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Pesticide residues in food 2001

Joint FAO/WHO Meeting on Pesticide Residues

EVALUATIONS

2001

PART I - RESIDUES

Rome, 2002

CONTENTS

* New compound
** Evaluated within the periodic review programme of the Codex Committee on Pesticide Residues

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2001 Joint FAO/WHO Meeting on Pesticide Residues
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Abbreviations

*	at or about the limit of quantification
ADI	acceptable daily intake
ai	active ingredient
AUC	area under the curve for concentration–time
bw	body weight
CCN	Codex classification number (for compounds or commodities)
CCPR	Codex Committee on Pesticide Residues
CXL	Codex level
2,4-D IPE	(2,4-dichlorophenoxy)acetic acid isopropyl ester
DT_{50}	time to 50% decomposition
DT_{90}	time to 90% decomposition
ECD	electron capture detection
F	fat
F_1	first filial generation
F_2	second filial generation
FAO	Food and Agricultural Organization of the United Nations
GAP	good agricultural practice
GC	gas chromatography
GLC	gas–liquid chromatography
GPC	gel-permeation chromatography
GEMS/Food	Global Environment Monitoring System–Food Contamination Monitoring and Assessment Programme
GSH	glutathione
HPLC	high-performance liquid chromatography
HR	highest residue in the edible portion of a commodity found in trials used to estimate a maximum residue level in the commodity
HR-P	highest residue in a processed commodity calculated by multiplying the HR of the raw commodity by the corresponding processing factor
IARC	International Agency for Research on Cancer
IEDI	international estimated daily intake
IESTI	international estimate of short-term dietary intake
JECFA	Joint Expert Committee on Food Additives
JMPR	Joint Meeting on Pesticide Residues
LC	liquid chromatography
LC_{50}	median lethal concentration
LD_{50}	median lethal dose
LOAEL	lowest-observed-adverse-effect level
LOAEC	lowest-observed-adverse-effect concentration
LOD	limit of detection
LOQ	limit of quantification
MDL	method detection limit
MLD	minimum level of detection
MRL	maximum residue limit
MS	mass spectrometry
MS/MS	tandem mass spectrometry
NOAEL	no-observed-adverse-effect level
NPD	nitrogen–phosphorus detector
OECD	Organization for Economic Co-operation and Development
PF	processing factor

PHI	pre-harvest interval
P_{ow}	octanol–water partition coefficient
RfD	reference dose
STMR	supervised trials median residue
STMR-P	supervised trials median residue in a processed commodity calculated by multiplying the STMR of the raw commodity by the corresponding processing factor
TRR	total radiolabelled residue
TMDI	theoretical maximum daily intake
UV	ultraviolet radiation
W	the previous recommendation is withdrawn
WHO	World Health Organization

Use of JMPR reports and evaluations by registration authorities

Most of the summaries and evaluations contained in this report are based on unpublished proprietary data submitted for use by JMPR in making its assessments. A registration authority should not grant a registration on the basis of an evaluation unless it has first received authorization for such use from the owener of the data submitted for the JMPR review or has received the dat on which the summaries are based, either from the owner of the data or from a second party that has obtained permission from the owner of the data for this purpose.

ALDICARB (117)

EXPLANATION

Aldicarb was re-evaluated for residues in 1994 under the CCPR Periodic Review Programme. The JMPR recommended MRLs for a wide range of commodities, including a temporary MRL of 0.5 mg/kg for potatoes, and the withdrawal of the MRL for bananas. The TMRL for potatoes was recommended as an MRL in 1996. At the 30th Session of the CCPR, it was noted that new data on bananas and potatoes, based on amended GAP, would be reported to the 2000 JMPR (ALINORM 99/24). The 2000 JMPR decided to postpone evaluation until 2001. The present Meeting received the results of residue trials on bananas and potatoes, information on GAP for potatoes in Europe, a processing study on potatoes, and estimates of acute dietary intake based on the Monte Carlo model.

USE PATTERN

Aldicarb is registered for use on bananas in Argentina, Belize, Cameroon, Egypt, France (Guadeloupe and Martinique), the Ivory Coast, South Africa and Zimbabwe. GAP in France and in Côte d'Ivoire allows 2 applications/2 g ai/plant, with a PHI of 180 days.

Aldicarb is registered for use on potatoes in the USA, using positive-displacement (PDA) application of 3.36 kg ai/ha; the PHI is 100 and 150 days in the Florida and Pacific Northwest States, respectively. GAP in The Netherlands is a furrow application at 12.8 g ai/100 m, equivalent to 1.7 kg ai/ha, or a broadcast application at 3.36 kg ai/ha with a PHI of 90 days. In Italy, Greece and Spain, critical GAP is a furrow application of 2.5 kg ai/ha, and a PHI of 90 days.

ANALYTICAL METHODS

The analytical method used in all trials determines the residues separately by high-performance liquid chromatography with post-column reaction and fluorescence detection. The analytical recoveries from banana peel and pulp and potato tubers at fortification levels of 0.01 to 5.0 mg/kg ranged from 68 to 121% for aldicarb, aldicarb sulfoxide and aldicarb sulfone. The limit of quantification (LOQ) was 0.01 or 0.03 mg/kg for each compound.

Stability of residues in stored analytical samples

In a study in 1998 to determine the stability of aldicarb and its metabolites a fortification level of 0.1 mg/kg was used. Bananas and their processed fractions were stored for up to 6 months at -29 to -15°C. 64-87% of the added compounds remained after 5 months in the pulp, 56-80% in the peel, 61-98% in purée and 57-71% in chips (Table 1).

Table 1. Storage stability of bananas and their processed products, % remaining.

Sample	Storage, months	Aldicarb	Aldicarb sulfoxide	Aldicarb sulfone
Pulp	0	84, 83	79, 87	77, 104
	1	87, 85	77, 74	93, 91
	3	78, 77	68, 78	83, 87
	5	84, 76	68, 64	72, 82
Peel	0	81, 81	70, 77	94, 88
	1	78, 66	62, 66	80, 83
	3	56, 56	67, 68	93, 91
	5	60, 56	58, 62	80, 78
Purée	0	93, 89	81, 83	102, 110
	1	91, 90	77, 81	87, 87

Sample	Storage, months	Aldicarb	Aldicarb sulfoxide	Aldicarb sulfone
	3	88, 90	81, 69	87, 79
	5	95, 86	74, 61	94, 98
Chips	0	82, 77	90, 77	93, 95
	1	45, 49	49, 63	58, 69
	3	52, 51	62, 61	67, 65
	5	57, 66	61, 64	66, 71

RESIDUES RESULTING FROM SUPERVISED TRIALS

The total residue is the sum of the parent aldicarb and the metabolites aldicarb sulfone and aldicarb sulfoxide, expressed as aldicarb.

Soil application was used in all trials, and aldicarb was not detected in any samples. In the following Tables, underlined residues were used for the estimation of maximum residue levels and double underlined for estimation of STMRs and HRs (highest residues).

Bananas. Trials were conducted in major banana production sites in Guadeloupe and Martinique from 1996 to 1998 and in the Ivory Coast from 1997 to 1999 (Table 2). A rate of 2 g of aldicarb/plant was applied to each generation up to 5 months after planting, and samples harvested after 134 to 286 days. Samples consisted of 12 bananas (bagged or unbagged) taken from the lower, middle and upper position of the bunch. Each banana finger was halved. One half was peeled and the pulp and peel composited separately for analysis (Table 2). The pulp of the other half was used to determine the residues in the pulp of individual bananas (Tables 3-5). Individual peel samples were not analysed separately.

Table 2. Residues of aldicarb in bananas after single applications to the soil per generation.

Location	Generation	Application (g ai/plant)	PHI, days	Sample	Residues (mg/kg)			
					Aldicarb	Aldicarb sulfone	Aldicarb sulfoxide	Total, as aldicarb
Guadeloupe[1,2] bagged	1st	2	286	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2	161	fruit	<0.003	0.010	<0.005	0.02
				pulp	<0.003	0.010	<0.005	0.02
		2.2	134	fruit	<0.003	0.10	0.013	0.12
				pulp	<0.003	0.10	0.010	0.10
unbagged	2nd	2.2	249	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2.2	180	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2.2	150	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
Guadeloupe[1,2] unbagged	1st	2	286	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2	161	fruit	<0.003	0.010	<0.005	0.02
				pulp	<0.003	0.010	<0.005	0.02
		2.2	134	fruit	<0.003	0.091	0.011	0.10
				pulp	<0.003	0.090	0.010	0.09
Ivory Coast[3] unbagged	1st	1.63	249	fruit	<0.01	<0.01	<0.01	<0.03
				pulp	<0.01	<0.01	<0.01	<0.03
		2.04	186	fruit	<0.01	<0.01	<0.01	<0.03
				pulp	<0.01	<0.01	<0.01	<0.03
		2.04	158	fruit	<0.01	<0.01	<0.01	<0.03

Location	Generation	Application (g ai/plant)	PHI, days	Sample	Residues (mg/kg)			
					Aldicarb	Aldicarb sulfone	Aldicarb sulfoxide	Total, as aldicarb
				pulp	<0.01	<0.01	<0.01	≤0.03
bagged	2nd	1.84	252	fruit	<0.01	<0.01	<0.01	<0.03
				pulp	<0.01	<0.01	<0.01	<0.03
		1.84	221	fruit	<0.01	<0.01	<0.01	≤0.03
				pulp	<0.01	<0.01	<0.01	,0.03
		1.84	190	fruit	<0.01	<0.01	<0.01	≤0.03
				pulp	<0.01	<0.01	<0.01	≤0.03
Martinique[1,2] bagged	1st	2.2	257	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2.2	178 ± 14	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2.2	150 ± 14	fruit	<0.003	0.010	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
unbagged	2nd	2.2	199	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2.2	167	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	0.010	<0.005	0.01
		2.2	136	fruit	<0.003	0.005	0.005	0.02
				pulp	<0.003	0.005	0.005	0.02
Martinique[1,2,3] unbagged	1st	2.2	257	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2.2	178 ± 14	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01
		2.2	150 ± 14	fruit	<0.003	<0.005	<0.005	0.01
				pulp	<0.003	<0.005	<0.005	0.01

[1] Residues in fruit (pulp + peel) were calculated from residues in the composite pulp and peel samples and % of each substrate in the sample
[2] It was assumed that undetected residues were at limit of detection for each substrate (pulp and peel 0.003 and 0.005 for aldicarb and aldicarb sulfone respectively, and 0.005 and 0.004 for aldicarb sulfoxide)
[3] Residues in fruit, peel and pulp were <LOQ (0.01 mg/kg) for each analyte.

Table 3. Residues of aldicarb in pulp samples from individual bagged and unbagged bananas in a trial in Guadeloupe, 1st generation, PHI 161 days at 2 g ai/plant.

Sample ref.	Position in bunch	Aldicarb (mg/kg)	Aldicarb sulfoxide (mg/kg)	Aldicarb sulfone (mg/kg)	Total as aldicarb (mg/kg)
BAGGED					
RR21845	Upper	<0.003	0.01	<0.005	0.015
RR21853	Upper	<0.003	0.021	0.005	0.025
RR21861	Upper	<0.003	<0.0054	<0.005	0.011
RR21869	Upper	<0.003	0.008	<0.005	0.014
RR21909	Middle	<0.003	0.005	<0.005	0.011
RR21917	Middle	<0.003	0.006	<0.005	0.012
RR21925	Middle	<0.003	0.005	<0.005	0.011
RR21933	Middle	<0.003	0.008	<0.005	0.014
RR21963	Lower	<0.003	<0.0054	<0.005	0.011
RR21969	Lower	<0.003	<0.0054	<0.005	0.011

Sample ref.	Position in bunch	Aldicarb (mg/kg)	Aldicarb sulfoxide (mg/kg)	Aldicarb sulfone (mg/kg)	Total as aldicarb (mg/kg)
RR21975	Lower	<0.003	0.011	<0.005	0.016
RR21981	Lower	<0.003	0.005	<0.005	0.011
Mean total as aldicarb 0.0135 mg/kg; SD 0.0041; RSD 30.0%; highest/mean 1.85					
UNBAGGED					
RR21877	Upper	<0.003	0.007	<0.005	0.013
RR21885	Upper	<0.003	0.007	<0.005	0.013
RR21893	Upper	<0.003	0.009	0.004	0.014
RR21901	Upper	<0.003	0.009	0.004	0.014
RR21939	Middle	<0.003	0.007	<0.005	0.013
RR21945	Middle	<0.003	0.006	<0.005	0.012
RR21951	Middle	<0.003	0.005	<0.005	0.011
RR21957	Middle	<0.003	0.007	<0.005	0.013
RR21987	Lower	<0.003	0.007	<0.005	0.013
RR21993	Lower	<0.003	0.016	0.005	0.021
RR21999	Lower	<0.003	0.006	ND	0.012
RR22005	Lower	<0.003	0.005	ND	0.011
Mean total as aldicarb 0.0133 mg/kg; SD 0.0026; RSD 19.5%; highest/mean 1.575					

Table 4. Residues of aldicarb in banana pulp in trial in Guadeloupe, 1st generation, PHI 134 days at 2 g ai/plant on bagged and unbagged bananas.

Sample ref	Sample	Aldicarb (mg/kg)	Aldicarb sulfoxide (mg/kg)	Aldicarb sulfone (mg/kg)	Total, as aldicarb (mg/kg)
BAGGED					
RR21846	Upper	<0.003	0.067	0.008	0.067
RR21854	Upper	<0.003	0.043	0.005	0.044
RR21862	Upper	<0.003	0.071	0.008	0.07
RR21870	Upper	<0.003	0.102	0.011	0.099
RR21910	Middle	<0.003	0.112	0.012	0.109
RR21918	Middle	<0.003	0.100	0.011	0.098
RR21926	Middle	<0.003	0.079	0.008	0.077
RR21934	Middle	<0.003	0.138	0.013	0.132
RR21964	Lower	<0.003	0.044	0.006	0.045
RR21970	Lower	<0.003	0.047	0.006	0.048
RR21976	Lower	<0.003	0.049	0.006	0.05
RR21982	Lower	<0.003	0.124	0.011	0.117
Mean total as aldicarb 0.0797 mg/kg; SD 0.0306; RSD 38.4%; highest/mean 1.657					
UNBAGGED					
RR21878	Upper	<0.003	0.057	0.007	0.057

Sample ref	Sample	Aldicarb (mg/kg)	Aldicarb sulfoxide (mg/kg)	Aldicarb sulfone (mg/kg)	Total, as aldicarb (mg/kg)
RR21886	Upper	<0.003	0.111	0.012	0.108
RR21894	Upper	<0.003	0.153	0.018	0.149
RR21902	Upper	<0.003	0.153	0.016	0.147
RR21940	Middle	<0.003	0.151	0.009	0.14
RR21946	Middle	<0.003	0.073	0.010	0.074
RR21952	Middle	<0.003	0.033	0.006	0.036
RR21958	Middle	<0.003	0.093	0.011	0.092
RR21988	Lower	<0.003	0.036	0.006	0.039
RR21994	Lower	<0.003	0.050	0.007	0.051
RR22000	Lower	<0.003	0.043	0.007	0.045
RR22006	Lower	<0.003	0.035	0.007	0.039
Mean total as aldicarb 0.0714 mg/kg; SD 0.0448; RSD 55.0%; highest/mean 1.83					

Table 5. Residues of aldicarb in banana pulp in a trial in Martinique, 2nd generation, PHI 136 and 167 days at 2 g ai/plant on bagged bananas.

Sample ref	Sample	Aldicarb (mg/kg	Aldicarb sulfoxide (mg/kg	Aldicarb sulfone (mg/kg)	Total, as aldicarb (mg/kg)
167 days					
RR22184	Upper	<0.003	0,006	<0.005	0,012
RR22192	Upper	<0.003	<0.0054	<0.005	0,011
RR22200	Upper	<0.003	0,008	0,005	0,014
RR22208	Upper	<0.003	<0.0054	<0.005	0,011
RR22248	Middle	<0.003	0,005	<0.005	0,011
RR22256	Middle	<0.003	0,006	<0.005	0,012
RR22264	Middle	<0.003	0,009	<0.005	0,015
RR22272	Middle	<0.003	0,005	<0.005	0,011
RR22302	Lower	<0.003	<0.0054	<0.005	0,011
RR22308	Lower	<0.003	0,008	<0.005	0,014
RR22314	Lower	<0.003	0,007	<0.005	0,013
RR22320	Lower	<0.003	0,009	<0.005	0,015
Mean total as aldicarb 0.0125 mg/kg; SD 0.0016; RSD 13.0%; highest/mean 1.2					
136 days					
RR22186	Upper	<0.003	0,012	ND	0,017
RR22194	Upper	<0.003	0,007	ND	0,013
RR22202	Upper	<0.003	0,008	ND	0,014
RR22210	Upper	<0.003	0,012	0,004	0,017
RR22250	Middle	<0.003	0,007	ND	0,013
RR22258	Middle	<0.003	0,012	0,005	0,017

Sample ref	Sample	Aldicarb (mg/kg	Aldicarb sulfoxide (mg/kg	Aldicarb sulfone (mg/kg)	Total, as aldicarb (mg/kg)
RR22266	Middle	<0.003	0,007	ND	0,013
RR22274	Middle	<0.003	0,008	ND	0,014
RR22304	Lower	<0.003	0,01	ND	0,015
RR22310	Lower	<0.003	0,005	ND	0,011
RR22316	Lower	<0.003	0,009	ND	0,015
RR22322	Lower	<0.003	0,012	ND	0,017
Mean total as aldicarb 0.0147 mg/kg; SD 0.002; RSD 13.7%; highest/mean 1.159					

Data from the 1996 JMPR Evaluation

Bananas. In two trials in Martinique in 1987, reported to the 1996 JMPR, after two applications of 2 g ai/plant and PHIs of 148-205 days, the residues as total aldicarb were 0.02 and 0.03 mg/kg in the pulp.

Potatoes. Twenty three residue trials were conducted in Europe (Greece, Italy, The Netherlands, Spain and the UK) using 1 soil application of 2.5 to 3.4 kg ai/ha or 13 g ai/100 m. Some of the trials were decline studies with samples harvested from 90 to 120 days after treatment. Each tuber was halved and one half was used to make a composite sample for analysis. The other half was used to determine residues in individual tubers, which are reported in Tables 7 to 9. In sixteen trials in the USA with single soil applications at-planting PDA of 3.6 kg ai/ha two samples were collected each consisting of 24 tubers taken at random from the plot after 120 days. Residues in the tubers in all trials ranged from <0.03 to 0.45 mg/kg (Table 6).

Samples from sixty commercial potato fields randomly selected in Washington, Idaho and Oregon collected within a five-day window before harvest at PHIs of 150 to 192 days were analysed for aldicarb and its metabolites. The limit of quantification was about 0.02 mg/kg for each analyte. The maximum residue was 0.126 mg/kg as aldicarb, with an average of 0.041 $\pm$ 0.02 mg/kg, but full details of the trials were not provided.

Table 6. Residues of aldicarb in potato samples after 1 soil application.

Country. year	Type of application	Application rate	PHI, days	Residue (mg/kg)				Site
				Aldicarb	Aldicarb sulfone	Aldicarb sulfoxide	Total as aldicarb	
Greece, 1996	In furrow	2.5 kg ai/ha	87	<0.01	0.019	<0.01	0.04	96662 GR1
1998	In furrow	2.8 kg ai/ha	91	<0.01	<0.01	0.013	0.03	98694GR1
			101	<0.01	<0.01	0.017	0.03	
			112	<0.01	<0.01	0.011	0.03	
			121	<0.01	<0.01	0.013	0.03	
	In furrow	2.8 kg ai/ha	89	<0.01	0.013	0.018	0.04	98694GR2
			99	<0.01	0.024	0.033	0.06	
			110	<0.01	0.022	0.030	0.06	
			123	<0.01	<0.01	0.022	0.04	
Italy. 1998	In furrow	2.6 kg ai/ha	90	<0.01	<0.01	<0.01	0.03	98702BO1
			100	<0.01	0.021	<0.01	0.04	
			110	<0.01	<0.01	<0.01	0.03	
			120	<0.01	<0.01	<0.01	0.03	
	In furrow	2.6 kg ai/ha	90	<0.01	<0.01	<0.01	0.03	98694GR2
			100	<0.01	<0.01	<0.01	0.03	

Country. year	Type of application	Application rate	PHI, days	Residue (mg/kg)				Site
				Aldicarb	Aldicarb sulfone	Aldicarb sulfoxide	Total as aldicarb	
			110	<0.01	<0.01	<0.01	0.03	
			120	<0.01	<0.01	<0.01	0.03	
Netherlands. 1998	broadcast	3.4 kg ai/ha	90	<0.01	0.14	0.13	0.24	NL1
			100	<0.01	0.14	0.16	0.27	
			111	<0.01	0.077	0.073	0.14	
			120	<0.01	0.069	0.067	0.13	
	In furrow	13 g/100m	90	<0.01	0.039	0.097	0.13	NL1
			100	<0.01	0.034	0.073	0.11	
			111	<0.01	0.051	0.13	0.17	
			120	<0.01	0.041	0.076	0.11	
	broadcast	3.4 kg ai/ha	90	<0.01	0.083	0.13	0.20	NL2
			100	<0.01	0.050	0.078	0.12	
			111	<0.01	0.037	0.047	0.08	
			120	<0.01	0.038	0.064	0.10	
	In furrow	13 g ai/100m	100	<0.01	0.019	0.056	0.08	NL2
			111	<0.01	0.024	0.072	0.10	
			120	<0.01	0.024	0.075	0.10	
Spain. 1996 1998	In furrow	3 kg ai/ha	99	<0.01	0.41	0.074	0.45	96642M1
	In furrow	3 kg ai/ha	104	<0.01	0.035	0.015	0.06	96642V1
	In furrow	2.5 kg ai/ha	90	<0.01	0.038	0.25	0.27	98580SE1
			100	<0.01	0.028	0.22	0.24	
			110	<0.01	0.031	0.16	0.18	
			120	<0.01	0.020	0.17	0.18	
	In furrow	2.5 kg ai/ha	93	<0.01	<0.01	0.028	0.04	98580SE2
			100	<0.01	<0.01	0.027	0.04	
			111	<0.01	<0.01	0.018	0.04	
			120	<0.01	<0.01	0.019	0.04	
UK.1998 Study 98661	In furrow	13 g ai/100m	90	<0.01	0.033	0.075	0.11	RP1
		13 g ai/100m	91	<0.01	0.038	0.070	0.11	RP2
		13 g ai/100m	90	<0.01	0.036	0.044	0.08	RP3
		12 g ai/100m	90	<0.01	0.035	0.066	0.10	IRI
Study 98662	broadcast	3.3 kg ai/ha	90	<0.01	0.014	<0.01	0.03	RP1
		3.2 kg ai/ha	91	<0.01	0.089	0.10	0.18	RP2
		3.2 kg ai/ha	90	<0.01	0.14	0.25	0.36	RP3
		3.4 kg ai/ha	90	<0.01	0.065	0.06	0.12	IRI
Study 98667	In furrow	13 g ai/100m	91	<0.01	0.027	0.092	0.12	RP1
			100	<0.01	0.018	0.060	0.08	
			110	<0.01	0.016	0.033	0.05	
			120	<0.01	0.014	0.025	0.04	
	In furrow	13 g ai/100m	90	<0.01	<0.01	<0.01	<0.03	RP2
			100	<0.01	<0.01	<0.01	<0.03	
			110	<0.01	<0.01	<0.01	<0.03	
			120	<0.01	<0.01	<0.01	<0.03	
	In furrow	13 g ai/100m	91	<0.01	0.023	0.044	0.07	RP3
			100	<0.01	0.017	0.032	0.05	
			110	<0.01	0.018	0.036	0.06	
			120	<0.01	0.011	0.030	0.05	
	In furrow	13g ai/100m	90	<0.01	0.011	0.035	0.05	IRI
			100	<0.01	<0.010	<0.01	0.09[1]	
			110	<0.01	0.011	0.022	0.04	
			120	<0.01	0.027	0.075	0.10	

Country. year	Type of application	Application rate	PHI, days	Residue (mg/kg)				Site
				Aldicarb	Aldicarb sulfone	Aldicarb sulfoxide	Total as aldicarb	
Study 98668	broadcast	3.3 kg ai/ha	91	<0.01	<0.01	<0.01	≤0.03	RP1
			100	<0.01	<0.01	<0.01	<0.03	
			110	<0.01	<0.01	<0.01	<0.03	
			120	<0.01	<0.01	<0.01	<0.03	
	broadcast	3.2 kg ai/ha	90	<0.01	<0.01	<0.01	≤0.03	RP2
			100	<0.01	<0.01	<0.01	<0.03	
			110	<0.01	<0.01	<0.01	<0.03	
			120	<0.01	<0.01	<0.01	<0.03	
	broadcast	3.2 kg ai/ha	91	<0.01	0.045	0.043	0.09	RP3
			100	<0.01	0.019	0.013	0.04	
			110	<0.01	0.023	0.020	0.05	
			120	<0.01	0.19	0.017	0.04	
	broadcast	3.4 kg ai/ha	90	<0.01	0.031	0.11	0.13	IRI
			100	<0.01	0.033	0.11	0.14	
			110	<0.01	<0.01	0.015	0.03	
			120	<0.01	0.015	0.048	0.07	
USA. 1996[2]	PDA	3.6 kg ai/ha	120	<0.003	0.011	0.02	0.03	11218-05
CO	PDA	3.6 kg ai/ha	120	<0.003	0.043	0.176	0.20	11218-06
ID	PDA	3.6 kg ai/ha	120	<0.003	<0.02	<0.02	0.03	10525-01
	PDA	3.6 kg ai/ha	120	<0.003	<0.003	<0.003	≤0.02	10525-02
	PDA	3.6 kg ai/ha	120	<0.003	<0.02	<0.02	0.03	10525-08
	PDA	3.6 kg ai/ha	120	<0.003	0.02	0.03	0.04	10528-10
MI	PDA	3.6 kg ai/ha	120	<0.003	0.05	0.081	0.11	11218-01
	PDA	3.6 kg ai/ha	120	<0.003	0.021	0.029	0.04	11218-02
ND	PDA	3.6 kg ai/ha	120	<0.003	0.05	0.09	0.13	11218-04
OR	PDA	3.6 kg ai/ha	120	<0.003	<0.003	<0.02	0.02	10523-03
	PDA	3.6 kg ai/ha	120	<0.003	<0.003	<0.02	0.02	10525-04
	PDA	3.6 kg ai/ha	120	<0.003	0.02	0.03	0.04	10525-09
SD	PDA	3.6 kg ai/ha	120	<0.003	0.039	0.072	0.10	11218-03
WA	PDA	3.6 kg ai/ha	120	<0.003	0.02	0.06	0.06	10525-05
	PDA	3.6 kg ai/ha	120	<0.003	<0.02	0.04	0.05	10525-06
	PDA	3.6 kg ai/ha	120	<0.003	0.03	0.06	0.06	10525-07

[1] Result obtained on sample labelled "untreated". As <0.028 mg/kg was found on sample labelled "treated", labels were assumed to have been reversed

[2] In calculating total residue, 0.00 mg/kg is used for values reported as undetected (<0.003 mg/kg) and 0.02 mg/kg for those reported as <0.02 mg/kg

The results of further trials on potatoes conducted according to GAP, reported to the 1999 JMPR, in rank order were <0.03 (5), 0.03-0.048 (5), 0.053-0.08 (7), 0.09 (2), 0.1-0.18 (6), 0.23 (2), 0.24, 0.25 (2), 0.3 (2), 0.35, 0.4 (2), 0.43 and 0.7 mg/kg as aldicarb sulfone. To be expressed as aldicarb, the results were multiplied by 0.856 giving residues of <0.03 (5), 0.03-0.04 (5), 0.04-0.07 (7), 0.08 (2), 0.08-0.15 (6), 0.20 (3), 0.21(2), 0.26(2), 0.3, 0.34 (2), 0.39 and 0.6 mg/kg.

Table 7. Residues of aldicarb in individual potato tubers in trials in the UK and The Netherlands.

Trial 98-661 – UK plot AK/4092RP1		Trial 98-661 – UK plot IR392338/1		Trial 98-687NL1/ND – plot 3 R1	
Sample reference	Total aldicarb, mg/kg	Sample reference	Total aldicarb, mg/kg	Sample reference	Total aldicarb, mg/kg
45815/1	0.033	52976/1	0.081	145831	0.037
45815/2	0.079	52976/2	0.050	145832	0.249

Trial 98-661 – UK plot AK/4092RP1		Trial 98-661 – UK plot IR392338/1		Trial 98-687NL1/ND – plot 3 R1	
Sample reference	Total aldicarb, mg/kg	Sample reference	Total aldicarb, mg/kg	Sample reference	Total aldicarb, mg/kg
45815/3	0.046	52976/3	0.107	145833	0.116
45815/4	0.112	52976/4	0.057	145834	0.046
45815/5	0.057	52976/5	0.074	145835	0.137
45815/6	0.197	52976/6	0.286	145836	0.075
45815/7	0.130	52976/7	0.070	145837	0.174
45815/8	0.262	52976/8	0.184	145838	0.426
45815/9	0.063	52976/9	0.072	145839	0.201
45815/10	0.111	52976/10	0.080	145840	0.051
45815/11	0.039	52976/11	0.124	145841	0.058
45815/12	0.043	52976/12	0.055	145842	0.289
45815/13	0.103	52976/13	0.066	145843	0.075
45815/14	0.098	52976/14	0.033	145844	0.124
45815/15	0.048	52976/15	0.050	145845	0.077
45815/16	0.055	52976/16	0.090	145846	0.073
45815/17	0.068	52976/17	0.030	145847	0.084
45815/18	0.087	52976/18	0.338	145848	0.034
45815/19	0.091	52976/19	0.040	145849	0.079
45815/20	0.098	52976/20	0.181	145850	0.244
45815/21	0.047	52976/21	0.095	145851	0.401
45815/22	0.169	52976/22	0.064	145852	0.211
45815/23	0.169	52976/23	0.052	145853	0.028
45815/24	0.115	52976/24	0.067	145854	0.158
45815/25	0.133	52976/25	0.028	145855	0.041
45815/26	0.111	52976/26	0.069	145856	0.031
45815/27	0.197	52976/27	0.039	145857	0.097
45815/28	0.045	52976/28	0.109	145858	0.032
45815/29	0.225	52976/29	0.110	145859	0.128
45815/30	0.059	52976/30	0.340	145860	0.048
45815/31	0.048	52976/31	0.079	145861	0.074
45815/32	0.191	52976/32	0.028	145862	0.033
45815/33	0.081	52976/33	0.030	145863	0.044
45815/34	0.195	52976/34	0.143	145864	0.063
45815/35	0.203	52976/35	0.058	145865	0.067
45815/36	0.075	52976/36	0.055	145866	0.071
45815/37	0.091	52976/37	0.091	145867	0.045
45815/38	0.121	52976/38	0.072	145868	0.034
45815/39	0.148	52976/39	0.052	145869	0.078
45815/40	0.051	52976/40	0.209	145870	0.052

Trial 98-661 – UK plot AK/4092RP1		Trial 98-661 – UK plot IR392338/1		Trial 98-687NL1/ND – plot 3 R1	
Sample reference	Total aldicarb, mg/kg	Sample reference	Total aldicarb, mg/kg	Sample reference	Total aldicarb, mg/kg
45815/41	0.107	52976/41	0.039	145871	0.048
45815/42	0.049	52976/42	0.028	145872	0.085
45815/43	0.034	52976/43	0.088	145873	0.034
45815/44	0.084	52976/44	0.138	145874	0.089
45815/45	0.083	52976/45	0.059	145875	0.364
45815/46	0.076	52976/46	0.071	145876	0.064
45815/47	0.042	52976/47	0.115	145877	0.330
45815/48	0.146	52976/48	0.181	145878	0.070
45815/49	0.033	52976/49	0.052	145879	0.085
45815/50	0.067	52976/50	0.067	145880	0.075
Max	**0.262**	**Max**	**0.340**	**Max**	**0.426**
Mean	**0.100**	**Mean**	**0.094**	**Mean**	**0.113**
St Dev	**0.057**	**St Dev**	**0.072**	**St Dev**	**0.101**
Median	**0.086**	**Median**	**0.071**	**Median**	**0.075**
Max/mean	**2.61**	**Max/mean**	**3.62**	**Max/mean**	**3.79**
RSD	**57%**	**RSD**	**77%**	**RSD**	**89%**

Table 8. Residues of aldicarb in individual potato tubers in trials in Spain and Italy.

Trial 98580/Spain/SE1		Trial 98580/Spain/SE1		Trial 98702BO1/ Italy		Trial 98702BO2/Italy	
Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg
9	0.230	19	<0.028	9	0.030	52	<0.028
10	0.263	20	0.037	10	<0.028	54	<0.028
11	0.379	21	0.031	11	0.029	81	<0.028
12	0.205	22	0.033	12	0.030	91	<0.028
13	0.394	23	<0.028	13	<0.028	79	<0.028
14	0.393	24	0.067	14	0.032	93	<0.028
15	0.094	25	0.050	15	<0.028	84	<0.028
16	0.309	26	0.107	16	<0.028	62	<0.028
17	0.079	27	0.032	17	0.029	122	<0.028
18	0.709	28	0.032	18	<0.028	74	<0.028
19	0.206	29	0.031	19	0.030	112	0.029
20	0.184	30	0.047	20	0.038	138	0.043
21	0.297	31	0.033	21	0.031	78	<0.028
22	0.390	32	0.033	22	0.031	61	<0.028
23	0.534	33	0.067	23	0.037	82	<0.028
24	0.173	34	0.036	24	<0.028	115	<0.028

Trial 98580/Spain/SE1		Trial 98580/Spain/SE1		Trial 98702BO1/ Italy		Trial 98702BO2/Italy	
Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg
25	0.309	35	0.037	25	<0.028	109	<0.028
26	1.068	36	0.044	26	0.043	68	0.031
27	0.724	37	<0.028	27	0.031	61	<0.028
28	0.325	38	0.067	28	0.034	107	<0.028
29	0.493	39	0.031	29	<0.028	112	<0.028
30	0.218	40	<0.028	30	0.032	105	0.053
31	0.477	41	<0.028	31	0.035	133	<0.028
32	0.291			32	0.138	194	<0.028
33	0.221			33	0.037	53	<0.028
34	0.141			34	0.083	65	<0.028
35	0.472			35	0.034	72	<0.028
36	0.207			36	0.031	75	<0.028
37	0.412			37	0.031	70	<0.028
38	0.299			38	<0.028	76	<0.028
39	0.291			39	0.040	101	<0.028
40	0.143			40	0.044	137	<0.028
41	0.211			41	0.030	111	<0.028
42	0.111			42	<0.028	143	<0.028
43	0.200			43	0.053	62	<0.028
44	0.182			44	<0.028	65	<0.028
45	0.325			45	0.035	92	<0.028
46	0.146			46	<0.028	72	<0.028
47	0.433			47	0.058	59	<0.028
48	0.280			48	0.034	69	<0.028
49	0.242			49	0.032	58	<0.028
50	0.273			50	<0.028	102	0.053
51	0.203			51	<0.028	79	<0.028
52	0.246			52	<0.028	60	<0.028
53	0.290			53	0.037	54	<0.028
54	0.192			54	<0.028	275	0.065
55	0.310			55	0.076	128	0.047
56	0.236			56	0.034	68	<0.028
57	0.190			57	0.030	139	0.037
58	0.629			58	<0.028	120	<0.028
Max	**1.068**	**Max**	**0.107**	**Max**	**0.138**	**Max**	**0.065**
Mean	**0.313**	**Mean**	**0.042**	**Mean**	**0.037**	**Mean**	**0.031**
St Dev	**0.181**	**St Dev**	**0.019**	**St Dev**	**0.018**	**St Dev**	**0.008**
Median	**0.276**	**Median**	**0.033**	**Median**	**0.031**	**Median**	**<0.028**

Trial 98580/Spain/SE1		Trial 98580/Spain/SE1		Trial 98702BO1/ Italy		Trial 98702BO2/Italy	
Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg
Max/mean	**3.42**	**Max/mean**	**2.57**	**Max/mean**	**3.79**	**Max/mean**	**2.11**
RSD	**58%**	**RSD**	**46%**	**RSD**	**51%**	**RSD**	**25%**

Table 9. Residues of aldicarb in individual potato tubers in trials in Greece (Trials 98694R1 and 98694/R2, Greece Rep 2).

Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg
153312	0.032	153362	0.029	153412	0.045	153462	<0.028
153313	0.032	153363	0.036	153413	0.036	153463	0.030
153314	0.041	153364	0.037	153414	0.051	153464	<0.028
153315	0.031	153365	<0.028	153415	0.071	153465	<0.028
153316	0.039	153366	<0.028	153416	0.059	153466	<0.028
153317	<0.028	153367	0.033	153417	0.042	153467	0.037
153318	0.031	153368	0.032	153418	0.103	153468	<0.028
153319	0.031	153369	0.031	153419	0.046	153469	0.033
153320	0.043	153370	<0.028	153420	0.082	153470	<0.028
153321	0.030	153371	0.039	153421	0.078	153471	0.030
153322	<0.028	153372	0.031	153422	0.113	153472	0.031
153323	0.034	153373	<0.028	153423	0.039	153473	0.050
153324	0.031	153374	0.030	153424	<0.028	153474	0.037
153325	0.033	153375	0.047	153425	0.074	153475	<0.028
153326	0.029	153376	0.041	153426	0.074	153476	0.071
153327	0.036	153377	0.042	153427	0.088	153477	0.054
153328	<0.028	153378	0.035	153428	0.036	153478	0.046
153329	0.029	153379	0.031	153429	0.050	153479	0.041
153330	<0.028	153380	<0.028	153430	0.087	153480	0.065
153331	0.050	153381	0.031	153431	0.032	153481	0.046
153332	<0.028	153382	<0.028	153432	<0.028	153482	0.053
153333	<0.028	153383	0.030	153433	<0.028	153483	0.032
153334	0.036	153384	<0.028	153434	0.063	153484	0.079
153335	0.041	153385	0.034	153435	0.087	153485	0.034
153336	<0.028	153386	<0.028	153436	0.038	153486	0.033
153337	<0.028	153387	0.035	153437	0.052	153487	0.029
153338	0.036	153388	<0.028	153438	0.071	153488	0.030
153339	0.044	153389	0.035	153439	0.102	153489	<0.028
153340	0.035	153390	0.045	153440	0.040	153490	0.088
153341	0.044	153391	0.030	153441	<0.028	153491	0.038
153342	<0.028	153392	0.037	153442	<0.028	153492	0.032

Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg	Sample no.	Total aldicarb, mg/kg
153343	0.040	153393	0.040	153443	<0.028	153493	0.031
153344	0.036	153394	0.037	153444	<0.028	153494	0.063
153345	<0.028	153395	<0.028	153445	0.032	153495	0.092
153346	<0.028	153396	0.043	153446	<0.028	153496	0.071
153347	0.042	153397	0.033	153447	<0.028	153497	0.074
153348	0.030	153398	0.043	153448	0.042	153498	<0.028
153349	0.027	153399	0.031	153449	0.035	153499	<0.028
153350	0.035	153400	0.042	153450	<0.028	153500	<0.028
153351	0.036	153401	0.036	153451	<0.028	153501	0.085
153352	0.030	153402	<0.028	153452	0.044	153502	0.045
153353	0.042	153403	0.043	153453	0.030	153503	0.030
153354	<0.028	153404	<0.028	153454	0.056	153504	0.037
153355	<0.028	153405	0.039	153455	0.052	153505	0.051
153356	0.037	153406	0.031	153456	0.080	153506	0.081
153357	0.031	153407	0.035	153457	0.031	153507	<0.028
153358	0.030	153408	0.051	153458	0.029	153508	0.040
153359	0.032	153409	0.038	153459	0.056	153509	0.042
153360	0.042	153410	0.043	153460	0.051	153510	<0.028
153361	<0.028	153411	0.031	153461	0.039	153511	0.100
Max	**0.050**	**Max**	**0.051**	**Max**	**0.113**	**Max**	**0.100**
Mean	**0.033**	**Mean**	**0.035**	**Mean**	**0.051**	**Mean**	**0.044**
St Dev	**0.006**	**St Dev**	**0.006**	**St Dev**	**0.024**	**St Dev**	**0.020**
Median	**0.031**	**Median**	**0.033**	**Median**	**0.043**	**Median**	**0.035**
Max/mean	**1.49**	**Max/mean**	**1.49**	**Max/mean**	**2.22**	**Max/mean**	**2.24**
RSD	**17%**	**RSD**	**18%**	**RSD**	**46%**	**RSD**	**46%**

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

The stability at room temperature of aldicarb and its metabolites was studied in banana pulp and peel samples fortified at 0.1 mg/kg. The results are shown on Table 10.

Table 10. Stability of residues of aldicarb and metabolites in bananas at room temperature (% remaining).

Sample	Storage, days	Aldicarb	Aldicarb sulfoxide	Aldicarb sulfone
pulp	0	84, 87	71, 70	87, 86
	2	74, 84	77, 78	94, 91
	4	75, 77	97, 73	84, 84
	6	63, 73	0, 0	85, 89
peel	0	68, 68	68, 72	98, 91
	2	28, 32	80, 82	100, 97

	4	27, 30	67, 70	98, 94
	6	37, 36	77, 70	82, 81

In processing

A processing study was carried out on potatoes from 3 fields in Spain commercially treated with aldicarb at planting. Tuber samples (average size 3-4 cm) taken 67 to 88 days after treatment had total aldicarb residues expressed as aldicarb of 0.06. 0.15 and 0.45 mg/kg. After microwave boiling, tubers had on average 70% of the residues before cooking (processing factors: 0.72; 0.72 and 0.65).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Preliminary evaluations of dietary intake in Europe show the UK population as a high consumer of foods identified as the main potential sources of residues of aldicarb (potatoes, bananas, carrots and citrus fruit). Data from field trials, adjusted to reflect market share information and import statistics, were combined with consumption data for the UK adult (16 to 64 years) and toddler population (2½ to 4½ years) to estimate the potential exposure of the population to aldicarb (Barraj and Petersen, 1999). The probabilistic Monte Carlo exposure model was used, following guidelines outlined by the UK Ministry of Agriculture, Fisheries and Food. The results indicate that potential dietary exposure is well below the acute reference dose (acute RfD) of 0.003 mg/kg bw/day (JMPR, 1995). The UK adult and toddler exposures at the 97.5th percentile are 0.00014 mg/kg bw/day (4.7% of acute RfD) and 0.00023 mg/kg bw/day (7.7% of the acute RfD).

A reanalysis of the dietary exposure assessment using the Monte Carlo exposure model was conducted to include new results from June 1999 and detailed consumption data for the UK infant (less than 1 year). The estimated UK adult and toddler exposures at the 99th percentile are 0.000449 mg/kg (15% of the acute RfD) and 0.000776 mg/kg (26% of the acute RfD) respectively. The estimated UK infant exposure at the 99th percentile is 0.000626 mg/kg (21% of the acute RfD).

APPRAISAL

Aldicarb was last evaluated for residues in 1994 by the JMPR within the CCPR periodic review programme. The 1994 Meeting estimated maximum residue levels for a wide range of commodities and estimated a temporary maximum residue level of 0.5 mg/kg for potato, pending the submission of data from supervised trials corresponding to current use patterns; it withdrew the MRL for banana. In 1996, new data on residues in banana and potato were evaluated, and the MRL of 0.5 mg/kg on potatoes was confirmed. At its Thirtieth Session, the CCPR noted that new data on banana and potato based on amended GAP use would become available (ALINORM 99/24). At the present Meeting, data on residues in trials on banana and potato, residues in individual units of banana and potato, a study on processing of potato, and an estimate of short-term dietary intake by a probabilistic method were provided.

Stability of residues in stored analytical samples

Aldicarb and its metabolites were relatively stable at a concentration of 0.1 mg/kg in banana and in processed fractions stored for up to 5 months in a freezer. After storage, 64–87% of the added compounds remained in banana pulp, 56–80% in peel, 61–98% in purée and 57–71% in banana chips. No new studies were provided on potato samples.

Results of supervised trials

In Guadeloupe, Martinique and Côte d'Ivoire, the GAP for banana is 2 g ai/plant. The labels either states that a period of 180 days is necessary between the last treatment and the expected harvesting date or specifies a PHI of 180 days. The Meeting agreed that, if bananas were treated with aldicarb with the intention of harvesting 180 days later, the use would be considered at GAP if the bananas were harvested at maturity.

Twenty-four trials were conducted in these countries, with 1 x 2 g/plant applied to the first and/or the second generation, on bagged and/or unbagged bananas (PHI, 134–286 days). The concentrations of residues of aldicarb in bagged banana were 0.01 (4), 0.02, < 0.03 (3) and 0.12 mg/kg, and those in bagged banana pulp were 0.01 (4), 0.02, < 0.03 (2), 0.03 and 0.10 mg/kg. The concentrations in unbagged banana fruit were 0.01 (9), 0.02 (2), < 0.03 (3) and 0.10 mg/kg, and those in unbagged banana pulp were 0.01 (9), 0.02 (2), < 0.03 (3) and 0.09 mg/kg, as aldicarb. Residues after culture by GAP on bagged and unbagged banana applied to a single population, and were combined. The residue concentrations in fruit, in ranked order (median underlined), were: 0.01 (13), 0.02 (3), < 0.03 (6), 0.10 and 0.12 mg/kg, and those in pulp were 0.01 (13), 0.02 (3), < 0.03 (5), 0.03, 0.09 and 0.10 mg/kg, as aldicarb.

On the basis of the concentrations in the fruit, the Meeting estimated a maximum residue level of 0.2 mg/kg for aldicarb in banana. On the basis of the concentrations in pulp, the Meeting estimated an STMR of 0.01 mg/kg, and an HR of 0.10 mg/kg for aldicarb in banana.

Individual pulp units from four trials (12 units per trial from four bunches) conducted in Guadeloupe (first-generation; PHI, 134 days for bagged and 161 days for unbagged bananas) and from two trials conducted in Martinique (second-generation; PHI, 167 and 136 days for bagged banana) were analysed. The distribution of residues in the 12 units did not represent the expected distribution of residues among plants on a treated field. Aldicarb is a systemic insecticide, which is taken up by the plant from the soil. The residues are equally distributed in the peel and the pulp, and there is no difference between the concentrations in bagged and unbagged banana. Furthermore, the main source of variation in concentrations is differences in uptake. The sampling plan used, in which only four bunches were selected from the treated area, would not indicate the probable variation in concentrations, and, consequently, no variability factor could be estimated. The Meeting agreed that a default variability factor of 5 should be used to estimate short-term dietary intake of aldicarb from banana; the unit weight of the whole portion includes more than one finger and is > 250 g (see section 3).

Overall, 29 trials were conducted with aldicarb on potato in Europe (three in Greece, four in The Netherlands, two in Italy, four in Spain and 16 in the United Kingdom). GAP in The Netherlands involves furrow application of a dose of 12.8 g/100 m, equivalent to 1.7 kg ai/ha, or broadcast application of 3.36 kg/ha and a PHI of 90 days. The residue concentrations in four trials conducted in The Netherlands according to GAP were 0.10, 0.17, 0.20 and 0.27 mg/kg. Seventeen trials conducted in the United Kingdom according to GAP in The Netherlands gave concentrations of < 0.03 (3), 0.03, 0.07, 0.08, 0.09, 0.10 (2), 0.11 (2), 0.12 (2), 0.14, 0.18 and 0.36 mg/kg. In Greece, Italy and Spain, critical GAP is furrow application of 2.5 kg ai/ha and a PHI of 90 days. The concentrations in trials conducted according to GAP were 0.04, 0.03 and 0.06 mg/kg in Greece, 0.04 and 0.03 mg/kg in Italy and 0.45, 0.06, 0.27 and 0.04 mg/kg in Spain.

In the USA, 16 trials were conducted according to the GAP rate of 3.36 kg ai/ha, a PHI of 100 or 150 days and positive displacement application, in Colorado, Idaho, Michigan, North Dakota, South Dakota and Washington. The concentrations of aldicarb residues in tubers after 120 days were < 0.02, 0.02 (2), 0.03 (3), 0.04 (3), 0.05, 0.06 (2), 0.10, 0.11, 0.13 and 0.20 mg/kg.

The concentrations of residues in trials conducted in Europe and the USA were considered to apply to a single population and were combined, in ranked order, as follows: < 0.02, 0.02 (2), < 0.03

(3), 0.03 (6), 0.04 (5), 0.05, 0.06 (4), 0.07, 0.08, 0.09, 0.10 (3), 0.11 (3), 0.12 (2), 0.13, 0.14, 0.18, 0.20, 0.27, 0.36 and 0.45 mg/kg, as aldicarb equivalents. The Meeting confirmed the previous recommended MRL of 0.5 mg/kg and estimated an STMR values of 0.06 mg/kg and a highest residue of 0.45 mg/kg for aldicarb in potato, as aldicarb equivalents.

The Meeting considered the database from 26 supervised field trials on potato submitted to the 1996 JMPR that had been carried out in the USA with the recommended positive displacement application of aldicarb. In each trial, 30–100 individual potato tubers were analysed. The observed maximum concentrations of residues in individual tubers in each trial were, in rank order, 0.045 (2), 0.046, 0.048, 0.063, 0.065, 0.072, 0.11, 0.17 (2), 0.20, 0.22, 0.23, 0.25, 0.26, 0.27, 0.29, 0.31, 0.32, 0.34, 0.51, 0.61, 0.94, 1.1 and 1.2 (2) mg/kg. Data on individual tubers were submitted to the present Meeting from 11 supervised trials conducted in Europe according to GAP, with furrow application. In each trial, 27–50 individual potato tubers were analysed. The observed maximum concentrations of residues in individual tubers in each trial were, in rank order, 0.05, 0.051, 0.065, 0.10 (2), 0.11, 0.138, 0.262, 0.34, 0.426 and 1.07 mg/kg. The Meeting agreed that the maximum residue levels in individual tubers in Europe and the USA comprised a single population and could be combined, in ranked order, as follows: 0.045 (2), 0.046, 0.048, 0.05, 0.051, 0.063, 0.065 (2), 0.072, 0.1 (2), 0.112, 0.11, 0.14, 0.17 (2), 0.2, 0.22, 0.23, 0.25, 0.26, 0.262, 0.27, 0.29, 0.31, 0.32, 0.34 (2), 0.43, 0.51, 0.61, 0.94, 1.1 (2) and 1.2 (2) mg/kg.

The Meeting agreed that the highest residue in this data set (1.2 mg/kg) could be used to estimate short-term intake of aldicarb from consumption of potato. When this value is used, no variability factor need be applied to the first part of the equation for calculation of the IESTI in case 2a (see section 3). The HR value estimated from the composite sample, 0.45 mg/kg, was used in the second part of the equation.

Fate of residues during storage

A study of the fate of residues of aldicarb and its metabolites present at 0.1 mg/kg in banana pulp and peel at room temperature showed that 36–82% of the residues remained after 6 days.

Fate of residues during processing

A study was conducted on processing of potato obtained from three fields in Spain that had been commercially treated with aldicarb at the time of planting. Samples taken 67–88 days after treatment (average size of tubers, 3–4 cm) contained residues of total aldicarb, expressed as aldicarb, at concentrations of 0.06, 0.15 and 0.45 mg/kg. After microwave boiling, the tubers contained an average of 70% of the residues present before cooking (processing factors, 0.72, 0.72 and 0.65). On the basis of the average processing factor for microwaved potato (0.7), the estimated STMR of 0.06 mg/kg and an HR of 0.45 mg/kg for potato, the Meeting estimated an STMR-P of 0.042 and an HR-P of 0.315 mg/kg for aldicarb in microwaved potato.

On the basis of the highest residue of 1.2 mg/kg for potato, the Meeting estimated a highest residue of 0.84 mg/kg for aldicarb in microwaved potato. This value can be used to estimate short-term intake of aldicarb from the consumption of microwaved potato, and no variability factor need be applied to the first part of the equation for calculation of the IESTI in case 2a (see section 3). The HR-P value estimated for the composite sample (0.315 mg/kg) was used in the second part of this equation.

In processing studies submitted to the 1996 JMPR, the average processing factors were 0.75 for potato flakes, 0.48 for chips, 0.29 for frozen fries and 0.39 for cooked fries. On the basis of the estimated STMR and HR values for potato, the Meeting estimated an STMR-P value for aldicarb in potato flakes of 0.045 mg/kg and an HR-P value of 0.338 mg/kg; an STMR-P value for potato chips

of 0.0288 mg/kg and an HR-P value of 0.216 mg/kg; an STMR-P value for frozen fries of 0.0174 mg/kg and an HR-P value of 0.131 mg/kg; and an STMR-P value for cooked fries of 0.0234 mg/kg and an HR-P value of 0.176 mg/kg for aldicarb in potato.

The Meeting received the result of use of a probabilistic method for estimating short-term dietary intake. The model and data applied only to the situation in the United Kingdom.

RECOMMENDATIONS

On the basis of data from supervised residue trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and estimation of dietary intake for plant commodities: sum of aldicarb, aldicarb sulfoxide and aldicarb sulfone, expressed as aldicarb. Acute RfD: 0.003 mg/kg bw

ADI (mg/kg bw)	Commodity		Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
	CCN	Name	New	Previous		
0-0.003	FI 0327	Banana	0.2	W	0.01	0.10
	VR 0589	Potato	0.5	0.5	0.06	0.45
		Potato, microwaved			0.042	0.315
		Potato flakes			0.045	
		Potato chips			0.228	
		Potato frozen fries			0.0174	
		Potato cooked fries			0.0234	

Dietary risk assessment

Long-term intake

Currently (1995), the ADI for aldicarb is 0–0.003 mg/kg bw. The dietary intake was calculated of the 21 commodities for human consumption for which CXLs exist and for banana and potato on the basis of the STMRs estimated in this evaluation. The results are shown in Annex 3 (Report 2001). The estimated dietary intake of aldicarb ranged from 6% of the ADI in the African diet to 20% in the Middle Eastern diet. The Meeting concluded that the intake of residues of aldicarb resulting from uses that have been considered by the JMPR is unlikely to present a public heath concern.

Short-term intake

An acute RfD of 0.003 mg/kg bw for aldicarb was established by the 1999 JMPR. The IESTI for aldicarb was calculated for banana and potato (Annex 4-Report 2001). For banana, it was 140% of the acute RfD for the general population and 330% of the acute RfD for children. For potato, it was 230% of the acute RfD for the general population and 560% of the acute RfD for children. The IESTI for microwaved potato was 160 and 400% of the acute RfD for the general population and children, respectively. The information provided to the Meeting precluded a conclusion that the acute dietary intake of banana and potato by children and adults would be below the acute RfD.

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CHLORPROPHAM (201)

IDENTITY

ISO common name: chlorpropham

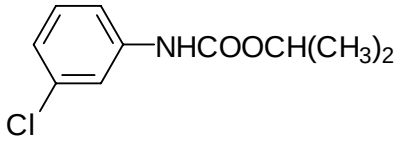
Chemical name:
IUPAC: isopropyl 3-chlorocarbanilate
CA: 1-methylethyl (3-chorophenyl)carbamate

CAS Registry no.: 101-21-3

CIPAC no.: 0043

Synonyms: CIPC

Structural formula:



Molecular formula: $C_{10}H_{12}ClNO_2$

Molecular weight: 213.7

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Appearance:	Light cream coloured crystalline solid with slight sweet ester odour (Wojcieck, 1993)		
Density:		1.17 g/cm^3 at 24°C	(Wojcieck, 1993)
Vapour pressure:		$2.46 \cdot 10^{-2}$ Pa at 25°C	(Lorence, 1993a)
		$8.02 \cdot 10^{-2}$ Pa at 35°C	(Lorence, 1993a)
		$2.65 \cdot 10^{-1}$ Pa at 45°C	(Lorence, 1993a)
Melting point:		38-41°C	(Wojcieck, 1993)
Octanol/water partition coefficient:		log P_{ow} = 3.4	(Lorence, 1993b)
Solubility:	water	0.017 g/100 g at 25°C	(Lorence, 1993c)
	n-octanol	>95 g/100 g at 25°C	(Lorence, 1993c)
	acetonitrile	>95 g/100 g at 25°C	(Lorence, 1993c)
	acetone	>95 g/100 g at 25°C	(Lorence, 1993c)
Hydrolysis:		no data submitted	
Photolysis:		no data submitted	
Dissociation constant:		pKa 13.3 at 20 ± 1°C in 19% ethanol (Hambrick, 1993)	
Thermal stability:		25-150°C range without decomposition (Malone, 1993)	

Technical material

Minimum purity:	>98%
Colour:	off-white to light brown
Physical State:	solid

Melting point: 38-40°C
Stability: stable indefinitely (Lorence, 1993d; Dewitt and Lorence, 1994)

FORMULATIONS

Commercially available formulations: DP, HN, TC, EC, SL

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Metabolism in rats (Robinson and Liu, 1991), lactating goats (Wu, 1991a) and laying hens (Wu, 1991b) was evaluated for toxicology by the 2000 JMPR. The same trials were reported to the 2001 Meeting for residue evaluation.

Rats (Robinson and Liu, 1991). Groups of male and female Sprague-Dawley rats were given single oral low and high doses, and single intravenous injections of ^{14}C-ring-labelled chlorpropham at 5, 200, and 0.5 mg/kg bw respectively. An additional group was dosed orally once daily for 14 days with 5 mg/kg of unlabelled chlorpropham, followed by single doses of the radiolabelled compound on day 15. An open test system was used because a negligible amount of $^{14}CO_2$ elimination was observed in the preliminary range-finding study. Urine and faeces were collected over 7-day intervals. 89-97% of the dose was excreted in the urine and 4-7% in the faeces over 7 days, most within 24 hours and minor amounts during days 2 and 3. Excretion did not vary significantly according to dose or sex. No significant levels of the administered dose were released into respired gases after oral dosing.

Analysis of tissues and organs showed that none of the low-dosed groups showed ^{14}C residues exceeding 0.05 mg/kg as chlorpropham. No ^{14}C residues were detected in the tissues or organs of the intravenous-dosed group. Tissues from the high-dose group showed higher residues than the other groups as expected.

Urine and faeces samples collected over the first 24 h were pooled according to sex, excreta type, and dose regimen. Filtered urine and acetonitrile extracts of faeces homogenates were analysed by reverse-phase HPLC. Major radioactive peaks of representative excreta samples were also isolated and compared with radioactive metabolite standards by normal-phase TLC for qualitative confirmation of structures.

A total of 21 metabolites, plus the parent chemical, were detected. Thirteen metabolites accounting for 88-95% of the administered dose were identified (Table 1). Most of the metabolites were found in the urine. No appreciable differences in the metabolite profiles were seen between dose groups or between males and females. In the urine, aryl *O*-sulfate conjugates accounted for approximately 58-70% of the administered dose. The main metabolites were *p*-hydroxy-chlorpropham *O*-sulfate, 3-chloro-4-hydroxyacetanilide *O*-sulfate and *p*-hydroxy-chlorpropham. The structures are shown in Figure 1. Most of the radioactivity in faeces was detected as free metabolites. Unchanged chlorpropham was detected in some faecal samples but not in urine. Three major metabolic pathways were proposed. In addition to aromatic hydroxylation, there is oxidation of the isopropyl side chain and hydrolysis to 3-chloroaniline.

Table 1. Combined distribution of chlorpropham and its metabolites in rat urine and faeces. Mean percentages of orally administered dose (Robinson and Liu, 1991). Structures of compounds are shown in Figure 2.

Compound		%
No.	Name	
	Chlorpropham (parent compound)	0.3

Compound		%
No.	Name	
M1	Chlorpropham alcohol	0.4
M3	Chlorpropham carboxylic acid	4.0
M4	*p*-Hydroxychlorpropham alcohol	1.7
	M4 sulfate	6.2
M2	*p*-Hydroxychlorpropham	14.3
	M2 sulfate	39.0
	M2 glucuronide	1.7
M5	3-Chloroaniline	0.6
	3-Chloro-4-hydroxyaniline sulfate (M6 sulfate)	2.4
	3-Chloro-4-hydroxyaniline *N*-glucuronide *O*-sulfate	1.1
M9	3-Chloro-4-hydroxyacetanilide	1.0
	M9 sulfate	15.5
	M9 glucuronide	0.7
	Unknown (8 metabolites)	1.0
	Total sulfate conjugates	64.1
	TOTAL (parent compound and all metabolites)	90.0

Goats (Wu, 1991a). Two lactating goats were dosed with capsules containing ^{14}C-ring-labelled chlorpropham plus lactose at a rate of 75 mg/day (equivalent to dietary exposure levels of 31.5-36 ppm in the feed or 1.6–1.9 mg/kg bw) for seven days. A control goat received capsules containing only lactose. Urine and faeces were collected daily and milk twice daily, and blood samples were taken on days 1, 3 and 5 and before slaughter. The goats were killed 24 hours after the last dose and liver, kidneys, heart, loin muscle, leg muscle, omental and peripheral fat were collected for analysis.

Extraction and fractionation procedures were combined with combustion, liquid scintillation counting (LSC), HPLC, TLC including two-dimensional TLC, and radiochromatography to characterize significant metabolites.

Mean excretion of the radioactivity in the urine, faeces and milk for 7 days and up to 24 h after the last dose was approximately 99%, 6% and 1% of the cumulative dose respectively. Transfer to liver was about 1%; to fat and muscle lower by 1 or 2 orders of magnitude.

Radioactivity in the milk, expressed as mg chlorpropham equivalents/kg, was constant throughout the study. Residues ranged from 0.32 to 0.45 mg/kg in the milk, 0.18-0.32 mg/kg in the liver, and 0.05 mg/kg in the kidneys, and was below the limit of detection in the hearts, muscles, and fat (<0.03 mg/kg). Residues in the blood were <0.03 mg/kg on day 1, <0.03-0.046 mg/kg on day 3, 0.06 mg/kg on day 5 and 0.09 mg/kg on day 7. The main metabolites identified in the milk, liver and kidneys are shown in Table 2 (average values expressed as a percentage of the TRR and as mg chlorpropham/kg). An unknown metabolite which had been detected in rat urine was found in the goat kidneys (3.7% of the TRR). In the fat chlorpropham was 88.5% of the TRR (0.03 mg/kg). No data on metabolite identification in excreta or blood were reported. The metabolic pathways are shown in Figure 1.

Table 2. Distribution of chlorpropham and its metabolites in milk and tissues of goats (Wu, 1991a). Structures are shown in Figure 1.

Substance		Milk		Liver		Kidney	
		% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
1	3-Chloro-4-hydroxyaniline sulfate (M6 sulfate)		<0.001		<0.001		<0.001

	Substance	Milk		Liver		Kidney	
		% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
2	3-Chloro-4-hydroxyacetanilide *O*-glucuronide (M9 glucuronide)						<0.001
3	3-Chloro-4-hydroxyacetanilide (M9)					3.8	0.003
4	*p*-Hydroxychlorpropham alcohol (M4)			1.0	0.003	0.55	<0.001
5	*p*-Hydroxy-chlorpropham *O*-glucuronide (M2 glucuronide)	3.7	0.014			3.5	0.002
6	3-Chloro-4-hydroxyacetanilide *O*-sulfate (M9 sulfate)	4.5	0.02	0.4	0.001	4.1	0.003
7	M4 aryl sulfate	5.0	0.02			1.1	0.001
8	Chlorpropham alcohol (M1)						
9	*p*-Hydroxy-chlorpropham (M2)	0.89	0.005	3.2	0.008		
10	3-Chloro-4-hydroxyaniline *N*-glucuronide *O*-sulfate						
11	Chlorpropham carboxylic acid (M3)			0.5	0.001		<0.001
12	Chlorpropham (parent)					1.1	0.001
13	*p*-Hydroxy-chlorpropham *O*-sulfate (M2 sulfate)	81	0.3			16.5	0.01
14	3-Chloraniline (M5)						<0.001
15	3-Chloro-4-hydroxyaniline (M6)						<0.001
16	3-Chloroacetanilide (M7)			1.95	0.004	1.3	0.001
17	3-Chloro-6-hydroxyacetanilide (M10)						<0.001
18	3-Chloro-6-hydroxyaniline (M8)					0.65	<0.001
19	3-Chloroaniline-*N*-sulfamate, potassium salt	0.89	0.005	3.2	0.008		<0.001
20	*p*-Methoxy-chlorpropham					1.1	0.001
	B-6, structure unknown (found in rat urine)					3.7	0.003
	Unknowns	3.3	0.013	1.5	0.005	14	0.009
	Nonpolar lipids	0.46	0.002	2.2	0.007	1.7	0.001
	Aqueous			4.2	0.01		
	Protease-hydrolyzable			59	0.16	23	0.014
	Acid-hydrolyzable			22	0.06	16	0.01
	Bound residues	0.75	0.003	4.4	0.01	8.8	0.005
	Total	100.5	0.38	103.5	0.28	100.9	0.064

Poultry (Wu, 1991b). Ten laying hens were dosed once daily with gelatine capsules containing 6 mg of ^{14}C-chlorpropham for seven days (3.3-4.2 mg/kg bw or 50 ppm in the diet). Five control hens received lactose only by capsule. During treatment excreta were collected once daily and eggs twice daily. Eight hours after the last dose the hens were killed and blood, breast and thigh muscle, fat, heart, gizzard, kidney, liver and skin were collected for analysis. During the dosing period, eggs and excreta were also collected for analysis. The methods used were as described above for goats.

During the 7 days and for 8 hours after the last dose 83% of the cumulative dose was recovered from the excreta and 0.03% from the total of eggs laid (0.01% in the whites and 0.02% in the yolks). Radioactivity in the yolks, expressed as mg chlorpropham equivalents/kg, was undetectable during the first 3 days then increased from 0.1 mg/kg on day 4 to 0.23 mg/kg on day 7, when a steady state had not been reached. In the whites residues ranged from 0.007 to 0.074 mg/kg reaching a plateau on day 6. ^{14}C residues in the liver and kidneys were 0.47 and 0.46 mg/kg, in the

skin and fat 0.15 and 0.19 mg/kg, in the gizzard, heart and blood 0.09, 0.04 and 0.09 mg/kg, and in thigh and breast muscle 0.015 and 0.006 mg/kg respectively. The main compounds in the eggs, liver and kidney, expressed as a percentage of the TRR and in mg/kg as chlorpropham are shown in Table 3. Parent chlorpropham was the main compound identified in the fat (92% of the TRR) and skin (68% of the TRR). *p*-Hydroxy-chlorpropham *O*-sulfate constituted 19% of the TRR in the skin. The metabolic pathways are shown in Figure 1.

Table 3. Distribution of chlorpropham and its metabolites in the eggs and tissues of hens (Wu, 1991b).

	Substance	White		Yolk		Liver		Kidney	
		% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
1	3-Chloro-4-hydroxyaniline sulfate (M6 sulfate)	22	0.016					3.8	0.015
2	3-Chloro-4-hydroxyacetanilide *O*-glucuronide (M9 glucuronide)							8.1	0.037
3	3-Chloro-4-hydroxyacetanilide (M9)					0.35	0.002	0.4	0.002
4	*p*-Hydroxychlorpropham alcohol (M4)							5.0	0.023
5	*p*-Hydroxy-chlorpropham *O*-glucuronide (M2 glucuronide)							9.3	0.042
6	3-Chloro-4-hydroxyacetanilide *O*-sulfate (M9 sulfate)							3.7	0.017
7	M4 sulfate	1.1	0.001						
8	Chlorpropham alcohol (M1)	2.3	0.002	3.4	0.007				
9	*p*-Hydroxy-chlorpropham (M2)					3.7	0.017		
10	3-Chloro-4-hydroxyaniline *N*-glucuronide *O*-sulfate	3.9	0.003						
11	Chlorpropham carboxylic acid (M3)	3.3	0.002					3.0	0.014
12	Chlorpropham (parent)	3.1	0.002	20	0.04	0.5	0.002	7.4	0.033
13	*p*-Hydroxy-chlorpropham *O*-sulfate (M2 sulfate)	7.7	0.006	32	0.06	4.3	0.02		
14	3-Chloraniline (M5)								
15	3-Chloro-4-hydroxyaniline (M6)							3.4	0.015
16	3-Chloroacetanilide (M7)	1.4	0.001	1.5	0.003				
	B-6, Unknown found in rat urine							5.5	0.025
	Organosoluble and water-soluble unknowns	39[1]	0.03'	10	0.02	12	0.055	6	0.027
	Lipophilic radioactivity			13	0.025	2.5	0.012		
	Protease-hydrolyzable			21	0.04				
	Enzyme- or acid-hydrolyzable 3-chloro-4-hydroxyaniline-related metabolites					64	0.3	25	0.11
	Other unknowns	16	0.01			12.5	0.06	20	0.09
	Total	99.8	0.073	100.9	0.195	99.85	0.468	100.6	0.45

[1]Seven unknowns, none exceeding 0.014 mg/kg

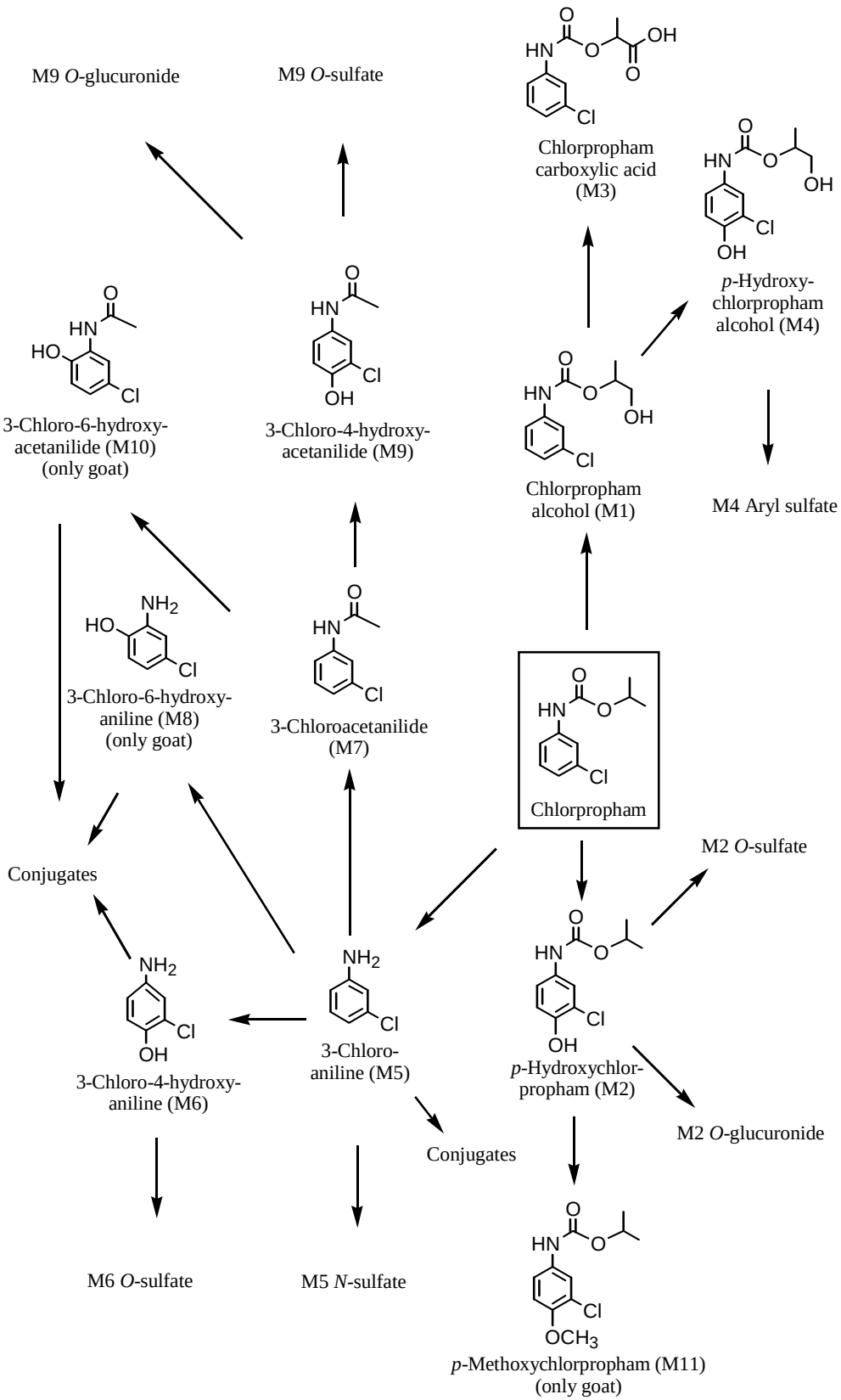


Figure 1. Proposed metabolic pathways in lactating goats and laying hens.

Plant metabolism

Potatoes (Kim-Kang, 1991). 164 potatoes, with an average size of 170 g, were treated with 1.5% ^{14}C-ring-labelled chlorpropham diluted from a 26% w/w emulsion at a nominal dose level of 40 mg/kg and stored in an incubator (8 ± 2°C) with circulating moist air simulating cold storage. Eight potatoes were sampled at 2 hours, 2 days, and 1, 3, 6, 9, 12, 16, 20, 24, 28, 32, 40, 44, 48 and 52 weeks after treatment, and the tubers washed with methanol to remove surface residues. Two potatoes from each sampling were homogenised as whole tubers, and 6 were peeled twice to yield peel, first layer and pulp. Each sample was diced, frozen in liquid nitrogen and homogenized for determination of the TRR.

Peel, pulp, first layer, and whole potatoes were extracted by blending with a modified Bligh-Dyer solvent mixture of methanol/water/chloroform ($MeOH/H_2O/CHCl_3$, 11:5:5). The $CHCl_3$ fraction was further partitioned with a mixture of acetonitrile (ACN) and hexane (1:1). The percentage of the TRR in each extracted fraction was determined for each sample. The final TRR levels after one year's storage (mg/kg as chlorpropham) were 1.2, 1.9, 20, and 4.2 mg/kg in the pulp, first layer, peel and whole potato respectively. A gradual decrease in the proportion of the TRR in the ACN fraction from the pulp and a gradual increase in the $MeOH/H_2O$ fraction was observed. Comprehensive analyses of the peel and pulp samples from the final harvest (52 weeks) showed 49.7% of the TRR in the ACN fraction, 39.5% in the $MeOH/H_2O$ fraction, 1.8% in the hexane fraction, and 9% in the post extraction solids (PES) from the pulp and 71%, 9.4%, 6.4%, and 13% in the ACN, MeO/H_2O, hexane, and PES fractions respectively from the peel.

Unextractable residues in the pulp PES digested with α-amyloglucosidase and yielded 6.7% of a non-starch material related to protein, cellulose, hemicellulose and lignin. The peel PES were treated with cellulase, then α-amyloglucosidase, followed by Bleidner distillation-extraction, giving ^{14}C residues of 2.75% in the cellulose, 1.25% in the starch and 8.8% in the cellulose/lignin subfractions.

In summary, under cold storage translocation of the radioactivity from the peel to the pulp was slow (Table 4). About 86% of the radioactivity remained on the surface of the potatoes after 364 days.

Table 4. Distribution of radioactivity in potatoes (Kim-Kang, 1991).

Days after treatment	^{14}C, % of TRR				Days after treatment	^{14}C, % of TRR	
	Methanol wash	Peel	1st layer	Pulp		Methanol wash	Whole potato
0 (2h)	98	1.9	0.02	0.04	0 (2h)	99	1.1
2	95.5	4.4	0.03	0.05	2	94	5.6
7	97	2.6	0.03	0.05	7	97	3.2
21	97	3.1	0.06	0.11	21	97	2.85
42	96	3.4	0.11	0.27	42	96	3.9
63	95	4.3	0.13	0.35	63	96	4.2
84	94	5.6	0.16	0.56	84	94	6.2
112	92	7.0	0.24	0.68	112	93	7.2
140	92	7.2	0.21	0.57	140	90.5	9.5
168	91.5	6.9	0.42	1.1	168	91.5	8.55
196	92	6.3	0.54	1.6	196	91	8.9
224	89.5	8.3	0.51	1.7	224	88.5	11.5
252	87	9.2	0.87	3.1	252	88	12
280	85	13	0.63	2.0	280	79	21
308	87	10.5	0.70	2.2	308	87.5	12.5
336	85	11	0.75	2.8	336	78	22
364	86	9.8	0.90	2.9	364	85	15

The compounds in the peel and pulp samples were determined at 52 weeks by two-dimensional TLC and radiochromatography. Seven compounds, including the parent, were identified. Most of the residue remained as chlorpropham. The main metabolites identified were an oligosaccharide conjugate of *p*-hydroxy-chlorpropham, a novel amino acid conjugate of *p*-hydroxy-chlorpropham found in the pulp and as a minor metabolite in the peel, and also included 3-chloroaniline, *p*-methoxy-chlorpropham, 3-chloro-*N*-glucosylaniline and an oligosaccharide conjugate of chlorpropham alcohol. Enzyme hydrolysis of PES (cellulase and α-amyloglucosidase) yielded some of the parent compound indicating that part of the chlorpropham was probably physically bound to endogenous carbohydrate material unextractable by conventional solvent-solvent extraction. The MeOH washes were also analysed by HPLC and 2-D TLC; chlorpropham was the only surface residue identified. The results are shown in Table 5. The three potential metabolic pathways listed below are shown in Figure 2.

1) Decarboxylation to 3-chloroaniline, followed by conjugation with glucose and other biomolecules.
2) Hydroxylation and subsequent conjugation with either oligosaccharides or amino acids at the position para to the amino moiety or methylation of *p*-hydroxy-chlorpropham to *p*-methoxy-chlorpropham.
3) Oxidation of the isopropyl side chain and subsequent conjugation with oligosaccharide(s).

Table 5. Distribution of ^{14}C residues in potato peel and pulp (Kim-Kang, 1991).

Substance (52 weeks after treatment)	Peel		Pulp	
	% of TRR	mg/kg as chlorpropham	% of TRR	mg/kg as chlorpropham
identified				
Chlorpropham	85	17	42	0.52
p-methoxy-chlorpropham			1.9	0.023
3-Chloroaniline	3.6	0.72		
3-Chloro-*N*-glucosylaniline	0.54	0.11	6.1	0.075
Oligosaccharide conjugate of *p*-hydroxy-chlorpropham	7.6	1.5	18	0.22
Oligosaccharide conjugate of chlorpropham alcohol	0.27	0.05		
Amino acid conjugate of *p*-hydroxy-chlorpropham	0.58	0.12	18	0.22
unknowns				
Polar unidentified	1.2	0.24	5.0	0.062
Non polar hexane soluble			1.8	0.022
Enzyme-hydrolyzed water-soluble	1.7	0.34	1.3	0.016
Bound residues			6.7	0.083
Total	100	20	100	1.24

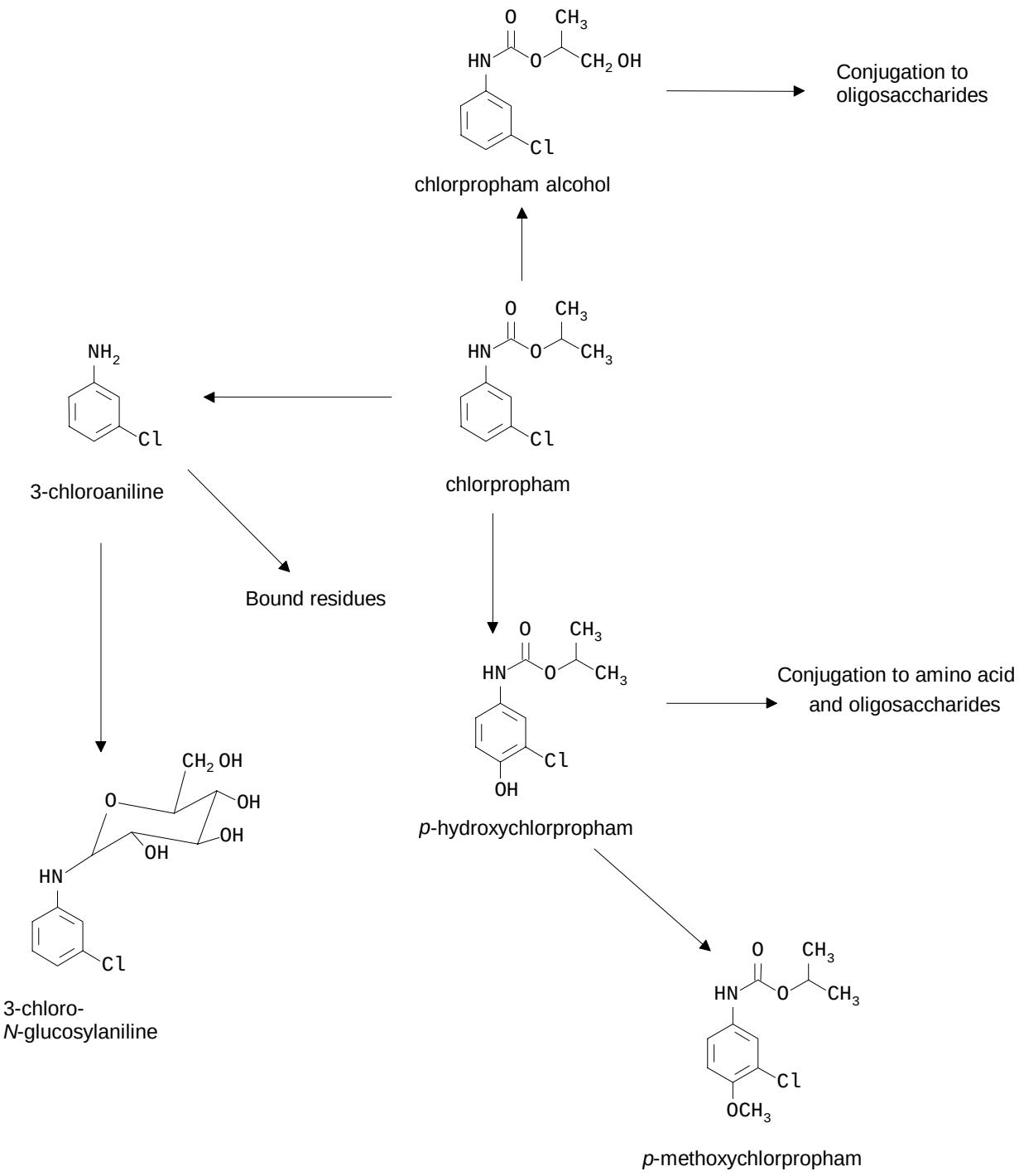


Figure 2. Proposed metabolic pathways in stored potatoes (Kim-Kang, 1991).

Environmental fate in soil

No information.

Environmental fate in water/sediment systems

No information.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Plant material

Potatoes. Analytical methods were reported for the determination of residues of chlorpropham alone or of the parent and three metabolites (3-chloroaniline, *p*-hydroxy-chlorpropham, *p*-methoxy-chlorpropham).

(Roland, 1998a,b). In the supervised trials (Tables 26-28) potatoes were rinsed in running water to remove any adhering soil and divided into representative parts before being completely thawed, to ensure subsampling homogeneity. The potatoes were peeled with a stainless steel paring knife as soon as the surfaces were sufficiently tenderized. The thickness of the peel was 1.3 ± 0.2 mm and fortification rates were 0.1, 1, 2 and 5 mg/kg for entire tubers, 0.02, 0.2, 0.5, 1 mg/kg for peeled and 0.02 and 0.1 mg/kg for cooked potatoes. Two independent analyses were made using separate subsamples of each part of the sample. 50 g of sample was homogenized with 200 ml of petroleum ether/acetone (1/1) and filtered. The apparatus and cake were then rinsed with 50 ml of the extraction mixture, and the extracts partitioned with 500 ml of water and 20 ml of saturated NaCl solution. The petroleum ether extract was filtered through anhydrous sodium sulfate and the aqueous phase re-extracted with 75 ml of methylene chloride. The methylene chloride extract was filtered through anhydrous sodium sulfate. The combined organic extracts were evaporated under vacuum and the dry residue dissolved in 5 ml of iso-octane. After further purification on a Florisil column, chlorpropham was eluted with 60 ml of hexane saturated with CH_3CN, the eluate evaporated under vacuum, and the dry residue dissolved in 2.5 ml of iso-octane. Determination was carried out by GLC with an NPD. The results are shown in Table 6.

Table 6. Recovery of chlorpropham from potatoes (Roland, 1998a,b).

Sample	Fortification level (mg/kg)	Chlorpropham recovered (mg/kg)	Recovery (%)
Entire tubers Untreated	0	<0.02	-
	0	<0.02	-
	0	<0.02	-
	0	<0.02	-
	0.1	0.106	106
	0.1	0.103	103
	0.1	0.104	104
	0.1	0.1	100
	2	1.9	95
	2	1.8	90
Peeled potatoes Untreated	0	<0.02	-
	0	<0.02	-
	0	<0.02	-
	0	<0.02	-
	0.02	0.02	100
	0.02	0.018	90
	0.02	0.021	105
	0.02	0.019	95
	0.5	0.5	100
	0.5	0.45	90
	0.5	0.49	98
	0.6	0.47	94

Sample	Fortification level (mg/kg)	Chlorpropham recovered (mg/kg)	Recovery (%)
Cooked potatoes Untreated	0	<0.02	-
	0	<0.02	-
	0.02	0.02	100
	0.02	0.018	90
	0.1	0.092	92
	0.1	0.089	89

(Brielbeck and Marx, 1996a,b). Recoveries of chlorpropham residues from unpeeled (1996a) and peeled potatoes (1996b) determined by GLC with an ECD after bromination were 88-94% at fortification levels of 0.3-0.4 mg/kg.

(Brielbeck and Marx, 1999c). Recoveries of chlorpropham residues from peeled and cooked and peeled and unpeeled raw potatoes determined by GLC with an NPD were 94-101% at fortification levels of 0.02-5 mg/kg.

(Moeller, 1991). In a method for the determination of chlorpropham and the three metabolites 3-chloroaniline, *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham potatoes are chopped in a food processor, and 50 g subsamples in a tall square bottle are homogenized in 100 ml of 50:50 methanol/0.5 N HCl using a polytron insertion homogenizer. The bottle is then heated to near boiling for 3 min at 50% power in a 1500 W microwave oven, cooled and 200 ml of 50:50 hexane/ethyl acetate added and shaken, followed by 20 ml of pH 7 phosphate buffer plus 25 ml of a 1 N NaOH solution, and the bottle is capped and shaken. The emulsion separates rapidly especially when chilled or set on a slow orbital shaker. After separation 100 ml of the upper hexane-ethyl acetate layer is filtered through sodium sulfate, 100 ml of extract is collected and evaporated in a turbo-vap evaporator under nitrogen and twice exchanged with n-hexane without going to dryness. The final exchange is automatically reduced to 0.5 ml of n-hexane which is then brought to 5 ml with mixing to obtain a final concentration of 5 g of sample per ml of n-hexane. The extract is analysed by gas chromatography with a nitrogen-phosphorus detector on a 15 m DB-5 megabore column equipped with a 1 m uncoated guard.

A recovery study was carried out on whole potatoes spiked with the analytes at 0.4 mg/kg and 1.2 mg/kg (n = 6 or 7). The recoveries at 1.2 mg/kg level were 69% for chlorpropham, 41% for 3-chloroaniline, 83% for *p*-hydroxy-chlorpropham and 78% for *p*-methoxy-chlorpropham, and at 0.4 mg/kg were 68% for chlorpropham, 38% for 3-chloroaniline, 87% for *p*-hydroxy-chlorpropham and 78% for *p*-methoxy-chlorpropham. The low recovery of 3-chloroaniline is similar to the results of the metabolism study (Kim-Kang, 1991) and appears to confirm the reactive incorporation of this compound into the insoluble post-extraction solids. The stability of the compounds under acidic hydrolysis conditions is verified.

(Walker *et al.*, 1993). In a multi-residue method for the determination of chlorpropham, 3-chloroaniline, *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham in potatoes, their processed products, and canola cooking oil the primary methanol-water extract is partitioned with methylene chloride. The post-extraction solids are filtered, mixed with a pH 6.5 NaCl-saturated phosphate buffer, sonicated, and partitioned with methylene chloride which is combined with the first extract. For oil-processed samples a GPC clean-up is necessary. The methylene chloride is evaporated in a stream of nitrogen and exchanged with n-hexane for analysis by capillary gas chromatography with a nitrogen-phosphorus detector. This method has been validated for the determination of chlorpropham and its metabolites in whole potatoes, potato peel and pulp, French fries and chips with and without skins, processed dried and wet peels, dehydrated granules and canola oil. The detection limits and practical limits of quantification for chlorpropham, *p*-hydroxy-chlorpropham, *p*-methoxy-chlorpropham and 3-chloroaniline were 0.08 and 0.45 mg/kg in whole potatoes, fresh pulp and peel, and processed wet peel, 0.2 and 1.1 mg-kg in French fries, 0.45 and 2.2 mg/kg in chips, 0.38 and 1.9 mg/kg in dehydrated granules and processed dried peel, and 2.9 and 14 mg/kg in canola oil.

Experimental recoveries (n = 6) at spiking levels of 5.3 and 13 mg/kg (8 and 20 mg/kg for canola oil) were above 60% with the exception of 3-chloroaniline in fresh potato peels which was not recovered. It is suggested that irreversible binding of 3-chloroaniline with the substrate could prevent extraction. Sonication gave recoveries of all analytes equal to or better than were achieved after 12 hours of refluxing at alkaline pH. The results are shown in Table 7.

Table 7. Recoveries of chlorpropham and its metabolites from fortified potato samples (Walker *et al*., 1993).

Analyte	Sample	Fortification level (mg/kg)	No. of samples[1]	Recovery, %
Chlorpropham	Whole potato	5.3	6 (1)	81-121
		13	6	70-95
	Potato pulp	5.3	6	72-94
		13	6 (1)	68-101
	Potato peel	5.3	6 (2)	36-126
		13	6 (1)	73-128
	Canola oil	8.0	6 (1)	68-82
		20	6	91-116
	French fries	5.3	6	77 -90
		13	6	77-11
	Potato chips	5.3	6	74-98
		13	6 (1)	80-151
	Dried peel	5.3	6 (2)	66-124
		13	6 (1)	80-140
	Wet peel	5.3	6	70-113
		13	6 (2)	65-92
	Dehydrated granule	5.3	6	81-104
		13	6	87-95
	MeOH/water	5.3	6 (1)	75-121
		13	6 (1)	86-121
p-Hydroxy-chlorpropham	Whole potato	5.3	6	74-104
		13	6	80-120
	Potato pulp	5.3	6 (3)	57-79
		13	6 (3)	62-94
	Potato peel	5.3	6 (3)	51-102
		13	6 (3)	57-97
	Canola oil	8.0	6 (1)	69-91
		20	6 (2)	94-124
	French fries	5.3	6	106-117
		13	6	74-112
	Potato chips	5.3	6	87-106
		13	6	83-104
	Dried peel	5.3	6 (1)	62-117
		13	6 (2)	65-134
	Wet peel	5.3	6	70-98
		13	6	80-97
	Dehydrated granule	5.3	6	77-102
		13	6	85-98
	MeOH/water	5.3	6	72-111
		13	6	80-113

Analyte	Sample	Fortification level (mg/kg)	No. of samples[1]	Recovery, %
p-methoxy-chlorpropham	Whole potato	5.3	6 (1)	81-123
		13	6	73-101
	Potato pulp	5.3	6	75-98
		13	6	72-98
	Potato peel	5.3	6 (3)	74-149
		13	6	72-119
	Canola oil	8.0	6 (1)	66-89
		20	6 (1)	94-126
	French fries	5.3	6	83-98
		13	6	77-114
	Potato chips	5.3	6	81-96
		13	6	88-113
	Dried peel	5.3	6	70-113
		13	6 (1)	80-132
	Wet peel	5.3	6	83-102
		13	6	87-102
	Dehydrated granule	5.3	6	90-115
		13	6	88-100
	MeOH/water	5.3	6 (1)	81-123
		13	6 (1)	88-131
3-Chloroaniline	Whole potato	5.3	6 (1)	68-77
		13	6 (5)	65-71
	Potato pulp	5.3	6 (5)	64-72
		13	6 (6)	51-68
	Potato peel	5.3	6 (6)	not detected
		13	6 (6)	not detected
	Canola oil	8.0	6 (6)	26-60
		20	6 (5)	54-72
	French fries	5.3	6	89-94
		13	6 (6)	59-68
	Potato chips	5.3	6	87-106
		13	6 (3)	62-77
	Dried peel	5.3	6 (1)	49-90
		13	6 (3)	55-108
	Wet peel	5.3	6 (1)	68-89
		13	6 (1)	60-85
	Dehydrated granule	5.3	6 (2)	34-89
		13	6	72-87
	MeOH/Water	5.3	6	75-117
		13	6 (1)	65-101

[1]Numbers in parentheses: nos. of samples with recoveries outside 70-120% range.

Goodrick *et al.* (1994) modified the method by using hexane-based calibration standards. (In the original method substrate-based standards were used with the aim of limiting the effects of interference.)

As before a methanol-water extract is partitioned with methylene chloride but the primary extractant is a 50:50 mixture of methanol and 0.5N HCl. The analysis is completed as before. The method has been validated for the determination of chlorpropham and 3-chloroaniline in whole potatoes, chips with peel, processed dried and wet peel, and dehydrated granules. The results are shown in Table 8.

Table 8. Recoveries of chlorpropham and 3-chloroaniline from fortified potato samples (Goodrick *et al.*, 1994).

Analyte	Sample	Fortification level (mg/kg)	No. of samples [1]	Recovery, %
Chlorpropham	Whole	0.5	6	82-106
		2	6	83-113
		8	6 (1)	43-105
	Chips with peel	4	6 (2)	94-141
		10	6 (4)	113-149
		20	6	70-105
	Processed wet peel	0.8	6	71-88
		2	6	85-104
		8	6 (3)	68-91
	Processed dried peel	2	6	73-93
		10	6 (1)	67 -92
		40	6 (1)	64-80
	Dehydrated granules	2	6	72-101
		10	6 (1)	ND-97
		40	6 (4)	41-73
3-Chloroaniline	Whole	0.5	6 (6)	20-26
		2	6 (6)	15-22
		8	6 (6)	17-37
	Chips with peel	4	6 (6)	34-67
		10	6 (6)	36-48
		20	6 (6)	8-28
	Processed wet peel	0.8	6 (6)	49-62
		2	6 (6)	36-50
		8	6 (6)	38-54
	Processed dried peel	2	6 (6)	46-62
		10	6 (6)	46-62
		40	6 (6)	24-55
	Dehydrated granules	2	6 (6)	46-57
		10	6 (6)	ND-62
		40	6 (5)	37-72

[1]Numbers in parentheses: nos. of samples with recoveries outside 70-120% range

Bogess (1993) validated a method for the determination of chlorpropham, 3-chloroaniline, *p*-hydroxy-chlorpropham, and *p*-methoxy-chlorpropham in whole potatoes, potato pulp, fresh and processed wet and dry peel, dehydrated granules, and chips and French fries with and without peel using gas chromatography with a specific nitrogen-phosphorus detector. The results are shown in Table 9.

Table 9. Recoveries of chlorpropham and metabolites from fortified potato samples (Bogess, 1993).

Analyte	Sample	Fortification level (mg/kg)	No. of samples[1]	Recovery, %
Chlorpropham	Whole	0.4	2 (2)	138-183
		1	2 (2)	169-177
	Pulp	0.4	2 (2)	122-155
		1	1	99
	Fresh peel	0.4	2 (1)	65-89
		1	2	76-78

Analyte	Sample	Fortification level (mg/kg)	No. of samples[1]	Recovery, %
	Processed wet peel	0.4	2 (1)	98-141
		1	2	80-81
	Processed dry peel	2	2	72-96
		5	2 (1)	108-126
	Dehydrated granules	2	2	83 -94
		5	2	89-94
	Potato chips	2	2	105-108
	French fries	0.4	2	76-78
		1	2	79-81
4'-Hydroxy-chlorpropham	Whole potato	0.4	2 (2)	59-126
		1	2 (2)	147-150
	Potato pulp	0.4	2 (2)	29-32
		1	1 (1)	40
	Fresh peel	0.4	2 (1)	60-78
		1	2 (1)	66-72
	Processed wet peel	0.4	2 (1)	56-113
		1	2	74-93
	Processed dry peel	2	2 (1)	56-113
		5	2 (2)	122-140
	Dehydrated granules	2	2	91-98
		5	2	96-98
	Potato chips	2	2	72-97
	French fries	0.4	2	86-89
		1	2	83-83
p-methoxy-chlorpropham	Whole potato	0.4	2 (1)	94-150
		1	2 (2)	153-158
	Potato pulp	0.4	2 (1)	109-134
		1	1	102
	Fresh peel	0.4	2 (1)	69-91
		1	2	79-82
	Processed wet peel	0.4	2 (1)	94-137
		1	2	89-92
	Processed dry peel	2	2 (1)	66-109
		5	2 (2)	132- 150
	Dehydrated granules	2	2	93-106
		5	2	95-99
	Potato chips	2	2	71-75
	French fries	0.4	2	83-87
		1	2	83-84
3-Chloroaniline	Whole potato	0.4	2 (2)	39-51
		1	2 (2)	38-55
	Potato pulp	0.4	2 (2)	39-40
		1	1 (1)	41
	Fresh peel	0.4	2 (2)	44-57
		1	2 (2)	48-68
	Processed wet peel	0.4	2 (2)	40-56
		1	2 (2)	41-43
	Processed dry peel	2	2 (2)	33-53
		5	2 (1)	57-77
	Dehydrated granules	2	2 (2)	51-63
		5	2 (2)	62-63

Analyte	Sample	Fortification level (mg/kg)	No. of samples[1]	Recovery, %
	Potato chips	2	2 (2)	36-38
	French fries	0.4	2 (2)	23-39
		1	2 (2)	27-29

[1]Numbers in parentheses: nos. of samples with recoveries outside 70-120% range.

Bogess (1994) conducted a supplementary study on whole potatoes spiked with chlorpropham at higher levels. The results are shown in Table 10.

Table 10. Recoveries of chlorpropham from fortified samples of whole potatoes (Bogess, 1994).

Analyte	Fortification level (mg/kg)	No. of samples	Recovery, %
Chlorpropham	2	2	58, 73
	5	2	81, 85

Animal material

Note: *p*-Hydroxy-chlorpropham *O*-sulfate has been widely referred to as 4'-hydroxy-chlorpropham-*O*-sulfonic acid, with the abbreviation HSA. In the following sections the compound will be named *p*-hydroxy-chlorpropham sulfate, but the abbreviation HSA will be used.

Daun (1995a,b, 1996a,b) developed and validated a method for the determination of residues of chlorpropham and *p*-hydroxy-chlorpropham sulfate (HSA) in meat and milk. Homogenized samples of whole milk, skimmed milk, cream, muscle, liver, kidney, and fat are ground in a glass mortar with 40 μm C-18 solid-phase material (Bakerbond Octadecyl (C_{18}) Prep LC Packing). The mixture is packed into a polymeric column and eluted sequentially with 1:1 hexane/dichloromethane (DCM), pure DCM, and methanol/water (5:1). The hexane/DCM eluate is evaporated to near dryness, reconstituted in hexane, partitioned with acetonitrile (ACN), concentrated under vacuum and, after water is added, partitioned back into hexane and diluted to known volume for determination of chlorpropham by gas chromatography with mass-selective detection (GLC-MSD). The DCM fraction is discarded.

The methanol/water eluate is passed through a solid-phase extraction (SPE) cartridge containing a quaternary ammonium bonded phase. The cartridge is washed with methanol and water and the *p*-hydroxy-chlorpropham-*O*-sulfonic acid eluted with dilute alkali. The fraction containing the *p*-hydroxy-chlorpropham-*O*-sulfonic acid is analysed by HPLC on a reverse-phase column with detection and measurement at 238 nm.

Table 11. Recoveries of chlorpropham and HSA from fortified control samples of milk and tissues of cattle (Daun, 1995a,b, 1996b).

Analyte	Sample	Fortification level (mg/kg)	No. of samples [1]	Recovery, %
Chlorpropham	Whole milk	0.01	3 (1)	113-130
		0.1	3 (1)	109-129
	Skimmed milk	0.01	3	72-86
		0.1	3	78-106
	Cream	0.01	3 (1)	12-108
		0.1	3	103-127
	Muscle	0.01	3	89-113
		0.1	3 (1)	85-122

Analyte	Sample	Fortification level (mg/kg)	No. of samples [1]	Recovery, %
	Liver	0.01	3 (3)	123-143
		0.1	3	106-114
	Kidney	0.01	3 (1)	100-165
		0.1	3	87-94
	Fat	0.01	3 (1)	25-118
		0.1	3	99-102
HSA	Whole milk	0.05	3	85-95
		0.5	3	83-87
	Skimmed milk	0.05	3	75-88
		0.5	3	81-83
	Cream	0.05	3 (1)	67-81
		0.5	3	82-97
	Muscle	0.05	3	87-95
		0.5	3 (1)	69-72
	Liver	0.05	3 (2)	66-80
		0.5	3	71-104
	Kidney	0.05	3	75-95
		0.5	3	70-105
	Fat	0.05	3	92-101
		0.5	2	79, 95

[1]Numbers in parentheses: nos. of samples with recoveries outside 70-120% range.

Daun and Zeller (1995) determined chlorpropham in the milk and tissues of dairy cows after solid-phase extraction followed by elution with organic solvents and further isolation through partition between immiscible solvents. Chlorpropham is determined in the purified extract by gas chromatography with mass selective detection (GC-MSD).

p-Hydroxy-chlorpropham-*O*-sulfonic acid (HSA) is determined in whole and skimmed milk by dilution with acetonitrile, selective precipitation of interfering substances and analysis of the resulting solution by reverse-phase HPLC with UV detection. HSA is isolated from tissues and cream using a single-phase extraction system. The aqueous phase is reduced in volume and further purified on a C-18 SPE cartridge. HSA is determined in the eluate by reverse-phase HPLC as before.

The limits of quantification (LOQs) of chlorpropham and HSA were 0.01 and 0.05 mg/kg respectively. The recoveries are shown in Tables 12-14.

Table 12. Recoveries of chlorpropham and HSA from whole milk (Daun and Zeller, 1995).

Day of treatment	Fortification level (mg/kg)	Recovery, %	
		Chlorpropham	HSA
0	0.01	100, 118	
	0.05	113	71, 77, 83
	0.1	87, 77, 119	
	0.5	85, 83, 77	
1	0.01	163, 191	
	0.05	116	87, 93
	0.1	101, 88, 57	
	0.5	98, 87, 75	
4	0.05	101, 91, 97	73, 70
	0.1	104, 82	101
	0.5	83	85, 82

Day of treatment	Fortification level (mg/kg)	Recovery, %	
		Chlorpropham	HSA
	10		72
	0.01	97	
	0.05	72, 65	83
	0.1	49, 78, 75	70, 87
	0.5		77
7	10		88, 73
	0.05	88, 92, 76	87, 74, 57
	0.1	95, 100, 96	
10	0.5		86, 76, 82
	0.05	118, 105	65, 90, 54
	0.1	132, 102, 98	
14	0.5		72, 77, 71
24	0.05	62	
	0.05	84	
	0.1	154	
28	0.5		72

Table 13. Recoveries from skimmed milk and cream samples fortified with chlorpropham or HSA (Daun and Zeller, 1995).

Sample	Fortification level (mg/kg)	Recovery, %	
		Chlorpropham	HSA
Skimmed milk	0.05	117, 116	68, 78
	0.1	63, 112	
	0.5		79, 85
Cream	0.05	106, 103	102, 86
	0.1	89, 82	
	0.5		89, 108

Table 14. Recoveries from tissue samples fortified with chlorpropham or HSA (Daun and Zeller, 1995).

Sample	Fortification level (mg/kg)	Recovery, %	
		Chlorpropham	HSA
Liver	0.01	261, 228	
	0.05		88, 108
	0.1	105, 88	
	0.5		78, 81
Muscle	0.01	134, 173, 209	
	0.05		86, 74
	0.1	91, 100, 80	
	0.5		77, 71
Kidney	0.01	128, 389, 273	
	0.05		96, 142
	0.1	99, 72, 71	
	0.5		83
	5		102
Fat	0.01	224	
	0.05	83, 129	97, 86

Sample	Fortification level (mg/kg)	Recovery, %	
		Chlorpropham	HSA
	0.1	109	
	0.5		100, 96
	5	110	
	10	73	

Stability of pesticide residues in stored analytical samples

Plants

Goodrick *et al.* (1993a) investigated the storage stability of chlorpropham and metabolites in fortified untreated tuber samples which were also processed into pulp, peel, French fries, chips, processed wet and dried peel and dehydrated granules. Subsamples of each were spiked with 2 or 20 mg/kg of chlorpropham, 3-chloroaniline, *p*-hydroxy-chlorpropham or *p*-methoxy-chlorpropham and stored frozen at –20 to -21°C before analysis at 0 and 14 days, 1 and 2 months, and monthly thereafter up to 390 days for whole potatoes and fresh peel, 360 days for pulp and processed dried peel, 272 days for French fries, 240 days for chips and dehydrated granules, and 180 days for processed wet peel. The results are shown in Tables 15 and 16.

The stabilities of all the analytes were broadly similar at the two fortification levels but were low for 3-chloroaniline and *p*-hydroxy-chlorpropham. Of the 64 sample-analyte combinations 40 decreased by 3% or less per month and 15 showed monthly negative rates from 3.4-6.8%. 3-Chloroaniline and *p*-hydroxy-chlorpropham were unstable in whole potatoes, pulp and peel after 90 days, and 3-chloroaniline in processed wet peel. The instability in the fresh samples may be because of reaction with the substrate.

Table 15. Highest and lowest percentages of chlorpropham and its metabolites remaining in processed potato products after frozen storage (Goodrick *et al*., 1993a).

Compound	Highest remainder		Lowest remainder	
	mean ± sd	Product/fort. level/days	mean ± sd	Product/fort. level/days
Chlorpropham	98 ± 26	Dried peel/20 mg/kg/360	60 ± 28	French fries/2 mg/kg/272
3-Chloroaniline	64 ± 21	Dried peel/20 mg/kg/360	24 ± 12	Fresh peel/2 mg/kg/390
p-Hydroxy-chlorpropham	91 ± 30	Dried peel/2 mg/kg/360	28 ± 19	Pulp/20 mg/kg/360
p-Methoxy-chlorpropham	105 ± 32	Dried peel/20 mg/kg/360	63 ± 24	French fries/2 mg/kg/272

Table 16. Storage stability of analytes in potatoes and their processed products fortified with chlorpropham or its metabolites (Goodrick *et al*., 1993a).

Sample	% Change per month[1]							
	Chlorpropham		3-chloroaniline		*p*-hydroxychlor-propham		*p*-methoxychlor-propham	
	2 mg/kg	20 mg/kg	2 mg/kg	20 mg/kg	2 mg/kg	20 mg/kg	2 mg/kg	20 mg/kg
Whole potato	-2.7	-1.2	-2.3	-8.7	-5.2	-9.1	-2.1	0.6
Pulp	-2.1	-0.1	-6.2	-9.1	-6.1	-10	-0.8	1.7
Fresh peel	-2.0	-2.4	1.5	-7.0	0.6	-8.8	-1.9	-2.1

Sample	% Change per month[1]							
	Chlorpropham		3-chloroaniline		*p*-hydroxychlor-propham		*p*-methoxychlor-propham	
	2 mg/kg	20 mg/kg	2 mg/kg	20 mg/kg	2 mg/kg	20 mg/kg	2 mg/kg	20 mg/kg
Dehydrated granules	-5.9	-4.2	-6.8	-5.2	-4.9	-4.9	-4.5	-2.5
French fries	-4.1	-4.7	-2.0	-1.4	-3.0	-3.0	-2.9	-3.4
Chips	-2.7	7.8	-4.4	3.2	-0.5	4.1	-1.1	2.5
Processed wet peel	0.8	-2.0	-13	-12	6.8	6.0	1.5	0.5
Processed dried peel	2.5	1.2	-5.3	-6.3	-0.5	3.5	1.0	0.7

[1] Calculated using secular trend analysis, based on expected 365 days value using a linear regression model. Positive rates of change are artefacts of the measurement system according to the author.

Haws *et al.* (1993a,b) investigated the storage stability of chlorpropham in field-treated potato tubers and their products. The potatoes were treated under practical conditions (aerosol fogging) and processed to produce fresh peel, chips and French fries with skin, dehydrated granules, and dried and wet peel, then homogenized and stored at -20 to -21°C. Residues were determined at intervals up to 272-391 days. As different field samples were analysed at successive storage times the results (Table 17) are of limited use. The initial concentrations of 3-chloroaniline, *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham were below practical limits of quantification and detection and therefore not suitable for a stability study.

Table 17. Stability of chlorpropham in field-treated potatoes and their processed products stored at -20 to -21°C (Haws *et al.*, 1993a,b).

Sample	Chlorpropham (mg/kg), mean of two samples												
	Days in freezer at -20 to -21°C												
Whole potatoes	**9**	**20**	**30**	**62**	**91**	**121**	**184**	**218**	**283**	**305**	**333**	**361**	**391**
	11	9.9	8.7	10	10	8.6	6.5	5.1	12	6.1	8.0	6.7	11
Fresh peel	**Days in freezer at -20 to -21°C**												
	9	**20**	**30**	**62**	**91**	**121**	**184**	**218**	**283**	**300**	**333**	**361**	**391**
	62	51	46	58	61	17	61	39	59	43	58	46	56
Potato chips with skin	**Days in freezer at -20 to -21°C**												
	20	**62**	**91**			**121**	**156**	**182**	**215**	**231**	**282**		
	4.5	5.2	3.7			5.8	9.9	12	13	3.4	3.1		
French fries with skin	**Days in freezer at -20 to -21°C**												
	20	**30**	**62**	**91**	**121**	**154**	**182**	**215**	**282**	**304**			
	2.5	3.5	2.5	2.4	3.2	3.0	3.0	2.8	2.3	3.2			
Dehydrated granules	**Days in freezer at -20 to -21°C**												
	5	**13**	**29**	**61**	**95**	**152**	**179**	**209**	**272**				
	1.8	2.4	2.7	2.1	2.3	2.5	2.6	2.3	1.9				
Processed dried peels	**Days in freezer at -20 to -21°C**												
	6	**14**	**30**	**62**	**96**	**120**	**153**	**180**	**210**	**272**	**300**	**330**	**362**
	88	96	78	94	58	49	154	137	105	125	135	160	133
Processed wet peels	**Days in freezer at -20 to -21°C**												
	9	**42**	**62**	**91**	**121**	**153**	**183**	**217**		**272**			
	33	34	27	37	22	23	26	37		39			

Mammalian products

Storage stability studies were conducted on liver, muscle and milk (Daun and Zeller, 1995; Daun, 1996b). Samples were fortified with 0.1 mg/kg chlorpropham or HSA and stored under the same conditions as samples collected from treated cows (-20°C) to provide for a minimum of duplicate analyses at each of 6 time points plus several contingency samples. Samples were analysed on the day of fortification and after various periods of storage (Tables 18 and 19).

Table 18. Storage stability at -20°C of chlorpropham in fortified samples of milk, liver and muscle of cows (Daun and Zeller, 1995; Daun, 1996b).

Sample	Storage period (days)	Fortification level (mg/kg)	Chlorpropham found (mg/kg)	% remaining	% of fresh fortification
Whole milk	NA	Control	<0.01	NA	
	0	0.1	0.112	112	
	0	0.1	0.079	79	
	NA	Control	<0.01	NA	
	0	0.1	0.094	94	
	7	0.1	0.096	96	102
	7	0.1	0.087	87	92
	NA	Control	<0.01	NA	
	0	0.1	0.113	113	
	29	0.1	0.079	79	70
	29	0.1	0.083	83	73
	NA	Control	<0.01	NA	
	0	0.1	0.088	88	
	59	0.1	0.07	70	79
	59	0.1	0.062	62	70
	NA	Control	0.019	NA	
	0	0.1	0.093	93	
	127	0.1	0.078	78	84
	127	0.1	0.089	89	96
Liver	NA	Control	0.011	NA	
	0	0.1	0.081	81	
	0	0.1	0.073	73	
	NA	Control	0.018	NA	
	0	0.1	0.078	78	
	7	0.1	0.104	104	133
	7	0.1	0.057	57	73
	NA	Control	0.01	NA	
	0	0.1	0.103	103	
	14	0.1	0.089	89	87
	NA	Control	0.012	NA	
	0	0.1	0.094	94	
	28	0.1	0.085	85	91
	28	0.1	0.091	91	98
Muscle	NA	Control	0.022	NA	
	0	0.1	0.082	82	
	0	0.1	0.094	94	
	NA	Control	0.01	NA	
	0	0.1	0.102	102	
	7	0.1	0.104	104	102
	7	0.1	0.08	80	78
	NA	Control	0.021	NA	
	0	0.1	0.096	96	
	15	0.1	0.076	76	80
	15	0.1	0.077	77	80
	NA	Control	<0.01	NA	
	0	0.1	0.105	105	
	29	0.1	0.112	112	107
	29	0.1	0.126	126	120
	NA	Control	<0.01	NA	
	0	0.1	0.091	91	
	59	0.1	0.092	92	102
	59	0.1	0.084	84	93

NA: not applicable

Table 19. Storage stability at -20°C of HSA in fortified samples of milk, liver and muscle of cows (Daun and Zeller, 1995; Daun, 1996b).

Sample	Storage period (days)	Fortification level (mg/kg)	HSA found (mg/kg)	% remaining	% of fresh fortification
Whole milk	NA	Control	<0.05		
	0	0.1	0.077	77	
	0	0.1	0.075	75	
	NA	Control	<0.05	NA	
	0	0.1	0.076	76	
	7	0.1	0.064	64	86
	7	0.1	0.08	80	105
	NA	Control	<0.05	NA	
	0	0.1	0.085	85	
	14	0.1	0.086	86	101
	14	0.1	0.084	84	99
	NA	Control	<0.05	NA	
	0	0.1	0.078	78	
	31	0.1	0.083	83	107
	31	0.1	0.082	82	106
	NA	Control	<0.05	NA	
	0	0.1	0.081	81	
	59	0.1	0.046	46	57
	59	0.1	0.076	76	94
	NA	Control	<0.05	NA	
	0	0.1	0.076	76	
	133	0.1	0.073	73	96
	133	0.1	0.07	70	91
Liver	NA	Control	<0.05	NA	
	0	0.1	0.071	71	
	0	0.1	0.069	69	
	NA	Control	<0.05	NA	
	0	0.1	0.103	103	
	7	0.1	0.079	79	77
	7	0.1	0.075	75	73
	NA	Control	<0.05	NA	
	0	0.1	0.108	108	
	16	0.1	0.076	76	70
	16	0.1	0.07	70	64
	NA	Control	0.06	NA	
	0	0.1	0.155	155	
	30	0.1	0.111	111	72
	30	0.1	0.103	103	67
	NA	Control	<0.05	NA	
	0	0.1	0.135	135	
	59	0.1	0.102	102	76
	59	0.1	0.099	99	73
Muscle	NA	Control	<0.05	NA	
	0	0.1	0.04	40	
	0	0.1	0.054	54	
	NA	Control	<0.05	NA	
	0	0.1	0.066	66	
	7	0.1	0.06	60	91
	7	0.1	0.052	52	79
	NA	Control	0.001	NA	
	0	0.1	0.061	61	
	21	0.1	0.044	44	73
	21	0.1	0.052	52	85
	NA	Control	<0.05	NA	
	0	0.1	0.041	41	
	34	0.1	0.055	55	132

Sample	Storage period (days)	Fortification level (mg/kg)	HSA found (mg/kg)	% remaining	% of fresh fortification
	34	0.1	0.051	51	123
	NA	Control	<0.05	NA	
	0	0.1	0.069	69	
	41	0.1	0.047	47	68
	41	0.1	0.056	56	81
	NA	Control	<0.05	NA	
	0	0.1	0.066	66	
	63	0.1	0.028	28	43
	63	0.1	0.075	75	114
	NA	Control	0.003	NA	
	0	0.1	0.079	79	
	92	0.1	0.068	68	86
	92	0.1	0.066	66	84
	NA	Control	0.006	NA	
	0	0.1	0.066	66	
	122	0.1	0.059	59	90
	122	0.1	0.055	55	84

NA: not applicable

Definition of the residue

Plants (potatoes). Metabolism studies on stored potatoes established that 10% of the applied radioactivity was in the peel after washing and 3% in the pulp. 85% of the residue in the peel was chlorpropham and 3.5% 3-chloroaniline. In the pulp 42% was chlorpropham, two different conjugates of *p*-hydroxy-chlorpropham each accounted for 18%, and 6% was a conjugate of 3-chloroaniline. Thus the main metabolic pathway was hydroxylation at the *p*- position and subsequent conjugation. A minor pathway was decarboxylation to 3-chloroaniline.

In a supervised residue trial on stored potatoes the only metabolite detected was 3-chloroaniline at about 2% of the level found for chlorpropham but the analytical method for 3-chloroaniline showed insufficient recoveries (approximately 40-70% from whole potato, pulp and peel at a fortification level of 0.4 mg/kg). Residues of *p*-methoxy-chlorpropham and *p*-hydroxy-chlorpropham or its conjugates were not detected. Although the samples were kept frozen for several months before analysis, the absence of these metabolites was confirmed in the storage stability study included in this trial, and they were not detected shortly after sampling and processing.

On the basis of these findings the Meeting recommended that the definition of the residue in potatoes for enforcement and risk assessment purposes should be chlorpropham *per se*.

Animal products. In metabolism studies on rats, goats and hens chlorpropham was rapidly virtually fully absorbed, extensively metabolised and quickly excreted. However there were differences between the ultimate residue composition in the edible products of hens and goats.

In hens 92% and 68% of the residue in the fat and skin respectively was chlorpropham, and in other tissues and in eggs it was 3-chloro-4-hydroxyaniline conjugates ranging from 22-70%, in eggs the main compound is the *O*-sulfonic acid conjugate. Since these conjugates together are a major residue in these tissues and in eggs, they should be included in the definition of the residue. As potatoes are less than 10% of the feed for poultry (see FAO Manual p125), and no hen feeding study nor analytical method for poultry products were submitted, no definition of the residue in poultry products is recommended.

In goats, the main residue in milk and kidney is *p*-hydroxy-chlorpropham *O*-sulfonate (HSA; 81% and 16% of the TRR respectively), and in fat tissues it is chlorpropham (88%). No methods of analysis are available to determine the two residues simultaneously. As the metabolite was

considered to be of no toxicological significance by the 2000 JMPR, the Meeting agreed that the residue definition for animal products for compliance with the MRL and dietary risk assessment should be chlorpropham only.

The chlorpropham log P_{OW} of 3.4 and the presence of chlorpropham in fat and cream but not in muscle or skimmed milk in the dairy cow feeding study indicate fat-solubility. No octanol/water partition coefficient was reported for HSA but the chemical nature of the molecule suggests that its fat-solubility would be low.

USE PATTERN

Chlorpropham is used as a growth regulator to suppress potato sprouting during storage after harvest. This use is registered in Australia, Europe and the USA (Table 20). Labels were submitted by Australia (Simpson and Hamilton, 2001) and the Chlorpropham Task Force in the USA. Germany provided information on GAP, but without labels.

Further uses are for weed control as a pre- or post-emergence herbicide for vegetables and flower bulbs in Europe (Table 21). As the product is applied at an early stage, a post-harvest interval is not specified. Labels were submitted by the Chlorpropham Task Force in the USA.

Table 20. Registered uses of chlorpropham for the post-harvest treatment of ware potatoes for sprout control.

Country	Form, conc. ai	Application				WhP[1] (days)
		Method	Remarks/label information	Rate (kg ai/t)	No.	
Australia	DP 25 g/kg	dusting	Treatment must be managed so that potatoes removed from storage and sent for processing contain less than 30 mg/kg chlorpropham	0.038		
	SL 500 g/l	fogging	Application rate will depend upon storage conditions. Retreatment may be necessary if residues fall below 25 mg/kg.	0.03		
Belgium	DP 10 g/kg	dusting		0.018-0.02		
	HN 300 g/l	hot fogging	In air-cooled storage	0.018		
	EC 300 g/l	spraying or fogging	On the conveyor belt (no hot fogging)	0.018	1	
France	DP 10 g/kg	dusting		0.01		
Germany	DP 10 g/kg	dusting		0.01-0.02	1	
Netherlands	DP 10 g/kg	dusting	In air-cooled boxes up to 6°C Re-treatments are possible	0.01		60
		dusting	Normal cool storage	0.02	1	
	HN 300 g/l	fogging		0.018[2]	1-3	
UK	HN 500 g/l	hot fogging in boxes	Retreatments should be after 80-100 days, 45 days apart, if the storage period is uncertain, use half dose rate.	0.045[2] 0.015		21
		hot fogging in bulk	Minimum interval of 45 days between treatments	0.053[2] 0.018		
	M 300 g/l	fogging in boxes and bulk	Retreatments should be after 45-90 days	0.064[2] 0.014-0.021	3	21
	LF 500 g/l	fogging in boxes	Retreatments should be after 45-90 days	0.014-0.021	3	21
		fogging in bulk	1st application 2nd and 3rd application	0.021 0.014	3	21
	M 500 g/l	fogging in boxes	Retreatments should be after 45-90 days	0.014-0.021	3	21
		fogging in bulk	1st application 2nd and 3rd application	0.021 0.014	3	21

Country	Form, conc. ai	Application				WhP[1] (days)
		Method	Remarks/label information	Rate (kg ai/t)	No.	
	GR 50 g/kg	Sprinkling of granules over the top of boxes and bulk	Retreatments by fogging should be made using other formulations, 45-90 days between applications	0.025	3	21
	M 500 g/l	fogging boxes		0.021	5	21
		fogging n bulk		0.014	5	21
	M 600 g/l	hot fogging in boxes	Retreatments should be after 80-100 days.	0.018		21
		hot fogging in bulk	If the storage period is uncertain use half dose rate	0.015		21
USA	EC 250 g/l	spraying	Spraying on the conveyor belt during transport into storage	0.01		
	EC 240 g/l	spraying	Spraying on the conveyor belt during transport into storage	0.01		
	Aerosol 1000 g/l	fogging	Re-treatments are possible; adapt rate to storage period and temperature	0.015-0.025		
	Aerosol 840 g/l	fogging	Re-treatments are possible; adapt rate to storage period and temperature	0.015-0.022		

[1] Withholding period
[2] Maximum total dose

Table 21. Registered uses of chlorpropham for weed control.

Crop	Country	Form, conc. ai	Application			
			Method	Remarks	Rate (kg ai/ha)	No.
Carrots	UK	EC 400 g/l	spraying pre-emergence	within 3 days of drilling	1.1-1.7	1
Grassland	Netherlands	EC 400 g/l			1.2-1.6	
Leek	UK	EC 400 g/l	spraying pre-emergence		1.1-4.5 4.5	1
Lettuce	UK	EC 400 g/l	spraying pre-emergence		1.1	1
Onion	UK	EC 400 g/l	spraying pre-emergence post-emergence to 4 leaf stage		1.1-4.5 2.2	1
Flower bulbs	Netherlands	EC 400 g/l			1.6	
Flower bulbs	UK	EC 400 g/l	spraying pre-emergence	to weed-free soil	1.6-4.5	1
	UK	EC 400 g/l	spraying post-emergence	at plant height of 5 cm and post-flowering	2.2-3.4	1
	UK	EC 400 g/l	spraying post-emergence	before leaves unfold	2.2	1
Parsley	UK	EC 400 g/l	spraying pre-emergence	immediately after drilling	0.8-1.1	1

RESIDUES RESULTING FROM SUPERVISED TRIALS

Animal products

Cows (Daun and Zeller, 1995). In a feeding study on cows to determine chlorpropham and HSA (*p*-hydroxy-chlorpropham sulfate) residues in edible tissues and milk four groups consisting of three animals each were fed at nominally 0, 290, 870 and 2900 ppm in the feed for 28 days. Actual mean chlorpropham dietary burdens were 322 ppm, 955 ppm, and 3111 ppm based on feed consumption during the study. No changes in milk production or feed consumption, or any other adverse reactions were observed.

Samples of milk were collected twice daily from each animal from day -1. Afternoon samples were stored at approximately 5°C until combined with the next morning's sample, then stored frozen at -20°C. Tissue samples were collected within 16-24 hours after the last dose. Extreme care was taken to maintain tissue sample integrity through processing, extraction, and analysis. The tissue samples were kept on wet ice until ground with liquid nitrogen, and stored at -20°C until extraction.

Low levels of chlorpropham were found in the whole milk, muscle, liver, and kidneys. The fat contained levels from 0.09 mg/kg in one of the cows treated at 332 ppm to 2.8 mg/kg in one treated at 3111 ppm. Chlorpropham in the cream varied from 0.02 mg/kg (cow No. 5, 322 ppm) to 0.64 mg/kg (cow No. 11, 3111 ppm). Minor background chromatographic responses were present in many of the control chromatograms, representing mean apparent concentrations from 0.002 to 0.02 mg/kg.

Residues of HSA calculated as chlorpropham in the tissues, skimmed milk and cream ranged from below the limit of detection (<0.03 mg/kg) to 3.9 mg/kg in one skimmed milk sample (3111 ppm). Residues in the whole milk were higher and roughly proportional to feeding level, ranging from undetected in the samples from the control cows to 6.7 mg/kg in one of the 3111 ppm group. Residues of HSA in whole milk reached nearly maximum levels by the 4th day of dosing and fluctuated throughout the remainder of the dosing period. Although the concentration of HSA in whole milk varied between cows in a given treatment group, the cow producing the highest level of HSA did so consistently over the treatment period.

The levels of chlorpropham and HSA in whole milk and tissues (Tables 22-24) were consistent with those found in the ruminant metabolism study.

Table 22. Residues in whole milk from three treatment groups (3 animals per group) after various periods of treatment (Daun and Zeller, 1995).

Compound	Day of treatment	Treatment groups, residues calculated as chlorpropham[1] (mg/kg)			
		Control	322 ppm	955 ppm	3111 ppm
Chlorpropham	0	<0.01	<0.01	<0.01	<0.01
		<0.01	<0.01	<0.01	<0.01
		<0.01	<0.01	<0.01	<0.01
	1	<0.01	<0.01	<0.01	<0.01
		0.01	<0.01	<0.01	0.032
		<0.01	<0.01	<0.01	<0.01
	4	<0.01	<0.01	<0.01	0.03
		<0.01	<0.01	<0.01	0.06
		<0.01	<0.01	<0.01	0.04
	7	<0.01	<0.01	<0.01	0.03
		<0.01	<0.01	0.01	0.03
		<0.01	<0.01	<0.01	0.03
	10	<0.01	<0.01	<0.01	0.015
		<0.01	<0.01	<0.01	0.03
		<0.01	<0.01	<0.01	0.04
	13	<0.01	<0.01	<0.01	0.02
		<0.01	<0.01	<0.01	0.05
		0.01	<0.01	<0.01	0.03
	14	0.01	<0.01	<0.01	0.04
		<0.01	<0.01	<0.01	0.04
		<0.01	<0.01	<0.01	0.02
	18	<0.01	0.06	<0.01	0.02
		<0.01	0.04	<0.01	0.04
		<0.01	0.03	<0.01	0.02
	21	<0.01	0.03	0.01	0.02
		<0.01	0.03	<0.01	0.05
		<0.01	0.04	<0.01	0.02

Compound	Day of treatment	Treatment groups, residues calculated as chlorpropham[1] (mg/kg)			
		Control	322 ppm	955 ppm	3111 ppm
		<0.01	<0.01	<0.01	0.01
		<0.01	<0.01	<0.01	0.03
	24	<0.01	<0.01	<0.01	0.02
		<0.01	<0.01	<0.01	0.01
		<0.01	<0.01	<0.01	0.04
	28	<0.01	<0.01	0.014	0.02
		<0.03	<0.03	<0.03	<0.03
HSA		<0.03	<0.03	<0.03	<0.03
	0	<0.03	<0.03	<0.03	<0.03
		0.08	0.17	0.52	1.7
		<0.03	0.23	0.55	1.4
	1	<0.03	0.33	0.32	4.1
		<0.03	0.21	0.50	3.2
		<0.03	0.31	0.58	2.5
	4	<0.03	0.5	1.1	6.2
		<0.03	0.22	0.48	3.2
		<0.03	0.46	1.4	2.5
	7	<0.03	0.20	1.2	5.4
		<0.03	0.10	0.54	1.2
		<0.03	0.29	0.76	0.55
	10	<0.03	0.48	1.1	2.2
		<0.03	0.22	0.20	3.7
		<0.03	0.32	0.18	2.9
	13	<0.03	0.54	0.46	5.7
			0.23	0.43	1.0
			0.34	0.45	0.86
	14		0.59	1.1	2.9
		<0.03	0.24	0.46	2.6
		<0.03	0.37	0.52	2.5
	18	<0.03	0.57	1.1	6.7
		<0.03	0.20	0.33	0.50
		<0.03	0.26	0.79	0.55
	21	<0.03	0.46	0.57	3.2
		<0.03	0.22	0.21	0.83
		<0.03	0.52	0.20	0.37
	24	<0.03	0.58	0.26	3.0
		<0.03	0.61	0.56	0.83
		<0.03	0.15	0.46	0.55
	28	<0.03	0.44	0.64	3.4

[1] Conversion factor from HSA (MW 309.7) to chlorpropham (MW 213.7): 0.69

Table 23. Residues of chlorpropham and HSA in skimmed milk and cream from day 14 of treatment (Daun and Zeller, 1995).

Sample	Compound	Treatment groups, residues calculated as chlorpropham (mg/kg)			
		Control	322 ppm	955 ppm	3111 ppm
		0.01	<0.01	<0.01	<0.01
		<0.01	<0.01	<0.01	<0.01
Skimmed Milk	Chlorpropham	<0.01	<0.01	<0.01	<0.01
		<0.03	0.14	0.42	2.2
		<0.03	0.20	0.65	1.9
	HSA	<0.03	0.50	0.76	3.9
		<0.01	0.03	0.05	0.18
		0.01	0.02	0.05	0.64
Cream	Chlorpropham	<0.01	0.03	0.09	0.21
		<0.03	0.15	0.4	2.3
		<0.03	0.23	0.66	1.7
	HSA	<0.03	0.37	0.97	3.6

Table 24. Residues of chlorpropham and HSA in cattle tissues (Daun and Zeller, 1995).

Sample	Compound	Treatment groups, residues calculated as chlorpropham (mg/kg)			
		Control	322 ppm	955 ppm	3111 ppm
Liver	Chlorpropham		0.01	<0.01	0.02
		0.01	0.02	0.012	0.01
		0.02	<0.01	<0.01	0.02
	HSA	<0.03	<0.03	<0.03	0.06
		<0.03	<0.03	<0.03	0.04
		<0.03	<0.03	<0.03	<0.03
Kidney	Chlorpropham	0.01	<0.01	<0.01	<0.01
		<0.01	<0.01	<0.01	0.02
		0.02	<0.01	<0.01	<0.01
	HSA	<0.03	0.12	0.76	1.0
		<0.03	0.24	1.0	2.3
		<0.03	0.26	1.2	1.5
Muscle	Chlorpropham	<0.01	<0.01	<0.01	0.11
		0.01	0.01	0.01	0.02
		0.01	<0.01	<0.01	<0.01
	HSA	<0.03	<0.03	<0.03	<0.03
		<0.03	<0.03	<0.03	<0.03
		<0.03	<0.03	<0.03	<0.03
Fat	Chlorpropham	0.02	0.11	0.34	0.97
		<0.01	0.09	0.18	2.8
		0.02	0.13	0.26	0.15
	HSA	<0.03	<0.03	<0.03	<0.03
		<0.03	<0.03	<0.03	<0.03
		<0.03	<0.03	<0.03	<0.03

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

Potatoes. The results of the supervised trials on ware potatoes are shown in Tables 25-32. When residues were not detected, they are shown as below the method detection limit (MDL). The lowest validated fortification level, the limit of quantification (LOQ), was about 5 times higher. Residues of chlorpropham and its metabolites as well as application rates have generally been rounded to 2 significant figures or, for residues near the MDL, to 1 significant figure. Although all trials included control plots residues in control samples are recorded only when they exceeded the MDL. Values are not corrected for recoveries. Residues from trials according to GAP are underlined; results used to estimate STMRs are double underlined.

Kleinkopf and Thomson (1992); Goodrick *et al*. (1993b-d). An extensive trial on mature potato tubers stored under commercial conditions in bins was conducted according to GLP and EPA pesticide Assessment Guidelines Subdivision 0 - Residue Chemistry Series 171-4, Magnitude of the Residue. The storage capacity of the bins ranged from approximately 54 to 68 tonnes. Each bin had its own air ventilation equipment, refrigeration unit and computer-controlled monitoring systems to measure sampling pile conditions accurately, and was designed to allow tuber sampling during storage. Industry standards of relative humidity and temperature with continuous air flow were followed. Each bin was aerosol-fogged separately. Before placing the potatoes in the fumigation/storage bins, hand removal of rocks, dirt clods, vegetative debris and rotten tubers was attempted. Five bins were filled to 75% with potatoes and stored at 14°C for two weeks. Thereafter, bin temperatures were gradually reduced to:

a) 5°C in bin 1, the untreated control, to help prevent sprouting, and to 4°C in week 27 to prolong the sprout-free condition
b) 7.2°C in bins 2 and 3 for storage of potatoes for the fresh market or for processing into frozen or dehydrated products

c) 10°C in bins 4 and 5 for storage of potatoes for processing into chips.

Three commercial formulations of chlorpropham were applied to the stored potatoes at the prescribed maximum rates in a manner consistent with standard practices in the potato industry:

- Bins 2, 3, 4 and 5, each containing approximately 63.4 tonnes of potatoes, served as the fumigation chambers for thermal fogging with two aerosol formulations (Decco 273 Aerosol containing 50% ai, and Sprout Nip 4A Aerosol containing 47% ai).
- The other formulation, an emulsifiable concentrate (Decco 276 EC, containing 26% ai), was applied as 1% aqueous direct spray to samples of potatoes from bins 2 and 3 that were also thermally fogged. (The application of a 1% aqueous emulsion to potato tubers moving along a conveyor line is called a "direct spray".) The EC formulation was applied once before and once after thermal fogging at 5 different times to tubers collected from three sampling depths in storage bins 2 and 3. After collecting a 60-tuber composite sample, the tubers were washed in water and allowed to air-dry until damp. Rotten tubers were discarded, and those remaining were weighed and the weight used to calculate the amount of 1% chlorpropham emulsion required for an application rate of 0.01 kg ai/t potatoes. Some samples from the untreated control (bin 1) were treated once by direct spray.

Two sampling pipes were inserted into each bin before filling the bins with potatoes to facilitate sampling at various depths. The pipes allowed personnel access to selected parts of the potato pile for sampling at 0.3, 2.4 and 4.6 m above the air ducts in the bin floor.

Duplicate top, middle and bottom samples (A and B) were thus collected 0, 5, 91, 96, 140, 145 and 215 days after initial sampling from various locations within the piles, stored at 3.3-4.4 °C, and shipped as soon as possible under ambient conditions (shipment lasted for 2 days) to an analytical laboratory or processing plant. Samples were prepared, homogenized, and frozen until extraction. Upon arrival, samples were stored at 1.1-4.4 °C until composited and homogenized, then stored at -20 to -21°C for 3-12 months. Samples were extracted, and chlorpropham, 3-chloroaniline, conjugates of *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham were quantified by GLC with an NPD. The results are shown in Table 25.

Table 25. Residues of chlorpropham and its metabolites in whole potatoes (Kleinkopf and Thomson, 1992; Goodrick *et al*., 1993b-d).

Treatment	Days after initial treatment	Bin no., location in pile[1]	Residue[2] (mg/kg]			
			chlorpropham	3-chloroaniline	4'-hydroxy-chlorpropham	*p*-methoxy-chlorpropham
Report 92CIPC04, 3 different treatments: 1 x direct spray; 1 x fogging + direct spray; 2 x fogging + direct spray						
EC direct spray 0.01 kg ai/t potatoes, applied 19-11-91	0	1, top A	4.3	<0.08	<0.08	<0.08
		1, top B	4.3	<0.08	<0.08	<0.08
		1, top C	6.4	<0.08	<0.08	<0.08
		1, top D	8.2	<0.08	<0.08	<0.08
EC direct spray 0.02 kg ai/t potatoes, applied 14-11-91	0	2, bottom A	3.8	<0.08	<0.08	<0.08
		2, bottom B	3.6	<0.08	<0.08	<0.08
		2, middle A	4.3	<0.08	<0.08	<0.08
		2, middle B	3.6	<0.08	<0.08	<0.08
		2, top A	3.9	<0.08	<0.08	<0.08
		2, top B	3.6	<0.08	<0.08	<0.08
		3, bottom A	2.7	<0.08	<0.08	<0.08
		3, bottom B	3.5	<0.08	0.10	<0.08
		3, middle A	3.3	<0.08	<0.08	<0.08
		3, middle B	2.9	<0.08	<0.08	<0.08
		3, top A	3.6	<0.08	<0.08	<0.08
		3, top B	3.8	<0.08	<0.08	<0.08

Treatment	Days after initial treatment	Bin no., location in pile[1]	Residue[2] (mg/kg]			
			chlorpropham	3-chloroaniline	4'-hydroxy-chlorpropham	*p*-methoxy-chlorpropham
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 + EC direct spray 0.01 kg ai/t potatoes, applied 19-11-91	5	2, bottom A	9.5	<0.08	<0.08	<0.08
		2, bottom B	11	<0.08	<0.08	<0.08
		2, middle A	7.2	<0.08	<0.08	<0.08
		2, middle B	7.6	<0.08	<0.08	<0.08
		2, top A	6.9	<0.08	<0.08	<0.08
		2, top B	7.0	<0.08	<0.08	<0.08
		3, bottom A	7.5	<0.08	<0.08	<0.08
		3, bottom B	7.2	<0.08	<0.08	<0.08
		3, middle A	5.0	<0.08	<0.08	<0.08
		3, middle B	4.8	<0.08	<0.08	<0.08
		3, top A	9.1	0.08	<0.08	<0.08
		3, top B	8.0	<0.08	<0.08	<0.08
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 + EC direct spray 0.01 kg ai/t potatoes, applied 13-02-92	91	2, bottom A	8.9	0.11	<0.08	<0.08
		2, bottom B	8.6	0.10	<0.08	<0.08
		2, middle A	9.3	0.10	<0.08	<0.08
		2, middle B	8.3	0.10	<0.08	<0.08
		2, top A	6.5	0.09	<0.08	<0.08
		2, top B	7.3	0.09	<0.08	<0.08
		3, bottom A	7.6	0.10	<0.08	<0.08
		3, bottom B	9.4	0.11	<0.08	<0.08
		3, middle A	6.1	0.10	<0.08	<0.08
		3, middle B	6.3	0.10	<0.08	<0.08
		3, top A	9.1	0.10	<0.08	<0.08
		3, top B	9.0	0.12	<0.08	<0.08
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 + Aerosol fogging 0.02 kg ai/t potatoes, applied 14-02-92 + EC direct spray 0.01 kg ai/t potatoes, applied 18-02-92	96	2, bottom A	8.3	0.16	<0.08	<0.08
		2, bottom B	9.7	0.14	<0.08	<0.08
		2, middle A	8.5	0.12	<0.08	<0.08
		2, middle B	7.0	0.12	<0.08	<0.08
		2, top A	6.0	<0.08	<0.08	<0.08
		2, top B	7.2	<0.08	<0.08	<0.08
		3, bottom A	12	0.13	<0.08	<0.08
		3, bottom B	14	0.16	<0.08	<0.08
		3, middle A	9.3	0.12	<0.08	<0.08
		3, middle B	8.8	0.12	<0.08	<0.08
		3, top A	10	0.13	<0.08	<0.08
		3, top B	9.5	0.12	<0.08	<0.08
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 + Aerosol fogging 0.02 kg ai/t potatoes applied 14-02-92 + EC direct spray 0.01 kg ai/t potatoes applied 02-04-92	140	2, bottom A	11	0.12	<0.08	<0.08
		2, bottom B	10.5	0.1	<0.08	<0.08
		2, middle A	8.4	0.12	<0.08	<0.08
		2, middle B	8.9	0.1	<0.08	<0.08
		2, top A	9.0	0.11	<0.08	<0.08
		2, top B	7.5	0.1	<0.08	<0.08
		3, bottom A	13	0.12	<0.08	<0.08
		3, bottom B	12	0.12	<0.08	<0.08
		3, middle A	12	0.12	<0.08	<0.08
		3, middle B	9.4	0.12	<0.08	<0.08
		3, top A	13	0.13	<0.08	<0.08
		3, top B	12	0.12	<0.08	<0.08
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 + Aerosol fogging 0.02 kg ai/t potatoes, applied 14-02-92 + EC direct spray 0.01 kg ai/t potatoes, applied 16-06-92	215	2, bottom A	8.2	0.14	<0.08	<0.08
		2, bottom B	7.7	0.12	<0.08	<0.08
		2, middle A	7.5	0.12	<0.08	<0.08
		2, middle B	8.0	0.14	<0.08	<0.08
		2, top A	7.6	0.14	<0.08	<0.08
		2, top B	7.1	0.13	<0.08	<0.08
		3, bottom A	11	0.14	<0.08	<0.08
		3, bottom B	9.8	0.15	<0.08	<0.08
		3, middle A	7.6	0.13	<0.08	<0.08
		3, middle B	8.3	0.14	<0.08	<0.08

Treatment	Days after initial treatment	Bin no., location in pile[1]	Residue[2] (mg/kg]			
			chlorpropham	3-chloroaniline	4'-hydroxy-chlorpropham	*p*-methoxy-chlorpropham
		3, top A	7.4	0.12	<0.08	<0.08
		3, top B	8.2	0.13	<0.08	<0.08
Report 92CIPC05, 2 different treatments: 1 x fogging; 2 x fogging						
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 sampling at 19-11-91	5	2, bottom A	8.7	<0.08	<0.08	<0.08
		2, bottom B	7.3	<0.08	<0.08	<0.08
		2, middle A	4.2	<0.08	<0.08	<0.08
		2, middle B	3.2	<0.08	<0.08	<0.08
		2, top A	3.6	<0.08	<0.08	<0.08
		2, top B	3.2	<0.08	<0.08	<0.08
		3, bottom A	7.9	0.2	<0.08	<0.08
		3, bottom B	8.9	0.21	<0.08	<0.08
		3, middle A	7.3	0.2	<0.08	<0.08
		3, middle B	6.1	0.19	<0.08	<0.08
		3, top A	6.7	0.19	<0.08	<0.08
		3, top B	6.3	0.19	<0.08	<0.08
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 sampling at 13-02-91	91	2, bottom A	2.8	0.13	<0.08	<0.08
		2, bottom B	4.1	0.12	<0.08	<0.08
		2, middle A	3.6	0.12	<0.08	<0.08
		2, middle B	2.6	0.12	<0.08	<0.08
		2, top A	1.4	0.12	<0.08	<0.08
		2, top B	2.0	0.12	<0.08	<0.08
		3, bottom A	5.2	0.14	<0.08	<0.08
		3, bottom B	4.5	0.14	<0.08	<0.08
		3, middle A	4.3	0.15	<0.08	<0.08
		3, middle B	6.1	0.14	<0.08	<0.08
		3, top A	7.1	0.17	<0.08	<0.08
		3, top B	5.1	0.14	<0.08	<0.08
Aerosol fogging 0.02 kg ai/t potatoes applied 15-11-91 + Aerosol fogging 0.02 kg ai/t potatoes, applied 14-02-92 sampling at 18-02-92	96	2, bottom A	9.8	<0.08	<0.08	<0.08
		2, bottom B	9.9	<0.08	<0.08	<0.08
		2, middle A	6.9	<0.08	<0.08	<0.08
		2, middle B	6.4	<0.08	<0.08	<0.08
		2, top A	6.0	<0.08	<0.08	<0.08
		2, top B	4.5	<0.08	<0.08	<0.08
		3, bottom A	16	0.18	<0.08	<0.08
		3, bottom B	10	0.18	<0.08	<0.08
		3, middle A	9.4	0.14	<0.08	<0.08
		3, middle B	9.5	0.13	<0.08	<0.08
		3, top A	12	0.15	<0.08	<0.08
		3, top B	11	0.13	<0.08	<0.08
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 + Aerosol fogging 0.02 kg ai/t potatoes, applied 14-02-92 sampling at 07-04-92	140	2, bottom A	7.1	0.1	<0.08	<0.08
		2, bottom B	9.7	0.12	<0.08	<0.08
		2, middle A	8.1	0.09	<0.08	<0.08
		2, middle B	9.2	0.1	<0.08	<0.08
		2, top A	4.7	0.08	<0.08	<0.08
		2, top B	4.4	0.09	<0.08	<0.08
		3, bottom A	11	0.1	<0.08	<0.08
		3, bottom B	18	0.12	<0.08	<0.08
		3, middle A	12	0.08	<0.08	<0.08
		3, middle B	11	0.08	<0.08	<0.08
		3, top A	6.8	0.09	<0.08	<0.08
		3, top B	9.4	0.09	<0.08	<0.08

Treatment	Days after initial treatment	Bin no., location in pile[1]	Residue[2] (mg/kg]			
			chlorpropham	3-chloroaniline	4'-hydroxy-chlorpropham	*p*-methoxy-chlorpropham
Aerosol fogging 0.02 kg ai/t potatoes, applied 15-11-91 + Aerosol fogging 0.02 kg ai/t potatoes, applied 14-02-92 sampling at 16-06-92	215	2, bottom A	7.8	<0.08	<0.08	<0.08
		2, bottom B	7.0	<0.08	<0.08	<0.08
		2, middle A	6.6	<0.08	<0.08	<0.08
		2, middle B	6.8	<0.08	<0.08	<0.08
		2, top A	6.8	<0.08	<0.08	<0.08
		2, top B	5.4	<0.08	<0.08	<0.08
		3, bottom A	8.2	0.09	<0.08	<0.08
		3, bottom B	8.8	0.08	<0.08	<0.08
		3, middle A	11	0.08	<0.08	<0.08
		3, middle B	8.2	<0.08	<0.08	<0.08
		3, top A	7.8	<0.08	<0.08	<0.08
		3, top B	8.2	<0.08	<0.08	<0.08
Report 92CIPC06, 2 different treatments: 1 x fogging; 2 x fogging						
Aerosol fogging 0.03 kg ai/t potatoes, applied 19-11-91 sampling at 19-11-92	5	4, bottom A	23	0.23	<0.08	<0.08
		4, bottom B	21	0.18	<0.08	<0.08
		4, middle A	7.6	0.11	<0.08	<0.08
		4, middle B	6.4	0.1	<0.08	<0.08
		4, top A	4.7	0.1	<0.08	<0.08
		4, top B	4.7	0.09	<0.08	<0.08
		5, bottom A	16	0.16	<0.08	<0.08
		5, bottom B	13	0.19	<0.08	<0.08
		5, middle A	11	0.15	<0.08	<0.08
		5, middle B	13	0.15	<0.08	<0.08
		5, top A	13	0.17	<0.08	<0.08
		5, top B	10	0.13	<0.08	<0.08
Aerosol fogging 0.03 kg ai/t potatoes, applied 19-11-91 sampling at 13-02-92	91	4, bottom A	7.8	0.15	<0.08	<0.08
		4, bottom B	11	0.15	<0.08	<0.08
		4, middle A	7.0	0.15	<0.08	<0.08
		4, middle B	11	0.16	<0.08	<0.08
		4, top A	5.4	0.16	<0.08	<0.08
		4, top B	3.2	0.14	<0.08	<0.08
		5, bottom A	7.0	<0.08	<0.08	<0.08
		5, bottom B	7.8	<0.08	<0.08	<0.08
		5, middle A	5.6	<0.08	<0.08	<0.08
		5, middle B	14	<0.08	<0.08	<0.08
		5, top A	9.2	<0.08	<0.08	<0.08
		5, top B	7.4	<0.08	<0.08	<0.08
Aerosol fogging 0.03 kg ai/t potatoes, applied 15-11-91 sampling at 02-04-92	140	4, bottom A	8.6	0.26	<0.08	<0.08
		4, bottom B	8.2	0.23	<0.08	<0.08
		4, middle A	10	0.22	<0.08	<0.08
		4, middle B	12	0.25	<0.08	<0.08
		4, top A	7.1	0.23	<0.08	<0.08
		4, top B	5.9	0.22	<0.08	<0.08
		5, bottom A	13	0.16	<0.08	<0.08
		5, bottom B	13	0.19	<0.08	<0.08
		5, middle A	10	0.15	<0.08	<0.08
		5, middle B	12	0.14	<0.08	<0.08
		5, top A	9.8	0.14	<0.08	<0.08
		5, top B	11	0.14	<0.08	<0.08
Aerosol fogging 0.03 kg ai/t potatoes, applied 15-11-91 + 0.015 kg ai/t potatoes, applied 03-04-92 sampling at 07-04-92	145	4, bottom A	13	0.22	<0.08	<0.08
		4, bottom B	12	0.22	<0.08	<0.08
		4, middle A	12	0.2	<0.08	<0.08
		4, middle B	14	0.19	<0.08	<0.08
		4, top A	5.5	0.17	<0.08	<0.08
		4, top B	6.0	0.19	<0.08	<0.08
		5, bottom A	14	0.23	<0.08	<0.08

Treatment	Days after initial treatment	Bin no., location in pile[1]	Residue[2] (mg/kg]			
			chlorpropham	3-chloroaniline	4'-hydroxy-chlorpropham	*p*-methoxy-chlorpropham
		5, bottom B	14	0.18	<0.08	<0.08
		5, middle A	12	0.19	<0.08	<0.08
		5, middle B	16	0.22	<0.08	<0.08
		5, top A	10	0.19	<0.08	<0.08
		5, top B	12	0.20	<0.08	<0.08
Aerosol fogging 0.03 kg ai/t potatoes, applied 15-11-91 + 0.015 kg ai/t potatoes, applied 03-04-92 sampling at 16-06-92	215	4, bottom A	7.8	0.09	<0.08	<0.08
		4, bottom B	8.2	0.09	<0.08	<0.08
		4, middle A	8.0	<0.08	<0.08	<0.08
		4, middle B	7.8	<0.08	<0.08	<0.08
		4, top A	6.7	<0.08	<0.08	<0.08
		4, top B	8.1	<0.08	<0.08	<0.08
		5, bottom A	8.9	0.13	<0.08	<0.08
		5, bottom B	10	0.13	<0.08	<0.08
		5, middle A	11	0.12	<0.08	<0.08
		5, middle B	15	0.13	<0.08	<0.08
		5, top A	11	0.12	<0.08	<0.08
		5, top B	9.5	0.11	<0.08	<0.08

[1] Bottom, middle, top: 0.3, 2.4, 4.6 m above floor ducts respectively
[2] 0.08 mg/kg is method detection limit (MDL), not LOQ

Roland (1998b). In a field study to determine chlorpropham residues in potatoes in France (field part) and Belgium (analytical part) two fogging applications were made, firstly in October 1997 at 7 g ai/t, and secondly in January 1998 at 6 g ai/t. Samples were taken 1 day before and 0, 30 and 60 days after the first application and 0, 30, 60, 90 and 120 days after the second. The potatoes were stored on wooden pallets in a warehouse in piles 5 or 6 pallets high each containing about 1 tonne. The samples were taken in four places sited diagonally in the warehouse from the bottom, the middle and top pallets of the piles. The whole tubers were frozen. After removal of adhering soil by rinsing in running water, the potatoes (not completely thawed) were divided into representative parts. They were peeled with a knife as soon as the surface part was sufficiently tenderised. The residues in tubers and pulp are shown in Tables 26 and 27 respectively. Each value is the mean of two analyses, obtained from separate sub-samples.

Table 26. Residues of chlorpropham in whole tubers after fogging (Roland, 1998b).

Treatment	Days after application	Pallet location, residues (mg/kg)		
		bottom	middle	top
Fogging, pile, NeoStop L 500 (HN, Chlorpropham 500 g/l) 1x 7 g ai/t at 31-10-1997 + 1x 6 g ai/t at 06-01-1998	-1 (before 1st application)	0.5, 0.18, 0..21, 0.29	0.24, 0.2, 0.18, 0.20	0.29, 0.44, 0.33, 0.34
	0 (1st application)	1.2, 1.6, 3.1, 1.7	1.1, 2.0, 1.6, 0.86	3.3, 6.4, 3.2, 2.0
	30 (1st application)	1.2, 1.7, 1.6, 2.0, 1.6	1.1, 2.1, 2.0, 1.7, 1.4	3.4, 13, 6.0, 1.9
	60 (1st application)	0.75, 0.92, 1.8, 1.1	0.67, 1.5, 1.1, 1.1	1.1, 6.1, 3.6, 1.8
	0 (2nd application)	1.5, 1.8, 3.4, 2.6	1.9, 4.0, 3.2, 3.3	4.1, 11, 7.1, 4.1
	30 (2nd application)	1.2, 1.7, 3.5, 2.5	1.6, 3.5, 3.3, 2.9	3.8, 9.0, 8.0, 3.4
	60 (2nd application)	1.4, 1.4, 2.2, 2.4	3.3, 3.1, 3.5, 2.3	1.4, 13, 5.1, 2.4
	90 (2nd application)	1.2, 1.1, 2.2, 1.6	1.1, 2.2, 0.99, 1.6	1.7, 8.3, 4.9, 1.9
	120 (2nd application)	1.2, 0.92, 2.3, 1.9	1.6, 1.9, 1.0, 1.6	1.7, 7.5, 5.6, 2.0

Table 27. Residues of chlorpropham in the pulp of peeled potatoes after fogging (Roland, 1998b).

Days after application	Pallet location, residues (mg/kg)		
	bottom	middle	top
-1 (before 1st application)	<0.02	<0.02	<0.02
0 (1st application)	0.02	0.04	0.05
30 (1st application)	0.03	<0.02	0.04
60 (1st application)	<0.02	0.02	0.03
0 (2nd application)	0.04	0.04	0.23
30 (2nd application)	0.07	0.05	0.08
60 (2nd application)	0.07	0.07	0.07
90 (2nd application)	0.06	0.06	0.14
120 (2nd application)	0.11	0.07	0.24

Roland (1998a). In a field trial in Belgium potatoes given one fogging application of NeoStop (DP 1% chlorpropham) at 150 g/100 kg (equal to 15 g ai/t potatoes) during storage were sampled after 0, 1, 3, 7, 14, 38 and 45 days, and 2, 3, 4, 6 and 8 months. The residues of chlorpropham are shown in Table 28.

Table 28. Residues of chlorpropham in potatoes (Roland, 1998a).

Treatment	Interval after application	Residues (mg/kg)		
		Whole tubers	Peeled potatoes	Cooked potatoes
Manually powdering of the exact quantity above each paper bag filled with potatoes, shaking of the bag. NeoStop (DP, 1% chlorpropham) 1x 15 g ai/t at 12-11-1997	Untreated before application	<0.02	<0.02	<0.02
	0 day following application	3.6	0.11	
	1 day after application	7.9	0.23	
	3 days after application	5.5	0.12	
	7 days after application	8.8	0.18	
	14 days after application	5.8	0.19	
	28 days after application	6.1	0.27	
	45 days after application	4.6	0.24	0.08
	2 months after application	5.3	0.22	
	3 months after application	4.9	0.37	
	4 months after application	3.1	0.36	
	6 months after application	3.2	0.45	
	8 months after application	2.6	0.33	

Brielbeck and Marx (1999a). Seven trials (one a decline trial) were conducted to determine residues of chlorpropham in peeled and unpeeled potato tubers following two fogging applications of Neo-Stop L 500 (chlorpropham 500 g/l HN) equal to 7 and 6 g ai/t in Belgium. For unpeeled samples, tubers were washed with water before weighing and freezing. For peeled samples, tubers were washed, weighed and peeled. Peels and peeled tubers were weighed separately and peels discarded. Peeled tubers were washed again with water, weighed and frozen. The residues in duplicate field samples, each the mean of duplicate analyses, are shown in Table 29.

Table 29. Residues of chlorpropham in potatoes, Saint-Amand, Belgium (Brielbeck and Marx, 1999a).

Treatment	Sample	Time of sampling	Residues (mg/kg)	
			Unpeeled potatoes	Peeled potatoes
Fogging, box, Neo-Stop L 500 (HN, chlorpropham 500 g/l) 1x 7 g ai/t at 17-11-1998 + 1x 6 g ai/t at 18-01-1999	G-09	before treatment 1	<0.02, <0.02	<0.02, <0.02
		1 day after treatment 1	0.49, 0.45	0.03, 0.08
		before treatment 2	0.64, 0.63	0.11, 0.03
		1 day after treatment 2	1.1, 1.2	0.09, 0.07
		29 days after treatment 2	0.70, 0.76	0.09, 0.07
		91 days after treatment 2	0.58, 0.65	0.08, 0.07
	G 10	before treatment 1	<0.02, <0.02	<0.02, <0.02
		7 days after treatment 2	0.70, 0.85	0.06, 0.05
	G 11	before treatment 1	<0.02, <0.02	<0.02, <0.02
		7 days after treatment 2	0.89, 0.67	0.08, 0.08
	G 12	before treatment 1	<0.02, <0.02	<0.02, <0.02
		7 days after treatment 2	0.61, 0.58	0.10, 0.10
	G 13	before treatment 1	<0.02, <0.02	<0.02, <0.02
		7 days after treatment 2	0.96, 0.68	0.14, 0.16
	G 14	before treatment 1	<0.02, <0.02	<0.02, <0.02
		7 days after treatment 2	1.1, 1.2	0.18, 0.22
	G 15	before treatment 1	<0.02, <0.02	<0.02, <0.02
		7 days after treatment 2	1.1, 0.77	<0.02, <0.02

Brielbeck and Marx (1999b). A similar set of seven trials was conducted in Germany with single applications of 1.5 kg/t Neo-Stop (chlorpropham 1% DP, equal to 15 g ai/t). The samples were prepared as above. The results (each the mean of duplicate analyses) are shown in Table 30.

Table 30. Residues of chlorpropham in potatoes, Goch Hülm, Germany (Brielbeck and Marx, 1999b).

Treatment	Sample, variety	Time of sampling	Residues (mg/kg)	
			Unpeeled potatoes	Peeled potatoes
Dusting, box, Neo-Stop, (DP, 1% chlorpropham) 1x 15 g ai/t at 28-10-98	ASU 52, Bintje	before treatment	<0.02, <0.02	<0.02, <0.02
		1 day after treatment	2.6, 2.3	0.10, 0.10
		7 days after treatment	3.8, 2.9	0.08, 0.08
		28 days after treatment	2.1, 1.9	0.14, 0.13
		61 days after treatment	2.7, 2.3	0.04, 0.05
		92 days after treatment	1.4, 1.3	0.11, 0.10
		118 days after treatment	2.0, 1.2	0.13, 0.15
		181 days after treatment	1.9, 2.4	0.07, 0.08
	ASU 46, Bintje	before treatment	<0.02, <0.02	<0.02, <0.02
		30 days after treatment	2.9, 3.4	0.09, 0.11
		61 days after treatment	2.9, 3.2	0.05, 0.06
		92 days after treatment	3.5, 2.8	0.09, 0.09
	ASU 47, Bintje	before treatment	<0.02, <0.02	<0.02, <0.02
		30 days after treatment	4.3, 4.3	0.09, 0.11
		61 days after treatment	4.8, 4.0	0.05, 0.06
		92 days after treatment	2.4, 1.7	0.09, 0.09
	ASU 48, Mentor	before treatment	<0.02, <0.02	<0.02, <0.02
		30 days after treatment	2.2, 2.9	0.04, <0.02
		61 days after treatment	3.0, 3.1	0.06, 0.05
		92 days after treatment	1.7, 1.7	0.06, 0.06

Treatment	Sample, variety	Time of sampling	Residues (mg/kg)	
			Unpeeled potatoes	Peeled potatoes
	ASU 49, Russet Burbank	before treatment	<0.02, <0.02	<0.02, <0.02
		30 days after treatment	3.2, 3.3	0.06, 0.07
		61 days after treatment	2.2, 2.7	0.09, 0.13
		92 days after treatment	2.6, 3.5	0.07, 0.08
	ASU 50, Helmond	before treatment	<0.02, <0.02	<0.02, <0.02
		30 days after treatment	4.6, 4.9	0.13, 0.14
		61 days after treatment	2.7, 2.8	0.11, 0.05
		92 days after treatment	3.9, 4.6	0.35, 0.34
	ASU 51, Nierswalde	before treatment	<0.02, <0.02	<0.02, <0.02
		30 days after treatment	3.0, 4.3	0.14, 0.17
		61 days after treatment	2.7, 2.0	0.48, 0.44
		92 days after treatment	2.8, 2.4	0.15, 0.17

Brielbeck and Marx (1996a,b). In further trials potatoes stored in separate boxes were treated with 1 kg CIPC 1% DP/t (10.6 g ai/t) which is equivalent to AU 95395 and NEO Stop. Samples were taken from the top, the middle and the bottom of the boxes and prepared as before. The results are shown in Table 31.

Table 31. Residues of chlorpropham in potatoes, Keppeln, Germany (Brielbeck and Marx, 1996a,b).

Treatment	Sample source, variety	Time of sampling	Chlorpropham (mg/kg)	
			Unpeeled potatoes	Peeled potatoes
Powdering, box, Neo-Stop, (DP, 1% chlorpropham), 1x 11 g ai/t at 28-02-96	ASU 32, Bintje	before treatment	<0.02, <0.02	<0.025, <0.025
		1-2 hours after treatment	2.9, 3.0	<0.025, <0.025
		30 days after treatment	1.9, 3.0	0.08, 0.07
	ASU 33, Gloria	before treatment	<0.02, <0.02	<0.025, <0.025
		1-2 hours after treatment	2.5, 1.2	<0.025, <0.025
		30 days after treatment	2.1, 2.2	0.06, 0.06
	ASU 34, Hansa	before treatment	<0.02, <0.02	<0.025, <0.025
		1-2 hours after treatment	1.8, 1.7	<0.025, <0.025
		30 days after treatment	1.9, 0.96	<0.025, 0.032
	ASU 35, Cilena	before treatment	<0.02, <0.02	<0.025, <0.025
		1-2 hours after treatment	1.3, 1.2	0.03, <0.025
		30 days after treatment	2.0, 1.4	0.03, 0.06

Brielbeck and Marx (1999c). In four trials potatoes were treated with 1.0 kg of Neo Stop 1% DP/t (10 g ai/t) by dusting immediately before being taken into the warehouse. After sampling, some of the tubers were washed with water and some were washed and peeled as before. The results are shown in Table 32.

Table 32. Residues of chlorpropham in potatoes, Goch Hülm, Germany (Brielbeck and Marx, 1999c).

Treatment	Sample, variety	Time of sampling	Residues (mg/kg)	
			Unpeeled	Peeled
Powdering, box, Neo-Stop (DP, 1% chlorpropham) 1x 10 g ai/t	ASU 42, Bintje	before treatment	<0.02, <0.02	<0.02, <0.02
		1 day after treatment	3.0, 2.9	0.21, 0.12
		30 days after treatment	2.9, 2.6	0.21, 0.30
	ASU 43, Cilena	before treatment	<0.02, <0.02	<0.02, <0.02
		1 day after treatment	1.5, 1.7	0.37, 0.13
		30 days after treatment	1.1, 1.2	0.24, 0.19
		before treatment	<0.02, <0.02	<0.02, <0.02

Treatment	Sample, variety	Time of sampling	Residues (mg/kg)	
			Unpeeled	Peeled
	ASU 44, Hansa	1 day after treatment	2.3, 2.5	0.08, 0.14
		30 days after treatment	2.2, 2.0	0.23, 0.21
	ASU 45, Secura	before treatment	<0.02, <0.02	<0.02, <0.02
		1 day after treatment	3.2, 2.7	0.07, 0.05
		30 days after treatment	2.8, 2.2	0.06, 0.06

Further incomplete residue data were reported by Germany (Anon., 2001) including the results of one trial in 1970 on stored potatoes treated twice with 6.4-13 kg ai/t, WhP 65 days. Chlorpropham residues were reported for peeled potatoes only and ranged from <0.05 to 0.3 mg/kg. No data were available for whole tubers. These results could not be used for evaluation.

In processing

Potatoes (Roland, 1998a). Potatoes stored for 45 days were peeled, put in boiling water and cooked for 20 minutes. The residues in fresh whole tubers were 4.6 mg/kg, in fresh peeled potatoes 0.24 mg/kg and in cooked peeled potatoes 0.08 mg/kg (see also Table 28).

(Swanson *et al.*, 1993; Haws *et al.*, 1993c). The storage conditions and chlorpropham treatments used in industry and in the study reported by Kleinkopf and Thomson (1992) vary with the intended use of the raw commodity for chips, or frozen and dehydrated products. The scheme used by Kleinkopf and Thomson is shown in Table 33.

Table 33. Storage conditions and treatment of potatoes for processing as chips, or frozen or dehydrated products (Kleinkopf and Thomson, 1992).

	For chips	For frozen or dehydrated products
Storage bins	4 and 5	2 and 3
Storage conditions	10°C, 5% relative humidity	7.2°C, 95% relative humidity
Chlorpropham treatments	aerosol fogging	aerosol fogging
Chlorpropham formulations	Sprout Nip 4A Aerosol	Decco 273 Aerosol
Chlorpropham rates	0.033 kg ai/t potatoes-initial fogging 0.017 kg ai/t potatoes-second fogging	0.02 kg ai/t potatoes-initial fogging 0.02 kg ai/t potatoes-second fogging
Treatment schedule	15-11-1991 initial aerosol fogging 03-04-1992 second aerosol fogging	15-11-1991 initial aerosol fogging 14-02-1992 second aerosol fogging

The tubers were processed by standard industrial procedures. Stored tubers were shipped intact and unfrozen to a pilot processing plant. They were stored at 3.3°C before being processed into frozen French fries and chips with and without skin, dehydrated granules and wet and dry peel. Thereafter the products were homogenized and stored at -20 to -21°C for 2-10 months. Chlorpropham and its metabolites 3-chloroaniline, *p*-hydroxy-chlorpropham (including conjugates) and *p*-methoxy-chlorpropham were determined in the French fries, chips and in the canola oil used during processing. The wet and dried peel removed during processing was retained for analysis (Swanson *et al.*, 1993).

Chips. Although commercial potato processing includes a water wash to remove starch the procedure did not include this, maximizing the potential residue of chlorpropham in the chips. Neither did it include salting the chips. Figure 3 shows the processing of chips at the pilot plant.

Table 34 shows the residues of chlorpropham and 3-chloroaniline in chips. Residues of *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham were undetectable in any fresh or processed product. Processing factors could not be determined as different samples were used for the determination of residues in the raw agriculture commodity (RAC) and the processed product.

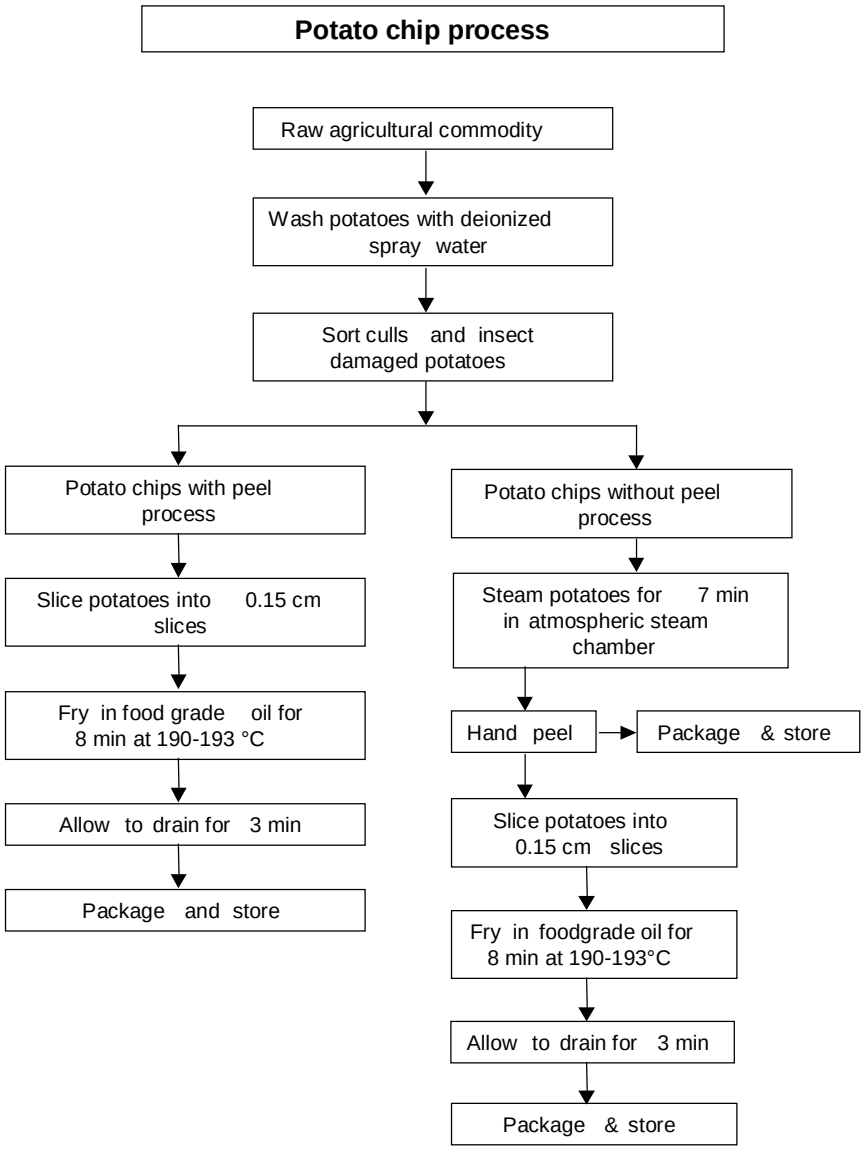


Figure 3. Processing of potatoes to chips at a pilot plant (Swanson *et al.*, 1993).

Table 34. Residues of chlorpropham and 3-chloroaniline in potato chips (Haws *et al.*, 1993c).

Treatment	Bin no. Location in pile	Days after first treatment	Chlorpropham residues (mg/kg)		3-Chloroaniline residues (mg/kg)	
			With skin	Without skin	With skin	Without skin
Aerosol fogging	4, bottom A	5	3.4	<0.45	<0.45	<0.45
at 15-11-91	4, bottom B	5	2.7	<0.45	<0.45	<0.45
0.03 kg ai/t	4, middle A	5	1.3	<0.45	<0.45	<0.45
potatoes	4, middle B	5	1.4	<0.45	<0.45	<0.45
	4, top A	5	0.72	<0.45	<0.45	<0.45
	4, top B	5	0.7	<0.45	<0.45	<0.45
sampling at	5, bottom A	5	3.6	<0.45	<0.45	<0.45

Treatment	Bin no. Location in pile	Days after first treatment	Chlorpropham residues (mg/kg)		3-Chloroaniline residues (mg/kg)	
			With skin	Without skin	With skin	Without skin
19-11-91	5, bottom B	5	3.3	<0.45	<0.45	<0.45
	5, middle A	5	1.5	<0.45	<0.45	<0.45
	5, middle B	5	1.6	<0.45	<0.45	<0.45
	5, top A	5	1.8	<0.45	<0.45	<0.45
	5, top B	5	1.7	<0.45	<0.45	<0.45
Aerosol fogging	4, bottom A	91	5.7	<0.45	<0.45	<0.45
at 15-11-91	4, bottom B	91	6.4	<0.45	<0.45	<0.45
0.03 kg ai/t	4, middle A	91	2.8	<0.45	<0.45	<0.45
potatoes	4, middle B	91	3.7	<0.45	<0.45	<0.45
	4, top A	91	2.9	<0.45	<0.45	<0.45
	4, top B	91	2.3	<0.45	<0.45	<0.45
sampling at	5, bottom A	91	4.0	<0.45	<0.45	<0.45
13-02-92	5, bottom B	91	5.1	<0.45	<0.45	<0.45
	5, middle A	91	4.7	<0.45	<0.45	<0.45
	5, middle B	91	5.0	<0.45	<0.45	<0.45
	5, top A	91	4.6	<0.45	<0.45	<0.45
	5, top B	91	4.9	<0.45	<0.45	<0.45
Aerosol fogging	4, bottom A	140	4.5	<0.45	<0.45	<0.45
at 15-11-91	4, bottom B	140	3.7	<0.45	<0.45	<0.45
0.03 kg ai/t	4, middle A	140	1.2	<0.45	<0.45	<0.45
potatoes	4, middle B	140	2.0	<0.45	<0.45	<0.45
	4, top A	140	2.4	<0.45	<0.45	<0.45
	4, top B	140	2.6	<0.45	<0.45	<0.45
sampling at	5, bottom A	140	3.8	<0.45	<0.45	<0.45
02-04-92	5, bottom B	140	4.0	<0.45	<0.45	<0.45
	5, middle A	140	3.8	<0.45	<0.45	<0.45
	5, middle B	140	4.1	<0.45	<0.45	<0.45
	5, top A	140	7.9	<0.45	<0.45	<0.45
	5, top B	140	6.4	<0.45	<0.45	<0.45
Aerosol fogging	4, bottom A	145	4.4	≤0.45	<0.45	<0.45
at 15-11-91	4, bottom B	145	4.2	≤0.45	<0.45	<0.45
0.03 kg ai/t	4, middle A	145	4.0	≤0.45	<0.45	<0.45
potatoes	4, middle B	145	8.1	≤0.45	<0.45	<0.45
	4, top A	145	4.1	≤0.45	<0.45	<0.45
+	4, top B	145	1.5	≤0.45	<0.45	<0.45
0.015 kg ai/t	5, bottom A	145	0.82	≤0.45	<0.45	<0.45
	5, bottom B	145	1.5	≤0.45	<0.45	<0.45
03-04-92	5, middle A	145	1.9	≤0.45	<0.45	<0.45
	5, middle B	145	1.7	≤0.45	<0.45	<0.45
sampling at	5, top A	145	1.2	≤0.45	<0.45	<0.45
07-04-92	5, top B	145	-		<0.45	<0.45
Aerosol fogging	4, bottom A	215	3.8	1.2	<0.45	<0.45
at 15-11-91	4, bottom B	215	5.0	1.4	<0.45	<0.45
0.03 kg ai/t	4, middle A	215	4.6	1.5	<0.45	<0.45
potatoes	4, middle B	215	6.3	1.1	<0.45	<0.45
	4, top A	215	4.6	1.4	<0.45	<0.45
+	4, top B	215	6.4	1.3	<0.45	<0.45
0.015 kg ai/t	5, bottom A	215	7.0	1.5	<0.45	<0.45
potatoes	5, bottom B	215	5.3	1.6	<0.45	<0.45

Treatment	Bin no. Location in pile	Days after first treatment	Chlorpropham residues (mg/kg)		3-Chloroaniline residues (mg/kg)	
			With skin	Without skin	With skin	Without skin
03-04-92	5, middle A	215	6.3	1.8	<0.45	<0.45
	5, middle B	215	7.9	1.4	<0.45	<0.45
sampling at	5, top A	215	4.6	1.5	<0.45	<0.45
16-06-92	5, top B	215	7.1	1.5	<0.45	<0.45

[1] 0.45 mg/kg is method detection limit (MDL), not LOQ

French fries. Commercial processing incorporates sequential water blanching, air-drying and a glucose dip to control colour and solid concentrations in pan-fried French fries. The experimental procedure included a minimal single water blanching to gelatinize starch which results in maximum chlorpropham residues. Figure 4 shows the process at a pilot plant.

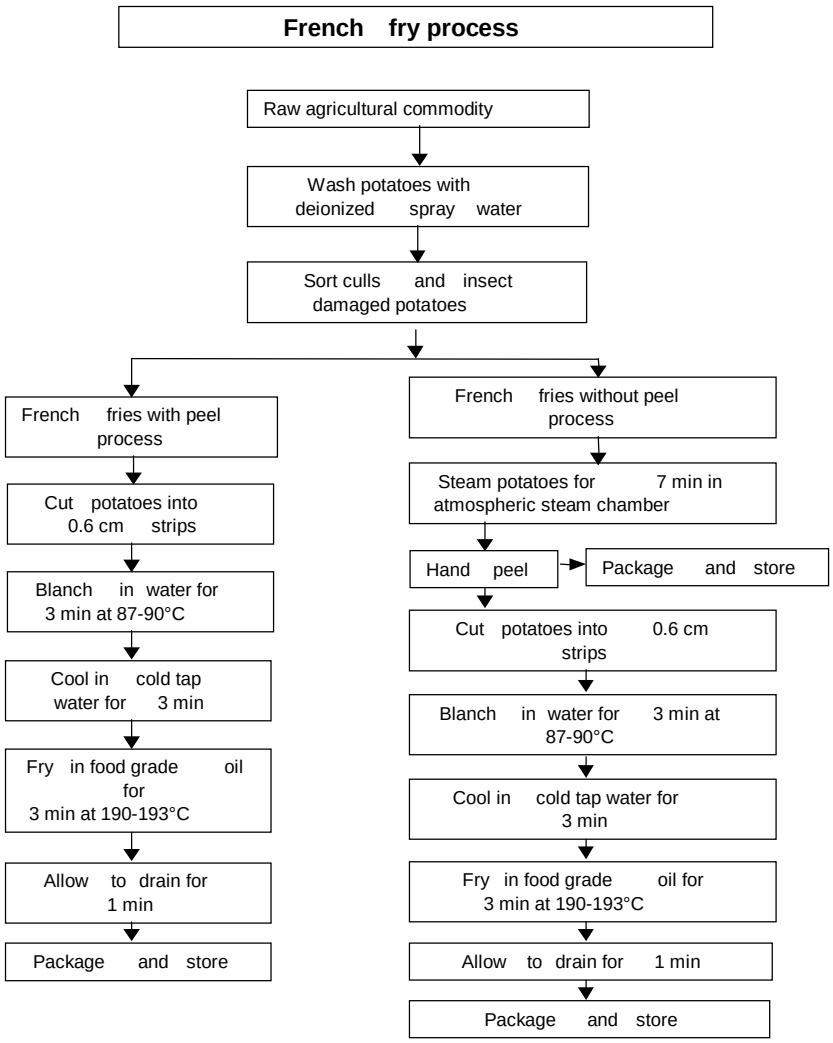


Figure 4. Processing of potatoes to French fries at a pilot plant (Swanson *et al.*, 1993).

Table 35 shows the residues of chlorpropham and 3-chloroaniline in fries with and without skin. Residues of *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham were undetectable in any fresh or processed product. Processing factors could not be determined as different samples were used for determination of residues in the raw agriculture commodity (RAC) and the processed product.

Table 35. Residues of chlorpropham and 3-chloroaniline in French fries (Haws *et al.*, 1993c).

Treatment	Bin No.	Days after initial treatment	Chlorpropham residues[1] (mg/kg)		3-Chloroaniline residues[1] (mg/kg)	
	Location in pile		with skin	without skin	with skin	without skin
Aerosol fogging	2, bottom A	5	0.47	<0.2	<0.2	<0.2
at 15-11-91	2, bottom B	5	0.56	<0.2	<0.2	<0.2
0.02 kg ai/t	2, middle A	5	0.26	<0.2	<0.2	<0.2
potatoes	2, middle B	5	0.31	<0.2	<0.2	<0.2
	2, top A	5	<0.2	<0.2	<0.2	<0.2
	2, top B	5	<0.2	<0.2	<0.2	<0.2
sampling at	3, bottom A	5	0.41	<0.2	<0.2	<0.2
19-11-91	3, bottom B	5	0.49	<0.2	<0.2	<0.2
	3, middle A	5	0.39	<0.2	<0.2	<0.2
	3, middle B	5	0.42	<0.2	<0.2	<0.2
	3, top A	5	0.34	<0.2	<0.2	<0.2
	3, top B	5	0.37	<0.2	<0.2	<0.2
Aerosol fogging	2, bottom A	91	1.3	<0.2	<0.2	<0.2
at 15-11-91	2, bottom B	91	1.5	<0.2	<0.2	<0.2
0.02 kg ai/t	2, middle A	91	1.6	<0.2	<0.2	<0.2
potatoes	2, middle B	91	1.1	<0.2	<0.2	<0.2
	2, top A	91	0.73	<0.2	<0.2	<0.2
	2, top B	91	0.78	<0.2	<0.2	<0.2
sampling at	3, bottom A	91	1.1	<0.2	<0.2	<0.2
13-02-92	3, bottom B	91	1.4	<0.2	<0.2	<0.2
	3, middle A	91	2.0	<0.2	0.23	<0.2
	3, middle B	91	2.0	<0.2	0.23	<0.2
	3, top A	91	1.2	<0.2	<0.2	<0.2
	3, top B	91	1.5	<0.2	<0.2	<0.2
Aerosol fogging	2, bottom A	96	1.9	<0.2	<0.2	<0.2
at 15-11-91	2, bottom B	96	2.2	<0.2	<0.2	<0.2
0.02 kg ai/t	2, middle A	96	2.0	<0.2	<0.2	<0.2
potatoes	2, middle B	96	2.3	<0.2	<0.2	<0.2
	2, top A	96	1.4	<0.2	<0.2	<0.2
+	2, top B	96	1.4	<0.2	<0.2	<0.2
0.02 kg ai/t	3, bottom A	96	2.6	<0.2	<0.2	<0.2
potatoes	3, bottom B	96	2.7	<0.2	<0.2	<0.2
14-02-92	3, middle A	96	2.0	<0.2	<0.2	<0.2
	3, middle B	96	2.0	<0.2	<0.2	<0.2
sampling at	3, top A	96	1.3	<0.2	<0.2	<0.2
18-02-92	3, top B	96	1.6	<0.2	<0.2	<0.2
Aerosol fogging	2, bottom A	140	1.5	0.41	<0.2	<0.2
at 15-11-91	2, bottom B	140	0.97	0.54	<0.2	<0.2
0.02 kg ai/t	2, middle A	140	2.8	0.37	<0.2	<0.2
potatoes	2, middle B	140	4.0	0.31	<0.2	<0.2
	2, top A	140	1.1	0.37	<0.2	<0.2
+	2, top B	140	1.4	0.34	<0.2	<0.2
0.02 kg ai/t	3, bottom A	140	2.1	0.28	<0.2	<0.2
potatoes	3, bottom B	140	2.6	0.29	<0.2	<0.2
14-02-92	3, middle A	140	2.2	0.32	<0.2	<0.2
	3, middle B	140	2.2	0.40	<0.2	<0.2
sampling at	3, top A	140	1.3	0.36	<0.2	<0.2

Treatment	Bin No.	Days after initial treatment	Chlorpropham residues[1] (mg/kg)		3-Chloroaniline residues[1] (mg/kg)	
	Location in pile		with skin	without skin	with skin	without skin
07-04-92	3, top B	140	2.1	0.33	<0.2	<0.2
Aerosol fogging	2, bottom A	215	1.4	≤0.2	<0.2	<0.2
at 15-11-91	2, bottom B	215	1.6	<0.2	<0.2	<0.2
0.02 kg ai/t	2, middle A	215	1.6	≤0.2	<0.2	<0.2
potatoes	2, middle B	215	1.4	<0.2	<0.2	<0.2
	2, top A	215	1.7	≤0.2	<0.2	<0.2
+	2, top B	215	1.6	<0.2	<0.2	<0.2
0.02 kg ai/t	3, bottom A	215	1.6	0.34	<0.2	<0.2
potatoes	3, bottom B	215	1.5	0.35	<0.2	<0.2
14-02-92	3, middle A	215	1.5	≤0.2	<0.2	<0.2
	3, middle B	215	2.3	0.23	<0.2	<0.2
sampling at	3, top A	215	1.2	0.28	<0.2	<0.2
16-06-92	3, top B	215	1.2	<0.2	<0.2	<0.2

[1] 0.2 mg/kg is method detection limit (MDL), not LOQ

Peels and granules. Peeling was very similar to commercial practice. Steamed potatoes were peeled by hand in the experimental process because of the small sample size. Figure 5 shows the production of peel at a pilot plant.

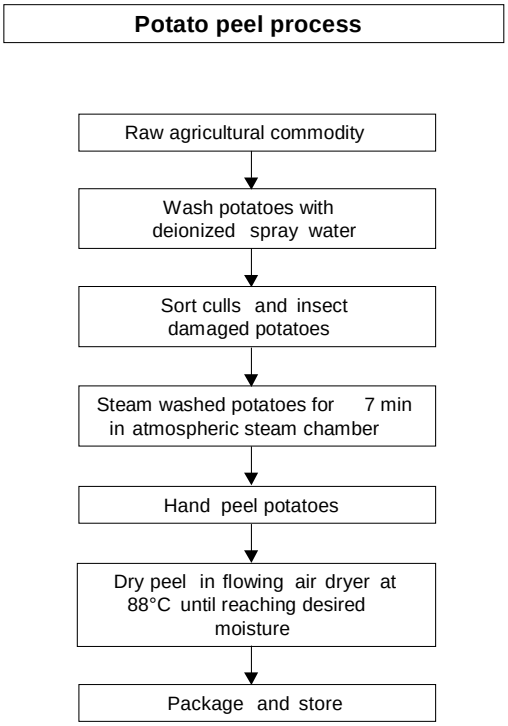


Figure 5. Potato peeling process at a pilot plant (Swanson *et al.*, 1993).

The commercial granule drying process was closely simulated in the experimental procedure. Figures 6a and 6b show granule production at a pilot plant.

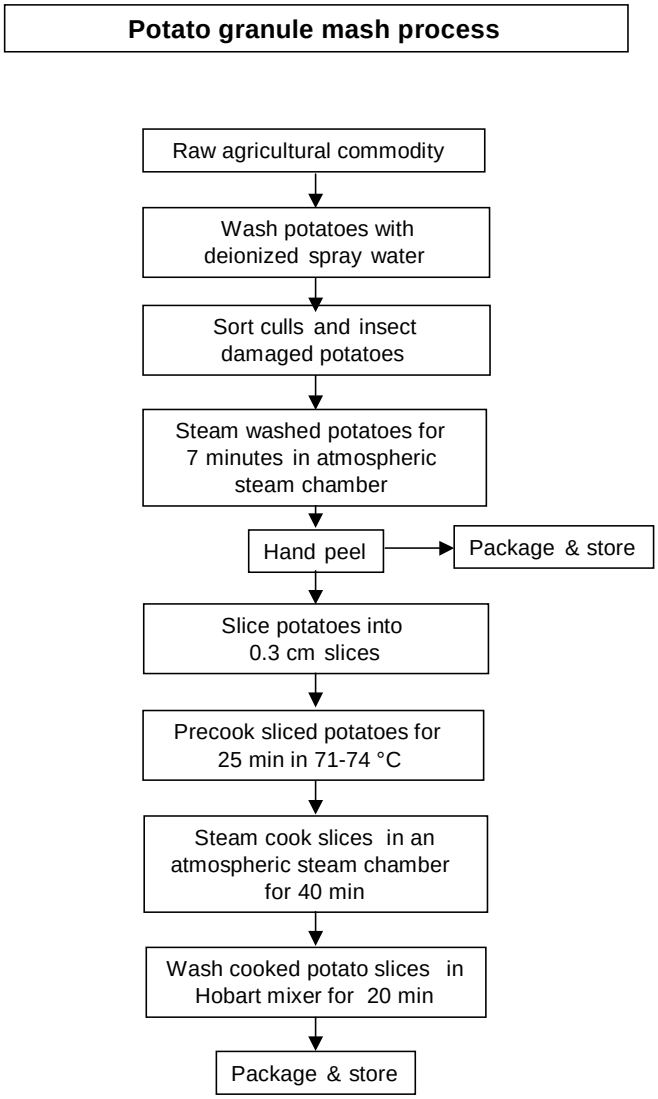


Figure 6a. Potato granule mash production at a pilot plant (Swanson *et al.*, 1993).

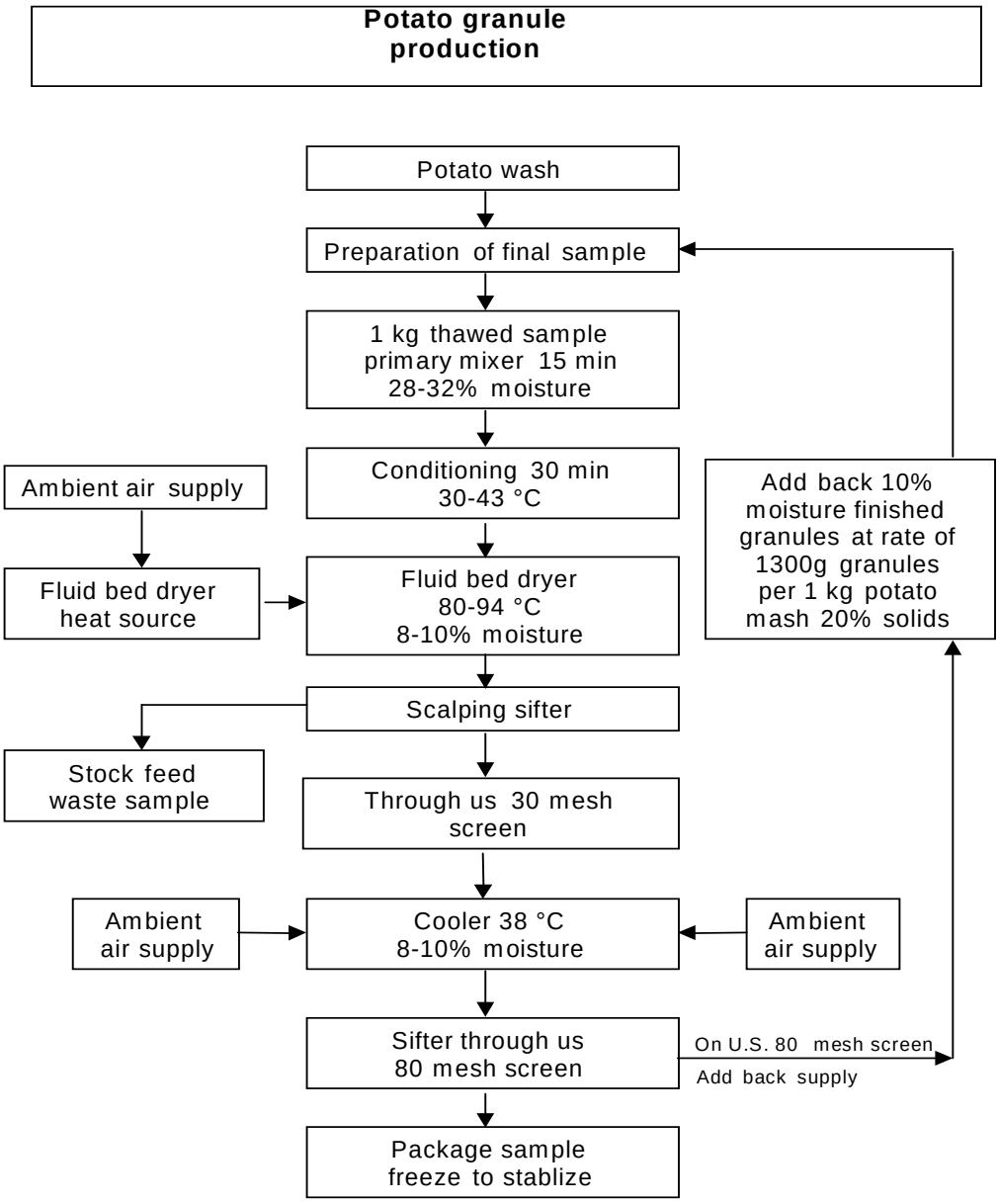


Figure 6b. Potato processing to dry granules at a pilot plant (Swanson *et al.*, 1993).

Table 36 shows the residues of chlorpropham and 3-chloroaniline in dried and wet potato peel as well as in dehydrated granules. Residues of *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham were undetectable in any fresh or processed product. Processing factors could not be determined as different samples were used for determination of residues in the raw agriculture commodity (RAC) and the processed product.

Table 36. Residues of chlorpropham and 3-chloroaniline in potato peel and granules (Haws *et al.*, 1993c).

Treatment	Bin no., location in pile	Days after initial treatment	Chlorpropham residues[1] (mg/kg)			3-Chloroaniline residues[1] (mg/kg)		
			Dried peel	Wet peel	Dehydr. granules	Dried peel	Wet peel	Dehydr. granules
Aerosol fogging	2, bottom A	5	89	11	<0.38	0.69	0.12	<0.38
at 15-11-91	2, bottom B	5	61	12	<0.38	<0.38	0.18	<0.38
0.02 kg ai/t	2, middle A	5	38	8.8	<0.38	<0.38	0.11	<0.38
potatoes	2, middle B	5	32	9.0	<0.38	<0.38	0.08	<0.38
	2, top A	5	29	7.0	<0.38	<0.38	<0.08	<0.38
	2, top B	5	33	7.2	<0.38	<0.38	<0.08	<0.38
sampling at	3, bottom A	5	59	14	<0.38	2.7	0.18	<0.38
19-11-91	3, bottom B	5	60	13	<0.38	0.67	0.15	<0.38
	3, middle A	5	67	13	<0.38	0.50	1.16	<0.38
	3, middle B	5	76	9.7	<0.38	1.0	0.14	<0.38
	3, top A	5	60	10	<0.38	2.2	0.11	<0.38
	3, top B	5	42	10	<0.38	<0.38	0.12	<0.38
Aerosol fogging	2, bottom A	91	26	7.3	0.77	0.48	0.08	<0.38
at 15-11-91	2, bottom B	91	40	10	0.78	0.61	0.14	<0.38
0.02 kg ai/t	2, middle A	91	52	9.2	0.47	0.57	0.08	<0.38
potatoes	2, middle B	91	30	7.2	0.50	0.40	<0.08	<0.38
	2, top A	91	45	3.7	0.83	0.55	<0.08	<0.38
	2, top B	91	20	3.4	0.84	0.42	<0.08	<0.38
sampling at	3, bottom A	91	47	9.9	0.78	0.84	0.16	<0.38
13-02-92	3, bottom B	91	44	9.7	0.78	0.78	0.18	<0.38
	3, middle A	91	35	8.8	0.79	0.50	0.12	<0.38
	3, middle B	91	43	9.8	0.78	0.58	0.12	<0.38
	3, top A	91	56	11	0.76	0.68	0.13	<0.38
	3, top B	91	51	10	0.72	0.60	0.16	<0.38
Aerosol fogging	2, bottom A	96	81	31	1.2	1.6	0.31	<0.38
at 15-11-91	2, bottom B	96	76	33	1.0	1.8	0.28	<0.38
0.02 kg ai/t	2, middle A	96	65	17	<0.38	1.0	0.13	<0.38
potatoes	2, middle B	96	70	14	<0.38	1.3	0.15	<0.38
	2, top A	96	48	19	0.75	0.64	0.18	<0.38
+	2, top B	96	44	14	0.65	<0.38	0.15	<0.38
0.02 kg ai/t	3, bottom A	96	145	34	0.69	3.5	0.25	<0.38
potatoes	3, bottom B	96	90	34	0.57	1.6	0.39	<0.38
14-02-92	3, middle A	96	81	32	0.64	1.1	0.29	<0.38
	3, middle B	96	106	30	0.71	1.3	0.23	<0.38
sampling at	3, top A	96	93	33	0.41	1.1	0.24	<0.38
18-02-92	3, top B	96	102	26	<0.38	1.0	0.11	<0.38
Aerosol fogging	2, bottom A	140	60	35	0.67	0.38	0.36	<0.38
at 15-11-91	2, bottom B	140	57	26	0.81	0.38	0.23	<0.38
0.02 kg ai/t	2, middle A	140	51	26	0.63	0.38	0.23	<0.38
potatoes	2, middle B	140	41	31	0.87	0.38	0.26	<0.38
	2, top A	140	44	17	0.75	0.38	0.18	<0.38
+	2, top B	140	30	21	0.76	0.38	0.22	<0.38
0.02 kg ai/t	3, bottom A	140	61	45	0.75	0.38	0.34	<0.38
potatoes	3, bottom B	140	63	41	0.87	0.38	0.32	<0.38
14-02-92	3, middle A	140	67	35	0.95	0.38	0.25	<0.38

Treatment	Bin no., location in pile	Days after initial treatment	Chlorpropham residues[1] (mg/kg)			3-Chloroaniline residues[1] (mg/kg)		
			Dried peel	Wet peel	Dehydr. granules	Dried peel	Wet peel	Dehydr. granules
	3, middle B	140	78	42	0.96	0.53	0.27	<0.38
sampling at	3, top A	140	71	43	0.69	0.48	0.30	<0.38
07-04-92	3, top B	140	77	31	0.82	0.53	0.28	<0.38
Aerosol fogging	2, bottom A	215	56	11	1.2	1.0	0.21	<0.38
at 15-11-91	2, bottom B	215	59	12	0.91	0.93	0.2	<0.38
0.02 kg ai/t	2, middle A	215	53	14	1.3	1.1	0.18	<0.38
potatoes	2, middle B	215	57	14	1.4	1.1	0.16	<0.38
	2, top A	215	47	15	1.1	0.92	0.21	<0.38
+	2, top B	215	57	15	1.2	1.2	0.22	<0.38
0.02 kg ai/t	3, bottom A	215	26	14	1.5	1.4	0.22	<0.38
potatoes	3, bottom B	215	25	13	1.5	1.5	0.19	<0.38
14-02-92	3, middle A	215	24	15	1.9	1.1	0.19	<0.38
	3, middle B	215	25	10	2.1	1.1	0.21	<0.38
sampling at	3, top A	215	27	17	1.6	1.6	0.24	<0.38
16-06-92	3, top B	215	25	17	1.5	1.4	0.23	<0.38

[1] 0.38 mg/kg is method detection limit (MDL) for granules and dried peel; 0.08 mg/kg is MDL for wet peel

Canola oil. Samples of oil used in frying French fries and chips, with and without skins, were taken before and after each frying. The samples were delivered to the analytical laboratory and stored frozen. The oil did not show a residue above the method detection limit (MDL) of 2.9 mg/kg each for chlorpropham, 3-chloroaniline, *p*-hydroxy-chlorpropham and *p*-methoxy-chlorpropham.

Residues in the edible portion of food commodities

Potatoes (Kleinkopf and Thomson, 1992; Goodrick *et al*., 1993b-d). In a study on mature potato tubers stored in bins under commercial conditions (see Table 25 above) whole tubers (Kleinkopf and Thomson, 1992) were processed into pulp and peel. The results from the three types of treatment are reported by Goodrick *et al.* (1993b-d) in reports 92CIPC04, 92CIPC05 and 92CIPC06. The chlorpropham and 3-chloroaniline residues in whole potatoes, pulp and peel, and processing factors calculated for 3-chloroaniline only if residues in the raw agriculture commodity were higher than the MDL, are shown in Tables 37 and 38.

Table 37. Residues of chlorpropham in the edible portions of potatoes (Goodrick *et al*., 1993b-d).

Treatment, Report No.	Bin no. Location in pile	Days after initial treatment	Chlorpropham residues[1] (mg/kg)				
			Whole	Pulp	Process factor (pulp)	Peel	Process factor (peel)
Aerosol fogging	2, bottom A	5	9.5	0.22	0.023	31	3.3
at 15-11-91	2, bottom B	5	11	0.22	0.02	35	3.2
0.02 kg ai/t	2, middle A	5	7.2	0.23	0.031	28	3.9
potatoes	2, middle B	5	7.6	0.23	0.03	32	4.2
	2, top A	5	6.9	0.25	0.036	33	4.8
+	2, top B	5	7.0	0.26	0.037	34	4.8
EC direct spray	3, bottom A	5	7.5	<0.08	0.011	37	4.9
at 19-11-91	3, bottom B	5	7.2	<0.08	0.011	32	4.4
0.01 kg ai/t	3, middle A	5	5.0	<0.08	0.016	41	8.2
potatoes	3, middle B	5	4.8	<0.08	0.017	43	9
	3, top A	5	9.1	0.12	0.013	46	5.1

Treatment, Report No.	Bin no. Location in pile	Days after initial treatment	Chlorpropham residues[1] (mg/kg)				
			Whole	Pulp	Process factor (pulp)	Peel	Process factor (peel)
Rep. 92CIPC04	3, top B	5	8.0	0.17	0.021	40	5
Aerosol fogging	2, bottom A	91	8.9	0.14	0.016	37	4.2
at 15-11-91	2, bottom B	91	8.6	0.15	0.017	36	4.2
0.02 kg ai/t	2, middle A	91	9.3	0.15	0.016	47	5.1
potatoes	2, middle B	91	8.3	0.14	0.017	55	6.6
	2, top A	91	6.5	0.17	0.026	30	4.6
+	2, top B	91	7.3	0.15	0.021	32	4.4
EC direct spray	3, bottom A	91	7.6	0.18	0.024	52	6.8
at 13-02-92	3, bottom B	91	9.4	0.18	0.019	64	6.8
0.01 kg ai/t	3, middle A	91	6.1	0.12	0.02	60	9.8
potatoes	3, middle B	91	6.3	-	-	65	10.3
	3, top A	91	9.1	0.17	0.019	51	5.6
Rep. 92CIPC04	3, top B	91	9.0	-	-	59	6.6
Aerosol fogging	2, bottom A	96	8.3	0.12	0.014	95	11
at 15-11-91	2, bottom B	96	9.7	0.13	0.013	77	8
0.02 kg ai/t	2, middle A	96	8.5	0.09	0.011	65	7.6
potatoes	2, middle B	96	7.0	0.09	0.013	55	7.9
+	2, top A	96	6.0	<0.08	0.013	52	8.7
0.02 kg ai/t	2, top B	96	7.2	<0.08	0.011	50	6.9
potatoes	3, bottom A	96	12	0.13	0.011	68	5.7
14-02-92	3, bottom B	96	14	0.14	0.01	83	5.9
+	3, middle A	96	9.3	0.12	0.013	60	6.4
EC direct spray	3, middle B	96	8.8	0.18	0.02	62	7.1
at 18-02-92	3, top A	96	10	0.13	0.013	49	4.9
0.01 kg ai/t Rep. 92CIPC04	3, top B	96	9.5	0.15	0.016	58	6.1
Aerosol fogging	2, bottom A	140	11	0.15	0.014	14	1.3
at 15-11-91	2, bottom B	140	11	0.18	0.016	25	2.3
0.02 kg ai/t	2, middle A	140	8.4	0.12	0.014	15	1.8
potatoes	2, middle B	140	8.9	0.16	0.018	23	2.6
+	2, top A	140	9.0	0.14	0.016	20	2.2
0.02 kg ai/t	2, top B	140	7.5	0.13	0.017	18	2.4
potatoes	3, bottom A	140	13	0.42	0.032	19	1.5
14-02-92	3, bottom B	140	12	0.13	0.011	19	1.6
+	3, middle A	140	12	0.71	0.059	27	2.2
EC direct spray	3, middle B	140	9.4	0.73	0.078	18	1.9
at 02-04-92	3, top A	140	13	0.42	0.032	18	1.4
0.01 kg ai/t Rep. 92CIPC04	3, top B	140	12	0.34	0.041	-	-
Aerosol fogging	2, bottom A	215	8.2	0.39	0.048	30	3.6
at 15-11-91	2, bottom B	215	7.7	0.32	0.042	28	3.6
0.02 kg ai/t	2, middle A	215	7.5	0.24	0.032	30	4
potatoes	2, middle B	215	8.0	0.30	0.038	39	4.9
+	2, top A	215	7.6	0.28	0.037	28	3.7
0.02 kg ai/t	2, top B	215	7.1	0.33	0.046	32	4.5
14-02-92	3, bottom A	215	11	0.36	0.033	43	3.9
+	3, bottom B	215	9.8	0.30	0.031	48	4.9
EC direct spray	3, middle A	215	7.6	0.45	0.059	38	5
at 16-06-92	3, middle B	215	8.3	0.40	0.048	31	3.7

Treatment, Report No.	Bin no. Location in pile	Days after initial treatment	Chlorpropham residues[1] (mg/kg)				
			Whole	Pulp	Process factor (pulp)	Peel	Process factor (peel)
0.01 kg ai/t	3, top A	215	7.4	0.42	0.057	51	6.9
Rep. 92CIPC04	3, top B	215	8.2	0.44	0.054	54	6.6
Mean processing factor				pulp (n = 58)	0.03	peel (n-59)	**5.1**
Median processing factor				pulp (n = 58)	0.0195	peel (n=59)	**4.9**
Aerosol fogging	2, bottom A	5	8.7	<0.08	0.009	34	3.9
at 15-11-91	2, bottom B	5	7.3	-	-	40	5.5
0.02 kg ai/t	2, middle A	5	4.2	<0.08	0.019	16	3.8
potatoes	2, middle B	5	3.2	<0.08	0.025	21	6.6
	2, top A	5	3.6	<0.08	0.022	17	4.7
	2, top B	5	3.2	-	-	19	5.9
Rep. 92CIPC05	3, bottom A	5	7.8	-	-	47	6.0
	3, bottom B	5	8.9	0.11	0.012	62	7.0
	3, middle A	5	7.3	-	-	42	5.8
	3, middle B	5	6.1	0.12	0.02	33	5.4
	3, top A	5	6.7	-	-	33	4.9
	3, top B	5	6.3	0.13	0.021	40	6.3
Aerosol fogging	2, bottom A	91	2.8	<0.08	0.029	39	13.9
at 15-11-91	2, bottom B	91	4.1	<0.08	0.02	46	11.2
0.02 kg ai/t	2, middle A	91	3.6	<0.08	0.022	34	9.4
potatoes	2, middle B	91	2.6	<0.08	0.031	29	11.2
	2, top A	91	1.4	<0.08	0.057	25	17.9
	2, top B	91	2.0	<0.08	0.04	23	11.5
Rep. 92CIPC05	3, bottom A	91	5.2	-	-	47	9.0
	3, bottom B	91	4.5	<0.08	0.018	37	8.2
	3, middle A	91	4.3	<0.08	0.019	67	15.6
	3, middle B	91	6.1	<0.08	0.013	37	6.1
	3, top A	91	7.1	<0.08	0.011	43	6.1
	3, top B	91	5.1	<0.08	0.016	39	7.6
Aerosol fogging	2, bottom A	96	9.8	0.11	0.011	-	-
at 15-11-91	2, bottom B	96	9.9	0.16	0.016	78	8.0
0.02 kg ai/t	2, middle A	96	6.9	<0.08	0.012	37	5.4
potatoes	2, middle B	96	6.4	0.09	0.014	32	5.0
	2, top A	96	6.0	0.09	0.015	35	5.8
+	2, top B	96	4.5	<0.08	0.018	26	5.8
0.02 kg ai/t	3, bottom A	96	16	-	-	74	4.6
potatoes	3, bottom B	96	10	-	-	61	6.1
14-02-92	3, middle A	96	9.4	-	-	64	6.8
	3, middle B	96	9.5	<0.08	0.008	51	5.4
	3, top A	96	12	<0.08	0.007	58	4.8
Rep. 92CIPC05	3, top B	96	11	<0.08	0.007	52	4.7
Aerosol fogging	2, bottom A	140	7.1	<0.08	0.011	51	7.2
at 15-11-91	2, bottom B	140	9.7	<0.08	0.008	48	5.0
0.02 kg ai/t	2, middle A	140	8.1	<0.08	0.01	35	4.3
potatoes	2, middle B	140	9.2	-	-	38	4.2
	2, top A	140	4.7	0.15	0.032	36	7.7
+	2, top B	140	4.4	<0.08	0.018	23	5.2
0.02 kg ai/t	3, bottom A	140	11	0.23	0.021	52	4.7
potatoes	3, bottom B	140	18	0.24	0.013	45	2.4
14-02-92	3, middle A	140	12	0.25	0.021	40	3.3

Treatment, Report No.	Bin no. Location in pile	Days after initial treatment	Chlorpropham residues[1] (mg/kg)				
			Whole	Pulp	Process factor (pulp)	Peel	Process factor (peel)
	3, middle B	140	11	0.25	0.023	37	3.4
Rep. 92CIPC05	3, top A	140	6.8	0.25	0.037	52	7.6
	3, top B	140	9.4	0.32	0.034	76	8.1
Aerosol fogging	2, bottom A	215	7.8	0.53	0.068	40	5.1
at 15-11-91	2, bottom B	215	7.0	0.70	0.1	82	11.7
0.02 kg ai/t	2, middle A	215	6.6	0.53	0.08	32	4.8
potatoes	2, middle B	215	6.8	0.38	0.056	38	5.6
	2, top A	215	6.8	0.28	0.041	23	3.4
+	2, top B	215	5.4	0.35	0.065	27	5.0
0.02 kg ai/t	3, bottom A	215	8.2	0.41	0.05	43	5.2
potatoes	3, bottom B	215	8.8	0.61	0.069	-	-
14-02-92	3, middle A	215	11	0.49	0.045	53	4.8
	3, middle B	215	8.2	0.75	0.091	49	6.0
Rep. 92CIPC05	3, top A	215	7.8	0.52	0.067	58	7.4
	3, top B	215	8.2	0.73	0.089	50	6.1
Mean processing factor (n = 50)				pulp (n = 50)	0.03	peel (n=58)	**6.6**
Median processing factor (n = 50)				pulp (n = 50)	0.021	peel (n=58)	**5.8**
Aerosol fogging	4, bottom A	5	23	0.14	0.006	101	4.4
at 15-11-91	4, bottom B	5	21	0.12	0.006	152	7.2
0.03 kg ai/t	4, middle A	5	7.6	-	-	56	7.4
potatoes	4, middle B	5	6.4	<0.08	0.012	43	6.7
	4, top A	5	4.7	<0.08	0.017	39	8.3
	4, top B	5	4.7	<0.08	0.017	31	6.6
sampling at	5, bottom A	5	16	0.14	0.009	95	5.9
19-11-91	5, bottom B	5	13	<0.08	0.006	75	5.8
	5, middle A	5	11	<0.08	0.007	63	5.7
Rep. 92CIPC06	5, middle B	5	13	<0.08	0.006	67	5.2
	5, top A	5	13	0.16	0.012	85	6.5
	5, top B	5	10	<0.08	0.008	68	6.8
Aerosol fogging	4, bottom A	91	7.8	0.22	0.028	61	7.8
at 15-11-91	4, bottom B	91	11	0.16	0.014	64	5.8
0.03 kg ai/t	4, middle A	91	7.0	-	-	45	6.4
potatoes	4, middle B	91	11	0.16	0.014	48	4.4
	4, top A	91	5.4	0.22	0.041	28	5.2
sampling at	4, top B	91	3.2	<0.08	0.025	18	5.6
13-02-92	5, bottom A	91	7.0	0.23	0.033	60	8.6
	5, bottom B	91	7.8	0.26	0.033	52	6.7
Rep. 92CIPC06	5, middle A	91	5.6	0.24	0.043	52	9.3
	5, middle B	91	14	0.35	0.025	62	4.4
	5, top A	91	9.2	0.30	0.033	63	6.8
	5, top B	91	7.4	0.26	0.035	53	7.2
Aerosol fogging	4, bottom A	140	8.6	0.53	0.062	36	4.2
at 15-11-91	4, bottom B	140	8.2	0.54	0.066	60	7.3
0.03 kg ai/t	4, middle A	140	10	0.62	0.062	44	4.4
potatoes	4, middle B	140	12	0.52	0.043	57	4.8
	4, top A	140	7.1	0.35	0.049	45	6.3
	4, top B	140	5.9	0.28	0.047	46	7.8
sampling at	5, bottom A	140	13	0.49	0.038	58	4.5
02-04-92	5, bottom B	140	13	0.47	0.036	55	4.2

Treatment, Report No.	Bin no. Location in pile	Days after initial treatment	Chlorpropham residues[1] (mg/kg)				
			Whole	Pulp	Process factor (pulp)	Peel	Process factor (peel)
	5, middle A	140	10	0.57	0.057	58	5.8
Rep. 92CIPC06	5, middle B	140	12	0.55	0.046	78	6.5
	5, top A	140	9.8	0.64	0.065	58	5.9
	5, top B	140	11	0.54	0.049	90	8.2
Aerosol fogging	4, bottom A	145	13	0.52	0.04	90	6.9
at 15-11-91	4, bottom B	145	12	0.35	0.029	71	5.9
0.03 kg ai/t	4, middle A	145	12	0.57	0.048	81	6.8
potatoes	4, middle B	145	14	0.42	0.03	58	4.1
+	4, top A	145	5.5	0.35	0.064	53	9.6
0.015 kg ai/t	4, top B	145	6.0	0.30	0.05	51	8.5
potatoes	5, bottom A	145	14	0.55	0.039	69	4.9
03-04-92	5, bottom B	145	14	0.39	0.028	72	5.1
sampling at	5, middle A	145	12	0.54	0.045	74	6.2
07-04-92	5, middle B	145	16	0.52	0.032	73	4.6
	5, top A	145	10	0.48	0.048	50	0.5
Rep. 92CIPC06	5, top B	145	12	0.42	0.035	98	8.2
Aerosol fogging	4, bottom A	215	7.8	1.0	0.13	61	7.8
at 15-11-91	4, bottom B	215	8.2	1.2	0.15	73	8.9
0.03 kg ai/t	4, middle A	215	8.0	1.2	0.15	56	7
potatoes	4, middle B	215	7.8	1.1	0.14	46	5.9
+	4, top A	215	6.7	0.99	0.15	49	7.3
0.015 kg ai/t	4, top B	215	8.1	1.0	0.12	54	6.7
potatoes	5, bottom A	215	8.9	1.0	0.11	66	7.5
03-04-92	5, bottom B	215	10	1.0	0.1	61	6.1
sampling at	5, middle A	215	11	1.4	0.13	53	4.8
16-06-92	5, middle B	215	15	1.1	0.073	77	5.1
	5, top A	215	11(1)	1.3	0.12	74	6.7
Rep. 92CIPC06	5, top B	215	9.5	1.3	0.14	75	7.9
Mean processing factor				pulp (n = 58)	0.05	peel (n=59)	**6.3**
Median processing factor				pulp (n = 58)	0.041	peel (n=59)	**6.4**
Overall mean processing factor				pulp (n = 166)	0.037	peel (n=177)	**6.0**
Overall median processing factor				pulp (n = 166)	0.027	peel (n=177)	**5.8**

[1] 0.08 mg/kg is method detection limit (MDL) for pulp, not LOQ.

Table 38. Residues of 3-chloroaniline in edible portions of potatoes (Goodrick *et al.*, 1993b-d).

Treatment, Report No.	Bin no., location in pile	Days after initial treatment	3-Chloroaniline residues[1] (mg/kg)			
			Whole	Pulp	Peel	Processing factor (peel)
Aerosol fogging	2, bottom A	5	<0.08	<0.08	<0.08	-
at 15-11-91	2, bottom B	5	<0.08	<0.08	<0.08	-
0.02 kg ai/t	2, middle A	5	<0.08	<0.08	<0.08	-
potatoes	2, middle B	5	<0.08	<0.08	<0.08	-
	2, top A	5	<0.08	<0.08	<0.08	-
+	2, top B	5	<0.08	<0.08	<0.08	-
EC direct spray	3, bottom A	5	0.09	<0.08	<0.08	-
at 19-11-91	3, bottom B	5	0.08	<0.08	0.08	-
0.01 kg ai/t	3, middle A	5	<0.08	<0.08	<0.08	-

Treatment, Report No.	Bin no., location in pile	Days after initial treatment	3-Chloroaniline residues[1] (mg/kg)			
			Whole	Pulp	Peel	Processing factor (peel)
	3, middle B	5	<0.08	<0.08	<0.08	-
	3, top A	5	0.08	<0.08	<0.08	-
Rep. 92CIPC04	3, top B	5	<0.08	<0.08	0.11	-
Aerosol fogging	2, bottom A	91	0.11	<0.08	0.20	1.8
at 15-11-91	2, bottom B	91	0.10	<0.08	0.19	1.9
0.02 kg ai/t	2, middle A	91	0.10	<0.08	0.20	2.0
potatoes	2, middle B	91	0.10	<0.08	0.23	2.3
	2, top A	91	0.09	<0.08	0.21	2.3
+	2, top B	91	0.09	<0.08	0.20	2.2
EC direct spray	3, bottom A	91	0.10	<0.08	0.20	2.0
at 13-02-92	3, bottom B	91	0.11	<0.08	0.21	1.9
0.01 kg ai/t	3, middle A	91	0.10	-	0.20	2.0
	3, middle B	91	0.10	<0.08	0.21	2.1
	3, top A	91	0.10	-	0.23	2.3
Rep. 92CIPC04	3, top B	91	0.12	<0.08	0.20	1.7
Aerosol fogging	2, bottom A	96	0.16	<0.08	0.30	1.9
at 15-11-91	2, bottom B	96	0.14	<0.08	0.23	1.6
0.02 kg ai/t	2, middle A	96	0.12	<0.08	0.26	2.2
potatoes	2, middle B	96	0.12	<0.08	0.22	1.8
+	2, top A	96	<0.08	<0.08	0.20	-
0.02 kg ai/t	2, top B	96	<0.08	<0.08	0.20	-
potatoes	3, bottom A	96	0.13	<0.08	0.21	1.6
14-02-92	3, bottom B	96	0.16	<0.08	0.33	2.1
+	3, middle A	96	0.12	<0.08	0.19	1.6
EC direct spray	3, middle B	96	0.12	<0.08	0.19	1.6
at 18-02-92	3, top A	96	0.13	<0.08	0.21	1.6
0.01 kg ai/t Rep. 92CIPC04	3, top B	96	0.12	<0.08	0.21	1.8
Aerosol fogging	2, bottom A	140	0.12	<0.08	0.25	2.1
at 15-11-91	2, bottom B	140	0.10	<0.08	0.24	2.4
0.02 kg ai/t	2, middle A	140	0.12	<0.08	0.24	2.0
potatoes	2, middle B	140	0.10	<0.08	0.24	2.4
+	2, top A	140	0.11	<0.08	0.25	2.3
0.02 kg ai/t	2, top B	140	0.10	<0.08	0.25	2.5
potatoes	3, bottom A	140	0.12	<0.08	0.29	2.4
14-02-92	3, bottom B	140	0.12	<0.08	0.27	2.2
+	3, middle A	140	0.12	<0.08	0.25	2.1
EC direct spray	3, middle B	140	0.12	<0.08	-	-
at 02-04-92	3, top A	140	0.13	<0.08	0.29	2.2
0.01 kg ai/t Rep. 92CIPC04	3, top B	140	0.12	<0.08	0.29	2.4
Aerosol fogging	2, bottom A	215	0.14	<0.08	0.28	2.0
at 15-11-91	2, bottom B	215	0.12	<0.08	0.32	2.7
0.02 kg ai/t	2, middle A	215	0.12	<0.08	0.25	2.1
potatoes	2, middle B	215	0.14	<0.08	0.26	1.9
+	2, top A	215	0.14	<0.08	0.22	1.6
0.02 kg ai/t	2, top B	215	0.13	<0.08	0.23	1.8
14-02-92	3, bottom A	215	0.14	<0.08	0.33	2.4
+	3, bottom B	215	0.15	<0.08	0.31	2.1
EC direct spray	3, middle A	215	0.13	<0.08	0.24	1.8

Treatment, Report No.	Bin no., location in pile	Days after initial treatment	3-Chloroaniline residues[1] (mg/kg)			
			Whole	Pulp	Peel	Processing factor (peel)
at 16-06-92	3, middle B	215	0.14	<0.08	0.24	1.7
0.01 kg ai/t	3, top A	215	0.12	<0.08	0.29	2.4
Rep. 92CIPC04	3, top B	215	0.13	<0.08	0.29	2.2
Aerosol fogging	2, bottom A	5	<0.08	<0.08	0.22	-
at 15-11-91	2, bottom B	5	<0.08	-	0.21	-
0.02 kg ai/t	2, middle A	5	<0.08	<0.08	0.20	-
potatoes	2, middle B	5	<0.08	<0.08	0.19	-
	2, top A	5	<0.08	<0.08	0.19	-
	2, top B	5	<0.08	-	0.19	-
	3, bottom A	5	0.20	<0.08	0.18	0.90
Rep. 92CIPC05	3, bottom B	5	0.21	<0.08	0.19	0.90
	3, middle A	5	0.20	<0.08	0.17	0.85
	3, middle B	5	0.19	<0.08	0.24	1.3
	3, top A	5	0.19	<0.08	0.20	1.1
	3, top B	5	0.19	<0.08	0.16	0.84
Aerosol fogging	2, bottom A	91	0.13	<0.08	0.16	1.2
at 15-11-91	2, bottom B	91	0.12	<0.08	0.16	1.3
0.02 kg ai/t	2, middle A	91	-	<0.08	0.15	-
potatoes	2, middle B	91	0.12	<0.08	0.15	1.2
	2, top A	91	0.12	<0.08	0.15	1.2
	2, top B	91	0.12	<0.08	0.14	1.2
	3, bottom A	91	0.15	<0.08	0.31	2.1
Rep. 92CIPC05	3, bottom B	91	0.14	<0.08	0.30	2.1
	3, middle A	91	0.15	<0.08	0.32	2.1
	3, middle B	91	0.14	<0.08	0.34	2.4
	3, top A	91	0.17	<0.08	0.31	1.8
	3, top B	91	0.14	<0.08	0.31	2.2
Aerosol fogging	2, bottom A	96	<0.08	<0.08	-	-
at 15-11-91	2, bottom B	96	<0.08	<0.08	0.36	-
0.02 kg ai/t	2, middle A	96	<0.08	<0.08	0.26	-
potatoes	2, middle B	96	<0.08	<0.08	0.24	-
	2, top A	96	<0.08	<0.08	0.27	-
+	2, top B	96	<0.08	<0.08	0.28	-
0.02 kg ai/t	3, bottom A	96	0.18	-	0.34	1.9
potatoes	3, bottom B	96	0.18	-	0.28	1.6
14-02-92	3, middle A	96	0.14	<0.08	0.27	1.9
	3, middle B	96	0.13	<0.08	0.25	1.9
	3, top A	96	0.15	<0.08	0.24	1.6
Rep. 92CIPC05	3, top B	96	0.13	<0.08	0.22	1.7
Aerosol fogging	2, bottom A	140	0.10	<0.08	0.26	2.6
at 15-11-91	2, bottom B	140	0.12	<0.08	0.20	1.7
0.02 kg ai/t	2, middle A	140	0.09	<0.08	0.17	1.9
potatoes	2, middle B	140	0.10	<0.08	0.15	1.5
	2, top A	140	0.08	<0.08	0.17	2.1
+	2, top B	140	0.09	<0.08	0.15	1.7
0.02 kg ai/t	3, bottom A	140	0.10	<0.08	0.14	1.4
potatoes	3, bottom B	140	0.12	<0.08	0.13	1.1
14-02-92	3, middle A	140	-	<0.08	0.10	-
	3, middle B	140	-	<0.08	0.09	-

Treatment, Report No.	Bin no., location in pile	Days after initial treatment	3-Chloroaniline residues[1] (mg/kg)			
			Whole	Pulp	Peel	Processing factor (peel)
Rep. 92CIPC05	3, top A	140	0.09	<0.08	0.15	1.7
	3, top B	140	0.09	<0.08	0.19	2.1
Aerosol fogging	2, bottom A	215	<0.08	<0.08	0.33	-
at 15-11-91	2, bottom B	215	<0.08	<0.08	0.51	-
0.02 kg ai/t	2, middle A	215	<0.08	<0.08	0.29	-
potatoes	2, middle B	215	<0.08	<0.08	0.34	-
	2, top A	215	<0.08	<0.08	0.26	-
+	2, top B	215	<0.08	<0.08	0.57	-
0.02 kg ai/t	3, bottom A	215	0.09	<0.08	0.37	4.1
potatoes	3, bottom B	215	-	<0.08	-	-
14-02-92	3, middle A	215	-	<0.08	0.30	-
	3, middle B	215	<0.08	<0.08	0.57	-
Rep. 92CIPC05	3, top A	215	<0.08	<0.08	0.35	-
	3, top B	215	<0.08	<0.08	0.38	4.8
Aerosol fogging	4, bottom A	5	0.23	<0.08	0.64	2.8
at 15-11-91	4, bottom B	5	0.18	<0.08	0.62	3.4
0.03 kg ai/t	4, middle A	5	0.11	<0.08	0.27	2.4
potatoes	4, middle B	5	0.10	<0.08	0.23	2.3
	4, top A	5	0.10	<0.08	0.22	2.2
	4, top B	5	0.09	<0.08	0.22	2.4
sampling at	5, bottom A	5	0.16		0.31	1.9
19-11-91	5, bottom B	5	0.19	<0.08	0.31	1.6
	5, middle A	5	0.15	<0.08	0.32	2.1
	5, middle B	5	0.15	<0.08	0.29	1.9
Rep. 92CIPC06	5, top A	5	0.17	<0.08	0.31	1.8
	5, top B	5	0.13	<0.08	0.26	2.0
Aerosol fogging	4, bottom A	91	0.15	<0.08	0.50	3.3
at 15-11-91	4, bottom B	91	0.15	<0.08	0.73	4.9
0.03 kg ai/t	4, middle A	91	0.15	-	0.22	1.5
potatoes	4, middle B	91	0.16	<0.08	0.28	1.8
	4, top A	91	0.16	<0.08	0.24	1.5
	4, top B	91	0.14	<0.08	0.18	1.3
sampling at	5, bottom A	91	<0.08	<0.08	0.22	-
13-02-92	5, bottom B	91	<0.08	<0.08	-	-
	5, middle A	91	<0.08	<0.08	-	-
Rep. 92CIPC06	5, middle B	91	<0.08	<0.08	-	-
	5, top A	91	<0.08	<0.08	0.15	-
	5, top B	91	<0.08	<0.08	0.13	-
Aerosol fogging	4, bottom A	140	0.26	<0.08	0.44	1.7
at 15-11-91	4, bottom B	140	0.23	<0.08	1.1	4.8
0.03 kg ai/t	4, middle A	140	0.22	<0.08	0.18	0.82
potatoes	4, middle B	140	0.25	<0.08	0.20	0.80
	4, top A	140	0.23	<0.08	0.24	1.0
	4, top B	140	0.22	<0.08	0.29	1.3
sampling at	5, bottom A	140	0.16	<0.08	0.44	2.8
02-04-92	5, bottom B	140	0.19	<0.08	0.41	2.2
	5, middle A	140	0.15	<0.08	0.39	2.6
	5, middle B	140	0.14	<0.08	0.37	2.6
Rep. 92CIPC06	5, top A	140	0.14	<0.08	0.37	2.6

Treatment, Report No.	Bin no., location in pile	Days after initial treatment	3-Chloroaniline residues[1] (mg/kg)			
			Whole	Pulp	Peel	Processing factor (peel)
	5, top B	140	0.14	<0.08	0.36	2.6
Aerosol fogging	4, bottom A	145	0.22	<0.08	0.21	0.95
at 15-11-91	4, bottom B	145	0.22	<0.08	0.23	1.1
0.03 kg ai/t	4, middle A	145	0.20	<0.08	0.12	0.60
potatoes	4, middle B	145	0.19	<0.08	0.11	0.58
	4, top A	145	0.17	<0.08	0.10	0.59
+	4, top B	145	0.19	<0.08	0.11	0.58
0.015 kg ai/t	5, bottom A	145	0.23	<0.08	0.15	0.65
potatoes	5, bottom B	145	0.18	<0.08	0.17	0.94
03-04-92	5, middle A	145	0.19	<0.08	0.18	0.95
sampling at	5, middle B	145	0.22	<0.08	0.16	0.73
07-04-92	5, top A	145	0.19	<0.08	0.15	0.79
Rep. 92CIPC06	5, top B	145	0.20	<0.08	0.21	1.1
Aerosol fogging	4, bottom A	215	0.09	<0.08	0.28	-
at 15-11-91	4, bottom B	215	0.09	<0.08	0.31	-
0.03 kg ai/t	4, middle A	215	<0.08	<0.08	0.23	-
potatoes	4, middle B	215	<0.08	<0.08	0.24	-
	4, top A	215	<0.08	<0.08	0.32	-
+	4, top B	215	<0.08	<0.08	0.24	-
0.015 kg ai/t	5, bottom A	215	0.13	<0.08	0.49	3.8
potatoes	5, bottom B	215	0.13	<0.08	0.40	3.1
03-04-92	5, middle A	215	0.12	<0.08	0.55	4.6
sampling at	5, middle B	215	0.13	<0.08	0.30	2.3
16-06-92	5, top A	215	0.12	<0.08	0.48	4.0
Rep. 92CIPC06	5, top B	215	0.11	<0.08	0.33	3.0
Mean processing factor peel (n = 127)						1.94
Median processing factor (n = 127)						1.9

[1] 0.08 mg/kg is method detection limit (MDL) for whole potato, pulp, peel, not LOQ.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Table 39 shows a summary of results from the USDA Pesticide Data Program for 1992, 1993, 1994, 1995, 1996, 1997 and 1998.

Table 39. Chlorpropham monitoring data from the USDA Pesticide Data Program.

Year	No. of samples analysed	No. of residues detected	Number of samples in chlorpropham residue range (mg/kg)										
			>0.002 ≤0.01	>0.01 ≤0.05	>0.05 ≤0.1	>0.1 ≤0.5	>0.5 ≤1	>1 ≤2	>2 ≤3	>3 ≤4	>4 ≤5	>5 ≤10	>10 ≤20
Apples													
1992		1		1									
1993		2		2									
1994	687	2	2										
1995	693	0											
1996	530	2		2									
Apple juice													
1996	171	0											
1997	683	0											

Year	No. of samples analysed	No. of residues detected	Number of samples in chlorpropham residue range (mg/kg)										
			>0.002 ≤0.01	>0.01 ≤0.05	>0.05 ≤0.1	>0.1 ≤0.5	>0.5 ≤1	>1 ≤2	>2 ≤3	>3 ≤4	>4 ≤5	>5 ≤10	>10 ≤20
1998	694	0											
Bananas													
1994	640	0											
1995	486	0											
Broccoli													
1994	679	0											
Cantaloupe													
1998	408	0											
Carrots													
1994	687	4		4									
1995	701	0											
1996	500	0											
Celery													
1994	176	0											
Corn syrup													
1998	298	0											
Corn, sweet													
1994	462	0											
1995	671	0											
1996	173	0											
Green beans													
1993		1		1									
1994	591	0											
1995	587	19		14	3	2							
1996	531	0											
1997	707	0											
1998	359	0											
Grapes													
1994	669	0											
1995	689	1		1									
1996	525	1		1									
Grape juice													
1998	665	0											
Lettuce													
1994	691	0											
Milk													
1996	570	0											
1997	727	0											
1998	594	1	1										
Oranges													
1994	683	0											
1995	691	0											
1996	518	0											
Orange juice													
1997	692	0											
1998	700	0											
Peaches													
1994	396	0											
1995	367	1		1									
1996	324	0											
1997	756	0											
Pears													
1997	708	0											
1998	712	0											

Year	No. of samples analysed	No. of residues detected	Number of samples in chlorpropham residue range (mg/kg)										
			>0.002 ≤0.01	>0.01 ≤0.05	>0.05 ≤0.1	>0.1 ≤0.5	>0.5 ≤1	>1 ≤2	>2 ≤3	>3 ≤4	>4 ≤5	>5 ≤10	>10 ≤20
Peas, sweet													
1994	433	0											
1995	670	0											
1996	355	0											
Potatoes													
1992		337		52	32	62	42	71	30	17	17	14	
1993		399		60	25	64	62	74	59	20	9	26	
1994	693	419	1	68	43	63	52	67	45	35	19	24	2
1995	707	482		107	25	59	75	74	58	35	17	29	3
Potatoes, sweet													
1996	507	1		1									
1997	681	0											
1998	357	1		1									
Spinach													
1995	610	0											
1996	517	1		1									
1997	680	0											
1998	695	0											
Strawberries													
1998	656	0											
Tomatoes													
1996	174	0											
1997	722	0											
1998	717	3		2		1							
Winter squash													
1997	661	1		1									
1998	679	1			1								

Table 40 gives a summary of the results from a review of the US Food and Drug Administration Pesticide Monitoring Database for Fiscal years 1992, 1993, 1994, 1995, 1996, 1997 and 1998. This database only reports detected residues not analysed samples in which residues were not detected.

Table 40. Results of monitoring of chlorpropham in the USA.

Crop/year	No. of residues detected	Number of samples in chlorpropham residue range (mg/kg)										
		≤0.01	>0.01 ≤0.05	>0.05 ≤0.1	>0.1 ≤0.5	>0.5 ≤1	>1 ≤2	>2 ≤3	>3 ≤4	>4 ≤5	>5 ≤10	>10 ≤20
Carrots												
1998	1	1										
Peppers												
1998	1	1										
Potatoes												
1992	24	7	4		1		7	3	2			
1993	70	10	2	9	13	10	6	11	2	3	4	
1994	56	3	3	7	21	7	9	4	2			
1995	100	57	11	4	7	4	3	8	3	1	1	1
1996	43	1	2	1	14	3	8	2	3	3	6	
1997	43	1			6	3	6	5	5	4	12	1
1998	37	5	1	5	4	4	5	2		5	6	
Yams												
1992	3		1		2							

Crop/year	No. of residues detected	Number of samples in chlorpropham residue range (mg/kg)										
		≤0.01	>0.01 ≤0.05	>0.05 ≤0.1	>0.1 ≤0.5	>0.5 ≤1	>1 ≤2	>2 ≤3	>3 ≤4	>4 ≤5	>5 ≤10	>10 ≤20
1995	2		2									

Chlorpropham was included in the 1994 and 1996 Australian Market Basket Surveys (Marro, 1996; Hardy, 1998).

In the 1994 survey chlorpropham was not detected (limit of reporting not stated) in the only food examined which was potatoes.

In the 1996 survey chlorpropham was detected in one sample at 0.2 mg/kg. Potatoes were the only food examined. The calculated dietary intakes of chlorpropham were very low for both the mean energy diets and the 95th percentile energy diets (Table 41).

Table 41. Estimated dietary intakes of chlorpropham from the Australian Market Basket Survey (Hardy, 1998).

	Body weight, kg	Potato consumption, g/day		Intake, ng/kg bw/day	
		mean	95th percentile	mean	95th percentile
Adults males	75	151	244	1.9	3.1
Adults females	59.1	87	144	1.4	2.3
Boys aged 12	39.8	116	183	2.8	4.4
Girls aged 12	41.5	104	150	2.4	3.4
Toddlers aged 2	12.3	23	27	1.8	2.1
Infants 9 months	9.1	13	15	1.3	1.6

NATIONAL MAXIMUM RESIDUE LIMITS

The governments of Australia and Germany submitted their MRLs. Australian MRLs for chlorpropham were revised in December 2000 (Simpson and Hamilton, 2001).

National MRLs reported to the Meeting.

Country	Crop	MRL (mg/kg)
Australia	Potatoes	30
	Onion, bulb	0.05*
	Garlic	0.05*
Germany	Potatoes, washed	5
	Carrot, leaf of root celery, chervil, parsnips, parsley, celery stock	0.2
	Other foods of plant origin	0.1
USA	Post-harvest application on potatoes	50
	Soya beans	0.2

* MRL set at or about the LOQ

APPRAISAL

Chlorpropham (isopropyl 3-chlorophenylcarbamate) was reviewed only for toxicology by the JMPR in 1963, 1965 and 2000. The compound was identified as a candidate for evaluation of residues as a new compound by the JMPR 2001 by the CCPR at its Thirtieth Session (1998) (ALINORM 99/24).

Chlorpropham is used as a growth regulator to suppress the post-harvest sprouting of ware

potatoes during storage. As a herbicide, it controls a broad spectrum of annual weeds. Only information on its use as a growth regulator for ware potatoes was made available to the Meeting by the Chlorpropham Manufacturers Task Force in the USA. This comprised studies on metabolism in animals and plants, methods of residue analysis, stability of residues in stored analytical samples, uses, results of supervised residue trials under commercial storage conditions and processing data. Information on national trials conducted according to GAP was provided by the governments of Australia and Germany.

Pure chlorpropham is a cream-coloured, crystalline solid of moderate volatility. It has limited solubility in water but is highly soluble in certain organic solvents. The log P_{ow} of 3.4 suggests that bioaccumulation may occur.

The trials summarized below were based on post-harvest use of chlorpropham on stored potatoes only.

Metabolism

Animals

The metabolism of chlorpropham in rats, lactating goats and laying hens is qualitatively similar. In rats, chlorpropham was rapidly absorbed and essentially completely metabolized before excretion in urine and, in small amounts, in faeces. Within 24 h, 82–92% of the radiolabel was recovered in the urine and 3–5% in the faeces. Three major metabolic routes were proposed: (1) hydroxylation at the 4-position and subsequent conjugation with sulfate or glucuronide; (2) oxidation of the isopropyl side-chain to the alcohol and subsequently the acid; and (3) decarbanilation to form 3-chloroaniline followed by *N*-acetylation, 4-hydroxylation and conjugation.

After administration of [^{14}C-ring]chlorpropham in capsules at a dose of 1.6–1.9 mg/kg bw (32–36 ppm in the feed) to two lactating goats for 7 days, rapid absorption and elimination *via* urine and faeces were seen (about 99%). About 1% was transferred to milk and liver, and one or two orders of magnitude less to fat and muscle. The goats metabolized chlorpropham readily. The main metabolic pathways included hydroxylation at the 4-position and subsequent formation of conjugates of sulfate or glucuronide. The main residue in the milk and kidney was the metabolite 4-hydroxy-chlorpropham-*O*-sulfonic acid (81% and 16% of TRR, respectively), while the main residue in fat tissues was chlorpropham (88% of TRR).

In laying hens receiving a daily dose of 6 mg [^{14}C-ring]chlorpropham by capsule (3.3–4.2 mg/kg bw or 50 ppm in the feed) for 7 days, 83% of the cumulative dose was recovered from excreta and only 0.03% from the egg production. The maximum concentrations of residues were 0.07 mg/kg in egg white and 0.23 mg/kg in egg yolk. The concentrations of TRR in tissues and organs were low (~0.5 mg/kg in liver and kidneys, ~0.2 mg/kg in fat and skin; 0.015 and 0.006 mg/kg in thigh and breast muscle, respectively). Chlorpropham was the main residue in hen fat and skin (92% and 68% of TRR, respectively), while the main residues in liver and kidney were 3-chloro-4-hydroxyaniline conjugates (25–64%). The *O*-sulfonic acid conjugate of 3-chloro-4-hydroxyaniline was the main compound in eggs (22% of TRR).

Plants: potato

Studies on metabolism and residues in crops other than potato were not provided. Translocation and formation of metabolites in potatoes were investigated after treatment by surface coating with [^{14}C-ring]chlorpropham and simulation of cold-storage conditions. Translocation was slow; approximately 86% of the TRR still being present in the surface methanol-wash fraction as chlorpropham after 52 weeks of storage. About 10% of TRR was recovered from the peel and about 3% from the pulp, mainly as unchanged chlorpropham.

The main metabolite in peel was an oligosaccharide of 4-hydroxy-chlorpropham. 3-Chloroaniline was the second main metabolite in peel. It was not identified as a free metabolite in pulp but in conjugated form, as 3-chloroaniline-*N*-glucosylamine (6% of TRR in pulp). The main metabolites in pulp, both representing about 18% of TRR, were an oligosaccharide and an amino acid conjugate of 4-hydroxy-chlorpropham. About 10% of TRR in peel and pulp was not extractable. Three potential metabolic pathways in plants were proposed:

- hydroxylation and subsequent conjugation with glucose, oligosaccharides or amino acids at the 4-position (*para* to the amino moiety) or conjugation of 4-hydroxy-chlorpropham with a methyl moiety to *para*-methoxy-chlorpropham or to an *S*-cysteinyl-hydroxy-chlorpropham;
- decarboxylation to 3-chloroaniline, followed by conjugation with glucose and other biomolecules;
- oxidation of the isopropyl chain and subsequent conjugation with oligosaccharide(s).

Methods of analysis

Plant matrices: potato

Most of the methods submitted for the analysis of chlorpropham residues in potato involved homogenization with an organic solvent (e.g. methanol, petroleum ether/acetone, hexane/acetone) followed by partition into dichloromethane. For further purification of the extract, an adsorbent column (e.g. Florisil) can be used. Chlorpropham is determined by GLC–NPD or after bromination as the bromo derivative by GLC–ECD. The LOQ was validated as 0.02 mg/kg.

Methods for the determination of chlorpropham and its three metabolites 3-chloroaniline, 4-hydroxy-chlorpropham and *para*-methoxy-chlorpropham in potato and potato products were submitted. They involved methanol/water as the primary extraction solvent, sometimes acid or alkaline hydrolysis and sonication for splitting conjugates, with subsequent clean-up by liquid–liquid partition with other organic solvents or phosphate buffer. For oil-processed samples, GPC clean-up follows. Determination was made by GLC–NPD. The methods have been validated for analysis of the parent compound and metabolites in whole potato, fresh peel and pulp, fries with and without skins, canola oil, potato chips with and without skins, processed dried peels, processed wet peels and dehydrated granules.

The recoveries of chlorpropham, 4'-hydroxy-chlorpropham and *para*-methoxy-chlorpropham were satisfactory. 3-Chloroaniline was recovered from fortified samples with varying consistency (40–70% from whole potato, pulp, peel with a fortification level of 0.4 mg/kg), as a large proportion of the aniline moiety can remain bound on biological material and occur as e.g. *N*-glucosyl or *N*-malonyl conjugates. Therefore, for each batch of samples from supervised trials, three untreated samples of each matrix were extracted, two of which were fortified with chlorpropham and the three metabolites to document recovery levels. The third sample served as a blank matrix to monitor contamination and interfering background matrix. Furthermore, matrix-based calibration standards were used. The method detection limits (MDL) and the LOQ for chlorpropham, 3-chloroaniline, *para*-hydroxy-chlorpropham and *para*-methoxy-chlorpropham (MDL / LOQ) were:

– 0.08 / 0.45 mg/kg in whole potato, fresh pulp, fresh peel and processed wet peel,
– 0.2 / 1.1 mg/kg in fries,
– 0.45 / 2.2 mg/kg in chips,
– *0.38 / 1.9 mg/kg in dehydrated granules and processed dried peel,*
– 2.9 / 14 mg/kg in canola oil.

Animal matrices

The parent and the metabolite *p*-hydroxy-chlorpropham-*O*-sulfonic acid cannot be determined together in ruminant matrices. The method for chlorpropham involves solid phase matrix dispersion

followed by GLC–MS detection. The recoveries of the lowest fortification level of 0.01 mg/kg in whole milk, liver, muscle, kidney and fat were about 200% in some cases. Therefore, the LOQ for chlorpropham achievable in whole milk, skim milk and cream should be 0.05 mg/kg and that for liver, muscle, kidney and fat should be 0.1 mg/kg.

4-Hydroxy-chlorpropham-*O*-sulfonic acid is determined in whole and skim milk by dilution with acetonitrile, selective precipitation of interfering substances and analysis by reversed-phase HPLC with UV detection. In tissues and cream, 4-hydroxy-chlorpropham-*O*-sulfonic acid is isolated by solid phase extraction and is determined by reversed-phase HPLC and UV detection. The achievable LOQ for this metabolite in whole milk, skim milk, cream, liver, muscle, kidney and fat is 0.05 mg/kg.

Stability of residues in stored analytical samples

Plant matrices: potato

A study of stability in freezer storage at –20 to –21 °C with fresh whole tubers, pulp and peel and processed potato products (chips, fries, dehydrated granules, processed wet and dried peel), fortified at two levels with chlorpropham or one of the metabolites 3-chloroaniline, 4-hydroxy-chlorpropham or *para*-methoxy-chlorpropham, showed that 3-chloroaniline and 4-hydroxy-chlorpropham were unstable in whole potatoes, potato pulp and potato peel after 90 days of storage. 3-Chloroaniline was also unstable in processed wet peels. The low initial recoveries of these analytes and their instability in fresh products may be due to bioreactivity with the potato matrix. An acceptable stability of 5–6 months' storage was found for chlorpropham and *para*-methoxy-chlorpropham.

Animal matrices

Cow liver, muscle and milk were fortified with 0.1 mg/kg chlorpropham and 4′-hydroxy-chlorpropham-*O*-sulfonic acid and stored at –20 °C. There was no significant degradation of either compound in any of the matrices over the storage period: chlorpropham, 28 days in liver, 59 days in muscle and 127 days in milk; 4-hydroxy-chlorpropham-*O*-sulfonic acid, 59 days in liver, 122 days in muscle and 133 days in milk.

Definition of the residue

Plant material

Studies of metabolism in stored potatoes established that most of the radiolabel was in the peel (10% of the applied amount after washing) and only a small proportion (3% of the applied amount) in the pulp. Most of the residue in the peel consisted of chlorpropham (85%) and only a minor part (3.5%) was 3-chloroaniline. Chlorpropham made up 42% of the residue in pulp.

In a supervised trial with stored potatoes, the only metabolite detected was 3-chloroaniline, less than 2% of the chlorpropham residue. Residues of *para*-methoxy-chlorpropham and (conjugates of) 4-hydroxy-chlorpropham were not detected.

The 2000 JMPR identified 3-chloroaniline as a toxicologically significant compound, apart from the parent chlorpropham. As 3-chloroaniline forms only a minor part of the residue, the Meeting agreed that residues in potatoes can be defined as chlorpropham *per se* for enforcement and risk assessment purposes.

Animal products

Studies of metabolism were carried out in rats, goats and hens. Chlorpropham was rapidly and virtually completely absorbed, extensively metabolized and rapidly excreted in both domestic

animals and rats. As potatoes are a minor feed item for chicken (< 10% of feed, see *FAO Manual*, p. 125), the Meeting focused on the study of metabolism in goats.

The main residue in milk and kidney of goats was the low-fat-soluble metabolite 4-hydroxy-chlorpropham-*O*-sulfonic acid (81% and 16% of measured TRR), while the fat-soluble chlorpropham was the main residue in fat (88%). No methods of analysis are available to determine the two residues simultaneously. As the metabolite was considered to be of no toxicological significance by the 2000 JMPR, the Meeting agreed that the residue definition for animal products for compliance with MRLs and dietary risk assessment should be chlorpropham only.

The presence of chlorpropham in fat and cream but not in muscle or skim milk in the feeding study in dairy cows and its log P_{OW} of 3.4 imply solubility in fat. The Meeting agreed that the residue is fat-soluble.

Fate of residues during storage

Chlorpropham is registered in the USA for post-harvest treatment on potato as an emulsifiable concentrate used by direct spray of a 1% aqueous emulsion on potato tubers moving along a conveyor line or as an aerosol fog at a standard application rate of 0.015 kg ai/t. The rate should be adapted to the storage period and temperature. Re-treatments can be made with one of the following regimens:

- aerosol fog at 0.02 kg ai/t at each of two applications 90 days apart, followed by direct spray at 0.01 kg ai/t, or
- aerosol fog at 0.03 kg ai/t and a second aerosol fog at 0.015 kg ai/t 140 days later.

A withholding period in days was not identified.

Extensive data were provided from a supervised trial in the USA on various treatment schedules on ware potatoes stored in bins. Each bin had its own air ventilation, refrigeration unit and computer-controlled monitoring system for accurate measurement of sampling pile conditions. The bins, each containing approximately 63.5 t of potatoes, were designed to allow access for tuber sampling during storage. Industry standards for relative humidity and temperature with continuous air flow were followed. Each bin was fogged with aerosol separately. Each bin was therefore considered as a separate trial. Furthermore, applications carried out at different times and different rates were considered separate treatments and equal a separate trial. The residue values used for evaluation were selected as either the highest value of the six samples taken from each bin or, in the case of a decline study, only one value (the highest) was selected. The concentrations of residues of chlorpropham in whole unwashed tubers resulting from various treatments according to GAP were:

Treatment (kg ai/t potatoes)	Residues (mg/kg)	Time after initial treatment (days)
1 x EC direct spray 0.01	8.2	0
1 x aerosol fog 0.02 + 1 x EC direct spray 0.01	9.1, 9.3, 9.4, 11	5, 91, 96
1 x aerosol fog 0.02	8.7, 8.9	5
1 x aerosol fog 0.03	16, 23	5,
2 x aerosol fog 0.02	9.9, 18	96, 140
1 x aerosol fog 0.03 + aerosol fog 0.015	14, 16	145
2 x aerosol fog 0.02 + 1 x EC direct spray 0.01	8.2, 9.7, 11, 11, 13, 14	96, 140, 215

The concentrations, in ranked order (median underlined), were: 8.2 (2), 8.7, 8.9, 9.1, 9.3, 9.4, 9.7, 9.9, <u>11</u> (3), 13, 14 (2), 16 (2), 18 and 23 mg/kg.

Chlorpropham is registered in Belgium, France and Germany for spraying, dusting or hot fogging of ware potatoes at 0.01–0.02 kg ai/t without a withholding period in days. The same treatment rates are registered in The Netherlands, with a withholding period of 60 days. The potatoes

can be stored in boxes or in bulk.

One trial carried out in France in 1998 (1 x 0.007 + 1 x 0.006 kg ai/t, pile from pallox) and one trial from Belgium in 1997 (1 x 0.015 kg ai/t, manual treatment of potatoes in paper bags) resulted in maximum residue concentrations of 8.8 and 13 mg/kg. The tubers were not washed before freezing of the analytical samples.

Treatment of potatoes stored in boxes was investigated in several trials, in which some of the potatoes were washed and some were washed and peeled after sampling. Seven trials in Belgium (1997) with hot fogging application of 1 x 0.007 kg ai/t plus 1 x 0.006 kg ai/t resulted in values of 0.61, 0.85, 0.89, 0.96, 1.1 and 1.2 (2) mg/kg. Seven trials in Germany in 1998 (dusting, 1 x 0.015 kg ai/t) resulted in concentrations of 0.06, 0.11, 3.5 (2), 3.8, 4.3 and 4.9 mg/kg. Four trials carried out in Germany in 1996 and 1999 with powdering of 1 x 0.01 kg ai/t, resulted in values of 1.7, 1.9, 2.0, 2.5, 2.5, 3.0, 3.0 and 3.2 mg/kg. The concentrations in washed whole potato tubers were, in ranked order (median underlined), 0.61, 0.85, 0.89, 0.96, 1.1, 1.2 (2), 1.7, 1.9, 2.0, 2.5 (2), 3.0 (2), 3.1, 3.2, 3.5 (2), 3.8, 4.3, 4.8 and 4.9 mg/kg.

The data on residues received from the European studies of box-stored, washed potatoes are different from those from the study of bin storage of unwashed tubers in the USA. The MRL, STMR and highest residues were derived from the USA data on unwashed potatoes and the two trials with unwashed potatoes in France and Belgium. The residue concentrations, in ranked order, were: 8.2 (2), 8.7, 8.8, 8.9, 9.1, 9.3, 9.4, 9.7, 9.9, 11 (3), 13 (2), 14 (2), 16 (2), 18 and 23 mg/kg.

The Meeting estimated a maximum residue level of 30 mg/kg, an STMR value of 11 mg/kg and a highest residue of 23 mg/kg for ware potatoes.

Fate of residues during processing

No information on the fate or nature of the residue after hydrolysis under cooking conditions was submitted.

Cooked potatoes were prepared from one fresh whole tuber sample containing 4.6 mg/kg chlorpropham. The concentration of residues decreased to 0.24 mg/kg in peeled fresh potatoes and to 0.08 mg/kg in peeled cooked potatoes after cooking for 20 min. Cooking reduced the value to 33% (processing factor, 0.33). From the STMR and the HR values for fresh ware potatoes of 11 and 23 mg/kg, an STMR-P value of 3.6 mg/kg and an HR-P value of 7.6 mg/kg were calculated for cooked potatoes with skin.

Cooked and peeled potatoes: The median processing factor for chlorpropham on raw peeled potatoes, based on 166 samples, was 0.027. Application of this factor to the STMR of 11 mg/kg and the HR of 23 mg/kg for raw ware potatoes provided a median value of 0.297 mg/kg and a highest residue of 0.62 for raw peeled potatoes. With the processing factor for cooking (0.33), an STMR-P value of 0.098 mg/kg and a HR-P value of 0.2 mg/kg were calculated for cooked potatoes without skin.

An adequate, extensive study of potato processing by standard industrial procedures provided information on the distribution of residues of chlorpropham and 3-chloroaniline in whole potato, pulp and peel, chips, and frozen and dehydrated products. Processing factors could be derived for fresh peeled potato and fresh peel, but not for chips, fries, dehydrated granules or processed peel, as different samples were used for the determination of residues in the raw agricultural commodity and in the processed product. For this reason, the concentrations used for evaluation of chips, fries, dehydrated granules and processed peel were selected from the data in trials conducted according to GAP.

Chips[1]: The concentrations of chlorpropham residues in chips with and without skin were 0.82, 1.2, 1.5 (2), 1.7, 1.9, 3.8, 4.0, 4.1, 4.2, 4.4, 4.6 (3), 5.0, 5.3, 6.3 (2), 6.4, 7.0, 7.1, 7.9 and 8.1 mg/kg and < 0.045 (11), 1.1, 1.2, 1.3, 1.4 (3), 1.5 (4), 1.6 and 1.8 mg/kg. The Meeting estimated STMR-P values of 4.6 and 1.1 mg/kg for chips with and without skin, respectively.

Fries[2]: The concentrations of chlorpropham residues in fries with and without skin were 0.97, 1.1, 1.2 (2), 1.3 (2), 1.4 (5), 1.5 (3), 1.6 (5), 1.7, 1.9, 2.0 (3), 2.1 (2), 2.2 (3), 2.3 (2), 2.6 (2), 2.7, 2.8 and 4.0 mg/kg and ≤ 0.2 (20), 0.23, 0.28 (2), 0.29, 0.31, 0.32, 0.33, 0.34 (2), 0.35, 0.36, 0.37 (2), 0.4, 0.41 and 0.54 mg/kg, respectively. The Meeting estimated STMR-P values of 1.6 and 0.2 mg/kg for fries with and without skin, respectively.

Dehydrated granules[2]: The concentrations of residues in dehydrated granules were < 0.38 (3), 0.41, 0.57, 0.63, 0.64, 0.65, 0.67, 0.69 (2), 0.71, 0.75 (3), 0.76, 0.81, 0.82, 0.87 (2), 0.91, 0.95, 0.96, 1.0, 1.1, 1.2 (3), 1.3, 1.4, 1.5 (3), 1.6, 1.9 and 2.1 mg/kg. The Meeting estimated an STMR-P value for chlorpropham of 0.845 mg/kg in dehydrated granules.

Potato peel, processed[2]: The concentrations of residues in industrially produced wet peel were 10, 11, 12, 13, 14 (5), 15 (3), 17 (4), 19, 21, 26 (3), 30, 31 (3), 32, 33 (2), 34 (2), 35 (2), 41, 42, 43 and 45 mg/kg The Meeting estimated an STMR-P value of 23.5 mg/kg for processed potato wet peel.

Residues in animal commodities

The Meeting estimated the dietary burden of chlorpropham and 3-chloroaniline in farm animals on the basis of the feeds listed in Appendix IX of the *FAO Manual.* The Meeting agreed to use only the STMR value for calculation of the dietary burden from processed animal feed as wet potato peel. It is suitable for estimating MRLs and HRs for animal commodities.

Dietary burden of chlorpropham

Commodity	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
					Beef cattle	Dairy cattle	Poultry	Beef cattle	Dairy cows	Poultry
Potato wet peel, processed	23.5	STMR-P	15	157	75	40	–	118	63	–

The dietary burden of chlorpropham in ruminant commodities (expressed as dry weight) used to estimate the MRL and STMR value was 118 mg/kg for beef cattle and 63 mg/kg for dairy cows.

In a 28-day study of cows given chlorpropham by capsule at a level equivalent to 0, 322, 955 or 3111 ppm in the feed (dry weight basis), only minor concentrations of chlorpropham residues (< 0.01–0.06 mg/kg) were found in milk at the highest level tested. The concentrations of the metabolite 4-hydroxy-chlorpropham-*O*-sulfonic acid (calculated as chlorpropham) were higher and roughly proportional to the feeding level, ranging from 0.1 to 0.61 mg/kg at the lowest level to 0.37–6.7 mg/kg at the highest level. Chlorpropham residues could not be detected in skim milk, but in cream the concentrations were 0.02–0.03 at the lowest level and 0.21–0.64 at the highest level. The residues of 4-hydroxy-chlorpropham-*O*-sulfonic acid were nearly equally distributed in skim milk and cream, the concentrations (calculated as chlorpropham) being 1.9–3.9 mg/kg and 1.7–3.6 mg/kg, respectively, in the group given the highest dose.

[1] Treatment of potatoes intended for chips: aerosol fogging 0.03 + 0.015 kg ai/t, treatment interval, 4.5 months
[2] Treatment of potatoes intended for frozen or dehydrated products: aerosol fogging 0.02 + 0.02 kg ai/t, treatment interval, 3 months

Minor concentrations of parent chlorpropham were found in muscle, liver and kidney. In the group at the highest level, the maximum values were 0.02 mg/kg in liver and kidney and 0.1 mg/kg in muscle. In fat, the chlorpropham residue values were 0.1–0.13, 0.19–0.39 and 0.15–2.8 mg/kg at the lowest, intermediate and highest level, respectively. Residues of 4-hydroxy-chlorpropham-*O*-sulfonic acid (calculated as chlorpropham) were found predominantly in kidney, with concentrations of 0.12–0.26 mg/kg, 0.76–1.2 mg/kg and 1.0–2.3 mg/kg at the three levels, respectively. No residues of the metabolite were detected (< 0.03 mg/kg) in muscle or fat. In liver, it was found only in cows at the highest level, at a maximum of 0.06 mg/kg.

The MRL and the STMR value for chlorpropham in milk were calculated from the interpolated dietary burden of 63 mg/kg (based on the STMR) for dairy cows; and the MRLs and the STMRs for meat, liver and kidney were derived from the dietary burden of 118 mg/kg for beef cattle. The interpolation is based on the actual concentration of residue in the group at the lowest level (322 ppm). As the compound is fat-soluble, the maximum residue level and the STMR value for milk were based on the concentrations of residue in cream. The following table shows the highest and the mean actual and interpolated residues used for estimating MRLs and STMR values for chlorpropham.

Feeding level (ppm) *Interpolated* / Actual	Chlorpropham residues (mg/kg)							
	Cream (mean)	Liver		Kidney		Muscle		Fat	
		High	Mean	High	Mean	High	Mean	High	Mean
MRL Beef cattle		*0.007* / 0.02		*< 0.004* / < 0.01		*0.004* / 0.01		*0.048* / 0.13	
STMR Beef cattle			*0.005* / 0.013		*< 0.004* / < 0.01		*< 0.004* / < 0.01		*0.04* / 0.11
MRL Dairy cows	*0.006* / 0.03								
STMR Dairy cows	*0.006* / 0.03								

118 / 322 (Beef cattle); *63* / 322 (Dairy cows)

The Meeting estimated maximum residue levels for chlorpropham of 0.0005* mg/kg F for milk, 0.01* mg/kg for edible offal of cattle and 0.1 mg/kg (fat) for cattle meat. The estimated STMR values are 0.0003 mg/kg for cattle milk, 0.005 mg/kg for edible offal of cattle and 0.004 mg/kg for cattle meat. The estimated highest residues are 0.007 mg/kg for edible offal of cattle and 0.004 mg/kg for cattle meat.

Recommendations

On the basis of the data from supervised trials, the Meeting concluded that the concentrations of residues listed below are suitable for establishing maximum residue limits and for assessing the IEDI and IESTI.

Definition of residue (for compliance with MRLs and for estimation of dietary intake): Chlorpropham. The residue is fat-soluble.

Commodity		Recommendation (mg/kg)			
CCN	Name	MRL		STMR, STMR-P	HR, HR-P
		New	Previous		
MO 0812	Cattle, edible offal of	0.01*	-	0.005	0.007
MM 0812	Cattle meat	0.1 (fat)	-	0.004	0.004
ML 0812	Cattle milk	0.0005*F	-	0.0003	
VR 0589	Potato	30 Po	–	11	23
	Potato, cooked[1]			3.6	7.6
	Potato, peeled and cooked			0.098	0.2
	Potato chips with skin			4.6	
	Potato chips without skin			1.1	
	Potato French fries with skin			1.6	
	Potato French fries without skin			0.2	
	Potato dehydrated granules			0.845	

[1]The information provided to the JMPR precludes an estimate that the dietary intake would below the acute RfD.

Further work or information

Desirable

1. A study on hydrolysis with radiolabelled chlorpropham to clarify the effect of cooking on the nature of residues (Annex 5, reference 86, pp. 12–15)
2. Processing studies on cooked potatoes with skin and for microwaved and oven-baked potatoes

Dietary risk assessment

Long-term intake

STMR or STMR-P values for chlorpropham were estimated by the Meeting for animal products, potatoes and six processed potato commodities. When data on consumption were available, these values were used to estimate dietary intake. The results are shown in Annex 3 (Report 2001).

The IEDIs, based on the estimated STMR values, were 1–50% of the ADI for the five GEMS/Food regional diets. The Meeting concluded that long-term intake of residues of chlorpropham from use on potatoes is unlikely to present a public health concern.

Short-term intake

The IESTI for chlorpropham was calculated for animal products and for potatoes (and their processing fractions) for which maximum residue levels and STMR values were estimated and for which data on consumption were available. The results are shown in Annex 4 (Report 2001).

The 2000 JMPR established an acute RfD of 0.03 mg/kg bw, on the basis of a NOAEL of 10 mg/kg bw per day in a 90-day study of toxicity in rats and a safety factor of 300. This value includes an additional safety factor of 3 to take account of inadequacies in the assessment of

methaemoglobinaemia, the critical toxicological effect. The current Meeting stated that the assessment of acute risk might require refinement of the acute RfD by submission of new studies that more appropriately address the end-point of concern.

The IESTI represented 0–1600% of the acute RfD for the general population and 0–4600% of the acute RfD for children. The values of 510 and 1500% represent the estimated short-term intake of cooked potatoes with skin. Peeling and cooking of potatoes reduced the concentration of chlorpropham residue, resulting in IESTIs of 10% of the acute RfD for the general population and 40% of the acute RfD for children. The Meeting concluded that short-term intake of chlorpropham residues is unlikely to present a public health concern, when peeled potatoes are consumed.

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2,4-D (020)

EXPLANATION

2,4-D was evaluated for residues within the CCPR Periodic Review Programme by the JMPR in 1998. The Meeting recommended numerous MRLs including an MRL of 0.1 mg/kg for grapefruit and oranges based on four supervised trials of the minor pre-harvest use as a plant growth regulator, and recommended withdrawal of the existing CXL of 2 mg/kg for citrus fruits.

The 32nd Session of the CCPR in 2000 decided to retain the CXL for citrus fruits, as the governments of South Africa, Uruguay and the USA wished to accommodate post-harvest use, and Spain also preferred not to have MRLs for individual citrus fruits. The governments of the USA and Spain informed the CCPR that additional residue trials would be reported to the JMPR. The Netherlands and South Africa disagreed with the evaluation of the data on which the proposed separate MRLs for oranges and grapefruit was based (ALINORM 01/24, para 89).

The 2001 Meeting received information on GAP and supervised residue trials for the post-harvest use of 2,4-D on lemons and oranges.

USE PATTERN

The post-harvest use of 2,4-D isopropyl ester (common name 2,4-D-isopropyl) is registered on lemons in the USA and on citrus fruits in Uruguay. 2,4-D-isopropyl is applied in a water-wax emulsion or as a diluted flush or spray followed by waxing in the packing house to inhibit abscission of buttons on harvested fruits. The registered uses are shown in Table 1 where application rates are expressed as acid equivalents (kg ae/hl).

Table 1. Registered post-harvest uses of the 2,4-D isopropyl ester.

Crop	Country	Method, label instructions	Spray conc. (kg ae/hl)[1]	No.	WhP[2], days
Lemons	USA	Post-harvest packing house use to maintain healthy buttons on lemons. Added to wax emulsions on lemons waxed before storage. Otherwise as a special treatment (flush or spray) after the last fresh-water rinse.	0.042	1	-
Grapefruit Lemons Mandarins Oranges	Uruguay	Post-harvest, as wax or as a pre-waxing spray.	0.042	1	-

[1] Factor 0.84 (molecular weight 2,4-D acid 221, molecular weight 2,4-D-isopropyl 263.12)
[2] Withholding period

RESIDUES RESULTING FROM SUPERVISED TRIALS

Johnson and Strickland (1995). Two supervised trials on the post-harvest use of 2,4-D on lemons in California, USA, were reported to the 1998 JMPR. However there were too few trials for the estimation of a maximum residue level. The results are repeated in Table 2.

Table 2. Results of two US trials on the use of 2,4-D on lemons reported to the 1998 JMPR (Johnson and Strickland, 1995). Whole fruit analysed.

Site no./Location	Variety	Application rate		Date of treatment	Growth stage	Residue (mg/kg)	PHI or WHP (days)	Remarks
		g ae/ha (g ae/hl)	water (l/ha)					
Site 1 Tulare County, CA	Eureka	56 (1.3)	4456	12/6/94	Immature	0.06, 0.05 <0.05 (2)	0 7	pre-harvest
		(50)		12/15/94		0.42 0.29 0.61 0.41	0 28 56 112	post-harvest[1] in storage
Site 2 Ventura County, CA	Lisbon	56 (1.2)	4663	12/20/94	Immature	<0.05, 0.05 <0.05 (2)	0 7	pre-harvest
		(50)		12/28/94		0.54 0.4 0.52 0.5	0 28 56 112	post-harvest[1] in storage

[1] Fruits harvested 7 days after pre-harvest treatment were treated in storage.

Johnson and Strickland (2001). In 2001 six groups of Navel oranges and four of lemons were treated, and one group of each used as controls. Fifty individual Navel oranges and 50 lemons (1st 4 trials) and 50 Navel oranges (5th and 6th trials) were sprayed with a 0.05 kg ai/hl 2,4-D-isopropyl solution (0.042 kg ae/hl). Twenty oranges and 20 lemons were randomly collected from each trial. All trials complied with label directions and simulated standard industry practices. Duplicate solutions were prepared for duplicate treatments.

For post-harvest use 2,4-D-isopropyl is applied in a water-wax emulsion or as a diluted flush or spray followed by waxing in the packing-house. Trials conducted before preparation of the protocol indicated that 2,4-D residues were slightly higher after aqueous spray applications (mean 0.26 mg/kg) than after wax emulsions (mean 0.16 mg/kg). Post-harvest aqueous spray applications were therefore made to maximize potential residues.

Control samples were handled in the same way as treatment samples except that they were sprayed with a blank formulation. Each replicate consisted of 20 fruits weighing an average of 2.5 kg (Navel oranges) or 1.3 kg (lemons). All were frozen immediately after treatment and subdivided into two 10-fruit samples. The fruits were homogenized and two 10-g sub-samples from each batch were extracted and analysed for 2,4-D residues by gas chromatography (GLC).

The Navel oranges were harvested on 17 January 2001 and collected from the packing house on the next day. The Lisbon lemons were harvested on 16 January 2001 and collected the next day. The fruit were transported on the day of collection to the Sunkist Research Station and placed in a cold room (approximately 1.7°C). The fruit did not receive any pre-harvest 2,4-D treatments or post-harvest applications of any kind.

In the first four treatments on 23 January 2001 50 Navel oranges and 50 lemons were treated at the same time according to label directions and industrial practice. Two extra treatments were applied to the oranges. All the fruit were put through a 10% solution of a commercial foamer wash, rinsed with fresh water, and dried. Control fruit were then sprayed with a blank formulation, and the treated fruit at 0.05 kg ai/hl 2,4-D-isopropyl.

For each run the fruit were placed on a conveyor belt and rubber balls were used to push the sample through the line to ensure the samples maintained a constant flow rate. The treatment and control solutions were applied through four nozzles which coated the fruit as they passed underneath. The spray solution and wet fruit also coated several rows of plastic brushes that the fruit rolled through after being sprayed. The total contact time measured with a stopwatch was approximately 22

seconds. The fruit were next conveyed through foam brushes, where they were partially dried and then onto wax brushes to apply a commercial storage wax solution consisting of 12.5% storage wax and 87.5% soft water. Then the fruit were conveyed through a forced-air dryer (52 - 57°C) to dry the wax and samples were placed in plastic bags off the packing line, labelled, placed in a second plastic bag, and immediately placed in freezers. The next day samples were shipped on dry ice via overnight express for determination of the residues.

One approximately 50-ml sample of each control and treatment solution was collected immediately before each treatment and analysed to establish the actual concentration of active ingredient in the application solutions.

Analytical methods. 2,4-D in unpeeled raw citrus fruit was determined by a fully-validated method. All individual fruit included in each 10-fruit sample were homogenized. The ground samples were stored frozen at approximately -20°C. Two 10 g sub-samples of the homogenized sample were analysed. 2,4-D was isolated by extraction with 0.7 M NaOH for 1 hour at 100°C. An aliquot of the extract was acidified with sulfuric acid and extracted with ether. The 2,4-D in the extract was then converted to its methyl ester using a boron trifluoride/methanol solution. After water was added, the sample was taken up in hexane and analysed by gas chromatography with a mass selective detector (GLC-MSD). The limit of quantification (LOQ) for raw citrus fruit was 0.05 mg/kg. All samples were analysed within 20 days of treatment.

5-ml samples of application solution mixes were hydrolyzed in aqueous sodium hydroxide solution to convert any esters or salts of 2,4-D to the sodium salt. The sample was then acidified with sulfuric acid to convert all 2,4-D to the free acid, saturated with sodium chloride, and partitioned into ethyl ether. The ether was evaporated and the residue treated with boron trifluoride-methanol solution to convert 2,4-D acid to the methyl ester. Water was added to the reaction mixture and 2,4-D-methyl partitioned into hexane and determined by GLC-MSD. The concentration in the application solution was calculated as 2,4-D-isopropyl. The LOQ was 0.1 mg/kg for application solutions.

Results. Residues were calculated as acid equivalents in mg ae/kg. 2,4-D residues in all control orange and lemon samples were <0.05 mg/kg. Mean 2,4-D residues in orange samples treated with the 0.05 kg ai/hl 2,4-D-isopropyl spray solution were 0.2 mg/kg. The maximum residue found in any Navel orange sample was 0.27 mg/kg (Table 3). Mean residues in lemons treated with the 0.05 kg ai/hl 2,4-D-isopropyl spray solutions were 0.395 mg/kg, and the maximum residue found in any lemon sample was 0.65 mg/kg (Table 4).

Table 3. 2,4-D residues at day 0 in Navel oranges, whole fruit (Johnson and Strickland, 2001).

Sample No.	Treatment (kg ae/hl)	Treatment sample	Analytical sample	2,4-D residues (mg ae/kg)	
				measured	mean
101-014-05	Trial 1 0.042	1	1	0.154	0.16
			2	0.166	
101-014-06		2	1	0.270	0.24
			2	0.214	
101-014-07	Trial 2 0.042	1	1	0.235	0.22
			2	0.207	
101-014-08		2	1	0.252	0.22
			2	0.186	
101-014-09	Trial 3 0.042	1	1	0.144	0.16
			2	0.172	
101-014-10		2	1	0.179	0.2
			2	0.218	

Sample No.	Treatment (kg ae/hl)	Treatment sample	Analytical sample	2,4-D residues (mg ae/kg)	
				measured	mean
101-014-11	Trial 4 0.042	1	1	0.197	0.19
			2	0.189	
101-014-12		2	1	0.218	0.21
			2	0.204	
101-014-13	Trial 5 0.042	1	1	0.204	0.2
			2	0.194	
101-014-14		2	1	0.213	0.21
			2	0.210	
101-014-15	Trial 6 0.042	1	1	0.183	0.19
			2	0.203	
101-014-16		2	1	0.183	0.19
			2	0.192	

Table 4. 2,4-D residues at day 0 in whole lemons (Johnson and Strickland, 2001).

Sample No.	Treatment (kg ae/hl)	Treatment sample	Analytical sample	2,4-D residues (mg ae/kg)	
				measured	mean
101-014-17	Trial 1 0.042	1	1	0.337	0.33
			2	0.315	
101-014-18		2	1	0.654	0.6
			2	0.554	
101-014-19	Trial 2 0.042	1	1	0.297	0.33
			2	0.354	
101-014-20		2	1	0.382	0.41
			2	0.429	
101-014-21	Trial 3 0.042	1	1	0.338	0.36
			2	0.375	
101-014-22		2	1	0.352	0.37
			2	0.383	
101-014-23	Trial 4 0.042	1	1	0.404	0.44
			2	0.477	
101-014-24		2	1	0.310	0.33
			2	0.344	

The formulation blank solution used to spray control orange and lemon samples contained 0.145 mg/l 2,4-D-isopropyl. Mean 2,4-D-isopropyl concentration in the six treatment solutions ranged from 106% to 136% of the nominal concentration of 0.05 kg ai/hl (Table 5), and the mean for all six treatments was 121% of nominal.

Table 5. 2,4-D-isopropyl concentrations in applied solutions (Johnson and Strickland, 2001).

Sample No.	Solution	Analysis	2,4-D-isopropyl (kg ai/hl)	Treatment mean (kg ai/hl)	% of nominal
101-014-25	Control 1	1	0.000015	0.000014	
		2	0.000014		
101-014-26	Trial 1	1	0.075	0.068	136
		2	0.062		
101-014-27	Trial 2	1	0.062	0.061	122
		2	0.059		
101-014-28	Trial 3	1	0.058	0.062	124
		2	0.067		
101-014-29	Trial 4	1	0.054	0.054	108
		2	0.054		
		1	0.051		

Sample No.	Solution	Analysis	2,4-D-isopropyl (kg ai/hl)	Treatment mean (kg ai/hl)	% of nominal
101-014-30	Trial 5	2	0.056	0.053	106
101-014-31	Trial 6	1	0.060	0.064	128
		2	0.068		

APPRAISAL

2,4-D was evaluated for residues in a periodic review by the JMPR in 1998, and many MRLs were recommended. In the case of citrus fruits, the JMPR estimated a maximum residue level of 0.1 mg/kg for grapefruit and orange on the basis of four supervised trials conducted according to minor pre-harvest use as a plant growth regulator, and recommended withdrawal of the current CXL of 2 mg/kg for citrus fruit.

The CCPR at its thirty-second session in 2000 decided to retain the CXL for citrus fruits, as the Delegations of South Africa, Uruguay and the USA preferred to do so in order to accommodate post-harvest use. The Delegation of Spain also preferred the CXL to MRLs for individual commodities. Spain and the USA informed the CCPR that the results of additional trials would become available for the JMPR. The Netherlands and South Africa disagreed with evaluation of data for the proposed separate MRLs for orange and grapefruit (ALINORM 01/24).

The 2001 JMPR received information on trials conducted in Uruguay and the USA on citrus fruit by GAP and on supervised trials of post-harvest use of 2,4-D on lemons and oranges.

Residues of supervised trials

2,4-Dichlorophenoxyacetic acid isopropyl ester (2,4-D IPE) is currently registered and is applied after harvest to commercial citrus species in order to inhibit abscission of buttons on harvested fruit in Uruguay (grapefruit, orange, mandarin, lemon) and in the USA (lemon). The solutions of 2,4-D IPE can be applied as a treatment in a water–wax emulsion in packing houses or as a diluted flush or spray.

The 1998 JMPR evaluated two post-harvest trials on lemons in California conducted according to current GAP in Uruguay and the USA. The concentrations of residues in whole fruit were 0.54 and 0.61 mg/kg.

Post-harvest treatments were made to navel oranges (six trials) and lemons (four trials) with experimental packing-line equipment at a research centre in California in 2001. Applications were made in accordance with current label requirements in Uruguay and the USA at maximum rates. Commercial application and fruit handling practices were followed. The fruit were sprayed with 2,4-D IPE solution containing 0.05 kg ai/hl (2,4-D acid equivalent, 0.04 kg ai/hl). The concentrations of residues on whole orange fruit were, in ranked order (median underlined), 0.19, 0.2, <u>0.21</u> (2), 0.22 and 0.24 mg/kg. The concentrations on whole lemon fruit were, in ranked order, 0.37, 0.41, 0.44 and 0.6 mg/kg.

The Meeting acknowledged that the data for oranges (median, 0.21 mg/kg) and lemons (median, 0.49 mg/kg) were different. However, on the basis of Uruguayan use on oranges, grapefruit, mandarins and lemons, the Meeting decided to recommend an MRL for citrus fruits based on the whole data set. The concentrations on whole fruit after post-harvest treatment of oranges and lemons were, in ranked order, 0.19, 0.20, 0.21 (2), 0.22, <u>0.24</u>, <u>0.37</u>, 0.41, 0.44, 0.54, 0.60 and 0.61 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg for citrus fruit. As no data were submitted for the edible portion, the Meeting estimated an STMR value of 0.3 mg/kg, based on the residues in whole fruit.

Fate of residues during processing

The 1998 JMPR estimated processing factors of 0.1 for citrus juice and < 1 for citrus oil. The Meeting applied these factors to the STMR value of 0.3 mg/kg for citrus fruit and estimated STMR-P values of 0.03 mg/kg for citrus juice and 0.3 mg/kg for citrus oil.

Recommendations

On the basis of the data from supervised trials, the Meeting concluded that the residue concentrations listed below are suitable for establishing maximum residue limits and for assessing the IEDI.

Definition of the residue (for compliance with MRLs and for estimation of dietary intake): 2,4-D

Commodity		Recommendation, values in mg/kg			
CCN	Name	MRL		STMR, STMR-P[1]	HR
		New	Previous		
FC 0001	Citrus fruits	1 Po	–	0.3	
	Citrus juice			0.03	
	Citrus oil			0.3	
FC 0203	Grapefruit	W	0.1		
FC 0004	Oranges, Sweet, Sour	W	0.1		

W: The previous recommendation is withdrawn.
[1] As no data for edible portions were available, the STMR values are based on results for whole fruits.

Dietary risk assessment

Long-term intake

STMR or STMR-P values for 2,4-D were estimated by the current Meeting for citrus fruits and the processed commodities citrus juice and oil. Further STMR or STMR-P values were estimated by the 1998 JMPR for 22 commodities. When data on consumption were available, these values were used to estimate dietary intake. The results are shown in Annex 3.

The IEDIs for the five GEMS/Food regional diets, based on the estimated STMRs, were 3–20% of the ADI. The Meeting concluded that long-term intake of residues of 2,4-D from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The 2001 JMPR concluded that it was unnecessary to establish an acute RfD for 2,4-D. The Meeting therefore concluded that the short-term intake of 2,4-D residues is unlikely to present a risk to consumers.

REFERENCES

Johnson, G. D. and Strickland, M. D. 1995. Magnitude of residues in/on California citrus fruit after growth regulator treatments with (2,4-Dichlorophenoxy) acetic acid isopropylester. Final report: Lab Project No. 101-004: R28941: R289402. Western EcoSystems

Technology; Research for Hire; and Corning Hazleton. Unpublished.

Johnson, G. D. and Strickland, M. D. 2001. Magnitude of residues in/on citrus fruit after post harvest treatments with (2,4-Dichlorophenoxy) acetic acid isopropylester. June 27, 2001. California Citrus Quality Council, Auburn, CA 95603, USA. Project ID CCQC 00-01. Unpublished.

DIMETHIPIN (151)

EXPLANATION

Dimethipin was evaluated in 1985, 1987 and in 1988. It was identified for re-evaluation at the 1997 CCPR (ALINORM 97/24 A) and scheduled for consideration by the 2001 JMPR.

Data to support the existing CXLs for cotton, linseed, potatoes, rape seed, sunflower seed and animal commodities and other critical data required for the recommendation of MRLs have been reported by the manufacturer. The governments of Australia and Germany have reported information on GAP and/or residue data.

IDENTITY

ISO Common name: dimethipin

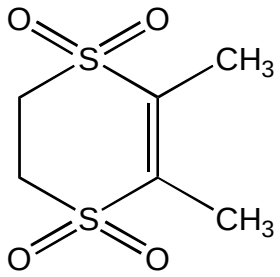
Chemical name:
IUPAC: 2,3-dihydro-5,6-dimethyl-1,4-dithiine 1,1,4,4-tetraoxide
CA: 2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetraoxide

CAS No.: 55290-64-7

CIPAC No.: 151

Synonyms/trade names: Harvade, UBI-N252, oxidimethiin, tetrathiin.

Structural formula:



Molecular formula: $C_6H_{10}O_4S_2$

Molecular weight: 210.3

Physical and chemical properties

Technical material

Appearance: white crystalline (Riggs, 1990a)
Odour: sweet molasses-like (Riggs, 1990b)
Density: 1.5935 g/cm^3 at 23°C (Thomson, 1989)
Melting point: 162-172°C

Solubility (Spare, 1987a, Young 1991)

Solvent	Solubility at 25°C (g/100 ml solvent)
Water	0.46

Solvent	Solubility at 25°C (g/100 ml solvent)
Aqueous buffer pH 4	0.21
Aqueous buffer pH 7	0.18
Aqueous buffer pH 10	0.17
Acetone	9.7
Acetonitrile	18
1-Butanol	0.16
Methanol	1.07
1-Octanol	7.9×10^{-2}
Propylene glycol	0.76
Toluene	0.90
Hexane	$1.2\text{-}1.7\times10^{-3}$

pH of 1% solution in 50% (v/v) aqueous dioxane = 4.52 at 30.2°C (Thomson, 1990a)
Dissociation constant: $pK_a = 10.88 \pm 0.39$ at 25°C (Thomson, 1990b)
Vapour pressure: less than 3.81×10^{-7} Torr at 24°C (Spare 1987b)
Partition coefficient (*n*-octanol/water): $\log P_{ow} = -0.174$ (Steeves 1986)
Stability in presence of transition metals: the technical material is stable when mixed with stainless steel particles or sodium tungstate dihydrate and stored at 25°C for sixteen weeks (Riggs 1990c).
Technical dimethipin is stable when stored at 20°C and 50% RH in polyethylene containers for 12 months (Thomson 1991).

Hydrolysis (Fitzpatrick 1981, Lengen 1982)

25°C	stable at pH 3
	stable at pH 6
	estimated half-life 0.9-2 years based on data from 57 days storage at pH 9
45°C	stable at pH 3
	stable at pH 6
	half-life 330 days based on data from 57 days storage at pH 9

At 70°C and pH 9, [^{14}C]dimethipin accounted for 24% of the radioactivity giving a half-life of about 4 months. Major hydrolysis products were 2-hydroxymethyl-3-methyl-1,4-dithiane 1,1,4,4-tetraoxide and 1,4-dithiane 1,1,4,4-tetraoxide (Fitzpatrick and Wong, 1981).

Photolysis:
Stability in sunlight: the technical material is stable on exposure to continuous simulated sunlight for 7 days (Riggs, 1990d).

UV absorption: $\lambda_{max} = 219$ nm, $\varepsilon = 5.16\times10^{-2}$ (Pierce, 1996)

Formulations

The following formulation types are available: flowable powder (DF), suspension concentrate (SC)

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

In metabolism studies on rats, goats and hens [^{14}C]dimethipin and [$^{13/14}$C]dimethipin were used to trace the fate of different parts of the dimethipin molecule.

The following abbreviations are used for the metabolites:

red-DMP = 2,3-dimethyl-1,4-dithiane 1,1,4,4-tetraoxide

acetyl dithiane = 2-acetyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-S-cys = *S*-(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian 2-yl)-L-cysteine
glu-cys-S-DMP = *S*-(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian-2-yl)-L-cysteinyl-γ-glutamic acid
DMP-S-acetate = 2-[(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian-2-yl)thio]acetic acid
DMP-GSH = *S*-(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian-2-yl)-L-glutathione
DMP-SH = 2-mercapto-2,3-dimethyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-S-methyl = 2,3-dimethyl-2-methylthio-1,4-dithiane 1,1,4,4-tetraoxide
DMP-tert-OH = 2-hydroxy-2,3-dimethyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-prim-OH = 2-hydroxymethyl-3-methyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-SO-methyl = 2,3-dimethyl-2-(methylsulfinyl)-1,4-dithiane 1,1,4,4-tetraoxide
hydroxy-DMP = 2,3-dihydro-5-hydroxymethyl-6-methyl-1,4-dithiine 1,1,4,4-tetraoxide
demethyl-hydroxy-DMP = 2,3-dihydro-5-hydroxymethyl-1,4-dithiine 1,1,4,4-tetraoxide
methylene-DMP = 2-methyl-3-methylene-1,4-dithiane 1,1,4,4-tetraoxide
demethyl-DMP = 1,4-dithiane 1,1,4,4-tetraoxide
N-acetyl-cys-DMP = *N*-acetylcysteinyl conjugate
Cys-gly-DMP = cysteinyglycine conjugate
HESB = 3-(2-hydroxyethylsulfonyl)butan-2-one

Rats. Charles River rats were dosed orally with 1 mg of [^{14}C]dimethipin labelled at the 2 and 3 positions of the dithi-ine ring and killed after 96 hours (Caplan and Merricks, 1978). 93% of the dose was excreted in the urine and faeces, 89% being excreted within 48 hours. Less than 0.1% was recovered as volatiles or expired carbon dioxide. Radioactivity was highest in blood and low levels were detected in tissues and the gastrointestinal tract. In both the pooled urine and faecal samples (Smilo *et al.*, 1978) less than 5% of the radioactivity was extractable with organic solvents, and 80-90% was polar. Comparisons of retention times indicated that approximately 5% of the radioactivity was associated with unchanged dimethipin.

In another study Byrd and Billings (1989) compared the absorption, distribution and excretion of [^{14}C]dimethipin in groups of Sprague-Dawley rats dosed orally with [^{14}C]dimethipin at 50 mg/kg bw and 1.2 mg/kg bw as well as intravenously at 2 mg/kg bw. Another group was pre-dosed at 1000 mg/kg in the diet with unlabelled dimethipin before being given single oral doses of 50 mg/kg [^{14}C]dimethipin. 27-57% of the dose after oral dosing was recovered in the urine and 27-62% in the faeces within 96 hours of the last dose. Residues in the tissues accounted for 0.2-4% of the administered radioactivity at 96 hours. Total radioactive residues (TRR) were highest in the liver with lower levels in the fat, kidney and muscle.

Five products were detected in all samples of the urine from all dose groups: unchanged dimethipin, the *N*-acetylcysteine conjugate, red-DMP, a cysteinylglycine conjugate and a polar fraction supporting the involvement of glutathione conjugation in the metabolic pathway (Mcmanus, 1987a).

In a separate study, rats were dosed orally at 800 mg/kg bw with [2,3-^{14}C]dimethipin and urine was collected for 72 hours after dosing (Mcmanus, 1987b). 29% of the radioactive dose was excreted in the urine with most recovered in the first 24 hours. Almost no unchanged dimethipin was detected. Seven metabolites were detected by HPLC. Of these three were identified and accounted for 77% of the radioactivity in the urine: a cysteinylglycine conjugate (54%), an *N*-acetylcysteine conjugate (12%) and red-DMP (11%). It was considered that metabolism involves conjugation with glutathione and degradation to cysteinylglycine and cysteine conjugates and the formation of mecapturic acid conjugates.

To study dermal absorption of [^{14}C]dimethipin by rats it was applied to their backs at a rate of 682 μg ai/cm^2. Approximately 0.6 and 0.9% of the dose had been absorbed through the skin in both male and female rates after 12 hours (Frederick, 1983). Most of the absorbed dose was excreted with minor residues detected in the blood, with lower levels in the tissues when the rats were killed 72 hours after application.

Goats. Singh (1982) dosed a lactating and a non-lactating goat weighing 46 and 50 kg bw with gelatine capsules containing 500 mg [2,3-^{14}C]dimethipin twice daily for three consecutive days. The bile duct of the non-lactating goat was cannulated and the daily dose was about 20 mg/kg bw equivalent to a nominal feeding rate of about 700 ppm in the feed. Milk and excreta were collected throughout and the goats were slaughtered 18 hours after the last dose. Samples of blood, liver and kidneys were collected and residues characterized by a variety of techniques including chromatography, mass spectrometry, NMR and acid and enzymatic hydrolysis.

The TRRs were highest in urine. Approximately 25% of the radioactivity was extracted from urine with ethyl acetate after acidification with dilute HCl. Five compounds were isolated from the ethyl acetate extract by HPLC and TLC. Three of the compounds accounting for less than 3% of the TRR in the urine were identified as dimethipin, and 2-ethyl-2-methyl-1,3-dithiolane 1,1,4,4-tetraoxide and 2-ethyl-1,3-dithiolane 1,1,4,4-tetraoxide, thought to be impurities. The other two compounds were identified by MS and ^{1}H NMR as the alcohols DMP-prim-OH and DMP-tert-OH, accounting for 24 and 16% of the TRR in the urine respectively. At least four polar metabolites were detected in the HPLC profile of the aqueous urine extract, three of which were isolated by repetitive HPLC and analysed by NMR and MS. Structures consistent with the data were hydroxy-DMP, demethyl-hydroxy-DMP and DMP-prim-OH. Most of the residues in the aqueous extract were not identified but were thought to be polar conjugates. Alcohols hydroxy-DMP, demethyl-hydroxy-DMP, DMP-tert-OH and DMP-prim-OH would be expected ultimately to be conjugated to endogenous materials in the goat.

Acidification of the bile and extraction with ethyl acetate recovered 41% of the TRR with 59% remaining in the aqueous phase. Dimethipin and seven metabolites were detected in the ethyl acetate extract. A comparison of the ethyl acetate and aqueous extracts indicated incomplete partitioning of the polar metabolites. A major metabolite representing approximately 40% of the TRR in the bile was identified as the ring-opened product HESB (M+1 181 m/e). Additional polar metabolites were identified by acid and β-glucuronidase hydrolysis by which 18 and 26% respectively of the ^{14}C in the aqueous fraction was made extractable with ethyl acetate. Comparison of TLC of the extracts before and after hydrolysis indicated the formation of less polar compounds on hydrolysis, suggesting that some of the polar metabolites in the bile were glucuronides. Comparison of the chromatographic properties of dimethipin reaction mixtures with L-cysteine and *N*-acetylcysteine confirmed the presence of their conjugates in the bile.

The TRR in livers were 14 and 19 mg/kg for the lactating and dry goat respectively and in the kidneys were 17 and 24 mg/kg (all expressed as dimethipin). Acetone/water extraction of liver and kidney homogenates removed 58 and 81% of the TRR respectively. For liver, hydrolysis with acid and base did not release any more radioactivity. Partitioning of the acetone/water extracts with ethyl acetate and analysis by TLC resulted in chromatograms qualitatively the same for liver, kidney and urine, with HESB and DMP-tert-OH identified in liver and kidney samples. Analysis of the liver and kidney extracts by gel permeation chromatography and β-glucuronidase hydrolysis indicated a glucuronide conjugate. The high levels of polar and bound residues also indicated extensive conjugation.

Bile and urine samples collected 12 hours after the first dose were further studied by McManus (1989). Samples were centrifuged and filtered through LID-X 0.2 μm nylon before analysis by HPLC. The profiles for urine and bile samples showed essentially the same metabolic pattern with most of the metabolites classed as polar. At least 6 metabolites more polar than dimethipin were detected. Four metabolites common to urine and bile were identified: a reduced product, a carboxylic acid, a demethylated product related to an impurity present in dimethipin (2-ethyl-1,3-dithiolane 1,1,4,4-tetraoxide) and an *N*-acetylcysteine conjugate. However, it was not possible to identify the two dominant metabolites, though reduction with Raney nickel or dithiothreitol resulted in an increase of the reduced product suggesting the presence of a sulfur conjugate.

Table 1. Identity of metabolites and their distribution in the milk and tissues of goats dosed with [^{14}C]dimethipin equivalent to 500 ppm in the diet for 3 days (Singh, 1982; Mcmanus, 1984).

	Liver	Bile	Kidney	Urine
TRR (mg/kg as dimethipin)	19	500	24	1800
Compound	% of TRR			
Dimethipin	2	8	2	2
Hydroxy-DMP				6
demethyl-hydroxy-DMP				10
HESB	9	30	8	20
DMP-tert-OH	6		5	16
DMP-prim-OH				24
N-acetyl-cys-DMP		12		
2-ethyl-2-methyl-1,3-dithiolane-1,1,3,3-tetraoxide				0.5
2-(1-hydroxyethyl)-2-methyl-1,3-dithiolane-1,1,3,3-tetraoxide	1			
2-ethyl-1,3-dithiolane-1,1,3,3-tetraoxide				0.5
Polar metabolites[1]	40	50	65	21
Bound[2]	42		19	

[1]acid hydrolysis showed numerous ethyl acetate-extractable products
[2]mainly high molecular weight residues (>500)

Lactating goats were dosed orally with 0.15 and 50 mg/kg bw 2,3-ring-labelled [^{14}C] or 50 mg/kg bw 2,3-ring-labelled [^{14}C] and 5,6-ring- and methyl-labelled [^{13}C]dimethipin once daily for five days (Byrd, 1992; Lau and Gay, 1996), equivalent to 3, 1010 and 1290 ppm in the feed based on mean daily feed consumptions. Milk was collected twice daily, and urine and faeces daily. The goats were slaughtered 22-24 hours after the last dose. The radioactive residues in the tissues were characterized by HPLC, GC-MS, LC-MS and ^{13}C-NMR.

Radioactivity in faeces and urine collected up to 22 hours after the last dose accounted for 95% of the administered dose for both ^{14}C-animals with 39% and 54% excreted in faeces and urine for the low-dose group and 51% and 42% in faeces and urine respectively for the high. Approximately 0.1% and 0.2% was eliminated in milk of the low- and high-dose animals and approximately 97% and 96% of the total dosed radioactivity was recovered from the low- and high-^{14}C-dose animals respectively.

Table 2. Distribution of radioactivity in the blood, milk and tissues of lactating goats dosed orally with [^{14}C] or [$^{13/14}$C]dimethipin for 5 days (Byrd, 1992; Lau and Gay, 1996).

Sample	TRR (mg/kg calculated as dimethipin)		
	^{14}C-Low dose goat (3 ppm)	^{14}C-High dose goat (1010 ppm)	$^{13/14}$C-High dose goat (1290 ppm)
Whole blood	0.006	2.75	
Milk	0.005-0.006	0.68-1.2	3.1-4.3
Muscle	0.002	0.64	2.04
Fat	0.001	0.32	0.99
Kidney	0.15	28	55
Liver	0.27	79	45
Gastrointestinal tract	0.05	11	

In centrifuged milk samples the aqueous layer accounted for 69-86% of the radioactivity in the milk, and the only significant metabolite was DMP-S-cys, confirmed by co-chromatography with an authentic standard.

Less than 13% of the TRR from the high-dose liver was extracted with organic solvents, but about 50% with water or phosphate buffers (pH 7.5). Most of the extracted radioactivity was

associated with protein precipitates. The radioactive residues would not pass through a 50 kDa molecular weight cut-off filter. Enzymatic digestion released all the radioactivity which HPLC revealed to be associated with ethane-1,2-disulfonic acid and peptide conjugates. Reduction of the liver homogenate gave red-DMP as the major product while HCl-butanol hydrolysis resulted in a single product, acetyl dithiane. It is proposed that metabolites in liver are covalently bound to proteins.

It appears that the double bond of dimethipin forms a thioether bond with protein sulfhydryl groups, which upon digestion with proteases give multiple peptide fragments conjugated to red-DMP. Scission of the thioether bonds gives reduced dimethipin. Acid hydrolysis cleaves the peptide and thioether bonds to form an intermediate that rearranges to acetyl dithiane. The protease digestion also required addition of acid, yielding an intermediate that can fragment to give ethane-1,2-disulfonic acid.

All of the radioactivity from the kidney samples was extracted with water. Ethane-1,2-disulfonic acid was the only metabolite observed in the low-dose (3 ppm) goat, and in the high-dose (1010 ppm) goat ethane-1,2-disulfonic acid was the only free metabolite together with conjugated products released on acid hydrolysis to give acetyl dithiane.

The main metabolite in muscle was red-DMP present at approximately 30% of the TRR: no other metabolite accounted for more than 8% of the TRR.

The levels of ^{14}C in fat were too low to allow further characterization.

Table 3. Distribution of ^{14}C and identities of metabolites in the milk and tissues of lactating goats dosed with [^{14}C]dimethipin for 5 days (Byrd, 1992; Lau and Gay, 1996).

	^{14}C-low-dose goat (3 ppm)			^{14}C-high-dose goat (1010 ppm)			
	Milk	Liver	Kidney	Milk	Liver	Kidney	Muscle
TRR (mg/kg as dimethipin)	0.005	0.27	0.15	1.01	79	28	0.64
Aqueous extract recovery (%)	70	<50	99.7	>85	<50	104	50
HCl-BuOH recovery (%)	-	106	-	-	91	92	95
acetyl dithiane[1]	-	0.12 (44%)	-	-	46 (59%)	9.2 (32%)	-
ethane-1,2-disulfonic acid[1]	-	0.035 (15%)	0.11 (76%)	-	20 (45%)[2]	7.8 (28%)	-
red-DMP[1]	-	-	-	-	-	-	0.19 (30%)
DMP-S-cys[1]	0.001 (20%)	-	-	0.37 (37%)	-	-	-

[1] mg/kg as dimethipin (% of TRR)
[2] Metabolites were not determined for the liver of the ^{14}C-high dose goat (1010 ppm). The value reported is for the trypsin-pepsin digest of liver from $^{13/14}C$-high dose goat (1290 ppm) for which the liver TRR was 45 mg/kg calculated as dimethipin.

Liver homogenates from the three goats were hydrolysed and stored frozen for 1 (1290 ppm), 31 (3 ppm) and 26-30 (1010 ppm) months resulting in the same single ^{14}C product, acetyl dithiane. The aqueous extracts from kidneys were analysed after 25 (3 ppm), 25 (1010 ppm) and 4 (1290 ppm) months' storage and showed the same metabolite, ethane-1,2-disulfonic acid.

The main metabolic pathway for dimethipin is via a Michael addition of sulfhydryl to the double bond. Glutathione addition yields DMP-S-cys, via the mercapturic acid pathway, which is eliminated in urine and milk. This conjugate was not observed in edible tissues. Protein addition yields protein-bound reduced dimethipin which is the only residue observed in liver and muscle, and approximately half the residue observed in kidney. Hydrolysis of the bound residue and subsequent rearrangement yielded three products: red-DMP, acetyl dithiane and ethane-1,2-disulfonic acid. The

last was the only metabolite observed in the kidney of the ^{14}C low-dose goat and accounted for about one third of the ^{14}C in the high-dose.

Hens. Of seven groups of five single-comb White Leghorn pullets (1.3-2.4 kg bw) (Bodden *et al*., 1982), two groups were dosed with [^{14}C]dimethipin at nominal levels equivalent to 1 (0.06 mg/kg bw), 6 (0.34 mg/kg bw) and 30 (1.7 mg/kg bw) ppm in the feed. The remaining group was an untreated control. The hens were dosed by capsule with doses calculated on average consumption figures of 110 g feed per day for 30 days. One group at each dose level was then slaughtered. The remaining 5 birds at each dose level were slaughtered 11 days later. Egg and excreta samples were collected daily, and muscle (1:1 white and dark), liver and kidney after slaughter. Radioactive residues were determined by LSC.

The total recovery of radioactivity in the excreta was 90, 92 and 92% of the administered dose for the 1, 6 and 30 ppm dose groups respectively. Samples from days 30-34 and 36-40 were not analysed, so the true recovery figures are likely to be higher. Approximately 0.3% of the dose was found in tissues after the last dose with about 0.1% remaining in the withdrawal group after 11 days. Residues in eggs accounted for 0.2% of the dose at the end of feeding decreasing to below the limit of detection of 6 μg/kg after 5 days in the 1 ppm dose group and 11 days in the 5 ppm group. It was near the limit of detection after 11 days at 30 ppm. ^{14}C residues in eggs reached a plateau 10 days after the start of dosing reaching maximum levels of 11, 41 and 198 μg/kg for the 1, 6 and 30 ppm dose groups respectively. The TRR was highest in liver and lowest in fat. Residues were roughly proportional to dosage rates.

Table 4. Distribution of ^{14}C in tissues of hens dosed with [^{14}C]dimethipin for 30 days (Bodden *et al*., 1982).

Nominal dose (ppm)	TRR (μg/kg as dimethipin)				
	Kidney	Liver	Muscle	Fat	Blood
30 days feeding					
1	23 ± 4.4	74 ± 22	<8	<19	56 ± 20
6	114 ± 25	365 ± 90	30 ± 4.7	<18	303 ± 58
30	490 ± 23	1430 ± 158	129 ± 22	29 ± 5.9	1450 ± 114
11 days withdrawal					
1	<7	<7	<7	<18	14 ± 3.9
6	10 ± 2	28 ± 5.0	12 ± 2.0	<18	79 ± 15
30	72 ± 11	137 ± 30	53 ± 7.2	19 ± 2.4	363 ± 55

Residues of dimethipin were <0.01 mg/kg in liver at all doses (Abdel-Kader and Blaszczynski, 1984).

Lau and Gay (1993) dosed White Leghorn laying hens with [^{14}C]dimethipin for five days at 15.8 or 152 mg/bird, equivalent to 203 or 2770 ppm in the diet. Egg and excreta samples were collected daily and the birds killed within 24 hours of the last dose. Samples of liver, kidney, gizzard, muscle and fat were collected for characterization by HPLC and co-chromatography with authentic standards, LC-MS and ^{1}H NMR.

The recovery of radioactivity from excreta, expired-air traps and carcases was >95% with 90-91% excreted within 24 hours of the last dose. Only 5.1-5.6% of the dose was recovered in edible tissues and eggs. Radioactive residues in eggs did not reach a plateau during the 5 days of the study.

Table 5. Radioactive residues in eggs and tissues of laying hens dosed orally with [^{14}C]dimethipin for 5 days (Lau and Gay, 1993).

	TRR (mg/kg as dimethipin)	
Sample	Low-dose hens (203 ppm)	High-dose hens (2770 ppm)
Liver	9.7	65

Sample	TRR (mg/kg as dimethipin)	
	Low-dose hens (203 ppm)	High-dose hens (2770 ppm)
Kidney	4.5	39
Gizzard	1.4	20
Muscle (breast)	0.63	10
Muscle (thigh)	0.72	10
Egg yolk	1.1	6.9
Egg white	0.68	6.6
Fat	0.20	2.4

20-50% of the TRR was extracted from the egg and tissue samples with organic solvents and water. A further 25-50% was released by acid and base extraction, and proteolytic digestion of the post-extraction solids released nearly all the remainder. Significant bound radioactivity was only found in egg white (20% of the TRR) and fat (24% of the TRR).

Table 6. Distribution of radioactivity in extracts of eggs and tissues of laying hens dosed orally with [^{14}C]dimethipin for 5 days (Lau and Gay, 1993).

Sample	% of TRR			
	Solvent extracted[1]	Enzyme hydrolysate of post extraction solids[2]	Bound[3]	Total recovery
Liver	75	23	1.3	99
Kidney	49	27	2.3	78
Gizzard	63	33	1.3	97
Muscle (breast)	58	29	0.1	87
Muscle (thigh)	59	18	0.2	77
Egg yolk	85	16	0.1	100
Egg white	80	4.3	20	100
Fat	54	-	24	78

[1] sum of solvent extracts, hexane, ethyl acetate, methanol, water, acid/base
[2] based on the most effective enzyme of proteases, sulfatases, β-glucuronidase, β-glucosidase, pepsin, trypsin and esterases, all incubated at 37°C.
[3] based on combustion of post-hydrolysis solids.

To further characterize the metabolites present the various extracts were purified on C-18 solid-phase extraction and silica gel columns and by HPLC. Individual metabolites were identified in the excreta by co-chromatography with authentic standards, mass spectrometry and ^{1}H NMR.

The main metabolite was DMP-S-cys in hen livers and glu-cys-S-DMP in other tissues. It is proposed that the addition of glutathione to dimethipin (glutathione S-transferase-catalysed or spontaneous) gives DMP-GSH which can be transported out of the cells in which it is formed and the glutathione moiety degraded by endogenous peptidases to produce glu-cys-S-DMP and DMP-S-cys. Oxidative transamination and loss of pyruvic acid or decarboxylation can give DMP-SH and DMP-S acetate. Methylation of DMP-SH in the presence of S-adenosine-methionine (SAM) would produce DMP-S-methyl which could be further oxidised to DMP-SO-methyl. Another product could be the *N*-acetylcysteinyl conjugate, a compound expected to be retained by the strong anion exchange columns used. An unidentified metabolite found in several of the extracts had similar chromatographic behaviour to products obtained by reacting dimethipin with *N*-acetylcysteine. Reduction and hydroxylation reactions are also possible as evidenced by the presence of red-DMP and the hydroxylated metabolites DMP-tert-OH and DMP-prim-OH.

Samples of excreta were extracted successively with methanol/methylene chloride (1:1), methanol, methanol/water (1:1) and water. The methanol/methylene chloride and methanol extracts were combined to form an organic extract, and the methanol/water and water to form an aqueous extract. Following extensive chromatography on C-18 solid-phase extraction and silica gel columns and HPLC, DMP-prim-OH, DMP-SO-methyl, DMP-tert-OH and glu-cys-S-DMP, DMP-S-cys, DMP-S-acetate and DMP-SH metabolites were identified in the excreta by co-chromatography with authentic standards, mass spectrometry and ^{1}H NMR.

Table 7. Identity and distribution of metabolites in the edible tissues and eggs of hens dosed with [^{14}C]dimethipin for 5 days (Lau and Gay, 1993).

Compound or fraction	% of TRR							
	Liver	Kidney	Muscle (breast)	Muscle (thigh)	Fat	Gizzard	Egg yolk	Egg white
Unknown #1	1.3	-	0.13	1.7	3.1	0.3	-	0.25
Unknown #2	3.1	17	28	16	-	15	7.6	1.1
Unknown #3	0.45	-	-	-	-	-	-	-
Unknown #4	2.4	2.8	2.2	-	-	-	-	-
Unknown #5	0.58	1.6	-	-	-	-	-	-
DMP-S-methyl	7.3	-	-	-	-	-	0.62	-
DMP-prim-OH	3.1	-	-	-	-	0.8	2.9	2.3
DMP-tert-OH	2.9	4.4	-	-	-		-	1.2
DMP-SO-methyl	0.95	1.2	0.18	-	-		0.95	6.0
DMP-S-cys	22	7.0	2.3	5.0	-	11	3.9	0.01
red-DMP	7.6	0.98	2.1	-	-	2.5	4.7	7.8
DMP-GSH	5.9	3.5	1.0	-	-	4.1	8.1	3.4
Unknown #6	0.36	-	-	-	-		5.0	-
glu-cys-S-DMP	7.4	19	32	28	20	21	36	25
DMP-SH	0.92	-	-	-	-	0.7	0.22	3.8
DMP-S-acetate	-	-	-	-	-		6.8	2.1
Unknown #7	-	-	-	-	-		-	3.8
Unknown #8	0.91	4.0	3.4	3.6	-	8.8	4.1	12
Unknown #9	0.25	-	-	0.51	-	0.86	-	-
Baseline	26	12	14	13	16	31	15	20
Bound	1.3	2.3	0.96	2.1	5	1.3	1.9	20
Total	95	76	87	74	74[1]	97	98	110

[1] includes 11% not analysed and 19% combustion loss

The results in rats, goats and hens show that dimethipin is extensively metabolized with almost no residual parent compound retained. The main residues in animals form as the result of glutathione, amino acid and protein conjugation and subsequent degradation. Minor metabolites are formed as a result of hydrolytic hydroxylation and/or oxidation to form hydroxy-DMP, DMP-tert-OH and DMP-prim-OH. The proposed metabolic pathway for dimethipin in domestic animals and birds is shown in Figure 1.

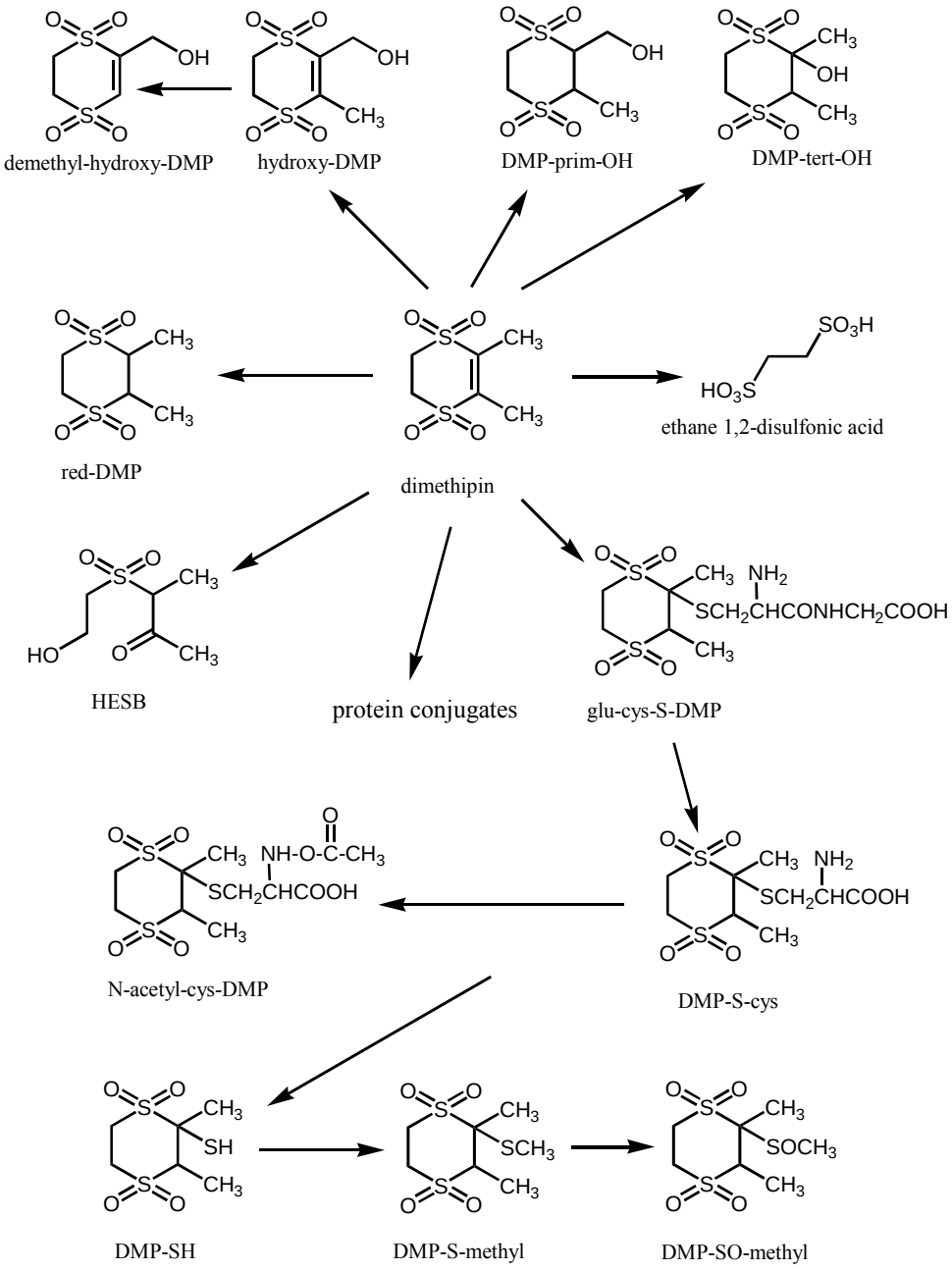


Figure 1. Proposed metabolic pathway of dimethipin in goats and hens.

Plant metabolism

Studies on cotton, potatoes, sunflowers, rice and grapes were reported to the Meeting.

Cotton and potatoes. In a study by Lengen (1987) cotton seedlings entering the second trifoliate stage were removed from their potting soil, their roots were rinsed and the seedlings grown hydroponically for 3 days in half-strength nutrient solution (Murashige Skoog) containing 75 mg/kg [^{14}C]dimethipin. Samples of the desiccated leaves (wilting, dry and brittle) were collected. Cotton callus was initiated from roots of asceptically germinated Stoneville seeds maintained on the nutrient medium. At 4-week intervals the medium was changed and the callus injected with [^{14}C]dimethipin. Potato callus was initiated in a similar fashion and also injected with [^{14}C]dimethipin.

The cotton leaves were extracted with $CHCl_3$/methanol/water and the combined extracts partitioned with $CHCl_3$ to produce a two-phase system; $CHCl_3$ and aqueous. Approximately 98% of the radioactivity was extracted, 20% in the $CHCl_3$ phase and 78% in the aqueous phase. HPLC analysis of the $CHCl_3$ phase revealed a single peak that co-chromatographed with dimethipin, and the identity was confirmed by mass spectrometry. The aqueous phase contained five metabolites of which dimethipin accounted for 51% of the radioactivity. Two of the metabolites, at 1.2 and 3.6% of the TRR, co-chromatographed with reaction products from a mixture of [^{14}C]dimethipin and L-cysteine, although their identity could not be established. Comparison of the plant extract HPLC profile with that from urine in a rat feeding study (Mcmanus, 1987a) indicated that one of the metabolites was cys-gly-DMP. An additional two metabolites which co-chromatographed with reaction products from a mixture of [^{14}C]dimethipin and glutathione represented 11 and 8.8% of the TRR. The former also co-chromatographed with the rat metabolite *N*-acetylcysteinyl-dimethipin while the latter was identified as red-DMP. Reduction of an aliquot of the aqueous phase to confirm the presence of intact dimethipin or red-DMP in the unidentified metabolites proved inconclusive. Enzymatic hydrolysis of an aliquot of the aqueous phase with glucosidase and cellulase resulted in no significant changes indicating that the metabolites were neither sugar- nor cellulose-based conjugates.

The cotton callus cultures gave extracts with similar metabolite profiles to the hydroponically treated plants except the dimethipin/L-cysteine reaction products increased and red-DMP decreased. The potato callus culture produced extracts with an additional polar peak over and above the other five peaks in the HPLC chromatogram, which had an identical retention time to an unidentified polar rat metabolite.

As dimethipin is applied to plants close to natural senescence at or about harvest, biochemical activity is very limited resulting in minimal metabolism, and the main residue is the parent compound. In a study of the fate of dimethipin in cotton seedlings and callus cell cultures of cotton and potatoes most of the plant metabolites resulted from the conjugation of dimethipin with glutathione and/or cysteine and subsequent degradation to yield cyclic and acyclic dimethipin derivatives.

Cotton. Four mature indoor-grown plants, each with 1-4 bolls open, were treated with a single application of a flowable formulation of [^{14}C]dimethipin at 1.12 kg ai/ha (Curtiss, 1980). The bolls were harvested 7 days after spraying and seeds and linters removed. Approximately 94% of the TRR in seeds with linters (0.81 mg/kg as dimethipin) was removed by Soxhlet extraction with methanol of which 94% or 0.76 mg/kg was identified as unchanged parent compound by TLC with LSC using an SiO_2 IBF TLC plate developed with acetone/$CHCl_3$. In seeds delinted by acid (H_2SO_4), rinsed with water, air-dried and homogenized, 18% of the TRR was extractable with methanol (0.18 mg/kg calculated as dimethipin) of which 38% was identified by TLC as unchanged dimethipin. The methanol extract was partitioned with hexane with the oil fraction accounting for 1.1% of the total extractable residue.

Burke and Johnson (1994) treated mature indoor-grown Stoneville 215 cotton plants with [^{13,14}C]dimethipin at 0.34 and 1.6 kg ai/ha two weeks before harvest. Samples of bolls and foliage were separated into foliage, carpel walls, fibre and seed and ^{14}C determined by combustion LSC. Samples were extracted and profiled by reverse-phase and anion-exchange chromatography, NMR and mass spectrometry. Approximately 98% of the ^{14}C in foliage was extracted with acetone and methanol/water. The main residue was unchanged dimethipin (72%) with no other individual compound accounting for more than 5% of the TRR. Approximately 85% of the radioactivity in mature seeds harvested from plants treated at 0.34 kg ai/ha was removed by rinsing with acetone. The major compound in the surface rinse was unchanged dimethipin. Extraction of ground seeds with acetone, hexane and methanol/water recovered 77-80% of the TRR. 80-90% of the residue in seeds was identified as dimethipin: no other component accounted for more than 5.2%. The minor metabolites were a group of closely-related highly polar anionic compounds that could be extracted into polar solvents but were not associated with cellular components of cotton seeds.

Table 8. Distribution of radioactivity in cotton plants treated with [^{14}C]dimethipin (Burke and Johnson, 1994).

Sample	TRR (mg/kg as dimethipin)	
	0.34 kg ai/ha	1.55 kg ai/ha
Cotton fibre	12 ± 9.3	97 ± 95
Carpel walls	8.7 ± 1.1	37 ± 4
Foliage	97 ± 6	341 ± 18
Immature seed	0.084 ± 0.036	-
Mature seed	0.29 ± 0.18	1.4 ± 1.1
Homogenized seed	0.20 ± 0.02	1.1 ± 0.07

Potatoes. A field-grown Kennebec plant was sprayed with a flowable formulation of [^{14}C]dimethipin at 2.24 g ai/ha (Lengen and Harned, 1981a), and the potatoes harvested after 14 days. The unwashed, unpeeled potatoes were analysed by LSC after dry combustion. Residues in soil and potatoes were characterized by TLC (Whatman silica gel LK_6 glass-backed plates) or GLC with an ECD. The TRR in the tubers was 0.059 mg/kg calculated as dimethipin. Unchanged dimethipin, determined by methanol extraction and the standard GLC analytical method, accounted for 20-25% of the TRR (0.012-0.015 mg/kg). The low levels of radioactivity precluded analysis of the unextracted material. Untreated control samples contained low levels of radioactive residue (0.005 mg/kg as dimethipin). The TRRs in the soil at depths of 0-15 cm and 15-30 cm were 1.1 and 0.04 mg/kg respectively, as dimethipin. Residues of unchanged dimethipin in soil from the 0-15 cm profile measured using TLC with LSC were 0.8 mg/kg.

Sunflowers. The backs of the seed heads of six mature plants grown outdoors in plastic-lined wooden bins were sprayed with flowable [^{13,14}C]dimethipin at 1.4 kg ai/ha (Curtiss and Harned, 1980). Seeds were harvested after a two-week senescence period (outdoors) and a two week drying period (indoors), and homogenized and Soxhlet-extracted with acetonitrile. Hexane was used to partition the oil from the acetonitrile. Extracts were analysed by TLC with LSC and GLC with an ECD. Samples of seed were also sequentially extracted with methanol and methanol/water/HCl to ensure that all the extractable material had been removed.

The TRRs in seeds at harvest (calculated as dimethipin) were 19 mg/kg of which 14 mg/kg was extractable with a variety of solvents. 61% of the extractable residue was dimethipin. No other single component exceeded 5.7% of the TRR.

Table 9. Distribution of radioactivity in sunflower seed from plants treated with [^{14}C]dimethipin (Curtiss and Harned, 1980).

	TRR (mg/kg as dimethipin)	% dimethipin
CH_3CN extract	10	89
Hexane partition of CH_3CN extract (oil)	0.14	11
Methanol extract	3.5	-
Methanol/water/HCl (Soxhlet)	0.34	-
Methanol/water/HCl (room temperature)	0.23	-
Unextractable	4.5	-
Total	19	

Rice. Balba and Dzialo (1983) treated indoor-grown plants with [^{14}C]dimethipin at 2.24 g ai/ha. The plants were harvested 17 days later and separated into straw, hulls and seed. Radioactivity was determined by combustion and LSC. Residues in the straw, hulls and seed were extracted with $CHCl_3$/water with further extraction of the seed using methanol/water. Analysis was by TLC and GLC. TRRs in straw, hulls and seed were 162, 325 and 8 mg/kg respectively, calculated as dimethipin. Solvent-extractable residues represented 89, 90 and 78% of the TRR in straw, hulls and seed respectively with unchanged dimethipin representing 67 (108 mg/kg), 80 (261 mg/kg) and 50%

(4.1 mg/kg) respectively of the extractable TRR. Three metabolites were separated by TLC or GLC but were not identified.

Grapes. Six field-grown Mueller-Thurgau vines were sprayed with an EC formulation at 115 mg [^{14}C]dimethipin/vine (Ellgehausen and Fisher, 1982). Samples of leaves and grapes were collected 2 hours, 6 days and (at harvest) 24 days after application. Grapes were separated from the stems and crushed. The resulting juice was separated from skins and seed by filtration, and also processed into wine. The total radioactive residues were determined by LSC. The TRRs in leaves were 16, 7.8 and 3.6 mg/kg as dimethipin 2 hours and 6 and 24 days after application respectively.

Table 10. Distribution of radioactivity in grapes treated with [^{14}C]dimethipin at 115 mg/vine (Ellgehausen and Fisher, 1982).

Sample	TRR (mg/kg as dimethipin)		
	2 hours	6 days	24 days
Juice	0.70 (44%)	0.44 (33%)	0.26 (33%)
Skins & seed	0.78 (32%)	0.72 (44%)	0.43 (47%)
Stems	4.1 (24%)	3.1 (24%)	1.4 (20%)

Figures in parentheses are % of TRR in whole grapes.

Table 11. Characterisation of ^{14}C radioactivity in grapes and processed products (Ellgehausen and Fisher, 1982).

	Compound or fraction	% of TRR						
		2 hours		6 days		24 days		
		Juice	Seeds + skins	Juice	Seeds + skins	Juice	Seeds + skins	Wine
$CHCl_3$ extract								
	Polar			11	21	0.6		5.9
	M1		4.3			1.0	0.4	
	M2		2.1			0.2		
	M3				2.3	0.8	0.6	11
	M4			8.0		4.4		29
	Dimethipin	97	77	50	14	14	1.0	54
	M6				0.7		1.9	
	M7, other						<0.01, 8.1	
Sub-total		97	84	68	38	21	12	99.9
MeOH			7.6		-			
MeOH/water			4.7		52		48	
Unextractable			4.0		9.8		40	
Water- soluble		3.0		32		79		

Owing to the low levels of radioactivity in the aqueous extracts of juice they were first fractionated by ultrafiltration. Samples of the filtrate were passed down a Bio-Bead column or treated with pectinase. Nine metabolites were resolved by TLC of the Bio-Bead fraction with no single metabolite accounting for more than 3.2% of the juice TRR. No conjugates were released by HCl- or β-glucosidase hydrolysis.

Approximately 96, 90 and 60% of the radioactivity in skins and seed was extractable with $CHCl_3$, methanol, methanol/water at 2 hours, 6 days and 24 days respectively after treatment. At least seven metabolites were determined by TLC of the $CHCl_3$ extract, and no single metabolite accounted for more than 10% of the TRR.

The radioactivity in the methanol extract from the skin and seed samples collected 6 hours after treatment was too low for further analysis. Methanol extracts from 6- and 24-day samples were partitioned with $CHCl_3$ and first incubated with pectinase and then partitioned with $CHCl_3$, then incubated with β-glucosidase and partitioned with ethyl acetate. Most of the radioactivity was in the

$CHCl_3$ extract as the two metabolites D6 and D8. Only 1.7% of the skin and seed radioactivity was extractable with $CHCl_3$ after pectinase incubation with metabolites D5, D6 and D8 observed.

Residues of dimethipin were 0.036, 0.004 and 0.033 mg/kg in juice, stems/seeds and wine respectively of the combined 6- and 24-day samples. Numerous metabolites were detected although none were identified. The major metabolite, M4, accounted for 0.06 and 0.02 mg/kg in juice and wine respectively, calculated as dimethipin.

Samples of juice were processed into wine by alcoholic fermentation, then filtered. No radioactive CO_2 was evolved during fermentation. 11% of the radioactivity was in the yeast and solids and 89% in the clear wine.

Environmental fate in soil

Degradation

Aerobic degradation. The aerobic degradation of [^{14}C]dimethipin in a silt loam (sand 24%, silt 56%, clay 16%; pH 5.6; organic matter 4.4%; CEC 34 meq/100 g) and a sand (sand 96%, silt 3.6%, clay 0%; pH 6.1; organic matter 1.8%; CEC 7.3 meq/100 g) kept at 25°C in the dark was studied by Fitzpatrick (1982). Dimethipin was applied to the soils at a rate of 1 mg/kg, equivalent to 1.12 kg ai/ha, and incubated for up to a year. Extractable dimethipin accounted for 50% of the applied radioactivity in the silt loam after a year while bound residue and $^{14}CO_2$ accounted for 23 and 1.4% respectively. In the sand, 76-84% of the applied radioactivity was recovered of which 51-66% was identified as dimethipin. Bound residues and $^{14}CO_2$ accounted for 2.6 and 0.26% of the applied radioactivity after a year of aerobic ageing.

The aerobic metabolism of [^{14}C]dimethipin was studied in two standard German soils (standard 1: loamy sand high; sand 86%, silt 7.1%, clay 4.9%; pH 6.0; organic matter 2.6%; CEC 7.5 meq/100 g; standard 2: loamy sand low; sand 76%, silt 13%, clay 11%; pH 6.6; organic matter 0.7%; CEC 4.5 meq/100 g) and a field loam (sandy loam: sand 69%, silt 13%, clay 19%; pH 6.3; organic matter 1.9%; CEC 18 meq/100 g) for 168 days (Ellgehausen, 1985). Sieved samples were mixed with [^{14}C]dimethipin at 0.99 mg/100 g soil and the mixture adjusted with water to 40% maximum holding capacity. Dimethipin was the only compound detected in the extractable radioactivity from the German standard soil 2 and the field loam. It accounted for 33, 38 and 40% of the applied radioactivity in German standard soils 1 and 2 and the field loam respectively after 168 days. In standard soil 1 three metabolites were detected in addition to parent dimethipin in the extractable ^{14}C. Two were tentatively identified as methylene-DMP (up to 5.3%) and demethyl-DMP (up to 6.8%) by co-chromatography with authentic standards, and the third tentatively identified in a separate study by mass spectrometry as the carboxylic acid DMP-COOH (M + 1 243 m/e) (Mcmanus, 1985). Approximately 30% of the radioactivity applied to the field loam was converted to $^{14}CO_2$. Unextractable radioactivity increased with time in all soils reaching 25, 19 and 25% of the applied radioactivity respectively for standard soils 1 and 2 and the field loam. Recoveries of radioactivity were 94-101%.

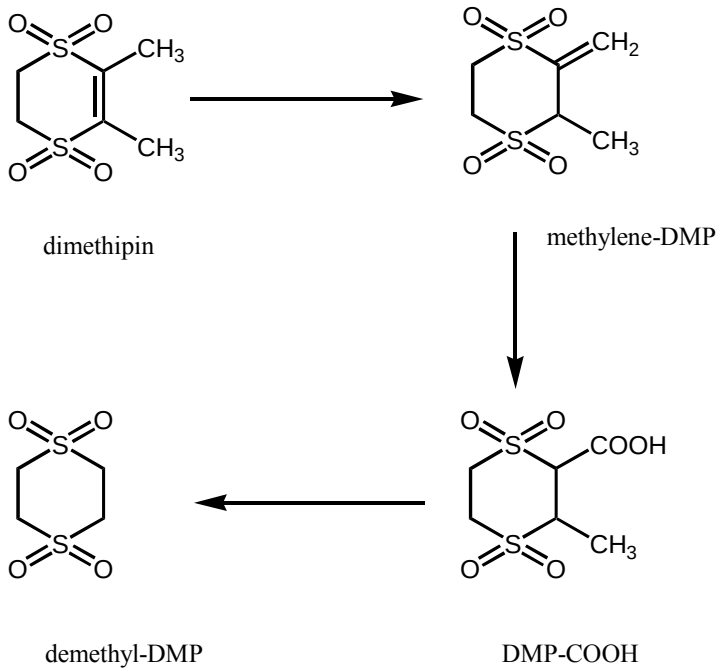


Figure 2. Proposed aerobic degradation pathway of dimethipin in soil

Anaerobic degradation. The same types of soil were again used by Fitzpatrick (1982) to study the anaerobic degradation of [^{14}C]dimethipin stored at 25°C in the dark. Dimethipin was applied at 1 mg/kg and the soils were incubated under aerobic conditions for one month before flooding with oxygen-free sterile water. ^{14}C desorbed from the soils into the water from 0 to 30 days: 76% desorbed from sand at day 0 and 87% after 30 days. Approximately 13% of the applied radioactivity was extractable from the silt loam soil with acetone with bound residues accounting for 5.2% of the ^{14}C. Dimethipin accounted for 70% of the radioactivity in the aqueous extracts. After 60 days 60-69% of the applied radioactivity was dimethipin. Recovery of ^{14}C was 88%.

In the sand, negligible ^{14}C was extracted with acetone (<2% at 60 days). Most of the radioactivity was desorbed into the aqueous phase (85% of the ^{14}C of which 80% was dimethipin). Bound residues accounted for 2% of the ^{14}C at 60 days. The recovery of ^{14}C at 60 days was greater than 90%.

Aqueous photolysis. Lengen and Harned (1981b) found the degradation of [^{14}C]dimethipin in a 2900 mg/kg aqueous solution to be slow with 92 and 89% of the radioactivity in control and photolyzed solutions respectively shown to be dimethipin after 28 days. The degradation was much more rapid when air was continuously bubbled through the solutions, when after 14 days only 51-52% of the radioactivity was present as dimethipin in both control and photolysed solutions. In a parallel study with argon-saturated solutions, degradation products in both solutions accounted for less than 15%. Degradation products were not amenable to analysis by chromatography or mass spectrometry, possibly owing to low molecular weights.

Fackler (1991) studied the photolytic stability of aqueous solutions of dimethipin at pH 5, 7 and 9 under natural sunlight. The temperature of the solutions varied diurnally and with weather conditions. Significant hydrolysis was not observed in control solutions maintained in the dark. Estimated half-lives at pH 5 and 9 were 35 and 47 days respectively. No significant degradation occurred at pH 7.

Soil photolysis. Lengen and Harned (1981b) applied dimethipin to thin films of sandy loam soil at a rate equivalent to 1.68 kg ai/ha exposing the films to ultraviolet light for 28 days. Dimethipin accounted for 89-99% and 47-51% of the ^{14}C in control and irradiated films respectively.

Fackler (1992) determined the half-life of [^{14}C]dimethipin in Paxton sandy loam soil exposed to sunlight for 30 days at 25°C. After 30 days dimethipin accounted for 81-87% and 58-65% of the ^{14}C in control and irradiated samples respectively. Volatile components accounted for less than 1% of the applied radioactivity. Recoveries of ^{14}C at each sampling interval were 92 ± 7% for exposed samples and 94 ± 9% for dark samples.

Field studies. In a study of the field dissipation of dimethipin by Harned (1981a) Kats potatoes were treated with a flowable formulation at 1.12 kg ai/ha (748 l/ha). Samples of gravely silt loam soil (pH 5.3, organic matter content 3.5%) were taken at 0-15 and 15-30 cm depths before and after treatment. The pre-treatment soil samples had the highest levels of dimethipin at 13.2 mg/kg in the 0-15 cm core, with 0.048 mg/kg in the 15-30 cm core, and the next highest were 2.1 mg/kg in the 0-15 cm core collected 4 days after spraying. The study cannot be used to determine the degradation of dimethipin under field conditions owing to the pre-treatment results.

Dimethipin was applied as one or two sprays at 0.56 kg ai/ha to cotton in Mississippi, Georgia and Arizona, USA (Harned, 1981b) grown in silt loam in Mississippi (sand 26%, silt 58%, clay 16%; pH 4.3; organic matter 1.1%; CEC 24 meq/100 g), loamy sand in Georgia (sand 85%, silt 11%, clay 3%; pH 4.9; organic matter 1.6%; CEC 14 meq/100 g) and clay loam in Arizona (sand 28%, silt 36%, clay 35%; pH 7.9; organic matter 1.4%; CEC 42 meq/100 g). Soils were sampled at 0-15 cm and 15-30 cm (Wong, 1976). Residues of dimethipin in Mississippi at the 0-15 cm depth were 0.086 mg/kg on the day of application decreasing to 0.083 mg/kg at 30 days and <0.025 mg/kg at 164 days after spraying. Maximum residues in the 15-30 cm cores were 0.033 mg/kg at 7 days. In Georgia, the highest residue of 0.36 mg/kg was determined immediately after the first of two applications. 164 days after the second application residues had decreased to 0.043 and 0.039 mg/kg at 0-15 and 15-30 cm respectively. At the Arizona site there was no clear decline pattern with the highest residues observed at 164 and 14 days at 0.59 mg/kg for the 0-15 cm core and 0.56 mg/kg for the 15-30 cm core respectively. The Arizona field was disced and deep-ploughed between days 30 and 164 resulting in some mixing of sampling depths. At 249 days residues were 0.26 and 0.028 mg/kg for the 0-15 and 15-30 cm sampling depths respectively. Residues in soil decreased at the Mississippi and Georgia sites where rainfall was significantly greater (117 and 31 cm respectively for 6 months after application) than in Arizona (7.3 cm) which has a year-round dry, warm to hot climate.

Table 15. Field studies on the dissipation of dimethipin in soil in the USA (Harned, 1981b).

Crop/variety/location/ year	Soil	Application rate (kg ai/ha)	DALA	Accumulated rainfall (cm)	Residue (mg/kg)	
					0-15 cm	15-30 cm
Cotton/Stoneville-213/Mississippi/1981	Silt loam	0.56	-0	-	<0.025	<0.025
			0	-	0.086	<0.025
			7	0.0	0.11	0.033
			14	2.8	0.10	<0.025
			30	2.8	0.083	<0.025
			164	117	<0.025	<0.025
Cotton/DPL-41/Georgia/1981	Loamy sand	2×0.56	-0	-	0.031	0.043
			0 1st spray	-	0.36	0.075
			3 1st spray	0.05	0.082	0.064
			7 1st spray	0.15	0.10	0.030
			0 2nd spray	0.15	0.21	0.066
			3	0.79	0.21	<0.025
			7	2.0	0.19	<0.025
			14	2.0	0.15	<0.025
			30	4.0	0.18	<0.025
			170	31	0.043	0.039

Crop/variety/location/ year	Soil	Application rate (kg ai/ha)	DALA	Accumulated rainfall (cm)	Residue (mg/kg)	
					0-15 cm	15-30 cm
Cotton/DPL-61/Arizona/1981	Clay loam	2×0.56	-0	-	<0.025	<0.025
			0 1st spray	-	0.084	0.059
			7 1st spray	0.00	0.12	0.029
			0 2nd spray	0.00	0.18	0.037
			3	0.00	0.26	0.46
			7	0.05	0.48	0.25
			14	0.05	0.43	0.56
			30	0.05	0.43	0.031
			164	7.3	0.59	0.23
			249	[1]	0.26	0.028

DALA: days after last application
[1]plot received 61 cm of irrigation water

Residues of dimethipin were also determined in two Californian field plots planted with cotton and rotational crops of lettuce, carrots and beets for four years. The cotton crops were defoliated with dimethipin at 0.28 or 2 × 0.28 kg ai/ha. The soil was adobe clay with 4% organic matter, the crops were irrigated with about 76-91 cm/year by furrows and the rainfall was 52, 30, 29 and 26 cm. Residues in core samples at depths of 0-15 and 15-30 cm were <0.02 mg/kg 337-347 days after the last application.

Dzialo *et al*. (1994a) studied the field dissipation of dimethipin on bare ground and a cotton crop in Georgia. Both plots were harrowed and roto-tilled twice to a depth of 8 cm before planting. The cotton plot was planted with the variety Coker 315 and the bare-ground plot was roto-tilled once more before treatment. Dimethipin was applied as two sprays at 0.34 kg ai/ha and 0.26 kg ai/ha seven days apart with the first application at about the 50% boll-open stage, and the soil was sampled at various intervals up to 547 days later. The samples sectioned into increments of 0-15, 15-30, 30-46, 46-61, 61-76, 76-91, 91-107 and 107-122 cm were analysed for dimethipin by GLC with an ECD with residues in selected samples confirmed by GC-MS. The soil at the 0-15 cm depth was sandy clay loam (sand 76%, silt 0.0%, clay 24%, pH 6.2, organic matter 1.1%, CEC 2.9 meq/100 g) for both the cotton crop and bare ground plots. The average monthly minimum and maximum temperatures were 7 and 23°C while the total irrigation and rainfall for the two plots was 239-241 cm.

In the cropped plot residues peaked at 0.10 mg/kg 14 days after the second application, probably a result of treated foliage transferring residues to the soil. Residues decreased to <0.01 mg/kg at 547 days after the first spray.

Table 16. Residues of dimethipin in cores of soil treated with two sprays of a flowable formulation on a cotton crop in Georgia (average of three replicates).

Sample interval (days)	Dimethipin (mg/kg)							
	0-15 cm	15-30 cm	30-46 cm	46-61 cm	61-76 cm	76-91 cm	91-107 cm	Total
-1	ND	ND	ND	ND	ND	ND	ND	ND
0	0.042	ND	ND	ND	NA	NA	NA	0.042
1	0.059	ND	ND	ND	NA	NA	NA	0.059
2	0.063	ND	ND	ND	NA	NA	NA	0.063
6	0.066	ND	ND	ND	NA	NA	NA	0.066
7[1]	0.084	ND	ND	ND	NA	NA	NA	0.084
10	0.090	ND	ND	ND	NA	NA	NA	0.090
14	0.084	ND	ND	ND	NA	NA	NA	0.084
21	0.10	ND	ND	ND	NA	NA	NA	0.10
35	0.098	ND	ND	ND	NA	NA	NA	0.098
67	0.065	0.01	ND	ND	NA	NA	NA	0.075
97	0.047	0.018	ND	ND	NA	NA	NA	0.065
127	0.051	0.020	ND	ND	NA	NA	NA	0.071
157	0.044	0.021	ND	ND	NA	NA	NA	0.065
187	0.037	0.018	0.015	0.012	ND	ND	NA	0.082

Sample interval (days)	Dimethipin (mg/kg)							
	0-15 cm	15-30 cm	30-46 cm	46-61 cm	61-76 cm	76-91 cm	91-107 cm	Total
247	0.014	0.012	0.010	ND	ND	0.011	ND	0.047
367	ND	ND	ND	ND	ND	ND	NA	ND
490	ND	0.011	ND	ND	ND	ND	NA	0.011
547	ND	ND	ND	ND	ND	ND	NA	ND

ND: not detected
NA: not analysed
[1] second application

Residues in the bare-ground plot peaked on the day of the second application at 0.209 mg/kg decreasing to below the limit of detection by day 490.

Table 17. Residues of dimethipin in cores of soil from a bare-ground plot in Georgia treated with two sprays of a flowable formulation. Average of three replicates.

Sample interval (days)	Dimethipin (mg/kg)							
	0-15 cm	15-30 cm	30-46 cm	46-61 cm	61-76 cm	76-91 cm	91-107 cm	Total
-1	ND	ND	ND	ND	ND	ND	ND	ND
0	0.081	ND	ND	ND	NA	NA	NA	0.081
1	0.075	ND	ND	ND	NA	NA	NA	0.075
2	0.090	ND	ND	0.011	ND	ND	NA	0.090
6	0.073	ND	ND	ND	NA	NA	NA	0.073
7[1]	0.209	ND	ND	ND	NA	NA	NA	0.209
10	0.193	ND	ND	ND	NA	NA	NA	0.193
14	0.134	ND	ND	ND	NA	NA	NA	0.134
21	0.131	ND	ND	ND	NA	NA	NA	0.131
35	0.126	ND	ND	ND	NA	NA	NA	0.126
67	0.078	ND	ND	ND	NA	NA	NA	0.078
97	0.072	0.018	0.013	ND	0.010	ND	ND	0.113
127	0.040	0.035	0.011	0.012	ND	ND	NA	0.098
157	0.064	0.029	0.016	0.015	ND	ND	NA	0.124
187	0.053	0.026	0.014	0.010	ND	ND	NA	0.103
247	0.034	0.028	0.016	0.014	ND	ND	NA	0.092
367	0.013	0.019	0.014	0.015	ND	ND	NA	0.061
490	ND	ND	ND	ND	ND	ND	NA	ND
547	ND	ND	ND	ND	ND	ND	NA	ND

ND: not detected
NA: not analysed
[1] second application

The half-lives of dimethipin, calculated from the first-order constants using linear regression analysis, in the cropped and bare-ground plots were 168 and 177 days respectively.

Dzialo *et al*. (1994b) studied the dissipation of dimethipin on a cotton field crop in Mississippi tilled to a depth of 5-8 cm three times during the study to remove weeds and stubble. The plot was planted with variety DES 119 and dimethipin was sprayed twice seven days apart at 0.34 kg ai/ha and 0.26 kg ai/ha, with the first application when the crop was at about the 75% boll-open stage and the second at the 90% stage. Soil samples sectioned into increments of 0-15, 15-30, 30-46, 46-61, 61-76, 76-91, 91-107 and 107-122 cm were collected at various intervals up to 548 days after the first application. The soil for the 0-15 cm depth samples was sandy loam (sand 33%, silt 58%, clay 9.2%, pH 6.8, organic matter 0.8%, CEC 5.5 meq/100 g). Average monthly minimum and maximum temperatures were 5 and 17°C while the total rainfall was 171 cm. Analysis for dimethipin in the soil samples was by GLC with an ECD with residues in selected samples confirmed by GC-MS.

Residues peaked at 0.16 mg/kg on the day of the second application and decreased to 0.019 mg/kg 548 days after the first spraying.

Table 18. Residues of dimethipin in cores of soil from a cotton plot in Mississippi treated with two sprays of a flowable formulation. Average of three replicates.

Interval (days)	Dimethipin (mg/kg)							
	0-15 cm	15-30 cm	30-46 cm	46-61 cm	61-76 cm	76-91 cm	91-107 cm	Total
-1	ND	ND	ND	ND	ND	ND	ND	ND
0	0.031	ND	ND	ND	NA	NA	NA	0.031
1	0.080	ND	ND	ND	NA	NA	NA	0.080
2	0.017	ND	ND	ND	NA	NA	NA	0.017
6	0.078	0.012	ND	ND	NA	NA	NA	0.090
7[1]	0.147	0.011	ND	ND	NA	NA	NA	0.158
10	0.061	0.011	ND	ND	NA	NA	NA	0.072
14	0.123	0.016	ND	ND	NA	NA	NA	0.139
21	0.096	0.017	ND	ND	NA	NA	NA	0.113
35	0.088	0.018	ND	ND	NA	NA	NA	0.106
65	0.016	0.031	0.057	0.014	ND	ND	NA	0.118
97	0.012	0.032	0.042	0.022	ND	ND	NA	0.108
126	ND	0.021	0.047	0.050	0.015	ND	ND	0.133
159	ND	0.014	0.019	0.045	0.026	ND	ND	0.104
187	ND	0.008	0.017	0.024	0.025	ND	ND	0.074
247	ND	0.007	0.011	0.033	0.030	ND	ND	0.081
367	ND	ND	0.009	0.024	0.024	ND	ND	0.057
489	ND	ND	ND	ND	0.015	ND	ND	0.015
548	ND	ND	ND	ND	0.019	ND	NA	0.019

[1] second application

The half-life of dimethipin in the 0-122 cm depth calculated from first-order constants using linear regression analysis was 196 days.

Dimethipin was applied as a single spray at 2.24 kg ai/ha to sunflowers 14 days before harvest in North Dakota, USA (Harned, 1982). The soil was clay loam (sand 40%, silt 40%, clay 19%; pH 7.0; organic matter 16%; CEC 54 meq/100 g). 21 days after spraying the plot was disced to a depth of 10-13 cm. Soils were sampled to a depth of 30 cm as two cores, 0-15 cm and 15-30 cm and analysed for dimethipin (Wong, 1976). Under the climate conditions typical of North Dakota severe cold and low precipitation occurred for the seven months after application that autumn. The delayed dissipation of dimethipin appears to be related to the onset of warm weather. A possible reason for the variability in results is the incorporation of sunflower stubble/organic matter in the soil, discing at 21 days

In another trial a single spray of dimethipin was applied at 1.12 kg ai/ha to sunflowers 14 days before harvest in North Dakota (Fitzpatrick, 1983). The soil was silt loam (sand 36%, silt 51%, clay 13%; pH 7.0; organic matter 5.2%; CEC 52 meq/100 g). The crop was harvested so that no part of the normal harvested portion remained on the plot and the plot was not disced or ploughed. Soils were sampled to a depth of 30 cm as two cores, 0-15 cm and 15-30 cm and analysed for dimethipin. The initial residue at 0-15 cm was 0.10 mg/kg and decreased to <0.02 mg/kg after 18 months. The highest residue of 0.18 mg/kg correlated with an increase in precipitation and the seasonal thaw with subsequent stubble run-off.

Table 19. Field studies on the dissipation of dimethipin in soil in the USA (Harned, 1982, Fitzpatrick, 1983).

Crop/variety/location/year	Soil	Application rate (kg ai/ha)	DALA	Accumulated rainfall (cm)	Residue (mg/kg)	
					0-15 cm	15-30 cm
Sunflower/894-oil type /North Dakota /1982	Clay loam	2.24	-0	-	0.025	<0.025
			+0	-	0.43	0.035
			3	0.064	0.37	<0.025
			7	0.064	0.28	<0.025
			14	0.064	0.54	<0.025
			30[1]	3.7	0.38	<0.025

Crop/variety/location/year	Soil	Application rate (kg ai/ha)	DALA	Accumulated rainfall (cm)	Residue (mg/kg)	
					0-15 cm	15-30 cm
			180	10	0.49	<0.025
			270	24	0.54	<0.025
			365	52	0.087	<0.025
			545	70	0.055	0.055[2]
Sunflower/894-oil type/ North Dakota /1982	Silt loam	1.12	-0	-	<0.02	<0.02
			+0	-	0.10	<0.02
			14	4.0	0.10	<0.02
			30	4.4	0.07	<0.02
			90	12	0.06	<0.02
			180	30	0.18	<0.02
			270	44	0.04	<0.02
			365	61	0.04	<0.02
			540	81	<0.02	<0.02

DALA: days after last application
[1] plot disced to a depth of 10-13 cm 21 days after application
[2] residues in 0-30 and 30-58 cm cores were 0.065 and <0.025 mg/kg indicating the absence of significant deep soil leaching

Residues in rotational crops. In a confined rotational crop study (Perhach and Jalal, 1993) a small outdoor plot of Hanford sandy loam soil 0.61 m × 2.44 m was sprayed with [^{14}C]dimethipin at 0.6 kg ai/ha and subplots planted with Waldmann lettuce, var. 425 barley and Imperator carrots after 30 days. Samples of lettuce, barley (heads and straw) and carrots (tops and roots) were collected at half-mature growth and at maturity together with soil samples to a depth of 30 cm. The ^{14}C was determined by combustion and LSC. Crop samples were extracted twice with acetone followed by methanol/water. The acetone extracts were pooled as were the aqueous methanol extracts. The extracts were analysed by HPLC in a C-18 reverse-phase column with UV detection. Radio-chromatograms were constructed from LSC analysis of column fractions. Identification of compounds was by TLC on silica gel 60 F254 plates and co-chromatography with authentic standards. Further characterization was by column chromatography (Sephadex A-25 anion exchanger, Sephadex LH 20 and Biogel P2) combined with mass spectrometry in electron impact, chemical ionisation and fast atom bombardment modes.

Radioactive residues in 0-15 cm soil cores were 0.19, 0.06 and 0.39 mg/kg as dimethipin respectively in the lettuce, carrot and barley subplots immediately after application. At planting 30 days after treatment the levels were 0.25, 0.15 and 0.14 mg/kg respectively, and at harvest were 0.03 (100 DAT), 0.02 (238 DAT) and 0.03 (296 DAT) mg/kg. The variation in observed TRR is probably due to inhomogeniety in the application (stated to be made uniformly) and reflects the small number of core samples collected.

Most of the radioactivity in the soil at application and planting was extracted with acetonitrile (85-100% of the TRR), dimethipin being the only compound extracted. The percentage of bound, unextractable residue increased with time after application reaching 60-93% of the TRR at harvest.

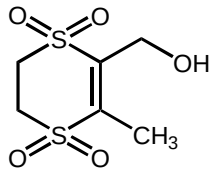
The concentrations of radioactivity were highest in barley forage, carrot tops and lettuce leaves. Only low levels of dimethipin were detected in the crops at harvest with residues ranging from undetectable in barley grain to 0.05 mg/kg in carrot roots.

Table 20. Radioactive residues in rotational crops after application of [^{14}C]dimethipin (Perhach and Jalal, 1993).

		Lettuce		Carrot				Barley		
		Immature	Mature leaf	Immature		Mature		Immature	Mature	
				Tops	Root	Tops	Root	Forage	Straw	Grain
TRR (mg/kg[1])		1.4	0.42	1.8	0.10	0.69	0.10	2.5	0.34	0.02
Fraction		% of TRR								
Organic	dimethipin	7.3	13	-	46	3.7	14	1.8	4.3	-
	hydroxy-DMP								3.3	
	U1						36			
	U2	10	22	32	4.3	29		14		
	U3		0.02					5.6	4.7	
	Other	7.3				2.5				
	Total	29	36	37	50	37	50	22	12	21
Aqueous/ MeOH	U1	5.7	8.9	5.9	27	7.2	26	48	30	
	U2	1.1	-	2.2		6.4				
	U3		0.4	-		-				
	Other	4.5	1.1	2.9		7.0				
	Total	11	10	13	27	21	26	48	30	18
Bound		60	54	50	23	42	24	31	58	61
Total		92	115	70	83	83	107	53	82	101

[1]calculated as dimethipin

In addition to dimethipin and hydroxy-DMP, three compounds, U1, U2 and U3 were detected in plant extracts. They did not co-chromatograph with the prepared standards but appeared to be related. When U2 and U3 were exposed to aqueous methanol they were converted into U1, and U2 and U3 formed at different stages of U1's purification. Mass spectra (EI, CI and FAB modes) of the compounds revealed fragments of hydroxy-DMP so the products are probably derivatives of hydroxy-DMP conjugated to the hydroxyl oxygen through ester or ether linkages. The FAB mass spectra of a mixture of U2 and a related compound, U4, showed a large number of ion peaks in the range m/z 450-650, though none corresponded to glucose, glucuronic acid or glutathione, the most likely candidates for conjugation to hydroxy-DMP. Hydrolysis of U1 in acid resulted in hydroxy-DMP, U2 and U3.



hydroxy-DMP

Korpalski (1996a) determined dimethipin in rotational crops after spraying it on cotton. In two field trials in Mississippi and Texas in sandy loam soil (Mississippi: sand 66%, silt 30%, clay 4%; pH 5.8; organic matter 1.2%; CEC 5.1 meq/100 g; Texas: sand 68%, silt 16%, clay 16%; pH 8.3; organic matter 0.9%; CEC 25 meq/100 g) dimethipin was sprayed twice on maturing cotton at 0.34-0.35 and 0.25-0.26 kg ai/ha. Approximately 30 days after the second application (after harvest) lettuce, carrots and wheat were planted. A sample of wheat forage was collected before harvest. Residues in lettuce at harvest were 0.02 to 0.03 mg/kg in Mississippi but quantifiable residues were not detected in Texas, nor in carrot roots or wheat grain at either site.

Table 21. Residues of dimethipin in rotational crops after application of dimethipin to mature cotton, 1 month plant back period (Korpalski, 1996a).

Crop	Location	Variety	Plant back interval (days)	Days from planting to harvest	Residue (mg/kg)
Lettuce	Mississippi	Black-seeded Simpson	28	217	0.02, 0.03, 0.03
	Texas	Golden State D	30	96	<0.02 (3)
Carrot (roots)	Mississippi	Early Coreless	28	232	<0.02 (3)
	Texas	Imperator 58	30	96	<0.02 (3)
Carrot (tops)	Mississippi	Early Coreless	28	232	0.04, 0.06, 0.07
	Texas	Imperator 58	30	96	0.03, 0.05, 0.04
Wheat (forage)	Mississippi	Mixed (mostly Cardinal)	28	157	0.03, 0.04, 0.04
	Texas	MIT	30	157	0.04, 0.04, 0.03
Wheat straw	Mississippi	Mixed (mostly Cardinal)	28	234	0.02, 0.02, 0.03
	Texas	MIT	30	230	<0.02 (3)
Wheat grain	Mississippi	Mixed (mostly Cardinal)	28	234	<0.02 (3)
	Texas	MIT	30	230	<0.02 (3)

Recoveries at fortifications of 0.1 and 0.5 mg/kg 83-109%.
Residues corrected for analytical recoveries when below 100%

Korpalski (1995a) also studied residues in rotational crops of lettuce, carrots and oats after dimethipin was sprayed twice on growing cotton in two field trials in Mississippi and Texas at 0.35-0.36 and 0.26 kg ai/ha. The soils were sandy loam at both sites (Mississippi: pH 6.3; organic matter 0.7%; Texas: pH 5.0; organic matter 0.5%). Approximately 6 months after the second application, after the cotton crop was harvested, lettuce, carrots and oats were planted. A sample of oat forage was collected before harvest of the grain.

The residues in the rotational crops were all <0.02 mg/kg, except in carrot tops and oat straw at the Texas site. A plant back interval of 6 months results in lower residues in rotational crops than an interval of 3 months.

Table 22. Residues of dimethipin in rotational crops after spray applications of dimethipin to cotton, 6 month plant back period (Korpalski, 1995a).

Crop	Location	Variety	Plant back interval (days)	Days from planting to harvest	Residue (mg/kg)
Lettuce	Mississippi	Black-seeded Simpson	184	55	<0.02 (3)
	Texas	Salad Bowl	179	52	<0.02 (3)
Carrot (roots)	Mississippi	Coreless	184	82	<0.02 (3)
	Texas	Imperator 58	179	95	<0.02, 0.02 (2)
Carrot (tops)	Mississippi	Coreless	184	82	<0.02 (3)
	Texas	Imperator 58	179	95	0.06, 0.13, 0.18
Oat (forage)	Mississippi	Bob	184	52	<0.02 (3)
	Texas	Troy	179	52	<0.02 (3)
Oat straw	Mississippi	Bob	184	92	<0.02 (3)
	Texas	Troy	179	80	0.03 (3)
Oat grain	Mississippi	Bob	184	92	<0.02 (3)
	Texas	Troy	179	80	<0.02 (3)

Recoveries at fortifications of 0.1 and 0.5 mg/kg 74-106%.
Residues corrected for analytical recoveries when below 100%

The results showed that dimethipin is extensively metabolized with the parent compound accounting for ≤14% of the TRR in crops. Residues in rotational crops after application at the USA label rate for cotton were <0.02-0.07 mg/kg at a plant-back interval of 1 month and <0.02 mg/kg in

crops planted 6 months after spraying, but in carrot tops the residues were up to 0.18 mg/kg at harvest in crops planted 6 months after the last application.

Adsorption/desorption. The adsorption/desorption of [^{14}C]dimethipin was studied in the USA and Canada (Curry, 1980). The soil in the US trial was Bethany sandy loam (sand 61%, silt 24%, clay 15%; pH 5.5; organic matter 1.9%; CEC 8.5 meq/100 g), and in Ontario the five soils were Haldimand silty clay loam (sand 9.3%, silt 60%, clay 31%; pH 6.1; organic matter 3.8%; CEC 36 meq/100 g), Berrin sand (sand 82%, silt 13%, clay 5.8%; pH 6.6; organic matter 2.8%; CEC 19 meq/100 g), Fox sandy loam (sand 69%, silt 22%, clay 9.1%; pH 7.0; organic matter 3.0%; CEC 21 meq/100 g), Huron silt loam (sand 24%, silt 54%, clay 22%; pH 6.9; organic matter 4.5%; CEC 38 meq/100 g) and Bradford muck (pH 5.3; organic matter 89%; CEC 204 meq/100 g). All were treated at four application rates of [^{14}C]dimethipin, 1, 2, 4 and 8 µg/ml. The adsorption isotherms were modelled using the Freundlich[1] adsorption equation.

Dimethipin was weakly adsorbed by all the soils and there was a close relationship between adsorbtion and percentage of organic matter. Average adsorption partition coefficients (K_a) were 0.04 for Bethany sandy loam, 0.20 Haldimand silty clay loam, 0.20 Berrien sand, 0.27 Fox sandy loam, 0.36 Huron silt loam and 13.6 Bradford muck. Correlation coefficients were 0.94, 0.97, 0.98, 1.00, 0.99 and 0.99 respectively. The corresponding K_{oc} values were 4, 9, 12, 15, 14 and 26. Adsorption was essentially completely reversible with almost all dimethipin desorbed after 6 extractions with water from all the soils except Bethany muck which required more than 8 extractions.

Spare (1990) studied the adsorption/desorption of [^{14}C]dimethipin in four US Department of Agriculture soils; Sharkey clay (sand 25%, silt 33%, clay 42%; pH 6.5; organic matter 4.8%; CEC 24 meq/100 g), Sassafras sand (sand 96%, silt 2%, clay 2%; pH 6.5; organic matter 0.9%; CEC 1.8 meq/100 g), Paxton sandy loam (sand 64%, silt 29%, clay 7%; pH 6.3; organic matter 3.1%; CEC 8.5 meq/100 g) and Hesperia loam (sand 44%, silt 47%, clay 9%; pH 6.7; organic matter 0.8%; CEC 4.3 meq/100 g) by batch equilibrium at concentrations of 0, 0.2, 0.5, 1.0, 5.0 and 10 µg/ml. Sharkey clay was the only soil for which the Freundlich isotherm was applicable, with an adsorption partition coefficient of 0.092 (K_{oc} 3.3), because adsorption by the other soils was too weak. Desorption constants could not be determined. The recovery of ^{14}C from the soils and solutions ranged from 100 to 105%.

From the adsorption K_a values the mobility of dimethipin was very high in all soils studied.

Mobility. The mobility of dimethipin was studied in four soils, sand (sand 99%, silt 0.2%, clay 1.3%; pH 7.2; organic matter 1.0%; CEC - meq/100 g), loamy sand (sand 87%, silt 4.6%, clay 8.0%; pH 7.7; organic matter 0.9%; CEC 5.8 meq/100 g), sandy loam (sand 61%, silt 24%, clay 15%; pH 5.5; organic matter 1.9%; CEC 8.5 meq/100 g) and silt (sand 10%, silt 78%, clay 12%; pH 4.4; organic matter 2.1%; CEC 12 meq/100 g) (Erdmann *et al*., 1981). ^{14}C-labelled dimethipin was applied to the tops of 30 cm soil columns, moistened to field capacity, at the equivalent of 1.68 kg ai/ha. The columns were leached with 51 cm of distilled water. An aged soil column was prepared by treating 7.6 column cm of sandy loam with [^{14}C]dimethipin which was then aerobically aged in the dark at ambient temperature for 30 days, poured onto a 23 cm column of sandy loam and leached with 1.25 column cm of distilled water daily for 45 days. The eluate and 7.6 cm soil sections were analysed by

[1] The Freundlich equation was used to interpret the adsorption data

$$\frac{x}{m} = KC_e^{\frac{1}{n}}$$

x/m: soil equilibrium concentration in µg/g
C_e: aqueous phase equilibrium concentration in µg/ml
K_a: Freundlich adsorption constant or coefficient
n is a constant
K_{oc}: adsorption coefficient based on soil organic carbon content = $K \times 100$ / %OC
%OC: organic carbon content = % organic matter divided by 1.7

LSC and TLC with LSC. 77 to 102% of the applied radioactivity was eluted, with dimethipin accounting for 71-96% of the eluted radioactivity. The ^{14}C retained in the soil, as a percentage of the applied radioactivity, was 23, 1.0, 4.8, 0.8 and 8.3% respectively for sand, loamy sand, sandy loam, silt loam and aged sandy loam. Elution of the radioactivity was faster from the loamy sand, silt loam and aged sandy loam than from the sand and sandy loam soils.

Dimethipin is highly mobile and is not degraded significantly under simulated leaching conditions.

Environmental fate in water/sediment systems

Dzalio (1993) studied the anaerobic aquatic degradation of dimethipin in a water/sediment mixture from a pond in a cotton-producing region of Seminole County, Georgia, USA. The sediment (#90877) was a loamy sand (sand 86%, silt 6%, clay 8%; pH 6.4; organic matter 1.2%; CEC 2.6 meq/100 g). The sediment/water system was maintained under a nitrogen atmosphere for 31 days before treating with [^{14}C]dimethipin at 5.2 mg/kg. Samples were analysed at intervals after treatment and degradation and product formation were monitored by HPLC and LSC. At the start of the experiment 97% of the applied ^{14}C was present in the aqueous filtrate, and after 365 days 56% was associated with the water filtrate with dimethipin accounting for 65% of the ^{14}C in water or 37% of the applied radioactivity. Extractable residues from the soil accounted for 5% of the applied ^{14}C, with dimethipin accounting for 89%. Bound residues accounted for 17 and $^{14}CO_2$ for 7% of the applied ^{14}C. The half-life of dimethipin under anaerobic aquatic conditions was 277 days calculated by linear regression.

The bound residues were sonicated and extracted with methanol/acetone/$CHCl_3$/distilled water, then treated by Soxhlet extraction with 0.1 M formic acid and room-temperature extraction with 0.1 M ammonium hydroxide. 3% of the applied radioactivity was liberated from the sample aged for 9 months with thirteen peaks observed in the HPLC profile of the combined extracts. To aid the identification of degradation products an accelerated ageing study was conducted at 35°C using 15 mg/kg [^{14}C]dimethipin, but no significant degradation was observed even after over a year. To investigate whether some of the degradation products had been formed by anaerobic oxidation, activated sludge from a municipal waste treatment plant was treated with [^{14}C]dimethipin and incubated under aerobic conditions in an attempt to generate substantial quantities of oxidation products for comparison with the anaerobic products. This produced a variety of metabolites, but comparing retention times on a variety of chromatography columns proved inconclusive.

In summary, dimethipin is degraded only slowly under aerobic aquatic conditions, and in or on soil under aerobic and anaerobic conditions. It is relatively persistent in the environment and considered highly mobile in all the soils studied.

Bioconcentration. Kuc (1980) studied the bioconcentration of dimethipin in bluegill sunfish over a 30-day exposure with a mean [^{14}C]dimethipin concentration in the water of 2.7 mg/kg and a 14-day depuration period. The maximum bioconcentration factor (BCF) in the whole fish was 3.4 with a maximum residue level of 8.4 mg/kg during uptake. The BCF for edible tissues was 2.8 with a maximum residue of 7.1 mg/kg. After 14 days depuration, the ^{14}C concentration was 3.8 mg/kg in the whole fish and 4.1 mg/kg in the edible parts, as dimethipin.

Residues in channel catfish were also studied after 30 days exposure to an aerobically aged sandy loam soil which was then aged for 14 days under flooded conditions and treated with [^{14}C]dimethipin at 1.12 kg ai/ha (Harned *et al.*, 1981). Bioconcentration factors were 3.6 for edible tissues and 4.0 for whole fish. After 15 days depuration, residues in edible tissues and whole fish had decreased to 70 and 57% of the maximum levels respectively. Parent dimethipin was the only ^{14}C compound detected in the water after the 30-day uptake period.

METHODS OF RESIDUE ANALYSIS

Cotton seed (Womer and Sisken, 1974). Ground seed was extracted with acetone/water and the combined filtered extracts washed with petroleum ether (5% NaCl solution was added to aid separation) and the petroleum ether was back-washed with acetone/water. The residue was partitioned with $CHCl_3$, and the organic layer concentrated by rotary evaporation (40°C) and cleaned up on a column of Florisil and alumina. Further clean-up was by partitioning with octanol-nitromethane. The sample was then concentrated by rotary evaporation at 40°C and analysed by GLC with a sulfur-specific detector. Recoveries through the extraction procedure determined using samples fortified with radiolabelled dimethipin (levels not specified) were 88-99% (average 94%, n=6), and for the corresponding GLC analyses were 85-105% (average 93%).

In the US FDA Pesticide Analytical Method Volume II, §180.406 (1975), cotton seed is extracted with methanol/water (9:1) and the oil removed by a hexane wash with aqueous NaCl to prevent emulsion formation. The methanol/water layer is partitioned with $CHCl_3$, and the $CHCl_3$ concentrated and cleaned up on a Florisil and alumina column. Dimethipin is eluted with $CHCl_3$/acetone (23:2) and the eluate evaporated to dryness. The residue is dissolved in acetone for analysis by GLC with an FPD (sulfur mode). Recoveries from samples fortified at 0.5 mg/kg were 77-97%.

Koch and Cooper (1994) and Korpalski (1992a, 1993a) validated a revision of this method by Wormer and Sisken (1975), described by Brookey *et al*. (1993), for cotton seed and cotton seed processed products. The initial extraction procedure was different for the different samples. Ground ginned cotton seed or cotton seed hulls were extracted twice with methanol/water (9:1) and the combined extracts partitioned with hexane. The hexane layer was discarded and the aqueous phase was extracted three times with $CHCl_3$. The $CHCl_3$ was dried over anhydrous sodium sulfate and 10% decanol in acetone was added before concentration to a volume of 2 ml by rotary evaporation at 40°C. The decanol-acetone keeper solution was added at each of the solvent concentration steps. The remaining liquid was evaporated to dryness under a stream of nitrogen before redissolving in dichloromethane. Soapstock samples were blended with Celite and acetonitrile and the extracts dried with anhydrous sodium sulfate before partitioning with hexane. The acetonitile phase was evaporated to dryness and the residue dissolved in dichloromethane. Oil samples were mixed with hexane and the residue partitioned with acetonitrile. The hexane layer was discarded and the acetonitrile layer evaporated to dryness and the residue dissolved in dichloromethane.

The dichloromethane solutions were cleaned up on a gel permeation column. The cotton seed solution was passed through a 0.45 µm disposable cartridge filter before loading on the column. The eluate was concentrated by rotary evaporation followed by evaporation under nitrogen and the remaining residue dissolved in toluene/$CHCl_3$ (4:1). The solution was cleaned up on an alumina/Florisil column eluted with 8% acetone in $CHCl_3$. The solution was evaporated to dryness as previously and the residue dissolved in ethyl acetate for analysis by GLC with an FPD (sulfur mode). Recoveries determined by fortification with dimethipin at 0.5-2.0 mg/kg were 70-90%. It was noted that successful application of the method required proper calibration of the alumina-Florisil clean-up column owing to the variable performance of commercially purchased alumina. In addition, low recoveries were observed if on concentration of the solutions by rotary evaporation, they were allowed to go dry.

Table 23. Validation data for the analysis of cotton seed and processed commodities (Koch and Cooper, 1994, Korpalski, 1992a, 1993a).

Sample	Fortification level (mg/kg)	Recovery (%)
Cotton seed	0.1	100, 88, 105, 95
	0.2	88, 85, 92, 90
	0.5	86, 78, 100, 110, 70, 73
	2.0	89, 90

Sample	Fortification level (mg/kg)	Recovery (%)
Cotton seed hulls	0.1	88, 88, 105, 105
	0.2	82, 78, 96, 100
	0.5	78, 72, 102, 96
Cotton seed oil	0.1	97, 92, 100,100
	0.2	71, 91, 75, 95
	0.5	85, 85, 88, 78
Cotton soapstock	0.1	69, 69
	0.2	68, 82
	0.1	66, 90

In an independent laboratory validation of the method of Womer and Sisken (1975) to determine residues of dimethipin in cotton seed, essentially as described above, average recoveries were 92% from samples fortified at 0.1, 0.2 and 0.5 mg/kg (range 83-100%).

In another independent laboratory validation (PTRL-West Inc Method No. P671W/RP97009 for cereal substrates) residues of dimethipin were extracted from grain forage and straw by being homogenized twice with acetone/water (9:1) and the extract filtered, diluted with water and partitioned twice with hexane. The aqueous phase was partitioned twice with dichloromethane and the combined dichloromethane extracts dried and concentrated after adding 10% decanol in acetone as a keeper [taken from yellow note]. Hexane was added and the solution cleaned up on a silica "BondElut" cartridge sequentially washed with toluene and hexane/acetone (95:5). The dimethipin was eluted with hexane/acetone (75:25) and the eluate concentrated by rotary evaporation after adding 1% decanol in acetone as a keeper. The extracts were analysed by GLC with an FPD (sulfur mode). Minor modifications included adding saturated NaCl solution before hexane partition to minimise emulsion formation. Recoveries were 74-113% at 0.02-0.05 mg/kg from fortified samples of wheat grain, 71-88% at 0.02-0.5 mg/kg from wheat forage and 104-110% at 0.02-0.5 mg/kg from barley straw. The results confirmed an LOQ of 0.02 mg/kg.

Korpalski (1995b) described the validation of a method based on the "Determination of dimethipin (Harvade®) residues in various wet and dry crops", Morse Laboratories SOP#Meth-74, 10/94 for rotational crops (lettuce, carrot roots, carrot tops, oat straw, oat forage, oat grain and wheat grain). All samples were ground to a fine consistency with dry ice and extracted twice with acetone/water (9:1), partitioned with $CHCl_3$, the $CHCl_3$ dried with sodium sulfate and concentrated at less than 40°C using a rotary evaporator after adding 10% decanol in acetone. The remaining solvent was removed under a stream of nitrogen and the residue dissolved in dichloromethane for clean-up on a gel permeation column followed by a Florisil column. Residues of dimethipin were determined by GLC with an FPD (sulfur mode). Recoveries from fortified samples of lettuce at 0.02-0.3 mg/kg were 90-108%, carrot roots at 0.02-0.29 mg/kg 87-115%, carrot tops at 0.02-0.34 mg/kg 85-113%, oat forage at 0.02-0.29 mg/kg 83-100%, oat straw at 0.02-0.28 mg/kg 87-112%, oat grain at 0.02-0.3 mg/kg 81-92% and wheat grain at 0.02-0.3 mg/kg 92-110%. The results confirm a limit of quantification of 0.02 mg/kg.

In the US FDA Pesticide Analytical Method Volume II, §180.406 (1975), beef liver is extracted with acetonitrile, the filtrate dried over anhydrous sodium sulfate and washed with petroleum ether. The acetonitrile layer is concentrated and the residue dissolved in benzene-$CHCl_3$ (1:1) and cleaned up on a Florisil and alumina column. Dimethipin is eluted with $CHCl_3$/acetone (23:2) and the eluate evaporated to dryness. The residue is dissolved in ethyl acetate for analysis by GLC with an ECD or GC-MS with selected ion monitoring at m/z 118. Recoveries from samples fortified at 0.02-0.04 mg/kg were 85-102% and 71-99% for GLC with an ECD and GC-MS analysis respectively.

A method for the determination of dimethipin in animal tissues was described by Singh and Eckhert (1996) (SOP EBT #270, 10/11/95). Animal tissues (muscle, kidney and liver) were homogenized with acetonitrile, anhydrous sodium sulfate and Celite®. The filtered acetonitrile extract was washed with petroleum ether and evaporated to dryness on a rotary evaporator at 40-50°C. The

residue was dissolved in 50% $CHCl_3$/benzene, cleaned up on an alumina/Florisil column and eluted with 8% acetone in $CHCl_3$. The eluate was reduced by rotary evaporation followed by evaporation under a stream of nitrogen. The residue was dissolved in acetone for analysis by GLC with an ECD. Average recoveries (n=18) for samples fortified at 0.01, 0.05 and 1.0 mg/kg were 95 ± 4.2% for muscle, 95 ± 5.8% for liver and 98 ± 9.5% for kidney.

A method for the determination of dimethipin in chicken liver was described by Abdel-Kader and Blaszczynski (1984). Samples were extracted by blending with acetonitrile, filtered and cleaned by partitioning twice with petroleum ether. The acetonitrile layer was dried over anhydrous sodium sulfate, evaporated to dryness and redissolved in 50% $CHCl_3$ in toluene, cleaned up on a mixed alumina/Florisil column and eluted with 8% acetone in $CHCl_3$. The solution was evaporated to dryness and the residue redissolved in ethyl acetate for analysis by GLC with an ECD. Recoveries from samples fortified at 0.01, 0.02, 0.04 and 0.1 mg/kg were 109, 95, 97 and 99% respectively.

In a method for the determination of the dimethipin metabolite ethane-1,2-disulfonic acid in beef kidney reported by Batorewicz (1993) the kidney is diced, homogenized and water is added. Proteins are precipitated with aqueous potassium ferrocyanide and zinc acetate. The suspension is centrifuged and the supernatant filtered. An aliquot of the filtrate is cleaned up on a solid-phase extraction strong anion-exchange column. The column is washed with 1% trifluoroacetic acid (TFA) with the analyte eluted with 3% TFA, the solution evaporated to dryness and the residue reconstituted in water for analysis by ion-exchange chromatography with conductivity detection. Recoveries from samples fortified with ethane-1,2-disulfonic acid at 0.2 and 0.5 mg/kg ranged from 70 to 108% (mean 95%, n=6). The performance of the method was re-examined by Batorewicz and Long (1996). Three kidney samples from an animal feeding study were analysed together with samples fortified at 0.2 and 0.5 mg/kg. The fortified samples gave recoveries of 90 and 78% respectively, with average incurred residues in the three kidney samples of 0.47 ± 0.05 mg/kg in the original feeding study and 0.34 ± 0.05 mg/kg in the performance study.

In a method described by Henderson (1981) residues of dimethipin in milk are extracted by blending samples with ethyl acetate. The filtered ethyl acetate is concentrated by evaporation and the solution partitioned with acetonitrile and petroleum ether. The acetonitrile layer is evaporated to near dryness, and the sample dissolved in dichloromethane and purified by passage through a silica column. The eluted dichloromethane is concentrated by rotary evaporation to near dryness, followed by evaporation under a stream of nitrogen. The residue is dissolved in acetone for analysis by GLC with an ECD. Recoveries from samples fortified at 0.01 mg/kg were 70, 80 and 98% and from a sample fortified at 0.05 mg/kg 76%. The limit of quantification is 0.01 mg/kg. Validation was carried out without any modification (Milad, 1981). Recoveries from milk samples fortified at 0.5-3.0 mg/kg were 70-100%. Analytical verification recoveries in a dairy cow feeding study were 98 ± 9.4% for milk (Singh and Ekert, 1996).

In the determination of dimethipin in soil, samples were extracted by Soxhlet with acetone (Wong, 1976). The extract was evaporated to dryness and the residue dissolved in 20% chloroform in toluene, dried over anhydrous sodium sulfate and cleaned up on a mixed alumina/Florisil column eluted with 8% ethyl acetate in chloroform. The eluate was evaporated to dryness, and the residue dissolved in acetone for analysis by GLC with an FPD (sulfur mode). Recoveries from five different soils (Agawam sandy loam, Foster fine sandy loam, Tifton sandy loam, slit loam and Bethany sandy loam) fortified at 0.2 mg/kg with [^{14}C]dimethipin were 99-110%. In a study reported by Vithala and DeMatteo (1999) recoveries of dimethipin from soil ranged from 66 to 96% but fortification levels were not specified. The reported limit of detection was 0.04 mg/kg.

Dimethipin was determined in fresh water after filtering through a 0.45 µm disposable cartridge by HPLC with UV detection at 210 nm (Stauffer, 1990). The limit of detection was stated to be 0.1 mg/kg. Recoveries from samples fortified at 1 and 100 mg/kg were 87-93% and 90-99% respectively.

Stability of pesticide residues in stored analytical samples

The freezer storage stability of dimethipin in a variety of crops and processed commodities was studied by Korpalski (1998). Ground samples of lettuce, carrot roots, wheat grain and oat straw fortified with dimethipin at 0.2 mg/kg and stored at -20 ± 5°C were analysed at regular intervals for 12 months. The analytical method used was the "Determination of dimethipin (Harvade®) residue in various wet and dry crops" (Morse Laboratories Ltd. SOP #Meth-74, Rev 2, 01/95, LOQ 0.02 mg/kg). Residues were uncorrected for procedural recoveries.

Table 24. The stability of dimethipin in fortified samples stored at -20°C (Korpalski, 1998).

Storage period (days)	% remaining after storage			
	Lettuce	Carrot roots	Wheat grain	Oat straw
0	95, 105	105, 100	83, 83	95, 88
37	108, 93	100, 110	100, 93	88, 90
92	94, 97	103, 103	94, 94	94, 91
180	97, 97	97, 100	88, 94	113, 100
280	103, 106	100, 91	97, 103	97, 97
366	106, 110	100, 103	100, 100	98, 95

Procedural recoveries from samples fortified at 0.05 and 0.3 mg/kg were 87-107% for lettuce, 82-105% for carrot root, 73-105% for wheat grain and 82-116% for oat straw.

Korpalski (1993b, 1996b) studied the freezer storage stability of dimethipin in cotton seed and processed products using the Morse Laboratories Ltd. MLSOP #Meth-60 method (LOQ 0.02 mg/kg). Samples of ground cotton seed, meal, hulls and crude oil were fortified with dimethipin at 0.2 or 0.5 mg/kg and stored at -20 ± 5°C. The seed was stored for 12 months and all the other samples for 7 months.

Table 25. The stability of dimethipin in fortified samples stored at -20°C (Korpalski, 1993b, 1996b).

Storage period (months)	% remaining after storage			
	Seed (0.5 mg/kg)	Meal (0.2 mg/kg)	Hulls (0.5 mg/kg)	Crude oil (0.2 mg/kg)
0	81, 82	75, 73	78, 90	98, 100
1	82, 84	73, 78	86, 84	100, 115
2 + 23 days	80, 83	60, 80	82, 78	100, 105
3		75, 39	68, 72	63, 83
4	87, 81			
5		78, 78	72, 68	83, 83
7		85, 78	79, 73	90, 96
8	82, 84			
12	89, 81			

Procedural recoveries from cotton seed fortified at 0.5 mg/kg were 85-105%, and from meal, hulls and crude oil fortified at 0.1 or 0.5 mg/kg 74-94%, 62-89% and 74-120% respectively

Hughes and Halverson (1996) studied the freezer storage stability of ethane-1,2-disulfonic acid in beef kidney. Samples containing incurred residues of ethane-1,2-disulfonic acid were analysed after 0, 93 and 178 days of freezer storage. Mean residues were 0.41, 0.44 and 0.45 mg/kg after 0, 93 and 178 days respectively.

The frozen storage stability of dimethipin in milk and tissues of dairy cows was studied by Singh and Eckert (1996). Samples of milk and homogenized muscle, liver and kidney were fortified with dimethipin at 0.05 mg/kg and analysed after 0, 1 and 2 months frozen storage.

Table 26. The stability of dimethipin in fortified samples stored at -20°C (Singh and Eckert, 1996).

Storage period (months)	% remaining			
	Milk	Muscle	Liver	Kidney
0	103, 106	82, 84	90, 92	79, 79
1	94, 95	83, 78	81, 78	80, 83
2	97, 98	91, 91	95, 86	89, 94

Definition of the residue

Dimethipin is not significantly metabolized by plants when applied close to harvest. The main component of the extractable residue in plants is dimethipin, accounting for 38-72, 61, 20-25, 50 and 14-50% of the extractable residue in cotton, sunflower seeds, potatoes, rice grain and grape juice respectively. In animals dimethipin is extensively metabolized with the main pathways involving conjugation to glutathione, amino acids and peptides and subsequent degradation. Minor routes of metabolism include hydrolytic hydroxylation and oxidation.

The definition of the residue for commodities derived from plants and animals should be dimethipin for compliance with MRLs and the estimation of dietary intake.

USE PATTERN

Dimethipin is registered as a flowable formulation in many countries. It is a plant growth regulator and is used as a defoliant, to enhance maturation and reduce seed moisture in grain and oil seed crops.

The information available to the Meeting on registered uses is shown in Table 19.

Table 27. Registered uses of dimethipin. All foliar applications.

Crop	Country	Form.	Application			PHI (days)
			Rate (kg ai/ha)	Spray conc., (kg ai/hl)	No.	
Barley (malt)	Poland	25F	0.38-0.5			
Bean	Poland	25F	0.38-0.5			14-21
Bean (broad)	Poland	25F	0.38-0.5			14-21
Bean (horse)	Poland	25F	0.38-0.5			14-21
Buckwheat	Poland	25F	0.38-0.5			
Cabbage	Czech Republic	25F	0.63-1.0			10-14
Cabbage	Poland	25F	0.5			
Cabbage	Slovakia	25F	0.63			
Carrot	Poland	25F	0.5-0.75			
Cauliflower	Poland	25F	0.5			
Cauliflower	Slovakia	25F	0.63-1.0			
Clover (red)	Poland	25F	0.75			
Cotton	Bulgaria	25F 25% FS	0.4			apply to cotton at 10-150 open bolls per 100 plants stage
Cotton	Egypt	25F	0.5-0.63			
Cotton	France	25F	0.31	6.9		14-21
Cotton	Greece	25F	0.31	0.039-0.063		None
Cotton	Greece	5F, 60%FL		0.05-0.1		
Cotton (medium fibre)	Kazakhstan	25F	0.38-0.55			10-14
Cotton (fine fibre)	Kazakhstan	25F	0.5-0.63			10-14
Cotton	South Africa	25F	0.31-0.63			
Cotton	Spain	25F	0.31			
Cotton	Turkey	25F	0.31			
Cotton	Turkmenistan	25F				

Crop	Country	Form.	Application			PHI (days)
			Rate (kg ai/ha)	Spray conc., (kg ai/hl)	No.	
Cotton	USA	5F (48%)	0.23-0.28	0.12-0.30 grd 0.49-1.5 air	2	7-21
Cotton	USA	25F (22%)	0.26-0.32		2	7-21
Cotton	Uzbekistan	25F	0.38-0.63			
Facelia	Poland	25F	0.75			
Fodder beet	Poland	25F	0.75-1.0			
Fruit trees	Czech Republic	25F		1%		14
Fruit (nursery)	Slovakia	25F		0.3-1%		
Grass (seed)	Poland	25F	0.38-0.5			
Kohlrabi	Poland	25F	0.5			
Kohlrabi	Slovakia	25F	0.63			
Lettuce	Czech Republic	25F	0.63-1.0			10-14
Lettuce	Poland	25F	0.5-0.75			14-21
Lettuce	Slovakia	25F	0.63-1.0			
Linseed (flax seed crop)	Belarus	25F, 25% FS	0.38-0.55			
Linseed (flax)	Bulgaria	25F, 25% FS	0.5			14
Linseed (flax)	Czech Republic	25F	0.5			10-15
Linseed (flax)	Eire	25F	0.5	0.13-0.2		21-28 after full flowering
Linseed (flax)	Kazakhstan	25F	0.38-0.5			10-14
Linseed (flax floret seed)	Poland	25F	0.5			
Linseed	Slovakia	25F	0.5			
Lupin	Poland	25F	0.38-0.5			14-21
Maize	Czech Republic	25F	0.5-0.63			21
Maize	Hungary	25F	0.45-0.63			14
Maize	Slovakia	25F	0.5-0.63			
Onion	Czech Republic	25F	0.63			10-14
Onion (sets)	Poland	25F	0.38-0.5			
Onion	Slovakia	25F	0.63			
Parsnip	Poland	25F	0.5-0.75			14-21
Pea	Czech Republic	25F	0.5-0.63			14
Pea	Hungary	25F	0.3-0.5			14
Pea	Poland	25F	0.38-0.5			14-21
Pea	Slovakia	25F	0.5-0.63			
Pepper (red)	Bulgaria	25F, 25% FS	0.3			
Pisum sativum convar speciosum	Slovakia	25F	0.5-0.63			
Potato (seed)	Belarus	25F, 25% FS	0.75			
Potato	Belarus	25F, 25% FS	0.75			
Potato	Bulgaria	25F, 25% FS	0.63			14
Potato	Czech Republic	25F	0.5-0.75			14
Potato	Eire	25F	0.63	0.13-0.31		21
Potato	Hungary	25F	0.5-0.63			14
Potato	Kazakhstan	25F	0.75			18-21
Potato (seed)	Kazakhstan	25F	0.75			18-21
Potato	Poland	25F	0.5-0.75			14-21
Potato	Romania	25F	0.63			7
Potato	Slovakia	25F	0.5-0.75			
Radish	Czech Republic	25F	0.63-1.0			10-14
Radish	Poland	25F	0.5			
Radish	Slovakia	25F	0.63-1.0			
Rape seed	Czech Republic	25F	0.38-0.5			10-14
Rape seed	Croatia	25F	0.38-0.5			
Rape seed	Eire	25F	0.5	0.1-0.25		10-14
Rape seed	Hungary	25F	0.3-0.5			14
Rape seed	Kazakhstan	25F	0.38			10-14
Rape seed	Kyrgyzstan	25F	0.38-0.5			10-14

Crop	Country	Form.	Application			PHI (days)
			Rate (kg ai/ha)	Spray conc., (kg ai/hl)	No.	
Rape seed	Poland	25F	0.38-0.5			
Rape seed	Slovakia	25F	0.38-0.5			
Red beet	Poland	25F	0.75-1.0			
Rice	Bulgaria	25F, 25% FS	0.38-0.5			14
Rice	Hungary	25F	0.25-0.3			14
Rice	Romania	25F	0.5			7
Soya bean	Czech Republic	25F	0.5-0.63			21
Soya bean	Croatia	25F	0.38-0.5			
Soya bean	Hungary	25F	0.38-0.5			14
Soya bean	Poland	25F	0.38-0.5			14-21
Soya bean	Slovakia	25F	0.5-0.63			
Sugar beet	Poland	25F	0.75-1.0			
Sunflower	Belarus	25F, 25% FS	0.3			
Sunflower	Bulgaria	25F, 25% FS	0.38-0.5			14
Sunflower	Czech Republic	25F	0.5			10-14
Sunflower	Croatia	25F	0.38-0.5			
Sunflower	Hungary	25F	0.38-0.5			14
Sunflower	Kazakhstan	25F	0.3			10-14
Sunflower	Poland	25F	0.5			
Sunflower	Romania	25F	0.38			7
Sunflower	Slovakia	25F	0.5			
Sunflower	Spain	25F	0.5			
Sunflower	Turkey	25F	0.5			
Tomato	Bulgaria	25F, 25% FS	0.31			14
Tomato (processing)	Czech Republic	25F	0.38			21
Tomato	Slovakia	25F	0.38			
Tomato	Turkey	25F	0.31			

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of the residue trials are shown in Tables 28-32 and are reviewed in order of the Codex Alimentarius Classification of Foods and Feeds.

Table 28 *Potato.* France, Germany, Netherlands, Norway, Sweden, UK.
Table 29 *Cotton seed.* Spain, USA.
Table 30 *Linseed.* Czech Republic.
Table 31 *Rape seed.* Czech Republic, Germany, Hungary, Norway, UK.
Table 32 *Sunflower seed.* Hungary.

Where residues were not detected the results are reported as below the limit of quantification (LOQ), e.g. <0.05 mg/kg. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures. Although trials included results for untreated controls these are not reported in the Tables unless they were greater than the LOQ. The prefix "c" indicates samples from control plots. Where possible residues are reported uncorrected for analytical recoveries. It should be noted that unless stated otherwise concurrent recoveries were acceptable and any corrections were small.

Except for the trials on flax and linseed in Hungary and Czechoslovakia, trials were fully reported.

In supervised trials on potatoes in France, Germany, Norway, The Netherlands, Sweden and the UK the plots were 10 - 3240 m^2. Dimethipin was sprayed on the leaves using knapsack sprayers, hand-held boom sprayers and tractor-mounted boom sprayers. The period of frozen storage before analysis was 247-381 days for the trials in Germany and Norway.

Table 28. Residues of dimethipin in potatoes after foliar applications of various dimethipin formulations. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used for the estimation of maximum residue levels.

Location, year, variety	Form	Application			PHI (days)	Dimethipin (mg/kg)	Reference
		kg ai/ha	kg ai/hl	No.			
Lillers, France (1984) Bintje	25F	0.75	0.15	1	34	Peel 0.03, 0.04, 0.02, <0.01	N6.2.3.13
						Peeled tuber <0.01 (4)	
						Whole tuber <0.01 (4)	
St Remy, France (1984) Bintje	25F	0.75	0.13	1	21	≤0.1 (different analytical laboratory, LOQ 0.1, whole tubers analysed)	N6.2.3.13
Dom Loup, France (1984) Sirtema	25F	0.75	0.15	2	25	Peel 0.02 (3), 0.01	N6.2.3.13
						Peeled tuber <0.01 (4)	
						Whole tuber <0.01 (4)	
					18	Peel 0.015, 0.01, 0.02, <0.01	
						Peeled tuber <0.01 (4)	
						Whole tuber ≤0.01 (4)	
					14	Peel 0.03	
						Peeled tuber <0.01	
						Whole tuber <0.01	
					10	Peel <0.01	
						Peeled tuber <0.01	
						Whole tuber <0.01	
Pocany, France (1984) Bintje	25F	0.75	0.15	2	32	Peel <0.01 (6), 0.01 (2)	N6.2.3.13
						Peeled tuber <0.01 (8)	
						Whole tuber <0.01 (8)	
Brillit, Germany (1986) Roxy	25F	0.75	0.19	1	14	≤0.02	N6.2.3.24
Kalen Born, Germany (1986) Grata	25F	0.75	0.19	1	14	≤0.02	N6.2.3.24
Nordheim, Germany (1986) Ulla	25F	0.75	0.19	1	14	≤0.02	N6.2.3.24
Winzerhavsen, Germany (1986) Granola	25F	0.75	0.19	1	14	≤0.02	N6.2.3.24
Otter Weier, Germany (1986) Sieglinde	25F	0.75	0.19	1	15	≤0.02	N6.2.3.24
Mattenkofen, Germany (1986) Juliver	25F	0.75	0.19	1	14	≤0.02	N6.2.3.24
Dinteloord, Netherlands (1983) Bintje	25F	0.5	0.08	1	9-40[1]	≤0.05	N6.2.3.14
Luttelgeest, Netherlands (1983) Bintje	25F	0.5	0.08	1	9-40[1]	≤0.05	N6.2.3.14
Ottersum, Netherlands (1983) Bintje	25F	0.5	0.08	1	9-40[1]	≤0.05	N6.2.3.14
Ottersum, Netherlands (1984) Bintje	25F	0.63	0.1	1	[4]	≤0.05 (4)	N6.2.3.23
Rilland, Netherlands (1984) Bintje	25F	0.63	0.1	1	[4]	≤0.05 (4)	N6.2.3.23
Tollebeek, Netherlands (1984) Bintje	25F	0.63	0.1	1	[4]	≤0.05 (4)	N6.2.3.23
Mohn Kirkenaer, Norway (1985) Beate	25F	0.5	0.1	1	23	<0.05	N6.2.1.21
Mohn Kirkenaer, Norway (1985) Beate	25F	0.75	0.15	1	23	<0.05	N6.2.1.21
Mohn Kirkenaer, Norway (1985) Beate	25F	1.0	0.2	1	23	<0.05	N6.2.1.21
Gjesasen, Norway (1985) Ostara	25F	0.5	0.1	1	34	<0.05	N6.2.1.21
Gjesasen, Norway (1985) Ostara	25F	0.75	0.15	1	34	<0.05	N6.2.1.21

Location, year, variety	Form	Application			PHI	Dimethipin	Reference
		kg ai/ha	kg ai/hl	No.	(days)	(mg/kg)	
Gjesasen, Norway (1985) Ostara	25F	1.0	0.2	1	34	<0.05	N6.2.1.21
Skännige, Sweden (1983) Magnum bonum	25F	1.5	0.3	1	22-52[2]	<0.003	N6.2.3.15
Skepparslöv, Sweden (1983) Dianella	25F	1.5		1	22-52[2]	0.009	N6.2.3.15
Ugerup, Sweden (1983) Dianella	25F	1.5	0.38	1	22-52[2]	<0.003	N6.2.3.15
Ultuna, Sweden (1983) Bintje	25F	1.5	0.3	1	22-52[2]	<0.003[3]	N6.2.3.15
Röbäcksdalen, Sweden (1983) Sabina	25F	1.5	0.38	1	22-52[2]	0.010	N6.2.3.15
Skännige, Sweden (1983)	25F	1.5		1	22-52[2]	<0.003	N6.2.3.15
Pershore, UK (1982) Desiree	25F	0.5		1	21-28[4]	<u>≤0.005</u> (5)	N6.2.3.12
Cutsdean, UK (1982) Maris piper	25F	0.5		1	21-28[4]	<u>≤0.005</u> (5)	N6.2.3.12
Northleach, UK (1982) Desiree	25F	0.5		1	21-28[4]	<u>≤0.005</u> (5)	N6.2.3.12
Northleach, UK (1982) Desiree	25F	1.0		1	21-28[4]	<u>≤0.005</u> (5)	N6.2.3.12

[1]when potato haulm had dried off, 9-40 days after application
[2]when potato haulm had dried off, 22-52 days after application
[3]residues in soil were 0.16 mg/kg
[4]when the potato haulm had died down.
Peel constituted 8-19% of total weight for the Dom Loup trial, 14-19% for the Lillers trial and 14-18% for the Pocany trial
Recoveries: 98, 91 and 80% at 0.0198, 0.0988 and 0.988 mg/kg respectively N6.2.3.24; 80, 93 and 85% at 0.051, 0.25 and 1.01 mg/kg respectively N6.2.3.21; 82, 76 and 84% at 0.051, 0.51 and 1.03 mg/kg respectively N6.2.3.14; 82, 87 and 86% at 0.050, 0.50 and 1.01 mg/kg respectively N6.2.3.23; 112, 91, 82, 81 and 79% at 0.0052, 0.010, 0.103, 0.52 and 1.03 mg/kg respectively N6.2.3.12

Supervised trials were reported on cotton in Spain and the USA. In the USA trials dimethipin was sprayed using CO_2 (or compressed air) backpack or tractor-mounted boom sprayers and from aircraft. The first application was made with at least 70% bolls open and the second 5 days later. Plot sizes for the ground applications ranged from 8 rows × 15 m to 4 rows × 91 m and for aerial application were 0.25 and 0.8 ha. Samples were stored frozen for 49-191 days. The plot sizes for the Spanish trials ranged from 4-50 ha and were sprayed from the air; samples were stored frozen for 125-134 days.

Table 29. Residues of dimethipin in cotton seed after foliar applications of various dimethipin formulations. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP used to estimate maximum residue levels.

Location, year, variety	Form	Application			PHI	Dimethipin	Reference
		kg ai/ha	kg ai/hl	No.	(days)	(mg/kg)	
Diaz Martinez, Spain (1986) Coker 304	25F ✈	0.31	0.31	1	14	<u>0.03</u>, 0.02	N6.2.1.3
Las Baracas, Spain (1986)	25F ✈	0.31	0.31	1	7	<u>0.07</u>, 0.04	N6.2.1.3
Laura Abad El Ruidero, Spain (1986) Copa	25F ✈	0.31	0.31	1	5	<u>0.07</u>, 0.04, <0.02	N6.2.1.3
Sotillo Gallego, Spain (1986)	25F ✈	0.31	0.31	1	14	<u>0.02</u>, 0.02, <0.02	N6.2.1.3
Helm, California (1993) GC 510	5F	0.35 0.26	0.34 0.25	2	7	0.2, <u>0.2</u>	RP-92026
Donna, Texas (1993) Delta Pine 50	5F	0.35 0.26	0.37 0.28	2	7	<u>0.2</u>, 0.1	RP-92026
Hawkinsville, Georgia (1993) Stoneville 825	5F	0.35 0.26	0.38 0.28	2	7	<0.1, <u>0.1</u>	RP-92026

Location, year, variety	Form	Application			PHI	Dimethipin	Reference
		kg ai/ha	kg ai/hl	No.	(days)	(mg/kg)	
Senatobia, Mississippi (1993) DPL-50	5F	0.35 0.26	0.37 0.28	2	7	0.2, 0.3	RP-92026
Proctor, Arizona (1992) Stoneville 453	5F	0.35 0.26	0.19 0.14	2	7	<0.1, ≤0.1	RP-91034
Proctor, Arizona (1992) Stoneville 453	5F	0.35 0.26	0.19 0.14	2	7	≤0.1, <0.1	RP-91034
Senatobia, Mississippi (1992) DPL-50	5F	0.35 0.26	0.19 0.14	2	7	0.2, 0.12	RP-91034
Senatobia, Mississippi (1992) DPL-50	5F ✈	0.35 0.26	0.75 0.56	2	7	0.1, 0.1	RP-91034
Charleston, Mississippi (1992) DPL-50	5F	0.35 0.26	0.19 0.14	2	7	0.1, 0.2	RP-91034
Toone, Tennesse (1992) DPL-50	5F	0.35 0.26	0.19 0.14	2	7	0.7, 0.6, 0.7, 0.7	RP-91034
Raymondville, Texas (1992) DPL-5690	5F	0.35 0.26		2	7	0.1, 0.2	RP-91034
Raymondville, Texas (1992) DPL-5690	5F ✈	0.35 0.26		2	7	<0.1, ≤0.1	RP-91034
Donna, Texas (1992) Stoneville 453	5F	0.35 0.26	0.25 0.19	2	7	<0.1, ≤0.1	RP-91034
Meigs, Georgia (1992) DPL-90	5F	0.35 0.26	0.19 0.14	2	7	<0.1, 0.1	RP-91034
Opelousas, Louisiana (1992) DPL-50	5F	0.35 0.26	0.38 0.28	2	7	0.2, 0.2	RP-91034

Loamy sand (pH 8.7), sandy loam (pH 7.9), sand (pH 7.3-7.9), silt loam (pH 6.1), loam (pH 6.0), loam (pH 5.9), silt loam (pH 6.9), silt loam (pH 5.3), silt loam (pH 6.6), silt loam (pH 7.6), silt loam (pH 8.3), sandy loam (pH 8.4), loamy sand (pH 6.6), loam (pH 4.4)
Recoveries: 80, 95% at 0.1 mg/kg, 90, 76% at 0.5 mg/kg, LOQ 0.1 mg/kg RP-92026; 95, 77, 79, 77, 84, 78% at 0.1 mg/kg, 92, 80, 78, 75, 90, 78% at 0.5 mg/kg, LOQ 0.1 mg/kg RP-91034; 118 and 80% at 0.071 mg/kg, LOQ 0.02 mg/kg N6.2.1.3
✈ aerial application

Table 30. Residues of dimethipin in linseed after foliar applications of various dimethipin formulations. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Location, year, variety	Form	Application			PHI	Dimethipin (mg/kg)		Reference
		kg ai/ha	kg ai/hl	No.	(days)	Seed	Straw	
Czech Republic	-	-		-	-	<0.1	7.0	N6.2.7.3/4
Czech Republic	-	-		-	-	0.1	10	N6.2.7.3/4
Czech Republic	-	-		-	-	<0.1	6.3	N6.2.7.3/4
Czech Republic	-	-		-	-	<0.1	8.2	N6.2.7.3/4
Czech Republic	-	-		-	-	<0.1	0.4	N6.2.7.3/4
Czech Republic	-	-		-	-	<0.1	<0.1, <0.1	N6.2.7.3/4
Czech Republic	-	-		-	-	<0.1	<0.1, <0.1	N6.2.7.3/4
Czech Republic	-	-		-	-	<0.1		N6.2.7.3
Rýmařov, Czech Republic (1982)	WP	1.3			8	<0.1	25	N6.2.7.1/2
Kežmarok, Czech Republic (1982)	WP	1.0			11	<0.1	13	N6.2.7.1/2
Kežmarok, Czech Republic (1982)	WP	1.5			11	<0.1	<0.1	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.0			11	<0.1	4.8	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.0			14	<0.1	8.9	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.0			17	<0.1	11	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.0			20	<0.1	9.1	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.0			7	0.9	10 c0.3	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.0			10	0.2	7.3	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	0.5			14	≤0.1	4.5	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	0.5			14	≤0.1	4.0	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.0			14	0.1	12	N6.2.7.1/2

Location, year, variety	Form	Application			PHI (days)	Dimethipin (mg/kg)		Reference
		kg ai/ha	kg ai/hl	No.		Seed	Straw	
Všúptl, Czech Republic (1982)	WP	1.0			14	<0.1	18	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.5			14	0.1	20	N6.2.7.1/2
Všúptl, Czech Republic (1982)	WP	1.5			14	0.1	18	N6.2.7.1/2

Recoveries: 80, 75 and 78% at 0.52, 2.6 and 5.2 mg/kg respectively N6.2.7.1, LOQ 0.1 mg/kg; 110, 94 and 95% at 0.10, 0.52 and 1.04 mg/kg respectively N6.2.7.2, LOQ 0.1 mg/kg; 85, 83 and 88% at 0.098, 0.492 and 0.985 mg/kg respectively N6.2.7.3, LOQ 0.1 mg/kg; 86, 104 and 85% at 0.197, 0.985 and 9.85 mg/kg respectively N6.2.7.4, LOQ 0.4 mg/kg.

Supervised trials were reported on rape seed from the Czech Republic, Germany, Hungary, Norway and the UK. Dimethipin was applied using knapsack sprayers and tractor-mounted boom sprayers. Plot sizes ranged from 7.5 m^2 to 5 ha. Samples were stored frozen for 14 to 405 days.

Table 31. Residues of dimethipin in rape seed after foliar applications of various dimethipin formulations. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Location (year) variety	Form	Application			PHI (days)	Dimethipin (mg/kg)	Reference
		kg ai/ha	kg ai/hl	N			
Moravia, Czech Republic (1983)	50W	0.25	0.063	1	7	<0.1	N6.2.13.2
					11	<0.1	N6.2.13.2
					14	<0.1	N6.2.13.2
Moravia, Czech Republic (1983)	50W	0.5	0.13	1	7	<0.1	N6.2.13.2
					11	<u><0.1</u>	N6.2.13.2
					14	<0.1	N6.2.13.2
Moravia, Czech Republic (1983)	50W	0.75	0.19	1	7	<0.1	N6.2.13.2
					11	<0.1	N6.2.13.2
					14	<0.1	N6.2.13.2
Moravia, Czech Republic (1983) Jet neuf	5F	0.6	0.15	1	7	<u><0.1</u>	N6.2.13.2
Moravia, Czech Republic (1983) Jet neuf	25F	0.38	0.094	1	7	<u><0.1</u>	N6.2.13.2
Straubing, Germany (1985) Jet neuf	25F	0.25	0.063	1	16	<0.05, <0.05	N6.2.13.4
Straubing, Germany (1985) Jet neuf	25F	0.5	0.13	1	16	<0.05, <u><0.05</u>	N6.2.13.4
Matting, Germany (1986) Belinda	25F	0.5	0.13	1	0 3 6 10	1.2 0.2 <0.1 <u><0.1</u>	N6.2.13.7
Gutrohlstorp, Germany (1986) Jet neuf	25F	0.5		1	0 pod 3 pod 7 pod 10 pod 11 seed	4.6 c0.3 0.5 0.3 0.3 <u><0.1</u>	N6.2.13.7
Gutrohlstorp, Germany (1986) Miranda	25F	0.5		1	0 pod 3 pod 7 pod 10 pod 11 seed	4.8 0.5 0.3 0.3 <u><0.1</u>	N6.2.13.7
Lichtenau, Germany (1986) Loras	25F	0.5		1	3 7 10	0.3 <0.1 <0.1, <u>0.1</u>	N6.2.13.7

Location (year) variety	Form	Application			PHI (days)	Dimethipin (mg/kg)	Reference
		kg ai/ha	kg ai/hl	N			
Ausserhienthal, Germany (1986) Jet neuf	25F	0.5		1	0 pod 0 3 6 10	12 0.9 0.3 <0.1 ≤0.1	N6.2.13.7
Fejer County, Hungary (1998)	25EC	0.45	0.19	1	23	≤0.05 (3)	98 UNI AB 01 02
Østfold, Norway (1985)	25F	0.25	0.05	1	13	<0.05	N6.2.13.6
Østfold, Norway (1985)	25F	0.5	0.1	1	13	<0.05	N6.2.13.6
Cirencester, UK (1983) Jet neuf	25F	0.25	0.071	1	8	0.033[1]	N6.0.3
Pershore, UK (1983) Jet neuf	25F	0.25	0.071	1	7		N6.0.3
Stow, UK (1983) Jet neuf	25F	0.25	0.071	1	15		N6.0.3
Stow, UK (1983) Jet neuf	25F	0.25	0.071	1	15		N6.0.3
Pershore, UK (1983) Jet neuf	25F	0.5	0.14	1	7	0.025[2]	N6.0.3
Stow, UK (1983) Jet neuf	25F	0.5	0.14	1	15		N6.0.3
Stow, UK (1983) Jet neuf	25F	0.5	0.14	1	15		N6.0.3
Pershore, UK (1984) Jet neuf	25F	0.5	0.31	1	21	0.04[3] c0.015	N6.0.3
Pershore, UK (1985) Bien venu	25F	0.63	0.23	1	20	<0.05[4] (4)	N6.2.13.4
Tenbury, UK (1985) Bien venu	25F	0.63	0.23	1	25		N6.2.13.4
Essex, UK (1986) Mikado	25F	0.5	0.13	1	22	<0.05 (oil)	N6.2.13.5
Essex, UK (1986) Mikado	25F	1.0	0.25	1	22	<0.05 (oil)	N6.2.13.5
Essex, UK (1986) Bienvenu	25F	0.5	0.13	1	19	<0.05 (oil)	N6.2.13.5
Essex, UK (1986) Bienvenu	25F	1.0	0.25	1	19	<0.05 (oil)	N6.2.13.5
Essex, UK (1986) Mikado	25F	0.5	0.13	1	11	<0.05 (oil)	N6.2.13.5
Essex, UK (1986) Mikado	25F	1.0	0.25	1	11	<0.05 (oil)	N6.2.13.5
Essex, UK (1986) Rafal	25F	0.5	0.13	1	16	<0.05 (oil)	N6.2.13.5
Essex, UK (1986) Rafal	25F	1.0	0.25	1	16	0.06 (oil) (<0.05)	N6.2.13.5

[1]average of the 4 trials carried out at 0.25 kg ai/ha in UK in 1983
[2]average of the 3 trials carried out at 0.5 kg ai/ha in UK in 1983
[3]average of 2 replicates
[4] average of 2 trials, 8 replicates, carried out at 0.625 kg ai/ha in UK in 1985
Recoveries: 93, 94, 72 and 78% at 0.05, 0.1, 0.2 and 0.5 mg/kg respectively 98 UNI AB 01 02; 87, 97 and 97% at 0.051, 0.25 and 1.01 mg/kg respectively N6.2.13.5; 106, 88 and 98% at 0.0988, 0.25 and 0.988 mg/kg respectively N6.2.13.7; 82, 70 and 93% at 0.051, 0.26 and 1.01 mg/kg respectively N6.2.13.6; 85, 84, 101 and 108% at 0.975, 0.244, 0.098 and 0.049 mg/kg respectively for oilseed, 83, 95 and 80% at 0.982, 0.246 and 0.049 mg/kg respectively for oil, 94, 104 and 76% at 0.975, 0.244 and 0.049 mg/kg respectively for cake N6.2.13.4; 105, 99 and 105% at 0.098, 0.492 and 0.985 mg/kg respectively N6.2.13.2

Supervised trials were reported on sunflowers from Hungary. Foliar application of dimethipin was by aircraft to plots that ranged in size from 5 to 249 ha.

Table 32. Residues of dimethipin in sunflowers after foliar applications of various dimethipin formulations. Analyses of replicate field samples from one plot or from duplicate plots in one trial are shown separately. Double-underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Location, year, variety	Form	Application			PHI	Dimethipin	Recoveries	Ref.
		kg ai/ha	kg ai/hl	No.	(days)	(mg/kg) [1]		
Hunyadi, Hungary (1984)	25F ✈	0.38	0.75	1	20	0.4, 0.55, 0.35, 0.4, 0.7, 0.35, 0.2	71 ± 11%	N6.2.5.5
Dunaföldvár, Hungary (1984)	25F ✈	0.38	0.75	1	22	≤0.1 (7)	75 ± 8%	N6.2.5.5
Hajdu, Hungary (1986) Iregi	25F ✈	0.38	0.63	1	10	0.11, 0.08, 0.30, 0.25, 0.21, 0.11, 0.14	88%	N6.2.5.8
Hajdu, Hungary (1986) Iregi	25F ✈	0.38	0.63	1	10	0.02, 0.03, 0.03, 0.09, 0.04, 0.03, 0.01	0.01-0.2 mg/kg, 80-95%	N6.2.5.8
Baranya, Hungary (1986) Ihnk-81	25F ✈	0.38	0.75	1	10	≤0.01 (5)	64 ± 6% at 0.3 mg/kg, 78 ± 5% at 0.5 mg/kg	N6.2.5.8
Baranya, Hungary (1986) Nsh-26	25F ✈	0.38	0.75	1	10	≤0.01 (5)	64 ± 6% at 0.3 mg/kg, 78 ± 5% at 0.5 mg/kg	N6.2.5.8
Jászalsózentgyörgy, Hungary (1986) Iregi	25F ✈	0.38	0.75	1	32	0.18, <0.05, 0.26, 0.11, 0.17	94 ± 4% at 0.1 mg/kg	N6.2.5.8
Jászalsózentgyörgy, Hungary (1986) Nsh-26	25F ✈	0.38	0.75	1	32	0.77, 0.25, 0.71, 0.43, 0.58	94 ± 4% at 0.1 mg/kg	N6.2.5.8
Balatonfökajár, Hungary (1986) Nsh-26	25F ✈	0.38	0.75	1	13	≤0.01 (7)	68 ± 3% at 0.1 mg/kg	N6.2.5.8
Balatonfökajár, Hungary (1986) Nsh-26	25F ✈	0.38	0.75	1	13	≤0.01 (7)	68 ± 3% at 0.1 mg/kg	N6.2.5.8
Tolna, Hungary (1986) Topflor	25F ✈	0.25	0.42	1	9	0.06, 0.15, 0.05, 0.22, 0.08	78 ± 8%	N6.2.5.8
Tolna, Hungary (1986) Topflor	25F ✈	0.38	0.63	1	9	0.10, 0.08, 0.25, 0.38, 0.35	78 ± 8%	N6.2.5.8

✈ aerial application
[1] corrected for average analytical recovery

Animal feeding studies

Lactating cows. Groups of 3 lactating Holstein dairy cattle (487-737 kg bw) were dosed with dimethipin in the diet for 28 days (Singh and Eckert, 1996). The average feed consumption before commencement of dosing was 14.5 kg per day. Doses, calculated using the average consumption figure and administered in gelatine capsules by balling gun after the morning milking, were nominally equivalent to 5, 15 or 50 ppm in the feed (72.5, 217.5 or 725 mg ai per capsule). Daily composite milk samples were collected for each cow, with proportionate quantities of morning and evening milk mixed. Cows from each group were slaughtered twenty-four hours after receiving the final dose. Samples of muscle, liver and kidney collected at slaughter and milk were analysed for dimethipin. Kidney samples were also analysed for the metabolite ethane-1,2-disulfonic acid (Hughes and Patzer, 1996).

Residues in milk from the highest dose group were <0.01 mg/kg in all samples analysed, from days 0, 7, 14, 21 and 28 of dosing. Residues in muscle, liver and kidney in the highest group were also <0.01 mg/kg. It was therefore decided not to analyse milk and tissues from the other dose groups.

Residues of ethane-1,2-disulfonic acid were <0.01, <0.01 and <0.01 mg/kg in the 5 ppm, 0.22, 0.27 and 0.38 mg/kg in the 15 ppm and 0.32, 0.66 and 0.44 mg/kg in the 50 ppm dose groups.

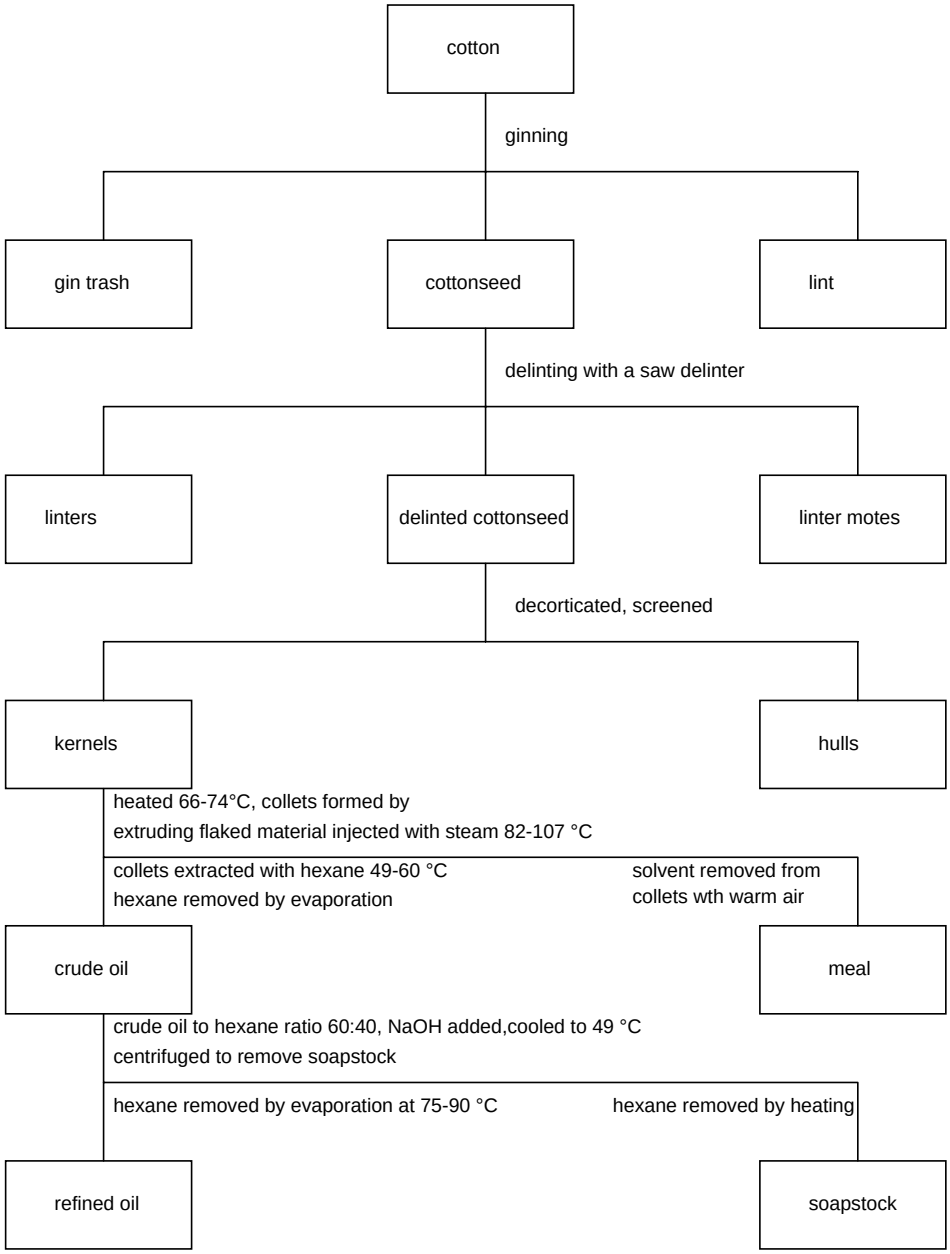
FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Processing studies on cotton (Korpalski, 1993d) were provided to the Meeting.

Dimethipin was applied to cotton as two sprays 5 days apart at 0.68 and 0.51 kg ai/ha with harvest 7 days after the last application. The trials were in Texas and Mississippi with replicate samples taken from the two sites. The cotton seed was ginned to separate the seed cotton into seed and lint as well as ginning trash. Ginned seed was passed through a saw delinter to remove excess lint before hulling. The delinted seed was mechanically decorticated and screened to separate the majority of the hull material from the kernel and samples of hulls were collected. The kernel material was heated (66-74°C), flaked, and expanded into collets by extruding flaked material injected with steam (82-107°C). The collets were then extracted three times with hexane at 49-60°C. Solvent was removed from the spent collets with warm forced air. Meal samples were collected from the spent collets. Crude oil samples were obtained by evaporation of the hexane. Refined oil was obtained after adjusting the crude oil and hexane mixture to the proper ratio, and the miscella refined by distillation. The hexane was evaporated from the original miscella to bring the crude oil to hexane ratio to 60:40. NaOH was added with vigorous mixing and the mixture cooled to 49°C without stirring. Refined oil was separated from the soapstock by centrifugation and recovered from the miscella by evaporation of the hexane at 75-90°C. The soapstock was heated to remove residual hexane.

Figure 3. Cotton processing (Korpalski, 1993d).



Processing factors were all less than one, indicating that dimethipin is not concentrated in processed cotton commodities.

Table 33. Residues of dimethipin in cotton seed and processing fractions (Korpalski, 1993d).

Sample	Ginned seed	Meal	Hulls	Soapstock	Crude oil	Refined oil
1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2	0.50	0.12	0.54	<0.1	<0.1	<0.1
3	0.46	0.11	0.44	<0.1	<0.1	<0.1
4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
5	0.61	<0.1	0.42	<0.1	<0.1	<0.1
6	0.68	<0.1	0.40	<0.1	<0.1	<0.1
Average	0.56	0.11	0.45	<0.1	<0.1	<0.1

Sample	Ginned seed	Meal	Hulls	Soapstock	Crude oil	Refined oil
Processing factor	-	0.2	0.8	<0.2	<0.2	<0.2

Recoveries from samples fortified with dimethipin at 0.1 and 0.5 mg/kg were 82-86, 88-94, 94-100, 100, 106-115 and 88-120% for seed, meal, hulls, soapstock, crude oil and refined oil respectively.
Residues were corrected for analytical recoveries where recoveries were less than 100%

Residues in the edible portions of food commodities

No additional information.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Dimethipin was determined in foods prepared for consumption in the 1997, 1998 and 1999 USA Food and Drug Administration Pesticide Program Residue Monitoring Total Diet Studies. It was reported that the incidence of detections was less than 2%.

NATIONAL MAXIMUM RESIDUE LIMITS

The residue is defined as dimethipin in Australia, the countries of the EU and the USA, the only countries for which information was provided. The Meeting was made aware that the following national MRLs had been established.

COUNTRY	COMMODITY	MRL (mg/kg)
Australia	Cotton seed	0.5
	Cotton seed oil, crude ; Cotton seed oil, refined	*0.1
	Milks, meat (mammalian), edible offal (mammalian), poultry meat, poultry edible offal	*0.01
	Eggs	*0.02
Japan	Sunflower seed	0.5
	Cotton seed	0.5
	Rape seed	0.1
	Other oil seeds	0.2
	Potato	0.05
Taiwan	Rice	0.5
USA	Cotton, undelinted seed	0.5
	Cotton, hulls	0.7
	Cattle meat by-products including offal, cattle fat, cattle meat, goat meat by-products including offal, goat fat, goat meat, horse meat by-products including offal, horse fat, horse meat, sheep meat by-products including offal, sheep fat, sheep meat, hog meat by-products including offal, hog fat, hog meat	0.02

APPRAISAL

Dimethipin is a plant growth regulator used mainly as a defoliant and harvest aid to accelerate desiccation of plant material. Dimethipin was first evaluated in 1985. It was listed by the 1997 CCPR (ALINORM 95/24 A) for periodic re-evaluation and was scheduled for consideration by the FAO Panel of the 2001 JMPR. The Meeting received information on its physicochemical properties, metabolism, environmental fate, analytical methods, stability in storage, registered uses, and residues in supervised trials and processing studies.

The Meeting was provided with studies in which dimethipin radiolabelled at the 2 and 3 positions of the dithiin ring was used in order to follow its distribution and metabolism in animals and plants. The following abbreviations are used for the metabolites discussed below:

red-DMP = 2,3-dimethyl-1,4-dithiane 1,1,4,4-tetraoxide
acetyl dithiane = 2-acetyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-S-cys = *S*-(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian 2-yl)-L-cysteine

glu-cys-S-DMP = *S*-(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian-2-yl)-L-cysteinyl-γ-glutamic acid
DMP-S-acetate = 2-[(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian-2-yl)thio]acetic acid
DMP-GSH = *S*-(2,3-dimethyl-1,1,4,4-tetraoxo-1,4-dithian-2-yl)-L-glutathione
DMP-SH = 2-mercapto-2,3-dimethyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-S-methyl = 2,3-dimethyl-2-methylthio-1,4-dithiane 1,1,4,4-tetraoxide
DMP-tert-OH = 2-hydroxy-2,3-dimethyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-prim-OH = 2-hydroxymethyl-3-methyl-1,4-dithiane 1,1,4,4-tetraoxide
DMP-SO-methyl = 2,3-dimethyl-2-(methylsulfinyl)-1,4-dithiane 1,1,4,4-tetraoxide
hydroxy-DMP = 2,3-dihydro-5-hydroxymethyl-6-methyl-1,4-dithiine 1,1,4,4-tetraoxide
demethyl-hydroxy-DMP = 2,3-dihydro-5-hydroxymethyl-1,4-dithiine 1,1,4,4-tetraoxide
methylene-DMP = 2-methyl-3-methylene-1,4-dithiane 1,1,4,4-tetraoxide
demethyl-DMP = 1,4-dithiane 1,1,4,4-tetraoxide
N-acetyl-cys-DMP = *N*-acetylcysteinyl conjugate
Cys-gly-DMP = cysteinyglycine conjugate
HESB = 3-(2-hydroxyethylsulfonyl)butan-2-one

Metabolism

Animals

After oral administration of [^{14}C]dimethipin to rats, unchanged dimethipin, *N*-acetylcysteine conjugate, red-DMP, a cysteinylglycine conjugate and a polar fraction were identified in urine.

Two female goats (one lactating) were given [^{14}C]dimethipin orally at a dose of 20 mg/kg bw, equivalent to a nominal feeding rate of 500 ppm, for 3 consecutive days. The metabolites identified in urine were DMP-*prim*-OH, DMP-*tert*-OH, hydroxy-DMP and 2,3-dihydro-5-hydroxymethyl-1,4-dithiine-1,1,4,4-tetraoxide. Most of the residue in urine was not characterized, but was thought to consist of polar conjugates. Bile extracts contained dimethipin and seven metabolites, including the ring-opened product 3-(2-hydroxyethylsulfonyl)butan-2-one and dimethipin L-cysteine and *N*-acetyl cysteine conjugates. The concentrations of radiolabelled residues in edible tissues were highest in liver and kidney and much lower in muscle and fat. Intact dimethipin accounted for 2% of the TRR in liver and kidney. The metabolites 3-(2-hydroxyethylsulfonyl)butan-2-one and DMP-*tert*-OH were identified in liver and kidney, while β-glucuronidase hydrolysis indicated the presence of a glucuronide conjugate. The high concentrations of polar and bound residues in liver and kidney indicated extensive conjugation.

Lactating goats were dosed orally with radiolabelled dimethipin once daily for 5 consecutive days, at doses of 0.15 and 50 mg/kg bw [^{14}C]dimethipin and 50 mg/kg bw [$^{13/14}$C]dimethipin, equivalent to feeding at 3, 1010 and 1290 ppm in the diet. Radiolabel in excreta collected up to 22 h after the last dose (slaughter) accounted for 95% of the administered dose, while 0.1–0.2% of the dose was eliminated in milk. The only metabolite detected in milk in significant quantities was DMP-S-cys. The association of most of the ^{14}C in liver with protein suggests that the metabolites in liver were protein conjugates. In kidney, 1,2-ethane disulfonic acid was the only metabolite found in the goat given the low dose, while 1,2-ethane disulfonic acid was the only free metabolite in the goat given the high dose, with conjugated products that were released on acid hydrolysis. The main metabolite in muscle was red-DMP, which was present at approximately 30% of the TRR; no other metabolite accounted for more than 8% of the TRR. The concentrations of radiolabel in fat were too low to permit characterization of metabolites.

The main route of transformation of dimethipin is a Michael addition of a sulfhydryl to the double bond. Addition of glutathione yields DMP-S-cys, via the mercapturic acid pathway, which is eliminated in urine and milk. This conjugate was not observed in edible tissues. If the addition is made to a protein sulfhydryl, the result is protein-bound reduced dimethipin, which was the only residue observed in liver and muscle and approximately half that observed in kidney. Hydrolysis of the bound residue and subsequent rearrangement gave three products: red-DMP, acetyl dithiane and

1,2-ethane disulfonic acid. The latter was the only metabolite observed in kidney in the goat given the lower radiolabelled dose but represented about one-third of the radiolabelled residues in kidney in the goat given the higher dose.

White Leghorn pullets (1.3–2.4 kg bw) were given [^{14}C]dimethipin at nominal levels equivalent to 1 (0.06 mg/kg bw), 6 (0.34 mg/kg bw) and 30 (1.7 mg/kg bw) ppm in the feed. The concentration of radiolabelled residues in eggs plateaued 10 days after the start of dosing and reached maxima of 11, 41 and 198 μg/kg at the three doses, respectively. The TRR in eggs decreased to below the limit of detection of 6 μg/kg after 5 days' withdrawal from dosing at 1 ppm. After 11 days' withdrawal, the concentration of radiolabel in eggs was below the limit of detection for the group given 5 ppm and near the limit of detection for that given 30 ppm. Of the edible tissues, liver and kidney had the highest TRR and fat had the lowest. The concentration of dimethipin residues in liver was < 0.01 mg/kg at all doses.

The material balance after oral dosing of white Leghorn laying hens with [^{14}C]dimethipin for 5 days at 15.8 or 152 mg/bird (equivalent to feeding at 203 or 2770 ppm in the diet) was > 95%. Most of the radiolabel was eliminated in excreta (90–91%) within 24 h of the last treatment, and 5.1–5.6% of the amount given was recovered in edible tissues and eggs. The concentrations of radiolabelled residues were greatest in liver followed by kidney, muscle, eggs and fat. The main metabolite identified in hen liver was DMP-S-cys, and glu-cys-*S*-DMP was the main metabolite detected in other tissues. Other metabolites identified in liver included DMP-*prim*-OH, DMP-*tert*-OH, hydroxy-DMP, DMP-SH, DMP-*S*-methyl, DMP-SO-methyl and DMP-*S*-acetate.

It has been proposed that addition of glutathione to dimethipin (catalysed by glutathione *S*-transferase or spontaneous) gives DMP-GSH, which can be transported out of the cells in which it is formed and the glutathione moiety degraded by endogenous peptidases to produce glu-cys-*S*-DMP and DMP-*S*-cys. Oxidative transamination and loss of pyruvic acid or decarboxylation can give DMP-SH and DMP-*S*-acetate. Methylation of DMP-SH in the presence of *S*-adenosine-methionine would produce DMP-*S*-methyl, which could be further oxidized to DMP-SO-methyl. Another product that could be formed is the *N*-acetylcysteinyl conjugate, which would be expected to be retained by the strong anion-exchange columns used. An unidentified metabolite found in several extracts had chromatographic behaviour similar to that of products obtained by reacting dimethipin with *N*-acetylcysteine. Reduction and hydroxylation reactions are also possible, as evidenced by the presence of red-DMP and the hydroxylated metabolites DMP-*tert*-OH and DMP-*prim*-OH.

The data on metabolism in rats, goats and hens show that dimethipin is extensively metabolized, almost no residual parent compound being retained in any of these species. The main residues in animals form as the result of glutathione, amino acid and protein conjugation and subsequent degradation. Minor metabolites are formed as a result of hydrolytic hydroxylation and/or oxidation.

Plants

Studies on metabolism in cotton, sunflower, potato, grape and rice were made available to the Meeting.

When mature indoor-grown cotton plants, each with one to four bolls open, were treated with a single application of [^{14}C]dimethipin at 1.12 kg ai/ha, the extractable residue in seeds with linters accounted for 94% of the TRR, of which 94% was identified as dimethipin. In acid-delinted seeds, 18% of the TRR was extractable with methanol, of which 38% was dimethipin.

Dimethipin was the major component (72%) of the residue in foliage of cotton plants treated with [^{13}C/^{14}C]dimethipin at 0.34 and 1.6 kg ai/ha 2 weeks before harvest. No other individual compound accounted for more than 5% of the TRR. Most of the radiolabelled residue (80–90%) in

seeds was identified as dimethipin, no other component accounting for more than 5.2% of the extracted residue.

When the backs of the seed heads of mature sunflower plants were sprayed with [^{13}C/^{14}C]-dimethipin at 1.4 kg ai/ha and harvested 4 weeks later, dimethipin accounted for 61% of the extractable residue, with no other single component exceeding 5.7% of the TRR.

A field-grown potato plant (*cv.* Kennebec) was sprayed with a flowable formulation of [^{14}C]dimethipin at 2.24 g ai/ha and harvested 14 days later. Unchanged dimethipin accounted for 20–25% of the TRR (0.012–0.015 mg/kg) in unwashed potato tubers.

Indoor-grown rice plants were treated with [^{14}C]dimethipin at 2.24 g ai/ha, and the plants were harvested 17 days later. The TRRs in straw, hulls and seed were 162, 325 and 8 mg/kg, respectively, calculated as dimethipin. More than 78% of the radiolabelled residues in straw, hulls and grain were extractable in solvents, dimethipin representing 50–80% of the extractable TRR.

When Mueller-Thurgau grape vines were sprayed with [^{14}C]dimethipin at 115 mg/vine, the TRRs in leaves were 16, 7.8 and 3.6 mg/kg (calculated as dimethipin) 2 h and 6 and 24 days after application, respectively. The concentrations of dimethipin residues were 0.036 mg/kg in juice, 0.004 mg/kg in stems and seeds and 0.033 mg/kg in wine in combined 6- and 24-day samples. Numerous metabolites were detected, although none was identified. When samples of juice were processed into wine by alcoholic fermentation, no $^{14}CO_2$ evolved. In wine filtered after fermentation, 11% of the radiolabel was in yeast and solids and 89% in the clear wine.

Most of the radiolabel in the leaves of cotton seedlings grown hydroponically with [^{14}C]-dimethipin in the nutrient medium for 3 days were dimethipin (79%). Metabolites identified as minor constituents were cysteine and glutathione conjugates of dimethipin. Extracts of cotton callus cultures treated with [^{14}C]dimethipin had metabolite profiles similar to that of hydroponically treated cotton plants, but with more dimethipin–L-cysteine reaction product. An additional polar metabolite with an identical HPLC retention time to an unidentified rat metabolite was observed in [^{14}C]dimethipin-treated potato callus cultures

As dimethipin is applied to plants close to harvesting, when the plants are close to natural senescence, the biochemical activity is very limited, resulting in minimal metabolism. As a result, the main plant residue is the parent compound. In a study of the fate of dimethipin in cotton seedlings and callus cell cultures of cotton and potato, most of the plant metabolites resulted from conjugation of dimethipin with glutathione and/or cysteine.

Environmental fate

Studies were reported on degradation, dissipation and mobility in soil, adsorption and desorption, photodegradation on soil, confined rotational crops and aquatic dissipation.

Soil

The aerobic metabolism of [^{14}C]dimethipin was studied on a silt loam, a sand, two loamy sands and a field loam at 25 °C. Under aerobic conditions, bound residues and $^{14}CO_2$ accounted for < 25 and 30% of the radiolabel, respectively. After 168 days of incubation, 50–66% of the radiolabel was recovered as dimethipin. The main metabolites identified were 2-methyl-3-methylene-1,4-dithiane-1,1,4,4-tetraoxide, 1,4-dithiane-1,1,4,4-tetraoxide and a carboxylic acid derivative of dimethipin. The mass balances for the radiolabel were 94–101%.

The anaerobic metabolism of [^{14}C]dimethipin was studied on a silt loam and a sand. Desorption of radiolabel from the soils to the water used to maintain anaerobic conditions was noted.

On silt loam and sand, 60–80% of the radiolabel was present as dimethipin after incubation for 60 days at 25 °C. The mass balances for the radiolabel were 88–90% after 60 days' incubation.

Dimethipin is not susceptible to anaerobic photolytic degradation. In aerated solutions, the photolytic half-time was reduced to 14 days. The rate of photolysis was observed to be pH-dependent, with no significant degradation at pH 7 but half-times at pH 5 and 9 of 35 and 47 days, respectively.

Significant photolytic losses were seen after irradiation of [^{14}C]dimethipin on sandy loam soils when compared with degradation by hydrolysis and soil metabolism. After 30 days, dimethipin accounted for 47–65% and 81–99% of the radiolabel in irradiated and dark control samples, respectively. Volatile components accounted for < 1% of the applied radiolabel. The mass balances were 92 ± 7% for exposed samples and 94 ± 9% for dark samples.

The Meeting concluded that dimethipin is relatively persistent in soils.

Dimethipin was weakly adsorbed onto each of the soils, and a strong relationship was observed between adsorbed dimethipin and percentage of organic matter. The desorption was essentially completely reversible. The adsorption K_a values (< 15) and ease of desorption indicate that the mobility of dimethipin was high in all soils studied.

Studies of leaching were reported for four soil types, sand, loamy sand, sandy loam and silt, treated with dimethipin at 1.7 kg ai/ha. Dimethipin was readily leached from 30-cm soil columns with 51 column cm of water. Between 77 and 102% of the applied radiolabel eluted, of which 71–96% was dimethipin. The rate of elution of the radiolabel was fastest in loamy sand, silt loam and aged sandy loam soil columns, with a more gradual rate in sand and sandy loam soils. Dimethipin is considered to be highly mobile and does not degrade significantly under conditions simulating leaching.

Field studies were conducted under natural conditions of rainfall and irrigation in several states of the USA at sites with loamy sand, clay loam and silt loam soils. The soils were treated according to GAP in the USA for cotton (two sprays, 0.35 and 0.25 kg ai/ha) and sunflowers (2.24 kg ai/ha). Dimethipin migrated below the top 30 cm of soil, and low concentrations of residue were detected at depths down to 91 cm (0.01 mg/kg). The half-time for degradation of dimethipin in the 0–122-cm depth was 168–196 days.

In a study of confined rotational crops, lettuce, barley and carrots were planted in soil treated with [^{14}C]dimethipin at 0.6 kg ai/ha after a fallow period of 30 days and grown to maturity. Dimethipin accounted for most of the radiolabel in soil at application and planting (85–100% of TRR). The percentage of bound, unextractable residue increased with time after application, reaching 60–93% of the TRR in soil samples at harvest. The concentrations of residues of dimethipin in immature and mature crops were 0.01–0.10 mg/kg. No residues of dimethipin were detected in wheat grain. Three crop metabolites were isolated, one of which was identified as hydroxy-DMP.

Lettuce, carrot and wheat or oats were planted in soil treated with two sprays of dimethipin at 0.35 and 0.26 kg ai/ha (GAP for cotton in the USA) after fallow periods of 1 and 6 months. The concentrations of residues of dimethipin in these rotational crops were significant (< 0.02–0.07 mg/kg) at a plant-back interval of 1 month and mostly negligible (< 0.02 mg/kg) in crops planted 6 months after application. The notable exception was carrot tops, which had concentrations ≤ 0.18 mg/kg at harvest in crops planted 6 months after the last application.

The Meeting concluded that the concentrations of inadvertent residues of dimethipin in rotational crops would not be significant after a 6-month plant-back period and that the carryover of dimethipin under field conditions should be < 0.02 mg/kg. Dimethipin is degraded only slowly under aerobic aquatic conditions or on soil under aerobic and anaerobic conditions. It is relatively persistent in the environment and considered to be highly mobile in all the soil types studied.

Water–sediment systems

The half-time of dimethipin in an anaerobic water–sediment system was 277 days. At the start of the experiment, 97% of the applied ^{14}C was present in the aqueous filtrate. By the end of the experiment (365 days), 56% of the applied radiolabel was associated with the water filtrate, dimethipin accounting for 65% of the radiolabel in water or 37% of that applied. Extractable residues from the soil accounted for 5% of the applied radiolabel, dimethipin comprising 89%. Bound residues and $^{14}CO_2$ accounted for 17 and 7% of the applied radiolabel, respectively.

Methods of analysis

Adequate methods have been developed for the analysis of residues of dimethipin on crops and of dimethipin and 1,2-ethane disulfonic acid in animal commodities. Dimethipin is extracted from the matrix with a polar solvent (methanol, aqueous methanol or acetonitrile). The extract is cleaned up with a hexane wash, GPC and a Florisil column. Dimethipin is quantified by GC with a sulfur-specific flame photometric detector, ECD or mass-selective detector. The LOQ and LOD depended on the detector used. The LOQs for most matrices were generally 0.01–0.05 mg/kg.

The Meeting concluded that adequate analytical methods are available for enforcement of MRLs and monitoring purposes.

Stability of residues in stored analytical samples

The stability of dimethipin during frozen storage of fortified samples of cotton seed, meal, hulls and crude oil, lettuce, carrot and wheat grain as well as bovine milk, muscle, kidney and liver was reported. The stability of the metabolite 1,2-ethane disulfonic acid in samples of bovine kidney with incurred residues was also reported.

The periods for which the concentrations of residues of dimethipin remained > 70% of the initial concentration were at least 12 months for lettuce, carrot root, wheat grain and cotton seed; 7 months for cotton seed meal, hulls and crude oil; and 2 months for bovine milk, muscle, kidney and liver. Residues of 1,2-ethane disulfonic acid in bovine kidney were stable for at least 6 months.

The Meeting concluded that dimethipin is stable in crop matrices stored frozen for periods of up to 12 months.

Definition of the residue

Dimethipin is not significantly metabolized by plants when applied close to harvest. The main component of the extractable residue in plants is dimethipin, comprising 38–72, 61, 20–25, 50 and 14–50% of the extractable residue in cotton, sunflower seeds, potatoes, rice grain and grape juice, respectively. In animals, dimethipin is extensively metabolized, the main pathways involving conjugation to glutathione, amino acids and peptides and subsequent degradation. Minor routes of metabolism include hydrolytic hydroxylation and oxidation. There is no reasonable expectation that feeding of dimethipin-treated commodities to animals would result in residues of dimethipin or metabolites in animal commodities that are above typical LOQs.

On the basis of the metabolism of dimethipin in plants, the conclusions of the 1999 JMPR on the toxicology of the compound and the available analytical methods, the Meeting concluded that the residue for compliance with MRLs and for estimation of dietary intake should continue to be defined as dimethipin.

Results of supervised trials

Dimethipin is registered as a plant growth regulator for use as a crop defoliant and harvest aid to accelerate desiccation of plant material. It is applied at the end of plant maturity and close to its natural senescence. At this time, the biochemical activity in plants is very limited, and the penetration, translocation and metabolism of dimethipin in plants are slow. As dimethipin is used as a growth regulator in crops, it is usually best to harvest crops at the appropriate stage of desiccation or defoliation rather than to set minimum pre-harvest intervals. Considerable latitude with respect to the PHI has been allowed in assessing compliance with GAP. Supervised trials were reported on potato, cotton, rape, linseed and sunflowers.

Data were available from supervised trials on potato in France, Germany, The Netherlands, Norway, Sweden and the United Kingdom, but with no corresponding GAP. The Meeting decided to evaluate the trials from France, Germany, The Netherlands and the United Kingdom according to the GAP of Ireland.

In Ireland, dimethipin is registered for application to potatoes at a rate of 0.63 kg ai/ha with a 21-day PHI. The concentrations of residues of dimethipin in four trials in France with application of 0.75 kg ai/ha and PHIs of 18–34 days were < 0.01 (3) and < 0.1 mg/kg. In six trials in Germany at 0.75 g ai/ha with PHIs of 13–14 days, the concentrations of residues of dimethipin were < 0.02 mg/kg (6). Six trials in The Netherlands conducted at 0.5–0.63 kg ai/ha with PHIs of 9–40 days showed concentrations < 0.05 (6) mg/kg. The concentrations in three trials in the United Kingdom at 0.5 kg ai/ha and PHIs of 21–28 days were < 0.005 mg/kg (3).

The concentrations of residues of dimethipin in potatoes in 19 trials, in ranked order (median underlined), were < 0.005 (3), < 0.01 (3), < 0.02 (6), < 0.05 (6) and < 0.1 mg/kg. All the values in potato tubers were below the LOD. The Meeting considered that an appropriate LOQ for a regulatory analytical method is 0.05 mg/kg. The observation of detectable residues of dimethipin in a trial of metabolism in potatoes after application at an exaggerated rate led to the conclusion that the concentration could not be considered zero. The Meeting estimated a maximum residue level, an STMR value and a highest residue for dimethipin in potatoes of 0.05(*), 0.02 and 0.02 mg/kg respectively. The results of a number of trials conducted in countries without corresponding GAP but with PHIs and similar or excessive application rates in comparison with GAP in Ireland support the conclusion that the concentrations of residues are < 0.05 mg/kg. The estimated maximum residue level confirms the current recommendation (0.05(*) mg/kg) for potato.

Supervised field trials on cotton were reported from Spain and the USA.

The registered use pattern in Spain is 0.31 kg ai/ha with no specified PHI. The concentrations of residues in cotton seed in four trials at an application rate of 0.31 kg ai/ha were 0.02, 0.03 and 0.07 (2) mg/kg 5–14 days after application.

Fifteen trials in the USA followed GAP in that country, which is two sprays at 0.23–0.32 kg ai/ha with a minimum re-treatment interval of 5 days and a PHI of 7 days. The concentrations of residues of dimethipin were < 0.1 (4), 0.1 (3), 0.2 (6), 0.3 and 0.7 mg/kg.

The concentrations of dimethipin in cotton seed in the 19 trials, in ranked order, were 0.02, 0.03, 0.07 (2), < 0.1 (4), 0.1 (3), 0.2 (6), 0.3 and 0.7 mg/kg. The Meeting estimated a maximum residue level, an STMR value and a highest residue for dimethipin in cotton seed of 1, 0.1 and 0.7 mg/kg respectively. The estimated maximum residue level replaces the current recommendation (0.05(*) mg/kg) for cotton seed.

Supervised trials on linseed were provided from the Czech Republic. In two trials approximating GAP in that country (0.5 kg ai/ha; PHI, 10–15 days), the concentrations of residues of dimethipin were < 0.1 (2) mg/kg.

The number of trials with linseed is insufficient for setting a maximum residue level. The Meeting recommended withdrawal of the current maximum residue level of 0.2 mg/kg for linseed.

Supervised field trials on rape seed were reported from the Czech Republic, Germany, Hungary, Norway and the United Kingdom. Details of GAP in Norway were not provided. The trials in the United Kingdom did not approximate the relevant GAP and/or were not adequately described.

The registered use pattern in the Czech Republic is 0.38–0.5 kg ai/ha with a PHI of 10–14 days. The concentrations of residues in rape seed in three trials with application rates of 0.38–0.6 kg ai/ha were < 0.1 mg/kg 7–14 days after application.

Six trials in Germany approximated GAP in Hungary, which is application at 0.3–0.5 kg ai/ha with a PHI of 14 days. The concentrations of residues of dimethipin were < 0.1 (5) and 0.1 mg/kg.

In one trial in Hungary conducted according to GAP, the concentration in rape seed was < 0.05 mg/kg.

The concentrations of residues of dimethipin in rape seed in the 10 trials were < 0.05, ≤ 0.1 (8) and 0.1 mg/kg. The Meeting estimated a maximum residue level, an STMR value and a highest residue for dimethipin in rape seed of 0.2, 0.1 and 0.1 mg/kg, respectively.

Data were available on a supervised trials on sunflowers conducted according to GAP in Hungary, which is application at 0.38–0.5 kg ai/ha with harvesting 14 days after the final spray. In 11 trials approximating GAP, the concentrations of residues of dimethipin were < 0.01 (4), < 0.1, 0.09, 0.26, 0.30, 0.38, 0.70 and 0.77 mg/kg.

The concentrations of residues of dimethipin in sunflower seed in the 11 trials in ranked order were < 0.01 (4), 0.09, ≤ 0.1, 0.26, 0.30, 0.38, 0.70 and 0.77 mg/kg. The Meeting estimated a maximum residue level, an STMR value and a highest residue for dimethipin in sunflower seed of 1, 0.1 and 0.77 mg/kg respectively. The estimated maximum residue level replaces the current recommendation (0.5 mg/kg) for sunflower seed.

Fate of residues during processing

Information was provided to the Meeting on the fate of dimethipin residues during processing of cotton seed. Processing factors were calculated for dimethipin residues in processed commodities derived from this raw agricultural commodity only when dimethipin was the residue of concern for surveillance and estimation of dietary intake. When the concentrations of residues in a processed commodity did not exceed the LOQ, the processing factor was calculated from the LOQ and is prefixed with a 'less than' symbol (<).

The average factor for processing of cotton seed to meal was 0.2, that for cotton seed to hulls was 0.8, that for cotton seed to soapstock was < 0.2, that for cotton seed to crude oil was < 0.2 and that for cotton seed to refined oil was < 0.2. Application of a processing factor of 0.2 to the STMR of 0.1 mg/kg for cotton seed gives an STMR-P value for crude and refined oil of 0.02 mg/kg. The Meeting estimated maximum residue levels of 0.1 mg/kg for crude cotton seed oil and edible cotton seed oil. The estimated maximum residue level for crude cotton seed oil confirms the current recommendation (0.1 mg/kg), while that for edible cotton seed oil replaces the current recommendation (0.02 * mg/kg).

Residues in animal commodities

The studies of animal transfer indicate that feeding dimethipin at concentrations up to 50 ppm in the diet will not result in residues in milk and tissues that exceed 0.01 mg/kg, the LOQ for dimethipin in milk and tissues with the analytical method provided.

The dietary burden of dimethipin residues in farm animals was estimated by the Meeting on the basis of the diets listed in Appendix IX of the *FAO Manual*. Potential feed items for which information on residues was available were cotton seed, cotton seed meal and hulls, rape seed and sunflower seed. The estimated intakes of dimethipin by beef and dairy cattle are shown in the table below.

Commodity	Group	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poul-try	Beef cattle	Dairy cows	Poul-try
Cotton seed	SO	1	MRL	90	1.1	10	10		0.11	0.11	
Cotton seed meal	SO	0.02	STMR-P	88	0.02						
Cotton seed hulls	SO	0.08	STMR-P	90	0.09						
Potato culls		0.02	STMR	20	0.1						
Rape seed	SO	0.2	MRL	88	0.23						
Sunflower seed	SO	1	MRL	92	1.08	15	15	30	0.16	0.16	0.32
Total						25[a]	25[a]	30[b]	0.27	0.27	0.32

[a] Assuming that total oilseed products will not be fed at more than 25% of the diet to beef cattle and dairy cows
[b] Assuming that total oilseed products will not be fed at more than 30% of the diet to poultry

The dietary burden of dimethipin for beef and dairy cattle is 0.27 mg/kg. No residues of dimethipin were detected in milk or tissues of dairy cows fed at 50 ppm in the diet for 28 days, a level that is 185 times the estimated dietary burden for cattle. The Meeting estimated maximum residue levels, STMR values and highest residues for dimethipin in edible offal (mammalian) and meat (mammalian) of 0.01*, 0 and 0 mg/kg respectively. The Meeting also estimated a maximum residue level and STMR of *0.01 mg/kg and 0 mg/kg for milk. The estimated maximum residue levels replace the current recommendations (0.02* mg/kg) for edible offal (mammalian), meat (mammalian) and milk.

The dietary burden of dimethipin for poultry is 0.32 mg/kg. No residues of dimethipin were detected in eggs or tissues of hens dosed orally for 5 days at a rate equivalent to feeding at 2770 ppm, a level that is > 8000 times the estimated dietary burden for poultry. The concentrations of TRRs in tissues and eggs of hens dosed at up to 30 ppm in the diet for 30 days were < 1.4 mg/kg (calculated as dimethipin). The studies with radiolabelled compound indicate that there is no reasonable expectation that detectable residues of dimethipin will be found in eggs or tissues of hens fed at the estimated dietary burden of 0.32 mg/kg. The Meeting estimated maximum residue levels, STMR values and highest residues for dimethipin in eggs, edible offal of poultry and poultry meat of 0.01*, 0 and 0 mg/kg, respectively. The estimated maximum residue levels replace the current recommendations (0.02* mg/kg) for eggs, poultry, edible offal and poultry meat.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the concentrations of residue listed below are suitable for establishing maximum residue limits and for assessing IEDIs and IESTIs.

Definition of the residue (for compliance with MRL and estimation of dietary intake): agricultural commodities: Dimethipin.

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P	HR or HR-P
CCN	Name	New	Previous	(mg/kg)	(mg/kg)
SO 0691	Cotton seed	1	0.5	0.1	0.7
OC 0691	Cotton seed oil, crude	0.1	0.1	0.02	
OR 0691	Cotton seed oil, edible	0.1	0.02 (*)	0.02	
MO 0105	Edible offal (mammalian)	0.01 (*)	0.02 (*)	0	0
PE 0112	Eggs	0.01 (*)	0.02 (*)	0	0
SO 0693	Linseed	W	0.2		
MM 0095	Meat (from mammals other than marine mammals)	0.01 (*)	0.02 (*)	0	0
ML 0106	Milks	0.01 (*)	0.02 (*)	0	
VR 0589	Potato	0.05 (*)	0.05 (*)	0.02	0.02
PM 0110	Poultry meat	0.01 (*)	0.02 (*)	0	0
PO 0111	Poultry, edible offal	0.01 (*)	0.02 (*)	0	0
SO 0495	Rape seed	0.2	-	0.1	0.1
SO 0702	Sunflower seed	1	0.5	0.1	0.77
OC 0702	Sunflower seed oil, crude	W	0.1		
OR 0702	Sunflower seed oil, edible	W	0.02 (*)		

W: the previous recommendation is withdrawn

Dietary risk assessment

Long-term intake

The periodic review of dimethipin resulted in recommendations for new and revised MRLs and new STMRs for raw and processed commodities. Data on consumption were available for 12 food commodities and were used in the dietary intake calculation. The results are shown in Annex 3 (Report 2001).

The IEDIs for the five GEMS/Food regional diets, based on estimated STMRs, were 3-20% of the ADI of 0–0.02 mg/kg bw. The Meeting concluded that long-term intake of residues of dimethipin from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The IESTI for dimethipin was calculated for processed cotton seed products, potatoes, rape seed and sunflower seed as well as animal products for which maximum residue levels and STMRs were estimated and for which data on consumption were available. The results are shown in Annex 4 (Report 2001). The IESTI represented 0–10% of the acute RfD (0.02 mg/kg bw) for the general population and 0–10% of the acute RfD for children.

The Meeting concluded that short-term intake of dimethipin residues is unlikely to present a public health concern.

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DINOCAP (087)

EXPLANATION

Dinocap was last evaluated for residues by the 1999 JMPR. In 2000 the Meeting conducted a short-term dietary risk assessment from the consumption of grapes, apples, curcubits, strawberries, peppers, peaches, and tomatoes. The International Estimated Short-Term Intake (IESTI) of grapes exceeded the acute RfD for children (120% of the acute RfD) and for women of child-bearing age (140% of the acute RfD).

At the 33rd Session of the CCPR (2001) the representative of the manufacturer disagreed with the short-term intake calculation because it was based on data on wine grapes grown in northen Europe, which have high residues levels, and considered that data on table grapes grown in southern Europe should have been used. The Committee, noting that the proposed draft MRL for grapes was based on European GAP, agreed to consider this compound at its next session (ALINORM 01/24A).

APPRAISAL

The IESTI estimated at the 2000 JMPR was based on supervised trials submitted to the 1998 JMPR when dinocap was evaluated as a new compound. An HR value of 0.66 mg/kg for dinocap from a trial in Germany on wine grapes according to French GAP was used to estimate short-term intake. At the present Meeting a current French label was provided by the manufacturer and the trials in France and Germany provided to the 1998 JMPR were re-evaluated. The new label specifies a dose rate of 0.21 kg ai/ha. The residues in the trials in northern France and Germany on wine grapes were, in rank order, 0.22, 0.27, 0.28 and 0.35 mg/kg. Those in trials in southern France on table grapes were <0.04 and 0.05 (2) mg/kg. In 21 trials on table grapes in Greece, Italy and Portugal according to GAP (0.021 to 0.073 kg ai/hl) residues were, in rank order, <0.02 (2), <0.04 (8), <0.05 (6), 0.06, 0.08, 0.09, 0.11 (2), 0.20 (2) and 0.30 (2) mg/kg. The Meeting agreed that the residues in northern and southern Europe represented a single population and could be combined for the estimate as follows: <0.02 (2), <0.04 (9), <0.05 (8), 0.06, 0.08, 0.09, 0.11 (2), 0.20 (2), 0.22, 0.27, 0.28, 0.30 (2) and 0.35 mg/kg.

The Meeting withdrew the previous recommendations and estimated a maximum residue level of 0.5 mg/kg, an STMR of 0.05 mg/kg and an HR of 0.35 mg/kg for dinocap in grapes. Although this HR value comes from a supervised trial on wine grapes, the two next highest values (0.30 mg/kg) are from a trial on table grapes, indicating that wine and table grapes can contain similar residues. The short-term intake estimate should reflect the consumption of a single unit of a given commodity from any source, and no information is provided in the French label that wine variety grapes cannot be used for human consumption.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels shown below are suitable for establishing maximum residue limits and for dietary intake assessment.

Definition of residue for compliance with MRLs and for estimation of dietary intake: sum of dinocap isomers and dinocap phenols, expressed as dinocap.

CCN	Commodity	MRL (mg/kg) New	MRL (mg/kg) Previous	STMR or STMR-P (mg/kg)	HR or HR-P (mg/kg)
FB 0269	Grapes	0.5	1	0.05	0.35

DIETARY RISK ASSESSMENT

Chronic intake. Currently, the ADI for dinocap is 0.01 mg/kg body weight/day. At the 1998 JMPR, the International Estimated Daily Intake (IEDI) calculated for commodities of human consumption which STMRs were estimated ranged from 0 to 1 % of the ADI for the five GEMS/Food regional diets. At this Meeting the STMR recommendation for grapes of 0.105 mg/kg was replaced by 0.05 mg/kg. The Meeting confirms the previous conclusion that the intake of residues of dinocap resulting from its uses that have been considered by the JMPR is unlikely to present a public heath concern.

Short-term intake: An acute RfD of 0.03 mg/kg bw for dinocap was allocated for children and for general population and of 0.008 mg/kg bw for women of child-bearing age by the 2000 JMPR. International Estimate of Short-Term Intakes (IESTI) were calculated for grapes and the results are shown in Annex IV. The IESTI was 20 % of acute RfD for the general population, 60% of acute RfD for children, and 80 % for women of child-bearing age. The Meeting concluded that the short-term intake of dinocap from use in grapes is unlikely to present a public heath concern.

DIPHENYLAMINE (030)

EXPLANATION

Diphenylamine was originally evaluated in 1969 and subsequently in 1976, 1979, 1984 and 1998. It was identified for re-evaluation within the CCPR Periodic Review Programme at the 1996 CCPR (ALINORM 97/24), proposed for consideration by the 2000 JMPR at the 1997 CCPR (ALINORM 97/ 24A) and the evaluation deferred until 2001. An ADI of 0-0.08 mg/kg bw was established by the 1998 JMPR replacing the previous ADI of 0-0.02 mg/kg bw.

Because of toxicological concerns, attention was given to the various method of synthesising and purifying diphenylamine to produce a quality acceptable for the treatment of apples and pears. It was proposed that a specification for a pure (food grade) diphenylamine should be drawn up.

The manufacturer reported new studies of physical and chemical properties, animal, plant and soil degradation, analytical methods, storage stability, farm animal feeding, supervised residue trials and food processing.

The governments of Australia and The Netherlands have reported information on national GAP and/or residue data.

IDENTITY

ISO common name: none

Chemical name

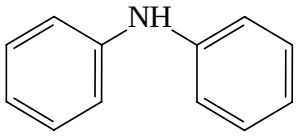
IUPAC: diphenylamine

CA: *N*-phenylbenzenamine

CAS Registry No.: 122-39-4

Synonyms: DPA

Structural formula:



Molecular formula: $C_{12}H_{11}N$

Molecular weight: 169.22

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Vapour pressure:	6.39×10^{-4} torr. (=8.52×10^{-2} Pa) at 25°C 2.32×10^{-3} torr. (=3.09×10^{-1} Pa) at 35°C 7.09×10^{-3} torr. (=9.46×10^{-1} Pa) at 45°C (gas saturation method) (Douglass, 1993a)	
Octanol/water partition coefficient:	K_{ow} = 3860, log K_{ow} = 3.6 at 25°C (batch method) (Douglass, 1993b)	
Solubility (99.4% purity):	water at 25°C acetonitrile at 25°C methanol at 25°C octanol at 25°C hexane at 25°C	0.039 mg/ml 860 mg/ml 474 mg/ml 230 mg/ml 57 mg/ml (Schetter, 1993)
Hydrolysis (sterile solution) (Baur, 1993):	half-life at 25°C	pH 5: 320 days pH 7: 350 days pH 9: 360 days (Baur, 1993)

Baur demonstrated that diphenylamine was substantially stable to hydrolysis under sterile conditions in the dark at 25°C for 30 days. The calculated half-lives are based on these 30-day tests.

Photolysis:	half-life 4.4 hours in aqueous buffer, pH 7, under a xenon arc lamp (157 W/m^2 (330-800 nm) (Baur and Robinson, 1993)
Dissociation constant:	pKa 1.03 at 20 ± 1.0°C (Hambrick, 1993)

Technical material

Appearance:	Cream solid flakes with a sharp creosote odour	(Wojcieck, 1992)
Relative density:	1.177 g/cm^3 at 25°C	(Wojcieck, 1992)
Melting point:	52.7-54.7°C	(Wojcieck, 1992)
Minimum purity:	>99%	
Solubility at 25ºC:	water acetonitrile methanol octanol hexane	0.038-0.042 mg/ml 808-897 mg/ml 454-492 mg/ml 204-237 mg/ml 53-66 mg/ml
Thermal stability:	25-150°C range without decomposition (Malone, 1993)	
Stability:	stable indefinitely	

FORMULATIONS

Diphenylamine is commercially available in EC and SL formulations.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The Meeting received information on animal metabolism studies on rats, lactating goats and laying hens, all with diphenylamine uniformly labelled with ^{14}C in both rings of the molecule.

Rats. A metabolism study on diphenylamine (Wu, 1993) was evaluated by the JMPR in 1998 for the toxicological evaluation. Male and female Sprague-Dawley rats were treated orally with single doses of [^{14}C]diphenylamine at 5 and 750 mg/kg bw, and multiple doses of 5 mg/kg bw (repeated doses of 5 mg/kg bw/day of unlabelled diphenylamine for 14 days followed by single doses of 5 mg/kg bw of labelled compound). Diphenylamine was extensively absorbed and then excreted mainly in urine. Only 0.14-0.28% of the low dose remained in the tissues and organs of animals after 168 hours. ^{14}C in the expired air accounted for less than 0.01% of the administered dose. Twelve metabolites were identified. The parent and these metabolites in the excreta accounted for 81-93% of the dose. The metabolites were

4,4'-dihydroxydiphenylamine (4,4'-di-OH-DPA)	unconjugated
	O-sulfate
	O,*O*-disulfate
4-hydroxydiphenylamine (4-OH-DPA)	unconjugated
	O-glucuronide
	N-glucuronide
	O-sulfate
	O,*N*-diglucuronide
indophenol	unconjugated
	O-sulfate
3-hydroxydiphenylamine (3-OH-DPA)	unconjugated
2-hydroxydiphenylamine (2-OH-DPA)	unconjugated

Note: The hydroxy(di)phenylamines should be named as substituted phenols according to IUPAC nomenclature, but they are named as substituted phenylamines for clarity.

Goats. Two lactating goats were dosed orally with capsules containing [^{14}C]diphenylamine for seven successive days at a level equivalent to 45.5 ppm in the feed for Goat A (54 kg) and 46.6 ppm for Goat B (48 kg) (Kim-Kang, 1994c). Their diet consisted of a commercial grain ration and alfalfa mixed hay; average feed consumption per day was 2.38 kg and 1.94 kg respectively (moisture or dry weight content of the feed not stated). Milk was collected twice daily during the treatment period, and urine and faeces continuously throughout the treatment period. At the end of each 24-hour sampling each animal's cage was rinsed with isopropyl alcohol/water (IPA/H_2O, 1:1). The goats were slaughtered 24-26 hours after the last dose. Liver, kidneys, omental and back fat, tenderloin and hindquarter muscle were collected.

Approximately 97% of the administered dose was recovered from the urine, faeces, milk, cage wash, gastrointestinal tract contents and rumen contents (Table 1). Most of the radioactive residues were recovered in urine (>87%), and the total excretion through urine and faeces accounted for about 94%.

The total ^{14}C residues in the milk reached a plateau within a few hours. Because of rapid elimination after each daily administration the ^{14}C levels fluctuated regularly between the two milkings (Table 2). ^{14}C levels in the tissues were low, but higher in the kidneys and liver than in fat or muscle.

The levels of parent and metabolites identified in milk and tissues are shown in Table 3. 30-36% of the residues in fat and kidney remained as the unmetabolized parent compound, and 4-12% in the liver and milk. In addition to diphenylamine, several polar metabolites including 4-OH-DPA, 4,4'-dihydroxy-DPA, indophenol, the sulfate conjugate of 4-OH-DPA and the glucuronic acid conjugate of 4-OH-DPA were detected. A number of components of the residues in the liver including polar and non-polar unknowns were unidentifiable. Ring-hydroxylation followed by conjugation with either a sulfate moiety or glucuronic acid was the main metabolic pathway. In addition, hydroxylation on both rings followed by conjugation with either sulfate or glucuronic acid at only one position or at both positions were observed.

Table 1. Distribution of ^{14}C in 2 goats after dosing with [^{14}C]diphenylamine for seven days at a level equivalent to 45.5 or 46.6 ppm in the feed (Kim-Kang, 1994c).

	% of total ^{14}C dose						
	Urine	Faeces	Milk	Cage wash	GI tract contents	Rumen contents	Total recovery
Goat A	87.3	6.4	0.54	2.2	0.08	0.09	96.7
Goat B	89.1	5.5	0.56	1.4	0	0.05	96.6

Table 2. ^{14}C levels in milk of 2 goats during dosing at a level equivalent to 45.5 or 46.6 ppm in the feed for seven days and in the tissues after slaughter (Kim-Kang, 1994c).

Sample	Time (h)	^{14}C, mg/kg (as diphenylamine)	
		Goat A	Goat B
Milk	0	<0.01	<0.01
	8	0.78	0.53
	24	0.26	0.23
	32	0.89	0.64
	48	0.22	0.23
	56	0.79	0.63
	72	0.26	0.24
	80	0.77	0.66
	96	0.29	0.23
	104	0.86	0.66
	120	0.26	0.22
	128	0.75	0.62
	144	0.26	0.23
	152	0.85	0.63
	168 (7 days)	0.24	0.22
Liver	after slaughter	0.11	0.10
Kidneys	after slaughter	0.12	0.07
Leg muscle	after slaughter	0.007	0.006
Loin muscle	after slaughter	0.008	0.006
Back fat	after slaughter	0.026	0.02
Omental fat	after slaughter	0.02	0.02

Table 3. Parent compound and metabolites determined in the milk and tissues of goats dosed for 7 days with [^{14}C]diphenylamine (Kim-Kang, 1994c).

Compound	^{14}C expressed as diphenylamine, mg/kg							
	Milk [1]		Liver		Kidney		Omental fat	
	Goat A	Goat B	Goat A	Goat B	Goat A	Goat B	Goat A	Goat B
DPA	0.063	0.075	0.006	0.003	0.043	0.023	0.008	0.004
4-OH-DPA			0.002					
4,4'-di-OH-DPA			0.002	0.002				
Indophenol			0.002		0.002			
Metab A [2]	0.33	0.26	0.003		0.014	0.011		
Metab B [3]	0.40	0.25	0.009	0.006	0.029	0.018		
Metab I [4]	0.009		0.006		0.002			
Metab J [5]	0.013				0.002			
TOTAL [6]	0.85	0.63	0.11	0.10	0.12	0.07	0.02	0.02

[1] Milk: sampling time 152 hours
[2] Metab A: glucuronic acid conjugate of 4-OH-DPA
[3] Metab B: sulfate conjugate of 4-OH-DPA
[4] Metab I: sulfate conjugate of 4,4'-dihydroxy-DPA ?
[5] Metab J: disulfate conjugate of dihydroxy-DPA ?
[6] Total residue: ^{14}C measurement, see Table 2.

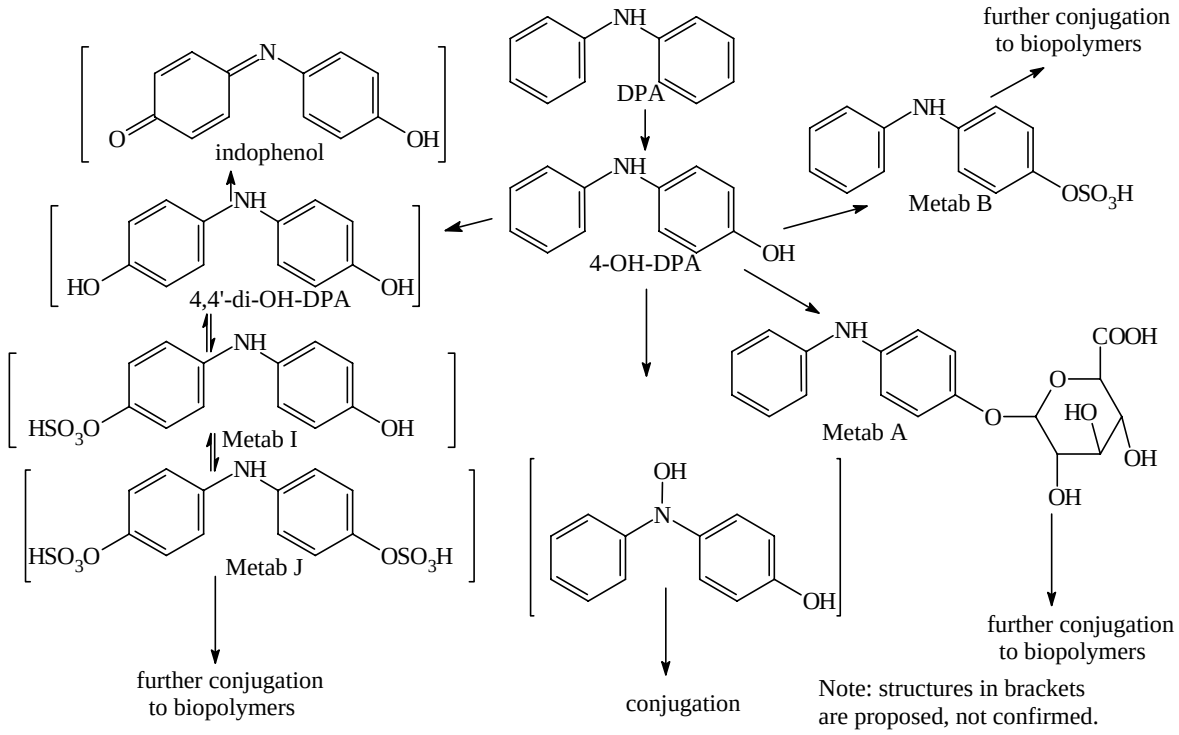


Figure 1. Proposed metabolic pathways of diphenylamine in the lactating goat.

Poultry. Fifteen laying hens were dosed orally with capsules containing [^{14}C]diphenylamine for seven days at levels equivalent to 50 ppm in feed, based on an average feed consumption (as fed, not expressed as dry weight) of 115 g/chicken/day (Kim-Kang, 1994d). Eggs were collected in the morning and in the afternoon and composited at each sampling for analysis. Hens were slaughtered approximately 22-24 hours after the last dose for analysis of liver, kidney, skin with adhering fat, and thigh and breast muscle.

Extraction and fractionation procedures were applied in conjunction with combustion, liquid scintillation counting (LSC), HPLC, and one- and two-dimensional TLC and radio-chromatography, to isolate and characterize significant metabolites. Preparative isolations of unknown metabolites were achieved by HPLC in order to obtain sufficient quantities for additional characterization by TLC. Two-dimensional TLC, in conjunction with base hydrolysis (sodium hydroxide), was employed to elucidate the structures of the aglycones of the conjugated metabolites.

Approximately 91% of the administered dose was excreted. The total ^{14}C as diphenylamine was 0.15 mg/kg in the liver, 0.21 in kidneys, <0.01 in breast and thigh muscle and 0.04 mg/kg in the fat/skin samples. The levels in the egg yolks ranged from <0.01 to 0.38 mg/kg (Table 4) and in the whites were less than 0.01 mg/kg.

Table 4. ^{14}C levels in eggs from 15 hens dosed at a level equivalent to 50 ppm in the feed during a seven-day study (Kim-Kang, 1994d).

Day	^{14}C, mg/kg (as diphenylamine)			
	Whites		Yolks	
	am	pm	am	pm
0		<0.01		<0.01
1	<0.01	<0.01	<0.01	<0.01
2	<0.01	<0.01	0.037	0.069
3	<0.01	<0.01	0.088	0.15
4	<0.01	<0.01	0.18	0.24
5	<0.01	<0.01	0.25	0.30
6	<0.01	<0.01	0.27	0.38
7	<0.01		0.31	

Table 5. Parent compound and metabolites in the eggs and tissues of hens dosed for 7 days with [^{14}C]diphenylamine at a level equivalent to 50 ppm in the feed (Kim-Kang, 1994d).

Compound	Metabolite levels, ^{14}C expressed as diphenylamine , mg/kg			
	Egg yolk [1]	Liver	Kidney	Fat + skin
DPA	0.065	0.011	0.003	0.014
2-OH-DPA		0.007	0.001	
4-OH-DPA	0.018			
4,4'-di-OH-DPA	0.002	0.004		
Indophenol		0.002		
Metab A [2]	0.012	0.002		
Metab B [3]	0.22	0.012		0.009
Metab C [4]	0.007	0.007	0.078	
Metab I [5]	0.005	0.003	0.020	
Metab J [6]	0.001		0.024	
TOTAL [7]	0.38	0.15	0.21	0.04

[1] Eggs: day 6 pm sample
[2] Metab A: glucuronic acid conjugate of 4-OH-DPA
[3] Metab B: sulfate conjugate of 4-OH-DPA
[4] Metab C: polar conjugate of 4-OH-DPA
[5] Metab I: sulfate conjugate of 4,4'-dihydroxy-DPA ?
[6] Metab J: disulfate conjugate of dihydroxy-DPA ?
[7] Total residue: ^{14}C measurement.

A significant proportion of the residues in the fat, skin and egg yolks remained as unmetabolized diphenylamine (7-35% of the ^{14}C) but most of the residue in the yolks was a sulfate conjugate of 4-OH-DPA (metabolite B, 57% of the ^{14}C). Minor residues in the yolks and liver were glucuronic conjugates of 4-OH-DPA. Some parent compound (1-8% of the ^{14}C) was also present in

the liver and kidneys. The main metabolite in the kidneys was a more polar conjugate of 4–OH-DPA (metabolite C, 38% of the ^{14}C). Only 32% of the ^{14}C in the liver was attributable to identified compounds (including metabolite C, Table 5) with two unidentified isomeric metabolites accounting for 48% of the residue.

The study of metabolism in hens demonstrated that diphenylamine can be hydroxylated on the ring at position 4 and subsequently conjugated with glucuronic acid, sulfate, and other groups, and also at position 2 to form 2-OH-DPA which can be conjugated subsequently with either a sulfate or glucuronic acid moiety. 4-OH-DPA can be further hydroxylated on the second ring to form dihydroxy-DPA, which can form either monoconjugates or diconjugates. Significant residues of diphenylamine and its degradation products formed by hydroxylation and conjugation with endogenous substrates were transferred into egg yolk and some tissues. Residues in egg white and muscles were below the limit of quantification.

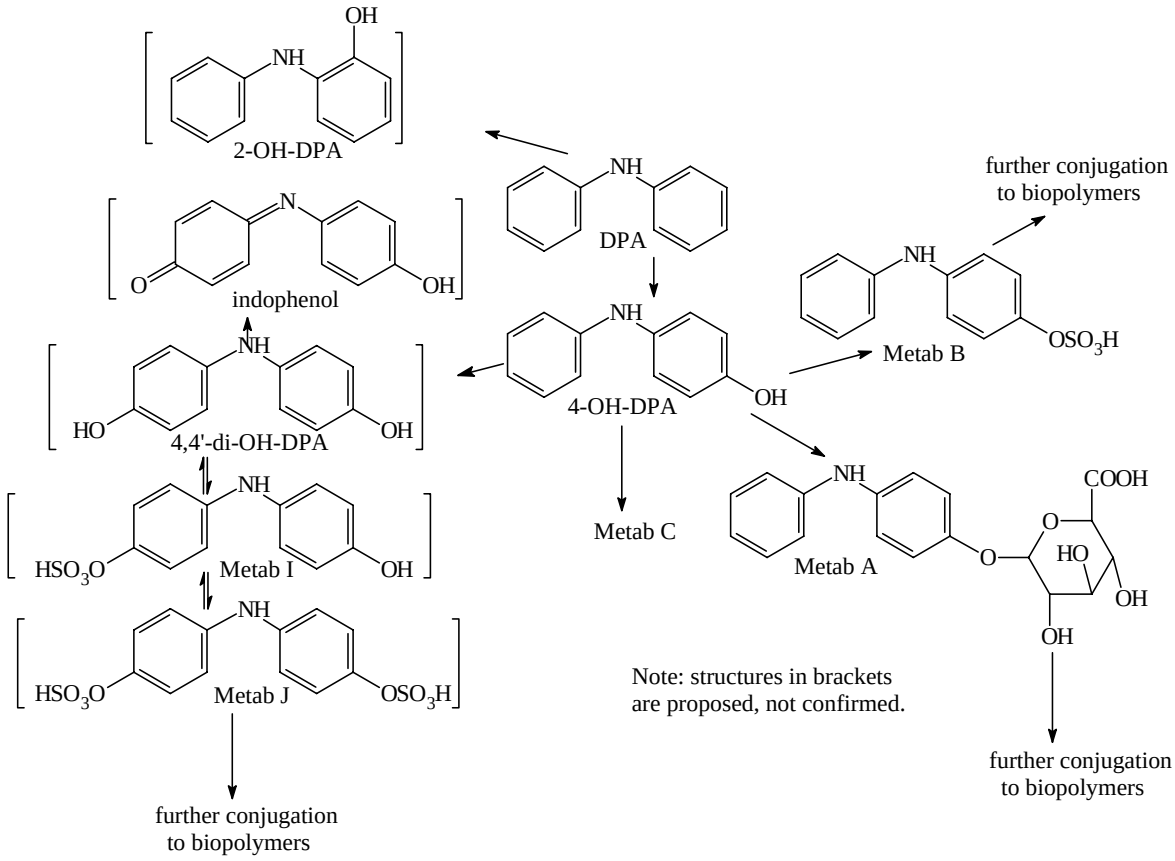


Figure 2. Proposed metabolic pathways of diphenylamine in laying hens.

Plant metabolism

A study of the metabolism of stored apples was reported to the Meeting (Kim-Kang, 1993, 1994a,b).

One hundred and forty-four Red Delicious apples, unit size about 200 g, were treated with an emulsion of [^{14}C]diphenylamine (uniform ring label). A residue of approximately 50 mg/kg resulted. All treated apples except eight used for zero-time measurement were stored in cabinets at 0 ± 2°C and 95 ± 5% relative humidity. Air was passed through the cabinets and an exit trap to collect volatile metabolites. Negligible amounts of the ^{14}C were found in the trap demonstrating that volatile

metabolites were not produced. Apples were sampled at intervals up to 40 weeks after treatment, with separation into peel and pulp for determination of the ^{14}C residues.

Most of the residue was absorbed into the peel within 2 days (Table 6), then it slowly migrated into the pulp which after 40 weeks contained 32% of the residue.

Under cold storage conditions the parent chemical is initially converted to a number of free hydroxylated products, including 2-hydroxydiphenylamine, 3-hydroxydiphenylamine, 4-hydroxydiphenylamine, and a dihydroxydiphenylamine (Table 7). The hydroxylated metabolites then conjugate with glucose and oligosaccharides. Diphenylamine is the main component of the residue in whole fruit.

Diphenylamine, in a simulation of commercial post-harvest treatment, was initially found on the surface of the apples. After 40 weeks' storage, the parent compound accounted for approximately 41% of the total ^{14}C residue with 37% present as conjugates and 8% as hydroxydiphenylamines. The proposed metabolic pathway is shown in Figure 3.

The unidentified non-polar metabolites found in the study were not related to either 4-aminobiphenyl, 2-aminobiphenyl, or *N*-nitrosodiphenylamine.

Table 6. Percentage distribution of the ^{14}C in methanol rinse, pulp and peel of apples treated post-harvest with [^{14}C]diphenylamine and stored at 0 ± 2°C and 95 ± 5% relative humidity(Kim-Kang, 1993).

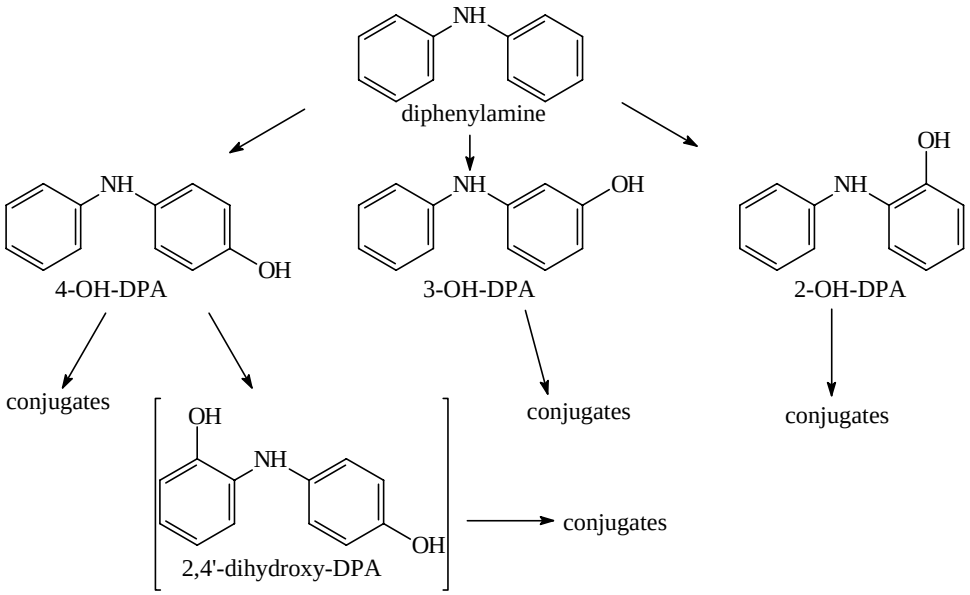
Days after treatment	% of the ^{14}C		
	Rinse (MeOH)	Pulp	Peel
0 (3.5 h)	77	0.13	23
2	29	3.0	68
7	22	5.6	73
14	23	7.4	69
28	21	9.9	69
42	16	14	69
56	16	17	67
69	15	19	66
84	14	15	71
112	15	22	63
140	11	22	67
168	10	26	65
196	10	31	59
224	8.2	27	64
252	9.3	28	62
280	7.0	32	61

Table 7. Distribution of diphenylamine and its metabolites in apples treated post-harvest with [^{14}C]diphenylamine and stored at 0 ± 2°C and 95 ± 5% relative humidity for 40 weeks (Kim-Kang, 1993).

Compound	Pulp		Peel		Rinse (MeOH)		Total fruit	
	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]
Diphenylamine	12	2.0	50	76	87	2.4	41	17
2-OH-diphenylamine	0.51	0.09	1.6	2.4	1.7	0.05	1.3	0.54
3-OH-diphenylamine	1.0	0.16					0.33	0.14
4-OH-diphenylamine	3.5	0.57	7.2	11	7.7	0.21	6.1	2.6
Glucose conjugate of 4-OH-diphenylamine	21	3.4	13	19	1.3	0.04	14	6.1

Compound	Pulp		Peel		Rinse (MeOH)		Total fruit	
	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]
Oligosaccharide conjugate of dihydroxy-diphenylamine	14	2.3	0.99	1.5			5.1	2.2
Oligosaccharide conjugate of 2-OH-diphenylamine	16	2.6	0.39	0.59			5.2	2.2
Oligosaccharide conjugate of 4-OH-diphenylamine	14	2.4	8.6	13			9.9	4.2
Oligosaccharide conjugate of 3-OH-diphenylamine	4.1	0.67	1.6	2.4	2.0	0.06	2.4	1.0
Polar unidentified	3.9	0.64					1.3	0.53
Polar unknowns 2 (9 metabs)	8.5	1.4	13	20			11	4.5
Nonpolar unknowns (2 metabs)	0.72	0.12	0.48	0.72			0.52	0.22
Bound residue	1.1	0.19	2.9	4.3			2.1	0.89
Total	100	16.5	100	151.1	100	2.76	100	42

[1] As diphenylamine



Conjugates: with glucose or oligosaccharides

Figure 3. Proposed metabolic pathways of diphenylamine in stored apples.

Environmental fate in soil

The Meeting received information on aerobic degradation, adsorption-desorption and mobility of aged residues.

Aerobic degradation. Liu (1993a) incubated ring-labelled [^{14}C]diphenylamine in a loam soil (45% sand, 36% silt, 19% clay, 0.6% organic matter, pH 7.3) at a nominal 10 mg/kg under aerobic conditions at 25°C in the dark for 12 months with soil moisture levels maintained at approximately 75% of field capacity. Recovery of ^{14}C, including volatiles, was in the range 91.4-103%.

The levels of diphenylamine, unextractables and $^{14}CO_2$ are shown in Table 8. Diphenylamine decreased rapidly in the initial stages, but more slowly after about 7 days. The products were polymeric and not identified. Mineralization was slow.

Table 8. Disappearance of diphenylamine and generation of CO_2 and unextractable residues during aerobic incubation of labelled diphenylamine in a loam soil (Liu, 1993a).

Day	Total ^{14}C	CO_2	Unextractable	diphenylamine
	^{14}C as % of applied			
0	101		4.5	91
4 h	103	0.01	12	83
8 h	103	0.06	22	42
1	100	0.30	26	54
3	101	1.4	48	31
7	99	2.3	53	21
14	99	3.7	53	18
30	99	5.3	57	9.9
60	97	7.9	46	21
91	94	10	49	11.3
120	99	11	55	15
184	101	14	58	21
270	91	17	48	18
365	98	18	49	15

Adsorption and desorption. Reynolds (1994) measured the adsorption and desorption of ring-labelled [^{14}C]diphenylamine on 4 soils and a sediment. Diphenylamine at 0.1-10 ng/g dissolved in 25 ml aqueous 0.01M $CaCl_2$ was added to 5 g of soil or sediment (the clay was tested at a soil:solution ratio of 1:100) and shaken at ambient temperature for 72 hours. ^{14}C was measured in clear solution removed after centrifugation; adsorption to the soil or sediment was calculated (Table 9). For the desorption test, 25 ml aqueous 0.01M $CaCl_2$ was added to the tube which was shaken for 72 hours at ambient temperature. ^{14}C was measured as above (Table 9). The stability of diphenylamine was tested by TLC analysis of the supernatants and residual desorption solids. The levels of diphenylamine accounted for 46-79% of the ^{14}C. According to the classification system based on K_{OC} diphenylamine was immobile (K_{OC} > 5000) in 2 soils, slightly mobile (K_{OC} 2000-5000) in 2 soils and of low mobility (K_{OC} 500-2000) in one soil.

Table 9. Adsorption and desorption of diphenylamine on 4 soils and a sediment (Reynolds, 1994).

Soil	Soil properties						Adsorption		Desorption		Mobility
	sand, %	silt, %	clay, %	organic matter, %	PH	CEC, meq/100 g	K_d	K_{oc}	K_d	K_{oc}	rating
Loam	45	36	19	0.60	7.3	9.6	13.8	3960	23.5	6750	slight
Silty clay loam, lake sediment	9.6	51	40	0.43	6.7	20	16.4	6590	40	15870	immobile
Clay	28	22	50	5.1	5.6	36	152	5140	307	10400	immobile
Loamy sand	78	16	6.0	1.0	6.6	9.0	21.4	3620	35	5860	slight
Silt loam	36	58	6.	0.7	7.8	14	4.9	1212	8.7	2150	low

Aged leaching. Kammerer (1994a) incubated ring-labelled [^{14}C]diphenylamine at 10 mg/kg in a loam, a loam sand, a silt loam and a clay soil under aerobic conditions in the dark at 25°C for 1 day and used the resulting aged residues for leaching experiments. On top of soil columns 30 cm high and 3.6 cm diameter were placed plugs (50 g) of the incubated soil, and the columns were then leached with 510 ml of 0.01M $CaCl_2$. Only 0.12-4.3% of the recovered ^{14}C appeared in the leachate, and 36-95% remained in the treated soil or the two top 6-cm segments (4.3-48% of that recovered) of the column. The mobility of aged diphenylamine in the 4 soils was loam, slight; loam sand and silt loam, low; and clay, immobile. Aged soils extracted with aqueous acetonitrile produced diphenylamine (14-56% of the dose) and the identified products *N,N*-diphenylformamide (2.0-4.7% of dose) and 4-nitro-*N*-phenyl-benzenamine (1.3-5.3% of dose).

Environmental fate in water-sediment systems

The Meeting received information on the photolysis of diphenylamine in aqueous solution and its anaerobic degradation in a sediment-water system.

Photolysis. Bauer (1993) UV-irradiated diphenylamine in an aqueous solution. Approximately 7% carbazole was formed in 0.5 hours peaking at 52% at 10.5 hours, hydroxydiphenylamine was about 1% after 1 hour and peaked at 16% by 36 hours, and D3, a cyclopentenohydroxyindole, reached 93% after 192 hours' irradiation. Minor amounts of trimeric products were also formed, with proposed structures based on molecular ions (M+1) at m/z 508, 515 and 534. Structures and proposed structures are shown in Figure 4.

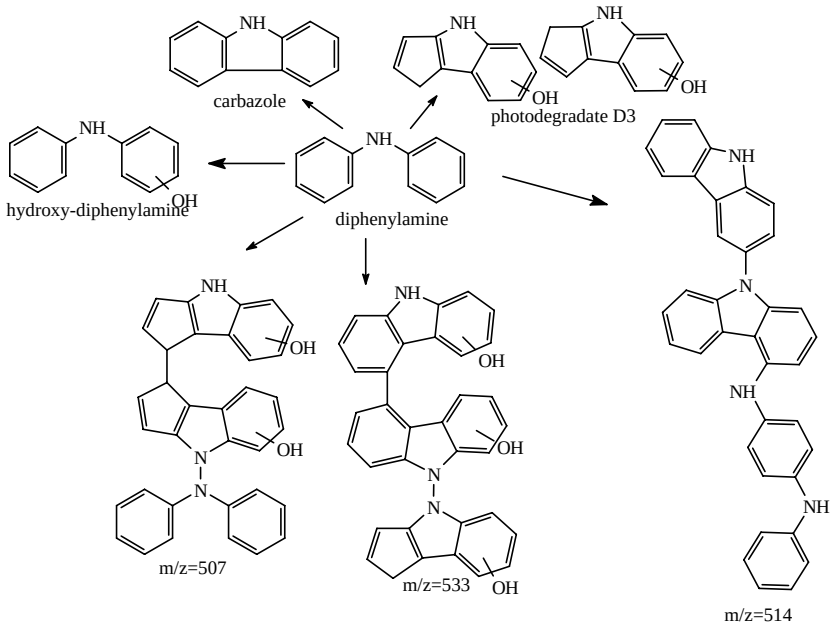


Figure 4. Photolytic degradation of diphenylamine.

Anaerobic aquatic degradation. Liu (1993b) incubated lake water (44 ml) and its sediment, a silty clay loam, (20 g dry weight or 26 g wet weight) with ring-labelled [^{14}C]diphenylamine at 10 mg/kg sediment in the dark at 25°C under anaerobic conditions for 1 year. Before incubation the water-sediment systems in the tubes had been flushed with nitrogen, dosed with 0.5 g glucose and incubated for 30 days to ensure anaerobicity. The lake water had a pH of 8.4 and an alkalinity of 112 mg/l expressed as $CaCO_3$. The sediment was the same as used in the adsorption-desorption experiments (Table 9). Evolved $^{14}CO_2$ was trapped. At sampling, sediment and water were extracted with acidified acetonitrile. ^{14}C recovery was acceptable, but was low at days 31 and 61 until it was realised that ^{14}C had been volatilized and incorporated into the rubber stoppers. Diphenylamine was identified as part

of the residue in the stoppers. The half-life of diphenylamine was approximately 60 days (Table 10). The degradation products were soil-bound or soil-incorporated residues, which very slowly mineralized.

Table 10. Residues of diphenylamine and its degradation products in lake sediment and water after anaerobic incubation at 25°C of ring-labelled [^{14}C]diphenylamine at 10 mg/kg sediment (Liu 1993b).

Days	Distribution of ^{14}C expressed as % of dose		
	$^{14}CO_2$	diphenylamine	unextractable
0		100	0.12
3	0.08	97	2.2
7	0.12	97	1.2
14	9.19	96	5.0
31	0.60	74	3.2
61	0.55	50	3.3
90	0.59	43	2.8
123	0.71	28	4.1
180	0.47	26	12
270	1.5	19	8.8
364	2.7	17	34

METHODS OF RESIDUE ANALYSIS

Analytical methods

The Meeting received information on methods of analysis for diphenylamine in crops, and for processed and animal commodities.

Apples. Tshabalala (1994a) described an analytical method for determining residues of diphenylamine in apples and their processed products.

Whole apples are homogenized in a food processor with liquid nitrogen to produce a white powder. An analytical sample is then blended with acetone and filtered. A portion of the filtrate is partitioned with hexane and water, from which the diphenylamine residue is recovered in the hexane extract, which is taken to dryness. The residue is taken up in dichloromethane for derivatization by reaction with trifluoroacetic anhydride reagent in dichloromethane in a sealed vial at 50°C for 1 hour. The acetylated diphenylamine is determined by GC-MS, and quantified using single-ion monitoring at 265 amu. Diphenylamine standards are also derivatized. The procedure for wet pomace, dry pomace and apple juice begins with the acetone extraction step. Recoveries are shown in Table 11.

The determined diphenylamine residues of 0.0686 and 0.085 mg/kg in control apples precluded reliable recovery tests at the lower levels. Tshabalala (1994b), in a supplementary report, showed that the LOQ for diphenylamine residues in apples, juice and wet pomace was 0.08 mg/kg, and in dry pomace 1 mg/kg.

Table 11. Recoveries of diphenylamine from apples and their processed commodities (Tshabalala, 1994a,b).

Sample	Fort. level, mg/kg	n	Mean recovery [1]	Recoveries [1]
Red Delicious whole apple	control	1	0.0686 mg/kg	0.0686 mg/kg
Red Delicious whole apple	0.02	3	125	96, 130, 150
Red Delicious whole apple	0.20	1	93	93
Red Delicious whole apple	2.0	5	91	110, 84, 88, 80, 95
Red Delicious whole apple	2.8	2	87	81, 92
Red Delicious juice	control	3	<0.08 mg/kg	<0.08, <0.08, <0.08 mg/kg
Red Delicious juice	0.40	3	83	62, 100, 86
Red Delicious juice	1.0	3	82	78, 80, 89

Sample	Fort. level, mg/kg	n	Mean recovery [1]	Recoveries [1]
Red Delicious juice	2.0	3	113	110, 120, 110
Red Delicious wet pomace	control	3	<0.08 mg/kg	<0.08, <0.08, <0.08 mg/kg
Red Delicious wet pomace	1.0	3	72	73, 70, 73
Red Delicious wet pomace	2.0	3	78	80, 78, 76
Red Delicious dry pomace	control	3	<0.40 mg/kg	<0.40, <0.40, <0.40 mg/kg
Red Delicious dry pomace	1.0	3	74	76, 70, 77
Red Delicious dry pomace	2.0	3	80	82, 79, 79
Granny Smith whole apple	control	3	0.085 mg/kg	0.094, 0.0803, 0.0802 mg/kg
Granny Smith whole apple	0.02	3	61	62, 67, 55
Granny Smith whole apple	0.20	3	80	86, 79, 75
Granny Smith whole apple	2.0	5	85	75, 78, 85, 96, 90
Granny Smith juice	control	3	<0.08 mg/kg	<0.08, <0.08, <0.08 mg/kg
Granny Smith juice	0.40	3	90	93, 90, 88
Granny Smith juice	1.0	3	91	91, 84, 99
Granny Smith juice	2.0	3	107	100, 110, 110
Granny Smith wet pomace	control	3	<0.086 mg/kg	<0.08, 0.099, <0.08 mg/kg
Granny Smith wet pomace	0.40	3	99	94, 110, 94
Granny Smith wet pomace	1.0	3	86	91, 76, 90
Granny Smith wet pomace	2.0	3	70	51, 86, 73
Granny Smith dry pomace	control	3	<0.08 mg/kg	<0.08, <0.08, <0.08 mg/kg
Granny Smith dry pomace	1.0	3	80	93, 78, 70
Granny Smith dry pomace	2.0	3	78	76, 74, 83
Supplementary report by Tshabalala, 1994b				
Red Delicious whole apple	control	1	<0.08 mg/kg	<0.08 mg/kg
Red Delicious whole apple	0.08	2	90	89, 90
Red Delicious whole apple	10.0	2	92	89, 95
Red Delicious juice	control	1	<0.08 mg/kg	<0.08 mg/kg
Red Delicious juice	0.08	1	69	69
Red Delicious juice	10.0	2	91	91, 90
Red Delicious wet pomace	control	1	<0.08 mg/kg	<0.08 mg/kg
Red Delicious wet pomace	0.08	2	83	83, 83
Granny Smith whole apple	control	1	<0.08 mg/kg	<0.08 mg/kg
Granny Smith whole apple	0.08	2	115	120, 110
Granny Smith whole apple	10.0	2	110	110, 110
Granny Smith juice	control	1	<0.08 mg/kg	<0.08 mg/kg
Granny Smith juice	0.08	2	93	93, 93
Granny Smith juice	10.0	2	87	81, 93
Granny Smith wet pomace	control	1	<0.08 mg/kg	<0.08 mg/kg
Granny Smith wet pomace	0.08	1	81	81

[1] % recovery for fortified samples, residue concentration for control samples

Thompson (2000) described the analytical method used in supervised trials on pears. The sample was extracted with acetone and cleaned up by repeated solvent partitioning. The residue in the final solution was analysed without derivatization by GLC with an NPD. The LOQ was 0.1 mg/kg. Recoveries were determined from 0.1-24 mg/kg and were generally low but adequate (mean 77%, range 58-93% n=20).

Animal tissues and milk. Keller and Weber (1996b) applied the enforcement analytical method for the determination of diphenylamine residues to samples of milk, liver, kidney and fat from a goat metabolism study (Kim-Kang, 1994c).

Diphenylamine is extracted from whole milk with acetonitrile, which is partitioned with hexane to remove fats. The acetonitrile extract is then evaporated to dryness, redissolved in hexane, and analysed by GC-MSD. The method for tissues is similar, except that after evaporation to dryness the residue is redissolved in a small volume of acetonitrile, diluted with water and partitioned into

hexane. The hexane solution is then analysed by GC-MSD. Recoveries are shown in Table 12. LOQs were 0.01 mg/kg.

Table 12. Recoveries of diphenylamine from goat milk and tissues (Keller and Weber, 1996b).

Sample	Fortification levels (mg/kg)	Mean % recovery	Recoveries, %
Milk	0.01	103	100, 105
Milk	0.10	93	80, 105
Kidney	0.01	111	101, 112, 106, 124
Kidney	0.025	97	97
Liver	0.01	106	100, 111
Fat	0.01	109	139, 80
Fat	0.025	131	131

Determinations by the analytical method are compared with ^{14}C measurements from the metabolism study in Table 13. The results are quite different for milk and kidney, but the measurements were made approximately 3 years apart and diphenylamine may have decreased during storage.

Table 13. Residues of diphenylamine in goat milk and tissues determined by the analytical method (Keller and Weber, 1996b) and by ^{14}C measurement (Kim-Kang, 1994c).

Sample	DPA by analysis (Nov 1995), mg/kg	DPA by ^{14}C measurement (Dec 1992), mg/kg
Milk	0.002	0.063
Kidney	0.002	0.043
Liver	0.004	0.006
Fat	0.006	0.008

Keller and Weber (1996a) used the same method for analysis of milk and tissues from a feeding trial on lactating dairy cows described later and provided validation data (Table 14). The LOQ was 0.01 mg/kg.

Table 14. Recoveries of diphenylamine from the milk and tissues of dairy cows (Keller and Weber, 1996a).

Sample	Fortification levels (mg/kg)	No.	Mean % recovery	Recoveries, %
Whole milk	0.01	3	98	105 94.9 93.9
Whole milk	1.0	3	91	90 91.6 91.6
Skimmed milk	0.01	3	85	103 90.5 61.8
Skimmed milk	1.0	3	88	89.7 85.9 87.9
Cream	0.01	3	112	105 115 115
Cream	1.0	3	96	94.1 98.6 94.6
Muscle	0.01	3	92	96.3 94.4 86.4
Muscle	1.0	3	97	111 74.8 106
Kidney	0.01	3	87	82.6 104 73.7
Kidney	1.0	3	93	100 85.6 91.9
Liver	0.01	3	83	86.5 90.5 71.7
Liver	0.10	3	104	109 104 99
Liver	0.30	3	95	104 96.4 84.2
Fat	0.01	3	95	95 106 85
Fat	0.10	3	94	71.5 106 103
Fat	0.20	3	94	95.5 96.5 90.1

Stability of residues in stored analytical samples

A trial on the stability of diphenylamine residues in fresh apples and processed commodities during frozen storage was reported to the Meeting (Johnson and Strickland, 1995a).

Red Delicious and Granny Smith apples were treated with a 0.20 kg ai/hl dip and 0.22 kg ai/hl drench respectively to simulate commercial post-harvest treatment and samples of whole apples, juice and pomace from the processed apple study described below (Johnson and Strickland, 1995c) were stored in freezers at temperatures between -24°C and -12°C. The results are shown in Table 15.

Degradation rates and the time required for 30% decrease of the residue were calculated from each test by assuming a first-order decrease (rate of decrease proportional to concentration). In each case the time required for 30% decrease exceeded the duration of the test (Table 15).

There were no measurable losses of diphenylamine residues in whole apple, juice or wet and dried pomace over the 155-202 days of the trial.

Table 15. Storage stability of diphenylamine in apples and their processed commodities (Johnson and Strickland, 1995a) Apples were dipped in diphenylamine solutions to simulate commercial post-harvest treatment and stored whole at -24°C to -12°C. Day zero samples from the processed apple residue study (Johnson and Strickland, 1995c) were used in the storage stability study on juice and pomace.

Commodity	Storage period days	DPA residues, mg/kg	Procedural analytical recoveries
Apple, Granny Smith, whole	7	4.3 4.2	
	21	4.4 4.8	
	41		75-86% (0.2-2 mg/kg)
	44	3.5 3.4	90% 96% (2 mg/kg)
	64	4.0 3.8	81% 88% (2 mg/kg)
	94	3.4 3.3	91% 95% (2 mg/kg)
	125	4.1 3.9	110% 110% (10 mg/kg)
	155	3.7 3.9	90% 110% (3.2 mg/kg)
Months for 30% decrease	>5		
Juice, Granny Smith	0	0.40 0.54	86% 94% (1 mg/kg)
	14	0.65 0.58	83% 94% (1 mg/kg)
	28	0.56 0.51	92% 98% (2 mg/kg)
	58	0.54 0.49	70% 86% (0.4 mg/kg)
	106	0.60 0.55	90% 97% (1 mg/kg)
	126	0.82 1.05	93% 110% (1.6 mg/kg)
	202	0.47 0.45	85% 90% (0.4 mg/kg)
Months for 30% decrease	>7		
Wet pomace, Granny Smith	0	98 97	73% 77% (200 mg/kg)
	14	105 88	80% 90% (200 mg/kg)
	28	124 105	89% 93% (200 mg/kg)
	58	117 102	92% 92% (120 mg/kg)
	91	96 106	86% 87% (120 mg/kg)
	122	107 120	110% 110% (120 mg/kg)
	161	92 85	79% 82% (120 mg/kg)
Months for 30% decrease	>6		
Dry pomace, Granny Smith	0	89 104	73% 77% (100 mg/kg)
	14	107 88	73% 87% (100 mg/kg)
	28	109 92	89% 88% (100 mg/kg)
	58	122 122	83% 88% (100 mg/kg)
	91	107 104	93% 100% (120 mg/kg)
	126	(101 108) [1]	64% 69% (100 mg/kg)
	167	86 91	77% 78% (100 mg/kg)

Commodity	Storage period days	DPA residues, mg/kg	Procedural analytical recoveries
Months for 30% decrease	>7		
Apple, Red Delicious, whole	7	2.6 2.5	80% 95% (2 mg/kg)
	12		81% 92% (2.8 mg/kg)
	21	2.9 3.2	93% 110% (0.2 2.0 mg/kg)
	44	3.6 3.6	84% 88% (2 mg/kg)
	64	4.7 4.8	87% 94% (2 mg/kg)
	94	3.6 3.9	94% 100% (2 mg/kg)
	125	2.8 3.2	89% 95% (10 mg/kg)
	155	3.4 3.7	87% 93% (3.2 mg/kg)
Months for 30% decrease	>5		
Juice, Red Delicious	0	0.80 0.76	96% 100% (2 mg/kg)
	14	0.78 0.95	85% 88% (2 mg/kg)
	28	0.80 0.87	85% 93% (2 mg/kg)
	58	0.81 0.86	83% 90% (0.4 mg/kg)
	106	0.90 0.87	98% 99% (1.6 mg/kg)
	126	0.65 0.78	77% 100% (1.6 mg/kg)
	202	0.62 0.62	86% 91% (0.4 mg/kg)
Months for 30% decrease	>7		
Wet pomace, Red Delicious	0	148 137	76% 98% (200 mg/kg)
	14	(117 110) [1]	67% 79% (200 mg/kg)
	28	147 126	86% 97% (200 mg/kg)
	58	132 151	82% 82% (160 mg/kg)
	91	146 134	99% 94% (160 mg/kg)
	122	126 155	79% 86% (120 mg/kg)
	161	137 131	81% 93% (160 mg/kg)
Months for 30% decrease	>6		
Dry pomace, Red Delicious	0	75 72	77% 91% (100 mg/kg)
	14	81 71	75% 74% (100 mg/kg)
	28	67 78	86% 98% (100 mg/kg)
	58	83 87	94% 99% (100 mg/kg)
	91	78 80	91% 97% (80 mg/kg)
	126	(62 59) [1]	59% 83% (100 mg/kg)
	167	72 78	77% 81% (100 mg/kg)
Months for 30% decrease	>6		

[1] Values in parentheses not taken into account because of poor procedural recoveries

In a storage stability study on animal products conducted as part of a livestock feeding study, whole milk, muscle and liver samples fortified at 0.101 mg/kg were stored at -20ºC ± 10ºC for 34 to 54 days. The results are shown in Table 16. During storage diphenylamine residues did not decrease significantly, but analytical variability may have camouflaged small losses.

Table 16. Stability of diphenylamine residues in milk, muscle and liver during freezer storage (Keller and Weber, 1996a).

Sample	Storage period (days)	Fort level, mg/kg	Residues mg/kg	% remaining	Procedural analytical recoveries
Whole milk	0	0.101	0.11, 0.11	109	
	14	0.101	0.090, 0.089	89	101% (0.101 mg/kg)
	31	0.101	0.095, 0.099	96	95% (0.101 mg/kg)
	54	0.101	0.093, 0.095	93	103% (0.101 mg/kg)
Muscle	0	0.101	0.100, 0.108	103	
	15	0.101	0.076, 0.076	75	85% (0.101 mg/kg)
	28	0.101	0.054, 0.062	57	66% (0.101 mg/kg)
	37	0.101	0.103, 0.098	100	111% (0.101 mg/kg)
Liver	0	0.101	0.114, 0.106	109	

Sample	Storage period (days)	Fort level, mg/kg	Residues mg/kg	% remaining	Procedural analytical recoveries
	15	0.101	0.096, 0.096	95	100% (0.101 mg/kg)
	28	0.101	0.101, 0.095	97	106% (0.101 mg/kg)
	38	0.101	0.105, 0.114	108	111% (0.101 mg/kg)

Definition of the residue

The plant metabolism study indicates that the parent compound diphenylamine is the main residue in apples.

The animal metabolism studies on rats, goats and laying hens indicate that the glucuronic and sulfate conjugates of 4-OH-DPA and the parent compound are the main components in animal tissues, milk and eggs.

The Meeting concluded that the current definition (diphenylamine only) is suitable for compliance with MRLs and for the estimation of dietary intake.

The measured log P_{ow} for diphenylamine is 3.6. The animal feeding study showed that diphenylamine residues in fat were higher than in muscle and in milk were associated with the cream, suggesting the compound should be designated fat-soluble. The Meeting recommended that diphenylamine should be described as fat-soluble.

USE PATTERN

Long-term exposure of apples to low temperatures in controlled-atmosphere storage commonly induces a physiological disorder known as scald. Diphenylamine is registered in a number of countries for post-harvest application to apples for reducing scald during storage. The two most commonly treated varieties are Red Delicious and Granny Smith. The information reported to the Meeting on registered uses is shown in Table 17.

Table 17. Registered uses of diphenylamine.

Crop	Country	Form	Application			Notes
			Method	Dip conc. kg ai/hl	Contact time	
Apples	Australia	EC 310 g/l	dip	0.05-0.36	minimum 10-30 secs	[1] [2]
Apples	France		dip	0.04-0.20	30 secs	[3]
Apples	France		drench	0.04-0.20	30 secs to 2 mins	[3]
Apples	Greece		dip, drench or fog	0.075-0.20	max 2 mins	[4]
Apples	Israel		drench or dip	0.20-0.30	max 2 mins	
Apples	Italy		dip, drench or fog	0.075-0.20	max 2 mins	[4]
Apples	Lebanon		dip, drench or fog	0.075-0.20	max 2 mins	[4]
Apples	South Africa		dip or spray	0.20	30 secs to 2 mins	general case
Apples	South Africa		dip or spray	0.20-0.30	30 secs to 2 mins	Granny Smith
Apples	Syria		dip, drench or fog	0.075-0.20	max 2 mins	[4]
Apples	Turkey		dip, drench or fog	0.075-0.20	max 2 mins	[4]
Apples	UK		dip	0.04-0.20	30 secs	[3]
Apples	UK		drench	0.04-0.20	30 secs to 2 mins	[3]
Apples	USA	EC 150 g/l	dip, spray or drench	0.10-0.22	max 2 mins	[5] [2]
Pears	Australia	EC 310 g/l	dip	0.037-0.26	minimum 10-30 secs	[1] [2]

Crop	Country	Form	Application			Notes
			Method	Dip conc. kg ai/hl	Contact time	
Pears	Greece		dip, drench or fog	0.075	max 2 mins	
Pears	Italy		dip, drench or fog	0.075	max 2 mins	
Pears	Lebanon		dip, drench or fog	0.075	max 2 mins	
Pears	Syria		dip, drench or fog	0.075	max 2 mins	
Pears	Turkey		dip, drench or fog	0.075	max 2 mins	

[1] Concentration depends on variety and intended storage. DPA moves into pears, thin-skinned and russet apples and pears faster than into thick-skinned apples such as Granny Smith. The rates for different varieties therefore vary.
[2] Label provided
[3] American red, Granny or Melrose : 1800-2000 ppm ; Idared, Jonagold, 2-colour variety : 900-1000 ppm ; Golden : 400-620 ppm
[4] Concentration depends on variety
[5] Use 0.10 kg ai/hl for Cortland McIntosh, Roma Beauty, Turley, Stayman and Winesap varieties; 0.20 kg ai/hl for Red Delicious and Fuji; 0.22 kg ai/hl for Granny Smith.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised trials on apples and pears were reported to the Meeting in full, with recoveries from fortified samples at appropriate levels and duration of sample storage. The results and dip concentrations have generally been rounded to 2 significant figures. The results are unadjusted for % recovery. Procedural recoveries for the Granny Smith and Delicious apples were mean 83% and 95%, SD 7.6% and 20% respectively.

In a trial from local orchards in the USA Red Delicious apples were dipped post-harvest and Granny Smith apples drenched, using duplicate treatment solutions and 75 apples of each kind weighing a minimum of 13 kg. Treated and control samples were placed in a controlled atmosphere and stored mainly at 0-1.5°C, 1.5% O_2 and 1.5-2% CO_2. The cold store for the Granny Smiths was opened on day 202 and until day 260 the temperature was approximately 5°C, and CO_2 and O_2 levels uncontrolled. Samples were withdrawn at intervals for analysis (Johnson and Strickland, 1995b). The results are shown in Table 18.

Pears from each of two local orchards in the USA were dipped. Four separate batches of diphenylamine dip solution were prepared and the pears (50 per batch) were dipped at the label rate for 2 min and set aside to dry (Thompson, 2000). Samples of 24 pears were then selected from each batch and stored in a freezer for 256 days. Three samples of pears spiked with diphenylamine at 9.6 mg/kg and stored in a freezer for 266 days retained 77-83% of the added diphenylamine. The results are shown in Table 19.

Table 18. Diphenylamine residues in apples from supervised trials with post-harvest treatments in WA, USA, 1993. Double-underlined residues are from treatments according to GAP and are valid for the estimation of an MRL. All EC formulations.

Variety	Application			Days[1]	Residues, mg/kg	Ref
	kg ai/hl	Type	No.			
Red Delicious	0.20	dip	1	0 90 181 281 0 90 181 261	<u>5.5</u> 4.6 4.3 3.5 c <0.08 (2) c <0.08 (2) c 0.16 0.13 c 0.15 0.21	DPA 93-01
Red Delicious	0.20	dip	1	0 90 181 281 0 90 181 261	6.2 <u>6.3</u> 3.6 2.9 c <0.08 (2) c <0.08 (2) c 0.16 0.13 c 0.15 0.21	DPA 93-01
Granny Smith	0.22	drench	1	0 91 181 260 0 91 175 240	<u>3.4</u> 2.5 2.0 1.1 c <0.08 (2) c 0.14 0.092 c 0.14 0.14 c 0.21 0.26	DPA 93-01
Granny Smith	0.22	drench	1	0 91 181 260 0 91 175 240	<u>3.4</u> 2.4 2.1 0.96 c <0.08 (2) c 0.14 0.092 c 0.14 0.14 c 0.21 0.26	DPA 93-01

[1] Treatment to sampling interval during controlled atmosphere storage
c: sample from untreated control

Table 19. Diphenylamine residues in Bartlett pears from supervised trials with post-harvest treatments in the USA in 2000 (Thompson, 2000). Double-underlined residues are from treatments according to GAP and are valid for MRL estimation. All EC formulations. All analyses on day of treatment.

Location	Application			Residues, mg/kg	Ref
	kg ai/hl	Type	No.		
ID	0.20	dip	1	2.1	06879.98-ID05
ID	0.20	dip	1	2.1	06879.98-ID05
ID	0.20	dip	1	2.9	06879.98-ID05
ID	0.20	dip	1	2.5	06879.98-ID05
WA	0.20	dip	1	2.3	06879.98-WA21
WA	0.20	dip	1	2.0	06879.98-WA21
WA	0.20	dip	1	2.4	06879.98-WA21
WA	0.20	dip	1	1.8	06879.98-WA21

Livestock feeding trials

In a feeding study reported to the Meeting (Keller and Weber, 1996a) lactating Holstein dairy cows (body weights ranging from 460-656 kg on the day before trial began) which had produced more than 19.3 kg of milk/day as an average during acclimatization, were given twice daily (after each milking) gelatine capsules containing diphenylamine for 28 days and slaughtered on day 29. Control animals were given empty gelatine capsules. Three groups each consisting of three cows were given doses equivalent to approximately 30, 90 and 300 ppm in the diet (dry-weight basis). Daily dry feed intake per animal ranged from 16.2 kg to 27.2 kg, mean 21.4 kg.

Samples of milk were collected on acclimatisation day 5 in the morning and then from each morning and afternoon milking from the day before the first dose until the morning of day 29. The animals were slaughtered within 22 hours of the last dose. Samples of liver, kidney, fat and muscle were homogenized and stored in a freezer for 1-54 days (milk), 34–35 days (muscle), 35-36 days (liver), 26-27 days (kidney), 19-20 days (fat) 12-15 days (cream) and 21-26 days (skimmed milk) before analysis. The results are shown in Table 21.

Levels of diphenylamine below the LOQ were detected in the milk on days 14, 21 and 24 in control samples, and at or about the LOQ (0.005 mg/kg) in the 30 and 90 ppm groups sometimes. Residues in milk from the 300 ppm feeding group were up to 0.014 mg/kg. When day 14 milk was separated into cream and skimmed milk residues partitioned into the fat fraction.

No residues were present in muscle at any dosage level and in kidneys only at the highest level. Residues were determined in fat, liver and cream at all feeding levels, allowing calculation of transfer factors (Table 20). Transfer factors for body fat and cream are quite similar, and in cream and liver appear to decrease with increased feeding levels.

Table 20. Transfer factors for diphenylamine in dairy cattle feed. Values are calculated for the mean and maximum residues in the 3 animals in the feeding group.

Feeding level, diphenylamine, ppm dry weight	Mean residue, mg/kg			Transfer factor = residue in sample ÷ feeding level		
	cream	liver	fat	cream	liver	fat
30	0.0098	0.034	0.006	0.00033	0.0011	0.00020
90	0.0190	0.053	0.0177	0.00021	0.00059	0.00020
300	0.0492	0.153	0.0533	0.00016	0.00051	0.00018
	Max residue, mg/kg					
		liver	fat	cream	liver	fat
30		0.068	0.006		0.0027	0.0002
90		0.070	0.020		0.00078	0.00022
300		0.257	0.109		0.00086	0.00036

Table 21. Residues in the milk and tissues of lactating Holstein dairy cattle, 3 animals per group, dosed twice daily for 28 days with diphenylamine equivalent to 30, 90 and 300 ppm in the diet on a dry-weight basis and slaughtered on day 29 (Keller and Weber, 1996a). Each recorded residue is from a single animal.

Sample	Diphenylamine, mg/kg [2]		
	Low dose (30 ppm)	Medium dose (90 ppm)	High dose (300 ppm)
Milk			
Day -1	<0.005, ND(2)	<0.005 (2), ND	<0.005, ND, <0.005
Day 1	<0.005 (3)	ND (2), <0.005	ND, <0.005, 0.005
Day 4	<0.005, ND, <0.005	<0.005 (3)	<0.005, 0.005, <0.005
Day 7	0.005 (3)	0.005, <0.005, 0.005	0.005, 0.006 (2)
Day 10	<0.005 (3)	<0.005 (3)	<0.005, 0.014, 0.008
Day 14 evening [1]	<0.005, 0.005, <0.005	0.006, 0.005, 0.006	<0.005, 0.006, 0.008
Day 14 morning	0.005, ND (2)	ND, 0.005 (2)	ND, 0.006, 0.005
Day 18	<0.005 (2), 0.005	<0.005 (3)	<0.005, 0.005 (2)
Day 21	0.005 (2), <0.005	0.005 (3)	0.006, 0.010, 0.008
Day 24	<0.005 (3)	<0.005, 0.005, <0.005	0.005, 0.012, 0.008
Day 28	<0.005 (3)	<0.005 (3)	<0.005, 0.005, <0.005
Skimmed milk			
Day 14 evening	ND (3)	ND (3)	ND (2), 0.005
Day 14 morning	<0.005, 0.011, ND	<0.005 (3)	<0.005 (3)
Cream			
Day 14 evening	0.011, 0.010, 0.008	0.028, 0.013, 0.020	0.014, 0.061, 0.059
Day 14 morning	0.009, 0.010, 0.011	0.017, 0.016, 0.020	0.013, 0.103, 0.045
Mean residue	0.0098	0.0190	0.0492
Liver			
	0.018, 0.016, 0.068	0.044, 0.045, 0.070	0.064, 0.257, 0.137
Mean residue	0.034	0.053	0.153
Kidney			
	<0.005 (3)	<0.005 (3)	0.006, 0.010, 0.006
Muscle			
	<0.005 (3)	<0.005 (3)	<0.005 (3)
Fat			
	0.006 (3)	0.020, 0.014, 0.019	0.022, 0.109, 0.029
Mean residue	0.006	0.0177	0.0533

[1] Note that "Day" refers to study day, which began when the first half-dose was given after the morning milking, so that the evening milking on study day 14 preceded the morning milking on study day 14.
[2] LOQ 0.01 mg/kg, LOD 0.005 mg/kg
ND: not detected

FATE OF RESIDUES IN STORAGE AND PROCESSING

Stability in commercial storage.

The Meeting received information on the stability of diphenylamine in whole apples after post-harvest treatments stored in controlled atmospheres at approximately 0-1°C, 1.2 -1.5% O_2 and 1.9% CO_2. The results are shown in Table 18.

Meherink *et al.* (1988) showed that diphenylamine residues on freshly-dipped Red Delicious apples at 20°C placed in a storage cabinet at 0°C were partially transferred to untreated pears already in the cabinet. After 30 days the levels of diphenylamine in the pears in the top and bottom of the container were 0.6 and 0.2 mg/kg respectively. It would appear that diphenylamine evaporated from the warm apples and condensed on the cold pears in storage.

Bramlage *et al.* (1996) investigated whether diphenylamine is endogenous in apples. Hexane rinses from the surface of freshly harvested apples from a number of sources, when examined by GC-MS, contained a diphenylamine-like substance. It may have been diphenylamine contaminated with a similar compound or a related compound that after derivatization with heptafluorobutyric anhydride produced three mass spectral ions at 168, 278 and 365 as in derivatized diphenylamine, but with different abundances. The authors concluded that the presence of endogenous diphenylamine was not proved but in any case its concentration would not exceed 0.01 mg/kg.

In processing

The Meeting received information on the fate of diphenylamine during commercial processing of apples (Johnson and Strickland, 1995c).

Red Delicious apples were dipped in 2.0 kg ai/hl diphenylamine and Granny Smith apples drenched at 2.2 kg ai/hl, both treatments at 10 times the US label rate. Including controls, all treatments included the fungicide thiabendazole at 0.053 kg ai/hl to prevent spoilage in storage, which is standard industrial practice. Some treated and control apples were processed directly while others were placed in a commercial controlled atmosphere store before processing. Six samples of both varieties were treated; the day 0 samples each consisted of 150 apples (approximately 27 kg), and the stored samples 75 apples (approximately 13 kg). Duplication in the experiment was based on duplicated treatment solutions.

Apples were processed into juice, wet pomace and dried pomace using simulated small-scale industrial procedures. The apples were washed in a tub, sorted, crushed, and pressed to wet pomace which was dried in a bin air dryer at 79-93°C to less than 10% moisture to produce dried pomace. The juice was filtered to produce a fresh juice fraction. The results and calculated processing factors are shown in Table 22.

Calculated processing factors from unwashed apples to processed products were juice, mean 0.051, range 0.022-0.12; wet pomace, mean 4.7, range 2.3-8.4; dry pomace, mean 2.4, range 1.4-3.6. Diphenylamine is volatilized during drying resulting in a lower processing factor for dry than for wet pomace.

Table 22. Diphenylamine residues in apples, juice and pomace from processing treated apples after treatment or after controlled atmosphere storage.

Apple variety	Commodity	Apple storage period, days [1]	Diphenylamine, mg/kg	Processing factor [2]
Red Delicious	unwashed apples	0	33.6	
	juice	0	1.27	0.038
	wet pomace	0	128	3.8
	dried pomace	0	63.5	1.9
Red Delicious	unwashed apples	0	25.6	
	juice	0	1.48	0.058
	wet pomace	0	160	6.3
	dried pomace	0	46.2	1.8
Red Delicious	unwashed apples			
	juice	181	0.93	
	wet pomace	181	74.1	
	dried pomace	181	52.5	
Red Delicious	unwashed apples			
	juice	181	1.10	
	wet pomace	181	92.8	
	dried pomace	181	55.6	
Red Delicious	unwashed apples	281	28.8	
	juice	281	0.85	0.030
	wet pomace	281	66.7	2.3
	dried pomace	281	40.4	1.4
Red Delicious	unwashed apples	281	10.3	
	juice	281	0.66	0.064
	wet pomace	281	62.4	6.1
	dried pomace	281	34.0	3.3
Granny Smith	unwashed apples	0	31.6	
	juice	0	0.694	0.022
	wet pomace	0	99.0	3.1
	dried pomace	0	99.8	3.2
Granny Smith	unwashed apples	0	25.3	
	juice	0	0.628	0.025
	wet pomace	0	89.5	3.5
	dried pomace	0	38.3	1.5
Granny Smith	unwashed apples			
	juice	181	0.910	
	wet pomace	181	72.6	
	dried pomace	181	35.6	
Granny Smith	unwashed apples			
	juice	181	0.494	
	wet pomace	181	51.9	
	dried pomace	181	15.0	
Granny Smith	unwashed apples	260	4.63	
	juice	260	0.558	0.121
	wet pomace	260	38.8	8.4
	dried pomace	260	16.5	3.6
Granny Smith	unwashed apples	260	5.68	
	juice	260	0.284	0.050
	wet pomace	260	23.4	4.1
	dried pomace	260	13.8	2.4

[1] Controlled atmosphere

[2] Processing factor: residue in processed commodity ÷ residue in unwashed apples

RESIDUES IN FOOD IN COMMERCE OR CONSUMPTION

Monitoring data

The government of The Netherlands reported data for diphenylamine on several commodities to the Meeting. The results are summarized in Table 23.

Table 23. Monitoring data for diphenylamine on several commodities in The Netherlands.

Commodity	No. of samples	No. of samples with residues [1]	MRL, mg/kg	No. of samples >MRL	Year
Apples	1495	57	5		1994-1996
Apples	398	10	5		1997
Apples	93	5	5		1998
Asparagus	244	0	0.05*		1994-1996
Aubergines	148	1	0.05*	1	1994-1996
Bananas	57	0	0.05*		1994-1996
Beans (with pods)	133	1	0.05*	1	1998
Beetroot	83	0	0.05*		1994-1996
Carrots	407	0	0.05*		1994-1996
Courgettes	206	0	0.05*		1994-1996
Cucumbers	951	0	0.05*		1994-1996
Endive	1137	0	0.05*		1994-1996
Grapes	667	0	0.05*		1994-1996
Iceberg lettuce	471	0	0.05*		1994-1996
Lettuce	3306	0	0.05*		1994-1996
Mangoes	191	0	0.05*		1994-1996
Mushrooms	384	0	0.05*		1994-1996
Onion	97	0	0.05*		1994-1996
Oranges	902	0	0.05*		1994-1996
Passion fruit	40	0	0.05*		1994-1996
Pears	34	3	0.05*	3	1998
Peppers	1525	0	0.05*		1994-1996
Plums	437	0	0.05*		1994-1996
Pulses	42	0	0.05*		1994-1996
Strawberries	2378	1	0.05*	1	1994-1996
Swedes	9	0	0.05*		1994-1996
Sweet corn	27	0	0.05*		1994-1996
Tomatoes	1108	0	0.05*		1994-1996

[1] Limit of quantification 0.05 mg/kg

Monitoring data from the USDA Pesticide Data Program for 1994, 1995, 1996 and 1997 are summarized in Table 24.

Table 24. Monitoring data from the USDA Pesticide Data Program.

Commodity	No. of samples	No. of samples with residues	Number of samples in residue range (mg/kg)							Year
			<0.05	<0.5	<1.0	<2.0	<3.0	<5.0	>5.0	
Apple juice	171	17	14	3						1996
Apple juice	668	57	45	12						1997
Apples	629	438	76	117	125	93	16	10	1	1994
Apples	691	489	73	138	118	131	21	7	1	1995
Apples	524	452	52	121	146	105	22	6	0	1996
Bananas	508	0								1994
Bananas	479	1		1						1995
Broccoli	545	0								1994
Carrots	554	0								1994
Carrots	701	0								1995
Carrots	500	0								1996

Commodity	No. of samples	No. of samples with residues	Number of samples in residue range (mg/kg)							Year
			<0.05	<0.5	<1.0	<2.0	<3.0	<5.0	>5.0	
Celery	143	0								1994
Grapes	537	1	1							1994
Grapes	677	1	1							1995
Grapes	519	0								1996
Green beans	473	0								1994
Green beans	587	0								1995
Green beans	525	0								1996
Green beans	693	6	5	1						1997
Lettuce	542	0								1994
Milk	346	0								1996
Orange juice	678	2	2							1997
Oranges	506	0								1994
Oranges	549	0								1995
Oranges	454	1		1						1996
Peaches	299	0								1994
Peaches	285	1	1							1995
Peaches	735	1		1						1997
Peaches	280	5	2	3						1996
Potatoes	539	0								1994
Potatoes	692	1		1						1995
Spinach	477	0								1995
Spinach	441	0								1996
Spinach	498	0								1997
Spinach, canned	168	2	1	1						1997
Squash	426	1	1							1997
Sweet corn	327	0								1994
Sweet corn	671	0								1995
Sweet corn	173	0								1996
Sweet peas	245	0								1994
Sweet peas	601	0								1995
Sweet peas	355	0								1996
Sweet potatoes	507	1	1							1996
Sweet potatoes	695	1	1							1997
Tomatoes	168	0								1996
Tomatoes	707	4	4							1997

Monitoring data from a review of the US Food and Drug Administration Pesticide Monitoring Database for Fiscal years 1992, 1993, 1994, 1995, 1996, 1997 and 1998 are shown in Table 25.

Table 25. US FDA pesticide monitoring data for diphenylamine.

Commodity	No. of samples with residues	Number of samples in residue range (mg/kg)							Year
		<0.05	<0.5	<1.0	<2.0	<3.0	<5.0	>5.0	
Apples	45			4	4	16	15	6	1992
Apples	8		2	1	2	3			1993
Apples	6	1	1	2	2				1994
Apples	16	5	3	2	4	2			1995
Apples	28	13	15						1996
Apples	18	4	6	4	1	2	1		1997
Apples	31	15	10	2	4	1			1998
Apple juice	1			1					1993
Apple juice	1		1						1994
Apple juice	2	2							1996
Apple juice	5	5							1997

Commodity	No. of samples with residues	Number of samples in residue range (mg/kg)							Year
		<0.05	<0.5	<1.0	<2.0	<3.0	<5.0	>5.0	
Apple juice	1	1							1998
Pear	6	2	4						1995
Pear	1	1							1996
Pear	5	2	3						1997
Pear	4	3	1						1998

Data for diphenylamine residues in pears from the targeted monitoring program in Victoria, Australia, were reported for 1995-97. The results are shown in Table 26.

Table 26. Diphenylamine residues in pears from the targeted monitoring program from Victoria, Australia, for 1995-97.

No. of samples analysed	No. of samples with diphenylamine	No. of samples in range (mg/kg)						
		<0.1	<0.5	<1.0	<2.0	<3.0	<4.0	<5.0
26	26	0	7	4	7	3	3	2

Diphenylamine was included in the 1996 Australian Market Basket Survey (Hardy, 1998). The estimated daily dietary intake for diphenylamine residues in food expressed as % ADI for diets based on mean energy intake were 2.1% for adult males, 2.8% for adult females, 3.2% for boys aged 12, 2.6% for girls aged 12, 11.8% for toddlers and 8.6% for infants (ADI 0.02 mg/kg bw).

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed of the following national MRLs.

Country	MRL, mg/kg	Commodity
Australia	5	Apples
	7	Pears
USA	10	Apples
	0	Meat, milk
Netherlands	5	Apples
	0.05*	Other food commodities

APPRAISAL

Diphenylamine was first evaluated in 1969. Its toxicology was reviewed by the 1998 JMPR, which allocated an ADI of 0–0.08 mg/kg bw and concluded that an acute RfD was unnecessary. Diphenylamine was reviewed by the present Meeting within the CCPR periodic review programme.

The Meeting received information on physical and chemical properties, metabolism and environmental fate, analytical methods, stability on storage, farm animal feeding, use pattern, residues in supervised trials on apples and pears and a study of processing.

METABOLISM

Animals

When rats were dosed orally with [^{14}C-ring]diphenylamine at 5 or 750 mg/kg bw, the compound was extensively absorbed and was excreted mainly in urine. Only 0.14–0.28% of the dose remained in tissues and organs of animals at the low dose 168 h after dosing. The radiolabel in expired air accounted for < 0.01% of the administered dose. Twelve metabolites were identified, most of which were hydroxylated diphenylamines and their glucuronide and sulfate conjugates. The parent and these 12 metabolites accounted for 81–93% of the dose in excreta.

When two lactating goats were dosed orally with encapsulated [^{14}C]diphenylamine for 7 days at a level equivalent to 46 ppm in the feed, the total amount excreted in urine and faeces accounted for about 94% of the dose. TRRs in milk reached equilibrium rapidly. The concentrations of radiolabel in tissues were low, but more was found in kidney and liver than in fat or muscle. A significant proportion of the residues in fat and kidney (30–36%) and some residues in liver and milk (4–12%) were unmetabolized parent compound.

Several polar metabolites were identified, including 4-hydroxydiphenylamine, 4,4'-dihydroxy-diphenylamine, indophenol and the sulfate and glucuronic acid conjugates of 4-hydroxydiphenylamine. Ring hydroxylation followed by conjugation with either a sulfate moiety or glucuronic acid was the main metabolic pathway.

Approximately 91% of the administered dose was recovered in the excreta of 15 laying hens dosed orally with encapsulated [^{14}C]diphenylamine for 7 successive days at a level equivalent to 50 ppm in feed. The concentrations of TRR (as diphenylamine) in liver, kidneys, breast muscle, thigh muscle and fat/skin samples were 0.15, 0.21, < 0.01 < 0.01, and 0.04 mg/kg, respectively, while those in egg yolk ranged from < 0.01 to 0.38 mg/kg and those in egg whites were < 0.01 mg/kg. A significant proportion of the residues in fat and skin and egg yolk were unmetabolized parent compound (17–35%); however, most (58%) of the residues in egg yolk were identified as a sulfate conjugate of 4-hydroxydiphenylamine, which also appeared in the other tissues.

The study of metabolism in hens showed that diphenylamine can be hydroxylated on the ring at position 4 or 2 and hydroxylated on the second ring. All these metabolites may subsequently be conjugated with glucuronic acid, sulfate and other groups.

PLANTS

In a study of the metabolism of diphenylamine in stored Red Delicious apple, the fruit were treated with an emulsion of [U-^{14}C-ring]diphenylamine, resulting in a residue of approximately 50 mg/kg, and stored at 2 °C and 95% relative humidity for 40 weeks. Most of the pesticide was absorbed into the peel within 2 days. The residue then slowly migrated into the pulp, and, after 40 weeks, the pulp contained 32% of the residue. After 40 weeks' storage, the parent compound accounted for approximately 41% of the TRR in the apples, with 37% as conjugates and 8% as hydroxydiphenylamines. Diphenylamine was converted to 2-, 3- and 4-hydroxydiphenylamines and a dihydroxydiphenylamine, which was then conjugated with glucose and oligosaccharides. The unknown non-polar metabolites, accounting for 0.52% of the residue in the apples, were not related to 4-aminobiphenyl, 2-aminobiphenyl or *N*-nitrosodiphenylamine.

ENVIRONMENTAL FATE

SOIL

When [^{14}C-ring]diphenylamine was incubated in a loam soil at a nominal rate of 10 mg/kg under aerobic conditions at 25 °C in the dark for 12 months, diphenylamine initially disappeared rapidly, but after about 7 days the disappearance was quite slow. After 12 months 15% of the dose remained as diphenylamine, 49% was unextractable, and 18% was mineralized. The metabolites were polymeric and not identified.

When [^{14}C-ring]diphenylamine was tested for adsorption and desorption on four soils and a sediment, its mobility ratings were slight, immobile, immobile, slight and low in a loam, a silty clay loam lake sediment, a clay, a loamy sand and a silt loam, respectively.

Residues of [^{14}C-ring]diphenylamine were aerobically aged on four soils for 1 day and then leached through columns of the soils with 0.01 mol/L $CaCl_2$. The mobility ratings for the aged residues were: loam, slight; loam sand, low; silt loam, low; clay, immobile. Metabolites were identified in extracts from the soil columns as *N*,*N*-diphenylformamide (2.0–4.7% of dose) and 4-nitro-*N*-phenylbenzenamine (1.3–5.3% of dose).

WATER–SEDIMENT SYSTEMS

In a photolysis study, carbazole was identified as a major product when diphenylamine in an aqueous solution was subjected to UV irradiation, with approximately 7% formed within 0.5 h and a maximum of 52% at 10.5 h. Hydroxydiphenylamine was also identified, reaching a maximum value of 16% by 36 h. A third product, an indenohydroxyindole, reached a value of 93% by the end of the 192-h irradiation period. Small amounts of trimeric products were also formed.

When [^{14}C-ring]diphenylamine was incubated with a lake water and sediment under anaerobic conditions in the dark at 25 °C, the half-life for disappearance was approximately 60 days. The products of decomposition were soil-bound or soil-incorporated residues, which mineralized slowly (2.7% of the dose in 1 year).

METHODS OF ANALYSIS

The Meeting received information on GLC methods for the analysis of diphenylamine residues in fruit, processed apples and animal commodities.

Plant matrices

Whole apples were homogenized in a food processor with liquid nitrogen to produce a white powder, and an analytical sample of homogenized whole apples or wet pomace, dry pomace or apple juice was blended with acetone and filtered. Diphenylamine residues were extracted from the aqueous acetone

with hexane and then derivatized with trifluoroacetic anhydride in dichloromethane to produce trifluoroacetylated diphenylamine for GLC–MS analysis. The LOQ for diphenylamine residues in apples, juice and wet pomace was 0.08 mg/kg, and that for dry pomace was 1 mg/kg. The mean recovery from the four matrices was 85% (range, 51–150%, *n* = 85).

In the analytical method used in a supervised trial on pears, the sample was extracted with acetone and subjected to a number of solvent partitioning clean-up steps. The residue in the final solution was analysed, without derivatization, by GLC–NPD. The LOQ was 0.1 mg/kg. Recoveries were tested after addition of 0.1–24 mg/kg and were generally low, but satisfactory (mean, 77%; range, 58–93%; *n* = 20).

Animal matrices

In the method of analysis for diphenylamine residues in milk and animal tissues, the matrix was extracted with acetonitrile, which was partitioned with hexane to remove fats. The acetonitrile extract was then evaporated to dryness, redissolved in hexane, and analysed by GLC with mass-selective detection. The LOQ was 0.01 mg/kg. In validation testing for whole milk, skim milk, cream, muscle, kidney, liver and fat after spiking with 0.01–1 mg/kg, the mean recovery was 94% (range, 62–115%; *n* = 96).

Tissues and milk from goats in the study of metabolism were analysed for diphenylamine for comparison with the measurement of [^{14}C]diphenylamine. The results were reasonably close for liver and fat, but not for milk and kidney. However, the measurements were made approximately 3 years apart, and diphenylamine may have depleted during storage.

STABILITY OF RESIDUES IN STORED ANALYTICAL SAMPLES

Data on stability during freezer storage were provided for diphenylamine residues in whole apples, juice, wet pomace, dry pomace, whole milk, muscle and liver. The residues in whole apples, juice, wet pomace, and dry pomace were stable for 5–7 months, those in whole milk for 8 weeks and those in muscle and liver for 6 weeks.

DEFINITION OF THE RESIDUE

The parent compound diphenylamine is the main component of the residue in apples. The gluconic and sulfate conjugates of 4-hydroxydiphenylamine and the parent compound are the main components in animal tissues, milk and eggs. The conjugates of 4-hydroxydiphenylamine can be regarded as intermediates in the process of detoxication and excretion and need not be included in the residue definition for dietary risk assessment. All the plant metabolites were also animal metabolites.

The Meeting concluded that the current definition (diphenylamine only) is suitable for assessing compliance with MRLs and for estimating dietary intake.

The measured log P_{ow} for diphenylamine is 3.6. The animal feeding study showed that the concentrations of diphenylamine residue in fat were higher than in muscle, and that in milk diphenylamine was associated with the cream, suggesting the compound should be designated fat-soluble. The Meeting recommended that diphenylamine be described as fat-soluble.

RESULTS OF SUPERVISED TRIALS

Diphenylamine is registered for post-harvest use on apple in the USA as a dip, spray or drench at a concentration of 0.20 kg ai/hl for Red Delicious and 0.22 kg ai/hl for Granny Smith and a maximum contact time of 2 min. The concentrations of residues in apples in four trials meeting GAP in the USA were 3.4, 3.4, 5.5 and 6.3 mg/kg.

Although data were available on residues from only four trials, the Meeting agreed that the data were sufficient because post-harvest trials need not cover the range of variables that occur in a field situation. The trials did include dip and drench methods of application.

The Meeting estimated a maximum residue level and an STMR value for diphenylamine in apples of 10 and 4.45 mg/kg respectively. The estimated maximum residue level replaces the current recommendation (5 mg/kg) for apple.

Diphenylamine is registered for post-harvest use on pears in Australia as a dip at a concentration of 0.037–0.26 kg ai/hl and a minimum contact time of 10–30 s. The concentrations of residues in pears in eight trials in the USA that matched Australian GAP (The dip concentration of 0.20 kg ai/hl was 23% below specified GAP, but sufficiently close.), in rank order (median underlined), were: 1.8, 2.0, 2.1 (2), 2.3, 2.4, 2.5 and 2.9 mg/kg.

The Meeting agreed that Australian GAP could be applied to the trials in the USA for post-harvest use. The Meeting estimated a maximum residue level and an STMR value for diphenylamine in pears of 5 and 2.2 mg/kg, respectively.

FATE OF RESIDUES DURING STORAGE AND PROCESSING

Treated apples from the supervised trials were held in commercial cold storage, and diphenylamine residues were measured at intervals. The concentrations declined with an average half-life of 7–8 months. There is some evidence that small amounts of diphenylamine may be transferred from treated to untreated fruit in the same store.

Fate of residues during processing

When diphenylamine-treated apples were processed into juice, wet pomace and dried pomace by procedures that simulated small-scale industrial practices, the residues tended to concentrate in the pomace and deplete in the juice. The first step in the process was washing, which would be expected to reduce surface residues.

The calculated processing factors for unwashed apples to processed commodity were: juice, mean 0.051, range 0.022–0.12; wet pomace, mean 4.7, range 2.3–8.4; dry pomace, mean 2.4, range 1.4–3.6. Diphenylamine is volatilized during drying, resulting in a lower processing factor for dry pomace than for wet pomace.

The Meeting applied these processing factors to the estimated maximum residue level (10 mg/kg) and STMR value (4.45 mg/kg) for apples to provide estimates for the processed commodities. The Meeting estimated a maximum residue level and an STMR-P value for diphenylamine in apple juice of 0.5 and 0.23 mg/kg respectively, an STMR-P value for diphenylamine in wet apple pomace of 21 mg/kg, and a maximum residue level and an STMR-P value for diphenylamine in dry apple pomace of 25 and 10.6 mg/kg, respectively.

RESIDUES IN ANIMAL COMMODITIES

DIETARY BURDEN IN FARM ANIMALS

The Meeting estimated the dietary burden of diphenylamine residues in farm animals on the basis of the diets listed in Appendix IX of the *FAO Manual*. As the only feed commodities listed are processed, the dietary burdens for the estimated MRL and STMR value are the same.

Commodity	Group	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Apple pomace, wet	AB	21	STMR-P	40	53	40	20		21	11.5	
Apple pomace, dry	AB	10.6	STMR-P	90	11.8						
					Total	40	20		21	11.5	

FEEDING STUDIES

Groups of three lactating Holstein dairy cows were dosed orally by capsule twice daily for 28 days (once after each milking) at a dose equivalent to 30, 90 and 300 ppm in the diet (dry weight). The animals were slaughtered on day 29 for tissue collection and analysis.

Diphenylamine residues were detected in milk on some occasions in the groups given 30 or 90 ppm, but at or about the LOQ (0.005 mg/kg). The concentrations of residues in milk from cows at 300 ppm were up to 0.014 mg/kg. When milk collected on day 14 was separated into cream and skim milk, the residues partitioned into the fat fraction.

The concentration of residues in muscle was < 0.005 mg/kg, even at the highest feeding level, and those in kidney were just measurable (0.006–0.01 mg/kg) at this level. Residues were measured in liver, fat and day-14 cream in cows at all three feeding levels, the mean values being 0.034, 0.053 and 0.153 mg/kg in liver; 0.006, 0.0177 and 0.053 mg/kg in fat; and 0.0098, 0.019 and 0.0492 mg/kg in

cream at the three feeding levels. The transfer factor (residue in tissue ÷ residue in feed) for fat was consistent across feeding levels: 0.00020, 0.00020 and 0.00018, but the factors for cream and liver were less consistent.

MAXIMUM RESIDUE LEVELS

The dietary burdens of diphenylamine for estimation of MRL and STMR values in animal commodities (residue concentrations in animal feeds expressed in dry weight) were 21 mg/kg for beef cattle and 11.5 mg/kg for dairy cows. As the dietary burden for beef cattle is higher than that for dairy cows, it should be used to estimate residues in tissues. The dietary burdens were lower than the lowest feeding level (30 ppm), so the resulting residues in tissues and milk were calculated by applying the transfer factors at the lowest feeding level to those dietary burdens.

The highest individual concentration of tissue residue in the relevant feeding group was used in conjunction with the dietary burden to calculate the probable highest residue in animal commodities. The mean value in tissues from animals in the relevant feeding group was used in conjunction with the dietary burden to estimate the STMR values for animal commodities. For milk (cream), the mean residue in milk (cream) at the plateau level in the relevant feeding group was used to estimate both the highest residue and the STMR value.

Feeding level (ppm) *Interpolated* / Actual	Diphenylamine residues (mg/kg)				
	Cream	Fat		Liver	
	(mean)	High	Mean	High	Mean
MRL beef cattle *21* / 30		*0.0042* / 0.006		*0.048* / 0.068	
MRL dairy cows *11.5* / 30	*0.0038* / 0.0098				
STMR beef cattle *21* / 30			*0.0042* / 0.006		*0.024* / 0.034
STMR dairy cows *11.5* / 30	*0.0038* / 0.0098				

The concentrations of residues in muscle and kidney were < 0.005 mg/kg and 0.007 mg/kg, respectively, at the highest feeding level (300 ppm). The Meeting agreed that residues in muscle and kidney at a feeding level of 21 mg/kg were unlikely to exceed 0.0005 and 0.0007 mg/kg, respectively.

The Meeting estimated a maximum residue level and an STMR value for diphenylamine in cattle meat of 0.01* (fat) and 0.0005 mg/kg, respectively; a maximum residue level and an STMR value for diphenylamine in cattle liver of 0.05 and 0.024 mg/kg, respectively; a maximum residue level and an STMR value for diphenylamine in cream of 0.01* and 0.0038 mg/kg, respectively, which are equivalent to 0.0004* F and 0.00015 mg/kg for milk; and a maximum residue level and an STMR value for diphenylamine in cattle kidney of 0.01* and 0.0007 mg/kg, respectively.

Recommendations

On the basis of the available data on residues resulting from supervised trials, the Meeting estimated the maximum residue levels and STMR values listed below. The maximum residue levels are recommended for use as MRLs.

Definition of residue (for compliance with the MRL and for estimation of dietary intake): Diphenylamine. The residue is fat-soluble.

Commodity		MRL (mg/kg)		STMR/STMR-P (mg/kg)
CCN	Name	New	Current	
FP 0226	Apple	10 Po	5 Po	4.45
JF 0226	Apple juice	0.5 PoP		0.23
AB 0226	Apple pomace (dry)	25 PoP		10.6
	Apple pomace (wet)			21
MO 1280	Cattle, kidney	0.01*		0.0007
MO 1281	Cattle, liver	0.05		0.024
ML 0812	Cattle milk	0.0004* F[1]		0.00015
MM 0812	Cattle meat	0.01* (fat)		0.0005
FP 0230	Pear	5 Po		2.2

* At or about the LOQ
[1] Equivalent to 0.01* mg/kg in milk fat.

Dietary risk assessment

Long-term intake

The periodic review of diphenylamine resulted in recommendations for new and revised MRLs and new STMR values for raw and processed commodities. Data on consumption were available for the food commodities and were used in calculating dietary intake. The results are shown in Annex 3.

The IEDIs for the five GEMS/Food regional diets, based on estimated STMRs, were 0–4% of the ADI. The Meeting concluded that long-term intake of residues of diphenylamine from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The 1998 JMPR concluded that an acute RfD for diphenylamine was unnecessary. The Meeting therefore concluded that the short-term dietary intake of diphenylamine residues is unlikely to present a risk to consumers.

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FIPRONIL (202)

Fipronil belongs to a new class of insecticides known as phenylpyrazoles. It was first reviewed by the 1997 JMPR for toxicology only, and was identified as a candidate for residue evaluation by the 2000 JMPR by the 1998 CCPR (ALINORM 99/24). The evaluation was postponed to the 2001 JMPR.

Information was reported to the Meeting by the manufacturer Aventis CropScience on metabolism in animals and plants, environmental fate in soil and water, methods of residue analysis and stability of residues in stored analytical samples, registered uses, residues in supervised trials, fate during processing and national MRLs. Information on national GAP was provided by the governments of Australia and Poland. The Meeting was informed that no authorized uses exist in Germany or The Netherlands.

IDENTITY

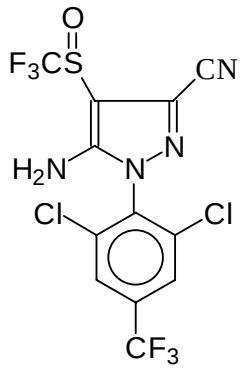
BSI common name: fipronil

Chemical name:

IUPAC (±)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*-tolyl)-4-trifluoromethylsulfinylpyrazole-3-carbonitrile

CA (±)5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[trifluoromethyl)sulfinyl]-1*H*-pyrazole-3-carbonitrile

CAS No: 120068-37-3
CIPAC No: 581
Synonyms: MB 46030
Structural formula:



Molecular formula: $C_{12}H_4Cl_2F_6N_4OS$
Molecular weight: 437.1

Physical and chemical properties

Pure active ingredient

Appearance:	White powder	(Chabert and Lecourt, 1996)
Melting point:	203°C	(Chabert and Lecourt, 1996)

Octanol/water partition coefficient:		
HPLC method	log P_{OW} 3.5 at 20°C	(Cousin, 1997a)
Shake-flask method	log P_{OW} 4.0 at 20°C	(Chabassol and Reynaud, 1991a)
Hydrolysis:		
pH 5 (buffered)	Stable	(Corgier and Plewa, 1992a)
pH 7 (buffered)	Nearly stable (2% loss on 30 days)	
pH 9 (buffered)	DT-50 approximately 28 days	
Photolysis:		
	DT-50 0.33 days (k=-0.0176 $days^{-1}$)	(Corgier and Plewa, 1992b)
	Quantum yield (Φ_{300}) at 300 nm, 1.99 x 10^{-1}	(Boinay, 1997)
Dissociation constant:	Not determinable due to low water solubility	

Technical material

Physical and chemical properties:

Dry technical:[1]		
Minimum purity	95% (950 g/kg)	
Wet technical:[1]		
Minimum purity	87% (870 g/kg)	
Water	6% (6.0 g/kg)	
Vapour pressure:	3.7 x 10^{-9} h Pa at 25°C	((Chabassol and Reynaud, 1991b)
Solubility:		
Water, distilled (20°C)	1.9 mg/l	(Chabassol and Reynaud, 1991c)
buffered (pH 5, 20°C)	2.4 mg/l	((Chabassol and Reynaud, 1991c)
buffered (pH 7, 25°C)	3 mg/l	(Buddle, 1991)
buffered (pH 9, 20°C)	2.2 mg/l	(Chabassol and Reynaud, 1991c)
Organic solvents, g/100 ml		(Chabassol and Reynaud, 1991d)
acetone	54.6	
dichloromethane	2.2	
ethyl acetate	26.5	
hexane	0.003	
methanol	13.8	
1-octanol	1.2	
2-propanol	3.6	
toluene	0.3	
Relative density:	1.48-1.63 (20°C)	(Chabassol and Hunt, 1991a)
Stability:		
Thermal	No degradation at 30-150°C	(Chabassol, 1992)
Flammability	Not highly flammable; not autoflammable	(Fillion, 1996)
Oxidizing potential	Unreactive in water, ammonium dihydrogen phosphate, metallic zinc, diute neutral potassium permanganate	(Chabassol and Hunt, 1991b; Tran Thahn Phong, 1999)
Explosivity:	Not explosive	

Pure metabolites

Vapour pressure:		
MB 46136	7.6×10^{-7} Pa at 25°C	(Cousin, 1996a)
MB 45950	2.3×10^{-6} Pa at 25°C	(Cousin, 1996b)
MB 46513	0.4×10^{-5} Pa at 25°C	(Cousin, 1995)
Water solubility: (distilled, 20°C)		
MB 46136	0.16 mg/l	(Cousin, 1997c)
MB 45950	1.1 mg/l	(Cousin, 1998a)
MB 46513	0.95 mg/l	(Cousin, 1997e)
Octanol/water partition coefficient:		
MB 46136	Log P_{OW} 3.8, 20°C	(Cousin, 1997b)
MB 45950	Log P_{OW} 3.7, 20°C	(Cousin, 1998b)
MB 46513	Log P_{OW} 3.4, 20°C	(Cousin, 1997d)

Formulations

The following list includes the main formulations developed for crop uses:

Formulation type	ai content	Principal formulation names
Suspension concentrate (SC)	50, 200, 400, 750 g/l	Regent®, Ascend®, Klap®
Seed treatment suspension concentrate (FS)	10, 20, 50, 250, 500, 750 g/l	LeSak® Regent, Cosmos®, Icon®
Water-dispersible granule (WG)	800 g/kg	Regent, Cazador®, Schuss®
Microgranule (GR), sand, Biodac® or clay based	3, 5, 10, 15, 20 g/kg	Regent, Prince®
Ultra low volume (UL)	Range of 2-25 g/l	Adonis®
Emulsifiable concentrate (EC)	25, 300 g/l	Regent, Adonis
Granular bait	0.03 g/kg	Blitz®

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METABOLISM AND ENVIRONMENTAL FATE

Compounds are identified by code numbers as shown below. The chemical names do not conform to either IUPAC or CA nomenclature, but have been used to emphasize the relation between the compounds.

Code	Chemical name
fiponil (MB 46030)	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole
MB 45950	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthiopyrazole
MB 45897	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole
MB 46136	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonylpyrazole
fipronil-desulfinyl (MB 46513)	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylpyrazole
MB 46400	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole-4-carboxylic acid
RPA 106889	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole-3,4-dicarboxylic acid
RPA 104615	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole-4-sulfonic acid
RPA 105320	5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonylpyrazole

Code	Chemical name
RPA 105048	5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylpyrazole
RPA 200761	5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole-3-carboxylic acid
RPA 200766	5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole

Animal metabolism

Animal metabolism studies (Powles, 1992; Totis and Fisher, 1994; Steward, 1994a,b) were reviewed by the JMPR in 1997 for toxicology.

Rats. In an ADME (absorption, distribution, metabolism and excretion) study (Powles, 1992), rats were dosed orally with ^{14}C-phenyl ring-labelled fipronil in aqueous methyl cellulose (0.5% w/v) containing Tween 80 (0.01% w/v). Groups of 5 males and 5 females were treated as follows.

- Group A: single oral doses of 4 mg/kg bw [^{14}C]fipronil
- Group B: 14 daily oral doses of unlabelled fipronil followed by single labelled doses, all 4 mg/kg bw
- Group C: single oral doses of 150 mg/kg bw [^{14}C]fipronil.

After treatment the rats were placed in metabolism cages and urine, faeces and blood were collected over 7 days. Expired air was passed through organic traps to ensure the recovery of all radioactive residues. After seven days, the rats were killed and blood and selected tissues were sampled. There were no significant differences in the disposition of radiolabelled materials between the sexes within any treatment group. Recoveries of ^{14}C were all greater than 95%.

Table 1. Percentage recoveries of radioactivity from rats after dosing with [^{14}C]fipronil, group mean values (Powles, 1992).

Group	Sex	Urine	Faeces	Cage washes	Cage debris	Tissues	Total
A	Male	5.6	45.6	0.88	0.022	46.1	98.2
A	Female	5.6	46.0	1.2	ND	45.8	98.6
B	Male	16.2	56.1	1.6	0.03	23.7	97.6
B	Female	13.8	61.4	2.9	0.22	20.2	98.5
C	Male	29.3	66.9	3.8	0.68	2.9	103.6
C	Female	22.0	75.1	3.0	1.02	5.3	106.4

Absorption/kinetics

The amount of dose absorbed appeared to be dependent on dosage and regimen when the urine and tissue results were combined. Group A absorbed approximately 50%, group B about 40% and group C about 30% of the radioactivity. The absorbed fipronil was readily metabolized. No unconjugated [^{14}C]fipronil was detected in the urine or tissues.

In Groups A and C the rate of decrease of radioactivity in the blood was similar for both sexes. The half-lives in Group A for males were 149 ± 11 h and for females 200 ± 59 h, which may be due to the slow release of radioactivity from a tissue such as fat. In Group C residues decreased more rapidly than in group A, with half-lives of 54.4 ± 20 h for males and 51 ± 10.5 h for females.

Excretion

Most of the radioactivity was eliminated in the faeces in all groups. Proportions varied with the dosage, but were the same for males and females. Metabolites were selectively cleared by renal and/or hepatic mechanisms. The presence of metabolites in faeces would suggest biliary excretion.

Table 2. Elimination as % of applied radioactivity at 168 h - group mean values (Powles, 1992).

Group	Sex	Faeces	Urine	Total excreted
A	Male	45.6	5.6	51.2
A	Female	46.0	5.6	51.6
B	Male	56.1	16.2	72.3
B	Female	61.4	13.8	75.2
C	Male	66.9	29.3	96.2
C	Female	75.1	22.0	97.1

Distribution

Seven days after exposure to [^{14}C]fipronil residues were highest in the fat, with moderate levels in the adrenal gland, pancreas, skin, liver, kidney, muscle, thyroid, and ovaries and uterus in females. The levels were lower in other tissues.

Table 3. Concentrations of radioactivity in the tissues of rats after oral administration of [^{14}C]fipronil - group mean values (Powles, 1992).

Sample	^{14}C, µg/g as fipronil					
	A male	A female	B male	B female	C male	C female
Abdominal fat	14.7	18.8	5.8	5.8	29.4	54.5
Adrenals	4.3	4.7	1.5	1.4	7.6	14.6
Kidney	1.3	1.5	0.5	0.5	4.1	6.6
Liver	2.5	2.7	1.1	0.97	6.5	11.2
Muscle	0.83	0.98	0.39	0.31	1.8	3.2
Pancreas	3.6	6.0	2.1	1.98	8.9	15.0
Skin	2.5	3.7	1.3	1.1	7.9	17.5
Thyroids	2.3	3.5	0.88	1.5	1.4	7.7
Ovaries	-	5.1	-	1.7	-	15.6
Uterus	-	2.3	-	1.1	-	10.5

Biotransformation

Analysis by HPLC of fat, liver, kidney, muscle and uterus samples containing moderate to high levels of radioactivity indicated that the same main component was present in all tissues. This was characterized by co-chromatography with an authentic standard as the sulfonyl analogue MB 46136 and confirmed by mass spectrometry.

At least 11 radiolabelled metabolites from faeces extracts were resolved by HPLC. The main metabolites apart from polar components (probably conjugates) were identified. At early samplings, the main compound was unchanged fipronil with lesser amounts of MB 46136 and the trifluoromethylthio reduction product MB 45950, with the amide RPA 200766 identified in some samples. At later samplings the main metabolite was MB 46136.

High levels of very polar radiolabelled material were found by HPLC in unextracted undiluted urine samples. After deconjugation with enzyme preparations specific for cleavage of glucuronide and sulfate conjugates and chromatographic separation using a more polar solvent system, 14 compounds were resolved of which seven were characterized by chromatography and mass spectrometry. The two main components in the urine were evidently pyrazole-ring-opened compounds retaining two nitrogen atoms and the nitrile ligand. The five other identified compounds were the parent compound, MB 46136, MB 45950, MB 45897 formed by loss of the trifluoromethylsulfinyl group, and the amide RPA 200766. All were probably excreted as *N*-glucuronides in the urine since the pyrazole or

pyrazole-derived moieties of the aglycones possess more than one possible site for the formation of glucuronide adducts.

In summary, when single doses of [^{14}C]fipronil were given to male and female rats at 4 or 150 mg/kg/bw or after exposure to 4 mg/kg/bw after pre-treatment with 14 daily unlabelled doses the ^{14}C was quantitatively recovered. The proportion of dose absorbed appeared to depend on dosage and regimen for both sexes with the highest absorption after the single low doses. Metabolism was rapid. No unmetabolized fipronil was detected in any tissues or urine. Most of the radioactivity was excreted in the faeces which contained unchanged [^{14}C]fipronil and metabolites, suggesting bilary elimination of absorbed and metabolized fipronil, and direct elimination of unabsorbed fipronil. This implies some excretion in the bile. Tissue concentrations were high 7 days after dosing, with the highest levels in the fat. The main residue in the fat and other tissues was MB 46136.

Kinetics

In another study by Totis and Fisher (1994) radioactivity was measured in the blood and tissues of Charles River CD strain (Sprague-Dawley) male and female rats after single oral doses of 4 or 40 mg/kg of [^{14}C]fipronil.

Blood radioactivity was determined in groups of 5 rats of each sex over 336 hours. Absorption was rapid for the 4 mg/kg group (mean T_{max} 5.5 h) but elimination was relatively slow. Absorption was much slower for the 40 mg/kg group (mean T_{max} 36 h) in which an initial period of rapidly falling levels in the blood was followed by much slower elimination. Half-lives were similar at both doses (40 mg/kg group half-life: 135 $\pm$ 16 h (males), 171 $\pm$ 27 h (females); 4 mg/kg group half-life: 185 $\pm$ 22 h (males), 245 $\pm$ 35 h (females).

Tissue samples from groups of 3 male and 3 female rats were analysed for total radioactivity by LSC at 4 sampling times. The results are shown in Table 4. Concentrations in the tissues peaked at the blood T_{max} for males and females except in the stomach and gastrointestinal tract which were involved in absorption.

Table 4. Radioactivity in the tissues of rats - group mean values (Totis and Fisher, 1994).

Sample	^{14}C, µg equivalents as fipronil							
	4 mg/kg bw				40 mg/kg bw			
	0.75h	4.8h	96h	168h	3h	33.6h	77h	168h
Males								
Stomach and contents	147	0.5	0.33	0.56	381	64	10	0.88
Abdominal fat	11	31	24	16	69	229	115	32
Adrenals	9.0	11	8.3	5.2	34	54	20	16
Kidney	3.3	3.5	2.1	1.5	14	17	8.8	3.3
Liver	9.2	6.8	3.4	2.4	31	36	17	5.8
Muscle	1.8	3.0	0.91	0.76	7.6	10	4.6	1.5
Pancreas	5.2	6.7	6.5	4.5	31	38	13	6.2
Skin and fur	1.9	5.1	4.1	3.3	17	30	16	6.4
Thyroids	3.7	5.1	2.7	2.2	25	29	17	10
Females								
	0.83h	6.2h	94h	168h	3h	38.4h	78h	168h
Stomach and contents	53	0.73	0.40	0.57	185	148	8.7	1.3
Abdominal fat	13	31	25	22	80	201	135	39
Adrenals	10	9.7	5.1	3.9	39	47	29	14
Kidney	4.1	3.4	1.8	1.6	16	16	11	1.1
Liver	12	7.7	3.2	2.9	32	32	20	6.3
Muscle	1.8	2.1	0.99	1.3	7.4	8.8	5.9	2.0
Pancreas	6.1	5.3	3.2	2.6	26	32	20	5.6
Skin & fur	2.4	5.4	3.8	3.9	20	29	19	6.2
Thyroids	4.2	4.1	2.7	2.9	16	16	23	13

Sample	^{14}C, µg equivalents as fipronil							
	4 mg/kg bw				40 mg/kg bw			
	0.75h	4.8h	96h	168h	3h	33.6h	77h	168h
Ovaries	5.9	5.6	5.4	4.6	20	44	20	9.9
Uterus	2.1	3.9	3.3	2.5	18	30	11	7.2

Goats. In a study by Stewart (1994b) repeated daily oral doses of [^{14}C]fipronil in capsules were given to three dairy goats at 0.05, 2 or 10 ppm in the diet (dry matter basis) for 7 days. The doses were given in the morning and afternoon before feeding after milk and excreta collections. The radiolabelled fipronil-derived material retained in tissues or excreta was characterized by a combination of chromatography and spectrometry.

83% of the total dose was recovered from the 0.05 ppm dose, 64% of which was in the faeces (Table 5). 18% was estimated to have been retained in the tissues, none was detected in the urine, and 0.86% was recovered from the milk. At 2 ppm 50% was recovered, 25% in tissues with 2.5%, 18% and 4.6% in the urine, faeces and milk respectively. At 10 ppm 77% was recovered: 61% in the faeces, 6.6% in urine, 1.3% in milk and 7.4% in tissues. It was suggested that the unrecovered radioactivity was retained in the carcase.

Table 5. Recovery of applied radioactivity after oral administration of [^{14}C]fipronil to lactating goats (Stewart, 1994b).

Sample	^{14}C, % of dose		
	0.05 ppm	2 ppm	10 ppm
Urine	ND	2.45	6.58
Faeces	64.16	17.8	61.28
Whole milk	0.86	4.64	1.33
Cage washes	ND	0.04	0.14
Cage debris	ND	ND	0.54
Tissues	18.31	25.41	7.44
Total	83.32	50.32	77.3

ND: not detectable

After day 1, over 40% of the daily radioactive dose was recovered from the low- and high-dose groups. From days 2 to 6, daily recoveries were approximately 58% and 74% respectively and excretion appeared to reach a plateau after dosing at 0.05 ppm. At 10 ppm recoveries were erratic, but on days 2 and 3, this animal received only half the daily dose which may have influenced the pattern of elimination. Excretion of the daily dose increased over the study at 2 ppm, with a maximum of 47% recovered on day 7.

No radioactivity was detected in blood or plasma from the 0.05 ppm dose, and at 2 ppm levels were 0.023 mg/kg fipronil equivalents in the blood and 0.034 mg/kg in plasma. Concentrations increased during the study. A similar pattern was observed in the blood at 10 ppm where concentrations increased from 0.016 to 0.052 mg/kg before the afternoon dose on days 1 and 7 respectively, but in the plasma no definite pattern was identified: concentrations varied from 0.011 to 0.086 mg/kg during the study.

At all intervals levels of radioactivity from the low dose in the milk were <0.001 mg/kg as fipronil. At 2 and 10 ppm however, residues in the milk increased from 0.02 to 0.11 mg/kg and from 0.052 to 0.17 mg/kg respectively from days 1 to 7.

23.5 hours after the last dose at 0.05 ppm, the TRR (total radioactive residue) in the tissues was <0.01 mg/kg as fipronil. At 2 and 10 ppm, the highest residues were in fat: 1.3 and 1.9 mg/kg in omental and 1.3 and 1.95 mg/kg in renal respectively. At 2 ppm, residues were 0.07, 0.1 and 0.4 mg/kg in muscle, kidney and liver respectively and at 10 ppm 0.08 mg/kg in muscle, 0.15 mg/kg in

kidney and 0.86 mg/kg in liver. As in milk, residues at 2 ppm were 24 to 165 times higher than at 0.05 ppm, but after a fivefold increase in the dose from 2 to 10 ppm, the residues in tissues rose only about twofold.

Extracts of urine, faeces and milk (day 7), muscle, kidney, liver and omental and renal fat from the intermediate and high-dose groups were analysed by HPLC. Samples from the high-dose group were subjected to GC-MS and/or LC-MS. The combination of techniques produced strong evidence that fipronil was the main residue in the high-dose milk and fat: 0.1 and about 1.4 mg/kg respectively. Metabolites MB 45950 and MB 46136 were also present. Although the individual components comprising the TRR in kidney and muscle represented <0.05 mg/kg fipronil equivalents, the parent compound plus MB 46136 were confirmed to be present. In the liver, the main metabolite was MB 46136 (0.46 mg/kg as fipronil) representing approximately 53% of the TRR; minor metabolites identified were RPA 200766 (0.098 mg/kg fipronil equivalents) and fipronil (0.013 mg/kg). Several minor metabolites in liver were not identified, but none were present at >0.052 mg/kg fipronil equivalents. HPLC analysis of equivalent extracts after the intermediate dose confirmed MB 46136 to be the main component of the TRR in all samples.

At both doses, most of the radioactivity was associated with polar compounds. Deconjugation with an enzyme preparation specific for cleavage of glucuronide and sulphate conjugates appeared not to change the elution profile, although this does not necessarily indicate the absence of glucuronide and sulfate conjugates. At the high dose, MB 46136 was a minor constituent in deconjugated and original urine. HPLC and GC-MS analysis confirmed that the main component present in the faeces was MB 46136. Parent compound, MB 45950 and a polar component were also identified as constituents of the residue. Although not verified by GC-MS, these components also apparently contributed to the total radioactivity at 2 ppm. The results are shown in Table 6.

In conclusion, after seven daily oral doses of [^{14}C]fipronil to dairy goats at nominal levels of 0.05 and 10 ppm, the administered radioactivity was extensively excreted, mainly in the faeces. At 2 ppm a greater proportion of the administered dose was retained in the animal. Recoveries from urine, milk and tissues indicated a minimum absorption of approximately 19%, 33% and 15% at 0.05, 2 and 10 ppm respectively. At 0.05 ppm the percentage of the TRR in the milk was negligible. At 2 and 10 ppm, the TRR in milk increased during the study. At the intermediate dose, the levels in milk attained a steady state. Consistently with the lipophilic nature of the compound and its metabolites, the main residues were in fat, providing supportive evidence that unrecovered radioactivity was retained in the animal. The parent compound and the metabolites MB 46136, MB 45950 and RPA 200766 were the principal compounds, although the proportions varied with the dose.

Table 6. Compounds in the milk and tissues of a dairy goat dosed with fipronil at a level equivalent to 10 ppm in the diet (Stewart, 1994b).

Sample	Peak identified	Retention time (min)	Compound	Residues	
				% of TRR	mg/kg fipronil equivalents
Milk	M1.10	46.0	fipronil	59.8	0.099
	M2.10	55.5	MB 45950	11.7	0.019
	M3.10	60.0	MB 46136	22.5	0.037
	M4.10	64.5	Unknown	1.53	0.003
			Remainder	4.5	
Kidney	K1.10	22.0	Unknown	1.51	0.002
	K2.10	24.0	Unknown	3.22	0.005
	K3.10	25.0	Unknown	3.40	0.005
	K4.10	26.0	fipronil	3.21	0.005
	K5.10	28.3	MB 46136	75.06	0.113
	K6.10	32.3	Unknown	0.39	0.001
			Remainder	13.21	
Liver	L1.10	19.1	Mwt 330[1]	4.49	0.039
	L2.10	21.2	RPA 200766	11.32	0.098

Sample	Peak identified	Retention time (min)	Compound	Residues	
				% of TRR	mg/kg fipronil equivalents
	L3.10	21.3	Unknown	2.67	0.023
	L4.10	22.3	Mwt 355[1]	6.0	0.052
	L5.10	22.5	Unknown	2.13	0.018
	L6.10	24.4	Mwt 353[1]	10.7	0.092
	L7.10	25.2	Unknown	2.42	0.021
	L8.10	25.4	Unknown	0.53	0.005
	L9.10	26.3	Mwt 313[1]	1.12	0.010
	L10.10	27.3	fipronil	1.54	0.013
	L11.10	29.1	MB 46136	52.93	0.456
	L12.10	41.2	Unknown	2.22	0.019
			Remainder	1.95	
Muscle	MU1.10	13.0	RPA 200766	7.22	0.006
	MU2.10	46.0	fipronil	60.76	0.048
	MU3.10	54.5	MB 45950	8.26	0.007
	MU4.10	59.5	MB 46136	20.51	0.016
	MU5.10	61.0	Unknown	1.79	0.001
			Remainder	1.45	
Fat, omental	OM1.10	12.5	RPA 200766	0.64	0.012
	OM2.10	45.5	fipronil	73.19	1.405
	OM3.10	54.0	MB 45950	5.47	0.105
	OM4.10	59.0	MB 46136	16.85	0.323
	OM5.10	62.0	Unknown	0.94	0.018
			Remainder	2.91	
Fat, renal	RF1.10	13.0	RPA 200766	0.74	0.014
	RF2.10	45.5	fipronil	72.72	1.414
	RF3.10	54.5	MB 45950	6.04	0.117
	RF4.10	59.5	MB 46136	17.95	0.349
	RF5.10	62.0	Unknown	0.94	0.018
			Remainder	1.60	

[1]Proposed molecular ions

Hens. In a study by Stewart (1994a) oral capsules containing levels equivalent to 0.05, 2 or 10 ppm in the diet (dry matter basis) were given to three groups of five laying hens daily for 28 days. The birds were dosed in the morning before feeding after egg and excreta collections, with an additional hen as a control. Residues were determined by chromatography and spectometry.

At 0.05 ppm a mean of 52% of the radioactivity was recovered within 23.5 hours of the last dose, and at 2 and 10 ppm mean recoveries were 55% and 58% respectively. At all doses the highest recoveries were from excreta, and egg yolks and whites (Table 7).

Table 7. Total recoveries of applied radioactivity from laying hens (Stewart, 1994a).

Sample	^{14}C, % of total administered dose		
	0.05 ppm	2 ppm	10 ppm
Excreta	28.35	36.28	41.47
Egg yolk	16.11	15.11	13.26
Egg white	1.99	1.68	1.44
Tissues (skin, fat, muscle, liver)	5.40	0.82	0.65
Cage wash	ND	0.06	0.07
Cage debris	ND	0.57	0.43
Total (mean)	51.9	54.53	57.53

ND: not detectable

Mean daily recoveries of radioactivity in excreta and eggs (expressed as a percentage of the daily dose) increased throughout the study.

Group mean maximum levels of 0.18, 7.02 and 30 mg/kg as fipronil were determined in egg yolks from the low-, intermediate- and high-dose groups respectively, and towards the end of the study almost reached a plateau. In all groups the residues in the egg yolks were higher than in the whites (low dose up to 78 times, intermediate and high up to 20 and 24 times respectively) consistent with the lipophilic nature of the compound. Concentrations of radioactivity in the whites were 0.011 mg/kg fipronil equivalents at the low dose, 0.3 mg/kg at the intermediate and 1.1 mg/kg at the high dose. The residues in the yolks at all doses displayed apparent dose proportionality, and in the whites only at the intermediate and high doses.

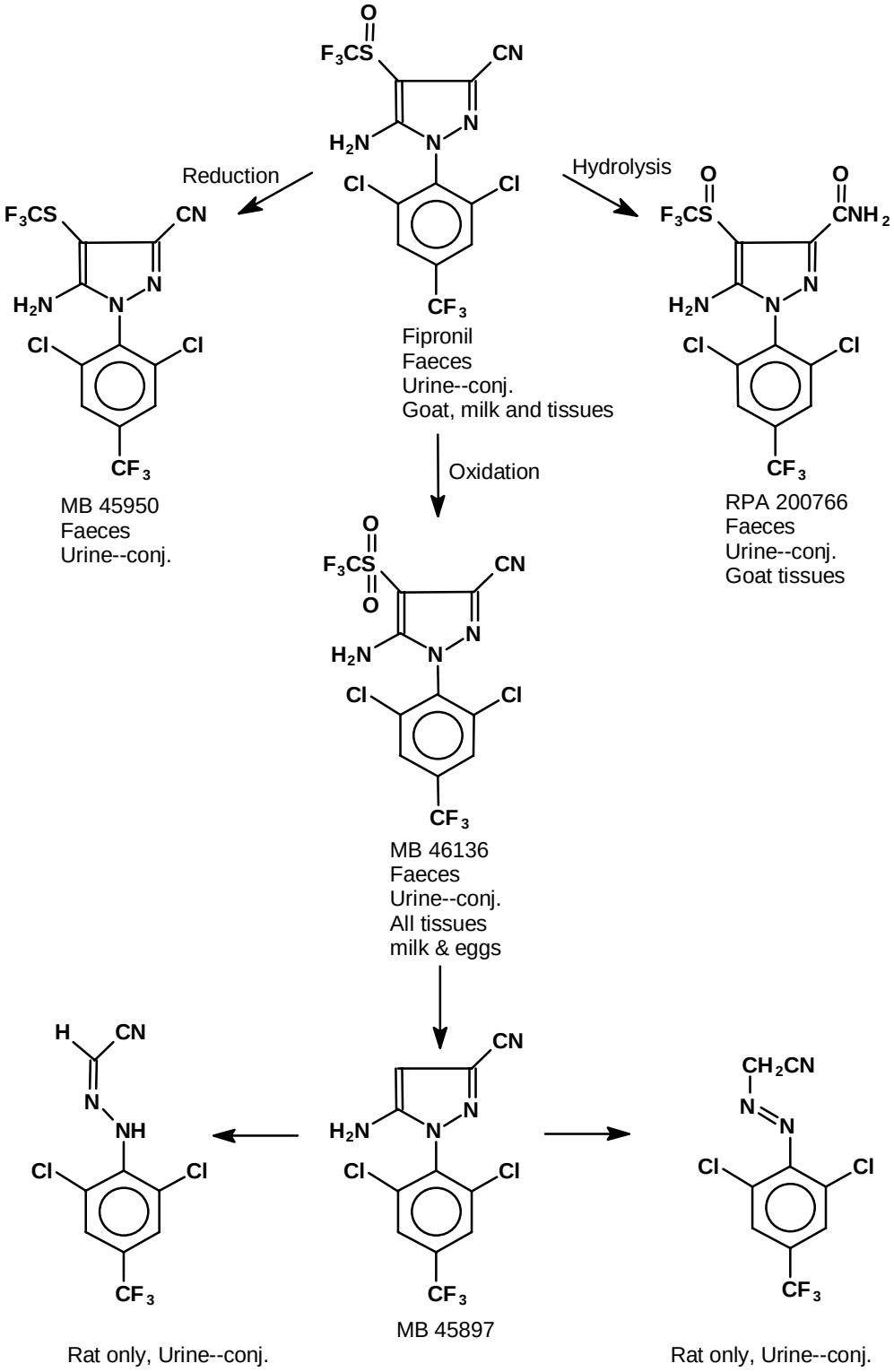
At the end of the study, 23.5 hours after the last dose, residues were highest in the skin, 0.1, 3.9 and 17 mg/kg as fipronil and in the peritoneal fat, 0.29, 12 and 56 mg/kg, at 0.05, 2 and 10 ppm respectively. Mean concentrations in liver and muscle were 0.03 mg/kg (low dose), 1.2 mg/kg (intermediate dose) and 4.9 mg/kg (high dose). In all tissues, residues were proportional to dose.

Extracts of egg yolk and white at day 27, and skin, peritoneal fat, liver and muscle from all groups were analysed by HPLC, and samples from the high-dose group by GC-MS. There was strong evidence that MB 46136 was the main component in egg yolks and whites and tissues of the high-dose group. Fipronil was a minor component in egg yolk, skin, fat and liver. Although samples from the other two groups were not analysed by GC-MS, the similar chromatography of these extracts strongly indicated that MB 46136 was also the main metabolite in the eggs and tissues at all doses.

Analysis of excreta by the same methods at day 27 confirmed that the main components were MB 46136 and fipronil. At the low and intermediate doses, the main residue was MB 46136, and at the high dose fipronil was the main component which may indicate that absorption of fipronil was incomplete at this dosage.

In summary approximately 52 to 58% of the administered radioactivity was eliminated, mainly in the excreta, at all doses and radioactive residues in both excreta and egg yolks and whites were close to reaching plateau levels. The elevated residues in egg yolk, skin and fat are consistent with the lipophilic nature of the compound. The metabolite MB 46136 was identified as the main residue in eggs and tissues at all doses. Figure 1 shows the metabolic pathway of fipronil in animals.

Figure 1. Metabolic pathways of fipronil in animals.



Animal metabolism of fipronil-desulfinyl (MB 46513)

Rats. In the ADME study (Totis, 1996) reviewed by the 1997 JMPR groups of male and female Sprague Dawley rats were dosed with [^{14}C]fipronil-desulfinyl labelled in the phenyl ring as follows.

- Single oral low doses (SOLD) of 1 mg/kg bw [^{14}C]fipronil-desulfinyl
- Single oral high doses (SOHD) of 10 mg/kg bw [^{14}C]fipronil-desulfinyl
- Repeat oral low doses (ROLD): 14 daily oral doses of 1 mg/kg bw unlabelled fipronil-desulfinyl followed by a single dose of 1 mg/kg bw [^{14}C]fipronil-desulfinyl.

After treatment the rats were placed in cages and urine and faeces were collected for 7 days. Exhaled carbon dioxide was not trapped during the study as results from an earlier group dosed at 15 mg/kg/day had shown <0.1% of the radioactivity was eliminated via this route during the first 48 hours. The rats were killed and samples of blood and selected tissues were collected. Recoveries of ^{14}C during the seven days were essentially quantitative, ranging from 93 to 100% (mean 97%, SD $\pm$ 3.7%).

In addition rats given single doses at 1 and 10 mg/kg were housed in wire cages and blood samples were taken approximately 0.5, 1, 2, 3, 4, 6, 8, and 24 hours after dosing, and then at 24 hour intervals until c. 360 hours (low-dose group) or 408 hours (high-dose group) after dosing, and finally at 48-72 hour intervals until 648 hours after dosing.

Absorption/kinetics

In all three regimes the percentage of [^{14}C]fipronil-desulfinyl absorbed was very similar, with a higher proportion absorbed by the females. The mean estimated percentage absorbed was calculated from the radioactivity detected in the urine, cage washes and tissues: approximately 31/44% (male/female), 34/46% (male/female) and 35/45% (male/female) for the high-, low- and repeated-dose groups respectively. The pharmacokinetic experiments indicated a relatively slow absorption at both doses with mean maximum blood concentrations approximately 46-73 hours after dosing (Table 8). The maximum concentrations in the blood appear to be proportional to the administered dose.

Table 8. Blood pharmacokinetic parameters of fipronil-desulfinyl in rats (Totis, 1996).

Parameter	Males		Females	
	Mean	SD	Mean	SD
C_{max} (µg equiv/g)				
SOHD	2.03	0.47	2.3	0.9
SOLD	0.14	0.02	0.15	0.03
T_{max} (hours)				
SOHD	73	9.1	71	8.3
SOLD	46	13.6	61	17.1
Half-life (hours)				
SOHD	170	21	221	55
SOLD	156	18	210	14

SD: Standard deviation

Distribution

The radioassay of tissues sampled seven days after administration of [^{14}C]fipronil-desulfinyl indicated that radioactivity was widely distributed; no residues were below the minimum limit of detection (MLD) after 168 hours. Residues were highest in the fat in all groups, and moderate to low in the liver, kidney, adrenals, lungs, thyroid, skin and fur, pancreas and uterus. Mean percentages of the dosed ^{14}C remaining in the tissues after seven days were 20 and 30% for SOHD males and females

respectively; 27 and 41% for SOLD males and females respectively; and 22 and 32% for ROLD males and females respectively.

In all three groups, levels of radioactivity after 168 hours were indicative of a relatively slow elimination rate.

Elimination

In the three groups, the faeces were the main route of elimination for fipronil-desulfinyl, accounting for approximately 46% to 70% of the administered dose, and the urine for approximately 4% to 11%. After 24 hours, elimination was at a steady rate until the end of the study. More than 70% of the total was excreted after 96-120 hours in both the faeces and the urine. The proportion eliminated in the faeces was similar in all three groups. Mean levels in the faeces of males were slightly higher than in females (64% and 52% respectively). This difference was not apparent in the urine (8.4% and 8.6% respectively) but corresponds to the slightly higher radioactivity found in the tissues of females at slaughter.

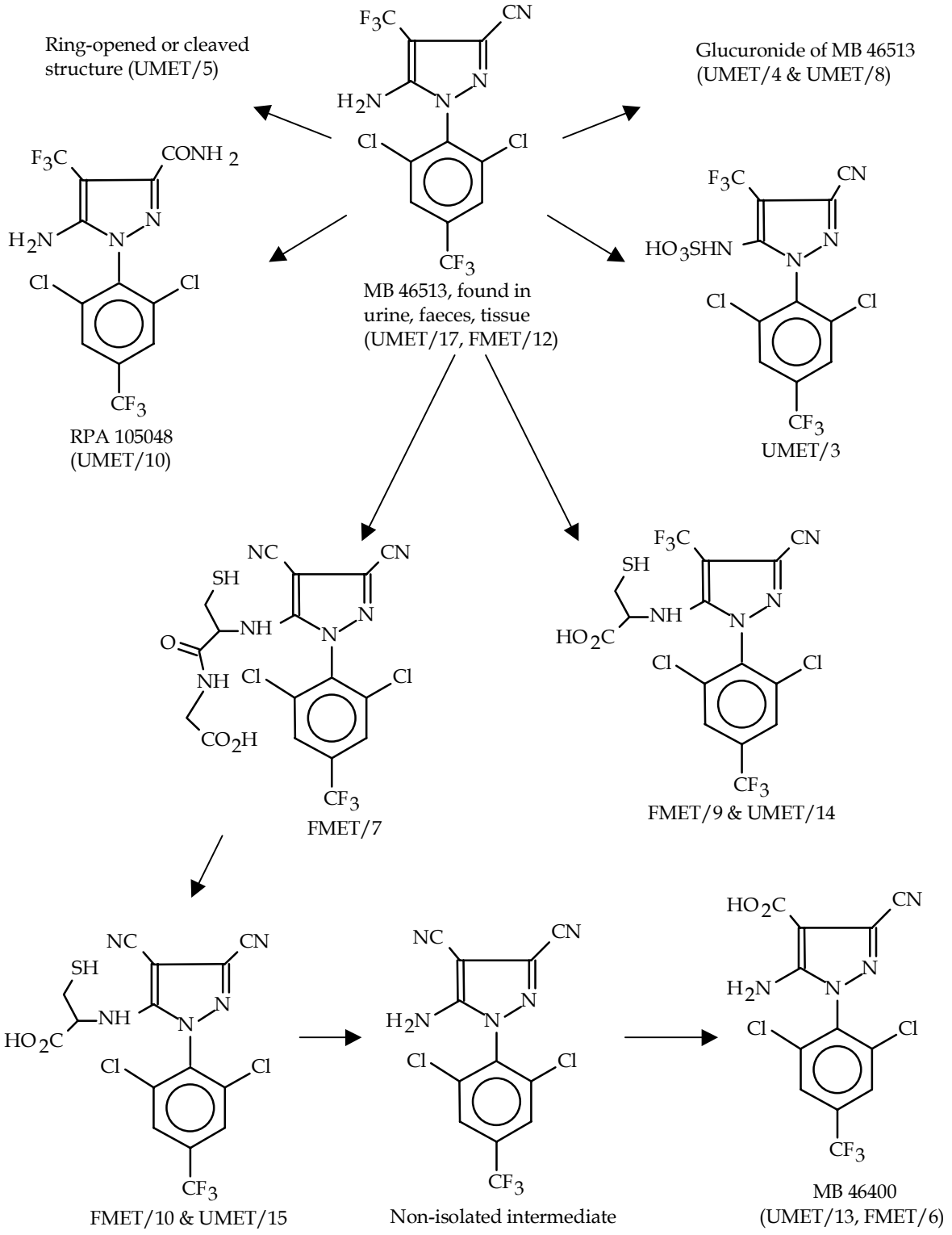
Metabolism

About 13 radiolabelled metabolites in the faeces and 17 in the urine extracts were resolved by HPLC, with identification by mass spectrometry (LC-MS, LC-MS-MS and/or GC-MS) and ^{19}F NMR. Trace levels of fipronil were detected in urine and it was the main component in the faeces in all the groups, which suggests that a large part of the administered dose was excreted in the faeces without absorption or as a conjugate via the bile which was de-conjugated by hydrolytic enzymes in the gut.

In the urine only the 4-carboxylic derivative MB 46400 (UMET/13. FMET/6. Figure 2) accounted for more than 5% of the dose. A second metabolite, UMET/3, accounted for over 2% in the animals from the repeat low-dose group; it was identified as a sulfate conjugate of fipronil-desulfinyl. Extracts from urine samples, including those from samples treated with enzyme preparations specific for cleavage of glucuronide and sulfate conjugates and those subjected to acid hydrolysis, were analysed by HPLC. Results obtained from incubations with the de-conjugating enzymes did not definitely demonstrate the presence of glucuronide or sulfate conjugates, but after acidic hydrolysis two other polar metabolites were thought to be amino acid conjugates of fipronil-desulfinyl. Structural identification using LC-MS indicated that UMET/8 was also a conjugate, tentatively identified as a 5-aminoglucuronide conjugate of the parent. UMET/10 was clearly identified as the amide RPA 105048. UMET/15 was proposed to be the 4-cyano-5-(*N*-cysteinyl) derivative of fipronil-desulfinyl. In faeces the second most abundant compound after the parent was FMET/10; after acidic hydrolysis, this metabolite was seen to decrease and therefore indicated to be a conjugate. LC-MS-MS and ^{19}F NMR showed that FMET/10 was the same compound as UMET/15, the 4-cyano-5-(*N*-cysteinyl) compound. FMET/6 was identified as the 4-carboxylic acid derivative of fipronil-desulfinyl. Acidic hydrolysis indicated that both FMET/9 and FMET/7 were conjugates; LC-MS-MS and ^{19}F NMR identified FMET/9 as the 5-(*N*-cysteinyl) conjugate of fipronil-desulfinyl and FMET/7 as a 4-cyano-5-(*N*-cysteinylglycine) conjugate linked through the cysteine residue. Polar metabolites FMET/1, FMET/2, and FMET/4 were found to be thermo-sensitive during hydrolysis experiments; LC-MS demonstrated that these were probably conjugates because of their high molecular weights.

Structures have been proposed for urinary metabolites which account for approximately 90% of the radioactivity eliminated in the urine and for faecal metabolites representing approximately 93% of that eliminated in the faeces. Only one radioactive residue was identified from tissue samples, this being the unchanged compound fipronil-desulfinyl. The proposed metabolic pathways of fipronil-desulfinyl in the rat are shown in Figure 2.

Figure 2. Proposed metabolic pathways of fipronil-desulfinyl in the rat.



Goats. In a study of distribution, metabolism, and elimination of radioactivity three diary goats were given repeated oral doses of [^{14}C]fipronil-desulfinyl in capsules at levels equivalent to 0.05, 2 and 10 ppm in the diet (dry matter basis) for seven days (Johnson *et al.*, 1996). Radioactive residue levels in the milk and selected tissues were determined.

The goats were dosed after milk and excreta collections before being fed in the morning and afternoon, and killed 23 hours after the last dose.

Recoveries were as follows. At 0.05 ppm, 72% of the total dose was recovered, with 19.5% in the faeces and 7.1% in urine, at 2 ppm, 52% with 26% and 4.7% in the faeces and urine respectively, and at 10 ppm, 69%, with 50% in faeces and 3.2% in urine. The highest residues in the tissues at all levels were in the liver and fat, with higher concentrations than in circulating plasma, and the lowest in muscle (Table 9).

Table 9. Mean recoveries of total radioactivity as % of administered dose after repeated oral dosing of lactating goats with [^{14}C]fipronil-desulfinyl (Johnson *et al.*, 1996).

Sample	^{14}C, % of total administered dose		
	0.05 ppm	2 ppm	10 ppm
Urine	7.1	4.7	3.2
Faeces	19.5	26	50
Cages wash	0.79	0.14	0.19
Milk	5.3	0.96	2.6
Total body fat	26	9.0	7.4
Kidneys	0.13	0.11	0.06
Liver	4.4	2.7	2.2
Skeletal Muscle	9.2	8.3	4.1

Concentrations of radioactivity in milk at each dose level approached a steady state about 104 hours after the first dose, and peaked at 0.008, 0.056, and 0.36 mg/kg fipronil-desulfinyl equivalents at the 0.05, 2, and 10 ppm dose levels respectively. Residues in the tissues 23 hours after the last dose are shown in Table 10.

Table 10. Total radioactivity in tissues after repeated oral dosing of lactating goats with [^{14}C]fipronil-desulfinyl (Johnson *et al.*, 1996).

Sample	TRR (mg/kg fipronil-desulfinyl equivalents)		
	0.05 ppm	2 ppm	10 ppm
Omental fat	0.078	0.57	2.7
Renal fat	0.066	0.53	2.2
Kidneys	0.0075	0.13	0.47
Liver	0.037	0.76	2.8
Skeletal muscle	0.0035	0.068	0.18

Samples from the 10 ppm goat were extracted for identification of residues. Extraction of radioactivity was essentially quantitative (>91%) from milk and all tissues except kidney (86%). Residues in urine were isolated by solid phase extraction and solvent elution. Extracts of milk, urine, faeces, liver, muscle, kidney and fat were examined using radio-HPLC and LC-MS. For metabolite profile comparison, liver and omental fat from the 0.05 ppm group and liver, omental fat, and milk from the 2 ppm group were analysed by HPLC. The chromatographic properties of components in these extracts were similar to those in the high-dose extracts indicating similar metabolism at all doses.

Analysis by radio-HPLC and LC-MS indicated that fipronil-desulfinyl was the only residue in faeces, renal fat, omental fat, and milk and also the main residue in liver, muscle, and kidney. Analysis of liver extracts by LC-MS indicated the presence of the deaminated ring-opened derivatives of RPA 106889 and RPA 105048, and ring-opened metabolite RPA 108058 (see Figure 3). One other unidentified metabolite, less than 10% of the TRR, was characterized by HPLC retention time as polar, possibly a derivative with the pyrazole ring intact. In muscle, one minor unidentified component (<0.02 mg/kg, 0.95% of the TRR) was detected in addition to fipronil-desulfinyl. In kidneys, all compounds except fipronil-desulfinyl were minor (0.82-5.07% of the TRR, 0.004 to 0.024

mg/kg. In addition to low levels of fipronil-desulfinyl, residues in urine were tentatively identified as 5-amino sulfate and glucuronide conjugates of fipronil-desulfinyl, its 5-(*N*-cysteine) conjugate and its *N*-oxide.

In conclusion, excretion occurred mainly in the faeces, the proportion excreted decreasing as the dose decreased. Residues in the milk appeared to indicate that a plateau was reached after 104 hours. The high residues in fat were consistent with the lipophilic nature of the compound. Fipronil-desulfinyl was the principal component of the total radioactive residue in milk and tissues at all doses.

Hens. McCorquodale *et al.* (1996) gave repeated oral doses of [^{14}C]fipronil-desulfinyl in capsules at nominal doses of 0.05, 2 and 10 ppm in the diet (dry matter basis) to three groups of five laying hens. After egg and excreta collection the hens were dosed for 14 days with [^{14}C]fipronil-desulfinyl in the morning before feeding. Three additional hens were the controls. The hens were killed 23 hours after the last dose. The residues in selected tissues and excreta were characterized by chromatography and spectometry, the initial chromatographic analysis being within 6 months. Storage stability was established by radio-HPLC analyses of liver and egg white and yolk extracts at intervals several months apart.

At 0.05, 2 and 10 ppm the mean recoveries of the total administered radioactivity within approximately 23 hours of the last dose were 68%, 79% and 81% respectively. At all doses most of the radioactivity was found in the excreta (Table 11).

Table 11. Mean recoveries of total radioactivity, % of administered dose, from laying hens after repeat oral doses of [^{14}C]fipronil-desulfinyl (McCorquodale *et al.*, 1996).

	^{14}C, % of total administered dose		
Sample	0.05 ppm	2 ppm	10 ppm
Excreta	53	69	71
Cages wash	1.6	1.4	1.2
Egg white	1.9	1.3	1.3
Egg yolk	4.8	2.9	3.6
Tissues	4.0	4.2	6.3

The distribution of the TRR between egg whites and yolks during the study was similar at all doses, and the residues appeared to reach a plateau. Maximum residues in the three groups were 0.005, 0.18, and 0.85 mg/kg fipronil-desulfinyl equivalents in the whites and 0.052, 1.55 and 7.5 mg/kg in the yolks. At the end of the study the highest levels were in omental fat, partially-formed eggs, liver, and skin plus fat (Table 12) and were higher than in plasma. In muscle the residues were lower than in plasma.

Table 12. Mean residues in the tissues and eggs of laying hens after repeat oral doses of [^{14}C]fipronil-desulfinyl (McCorquodale *et al.*, 1996).

	TRR (mg/kg fipronil-desulfinyl equivalents)		
Sample	0.05 ppm	2 ppm	10 ppm
Eggs partially formed	0.058	1.55	8.7
Omental fat	0.058	1.61	8.8
Breast muscle	0.002	0.056	0.25
Thigh muscle	0.004	0.13	0.6
Liver	0.038	1.02	4.1
Skin plus fat	0.034	0.93	5.8

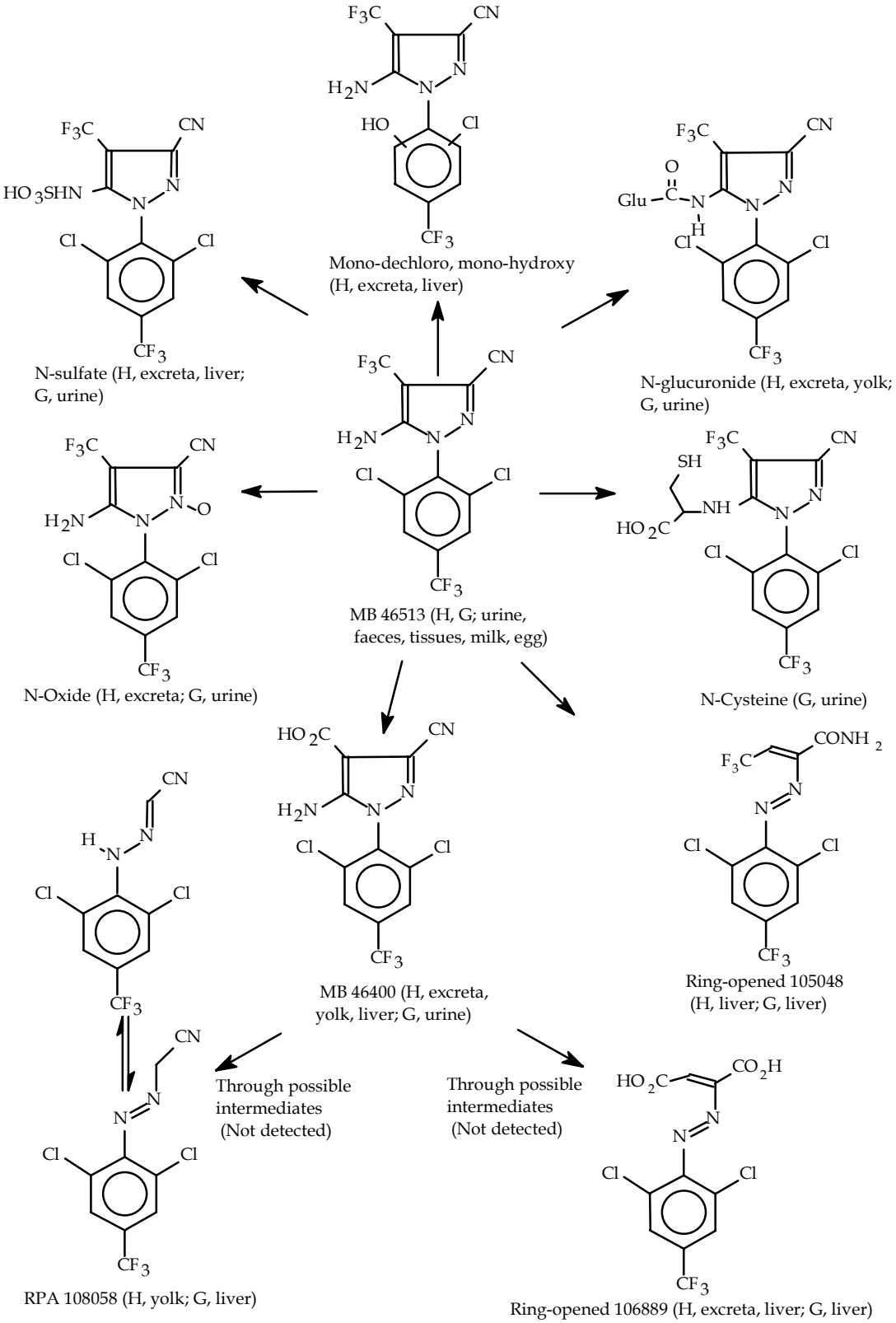
Samples from the 10 ppm group were extracted for identification of residues. Extraction of ^{14}C was essentially quantitative (>88%) except from one liver sample. Extracts of excreta, egg yolk and white, liver, muscle and fat were examined using radio-HPLC and LC-MS. For metabolite profile

comparison, liver and omental fat from the 0.05 ppm group and liver, omental fat, and eggs from the 2 ppm group were analysed by HPLC. The similar chromatographic properties of the components in these extracts to those from the high-dose group indicate that metabolism was the same at all doses.

The combination of radio-HPLC and LC-MS analysis indicated that fipronil-desulfinyl was the only residue in skin and fat, omental fat, and egg white and the main component in excreta, liver, muscle, and egg yolk. Other residues in excreta were tentatively identified as 5-amino sulfate and glucuronide conjugates of fipronil-desulfinyl, MB 46400, a mono-dechloro, monohydroxy derivative of fipronil-desulfinyl, a deaminated ring-opened metabolite of RPA 106889, and the pyrazole *N*-oxide of the parent. In liver, LC-MS indicated the presence of the deaminated ring-opened derivatives of RPA 106889 and RPA 105048. Other unidentified metabolites present at much less than 10% of the TRR were characterized by HPLC retention time as being polar in nature, and thought to be derivatives or conjugates with the pyrazole ring intact. In muscle, three minor unidentified components (<0.02 mg/kg, 1.8-3.9% of the TRR) were detected in addition to fipronil-desulfinyl. In egg yolk, a minor component was tentatively identified as RPA 108058 and additional components characterized as more polar than the parent, probably derivatives or conjugates with the pyrazole ring intact. Proposed metabolic pathways are shown in Figure 3.

In conclusion, after repeated oral administration of [^{14}C]fipronil-desulfinyl to laying hens at doses of 0.05, 2 and 10 ppm, approximately 53 to 71% of the administered radioactivity was eliminated in the excreta. Residues seemed to reach a plateau by the end of the dosing period on the basis of radioactivity measurements in eggs. The elevated radioactive residues in egg yolk, omental fat, and skin plus fat were consistent with the lipophilic nature of the compound. Fipronil-desulfinyl was identified as the principal component of the total radioactive residue in eggs and tissues at all doses.

Figure 3. Proposed metabolic pathways of fipronil-desulfinyl in livestock.



Summary of animal metabolism

The fate of fipronil in mammals was similar in all species studied. It is relatively well absorbed, dependent on dose level and formulation, and extensively distributed in the tissues particularly those with high lipid content. Excretion is mainly via the faeces which contained both free (Phase I) and conjugated (Phase II) metabolites. Both biliary and direct intestinal excretion is involved. Much less is excreted in the urine and urine metabolites are almost exclusively conjugates.

The metabolic pathways of fipronil-desulfinyl in livestock are consistent with those in rats. Fipronil-desulfinyl is metabolized to more polar derivatives or forms polar conjugates which are excreted. The compound is unmetabolized fipronil-desulfinyl is distributed into eggs, milk, and/or tissues, with the highest levels in fat. This is consistent with the lipophilic nature of the molecule. On the basis of these results, it appears that only fipronil-desulfinyl could be transferred to animal substrates in measurable quantities.

Plant metabolism

Soil application

Metabolism by maize, sugar beet, cotton and sunflower was studied after soil application.

Maize. In the first of two trials Yenne and Stone (1994) applied phenyl-labelled [^{14}C]fipronil as a 1.5% granular formulation at 420 g ai/ha (granular proposed use rate 150 g ai/ha), and also at 10 times this rate, and as a stem injection. Both applications were intended to induce higher than normal metabolite levels to facilitate analysis. However results were only reported for plants treated at the lower rate.

The granular formulation was applied to the soil surface before planting, then seeds and granules were covered with approximately 3.8 cm of soil. Plants were harvested at the forage stage (whole green plants, 42 days after treatment) and at maturity (grain at 98 days after treatment and fodder at 106 days after treatment).

The forage contained 0.21 mg/kg fipronil equivalents, fodder 3.7 mg/kg and grain 0.16 mg/kg. The harvested samples contained less than 4.5% of the applied radioactivity (Table 13).

Table 13. Distribution of ^{14}C in field maize after soil treatment with fipronil (Yenne and Stone, 1994).

Sample	^{14}C % of applied	% of TRR	mg/kg as fipronil
Forage	4.0	100	0.21
Mature Plant	4.3		
Fodder	4.0	92.5	3.7
Grain	0.3	7.5	0.16

A series of solvents were used for extraction. Analysis was by ^{14}C-HPLC and MS. 76%, 106% and 99% of the TRR was accounted for in forage, fodder, and grain respectively, after the extractions (including mild acid hydrolysis), distributed as follows. Fipronil (0.08 mg/kg, 39.9% of the TRR), RPA 200766 (0.03 mg/kg, 12.7% of the TRR), and MB 46136 (0.02 mg/kg, 8.7% of the TRR) were in the forage. Two unidentified metabolites at <0.01 mg/kg were also observed. There were seven significant compounds (>0.05 mg/kg) in the fodder, five of which were identified: fipronil (0.45 mg/kg, 12.1% of the TRR), RPA 200761 (0.29 mg/kg, 7.7% of the TRR), RPA 200766 (0.94 mg/kg, 25.3% of the TRR), MB 45950 (0.06 mg/kg, 1.7% of the TRR), and MB 46136 (1.02 mg/kg, 27.6% of the TRR. There were five minor unidentified metabolites at levels of 0.01-0.02 mg/kg. Only one metabolite, a conjugate of RPA 200766, was found in the grain extracts at 0.14 mg/kg (87.5% of the TRR). The results are shown in Table 14.

Table 14. Distribution of fipronil and metabolites in maize tissues (Yenne and Stone, 1994).

Sample	Compound	Residues (mg/kg)	% of TRR[1]
Forage	Fipronil	0.08	39.9
	MB 46136	0.02	8.7
	RPA 200766	0.03	12.7
Fodder	Fipronil	0.45	12.1
	RPA 200761	0.29	7.7
	RPA 200766	0.94	25.3
	MB 45950	0.06	1.7
	MB 46136	1.02	27.6
	2 major unidentified metabolites	0.10 0.20	2.8 5.4
Grain	RPA 200766 conj.	0.14	87.5

[1] Calculated from total residues in individual samples

To establish that fipronil residues in maize had been stable throughout the 3 years of the study and to determine the distribution of residues in maize more clearly, a supplementary study (Yenne and Jesudason, 1995) was conducted. An acetonitrile solution of [^{14}C]fipronil was applied to soil at 146 g ai/ha, and seeds planted and covered with 3.8 cm of soil. Some plants were harvested at the forage stage (whole green plants, 35 days after treatment) and some at maturity (grain at 90 to 106 days after treatment and fodder at 106 days after treatment). Forage samples were cut into 30-cm segments, and plants harvested at maturity were divided into grain, cobs, and 60-cm stalk segments.

The bottom stalk segments of both forage and mature plants contained the highest percentages of radioactivity. Forage from all segments combined contained 0.11 mg/kg fipronil equivalents, fodder 0.51 mg/kg, the cob 0.025 and grain 0.013 mg/kg. At mature harvest the above-ground plant sections contained 0.81% of the radioactivity applied to the soil (Table 15).

Table 15. Distribution of radioactivity in maize plants (Yenne and Jesudason, 1995).

Sample	^{14}C, % of applied	% of TRR	mg/kg as fipronil
Forage	0.45	100	0.11
Mature plant	0.81		
Fodder	0.78	95.1	0.51
Cobs	0.01	1.84	0.025
Grain	0.02	3.09	0.013

Forage, fodder and grain samples were extracted in order to isolate metabolites for identification; cobs were not extracted because of the low level of uptake. Two extraction procedures were compared in order to provide radio-validation of the method of analysis for residue trials. In procedure 1 the first extraction solvent was 100% acetonitrile whereas in procedure 2 it was acetonitrile/water (75/25); subsequent extractants were identical. The second extraction procedure gave more than 96% recovery of the TRR from all tissues. Extracts were analysed by ^{14}C-HPLC followed by MS to identify and confirm metabolites. Fipronil at 0.044 mg/kg (39% of the TRR), RPA 200766 at 0.033 mg/kg (30% of the TRR), MB 46136 at 0.013 mg/kg (11.6% of the TRR), and RPA 200761 at 0.012 mg/kg (10% of the TRR) were identified in the forage. In fodder, fipronil (0.061 mg/kg, 12% of the TRR), RPA 200766 (0.19 mg/kg, 38% of the TRR), MB 46136 (0.082 mg/kg, 16% of the TRR), and RPA 200761 (0.008 mg/kg, 1.6% of the TRR) were also observed, together with an additional minor metabolite RPA 105320 (0.007 mg/kg, 1.4% of the TRR). In grain, only RPA 200766 was identified at 0.008 mg/kg (60% of the TRR).

Table 16. Distribution of ^{14}C residues in maize tissues (Yenne and Jesudason, 1995).

Sample	Compound	Residues (mg/kg)	% of TRR[1]
Forage	Fipronil	0.044	39.1
	MB 46136	0.013	11.6
	RPA 200766	0.033	29.9
	RPA 200761	0.012	10.3
	Unextracted	0.001	0.8
Fodder	Fipronil	0.061	12.1
	MB 46136	0.082	16.2
	RPA 200766	0.194	38.4
	RPA 200761	0.008	1.6
	RPA 105320	0.007	1.4
	Unextracted	0.017	3.4
Grain	RPA 200766	0.008	60.4
	Unextracted	<0.01	0

[1] Calculated from total residues in individual samples.

Fipronil, MB 46136, and RPA 200766 were the main metabolites found in forage and fodder in both the metabolism studies on maize. Only RPA 200766 or its conjugate was found in the grain.

Sugar beet. In a study by Oliver *et al.* (1993) investigating the distribution and metabolism of phenyl ring-labelled [^{14}C]fipronil, the compound was applied with seed at sowing as a 2% granular formulation at the equivalent of 200 g ai/ha and, for the identification of metabolites, at 10 times this rate.

After harvest the leaves and beets were analysed separately; two individual plants were analysed, and the remainder bulked and three replicate samples taken. Sufficient activity was present at 200 g ai/ha for analysis so only these results are reported.

Residues were isolated by sequential acetone, methanol/water, and Soxhlet extractions followed by acid digestion. The leaves contained residues equivalent to a mean of 92% of the TRR, of which 86-91% (0.57-0.59 mg/kg) was extractable. Mild and strong acid hydrolysis released 1.5% to 3.2% (0.01 to 0.021 mg/kg). In the root tissue, 80% to 91% of the activity (0.037 to 0.061 mg/kg) was released after extractions with acetone and methanol/water only. Metabolites were identified by co-chromatography against standards and GC-MS.

In the leaves, 85% to 88% of the extracted activity was in the methanol extract. The residue comprised MB 46136 (0.18 to 0.23 mg/kg) the main component, followed by RPA 105320 (0.11 to 0.12 mg/kg), MB 45950 (0.017 to 0.029 mg/kg), and MB 45897 (0.01 to 0.019 mg/kg). Low levels of fipronil were detected by GC-MS. Polar material (0.087 to 0.09 mg/kg) was shown to consist of at least four components by reverse phase TLC.

In the beets, organosoluble material accounted for 96.7% to 98% of the extracted activity. MB 46136 (0.028 to 0.053 mg/kg) was again the main component. Fipronil (0.005 to 0.012 mg/kg) and RPA 200766 (0.002 to 0.003 mg/kg) were also found. Low levels of MB 45950 were detected by GC-MS (Table 17).

Table 17. Distribution of ^{14}C residues in sugar beet (Oliver *et al.*, 1993).

Sample	Compound	mg/kg as fipronil[1]
Leaves	Fipronil	NA[2]
	MB 46136	0.19
	MB 45950	0.024[3]
	MB 45897	0.011
	RPA 105320	0.12

Sample	Compound	mg/kg as fipronil[1]
	RPA 200766	0.025
	4 polar components	total 0.088
Beet	Fipronil	0.009
	MB 46136	0.033
	MB 45950	NA[2]
	RPA 200766	0.003

[1] Mean of replicates
[2] NA: not analysed. Observed at low levels by GC-MS
[3] Not confirmed by GC-MS

Cotton. Yenne and Stone (1995) investigated the metabolism of phenyl ring-labelled [^{14}C]fipronil in and on cotton plants after soil incorporation (a further study on foliar application is described later).

An in-furrow treatment at planting of an acetonitrile solution of [^{14}C]fipronil was applied to the cotton at approximately 224 g ai/ha. Plants were harvested at maturity (plants dessicated, seeds hard, 140 days after planting) and the above-ground parts separated into seed, lint, bolls and foliage.

Only 2.3% of the applied radioactivity was found in the above-ground plant parts. Foliage contained 2.2 mg/kg fipronil equivalents (more than 97% of the TRR in the plant at harvest), bolls 0.16 mg/kg, lint 0.02 and seed <0.01 mg/kg respectively.

Table 18. Distribution of ^{14}C in cotton plants (Yenne and Stone, 1995).

Sample	% of applied ^{14}C	% of TRR	mg/kg as fipronil
Foliage	2.29	97.4	2.17
Bolls	0.05	2.1	0.16
Lint	0.3	0.3	0.02
Seed	0.1	0.1	<0.01

More than 76% of the TRR was extracted with a sequence of organic solvents followed by acid and base digestion from the foliage and bolls. Lint was digested with cellulase; insufficient radioactivity was present for identification of metabolites. Seed was not extracted, as it contained <0.01 mg/kg fipronil equivalents.

Extracts were analysed by radio-HPLC followed by MS. In the foliage fipronil was determined at 0.01 mg/kg (0.3% of the TRR), and the metabolites RPA 200766 at 0.9 mg/kg (41.5% of the TRR), MB 46136 at 0.15 mg/kg (6.9% of the TRR), and RPA 200761 at 0.17 mg/kg (8.1% of the TRR). Two unknown metabolites (<0.05 mg/kg) were more polar than fipronil and its metabolites on the basis of partitioning and retention time characteristics. An additional 12 metabolites were detected at <0.01 mg/kg. No MB 45950 was determined. In bolls, fipronil (0.02 mg/kg, 12% of the TRR) and RPA 200766 (0.03 mg/kg, 21% of the TRR) were identified; and two other metabolites, more polar than fipronil, at <0.01 mg/kg (Table 19). The results indicate that measurable residues in cotton seed would be unlikely.

Table 19. Radioactive residues in cotton plants (Yenne and Stone, 1995).

Sample	Compound	Residues (mg/kg as compound, not as fipronil)	% of TRR[1]
Foliage	Fipronil	0.01	0.3
	MB 46136	0.15	6.9
	RPA 200766	0.90	41.5
	RPA 200761	0.17	8.1
Bolls	Fipronil	0.02	12
	RPA 200766	0.03	21

[1] Calculated from total residues in individual samples

Sunflower. In a study by Bellet *et al.* (1993) [^{14}C]fipronil (phenyl-labelled) was applied in furrow with seed at sowing as a 2% granular formulation at 200 g ai/ha, the intended use rate. Plants were sampled at intervals and at harvest. The TRR was measured in the aerial parts of the pre-harvest samples, and the leaves, trunk, heads and seeds taken at harvest were analysed separately.

Samples one month after planting showed absorption of 1.3% of the applied ^{14}C (0.17 mg/kg fipronil equivalents) and at harvest contained 4.8% in total. The distribution of the ^{14}C within the plants at harvest is shown in Table 20. More than 80% of the radioactivity was in the leaves.

Table 20. Distribution of radioactivity in sunflowers at harvest (Bellet *et al.*, 1993).

Sample	% of applied ^{14}C	% of TRR	mg/kg as fipronil
Leaves	4.0	83	1.4
Trunk	0.6	13	0.13
Head	0.08	1.7	0.033
Seed	0.12	2.9	0.034

Residues were isolated by sequential acetone, methanol/water, and Soxhlet extractions followed by digestion of tissues with acid. Extractability of radioactivity from the four substrates ranged from 83 to 95%. Metabolites were identified by co-chromatography with standards and GC-MS.

The main residue in the leaves was unchanged fipronil (0.48 mg/kg; 30% of the TRR). MB 46136 was a major metabolite (0.22 mg/kg, 14% of the TRR) together with RPA 200766 (0.11 mg/kg; 7.1% of the TRR). Numerous minor metabolites were found but none exceeded 0.05 mg/kg. The trunk also contained unchanged fipronil and MB 46136 was a main metabolite. Again, no other metabolites were identified which exceeded 0.01 mg/kg. The head contained no components above 0.01 mg/kg. The metabolite pattern in the seeds (which contained 0.029 mg/kg extractable ^{14}C, 2.7% of the TRR) differed in that extracts contained 14 components, all at levels below 0.01 mg/kg. Fipronil and closely related metabolites were not present in the seeds (Table 21).

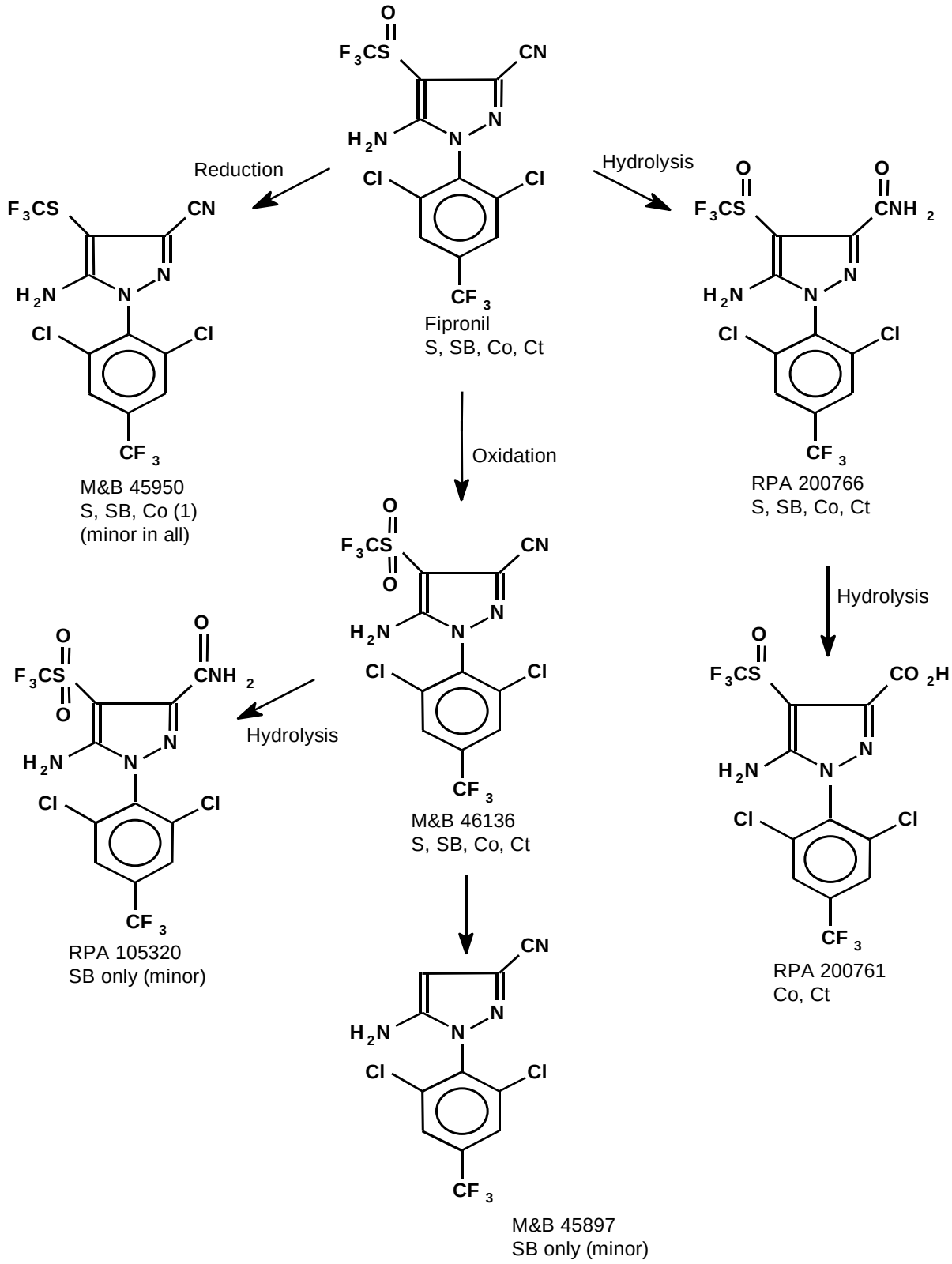
Table 21. Distribution of fipronil and metabolites in sunflower plants (Bellet *et al.*, 1993).

Sample	Compound	Residue (mg/kg)	% of total residue
Leaves			
Organic extract	Fipronil	0.48	30
	MB 46136	0.22	14
	MB 45950	0.04	2.6
	RPA 200766	0.11	7.1
	6 unknowns	0.015 to 0.045, total 0.16	9.9
Acid fraction	5 components	each <0.01, total 0.017	1.1
Trunk	Fipronil	0.034	4.3
	MB 46136	0.12	1.5
	2 unknowns	each <0.01, total 0.01	1.2
	polar (baseline) compound(s)	total 0.019	2.4
Head	multiple components	each <0.01, total 0.021	1.5
Seed	14 unknowns	each <0.01, total 0.029	2.7

In summary three pathways of metabolism of fipronil in plants after application by soil incorporation were identified:

(1) reduction to sulfide MB 45950, a minor pathway observed in some plants
(2) oxidation to MB 46136
(3) hydrolysis to amide RPA 200766. Further hydrolysis of metabolites RPA 200766 and MB 46136 to metabolites RPA 200761 and RPA 105320 also occurs in some plant tissues.

The proposed metabolic pathways are shown in Figure 4.



C: corn (maize), Co: cotton, S: sunflower, SB: sugar beet.

Figure 4. Plant metabolism after soil incorporated application.

Foliar application

Rice. In a study by Cooper *et al*. (1994) phenyl ring-labelled [^{14}C]fipronil was applied to transplanted rice plants as either a granular treatment or as a foliar spray.

Seedlings were transplanted into plots resembling paddy-fields (Thailand) with water levels between 9 and 15 cm. In two plots a 0.3% granule formulation was broadcast at 50 g ai/ha 20 days after the seedlings had been transplanted. In another two plots, the plants were sprayed twice with a 5% suspo-emulsion of fipronil at 20 and 50 days after being transplanted at 50 g ai/ha per treatment. There were also two control plots. The plots were maintained according to GAP for rice growing in Thailand.

Plants from all six plots were randomly sampled 51 days after transplanting (1 day after the second foliar spray and 31 days after the single granular treatment). At harvest, 92 days after transplanting, root, straw and ear samples were processed to provide pannicle, husk, brown rice, polished rice, and bran. The TRR was measured in all the samples. The results demonstrated that fipronil applied either as a granule or foliar application was absorbed and distributed throughout the whole plant. The residues at harvest after the granule application were lower than those in the sprayed plants (Table 22).

Table 22. Radiolabelled residues in rice plants at harvest, 72 days after granular treatment and 42 days after the second foliar treatment (Cooper *et al*., 1994).

Sample	^{14}C, mg/kg as fipronil					
	Foliar application			Granule application		
	Plot 1	Plot 3	Mean	Plot 2	Plot 5	Mean
Root	0.109	0.092	0.101	0.076	0.055	0.065
Straw	0.248	0.266	0.257	0.111	0.086	0.099
Pannicle	2.046	2.145	2.096	0.337	0.315	0.326
Husk	0.495	0.545	0.520	0.075	0.073	0.074
Bran	0.155	0.128	0.142	0.022	0.022	0.022
Brown Rice	0.025	0.023	0.024	0.005	0.006	0.006
Polished Rice	0.012	0.014	0.013	0.004	0.004	0.004
Total[1]	0.28	0.3	0.29	0.1	0.078	0.089

[1] Brown rice: polished rice + bran. Results for polished rice and bran, but not brown rice, have therefore been included in the total

74%-94% of the TRR was extractable. Extracts were analysed by ^{14}C-HPLC and by MS. Fipronil was present in all samples and no MB 46136 was detected in any. The photodegradation product fipronil-desulfinyl was detected only in samples from the foliar-treated plots (brown rice 0.45 µg/kg, polished rice 0.19 µg/kg), as was MB 45897. RPA 200766 was detected in all rice samples but at higher levels in samples from the granule-treated plots. Low levels of MB 45950 and RPA 104615 were present in all samples. The results are shown in Table 23.

Table 23. Residues in brown and polished rice (Cooper *et al*., 1994).

Indicated identity	Residue, µg/kg as compound, not as fipronil, and (% of TRR)			
	Brown rice		Polished rice	
	Granule	Foliar	Granule	Foliar
Fipronil	1.3 (25.4%)	12.3 (51.6%)	0.72 (17.6%)	4.97 (38%)
MB 46136	ND[2]	ND	ND	ND
MB 45950	0.21 (4.1%)	1.02 (4.3%)	0.21 (5.1%)	0.36 (2.8%)
fipronil-desulfinyl	ND	0.45 (1.9%)	ND	0.19 (1.5%)
MB 45897	ND	0.85 (3.6%)	ND	0.61 (4.7%)
RPA 200766	0.62 (12.1%)	2.27 (9.5%)	0.93 (22.8%)	1.81 (13.8%)

Indicated identity	Residue, µg/kg as compound, not as fipronil, and (% of TRR)			
	Brown rice		Polished rice	
	Granule	Foliar	Granule	Foliar
RPA 104615	0.11 (2.1%)	0.43 (1.8%)	0.1 (2.5%)	0.45 (3.4%)
Unascribed[1]	1.56 (30.5%)	2.18 (9.1%)	1.13 (27.7%)	2.46 (18.8%)
Unextracted	1.36 (26.6%)	4.6 (19.3%)	1.06 (26.0%)	2.54 (19.4%)

[1] Unascribed: radioactivity that could not be assigned to discrete peaks on the chromatogram
[2] ND: not detectable

To investigate the unextracted residue, brown rice samples were treated with methanol and ammonia, then refluxed with methanol and increasing concentrations of potassium hydroxide. Approximately 82% of the residual 20% was released, about 56% of which was partitioned into dichloromethane; the remaining 26% did not. It was concluded that most of the unextracted residue was not incorporated into natural products but consisted of fipronil and/or metabolites chemically bound to varying degrees.

A number of metabolites were detected in the granule- and foliar-treated green plant samples and harvested plant parts (excluding rice) (Table 24).

Table 24. Residues in granule- (GR) and foliar-treated plants (Cooper *et al*., 1994).

Interval	Sample and application		Residue, mg/kg as compound, not as fipronil					
			fipronil	MB 45950	MB 46136	Fipronil-desulfinyl	MB 45897	RPA 200766
51 DAT	Root	GR	0.01	0.013	0.004	0.008	0.001	0.001
		Foliar	0.096	0.015	0.005	0.016	0.001	0.001
	Plant	GR	0.008	0.003	0.003	0.01	<0.001	0.001
		Foliar	0.27	0.13	0.013	0.053	0.004	0.006
Harvest	Root	GR	0.004	0.016	0.010	0.01	ND	ND
		Foliar	0.025	0.013	0.015	0.019	ND	0.002
	Straw	GR	0.012	0.015	0.017	0.023	ND	0.005
		Foliar	0.1	0.023	0.029	0.047	ND	0.004
	Pannicle	GR	0.027	0.12	0.029	0.24	0.005	0.006
		Foliar	0.48	0.24	0.1	0.57	0.019	0.018
	Husk	GR	0.015	0.037	0.004	0.017	ND	0.006
		Foliar	0.11	0.027	0.021	0.053	0.006	0.013
	Bran	GR	0.004	0.003	ND	0.006	ND	<0.001
		Foliar	0.065	0.011	0.007	0.018	0.001	0.005

DAT: days after treatment
ND: not detectable

The number and nature of the metabolites demonstrated that rice plants are metabolized extensively by oxidative as well as reductive mechanisms, and the distribution throughout the plants also demonstrated that fipronil and its metabolites can be translocated.

Cabbage. In a study by Lowden and French (1995) HISPI cabbages grown from seed were foliar-sprayed twice with [^{14}C]fipronil (phenyl-labelled), once at the onset of heart formation and again 14 days later, at a rate equivalent to 200 g ai/ha per treatment.

Two treated plants were sampled 0, 17, 21, 24 and 28 days after the first spray, and four taken 14 days after the first dose (two before and two after the second dose: 14a and 14b). The remaining plants were harvested 35 days after the first spray. Control plants were sampled 0, 14, 28 and 35 days after the first spray. The TRR was measured in all samples, which were sequentially extracted with acetonitrile/water (1/1), acetonitrile, and hexane and the residues identified by HPLC, MS, and NMR.

A summary of the results is shown in terms of concentration in Table 25 and in percentage of the TRR in Table 26.

Table 25. Concentrations of fipronil and metabolites in cabbages, expressed as mg/kg fipronil equivalents (Lowden and French, 1995).

Component	Days after application									
								35 (Harvest)		
	0	14a	14b	17	21	24	28	Total	Leaves	Heart
Fipronil	1.98	0.53	1.65	0.91	0.83	0.54	0.57	0.66	1.08	0.38
MB 46136	0	0	0	0.01	0.01	0.01	0	0.01	0.03	0
MB 45950	0	0	0	0	0.03	0	0.01	0	0	0
fipronil-desulfinyl	0	0.14	0.3	0.21	0.22	0.21	0.2	0.17	0.35	0.03
RPA 200766	0	0	0	0.03	0.05	0.05	0	0.16	0.29	0.06
RPA 104615	0	0.05	0	0.05	0.04	0.04	0.15	0.21	0.4	0.08
Bound	0	0.06	0.1	0.08	0.08	0.09	0.1	0.07	0.13	0.03

Table 26. Fipronil and metabolites in cabbages, expressed as % of TRR (Lowden and French, 1995).

Component	Days after application									
								35 (Harvest)		
	0	14a	14b	17	21	24	28	Total	Leaves	Heart
Fipronil	100	68	81	71	66	57	55	52	47	66
MB 46136	0	0	0	0.8	0.8	1.1	0	0.8	1.3	0
MB 45950	0	0	0	0	2.4	0	1.0	0	0	0
fipronil-desulfinyl	0	18	15	16	17.5	22	19.4	13	15	5.2
RPA 200766	0	0	0	2.3	4.0	5.3	0	12.5	13	10
RPA 104615	0	6.4	0	3.9	3.2	4.3	15	16	18	14
Bound	0	7.7	4.9	6.2	6.3	9.6	9.7	5.5	5.7	5.2

This study demonstrated that the photodegradation products of fipronil, fipronil-desulfinyl and RPA 104615 are two of the main degradation products of fipronil found in cabbage plants after foliar application. At harvest (35 days after first application), these compounds accounted for 13% and 16% of the TRR respectively. RPA 200766, the amide metabolite, was also a major product (13% of the TRR at harvest).

Potatoes. In a study by Mislankar (1995) plants were sprayed twice with [^{14}C]fipronil at 112 g ai/ha/application (season rate) or 560 g ai/ha/application (5 times the season rate), the first 7 weeks and the second 10 weeks after planting, 28 days before harvest. Potatoes were harvested as they matured and tubers composited. The TRR was determined in the vines and potatoes at both rates.

Table 27. Total radioactive residues in potato plants (Mislankar, 1995).

Sample	Rate (g ai/ha)	% of TRR	mg/kg as fipronil
Potato	2 x 112	1.05	0.005
Vine	2 x 112	99	0.47
Potato	2 x 560	0.54	0.02
Vine	2 x 560	99.5	3.7

Only tubers, the edible portions of the plants, were extracted. As the TRR in the potatoes sprayed at the low rate was only 0.005 mg/kg as fipronil, only extracts from the potatoes sprayed at the high rate were analysed.

Sequential solvent extractions extracted almost 95% of the TRR (0.019 mg/kg) from the high-rate tubers. Analysis was by HPLC with LSC; all metabolites were below 0.005 mg/kg. Metabolites were identified by HPLC retention time compared to standards and confirmed by mass spectrometry.

Four metabolites were identified in the tubers: fipronil at 0.0034 mg/kg (18% of the TRR), MB 46136 at 0.0013 mg/kg (6.6% of the TRR), fipronil-desulfinyl at 0.003 mg/kg (16% of the TRR), MB 45897 at 0.0012 mg/kg (6.4% of the TRR), and RPA 104615 at 0.0018 mg/kg (9.6% of the TRR). Five unknown metabolites, all below 0.002 mg/kg, accounted for a total of 0.005 mg/kg. Trace amounts of MB 45950, RPA 200766, and RPA 200761 were detected by MS only.

Table 28. Fipronil and its metabolites in potato tubers (Mislankar, 1995).

Sample	Compound	Residue (mg/kg as compound, not as fipronil)	% of TRR[1]
Tuber (5 times rate)	Fipronil	0.0034	18
	MB 46136	0.0013	6.6
	fipronil-desulfinyl	0.003	15.8
	MB 45897	0.0012	6.4
	RPA 104615	0.0018	9.6
	5 compounds	all <0.002, total 0.005	26

[1] Calculated from total residues in individual samples

The residue levels at the fivefold rate indicate that fipronil and its metabolites are poorly translocated from the foliage to the tubers, and therefore there should not be measurable residues in tubers at the proposed rate.

After foliar application to potatoes, fipronil is oxidized to the sulfone MB 46136 or photolysized to fipronil-desulfinyl. The sulfone undergoes further transformation to the sulfonic acid RPA 104615 followed by loss of the sulfonic acid group to form MB 45897.

Cotton. In a study by Yenne and Stone (1995) an acetonitrile solution of [^{14}C]fipronil was sprayed twice on cotton foliage at 112 g ai/ha/application, the second time at the soft-boll stage 49 days before harvest. The mature dessicated plants with hard seeds were harvested 140 days after planting and the above-ground portion of the plants separated into seed, lint, bolls and foliage. The TRR was determined in all tissues.

The foliage contained 8.3 mg/kg fipronil equivalents (97% of the TRR in the plant at harvest), bolls 0.81 mg/kg, lint 0.1 and seed <0.01 mg/kg.

Table 29. Distribution of radioactivity in cotton plants (Yenne and Stone, 1995).

Sample	^{14}C, % of TRR	Residue (mg/kg as fipronil)
Foliage	97	8.3
Bolls	2.7	0.81
Lint	0.3	0.1
Seed	0	<0.01

Cotton foliage and bolls were extracted with a sequence of organic solvents followed by acid and base digestion. More than 90% of the TRR was extractable. Lint was digested with cellulase; seed was not extracted as it contained <0.01 mg/kg fipronil equivalents.

Foliage, boll extracts and digested lint were analysed by ^{14}C-HPLC and TLC followed by MS to identify and confirm metabolites. The compounds in the foliage were fipronil at 4.4 mg/kg (53% of the TRR), MB 46136 at 0.55 mg/kg fipronil equivalents (6.6% of the TRR), RPA 200761 at 1.3 mg/kg (15.5% of the TRR), and fipronil-desulfinyl at 0.01 mg/kg (0.1% of the TRR), two unknown significant metabolites (0.05 mg/kg) which were more polar than fipronil and the identified metabolites from their partitioning and retention time characteristics, and an additional 6 metabolites at 0.01 mg/kg. Trace amounts of MB 45950, RPA 105320, and RPA 200766 were detected by LC-MS only. In bolls, the same main metabolites were identified, but in different proportions: fipronil (0.52

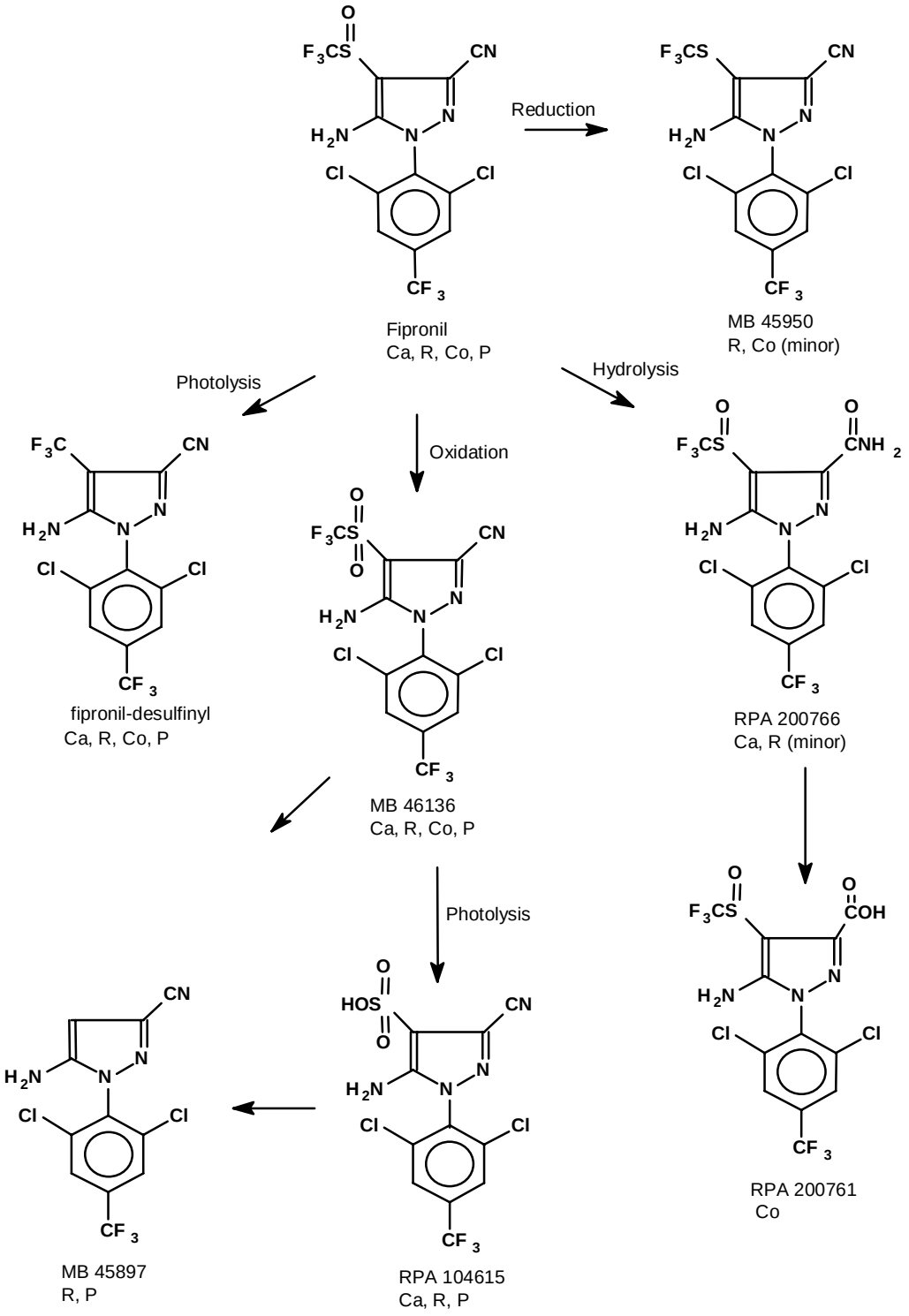
mg/kg, 64% of the TRR), MB 46136 (0.11 mg/kg, 14% of the TRR), RPA 200761 (<0.01 mg/kg, 0.3% of the TRR), and fipronil-desulfinyl (0.01 mg/kg, 0.9% of the TRR). Lint contained only 2 metabolites above 0.01 mg/kg, fipronil and MB 46136. Low levels (<0.01 mg/kg) of fipronil-desulfinyl, RPA 200761, and MB 45950 were also confirmed; 5 additional unknowns were observed, all at levels below 0.01 mg/kg (Table 30).

Table 30. Radioactive residues in cotton plants (Yenne and Stone, 1995).

Sample	Compound	mg/kg as fipronil	% of TRR
Foliage	Fipronil	4.4	53
	MB 46136	0.55	6.6
	RPA 200761	1.3	15.5
	fipronil-desulfinyl	0.01	0.1
	Polar unknowns	0.18	2.2
	6 compounds	all <0.01	total 0.8
Bolls	Fipronil	0.52	64
	MB 46136	0.11	14
	RPA 200761	<0.01	0.3
	fipronil-desulfinyl	0.01	0.9
Lint	Fipronil	0.05	48
	MB 46136	0.11	14
	RPA 200761	<0.01	1.2
	fipronil-desulfinyl	<0.01	2.0
	MB 45950	<0.01	4.2
	5 compounds	all <0.01	total 14

The metabolic pathways in plants after foliar application of fipronil may be summarized as follows. In addition to the formation of metabolites *via* oxidation (MB 46136), reduction (MB 45950) and hydrolysis (RPA 200766 and RPA 200761), the photodegradation products fipronil-desulfinyl and RPA 104615 have been shown to be terminal residues. Cleavage of the sulfonic acid group from RPA 104615 can also occur to give MB 45897 (minor). Fipronil, MB 46136 and fipronil-desulfinyl were the main compounds observed in all studies. Proposed metabolic pathways in foliar-treated plants are shown in Figure 5.

Figure 5. Metabolic pathways in plants after foliar applications.



Ca: Cabbage; R: Rice; Co: Cotton; P: Potato

Plant metabolism – summary of results

Soil incorporated applications. The metabolism of fipronil was studied in sunflowers, sugar beet, field maize, and cotton after the application of fipronil to soil with incorporation. Formulations, rates, and samples analysed are shown in Table 31.

Table 31. Summary details of soil-incorporated fipronil metabolism studies.

Crop	Method of application	Time of application	Rate (g ai/ha)	Sample analysed	Sampling time
Sunflower	Granule	at planting	200	Leaves, trunk, head, seeds	at harvest
Sugar beet	Granule	at planting	200	Beet, leaves	at harvest
Field maize	a) Granule b) Soil spray	at planting	a) 420 b) 146	Green forage Fodder, grain	a) 42 DAP[1] at harvest b) 35 DAP at harvest
Cotton	Soil spray	at planting	224	Foliage, bolls, lint, seed	at harvest

[1] Days after planting

In all studies the samples indicated in the above table were analysed quantitatively for radioactivity, and subjected to solvent extraction followed by extract analysis to give qualitative information. Methods of analysis included TLC, HPLC-MS and GC-MS.

Measurement of radioactivity showed that the uptake of soil-applied fipronil into plants is low (less than 5% based upon total radioactivity measured in whole plants at harvest). Analysis of extracts from maize forage samples revealed fipronil, the sulfone MB 46136 and the amide RPA 200766 as the main metabolites in both studies; RPA 200761 was also found in the second study. In harvest samples, sugar beet and sunflower leaves as well as maize fodder and cotton foliage contained the metabolites MB 46136 and RPA 200766 and varying amounts of the parent compound. RPA 105320 and MB 45897 were identified only in beet leaves; RPA 200761 was identified in maize fodder and cotton foliage.

In edible plant parts, MB 46136 and RPA 200766 were present in sugar beet. In maize grain only RPA 200766 was found. Sunflower seed extracts contained a complex mixture of substances dissimilar to those in the leaves; a number of components each representing <0.01 mg/kg were separated. Cotton seed was not analysed as it contained less than 0.01 mg/kg of TRR. The distribution of identified compounds in all the studies is shown in Table 32.

Table 32. Compounds identified in soil-applied fipronil metabolism.

TRR, mg/kg as fipronil	Fipronil	MB 45897	MB 45950	MB 46136	RPA 105320	RPA 200761	RPA 200766
Sunflower							
Leaves 1.43	M	--	vm	M	--	--	m
Seed 0.034[1]	--	--	--	--	--	--	--
Sugar beet							
Leaves 0.45	MSO	vm	vm, NC	M	M	--	vm
Root 0.05	M	--	MSO	M	--	--	m
Maize-1							
Forage 0.21	M	--	--	m	--	--	M
Fodder 3.7	M	--	vm	M	--	m	M
Grain 0.16	--	--	--	--	--	--	M
Maize-2							
Forage 0.11	M	--	--	M	--	M	M
Fodder 0.51	M	--	--	M	vm	vm	M
Grain 0.01	--	--	--	--	--	--	M
Cotton							
Foliage[2] 2.33	vm	--	--	m	--	m	M
Lint 0.02[3]	--	--	--	--	--	--	--

TRR, mg/kg as fipronil	Fipronil	MB 45897	MB 45950	MB 46136	RPA 105320	RPA 200761	RPA 200766
Seed <0.01 [3]	--	--	--	--	--	--	--

M: major, >10% of TRR; m: minor, 5-10% of TRR; vm: very minor, <5% of TRR
NC: not confirmed by MS; MSO: observed by MS only
[1] 14 components, all <0.01 mg/kg
[2] Including bolls
[3] Not analysed

In summary, for soil-incorporated uses of fipronil, identification of residues in plant tissues shows that the metabolism proceeds mainly by oxidation to sulfone MB 46136 and hydrolysis to amide RPA 200766. Further hydrolysis of these metabolites can also occur. Very small amounts of sulfide MB 45950 can occur by reduction, but in no case was it >5% of the total radioactive residue.

Foliar applications. The metabolism of [^{14}C]fipronil has been studied after foliar spray application to cabbages, rice, cotton, and potatoes. The timing rates of application, and samples analysed at harvest are shown in Table 33.

Table 33. Summary details of foliar-applied fipronil metabolism studies.

Crop	Time of application	Rate (g ai/ha)	Sample analysed	Sampling
Cabbage	First spray at onset of heart formation; 14 day spray interval	2 x 200	Leaves, heart	21 DALT[1]
Rice[2]	First spray 20 days after transplant; 30 day spray interval	2 x 50	Straw, panicle, husk, bran, brown rice, polished rice	42 DALT
Cotton	First spray pre-first bloom; second spray at soft boll stage	2 x 112	Foliage, bolls, lint, seed	49 DALT
Potato	First spray to immature foliage, 7 weeks after planting; 21 day spray interval	2 x 560[3]	Tuber	28 DALT

[1]Days after last treatment
[2]The study also included a granular application to the rice paddy 20 days after the transplant of rice; only data from the foliar portion of the study are reported.
[3]Rate applied is 5 times proposed use rate to allow identification of metabolites.

Radioactive residues were quantified in all samples. Organic solvents were used for extraction and extracts were used for identification. Methods of analysis were similar to those for the extracts after soil-incorporation.

In addition to the formation of previously known fipronil metabolites from oxidation (MB 46136), reduction (MB 45950) and hydrolysis (RPA 200766, RPA 200761), photodegradation products fipronil-desulfinyl and RPA 104615 have been identified as possible terminal residues after foliar application of fipronil. The main residues are consistently parent and fipronil-desulfinyl; lesser amounts of MB 45950 and MB 46136 can also form. Table 34 shows the distribution of identified compounds in all the studies.

Table 34. Compounds identified in foliar-applied fipronil metabolism.

Sample and TRR, mg/kg as fipronil	Compound							
	Fipronil	MB 45897	MB 45950	MB 46136	fipronil-desulfinyl	RPA 104615	RPA 200761	RPA 200766
Cabbage								
Whole plant 1.28	M	--	--	vm	M	M	--	M
Cotton								
Foliage[1] 9.13	M	--	--	m	vm	--	M	--
Lint 0.1	M	--	vm	M	vm	--	vm	--
Seed[2] <0.01	--	--	--	--	--	--	--	--

Sample and TRR, mg/kg as fipronil	Compound							
	Fipronil	MB 45897	MB 45950	MB 46136	fipronil-desulfinyl	RPA 104615	RPA 200761	RPA 200766
Potato								
Tuber 0.021[3]	M	m	MSO	m	M	m	MSO	--
Rice								
Straw 0.26	M	--	M	M	M	--	--	vm
Panicle 2.1	M	vm	M	m	M	--	--	vm
Husk 0.52	M	vm	M	m	M	--	--	m
Bran 0.14	M	vm	M	m	M	--	--	vm
Brown rice 0.024	M	vm	vm	--	vm	vm	--	m
Polished rice 0.013	M	vm	vm	--	vm	vm	--	M

M: major, >10% of TRR; m: minor, 5-10% of TRR; vm: very minor, <5% of TRR
MSO: observed by MS only
[1] Including bolls
[2] Not analysed, TRR <0.01 mg/kg
[3] 5-times rate; single rate TRR was only 0.005 mg/kg

Environmental fate in soil

Photolysis

The photolytic degradation of [^{14}C]fipronil after surface application to a clay-loam soil has been studied by Burr and Austin (1992). Soil at 75% of its 1/3 bar moisture holding capacity was treated with [^{14}C]fipronil at a rate equivalent to 0.25 kg ai/ha.

All soil samples were incubated under aerobic conditions. Control samples were maintained in the dark; test samples were irradiated with a xenon lamp, filtered to provide light in the wavelength range 290-800 nm. An 8/16 h light/dark irradiation cycle was used to simulate natural sunlight equivalent to a typical day in Florida, USA, and samples were taken after 0, 3, 7, 14, 21 and 30 days. The extracts were analysed by thin-layer and high-performance liquid chromatography.

The nature and number of degradation products found differed between the control and irradiated samples. In the control sample extracts, the metabolites MB 45950, MB 46136 and RPA 200766 were identified and by day 30 all were at approximately equal proportions of the applied nominal dose, about 10%. The remainder of the radioactivity was identified as being from fipronil.

In the irradiated samples the products MB 45950, MB 46136, RPA 200766, fipronil-desulfinyl and RPA 104615 were identified. The proportion of RPA 200766 was very similar in the control and irradiated samples, indicating that its production is not related to photolytic degradation. MB 45950 was only a very minor product under irradiation, <2% by day 30. The two photoproducts RPA 104615 and fipronil-desulfinyl each accounted for about 7% of the applied nominal dose and were not found in the control samples.

Fipronil was degraded rapidly with and without irradiation with half-lives of about 49 and 34 days respectively. Irradiation yielded RPA 104615 and fipronil-desulfinyl which were also observed in an aqueous photolysis study described below but not in the control samples in either study.

Aerobic degradation

The degradation of [^{14}C]fipronil applied at 200 g ai/ha to a sandy loam soil in Manningtree, UK, and Speyer 2.2 soil in Germany over a 336-day period was studied by Waring (1993). Key characteristics of the soil were as follows.

Soil	Textural class	Cation exchange capacity (me/100g)	Organic matter (%)	pH
Speyer 2.2	Sand	3.3	3.3	6.1
Manningtree Soil	Sandy loam	6.4	1.7	7.8

Aliquots of the soils (50 g dry weight equivalent) were incubated in crystallizing dishes housed in glass chambers. Moistened CO_2-free air was drawn through each chamber before being passed through various traps to collect polar and non-polar volatiles and $^{14}CO_2$. Duplicates of each soil were sampled at intervals of 0, 1, 3, 7, 14, 30, 41, 80, 149, 252 and 336 days after treatment.

Initially, [^{14}C]fipronil accounted for >98% of the applied radioactivity. Over the study period, the amount of parent compound decreased to 12-20% in the Manningtree and 44%-46% in the Speyer soil.

RPA 200766 and MB 46136 were the main degradation products, accounting for a maximum of 38% and 24% of the applied radioactivity respectively in Manningtree and 27% and 14% in Speyer 2.2 soil. Smaller quantities of MB 45950 (<5%) and the photodegradation product fipronil-desulfinyl (1%, assumed to be an artifact) were also detected in both soils, and MB 45897 (<1%) in Speyer 2.2 soil.

The initial half-lives determined by HPLC were 128 and 308 days in Manningtree and Speyer soils respectively.

A study was conducted to investigate the rate of degradation of phenyl ring-labelled [^{14}C]fipronil in four European soils incubated under aerobic conditions at 22°C and 10°C (Humphreys *et al.*, 1994). It used radiolabelled test material to determine the nature of the bound residues. The characteristics of the soils used are shown in Table 35.

Table 35. Soil characteristics (Humphreys *et al.*, 1994).

Soil	Origin	% Clay	% Silt	% Sand	% Organic matter	pH
Speyer 2.2	Germany	8	9	83	5.7	6.3
Sandy loam	UK	9	11	80	0.75	6.4
Sandy clay loam 1	France	26	27	47	1.2	6.16
Sandy clay loam 2	France	24	26	50	2.2	6.18

The soils were allowed to equilibrate for 14 days at 0.33 bar moisture holding capacity (MHC) and then raised to 0.1 bar MHC for dosing and incubation. Dishes containing 75 g of the appropriate soil (oven-dried equivalent) were dosed with [^{14}C]fipronil at a rate equivalent to 200 g ai/ha and incubated in the dark under aerobic conditions. Sample traps were used to retain any volatile products. Duplicate soil and trap samples were taken at 7 days and at 1, 3, 5 (sandy clay loam 1 only), 6, 9 and 12 months. Good radiochemical recoveries were achieved and most of the radioactivity was extracted. Radio-HPLC analysis showed a reduction of fipronil content with time for each soil. Half-lives from the Timme model (Timme *et al.*, 1986) are shown in Table 36.

Table 36. Estimated half-lives of fipronil in soil treated with [^{14}C]fipronil at 200 g ai/ha (Humphreys *et al.*, 1994).

Soil	Half-life (days), 10° C	Half-life (days), 22° C
Speyer 2.2 (Germany)	247	62
Sandy loam (UK)	163	117
Sandy clay loam 1 (France)	61	18
Sandy clay loam 2 (France)	62	40

The main degradation product in all cases was RPA 200766 (about 30-47%), with MB 46136 about 20%. MB 45950 was found at levels below 10% (below 5% in most cases), and RPA 105320

and MB 45897 at very low levels. These compounds accounted for more than 85% of the extractable radioactivity in the Speyer and sandy loam soils, and more than 60% in the sandy clay loam.

Polar products not previously detected were found in significant amounts (from 5.9% to 29% collectively) in the later stages of the study, at higher levels in the sandy clay loams than in the other soils. These were acid analogues of fipronil and its degradation products, the result of hydrolysis of nitrile to amide and thence to carboxylic acid, found at levels reflective of the abundance of their precursors. RPA 200761, the acid derived from amide RPA 200766, was detected at the highest level in all soils followed by RPA 106881, the acid of MB 46136. MB 46233, the acid of MB 45950, was observed at much lower concentrations. Of these acids, only RPA 200761 was found, in some samples, at levels above 10% of the applied dose.

Adsorption/desorption

The adsorption/desorption characteristics of fipronil, MB45950, MB 46136 and fipronil-desulfinyl have all been studied.

Fipronil. Godward *et al.* (1992) studied the soil adsorption and desorption of [^{14}C]fipronil in five European soils: Speyer 2.2 (Germany), sandy loam and loam (UK), and sandy clay loam 1 and 2 (France).

Recoveries of ^{14}C throughout the study were essentially quantitative for all soils and [^{14}C]fipronil was stable throughout. K_{oc} values calculated for each soil and the Freundlich isotherm constants for adsorption and desorption are shown in Table 37.

Table 37. Freundlich adsorption/desorption constants for fipronil (Godward *et al.*, 1992).

Soil	% organic C	K	1/n	K_{OC}
Adsorption				
German Speyer 2.2	3.35	14.32	0.947	427
UK sandy loam	0.34	4.19	0.950	1248
UK loam	4.25	20.69	0.938	486
French sandy-clay-loam-1	1.16	9.32	0.969	800
French sandy-clay-loam-2	1.59	10.73	0.949	673
Desorption				
German Speyer 2.2	3.35	13.35	0.905	398
UK sandy loam	0.34	7.25	0.986	2162
UK loam	4.25	21.51	0.910	506
French sandy-clay-loam-1	1.16	10.14	0.960	870
French sandy-clay-loam-2	1.59	12.88	0.948	808

Comparison of the adsorption and desorption isotherms indicates that the processes involved in adsorption and desorption are similar.

The results indicate that fipronil is unlikely to show much mobility in soil. According to McCall's designation, fipronil would be expected to be of medium to low mobility (McCall *et al.*, 1980).

MB 45950. The adsorption and desorption properties of [^{14}C]MB 45950 (phenyl-labelled), a soil degradation product of fipronil, have been investigated in four soils: silt and sandy loam (USA), loam and silt loam (UK) and a sediment sandy clay loam (UK) (McMillan, 1997b).

Recoveries throughout the study were essentially quantitative and ^{14}C-MB 45950 was stable. The K_{oc} values calculated for each soil and the Freundlich equation constants for adsorption and desorption are shown in Table 38.

Table 38. Freundlich adsorption/desorption constants for MB 45950 (McMillan, 1997b).

Soil	% organic C	K	1/n	K_{OC}
Adsorption				
US Silt loam	0.5	28.1	1.046	5621
US Sandy loam	1.2	42.36	0.950	3530
UK Loam	2.2	9.97	0.997	4362
UK Silt loam	1.9	32.2	0.932	1695
UK Sediment	2.3	100.02	0.970	4349
Desorption				
US Silt loam	0.5	27.87	0.958	5574
US Sandy loam	1.2	48.48	0.945	4040
UK Loam	2.2	94.59	0.968	4300
UK Silt loam	1.9	37.92	0.923	1996
UK Sediment	2.3	97.59	0.953	4243

Comparison of the isotherms derived from the adsorption and desorption data indicates that adsorption is reversible with substantial hysteresis in the adsorption/desorption curve. The results show that MB 45950 would not be expected to show any significant movement in soil. According to the McCall classification MB 45950 should be classified as having low mobility.

MB 46136. The adsorption and desorption of the degradation product [^{14}C]MB 46136 (phenyl-labelled) have been investigated in four soils, silt and sandy loam (USA), loam and silt loam (UK), and a sediment (UK) classified as sandy clay loam according to the USDA classification (McMillan, 1997a).

Because of the low solubility of MB 46136 in water only low concentrations could be used. This, and the fact that the compound is adsorbed to glass, contributed to some variability in recoveries, which occasionally fell outside the target range of 90-110%. [^{14}C]MB 46136 was stable throughout.

The K_{oc} values calculated for each soil and the Freundlich equation constants for adsorption and desorption are shown in Table 39.

Table 39. Freundlich adsorption/desorption constants for MB 46136 (McMillan, 1997a).

Soil	% organic C	K	1/n	K_{OC}
Adsorption				
US silt loam	0.5	26.55	1.141	5310
US sandy loam	1.2	48.64	0.996	4054
UK loam	2.2	148.4	1.054	6745
UK silt loam	1.9	27.51	0.947	1448
5 UK sediment	2.3	80.18	0.970	3486
Desorption				
US silt loam	0.5	659.1	1.696	131815
US sandy loam	1.2	72.1	1.024	6008
UK loam	2.2	231	1.085	10500
UK Silt loam	1.9	33.8	0.947	1777
UK Sediment	2.3	95.1	0.979	4136

The shape of the isotherms suggest a single adsorption mechanism. In all cases, the desorption mechanism is relatively independent of the treatment concentration.

The results indicate that MB 46136 would not be expected to show any significant movement in soil. According to McCall *et al.* (1980) MB 45950 should be classified as having low to negligible mobility.

Fipronil-desulfinyl. The soil adsorption and desorption properties of the photodegradation product [^{14}C]fipronil-desulfinyl (phenyl-labelled) were investigated in four soils and a sediment in the USA:

silt loam, clay, sand and loamy sand, and a sediment classified as loam according to the USDA classification (Feung and Mislankar, 1996).

Recoveries throughout the study were essentially quantitative for all soils, and [^{14}C]fipronil-desulfinyl was stable throughout. The K_{OC} values calculated for each soil and the Freundlich equation constants for adsorption and desorption are shown in Table 40.

Table 40. Freundlich adsorption/desorption constants for fipronil-desulfinyl (Feung and Mislankar, 1996).

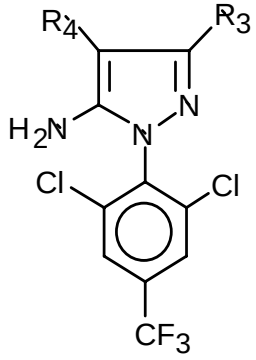
Soil	% organic C	K	1/n	K_{OC}
Adsorption				
Silt loam	0.5	5.47	0.738	1094
Clay	1.2	15.2	1.183	1267
Sand	0.4	4.34	0.920	1085
Loamy sand	0.3	5.13	0.953	1710
Sediment	5.0	69.3	0.947	1386
Desorption				
Silt loam	0.5	6.21	0.793	1242
Clay	1.2	14.7	0.916	1225
Sand	0.4	5.77	0.932	1443
Loamy sand	0.3	5.93	0.951	1977
Sediment	5.0	66.2	0.913	1324

The desorption results demonstrated that fipronil-desulfinyl, once adsorbed, was tightly bound to soil. According to McCall *et al.* (1980) fipronil-desulfinyl should be classified as having low mobility.

Accumulation of fipronil in confined rotational crops.

The reference standards used in confined rotational crop studies are listed in Figure 6.

Figure 6. Structures of fipronil and standards representing potential metabolites.



Compound	R_3	R_4
Fipronil	CN	$SOCF_3$
MB 45950	CN	SCF_3
MB 46136	CN	SO_2CF_3
RPA 200766	$CONH_2$	$SOCF_3$
Fipronil-desulfinyl	CN	CF_3
MB 200761	COOH	$SOCF_3$
MB 45897	CN	H
RPA 105048	$CONH_2$	CF_3
RPA 104615	CN	SO_3H
RPA 105320	$CONH_2$	SO_2CF_3

Soil incorporation treatment

In a study by Jesudason and Mackie (1995) phenyl ring-labelled [^{14}C]fipronil was applied to a sandy loam soil at 157 g ai/ha and incorporated. Samples were collected after application to determine whether the soil had retained radioactivity approximating the theoretical application rate. The treated soil was then planted with carrots, radishes or lettuce, and sorghum or wheat at 30, 153 and 365 days after treatment (DAT). Lettuce leaf was harvested 36-196 days, radish leaf and root 36 to 51 days, carrot leaf and root 83 days, wheat forage 51 days, wheat straw and grain 231 days, sorghum forage 20-36 days and sorghum grain 107 to 112 days after planting. The total ^{14}C residues are shown in Table 41.

Table 41. TRR in rotational crops treated with [^{14}C]fipronil (Jesudason and Mackie, 1995).

Sample	TRR (DPM/g[1] and mg/kg [^{14}C]fipronil equivalents)					
	30 DAT		153 DAT		365 DAT[2]	
	DPM/g	mg/kg	DPM/g	mg/kg	DPM/g	mg/kg
Lettuce leaf	161	0.003[3]	274	0.006[3]	425	0.009[3]
Carrot leaf	1047	0.021	--	--	--	--
Carrot root	796	0.016	--	--	--	--
Radish leaf	--	--	199	0.004[3]	317	0.006[3]
Radish root	--	--	131	0.003[3]	171	0.003[3]
Wheat forage	--	--	837	0.017	--	--
Wheat straw	--	--	8495	0.172	--	--
Wheat grain	--	--	590	0.012	--	--
Sorghum forage	1380	0.028	--	--	667	0.014
Sorghum stover	1761	0.036	--	--	1169	0.024
Sorghum grain	410	0.008[3]	--	--	803	0.016

[1] DPM/g:-disintegrations per min/g tissue
[2] DAT: days after treatment
[3] <0.01 mg/kg, not analysed further

All crops that had TRR values at or above 0.01 mg/kg were extracted and the extracted residues characterized and identified. Total recoveries were more than 88% of the TRR in all samples at the three rotational intervals. All extracted residues were organosoluble in 30 DAT carrot leaf, carrot root and sorghum forage, 153 DAT wheat forage, and 365 DAT sorghum forage. Water-soluble residues in 30 DAT sorghum stover, 153 DAT wheat grain, and 365 DAT sorghum were below 0.01 mg/kg. Unextractable residues were below 0.01 mg/kg in all samples.

Organosoluble compounds were identified by two reverse-phase HPLC methods using a Spherisorb ODS column and a Hichrom spherisorb semi-preparative column with UV (280 nm) and radiometric detection. The LOQ ranged from 0.001 to 0.003 mg/kg. The distribution of organosoluble compounds found in the analysed rotational crops is shown in Table 42.

Table 42. Organosoluble residues identified in rotational crops (Jesudason and Mackie, 1995).

Residues in organosoluble extracts, mg/kg as compound, not ^{14}C as fipronil											
Sample	TRR	fipronil	RPA 200761	RPA 200766	MB 46136	Fipronil-desulfinyl	RPA 105320	MB 45950	RPA 104615	RPA 105048	un-known
30 DAT											
Carrot											
Leaf	0.021	0.005	0.001[1]	0.010	0.001	ND	0.001	ND	0.001[1]	ND	ND
Root	0.016	0.005	<LOQ	0.002	0.005	ND	ND	0.004	<LOQ	ND	ND

Residues in organosoluble extracts, mg/kg as compound, not ^{14}C as fipronil											
Sample	TRR	fipronil	RPA 200761	RPA 200766	MB 46136	Fipronil-desulfinyl	RPA 105320	MB 45950	RPA 104615	RPA 105048	un-known
Sorghum											
Forage	0.028	0.013	0.004[1]	0.003	0.003	ND	ND	ND	0.004[1]	ND	ND
Stover	0.036	0.003	0.003	0.004	0.008	0.001	ND	ND	0.003	ND	0.002
153 DAT											
Wheat											
Forage	0.017	0.003	ND	0.003	0.003	ND	ND	ND	ND	ND	0.006
Straw	0.172	0.020	0.015	0.067	0.044	0.019	0.012	ND	ND	0.003	0.007
Grain	0.012	ND	0.006	0.001	ND	ND	ND	ND	ND	ND	0.002
365 DAT											
Sorghum											
Forage	0.014	0.001	0.002	0.001	0.001	ND	ND	ND	0.003	ND	ND
Stover	0.024	0.001	0.003	0.005	0.004	ND	ND	ND	ND	ND	0.003
Grain	0.016	ND	0.009	ND	ND	ND	ND	ND	ND	ND	ND

[1] The concentration of RPA 200761 and RPA 104615 together, not individually
ND: not detectable

The results are consistent with established routes of environmental degradation and plant metabolism of fipronil and demonstrate common pathways in rotated crops, and indicate that:

- The uptake of the TRR is low, in this study less than 0.01 mg/kg in 8 of 18 samples analysed at the three rotational intervals and between 0.01 and 0.05 mg/kg in 9 of 18.
- Fipronil and its metabolites are not highly systemic. No significant residues were found in the edible substrates analysed (those with TRR >0.01 mg/kg). Only cereal straw and forage, both animal feed items, contained residues higher than 0.01 mg/kg.

Soil surface treatment

In a study by Jesudason and Mackie (1999) phenyl ring-labelled [^{14}C]fipronil was applied to the surface of a sandy loam soil at 369 g ai/ha, and the plots planted with lettuce (*Lactuca sativa*), and radish (*Raphanus sativus*), and sorghum (*Sorghum vulgare*) or wheat (*Triticum aestivum*) 30, 150 and 365 days after treatment. All crops were grown to maturity and sampled, and sorghum and wheat were also sampled at the forage stage. The crops were harvested at intervals after planting of 32-43 days for lettuce, 32-43 days for radish, 196 days for wheat forage, 259 days for wheat straw and grain, 33-74 days for sorghum forage and 118-171 days for sorghum grain and fodder. Recoveries of ^{14}C are shown in Table 43.

Table 43. TRR in rotational crops after surface treatment of soil with [^{14}C]fipronil (Jesudason and Mackie, 1999).

Sample	TRR (DPM/g and mg/kg [^{14}C]fipronil equivalents)					
	30 DAT		150 DAT		365 DAT	
	DPM/g	mg/kg	DPM/g	mg/kg	DPM/g	mg/kg
Lettuce leaf	2562	0.040	608	0.009	1624	0.025
Radish leaf	6812	0.11	631	0.010	1667	0.026
Radish root	1615	0.025	196	0.003[1]	362	0.006[1]
Wheat forage	--	--	3007	0.047	--	--
Wheat straw	--	--	13345	0.21	--	--
Wheat grain	--	--	789	0.012	--	--
Sorghum forage	3320	0.052	--	--	3100	0.048
Sorghum fodder	7757	0.12	--	--	2350	0.037
Sorghum grain	1712	0.027	--	--	1006	0.016

DAT: days after treatment
DPM/g: disintegrations per min/g tissue
[1] Not analysed further

The recovery of ^{14}C was >97% from the extracted samples except radish leaves (70% of 0.001 mg/kg). Recoveries of extractable ^{14}C from samples with >0.01 mg/kg ranged from 86% to 110% of the TRR, and the total identified compounds in solvent-extractable fractions from 31% to 84%. The unidentified radioactive compounds (each ≥0.01 mg/kg) were characterized. The processed samples were extracted with an organic solvent, followed by a mildly acidified organo-aqueous mixture, and the combined extracts were turbo-evaporated and/or further cleaned up, if necessary, through a C-18-Sep-Pak cartridge before HPLC analysis. The unextractable residue was combusted and radioassayed to determine the bound residue. The LOQ for extracts counted by liquid scintillation ranged from 0.001 to 0.006 mg/kg. The metabolites were consistent with those found in earlier studies. The results are summarized in Table 44.

Table 44. Identified residues in rotational crops (Jesudason and Mackie, 1999).

Sample	Residues in organosoluble extracts (mg/kg of compound, not ^{14}C)												
	Solvent extractable (mg/kg)	Fipronil	MB 46136	MB 46513	MB 45950	RPA 200761	RPA 200766	RPA 105320	RPA 104615	RPA 105048	% of TRR Identified	Unknown	Total as % TRR
30 DAT													
Lettuce leaf [1]	0.024	0.006	0.003	0.001	ND	<LOQ	0.006	0.001	0.002	0.003	56	0.002	61
Radish leaf	0.083	0.002	0.006	0.001	ND	0.002	0.011	ND	0.054	0.005[2]	77	0.002	79
Radish root	0.021	0.003	0.007	0.001	ND	ND	0.002	ND	0.008	ND	84	0.001	88
Sorghum forage	0.037	0.006	0.002	0.001	ND	0.004	0.002	ND	0.016	0.001[2]	62	0.005	72
Sorghum fodder	0.068	ND	0.013	ND	ND	0.010	ND	ND	0.045	ND	57	ND	57
Sorghum grain	0.014	ND	ND	ND	ND	0.006	ND	ND	0.005	ND	39	0.003	50
150 DAT													
Lettuce leaf	0.004	ND	ND	ND	ND	ND	0.002	ND	ND	ND	22	0.004	67
Radish leaf	0.004	ND	ND	ND	ND	0.002	ND	ND	ND	ND	23	0.002	45
Wheat forage	0.034	0.007	0.008	0.003	ND	ND	0.011	0.003[2]	ND	0.003[2]	77	ND	77
Wheat straw	0.152	0.007	0.051	0.012	ND	ND	0.039	ND	0.027	ND	65	0.016	73
Wheat grain	0.009	ND	ND	ND	ND	ND	ND	ND	0.001	ND	8	0.008	79
365 DAT													
Lettuce leaf	0.024	0.004	0.008	0.001	0.001	ND	0.004	0.002	ND	0.001	84	0.003	96
Radish leaf	0.02	ND	ND	ND	ND	0.012	0.004	ND	ND	ND	61	0.004	76
Sorghum forage	0.035	ND	ND	ND	ND	0.013	0.002	ND	ND	ND	31	0.021	74
Sorghum fodder[3]	0.031	ND	0.006	ND	ND	0.011	ND	ND	0.009	ND	83	0.005	70
Sorghum grain[4]	0.011	ND	ND	ND	ND	0.005	0.003	ND	ND	ND	37	0.003	69

ND: not detectable

[1] Metabolite MB 45897 was <LOQ

[2] Confirmed by LC-MS-MS in 30 DAT lettuce only

[3] Trace of parent detected by LC-MS-MS

[4] Trace of RPA 104615 detected by LC-MS-MS; presence of RPA200766 unconfirmed by LC-MS-MS

The sum of the residues of fipronil, MB 46136, fipronil-desulfinyl and MB 45950 ranged from 0.006 to 0.07 mg/kg. MB 45950 was detected in only one sample, at 0.001 mg/kg, at the last rotation. The study demonstrates that neither fipronil nor its significant metabolites are likely to be found in grain at any plant-back interval of a month or more, or in root crops planted 5 or more months after foliar applications at 369 g ai/ha.

Accumulation in field rotational crops

In a field rotational crop study at two sites, North Carolina and California, USA, one plot at each site was treated once at the maximum US proposed labelled rate of 0.34 kg ai/ha as a soil-surface, fallow-soil application with commercial equipment (Carringer, 1998b). The test and control plots were divided into 16 subplots, and examples of root, leafy and legume vegetables and small grain were planted 30, 120, 240 and 365 days after treatment. At each plant-back interval, four crops from the

crop groups were sampled at normal harvest maturity. The minimum limit of detection (MLD) and LOQ were 0.002 and 0.005 mg/kg respectively. The results are summarized in Tables 45 and 46.

Residues of fipronil, fipronil-desulfinyl, MB 45950, and MB 46136 were below the MLD in all control samples except in one 119-day untreated green pea forage sample from the California site which had residues between the MLD and LOQ, and below the LOQ in treated samples from the North Carolina site, except in a 120-day treated winter wheat sample with residues of 0.006 mg/kg MB 46136 and 0.022 mg/kg fipronil-desulfinyl in the straw.

Significant residues were found only at the California site where they were exclusively in the vegetative portion of the crops not in the reproductive portion (i.e. grain). At 119, 239 and 367-day plant-back intervals residues from <0.005 to 0.026 mg/kg were found only in animal feedstuffs (small grain forage and straw, and legume forage). Only at the 31-day plant-back interval were quantifiable residues found in lettuce and radish tops, ranging from 0.008 to 0.016 mg/kg.

Table 45. Residues of fipronil, MB 45950, MB 46136 and fipronil-desulfinyl in treated rotational crops, California site (Carringer, 1998b).

Plant-back interval (DAT)	Sample	Days after planting	Residues (mg/kg)[1]			
			Fipronil	fipronil-desulfinyl	MB 45950	MB 46136
31	Radish top	32	ND, ND	0.011, 0.014	ND, ND [2]	<0.005, <0.005
	Radish root	32	ND, ND	ND, <0.005	ND, ND	ND, ND
	Cowpea forage	52	ND, ND	0.009, 0.009	ND, ND	ND, ND
	Cowpea grain	144	ND, ND	ND, ND	ND, ND	ND, ND
	Cowpea straw	144	ND, ND	ND, ND	ND, ND	ND, ND
	Red leaf lettuce	50	ND, ND	0.011, 0.016	ND, ND	0.008, 0.012
	Sorghum forage	33	ND, ND	0.01, 0.007	ND, ND	<0.005, <0.005
	Sorghum grain	122	ND, ND	ND, ND	ND, ND	ND, ND
	Sorghum straw	122	<0.005,ND	0.031, 0.032	ND, ND	0.024, 0.021
119	Radish top	33	ND, ND	<0.005, <0.005	ND, ND	ND, ND
	Radish root	33	ND, ND	ND, ND	ND, ND	ND, ND
	Green pea forage	57	<0.005, ND	ND, ND	ND, ND	<0.005,ND
	Green pea grain	140	ND, ND	ND, ND	ND, ND	ND, ND
	Green pea straw	140	ND, ND	<0.005, ND	ND, ND	<0.005, <0.005
	Green leaf lettuce	57	ND, ND	<0.005, <0.005	ND, ND	ND, ND
	W. wheat forage	57	ND, ND	<0.005, <0.005	ND, ND	ND, ND
	W. wheat grain	176	ND, ND	ND, ND	ND, ND	ND, ND
	W. wheat straw	176	ND, ND	0.022, 0.019	ND, ND	<0.005, <0.005
239	Radish top	55	NA[3]	NA	NA	NA
	Radish root	55	NA	NA	NA	NA
	Cowpea forage	132	ND, ND	0.006, 0.005	ND, ND	<0.005, <0.005
	Cowpea grain	191	NA	NA	NA	NA
	Cowpea straw	191	NA	NA	NA	NA
	Red leaf lettuce	90	NA	NA	NA	NA
	W. wheat forage	83	ND, ND	<0.005, <0.005	ND, ND	ND, ND
	W. wheat grain	132	NA	NA	NA	NA
	W. wheat straw	132	ND, ND	0.026, 0.022	ND, ND	0.016, 0.013
367	Radish top	36	NA	NA	NA	NA
	Radish root	36	NA	NA	NA	NA
	Cowpea forage	60	NA	NA	NA	NA
	Cowpea grain	105	NA	NA	NA	NA
	Cowpea straw	105	NA	NA	NA	NA
	Red leaf lettuce	60	NA	NA	NA	NA
	Sorghum forage	60	ND, ND	<0.005, <0.005	ND, ND	ND, <0.005
	Sorghum grain	142	NA	NA	NA	NA
	Sorghum straw	142	ND, ND	0.010, 0.018	ND, ND	0.013, 0.02

ND: not detectable W: winter

[1] Duplicate samples analysed

[2] Not detectable, MLD: 0.002 mg/kg

[3] NA: not analysed if residues not above the LOQ at the previous plant-back interval

Table 46. Residues of fipronil, MB 45950, MB 46136 and fipronil-desulfinyl in treated rotational crops, North Carolina site (Carringer, 1998b).

Plant-back Interval (DAT)	Crop sample	Age of crop at sampling (days)	Residues (mg/kg) [1]			
			Fipronil	fipronil-desulfinyl	MB 45950	MB 46136
31	Radish top	34	ND, ND [1,2]	ND, ND	ND, ND [2]	ND, ND
	Radish root	34	ND, ND	ND, ND	ND, ND	ND, ND
	Soya bean forage	34	ND, ND	<0.005, ND	ND, ND	ND, ND
	Soya bean grain	146	ND, ND	ND, ND	ND, ND	ND, ND
	Soya bean straw	146	ND, ND	<0.005, <0.005	ND, ND	<0.005, <0.005
	Collard foliage	125	ND, ND	ND, ND	ND, ND	ND, ND
	Sorghum forage	34	ND, ND	ND, ND	ND, ND	ND, ND
	Sorghum grain	124	ND, ND	ND, ND	ND, ND	ND, ND
	Sorghum straw	124	ND, ND	ND, ND	ND, ND	ND, ND
120	Radish top	57	ND, ND	ND, ND	ND, ND	ND, ND
	Radish root	57	ND, ND	ND, ND	ND, ND	ND, ND
	Wando pea forage	Not collected	--	--	--	--
	Wando pea grain	Not collected	--	--	--	--
	Wando pea straw	Not collected	--	--	--	--
	Mustard foliage	215	ND, ND	ND, ND	ND, ND	ND, ND
	W. wheat forage	201	ND, ND	ND, ND	ND, ND	ND, ND
	W. wheat grain	285	ND, ND	ND, ND	ND, ND	ND, ND
	W. wheat straw	286	ND, ND	0.022, 0.019	ND, ND	<0.005, 0.006
296	Radish top	60	NA [3]	NA	NA	NA
	Radish root	60	NA	NA	NA	NA
	Wando pea forage	60	NA	NA	NA	NA
	Wando pea grain	109	NA	NA	NA	NA
	Wando pea straw	110	NA	NA	NA	NA
	Mustard foliage	60	NA	NA	NA	NA
335	S. wheat forage	92	NA	NA	NA	NA
	S. wheat grain	Not collected	NA	NA	NA	NA
	S. wheat straw	Not collected	NA	NA	NA	NA
365	Radish top	40-41	NA	NA	NA	NA
	Radish root	40-41	NA	NA	NA	NA
	Soya bean forage	64	NA	NA	NA	NA
	Soya bean grain	177	NA	NA	NA	NA
	Soya bean straw	177	NA	NA	NA	NA
	Mustard foliage	64	NA	NA	NA	NA
	Sorghum forage	40-41	NA	NA	NA	NA
	Sorghum grain	141	NA	NA	NA	NA
	Sorghum straw	141	NA	NA	NA	NA

W.: winter
S.: spring
[1] Duplicate field samples analysed
[2] ND: not detectable, MLD: 0.002 mg/kg
[3] NA: not analysed if residues were not above the LOQ at the previous plant-back interval

The results indicated that no residues would be found in cereal grain at any interval. The low levels in animal feed supported a 31-day plant-back interval for soya beans and a 120-day plant-back interval for leafy vegetables and root crops after a foliar application of fipronil at a rate of 0.34 kg ai/ha.

Summary

When fipronil is applied to the soil at 157 g ai/ha uptake is low in rotational crops. Only two animal feed items from the small grain crops contained residues above 0.01 mg/kg, indicating that fipronil and its relevant metabolites are not highly systemic.

After surface application of fipronil at 369 g ai/ha to the soil neither fipronil nor its relevant metabolites are likely to be found in grain after 30 to 365 days, nor in root crops or leafy vegetables after 5 months.

A field crop rotational study confirmed that after application at 340 g ai/ha to the soil surface residues in the vegetative portions of crops are low and undetectable in grain. At plant-back intervals of 119-367 days after treatment residues ranged from <0.005 mg/kg to 0.026 mg/kg in animal feedstuff samples. Only at short plant-back intervals (30 DAT) were residues found in leafy and root crops (<0.002 to 0.032 mg/kg).

Environmental fate in water/sediment systems

Hydrolysis

The hydrolysis of [^{14}C]fipronil at 25°C was determined by Corgier and Plewa (1992a) in a study in the dark, under sterile conditions, at pH 5, 7, and 9 at an initial concentration of 0.89 mg/l of buffer solution. The results were as follows.

pH 5 (buffered)	stable
pH 7 (buffered)	nearly stable (2% loss in 30 days)
pH 9 (buffered)	DT-50 approximately 28 days

At pH 9 fipronil was converted exclusively to RPA 200766, according to pseudo-first-order kinetics, with a half-life of 28 days and rate constant k = -0.0243 day^{-1}. No volatile compounds were found at any pH. Recoveries of ^{14}C ranged from 96.4% to 101.6%.

Aqueous photolysis

Corgier and Plewa (1992b) determined a half-life of 0.33 days.

In another study by Boinay (1997) at pH 5 and 25°C under sterile conditions at an initial concentration of 0.9 mg/l with 1% acetonitrile as co-solvent, light was provided by a xenon lamp with radiation of less than 290 nm filtered out. Time under the lamp was converted to equivalents of 'Florida summer days'. Irradiation was for 0, 1, 2, 4 or 6 hours. Control samples were maintained in darkness for 6 hours. Analyses of test and trap solutions showed good recoveries ranging from 99.8 to 103% of the applied radioactivity. Practically no volatile compounds were formed.

After 6 hours the main organoextractable photoproduct was fipronil-desulfinyl, with a minor unknown (HPLC RT = 2 min) accounting for 43% and 4% of the applied radioactivity respectively. The aqueous extract contained RPA 104615 and a minor unknown (HPLC RT = 3.3 min) accounting for 8.2% and 5.6% respectively. The remaining 32% was accounted for by the parent compound. Dark controls showed no appreciable degradation.

The kinetics of photolytic degradation were pseudo first order with a DT-50 of 0.33 days and k = -0.0176 days^{-1}. The quantum yield of the direct photolysis of fipronil in an aqueous solution was determined in a radiometer irradiation apparatus at 300 nm and was 0.199 (mean of two values).

Biodegradability

In a study to assess the biodegradability of fipronil in an aerobic aqueous medium (Mead, 1997) fipronil was exposed to activated sewage sludge micro-organisms at 19.05 mg/l with culture medium in sealed vessels stored in the dark at 21°C for 28 days. Degradation of the test material was assessed by measuring the carbon dioxide produced.

Preliminary assessment of the toxicity of fipronil to the micro-organisms was not possible because of the insolubility of the test material. Therefore fipronil and sodium benzoate were included as a toxicity control for validation, in addition to innoculum and standard sodium benzoate controls.

After 28 days, degradation of fipronil was 47% and of sodium benzoate 100% confirming the suitability of the inoculum and test conditions. The toxicity control achieved 42% degradation, confirming that the test substance was not toxic to the micro-organisms.

Anaerobic aquatic degradation

The anaerobic aquatic degradation of [^{14}C]fipronil after application at 10 µg/cm^2 to a flooded sandy loam soil, already incubated for 53 days to establish stable anaerobic conditions, was studied for a year (Waring, 1993a). Soil 5 cm deep was covered by 12 cm of deionized water and kept in the dark at 25 ± 1°C in glass cylinders. Moistened nitrogen gas was passed over the water surface of each cylinder and then through a variety of traps to collect radiolabelled volatiles. Duplicate samples were removed for analysis at 0, 1, 3, 7, 14, 30, 59, 120, 179, 269 and 365 days after application.

Recoveries from the surface water decreased from >93% initially to 13-21% after 365 days incubation. The soil contained 69% of the applied ^{14}C after 365 days. Most of the radioactivity in the soil (>62%) was extracted with acetonitrile. Less than 0.1% was collected in the traps.

Initially [^{14}C]fipronil accounted for >92% of the applied ^{14}C, but decreased during the course of the study to <16%. Decomposition resulted mainly in the formation of the reduced product MB 45950 and the amide RPA 200766, accounting for 32 and 47% of the applied radioactivity respectively, after 365 days. Several unidentified minor degradation products were detected in the soil samples by TLC or HPLC. The initial half-life of [^{14}C]fipronil in flooded Manningtree, UK, sandy loam soil under anaerobic conditions was about 123 days.

Degradation in water/sediment systems

The degradation of both fipronil and fipronil-desulfinyl has been studied.

Fipronil. The degradation of [^{14}C]fipronil under aerobic conditions in two systems each comprising an aerobic water phase and a sediment phase under reducing conditions (system 1 “Ongar, UK” and system 2 “Manningtree, UK”) over a period of 121 days was studied by Ayliffe (1998). Glass flasks containing 4 cm of soil sediment covered by 11 cm of associated water were incubated in the dark at 20 ± 2°C. The ratio of water to oven-dry equivalent weight of sediment was approximately 1:4. The systems were acclimatized for 28 days before the single application of [^{14}C]fipronil at the equivalent of 200 g ai/ha to the surface water of each flask. Moistened air was supplied under positive pressure into the water surface and the effluent air passed through two 1 M potassium hydroxide traps to collect any liberated CO_2. Samples were analysed 0, 0.02, 0.25, 1, 2, 7, 14, 29, 58, 93 and 121 days after [^{14}C]fipronil application.

Mean recoveries were above 94% in the two systems. The radioactivity was gradually transferred from the water to the sediment. By the end of the study, ^{14}C levels in the water were about 12.4% and 2.5% of the total applied in systems 1 and 2 respectively, and in extracts of the two sediments c. 83% and 94% respectively. The unextractable residues recovered by combustion were generally below 5%. Volatiles accounted for less than 1% of the applied radioactivity in both systems.

The main degradation product was the sulfide MB 45950, with maximum concentrations of 88% in system 1 and 80% in system 2. Up to 4 minor products generally accounted for less than 2% of the applied ^{14}C at any time. These included RPA 200766 and the amide of MB 45950, MB 46126.

The half-lives of fipronil in the water phase, sediment and the total system were characterized by HPLC of extracts, and were less than 14 and 6 days in water, 48 and 75 days in sediment and 22 and 32 days in the total system for systems 1 and 2 respectively.

Fipronil-desulfinyl. Lowden and Mahay (2000) determined the route and rate of degradation of ^{14}C-labelled fipronil-desulfinyl in systems with "Manningtree-UK" and "Ongar-UK" water phases treated at the equivalent of 100 g ai/ha in the water phase and incubated in the dark at 20°C for up to 365 days, with sampling at 0 h and 6 h and 1, 2, 7, 14, 30, 61, 100, 152 and 365 days after treatment. The water was separated from the sediment, then water and sediments were radioassayed and examined by HPLC. The recoveries of applied radioactivity had an overall mean value of 94.5%. Analysis of the water phases showed that there was initially a relatively rapid transfer of radiolabelled material from the water phases to the sediments in both systems, with a reduction in the rate of transfer after about 30 days. There was simultaneous degradation in the water and sediment resulting in the formation of four minor products. No significant quantities of volatile products were formed, <0.5% applied radioactivity (a.r.).

Two minor products were MB 46400 and RPA 105048 which reached a maximum of 6.8% and 4.3% of the a.r. in the total systems respectively. Two other minor products were also detected. Compound A was detected in the sediment extracts only, accounting for only 1.07% of the a.r. at 61 days before disappearing. Compound B appeared in both the water and sediment phases reaching a maximum of 1.6% of the a.r. in the total systems at 365 days. At 30 days the products accounted for 1.6% of the 22% of the a.r. in the water of the Manningtree system and 3.6% of 32% of the a.r. in the water of the Ongar system. At 365 days however, the products accounted for 5.7% of totals of 11% and 10% of the a.r. in the waters of the Manningtree and Ongar systems respectively.

In the sediments, the main component of the extractable materials was fipronil-desulfinyl which was accompanied by small amounts of MB 46400, RPA 105048 and compound B (Manningtree sediment only).

These results indicate that in the environment, any fipronil-desulfinyl reaching or formed in the water of a water/sediment system from a fipronil application will move to the sediment at an initially rapid rate. The degradation (principally hydrolysis) of the compound is likely to proceed steadily in both the water and sediment phases. The movement of the compound from water to sediment plus the degradation resulted in DT-50 values of 4.2 days and 9.9 days and DT-90 values of 174 days and 146 days for the Manningtree and Ongar water phases respectively.

Bioaccumulation in fish

In studies by Chapleo and Hall (1992) and Roohi *et al.* (1992) bluegill sunfish were exposed to a continuous flow of water containing 850 ng/l [^{14}C]fipronil for 35 days (uptake phase). Daily water samples showed that the test concentration remained between 810 and 990 ng/l (mean 900 ng/l) fipronil equivalents.

The fish were then exposed to a continuous flow of dilution water alone for two weeks (depuration phase), as were a control group. The radioactivity in edible (muscle) and non-edible (viscera) tissues during the uptake and depuration phases of the control fish was low: all results were below the limit of reliable determination.

After 14 days' exposure the residues in whole fish and edible and inedible portions appeared to be stable.

In whole fish, concentrations of the TRR increased to a mean maximum of 315 ng/g fipronil equivalents fresh weight, corresponding to a bioconcentration factor of 380 after 35 days exposure to [^{14}C]fipronil. The apparent steady-state bioconcentration factor was 321, corresponding to 273 ng/g fipronil equivalents fresh weight. Over 99% of the radioactivity accumulated at the steady state was eliminated during the depuration phase.

During the uptake phase, most of the radioactivity (>69%) was in the inedible fraction, where the apparent steady-state bioconcentration factor was 575 corresponding to 489 ng/g fipronil

equivalents fresh weight. Over 97% of the radioactivity at steady-state was eliminated during the depuration phase.

In the edible fraction, the apparent steady-state bioconcentration factor was 164, corresponding to 139 ng/g fipronil equivalents fresh weight. Over 96% of the radioactivity at the steady state was eliminated during the depuration phase.

The muscle and viscera (edible and inedible respectively), were subjected to extraction procedures designed to isolate the radiolabelled components. These extracts were then analysed using chromatographic and spectrometric techniques for the identification of individual components.

The results demonstrate that absorbed fipronil is metabolized to MB 46136, MB 45950 and MB 45897. The parent compound and its metabolite MB 45950 each accounted for approximately 11% of the TRR, and MB 45897 and MB 46136 for 26 and 44% respectively. The amide RPA 200766, was also present in lesser amounts. The percentage of these metabolites in the inedible lipophilic fraction exceeded that in the less lipophilic edible fraction by a factor of 3 to 4, consistent with the octanol/water partition coefficients of the compounds.

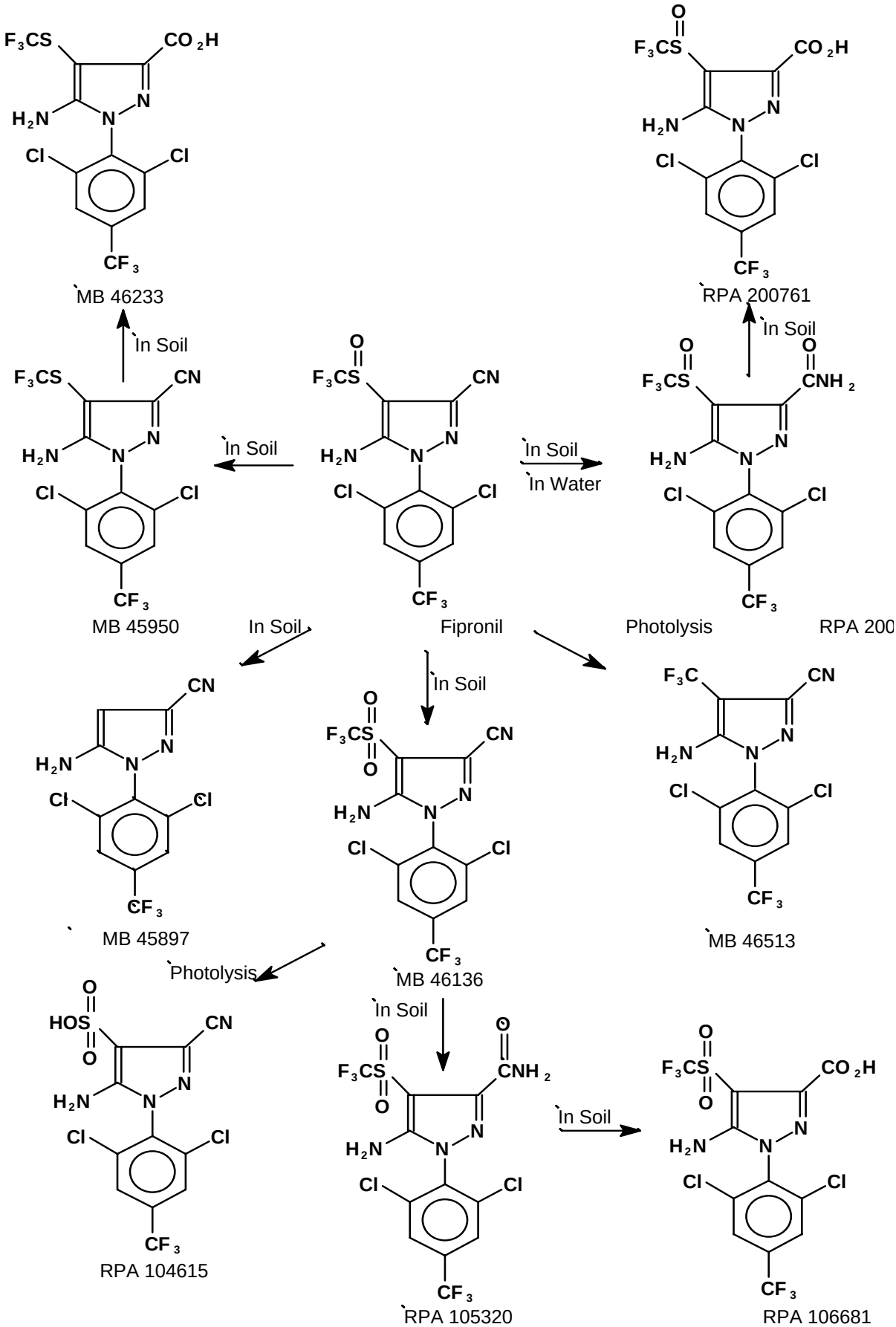
Analysis of the samples from days 1 to 3 of the depuration phase revealed the same compounds as at day 7, when approximately 90% of the TRR had been eliminated. In both cases and in common with the uptake phase, MB 46136 was the main metabolite, but results indicated that metabolism of the parent compound continued during the depuration phase and that no single metabolite was preferentially eliminated. The proportions of the metabolites in the edible and inedible fractions were found, in the initial phase of depuration, to be approximately the same as in the uptake phase, but the ratio decreased to 1.5 by day 7, consistent with the reasonably rapid elimination of the compounds from both fractions.

It is concluded that fipronil in fresh water is both accumulated by and eliminated from bluegill sunfish. The pattern of accumulation and elimination of [^{14}C]fipronil indicates that a simple, two-compartment model is approached. In all tissues and in whole fish, the accumulated radioactivity was almost completely eliminated (>96%) after 14 days depuration, with no indication of preferential elimination of any metabolite.

Summary of environmental fate

It has been demonstrated in laboratory studies that fipronil undergoes oxidation to the sulfone MB 46136 (a major degradation product in aerobic soil studies), reduction to the sulfide MB 45950 (a minor product in aerobic soil and a major product in aerobic and anaerobic aquatic studies), hydrolysis to the amide RPA 200766 (a major product in aerobic soil and hydrolysis studies and a minor product in the aquatic studies), and photolysis to the desulfinylated degradation product fipronil-desulfinyl (the major product in the aqueous photolysis study and minor in the soil photolysis study) and to a lesser extent the sulfonic acid RPA 104615 (only a minor product in aqueous degradation and soil photolysis). Figure 7 shows the proposed degradation pathways of fipronil in soil and water.

Figure 7. Degradation pathways of fipronil in the environment.



METHODS OF RESIDUE ANALYSIS

Analytical methods

Plant material

A multi-residue enforcement analytical method, DFG S19 modified, was validated for the determination of residues of fipronil, MB 45950, MB 4613, fipronil-desulfinyl, and RPA 200766 in maize, peaches and potatoes (Haussman, 1998). The modified method is outlined below:

- extraction with water/acetone
- subsequent partition into an organic phase after addition of ethyl acetate/cyclohexane
- gel permeation chromatography
- silica gel column fractionation
- GLC with electron capture detection

The method was validated at 0.002 mg/kg (the LOQ) and 0.02 mg/kg per analyte and gave acceptable average recoveries of 70-110% and relative standard deviations of $\leq$20% at both fortification levels in the three commodities, except of MB 45950 from maize at 0.02 mg/kg and of MB 46136 from maize and potatoes at 0.02 mg/kg, where mean recoveries were slightly below 70%. The average recovery of RPA 200766 from potato at 0.002 mg/kg was slightly above 110% (relative standard deviation of 25%). Residues in control samples were all $\leq$30% of the LOQ.

In an early general GLC method (Manley, 1993) fipronil and its metabolites are extracted with acetonitrile from plant material, water is added and the solution partitioned with hexane for clean-up. Residues are extracted with dichloromethane, and purified using solid-phase extraction before quantification by GLC with electron capture detection. The method was validated at 0.01 mg/kg for apples, rice bran, cabbage, grapes, maize grain, maize plant, maize silage, rice, sugar beet and sunflower. The limit of detection was estimated at 0.003 mg/kg for fipronil and its metabolites.

In an analytical method (Communal, 1994) to determine residues in vegetables, cereals and fruits fipronil, MB 45950, MB 46136, fipronil-desulfinyl, and RPA 200766 are extracted with acetonitrile, and the crude extract purified on a C-18 cartridge followed by activated charcoal. Analysis is by gas liquid chromatography with electrochemical detection (ELCD). The method has been validated for cabbage, watermelon, mango, maize, sunflower (including oil and oilcake), winter wheat, citrus fruits, cane sugar, potato, mushroom and banana. The LOQ for each compound in various substrates is shown in Table 47.

Table 47. LOQ for fipronil and degradation products in various substrates (Communal, 1994).

Substrate	Validated LOQs (mg/kg)				
	Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA200766
Cabbage	0.005	0.005	0.005	0.005	0.005
Watermelon	0.005	0.005	0.005	0.005	0.005
Mango	0.005	0.005	0.005	0.005	0.005
Maize silage	0.005	0.005	0.005	0.005	0.005
Maize grain	0.002	0.002	0.002	0.002	0.002
Wheat straw	0.01	0.01	0.01	0.01	0.01
Wheat grain	0.002	0.002	0.002	0.002	0.002
Wheat forage	0.01	0.01	0.01	0.01	0.01
Sunflower seed	0.002	0.002	0.002	0.002	0.002
Sunflower oil	0.002	0.002	0.002	0.002	0.002
Sunflower cake	0.002	0.002	0.002	0.002	0.002
Citrus	0.002	0.002	0.002	0.002	0.002
Sugar cane	0.01	0.01	0.01	0.01	0.01
Potato	0.002	0.002	0.002	0.002	0.002
Mushroom	0.002	0.002	0.002	0.002	0.002
Banana	0.002	0.002	0.002	0.002	0.002

In a method to determine residues of fipronil, MB 45950, MB 46136 and fipronil-desulfinyl in maize, cotton, potato and rice substrates (Baillargeon and Plaisance, 1998), residues are extracted from seed, meal, hulls, grain, forage, fodder and straw with acetonitrile/water and partitioned with hexane. After removal of the acetonitrile, the residues are partitioned with dichloromethane. Crude and refined oils are diluted with hexane before extraction. Residues are extracted from potato tubers, flakes, wet and dry peel and chips with acetonitrile/acetone. Column chromatography (various combinations of charcoal, silica gel, alumina, Florisil, amino) is used for clean-up of extracts. Quantification of fipronil and it metabolites is accomplished by gas chromatography using an electron capture or mass selective detector. The LOQs are shown in Table 48.

Table 48. LOQs in various substrates of maize, cotton, potato and rice (Baillargeon and Plaisance, 1998).

LOQ (mg/kg)	GLC/ECD
0.003	Potato - tuber, flakes, wet and dry peel, chips
0.005	Cotton - seed, meal, hulls, crude and refined oil
0.01	Rice - grain
0.01	Maize - grain, crude oil
0.02	Maize - forage, fodder, starch
	GLC/MSD
0.005	Maize - grain, crude oil
0.005	Cotton - crude and refined oil
0.01	Maize - forage, fodder, starch
0.01	Cotton - seed, meal, hulls
0.01	Rice - grain, straw
0.1	Cotton by-product (gin trash)

In a method developed by Le Galliot and Communal (1994) to determine residues of fipronil, MB 45950, MB 46136, fipronil-desulfinyl and RPA 200766 in cabbage, residues are extracted with acetonitrile and the crude extract is purified on a C-18 cartridge followed by activated charcoal. Analysis is by gas liquid chromatography with electrochemical detection (ELCD, Hall detector). The LOQ is 0.005 mg/kg for each compound.

In another method (Maycey *et al.*, 1995) to determine residues of fipronil and its possible metabolites MB 45897, MB 45950, MB 46136, fipronil-desulfinyl and RPA 200766 in rice (green plant, straw, bran, brown and white rice) residues in green plant and straw are extracted with methanol and in bran, brown and white rice with acetonitrile. After liquid/liquid partition, solid-phase extraction and gel-permeation chromatography, residues are quantified by GLC with an electron capture detector. The LOQs were 0.005-0.01 mg/kg in green plant, 0.005 mg/kg in straw and 0.001 mg/kg in brown and white rice and bran.

In a method to determine residues of fipronil and its metabolites in agricultural maize and its processed commodities (Upalawanna, 1993; Baillargeon, 1995a,b, 1996), residues are extracted from grain and fodder with 75% actonitrile/25% water and from forage, crude oil and starch with acetonitrile. After clean-up by partition with hexane and removal of acetonitrile, residues are extracted into dichloromethane, cleaned up by column chromatography on silica gel and charcoal and determined by gas chromatography with a ^{63}Ni electron capture detector. LOQs for fipronil and MB 45950, MB 46136, fipronil-desulfinyl and RPA 200766 were estimated by rounding up to the highest LOQ of any analyte in a substrate and applying that value to all analytes. They were 0.01 mg/kg in grain and crude oil and 0.02 mg/kg in forage, fodder and starch. No major interferences were found from the 45 compounds tested.

In the method of Maycey and Savage (1992) to determine residues of fipronil, MB 45950, MB 46136, fipronil-desulfinyl, and RPA 200766 in bananas residues are extracted with methanol,

cleaned up using solid-phase extraction followed by silica column chromatography, and quantified by electron capture gas chromatography with a megabore capillary column. The LOQ was 0.01 mg/kg.

In addition to the method of Baillargeon and Plaisance (1998) which determined residues of fipronil and its metabolites in potato tubers and their processed commodities, an earlier method was validated (Baillargeon, 1995c; Shaffer, 1995). The residues are extracted with acetonitrile, cleaned up by liquid-liquid partition and alumina and silica gel column chromatography, and quantified by GLC with an electron-capture detector. The LOQ was 0.05 mg/kg, and recoveries were 85% (mean of five levels).

Animal material

The multi-residue enforcement analytical method DFG S19 was modified and validated for the determination of residues of fipronil, MB 45950, MB 46136 and fipronil-desulfinyl in bovine muscle, milk and fat, and chicken eggs (Haussman, 1999). The modified method in outline is as follows:

- extraction with water/acetone
- partition into an organic phase after addition of ethyl acetate/cyclohexane (for bovine muscle and milk)
- extraction (2): add acetonitrile/acetone (for bovine fat and eggs)
- gel permeation chromatography
- silica gel column fractionation
- GLC with electron capture detection.

Samples were fortified at 0.002 mg/kg (LOQ) and 0.02 mg/kg with the four analytes, and the method successfully validated in bovine muscle, milk and fat and chicken eggs at these levels. Recoveries ranged from 70% to 108%.

A method of analysis was developed and validated by Wargo (1997) to determine residues of fipronil and its sulfide and sulfone animal metabolites MB 45950 and MB 46136 as the sulfone MB 46136, and the photolysis product fipronil-desulfinyl as a separate entity in bovine milk, muscle, liver, fat and kidney and poultry eggs, muscle, liver, and skin and fat. Residues are extracted with 30:70% acetone/acetonitrile. After column chromatography, the extract is treated with sodium periodate and rhuthenium trichloride to oxidize the sulfide and sulfoxide to sulfone MB 46136. MB 46136 and fipronil-desulfinyl are processed through the method intact, and quantified by gas chromatography using a ^{63}Ni electron capture detector. The performance criteria for validation included LOQ and MLD determination, accuracy, precision, extraction efficiency, linearity, specificity and ruggedness. A confirmatory GC-MSD method was also validated. The method was assessed from average recoveries from all nine substrates; fortification levels ranged from 0.005 to 0.055 mg/kg each of fipronil, MB 45950, MB 46136 and fipronil-desulfinyl. Fipronil-desulfinyl and MB 46136 were both quantified at 0.005 mg/kg. In addition, recoveries of MB 46136 from fortifications with 0.002 mg/kg each of MB 45950, fipronil and MB 46136 were determined. The method is capable of quantifying fipronil-desulfinyl and MB 46136 (intact or from oxidation of MB 45950 and/or fipronil) at less than 0.005 mg/kg each in animal tissues. The MLD was estimated to be approximately 0.0004 mg/kg.

In an individual analyte method to determine residues of fipronil, MB 45950 and MB 46136 in muscle, fat, liver, kidney, milk and eggs the residues are extracted from substrates with 30% acetone in acetonitrile. After column clean-up, residues are quantified by GLC using a ^{63}Ni electron capture detector. Chicken eggs, cattle kidney and fat were used as representative substrates for validation. No interferences were found from the 115 compounds with tolerances in animal substrates that were tested. The LOQ was 0.01 mg/kg for each compound in all the substrates. The method was independently validated (Yarko and Davis, 1994).

An independent laboratory validation of “Method of analysis for the determination of fipronil, (MB 45950 and MB46136) in milk, eggs, liver, kidney, muscle and fat tissues” (Hudson, 1994, Robinson, 1995) was carried out according to US EPA requirements (Yarko and Davis, 1994) by

measuring recoveries from beef fat fortified at two levels, using the original version of the method (18 October, 1993): 0.01 and 0.05 mg/kg of fipronil and MB 45950, and 0.06 and 0.3 mg/kg of MB46136. In general the results demonstrated no background interference and recoveries were all within the acceptable limits of 70%-120%.

Soil

Methods have been developed for the determination of fipronil, MB 46136, MB 45950, fipronil-desulfinyl and RPA 200766 in soil (Ibrahim, 1992). The basic method can be adapted to any soil substrate by modifying clean-up procedures to remove chromatographic interference. Residues are extracted from the soil with acetonitrile/acetone (70/30), the sample is centrifuged and the extract dried with sodium sulfate, the analytes are adsorbed onto activated charcoal and eluted with acetonitrile. Quantification is by GLC with electron capture detection. The LOQ is 0.005 mg/kg.

Stability of residues in stored analytical samples

Animal substrates

The results of the studies of the storage stability of fipronil, MB 45950 and MB 46136 in animal commodities (Byrd, 1994a,b) are shown in Table 49. Samples of each of the five substrates were fortified at 0.1 mg/kg with a standard solution containing fipronil and its metabolites.

Table 49. Storage stability in animal substrates, unadjusted for procedural recoveries (Byrd, 1994a,b).

Animal	Sample	Storage temp. (°C)	Storage, months	% remaining, average of 3 samples		
				Fipronil	MB 45950	MB 46136
Cow	Milk	fresh spike	0	90	86	104
		≤-10	1	92	94	99
		≤-10	3	85	88	97
	Liver	fresh spike	0	96	88	106
		≤-10	1	90	92	97
		≤-10	3	83	79	93
	Kidney	fresh spike	0	87	91	92
		≤-10	1	88	90	89
		≤-10	3	82	78	107
	Muscle	fresh spike	0	94	91	104
		≤-10	1	86	90	93
		≤-10	3	83	84	92
	Fat	fresh spike	0	86	84	92
		≤-10	1	84	88	91
		≤-10	3	81	87	86
Hen	Egg	fresh spike	0	79	83	84
		≤-10	1	89	84	100
		≤-10	3	78	82	82
	Liver	fresh spike	0	82	85	88
		≤-10	1	92	87	100
		≤-10	3	77	84	86
	Muscle	fresh spike	0	88	88	96
		≤-10	1	82	83	92
		≤-10	3	78	79	83
	Skin	fresh spike	0	85	87	90
	with fat	≤-10	1	89	87	100
		≤-10	3	81	78	81

In addition as a part of the study on cows (Byrd, 1994a) the storage stability of refrigerated analytical standards was investigated. The results indicate that all the compounds are stable for at least 4 months.

Plant substrates and processed fractions

The stabilities of fipronil, MB 45950, MB 46136 and fipronil-desulfinyl in plant commodities are shown in Tables 50-54.

Table 50. Storage stability in lettuce spiked with 1 mg/kg of each compound (Plaisance, 1998).

Sample	Storage temp. (°C)	Months of storage	% remaining, 2 samples			
			Fipronil	MB 45950	MB 46136	fipronil-desulfinyl
Leaves	fresh spike	0	89 96	93 96	103 108	94 98
	- 20	6	95 93	98 93	99 94	97 96
	- 20	12	82 88	93 92	76 80	84 93

The stability of analytical standard solutions was also reported in the study. Acetonitrile solutions were stable at –20°C over 13 months.

Table 51. Storage stability in potato tubers spiked at 0.1 mg/kg (Eng, 1996b).

Storage temp. (°C)	Storage, months	% remaining, 2 samples			
		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl
fresh spike	0	92 87	86 91	78 72	92 89
- 20	6	92 94	85 90	88 90	88 90
- 20	12	72 85	71 82	67 80	76 89
- 20	24	94 116	93 110	91 106	78 106

Table 52. Stability in whole brassica vegetables stored at -20°C and spiked with 0.1 mg/kg of each compound (Keats, 1997h).

Crop	Storage, months	% remaining, 2 samples			
		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl
Broccoli	11	83 83	90 93	80 78	96 93
Cabbage	11	85 97	91 89	84 82	92 89
Cauliflower	12	86 88	85 85	80 76	88 84

Table 53. Storage stability in maize grain, forage, fodder and processed products, spiked with 0.1 mg/kg of each compound (Upalawanna, 1994).

Sample	Storage temp. (°C)	Storage, months	Corrected % remaining[1], 2 samples			
			Fipronil	MB 45950	MB 46136	fipronil-desulfinyl
Grain	fresh spike	0	103 120	95 108	102 118	NA
	≤-10	5.8	98 118	90 100	98 109	NA

Sample	Storage temp. (°C)	Storage, months	Corrected % remaining[1], 2 samples			
			Fipronil	MB 45950	MB 46136	fipronil-desulfinyl
	≤-10	11.5	88 84	88 86	105 105	NA
Forage	fresh spike	0	106 104	101 99	104 98	NA
	≤-10	5.9	104 102	96 85	110 95	NA
	≤-10	11.6	91 89	81 85	80 83	NA
Fodder	fresh spike	0	93 97	101 107	100 112	NA
	≤-10	6.4	107 99	103 102	103 101	NA
	≤-10	12	91 88	100 93	108 105	NA
Silage	fresh spike	0	109 111	105 107	103 105	NA
	≤-10	5.6	110 101	119 107	122 110	NA
	≤-10	11.6	92 98	91 96	98 92	NA
Crude oil	fresh spike	0	86 92	88 93	84 92	NA
	≤-10	6.1	82 95	78 92	87 98	NA
	≤-10	11.8	116 102	113 105	124 129	NA
Refined oil	fresh spike	0	114 121	105 108	118 128	NA
	≤-10	6.1	110 110	107 116	122 129	NA
	≤-10	11.9	95 109	100 107	109 116	NA
Grain dust	fresh spike	0	116 107	114 110	108 101	NA
	≤-10	6.1	107 110	107 106	122 113	NA
	≤-10	11.7	91 92	92 94	107 108	NA
Meal	fresh spike	0	94 102	91 97	90 100	NA
	≤-10	6.1	84 80	92 86	88 91	NA
	≤-10	11.7	73 79	87 87	92 84	NA
Starch	fresh spike	0	112 116	108 107	103 103	NA
	≤-10	5.9	107 95	103 101	108 104	NA
	≤-10	11.7	90 84	92 97	92 102	NA

[1] All results were corrected for analytical recoveries

Table 54. Storage stability in cotton spiked with 0.1 mg/kg of each compound (Eng, 1996a, 1997).

Sample	Storage temp. (°C)	Storage, months	Corrected % remaining[1], 2 or 3 samples			
			Fipronil	MB 45950	MB 46136	fipronil-desulfinyl
Eng (1996a)						
Ginned seed	fresh spike	0	106 95 92	93 79 79	103 99 105	98 88 76

Sample	Storage temp. (°C)	Storage, months	Corrected % remaining[1], 2 or 3 samples			
			Fipronil	MB 45950	MB 46136	fipronil-desulfinyl
	- 20	5	99	99	98	100
			103	100	107	103
	- 20	12	103	94	103	105
			102	94	94	106
Hulls	fresh spike	0	108	93	110	95
			104	94	104	99
			107	98	100	107
	- 20	5	88	97	86	88
			111	110	121	95
	- 20	12	103	87	92	99
			106	91	102	102
Meal	fresh spike	0	99	92	108	93
			93	89	99	95
			83	82	83	85
	- 20	5	93	93	92	91
			91	95	89	91
	- 20	12	102	99	102	110
			95	94	96	104
Crude oil	fresh spike	0	124	110	118	113
			102	94	99	99
			102	97	104	103
	- 20	5	104	106	102	101
			104	106	104	103
	- 20	12	109	101	110	104
			105	102	102	107
Refined oil	fresh spike	0	117	116	115	110
			115	111	112	111
			110	100	111	97
	- 20	5	104	98	100	103
			102	97	94	100
	- 20	12	101	99	99	99
			98	95	95	93
Eng (1997)						
Gin trash	Fresh spike	0	96	86	98	92
			93	88	99	04
			86	83	100	89
	- 20	5	101	101	93	98
			97	100	94	95
	- 20	14	104	107	104	105
			99	109	104	100

[1] All results were corrected for analytical recoveries

The stability of analytical standard solutions was also reported in the studies (Eng, 1996a, 1997). It was determined that the acetonitrile solutions were stable at -20°C over 15 months.

In a study to examine the stability of residues in maize and cotton samples after a freeze/thaw cycle (Reed, 1998), residues were shown to be stable for at least 9 to 10 days when stored under ambient conditions.

Definition of the residue

Toxicological background. Fipronil was evaluated for toxicology by the 1997 and the 2000 JMPR. The 1997 Meeting concluded that the mammalian metabolites have toxicities comparable to or substantially less than that of fipronil. Because the photodegradation product fipronil-desulfinyl (fipronil-desulfinyl) is of toxicological concern but not a mammalian metabolite of fipronil, it was reviewed separately.

The 1997 JMPR established an ADI of 0-0.0002 mg/kg bw for fipronil, and considered that a separate ADI should be established for fipronil-desulfinyl because it could be a significant residue and

its toxicity is greater than that of fipronil. A temporary ADI of 0.00003 mg/kg bw was established for fipronil-desulfinyl, and an acute RfD of 0.003 mg/kg bw for both fipronil and fipronil-desulfinyl.

The 2000 JMPR revised the above and established a group ADI of 0-0.0002 mg/kg bw for fipronil and fipronil-desulfinyl alone or in combination. The acute RfD established by the 1997 JMPR for fipronil and fipronil-desulfinyl alone or in combination was confirmed. Other toxicologically significant compounds are fipronil sulfone (MB 46136) and fipronil sulfide (MB 45950). The Meeting concluded that the metabolite RPA 200766 is significantly less toxic than fipronil and the acknowledged relevant metabolites MB 45950 and MB 46136 as well as the degradation product fipronil-desulfinyl. For this reason, RPA 200766 should not be relevant for dietary risk assessment.

Plant products. Studies of plant metabolism have shown that for soil-incorporated uses, residues of the parent and MB 46136 account for most of the residue, with MB 45950 levels being generally very low.

After foliar application the majority of the residues in human food items (cabbage, potato tubers) consisted of the parent compound and the photodegradation product fipronil-desulfinyl, whereas in animal feed items (rice straw, husk, bran), the parent compound, MB 46136, fipronil-desulfinyl and MB 45950 are potential residues for consideration.

The results of supervised residue trials indicated that the parent compound is the main component of the residue. The Meeting concluded that fipronil should be a good indicator compound for enforcement purposes in plant commodities.

The Meeting concluded that for chronic and acute dietary risk assessment purposes, the residue in plant commodities should be defined as the sum of fipronil, MB 46136, fipronil-desulfinyl and MB 45950, expressed as fipronil.

Animal products. In a goat metabolism study fipronil and the metabolites MB 46136 and MB 45950 were identified as the principal compounds. In a laying hen metabolism study, MB 46136 was identified as the main component of the total radioactive residue in eggs and tissues. The results of feeding studies with fipronil on cows and hens show that most of the residue in milk, eggs and tissues consisted of MB 46136.

The Meeting concluded that the definition of the residue in animal commodities for enforcement purposes should be the sum of fipronil and MB 46136, expressed as fipronil. For long- and short-term dietary risk assessment purposes, the residue should be defined as the sum of fipronil, MB 46136, fipronil-desulfinyl and MB 45950, expressed as fipronil.

Summary - definition of the residue

- For compliance with MRLs for plant commodities: fipronil.
- For compliance with MRLs for animal commodities: sum of fipronil and MB 46136, expressed as fipronil.
- For estimation of chronic and acute dietary intake for plant and animal commodities: sum of fipronil, fipronil-desulfinyl, MB 46136 and MB 45950, expressed as fipronil.

The residue is fat-soluble.

USE PATTERN

Fipronil belongs to a new class of insecticides known as phenylpyrazoles. The main pests controlled are shown in Table 55.

Table 55. Main pests controlled by fipronil.

Crop	Main pests controlled	Application timing
Bananas	banana weevil borer, rust and flower thrips	mat application at any time relative to fruit stage depending upon pest pressure; bud injection after emergence of flower bud
Brassica vegetables	Diamondback moth, white butterfly, cabbage looper, leaf miner, flea beetle, thrips	1 to multiple foliar applications a year, typically depending upon pest pressure and official recommendations
Cereals (rye, wheat, barley)	wireworm, wheat bulbfly, cereal leaf beetle	seed treatment; 1 to 2 foliar applications per year
Cotton	bollworm, boll weevil, plant bugs, thrips, false wireworm, leafworm, green mirid	seed treatment; 1 to multiple foliar applications a year, typically depending upon pest pressure and official recommendations
Maize	maize rootworm, wireworm, maize borers, agricultural termites, click beetle, leaf weevil	seed treatment; at plant in furrow application; ppi[1] soil broadcast application; 1 to 2 foliar applications per year
Pasture grasses	grasshoppers and locusts, beetle, click beetle, stalk borer	1 to multiple broadcast or barrier foliar applications a year, typically depending upon pest pressure and official recommendations
Potato	wireworm, rootworm, thrips, weevils, Colorado potato beetle	at plant in furrow application; ppi banded or broadcast soil application; 1 to multiple foliar applications a year, typically depending upon pest pressure and official recommendations
Rice	rice weevils, stem borers, plant hoppers, leaf folders, gall midges, thrips, bloodworm, maggots	seed treatment; ppi broadcast soil application; nursery box treatment; post transplant broadcast granules in flooded paddy; 1 to 3 foliar applications a year, typically depending upon pest pressure and official recommendations
Sorghum	wireworm, chinch bug, black earwig	ppi soil broadcast application; seed treatment
Sugar beet	click beetle, grubs, wireworm, leaf weevil, root weevil	seed treatment; ppi broadcast soil application; at plant in furrow application; 1 to 2 foliar applications per year
Sugar cane	termites, borers, weevils, beetles, hoppers	at plant in furrow application; inter-row spray application post planting
Sunflower	wireworm, leaf weevil	ppi soil broadcast application; seed treatment

[1] ppi: pre-plant soil incorporation

The following Tables give registered use patterns for the use of fipronil on bananas (Table 56), brassica vegetables (Table 57), root and tuber vegetables (Table 58), cereals (Table 59), oilseeds (Table 60), and pasture grass and sugar cane (Table 61). Because fipronil is a highly effective insecticide on many insect pests, application rates have been expressed as grams of active ingredient rather than kilograms. For spray applications expressed as g ai/ha where application volumes have been recommended on the label, g ai/100 l values have been calculated. Unless otherwise specified, application is outdoor/field only. Copies of the associated national labels were submitted.

Table 56. Uses of fipronil on bananas.

Country	Formulation	Application				PHI
		Method	g ai/ha	g ai/100 l	No.	days
Australia	WG 800 g/kg; SC 200 g/l	soil/lower stem spray	~300 (0.12-0.2 g ai/ stool)	24-40	not specified; CP 2	0
Cameroon	GR 5 g/kg	soil broad-cast at base of plant	300-400 (0.15-0.2 g ai/plant)		not specified	not specified
Ivory Coast	GR 5 g/kg	soil broad-cast at base of plant	300-400 (0.15-0.2 g ai/plant)		not specified	not specified
France (Guadeloupe)	GR 5 g/kg	apply at base of plant, in-corporate	~400 (0.2 g ai/plant)		not specified	not specified
Myanmar	GR 3 g/kg	soil broad-cast at base of plant	90-300 (0.045-0.15 g ai/plant)		not specified; CP 1	7
Philippines	SC 50 g/l	bud injection	0.02 g ai/bud (70 ml diluted suspension)	30	not specified; CP 1	not specified

CP: common practice

Table 57. Uses of fipronil on brassica vegetables. All foliar applications.

Crop	Country	Formulation	Application			PHI
			g ai/ha	g ai/100 l	No.	days
Brassicas, general	Ivory Coast	SC 50 g/l	50 -75	10-37.5	not specified	7
	Kenya	SC 50 g/l	50	6.25-12.5	not specified	3
	Myanmar	SC 50 g/l	25-50	2.8-5.6	not specified; WCP 4-5	7
Broccoli	Australia	WG 800 g/kg; SC 200 g/l	24-48 50	5-12.5	4	7
	Ecuador	WG 800 g/kg	31.5-62.5		not specified	45
Brussels sprouts	Australia	WG 800 g/kg; SC 200 g/l	24-48 50	5-12.5	4	7
Cabbage	Australia	WG 800 g/kg; SC 200 g/l	24-48 50	5-12.5	4	7
	Colombia	WG 200 g/kg	48		not specified	not specified
	Ecuador	WG 200 g/kg	31.5-62.5		not specified	45
	India	SC 50 g/l	40-50	8-10	2-3	7
	Indonesia	SC 50 g/l	12.5-25	2.5-5	not specified; WCP 6-8	14
	Malaysia	SC 50 g/l	36	4.5	not specified; WCP 4-6	5
	New Zealand	SC 200 g/l	24	4.8	4	7
	Panama	WG 200 g/kg; SC 200 g/l	50	16.7-25 by ground	not specified (but requires 15 day spray interval)	not specified
	Peru	SC 200 g/l	40-50	11-12.5	not specified (but requires 15 day spray interval)	14
	Philippines	SC 50 g/l	25-50	5-16	not specified; WCP 6-8	7
	Taiwan	SC 50 g/l	12.5-25	2.5	not specified; WCP 3-4	9
	Venezuela	SC 200 g/l	15-25		not specified	14
Cauliflower	Australia	WG 800 g/kg; SC 200 g/l	24-48 50	5-12.5	4	7
	Ecuador	WG 800 g/kg	31.5-62.5		not specified	45
	Peru	SC 200 g/l	40-50	11-12.5	not specified	14
Crucifers, general	China	SC 50 g/l	12.8-24.8	1.3-4.1	not specified; WCP 4	not specified
	Thailand	SC 50 g/l	50-200	5	not specified; WCP 3-4	7
	Vietnam	WG 800 g/kg	25.6	8.5	not specified; WCP 5	15
Crucifers, leafy	Malaysia	SC 50 g/l	36	4.5	not specified; WCP 4-6	5
Kohlrabi	Australia	WG 800 g/kg; SC 200 g/l	24-48 50	5-12.5	4	7

WCP: worst case practice; estimated from field development expertise and observation

Table 58. Uses of fipronil on root and tuber vegetables.

Crop	Country	Formulation	Application				PHI
			Method	g ai/ha	g ai/100 l	No.	days
Potato	Australia	SC 200 g/l	soil broadcast ppi spray	50		1	NA
	Belarus/Russia	EC 25 g/l	foliar	12.5-15	2.5	2	30
	Belarus/Russia	WG 800 g/kg	foliar	16-20	4-10	2	30
	Brazil	GR 20 g/kg	soil, in furrow at planting	100		1	NA
	Colombia	SC 200 g/l	soil in furrow spray or hill spray	120		2	not specified
	Czech/Slovak	WG 800 g/kg	foliar	20	6.67-10	not specified, CP 2	14
	Ecuador	WG 800 g/kg	soil spray	50-100		2, 2nd application at hilling	30
	Hungary	WG 800 g/kg	foliar	20	4-6.7 by ground	not specified, CP 1-2 (requires 2-3 wk spray interval)	14
	Indonesia	SC 50 g/l	foliar	12.5-50	2.5-5	not specified, CP 2-3	14

Crop	Country	Formulation	Application				PHI
			Method	g ai/ha	g ai/100 l	No.	days
	Italy	GR 20 g/kg	soil, in furrow at planting	150		1	NA
	Myanmar	GR 3 g/kg	soil broadcast or incorporated	75-110		not specified, CP 1	14
	Myanmar	SC 50 g/l	foliar	unclear	2.5-5	4-5	14
	Panama	SC 200 g/l WG 800 g/kg	at plant soil spray or foliar	50-150	16.7-50 by ground	not specified, CP 1-2 (requires 15d spray interval)	not specified
	Peru	SC 200 g/l	soil spray	50-100	12.5-25	not specified	14
	Poland	SC 200 g/l	foliar	20	5-13.3	not specified	14
	Romania	SC 200 g/l	foliar	18-20	2.25-5	3	30
	Spain	WG 800 g/kg	foliar	20-24	2.25-6	3	14
	Turkey	WG 800 g/kg	foliar	16		2	14
	Ukraine	EC 25 g/l	foliar	16		1	28
	Ukraine	WG 800 g/kg	foliar	16-20		2	20
Sugar beet	Belgium	GR 14 g/kg with aldicarb	soil, in furrow at planting	77-154		1	NA
	Belgium GAP pending	WG 800 g/kg	broadcast soil ppi spray	200		1	NA
	Chile	FS 250 g/l	seed treatment	200-400 g ai/ 100 kg seed		1	NA
	France	GR 14 g/kg with aldicarb	soil, in furrow at planting	160		1	NA
	France	WG 800 g/kg	broadcast soil ppi spray	200		1	NA
	Hungary	WG 800 g/kg	foliar	20-24	4-8 by ground	not specified, CP 1-2 (requires 2-3 wk spray interval)	30
	Italy	GR 20 g/kg	soil, in furrow at planting	150		1	NA
	Romania	FS 250 g/l	seed treatment	375 g ai/100 kg seed		1	NA
	Romania	SC 200 g/l	foliar	20	2.25-5	3	30
	Ukraine	FS 500 g/l	seed treatment	25 g ai/100,000 seeds		1	NA

NA: not applicable
CP: common practice

Table 59. Uses of fipronil on cereals.

Crop	Country	Formulation	Application				PHI
			Method	g ai/ha	g ai/100 l	No.	days
Barley	Belarus/ Russia	WG 800 g/kg	Foliar	16	4-8	1	30
Cereals, general	Czech/Slovak	WG 800 g/kg	foliar	20	6.66-10	not specified; CP 1	44
	France	FS 250 g/l plus combination products w/fungicides	seed treatment	100 (50 g ai/ 100 kg seed)		1	NA
	Hungary	WG 800 g/kg	foliar	12	2.4-4	not specified, CP 1-2, (requires 2-3 wk spray interval)	30
	Romania	SC 200 g/l	foliar	18	2.25-4.5	3	30
	Switzerland	FS 500 g/l	seed treatment	Only bag label warning put on treated seed imported into Switzerland from other countries			

Crop	Country	Formulation	Application				PHI
			Method	g ai/ha	g ai/100 l	No.	days
	Turkey	WG 800 g/kg	foliar	20		1	not specified; pest appears during or after tillering
Maize	Belgium	FS 500 g/l GAP pending	seed treatment	40 g ai/50,000 seeds		1	NA
	Belgium	WG 800 g/kg GAP pending	soil broad-cast ppi spray	200		1	NA
	Chile	FS 250 g/l	seed treatment	100-125 g ai/ 100 kg seed		1	NA
	Ivory Coast	SC 50 g/l	soil spray at planting, incorporated	100-200	20-100	1	NA
	France	FS 500 g/l	seed treatment	50-70 (250 g ai/100 kg seed; 27.5 g ai / 50,000 seeds)		1	NA
	France	GR 20 g/kg (w/aldicarb)	soil, in furrow at planting	160		1	NA
	France	WG 800 g/kg	soil broad-cast ppi spray	200		1	NA
	Hungary	WG 800 g/kg	foliar	20	4-6.7 by ground	not specified, CP 1-2 (requires 2-3 wk spray interval)	30
	Italy	FS 500 g/l	seed treatment	250 g ai/100 kg seed (15 g ai / 25,000 seeds)		1	NA
	Italy	GR 20 g/kg	soil, in furrow at planting	100-150		1	NA
	Kenya	GR 3 g/kg	soil, in furrow at planting	90		1	90
	Mexico	GR 20 g/kg	soil, in furrow at planting	200		1	NA
	Mozambique	FS 250 g/l	seed treatment	100 (400 g ai/100 kg seed)		1	NA
	Mozambique	GR 3 g/kg	soil, in furrow at planting	99		1	NA
	Mozambique	SC 200 g/l	soil, in furrow spray at planting	100		1	30
	Myanmar	GR 3 g/kg	soil broad-cast or incorporated	75-110		1	7
	Myanmar	SC 50 g/l	soil spray	100-200	0.2-0.4	1	7
	Panama	SC 200 g/l	soil ppi spray or seed treatment	100	33.3-50 by ground	1	NA
	Panama	WG 800 g/kg	soil ppi spray or seed treatment	50-100	16.7-50 by ground	1	NA
	Romania	FS 250 g/l	seed treatment	125 g ai/100 kg seed		1	NA
	Switzerland	FS 500 g/l	seed treatment	Only bag label warning put on treated seed imported into Switzerland from other countries			
	Turkey	FS 500 g/l	seed treatment	25 g ai/100 kg seed		1	NA
	Ukraine	FS 500 g/l	seed treatment	100 g ai/100 kg seed		1	NA
	USA	GR 15 g/kg	soil, in furrow at planting	112-146		1	NA
	USA	SC 400 g/l WG 800 g/kg	soil, in furrow spray at planting	112-146		1	90
	Zimbabwe	FS 250 g/l FS 500 g/l	seed treatment	400 g ai/100 kg seed		1	NA
	Zimbabwe	SC 200 g/l	soil, in furrow at planting or broad-cast ppi spray	50-150		1	NA
Rice	Argentina	FS 250 g/l	seed treatment	30 g ai/100 kg seed		1	NA
	Australia	FS 500 g/l	seed treatment	12.5 (10 g ai/ 100 kg seed)		1	NA

Crop	Country	Formulation	Application				PHI days
			Method	g ai/ha	g ai/100 l	No.	
	Bangladesh	GR 3 g/kg	broadcast into paddy	30		1 within 25 d post transplant	not specified
	Bangladesh	SC 50 g/l	foliar	25	5	not specified, CP 1-3	7
	Brazil	FS 250 g/l	seed treatment	62.5 g ai/100 kg seed		1	NA
	China	FS 50 g/l	seed treatment	16-125 (0.8-4.5 g ai/kg seed, seeding rate 20-30 kg/ha)		1	NA
	China	GR 3 g/kg	nursery or broad-cast into paddy	49.5-81		1 just before or after sowing or transplant	not specified
	China	SC 50 g/l	foliar	22.5-45	3-10	not specified, CP 1-2	not specified
	Colombia	SC 200 g/l	foliar	60-70		not specified	not specified
	Colombia	WG 800 g/kg	foliar	50-60		not specified	not specified
	France	FS 500 g/l GAP pending	seed treatment	25 (12.5 g ai/ 100 kg seed)		1	NA
	India	GR 3 g/kg	broadcast into paddy	50-75		1	32
	India	SC 50 g/l	foliar	50-75	10-12.5	1 from 25-30d post transplant	32
	Indonesia	FS 50 g/l	seed treatment	12.5-25 (0.6-1.25 g ai/kg seed)		1	NA
	Indonesia	GR 3 g/kg	broadcast into paddy	30		2	25
	Indonesia	SC 50 g/l	foliar	12.5-25	2.5-8.33	not specified, CP 1-2	14
	Ivory Coast	GR 3 g/kg	broadcast into paddy	45		2, 2nd appl. 42 days after sowing or 30 days after transplant	not specified
	Ivory Coast	SC 50 g/l	foliar	25-75	5-37.5	not specified	7
	Japan	GR 10 g/kg	broadcast nursery box	100 (0.5 g ai/box)		1, 3 d before to day of transplant	NA
	Madagascar	SC 50 g/l	foliar	50	25	1	50
	Malaysia	GR 3 g/kg	broadcast into paddy	25-50		1, 15-30 d post sowing	90 (14d proposed)
	Myanmar	GR 3 g/kg	broadcast into paddy	37-75		1, 5-30 d post sowing	7
	Myanmar	GR 3 g/kg	nursery box	0.15 g ai/box		1	NA
	Myanmar	SC 50 g/l	foliar	25-50		not specified, CP 1	7
	Panama	SC 200 g/l	foliar	50-150	16.7-75 by ground; 50-150 by air	not specified, CP 1-2 (requires 15 d spray interval)	not specified
	Panama	WG 800 g/kg	foliar	50-100	16.7-50 by ground; 50-100 by air	not specified, CP 1-2 (requires 15 d spray interval)	not specified
	Philippines	GR 3 g/kg	broadcast into paddy	30-51		1 no more than 45 d post transplant or 55 d post seeding	not specified
	Philippines	SC 50 g/l	foliar	20-30	3.9-12	not specified, CP 1	7
	Sri Lanka	GR 3 g/kg	broadcast into paddy	36		not specified, CP 1	not specified
	Sri Lanka	SC 50 g/l	foliar	9	2-2.5	not specified	5
	Taiwan	GR 3 g/kg	broadcast into paddy	60		2, last one at tillering	not specified
	Taiwan	GR 3 g/kg	nursery box	0.15 g ai/ box		1	NA

Crop	Country	Formulation	Application				PHI days
			Method	g ai/ha	g ai/100 l	No.	
	Thailand	GR 2 or 3 g/kg	broadcast into paddy	25-50		1-2	7[1]
	Thailand	SC 50 g/l	foliar	25-62.5	5-12.5	not specified, CP 1-2	7[1]
	USA	FS 750 g/l	seed treatment	28-56 (60-120 g ai/100 kg seed)		1	NA
	USA	SC 750 g/l WG 800 g/kg	soil ppi spray	28-56	0.1-0.6 by ground; 1.2-2.4 by air	1	NA
	Venezuela	FS 250 g/l	seed treatment	56 g ai/100 kg seed		1	NA
	Venezuela	SC 200 g/l	foliar	62		not specified	7
	Vietnam	GR 3 g/kg	broadcast into paddy	30		not specified, CP 1	not specified
	Vietnam	WG 800 g/kg	foliar	26	8	not specified, CP 1	15
Sorghum	Australia	FS 500 g/l GAP pending	seed treatment	75 g ai/100 kg seed		1	NA
	Australia	SC 200 g/l WG 800 g/kg	foliar	1.25	3-7.5	not specified	14
	Australia	UL 8.5 g/l	foliar (aerial)	1.3		not specified	14
	France	WG 800 g/kg	soil broadcast ppi spray	200		1	NA
	Myanmar	GR 3 g/kg	soil broadcast or incorporated	75-111		1	7
	Panama	SC 200 g/l WG 800 g/kg	foliar or seed treatment	25-30	8.3-15 by ground	not specified, CP 1-2 (requires 15d spray interval)	not specified
Wheat	Belarus/ Russia	WG 800 g/kg	foliar	18-24	4.5-12	1	30
	Belgium	FS 125 g/l (in combination w/ fungicides)	seed treatment	50 g ai/100 kg seed		1	NA
	Chile	FS 250 g/l	seed treatment	50-100 g ai/100 kg seed		1	NA
	Romania	SC 200 g/l	foliar	15-18 (depending on pest)	1.88-4.5	3	30

NA: not applicable
CP: common practice
[1] The label PHI of 7 days represents the standard PHI for fipronil in Thailand. However, the pest spectrum dictates the timing of applications. Fipronil is used in Thailand on rice to control thrips, leaffolder, stemborer and brown plant hopper. Common practice is 1-2 foliar applications at 12.5-37.5 g ai/ha made from 7 to a maximum 60 days after planting (rice is harvested 110-120 days after planting).

Table 60. Uses of fipronil on oilseeds.

Crop	Country	Formulation	Application				PHI days
			Method	g ai/ha	g ai/100 l	No.	
Cotton	Australia	FS 500 g/l	seed treatment	50 g ai/100 kg seed		1	NA
	Australia	SC 200 g/l WG 800 g/kg	foliar	12.5-24	1.3-70	not specified, CP 1-2	28
	Bolivia	WG 800 g/kg	foliar	12-80 ground 24-80 air	3-80 ground; 75-400 air	4-7 at 7 day intervals WCP 2-3	15
	Brazil	WG 800 g/kg	foliar	12-80 ground 24-80 air	3-80 ground; 75-400 air	4-7 at 7 day intervals; WCP 2-3	15
	Colombia	SC 200 g/l	foliar	65-70	172-308 air	not specified; WCP 2-3	not specified
	Colombia	WG 800 g/kg	foliar	64-68		not specified; WCP 2-3	not specified

Crop	Country	Formulation	Application				PHI
			Method	g ai/ha	g ai/100 l	No.	days
	Ivory Coast	SC 50 g/l	foliar	12.5-80	2.5-40	not specified	7
	Mexico	SC 200 g/l	foliar	50		2 at 7 day intervals	45
	Mexico	WG 800 g/kg	foliar	32-48		2 at 5-7 day intervals	45
	Mozambique	FS 250 g/l	seed treatment	100 (400 g ai/100 kg seed)		1	NA
	Mozambique	GR 3 g/kg	soil, in furrow at planting	99		1	NA
	Myanmar	SC 50 g/l	foliar	12.5-370		not specified, CP 1	7
	Paraguay	WG 800 g/kg	foliar	12-80	3-80 ground; 30-400 air	4-7 at 7 day intervals; WCP 2-3	15
	Peru	SC 200 g/l	foliar	60-70	15-18 ground; 120-150 air	not specified; WCP 2-3	14
	USA (GAP pending)	EC 300 g/l WG 800 g/kg	foliar	28-56	12-188	maximum 224 g ai/ ha/ season	60
	Venezuela	SC 200 g/l	foliar	70		not specified; WCP 2-3	15
	Zimbabwe	FS 250 g/l FS 500 g/l	seed treatment	400 g ai/100 kg seed		1	NA
	Zimbabwe	SC 200 g/l	soil, in furrow spray at planting	100		1	NA
Sunflower	Australia	FS 500 g/l GAP pending	seed treatment	75 g ai/100 kg seed		1	NA
	France	FS 500 g/l	seed treatment	50-70 (500 g ai/100 kg seed)		1	NA
	France	GR 20 g/kg w/aldicarb	soil in furrow	160		1	NA
	France	WG 800 g/kg	broadcast soil ppi spray	200		1	NA
	Italy	GR 20 g/kg	soil, in furrow at planting	100-150		1	NA
	Myanmar	GR 3 g/kg	soil broadcast or incorporated	111-148		not specified, CP 1 at planting	7
	Romania	FS 250 g/l	seed treatment	125 g ai/100 kg seed		1	NA
	Ukraine	FS 500 g/l	seed treatment	100 g ai/100 kg seed		1	NA

NA: not applicable
CP: common practice
WCP: worst-case practice

Table 61. Uses of fipronil on pasture grasses and sugar cane.

Crop	Country	Formulation	Application				PHI
			Method	g ai/ha	g ai/100 l	No.	days
Grassland	China	UL 4 g/l	foliar	4-8		not specified	not specified
Uncultivated land	Ethiopia*	UL 12.5 g/l	foliar	1-6.25		not specified	7
	Mozambique	UL 7.5 g/l	foliar	7.5		1	21
	Sudan	UL 12.5 g/l	foliar	1-6.25		not specified	7
	Madagascar	UL 4 g/l	foliar	2-4		not specified	3
Pasture	Australia	UL 8.5 g/lSC 200 g/l WG 800 g/kg	foliar	1.3		not specified	14
	South Africa	UL 2, 3, 5 & 7.5 g/l	foliar	7.5		not specified	21

Crop	Country	Formulation	Application				PHI days
			Method	g ai/ha	g ai/100 l	No.	
Sugar cane	Australia	SC 200 g/l WG 800 g/kg	inter row directed spray to soil and bottom 40 cm stalk	75	37.5	1	84
	Bangladesh	GR 3 g/kg	soil, in furrow at planting	100		1	NA
	Bangladesh	SC 50 g/l	soil, in furrow drench at planting	100	20	1	NA
	Bolivia	WG 800 g/kg	soil, in furrow spray at planting	200	50-200	1	NA
	Brazil	GR 20 g/kg	soil, in furrow at planting	200		1	NA
	Brazil	WG 800 g/kg	soil, in furrow spray at planting	160-200	80-200	1	NA
	China	GR 3 g/kg	soil, in furrow at planting	100-150		1	NA
	Ivory Coast	SC 50 g/l	soil incorporated spray	50-200	10-100	not specified	7
	Indonesia	FS 50 g/l	cane set dipping	125-250 ppm ai in solution		1	NA
	Indonesia	GR 3 g/kg	soil incorporated	75-150		2	25
	Malaysia	SC 50 g/l	soil, in furrow spray at planting	20	2.5	1	NA
	Mozambique	SC 200 g/l	soil, in furrow spray	100		1	60
	Myanmar	GR 3 g/kg	soil, in furrow at planting	37-111		1	NA
	Myanmar	SC 50 g/l	soil, in furrow spray at planting	100	11	1	NA
	Panama	SC 200 g/l	soil spray or foliar spray	50-60	16.7-30 by ground; 50-60 by air	not specified	not specified
	Panama	WG 800 g/kg	soil spray or foliar spray	50-200	16.7-100 by ground; 50-200 by air	not specified	not specified
	Paraguay	WG 800 g/kg	soil, in furrow spray at planting	160 (2.8 g ai/100 m of furrow)	40-160	1	NA
	Sudan	SC 50 g/l	soil, in furrow spray at planting	120	5	1	NA
	Thailand	SC 50 g/l	soil, in furrow at planting	100	20	1	7
	Zimbabwe	SC 200 g/l	soil, in furrow spray at planting	100	50	1	NA

* the same label is used in Kenya, Tanzania and Uganda

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received supervised trials residue data on plants as well as animal feeding studies. Residue data on bananas, potatoes, sugar beet, vegetables, cereals, grasses and oilseeds are summarized in Tables 62-84.

Table 62. Bananas.
Table 63. Broccoli and cauliflower.
Table 64. Cabbages.
Table 65. Potatoes.
Table 66. Sugar beet roots.
Table 67. Barley grain.
Table 68. Maize grain.
Table 69. Rice grain.
Table 70. Sorghum grain.
Table 71. Wheat grain.
Table 72. Sugar cane.
Table 73. Cotton seed.
Table 74. Sunflower seed.
Table 75. Sugar beet tops.
Table 76. Maize cobs, silage, forage and fodder.
Table 77. Pasture grass.
Table 78. Barley straw.
Table 79. Rice straw.
Table 80. Sorghum forage and straw.
Table 81. Wheat straw.
Table 82. Cotton fodder.
Table 83. Sunflower forage and fodder.
Table 84. Sugar cane forage and fodder.

The concentrations of fipronil and the metabolites MB 45950, MB 46136, fipronil-desulfinyl and RPA 200766 are expressed in the Tables below as individual residues, but in the appraisal were calculated as fipronil according to the appropriate definition of the residue: MB 45950 (421.1 g/mol) factor 1.04, MB 46136 (453.1 g/mol) factor 0.965, fipronil-desulfinyl (389.02 g/mol) factor 1.1 and RPA 200766 (455.08 g/mol) factor 0.96.

Where residues were not detected they are recorded as below the LOQ, e.g. <0.002 mg/kg, except in the US data where "less than the minimum limit of detection (MLD)" is shown; for residues between the MLD and LOQ, <LOQ is shown. The explanation is noted in the Tables containing US data.

Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOQ, to 1 significant figure. Residues from trials according to GAP are underlined, those used for the estimation of STMRs and HRs are double underlined.

Bananas (Table 62). The common practice is to apply granules or spray the soil around the base of the plant stem to control banana weevil as pest pressure dictates, generally without incorporation but with incorporation in Guadeloupe. The trials listed in Table 62 were according to common practice.

Table 62. Results of supervised trials on bananas.

Country, Year, reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/ha	No.	Comments; time between appl.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1992-1993, PR93725AT1 Richard and Muller, 1994a	SC	800	1	no decline study, separate	63	<0.002	<0.002	<0.002	<0.002	<0.002
			1	treatments,	91	<0.002	<0.002	<0.002	<0.002	<0.002
			1	spraying to stem and soil	141	<0.002	<0.002	<0.002	<0.002	<0.002
			1		166	<0.002	<0.002	<0.002	<0.002	<0.002
Australia, 1994, 94663AU1, Richard and Muller, 1995a	SC	300	1	no decline study, separate	0	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
			1	treatments,	1	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
			1	spraying to stem and soil	7	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
			1		14	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
			1		28	≤0.002	≤0.002	≤0.002	NR	<0.002
			1		60	≤0.002	≤0.002	≤0.002	NR	<0.002
Australia, 1994, 94663AU1 Richard and Muller, 1995a	SC	600	1	no decline study, separate treatments,	0	0.003[1] <0.002	<0.002	<0.002	<0.002	<0.002
			1	spraying to stem and soil	1	<0.002	<0.002	<0.002	<0.002	<0.002
			1		7	<0.002	<0.002	<0.002	<0.002	<0.002
			1		14	<0.002	<0.002	<0.002	<0.002	<0.002
			1		28	<0.002	<0.002	<0.002	<0.002	<0.002
			1		60	<0.002	<0.002	<0.002	<0.002	<0.002
Australia, 1994, 94663AU2 Richard and Muller, 1995a	SC	300	1	no decline study, separate	1	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
			1	treatments,	7	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
			1	spraying to stem and soil	17	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
			1		29	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
Australia, 1994, 94663AU2 Richard and Muller, 1995a	SC	600	1	no decline study, separate	1	<0.002	<0.002	<0.002	<0.002	<0.002
			1	treatments,	7	<0.002	<0.002	<0.002	<0.002	<0.002
			1	spraying to stem and soil	17	<0.002	<0.002	<0.002	<0.002	<0.002
			1		29	<0.002	<0.002	<0.002	<0.002	<0.002
Cameroon, 1992-1993, 90CAM04I Richard and Muller, 1993c	GR	200	1		295	<0.002	<0.002	<0.002	<0.002	<0.002
		400	1	soil treatment	295	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Guadeloupe, 1992-1993, GU-NEU 196, 92-319 Meteo III, Richard and Muller, 1993a	GR	400	1	no decline study, separate	0	≤0.002	≤0.002	≤0.002	<0.002	<0.002
			1	soil treatments	14	≤0.002	≤0.002	≤0.002	<0.002	<0.002
			1		21	≤0.002	≤0.002	≤0.002	<0.002	<0.002
			1		58	≤0.002	≤0.002	≤0.002	<0.002	<0.002
			1		92	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Guadeloupe, 1992-1993 92-319 GU-NEU 196 Garage IV, Richard and Muller, 1993a	GR	400	1	no decline study, separate	0	≤0.002	≤0.002	≤0.002	<0.002	<0.002
			1	soil treatments	14	≤0.002	≤0.002	≤0.002	<0.002	<0.002
			1		21	≤0.002	≤0.002	≤0.002	<0.002	<0.002
			1		58	0.003[2]	≤0.002	≤0.002	<0.002	<0.002
			1		92	0.025[3]	<0.002	<0.002	<0.002	<0.002

Country, Year, reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/ha	No.	Comments; time between appl.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Guadeloupe, 1992-1993[2] GU-NEU 196, 92-319, Meteo II, Richard and Muller, 1993a	GR	400	2	interval 6 months, soil treatment	149	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Guadeloupe, 1992-1993[2] GU-NEU 196 Meteo III, 92-319 Richard and Muller, 1993a	GR	400	2	interval 4 months, soil treatment	43	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Guadeloupe, 1992-1993[2] GU-NEU 196, Garage IV, 92-319 Richard and Muller, 1993a	GR	400	2	interval 4 months, soil treatment	43	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Guadeloupe, 1992-1993[2] GU-NEU 196 Meteo II, 92-319 Richard and Muller, 1993a	GR	200	3	interval 3 months, soil treatment	86	<0.002	<0.002	<0.002	<0.002	0.002
Ivory Coast, 1993[2] BACJEX 420 Richard and Muller, 1993b	GR	800	1 1 1 1 1	no decline study, separate soil treatments	3 19 33 63 94	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002
Ivory Coast, 1993[2] BACJEX 420 Richard and Muller, 1993b	GR	1600	1 1 1 1 1	no decline study, separate soil treatments	3 19 33 63 94	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002
Ivory Coast, 1993-1994[2] CAD93I05 Richard and Muller, 1994e	GR	250 500 1000	2 2 2	interval 3 months, soil treatment	78 78 78	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	NR NR NR	<0.002 <0.002 <0.002

NR: not reported owing to analytical problems
[1]Fipronil was reported at 0.003 mg/kg, but the untreated control contained a quantifiable quantity of parent (0.006 mg/kg). Value at day 0 is considered to be contamination.
[2] Three individual field samples of fruit from the lower, middle and upper portions of the bunch were analysed at each interval (in trial 92-319: 0.003 mg/kg is mean of 0.005, 0.002, 0.002 mg/kg).
[3] Contamination, not included in evaluation.

Broccoli and cauliflower (Table 63). Fipronil was applied as a foliar spray, so residues of parent, MB 45950, MB 46136 and the photoproduct fipronil-desulfinyl were reported.

Table 63. Residues from supervised trials in Australia on flowering brassicas. All WG formulation.

CROP Year Reference	Application				PHI, days	Residues, mg/kg				
	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Keats, 1996a										
BROCCOLI 1996 AK96052 4/2	12	2	4	7,7,7	0 1 2 3 5 7 14 21	0.026 0.023 0.015 0.007 <0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002	0.003 0.004 0.003 <0.002 <0.002 <0.002 <0.002 <0.002	0.005 0.006 0.003 <0.002 <0.002 <0.002 <0.002 <0.002	NR
BROCCOLI 1996 AK96052 4/3	24	4	4	7,7,7	0 1 2 3 5 7 14 21	0.027 0.025 0.015 0.003 <0.002 <0.002 <0.002 <0.002	0.003 0.003 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002	0.004 0.005 0.002 <0.002 <0.002 <0.002 <0.002 <0.002	0.008 0.007 0.003 <0.002 <0.002 <0.002 <0.002 <0.002	NR

CROP Year Reference	Application				PHI, days	Residues, mg/kg				
	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
BROCCOLI 1996 AK96052 4/4	48	8	4	7,7,7	0	0.049	0.003	0.005	0.009	NR
					1	0.036	<0.002	0.007	0.005	
					2	0.013	<0.002	0.003	0.006	
					3	0.008	<0.002	<0.002	0.004	
					5	0.004	<0.002	<0.002	<0.002	
					7	0.006	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 4/5	96	16	4	7,7,7	0	0.043	0.004	0.006	0.011	NR
					1	0.031	0.003	0.005	0.01	
					2	0.020	0.002	0.007	0.009	
					3	0.012	<0.002	0.003	0.007	
					5	0.009	<0.002	0.003	0.01	
					7	0.004	<0.002	<0.002	0.005	
					14	0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 6/2	12	2	6	7,7,7,8,7	0	0.033	0.003	0.003	0.008	NR
					1	0.023	<0.002	0.003	0.005	
					2	0.011	<0.002	0.002	0.004	
					3	0.008	<0.002	<0.002	0.002	
					5	<0.002	<0.002	<0.002	<0.002	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 6/3	24	4	6	7,7,7,8,7	0	0.046	0.003	0.004	0.01	NR
					1	0.015	<0.002	0.004	0.004	
					2	0.014	<0.002	0.003	0.006	
					3	0.009	<0.002	<0.002	0.004	
					5	0.009	<0.002	<0.002	<0.002	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 6/4	48	8	6	7,7,7,8,7	0	0.049	0.004	0.005	0.014	NR
					1	0.036	0.004	0.007	0.02	
					2	0.037	0.005	0.008	0.022	
					3	0.008	<0.002	<0.002	0.005	
					5	0.008	<0.002	0.002	0.005	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 6/5	96	16	6	7,7,7,8,7	0	0.060	0.006	0.007	0.022	NR
					1	0.041	0.005	0.011	0.022	
					2	0.041	0.004	0.009	0.021	
					3	0.031	0.004	0.006	0.016	
					5	0.009	<0.002	0.003	0.005	
					7	0.007	<0.002	<0.002	0.004	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 10/2	12	2	10	7,7,7,8,7, 6,6,8,7	0	0.034	0.003	<0.002	0.011	NR
					1	0.014	<0.002	<0.002	<0.002	
					2	0.013	<0.002	<0.002	<0.002	
					3	0.005	<0.002	<0.002	<0.002	
					5	0.004	<0.002	<0.002	<0.002	
					7	0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 10/3	24	4	10	7,7,7,8,7, 6,6,8,7	0	0.029	0.003	0.005	0.01	NR
					1	0.016	<0.002	0.002	0.005	
					2	0.007	<0.002	<0.002	<0.002	
					3	0.007	<0.002	0.002	0.002	
					5	0.005	<0.002	<0.002	<0.002	
					7	0.003	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	

CROP Year Reference	Application				PHI, days	Residues, mg/kg				
	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
BROCCOLI 1996 AK96052 10/4	48	8	10	7,7,7,8,7, 6,6,8,7	0	0.068	0.005	0.008	0.019	NR
					1	0.055	0.006	0.008	0.016	
					2	0.025	0.003	0.004	0.009	
					3	0.007	<0.002	0.004	0.004	
					5	0.007	<0.002	0.003	0.003	
					7	0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
BROCCOLI 1996 AK96052 10/5	96	16	10	7,7,7,8,7, 6,6,8,7	0	0.079	0.017	0.008	0.022	NR
					1	0.058	0.006	0.01	0.019	
					2	0.030	0.004	0.006	0.011	
					3	0.021	0.002	0.004	0.009	
					5	0.009	<0.002	0.004	0.004	
					7	0.006	<0.002	0.004	0.003	
					14	0.004	<0.002	0.003	0.002	
					21	0.003	<0.002	<0.002	<0.002	
Keats, 1996d										
CAULIFLOWER 1995 AUS 94i47aR	12	2.4	2	7	0	0.014	<0.002	<0.002	<0.002	NR
					1	0.009	<0.002	<0.002	<0.002	
					3	0.004	<0.002	<0.002	<0.002	
					5	0.003	<0.002	<0.002	<0.002	
					7	0.003	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER 1995 AUS 94i47aR	24	4.8	2	7	0	0.018	<0.002	<0.002	<0.002	NR
					1	0.014	<0.002	<0.002	<0.002	
					3	0.007	<0.002	<0.002	<0.002	
					5	0.003	<0.002	<0.002	<0.002	
					7	0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER 1995 AUS 94i47aR	48	9.6	2	7	0	0.019	<0.002	0.002	<0.002	NR
					1	0.016	<0.002	<0.002	<0.002	
					3	0.006	<0.002	<0.002	<0.002	
					5	0.002	<0.002	<0.002	<0.002	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER 1995 AUS 94i47aR	96	19.2	2	7	0	0.024	<0.002	0.004	<0.002	NR
					1	0.018	<0.002	0.004	<0.002	
					3	0.009	<0.002	<0.002	0.002	
					5	0.004	<0.002	<0.002	<0.002	
					7	0.003	<0.002	0.002	<0.002	
					14	0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER 1995 AUS 94i47aR	12	2.4	4	7,7,7	0	0.013	<0.002	<0.002	<0.002	NR
					1	0.01	<0.002	<0.002	<0.002	
					3	0.006	<0.002	<0.002	<0.002	
					5	0.003	<0.002	<0.002	<0.002	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER 1995 AUS 94i47aR	24	4.8	4	7,7,7	0	0.016	<0.002	<0.002	<0.002	NR
					1	0.01	<0.002	<0.002	<0.002	
					3	0.005	<0.002	<0.002	<0.002	
					5	0.002	<0.002	<0.002	<0.002	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER 1995 AUS 94i47aR	48	9.6	4	7,7,7	0	0.017	<0.002	<0.002	<0.002	NR
					1	0.008	<0.002	<0.002	<0.002	
					3	0.006	<0.002	<0.002	<0.002	
					5	0.005	<0.002	<0.002	<0.002	
					7	0.003	<0.002	<0.002	<0.002	
					14	0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	

CROP Year Reference	Application				PHI, days	Residues, mg/kg				
	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
CAULIFLOWER	96	19.2	4	7,7,7	0	0.024	<0.002	<0.002	<0.002	NR
1995					1	0.015	<0.002	<0.002	<0.002	
AUS 94i47aR					3	0.006	<0.002	<0.002	<0.002	
					5	0.004	<0.002	<0.002	<0.002	
					7	0.003	<0.002	<0.002	<0.002	
					14	0.003	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	12	2.4	8	7,7,7,8,7	0	0.018	<0.002	<0.002	<0.002	NR
1995				,6,8,7	1	0.012	<0.002	<0.002	<0.002	
AUS 94i47aR					3	0.012	<0.002	0.003	<0.002	
					5	0.009	<0.002	0.002	<0.002	
					7	0.009	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	24	4.8	8	7,7,7,8,7	0	0.020	<0.002	<0.002	<0.002	NR
1995				,6,8,7	1	0.014	<0.002	<0.002	<0.002	
AUS 94i47aR					3	0.006	<0.002	<0.002	<0.002	
					5	0.004	<0.002	<0.002	<0.002	
					7	0.004	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	48	9.6	8	7,7,7,8,7	0	0.026	<0.002	<0.002	<0.002	NR
1995				,6,8,7	1	0.016	<0.002	<0.002	<0.002	
AUS 94i47aR					3	0.005	<0.002	<0.002	<0.002	
					5	0.005	<0.002	<0.002	<0.002	
					7	0.003	<0.002	<0.002	<0.002	
					14	0.003	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	96	19.2	8	7,7,7,8,7	0	0.061	<0.002	0.009	<0.002	NR
1995				,6,8,7	1	0.028	<0.002	0.003	<0.002	
AUS 94i47aR					3	0.013	<0.002	0.004	0.003	
					5	0.008	<0.002	<0.002	<0.002	
					7	0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
Keats, 1996c										
CAULIFLOWER	12	2	2	7	0	0.011	<0.002	<0.002	<0.002	NR
1995					1	0.008	<0.002	<0.002	<0.002	
AUS 94i47R					3	0.002	<0.002	<0.002	<0.002	
					5	0.003	<0.002	<0.002	<0.002	
					7	0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	24	4	2	7	0	0.012	<0.002	<0.002	0.003	NR
1995					1	0.008	<0.002	<0.002	0.003	
AUS 94i47R					3	0.006	<0.002	<0.002	<0.002	
					5	0.004	<0.002	<0.002	<0.002	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	48	8	2	7	0	0.015	<0.002	<0.002	<0.002	NR
1995					1	0.016	<0.002	0.002	<0.002	
AUS 94i47R					3	0.011	<0.002	<0.002	<0.002	
					5	0.007	<0.002	<0.002	<0.002	
					7	0.003	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	96	16	2	7	0	0.037	<0.002	0.003	<0.002	NR
1995					1	0.029	<0.002	0.005	0.002	
AUS 94i47R					3	0.014	<0.002	<0.002	0.002	
					5	0.008	<0.002	<0.002	0.011	
					7	0.008	<0.002	<0.002	0.003	
					14	0.003	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	12	2	5	7,7,8	0	0.014	<0.002	<0.002	<0.002	NR
1995					1	0.012	<0.002	<0.002	<0.002	
AUS 94i47R					3	0.011	<0.002	<0.002	<0.002	
					5	0.006	<0.002	<0.002	<0.002	
					7	<0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	

CROP Year Reference	Application				PHI, days	Residues, mg/kg				
	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
CAULIFLOWER	24	4	5	7,7,8	0	0.044	0.003	0.01	0.011	NR
1995					1	0.040	0.002	0.009	0.009	
AUS 94i47R					3	0.036	<0.002	0.008	0.008	
					5	0.012	<0.002	<0.002	0.004	
					7	0.004	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	48	8	5	7,7,8	0	0.048	0.003	0.009	0.011	NR
1995					1	0.040	0.002	0.006	0.008	
AUS 94i47R					3	0.032	<0.002	0.005	0.008	
					5	0.012	<0.002	<0.002	0.003	
					7	0.008	≤0.002	≤0.002	≤0.002	
					14	0.003	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	96	16	5	7,7,8	0	0.065	0.004	0.014	0.016	NR
1995					1	0.045	0.003	0.009	0.012	
AUS 94i47R					3	0.042	<0.002	0.009	0.011	
					5	0.009	<0.002	<0.002	<0.002	
					7	0.003	<0.002	<0.002	<0.002	
					14	0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	12	2	9	7,7,8,7,8	0	0.022	<0.002	0.002	0.004	NR
1995				,6,8,6	1	0.015	<0.002	0.002	0.003	
AUS 94i47R					3	0.008	<0.002	<0.002	<0.002	
					5	0.003	<0.002	<0.002	<0.002	
					7	0.002	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	24	4	9	7,7,8,7,8	0	0.037	<0.002	0.01	0.005	NR
1995				,6,8,6	1	0.039	<0.002	0.009	0.005	
AUS 94i47R					3	0.007	<0.002	0.008	<0.002	
					5	0.008	<0.002	<0.002	<0.002	
					7	0.004	<0.002	<0.002	<0.002	
					14	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
CAULIFLOWER	48	8	9	7,7,8,7,8	0	0.081	0.004	0.016	0.015	NR
1995				,6,8,6	1	0.062	0.003	0.011	0.013	
AUS 94i47R					3	0.012	<0.002	<0.002	<0.002	
					5	0.009	<0.002	<0.002	<0.002	
					7	0.005	<0.002	<0.002	<0.002	
					14	0.006	<0.002	<0.002	<0.002	
					21	0.003	<0.002	<0.002	<0.002	
CAULIFLOWER	96	16	9	7,7,8,7,8	0	0.168	0.013	0.033	0.046	NR
1995				,6,8,6	1	0.100	0.006	0.015	0.024	
AUS 94i47R					3	0.012	<0.002	<0.002	0.002	
					5	0.011	<0.002	<0.002	0.002	
					7	0.005	<0.002	<0.002	<0.002	
					14	0.003	<0.002	<0.002	<0.002	
					21	0.003	<0.002	<0.002	<0.002	

NR: not reported owing to analytical problems

Head and leafy cabbages (Table 64). Fipronil was applied as a foliar spray so residues of the degradation product fipronil-desulfinyl were reported.

Table 64. Supervised trials on head and leafy cabbages.

CROP, Country, Year, Reference, Remarks	Application					PHI, days	Residues, mg/kg				
	Form	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
BRUSSELS SPROUTS	SC	50	12.5	5	8,6,8,7	0	0.223	0.004	0.022	0.021	NR
							0.232	0.005	0.024	0.023	
Australia, 1997,						3	0.104	0.004	0.011	0.024	
AK97023 R1 & R2							0.113	0.004	0.013	0.025	
Keats, 1997 j,						5	0.097	0.004	0.013	0.024	
2 replicates							0.099	0.003	0.015	0.025	
						7	0.017	0.003	0.006	0.008	
							0.016	0.002	0.004	0.007	
CABBAGE	SC	50	5	4	9,10,8	0	0.016	<0.002	<0.002	0.004	<0.002

CROP, Country, Year, Reference, Remarks	Application					PHI, days	Residues, mg/kg				
	Form	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1994,							0.014	<0.002	<0.002	0.003	<0.002
93AUS09i South						4	0.005	<0.002	<0.002	0.004	<0.002
Australia R1 & R2							0.005	<0.002	<0.002	0.004	<0.002
Keats, 1996 b,						8	0.004	<0.002	<0.002	<0.002	<0.002
2 replicates							0.004	<0.002	<0.002	<0.002	<0.002
						14	<0.002	<0.002	<0.002	<0.002	<0.002
							<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	SC	100	10	4	9,10,8	0	0.027	<0.002	<0.002	0.005	<0.002
Australia, 1994,							0.026	<0.002	<0.002	0.005	<0.002
93AUS09i South						4	0.011	<0.002	<0.002	0.006	<0.002
Australia R1 & R2,							0.011	<0.002	<0.002	0.007	<0.002
Keats, 1996 b,						8	0.005	<0.002	<0.002	<0.002	<0.002
2 replicates							0.006	<0.002	<0.002	<0.002	<0.002
						14	<0.002	<0.002	<0.002	<0.002	<0.002
							0.002	<0.002	<0.002	<0.002	<0.002
Keats, 1994											
CABBAGE	WG	12.5	3.1	8	4,4,6,13,11,	0	<0.002	<0.002	<0.002	<0.002	<0.002
Australia, 1994,							0.002				
93AUS09i DMG					8,7	1	<0.002	<0.002	<0.002	0.004	<0.002
94007 Trial 1 R1 &										<0.002	
R2						3	<0.002	<0.002	<0.002	<0.002	<0.002
2 replicates						5	<0.002	<0.002	<0.002	<0.002	<0.002
						7	<0.002	<0.002	<0.002	<0.002	<0.002
						14	<0.002	<0.002	<0.002	<0.002	<0.002
						21	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	25	6.1	8	4,4,6,13,11,	0	0.008	<0.002	<0.002	0.004	<0.002
Australia, 1994,							0.008			0.005	<0.002
93AUS09i DMG					8,7	1	0.004	<0.002	<0.002	0.003	<0.002
94007 Trial 1 R1 &							0.005			0.003	<0.002
R2,						3	<0.002	<0.002	<0.002	0.004	<0.002
2 replicates							0.002			0.004	<0.002
						5	<0.002	<0.002	<0.002	0.003	<0.002
evaluated acc. to										0.003	<0.002
New Zealand's						7	<0.002	<0.002	<0.002	<0.002	<0.002
GAP						14	<0.002	<0.002	<0.002	<0.002	<0.002
						21	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	50	12.5	8	4,4,6,13,11,	0	0.011	<0.002	<0.002	0.006	<0.002
Australia, 1994,							0.01	<0.002	<0.002	0.006	<0.002
93AUS09i DMG					8,7	1	0.006	<0.002	<0.002	0.003	<0.002
94007 Trial 1 R1 &							0.006	<0.002	<0.002	0.003	<0.002
R2,						3	0.002	<0.002	<0.002	0.007	<0.002
2 replicates							0.002	0.002	<0.002	0.007	<0.002
						5	0.002	<0.002	<0.002	0.005	<0.002
							0.002	<0.002	<0.002	0.005	<0.002
						7	0.002	<0.002	<0.002	0.003	<0.002
							0.002	<0.002	<0.002	0.003	<0.002
						14	<0.002	<0.002	<0.002	0.002	<0.002
							<0.002	<0.002	<0.002	0.002	<0.002
						21	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	100	25	8	4,4,6,13,11,	0	0.018	<0.002	<0.002	0.006	<0.002
Australia, 1994							0.017	<0.002	<0.002	0.006	<0.002
93AUS09i DMG					8,7	1	0.01	<0.002	<0.002	0.005	<0.002
94007 Trial 1 R1 &							0.01	<0.002	<0.002	0.005	<0.002
R2,						3	0.004	<0.002	<0.002	0.011	<0.002
2 replicates							0.004	<0.002	<0.002	0.011	<0.002
						5	0.004	<0.002	<0.002	0.008	<0.002
							0.004	<0.002	<0.002	0.008	<0.002
						7	0.003	<0.002	<0.002	0.005	<0.002
							0.003	<0.002	<0.002	0.005	<0.002
						14	<0.002	<0.002	<0.002	0.003	<0.002
							<0.002	<0.002	<0.002	0.003	<0.002
						21	<0.002	<0.002	<0.002	<0.002	<0.002
							<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	25	6.1	2	7	0	<0.002	<0.002	<0.002	<0.002	<0.002
Australia, 1994						1	0.003	<0.002	<0.002	<0.002	<0.002
93AUS09i DMG						3	<0.002	<0.002	<0.002	0.003	<0.002
94007 Trial 2						5	<0.002	<0.002	<0.002	<0.002	<0.002
evaluated acc. to						7	<0.002	<0.002	<0.002	<0.002	<0.002
New Zealand's						14	<0.002	<0.002	<0.002	<0.002	<0.002
GAP						21	<0.002	<0.002	<0.002	0.002	<0.002
CABBAGE	WG	50	12.5	2	7	0	0.003	<0.002	<0.002	<0.002	<0.002

CROP, Country, Year, Reference, Remarks	Application					PHI, days	Residues, mg/kg				
	Form	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1994						1	0.005	<0.002	<0.002	0.002	<0.002
93AUS09i DMG						3	<0.002	<0.002	<0.002	<0.002	<0.002
94007 Trial 2						5	0.002	<0.002	<0.002	0.002	<0.002
						7	<0.002	<0.002	<0.002	<0.002	<0.002
						14	<0.002	<0.002	<0.002	0.003	<0.002
						21	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	100	25	2	7	0	0.004	<0.002	<0.002	0.003	<0.002
Australia, 1994						1	0.007	<0.002	<0.002	0.004	<0.002
93AUS09i DMG						3	0.002	<0.002	<0.002	0.003	<0.002
94007 Trial 2						5	0.002	<0.002	<0.002	0.003	<0.002
						7	0.002	<0.002	<0.002	0.003	<0.002
						14	<0.002	<0.002	<0.002	0.002	<0.002
						21	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	25	6.1	2	7	0	0.003	<0.002	<0.002	<0.002	<0.002
Australia, 1994						1	0.003	<0.002	<0.002	<0.002	<0.002
93AUS09i DMG						3	<0.002	<0.002	<0.002	0.002	<0.002
94007 Trial 2, no						5	<0.002	<0.002	<0.002	<0.002	<0.002
sticker, *evaluated acc. to New Zealand's GAP*						7	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	50	12.5	2	7	0	0.003	<0.002	<0.002	0.003	<0.002
Australia, 1994						1	0.004	<0.002	<0.002	<0.002	<0.002
93AUS09i DMG						3	0.002	<0.002	<0.002	0.004	<0.002
94007 Trial 2, no						5	<0.002	<0.002	<0.002	0.002	<0.002
sticker						7	<0.002	<0.002	<0.002	0.002	<0.002
CABBAGE	WG	100	25	2	7	0	0.005	<0.002	<0.002	0.003	<0.002
Australia, 1994						1	0.006	<0.002	<0.002	0.004	<0.002
93AUS09i DMG						3	0.002	<0.002	<0.002	0.003	<0.002
94007 Trial 2, no						5	0.002	<0.002	<0.002	0.002	<0.002
sticker						7	0.002	<0.002	<0.002	0.002	<0.002
CABBAGE	WG	25	6.1	4	11,8,7	0	0.003	<0.002	<0.002	<0.002	<0.002
Australia, 1994						1	0.003	<0.002	<0.002	<0.002	<0.002
93AUS09i DMG						3	<0.002	<0.002	<0.002	0.004	<0.002
94007 Trial 2						5	<0.002	<0.002	<0.002	0.002	<0.002
evaluated acc. to New Zealand's GAP						7	<0.002	<0.002	<0.002	<0.002	<0.002
						14	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	50	12.5	4	11,8,7	0	0.008	<0.002	<0.002	<0.002	<0.002
Australia, 1994						1	0.005	<0.002	<0.002	0.003	<0.002
93AUS09i DMG						3	0.002	<0.002	<0.002	0.005	<0.002
94007 Trial 2						5	<0.002	<0.002	<0.002	0.003	<0.002
						7	<0.002	<0.002	<0.002	0.002	<0.002
						14	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	100	25	4	11,8,7	0	0.012	<0.002	<0.002	0.003	<0.002
Australia, 1994						1	0.007	<0.002	<0.002	0.004	<0.002
93AUS09i DMG						3	0.002	<0.002	<0.002	0.004	<0.002
94007 Trial 2						5	0.002	<0.002	<0.002	0.003	<0.002
						7	0.002	<0.002	<0.002	0.004	<0.002
						14	<0.002	<0.002	<0.002	<0.002	<0.002
CABBAGE	WG	25	6.1	7	4,6,13,11,	0	0.004	<0.002	<0.002	<0.002	<0.002
Australia, 1994		50	12.5		8,7		0.012	<0.002	<0.002	0.002	<0.002
93AUS09i DMG		100	24				0.022	<0.002	<0.002	0.003	<0.002
94007 Trial 2											
Muller, 1994a											
Brassica Juncea	SC	25	5, 3.1	2	7	1	0.091	<0.005	0.022	0.092	<0.005
(Leafy brassica)						3	0.020	<0.005	0.011	0.033	<0.005
Malaysia, 1993						5	<0.005	<0.005	<0.005	0.016	<0.005
93-712 Trial 1						7	0.008	<0.005	0.005	0.033	<0.005
						10	<0.005	<0.005	<0.005	0.005	<0.005
Brassica Juncea	SC	50	10,	2	7	1	0.19	<0.005	0.048	0.23	<0.005
(Leafy brassica)			6.2			3	0.037	<0.005	0.018	0.090	<0.005
Malaysia, 1993						5	0.009	<0.005	0.007	0.035	<0.005
93-712 Trial 1						7	<0.005	<0.005	<0.005	0.036	<0.005
						10	<0.005	<0.005	<0.005	0.019	<0.005
Brassica Juncea	SC	25	4.5,	2	7	1	0.025	<0.005	0.005	0.016	<0.005
(Leafy brassica)			3,6			2	0.012	<0.005	<0.005	0.019	<0.005
Malaysia, 1993						4	<0.005	<0.005	<0.005	0.009	<0.005
93-712 Trial 2											
Brassica Juncea	SC	50	9.1,	2	7	1	0.042	<0.005	0.008	0.033	<0.005
(Leafy brassica)			7.1			2	0.033	<0.005	0.01	0.041	<0.005
Malaysia, 1993						4	0.007	<0.005	0.006	0.020	<0.005

CROP, Country, Year, Reference, Remarks	Application					PHI, days	Residues, mg/kg				
	Form	g ai/ha	g ai/hl	No.	Interval, days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
93-712 Trial 2											
Keats, 1997l											
CABBAGE New Zealand, 1997 97NZL03	SC	24		4	10,10,11	0 1 3 7 14	0.082 0.041 0.018 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002	0.003 0.002 0.002 <0.002 <0.002	0.003 0.003 0.003 <0.002 <0.002	NR
CABBAGE New Zealand, 1997 97NZL03 *evaluated acc. to Australian GAP*	SC	48		4	10,10,11	0 1 3 7 14	0.192 0.083 0.045 0.014 0.004	0.002 <0.002 <0.002 <0.002 <0.002	0.01 0.005 0.004 0.002 <0.002	0.007 0.008 0.012 0.005 0.002	NR

NR: not reported owing to analytical problems
NA: not analysed

Potatoes (Table 65). Both soil and foliar pests can be controlled with fipronil. In some trials where fipronil was applied as a seed treatment, a broadcast incorporated soil spray or as granules applied in furrow, only the residues of fipronil, RPA 200766, MB 45950 and MB 46136 are reported here. Trials with foliar applications, except in Spain, also include fipronil-desulfinyl.

Table 65. Residues from supervised trials on potatoes.

Country, Year, Reference, Remarks	Application			PHI, days	Residues, mg/kg				
	Form.	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Foliar (Orosz, 1995)									
Hungary, 1995 95-RHOP-AB-14-001	WG	20	1	1 3 7 10 14	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	0.01 <0.01 0.01 <0.01 <0.01
Hungary, 1995 95-RHOP-AB-14-001	WG	20	2	1 3 7 10 14	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	0.01 <0.01 <0.01 <0.01 <0.01
Foliar (Maestracci, 1998g)									
Germany, 1997 97746de1 Lower Saxony *evaluated acc. to Romanian GAP*	WG	20*	3	27	<0.002	<0.002	<0.002	<0.002	<0.002
Germany, 1997 97746de1 Lower Saxony *evaluated acc. to Polish GAP*	WG	20*	4	14 21	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002
Germany, 1997 97746DE2 Rheinland-Pfalz *evaluated acc. to Romanian GAP*	WG	20*	3	31	<0.002	<0.002	<0.002	<0.002	<0.002
Germany, 1997 97746DE2 Rheinland-Pfalz *evaluated acc. to Polish GAP*	WG	20*	4	14 21	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002
Germany, 1997 97746DE3, North Rhine Westphalia *evaluated acc. to Romanian GAP*	WG	20*	3	20	<0.002	<0.002	<0.002	<0.002	<0.002
Germany, 1997 97746DE3, North Rhine Westphalia *evaluated acc. to Polish GAP*	WG	20*	4	14 21	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002
Germany, 1997 97746DE4 Bavaria *evaluated acc. to Romanian GAP*	WG	20*	3	27	<0.002	<0.002	<0.002	<0.002	<0.002

Country, Year, Reference, Remarks	Application			PHI, days	Residues, mg/kg				
	Form.	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Germany, 1997 97746DE4 Bavaria *evaluated acc. to Polish GAP*	WG	20*	4	14 21	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002
Foliar (Yslan and Baudet, 1999d)									
Germany, 1998 98670DE1 Lower Saxony *evaluated acc. to Romanian GAP*	WG	20*	3	21	≤0.002	≤0.002	≤0.002	≤0.002	NR
Germany, 1998 98670DE1 Lower Saxony *evaluated acc. to Polish GAP*	WG	20*	4	14 21	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	NR
Germany, 1998 98670DE2 North Rhine Westphalia *evaluated acc. to Polish GAP*	WG	20*	3	15	≤0.002	≤0.002	≤0.002	≤0.002	NR
Germany, 1998 98670DE2 North Rhine Westphalia *evaluated acc. to Polish GAP*	WG	20*	4	14 21	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	NR
Germany, 1998 98670DE3 Rhine Palinate *evaluated acc. to Polish GAP*	WG	20*	3	20	≤0.002	≤0.002	≤0.002	≤0.002	NR
Germany, 1998 98670DE3 Rhine Palinate	WG	20*	4	14 21	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	NR
Germany, 1998 98670DE4 Hesse *evaluated acc. to Polish GAP*	WG	20*	3	21	≤0.002	≤0.002	≤0.002	≤0.002	NR
Germany, 1998 98670DE4 Hesse *evaluated acc. to Polish GAP*	WG	20*	4	14 21	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	NR
Foliar									
Poland, 1994/95 95794PL1 Bonin (after flowering) Muller, 1996d	WG	20	1	14	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
Poland, 1994/95 95794PL2 Bonin (after planting) Muller, 1996d	WG	20	1	14	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
Poland, 1994/95 95794PL3 Poznan (after flowering) Muller, 1996d *evaluated acc. to Romanian GAP*	WG	20	1	28	≤0.002	≤0.002	≤0.002	≤0.002	<0.002
Spain, 1994 94666SE1 Madrid Muller, 1996b, 2 replicates	WG	24	3	0 3 7 14 21	<0.002 <0.002 <0.002 ≤0.002 <0.002	<0.002 <0.002 <0.002 ≤0.002 <0.002	<0.002 <0.002 <0.002 ≤0.002 <0.002	NR	<0.002 <0.002 <0.002 <0.002 <0.002
Spain, 1994 94666SE2 Seville Muller, 1996 b, 2 replicates	WG	24	2	0 3 7 14 21 	0.002 0.004 0.002 0.002 0.002 0.003 <0.002 0.003 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002 < 0.002 <0.002 ≤0.002 <0.002 <0.002	<0.002 <0.002 <0.002 0.004 <0.002 <0.002 <0.002 0.002 <0.002 <0.002	NR	<0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002
Spain, 1994 94666SE3 Valencia Muller, 1996 b, 2 replicates	WG	24	2	15	≤0.002	≤0.002	≤0.002	NR	<0.002
Spain, 1994 94666SE4 Avila Muller, 1996b, 2 replicates	WG	24	2	15	≤0.002	≤0.002	≤0.002	NR	<0.002
Spain, 1995 95715SE1 Madrid Richard and Muller, 1996a, 2 replicates	WG	24	3	0 3 7 14 21	<0.002 <0.002 <0.002 ≤0.002 <0.002	<0.002 <0.002 <0.002 ≤0.002 <0.002	<0.002 <0.002 <0.002 ≤0.002 <0.002	<0.002 <0.002 <0.002 ≤0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002

Country, Year, Reference, Remarks	Application			PHI, days	Residues, mg/kg				
	Form.	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Spain, 1995 95715SE2 Valencia Richard and Muller, 1996a, 2 replicates	WG	24	3	0 3 7 14	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002
Spain, 1995 95762SE1 Avila Richard and Muller, 1996b, 2 replicates	WG	24	2	16	<0.002	<0.002	<0.002	<0.002	<0.002
Spain, 1995 95762SE2 Seville Richard and Muller, 1996b, 2 replicates	WG	24	2	14	<0.002	<0.002	<0.002	<0.002	<0.002
Soil, granules applied in furrow at planting									
Greece, 1993 R93702XX1 Richard and Muller, 1994d, 2 replicates	GR	200 400	1	96	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR	<0.002 <0.002
Greece, 1994 94673GR1 Richard and Muller, 1995b, 2 replicates	GR	200 400	1	113	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR	<0.002 <0.002
Italy, 1993 R93636BO1 Bologna Richard and Muller, 1994j, 2 replicates	GR	150 300	1	118	0.017 0.005 0.008 0.009	0.002 <0.002 0.002 <0.002	0.009 0.003 0.004 0.004	NR	0.007 0.002 0.003 0.003
Italy, 1993 Corticelle, Bologna R93641BO1 Richard and Muller, 1994i, 2 replicates	GR	105 210	1	118	0.003 0.003 0.007 0.008	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 0.002 0.002	NR	<0.002 <0.002 <0.002 <0.002
Italy, 1995 95739BO1 Corticella Muller, 1996h, 2 replicates	GR	143	1	123	<0.002	<0.002	<0.002	<0.002	<0.002
Italy, 1995 95739BO2 Minerbio Muller, 1996h, 2 replicates	GR	176	1	129	<0.002	<0.002	<0.002	<0.002	<0.002
Italy, 1995 95746BO1 Corticella Muller,1996f, 2 replicates	GR	102 163	1	123	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002
Italy, 1995 95746BO2 Minerbio Muller, 1996f, 2 replicates	GR	162	1	129	0.003 0.005	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 0.002
Italy, 1996 96705BO1 Bologna Maestracci, 1997d, 2 replicates	GR	111 141	1	90	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002

*Target rate; achieved rate per application in some cases varied by ±5% (1 g ai/ha).
NR: not reported

Table 66. Supervised trials on sugar beet roots (most trials include duplicate plots).

Country, Year, Reference	Application			PHI days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Soil treatment at sowing (Claviere and Muller, 1990, 1991)									
France, 1990 Rachecourt, France (52) XE190I11	GR	100 200 300	1	148	<0.01 <0.01 0.16 <0.01 0.011	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 0.015 0.011 0.018	NR	<0.01 <0.01 <0.01 <0.01 <0.01
France, 1990 Allogny, France (45) XB290I11	GR	100 200 300	1	179	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	NR	<0.01 <0.01 <0.01 <0.01 <0.01

Country, Year, Reference	Application			PHI days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
					<0.01	<0.01	<0.01		<0.01
France, 1990	GR	100	1	181	<0.01	<0.01	<0.01	NR	<0.01
Beaulieu, France					<0.01	<0.01	<0.01		<0.01
(45)		200			≤0.01	≤0.01	≤0.01		<0.01
XB190I11					<0.01	<0.01	<0.01		<0.01
		300			<0.01	<0.01	<0.01		<0.01
					<0.01	<0.01	<0.01		<0.01
France, 1990	GR	100	1	168	0.015	<0.01	<0.01	NR	<0.01
Le Meillard, France					0.016	<0.01	<0.01		<0.01
(80)		200			<0.01	<0.01	<0.01		<0.01
XD290I11					0.014	≤0.01	≤0.01		<0.01
		300			0.012	<0.01	<0.01		<0.01
					0.032	<0.01	0.011		<0.01
France, 1990	GR	100	1	167	<0.01	<0.01	<0.01	NR	<0.01
Allas, France (17)					<0.01	<0.01	<0.01		<0.01
FRX90I11		200			≤0.01	≤0.01	≤0.01		<0.01
					<0.01	<0.01	<0.01		<0.01
		300			<0.01	<0.01	<0.01		<0.01
					<0.01	<0.01	<0.01		<0.01
France, 1990	GR	100	1	176	<0.01	<0.01	NR	NR	NR
Mericourt, France					0.017	<0.01	NR		NR
(80)		200[1]			<0.05	<0.01	NR		NR
XD190I11					<0.05	<0.01	NR		NR
		300			0.043	<0.01	NR		NR
					0.028	<0.01	NR		NR
France, 1990	GR	300	1	144	0.016	<0.01	<0.01	NR	<0.01
Mezerolles, France									
(80) XD190I12									
Claviere and Muller, 1991									
Soil treatment at sowing (Dupont and Muller, 1992)									
France, 1991	GR	150	1	178	≤0.01	≤0.01	≤0.01	NR	<0.01
Faverolles, France					NR	<0.01	<0.01		<0.01
(51) LE291I15		200			≤0.01	≤0.01	≤0.01		<0.01
					<0.01	<0.01	<0.01		<0.01
France, 1991	GR	150	1	181	<0.01	<0.01	<0.01	NR	<0.01
Guignonville,					0.018	≤0.01	≤0.01		<0.01
France (45)		200			0.018	≤0.01	≤0.01		<0.01
LB391I15					<0.01	<0.01	<0.01		<0.01
France, 1991	GR	150	1	161	≤0.01	≤0.01	≤0.01	NR	<0.01
Autruche, France					<0.01	<0.01	<0.01		<0.01
(51) LE191I15		200			≤0.01	≤0.01	≤0.01		<0.01
					<0.01	<0.01	<0.01		<0.01
France, 1991	GR	150	1	198	<0.01	<0.01	<0.01	NR	<0.01
Bellegarde, France					0.011	≤0.01	≤0.01		<0.01
(45) LB191I15		200			≤0.01	≤0.01	≤0.01		<0.01
					<0.01	<0.01	<0.01		<0.01
France, 1991	GR	150	1	213	≤0.01	≤0.01	≤0.01	NR	<0.01
Meranville, France					<0.01	<0.01	<0.01		<0.01
(45) LB491I15		200			<0.01	<0.01	<0.01		<0.01
					0.072	≤0.01	≤0.01		<0.01
Soil treatment at sowing (Muller, 1994j)									
France, 1993	GR	305	1	193	<0.002	<0.002	<0.002	NR	<0.002
R93568B1					<0.002	<0.002	<0.002		<0.002
Gidy (45)									
France, 1993	GR	243	1	196	0.006	<0.002	0.007	NR	<0.002

Country, Year, Reference	Application			PHI days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
R93568B2 Patay (45)		 334			0.013 0.005 0.006	<0.002 <0.002 <0.002	0.011 0.006 0.005		0.002 <0.002 <0.002
France, 1993 R93568D1 Frohen le Grand (80)	GR	179 251	1	181	0.003 <0.002 <0.002 <0.002	≤0.002 <0.002 <0.002 <0.002	0.002 <0.002 0.002 0.002	NR	<0.002 <0.002 <0.002 <0.002
France, 1993 R93568D2 Frohen le Grand (80)	GR	188[2] 281	1	190	0.009 0.002 <0.002	≤0.002 <0.002 <0.002	0.005 <0.002 <0.002	NR	<0.002 <0.002 <0.002
France, 1993 R93568D3 Frohen le Grand (80)	GR	174[2] 211	1	175	0.013 0.002 0.002 <0.002 0.003	≤0.002 <0.002 <0.002 <0.002 ≤0.002	0.005 0.004 0.004 <0.002 0.005	NR	<0.002 <0.002 <0.002 <0.002 <0.002
France, 1993 R93568E1 Bazancourt (51)	GR	159 253	1	166	0.007 0.005 0.017 0.024	≤0.002 <0.002 <0.002 <0.002	0.004 0.003 0.007 0.008	NR	<0.002 <0.002 <0.002 <0.002
Soil treatment at sowing (Muller, 1995e)									
France, 1994 945520R1 Patay (45)	GR	161 245	1	189	0.002 0.003 0.004 <0.002	<0.002 ≤0.002 <0.002 <0.002	0.004 0.004 0.008 0.003	NR	<0.002 <0.002 0.002 <0.002
France, 1994 94552AM1 Barly (80)	GR	161 240	1	153	0.002 0.003 0.004 <0.002	0.002 ≤0.002 <0.002 <0.002	0.003 0.006 0.003 <0.002	NR	<0.002 <0.002 <0.002 <0.002
France, 1994 94552RS1 Muizon(51)	GR	161 244	1	174	0.003 0.002 0.003 0.003	≤0.002 <0.002 <0.002 <0.002	0.005 0.004 0.005 0.003	NR	<0.002 <0.002 <0.002 <0.002
Soil treatment before sowing (Maestracci, 1998b)									
France, 1997 97521AM1 Barly (80)	WG	200	1	168	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	<0.002 <0.002
France, 1997 97521DJ1 Neuilly les Dijon (21)	WG	210	1	188	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	<0.002 <0.002
France, 1997 97521OR1 Merevile (91)	WG	200	1	181	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	<0.002 <0.002
France, 1997 97521RS1 Reims (51)	WG	200	1	186	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	<0.002 <0.002
Foliar treatment (Lantos, 1997a)									
Hungary, 1996 RP AB 15003	WG	24	1	30	≤0.01 <0.01 <0.01	≤0.01 <0.01 <0.01	≤0.01 <0.01 <0.01	≤0.01 <0.01 <0.01	<0.01 <0.01 <0.01
Soil treatment at sowing (Richard and Muller, 1994b)									
Italy, 1993 93640BO1 CNS Bologna	GR	105 210	1	169	0.003 <0.002 0.005 <0.002	<0.002 <0.002 ≤0.002 <0.002	0.002 0.003 0.005 <0.002	NR	<0.002 <0.002 <0.002 <0.002
Italy, 1993 93630BO1 CNS Bologna	GR	150 300	1	169	0.003 <0.002 0.002	≤0.002 <0.002 <0.002	0.004 <0.002 0.003	NR	<0.002 <0.002 <0.002

Country, Year, Reference	Application			PHI days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
					0.003	<0.002	0.006		<0.002
Soil treatment in furrow at sowing (Muller, 1996e)									
Italy, 1995 95742BO1 CNS Corticella (BO)	GR	124	1	140	0.002	<0.002	0.003	<0.002	<0.002
					0.004	<0.002	0.004	<0.002	<0.002
		166			≤0.002	≤0.002	≤0.002	<0.002	<0.002
					<0.002	<0.002	<0.02	<0.002	<0.002
Italy, 1995 95742BO2 Minerbio (BO)	GR	103	1	136	0.002	<0.002	0.002	<0.002	<0.002
					0.002	<0.002	0.002	<0.002	<0.002
		146			<0.002	<0.002	<0.002	<0.002	<0.002
					0.002	≤0.002	0.003	<0.002	<0.002
Soil treatment (Muller, 1996l)									
Italy, 1995 95741BO1 CNS Corticella (BO)	GR	90	1	140	<0.002	<0.002	<0.002	<0.002	<0.002
					<0.002	<0.002	<0.002	<0.002	<0.002
		141			≤0.002	≤0.002	≤0.002	<0.002	<0.002
					<0.002	<0.002	<0.002	<0.002	<0.002
Italy, 1995 95741BO2 Minerbio (BO)	GR	106	1	136	0.002	<0.002	0.002	<0.002	<0.002
					0.003	<0.002	0.004	<0.002	<0.002
		140			0.004	<0.002	<0.002	<0.002	<0.002
					0.005	≤0.002	≤0.002	<0.002	<0.002
Soil treatment (Yslan and Baudet, 1999c)									
Spain, 1998 98589M1 Sta. Olalla Toledo	WG	197	1	198	≤0.002	≤0.002	≤0.002	<0.002	NR
					<0.002	<0.002	<0.002	<0.002	

NR: not reported
[1]LOQ increased to 0.05 mg/kg owing to interference; not included in evaluation
[2]only one plot

Cereal grains (barley, maize, rice, sorghum, wheat, Tables 67-71). Soil and foliar pests can be controlled with fipronil. In terrestrial trials where fipronil has been applied as a seed treatment, as granules in furrow or as an incorporated soil spray, only the residues of fipronil, RPA 200766, MB 45950 and MB 46136 have generally been reported. Trials with foliar and aquatic applications (flooded rice paddy) also include fipronil-desulfinyl.

Barley (Table 67). Residue trials in France were 2-3 times overdosed but show a 'nil residue situation' in the grain.

Table 67. Supervised trials on barley grain (seed treatment) in France, 1993-94.

Reference	Application			PHI, days	Residues, mg/kg				
	Form	g ai/t	No.		Fipronil	MB 45950	MB 46136	Fipronil-desulfinyl	RPA 200766
Muller, 1995a									
94501OR1	FS	1500	1	260	≤0.002	≤0.002	≤0.002	NR	<0.002
94501AM1	FS	1500	1	271	≤0.002	≤0.002	≤0.002	NR	<0.002
94501RS1	FS	1500	1	260	≤0.002	≤0.002	≤0.002	NR	<0.002
94501DJ1	FS	1500	1	250	≤0.002	≤0.002	≤0.002	NR	<0.002
94501LY1	FS	1500	1	249	≤0.002	≤0.002	≤0.002	NR	<0.002
Muller, 1995c									
94502OR1	FS	1000	1	260	≤0.002	≤0.002	≤0.002	NR	<0.002

NR: not reported

Maize (Table 68). The supervised trials on maize included applications by seed treatment, incorporated granules in furrow at sowing, incorporated soil spray in furrow at sowing, pre-sowing

incorporated broadcast soil spray, and foliar spray. Each trial was with duplicate plots, the US trials with two or three plots.

Table 68. Supervised trials on maize. Residues in grain.

Country, Year, Reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Seed treatment (Muller, 1994c)										
France, 1993, R93562H1	FS	2500			161	≤0.002	≤0.002	≤0.002	NR	<0.002
Seed treatment (Muller, 1994f)										
France, 1993, R93565A1	FS	3750			151	≤0.002	≤0.002	≤0.002	NR	<0.002
France, 1993, R93565B1	FS	3750			165	≤0.002	≤0.002	≤0.002	NR	<0.002
France, 1993, R93565G1	FS	3750			182	≤0.002	≤0.002	≤0.002	NR	<0.002
France, 1993, R93565H1	FS	3750			152	≤0.002	≤0.002	≤0.002	NR	<0.002
France, 1993, R93565H2	FS	3750			154	≤0.002	≤0.002	≤0.002	NR	<0.002
France, 1993, R93565K1	FS	3750			154	≤0.002	≤0.002	≤0.002	NR	<0.002
Soil treatment incorporated granules in furrow (Muller, 1996i)										
France, 1995, 95535BX1	GR		298		150	<0.002	<0.002	<0.002	<0.002	<0.002
France, 1995, 95535AM1	GR		177		147	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Soil treatment pre-sowing, 2 replicates (Maestracci, 1998d)										
France, 1997, 97540AM1	WG		200	66.7	180*	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97540OR1	WG		200	60.6	174*	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97540RS1	WG		200	84.7	169*	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97540RS2 **replicate 1**	WG		200	100	156*	<0.002[3]	<0.002[3]	<0.002[3]	<0.002[3]	<0.002[3]
France, 1997, 97540RS2 **replicate 2**	WG		200	100	156*	0.004[3]	≤0.002[3]	≤0.003[3]	<0.002[3]	0.008[3]
France, 1997, 97540BX1 **replicate 1**	WG		200	60.6	159*	<0.002[3]	<0.002[3]	<0.002[3]	<0.002[3]	<0.002[3]
France, 1997, 97540BX1 **replicate 2**	WG		200	60.6	159*	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97540BX2	WG		200	60.6	159*	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97540TL1 **replicate 1**	WG		200	60.6	154*	≤0.002[3]	≤0.002[3]	≤0.002[3]	<0.002[3]	<0.002[3]
France, 1997, 97540TL1 **replicate 2**	WG		200	60.6	154*	<0.002[3]	<0.002[3]	<0.002[3]	<0.002[3]	<0.002[3]
France, 1997, 97540TL2	WG		200	60.6	159*	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Seed treatment (Muller, 1994d)										
France, 1993, R933563A1 (maize, sweet)	FS	2500			109	≤0.002 (ear)	≤0.002 (ear)	≤0.002 (ear)	NR	<0.002 (ear)
Soil treatment at sowing (Richard and Muller, 1994k)										
France, 1993, 93735 Sevignacq (maize, sweet)	GR		200		99	≤0.002 (ear)	≤0.002 (ear)	≤0.002 (ear)	NR	<0.002 (ear)
Soil treatment at sowing (Muller, 1995d)										
Greece, 1994, 94672GR2	GR		200		99	≤0.002	≤0.002	≤0.002	NR	<0.002
Greece, 1994, 94672GR2	GR		400		99	<0.002	<0.002	<0.002	NR	<0.002
Foliar spray (Lantos, 1997b)										
Hungary, 1997, RP AB 15 004	WG		24	6	30	≤0.01	≤0.006	≤0.01	≤0.005	<0.014
Soil treatment at sowing (Richard and Muller, 1994g)										
Italy, 1993, R93633BO1	GR		240		143	<0.002	<0.002	<0.002	NR	<0.002
Soil treatment at sowing, 2 replicates (Muller, 1996c)										
Italy, 1995, 95744BO1	GR		112		174	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Italy, 1995, 95744BO2	GR		153		161	0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	<0.002 <0.002
Seed treatment (Richard and Muller, 1995d)										
Spain, 1994, 94665SE1	FS	2500			174	≤0.002	≤0.002	≤0.002	NR	<0.002
Seed treatment (Maestracci, 1996b)										
Spain, 1995, 95712SE1	FS	2500			155	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Spain, 1995, 95712SE2	FS	2500			153	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Soil treatment pre-sowing (Yslan and Baudet, 1999b)										
Spain, 1998, 98588SE1	WG		195.2	42.4	163*	≤0.002	≤0.002	≤0.002	<0.002	NR
Spain, 1998, 98588SE2	WG		176.6	40.8	147*	≤0.002	≤0.002	≤0.002	<0.002	NR
Soil treatment at sowing, 3 replicates (Kowite, 1993a)										
USA, 1992[1], 92-015 INC	GR		146		146	≤0.002	≤0.002	≤0.003	<0.002	<0.003

Country, Year, Reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1992[1], 92-015 T-band	GR		146		146	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-016	GR		146		157	<0.002 <0.002 ≤0.002	<0.002 <0.002 ≤0.002	<0.003 <0.003 ≤0.003	<0.002 <0.002 <0.01	<0.003 <0.003 <0.003
USA, 1992[1], 92-019 INC	GR		146		191	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-019 T-band	GR		146		191	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-029	GR		157		153	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-039	GR		135		156	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-058 INC	GR		157		159	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-058 T-band	GR		157		159	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-076	GR		135		151	<0.002 ≤0.01 <0.002	<0.002 ≤0.002 <0.002	<0.003 ≤0.003 <0.003	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003
USA, 1992[1], 92-094	GR		146		173	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-097	GR		146		162	≤0.002	≤0.002	≤0.003	<0.002	<0.003
USA, 1992[1], 92-097 T-band	GR		146		169	≤0.002	≤0.002	≤0.003	<0.002	<0.003
Soil treatment at sowing, 3 replicates (Kowite, 1994)										
USA, 1993[1], 93-206 T-band	GR		146		148	≤0.002	≤0.002	≤0.003	NR	<0.003
USA, 1993[1], 93-206 INC	GR		146		148	≤0.002	≤0.002	≤0.003	NR	<0.003
USA, 1993[1], 93-207	GR		146		140	≤0.002	≤0.002	≤0.003	NR	<0.003
USA, 1993[1], 93-208	GR		146		125	<0.002 <0.002 ≤0.01	<0.01 <0.002 ≤0.01	<0.003 <0.003 ≤0.003	NR	<0.003 <0.003 <0.003
USA, 1993[1], 93-209	GR		146		168	≤0.002	≤0.002	≤0.003	NR	<0.003
USA, 1993[1], 93-210	GR		146		128	<0.002 <0.002 ≤0.002	<0.002 <0.002 ≤0.002	<0.003 <0.003 ≤0.01	NR	<0.003 <0.003 <0.003
USA, 1993[1], 93-211	GR		146		124	<0.002 <0.002 ≤0.002	<0.002 <0.002 ≤0.002	<0.003 <0.003 ≤0.003	NR	<0.003 <0.01 <0.01
USA, 1993[1], 93-212 T-band	GR		146		171	≤0.002	≤0.002	≤0.003	NR	<0.003
USA, 1993[1], 93-212 INC	GR		146		171	≤0.002	≤0.002	≤0.003	NR	<0.003
USA, 1993[1], 93-213 T-band	GR		146		171	<0.002 <0.002 ≤0.002	<0.002 <0.002 ≤0.002	<0.003 <0.003 ≤0.003	NR	<0.003 <0.01 <0.01
USA, 1993[1], 93-213 INC	GR		146		171	≤0.002 <0.002 <0.002	≤0.002 <0.002 <0.002	≤0.003 <0.003 <0.003	NR	<0.01 <0.003 <0.003
USA, 1993[1], 93-214 T-band	GR		146		131	≤0.002 <0.002 <0.002	≤0.002 <0.002 <0.002	≤0.003 <0.003 <0.003	NR	<0.003 <0.003 <0.01
USA, 1993[1], 93-214 INC	GR		146		131	<0.002 <0.002 ≤0.002	<0.002 <0.002 ≤0.002	<0.003 <0.003 ≤0.01	NR	<0.01 <0.01 <0.01
USA, 1993[1], 93-215 T-band	GR		146		140	≤0.002	≤0.002	≤0.003	NR	<0.003
USA, 1993[1], 93-215 INC	GR		146		140	≤0.002	≤0.002	≤0.003	NR	<0.003
Soil treatment at sowing, 2 replicates (Kowite, 1996)										
USA, 1995[1], 95-0212 GR INC	GR		146		126	≤0.01 <0.004	≤0.01 <0.01	≤0.003 <0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0212 SS INC	WG		146		126	≤0.004 <0.004	≤0.01 <0.004	≤0.003 <0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0213 GR INC	GR		146		148	<0.004	<0.01[2]	<0.003	NR	<0.002
USA, 1995[1], 95-0213 SS INC	WG		146		148	<0.004	<0.01[2]	<0.003	NR	<0.002
USA, 1995[1], 95-0214 GR INC	GR		146		153	≤0.004 <0.004	≤0.01 <0.004	≤0.003 <0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0214 SS INC	WG		146		153	≤0.004	≤0.004	≤0.003	NR	<0.002

Country, Year, Reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1995[1], 95-0215 GR INC	GR		146		159	≤0.01 <0.004	≤0.01 <0.004	≤0.01 0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0215 SS INC	WG		146		159	≤0.004	≤0.004	≤0.003	NR	<0.002
USA, 1995[1], 95-0216 GR INC	GR		146		136	≤0.004	≤0.004	≤0.003	NR	<0.002
USA, 1995[1], 95-0216 SS INC	WG		146		136	≤0.004	≤0.004	≤0.003	NR	<0.002
USA, 1995[1], 95-0217 GR INC	GR		146		122	≤0.004	≤0.01	≤0.003	NR	<0.002
USA, 1995[1], 95-0217 SS INC	WG		146		122	≤0.004	≤0.01	≤0.003	NR	<0.002
USA, 1995[1], 95-0218 GR INC	GR		146		122	<0.004	<0.01[2]	<0.003	NR	<0.002
USA, 1995[1], 95-0218 SS INC	WG		146		122	<0.004	<0.01[2]	<0.003	NR	<0.002
USA, 1995[1], 95-0219 GR INC	GR		146		116	<0.004	<0.01[2]	<0.003	NR	<0.002
USA, 1995[1], 95-0219 SS INC	WG		146		116	<0.004	<0.01[2]	<0.003	NR	<0.002
USA, 1995[1], 95-0220 GR INC	GR		146		143	≤0.004 <0.004	≤0.01 <0.004	≤0.003 <0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0220 SS INC	WG		146		143	≤0.004 <0.004	≤0.01 <0.004	≤0.003 <0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0221 GR INC	GR		146		160	≤0.004	≤0.004	≤0.003	NR	<0.002
USA, 1995[1], 95-0221 SS INC	WG		146		160	≤0.004	≤0.004	≤0.003	NR	<0.002
USA, 1995[1], 95-0222 GR INC	GR		146		150	≤0.004 <0.004	≤0.01 <0.004	≤0.003 <0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0222 SS INC	WG		146		150	≤0.004	≤0.004	≤0.003	NR	<0.002
USA, 1995[1], 95-0223 GR INC	GR		146		125	≤0.004 <0.004	≤0.01 <0.004	≤0.003 <0.003	NR	<0.002 <0.002
USA, 1995[1], 95-0223 SS INC	WG		146		125	≤0.004	≤0.004	≤0.003	NR	<0.002

*days between sowing and harvest, not between soil spray and harvest
NR: not reported
AP: analytical problem
[1] LOQ for each compound 0.01 mg/kg (lowest fortification level). Residues reported as ND (not detected) in the original report are shown as <0.00x (i.e. <MLD)
[2] Contamination of control reported
[3] Result confirmed by GC-MS-MS

Rice (Table 69). The results of supervised trials after seed treatment, granules broadcast into the flooded paddy, granules in nursery boxes, pre-plant incorporated broadcast soil spray, and foliar applications were reported. Although many of the registered labels for liquid formulations either show no PHI restriction or indicate PHIs of a week or so (generally applicable to all crops and not specific to rice), fipronil's pest spectrum and insect pest timing needs to be taken into account to understand what a normal PHI would be for rice. Except in Indonesia where the stink bug, a late-season pest, is present, PHIs of 28 days or more are common practice. In many countries, one application of fipronil per crop is made early, in which case PHIs are longer than 40 days.

Table 69. Residues in rice grain.

Commodity, Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Seed box treatment, 2 replicates (Anon., 1994)											
Unpolished rice, Japan, 1993, I.E.T. Official residue trial, Ushuku	GR		0.5 g ai/box		1	132	≤0.001	≤0.001	≤0.001	<0.001	0.003

Commodity, Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Unpolished rice, Japan, 1993, I.E.T. Official residue trial, Shiga	GR		0.5 g ai/box		1	141	≤0.001	≤0.001	≤0.001	<0.001	<0.001
Seed box treatment, 2 replicates (Anon., 1995a)											
Rice, brown, Japan, 1995, Nihon Noyaku	GR		0.5 g ai/box		1	123	≤0.001	≤0.001	≤0.001	<0.001	0.003
Seed box treatment, 2 replicates (Anon., 1995b)											
Rice, brown, Japan, 1995, Nissan Fukui	GR		0.5 g ai/box		1	140	≤0.001	≤0.001	≤0.001	<0.001	<0.001
Rice, brown, Japan, 1995, Nissan Mie	GR		0.5 g ai/box		1	118	≤0.001	≤0.001	≤0.001	<0.001	<0.001
Seed treatment, 2 replicates (Keats, 1996e)											
Australia, 1996, AK96059	FS		25 50 100		1	167	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	NR
Seed treatment, 2 replicates (Keats, 1996h)											
Australia, 1996, AK96060	FS		25 50 100		1	215	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	NR
Seed treatment, 2 replicates (Keats, 1996i)											
Australia, 1996, AK96061	FS		12.5 25 50		1	144	≤0.002 <0.002 <0.002	≤0.002 <0.002 <0.002	≤0.002 <0.002 <0.002	<0.002 <0.002 <0.002	NR
Seed treatment (Yslan and Baudet, 1999a)											
Spain, 1998, 98639TR1	FS	263	52.6		1	133	<0.002	<0.002	<0.002	<0.002	NR
Seed treatment (Maestracci, 1997c)											
France, 1996, 96561AV1	FS	130			1	119 143	<0.002 ≤0.002	<0.002 ≤0.002	<0.002 ≤0.002	<0.002 <0.002	<0.002 <0.002
Seed treatment (Maestracci, 1998e)											
France, 1997, 97545AV1 variety Thaibonnet	FS	130			1	127[2] 149	<0.002 ≤0.002	<0.002 ≤0.002	<0.002 ≤0.002	<0.002 <0.002	<0.002 <0.002
France, 1997, 97545AV2 variety Ariete	FS	130			1	127[2] 149	<0.002 ≤0.002	<0.002 ≤0.002	<0.002 ≤0.002	<0.002 <0.002	<0.002 <0.002
Seed treatment (Maestracci, 1998f)											
France, 1997, 97546AV1 variety Ariete	FS	130			1	133	≤0.002	≤0.002	≤0.002	<0.002	NR
France, 1997, 97546AV2 variety Thaibonnet	FS	130			1	133	≤0.002	≤0.002	≤0.002	<0.002	NR
Seed treatment, 2 replicates (Keats, 1996m)											
Thailand, 1996, 95THA01i	FS		50		1	116	0.003 0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
Thailand, 1996, 95THA01i	FS		100		1	116	<0.002 0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
Seed treatment, 2 replicates (Mede, 1996b)											
USA, 1995[1], 95-0248AR	FS		56		1	119	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0249AR	FS		56		1	134	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0250CA	FS		56		1	139	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0251CA	FS		56		1	139	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0252LA	FS		56		1	107	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0253LA	FS		56		1	112	<0.003 ≤0.01	<0.003 ≤0.003	<0.003 ≤0.003	<0.003 <0.003	<0.003 <0.003
USA, 1995[1], 95-0254MS	FS		56		1	128	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0255TX	FS		56		1	119	≤0.003	≤0.003	≤0.003	<0.003	<0.003

Commodity, Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1995[1], 95-0256MS	FS		56		1	130	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0257LA	FS		56		1	109	≤0.003	≤0.003	≤0.003	<0.003	<0.003
Seed treatment, 2 replicates (Mede, 1997)											
USA, 1996[1], 10392-01	FS		54		1	126	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-02	FS		58		1	125	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-03	FS		57		1	129	≤0.01 <0.003	≤0.003 <0.003	≤0.003 <0.003	<0.003 <0.003	NR
USA, 1996[1], 10392-04	FS		56		1	110	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-05	FS		56		1	117	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-07	FS		56		1	128	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-08	FS		57		1	138	≤0.003	≤0.003	≤0.003	<0.003	NR
Soil pre-plant incorporated broadcast treatment, 2 replicates (Mede, 1996b)											
USA, 1995[1], 95-0248AR	WG		56		1	119	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0249AR	WG		56		1	134	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0250CA	WG		56		1	141	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0251CA	WG		56		1	140	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0252LA	WG		56		1	112	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0253LA	WG		56		1	114	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0254MS	WG		56		1	128	≤0.003	≤0.003	≤0.003	<0.003	<0.01
USA, 1995[1], 95-0255TX	WG		56		1	119	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0256MS	WG		56		1	130	≤0.003	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0257LA	WG		56		1	110	≤0.003	≤0.003	≤0.003	<0.003	<0.003
Soil pre-plant incorporated broadcast treatment, 2 replicates (Mede, 1997)											
USA, 1996[1], 10392-01	SC		57		1	133	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-02	SC		57		1	125	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-03	SC		57		1	136	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-04	SC		56		1	113	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-05	SC		57		1	120	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-07	SC		59		1	128	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-08	SC		56		1	143	≤0.01 <0.01	≤0.01 <0.003	≤0.003 <0.003	<0.003 <0.003	NR
Broadcast into flooded paddy, 2 replicates (Garcia and Oiveira, 1994c)											
Brazil, 1994, 032/94PC	GR		100 200		1	30	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01
Broadcast into flooded paddy, 2 replicates (Garcia and Oiveira 1994e)											
Brazil, 1994, 062/94PC	GR		100 200		1	30	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01
Broadcast into flooded paddy, 3 replicates (Maycey *et al.*, 1994d)											
Rice, brown, Indonesia, 1992/3, P92/278 Pusaharuta	GR		50		1	98	<0.001	NR	NR	<0.001	NR
Rice, brown, Indonesia, 1992/3, P92/278 Kutasari	GR		50		1	97	<0.001	NR	NR	<0.001	NR

Commodity, Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Rice, brown, Indonesia, 1992/3, P92/278 Mundu	GR		50		1	97	0.003 <0.001 <0.001	NR	NR	<0.001 <0.001 <0.001	NR
Broadcast treatment into flooded paddy (Maycey *et al.*, 1994a)											
Rice, brown, Philippines, 1992, 92/277 Luzon	GR		50		1	81	<0.001	NR	NR	<0.001	NR
Rice, white Philippines, 1992, 92/277 Luzon	GR		50		1	81	<0.001	NR	NR	<0.001	NR
Rice, brown, Philippines, 1992, 92/277 Visayas	GR		50		1	76	<0.001	NR	NR	<0.001	NR
Rice, white, Philippines, 1992, 92/277 Visayas	GR		50		1	76	<0.001	NR	NR	<0.001	NR
Rice, brown, Philippines, 1992, 92/277 Mindanao	GR		50		1	76	<0.001	NR	NR	<0.001	NR
Rice, white, Philippines, 1992, 92/277 Mindanao	GR		50		1	76	<0.001	NR	NR	<0.001	NR
Broadcast treatment into flooded paddy, (Maycey *et al.*, 1994b)											
Rice, brown Taiwan, 1993, 92/275 Hsinung Li **Plot 1**	GR		50		1	89	<0.001	NR	NR	<0.001	NR
Rice, brown Taiwan, 1993, 92/275 Hsinung Li **Plot 2**	GR		50		1	89	<0.001	NR	NR	<0.001	NR
Broadcast treatment into flooded paddy (Maycey *et al.*, 1994c)											
Rice, brown Thailand, 1992/1993, 92/276 Supanuri Rice Research Station **replicate 1**	GR		50		1	79	<0.001	NR	NR	<0.001	NR
Rice, white Thailand, 1992/1993, 92/276 Supanuri Rice Research Station **replicate 1**	GR		50		1	79	<0.001	NR	NR	<0.001	NR
Rice, brown Thailand, 1992/1993, 92/276 Supanuri Rice Research Station **replicate 2**	GR		50		1	75	<0.001	NR	NR	<0.001	NR
Rice, white Thailand, 1992/1993, 92/276 Supanuri Rice Research Station **replicate 2**	GR		50		1	75	<0.001	NR	NR	<0.001	NR
Rice, brown Thailand, 1992/1993, 92/276 Supanuri	GR		50		1	78	<0.001	NR	NR	<0.001	NR
Rice, white Thailand, 1992/1993, 92/276 Supanuri	GR		50		1	78	<0.001	NR	NR	<0.001	NR
Rice, brown Thailand, 1992/1993, 92/276 Nontaburi	GR		50		1	75	<0.001	NR	NR	<0.001	NR

Commodity, Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Rice, white Thailand, 1992/1993, 92/276 Nontaburi	GR		50		1	75	<0.001	NR	NR	<0.001	NR
Foliar treatment, 3 replicates (Maycey *et al.*, 1994d)											
Indonesia, 1992/3, P92/278 Kutasari	SC		50		1	67	<0.001	NR	NR	<0.001	NR
Indonesia, 1992/3, P92/278 Mundu	SC		50		1	67	<0.001	NR	NR	<0.001	NR
Indonesia, 1992/3, P92/278 Pusaharuta	SC		50		1	67	<0.001	NR	NR	<0.001	NR
Foliar treatment, residues for rice with husks/without husks (Keats, 1997 a,d)											
Indonesia, 1996, AK97004/AK97012	SC		12.5	3.1	1	7	0.028/ 0.002	0.002/ <0.002	0.005/ <0.002	0.022/ <0.002	NR
Indonesia, 1996, AK97004/AK97012	SC		12.5	3.1	1	14	0.029/ 0.002	<0.002/ <0.002	0.007/ <0.002	0.02/ 0.002	NR
Indonesia, 1996, AK97004/AK97012	SC		12.5	3.1	2	7	0.069/ 0.006	0.005/ <0.002	0.013/ <0.002	0.047/ 0.003	NR
Indonesia, 1996, AK97004/AK97012	SC		25	6.2	1	14	0.037/ 0.008	<0.002/ <0.002	0.009/ 0.002	0.029/ 0.005	NR
Indonesia, 1996, AK97004/AK97012	SC		25	6.2	1	7	0.086/ 0.013	0.011/ <0.002	0.159/ 0.004	0.076/ 0.011	NR
Indonesia, 1996, AK97004/AK97012	SC		25	6.2	2	7	0.099/ 0.03	0.016/ 0.002	0.042/ 0.009	0.103/ 0.019	NR
Indonesia, 1996, AK97004/AK97012	SC		50	12.5	1	7	0.099/ 0.017	0.017/ <0.002	0.028/ 0.004	0.093/ 0.009	NR
Indonesia, 1996, AK97004/AK97012	SC		50	12.5	1	14	0.097/ 0.013	0.005/ <0.002	0.024/ 0.003	0.082/ <0.002	NR
Indonesia, 1996, AK97004/AK97012	SC		50	12.5	2	7	0.101/ 0.029	0.026/ 0.002	0.065/ 0.008	0.12/ 0.019	NR
Foliar treatment (Maycey *et al.*, 1994a)											
Rice, brown Philippines, 1992, 92/277 Luzon	SC		50		1	51	<0.001	NR	NR	<0.001	NR
Rice, white Philippines, 92/277 Luzon	SC		50		1	51	<0.001	NR	NR	<0.001	NR
Rice, brown Philippines, 1992, 92/277 Visayas	SC		50		1	46	<0.001	NR	NR	<0.001	NR
Rice, white Philippines, 1992, 92/277 Visayas	SC		50		1	46	<0.001	NR	NR	<0.001	NR
Rice, brown Philippines, 1992, 92/277 Mindanao	SC		50		1	46	<0.001	NR	NR	<0.001	NR
Rice, white Philippines, 1992, 92/277 Mindanao	SC		50		1	46	<0.001	NR	NR	<0.001	NR
Broadcast treatment after transplanting followed by foliar treatment (Maycey *et al.*, 1994a)											
Rice, brown Philippines, 1992, 92/277 Luzon	GR SC		50		2	51	<0.001	NR	NR	<0.001	NR
Rice, white Philippines, 1992, 92/277 Luzon	GR SC		50		2	51	<0.001	NR	NR	<0.001	NR
Rice, brown Philippines, 1992, 92/277 Visayas	GR SC		50		2	46	<0.001	NR	NR	<0.001	NR
Rice, white Philippines, 1992, 92/277 Visayas	GR SC		50		2	46	<0.001	NR	NR	<0.001	NR
Rice, brown Philippines, 1992, 92/277 Mindanao	GR SC		50		2	46	<0.001	NR	NR	<0.001	NR
Rice, white, Philippines, 1992, 92/277 Mindanao	GR SC		50		2	46	<0.001	NR	NR	<0.001	NR

Commodity, Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Foliar treatment, (Maycey *et al.*, 1994b)											
Rice, brown Taiwan, 1993, 92/275 Chitong Li **Plot 1**	SC		50		1	79	<0.001	NR	NR	<0.001	NR
Rice, brown Taiwan, 1993, 92/275 Chitong Li **Plot 2**	SC		50		1	79	<0.001	NR	NR	<0.001	NR
Foliar treatment, 3 replicates (Maycey *et al.*, 1994c)											
Rice, brown Thailand, 1992/1993, 92/276 Supanuri Rice Research Station	SC		50		1	49	<0.001 <0.001 <0.001	NR	NR	<0.001 0.001 0.001	NR
Rice, white Thailand, 1992/1993, 92/276 Supanuri Rice Research Station	SC		50		1	49	<0.001	NR	NR	<0.001	NR
Rice, brown Thailand, 1992/1993, 92/276 Supanuri Rice Research Station	SC		50		1	45	<0.001 <0.001 <0.001	NR	NR	0.001 0.001 0.001	NR
Rice, white Thailand, 1992/1993, 92/276 Supanuri Rice Research Station	SC		50		1	45	<0.001	NR	NR	<0.001	NR
Rice, brown Thailand, 1992/1993, 92/276 Supanuri	SC		50		1	48	<0.001 0.002 0.001	NR	NR	<0.001 <0.001 <0.001	NR
Rice, white Thailand, 1992/1993, 92/276 Supanuri	SC		50		1	48	<0.001	NR	NR	<0.001	NR
Rice, brown Thailand, 1992/1993, 92/276 Nontaburi	SC		50		1	45	<0.001 0.001 <0.001	NR	NR	<0.001 <0.001 <0.001	NR
Rice, white Thailand, 1992/1993, 92/276 Nontaburi	SC		50		1	45	<0.001 <0.001 <0.001	NR	NR	<0.001 <0.001 0.001	NR

[1] residues reported as ND (not detectable) in the original report are shown as <0.00x (i.e. MLD)
[2] analysed sample: ear
NR: not reported

Table 70. Residues in sorghum grain from seed treatment or foliar applications.

Country, Year Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Foliar treatment at stage BBCH 85**, 2 replicates (Keats, 1996n)**											
Australia, 1995, AK96074	UL		10		1	0	0.24 0.18	0.004 0.003	0.002 0.003	0.004 0.003	NR
						1	0.11 0.099	0.002 0.002	0.04 0.04	0.019 0.017	
						3	0.049 0.05	<0.002 <0.002	0.011 0.01	0.008 0.009	
						7	0.052 0.049	<0.002 <0.002	0.009 0.01	0.008 0.008	
						21	0.011 0.011	<0.002 <0.002	0.011 0.008	0.004 0.003	
Australia, 1995, AK96074	UL		20		1	0	0.33 0.29	0.008 0.006	0.007 0.005	0.002 0.002	NR
						1	0.18	0.004	0.017	0.005	

Country, Year Reference	Application					PHI,	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.	days	Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
							0.17	0.004	0.018	0.006	
						3	0.065	0.002	0.012	0.007	
							0.061	<0.002	0.01	0.007	
						7	0.059	<0.002	0.013	0.009	
							0.057	<0.002	0.013	0.009	
						21	0.017	<0.002	0.009	0.005	
							0.015	<0.002	0.01	0.005	
Foliar treatment at stage BBCH 75 (Keats, 1996o)											
Australia, 1996, AK96075	UL		10		1	0	0.093	0.004	0.008	0.002	NR
						1	0.066	0.003	0.01	0.003	
						3	0.025	0.002	0.014	0.005	
						7	0.024	<0.002	0.013	0.005	
						17	0.027	<0.002	0.013	0.004	
Australia, 1996, AK96075	UL		20		1	0	0.12	0.005	0.004	<0.002	NR
						1	0.092	0.003	0.005	0.002	
						3	0.071	0.002	0.006	0.003	
						7	0.058	0.002	0.006	0.004	
						17	0.031	<0.002	0.006	0.006	
Foliar treatment at maturity, BBCH 87, 2 replicates (Keats, 1996p)											
Australia, 1996, AK96076	UL		10		1	0	0.27	0.058	0.01	<0.002	NR
							0.29	0.055	0.011	<0.002	
						1	0.14	0.023	0.099	0.007	
							0.13	0.021	0.074	0.006	
						3	0.10	0.017	0.039	0.003	
							0.11	0.016	0.041	0.004	
						7	0.087	0.013	0.034	0.004	
							0.077	0.013	0.032	0.004	
						21	0.019	0.002	0.022	<0.002	
							0.013	0.002	0.015	<0.002	
Australia, 1996, AK96076	UL		20		1	0	0.42	0.078	0.025	<0.002	NR
							0.43	0.079	0.022	<0.002	
						1	0.35	0.059	0.059	0.003	
							0.34	0.053	0.062	0.003	
						3	0.12	0.019	0.044	0.003	
							0.12	0.018	0.04	0.003	
						7	0.11	0.016	0.052	0.006	
							0.11	0.016	0.052	0.006	
						21	0.032	0.005	0.032	0.003	
							0.032	0.004	0.03	0.003	
Foliar treatment at maturity, BBCH 87**, 2 replicates (Keats, 1998a)**											
Australia, 1998, AK98024	SC		1.25		1	0	0.011	0.002	<0.002	<0.002	NR
							0.01	0.002	<0.002	<0.002	
						4	0.002	<0.002	<0.002	<0.002	
						7	0.008	<0.002	<0.002	<0.002	
							0.008	<0.002	0.002	<0.002	
						15	0.002	<0.002	<0.002	<0.002	
						21	<0.002	<0.002	<0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98024	SC		2.5		1	0	0.036	0.008	0.002	<0.002	NR
							0.038	0.008	0.002	<0.002	
						4	0.002	<0.002	<0.002	<0.002	
						7	0.008	<0.002	0.003	<0.002	
						15	0.003	<0.002	<0.002	0.002	
						21	<0.002	<0.002	<0.002	<0.002	
						29	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98024	SC		5.0		1	0	0.086	0.02	0.007	0.009	NR
							0.082	0.021	0.006	0.009	
						4	0.003	<0.002	<0.002	<0.002	
						7	0.009	<0.002	0.004	<0.002	
							0.008	<0.002	0.003	0.003	
						15	0.01	<0.002	<0.002	0.003	
							0.009	<0.002	<0.002	<0.002	
						21	0.002	<0.002	<0.002	<0.002	
						29	<0.002	<0.002	<0.002	<0.002	
Foliar treatment at maturity, BBCH 87, 2 replicates (Keats, 1998b)											
Australia, 1998, AK98025	UL		1.25		1	0	0.008	0.002	<0.002	<0.002	NR
							0.01	0.002	<0.002	<0.002	
						2	0.005	0.002	<0.002	<0.002	
							0.003	<0.002	<0.002	0.003	
						4	0.002	<0.002	0.002	<0.002	
							0.002	<0.002	<0.002	<0.002	

Country, Year Reference	Application					PHI,	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.	days	Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
						7	0.002	<0.002	0.002	<0.002	
						15	<0.002	<0.002	<0.002	<0.002	
						21	0.002	<0.002	<0.002	<0.002	
							<0.002	<0.002	<0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98025	UL		2.5		1	0	0.009	0.003	<0.002	0.002	NR
							0.011	0.005	<0.002	<0.002	
						2	0.014	<0.002	<0.002	0.005	
							0.01	<0.002	0.003	0.007	
						4	0.004	<0.002	0.007	<0.002	
							0.006	<0.002	0.005	<0.002	
						7	0.005	<0.002	0.004	<0.002	
							0.005	<0.002	0.004	<0.002	
						15	0.002	<0.002	0.002	<0.002	
							0.002	<0.002	0.002	<0.002	
						21	<0.002	<0.002	0.002	<0.002	
							<0.002	<0.002	<0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98025	UL		5.0		1	0	0.024	0.006	<0.002	0.008	NR
							0.02	0.008	<0.002	0.004	
						2	0.011	0.002	0.003	0.004	
							0.017	0.003	<0.002	0.004	
						4	0.005	<0.002	0.006	0.004	
							0.003	0.003	0.005	0.003	
						7	0.01	<0.002	0.006	<0.002	
							0.009	<0.002	0.006	<0.002	
						15	0.004	<0.002	0.004	<0.002	
							0.002	<0.002	0.004	<0.002	
						21	0.002	<0.002	0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98025	UL		7.5		1	0	0.035	0.006	<0.002	0.012	NR
							0.041	0.006	<0.002	0.008	
						2	0.018	0.002	0.002	0.006	
							0.014	0.002	<0.002	0.008	
						4	0.012	<0.002	0.008	0.003	
							0.009	0.003	0.009	0.005	
						7	0.016	<0.002	0.013	<0.002	
							0.017	<0.002	0.013	<0.002	
						15	0.002	<0.002	0.006	<0.002	
							0.006	<0.002	0.005	<0.002	
						21	0.003	<0.002	0.004	<0.002	
							0.004	<0.002	0.004	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Foliar treatment at stage BBCH 73, 2 replicates (Keats, 1998c)											
Australia, 1998, AK98027	UL		1.25		1	0	0.008	<0.002	<0.002	<0.002	NR
							0.002	<0.002	<0.002	<0.002	
						2	0.006	<0.002	<0.002	0.002	
							0.002	<0.002	<0.002	0.002	
						4	<0.002	<0.002	0.002	<0.002	
							<0.002	<0.002	<0.002	<0.002	
						7	<0.002	<0.002	0.002	<0.002	
						15	<0.002	<0.002	<0.002	<0.002	
						21	<0.002	<0.002	<0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98027	UL		2.5		1	0	0.007	0.003	<0.002	<0.002	NR
							0.013	<0.002	<0.002	<0.002	
						2	0.01	<0.002	<0.002	0.004	
							0.014	<0.002	0.003	0.008	
						4	0.003	<0.002	0.005	<0.002	
							0.002	<0.002	0.003	0.003	
						7	0.002	<0.002	0.002	<0.002	
							0.002	<0.002	0.002	<0.002	
						15	<0.002	<0.002	<0.002	<0.002	
						21	<0.002	<0.002	<0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98027	UL		5.0		1	0	0.017	0.006	<0.002	0.002	NR
							0.011	0.002	<0.002	0.003	
						2	0.012	0.002	0.003	0.002	
							0.016	0.002	<0.002	0.004	
						4	0.003	<0.002	0.003	0.004	
							0.005	<0.002	0.005	0.003	
						7	0.002	<0.002	0.002	<0.002	

Country, Year Reference	Application					PHI,	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.	days	Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
							0.003	<0.002	0.004	<0.002	
						15	<0.002	<0.002	<0.002	<0.002	
						21	<0.002	<0.002	<0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK98027	UL		7.5		1	0	0.025	0.003	<0.002	0.006	NR
							0.017	0.005	0.003	0.002	
						2	0.016	0.002	<0.002	0.006	
							0.015	0.002	0.003	0.008	
						4	0.009	<0.002	0.006	0.006	
							0.005	0.003	0.004	0.002	
						7	0.004	<0.002	0.007	<0.002	
							0.002	<0.002	0.003	<0.002	
						15	<0.002	<0.002	<0.002	<0.002	
						21	<0.002	<0.002	<0.002	<0.002	
						28	<0.002	<0.002	<0.002	<0.002	
Seed treatment, GAP pending, 2 replicates (Keats, 1998g)											
Australia, 1998, AK98030	FS	750			1	138	≤0.002	≤0.002	≤0.002	<0.002	NR
		1500					<0.002	<0.002	<0.002	<0.002	
Seed treatment, GAP pending, 2 replicates (Keats, 1998h)											
Australia, 1998, AK98031	FS	750			1	104	≤0.002	≤0.002	≤0.002	<0.002	NR
		1500					<0.002	<0.002	<0.002	<0.002	

Table 71. Residues in wheat grain from seed treatment or foliar applications (most trials include 2 replicates).

Crop, Country, Year, Reference	Application					PHI,	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.	days	Fipronil	MB 45950	MB 46136	fipronil - desulfinyl	RPA 200766
Seed treatment (Muller, 1994k)											
Wheat, winter, France, 1992/3, 93-507E1	FS	1000			1	251	<0.002	<0.002	<0.002	NR	<0.002
Seed treatment (Richard and Muller, 1994h)											
Wheat, winter, France, 1992/3, 93-508B1	FS	1500			1	279	<0.002	<0.002	<0.002	NR	<0.002
Wheat, winter, France, 1992/3, 93-508C1	FS	1000			1	286	<0.002	<0.002	<0.002	NR	<0.002
		1500					<0.002	<0.002	<0.002		<0.002
Wheat, winter, France, 1992/3, 93-508D1	FS	1500			1	269	<0.002	<0.002	<0.002	NR	<0.002
Wheat, winter, France, 1992/3, 93-508E1	FS	1500			1	264	<0.002	<0.002	<0.002	NR	<0.002
Wheat, winter, France, 1992/3, 93-508F1	FS	1500			1	268	<0.002	<0.002	<0.002	NR	<0.002
Wheat, winter, France, 1992/3, 93-508K1	FS	1000			1	226	<0.002	<0.002	<0.002	NR	<0.002
		1500					<0.002	<0.002	<0.002		<0.002
Seed treatment (Muller, 1995b)											
Wheat, winter, France, 1993/4, 94-500BX1	FS	1500			1	244	<0.002	<0.002	<0.002	NR	<0.002
							0.003	<0.002	<0.002		0.002
Wheat, winter, France, 1993/4, 94-500RN1	FS	1500			1	260	<0.002	<0.002	<0.002	NR	<0.002
Wheat, winter, France, 1993/4, 94-500AM1	FS	1500			1	286	<0.002	<0.002	<0.002	NR	<0.002
Wheat, winter, France, 1993/4, 94-500DJ1	FS	1500			1	262	<0.002	<0.002	<0.002	NR	<0.002

Crop, Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil - desulfinyl	RPA 200766
Wheat, winter, France, 1993/4, 94-500LY1	FS	1500			1	245	<0.002	<0.002	<0.002	NR	<0.002
Wheat, winter, France, 1993/4, 94-500AV1	FS	1500			1	245	<0.002	<0.002	<0.002	NR	<0.002
Seed treatment (Muller, 1996k)											
Wheat, spring, France, 1995, 95-507BX1	FS	500			1	140	≤0.002	≤0.002	≤0.002	NR	<0.002
Wheat, spring, France, 1995, 95-507AM1	FS	500			1	128	≤0.002	≤0.002	≤0.002	NR	<0.002
Wheat, spring, France, 1995, 95-507RS1	FS	500			1	131	≤0.002	≤0.002	≤0.002	NR	<0.002
Wheat, spring, France, 1995, 95-507LY1	FS	500			1	145	≤0.002	≤0.002	≤0.002	NR	<0.002
Seed treatment (Muller, 1996j)											
Wheat, spring, France, 1995 95-518RS1	FS	500			1	131	≤0.002	≤0.002	≤0.002	NR	<0.002
Seed treatment (Maestracci, 1998a)											
Wheat, winter, Greece, 1997/8, 96600GR1	FS	750			1	152	0.004 0.03	<0.002 <0.002	<0.002 0.003	<0.002 <0.002	<0.002 <0.002
Seed treatment (Souvinet, 1999)											
Wheat, winter, Greece, 1997/8, 97741GR1	FS	750			1	181	0.003 0.003	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
Foliar treatment at stage BBCH 51 (Muller, 1996a)											
Wheat, winter, Poland, 1995, 95795PL1	WG		20	6.67	1	44	<0.002	<0.002	<0.002	<0.002	<0.002
Foliar treatment no reference (summary table, no GLP report available)											
Wheat, winter, Russia, 1997, Krasnodar	EC		24	12	1	27	<0.005	NR	NR	NR	NR
Wheat, winter, Russia, 1997, Rostov	EC		20	10	1	25	<0.005	NR	NR	NR	NR
Wheat, winter, Russia, 1997, Voronesh	EC		20	10	1	38	<0.005	NR	NR	NR	NR
Wheat, spring, Russia, 1998, Volgograd	EC		21	10.5	1	49	<0.005	NR	<0.004	<0.005	NR
Wheat, spring, Russia, 1998, Saratov	EC		21	10.5	1	48	<0.005	NR	<0.004	<0.005	NR

NR: not reported

Table 72. Residues in sugar cane from soil and foliar applications.

Country, Year, Reference	Application			PHI, days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Soil treatment, in furrow spray at planting, 2 replicates (Keats, 1997n)									
Australia, 1995, AUS94i48r Tully Queensland	WG	100 200 400	1	340	≤0.002 0.002 0.002	≤0.002 <0.002 <0.002	≤0.002 <0.002 0.003	<0.002 <0.002 <0.002	NR

Country, Year, Reference	Application			PHI, days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1995, AUS94i48r Tully Queensland	WG	100 200 400	2	245	0.002 <0.002 0.002 0.003	≤0.002 <0.002 <0.002 <0.002	≤0.002 <0.002 <0.002 0.003	<0.002 <0.002 <0.002 <0.002	NR
Spray on the bottom of the stalk, 2 replicates (Keats, 1997m)									
Australia, 1995, AUS94i74r Mowilyan Queensland	WG	100	1	181	0.002	<0.002	0.002	<0.002	NR
Australia, 1995, AUS94i74r Mowilyan Queensland	WG	200	1	181	0.002	<0.002	0.002	0.002	NR
Australia, 1995, AUS94i74r Mowilyan Queensland	WG	50	2	134	<0.002 0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
Australia, 1995, AUS94i74r Mowilyan Queensland	WG	100	2	53	0.025 0.02	<0.002 <0.002	0.008 0.007	0.003 0.003	NR
Spray on the bottom of the stalk, 2 replicates (Keats, 1997k)									
Australia, 1996, 97NST14 Kurrimine Beach Queensland	SC	75	1	101	≤0.002	≤0.002	≤0.002	≤0.002	NR
Soil treatment, in furrow spray followed by stool spray, 2 replicates (Keats, 1997k)									
Australia, 1996, AUS94i74cr Kurrimine Beach Queensland	WG + SC	100 soil + 50 foliar	1 + 2	95	0.002	≤0.002	0.002	≤0.002	NR
Australia, 1996, AUS94i74cr Kurrimine Beach Queensland	WG + SC	200 soil + 100 foliar	1 + 2	95	0.002 0.003	<0.002 <0.002	0.003 0.003	0.002 0.002	NR
AUS94i74cr Kurrimine Beach Queensland	WG + SC	400 soil + 200 foliar	1 + 2	95	0.005	<0.002	0.006	0.008	NR
Soil treatment, in furrow spray at planting, 2 replicates (Garcia and Oliveira, 1994a)									
Brazil, 1994, 154/94 Sao Paulo	WG	400 800	1	87	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01
Soil treatment, in furrow spray at planting, 2 replicates (Garcia and Oliveira, 1994b)									
Brazil, 1994 155/94 Sao Paulo	WG	400 800	1	87	<0.01 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 0.01

NR: not reported

Oilseeds - cotton and sunflower (Tables 73, 74). Both soil and foliar pests can be controlled with fipronil. For trials where fipronil has been applied as a seed treatment, as in-furrow granules or as a soil incorporated pre-plant spray, only the residues of fipronil and its soil degradation products MB 45950, MB 46136 and RPA 200766 have been reported. For trials using foliar or combined soil/foliar applications fipronil-desulfinyl residues are included.

Table 73. Residues in cotton seed after varied applications of fipronil.

Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Seed treatment, 2 replicates(Keats, 1997i)											
Australia, 1995, AK97018 Clare, QLD	FS	5000 10 000			1	169	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
Foliar treatment, 2 replicates (Keats, 1997e)											
Australia, 1996, AK97016 Breeza, NSW	EC		200		4	14	<0.002 0.002	<0.002 <0.002	<0.002 <0.002	0.002 <0.002	NR
Seed treatment followed by foliar treatments, 2 replicates (Keats, 1997f)											
Australia, 1996, AK97015 Kincora Queensland	FS + SC +	5000	25		1 1						

Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
	ULV		25		1	113	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97015 Kincora Queensland	FS + SC + ULV	10 000	50 50		1 1 1	113	<0.002 <0.002	<0.002 <0.002	<0.002 0.002	<0.002 <0.002	NR
Australia, 1996, AK97015 Kincora Queensland	FS + SC + ULV	10 000	100 100		1 1 1	113	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97015 Kincora Queensland	FS + SC + ULV	5000	25 25		1 1 3	28	0.003 0.002	0.002 <0.002	0.003 0.003	0.002 <0.002	NR
Australia, 1996, AK97015 Kincora Queensland	FS + SC + ULV	10 000	50 50		1 1 3	28	0.002 <0.002	<0.002 <0.002	0.002 0.002	0.002 0.002	NR
Australia, 1996, AK97015 Kincora Queensland	FS + SC + ULV	10 000	100 100		1 1 3	28	0.002	<0.002	0.002	<0.002	NR
Seed treatment followed by foliar treatments, 2 replicates (Keats, 1997g)											
Australia, 1996, AK97014 Breeza NSW	FS + SC + ULV	5000	25 25		1 1 1	109	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97014 Breeza NSW	FS + SC + ULV	10 000	50 50		1 1 1	109	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97014 Breeza NSW	FS + SC + ULV	10 000	100 100		1 1 1	109	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97014 Breeza NSW	FS + SC + ULV	5000	25 25		1 1 3	31	0.004 0.002	<0.002 <0.002	0.004 0.003	<0.002 <0.002	NR
Australia, 1996, AK97014 Breeza NSW	FS + SC + ULV	10 000	50 50		1 1 3	31	0.002	<0.002	0.003	<0.002	NR
Australia, 1996, AK97014 Breeza NSW	FS + SC + ULV	10 000	100 100		1 1 3	31	<0.002	<0.002	<0.002	<0.002	NR
Foliar treatment, 2 replicates (Lynch, 1998)											
Australia, 1998, AK99029 Jambin, QLD **Single applications to separate plots**	SC		35.4	44.8	1 1 1 1 1	0 15 30 43 57	0.014 0.016 0.01 0.008 0.002 0.005 <0.002 <0.002 <0.002	0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002	0.004 0.009 0.004 0.006 0.005 0.004 0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002 <0.002	NR

Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
					1	71	<0.002	<0.002	<0.002	<0.002	
					1	85	<0.002	<0.002	<0.002	<0.002	
					1	99	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99029	SC		71.4	92.7	1	0	0.027	0.002	<0.002	<0.002	NR
							0.034	0.004	0.004	<0.002	
Jambin, QLD					1	15	0.02	0.006	0.007	<0.002	
							0.026	0.009	0.007	<0.002	
Single					1	30	0.011	0.004	0.006	<0.002	
applications							0.018	0.003	0.005	<0.002	
to separate plots					1	43	0.005	0.002	0.006	<0.002	
							0.009	0.004	0.01	<0.002	
					1	57	0.002	<0.002	0.002	<0.002	
							<0.002	<0.002	0.004	<0.002	
					1	71	<0.002	<0.002	<0.002	<0.002	
					1	85	<0.002	<0.002	<0.002	<0.002	
					1	99	<0.002	<0.002	<0.002	<0.002	
Foliar treatment, 2 replicates (Lynch, 1999)											
Australia, 1998, AK99032	SC		25	28.4	1	0	<0.002	<0.002	<0.002	<0.002	NR
					1	15	<0.002	<0.002	<0.002	<0.002	
Wee Waa					1	29	<0.002	<0.002	<0.002	<0.002	
NSW					1	43	<0.002	<0.002	<0.002	<0.002	
Single					1	57	<0.002	<0.002	<0.002	<0.002	
applications					1	71	<0.002	<0.002	<0.002	<0.002	
to separate plots					1	85	<0.002	<0.002	<0.002	<0.002	
					1	99	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99032	SC		50	56.8	1	0	0.003	<0.002	<0.002	<0.002	NR
							0.003	<0.002	<0.002	<0.002	
Wee Waa					1	15	<0.002	<0.002	<0.002	<0.002	
NSW					1	29	<0.002	<0.002	<0.002	<0.002	
Single					1	43	<0.002	<0.002	<0.002	<0.002	
applications					1	57	<0.002	<0.002	<0.002	<0.002	
to separate plots					1	71	<0.002	<0.002	<0.002	<0.002	
					1	85	<0.002	<0.002	<0.002	<0.002	
					1	99	<0.002	<0.002	<0.002	<0.002	
Foliar treatment, 2 replicates (Garcia and Oliveira, 1994d)											
Brazil, 1994, 028/94PC	WG		100		2	15	<0.01	<0.01	<0.01	<0.01	<0.01
			200		2	15	0.01	<0.01	<0.01	<0.01	<0.01
							<0.01	<0.01	<0.01	<0.01	<0.01
Foliar treatment, 2 replicates (Carringer, 1998a)											
Mexico, 1996, 12046-01	WG		50		6	16	<0.004	<0.002	<0.005	<0.01	NR
						31	<0.004	<0.002	<0.005	<0.01	
							<0.01	<0.01	<0.01	<0.01	
						54	<0.004	<0.002	<0.005	<0.01	
						61	<0.004	<0.002	<0.01	<0.01	
Mexico, 1996, 12046-01	WG		250		6	54	<0.01	<0.002	<0.01	<0.01	NR
Mexico, 1996, 12046-02	WG		50		6	17	<0.01	<0.002	<0.01	<0.01	NR
						31	<0.004	<0.002	<0.01	<0.01	
						46	<0.01	<0.002	<0.01	<0.01	
						61	<0.01	<0.002	<0.01	<0.01	
Mexico, 1996, 12046-02	WG		250		6	46	0.037	<0.002	0.037	0.067	NR
							<0.01	<0.002	<0.01	0.02	
Soil treatment in-furrow at sowing followed by foliar treatments, or foliar only, 2 replicates (Norris, 1995a)											
USA, 1994, 94-0343TX	WG		168 inc + 84 foliar		1						
					2	45	<0.004	<0.002	<0.005	<0.003	<0.005
							<0.004	<0.002	<0.005	<0.01	<0.005
USA, 1994, 94-0343TX	WG		84 foliar		4	45	<0.004	<0.002	<0.005	<0.003	<0.005
							<0.01	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0344NC	WG		168 inc + 84 foliar		1						
					2	45	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0344NC	WG		84 foliar		4	45	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0345AZ	WG		168 inc + 84 foliar		1						
					2	45	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0345AZ	WG		84 foliar		4	45	<0.004	<0.002	<0.005	<0.01	<0.005
USA, 1994, 94-0346CA	WG		168 inc +		1						

Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
			84 foliar		2	46	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0346CA	WG		84 foliar		4	46	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0347AR	WG		168 inc + 84 foliar		1 2	45	<0.01 <0.004	<0.002 <0.002	<0.005 <0.005	<0.003 <0.003	<0.005 <0.005
USA, 1994, 94-0347AR	WG		84 foliar		4	45	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0348MS	WG		168 inc + 84 foliar		1 2	45	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0348MS	WG		84 foliar		4	45	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0349AR	WG		168 inc + 84 foliar		1 2	46	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0349AR	WG		84 foliar		4	46	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0350LA	WG		168 inc + 84 foliar		1 2	57	<0.004 <0.004	<0.002 <0.002	<0.005 <0.005	<0.01 <0.003	<0.005 <0.005
USA, 1994, 94-0350LA	WG		84 foliar		4	57	<0.004	<0.002	<0.005	<0.01	<0.005
USA, 1994, 94-0351TX	WG		168 inc + 84 foliar		1 2	46	<0.004 <0.004	<0.002 <0.002	<0.005 <0.005	<0.003 <0.01	<0.005 <0.005
USA, 1994, 94-0351TX	WG		84 foliar		4	46	<0.004 <0.004	<0.002 <0.002	<0.01 <0.005	<0.01 <0.01	<0.005 <0.005
USA, 1994, 94-0352GA	WG		168 inc + 84 foliar		1 2	44	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0352GA	WG		84 foliar		4	44	<0.004	<0.002	<0.005	<0.003	<0.005
USA, 1994, 94-0353TX	WG		1681 inc + 420 foliar		1 4	45	0.056 0.049	0.021 0.017	0.069 0.066	0.173 0.143	<0.004 <0.004
Soil treatment in furrow at sowing followed by foliar treatments, or foliar only, 2 replicates (Norris, 1997a)											
USA, 1995, 95-0023NC	WG		168 inc + 84 foliar		1 2	44	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0023NC	WG		84 foliar		4	44	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0026AR	WG		168 inc + 84 foliar		1 2	45	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0026AR	WG		84 foliar		4	45	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0027MS	WG		168 inc + 84 foliar		1 2	44	<0.003 <0.003	<0.003 <0.003	<0.004 <0.01	<0.003 <0.003	<0.004 <0.01
USA, 1995, 95-0027MS	WG		84 foliar		4	44	<0.003	<0.003	<0.01	<0.003	<0.01
USA, 1995, 95-0028LA	WG		168 inc + 84 foliar		1 2	45	<0.003 <0.003	<0.003 <0.003	<0.004 <0.004	<0.01 0.012	<0.004 <0.004
USA, 1995, 95-0028LA	WG		84 foliar		4	45	<0.003	<0.003	<0.004	<0.01 <0.01	<0.004
USA, 1995, 95-0029TX	WG		168 inc + 84 foliar		1 2	43	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0029TX	WG		84 foliar		4	43	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0030TX	WG		168 inc + 84 foliar		1 2	44	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995,	WG		84 foliar		4	44	<0.003	<0.003	<0.004	<0.003	<0.004

Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
95-0030TX											
USA, 1995, 95-0031OK	WG		168 inc + 84 foliar		1 2	44	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0031OK	WG		84 foliar		4	44	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0032TX	WG		168 inc + 84 foliar		1 2	46	<0.003	<0.003	<0.004	<0.003	<0.004
USA, 1995, 95-0032TX	WG		84 foliar		4	46	<0.003 <0.003	<0.003 <0.003	<0.01 <0.004	<0.01 <0.01	<0.004 <0.004
USA, 1995, 95-0033TX	WG		168 inc + 84 foliar		1 2	46	<0.003 <0.003	<0.003 <0.003	<0.004 <0.004	<0.003 <0.01	<0.004 <0.004
USA, 1995, 95-0033TX	WG		84 foliar		4	46	<0.003	<0.003	<0.004	<0.01	<0.004
USA, 1995, 95-0034AZ	WG		168 inc + 84 foliar		1 2	45	<0.01 <0.003	<0.003 <0.003	<0.004 <0.004	<0.01 <0.003	<0.004 <0.004
USA, 1995, 95-0034AZ	WG		84 foliar		4	45	<0.003 <0.01	<0.003 <0.01	<0.004 <0. 010	<0.003 <0.01	<0.004 <0.004
USA, 1995, 95-0035CA	WG		168 inc + 84 foliar		1 2	45	<0.01 <0.01	<0.003 <0.003	<0.004 <0.004	0.011 <0.01	<0.004 <0.004
USA, 1995, 95-0035CA	WG		84 foliar		4	45	0.011 <0.01	<0.003 <0.003	<0.01 <0.004	0.025 0.013	<0.004 <0.004
USA, 1995, 95-0036CA	WG		168 inc + 84 foliar		1 2	46	<0.003 <0.01	<0.003 <0.003	<0.004 <0.01	<0.01 0.021	<0.004 <0.004
USA, 1995, 95-0036CA	WG		84 foliar		4	46	<0.01 <0.01	<0.003 <0.003	<0.01 <0.004	0.019 0.018	<0.004 <0.004
Foliar treatment, 2 replicates (Norris, 1997b)											
USA, 1995, 95-0276GA	WG		56		6	43	<0.003 <0.01	<0.003 <0.003	<0.01 <0.01	<0.01 <0.01	<0.004 <0.004
USA, 1995, 95-0277LA	WG		56		6	45	<0.003 0.015	<0.003 <0.003	<0.01 <0.01	<0.01 <0.01	<0.004 <0.004
USA, 1995, 95-0278TX	WG		56		6	46	<0.01 <0.01	<0.003 <0.003	<0.01 <0.01	<0.01 <0.01	<0.004 <0.004
USA, 1995, 95-0279TX	WG		56		6	44	<0.01 <0.01	<0.003 <0.003	<0.01 <0.01	<0.01 0.01	<0.004 <0.004
USA, 1995, 95-0280CA	WG		56		6	46	<0.01 0.015	<0.003 <0.003	<0.01 <0.01	0.015 0.025	<0.004 <0.004
Foliar treatment, 2 replicates (Norris, 1998)											
USA, 1996, 10669-01NC	EC		56		6	43	<0.003	<0.003	<0.004	<0.003	NR
USA, 1996, 10669-02GA	EC		56		6	44	<0.003 <0.003	<0.003 <0.003	<0.004 <0.01	<0.01 <0.01	NR
USA, 1996, 10669-03AR	EC		56		6	45	<0.003	<0.003	<0.004	<0.01	NR
USA, 1996, 10669-04AR	EC		56		6	46	<0.003 <0.003	<0.003 <0.003	<0.004 <0.01	<0.01 <0.01	NR
USA, 1996, 10669-05MS	EC		56		6	45	<0.003	<0.003	<0.004	<0.01	NR
USA, 1996, 10669-06LA	EC		56		6	45	<0.003	<0.003	<0.004	<0.01	NR
USA, 1996, 10669-07TX	EC		56		6	47	<0.01	<0.003	<0.01	<0.01	NR
USA, 1996, 10669-08TX	EC		56		6	45	<0.01	<0.003	<0.01	<0.01	NR
USA, 1996, 10669-09OK	EC		56		6	45	<0.003 <0.01	<0.003 <0.003	<0.01 <0.01	<0.01 <0.01	NR
USA, 1996, 10669-10TX	EC		56		6	47	<0.01	<0.003	<0.01	<0.01	NR
USA, 1996, 10669-11TX	EC		56		6	46	<0.01	<0.003	<0.01	<0.01	NR
USA, 1996, 10669-12AZ	EC		56		6	45	<0.01	<0.003	<0.01	<0.01	NR
USA, 1996, 10669-13CA	EC		56		6	44	<0.01	<0.003	<0.01	<0.01	NR
USA, 1996,	EC		56		6	45	<0.01	<0.003	<0.004	<0.01	NR

Country, Year, Reference	Application					PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
100669-14CA							<0.01	<0.003	0.011	<0.01	
Foliar treatment, GAP pending, 2 replicates (Gough, 1999)											
USA, 1997, 13499-01 Kerman CA	EC		56		3	75	<0.003	<0.003	<0.004	<0.01	NR
USA, 1997, 13499-01 Kerman CA	EC		56		4	75	<0.003 <0.003	<0.003 <0.003	<0.004 <0.004	<0.01 <0.003	NR
USA, 1997, 13499-02 Tulare CA	EC		56		3	75	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13499-02 Tulare CA	EC		56		4	75	<0.003 <0.003	<0.003 <0.003	<0.004 <0.01	<0.003 <0.01	NR
USA, 1997, 13499-03 Brawley CA	EC		56		3	76	<0.003 <0.003	<0.003 <0.003	<0.004 <0.01	<0.003 <0.01	NR
USA, 1997, 13499-03 Brawley CA	EC		56		4	76	<0.003	<0.003	<0.01	<0.01	NR
Foliar treatment, GAP pending, 2 replicates (Macy, 1998)											
USA, 1997, 13501-01AR	EC		56		3	58	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-01AR	EC		56		4	58	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-02AR	EC		56		3	61	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-02AR	EC		56		4	61	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-03LA	EC		56		3	60	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-03LA	EC		56		4	60	<0.003	<0.003	<0.004	<0.01	NR
USA, 1997, 13501-04LA	EC		56		3	61	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-04LA	EC		56		4	61	<0.003 <0.003	<0.003 <0.003	<0.004 <0.004	<0.01 <0.003	NR
USA, 1997, 13501-05MS	EC		56		3	61	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-05MS	EC		56		4	61	<0.003	<0.003	<0.004	<0.003	NR
USA, 1997, 13501-06AR	EC		56		3	57	<0.003	<0.003	<0.004	<0.01	NR
USA, 1997, 13501-06AR	EC		56		4	57	<0.003 <0.003	<0.01 <0.003	<0.004 <0.004	<0.01 <0.003	NR

NR: not reported inc: soil incorporation

Table 74. Residues in sunflower seed from seed treatment, in-furrow granular or pre-sowing incorporated spray application (each trial includes 2 replicates). All single applications.

Country, Year, Reference	Application			PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Seed treatment (Keats, 1998l)									
Australia, 1998, AK 98032, 96i38gR	FS	750 1500		113 113	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	NR
Seed treatment (Keats, 1998k)									
Australia, 1998, AK 98035, 96i38bR	FS	750 1500		144 144	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	NR
Seed treatment (Keats, 1998i)									
Australia, 1998, AK 98033, 97i004a	FS	750 1500		138 138	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	NR
Seed treatment (Keats, 1998j)									
Australia, 1998, AK 98034, 97i004b	FS	750 1500		112 112	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	NR
Soil application at sowing (Diot and Muller, 1992)									

Country, Year, Reference	Application			PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
France, 1990, 91-214, LA19I27 Leovillle	GR		200	147	<0.01	<0.01	<0.01	NR	<0.01
France, 1990, 91-214, LA19I27 Chadenac	GR		200	151	<0.01	<0.01	<0.01	NR	<0.01
France, 1990, 91-214, LA19I27 Castlenaudary	GR		200	149	<0.01	<0.01	<0.01	NR	<0.01
France, 1990, 91-214, LA19I27 St. Gilles	GR		200	140	<0.01	<0.01	<0.01	NR	<0.01
Soil application at sowing (Muller, 1993a)									
France, 1992, 92-142 part 1, XA192R84	GR		200 294	146 146	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1992, 92-142 part 1, XH192R84	GR		206 295	137 137	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1992, 92-142 part 1, XK192R84	GR		200 300	140 140	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
Soil application at sowing (Muller, 1993b)									
France, 1992, 92-143 XK192R85	GR		206	136	<0.01	<0.01	<0.01	NR	<0.01
Seed treatment (Muller, 1993c)									
France, 1992, 92-178 XH192R112	FS	10 000 15 000		124 124	<0.01 0.014 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	NR	<0.01 <0.01 <0.01
France, 1992 92-178 XK192R112	FS	10 000 15 000		140 140	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1992, 92-178 XE192R112	FS	10 000 15 000		148 148	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
Seed treatment (Muller, 1994g)									
France, 1993, R93566H1	FS	2500		124	<0.002	<0.002	<0.002	NR	<0.002
Seed treatment (Muller, 1994h)									
France, 1993, R93567A1	FS	3750		146	≤0.002 <0.002	≤0.002 <0.002	0.002 <0.002	NR	<0.002 <0.002
France, 1993, R93567A2	FS	3750		147	<0.002 ≤0.002	<0.002 0.004	0.003 ≤0.002	NR	<0.002 <0.002
France, 1993, R93567E1	FS	3750		165	<0.002 ≤0.002	<0.002 0.002	<0.002 0.003	NR	<0.002 <0.002
France, 1993, R93567F1	FS	3750		148	≤0.002	≤0.002	≤0.002	NR	<0.002
France, 1993, R93567H1	FS	3750		166	≤0.002	≤0.002	≤0.002	NR	<0.002
France, 1993, R93567K1	FS	3750	1	89	≤0.002	≤0.002	≤0.002	NR	<0.002
Soil application at sowing (Muller, 1996g)									
France, 1995, 95536OR1	GR		252	153	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1995, 95536AV1	GR		174	139	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Soil application at sowing (Maestracci, 1996a)									
France, 1995, 95537DJ1	GR		190	154	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1995, 95537TL1	GR		187	164	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Soil application before sowing (Maestracci, 1998c)									
France, 1997, 97542DJ1	WG		200	160	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97542OR1	WG		200	146	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97542BX1	WG		200	146	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97542LY1	WG		200	134	≤0.002	≤0.002	≤0.002	<0.002	<0.002
France, 1997, 97542TL1	WG		200	140	≤0.002	≤0.002	≤0.002	<0.002	<0.002
Soil application before sowing (Richard and Muller, 1994f)									
Italy, 1993, R93635BO1	GR		240	112	<0.002	<0.002	<0.002	NR	<0.002
Seed treatment (Muller, 1995f)									
Spain, 1994, 94667SE1	FS	10 000		133	<0.002	<0.002	<0.002	NR	<0.002
Seed treatment (Maestracci, 1997b)									
Spain, 1996, 96637M1	FS	10 000		179	<0.002	<0.002	<0.002	<0.002	<0.002
Spain, 1996, 96637SE1	FS	10 000		161	<0.002	<0.002	<0.002	<0.002	<0.002

NR: not reported

Table 75. Supervised trials on sugar beet, leaves and tops analysed (each trial 2 replicates). All single applications.

Country, Year, Location, Reference	Application		PHI	Residues, mg/kg				
	Form	g ai/ha	days	Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Soil treatment at sowing (Claviere and Muller, 1990)								
France, 1990	GR	100	148	<0.01	<0.01	0.011	NR	<0.01
Rachecourt,				0.015	<0.01	0.013		<0.01
XE190I11		200	148	0.027	<0.01	<0.01		<0.01
				0.029	<0.01	0.012		<0.01
		300	148	0.028	<0.01	<0.01		<0.01
				0.029	<0.01	0.015		<0.01
France, 1990	GR	100	179	0.021	<0.01	<0.01	NR	<0.01
Allogny,				0.013	<0.01	<0.01		<0.01
XB290I11		200	179	<0.01	<0.01	0.012		<0.01
				<0.01	<0.01	0.013		<0.01
		300	179	<0.01	<0.01	0.011		<0.01
				0.012	<0.01	0.013		<0.01
France, 1990	GR	100	181	<0.01	<0.01	<0.01	NR	<0.01
Beaulieu,				<0.01	<0.01	<0.01		<0.01
XB190I11		200	181	<0.01	<0.01	<0.01		<0.01
				<0.01	<0.01	<0.01		<0.01
		300	181	<0.01	<0.01	0.011		<0.01
				0.013	<0.01	0.012		<0.01
France, 1990	GR	100	168	0.013	<0.01	<0.01	NR	<0.01
Le Meillard,				0.018	<0.01	<0.01		<0.01
XD290I11		200	168	0.017	<0.01	<0.01		<0.01
				0.021	<0.01	0.012		<0.01
		300	168	0.011	<0.01	0.011		<0.01
				0.017	<0.01	0.012		<0.01
France, 1990	GR	100	176	<0.01	<0.01	0.012	NR	<0.01
Mericourt,				<0.01	<0.01	0.016		<0.01
XD190I11		200	176	<0.01	<0.01	0.011		<0.01
				0.012	<0.01	0.018		<0.01
		300	176	0.01	<0.01	0.012		<0.01
				0.014	<0.01	0.017		<0.01
Soil treatment at sowing (Dupont and Muller, 1992)								
France, 1991	GR	150	178	<0.01	<0.01	<0.01	NR	<0.01
Faverolles, LE291I15				<0.01	<0.01	<0.01		<0.01
		200		<0.01	<0.01	<0.01		<0.01
				<0.01	<0.01	<0.01		<0.01
France, 1991	GR	150	181	<0.01	<0.01	<0.01	NR	<0.01
Guignonville,				0.014	<0.01	<0.01		<0.01
LB391I15		200	181	<0.01	<0.01	<0.01		<0.01
				0.011	<0.01	<0.01		<0.01
France, 1991	GR	150	161	<0.01	<0.01	<0.01	NR	<0.01
Autruche, LE191I15				<0.01	<0.01	<0.01		<0.01
		200	161	<0.01	<0.01	<0.01		<0.01
				<0.01	<0.01	<0.01		<0.01
France, 1991	GR	150	198	0.012	<0.01	<0.01	NR	<0.01
Bellegarde, LB191I15				0.015	<0.01	<0.01		<0.01
		200	198	<0.01	<0.01	<0.01		<0.01
				0.017	<0.01	<0.01		<0.01

Country, Year, Location, Reference	Application		PHI	Residues, mg/kg				
	Form	g ai/ha	days	Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
France, 1991 Meranville, LB491I15	GR	150	213	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01	NR	<0.01 <0.01
		200	213	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01		0.016 0.012
Soil treatment at sowing (Muller, 1994j)								
France, 1993 R93568B1 Gidy	GR	305	193	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1993 R93568B2 Patay	GR	334	196	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1993 R93568D1 Frohen le Grand	GR	251	181	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1993 R93568D2 Frohen le Grand	GR	281	190	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1993 R93568D3 Frohen le Grand	GR	211	175	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01	NR	<0.01 <0.01
France, 1993 R93568E1 Bazancourt	GR	253	166	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
Soil treatment at sowing (Muller, 1995e)								
France, 1994 945520R1 Patay	GR	245	189	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1994 94552AM1 Barly	GR	240	153	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
France, 1994 94552RS1 Muizon	GR	244	174	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
Soil treatment before sowing (Maestracci, 1998b)								
France, 1997 97521AM1 Barly	WG	200	168	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	<0.002 <0.002
France, 1997 97521DJ1 Neuilly les Dijon	WG	210	188	≤0.002 <0.002	≤0.002 <0.002	≤0.002 <0.002	<0.002 <0.002	<0.002 <0.002
France, 1997 97521OR1 Merevile	WG	200	181	≤0.002 <0.002	≤0.002 <0.002	0.006 0.005	<0.002 <0.002	<0.002 0.004
France, 1997 97521RS1 Reims	WG	200	186	≤0.002 <0.002	≤0.002 <0.002	0.003 0.002	<0.002 <0.002	<0.002 <0.002
Soil treatment at sowing (Richard and Muller, 1994b)								
Italy, 1993 93640BO1 CNS Bologna	GR	210	169	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01	NR	<0.01 <0.01
Italy, 1993 93630BO1 CNS Bologna	GR	150	169	<0.01 0.018	<0.01 ≤0.01	<0.01 0.01	NR	<0.01 <0.01
		300		<0.01 <0.01	<0.01 <0.01	<0.01 <0.01		<0.01 <0.01
Soil treatment in furrow at sowing (Muller, 1996e)								
Italy, 1995 95742BO1 CNS Corticella	GR	166	140	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01	<0.01 <0.01	<0.01 <0.01
Italy, 1995 95742BO2 Minerbio	GR	146	136	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01	<0.01 <0.01	<0.01 <0.01
Soil treatment (Muller, 1996l)								
Italy, 1995 95741BO1 CNS Corticella	GR	90	140	≤0.01	≤0.01	≤0.01	<0.01	<0.01
		141	140	<0.01	<0.01	<0.01	<0.01	<0.01
Italy, 1995 95741BO2 Minerbio	GR	106	136	≤0.01	≤0.01	≤0.01	<0.01	<0.01
		140	136	<0.01	<0.01	<0.01	<0.01	<0.01

Country, Year, Location, Reference	Application		PHI days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Soil treatment (Yslan and Baudet, 1999c)								
Spain, 1998 98589M1 Sta. Olalla Toledo	WG	197 1	197	≤0.002 <0.002	≤0.002 <0.002	0.002 <0.002	<0.002 <0.002	NR

NR: not reported

Table 76. Residues in maize forage, fodder, and green plant (forage) for use as silage. All single applications.

Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Seed treatment, 2 replicates (Muller, 1994c)											
France, 1993, R9356A1	silage green plant	FS	2500			118 60	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01	NR NR	<0.01 <0.01
Seed treatment, 2 replicates (Muller, 1994e)											
France, 1993, R93564A1	silage	FS	3750			118	≤0.005	≤0.005	≤0.005	NR	<0.005
France, 1993, R93564B1	silage	FS	3750			118	≤0.005	≤0.005	≤0.005	NR	<0.005
France, 1993, R93564C1	silage	FS	3750			118	≤0.005	≤0.005	≤0.005	NR	<0.005
France, 1993, R93564E	silage	FS	3750			118	≤0.005	≤0.005	≤0.005	NR	<0.005
France, 1993, R93564F1	silage	FS	3750			118	≤0.005	≤0.005	≤0.005	NR	<0.005
France, 1993, R93564K1	silage	FS	3750			118	≤0.005	≤0.005	≤0.005	NR	<0.005
Soil treatment incorporated granules in furrow, 2 replicates (Muller, 1996i)											
France, 1995, 95535BX1	silage	GR		298		116	<0.005	<0.005	<0.005	<0.005	<0.01
France, 1995, 95535AM1	silage	GR		177		112	≤0.005	≤0.005	≤0.005	<0.005	<0.005
Soil treatment pre-sowing (Maestracci, 1998d)											
France, 1997, 97540AM1	green plant	WG		200	66.7	159*	≤0.005	≤0.005	≤0.005	<0.005	NR
France, 1997, 97540OR1	green plant	WG		200	60.6	141*	≤0.005	≤0.005	≤0.005	<0.005	NR
France, 1997, 97540RS1	green plant	WG		200	84.7	139*	≤0.005	≤0.005	≤0.005	<0.005	NR
France, 1997, 97540RS2	green plant	WG		200	100	141*	≤0.005	≤0.005	≤0.005	<0.005	NR
France, 1997, 97540BX1	green plant cob	WG		200	60.6	132* 118	≤0.005 ≤0.002	≤0.005 ≤0.002	≤0.005 ≤0.002	<0.005 <0.002	NR <0.002
France, 1997, 97540BX2	green plant cob	WG		200	60.6	132* 118	≤0.005 ≤0.002	≤0.005 ≤0.002	≤0.005 ≤0.002	<0.005 <0.002	NR <0.002
France, 1997, 97540TL1	green plant cob	WG		200	60.6	127* 105	≤0.005 <0.002 <0.002	≤0.005 <0.002 0.003	≤0.005 <0.002 <0.002	<0.005 <0.002 <0.002	NR <0.002 <0.002
France, 1997, 97540TL2	green plant cob	WG		200	60.6	132* 110	≤0.005 <0.002 0.003	≤0.005 0.003 0.005	≤0.005 <0.002 <0.002	<0.005 <0.002 <0.002	NR <0.002 <0.002
Soil treatment at sowing (Muller, 1995d)											
Greece, 1994, 94672GR1	silage	GR		200		77	≤0.002	≤0.002	≤0.002	NR	≤0.002
Greece, 1994, 94672GR1	silage	GR		400		77	<0.002	<0.002	<0.002	NR	<0.002
Soil treatment at sowing (Richard and Muller, 1994g)											
Italy, 1993, R93633BO1	shoot	GR		240		122	<0.01	<0.01	<0.01	NR	0.01

Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Soil treatment at sowing, 2 replicates (Muller, 1996c)											
Italy, 1995, 95744BO1	shoot	GR		153		115	≤0.005	≤0.005	≤0.005	<0.005	≤0.005
Italy, 1995, 95744BO2	shoot	GR		155		100	≤0.005	≤0.005	≤0.005	<0.005	≤0.005
Soil treatment at sowing, 3 replicates (Kowite, 1993a)											
USA, 1992, 92-015 INC	forage	GR		146		45	<0.02 <0.001 (2)	<0.003 <0.003 (2)	<0.005 <0.005 (2)	<0.004 <0.004 (2)	<0.02 <0.003 (2)
	silage					110	≤0.007 <0.007 <0.007	≤0.004 <0.004 <0.004	≤0.02 <0.005 <0.005	<0.003 <0.003 <0.003	<0.02 <0.004 <0.02
	fodder					146	≤0.02 <0.003	≤0.007 <0.007	≤0.02 <0.02	<0.004 <0.004	<0.02 <0.006
USA, 1992, 92-015 T-band	forage	GR		146		45	<0.001 (2) <0.02	<0.003 (2) <0.003	<0.005 (2) <0.005	<0.004 (2) <0.004	<0.003 (2) <0.003
	silage					110	≤0.007	≤0.004	≤0.005	<0.003	<0.004
	fodder					146	<0.003 ≤0.02 <0.02	<0.007 ≤0.007 <0.007	<0.02 0.022 <0.02	<0.004 <0.004 <0.004	<0.02 <0.02 <0.02
USA, 1992, 92-016	forage	GR		146		45	<0.001(2) <0.001	<0.003 (2) <0.003	<0.005 (2) <0.005	<0.004 (2) <0.004	<0.003 (2) <0.02
	silage					109	≤0.007 <0.007 <0.007	≤0.004 <0.004 <0.004	≤0.02 <0.02 <0.005	<0.003 <0.003 <0.003	<0.02 <0.02 <0.004
	fodder					157	<0.02 <0.02 ≤0.02	<0.007 <0.007 ≤0.007	0.031 0.022 0.033	<0.02 <0.02 <0.02	<0.02 <0.02 <0.02
USA, 1992, 92-019 INC	forage	GR		146		45	<0.001	<0.003	<0.005	<0.004	<0.003
	silage					137	<0.007 (2) ≤0.007	<0.004 (2) ≤0.004	<0.005(2) 0.005	<0.003 (2) <0.02	<0.004 <0.004
	fodder					191	≤0.003 (2) <0.003	≤0.007 (2) <0.007	≤0.02 (2) <0.005	<0.004 (2) <0.004	2<0.006 <0.006
USA, 1992, 92-019 T-band	forage	GR		146		45	<0.02 (2) <0.02	<0.003 (2) <0.003	<0.005 (2) <0.005	<0.004 (2) <0.004	2<0.003 <0.02
	silage					137	<0.007 <0.007 ≤0.02	<0.004 <0.004 ≤0.02	<0.005 <0.005 ≤0.02	<0.003 <0.02 <0.02	<0.004 <0.004 <0.004
	fodder					191	≤0.02	≤0.007	≤0.02	<0.004	<0.006
USA, 1992, 92-029	forage	GR		157		45	<0.02 (2) <0.02	<0.003 (2) <0.003	<0.005 (2) <0.005	<0.004 (2) <0.004	<0.003 (2) <0.02
	silage					117	≤0.007	≤0.004	≤0.005	<0.003	<0.004
	fodder					153	≤0.02	≤0.007	≤0.02	<0.004	<0.006
USA, 1992, 92-039	forage	GR		135		45	<0.001	<0.003	<0.005	<0.004	<0.003
	silage					102	≤0.007	≤0.004	≤0.005	<0.003	<0.004
	fodder					156	≤0.003 (2) <0.003	≤0.02 (2) <0.007	≤0.005 (2) <0.005	<0.004 (2) <0.004	<0.006 (2) <0.006
USA, 1992, 92-058 INC	forage	GR		157		45	<0.02	<0.003	<0.005	<0.004	<0.003
	silage					129	≤0.007	≤0.004	≤0.005	<0.003	<0.004
	fodder					159	≤0.003	≤0.007	≤0.02	<0.004	<0.006

Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1992, 92-058 T-band	forage	GR		157		45	<0.02	<0.003	<0.005	<0.004	<0.003
	silage					129	<0.007 (2) ≤0.007	<0.004 (2) 0.004	<0.005 (2) ≤0.005	<0.003 (2) <0.003	<0.004 (2) <0.02
	fodder					159	<0.003 ≤0.02 <0.003	<0.007 ≤0.007 <0.007	<0.02 ≤0.02 <0.005	<0.004 <0.004 <0.004	<0.006 <0.006 <0.02
USA, 1992, 92-076	forage	GR		135		45	<0.02	<0.003	<0.02	<0.004	<0.02
	silage					115	<0.007 (2) ≤0.02	<0.004 (2) ≤0.004	<0.02 (2) ≤0.02	2<0.003 <0.003	<0.02 (2) <0.02
	fodder					151	<0.02 ≤0.02 <0.02	<0.007 ≤0.007 <0.007	<0.02 0.024 0.021	<0.02 <0.004 <0.02	<0.02 <0.02 <0.02
USA, 1992, 92-094	forage	GR		146		45	<0.02	<0.003	<0.02	<0.004	<0.02
	silage					121	≤0.007 (2) <0.007	≤0.004 (2) <0.004	≤0.02 (2) <0.005	2<0.003 <0.003	<0.004 (2) <0.004
	fodder					173	<0.02 ≤0.02 <0.02	<0.02 ≤0.007 <0.007	0.029 0.042 0.03	<0.004 <0.004 <0.004	<0.02 <0.02 <0.02
USA, 1992, 92-097	forage	GR		146		46	<0.02	<0.003	<0.005	<0.004	<0.02
	silage					130	≤0.007	≤0.004	≤0.005	<0.02	<0.02
	fodder					162	≤0.02	≤0.007	≤0.02	<0.004	<0.02
USA, 1992, 92-101 INC	forage	GR		146		71	<0.02 (2) <0.02	<0.003 (2) <0.003	<0.005 (2) <0.005	<0.004 (2) <0.004	<0.02 (2) <0.003
	silage					126	≤0.02	≤0.004	≤0.02	<0.003	<0.02
	fodder					169	NR	NR	NR	NR	NR
USA, 1992, 92-101 T-band	forage	GR		146		71	<0.02	<0.003	<0.005	<0.004	<0.02
	silage					126	<0.007 (2) ≤0.02	<0.004 (2) 0.004	<0.02 (2) ≤0.02	2<0.003 <0.003	<0.02 (2) <0.02
	fodder					169	<0.02 <0.02 ≤0.02	<0.007 <0.007 ≤0.007	0.029 0.034 0.038	<0.02 <0.02 <0.02	<0.02 0.02 <0.02
Soil treatment at sowing, 3 replicates (Kowite, 1994)											
USA, 1993, 93-206 T-band	forage	GR		146		45	<0.001	<0.003	<0.005	NR	<0.003
	silage					113	≤0.02	≤0.004	≤0.02		<0.02
	fodder					148	<0.02 ≤0.02 <0.02	<0.007 ≤0.02 <0.02	0.022 0.031 0.027		<0.02 <0.02 <0.02
USA, 1993, 93-206 INC	forage	GR		146		45	<0.02 (2) <0.02	<0.003 (2) <0.003	<0.02 (2) <0.02	NR	2<0.003 <0.02
	silage					113	≤0.02	≤0.004	≤0.02		<0.02
	fodder					148	<0.02 <0.02 0.02	<0.007 <0.02 ≤0.007	0.047 0.045 0.073		0.025 0.024 0.03
USA, 1993. 93-207	forage	GR		146		45	<0.001	<0.003	<0.005	NR	<0.003
	silage					103	≤0.02 <0.007 (2)	≤0.004 <0.004 (2)	≤0.02 <0.005 (2)		<0.02 <0.02 (2)
	fodder					140	≤0.02 <0.02 <0.02	≤0.02 <0.007 <0.02	≤0.02 <0.02 <0.02		<0.02 <0.02 <0.006

Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1993, 93-208	forage	GR		146		44	<0.02 <0.02 <0.02	<0.02 <0.003 <0.02	<0.005 <0.005 <0.005	NR	<0.003 <0.02 <0.003
	silage					96	0.022 <0.02 <0.02	≤0.004 <0.004 <0.004	≤0.02 <0.02 0.021		<0.02 <0.02 <0.02
	fodder					125	≤0.02	≤0.007	≤0.02		<0.02
USA, 1993, 93-209	silage	GR		146		96	≤0.007 <0.007 <0.007	≤0.004 <0.004 <0.004	≤0.005 <0.005 <0.005	NR	<0.02 <0.02 <0.004
	fodder					168	≤0.003	≤0.02	≤0.02		<0.006
USA, 1993, 93-210	forage	GR		146		45	<0.02	<0.003	<0.005	NR	<0.003
	silage					106	≤0.007	≤0.004	≤0.005		<0.004
	fodder					128	≤0.02	≤0.02	≤0.02		<0.02
USA, 1993, 93-211	forage	GR		146		45	0.056 0.03 0.03	<0.02 <0.003 <0.003	0.044 0.024 0.027	NR	0.031 0.022 <0.02
	silage					109	≤0.02 <0.02 <0.02	≤0.004 <0.004 <0.004	0.036 <0.02 0.024		<0.02 <0.02 <0.02
	fodder					124	≤0.02 <0.02 <0.02	≤0.007 <0.007 <0.007	0.025 0.022 <0.02		<0.02 <0.02 <0.02
USA, 1993, 93-212 T-band	forage	GR		146		45	<0.02	<0.003	<0.005	NR	<0.003
	silage					115	≤0.007	≤0.004	≤0.005		<0.004
	fodder					171	≤0.003	≤0.007	≤0.005		<0.006
USA, 1993, 93-212 INC	forage	GR		146		45	<0.02	<0.002	<0.005	NR	<0.003
	silage					115	<0.007 (2) ≤0.007	<0.004 (2) ≤0.004	<0.005 (2) ≤0.02		<0.02 (2) <0.02
	fodder					171	≤0.02 (2) <0.02	≤0.007 (2) <0.007	≤0.02 (2) <0.02		<0.02 (2) <0.006
USA, 1993, 93-213 T-band	forage	GR		146		45	<0.02 (2) 0.021	2<0.003 <0.003	<0.02 (2) <0.02	NR	<0.02 (2) <0.02
	silage					129	<0.007 (2) ≤0.007	<0.004 (2) ≤0.02	<0.005 (2) ≤0.005		<0.004 (2) <0.004
	fodder					171	<0.02 (2) 0.02	<0.02 (2) 0.007	<0.02 (2) 0.02		2<0.006 0.006
USA, 1993, 93-213 INC	forage	GR		146		45	0.026 0.025 0.028	<0.003 <0.003 <0.003	<0.02 <0.02 <0.02	NR	<0.02 <0.02 <0.02
	silage					129	<0.007 (2) ≤0.007	<0.004 (2) ≤0.004	<0.005 (2) ≤0.005		<0.004 (2) <0.02
	fodder					171	≤0.02	≤0.02	≤0.02		<0.006
USA, 1993, 93-214 T-band	forage	GR		146		47	<0.02 (2) <0.02	2<0.003 <0.003	<0.02 (2) <0.005	NR	<0.02 (2) <0.02
	silage					103	<0.007 <0.02 ≤0.02	<0.004 <0.004 ≤0.004	<0.005 <0.02 ≤0.02		<0.02 <0.02 <0.02
	fodder					131	<0.02 ≤0.02 <0.003	<0.007 ≤0.007 <0.007	<0.02 ≤0.02 <0.02		<0.006 <0.02 <0.006

Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1993, 93-214 INC	forage	GR		146		47	0.024 <0.02 0.022	<0.003 <0.003 <0.003	<0.02 <0.02 <0.02	NR	<0.02 <0.02 <0.02
	silage					103	<0.007 (2) <u><0.02</u>	<0.004 (2) <u><0.004</u>	<0.005 (2) <u><0.02</u>		<0.004 (2) <0.02
	fodder					131	<0.02 (2) <u><0.02</u>	<0.007 (2) <u><0.007</u>	<0.02 (2) <u><0.02</u>		2<0.006 <0.02
USA, 1993, 93-215 T-band	forage	GR		146		45	<0.02 (2) <0.02	2<0.003 <0.003	<0.005 (2) <0.005	NR	<0.02 (2) <0.003
	silage					111	<0.007 (2) <u><0.007</u>	<0.004 (2) <u><0.004</u>	<0.005 (2) <u><0.005</u>		<0.004 (2) <0.02
	fodder					140	<u><0.02</u>	<u><0.007</u>	<u><0.02</u>		<0.006
USA, 1993, 93-215 INC	forage	GR		146		45	<0.02 <0.001 <0.02	<0.003 <0.003 <0.003	<0.005 <0.005 <0.005	NR	<0.003 <0.003 <0.02
	silage					111	<u><0.007</u> <0.007 <0.007	<u><0.004</u> <0.004 <0.004	<u><0.02</u> <0.02 <0.005		<0.02 <0.02 <0.02
	fodder					140	<u><0.02</u>	<u><0.007</u>	<u><0.02</u>		<0.02
Soil treatment at sowing, 2 replicates (Kowite, 1996)											
USA, 1995, 95-0212 GR INC	forage	GR		146		88	<u><0.02</u>	<u><0.02</u>	<u><0.02</u>	NR	<0.02
	fodder					126	<u>0.04</u> 0.032	<u><0.02</u> <0.02	<u>0.055</u> 0.051		0.028 0.024
USA, 1995, 95-0212 SS INC	forage	WG		146		88	<u>0.023</u> <0.02	<u><0.02</u> <0.02	<u>0.03</u> <0.02	NR	<0.02 <0.02
	fodder					126	0.022 <u>0.025</u>	<0.02 <u><0.02</u>	0.04 <u>0.043</u>		0.02 0.02
USA, 1995, 95-0213 GR INC	forage	GR		146		105	<u><0.02</u>	<u><0.004</u>	<u><0.02</u>	NR	<0.02
	fodder					148	<0.02 <u><0.02</u>	<0.003 <u><0.02</u>	<0.02 <u><0.02</u>		<0.02 <0.02
USA, 1995, 95-0213 SS INC	forage	WG		146		105	<0.005 <u><0.02</u>	<0.004 <u><0.004</u>	<0.02 <u><0.02</u>	NR	<0.02 <0.02
	fodder					148	<u><0.02</u>	<u><0.003</u>	<u><0.02</u>		<0.02
USA, 1995, 95-0214 GR INC	forage	GR		146		105	<u><0.02</u>	<u><0.004</u>	<u><0.02</u>	NR	<0.02
	fodder					153	<u><0.02</u> <0.02	<u><0.003</u> <0.003	<u>0.034</u> 0.024		<0.02 <0.02
USA, 1995, 95-0214 SS INC	forage	WG		146		105	<u><0.02</u>	<u><0.004</u>	<u><0.02</u>	NR	<0.02
	fodder					153	<u><0.02</u> <0.02	<u><0.003</u> <0.003	<u>0.021</u> <0.02		<0.02 <0.02
USA, 1995, 95-0215 GR INC	forage	GR		146		120	<u><0.02</u> <0.005	<u><0.02</u> <0.004	<u><0.02</u> <0.02	NR	<0.02 <0.02
	fodder					159	<u><0.02</u> <0.02	<u><0.003</u> <0.003	<u><0.02</u> <0.008		<0.008 <0.008
USA, 1995, 95-0215 SS INC	forage	WG		146		120	<u><0.02</u>	<u><0.004</u>	<u><0.02</u>	NR	<0.02
	fodder					159	<u><0.02</u>	<u><0.003</u>	<u><0.02</u>		<0.008
USA, 1995, 95-0216 GR INC	forage	GR		146		88	<u><0.02</u>	<u><0.004</u>	<u><0.02</u>	NR	<0.02
	fodder					136	<0.02 <u><0.02</u>	<0.02 <u><0.02</u>	0.023 <u>0.025</u>		<0.02 <0.02
USA, 1995, 95-0216 SS INC	forage	WG		146		88	<u><0.02</u>	<u><0.004</u>	<u><0.02</u>	NR	<0.02
	fodder					136	<u><0.02</u>	<u><0.02</u>	<u>0.021</u>		<0.02

Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1995, 95-0217 GR INC	forage	GR		146		84	≤0.02	≤0.004	≤0.02	NR	<0.02
	fodder					122	≤0.02	≤0.003	0.036		<0.02
							<0.02	<0.003	0.03		<0.02
USA, 1995, 95-0217 SS INC	forage	WG		146		84	≤0.02	≤0.02	0.022	NR	<0.02
							<0.02	<0.02	<0.02		<0.02
	fodder					122	<0.02	<0.003	0.034		<0.02
							≤0.02	≤0.003	0.051		<0.02
USA, 1995, 95-0218 GR INC	forage	GR		146		84	<0.02	<0.004	0.022	NR	<0.02
							≤0.02	≤0.004	0.029		<0.02
	fodder					122	<0.02	<0.003	0.038		<0.02
							≤0.02	≤0.003	0.048		0.03
USA, 1995, 95-0218 SS INC	forage	WG		146		84	≤0.02	≤0.004	0.026	NR	<0.02
							<0.02	<0.004	0.024		<0.02
	fodder					122	≤0.02	≤0.02	0.046		0.024
							<0.02	<0.02	0.044		0.021
USA, 1995, 95-0219 GR INC	forage	GR		146		94	≤0.02	≤0.02	≤0.02	NR	<0.02
	fodder					116	≤0.02	≤0.003	0.025		<0.02
USA, 1995, 95-0219 SS INC	forage	WG		146		94	≤0.02	≤0.02	≤0.02	NR	<0.02
	fodder					116	≤0.02	≤0.003	≤0.02		<0.02
USA, 1995, 95-0220 GR INC	forage	GR		146		101	≤0.02	≤0.004	≤0.02	NR	<0.02
	fodder					143	≤0.02	≤0.02	0.025		<0.02
							<0.02	<0.02	0.024		<0.02
USA, 1995, 95-0220 SS INC	forage	WG		146		101	≤0.02	≤0.004	≤0.02	NR	<0.02
	fodder					143	0.023	<0.02	0.039		<0.02
							0.022	≤0.02	0.041		<0.02
USA, 1995, 95-0221 GR INC	forage	GR		146		105	<0.005	<0.004	<0.02	NR	<0.003
							≤0.005	≤0.004	≤0.02		<0.02
	fodder					160	≤0.02	≤0.003	≤0.02		<0.02
USA, 1995, 95-0221 SS INC	forage	WG		146		105	≤0.005	≤0.004	≤0.02	NR	<0.003
	fodder					160	≤0.02	≤0.003	≤0.02		<0.02
USA, 1995, 95-0222 GR INC	forage	GR		146		103	≤0.02	≤0.004	≤0.02	NR	<0.02
	fodder					150	≤0.02	≤0.003	0.038		<0.02
							<0.02	<0.003	<0.02		<0.008
USA, 1995, 95-0222 SS INC	forage	WG		146		103	≤0.02	≤0.004	≤0.02	NR	<0.02
	fodder					150	≤0.005	≤0.003	≤0.02		<0.008
USA, 1995, 95-0223 GR INC	forage	GR		146		92	0.022	≤0.02	0.028	NR	<0.02
							<0.02	<0.004	0.022		<0.02
	fodder					125	<0.02	<0.02	0.044		<0.02
							≤0.02	≤0.02	0.054		<0.02
USA, 1995, 95-0223 SS INC	forage	WG		146		92	0.038	≤0.02	0.043	NR	<0.02
							0.029	<0.004	0.032		<0.02
	fodder					125	0.032	<0.02	0.098		0.028
							0.04	≤0.02	0.106		0.029
Seed treatment, 2 replicates (Richard and Muller, 1995d)											
Spain, 1994, 94665SE1	fodder	FS	2500			174	≤0.002	≤0.002	≤0.002	NR	<0.002
Seed treatment, 2 replicates (Maestracci, 1996b)											
Spain, 1994, 95712SE1	fodder	FS	2500			155	≤0.005	≤0.005	≤0.005	<0.005	<0.005
Spain, 1994, 95712SE2	fodder	FS	2500			153	≤0.005	≤0.005	≤0.005	<0.005	<0.005

NR: not reported
*days between sowing and harvest, not between soil spray and harvest

Table 77. Residues in pasture grass after single foliar applications (each trial includes 2 replicates).

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Keats, 1996 f								
Australia, 1995, 94i55 Clermont Central Queensland	UL	5	0	0.051	<0.002	0.005	<0.002	NR
				0.051	<0.002	0.005	0.002	
			1	0.029	<0.002	0.004	<0.002	
				0.029	<0.002	0.005	<0.002	
			3	0.01	<0.002	0.006	0.002	
				0.011	<0.002	0.006	0.002	
			5	0.009	<0.002	0.007	0.003	
				0.009	<0.002	0.007	0.004	
			7	0.003	<0.002	0.003	<0.002	
				0.005	<0.002	0.003	<0.002	
Australia, 1995, 94i55 Clermont Central Queensland	UL	10	0	0.13	<0.002	0.013	0.003	NR
				0.14	<0.002	0.013	0.003	
			1	0.082	<0.002	0.01	0.003	
				0.071	<0.002	0.012	0.003	
			3	0.017	<0.002	0.01	0.005	
				0.019	<0.002	0.012	0.005	
			5	0.021	<0.002	0.016	0.007	
				0.017	<0.002	0.016	0.008	
			7	0.01	<0.002	0.01	0.004	
				0.011	<0.002	0.01	0.004	
Australia, 1995, 94i55 Clermont Central Queensland	UL	20	0	0.25	0.002	0.029	0.025	NR
				0.17	<0.002	0.029	0.025	
			1	0.13	<0.002	0.022	0.02	
				0.12	<0.002	0.023	0.019	
			3	0.04	<0.002	0.019	0.015	
				0.041	<0.002	0.019	0.015	
			5	0.023	<0.002	0.017	0.012	
				0.021	<0.002	0.017	0.013	
			7	0.011	<0.002	0.008	0.007	
				0.018	<0.002	0.008	0.008	
Australia, 1995, 94i55 Clermont Central Queensland	UL	30	0	0.52	0.003	0.045	0.042	NR
				0.52	0.003	0.041	0.043	
			1	0.29	0.003	0.04	0.036	
				0.29	0.003	0.034	0.037	
			3	0.17	0.002	0.047	0.048	
				0.18	0.003	0.045	0.048	
			5	0.08	<0.002	0.036	0.034	
				0.083	<0.002	0.036	0.035	
			7	0.029	<0.002	0.022	0.022	
				0.028	<0.002	0.023	0.023	
Keats, 1996 k								
Australia, 1995, AUS94i55b Springfield via Orange, NSW	WG	5	0	0.005	<0.002	<0.002	<0.002	NR
				0.005	<0.002	<0.002	<0.002	
			1	0.003	<0.002	<0.002	<0.002	
				0.003	<0.002	<0.002	<0.002	
			3	0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
			5	0.002	<0.002	<0.002	<0.002	
				0.002	<0.002	<0.002	<0.002	
			7	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1995, AUS94i55b Springfield via Orange, NSW	WG	10	0	0.011	<0.002	<0.002	<0.002	NR
				0.011	<0.002	<0.002	0.002	
			1	0.006	<0.002	<0.002	<0.002	
				0.006	<0.002	<0.002	<0.002	
			3	0.004	<0.002	<0.002	<0.002	
				0.004	<0.002	<0.002	<0.002	
			5	0.003	<0.002	<0.002	<0.002	
				0.003	<0.002	<0.002	<0.002	
			7	0.003	<0.002	<0.002	<0.002	
				0.003	<0.002	<0.002	<0.002	
Australia, 1995, AUS94i55b Springfield via Orange, NSW	WG	20	0	0.021	<0.002	<0.002	0.004	NR
				0.02	<0.002	<0.002	0.004	
			1	0.014	<0.002	<0.002	0.003	
				0.014	<0.002	<0.002	0.003	
			3	0.009	<0.002	<0.002	0.003	
				0.009	<0.002	<0.002	0.002	
			5	0.005	<0.002	<0.002	0.002	
				0.005	<0.002	<0.002	0.002	
			7	0.006	<0.002	<0.002	<0.002	
				0.005	<0.002	<0.002	<0.002	
Australia, 1995, AUS94i55b Springfield via Orange, NSW	WG	30	0	0.032	<0.002	<0.002	0.005	NR
				0.032	<0.002	<0.002	0.004	
			1	0.02	<0.002	<0.002	0.005	
				0.02	<0.002	<0.002	0.005	
			3	0.014	<0.002	<0.002	0.003	
				0.014	<0.002	<0.002	0.004	
			5	0.007	<0.002	<0.002	0.003	
				0.007	<0.002	<0.002	0.003	
			7	0.008	<0.002	<0.002	0.002	
				0.009	<0.002	<0.002	0.002	
Keats, 1996 g								
Australia, 1995, AUS95i55R Binguy New South Wales	UL	5	1	0.11	<0.002	0.009	0.003	NR
				0.091	<0.002	0.009	0.003	
			3	0.03	<0.002	0.011	0.005	
				0.026	<0.002	0.011	0.005	
			5	0.021	<0.002	0.014	0.007	
				0.019	<0.002	0.014	0.007	
			7	0.007	0.006	0.007	<0.002	
				0.009	<0.002	0.007	0.003	
Australia, 1995, AUS95i55R Binguy New South Wales	UL	10	1	0.23	<0.002	0.021	0.005	NR
				0.2	<0.002	0.01	0.003	
			3	0.045	<0.002	0.01	0.006	
				0.039	<0.002	0.022	0.01	
			5	0.045	<0.002	0.033	0.016	
				0.042	<0.002	0.031	0.016	
			7	0.027	<0.002	0.02	0.008	
				0.029	<0.002	0.021	0.008	
Australia, 1995, AUS95i55R Binguy New South Wales	UL	15	1	0.42	0.003	0.044	0.034	NR
				0.38	0.003	0.038	0.027	
			3	0.14	0.004	0.033	0.021	
				0.13	0.004	0.025	0.022	
			5	0.066	<0.002	0.023	0.018	
				0.057	<0.002	0.031	0.019	
			7	0.028	<0.002	0.015	0.014	
				0.037	<0.002	0.016	0.014	

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1995, AUS95i55R Binguy New South Wales	UL	30	1	0.78	0.004	0.06	0.054	NR
				0.71	0.004	0.053	0.051	
			3	0.44	0.004	0.07	0.077	
				0.44	0.004	0.067	0.067	
			5	0.22	0.002	0.056	0.044	
				0.21	0.002	0.046	0.022	
			7	0.075	<0.002	0.031	0.031	
				0.073	<0.002	0.031	0.03	
Keats, 1996 l								
Australia, 1995, AUS94i55cR Gingin Western Autralia	SC	5	0	0.18	0.005	0.004	0.042	NR
				0.18	0.004	0.005	0.044	
			1	0.067	0.005	0.005	0.05	
				0.065	0.005	0.005	0.05	
			3	0.032	0.008	0.004	0.026	
				0.031	0.008	0.004	0.026	
			5	0.004	0.004	<0.002	0.004	
				0.003	0.004	<0.002	0.004	
			7	0.003	0.004	<0.002	0.003	
				0.003	0.004	<0.002	0.004	
Australia, 1995, AUS94i55cR Gingin Western Australia	SC	10	0	0.36	0.014	0.017	0.15	NR
				0.36	0.015	0.018	0.15	
			1	0.27	0.014	0.01	0.13	
				0.27	0.014	0.011	0.14	
			3	0.17	0.015	0.017	0.15	
				0.18	0.015	0.018	0.16	
			5	0.072	0.018	0.01	0.058	
				0.069	0.017	0.008	0.056	
			7	0.005	0.005	<0.002	0.006	
				0.005	0.004	<0.002	0.006	
Australia, 1995, AUS94i55cR Gingin Western Autralia	SC	20	0	0.44	0.027	0.052	0.30	NR
				0.44	0.024	0.058	0.29	
			1	0.39	0.014	0.023	0.18	
				0.41	0.018	0.041	0.21	
			3	0.24	0.026	0.047	0.27	
				0.24	0.026	0.047	0.28	
			5	0.22	0.033	0.059	0.36	
				0.21	0.024	0.043	0.31	
			7	0.14	0.031	0.038	0.23	
				0.14	0.034	0.042	0.24	
Australia, 1995, AUS94i55cR Gingin Western Australia	SC	30	0	0.5	0.056	0.1	0.27	NR
				0.5	0.056	0.1	0.25	
			1	0.46	0.046	0.082	0.24	
				0.46	0.045	0.086	0.24	
			3	0.26	0.031	0.073	0.21	
				0.26	0.031	0.076	0.20	
			5	0.23	0.024	0.056	0.23	
				0.24	0.025	0.056	0.23	
			7	0.23	0.027	0.077	0.27	
				0.23	0.028	0.077	0.26	

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Keats, 1996 j								
Australia, 1996, AUS94i55d Springfield via Orange, NSW	SC	5	0	0.009	<0.002	<0.002	<0.002	NR
				0.009	<0.002	<0.002	<0.002	
			1	0.005	<0.002	<0.002	<0.002	
				0.005	<0.002	<0.002	<0.002	
			3	0.004	<0.002	<0.002	<0.002	
				0.004	<0.002	<0.002	<0.002	
			5	0.002	<0.002	<0.002	<0.002	
				0.002	<0.002	<0.002	<0.002	
			7	0.002	<0.002	<0.002	<0.002	
				0.002	<0.002	<0.002	<0.002	
Australia, 1996, AUS94i55d Springfield via Orange, NSW	SC	10	0	0.015	<0.002	<0.002	<0.002	NR
				0.015	<0.002	<0.002	<0.002	
			1	0.009	<0.002	<0.002	<0.002	
				0.009	<0.002	<0.002	<0.002	
			3	0.006	<0.002	<0.002	<0.002	
				0.006	<0.002	<0.002	<0.002	
			5	0.004	<0.002	<0.002	<0.002	
				0.004	<0.002	<0.002	<0.002	
			7	0.003	<0.002	<0.002	<0.002	
				0.004	<0.002	<0.002	<0.002	
Australia, 1996, AUS94i55d Springfield via Orange, NSW	SC	15	0	0.038	<0.002	<0.002	0.004	NR
				0.039	<0.002	<0.002	0.004	
			1	0.023	<0.002	<0.002	0.003	
				0.023	<0.002	<0.002	0.003	
			3	0.014	<0.002	<0.002	0.002	
				0.015	<0.002	<0.002	0.002	
			5	0.008	<0.002	<0.002	0.002	
				0.008	<0.002	<0.002	0.002	
			7	0.008	<0.002	<0.002	<0.002	
				0.009	<0.002	<0.002	<0.002	
Australia, 1996, AUS94i55d Springfield via Orange, NSW	SC	30	0	0.087	<0.002	<0.002	0.006	NR
				0.072	<0.002	<0.002	0.005	
			1	0.04	<0.002	<0.002	0.005	
				0.043	<0.002	<0.002	0.005	
			3	0.026	<0.002	<0.002	0.004	
				0.025	<0.002	<0.002	0.004	
			5	0.011	<0.002	<0.002	0.003	
				0.012	<0.002	<0.002	0.003	
			7	0.013	<0.002	<0.002	0.002	
				0.012	<0.002	<0.002	0.002	

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Keats, 1998e								
Australia, 1998, 98NST08 Mt. Mclaren Queensland	UL	1.25	0	0.035	<0.002	0.005	0.002	NR
				0.041	0.003	0.003	0.006	
			2	0.032	<0.002	<0.002	0.004	
				0.026	0.004	0.004	0.004	
			4	0.014	0.004	0.003	<0.002	
				0.023	0.003	0.005	0.003	
			7	0.009	<0.002	0.005	<0.002	
				0.007	<0.002	0.005	<0.002	
			15	0.004	<0.002	0.003	<0.002	
				0.004	<0.002	0.003	<0.002	
			21	0.002	<0.002	<0.002	<0.002	
				0.003	<0.002	0.002	<0.002	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
Australia, 1998, 98NST08 Mt. Mclaren Queensland	UL	2.5	0	0.067	0.002	0.004	0.005	NR
				0.058	0.002	0.004	0.009	
			2	0.029	0.004	0.002	0.01	
				0.033	0.004	0.006	0.014	
			4	0.018	0.002	0.007	0.004	
				0.024	0.002	0.009	0.008	
			7	0.021	0.002	0.015	<0.002	
				0.021	0.002	0.013	<0.002	
			15	0.008	<0.002	0.003	<0.002	
				0.008	<0.002	0.003	<0.002	
			21	0.007	<0.002	0.006	0.002	
				0.005	<0.002	0.006	0.002	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
Australia, 1998, 98NST08 Mt. Mclaren Queensland	UL	5.0	0	0.20	0.009	0.008	0.02	NR
				0.22	0.003	0.004	0.019	
			2	0.09	0.004	0.003	0.02	
				0.098	0.003	0.005	0.024	
			4	0.059	0.003	0.005	0.006	
				0.047	0.005	0.009	0.01	
			7	0.027	0.002	0.006	<0.002	
				0.027	0.002	0.011	<0.002	
			15	0.014	<0.002	0.009	0.003	
				0.02	0.002	0.011	0.004	
			21	0.02	0.002	0.007	0.003	
				0.021	0.002	0.008	0.003	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1998, 98NST08 Mt. Mclaren Queensland	UL	7.5	0	0.29	0.01	0.012	0.024	NR
				0.31	0.014	0.006	0.034	
			2	0.19	0.008	0.007	0.035	
				0.21	0.012	0.013	0.045	
			4	0.089	0.011	0.026	0.01	
				0.079	0.005	0.012	0.01	
			7	0.073	<0.002	0.035	0.002	
				0.073	0.005	0.034	0.005	
			15	0.022	0.002	0.015	0.004	
				0.018	0.002	0.013	0.003	
			21	0.027	0.003	0.012	0.004	
				0.024	0.003	0.013	0.004	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
Keats, 1998f								
Australia, 1998, 98NST10 Clermont Queensland	UL	1.25	0	0.026	<0.002	0.004	0.002	NR
				0.03	0.002	0.003	0.004	
			2	0.022	<0.002	0.004	0.014	
				0.018	0.003	0.004	0.01	
			4	0.01	0.002	0.002	0.004	
				0.009	0.003	0.005	0.003	
			7	0.007	<0.002	<0.002	<0.002	
				0.009	<0.002	<0.002	0.003	
			16	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
			21	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
Australia, 1998, 98NST10 Clermont Queensland	UL	2.5	0	0.045	0.004	0.004	0.006	NR
				0.053	0.004	0.004	0.01	
			2	0.034	0.002	0.008	0.011	
				0.028	0.002	0.004	0.009	
			4	0.01	0.002	0.01	0.004	
				0.018	0.003	0.006	0.004	
			7	0.007	<0.002	<0.002	0.003	
				0.011	<0.002	<0.002	<0.002	
			16	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
			21	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1998. 98NST10 Clermont Queensland	UL	5.0	0	0.13	0.005	0.009	0.016	NR
				0.14	0.009	0.013	0.012	
			2	0.07	0.003	0.013	0.016	
				0.078	0.005	0.009	0.02	
			4	0.03	0.002	0.002	0.008	
				0.038	0.006	0.002	0.004	
			7	0.016	0.002	0.002	0.003	
				0.008	0.002	0.002	0.003	
			16	0.004	<0.002	0.003	<0.002	
				0.004	<0.002	0.003	<0.002	
			21	0.002	<0.002	<0.002	<0.002	
				0.002	<0.002	<0.002	<0.002	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
Australia, 1998, 98NST10 Clermont Queensland	UL	7.5	0	0.16	0.01	0.01	0.018	NR
				0.18	0.01	0.014	0.02	
			2	0.10	0.006	0.003	0.03	
				0.12	0.012	<0.002	0.026	
			4	0.049	0.007	0.009	0.01	
				0.057	0.005	0.011	0.008	
			7	0.014	<0.002	0.005	0.003	
				0.023	0.004	0.003	0.005	
			16	0.003	<0.002	0.002	<0.002	
				0.003	<0.002	0.003	<0.002	
			21	0.005	<0.002	0.003	<0.002	
				0.005	<0.002	0.005	0.002	
			28	<0.002	<0.002	<0.002	<0.002	
				<0.002	<0.002	<0.002	<0.002	
Richard and Muller, 1995c								
Mauritania, 1994, Mauritania 94686XX1	UL	11.04	2	0.095	<0.01	0.011	<0.01	<0.01
				0.011	<0.01	<0.01	<0.01	<0.01
				0.047	<0.01	0.028	<0.01	<0.01
				0.044	<0.01	0.029	<0.01	<0.01
				0.26	0.024	0.120	0.025	<0.01
			9	<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	0.012	<0.01	<0.01
				0.016	<0.01	0.021	<0.01	<0.01
				0.031	<0.01	0.04	<0.01	<0.01
				0.023	<0.01	0.047	<0.01	<0.01
				<0.01	<0.01	0.014	<0.01	<0.01
			16	<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	0.012	<0.01	<0.01
				<0.01	<0.01	0.017	<0.01	<0.01
				0.034	<0.01	0.077	<0.01	<0.01
				0.02	<0.01	0.018	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
			23	<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
			30	<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
				0.014	<0.01	0.025	<0.01	<0.01
				0.013	<0.01	0.034	<0.01	<0.01
				<0.01	<0.01	<0.01	<0.01	<0.01
Yslan, 1999								
Russia, 1998	EC	4	0	0.20	<0.01	0.04	0.015	NR
982008STA1				0.26	<0.01	0.041	<0.01	
Levokoumsk			1	0.068	<0.01	0.044	0.02	
(STRAVOPOL				0.14	<0.01	0.058	0.017	
KRAI)			3	0.046	<0.01	0.05	0.02	
Russia North				0.039	<0.01	0.044	0.017	
			7	0.019	<0.01	0.019	<0.01	
				NA	NA	NA	NA	
			14	0.118	<0.01	0.018	<0.01	
				NA	NA	NA	NA	
			21	<0.01	<0.01	<0.01	<0.01	
				NA	NA	NA	NA	
			28	<0.01	<0.01	<0.01	<0.01	
				<0.01	<0.01	<0.01	<0.01	
Viljoen and van Zyl, 1998								
South Africa, 1997, RS97101 De Ar Hanover grassveld	UL	7.5	1 h	3.8	0.14	0.45	<0.01	<0.01
				5.9	0.13	0.68	<0.01	<0.01
			1	3.0	0.04	0.82	0.04	<0.01
				2.6	0.04	0.70	0.01	0.01
			3	0.55	<0.01	0.26	0.11	<0.01
				0.55	<0.01	0.26	0.16	<0.01
			7	0.17	<0.01	0.33	0.18	<0.01
				0.17	<0.01	0.33	0.19	<0.01
			14	0.04	<0.01	0.21	0.06	<0.01
				0.04	<0.01	0.22	0.06	<0.01
			21	0.21	<0.01	0.32	0.13	<0.01
				0.2	<0.01	0.28	0.13	<0.01
South Africa, 1997, RS97101 De Ar Hanover grassveld		15	1 h	8.5	0.19	0.87	<0.01	<0.01
				8.7	0.15	0.81	<0.01	<0.01
			1	2.9	0.03	0.67	<0.01	<0.01
				4.2	0.06	1.0	0.07	0.01
			3	2.1	<0.01	0.78	0.14	<0.01
				2.1	<0.01	0.80	0.14	<0.01
			7	1.9	<0.01	1.0	0.41	<0.01
				1.8	<0.01	1.0	0.41	<0.01
			14	0.67	<0.01	0.61	0.26	<0.01
				0.66	<0.01	0.61	0.26	<0.01
			21	0.33	<0.01	0.48	0.22	<0.01
				0.36	<0.01	0.49	0.22	<0.01

Country, Year, Reference	Application		PHI, days	Residues, mg/kg				
	Form	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
South Africa, 1997, RS97101 De Ar Hanover bossieveld	UL	7.5	1 h	0.69	0.61	0.46	<0.01	0.42
				0.67	0.64	0.44	<0.01	0.37
			1	0.60	0.01	0.37	<0.01	0.19
				0.60	<0.01	0.37	<0.01	0.19
			3	0.40	0.09	0.11	<0.01	0.02
				0.39	0.09	0.11	<0.01	0.03
			7	0.06	0.04	0.12	0.01	<0.01
				0.06	0.04	0.14	0.02	<0.01
			14	0.04	0.02	<0.01	<0.01	0.16
				0.03	0.02	<0.01	<0.01	0.19
			21	<0.05	<0.01	0.02	<0.01	<0.01
				NA	<0.01	0.02	<0.01	<0.01
South Africa, 1997, RS97101 De Ar Hanover bossieveld	UL	15	1 h	0.21	0.33	0.19	<0.01	0.24
				0.21	0.30	0.19	<0.01	0.24
			1	0.21	0.17	0.22	<0.01	0.11
				0.22	0.17	0.22	<0.01	0.11
			3	0.98	0.12	0.16	0.65	<0.01
				1.1	0.20	0.21	0.73	<0.01
			7	0.07	0.04	0.07	0.07	0.08
				0.08	0.04	0.07	0.07	0.09
			14	0.04	<0.01	0.04	0.81	<0.01
				0.04	<0.01	0.06	0.85	<0.01
			21	0.04	0.10	0.25	<0.01	0.04
				0.04	0.10	0.25	<0.01	0.04
South Africa, 1997, RS97101 De Ar Hanover mixedveld	UL	7.5	1 h	2.1	<0.01	0.03	<0.01	0.04
				2.1	<0.01	0.03	<0.01	0.04
			1	1.4	<0.01	0.04	<0.01	0.04
				1.4	<0.01	0.34	<0.01	0.04
			3	0.76	0.09	<0.01	0.06	0.07
				0.73	0.11	<0.01	0.05	0.07
			7	1.1	<0.01	<0.01	0.15	0.07
				0.82	<0.01	<0.01	0.13	0.07
			14	0.38	<0.01	<0.01	0.06	0.07
				0.71	<0.01	<0.01	0.07	0.10
			21	0.43	<0.01	<0.01	0.05	0.09
				0.44	<0.01	<0.01	0.05	0.09
South Africa, 1997, RS97101 De Ar Hanover mixedveld	UL	15	1 h	2.8	<0.01	0.03	<0.01	0.03
				2.8	<0.01	0.02	<0.01	0.03
			1	2.6	<0.01	0.01	<0.01	0.09
				2.6	<0.01	0.01	<0.01	0.10
			3	2.3	0.06	<0.01	<0.01	0.09
				2.3	<0.01	<0.01	<0.01	0.09
			7	1.9	0.11	<0.01	0.18	0.04
				1.9	0.10	<0.01	0.18	0.04
			14	0.86	<0.01	0.09	<0.01	0.15
				0.82	<0.01	0.09	0.14	0.15
			21	0.17	<0.01	0.13	0.02	0.11
				0.33	<0.01	0.17	<0.01	0.09

NR: not reported NA: not analysed

Table 78. Residues in barley straw after single seed treatments.

Country, Year, Reference	Sample	Application		PHI, days	Residues, mg/kg				
		Form	g ai/t		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Seed treatment, 2 replicates (Muller, 1995a)									
France, 1993-1994, 94501OR1	straw	FS	1500	260	<0.01	<0.01	<0.01	NR	<0.01
France, 1993-1994, 94501AM1	straw	FS	1000	271	0.01 <0.01	<0.01 <0.01	0.024 0.024	NR	<0.01 0.01
			1500	271	<0.01 <0.01	<0.01 <0.01	0.038 0.032		0.014 0.01
France, 1993-1994, 94501RS1	straw	FS	1500	260	<0.01	<0.01	<0.01	NR	<0.01
France, 1993-1994, 94501DJ1	straw	FS	1000	250	<0.01 <0.01	<0.01 <0.01	0.016 0.023	NR	<0.01 <0.01
			1500	250	<0.01 <0.01	<0.01 <0.01	0.015 0.013		<0.01 <0.01
France, 1993-1994, 94501LY1	straw	FS	1000	249	0.014 <0.01	<0.01 <0.01	0.013 0.014	NR	<0.01 <0.01
			1500	249	<0.01 <0.01	<0.01 <0.01	0.012 0.014		<0.01 <0.01

NR: not reported

Table 79. Residues in rice straw. All single applications.

Commodity, Country, Year, Reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Seed treatment, 2 replicates (Keats, 1996e)										
Australia, 1996, AK96059	FS		25 50 100	1	167	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 0.003 0.005	NR
Seed treatment, 3 replicates (Keats, 1996h)										
Australia, 1996, AK96060	FS		25 50 100	1	215	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	NR
Seed treatment, 2 replicates (Keats, 1996i)										
Australia, 1996, AK96061	FS		12.5 25 50	1	144	≤0.002 <0.002 <0.002 <0.002	≤0.002 <0.002 <0.002 <0.002	≤0.002 <0.002 <0.002 <0.002	<0.002 <0.002 0.007 0.008	NR
Seed treatment (Maestracci, 1997c)										
France, 1996, 96561AV1	FS	130		1	143	≤0.002	≤0.002	≤0.002	<0.002	≤0.002
Seed treatment (Maestracci, 1998e)										
France, 1997, 97545AV1 variety Thaibonnet	FS	130		1	149	≤0.005	≤0.005	≤0.005	<0.005	NR
France, 1997, 97545AV2 variety Ariete	FS	130		1	149	≤0.005	≤0.005	≤0.005	<0.005	NR
Seed treatment (Maestracci, 1998f)										
France, 1997, 97546AV1 variety Ariete	FS	130		1	133	≤0.005	≤0.005	≤0.005	<0.005	NR
France, 1997, 97546AV2 variety Thaibonnet	FS	130		1	133	≤0.005	≤0.005	≤0.005	<0.005	NR
Seed treatment, 2 replicates (Yslan and Baudet, 1999a)										
Spain, 1998, 98639TR1	FS	263	52.6	1	133	<0.002	<0.002	<0.002	<0.002	NR
Seed treatment, 2 replicates (Mede, 1996b)										
USA, 1995[1], 95-0248AR	FS		56	1	119	≤0.01 <0.01	≤0.01 <0.01	0.017 0.012	<0.003 <0.003	<0.01 <0.01

Commodity, Country, Year, Reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA, 1995[1], 95-0249AR	FS		56	1	134	<0.01 ≤0.01	<0.003 ≤0.01	<0.01 0.012	<0.01 <0.01	<0.003 <0.003
USA, 1995[1], 95-0250CA	FS		56	1	139	≤0.01 <0.003	≤0.003 <0.003	≤0.003 <0.003	<0.003 <0.003	<0.003 <0.003
USA, 1995[1], 95-0251CA	FS		56	1	139	≤0.003 <0.003	≤0.01 <0.01	≤0.003 <0.003	<0.01 <0.003	<0.003 <0.003
USA, 1995[1], 95-0252LA	FS		56	1	107	≤0.01	≤0.01	0.011	<0.01	<0.01
USA, 1995[1], 95-0253LA	FS		56	1	112	≤0.01 <0.01	≤0.01 <0.01	0.01 <0.01	<0.01 <0.01	<0.003 <0.003
USA, 1995[1], 95-0254MS	FS		56	1	128	≤0.01 <0.01	≤0.01 <0.01	0.024 0.014	<0.01 <0.01	0.014 0.011
USA, 1995[1], 95-0255TX	FS		56	1	119	<0.003 ≤0.01	<0.003 ≤0.01	<0.01 0.01	<0.003 <0.003	<0.003 <0.003
USA, 1995[1], 95-0256MS	FS		56	1	130	≤0.01	≤0.01	≤0.01	<0.003	<0.003
USA, 1995[1], 95-0257LA	FS		56	1	109	0.012 <0.01	≤0.01 <0.01	0.02 0.015	<0.01 <0.01	0.014 <0.01
Seed treatment, 2 replicates (Mede, 1997)										
USA, 1996[1], 10392-01	FS		54	1	126	≤0.003	≤0.003	≤0.003	<0.01	NR
USA, 1996[1], 10392-02	FS		58	1	125	<0.01 ≤0.01	<0.01 ≤0.01	0.012 0.013	<0.003 <0.003	NR
USA, 1996[1], 10392-03	FS		57	1	129	<0.01 ≤0.01	<0.01 ≤0.01	<0.01 0.014	<0.003 <0.003	NR
USA, 1996[1], 10392-04	FS		56	1	110	≤0.003	≤0.003	≤0.003	≤0.003	NR
USA, 1996[1], 10392-05	FS		56	1	117	≤0.01	≤0.01	≤0.01	<0.003	NR
USA, 1996[1], 10392-07	FS		56	1	128	≤0.01	≤0.01	≤0.01	<0.003	NR
USA, 1996[1], 10392-08	FS		57	1	138	≤0.01	≤0.01	≤0.003	<0.01	NR
Seed box treatment, 3 replicates (Anon., 1994)										
Japan, 1993, I.E.T. Official residue trial, Ushuku	GR		0.5 g ai/box	1	132	0.01 0.01 0.01	0.09 0.06 0.06	≤0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01
Japan, 1993, I.E.T. Official residue trial, Shiga	GR		0.5 g ai/box	1	141	0.04 0.03 0.03	0.19 0.16 0.12	0.03 0.03 0.02	0.01 0.01 0.01	0.01 0.01 0.01
Seed box treatment, 2 replicates (Anon., 1995a)										
Japan, 1995, Nihon Noyaku	GR		0.5 g ai/box	1	123	0.04	≤0.01	≤0.01	<0.01	<0.01
Seed box treatment, 2 replicates (Anon., 1995b)										
Japan, 1995, Nissan, Fukui	GR		0.5 g ai/box	1	140	≤0.01	0.01	≤0.01	<0.01	<0.01
Japan, 1995, Nissan, Mie	GR		0.5 g ai/box	1	118	0.01	0.04	0.02	<0.01	<0.01
Soil pre-plant incorporation broadcast treatment, 2 replicates (Mede, 1996b)										
USA, 1995[1], 95-0248AR	WG		56	1	119	<0.01 ≤0.01	<0.01 ≤0.01	0.012 0.017	<0.003 <0.003	<0.01 <0.01
USA, 1995[1], 95-0249AR	WG		56	1	134	≤0.01	≤0.003	≤0.01	<0.003	<0.003
USA, 1995[1], 95-0250CA	WG		56	1	141	≤0.01	≤0.003	≤0.003	<0.003	<0.003
USA, 1995[1], 95-0251CA	WG		56	1	140	≤0.01 <0.003	≤0.01 <0.01	≤0.01 <0.01	<0.01 <0.01	<0.003 <0.003
USA, 1995[1], 95-0252LA	WG		56	1	112	0.016 <0.01	≤0.01 <0.01	0.015 0.014	<0.003 <0.01	0.019 0.014
USA, 1995[1], 95-0253LA	WG		56	1	114	≤0.01 <0.01	≤0.01 <0.01	≤0.01 <0.01	<0.01 <0.003	<0.003 <0.003
USA, 1995[1], 95-0254MS	WG		56	1	128	<0.003 ≤0.01	<0.01 ≤0.01	<0.01 0.013	<0.003 <0.003	<0.01 0.011
USA, 1995[1], 95-0255TX	WG		56	1	119	≤0.01 <0.003	≤0.01 <0.01	≤0.01 <0.01	<0.003 <0.01	<0.003 <0.003
USA, 1995[1], 95-0256MS	WG		56	1	130	≤0.01	≤0.01	≤0.01	<0.003	<0.003
USA, 1995[1], 95-0257LA	WG		56	1	110	≤0.01 <0.01	≤0.01 <0.01	0.014 0.012	<0.01 <0.01	<0.01 <0.01

Commodity, Country, Year, Reference	Application				PHI, days	Residues, mg/kg				
	Form	g ai/t	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Soil pre-plant incorporation broadcast treatment, 2 replicates (Mede, 1997)										
USA, 1996[1], 10392-01	SC		57	1	133	≤0.01	≤0.01	≤0.01	<0.003	NR
USA, 1996[1], 10392-02	SC		57	1	125	≤0.01	≤0.01	≤0.01	<0.003	NR
USA, 1996[1], 10392-03	SC		57	1	136	<0.003 ≤0.01	<0.01 ≤0.01	<0.01 ≤0.01	<0.003	NR
USA, 1996[1], 10392-04	SC		56	1	113	≤0.003	≤0.003	≤0.003	<0.003	NR
USA, 1996[1], 10392-05	SC		57	1	120	≤0.01	≤0.01	≤0.01	<0.003	NR
USA, 1996[1], 10392-07	SC		59	1	128	≤0.01	≤0.01	≤0.01	<0.003	NR
USA, 1996[1], 10392-08	SC		56	1	143	≤0.01	≤0.01	≤0.01	<0.01	NR
Foliar treatment, 3 replicates (Maycey *et al*., 1994c)										
Thailand, 1992/1993, 92/276 Supanuri Rice Research Station	SC		50	1	49	0.039 0.061 0.042	0.01 0.01 0.009	0.028 0.047 0.059	0.048 0.075 0.051	NR
Thailand, 1992/1993, 92/276 Supanuri Rice Research Station	SC		50	1	45	0.017 0.006 0.014	0.006 <0.005 0.005	0.016 0.01 0.011	0.028 0.013 0.017	NR
Thailand, 1992/1993, 92/276 Supanuri	SC		50	1	48	0.038 0.072 0.13	0.009 0.014 0.03	0.044 0.053 0.18	0.046 0.068 0.2	NR
Thailand, 1992/1993, 92/276 Nontaburi	SC		50	1	45	0.041 0.022 0.09	0.006 0.005 0.012	0.041 0.059 0.095	0.045 0.032 0.095	NR
Foliar treatment, 3 replicates, (Maycey *et al*., 1994a)										
Philippines, 1992, 92/277 Luzon	SC		50	1	51	0.022 0.027 0.018	0.005 0.009 0.006	0.037 0.043 0.027	0.065 0.084 0.059	NR
Foliar treatment, 3 replicates (Maycey *et al*., 1994b)										
Taiwan, 1993, 92/275 Chitong Li	SC		50	1	79	≤0.005	≤0.005	≤0.005	≤0.005	NR
Broadcast treatment after transplanting followed by foliar treatment, 3 replicates, (Maycey *et al*., 1994a)										
Philippines, 1992, 92/277 Luzon	GR SC		50	2	51	0.014 0.018 0.02	0.009 0.008 ≤0.005	0.024 0.042 0.039	0.046 0.053 0.049	NR
Broadcast treatment into flooded paddy, 3 replicates (Maycey *et al*., 1994a)										
Philippines, 1992, 92/277 Luzon	GR		50	1	81	0.009 0.006 0.008	<0.005 ≤0.005 0.005	0.008 0.008 0.01	0.018 0.025 0.021	NR
Broadcast treatment into flooded paddy, 3 replicates (Maycey *et al*., 1994b)										
Taiwan, 1993, 92/275 Hsinung Li	GR		50	1	89	≤0.005	≤0.005	≤0.005	≤0.005	NR
Broadcast treatment into flooded paddy, (Maycey *et al*., 1994c)										
Thailand, 1992/1993, 92/276 Supanuri Rice Research Station, **replicate 1**	GR		50	1	79	<0.005	0.008	<0.005	0.01	NR
Thailand, 1992/1993, 92/276 Supanuri Rice Research Station, **replicate 2**	GR		50	1	75	≤0.005	0.008	0.006	0.012	NR
Thailand, 1992/1993, 92/276 Supanuri	GR		50	1	79	≤0.005 <0.005 <0.005	0.011 0.012 0.013	0.008 <0.005 <0.005	0.021 0.017 0.015	NR
Thailand, 1992/1993, 92/276 Nontaburi	GR		50	1	75	<0.005 <0.005 ≤0.005	<0.005 <0.005 ≤0.005	<0.005 <0.005 0.006	<0.005 <0.005 0.006	NR

NR: not reported

[1]residues reported as ND (not detected) in the original report are shown as <0.00x, i.e. the minimum limit of detection (MLD)

Table 80. Residues in sorghum forage and straw from trials in Australia. All single applications.

Year, Reference	Sample	Application			PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Foliar treatment at stage BBCH 85, 2 replicates (Keats, 1996n)										
1995, AK96074	forage	UL		10	0	0.019	0.003	0.002	<0.002	NR
						0.017	0.003	<0.002	<0.002	
					1	0.016	0.003	0.008	<0.002	
						0.016	0.003	0.007	<0.002	
					3	0.011	0.002	0.002	<0.002	
						0.011	0.002	<0.002	<0.002	
					7	0.002	<0.002	<0.002	<0.002	
						0.003	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
	straw				35	<0.002	<0.002	<0.002	<0.002	
					48	<0.002	<0.002	<0.002	<0.002	
1995, AK96074	forage	UL		20	0	0.065	0.005	<0.002	<0.002	NR
						0.055	0.005	<0.002	<0.002	
					1	0.019	0.002	0.003	<0.002	
						0.018	0.002	0.002	<0.002	
					3	0.007	0.003	0.003	<0.002	
						0.007	<0.002	0.002	<0.002	
					7	0.004	<0.002	<0.002	<0.002	
						0.004	<0.002	<0.002	<0.002	
					21	0.002	<0.002	<0.002	<0.002	
						0.002	<0.002	<0.002	<0.002	
	straw	UL		20	35	0.004	<0.002	0.003	<0.002	
						0.002	<0.002	0.002	<0.002	
					48	<0.002	<0.002	<0.002	<0.002	
Foliar treatment at stage BBCH 75 (Keats, 1996o)										
1996, AK96075	forage	UL		10	0	0.067	<0.002	0.003	<0.002	NR
					1	0.057	<0.002	0.004	<0.002	
					3	0.038	<0.002	0.003	<0.002	
					7	0.018	<0.002	0.003	<0.002	
					17	0.005	<0.002	0.003	<0.002	
	straw				42	<0.002	<0.002	<0.002	<0.002	
1996, AK96075	forage	UL		20	0	0.13	0.002	<0.002	<0.002	NR
					1	0.14	<0.002	<0.002	<0.002	
					3	0.078	<0.002	<0.002	<0.002	
					7	0.075	<0.002	<0.002	<0.002	
					17	0.005	<0.002	<0.002	<0.002	
	straw				42	0.002	<0.002	<0.002	<0.002	
Foliar treatment at maturity, BBCH 87, 2 replicates (Keats, 1996p)										
1996, AK96076	forage	UL		10	0	0.021	0.003	<0.002	<0.002	NR
						0.019	0.003	<0.002	<0.002	
					1	0.013	0.002	0.002	<0.002	
						0.013	0.002	<0.002	<0.002	
					3	0.015	0.003	0.003	<0.002	
						0.009	0.002	<0.002	<0.002	
					7	0.002	<0.002	<0.002	<0.002	
						0.003	<0.002	<0.002	<0.002	
					21	0.002	<0.002	<0.002	<0.002	
						<0.002	<0.002	<0.002	<0.002	
	straw				42	<0.002	<0.002	<0.002	<0.002	
1996, AK96076	forage	UL		20	0	0.054	0.009	0.002	<0.002	NR
						0.052	0.009	0.002	<0.002	
					1	0.019	0.003	<0.002	<0.002	
						0.022	0.004	0.002	<0.002	
					3	0.017	0.003	<0.002	<0.002	
						0.017	0.003	0.002	<0.002	
					7	0.008	<0.002	0.002	<0.002	
						0.007	<0.002	0.002	<0.002	
					21	0.007	<0.002	0.002	<0.002	
						0.006	<0.002	0.002	<0.002	
	straw				42	0.004	<0.002	0.002	<0.002	
						0.004		0.002		

Year, Reference	Sample	Application			PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Foliar treatment at maturity, BBCH 87, 2 replicates (Keats, 1998a)										
1998, AK98024	forage	SC		1.25	0	0.072	0.002	0.002	0.002	NR
						0.08	0.003	0.003	0.002	
					4	0.004	<0.002	<0.002	<0.002	
					7	0.004	<0.002	<0.002	<0.002	
					15	<0.002	<0.002	<0.002	<0.002	
						0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
						0.002	<0.002	<0.002	<0.002	
					29	<0.002	<0.002	<0.002	<0.002	
1998, AK98024	forage	SC		2.5	0	0.12	0.006	0.004	0.009	NR
						0.13	0.007	0.004	0.01	
					4	0.02	<0.002	0.003	0.003	
						0.018	<0.002	0.002	0.003	
					7	0.007	<0.002	<0.002	<0.002	
						0.006	<0.002	<0.002	<0.002	
					15	<0.002	<0.002	0.002	<0.002	
						0.002	<0.002	<0.002	<0.002	
					21	0.002	<0.002	<0.002	<0.002	
						0.002	<0.002	<0.002	<0.002	
					29	<0.002	<0.002	<0.002	<0.002	
1998, AK98024	forage	SC		5.0	0	0.37	0.015	0.022	0.025	NR
						0.39	0.015	0.023	0.034	
					4	0.048	0.002	<0.002	<0.002	
						0.043	0.002	<0.002	<0.002	
					7	0.011	0.002	<0.002	<0.002	
						0.01	0.002	0.003	<0.002	
					15	0.002	<0.002	0.002	<0.002	
						0.003	<0.002	<0.002	<0.002	
					21	0.002	<0.002	<0.002	0.002	
					29	<0.002	<0.002	<0.002	<0.002	
Foliar treatment at maturity, BBCH 87, 2 replicates (Keats, 1998b)										
1998, AK98025	forage	UL		1.25	0	0.049	0.002	<0.002	0.005	NR
						0.053	0.003	<0.002	0.004	
					2	0.01	0.002	<0.002	0.002	
						0.009	<0.002	<0.002	0.002	
					4	0.004	<0.002	<0.002	0.002	
						0.003	<0.002	<0.002	<0.002	
					7	0.006	<0.002	0.004	<0.002	
						0.005	<0.002	0.004	<0.002	
					15	<0.002	<0.002	<0.002	<0.002	
					21	0.002	<0.002	<0.002	<0.002	
					28	<0.002	<0.002	<0.002	<0.002	
1998, AK98025	forage	UL		2.5	0	0.067	0.004	<0.002	0.007	NR
						0.072	0.004	<0.002	0.01	
					2	0.011	0.002	<0.002	0.002	
						0.012	<0.002	<0.002	0.002	
					4	0.014	0.002	<0.002	0.003	
						0.016	0.002	<0.002	<0.002	
					7	0.007	<0.002	0.006	<0.002	
						0.007	<0.002	0.007	<0.002	
					15	0.003	<0.002	0.004	<0.002	
						0.004	<0.002	0.004	<0.002	
					21	0.005	<0.002	0.005	<0.002	
					28	<0.002	<0.002	<0.002	<0.002	
1998, AK98025	forage	UL		5.0	0	0.11	0.005	0.005	0.028	NR
						0.1	0.007	0.003	0.032	
					2	0.039	0.002	0.005	0.009	
						0.035	<0.002	0.003	0.011	
					4	0.035	0.002	0.002	0.004	
						0.039	<0.002	0.002	0.003	
					7	0.01	0.004	0.017	<0.002	
						0.009	0.005	0.023	<0.002	
					15	0.008	<0.002	0.005	<0.002	
					21	0.008	<0.002	0.002	<0.002	
						0.008	<0.002	0.003	<0.002	
					28	<0.002	<0.002	<0.002	<0.002	

Year, Reference	Sample	Application			PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
1998, AK98025	forage	UL		7.5	0	0.27	0.009	0.006	0.042	NR
						0.27	0.011	0.01	0.04	
					2	0.067	0.002	0.006	0.012	
						0.073	0.002	0.008	0.015	
					4	0.059	0.008	0.002	0.009	
						0.065	0.004	0.002	0.011	
					7	0.061	0.005	0.034	0.002	
						0.032	0.004	0.034	0.002	
					15	0.015	0.002	0.011	0.002	
						0.02	<0.002	0.012	0.003	
					21	0.018	0.002	0.011	0.002	
						0.017	0.002	0.011	0.002	
					28	<0.002	<0.002	<0.002	<0.002	
Foliar treatment at stage BBCH 73, 2 replicates (Keats, 1998c)										
1998, AK98027	forage	UL		1.25	0	0.029	<0.002	<0.002	0.002	NR
						0.033	<0.002	<0.002	0.002	
					2	0.009	<0.002	<0.002	0.004	
						0.013	<0.002	0.003	<0.002	
					4	0.004	<0.002	<0.002	<0.002	
						0.003	<0.002	<0.002	<0.002	
					7	0.003	<0.002	0.002	<0.002	
						0.005	<0.002	0.002	<0.002	
					15	<0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
					28	<0.002	<0.002	<0.002	<0.002	
1998, AK98027	forage	UL		2.5	0	0.047	0.002	<0.002	0.005	NR
						0.053	0.003	<0.002	0.004	
					2	0.011	<0.002	0.002	0.002	
						0.013	<0.02	0.002	0.002	
					4	0.014	<0.002	<0.002	<0.002	
						0.006	0.002	<0.002	<0.002	
					7	0.007	0.003	0.002	<0.002	
						0.005	<0.002	<0.002	<0.002	
					15	0.002	<0.002	<0.002	<0.002	
					21	<0.002	<0.002	<0.002	<0.002	
					28	<0.002	<0.002	<0.002	<0.002	
1998, AK98027	forage	UL		5.0	0	0.13	0.002	0.002	0.01	NR
						0.12	0.003	0.003	0.014	
					2	0.039	<0.002	0.002	0.012	
						0.041	0.003	0.005	0.008	
					4	0.019	0.002	0.002	0.003	
						0.022	<0.002	0.002	0.002	
					7	0.01	0.002	0.006	0.003	
						0.014	0.002	0.012	0.002	
					15	0.002	<0.002	0.003	<0.002	
					21	<0.002	<0.002	0.002	<0.002	
					28	<0.002	<0.002	<0.002	<0.002	
1998, AK98027	forage	UL		7.5	0	0.32	0.005	0.004	0.019	NR
						0.32	0.006	0.01	0.023	
					2	0.073	<0.002	0.007	0.015	
						0.069	0.003	0.006	0.013	
					4	0.03	0.002	0.002	0.004	
						0.038	0.006	0.002	0.008	
					7	0.022	<0.002	0.011	0.002	
						0.03	0.003	0.015	0.002	
					15	0.003	<0.002	0.003	<0.002	
						0.002	<0.002	0.004	<0.002	
					21	<0.002	<0.002	0.002	<0.002	
						<0.002	<0.002	0.003	<0.002	
					28	<0.002	<0.002	<0.002	<0.002	
Seed treatment before sowing, GAP pending, 2 replicates (Keats, 1998g)										
1998, AK98030	forage	FS	750		35	<0.002	<0.002	<0.002	<0.002	NR
			1500			<0.002	<0.002	<0.002	<0.002	
	straw		750		138	<0.002	<0.002	<0.002	<0.002	
			1500			<0.002	<0.002	<0.002	<0.002	
Seed treatment before sowing, GAP pending, 2 replicates (Keats, 1998h)										
1998, AK98031	forage	FS	750		33	<0.002	<0.002	<0.002	<0.002	NR
			1500			<0.002	<0.002	<0.002	<0.002	

Year, Reference	Sample	Application			PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
	straw		750		104	<0.002	<0.002	<0.002	<0.002	
			1500			<0.002	<0.002	<0.002	<0.002	

NR: not reported

Table 81. Residues in wheat straw. All single applications.

Crop, Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
Seed treatment, 2 replicates (Muller, 1994k)											
Wheat, winter, France 1992/3, 93-507E1	forage[1]	FS	1000			121	0.016 0.016	<0.01 <0.01	<0.01 <0.01	NR	<0.01 0.01
						182	<0.01	<0.01	<0.01		<0.01
	straw					251	<0.01	<0.01	<0.01	NR	<0.01
Seed treatment, 2 replicates (Muller, 1996j)											
Wheat, spring, France, 1995, 95-518RS1	forage	FS	500			74	<0.01	<0.01	<0.01	NR	<0.01
	straw					131	<0.01	<0.01	<0.01		<0.01
Seed treatment, 2 replicates (Richard and Muller, 1994h)											
Wheat , winter, France 1992/3, 93-508B1	straw	FS	1000			279	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	0.017 0.02
			1500				0.017 0.023	<0.01 <0.01	0.011 0.012		0.017 0.015
Wheat, winter, France 1992/3, 93-508C1	straw	FS	1500			286	<0.01	<0.01	<0.01	NR	<0.01
Wheat, winter, France 1992/3, 93-508D1	straw	FS	1000			269	<0.01	<0.01	<0.01	NR	<0.01
			1500				<0.01 <0.01	<0.01 <0.01	<0.01 0.011		<0.01 <0.01
Wheat, winter, France 1992/3, 93-508E1	straw	FS	1500			264	<0.01	<0.01	<0.01	NR	<0.01
Wheat, winter, France 1992/3, 93-508F1	straw	FS	1500			268	<0.01	<0.01	<0.01	NR	<0.01
Wheat, winter, France 1992/3, 93-508K1	straw	FS	1000			226	<0.01	<0.01	<0.01	NR	<0.01
			1500				<0.01	<0.01	<0.01		<0.01
Seed treatment, 2 replicates (Muller, 1995b)											
Wheat, winter, France, 1993/4, 94-500BX1	straw	FS	1000			244	<0.01 0.01	<0.01 <0.01	0.013 <0.01	NR	<0.01 <0.01
			1500				<0.01 0.012	<0.01 <0.01	<0.01 0.013		<0.01 <0.01
Wheat, winter, France, 1993/4, 94-500RN1	straw	FS	1000			260	<0.01	<0.01	<0.01	NR	<0.01
			1500				<0.01 0.011	<0.01 <0.01	0.06 0.036		0.012 0.01
Wheat, winter, France, 1993/4, 94-500AM1	straw	FS	1000			286	<0.01	<0.01	<0.01	NR	<0.01
			1500				<0.01 <0.01	<0.01 <0.01	0.023 0.025		0.01 0.011
Wheat, winter, France, 1993/4, 94-500DJ1	straw	FS	1000			262	<0.01 <0.01	<0.01 <0.01	<0.01 0.01	NR	<0.01 <0.01
			1500				<0.01 <0.01	<0.01 <0.01	0.015 0.019		<0.01 <0.01
Wheat, winter, France, 1993/4, 94-500LY1	straw	FS	1000			245	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	NR	0.014 0.012
			1500				<0.01 0.011	<0.01 <0.01	<0.01 <0.01		0.013 0.01
Wheat, winter, France, 1993/4, 94-500AV1	straw	FS	1500			245	<0.01	<0.01	<0.01	NR	<0.01

Crop, Country, Year, Reference	Sample	Application				PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
Seed treatment, 2 replicates (Muller, 1996k)											
Wheat, spring, France, 1995, 95-507BX1	straw	FS	500			140	0.011 0.014	<0.01 <0.01	0.014 <0.01	NR	<0.01 <0.01
Wheat, spring, France, 1995, 95-507AM1	straw	FS	500			128	<0.01	<0.01	<0.01	NR	<0.01
Wheat, spring, France, 1995, 95-507RS1	straw	FS	500			131	<0.01	<0.01	<0.01	NR	<0.01
Wheat, spring, France, 1995, 95-507LY1	straw	FS	500			145	0.011 <0.01	<0.01 <0.01	<0.01 <0.01	NR	<0.01 <0.01
Foliar treatment, 2 replicates (Muller, 1996a)											
Wheat, winter, Poland, 1995, 95795PL1 *evaluated acc. to Czech/Slovak GAP*	straw	WG		20	6.67	44	0.017 0.014	<0.005 <0.05	0.015 0.006	0.029 0.013	<0.005 <0.005
Foliar treatment, no reference (summary table, no GLP report available)											
Wheat, winter, Russia, 1997, Krasnodar	straw	EC		24	12	27	<0.01	NR	NR	NR	NR
Wheat, winter, Russia, 1997, Rostov	straw	EC		20	10	25	<0.01	NR	NR	NR	NR
Wheat, winter, Russia, 1997, Voronesh	straw	EC		20	10	38	<0.01	NR	NR	NR	NR
Wheat, spring, Russia, 1998, Volgograd	straw	EC		21	10.5	49	<0.01	NR	<0.01	<0.01	NR
Wheat, spring, Russia, 1998, Saratov	straw	EC		21	10.5	49	<0.01	NR	<0.01	<0.01	NR

[1] data from green plant residues, early March and early May samplings, should cover 15-20 cm stage to stem elongation
NR: not reported

Table 82. Residues in cotton plants and gin trash.

Country, Year, Reference	Sample	Application					PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
Seed treatment, 2 replicates (Keats, 1997i)												
Australia, 1995, AK97018 Clare, QLD	plant	FS	5000 10 000			1	169	0.007 0.006 0.01 0.009	<0.002 <0.002 <0.002 <0.002	<0.002 <0.002 <0.002 <0.002	0.002 0.002 0.002 0.002	NR
Foliar treatment, 2 replicates (Keats, 1997e)												
Australia, 1995, AK97016 Breeza, NSW	Plant (trash)	EC		200		4	14 24 28	0.64 0.29 0.093 0.12 0.16 0.19	0.21 0.08 0.024 0.035 0.041 0.058	0.079 0.002 <0.002 0.004 0.004 0.005	0.82 0.58 0.29 0.30 0.31 0.36	NR
Seed treatment followed by foliar treatments, 2 replicates (Keats, 1997f)												
Australia, 1996, AK97015 Kincora Queensland	Plant	FS + SC + ULV	5000	 25 25		1 1 1	113	0.003 0.003	<0.002 <0.002	0.011 0.009	0.002 0.002	NR
Australia, 1996, AK97015 Kincora Queensland	plant	FS + SC + ULV	10 000	 50 50		1 1 1	113	0.004 0.004	<0.002 <0.002	0.009 0.008	0.002 0.002	NR

Country, Year, Reference	Sample	Application					PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
Australia, 1996, AK97015 Kincora Queensland	plant	FS + SC + ULV	10 000	100 100		1 1 1	113	0.01 0.01	0.002 <0.002	0.024 0.022	0.008 0.007	NR
Australia, 1996, AK97015 Kincora Queensland	plant	FS + SC + ULV	5000	25 25		1 1 3	4 7 14 21 28	0.048 0.053 0.057 0.052 0.023 0.021 0.019 0.018 0.016 0.017	0.004 0.004 0.006 0.005 0.002 0.002 <0.002 <0.002 <0.002 <0.002	0.3 0.35 0.30 0.27 0.33 0.31 0.076 0.078 0.18 0.17	0.016 0.017 0.01 0.009 0.013 0.013 0.006 0.005 0.004 0.004	NR
Australia, 1996, AK97015 Kincora Queensland	plant	FS + SC + ULV	10 000	50 50		1 1 3	4 7 14 21 28	0.33 0.29 0.078 0.074 0.068 0.066 0.047 0.046 0.032 0.027	0.012 0.011 0.004 0.003 0.003 0.003 0.002 0.005 0.004 <0.002	1.5 1.3 0.62 0.52 0.32 0.34 0.4 0.38 0.3 0.27	0.059 0.059 0.02 0.018 0.013 0.014 0.015 0.017 0.011 0.011	NR
Australia, 1996, AK97015 Kincora Queensland	plant	FS + SC + ULV	10 000	100 100		1 1 3	4 7 14 21 28	0.41 0.35 0.36 0.34 0.11 0.10 0.084 0.077 0.019 0.015	0.005 0.004 0.007 0.007 0.003 0.002 0.002 0.002 <0.002 <0.002	1.3 1.1 1.6 1.5 1.0 0.89 0.59 0.49 0.13 0.072	0.032 0.024 0.086 0.085 0.034 0.049 0.022 0.019 0.005 0.004	NR
Seed treatment followed by foliar treatments, 2 replicates (Keats, 1997g)												
Australia, 1996, AK97014 Breeza NSW	plant	FS + SC + ULV	5000	25 25		1 1 1	109	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97014 Breeza NSW	plant	FS + SC + ULV	10 000	50 50		1 1 1	109	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97014 Breeza NSW	plant	FS + SC + ULV	10 000	100 100		1 1 1	109	<0.002	<0.002	<0.002	<0.002	NR
Australia, 1996, AK97014 Breeza NSW	plant	FS + SC + ULV	5000	25 25		1 1 3	0 6 15 31	0.87 0.94 0.17 0.14 0.064 0.057 0.025 0.013	0.01 0.01 0.006 0.006 0.003 0.002 <0.002 <0.002	0.062 0.056 0.08 0.10 0.073 0.075 0.005 0.004	0.006 0.006 0.016 0.016 0.012 0.011 0.003 0.003	NR
Australia, 1996, AK97014 Breeza NSW	plant	FS + SC + ULV	10 000	50 50		1 1 3	0 6 15 31	1.7 1.3 0.064 0.054 0.05 0.044 0.027 0.025	0.03 0.014 0.004 0.003 0.002 0.002 0.002 <0.002	0.069 0.033 0.086 0.079 0.087 0.089 0.024 0.016	0.005 0.003 0.008 0.006 0.006 0.005 0.005 0.005	NR
Australia, 1996, AK97014 Breeza	plant	FS + SC +	10 000	100		1 1	0 6	2.5 2.1 0.15 0.09	0.024 0.016 0.005 0.005	0.076 0.055 0.12 0.15	0.004 0.003 0.006 0.005	NR

Country, Year, Reference	Sample	Application					PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
NSW		ULV		100		3	15	0.059	0.003	0.10	0.005	
								0.069	0.003	0.17	0.012	
							31	0.045	0.002	0.032	0.002	
								0.038	<0.002	0.03	0.003	
Single foliar treatments, 2 replicates (Lynch, 1998)												
Australia, 1998, AK99029 Jambin Queensland **Single applications to separate plots**	plant	SC		35.4	44.8	1	0	0.086	<0.002	0.056	0.024	NR
								0.09	<0.002	0.061	0.023	
						1	15	0.053	0.004	0.053	0.015	
								0.058	0.003	0.058	0.009	
						1	30	0.01	0.003	0.036	0.008	
								0.014	0.004	0.042	0.007	
						1	43	0.004	<0.002	0.032	0.003	
								0.005	<0.002	0.028	0.003	
						1	57	<0.002	<0.002	0.026	<0.002	
								<0.002	<0.002	0.021	<0.002	
						1	71	<0.002	<0.002	0.022	<0.002	
								<0.002	<0.002	0.016	<0.002	
						1	85	<0.002	<0.002	0.008	<0.002	
								<0.002	<0.002	0.006	<0.002	
						1	99	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99029 Jambin Queensland **Single applications to separate plots**	gin trash	SC		35.4	44.8	1	0	0.26	0.01	0.031	0.011	NR
								0.28	0.01	0.038	0.014	
						1	15	0.16	0.012	0.043	0.02	
								0.15	0.012	0.036	0.015	
						1	30	0.098	0.009	0.032	0.009	
								0.086	0.006	0.027	0.006	
						1	43	0.035	0.005	0.021	<0.002	
								0.028	0.003	0.013	<0.002	
						1	57	0.008	<0.002	0.008	<0.002	
								0.005	<0.002	0.004	<0.002	
						1	71	0.003	<0.002	0.003	<0.002	
								<0.002	<0.002	0.005	<0.002	
						1	85	<0.002	<0.002	0.002	<0.002	
						1	99	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99029 Jambin Queensland **Single applications to separate plots**	plant	SC		71.4	92.7	1	0	0.36	0.028	0.05	0.034	NR
								0.38	0.023	0.042	0.044	
						1	15	0.23	0.014	0.066	0.047	
								0.26	0.018	0.085	0.059	
						1	30	0.13	0.007	0.062	0.012	
								0.14	0.004	0.062	0.005	
						1	43	0.06	0.002	0.052	0.003	
								0.033	<0.002	0.048	<0.002	
						1	57	0.011	<0.002	0.044	<0.002	
								0.008	<0.002	0.032	<0.002	
						1	71	0.003	<0.002	0.024	<0.002	
								0.003	<0.002	0.012	<0.002	
						1	85	<0.002	<0.002	0.008	<0.002	
								<0.002	<0.002	0.005	<0.002	
						1	99	<0.002	<0.002	0.003	<0.002	
								<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99029 Jambin Queensland **Single applications to separate plots**	gin trash	SC		71.4	92.7	1	0	0.52	0.024	0.031	0.016	NR
								0.5	0.03	0.038	0.022	
						1	15	0.26	0.019	0.042	0.03	
								0.29	0.023	0.06	0.029	
						1	30	0.13	0.016	0.057	0.01	
								0.16	0.019	0.049	0.014	
						1	43	0.036	0.009	0.042	0.003	
								0.041	0.012	0.035	0.004	
						1	57	0.02	0.004	0.036	<0.002	
								0.013	<0.002	0.027	<0.002	
						1	71	0.007	<0.002	0.03	<0.002	
								0.003	<0.002	0.023	<0.002	
						1	85	<0.002	<0.002	0.012	<0.002	
								<0.002	<0.002	0.008	<0.002	
						1	99	<0.002	<0.002	0.003	<0.002	
								<0.002	<0.002	<0.002	<0.002	
Single foliar treatments, 2 replicates (Lynch, 1999)												
Australia, 1998, AK99032 Wee Waa NSW	plant	SC		25	28.4	1	0	0.062	0.003	0.017	0.018	NR
								0.059	0.004	0.014	0.016	
						1	15	0.017	<0.002	0.011	0.013	
								0.023	<0.002	0.012	0.013	
						1	29	0.003	<0.002	0.009	0.009	

Country, Year, Reference	Sample	Application					PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
								0.005	<0.002	0.008	0.01	
Single applications to separate plots						1	43	<0.002	<0.002	0.004	<0.002	
								<0.002	<0.002	0.003	<0.002	
						1	57	<0.002	<0.002	0.002	<0.002	
						1	71	<0.002	<0.002	<0.002	<0.002	
						1	85	<0.002	<0.002	<0.002	<0.002	
						1	99	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99032 Wee Waa NSW	gin trash	SC		25	28.4	1	0	0.25	0.014	0.026	0.02	NR
								0.26	0.016	0.022	0.017	
						1	15	0.071	0.009	0.011	0.016	
								0.078	0.003	0.009	0.014	
						1	29	0.008	<0.002	0.009	0.01	
								0.005	<0.002	0.012	0.012	
Single applications to separate plots						1	43	0.002	<0.002	0.007	0.003	
								<0.002	<0.002	0.006	0.004	
						1	57	<0.002	<0.002	0.002	<0.002	
								<0.002	<0.002	<0.002	<0.002	
						1	71	<0.002	<0.002	<0.002	<0.002	
						1	85	<0.002	<0.002	<0.002	<0.002	
						1	99	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99032 Wee Waa NSW	plant	SC		50	56.8	1	0	0.13	0.008	0.016	0.006	NR
								0.019	0.009	0.025	0.015	
						1	15	0.075	0.004	0.021	0.018	
								0.057	0.005	0.017	0.016	
						1	29	0.007	0.002	0.016	0.011	
								0.004	<0.002	0.012	0.011	
Single applications to separate plots						1	43	0.002	<0.002	0.008	0.002	
								0.003	<0.002	0.007	<0.002	
						1	57	0.002	<0.002	0.003	<0.002	
								<0.002	<0.002	0.002	<0.002	
						1	71	<0.002	<0.002	0.002	<0.002	
						1	85	<0.002	<0.002	<0.002	<0.002	
						1	99	<0.002	<0.002	<0.002	<0.002	
Australia, 1998, AK99032 Wee Waa NSW	gin trash	SC		50	56.8	1	0	0.45	0.02	0.023	0.025	NR
								0.46	0.02	0.025	0.024	
						1	15	0.16	0.011	0.2	0.016	
								0.15	0.007	0.18	0.008	
						1	29	0.018	0.002	0.017	0.013	
								0.01	<0.002	0.019	0.016	
Single applications to separate plots						1	43	0.007	<0.002	0.013	0.007	
								0.005	<0.002	0.01	0.008	
						1	57	0.003	<0.002	0.007	0.003	
								0.004	<0.002	0.009	<0.002	
						1	71	0.002	<0.002	0.005	<0.002	
								0.003	<0.002	0.004	<0.002	
						1	85	<0.002	<0.002	0.003	<0.002	
								<0.002	<0.002	<0.002	<0.002	
						1	99	<0.002	<0.002	<0.002	<0.002	
Soil treatment in-furrow at sowing followed by foliar treatments, or foliar only (Norris, 1997a)												
USA, 1995, 95-0023NC	gin trash	WG		168 inc + 84 foliar		1 2	44	<0.04 <0.04	<0.04 <0.04	0.33 0.26	0.48 0.43	<0.05 <0.05
USA, 1995, 95-0023NC	gin trash	WG		84 foliar		4	44	<0.04 <0.1	<0.04 <0.04	0.37 0.41	0.5 0.6	<0.05 <0.05
USA, 1995, 95-0026AR	gin trash	WG		168 inc + 84 foliar		1 2	45	<0.1 <0.1	<0.04 <0.04	0.17 0.21	0.59 0.64	<0.05 <0.05
USA, 1995, 95-0026AR	gin trash	WG		84 foliar		4	45	0.11 <0.1	<0.04 <0.04	0.42 0.43	1.3 1.1	<0.05 <0.05
USA, 1995, 95-0027MS	gin trash	WG		168 inc + 84 foliar		1 2	44	<0.1 <0.1	<0.04 <0.04	<0.1 <0.1	0.23 0.25	<0.05 <0.05
USA, 1995, 95-0027MS	gin trash	WG		84 foliar		4	44	<0.1 <0.1	<0.04 <0.04	0.27 0.19	0.51 0.47	<0.05 <0.05

Country, Year, Reference	Sample	Application					PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
USA, 1995, 95-0028LA	gin trash	WG		168 inc + 84 foliar		1 2	45	<0.04 <0.04	<0.04 <0.04	0.25 0.29	0.61 0.68	<0.05 <0.05
USA, 1995, 95-0028LA	gin trash	WG		84 fol		4	45	<0.1 <0.1	<0.04 <0.04	0.449 0.435	1.0 1.1	<0.05 <0.05
USA, 1995, 95-0029TX	gin trash	WG		168 inc + 84 foliar		1 2	43	0.11 <0.1	<0.04 <0.04	0.21 0.2	0.17 0.16	<0.05 <0.05
USA, 1995, 95-0029TX	gin trash	WG		84 foliar		4	43	0.12 0.13	<0.1 <0.04	0.37 0.40	0.39 0.41	<0.05 <0.05
USA, 1995, 95-0030TX	gin trash	WG		168 inc + 84 foliar		1 2	44	<0.04	<0.04	<0.05	<0.04	<0.05
USA, 1995, 95-0030TX	gin trash	WG		84 foliar		4	44	<0.04	<0.04	<0.05	<0.04	<0.05
USA, 1995, 95-0031OK	gin trash	WG		168 inc + 84 foliar		1 2	44	<0.04 <0.04	<0.04 <0.04	<0.05 <0.1	<0.04 <0.04	<0.05 <0.05
USA, 1995, 95-0031OK	gin trash	WG		84 foliar		4	44	<0.04	<0.04	<0.05	<0.1	<0.05
USA, 1995, 95-0032TX	gin trash	WG		168 inc + 84 foliar		1 2	46	<0.1 <0.1	<0.04 <0.04	0.17 <0.05	<0.1 <0.1	<0.05 <0.05
USA, 1995, 95-0032TX	gin trash	WG		84 foliar		4	46	<0.1 0.1	<0.04 0.04	<0.05 0.17	<0.1 0.18	<0.05
USA, 1995, 95-0033TX	gin trash	WG		168 inc + 84 foliar		1 2	46	<0.04	<0.04	<0.05	<0.1	<0.05
USA, 1995, 95-0033TX	gin trash	WG		84 foliar		4	46	<0.04	<0.04	<0.05	<0.1	<0.05
USA, 1995, 95-0034AZ	gin trash	WG		168 inc + 84 foliar		1 2	45	0.29 0.31	<0.04 <0.04	0.31 0.30	0.49 0.48	<0.05 <0.05
USA, 1995, 95-0034AZ	gin trash	WG		84 foliar		4	45	0.36 0.4	<0.1 <0.1	0.56 0.6	0.86 0.83	<0.05 <0.05
USA, 1995, 95-0035CA	gin trash	WG		168 inc + 84 foliar		1 2	45	0.57 0.62	0.12 0.13	0.33 0.38	1.7 2.0	<0.05 <0.05
USA, 1995, 95-0035CA	gin trash	WG		84 foliar		4	45	1.4 1.6	0.23 0.25	0.95 1.0	4.4 4.7	<0.05
USA, 1995, 95-0036CA	gin trash	WG		168 inc + 84 foliar		1 2	46	0.52 0.43	0.1 <0.1	0.46 0.37	1.7 1.8	<0.05 <0.05
USA, 1995, 95-0036CA	gin trash	WG		84 foliar		4	46	0.36 0.58	<0.1 0.11	0.24 0.5	1.3 2.4	<0.05
Foliar treatment, 2 replicates (Norris, 1997b)												
USA, 1995, 95-0276GA	gin trash	WG		56		6	43	0.32 0.23	<0.1 <0.1	0.79 0.62	0.89 0.77	<0.05
USA, 1995, 95-0277LA	gin trash	WG		56		6	45	0.11 0.1	<0.04	0.52 0.56	1.0 1.2	<0.05
USA, 1995, 95-0278TX	gin trash	WG		56		6	46	<0.1 <0.1	<0.1 <0.1	0.12 0.11	0.1 0.11	<0.05
USA, 1995, 95-0279TX	gin trash	WG		56		6	44	0.11 0.11	<0.1 <0.1	0.15 0.14	0.18 0.18	<0.05
USA, 1995, 95-0280CA	gin trash	WG		56		6	46	1.6 1.6	0.25 0.25	1.2 1.2	4.8 4.6	<0.05
Foliar treatment, 2 replicates (Norris, 1998)												
USA, 1996, 10669-01NC	gin trash	EC		56		6	43	<0.1 <0.1	<0.1 <0.1	0.37 0.23	0.24 0.15	NR
USA, 1996,	gin	EC		56		6	44	0.13	<0.1	0.67	0.5	NR

Country, Year, Reference	Sample	Application					PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
10669-02GA	trash							0.2	<0.1	1.1	0.9	
USA, 1996, 10669-03AR	gin trash	EC		56		6	45	<0.1 <0.1	<0.1 <0.1	0.15 0.28	0.11 0.29	NR
USA, 1996, 10669-04AR	gin trash	EC		56		6	46	<0.1 <0.1	<0.1 <0.1	0.22 0.32	0.21 0.31	NR
USA, 1996, 10669-05MS	gin trash	EC		56		6	45	<0.1 <0.1	<0.1 <0.1	0.63 0.3	0.34 0.15	NR
USA, 1996, 10669-06LA	gin trash	EC		56		6	45	<0.1 <0.1	<0.1 <0.1	0.36 0.45	0.45 0.54	NR
USA, 1996, 10669-07TX	gin trash	EC		56		6	47	<0.1 <0.1	<0.04 <0.04	0.55 0.5	0.47 0.4	NR
USA, 1996, 10669-08TX	gin trash	EC		56		6	45	<0.1 0.12	<0.1 <0.1	0.29 0.57	0.19 0.36	NR
USA, 1996, 10669-09OK	gin trash	EC		56		6	45	<0.04 <0.04	<0.04 <0.04	<0.1 <0.05	<0.1 <0.1	NR
USA, 1996, 10669-10TX	gin trash	EC		56		6	47	<0.1 <0.1	<0.04 <0.04	<0.1 <0.1	<0.1 <0.1	NR
USA, 1996, 10669-11TX	gin trash	EC		56		6	46	<0.1 <0.1	<0.04 <0.04	<0.1 <0.1	<0.1 <0.1	NR
USA, 1996, 10669-12AZ	gin trash	EC		56		6	45	0.23 0.34	<0.04 <0.1	0.53 0.80	0.45 0.8	NR
USA, 1996, 10669-13CA	gin trash	EC		56		6	44	0.16 0.27	<0.1 <0.1	0.57 0.97	0.64 1.4	NR
USA, 1996, 10669-14CA	gin trash	EC		56		6	45	0.26 0.19	<0.1 <0.1	1.5 0.96	1.0 0.7	NR
Foliar treatment, GAP pending, 2 replicates (Gough, 1999)												
USA, 1997, 13499-01 Kerman CA	gin trash	EC		56		3	75	<0.04 <0.01	<0.04 <0.004	<0.1 0.11	0.22 0.30	NR
USA, 1997, 13499-01 Kerman CA	gin trash	EC		56		4	75	<0.1 <0.1	<0.04 <0.004	<0.1 0.16	0.12 0.38	NR
USA, 1997, 13499-02 Tulare CA	gin trash	EC		56		3	75	<0.1 <0.1	<0.1 <0.1	0.32 0.29	0.32 0.27	NR
USA, 1997, 13499-02 Tulare CA	gin trash	EC		56		4	75	<0.1 <0.1	<0.1 <0.1	0.22 0.29	0.25 0.34	NR
USA, 1997, 13499-03 Brawley CA	gin trash	EC		56		3	76	<0.1 <0.1	<0.04 <0.04	0.12 <0.1	0.31 0.24	NR
USA, 1997, 13499-03 Brawley CA	gin trash	EC		56		4	76	<0.1 <0.1	<0.04 <0.04	0.14 0.17	0.39 0.45	NR
Foliar treatment, GAP pending, 2 replicates (Macy, 1998)												
USA, 1997, 13501-01AR	gin trash	EC		56		3	58	<0.04 <0.04	<0.04 <0.04	0. 16 0. 11	<0.1 <0.1	NR
USA, 1997, 13501-01AR	gin trash	EC		56		4	58	<0.04 <0.04	<0.04 <0.04	0. 17 0.15	<0.1 <0.1	NR
USA, 1997, 13501-02AR	gin trash	EC		56		3	61	<0.04 <0.04	<0.04 <0.04	0.1 0.21	0.15 <0.1	NR
USA, 1997, 13501-02AR	gin trash	EC		56		4	61	<0.04 <0.04	<0.04 <0.04	0.14 0.13	<0.1 <0.1	NR
USA, 1997, 13501-03LA	gin trash	EC		56		3	60	<0.04	<0.04	<0.1	<0.1	NR
USA, 1997, 13501-03LA	gin trash	EC		56		4	60	<0.04 <0.04	<0.04 <0.04	<0.1 <0.1	<0.1 0.14	NR
USA, 1997, 13501-04LA	gin trash	EC		56		3	61	<0.04	<0.04	<0.1	<0.1	NR
USA, 1997, 13501-04LA	gin trash	EC		56		4	61	<0.04 <0.04	<0.04 <0.04	0.19 0.2	0.15 0.16	NR
USA, 1997, 13501-05MS	gin trash	EC		56		3	61	<0.04 <0.04	<0.04 <0.04	<0.1 0.12	<0.1 <0.1	NR

Country, Year, Reference	Sample	Application					PHI, days	Residues, mg/kg				
		Form	g ai/t	g ai/ha	g ai/hl	No.		Fipronil	MB 45950	MB 46136	MB 46513	RPA 200766
USA, 1997, 13501-05MS	gin trash	EC		56		4	61	<0.04 <0.04	<0.04 <0.04	0.1 0.19	<0.1 0.13	NR
USA, 1997, 13501-06AR	gin trash	EC		56		3	57	<0.04 <0.04	<0.04 <0.04	0.1 <0.1	0.17 0.11	NR
USA, 1997, 13501-06AR	gin trash	EC		56		4	57	<0.04 <0.04	<0.04 <0.04	0.15 0.13	0.16 0.14	NR

NR: not reported
inc: soil incorporation

Table 83. Residues in sunflower forage and straw from seed treatment (each trial with 2 replicates), Australia, all single applications.

Year, Reference	Application			PHI, days	Residues, mg/kg				
	Sample	Form	g ai/ ton		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
(Keats, 1998l)									
1997, AK 98032, 96i38gR	forage	FS	750 1500	36	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
	straw		750 1500	113	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	
(Keats, 1998k)									
1998, AK 98035, 96i38bR	forage	FS	750 1500	40	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
	straw		750 1500	144	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	
(Keats, 1998i)									
1998, AK 98033, 97i004a	forage	FS	750 1500	53	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	0.002 <0.002	NR
	straw		750 1500	138	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	
(Keats, 1998j)									
1998, AK 98034, 97i004b	forage	FS	750 1500	22	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
	straw		750 1500	112	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	

NR: not reported

Table 84. Residues in sugar cane leaves resulting from soil and foliar applications in Australia.

Year, Reference, Location	Application			PHI, days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Foliar spray, 2 replicates (Keats, 1997m)									
1995, AUS94i74r Mowilyan Queensland	WG	100	1	181	<0.002 0.002	<0.002 <0.002	<0.002 <0.002	<0.002 <0.002	NR
1995, AUS94i74r Mowilyan Queensland	WG	200	1	181	0.002 0.002	<0.002 <0.002	<0.002 <0.002	0.003 0.002	NR
1995, AUS94i74r Mowilyan Queensland	WG	50	2	134	0.002 0.002	<0.002 <0.002	<0.002 <0.002	0.002 0.002	NR
1995, AUS94i74r Mowilyan Queensland	WG	100	2	53	0.005 0.007	<0.002 <0.002	<0.002 <0.002	0.002 0.002	NR
Soil treatment and stool spray, 2 replicates (Keats, 1997k)									
1996, AUS94i74cr Kurrimine Beach Queensland	WG + SC	100 soil + 50 foliar	1 + 2	95	<0.002	<0.002	<0.002	<0.002	NR

Year, Reference, Location	Application			PHI, days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
1996, AUS94i74cr Kurrimine Beach Queensland	WG + SC	200 soil 100 foliar	1 + 2	95	<0.002	<0.002	<0.002	<0.002	NR
1996, AUS94i74cr Kurrimine Beach Queensland	WG + SC	400 soil 200 foliar	1 + 2	95	<0.002	<0.002	<0.002	<0.002	NR
Foliar application, 2 replicates (Keats, 1997k)									
1997, 97NST14 Kurrimine Beach Queensland	SC	75	1	101	<0.002	<0.002	<0.002	<0.002	NR
Foliar application to base on cane stalks, 2 replicates (Keats, 1997c)									
1996, AUS94i74br Rocky Point Queensland	WG	50	2	0	0.11	0.003	0.005	0.002	NR
					0.11	0.004	0.005	0.002	
				1	0.22	0.009	0.02	0.036	
					0.18	0.008	0.014	0.032	
				3	0.093	0.004	0.009	0.016	
					0.096	0.004	0.011	0.016	
				5	0.12	0.004	0.008	0.007	
					0.13	0.004	0.008	0.006	
				7	0.058	0.003	0.008	0.013	
					0.061	0.003	0.009	0.012	
				14	0.01	<0.002	0.004	0.006	
					0.009	<0.002	0.004	0.005	
				26	0.015	<0.002	0.004	0.003	
					0.014	<0.002	0.004	0.003	
1996, AUS94i74br Rocky Point Queensland	WG	100	2	0	0.34	0.008	0.012	0.005	NR
					0.33	0.008	0.014	0.005	
				1	0.26	0.007	0.016	0.016	
					0.23	0.007	0.015	0.015	
				3	0.21	0.01	0.048	0.059	
					0.2	0.01	0.048	0.059	
				5	0.15	0.007	0.023	0.033	
					0.17	0.008	0.023	0.035	
				7	0.15	0.004	0.012	0.014	
					0.14	0.005	0.013	0.016	
				14	0.097	0.004	0.01	0.014	
					0.099	0.004	0.01	0.015	
				26	0.079	0.005	0.019	0.026	
					0.058	0.004	0.015	0.017	
1996, AUS94i74br Rocky Point Queensland	WG	100	1	0	0.7	0.012	0.021	0.006	NR
					0.75	0.012	0.022	0.005	
				1	0.54	0.01	0.025	0.013	
					0.5	0.011	0.02	0.012	
				3	0.46	0.019	0.061	0.035	
					0.57	0.018	0.058	0.028	
				5	0.19	0.01	0.029	0.015	
					0.2	0.01	0.032	0.02	
				7	0.075	0.003	0.009	0.008	
					0.067	0.002	0.007	0.009	
				14	0.038	0.002	0.007	0.003	
					0.029	0.002	0.007	0.003	
				26	0.018	0.002	0.007	0.003	
					0.016	0.002	0.006	0.003	

Year, Reference, Location	Application			PHI, days	Residues, mg/kg				
	Form	g ai/ha	No.		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
1996, AUS94i74br	WG	200	1	0	0.86	0.014	0.026	0.006	NR
Rocky Point					0.94	0.016	0.025	0.005	
Queensland				1	1.1	0.023	0.053	0.056	
					1.2	0.023	0.054	0.056	
				3	0.51	0.015	0.039	0.062	
					0.5	0.014	0.038	0.059	
				5	0.39	0.017	0.061	0.098	
					0.36	0.016	0.063	0.103	
				7	0.32	0.015	0.046	0.093	
					0.32	0.017	0.046	0.091	
				14	0.19	0.007	0.02	0.031	
					0.17	0.007	0.017	0.028	
				26	0.085	0.004	0.016	0.033	
					0.072	0.005	0.015	0.026	

NR: not reported

Animal feeding studies

Cows. Three feeding studies were reported on the transfer of residues of fipronil into meat, animal fat, meat by-products and milk, and a further study for residues of fipronil-desulfinyl in lactating animals.

In the first study (Byrd, 1994a) groups of three lactating cows were dosed daily with fipronil by bolus at a rate equivalent to 0.04, 0.13 or 0.43 ppm in the diet for 35 days. Milk was collected twice daily. Equal samples of morning and evening milk were combined and analysed for fipronil, MB 45950 and MB 46136. Fipronil-derived residues reached a plateau after 25 days at the high-dose, and consisted almost entirely of MB 46136. MB 45950 was detected in a single milk sample and trace amounts of fipronil (<0.01 mg/kg) at the high dose. The results are shown in Table 85.

Table 85. Residues in milk, mg/kg (Byrd, 1994a).

Day	0.04 ppm dose			0.13 ppm dose			0.43 ppm dose		
	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136
0	ND (3)[1]	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)
1	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	<0.01 (3)[2]	<0.01 (3)	ND (3)	<0.01 (3)
3	ND (3)	ND (3)	<0.01 (3)	ND ND <0.01	ND ND ND	<0.01 <0.01 <0.01	<0.01 (3)	ND (3)	<0.01 (3)
7	ND ND ND	ND ND ND	<0.01 ND <0.01	ND (3)	ND (3)	<0.01 (3)	<0.01 <0.01 <0.01	ND ND <0.01	0.014 0.013 0.023
12	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.013 <0.01 <0.01	<0.01 <0.01 <0.01	ND ND ND	0.025 0.019 0.025
15	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.016 <0.01 <0.01	<0.01 <0.01 <0.01	ND ND ND	0.024 0.025 0.027
20	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.014 <0.01 0.01	<0.01 <0.01 <0.01	ND ND ND	0.025 0.026 0.029
25	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.012 <0.01 0.013	<0.01 <0.01 <0.01	ND ND ND	0.030 0.024 0.040
29	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.012 <0.01 0.012	ND <0.01 ND	ND ND ND	0.030 0.038 0.052
34	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.018 <0.01 0.013	<0.01 <0.01 <0.01	ND ND ND	0.035 0.032 0.041

[1] ND: not detectable [2] <0.01: residue lower than the LOQ, traces detected

After 35 days the cows were slaughtered and the liver, kidney, fat and muscle were collected for analysis in triplicate from each animal. Fat contained the highest concentration of fipronil residues, but only at levels slightly above the LOQ in the high-dose group. Most of the residue was MB 46136. The results are shown in Table 86.

Table 86. Residues in cow tissues, mg/kg (Byrd, 1994a).

Sample	0.04 ppm group			0.13 ppm group			0.43 ppm group		
	fipronil	MB 45950	MB 46136	Fipronil	MB 45950	MB 46136	Fipronil	MB 45950	MB 46136
Muscle	ND[1]	ND	<0.01[2]	ND	ND	0.01	ND	ND	ND
	ND	ND	<0.01	ND	ND	0.015	ND	ND	ND
	ND	ND	<0.01	ND	ND	0.01	ND	ND	ND
Liver	ND	ND	0.013	ND	ND	0.061	ND	ND	0.16
	ND	ND	0.011	ND	ND	0.039	ND	ND	0.122
	ND	ND	0.012	ND	ND	0.046	ND	ND	0.117
Kidney	ND	ND	<0.01	ND	ND	0.014	<0.01	ND	0.034
	ND	ND	<0.01	<0.01	ND	<0.01	<0.01	ND	0.027
	ND	ND	<0.01	<0.01	ND	0.01	<0.01	ND	0.027
Fat	<0.01	ND	0.046	<0.01	<0.01	0.218	0.042	<0.01	0.546
	<0.01	ND	0.036	<0.01	<0.01	0.134	0.031	<0.01	0.446
	<0.01	ND	0.063	<0.01	<0.01	0.146	0.026	<0.01	0.413

[1]ND: not detectable
[2] <0.01: residue lower than the LOQ, traces detected

In a second study (Tew, 1999) two cows were dosed with fipronil at a rate equivalent to 1 ppm in the feed (dry weight basis) for 20 days. Milk samples were collected on 4 non-consecutive days before and on the 1st, 2nd, 4th, 7th and 19th days after the last dose. Milk fat was separated from whole milk collected on the last day of dosing by centrifuging. Whole milk and milk fat samples were analysed for residues of fipronil, MB 46136 and MB 45950 to determine the rate at which residues decreased in whole milk and the degree to which fipronil was concentrated in the fat. Analysis of samples from days 14-20 of dosing confirmed that residues had reached a plateau, and throughout the study consisted almost entirely of the metabolite MB 46136. The mean plateau residue of days 14,16, 18 and 20 was 0.033 mg/kg). No measurable residues of fipronil or MB 45950 (LOQ 0.003 mg/kg) were found in any whole milk samples.

Residues in the milk decreased slowly at the end of dosing. After one week MB 46136 residues were approximately 66% of their plateau level. Samples 19 days after the last dose had decreased to near the LOQ with average MB 46136 residues of 0.004 mg/kg. The calculated half-life of fipronil was 5.2 days.

The residues in milk fat samples were compared to those in day 20 whole milk. Similarly, residues consisted mainly of MB 46136 but because the residue was concentrated, minor amounts of MB 45950 (0.006 mg/kg) were detected. Average total residues as MB 46136 equivalents in whole milk and milk fat from day 20 were 0.039 mg/kg and 0.552 mg/kg respectively, indicating a concentration factor of 14.2.

In a feeding study by Keats (1998) in Australia to determine maximum residues in rangeland cattle oversprayed and then fed on fipronil-treated pasture grasses and the rate at which the residues decreased in various edible tissues, 32 cows were divided into 10 groups of 3 animals (groups 1-10), plus two control animals. On day 1, groups 1-10 were sprayed once dermally at the proposed commercial rate of 2.5 g ai/ha and the total applied to each was 0.75 mg as fipronil, calculated on an average hide area of 3 m^2. The treated cows were then dosed orally once a day with fipronil for up to 14 days. Animals from groups 1-7 and groups 8-10 were dosed with capsules at rates to give dietary exposures corresponding to twice the commercial rate (5 g ai/ha) and the commercial rate of 2.5 g ai/ha respectively. The fipronil concentration in the capsules decreased from day 1 to 14,

corresponding to the fipronil levels found in Australian pasture decline studies. The doses were as follows:

Day	Fipronil/capsule (mg)	
	Groups 8-10	Groups 1-7
1	2.5	5.0
2	1.9	3.9
3	1.4	2.7
4	0.8	1.5
5	0.7	1.5
6	0.7	1.4
7	0.6	1.1
8	0.4	0.8
9	0.4	0.7
10	0.3	0.6
11	0.3	0.5
12	0.2	0.4
13	0.2	0.4
14	0.1	0.3

The details of dosing are shown in Table 87. Fipronil, MB 45950 and MB 46136 were measured in renal, subcutaneous and abdominal fat, loin, round and diaphragm muscle, kidney and liver at 3 time points through the 14 days (3 animals per time point) and at 4 time points through the depuration period (again 3 animals per time point) at the double rate, and twice during uptake and once during depuration at the lower rate. The samples were stored at $\leq$-20°C and analysed within 2 months.

Table 87. Details of dosing in rangeland cattle study (Keats, 1998).

Group (3 animals/group)	Dermal dose (mg/animal)	Days dosed orally	Oral dose (mg/animal)	Pre-slaughter depuration (days)
1	0.75	5	14.6	0
2	0.75	10	19.2	0
3	0.75	14	20.8	0
4	0.75	14	20.8	6
5	0.75	14	20.8	13
6	0.75	14	20.8	20
7	0.75	14	20.8	27
8	0.75	10	9.7	0
9	0.75	14	10.5	0
10	0.75	14	10.5	13
Control	0	0	0	NA

Samples from the control animal contained no quantifiable residues. No residues of fipronil-desulfinyl were found, indicating that the photodegradation product, if formed on the animal after over-spray, will not be absorbed to any measurable extent. The highest residues were in the fat followed by liver in all dose groups, with very little residue transferred to muscles or kidneys (Tables 88-89).

Table 88. Residues in cattle fat, mg/kg (Keats, 1998).

Group	Renal fat			Abdominal fat			Subcutaneous fat		
	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136
Double dose									
1	0.027	0.008	0.078	0.024	0.007	0.061	0.026	0.005	0.064
	0.028	0.008	0.092	0.029	0.009	0.091	0.030	0.009	0.091
	0.035	0.013	0.059	0.029	0.009	0.044	0.026	0.009	0.050
2	0.018	0.004	0.078	0.021	0.005	0.083	0.021	0.003	0.08
	0.022	0.007	0.097	0.021	0.007	0.09	0.012	0.002	0.045
	0.02	0.005	0.11	0.014	0.003	0.081	0.017	0.003	0.088

Group	Renal fat			Abdominal fat			Subcutaneous fat		
	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136
3	0.009	0.005	0.154	0.009	0.005	0.145	0.01	0.004	0.156
	0.009	0.003	0.109	0.009	0.003	0.111	0.009	0.002	0.128
	0.012	0.002	0.069	0.012	0.002	0.068	0.011	0.002	0.048
4	0.004	0.005	0.067	0.004	0.004	0.065	0.006	0.006	0.065
	0.002	0.002	0.068	0.006	0.002	0.064	0.008	0.002	0.072
	0.003	0.002	0.077	0.002	0.002	0.079	0.006	0.002	0.067
5	<0.002	0.002	0.089	0.002	0.002	0.087	0.003	0.003	0.094
	0.003	0.002	0.084	0.003	0.002	0.071	0.004	0.002	0.057
	0.002	<0.002	0.045	<0.002	<0.002	0.033	0.003	<0.002	0.046
6	0.003	<0.002	0.034	<0.002	<0.002	0.040	<0.002	<0.002	0.033
	<0.002	<0.002	0.031	<0.002	<0.002	0.020	<0.002	<0.002	0.033
	<0.002	<0.002	0.059	0.002	<0.002	0.055	<0.002	<0.002	0.069
7	<0.002	<0.002	0.023	<0.002	<0.002	0.028	<0.002	<0.002	0.031
	<0.002	<0.002	0.08	<0.002	<0.002	0.063	0.002	<0.002	0.07
	0.002	<0.002	0.037	<0.002	<0.002	0.035	0.002	0.002	0.048
Single dose									
8	0.011	0.005	0.085	0.009	0.002	0.08	0.006	<0.002	0.051
	0.01	0.004	0.05	0.01	0.004	0.045	0.011	0.003	0.04
	0.01	0.006	0.062	0.011	0.007	0.064	0.012	0.006	0.08
9	0.008	0.004	0.066	0.007	0.002	0.057	0.007	<0.002	0.056
	0.01	0.005	0.085	0.01	0.005	0.070	0.008	0.002	0.066
	0.004	<0.002	0.034	0.005	<0.002	0.041	0.007	<0.002	0.052
10	<0.002	<0.002	0.033	<0.002	<0.002	0.030	<0.002	<0.002	0.026
	<0.002	<0.002	0.026	<0.002	<0.002	0.026	<0.002	<0.002	0.03
	<0.002	<0.002	0.036	<0.002	<0.002	0.034	0.002	<0.002	0.03

Table 89. Residues in cattle tissues, mg/kg (Keats, 1998).

Group	Diaphragm muscle			Loin and round muscle			Liver			Kidney		
	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136
Double dose												
1	0.004	<0.002	0.011	<0.002	<0.002	0.002	<0.002	<0.002	0.018	0.002	<0.002	0.006
	<0.002	<0.002	0.011	<0.002	<0.002	0.002	<0.002	<0.002	0.01	0.003	<0.002	0.003
	0.003	0.002	0.004	<0.002	<0.002	<0.002	<0.002	<0.002	0.005	<0.002	<0.002	0.003
2	0.002	<0.002	0.006	<0.002	<0.002	<0.002	<0.002	<0.002	0.004	0.002	<0.002	0.003
	0.003	<0.002	0.006	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	0.002	<0.002	0.002
	<0.002	<0.002	0.005	<0.002	<0.002	0.002	0.002	<0.002	0.003	<0.002	<0.002	0.002
3	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.01	<0.002	<0.002	0.003
	<0.002	<0.002	0.003	<0.002	<0.002	<0.002	<0.002	<0.002	0.006	<0.002	<0.002	0.004
	<0.002	<0.002	0.002	<0.002	<0.002	0.002	<0.002	<0.002	0.002	<0.002	<0.002	<0.002
4	<0.002	<0.002	0.007	<0.002	<0.002	0.002	<0.002	<0.002	0.005	<0.002	<0.002	0.005
	<0.002	<0.002	0.004	<0.002	<0.002	<0.002	0.002	<0.002	0.006	<0.002	<0.002	0.006
	<0.002	<0.002	0.006	<0.002	<0.002	0.002	<0.002	<0.002	0.007	<0.002	<0.002	0.002
5	<0.002	<0.002	0.004	<0.002	<0.002	<0.002	<0.002	<0.002	0.020	<0.002	<0.002	0.006
	<0.002	<0.002	<0.002	<0.002	<0.002	0.003	<0.002	<0.002	0.01	0.002	<0.002	0.005
	<0.002	<0.002	0.002	<0.002	<0.002	0.002	<0.002	<0.002	0.005	<0.002	<0.002	0.003
6	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002	<0.002	<0.002	<0.002
	<0.002	<0.002	0.003	<0.002	<0.002	0.003	0.002	<0.002	0.002	<0.002	<0.002	<0.002
	<0.002	<0.002	0.003	<0.002	<0.002	0.002	<0.002	<0.002	0.005	<0.002	<0.002	0.002
7	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002	<0.002	<0.002	<0.002
	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002	0.002	<0.002	0.002
	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002	<0.002	<0.002	0.002
Single Dose												
8	<0.002	<0.002	0.003	<0.002	<0.002	0.002	<0.002	<0.002	0.003	<0.002	<0.002	0.002
	<0.002	<0.002	0.003	<0.002	<0.002	0.002	<0.002	<0.002	0.004	<0.002	<0.002	0.002
	0.002	<0.002	0.003	<0.002	<0.002	0.002	<0.002	<0.002	0.003	<0.002	<0.002	0.002
9	<0.002	<0.002	0.003	<0.002	<0.002	0.002	<0.002	<0.002	0.003	<0.002	0.002	0.002
	<0.002	<0.002	0.003	<0.002	<0.002	0.002	<0.002	<0.002	0.003	<0.002	<0.002	0.002
	<0.002	<0.002	0.002	<0.002	<0.002	0.002	<0.002	<0.002	0.003	<0.002	<0.002	0.002
10	<0.002	<0.002	0.002	<0.002	<0.002	0.002	<0.002	<0.002	0.006	<0.002	<0.002	0.002
	<0.002	<0.002	<0.002	<0.002	<0.002	0.002	<0.002	<0.002	0.002	<0.002	<0.002	0.002
	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.003

In a study by Williams (1997) groups of three lactating cows were dosed daily with fipronil-desulfinyl by bolus at a rate equivalent to 0.025, 0.075, 0.3 or 1 ppm in the diet for 35 days. An additional animal was administered the highest dose and depurated for 7 days after the 35 days. Milk was collected twice daily on 10 days during the dosing period at pre-determined times and on days 37, 39 and 42 from the single depuration animal. Equal portions of morning and evening milk samples were combined and analysed for fipronil-desulfinyl. Milk fat samples were prepared from day 35 high-dose samples for analysis.

Fipronil-desulfinyl reached a plateau in milk in the 15- to 20-day interval, and the concentration of the analyte paralleled the administered dose in all but the high-dose group (Table 90). fipronil-desulfinyl residues were mainly in the milk fat rather than the skimmed milk, by a factor of about 16.

Table 90. Plateau residues of fipronil-desulfinyl in whole milk (Williams, 1997).

Group	Measured fipronil-desulfinyl dietary level (ppm)	fipronil-desulfinyl mean plateau concentration (mg/kg)	fipronil-desulfinyl range at day 35 (mg/kg)
1	0	<0.002	Not detected
2	0.025	0.003	0.003-0.005
3	0.076	0.008	0.009-0.01
4	0.31	0.027	0.026-0.031
5[1]	1.03	0.058	0.046-0.072
5 (d)	1.03	0.072 at day 35	0.027 at day 42[2]

[1] average of 4 animals
[2] milk level in 1 high-dose animal after 7 days of depuration

After 35 days of dosing, all treated cows except the depuration animal were slaughtered and the liver, kidney, fat and muscle collected for analysis. The depuration cow was slaughtered and sampled 7 days later. The results reported are the means of 2 analyses. Of the tissues examined, fat and liver contained significant levels of fipronil-desulfinyl and muscle and kidney very little (Table 91). The tissue levels in the depurated animal, in conjunction with the milk residues, support a half-life value for MB 46136 in lactating cows of somewhat less than one week.

Table 91. Fipronil-desulfinyl residues in the tissues of lactating cows, mg/kg (Williams, 1997).

Sample	0.025 ppm group	0.076 ppm group	0.3 ppm group	1.03 ppm group[1]	1.03 ppm (dep)[2]
Muscle	<0.002	0.005	0.015	0.028	0.018
	<0.002	0.003	0.011	0.035	
	0.003	0.003	0.019	0.037	
Liver	0.038	0.094	0.27	0.61	0.25
	0.036	0.069	0.25	0.49	
	0.033	0.098	0.28	0.59	
Kidney	0.004	0.013	0.044	0.12	0.052
	0.005	0.012	0.030	0.094	
	0.006	0.01	0.041	0.093	
Fat	0.039	0.12	0.41	1.06	0.48
	0.039	0.091	0.35	0.79	
	0.043	0.094	0.33	1.07	

[1]excluding the depurated cow
[2]depurated cow

Hens. Byrd (1994b) dosed laying hens, ten per dose group, daily by bolus at rates equivalent to 0.01 ppm, 0.031 ppm, or 0.103 ppm in the diet for 42 days. Eggs were collected throughout and residues reached a plateau after approximately 15 days. The hens were killed after the last doses and liver, skin

with adhering fat and muscle were collected. The eggs and tissues were analysed for fipronil, MB 46136 and MB 45950.

Average MB 46136 residues in eggs in the medium- and high-dose groups reached a plateau at about 25-28 days. Those from the low-dose group contained ≤0.01 mg/kg throughout, except from one bird at 25 days (0.013 mg/kg). No MB 45950 was observed in eggs from any group and only trace amounts of fipronil (<0.01 mg/kg) in the high-dose group (Table 92).

Table 92. Residues in eggs, mg/kg (Byrd, 1994b).

Day	0.01 ppm dose			0.031 ppm dose			0.103 ppm dose		
	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136	fipronil	MB 45950	MB 46136
0	ND (3) [1]	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)
1	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)
3	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	ND (3)	ND (3)	ND (3)	<0.01 (3) [2]
7	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	<0.01 (3)	<0.01 (3)	ND (3)	0.033 0.025 0.026
12	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.013 0.01 0.013	<0.01 (3)	ND (3)	0.049 0.040 0.039
15	ND (3)	ND (3)	<0.01 (3)	ND (2)	ND (2)	0.018 0.019	<0.01 (3)	ND (3)	0.051 0.045 0.042
20	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.019 0.02 0.015	<0.01 (3)	ND (3)	0.102 0.081 0.091
25	ND (3)	ND (3)	<0.01 0.013 <0.01	ND (3)	ND (3)	0.023 0.021 0.022	<0.01 (3)	ND (3)	0.116 0.092 0.096
28	ND (3)	ND (3)	<0.01 0.01 <0.01	ND (3)	ND (3)	0.029 0.027 0.03	<0.01 (3)	ND (3)	0.115 0.077 0.083
34	ND (3)	ND (3)	<0.01 0.012 <0.01	ND (3)	ND (3)	0.036 0.017 0.02	<0.01 (3)	ND (3)	0.097 0.092 0.087
41	ND (3)	ND (3)	<0.01 (3)	ND (3)	ND (3)	0.021 0.029 0.023	<0.01 (3)	ND (3)	0.112 0.086 0.09

[1]ND: not detectable
[2] <0.01: residue lower than the LOQ, traces detected

Residues of MB 46136 in the low-dose group were at or below 0.01 mg/kg in muscle and liver and 0.013 mg/kg in skin with adhering fat. At all doses MB 46136 was present at much higher levels in the skin with adhering fat than in the other tissues. The total residue in the fat was almost entirely MB 46136 with fipronil constituting less than 10% in the high-dose group (Table 93).

Table 93. Residues in the tissues of laying hens, mg/kg (Byrd, 1994b).

Sample	0.01 ppm group			0.031 ppm group			0.103 ppm group		
	fipronil	45950	46136	fipronil	45950	46136	fipronil	45950	46136
Muscle	ND (3) [1]	ND (3)	<0.01 (3)	ND (3)	ND (3)	<0.01 (3) [2]	ND (3)	ND (3)	0.014 0.012 0.01
Liver	ND (3)	ND (3)	<0.01 (3)	<0.01 ND ND	ND (3)	0.019 0.020 0.020	<0.01 (3)	ND (3)	0.071 0.067 0.069
Skin with fat	ND (3)	ND (3)	0.013 0.013 0.014	ND <0.01 <0.01	ND ND <0.01	0.046 0.057 0.060	<0.01 (3)	ND (3)	0.161 0.208 0.204

[1]ND: not detectable
[2] <0.01: residue lower than the LOQ, traces detected

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Potatoes (Tables 94-95). In a processing study by Macy (1997) potatoes in Washington state, USA, were foliar-sprayed four times with a 200 g/l SC formulation at an exaggerated rate of 280 g ai/ha/application (total rate 1120 g ai/ha) and the tubers harvested 28 days after the last application. All potatoes were washed and inspected for culls.

For chips, potatoes were peeled using an abrasive peeler, trimmed by hand, sliced into chips and placed in warm water. Slices were fried in a restaurant-style deep-fat fryer and drained.
For flakes, potatoes were steam-peeled, scrubbed to remove skins, hand trimmed, cut into 12 mm slices and then washed. Slices were then cooked in a pre-cooker, culled and cooked in a steam cooker. The cooked potatoes were mashed, mixed with additives, dried and broken into flakes.

The peels removed in the flake process were hydraulically pressed and mixed with cut trim waste to make up wet peel for analysis.

Table 94 shows the results (mean of 2 analysed samples).

Table 94. Residues in potatoes and their processed fractions (Macy, 1997).

Location,, Year, Reference	Application			PHI,	Commodity	Residues, mg/kg				
	Form	g ai/ha	No.	days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA (WA), 1996 96V11660[1]	SC	280	4	28	Tuber	0.003	ND	<0.003	0.003	NR
					Chips	<0.003	ND (2)	ND (2)	ND (2)	NR
					Flakes	<0.002	ND (2)	<0.003 (2)	ND (2)	NR
					Wet peel	0.03	0.009	0.008	0.024	NR

[1] <0.003 means residues were detected at >MLD but <LOQ
ND: not detectable (<MLD)
NR: not reported

In another US processing study Macy (1996) sprayed potatoes in Washington state in furrow at 1120 g ai/ha and then 4 times foliarly at 280 g ai/ha/application (total rate applied 2240 g ai/ha, at highly exaggerated rates for both application methods) with an 800 g/kg WG formulation. Tubers were harvested 28 days after the last application. The same processing procedures as above were used. The results are shown in Table 95 (mean of 2 analysed samples).

Table 95. Residues in potatoes and their processed fractions, Washington state, USA, 1996 (Macy, 1996).

Reference	Application			PHI,	Commodity	Residues, mg/kg				
	Form	g ai/ha	No.	days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
US95V03R	WG	1120 soil, 280 foliar	4	28	tuber	0.034	0.003	0.008	0.011	NR
					chips	0.003	ND	0.008	ND	NR
					flakes	0.011	0.001	0.002	0.001	NR
					wet peel	0.252	0.019	0.084	0.035	NR

ND: not detectable
NR: not reported

In two studies of 8 trials each (Maestracci, 1998; Yslan and Baudet, 1999) on potatoes in Germany 4 foliar applications of WG formulation were made at a seasonal rate corresponding to 80 g ai/ha, with a 28-day PHI. Tuber samples were harvested with attached soil that was removed by washing in cold tap water. Tubers were dried with paper towels and peeled. The wet peel and peeled tubers were frozen separately for subsequent analysis. Residues of the parent compound and the metabolites in all unpeeled tuber samples were below the LOQ, and were undetectable in peeled potatoes.

Rice. A rice processing study was planned in the USA but after a fivefold application rate there were no residues above the LOQ of 0.01 mg/kg in rice grain samples so the processed products were not analysed (Mede, 1996a).

Maize (Table 96). In a maize processing study by Kowite (1993b) in the USA single in-furrow applications of 20 g/kg granules at an exaggerated application rate of 2912 g ai/ha (20 times the US label rate) were made at planting. At harvest, triplicate samples were taken from treated and control plots for use in dry and wet milling processes. The procedures are outlined below.

- *Dry milling:* The moisture content of the grain was between 20 and 28% by weight. The maize samples were dried and cleaned by aspiration and screening. The light impurities from aspiration were classified as grain dust. The cleaned grain was moisture-adjusted and impact-milled to produce hull, grits, meal, flour and germ. The germ was heat-conditioned, flaked and pressed in an expeller to liberate most of the crude oil. The residual crude oil in the solid material (presscake) exiting the expeller was later extracted with hexane. The solvent was removed from the presscake and the crude oils recovered from the expeller and solvent extraction were combined and refined.

- *Wet milling:* The dried and cleaned grain was steeped in water and then milled to recover germ, hull, coarse gluten-starch, gluten and starch in that order. After drying, the processing was completed as before.

Validation of the method with fortification levels of 0.01 mg/kg for each compound and commodity, except starch (0.02 mg/kg), gave recoveries of >75%. The results are shown in Table 96. Undetectable residues are recorded as less than the reported minimum limit of detection (MLD); actual values between the MLD and LOQ (0.01 for all samples, except starch 0.02 mg/kg) are reported as found.

Table 96. Residues in maize and its processed fractions, Nebraska, USA, 1992. Ref. 92-059 (Kowite, 1993b).

Application			PHI, days	Commodity	Residues, mg/kg				
Form	g ai/ha	No.			Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
GR	2912	1	179	Whole seed Dry milling	3<0.002	3<0.002	3<0.003	3<0.002	3<0.003
				Grit Dry milling	3<0.002	3<0.002	3<0.003	3<0.002	3<0.003
				Meal Dry milling	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003	**0.004**[1] **0.01**[1] **0.005**[1] **UTC: 0.007**	<0.003 <0.003 <0.003
				Flour Dry milling	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003	**0.002**[2] **0.018**[2] <0.002 **UTC: <0.002**	<0.003 <0.003 <0.003
				Crude oil Dry milling	<0.002 **0.002**[1] <0.002 **UTC: 0.005**	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003	<0.004 <0.004 <0.004
				Refined oil Dry milling	**0.002**[1] **0.003**[1] **0.002**[1] **UTC: 0.005**	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003	**0.03**[1] **0.005**[1] **0.0007**[1] **UTC: 0.027**
				Grain dust Dry milling	3<0.002	3<0.002	3<0.003	3<0.002	3<0.003
				Whole seed Wet milling	3<0.002	3<0.002	3<0.003	3<0.002	3<0.003
				Starch Wet milling	3<0.004	3<0.003	3<0.004	3<0.003	3<0.006
				Crude oil Wet milling	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003	**0.006** **0.005** **0.004** **UTC: <0.004**
				Refined oil Wet milling	**0.003** <0.002 <0.002 **UTC: <0.002**	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003	<0.003 <0.003 <0.003	**0.016** **0.006** **0.018** **UTC: <0.004**
				Grain dust Wet milling	**0.004** **0.004** **0.003** **UTC: <0.002**	<0.002 <0.002 <0.002	**0.004** **0.004** **<0.003** **UTC: <0.003**	<0.002 <0.002 <0.002	<0.003 <0.003 <0.003

[1] Stated to be contamination
[2] Thought to be contamination (variability of the results and improbability of photolytic reaction occurring during processing make the findings suspect)
UTC: untreated control sample

Cotton seed (Table 97). In a processing study in the USA by Norris (1995) duplicate plots were treated with an in-furrow spray at 1680 g ai/ha followed by 4 foliar applications each at 420 g ai/ha with 800 WG formulation (5-10 times normal rates for both foliar and soil applications). The cotton was harvested 45 days after the last foliar application and ginned. The resulting cotton seed was processed by

- delinting
- hulling and separation of seed kernels from hulls

- expansion and solvent extraction of kernels, separation into meal and crude oil
- addition of alkali and refining of crude oil

The LOQ for each compound in cotton seed as well as the processed fractions was 0.01 mg/kg. Residues below the LOQ but above the MLD were reported as the calculated value in the analytical report.

A limited processing study (2 trials) was carried out by Carringer (1998) in Mexico to produce crude oil from cotton seed from plants treated with 6 applications at the exaggerated rate of 250 g ai/ha. No evidence of concentration was observed.

Table 97. Residues in cotton seed and its processed fractions (Norris, 1995). All WG formulations

Location, Year, Reference	Application		PHI, days	Commodity	Residues, mg/kg				
	g ai/ha	No.			Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
USA (Texas), 1994 94-0353 Replicate 1 Norris, 1995	1680 soil + 420 foliar	1 + 4	45	Seed	0.056	0.021	0.07	0.173	<0.004
				Meal	<0.002	<0.001	<0.002	0.004	<0.002
				Hulls	0.008	0.003	0.008	0.021	<0.002
				Crude oil	0.009	0.044	0.013	0.041	<0.005
				Refined oil	0.01	0.005	0.016	0.039	<0.005
USA (Texas), 1994 94-0353 Replicate 2 Norris, 1995	1680 soil + 420 foliar	1 + 4	45	Seed	0.049	0.017	0.066	0.0143	<0.004
				Meal	<0.002	<0.002	0.003	0.007	<0.002
				Hulls	0.014	0.003	0.013	0.0029	<0.002
				Crude oil	0.017	0.006	0.019	0.061	<0.005
				Refined oil	0.013	0.006	0.019	0.054	<0.005
Mexico, 1996 12046-01 Carringer, 1998	250	6	54	Seed	<0.01	<0.002	<0.01	<0.01	NR
				Crude oil	<0.01	<0.001	<0.003	<0.01	NR
Mexico, 1996 12046-02 Carringer, 1998	250	6	46	Seed	0.037	<0.01	0.037	0.067	NR
				Crude oil	<0.01	<0.01	<0.01	<0.01	NR

NR: not reported

Sunflower seed (Table 98). In various residue trials in Southern Europe residues were determined in the oil extracted from the seeds and the seed-cake solid residue.

Table 98. Residues in sunflower seeds and their processed fractions.

Country, Year, Reference	Application				PHI,	Commodity	Residues, mg/kg			
	Form	g ai/t	g ai/ha	No.	days		Fipronil	MB 45950	MB 46136	RPA 200766
France, 1990 Leovillle 91-215, LA19I27 Maiano and Muller, 1991	GR		200	1	147	Seed Oil Seed cake	NR <0.01 (2) 0.01 <0.01	NR <0.01 (2) <0.01 <0.01	NR <0.01 (2) <0.01 <0.01	NR <0.01 (2) <0.01 <0.01
France, 1990 Chadenac 91-215, LA19I27 Maiano and Muller, 1991	GR		200	1	151	Seed Oil Seed cake	NR <0.01 (2) <0.01 (2)	NR <0.01 (2) <0.01 (2)	NR <0.01 (2) <0.01 (2)	NR <0.01 (2) <0.01 (2)
France, 1990 91-215, LA19I27 St. Gilles Maiano and Muller, 1991	GR		200	1	140	Seed Oil Seed cake	NR <0.01 (2) <0.01 (2)	NR <0.01 (2) <0.01 (2)	NR <0.01 (2) <0.01 (2)	NR <0.01 (2) <0.01 (2)

Country, Year, Reference	Application				PHI,	Commodity	Residues, mg/kg			
	Form	g ai/t	g ai/ha	No.	days		Fipronil	MB 45950	MB 46136	RPA 200766
France, 1992 92-142 part 2, XA192R84 Muller, 1994	GR		294	1	146	Seed Oil Seed cake	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)	NR <0.005 (2) <0.005 (2)	NR <0.005 (2) NR
France, 1992 92-142 part 2, XH192R84 Muller, 1994	GR		206 295	1	137	Seed Oil Seed cake	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)	NR <0.005 (2) <0.005 0.006	NR <0.005 (2) NR
France, 1992 92-142 part 2, XK192R84 Muller, 1994	GR		200 300	1	140	Seed Oil Seed cake	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)	NR <0.005 (2) <0.005 (2)	NR <0.005 (2) NR
France, 1993 R93567A2 Muller, 1994 g	FS	3750		1	147	Seed Oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)
France, 1993 R93567H1 Muller, 1994 g	FS	3750		1	166	Seed Oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)
France, 1993 R93567K1 Muller, 1994 g	FS	3750		1	89	Seed Oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) 0.011, 0.013 <0.002 (2)
France, 1995 95537DJ1 Maestracci, 1996	GR		190	1	154	Seed Oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)
France, 1995 95537TL1 Maestracci, 1996	GR		187	1	164	Seed oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)
Italy, 1995 95743BO1 Maestracci, 1997	GR		153	1	153	Seed Oil Seed cake	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)
Italy, 1995 95743BO2 Maestracci, 1997	GR		150	1	154	Seed Oil Seed cake	NR <0.002 <0.002	NR <0.002 <0.002	NR <0.002 <0.002	NR <0.002 <0.002
Italy, 1995 95743BO3 Maestracci, 1997	GR		150	1	154	Seed Oil Seed cake	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)	NR <0.002 (2) <0.002 (2)
Spain, 1994 94667SE1 Muller, 1995	FS	10,000		1	133	Seed Oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) 0.002 <0.002 <0.002 (2)	<0.002 (2) 0.002 0.002 <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)
Spain, 1996 96637M1 Maestracci, 1997	FS	10,000		1	192	Seed Oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) 0.002 <0.002	<0.002 (2) <0.002 (2) <0.002 (2)
Spain, 1996 96637SE1 Maestracci, 1997	FS	10,000		1	164	Seed Oil Seed cake	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)	<0.002 (2) <0.002 (2) <0.002 (2)

NR: not reported

Sugar cane (Table 99). A number of studies were conducted in Australia to measure residues in various processed fractions of sugar cane treated with fipronil by soil or foliar application.

Table 99. Residues in sugar cane and its processed fractions.

Country, Year, Reference	Application			PHI,	Commodity	Residues, mg/kg				
	Form	g ai/ha	No.	days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1996 AUS94i74br Rocky Point Queensland Keats, 1997b	WG	100 foliar	2	116	Cane	NR	NR	NR	NR	NR
					Bagasse	0.003 0.002	<0.002 (2)	0.002 <0.002	<0.002 (2)	NR
					Juice	<0.002 0.002	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR
					Molasses	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR
					Sugar	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR

Country, Year, Reference	Application			PHI,	Commodity	Residues, mg/kg				
	Form	g ai/ha	No.	days		Fipronil	MB 45950	MB 46136	fipronil-desulfinyl	RPA 200766
Australia, 1996 AUS94i74cr Kurrimine Beach Queensland Keats, 1997k	WG + SC	100 soil 50 foliar	1 + 2	95	Cane	0.002 0.002	<0.002 (2)	0.002 0.002	<0.002 (2)	NR
					Bagasse	0.004 0.004	<0.002 (2)	0.003 0.002	<0.002 (2)	
					Juice	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	
					Cane	0.002 0.003	<0.002 (2)	0.003 0.003	0.002 0.002	NR
					Bagasse	0.004 0.004	<0.002 (2)	0.004 0.003	0.002 <0.002	
					Juice	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	
					Cane	0.005 0.005	<0.002 (2)	0.006 0.006	0.008 0.008	NR
					Bagasse	0.005 0.006	<0.002 (2)	0.004 0.005	0.003 0.004	
					Juice	0.003 0.003	<0.002 (2)	<0.002 (2)	<0.002 (2)	
Australia, 1995 AUS94i74r Mowilyan Queensland Keats, 1997m	WG	50 foliar	2	134	Cane	<0.002 0.002	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR
					Bagasse	<0.002 0.002	<0.002 (2)	<0.002 0.002	<0.002 (2)	
					Juice	0.002 <0.002	<0.002 (2)	<0.002 (2)	<0.002 (2)	
		100 foliar	2	53	Cane	0.025 0.02	<0.002 (2)	0.008 0.007	0.003 0.003	NR
					Bagasse	0.013 0.018	0.002 0.002	0.003 0.005	0.003 0.003	
					Juice	0.004 0.005	<0.002 (2)	<0.002 (2)	<0.002 (2)	
		100 foliar	1	181	Cane	0.002 0.002	<0.002 (2)	0.002 0.002	<0.002 (2)	NR
					Bagasse	0.004 0.004	<0.002 (2)	0.002 <0.002	<0.002 (2)	
					Juice	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	
		200 foliar	1	181	Cane	0.002 0.002	<0.002 (2)	0.002 0.002	0.002 0.002	NR
					Bagasse	<0.002 (2)	<0.002 (2)	<0.002 (2)	0.002 0.002	
					Juice	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	
Australia, 1996 97NST14 Kurrimine Beach Queensland Keats, 1997k	SC	75 foliar	1	101	Cane	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR
					Bagasse	0.002 0.002	<0.002 (2)	<0.002 (2)	0.002 0.002	NR
					Juice	0.002 0.002	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR
					Molasses	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR
					Sugar	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	NR

NR: not reported

Residues in the edible portion of food commodities

Data are reported in “Fate of residues in storage and processing”.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No monitoring or enforcement data were received.

NATIONAL MAXIMUM RESIDUE LIMITS

Information, as of 7 March 2000, on world-wide national MRLs submitted by the manufacturer is tabulated below.

Country	Commodity	MRL (mg/kg)	Definition of the residue
Australia	Bananas	0.01	Sum of Fipronil, MB 45950 and MB 46136
	Brassica vegetables (head cabbage, cauliflower, broccoli, Brussels sprouts, kohlrabi)	0.05 (temporary)	Sum of Fipronil, MB 45950, MB 46136 and fipronil-desulfinyl
	Cotton (seed, crude oil, meal, hull)	0.01	Sum of Fipronil, MB 45950, MB 46136 and fipronil-desulfinyl
	Edible offal	0.02	
	Eggs	0.02	
	Meat of mammals (fat)	0.05	
	Milk (fat)	0.01	
	Mushrooms	0.02	Sum of Fipronil, MB 45950 and MB 46136
	Peanuts (nut, crude oil, forage, fodder)	0.01	Sum of Fipronil, MB 45950 and MB 46136
	Potatoes	0.01	Sum of Fipronil, MB 45950 and MB 46136
	Poultry, edible offal	0.01	
	Poultry meat (fat)	0.02	
	Rice	0.005	Sum of Fipronil, MB 45950 and MB 46136
	Sugar cane (cane, fodder)	0.01	Sum of Fipronil, MB 45950 and MB 46136
	Sweet potatoes	0.01	Sum of Fipronil, MB 45950 and MB 46136
Brazil	Cotton	0.01	Fipronil
	Potatoes	0.05	Fipronil
	Rice	0.01	Fipronil
	Sugar cane	0.01	Fipronil
Belgium	Cereals	0.02	Sum of Fipronil and MB 46136
Czech Republic	Potatoes	0.01	
France	Bananas	0.01	Fipronil
	Maize (grain, silage)	0.01	Fipronil
	Sugar beet	0.01	Fipronil
	Sunflower	0.01	Fipronil
	Cereals	0.01	
Hungary	Cereals	0.05	
	Maize grain	0.05	
	Potatoes	0.05	
	Sugar beet	0.05	
India	Cabbage	0.05	
	Chillies	0.05	
Italy	Maize grain Maize silage	0.01 0.02	
	Sugar beet (root)	0.02	
	Sunflower seed	0.01	
	Potatoes	0.03	
	Tomatoes	0.01	
Japan	Rice	0.01	
	Water	0.0005	
Korea	Cucumber	0.06	
	Rice	0.01	
Mexico	Maize	0.01	
Peru	Cotton seed	0.01	
	Grapes	0.05	
	Mangold	0.05	
	Potatoes	0.05	
	Tomatoes	0.05	
Russia	Cereals	0.005	
	Potatoes	0.005	
South Africa	Citrus	0.05 (at LOQ)	Sum of Fipronil, MB 45950, MB 46136, fipronil-desulfinyl and RPA 200766
	Mango	0.05 (at LOQ)	Sum of Fipronil, MB 45950, MB 46136, fipronil-desulfinyl and RPA 200766

Country	Commodity	MRL (mg/kg)	Definition of the residue
Spain	Potatoes	0.01	Sum of Fipronil, MB 45950, MB 46136 and RPA 200766
Switzerland	Cereals	0	Fipronil
	Maize	0.01	Fipronil
Taiwan	Cabbage (headed leafy vegetables)	0.1	Sum of Fipronil and MB 46136
	Cabbage (non-headed leafy vegetables)	0.5	Sum of Fipronil and MB 46136
	Rice	0.01	
USA	Maize forage Maize grain Maize stover	0.15 0.02 0.3	Sum of Fipronil, MB 45950 and MB 46136
	Eggs	0.03	
	Fat - Cattle, goat, horse, sheep - Hog - Poultry	 0.4 0.03 0.05	
	Liver - Cattle, goat, horse, sheep - hog	 0.1 0.02	
	Meat - Cattle, goat, horse, sheep - Hog - Poultry	 0.04 0.01 0.02	
	Meat by-products, poultry	0.02	
	Meat by-products (except liver) - cattle, goat, horse, sheep - hog	 0.04 0.01	
	Milk (fat, reflecting 0.05 mg/kg in whole milk)	1.5	
	Rice grain	0.04	Sum of Fipronil, MB 45950, MB 46136 and fipronil-desulfinyl
	Rice straw	0.1	Sum of Fipronil, MB 45950, MB 46136 and fipronil-desulfinyl
Uzbekistan	Cabbage	0.01	
Venezuela	Cabbage	0.5	
	Cotton seed	<0.01	
	Rice	0.01	

APPRAISAL

Fipronil belongs to a new class of insecticides known as phenylpyrazoles and was first reviewed by the 1997 JMPR for toxicology only. The compound was identified by the 1998 CCPR as a candidate for the residue evaluation of a new compound by the 2000 JMPR. The evaluation was postponed to the Meeting in 2001.

The manufacturer sent the Meeting information on metabolism in animals and plants, environmental fate in soil and water, methods of residue analysis, stability of residues in stored analytical samples, uses, supervised trials and processing data as well as national MRLs. Information on national GAP was provided by the governments of Australia, The Netherlands and Poland.

Pure fipronil is a white powder with a melting-point of 203 °C and low volatility. It has limited solubility in water and medium–high solubility in certain organic solvents. The log P_{OW} for the parent and relevant metabolites of 3.5–4 suggests that bioaccumulation may occur.

The parent, metabolites and degradation products are identified by the code numbers shown below.

Code	Chemical name
fiponil (MB 46030)	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole
MB 45950	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthiopyrazole
MB 45897	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole
MB 46136	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4 trifluoromethylsulfonylpyrazole
fipronil-desulfinyl (MB 46513)	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylpyrazole
MB 46400	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole-4-carboxylic acid
RPA 106889	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole-3,4-dicarboxylic acid
RPA 104615	5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole-4-sulfonic acid
RPA 105320	5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4 trifluoromethylsulfonylpyrazole
RPA 105048	5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylpyrazole
RPA 200761	5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole-3-carboxylic acid
RPA 200766	5-amino-3-carbamoyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole

Metabolism

Animals

The absorption, distribution, metabolism and excretion of [phenyl ring ^{14}C]fipronil and its toxicologically relevant photodegradation product fipronil-desulfinyl were studied in rats, goats and hens.

Parent fipronil: Rats were given a single dose of 4 or 150 mg/kg bw or 4 mg/kg bw [^{14}C]fipronil after pretreatment with 14 daily non-radiolabelled doses. After absorption, metabolism was rapid, and no unmetabolized fipronil was detected in any tissues or urine. Most of the radiolabel was eliminated in faeces, which contained unchanged [^{14}C]fipronil and metabolites, suggesting both bilary elimination of absorbed fipronil (metabolized) and elimination of unabsorbed fipronil. This observation indicates that some metabolites are probably excreted in the bile. The tissue concentrations of total radioactive residues (TRR) were high 7 days after dosing, with the highest levels in fat. The main residue in fat and other tissues examined was fipronil-sulfone.

Goats were given seven daily oral doses of [^{14}C]fipronil by capsule, equivalent to 0.05, 2 or 10 ppm in the diet (dry matter basis). Animals given the lowest and highest concentrations excreted the radiolabel extensively, mainly in the faeces. In contrast, those at 2 ppm appeared to retain a greater proportion of the administered dose. After administration at 0.05 ppm in the diet, 83% of the total dose was recovered, most (64%) being found in faeces. Much of the remaining radiolabel was estimated to have been retained in tissues (18%). At this concentration, no radiolabel was detected in urine, and negligible amounts were recovered in milk (0.86%). At the concentration of 2 ppm, a total of 50% of the radiolabel was recovered, most of which was sequestered in tissues (25%), with 2.5%, 18% and 4.6% in urine, faeces and milk, respectively. At the nominal concentration of 10 ppm, 77% of the administered radiolabel was recovered, principally in faeces (61%), with the remainder in urine (6.6%), milk (1.3%) and tissues (7.4%).

Consistent with the lipophilic nature of the compound and its metabolites, most of the radiolabelled residues were found in fat, providing supporting evidence that the radiolabel that was not recovered was retained in the animal. The parent compound was the main residue in milk and fat in animals at the highest concentration, representing 0.099 and 1.4 mg/kg, respectively. The metabolites fipronil-thioether and fipronil-sulfone were also present in these samples. Although the individual components of the TRR in kidney and muscle represented < 0.05 mg/kg fipronil equivalents, the parent compound and fipronil-sulfone were also present. In the liver, the main metabolite was fipronil-sulfone (0.46 mg/kg fipronil equivalents), representing 53% of TRR; compounds identified in smaller amounts were RPA 200076 (0.098 mg/kg fipronil equivalents) and the parent compound (0.013 mg/kg).

Hens were given repeated oral doses of [^{14}C]fipronil by capsule at a concentration of 0.05, 2 or 10 ppm in the diet (dry matter basis). Approximately 52–58% of the administered radiolabel was eliminated, principally in the excreta. Plateau levels for both the excretion of radiolabel and residue concentrations in egg yolk and white were close to being attained. The high concentrations in egg yolk, skin and fat were consistent with the lipophilic nature of the compound. The metabolite fipronil-sulfone was identified as the principal component of the TRR in eggs and tissues at all concentrations.

The fate of fipronil has been shown to be similar in all species studied. It is relatively well absorbed and extensively distributed in the tissues, with a preference for tissues with a high lipid content. Faeces and then urine were the major routes of elimination of fipronil. Its biotransformation involved changes in the functional groups attached to the pyrazole ring. The compounds identified in faeces and urine were the parent and the fipronil-sulfone, the amide (RPA 200766) derived from the nitrile group, a reduction product (fipronil-thioether), a cleavage product (MB 45897) of the sulfone and its derivatives formed by further cleavage. The fipronil-sulfone was the main compound in eggs and tissues. Parent compound and fipronil-sulfone were identified as major compounds in milk and fat.

Fipronil-desulfinyl: Rats: The absorption, distribution, metabolism and excretion of [^{14}C]fipronil-desulfinyl were studied in rats that received either a single oral dose of 1 or 10 mg/kg bw or 14 daily oral doses of unlabelled fipronil-desulfinyl at 1 mg/kg bw per day followed by a single oral radiolabelled dose. Much more of the dose was eliminated in the faeces (46–70%) than in the urine with all dosing regimens. Appreciable quantities of residues were found in the tissues 1 week after treatment, the highest concentrations being present in fat and fatty tissues. Numerous metabolites or conjugates of fipronil-desulfinyl were present in urine and faeces. Biotransformation of the compound involved changes at the functional groups attached to the pyrazole ring. Only unchanged fipronil-desulfinyl was identified in the liver, fat, skin and residual carcass.

Goats were given repeated oral doses of [^{14}C]fipronil-desulfinyl by capsule at concentrations equivalent to 0.05, 2 and 10 ppm in the diet (dry matter basis) for 7 days. Excretion was mainly in the faeces, the percentage excreted declining with decreasing dose. Plateau levels appeared to have been attained after 104 h on the basis of measurements of radiolabel in milk. The high concentrations in fat were consistent with the lipophilic nature of the compound. Fipronil-desulfinyl was identified as the principal component of the TRR in milk and tissues at all concentrations.

Hens received 14 daily doses of [^{14}C]fipronil-desulfinyl by capsule at concentrations equivalent to 0.05, 2 and 10 ppm in the diet (dry matter basis). Approximately 53–71% of the administered radiolabel was eliminated in the excreta. Measurements of radiolabel in eggs indicated that plateau levels had been attained by the end of the dosing period. The high concentrations in egg yolk, omental fat, and skin with fat were consistent with the lipophilic nature of the compound. Fipronil-desulfinyl was identified as the principal component of the TRR in egg and tissues at all concentrations.

The metabolic pathway of the photodegradation product fipronil-desulfinyl in livestock is consistent with that in rats. Fipronil-desulfinyl is metabolized to more polar derivatives or forms polar conjugates, which are excreted. Unmetabolized fipronil-desulfinyl is distributed to eggs, milk, and/or tissues, the highest concentrations being found in fat, consistent with the lipophilic nature of the molecule. These results indicate that only unchanged fipronil-desulfinyl has the potential to transfer to animal substrates in measurable quantities.

Plants

The metabolism of [phenyl ring-^{14}C]fipronil was investigated after application to the soil or to the aerial part of the plant.

Studies of metabolism after soil incorporation were carried out on maize, sugar beet, cotton and sunflowers. Quantitative analysis of radiolabel showed that the uptake of soil-applied fipronil by plants is low (< 5% on the basis of the total radiolabel measured in whole plants at harvest). Analysis of extracts of maize forage samples revealed fipronil, fipronil-sulfone and amide RPA 200766 as the major metabolites; RPA 200761 was also found. In samples taken at harvest, sugar beet and sunflower leaves, maize fodder and cotton foliage contained two common metabolites, fipronil-sulfone and RPA 200766, in addition to various amounts of the parent compound. RPA 105320 and MB 45897 were identified only in beet leaves; RPA 200761 was identified in maize fodder and cotton foliage.

With regard to edible plant parts, fipronil-sulfone and RPA 200766 were present in sugar beet, but only amide RPA 200766 was found in field maize grain. Investigation of sunflower seed extract revealed a complex mixture of substances different from those found in the leaves; a number of components each representing < 0.01 mg/kg were separated. Cotton seed was not analysed as it was found to contain < 0.01 mg/kg of the TRR.

In summary, identification of residues in plant tissues after soil incorporation of fipronil showed that the metabolism proceeded mainly by oxidation to fipronil-sulfone and hydrolysis to amide RPA 200766. Further hydrolysis of metabolites RPA 200766 and fipronil-sulfone can also occur. Very small amounts of fipronil-thioether can be formed by reduction, but in no case was it found at > 5% of the TRR

Studies of metabolism after application by foliar spray were carried out on cabbage, rice, cotton and potato. Radiolabelled residues were quantified in all plant parts. In addition to the formation of previously known fipronil metabolites by oxidation (fipronil-sulfone), reduction (fipronil-thioether) and hydrolysis (RPA 200766, RPA 200761), the photodegradates fipronil-desulfinyl and RPA 104615 were shown to be possible terminal residues after foliar application of fipronil. The main residues found consistently after foliar application were the parent and fipronil-desulfinyl; lesser amounts of fipronil-thioether and fipronil-sulfone were also formed.

Environmental fate

Soil

The photolytic degradation of [^{14}C]fipronil was studied after surface application to a clay loam soil. Fipronil degraded rapidly in both the control (no irradiation) and irradiated phase of the study, with estimated half-times of 49 and 34 days, respectively. The enhanced degradation stimulated by photolysis yielded the photodegradates RPA 104615 and fipronil-desulfinyl, which were also observed after aqueous photolysis but not in the dark control experiments nor in studies of hydrolysis (dark).

Aerobic soil degradation of [^{14}C]fipronil in various soils (sandy loam, sandy clay loam, sand) resulted in DT_{50} values of 40–308 days, depending on the soil type and temperature. The main breakdown product of fipronil in all cases was RPA 200766 (30–47%). Fipronil-sulfone was also identified as a significant degradate (about 20%). Fipronil-thioether was found, but at levels < 10%; RPA 105320 and MB 45897 were present at very low levels. Polar metabolites not previously found appeared in the later stages of the study and were generated in significant amounts (5.9–29.2%, collectively). These metabolites occurred at higher concentrations in the sandy clay loams than in the other soils. The polar metabolites were identified as acid homologues of fipronil and its metabolites, the result of hydrolysis of nitrile to amide and to carboxylic acid.

In a study of adsorption and desorption in soil, fipronil, fipronil-thioether and fipronil-desulfinyl showed medium–low mobility, and fipronil-sulfone was classified as having low mobility to immobility.

Studies of rotational crops were carried out with [^{14}C]fipronil at recommended use rates for soil incorporation or surface treatment. The results were consistent with the established pathways of environmental degradation and plant metabolism.

[^{14}C]Fipronil incorporated into soil at 157 g ai/ha was taken up at a low rate by carrot, radish, lettuce, mustard, sorghum and wheat. Only cereal forage and fodder contained concentrations of residues > 0.01 mg/kg.

After application of [^{14}C]fipronil to soil surface at 369 g ai/ha, neither fipronil nor its relevant metabolites were found in cereal grains 30–365 days later. Further, residues were not found in root crops or leafy vegetables 5 months after treatment.

A field study on radish, soya bean, pea, mustard, lettuce, sorghum and wheat confirmed that soil-surface application at 340 g ai/ha would result in low residues of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone in the vegetative portions of crops, and none in grains. At plant-back intervals of 119–367 days after treatment, concentrations of residues of the parent and its relevant metabolites ranging from < 0.005 to 0.026 mg/kg were found. Only at a short plant-back interval of 31 days were residues found in leafy and root crops (< 0.002–0.016 mg/kg).

Water–sediment systems

A study of the fate and behaviour of [^{14}C]fipronil in two water–sediment systems showed that the major degradate under aerobic conditions was the fipronil-thioether (80–88% of applied radiolabel). The DT_{50} values were 6–14 days in water, 48–75 days in sediment and 22–32 days in the total systems. Under anaerobic conditions, decomposition resulted mainly in the formation of fipronil-thioether and the amide RPA 200766, accounting for 32 to 47% of applied radiolabel, respectively. The DT_{50} value for fipronil under anaerobic conditions was 123 days.

In an investigation of the fate and behaviour of the photodegradation product [^{14}C]fipronil-desulfinyl in two water–sediment test systems (Manningtree, UK, and Ongar, UK), it was found that any fipronil-desulfinyl reaching or formed in the water after an application of fipronil moved to the sediment at an initially rapid rate. The degradation (principally hydrolysis) of the compound then proceeded steadily in both water and sediment phases. The movement of the compound from water to sediment and the degradation resulted in DT_{50} values of 4.2 days and 9.9 days and DT_{90} values of 174 days and 146 days in the two test systems.

Methods of analysis

Plant material is extracted with acetonitrile or water:acetone, and the crude extract is purified by liquid–liquid partition and column chromatography (e.g. silica gel, alumina, Florisil or C18 cartridge). Determination is conducted by GLC with an ECD, MSD or electrochemical detector. The methods have been validated for fipronil, fipronil-thioether, fipronil-sulfone, fipronil-desulfinyl and RPA 200766 in numerous matrices. The LOQs of all compounds ranged from 0.002 mg/kg in e.g. cereal grains, banana and potato to 0.01 mg/kg in cereal straw and forage.

The analytical methods for animal products follow the same steps described above. Numerous validation studies resulted in LOQs for fipronil, fipronil-desulfinyl, fipronil-thioether and MB 56136 of 0.002– 0.01 mg/kg in bovine muscle, milk, liver, kidney, fat and eggs.

The multi-residue analytical method DFG S19, suitable for enforcement, was modified and successfully validated for the determination of residues of fipronil and its metabolites (fipronil-thioether, fipronil-sulfone, fipronil-desulfinyl) in plants and animal products at 0.002 mg/kg per analyte (LOQ) and 0.02 mg/kg per analyte (10 x LOQ).

Methods were developed for the analysis of fipronil, fipronil-sulfone, fipronil-thioether, fipronil-desulfinyl, and RPA 200766 in soil. The residues are extracted from soil with acetonitrile:acetone (70:30). The sample is centrifuged, the extract is dried with Na_2SO_4, and the analytes are adsorbed onto activated charcoal and eluted with acetonitrile. The residues are quantified by GC with ECD. The LOQ is 0.005 mg/kg for all compounds.

Stability of residues in stored analytical samples

Studies of the stability of fipronil, fipronil-thioether and fipronil-sulfone on animal products (milk, liver, kidney, muscle, fat, eggs) under storage conditions indicated that they are stable at –10 °C for at least 3 months. Studies of stability in storage were also reported for residues of fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl in lettuce, potato, broccoli, cabbage, cauliflower, maize (grain, forage, fodder, oil, starch) and cotton (seed, hulls, meal, oil, gin trash). The residues were shown to be stable at –20 °C for 12–24 months.

Definition of the residue

Toxicological background

Fipronil was evaluated for toxicology by the 1997 and the 2000 JMPR. The 1997 Meeting concluded that the toxicity of the mammalian metabolites is comparable to or substantially less than that of fipronil. Because the photodegradation product fipronil-desulfinyl is of toxicological concern but not a mammalian metabolite of fipronil, it was reviewed separately.

After considering additional data, the 2000 JMPR established a group ADI of 0–0.0002 mg/kg bw for fipronil and fipronil-desulfinyl, alone or in combination. The acute RfD established by the 1997 JMPR of 0.003 mg/kg bw for fipronil and fipronil-desulfinyl, alone or in combination, was confirmed. Other toxicologically significant compounds are fipronil-sulfone and fipronil-thioether. The 2000 JMPR concluded that the metabolite RPA 200766 is significantly less toxic than fipronil, the acknowledged relevant metabolites fipronil-thioether and fipronil-sulfone and the degradation product fipronil-desulfinyl. Therefore, RPA 200766 should not be relevant for dietary risk assessment.

Plant material

Studies of plant metabolism have shown that, after soil incorporation, residues of the parent and fipronil-sulfone represent most of the total residues, the concentrations of fipronil-thioether usually being low.

In studies of foliar metabolism, most of the residues in edible plant parts (cabbage, potato tubers) consisted of the parent compound and fipronil-desulfinyl, whereas in animal feed items (rice straw, husk, bran), the parent compound, fipronil-sulfone, fipronil-desulfinyl and fipronil-thioether were the residues most relevant for consideration.

The results of supervised residue trials indicated that the parent compound is the main component of the residue. The Meeting concluded that fipronil is a good indicator compound for enforcement purposes for plant commodities. The Meeting considered that, for the purposes of long-term and short-term dietary risk assessment, the residue should be defined as the sum of fipronil, fipronil-sulfone, fipronil-desulfinyl and fipronil-thioether, calculated as fipronil.

Animal products

In a study of metabolism in goats, fipronil, fipronil-sulfone and fipronil-thioether were the principal compounds. In a study of metabolism in laying hens, fipronil-sulfone was identified as the major component of the TRR in eggs and tissues. The results of studies in which fipronil was fed to cows and hens showed that most of the residues in milk, eggs and tissues consisted of fipronil-sulfone.

The Meeting concluded that the definition of residue for enforcement purposes should be the sum of fipronil and fipronil-sulfone, expressed as fipronil. For the purposes of long-term and short-term dietary risk assessment, the residue should be defined as the sum of fipronil, fipronil-sulfone, fipronil-desulfinyl and fipronil-thioether, calculated as fipronil.

The residue definitions are thus:

- for compliance with MRLs for plant commodities: fipronil
- for compliance with MRLs for animal commodities: sum of fipronil and fipronil-sulfone, expressed as fipronil.
- for estimation of long-term and short-term dietary intake from plant and animal commodities: sum of fipronil, fipronil-desulfinyl, fipronil-sulfone and fipronil-thioether, expressed as fipronil.

The Meeting concluded that the residue is fat-soluble.

Results of supervised trials

The residues reported in supervised trials consisted of three (after soil treatment) or four (after foliar spray) components. The studies of metabolism and the supervised trials showed that after soil incorporation, residues of parent and fipronil-sulfone represented most of the total residues. After foliar uses (including soil surface treatment; broadcast treatment of flooded paddy rice), most of the residues in edible plant parts consisted of fipronil and fipronil-desulfinyl, whereas those in animal feed items were fipronil, fipronil-sulfone and fipronil-desulfinyl. If the concentrations of all components are below the LOQ (or MLD[1]), a reasonable assumption is that the concentrations of combined residues are:

- after soil incorporation and seed treatment, for food and feed commodities *(banana, potato, sugar beet, barley, wheat, maize, rice, sweet corn, sorghum, sugar cane, sunflower seed, sugar beet leaves or tops, maize forage and fodder, cereal straw)*: lower than the combined LOQs for fipronil and fipronil-sulfone;
- after foliar and soil surface use and treatment of flooded paddy rice, for food commodities *(banana, flowerhead brassicas, head cabbage, potato, rice, sorghum, cotton seed)*: lower than the combined LOQs for fipronil and fipronil-desulfinyl;
- after foliar and soil surface use and treatment of flooded paddy rice, for feed items *(pasture grass, cereal straw, sorghum forage and fodder, cotton gin trash)* and sugar cane: lower than the combined LOQs for fipronil, fipronil-sulfone and fipronil-desulfinyl.

When the concentration of one component is above and the other below the LOQ, that of the combined residue is assumed to be close to the measurable component plus the LOQ of the other. To indicate that one of the results was a real measurement, the Meeting agreed to express the sum of the values as a real figure (e.g. < 0.002 + 0.004 mg/kg = 0.006 mg/kg). The method for calculating the total residue in various situations is illustrated below.

Fipronil	Fipronil-sulfone or fipronil-desulfinyl	Total
< 0.002	< 0.002	< 0.004
< 0.002	0.004	0.006
0.003	0.005	0.008

The concentrations of residues of fipronil (437.2 g/mol) and the metabolites fipronil-thioether (421.1 g/mol, factor 1.04), fipronil-sulfone (453.1 g/mol, factor 0.965) and fipronil-desulfinyl (389.02 g/mol, factor 1.1) are given in the evaluation tables for the individual compounds but were calculated

[1]For data on maize and rice grain in the USA only: when no detectable residues were found, “less than the minimum limit of detection (MLD) ” is shown in the evaluation tables.

in the appraisal according to the respective residue definition. The LOQs of the individual compounds are not corrected by these factors.

Banana: Common practice worldwide is to apply 300–400 g ai/ha fipronil around the base of the banana stem or plant with or without incorporation into the soil. The number of treatments and the PHI are not specified in most countries.

Two studies, each of 300 and 600 g ai/ha, and one study with 800 g ai/ha were available from Australia. As separate plots were treated on different dates and the bananas were harvested at different times (PHI, 0–166 days), these were considered to be individual trials. In all 10 trials conducted according to Australian GAP (stem and soil surface treatment, 300 g ai/ha), the concentrations of fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl residues were no higher than the LOQ of 0.002 mg/kg.

Five studies of soil treatment in Guadeloupe (10 trials, 1 x 400 kg ai/ha; three trials, 2 x 400 g ai/ha) with PHIs of 0–149 days were carried out according to French GAP. A further soil treatment trial was carried out according to GAP (400 g ai/ha, soil broadcast at base of plant) in Cameroon. The ranked orders of concentrations of residues after stem and soil surface spray were < 0.002 (10) mg/kg for fipronil and < 0.004 (10) mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil). The ranked orders of concentrations of residues after soil incorporation were < 0.002 (12) and 0.003 mg/kg for fipronil and < 0.004 (12) and 0.005 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The combined results of 23 trials with foliar spray and soil incorporation were, in ranked order (median underlined), < 0.002 (22) and 0.003 mg/kg for fipronil and ≤ 0.004 (22) and 0.005 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting estimated the following residue levels in bananas: maximum residue level (fipronil), 0.005 mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.004 mg/kg; highest residue (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.005 mg/kg.

Foliar spray use of fipronil on broccoli and cauliflower is registered in Australia with a maximum GAP of 4 x 48 g ai/ha and a PHI of 7 days. Numerous trials were carried out in Australia, but only one trial on broccoli and two on cauliflower were conducted in accordance with the maximum GAP (4 or 5 x 48 g ai/ha; PHI, 7 days). The results of further trials with two to ten applications at an interval of 7 days showed that the number of applications is of secondary relevance to the residue concentration. Therefore, further trials with 48 g ai/ha and a PHI of 7 days were used for evaluation, two on broccoli (six or ten treatments) and four on cauliflower (two, eight or nine treatments). The ranked orders of concentrations of residues after foliar spray were < 0.002 (2), 0.002, 0.003 (3), 0.005, 0.006 and 0.008 mg/kg for fipronil and < 0.004 (2), 0.004, 0.005 (3), 0.007, 0.008 and 0.01 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Foliar spray use of fipronil in head cabbage is registered in Australia (4 x 24–48 g ai/ha; PHI, 7 days), in New Zealand (4 x 24 g ai/ha; PHI, 7 days), the Philippines (6–8 x 25–50 g ai/ha; PHI, 7 days) and other countries in Asia and Latin America. Supervised trials with various numbers of applications were available from Australia and New Zealand. The Meeting noted that the number of applications is of secondary importance for the concentration of residue, and therefore the results from trials with two, four and eight applications were combined.

In four of the trials in Australia and one in New Zealand that conformed to New Zealand GAP (24 g ai/ha), the concentrations of residues were lower than the LOQ of 0.002 mg/kg.

In five trials in Australia and one in New Zealand that complied with the Australian maximum GAP (48 g ai/ha) and in which there were detectable residues, the ranked orders of concentrations of residues were < 0.002 (3), 0.002, 0.004 and 0.014 mg/kg for fipronil and < 0.004, 0.004, 0.0042, 0.0053, 0.0062 and 0.0215 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting noted that the data on flowerhead brassica and head cabbage were similar and could be combined for mutual support. The combined residues were, in ranked order, for fipronil: < 0.002 (6), 0.002 (2), 0.003 (3), 0.004, 0.005, 0.006, 0.008 and 0.14 mg/kg, and for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil) (median underlined): < 0.004 (3), 0.004 (2), 0.0042, 0.005 (3), 0.0053, 0.0062, 0.007, 0.008, 0.01 and 0.0215 mg/kg.

The Meeting estimated the following residue levels for flowerhead brassicas and cabbages, head: maximum residue level (fipronil), 0.02 mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.005 mg/kg; and HR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.0215 mg/kg.

The use of fipronil on Brussels sprouts is registered in Australia (4 x 24–48 g ai/ha; PHI, 7 days), but the results of only one trial were received. The Meeting could not recommend extrapolation of the results for cabbages, head or flowerhead brassicas to Brussels sprouts and concluded that there were insufficient data to estimate a maximum residue level.

The results of four trials on brassica leafy vegetables in Malaysia with 2 x 25 or 50 g ai/ha (GAP, 4–6 x 36 g ai/ha) were received. The Meeting could not recommend extrapolation from the results for cabbages, head or flowerhead brassicas to brassica leafy vegetables and concluded that there were insufficient data to estimate a maximum residue level.

Fipronil may be used on potato as a foliar spray e.g. in Hungary (1–2 x 20 g ai/ha; PHI, 14 days), in Spain (3 x 20–24 kg ai/ha; PHI, 14 days), the Czech Republic, Poland and Slovakia (20 g ai/ha; PHI, 14 days; number of treatments not specified) and Romania (3 x 20 g ai/ha; PHI, 30 days). Another use is soil incorporation at planting, e.g. in Italy (1 x 150 g ai/ha).

For foliar spray, the results of 29 European trials conducted according to the above GAPs were submitted. Most of the samples were analysed for fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone at an LOQ of 0.002 mg/kg for each. Two trials in Hungary were analysed with a less sensitive method (LOQ, 0.01 mg/kg), resulting in unquantifiable concentrations of residues of each compound. These trials were considered to belong to another population and were excluded from the evaluation. The concentrations of residues, in ranked order, were < 0.002 (26) and 0.003 mg/kg for fipronil and < 0.004 (23) mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

For soil incorporation, six trials were carried out according to Italian GAP. The samples were analysed for fipronil, fipronil-thioether and fipronil-sulfone. One study showed high concentrations of 0.017 mg/kg fipronil and 0.009 mg/kg fipronil-sulfone. No residue was determined in the corresponding untreated sample. The Meeting considered that there was no reason to exclude this value from the evaluation. The concentrations of residues, in ranked order, were < 0.002 (4), 0.005 and 0.017 mg/kg for fipronil and < 0.004 (4), 0.007 and 0.028 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The combined results of the 27 trials with foliar spray and the six trials with soil incorporation were, in ranked order: < 0.002 (30), 0.003, 0.005 and 0.017 mg/kg for fipronil and < 0.004 (27), 0.007 and 0.028 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting estimated the following residue levels for potato: maximum residue level (fipronil), 0.02 mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.004 mg/kg; highest residue (sum of fipronil, fipronil-desulfinyl, fipronil-thioetherand fipronil-sulfone), 0.028 mg/kg.

Fipronil can be used on sugar beet by soil application, e.g. in France and Italy (1 x 150–160 g ai/ha). In France, another GAP is broadcast soil incorporation before sowing at 200 g ai/ha. A further use is by foliar spray at 20–24 g ai/ha (PHI, 30 days) in Hungary and Romania.

For foliar spray, only one trial conducted in Hungary according to the GAP was reported. The concentrations of the residues of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone were lower than the LOQ of 0.01 mg/kg. The Meeting considered that one trial was inadequate to allow assessment the residue of fipronil in sugar beet after foliar spray.

Numerous trials (34) by soil treatment were carried out in France at 150–200 g ai/ha according to French or Italian GAP. Ten were analysed with a method with a LOQ of 0.01 mg/kg, but concentrations greater than the LOQ were determined in three of the trials. Hence, these trials were included in the assessment. One study showed high values of 0.16 mg/kg for fipronil and 0.015 mg/kg for fipronil-sulfone. No residue was determined in the corresponding untreated sample. The Meeting noted that there was no reason to exclude this value from the evaluation. The concentrations of residues, in ranked order, were: < 0.002 (7), 0.002, 0.003 (6), 0.005 (2), 0.007, 0.009, < 0.01 (9), 0.011, 0.013, 0.014, 0.018 (2), 0.072 and 0.16 mg/kg for fipronil and < 0.004 (7), 0.005 (2), 0.007 (3), 0.008 (2), 0.008, 0.009, 0.01, 0.011, 0.014, 0.018, < 0.02 (9), 0.021, 0.024, 0.028 (2), 0.082 and 0.17 mg/kg for the sum of fipronil, fipronil-thioether, fipronil-sulfone (calculated as fipronil).

The Meeting estimated the following residue levels for sugar beet on the basis of use by soil incorporation: maximum residue level (fipronil), 0.2 mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.0125 mg/kg; highest residue (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.17 mg/kg.

Fipronil is registered for use as a foliar spray on cereal grains (barley, oats, rye, triticale, wheat) in many countries, but adequate data on residues have not been submitted. In France, fipronil may be used as a seed treatment at 50 g ai/100 kg in cereals. There is specific GAP for wheat in Belgium (50 g ai/100 kg seed) and in Chile (50–100 g ai/100 kg seed).

Six seed treatment trials with two- to threefold excess doses on barley were reported from France (treatment with 100 or 150 g ai/100 kg of seed). The grains were analysed for fipronil, fipronil-thioether and fipronil-sulfone. At harvest, 249–271 days after sowing, the concentrations of residues of all analytes were below the LOQ of 0.002 mg/kg of grain.

Five trials on wheat seed treatment that complied with GAP (50 g ai/100 kg seed) were carried out in France. The grains were analysed for fipronil, fipronil-thioether and fipronil-sulfone. At harvest, 128–145 days after sowing, the concentrations of residues of all analytes were below the LOQ of 0.002 mg/kg of grain. In 17 trials conducted in France and Greece trials at higher application rates (75–150 g ai/100 kg seed), the concentrations of residues in the analytes were < 0.002–0.003 mg/kg. The concentrations of residues in barley and wheat after seed treatment were < 0.002 (11) mg/kg for fipronil and ≤ 0.004 (11) mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting agreed to extrapolate the data on residues in barley and wheat to oats, rye and triticale for seed treatment use, and estimated the following residue levels: maximum residue level (fipronil), 0.002* mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.004 mg/kg; and highest residue (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.004 mg/kg.

The use of fipronil as seed treatment of maize is registered in many countries: e.g. France and Italy 250 g ai/100 kg seed; Mozambique and Zimbabwe, 400 g ai/100 kg seed. Eleven trials were reported from France and Spain at 250–375 g ai/100 kg seed. The samples were analysed for fipronil, fipronil-thioether and fipronil-sulfone. Residues of all analytes were undetectable (< 0.002 mg/kg). The ranked orders were thus: < 0.002 (11) mg/kg for fipronil and < 0.004 (11) mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Another use is by soil treatment before or at sowing (e.g. France 200, Italy 100–150, USA 112–146 g ai/ha). Fifteen southern European trials complied with French and Italian GAP and 46 North American trials with GAP in the USA. The ranked orders of residues were < 0.002 (39), 0.002, < 0.004 (16), 0.004 and < 0.01 (4) mg/kg for fipronil and < 0.004 (13), 0.004, < 0.005 (24), < 0.007 (16), 0.007, < 0.012 (2), <0.013 (3) and < 0.02 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Hungarian GAP allows one foliar spray at 20 g ai/ha and a 30-day PHI. The concentration of residues in maize grain in a trial that complied with GAP was < 0.01 mg/kg for fipronil and its metabolites. The Meeting considered that one trial was inadequate to allow assessment of residues of fipronil in maize after foliar spray.

The combined results of trials with seed treatment and soil incorporation for maize were, in ranked order, < 0.002 (50), 0.002, < 0.004 (16), 0.004 and < 0.01 mg/kg for fipronil and < 0.004 (24), 0.004, < 0.005 (24), < 0.007 (16), 0.007, < 0.012 (2), <0.013 (3) and < 0.02 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting estimated the following levels for maize: maximum residue level (fipronil), 0.01 mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.005 mg/kg; and highest residue (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.02 mg/kg.

Sweet corn (corn-on-the-cob) was analysed in four French trials after soil treatment with fipronil before or at sowing at 200 g ai/ha. The concentrations of residues, in ranked order, were: < 0.002 (3) and 0.003 mg/kg for fipronil and < 0.004, < 0.004, 0.007 and 0.01 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting decided that four trials were insufficient to allow estimation of a maximum residue level for sweet corn.

Fipronil may be used on rice worldwide as a seed treatment, as soil or flooded paddy application or as a foliar spray. Numerous supervised trials with various application scenarios were reported. The following trials were conducted in accordance with GAP:

- seed treatment at 10–13 g ai/100 kg seed: one trial in Australia, five trials in France
- seed treatment at 120 g ai/100 kg seed, equal to 56 g ai/ha: 17 trials in the USA
- seed-box treatment at 0.5 g ai/nursery box: five trials in Japan
- soil incorporation before planting at 56 g ai/ha: 17 trials in the USA
- broadcast treatment on flooded paddy at 1 x 50 g ai/ha: three trials in the Philippines, one trial in Taiwan, three trials in Thailand (with no analysis for fipronil-thioether or fipronil-sulfone)
- foliar treatment: six trials in the Philippines at 1 x 50 g ai/ha and four trials in Thailand at 1 x 50 g ai/ha, with no analysis for fipronil-thioether or fipronil-sulfone; one trial in Indonesia at 1 x 25 g ai/ha, with analysis for fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl.

The concentrations of residues after seed treatment, including seed boxes and soil incorporation, in ranked order, were: < 0.001 (5), < 0.002 (6), < 0.003 (31) and < 0.01 (3) mg/kg for

fipronil and < 0.002 (5), < 0.004 (6), ≤ 0.006 (31) and < 0.013 (3) mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The concentrations after broadcast treatment on flooded paddy, were < 0.001 (7) mg/kg for fipronil and ≤ 0.001 (7) mg/kg for fipronil-desulfinyl. The sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone could not be calculated, as fipronil-thioether and fipronil-sulfone were not analysed.

The concentrations after foliar spray were < 0.001 (9), 0.002 and 0.008 mg/kg for fipronil; < 0.001 (8), 0.001 (3) and 0.005 mg/kg for fipronil-desulfinyl; and 0.016 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil; only one sample was analysed for fipronil-thioether and fipronil-sulfone).

The Meeting decided that the data on use as a foliar spray and by broadcast onto flooded paddy were insufficient because most of the samples were not analysed according to the residue definition. It decided to derive the maximum residue levels from the data for seed or seed-box treatment and soil incorporation. The Meeting estimated the following residue levels for rice: maximum residue level (fipronil), 0.01 mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.006 mg/kg; highest residue (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.013 mg/kg.

Use of fipronil on sorghum is registered in Australia for seed treatment (75 g ai/100 kg seed) and as a foliar spray (1.5 g ai/ha; PHI, 14 days). The results of supervised trials were available only from Australia. Three trials by foliar spray and two by seed treatment were conducted according to GAP. The samples were analysed for fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl. The concentrations of residues after seed treatment, in ranked order, were: < 0.002 (2) mg/kg for fipronil and < 0.004 (2) mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil). The concentrations of residues after foliar treatment, in ranked order, were: < 0.002 and 0.002 (2) mg/kg for fipronil and < 0.004 and 0.004 (2) mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting concluded that two trials of seed treatment and three of foliar treatment were inadequate for estimating a maximum residue level or STMR for a major crop such as sorghum.

The registered Australian use pattern on sugar cane allows application of 75 g ai/ha as one spray directed at the soil at the time of planting and/or spray to the bottom 40 cm of the stalk (PHI, 84 days). In Brazil, 200 g ai/ha are used as a soil spray in furrows at the time of planting.

Five trials of soil treatment were received from Australia, but only two complied approximately with GAP. The samples were analysed for fipronil, fipronil-thioether and fipronil-sulfone. The concentrations of residues for all analytes were lower or at the LOQ of 0.002 mg/kg at PHIs of 245 and 340 days.

Five trials in which the last treatment was spray to the bottom of the stalk were carried out in Australia. Two were approximately in accordance with Australian GAP. The concentrations of residues were lower than or at the LOQ of 0.002 mg/kg, with PHIs of 95 and 101 days for all analytes (fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl).

The Meeting concluded that there were insufficient data to estimate a maximum residue level.

Fipronil may be used worldwide for seed treatment of cotton (e.g. in Australia at 50 g ai/100 kg seed) or as foliar spray (e.g. in Mexico at 2 x 50 g ai/ha; PHI, 45 days; Brazil at 4–7 x 12–80 g ai/ha; PHI, 15 days). In the USA, GAP for foliar treatment at 28–56 g ai/ha (maximum, 224 g ai/ha per season) and a PHI of 60 days is pending approval. Numerous supervised trials of seed or soil

treatment followed by foliar spray or foliar spray only were reported from Australia, Brazil, Mexico and the USA. Three from Australia and one from Brazil complied with GAP.

The concentrations of residues after foliar treatment were < 0.002, 0.003, 0.004 and < 0.01 mg/kg for fipronil and < 0.004, 0.01 (2) and < 0.02 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Forty trials in the USA complied with the pending GAP. These trials were not evaluated as pending GAP is not considered by the Meeting.

The Meeting concluded that four trials were inadequate to allow estimation of a maximum residue level or an STMR for cotton seed, as it is a major crop.

Australian GAP permits treatment of sunflower seed at 75 g of fipronil per 100 kg. Data were available from four supervised trials conducted according to GAP and four trials with a twofold overdose. The samples were analysed for fipronil, fipronil-thioether and fipronil-sulfone. The concentrations of residues of all analytes were < 0.002 mg/kg.

French GAP permits seed treatment with 500 g of fipronil per 100 kg of sunflower seed. Data were available from six supervised trials conducted approximately according to GAP (375 g ai/100 kg seed) and three trials in Spain with a twofold overdose (1 kg ai/100 kg seed). The samples were analysed for fipronil, fipronil-thioether and fipronil-sulfone. The concentrations of residues were < 0.002 mg/kg (6) for fipronil and from < 0.002 to 0.004 for the other analytes.

GAP in France also allows application of 200 g ai/ha as a spray directed at the soil. Data were available from eight supervised trials in France conducted approximately according to GAP, and one trial in France and one in Italy at overdoses. The samples were analysed for fipronil, fipronil-thioether and fipronil-sulfone The concentration of residues was < 0.002 mg/kg (9) for each analyte. Eight further trials in France that complied with GAP resulted in concentrations below the LOQ of 0.01 mg/kg. As no concentration > 0.01 mg/kg was detected, the Meeting did not consider the data from France based on an LOQ of 0.01 mg/kg.

The concentrations of residues after soil and seed treatment, in ranked order, were: < 0.002 (19) mg/kg for fipronil and ≤ 0.004 (17), 0.007 and 0.008 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting estimated the following levels from trials with an LOQ of 0.002 mg/kg for sunflower seed: maximum residue level (fipronil), 0.002* mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.004 mg/kg; and highest residue (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.008 mg/kg.

A total of 27 trials were carried out in France on soil treatment of sugar beet leaves or tops at 150–200 g ai/ha according to French (160 g ai/ha) or Italian GAP (150 g ai/ha). The concentrations of residues on a fresh weight basis were < 0.002 (5), < 0.01(14), 0.011, 0.012, 0.014, 0.015, 0.017, 0.018, 0.021 and 0.029 mg/kg for fipronil and < 0.004 (2), 0.004, 0.005, 0.008, ≤ 0.02 (13), 0.021, 0.023, 0.024, 0.025, 0.027, 0.028, 0.029, 0.033 and 0.041 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Allowing for the standard 23% dry matter (*FAO Manual*), the Meeting estimated the following residue levels (dry weight) in sugar beet leaves or tops for soil incorporation use: maximum residue level (fipronil), 0.2 mg/kg; STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.087 mg/kg (0.02/0.23).

Numerous supervised trials were available on maize forage (n = 72) and fodder (n = 55) after seed or soil treatment. To prepare silage for feed, the whole aerial portion of the immature plant must

be cut at the late dough or early dent stage. Hence, the data on residues in fodder 77–120 days after treatment were used for evaluation.

The ranked orders of concentrations of residues in forage or silage on a fresh weight basis after seed treatment and soil incorporation were: < 0.002, < 0.005 (19), < 0.007 (18), < 0.01, < 0.02 (29), 0.022 (2), 0.023 and 0.038 mg/kg for fipronil and < 0.004, < 0.01 (17), < 0.012 (11), 0.012, 0.016, < 0.02, < 0.025 (2), ≤ 0.027 (5), < 0.04 (24), 0.041, 0.042, 0.044, 0.046, 0.048, 0.05, 0.053, 0.055 and 0.079 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Allowing for the standard 40% dry matter (*FAO Manual*), the Meeting estimated the following residue levels (dry weight) in maize forage: maximum residue level (fipronil), 0.1 mg/kg; and STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.0675 mg/kg (0.027/0.4).

The ranked orders of residues in the corresponding dry maize fodder samples taken at harvest, on a fresh weight basis (seed treatment and soil incorporation) were: < 0.002, < 0.003 (5), < 0.005 (3), < 0.02 (41), 0.02, 0.022, 0.025 and 0.04 (2) mg/kg for fipronil and < 0.004, < 0.005, < 0.008 (2), < 0.01 (2), < 0.023 (2), < 0.025, ≤ 0.04 (23), 0.041, 0.043, 0.044 (4), 0.046, 0.05, 0.052, 0.053, 0.055, 0.057 (2), 0.061, 0.062, 0.064, 0.066 (2), 0.069, 0.072, 0.09, 0.093 and 0.14 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Allowing for the standard 83% dry matter in maize stover (*FAO Manual*), the Meeting estimated the following residue levels (dry weight) in maize fodder: maximum residue level (fipronil), 0.1 mg/kg, and STMR (sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone), 0.048 mg/kg (0.04/0.83).

Use of fipronil as a foliar spray on pasture grass is registered in Australia (1 x 1.3 g ai/ha; PHI, 14 days) and South Africa (1 x 7.5 g ai/ha; PHI, 21 days). Numerous supervised trials on pasture grass were carried out in Australia with one application of 1.25, 2.5, 5, 7.5, 10, 20 or 30 g ai/ha; one trial was conducted in Mauritania with 11 g ai/ha; one trial was conducted in the Russian Federation with 4 g ai/ha and three trials in South Africa, each with 7.5 g ai/ha and 15 g ai/ha, were submitted. Of the trials submitted, two from Australia and the three from South Africa were in accordance with the respective GAP. The ranked orders of concentrations of residues on a fresh weight basis were < 0.002, 0.004, < 0.05, 0.21 and 0.44 mg/kg for fipronil, and < 0.006, 0.009, 0.079, 0.51 and 0.66 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting decided that five trials were insufficient to estimate a maximum residue level or an STMR for pasture grass.

Straw and fodder (dry) of cereal grains (barley, oats, rye, triticale, wheat): The two- to threefold overdoses used in the French trials of seed treatment for barley showed residues of fipronil-sulfone (maximum 0.038 mg/kg) in the straw. These results could not be used for evaluation because the trials were not conducted according to GAP and the results do not indicate a ‘nil residue situation’ as in the corresponding grain samples.

Five trials of treatment of wheat seed that complied with GAP (50 g ai/100 kg seed) were carried out in France. Samples were taken at harvest, 128–286 days after sowing. The ranked orders of concentrations of residues in wheat straw, on a fresh weight basis, were < 0.01 (3) and 0.011 (2) mg/kg for fipronil and < 0.02 (3), 0.021 and 0.025 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

For foliar spray use, only one trial in Poland was received, which complied with Czech and Slovak GAP. The concentrations of residues (fresh weight) were 0.017 mg/kg for fipronil and

0.063 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting concluded that five trials with soil treatment and one with foliar treatment were insufficient to estimate a maximum residue level and an STMR for cereal straw and fodder, dry.

Numerous supervised trials with different applications to rice straw and fodder, dry were reported. The trials conducted in accordance with GAP were:

- seed treatment at 10–13 g ai/100 kg seed: one trial in Australia, five trials in France
- seed treatment at 120 g ai/100 kg seed: 17 trials in the USA
- seed-box treatment at 0.5 g ai/box: five trials in Japan
- soil incorporation before planting (56 g ai/ha): 17 trials in the USA
- broadcast treatment on flooded paddy (1 x 50 g ai/ha): one trial in the Philippines, one in Taiwan and three in Thailand
- foliar treatment (1 x 50 g ai/ha): four trials in Thailand, one in the Philippines (at Thai GAP) and one in Taiwan (at Thai GAP)
- broadcast treatment after transplanting, followed by foliar treatment (2 x 50 g ai/ha): one trial in the Philippines.

Rice straw was the only feed item used in the calculation of the dietary burden of cattle with detectable residues of the photodegradation product fipronil-desulfinyl. As separate studies of cattle feeding were carried out with fipronil and fipronil-desulfinyl, the dietary burden must be calculated differently than for other feed items, and different STMR values are needed.

The ranked orders of concentrations of residues, on a fresh weight basis, after seed treatment, including seed box and soil incorporation, were: < 0.002 (2), < 0.003 (4), < 0.005 (4), < 0.01 (29), 0.01 (2), 0.012, 0.016 and 0.04 (2) mg/kg for fipronil and < 0.004 (2), < 0.006 (4), < 0.01 (4), < 0.013 (3), ≤ 0.02 (15), 0.02, 0.021, 0.022, 0.023 (2), 0.024 (2), 0.026 (2), 0.03 (2), 0.031, 0.033, 0.06, 0.069, 0.11 and 0.26 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The ranked orders of concentrations of residues, on a fresh weight basis, after foliar and broadcast onto flooded paddy were: < 0.005 (5), 0.006, 0.017, 0.02, 0.027, 0.061, 0.09 and 0.13 mg/kg for fipronil; < 0.005 (2), 0.006, 0.012, 0.021, 0.025, 0.028, 0.049, 0.075, 0.084, 0.095 and 0.2 mg/kg for fipronil-desulfinyl; < 0.01 (2), 0.011, 0.014, 0.019, 0.024, 0.038, 0.058, 0.077, 0.12, 0.19 and 0.33 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil); and < 0.015 (2), 0.018, 0.032, 0.039, 0.047, 0.069, 0.11, 0.17, 0.2, 0.3 and 0.55 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

The Meeting noted that the data resulting from different uses (seed treatment including seed box and soil incorporation on the one hand and foliar and broadcast onto flooded paddy on the other hand)constituted one population. The combined results of the two data sets were: < 0.002 (2), < 0.003 (4), < 0.005 (9), 0.006, < 0.01 (29), 0.01 (2), 0.012, 0.016, 0.017, 0.02, 0.027, 0.04 (2), 0.061, 0.09 and 0.13 mg/kg for fipronil; < 0.005 (2), 0.006, 0.012 (2), 0.025, 0.028, 0.049, 0.075, 0.084, 0.095 and 0.2 mg/kg for fipronil-desulfinyl; < 0.004 (2), < 0.006 (4), < 0.01 (6), 0.011, < 0.013 (3), 0.014, 0.019, ≤ 0.02 (15), 0.02, 0.021, 0.022, 0.023 (2), 0.024 (3), 0.026 (2), 0.03 (2), 0.031, 0.033, 0.038, 0.058, 0.06, 0.069, 0.077, 0.11, 0.12, 0.19, 0.26 and 0.33 mg/kg for the sum of fipronil, fipronil-thioether and fipronil-sulfone (calculated as fipronil); and < 0.004 (2), < 0.006 (4), < 0.01 (4), < 0.013 (3), < 0.015 (2), 0.018, ≤ 0.02 (15), 0.02, 0.021, 0.022, 0.023 (2), 0.024 (2), 0.027 (2), 0.03, 0.031, 0.032 (2), 0.034, 0.039, 0.047, 0.06, 0.07 (2), 0.11 (2), 0.17, 0.2, 0.26, 0.3 and 0.55 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether and fipronil-sulfone (calculated as fipronil).

Allowing for the standard 90% dry matter (*FAO Manual*), the Meeting estimated the following residue levels (dry weight) for rice straw: maximum residue level (fipronil), 0.2 mg/kg;

STMR (fipronil-desulfinyl), 0.029 mg/kg (0.0265/0.9); STMR (sum of fipronil, fipronil-thioether, fipronil-sulfone), 0.022 mg/kg (0.02/0.9).

Sorghum forage and fodder: Fipronil is registered for use as a foliar spray on sorghum at 1.5 g ai/ha (PHI, 14 days). Registration as a seed treatment at 75 g ai/100 kg seed is pending. The results of supervised trials were available only from Australia. Forage samples from trials conducted in accordance with registered or pending GAP were available from three trials with foliar spraying and two with seed treatment, but straw samples were available only from the two seed treatment trials. The samples were analysed for fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl. The concentration of residues in each analyte was < 0.002 mg/kg.

The concentrations of residues, in ranked order, in forage on a fresh weight basis after foliar spray were: < 0.002 (2) and 0.002 mg/kg for fipronil and < 0.006 (2) and 0.006 mg/kg for the sum of fipronil, fipronil-desulfinyl, fipronil-thioether, fipronil-sulfone (calculated as fipronil).

The Meeting did not consider trials conducted according to a pending GAP and concluded that three trials of foliar treatment were inadequate for estimating a maximum residue level or STMR for sorghum forage or fodder.

Cotton gin trash used as animal feed includes plant parts resulting from ginning cotton, which consist of burrs, leaves, stems, lint and seeds. Data on residues after foliar spray use were reported from one trial in Australia and 30 in the USA conducted according to the pending GAP in the USA. The Meeting does not consider trials according to a pending GAP and concluded that the data were inadequate for estimating a maximum residue level or an STMR for cottonseed.

Sunflower forage and fodder samples were taken from each of four seed treatment trials conducted in Australia at 75 or 150 g ai/100 kg seed and analysed for fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl. The concentration of residues was < 0.002 mg/kg in each analyte in all samples.

The Meeting noted that sunflower forage and fodder is not a feed item and did not recommend an MRL or STMR.

The results of analyses for residues in sugar cane leaves for forage and fodder in numerous trials conducted in Australia were submitted, but only two had been conducted according to GAP. The concentrations of all the residues (parent, fipronil-thioether, fipronil-sulfone, fipronil-desulfinyl) were < 0.002 mg/kg (fresh weight).

The Meeting considered that two trials were insufficient to allow estimation of a maximum residue level or an STMR.

Fate of residues during processing

The effect of processing on the concentrations of residues of fipronil has been studied in potatoes, maize, cotton seed, sunflower seed and sugar cane. No study on the effects of processing on the nature of the residue was received. As cauliflower, broccoli, cabbages and potatoes are usually eaten cooked, studies of the effects of processing would be desirable, as the proportions of parent compound and the relevant metabolites might be changed by cooking.

In one trial on potato treated by foliar spray in the USA, 0.0035 mg/kg of fipronil and 0.003 mg/kg of fipronil-desulfinyl were detected in the tubers. The concentrations of residues of fipronil-thioether and fipronil-sulfone were lower than the LOQ/MLD of 0.003/0.001 mg/kg. When the tubers were processed to chips, flakes and wet peel, the following processing factors were calculated:

Commodity	Fipronil + fipronil-desulfinyl (mg/kg), calculated as fipronil	Processing factor
Tuber	0.0068	
Chips	< 0.004	< 0.59
Flakes	< 0.004	< 0.59
Wet peel	0.056	8.2

In a second processing study in the USA, potatoes were treated in the furrow and then by spraying of foliage. Residues of fipronil, fipronil-thioether, fipronil-sulfone and fipronil-desulfinyl were detected in the tubers, which were processed to chips, flakes and wet peel. The following processing factors were calculated:

Commodity	Fipronil + fipronil-thioether + fipronil-sulfone + fipronil-desulfinyl (mg/kg), calculated as fipronil	Processing factor
Tuber	0.057	
Chips	< 0.0126	< 0.221
Flakes	0.0156	0.274
Wet peel	0.394	6.91

As the concentrations of residues in raw agricultural commodities in the first study were near the LOQ, the Meeting applied only the processing factors from the second study to the STMR value of 0.004 mg/kg for whole potatoes in order to calculate the following STMR-P values: chips, 0.0009 mg/kg; flakes, 0.0011 mg/kg; wet peel, 0.0276 mg/kg.

A study of maize processing was carried out in the USA after a single in-furrow application at planting at an exaggerated application rate. No detectable residues were reported in raw or processed commodities. No STMR-P value could be estimated.

The results of two processing studies carried out in the USA on cotton seed were submitted. The processed fractions were meal, hulls, crude and refined (edible) oil. Two further, limited studies carried out in Mexico show no fipronil or its metabolites in oil. The processing factors were based on the studies in the USA and the second Mexican study and are shown below:

Commodity	Fipronil + fipronil-thioether + fipronil-sulfone + fipronil-desulfinyl (mg/kg), calculated as fipronil	Processing factor
Seed	0.337	
Meal	< 0.008	< 0.025
Hulls	0.042	0.12
Crude oil	0.111	0.33
Refined oil	0.074	0.22
Seed	0.289	
Meal	< 0.0126	< 0.044
Hulls	0.062	0.21
Crude oil	0.109	0.38
Refined oil	0.097	0.34
Seed	< 0.031	
Crude oil	<0.024	< 0.77
Seed	0.148	
Crude oil	< 0.031	0.21

The mean processing factors were 0.035 for cotton meal, 0.165 for cotton hulls, 0.307 for cotton crude oil and 0.28 for cotton refined oil. As no STMR value was derived for cotton seed, no STMR-P values were estimated.

In numerous supervised trials conducted on sunflower seed in southern Europe, residues in sunflower oil extracted from the seeds and the cake solid were also measured. As neither fipronil nor its metabolites were detected in raw agricultural commodities, no STMR-P value could be estimated.

Nine studies on processing of sugar cane were submitted, but only two (each with two independent trials) showed residues in raw agricultural commodities and could be used to estimate processing factors:

Commodity	Fipronil + fipronil-thioether + fipronil-sulfone + fipronil-desulfinyl (mg/kg), calculated as fipronil	Processing factor
	1 x 100 g ai/ha soil treatment + 2 x 50 g ai/ha foliar treatment	
Cane	0.0198	
Bagasse	0.0123	0.621
Juice	< 0.007	< 0.35
Cane	0.0198	
Bagasse	0.0154	0.778
Juice	0.007	0.35
	2 x 100 g ai/ha foliar treatment	
Cane	0.0363	
Bagasse	0.0213	0.587
Juice	< 0.008	< 0.22
Cane	0.0303	
Bagasse	0.0283	0.934
Juice	< 0.009	< 0.297

A mean processing factor of 0.73 was calculated for bagasse, the material left over after pressing out the juice; the juice is made into molasses and sugar. The mean processing factor was < 0.3 for sugar juice. As no STMR value was derived for sugar cane, no STMR-P values were estimated.

Residues in animal commodities

Dietary burden in animals

The Meeting estimated the dietary burden of fipronil residues and its toxicologically significant metabolites in farm animals on the basis of the diets listed in Appendix IX of the *FAO Manual*.

Separate feeding studies were carried out in cattle to determine the residues of fipronil and of its photodegradation product fipronil-desulfinyl. Detectable amounts of fipronil-desulfinyl were found only in rice straw among all the feed items considered for cows. The dietary burden was therefore calculated separately for comparison with the results of:

- the feeding study of fipronil by summing the concentrations of residues of fipronil, fipronil-thioether and fipronil-sulfone, calculated as fipronil (all animal feed)
- the feeding study of fipronil-desulfinyl by summing the concentrations of residues of fipronil-desulfinyl (rice straw only).
-

As the plateau concentration of fipronil in milk in the feeding study in dairy cows was reached slowly (> 2 weeks), the STMR and STMR-P values of the feed item were used to calculate

the dietary burden for estimation of MRLs, STMR values and HR values for animal commodities, as follows:

Dietary burden of sum of fipronil, fipronil-thioether and fipronil-sulfone, calculated as fipronil

Commodity	Group	STMR or STMR-P (mg/kg)	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
					Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Barley grain	GC	0.004	88	0.0045						
Maize	GC	0.005	88	0.0057			80			0.00456
Maize forage	AF	0.0675	100	0.0675	5	50		0.0034	0.0338	
Maize fodder	AS	0.048	100	0.048						
Oats	GC	0.004	89	0.0045						
Potato, wet peel		0.0276	15	0.184	75	40		0.138	0.0736	
Rice	GC	0.006	88	0.0068			20			0.00136
Rice straw and fodder	AS	0.022	100	0.022						
Rye	GC	0.004	88	0.0045						
Sugar beet leaves or tops		0.087	100	0.087	20	10	–	0.0174	0.0087	
Wheat	GC	0.004	89	0.0045						
		Total			100	100	100	0.159	0.116	0.006

Dietary burden of fipronil-desulfinyl

Commodity	Group	STMR (mg/kg)	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
					Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Rice straw and fodder	AS	0.029	100	0.029	10	10	–	0.0029	0.0029	–

Feeding studies

Cows, fipronil: Groups of three lactating cows were given fipronil in bolus doses equivalent to 0.04, 0.13 or 0.43 ppm in the diet, daily for 35 days. Milk was analysed for fipronil and for fipronil-thioether and fipronil-sulfone. A plateau concentration of fipronil-derived residues was observed in milk after 25 days at the high dose. The residue in milk consisted almost entirely of fipronil-sulfone. Fipronil-thioether was detected in a single sample of milk; trace amounts of fipronil (< 0.01 mg/kg) were detected at the high dose. After 35 days of dosing, the cows were killed, and liver, kidney, fat and muscle were collected for analysis from each animal. Of the four tissues examined, fat contained the highest concentration of fipronil residues. Most of the residues consisted of fipronil-sulfone; fipronil was detected in fat of cows at the high dose at a concentration slightly above the LOQ.

The residue for compliance with the MRL is defined as the sum of fipronil and fipronil-sulfone, and that for the STMR as the sum of fipronil, fipronil-sulfone, fipronil-thioether and fipronil-desulfinyl. Fipronil-desulfinyl was not determined. As no concentrations of fipronil-thioether or fipronil above the LOQ were determined in milk, muscle, kidney or liver at the highest dose, the Meeting decided to calculate both the maximum residue levels and the STMR values on the basis of the fipronil-sulfone residues. Both fipronil and fipronil-sulfone were found in fat samples from cows at the highest dose. If all concentrations are below the LOQ, it is reasonable to assume that the concentration of combined residues is lower than the LOQ for fipronil-sulfone in milk, muscle,

kidney and liver and lower than the combined LOQs for fipronil and fipronil-sulfone in fat. When one component is above and the other below the LOQ, the concentration of combined residue is assumed to be below or close to that of the measurable component plus the LOQ of the other.

The dietary burden was calculated as follows: 0.159 mg/kg (typical residue value in beef cattle) and 0.116 mg/kg (typical residue value in dairy cows). The table below shows the actual and interpolated concentrations of residues used to estimate dietary intake as the sum of fipronil and fipronil-sulfone (calculated as fipronil), on the basis of actual concentrations in cows given the intermediate dose (0.13 ppm):

Feed level (ppm) *Interpolated* / actual	Fipronil and fipronil-sulfone residues (mg/kg), calculated as fipronil								
	Milk (mean)	Muscle		Liver		Kidney		Fat	
		Highest	Mean	Highest	Mean	Highest	Mean	Highest	Mean
MRL beef cattle *0.159* / 0.13		*0.0183* / 0.015		*0.0746* / 0.061		*0.0171* / 0.014		*0.279* / 0.228	
MRL dairy cows *0.116* / 0.13	*0.0107* / 0.012								
STMR beef cattle *0.159* / 0.13			*0.0143* / 0.0117		*0.0596* / 0.0487		*0.0134* / 0.011		*0.215* / 0.176
STMR dairy cows *0.116* / 0.13	*0.0107* / 0.012								

Cows, fipronil-desulfinyl: The concentrations of fipronil-desulfinyl residues were determined in animal commodities after repeated dosing of groups of three lactating given bolus doses of fipronil-desulfinyl equivalent to 0.025, 0.075, 0.3 or 1 ppm in the diet, daily for 35 consecutive days. At the plateau (after 15–20 days), the concentration of the analyte in milk paralleled the administered dose in all but the high-dose group. Fipronil-desulfinyl residues were associated more with milk fat rather than skim milk; the milk fat concentration factor was determined to be approximately 16.

The dietary burden was calculated as 0.0029 mg/kg (STMR for beef and dairy cattle). The following table shows the highest and the mean actual and interpolated concentrations of residues of fipronil-desulfinyl, on the basis of the actual concentrations in the group given the lowest dose (0.025 ppm):

Feeding level (ppm) *Interpolated* / actual	Fipronil-desulfinyl residues (mg/kg), calculated as fipronil								
	Milk (mean)	Muscle		Liver		Kidney		Fat	
		Highest	Mean	Highest	Mean	Highest	Mean	Highest	Mean
MRL, beef and dairy cattle *0.0029* / 0.025	*0.0004* / 0.0033	*0.0004* / 0.0033		*0.0048* / 0.0418		*0.0008* / 0.0066		*0.0055* / 0.0473	
STMR, beef and dairy cattle *0.0029* / 0.025	*0.0004* / 0.0033		*0.0003* / < 0.0022		*0.0046* / 0.0396		*0.0006* / 0.0055		*0.0051* / 0.044

The following tables show the combined data from the two feeding studies and the values selected for estimation of MRLs, STMR values and HR values for animal commodities. The residue concentrations are calculated as fipronil.

MRLs for animal commodities:

Commodity	Sum of fipronil and fipronil-sulfone (mg/kg)	Proposed MRL (mg/kg)
Milk	0.0107	0.02
Liver	0.0746	0.1
Kidney	0.0171	0.02
Meat (fat)	0.279	0.5 (fat)

Highest residues for animal commodities:

Commodity	Sum of fipronil and fipronil-sulfone (mg/kg)	Fipronil-desulfinyl (mg/kg)	Sum of fipronil, fipronil-sulfone and fipronil-desulfinyl (mg/kg)	Proposed HR (mg/kg)
Liver	0.0746	0.0048	0.0794	0.079
Kidney	0.0171	0.0008	0.0179	0.018
Meat (muscle)	0.0183	0.0004	0.0187	0.019

STMR values for animal commodities:

Commodity	Sum of fipronil and fipronil-sulfone (mg/kg)	Fipronil-desulfinyl (mg/kg)	Sum of fipronil, fipronil-sulfone and fipronil-desulfinyl (mg/kg)	Proposed STMR (mg/kg)
Milk	0.0107	0.0004	0.0111	0.011
Liver	0.0596	0.0046	0.0642	0.064
Kidney	0.0134	0.0006	0.014	0.014
Meat (muscle)	0.0143	0.0003	0.0146	0.015

The Meeting estimated maximum residue levels of 0.02 mg/kg for cattle milk, 0.1 mg/kg for cattle liver, 0.02 mg/kg for cattle kidney and 0.5 mg/kg (fat) for cattle meat. It recommended that the HR values be 0.079 mg/kg for cattle liver, 0.018 mg/kg for cattle kidney and 0.019 mg/kg for cattle meat. The estimated STMR values are 0.011 mg/kg for cattle milk, 0.064 mg/kg for cattle liver, 0.014 mg/kg for cattle kidney and 0.015 mg/kg for cattle meat.

Hens, fipronil: The concentrations of fipronil-derived residues in poultry commodities were determined after repeated dosing of groups of 10 laying hens given bolus doses equivalent to 0.01, 0.031 or 0.103 ppm, daily for 42 consecutive days. Eggs were collected and analysed during this period. A plateau concentration of fipronil-derived residues was observed in eggs after about 15 days of dosing. The hens were killed 42 days after dosing was initiated, and liver, skin with adhering fat and muscle were collected for analysis; eggs and tissues were analysed for fipronil, fipronil-sulfone and fipronil-thioether.

The average concentration of fipronil-sulfone equivalents in eggs from hens at the lowest dose reached a plateau by day 12 of treatment, when there were only trace amounts (< 0.01 mg/kg) of fipronil-sulfone equivalents. In hens given the intermediate and highest doses, plateau concentrations

were reached after about 28 days. No fipronil-thioether was observed in eggs at any dose, and only trace amounts of fipronil (< 0.01 mg/kg) were observed at the high dose.

The concentrations of residues were < 0.01 mg/kg in muscle and liver in hens on the low-dose regime and 0.013 mg/kg in skin with adhering fat. At all doses, fipronil-sulfone was found at much higher concentrations in skin with adhering fat than in all other tissues. The total residue in fat comprised almost entirely fipronil-sulfone, fipronil constituting < 10% in the high-dose group.

The dietary burden was calculated as 0.006 mg/kg (STMR). The following table shows the highest and the mean actual and interpolated concentrations of the sum of fipronil and fipronil-sulfone, based on the actual concentrations found in the group given the low dose (0.01 ppm):

Feed level (ppm) *Interpolated* / actual	Fipronil and fipronil-sulfone residues (mg/kg), calculated as fipronil							
	Eggs		Muscle		Liver		Skin with fat	
	Highest	Mean	Highest	Mean	Highest	Mean	Highest	Mean
MRL *0.006* / 0.01	*0.0078* / 0.013		*< 0.006* / < 0.01		*< 0.006* / < 0.01		*0.0084* / 0.014	
STMR *0.006* / 0.01		*0.006* / 0.01		*< 0.006* / < 0.01		*0.006* / < 0.01		*0.008* / 0.0133

Hens, fipronil-desulfinyl: A separate feeding study was not provided, but in a study of metabolism in hens given [^{14}C]fipronil-desulfinyl 50–70% of the dose was recovered in the excreta. The edible tissues and eggs contained < 6% of the total applied dose, with 1–2% in egg white, 3–5% in yolk and 4–6% in tissues. The only poultry feed item that contained detectable residues of fipronil-desulfinyl was rice grain. The concentrations of residues in 29 samples of rice treated by foliar spray or in flooded paddies were < 0.001 (27), 0.002 and 0.005 mg/kg. The Meeting concluded that quantifiable residues of fipronil-desulfinyl are unlikely to occur in eggs or edible poultry tissues.

On the basis of the results of the feeding study with 0.01 ppm fipronil, the Meeting estimated maximum residue levels of 0.02 mg/kg for eggs, 0.02 mg/kg for poultry, edible offal and 0.0* for poultry meat. It recommended HR values of 0.0078 mg/kg for eggs, 0.0084 mg/kg for poultry, edible offal and 0.006 mg/kg for meat. The estimated STMRs were 0.006 mg/kg for eggs, 0.008 mg/kg for poultry, edible offal and 0.006 mg/kg for meat.

Recommendations

The Meeting estimated the following maximum residue levels and STMR values and recommended them for use as MRLs, STMR values and HR values:

Definition of the residue:

- for compliance with MRLs for plant commodities: fipronil
- for compliance with MRLs for animal commodities: sum of fipronil and 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonyl pyrazole (fipronil sulfone), expressed as fipronil.
- for estimation of dietary intake of plant and animal commodities: sum of fipronil, 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonyl-pyrazole (fipronil-sulfone), 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoro-methylthio-

pyrazole (fipronil thioether) and 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylpyrazole (fipronil-desulfinyl), expressed as fipronil

The residue is fat-soluble.

Commodity		Recommendation			
CCN	Name	MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR (mg/kg)
		New	Previous		
FI 0327	Banana	0.005	–	0.004	0.005
GC 0640	Barley	0.002*	–	0.004	0.004
VB 0041	Cabbages, Head	0.02	–	0.005	0.0215
MO 1280	Cattle, kidney	0.02	–	0.014	0.018
MO 1281	Cattle, liver	0.1	–	0.064	0.079
MM 0812	Cattle meat	0.5 (fat)	–	0.015	0.019
ML 0812	Cattle milk	0.02	–	0.011	
PE 0112	Eggs	0.02	–	0.006	0.0078
VB 0042	Flowerhead brassicas	0.02	–	0.005	0.0215
GC 0645	Maize	0.01	–	0.005	0.02
AF 0645	Maize forage	0.1[1]	–		
AS 0645	Maize fodder	0.1[1]	–		
GC 0647	Oats	0.002*	–	0.004	0.004
VR 0589	Potato	0.02	–	0.004	0.028
	Potato chips			0.0009	
	Potato flakes			0.0011	
PO 0110	Poultry, edible offal of	0.02	–	0.008	0.0084
PM 0110	Poultry meat	0.01*	–	0.006	0.006
GC 0649	Rice	0.01	–	0.006	0.013
AS 0649	Rice straw and fodder, dry	0.2[1]	–		
GC 0650	Rye	0.002*	–	0.004	0.004
VR 0596	Sugar beet	0.2	–	0.0125	0.17
AV 0596	Sugar beet leaves or tops	0.2[1]	–		
SO 0702	Sunflower seed	0.002*	–	0.004	0.008
GC 0653	Triticale	0.002*	–	0.004	0.004
GC 0654	Wheat	0.002*	–	0.004	0.004

[1] Expressed on dry weight basis

Further work or information

Desirable

1. Study of hydrolysis to determine the nature of residues after processing
2. Studies of processing of cabbages (cooking, sauerkraut preparation)
3. Studies of processing of potatoes (cooking, oven baking, microwaving)

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Dietary risk assessment

Long-term intake

The Meeting estimated 22 STMR values for fipronil, which were used to calculate dietary intake. The results are shown in Annex 3 (Report 2001).

The IEDIs for the five GEMS/Food regional diets, based on estimated STMR values, were 20–60% of the ADI. The Meeting concluded that dietary intake of fipronil residues is unlikely to present a public health concern.

Short-term intake

The IESTI of fipronil was calculated for the food commodities (and their processing fractions) for which MRLs, STMR values and/or HR values were established and for which data on consumption were available. The results are shown in Annex 4 (Report 2001).

The calculated short-term intakes were less than 100% of the acute RfDs for children and for the general population. The Meeting concluded that short-term intake of residues of fipronil, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

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HALOXYFOP (194)

EXPLANATION

Haloxyfop was first evaluated in 1995 and again in 1996. The Meeting noted that the expected levels of residue intake by cattle would exceed the maximum dose used in the animal feeding studies and therefore requested further ruminant feeding studies at feeding levels comparable to the maximum residue levels found in fodder crops. Information on the moisture content of fodder crops was also considered desirable.

METHODS OF RESIDUE ANALYSIS

Muscle, liver and kidney samples were extracted with methanolic sodium hydroxide, ether and sodium hydrogen carbonate solution. Rendered fat was dissolved in toluene and the fat precipitated with acetonitrile, which was evaporated. Milk was acidified and extracted with ether, which was evaporated and the residue dissolved in toluene. Acetonitrile was added and subsequently removed by evaporation. Haloxyfop was derivatized to the methyl ester, which was cleaned up by gel permeation chromatography and determined by GLC with an ECD (Anon., 1999a). *o,p*-DDE was used as an internal standard. Mean recoveries were 117, 98, 99, 108 and 113% at 0.01 mg/kg for liver, kidney, muscle, fat and milk respectively (Anon., 1999c).

Animal feeding studies

Twelve Friesian cows each weighing 452-568 kg were dosed twice daily for 28 days with gelatin capsules containing haloxyfop-R equivalent to 10, 20 or 30 ppm in the diet (100, 200 or 300 mg/animal/day). Milk was collected morning and evening to form a daily sample although samples from every collection day were not analysed.

One of the control cows became photosensitive resulting in superficial mastitis with a painful udder and was withdrawn from the study. Three weeks after the trial a control cow aborted. Post-mortem examination revealed that the abortion was Aspergillus-induced. All other cows remained healthy throughout the trial (Anon., 1999b).

Table 1. Residues of haloxyfop-R in milk (Anon., 1999b).

Day	Residue, mg/kg			
	Control	10 ppm	20 ppm	30 ppm
-2	0.02, ND, ND	0.008, ND, ND	ND, ND, ND	ND, ND, ND
1	ND, 0.01, 0.01	0.008, 0.008, 0.01	0.02, 0.01, 0.02	0.03, 0.02, 0.02
2		0.12, 0.14, 0.20	0.33, 0.19, 0.39	0.24[1], 0.42, na
6		0.18, 0.20, 0.23	0.40, 0.24, 0.43	0.27[1], 0.57, 0.54
10		0.33, 0.31, 0.38	0.59, 0.48, 0.87	0.42[1], 1.83, 1.29
14		0.28, 0.20, 0.27	0.56, 0.36, 0.54	0.28[1], 0.73, 0.60
18		0.22, 0.22, 0.29	0.54, 0.28[2], 0.70	0.33[1], 0.74, 0.70
22		0.23, 0.17, 0.25	0.56, 0.20[2], 0.59	0.20[1], 0.72, 0.63
26		0.58, 0.37, 0.65	0.91, 0.22[2], 0.97	0.37[1], 2.21, 1.01
29	ND			
30		0.40, 0.09, 0.32	0.59, 0.09[2], 0.48	0.19[1], 0.95, 0.61
34		0.13, 0.008, 0.07	0.06, 0.03, 0.04	0.02[1], 0.52, 0.04
38		0.008, ND, 0.009	0.01, ND, 0.005	ND[1], 0.07, 0.07
42	ND, ND	ND, ND, ND	0.005, ND, 0.01	ND[1], 0.11, 0.003

ND: undetectable, <0.002 mg/kg
NA: not analysed
[1] One cow (cow 95) in group consistently showed low residues
[2] One cow (cow 54) in group consistently showed low residues particularly from days 14-30

In the trial reported to the 1995 Meeting residues in the milk of cows fed the equivalent of 2.5 ppm haloxyfop in the diet for 28 days (Gardner, 1984) reached a maximum of 0.04 mg/kg at day 20.

In another trial 24 beef cattle weighing 450-650 kg were dosed twice daily for 28 days with gelatin capsules containing the equivalent of 10, 20 or 30 ppm haloxyfop-R in the diet. Cattle were slaughtered on day 28, and some animals in the 30 ppm group on days 35, 42, 49 and 56. Animals remained healthy throughout the study except one cow which suffered a haematoma and another a heel abscess. No abnormalities were seen on post mortem examination (Anon., 1999d).

Table 2. Residues of haloxyfop-R in the tissues of beef cattle (Anon., 1999d)

Sample	Residue, mg/kg			
	Control	10 ppm diet	20 ppm diet	30 ppm diet (day 28)
Liver	ND, ND, ND	0.23, 0.33, 0.20	0.38, 0.45, 0.30	0.46, 0.20, 0.18
Kidney	0.02, 0.01, 0.01	0.51, 0.53, 0.57	1.13, 1.49, 0.53	1.17, 0.48, 1.81
Muscle	ND, ND, ND	0.02, 0.05, 0.02	0.06, 0.06, 0.03	0.05, 0.01, 0.05
Abdominal fat	ND, ND, ND	0.02, 0.008, 0.01	0.05, 0.03, 0.03	0.02, 0.02, 0.04
Renal fat	0.009, 0.007, ND	0.02, 0.005, 0.01	0.04, 0.02, 0.02	0.02, 0.02, 0.04
Subcutaneous fat	ND, ND, ND	0.02, 0.01, 0.008	0.03, ND, 0.03	0.02, 0.01, 0.03
	30 ppm diet (day 35)	30 ppm diet (day 42)	30 ppm diet (day 49)	30 ppm diet (day 56)
Liver	0.09, 0.12, 0.06	0.02, 0.01, 0.03	0.01, 0.02, 0.006	0.007, 0.006, ND
Kidney	0.07, 0.11, 0.07	0.02, 0.01, 0.02	0.02, 0.01, 0.009	0.006, 0.018, 0.009
Muscle	0.006, ND ,ND	ND, ND, ND	ND, ND, ND	ND, ND, ND
Abdominal Fat	0.02, 0.008, 0.01	0.007, ND, 0.007	0.02, ND, 0.03	0.02, 0.008, 0.006
Renal Fat	0.008, 0.01, 0.02	0.009, 0.007, 0.007	0.05, 0.02, 0.04	0.03, 0.02, 0.03
Subcutaneous Fat	0.008, ND, ND	ND, ND, ND	ND, ND, ND	ND, ND, ND

ND: undetectable (<0.005 mg/kg liver, kidney, muscle, 0.003 mg/kg fat)

Residues of haloxyfop-R were not closely correlated with dose levels, with residues in the 20 and 30 ppm groups at similar levels.

In an earlier trial reported to the 1995 JMPR beef calves had been dosed with haloxyfop daily for 28 days at levels equivalent to 0, 0.25, 0.5, 1, 5 and 10 ppm in the diet on a dry matter basis (Kutschinski and Bjerk, 1984a). Three animals at each feeding level were slaughtered without a withdrawal period and three at the highest feeding level were slaughtered seven days and three fourteen days after the last dose. The residues relevant to the estimation of maximum residue levels and STMRs are shown below (FAO/WHO, 1996b).

Table 3. Residues of haloxyfop in the tissues of calves after dosing for 28 days (Kutschinski and Bjerk, 1984a).

Tissue	Residue, mg/kg at indicated intake		
	5 ppm diet	10 ppm diet	10 ppm diet (7 days withdrawal)
Muscle	0.01	0.02 – 0.06	<0.01
Liver	0.14 - 0.15	0.40 – 0.72	0.02 – 0.03
Kidney	0.35 - 0.51	0.83 – 1.90	0.03 – 0.06
Fat	0.06 - 0.09	0.24 – 0.53	0.07 – 0.21

Only residues in muscle occurred at similar levels in the two studies; in all other cases, residues were higher from the earlier trial in which dosing was with the racemate.

In another trial reported to the 1995 JMPR laying hens were fed haloxyfop each day for 28 days at 0, 0.25, 0.75 and 2.5 ppm in the diet on a dry matter basis (Kutschinski and Bjerk, 1984b). Hens in all groups were killed immediately after the last dose, and one high-level group was killed seven days and one fourteen days after the last dose. Eggs from each group were collected daily and eggs, muscle with attached skin, liver and fat were analysed for residues of haloxyfop and its conjugates by GLC with a limit of quantification of 0.01 mg/kg. The results are shown in Table 4.

Table 4. Residues in chicken tissues and eggs resulting from ingestion of haloxyfop

Tissue	Residue, mg/kg, at indicated intake				
	0.25 ppm	0.75 ppm	2.5 ppm	2.5 ppm [1]	2.5 ppm [2]
Muscle/Skin	<0.01	<0.01 – 0.02	0.02 – 0.12	<0.01 – 0.02	<0.01 – 0.03
Liver	0.01 – 0.09	0.06 – 0.20	0.19 – 0.68	<0.01 – 0.02	<0.01 – 0.01
Fat	<0.01 – 0.03	0.02 – 0.12	0.12 – 0.60	0.04 – 0.75	0.06 – 0.34
Eggs	<0.01	0.02	0.04	0.01	<0.01

[1] After 7 days withdrawal
[2] After 14 days withdrawal

APPRAISAL

Haloxyfop was evaluated for the first time in 1995 and again in 1996. The 1995 JMPR provisionally estimated maximum residue levels for a number of commodities, including fodder crops and commodities of animal origin, noting the lack of critical supporting data on the uptake of the soil degradation products by crops. The 1996 JMPR received reports of studies on the uptake of the parent compound or its degradation products from soil treated with haloxyfop but agreed to withdraw the provisional maximum residue levels for fodder crops and cattle tissues and milk, as no information was available on the moisture content of fodder crops, and the expected intake of residues by cattle would exceed the maximum dose used in the feeding studies. It therefore requested the results of further feeding studies in which ruminants were fed a concentration comparable to the maximum residue level found in fodder crops. Information on the moisture content of fodder crops was also noted as desirable.

The Meeting received information on methods of analysis for milk and cattle tissues and feeding studies in dairy and beef cattle.

Results of supervised trials

Estimation of STMR values for fodder crops for which provisional maximum residue levels were estimated by the 1995 JMPR

The 1995 JMPR estimated provisional MRLs of 5.0 mg/kg for alfalfa forage (green), 0.3 mg/kg for beet leaves or tops, and 0.3 mg/kg for sugar beet leaves or tops. The 1996 JMPR agreed to withdraw these provisional recommendations because the concentrations of residues found in supervised trials on these fodder crops were expressed on a wet weight basis, whereas the Codex Classification of Food and Feeds indicates that MRLs for fodder and forage crops should, if relevant, preferably be set and expressed on a ‘dry weight’ basis; furthermore, no information was available on the moisture content of these commodities. The current Meeting agreed to reinstate the recommended MRLs for these commodities, with a footnote to indicate that the MRLs are set on a fresh weight basis.

The concentrations of residues on alfalfa from two trials conducted in Australia in compliance with the maximum GAP for haloxyfop (0.16 kg ai/ha; PHI 21 days) and two trials conducted in

Australia in compliance with the maximum GAP of Australia for haloxyfop-R (0.078 kg ai/ha; PHI, 21 days), in ranked order, were (median underlined): 1.8, 2.2, 2.4 and 3.1 mg/kg.

The Meeting agreed to reinstate the recommended MRL of 5 mg/kg (on a fresh weight basis) and estimated an STMR value of 2.3 mg/kg and an HR of 3.1 mg/kg.

Both the 1995 and the 1996 JMPR agreed to consider the data for beet and sugar beet fodder together, as these crops and the use pattern of haloxyfop on them are similar.

In 13 trials on sugar beet carried out in the United Kingdom with racemic haloxyfop according to the maximum French GAP (0.21 kg ai/ha, up to early weed tillering), the concentrations of residues in the leaves and tops were < 0.02 (3), 0.02, < 0.03 (3), 0.03, 0.04 (2), 0.09, 0.11 and 0.28 mg/kg. In eight trials on sugar beet carried out in Germany with racemic haloxyfop according to the maximum German GAP (0.21 kg ai/ha; PHI, 90 days), the concentrations in the leaves and tops were < 0.01, < 0.02 (2), 0.03, 0.04, 0.08, 0.28 and 0.3 mg/kg. In four trials on sugar beet with haloxyfop-R in Germany and Italy conducted according to maximum French GAP (0.1 kg ai/ha, up to early weed tillering), the concentrations of residues in the leaves and tops were < 0.02, 0.09 (2) and 0.14 mg/kg.

In five trials on fodder beet with racemic haloxyfop conducted in Germany according to maximum German GAP (0.21 kg ai/ha; PHI, 90 days), the concentrations in the leaves or tops were < 0.02 (3), 0.03 and 0.05 mg/kg.

The concentrations of residues in the leaves or tops in a total of 30 trials, in ranked order, were: < 0.01, < 0.02 (9), 0.02, < 0.03 (3), 0.03 (3), 0.04 (3), 0.05, 0.08, 0.09 (3), 0.11, 0.14, 0.28 (2) and 0.3 mg/kg. The Meeting agreed to reinstate the recommended MRL of 0.3 mg/kg (on a fresh weight basis) and estimated an STMR value of 0.03 mg/kg and a highest residue of 0.3 mg/kg.

In four supervised trials on pasture with racemic haloxyfop and two with haloxyfop-R in Australia conducted in accordance with maximum Australian GAP (0.1 kg ai/ha with racemic haloxyfop, 0.052 kg ai/ha with haloxyfop-R; PHI, 7 days in both cases), the concentrations of residues, in ranked order, were 0.49, 0.99, 1.5, 1.7, 2.0 and 3.4 mg/kg.

The Meeting estimated an STMR value of 1.6 mg/kg and an HR value of 3.4 mg/kg. As pasture is not traded internationally in bulk, no maximum residue level was estimated.

Residues in animal commodities

Feeding studies

Haloxyfop-R (as its methyl ester) was determined in milk and cattle tissues by GC–ECD after solvent extraction and derivatization, with 98–117% recovery.

Dairy cows were dosed with haloxyfop-R at rates equivalent to 0, 10, 20 or 30 ppm of diet for 28 days. Residues were detected rapidly in milk (1 day after treatment), and the concentration appeared to reach a plateau by day 10 and a peak at day 26. The maximum concentrations in milk were 0.65 mg/kg at 10 ppm of diet, 0.97 mg/kg at 20 ppm and 2.2 mg/kg at 30 ppm. The concentrations varied widely between cows, and one cow each at 20 and 30 ppm had consistently low values. In the study considered by the 1995 Meeting, in which cows were dosed with haloxyfop for 28 days at 2.5 ppm of diet, the concentration in milk reached a maximum of 0.04 mg/kg at day 20.

Beef cattle were dosed with haloxyfop-R at a rate equivalent to 0, 10, 20 or 30 ppm of diet for 28 days. Low concentrations of residue were detected in kidney and renal fat in the control group. The concentrations in animals at the highest dietary rate on day 28 were highest in the kidney (1.8 mg/kg at 30 ppm) and liver (0.46 mg/kg at 30 ppm). The mean concentrations in muscle did not exceed 0.06 mg/kg in any group, and the highest levels in abdominal, renal and subcutaneous fat were similar in

all groups: 0.05, 0.04 and 0.03 mg/kg, respectively. Residues were detectable 28 days after cessation of dosing in all tissues except muscle. The concentrations did not appear to be strongly correlated to dietary rate, those in animals at 20 and 30 ppm being similar.

The 1995 Meeting noted that haloxyfop-S undergoes rapid and nearly complete inversion to haloxyfop-R. In rats dosed with haloxyfop, nearly all of the residue recovered from urine and faeces was in the form of haloxyfop-R. The current Meeting therefore considered that the new studies in cattle dosed with haloxyfop-R could be used in estimating maximum residue levels, STMR values and highest residues in cattle tissues and milk.

Dietary burden of farm animals

The 1996 Meeting calculated that the intake by cattle was 17 ppm in the diet, on the basis of the highest residue in pasture of 3.35 mg/kg and 80% moisture content. This was higher than the maximum concentration of 10 ppm used in the studies available to the Meeting. However, the 1997 and 1998 Meetings elaborated principles for estimating maximum residue levels and STMR values for commodities of animal origin, and the 1997 JMPR distinguished situations in which the plateau was reached rapidly and those in which it was reached slowly. It recommended that the MRLs of feed items should be used to calculate the dietary burden of animals for estimating maximum residue levels if the plateau was reached rapidly, while STMR values should be used if the plateau was reached slowly. For estimating STMR values, it recommended that, in both cases, the STMR values of feed items should be used to calculate the dietary burden of animals.

The concentrations of residues of haloxyfop in milk reached a plateau on day 10 in the study provided to the current Meeting; they reached a maximum on day 20 in a study reviewed by the 1995 JMPR. The current Meeting agreed that the plateau concentration of haloxyfop residues in milk was reached slowly and re-estimated the dietary burden of cattle on the basis of the diets in Appendix IX of the *FAO Manual*. Calculation from STMRs provided feed concentrations suitable for estimating both maximum residue levels and STMRs for cattle commodities.

The 1995 JMPR estimated maximum residue levels of 0.01 mg/kg for chicken meat, 0.1 mg/kg for edible offal of chicken and 0.01 mg/kg (*) for chicken eggs. The 1996 JMPR re-calculated an intake of 0.035 ppm (dry weight basis) by poultry on the basis that feed could contain up to 50% pulses, 7% rape seed meal and 30% soya bean meal and using the STMR values of 0.03, 0.15 and 0.03 mg/kg for these three feed items, respectively. The current Meeting re-estimated the dietary burden of haloxyfop residues for poultry on the basis of the diets in Appendix IX of the *FAO Manual*. As no information was available on the time at which the concentrations reached a plateau in chicken, the maximum and STMR dietary burdens were calculated on the basis of the highest residue level or STMR-P value and STMR or STMR-P value, respectively.

Estimated dietary burden of cattle

Commodity	Group	STMR or STMR-P (mg/kg)	Dry matter (%)	Residue, dry weight (mg/kg)	Per cent of diet		Residue contribution (mg/kg)	
					Beef cattle	Dairy cows	Beef cattle	Dairy cows
Pasture	AF	1.59	25	6.36	30	40	1.9	2.5
Alfalfa forage (green)	AL	2.33	35	6.66	70	60	4.7	4.0
Fodder beet, leaves or tops	AV	0.04	23	0.17				
Sugar beet, leaves or tops	AV	0.04	23	0.17				
Pulses (field pea, dry)	VP	0.03	90	0.04				
Rape seed meal	SO	0.15	88	0.17				
Rice bran	CM	0.02	90	0.02				
Soya bean meal	VP	0.03	92	0.03				
				Total	100	100	6.6	6.5

Maximum dietary burden of poultry

Commodity	Group	MRL or STMR-P (mg/kg)	Dry matter (%)	Residue on dry basis (mg/kg)	Per cent of diet	Residue contribution (mg/kg)
Pulses (field pea, dry)	VD	0.2	90	0.22	20	0.044
Rape seed meal	SO	0.15	88	0.17	15	0.026
Rice bran	CM	0.02	90	0.02	25	0.006
Soya bean meal	VD	0.03	92	0.03	20	0.007
				Total	80	0.082

Dietary burden of poultry at STMR

Commodity	Group	STMR or STMR-P (mg/kg)	Dry matter (%)	Residue on dry basis (mg/kg)	Per cent of diet	Residue contribution (mg/kg)
Pulses (field pea, dry)	VD	0.03	90	0.04	20	0.008
Rape seed meal	SO	0.15	88	0.17	15	0.026
Rice bran	CM	0.02	90	0.02	25	0.006
Soya bean meal	VD	0.03	92	0.03	20	0.007
				Total	80	0.044

The dietary burden of haloxyfop for estimating the maximum residue levels and STMR values for cattle commodities (residue concentrations in animal feeds expressed as dry weight) was calculated to be 6.6 mg/kg for beef cattle and 6.5 mg/kg for dairy cows. The dietary burden for poultry commodities was calculated to be 0.082 mg/kg for estimating the maximum residue level and 0.044 mg/kg for the STMR.

A study in which cattle were fed a diet containing 10 ppm haloxyfop for 28 days was considered by the 1995 JMPR, and the current Meeting agreed to use the data from this study in estimating maximum residue levels and STMRs and highest residues for various tissues of cattle. The highest individual values in the group at 5 and 10 ppm were used in conjunction with the dietary burden at the STMR to calculate the probable highest concentration of residues in animal commodities. The mean concentrations in animal tissues at 5 and 10 ppm were used in conjunction with the dietary burden at the STMR to estimate the STMR values for animal commodities. For milk, the mean plateau concentration of residues in the group fed a diet containing 10 ppm haloxyfop-R was used to estimate both the STMR and the highest residue.

Feeding level (ppm) *Interpolated* / actual	Residues of haloxyfop (mg/kg)								
	Milk (mean)	Liver		Kidney		Muscle		Fat	
		High	Mean	High	Mean	High	Mean	High	Mean
MRL beef									
6.6 /		*0.33* /		*0.95* /		*0.03* /		0.23 /	
5		0.15		0.51		0.01		0.09	
10		0.72		1.90		0.06		0.53	
MRL dairy									
6.5 /	*0.22* /								
10	0.34								
STMR beef									
6.6 /			*0.28* /		*0.73* /		0.02 /		0.18 /
5			0.15		0.43		0.01		0.08
10			0.56		1.37		0.04		0.39
STMR dairy									
6.5 /	*0.22* /								
10	0.34								

The Meeting estimated a maximum residue level and STMR value in milk of 0.3 and 0.22 mg/kg; a maximum residue level, STMR value and highest residue in cattle liver of 0.5, 0.28 and 0.33 mg/kg; a maximum residue level, STMR value and highest residue in cattle kidney of 1, 0.73 and

0.95 mg/kg; and a maximum residue level, STMR value and highest residue in cattle meat of 0.05, 0.02 and 0.03 mg/kg, respectively.

The 1995 and 1996 JMPR considered a study in which laying hens were fed a diet containing 0.25–2.5 ppm haloxyfop for 28 days.

Feeding level (ppm) *Interpolated* / actual	Residues of haloxyfop (mg/kg)							
	Muscle and skin		Liver		Fat		Eggs	
	High	Mean	High	Mean	High	Mean	High	Mean
MRL	*< 0.003* /		*0.030* /		*0.010* /		*< 0.003* /	
0.082 / 0.25	< 0.01		0.09		0.03		< 0.01	
STMR		*< 0.002* /		*0.009* /		*0.004* /		*< 0.002* /
0.044 / 0.25		< 0.01		0.05		0.02		< 0.01

The Meeting estimated a maximum residue level, STMR value and highest residue in chicken meat (with adhering skin) of 0.01(*), 0.002 and 0.003 mg/kg; a maximum residue level, STMR value and HR value in chicken, edible offal of 0.05, 0.009 and 0.030 mg/kg; and a maximum residue level, STMR value and highest residue in chicken eggs of 0.01(*), 0.002 and 0.003 mg/kg, respectively.

Recommendations

On the basis of the data provided, the Meeting recommended the following values:

Definition of residue (for compliance with MRL and for estimation of dietary intake of commodities of plant and animal origin): haloxyfop esters, haloxyfop and its conjugates expressed as haloxyfop

Commodity		MRL (mg/kg)		STMR (mg/kg)	HR (mg/kg)
CCN	Name	New	Previous		
AL 1021	Alfalfa forage (green)	5[a]	W	2.33	–
MM 0812	Cattle meat	0.05	W	0.02	0.03
ML 0812	Cattle milk	0.3	W	0.22	–
MO 0812	Cattle, edible offal of	–	W	–	–
MO 1280	Cattle, kidney	1	–	0.73	0.95
MO 1281	Cattle, liver	0.5	–	0.28	0.33
PE 0840	Chicken eggs	0.01(*)	0.01 (*)	0.002	0.003
PM 0840	Chicken meat	0.01(*)[b]	0.01 (*)	0.002	0.003
PO 0840	Chicken, edible offal of	0.05	0.1	0.009	0.030
AV 1051	Fodder beet leaves or tops	0.3 [a]	W	0.03	–
AV 0596	Sugar beet leaves or tops	0.3 [a]	W	0.03	–

[a] Fresh weight basis
[b] With adhering skin

The information provided to the JMPR precluded an estimate that the dietary intake would be below the ADI in three regional diets.

Dietary risk assessment

Long-term intake

The Meeting estimated 10 STMR values for four commodities of cattle origin, three commodities of chicken origin and three fodder crops. These STMR values were used in combination with the STMR and STMR-P values estimated by the 1996 Meeting to calculate the long-term dietary intake of haloxyfop. The result is shown in Annex 3.

The IEDIs for the five GEMS/Food regional diets, on the basis of the estimated STMRs, were in 50–440% of the ADI. The Meeting concluded that long-term dietary intake of haloxyfop residues

from uses that have been considered by the JMPR might exceed the ADI in three GEMS/Food regional diets.

Short-term intake

The IESTI of haloxyfop by children and adults was calculated for commodities derived from cattle and chicken. The results are shown in Annex 4. The Meeting concluded that it might be necessary to establish an acute reference dose for haloxyfop. As one has yet been established, the acute risk assessment for haloxyfop was not finalized

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IPRODIONE (111)

EXPLANATION

Iprodione was first evaluated for residues in 1977 and again in 1980, and in 1994 under the CCPR Periodic Review Programme, and for toxicology in 1992 and 1995. In the 1994 periodic review, the Meeting recommended withdrawal of the existing CXL of 5 mg/kg in tomato because an insufficient number of trials according to GAP had been carried out, but the 28th Session of the CCPR recommended maintaining the existing CXL, pending provision of new data. The 30th CCPR retained the CXL as the manufacturer confirmed the availability of new data from indoor trials. The 31st CCPR agreed to extend the 4-year period under the Periodic Review procedure and the evaluation was scheduled for 2001.

METHODS OF RESIDUE ANALYSIS

Analytical methods

In the 1977 evaluation of iprodione, limits of quantification ranging from 0.01 to 0.02 mg/kg were reported for most fruits and vegetables and 0.05 to 0.1 mg/kg for samples where interferences occurred. Quantification was by GLC with an ECD.

As part of a storage stability study, Plaisance (1994a) reported an analytical method for the determination of iprodione, its isomer *N*-(3,5-dichlorophenyl)-3-isopropyl-2,4-dioxoimidazolidine-1-carboxamide (RP 30228) and metabolite 3-(3,5-dichlorophenyl)-2,4-dioxoimidazolidine-1-carboxamide (RP 32490) in a number of whole commodities and processed fractions. The treated samples are blended with CH_3CN and filtered, before being partitioned with hexane. The lower CH_3CN/H_2O phase is collected and partitioned repeatedly with hexane. The hexane fractions are discarded and the aqueous CH_3CN is evaporated to a small volume. A 50:50 mixture of hexane and CH_2Cl_2 is added to the CH_3CN and the mixture is cleaned up on a Florisil column. The eluate is evaporated to 1-2 ml and filtered before analysis by HPLC with UV detection (λ = 200 or 210 nm). pH adjustment was required for grape samples. No modifications of the method were required for tomatoes. Iprodione, its isomer RP-30228 and its metabolite RP-32490 are observed on one chromatogram with retention times of 6.47, 8.91 and 3.84 min respectively. The limit of quantification is 2.5 mg/kg for each compound. Representative chromatograms of each of 43 commodities were provided. Validation recoveries were determined for all commodities, with fortifications at 2.5 and 5 mg/kg and the results for whole tomatoes are shown in Table 1.

Table 1. Recoveries of iprodione, its isomer and metabolite from whole tomatoes.

Compound	Fortification level (mg/kg)	Recovery (%)
Iprodione	2.5 5	90, 90, 91, 94 91, 93, 96, 96
RP-30228	2.5 5	86, 90, 91, 92 94, 96, 96, 96
RP-32490	2.5 5	84, 85, 89, 90 86, 86, 86, 91

Bourgade *et al.* (1997) reported a version of method CNG-An no. 20610E revised to meet contemporary registration requirements (AR 144-97) that involves extracting residues of iprodione from plant samples by homogenizing in acetone and clean-up by partitioning with CH_2Cl_2. For fruit, vegetable and cereal samples (citrus fruit, stone fruit, berries and other small fruit; root and tuber vegetables,

fruiting vegetables, brassicas, leafy vegetables and fresh herbs, legume vegetables and pulses; cereals), the extracts are purified on a Florisil cartridge. For difficult samples (almonds, hazelnuts, grapes; carrots, stalk and stem vegetables; oilseeds) the extracts are purified on a diol cartridge. For oily products such as tree nuts and oilseeds, the extracts are washed with *n*-hexane before the diol cartridge. Quantification is by GLC on a semi-capillary column with an ECD and external standardization. The limit of quantification (LOQ) is 0.02 mg/kg. Specimen chromatograms of various samples were provided together with those of standard solutions. Recoveries from control samples taken from residue trials are shown in Table 2.

Table 2. Reported recoveries of iprodione from fruits and vegetables.

Sample	Fortification level (mg/kg)	Recovery (%)
Lemons	0.02 2 5	95, 96 80, 120 72
Oranges	0.02 0.1	106, 108 73
Cherries	0.02 0.1 1 2	74 76 91 94
Strawberries	0.02 5	121 96
Blackcurrants	8	80
Celeriac	0.02 10	112 106
Radish	0.02 0.5	83 115
Cucumbers	0.02 0.1 0.2 1	76, 102 98, 111 104 71
Melon	0.02 0.05 0.1 0.2 0.3	85 103 91, 92 81 94
Watermelon	0.05 0.1 0.2 0.4	109 118 128 71
Cauliflower	0.02 0.04 1	96, 133 87, 99 81
Broccoli	0.02 1	120 81
Brussels sprouts	0.02 0.1 0.2	100, 115 76 71
Chinese cabbage	0.02 0.1 2 5 15	81 119 85 100 119
Cabbage	0.02 0.05 0.1	93, 102 91 92, 108

Sample	Fortification level (mg/kg)	Recovery (%)
	0.25 0.5 1	80 92 107
Chicory	0.02	78, 88
Peas	0.02 0.1 1	81, 88 91, 93 90
Peas with pods	0.02 2	88 71
Lentils	0.02 0.1	99, 105 93, 109
Green beans	0.02 0.05 0.1 0.2 0.4 0.5 1 2	85, 95, 96, 106, 109 91 97, 113, 121 77, 83 73 87 87, 93, 99 78, 103
Wheat (grain)	0.02 0.05	86, 132 90, 91
Wheat straw	0.05 0.2 1	92, 99 80 91
Barley (grain)	0.02 0.05 0.1	86, 104 88, 111 101
Barley (straw)	0.05 0.2 1 2	79, 101 111 81 103
Sorghum	0.02	125

The modified method AR 144-97 was used to analyse tomatoes in many of the residue trials. Recoveries from some of the trials are shown below.

Table 3. Recoveries from tomatoes as determined in supervised residues trials.

Trial Ref.	Reported LOQ	Fortification level (mg/kg)	Recovery (%)
446165	0.02	0.02 0.4 0.8	80, 84, 95 94 90
444928	0.02	0.02 2	80, 84 96
427141	0.05	0.05	98
427214	0.05	0.05 0.09	95 100
412155	0.05	1 0.92 1.8	100 92 90
412161	0.05	0.5 0.95 2	100 95 98
405735	0.1	0.1	97

Stability of pesticide residues in stored analytical samples

The Meeting received several storage stability studies from the manufacturer. Maycey and Savage (1991) reported the stability of iprodione in strawberries, lettuce, blackcurrants, blackcurrant juice and prepared tomato extracts. Samples containing incurred residues obtained from residue trials were stored at -20°C for a maximum of 14 months after initial analysis. At varying intervals treated and control samples were re-analysed. Tomato extracts were prepared by homogenizing tomatoes with acetone, filtering, and evaporating the remaining filtrate to leave an aqueous sample. The samples were frozen until required, with further work-up before re-analysis. Concurrent recoveries were determined in the different samples at each interval. The results are shown in Table 4.

Table 4. Frozen storage stability of incurred iprodione residues in strawberries, lettuce, blackcurrants and blackcurrant juice and tomato extract.

Sample	Storage period (months)	Residue (mg/kg)		Concurrent recovery range (%)
		Initial analysis	Re-analysis	
Strawberries	8 14	2.4, 2.9 3.1, 3.1	2.5, 2.4 3.0, 3.1	93-95 (n = 3)
Lettuce	1 2.5 7 9 10	19.0, 20.3 19.0, 20.3 4.1, 4.2 5.0, 5.3 4.3, 4.7	20.4, 21.6 19.6, 21.0 3.4, 3.7 4.7, 4.4 5.4, 5.0	71-93 (n = 8)
Blackcurrants Juice	12 12	1.4, 1.5 1.8, 2.2 0.69, 0.78 0.60, 0.61	1.2, 1.3 1.4, 1.6 0.74, 0.75 0.58, 0.60	82, 83 86, 90
Tomato extract	6 days 6.5 12.8	0.99, 1.0	0.93, 0.98 1.1, 1.1 0.84, 0.99	95-97 (n = 5)

The results show that iprodione residues in strawberries stored up to 14 months, lettuce for 10 months, blackcurrants and blackcurrant juice for 12 months and tomato extract for almost 13 months decrease negligibly.

Plaisance (1994b) investigated the stability of iprodione, its isomer RP 30228 and metabolite RP 32490 in 43 commodities and processed fractions during storage at -10°C but only the results for tomato are reported here. Samples of tomatoes were individually fortified with 5 mg/kg of iprodione, its isomer and its metabolite and stored up to 12 months. At 3-month intervals, the stored commodities were analysed and the results compared to those from freshly fortified samples; duplicate samples were analysed at each time. The method was validated by analysis of samples fortified with 2.5 and 5 mg/kg of iprodione, its isomer and its metabolite to demonstrate acceptable recoveries (Table 1).

In a continuation of the Plaisance study, Gillings (1995) investigated the storage stability of tomato samples over 24 months, and reported a modified analytical method. Data from both studies are shown in Table 5.

Table 5: Storage stability of iprodione, its isomer RP-30228 and metabolite RP-32490 in tomatoes fortified at 5 mg/kg (Plaisance, 1994; Gillings, 1995).

Analyte	Storage period (months)	Apparent % remaining in stored sample	Concurrent recovery (%)	Corrected %remaining
Iprodione	0	95, 98	106	90, 93
	3	82, 86	80	102, 107
	6	(88), (92)[1]	67	131, 137
	9	94, 88	97	97, 91
	12	90, 91	95	95, 95
	24	92, 91	84	103, 101
RP-30228	0	92, 89	101	91, 89
	3	74, 78	87	85, 90
	6	68, 82	83	83, 100
	9	89, 88	108	83, 81
	12	85, 88	94	91, 93
	24	87, 87	83	104, 104
RP-32490	0	92, 91	101	90, 90
	3	85, 80	86	99, 93
	6	115, 117	104	111, 112
	9	89, 87	96	92, 90
	12	97, 95	104	93, 91
	24	89, 87	88	100, 99

[1]Values in parentheses not taken into account because of poor procedural recoveries on that day.

The proportions of the original fortification remaining in tomatoes ranged from 81 to 137% for iprodione, its isomer and its metabolite:

Compound	Range, %	Mean, %
Iprodione	90-137	104
Isomer RP-30228	81-104	91
Metabolite RP-32490	90-112	97

The results show that residues of iprodione, its isomer and its metabolite in tomatoes are stable during frozen storage for at least 24 months.

USE PATTERN

Iprodione is registered as a contact fungicide on *solanaceae*, more specifically tomatoes, in Africa (Algeria, Ivory Coast, Cameroon, Kenya, Mauritius, Morocco, South Africa, Senegal, Togo, Tunisia, Zambia), North America (Canada), Latin America (Bolivia, Brazil, Chile, Costa Rica, Honduras, Nicaragua), EU (Belgium, France, Finland, Greece, Hungary, Italy, Portugal, Romania, Spain, Sweden, The Netherlands, the UK), Asia and Australasia (Australia, New Zealand, Japan, China, Thailand, Malaysia, Myanmar). Iprodione is used to control the fungal diseases *Alternaria spp.*, *Sclerotinia spp.* and *Botrytis spp.* in tomatoes. It is formulated as a wettable powder, suspension concentrate and water-dispersible granules for use in field and glasshouse. WP and WDG products are typically 500 g/kg, while SC products are 255 or 500 g/l.

The information reported to the Meeting on the registered uses on tomatoes is shown in Table 6.

Table 6: Registered uses of iprodione on tomatoes. All foliar applications.

Country	Form.	Field/ indoor	Application			PHI (days)
			Rate (kg ai/ha)	Spray conc. (kg ai/hl)	No.	
Belgium	WP 500 SC 500	[1]		0.05	6[2]	3
Brazil	WP 500 SC 500	Field	0.6-0.75	0.075[3]	1-3	1
Canada	WP 500 WG 500	Indoor		0.05	NS[4]	2
China	WP 500 SC 500	Field and indoor	0.375-0.75	0.056-0.17[5]	1-3	7
Denmark	SC 500 WP 750	Field and indoor		0.025-0.05 0.022-0.052	NS	3
France	SC 500	Field and indoor	0.75-1		NS[6]	3
Italy	WP 500 FL 250	Field		0.05-0.075[7]		21
Japan	WP 500 SC 40	Field and indoor	1	0.033-0.05 0.026-0.040	3[8]	1
Netherlands	SC 500	Field and indoor		0.025		3
UK	WP 500	Field and indoor		0.05	6[2]	1 (Indoor) 2 (Field)

[1] For use in market gardens.
[2] Re-treatment interval 14 days.
[3] Spray volumes 800-1000 l/ha; repeat at 7-day intervals.
[4] Application from 2nd flower stage; repeat at weekly intervals.
[5] Spray volumes 450-675 l/ha.
[6] Apply from 2nd flower stage; re-treatment interval 10-15 days indoors or 15-20 days in field.
[7] Similar rates for combination product with thiram.
[8] Application from flowering stage.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results from supervised residue trials are shown in Tables 7-15.

Tables 7-12 *Europe:* Belgium, Denmark, France, UK, Italy, The Netherlands
Table 13 Canada
Table 14 China
Table 15 Japan

Where residues were not detected the results are reported as below the limit of quantification (LOQ), e.g. <0.05 mg/kg. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures. Although trials included results for untreated controls, these results are not reported in the Tables unless the residues in the control samples were above the LOQ. The prefix *"c"* in the Tables indicates samples from control plots. Where possible, residues are recorded uncorrected for analytical recoveries. It should be noted that unless stated otherwise concurrent recoveries were acceptable and any corrections small. NS indicates that a particular detail was not stated in the field report.

It is noted that a number of the trials described below were reviewed in the 1994 evaluation of iprodione. Unless otherwise stated, WP or WDG formulations were used in most trials.

Results from a single trial in Belgium were reported to the Meeting, but it was not stated whether the trial was in the field or under glass. Four foliar sprays were applied at intervals of 11, 21 and 14 days, and samples taken 3 hours after the last spray. The LOQ was reported as 0.01 mg/kg, although analytical details were not given.

Table 7. Residues in tomatoes from a trial in Belgium.

Location, year	Application				PHI	Residues	Ref.
	kg ai/ha	kg ai/hl	No.	Interval		(mg/kg)	
Moerzeke, 1983	–	0.025	4	11, 21, 14	3 h	0.28	Nangniot, 1983, Report 83/128 319549
	–	0.05	4		3 h	1.60	

Two glasshouse trials in Denmark were conducted in 1980 and 1981. In the 1980 trial, maturing fruit received a single foliar application by knapsack sprayer. Plots of 6 single plants were sprayed to run-off. Samples were analysed within 3-4 months of collection. In the 1981 trial, 7 sprays were applied to 15 plants at 14-day intervals, using a knapsack sprayer. The LOQ was reported as 0.1 mg/kg, the lowest fortification level for analytical recoveries.

Table 8: Residues in tomatoes from indoor trials in Denmark.

Location, year (variety)	Application				PHI (days)	Residues (mg/kg)	Ref.
	kg ai/ha	kg ai/hl	No.	Interval			
Koebenhavn, 1980 (Ida)	–	0.05	1	–	0	1.3 *c* 0.018	Brockelsby and Cooper, 1981 403185
					4	0.74	
					7	0.49	
Marslev, 1981 (Ida)	1.4		7	14 days	1	1.9 *c* 0.035	Maycey, 1982b 404347
					3	1.7 *c* 0.02	
					5	0.9	
					7	1.0	
					14	1.0	

Several field trials in Northern and Southern France, from 1978 to 1998, were reported. In the 1978 trials, either single or 4 foliar applications were made by pneumatic sprayer to tomatoes under cover. No detailed description of analysis was given.

In the first of the 1991 trials (at Coustellet) 2 foliar applications of an SC formulation were made by pneumatic sprayer, the first at flowering and the second 25 days later at orange fruit. The limit of quantification was 0.05 mg/kg; a full analytical report was provided. In the second trial, 3 sprays of an SC product were applied by pneumatic sprayer at intervals of 14 and 15 days. Rain fell 5 days after the last spraying and temperatures during the spraying were 26-29°C. Samples from both trials were analysed within 3 months but details of the field phase of the trials were in summary form only.

In 1998 in two glasshouse trials on tomatoes in Northern France an SC formulation was applied five times at 7-day intervals using a backpack sprayer, starting at BBCH 66 through to BBCH 81, to duplicate plots of 9 and 8 m^2 each consisting of 10 plants. Samples from the replicate plots were analysed individually within 3 months. A full description of the analytical method was provided with chromatograms, LOQ 0.02 mg/kg.

In another glasshouse trial in 1998 in Southern France 4 sprays of an SC formulation were applied by backpack sprayer at 7-day intervals to duplicate plots (8 m^2, 20 plants) at growth stages ranging from BBCH 64-71 to BBCH 65-74. Samples from each replicate plot were analysed within 5 months: a full method with chromatograms was provided.

Table 9. Residues in tomatoes from trials in France.

Location, year (variety)	Application				Field/ indoor	PHI (days)	Residues (mg/kg)	Ref.
	kg ai/ha	kg ai/hl	No.	Interval, days				
Avignon, France (Sth), 1978, (63-5)	0.83	0.15	1	–	indoor	9	0.19	Laurent and Chabassol, 1979 402126
Chavanne, France (Sth), 1978, (63-4)	0.75	0.15	4	17, 22, 33	indoor	7	0.85	
Coustellet. France (Sth), 1991, (Delta)	0.75		2	25	field	19	<0.05	Muller, 1991b 427141 (Study 91-261)
Robion, France (Sth), 1991, (Roma)	2.2		3	14, 15	field	0 4 7 14	0.1 <0.05 <0.05 <0.05	Muller, 1991a 427214 (Study 91-198)
Janze, France (Nth), 1998 (Felicia)		0.05	5	7	indoor	3	1.7, 1.6	Baudet, 1991b 444928 (Study 98-574)
St. Coulomb, France (Nth), 1998, (Felicia)		0.05	5	7	indoor	3	1.5, 1.7	
Vaucluse, France (Sth), 1998, (Felicia)		0.15	4	7	indoor	3	1.9, 1.3	Baudet, 1991c 446068 (Study 98-755

Several glasshouse trials were conducted in the UK during 1974, 1977 and 1981.

In 1974, trials were carried out at two sites in Essex, one in polythene greenhouses at Writtle and the other in a multispan glasshouse at Brentwood.

At Writtle 5 to 8 applications at 13- to 14-day intervals using a knapsack sprayer were made to plots of 12 plants, 30 cm apart (3 replicates of 4 plants). Crops were sprayed to run-off but spray volumes were not reported. Samples from each replicate (3 × 1 kg) were collected 14 days after the last spraying and analysed individually within 5 months. The reported LOQ was 0.05 mg/kg.

At Brentwood, in the first of two trials 5 applications were made at 14-day intervals to a plot of 36 plants, 45 cm apart (3 replicates of 12 plants), sprayed to run-off using a knapsack sprayer. Samples were collected 0-14 days after treatment and analysed within 4 months. In the other trial, 4 to 8 sprays were applied using a knapsack sprayer at 14-day intervals and samples collected 14 or 15 days after the last spraying (14 and 28 days later after 8 sprays) were analysed within 4 months. Treated plots consisted of 18 plants, 45 cm apart (3 replicates of 6 plants). The LOQ was 0.05 mg/kg.

An SC formulation was used in the 1981 UK trials. At Chichester, 6 sprays were applied by motorised knapsack sprayer at intervals of 10 to 17 days from early flowering to mature fruit stages. The plot consisted of 5 rows or 115 m^2; samples were analysed within 4 months. In the Ipswich trial 6 sprays were applied by hand-held lance sprayer at intervals of 5 to 48 days, from 2nd flowers to red fruit stages; plot size 3 double rows. Samples were analysed within 2 months of collection. In the Pershore trial, 11 sprays were applied by hand-held knapsack at 14- to 21-day intervals; no indication of growth stages or plot size was given. Samples were analysed one month after collection. Finite residues were found in all control samples. Replicate samples were analysed individually. The lowest fortification to test recovery was 0.2 mg/kg, although the limit of quantification was reported as 0.01 mg/kg.

In the 1977 glasshouse trials in England and Scotland a variety of formulations of iprodione were used. At Kirkham 2 applications were made at 14-day intervals by thermal fogging at a rate equivalent to 1.1 kg ai/ha, and at Milford 4 were made at 14-day intervals by fogging to a 0.4 ha plot and 2 replicate samples and a control were collected 2 days after treatment. In the first of two trials at Lea Valley 2

applications were made by spraying or fogging on the same day to 4 replicate plots, and in the second trial 4 or 5 applications by spraying or fogging but plot sizes were not reported. At Ayr in Scotland 4 applications were made by spraying using a hand-held lance or by a fogging machine to each replicate plot (size 9.7 × 35m). Samples from all the UK trials were analysed within 1 to 2 months of collection. The limit of quantification was reported as 0.02 mg/kg.

Table 10. Residues in tomatoes from indoor trials in the UK.

Location, year (variety)	Application				PHI (days)	Residues (mg/kg)	Ref.
	kg ai/ha	kg ai/hl	No.	Interval			
Writtle, Essex, 1974, (Eurocross B.B.)		0.05	5	16, 14, 14, 13	14	1.8, 2.6, 3.8	Laurent and Buys, 1975 445075 Spray to run-off
			6	16, 14, 14, 13, 14	14	2.9, 4.7, 3.7	
			7	16, 14, 14, 13, 14, 14	14	4.9, 5.0	
			8	16, 14, 14, 13, 14, 14, 14	14 27 41	2.9, 5.0, 4.6 1.8, 3.1, 1.9 3.2, 3.4	
Brentwood, Essex, 1974, (Sonato)		0.05	4 5 6 7 8	14 (3) 14 (3), 15 14 (3), 15, 14 14 (3), 15, 14 (2) 14 (3), 15, 14 (3)	15 14 14 14 14 28	1.4, 1.9, 2.0, 2.7 3.3, 2.4 4.9, 3.1, 3.1 4.1, 4.3 6.4, 5.3	445075
Brentwood, Essex, 1974, (Sonato)		0.05	5	14 (4)	0 2 5 7 9 14	2.2, 3.1, 3.9 4.2, 3.7, 2.4 3.5, 3.0, 2.5 1.2, 3.6, 2.7 1.4, 1.6, 3.4 3.6, 2.7, 1.7	445075
Chichester, 1981, (Sonatine)		0.05	6	14, 14, 14, 10, 17	1	2.6, 2.8 *c* 0.06	Maycey, 1982a 403960
Ipswich, 1981, (Shirley)		0.05	6	14, 20, 5, 44, 48	1	1.4, 2.1 *c* 0.40	
Pershore, 1981, (Sonatine)		0.05	11	14 (5), 21 (2), 14(2), 17	1	1.5, 1.4 *c* 0.47	
Kirkham, 1977, (Sonato)	1.1	0.08	2	14	2	0.85, 1.0, 0.24	Woods, 1978 445076
Milford, 1977 (Kirdford Cross)	1.1	0.06	4	14, 14, 14	2	1.4	
Lea Valley, 1977, (Sonato)	0.56	0.06	2	0 days	2	0.1	
Lea Valley, 1977, (Sonato)	0.56	0.06	4	14, 14, 7	3	0.23	
			5	14, 14, 7, 14	3	0.28	
Ayr, 1977 (Curabelle)	0.56	0.06	4	14, 15, 14	2	1.4	

In a single Italian field trial 3 sprays of a 250 SC formulation were applied by compressor. Plots were replicated with samples of 1.5 kg analysed individually within 2 months of collection. The limit of quantification was 0.03 mg/kg.

Table 11. Residues in tomatoes from a field trial in Italy.

Location, year (variety)	Application				PHI (days)	Residues (mg/kg)	Ref.
	kg ai/ha	kg ai/hl	No.	Interval			
Alfonsine, 1982 (UC 90)	0.75	0.075	3	15, 17	15 28	0.06 0.03	Chabassol and Aublet, 1983 405735

In three glasshouse trials in The Netherlands five foliar sprays were applied at intervals of 10 to 14 days (BBCH 60-89) using a motor sprayer with a spraystick at 1.1 kg ai/ha or 0.073 kg ai/hl to control and treated plots of 16 m^2 (1 double row 1.6 m wide by 10 m long). Samples were analysed within 4 months of collection. Replicate samples (12 fruits) were taken randomly from each plot. Quantification was by GLC with an ELCD (electroconductivity detector). The LOQ was 0.02 mg/kg.

Table 12. Residues in tomatoes from indoor trials in The Netherlands.

Year (variety)	Application			PHI (days)	Residues (mg/kg)	Ref.
	kg ai/hl	No.	Interval			
1998 (Elegance)	0.073	5	13, 10, 10, 11	3	0.58, 0.79	Baudet, 1999a 446165
	0.073	5	13, 10, 10, 11	3	0.50, 0.54	
	0.073	5	13, 10, 10, 11	3	0.86, 1.1	

In glasshouse trials in Canada in 1981/1982 two or three foliar sprays were applied at intervals of 37 or 14 and 35 days respectively by knapsack (1981 trial) or by electric greenhouse sprayer (1982). In the 1981 trial plots consisted of 10 plants by 4 replicates and spray volumes were 250 l/ha, and in the 1982 plots of 4 rows by 10m (row spacing 102 cm; plant spacing 31 cm) were sprayed to run-off. Composite samples were taken from 4 replicate plots. In the 1982 trials, residues in individual 1 kg samples were determined. All samples were analysed within 4 months of collection. The LOQ was 0.1 mg/kg; controls <0.03 mg/kg.

Table 13. Residues in tomatoes from indoor trials in Canada.

Location, year (variety)	Application			PHI (days)	Residue (mg/kg)	Ref.
	kg ai/hl	No.	Interval			
Ontario, 1981, (MR 13)	0.05	3	14, 35	2 7	0.2 0.4	Maycey, 1983 318322
	0.1	3	14, 35	2 7	0.5 0.5	
Ontario, 1982, (Vendor)	0.05	2	37	3	0.1, <0.1, 0.2, 0.2[1]	
(Jumbo)	0.05	2	37	3	0.2, 0.2, 0.3, 0.3	
(MR 13)	0.05	2	37	3	0.2, 0.3, 0.4, 0.2	

[1] 4 × 1 kg samples analysed individually instead of composite.

For trials in China only summary sheets were provided in English with field- and analytical-phase reports in Chinese. Recoveries were 85-87% with an LOQ of 0.01 mg/kg.

Table 14. Residues in tomatoes from field trials in China.

Location, year	Application			PHI (days)	Residue (mg/kg)	Ref.
	kg ai/ha	No.	Interval			
Hang Zhou, 1990	0.75	3	NS	3 7 10	1.7 1.6 1.9	Aventis 448474
		5	NS	3 7	0.71 1.1	

Location, year	Application			PHI	Residue	Ref.
	kg ai/ha	No.	Interval	(days)	(mg/kg)	
				10	0.60	
	1.5	3	NS	3 7 10	1.7 1.7 0.69	
		5	NS	3 7 10	1.1 2.0 2.0	
Shi Jia, 1990	0.75	3	NS	3 7 10	1.1 0.53 0.25	448474
		5	NS	3 7 10	1.1 0.99 0.23	
	1.5	3	NS	3 7 10	1.6 1.0 0.38	
		5	NS	3 7 10	2.1 1.3 0.26	
Hang Zhou, 1991	0.75	3	NS	3 7 10	0.24 0.15 0.04	448474
		5	NS	3 7 10	1.0 0.21 0.08	
	1.5	3	NS	3 7 10	1.7 0.15 0.12	
		5	NS	3 7 10	0.43 0.29 0.14	
Shi Jia, 1991	0.75	3	NS	3 7 10	0.26 0.09 0.05	
		5	NS	3 7 10	0.58 0.19 0.14	
	1.5	3	NS	3 7 10	0.51 0.40 0.16	
		5	NS	3 7 10	0.31 0.30 0.21	

A number of Japanese trials from 1975 to 1988 were reported to the Meeting. In the 1975 trials at Nagasaki, 3, 4 or 5 sprays were applied at 7-day intervals. Field details were brief, with no indication of plot sizes or samples sizes. Samples were analysed for iprodione and its isomer RP30228 within 7 months of collection. The limits of quantification were 0.05 mg/kg for iprodione and 0.1 mg/kg for RP-30228.

In the 1975 Ibaraki trial 1, 3 or 4 sprays of iprodione were applied at 7-day intervals. Field details were again brief with no indication of plot or sample sizes. Samples were analysed for iprodione and RP-30228 within 4 months of collection. The limits of quantification were 0.05 mg/kg for both compounds.

Table 15. Residues in tomatoes from indoor trials in Japan.

Location, year (variety)	Application				PHI (days)	Residue[1] (mg/kg)	Ref.
	kg ai/ha	kg ai/hl	No.	Interval			
Nagasaki, 1975	3	0.1	3	7, 7	1 3 7 14	2.1 3.4 1.8 3.0	Laurent and Buys, 1976a 412155
	3	0.1	4	7, 7, 7	1 3 7 14	4.6 3.6 4.1 2.8	
	3	0.1	5	7, 7, 7, 7	1 3 7 14	4.5 4.1 3.9 3.8	
Ibaraki, 1975	2.5	0.1	1		1 3 7 14	1.3 1.4 1.2 0.79	Laurent and Buys, 1976b 412161
	2.5	0.1	3	7, 7	1 3 7 14	5.3 3.5 3.0 2.4	
	2.5	0.1	4	7, 7, 7	1 3 7 14	5.6 5.4 4.3 3.5	
Gunma, 1978, (Ogata zuiko)	0.75-1	0.05	3	7, 7	3 7	1.1 0.90	IETJ 1978
	0.75 - 1.3		6	7, 7, 7, 7, 7	3 7	0.45 1.2	
Chiba, 1978, (Toko K)	1.5	0.05	3	7, 7	1 3 7	0.61 0.60 0.52	
			6	7, 7, 7, 7, 7	1 3 7	1.6 0.82 1.0	
Ibaraki, 1988, (TVR-2)	0.46	0.023	4	7, 7, 7	1 3 7	0.01 0.02 0.02	IETJ 1988a
Ishikawa, Japan 1998 (Kyoryoku reigyoku)	0.46	0.023	4	7, 7, 7	1 3 7	0.04 0.02 0.03	
Ibaraki, 1988, (TVR-2)	0.46	0.023	4	7, 7, 7	1 3 7	0.16 0.22 0.22	IETJ 1988b
Ishikawa, Japan 1998 (Kyoryoku reigyoku)	0.46	0.023	4	7, 7, 7	1 3 7	0.72 0.56 0.74	

IETJ: Institute of Environmental Toxicology, Japan

[1] Residues of RP30228 were determined in all samples, but were below the limits of quantification of 0.1 mg/kg in the Nagasaki trials and 0.05 mg/kg in the other trials.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

In trials in the USA tomatoes were sprayed five times with a wettable powder formulation at 7- or 14-day intervals at rates equivalent to 1.1 or 2.2 kg ai/ha. Samples of 0.9-2.2 kg of fruit were taken on the same day as the last application from each of 6 trial sites: Florida, California (2), New Jersey and Ohio (2) and analysed within 2 months of collection. Samples from one of the California trials were processed into wet and dry pomace, purée, juice and ketchup. Pilot plant scale equipment was used and the processing simulated commercial conditions. Iprodione, its isomer and metabolite were determined in all samples. The limit of quantification was 0.05 mg/kg for each compound. The results are shown in Tables 16 and 17.

Table 16. Residues of iprodione, RP-30228 and RP-32490 in whole treated tomatoes (Guyton, 1987).

Trial	Application (kg ai/ha)	PHI (days)	Residues (mg/kg)		
			Iprodione	RP-30228	RP-32490
Ohio site 1	1.1	0	0.22	<0.05	<0.05
	2.2	0	2.4	0.15	0.07
Ohio site 2	1.1	0	1.6	0.11	<0.05
	2.2	0	1.6	0.11	0.08
Florida	1.1	0	0.25	<0.05	<0.05
	2.2	0	1.9	0.07	0.08
California site 1	1.1	0	0.27	<0.05	<0.05
	2.2	0	0.46	<0.05	<0.05
California site 2	1.1	0	1.5	0.07	<0.05
	2.2	0	2.8	0.14	0.10
New Jersey	1.1	0	0.37	0.05	0.08
	2.2	0	0.76	0.06	0.06

Table 17. Residues of iprodione, RP-30228 and RP-32490 in processed tomato fractions from fruit treated in California at site 1 (Guyton 1987).

Sample	Application (kg ai/ha)	Residues (mg/kg)		
		Iprodione	RP-30228	RP-32490
Tomato	1.1	0.27	<0.05	<0.05
	2.2	0.46	<0.05	<0.05
Wet pomace	1.1	1.4	0.16	<0.05
	2.2	1.4	0.06	0.13
Dry pomace	1.1	5.7	0.44	0.24
	2.2	9.8	0.35	0.41
Juice	1.1	0.15	0.14	<0.05
	2.2	0.21	0.12	<0.05
Purée	1.1	0.09	<0.05	0.05
	2.2	0.33	0.05	0.08
Ketchup	1.1	0.16	<0.05	<0.05
	2.2	0.59	0.10	0.10

Mean processing factors for various fractions were calculated from residues in samples treated at 1.1 and 2.2 kg ai/ha.

Table 18. Calculated processing factors for residues of iprodione in processed tomato fractions.

Commodity	Processing factor		
	1.1 kg ai/ha	2.2 kg ai/ha	Mean
Tomato	-	-	-
Wet pomace	5.2	3.0	4.1
Dry pomace	21	21	21
Juice	0.6	0.5	0.5
Purée	0.3	0.7	0.5
Ketchup	0.6	1.3	0.9

Concentration of iprodione residues occurs in wet and dry pomace prepared from treated tomatoes.

Recoveries of iprodione, RP-30228 and RP-32490 from tomatoes and their processed fractions are shown in Table 19.

Table 19. Recoveries of iprodione, RP-30228 and RP-32490 from fortified tomatoes and their processed fractions.

Sample	Fortification (mg/kg)	Recoveries (%)		
		Iprodione	RP-30228	RP-32490
Tomato	5	99		
	4	93		
	2	102		
	1	130, 107	105	
	0.5	96	130	117
	0.2		86, 113	134, 104
Juice	0.05	127	99	92
Purée	0.2	116		
Wet pomace	5	105		
Dry pomace	10	113		

NATIONAL MAXIMUM RESIDUE LIMITS

The manufacturer reported the following national MRLs for iprodione in tomatoes.

Country	MRL (mg/kg)
Canada	0.5
Australia, Hungary, South Africa, Zambia	2
Bolivia, Brazil	4
China, Costa Rica, EU, Honduras, Israel, Japan, Kenya, New Zealand, Nicaragua, Switzerland, Tunisia	5
Peru	10

The current Codex CXL is 5 mg/kg.

APPRAISAL

Iprodione was first evaluated in 1977 and was subsequently reviewed for residues in 1980 and 1994. In the periodic review of iprodione in 1994, the Meeting recommended withdrawal of the CXL for tomato of 5 mg/kg, as there were insufficient supervised trials with corresponding GAP. The CCPR at its Twenty-eighth Session maintained the existing CXL, pending provision of new data. At its 30th Session, the CCPR retained the CXL, as the manufacturer confirmed the availability of new data from indoor trials. The evaluation was scheduled for 2001 by the CCPR at its Thirty-first Session.

The Meeting received information on analytical methods and GAP as well as supplementary data on residues, stability in storage and processing of tomatoes.

Methods of analysis

The Meeting received information on an HPLC and a GLC method for the determination of iprodione in crops and processed commodities. In the HPLC method, iprodione, its isomer N-(3,5-dichlorophenyl)-3-isopropyl-2,4-dioxoimidazolidine-1-carboxamide (RP-30228) and its metabolite 3-(3,5- dichlorophenyl_-2,4- dioxoimidazolidine-1-carboxamide (RP-34290) were measured, while the GC method can be used to determine residues of iprodione. The LOQs were 2.5 and 0.02 mg/kg for the HPLC and GC method, respectively. Both methods were validated for at least 25 crops, including tomatoes.

Stability of residues in stored analytical samples

Iprodione was stable in tomato extracts for at least 13 months when stored at −20°C. In another study, the stability of iprodione, its isomer RP-30228 and its metabolite RP-32490 in 43 commodities and processed fractions was investigated. Residues in tomatoes were stable for at least 24 months when stored at −10 °C.

Results of supervised trials

Labels from products registered in Belgium, Brazil, Canada, China, Denmark, France, Italy, Japan, The Netherlands and the UK were provided to the Meeting. Many of the labels indicated use indoors (glasshouse or under cover) and in the field. In the UK, two PHIs are indicated, one for indoor use and another for field use. The manufacturer indicated that re-registration of the compound in the European Union is pending; therefore, use in some of the more recent European trials did not correspond to existing labels.

Several of the trials provided to the Meeting had been reviewed by the 1994 JMPR. Data from field and indoor trials on tomato were provided.

Field trials

In China, iprodione is registered for use (in the field or under cover) at rates ranging 0.37 to 0.75 kg ai/ha, with a PHI of 7 days. One to three sprays are recommended. Concentrations of 1.6, 0.53, 0.15 and 0.09 mg/kg were found in trials corresponding to GAP, with samples taken 7 days after treatment at 0.75 kg ai/ha.

Iprodione is registered in Italy for field use only, with application at concentrations of 0.05-0.075 kg ai/hl and a PHI of 21 days. In one trial in Italy that did not correspond to GAP, iprodione was applied three times at 0.075 kg ai/hl, and samples were taken 15 and 28 days after treatment. A single value of 0.03 mg/kg was obtained 28 days after treatment.

Registered labels in France allow use of iprodione on tomatoes in the field at rates of 0.75–1 kg ai/ha and a re-treatment interval of 15–20 days; the PHI is 3 days. The field trials did not correspond to GAP, as the PHI was 19 days in one trial and the application rate was 2.2 kg ai/ha in the other.

The Meeting considered that there were inadequate data from field trials, which could not be pooled or directly compared with data from trials conducted under cover. Therefore, these data were not used in estimating a maximum residue level.

Indoor trials

Trials in glasshouses were conducted in Canada, Denmark, France, Japan, The Netherlands and the UK.

In four trials in Canada which approximated national GAP (0.05 kg ai/hl; PHI, 2 days), the concentrations of residues were 0.2, 0.3, 0.4 and 0.4 mg/kg 2–3 days after spraying at 0.05 kg ai/hl.

In one trial in Denmark, iprodione was applied once at 0.05 kg ai/hl, and samples were collected 0, 4 and 7 days after treatment. The trial approximated GAP in Denmark (0.022–0.052 kg ai/hl; PHI, 3 days). A concentration of 0.74 mg/kg was found on day 4. In a second trial, the spray volumes used were not reported, and low concentrations of iprodione were present in control samples taken on days 1 and 3. These data were not considered in estimating an MRL.

Registered labels in France allow use of iprodione on tomatoes under cover at rates of 0.75–1 kg ai/ha and a re-treatment interval of 10–15 days; the PHI is 3 days. Five trials conducted under cover in northern and southern France did not approximate national GAP. The data were evaluated by comparison with GAP in the UK (0.05 kg ai/hl; PHI, 1 day). A concentration of 1.7 mg/kg (2) was found in crops treated five times at 0.05 kg ai/hl and sampled 3 days after treatment.

The results of numerous trials conducted in Japan were provided to the Meeting. Iprodione is registered for use on tomatoes (in the field and under cover) at spray concentrations of 0.026–0.05 kg ai/hl and a PHI of 1 day; a maximum number of three sprays is recommended. Four trials which approximated national GAP showed concentrations of residues of 0.61, 1.1, 1.2 and 1.6 mg/kg 1–3 days after spraying at 0.05 kg ai/hl.

In three trials conducted in glasshouses in The Netherlands, a spray concentration of 0.075 kg ai/hl was applied five times to tomatoes. However, the trial did not correspond to registered uses in The Netherlands, which allow application at a spray concentration of 0.025 kg ai/hl and a PHI of 3 days.

In the UK, iprodione may be applied to tomatoes under cover at a spray concentration of 0.05 kg ai/hl. A maximum of six sprays may be applied, with a PHI of 1 day. In trials conducted in 1981, iprodione was present in untreated samples at concentrations 20–30% lower than in treated samples in two trials and 3% lower in a third trial. Only data from the trial with low contamination in the control sample were considered in estimating an MRL. Four trials conducted in 1977 approximated GAP in the UK, with application at 0.05 kg ai/hl and sampling 2 days after the last spray. The concentrations of residues in these trials were 0.23, 0.28, 1.4, 1.4, 2.8 and 4.2 mg/kg, in samples taken 1–2 days after treatment at 0.05 kg ai/hl.

The results of all indoor trials conducted at GAP showed concentrations, in ranked order (median underlined), of: 0.2, 0.23, 0.28, 0.3, 0.4 (2), 0.61, 0.74, <u>1.1</u>, 1.2, 1.4 (2), 1.6, 1.7 (2), 2.8 and 4.2 mg/kg. The Meeting estimated a maximum residue level of 5 mg/kg, an STMR value of 1.1 mg/kg and a highest residue value for iprodione in tomatoes of 4.2 mg/kg. The estimated maximum residue level confirms the current recommendation (5 mg/kg) for tomato.

Fate of residues during processing

A study of processing conducted in the USA which was reviewed by the 1994 JMPR was re-submitted by the manufacturer. Iprodione was applied five times at 7–14-day intervals, at a rate equivalent to 1.1 or 2.2 kg ai/ha. Samples of treated fruit were taken on the day of the final application. Residues of iprodione, its isomer and its metabolite were determined in all samples. The concentrations were 0.22–1.6 mg/kg after application at 1.1 kg ai/ha and 0.46–1.9 mg/kg after application at 2.2 kg ai/ha.

Tomatoes collected after both treatments were processed into wet and dry pomace, juice, purée and ketchup. The calculated processing factors for the concentration of iprodione were 4.2 in wet pomace and 21 in dry pomace. In the 1994 evaluation, factors of 5 and 21, respectively, were reported; however, the data had not been corrected for recovery. Processing factors of 0.5, 0.5 and 0.9 were calculated for juice, purée and ketchup, resulting in corresponding STMR-P values of 0.55, 0.55 and 0.99.

Recommendations

On the basis of the data from supervised trials, the Meeting concluded that the concentrations of residues listed below were suitable for establishing maximum residue limits and for assessing IEDI.

Definition of the residue (for compliance and for estimation of dietary intake): iprodione

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)	HR or HR-P (mg/kg)
CCN	Name	New	Previous		
VO 0448	Tomato	5	5	1.1	4.2
JF 0448	Tomato juice			0.55	
	Tomato purée			0.55	
	Tomato ketchup			0.99	

Dietary risk assessment

Long-term intake

The IEDIs for the five GEMS/Food regional diets, on the basis of the estimated STMR values, were 3–50% of the ADI. The Meeting concluded that long-term intake of residues of iprodione from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The present Meeting considered that the toxicological profile of iprodione includes effects of concern that might indicate a need for an acute RfD. The IESTI for iprodione was calculated as described in Section 3 for commodities for which maximum residue levels and STMR values were estimated and for which data on consumption were available. The results are shown in Annex 4 (Report 2001). The IESTI for tomatoes was 0.060 mg/kg bw for the general population and 0.244 mg/kg bw for children. As no acute RfD has been established, the risk assessment for iprodione was not finalized.

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KRESOXIM-METHYL (199)

EXPLANATION

Kresoxim-methyl was evaluated for the first time by the JMPR in 1998. The 1998 Meeting recommended MRLs for pome fruits, barley, cucumber, grapes, dried grapes, rye, straw and fodder (dry) of cereal grains, wheat, edible offal (mammalian), mammalian fats (except milk fats), meat (from mammals other than marine mammals), milks and poultry meat.

New information on registered uses, supervised residue trials, processing studies on citrus fruits, olives and sunflower, and metabolism in sugar beet was made available by the manufacturer to the Meeting. Information on current GAP was received from Germany and Japan.

The code numbers, names and structures of kresoxim-methyl and its metabolites referred to in this Evaluation are shown in Figure 1.

IDENTITY

Physical and chemical properties

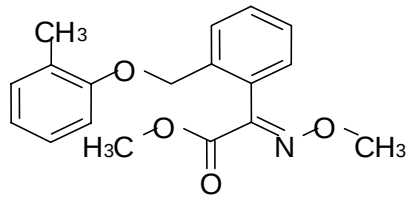
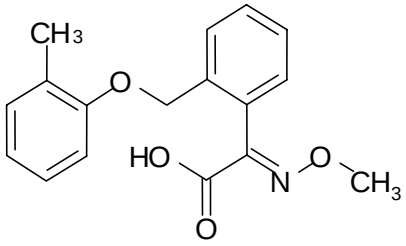
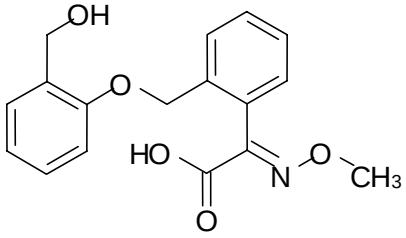
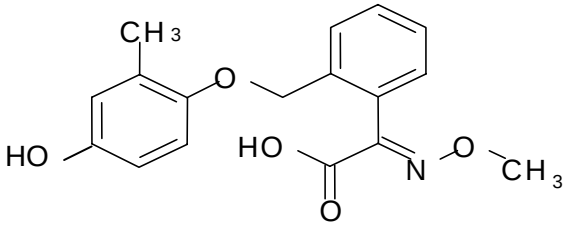
Information on vapour pressure was inadvertently reported for the (*Z*)-isomer of kresoxim-methyl instead of the free acid metabolite (BF 490-1 or 490M1) in the 1998 JMPR Evaluation, Part I. The entry should read:

Vapour pressure: kresoxim-methyl: 2.3×10^{-6} Pa at 20°C (extrapolated)
free acid (BF 490-1): $<1 \times 10^{-5}$ Pa
(Gückel, 1992; Kästel, 1996)

The current Meeting received additional information on the octanol/water partition coefficient of the free acid at pH 4 and 9 as follows.

Octanol/water partition: kresoxim-methyl (99.4%): log K_{ow} = 3.40 at 25°C
free acid (BF 490-1): log K_{ow} = 0.15 (pH 7; 20°C),
log K_{ow} = 2.74 (pH 4; 20°C),
log K_{ow} = -2.85 (pH 9; 20°C)
(Redeker, 1990; Türk, 1996)

Figure 1. Structures and codes of kresoxim-methyl and related substances referred to in the monograph.

Code/Name	Chemical name Structure
Kresoxim-methyl BAS 409 F LAB 242 009	methyl (*E*)-methoxyimino[α-(*o*-tolyloxy)-*o*-tolyl]acetate 
490M1 BF 490-1	(E)-methoxyimino[α-(*o*-tolyloxy)-*o*-tolyl]acetic acid 
490M2 BF 490-2	α-[(*o*-hydroxymethyl)phenoxy]-*o*-tolyl(methoxyimino)acetic acid 
490M9 BF 490-9	α-(*p*-hydroxy-*o*-tolyloxy)-*o*-tolyl(methoxyimino)acetic acid 

METABOLISM AND ENVIRONMENTAL FATE

Plant metabolism

Sugar beet In German studies carried out in 1998-1999, [*phenyl*-^{14}C]kresoxim-methyl, in a 50% water dispersible granular formulation, was applied twice as a foliar spray to sugar beet (Victoria variety), at 150 g ai/ha (Veit, 1999). The first application took place 91 days after sowing (11/08/1998), corresponding to a growth stage of 39 (BBCH code), and the second 3 weeks later or 28 days before harvest (01/09/1998).

Samples were taken before and after the second treatment and at harvest, and stored in a freezer

at –18ºC until extraction. An aliquot of a methanol extract of the leaves was stored in a freezer at –18ºC for 212 days to establish the stability of the residues during frozen storage.

High total radioactive residues (TRR) were found in the leaves (1.26 mg/kg as kresoxim-methyl equivalents at harvest and 1.43 mg/kg on the day of the last treatment as the sum of ^{14}C in methanol and water extracts and unextracted residue). The low TRR in the roots (0.009 mg/kg at harvest and 0.024 mg/kg on the day of the last treatment) indicated that only a small amount of the applied radioactivity was translocated from the leaves to the roots (Table 1).

Table 1. Total radioactive residues in sugar beet after [^{14}C]kresoxim-methyl treatment (2 x 150 kg ai/ha).

Sample, days after 2nd treatment	TRR determined by direct combustion, mg/kg	TRR calculated[1], mg/kg
Roots before 2nd treatment	0.007	0.007
Roots, 0 [2]	0.053	0.024
Leaves before 2nd treatment	0.610	0.543
Leaves, 0	1.846	1.434
Roots, 28	0.008	0.009
Leaves, 28	1.735	1.255

[1] Sum of the extracts (methanol and water) and the post-extraction residue (PES).
[2] Roots after 2nd treatment were harvested with the green part of the crop.

To determine the nature of the residue, methanol extraction was followed by two extractions with water and the determination of radioactivity by LSC. The radioactive residues in leaves were extracted by methanol and water at rates between 91.1% and 98.9% of the TRR. In root samples, where the levels of the TRR were much lower, the extractability was also lower and ranged from 63.3% to 93.2% (Table 2).

Table 2. Extractability of radioactivity in sugar beet after [^{14}C]kresoxim-methyl treatment (2 x 150 g ai/ha).

Sample, days after 2nd treatment	^{14}C, mg/kg as kresoxim-methyl and % of TRR								
	TRR[1]	methanol		H_2O		ERR[2]		PES[3]	
		mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
Roots before 2nd treatment	0.007	0.004	65.7	0.001	10.1	0.005	75.8	0.002	24.2
Roots, 0	0.024	0.022	91.4	<0.001	1.5	0.022	93.2	0.002	6.8
Leaves before 2nd treatment	0.543	0.526	96.7	0.005	1.0	0.531	97.7	0.012	2.3
Leaves, 0	1.434	1.409	98.3	0.008	0.6	1.417	98.9	0.017	1.2
Roots, 28	0.009	0.005	60.8	<0.001	2.5	0.005	63.3	0.003	36.6
Leaves, 28	1.255	1.110	88.5	0.033	2.6	1.143	91.1	0.112	8.9

[1] Calculated; see Table 1
[2] Extractable radioactive residues: sum of methanol and water extracts
[3] Post-extraction solids

The radioactivity in the methanol extracts of roots and leaves was characterized by solvent partition. Most of the radioactivity in the extract of leaves was found in the ethyl acetate phase (94.2% of the TRR on the day of the last treatment and 69.1% 28 days after the last treatment). The radioactivity in the methanol extract of roots taken 28 days after the second application was about equally divided between the ethyl acetate and water phases (Table 3).

Table 3. Partition characteristics of methanol-extracted radioactivity in sugar beet after [^{14}C]kresoxim-methyl treatment (2 x 150 g ai/ha).

Sample, days after last treatment	methanol mg/kg[1]	% recovery[2]	Ethyl acetate		Water	
			mg/kg[1]	% of TRR	mg/kg[1]	% of TRR
Roots, 0	0.022	90.9	0.017	68.4	0.003	10.9
Leaves, 0	1.409	105.0	1.351	94.2	0.129	9.0
Roots, 28	0.005	120.0	0.003	29.7	0.003	37.0
Leaves, 28	1.110	111.1	0.867	69.1	0.366	29.2

[1] As kresoxim-methyl
[2] 100 (mg/kg in ethyl acetate + mg/kg in water) ÷ (mg/kg in methanol)

Characterization and identification of radioactive residues in the extracts by HPLC indicated that the unchanged parent compound was the predominant residue in leaves and roots taken 28 days after the last application. A small amount of BF 490-1 (free acid metabolite) was detected in the water extracts and some water phases after solvent partition. In some cases an additional small peak was present in leaves corresponding to the sugar conjugate of BF 490-2. The extraction of the residual radioactive residues with aqueous ammonia released only a part of them.

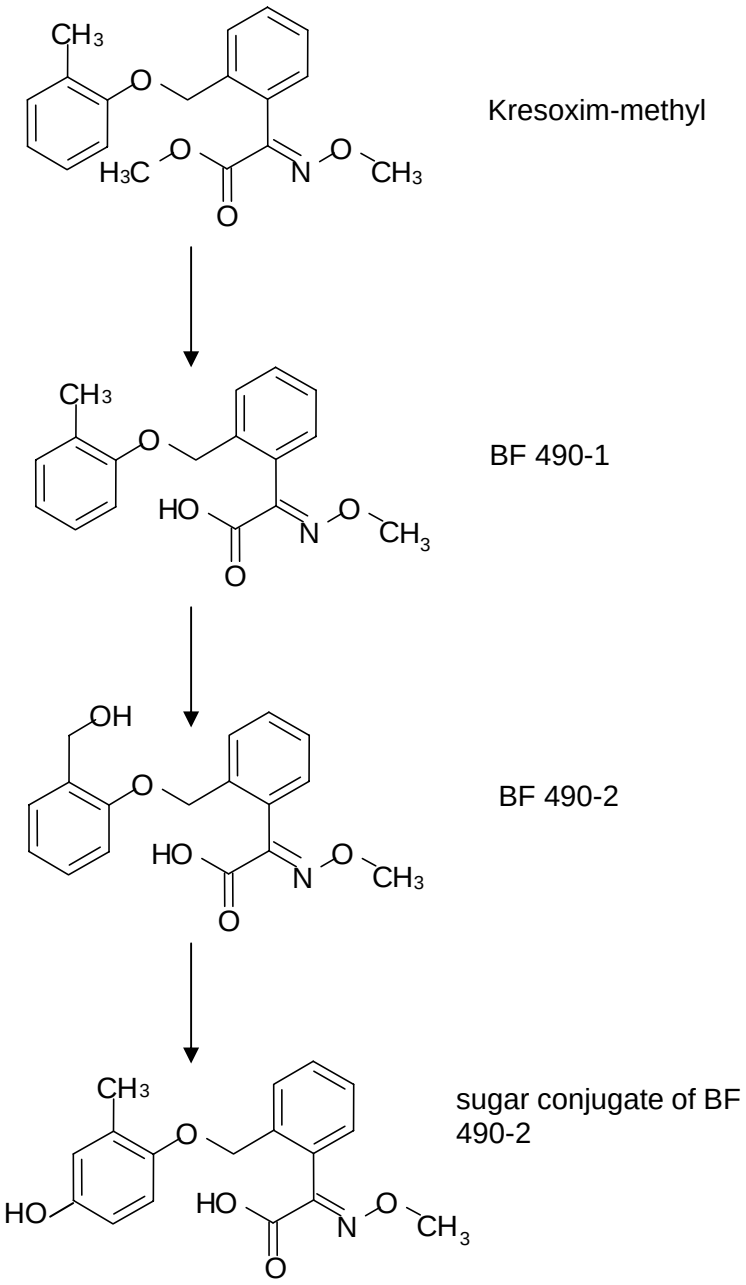
Table 4. Characterization of residues in the extracts of sugar beet leaves by HPLC.

Sample, Days after the last treatment	Compound or fraction	% of TRR	Concentration mg/kg
Leaves, 0	Kresoxim-methyl BF 490-1	98.3 0.6	1.409 0.008
	Total identified	98.9	1.417
	Unidentified radioactive residue	1.2	0.017
	Total	100.1	1.434
Leaves, 28	Kresoxim-methyl BF 490-1	88.5 2.6	1.110 0.033
	Total identified	91.1	1.143
	NH_4OH extract Final residue	2.3 2.0	0.029 0.026
	Total	95.4	1.198

In the storage stability study with the methanol extract of the leaves mentioned earlier the radiochromatogram of the stored extract of leaves sampled 28 days after the last application was similar to that of the extract before storage, indicating that the radioactive residues in the extract were stable in a freezer for approximately 7.5 months.

The metabolic pathway of kresoxim-methyl in sugar beet is shown in Figure 2. Besides the parent compound only two metabolites could be detected, the free acid and the sugar conjugate of BF 490-2. These results were similar to the results of the other metabolism studies on apples and wheat (FAO/WHO, 1999) in which the parent compound was also the dominant radioactive residue and the same metabolites, BF 490-1 and the sugar conjugate of BF 490-2, were found.

Figure 2. The metabolic pathway of kresoxim-methyl in sugar beet.



USE PATTERN

Information on use patterns was received from Germany and Japan. The manufacturer provided information on new uses on citrus fruits and olives together with the relevant labels. The registered uses are summarized in Tables 5-8.

Table 5. Registered uses of kresoxim-methyl on fruit (field applications unless otherwise stated).

Commodity	Country	Form	Application			Max. no.	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
Apple	Japan	WG	0.016			3	1	Fruit spot Scab Powdery mildew Blossom blight
	Japan	WG	0.016-0.024			3	1	Anthracnose Ring rot Fly speck Sooty blotch Blotch
	Japan	WG	0.016-0.031			3	1	Alternaria blotch Rust
Citrus fruits	Japan	WG	0.016-0.024			3	14	Scab Melanose Grey mould Freckle
	Japan	WG	0.024			3	14	Brown spot
	South Africa	WG	0.01 + 0.5 l narrow range mineral oil			2	56	Guignardia citricarpa Apply only in combination with mineral oil as indicated. Apply as a medium- or full cover spray during mid November and follow up in mid January. Not to be sprayed on lemons.
Grapes	Germany	WG	0.0075	400-1600	0.03-0.12	3	35	Unicinula necator Wine grapes
	Japan	WG	0.016			3	14	Powdery mildew Rust
	Japan	WG	0.016-0.024			3	14	Anthracnose (Elisinoe ampelina) Downy mildew Swelling arm Ripe rot Gray mould Isariopsis leaf spot
Kiwifruit	Japan	WG	0.016-0.024			3	1	Gray mould
Olive	Spain	WG	0.005-0.01	1000		See note	30	Phomopsis helianthi Number of applications: 1 for oil olives when fruits are present (growth stage 85 BBCH), and 2 between harvest and flowering (growth stage 59 BBCH) (fresh green olives and oil olives)
Peach	Japan	WG	0.024			3	1	Scab Powdery mildew Brown rot Black spot
Pear, Oriental	Japan	WG	0.016			3	1	Scab
	Japan	WG	0.016-0.024			3	1	Physalospora canker Black spot Powdery mildew
Persimmon (Kaki)	Japan	WG	0.016			3	14	Powdery mildew Leaf spot Anthracnose Gray mould
Plum (*Prunus mume*)	Japan	WG	0.016-0.024			3	7	Scab
	Japan	WG	0.024			3	7	Powdery mildew

Commodity	Country	Form	Application			Max. no.	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
								Gray mould Shooty blotch
Pome fruits	Germany	WG	0.006	500 l/ha & m height of tree crown	0.0313 and m height of tree crown	4	35	Scab Powdery mildew Application rate for standard tree of 3 m height equivalent to 0.0938 kg ai/ha and 1500 l water/ha. Atomizing spraying: reduction of water up to fivefold
Strawberry	Germany	WG	0.0078	2000	0.155	3: 3	F	Powdery mildew Before flowering and post harvest
	Japan	SC	0.008-0.014			3	1	Powdery mildew

Table 6. Registered uses of kresoxim-methyl on vegetables.

Commodity	Country	Form	For B	Application			Max. no	PHI, days	Pest or disease, notes
				Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
Carrot	Japan	SC	B	0.014			3	7	Cecospora leaf spot
	Japan	SC	B	0.014-0.021			3	7	Leaf blight
Chinese cabbage	Japan	SC	B	0.014			3	3	Alternaria leaf spot White spot Downy mildew
Cucumber	Japan	SC	B	0.014			3	1	Powdery mildew Downy mildew Corynesporaa leaf spot
Egg plant	Japan	SC	B	0.014			3	1	Powdery mildew Leaf mould
Garlic	Japan	SC	B	0.021			3	7	Rust
Melon	Japan	SC	B	0.014-0.021			3	1	Downy mildew Powdery mildew Gummy stem blight
Onion, Welsh	Japan	SC	B	0.021			3	7	Rust Alternaria leaf spot
Pepper, Sweet	Japan	SC	B	0.014			3	7	Powdery mildew
Pumpkin	Japan	SC	B	0.014			3	1	Powdery mildew
Sugar and fodder beets	Germany	SC	F	0.031-0.042	300-400	0.125	1	28	Powdery mildew Cercospora beticola, Rust In all not more than 1 treatment/year for this crop
Sugar beet	Japan	SC	B	0.014-0.021			3	21	Cercospora leaf spot
	Japan	SC	B	0.014			3	21	Leaf spot
Watermelon	Japan	SC	B	0.014-0.021			3	1	Anthracnose Gummy stem blight
	Japan	SC	B	0.021			3	1	Powdery mildew
Yam	Japan	SC	B	0.021			3	7	Cylindrosporium dioscoreae

F: field; B: both field and glasshouse.

Table 7. Registered uses of kresoxim-methyl on cereals (field applications).

Commodity	Country	Form	Application			Max. no.	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
Barley	Germany	SE	0.03	400	0.125	2	35	Powdery mildew Puccinia hordei Rhynchosporium secalis Net blotch
	Germany	SE	0.026-0.053	200-400	0.105	2	35	Powdery mildew

Commodity	Country	Form	Application			Max. no.	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
	Germany	SC	0.03-0.06	200-400	0.125	2	35	Powdery mildew Puccinia hordei Rhynchosporium secalis Net blotch
	Japan	SC	0.014-0.021			3	14	Erysiphe graminis Fusarium nivale Fusarium roseum
Rye	Germany	SC	0.03-0.06	200-400	0.125	2	35	Powdery mildew Brown rust Rhynchosporium secalis
	Germany	SE	0.03	400	0.125	2	35	Powdery mildew Brown rust Rhynchosporium secalis
	Germany	SE	0.026-0.053	200-400	0.105	2	35	Powdery mildew
Triticale	Germany	SE	0.03	400	0.125	1	35	Septoria nodorum
	Germany	SC	0.03-0.06	200-400	0.125	1	35	Septoria nodorum
Wheat	Germany	SE	0.03	400	0.125	1	35	Cereal eyespot Fusarium spp.
	Germany	SE	0.03	400	0.125	2	35	Powdery mildew Brown rust Yellow rust Drechslera tritici-repentis Septoria tritici Septoria nodorum
	Germany	SE	0.026-0.053	200-400	0.105	2	35	Powdery mildew
	Germany	SC	0.03-0.06	200-400	0.125	2	35	Powdery mildew Brown rust Yellow rust Drechslera tritici-repentis Septoria tritici Septoria nodorum
	Japan	SC	0.014-0.021			3	14	Erysiphe graminis Fusarium nivale Fusarium roseum

Table 8. Registered uses of kresoxim-methyl on tea (field applications).

Commodity	Country	Form	Application			Max. no.	PHI, days	Pest or disease, notes
			Spray conc., kg ai/hl	Water vol., l/ha	kg ai/ha			
Tea	Japan	SC	0.014			3	10	Pestalotia longiseta
	Japan	SC	0.014-0.021			3	10	Anthracnose Gray blight
	Japan	SC	0.021			3	10	Blister blight

RESIDUES RESULTING FROM SUPERVISED TRIALS

Trials were carried out under field conditions. They were reported in sufficient detail and acceptable analytical information was supplied. The residues were of parent kresoxim-methyl. In selecting residues for the estimation of maximum residue levels and STMRs the trials according to maximum GAP (i.e. minimum PHI, maximum dose rate and maximum number of treatments) have been used. The residues from these are double-underlined.

The residue trials were on citrus fruits, olives and sunflowers. The results are shown in Tables 9-11.

Table 9. Supervised residue trials on citrus fruits.

Location Variety	Date of last treatment	Form.	Application				Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.				
Nelspruit, South Africa Valencia	22/01/96	WG 500 g/kg		3000 (11.3 l/tree)	0.01	2	Pulp	<0.01	0	#97/11299
								<0.01	7	
								<0.01	14	
								<0.01	28	
								≤0.01	56	
								<0.01	116	
							Peel	0.80	0	
								0.72	7	
								0.51	14	
								0.40	28	
								0.21	56	
								0.29	112	
							Whole fruit	0.27	0	
								0.28	7	
								0.19	14	
								0.13	28	
								0.07	56	
								0.06	112	
	22/01/96	WG 500 g/kg		3000 (11.3/tree)	0.02	2	Pulp	0.03	0	
								0.03	7	
								0.02	14	
								<0.01	28	
								<0.01	56	
								<0.01	112	
							Peel	2.2	0	
								2.1	7	
								1.7	14	
								1.1	28	
								0.85	56	
								0.93	112	
							Whole fruit	0.82	0	
								0.68	7	
								0.55	14	
								0.34	28	
								0.26	56	
								0.23	112	
	22/01/96	WG 500 g/kg		3000 (11.3/tree)	0.02 +0.5 l mineral oil/hl	2	Pulp	0.03	0	
								0.02	7	
								0.01	14	
								<0.01	28	
								<0.01	56	
								<0.01	112	
							Peel	3.0	0	
								3.1	7	
								2.1	14	
								1.8	28	

Location Variety	Date of last treatment	Form.	Application				Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.				
								1.1	56	
								1.1	112	
							Whole fruit	1.1	0	
								1.1	7	
								0.80	14	
								0.57	28	
								0.32	56	
								0.30	112	
Nelspruit, South Africa Valencia	22/01/96	WG 500 g/kg		3000 (11.3/tree)	0.01	3	Pulp	<0.01	0	#97/11323
								<0.01	7	
								<0.01	14	
								<0.01	28	
								<0.01	56	
							Peel	0.61	0	
								0.75	7	
								0.71	14	
								0.49	28	
								0.28	56	
							Whole fruit	0.22	0	
								0.25	7	
								0.24	14	
								0.15	28	
								0.09	56	
	22/01/96	WG 500 g/kg		3000 (11.3/tree)	0.02	3	Pulp	0.03	0	
								0.01	7	
								0.01	14	
								<0.01	28	
								<0.01	56	
							Peel	2.5	0	
								2.3	7	
								2.1	14	
								1.3	28	
								1.2	56	
							Whole fruit	0.88	0	
								0.77	7	
								0.67	14	
								0.42	28	
								0.33	56	
	22/01/96	WG 500 g/kg		3000 (11.3/tree)	0.02 +0.5 l mineral oil/hl	3	Pulp	0.09	0	
								0.05	7	
								0.06	14	
								0.03	28	
								0.03	56	
							Peel	5.0	0	
								5.0	7	
								4.3	14	
								2.5	28	

Location Variety	Date of last treatment	Form.	Application				Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.				
								2.4	56	
							Whole fruit	1.9	0	
								1.8	7	
								1.6	14	
								0.77	28	
								0.64	56	
Malelane, South Africa Valencia	22/01/98	WG 500 g/kg		8000	0.01	2	Pulp	0.10	0	#99/10181
								<0.01	84	
							Peel	1.8	0	
								0.43	84	
							Whole fruit	0.69	0	
								0.21	84	
	22/01/98	WG 500 g/kg		8000	0.02	2	Pulp	0.24	0	
								0.02	84	
							Peel	3.1	0	
								0.73	84	
							Whole fruit	1.4	0	
								0.35	84	
	19/11/97	WG 500 g/kg		8000	0.01	1	Fresh	0.28	0	
								0.05	28	
								0.04	56	
								0.01	105	
							Peel	3.6	0	
								0.71	28	
								0.43	56	
								0.32	105	
							Whole fruit	2.2	0	
								0.39	28	
								0.21	56	
								0.15	105	
	19/11/97	WG 500 g/kg		8000	0.02	1	Fresh	0.76	0	
								0.04	28	
								0.04	56	
								<0.01	105	
							Peel	3.6	0	
								0.91	28	
								0.59	56	
								0.38	105	
							Whole fruit	2.0	0	
								0.43	28	
								0.26	56	
								0.14	105	
	22/01/98	WG 500 g/kg		8000	0.01	1	Pulp	0.12	0	
								<0.01 a	27	
								≤0.01 a	48	
								<0.01 a	90	

Location Variety	Date of last treatment	Form.	Application				Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.				
							Peel	1.6	0	
								<0.01 a	27	
								<0.01 a	48	
								<0.01 a	90	
							Whole fruit	0.74	0	
								<0.01 a	27	
								≤0.01 a	48	
								<0.01 a	90	
	22/01/98	WG 500 g/kg		8000	0.02	1	Pulp	0.17	0	
								<0.01 a	27	
								<0.01 a	48	
								<0.01 a	90	
							Peel	2.6	0	
								<0.01 a	27	
								<0.01 a	48	
								<0.01 a	90	
							Whole fruit	1.1	0	
								<0.01 a	27	
								<0.01 a	48	
								<0.01 a	90	
A van der Westhuizen, South Africa Valencia	20/01/98	WG 500 g/kg		2000 (5 l/tree)	0.01	2	Pulp	≤0.01	54	#98/11401
								<0.01	85	
							Peel	0.64	54	
								0.62	85	
							Whole fruit	0.57 b	0	
								0.26 b	28	
								0.19	54	
								0.16	85	
	17/11/97	WG 500 g/kg		2000 (5 l/tree)	0.01	1	Pulp	<0.01	118	
							Peel	0.29	118	
							Whole fruit	0.41 b	24	
								0.22 b	64	
								0.07 b	92	
								0.11	118	
	20/01/97	WG 500 g/kg		2000 (5 l/tree)	0.01	1	Pulp	≤0.01	54	
							Peel	0.45	54	
							Whole fruit	0.58 b	0	
								0.14 b	28	
								0.13	54	
	17/11/97	WG 500 g/kg		2000 (5 l/tree)	0.02	1	Fresh	<0.01	92	
								<0.01	118	
							Peel	0.44	92	
								0.55	118	
							Whole fruit	0.85 b	24	

Location Variety	Date of last treatment	Form.	Application				Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.				
								0.28 b	64	
								0.17	92	
								0.20	118	
	20/01/98	WG 500 g/kg		2000 (5 l/tree)	0.02	1	Pulp	<0.01	54	
							Peel	1.0	54	
							Whole fruit	1.2 b	0	
								0.59 b	28	
								0.34	54	
A van der Westhuizen, Letsitele, South Africa Marsh	20/01/98	WG 500 g/kg		2000 (5/tree)	0.01	2	Pulp	0.01	0	#98/11303
								≤0.01	14	
							Peel	1.1	0	
								0.60	14	
								0.67	28	
								0.52	44	
								0.42	63	
							Whole fruit	0.45	0	
								0.23	14	
								0.22	28	
								0.18	44	
								0.14	63	
	17/11/97	WG 500 g/kg		2000 (5/tree)	0.01	1	Pulp	<0.01	64	
							Peel	0.27	64	
								0.27	78	
								0.26	82	
								0.16	108	
								0.21	128	
							Whole fruit	0.11	64	
								0.10	78	
								0.09	82	
								0.06	108	
								0.07	128	
	20/1/98	WG 500 g/kg		2000 (5/tree)	0.01	1	Pulp	0.05	0	
								≤0.01	14	
							Peel	0.61	0	
								0.21	14	
								0.17	28	
								0.18	44	
								0.20	63	
							Whole fruit	0.30	0	
								0.08	14	
								0.06	28	
								0.06	44	
								0.06	63	
	17/11/97	WG 500 g/kg		2000 (5/tree)	0.02	1	Pulp	<0.01	64	

Location Variety	Date of last treatment	Form.	Application				Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.				
								<0.01	78	
								<0.01	92	
								<0.01	108	
								<0.01	128	
							Peel	0.38	64	
								0.39	78	
								0.34	92	
								0.41	108	
								0.31	128	
							Whole fruit	0.16	64	
								0.15	78	
								0.11	92	
								0.12	108	
								0.09	128	
	20/01/98	WG 500 g/kg		2000 (5/tree)	0.02	1	Pulp	0.11	0	
								0.04	14	
								0.03	28	
								<0.01	44	
								<0.01	63	
							Peel	1.5	0	
								1.6	14	
								0.89	28	
								0.58	44	
								0.67	63	
							Whole fruit	0.59	0	
								0.60	14	
								0.34	28	
								0.17	44	
								0.18	63	

[1] Re-analysed to confirm results.
[2] No data available for the pulp and peel.
The residue contents of the peel and pulp were determined separately and the content in the whole fruit calculated.

Table 10. Supervised residue trials on olives.

Location	Date of last treatment	Form.	Applications				Growth stage at last treatment[1]	Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.					
Andalusia, Spain Picual	03/11/98	WG 500 g/kg	0.10	1000	0.01	1	79-85	Fruit	≤0.05	29	#99/10705
								Pomace	<0.05	29	
								Crude oil	0.17	29	
								Waste water	<0.05		
	03/11/98	WG 500 g/kg	0.096	960	0.01	1	79-85	Fruit	≤0.05	29	
								Pomace	<0.05	29	
								Crude oil	0.12	29	
								Waste water	<0.05		
Andalusia, Spain Martena	03/11/98	WG 500 g/kg	0.10	1000	0.01	1	79-85	Fruit	≤0.05	30	
								Pomace	0.05	30	

Location	Date of last treatment	Form.	Applications				Growth stage at last treatment[1]	Sample	Residues mg/kg	PHI, days	Report no.
			kg ai/ha	Water l/ha	kg ai/hl	No.					
								Crude oil	0.13	30	
								Waste water	<0.05		
Andalusia, Spain Hoj. blanca	03/11/98	WG 500 g/kg	0.099	990	0.01	1	79-85	Fruit	0.11	30	
								Pomace	0.12	30	
								Crude oil	0.49	30	
								Waste water	<0.05	30	
Spain	97	WG 500 g/kg	0.10	1000	0.01	1		Fruit	0.23	0	#99/10706
									0.11	15	
									0.09	30	
									<0.05	43	
								Pomace	0.07	30	
								Crude oil	0.28	30	
								Waste water	<0.05	30	
	97	WG 500 g/kg	0.10	1000	0.01	1		Fruit	0.12	0	
									0.05	15	
									≤0.05	30	
									<0.05	43	
								Pomace	<0.05	30	
								Crude oil	0.20	30	
								Waste water	<0.05	30	
	97	WG 500 g/kg	0.10	1000	0.01	1		Fruit	0.09	0	
									<0.05	15	
									≤0.05	30	
									<0.05	43	
								Pomace	<0.05	30	
								Crude oil	0.23	30	
								Waste water	<0.05	30	
	97	WG 500 g/kg	0.10	1000	0.01	1		Fruit	0.13	0	
									0.09	15	
									≤0.05	30	
									<0.05	43	
								Pomace	0.06	30	
								Crude oil	0.24	30	
								Waste water	<0.05	30	

[1] Growth stage according to BBCH codes for olives

Table 11. Supervised residue trials on sunflowers.

Location	Date of last treatment	Form.	Applications				Growth stage at last treatment[1]	Sample	Residues mg/kg	PHI, days	Report No
			kg ai/ha	Water l/ha	kg ai/hl	No.					
Cote D'Or, France Albena	05/06/96	SE 150 g/l [2]	0.11	320		1	51	Plant without roots	2.96	0	#98/10582
								Seed	<0.05	63	
									<0.05	91	
Cote D'Or, France Albena	05/06/96	SE 150 g/l [2]	0.11	320		1	51	Plant without roots	5.67	0	

Location	Date of last treatment	Form.	Applications				Growth stage at last treatment[1]	Sample	Residues mg/kg	PHI, days	Report No
			kg ai/ha	Water l/ha	kg ai/hl	No.					
								Seed	<0.05	69	
									<0.05	92	
Haute Garonne, France Select	11/06/96	SE 150 g/l [2]	0.10	284		1	51	Plant without roots	4.42	0	
								Seed	<0.05	69	
									<0.05	88	
Haute Garonne, France Apisol	12/06/96	SE 150 g/l [2]	0.099	280		1	51	Plant without roots	4.23	0	
								Seed	0.07	79	
									<0.05	90	
Gard, France DK 37-90	11/06/97	SE 150 g/l [2]	0.11	310		1	51-53	Plant without roots	4.11	0	#98/10583
								Seed	<0.05	72	
									<0.05	82	
Cote D'Or, France Rigasol	10/6/97	SE 150 g/l [2]	0.11	324		1	53	Plant without roots	5.20	0	
								Seed	<0.05	71	
									<0.05	78	
Haute Garonne, France Andora	04/06/97	SE 150 g/l [2]	0.095	272		1	51	Plant without roots	3.32	0	
								Seed	<0.05	69	
									<0.05	82	
Haute Garonne, France Fantasol	11/06/97	SE 150 g/l [2]	0.11	304		1	51-53	Plant without roots	4.11	0	
								Seed	<0.05	68	
									<0.05	86	

[1] Growth stage according to BBCH codes for sunflowers
[2] with 300 g fenpropimorph /l

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

No information on processing of citrus fruits was available for the Meeting.

Residues in processed products of olives, crude oil and pomace, prepared according to the process shown in Figure 3, were determined in each residue trial on olives reported in Table 10. The figures are repeated, together with processing factors, in Table 12.

Figure 3. Extraction of oil from olives, industrial process. [1]

CSIC process

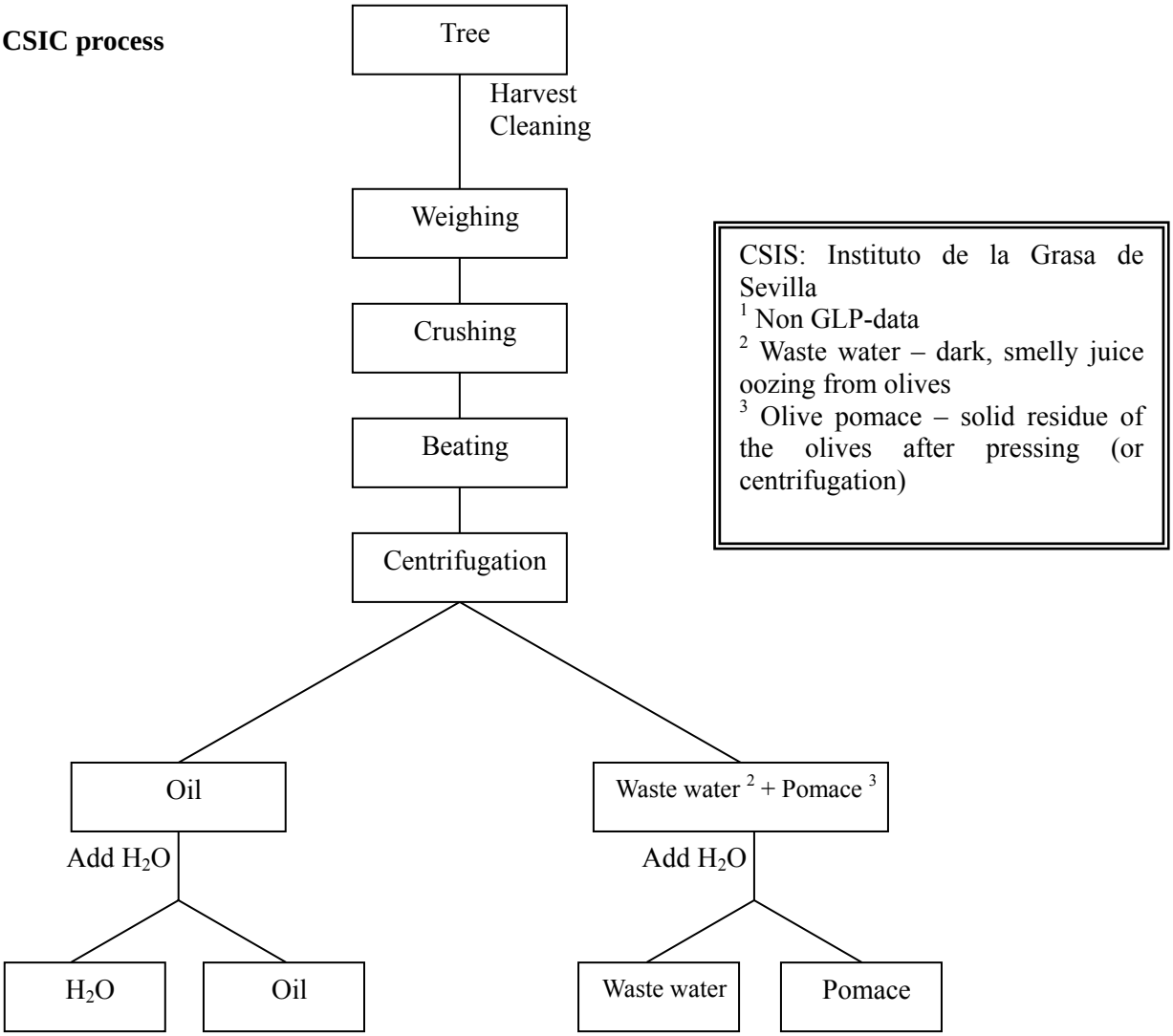


Table 12. Residues of kresoxim-methyl in processed products of olives.

Kresoxim-methyl, mg/kg, and (calculated processing factor)		
Fresh olive	Pomace	Crude oil
<0.05	<0.05	0.17 (>3.4)
<0.05	<0.05	0.12 (>2.4)
<0.05	0.05 (>1.0)	0.13 (>2.6)
0.11	0.12 (1.1)	0.49 (4.5)
0.09	0.07 (0.78)	0.28 (3.1)
<0.05	<0.05	0.20 (>4.0)
<0.05	<0.05	0.23 (>4.6)
<0.05	0.06 (>1.2)	0.24 (>4.8)
Mean factor (2 results)	0.94	3.8

Residues in the edible portion of food commodities

Apart from the processing studies on olives residues in the pulp of oranges and grapefruit are reported in Table 9.

NATIONAL MAXIMUM RESIDUE LIMITS

The national MRLs for citrus fruits, olive and sunflower seed and related products were reported (BASF, 2001).

Country	MRL, mg/kg, and commodity
European Union	0.05 citrus fruits 0.1 oilseeds 0.2 olives
France	0.20 sunflower seed oil (proposed)
Japan	2 mandarin, 10 citrus fruits other than mandarin
South Africa	0.5 citrus fruits
Spain	0.5 olive oil (proposed), 0.2 (grown for oil generation)(proposed), 0.05 olive (fresh green)

The definition of the residues in these commodities is kresoxim-methyl for all the MRLs listed.

APPRAISAL

Kresoxim-methyl was first evaluated for toxicology and residues by the Meeting in 1998. The 1998 Meeting allocated an ADI of 0–0.4 mg/kg bw and concluded that an acute RfD was unnecessary. The Meeting recommended that the definition of the residue both for compliance with MRLs and estimation of dietary intake be: 'commodities of plant origin, kresoxim-methyl; and commodities of animal origin, α-(*p*-hydroxy-*o*-tolyloxy)-*o*-tolyl(methoxyimino)acetic acid, expressed as kresoxim-methyl'. It estimated MRLs for pome fruits, barley, cucumber, grapes, dried grapes, rye, straw and fodder (dry) of cereal grains, wheat, edible offal (mammalian), mammalian fats (except milk fats), meat (from mammals other than marine mammals), milks and poultry meat. The IEDIs were 0% of the ADI for all of five GEMS/Food regional diets. The 1998 JMPR agreed that information was desirable on whether (E)-methoxyimino[α-*o*-tolyloxy)-*o*-tolyl]acetic acid was esterified to kresoxim-methyl when methanol was used for extraction in studies of metabolism and the analysis of samples from supervised trials.

New information on registered uses, the results of supervised residue trials and processing studies on citrus fruits, olive and sunflower and from a study of metabolism in sugar beet was made available by the manufacturer to the Meeting. Information on current GAP was received from Germany and Japan.

Metabolism

Plants

Sugar beet was sprayed with [phenyl-^{14}C]kresoxim-methyl at 0.15 kg ai/ha twice, the first time 91 days after sowing and the second 3 weeks later or 28 days before harvest. Most of the TRR was found in leaves at both 0 day (1.8 mg/kg determined by direct combustion and 1.4 mg/kg calculated as the sum of the methanol and water extracts and the residual residues) and 28 days after the second treatment (1.7 mg/kg by direct combustion and 1.2 mg/kg calculated). Only minor TRR were found in roots 0 day (0.053 mg/kg by combustion and 0.024 mg/kg calculated) and 28 days after the second application (0.008 mg/kg by combustion and 0.009 mg/kg calculated). These results indicate that only a small amount of the applied kresoxim-methyl was translocated from leaves to roots. Extraction with methanol and subsequently with water (twice) extracted most of radiolabelled residues (91.1–98.9% of the TRR in leaves and 63.3–93.3% in roots). The predominant component of the extracted residues was identified as the parent compound by HPLC. A small amount of a free acid metabolite, (E)-methoxyimino[α-(*o*-tolyloxy)-*o*-tolyl]acetic acid (BF 490-1), was detected in water extracts and some water phases after solvent partition, and an additional small peak corresponding to the sugar conjugate of α-[(*o*-hydroxymethyl)phenoxy]-*o*-tolyl(methoxyimino)acetic acid (BF 490-2) was found in some ases. The result of a study of stability in storage showed that the radiolabelled residues in the

methanol extract of sugar beet leaves were stable at –18ºC for approximately 7.5 months. These results confirm the definition of the residue in commodities of plant origin recommended by the 1998 JMPR and agree with the results of the studies of metabolism in apple and wheat, which also demonstrated that the parent compound kresoxim-methyl was the dominant radiolabelled residue, with minor amounts of BF 490-1 and the sugar conjugate of BF 490-2 in various matrices of these crops. The question of whether BF 490-1 is esterified to kresoxim-methyl during methanol extraction remained unanswered.

Results of supervised trials

GAP for citrus fruits was reported for Japan and South Africa. Fifteen trials on Valencia orange and five trials on Marsh grapefruit were conducted in South Africa. The label in South Africa states that the water-dispersible granule formulation should be applied only with 0.5 l of narrow-range mineral oil per hl of spray solution. Trials conducted with and without mineral oil (0.02 kg ai/hl) showed a similar percentage decline in residue concentration. Therefore, the Meeting concluded that seven trials on Valencia orange and three trials on Marsh grapefruit conducted in accordance with South African GAP (maximum of two applications at 0.01 kg ai/hl; PHI, 56 days) but without mineral oil could be considered for estimating the maximum residue level.

Kresoxim-methyl persisted in whole fruit after the PHI of 56 days. As in most cases the concentration of residues 56–84 days after the last application was < 30%, the concentration of 0.21 mg/kg (in Malelane, 0.01 kg ai/hl, 8000 l, 84 days after last application) was taken into consideration for estimating the MRL and STMR value. The concentrations in whole fruit were < 0.01, 0.07, 0.09, 0.13, 0.19, 0.21 (2) and 0.22 mg/kg for orange and 0.06, 0.11 and 0.18 mg/kg for grapefruit. These values are within the same range. The combined values, in ranked order (median underlined), were: < 0.01, 0.06, 0.07, 0.09, 0.11, 0.13, 0.18, 0.19, 0.21 (2) and 0.22 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg for oranges and grapefruit. The concentrations of residues in the edible portion (flesh) resulting from use at the maximum GAP and comparable conditions were: ≤ 0.01 (7) and 0.04 mg/kg. The Meeting estimated an STMR value of 0.01 mg/kg for the edible portion (flesh or pulp) of oranges and grapefruit.

GAP for olives was reported for Spain. Eight trials were conducted, four of which were on oil olives. These trials could be considered to comply with the Spanish GAP for oil olives (maximum of one application after flowering; 0.005–0.01 kg ai/ha; 1000 l/ha; PHI, 30 days). The concentrations of residues in fruit, in ranked order, were: ≤ 0.05 (7) and 0.09 mg/kg. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR value of 0.05 mg/kg for olives.

The results of eight trials on sunflower conducted in France, which were considered to comply with proposed French GAP (maximum of one application; 0.1 kg ai/ha; PHI, 60 days), and of a processing study became available to the Meeting. However, as the Committee was informed that there was no GAP for sunflower at the time of the review, the Meeting did not take action.

Fate of residues during processing

No information was available on the processing of citrus fruits to juice, pomace and citrus pulp, dry. As the concentration of residues of kresoxim-methyl in the flesh of oranges and grapefruits is usually < 0.01 mg/kg, the Meeting considered it unlikely that the concentrations in orange or grapefruit juice would significantly increase the dietary intake of kresoxim-methyl.

Olives were processed into oil and pomace in Spain according to the "Laboratories and Pilot Installations of the Experimental Oil Mill (Laboratorios e Instalaciones Piloto de la Almazara Experimental)", reflecting commercial practice. The concentrations of residues of kresoxim-methyl in crude oil and pomace were determined and reported in each trial. The concentrations in pomace were similar to those in fruit, while those in crude oil were about four times those in fruit (< 0.05–0.11 mg/kg in fruit, 0.12–0.49 mg/kg in crude oil).

The concentrations of residues in olive pomace and in crude oil in trials conducted according to GAP were ≤ 0.05 (4), 0.05, 0.06, 0.07 and 0.12 mg/kg and 0.12, 0.13, 0.17, 0.20, 0.23, 0.24, 0.28 and 0.49 mg/kg, respectively. The Meeting estimated a maximum residue level of 0.7 mg/kg and an STMR value of 0.22 mg/kg for olive oil, virgin. Since olive pomace is not generally regarded as a feedstuff, no maximum residue level was estimated.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the concentrations of residues listed below were suitable for establishing maximum residue limits and for assessing the IEDI.

Definition of residue (for compliance with MRL and for estimating dietary intake from plant commodities): kresoxim-methyl

Definition of residue (for compliance with MRLs and for estimating dietary intake from animal commodities): α-(p-hydroxy-o-tolyloxy)-o-tolyl(methoxyimino)acetic acid, expressed as kresoxim-methyl

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)
CCN	Name	New	Previous	
FC 0203	Grapefruit	0.5	-	
	Edible portion of grapefruit			0.01
FT 0305	Olives	0.2	-	0.05
OC 0305	Olive oil, virgin	0.7	-	0.22
FC 0004	Oranges, Sweet, Sour	0.5	-	
	Edible portion of oranges			0.01

Further work or information

Desirable

- Experimental determination of whether (E)-methoxyimino[α-(*o*-tolyloxy)-*o*-tolyl]acetic acid is methylated to kresoxim-methyl when methanol is used as an extractant in studies of metabolism or analysis of samples from supervised trials (1998 JMPR)

Dietary risk assessment

Long-term intake

STMR values have been estimated for three commodities, and concentrations of residues in the edible portion of oranges and grapefruit have been estimated. IEDIs were calculated for the five GEMS/Food regional diets from the STMR values for 16 commodities estimated by the current Meeting and by the 1998 JMPR (Annex 3). The calculated IEDIs were 0% of the ADI for all regional diets. The Meeting concluded that intake of residues of kresoxim-methyl resulting from uses considered by the 1998 and current JMPR was unlikely to present a public health concern.

Short-term intake

The 1998 JMPR concluded that an acute RfD for kresoxim-methyl was unnecessary. The Meeting therefore concluded that the short-term dietary intake of kresoxim-methyl residues is unlikely to present

a risk to consumers.

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METHOMYL (094)

EXPLANATION

A residue review for methomyl was conducted in 1975 and supervised field trial data for various crops and related data were considered in 1976-1978, 1987, 1988, 1990 and 1991. The 22nd Session of the CCPR decided to combine the MRLs for methomyl and thiodicarb (ALINORM 91/24 A, para. 126, p.21). Some aspects of the toxicology of methomyl are reviewed by the present Meeting. This review of residue aspects is within the CCPR Periodic Review Programme.

The manufacturer submitted data on product chemistry, metabolism, environmental fate, analytical methods, storage stability, animal feeding studies and survey samples. The governments of Queensland, Australia and Germany submitted information on labels.

IDENTITY

ISO common name: methomyl

Chemical name:

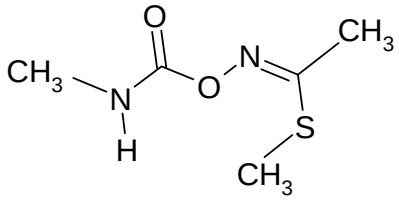
IUPAC: *S*-methyl *N*-(methylcarbamoyloxy)thioacetimidate

CA: methyl *N*-[[(methylamino)carbonyl]oxy]ethanimidothioate

CAS number: 16752-77-5

Synonyms and trade names: syn-methomyl; metomil; mesomil; OSM 1196; “Lannate”; “Nudrin”

Structural formula:



Molecular formula: $C_5H_{10}N_2O_2S$

Molecular weight: 162.20 g/mole

Physical and chemical properties

The physical and chemical properties of methomyl are summarized in Table 1. The material described is technical grade unless otherwise indicated.

Table 1. Physical and chemical properties of methomyl.

Property	Characteristics	Test material purity	Reference
Physical state	Crystalline solid		Silveira, 1990
Colour	White		Silveira, 1990
Odour	Slightly sulfurous		Silveira, 1990
Melting point	77°C		Silveira, 1990
Relative density	0.57 g/ml		Silveira, 1990
Solubility in water	5.48 ± 0.04 g/100 g water at 25°C	96.2%	Hoffman, 1988
Solubility in organic solvents, g/100 g at 25°C	Methanol: 100 Ethanol: 42 Isopropanol: 22 Acetone: 72 Toluene: 3 Ethyl acetate: 77.4 g/l at 20°C *n*-heptane: 0.097 1-Octanol: 24.0 *o*-xylene: 9.58 Acetonitrile: >25 at 20°C Dichloromethane: >25 Dimethylformamide: >25		Silveira, 1990. Moore, 2001
Vapour pressure	5.4×10^{-6} mm Hg at 25°C	>99.2%	Barefoot and Cooke, 1989
Dissociation constant	Non-ionizable		Silveira, 1990
Octanol/water partition coefficient (log)	1.24	99.3%	Singh, 1988
Hydrolysis	At pH 5 and 25°C, stable for 30 days At pH 7 and 25°C, stable for 30 days At pH 9 and 25°C, 50% loss in 30 days, with conversion to *S*-methyl *N*-hydroxythioacetimidate	95.5% radiochemical purity	Friedman, 1983

Photolysis	At a concentration of 100 mg/l in pH 5 aqueous medium at 25°C, the half-life under fluorescent UV lights (365 nm peak sensitivity, 1000 microwatts/cm^2) was 2-3 days, with acetonitrile the principal product.	95% methomyl, 3% *S*-methyl *N*-hydroxythioacetamidate, 2% unknown	Harvey, 1984
Storage stability	No significant degradation (<1%) over 9 years in ambient conditions		Silveira, 1990

Formulations

The formulations are listed in Table 2.

Table 2. Formulations of methomyl.

Registered Trademark	**Active Ingredient Content**	**Formulation Type**
Lannate Lannate SP Lannate 90	900 g/kg	Water soluble powder (SP)
Lannate 45	450 kg/kg	Water soluble powder (SP)
Lannate 40 SP	400 g/kg	Water soluble powder (SP)
Lannate 25	250 g/kg	Wettable powder (WP)
Lannate LV	290 g/l	Wettable powder (WP)
Lannate L	215 g/l	Soluble concentrate (SL)
Lannate 20L	200 g/l	Soluble concentrate (SL)
Lannate 12.5L	125 g/l	Soluble concentrate (SL)

METABOLISM AND ENVIRONMENTAL FATE

Unless otherwise noted [^{14}C]methomyl is labelled on the C doubly bound to N.

Animal metabolism

The metabolism of methomyl has been studied in various laboratory animals and livestock including rats, monkeys, goats, cows and poultry. In general, methomyl is rapidly absorbed, extensively metabolized and excreted as volatile or polar metabolites.

Rats. In a study by Harvey *et al*. (1973) two male rats were fed a diet containing 200 mg methomyl/kg bw for 8 days, followed by intragastric intubation of 1.2 mg [^{14}C]methomyl (about 5 mg/kg bw) and were killed 72 and 24 hours after treatment. A third male rat was treated similarly except that the [^{14}C]methomyl (3.5 mg/kg bw) was given after 19 days of preconditioning.

In three days the rats exhaled 50% of the administered ^{14}C (17% carbon dioxide and 33% acetonitrile, by GC-MS) and excreted 16-24% in the urine. Less than 3% of the administered dose was found in the faeces. Urinary and volatile metabolites were identified 1 or 3 days after the ^{14}C dose. Countercurrent distribution of the urine showed that almost all the radioactivity present was in polar material. Methomyl, methomyl *S*-oxide, methomyl *S*,*S*-dioxide and *S*-methyl *N*-hydroxythioacetimidate (MHTA) were not detected in the urine. Radioactivity was distributed among a range of tissues with about 10% of the dose in the tissues and carcase 1 or 3 days after dosing. Recovery of the total administered radioactivity did not exceed 60%.

In a second more detailed study (Hawkins *et al*., 1991) five male and five female rats were given single oral doses of syn-[^{14}C]methomyl (5 mg/kg) and held in metabolism cages for 7 days. The rats exhibited clinical signs of cholinesterase inhibition (muscle tremor and humped posture) which disappeared within 2 hours of the dose. Within 24 hours about 80% of the administered dose was eliminated in the urine and exhaled, but >90% elimination did not occur until 168 hours. No differences were found between males and females in rates of excretion or levels of residual radioactivity in tissues.

The radioactive components of the urine collected after 0-24 hours were separated by reverse-phase HPLC, ion partition chromatography (acetamide and acetate) and confirmed by TLC. The main metabolite was identified by NMR and mass spectroscopy (LC-MS-FAB) as a mercapturic acid derivative of methomyl, (L)-*N*-acetyl-*S*-[1-(methylcarbamoyloxyiminoethyl)]cysteine, equivalent to about 17% of the ^{14}C dose. There were many components, each constituting less than 5% of the administered dose, some tentatively identified as acetonitrile, acetate, MHTA sulfate and acetamide. Methomyl, MHTA, acetohydroxamic acid and the anti-isomer of methomyl were not detected.

Monkeys. Four male cynomolgus monkeys were each given a single oral dose of [^{14}C]methomyl (5 mg/kg bw). Over 24 hours about 36% of the administered dose was found in the exhaled air (4% as acetonitrile, range 2.7-5.2%; 32% carbon dioxide, range 30-36%) and about 27% in urine. A total of 32% was found in urine over 168 hours (Hawkins, 1992).

Approximately 5% of the radioactivity was still retained in the tissues after 168 hours. The highest concentrations were in the liver (0.7-0.9 mg/kg methomyl equivalents), fat (0.4-0.7 mg/kg) and kidney (0.4-0.5 mg/kg). Lower concentrations were found in other tissues but were generally higher than the blood levels of 0.1-0.2 mg/kg equivalents.

A combination of HPLC (reverse-phase, ion partition) and TLC characterized 18 radioactive metabolites in urine, with no metabolite accounting for more than 4% of the dose. Small amounts of acetonitrile (3%), acetate (0.6%), acetamide (0.5%) and MHTA sulphate (0.3%) were among the products found. The mercapturic acid derivative of methomyl accounted for about 1%. Methomyl, methomyl *S*-oxide, methomyl *S*,*S*-dioxide and *S*-methyl *N*-hydroxythioacetimidate (MHTA) were not detected.

Goats and cows. The metabolism of [^{14}C]methomyl has been examined in ruminants in three separate studies (two on goats and one on cows).

In the first study, (Harvey, 1980) a lactating goat was given [^{14}C]methomyl by capsule twice a day for 10 days at doses equivalent to 20 ppm in the feed. Milk, blood, urine and faeces were sampled daily and tissues within one day of the last dose. No methomyl or MHTA was detected in any of the samples. Approximately 16% and 7% of the radioactivity was excreted in the urine and faeces respectively and about 8% appeared in the milk and 17% in exhaled air. Residues in the milk reached a plateau after 3 days equivalent to approximately 2 mg/kg as methomyl, and the lactose contained about 11-13%, hexane extracts, containing the triglyceride components, 26-37% and the casein component 8-9% of the ^{14}C in the milk. This indicates that methomyl had been completely broken down and

incorporated into milk constituents. [^{14}C]acetonitrile was identified as a volatile metabolite in milk and blood.

Examination of the liver samples demonstrated that the radioactivity derived from methomyl was found in glycerol, glycerol-3-phosphate, fatty acids, neutral lipids and insoluble protein, indicating a metabolic pathway via acetonitrile and acetate into the naturally occurring constituents in the liver.

In the second study, a lactating cow was dosed twice daily by capsule for 28 days with [^{14}C]methomyl at a rate equivalent to 8 ppm in the feed. Milk samples were collected each day and selected tissues were taken within 24 h of the last dose. Radioactivity appeared in the milk within one day and reached a plateau of 0.5 mg/kg equivalents within 6 days, mostly because of the reincorporation of the radiolabel into fatty acids, lactose and other acetate-derived products. No methomyl or MHTA was detected; acetonitrile accounted for about 25% of the radioactivity. The highest concentrations of radioactivity, equivalent to 9.23 mg/kg, were in the liver, with only 2.01 mg/kg in the kidneys and lower concentrations in fat and muscle. Most of the radioactivity was considered to be the result of reincorporation of the radiolabel as acetate into natural constituents. No methomyl was detected in tissues (Monson and Ryan, 1991).

A more detailed goat study (Dietrich *et al.*, 1995) confirmed the results of the earlier ruminant studies. A lactating goat was dosed orally, once daily, for three days with 160 mg of [^{14,13}C]methomyl, nominally 80 ppm in the diet based on 2 kg food consumption/day, but was actually 162 ppm based on actual food consumption during the study. The specific activity was reported as 11.0 µCi/mg and the radiochemical purity was 97.8%. Milk was collected twice daily (morning and afternoon) and pooled each day. The goat was slaughtered 24 hours after the last dose. A portion of the samples were analysed immediately and the rest were frozen. More than 30% of the administered dose was collected as exhaled volatile metabolites with 18.5% identified as [^{14}C]carbon dioxide and 12.8% as [^{14}C]acetonitrile. Urine radioactivity accounted for 16.5%, while 5.0% was found in faeces. Approximately 3% was found in milk and radiolabelled residues in muscle, liver, fat and kidneys contained approximately 6% at slaughter. Overall recovery of the administered dose including stomach and gastrointestinal tract contents was 73%.

Tissue and milk samples were homogenized with methanol and chloroform and centrifuged, and the chloroform layer was drawn off with a pipette. The remaining pellet/methanol/water mixture was extracted twice with two additional 25 ml portions of chloroform on a wrist-shaker for 5 min, centrifuged and the chloroform fraction removed and combined with the first chloroform fraction.

The remaining pellet/methanol/water mixture was further extracted with methanol followed by separation of the methanol/water fraction by centrifugation. The pellet was again extracted with 25 ml of 50/50 methanol/water, centrifuged and the methanol/water supernatant combined with the first methanol/water fraction. The total radioactivity in the chloroform and methanol/water fractions was determined by LSC.

A portion of the remaining pellet was treated with Pronase. Further extractions were made after acid and base hydrolysis, saponification of neutral lipids and fatty acids and methylation of free fatty acids. The extracts analysed by HPLC.

The TRR was highest in liver (12.1 mg/kg as methomyl) with lower levels in kidney (4.67 mg/kg), muscle (1.45 mg/kg) and fat (0.32 mg/kg), and in the milk ranged from 4.09 mg/kg during the first 0-24 h to 9.31 mg/kg in samples during the 24 h after the last dose.

Tissues and milk were extracted on the day the goat was killed and analyses completed within 48 h. Special precautions were taken to minimize loss of volatile metabolites from tissues or further metabolism of initial metabolites. Methomyl, methomyl *S*-oxide, methomyl *S,S*-dioxide, *S*-methyl *N*-

hydroxythioacetimidate (MHTA) and hydroxymethyl-methomyl were not detected (LOD 0.007-0.018 mg/kg). [^{14}C]Acetonitrile was detected in all samples, at levels of 0.438 mg/kg as methomyl (18.6% of the TRR) in 48-72 h in milk, 10.2% (0.314 mg/kg) in liver, 62.3% (0.228 mg/kg) in muscle, 30.5% (0.360 mg/kg) in kidney and 39.4% (0.032 mg/kg) in fat. Low levels of [^{14}C]acetamide were detected in all samples, ranging from 0.005 mg/kg in fat to 0.08 mg/kg in milk and kidney, as well as [^{14}C]thiocyanate at 0.58 mg/kg as thiocyanate (17% of the TRR) in 48-72 h milk, 0.30 mg/kg (7% of the TRR) in liver, 0.097 mg/kg (19% of the TRR) in muscle, 0.59 mg/kg (35% of the TRR) in kidney, and 0.057 mg/kg (50% of the TRR) in fat. ^{12}C/^{13}C ratios determined by mass spectrometry of the pentafluorobenzyl derivative indicated that the thiocyanate isolated from milk was 50% methomyl-derived (presumably resulting from acetonitrile metabolism to cyanide which is then converted to thiocyanate, a known metabolic reaction for detoxification of cyanide) and 50% from natural sources.

Further analysis of the radioactivity in tissues indicated extensive metabolism of methomyl with incorporation of the radiolabel into natural products, which is consistent with the earlier goat and cow studies. Approximately 31% of the TRR in the milk was shown to be incorporated into fatty acids by saponification, methylation and chromatography with methylated fatty acid standards, and approximately 10% as [^{14}C]lactose by co-chromatography with an authentic radiolabelled reference standard. The presence of radiolabelled glucose and amino acids was confirmed in the milk and tissue samples. Most of the solvent-extractable radioactive compounds in the tissues apart from acetonitrile were highly polar compounds unrelated to methomyl, on the basis of HPLC retention times of available standards containing the methylcarbamoyloxy moiety. It is likely that the polar residues are natural products and low molecular weight compounds originating from acetonitrile or carbon dioxide, and the main component is radiolabelled thiocyanate (Table 3).

Table 3. Identification of radiolabelled residues from a lactating goat given 3 daily doses of 160 mg of [^{13,14}C]methomyl (Dietrich *et al.*, 1995).

Compound	Sample									
	Milk		Muscle		Liver		Kidney		Fat	
	mg/kg[1]	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR
Methomyl	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Methomyl oxime	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Acetonitrile	1.7	19	0.90	62	1.2	10	1.4	30	0.13	39
Acetamide	0.22	2	0.14	10	0.16	1	0.23	5	0.015	5
Thiocyanate	1.6	17	0.27	19	0.85	7	1.6	35	0.16	50
Fatty acids	2.9	31	0.02	1	0.24	2	0.06	1	0.02	7
Lactose	0.99	11	ND	NA	ND	NA	ND	NA	ND	NA
Acetate	0.28	3	0.24	16	5.7	45	0.88	19	0.03	9
Amino acids	1.2	13	0.19	13	1.6	13	0.63	13	0.03	8
Total	9.3	96	1.4	110	12.	77	4.7	98	0.32	110

[1] as methomyl
ND: not detected, LOD 0.02 mg/kg.
NA: not applicable

Poultry. Djanegara and Ryan (1994) dosed five white Leghorn laying hens orally once a day for three days with 5.1 mg [1-^{13,14}C]methomyl, equivalent to 45 ppm in the diet. The specific activity was reported as 23.3 µCi/mg and the radiochemical purity 98.5%. Eggs were collected twice daily, and samples of the whites and yolks pooled separately each day. The hens were killed 24 hours after the last dose. Exhaled acetonitrile and carbon dioxide accounted for 53% of the administered dose and the total recovery was 85% (Table 4).

Samples were analysed for methomyl, methomyl oxime, acetonitrile and acetamide (Table 5) within 48 hours. [^{14}C]Acetamide was detected in the whites and yolks at 0.02 and 0.01 mg/kg as methomyl respectively. No methomyl, methomyl oxime nor any metabolites (including methomyl sulfoxide, hydroxymethyl-methomyl and methomyl sulfone) with a retention time longer than acetonitrile were detected. [^{14}C]Acetamide was detected in the whites and yolks at 0.02 and 0.01 mg/kg as methomyl respectively.

In samples stored at -60^{o}C for 14 months more than 98% of the TRR in egg whites was extractable with methanol/water, of which 85-89% was acetonitrile and 1.4-2.6% acetamide (Table 6).

Tissue and yolk samples sequentially extracted with methylene chloride and methanol/water (2:1) were separated into polar, non-polar and residual solids fractions, and the solids pellets were treated with Pronase E overnight at 37^{o}C. The methylene chloride extracts were distilled to capture acetonitrile. The remaining residues were saponified and partitioned into petroleum ether, methylene chloride (after acidification) and ethanol/water extracts. The petroleum ether extracts were analysed for cholesterol and the methylene chloride extract methylated to characterize the fatty acids. Anaylses were by reverse-phase HPLC. The water/alcohol soluble fraction was not analysed further owing to low radioactivity (0.03 mg/kg). The methylated fatty acids were examined by GC-MS and palmitic, oleic, myristic and stearic acids and cholesterol were found.

The methanol/water extract and the supernatant from the Pronase E treatment of the residual solids were analysed by HPLC. Most of the radioactive residue was polar. The samples were hydrolyzed with concentrated HCl at 100^{o} C (to liberate amino acids) and analysed by another HPLC method (Table 6).

Table 4. TRR in the tissues and eggs of hens dosed orally for three days at 5 mg/day (Djanegara and Ryan, 1994).

Sample	TRR	
	mg/kg as methomyl	% of total dose administered
Liver	2.97	1.0
Muscle	0.54	1.4
Fat	0.79	0.8

Sample	TRR	
	mg/kg as methomyl	% of total dose administered
Egg whites		
0-24 h	0.99	0.2
24-48 h	1.1	0.3
48-72 h	1.5	0.3
Egg yolks		
0-24 h	0.46	<0.05
24-48 h	0.90	0.1
48-72 h	1.9	0.2
% of total dose: acetonitrile trap, 34.1; carbon dioxide trap, 19.2; excreta, 25.8; cage wash, 1.5.		

Table 5. Metabolism by poultry - initial analyses (Djanegara and Ryan, 1994).

Compound	Sample									
	Egg white (1.53 ppm)[1]		Egg yolk (1.94 ppm)[1]		Fat (0.794 ppm)		Liver (2.97 ppm)		Muscle (0.540 ppm)	
	% of TRR	mg/kg[2]	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Methomyl	ND[3]	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methomyl oxime	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acetamide	1.4	0.02	ND	ND	ND	ND	ND	ND	ND	ND
Acetonitrile	89	1.4	34	0.66	12	0.09	14	0.42	33	0.18

[1] mg/kg in 48-72 h eggs
[2] As methomyl.
[3] Not detected. Limit of detection estimated at 0.007-0.015 mg/kg.

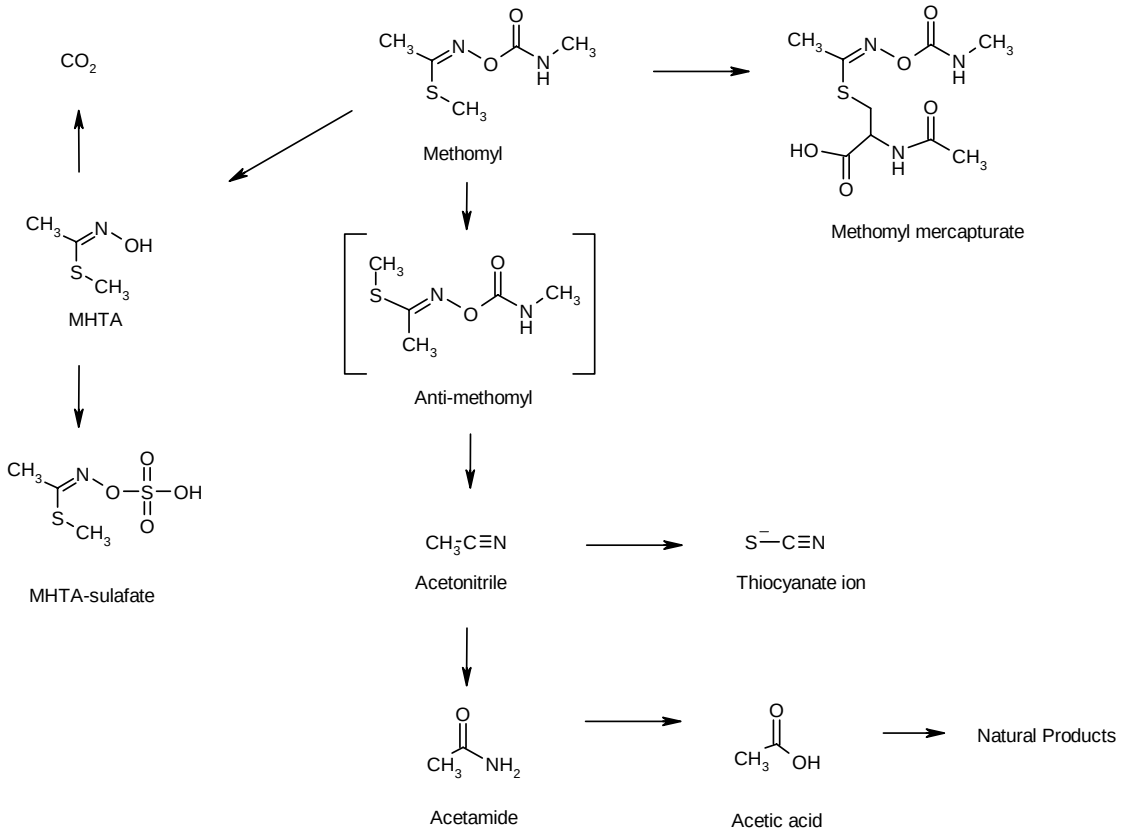
Table 6. Metabolism by poultry - additional analyses (Djanegara and Ryan, 1994).

Fraction/characterization or identification	Egg white (1.57 mg/kg)[1]		Egg yolk (1.94 mg/kg)[1]		Fat (0.794 mg/kg)		Liver (2.97 mg/kg)		Muscle (0.540 mg/kg)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
CH_2Cl_2 extract										
Acetamide	1.4	0.02	ND[2]	ND	ND	ND	ND	ND	ND	ND
Acetonitrile	90	1.4	21	0.41	7.1	0.056	9.3	0.28	26	0.14
Lipids			60[3]	1.2	87	0.69	32	0.96	15	0.083
MeOH/Water extract[4]			3.6	0.071	1.7	0.014	11.0	0.326	12	0.066
Acetamide			0.63	0.012			0.46	0.014	1.9	0.010
Acetonitrile			0.1	0.002			0.42	0.012	ND	ND
Polar metabolites			1.4	0.028			5.2	0.15	6.8	0.037
Unidentified			0.43	0.008			2.4	0.070	ND	ND
Pronase E supernatant[5]			7.9	0.15	3.8	0.030	36	1.08	39	0.22
Acetamide			ND	ND			0.3	0.009	ND	ND
Acetonitrile			ND	ND			6.5	0.19	ND	ND
Polar metabolites			5.2	0.102			18	0.53	33	0.18
Unidentified			0.95	0.018			9.6	0.28	5.7	0.031
Unextractable	3.0	0.05	6.6	0.13	0.55	0.004	11	0.32	6.6	0.036

[1] Residue in 48-72 h eggs
[2] Not detected
[3] Palmitic and oleic acids (36%), myristic acid (3.2%), stearic acid (5.7%), cholesterol (4.5%)
[4] Acid hydrolysis reduced polar metabolites. HPLC consistent with glycine, serine, glutamate and aspartate. Acetic acid (0.25% of TRR yolk, 1.7% of TRR liver, 2.3% of TRR muscle).
[5] Acid hydrolysis reduced combination of polar and unidentified metabolites. HPLC consistent with glycine, serine, glutamate and aspartate. Acetic acid (0.85% of TRR yolk, 9.8% of TRR liver, 7.9% of TRR muscle).

The metabolic pathways in poultry, rats, monkeys and ruminants are similar. The main pathway involves conversion of methomyl to the volatile metabolites acetonitrile and carbon dioxide with further metabolism of acetonitrile followed by the incorporation of one and two carbon units into a variety of natural products. Proposed pathways are shown in Figure 1.

Figure 1. Proposed metabolic pathways of methomyl in laboratory animals and livestock.



Plant metabolism

The metabolic fate of [^{14}C]methomyl in plants was studied in tobacco, maize and cabbage in the laboratory (Harvey, 1973a,b; Harvey and Reiser, 1973a; Harvey andYates, 1973a,b) and also under field conditions in maize, cabbage (Harvey and Reiser, 1973b) and cotton (Bull, 1974).

In the laboratory tobacco was grown from seedlings potted in sand. When the plants were 18 cm high the roots were exposed to a 10 mg/l solution of [^{14}C]methomyl for 28 days. The foliage of 42-day old greenhouse-grown cabbage and maize plants 28 cm high was treated with [^{14}C]methomyl in an aqueous solution containing Tween 20 surfactant, and a potted cabbage plant with 4.42 µc of radioactivity in 325 µl of solution. Four maize plants in a pot were treated with 5.44 µc of [1-C^{14}]methomyl pipetted into the whorls at the growing point. Each pot was placed in a glass metabolism apparatus equipped with cold traps, oxidizing furnaces and sodium hydroxide traps to measure the radioactivity of volatile products. Tobacco was harvested on the last day of treatment and cabbage and maize 7 and 10 days after treatment respectively.

96-97% of the radioactivity was accounted for in the two tobacco plants which absorbed 20-25% over 4 weeks. About 6% of the TRR (25% of the absorbed) was retained in the tissues and the remainder volatilized (14-19% of the dose). The volatile components [^{14}C]carbon dioxide and [^{14}C]acetonitrile were found in equal proportions.

About 108% of the radioactivity applied to the maize plants was accounted for, approximately 43% of which was volatilized within 10 days. The volatile components consisted of $^{14}CO_2$ and [^{14}C]acetonitrile in the ratio of 1:4. One week after treating the cabbage leaves, 20% of the radioactivity was volatized as $^{14}CO_2$ and [^{14}C]acetonitrile in approximately equal proportions, and approximately 96% of the applied was recovered.

The plant tissues were extracted by maceration in ethyl acetate (tobacco) or methanol. In cabbage 54% of the applied radioactivity was extractable and 22% unextractable, in tobacco 5% and 0.3%, in maize 26% and 19% respectively. The extracts of cabbage plants were analysed (counter-current distribution/LSC, TLC) for methomyl, methomyl *S*-oxide, methomyl *S*,*S*-dioxide and *S*-methyl *N*-hydroxythioacetimidate (MHTA) and components were characterized as more or less polar than methomyl. The cabbage leaf extract yielded 62% polar, 7% methomyl and 30% non-polar. The only terminal residue specifically detected was methomyl, with no evidence of structurally related compounds. Saponification of the non-polar residues yielded radiolabelled fatty acids. Palmitate, stearate and/or oleate, palmitoleic and arachidate were tentatively identified by gas chromatography, and polar compounds from the cabbage extracts by TLC as glycolic and tartaric acids and compounds which gave positive ninhydrin reactions indicating the reincorporation in amino acids.

[^{14}C]methomyl was also sprayed on tobacco leaves to determine whether it was translocated to untreated parts of the plant. Two plants were covered with plastic wrap, leaving the fifth leaf from the ground exposed, then sprayed with an aqueous solution of [^{14}C]methomyl (0.5 mg, 2.70 µc) containing surfactants. Three and seven days after treatment, plants were fractionated into growing tips, stems above treated leaf, treated leaf, mature leaves, stem below the treated leaf and roots, and separately extracted with ethyl acetate. No radioactivity was detected in any extracts except of the leaf treated originally in the 3-day sample but all segments of the 7-day sample contained residues indicating limited foliar translocation of methomyl. The radioactivity in the untreated segments was <1% of the residual radioactivity on the treated leaf.

The reports of the field studies (Harvey and Reiser, 1973g; Bull, 1974) lack adequate details to validate the findings. Field-planted cabbage approximately 6 weeks old received 8 weekly treatments of [^{14}C]methomyl applied at 0.56 kg /ha, specific activity 0.428 µCi/mg, with a commercial surfactant, and the plants were harvested 8 days after the last application. The outer leaves of the cabbage contained most of the residues of which 3-4% (0.8-0.9 mg/kg) was methomyl. The edible head contained 0.03-0.09 mg/kg methomyl (approximately 2-3% of the TRR), tentatively identified by countercurrent fractionation, with the remainder characterized as polar (31-51%) and non-polar (2-13%). Between 44 and 54% of the radioactivity was unextractable. No methomyl *S*-oxide, methomyl *S*,*S*-dioxide or *S*-methyl *N*-hydroxythioacetimidate (MHTA) was found in the outer leaves or heads.

In another study sweet corn plants approximately 8 weeks old received 7 weekly treatments of [^{14}C]methomyl at 0.56 kg /ha, specific activity 0.222 µCi/mg, with a commercial surfactant. Corn ears and fodder were harvested at an early mature stage 8 days after the last harvest. No methomyl was detected in the grain by countercurrent fractionation. 63% of the TRR was in a polar fraction and 37% was unextractable. The methomyl was equivalent to 2 mg/kg in fodder and 1.5 mg/kg in cannery waste (husks and cobs), and 35-49% was unextractable. 26-35% of the extractable TRR was polar and 3-6% non-polar. No methomyl *S*-oxide, methomyl *S*,*S*-dioxide or MHTA was found in the corn fractions.

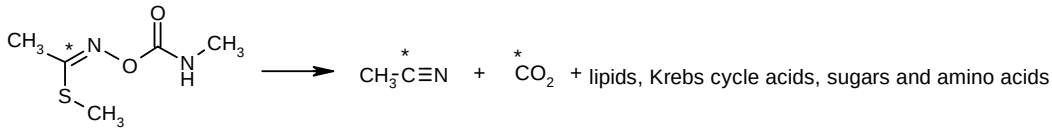
In a further study individual field-grown cotton leaves were treated with 50 µg of [^{14}C]methomyl in an aqueous solution containing a wetting agent and harvested 0, 4, 8, 24, 48, 96 and 192 hours later. About 40% of the methomyl penetrated the cotton leaves within the first four hours and 19% was on the leaf surface. Surface residues were largely lost within 48 hours (<2% remaining), presumably as $^{14}CO_2$ and [^{14}C]acetonitrile. Determination was by TLC and the parent compound was the only radioactive component on the leaf surface. [^{14}C]methomyl appeared to penetrate the leaf surface and was almost

completely degraded within 8 days (<2% degraded after 48 hours). No methomyl *S*-oxide, methomyl *S*,*S*-dioxide or *S*-methyl *N*-hydroxythioacetimidate (MHTA) was found in the leaves. The unextractable residue was about 6% of that applied.

In a study on rotational crops sandy loam soil (0.73% organic matter (OM), pH 5.9) in 28-l containers was surface-treated with [^{14}C]methomyl at 4.48 kg ai/ha and aged in a greenhouse (Harvey, 1978). Thirty and 120 days after treatment, cabbage, red beets and sunflower seeds were planted in the containers. The crops were grown to maturity and analysed for total ^{14}C and methanol-extractable ^{14}C, and the methanol extracts for ethyl acetate-soluble ^{14}C. After the 30 days of ageing, 26% of the original [^{14}C]methomyl remained in the soil, but only 8% after 120 days. Mature beets and cabbage harvested from soil aged 30 days after treatment contained ^{14}C levels equivalent to 0.1-0.2 mg/kg as methomyl, and mature sunflower seeds 2 mg/kg. Beets and cabbage planted 120 days after the soil was treated had ^{14}C levels of 0.04-0.05 mg/kg, and sunflower seeds 1.5 mg/kg. However all crops sampled after either 30 or 120 days ageing had levels of intact [^{14}C]methomyl or metabolites equivalent to 0.01 mg/kg or less (in the ethyl acetate fraction from hexane/ethyl acetate partition of concentrated methanol extract). The residue in the sunflower seeds was not analysed further.

The degradation pathway of methomyl is similar in the various crops studied. It is extensively metabolized to one- and two-carbon fragments, $^{14}CO_2$ and [^{14}C]acetonitrile, which are reincorporated into natural plant constituents in maize and cabbage, such as fatty acids. No apparent conjugates were observed in any of these studies. The only terminal residue specifically detected was methomyl.

Figure 2. Metabolism of [^{14}C]methomyl in plants.



Methomyl (* denotes position of the radiolabel)

The degradation or loss of unlabelled methomyl on cotton leaves was studied in cotton-growing areas of Mississippi, Texas and California in the USA. The potential wash-off from various leaf surfaces was tested in dislodgeable foliar studies (Eble and Tomic, 1990). Single applications of 0.76 kg ai/ha of a water-soluble formulation of methomyl were sprayed on the leaves during periods of no rainfall and sampled at 9 intervals from 0 to 144 hours after application. Residues were rinsed off with water for analysis by HPLC. The foliar half-life for methomyl was estimated to be 0.6 to 2.2 days, average 1.1 days, based on first-order kinetics.

Environmental fate in soil

The aerobic degradation of [^{14}C]methomyl was studied in a microbially active loam soil from Madera, California, USA (Zwick and Malik, 1990a). The organic matter content was 0.93% and the pH 7.8. The soil was treated with [^{14}C]methomyl at a rate equivalent to approximately 9 kg ai/ha and incubated at 75% maximum water holding capacity in a flow-through system at 25°C in the dark for 90 days. Duplicate samples taken at 9 dates were analysed for total ^{14}C, [^{14}C]methomyl and potential metabolites. [^{14}C]methomyl was rapidly degraded with a half-life of approximately 11 days, on the basis of first-order kinetics. The main product was $^{14}CO_2$ (75% of applied ^{14}C) during the three months. The degradation products extractable with methanol/water, 50/50, identified by TLC and HPLC, included minor amounts

of the hydrolysis product of methomyl, *S*-methyl *N*-hydroxythioacetimidate (MHTA) and two polar products, all of which were individually 3.3% or less of the applied radioactivity at any time. Unextractable radioactivity increased for the first month, reaching 24% then decreasing to 14% of the applied radioactivity at 3 months, mostly associated with soil organic matter. The soluble humin fraction, separated by sequential 0.1 N NaOH and 6N HCL treatments at 90°C, and the insoluble fraction contained about 8% each of the applied radioactivity.

[^{14}C]methomyl was added at a rate equivalent to 5.0 kg ai/ha to three moist agricultural soils and incubated in the dark in the laboratory for 42 days in a flow-through apparatus (Harvey and Pease, 1973e). Of the applied radioactivity 31-45% was found in the sodium hydroxide traps and identified as $^{14}CO_2$ and 12-14% was unextractable. The soil extracts contained 33-51% of the applied radioactivity, almost all as [^{14}C]methomyl, and degradation products and/or polar compounds represented less than 2%. Using the same experimental arrangement, a Minnesota muck soil (52% OM, pH 5.45) was treated at 4.5 kg ai/ha with [^{14}C]methomyl and incubated as described above for 42 days (Harvey, 1972). During the experiment 42% of the applied radioactive material was degraded to $^{14}CO_2$, unextractable residues accounted for 46% and 8% was extracted. The major component of the soil/water extract was [^{14}C]methomyl by TLC, representing 7.7% of the applied radioactivity. Minor degradation products were all below 0.3%.

In another laboratory study a Flanagan silt loam (8.26% OM, pH 6.5) was treated at 4 mg/kg with [^{14}C]methomyl and incubated for 45 days in a flow through system at 25°C in the dark. Soil moisture was maintained at approximately 70% of the maximum water holding capacity (Harvey, 1977b). A heat-sterilized soil replicate was also incubated in aseptic conditions. At the end of the experiment [^{14}C]methomyl was present in the active soil extracts at 47% of the applied radioactivity, $^{14}CO_2$ accounted for 22.5% and 26.2% was unextractable. 19% of the extractable fraction was methomyl and/or MHTA, equivalent to approximately 5% of the applied radioactivity. In the sterile replicate $^{14}CO_2$ was only 0.3%, and [^{14}C]methomyl was present at 89% of the applied radioactivity, indicating the importance of microbial processes for the degradation and subsequent mineralization of [^{14}C]methomyl and its transient products in soil.

Microbial transformation of methomyl was determined in Myrtleford sandy loam (2.1% OM, pH 6.1) and Ovens fine sandy clay loam (2.3% OM, pH 5.8). 10g of each soil was perfused with aqueous solutions (230 ml) containing 6 mg/l of methomyl (Fung and Uren, 1977). In one replicate, sodium azide was added to sterilize the soil. The soils were conditioned in the perfusion apparatus with polyvinyl alcohol (5%, w/v) to flocculate them to ensure adequate drainage, and equilibrated for 2 days. The solutions of 6 mg/l methomyl were then exchanged at a flow rate of 8 ml/min. at 25°C for up to 56 days. After 42 days 58% of the methomyl in the solution perfusing the Myrtleford soil and 38% in the Ovens soil solution had been degraded. The loss appeared to be about 5% in the azide-treated soil, suggesting the importance of microbial transformation.

The degradation of [^{14}C]methomyl under field conditions was studied at three US sites (Harvey and Pease, 1973) in a Keyport silt loam at Newark, Delaware; a Leon Immokalee fine sand at Bradenton, Florida; and Cecil loamy sand at Clayton, North Carolina. Stainless steel cylinders of approximately 10 cm in diameter and 38 cm in length were driven into undisturbed soil and the cylinders of soil were treated with [^{14}C]methomyl at rates equivalent to 5.04 kg ai/ha. Leachate from the more permeable Bradenton and Clayton soils was allowed to drain freely into a glass container. The cylinders were collected after 1, 3 and 12 months in Newark, after 3 months in Florida and 5 in North Carolina. The leachates contained no radioactivity. The soils were divided into four layers and the top layer was extracted with methanol and water and analysed for [^{14}C]methomyl and potential degradation products by countercurrent distribution. In all soils most of the residual radioactivity was in the top 8 cm, with less than 5% in the lower layers in Delaware, 8% in Florida and 27% in North Carolina. The results are shown in Table 7.

Table 7. Distribution of [^{14}C]methomyl (percentage of applied dose) in three soils under field conditions after application at 5 kg ai/ha (Harvey and Pease, 1973).

Fraction	% of applied ^{14}C at location/interval (months)/rainfall (cm)				
	Delaware/1/2.8	Delaware/3/28	Delaware/ 12/103	Florida/3/ 60	North Carolina/5/44
Unaccounted (volatilization assumed)	71	81	85	90	85
Unextracted (0-8 cm)	26	18	15	10	15
Methomyl (0-8 cm)	1.8	0.3	0.0	<0.005	<0.005
S-methyl *N*-hydroxy thioacetimidate (MHTA) (0-8 cm)	0.2	0.1	0.0	<0.005	<0.005
Polar (0-8 cm)	0.9	0.7	0.3	0.2	0.04

In another study [^{14}C]methomyl was added at 4.48 kg ai/ha to the surface of 1l containers filled with an agricultural sandy loam (0.73% OM, pH 5.9) and incubated in a greenhouse for 45 days (Harvey, 1977a). At the end of the experiment unextractable soil residues represented 20% of the applied radioactivity, and [^{14}C]methomyl 21%. The only degradation product, MHTA, was below 0.5% of the applied radioactivity at all 6 sampling dates. A polar fraction was found in all soil extracts, accounting for < 2% of the applied radioactivity. Most of the applied [^{14}C]methomyl was assumed to be lost through volatilization of $^{14}CO_2$. After extraction of the 45-day soil residue with hot caustic soda, about 25% of the unextractable radioactivity was recovered as MHTA, representing 3% of the applied radioactivity. The remainder was divided between all the normal soil organic matter fractions.

The anaerobic degradation of [^{14}C]methomyl in a microbially active loam soil from Madera, California, was studied by Zwick and Malik (1990b). The organic matter (OM) content of the soil was 0.93% and the pH 7.8. The soil was treated with [^{14}C]methomyl at a rate equivalent to approximately 8.97 kg ai/ha and first incubated aerobically at 75% maximum water holding capacity at 25°C in the dark for 14 days and then under anaerobic conditions for 60 days. Duplicate soil samples were taken 7, 14, 30 and 60 days later for analysis. [^{14}C]methomyl was rapidly degraded with a half-life (first order kinetics) of approximately 14 days under anaerobic conditions. The major product was $^{14}CO_2$ with approximately 35% of the applied radiolabel converted during the study period; however, 30% was formed during the aerobic phase. An additional 4% was found as volatile organic compounds during the anaerobic phase. Extractable compounds identified by HPLC and TLC included minor amounts of methomyl (0.6-5% of applied ^{14}C), MHTA (0.3-1%) and two polar products (each 0.3-7% of the applied radioactivity). Unextractable radioactivity was observed on anaerobic day 7 at 30% and decreased to 24% of the applied radioactivity at 60 days. Most of the unextractable radioactivity was associated with the soil organic matter.

Unlabelled methomyl was incubated at 10°C in soil samples from below shallow ground-water tables from four locations in The Netherlands (Smelt *et al.*, 1983). The subsoils were sand 0.5% OM, pH 7.6, loamy fine sands 2.3% OM, pH 7.5 and 1.0% OM, pH 7.8, and fine sand 0.1% OM, pH 4.5. All four subsoils are anaerobic in the field, and from each 100 g of water-saturated sediment was transferred into a jar and 25 ml of groundwater added. Anaerobic conditions were established by purging the container with nitrogen. After pre-incubation for 7-11 days at 10°C in the dark, 4 ml of methomyl solution was added (50 µg/ml) and the jars incubated under the same conditions as before. Conversion of methomyl in the

soil samples was very rapid. In three subsoils less than 5% of the applied material was measured after one day of incubation (half-life <5 hours), and in the fine sand the half-life was calculated to be 7 hours.

Bromilow *et al*. (1986) investigated the role of ferrous ions in the rapid degradation of methomyl in anaerobic soils. Subsoils were sampled from two locations in The Netherlands and anaerobic conditions were maintained during sampling and transport. The organic matter in the soils was 1.0 and 22.0%, the pHs were 5.7 and 6.7, and concentrations of ferrous ions (Fe^{2+}) 27 and 41 mg/l in the soil water. Suspensions of anaerobic soils (80-200 g dry basis) were incubated before the study began according to the procedure of Smelt *et al*. (1983) and 5 mg of unlabelled methomyl was added for further incubation at 20-24°C in the dark. Methomyl was very rapidly degraded in the anaerobic subsoils with half-lives of 1 and below 0.2 hours. Only methanethiol and dimethyl disulfide were detected in the headspace and soil water. Reactions of methomyl with metal ions was tested in an aqueous solution containing 250 mg/l Fe^{2+}. Solutions were deoxygenated with a gentle steam of nitrogen and incubated in sealed glass tubes under nitrogen. Methomyl was very rapidly degraded in the presence of Fe^{2+} with a half-life of 4.1 hours yielding methanethiol and presumably acetonitrile. However, the reactions in soil were about an order of magnitude faster than those in the aqueous solutions at comparable concentrations of ferrous ions in the water.

The rate of degradation was measured in three greenhouse soils in The Netherlands (Leistra *et al.*, 1984). The organic matter content of the soils ranged from 3.8-9.7% and the pH from 6.4-7.1. Methomyl was added at a rate equivalent to 3 kg ai/ha and the soils were incubated in the dark at 20°C for 60 days. Soil moisture was kept between 25 and 40% gravimetric water content. Half-lives determined using first-order kinetics were 2 to 14 days (average 6.7 days).

Methomyl, formulated as Lannate L insecticide, was applied at 4.48 kg ai/ha at a site in Greenville, Mississippi, USA (C.M. Kennedy, 1991d) to field cabbages planted in a loam and silt loam, average pH 6.4 and organic matter content 1% in the top 90 cm layer. Samples were taken down to 90 cm at 9 sampling dates up to 91 days later. The calculated half-life of methomyl was 5 days, and it remained in the top 15 cm of the soil throughout.

In another trial the same formulation was applied to cabbages at 10.09 kg ai/ha (S.M. Kennedy, 1989) at a field site in Madera, California, USA. The soil was a sandy loam with a pH of 7.9 and an organic matter content of 0.6% in the top 30 cm layer. Samples were taken down to 90 cm at 14 sampling dates up to 272 days after application. The half-life of methomyl was 54 days, owing to the low moisture content of the soil as the site bordering the California desert (2.5%-17.2% with an average of 10.7% during the study period). It was thought that the dry conditions may have adversely affected the soil microbial population, thus significantly reducing its bioactivity.

The photolysis of [^{14}C]methomyl by natural sunlight was studied at an application rate of 1.12 kg ai/ha (Swanson, 1986) with a dark control. Samples were analysed at intervals up to 30 days. A slurry of Keyport silt loam (5.0% sand, 67% silt, 28% clay, 1.4% OM, pH 6.8) was applied to glass microscope slides at 1 mm thickness and air dried. Using a water bath the temperature was maintained at 25°C during the exposure to sunlight. [^{14}C]methomyl decomposed with a half-life of 34 days to form acetonitrile, the only detected radioactive degradation product. The controls did not decompose.

The mobility of methomyl was investigated in batch equilibrium studies with [^{14}C]methomyl on two sandy loam and two silt loam soils (Priester, 1986). Aqueous solutions containing 0.2-6 mg/l [^{14}C]methomyl/l were mixed with 20 g of soil in a 1:1 ratio and shaken for 24 hours at 25°C. Radioactivity in the soil at equilibrium was determined from the change in concentration of radioactivity in the aqueous solution. For the desorption phase, the soil and water from the 6 mg/l adsorption experiment were used. The supernatant was removed and distilled water added to re-establish the initial total weight and 1:1 (w/w) soil to water ratio. The mixture was shaken for 24 hours at 25^{o}C and the

concentration of radioactivity in the supernatant was determined. This procedure was repeated five times, using fresh distilled water each time. The concentration of radioactivity in the soil at each step was calculated from the change in radioactivity in the water. Results are summarized in Table 8.

The mobility of [^{14}C]methomyl was also investigated in the four soils using soil thin-layer chromatography (Priester, 1984). TLC plates were made with each soil, spotted with an acetone solution of methomyl, and developed with water. The results are shown in Table 8.

Table 8. Adsorption/desorption of methomyl on sandy loam and silt loam soils (Priester, 1984, 1986).

Sample	pH	Organic matter (%)	K_{oc}, coefficient of adsorption per unit organic matter (l/kg)	Coefficient of desorption per unit organic matter (l/kg)	R_f for TLC plates developed with water
Cecil sandy loam	6.5	2.1	34	48	0.53
Woodstown sandy loam	6.6	1.1	21	45	0.82
Keyport silt loam	5.2	7.5	14	37	0.52
Flanagan silt loam	5.4	4.3	23	37	0.46

In another adsorption study by Cox *et al.* (1993) in southern Spain, 4 soils including subsoils were treated at concentrations of 20 and 50µM and soil:solution ratios of 1:2 and 1:5, w/v. Organic matter contents were 0.54-2.5%, and clay contents 20-68%. The soil-water distribution coefficient ranged from 0.06 l/kg for a subsurface soil with 0.29% organic matter and 24% clay to 1.4 l/kg for a surface soil with 1.67% organic matter and 68% clay. Regression analysis indicated some correlation between organic matter or clay content and adsorption.

Leistra *et al*. (1984) studied the adsorption of methomyl in three greenhouse soils (3.7-9.7% organic matter, pH 6.4-7.1) in The Netherlands. The soil:solution ratio was 1:1, with two concentrations of methomyl at 0.25 and 1 mg/l. Adsorption coefficients ranged from 0.43-1.30 l/kg and calculated K_{oc} from 11 to 13 l/kg. Adsorption was weak to moderate, with highest sorption in soils with higher clay and organic contents.

In a soil-column leaching study using sand, loamy sand and sandy loam soils, [^{14}C]methomyl was applied to the surface of 30 cm soil columns at a rate equivalent to 0.5 kg ai/ha and the columns were eluted with HPLC grade water equivalent to approximately 200 mm of rainfall within 24 hours (Langford-Pollard, 1994). The major radioactive component in the leachates corresponded to methomyl, as determined by HPLC and TLC. A minor component accounting for 0.8-2% of the applied radioactivity was identified as MHTA. Other radioactive fractions represented a maximum of 0.7% of applied radioactivity. Analysis of the soil column demonstrated the presence of [^{14}C]methomyl only.

Additional trials were conducted with aged Speyer 2.1 soil. 100 g soil fractions were mixed with sufficient HPLC grade water to bring the soil to 9% moisture content, and stored for 12 days in the dark at 20^{o}C in flasks, treated with the [^{14}C]methomyl solution and placed in a gas-flow system with traps for volatiles. After ageing [^{14}C]methomyl in the sandy Speyer 2.1 soil for 13 days at 20°C (half-life as determined from separate experiments), the contents of the flasks were transferred to columns packed with Speyer 2.1 soil, which were eluted with HPLC water. Extraction of an aged soil sample yielded 53% of the applied radioactivity; some 21% was not extracted and the radioactivity in the volatile traps during ageing accounted for 20% of the applied radioactivity which was shown to be due to $^{14}CO_2$. The main

radioactive component in the soil extracts before elution accounted for 48% of the applied radioactivity as [^{14}C]methomyl. MHTA was a minor component accounting for 0.8% of applied radioactivity. Column leaching of the aged soil sample showed limited mobility. [^{14}C]methomyl in the leachate represented 5% of the applied radioactivity.

The results are shown in Table 9.

Table 9. Leaching of ^{13}C-methomyl from three soils when applied at 200 g/ha and eluted with water equivalent to 20 cm of rainfall (Langford-Pollard, 1994).

Soil Organic % Sand %	% of applied radioactivity						
	Leachate	Soil 0-10 cm		Soil 10-20 cm		Soil 20-30 cm	
		Extract[1]	Residue	Extract	Residue	Extract	Residue
Unaged Speyer 2.1 1.07 90.9	52	5.1	1.6	12	2.0	27	3.3
Aged Speyer 2.1 1.07 90.9	6.7	10	22	7.6	2.0	13	2.9
Speyer 2.2 4.01 82.1	9.1	8.8	3.2	13	5.7	27	11
Speyer 2.3 2.11 64.7	8.1	9.7	3.3	22	4.1	46	7.7

[1] Methanol/water (2/1).

Environmental fate in water/sediment systems

The extent of indirect photolysis of methomyl in aqueous solutions was assessed by Armbrust and Reilly (1995). The rate constant for its reaction with hydroxyl radicals generated by direct photolysis of hydrogen peroxide, measured by competition kinetics against acetophenone as a reference, was 2.3×10^{12} /M-h indicating that methomyl is relatively reactive toward hydroxyl. In further experiments degradation was measured in sterile water buffered at pH 7 in the presence and absence of excess nitrate ions and in sterile natural water exposed to simulated sunlight at 25°C. Identical solutions were run as dark controls. After 360 hours (11,261 watt-hr/m^2), equivalent to about 42 summer days in Delaware, the degradation rate increased with increasing concentrations of nitrate ions, with half-lives of 45, 9.5 and 50 sunlight equivalent days for the 100 and 1000 molar excess nitrate solutions and the sterile natural water respectively. No significant degradation was observed in the controls, or in irradiated solutions that did not contain nitrate. These data suggest that methomyl would be rapidly degraded by indirect photolysis processes in shallow or near-surface natural waters.

The fate of [^{14}C]methomyl added at nominal concentrations of 0.45 µg/ml to two natural water/sediment systems was investigated by Mayo (1994). Test vessels with water/sediment samples (55-75 g) and sieved water (6 cm above sediment) were stored 28 days in the dark at 20^{o}C with a constant flow of humidified air passing over the water surface at a height of 3 cm and flow rate of 10-50 ml/min. The pH, temperature and oxygen concentration of the water and redox potential of water and sediment were measured periodically during the acclimatization period. An equilibrium in these parameters was established in 28 days as shown below, together with the characteristics of the soils.

Source of water/sediment	Auchingilsie, UK (moving water)	Hinchingbrooke, UK (pond)
pH	7.2-7.8	7.2-7.8
O_2 concentration	60%	65%
Redox potential (of sediment)	-40 to -50 mV	-40 to -50 mV
Sand %	41	44
Silt %	37	31
Clay %	22	25
Organic matter %	5.0	10.0

The mixtures in the vessels were treated with [^{14}C]methomyl at 0.45 µg/ml, and the vessels connected to a gas-flow system with traps (two vessels for each water/sediment system sampled at 0, 0.25, 1, 2, 7, 14, 29, 60 and 102 days). Samples of water taken at each interval were radio-assayed and then analysed by HPLC and TLC. Sediment samples were extracted with water/methanol. The redox potential of the sediment samples indicated that the sediment was anaerobic during the test period. The results are shown in Tables 10 and 11.

Table 10. Distribution of radioactivity after [^{14}C]methomyl was added to water/sediment systems (Mayo, 1994).

Sample	Days						
	0	0.25	1	7	14	60	102
	% of applied radioactivity[1]						
Auchingilsie							
Acetonitrile		0.98	1.1	19	23	27	27
CO_2		0.02	0.02	1.2	14	38	46
Water	85	88	88	49	15	1.4	1.7
Sediment extract	16	14	11	14	8.0	1.4	1.1
Sediment residue	0.42	0.62	0.48	8.0	14	12	10
Total recovery	101	104	101	91	74	80	86
Hinchingbrooke							
Acetonitrile		0.67	0.94	9.2	19	24	24
CO_2		<0.03	<0.07	0.48	5.9	28	32
Water	78	74	72	54	10	1.1	0.41
Sediment extract	22	25	25	19	7.8	0.94	0.67

Sample	Days						
	0	0.25	1	7	14	60	102
	% of applied radioactivity[1]						
Sediment residue	1.4	2.4	2.0	6.9	20	16	15
Total recovery	101	102	100	90	62[2]	70[2]	72[2]

[1] Average of two flasks
[2] Low recovery attributed to inefficient trapping of carbon dioxide.

Table 11. Percentage of the applied radioactivity in water and sediment after application of [^{14}C]methomyl at a nominal rate of 0.5 µg/ml (Mayo, 1994).

Day	% of applied ^{14}C in substrate[1]					
	Water		Sediment		Total	
	Hinchingbrooke	Auchingilsie	Hinchingbrooke	Auchingilsie	Hinchingbrooke	Auchingilsie
0	73	79	8.6	6.1	82	86
0.25	69	82	8.7	4.2	86	86
1	67	81	11	3.5	84	84
2	71	74	4.5	4.2	78	78
7	28	22	2.5	1.4	23	23
14	0.1	0.1	<0.4	<0.3	0.2	0.2
29	<0.1	<0.1	<0.2	<0.3	<0.4	<0.4

[1] Average of two flasks.

Methomyl was the main compound in the water and sediment. MHTA in the water fraction peaked at 7% of the applied radioactivity on day 2 in the Hinchingbrooke sample, 1% in The Auchingilsie sample. On day 7 [^{14}C]acetamide, identified by TLC and partition HPLC, accounted for up to 14% in the Auchingilsie system, and [^{14}C]acetonitrile peaked at 16% of the applied radioactivity in both systems on day 7. The total concentration of methomyl (water + sediment) decreased from 82% of the applied radioactivity on day 0 to 0.3% on day 14 in the Hinchingbrooke sample and from 86% to 0.2% in the Auchingilsie sample so assuming first-order kinetics the half-life was 3.5 days in the Auchingilsie system and 4.8 days in the Hinchingbrooke system.

HPLC and TLC analyses of water and sediment extracts confirmed the absence of *E*-methomyl, *E*-MHTA, methomyl sulfoxide, MHTA sulfoxide, acetaldehyde and acetic acid.

The degradation of methomyl in chlorinated water was investigated by Miles and Oshiro (1990). Solutions of methomyl at various pH levels stored in the dark at 24°C were treated with 1 µM hypochlorite. Methomyl disappeared rapidly from slightly alkaline solutions at a chlorine/methomyl ratio of 10. The degradation rate increased with higher hypochlorite concentrations when the pH was buffered

at 9, and with decreasing pH. Half-lives ranged from about 0.4 min. at pH 7.6 to 12 min. at pH 8.9. Reaction rates of methomyl with chloramine were 100 to 1000 times slower than with free chlorine and varied little over the pH range of 7 to 9.

Mason *et al.* (1990) investigated the removal of methomyl from water by chlorination and ozonation. Methomyl reacted rapidly with excess chlorine in the pH range 6.0-8.5 in proportion to chlorine concentrations. At fixed chlorine concentrations reaction rates decreased with increasing pH. At ratios below 2:1 chlorine:methomyl, the chlorine concentration was insufficient to destroy all the methomyl. Light had no effect on the reaction rate. No reaction was observed at pH 7 within 24 h when chlorine dioxide was used as the disinfecting agent at 14-18:1 ClO_2:methomyl on a molar ratio basis. When 1 mg/l of methomyl was reacted with ozone the reaction was too rapid to be followed spectrophotometrically, preventing kinetic studies.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Several analytical methods based on GLC or HPLC have been developed for the determination of methomyl in plant commodities which are suitable for data collection and some, as indicated, for enforcement (Table 12). Validation data are shown in Table 13.

Table 12. Methods for the determination of methomyl in or on plant commodities.

Report (reference)	Extraction/clean-up	Method of determination
ML/PC-12 (Pease and Kirkland, 1968)	Processed crop samples were extracted three times with ethyl acetate using a homogenizer, centrifuged and the supernatant decanted. The combined organic extracts were purified by liquid-liquid partitioning and concentrated. Sodium hydroxide was added to hydrolyse methomyl to MHTA, which was then extracted with ethyl acetate.	GLC - microcoulometric sulfur detector (Column: 120 cm glass containing 10% FFAP on 80- to 100-mesh Chromosorb W, Column temperature programmed from 100° to 200°C, Vaporiser, Transfer and Furnace Temperatures: 235°, 250° and 850°C respectively, Helium Carrier Gas Flow: 100 ml/min, Helium Purge Flow: 50 ml/min, Oxygen Flow, 50 ml/min)

Report (reference)	Extraction/clean-up	Method of determination
AMR 1806-90 (Clark and Kennedy, 1990)	Processed grape samples were extracted with acetonitrile using a homogenizer and the extract filtered. Sodium chloride was then added to the filtered extract for phase separation of acetonitrile and aqueous layers and direct partitioning of methomyl to the acetonitrile layer. The acetonitrile extract was separated, partitioned with hexane and passed through a Florisil solid-phase extraction cartridge where methomyl was retained. Following elution with 50:50 acetone:hexane, the samples were evaporated to dryness and reconstituted in 15:85 acetonitrile:water.	Reversed phase HPLC-UV (Column: 5.0 µm Zorbax ODS, 250 x 4.6 mm, Column temperature: 35°C, Mobile phase: 15/85 acetonitrile/water, Flow rate: 0.8 ml/min, Detection: 233 nm)
AMR 1405-89 Protocol A. (Labare, 1990)	Samples were extracted with methanol, followed by a three step solvent partitioning clean up of extract. The partially purified extract was passed through a Celite/charcoal column, concentrated and filtered.	Reverse-phase HPLC-fluorescence (Column: 5.0 µm Zorbax C8, 250 x 4.6 mm, Column temperature: 35°C, Mobile phase: acetonitrile/water , gradient elution, Flow rate: 1.5 ml/min, Detection: post-column hydrolysis with 0.05 N sodium hydroxide forming methylamine and derivatization using *o*-phthalaldehyde and mercaptoethanol, 0.5 ml/min flow rate, 100°C reactor temperature and excitation and emission wavelengths of 340 and 455 nm respectively)
AMR 3077-94 Revision No. 1, (Grigor, 1994)	Samples were soaked with water, followed by acetonitrile homogenization and the organic extract was separated and filtered. Sodium chloride was then added to the filtered extract for phase separation and direct partitioning of methomyl into the acetonitrile layer. The acetonitrile extract was separated, partitioned with hexane to remove fats, oils and other hexane-soluble coextractives and passed through a Florisil SPE cartridge. The eluate was evaporated to dryness and reconstituted in 15:85 acetonitrile/water. Note: Revision No. 1 supersedes and stands alone from the original report.	Reverse-phase HPLC-fluorescence (Column: 5.0 µm Zorbax RX-C8, 150 x 4.6 mm, Column temperature: 40°C, Mobile phase: acetonitrile/water , gradient elution, Flow rate: 1.0 ml/min, Detection: post-column hydrolysis with 0.2N sodium hydroxide forming methylamine and derivatization *o*-phthalaldehyde and *N*,*N*-dimethyl-2-mercaptoethylamine, 0.13 ml/min flow rate, 100°C reactor temperature and excitation and emission wavelengths of 330 and 466 nm respectively)

Report (reference)	Extraction/clean-up	Method of determination
AMR 3015-94 Revision No. 2 (Rühl, 1998)	Processed pea seed, pea hay, sorghum forage, sorghum hay, soya bean hay, or sugar beet foliage samples were soaked with water for 10-minutes, followed by an acetonitrile extraction using a homogenizer. For processed apple or grape samples, the same extraction procedure was used, but the water soak was omitted. Purification by acetonitrile/hexane partitioning, followed by a Florisil SPE clean up of the acetonitrile layer. After elution with 50:50 acetone:hexane, the eluate was evaporated to dryness and reconstituted in 15:85 acetonitrile:water. Note that Revision No. 2 contains the original method, adds watery fruit samples and includes upgrades of Revision No. 1.	Reverse-phase HPLC-fluorescence As Grigor, 1994.
AMR 4258-96 (Weidenauer *et al*., 1998)	Processed apple, orange, grape, or cotton seed samples were extracted with acetonitrile using a homogenizer. Sodium chloride added to the extract for phase separation and direct partitioning of methomyl to the acetonitrile layer. The acetonitrile extract was purified by hexane partitioning and passed through Florisil solid-phase extraction cartridge. Following elution with 50:50 acetone:hexane, the eluate was evaporated to dryness, reconstituted in 15:85 acetonitrile:water and filtered.	Reverse-phase HPLC-fluorescence As Grigor, 1994, except final flow rate 0.2 ml/min
Literature (Multi-residue Method 2, Inspectorate for Health Protection Part 1, 1996)	Processed crop samples were extracted with acetone and subsequently 50/50 dichloromethane/light petroleum using a homogenizer. After centrifugation, the organic extract was decanted, evaporated to dryness and redissolved in dichloromethane using an ultrasonic bath. The samples were passed through an aminopropyl-bonded silica solid-phase extraction column and the eluate was collected. Following elution with 99/1 dichloromethane/methanol , the eluate was evaporated to dryness, reconstituted in 20/80 acetonitrile/water using an ultrasonic bath and filtered.	Reverse-phase HPLC-fluorescence (Column: 4.0 µm Supersphere RP-8, 250 x 4.0 mm, Column temperature: 30°C, Mobile phase : 20/80 acetonitrile-water, 20/80 methanol/water and 60/40 acetonitrile/water (gradient elution), Flow rate: 0.75 ml/min, Detection: post-column hydrolysis using a 15 µm Aminex A27 strong anion exchange resin, 0.1 ml/min flow rate, 120°C reactor temperature, and excitation and emission wavelengths of 340 and 455 nm respectively)
Literature (de Kok *et al*., 1987)	Processed and cleaned up fruit or vegetable samples extracted as above, but finally reconstituted in 28/72 acetonitrile/water. Processed grain samples were extracted with 50/50 dichloromethane/acetone by soaking overnight. The organic extract was concentrated and purified as above.	Reverse-phase HPLC-fluorescence (Column: 5.0 µm Lichrosphere 100 RP-18, 250 x 4.0 mm, Column temperature: 30°C, Mobile phase: 28/72 acetonitrile/water , Flow rate: 1.0 ml/min, Detection: post-column hydrolysis with 0.05 N sodium hydroxide forming methylamine and derivatization with *o*-phthalaldehyde and 2-mercaptoethanol, 0.5 ml/min flow rate, 100°C reactor temperature and excitation and emission wavelengths of 340 and 455 nm respectively)

Report (reference)	Extraction/clean-up	Method of determination
Literature (de Kok and Hiemstra, 1992)	Processed fruit or vegetable samples extracted as above. The extract was purified by automated solid-phase extraction (SPE) with an aminopropyl cartridge. After elution with 99/1 dichloromethane/methanol , the collected fraction was evaporated to dryness by heating in nitrogen stream, then redissolved in 10/90 acetonitrile water and cleaned up as above.	On-line SPE-HPLC-fluorescence (Column: 4.0 µm Supersphere RP-8, 250 x 4.0 mm, Column temperature: 30°C, Mobile phase : 80/20 acetonitrile-water and 10/90 acetonitrile/water (gradient elution), Flow rate: 0.8 ml/min, Detection: post-column hydrolysis reaction using a 15 µm Aminex A27 strong anion exchange resin, 0.2 ml/min flow rate, 120°C reactor temperature, and excitation and emission wavelengths of 340 and 455 nm respectively)

Table 13. Validation of analytical methods for the determination of methomyl in plant products.

Report no. (reference)	Fortification (mg/kg)	Mean recovery (%)	Range or relative standard deviation (%) no. of samples	Sample	Control interference
ML/PC-12 (Pease and Kirkland, 1968)	0.02-4.0	98	86-110 (n=9)	Cabbage	Insignificant to none
	0.02-0.26	96	83-115 (n=11)	Sweet corn kernels	
	0.04-0.20	92	83-100 (n=3)	Sweet corn stalk	
	0.02-0.22	89	80-98 (n=7)	Soya bean leaves	
	0.02-0.20	90	84-95 (n=4)	Soya bean forage	
	0.02-0.20	81	75-86 (n=4)	Cotton seed	
	0.02-0.40	92	86-95 (n=5)	Tobacco	
	0.02-0.40	97	87-104 (n=8)	Snap beans, pods	
	0.02-0.40	90	83-104 (n=6)	Snap bean forage	
	0.02-1.0	86	80-96 (n=6)	Tomatoes	
	0.02-2.0	102	96-110 (n=7)	Celery	
	0.02-0.26	93	79-115 (n=6)	Lima beans	
	0.02-0.26	91	83-108 (n=6)	Potatoes	
	0.02-0.42	105	87-115 (n=5)	Peaches	
AMR 1806-90 (Clark and Kennedy, 1990)	0.02, 0.50 and 5.0	98	5.8 (n=6)	Grapes	Insignificant
AMR 1405-89 Protocol A (Labare, 1990)	0.05 and 5.0	89 32	15.7 (n=4) 9.4 (n=4)	Lettuce Peanuts	None

Report no. (reference)	Fortification (mg/kg)	Mean recovery (%)	Range or relative standard deviation (%) no. of samples	Sample	Control interference
AMR 3077-94 Revision No. 1 (Grigor, 1994)	10 and 20 0.20 and 0.40 1.0 and 2.0 1.0 and 2.0 2.0 and 4.0	103 94 96 94 103	9.9 (n=4) 9.0 (n=4) 20.4 (n=4) 6.4 (n=4) 3.9 (n=4)	Pea hay Pea seed Sorghum forage Sorghum hay Sugar beet foliage	None
AMR 3015-94 Revision No. 2 (Rühl, 1998)	0.02, 0.20, 0.40, 1.0, 2.0, 10 and 20	83 88 90 90 98 87 83 90	6.0 (n=9) 5.7 (n=9) 10.0 (n=9) 8.9 (n=9) 14.3 (n=16) 8.0 (n=21) 4.8 (n=45) 7.8 (n=33)	Pea seed Pea hay Sorghum forage Sorghum hay Soya bean hay Sugar beet foliage Apple Grapes	Insignificant to none
AMR 4258-96 (Weidenauer *et al*., 1998)	0.02 and 0.20	94 94 91 96	3.9 (n=6) 14.1 (n=6) 9.9 (n=6) 7.9 (n=6)	Apple Orange Grapes Cotton seed	None

Report no. (reference)	Fortification (mg/kg)	Mean recovery (%)	Range or relative standard deviation (%) no. of samples	Sample	Control interference
Literature (De Kok, *et al.*, 1987)	0.05 and 0.50	100	1.4 (n=10)	Grain	Insignificant to none
		88	(n=2)	Apple	
		82	(n=2)	Beans	
		79	(n=2)	Carrot	
		79	(n=2)	Cauliflower	
		80	(n=2)	Celery	
	0.20	80	(n=2)	Cucumber	
	0.20	82	(n=2)	Leek	
		81	(n=2)	Onion	
		83	(n=2)	Orange	
		79	(n=2)	Potato	
		81	(n=2)	Spinach	
		84	(n=2)	Strawberry	
		87	2.8 (n=5)	Carrot	
		80	2.8 (n=5)	Cauliflower	
Literature (De Kok and Hiemstra, 1992)	0.13	79	2.4 (n=5)	Apple	
		88	1.5 (n=5)	Beans	
		79	2.1 (n=5)	Carrot	
		78	1.7 (n=5)	Cauliflower	
		83	2.3 (n=5)	Endive	
		84	1.8 (n=5)	Onion	
		77	2.0 (n=5)	Orange	
		81	2.2 (n=5)	Paprika	
		78	1.2 (n=5)	Peach	
		81	2.3 (n=5)	Potato	
		78	3.0 (n=5)	Strawberry	
		91	1.9 (n=5)	Rice	

To determine the efficacy of acetonitrile as an extraction solvent for the determination of methomyl residues in dry and watery crop samples as described by Rühl, tests were conducted on pea seed and hay, sorghum fodder and hay, and sugar beet foliage using radiolabelled methomyl (Rühl, 1998). The average extraction efficiency was 103 ± 3 % (n=10).

Methods reported for the determination of methomyl in domestic animal commodities are generally modifications of those for plant products described above and are shown in Table 14, with validation data in Table 15.

Table 14. Methods for the determination of methomyl and its metabolites in animal tissues.

Reference (Author, Year)	Extraction/clean-up	Method of determination
ML/PC-12 (Pease and Kirkland, 1968)	As for plant samples (Table 12)	GC-Microcoloumetric sulfur detector GC conditions as for plant samples
AMR 898-87 (Powley, 1991a,b)	Methomyl was extracted from milk and tissue samples on a C-18 adsorbent and eluted with methylene chloride. The eluate was concentrated and further purified by passing it through a silica solid-phase extraction cartridge. Following elution with 3% methanol in methylene chloride, the samples were concentrated and reconstituted in 10:90 acetonitrile:5mM phosphate buffer (pH 3). Principal metabolites: (1) MHTA Processed tissue samples were extracted on C-18 adsorbent with ethyl acetate as eluent. The eluate was concentrated and further purified on a silica solid-phase extraction cartridge. Following elution with 10% methanol in ethyl acetate, the samples were concentrated. For milk samples, the same procedure was followed without silica clean-up.	Reverse-phase HPLC-UV (Column: 5-µm C-18 column, 15 cm x 4.6 mm i.d., Mobile Phase: 10/90 (v/v) acetonitrile/5 mM sodium dihydrogen phosphate (pH=3), Flow rate: 2.0 ml/min, Detection: 235 nm) GC-Nitrogen phosphorus thermionic detector (Column: 15 m x 530 µm fused silica capillary wall-coated with DB-Wax, Column temperature: Programmed from 130° to 150°C for milk and cream analysis and 60° to 200°C for animal tissue analysis, Injector and detector temperature: 250° and 300°C respectively, Helium carrier gas flow: 23 ml/min, Hydrogen flow: 1.5 ml/min, Air flow: 100 ml/min)

Reference (Author, Year)	Extraction/clean-up	Method of determination
AMR 898-87 (Powley, 1991a,b)	(2) [^{14}C]acetonitrile Milk or cream samples were homogenised, mixed with saturated sodium chloride solution and placed in a purge and trap sampler, which was then heated and purged with helium. Acetonitrile and other volatile components were trapped on Tenax® adsorbent, desorbed by heating the trap, and backflushed into a GC column packed with Porapak® Q adsorbent. The acetonitrile trapped at the head of the column was separated from other volatiles by temperature programming and collected in an impinger filled with xylene, which was then mixed with scintillation cocktail. Processed tissue samples were prepared and analysed as above, but homogenized after mixing with saturated sodium chloride solution. For processed fat samples, sodium hydroxide was added with homogenization before mixing with sodium chloride. (3) Acetamide Processed milk samples were extracted with acetone using a rotating mixer and centrifuged. Supernatant decanted, concentrated, washed with hexane, then diluted with methanol. Processed tissue samples were homogenised in 95:5 acetone:water, centrifuged, supernatant separated and evaporated until only the aqueous layer remained, then partitioned with hexane and ethyl acetate using a rotary mixer and diluted with methanol.	Liquid scintillation counting (LSC) Purge and trap conditions: (Temperatures: 100°, 40°, 100° and 100°C for transfer line, mount, bottom of trap and valve oven respectively, Purge gas: Helium at 20 ml/min, Prepurge time: 0.7 min, Heating time: 0.15 min, Sample temperature: 75°C, Purge time: 20 min, Dry purge: 2 min, Desorption: 4 min at 200°C, Bake time: 8 min at 225°C GC Conditions: column: Porapak® Q 100/120, 4 ft x 2 mm i.d., Carrier/desorb gas: Helium at 15 ml/min, Injector: 100°C, Detector temperature: FID, 300°C (about 1 ml/min split flow to detector), Valve switching time: flow was diverted to impinger 8 min into the run and diverted away 4 min later) GC-Nitrogen phosphorus detector (Column: 15 m x 0.26 mm i.d. x 0.25 µm DB-Wax fused silica, Column temperature: Programmed from 75° to 210°C, Injector and Detector temperatures: 275° and 300°C respectively, Helium carrier gas and make up gas flow rates: 2 and 30 ml/min respectively, Air and hydrogen Flow rates: optimum)
	Radiolabelled acetamide Processed milk samples were extracted with acetone transferred into water, washed with hexane, then diluted with methanol. Processed tissue samples were treated as above. The final extracts were fractionated using HPLC. The collected eluate was mixed with Formula-963 scintillation cocktail.	Liquid scintillation counting

Reference (Author, Year)	Extraction/clean-up	Method of determination
AMR 2964-94 (Daun, 1995)	Milk or processed tissue samples were extracted on a solid-phase matrix. Following elution with methylene chloride, the eluate was concentrated and further purified by passing through a silica solid-phase extraction cartridge and eluting with 3% methanol in methylene chloride. The eluate was concentrated and purified by partitioning with 9:1 acetonitrile:water and hexane. The acetonitrile:water layer was separated, concentrated, reconstituted in 10% acetonitrile in water and filtered.	Reverse-phase HPLC-fluorescence (Column: 5.0 µm C-18, 4.6 x 150 mm, Column temperature: 40°C, Mobile phase: acetonitrile/water, gradient elution, Flow rate: 1.0 ml/min, Detection: post-column hydrolysis with sodium hydroxide forming methylamine and derivatization using *o*-phthalaldehyde and 2-mercaptoethanol, 0.6 ml/min flow rate, 125°C reactor temperature and excitation and emission wavelengths of 330 and 465 nm respectively)
Literature (Ali, 1989))	Processed bovine, pig, or duck liver samples were mixed with anhydrous sodium sulfate and extracted twice with methylene chloride (CH_2Cl_2) using a homogenizer. The combined organic extracts were filtered twice through anhydrous sodium sulfate. The filtered extract was concentrated and dissolved in 1:1 methylene chloride-hexane solution, filtered and passed through a GPC SX-3 gel column for clean-up. The residue fraction was collected, evaporated to dryness and reconstituted in CH_2Cl_2. This was then passed through an aminopropyl solid-phase extraction cartridge and eluted with 1.5% methanol in CH_2Cl_2. The eluate was evaporated to dryness, reconstituted in methanol and filtered.	Reverse-phase HPLC-fluorescence (Conditions as above, but excitation and emission wavelengths 340 and 418 nm respectively)

Table 15. Validation of analytical methods for the determination of methomyl and metabolites in ruminant commodities and urine.

Report no. (reference)	Fortification (mg/kg)	Mean recovery (%)	Range or relative standard deviation (%) and number of samples	Sample	Control interference
ML/PC-1	0.08-1	94	88-100 (n=2)	Liver	None
(Pease and Kirkland, 1968)	0.08-0.2	98	90-105 (n=2)	Kidney	
	0.02-0.08	92	85-96 (n=3)	Muscle	
	0.04-0.12	96	93-98 (n=2)	Fat	
	0.2-1.4	90	80-97 (n=4)	Urine	

Report no. (reference)	Fortification (mg/kg)	Mean recovery (%)	Range or relative standard deviation (%) and number of samples	Sample	Control interference
AMR 898-87 (Powley, 1991a,b)	Methomyl				None
	0.02, 0.10, 0.20	89	7.5 (n=19)	Milk (whole/skimmed)	
	and 0.50	83	5.2 (n=5)	Cream	
		87	13.9 (n=18)	Fat	
		87	10.4 (n=10)	Kidney	
		79	10.8 (n=14)	Liver	
		88	11.8 (n=13)	Muscle	
	MHTA				
	0.02, 0.10 and	95	8.0 (n=16)	Milk	
	0.50	94	12.4 (n=6)	Cream	
		58	15.3 (n=14)	Fat	
		70	14.2 (n=9)	Kidney	
		65	17.2 (n=9)	Liver	
		68	10.7 (n=9)	Muscle	
	[^{14}C]Acetamide	99	4.6 (n=6)	Milk	
	0.02, 0.10 and 0.50	68	17.3 (n=3)	Muscle	
		73	4.8 (n=3)	Liver	
AMR 2964-94 (Daun, 1995)	0.01 and 0.05	91	7.7 (n=44)	Milk (whole/skimmed)	Insignificant to none
		88	8.2 (n=8)	Cream	
		99	8.2 (n=13)	Liver	
		91	4.8 (n=11)	Kidney	
		87	10.2 (n=11)	Muscle	
		94	11.5 (n=8)	Fat	
Literature	0.005, 0.01 and 0.02	69	24.3 (n=30)	Beef Liver	Insignificant to none
(Ali, (1989))		82	15.5 (n=36)	Pork Liver	
		91	17.5 (n=36)	Duck Liver	

Extraction efficiency studies were conducted for the determination of acetonitrile and acetamide using the method described by Powley. For [^{14}C]acetonitrile the average extraction was acceptable at 73 ± 13 % for the 4 samples of liver, kidney, muscle and fat, and for acetamide was also acceptable (overall 70 ± 13 %, n=24).

Methods were also reported for the determination of methomyl in environmental samples. The methods for soils are shown in Table 16.

Table 16. Methods for the determination of methomyl in soil.

Report (reference)	Extraction/clean-up	Method of determination
ML/PC-12 (Pease and Kirkland, 1968)	As for plant samples (Table 12)	GC-microcoloumetric sulfur detector GC conditions as for plant samples
ML/PC-12 Supplement 2 (Pease, 1969)	As above.	GC-flame photometric detector GC Conditions as for plant samples
AMR 1215-88 (S.M. Kennedy, 1989)	Soil samples were wetted with deionized water and extracted three times with ethyl acetate in a wrist-action shaker. The supernatant was filtered and the combined organic extracts concentrated and passed through a silica gel column. Following elution with 10% methanol in ethyl acetate, the eluate was blown to dryness and reconstituted in 84:15:1 water:acetonitrile:acetic acid.	Reverse-phase HPLC-UV (Column: 5.0 µm Zorbax ODS, 250 x 4.6 mm, Column temperature: ambient, Mobile phase: 14/85/1 acetonitrile/water/acetic acid, Flow rate: 0.8 ml/min, Detection: 233 nm)
AMR 1921-91 (C.M. Kennedy, 1991d)	As above except silica column omitted.	Reverse-phase HPLC-UV (Column: 5.0 µm Zorbax RX, 250 x 4.6 mm, Column temperature: 35°C, Mobile phase: 15/85 acetonitrile/water, Flow rate: 0.8 ml/min, Detection: 233 nm)
Literature (Honing *et al.*, 1996))	Sediment samples were sieved, freeze-dried and extracted with acetone-methylene chloride by Soxhlet. The extract was evaporated to dryness, reconstituted in hexane and passed through an aminopropyl-bonded silica column. Following elution with 25:75 acetone-methylene chloride, the eluate was evaporated to dryness and reconstituted in 20:80 methanol:water.	LC-Ionspray MS (Column: 3.0 µm Licrosphere 60 RP-select B base-deactivated phase, 125 x 3.0 mm , Mobile phase: methanol and water, gradient elution, Flow rate: 0.3 ml/min, MS Conditions: Flow rate: 350 L/h drying gas and 15 L/h nebulizer gas, Temperature: 125°C, ion source: Cone extraction voltage 20V, Mode: selected ion monitoring , $[M+Na]^+$ ion)

Report (reference)	Extraction/clean-up	Method of determination
AMR 2396-92 (Strahan and Wilfred, 1993) AMR 2513-92 (Leva and McKelvey, 1995)	Soil samples were extracted with acetone/phosphate buffered solution (PBS), centrifuged and supernatant filtered through a 0.45-µm Durapore membrane (a polyvinylidine difluoride filter). The filtered extract was evaporated near to dryness and reconstituted in PBS.	Enzyme-linked immunosorbent assay (ELISA)-UV (Separation: Rabbit polyclonal antibody was used forming methomyl hapten, Detection:405 nm, anti-rabbit antibody-enzyme/substrate reaction to produce *p*-nitrophenyl phosphate)
AMR 2759-93 (Rühl *et al*., 1994)	Soil samples were extracted twice with methanol using a wrist-action shaker and suction. The combined filtrates were evaporated to dryness, reconstituted in deionized water and passed through a C-18 solid-phase extraction column, where methomyl was retained. Methomyl was eluted with acetone, the eluate evaporated to dryness and the residue dissolved in 10:90 acetonitrile:water.	Reverse-phase HPLC-fluorescence LC conditions as for plant samples (Rühl, 1988) except mobile phase 20:80 acetonitrile/water
AMR 2311-92 (Rühl, 1995)	Soil samples were extracted twice with methanol using a wrist-action shaker and suction filtered. The filtrate was evaporated to dryness, reconstituted in deionized water and passed through a C-18 solid-phase extraction column, where methomyl was retained. Methomyl was eluted with acetone, the eluate evaporated to dryness and the residue dissolved in 10% acetonitrile in water.	Reverse-phase HPLC-fluorescence (Column: 5.0 µm Zorbax RX or ODS 2, 150 x 4.6 mm, Column temperature: 40°C, Mobile phase: 25/75 or 20/80 acetonitrile/water, Flow rate: 1.2 ml/min, Detection: as before, 100 or 125°C reactor temperature and excitation and emission wavelengths 228 and 418 or 330 and 466 nm respectively)
Literature (Johnson *et al.*, 1997))	Soil samples were extracted with 4% methanol in deionized water using an orbital shaker and centrifuged. The extract was decanted and passed through a graphite carbon solid-phase extraction cartridge for clean-up. Following elution with methanol, the eluate was diluted with methanol and filtered.	Reverse-phase HPLC-fluorescence (Column: 5.0 µm C-18 carbamate, 100 x 4.6 mm, Column temperature: 40°C, Mobile phase: methanol/water, gradient elution, Flow rate: 1.0 ml/min, Detection: post-column hydrolysis with sodium hydroxide and derivatization with *o*-phthalaldehyde and 2-mercaptoethanol, excitation and emission wavelengths of 330 and 466 nm respectively)

Table 17. Validation of analytical methods for the determination of methomyl in soil.

Report (reference)	Fortification levels (mg/kg)	Overall Mean recovery (%)	Range or Relative standard deviation (%) and number of samples	Control Interference
Literature (Pease and Kirkland, 1968)	0.04-4.0	63	(n=12)	Insignificant to none
AMR 1215-88 (S.M. Kennedy, 1989)	0.02, 0.04, 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 3.0, 4.0 and 5.0	90	11.3 (n=124)	Insignificant to none

Report (reference)	Fortification levels (mg/kg)	Overall Mean recovery (%)	Range or Relative standard deviation (%) and number of samples	Control Interference
AMR 1921-91 (C.M. Kennedy, 1991d)	0.02, 0.10 and 0.50	86	6.4 (n=29)	Insignificant
AMR 2396-92 (Strahan and Wilfred, 1993)	0.01, 0.05 and 0.10	111	12.6 (n=18)	None
AMR 2759-93 (Rühl *et al*., 1994)	0.01, 0.20, 0.50, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0	97	12.4 (n=9)	Insignificant to none
AMR 2311-92 (Rühl, 1995)	0.001, 0.002, 0.003, 0.004, 0.005, 0.01, 0.02, 0.03, 0.040, 0.05, 0.10, 0.20, 0.50 and 1.0	99	9.1 (n=71)	Insignificant to None
AMR 2513-92 Volume 2 (Leva and McKelvey, 1995)	0.01, 0.05, 0.10, 0.20, 0.30, 0.50, 5.0 and 10.0	96	13.5 (n=40)	None

A study of extraction efficiency using radiolabelled methomyl was summarised by C.M. Kennedy (1992). Recoveries of ^{14}C were greater than 90% from treated soil extracted with methanol/water and methanol after aerobic incubation for 0, 1, 2, 4, 8, 14 and 21 days and 1, 2 and 3 months. The overall extraction efficiency was 97 ± 3% (n=10).

Analytical methods submitted for the determination of methomyl in water are summarized in Table 18.

Table 18. Analytical methods for the determination of methomyl in water.

Report (reference)	Extraction/clean-up	Method
AMR 1091-88 (McIntosh, 1988)	Groundwater samples were treated with monochloroacetic acid buffer to adjust pH to 3.0, then filtered through a 0.2-µm polyester filter. (A multianalyte method for methylcarbamoyl oximes and methylcarbamates)	Reverse-phase HPLC-fluorescence (Column: 5.0 µm Altex Ultrasphere ODS, 250 x 4.6 mm, Column temperature: 40°C, Mobile phase: 15/85 methanol/water (v/v) and methanol, gradient elution, Flow rate: 1.0 ml/min, Detection: post-column hydrolysis with 0.05 N sodium hydroxide and derivatization with *o*-phthalaldehyde and 2-mercaptoethanol, 95°C reactor temperature and excitation and emission wavelengths of 230 and 418 nm respectively)

Report (reference)	Extraction/clean-up	Method
AMR 1392-89 (Battelle, 1991)	Groundwater samples were treated with sodium chloride, followed by HCl or NaOH to adjust pH to 3.0, then passed through a C-18 SPE cartridge, where methomyl was retained. Following elution with acetonitrile, the eluate was evaporated to dryness and the residue reconstituted in 40:60 methanol:1.0 M acetate buffer solution.	Reverse-phase HPLC-UV (Column: 5.0 μm Zorbax ODS, 250 x 4.6 mm, Column temperature: ambient, Mobile phase: 15/85 acetonitrile/water, Flow rate: 1.0 ml/min, Detection: 240 nm)
AMR 2311-92 (Rühl, 1995)	Groundwater, soil-pore water, tank mix, or irrigation water samples were centrifuged to remove sand and silt, then passed through a C-18 solid-phase extraction cartridge. Following elution with acetone, the eluate was evaporated to dryness and reconstituted in 10% acetonitrile in HPLC grade water.	Reverse-phase HPLC-fluorescence (LC conditions as above for soil samples)
AMR 2396-92 (Strahan and Wilfred, 1993)	Paddy, ditch, or stream water samples filtered through a 0.45 micron Durapore membrane (a polyvinylidine difluoride filter) and then diluted with phosphate buffered solution (PBS) (1:2) (to minimise any matrix effect)	Enzyme-linked immunosorbent assay (ELISA)-UV (Separation: Rabbit polycyclonal antibody was used forming methomyl hapten, Detection:405 nm, anti-rabbit antibody-enzyme/substrate reaction to produce p-nitrophenylphosphate)
AMR 2513-92 (Leva and McKelvey, 1995)	Pond, stream, or run-off water samples filtered and diluted with PBS as above	Enzyme-linked immunosorbent assay (ELISA)-UV (Separation and detection as above)
Literature (Johnson *et al.*, 1997))	Water samples were extracted and preconcentrated on a graphite carbon solid-phase extraction cartridge. Following elution with methanol, the eluate was diluted with methanol and filtered.	Reverse-phase HPLC-fluorescence (LC conditions as for soil)
Literature (Honing *et al.*, 1996))	Surface water samples were filtered through 0.45 μm PTFE fibre-glass, then extracted and concentrated using a C-18-bonded silica disk. Following elution with acetonitrile, the eluate was evaporated nearly to dryness and the residue dissolved in methanol.	LC-Ionspray MS (LC and MS Conditions as for soil)

Report (reference)	Extraction/clean-up	Method
Literature (Chiron *et al.*, 1995))	Groundwater samples were filtered, acidified to pH 2 with sulfuric acid, then extracted and preconcentrated using an automated on-line solid-phase extraction (SPE) system. The C-18 Empore extraction disk used was conditioned with methanol followed by acidified water (pH 3, trifluoroacetic acid) at 1.0 ml/min flow rate. Sample preconcentation flow rate was at 2.0 ml/min and desorption flow rate was initially 1.1 ml/min decreasing to 0.8 ml/min.	On-line SPE/HPLC-fluorescence (Column: 4.0 µm Supersphere 60 RP-8, 250 x 4.6 mm , Mobile phase: acetonitrile-methanol-water and acetonitrile-water (gradient elution), Flow rate: 0.8 ml/min Detection as above)
USA EPA Method 531.1 (Munch (ed.), 1995)	Water samples were treated with monochloroacetic acid buffer to adjust pH to 3, then filtered through a 0.45 µm Millipore type HA filter. An aliquot was injected onto a reversed-phase HPLC column.	Reverse-phase HPLC-fluorescence (Column: 4.0 µm Novapak C-18, 150 x 3.9 mm , Mobile phase: methanol and water, gradient elution, Flow Rate: 1.0 ml/min, , Detection as before)

Table 19. Validation of analytical methods for the determination of methomyl in water.

Report (reference)	Fortification (mg/kg)	Mean recovery (%)	Relative standard deviation/no. samples	Sample	Control interference
AMR 1091-88 (McIntosh, 1988)	2.50	98 105	4.0 (n=8) 9.0 (n=8)	Artificial Ground Water (Absopure Natural Artesian Spring Water) Organic-Contaminated Artificial Ground Water	None
AMR 1392-89 (Battelle, 1991)	0.10 and 0.15	97 85	17.5 (n=21) 23.9 (n=21)	Type 1 Groundwater (Artificial recharged Groundwater) Type 2 Groundwater (From mountain clefts)	None
AMR 2396-92 (Strahan and Wilfred, 1993)	0.05, 0.10, 0.25, 0.50 and 1.0	99	10.6 (n=45)	Paddy, Ditch and Stream Water	None
AMR 2311-92 (Rühl, 1995)	0.10, 0.20, 0.30, 0.40, 0.50, 1.0 and 2.0	90	11 (n=143)	Groundwater, Soil-pore water, Tank Mix samples and Irrigation Water	Insignificant to none
AMR 2513-92 Volume 2 (Leva and McKelvey, 1995)	0.20, 0.50, 1.0, 2.0, 5.0, 10, 100, 500 and 1000	97	13.4 (n=83)	Pond, Stream and Run-off Water	None

Report (reference)	Fortification (mg/kg)	Mean recovery (%)	Relative standard deviation/no. samples	Sample	Control interference
Literature. (Johnson *et al.*, 1997))	5.0 and 50	102	5 (n=6)	Hard Water	Insignificant to none
EPA Method 531.1. (Munch (ed.), 1995)	2.5	98 105	4.0 (n=7-8) 9.0 (n=7-8)	Synthetic Water 1 (Absopure Nature Artesian Spring Water) Synthetic Water 2 (Organic-Contaminated)	Insignificant to none

Stability of residues in stored analytical samples

Methomyl stability has been determined in a variety of crops, soil, water and animal tissues.

In crops, stability has been demonstrated in homogenized and/or whole crop samples representing root, grain, watery and oily commodities (Milby, 2000; Kennedy and Devine, 1993a-c; Kennedy and Tomic, 1993a,b; Behmke, 1998). The results are shown in Table 20.

Table 20. Storage stability of methomyl in various frozen plant commodities.

Sample	Fortification	Storage (^{o}C)	Storage (months)	Concurrent fortification recovery[1] (%)	Methomyl remaining[2] (%)	Reference/method
Soya bean hay	1.0 mg/kg	-20	0	91	87, 80 (84)	AMR2955-94
			3	88	88, 85 (87)	AMR1806-90
			6	87	79, 76 (78)	
			12	83	78, 78 (78)	
			18	87	85, 78 (82)	
			26	87	83, 79 (81)	
Maize (kernels)	0.10 mg/kg	-20	0	80	72, 76 (74)	AMR1770-90
			1	92	70, 70 (70)	AMR1806-90
			3	84	65, 59 (62)	
			6	65	75, 74 (74)	
			9	89	53, 56 (54)	
			12	81	74, 69 (72)	

Sample	Fortification	Storage (°C)	Storage (months)	Concurrent fortification recovery[1] (%)	Methomyl remaining[2] (%)	Reference/method
			18	65	66, 72 (69)	
			19.5	74	75, 79 (77)	
			24	82	75, 69 (72)	
Bean seed (whole pinto seed)	Field incurred 0.34 ± 0.04 (n=6)	-20	1	47[2] (91)	115, 129, 159 (135)	AMR3741-96 AMR1806-90 Average fresh fortification recovery
			3	42 (71)	79, 120, 91 (97)	
			6	43 (80)	102, 97, 112 (103)	
			12	41 (83)	68, 85, 97 (83)	
			18	65 (78)	109, 88, 91 (96)	
			26	41 (39)	88, 91, 94 (91)	
Potato (whole tuber)	Field incurred 0.47±0.07 (n=6)	-20	1	88[3] (90)	102, 81, 102 (95)	AMR3741-96 AMR1806-90
			3	85 (80)	87, 91, 85 (88)	
			6	81 (84)	81, 89, 96 (89)	
			12	84 (94)	104, 70, 87 (87)	
			18	85 (78)	117, 119, 119 (118)	
			26	76 (78)	94, 98, 89 (94)	
Peanut (whole kernels)	Field incurred 0.44±0.04	-20	1	76[2] (106)	109, 111, 130 (117)	AMR3741-96 AMR1806-90

Sample	Fortification	Storage (°C)	Storage (months)	Concurrent fortification recovery[1] (%)	Methomyl remaining[2] (%)	Reference/method
	(n=6)		3	68 (98)	91, 114, 111 (105)	
			8	72 (108)	70, 70, 64 (68)	
			12	64 (89)	95, 91, 111 (99)	
			18	74 (71)	141, 120, 100 (120)	
			26	61 (84)	66, 64, 73 (68)	
Sorghum forage (whole)	Field incurred 2.4±0.12	-20	1	78[3] (85)	75, 54, 110 (79)	AMR4344-97 AMR1806-90
			3	78 (82)	75, 54, 110 (110)	
			6	85 (82)	88, 92, 92 (92)	
			12	96 (96)	71, 120, 110 (100)	
			22	90 (81)	130, 110, 100 (110)	
			26	90 (107)	88, 130, 79 (96)	
Sorghum hay (whole)	Field incurred 3.2±0.36	-20	1	74[3] (78)	78, 120, 130 (110)	AMR4344-97 AMR1806-9
			3	69 (70)	110, 81, 140 (110)	
			6	120 (145)	150, 170, 150 (150)	
			12	74 (81)	100, 110,	

Sample	Fortification	Storage (°C)	Storage (months)	Concurrent fortification recovery[1] (%)	Methomyl remaining[2] (%)	Reference/method
					140 (120)	
			22	74 (82)	100, 170,	
					170 (150)	
			26	-[4] (96)[5]	130, 130,	
					110 (120)	
Sorghum fodder (stover)	Field incurred	-15 to -25	1	84[6]	0.41, 0.43,	AMR 3298-95
	0.48±0.03				0.41, 0.42,	AMR 3015-94
(homo-genized)					0.41(0.42)	
			3	88		
Lettuce, Head	5.0 mg/kg	-15 to -25	0	88[7]	96, 96 (96)	AMR 1806-90
						AMR1764-90
			1	88	88, 92 (90)	
			3	90	96, 100	
					(98)	
			6	70	68, 72 (70)	
			6.5	74	72, 76 (74)	
			9	94	96, 94 (96)	
			12	84	94, 84 (88)	
			18	108	98, 100	
					(100)	
			24	84	92, 88 (90)	
Broccoli	2.0 mg/kg	-15 to -25	0	95[8]	90, 90 (90)	AMR 1765-90
			1	85	85, 85 (85)	AMR 1806-90
			3	80	85, 85 (85)	
			6	95	90, 90 (90)	
			9	100	90, 95 (92)	
			12	100	100, 100	
					(100)	
			18	90	80, 80 (80)	

Sample	Fortification	Storage (°C)	Storage (months)	Concurrent fortification recovery[1] (%)	Methomyl remaining[2] (%)	Reference/method
			24	110	95, 90 (92)	
Orange (finely chopped)	2.0 mg/kg	-15 to -25	0 1 3 6 9 9.3 12 16 18 24	95[8] 75 100 95 90 95 75 85 90 105	95, 95 (95) 75, 90 (82) 85, 85 (85) 75, 70 (72) 55, 55 (55) 45, 49 (47) 46, 36 (41) 34, 34 (34) 30, 30 (30) 16, 18 (17)	AMR 1767-90 AMR 1806-90
Orange (half)	Field incurred 0.96	-15 to -25	24	100[9]	104	AMR 1767-90 AMR 1806-90
Apple	1.0 mg/kg	-15 to -25	0 1 3 6 9 12 18 24	92[9] 93 91 95 88 94 93 96	98, 94 (96) 97, 94 (96) 94, 93 (94) 91, 83 (87) 89, 87 (88) 102, 102 (103) 94, 91 (92) 97, 104 (100)	AMR 1768-90 AMR 1806-90
Grape	5.0 mg/kg	-15 to -25	0 1 3 6 9 12	76[7] 78 78 78 88 80	84, 80 (82) 84, 78 (80) 76, 80 (78) 76, 78 (77) 76, 84 (80) 84, 80 (82)	AMR 1768-90 AMR 1806-90

Sample	Fortification	Storage (°C)	Storage (months)	Concurrent fortification recovery[1] (%)	Methomyl remaining[2] (%)	Reference/method
			18	84	82, 80 (81)	
			24	78	74, 64 (69)	
			27	90	88, 80 (84)	
Onions, dry bulb (whole)	Field incurred 0.36 (0.35, 0.38)	-15 to -20	1	81[10]	106, 47 (mean 76)[11]	AMR 3746-96 AMR 1806-90
			3	87	120, 110 (115)	
			6	95	210, 140 (mean 175)[11]	
			12	84	160, 160 (160)	
			18	84	220, 220	
			24	96	230, 200 (215)	

[1] 0.10 mg/kg fortification of control samples immediately before extraction, except as otherwise noted. Results uncorrected for control sample recoveries.
[2] 0.10 mg/kg fortification of control sample homogenate, fortified at time zero and stored and analysed with the incurred residue samples. Values in parentheses are recoveries from beans or peanuts freshly fortified at 0.08 mg/kg.
[3] 0.20 mg/kg fortification of control sample homogenate, fortified at time zero and stored and analysed with the incurred residue samples. Values in parentheses are recoveries from fresh fortifications at 0.08 mg/kg for potato and 0.20 mg/kg for sorghum hay and forage.
[4] Interference in the control and 0.20 mg/kg fortification. Limit of determination 1.0 mg/kg.
[5] Fresh fortification recovery at 5.0 mg/kg.
[6] 0.5 mg/kg fortification of control samples homogenates immediately before extraction. Results uncorrected for control sample recoveries.
[7] 5.0 mg/kg fortification of control sample homogenates immediately before extraction. Results uncorrected for control sample recoveries.
[8] 2.0 mg/kg fortification of control samples immediately before extraction. Results uncorrected for control sample recoveries.
[9] 1.0 mg/kg fortification of control samples immediately before extraction. Results uncorrected for control sample recoveries.
[10] 0.08 mg/kg fortification of control samples immediately before extraction. Results uncorrected for control sample recoveries.
[11] The significant difference in replicate samples was attributed to variable concentration on the bulbs, with larger bulbs (exposed more above ground) receiving a larger dose of methomyl spray.

Methomyl was found to be unstable in beef liver fortified at 0.2 mg/kg and stored at -4°C (Ali *et al.*, 1993). 40-60% was lost when stored at room temperature for up to 8 hours, and residues decreased to 0% within two weeks. However methomyl was stable in ruminant milk, muscle and liver stored at -70°C (Daun, 1995). The results are shown in Table 21.

Table 21. Stability of residues in ruminant products fortified with methomyl and stored at –60 to -80 °C.

Sample	Fortification (mg/kg)	Storage period (days)	Methomyl remaining (%)	Method[1]
Milk, whole	0.10	0	88	Daun, 1995
		30	97	AMR 2964-94
		61	82	
		91	83	
		181	84	
Muscle	0.10	0	94	Daun, 1995
		2	93	AMR 2964-94
		9	91	
		15	88	
		33	102	
		61	88	
		91	89	
		181	86	
Liver	0.10	0	95	Daun, 1995
		11	102	AMR 2964-94
		20	93	
		31	88	
		60	94	
		90	94	
		165	94	

[1] Method validated for whole milk (0.01 mg/kg, 94% ± 6.6%, n = 16), liver (0.01 mg/kg, 106% ± 7.6%, n = 4) and muscle (0.01 mg/kg, 94% ± 8.6%, n = 3).

Rühl and Devine (1994) studied the stability of methomyl in soil samples from Madera, California, USA, fortified at 2.0, 20 and 200 µg/kg and stored frozen at -15 to -25° C, and in water from the American River, Sacramento, fortified at 0.1, 1.0 and 10 µg/kg and stored at 4°C and about -20°C. Methomyl was stable in the frozen soil and water for a minimum of 52 weeks and in cold water for a minimum of 14 weeks.

Definition of the residue

Metabolic studies on animals and plants have demonstrated that methomyl is substantially metabolized to carbon dioxide and acetonitrile. MHTA (methomyl oxime) was generally found to be absent, although its sulfate was found in some animal studies.

The older GC methods for analysis rely on conversion of methomyl to methomyl oxime, and thus, methomyl and methomyl oxime are determined. In the newer HPLC methods, only methomyl is determined, although thiodicarb may also be determined (separately) by the same method.

The Meeting noted that thiodicarb is readily metabolized to methomyl and that it is appropriate to combine the considerations for thiodicarb and methomyl. The Meeting agreed that the residue in both plant and animal commodities should be defined as methomyl for use of methomyl and as the sum of thiodicarb and methomyl, expressed as methomyl, for the use of thiodicarb. The Meeting further noted that expression of thiodicarb residue can be expressed as methomyl or thiodciarb, as the conversion factor from thiodicarb to methomyl is 0.92 and that from methomyl to thiodicarb is 1.1.

USE PATTERN

Methomyl is registered for use as a pesticide to control a large variety of chewing and sucking insects on a wide range of crops in many countries. Table 22 is a summary of the registered uses of methomyl based on labels or label translations provided by the manufacturer.

Table 22. Registered uses of methomyl.

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Alfalfa	Argentina	F	SP	900 g/kg	Foliar-aerial/ground	0.45	0.15 gnd 2.2aer	ns	10
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	7
	Cyprus	F	SP	900 g/kg	knapsack	1.0	0.2	2-3	7
	Hungary	F	SL	200 g/l	Foliar	0.12	0.024 (0/04 stubble)	ns	14
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	7
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	7
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.16	ns	7
	Peru	F	SL	240 g/l	Foliar	0.36	0.096	ns	5
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	15
	Peru	F	SP	400 g/kg	Foliar	0.27	0.18	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.27	0.18	ns	7
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.018	As needed	28
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	Grazing feeding-7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	Grazing feeding-7
Almonds	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
	Greece	F	SL	200 g/l	Foliar	1.1	0.09	1-3	20

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Greece	F	SP	900 g/kg	Foliar	1.1	0.09	1-3	20
	Greece	F	WP	250 g/kg	Foliar	1.1	0.09	1-3	20
Anise see Fennel									
Apple	Argentina		SP	900 g/kg	Foliar		0.054		14
	Australia	F	SL	225 g/l	Foliar-ground		0.045	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground		0.048	As needed	1
	Belgium	F	WP	250 g/kg	Foliar	0.75	0.05	ns	21
	Bulgaria	F	WP	250 g/kg	Foliar		0.02	3	7
	Canada	F	SL	215 g/l	Foliar-ground	1.9	0.065	As needed	8
	Canada	F	SP	900 g/kg	Foliar-ground	1.9	0.063	As needed	8
	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
	France	F	SL	200 g/l	Foliar		0.05-0.075	3	7
	Hungary	F	SL	200 g/l	Foliar	0.80	0.053	ns	14
	Italy	F	SL	200 g/l	Foliar		0.05	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.05	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	14
	Korea	F	SL	215 g/l	Foliar		0.0215	5	7
	Korea	F	SP	450 g/kg	Foliar		0.0675	2	14
	Kuwait	F	SP	900 g/kg	Foliar		0.032-0.045	ns	10-15
	Lebanon	F	SP	900 g/kg	Foliar		0.014-0.09	As needed	14
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.15-0.29	ns	8
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	0.73-1.16	ns	8
	Morocco	F	WP	250 g/kg	Foliar		0.0375	ns	7
	Oman	F	SP	900 g/kg	Foliar		0.032-0.045	As needed	10-15
	Qatar	F	SP	900 g/kg	Foliar		0.032-0.045	As needed	10-15
Apple	Romania	F	SP	900 g/kg	Foliar	0.45	0.03	3	7
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.014-0.018	As needed	15
	Syria	F	SP	900 g/kg	Foliar		.03-.06	As needed	14
	USA	F	SP	900 g/kg	Foliar-ground only	1.0	0.22	5	14 grazing-10
	USA	F	SL	290 g/l	Foliar-ground only	1.0	0.22	5	14 grazing-10
Apricot	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
	France	F	SL	200 g/l	Foliar		0.05-0.075	3	7
	Kuwait	F	SP	900 g/kg	Foliar		0.032-0.045	ns	10-15
	Morocco	F	WP	250 g/kg	Foliar		0.0375	ns	7
	Oman	F	SP	900 g/kg	Foliar		0.032-0.045	As needed	10-15
	Qatar	F	SP	900 g/kg	Foliar		0.032-0.045	As needed	10-15
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.014-0.018	As needed	15
Artichoke	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	.042-.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	7
	France	F	SL	200 g/l	Foliar	0.4		3	7
	France		SL	200 g/l	Foliar		0.04		
	Morocco	F	WP	250 g/kg	Foliar		0.0375	ns	7
	Tunisia	F	WP	250 g/kg	Foliar	0.038	0.038	3-4	7

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Venezuela	F	SL	223 g/l	traps		1.1	ns	
Asparagus	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	.042-.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	1
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.15-0.29	ns	1
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	0.73-1.16	ns	1
	Thailand	F	SL	184.5 g/l	Foliar		0.05	ns	3
	Thailand	F	SP	400 g/kg	Foliar		0.04-0.07	ns	6-14
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	8 (4.5 kg ai/ha/crop)	1
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	8 (5 kg ai/ha/crop)	1
Aubergine see Egg plant									
Avocado	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	1
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	2 (1 kg ai/ha/crop)	1
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	2 (1 kg ai/ha/crop)	1
Banana	Philippines	F	SP	400 g/kg	Bud injection		2-3kg/ha	As needed	
Bananas, Plantains	Colombia	F	SP	400 g/kg		2% solution		ns	-
	Venezuela	F	SL	223 g/l	traps		1.1	ns	
	Venezuela	F	SP	900 g/kg	traps		0.18	ns	
Barley	Australia	F	SL	225 g/l		0.45	1.0-2.1	As needed	14
	Australia	F	SP	400 g/kg		0.48	1.1-2.2	As needed	14
	Canada	F	SL	215 g/l	Foliar-ground	0.48	0.49	As needed	20
	Canada	F	SL	215 g/l	Foliar-aerial	0.48	2.2	As needed	20
	Canada	F	SP	900 g/kg	Foliar-ground	0.49	0.49	As needed	20
	Canada	F	SP	900 g/kg	Foliar-aerial	0.49	2.2	As needed	20
	Jordan	F	SP	900 g/kg	Foliar		.02-.05	ns	7
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	0.73-1.16	ns	7
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.15-0.29	ns	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	0.5	5.4	4	7 10-grazing
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	6.0	4	7 10-grazing
Beans	Australia	F	SL	225 g/l	Foliar-ground	0.45	0.023	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
	Central America	F	SL	216 g/l	Foliar	0.54	0.14-.027	ns	7 to 14
	Central America	F	SL	290 g/l	Foliar	0.58	0.15-0.29	ns	7 to 14
	Central America	F	SP	900 g/kg	Foliar	0.45	0.11-0.23	ns	3-15
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	.25-.5	ns	3-15
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	.042-.081	2-3	3
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	3
	Ecuador	F	SL	290 g/l	Foliar	0.36		6	
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.08-0.15	6	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.08-0.15	6	14

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	15
	Italy	F	SL	200 g/l	Foliar		.036-.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		.036-.04	ns	10
	Kuwait	F	SP	900 g/kg	Foliar		0.032-0.045	ns	3
	Lebanon	F	SP	900 g/kg	Foliar		0.014-0.09	As needed	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.15-0.29	ns	21
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	0.73-1.16	ns	21
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	2
	Oman	F	SP	900 g/kg	Foliar		0.023-0.045	As needed	3
	Peru	F	SP	400 g/kg	Foliar	0.4	0.135	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.4	0.135	ns	7
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	3
	Qatar	F	SP	900 g/kg	Foliar		0.023-0.045	As needed	3
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.014-0.032	As needed	10
	South Africa	F	SL	200 g/l	Foliar-aerial	0.225	0.75	ns	3
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	3
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.225	0.75	ns	3
	South Africa	F	SP	900 g/kg	Foliar-ground		0.045	ns	3
	Syria	F	SP	900 g/kg	Foliar		.03-.06	As needed	3
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	7-14
	Venezuela	F	SL	288 g/l	Foliar	0.86		ns	7-14
	Venezuela	F	SP	900 g/kg	Foliar	0.32		ns	7-14
Beans and legume seeds	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.480		As needed	1
Beans, Adzuki	Australia	F	SP	400 g/kg	Foliar-ground	0.480		As needed	7
Beans, Black	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	7-14
	Venezuela	F	SL	288 g/l	Foliar	0.86		ns	7-14
	Venezuela	F	SP	900 g/kg	Foliar	0.32		ns	7-14
Beans, Broad	Australia	F	SL	225 g/l	Foliar-ground	0.45	0.023	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.480			1
	Cyprus	F	SP	900 g/kg	Foliar-high volume	.42-.81	.042-.081	2-3	3
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	3
Beans, Castor	Thailand	F	SP	400 g/kg	Foliar		0.04-0.07	ns	3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Beans, dry	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10 (5 kg ai/ha/crop)	seed, vines, hay-14
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10 (5 kg ai/ha/crop)	seed, vines, hay-14
Beans, Fava	Lebanon	F	SP	900 g/kg	Foliar		0.014-0.09	As needed	3
	Syria	F	SP	900 g/kg	Foliar		.03-.06	As needed	3
Beans, French	Australia	F	SL	225 g/l	Foliar-ground	0.45	0.023	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.480		As needed	1
Beans, Green	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.15-0.29	ns	1
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	0.73-1.16	ns	1
Beans, long	Australia	F	SL	225 g/l	Foliar-ground	0.34	0.023	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
Beans, Mung See Mung bean									
Beans, Navy	Australia	F	SL	225 g/l	Foliar-ground	0.34	0.023	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
Beans, Snap	Canada	F	SL	215 g/l	Foliar-ground	0.50	0.5	As needed	7
	Canada	F	SP	900 g/kg	Foliar-ground	0.50	0.5	As needed	7
Beans, succulent	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10 (5 kg ai/ha/crop)	≤0.5 kg ai/ha=1 >0.5=3 vines-3 hay-7
Beans, succulent	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10 (4.5 kg ai/ha/crop)	≤0.56 kg ai/ha = 1 >0.56= 3 vines-3 hay-7
Beet, red	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	.042-.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
Beets	Austria	F	WP	250 g/kg	Foliar	0.25	0.05	ns	21
Beets, table	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	6.0 (4 kg ai/ha/crop)	8	roots-0 tops-14
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	6.0 (4 kg ai/ha/crop)	8	roots-0 tops-14
Bermuda grass pasture	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	4 (0.9 kg ai/ha/crop)	forage-7 dehydrated hay-3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	4 (0.9 kg ai/ha/crop)	forage-7 dehydrated hay-3
Binjal	India	F	SL	112 g/l	Foliar-high volume	0.04	0.08	ns	4
Blueberries	Australia	F	SL	225 g/l	Foliar-ground		0.023	ns	5
	USA	F	SL	900 g/kg	Foliar-aerial/ground	1.0	5.4	4	3
Broccoli	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
	Brazil	F	SL	215 g/l	Foliar		0.0215	5	3
	Canada	F	SL	215 g/l	Foliar-ground	0.48	0.19	As needed	7
	Central America	F	SL	216 g/l	Foliar	0.54	0.27	ns	3
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	6	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	6	14
	Japan	F	WP	450 g/kg	Foliar	.675-1.35	0.045	1-3	14
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.16	ns	3
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	4
	South Africa	F	SL	200 g/l	Foliar-aerial	0.225	0.75	ns	4
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.225	0.75	ns	4
	South Africa	F	SP	900 g/kg	Foliar-ground	0.225		ns	4
	South Africa	F	SP	900 g/kg	Foliar		0.045	ns	4
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	3
	Venezuela	F	SL	223 g/l	Foliar	0.7		ns	3
	Venezuela	F	SL	288 g/l	Foliar	0.86		ns	3
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	3
Brussels sprouts	Australia	F	SL	225 g/l	Foliar-ground	.23-.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	.24-.48		As needed	1
	Canada	F	SL	215 g/l	Foliar-ground	0.48	0.19	As needed	7
	Canada	F	SP	900 g/kg	Foliar-ground	0.48	0.19	As needed	7
	Poland	F	SL	200 g/l	Foliar	0.18	0 .09	3	7
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	4
	South Africa	F	SL	200 g/l	Foliar-aerial	0.225	0.75	ns	4
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	3
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.225	0.75	ns	4
	South Africa	F	SP	900 g/kg	Foliar-ground	0.225		ns	4
	South Africa	F	SP	900 g/kg	Foliar		0.045	ns	4
Bush and Canefruit	New Zealand	F	SL	200 g/l	Foliar		0.024	As needed	2
Cabbage	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	14
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		14
	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0- .48		As needed	1
	Brazil	F	SL	215 g/l	Foliar		0.0215	5	3
	Canada	F	SL	215 g/l	Foliar-ground	0.48	0.19	As needed	1
	Canada	F	SP	900 g/kg	Foliar-ground	0.49	0.20	As needed	1
	Central America	F	SL	216 g/l	Foliar	0.54	0.27	ns	3
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	3
	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	1
	China	F	SP	900 g/kg	Foliar	0.27	0.20	1-5	7
	Colombia	F	SP	400 g/kg	Foliar-ground	0.22	0.11	ns	14
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.22	0.8	ns	14
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.50	ns	1
	Cyprus	F	SP	900 g/kg	Foliar-high volume	.42-.81	0.081	2-3	1

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	1
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	6	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	6	14
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	
	France	F	SL	200 g/l	Foliar	0.3		1	7
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	- 0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	- 0.9		1	15
	India	F	SL	112 g/l	Foliar-high volume	0.05	0 .10	ns	3
	Indonesia	F	SL	200 g/l	Foliar		0.06	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		0.075	ns	14
	Italy	F	SL	200 g/l	Foliar		0.05	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.05	ns	10
	Japan	F	GR	1.5 g/kg	granule application	0.9		3	7
	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	3
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	1
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	1-3
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	1
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.16	ns	1
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	7
Cabbage	Oman	F	SP	900 g/kg	Foliar		0.023-0.045	As needed	1-3
	Pakistan	F	SP	400 g/kg	Foliar	0.16		ns	
	Peru	F	SP	400 g/kg	Foliar	0.4	0.14	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.4	0.14	ns	7
	Poland	F	SL	200 g/l	Foliar	0.18	0.09	3	14
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	1-3
	Romania	F	SP	900 g/kg	Foliar	0.9	0.09	3	3
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	15
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	4
	South Africa	F	SL	200 g/l	Foliar-aerial	0.225	0.75	ns	4
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.225	0.75	ns	4
	South Africa	F	SP	900 g/kg	Foliar-ground	0.225		ns	4
	South Africa	F	SP	900 g/kg	Foliar		0.045	ns	4
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	1

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Taiwan	F	WP	900 g/kg	Foliar		0.03(3000x)	ns	10
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11A	15	1
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11A	15	1
	Venezuela	F	SL	223 g/l	Foliar	0.7		ns	3
	Venezuela	F	SL	288 g/l	Foliar	0.86		ns	3
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	3
Cabbage, Chinese see Chinese cabbage									
Cacao	Indonesia	F	SL	200 g/l	Foliar		0.06	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		0.075	ns	14
Canola	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	7
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	7
	Canada	F	SL	215 g/l	Foliar-ground	0.27	0.11	As needed	8
	Canada	F	SL	215 g/l	Foliar-aerial	0.27	1.2	As needed	8
	Canada	F	SP	900 g/kg	Foliar-ground	0.46	0.18	As needed	8
	Canada	F	SP	900 g/kg	Foliar-aerial	0.46	2.0	As needed	8
Cantaloupe	Tunisia	F	WP	250 g/kg	Foliar	0.038	0.038	3-4	7
Carrots	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	1
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	1
	Cyprus	F	SP	900 g/kg	Foliar-high volume	.42-.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Japan	F	GR	1.5 g/kg	granule application	3-4.5		1	before seeding
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	1
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	1
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	1
Cauliflower	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	14
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		14
	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.36		As needed	1
	Canada	F	SL	215 g/l	Foliar-ground	0.48	0.19	As needed	7
Cauliflower	Canada	F	SP	900 g/kg	Foliar-ground	0.49	0.19	As needed	7
	Canada	F	SP	900 g/kg	Foliar-ground	0.49	0.19	As needed	7
	Central America	F	SL	216 g/l	Foliar	0.54	0.27	ns	3
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	3
	Colombia	F	SP	400 g/kg	Foliar-ground	0.22	0.11	ns	14
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.22	0.8	ns	14
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	15
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	3
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	1-3
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.16	ns	3
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	7
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	1-3
	Pakistan	F	SP	400 g/kg	Foliar	0.16		ns	
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	1-3
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	4
	South Africa	F	SL	200 g/l	Foliar-aerial	0.225	0.75	ns	4
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.225	0.75	ns	4
	South Africa	F	SP	900 g/kg	Foliar-ground	0.225		ns	4
	South Africa	F	SP	900 g/kg	Foliar		0.045	ns	4
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	3
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
	Turkey	F	SP	900 g/kg	Foliar	0.72		ns	3
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	3
	Venezuela	F	SL	223 g/l	Foliar	0.7		ns	3
	Venezuela	F	SL	288 g/l	Foliar	0.86		ns	3
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	3
Celery	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	7
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	7
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	7
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	7
	Venezuela	F	SL	223 g/l	Foliar	0.7		ns	
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	
Cereals	Kenya	F	SP	900 g/kg	Foliar-high volume	0.27	0.06	As needed	3
	New Zealand	F	SL	200 g/l	Foliar	0.4	0.4	As needed	7

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Cetrosema, Pascuorum seed crops	Australia	F	SL	225 g/l	Foliar	0.45		ns	-
Cherry	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
	France	F	SL	200 g/l	Foliar		0.05	3	7
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	10-15
	Morocco	F	WP	250 g/kg	Foliar		0.0375	ns	7
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	10-15
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	10-15
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.018	As needed	15
Chickpea	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	7
	Australia	F	SP	400 g/kg	Foliar-ground	0 .48		As needed	1
Chicory	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	2	80
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	2	80
Chinese cabbage	Japan	F	GR	1.5 g/kg	granule application	1.4		2	14
	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	14
	Korea	F	SP	450 g/kg	Foliar		0.068	As needed	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	0.43gnd 2.2aer	10 (9 kg ai/ha/crop)	10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	0.43gnd 2.2aer	10 (9 kg ai/ha/crop)	10
Citrus fruits	Algeria	F	SL	200 g/l	Foliar		0.03	ns	7
	Argentina	F	SP	900 g/kg	Foliar		0.054	ns	14
	Australia	F	SL	225 g/l	Foliar-ground		0.045	ns	2
	Australia	F	SP	400 g/kg	Foliar-ground		0.048	ns	2
	China	F	SP	900 g/kg	Foliar	300ppm	180 ppm	1-5	10
	Cyprus	F	SP	900 g/kg		0.65	0.054	1-2	1
	Greece	F	SL	200 g/l	Foliar	(1.35)	0.09	1-3	20
	Greece	F	SP	900 g/kg	Foliar	(1.35)	0.09	1-3	20
	Greece	F	WP	250 g/kg	Foliar	(1.35)	0.09	1-3	20
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	1
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	1
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	1
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	7
	South Africa	F	SL	200 g/l	Foliar		0.018	ns	2
	South Africa	F	SL	200 g/l	Foliar		0.018	ns	2
	South Africa	F	SL	200 g/l	Foliar		0.023	ns	28
	South Africa	F	SL	200 g/l	Foliar		0.09 + 3 L of Sunspray oil	1-late cultivars	28
	South Africa	F	SL	200 g/l	Foliar		0.018 + 500 ml mineral oil	ns	28
	South Africa	F	SL	200 g/l	Foliar		0.023	ns	28
	South Africa	F	SP	900 g/kg	Foliar-ground		0.018	ns	2
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.225	0.45	ns	
	South Africa	F	SP	900 g/kg	Foliar		0.018	ns	2

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	South Africa	F	SP	900 g/kg	Foliar		0.0225	ns	28
	South Africa	F	SP	900 g/kg	Foliar		0.09 + 3 L of Sunspray oil	1-late cultivars	28
	South Africa	F	SP	900 g/kg	Foliar		0.018 + 500 ml mineral oil	ns	28
	South Africa	F	SP	900 g/kg	Foliar		0.022	ns	28
	Spain	F	SL	200 g/l	Foliar-high volume	0.5	0.05	1-5	7
	Spain	F	WP	250 g/kg	Foliar-high volume	0.5	0.05	1-5	7
	Taiwan	F	WP	900 g/kg	Foliar		0.03	ns	
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
Clover	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	7
	Greece	F	SL	200 g/l	Foliar	0.54		1-3	20
	Greece	F	WP	250 g/kg	Foliar	0.54		1-3	20
Cocoa	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	
	Venezuela	F	SP	900 g/kg	Foliar	0.18		ns	
Coffee	Kenya	F	SP	900 g/kg	Foliar-high volume	0.9	0.11	As needed	7
Cole crops	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	14
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		14
	Peru	F	SL	296 g/l	Foliar	0.36	0.09	ns	3
Collards, fresh market	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	8	10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	8	10
Cotton	Argentina	F	SP	900 g/kg	Foliar	0.27	0.09	ns	14
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.027		14
	Australia	F	SL	225 g/l	Foliar-aerial	0.54	2.4	As needed	ns
	Australia	F	SP	400 g/kg	Foliar-aerial	0.56	2.5	As needed	15
	Brazil	F	SL	215 g/l	Foliar	0.33	-0.33	5	14
	Central America	F	SL	216 g/l	Foliar	0.54	0.027	ns	15
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	15
	Central America	F	SP	900 g/kg	Foliar	0.36	0.18	ns	15
	China	F	SP	900 g/kg	Foliar	0.18	0.105	1-5	ns
	Colombia	F	SL	216 g/l	Foliar-aerial	0.32	1.1	ns	7
	Colombia	F	SL	216 g/l	Foliar-ground	0.32	0.16	ns	7
	Colombia	F	SP	400 g/kg	Foliar-ground	0.44	0.22	ns	7
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.44	1.6	ns	
	Costa Rica	F	SP	900 g/kg	Foliar	0.72	0.36	ns	15
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	4	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15		14
	Greece	F	SL	200 g/l	Foliar	0.7		1-3	20
	Greece	F	SP	900 g/kg	Foliar	0.7		1-3	20
	Greece	F	WP	250 g/kg	Foliar	0.7		1-3	20
	India	F	SL	112 g/l	Foliar-high volume	0.06	0.12	ns	7
	India	F	SP	400	0.45	0.09	ns	10	

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
				g/kg4Foliar-					

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
				high volume					
	Indonesia	F	SL	200 g/l	Foliar		0.06	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		0.06	ns	14
	Kenya	F	SP	900 g/kg	Foliar-high volume	0.45	0.09	As needed	15
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	15
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	15
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	15
	Morocco	F	SL	200 g/l	Foliar		0.05	ns	7
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	7
	Pakistan	F	SP	400 g/kg	Foliar	0.4		ns	
	Peru	F	SP	400 g/kg	Foliar	0.4	0.18	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.4	0.18	ns	7
	Spain	F	SL	200 g/l	Foliar-high volume	0.4	0.05	2-3	7
	Spain	F	WP	250 g/kg	Foliar-high volume	0.4	0.05	2-3	7
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	15
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	-
	Turkey	F	SP	900 g/kg	Foliar	0.72		ns	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	0.76 west 0.50 east 0.67 Texas	8	8	15
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.76 west 0.50 east 0.67 Texas	15	8	15
	Venezuela	F	SL	223 g/l	Foliar	0.33		ns	15
	Venezuela	F	SL	288 g/l	Foliar-aerial	0.4	1.6	ns	15
	Venezuela	F	SP	900 g/kg	Foliar	0.45		ns	15
	Vietnam	F	SP	400 g/kg	Foliar	.0.72	0.12	ns	
Courgette	France	F/G	SL	200 g/l	Foliar	0.3		3	7
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	15
	Netherlands	F/G	SL	200 g/l	Foliar	0.4	0.025	1-3	3
	Netherlands	G	WP	250 g/kg	Foliar	0.4	0.08	1-3	3
Cowpea	Australia	F	SP	400 g/kg	Foliar-ground	0.48			7
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	3
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	3
Cucumber	Belgium	G	WP	250 g/kg	Foliar	0.5	0.031	ns	14

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Bulgaria	F	WP	250 g/kg	Foliar		0.023	3	7
	Central America	F	SL	216 g/l	Foliar	0.54	0.027	ns	3
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	3
	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	3
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	3
	Cyprus	F	SP	900 g/kg	Foliar-high volume	.42-.81	0.081	2-3	3
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	3
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	8	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	8	14
	France	F/G	SL	200 g/l	Foliar	0.3		3	7
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	20
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	20
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	20
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	20
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	20
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	20
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	20
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	20
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	- 0.9		1	20
	Hungary	F	SL	200 g/l	Foliar	0.4	0.07	ns	5
	Hungary	G	SL	200 g/l	Foliar	0.72	0.09	ns	5
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	3
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	3
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	3
	Netherlands	F/G	SL	200 g/l	Foliar	0.4	0.025	1-3	3
	Netherlands	G	WP	250 g/kg	Foliar	0.4	0.08	1-3	3
	New Zealand	G	SL	200 g/l	Foliar		0.024	4	2
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Pakistan	F	SP	400 g/kg	Foliar	0.16		ns	
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	3
	Poland	G	SL	200 g/l	Foliar		0.02	3	3
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Romania	G	SP	900 g/kg	Foliar	0.45	0.045	3	3
	Romania	F	SP	900 g/kg	Foliar	0.9	0.09	3	3
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	7
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
	Tunisia	F	WP	250 g/kg	Foliar	0.038	0.038	3-4	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	12	≤0.5 kg=1 >0.5 kg=3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	12	≤0.5 kg=1 >0.5 kg=3
	Venezuela	F	SL	223 g/l	Foliar	0.33		ns	3
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	3
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	3
	Canada	G	SL	215 g/l	Foliar-high volume		0.005	3	3
Duboisia	Australia	F	SL	225 g/l	Foliar-ground	0.23	0.023	As needed	ns
	Australia	F	SP	400 g/kg	Foliar-ground		0.024	As needed	2
Egg plant	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	France	F/G	SL	200 g/l	Foliar	0.45		3	7
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
Egg plant	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	15
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	5
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	6
	Netherlands	F/G	SL	200 g/l	Foliar	0.4	0.025	1-3	3
	Netherlands	G	WP	250 g/kg	Foliar	0.4	0.025-0.08	1-3	3
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	6
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	5
	Poland	G	SL	200 g/l	Foliar		0.02	3	3
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	6
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	15
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	6-14
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	10 (5 kg ai/ha/crop)	3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	10 (5 kg ai/ha/crop)	3
Endive, Escarole	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	8	10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	8	10
Fennel	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	7

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Fennel (anise)	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	7
Field crops	Morocco	F	SL	200 g/l	Foliar		0.038	ns	10
Figs	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
Flax	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	
	Canada	F	SL	215 g/l	Foliar-ground	0.27		As needed	8
	Canada	F	SL	215 g/l	Foliar-aerial	0.27	1.2	As needed	8
	Canada	F	SP	900 g/kg	Foliar-ground	0.24	0.24	As needed	8
	Canada	F	SP	900 g/kg	Foliar-aerial	0.24	1.1	As needed	8
	France	F	SL	200 g/l	Foliar	0.5		1	ns
	Taiwan	F	WP	900 g/kg	Foliar		0.05(2000x)	ns	
Forages	Morocco	F	SL	200 g/l	Foliar		0.05	ns	7
Fruit	Austria	F	WP	250 g/kg	Foliar	0.038	0.03	ns	21
	Macedonia	F	SL	200 g/l	Foliar		0.05	3	35
	Macedonia	F	SP	900 g/kg	Foliar		0.05	As needed	35
	Macedonia	F	WP	250 g/kg	Foliar		0.04	2	35
	Morocco	F	SL	200 g/l	Foliar		0.05	ns	7
Garlic	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	7
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	7
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	7
Garlic	USA	F	SL	290 g/l	Foliar-aerial/ground	0.5	2.7	6	7
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	2.7	6	7
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	5
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	5
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	5
Gherkin	France	F/G	SL	200 g/l	Foliar	0.3		3	7
Ginger	Australia	F	SL	225 g/l	Foliar-ground	0.34		ns	ns
	Australia	F	SP	400 g/kg	Foliar-ground	0.36		ns	
	Japan	F	WP		Foliar	1.35	0.045	1-3	7
Grape	Bulgaria	F	WP	250 g/kg	Foliar		0.02	4	21
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	4
	Algeria	F	WP	250 g/kg	Foliar		0.04	3-4	7
	Australia	F	SL	225 g/l	Foliar-ground		0.034	ns	7
	Australia	F	SP	400 g/kg	Foliar-ground		0.036	ns	7
	Austria	F	WP	250 g/kg	Foliar	0.38	0.05	ns	21
	Cyprus	F	SP	900 g/kg		0.54	0.054	1-2	10
	France	F	SL	200 g/l	Foliar	0.4	0.05	3	7
	Greece	F	SL	200 g/l	Foliar	(0.81)	0.054	1-3	20
	Greece	F	SP	900 g/kg	Foliar	(0.81)	0.054	1-3	20
	Greece	F	WP	250 g/kg	Foliar	(0.81)	0.054	1-3	20
	Hungary	F	SL	200 g/l	Foliar	0.48	0.05	ns	10
	Italy	F	SL	200 g/l	Foliar		0.05	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.05	ns	10

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	1
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	1-fresh 14-wine
	Macedonia	F	SL	200 g/l	Foliar		0.05	3	35
	Macedonia	F	SP	900 g/kg	Foliar		0.05	ns	35
	Macedonia	F	WP	250 g/kg	Foliar		0.05	2	35
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	table-1 industrial-10
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	table-1 industrial-10
	Morocco	F	WP	250 g/kg	Foliar		0.0375	ns	7
	New Zealand	F	SL	200 g/l	Foliar		0.024	As needed	7
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	1
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	1
	Romania	F	SP	900 g/kg	Foliar	0.9	0.06	3	7
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	7
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	fresh-1 wine-14
	Turkey	F	SP	900 g/kg	Foliar		0.054	ns	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	0.11	5	fresh, raisin-1 wine-14
Grape	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	0.11	5	fresh, raisin-1 wine-14
	Yugoslavia	F	SP	900 g/kg	Foliar		0.05	ns	35
Grapefruit	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	0.72	4	1 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	0.72	4	1 grazing-10
Grazing and other crops	South Africa	F	SL	200 g/l	Foliar-ground	0.045	0.011	ns	-
	South Africa	F	SP	900 g/kg	Foliar-ground	0.045	0.011	ns	-
Groundnuts	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	21
Guar	Australia	F	SL	225 g/l	Foliar-ground	0.45		ns	7
Hops	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	14
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	14
	Austria	F	WP	250 g/kg	Foliar	0.25	0.03	ns	21
	Belgium	F	WP	250 g/kg	Foliar	1.2	0.031	ns	21
	Poland	F	SL	200 g/l	Foliar		0.024	3	7
	Romania	F	SP	900 g/kg	Foliar	0.45		3	
	Spain	F	SL	200 g/l	Foliar-high volume	0.5	0.05	1-5	7
	Spain	F	WP	250 g/kg	Foliar-high volume	0.5	0.05	1-5	7
Horseradish	USA	F	SL	290 g/l	Foliar-ground only	0.5		4	65
	USA	F	SP	900 g/kg	Foliar-ground only	0.5		4	65
Indian jujubes	Taiwan	F	WP	900 g/kg	Foliar		0.03(3000x)	ns	6
Jewsmallow	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	10
Kale	Brazil	F	SL	215 g/l	Foliar		0.0215	5	3
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	6	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	6	14
Leafy vegetables	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.24		As needed	1
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	10
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	8	10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	8	10
Lemon	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	0.72	4	1 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	0.72	4	1 grazing-10
Lentils	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	7
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	2	21 forage-3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	2	21 forage-3
Lettuce	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	14
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		14
	Australia	F	SL	225 g/l	Foliar-ground	0-0.45	0.045	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground		0 0.048	As needed	3
	Belgium	G	WP	250 g/kg	Foliar	0.31	0.031	ns	14
	Canada	F	SL	215 g/l	Foliar-ground	0.97	0.39	As needed	7
	Canada	F	SP	900 g/kg	Foliar-ground	0.9	0.36	As needed	7
	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	7-10
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	7-10
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	6	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	6	14
	France	F	SL	200 g/l	Foliar	0.3		3	14
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	15
	Italy	F	SL	200 g/l	Foliar		0.05	ns	14
	Italy	F	WP	250 g/kg	Foliar		0.05	ns	14
	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	14
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	10
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	10
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	7
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	7
	Romania	F	SP	900 g/kg	Foliar	0.9	0.09	3	7
	Venezuela	F	SL	223 g/l	Foliar	0.7		ns	
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	
Lettuce, Head & Leaf	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	15-Head 8-Leaf	≤0.5 kg ai=7 >0.5=10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	15-Head 8-Leaf	≤0.5 kg ai=7 >0.5=10
Lime	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
Linseed	Australia	F	SL	225 g/l	Foliar-aerial	0.45	2.0	As needed	7
	Australia	F	SP	400 g/kg	Foliar-aerial	0.48		As needed	7
Lucerne	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	3-grazing
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	3-grazing
	South Africa	F	SL	200 g/l	Foliar-aerial	0.18	0.6	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground, low volume	0.18	0.18	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	7
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.18	0.6	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground, low volume	0.18	0.18	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground		0.045	ns	7
Lupin	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
	South Africa	F	SL	200 g/l	Foliar-aerial	0.18	0.6	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground, low volume	0.18	0.18	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground, low volume		0.18	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground, low volume	0.18	0.18	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground		0.045	ns	7
Maize	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	14
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	14
	Central America	F	SL	216 g/l	Foliar	0.54	0.29	ns	14
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	14
	Central America	F	SP	900 g/kg	Foliar	0.36	0.18	ns	7

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Kenya	F	SP	900 g/kg	Foliar-high volume	0.27	0.06	As needed	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	fresh-0 grain-3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	fresh-0 grain-3
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	7
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.18	0.6	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground, low volume		0.18	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground		0.045	ns	7
Maize	Argentina		SP	900 g/kg	Foliar	0.45	0.15	ns	10
	Brazil	F	SL	215 g/l	Foliar	0.129	0.09	5	14
	Colombia	F	SP	400 g/kg	Foliar-ground	0.33	0.17	ns	14
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.33	1.2	ns	14
	Costa Rica	F	SP	900 g/kg	Foliar	0.54	0.27	ns	ns
	Ecuador	F	SL	290 g/l	Foliar	0.36		2-3	14
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	2-3	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	2-3	14
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	7
	Greece	F	SL	200 g/l	Foliar	0.54		1-3	20
	Greece	F	WP	250 g/kg	Foliar	0.54		1-3	20
	Macedonia	F	SP	900 g/kg	ground application in bands	0.9		3	42
	Peru	F	SL	240 g/l	Foliar	0.19	0.06	ns	5
	Peru	F	SL	296 g/l	Foliar	0.26	0.06	ns	0
	Peru	F	SP	400 g/kg	Foliar	0.23	0.18	ns	7
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	0
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	6-14
	Tunisia	F	WP	250 g/kg	Foliar	0.038	0.038	3-4	7
	Turkey	F	SP	900 g/kg	Foliar	0.9		ns	3
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	0
	Venezuela	F	SP	900 g/kg	Foliar	0.45		ns	0
	Yugoslavia	F	SP	900 g/kg	ground application in bands	0.9		3	42
Maize, field	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	21
Maize, field and popcorn	USA	F	SL	290 g/l	Foliar-aerial/ground	0.5	11	10	ears-21 forage-3 fodder-21
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	11	10	ears-21 forage-3 fodder-21
Mango	Taiwan	F	WP	900 g/kg	Foliar		0.05(1800x)	ns	9,8
Melon	Central America	F	SL	216 g/l	Foliar	0.54	0.027	ns	3
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	3
	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	3
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	7
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	.042-.081	2-3	3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	3
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	8	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	8	14
	France	F/G	SL	200 g/l	Foliar	0.3		3	7
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	20
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	20
Melon	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	20
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	20
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	20
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	20
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	20
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	20
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	20
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	3
	Netherlands	F/G	SL	200 g/l	Foliar	0.4	0.025	1-3	3
	Netherlands	G	WP	250 g/kg	Foliar	0.4	0.08	1-3	3
	Pakistan	F	SP	400 g/kg	Foliar	16		ns	
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	3
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	1
	Romania	F	SP	900 g/kg	Foliar	0.9	0.09	3	3
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	3
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	12	1/2 lb.-1 >1/2 lb.-3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	12	1/2 lb.-1 >1/2 lb.-3
	Venezuela	F	SL	223 g/l	Foliar	0.33		ns	3
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	3
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	3
Mint	Australia	F	SL	225 g/l	Foliar-ground	0.45		ns	14
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		ns	14
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	9.1	4	14
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	9.1	4	14
Mung bean	Indonesia	F	SL	200 g/l	Foliar		0 .02	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		0.06	ns	14
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	3
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
	Vietnam	F	SP	400 g/kg	Foliar	0.72		ns	
Mung bean	Australia	F	SL	225 g/l	Foliar-aerial	0.45	2.1	As needed	7

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
(seed production)									
	Australia	F	SP	400 g/kg	Foliar-aerial	0.48	2.2	As needed	7
Muskmelon	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	3
Nashi	France	F	SL	200 g/l	Foliar		0.075	3	7
Nectarine	Australia	F	SL	225 g/l	Foliar-ground		0.034	As needed	1
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	1.0	3	1 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	1.0	3	1 grazing-10
Oats	Argentina		SP	900 g/kg	Foliar	045	0.15	ns	14
	Australia	F	SL	225 g/l		00.45	02.1	As needed	14
	Australia	F	SP	400 g/kg		00.48	02.2	As needed	14
	Canada	F	SL	215 g/l	Foliar-ground	0048	0.5		20
	Canada	F	SL	215 g/l	Foliar-aerial	048	2.2		20
	Canada	F	SP	900 g/kg	Foliar-ground	0.49	0.5	As needed	20
	Canada	F	SP	900 g/kg	Foliar-aerial	0.49	2.2	As needed	20
	USA	F	SL	290 g/l	Foliar-aerial/ground	0.5	5.4	4	7 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	5.4	4	7 grazing-10
Okra	India	F	SL	112 g/l	Foliar-high volume	0.04	0.08	ns	4
	Thailand	F	SL	184.5 g/l	Foliar		0.05	ns	3
Olive	Greece	F	SL	200 g/l	Foliar	(0.81)	0.09	1-3	20
	Greece	F	SP	900 g/kg	Foliar	(0.81)	0.09	1-3	20
	Greece	F	WP	250 g/kg	Foliar	(0.81)	0.09	1-3	20
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	7
	Peru	F	SL	296 g/l	Foliar	-	0.06	ns	15
Onion	Argentina	F	SP	900 g/kg	Foliar	0 .45	0.15	ns	14
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		14
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	6	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	6	14
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	7
	Hungary	F	SL	200 g/l	Foliar	0.4	0.07	ns	5
	Japan	F	WP	450 g/kg	Foliar	1.35	0.045	1-3	7
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	7
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	7
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	7
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	7
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	7
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	23
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	5
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	5

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	5
Onion, dry	Romania	F	SP	900 g/kg	Foliar	0.9	0.09	3	7
Onion, green and dry bulb	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4A	8 (6 kg ai/ha/crop green, 4 kg ai/ha/crop dry)	7
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4A	8(6 kg ai/ha/crop green, 4 kg ai/ha/crop dry)	7
Onion, Welsh	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	7
	Peru	F	SP	400 g/kg	Foliar		0.18	ns	7
	Peru	F	SP	900 g/kg	Foliar		0.18	ns	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	0.72	4	1 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5-1.0	0.72	4	1 grazing-10
Orchards	Yugoslavia	F	SP	900 g/kg	Foliar		0.05	As needed	Fruits-35
Palm, African & Coconut	Venezuela	F	SP	900 g/kg	traps		0.9	ns	
	Colombia	F	SP	400 g/kg				ns	-
Paprika	Hungary	F	SL	200 g/l	Foliar	0.4	0.07	ns	5
	Netherlands	F/G	SL	200 g/l	Foliar	0.4	0.025	1-3	3
	Netherlands	G	WP	250 g/kg	Foliar	0.4	0.08	1-3	3
	Poland	G	SL	200 g/l	Foliar		0.02	3	3
Pasture	Australia	F	SL	225 g/l	Foliar-aerial	0.45	2.1	As needed	3-grazing
	Australia	F	SP	400 g/kg	Foliar-aerial	0.48	2.2	As needed	3-grazing
	Kenya	F	SP	900 g/kg	Foliar-high volume	0.27	0.06	As needed	3
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	7
Pasture, legume seed crops	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	ns
Peach	Argentina	F	SP	900 g/kg	Foliar		0.054	ns	14
	Australia	F	SL	225 g/l	Foliar-ground		0.034	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground		0.36	As needed	1
	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
	France	F	SL	200 g/l	Foliar		0.075	3	7
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	10-15
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	4
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	7
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	10-15
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	10-15
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.018	As needed	15
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	4
	USA	F	SL	290 g/l	Foliar-aerial/ground	2.0	0.06gnd 4.8aer	6	4 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	2.0	0.06gnd 4.8aer	6	4 grazing-10
Peach, early cultivars	South Africa	F	SL	200 g/l	Foliar		0.045	2	16
	South Africa	F	SP	900 g/kg	Foliar		0.045	2	16
Peach, late	South Africa	F	SL	200 g/l	Foliar		0.045	3	16

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
cultivars									
	South Africa	F	SP	900 g/kg	Foliar		0.045	3	16
Peanut	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	14
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	14
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	21
	Indonesia	F	SL	200 g/l	Foliar		0.02	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		0.06	ns	14
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	21
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	21
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	8	21
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	8	21
	Venezuela	F	SL	223 g/l	Foliar	0.7		ns	
	Venezuela	F	SP	900 g/kg	Foliar	0.32		ns	7-14
Pear	Argentina	F	SP	900 g/kg	Foliar		0.054	ns	14
	Australia	F	SL	225 g/l	Foliar-ground		0.045	As needed	2
	Belgium	F	WP	250 g/kg	Foliar	0.75	0.05	ns	21
	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
	France	F	SL	200 g/l	Foliar		0.075	3	7
	Hungary	F	SL	200 g/l	Foliar	0.48	0.05	ns	10
	Italy	F	SL	200 g/l	Foliar		0.05	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.05	ns	10
	USA	F	SL	290 g/l	Foliar-ground	1.0	0.22	2	7 grazing-10
	USA	F	SP	900 g/kg	Foliar-ground	1.0	0.22	2	7 grazing-10
Peas	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	14
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		14
	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
	Canada	F	SL	215 g/l	Foliar-ground	0.484	0.48	As needed	1
	Canada	F	SP	900 g/kg	Foliar-ground	0.459	0.46	As needed	1
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	3
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	3
	France	F	SL	200 g/l	Foliar	0.3		1	7
	Hungary	F	SL	200 g/l	Foliar	0.4	0.07	ns	5
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	1
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	1
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	1
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	3
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	6 (3 kg ai/ha/crop)	1 forage-5 hay-14
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	6 (3 kg ai/ha/crop)	1 forage-5 hay-14

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Peas, field	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	7
	Australia	F	SP	400 g/kg	Foliar-ground	0.48	2.2	As needed	7
Pecans	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	5.4	7	30 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	7	30 grazing-10
Pepper	Bulgaria	F	WP	250 g/kg	Foliar		0.023	3	7
	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	3
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	3
	France	F/G	SL	200 g/l	Foliar	0.45		3	7
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	15
	Hungary	G	SL	200 g/l	Foliar	0.72	0.09	ns	5
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	7
	Mexico	F	SL	290 g/l	Foliar-ground	0.65	0.33	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.65	1.3	ns	3
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	7
	New Zealand	G	SL	200 g/l	Foliar		0.024	4	2
	Tunisia	F	WP	250 g/kg	Foliar	0.038	0.038	3-4	7
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	3
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	1
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	1
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	1
Pepper, Chili	Costa Rica	F	SP	900 g/kg	Foliar	0.54	0.27	ns	ns
	India	F	SL	112 g/l	Foliar-high volume	0.05	0.10	ns	4
	Peru	F	SL	240 g/l	Foliar	0.24	0.096	ns	5
	Peru	F	SP	400 g/kg	Foliar	0.4	0.14	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.4	0.14	ns	7
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	6-14
Pepper, Green	Romania	G	SP	900 g/kg	Foliar	0.45	0.045	3	3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Pepper, Green (field)	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	14
Pepper, Red	Korea	F	SL	215 g/l	Foliar		0.022	4	14
	Korea	F	SP	450 g/kg	Foliar		0.068	3	7
Pepper, Red and Green	Argentina	F	SP	900 g/kg	Foliar	0.45	1.5	ns	10
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		10
Pepper, Sweet	Australia	F	SL	225 g/l	Foliar-ground		0.045	As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground		0.048	As needed	1
Pigeon pea	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	7
	Australia	F	SP	400 g/kg	Foliar-ground	0.48	2.2	As needed	1
	India	F	SP	400 g/kg	Foliar-high volume	0.45	0.09	ns	7
Pistachio	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
Plantain, see Banana									
Plum	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	10-15
	Romania	F	SP	900 g/kg	Foliar	0.45	0.03	3	14
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.018	As needed	15
	France	F	SL	200 g/l	Foliar		0.075	3	7
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	7
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	10-15
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	10-15
Pome fruit	Algeria	F	WP	250 g/kg	Foliar		0.04	3-4	7
	Greece	F	SL	200 g/l	Foliar	(1.1)	0.09	1-3	20
	Greece	F	SP	900 g/kg	Foliar	(1.1)	0.09	1-3	20
	Greece	F	WP	250 g/kg	Foliar	(1.1)	0.09	1-3	20
	Spain	F	SL	200 g/l	Foliar-high volume	0.75	0.05	1-5	7
	Spain	F	WP	250 g/kg	Foliar-high volume	00.75	0.05	1-5	7
Pomegranates	USA	F	SL	290 g/l	Foliar-aerial/ground	1	4.4	2	14
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1	4.4	2	14
Poppies	Australia	F	SL	225 g/l	Foliar-ground	0 0.45		As needed	14
	Australia	F	SP	400 g/kg	Foliar-ground	0 0.48		As needed	14
Potato	Algeria	F	SL	200 g/l	Foliar		0.04	ns	7
	Algeria	F	WP	250 g/kg	Foliar		0.04	3-4	7
	Australia	F	SL	225 g/l	0	0.34-0.45		As needed	-
	Australia	F	SP	400 g/kg	Foliar-ground	0 0.48		As needed	
	Brazil	F	SL	215 g/l	Foliar		0.0215	3	9
	Canada	F	SL	215 g/l	Foliar-ground	0.48	0.19	As needed	3
	Canada	F	SP	900 g/kg	Foliar-ground	0.49	- 0.19	As needed	3
	Central America	F	SL	216 g/l	Foliar	0.65	0.33	ns	6
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	6
	Central America	F	SP	900 g/kg	Foliar	0.45	0.11-0.23	ns	6
	Colombia	F	SL	216 g/l	Foliar		0.054	ns	14
	Colombia	F	SP	400 g/kg			0.027	ns	14
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	6

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0- .81	0.081	2-3	7
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	7
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	6	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	6	ns
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	6
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	15
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	15
Potato	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	15
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	15
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	15
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	- 0.9		1	15
	Indonesia	F	SL	200 g/l	Foliar		0.075	ns	14
	Japan	F	GR	1.5 g/kg	granule application	0.9		5	7
	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	7
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	6
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	6
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	6
	Mexico	F	SL	290 g/l	Foliar-ground	0.65	- 0.33	ns	6
	Mexico	F	SL	290 g/l	Foliar-aerial	0.65	1.3	ns	6
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	7
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	6
	Pakistan	F	SP	400 g/kg	Foliar	016		ns	
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	6
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	15
	South Africa	F	SL	200 g/l	Foliar-aerial	0.45	1.5	Repeat weekly	3
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	Repeat weekly	3
	South Africa	F	SP	900 g/kg	Foliar-aerial	0.45	1.5	Repeat weekly	3
	South Africa	F	SP	900 g/kg	Foliar-ground		0.045	Repeat weekly	3
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	6
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3-14
	USA	F	SL	290 g/l	Foliar-aerial/ground	1.0	11	10	6
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	6
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	6
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	6
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	6
Prunes	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	
Pumpkin	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	3
	Venezuela	F	SL	223 g/l	Foliar	0.33		ns	
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	
Quince	France	F	SL	200 g/l	Foliar		0.075	3	7
Radish, Japanese	Japan	F	GR	1.5 g/kg	granule application	0.9		3	7
	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	7
Rice	Central America	F	SL	216 g/l	Foliar	0.54	.027	ns	7
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	7
	Colombia	F	SL	216 g/l	Foliar-aerial	0.3	1.1	ns	14
	Colombia	F	SL	216 g/l	Foliar-ground	0.3	0.15	ns	14
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.22	0.8	ns	14
	Colombia	F	SP	400 g/kg	Foliar-ground	0.22	0.11	ns	14
	Ecuador	F	SL	290 g/l	Foliar	0.23		3	14
	Ecuador	F	SP	400 g/kg	Foliar	0.22	0.11	3	14
	Ecuador	F	SP	900 g/kg	Foliar	0.22	0.11	3	14
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	3
	Taiwan	F	WP	900 g/kg	Foliar		0.05(1800x)	ns	15
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	
Rye	USA	F	SL	290 g/l	Foliar-aerial/ground	0.5	5.4	4	7 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	5.4	4	7 grazing-10
Scallion, Leek	Taiwan	F	WP	900 g/kg	Foliar		0.03(3000x)	ns	10
Sesame	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	7
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	-
	Venezuela	F	SL	223 g/l	Foliar	0.33		ns	ns
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	
Sesame seed	Australia	F	SL	225 g/l	Foliar-ground	0.45		As needed	14
	Australia	F	SP	400 g/kg	Foliar-ground	0.48	2.2	As needed	14
	Colombia	F	SP	400 g/kg	Foliar-ground	0.33	0.17	ns	14
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.33	1.2	ns	
Shallot	Indonesia	F	SL	200 g/l	Foliar		0.08	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		.075	ns	14
Sitao	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	3
Sorghum	Argentina	F	SP	900 g/kg	Foliar	0.45	0- .15	ns	10
	Australia	F	SL	225 g/l	Foliar-aerial	0.45	2.0	As needed	14
	Australia	F	SP	400 g/kg	Foliar-aerial	0.48	2.2	As needed	14
	Central America	F	SL	216 g/l	Foliar	0.54	.027	ns	14
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	14
	Central America	F	SP	900 g/kg	Foliar	0.36	0.18	ns	14
	Colombia	F	SL	216 g/l	Foliar-aerial	0.2	0.7	ns	14
	Colombia	F	SL	216 g/l	Foliar-ground	0.2	0.1	ns	14
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.33	1.2	ns	14

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Colombia	F	SP	400 g/kg	Foliar-ground	0.33	0.17	ns	14
	Costa Rica	F	SP	900 g/kg	Foliar	0.54	0.27	ns	14
	Ecuador	F	SL	290 g/l	Foliar	0.36		2-3	14
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	2-3	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	2-3	14
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	14
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	14
	Peru	F	SL	240 g/l	Foliar	0.24	0.096	ns	5
	Peru	F	SL	296 g/l	Foliar	0.26	0.06	ns	14
	Peru	F	SP	400 g/kg	Foliar	0.23	0.14	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.23	0.14	ns	7
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	14
	South Africa	F	SL	200 g/l	Foliar-aerial	0.18	0.6	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground, low volume	0.18	0.18	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground		0.045	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground, low volume	0.18	0.18	ns	7
	Taiwan	F	WP	900 g/kg	Foliar		0.03(3000x)	ns	15
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	6-14
	USA	F	SL	290 g/l	Foliar-aerial/ground	0.5	2.6A 0.53T	2	14 grazing-14
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	2.6A 0.53T	2	14 grazing-14
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	14
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	14
	Venezuela	F	SP	900 g/kg	Foliar	0.45		ns	14
Soya bean	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	10
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0.045		10
	Australia	F	SL	225 g/l	Foliar-aerial	0.45	2.0	As needed	7
	Australia	F	SP	400 g/kg	Foliar-aerial	0.48	2.2	As needed	7
	Brazil	F	SL	215 g/l	Foliar	0.43	0.43	3	14
	Central America	F	SL	216 g/l	Foliar	0.54	0.027	ns	7 to 14
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	7 to 14
	Colombia	F	SL	216 g/l	Foliar-aerial	0.2	0.7	ns	14
	Colombia	F	SL	216 g/l	Foliar-ground	0.2	0.1	ns	14
	Colombia	F	SP	400 g/kg	Foliar-aerial	0.33	1.2	ns	14
	Colombia	F	SP	400 g/kg	Foliar-ground	0.33	0.17	ns	14
	Ecuador	F	SL	290 g/l	Foliar	0.36		3	14
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	3	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	3	14
	Indonesia	F	SL	200 g/l	Foliar		0.06	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		0.06	ns	14
	Japan	F	GR	1.5 g/kg	granule application	0 .9		4	14
	Japan	F	WP	450 g/kg	Foliar	1.4	.0.045	1-3	14

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	14
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	14
	Peru	F	SP	400 g/kg	Foliar	0.23	0.14	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.23	0.14	ns	7
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	3
	Taiwan	F	WP	900 g/kg	Foliar		0.05(2000x)	ns	
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	8 -14
Soya bean	USA	F	SL	900 g/kg	Foliar-aerial/ground	0.5	10	3	14 bean <0.5 kg ai/ha: forage 3 hay 7 >0.5 kg ai/ha: forage 10 hay 12
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	10	3	14 bean <0.5 kg ai/ha: forage 3 hay 7 >0.5 kg ai/ha: forage 10 hay 12
	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	7-14
	Venezuela	F	SL	288 g/l	Foliar	0.86		ns	7-14
	Venezuela	F	SP	900 g/kg	Foliar	0.32		ns	7-14
Spinach	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	7
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0. 5	ns	7
	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	14
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	7
	Romania	F	SP	900 g/kg	Foliar	0.9	0.09	3	7
	USA	F	SL	900 g/kg	Foliar-aerial/ground	1.0	11	8	7
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	8	7
Spinach, leafy vegetables	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
Squash	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	10
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	3
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	7
	Tunisia	F	WP	250 g/kg	Foliar	0.038	0.038	3-4	7
Squash, Summer	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	7
	USA	F	SL	900 g/kg	Foliar-aerial/ground	1.0	4.5-9.1	12	1/2 lb.-1 > 1/2 lb.-3
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	4.5-9.1	12	1/2 lb.-1 > 1/2 lb.-3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Stone fruit	Algeria	F	WP	250 g/kg	Foliar		0.04	3-4	7
	Australia	F	SL	225 g/l	Foliar-ground		0.045	ns	1
	Australia	F	SP	400 g/kg	Foliar-ground		0.048	ns	1
	Greece	F	SL	200 g/l	Foliar	1.1	0.09	1-3	20
	Greece	F	SP	900 g/kg	Foliar	1.1	0.09	1-3	20
	Greece	F	WP	250 g/kg	Foliar	1.1	0.09	1-3	20
	Spain	F	SL	200 g/l	Foliar-high volume	0.75	0.05	1-5	7
	Spain	F	WP	250 g/kg	Foliar-high volume	0.75	0.05	1-5	7
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
Strawberry	Australia	F	SL	225 g/l	Foliar-ground		0.045	As needed	3
	Australia	F	SP	400 g/kg	Foliar-ground		0.048	As needed	3
	Canada	F	SL	215 g/l	Foliar-ground	0.70	0.3	1	14
	Canada	F	SP	900 g/kg	Foliar-ground	0.70	0.3	1	14
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	3
	Japan	F	WP	450 g/kg	Foliar	0.68	0.045	1-3	-
	Japan	F	WP	450 g/kg	Foliar	9.0	0.045	1-3	
	Japan	F	WP	450 g/kg	Foliar	13.5	0.045	1-3	
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	3
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	3-fresh 10-processing
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	3
	New Zealand	F	SL	200 g/l	Foliar		0.024	As needed	2
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	fresh-3 processed-10
	USA	F	SL	900 g/kg	Foliar-aerial/ground	1.0	1.1	10	fresh fruit-3 processing fruit-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	1.1	10	fresh fruit-3 processing fruit-10
Sugar beet	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	7
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	7
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	7
	Italy	F	SL	200 g/l	Foliar		0.05	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.05	ns	10
	Macedonia	F	SL	200 g/l	Foliar		0.08	3	42
	Macedonia	F	WP	250 g/kg	Foliar		0.06		42
	Poland	F	SL	200 g/l	Foliar	0.14	0.09	3	14
	Spain	F	SL	200 g/l	Foliar-high volume	0.3	0.05	1-5	7
	Spain	F	WP	250 g/kg	Foliar-high volume	0.3	0.05	1-5	7
	USA	F	SL	900 g/kg	Foliar-aerial/ground	1.0	11	10	7
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	11	10	7
	Yugoslavia	F	SP	900 g/kg	ground application in bands	0.9		3	42
Sugar cane	Indonesia	F	WP	250 g/kg	Foliar		0.18	4	14

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
Sunflower	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	10
	Australia	F	SP	400 g/kg	Foliar-aerial	0.48	2.2	As needed	7
	Australia	F	SL	225 g/kg	Foliar-aerial	0.45	2.0	As needed	7
	South Africa	F	SP	900 g/kg	Foliar-aerial	.09 + 100 ml Sumiciden	0.3	ns	-
	Venezuela	F	SL	223 g/l	Foliar	0.33		ns	7
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	7
	Venezuela	F	SP	900 g/kg	Foliar	0.18		ns	7
Sweet corn	Australia	F	SP	400 g/kg	Foliar-ground	0.48		As needed	1
	Australia	F	SP	400 g/kg	Foliar-ground	0.45		As needed	1
	Canada	F	SL	215 g/l	Foliar-ground	0.56	0.23	4	3
	Canada	F	SP	900 g/kg	Foliar-ground	0.56	0.23	4	3
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	3
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	7
	USA	F	SL	900 g/kg	Foliar-aerial/ground	0.5	5.4	28	ears-0 forage-3
Sweet potato	Japan	F	GR	1.5 g/kg	granule application	0.9		5	7
	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	7
	Taiwan	F	WP	900 g/kg	Foliar		0.05(1800x)	ns	
Tangelo, Tangerine	USA	F	SL	900 g/kg	Foliar-aerial/ground	1.0	0.6	4	1 grazing-10
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	0.6	4	1 grazing-10
Tea	Indonesia	F	SL	200 g/l	Foliar		0.05	3	14
	Indonesia	F	WP	250 g/kg	Foliar		0.05	3	14
	Japan	F	WP	450 g/kg	Foliar	1.8	0.045	1-3	21
	Taiwan	F	WP	900 g/kg	Foliar		0.05(2000x)	ns	21
Tea trees	Australia	F	SP	400 g/kg	Foliar-ground	0.5		ns	ns
Tomato	Argentina	F	SP	900 g/kg	Foliar	0.45	0.15	ns	10
	Argentina	F	SP	900 g/kg	Foliar-knapsack		0. 045		10
	Australia	F	SL	225 g/l	Foliar-ground		0.045	ns	1
	Australia	F	SP	400 g/kg	Foliar-ground		0.048	ns	1
	Belgium	G	WP	250 g/kg	Foliar	0.5	0.031	ns	14
	Brazil	F	SL	215 g/l	Foliar		0.02	5	3
	Bulgaria	F	WP	250 g/kg	Foliar		0.02	3	7
	Canada	F	SL	215 g/l	Foliar-ground	0.49	0.2	As needed	1
	Canada	F	SP	900 g/kg	Foliar-ground	0.49	- 0.2	As needed	1
	Central America	F	SL	216 g/l	Foliar	0.54	.027	ns	1
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	1
	Central America	F	SP	900 g/kg	Foliar	0.45	0.23	ns	1-2
	Costa Rica	F	SP	900 g/kg	Foliar	1.00	0.5	ns	1-2
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	1
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	1

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Ecuador	F	SL	290 g/l	Foliar	0.3		8	1
	Ecuador	F	SP	400 g/kg	Foliar	0.22	0.11	8	1
	Ecuador	F	SP	900 g/kg	Foliar	0.22	0.11	8	1
	Egypt	F	SP	900 g/kg	Foliar	0.64		ns	1
	France	F/G	SL	200 g/l	Foliar	0.5		3	7
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	7
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.9		1	7
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	7
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	7
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.9		1	7
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	7
Tomato	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	7
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.9		1	7
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	7
	Hungary	F	SL	200 g/l	Foliar	0.4	0.07	ns	5
	Hungary	G	SL	200 g/l	Foliar	0.72	0.09	ns	5
	India	F	SP	400 g/kg	Foliar-high volume	0.45	0.09	ns	5
	Indonesia	F	SL	200 g/l	Foliar		0.06	ns	14
	Indonesia	F	WP	250 g/kg	Foliar		0.038	ns	14
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	1
	Kuwait	F	SP	900 g/kg	Foliar		00.045	ns	1
	Lebanon	F	SP	900 g/kg	Foliar		0.09	As needed	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.65	- 1.3	ns	1
	Mexico	F	SL	290 g/l	Foliar-ground	0.65	0.33	ns	1
	Morocco	F	WP	250 g/kg	Foliar		0.038	ns	1-2
	Netherlands	F/G	SL	200 g/l	Foliar	0.4	0.025	1-3	3
	Netherlands	G	WP	250 g/kg	Foliar	0.4	0.08	1-3	3
	New Zealand	G	SL	200 g/l	Foliar		0.024	4	2
	New Zealand	F	SL	200 g/l	Foliar	0.4		As needed	2
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	1
	Pakistan	F	SP	400 g/kg	Foliar	0.16		ns	
	Peru	F	SL	240 g/l	Foliar	0.36	0.096	ns	5
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	1
	Peru	F	SP	400 g/kg	Foliar	0.4	0.18	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.4	0.18	ns	7
	Philippines	F	SP	400 g/kg	Foliar		0.09	As needed	1
	Poland	F	SL	200 g/l	Foliar	0.18	0.09	3	3
	Poland	G	SL	200 g/l	Foliar		0.02	3	3
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	1
Tomato	Romania	G	SP	900 g/kg	Foliar	0.45	0.045	3	3

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Romania	F	SP	900 g/kg	Foliar	0.90	0.09	3	3
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	15
	South Africa	F	SL	200 g/l	Foliar		0.045	ns	2
	South Africa	F	SP	900 g/kg	Foliar		0.045	ns	2
	Spain	F	SL	200 g/l	Foliar-high volume	0.50	0.05	1-5	3
	Spain	F	WP	250 g/kg	Foliar-high volume	0.50	0.05	1-5	3
	Syria	F	SP	900 g/kg	Foliar		0.06	As needed	1
	Taiwan	F	WP	900 g/kg	Foliar		0.03(3000x)	ns	4
	Thailand	F	SL	184.5 g/l	Foliar		0.05	ns	3
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
	Tunisia	F	WP	250 g/kg	Foliar	0.038	0.038	3-4	7
	Turkey	F	SP	900 g/kg	Foliar	0.72		ns	3
	USA	F	SL	900 g/kg	Foliar-aerial/ground	1.0	5.4	16	1
	USA	F	SP	900 g/kg	Foliar-aerial/ground	1.0	5.4	16	1
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	1
	Venezuela	F	SL	223 g/l		0.89		ns	1
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	1
Top fruit trees	Algeria	F	SL	200 g/l	Foliar		0.08	ns	7
Turf	USA	F	SL	900 g/kg	Foliar-aerial/ground	2.0		4	-
	USA	F	SP	900 g/kg	Foliar-aerial/ground	2.0		4	-
Vegetables	Algeria	F	SL	200 g/l	Foliar		0.04	ns	7
	Algeria	F	WP	250 g/kg	Foliar		0.04	3-4	7
	Austria	F/G	WP	250 g/kg	Foliar	0.38	0.06	ns	21
	Kenya	F	SP	900 g/kg	Foliar-high volume	0.9		As needed	5
	Macedonia	F	SL	200 g/l	Foliar		0.04	3	tomato-7 peppers, root vegetables-14 other veg-35
	Macedonia	F	SP	900 g/kg	Foliar		0.045	As needed	
	Macedonia	F	WP	250 g/kg	Foliar		0.04	2	
	Morocco	F	SL	200 g/l	Foliar		0.05	ns	7
	Yugoslavia	F	SP	900 g/kg	Foliar		0.05	As needed	14
Walnuts	Cyprus	F	SP	900 g/kg		0.82	0.041	1	8
Watermelon	Central America	F	SL	216 g/l	Foliar	0.54	0.027	ns	3
	Central America	F	SL	290 g/l	Foliar	0.58	0.29	ns	3
	Cyprus	F	SP	900 g/kg	Foliar-high volume	0.81	0.081	2-3	3
	Cyprus	F	SP	900 g/kg	knapsack	1.00	0.2	2-3	3
	Ecuador	F	SP	400 g/kg	Foliar	0.3	0.15	8	14
	Ecuador	F	SP	900 g/kg	Foliar	0.3	0.15	8	14
	Greece	F/G	SL	200 g/l	Foliar	0.45		1-3	20
	Greece	F/G	SL	200 g/l	soil spraying; incorporated	2.7		1	20
	Greece	F/G	SL	200 g/l	soil spraying followed by irrigation	0.90		1	20
	Greece	F/G	SP	900 g/kg	Foliar	0.45		1-3	20

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	Greece	F/G	SP	900 g/kg	soil spraying; incorporated	2.7		1	20
	Greece	F/G	SP	900 g/kg	soil spraying followed by irrigation	0.90		1	20
	Greece	F/G	WP	250 g/kg	Foliar	0.45		1-3	20
	Greece	F/G	WP	250 g/kg	soil spraying; incorporated	2.7		1	20
	Greece	F/G	WP	250 g/kg	soil spraying followed by irrigation	0.90		1	20
	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Kuwait	F	SP	900 g/kg	Foliar		0.045	ns	3
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	-1.2	ns	3
	Oman	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Peru	F	SL	296 g/l	Foliar	0.52	0.09	ns	3
	Peru	F	SP	400 g/kg	Foliar	0.41	0.18	ns	7
	Peru	F	SP	900 g/kg	Foliar	0.41	0.18	ns	7
	Qatar	F	SP	900 g/kg	Foliar		0.045	As needed	3
	Saudi Arabia	F	SP	900 g/kg	Foliar		0.032	As needed	10
	Thailand	F	SP	400 g/kg	Foliar		0.07	ns	3
	Venezuela	F	SL	223 g/l	Foliar	0.33		ns	3
	Venezuela	F	SL	288 g/l	Foliar	0.5		ns	3
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	3
Watermelon, field	Japan	F	WP	450 g/kg	Foliar	1.4	0.045	1-3	1
Wheat	Argentina	F	SP	900 g/kg	Foliar	0.45	.15	ns	14
	Australia	F	SL	225 g/l	Foliar-aerial	0.45	2.1	As needed	14
	Australia	F	SP	400 g/kg	Foliar-aerial	0.49	2.2	As needed	14
	Brazil	F	SL	215 g/l	Foliar	0.28	0.28	4	14
	Canada	F	SL	215 g/l	Foliar-ground	0.49	- 0.5	As needed	20
	Canada	F	SL	215 g/l	Foliar-aerial	0.49	2.2	As needed	20
	Canada	F	SP	900 g/kg	Foliar-ground	0.49	0.5	As needed	20
	Canada	F	SP	900 g/kg	Foliar-aerial	0.49	2.2	As needed	20
	China	F	SP	900 g/kg	Foliar	0.202	0.10	1-5	7
	Jordan	F	SP	900 g/kg	Foliar		0.05	ns	7
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	7
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	7
	South Africa	F	SL	200 g/l	Foliar-aerial	0.18	0.6	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground, low volume	0.18	0.18	ns	7
	South Africa	F	SL	200 g/l	Foliar-aerial		0.6	ns	7
	South Africa	F	SL	200 g/l	Foliar-ground		0.045	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground, low volume	0.18	0.18	ns	7
	South Africa	F	SP	900 g/kg	Foliar-ground		0.045	ns	7
Wheat	USA	F	SL	900 g/kg	Foliar-aerial/ground	0.5	5.4	4	7 grazing-10

Crop	Country	F/G[1]	Form type	Concen-tration	Application method	Rate[2] kg ai/ha	Spray conc., kg ai/hl	No. of applications	PHI (days)
	USA	F	SP	900 g/kg	Foliar-aerial/ground	0.5	5.4	4	7 grazing-10
Yucca	Venezuela	F	SL	223 g/l	Foliar	0.45		ns	
	Venezuela	F	SP	900 g/kg	Foliar	0.27		ns	
Zucchini	Italy	F	SL	200 g/l	Foliar		0.04	ns	10
	Italy	F	WP	250 g/kg	Foliar		0.04	ns	10
	Mexico	F	SL	290 g/l	Foliar-ground	0.58	0.29	ns	3
	Mexico	F	SL	290 g/l	Foliar-aerial	0.58	1.2	ns	3

[1] Outdoor or field use (F) or glasshouse application (G)
[2] The kg ai/hl value is calculated from label information, i.e., from maximum kg ai/ha and minimum spray volume per ha, except where no rate value is given or is in parenthesis.
ns: not stated

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised field trials were reported for numerous commodities. Where results were given as ND (not detected) and a substantiated value for ND was not provided, the ND was assigned 50% of the limit of quantification. Trials are listed in the following Tables, where underlined residues are from trials according to GAP and were used to esimate maximum residue levels.

Table Number	Commodity
23	Oranges and mandarins
24	Apples and pears (Europe)
25	Apples (USA)
26	Pears (USA)
27	Peaches and apricots (Europe)
28	Peaches (USA)
29	Nectarines (USA)
30	Plums (Europe)
31	Grapes (USA)
32	Grapes (Europe)
33	Onions, Bulb
34	Cabbage
35	Broccoli
36	Pears (USA)
36	Broccoli and cauliflower
37	Cucumbers and courgettes (Southern Europe)
38	Cucumbers and courgettes (Northern Europe)
39	Watermelon
40	Melons
41	Egg plant, tomatoes and peppers (USA)
42	Tomatoes and peppers (Europe)
43	Spinach, Head lettuce, Leaf lettuce
44	Beans (succulent), peas (podded), soya (immature)
45	Bean forage
46	Beans (dry)
47	Bean (dry) forage

Table Number	Commodity
48	Potato
49	Asparagus
50	Celery
51	Barley, oats, wheat
52	Barley, oats, wheat forage/straw
53	Sorghum grain
54	Sweet corn and maize
55	Sweet corn and maize forage and fodder
56	Cotton seed
57	Peanuts
58	Alfalfa
59	Soya hay
60	Sorghum forage and hay
61	Sorghum fodder
62	Sorghum fodder

Citrus fruits. In field trials in Greece, Italy and Spain SL or WP formulations were applied to oranges and mandarins in the 1996 (Weidenauer *et al.*, 1998m) and 1997 (Françon, 1999) growing seasons. Three foliar spray ground applications (4 in Greece) were made at one to three month intervals at a target rate of 500-1250 g ai/ha/application and 1000-2500 l/ha at concentrations of 0.04 kg ai/hl in Italy, 0.09 kg ai/hl in Greece and 0.05 kg ai/hl in Spain. In each year some trials were residue decline studies and others were at a PHI of 7 days. Samples were collected manually in duplicate and stored frozen at -18 to -20^{o}C for analysis by method AMR 3015-94 (Rühl, 1998). Storage was for a maximum of a year in the 1996 and 1.4 years in the 1997 trials. Samples were stored whole unhomogenized until 2 weeks or less before extraction in 1997 and until 4 months before extraction in 1996. The 1996 samples were then stored homogenized for a period that could have resulted in 30% loss of methomyl, on the basis of the storage stability studies (see above). Control samples fortified with methomyl at 0.02 mg/kg were extracted and analysed with the treated samples. For the 1996 samples recoveries were 88% $\pm$ 14%, n=13, and for 1997 96% $\pm$ 7%, n=13. The half-life, assuming first order kinetics, was 1-7 days for the former and 2-4 days for the latter. The results are shown in Table 23.

Table 23. Residues of methomyl in or on oranges and mandarins after foliar applications of WP or SL formulations in Greece, Italy and Spain in 1996 and 1997 (Trials AMR 4043-96; AMR 4500-97).

Location/Year/Variety	Spray application					PHI (days)	Methomyl (mg/kg)
	Form.	kg ai/hl	l/ha	No.	kg ai/ha		
Orange							
GAP:Spain	WP SL	0.05		5	0.6WP 0.5SL	7	
GAP:Greece	SL	0.09		3	1.35	20	
GAP:Italy	SL, WP	0.04				10	
Los Palacios, Spain/1996/Navelina	SL, 200 g/l	0.051	2131	3	1.09	-1h +1h 1 3 5 7	<0.02 0.17, 0.24 0.44, 0.29 0.24, 0.11 0.06, 0.02 ≤0.02, <0.02

Location/Year/Variety	Spray application					PHI (days)	Methomyl (mg/kg)
	Form.	kg ai/hl	l/ha	No.	kg ai/ha		
Los Palacios, Spain/1996/Navelina	WP, 250 g/kg	0.050	2131	3	1.06	-1h +1h 1 3 5 7	<0.02 0.37, 0.21 0.29, 0.26 0.11, 0.32 0.05, 0.15 0.03, <0.02
Los Palacios, Spain/1996/New Hall	SL, 200 g/l	0.050	2125	3	1.06	7	0.06, 0.03
Los Palacios, Spain/1996/Navelina	SL, 200 g/l	0.051	2131	3	1.09	7	<0.02, <0.02 <0.02, <0.02 (duplicate plots)
Los Palacios, Spain/1997/New Hall	SL, 200 g/l	0.051	1905	3	0.97	-1h +3h 1 3 5 7	<0.02 0.16, 0.03 0.05, 0.11 0.20, 0.04 <0.02, <0.02 0.02, <0.02
Los Pobla Llarga, Spain/1997/Salustiana	SL, 200 g/l	0.051	1003	3	0.51	7	0.43, 0.25
Los Pobla Llarga, Spain/1997/Salustiana	WP, 250 g/kg	0.051	1018	3	0.52	7	0.35, 0.15
Dalamanara-Argolis, Greece/1997/Merlin	SL, 200 g/l	0.050	2519	4	1.25	-1h +1h 1 3 5 7	0.07, 0.10 0.48, 0.78 0.69, 0.55 0.21, 0.49 0.27, 0.46 0.26, 0.30
Dalamanara-Argolis, Greece/1997/Merlin	SL, 200 g/l	0.050	2519	4	1.25	7	0.24, 0.25
Vergi Kostalii, Greece/1997 /Merlin	SL, 200 g/l	0.050	2014	3	1.0	7	0.30, 0.59
Catania, Italy/1996/Navalina	SL, 200 g/l	0.050	1500	3	0.75	7	0.06, 0.02
Catania, Italy/1996/Navalina	WP, 250 g/kg	0.050	1500	3	0.75	7	0.04, 0.09
C. da Desi, Italy/1997/Navelina	SL, 200 g/lg	0.050	2300	3	1.14	<0h +3 h 1 3 5 7	<0.02 0.66, 0.36 0.35, 0.22 0.17, 0.21 0.21, 0.17 0.14, 0.08
C. da Desi, Italy/1997/Navelina	WP, 250 g/l	0.051	2300	3	1.16	<0h +3 h 1 3 5 7	<0.02 0.79, 0.10 0.20, 0.76 0.55, 0.32 0.15, 0.17 0.07, 0.06
Mandarin							
GAP: Spain	SL, WP	0.05		5	0.5,0.6	7	
GAP: Greece	SL, WP	0.09		3	1.35	20	
GAP: Italy	SL, WP	0.04				10	

Location/Year/Variety	Spray application					PHI (days)	Methomyl (mg/kg)
	Form.	kg ai/hl	l/ha	No.	kg ai/ha		
Llira, Spain/1996/Clemenules	WP, 250 g/kg	0.050	2280	3	1.14	-1h +1h 1 3 5 7	0.03, 0.10 0.52, 0.97 0.76, 1.1 0.74, 0.50 0.61, 0.77 0.10, 0.19
Los Palacios, Spain /1996 /Clemenules	SL, 200 g/l	0.050	2111	3	1.06	7	0.05, 0.05
Lliria, Spain /1996 /Clemenules	WP, 250 g/kg	0.050	2280	3	1.14	7	0.14, 0.17
Castello de la Ribera, Spain /1997 /Clemenvilla	SL, 200 g/l	0.051	1813	3	0.93	-1h +3h 1 3 5 7	<0.02 0.44, 0.75 0.43, 0.53 0.37, 0.26 0.24, 0.15 0.17, 0.14
Los Placios, Spain /1997 /Clemenules	WP 250 g/l	0.051	1804	3	0.91	7	0.03, <0.02
Pyrgela-Argolis, Greece /1997 Clementines	SL, 200 g/l	0.050	2500	4	1.25	7	0.43, 0.16
Vergi Kostakii, Greece /1997 /Clementines	SL, 200 g/l	0.049	1930	3	0.96	-1h +3h 1 3 5 7	0.13, 0.09 1.7, 1.6 0.70, 0.80 0.42, 0.41 0.15, 0.74 0.32, 0.31
Vergi Kostakii, Greece /1997 /Clementines	WP, 250 g/kg	0.051	1944	3	0.98	-1h +3h 1 3 5 7	0.07, 0.02 1.8, 1.8 0.60, 0.59 0.48, 0.25 0.53, 0.27 0.11, 0.38
Catania, Italy/1997 /Avana	WP, 250 g/kg	0.050	2000	3	1.0	-1h +1h 1 3 5 7	<0.02 1.3, 0.98 0.74, 0.91 0.90, 0.75 0.49, 0.36 0.31, 0.30, 0.38, 0.31
C. da Campochiaro, Italy /1998 /Avana	SL, 200 g/l	0.051	2000	3	1.02	7	0.89, 0.51

Pome Fruit. Field trials on apples and pears were reported from Europe and the USA. Trials were conducted in Belgium, France and Italy in 1996 (Weidenauer *et al.*, 1998f,g) and in Belgium, France, Italy and Spain in 1997 (Françon and Larcinese, 1999d). WP or SL formulations were applied with ground equipment at a target rate of 0.60 or 0.90 kg ai/ha to pear and apple trees three times at one to two month intervals. Duplicate fruit samples were collected manually, stored frozen for a maximum of 1.9 years (-20^{o}C) and analysed by method AMR 3015-94. Control samples were fortified at 0.02 mg/kg and analysed with the treated samples. Recoveries were 84% $\pm$ 15% (n=11) for AMR 3941-96; 90% $\pm$ 12%% (n=14) for AMR 4505-97; and 88% $\pm$ 8% (n=4) for AMR 3942-96, and were similar at 0.20 mg/kg and 1.5 mg/kg fortifications. The results are shown in Table 24.

Table 24. Methomyl residues in or on apples and pears after the application of a WP or SL formulation at 0.60-0.90 kg ai/ha to trees in Europe in 1996-1997 (AMR 3941-96; AMR 3942-96; AMR 4505-97).

Location/Variety/ Year	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concentration (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
GAP: France	SL	0.075		3		7	
GAP: Italy	SL, WP	0.05				10	
GAP: Spain	SL, WP	0.05		5	0.6	7	
GAP: Belgium	WP	0.05			0.75	21	
Apple							
Fromenville-Rainecourt, France/Jomagol/1996 (AMR 3941-96)	SL, 200 g/l	0.060	1362	3	0.82	-1h +1h 1 3 5 7	<0.02 0.20, 0.24 0.11, 0.11 0.11, 0.15 0.10, 0.14 0.10, 0.13
Fromenville-Rainecourt, France/Jomagol/1996	WP, 250 g/kg	0.061	1283	3	0.78	-1h +1h 1 3 5 7	<0.02 0.17, 0.10 0.16, 0.12 <0.02, <0.02 0.08, 0.06 0.16, 0.08
Beano di Codroipo, Italy/Ozark Gold/1996	SL, 200 g/l	0.060	1500	3	0.90	-1h +1h 1 3 5 7	<0.02 0.47, 0.37 0.13, 0.22 0.18, 0.20 0.18, 0.17 0.08, 0.05
Beano di Codroipo, Italy/Ozark Gold/1996	WP, 250 g/kg	0.060	1500	3	0.90	-1h +1h 1 3 5 7	<0.02 0.53, 0.32 0.24, 0.18 0.13, 0.17 0.09, 0.12 0.09, 0.08
Sorgues, France/Golden/1996	SL, 200 g/l	0.060	994	3	0.60	-1h +1h 1 3 5 7	<0.02 0.12, 0.20 0.11, 0.09 0.10, 0.13 0.08, 0.11 0.05, 0.11
Fleurus, Belgium/Jonagold/1996	WP, 250 g/kg	0.060	1129	3	0.68	-1h +1h 1 3 5 7	<0.02 0.34, 0.18 <0.02, 0.21 0.10, 0.21 <0.02, 0.10 0.06, 0.05
St Jean de Braye, France/Golden/1996 (AMR 3942-96)	SL, 200 g/l	0.060	1152	3	0.69	7	0.03, 0.02
Montauban, France/Reine des Reinettes	SL, 200 g/l	0.060	964	3	0.58	7	0.07, 0.09
Nodebais, Belgium/Jonagold/1996	WP, 250 g/kg	0.061	1092	3	0.66	7	0.02, 0.15
Terrer-Zaragoza, Spain/Golden Delicious/1996	WP, 250 g/kg	0.060	1066	3	0.64	7	0.04, 0.06

Location/Variety/ Year	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concentration (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
St Loubes, France/Reinette/1997	WP, 250 g/kg	0.060	1611	3	0.967	<0 +3h 1 3 5 7	<0.02 0.14, 0.43 0.16, 0.22 0.17, 0.19 0.16, 0.16 0.10, 0.09
Lignieres de Tourraine, France/Granny Smith/1997	SL, 200 g/l	0.060	959	3	0.575	7	0.02, 0.09
Lignieres de Tourraine, France/Granny Smith/1997	WP, 250 g/kg	0.060	1010	3	0.606	7	0.17, 0.13
Assent, Belgium/Elstar/1997	WP, 250 g/kg	0.061	1176	3	0.714	7	0.05, 0.03
Ateca, Spain/Golden Delicious/1997	SL, 200 g/l	0.061	1032	3	0.633	7	0.07, 0.08
Pear							
Ittre, Belgium/Conference/ 1997	WP, 250 g/l	0.061	1157	3	0.702	-1h +3h 1 3 5 7	<0.02 0.58, 0.52 0.20, 0.24 0.17, 0.12 0.10, 0.10 0.09, 0.10
Chouze sur Loire, France/Williams/199 7	SL, 200 g/l	0.060	1230	3	0.738	-1h +3h 1 3 5 7	<0.02 0.19, 0.18 0.18, 0.09 0.08, 0.15 0.05, <0.02 0.03, <0.02
Modena, Italy/Decana del Comizio/1997	SL, 200 g/l	0.060	1020	3	0.612	-1h +3h 1 3 5 7	<0.02 1.1, 1.6 0.14, 0.11 0.17, 0.10 0.14, 0.13 0.11, 0.11
Modena, Italy/Decana del Comizio	WP, 250 g/l	0.060	1044	3	0.626	-1h +3h 1 3 5 7	<0.02 1.9, 0.96 0.07, 0.10 0.12, 0.13 0.05, 0.10 0.18, 0.10
Sorgues, France/Guyot/1997	SL, 200 g/l	0.060	992	3	0.596	7	0.04, 0.03

Two trials on apple trees were reported from the USA. In 1992 two plots at each of ten test sites received five foliar treatments (ground, airblast) of SP, WP or SL formulations at intervals of 5-7 days at 1 kg ai/ha or 1.5 kg ai/ha per treatment (Hausman and Devine, 1993b). Samples of mature fruit were taken 8, 10, 14 and 21 days after the last treatment and stored frozen at -15 to -25°C for up to 7 months. Analyses were by HPLC method AMR 1806-90. Control apple samples were fortified with methomyl at 0.02 mg/kg and analysed with the treated samples. The mean recovery was 96% ± 11% (n=4). For 35 fortifications from 0.02 to 1 mg/kg, the mean recovery was 95% ± 10%, range 78%-111%.

In the second trial in 1997 two plots were treated at 14 locations at different times to provide multiple PHIs with five applications by airblast sprayer (ground) at 1.0 kg ai/ha at approximately 7-day intervals (McCooey, 1998a). Duplicate samples from each plot were stored at -15 to -25°C for up to 5.5 months before extraction and analysis by method AMR 3015-94. Two trials were residue decline studies and half-lives of 5.0-9.5 days were calculated. Control samples were fortified with methomyl at 0.02 mg/kg and prepared and analysed with the treated samples. The recovery was 84% ± 4.7%, n=23.

The results are shown in Table 25.

Table 25. Residues of methomyl in or on apples after five foliar application of SP, WP or SL formulations at 1.0 or 1.5 kg ai/ha in the USA in 1992 and 1997 (AMR 2291-92; AMR 4345-97).

Location/Variety/year	Application			PHI (days)	Methomyl (mg/kg)
	Form.	Rate (kg ai/ha)	Spray volume (l/ha)		
GAP: USA	SP, SL	1.0	470	14	
Newark, Delaware/McIntosh/1992	SL, 216 g/l	1.0	460-470	8 14	0.44, 0.48, 0.56 0.24, 0.34, 0.24
	SL, 216 g/l	1.5	460-470	8 10 21	1.1, 1.1, 1.1 0.69 0.39, 0.21, 0.51
Upper Black Eddy, Pennsylvania/Cortland/1992	WP, 900 g/kg	1.0	480	8 14	0.66, 0.60, 0.68 0.31, 0.28, 0.26
	WP, 900 g/kg	1.5	480	8 10 21	0.96 0.94 0.42, 0.32, 0.36
Hamburg, Pennsylvania/Red Delicious/1997	SP, 900 g/kg	1.0	610-670	35 41	0.30, 0.32 0.17, 0.20
Hereford, Pennsylvania/Red Delicious/1997	SP, 900 g/kg	1.0	560	35 42	0.26, 0.27 0.33, 0.32
Alton, New York/Twenty Ounce/1992	SL, 216 g/l	1.0	470	8 14	0.43 0.42, 0.40, 0.33
	SL, 216 g/l	1.5	470	8 10	0.94 0.92
Sodus, New York/Monroe/1997	SL, 216 g/l	1.0	470	35 42	0.42, 0.33 0.29, 0.26
North Rose, New York/Idared/1997	SL, 216 g/l	1.0	480	35 42	0.38, 0.39 0.23, 0.31
Conklin, Michigan/Golden Delicious/1992	SL, 216 g/l	1.0	450	8 10 14 21	1.3, 1.4 0.86, 1.0, 0.89 0.43, 0.77, 0.60 0.19, 0.55, 0.50
	SL, 216 g/l	1.5	450	8 10 14 21	1.6, 1.9 2.1 1.3 0.80, 1.1, 1.1
Fennville, Michigan/Red Delicious/1992	SL, 216 g/l	1.0	470	8 14	0.46, 0.43, 0.35 0.39, 0.31, 0.16
	SL, 216 g/l	1.5	470	8 10	0.64, 0.44, 0.38 0.66
Conklin, Michigan/McIntosh/1997	SP 900 g/kg	1.0	580-650	35 42	0.099, 0.14 0.12, 0.094
Fennerville, Michigan/Red Delicious/1997	SP, 900 g/kg	1.0	450-470	35 42	0.24, 0.22 0.13, 0.12
North Rose, New York/Rhode Island Greening/1992	SP, 900 g/kg	1.0	470	8 14	0.64, 0.44, 0.38 0.31, 0.21, 0.14
	SL, 216 g/l	1.5	470	10	0.42

Location/Variety/year	Application			PHI (days)	Methomyl (mg/kg)
	Form.	Rate (kg ai/ha)	Spray volume (l/ha)		
Hickman, California, Granny Smith/1992	SP, 900 g/kg	1.0	470	8 14	0.23, 0.20, 0.12 0.12, 0.13, 0.16
	SP, 900 g/kg	1.5	470	10	0.20
Madera, California/Fuji/1997	SP, 900 g/kg	1.0	470	35 42	<0.02, <0.02 <0.02, <0.02
Granger, Washington/Red Delicious/1992	SL, 216 g/l	1.0	470	8 14	0.30, 0.40, 0.38 0.18, 0.22, 0.25
		1.5	470	10	0.22
Harrrah, Washington[1]/Red Delicious/1992	SL, 216 g/l	1.0	470	8 14	0.47, 0.42, 0.34 0.16, 0.23, 0.24
	SL, 216 g/l	1.5	470	10	0.54
Harrah, Washington[1]/Red Delicious/1992	SL, 216g/l	1.0	470	8 14	0.40, 0.71, 0.58 0.30, 0.48, 0.34
	SL, 216 g/l	1.5	470	10	0.46
Granger, Washington/Red Delicious/1997	SL, 216 g/l	1.0	460-500	35 42	0.17, 0.19 0.15, 0.11
Granger, Washington/Red Delicious	SP, 900 g/kg	1.0	460-490	21 28 35 42	0.50, 0.05 0.42, 0.40 0.18, 0.14 0.13, 0.12
Ephrata, Washington/Red Delicious/1997	SP, 900 g/kg	1.0	480	35 42	0.20, 0.25 0.15, 0.17
Elkton, Maryland/Golden Delicious/1997	SP, 900 g/kg	1.0	500	21 28 35 42	0.57, 0.46 0.23, 0.22 0.059, 0.030 0.058, 0.022
Cana, Virginia/Red Delicious/1997	SP, 900 g/kg	1.0	490	35 42	0.12, 0.096 0.064, 0.060
Austin, Colorado/Red Delicious/1997	SP 900 g/kg	1.0	570	35 42	0.15, 0.14 0.11, 0.080
Hood River, Oregon/1997/Red Delicious	SL, 216 g/l	1.0	480-560	35 42	0.300.42 0.49, 0.32

[1] Although two sites were in Harrah, different soil types were reported: loam for the first entry and silt loam for the second.

In six trials on pear trees in the USA four applications of an SL formulation with an airblast sprayer (ground) at 0.5 kg ai/ha were made at 5-7 day intervals (Hausmann and Devine, 1992b, 1993d). One to three samples, consisting of 16 or more fruit each, were collected at maturity at each location and stored frozen for a maximum of 8.5 months until extracted and analysed by method AMR 1806-90. Control samples fortified with methomyl were extracted and analysed with the treated samples. Recoveries were 100% at 0.2 mg/kg (n=2), 73% at 0.1 mg/kg, 92% at 0.5 mg/kg (n=2), 91% at 2 mg/kg and 98% at 4 mg/kg. The results are shown in Table 26.

Table 26. Residues of methomyl in or on pears after foliar ground applications of an SL or SP formulation to pear trees in the USA (AMR 2344-92; AMR 1970-91).

Location/Variety/year	Application					Methomyl (mg/kg)
	Form.	Rate (kg ai/ha)	Spray volume (l/ha)	No.	PHI (days)	
GAP: USA	SL, SP	1.0	470	2	7	
Upper Black Eddy,	SL, 216 g/l	0.5	480	4	7	0.52, 0.62, 0.56

Location/Variety/year	Application					Methomyl (mg/kg)
	Form.	Rate (kg ai/ha)	Spray volume (l/ha)	No.	PHI (days)	
Pennsylvania/Bartlett/1992						
Romney, West Virginia/Mangus/1992	SL, 216 g/l	0.5	410	4	7	1.1, 1.1, 1.2
Orwigsburg, Pennsylvania/Bosc/1992	SL, 216 g/l	0.5	470	4	7	0.17, 0.15, 0.23
Alton, New York/Bartlett/1991	SP, 900 g/kg	0.5	940	4	7 10 14	0.41 0.28 0.25
Alton, New York/Bartlett/1991	SL, 216 g/l	0.5	940	4	7 10 14	0.48 0.28 0.23
Winchester, Virginia/Delicious/1991	SL, 216 g/l	0.5	920	4	7 10 14	0.57, 0.58 0.56, 0.46 0.31, 0.36

Stone fruits. In field trials in France, Germany, Italy and Spain SL or WP formulations were applied to peaches or apricots in the 1996 and 1997 growing season (Weidenauer *et al.*, 1998b,c; Françon and Larcinese, 1999b). Three overall foliar sprays using ground equipment were made at a target rate of 600-900 g ai/ha, approximate spray volume 1000 l/ha. The retreatment interval was about one month. Samples were collected manually in duplicate at various intervals and stored at -20° C for up to 17 months (1996) or 13 months (1997). Residues of methomyl were determined by HPLC with post-column derivatization and fluorescence detection, based on method AMR 3015-94. In 1996 mean recoveries from concurrent control samples fortified at 0.02 mg/kg were 93% ± 14%, n = 8 (AMR 3886-96) and 84% ± 17%, n = 3 (AMR 3887-96), and in 1997, for samples fortified at 0.021 mg/kg, 81% ± 16%, n = 12, range 53%-110%. Even at a 0.21 mg/kg fortification, the standard deviation was still wide: 74% ± 13%, n = 7 (1996) and 72% ± 18%, n = 6 (1997). All control peach samples had methomyl concentrations below the limit of quantification (<0.02 mg/kg). Six trials were residue decline studies. The half-life ranged from 2 to 3 days for five of the trials and was 5 days for the sixth. The results are shown in Table 27.

Table 27. Residues of methomyl on peaches and apricots after three foliar applications of a WP or SL formulation at 600-900 g ai/ha, Europe, 1996 and 1997. Reference AMR 3886-96, AMR 3887-96, AMR 4499-97.

Location/Year/ Variety	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concen-tration (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
GAP:Spain	SL, WP	0.05		5	0.6	7	
GAP: Germany	SL			3	0.75	7	
GAP: Italy	WP, SL	0.04				10	
Almenar, Spain/1996/Catherine Peach	SL, 200 g/l	0.059	933	3	0.554	- 1 hr + 1 hr 1 3 5 7	<0.02, 0.02 0.75, 1.17 0.42, 0.46 0.05, 0.17 0.08, 0.05 0.09, 0.03
Hohnstedt, Germany/1996/ Sound Heaven Peach	WP, 250 g/kg	0.060	1000	3	0.600	- 1 hr 0 1 3 5 7	0.02, <0.02 0.43, 0.53 0.40, 0.45 0.12, 0.22 0.04, 0.07 0.04, 0.04

Location/Year/ Variety	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concen-tration (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
Sclaunicco di Lestizza, Italy/1996/Elegant Lady Peach	WP, 250 g/kg	0.060	1500	03	0.900	- 1 hr + 1 hr 1 3 5 7	<0.02, 0.03 0.70, 0.72 0.84, 0.33 0.43, 0.29 0.18, 0.33 0.06, 0.07
Almenar, Spain/1996/Catherine Peach	SL, 200 g/l	0.059	933	3	0.554	7	0.09, 0.03
Hohnstedt, Germany/1996/Sound Heaven Peach	WP, 250 g/kg	0.060	1000	3	0.600	7	0.04, 0.04
Scalunicco di Lestizza, Italy/1996/Elegant Lady Peach	WP, 250 g/kg	0.060	1500	3	0.900	7	0.06, 0.07
Az. Grigio Altedo, Italy/1996 Bella di Cesena Apricot	SL, 200 g/l	0.059	1228	3	0.728	7	0.15, 0.14
Az Grigio Altedo, Italy/1996 Bella di Cesena Apricot	WP, 250 g/kg	0.061	1214	3	0.737	7	0.03, 0.05
Watronville, France/1996/Early Red Haven Peach	SL, 200 g/l	0.060	989	3	0.593	7	0.17, 0.10
Watronville, France/1996/Early Red Haven Peach	WP, 250 g/kg	0.060	957	3	0.574	7	0.09, 0.05
Watronville, France/1996/Spring Lady Peach	SL, 200 g/l	0.060	1000	3	0.599	7	0.02, <0.02
Lignieres de Tourraine, France/1997/Dixired Peach	SL, 200 g/l	0.060	1025	3	0.615	- 1 hr + 3 hr 1 3 5 7	<0.02, <0.02 0.24, 0.19 0.10, 0.09 0.05, 0.11 0.02, 0.02 0.05, 0.03
Lignieres de Tourraine, France/1997/Dixired Peach	WP, 250 g/kg	0.060	1063	3	0.638	- 1 hr + 3 hr 1 3 5 7	0.02, <0.02 0.26, 0.32 0.18, 0.13 0.06, <0.02 0.03, 0.03 <0.02, 0.03
Collebeato, Italy/1997/Giulia Apricot	SL, 200 g/l	0.060	1540	3	0.924	- 1 hr + 3 hr 1 3 5 7	0.05, <0.02 0.44, 0.90 0.44, 0.25 0.08, 0.10 0.06, 0.04 0.04, 0.04
Collebeato, Italy/1997/Giulia Apricot	WP, 250 g/kg	0.060	1476	3	0.886	- 1 hr + 3 hr 1 3 5 7	0.03, 0.02 0.49, 0.46 0.32, 0.22 0.10, 0.09 0.09, 0.05 0.02,. 0.04

Location/Year/ Variety	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concen-tration (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
St-Gilles, France/1997/Royal Glory Peach	SL, 200 g/l	0.060	976	3	0.586	- 1 hr + 3 hr 1 3 5 7	<0.02, <0.02 0.11, 0.04 0.06, 0.02 0.02, <0.02 0.04, <0.02 0.04, <0.02
Hohnstedt, Germany/1997/Redhaven Peach	WP, 250 g/kg	0.060	1000	3	0.600	7	0.08, 0.05
Vigonovo, Italy/1997/2002 Peach	SL, 200 g/l	0.060	1000	3	0.600	7	<0.02, <0.02
Ateca, Spain/1997/Catherina Peach	WP, 250 g/kg	0.061	976	3	0.593	7	0.02, 0.05

Peach trees at 13 sites in the USA in 1998 were broadcast-sprayed by an airblast sprayer with an SP or SL formulation three times (Rühl, 2000). The retreatment interval was approximately 5 days. At a California site, a fourth application was made to ensure mature fruit at the desired PHI. Duplicate peach samples, each consisting of at least 24 fruits, were collected 4, 7 and 14 days after the last treatment. At two sites additional samples were collected to measure decline. Samples were stored frozen for 0.5-5 months and analysed by Method AMR 3015-94; the limit of quantification was 0.02 mg/kg. Recoveries from controls fortified with methomyl at 0.10 mg/kg were 97% $\pm$ 2%, n = 4. The results are shown in Table 28.

Table 28. Residues of methomyl on peaches after foliar applications of an SP or SL formulation in the USA in 1998 (AMR 4936-98).

Location/Variety	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concen-tration, (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
GAP: USA	Sl, SP	0.06A 4.8G		6	2.0	4	
Lyons, New York/Red Haven	SL, 288 g/l	0.11	935	3	1.0	4 7[1] 14	0.33, 0.28 0.15, 0.18 <0.02, <0.02
Elkton, Maryland/Glo Haven	SL, 288 g/l	0.16 0.17 0.18	626 589 570		1.0 1.0 1.0	 0 3 7[1] 14 21	 1.4, 1.2 0.32, 0.20 0.21, 0.21 0.14, 0.06 0.08, 0.08
Winterville, Georgia/Jefferson	SL, 288 g/l	0.13 0.17 0.16	767 589 617	3	1.0 1.0 0.98	 4 7[1] 12 14	 0.09, 0.14 0.03, 0.04 ND[2] ND
Garden Valley, Georgia/ Red Skin	SL, 288 g/l	0.18 0.15 0.16	542 654 608	3	1.0 1.0 1.0	 4 7[1] 14	 0.25, 0.29 0.06, 0.05 ND

Location/Variety	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concentration, (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
Taylorsville, North Carolina/Georgia Bell	SL, 288 g/l	0.21	468	3	1.0	4 7 14	0.60, 0.59 0.18, 0.23 0.04, 0.09
Washington, Louisiana/Tex Royal	SL, 288 g/l	0.19 0.20 0.22	524 496 505	3	1.0 1.0 1.1	 4 7 14[1]	 2.0, 1.5 0.36, 0.37 0.05, 0.05
Barto, Pennsylvania/ Redskin	SL, 288 g/l	0.15 0.15 0.14	682 682 692	3	1.0 1.0 1.0	 4 7 14[1]	 0.61, 0.62 0.20, 0.15 0.06, 0.07
Conklin, Michigan/Red Haven	SL, 288 g/l	0.16 0.16 0.16	636 645 636	3	1.0 1.0 1.0	 4 7[1] 14[1]	 0.38, 0.39 0.29, 0.31 0.06, 0.08
Chapel Hill, Texas/Sam Houston	SL, 288 g/l	0.11 0.11 0.11	907 898 898	3	1.0 0.97 1.0	 4 7 14[1]	 0.25, 0.34 0.05, 0.08 ND
Madera, California/Faye Elberta	SL, 288 g/l	0.17 0.17 0.17 0.17	561 561 561 561	4	0.96 0.96 0.97 0.97	 0 4 7 14 21[1]	 1.0, 1.8 0.46, 0.45 0.26, 0.27 0.13, 0.17 0.04, 0.06
Gridley, California/Loadels	SP, 900 g/kg	0.20 0.20 0.19	505 496 514	3	1.0 1.0 1.0	 4[1] 7[1] 14[1]	 0.70, 0.65 0.42, 0.30 0.1, 0.09
Traver, California/August Lady	SP, 900 g/kg	0.12 0.12 0.12	842 842 832	3	1.0 1.0 1.0	 4 7 14[1]	 0.28, 0.43 0.13, 0.18 0.02, 0.03
Woodville, California/Carson	SP, 900 g/kg	0.12 0.12 0.12	846 813 813	3	1.0 1.0 1.0	 4 7 14	 0.38, 0.31 0.28, 0.30 0.08, 0.18

[1] Normal harvest.
[2]The limit of detection was estimated at 0.007 mg/kg.

In field trials in the USA SP or SL formulations were applied three times to nectarines at 9 sites in 4 States in 1998 as a broadcast spray (airblast sprayer) at approximately 1.0 kg ai/ha (Rühl, 1999). The retreatment interval was 5 $\pm$ 1 days. At crop maturity (4-14 days after the last treatment), duplicate nectarine samples were collected and stored frozen for analysis by method AMR 3015-94. Control samples showed no methomyl residues, with an estimated limit of detection of 0.007 mg/kg. The storage

period ranged from 21 to 135 days. Concurrent control fortifications at 0.020 mg/kg yielded a mean recovery of 94% ± 10%, n = 12, range 75%-109%. The results are shown in Table 29.

Table 29. Residues of methomyl in or on nectarines after the foliar application of SP or SL formulations (3 x 1.0 kg ai/ha) in the USA in 1998 (AMR 4935-98).

Location/Variety	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concentration (kg ai/hl, calculated)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
GAP: USA	SL, SP	1.0		3	1.0	1	
Williamson, New York/Sunglo	SL, 288 g/l	0.11	940	3	1.0	4 7[1] 14	0.20, 0.18 0.065, 0.066 0.021, 0.025
Elkton, Maryland/Sunglo	SL, 288 g/l	0.16 0.17 0.17	630 590 570	3	1.0	0 3 7[1] 14 17	1.0, 1.4 0.49, 0.63 0.69, 0.25 0.094, 0.077 0.062, 0.040
Madera, California/Flavor Top	SL, 288 g/l	0.17 0.18 0.17	570 560 580	3	0.98	0 4 7 14 21[1]	0.78, 0.62 0.10, 0.14 0.060, 0.056 ND[2] ND
Parlier, California/Summer Grand	SP, 900 g/kg	0.14 0.14 0.14	700 710 700	3	1.0	4 7 14	0.24, 0.24 0.18, 0.13 <0.020
Linden, California/Midglow	SP, 900 g/kg	0.14	710	3	1.0	4 7[1] 14	0.24, 0.42 0.17, 0.16 0.028, 0.079
Exeter, California/August Glow	SP, 900 g/kg	0.14 0.14 0.15	700 690 680	3	1.0	4 7 14	0.039, 0.072 <0.02 ND
Madera, California/Fantasia	SP, 900 g/kg	0.15 0.16 0.16	710 780 710	3	1.1-1.2	4 7 14	0.15, 0.064 0.078, 0.060 <0.020
Hughson, California/Spring Red	SP, 900 g/kg	0.13 0.13 0.15	750 750 660	3	1.0	4 7[1] 14	0.45, 0.37 0.22, 0.19 0.023, 0.034
Zillah, Washington/Persica	SP, 900 g/kg	0.097 0.097 0.097	1020 1000 980	3	0.95-0.98	4 7 14[1]	1.1, 1.1 0.56, 0.47 0.26, 0.26

[1] Normal harvest (mature fruit, ripe).
[2] ND: none detected. Limit of detection estimated as 0.007 mg/kg.

In field trials on plums in Europe in the 1996 and 1997 growing season (Weidenauer *et al.*, 1998d,e; Françon and Larcinese, 1999c) SC or WP formulations were applied three times with a ground sprayer to run-off, generally at nominal rates of 0.60 or 0.90 kg ai/ha at 20-60 day intervals. Duplicate samples were stored frozen and analysed by method AMR 3015-94. Slight modifications were made to the HPLC gradient conditions. Fortified control samples were analysed with each set of samples. At a 0.02 mg/kg fortification the recoveries were 79% ± 11% (n=4) for AMR 3894-96; 74% ± 9% (n=7) for AMR 3895-96; and 76% ± 11% (n=10) for AMR 4501-97, and did not exceed 80% at 0.2 and 1.0 mg/kg fortifications. Samples were stored frozen for up to 1.8 years. The results are shown in Table 30. The calculated half-life was 4 days (first order kinetics).

Table 30. Residues of methomyl in or on plums from foliar applications of a WP or SL formulation at 0.6-0.9 kg ai/ha in Europe in 1996 and 1997 (AMR 3894-96; AMR 3895-96; AMR 5401-97).

Location/Variety/Year	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concentration (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
GAP: France	SL	0.075		3		7	
GAP: Spain	SP, SL	0.05		5	0.6	7	
GAP: Germany	None						
Beaumont, France/ Mirabel de Nancy/1996	SL, 200 g/l	0.060	1263	3	0.76	7	0.17, 0.28
Terrer-Zaragoza, Spain/President/1996	SL, 200 g/l	0.060	1454	3	0.87	7	<0.02, 0.02
Durrweitzschen, Germany/Stanley/1996	WP, 250 g/kg	0.060	1500	3	0.90	7	0.03, 0.10
Thillot, France/Mirabelle de Nancy/1996	SL, 200 g/l	0.060	275	3	0.16	-1h +3h 1 3 5 7	<0.02, <0.02 0.07, 0.05 0.02, 0.05 0.04, 0.05 0.06, 0.04 0.06, 0.05
Thillot, France/Mirabelle de Nancy/1996	WP, 250 g/kg	0.06	272	3	0.16	-1h +3h 1 3 5 7	<0.02, <0.02 0.03, 0.04 0.04, 0.05 0.04, <0.02 0.05, 0.06 0.06, 0.08
Durfort Lacapelette, France/Colbus/1996	SL, 200 g/l	0.06	788	3	0.47	-1h +1h 1 3 5 7	<0.02, <0.02 0.03, 0.04 0.03, 0.02 0.02, 0.02 0.02, 0.06 0.03, 0.03
Durweitzschen, Germany/Stanley/1996	WP, 250 g/kg	0.06	1500	3	0.90	-1h 0 1 3 5 8	<0.02 0.57, 0.45 0.54, 0.47 0.15, 0.21 0.20, 0.32 0.08, 0.19
Durweitzschen, Germany/Stanley/1997	SL, 200 g/l	0.06	1500	3	0.90	<0 0 1 4 6 8	<0.02 0.30, 0.42 0.33, 0.62 0.35, 0.45 0.28, 0.51 0.28, 0.28
Durweitzschen, Germany/Stanley/1997	WP, 250 g/kg	0.06	1500	3	0.90	<0 0 1 4 6 8	<0.02 0.49, 0.27 0.73, 0.72 0.37, 0.31 0.13, 0.34 0.22, 0.34
Thillot, France/Quetsche/1997	SL, 200 g/l	0.095	650	3	0.62	<0 +1h 1 3 5 7	<0.02 0.05, 0.08 0.06, 0.06 0.06, 0.05 0.03, 0.06 0.05, 0.08

Location/Variety/Year	Application					PHI (days)	Methomyl (mg/kg)
	Form.	Spray concen-tration (kg ai/hl)	Spray volume (l/ha)	No.	Rate (kg ai/ha)		
Aznalcazar, Spain/Black Amber/1997	WP, 250 g/kg	0.061	1127	3	0.68	-1h +3h 1 3 5 7	<0.02 0.28, 0.15 0.09, 0.09 <0.02, 0.03 0.04, 0.03 0.03, 0.03
Hohnstedt, Germany/Hauszwetsche /1997	SL, 200 g/l	0.060	1000	3	0.60	7	0.11, 0.10
Montauban, France/Golden Japan/1997	SL, 200 g/l	0.060	1140	3	0.68	7	0.02, 0.02
Creue, France/Mirabelle de Nancy	SL, 200 g/l	0.18	541	3	0.98	7	0.11, 0.13
Creue, France/Mirabelle de Nancy/1997	WP, 250 g/kg	0.11	553	3	0.60	7	0.03, 0.07

Berries and other small fruits

Grapes. An SL formulation was applied five times at 7-14 day intervals at 1.0 or 2.0 kg ai/ha by airblast or backpack sprayer to thirteen sites in New York, California, Michigan, Oregon and Washington, USA, in 1989 (S.M. Kennedy, 1990c). Samples were collected 1, 7, 10 and 14 days after the last treatment and stored frozen for 10 to 12 months until analysed by HPLC Method AMR-1806-90. Concurrent recoveries (30) from grapes fortified at 0.02 to 10.0 mg/kg methomyl gave recoveries of 107% ± 6%, n = 4 at 0.02 mg/kg. The overall average recovery was 94% ± 9%. All control samples contained <0.02 mg/kg except in Santa Maria, California, where the levels ranged from <0.02 to 0.18 mg/kg (Table 31).

In a further 12 trials in 1997-1998 in New York, Pennsylvania, Washington, Idaho and California, an SL or SP formulation was applied 4 times (airblast sprayer) at a rate of 1 kg ai/ha at 5 day intervals (McCooey, 1998b). From the two plots at each location two samples were taken at each of 2 or 3 intervals. Applications were planned so that mature grapes could be harvested from plot 1 about 29 days and from plot 2 14 days after the last treatment. Samples were stored frozen 4.5-7 months before analysis by HPLC (Method AMR-3015-94). Concurrent recoveries from controls fortified at 0.02 mg/kg, n = 15, were 91% ± 8%. All control samples were reported as "ND."

The results are shown in Table 31.

Table 31. Residues of methomyl after foliar application to grapes in the USA.

Location	Application				PHI (days)	Methomyl (mg/kg)	Report no.
	Form.	Rate (kg ai/ha)	Spray volume (l/ha)	No.			
GAP: USA	Sl, SP	1.0	910	5	1 fresh 14 wine		
Phelps, NY, 1989	SL, 0.22 kg ai/l (1.8 lb ai/gal)	1.0	935	5	1 7 10 14	3.5 2.8 2.1 2.0	AMR-1364-89
		1.0 2.0	935 935	3 2	- 1	 5.8	

Location	Application				PHI (days)	Methomyl (mg/kg)	Report no.
	Form.	Rate (kg ai/ha)	Spray volume (l/ha)	No.			
					7 10 14	4.4 2.3 2.9	
Comstock Park, Michigan, 1989	SL, 0.22 kg ai/l	1.0	1870	5	1 7 10 14	2.9 2.8 1.6 2.1	
Vancouver, Washington, 1989	SL, 0.22 kg ai/l	1.0	374	5	1 7 10 14	2.2 1.1 1.4 1.4	
		1.0 2.0	374	3 2	- 1 7 10 14	 11 6.8 4.2 5.7	
Cornelius, Oregon, 1989	SL, 0.22 kg ai/l	1.0	374	5	1 7 10 14	0.58 0.43 0.48 0.17	
		1.0 2.0	374	3 2	- 1 7 10 14	 1.2 0.42 0.96 0.28	
Corona, California, 1989	SL, 0.22 kg ai/l	1.0	1170	5	1 7 10 14	4.1 1.2 0.95 0.95	
		1.0 2.0	1170	3 2	- 1 7 10 14	 1.9 2.4 2.4 2.5	
Santa Maria, California, 1989	SL, 0.22 kg ai/l	1.0	785-898	5	1[1] 7 10 15	5.2, 1.3 4.5, 0.84 4.5, 0.74 3.9, 0.40	
		1.0 2.0	785- 898	3 2	- 1[1] 7 10 15	 18, 3.6 8.6, 1.9 12, 1.9 9.1, 0.87	
Fresno, California, 1989	SL, 0.22 kg ai/l	1.0	935	5	1 7 10 14	0.78 0.41 0.34 0.34	
		1.0 2.0	935	3 2	- 1 7 10 14	 1.9 1.6 0.95 1.4	
Porterville, California, (Flame seedless) 1989	SL, 0.22 kg ai/l	1.0	1170	5	1 7 10 14	0.93 0.50 0.37 0.16	
		1.0 2.0	1170	3 2	- 1	 1.0	

Location	Application				PHI (days)	Methomyl (mg/kg)	Report no.
	Form.	Rate (kg ai/ha)	Spray volume (l/ha)	No.			
					7 10 14	0.50 0.30 0.15	
Porterville, California, , (Thompson seedless) 1989	SL, 0.22 kg ai/l	1.0	1170	5	1 7 10 14	1.0 0.32 0.19 0.12	
Terra Bella, California, 1989	SL, 0.22 kg ai/l	1.0	1170	5	1 7 10 14	0.54 0.21 0.12 0.40	
		1.0 2.0	1170	3 2	- 1 7 10 14	 1.6 0.64 0.67 0.39	
Biola, California, 1989	SL, 0.22 kg ai/l	1.0	748	5	1 7 10 14	1.0 0.53 0.52 0.28	
Dundee, New York, 1997/Aurora= wine	SL, 0.29 kg ai/l (2.4 lb ai/gal)	0.9	468	4	13 21 29	2.3, 2.3 1.4, 1.6 0.89, 0.96	AMR 4346-97
Kempton, Pennsylvania, 1997/Cayuga= wine	SP, 900 g/kg (90%)	0.9	739-898	4	14 20 29	2.8, 2.8 2.5, 2.7 0.96, 1.3	
Orland, California, 1997/ Zinfandel= wine	SL, 0.29 kg ai/l	0.9	387-470	4	14 30	0.54, 0.65 0.10, 0.12	
Temecula, California, 1997/Zinfandel= wine	SP, 900 g ai/kg	0.9	688-713	4	14 29	1.3, 1.2 0.77, 0.67	
Porterville, California, /1997/Emperor =table	SP, 900 g ai/kg	0.9	544-574	4	14 29	0.60, 0.61 0.25, 0.22	
Orland, California, 1997/ Barbera= wine	SL, 0.29 kg ai/l	0.9	322-392	4	14 28	0.090, 0.15 0.095, 0.11	
Hughson, California, 1997/Thompson =table	SP, 900 g ai/kg	0.9	726-764	4	14 29	1.3, 1.4 0.54, 0.53	
Madera, California, 1997/Flame =table	SP, 900 g ai/kg	0.9	483-686	7 4	14 29	0.67, 0.26 0.057, 0.085	
Fresno, California, 1997/Flame = table	SP, 900 g ai/kg	0.9	701	4	14 21 29	0.26, 0.25 0.10, 0.12 0.094, 0.098	
Poplar, California, 1997/Thomas =table	SL, 0.29 kg ai/l	0.9	560	4	14 29	0.31, 0.26 0.37, 0.30	
Granger, Washington, 1997/Riesling =wine	SL, 0.29 kg ai/l	0.9	935	4	14 21 29	0.99, 1.2 0.63, 0.72 0.54, 0.85	
Payette, Idaho, 1997/Concord =table	SP, 500 g/kg	0.9	468	4	14 29	0.98, 0.45 0.31, 0.35	

[1] Duplicate values represent separate plots of 30 vines each at the same location. Some control samples showed methomyl concentrations of 0.02 mg/kg to 0.18 mg/kg.

In field trials on table and wine grapes during the 1997 season in France, Portugal and Italy a soluble concentrate, 200 g/l methomyl, and a wettable powder, 250 g/kg methomyl, were both applied 3 times at 30-day intervals as foliar sprays with ground equipment at a target rate of 300 g ai/ha per application (Françon and Larcinese, 1999a). The spray concentration was 0.060 kg ai/hl for both formulations The actual rate was adjusted to the foliar mass by spraying to run-off. Duplicate samples of bunches of grapes were collected 1 hour before and 3 hours and 1, 3, 5 and 7 days after the last application and stored at -18°C for approximately 2 months before analysis by an HPLC method based on AMR 3015-94. Concurrent recoveries from controls fortified at 0.021 mg/kg were 91% ± 7%, n = 14. Control samples were reported as <0.02 mg/kg The results are shown in Table 32.

Table 32. Residues of methomyl in or on grapes after three foliar sprays of SC or WP formulations at a nominal rate of 0.060 kg ai/hl, in Europe in 1997 (AMR 4498-97).

Location/Variety	Application				PHI (days)	Methomyl (mg/kg)
	Form.	Spray concentration (kg ai/hl)	Spray volume (l/ha)	Rate (kg ai/ha) Calculated		
GAP: France	SL	0.05		0.4	None	
GAP: Portugal	None (use Italy)					
GAP: Italy	SL, WP	0.05			10	
Avize, France/ Chardonnay	SL, 200 g/l	0.060	617	0.37	-1 h +1 h 1 3 5 7	0.03, 0.03 0.53, 0.33 0.20, 0.29 0.19, 0.22 0.14, 0.18 0.10, 0.09
	WP, 250 g/kg	0.060	597	0.358	- 1 h + 1 h 1 3 5 7	0.06, 0.06 0.32, 0.41 0.25, 0.25 0.16, 0.17 0.06, 0.13 0.14, 0.12
Rochecorbon, France/ Chenin Blanc	SL, 200 g/l	0.060	921	0.553	- 1 h + 3 h 1 3 5 7	<0.02, <0.02 0.06, 0.05 0.26, 0.15 0.16, 0.07 0.08, 0.18 0.09, 0.05
Villetelle, France/Carignan	WP, 250 g/kg	0.060	507	0.304	-1 h + 3 h 1 3 5 7	<0.02, <0.02 0.20, 0.17 0.13, 0.19 0.15, 0.11 0.06, 0.06 0.02, 0.03
C. da Biviere, Italy/ Calabrese	SL, 200 g/l	0.063	1200	0.756	-1 h + 3 h 1 3 5 7	0.03, 0.04 1.70, 1.72 1.26, 1.10 1.06, 0.38 0.79, 0.78 0.59, 0.48
C. da Biviere, Italy/ Calabrese I	WP, 250 g/kg	0.059	1200	0.710	-1 h + 3 h 1 3 5 7	0.04, 0.03 1.42, 1.31 1.30, 1.60 1.11. 0.97 0.65, 0.21 0.41, 0.38

Location/Variety	Application				PHI (days)	Methomyl (mg/kg)
	Form.	Spray concen-tration (kg ai/hl)	Spray volume (l/ha)	Rate (kg ai/ha) Calculated		
Vernou sur Brenne, France/ Chenin Blanc	SL, 200 g/l	0.060	947	0.568	7	0.09, 0.06
Hermonville, France/ Pinot Meunier	WP, 250 g/kg	0.060	600	0.360	7	0.07, 0.06
Sorgues, France/ Gros vert	SL, 200 g/l	0.060	507	0.304	7	0.12, 0.09
Sorgues, France/ Gros vert	WP, 250 g/kg	0.060	507	0.304	7	0.09, 0.06
Torres Vedras, Portugal/ Seminario	SL, 200 g/l	0.060	861	0.517	7	0.09, 0.09

Bulb vegetables

In twelve field trials on green onions in the USA from 1970-1975 1-6 applications using ground or air application equipment were made at rates of 0.28 to 2.0 kg ai/ha and 880-5100 l/ha (Ashley, 2001o). The samples were stored frozen, but no information was supplied on the storage interval nor on the analytical method and only summary results were provided. No information, except rainfall, was provided on the field conditions. Moreover, a supplement to the report states that low recoveries were found in fortified controls. The submission is deficient and was not considered.

Five field trials were reported on dry onion bulbs in the USA (S. M. Kennedy, 1990d). An SL formulation was applied 4 times with ground equipment at a rate of 1.0 kg ai/ha. Onions were harvested 7 days after the last application, stored frozen for up to one year and analysed by method AMR 1806-90. A sample consisted of at least twelve randomly collected bulbs. Control samples fortified with methomyl were extracted and analysed with the treated samples. At a fortification of 0.02 mg/kg the recovery was 87% $\pm$ 25%, n=3. The overall recovery from fortifications ranging from 0.02 to 3.0 mg/kg was 85% $\pm$ 14%, n=10 (Table 33).

Table 33. Residues of methomyl in or on bulb onions after the foliar application of an SL formulation (216 g ai/l) at 4 x 1.0 kg ai/ha, PHI 7 days, in the USA in 1989 (AMR 1365-89).

Location/Variety	Application Rate (kg ai/ha)	Spray volume (l/ha)	No. of applications	Residue (mg/kg)
GAP: USA	1.0		8	
Sodus, New York/Early Yellow Globe	1.0	240	4	0.056
Comstock Park, Michigan/Yellow Pungent Globe	1.0	140	4	0.072
Ephrata, Washington/Cima Hybrid	1.0	94	4	0.068
Irvine, California/Pecham Yellow Sweet Spanish	1.0	920	4	0.14
Porterville, California/Stockton Early Rev.	1.0	190	4	<0.02

Brassica vegetables

In trials on cabbage in the USA (C. M. Kennedy, 1991c) multiple applications of an SL or SP formulation were made at a rate of 1.0 kg ai/ha at three sites, at one with aerial equipment. Samples were collected at crop maturity (PHI 1 day, minimum 12 heads) and stored frozen for 8-12.5 months before analysis by method AMR 1806-90. Control samples were fortified at 0.05, 0.1, 0.5, 1 and 5 mg/kg and prepared and

analysed with the treated samples. The average recovery was 86% ± 7%, n=5. The results are shown in Table 34.

Table 34. Residues in or on cabbage after the foliar application of SL or SP formulations of methomyl at 10-20 x 1.0 kg ai/ha, PHI 1 day, in the USA in 1991 (AMR 1606-90).

Location/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Application Method	No. of applications	Residue (mg/kg)
GAP: USA	SL, SP	1.0	90A	Aerial/ground	15	
Bradenton, Florida/Bravo	SL, 216 g/l	1.0	450	Ground foliar plot sprayer	20 (heads present for 7 appls)	0.10
	SL, 216 g/l	1.0	450	Ground foliar plot sprayer	20 (heads present for 7 appls)	0.46
	SP, 900 g/kg	1.0	450	Ground foliar	20 (heads present for 7 appls)	0.27
Phelps, New York/A&C #5	SL, 216 g/l	1.0	280	Over-the-row ground with 12 ft boom	10 (heads present)	0.086
	SP, 900 g/kg	1.0	280	Over-the-row ground with 12 ft boom	10 (heads present)	0.18
Uvalde, Texas/Pennant	SL, 216 g/l	1.0	47	Aerial	10 (heads present)	0.52
	SP, 900 g/kg	1.0	47	Aerial	10 (heads present)	0.63

In field trials in the USA on broccoli and cauliflower in 1990 and 1992 (C. M. Kennedy, 1991a; Kennedy and Devine, 1994a) SL, SP or WP formulations were sprayed at 1 kg ai/ha in multiple ground or aerial applications at 2-day intervals to plots of brassica vegetables in California. Samples of about 12 heads or plants were collected at maturity (in triplicate for the 1992 trial) and stored frozen for 12.5 months until analysed by method AMR 1806-90. Control samples were fortified with methomyl at concentrations of 0.02, 0.10, 0.20 and 2.0 mg/kg and extracted and analysed with the treated samples. From broccoli the overall recovery was 99% ± 5.5%, n=9 and from cauliflower in 1990 87% ± 5.7%, n=10. The results are shown in Table 35.

Table 35. Residues after foliar ground or aerial application of methomyl to broccoli and cauliflower in California at 1.0 kg ai/ha, 3-day PHI (AMR 1600-90; AMR 1600-90 Supplement).

Location/Year/Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	Residue (mg/kg)
GAP: USA	SL, SP	1.0	90A	Aerial/ground	10	
Broccoli						
Madera, California/1990/ Packman	SL, 216 g/l	1.0	410	Over the top, tractor sprayer	10	0.35
	SP, 900 g/kg	1.0	410	Over the top, tractor sprayer	10	0.36
Salinas, California/1990/Shogun	SL, 216 g/l	1.0	400	Foliar ground, plot sprayer	13 + 1[1]	0.45
	SP, 900 g/kg	1.0	400	Foliar ground, plot sprayer	13 + 1[1]	0.44
Salinas, California/1990/Shogun	SL, 216 g/kg	1.0	140	Broadcast Aerial	13	0.68

Location/Year/Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	Residue (mg/kg)
	WP, 900 g/kg	1.0	140	Broadcast Aerial	13	1.1
Cauliflower						
Madera, California/1990/Long Island	SL, 216 g/l	1.0	370-420	Over-the-top broadcast. Tractor ground	17	5.6
	WP, 900 g/kg	1.0	370-420	Over-the-top broadcast. Tractor ground	17	3.8
Salinas, California. 1990/Silver Star	SL, 216 g/l	1.0	210 apps 1-7 420 apps 8-10	Broadcast over crop. Plot sprayer	10	0.18
	WP, 900 g/kg	1.0	210 apps 1-7 420 apps 8-10	Broadcast over crop. Plot sprayer	10	0.20
Salinas, California/1990/Silver Star	SL, 216 g/l	1.0	140	Broadcast Aerial	10	0.24
	WP, 900 g/kg	1.0	140	Broadcast Aerial	10	0.18
Madera, California/1992/Snowball Y Improved	SL, 216 g/l	1.0	310-380	Broadcast over crop, tractor with 10 ft boom.	10	1.6, 0.70, 0.58
Madera, California/1992/Snowball Y Improved	WP, 900 g/kg	1.0	310-380	Broadcast over crop, tractor with 10 ft boom	10	1.4, 2.0, 1.6

[1] An hour after the 13th application with ground equipment, the plots were accidentally sprayed at 1.0 kg ai/ha from a helicopter with the SL formulation.

Summaries of trials in the USA from 1967 to 1972 were reported by Ashley (2001j). Multiple applications of a 900 g ai/kg WS formulation or a 216 g/l SL formulation were made to broccoli and cauliflower at rates of 0.56 to 2.2 kg ai/ha using ground or aerial equipment. Samples were collected and analysed by GLC with a flame photometric detector (ML/PC-12 Supplement). The summary information is provided in Table 36.

Table 36. Residues of methomyl in or on broccoli and cauliflower after applications of WS or SL formulations, USA, 1967-1972 (4F1448).

Location/Year	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue[1] (mg/kg)
Broccoli							
Albion, New York/1967	WP, 900 g/kg	0.56	940	Foliar ground	6	1 3 7 10	1.0 0.15 0.04 0.02
Geneva, New York/1967	WP, 900 g/kg	0.56	260	Foliar ground	7	0 3 7 10 14	0.48 0.48 0.05 0.02 0.03
Milpitas, California/ 1968	WP, 900 g/kg	1.1	470	Foliar ground	[3]	0 3 5	0.46 0.09 <0.02

Location/Year	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue[1] (mg/kg)
						7	<0.02
Salinas, California/ 1967	WS, 900 g/kg	1.1	470	Foliar ground	[3]	0 3	8.6 0.20
	WS, 900 g/kg	2.2	470	Foliar ground	3	0 3	16. 0.46
Soledad, California/ 1967	WS, 900 g/kg	0.50	94	Foliar aerial	2	1 3 5 7	0.83 0.16 <0.02 0.05
	WS, 900 g/kg	1.0	94	Foliar aerial	2	1 3 5 7	1.2 0.21 0.12 0.08
Gilroy, California/ 1972	WP, 900 g/kg	0.50	94	Foliar aerial	2	1 3 5 7	0.44 0.30 0.10 0.05
	WP, 900 g/kg	1.0	94	Foliar aerial	2	1 3 5 7	1.0 0.73 0.22 0.32
Niles, Michigan/ 1972	WP, 900 g/kg	1.0	380	Foliar ground	5	1 3 7 14	3.5 0.70 0.20 0.06
	SL, 216 g/l	1.0	380	Foliar ground	5	1 3 7 14	4.4 2.8 0.09 0.08
Bradenton, Florida/1968	WP, 900 k/kg	1.1	240	Foliar ground	6	3 7 14	0.77 0.06 <0.02
Bradenton, Florida/1968	WP, 900 g/kg	1.3	660	Foliar ground	3	3 5 7	1.8 0.39 0.35
Bradenton, Florida/1971	WP, 900 g/kg	1.1	850	Foliar ground	1	1 3	5.1 0.51
Bradenton, Florida/1971	WP, 900 g/kg	0.56	770	Foliar ground	10	1 3	0.72 0.44
Bradenton, Florida/1971	WP, 900 g//kg	1.1	770	Foliar ground	10	1 3	3.6 0.96
Cauliflower							
Geneva, New York/1967	WP, 900 g/kg	0.56	260	Foliar ground	7	0 3 7	0.05 0.12 0.02
Bradenton, Florida/1972	WP, 900 g/kg	0.56	750	Foliar ground	6	1 3	0.32 0.10
Bradenton, Florida/1972	WP, 900 g/kg	1.1	750	Foliar ground	6	1 3	0.92 0.74
Sanger, California/ 1967	WP, 900 g/kg	0.56	340	Foliar ground	6	1 3 5 8	0.12 0.05 0.07 0.04
Gonzales, California/?	SL, 216 g/l	0.50	94	Foliar aerial	2	1 3 5 7	0.30 0.02 <0.02 0.02

Location/Year	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue[1] (mg/kg)
Gonzales, California/?	SL, 216 g/l	1.0	94	Foliar aerial	2	1 3 5 7	0.46 0.04 0.03 <0.02
Gilroy, California/?	SL, 216 g/l	0.50	94	Foliar aerial	2	1 3 5 7	0.26 0.12 0.089 0.13
Gilroy, California/?	SL, 216 g/l	1.0	94	Foliar aerial	2	1 3 5 7	0.48 0.51 0.13 0.05

[1] Summary results only. No details of sample storage, preparation, concurrent recovery data or details of the analyses.

Cucurbits

Field trials on cucumbers and courgettes (zucchini) in Belgium, Greece, Italy and The Netherlands were reported. In Italy and Greece a WP or SL formulation was applied (3 x 1000 l/ha, 3 x 50 g ai/hl) as a foliar ground spray to cucumbers and courgettes in the 1996 growing season (Weidenauer *et al.*, 1998h). Duplicate samples were collected at intervals and stored frozen (-20°C) for 11-13 months pending analysis by method AMR 3015-94. Fortified controls were analysed with the treated samples. At 0.02 mg/kg fortification, the average recovery was 76% ± 8%, n=4; at 0.2 mg/kg, 77% ± 22%, n=3. In further trials under similar conditions in the 1997 growing season in France, Greece and Italy samples were stored 14-16 months before extraction and analysis (Françon and Larcinese, 1999g). Recoveries from fortified control cucumbers were 84% ± 18%, n=3 at 0.021 mg/kg; and 89% ± 16%, n=3, at 0.21 mg/kg. Recoveries from courgettes were 85% ± 19%, n=6 at 0.021 mg/kg and 85% ± 11%, n=7 at 0.21 mg/kg. The results are shown in Table 37.

Table 37. Residues of methomyl in or on cucumbers and courgettes after foliar applications of a WP or SL formulation in Southern Europe (AMR 3977-96; AMR 4511-97).

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue (mg/kg)
Cucumber							
GAP: Italy	SL, WP	0.04 kg ai/hl				10	
GAP: Greece	SL	0.45			3	20	
GAP: France	SL	0.3			3	7	
Monta-naso Lombardo, Italy/1996/Potomac F1	SL, 200 g/l	0.52	1040	Ground foliar to run-off	3	-1h +3h 1 3 5 7	<0.02 0.03, 0.07 0.03, 0.02 <0.02, <0.02 <0.02:<0.02 <0.02, <0.02
Monta-naso Lombardo, Italy/1996/Potomac F1	WP, 250 k/kg	0.52	1030	Ground foliar to run-off	3	-1h +3h 1 3 5 7	<0.02 0.07, 0.03 0.07, 0.02 <0.02, <0.02 <0.02<0.02 <0.02:<0.02
Monta-naso	WP,	0.40	810	High volume	3	-1h	<0.02

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue (mg/kg)
Lombardo, Italy/1997/Potomac F1	250 g/kg			ground foliar to run-off		+3h 1 3 5 7	0.04, 0.04 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02
Cadriano Bologna, Italy/1996/Carine	SL, 200 g/l	0.33	666	Ground foliar to run-off	3	7	<0.02, <0.02
Fiesso di Castenaso, Italy/1997/Darina	SL, 200 g/l	0.49	966	Direct foliar	3	7	<0.02, <0.02
Kato Souli-Attica, Greece/1996/Ferri morse	SL, 200 g/l	0.50	994	Ground foliar to run-off	3	7	<0.02, <0.02
Beaucaire, France/1997/ Emeraude	SL, 200 g/l	0.31	612	Foliar spraying	3	-1 h +3 h 1 3 5 7	<0.02 0.08, 0.05 0.04, 0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02
Beaucaire, France/1997/ Emeraude	WP, 250 g/kg	0.30	601	Foliar spraying	3	-1h +3h 1 3 5 7	<0.02 <0.02, <0.02 0.03, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02
Courgette							
GAP: Italy	None Use France						
GAP: France	SL	0.3			3	7	
GAP: Greece	WP	0.45			3	15	
Mediglia, Italy/1996/?	SL, 200 g/l	0.52	1040	Ground foliar to run-off	3	7	<0.02, <0.02
Drosia, Michaniona, Greece/1997/ Verona	WP, 250 g/kg	0.25	508	Foliar appli-cation	3	-1h +3h 1 3 5 7	<0.02 0.02, 0.03 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02

Trials on cucumbers and courgettes in Northern Europe were also reported (Weidenauer *et al.*, 1998k; Françon and Larcinese, 1999k). WP or SL formulations were applied three times at 3-7 day intervals at a rate of 300-600 g ai/ha/application in glasshouses. Duplicate samples were collected at harvest, stored frozen (-20°C) and analysed by method AMR 3015-94. Control samples were fortified and analysed with the treated samples. At 0.02 mg/kg fortification the recovery was 87% ± 14%, n=10, and at 0.2 mg/kg, 84% ± 12%, n=9. The results are shown in Table 38.

Table 38. Residues in or on cucumbers and courgettes after foliar applications of WS or SL formulations in glasshouses in Northern Europe (AMR 4017-96; AMR 4521-97).

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue (mg/kg)
GAP:Belgium	WP	0.5	1600			14	

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue (mg/kg)
GAP: Netherlands	SL WP	0.4 0.4	1600 500		3	3	
Cucumber							
Oosterhout, Netherlands/ 1996/Dugan	SL, 200 g/l	0.50	982	Overall foliar by ground sprayer to run-off	3	-1h +3h 1 3 5 7	<0.02 0.03, 0.05 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02
Oosterhout, Netherlands/ 1996/Dugan	WP, 250 g/kg	0.49	972	Overall foliar by ground sprayer to run-off	3	-1h +3h 1 3 5 7	<0.02 0.04, 0.05 0.02, 0.03 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02
Oosterhout, Netherlands/19 97/Europa	SL, 200 g/l	0.47	1591	Ground sprayer (high volume) to run-off	3	-1h +3h 1 3 5 7	0.03, <0.02 0.02, 0.02 <0.02, 0.02 0.03, <0.02 <0.02, <0.02 <0.02, <0.02
Oosterhout, Netherlands/19 97/Dugan	SL, 200 g/l	0.48	1806	Ground sprayer (high volume) to run-off	3	7	<0.02, <0.02
Oosterhout, Netherlands/19 97/Dugan	WP, 250 g/kg	0.48	1594	Ground sprayer (high volume) to run-off	3	7	<0.02, <0.02
Melsele, Belgium/1997/ Nicolas	WP, 250 g/kg	0.55	1810	Overall foliar by ground sprayer to run-off	3	7	<0.02, <0.02
Bois de Nivelles, Belgium/1997/ Recento	WP, 250 g/kg	0.44	1465	Spraying	3	-1h +3h 1 3 5 7	<0.02, 0.03 0.18, 0.18 0.06, 0.06 0.03, 0.,02 <0.02, <0.02 <0.02, <0.02
Courgette							
St Gillis-Waas, Belgium/1997/ Bengale	WP, 250 g/kg	0.54	1253	Overall foliar by ground sprayer to run-off	3	-1h +1h 1 3 5 7	<0.02 0.06 0.08 <0.02 <0.02 <0.02
Bois de Nivelles, Belgium/1997/ Pandorex	WP, 250 g/gk	0.34	1117	Spraying	3	7	<0.02, <0.02
Honselersdijk, Netherlands	SL, 200 g/l	0.51	996	Overall foliar by ground sprayer to run-off	3	7	<0.02, <0.02

Field trials in 1969-1971 on watermelons were reported from the USA (Ashley, 2001f). A WD formulation was applied at rates of 0.56 to 1.12 kg ai/ha and whole watermelons were analysed by the GLC method ML/PC-12. The method was validated at 0.04 mg/kg. Detailed information on field trial conditions, sample collection, storage, extraction and analysis was not provided. Summary results are shown in Table 39.

Table 39. Residues of methomyl in or on watermelons after the application of a WD formulation in the USA.

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of applications	PHI (days)	Residue[1] (mg/kg)
GAP: USA	SL, SP	1.0	90A	Aerial/ground	12	3	
Leesburg, Florida/1969/?	WD, 900 g/kg	0.56	940	Broadcast	7	3	<0.04
Leesburg, Florida/1969/?	WD, 900 g/kg	1.12	940	Broadcast	2	4	<u>≤0.04</u>
Leesburg, Florida/1970/?	WD, 900 g/kg	0.56	940	Broadcast	7	3	<0.04, <0.04
Blythe, California/1970/?	WD, 900 g/kg	0.56	560	Broadcast	2	3	<0.04
Blythe, California/1970/?	WD, 900 g/kg	1.12	560	Broadcast	2	3	<u>≤0.04</u>
Bakersfield, California/1971/?	WD, 900 g/kg	0.56	140	Aerial	2	2 4	<0.04 (0.03) <0.04
Bakersfield, California/1971/?	WD, 900 g/kg	1.12	140	Aerial	2	2 4	<u>0.07</u> <0.04

[1] Values reported as <0.02 mg/kg, but method not validated below 0.04 mg/kg.

Field trials on melons were reported from Greece, Italy and The Netherlands in 1996 and 1997 (Weidenauer *et al.*, 1998i,n; Françon and Larcinese, 1999h,j). An SL or WP formulation was applied three times as a broadcast foliar spray at rates of 250-500 g ai/ha. Duplicate samples of mature fruits were collected and stored frozen for up to 16 months for analysis by method AMR 3015-94. Control samples of melons fortified with methomyl were extracted and analysed with the treated samples. At a 0.02 mg/kg fortification, the recovery was 86% <u>+</u> 12%, n=18. The results are shown in Table 40.

Table 40. Residues of methomyl in or on melons after three foliar applications of a WP or SL formulation in Europe.

Location/Year/Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	PHI (days)	Residue (mg/kg)	Reference
GAP: Netherlands	SL WP	0.4 0.4	1600 500		3		
GAP: Italy	SL, WP	0.04 kg ai/hl			10		
GAP: Spain	None Use Italy						
GAP: Germany	SL	0.45		3	20		
Monster, Netherlands/ 1996/Haon	SL, 200 g/l	0.46	897	Foliar Glass-house	-1h +4h 1 3 5 7	<0.02 0.02, 0.02 <0.02, 0.02 <u><0.02, <</u>0.02 <0.02, <0.02 <0.02, <0.02	Weidenauer *et al.*, 1998n AMR 4019-96
Monster, Netherlands/ 1996/Haon	WP, 250 g/kg	0.45	880	Foliar Glass-house	-1h +4h 1 3 5 7	<0.02 <0.02, 0.02 0.02, 0.02 <u><0.02</u>, <0.02 <0.02, <0.02 <0.02, <0.02	Weidenauer *et al.*, 1998n AMR 4019-96
Gravezande,	SL, 200 g/l	0.58	1986	Foliar	-1h	<0.02	Françon and Larcinese,

Location/Year/Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	PHI (days)	Residue (mg/kg)	Reference
Netherlands/ 1997/Haon				Glass-house	+0h 1 3 5 7	0.07, 0.06 0.10, 0.07 0.03, 0.10 <0.02, <0.02 0.03, <0.02	1999j AMR 4519-97
Gravezande, Netherlands/ 1997/Haon	WP, 250 g/kg	0.61	2011	Foliar Glass-house	7	<0.02, <0.02	Françon and Larcinese, 1999j AMR 4519-97
Gavello, Italy/1997/Pamir	SL, 200 g/l	0.26	515	Foliar Broad-cast	7	<0.02, <0.02	Françon and Larcinese, 1999h AMR 4513-97
Gavello, Italy/1997/Pamir	WP, 250 g/kg	0.26	518	Foliar Glass-house	7	<0.02, <0.02	Françon and Larcinese, 1999h AMR 4513-97
Caleppio de Settala, Italy/1997/Supermarket	WP, 250 g/kg	0.40	805	Foliar Glass-house	1 3 5 7	0.05, 0.04 0.02, 0.02 0.02, 0.02 <0.02, <0.02	Françon and Larcinese, 1999h AMR 4513-97
Montanaso Lombardo, Italy/1996/ Vector F-1	SL, 200 g/l	0.49	984	Foliar broad-cast	-1h +1h 3 5 7	<0.02 0.02, 0.03 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	Weidenauer *et al.*, 1998i AMR 3998-96
Montanaso Lombardo, Italy/1996/ Vector F-1	WP, 250 g/kg	0.50	990	Foliar Broad-cast	-1h +1h 3 5 7	<0.02 0.02, <0.02 <0.02, 0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	Weidenauer *et al.*, 1998i AMR 3998-96
Volania Ferrar, Italy/1996/Pamir	WP, 250 g/kg	0.41	808	Foliar Broad-cast	7	<0.02, <0.02	Weidenauer *et al.*, 1998i AMR 3998-96
Volania Ferrara, Italy/1996/Pamir	SL, 200 g/l	0.50	990	Foliar Broad-cast	-1h +1h 3 5 7	<0.02 0.03, 0.04 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	Weidenauer *et al.*, 1998i AMR 3998-96
Mesimeri-Thessaloniki, Greece/1996/ Thraklotica	SL, 200 g/l	0.50	985	Foliar Broad-cast	7	0.03, 0.03	Weidenauer *et al.*, 1998i AMR 3998-96
Metohi, Greece/1997/ Galli	SL, 200 g/l	0.25	502	Foliar Glass-house	1 3 5 7	0.03, 0.03 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	Françon and Larcinese, 1999h AMR 4513-97
Umbrete, Spain/1997/ Rochet	SL, 200 g/l	0.42	829	Foliar Broad-cast	7	<0.02, <0.02	Françon and Larcinese, 1999h AMR 4513-97

Other fruiting vegetables

Summary information on egg plant, pepper and tomato trials in the USA was provided and is summarized in Table 41(Ashley, 2001p). Samples were analysed by method ML-PC12 (1968).

Table 41. Residues of methomyl in or on egg plants, tomatoes and peppers after foliar application in the USA (9F 0814).

Location/Year	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of Applications	PHI (days)	Residue (mg/kg)
GAP: USA	SL, SP	1.0	19A	Aerial/ground	10 egg plant 10 pepper 16 tomato	3 egg plant 1 tomato 3 pepper	
Egg plant							
Wilmington, Delaware/1969	?	0.56	?	Foliar	9	2 5	0.10 0.04
Bradenton, Florida/1969	?	0.56	?	Foliar	2	2 4 6	0.05 0.04 <0.02
Bristol, Maryland/1969	?	0.56	?	Foliar	5	4	0.11
Wooster, Ohio/1969	?	0.56	?	Foliar	6	2 5	0.10 <0.02
Wooster, Ohio/1969	?	1.1	?	Foliar	6	2 5	0.30 0.11
Tomato							
Bradenton, Florida/1967	?	0.28	?	Foliar	4	0 4 8	0.02 <0.02 <0.02
Bradenton, Florida/1967	?	0.56	?	Foliar	4	3 5 7	0.08 0.02 0.02
Homestead, Florida/1967	?	0.56	?	Foliar	8	3 5 7	0.05 0.03 <0.02
Gillette, Florida/1967	?	0.56	?	Foliar	3	3 5 7	0.03 <0.02 <0.02
Gillette, Florida/1967	?	1.1	?	Foliar	3	3 5 7	0.03 0.04 0.02
Wilmington, Delaware /1968	?	0.56	?	Foliar	3	2 5	0.03 <0.02
Yolo, California		1.1	?	Foliar	3	0 10	<0.1 <0.1
Wooster, Ohio/1968	?	0.56	?	Foliar	6	2 5	0.03 <0.02
Wooster, Ohio/1968	?	1.1	?	Foliar	6	2 5	0.03 0.02
Bristol, Maryland/1968	?	0.56	?	Foliar	10	3 6	<0.02 <0.02
Weslaco, Texas/1968	?	0.56	?	Foliar	8	3 5	<0.02 <0.02
Weslaco, Texas/1968	?	1.1	?	Foliar	8	3 5	<0.02 <0.02
Weslaco, Texas/1968	?	2.2	?	Foliar	8	3 5	<0.02 <0.02
Pepper							
Bristol, Maryland/1968	?	0.56	?	Foliar	5	4	0.10
Wilmington, Delaware/1968	?	0.56	?	Foliar	9	2 5	0.16 0.05
Niles, Michigan	?	0.56	?	Foliar	4	2	0.28

Location/Year	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Method	No. of Applications	PHI (days)	Residue (mg/kg)
						4 8	0.12 0.07
Niles, Michigan	?	1.1	?	Foliar	4	2 4 8	0.44 0.11 0.10
Bradenton, Florida/1968	?	0.56	?	Foliar	6	3 5 7	0.39 0.38 0.28
Weslaco, Texas	?	0.56	?	Foliar	8	10	0.05
Weslaco, Texas	?	2.2	?	Foliar	8	10	0.19
Weslaco, Texas	?	1.1	?	Foliar	8	10	0.03
Wooster, Ohio/1968	?	0.56	?	Foliar	6	2 5	0.02 0.03
Wooster, Ohio/1968	?	1.1	?	Foliar	6	2 5	0.08 0.03

In pepper and tomato trials in Europe (Weidenauer *et al.*, 1998j,l; Françon and Larcinese, 1999e,i) plants were treated with a foliar spray 3 times, at 200-500 g ai/ha per application. Samples were collected in duplicate at intervals and stored frozen (-18^{o}C) for up to 17 months until analysed by method AMR 3015-94. Control tomatoes and peppers fortified with methomyl were extracted and analysed with the treated samples. Recoveries from peppers and tomatoes fortified at 0.02 mg/kg were 80 $\pm$ 2.0%, n=3, and 84% $\pm$ 12%, n=25 respectively. The results are shown in Table 42.

Table 42. Residues of methomyl in or on tomatoes and peppers after three foliar applications of a WP or SL formulation to plants in Europe.

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Application Method	PHI (days)	Residue (mg/kg)	Report no.
Tomato							
GAP: Netherlands	SL WP	0.4	1600 500		3 3		
GAP: Belgium	WP	0.5	1600		14		
GAP: Italy	SL, WP	0.04 kg ai/hl			10		
GAP: Spain	SL, WP	0.50	1000		3		
GAP: Portugal	None Use Spain						
Huissen, Netherlands/1996 /Jamaica	SL, 200 g/lg	0.50	975	Foliar with ground sprayer to run-off	-1h +1h 1 3 5 7	<0.02 0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 4018-96
Huissen, Netherlands/1996 /Jamaica	WP, 250 g/kg	0.50	982	Foliar with ground sprayer to run-off	-1h +1h 1 3 5 7	<0.02 <0.02, 0.02 <0.02:<0.02 <0.02, <0.02 <0.02:<0.02 <0.02, <0.02	AMR 4018-96
Bemmel, Netherlands/1997 /Jamaica	SL, 200 g/l	0.60	2020	Foliar with ground sprayer to run-off, high volume.	-1h +3h 1	<0.02 0.03, 0.03 <0.02, <0.02	AMR 4515-97

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Application Method	PHI (days)	Residue (mg/kg)	Report no.
				Glasshouse	3 5 7	<0.02, <0.02 <0.02, <0.02 <0.02, <0.02	
Huissen, Netherlands/1997 /Jamaica	WP, 250 g/kg	0.60	1980	Foliar with ground sprayer to run-off, high volume. Glasshouse	-1h +3h 1 3 5 7	<0.02 0.11, 0.07 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 4515-97
Harmelerwaard, Netherlands/1997 /Blitz	SL, 200 g/l	0.60	2006	Foliar with ground sprayer to run-off, high volume. Glasshouse	7	<0.02, <0.02	AMR 4515-97
Harmelerwaard, Netherlands/1997 /Blitz	WP, 250 g/kg	0.59	1953	Foliar with ground sprayer to run-off, high volume. Glasshouse	7	<0.02, <0.02	AMR 4515-97
Sint Katelinje Waver, Belgium/1996 /Durinta	WP, 250 g/kg	1.0	2013	Foliar with ground sprayer to run-off	7	0.06, 0.04	AMR 4018-96
Saint Amand, Belgium/1997 /Lucy	WP, 250 g/l	0.42	1384	Typical spraying. Glasshouse	-1h +3h 1 3 5 7	<0.02 0.08, 0.06 <0.02, 0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 4515-97
Bois de Nivelles, Belgium/1997 /Solar	SL, 200 g/l	0.45	1493	Typical spraying. Glasshouse	7	<0.02, <0.02	AMR 4515-97
Caleppio di Settala, Italy/1997 /Erminia	SL, 200 g/l	0.41	812	Foliar with ground sprayer to run-off, high volume.	-1h +3h 1 3 5 7	<0.02 0.07, 0.03 0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 4507-97
Caleppio di Settala, Italy/1997 /Erminia	WP, 250 g/kg	0.42	836	Foliar with ground sprayer to run-off, high volume. Glasshouse	7	<0.02, <0.02	AMR 4507-97
Montanaso Lombardo, Italy/1996/Red Setter/	SL., 200 g/l	0.50	994	Foliar with ground sprayer to run-off	-1h +1h 1 3 5 7	<0.02 0.04, 0.04 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 3999-96
Montanaso Lombardo, Italy/1996/Red Setter/	WP, 250 g/kg	0.48	960	Foliar with ground sprayer to run-off	-1h +1h 1 3 5 7	<0.02 0.04, 0.09 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 3999-96
Palacios, Spain/1997 /Empire	WP, 250 g/kg	0.45	885	Foliar spray	-1h +3h 1 3 5 7	<0.02 0.14, 0.21 0.03, 0.03 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 4507-97

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Application Method	PHI (days)	Residue (mg/kg)	Report no.
Utrera, Spain/1997/ Empire	WP, 250 g/kg	0.45	888	Foliar spray	7	<0.02, <0.02	AMR 4507-97
Ultrera, Spain/1996/ Nemared	SL, 200 g/l	0.30	607	Foliar with ground sprayer to run-off	-1h +3h 1 3 5 7	<0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 3999-96
Azambuja, Portugal/1997/ Heinz 8892	WP, 250 g/kg	0.41	813	Foliar application to run-off (atomizer)	7	<0.02, <0.02	AMR 4507-97
Azambuja, Portugal/1996/ Cannery row	SL, 200 g/l	0.48	965	Foliar with ground sprayer to run-off		No data	AMR 3999-96
Pepper							
GAP: Netherlands	None						
GAP: Belgium	None						
GAP: Italy	SL, WP	0.04 kg ai/hl			10		
Huissen, Netherlands/1996 /Spirit	SL, 200 g/lg	0.50	975	Foliar with ground sprayer to run-off	-1h +3h 1 3 5 7	<0.02 0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	AMR 4018-96
Montanaso Lombardo, Italy/1996/Indalo F1	SL, 200 g/l	0.50	990	Foliar with ground sprayer to run-off	7	<u>≤0.02</u>, <0.02	AMR 3999-96

<u>Leafy vegetables</u>

Summary data were provided on US trials on spinach from 1968-1972, using multiple applications of an SP (900 g/kg) or an SL formulation (216 g/l) at 0.56-1.1 kg ai/ha (Ashley, 2001j). No details were provided. The results are shown in Table 43.

Trials were reported for head and leaf lettuce in California and Arizona in 1990 (C. M. Kennedy, 1991b). 10-15 applications of an SL or SP formulation were made with ground or aerial equipment at 1.0 kg ai/ha/application and samples of at least 12 heads or bunches were collected and stored at -15 to -25^{o}C for up to 14 months for analysis by method AMR 1806-90. Control samples of leaf and head lettuce were fortified with methomyl (0.02-7.0 mg/kg) and analysed with the treated samples. The recovery from leaf lettuce was 93% <u>+</u> 7%, n=9 and from head lettuce, 94% <u>+</u> 7%, n=11. Some control samples showed residues up to 0.5 mg/kg in head and 0.07 mg/kg in leaf lettuce, but most controls were <0.02 mg/kg. The results are shown in Table 43.

Table 43. Residues of methomyl in or on leafy vegetables after the foliar application of an SL or SP formulation in the USA.

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Application method	No. of appli-cations	PHI (days)	Residue (mg/kg)	Report no.
Spinach								
GAP: USA	SL, SP	1.0	90A	Aerial/ground	8	7		
King City, California/1970/?	SP, 900 g/kg	1.1	660	Ground foliar	4	3 7 9	9.2 1.4 0.28	4F 1448
Chualar, California/1972/?	SP, 900 g/kg	0.84 0.56	380	Ground foliar	1 1	 7	 3.0	4F 1448
Chualar, California/1972/?	SP, 900 g/kg	0.84 1.1	750	Ground foliar	1 1	 3 7	 6.5 4.1	4F 1448
Chualar, California/1972/?	SL, 216 g/l	0.84 0.56	380	Ground foliar	1 1	 7	 1.7	4F 1448
Chualar, California/1972/?	SL, 216 g/l	0.84 1.1	750	Ground foliar	1 1	 3 7	 16 4.6	4F 1448
Salinas, California/1972/?	SL, 216 g/l	0.84 0.56	380	Ground foliar	1 1	 3 7	 5.1 2.6	4F 1448
Salinas, California/1972/?	SL, 216 g/l	0.84 1.1	750	Ground foliar	1 1	 3 7	 12. 4.6	4F 1448
Salinas, California/1969/?	SP, 900 g/kg	0.56	660	Ground foliar	1	1 3 9 15	8.8 3.0 1.2 0.60	4F 1448
Salinas, California/1969/?	SP, 900 g/kg	1.1	660	Ground foliar	1	1 3 9 15	4.3 3.2 1.3 0.56	4F 1448
Van Buren, Arizona/1968/?	SP, 900 g/kg	0.56	250	Ground foliar	3	3 7 14	1.7 0.25 0.07	4F 1448
Van Buren, Arizona/1968/?	SP, 900 g/kg	1.1	250	Ground foliar	3	3 7 14	5.6 0.07 0.05	4F 1448
Albion, New York/1968/?	SP, 900 g/kg	0.56	280	Ground foliar	4	3 7	0.44 0.07	4F 1448
Albion, New York/19689/?	SP, 900 g/kg	1.1	280	Ground foliar	4	3 7	1.3 0.34	4F 1448
Crystal City, Texas/1969/?	SP, 900 g/kg	0.56	660	Ground foliar	7	3 5 7 14	7.4 3.7 1.6 0.04	4F 1448
Crystal City., Texas/1969/?	SP, 900 g/kg	1.1	660	Ground foliar	7	3 5 7 14	12 5.7 5.00 0.13	4F 1448
Alma, Arkansas/1967/?	SP, 900 g/kg	0.56	380	Ground foliar	1	5 7 10	6.9 2.3 0.68	4F 1448
Bradenton, Florida/1967/?	SP, 900 g/kg	0.56	940	Ground foliar	4	1 3 5	32. 4.0 0.40	4F 1448

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Application method	No. of appli-cations	PHI (days)	Residue (mg/kg)	Report no.
						10 14	0.04 0.03	
Bradenton, Florida/1967/?	SP, 900 g/kg	1.1	940	Ground foliar	4	1 3 5 10 14	96. 12 2.1 0.22 0.04	4F 1448
Bradenton, Florida/1967/?	SP, 900 g/kg	1.1	630	Ground foliar	9	1 3 5	0.60 0.53 0.10	4F 1448
Dyersburg, Tennessee /1971/?	SP, 900 g/kg	0.34	75	Aerial foliar	1	4	0.40	4F 1448
Dyersburg, Tennessee /1971/?	SP, 900 g/kg	0.67	75	Aerial foliar	1	4 7	0.84 0.30	4F 1448
Dyersburg, Tennessee /1971/?	SP, 900 g/kg	1.3	75	Aerial foliar	1	4 7	3.2 0.74	4F 1448
Lettuce, Head								
GAP: USA	SP, SL	1.0	90A	Aerial/ground		<0.5 kg ai/ha= 7 >0.5 kg ai/ha =10		
Madera, California/1990 /Great Lakes	SL, 216 g/l	1.0	400-450	Tractor sprayer over-the-top	11 12 15	10 10 10	0.23 (0.039[1]) 0.70 (<0.020[1])	AMR 1601-90
Madera, California/1990 /Great Lakes	SP, 900 g/kg	1.0	400-450	Tractor sprayer over-the-top	11 12 15	10 10 10	0.13 (0.026[1]) 0.18 (0.026[1])	AMR 1601-90
Salinas, California /Pybas-101	SL, 216 g/l	1.0	140	Helicopter foliar	15 16	10 10	1.2 (0.028[1]) 1.2 (0.13[1])	AMR 1601-90
Salinas, California/1990 /Pybas-101	SP, 900 g/kg	1.0	140	Helicopter foliar	15 16	10 10	0.54 (0.043[1]) 0.54 (0.067[1])	AMR 1601-90
Salinas, California/1990 /Pybas-101[2]	SL, 216 g/l	1.0	200 for apps 1-10 430 for apps 11-15	CO_2 plot sprayer, broadcast over crop	10 12 15	10 10 10	2.2 (1.0[1]) 1.4 (0.62[1]) 1.8 (0.076[1])	AMR 1601-90
Salinas, California/1990 /Pybas-101[2]	SP, 900 g/kg	1.0	200 for apps 1-10 430 for apps 11-15	CO_2 plot sprayer, broadcast over crop	10 12 15	10 10 10	2.3 (0.79[1]) 1.1 (0.21[1]) 0.74 (0.080[1])	AMR 1601-90
Litchfield, Arizona/1990 /Vanguard	SP, 900 g/lg	1.0	56	Backpack broadcast	10 12 15	10 10 10	4.6 1.2 2.1	AMR 1601-90
Litchfield, Arizona/1990 /Vanguard	SL, 216 g/l	1.0	56	Backpack broadcast	10 12 15	10 10 10	2.2 1.6 3.3	AMR 1601-90
Litchfield, Arizona/1990 /Vanguard	SP, 900 g/kg	1.0	71	Fixed-wing aircraft foliar	15	10	4.8	AMR 1601-90
Litchfield, Arizona/1990 /Vanguard	SL, 216 g./l	1.0	71	Fixed-wing aircraft foliar	15	10	1.5	AMR 1601-90

Location/Year/ Variety	Form.	Application rate (kg ai/ha)	Spray volume (l/ha)	Application method	No. of appli-cations	PHI (days)	Residue (mg/kg)	Report no.
Lettuce, Leaf								
GAP: USA	See head lettuce							
Madera, California/1990 /Prize Head[3]	SL, 216 g/l	1.0	400-450	Tractor sprayer over-the-top	11 12 15	10 10 10	1.4 2.1 1.9	AMR 1601-90
Madera, California/1990 /Prize Head[3]	SP, 900 g/kg	1.0	400-450	Tractor sprayer over-the-top	11 12 15	10 10 10	2.1 0.92 1.4	AMR 1601-90
Salinas, California/1990 /Royal Green[4]	SL, 216 g/l	1.0	140	Helicopter foliar	15	10	0.62	AMR 1601-90
Salinas, California/1990 /Royal Green[4]	SP, 900 g/kg	1.0	140	Helicopter foliar	15	10	0.31	AMR 1601-90
Salinas, California/1990 /Royal Green[5]	SL, 216 g/l	1.0	200-220 for apps 1-10 430 for apps 11-15	CO_2 plot sprayer. Broadcast over crop.	10 12 15	10 10 10	0.88 2.9 0.58	AMR 1601-90
Salinas, California/1990 /Royal Green[5]	SP, 900 g/kg	1.0	200-220 for apps 1-10 430 for apps 11-15	CO_2 plot sprayer. Broadcast over crop.	10 12 15	10 10 10	1.2 2.5 1.0	AMR 1601-90
Litchfield, Arizona/1990 /Romaine	SL, 216 g/l	1.0	56	Backpack broadcast	10 12 15	10 10 10	5.4, 6.0, 5.4 6.1, 6.4, 5.4 6.6, 6.7, 6.3	AMR 1601-90
Litchfield, Arizona/1990 /Romaine	SP, 900 g/kg	1.0	56	Backpack broadcast	10 12 15	10 10 10	3.1 5.6, 4.9, 5.7 4.0	AMR 1601-90
Litchfield, Arizona/1990 Romaine	SL, 216 g/l	1.0	71	Fixed-wing aircraft foliar	15	10	3.6	AMR 1601-90
Litchfield, Arizona/1990 /Romaine	SP, 900 g/kg	1.0	71	Fixed-wing aircraft foliar	15	10	5.5, 5.3, 5.2	AMR 1601-90

[1] Trimmed.
[2] One of four controls showed residues of 0.38 mg/kg (trimmed), and 0.50 mg/kg (untrimmed).
[3] One of three controls showed residues of 0.049 mg/kg.
[4] Control showed a residue of 0.071 mg/kg.
[5] Controls showed residues of 0.047 and 0.021 mg/kg.

Legume vegetables

Results and limited descriptions of trial conditions and analytical methods were reported for trials on succulent beans, peas and soya in the late 1960s and early 1970s (Ashley, 2001b,g). Samples were analysed by GLC method ML/PC-12 or its modification. Storage conditions and periods were not reported but some recovery data were given for fortified controls. It appears that adequate recoveries were achieved at concentrations ≥0.02 mg/kg. Report 2F 1247 demonstrated adequate recoveries at 0.21-2.1 mg/kg from peas plus pods ranging from 76 to 88%, n=5 (Table 44).

Ten soya trials in 1967-1968 with PHIs ranging from 12 to 62 days were reported by Ashley (2001b). None of the trials were at the GAP PHI and it was not clear whether many of the trials were for immature beans. All residues were <0.02 mg/kg.

Table 44. Residues of methomyl in or on succulent beans and podded peas after multiple foliar applications of various formulations in the USA.

Location/type/year	Form.	Application rate (kg ai/ha)	No. of applications	PHI (days)	Residue (mg/kg)	Report no/ comment
GAP: USA	SL, SP	1.0	10	<0.5 6 kg ai/ha = 1 >0.5 6 kg ai/ha= 3		11 kg ai/ha max
Beans (Bush, Pole and Lima)						
Bradenton, Florida/bush bean/1968	SL, 360 g ai/l	0.56	6	2 5	0.02 0.07	1F- 1021
Bradenton, Florida/bush bean/1968	D, 20 g ai /kg	0.56	6	2 5	0.13 0.06	1F- 1021
Bradenton, Florida/bush bean/1968	SP, 900 g/kg	1.1	6	0 7	0.06 <0.02	1F- 1021
Bradenton, Florida/bush bean/1968	SP, 900 g/kg	0.56	7	1 3	0.05 <0.02	1F- 1021
Bradenton, Florida/bush bean/?	SP, 900 g/kg	0.22	7	1 3	<0.02 <0.02	1F- 1021
Bradenton, Florida/bush bean/?	SP, 900 g/kg	0.56	7	1 3	0.05 <0.02	1F- 1021
Bradenton, Florida/pole bean/1968	SP, 900 g ai/kg	0.56	3	2 6	<0.02 <0.02	1F- 1021
Homestead, Florida/1968/bush bean	SP, 900 g ai/kg	0.45	4	5	0.28	1F- 1021
Raleigh, North Carolina/1968/bush bean	D, 20 g ai/kg	1.1	4	1 3 7	0.62 0.03 0.04	1F- 1021
Raleigh, North Carolina/1968/bush bean	SP, 900 g/kg	0.56	7	1 3 7	0.06 0.04 <0.02	1F- 1021
Newark, Delaware/1965/lima bean	SP, 900 g/kg	1.1	11	7	<0.02	1F- 1021
Newark, Delaware/1965/lima bean	SP, 900 g/kg	0.56	11	7	<0.02	1F- 1021
Niles, Michigan/?/bush bean	SP, 900 g/kg	0.56	2	3 7	0.30 0.07	1F- 1021
Niles, Michigan/?/bush bean	SP, 900 g/kg	1.1	2	3 7	0.30 0.18	1F- 1021
Wooster, Ohio/?/lima bean	SP, 900 g/kg	1.1	6	2 5 8	0.68 0.05 0.03	1F- 1021
Peas + Pods (Peas only)						
Mt. Vernon, Washington/1969	SP, 900 g/kg	0.50	3	1 2 5 7	4.0 (0.12) 1.1 <0.02 (<0.02) <0.02	1F- 1021
Mt. Vernon, Washington/1969	SP, 900 g/kg	1.0	3	1 2 5 7	4.6 (0.40) 1.4 0.11 (<0.02) 0.04	1F- 1021

Location/type/year	Form.	Application rate (kg ai/ha)	No. of applications	PHI (days)	Residue (mg/kg)	Report no/ comment
Stanwood, Washington/1969	SP, 900 g/kg	0.56	2	6	0.09	1F- 1021
Stanwood, Washington/1969	SP, 900 g/kg	1.1	2	6	0.12	1F- 1021
Stanwood, Washington/1969	SP, 900 g/kg	2.2	2	6 13	0.93 (<0.02)	1F- 1021
Burlington, Washington/1969	SP, 900 g/kg	0.56	2	5	0.17	1F- 1021
Burlington, Washington/1969	SP, 900 g/kg	1.1	2	5	0.27	1F- 1021
Burlington, Washington/1969	SP, 900 g/kg	2.2	2	5 16	0.64 0.02 (<0.02)	1F- 1021
Waseco, Minnesota/1969	SP, 900 g/kg	0.56	1	14	<0.02	1F- 1021
Waseco, Minnesota/1969	SP, 900 g/kg	2.2	1	14	<0.02	2F- 1247
Marien, Wisconsin/1970	SP, 900 g/kg	0.56	1	1	0.12 (0.03)	2F- 1247
Marien, Wisconsin/1970	SP, 900 g/kg	1.1	1	1	0.20 (0.09)	2F- 1247
Waseca, Minnesota/1970	SP, 900 g/kg	0.56	1	1	0.18 (<0.02)	2F- 1247
Waseca, Minnesota/1970	SP, 900 g/kg	1.1	1	1	1.2 (0.52)	2F- 1247
Waseca, Minnesota/1970	SP, 900 g/kg	2.2	1	1	2.2 (1.1)	2F- 1247
Walla Walla, Washington/1971	SP, 900 g/kg	0.56	1	3 5	0.07 0.04	2F- 1247
Walla Walla, Washington/1971	SP, 900 g/kg	1.1	1	3 5	0.19 0.11	2F- 1247
Waseca, Minnesota/1971	SP, 900 g/kg	0.50	1	1 2	0.60 0.28	2F- 1247
Waseca, Minnesota/1971	SP, 900 g/kg	1.0	1	1 2	1.2 0.92	2F- 1247
Forest, Wisconsin/1971	SP, 900 g/kg	1.0	1	1 2 3	0.70 0.74 0.33	2F- 1247
Owatonna, Minnesota/1971	SP, 900 g/kg	0.50	1	1 2	0.83 0.51	2F- 1247
Owatonna, Minnesota/1971	SP, 900 g/kg	1.0	1	1 2	0.88 0.74	2F- 1247

Summary data were also reported for forage (Table 45).

Table 45. Residues of methomyl in or on the forage of beans (succulent), peas and soya (immature) from multiple foliar applications of various formulations in the USA.

Location/type/year	Form.	Application Rate (kg ai/ha)	No. of applications	PHI (days)	Residue (mg/kg)	Report no./ comment
GAP: USA	SL, SP	1.0	10	Bean: Vine 3 Hay 7 Pea: Forage 5		

Location/type/year	Form.	Application Rate (kg ai/ha)	No. of applications	PHI (days)	Residue (mg/kg)	Report no./ comment
				Hay 14		
Beans (Bush, Pole and Lima) - vines						
Bradenton, Florida/bush bean/1968	SL, 360 g ai/l	0.56	6	2 5	0.77 0.31	1F1021
Bradenton, Florida/bush bean/1968	D, 20 g ai /kg	0.56	6	2 5	4.0 1.2	1F1021
Bradenton, Florida/bush bean/?	SP, 900 g/kg	0.22	7	1 3 7	0.60 0.09 <0.02	1F1021
Bradenton, Florida/bush bean/?	SP, 900 g/kg	0.56	7	1 3 7 14	8.0 3.3 1.0 0.03	1F1021
Bradenton, Florida/pole bean/1968	SP, 900 g ai/kg	0.56	3	2 6	0.40 0.20	1F1021
Homestead, Florida/1968/bush bean	SP, 900 g ai/kg	0.45	4	3 7	0.62 0.11	1F1021
Raleigh, North Carolina/1968/bush bean	D, 20 g ai/kg	1.1	4	1 3 7	12. 4.3 1.4	1F1021
Raleigh, North Carolina/1968/bush bean	SP, 900 g/kg	0.56	7	1 3 7	6.8 3.1 0.06	1F1021
Podded pea forage						
Mt. Vernon, Washington/1969	SP, 900 g/kg	0.50	3	1 2 5 7	14 5.8 0.94 0.05	1F1021
Mt. Vernon, Washington/1969	SP, 900 g/kg	1.0	3	1 2 5 7	21 4.3 0.34 0.12	1F1021
Stanwood, Washington/1969	SP, 900 g/kg	0.56	2	1 6	6.0 2.7	1F1021
Stanwood, Washington/1969	SP, 900 g/kg	1.1	2	1 6	22 6.5	1F1021
Stanwood, Washington/1969	SP, 900 g/kg	2.2	2	1 6 13	27 14 4.9	1F1021
Burlington, Washington/1969	SP, 900 g/kg	0.56	2	1 5	15 3.1	1F1021
Burlington, Washington/1969	SP, 900 g/kg	1.1	2	1 5	33 7.6	1F1021
Burlington, Washington/1969	SP, 900 g/kg	2.2	2	1 5 16	48 10 0.30	1F1021
Waseco, Minnesota/1969	SP, 900 g/kg	0.56	1	14	<0.02	1F1021
Waseco, Minnesota/1969	SP, 900 g/kg	2.2	1	14	0.06	2F1247
Marien, Wisconsin/1970	SP, 900 g/kg	0.56	1	1	3.0	2F1247
Marien, Wisconsin/1970	SP, 900 g/kg	1.1	1	1	4.3	2F1247
Waseca, Minnesota/1970	SP, 900 g/kg	0.56	1	1	1.3	2F1247
Waseca, Minnesota/1970	SP, 900 g/kg	1.1	1	1	4.2	2F1247
Walla Walla, Washington/1971	SP, 900 g/kg	0.56	1	3 5 7	0.11 0.10 <0.02	2F1247
Walla Walla,	SP, 900 g/kg	1.1	1	3	3.7	2F1247

Location/type/year	Form.	Application Rate (kg ai/ha)	No. of applications	PHI (days)	Residue (mg/kg)	Report no./ comment
Washington/1971				5 7	1.3 0.08	
Soya bean forage						
Blackville, South Carolina/1967	?	1.1	2	12	0.30 (1.2 air-dried)	1F1021
Raleigh, North Carolina/1968	?	0.56	4	1 7 14	0.60 (2.4 air -dried) 0.03(0.10) 0.07(0.25)	1F1021
Raleigh, North Carolina/1968	?	1.1	4	14	0.08(0.29)	1F1021
Raleigh, North Carolina/1968	?	2.2	4	14	0.40(1.43)	1F1021
Bristol, Maryland/1968	?	0.56 (13.4 soil)	7	3 7	0.92(5.75 air-dried) 0.06(0.37)	1F1021
Quincey, Florida/1968	?	0.56	1	3	<0.02	1F1021
Quincey, Florida/1968	?	1.1	1	3	0.08(0.2 air-dried)	1F1021
Quincey, Florida/1968	?	0.56 ultralow volume	1	3	5.1(14 air-dried)	1F1021
Quincey, Florida/1968	?	1.0 ultralow volume	1	3	0.08(0.2 air-dried)	1F1021
Blackville, South Carolina/1968	?	0.56	2	3 7 10	5.1(14 air-dried) 0.80(2.2) 0.12(0.3)	1F1021
Blackville, South Carolina/1968	?	1.1	2	3 7 10	8.0(22 air-dried) 3.7(10) 0.88(2.4)	1F1021

In a succulent green bean trial in Plover, Wisconsin, USA an SL formulation, 215 g/l, was applied 5 times at 6-7 day intervals at a rate of 1.0 kg ai/ha (C.M. Kennedy and Devine, 1993d). The application was foliar with ground equipment (CO_2 tractor sprayer). Replicate samples were harvested 3 days after the last treatment and stored frozen ($-20^0 \pm 5^oC$) for 10 months before analysis by method AMR 1806-90. Control recoveries were 80, 92 and 88% at 0.01, 0.10 and 1.0 mg/kg. The residues on unwashed beans were 0.42, 0.58 and 0.36 mg/kg and on washed beans 0.13, 0.21 and 0.21 mg/kg.

Pulses

Field trials on dry beans were reported from the USA. Summary results were reported for trials in California in 1970-1972 (Ashley, 2001i). In additional trials in California in 1989 (Marxmiller and Tomic, 1991) and in Michigan, Colorado, Idaho and North Dakota in 1990 (Marxmiller and Hay, 1991d) samples stored for up to 31 months were analysed by Method AMR 1806-90. Recoveries ranged from 70% to 110% from beans fortified at 0.02-0.5 mg/kg. The results for dry beans are shown in Table 46 and for dry bean hay and forage in Table 47.

Table 46. Residues of methomyl in or on dry beans after the application of SP or SL formulations in the USA (4F1437; AMR 1465-89; AMR 1602-90).

Location/year/type	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
GAP: USA	SL, SP	1.0	10	10	Aerial/Ground	14	
San Lucas, California/1971 /Lima	SP, 900 g/kg	0.56	520	1	Ground	6	<0.02
San Lucas, California/1971 /Lima	SP, 900 g/kg	1.1	520	1	Ground	6	<0.02
Collegeville, California/1972/Kidney	SP, 900 g/kg	1.1	94	1	Aerial	3	<0.02
Newman, California/1972/Lima	SP, 900 g/kg	1.0	94	1	Aerial	14	<0.02
King City, California/1972/Lima	SP, 900 g/kg	0.50	470	1	Ground	0 4 7 13	<0.02 <0.02 <0.02 <0.02
King City, California/1972/Lima	SP, 900 g/kg	1.0	470	1	Ground	0 4 7 13	<0.02 <0.02 <0.02 <0.02
King City, California/1972/Lima	SP, 900 g/kg	0.50	49	1	Aerial	0 4 7	<0.02 <0.02 <0.02
King City, California/1972/Lima	SP, 900 g/kg	1.0	49	1	Aerial	0 4 7	<0.02 <0.02 <0.02
Dixon City, California/1972/Lima	SP, 900 g/kg	1.0	330	1	Ground	1 3 7	<0.02 <0.02 <0.02
Dixon City, California/1972/Lima	SP, 900 g/kg	1.0	94	1	Aerial	1 3 7	<0.02 <0.02 <0.02
Collegeville, California/1972/Kidney	SP, 900 g/kg	1.0	94	1	Aerial	3	<0.02
Farmington, California/1972/?	SP, 900 g/kg	1.0		1		3	<0.02
Tracey, California/1972/Pinto	SP, 900 g/kg	0.50	94	1	Aerial	5	<0.02
Tracey, California/1972/Pinto	SP, 900 g/kg	1.0	94	1	Aerial	5	<0.02
Greenfield, California/1971/Lima	SP, 900 g/kg	0.50	330	2	Ground	1 7	<0.02 <0.02
Madera, California/1989/Bush	SP, 900 g/kg	1.0	360	5	Tractor sprayer	0 3 7 14 21	<0.02 <0.02 <0.02 0.023 0.026[1]
Madera, California/1989/Bush	SP, 900 g/kg	2.0	360	5	Tractor sprayer	3 7 14	<0.02 <0.02 0.024
Madera, California/1989/Cowpea	SL, 215 g/l	1.0	390	5	Tractor sprayer	14 21	<0.02 <0.02
Madera, California/1989/Cowpea	SL, 215 g/l	2.0	390	5	Tractor sprayer	0 3 14 21	0.14 0.085 <0.02 <0.02
Tracy, California/1989/Lima	SL, 215 g/l	1.0	420	5	CO_2 plot sprayer	0 3 7	0.050 0.035 <0.02

Location/year/type	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
						14 21	<0.02 <0.02
Tracy, California/1989/Lima	SL, 215 g/l	2.0	420	5	CO_2 plot sprayer	0 3 7 14 21	0.16 0.24 0.035 <0.02 <0.02
Tracy, California/1989/Lima	SL, 215 g/l	1.0	100	5	aerial	0 3 7 14 21	<0.02 <0.02 <0.02 0.02 <0.02
Tracy, California/1989/Lima	SP, 900 g/kg	1.0	420	5	CO_2 plot sprayer	0 3 7 14 21	0.045 <0.02 <0.02 <0.02 0.026
Tracy, California/1989/Lima	SP, 900 g/kg	2.0	420	5	CO_2 plot sprayer	0 3 7 14 21	<0.02 0.070 0.050 <0.02 0.026
Conklin, Michigan/1990/Albion	SL, 215 g/l	1.0	210	5	CO_2 backpack sprayer	7	0.16, 0.17, 0.18
Eaton, Colorado/1990/Pinto	SL, 215 g/l	1.0	50	5	Aerial	7	0.045
Jerome, Idaho/1990/Pinto	SL, 215 g/l	1.0	120	5	CO_2 backpack sprayer	7	<0.02
Northwood, North Dakota/1990/Navy	SL, 215 g/l	1.0	50	5	Aerial broadcast	7	<0.02

[1] Control dry bean sample showed 0.03 mg/kg methomyl.

Table 47. Residues of methomyl in or on dry bean forage and hay after the application of SP or SL formulations in the USA (4F1437; AMR 1465-89; AMR 1602-90).

Location/year/type	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Collegeville, California/1971/Kidney	SP, 900 g/kg	1.0	94	1	Aerial	3	4.4 forage (80% water)
Patterson, California/1971/Lima	SP, 900 g/kg	1.0	140	1	Aerial	3 7	2.5 forage 1.3 (80% water)
Collegeville, California/1970/Kidney	SP, 900 g/kg	1.0	94	1	Aerial	5	0.60 forage (84% water)
Niles, Michigan/1972/Lima	SP, 900 g/kg	1.0	380	4	Ground	3	0.13 forage (80% water)
Madera, California/1989/Bush	SP, 900 g/kg	1.0	360	5	Tractor sprayer	0 3 7 14 21	18 forage 1.5 1.1 <0.50 hay <0.50
Madera, California/1989/Bush	SP, 900 g/kg	2.0	360	5	Tractor sprayer	0 3 7 14 21	30 forage 7.0 5.3 0.70 hay <0.50

Location/year/type	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Madera, California/1989/Cowpea	SL, 215 g/l	1.0	390	5	Tractor sprayer	0 3 7 14 21	22 forage 1.6 <0.50 <0.50 hay <0.50
Madera, California/1989/Cowpea	SL, 215 g/l	2.0	390	5	Tractor sprayer	0 3 14 21	<0.50 forage[1] 8.0 3.3 <0.50 hay <0.50
Tracy, California/1989/Lima	SL, 215 g/l	1.0	420	5	CO_2 plot sprayer	0 3 7 14 21	36 forage 6.0 4.8 9.0 hay 1.6
Tracy, California/1989/Lima	SL, 215 g/l	2.0	420	5	CO_2 plot sprayer	0 3 7 14 21	70 forage 9.2 5.3 1.8 hay <0.50
Tracy, California/1989/Lima	SL, 215 g/l	1.0	100	5	aerial	0 3 7 14 21	7.4 forage 4.6 1.8 1.1 hay <0.50
Tracy, California/1989/Lima	SP, 900 g/kg	1.0	420	5	CO_2 plot sprayer	0 3 7 14 21	36 forage 6.7 2.3 3.0 hay 1.0
Tracy, California/1989/Lima	SP, 900 g/kg	2.0	420	5	CO_2 plot sprayer	0 3 7 14 21	71 forage 8.5 2.7 10 hay 5.8

[1] Thought to be an error from mislabelling of samples.

Root and tuber vegetables

Summary results were reported for potato trials in the USA (Table 48). Samples were analysed by method ML/PC-12. Recoveries were adequate from fortified controls in the range 0.02-0.60 mg/kg.

Table 48. Methomyl residues in or on potato tubers after the foliar application of SL or SP formulations in the USA.

Location, Year	Application				mg/kg after PHI (days)		Report no.
	Form.	No.	Kg ai/hl	Kg ai/ha	6	7	
GAP:	SL, SP	8	11	1.1	6		
Hastings, FL 1968	SP, 900 g/kg	3	-	0.56	<0.02		0F 0886
Leipzig, DE 1975	SL, 215 g/l	5	0.50	1.0		<0.02	0F 0886
Smyrna, DE 1974	SL, 215 g/l	5	-	1.0		<0.02	0F 0886
Essexville, MI 1973	SL, 215 g/l	1	3.0	1.1		<0.02	0F 0886
Presque Isle, MA 1975	SL, 215 g/l	7	0.086	1.0		<0.02	0F 0886
Smyrna, DE 1974	SL, 215 g/l	5	-	0.50		<0.02	0F 0886

Location, Year	Application				mg/kg after PHI (days)		Report no.
	Form.	No.	Kg ai/hl	Kg ai/ha	6	7	
Smyrna, DE 1974	SL, 215 g/l	5	-	1.0		<0.02	
Smyrna, DE	SL, 215 g/l	1	-	0.5		<0.02	0F 0886
Smyrna, DE 1974	SL, 215 g/l	1	-	1.0		<0.02	
Smyrna, DE 1974	SL, 215 g/l	2	-	0.5		<0.02	0F 0886
Smyrna, DE 1974	SL, 215 g/l	2	-	1.0		<0.02	
Williamson, NY 1972	SP, 900 g/kg	1	-	0.56	<0.02		0F 0886
Williamson, NY 1972	SL, 215 g/l	1	-	0.56	<0.02		
Salinas, CA 1971	SP, 900 g/kg	1	-	0.56		<0.02 <0.02	0F 0886
Williamson, NY 1972	SP, 900 g/kg	1	-	1.1	<0.02		0F 0886
Williamson, NY 1972	SL, 215 g/l	1	-	4.4	<0.02		
Othello, WA 1972	SP, 900 g/kg	1	-	1.1	<0.02		0F 0886

Stalk and stem vegetables

Summary data were reported for field trials on asparagus in the USA in 1972-1973 (Ashley, 2001m). Samples were analysed by method ML/PC-12. Recoveries from fortified control asparagus samples were 150% at 0.04 mg/kg (n=1), and 90% and 105 % at 0.08 mg/kg. The results are shown in Table 49.

Table 49. Residues of methomyl in or on asparagus after the foliar application of SL or SP formulations in the USA (6F1654).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
GAP: USA	SL, SP	1.0	10	8	Aerial Ground	1	
El Centro, California/1972	SP, 900 g/kg	1.1	94	1	Aerial	1 14	0.15 <0.02
El Centro, California/1972	Sl, 215 G/L	1.1	470	1	Ground foliar	1 3 5	0.48 0.20 0.07
Hart, Michigan/1972	SP, 900 g/kg	0.56	700	1	Ground foliar	1-5	<0.04
Hart, Michigan/1972	SP, 900 g/kg	1.1	700	1	Ground foliar	1 2 3 5	0.12 0.08 <0.04 <0.04
Buchanan, Michigan/1972	SP, 900 g/kg	0.56	380	1	Ground foliar	1 2 4	0.12 <0.04 <0.04
Buchanan, Michigan/1972	SP, 900 g/kg	1.1	380	1	Ground foliar	1 2 4	0.14 0.06 <0.04
Lathrop, California/1974	SL, 215 g/l	2.0	470	5	Ground foliar	0 1 3	2.5 1.3 0.17
Lathrop, California/1974	SL, 215 g/l	1.0	470	5	Ground foliar	0 1 3	1.2 0.26 <0.02
Lathrop, California/1974	SL, 215 g/l	0.50	470	5	Ground foliar	0 1 3	0.68 0.05 <0.02
Stockton, California/1974	SL, 215 g/l	2.0	470	5	Ground foliar	0 1 3	2.3 0.87 0.07

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Stockton, California/1974	SL, 215 g/l	1.0	470	5	Ground foliar	0 1 3	0.70 0.40 0.07
Stockton, California/1974	SL, 215 g/l	0.50	470	5	Ground foliar	0 1 3	0.55 0.19 0.21
Bridgeton, New Jersey/1974	SL, 215 g/l	2.0	560	2	Ground foliar	1	0.81
Bridgeton, New Jersey/1974	SL, 215 g/l	1.0	560	2	Ground foliar	1	0.59
Grandview, Washington/1974	SL, 215 g/l	1.1	390	2	Ground Foliar	1 2 3 4 5	1.1 0.52 0.13 0.12 <0.02

Summary information was provided for US celery trials in Florida and California from 1968-1972 (Ashley, 2001j). Samples were analysed by method ML/PC-12. Some information on recoveries was provided for the fortification range 0.08-2.0 mg/kg. In two more recent trials in Florida and California in 1990 samples were stored up to 11 months and analysed by method AMR 1806-90 (Hay and Hausmann, 1991). Fortified control samples were analysed with the treated samples. The recovery was 110% at 0.02 mg/kg. The results are shown in Table 50.

Table 50. Residues of methomyl in or on celery after the foliar application of SP or SL formulations in the USA (4F1448; AMR 1605-90).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue [1] (mg/kg)
GAP: USA	SL, SP	1.0	10	10		7	
Sarasota, Florida/1968	WP, 900 g/kg	0.50	940	3	Foliar	3 7	2.3(0.27) 1.4(0.25)
Sarasota, Florida/1968	WP, 900 g/kg	2.0	940	3	Foliar	3 7	7.4(0.64) 4.3(0.53)
Belle Glade, Florida/1969	WP, 900 g/kg	0.50	940	1	Foliar	3 7 14	2.7(0.8) 0.52 0.06
Belle Glade, Florida/1969	WP, 900 g/kg	1.0	940	1	Foliar	3 7 14	3.4(0.80) 2.0 0.09
Zellwood, Florida/1969	WP, 900 g/kg	0.50	940	1	Foliar	2 5 7 14	1.1(0.09) 0.68 0.06 0.03
Zellwood, Florida/1969	WP, 900 g/kg	1.0	940	1	Foliar	2 5 7 14	3.2(0.25) 1.1 0.09 0.08
Salinas, California/1971	WP, 900 g/kg	1.0	140	6	Aerial	3 5 7	6.9(3.9) 3.7(1.5) 1.8(1.0)
Sarasota, Florida/1970	WP, 900 g/kg	0.50	940	1	Foliar	7 10 14	(<0.02) (<0.02) (<0.02)
Sarasota, Florida/1970	WP, 900 g/kg	1.0	940	1	Foliar	7	(<0.02)

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue [1] (mg/kg)
						10 14	(<0.02) (<0.02)
Bradenton, Florida/1967	WP, 900 g/kg	0.84	2800	11	Foliar	1 3 7 10	(1.6) (0.92) (0.10) (0.13)
Bradenton, Florida/1967	WP, 900 g/kg	1.7	2800	11	Foliar	1 3 7 10	(2.9) (2.3) (0.28) (0.14)
Sarasota, Florida/1971	WP, 900 g/kg	1.0	28	1	Aerial	1 3 7 13	22 3.2 2.0 0.17
Belle Glade, Florida/1972	SL, 215 g/l	0.50	28	2	Aerial	1 12	7.4 <0.02
Belle Glade, Florida/1972	SL, 215 g/l	0.50	490	2	Foliar	1 12	5.5 <0.02
Belle Glade, Florida/1972	SP, 900 g/kg	0.50	28	2	Aerial	1 12	7.4 <0.02
Belle Glade, Florida/1972	SP, 900 g/kg	0.50	490	2	Foliar	1 12	7.4 <0.02
Salinas, California/1972	SP, 900 g/kg	1.0	49	2	Aerial	14	(0.04)
Salinas, California/1972	SL, 215 g/l	1.0	49	2	Aerial	14	(0.02)
Belle Glade, Florida/1990	SL, 215 g/l	1.0	47	10	Aerial	7	<0.02
Belle Glade, Florida/1990	SP, 900 g/kg	1.0	47	10	Aerial	7	<0.02
Irvine, California/1990	SL, 215 g/l	1.0	1000	10	Foliar. Fix wet boom with drop nozzles	7	0.72
Irvine, California/1990	SP, 900 g/kg	1.0	1000	10	Foliar. Fix wet boom with drop nozzles	7	0.59

[1] Untrimmed. Values for trimmed celery are in parenthesis.

Cereal grains

Field trial data on barley, maize, oats, sorghum and wheat were provided from the USA. Summary information was submitted for barley, oats and wheat (Ashley, 2001k). Samples were analysed by method ML/PC-12. Fortified control recoveries from grain at concentrations of 0.02-1 mg/kg were adequate. Storage periods and conditions were not detailed. Findings for grain and for forage, hay and straw are shown in Tables 51 and 52 respectively.

Table 51. Residues of methomyl in or on cereal grains after the application of SL or SP formulations in the USA (5F 1615).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
GAP: USA	SL, SP	0.5	10	4	Aerial Ground	7	
Barley							
Stillwater, Oklahoma/1974	SP, 900 g/kg	0.50	280	4	Foliar	5	0.12

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
					ground	12	0.02
Stillwater, Oklahoma/1974	SP, 900 g/kg	1.0	280	4	Foliar ground	5 12	0.14 <0.02
Stillwater, Oklahoma/1974	SL, 215 g/l	0.50	280	4	Foliar ground	5 12	0.72 <0.02
Stillwater, Oklahoma/1974	SP, 900 g/kg	1.0	280	4	Foliar ground	5 12	1.1 0.04
Arthur, North Dakota/1974	SP, 900 g/kg	0.50	28	1	Aerial	15	<0.02
Bridgeville, Delaware/1975	SL, 215 g/l	0.50	-	1	Foliar	7 14	0.33 1.3
Oats							
Rosemont, Minnesota/1974	SP, 900 g/kg	0.50	380	2	Foliar ground	7 12	<0.02 <0.02
Rosemont, Minnesota/1974	SP, 900 g/kg	1.0	380	2	Foliar ground	7 12	<0.02 0.03
Rosemont, Minnesota/1974	SL, 215 g/l	0.50	380	2	Foliar ground	7 12	<0.02 0.02
Rosemont, Minnesota/1974	SL, 215 g/l	1.0	380	2	Foliar ground	7 12	0.02 0.03
Stillwater, Oklahoma/1974	SP, 900 g/kg	0.50	280	4	Foliar ground	5 12	<0.02 <0.02
Stillwater, Oklahoma/1974	SP, 900 g/kg	1.0	280	4	Foliar ground	5 12	<0.02 <0.02
Stillwater, Oklahoma/1974	SL, 215 g/l	0.50	280	4	Foliar ground	5 12	<0.02 <0.02
Stillwater, Oklahoma/1974	SL, 215 g/l	1.0	280	4	Foliar ground	5 12	<0.02 <0.02
Rosemont, Minnesota/1974	SP, 900 g/kg	0.50	380	2	Foliar ground	7 12	<0.02 <0.02
Rosemont, Minnesota/1974	SP, 900 g/kg	1.0	380	2	Foliar ground	7 12	<0.02 0.03
Rosemont, Minnesota/1974	SL, 215 g/l	0.50	380	2	Foliar ground	7 12	<0.02 0.02
Rosemont, Minnesota/1974	SL, 215 g/l	1.0	380	2	Foliar ground	7 12	0.02 0.03
Wheat							
Chesterfield, Missouri/1974	SP, 900 g/kg	0.50	400	2	Foliar ground	1 3 8	<0.02 <0.02 0.02
Chesterfield, Missouri/1974	SL, 215 g/l	0.50	400	2	Foliar ground	1 3 8	<0.02 0.04 <0.02
Olatho, Kansas/1974	SL, 215 g/l	0.50	360	4	Foliar ground	1 3 7	0.02 <0.02 <0.02
Buchanan, Missouri/1974	SP, 900 g/kg	0.56	360	5	Foliar ground	1 3 5 7	0.09 0.04 0.03 0.12
Buchanan, Missouri/1974	SP, 900 g/kg	1.0	360	5	Foliar ground	1	0.17
Buchanan, Missouri/1974	SL, 215 g/l	0.56	360	5	Foliar ground	1 3 5 7	0.04 0.07 0.05 0.06
Buchanan, Missouri/1974	SL, 215 g/l	1.0	360	5	Foliar ground	1 5	0.21 0.24

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Stillwater, Oklahoma/1974	SP, 900 g/kg	0.50	280	4	Foliar ground	5 12	0.30 0.09
Stillwater, Oklahoma/1974	SP, 900 g/kg	1.0	280	4	Foliar ground	5 12	0.33 0.02
Salisbury, Maryland/1984	SL, 215 g/l	0.56	38	2	Aerial	0 1 3 7 14	0.95 1.3 1.5 0.17 0.11
Salisbury, Maryland/1984	SL, 215 g/l	1.1	75	2	Aerial	0 1 3 7 14	1.3 2.83.50.110.0 8
Delmar, Delaware/1984	SL, 215 g/l	0.56	38	2	Aerial	0 1 3 7 14	0.14 0.10 0.11 <0.02 <0.02
Delmar, Delaware/1984	SL, 215 g/l	1.1	75	2	Aerial	0 1 3 7 14	0.89 0.16 0.20 0.04 <0.02
Mt. Gilead, Ohio/1984	WS,900 g/kg	0.56	94	2	Aerial	1 3 7 18	0.62 0.57 0.17 0.06
Mt. Gilead, Ohio/1984	WS,900 g/kg	1.0	94	2	Aerial	1 3 7 18	1.1 0.57 0.91 0.36
Amsterdam, Montana/1984	SL, 215 g/l	0.56	47	2	Aerial	1 3 7 14	0.53 0.36 0.40 0.13
Amsterdam, Montana/1984	SL, 215 g/l	1.1	47	2	Aerial	1 3 7 14	1.4 1.1 1.1 0.26
Phelps, New York/1974	SL, 215 g/l	0.50	560	3	Foliar	1 3 7 14	5.8 1.8 1.1 0.28
Phelps, New York/1974	SL, 215 g/l	1.0	560	3	Foliar	1 3 7 14	9.8 4.3 1.4 0.19
Phelps, New York/1974	SP, 900 g/kg	0.50	560	3	Foliar	1 3 7 14	2.9 2.0 0.69 0.04
Phelps, New York/1974	SP, 900 g/kg	1.0	560	3	Foliar	3	7.8
Chestertown, Maryland/1974	SL, 215 g/l	0.50	340	2	Foliar	1 14	2.1 0.15
Chestertown, Maryland/1974	SL, 215 g/l	0.50	340	1	Foliar	7 14	0.14 0.05
Chestertown, Maryland/1974	SP, 900 g/kg	0.50	340	1	Foliar	7	0.17

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
						14	0.07
Florence, South Carolina/1974	SL, 215 g/l	0.50	190	1	Foliar	3 7 14	0.26 <0.02 <0.02
Belleville, Illinois/1975	SL, 215 g/l	0.50	190	1	Foliar	6 14	0.02 <0.02
Louisville, Georgia/1974	SL, 215 g/l	0.50	130	1	?	5	0.20

Table 52. Residues of methomyl in or on cereal forage, hay and straw after the application of SL or SP formulations in the USA (5F 1615).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
GAP: USA	SL, SP	0.5	10	4	Aerial/ Ground	7	
Barley							
Stillwater, Oklahoma/1974	SP, 900 g/kg	0.50	280	2	Foliar ground	3 6 14	16 forage 11 0.15 (80% water)
Stillwater, Oklahoma/1974	SP, 900 g/kg	1.0	280	2	Foliar ground	3 6 14	54 forage 18 0.06 (80% water)
Stillwater, Oklahoma/1974	SL, 215 g/l	0.50	280	2	Foliar ground	3 14	14 forage 0.02 (80% water)
Stillwater, Oklahoma/1974	SP, 900 g/kg	1.0	280	2	Foliar ground	3 6 14	38 forage 14 0.47 (80% water)
Stillwater, Oklahoma/1974	SP, 900 g/kg	0.50	280	4	Foliar ground	5 12	2.8 straw <0.02
Stillwater, Oklahoma/1974	SP, 900 g/kg	1.0	280	4	Foliar ground	5 12	4.8 straw <0.02
Stillwater, Oklahoma/1974	SL, 215 g/l	0.50	280	4	Foliar ground	5 12	3.1 straw 0.05
Stillwater, Oklahoma/1974	SL, 215 g/l	1.0	280	4	Foliar ground	5 12	6.8 straw 0.16
Bridgeville, Delaware/1975	SL, 215 g/l	0.50	-	1	Foliar	7 14	0.41 forage 3.1
Oats							
Stillwater, Oklahoma/1974	Sl, 215 g/l	0.50	280	2	Foliar	14	0.05 forage (78% water)
Stillwater, Oklahoma/1974	Sl, 215 g/l	1.0	280	2	Foliar	14	0.27 forage (78% water)
Stillwater, Oklahoma/1974	SP, 900 g/kg	0.50	280	2	Foliar	14	0.08 forage (78% water)
Stillwater, Oklahoma/1974	Sl, 215 g/l	1.0	280	2	Foliar	14	0.09 forage (78% water)
Stillwater, Oklahoma/1974	SL, 215 g/l	0.50	280	4	Foliar	5 12	1.7 straw <0.02
Stillwater, Oklahoma/1974	SL, 215 g/l	1.0	280	4	Foliar	5 12	7.1 straw <0.05
Stillwater,	SP, 900 g/kg	0.50	280	4	Foliar	5	2.5 straw

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Oklahoma/1974						12	<0.05
Stillwater, Oklahoma/1974	SL, 215 g/l	1.0	280	4	Foliar	5 12	6.6 straw <0.05
Rosemont, Minnesota/1974	SL, 215 g/l	0.50	380	2	Foliar	7 12	0.16 forage 0.24
Rosemont, Minnesota/1974	SL, 215 g/l	1.0	380	2	Foliar	7 12	0.89 forage 0.14
Rosemont, Minnesota/1974	SP, 900 g/kg	0.50	380	2	Foliar	7 12	0.15 forage 0.10
Rosemont, Minnesota/1974	SP, 900 g/kg	1.0	380	2	Foliar	7 12	0.18 forage 0.24
Phelps, New York/1975	SL, 215 g/l	1.0	560	4	Foliar ground	7 21	0.65 forage <0.02
Phelps, New York/1975	SL, 215 g/l	0.50	560	4	Foliar ground	7 21	0.17 forage <0.02
Phelps, New York/1975	SL, 215 g/l	0.25	560	4	Foliar ground	7 21	0.05 forage <0.02
Wheat							
Chesterfield, Missouri/1974	SL, 215 g/l	0.50	400	2	Foliar ground	7 8 15	0.24 forage (70% water) 2.0 straw 1.0
Chesterfield, Missouri/1974	SL, 215 g/l	1.0	400	2	Foliar ground	7 14	0.87 forage 0.19 (70% water)
Chesterfield, Missouri/1974	SP, 900 g/kg	0.50	400	2	Foliar ground	8 15	2.0 straw 1.0
Chesterfield, Missouri/1974	SP, 900 g/kg	1.0	400	2	Foliar ground	7 14	0.87 forage 0.19 (70% water)
Olathe, Kansas/1974	SL, 215 g/l	0.50	360	2	Foliar ground	7 14	0.85 forage 0.03 (68% water)
Olathe, Kansas/1974	SL, 215 g/l	0.50	360	4	Foliar ground	3 7 14	0.90 straw 0.62 0.16
Buchanan, Missouri/1974	SP, 900 g/kg	0.56	380	2	Foliar ground	7 14	0.38 forage 0.03 (68% water)
Buchanan, Missouri/1974	SP, 900 g/kg	1.1	380	2	Foliar ground	7	0.52 forage (68% water)
Buchanan, Missouri/1974	SL, 215 g/l	0.56	380	2	Foliar ground	7 14	0.12 forage 0.03 (68% water)
Buchanan, Missouri/1974	SL, 215 g/l	1.1	380	2	Foliar ground	7	0.32 forage (68% water)
Buchanan, Missouri/1974	SP, 900 g/kg	0.56	380	5	Foliar ground	1 3	23 straw 12
Buchanan, Missouri/1974	SP, 900 g/kg	1.1	380	5	Foliar ground	1 7	55 15
Buchanan, Missouri/1974	SL, 215 g/l	0.56	380	5	Foliar ground	1 3 5 7	26 straw 20 11 0.43
Buchanan, Missouri/1974	SL, 215 g/l	1.1	380	5	Foliar ground	1 7	34 straw 15
Bennington, Nebraska/1974	SP, 900 g/kg	0.50	970	2	Foliar ground	8	0.59 forage (64% water)

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Bennington, Nebraska/1974	SP, 900 g/kg	0.50	970	2	Foliar ground	7	4.6 straw
Bennington, Nebraska/1974	SL, 215 g/l	0.50	970	2	Foliar ground	8	0.37 forage (64% water)
Bennington, Nebraska/1974	SL, 215 g/l	0.50	970	2	Foliar ground	7	2.8 straw
Stillwater, Oklahoma/1974	SP, 900 g/l	0.50	280	2	Foliar ground	1 3 6 14	48 forage 18 4.9 0.16 (80% water)
Stillwater, Oklahoma/1974	SP, 900 g/l	1.0	280	2	Foliar ground	1 3 6 14	36 forage 30 6.4 0.34 (80% water)
Stillwater, Oklahoma/1974	SP, 900 g/l	0.50	280	4	Foliar ground	5 12	3.7 straw 0.09
Stillwater, Oklahoma/1974	SP, 900 g/l	1.0	280	4	Foliar ground	5 12	1.8 straw 0.08
Stillwater, Oklahoma/1974	SL, 215 g/l	0.50	280	2	Foliar ground	1 3 6 14	22 forage 12 4.9 0.14 (80% water)
Stillwater, Oklahoma/1974	SP, 900 g/l	1.0	280	2	Foliar ground	`	46 forage 34 12 0.12 (80% water)
Stillwater, Oklahoma/1974 Triticale	SP, 900 g/kg	0.50	280	2	Foliar ground	14	<0.03 forage (80% water)
Stillwater, Oklahoma/1974 Triticale	SP, 900 g/kg	1.0	280	2	Foliar ground	14	0.09 forage (80% water)
Stillwater, Oklahoma/1974 Triticale	SL, 215 g/l	0.50	280	2	Foliar ground	14	0.12 forage (80% water)
Stillwater, Oklahoma/1974 Triticale	SL, 215 g/l	0.50	280	2	Foliar ground	5 12	3.0 straw 0.09
Stillwater, Oklahoma/1974 Triticale	SL, 215 g/l	1.0	280	2	Foliar ground	5 12	4.2 straw 0.15
Stillwater, Oklahoma/1974 Triticale	SP, 900 g/kg	0.50	280	2	Foliar ground	5 12	2.1 straw 0.92
Stillwater, Oklahoma/1974 Triticale	SP, 900 g/kg	1.0	280	2	Foliar ground	5 12	2.4 straw 0.07
Salisbury, Maryland/1984	SL, 215 g/l	0.56	38	2	Aerial	0 1 3 7 14	18 straw 8.1 3.4 0.39 0.20
Salisbury, Maryland/1984	SL, 215 g/l	1.1	75	2	Aerial	0 1	54 straw 28

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
						3 7 14	12 0.82 0.32
Delmar, Delaware/1984	SL, 215 g/l	0.56	38	2	Aerial	0 1 3 7 14	2.6 straw 1.7 0.82 <0.02 <0.02
Delmar, Delaware/1984	SL, 215 g/l	1.1	75	2	Aerial	0 1 3 7 14	6.4 straw 1.9 1.7 0.50 <0.02
Mt. Gilead, Ohio/1984	WS, 900 g/kg	0.56	94	2	Aerial	1 3 7 18	23 straw 40 6.5 0.53
Mt. Gilead, Ohio/1984	WS, 900 g/kg	1.1	94	2	Aerial	1 3 7 18	28 straw 35 10 2.4
Amsterdam, Montana/1984	WL, 215 g/l	0.56	47	2	Aerial	1 3 7 14	9.7 straw 5.3 5.7 0.8
Amsterdam, Montana/1984	WL, 215 g/l	1.1	47	2	Aerial	1 3 7 14	15 straw 12 9.1 1.7
Phelps, New York/1974	Sl, 215 g/l	0.50	560	3	Foliar	1 3 7 14	2.6 forage 3.2 0.53 0.09
Phelps, New York/1974	Sl, 215 g/l	1.0	560	3	Foliar	1 3 7 14	5.3 forage 5.8 3.5 0.18
Phelps, New York/1974	SP, 900 g/kg	0.50	560	3	Foliar	1 3 7 14	1.9 forage 3.7 0.26 0.10
Phelps, New York/1974	SP, 900 g/kg	1.0	560	3	Foliar	3	9.6 forage
Chestertown, Maryland/1974	SL, 215 g/l	0.50	560	1-2	Foliar	1 7 14	8.5 forage 2.7 1.8
Chestertown, Maryland/1974	SP, 900 g/kg	0.50	560	1-2	Foliar	7 14	3.1 forage 0.99
Florence, South Carolina/1974	SL, 215 g/l	0.50	190	2	Foliar	3 7 14	4.5 forage 0.05 0.02
Belleville, Illinois/1975	SL, 215 g/l	0.50	19	1	Aerial	6 14	0.12 forage 0.05
Chesterfield, Missouri/1974	SL, 215 g/l	0.50	400	2	Foliar	4 7	1.5 forage 0.06
Chesterfield, Missouri/1974	SL, 215 g/l	1.0	400	2	Foliar	4	1.9 forage
Chesterfield,	SP, 900 g/kg	0.50	400	2	Foliar	4	2.0 forage

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Missouri/1974							
Chesterfield, Missouri/1974	SP, 900 g/kg	1.0	400	2	Foliar	4 7	2.1 forage 1.5
Murrayville, Illinois/1974	SP, 900 g/kg	0.50	870	2	Foliar	4 7 14	1.6 forage 0.02 0.04
Murrayville, Illinois/1974	SP, 900 g/kg	1.0	870	2	Foliar	4 7 14	0.20 forage 0.17 0.03
Murrayville, Illinois/1974	SL, 215 g/l	0.50	870	2	Foliar	4 7 14	1.5 forage 0.57 0.07
Murrayville, Illinois/1974	SL, 215 g/l	1.0	870	2	Foliar	4 7 14	3.7 forage 2.6 0.16
Louisville, Georgia/1974	SL, 215 g/l	0.50	130	1	Aerial?	5	0.67 forage[1]
Buchanan, Michigan/1974	SL, 215 g/l	0.56	380	2	Foliar	3	2.4 forage
Buchanan, Michigan/1974	SL, 215 g/l	1.1	380	2	Foliar	3	1.2 forage
Buchanan, Michigan/1974	SP, 900 g/kg	0.56	380	2	Foliar	3	4.7 forage
Buchanan, Michigan/1974	SP, 900 g/kg	1.1	380	2	Foliar	3	3.9 forage
Bennington, Nebraska/1974	SP, 900 g/kg	0.50	970	2	Foliar	3	1.7 forage
Bennington, Nebraska/1974	SL, 215 g/l	0.50	970	2	Foliar	3	2.7 forage

[1] Control contained 0.27 mg/kg.

Sorghum field trials were conducted in the USA in 1967-1971 (Ashley, 2001h) and in 1991 (Hausmann and Devine, 1992a). Samples of grain and stover were analysed by method ML/PC-12 with the flame photometric detector modification in the early trials, with adequate recoveries from grain demonstrated from 0.02-1.0 mg/kg (0.02 mg/kg 94% and 114%). In 1991 samples of grain were collected randomly at maturity, stored frozen for a maximum of 8 months, and analysed by method AMR 1806-90. Recoveries of methomyl from fortified control grain samples at 0.02-1.0 mg/kg (at 0.02 mg/kg 115%) were adequate.

Table 53. Residues of methomyl in or on sorghum grain after the application of G, SP, or SL formulations in the USA (3F 1307; AMR 1926-91).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
GAP: USA	SL, SP	0.5	19	2	Aerial Ground	14	
Marana, Arizona/1970	G, 5 g ai/100g	1.1	-	1	Broadcast	57	<0.02
Weslaco, Texas/1967	G, 5 g ai/100g	0.56	-	1	Band	65	<0.02
Weslaco, Texas/1967	G, 5 g ai/100g	1.1	-	1	Band	65	<0.02
Tolleson, Arizona/1971	G, 5g ai/100g	1.1	-	1	Band	48	<0.02
Tolleson, Arizona/1971	G, 5g ai/100g	2.2	-	1	Band	48	<0.02
Tolleson, Arizona/1971	G, 5g ai/100g	0.45	-	1	Band	48	<0.02
Chandler, Arizona/1971	G, 5g ai/100g	0.6	-	1	Aerial	48	<0.02

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Buckeye, Arizona/1971	G, 5g ai/100g	0.84	-	1	Aerial	45	<0.02
Buckeye, Arizona/1971	G, 5g ai/100g	0.45	-	1	Band	45	<0.02
Harquella, Arizona/1971	G, 5g ai/100g	0.45	-	1	Aerial	39	<0.02
Tolleson, Arizona/1971	SP, 900 g/l kg	1.1	?	1	Ground broadcast	14	0.03
Tolleson, Arizona/1971	SP, 900 g/l kg	2.2	?	1	Ground broadcast	14	0.08
Clovis, New Mexico/1971	SP, 900 g/kg	0.78	?	1	Aerial	54	<0.02
Tolleson, Arizona/1971	SP, 900 g/kg	0.37	?	1	Aerial	5 15	0.09 0.07
Buckeye, Arizona/1971	G, 5g ai/ha SP, 900 g/kg	0.45 0.37	?	1 1	Band Aerial	3 13	0.36 <0.02
York, Nebraska/1991	SP, 900 g/kg	0.50	47	4	Ground. 3 pt tractor sprayer	14	0.029
Robinson, Kansas/1991	SL, 215 g/l	0.50	170	4	CO_2 backpack sprayer	14	<0.020
Eakly, Oklahoma/1991	SL, 215 g/l	0.50	140	4	CO_2 backpack sprayer	14	0.099
Oregon, Missouri/1991	SP, 900 g/kg	0.50	170	4	CO_2 backpack sprayer	14	0.12[1]

[1] Milo colouring dough stage at last treatment. At harvest, mature but still had high moisture content. Control sample contained 0.11 mg/kg.

Maize and sweet corn trials were reported from the USA (Hay, 1991b). Samples of sweet corn (kernel + cob, husk removed), maize grain, forage (entire plant, including ear) and fodder (plant without ear) were harvested at maturity and stored frozen as homogenates up to 11 months before extraction and analysis by method AMR 1806-90. Recoveries from fortified grain, fodder and forage were acceptable in the 0.02-0.20 mg/kg range for grain and 0.02-10 mg/kg range for fodder and forage. The overall recovery was 93% $\pm$ 10%, n=19. The results are shown in Tables 54 and 55.

The Tables indicate the results of earlier supervised field trials in the USA (1966-1967) (Ashley, 2001n). In most cases kernels without cobs were analysed.

Table 54. Residues of methomyl in or on sweet corn kernels and cobs and maize grain after the foliar application of SL or SP formulations in the USA (AMR 1607-90; 8F0677).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
Sweet corn							
GAP: USA	SL	0.5	10	28		Ear 0 Forage 3	
Belle Glade, Florida/1990	SL, 215 g/l	0.50	47	24	Aerial	0	<0.02
Belle Glade, Florida/1990	SL, 290 g/l	0.50	47	24	Aerial	0	<0.02
Phelps, New York/1990	SL, 215 g/l	0.50	280	16	Pressurized canister. Ground foliar.	0	<0.02
Phelps, New York/1990	SP, 900 g/kg	0.50	280	16	Pressurized canasta. Ground foliar.	0	<0.02
Hollandale, Minnesota/1990	SL, 215 g/l	0.50	180-230	16	Off-set boom. Foliar broadcast	0	0.021
Hollandale, Minnesota/1990	SP, 900 g/kg	0.50	180-230	16	Off-set boom. Foliar broadcast	0	<0.02
Newark, Delaware/1990	SL, 215 g/l	0.50	710-730	16	High clearance CO_2 sprayer. Foliar.	0	0.052
Newark, Delaware/1990	SP, 900 g/kg	0.50	710-730	16	High clearance CO_2	0	0.043

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
					sprayer. Foliar.		
Bradenton, Florida/1967	SP, 900 g/kg	0.56		4		1 3	<0.02 <0.02 kernel only
Bradenton, Florida/1967	SP, 900 g/kg	1.1		1		1	0.03
Wesalco, Texas 1967	SP, 900 g/kg	0.56		2		0 1	<0.02 <0.02 kernel only
Newark, Delaware 1967	SP, 900 g/kg	0.42		10		1	0.03 kernel only
Arlington, Wisconsin 1967	SP, 900 g/kg	0.56		2		3	<0.02 kernel only
Guckeen, Minnesota 1967	SP, 900 g/kg	0.56		2		3	<0.02 kernel only
Niles, Michigan 1967	SP, 900 g/kg	1.1		3		3	0.04
Rochelle, Illinois 1967	SP, 900 g/kg	1.1		5		3 8	<0.02 <0.02 kernel only
Rochelle, Illinois 1967	SP, 900 g/kg	1.7		5		3 8	0.07 0.02 kernel only
Portageville, Missouri 1967	SP, 900 g/kg	0.84		14		3	0.03 kernel only
Riverside, California 1967	SP, 900 g/kg	0.56		3		1	<0.02
Springfield, Tennessee 1967	SP, 900 g/kg	0.56		3		1	<0.02
Maize (Field corn)							
GAP: USA	SL, SP	0.5	5	10		Ear 21 Forage 3 Fodder 21	
Phelps, New York/1990	SL, 215 g/l	0.50	280	16	Pressurized canister. Ground foliar.	21	<0.02
Phelps, New York/1990	SP, 900 g/kg	0.50	280	16	Pressurized canasta. Ground foliar.	21	<0.02
Hollandale, Minnesota/1990	SL, 215 g/l	0.50	180-230	16	Off-set boom. Foliar broadcast	21	<0.02
Hollandale, Minnesota/1990	SP, 900 g/kg	0.50	180-230	16	Off-set boom. Foliar broadcast	21	<0.02
Newark, Delaware/1990	SL, 215 g/l	0.50	710-730	16	High clearance CO_2 sprayer. Foliar.	21	<0.02
Newark, Delaware/1990	SP, 900 g/kg	0.50	710-730	16	High clearance CO_2 sprayer. Foliar.	21	<0.02

Table 55. Residues of methomyl in or on sweet corn and maize forage and fodder after the foliar application of SL or SP formulations in the USA (AMR 1607-90; 8F 0677).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)[1]
Sweet corn forage							
GAP: USA	SL	0.5	10	28		Ear 0 Forage 3	
Phelps, New	SL, 215 g/l	0.50	280	16	Pressurized canister.	3	4.8

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)[1]
York/1990					Ground foliar.		
Phelps, New York/1990	SP, 900 g/kg	0.50	280	16	Pressurized canister. Ground foliar.	3	2.7
Hollandale, Minnesota/1990	SL, 215 g/l	0.50	180-230	16	Off-set boom. Foliar broadcast	3	3.2
Hollandale, Minnesota/1990	SP, 900 g/kg	0.50	180-230	16	Off-set boom. Foliar broadcast	3	3.3
Newark, Delaware/1990	SL, 215 g/l	0.50	710-730	16	High clearance CO_2 sprayer. Foliar.	3	2.5
Newark, Delaware/1990	SP, 900 g/kg	0.50	710-730	16	High clearance CO_2 sprayer. Foliar.	3	3.3
Chico, California/1990	SL, 215 g/l	0.50	94	16	Tractor mounted backpack sprayer. Foliar.	3	2.9
Chico, California/1990	SP, 900 g/kg	0.50	94	16	Tractor mounted backpack sprayer. Foliar.	3	2.3
Sweet corn fodder							
Bradenton, Florida 1966	SP, 900 g/kg	0.56		12		3 7 14	0.40 0.09 <0.02
Arlington, Wisconsin 1967	SP, 900 g/kg	0.56		2		3	0.56
Arlington, Wisconsin 1967	SP, 900 g/kg	1.1		2		3	1.0
Guckeen, Minnesota 1967	SP, 900 g/kg	0.56		3		4	0.22
Guckeen, Minnesota 1967	SP, 900 g/kg	1.1		3		4	0.26
Niles, Michigan 1967	SP, 900 g/kg	1.1		3		3	3.6 1.7
Portageville, Missouri 1967	SP, 900 g/kg	0.84		14		3	1.0
Rochelle, Illinois 1967	SP, 900 g/kg	1.1		3		3 7	7.2 1.7
Rochelle, Illinois 1967	SP, 900 g/kg	1.7		3		3 7	19 11
Maize forage and fodder							
GAP: USA	SL, SP	0.5	5	10		Forage 3 Fodder 21	
Phelps, New York/1990	SL, 215 g/l	0.50	280	16	Pressurized canister. Ground foliar.	3 21	6.9 forage 0.71 fodder
Phelps, New York/1990	SP, 900 g/kg	0.50	280	16	Pressurized canister. Ground foliar.	3 21	6.6 forage 0.30 fodder
Hollandale, Minnesota/1990	SL, 215 g/l	0.50	180-230	16	Off-set boom. Foliar broadcast	3 21	0.72 forage 0.029 fodder
Hollandale, Minnesota/1990	SP, 900 g/kg	0.50	180-230	16	Off-set boom. Foliar broadcast	3 21	1.0 forage 0.094 fodder
Newark, Delaware/1990	SL, 215 g/l	0.50	710-730	16	High clearance CO_2 sprayer. Foliar.	3 21	1.8 forage 0.094 fodder
Newark, Delaware/1990	SP, 900 g/kg	0.50	710-730	16	High clearance CO_2 sprayer. Foliar.	3 21	1.3 forage 0.053 fodder

[1] No information on moisture content.

Oilseed

Cotton seed trials were reported from the USA (Ashley, 2001e) and Europe (Weidenauer *et al.*, 1998o). Only summary information was provided for the US trials, 1966-1971, where the samples were analysed by method ML/PC-12 with a flame photometric detector. Recoveries of methomyl were adequate in the concentration range 0.02-8.0 mg/kg. In trials in Spain and Greece in 1996 duplicate samples from each plot were manually delinted, ground and frozen for up to 18 months (Greece) and 6 months (Spain) for analysis by method AMR 3015-94. The recovery of methomyl at 0.02 mg/kg was 80%, 71% and 106%. The results are shown in Table 56.

Table 56. Residues of methomyl in or on cotton seed after the foliar application of SP or SL formulations in the USA and Europe (1F 1162; AMR 4039-96).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
GAP: USA	SL SP	0.50 east 0.76 west 0.68 Texas	8 kg/hl SL 15 kg/hl SP	8	Aerial/ Ground	15	
GAP: Spain	SL	0.4	800	3		7	
GAP: Greece	SL	0.7		3		20	
Brawley, California/1970	SP, 900 g/kg	1.1		2		28	<0.02
Somerton, Arizona/1970	SP, 900 g/kg	0.56		6		36	<0.02
San Joaquin, California/1966	SP, 900 g/kg	0.56		3		59	<0.02
Bakersfield, California/1966	SP, 900 g/kg	1.1		1		39	<0.02
Kingsburg, California/1970	SP, 900 g/kg	1.1		1		2 8 15	0.1 <0.02 0.1
Tonopah, Arizona/1970	SP, 900 g/kg	0.56		2		61	<0.02
Liberty, Arizona/1970	SP, 900 g/kg	0.56		1		44	<0.02
Peoria, Arizona/1970	SP, 900 g/kg	0.56		2		36	<0.02
Buckeye, Arizona/1970	SP, 900 g/kg	0.56		1		39	<0.02
Buckeye, Arizona/1970	SP, 900 g/kg	1.1		3		60	<0.02
Sugarland, Texas/1970	SP, 900 g/kg	1.1		3		25	<0.02
Fingsburg, California/1970	SP, 900 g/kg	1.1	94	1	Aerial	2 8 15	0.1 <0.02 0.1
Sugarland, Texas/1970	SP, 900 g/kg	1.1	75	3	Aerial	25	<0.02
Texas A&M, Texas/1971	SP, 900 g/kg	0.74	19	8	Aerial	17	<0.02
Clay, Texas/1971	SP, 900 g/kg	0.74		14	Aerial	6	<0.02
Bloy, Arizona/1971	SP, 900 g/kg	0.56	66	3	Aerial	10	0.05
Peoria, Arizona/1971	SP, 900 g/kg	0.74	47	9	Aerial	11	<0.02
Buckeye, Arizona/1971	SP, 900 g/kg	0.56	47	3	Aerial	14	<0.02
Mercedes, Texas/1970	SP, 900 g/kg	0.56	28	1	Aerial	12 14	<0.02 <0.02
Ft. Valley, Georgia/?	SP, 900 g/kg	0.56	47	3	Aerial	25	<0.02
Ft. Valley, Georgia/?	SP, 900 g/kg	1.1	47	3	Aerial	25	<0.02
Villamanrique, Spain/1996	SL, 200 g/l	0.54	604	4	Foliar by ground sprayer	-1 h +3 h 3 7 14 21	<0.02 <0.02, <0.02 <0.02, <0.02 0.02, 0.02 <0.02, <0.02 <0.02, <0.02
Korifi, Greece/1996	SL, 200 g/l	0.72	770	4	Foliar by ground	21	<0.02

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)
					sprayer		

Summary information was reported for peanut trials in 1969-1970 in the USA (Ashley, 2001c). Samples were analysed by ML/PC-12. Recoveries of 65%-100% were adequate at 0.04-2.0 mg/kg fortifications of kernels. The US label forbids the feeding of treated foliage (forage or fodder). Results are shown in Table 57.

Table 57. Residues of methomyl in or on peanut kernels, hulls and foliage after the foliar application of a WP formulation (900 g ai/kg) in the USA (1F 1158).

Location/year	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue (mg/kg)		
						Kernel	Hull	Foliage
GAP: USA	SL, SP 1.0	11 kg ai/hl 10	8	Aerial/ Ground	21			
North Carolina/1969	0.50		4	Foliar	33			<0.02
North Carolina/1969	1.0		4	Foliar	33	<0.02	<0.02	0.04
Georgia/1970	0.50	190	1	Foliar	7 14	<0.02	<0.02	0.02 <0.02
Georgia/1970	1.0	190	1	Foliar	7 14	<0.02	<0.02	4.6 0.23
Virginia/1970	0.56	140	4	Foliar	82	<0.02	<0.02	<0.02
Alabama/1970	1.0	110	1	Foliar	8 15	<0.02	<0.09	1.4 0.34
Alabama/1970	0.56	380	1	Foliar	40	<0.02	<0.02	<0.02
North Carolina/1970	0.50	380	3	Foliar	1 3 7 21			20 14 1.8 0.34
North Carolina/1970	1.0	380	3	Foliar	1 3 7 21			46 27 5.5 0.48
North Carolina/1970	2.0	380	3	Foliar	1 3 7 21	<0.02	<0.02	>100 48 16 3.8

Legume animal feeds

Alfalfa. Supervised field trials were conducted in the USA in 1992 (C. M. Kennedy and Orescan, 1995). Applications, one at each cutting, with a total of 4 cuttings at each location, were made with carbon dioxide plot, backpack, or tractor sprayers about 7 days before harvest. The cut alfalfa was air dried for 3 days (PHI for hay refers to the day samples were frozen, cutting date + 3 days) and then frozen. Replicate samples were stored frozen up to 26 months before analysis by method AMR 2137-92. Recoveries from fortified controls were adequate at 0.05 mg/kg in both forage and hay. The results are shown in Table 58.

Additional US data were reported for trials in 1967 (Ashley, 2001d). A WS formulation was applied once, and the crop cut at 0-13 day intervals. Samples were analysed by method ML/PC-12 with an FPD. Adequate recovery was demonstrated at 0.04 mg/kg (Table 58).

Table 58. Residues of methomyl in or on alfalfa forage and hay after the application of SP or SL formulations in the USA (AMR 213792, 1F 1159).

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
GAP: USA	SP, SL	1.0	11 kg ai/hl 10	10	7 (grazing/feeding)	
FORAGE						
Newark, Delaware 1992	SL, 215 g/l	1.0	470 .	1	7	2.5
				1	10	0.72 0.90 0.96
			480	2	7	1.1
				2	10	0.12 0.047 0.39
			460	3	7	0.56
				3	10	0.077 0.083 0.16
			490	4	7	12.0[1]
				4	10	0.73[1] 0.68 0.78
Newark, Delaware 1992	SP, 900 g/kg	1.0	470	1	7	1.8
				1	10	0.45 0.91 0.64
			480	2	7	1.3
				2	10	0.16 0.075 0.13
			460	3	7	0.11
				3	10	0.13 0.43 0.20
			490	4	7	7.3[1]
				4	10	1.8[1] 1.7 1.2
Madera, California 1992	SL, 215 g/l	1.0	.47	1	7	1.9
				1	10	0.47 0.46 0.46
			47	2	7	3.8
				2	10	2.5[2] 5.9 1.5
			47	3	7	3.5
				3	10	1.8 2.2 0.94
			47	4	7	2.5 1.0 2.2
				4	10	0.021 0.024 0.061

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
Madera, California 1992	SP, 900 g/kg	1.0	47	1	7	-
				1	10	7.0 6.9 5.9
			47	2	7	-
				2	10	5.3[2] 3.2 2.4
			47	3	7	-
				3	10	
			47	4	7	2.2 2.9 3.6
				4	10	1.3 1.2 1.3
Ault, Colorado 1992	SL, 215 g/l	1.0	94	1	7	4.2
				1	10	4.0 3.6 1.6
			94	2	7	2.3
				2	10	0.60 0.42 0.50
			103	3	7	2.3
				3	10	0.95 0.80 1.5
			103	4	7	6.3 3.2 4.6
				4	10	2.9 2.3 2.7
Ault, Colorado 1992	SP, 900 g/kg	1.0	94	1	7	-
				1	10	3.8 2.6 2.6
			94	2	7	-
				2	10	0.70 0.56 0.68
			103	3	7	-
				3	10	0.73 1.2 0.29
			103	4	7	6.6 7.0 5.0
				4	10	3.0 1.5 2.4
Germansville, Pennsylvania 1992	SL, 215 g/l	1.0	200	1	7	-
				1	10	0.68
			190	2	7	0.044

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
				2	10	0.023
			240	3	7	0.70
				3	10	0.097
Germansville, Pennsylvania 1992	SP, 900 g/kg	1.0	200	1	7	-
				1	10	0.42
			190	2	7	-
				2	10	0.032
			240	3	7	0.57
				3	10	0.066
Rocehlle, Illinois 1992	SL, 215 g/l	1.0	130	1	7	4.2
				1	10	0.060
			140	2	7	0.98
				2	10	0.17
			140	3	7	2.0
				3	10	0.21
			150	4	7	0.10
				4	10	0.031
Rocehlle, Illinois 1992	SP, 900 g/kg	1.0	130	1	7	-
				1	10	0.079
			140	2	7	-
				2	10	0.17
			140	3	7	-
				3	10	0.19
			150	4	7	0.10
				4	10	0.028
Urbandale, Iowa 1992	SL, 215 g/l	1.0	47	1	7	0.64
				1	10	0.18
			47	2	7	1.8
				2	10	0.12
			47	3	7	0.15
				3	10	0.029
			47	4	7	0.43
				4	10	0.14
Urbandale, Iowa 1992	SP, 900 k/kg	1.0	47	1	7	-
				1	10	0.23
			47	2	7	-
				2	10	0.072
			47	3	7	-
				3	10	0.043
			47	4	7	1.5
				4	10	0.14
Madera, California 1992	SL, 215 g/l	1.0	270	1	7	4.0
				1	10	0.32 5.8 4.1
			230	2	7	8.8[2]
				2	10	3.8[2] 4.1 3.2
			250	3	7	4.6
				3	10	0.94

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
						1.1 1.9
			260	4	7	2.6 3.4 2.8
				4	10	0.76 1.3 0.85
Madera, California 1992	SP, 900 g/kg	1.0	270	1	7	-
				1	10	5.6
			230	2	7	-
				2	10	3.4[2] 2.1 7.5
			250	3	7	-
				3	10	1.2 1.5 1.4
			260	4	7	2.1 2.6 1.9
				4	10	0.64 1.0 0.61
Plainview, Texas 1992	SL, 215 g/l	1.0	110	1	7	2.1
				1	10	2.5
			120	2	7	0.081
				2	10	<0.020
			110	3	7	0.25
				3	10	0.058
			150	4	7	1.6 1.1 1.4
				4	10	0.41
Plainview, Texas 1992	SP, 900 g/kg	1.0	110	1	7	-
				1	10	1.2
			120	2	7	-
				2	10	0.023
			110	3	7	-
				3	10	0.053
			150	4	7	1.6 1.7 0.95
				4	10	0.73
Fallon, Nevada 1967	SP, 900 g/kg	0.56	190	1	0 3 7 13	20 6.5 1.8 0.2 (80% moisture)
Fallon, Nevada 1967	SP, 900 g/kg	1.1	190	1	0 3 7	100 26 4.0 (80% moisture)
Berino, New Mexico 1967	SP, 900 g/kg	1.1	360	1	1 4 6	18 4.0 1.5

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
						(80% moisture)
Niles, Michigan 1967	SP, 900 g/kg	0.56	380	1	3 8	3.2 0.41 (88% moisture)
Lebanon, Pennsylvania 1967	SP, 900 g/kg	0.56	470	1	3 7	2.0 0.34 (80% moisture)
French Camp, California 1970	SP, 900 g/kg	0.28	470	1	5	0.68 (72% moisture)
	SP, 900 g/kg	1.1	470	1	5	2.7 (72% moisture)
Tracy, California	SP, 900 g/kg	0.56	-	1	1 5	7.8 0.30 (76% moisture)
Lathrop, California 1970	SP, 900 g/kg	0.56	-	1	5	0.90 (76% moisture)
	SP, 900 g/kg	1.1	-	1	5	3.7 (76% moisture)
HAY						
Newark, Delaware 1992	SL, 215 g/l	1.0	470	1	7	3.5
				1	10	0.56 0.61 0.73
			480	2	7	6.2
				2	10	0.47 1.9 0.44
			460	3	7	1.1
				3	10	0.31 0.21 0.14
			490	4	7	13. 13. 15.
				4	10	0.60[1] 0.78 0.68
Newark, Delaware 1992	SP, 900 g/kg	1.0	470	1	7	3.3
				1	10	2.1 0.88 0.68
			480	2	7	1.4
				2	10	0.52 0.48 0.35
			460	3	7	1.1
				3	10	0.12 0.38 0.40
			490	4	7	14. 14. 13.
				4	10	1.1[1] 0.93 0.92
Madera, California 1992	SL, 215 g/l	1.0	.47	1	7	4.6
				1	10	0.64

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
						0.76 0.60
			47	2	7	14 17
				2	10	17[2] 6.5 7.2
			47	3	7	3.4
				3	10	2.7 2.9 2.9
			47	4	7	0.49 0.81 1.8
				4	10	0.081 0.049 0.043
Madera, California 1992	SP, 900 g/kg	1.0	47	1	7	-
				1	10	7.2 8.7 6.9
			47	2	7	-
				2	10	11[2] 13 6.8
			47	3	7	-
				3	10	5.3 1.7 3.5
			47	4	7	4.0
				4	10	2.5 3.0 3.6
Ault, Colorado 1992	SL, 215 g/l	1.0	94	1	7	1.5
				1	10	3.2 4.1 4.6
			94	2	7	1.9
				2	10	0.57 0.51 0.42
			103	3	7	1.5
				3	10	0.51 0.86 1.0
			103	4	7	7.2 6.8 7.5
				4	10	4.1 3.9 4.2
Ault, Colorado 1992	SP, 900 g/kg	1.0	94	1	7	-
				1	10	2.7 2.8 2.0
			94	2	7	-
				2	10	0.74

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
						0.26 1.1
			103	3	7	-
				3	10	0.98 0.66 0.54
			103	4	7	7.9 5.2 7.9
				4	10	3.5 3.1 4.6
Germansville, Pennsylvania 1992	SL, 215 g/l	1.0	200	1	7	-
				1	10	0.67
			190	2	7	0.25
				2	10	0.096
			240	3	7	0.32
				3	10	0.19
Germansville, Pennsylvania 1992	SP, 900 g/kg	1.0	200	1	7	-
				1	10	0.67
			190	2	7	-
				2	10	0.10
			240	3	7	0.28
				3	10	0.20
Rocehlle, Illinois 1992	SL, 215 g/l	1.0	130	1	7	5.6
				1	10	0.30
			140	2	7	0.92
				2	10	0.30
			140	3	7	2.4
				3	10	0.68
			150	4	7	0.24
				4	10	0.22
Rocehlle, Illinois 1992	SP, 900 g/kg	1.0	130	1	7	-
				1	10	0.29
			140	2	7	-
				2	10	0.78
			140	3	7	-
				3	10	0.75
			150	4	7	0.28
				4	10	0.19
Urbandale, Iowa 1992	SL, 215 g/l	1.0	47	1	7	1.1
				1	10	0.54
			47	2	7	3.4
				2	10	0.072
			47	3	7	0.26
				3	10	0.19
			47	4	7	0.41
				4	10	0.55
Urbandale, Iowa 1992	SP, 900 k/kg	1.0	47	1	7	-
				1	10	0.48
			47	2	7	-

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
				2	10	0.098
			47	3	7	-
				3	10	0.14
			47	4	7	2.7
				4	10	0.36
Madera, California 1992	SL, 215 g/l	1.0	270	1	7	10
				1	10	7.0 3.0
			230	2	7	17[2]
				2	10	5.7[2] 2.4 5.9
			250	3	7	4.0
				3	10	1.2 2.7 2.5
			260	4	7	2.9 2.4 3.1
				4	10	2.6 1.5 2.1
Madera, California 1992	SP, 900 g/kg	1.0	270	1	7	-
				1	10	7.8 10 11
			230	2	7	-
				2	10	4.3[2] 4.3 3.0
			250	3	7	-
				3	10	3.2 3.8 1.9
			260	4	7	3.1 3.7 1.2
				4	10	1.7 1.6 0.82
Plainview, Texas 1992	SL, 215 g/l	1.0	110	1	7	5.5
				1	10	2.8
			120	2	7	0.12
				2	10	0.084
			110	3	7	0.46
				3	10	0.11
			150	4	7	5.6 2.4 2.4
				4	10	0.68
Plainview, Texas 1992	SP, 900 g/kg	1.0	110	1	7	-
				1	10	1.8
			120	2	7	-
				2	10	0.12
			110	3	7	-

Location/year	Form.	Rate (kg ai/hg)	Spray vol. (l/ha)	Appl. no.	PHI (days)	Residue (mg/kg)
				3	10	0.14
			150	4	7	1.7 1.3 2.2
				4	10	0.56
Phelps, New York 1966	SP,900 g/kg	1.1	470	1	2 6 14	35 3.8 0.87
	SP, 900 g/kg	2.2	470	1	2 6 14	62 6.8 2.3
Dixon, California 1967	SP, 900 g/kg	0.56	350	1	1 3 7 14	13 4.1 0.92 0.30
El Centro, California 1970	SP, 900 g/kg	0.56	210	1	4 7 13	10 4.1 0.78
				2	2 4 6	2.4 1.2 0.90

[1] Samples invalid owing to atypical practice.
[2] Excessive application rate due to tractor speed.

Supervised field trials on the foliar application of methomyl with ground equipment to soya beans to determine residues in the hay were conducted in the USA at 8 locations (Rühl and Devine, 1994c). Triplicate storage samples were air- or hot-air dried (<49°C) from 1.5-10 days to 10-15% moisture content. Hay samples were stored frozen for up to 10 months before analysis by method AMR 3015-94. Adequate recovery was demonstrated at 0.02 mg/kg fortification of control samples. The results are shown in Table 59.

Table 59. Residues of methomyl in or on soya hay after the foliar application of SL or SP formulations in the USA (Rühl and Devine, 1994c).

Location, year	Form.	Application rate (kg ai/ha)	Spray volume (l/hg)	No. of applications	PHI (days)	Residue (mg/kg)
GAP: USA	SL SP	0.5	10 kg ai/hl 5	3	<0.5 kg ai/ha/crop forage 3 hay 7 >0.5 kg ai/ha/crop forage 10 hay 12	
Lonoke, Arkansas/1993	SP, 900 g/kg	0.5	85	3	12 21	0.021 0.020 <0.020 <0.020 <0.020 <0.020
Greenville, Mississippi/1993	SL, 215 g/l	0.5	56	3	12 21	0.031[1] 0.040 0.030 <0.020[1] <0.020

Location, year	Form.	Application rate (kg ai/ha)	Spray volume (l/hg)	No. of applications	PHI (days)	Residue (mg/kg)
						<0.020
Tellico Plains, Tennessee/1993	SP, 900 g/kg	0.5	94	3	12 21	0.033 0.032 0.026 <0.020 <0.020 <0.020
Rochelle, Illinois/1993	SP, 900 g/kg	0.5	200	3	12 21	0.076 0.057 0.054 <0.020 <0.020 <0.020
Paynesville, Minnesota/1993	SP, 900 g/kg	0.5	190	3	12 21	0.059 0.075 0.13 <0.020 <0.020 <0.020
Radcliffe, Iowa/1993	SP, 900 g/kg	0.5	190	3	12 21	0.034 0.050 0.041 <0.020 <0.020 <0.020
Oregon, Missouri/1993	SP, 900 g/kg	0.5	170	3	12 21	0.056 0.048 0.056 <0.020 <0.020 <0.020
Sheridan, Indiana/1993	SP, 900 g/kg	0.5	230	3	10 21	0.081 0.076 0.099 <0.020 <0.020 <0.020

[1] Controls contained methomyl: 0.026 mg/kg for 12 day and 0.069 mg/kg for 21 day.

In eight supervised field trials on sorghum to determine residues in the forage and hay in the USA an SL formulation was applied by various ground equipment to simulate commercial practices and samples of forage and air-dried hay were frozen for up to 15 months before analysis by method AMR 1806-90 or AMR 2676-93 (S. M. Kennedy, 1990e; Hausmann and Devine, 1993c). Recoveries were adequate from both fortified forage and hay in the range 0.02-1.0 mg/kg. The results are shown in Table 60.

Table 60. Residues of methomyl in or on sorghum green forage and hay after the application of a 215 g ai/l SL formulation in the USA (AMR 1367-89; AMR 2343-92).

Location, year	Application rate (kg ai/ha)	Spray volume (l/ha)	No. of applications	PHI (days)	Residue (mg/kg)
GAP: USA	0.5	2.7 kg ai/ha 19	2	14	
Sorghum forage (green)					

Location, year	Application rate (kg ai/ha)	Spray volume (l/ha)	No. of applications	PHI (days)	Residue (mg/kg)
Snook, Texas 1989	0.50	110	2	14	0.046
York, Nebraska 1989	0.50	190	2	14	0.068
Eakly, Oklahoma 1989	0.50	140	2	14	0.22
Lucas, Texas 1989	0.50	190	2	14	0.042
Donna, Texas 1992	0.50	94	2	13	<0.020
Halfway, Texas 1992	0.50	130	2	14	0.024
York, Nebraska 1992	0.50	94	2	14	<0.020
Troy, Kansas 1992	0.50	140	2	14	0.19 0.17 0.38
Little Rock, Arkansas 1992	0.50	140	2	14	<0.020
Sorghum hay					
Snook, Texas 1989	0.50	110	2	14	<0.02
York, Nebraska 1989	0.50	190	2	14	<0.02
Eakly, Oklahoma 1989	0.50	140	2	14	0.59
Lucas, Texas 1989	0.50	190	2	14	<0.02
Donna, Texas 1992	0.50	94	2	13	0.035 0.034 0.024
Halfway, Texas 1992	0.50	130	2	14	0.035 0.029 <0.020
York, Nebraska 1992	0.50	94	2	14	0.033 0.027 0.022
Troy, Kansas 1992	0.50	140	2	14	0.078 0.068 0.096
Little Rock, Arkansas 1992	0.50	140	2	14	0.024 0.039 0.026

In supervised field trials in the USA in 1995 (C.M. Kennedy, 1995) two foliar applications of a 290 g/l SL formulation were made to maturing grain, the second at the late hard dough growth stage. Duplicate samples of stover (fodder) were collected at each site and stored frozen for up to 8 months until analysed by method AMR 3015-94. Adequate recoveries were demonstrated for the range 0.02-20 mg/kg. The results are shown in Table 61. Earlier trials are shown in Table 62 (Ashley, 2001h).

Table 61. Residues of methomyl in or on sorghum fodder (stover) after the foliar application of a 290 g/lg SL formulation in the USA in 1995 (AMR 3298-95).

Location	Application rate (kg ai/ha)	Spray volume (l/ha)	No. of Applications	PHI (days)	Residue (mg/kg)
GAP: USA	0.5	2.7 kg ai/ha 19	2	14	
Donna, Texas	0.50	210	2	2	0.025[1] 0.028
York, Nebraska	0.50	190	2	13	1.0 0.99
Little Rock Arkansas	0.50	190	2	14	0.93 0.92
Plainview, Texas	0.50	120	2	14	0.081 0.026

Location	Application rate (kg ai/ha)	Spray volume (l/ha)	No. of Applications	PHI (days)	Residue (mg/kg)
Grand Island, Nebraska	0.50	190	2	14	2.4 2.5
Garden City, Kansas	0.50	180	2	13	3.1 3.4
Oregon, Missouri	0.50	160	2	14	0.41 0.50

[1] Fodder remained in the field for 13 days before collection. Grain was collected two days after the final application.

Table 62. Residues of methomyl in or on sorghum stover after the application of G or SP formulation in the USA (3F 1307).

Location/year	Form.	Rate (kg ai/ha)	Spray (l/ha)	No.	Method	PHI (days)	Residue[1] (mg/kg)
GAP: USA	SL, SP	0.5	2.7 kg ai/hl	2		14	
Marana, Arizona/1970	G, 5 g ai/100g	1.1	-	1	Broadcast	57	<0.02
Weslaco, Texas/1967	G, 5 g ai/100g	0.56	-	1	Band	65	<0.02
Weslaco, Texas/1967	G, 5 g ai/100g	1.1	-	1	Band	65	<0.02
Tolleson, Arizona/1971	G, 5g ai/100g	1.1	-	1	Band	48	<0.05
Tolleson, Arizona/1971	G, 5g ai/100g	2.2	-	1	Band	48	<0.05
Tolleson, Arizona/1971	G, 5g ai/100g	0.45	-	1	Band	29	0.09
Chandler, Arizona/1971	G, 5g ai/100g	0.6	-	1	Aerial	48	<0.05
Buckeye, Arizona/1971	G, 5g ai/100g	0.84	-	1	Aerial	45	<0.05
Buckeye, Arizona/1971	G, 5g ai/100g	0.45	-	1	Band	45	<0.05
Harquella, Arizona/1971	G, 5g ai/100g	0.45	-	1	Aerial	39	<0.05
Tolleson, Arizona/1971	SP, 900 g/kg	1.1	?	1	Ground broadcast	14	0.09
Tolleson, Arizona/1971	SP, 900 g/kg	2.2	?	1	Ground broadcast	14	-
Clovis, New Mexico/1971	SP, 900 g/kg	0.78	?	1	Aerial	54	<0.05
Tolleson, Arizona/1971	SP, 900 g/kg	0.37	?	1	Aerial	5 15	1.4 0.59
Buckeye, Arizona/1971	G, 5g ai/100g SP, 900 g/kg	0.45 0.37	?	1 1	Band Aerial	 3 13	 1.8 0.38

[1] Air dried.

RESIDUES IN ANIMAL COMMODITIES

Ruminant feeding studies

In two US studies in Madison, Wisconsin, twelve lactating Holstein dairy cattle (4 groups of 3 cows) were dosed with a balling gun, twice daily, for 28 days with capsules of methomyl containing the equivalent of 0 ppm, 8.1 ppm, 33.7 ppm or 85.8 ppm based on the measured feed consumption of each animal before and during the study (Daun, 1995). Milk samples collected daily and tissues at the end of the study were stored at -70^{o}C until analysed by an HPLC method with post-column derivatization, validated in milk and all tissues at 0.01 and 0.05 mg/kg. A concurrent storage stability study showed no significant loss of methomyl from fortified control samples stored and processed under the exact conditions of the study samples.

No samples, which included whole and skimmed milk, cream, liver, kidney, muscle and fat contained methomyl at or above the limit of quantification (0.01 mg/kg). The concentrations were in the same range as the control samples, <0.002-<0.005 mg/kg, in all samples at all feeding levels.

In a second study 4 groups of three lactating cows were dosed twice daily by balling gun after milking with a mixture of [^{14}C]methomyl and unlabelled methomyl for 28 days at feeding levels equivalent to 0, 2, 24 or 80 ppm in the diet, based on monitored feed consumption (Powley, 1991a,b). Milk and tissue samples were stored at -20^{o}C. Stability experiments conducted with the study indicated that methomyl would be stable in milk (up to two years), moderately stable in fat and muscle (up to 50% loss) and very unstable in liver and kidney. The lack of residues in liver, muscle, fat and kidney would be inconclusive for this study only.

Milk samples were analysed for methomyl by HPLC and for MHTA by capillary GLC with an NPD. The demonstrated limit of quantification of each was 0.02 mg/kg. The [^{14}C]acetonitrile in milk was determined by a purge and trap technique followed by GLC and LSC, and acetamide by acetone extraction and capillary GLC with an NPD. The [^{14}C]acetamide was extracted in the same manner, followed by HPLC fractionation and LSC.

In whole and skimmed milk and cream at the 24 ppm and 80 ppm feeding levels, methomyl and MHTA were not found (limit of quantification = 0.02 mg/kg) in any sample on days 1, 14 and 28. Methomyl was detected in one cream sample at about 0.02 mg/kg, but this sample was from a control animal. Methomyl and MHTA were also not detected in any tissue sample (<0.02 mg/kg). The results for acetonitrile and acetamide (total and labelled) are shown in Table 63.

Table 63. Residues of acetonitrile and acetamide in cow milk and tissues after dosing with methomyl for 28 days (AMR 898-87).

Sample	Residue (mg/kg) in group				Group mean (mg/kg)
	0 ppm	2 ppm	24 ppm	80 ppm	
ACETONITRILE					
Whole milk, day 1		<0.01 0.01 <0.01			0.01
Whole milk, day 7		0.07 0.07 0.08			0.07
Whole milk, day 10		0.07 0.07 0.05			0.06
Whole milk, day 18		0.07 0.08 0.05			0.07
Whole milk, day 21		0.07 0.06 0.04			0.06
Whole milk, day 24		0.09 0.06 0.08			0.08
Whole milk, day 28		0.05 0.08 0.06			0.06
Skimmed milk, day 14		0.06 0.05 0.05			0.05
Cream, day 14		0.03			0.02

Sample	Residue (mg/kg) in group				Group mean (mg/kg)
	0 ppm	2 ppm	24 ppm	80 ppm	
		0.02 0.02			
Liver		0.06 0.09 0.09			0.08
Kidney		0.04 0.03 0.04			0.04
Muscle		0.03 0.04 0.06			0.04
Subcutaneous fat		0.02 0.01 <0.01			0.01
Peritoneal fat		<0.01 <0.01 <0.01			<0.01
ACETAMIDE					
Whole milk, day 1	7.9 5.9 5.0			4.1 3.7 4.1	
Whole milk, day 4	7.5 4.9 4.2			4.5 4.3 4.3	
Whole milk, day 7	6.7 4.0 3.5			4.1 3.9 4.4	
Whole milk, day 10	6.1 3.2 3.5			6.6 4.1 5.0	
Whole milk, day 18	5.0 3.9 2.1			3.7 3.4 4.1	
Whole milk, day 21	5.2 3.4 1.6			2.8 3.4 3.6	
Whole milk, day 24	5.1 4.7 3.2			3.4 4.2 4.7	
Whole milk, day 28	5.0 4.2 2.2			3.6 4.0 4.0	
Skimmed milk, day 14	6.1 4.2 3.2			4.3 4.6 5.2	
Cream, day 14	0.5 1.6 <0.1			0.7 0.7 1.1	
Liver	14.6 16.7 14.5			13.5 14.2 13.2	
Kidney	9.6 (pooled sample)	4.9 5.8 6.7	7.3 7.3 9.2	8.8 10.2 7.6	
Muscle	7.2 6.8 7.9	9.9 8.5 8.1	8.1 8.3 8.3	9.2 8.0 9.6	
Subcutaneous fat	3.4	2.4	0.9	6.6	

Sample	Residue (mg/kg) in group				Group mean (mg/kg)
	0 ppm	2 ppm	24 ppm	80 ppm	
	3.7	2.0 1.8	1.7	1.9 4.9	
Peritoneal fat	3.8 3.1	5.0 4.8 3.7	3.6 3.7 3.5	11.6 2.4 7.8	
[^{14}C]ACETAMIDE					
Whole milk, day 1				0.006 <0.004 <0.003	0.006
Whole milk, day 4				0.068 0.033 0.019	0.040
Whole milk, day 18				0.088 0.034 0.026	0.049
Whole milk, day 28				0.053 0.050 0.037	0.047
Muscle				0.021 0.027 0.022	0.023
Liver				0.054 0.050 0.050	0.051

FATE OF RESIDUES IN STORAGE AND IN PROCESSING

In storage

No information.

In processing

Fifteen studies were reported for 13 different raw agricultural commodities processed to a total of approximately 65 fractions. Methomyl was concentrated in dried orange peel, apple peel and wheat bran. This suggests a surface residue. Methomyl is somewhat water-soluble and the octanol/water partition coefficient is low, so there would be no tendency to concentrate in oils (Table 64). All studies were conducted with RACs with field-incurred residues and processing procedures were commercially simulated unless otherwise indicated.

Table 64. Processing studies on raw agricultural commodities containing methomyl.

Commodity/sample	Methomyl (mg/kg)	Processing factor	Frozen storage, months	Reference/comment
Peanuts	0.44	---	18	Marxmiller and Hay, 1991a. AMR 1354-89. USA
Meal	<0.020	0.045	15.5	
Refined oil	<0.020	0.045	18	
Crude oil	<0.050	0.11	18	
Soapstock	0.020	0.045	18	

Commodity/sample	Methomyl (mg/kg)	Processing factor	Frozen storage, months	Reference/comment
Ginned Cotton seed	0.17	---	14.5	Kennedy and Hay, 1991a AMR 1355-89. USA
Refined oil	<0.020	<0.12	16	
Crude oil	<0.020	0.52	15.5	
Meal	0.065	0.38	16	
Soapstock	<0.020	<0.12	16	
Hulls	0.14	0.82	16	
Sorghum grain	0.17	---	3	Kennedy and Hay 1991b AMR 1356-89. USA
Flour	0.031	0.18	3	
Starch	<0.020	<0.12	3	
Soya beans	0.062	---	17	Kennedy and Hay, 1991c AMR 1357-89. USA
Refined oil	<0.020	<0.32	18	
Meal	<0.020	<0.32	18	
Crude oil	0.020	0.32	18	
Hulls	<0.020	<0.32	18	
Soapstock	<0.020	<0.32	18.5	
Wheat grain	0.13	---	13.5	Hay, 1991a AMR 1358-89. USA
Bran	0.31, 0.19 (average = 0.25)	1.9	14	
Middlings	0.026	0.20	13.5	
Shorts + germ	0.12	0.92	13.5	
Patent flour	<0.020	0.15	13.5	
Low grade flour	<0.020	0.15	13.5	
Maize	0.15, 0.060 (average = 0.11)	---	11.5	Marxmiller and Hay, 1991b, AMR 1359-89. USA
Dry mill				
Crude oil (expeller)	<0.020	0.18	11.5	
Refined oil	<0.020	0.18	10	
Medium grits	0.035	0.32	12.5	
Coarse meal	0.039	0.35	13.5	
Flour	0.11	1.0	13	
Wet mill				
Crude oil (expeller)	<0.020	0.18	10.5	
Refined oil	<0.020	0.18	10	
Starch	<0.020	0.18	12	
Succulent green beans, unwashed, untrimmed	0.36-0.58 (average = 0.45)	---	10	Kennedy and Devine, 1993d AMR 2134-91. Washing and trimming a consumer procedure. USA
Washed, trimmed	0.13-0.21 (average = 0.18)	0.4	10	
Canned	<0.020	<0.04	7.5	
Tomatoes	0.39, 0.42, 0.32 (average = 0.38)		12	Marxmiller and Hay, 1991c, AMR 1360-89. USA
Wet pomace	<0.020	0.053	12.5	
Dry pomace	<0.25	0.66	15	
Juice	<0.020	0.053	12.5	
Purée	<0.020	0.053	13	

Commodity/sample	Methomyl (mg/kg)	Processing factor	Frozen storage, months	Reference/comment
Lettuce	1.7-4.9 (average = 3.0)	---	8.5	Kennedy and Tomic, 1992 AMR 2106-91
Trimmed, unwashed	0.034-0.90 (average = 0.39)	0.13	8	Trimming as commercial process
Washed, untrimmed	0.10-0.52 (average = 0.28)	0.09	8	
Trimmed, washed	0.029-0.037 (average = 0.034)	0.01	8	Washing as consumer process. Washing of whole head.
Potatoes	0.042, <0.020, 0.050 (median = 0.042)	---	15	Kennedy and Hay, 1991e AMR 1370-89 RAC treatment = 5 x GAP. USA
Chips	<0.020	<0.48	14	
Granules	<0.020	<0.48	14	
Dry peel	<0.050	<1.0	14	
Wet peel	0.042, 0.050, <0.020 (median = 0.042)	1.0	14	
Oranges unwashed	0.96	---	19	Kennedy and Hay, 1991d AMR 1361-89. USA. Control = 0.034
Washed fruit	0.88	0.92	19	
Finisher pulp	<0.020	<0.021	20.5	
Juice	<0.020	<0.021	19.5	
Cold pressed oil	<0.020	<0.021	23	
Molasses	<0.20	<0.21	23	
Dried peel	2.8	2.9	22.5	
Oranges unwashed	0.095, 0.11 (average = 0.10)	---	10.5, 22	Hausmann and Devine, 1993a AMR 2090-91. Washed with soap and water in a commercial packing plant. Peeling is consumer practice. USA.
Washed fruit	0.038, 0.035 (average = 0.037)	0.37	10.5, 22	
Peel, unwashed fruit	0.49, 0.62 (average = 0.56)	5.6	13, 22	
Peel, washed fruit	0.29, 0.33 (average = 0.31)	3.1	13, 22	
Fruit, unwashed, peeled	<0.020, <0.020 (average = <0.020)	<0.2	12, 22	
Apples	0.77	---	7	Hausmann and Fillipone, 1993 AMR 2091-91. Washed in a commercial packing plant (brush + recycled water, then brush + fresh water, air-dried, no wax). Peeling and baking are consumer procedures. USA.
Washed fruit	0.55	0.71	7	
Peel, unwashed fruit	1.1	1.4	7	
Peel, washed fruit	1.1	1.4	7	
Fruit, unwashed, peeled	0.38	0.49	7	
Fruit, washed, peeled	0.64	0.83	7	
Baked, unwashed fruit	0.14	0.18	7	
Baked, washed fruit	0.15	0.19	7	
Apples	0.0466	---	---	Zabik *et al.*, 2000

Commodity/sample	Methomyl (mg/kg)	Processing factor	Frozen storage, months	Reference/comment
Slices	0.0102	0.22	---	
Sauce	0.0102	0.22	---	
Juice, concentrate	<0.005	0.11	---	
Juice, single	0.0133	0.29	---	
Peaches unwashed	0.21	---	4	Rühl, 2000 AMR 4936-98. Washing, peeling and baking are consumer procedures.
Washed fruit	0.030	0.14	3.5	
Fruit, peeled	0.051	0.24	3.5	
Fruit, lye-peeled	0.040	0.19	5.5	
Canned fruit	<0.007	0.03	5.5	
Baked fruit	0.025	0.12	5.5	

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The manufacturer participated in a market basket survey study to determine the distribution and level of residues of some *N*-methylcarbamate insecticides in samples of single-unit servings of vegetables and fresh fruits such as apples and peaches, or multiple-unit servings such as grapes and strawberries available to the US population (Carringer, 2000). Carbamate insecticides are an important class of pesticides used on a variety of fruits and vegetables to control various damaging insects. The carbamate market basket study (CMBS) was conducted according to a US EPA-approved study design.

During the one-year study commodities were collected from grocery stores throughout the USA. Subsequent residue data will be used to reflect the potential dietary and cumulative exposure risks to consumers using these commodities more accurately and to provide a basis for implementation of the US Food Quality Protection Act (FQPA) risk assessment mandate.

More then 400 samples from eight different crops including apples, tomatoes, lettuce, grapes, peaches, broccoli and oranges were analysed. An EPA-approved statistical sampling design for collecting the commodities and USDA Pesticide Data Program (PDP) sample preparation procedures (washing, peeling and coring) were used that are reflective of practices used by consumers. From a cumulative risk standpoint less than 0.4% of the samples contained detectable residues, and these were well below the EPA tolerance levels. Table 65 summarizes the commodities tested and methomyl residues detected.

Table 65. Distribution of detected methomyl residues (Carringer, 2000).

Commodity	No. of analyses	Samples with no residues ≤ 0.001 mg/kg		Samples with residues ≥0.001 mg/kg		Range of residues (mg/kg)	EPA tolerance (mg/kg)
		No.	%	No.	%		
Apple	400	394	99	6	2	ND-0.020	1.0
Tomato	399	398	100	1	0	ND-0.0019	1.0
Head lettuce	399	368	92	31	8	ND-0.083	5.0
Grape	393	336	85	57	15	ND-1.0	5.0
Peach	285	263	92	22	8	ND-0.19	5.0
Broccoli	395	386	98	9	2	ND-0.0086	3.0

Commodity	No. of analyses	Samples with no residues ≤ 0.001 mg/kg		Samples with residues ≥0.001 mg/kg		Range of residues (mg/kg)	EPA tolerance (mg/kg)
		No.	%	No.	%		
Orange	399	399	100	0	0	ND	2.0

The US Department of Agriculture's Pesticide Data Program collects data on pesticide residues in or on selected food commodities in the USA. The results for methomyl from 1993 to 1998 are shown in Tables 66-71.

Table 66. Distribution of detected methomyl residues (USDA, 1993).

Commodity	No. of samples	No. of detections	% of detections	Lowest residue (mg/kg)	Highest residue (mg/kg)	US tolerance level (mg/kg)
Apples	650	13	2.0	0.15	0.15	1
Broccoli	622	3	0.5	0.015	0.065	3
Celery	620	35	5.6	0.011	0.52	3
Green beans	554	23	4.2	0.013	0.49	2
Grapefruit	624	1	0.2	0.065	0.065	2
Grapes	612	39	6.4	0.013	2.0	5
Lettuce	639	27	4.2	0.013	1.6	5
Oranges	623	6	1.0	0.065	0.28	2
Peaches	358	4	1.1	0.065	0.21	5
Potatoes	638	1	0.2	0.065	0.065	0.2

Table 67. Distribution of detected methomyl residues, 1994 (USDA, 1994).

Commodity	No. of samples	No. of detections	% of detections	Lowest residue (mg/kg)	Highest residue (mg/kg)	US tolerance level (mg/kg)
Apples	687	26	3.8	0.013	0.12	1
Broccoli	679	5	0.7	0.015	0.070	3
Celery	176	7	4.0	0.013	0.099	3
Grapes	669	58	8.7	0.013	1.3	5
Green beans	591	21	3.6	0.013	0.70	2
Lettuce	691	35	5.1	0.013	1.5	5
Peaches	395	1	0.3	0.033	0.033	5
Sweet peas	433	2	0.5	0.025	0.025	5

Table 68. Distribution of detected methomyl residues, 1995 (USDA, 1995).

Commodity	No. of samples	No. of detections	% of detections	Lowest residue (mg/kg)	Highest residue (mg/kg)	US tolerance level (mg/kg)
Apples	693	24	3.5	0.012	0.13	1
Grapes	689	48	7.0	0.012	1.3	5
Green beans	587	23	3.9	0.012	0.30	2
Peaches	367	3	0.8	0.026	0.10	5
Spinach	610	65	10.7	0.012	1.3	6

Table 69. Distribution of detected methomyl residues, 1996 (USDA, 1996).

Commodity	No. of samples	No. of detections	% of detections	Lowest residue (mg/kg)	Highest residue (mg/kg)	US tolerance level (mg/kg)
Apple juice	177	0				1
Apples	530	11	2.1	0.012	0.096	1
Carrots	500	0				0.02
Grapes	525	39	7.4	0.013	1.3	5
Green beans	531	5	0.9	0.013	0.053	2
Oranges	518	0				2
Peaches	325	4	1.2	0.093	0.22	5
Spinach	517	62	12.0	0.012	5.4	6
Sweet corn	173	0				0.1
Sweet peas	355	0				5
Sweet potatoes	507	0				0.2
Tomatoes	174	0				1

Table 70. Distribution of detected methomyl residues, 1997 (USDA, 1997).

Commodity	No. of samples	No. of detections	% of detections	Lowest residue (mg/kg)	Highest residue (mg/kg)	US tolerance level (mg/kg)
Apple juice	683	0				1
Green beans	707	7	0.9	0.012	0.10	2
Orange juice	692	0				2
Peaches	756	0				5
Pears	708	0				4
Spinach, fresh	512	51	9.9	0.020	1.5	6
Spinach, canned	168	0				6
Sweet potatoes	695	0				0.2
Tomatoes	722	0				1
Winter squash, fresh	440	0				0.2
Winter squash, frozen	221	0				0.2

Table 71. Distribution of detected methomyl residues, 1998 (USDA, 1998).

Commodity	No. of samples	No. of detections	% of detections	Lowest residue (mg/kg)	Highest residue (mg/kg)	US tolerance level (mg/kg)
Apple juice	694	1	0.1	0.012	0.012	1
Cantaloupe	408	27	6.6	0.012	0.12	0.2
Grape juice	665	0				5
Green beans, C & F	359	3	0.8	0.034	0.16	2
Orange Juice	700	1	0.1	0.071	0.071	2
Pears	712	1	0.1	0.066	0.066	4
Spinach, canned	695	0				6
Strawberries, fresh	610	164	26.9	0.013	4.4	2
Strawberries, frozen	47	5	10.6	0.028	1.0	2
Sweet potatoes	357	0				0.2
Tomatoes	717	2	0.3	0.012	0.013	1

Commodity	No. of samples	No. of detections	% of detections	Lowest residue (mg/kg)	Highest residue (mg/kg)	US tolerance level (mg/kg)
Winter squash, fresh	530	0				0.2
Winter squash, frozen	149	0				0.2

NATIONAL MAXIMUM RESIDUE LIMITS

Information on national MRLs was provided by the manufacturer and is presented below. An asterisk * indicates absence of the analyte at the limit of quantification.

Country	Commodity	MRL, mg/kg
Argentina	Alfalfa (lucerne)	0.2
	Citrus	0.02
	Corn	0.1
	Cotton	0.1
	Flax	Exempt
	Forage (Winter cereals, sorghum, corn)	1
	Leafy vegetables	0.2
	Onion	0.02
	Pea	0.1
	Pepper, tomato, sweet corn	0.1
	Pome fruits	0.02
	Sorghum	0.2
	Soya bean	0.2
	Stone fruits	0.02
	Sunflower	0.2
	Tobacco	1
	Winter Cereals	0.1
Australia	Apples	1
	Avocado	T 0.1
	Blackberries	2
	Blueberries	2
	Cabbages, head	1
	Cereal grains	0.1*
	Cherries	2
	Citrus fruits	1
	Coffee beans	T 1
	Cotton seed	0.1*
	Dried grapes	0.05*
	Edible offal (mammal)	0.05
	Eggs	0.02*
	Fruit vegetables, other than Cucurbits	1
	Ginger root	0.1*
	Grapes	2
	Guava	T 0.5
	Hops, dry	0.5
	Herbs	T 1
	Leafy vegetables	1

Country	Commodity	MRL, mg/kg
	Legume vegetables	1
	Linseed	0.1*
	Meat (mammalian)	0.05
	Milks	0.05
	Mint	0.5
	Nectarine	1
	Peach	1
	Peanuts	0.05*
	Pears	3
	Plantago ovata seed	0.1
	Poppy seed	0.05*
	Potato	1
	Poultry, edible offal of	0.02*
	Poultry meat	0.02*
	Pulses	1
	Rape seed	0.5
	Sesame seed	0.1*
	Strawberry	0.5
	Sunflower seed	0.1*
	Sweet corn	0.1
T-Temporary *-at or about the limit of quantification		
Austria	Hops	10
	Grapes	3
	Spinach	2
	Apples	1
	Cotton seed	0.5
	Radish	0.5
	Cabbage	0.2
	Pears	0.2
	Stone fruit	0.2
	Cucurbitaceae	0.2
	Soya bean	0.2
	Peas with pods	0.2
	Beans with pods	0.2
	Herbs	0.2
	Fennel	0.2
	Tea	0.1
	Others	0.05
Belgium	Apple	0.05
	Cucumber	0.05
	Hops	2
	Lettuce	0.05
	Pear	0.05
	Tomato	0.05
Brazil	Broccoli	3
	Cabbage	3
	Corn	0.1

Country	Commodity	MRL, mg/kg
	Cotton	0.1
	Kale	3
	Potatoes	0.1
	Soya bean	0.1
	Tomato	1
	Wheat	0.1
Canada	Apples	0.5
	Barley	0.1*
	Beans, snap	0.1*
	Blueberry	6
	Broccoli	0.1*
	Brussels sprouts	0.1*
	Cabbage	5
	Canola	0.1*
	Celery	0.5
	Citrus	1
	Cucumbers	0.1*
	Flax	0.1*
	Grapes	4
	Lettuce	2
	Oats	0.1*
	Peas	0.1*
	Potatoes	0.1*
	Strawberries	1
	Sweet corn	0.1*
	Tobacco	0.1*
	Tomato	0.1*
	Wheat	0.1*
*0.1 is the default MRL for those crops that have not been assigned an MRL by the Food and Drug Act.		
China	Cabbage	1
	Citrus	n/a
	Cotton	n/a
	Tobacco	5
European Union	Grapefruit	0.5
	Lemons	1
	Limes	1
	Mandarins	1
	Oranges	0.5
	Pomelos	0.5
	Citrus, other	0.05*
	Tree nuts	0.05*
	Pome fruit	0.2
	Apricot	0.2
	Cherry	0.1
	Peach	0.2
	Plum	0.5
	Stone fruit, other	0.05*
	Grapes, table	0.05*
	Grapes, wine	1

Country	Commodity	MRL, mg/kg
	Strawberry	0.05*
	Canefruit	0.05*
	Small fruit and berries, other	0.05*
	Berries, wild	0.05*
	Miscellaneous fruits	0.05*
	Radish	0.5
	Root and tuber vegetables, other	0.05*
	Bulb vegetables	0.05*
	Tomato	0.5
	Aubergine	0.5
	Other fruiting vegetables	0.05*
	Cucurbits, edible peel	0.05*
	Cucurbits, inedible peel	0.05*
	Sweet corn	0.05*
	Brassica vegetables	0.05*
	Lettuce	2
	Leafy vegetables, other	0.05*
	Spinach	2
	Water cress	0.05*
	Witloof	0.05*
	Herbs	2
	Legume vegetables, fresh	0.05*
	Stem vegetables, fresh	0.05*
	Fungi	0.05*
	Pulses	0.05*
	Peanuts	0.1
	Soya bean	0.1
	Cotton	0.1
	Oil seed, other	0.05*
	Potatoes	0.05*
	Tea	0.1*
	Hops	10
* indicates the lower limit of analytical determination		
France	Citrus, large	0.5
	Citrus, small	1
	Fruits, other	0.02
	Vegetables, other	0.5
	Cereals	0.05
	Carrots	0.05
	Cotton	0.5
	Cucurbits with edible peel	0.2
	Spinach	0.5
	Stone fruit	0.2
	Plum	0.5
	Cherry	0.1
	Pome fruit	0.2
	Hops	10
	Lettuce	2
	Potatoes	0.05

Country	Commodity	MRL, mg/kg
	Radish	0.5
	Grapes	1
	Salads	2
	Soya beans	0.2
Indonesia	Apple	2
	Asparagus	2
	Barley	0.5
	Beans	0.1
	Cabbages	5
	Cauliflower	2
	Celery	2
	Citrus	1
	Common beans	2
	Cotton (seed oil)	0.1
	Cucumber	0.2
	Eggplant	0.2
	Eggs	0.05
	Grapes	5
	Hops (dry)	10
	Lettuce	5
	Maize flour	0.05
	Meat	0.02
	Melon	0.2
	Milk	0.02
	Onion	0.5
	Peanuts	0.1
	Peas	5
	Peppers	1
	Pineapple	0.2
	Potato	0.1
	Sorghum	0.2
	Soya bean	0.1
	Spinach	5
	Sugar beet	0.1
	Sweet corn	0.1
	Water melon	0.2
	Wheat	0.5
Italy	Apples	1
	Apricots	0.05
	Beans	0.05
	Cabbage	0.05
	Cherries	0.05
	Citrus	0.05
	Cucumbers	0.05
	Eggplant	0.1
	Grapes	3
	Lettuce	0.1
	Melon	0.3
	Olives	0.05

Country	Commodity	MRL, mg/kg
	Peas	0.05
	Peach	0.2
	Pears	0.2
	Peppers	0.1
	Plums	0.05
	Pumpkin	0.2
	Sugarbeet	0.05
	Tomato	0.1
	Watermelon	0.2
	Zucchini	0.1
Japan	Bell Pepper	0.5
	Broccoli	0.5
	Cabbage	0.5
	Carrot	0.5
	Ginger	0.5
	Grains	1
	Leek	0.5
	Lettuce	0.5
	Onion	0.5
	Pakchoi	0.5
	Potato	0.5
	Radish(Root)	0.5
	Soya bean	0.1
	Spinach	0.5
	Strawberry	0.5
	Sugarbeet	0.5
	Sweet potato	0.5
	Tea	3
	Watermelon	0.5
Korea	Apples	1
	Chinese cabbage	0.5
	Peppers, red	1
Netherlands	Cucumber	0.05
	Eggplant	0.05
	Melon	0.2
	Paprika	0.05
	Tomato	0.05
New Zealand	Small fruit	0.5
	Pome fruit	1
	Cereals, vegetables	0.2
Poland	Brussels sprouts	2
	Cabbage	2
	Cucumbers	0.5
	Egg plant	0.5
	Hops	4
	Paprika	0.5
	Sugarbeet	none
	Tomato	0.5

Country	Commodity	MRL, mg/kg
Portugal	Apples	1
	Grapes	3
	Peach	1
	Pears	1
	Tomato	1
South Africa	Beans	0.10
	Broccoli	0.20
	Brussels sprouts	0.20
	Cabbage	0.20
	Cauliflower	0.20
	Citrus	0.20
	Grazing crops	none
	Lucerne	0.10
	Lupines	0.10
	Maize	0.20
	Peach	0.20
	Potatoes	0.02
	Sorghum	0.20
	Sunflower	0.10
	Tobacco	0.20
	Tomato	0.10
	Wheat	0.20
Taiwan	Bulb vegetable	1
	Citrus	2
	Cucurbit	1
	Fruit vegetable	1
	Large berry	none
	Leafy vegetable	1
	Legume vegetable	1
	Maize	1
	Melon	none
	Mushroom	none
	Pome fruit	1
	Pulse	0.5
	Rice	0.5
	Root and tuber vegetable	0.5
	Small berry	2
	Stone fruit	2
	Sugarcane	none
	Tea	2
	Wheat	none
Thailand	Asparagus	2
	Cabbage	5
	Cauliflower	2
	Celery	none
	Cucumbers	0.2
	Eggplant	0.2
	Kale	none
	Lettuce	5

Country	Commodity	MRL, mg/kg
	Onion	0.2
	Other vegetables	none
	Peas, immature	none
	Peppers	1
	Potatoes	0.1
	Scallion	0.5
	Soya bean	0.2
	Soya bean, immature	0.1
	Tomato	1
	Watermelon	0.2
	Yard long bean	5
USA	Alfalfa	10
	Apples	1
	Asparagus	2
	Avocado	2
	Barley, grain	1
	Barley, hay	10
	Barley, stray	10
	Beans, dry	0.1*
	Beans, forage	10
	Beans, succulent	2
	Beet tops	6
	Blueberries	6
	Brassica (cole) leafy vegetables	6
	Broccoli	3
	Brussels sprouts	2
	Cabbage	5
	Cauliflower	2
	Celery	3
	Chinese cabbage	5
	Collards	6
	Corn, fodder	10
	Corn, forage	10
	Corn, fresh (inc. Sweet)	0.1*
	Corn, grain (Inc. Popcorn)	0.1*
	Cotton seed	0.1*
	Cucurbits	0.2*
	Dandelions	6
	Endive (escarole)	5
	Grapefruit	2
	Grapes	5
	Grass, Bermuda	10
	Grass, Bermuda, hay	40
	Kale	6
	Leeks	3
	Lemons	2
	Lentils	0.1
	Lettuce	5
	Mint hay	2

Country	Commodity	MRL, mg/kg
	Mustard greens	6
	Nectarine	5
	Oats, forage	10
	Oats, grain	1
	Oats, hay	10
	Oats, straw	10
	Onion, green	3
	Oranges	2
	Parsley	6
	Peach	5
	Peanuts	0.1*
	Peas	5
	Peas, vines	10
	Pecans	0.1
	Peppers	2
	Pomegranates	0.2*
	Rye, forage	10
	Rye, grain	1
	Rye, hay	10
	Rye, straw	10
	Sorghum, forage	1
	Sorghum, grain	0.2*
	Soya bean	0.2*
	Soya bean, forage	10
	Spinach	6
	Strawberries	2
	Swiss chard	6
	Tangerine	2
	Tomato	1
	Turnip greens	6
	Vegetables, fruiting	0.2*
	Vegetables, leafy	0.2*
	Vegetables, root crop	0.2*
	Watercress	6
	Wheat, forage	10
	Wheat, grain	1
	Wheat, hay	10
	Wheat, straw	10

APPRAISAL

Methomyl is a carbamate insecticide. It is registered throughout the world for foliar application to numerous agricultural crops.

Metabolism

Animals

The metabolism of [^{14}C]methomyl has been studied in rats, monkeys, goats, cows and hens. The radiolabel is located on C with a double-bond to N. The main metabolite identified in rat urine was a mercapturic acid derivative; acetonitrile, acetate, methomyl oxime sulfate and acetamide were tentatively identified in urine, but methomyl (both *syn* and *anti* isomers) and methomyl oxime (*S*-methyl *N*-hydroxythioacetimidate) were absent. About 75% of orally administered radiolabelled methomyl was eliminated within 3 days of the final treatment, with 50% in expired air and 25% in urine.

The findings in monkeys were similar to those in rats: 36% of the orally administered dose was found in expired air and 25% in urine. Urine also contained acetonitrile, acetate, acetamide, methomyl oxime sulfate and a trace of the mercapturic acid derivative of methomyl. Methomyl and methomyl oxime were absent. About 5% of the administered dose was found in tissues, the liver containing the largest portion (0.9 mg/kg as equivalents).

A definitive study of metabolism in goats confirmed the results of earlier studies on metabolism in goats and cows. A lactating goat was dosed orally for 3 consecutive days with radiolabelled methomyl at a concentration of about 160 ppm determined on the basis of actual feed consumption. About 30% was collected as expired volatile compounds (18% $^{14}CO_2$ and 13% [^{14}C]acetonitrile). The concentrations of radiolabel in milk and tissues were adequate to permit isolation and identification of metabolites (12 mg/kg of liver, 5 mg/kg of kidney, 1.5 mg/kg of muscle, 0.32 mg/kg of fat, 9 mg/kg of milk). Methomyl, methomyl *S*-oxide, methomyl *S*,*S*-dioxide, methomyl oxime and hydroxymethyl methomyl were not detected in any tissue or in milk, with an LOD of 0.007–0.018 mg/kg. Radiolabelled acetamide and thiocyanate were found in all tissues and milk, the latter constituting 7–50% of the total radiolabelled residue in the matrices.

Further characterization of the residues in tissues and milk indicated extensive incorporation of the radiolabel into natural components. About 30% of the TRR in milk was shown to be associated with fatty acids, and about 10% was [^{14}C]lactose. About 13% of the TRR in muscle, liver, kidney and fat was shown to be in amino acids.

The metabolism of [^{14}C]- or [^{13}C]methomyl was studied in white Leghorn laying hens dosed orally for 3 consecutive days at a rate equivalent to 45 ppm in the diet. Respired acetonitrile and CO_2 accounted for > 50% of the administered dose. The concentrations of equivalents of radiolabelled material in eggs and tissues were: 3 mg/kg in liver, 0.5 mg/kg in muscle, 0.8 mg/kg in fat, 1.5 mg/kg in egg white and 2 mg/kg in egg yolk. Methomyl and methomyl oxime were not detected in any tissue or in egg (LOD, 0.007–0.015 mg/kg.) Acetamide was found in egg white, and acetonitrile was found in all matrices, constituting 89% of the TRR in egg white.

Further characterization of the radiolabelled residue revealed that 60% of the TRR in egg yolk was associated with lipids, 87% with fat and 32% with liver. Small amounts (3% TRR) in the eggs and tissues were characterized as radiolabelled amino acids.

The Meeting concluded that the metabolism of methomyl is adequately understood in animals, and that similar mechanisms exist in rats, monkeys, ruminants and hens. Methomyl is degraded to acetonitrile, acetamide and CO_2, and these metabolites are incorporated into natural products. The Meeting further concluded that methomyl oxime is a probable intermediate, but neither it nor methomyl showed any propensity to bioaccumulate over the duration of the studies.

Plants

The metabolism of [^{14}C]methomyl was studied in tobacco, corn, cabbage and cotton. When tobacco plant roots were exposed to a solution of radiolabelled compound for 28 days, they absorbed 25% of the available radiolabel over 4 weeks. About 25% of that absorbed was retained, and the other 75% was released as CO_2 and acetonitrile, in equal proportions.

About 45% of a dose of [^{14}C]methomyl applied to the leaves of maize plants was volatilized within 10 days. About 26% of the radiolabel was extractable with methanol.

About 20% of a dose of [^{14}C]methomyl applied to the leaves of cabbage plants volatilized within 10 days, and 54% of the radiolabel was extractable with methanol. Methomyl constituted about 4% of the radiolabelled residue; no other related metabolite, such as methomyl oxime, was detected. Saponification of a non-polar fraction yielded radiolabelled fatty acids.

The translocation of methomyl was studied in tobacco plants by applying radiolabelled compound to the fifth leaf from the ground. No translocation was found after 3 days; after 7 days, < 1% of the residual radiolabel was found in plant parts other than the fifth leaves.

The metabolism of [^{14}C]methomyl was studied in maize, cabbage, and cotton under field conditions. Plants received repeated foliar treatments, and crops of maize and cabbage were harvested 8 days after the final treatment, while cotton leaves were harvested 0–192 hours after a single treatment. The outer leaves of cabbage heads contained methomyl at 0.9 mg/kg or 4% of the TRR, and the head contained 0.09 mg/kg. Methomyl oxime was not detected in head or leaves. Maize grain contained no methomyl or methomyl oxime, and most of the extractable radiolabel was associated with polar materials. Fodder contained about 2 mg/kg methomyl, and about 50% of the radiolabel could not be extracted.

In cotton, methomyl was the only component identified on the leaf surface. Radiolabel was initially found in leaves (extract) but disappeared within 48 h of treatment. Methomyl oxime was not found at any interval.

A study of confined rotational crops was conducted in sandy loam soil with cabbage, red beet and sunflower. Seeds were planted 30 and 120 days after treatment of the soil with [^{14}C]methomyl at a rate of 4.5 kg ai/ha, and the crops were harvested at normal maturity. At the 30-day plant-back interval, beets and cabbage contained 0.1–0.2 mg/kg methomyl equivalents, and sunflower seeds contained 2 mg/kg. At 120 days, the concentrations had declined to 0.05 mg/kg and 1.5 mg/kg, respectively. The concentrations of methomyl and its immediate metabolites, as determined by methanol extraction, were $\leq$ 0.01 mg/kg at both plant-back intervals.

The Meeting concluded that the nature of the residues in and on plants is adequately understood. Methomyl is degraded to CO_2 and acetonitrile, and these metabolites may then be incorporated into natural products. The Meeting further concluded that methomyl has little tendency to translocate and does not translocate (as methomyl) into rotational crops (< 0.01 mg/kg) at 30-day or longer plant-back intervals. The Meeting also noted that methomyl oxime, if present, occurs as a minor metabolite.

Environmental fate

Soil

Under anaerobic conditions, [^{14}C]methomyl degraded rapidly, with a first-order half-time of 11 days. Over a 3-month study period, the main degradate was $^{14}CO_2$, representing 75% of the applied material; methomyl oxime represented 3% of the applied material. In experiments with various soil types, 30–45% of the applied material was isolated as $^{14}CO_2$ after 42 days. The main component in soil extracts was

[^{14}C]methomyl, representing < 10% of the applied radiolabel. In sterile soil, [^{14}C]methomyl represented 89% of the applied radiolabel after 45 days.

[^{14}C]Methomyl had a first-order half-time of < 1 day to 14 days in various experiments under anaerobic conditions. Ferrous ion accelerated degradation to methanethiol and dimethyl disulfide.

The photolysis of [^{14}C]methomyl under natural sunlight for 30 days was studied after application at a rate of 1.1 kg ai/ha to silt loam, maintained at 25 ^{o}C. The radiolabelled compound decomposed with a half-time of 34 days, and the only decomposition product detected was acetonitrile. Controls showed no decomposition.

The mobility of [^{14}C]methomyl was studied on various types of loam soil. Methomyl was highly mobile in loams with a high sand content and less mobile in loams with more organic matter. Likewise, a higher clay content decreased the mobility of methomyl. In column leaching experiments performed with Speyer 2.1, 2.1 and 2.3 soils, the percentage of radiolabel in the leachate increased from 8% to 52% as the sand content of the soil increased from 65% to 91%. The leachate contained a maximum of 2% methomyl oxime.

The Meeting concluded that methomyl degrades at a moderate rate under both aerobic and anaerobic conditions and that microbes are essential to the degradation under aerobic conditions. CO_2 is the main degradate under aerobic conditions. Methomyl on soil is also subject to photodegradation. The Meeting further concluded that methomyl has low to moderate mobility in soil, greater mobility in sandy soils and less mobility in clay and in soils with a high content of organic matter.

Water–sediment systems

The fate of [^{14}C]methomyl added at a nominal concentration of 0.45 µg/ml to two natural water–sediment systems was studied. After an equilibrium had been established in the systems, the mixtures were spiked with the [^{14}C]methomyl, and sediment and water phases were taken and analysed at intervals up to 102 days. Acetonitrile accounted for about 25% of the applied radiolabel and CO_2 for about 40% after 102 days. Sediment contained about 15% of the radiolabel and water contained about 1%. By day 29, methomyl had virtually disappeared from both water and sediment. Analysis of extracts confirmed the absence of methomyl oxime, anti-methomyl, methomyl sulfoxide, acetaldehyde and acetic acid. The first-order half-time of methomyl was about 5 days.

The Meeting concluded that methomyl degrades rapidly in water–sediment systems, with the formation of acetonitrile and CO_2.

Methods of analysis

Methods were described for the determination of methomyl in plant commodities, animal commodities and environmental samples. The original methods for plant commodities consist of extraction with an organic solvent, liquid–iquid partition and hydrolysis with sodium hydroxide. The latter converts methomyl and thiodicarb to methomyl oxime. The final extract is analysed by GC, usually with a flame photometric detector in the sulfur mode.

The more recent method is based on HPLC. The plant matrix is extracted with solvent, cleaned up on a Florisil column and analysed by HPLC with post-column reaction to convert separated thiodicarb and methomyl to methylamine. Methylamine is derivatized (on-line) and detected by fluorescence.

The GC method has been validated for numerous plant commodities at an LOQ of 0.02 mg/kg. The HPLC method and its modifications have been validated at an LOQ of 0.02 mg/kg for methomyl.

Similar GC and HPLC methods exist for the determination of methomyl in meat, milk, poultry and eggs. The LOQs for the GC method are 0.080 mg/kg for liver, 0.080 mg/kg for kidney, 0.020 mg/kg for muscle and 0.040 mg/kg for fat. Difficulties were experienced in obtaining acceptable recoveries from milk. The HPLC method has an LOQ of 0.02 mg/kg or 0.01 mg/kg, depending on the extent of sample preparation.

The Meeting concluded that adequate methods exist for the determination of methomyl in plant and animal commodities.

Stability of residues in stored analytical samples

Information on stability in storage was provided for methomyl in soya bean hay, maize (kernels), bean seed, potato, peanut (nutmeat), grain sorghum forage, grain sorghum hay, grain sorghum stover, head lettuce, broccoli, orange (chopped), orange (half), apple, grape and onion (whole) stored frozen (nominal temperature, –20 °C). Adequate stability (> 80% remaining) was demonstrated after 24 months' storage for all commodities except chopped orange and onions. The residues on onions were incurred in the field, and the variability in the recovery at different times was attributed to differences in the portion of onion bulb exposed (above ground) at the time of methomyl application. The stability on an orange half was satisfactory.

Methomyl was unstable in or on liver stored at –4 to –20 °C, declining by at least 50% on day 1. The compound was stable in milk for 24 months at –20 °C but unstable in fat, muscle and kidney. Methomyl was stable in all ruminant commodities for 6 months when stored under cryogenic conditions (–70 °C).

These studies included use of the HPLC analytical method, in which methomyl is determined as methomyl. Any hydrolysis to methomyl oxime during storage would have been reflected as loss of methomyl. This was not observed.

The Meeting concluded that methomyl is stable under frozen conditions on most plant commodities for up to 24 months, the interval studied, but that it is not stable in ruminant fat, kidney, muscle or liver under ordinary freezer conditions. Special conditions must be used to store ruminant commodities for analysis.

Definition of the residue

Studies of the nature of the residue in animals and plants showed that methomyl is substantially metabolized to CO_2 and acetonitrile. Methomyl oxime was generally absent, although its sulfate was found in some studies in animals.

The older GC methods for analysis rely on conversion of methomyl to methomyl oxime, and thus, methomyl and methomyl oxime are determined. In the newer HPLC methods, only methomyl is determined, although thiodicarb may also be determined (separately) by the same method.

The Meeting noted that thiodicarb is readily metabolized to methomyl and that it is appropriate to combine the considerations for thiodicarb and methomyl. The Meeting agreed that the residue in both plant and animal commodities should be defined as methomyl for use of methomyl and as the sum of thiodicarb and methomyl, expressed as methomyl, for the use of thiodicarb. The Meeting further noted

that expression of thiodicarb residue can be expressed as methomyl or thiodicarb, as the conversion factor from thiodicarb to methomyl is 0.92 and that from methomyl to thiodicarb is 1.1.

Results of supervised trials

Supervised trials were conducted with foliar application of methomyl to numerous agricultural commodities, primarily in Europe and the USA.

Citrus

Supervised field trials were conducted on oranges and mandarin in Greece (GAP: soluble concentrate, 0.09 kg ai/hl, 1.4 kg ai/ha; one to three applications; PHI, 20 days), Italy (GAP: soluble concentrate, wettable powder; 0.04 kg ai/hl; PHI, 10 days) and Spain (GAP: wettable powder, soluble concentrate, 0.05 kg ai/hl; 0.6, 0.5 kg ai/ha; five applications; PHI, 7 days). Seven trials o oranges were conducted in Spain, three in Greece and four in Italy. Five trials on mandarin were conducted in Spain, three in Greece and two in Italy. When Spanish GAP is applied to the trials on orange, the ranked order of concentrations of residues was: < 0.02 (2), 0.02, 0.03, 0.06 (2), 0.07, 0.09, 0.14, 0.25, 0.30, 0.35, 0.43 and 0.59 mg/kg. There were five trials on mandarin in Spain, three in Greece and two in Italy. When Spanish GAP is applied to the trials on orange, the ranked order of concentrations of residues was: 0.05, 0.06, 0.17 (2), 0.19, 0.32, 0.38 (2), 0.43 and 0.89 mg/kg.

The Meeting considered the combined data sufficient for citrus. The ranked order of concentrations was therefore (median underlined): < 0.02 (2), 0.02, 0.03, 0.05, 0.06 (3), 0.07, 0.09, 0.14, 0.17 (2), 0.19, 0.25, 0.30, 0.32, 0.35, 0.38 (2), 0.43 (2), 0.59 and 0.89 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg for citrus. The Meeting agreed to maintain the current recommendation of 1 mg/kg. A study of consumer-type peeling showed that the concentration of residue on flesh is reduced by a factor of 0.2 when the peel is removed from unwashed oranges. Using this factor, the Meeting estimated an STMR value of 0.034 mg/kg and a highest residue of 0.18 mg/kg for citrus flesh.

Stone fruit

Supervised field trials were conducted on peach, apricot and nectarine. Trials on peach were conducted in Spain (GAP: soluble concentrate, wettable powder; 0.6 kg ai/ha, 0.05 kg ai/hl; one to five applications: PHI, 7 days), Germany (no GAP; uses that of France), France (GAP: 0.075 kg ai/ha; PHI, 7 days), Italy (wettable powder, soluble concentrate; 0.04 kg ai/ha; PHI, 10 days) and the USA (soluble concentrate, water-soluble powder; 2.0 kg ai/ha, 0.06 kg ai/hl terrestrial, 4.8 kg ai/hl aerial; six applications; PHI, 4 days). None of the 13 trials in the USA was conducted according to GAP. Applying the GAP of Spain for Italy, 15 trials in Europe (six in France, three in Germany, three in Italy and three in Spain) were at GAP, and the ranked order of concentrations of residues was: < 0.02, 0.02, 0.03, 0.04 (3), 0.05 (2), 0.07 (2), 0.08, 0.09 (3) and 0.10 mg/kg. The Meeting estimated an STMR value of 0.05 mg/kg and a maximum residue level of 0.2 mg/kg for peaches. The highest residue was estimated as 0.10 mg/kg. The Meeting agreed to withdraw the previous recommendation for peach (5 mg/kg).

Nine supervised trials were conducted on nectarine in the USA, two according to GAP (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.0 kg ai/hl; three applications; PHI, 1 day), resulting in concentrations of 0.78 and 1.4 mg/kg. The Meeting decided that there were insufficient data to estimate a maximum residue level or STMR value for nectarine from these data. Applying the European data for peach, the Meeting estimated a maximum residue level of 0.2 mg/kg, an STMR value of 0.05 mg/kg and a highest residue of 0.10 mg/kg for nectarine.

Four trials on apricot were conducted in Italy, all at the GAP of Spain (soluble concentrate, wettable powder; 0.05 kg ai/hl; PHI, 7 days). The ranked order of concentrations of residues was: 0.04 (2), 0.05 and 0.15 mg/kg. The Meeting considered that there were insufficient data from which to estimate a maximum residue level or an STMR value.

Supervised field trials were conducted on plums in Europe (GAP, France: soluble concentrate; 0.075 kg ai/hl; three applications; PHI, 7 days; Germany: none, uses that of France; Spain (stone fruit): soluble concentrate, wettable powder; 0.6 kg ai/ha, 0.05 kg ai/hl; one to five applications; PHI, 7 days). Of the 15 trials, 13 were conducted at GAP, and the ranked order of concentrations of residues was: 0.02 (2), 0.03 (2), 0.06, 0.08 (2), 0.10, 0.11, 0.19, 0.28, 0.34 and 0.51 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg, an STMR value of 0.08 mg/kg and a highest residue of 0.51 mg/kg for plums.

Pome fruit

Trials on apple and pear were conducted in France (soluble concentrate, 0.075 kg ai/h; three applications; PHI, 7 days), Germany (no GAP; uses that of France), Spain (soluble concentrate, wettable powder; 0.75 kg ai/ha, 0.05 kg ai/hl, one to five applications,; PHI, 7 days), Italy (soluble concentrate, wettable powder; 0.05 kg ai/hl; PHI, 10 days) and Belgium (wettable powder; 0.75 kg ai/ha, 0.05 kg ai/hl; PHI, 21 days). Of the trials on apple, 13 were at GAP (eight in France, two in Italy (GAP of Spain), two in Spain, one in Germany). The ranked order of concentrations of residues was: 0.03, 0.06, 0.08 (3), 0.09 (3), 0.11, 0.13, 0.16 and 0.17 (2) mg/kg.

Supervised field trials on apple were conducted in the USA (water-soluble powder, soluble concentrate; 1.0 kg ai/ha, 2.2 kg ai/hl; five applications; PHI, 14 days). Ten of 34 trials were at GAP, and the ranked order of concentrations of residues was: 0.16, 0.24, 0.25, 0.29, 0.31 (2), 0.34, 0.42, 0.48 and 0.77 mg/kg. The Meeting decided that the European and USA residues were from different populations and could not be combined. Supervised trials on apples were also conducted with thiodicarb, and the ranked order of concentrations of residues was: 0.30, 0.32, 0.40, 0.43, 0.48, 0.61, 0.68, 0.91 (2) and 1.6 mg/kg. The Meeting considered that the data on thiodicarb were from the same population as the data for methomyl and combined them, with a ranked order of concentrations of: 0.16, 0.24, 0.25, 0.30, 0.31(2), 0.32, 0.34, 0.39, 0.40, 0.42, 0.43, 0.48 (2), 0.61, 0.68 (2), 0.77, 0.91 (2), 1.5 and 1.6 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg, an STMR value of 0.41 mg/kg and a highest residue of 1.6 mg/kg for apple.

Supervised field trials were conducted on pear in Europe. Two trials were conducted in France, two in Belgium and one in Italy. GAP was applied in the trials in France (soluble concentrate; 0.075 kg ai/h; three applications; PHI, 7 days) and Italy (GAP of Spain: soluble concentrate, wettable powder; 0.05 kg ai/hl; five applications,; PHI, 7 days); the ranked order of concentrations of residues was: 0.03, 0.04, 0.11 and 0.18 mg/kg. Six field trials were conducted on pears in the USA, but none was at GAP. The Meeting decided that four trials were insufficient to estimate a maximum residue level or an STMR value for pears but agreed that the data on apple from Europe, with similar GAP and residue values, could be used to support the limited data set for pear. The concentrations in the combined data set, in ranked order, were: 0.03 (2), 0.04, 0.06, 0.08 (3), 0.09 (3), 0.11 (2), 0.13, 0.16, 0.17 (2) and 0.18 mg/kg. The Meeting estimated a maximum residue level of 0.3 mg/kg, an STMR value of 0.09 mg/kg and a highest residue of 0.18 mg/kg for pears.

The Meeting agreed to recommend the withdrawal of the draft MRL for pome fruit (2 mg/kg) and to replace it with the recommendations for apple (2 mg/kg) and pear (0.3 mg/kg).

Berries and small fruit

Supervised field trials on grapes were reported from the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; five applications; PHI, 1 day for fresh table grapes, 14 days for wine grapes). Seventeen trials were conducted at GAP. When the grape type (table or wine) was not specified, use on table grapes, with the shorter PHI, was assumed.

Supervised field trials on grapes were reported from France (GAP: soluble concentrate; 0.4 kg ai/ha, 0.05 kg ai/hl; three applications; no PHI), Italy (soluble concentrate, wettable powder; 0.05 kg ai/hl; PHI, 10 days) and Portugal (no GAP; uses that of Italy). Four trials from France were at GAP, with residue concentrations of 0.19, 0.25, 0.26 and 0.29 mg/kg. The results of these trials were combined with those of trials in the USA (foliar), and the ranked order of concentrations of residues was: 0.15, 0.19, 0.25, 0.26, 0.29, 0.54, 0.58, 0.65, 0.78, 0.93, 1.0 (2), 1.2, 1.3, 2.2, 2.3, 2.8, 2.9, 3.5, 4.1 and 5.2 mg/kg. Supervised field trials were also conducted with thiodicarb, giving a ranked order of concentrations of thiodicarb residues of: 0.59 and 0.7 (2) mg/kg. The combined values for methomyl and thiodicarb residues yields a ranked order of: 0.15, 0.19, 0.25, 0.26, 0.29, 0.54, 0.58, 0.59, 0.65, 0.7 (2), 0.78, 0.93, 1.0 (2), 1.2, 1.3, 2.2, 2.3, 2.8, 2.9, 3.5, 4.1 and 5.2 mg/kg. The Meeting estimated an STMR value of 0.86 mg/kg, a highest residue of 5.2 mg/kg and a maximum residue level of 7 mg/kg, which replaces the previous estimate (5 mg/kg).

Bulb vegetables

Five supervised trials were conducted on onions, bulb in the USA (GAP: 1.0 kg ai/ha, 5.4 kg ai/hl; eight applications; PHI, 7 days). All the trials were at GAP, and the ranked order of concentrations of residues was: < 0.02, 0.056, 0.068, 0.072 and 0.14 mg/kg. The Meeting estimated an STMR value of 0.068 mg/kg, a highest residue of 0.14 mg/kg and a maximum residue level of 0.2 mg/kg, which confirms the existing MRL.

Brassica vegetables

The GAP for cabbage in the USA is soluble concentrate or water-soluble powder formulation at 1.0 kg ai/ha, 1.1 kg ai/hl; 15 applications and a 1-day PHI. Seven trials were conducted at GAP, and the ranked order of concentrations of residues was: 0.086, 0.10, 0.18, 0.27, 0.46, 0.52 and 0.63 mg/kg. Supervised field trials on cabbage with thiodicarb yielded higher values: 0.08 (2), 0.12, 0.53, 0.76, 0.97, 1.2, 1.3, 2.1, 2.7, 2.8, 3.0, 3.1, 3.5, 3.8, 4.3, 4.8, 5.0 and 5.3 mg/kg. The Meeting considered the two sets of data to be from different populations and agreed to use the results for thiodicarb (higher values) for making estimates.

Supervised field trials were conducted on broccoli in the USA, where the GAP is use of the soluble concentrate or water-soluble powder formulation at 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications and a 3-day PHI. The ranked order of concentrations of residues in the 16 trials at GAP was: 0.09, 0.20, 0.21, 0.35, 0.36, 0.44, 0.45, 0.51, 0.68, 0.70, 0.73, 0.77, 0.96, 1.1, 1.8 and 2.8 mg/kg. Supervised field trials were also conducted on broccoli with thiodicarb, resulting in concentrations of: 1.1, 1.3, 1.6, 1.9, 2.6, 5.0 and 5.6 mg/kg. The Meeting considered the two data sets to be from different populations and agreed to use those for thiodicarb (higher values) for making estimates.

Supervised field trials were conducted on cauliflower in the USA, where the GAP is use of the soluble concentrate or water-soluble powder formulation at 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications and a PHI of 3 days. Eleven trials were conducted at GAP, and the ranked order of concentrations of residues was: 0.04, 0.18 (2), 0.20, 0.24, 0.51, 0.74, 1.6, 2.0, 3.8 and 5.6 mg/kg. Supervised field trials were also conducted with thiodicarb, resulting in concentrations of: 0.09, 0.16, 0.27, 0.45, 0.64, 0.71 and 2.3 (2)

mg/kg. The Meeting considered the two sets of data to correspond to the same population and agreed to combine them for making estimates.

The Meeting noted that GAP for broccoli, cabbage and cauliflower is similar and that the residue concentrations were similar. It therefore decided to combine the values for thiodicarb on cabbage, thiodicarb on broccoli and thiodicarb and methomyl on cauliflower (n = 45), as follows: 0.04, 0.08 (2), 0.09, 0.12, 0.16, 0.18 (2), 0.20, 0.24, 0.27, 0.45, 0.51, 0.53, 0.64, 0.71, 0.74, 0.76, 0.97, 1.1, 1.2, 1.3 (2), 1.6 (2), 1.9, 2.0, 2.1, 2.3 (2), 2.6, 2.7, 2.8, 3.0, 3.1, 3.5, 3.8 (2), 4.3, 4.8, 5.0 (2), 5.3 and 5.6 (2) mg/kg. The Meeting estimated a maximum residue level of 7 mg/kg, an STMR value of 1.3 mg/kg and a highest residue of 5.6 mg/kg for brassica vegetables.

The Meeting agreed to withdraw the previous recommendations for cabbages, head (5 mg/kg) and cauliflower (2 mg/kg), and to replace them by the recommendation for brassica vegetables (7 mg/kg).

Cucurbits

Supervised field trials on cucumbers were conducted in Belgium (wettable powder; 0.5 kg ai/ha, 0.031 kg ai/hl; PHI, 14 days), France (soluble concentrate; 0.3 kg ai/ha; three applications; PHI, 7 days), Greece (soluble concentrate; 0.45 kg ai/ha; one to three applications; PHI, 20 days), Italy (soluble concentrate, wettable powder; 0.04 kg ai/hl; PHI, 10 days) and The Netherlands (soluble concentrate, wettable powder; 0.4 kg ai/ha, 0.025 or 0.008 kg ai/hl; one to three applications; PHI, 3 days). The trials in Belgium and The Netherlands were conducted in glasshouses. The ranked order of concentrations of residues in the four trials conducted at GAP was: < 0.02 (2) and 0.03 (2) mg/kg. Eight trials on cucumber conducted outdoors (two in France, one in Greece and five in Italy) were at the respective GAP, and the ranked order of concentrations of residues was: < 0.02 (8) mg/kg. The Meeting considered that the data from the indoor and outdoor trials were from the same pool and combined them, resulting in a ranked order of concentrations in the 12 trials of: < 0.02 (10) and 0.03 (2) mg/kg.

Field trials on squash, summer were conducted in Belgium (no GAP; uses that of The Netherlands), Greece (wettable powder; 0.45 kg ai/ha; one to three applications; PHI, 15 day s), Italy (no GAP; uses that of France: 0.3 kg ai/ha; three applications; PHI, 7 days) and The Netherlands (soluble concentrate, wettable powder; 0.4 kg ai/hl, 0.025 kg ai/hl [0.08 kg ai/hl for wettable powder]; one to three applications; PHI, 3 days). The trials in Belgium and The Netherlands were conducted in glasshouses. Only one trial, in Belgium, was conducted at GAP, resulting in a residue concentration of < 0.02 mg/kg.

Supervised trials were conducted on watermelon in the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; 12 applications; PHI, 3 days). The ranked order of concentrations in the three trials conducted at GAP was < 0.04 (2) and 0.07 mg/kg.

Supervised trials on melons were conducted in Greece (soluble concentrate; 0.45 kg ai/ha; one to three applications; PHI, 20 days), Italy (soluble concentrate, wettable powder; 0.04 kg ai/hl; PHI, 10 days), The Netherlands (soluble concentrate, wettable powder; 0.4 kg ai/ha, 0.025 or 0.08 kg ai/hl; one to three applications; PHI, 3 days) and Spain (no GAP; uses that of Italy). Ten trials (seven in Italy, two in The Netherlands and one in Spain) were at GAP, and the ranked order of concentrations of residues was: < 0.02 (10) mg/kg.

The Meeting noted that the trials on melons, watermelon, summer squash and cucumbers yielded similar results, < 0.02– 0.07 mg/kg, and therefore decided to combine the values and estimate a maximum residue level for the cucurbit group. The ranked order of concentrations was: < 0.02 (21), 0.03 (2), < 0.04 (2) and 0.07 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg, a highest residue of 0.07 mg/kg and an STMR value of 0.02 mg/kg for the cucurbit vegetable group.

The Meeting agreed to withdraw the previous recommendations for cucumber (0.2 mg/kg), melon (0.2 mg/kg), summer squash (0.2 mg/kg) and watermelon (0.2 mg/kg) and to replace them by the recommendation for the cucurbit vegetable group (0.1 mg/kg).

Fruiting vegetables

Supervised trials were conducted on egg plant, tomato and peppers in the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 5.4 kg ai/hl; PHI, 3 days for egg plant, 1 day for tomato, 3 days for peppers). One of the trials on egg plant (residue concentration of 0.30 mg/kg), two on tomato (< 0.03 and 0.03 mg/kg) and two on peppers (0.08 and 0.44 mg/kg) were conducted at GAP.

Supervised trials on peppers and tomatoes were conducted in Europe. Trials on tomato were conducted in Belgium (wettable powder; 0.5 kg ai/ha, 0.031 kg ai/hl; PHI, 14 days), Italy (soluble concentrate, wettable powder; 0.04 kg ai/hl; PHI, 10 days), The Netherlands (soluble concentrate, wettable powder; 0.4 kg ai/ha, 0.025 or 0.08 kg ai/hl; one to three applications; PHI, 3 days), Portugal (no GAP; uses that of Spain), and Spain (soluble concentrate, wettable powder; 0.50 kg ai/ha, 0.05 kg ai/hl; one to five applications; PHI, 3 days). Two trials on pepper were reported, one from Italy (soluble concentrate, wettable powder; 0.04 kg ai/hl; PHI, 10 days) and one from The Netherlands (no GAP). The former was conducted at GAP, with a residue concentration of < 0.02 mg/kg. Nine trials on tomato (two in Belgium, four in Italy, two in The Netherlands and one in Spain) and one on peppers were conducted at GAP. The concentration of residues in tomato was < 0.02 (9). Supervised field trials on tomatoes were also conducted with thiodicarb, and the ranked order of concentrations was: 0.05, 0.06, 0.08, 0.09, 0.13, 0.16, 0.18, 0.23 (2), 0.33 and 0.73 mg/kg. The data on methomyl and thiodicarb were considered to represent different populations. Using only the data on thiodicarb (higher values), the Meeting estimated a maximum residue level of 1 mg/kg, an STMR value of 0.16 mg/kg and a highest residue of 0.73 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg for tomato, confirming the existing CXL.

The Meeting declined to estimate a maximum residue level or an STMR value for peppers, as there were only three trials at GAP, with concentrations of < 0.02, 0.08 and 0.44 mg/kg.

Sweet corn

Supervised trials were reported from the USA (GAP: soluble concentrate; 0.5 kg ai/ha, 5.4 kg ai/hl; 28 applications; no PHI for maize, 3 days for forage). Fourteen trials were at GAP, and the ranked order of concentrations of residues was: < 0.02 (9), 0.021, 0.03(2), 0.043 and 0.052. Supervised field trials were also conducted with thiodicarb, and the ranked order was: < 0.02, 0.02, < 0.03 (6), < 0.04, 0.04, 0.06, 0.07 (2), 0.08, 0.11, 0.13, 0.22, 0.28, 0.43, 0.54, 0.82 and 1.5 mg/kg. The Meeting ascertained that the two sets of data did not represent the same population and made estimates from the data on thiodicarb (higher values). The Meeting estimated a maximum residue level of 2 mg/kg, an STMR value of 0.065 mg/kg and a highest residue of 1.5 mg/kg. The Meeting agreed to maintain the current recommendation of 2 mg/kg (see report item on thiodicarb).

Leafy vegetables

Supervised field trials were conducted on lettuce, head in the USA (GAP: water-soluble powder, soluble concentrate; 1.0 kg ai/ha, 1.1 kg ai/hl; 15 applications; PHI, 7 days for rates < 0.5 kg ai/ha and 10 days for rates > 0.5 kg ai/ha). All the trials were conducted at the maximum rate with a 10-day PHI. The ranked order of concentrations in the 10 trials at GAP was: 0.18, 0.54, 0.70, 1.2, 1.5, 2.2, 2.3, 3.3, 4.6 and 4.8 mg/kg. The results of supervised trials with thiodicarb on head lettuce resulted in values of : < 0.04 (3), < 0.05, 0.07 (2), 0.09 (2), 0.12, 0.14, 0.19, 0.21, 0.25, 0.34, 0.35, 0.36, 0.42, 0.44, 0.48, 0.49, 0.71, 0.96,

1.1, 1.2, 1.5, 1.7 (2). 1.8, 1.9, 2.2, 2.6, 3.0, 3.2, 6.2, 6.3, 7.7, 10, 13, 17 and 18 mg/kg. The Meeting considered that the two data sets represented different populations and agreed to use those for thiodicarb data (higher concentrations but lower STMR value).

Supervised field trials were conducted on lettuce, leaf in the USA (GAP: water-soluble powder, soluble concentrate; 1.0 kg ai/ha, 1.1 kg ai/hl; eight applications; PHI, 7 days for rates < 0.5 kg ai/ha and 10 days for rates > 0.5 kg ai/ha). All the trials were conducted at the maximum rate, and the ranked order of concentrations of residues in the 10 trials at GAP was: 0.31, 0.62, 1.4, 2.1, 2.5, 2.9, 3.6, 5.5, 5.7 and 6.7 mg/kg.

Supervised field trials were conducted on spinach in the USA (GAP: water-soluble powder, soluble concentrate; 1.0 kg ai/ha, 1.1 kg ai/hl; eight applications; PHI, 7 days). Eight trials were at GAP, and the ranked order of concentrations of residues was: 0.07, 0.34, 0.74, 1.4, 4.1, 4.6 (2) and 5.0 mg/kg. Supervised trials also were conducted with thiodicarb, resulting in concentrations of : 0.04 (2), 0.21, 1.0, 3.2, 3.5, 4.1, 12 and 25 mg/kg. The Meeting considered the two data sets to represent the same population and combined them, resulting in a ranked order of: 0.04 (2), 0.07, 0.21, 0.34, 0.74, 1.0, 1.4, 3.2, 3.5, 4.1 (2), 4.6 (2), 5.0, 12 and 25 mg/kg. The existing MRL is 5 mg/kg.

Supervised trials were conducted on collards with thiodicarb (see report item). The ranked order of concentrations of residues was: 1.5 and 1.8 mg/kg.

The Meeting noted that the ranges of concentrations were similar for leaf lettuce (thiodicarb), spinach (methomyl and thiodicarb), collards (thiodicarb) and head lettuce (thiodicarb) and decided to pool the 69 values to estimate a maximum residue level for leafy vegetables. The ranked order of concentrations was: < 0.04 (3), 0.04 (2), < 0.05, 0.07 (3), 0.09 (2), 0.12, 0.14, 0.19, 0.21 (2), 0.25, 0.31, 0.34 (2), 0.35, 0.36, 0.42, 0.44, 0.48, 0.49, 0.62, 0.71, 0.74, 0.96, 1.0, 1.1, 1.2, 1.4 (2), 1.5 (2), 1.7 (2), 1.8 (2), 1.9, 2.1, 2.2, 2.5, 2.6, 2.9, 3.0, 3.2 (2), 3.5, 3.6, 4.1 (2), 4.6 (2), 5.0, 5.5, 5.7, 6.2, 6.3, 6.7, 7.7, 10, 12, 13, 17, 18 and 25 mg/kg. The Meeting estimated a maximum residue level of 30 mg/kg, an STMR value of 1.4 mg/kg and a highest residue of 25 mg/kg for leafy vegetables.

The Meeting agreed to withdraw the previous recommendations for kale (5 mg/kg), lettuce, head (5 mg/kg), and spinach (5 mg/kg) and to replace them by the recommendation for leafy vegetables (30 mg/kg).

Legume vegetables

Supervised trials were conducted on succulent beans in the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 1 day for single use at < 0.56 kg ai/ha and 3 days for single use at > 0.56 kg ai/ha). Six trials were at GAP, and the ranked order of concentrations of residues was: 0.03, 0.05 (2), 0.06, 0.30 and 0.68 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg, an STMR value of 0.055 mg/kg and a highest residue of 0.68 mg/kg for beans (succulent) or common bean.

Supervised trials were conducted on soya bean (immature seeds) in the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 1 day). None of the trials was conducted at GAP. The Meeting agreed to withdraw the recommendation for soya bean (immature seed) (0.1 mg/kg).

Supervised trials were conducted on peas (pods and succulent seeds) in the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 1 day for single use at < 0.56 kg ai/ha and 3 days for single use at > 0.56 kg ai/ha). Eight trials were at GAP, and the ranked

order of concentrations of residues was: 0.12, 0.18, 0.19, 0.33, 0.60, 0.83, 1.4 and 4.0. The Meeting estimated a maximum residue level of 5 mg/kg, an STMR value of 0.46 mg/kg and a highest residue of 4.0 mg/kg for peas (pods and succulent seeds). The Meeting agreed to maintain the current recommendation of 5 mg/kg.

Supervised trials were conducted in the USA on beans (dry) (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 14 days). In the 17 trials at GAP, the ranked order of concentrations of residues was: < 0.02 (15), 0.02 and 0.023 mg/kg. The Meeting estimated an maximum residue level of 0.05 mg/kg, an STMR value of 0.02 mg/kg and a highest residue of 0.023 mg/kg. The Meeting agreed to withdraw the previous recommendation (0.1 mg/kg) and to replaced it with the recommendation for beans (dry) (0.05 mg/kg).

Root and tuber vegetables

Supervised trials were conducted on potato in the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha; 10 applications; PHI, 6 days). In the nine trials at GAP, the ranked order of concentrations of residues was < 0.02 (9). Supervised field trials were also conducted with thiodicarb; the ranked order of concentrations of residues after foliar application was < 0.007 (2) and < 0.008 (2) mg/kg; and that after granular bait application was < 0.04 mg/kg (11). In all trials, neither thiodicarb nor methomyl was found at the LOQ (0.02 or 0.04 mg/kg). The Meeting therefore estimated a maximum residue level of 0.02(*) mg/kg, an STMR value of 0.00 mg/kg and a highest residue of 0.00 mg/kg. The Meeting agreed to withdraw the previous recommendation of 0.1 mg/kg and to replace it by the recommendation for potato (0.02(*) mg/kg).

Stalk and stem vegetables

Supervised field trials on asparagus were conducted in the USA (GAP: water-soluble powder, soluble concentrate; 1.0 kg ai/ha, 1.1 kg ai/hl; eight applications; PHI, 1 day). In the eight trials at GAP, the rank order of concentrations of residues was: 0.12, 0.14, 0.15, 0.26, 0.40, 0.48, 0.59 and 1.1 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg, an STMR value of 0.33 mg/kg and a highest residue of 1.1 mg/kg. The Meeting agreed to maintain the current recommendation of 2 mg/kg for asparagus.

Supervised field trials on celery were conducted in the USA (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 7 days). In the eight trials at GAP, the ranked order of concentrations of residues in untrimmed celery was: < 0.02 (2), 0.09, 0.59, 0.72, 1.8 and 2.0 (2) mg/kg. The Meeting estimated a maximum residue level of 3 mg/kg, an STMR value of 0.66 mg/kg and a highest residue of 2 mg/kg. The Meeting agreed to withdraw the previous recommendation for celery (2 mg/kg) and to replace it by the recommendation for celery (3 mg/kg).

Cereal grains

Supervised field trials were conducted on barley in the USA (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha, 5.4 (soluble concentrate) or 6.0 (water-soluble powder) kg ai/hl; four applications; PHI, 7 days). In the three trials at GAP, the ranked order of concentrations of residues on grain was: 0.12, 0.72 and 1.3 mg/kg (see below).

Supervised field trials were conducted on wheat in the USA (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha, 5.4 kg ai/hl; four applications; PHI, 7 days). In the 15 trials at GAP, the ranked order of concentrations of residues was: < 0.02 (4), 0.02 (2), 0.06, 0.12, 0.14, 0.17 (3), 0.40, 0.69 and 1.1 mg/kg. Supervised field trials were also conducted with application of thiodicarb to barley and

wheat, but the GAP was for granular bait use. The concentrations of residues ranged from < 0.02 to 0.06 mg/kg. Foliar application of methomyl was considered the critical use. The Meeting concluded that data on methomyl residues in barley and wheat resulting from identical foliar use were mutually supportive and pooled the data, with the ranked order: < 0.02 (4), 0.02 (2), 0.06, 0.12 (2), 0.14, 0.17 (3), 0.40, 0.69, 0.72, 1.1 and 1.3 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg, an STMR value of 0.14 mg/kg and a highest residue of 1.3 mg/kg for wheat grain and for barley grain. The Meeting agreed to withdraw the previous recommendations for wheat grain (0.5 mg/kg) and barley grain (0.5 mg/kg) and to replace them with the recommendations for wheat grain (2 mg/kg) and barley grain (2 mg/kg).

Supervised field trials were conducted on oats in the USA (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha, 5.4 kg ai/hl; four applications; PHI, 7 days). In the six trials at GAP, the ranked order of concentrations of residues was < 0.02 (6). The Meeting estimated a maximum residue level of 0.02(*) mg/kg, an STMR value of 0.02 mg/kg and a highest residue of 0.02 mg/kg for oat grain. The Meeting agreed to withdraw the previous recommendation for oat grain (0.5 mg/kg) and to replace it with the recommendation for oats (0.02(*) mg/kg).

Field trials on sorghum were conducted in the USA (GAP: water-soluble powder, soluble concentrate; 0.5 kg ai/ha, 0,53 kg ai/hl terrestrial, 2.6 kg ai/hl aerial; two applications; PHI, 14 days). In the five trials at GAP, the ranked order of concentrations of residues was: < 0.02 (2), 0.03, 0.07 and 0.1 mg/kg. The Meeting decided that five trials was insufficient to permit estimation of a maximum residue level or an STMR value and agreed to withdraw the recommendation for sorghum (0.2 mg/kg).

Supervised trials were conducted on maize in the USA (GAP: 0.5 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 21 days for ears). In the six trials at GAP, the ranked order of concentrations of residues was < 0.02 (6). The results for sweet corn support the finding of a maximum residue level of 0.05 mg/kg for maize with no PHI. Supervised field trials were also conducted with thiodicarb; all six trials yielded a residue concentration of < 0.1 mg/kg. Estimations were made on the basis of the data for methomyl, at the lower LOQ. The Meeting estimated an STMR value of 0.02 mg/kg and a maximum residue level of 0.02(*) mg/kg for maize grain to replace the previous recommendation (0.05(*) mg/kg).

Oilseed

Supervised trials of cotton seed were conducted in the USA (soluble concentrate, water-soluble powder; 0.5 kg ai/ha east of the Rocky Mountains, 0.67 kg ai/ha in Texas, 0.76 kg ai/ha west of the Rocky Mountains; 8 kg ai/hl (soluble concentrate), 15 kg ai/hl (water-soluble powder); PHI, 15 days for seed). Supervised trials were also conducted in Greece (soluble concentrate; 0.7 kg ai/ha; one to three applications; PHI, 20 days) and Spain (soluble concentrate; 0.4 kg ai/ha, 0.05 kg ai/hl; two to three applications,; PHI, 7 days). One trial from Spain (with a residue concentration of 0.02 mg/kg), one trial from Greece (< 0.02 mg/kg)and six from the USA were conducted at GAP. The ranked order of concentrations of residues was: ≤ 0.02 (5), 0.02 and 0.1 (2) mg/kg. In supervised field trials conducted with thiodicarb, the ranked order of concentrations of residues was: ≤ 0.04 mg/kg (12), < 0.05, 0.05, 0.09 and 0.10 (3) mg/kg. The Meeting considered that the data sets represented the same populations and combined them, with a ranked order of: < 0.02 (5), 0.02, < 0.04 (12), < 0.05, 0.05, 0.09 and 0.1 (5) mg/kg. The Meeting estimated an STMR value of 0.04 mg/kg, a highest residue of 0.1 mg/kg and a maximum residue level of 0.2 mg/kg for cotton seed to replace the previous recommendation (0.5 mg/kg).

Trials on peanut were conducted in the USA (soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; eight applications; PHI, 21 days). The two trials at GAP gave a concentration of < 0.02 (2) mg/kg. The Meeting concluded that two trials were insufficient to estimate a maximum residue level or STMR value and agreed to withdraw the recommendation for peanut (0.1 mg/kg).

Legume animal feeds

Supervised trials were conducted on alfalfa forage (green) in the USA (water-soluble powder, soluble concentrate; 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 7 days). In the 41 trials at GAP, the ranked order of concentrations of residues in forage was: 0.044, 0.081, 0.10 (2), 0.11, 0.15, 0.25, 0.43, 0.56, 0.57, 0.64, 0.70, 0.98, 1.1, 1.3, 1.5 (2), 1.6, 1.7, 1.8 (2), 1.9, 2.0, 2.1, 2.3 (2), 2.5 (2), 2.6, 3.4, 3.5, 3.6, 3.8, 4.0 (2), 4.2 (2), 4.6, 6.3 and 7.0 (2) mg/kg. Using the default value for dry matter for alfalfa forage (35%), the Meeting estimated an STMR value of 5.1 mg/kg for alfalfa forage and a maximum residue level of 25 mg/kg for alfalfa forage (green) on a dry weight basis. The current MRL is 10 mg/kg for alfalfa forage (green) on a fresh weight basis. The Meeting agreed to withdraw the previous recommendation and to replace it with the recommendation for alfalfa forage (green) (25 mg/kg, dry weight).

For alfalfa hay, 41 trials were at GAP; the ranked order of concentrations of residues was: 0.12, 0.24, 0.25, 0.26, 0.28 (2), 0.32, 0.41, 0.46, 0.92, 1.1 (3), 1.4, 1.5 (2), 1.8, 1.9, 2.2, 2.4, 2.7, 2.9, 3.3, 3.4 (2), 3.5, 3.7, 3.8, 4.0 (2), 4.6, 5.5, 5.6 (2), 6.2, 7.5, 7.9, 10,14, 15 and 17 mg/kg. The Meeting estimated a maximum residue level of 20 mg/kg, an STMR value of 3.0 mg/kg and a highest residue of 19 mg/kg for alfalfa hay on a dry weight basis from the default value for dry matter of 89%.

Supervised trials on bean, pea and soya bean forage were conducted in the USA, where the GAP for bean (succulent) is use of the water-soluble powder or soluble concentrate formulation at 1.0 kg ai/ha, 1.1 kg ai/hl, and a maximum of 10 applications. The PHI is 3 days for vines, 7 days for bean hay, 5 days for forage and 14 days for pea hay. One trial on succulent bean forage was at GAP, resulting in a concentration of 4.3 mg/kg. In four trials on pea vines at GAP, the ranked order of concentrations of residues was: 0.34, 1.3, 6.5 and 7.6 mg/kg. In three trials on soya bean (immature) forage at GAP, the concentrations were: 0.08 (2) and 8 mg/kg. The Meeting determined that the values for forage commodities represented the same population and could be combined to yield, in ranked order, concentrations of: 0.08 (2), 0.34, 1.3, 4.3, 6.5, 7.6 and 8 mg/kg. The default value for dry matter of 25% was used. The Meeting estimated a maximum residue level of 40 mg/kg, an STMR value of 11 and a highest residue of 32 mg/kg for pea vines and for soya bean forage. The Meeting agreed to withdraw the recommendations for pea vines (10 mg/kg fresh weight) and soya bean forage (green) and to replace them with the recommendations for pea vines (green) (40 mg/kg, dry weight) and soya bean forage (green) (40 mg/kg, dry weight).

Supervised trials were conducted in the USA on beans (dry) (GAP: soluble concentrate, water-soluble powder; 1.0 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 14 days). None of the trials for residues in forage was at GAP. In five trials for hay at GAP, the ranked order of concentrations of residues was: < 0.5 (2), 1.1, 3 and 9 mg/kg. The Meeting estimated a maximum residue level of 10 mg/kg, an STMR value of 1.1 mg/kg and a highest residue of 9 mg/kg for bean hay.

Supervised trials were conducted in the USA for soya bean hay (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha; three applications; PHI, 7 days at < 0.5 kg ai/ha, 12 days at > 0.5 kg ai/ha). In eight trials at GAP, the ranked order of concentrations of residues was: 0.021, 0.033, 0.040, 0.050, 0.056, 0.076, 0.099 and 0.13 mg/kg. The Meeting estimated a maximum residue level of 0.2 mg/kg, an STMR value of 0.06 mg/kg and a highest residue of 0.15 mg/kg for soya bean hay, using the default value for dry matter value of 85%.

Fodder and straw of cereal grains

Supervised field trials on barley were conducted in the USA (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha, 5.4 kg ai/hla (soluble concentrate), 6.0 kg ai/hl (water-soluble powder); four applications; PHI, 7 days). In two trials at GAP, the concentrations of residues in straw were 2.8 and

3.1 mg/kg. Trials were conducted with thiodicarb used as a granular bait, but the concentrations were lower (< 0.04 (6), < 0.2 (2) and 0.24 mg/kg). The values for thiodicarb and methomyl thus appear to represent different populations.

Supervised field trials on wheat were conducted in the USA (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha, 5.4 kg ai/hl; four applications; PHI, 7 days). In the 11 trials for wheat straw conducted at GAP, the ranked order of concentrations of residues was: < 0.02, 0.39, 0.43, 0.69, 2.0 (2), 2.8, 3.7, 4.6, 5.7 and 6.5 mg/kg. In trials conducted with thiodicarb as a granular bait, the concentrations of residues were < 0.02 mg/kg, a different population.

Supervised field trials on oats were conducted in the USA (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha, 5.4 kg ai/hl; four applications; PHI, 7 days). No trials on straw were conducted at GAP.

Supervised field trials were conducted in the USA for sorghum stover (GAP: water-soluble powder, soluble concentrate; 0.5 kg ai/ha, 0.53 kg ai/hl terrestrial, 2.6 kg ai/hl aerial; two applications; PHI, 14 days). In eight trials at GAP, the ranked order of concentrations of residues was: 0.38, 0.50, 0.59, 0.81, 0.93, 1.0, 2.5 and 3.4 mg/kg.

Supervised trials were conducted in the USA for maize fodder (GAP: 0.5 kg ai/ha, 1.1 kg ai/hl; 10 applications; PHI, 3 days for forage, 21 days for fodder). In six trials at GAP for fodder, the ranked order of concentrations of residues was: 0.029, 0.053, 0.094 (2), 0.30, and 0.71 mg/kg.

Supervised field trials were conducted in Japan with thiodicarb on rice straw (GAP: 1.2 kg ai/ha; PHI, 30 days). In four trials at GAP, the ranked order of concentrations of residues was: < 0.5, 0.62, and ≤ 1 (2) mg/kg.

Supervised field trials were conducted in the USA on sorghum (GAP: water-soluble powder, soluble concentrate; 0.5 kg ai/ha, 0.53 kg ai/hl terrestrial, 2.6 kg ai/hl aerial; two applications; PHI, 14 days). In nine trials for sorghum hay at GAP, the ranked order of concentrations of residues was: < 0.02 (3), 0.033, 0.035 (2), 0.039, 0.096 and 0.59 mg/kg

The Meeting considered that the values for residues in cereal grain commodities (fodder, stover, straw) represented the same population (except for use of thiodicarb as granular bait on wheat and barley) and combined the values, which, in ranked order, were: < 0.02 (4), 0.029, 0.033, 0.035 (2), 0.039, 0.053, 0.094 (2), 0.096, 0.30, 0.38, 0.39, 0.43, < 0.5, 0.50, 0.59 (2), 0.62, 0.69, 0.71, 0.81, 0.93, < 1 (2), 1.0, 2.0 (2), 2.5, 2.8 (2), 3.1, 3.4, 3.7, 4.6, 5.7 and 6.5 mg/kg. Using a default value for dry matter of 88%, the Meeting estimated a maximum residue level of 10 mg/kg, an STMR value of 0.67 mg/kg and a highest residue of 7.4 mg/kg for cereal grain fodder and straw. The Meeting agreed to withdraw the recommendations for barley straw and fodder, dry (5 mg/kg), maize fodder (50 mg/kg fresh weight), and oats straw and fodder, dry (5 mg/kg), and to replace them with the recommendation for cereal grain, straw, fodder (dry), hay (10 mg/kg).

Supervised field trials were conducted on sorghum forage (green) in the USA (GAP: water-soluble powder, soluble concentrate; 0.5 kg ai/ha, 0.53 kg ai/hl terrestrial, 2.6 kg ai/hl aerial; two applications; PHI, 14 days). In nine forage trials at GAP, the ranked order of concentrations of residues was: < 0.02 (3), 0.024, 0.042, 0.046, 0.068, 0.19 and 0.22 mg/kg. Using the default value for dry matter of 35%, the Meeting estimated a maximum residue level of 1 mg/kg, an STMR value of 0.12 mg/kg and a highest residue of 0.63. The Meeting agreed to maintain the current recommendation for sorghum forage (green) (1 mg/kg).

Supervised trials were conducted on sweet corn forage in the USA (GAP: soluble concentrate, 0.5 kg ai/ha, 5.4 kg ai/hl; 28 applications; no PHI for maize or fodder, 3 days for forage). In eight trials for forage at GAP, the ranked order of concentrations of residues was: 2.3, 2.5, 2.7, 2.9, 3.2, 3.3 (2) and 4.8. Supervised field trials were also conducted with thiodicarb; the ranked order of concentrations of residues in forage was: < 0.02, < 0.05, 0.06, 0.16, 0.21, 0.56, 1.1, 2.3, 5.2, 6.9, 11 and 18 mg/kg. The Meeting considered that the two sets of values represented the same population and combined them. They were, in ranked order: < 0.02, < 0.05, 0.06, 0.16, 0.21, 0.56, 1.1, 2.3 (2), 2.5, 2.7, 2.9, 3.2, 3.3 (2), 4.8, 5.2, 6.9, 11 and 18 mg/kg.

Supervised trials were also conducted in the USA on maize forage (GAP: 0.5 kg ai/ha, 1.1 kg ai/; 10 applications; PHI, 3 days for forage, 21 days for fodder). In six trials at GAP for forage, the ranked order of values was: 0.72, 1.0, 1.3, 1.8, 6.6 and 6.9 mg/kg.

The Meeting considered that the data for maize forage were part of the set for sweet corn forage and combined them. The ranked order of concentrations of residues was: < 0.02, < 0.05, 0.06, 0.16, 0.21, 0.56, 0.72, 1.0, 1.1, 1.3, 1.8, 2.3 (2), 2.5, 2.7, 2.9, 3.2, 3.3 (2), 4.8, 5.2, 6.6, 6.9 (2), 11 and 18 mg/kg. Using the default value for dry matter value of 40%, the Meeting estimated a maximum residue level of 50 mg/kg, an STMR value of 6.0 mg/kg and a highest residue of 45 mg/kg for maize forage on a dry weight basis. The Meeting agreed to withdraw the recommendation for maize forage (50 mg/kg, fresh weight) and to replace it with the recommendation for maize forage (50 mg/kg, dry weight).

Supervised field trials were conducted on wheat forage in the USA (GAP: soluble concentrate, water-soluble powder; 0.5 kg ai/ha, 5.4 kg ai/hl; four applications; PHI, 7 days). In 17 trials at GAP for forage, the ranked order of concentrations of residues was: 0.02, 0.05, 0.06, 0.12 (2), 0.24, 0.26, 0.37, 0.38, 0.53, 0.57, 0.59, 0.85, 2.7, 3.1 and 4.9 (2)mg/kg. Using the default value for dry matter of 25%, the Meeting estimated an STMR value of 1.5 mg/kg and a highest residue of 20 mg/kg. The Meeting did not estimate a maximum residue limit, as wheat forage is not a recognized commodity.

Unsupported uses

No supervised trials were reported for hops, dry, mint hay, onion, Welsh, peanut forage (green) or pineapple. The Meeting agreed to withdraw the previous recommendations for hops, dry (10 mg/kg), mint hay (2 mg/kg), onion, Welsh (0.5 mg/kg), peanut forage (5 mg/kg) and pineapple (0.2 mg/kg).

Fate of residues during processing

Fifteen studies were reported on processing of 13 raw agricultural commodities. In all the studies, the commodities contained field-incurred residues of methomyl, typically after application rates in excess of GAP. The studies simulated commercial practices, except where consumer practices were indicated. Methomyl occurred in only three matrices: dried orange peel, apple peel and wheat bran, supporting the observation that methomyl has little tendency to translocate. Furthermore, methomyl did not concentrate in oily fractions. Similarly, thiodicarb concentrated in soya bean hulls and sweet corn cannery waste.

The maximum residue levels, STMR values and highest residues given above were multiplied by the relevant processing factor to obtain the maximum residue level (where appropriate), the STMR-P value and the HR-P value for processed commodities of raw agricultural commodities. The results of similar studies with thiodicarb are also included, as appropriate (see the report item on thiodicarb). The calculations are summarized below.

Commodity	STMR	HR	MRL	Processed	Processin	STMR-	HR-P	MRL

(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	commodity	g factor	P (mg/kg)	(mg/kg)	(mg/kg)
Apple	0.41	1.6	2	Apple juice	0.29[a]	0.12	0.46	
				Apple pomace, wet	0.30[b]	0.12	0.48	
Citrus (orange)	0.17	0.89	1	Citrus juice	0.021	0.004	0.019	
				Citrus pulp, dry	2.9	0.49	2.6	3
Cotton seed	0.04	0.1	0.2	Cotton seed, edible oil	0.16[c]	0.006	0.016	0.04
				Cotton seed, hulls	0.96[d]	0.038	0.096	0.2
				Cotton seed, meal	0.32[e]	0.013	0.032	0.05
Grape	0.86	5.2	7	Wine	0.3[b]	0.26	1.6	
Maize	0.02	0.02	0.02 (*)	Maize, edible oil	0.18	0.004	0.004	0.02 (*)
Soya bean	0.04	0.15	0.2	Soya bean, hulls	3.6[b]	0.14	0.54	1
				Soya bean, meal	1	0.04	0.15	0.2
				Soya bean, oil crude	1	0.04	0.15	0.2
				Soya bean, oil refined	1	0.04	0.15	0.2
Sweet corn	0.065	1.5	2	Cannery waste	78[b]	5.1	120	
Tomato	0.16	0.73	1	Tomato paste	0.04[f]	0.006	0.030	
Wheat grain	0.14	1.3	2	Wheat flour	0.02	0.003	0.026	0.03
				Wheat bran	1.9	0.27	2.5	3
				Wheat germ	0.92	0.13	1.2	2

[a]Thiodicarb factor (0.014 for canned juice) and methomyl factor (0.29 for fresh juice)
[b]Thiodicarb processing study
[c]Average of thiodicarb factor (0.2) and methomyl factor (< 0.12)
[d]Average of thiodicarb factor (1.1) and methomyl factor (0.82)
[e]Average of thiodicarb factor (0.26) and methomyl factor (0.38)
[f]Average of thiodicarb factor (0.03) and methomyl factor (0.053)

A study of the results of peeling in a manner similar to that of consumers was conducted with unwashed oranges. The residue reduction factor was 0.2, and this factor was applied to the results of the field trial with citrus (see above) to give an STMR-P of 0.034 mg/kg.

Residues in animal commodities

Two feeding studies were conducted with lactating dairy cattle, one of which involved radiolabelled methomyl.

Lactating Holstein dairy cows were fed diets containing methomyl for 28 consecutive days at concentrations corresponding to 0, 8.1, 34, or 86 ppm. Milk was collected daily, and tissues were harvested immediately after the last day of treatment. The samples were stored at –70 °C to preclude degradation of methomyl. The compound was not found at the LOQ (0.01 mg/kg) in any tissue or milk

sample from cows at any feeding level. The apparent concentrations were similar to those in control samples, < 0.002 – < 0.005 mg/mg, for all samples.

A mixture of methomyl and [^{14}C]methomyl was given orally for 28 consecutive days to lactating dairy cows at a rate of 0, 2, 24 or 80 ppm, as ascertained from actual feed consumption. Milk and tissue samples were stored at –20 ^{o}C for up to 2 months before analysis. Studies of stability in storage showed that methomyl was stable in milk and muscle, variably stable in fat (up to 50% loss) and unstable in kidney and liver (> 90% loss over 24 months). Methomyl and methomyl oxime were not found at the LOQ of 0.02 mg/kg in whole milk, cream or skim milk from cows at 24 or 80 ppm. Methomyl was detected in only one sample, a sample of cream from a control animal, at about 0.02 mg/kg. Likewise, neither methomyl nor methomyl oxime was found in tissue samples. However, the storage conditions would have led to degradation of residues in fat, liver and kidney.

Acetonitrile and acetamide were determined in the milk and tissue samples. The maximum concentration of acetonitrile was 0.08 mg/kg in whole milk, while the concentrations in tissues were 0.08 mg/kg in liver, 0.04 mg/kg in kidney, 0.04 mg/kg in muscle and < 0.01–0.01 mg/kg in fat. Studies of stability in storage indicated that as much as 50% of the acetonitrile may have been lost during storage. The concentrations of acetamide in samples of whole milk from cows at 80 ppm contained 2.8–6.6 mg/kg, whereas the concentrations in tissues were 14 mg/kg in liver, 9 mg/kg in kidney, 9 mg/kg in muscle and 5 mg/kg ins subcutaneous fat. Acetamide is endogenous. Determinations of [^{14} C]acetamide showed concentrations attributable to methomyl of < 0.003–0.09 mg/kg in milk, 0.03 mg/kg in muscle and 0.05 mg/kg in liver.

The Meeting concluded that methomyl and methomyl oxime do not bioaccumulate. No residues were detectable in milk or tissues at the concentrations in feed that were studied.

The Meeting estimated the dietary burden of dairy and beef cattle (and poultry) from the diets listed in Appendix IX of the *FAO Manual*. Calculation from maximum residue levels yields the maximum theoretical dietary intake or the level of residues in feed suitable for estimating MRLs for animal commodities. Calculation from STMR values for feed yields estimated STMR values for animal commodities. The diets described are designed to maximize dietary exposure to thiodicarb, and nutritional requirements are not taken into account. The maximum residue levels for processed commodities were derived from the maximum or highest residue values estimated above for raw agricultural commodities, multiplied by the appropriate concentration or reduction factor from the processing studies. An exception is processed commodities that are considered to be blended, such as sweet corn cannery waste. For these, the STMR value of the raw agricultural commodity is multiplied by the processing factor to obtain the maximum residue level in the processed feed commodity.

Calculation of maximum theoretical dietary burden for animals

Commodity	Maximum or highest residue level (mg/kg)	STMR or STMR-P (mg/kg)	Group	Dry matter (%)	Per cent of diet				Residue contribution (mg/kg)			
					Beef cattle	Dairy cows	Poul-try	Pig	Beef cattle	Dairy cows	Poul-try	Pig
Alfalfa forage	25	0.12	AL	–	70	60	–	–				
Alfalfa hay	20		AL	–	70	60	–	–				
Apple pomace, wet			AB	40	40	20						
Barley grain	2	0.49	GC	88	50	40	75	80				
Cereal grain fodder	10		AS	–	10	10						
Citrus dry pulp		0.013	AB	91	20	20	–	–				
Cotton seed	0.2	0.038	SO	88	25	25	–	–				

Commodity	Maximum or highest residue level (mg/kg)	STMR or STMR-P (mg/kg)	Group	Dry matter (%)	Per cent of diet				Residue contribution (mg/kg)			
					Beef cattle	Dairy cows	Poul-try	Pig	Beef cattle	Dairy cows	Poul-try	Pig
Cotton seed meal			SO	89	15	15	20	15				
Cotton seed hulls				90	20	15	–	–				
Maize grain	0.02		GC	88	80	40	80	80				
Maize forage	50		AF	–	40	50	–	–	20	25		
Pea vine	40		AL	–	25	50						
Rape seed forage	0.2	0.04	SO	–	30	30						
Sorghum forage (green)	1	0.14	AF	–	40	50	–	–				
Soya bean meal			VD	92	15	15	40	25				
Soya bean hulls				90	20	20	20				0.03	
Soya bean hay	0.2	0.27	AL	–	30	30	–	–				
Sweet corn cannery waste	5.1			30	35	20	–	–	6.0	3.4		
Wheat bran			CF		59	40						
Wheat grain	2		GC	89	~~50~~ 25	~~40~~ 30	80	80	0.56	0.67	1.8	
Wheat forage	20			–	25	60	–	–				
Wheat straw	10		AS	88	10	10	–	–				
Total					100	100	100		27	29	2.0	

The average daily dietary burden of methomyl for ruminants is a fraction of the maximum daily burden, about 28 mg/kg. The maximum daily burden is expected to yield no quantifiable residues of methomyl in meat, meat by-products or milk, in view of the absence of residues in cows fed at 86 ppm and the absence of methomyl in the study of the nature of the residue in ruminants. Thus, the STMR values for milk, meat and meat by-products are estimated to be 0.000 mg/kg. The highest residue values for meat, edible offal and milk are also estimated to be 0.000 mg/kg; as there is no reasonable expectation that residues will occur. The maximum residue levels for meat, edible offal and milk are estimated to be 0.02(*) mg/kg, the typical LOQ. The Meeting agreed to maintain the current recommendations of 0.02(*) mg/kg for milks and for meat (from mammals other than marine mammals).

No study of poultry feeding was provided, but the study of the nature of the residue in poultry, conducted at a concentration equivalent to 45 ppm in feed, showed no methomyl or methomyl oxime in tissues or eggs at an LOQ of 0.015 mg/kg. As the study lasted only 3 days, the concentrations of residues may not have reached a plateau in eggs or tissues. A 21-day study with thiodicarb fed at 102 ppm also showed no accumulation of methomyl or thiodicarb. Thus, at a projected dietary intake of 2 mg/kg, no methomyl is anticipated to occur in the tissues or eggs.

The Meeting estimated a maximum residue level of 0.02(*) mg/kg for thiodicarb plus methomyl in eggs, in poultry meat and in edible offal of poultry. The Meeting also estimated highest residues and STMR values for these commodities, each at 0.00 mg/kg.

RECOMMENDATIONS

On the basis of the consideration of data from supervised trials and processing studies for methomyl and thiodicarb, the Meeting concluded that the values given in the report item on methomyl are suitable for establishing MRLs and for assessing long-term and short-term dietary intake.

<u>Definition of residue</u> (for compliance with the MRL and for estimation of dietary intake): sum of thiodicarb and methomyl, expressed as methomyl

CCN	Commodity	MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR (mg/kg)
		New	Previous		
AL 1021	Alfalfa forage (green)	25[a]	10 (fresh weight)		
AL 1020	Alfalfa fodder (hay)	20[a]	–		
FP 0226	Apple	2[b, c]	–	0.41	1.6
JF 0226	Apple juice	–	–	0.12	
VS 0621	Asparagus	2[a]	2	0.33	1.1
GC 0640	Barley	2[a]	0.5		
AS 0640	Barley straw and fodder, dry	W	5		
VD 0071	Beans (dry)	0.05[a]	0.1	0.02	0.023
AL 0061	Bean fodder (hay)	10[a]	–		
VP 0061	Beans (except broad and soya)	1[a]	–	0.005	0.68
VB 0040	Brassica (cole or cabbage) vegetables	7 [c, d]	–	1.3	5.6
VB 0041	Cabbages, Head	W	5		
VB 0404	Cauliflower	W	2		
VS 0624	Celery	3[a,c]	2	0.66	2
AS 0161	Cereal grain, straw, fodder (dry), hay	10[d]	–		
FC 0001	Citrus fruits	1[a]	1	0.034 pulp	0.18 pulp
AB 0001	Citrus pulp, dry	3	–		
JF 0001	Citrus juice	–		0.004	
VP 0526	Common bean (pods and/or immature seeds)	1[a]	2	0.055	0.68
SO 0691	Cotton seed	0.2[d]	0.5		
OR 0691	Cotton seed, edible oil	0.04		0.006	
	Cotton seed, meal	0.05	–		
	Cotton seed, hulls	0.2	–		
VC 0424	Cucumber	W	0.2		
MO 0105	Edible offal (from mammals other than marine mammals)	0.02(*)[d]	–	0.00	0.00
VO 0440	Egg plant	W	0.2		
PE 0112	Eggs	0.02 (*)[d]	–	0.00	0.00
VC 0045	Fruiting vegetables, cucurbits	0.1[a,e]		0.02	0.07
FB 0269	Grapes	7[a,c]	5	0.86	5.2
DH 1100	Hops, dry	W	10		
VL 0480	Kale	W	5		
VL 0482	Lettuce, Head	W	5		
VL 0053	Leafy vegetables	30[c,d]	–	1.4	25
GC 0645	Maize	0.02 (*)[a]	0.05(*)	0.02	0.02
AS 0645	Maize fodder	W	50 fresh weight		
AF 0645	Maize forage	50 [d]	50 fresh weight		
OR 0645	Maize, edible oil	0.02 (*)	–	0.004	
MM 0095	Meat (from mammals other than marine mammals)	0.02 (*)[d]	0.02 (*)	0.000	0.000
VC 0046	Melons, except watermelon	W	0.2		
ML 0106	Milks	0.02 (*)[d]	0.02 (*)	0.000	
AM 0738	Mint hay	W	2		
FS 0245	Nectarines	0.2[a]	5	0.05	0.10
AS 0647	Oat straw and fodder, dry	W	5		
GC 0647	Oats	0.02 (*)[a]	0.5		
VA 0385	Onion, Bulb	0.2[a]	0.2	0.068	0.14
VA 0387	Onion, Welsh	W	0.5		
AL 0528	Pea vines (green)	40[a]	10 fresh weight		

CCN	Commodity	MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR (mg/kg)
		New	Previous		
FS 0247	Peach	0.2[a]	5	0.05	0.10
SO 0697	Peanut	W	0.1		
AL1270	Peanut forage (green)	W	5		
FP 0230	Pear	0.3[a]	–	0.09	0.18
VP 0063	Peas (pods and succulent or immature seeds)	5[a]	5	0.46	4.0
VP 0064	Peas, shelled (succulent seeds)	W	0.5		
VO 0051	Peppers	W	1		
Fl 0353	Pineapple	W	0.2		
FS 0014	Plums	1[a]	–	0.08	0.51
FP 0009	Pome fruits	W	2		
VR 0589	Potato	0.02 (*)[d]	0.1	0.00	0.00
PM 0110	Poultry meat	0.02 (*)[d]	–	0.00	0.00
PO 0111	Poultry, edible offal of	0.02 (*)[d]	–	0.00	0.00
SO 0495	Rape seed	0.05[b]	–		
	Rape seed forage	0.2	–		
GC 0651	Sorghum	W	0.2		
AF 0651	Sorghum forage (green)	1[a]	1		
VD 0541	Soya bean (dry)	0.2[b]	0.2		
VP 0541	Soya bean (immature seed)	W	0.1		
AL 1265	Soya bean forage (green)	40[a]	10		
AL 0541	Soya bean hay	0.2[a]	–		
	Soya bean hulls	1	–		
	Soya bean meal	0.2			
OC 0541	Soya bean oil, crude	0.2	–	0.04	
OR 0541	Soya bean oil, refined	0.2	–	0.04	
VL 0502	Spinach	W	5		
VC 0431	Squash, Summer	W	0.2		
VR 0596	Sugar beet	W	0.1		
VO 0447	Sweet corn (corn-on-the-cob)	2[b,c]	2	0.065	1.5
VO 0448	Tomato	1[b,c]	1	0.16	0.73
VJ 0448	Tomato paste	–	–	0.007	
VC 0432	Watermelon	W	0.2		
GC 0654	Wheat	2[a]	0.5	0.14	1.3
CF 0121	Wheat flour	0.03	–	0.003	
CF 0654	Wheat bran	3	–	0.27	
CF 1210	Wheat germ	2	–	0.13	
–	Wine, of grape	–	–	0.26	

W, withdrawn
[a]Resulting from data on supervised field trials with methomyl
[b]Resulting from data on supervised field trials with thiodicarb
[c]The information provided to the JMPR precluded an estimate that the dietary intake would be below the acute RfD.
[d]Resulting from data on supervised field trials with methomyl plus thiodicarb
[e]The information provided to the JMPR precluded an estimate that the dietary intake of methomyl from watermelon would be below the acute RfD.

Dietary risk assessment

Long-term intake

STMR or STMR-P values were estimated by the present Meeting for 39 commodities. When data on consumption were available, these values were used in the estimates of dietary intake.

The dietary intakes in the five GEMS/Food regional diets, on the basis of the new STMR values, represented 1–20% of the ADI (Annex 3-Report 2001)). The Meeting concluded that the intake of residues of thiodicarb and methomyl resulting from the uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The IESTI for thiodicarb plus methomyl was calculated for the commodities for which maximum residue levels, STMR values and highest residues were established and for which data on consumption (of large portions and unit weight) were available. The results are shown in Annex 4.

The acute RfD for methomyl is 0.02 mg/kg bw. The IESTI represented 0–7200% of the acute RfD for children and 0–2800 % of the acute RfD for the general population. For children, the 100% of acute RfD was exceeded in: apples (770%), broccoli (1500%), Brussels sprouts (450%), head cabbage (1200%), cauliflower (1700%), celery (150%), watermelon (140%), grapes (1600%), kale (1100%), head lettuce (3000%), leaf lettuce (3800%), spinach (7200%), sweet corn (420%) and tomato (190%). For the general population, the acute RfD was exceeded in: apples (260%), broccoli (810%), Brussels sprouts (200%), head cabbage (320%), cauliflower (590%), grapes (470%), kale (670%), head lettuce (2000%), leaf lettuce (1500%), spinach (2800%) and sweet corn (140%).

The information provided to the Meeting precluded an estimate that the acute dietary intake of methomyl plus thiodicarb from the consumption of apples, broccoli, Brussels sprouts, head cabbage, cauliflower, celery (children only), watermelon (children only), grapes, kale, head lettuce, leaf lettuce, spinach, sweet corn and tomato (children only) would be below the acute RfD. The Meeting concluded that the short-term intake of residues of methomyl plus thiodicarb from uses, other than on these 14 commodities, that have been considered by the JMPR is unlikely to present a public health concern.

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PIPERONYL BUTOXIDE (062)

EXPLANATION

Piperonyl butoxide (PBO) is a synergist used to prolong the effects of the natural insecticides pyrethrin and rotenone, and many synthetic insecticides. The compound was reviewed by the 1992 JMPR for residues and toxicology, but the Meeting could not then evaluate the compound fully because the critical data were incomplete, particularly in relation to the metabolism of plants and animals. Stability and processing studies were reported for commercially stored wheat and wheat products only. The withdrawal of all MRLs was therefore recommended.

At its 26th Session (1994) the CCPR decided to withdraw the CXL for cereal grains and all other commodities except for wheat, which was advanced to step 5/8 (ALINORM 95/24). At its 27th Session the CCPR tentatively scheduled piperonyl butoxide under its Periodic Review Programme for residue re-evaluation by the 1999 JMPR but it was postponed to 2000 by the CCPR at its 30th Session (ALINORM 99/24 App.VII).

The present Meeting received information on physical and chemical properties, metabolism and environmental fate, analytical methods, freezer storage stability, registered uses, data from supervised trials on pre-and post-harvest uses, processing and animal feeding studies, residues in food in commerce and national residue limits from the manufacturer. The governments of Australia and Germany provided information on registered uses and national residue limits.

IDENTITY

ISO common name: piperonyl butoxide (accepted in lieu of common name)

Chemical name:

IUPAC: 5-[2-(2-butoxyethoxy)ethoxymethyl]-6-propyl-1,3-benzodioxole
2-(2-butoxyethoxy)ethyl 6-propylpiperonyl ether

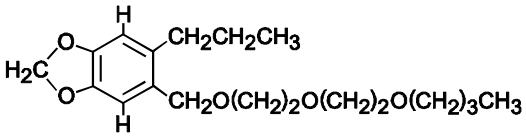
CA: 5-[[2-(2-butoxyethoxy)ethoxy]methyl]-6-propyl-1,3-benzodioxole

CAS No.: 51-03-6

CIPAC No: not listed

Other names: α-(2-butoxyethoxy)ethoxy-4,5-(methylenedioxy)-2-propyltoluene
α-(2-n-butoxyethoxy)ethoxy-4,5-(methylenedioxy)-2-propyltoluene
6-propylpiperonyl butyl diethyleneglycol ether

Structural formula:



Molecular formula: $C_{19}H_{30}O_5$

Molecular weight: 338.43

Physical and chemical properties (Endura, 1999)

Physical form:	oily liquid at room temperature
Colour:	pale to deep yellow (4.5 max Gardner scale)
Odour:	faint characteristic odour
Boiling point:	180°C at 1 mm Hg
Melting point:	liquid at room temperature
Flash point:	179°C (EEC method A9)
Autoflammability (ignition point):	>245°C
Explosion hazard:	none
Oxidizing properties:	none
Vapour pressure:	1.33×10^{-2} mPa at 25°C
Solubility in water:	14.3 mg/l at 25°C
Solubility:	highly soluble in most organic solvents
Purity :	90% min
Relative density:	1.05-1.07 (20°C)
Refractive index:	1.497-1.512 at 20°C
Stability:	the shelf life exceeds 2 years
Octanol-water partition coefficient (Log P_{ow}):	4.62
Henry's Law constant:	$<2.35 \times 10^{-4}$ l-atm/mole
Hydrolysis:	stable at pH 5-9 at 25°C
Photolysis:	half-life at pH 7 8.4 hours

METABOLISM AND ENVIRONMENTAL FATE

Piperonyl butoxide radiolabelled with ^{14}C in the glycol-derived side chain (Figure 1) or uniformly in the benzene ring was used in the studies.

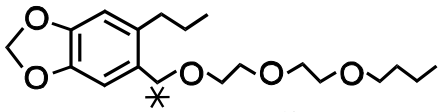


Figure 1. Site of radiolabel in [^{14}C]piperonyl butoxide

The names of the metabolites with the abbreviations found in the metabolism and environmental fate studies are listed below. The structures of metabolites A-Z are shown in Figure 2, those of M2-M12 and M14-M17 in Figure 3, M13 and HMDs in Figure 5, M20-M22 in Figure 9, and M23-M27 in Figure 11.

Metabolite A (MA): 1,3-benzodioxole-5,6-dicarboxylic acid
MB: 5,6-dihydroxyphthalide (4,5-dihydroxy-2-hydroxymethylbenzoic acid)
MC: lactone of (6-hydroxymethyl-1,3-benzodioxol-5-yl)acetic acid
MD: (6-propyl-1,3-benzodioxole-5-yl)methoxyacetic acid
ME: 6-propyl-1,3-benzodioxole-5-carboxylic acid or 4,5-methylenedioxy-2-propylbenzoic acid
MF: (2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}ethoxy)acetic acid
MG: 4-{[2-(2-butoxyethoxy)ethoxy]methyl}-5-propyl-1,2-benzenediol
MZ: 2-oxa-5,6-methylenedioxyindane
M2: 4-{[2-(2-butoxyethoxy)ethoxy]methyl}-2-methoxy-5-propylphenol
M4: 2-(2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}ethoxy)ethanol
M5: 2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}ethanol
M7: 2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}acetic acid
M8: 4-{[2-(2-butoxyethoxy)ethoxy]methyl}-5-propyl-1,2-benzenediol glucuronide
M9: 4-{[2-(2-butoxyethoxy)ethoxy]methyl}-2-methoxy-5-propylphenol glucuronide
M10: 2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}ethanol glucuronide
M11: 2-[2-(4-hydroxy-5-methoxy-2-propylbenzyloxy)ethoxy]ethoxyacetic acid
M12: 2-(4-hydroxy-5-methoxy-2-propylbenzyloxy)ethoxyacetic acid
M13: 4-{2-[2-(hydroxyethoxy)ethoxy]methyl}-5-propyl-1,2-benzenediol
M14: 2-[2-(5-hydroxy-2-propyl-4-sulfooxybenzyloxy)ethoxy]ethoxyacetic acid
M16: 4,5-dihydroxy-2-propylbenzyloxyacetic acid phenolic glucuronide
M17: 2-[2(4-hydroxy-5-methoxy-2-propylbenzyloxy)ethoxy]ethanol glucuronide
HMDS: hydroxymethyldihydrosafrole
M20: Glucose conjugate of HMDS
M21: Glucose conjugate of 2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethanol
M22: Glucose conjugate of 4-{2-[z-(6-propyl-1,3-benzodioxol-5-ylmethoxy)ethoxy]ethoxy}butan-1-ol
M23:4,5-methylenedioxy-2-propylbenzaldehyde
M24: bis(3,4-methylenedioxy-6-propylbenzyl) ether
M25: 2'-[2-(2-butoxyethoxy)ethoxy(hydroxy)methyl]4',5'-methylenedioxypropiophenone
M26: 2'-[2-(2-butoxyethoxy)ethoxymethyl]4',5'methylenedioxypropiophenone
M27: 2-ethylcarbonyl-4,5-methylenedioxybenzaldehyde

Animal metabolism

Rats. Lin and Selim (1991) dosed five male and five female Charles River DC rats orally with [^{14}C]PBO in three ways: single low doses at 50 mg/kg bw, single high doses at 500 mg/kg bw, and 13 daily doses with unlabelled piperonyl butoxide at 50 mg/kg bw followed by one radioactive dose at the same level.

Urine and faeces were collected at intervals and the rats were killed seven days after the (last) dose. Approximately two-thirds of the dosed ^{14}C in both male and female rats was excreted in the faeces, and the remainder in the urine, regardless of the dosage regimen. Recoveries from the tissues and carcase were less than 1.5% of the administered dose (Table 1).

Table 1. Radioactivity in the urine, faeces and tissues of rats (Lin and Selim, 1991).

Time (hours)	^{14}C, % of dose					
	Single low dose		Single high dose		Repeated low dose	
	Male	Female	Male	Female	Male	Female
URINE						
0-4	2.38	2.0	0.87	0.51	1.68	3.12
4-8	7.16	4.2	1.99	0.81	9.74	8.03
8-12	3.57	4.15	2.73	3.25	5.8	4.83
12-24	8.34	9.21	8.59	6.91	8.62	8.4
24-36	6.82	4.99	6.02	6.66	3.39	5.14
36-48	2.61	3.92	2.8	5.15	2.07	3.43
48-72	2.38	3.67	2.02	4.11	2.62	4.07
72-96	0.72	1.74	1.0	2.08	1.16	2.31
96-120	0.67	0.89	0.61	1.32	0.55	0.97
120-144	0.42	0.53	0.33	0.72	0.31	0.47
144-168	0.22	0.36	0.19	0.55	0.20	0.27
Final rinse	0.06	0.07	0.06	0.23	0.05	0.03
Total	35.6	35.7	27.2	32.3	36.2	38.1
FAECES						
0-4	NS	0.09	NS	NS	0.01	NS
4-8	NS	0.11	0.11	0.21	NS	0.10
8-12	NS	3.5	NS	0.06	2.1	6.05
12-24	20.6	28.3	28.6	25.4	31.8	26.7
24-36	13.4	9.17	14.0	11.09	8.7	4.04
36-48	15.4	7.64	11.4	10.4	7.55	7.16
48-72	6.06	3.88	6.78	7.32	5.41	5.41
72-96	3.3	2.89	2.66	4.13	2.01	3.0
96-120	2.05	1.21	1.6	2.04	1.14	1.35
120-144	0.97	0.63	0.70	0.82	0.57	0.59
144-168	0.61	0.34	0.40	0.37	0.54	0.40
Total	63.0	56.2	66.2	61.6	59.8	54.8
CARCASE AND TISSUES						
Total	1.49	0.89	1.0	1.19	1.14	0.77

NS: no sample excreted

In the tissues the highest residue levels were found in the liver (1.1-1.2 mg/kg) and gastro-intestinal tract (up to 2.0 mg/kg) and were 0.10-1.0 mg/kg in the kidneys, gastro-intestinal tract

contents, and residual carcases of the male rats and in the fat, spleen, adrenal and thyroid glands, gastro-intestinal tract contents, uterus, ovaries and residual carcase of female rats.

Piperonyl butoxide was extensively metabolized. There were only trace amounts of unchanged PB0 in the urine (Selim, 1991) (Table 2). Metabolism can occur at the propyl and glycol-derived side chains to produce the three metabolites MB, MC and MZ by cyclization, and in the heterocyclic ring (Figure 2). Oxidation on the glycol side chain is the main degradation pathway. In male rats MC was found to be the main metabolite in the urine. In females, MB and MZ predominated in the urine at the low dose, and MF at the high dose. Piperonyl butoxide, MF, MH and MD were the main compounds in the faeces of both sexes.

Table 2. Distribution of piperonyl butoxide and metabolites in rat excreta (Selim, 1991).

Dose group	^{14}C, % of dose, in								
	PBO	MA	MB	MC	MD	ME	MF	MG	MZ
Urine									
SOL-M	ND	2.6	2.1	6.8	0.7	1.7	0.5	ND	1.3
SOL-F	0.3	1.8	3.7	1.6	0.9	1.1	1.4	0.6	3.4
ROL-M	<0.2	2.7	2.4	6.7	1.2	1.1	1.1	<0.2	1.7
ROL-F	<0.2	1.2	4.1	2.1	1.4	1.2	2.1	2.4	3.5
SOH-M	<0.2	1.4	2.5	5.2	0.8	1.9	3.5	<0.2	1.8
SOH-F	<0.2	0.8	3.4	1.1	0.6	1.8	6.9	0.8	1.8
Faeces									
SOL-M	11.0	<0.2	<0.2	1.9	9.7	<0.2	7.2	13.8	<0.2
SOL-F	9.7	<0.2	<0.2	<0.2	3.1	<0.2	9.5	9.4	<0.2
ROL-M	2.2	<0.2	<0.2	2.1	8.3	<0.2	2.3	21.4	<0.2
ROL-F	3.6	<0.2	<0.2	<0.2	2.7	<0.2	4.8	26.1	<0.2
SOH-M	12.3	<0.2	<0.2	1.7	6.0	<0.2	4.3	15.5	<0.2
SOH-F	30.6	<0.2	<0.2	<0.2	<0.2	<0.2	2.6	15.0	<0.2

M: male; F: female; SOL: single oral low of 50 mg/kg bw; SOH: single oral high of 500 mg/kg bw; ROL: repeat oral low, 14 x 50 mg/kg bw.

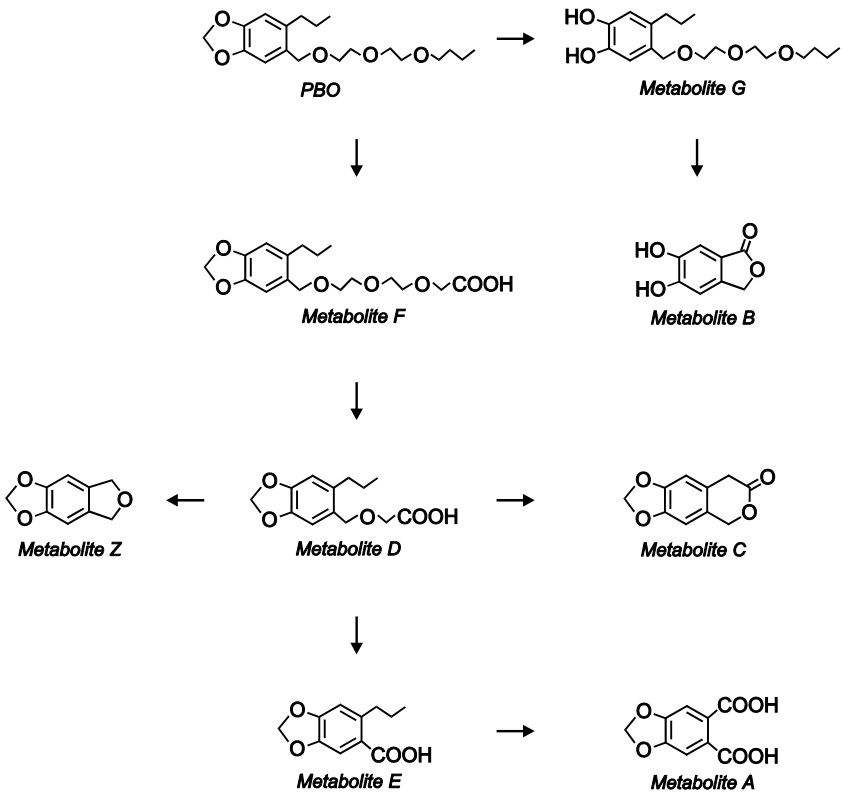


Figure 2. Proposed metabolic pathways of piperonyl butoxide in the rat (Selim, 1991).

Radiolabelled piperonyl butoxide in a typical formulation was sprayed onto discs of skin excised from five ten-week-old Sprague Dawley rats (Selim, 1994b). 5 min and 24 hours after application, the skin samples were washed with detergent solution, and then by ethanol and hexane. The samples were then tape-stripped to remove any radioactivity in the dead skin cells and homogenized. After 24 hours, a considerable proportion of the dose was recovered in the skin homogenate (Table 3).

Table 3. Average percentage recoveries of radioactivity from rat skin treated with [^{14}C]PBO (Selim, 1994b).

Time	Enclosure rinse	1st detergent wash	10 detergent washes	Ethanol rinse	Hexane rinse	Tape strips	Skin homogenate
5 min	1.75	92.5	3.73	0.08	0.11	0.04	0.67
24 h	7.18	35.0	16.6	0.87	0.87	0.50	31.1

In another study, four groups of four Sprague-Dawley CRL:CD rats seven to nine weeks old were given single doses of ring-labelled piperonyl butoxide, at a nominal rate of either 50 or 500 mg/kg bw (Bard *et al.*, 1999). After dosing, urine and faeces were collected for seven days. The rats were killed and the intact carcases were analysed for ^{14}C. Excretion was rapid and essentially 100%. Most of the radioactivity was eliminated within 48 hours after dosing, mainly in the faeces (Table 4).

Table 4. Distribution of radioactivity in rats dosed with piperonyl butoxide (Bard *et al.*, 1999).

Sample	^{14}C, % of dose			
	50 mg/kg bw		500 mg/kg bw	
	Male	Female	Male	Female
Urine	11.1	14.4	19.5	23.1
Faeces	85.1	82.9	75.9	69.9
Cage Wash	1.65	1.95	1.98	3.16
Carcase	0.44	0.37	0.30	0.28
Total [1]	98.3	99.6	97.9	97.4

[1] Calculated using unrounded percentages.

Analysis by HPLC showed little difference in metabolic profiles in the excreta at either dose, but radioactivity was higher in the excreta from the high-dose groups. HPLC with mass spectrometric detection was used to determine the structures of all major and many minor metabolites. Nuclear magnetic resonance spectrometry was used to confirm identities and to establish the position of functional groups in specific metabolites.

Piperonyl butoxide is vulnerable to metabolic attack in the dioxole ring and at the glycolate side chain (Figure 3). The former can open, producing either a pyrocatechol or an *o*-hydroxyanisole moiety. These products, either *per se* or conjugated, generally persist throughout subsequent metabolism. The pyrocatechol aglycones could be conjugated to gluconuride or sulfate at either of the two phenolic sites. Only one of each pair is shown in Figure 3.

Metabolites in the excreta collected in the first 48 hours after dosing at the higher rate were quantified by HPLC with UV and radiocarbon detection. The distribution of piperonyl butoxide and metabolites as percentages of the applied dose in male and female rats is shown in Table 5. Only piperonyl butoxide and M3 exceeded 10% of the applied dose in animals of either sex.

Table 5. Distribution of piperonyl butoxide and its metabolites in excreta from rats dosed at 500 mg/kg bw (Bard *et al.*, 1999).

	^{14}C, % of dose														
	PBO	M2	MG	M4	M5	MF	M7	M8	M9	M10	M11	M12	M14	M16	M17
Female	15.6	4.36	17.6	6.62		4.98	9.27[1]		0.62	0.28	NQ	NQ	0.78	0.98	NQ
Male	23.9	3.74	19.8	4.68		1.32		NQ[2]	NQ	NQ	NQ	NQ	3.07	0.78	NQ

[1] Total concentration of two metabolites unresolved by HPLC
[2] Not quantifiable by HPLC: identified by mass spectrometry

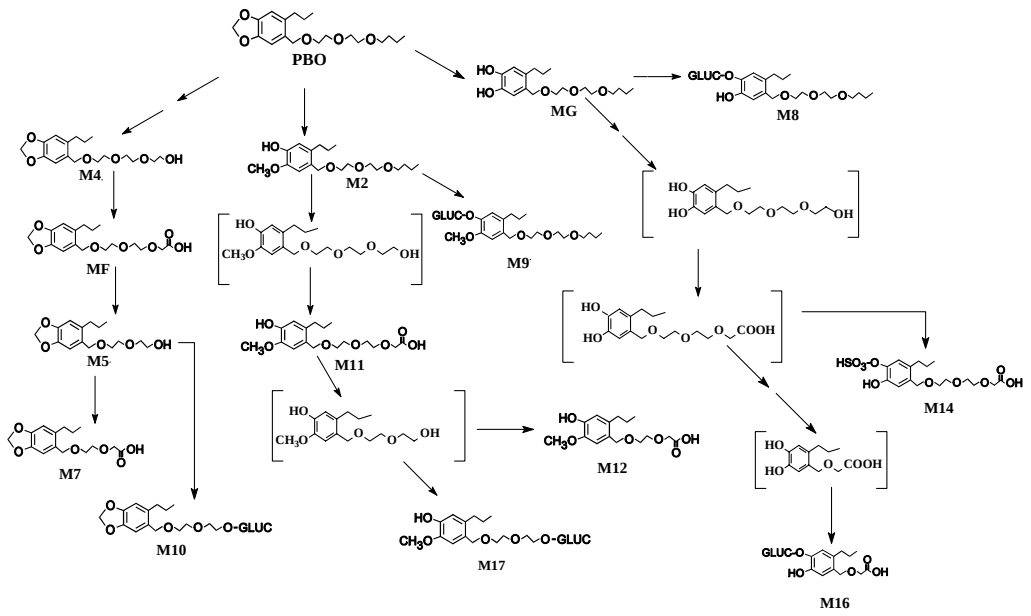
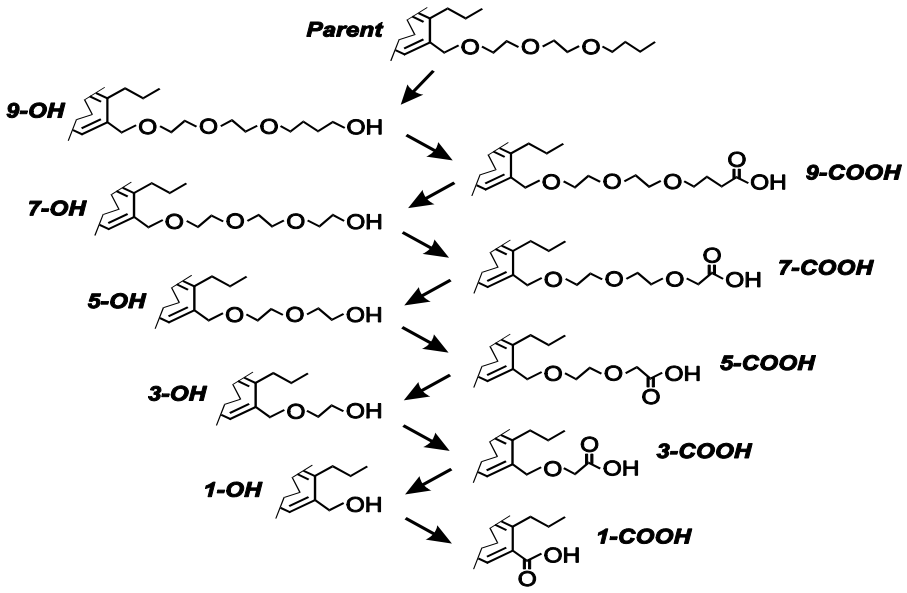


Figure 3. Proposed metabolic pathways of piperonyl butoxide in rats (Bard *et al.*, 1999).

Figure 4 shows the main steps in the metabolism of the glycolate side chain, showing the carbons remaining after each step. Initial hydroxylation followed by oxidation at the terminus of the original 9-carbon side chain produces C9-OH and then C8-COOH, from which is eliminated a 2-carbon (acetate) moiety; oxidation then results in the formation of 7-OH and 6-COOH. Successive losses of acetate followed by oxidation finally produce 1-OH and ring-COOH. In some cases the acid has been identified as an animal metabolite, but the corresponding alcohol is not found at a concentration high enough to measure although it is judged to be a necessary precursor.

Figure 4. Truncation of glycolate side chain of PBO in rats.



Goats. In a study by Selim (1995c) a dosing solution containing piperonyl butoxide uniformly labelled with ^{14}C in the benzene ring at a nominal concentration of 10% was applied to the skin of a lactating goat for 5 consecutive days. Using a balling gun two other lactating goats were given capsules containing [^{14}C]piperonyl butoxide levels nominally equivalent to intakes of 10 and 100 ppm in the feed daily for 5 days.

Urine, faeces, and milk were collected from all the goats at 12-hour intervals after the first application, and analysed for total ^{14}C. The radioactivity was excreted rapidly by the orally-dosed goats, and more slowly by the dermally-dosed goat. Most of the dose was excreted in the urine and faeces within 22 hours of the last dose by all the goats, and excretion in the milk was similar throughout the study (Table 6).

Table 6. Excretion of total radioactivity in the faeces, urine and milk from lactating goats treated with [^{14}C]PBO (Selim 1995c).

Time	^{14}C, % of dose								
	Dermal dose			Low oral dose			High oral dose		
(hours)	Faeces	Urine	Milk	Faeces	Urine	Milk	Faeces	Urine	Milk
0-12	0.03	2.26	0.03	0.50	10.8	0.04	0.14	11.2	0.04
12-24	0.38	3.14	0.02	2.72	2.39	0.02	1.53	3.99	0.02
24-36	0.55	3.12	0.06	0.89	9.0	0.03	1.0	8.5	0.05
36-48	0.79	4.20	0.04	2.73	5.93	0.02	2.19	6.0	0.03
48-60	0.88	4.82	0.06	2.18	12.7	0.04	3.82	10.1	0.04
60-72	0.79	4.47	0.06	3.35	4.62	0.03	2.08	4.23	0.02
72-84	1.74	5.48	0.07	1.97	12.3	0.05	2.65	11.8	0.05
84-96	0.97	5.26	0.06	3.48	4.48	0.02	3.42	4.28	0.02
96-108	1.63	5.34	0.07	1.44	11.6	0.05	2.58	8.6	0.04
108-120	1.15	6.29	0.06	2.55	5.25	0.03	2.88	3.54	0.02
Total	8.9	44.4	0.53	21.8	79.3	0.33	22.3	72.6	0.33

The goats were killed approximately 22 hours after the last dose, and samples of fat, liver, muscle and kidney were collected. Radioactivity was very low in muscle and was concentrated in the fat of the dermally-dosed goat and in the liver of the orally-dosed goats (Table 7).

Table 7. Total ^{14}C residues in the tissues of lactating goats after treatment with [^{14}C]piperonyl butoxide (Selim 1995c).

Sample	^{14}C as mg/kg PBO		
	Dermal dose	Oral low dose	Oral high dose
Fat	0.196	0.009	0.324
Leg muscle	0.023	0.005	0.007

Sample	^{14}C as mg/kg PBO		
	Dermal dose	Oral low dose	Oral high dose
Loin muscle	0.023	0.004	0.009
Liver	0.149	0.363	2.00
Kidney	0.113	0.071	0.398

The same metabolites were found in the tissues as in the urine by HPLC, and the urine from the goat dosed orally at 100 ppm was used as a source of materials for metabolite isolation and identification. Thus, metabolites in the milk and tissues from all three goats were characterized by comparison with metabolites identified in the urine.

The four main metabolites in the urine were isolated by semi-preparative HPLC, and their structures elucidated by LC-MS and GC-MS. A minor component in one of the purified fractions was identified as hydroxymethyldihydrosafrole (3,4-methylenedioxy-6-propylbenzyl alcohol, HMDS). It was not found in any of the analysed tissues.

Piperonyl butoxide was metabolized by cleavage of the glycol-derived side chain to produce a number of alcohols, and the alcohols were partially oxidized to the corresponding carboxylic acids. The proposed metabolic pathways for the metabolism of [^{14}C]piperonyl butoxide in lactating goats are shown in Figure 5.

Levels of piperonyl butoxide and metabolites identified in the milk, liver and kidneys are shown in Table 8. In milk, the residues consisted of the parent compound, M7 and MD.

Up to 11 metabolites were identified in liver, an indication of the extensive metabolism. The parent compound was a minor component in the liver from the oral low-dose goat and the dermally-dosed goat, but a major component in the oral high-dose goat.

Table 8. Piperonyl butoxide and metabolites in milk, liver and kidney from goats dosed with [^{14}C]piperonyl butoxide, in mg/kg PBO equivalents

Sample	Dose	^{14}C, mg/kg as PBO				
		PBO	MD	M5	M13	M7
Milk	Oral 10 ppm	0.002	0.002	-[1]	-	0.001
	Oral 100 ppm	0.006	0.005	-	-	0.016
	Dermal	0.012	0.001	-	-	0.001
Liver	Oral 10 ppm	0.002	<0.002	0.009	0.019	0.024
	Oral 100 ppm	0.115	0.040	<0.002	0.136	0.075
	Dermal	0.007	0.006	0.01	0.018	0.014
Kidney	Oral 10 ppm	<0.005	0.002	0.004	-	0.005
	Oral 100 ppm	0.010	0.024	0.023	-	0.045
	Dermal	0.007	<0.002	0.010	-	0.006
Fat	Oral 10 ppm	0.006	-	-	-	-
	Oral 100 ppm	0.129	-	-	-	-
	Dermal	0.155	-	-	-	-

[1] Not detected. Detection limits were not reported but can be assumed to be below the lowest concentration reported for detected residues.

In kidney the metabolic profiles were similar to those in liver, but concentrations were much lower. The parent compound was not detected in kidneys from the oral low-dose goat. Fourteen minor metabolite peaks were observed at or below 0.005 mg/kg.

The parent compound was the only radioactive component in the fat samples from the oral low-dose and dermal-dose goats, and in the leg and loin muscle from the dermal-dosed (0.31 mg/kg PBO equivalents), whereas the fat from the oral high-dose goat contained metabolite 15 (0.047 mg/kg PBO equivalents) as well, whose structure was not elucidated. Metabolites were not identified in muscle from the oral dose goats.

Hens. Selim (1995d) applied a solution containing [^{14}C]piperonyl butoxide uniformly labelled in the benzene ring dermally at a level nominally equivalent to 10 ppm piperonyl butoxide in the feed for 5 consecutive days to a group of 10 hens. About 24 hours earlier, feathers had been plucked from the hens' backs and the areas wiped with acetone. Containers 2.5 cm x 5 cm x 1.3 cm (maximum height) were stuck to their backs with cyanoacrylate glue and sealed with a medical adhesive silicone seal. The dosing solution contained 498 μCu, and 13.72 mg of piperonyl butoxide per g. Two other groups of 10 hens were dosed with capsules containing [^{14}C]piperonyl butoxide at nominal levels of 10 and 100 ppm piperonyl butoxide in the feed for 5 days.

Excreta and eggs were collected from each hen at 24-hour intervals after the first dose and analysed for ^{14}C. Excreta from the dermally-dosed hens contained 59% of the applied radioactivity, from the oral low dose group 89%, and from the oral high dose group 94%. In eggs, levels of radioactivity were low but were higher in whites than in yolks in the first 48 hours. After 48 hours, this pattern inverted and at day 5 the radioactivity in the yolks was approximately 5 times that in the whites (Table 9).

Table 9. Radioactive residues in the eggs of laying hens treated with [^{14}C]PBO (Selim 1995d).

Time	^{14}C, mg/kg as PBO					
	Dermal dose		Oral low dose		Oral high dose	
(hours)	White	Yolk	White	Yolk	White	Yolk
0-24	<0.001	<0.001	<0.001	<0.001	0.052	0.004
24-48	0.014	0.005	0.005	0.006	0.629	0.330
48-72	0.015	0.033	0.006	0.023	0.335	0.727
72-96	0.013	0.068	0.006	0.041	0.240	1.355
96-120	0.013	0.093	0.011	0.076	0.442	1.933

The hens were killed approximately 22 hours after the last dose, and samples of fat, liver, muscle, kidney and skin collected. In all groups, radioactivity was lower in muscle and skin and concentrated in fat. The total radioactive residues (TRR) in kidney and liver increased in proportion to oral dose levels (Table 10).

Table 10. Mean total radioactive residues in tissues of laying hens after treatment with ^{14}C piperonyl butoxide (Selim 1995d).

Sample	^{14}C, mg/kg as PBO		
	Dermal dose	Oral low dose	Oral high dose
Breast muscle	0.003	0.002	0.032
Thigh muscle	0.007	0.008	0.124
Fat	0.295	0.134	4.82
Kidney	0.192	0.136	1.19
Liver	0.147	0.109	1.59
Skin	0.077	0.029	0.807

Metabolites in the eggs and tissues were identified by comparison with urinary metabolites identified in a companion study with goats, using chemical tests, chromatography, LC-MS and GC-MS. The levels of piperonyl butoxide and the main metabolites found in eggs and most tissues from the three dose regimes are shown in Table 11. Total radioactive residues in breast muscle, skin from the low oral dose, and thigh muscle from the dermal and the oral low dose were too low (<0.05 mg/kg) for characterization of metabolites to be possible.

Table 11. Piperonyl butoxide and identified metabolites in the eggs and tissues of hens dosed with [^{14}C]PBO.

Sample	Dose	^{14}C, mg/kg as PBO				
		PBO	MD	M5	M13	M7
Egg whites	Oral-10 ppm	0.006	-[1]	-	-	-
	Oral-100 ppm	0.445	-	-	-	-
	Dermal	0.010	-	-	-	-
Egg yolks	Oral-10 ppm	0.035	0.026	-	-	-
	Oral-100 ppm	1.181	-	0.014	0.015	0.180
	Dermal	0 058	-	-	-	0.009
Fat	Oral-10 ppm	0.124	-	-	-	-
	Oral-100 ppm	4.295	-	-	-	-
	Dermal	0.274	-	-	-	-
Liver	Oral-10 ppm	-	0.003	0.002	0.003	0.016
	Oral-100 ppm	-	0.050	-	0.057	0.146
	Dermal	0.013	-	0.002	0.001	0.008
Kidney	Oral-10 ppm	-	-	0.008	-	0.040
	Oral-100 ppm	0.136	-	-	-	0.193
	Dermal	0.024	-	0.007	-	0.018
Untreated skin	Oral-100 ppm	0.445	-	-	0.123	0.130
	Dermal	0.060	-	-	-	-
Thigh muscle	Oral-100 ppm	0.115	-	-	-	0.001

[1] Not detected. Detection limits were not reported but can be assumed to be below the lowest concentration reported for detected residues.

In egg whites and yolks, the radioactive residue was mainly piperonyl butoxide and M7, an acid formed by oxidative metabolism (Figure 5). In all the fat samples piperonyl butoxide was the only radioactive component found, and in liver it was extensively metabolized and the predominant metabolite was M7. Kidney showed a metabolite profile similar to liver.

Piperonyl butoxide was the only radioactive component found in the untreated skin of the dermally-treated hens. The residue in thigh muscle from the oral high-dose hens was primarily piperonyl butoxide, with low amounts of M7. Breast muscle, thigh muscle from dermal or oral low dose, and skin from oral low dose did not contain enough total radioactivity to allow characterization of residues.

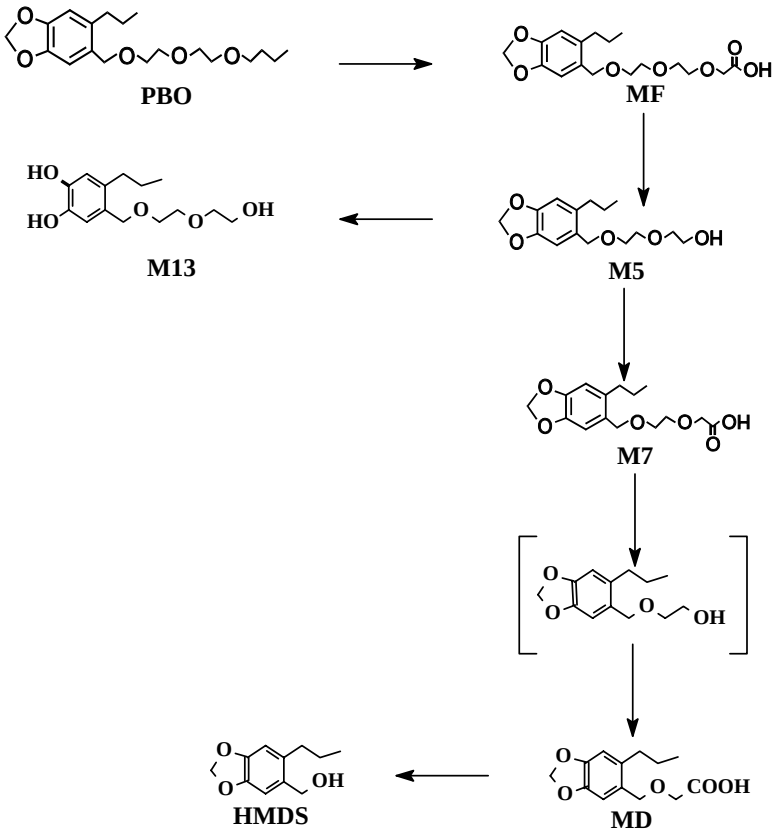


Figure 5. Metabolic pathways of piperonyl butoxide in goats and hens.

Plant metabolism

The metabolism of [^{14}C]PBO labelled in the glycol-derived side chain was studied in cotton (Selim 1994a), potatoes (Selim 1996e), and leaf lettuce (Selim 1995a). Plants were treated foliarly at the maximum label rate of 0.56 kg ai/ha. Five applications were made to lettuce at ten-day intervals, four to potatoes at fifteen-day intervals, and six to cotton five of which were at fifteen-day intervals and the sixth 2.5 months later.

The stability of the ^{14}C label at carbon 1 of the glycol side chain during metabolism was confirmed by the absence of dihydrosafrole (Figure 6) at a limit of detection of 0.05 mg/kg.

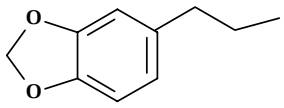


Figure 6. Dihydrosafrole.

Mild acid hydrolysis converts piperonyl butoxide and metabolites that retain the propyl side chain, the phenyl and dioxole rings, and the benzyl carbon into hydroxymethyldihydrosafrole (Figure 7). This is the basis for the analytical method for the determination of total metabolite residues.

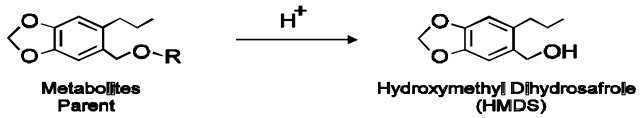


Figure 7. Conversion of piperonyl butoxide and its metabolites to HMDS.

Potato leaves and tubers were collected eight days after the last application, lettuce leaves on the day of the last application and ten days later, cotton leaves five weeks after the fifth application, and bolls sixteen days after the last (sixth) application. The bolls were separated into hulls, lint and seed. The samples were analysed by LSC and HPLC and metabolites identified by GC-MS. The distribution of radioactivity in the commodities is shown in Table 12.

Table 12. Distribution of radioactivity in plants foliar-sprayed with [^{14}C]piperonyl butoxide (Selim 1994a; 1995a; 1996e).

	Lettuce leaves		Potato		Cotton			
	0-Day PHI	10-Day PHI	Leaves	Tuber	Leaves	Hulls	Lint	Seed
TRR (mg/kg as PBO)	20.4	25.8	617	0.47	142	7.14	0.53	0.41
PBO (mg/kg)	10.4	6.3	241	<0.01	26.3	1.23	0.047	0.086
PBO (% of TRR)	51	24.4	39.1	<2	18.5	17	8.9	21
Bound (% of TRR)	19	29	18	51	25.9	51.0	35.9	84.5

TRR: Total radioactive residue

Uptake and translocation of parent or degradation products was minimal. The highest TRR in the cotton bolls was found in the hulls (5% of that on the leaves). In potatoes, the total radioactivity in the tubers was about 0.1% of that on the leaves. For undegraded piperonyl butoxide, levels in cotton lint, seed, and hulls were 0.2, 0.3 and 5%, respectively, of the levels in leaves.

In lettuce leaves, metabolism of piperonyl butoxide resulted in the formation of a series of related conjugates (Figure 8). At day 0, half of the radioactivity was present as the parent compound (petroleum ether extract) and 24.2 % remained in the aqueous fraction. At least 3 metabolites were found, including the glucose conjugate of HMDS and M10 (Figure 8), plus a small amount of PBO (1.5% of the radioactivity). The levels of the metabolites were not determined.

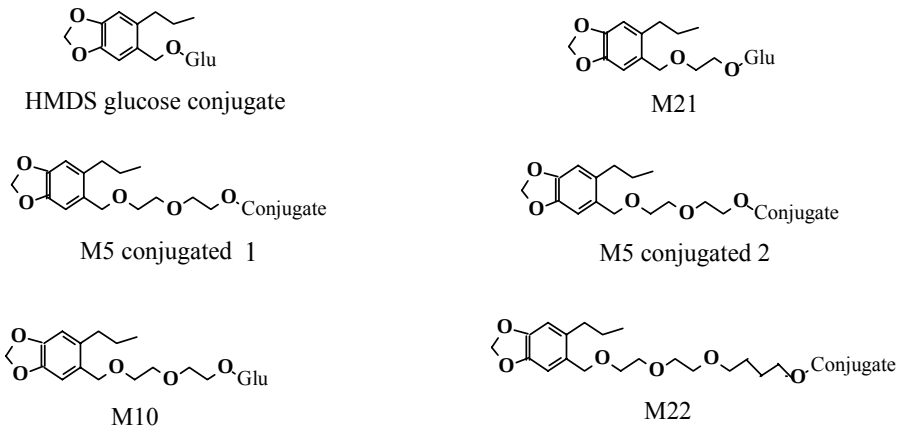


Figure 8. Metabolites of piperonyl butoxide in leaf lettuce.

A composite sample from plants 10 days after treatment was extracted with acetonitrile (71% of radioactivity), the extracts partitioned with petroleum ether containing piperonyl butoxide, and the aqueous fraction (40% of the radioactivity) analysed for metabolites. Five main plus at least 5 minor metabolites were identified (Table 13). Further investigation of the post-extraction solids (PES) of the lettuce leaves revealed small amounts of parent, some of the metabolites (Figure 8) and up to seven highly-polar degradation products at low levels (<10% of the TRR each).

Table 13. Distribution of [^{14}C]PBO and metabolites in lettuce aqueous extracts 10 days after last application (Selim 1995a).

	PBO	M20	M21	M5 conj1	M5 conj 2	M22	M10
Concentration (mg/kg)	6.3	2.0	0.6		0.2	0.5	1.8
% TRR	24.4	7.6	2.4		0.9	1.8	6.9

The potato leaf extracts contained at least seven organosoluble degradation products of high to moderate polarity, none exceeding 3% of the TRR. About 82% of the TRR was extracted from the tubers by organic solvent. The ethyl acetate extract of the unacidified aqueous fraction had at least five metabolite peaks (0.06-0.016 mg/kg) and the acidified aqueous fraction at least ten metabolite peaks with concentrations up to 0.018 mg/kg. No parent compound was found in either extract. The metabolite profile in the tubers was different from that of the leaves, indicating that further metabolism of PBO occurs in the tubers an/or during translocation to the tubers.

Bound residues in the PES from potato tubers were almost completely solubilized by mild acid hydrolysis. Degradation products were characterized as highly polar materials, most likely products of oxidation of one or both side chains to benzyl alcohols or carboxylic acids and of opening of the dioxole ring to a pyrocatechol structure (Figure 10). Bound materials did not include conjugates of aglycones, as mild hydrolysis did not result in the formation of HMDS.

Cotton leaves contained eleven or more organosoluble degradation products, of moderate polarity (<10% of the TRR). The predominant degradation product (7.5% of the TRR) was characterized as having an intact propyl side-chain and intact benzyl and dioxole rings. The glycol-derived side-chain had been oxidized or truncated, with one to three oxygen atoms remaining. The degradation product was probably a relatively polar conjugate, such as a sulfate or glucuronide. Similar metabolites were identified in lettuce leaves (Figure 8). Highly polar metabolites accounted for 24.9% of the radioactivity. The metabolites found in the leaves were not found in the hulls, seeds or lint.

In cotton seeds piperonyl butoxide was the only organosoluble residue. Mild acid hydrolysis of the post-extraction solids (PES) released almost 50% of the TRR. The hydrolysate yielded two peaks of high to moderate polarity, each below 0.05 mg/kg as PBO, and a third representing 44.6% of the TRR (0.12 mg/kg). This metabolite presented similar characteristics to those found in potato tubers: release from the PES by mild acid hydrolysis, water solubility, retention on and elution from C_{18} columns, elution at the HPLC solvent front, and failure to form HMDS on mild acid hydrolysis. Some proposed structures for metabolites in cotton seeds and potato tubers are shown in Figure 9.

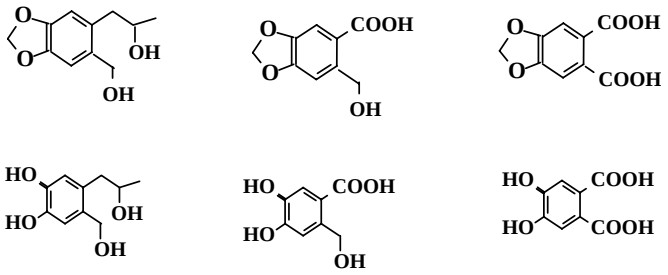


Figure 9**.** Probable PBO metabolites in cotton seed and potato tubers.

Cotton lint contained two organosoluble components, piperonyl butoxide and one highly polar material that was eluted at the HPLC solvent front (80.2% of the TRR, 0.19 mg/kg as PBO). Although this was not identified, it is possibly composed of highly-degraded metabolite(s), with the dioxole ring opened, similar to those found in potato tubers and cotton seed, except that it is not bound. Mild acid hydrolysis of the PES released less than 10% of the TRR (<0.05 mg/kg).

Cotton hulls contained the parent and five organosoluble degradation products, each at 0.1% of the TRR. At least ten degradation products were released by mild acid hydrolysis of the PES. The predominant degradation product, 5.1% of the TRR, was characterized as metabolite MD (1-(6-propyl-1,3-benzodioxol-5-yl)-2-oxabutan-4-oic acid). Mild base hydrolysis released four degradation products, none above 6.4% of the TRR. Subsequent strong base hydrolysis released an additional twenty or more products, none above 1.9% of the TRR.

Environmental fate in soil

Photolysis. The degradation of piperonyl butoxide, uniformly labelled in the phenyl ring, was studied in 2 mm layers of a sandy loam soil exposed to artificial sunlight from a Xenon arc lamp for 15 days, equivalent to 41 days natural sunlight (Anon., 1995b). The compound was applied at a rate equivalent to 10 kg ai/ha. Soil moisture levels were maintained at 75% water holding capacity at 1/3 bar for the period of the study. Controls were incubated in the dark.

Piperonyl butoxide was degraded both in the presence and absence of light with half-lives of one to 3 days (Table 14). The degradation products formed resulted from the loss of the

butoxyethoxyethyl side chain and oxidation of the resulting benzyl alcohol to the corresponding aldehyde and acid (Figure 10). In unirradiated soil the acid accumulated, whereas under the influence of light it was further degraded.

In both the irradiated and control soils, hydroxymethyldihydrosafrole (HMDS) reached a peak at day 3. Decomposition and oxidation of the phenyl ring was observed through the formation of CO_2, up to 28% in irradiated soil and 1.3% in the control dark soil.

Table 14. Percentage distribution of applied radioactivity in soil extracts (Anon., 1995b).

Compound	Days after application and (equivalent of natural sunlight)													
	0 (0)		0.25 (0.71)		1 (2.46)		3 (7.69)		6 (14.02)		10 (26.17)		15 (40.86}	
	D	I	D	I	D	I	D	I	D	I	D	I	D	I
PBO	95.7	95.7	95.7	82.4	91.9	81	21.2	8.4	5.6	3.4	3.1	8.6	2.6	15
ME	-	-	0.6	0.9	1.3	1.4	2.5	2.1	8.6	3.9	19.1	9.7	48.8	6.3
HMDS	-	-	0.7	3.2	0.4	1.3	63.3	44.0	57.4	33.5	32.2	11.2	1.9	3.1
M23	0.95	0.9	1.1	1.8	0.6	1.8	1.1	5.8	9.3	7.6	19.5	2.8	17.1	0.9
M24	-	-	-	-	-	-	7.5	4.8	7.6	3.7	7.6	4.0	5.9	1.6

D: dark control; I: irradiated

Aerobic degradation. The degradation of piperonyl butoxide labelled in the phenyl ring has been studied in soil incubated under aerobic conditions for up to 242 days (Anon., 1995c). Piperonyl butoxide was applied to sandy loam soil at a concentration of 10 kg ai/ha, and incubated in the dark at 25^{o}C at a moisture content of 75% water holding capacity at 1/3 bar. Duplicate or triplicate soil flasks were taken for analysis at intervals.

Piperonyl butoxide was rapidly degraded with a half-life of approximately 14 days, giving rise to four main degradation products (Table 15). More than half the applied piperonyl butoxide was mineralized to CO_2 at 242 days. Soil-bound residues increased to a maximum of approximately 37% after 128 days but were themselves further degraded. The proposed degradation pathways for piperonyl butoxide in aerobic soil are shown in Figure 10.

Table 15. Distribution of radioactivity in soil after application of [^{14}C]PBO (Anon., 1995c).

Compound	^{14}C, % of applied at intervals after application (days)											
	0	1	3	7	14	30	61	90	128	180	210	242
PBO	97.7	96.7	89.0	68.3	53.3	22.6	6.7	2.9	1.9	1.6	1.2	1.5
M25	<0.1	<0.1	0.6	2.7	4.6	8.9	6.3	3.2	1.2	1.5	1.8	1.0
M27	<0.1	0.1	2.4	5.8	4.9	3.0	2.6	2.3	2.2	2.1	2.0	1.4
ME	0.2	1.1	2.9	5.9	12.2	16.6	12.0	6.9	4.0	3.9	3.4	1.8
M26	<0.1	0.2	0.6	1.2	1.9	2.6	2.3	1.6	1.1	0.9	0.8	0.6

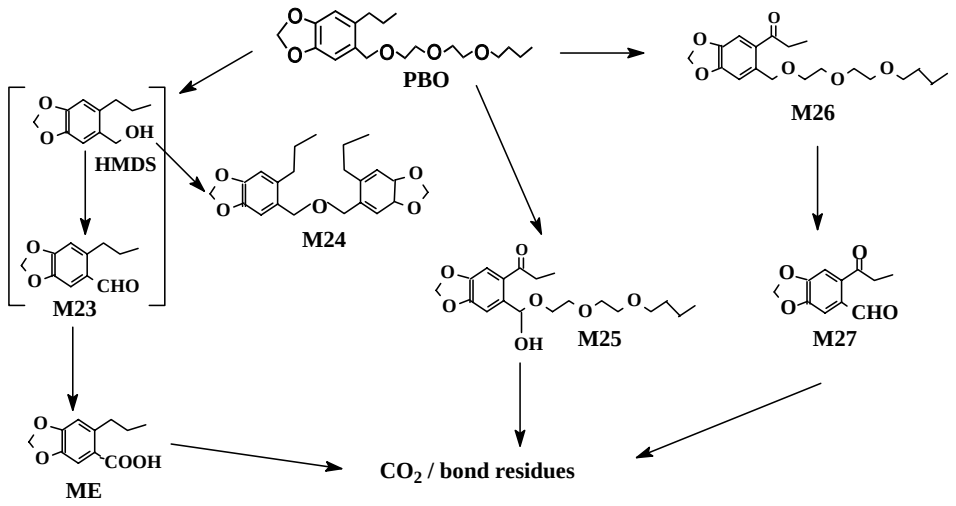


Figure 10. Proposed degradation pathways of piperonyl butoxide in aerobic soil.

Terrestrial dissipation. Studies were conducted under worst-case conditions at three sites in the USA: Georgia, California and Michigan (Hattermann,1992a,b). At each site a single application of a typical end-use formulation was made at a nominal rate of 5.2 kg piperonyl butoxide/ha to bare soil: ten times the proposed maximum single-application rate.

Before application, petri dishes 1.1 cm in depth were placed in the soil at each site with the tops level with the surface, and filled with soil from the site. At intervals from 5 min to 14 days after treatment the plates were removed, covered, chilled and the soil analysed for PBO. At all sites piperonyl butoxide was detected in the surface samples shortly after application but disappeared rapidly. Half-lives at the three sites were remarkably similar: 3.5 days in Michigan and 4.3 days in California and Georgia (Table 16).

Table 16. Piperonyl butoxide concentrations in petri dish soil samples after single applications (Hattermann, 1992a,b).

Site	PBO, mg/kg, at intervals after treatment										Half-life
	5 min	10 min	20 min	40 min	1 day	2 days	5 days	7 days	10 days	14 days	(days)
CA	1.0	1.0	1.2	0.92	0.53	0.48	0.43	0.40	0.20		4.3
GA	1.0	1.4	0.82	0.68	0.35	0.56	0.39	0.23	0.16	0.11	4.3
MI	1.5	2.1	1.7	1.4	0.67	0.29	0.29	0.16	0.19	0.11	3.5

Soil cores to a depth of 91 cm were also collected on a diagonal transect across the plots using a hydraulic probe with an acetate liner 24 hours before application and for 97 to 179 days thereafter. At each site within 14 to 30 days of application piperonyl butoxide had dissipated in the 0 to 15 cm soil layer to <0.10 mg/kg (Table 17), and was not detected at depths below 15 cm.

Table 17. Piperonyl butoxide concentration in soil at 0-15 cm depth after application of 5.2 kg ai/ha (Hattermann, 1992a,b).

Site	PBO, mg/kg, at days after treatment										
	-1	0	1	2	3	5	7	10	14	30	60
CA	<0.10	-	0.53	0.48	0.43	0.40	0.20	0.25	0.22	<0.10	<0.10
MI	-	<0.10	0.67	0.20	0.29	0.16[1]	0.20[2]	<0.10	0.11	<0.10	<0.10
GA	<0.10	-	0.35	0.56	0.39	0.23	0.16	0.15	0.11	<0.10	<0.10

[1] Sampled on day 4
[2] Sampled on day 8

Adsorption/desorption. The adsorption and desorption of piperonyl butoxide labelled in the phenyl ring were determined by batch equilibrium (Anon., 1995f). Four concentrations, 0.4, 2.0, 3.0, and 4.0 mg/l, were equilibrated on four soils: sand, clay loam, sandy loam, and silt loam for 24 hours at 25°C in the dark using a soil:solution ratio of 1:10. After the adsorption phase, the soil and solution were separated and two sequential desorption steps were carried out on the soil residue.

Piperonyl butoxide has low to moderate mobility in sandy loam, clay loam and silt loam soils and high mobility in sand (Table 18). Freundlich adsorption constants (K_a) ranged from 0.98 in sand to 29.9 in silt loam, and K_{oc} values from 399 in sand to 830 in silt loam. No desorption value (K_d) was determined for sand because of the low adsorption.

Table 18. Adsorption and desorption characteristics of piperonyl butoxide in four soils.

Soil	Organic matter (%)	Adsorption			Desorption[1]		
		K_a	K_{oc}	1/n	K_d	K_{oc}	1/n
Sandy loam	2.1	8.37	399	0.67	8.2/6.32	390/301	0.63/0.57
Sand	0.2	0.98	490	0.90	-	-	-
Clay loam	1.7	12.0	706	1.57	16.8/94.7	988/5571	1.28/2.07
Silt loam	3.6	29.9	830	0.84	41.5/58.1	1152/1614	0.87/0.83

[1] First/second desorption

Column leaching. The leaching behaviour of piperonyl butoxide labelled in the phenyl ring was investigated with unaged material in sand, silt loam, sandy loam, and clay loam, and with aged residues in sandy loam (Anon., 1995g).

For unaged leaching, [^{14}C]piperonyl butoxide was applied at a rate equivalent to 5 kg ai/ha to the tops of 30-cm columns and eluted with 0.01 M calcium chloride. Piperonyl butoxide did not leach readily in loam soils (Table 19). A distribution coefficient of 0.42 ml/g was calculated for sand soil, but not for the other soils as less than 5% of the radioactivity was eluted.

Table 19. Recoveries of ^{14}C from soil columns after application of [^{14}C]PBO at 1 mg/column (Anon., 1995g).

Fraction	^{14}C, % of applied			
	Sand	Clay loam	Sandy loam	Silt loam
Leachate	74.1	1.3	0.2	0.6
Extracted	16.9	88.4	96.0	94.4
Residues	2.8	5.1	1.4	5.2
Total	93.8	94.8	97.6	100.2

The unleached radioactivity was distributed fairly evenly throughout the columns (1.4-4.6% of the applied radioactivity) in the sand soil, but was in the top 10 cm of the loam soil columns.

Aged soil residues were prepared by incubation of [^{14}C]piperonyl butoxide in sandy loam soil under aerobic conditions for 18 days. After this period, 61% of the applied radioactivity was extracted from the soil, and 44.8% of the AR was piperonyl butoxide (Table 20). A mean of 4% was trapped as volatiles. The aged soil was placed on top of 30-cm soil columns and eluted with 0.01 M calcium chloride. Approximately 14% of the applied radioactivity was found in the column effluent. Most of the radioactivity remained in the aged soil applied to the soil columns. All three degradation products were more mobile than the parent compound (Table 20).

Table 20. Radioactive components in aged soil extract and column leachate after application and elution of [^{14}C]PBO (Anon., 1995g).

Fraction	^{14}C, % of applied[1]			
	PBO	HMDS	M23	ME
0-5 cm	7.6/42.8	5.2/2.8	2.4/1.8	1.8/2.5
5-10 cm	0.1/2.5	0.2/1.1	0.1/0.2	3.7/1.3
10-15 cm	<0.1/<0.1	0.7/0.6	0.1/0.1	3.8/1.3
15-20 cm	<0.1/<0.1	0.1/0.4	0.1/0.1	5.3/1.3
20-25 cm	<0.1/<0.1	0.5/0.5	0.1/<0.1	5.4/0.9
25-30 cm	<0.1/<0.1	<0.1/0.2	0.1/<0.1	7.1/0.6
Leachate[2]	0.1	4.7	1.6	7.4
Soil extract[3]	44.8	5.7	3.4	7.0

[1] Column 1/column 2
[2] Only from column 1
[3] Extract of a soil sample aged for 18 days.

Environmental fate in water/sediment systems

Hydrolysis. The stability of piperonyl butoxide labelled in the phenyl ring was investigated at a concentration of 1 mg/l at pH 5, 7, and 9 in sterile aqueous buffers (Anon., 1995a). Test systems were

incubated at 25°C in the dark for 30 days and 97 to 100 % of the applied radioactivity was recovered at the end of the experiment in each case.

Aqueous photolysis. The stability of piperonyl butoxide labelled in the phenyl ring was investigated in a 10 mM aqueous buffer at a concentration of 10 mg/l at pH 7 in California, USA (Selim, 1995b). The system was positioned in an area exposed to natural sunlight and the intensity of the sunlight was recorded. The period corresponded to 84 hours of exposure.

Piperonyl butoxide was rapidly degraded with a half-life of 8.4 hours with two major photoproducts observed (Table 21), and at least 5 other minor degradation products, each accounting for less than 10% of the applied radioactivity after 84 hours' exposure. The concentration of polar degradation products which eluted with the HPLC solvent front (0-5 min) increased over time, reaching 30% of the applied radioactivity at the end of the study. In control samples up to 2% of radioactivity represented degradation products.

Table 21. Distribution of applied radioactivity in aqueous piperonyl butoxide exposed to sunlight (Selim, 1995b).

Compound	^{14}C, % of initial, after exposure (hours)							
	0	4	8	12	24	36	72	84
PBO	95.7	62.6	51.5	44.4	18.3	8.6	1.9	0.9
HMDS		22.4	30.6	32.6	49.8	54.5	48.7	48.1
M23		5.7	7.6	7.9	11.5	12.2	9.8	10.8

The degradation of labelled piperonyl butoxide in ultraviolet light was also examined by Harbach (1995). Qualitative results mirrored the route of piperonyl butoxide degradation to 3,4-methylenedioxy-6-propylbenzyl alcohol (HMDS), then to 3,4-methylenedioxy-6-propylbenzaldehyde, and finally to 3,4-methylenedioxy-6-propylbenzoic acid.

Aquatic degradation. The degradation of piperonyl butoxide labelled in the phenyl ring was investigated in a water/sediment system using a sandy loam soil incubated under aerobic conditions in the dark for 30 days (Anon., 1995e). The application rate was equivalent to about 10 mg/kg sediment (dry weight) or 3.2 µg/ml of water. After application to the surface water, piperonyl butoxide partitioned into both sediment and water where it was further degraded (Table 22).

Table 22. Distribution of radioactivity after 30 days incubation of [^{14}C]piperonyl butoxide under aerobic aquatic conditions (Anon., 1995e).

Phase	^{14}C, % of applied					
	PBO	HMDS	M23	ME	Bound	Volatile
Water	22.5	3.8	1.8	3.4	-	-
Sediment	49.5	0.8	0.9	1.5	7.9	-
Total	72	4.5	2.7	4.9	7.9	0.9

The degradation of labelled piperonyl butoxide at a concentration of 10 mg/l was investigated in a water/sediment system using a sandy loam soil incubated under anaerobic conditions (N_2 gas) for 181 days in the dark (Anon., 1995d). Piperonyl butoxide decreased from 96.5% of the recovered

radioactivity at day 0 to 91.2 % at day 181. Two degradation products, 3,4-methylenedioxy-6-propylbenzyl alcohol (HMDS) and 3,4-methylenedioxy-6-propylbenzoic acid (ME) were detected (2.4% of the TRR or less as a combined residue).

METHODS OF RESIDUE ANALYSIS

Analytical methods

One method to determine residues of piperonyl butoxide and metabolites in raw and processed plant commodities involves extraction with acetonitrile, partition of piperonyl butoxide into petroleum ether, and analysis by HPLC with fluorescence detection. For dry samples such as sugar and sugar beet molasses, water is added before extraction. The solvent is evaporated and the aqueous fraction extracted with petroleum ether. PBO goes into the organic phase and the more polar metabolites remain in the aqueous phase, which is then subjected to mild acid hydrolysis to convert the metabolites quantitatively to HMDS. After neutralization, the reaction mixture is extracted with acetonitrile and the solution analysed for HMDS. Residues are expressed as piperonyl butoxide. Recovery was evaluated by fortification with piperonyl butoxide, which itself is degraded quantitatively to HMDS upon mild acid hydrolysis. PBO is determined as such in the petroleum ether fraction.

The limit of quantification (LOQ) for piperonyl butoxide and for total metabolites was 0.10 mg/kg in all samples. In grapes and cranberries, preliminary validation was unsuccessful for metabolites, as recoveries from fortified controls of these commodities were below 70%. The results of the method validation are shown on Table 23.

Untreated controls typically produced no elution peaks that interfered with piperonyl butoxide. Control orange oil contained a minor interferent, but the level of piperonyl butoxide in oil from treated oranges was more than twice as high. In all except two substrates, controls did not produce elution peaks that interfered with HMDS. Interferences were observed for metabolites in mustard greens from one of two trials and lemons from each of two trials, at levels that prevented determination of metabolite concentrations.

Table 23. Recoveries of piperonyl butoxide and metabolites in method validation and procedural verification.[1]

Analysis	% Recovery, overall mean	Var	CV	N
	Piperonyl butoxide			
Method validation	90.9	1.5	1.7%	596
Procedural verification	94.2	4.3	4.5%	112
	Total metabolites determined as HMDS			
Method validation[2]	90.9	1.6	1.7%	647
Procedural verification	92.6	3.3	3.5%	42

Var.: pooled variance for all analyses
CV: pooled coefficient of variation
N: No. of analyses.
[1] Method performance during each series of analyses
[2] Does not include data on legumes, citrus, cranberries or grapes

Residues of piperonyl butoxide in treated stored grains were determined by a variety of methods. Wheat and milled fractions were extracted with methanol (Halls, 1981; Ardley *et al.*, 1982;

Anon., 1999; Turnbull), hexane (Anon., 1999; Molinari, 1987; Australian Wheat Board, 1988) or ethyl acetate (Molinari, 1987), followed by HPLC analysis.

In studies on the treatment of warehouses (Meinen, 1991a,b) samples were extracted with an organic solvent and water. After clean-up by liquid-solid partition and partial evaporation of the eluate, the entire extract, including piperonyl butoxide, was brominated. The solution containing brominated piperonyl butoxide was further cleaned up in a solid phase extraction (SPE) column. The eluate was analysed by gas chromatography with electron-capture detection. The LOQ was 0.10 mg/kg, and the limit of detection 0.05 mg/kg, with average recoveries ranging from 56% in beans to 67% in peanuts. Control samples in general produced no interferents.

In the method used to determine residues of piperonyl butoxide in milk, eggs, and tissues of livestock in the feeding studies, samples were extracted with acetonitrile and fat was removed by partition with hexane. The acetonitrile fraction was concentrated, aqueous 1.5% NaCl was added, and piperonyl butoxide was partitioned into hexane. The hexane solution was cleaned up on a silica gel column and the eluate was analysed by GC-MS and GC-MS-MS. Untreated controls occasionally produced elution peaks that interfered with piperonyl butoxide. Overall, however, the specificity was considered adequate for the parent compound in all samples. LOQs were validated at 0.05 mg/kg in liver, kidney, muscle and fat with recoveries ranging from 70 to 108%, and at 0.01 mg/kg and 0.05 mg/kg in milk and in eggs from 67 to 120% and 71 to 104% respectively.

Stability of pesticide residues in stored analytical samples

The stability of piperonyl butoxide was examined by analyses at intervals of samples of raw and processed commodities fortified at 1.0 or 0.2 mg/kg, and stored under the same conditions of light and temperature as were used for the treated commodities in the field and processing studies. Analytical recoveries were checked with freshly fortified samples (Table 24).

Table 24. Stability of piperonyl butoxide in frozen raw and processed agricultural commodities stored in the dark.

Sample	Interval (months)	Analytical recoveries	% remaining
Fortified at 1 mg/kg			
Potato (Winkler, 1997) Tuber	0; 3; 6; 12	91; 97; 93.5; 86.5	93.5; 89.5; 87.5; 87.5
Granules	0; 3; 6; 12	95.5; 97.5; 93; 91.5	94; 93.5; 85; 53
Chips	0; 3; 6; 12	92; 100.5; 93; 96.5	93.5; 99; 90; 93.5
Wet peel	0; 3; 6; 12	84; 90.5; 85; 88.5	84; 74; 73; 68.5
Leaf lettuce (Hattermann, 1996f)	3; 6; 12	107.4; 97.2; 93.6	101.1; 102; 96.4
Broccoli (Selim, 1996d)	3; 6; 12	75; 89; 90.7	80.4; 79; 70.6
Cucumber (Hattermann, 1996I)	3; 6; 12	90.7; 91.7; 95.8	95.6; 92.8; 93.2
Grapes (Hattermann, 1996b)	3; 6; 12	88.9; 92.1; 80.4	91.4; 86.4; 81.7
Orange (Selim, 1996a) Fruit	3; 6; 12	86.0; 112.5; 87.9	85; 102.6; 89.5
Molasses	3; 6; 12	110; 95.2; 85.4	99.6; 94; 86.6
Juice	3; 6; 12	110; 82.4; 106.9	112; 87.5; 96.7
Dry pulp	3; 6; 12	95.2; 85; 86	95; 97.4; 97.1
Tomato (Hattermann, 1995m) Fruit	3; 6; 12	92; 94.7; 100.8	98.1; 100.9; 91.9
Juice	3; 6; 12	95.1; 103.5; 138	72.7; 76.9; 96.7
Dry pomace	3; 6; 12	99.2; 81; 105.9	88.4; 69.8; 95.3

Sample	Interval (months)	Analytical recoveries	% remaining
Purée	3; 6; 12	69.7; 88.5; 117.1	66.2; 55; 93.2
Wet pomace	3; 6; 12	97.1; 76.1; 101.3	96.7; 95; 93.3
Succulent Bean (Hattermann, 1995c) Vine	3; 6; 12	110; 85; 92.4	96.9; 90.9; 84.2
Pod	3; 6; 12	88.3; 91.4; 93.7	83; 90; 86
Hay	3; 6; 12	76; 77.3; 67	72; 61.8; 68.3
Cotton (Selim, 1996c) Oil-crude	3; 6; 12	107.2; 95.1; 100.8	106.2; 107.8; 108.5
Seed	3; 6; 12	99.2; 89; 76.2	89; 85.9; 75.7
Meal	3; 6; 12	80.0; 78; 85.7	75.6; 66.5; 65.8
Soapstock	3; 6; 12	74.6; 95.6; 93	106.3; 107.8; 85
Fortified at 0.2 mg/kg			
Candy (Meinen, 1991)	12	58-107	66
Meat (Meinen, 1991)	12	80-116	55.5
Bread (Meinen, 1991)	12	70-93	50.5
Sugar (Meinen, 1991)	12	58-65	63
Peanuts (Meinen, 1991)	12	65-85	69
Beans (Meinen, 1991)	12	80-107	81

DEFINITION OF THE RESIDUE

On the day of application, piperonyl butoxide accounted for 51% of the TRR in lettuce, and two metabolites for 24% in approximately equal amounts. After 10 days, levels of PBO decreased by 50% and 10 or more metabolites were formed at levels <10 % of the TRR. Piperonyl butoxide was not translocated to potato tubers or cotton products when applied to leaves of the plants. Some very polar material was found in cotton seed and lint, at 44 and 80% of the TRR respectively. Although these metabolites were not identified, they were highly degraded from piperonyl butoxide, and owing to their high polarity would not accumulate in animals if ingested.

The Meeting agreed that the definition of the residue for compliance with MRLs and for the estimation of dietary intake in plants should continue to be piperonyl butoxide.

Piperonyl butoxide has a log P_{ow} of 4.6, which indicates fat-solubility.

USE PATTERN

Tables 25, 26 and 27 summarize information on GAP for the uses of pesticides that contain piperonyl butoxide as a synergist

Table 25. Summary of GAP for pre-harvest uses.

Crop	Country	Form.	Application				PHI
			Method	kg ai/hl	kg ai/ha	No.	(days)
Almonds in bulk or bags	Costa Rica	NS	Surface treatment	0.62	NA [1]	NS[2]	NA
Almonds (shell-nuts)	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2

Crop	Country	Form.	Application				PHI (days)
			Method	kg ai/hl	kg ai/ha	No.	
Apple	Italy	NS	Spray, broadcast	0.04	NS	NS	2
Artichoke	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Asparagus	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Aubergine	Italy	LC	Spray, broadcast	0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.04	NS	NS	2
Avocado	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Beans	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Berries	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Germany	Liquid	Spray, broadcast	0.4	NS	3 max.	2
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Berries (except strawberries)	Germany	NS	Spray, broadcast	0.017	NS	NS	2
Brocolli	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Brassica plants	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Broad bean	Italy	NS	Spray, broadcast	0.04	NS	NS	2
Brussels sprouts	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Bulb vegetables	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Bush-beans, etc.	Germany	DP	Spray, broadcast	NS	0.75	NS	1
Bush-beans	Germany	DP	Dusting	NS	0.75	NS	NS
Cabbage	Italy	LC	Spray, broadcast	0.032 to 0.375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.12	NS	NS	2
	Germany	DP	Spray, broadcast	NS	0.75	NS	3
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Carrots	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Cauliflower	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Cereal grains	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Chayote	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0

Crop	Country	Form.	Application				PHI (days)
			Method	kg ai/hl	kg ai/ha	No.	
Cherry	Italy	NS	Spray, broadcast	0.04	NS	NS	2
Citrus fruits	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
Coffee	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Collards	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Cotton	Australia	NS	Spray, broadcast	NS	0.32 to 0.35	NS	NS
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Cucumbers	Germany	DP	Spray, broadcast	NS	0.75	NS	2
Cucurbit vegetables	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Egg plant	Italy	NS	Spray, broadcast	0.04	NS	NS	2
Field beans	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Figs	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Fruit trees	Australia	NS	Spray, broadcast	0.05 to 0.8	NS	NS	1
Fruiting vegetables	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
Fruits (except strawberries)	Germany	NS	Spray, broadcast	0.036	NS	4 max.	2
Fruits	Australia	XX [3]	Spray, broadcast	0.078	NS	NS	1
	Netherlands	Liquid	Spray, broadcast	0.04	NS	NS	2
General crops	Italy	NS	Spray, broadcast	0.04	NS	NS	2
Grape vines	Australia	NS	Spray, broadcast	0.10	NS	NS	1
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Grasses for seed, forage, fodder, and hay	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Greenhouse fruits	Costa Rica	NS	Spray, broadcast	0.11	NS	NS	0
Greenhouse vegetables	Costa Rica	NS	Spray, broadcast	0.11	NS	NS	0
	USA	NS	NS	NS	NS	NS	NS
Greenhouse & glasshouse crops	Australia	NS	Spray, broadcast	0.05 to 0.10	NS	NS	1
Haricot beans	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Harvested fruits and vegetables	USA	NS	Space spray	NS	NS	NS	NS
Harvested fruits	Costa Rica	NS	Direct Spray	0.05	NS	NS	NS
Hazelnuts	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2

Crop	Country	Form.	Application				PHI (days)
			Method	kg ai/hl	kg ai/ha	No.	
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Herbs and spices	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Hops	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Horticultural crops	Italy	NS	Spray, broadcast	0.037	NS	NS	2
Hydroponically grown vegetables	Costa Rica	NS	Spray, broadcast	0.0001	NS	NS	0
Jojoba	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Kohlrabi	Germany	DP	Spray, broadcast	NS	0.75	NS	3
Leaf vegetables	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Leek	Germany	DP	Dusting	NS	0.75	NS	NS
Legume vegetables	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Legume vegetables, including leaves	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
Legumes	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Lettuce	Germany	DP	Spray, broadcast	NS	0.75	NS	3
	Germany	DP	Dusting	NS	0.75	NS	NS
	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Kale	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Kohlrabi	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Mushrooms	USA	NS	Space spray	5.0 to 6.0	NS	NS	NS
Mustard greens	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Non-grass animal feeds	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Nuts	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Okra	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Olives	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Onion	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Onions and related species	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Oriental vegetables	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Pear	Italy	NS	Spray, broadcast	0.04	NS	NS	2

Crop	Country	Form.	Application				PHI (days)
			Method	kg ai/hl	kg ai/ha	No.	
Pineapple	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Plum	Italy	NS	Spray, broadcast	0.04	NS	NS	2
Pome fruits	Germany	Liquid	Spray, broadcast	0.04	NS	3 max.	2
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Germany	NS	Spray, broadcast	0.017	NS	NS	2
	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Potatoes	Germany	DP	Dusting	NS	0.75	NS	NS
	Italy	LC	Spray, broadcast	0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.04	NS	NS	2
	Germany	DP	Spray, broadcast	NS	0.75	NS	0
Rice	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
Root and tuber vegetables, including leaves	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
Root vegetables	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Root and tuber vegetables, leaves of	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Root and tuber vegetables	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Safflower	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Sesame	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Small-bush fruits	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Small fruits	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Spinach	Germany	DP	Dusting	NS	0.75	NS	NS
Stalk vegetables	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Stem vegetables	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Stone fruits	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
	Germany	NS	Spray, broadcast	0.017	NS	NS	2
	Germany	Liquid	Spray, broadcast	0.04	NS	3 max.	2
	USA	NS	Spray, broadcast	NS	0.045 to 0.56	NS	0.5
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Strawberries	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
	Germany	NS	Spray, broadcast	0.017	NS	NS	NS
	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
	Italy	EC	Spray, broadcast	0.032 to 0.04	NS	NS	2
Sub-tropical fruits	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0

Crop	Country	Form.	Application				PHI (days)
			Method	kg ai/hl	kg ai/ha	No.	
Sugar cane	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Sunflower	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Tea	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Tobacco	Italy	NS	Spray, broadcast	0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.032 to 0.0375	NS	NS	2
Tomato	Italy	NS	Spray, broadcast	0.032 to 0.04	NS	NS	2
	Italy	LC	Spray, broadcast	0.0375	NS	NS	2
	Italy	NS	Spray, broadcast	0.032 to 0.04	NS	NS	2
	Germany	DP	Spray, broadcast	NS	0.75	NS	2
Tree nuts	Costa Rica	NS	Spray, broadcast	NS	0.56	NS	0
Tuber vegetables	Netherlands	Liquid	Spray, broadcast	0.048	NS	NS	2
Vegetables (except capsicums and lettuce)	Australia	NS	Spray, broadcast	0.05	NS	NS	1
Vegetables	Australia	XX	Spray, broadcast	0.078	NS	NS	1
	Netherlands	Liquid	Spray, broadcast	0.04	NS	NS	2
	Australia	NS	Spray, broadcast	0.08	NS	NS	1

[1] Not applicable
[2] Not specified
[3] Microencapsulated timed release liquid concentrate

Table 26. Summary of GAP for post-harvest uses.

Crop	Country	Form.	Application				PHI (days)
			Method	kg ai/hl	mg ai/kg grain	No.	
Milking rooms	Costa Rica	NS	Space spray	0.94	NA	NS	NA
Milking parlours	Costa Rica	NS	Space spray	0.94	NA	NS	NA
Peanuts in bulk or in bags	Costa Rica	NS	Surface treatment	0.62	NA	NS	NA
Stored fruits	Italy	NS	Spray, broadcast	0.032	NS	NS	2
Stored fruits and vegetables	USA	NS	Space spray	NS	NS	NS	NS
	USA	NS	Direct spray	NS	NS	NS	NS
Stored cereals and legumes	Germany	RTU	Space spray	Max. 0.132 kg/1000m^3	NS	NS	NS
Stored food product in cloth bags, sacks, multi-walled paper bags, cardboard cartons	Australia	RTU		0.58 kg/hl	NS	NS	NS
Stored grain	Australia	EC	Spray, broadcast	0.43-0.85	4.3-8.5	NS	1
		EC	Spray, broadcast	0.8	8.0		NS
		RTU	Surface treatment	0.43	0.215/m^2	NS	1

Crop	Country	Form.	Application				PHI (days)
			Method	kg ai/hl	mg ai/kg grain	No.	
Stored grain and seed	Costa Rica	NS	Surface treatment	3	NA	NS	NA
	Italy	ULV	Direct spray	5.4	2.63-4.5*	NS	42
	USA	NS	Direct spray	NS	NA	NS	NA
Stored sweet potatoes	Costa Rica	NS	Space spray	3	NS	Ma x 10	NS
	USA	NS	Space spray	NS	NS	NS	NS
Walnuts in bulk or in bags	Costa Rica	NS	Surface treatment	0.62	NA	NS	NA
Warehouse & storage-dried foods	USA	NS	Space spray	5.0	0.25 kg/1000m^3	NS	NS
	USA	NS	Aerosol surface spray	3.0 to 5.0	NS	NS	NS
	USA	NS	Automatic sequential spray	17.7	NS	NS	NS
	USA	NS	Gas operated liquid dispenser	NS	NS	NS	NS
	USA	NS	Surface spray	5.0	0.30 kg/100 m^2	NS	NS
	USA	NS	Aerosol surface spray	1.25	NS	NS	NS
	USA	Dust	Dust crack and crevice	NS	NS	NS	NS
Warehouses	Costa Rica	NS	Space spray	1.25 to 5.0	NS	NS	NS
	Costa Rica	NS	Surface spray	1.0	NA	NS	NA

Table 27. Summary of GAP for use on animals and their living quarters.

Crop	Country	Form.	Application			
			Method	kg ai/hl	kg ai/ha	No.
Barns	Costa Rica	NS	Space spray	0.94	NA	NS
Cattle	Costa Rica	NS	Direct app.	0.1	NA	NS
Dairies	Costa Rica	NS	Space spray	0.94	NA	NS
Goats	Costa Rica	NS	Direct app.	0.1	NA	NS
Hogs	Costa Rica	NS	Direct app.	0.1	NA	NS
Horses	Costa Rica	NS	Direct app.	0.1	NA	NS
Livestock quarters and dairies	USA	NS	Space spray	0.62 to 1.25	NA	NS
Livestock and Poultry	Costa Rica	NS	Direct app.	0.23 to 1.0	NA	NS
Livestock and Poultry	USA	NS	Direct app.	1.0	NS	NS
Livestock	Costa Rica	NS	Direct app.	0.18	NA	NS
Poultry	Costa Rica	NS	Space spray	0.94	NA	NS
Poultry	Costa Rica	NS	Direct app.	0.94	NA	NS

Crop	Country	Form.	Application			
			Method	kg ai/hl	kg ai/ha	No.
Poultry Houses	Costa Rica	NS	Space spray	0.94	NA	NS
Sheep	Costa Rica	NS	Direct app.	0.1 to 0.12	NA	NS

RESIDUES RESULTING FROM SUPERVISED TRIALS

Pre-harvest uses

Crops were grown in the field in various locations in the USA, using typical agricultural practices. An insecticide containing piperonyl butoxide was applied ten to twelve times at the US maximum GAP rate of 0.56 kg/ha by broadcast ground spray at intervals of three to seven days. Raw agricultural commodities were collected on the day of the last spraying. In each trial, three plots were treated and the highest residue from the plots was selected for estimating maximum and median residue levels. The selected residues are double-underlined in the Tables.

Citrus fruits. Seven trials were conducted in 1992 in the USA (Hattermann, 1994a,b). Residues of PBO ranged from 0.90 to 3.1 mg/kg (Table 28).

Table 28. Residues of piperonyl butoxide in citrus fruits after 10 applications of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (Variety)	Application rate		Residues (mg/kg)
		Water (l/ha)	kg ai/hl	
AZ, Yuma	Lemons (Frost Newseller)	1337	0.042	1.7, 1.1, 1.3
CA, Porterville	Lemons (Lisbon)	2467	0.023	2.2, 2.6, 3.1
	Oranges (Washington Navel)	2454	0.026	0.90, 0.54, 0.65
FL, Oviedo	Oranges (Carrizo)	4072	0.014	0.84, 1.0, 0.77
TX, Raymondville	Oranges (Everhard Navel)	2365	0.024	0.82, 0.98, 0.73
FL, Oviedo	Grapefruit (Flame)	4072	0.014	1.4, 1.0, 1.2
TX, Raymondville	Grapefruit (Rio Red)	2369	0.024	0.49, 0.27, 0.45

Berries and small fruits. In seven trials in 1992/93 in different locations in the USA, one on blackberries, two on blueberries, one on cranberries, one on grapes and two on strawberries (Hattermann, 1994c) three plots were treated identically. Residues in the fruit ranged from 2.8 to 9.6 mg/kg (Table 29).

Table 29. Residues of piperonyl butoxide in grapes and berries after 10 applications of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate		Residues (mg/kg)
		Water (l/ha)	kg ai/hl	
OR, Salem	Blackberry (Evergreen)	823	0.068	2.6, 2.7, 2.8
MI, Conklin	Blueberry (Blue Crop)	1402	0.039	4.6, 4.9, 5.0
NC, Kenly	Blueberry (Woodard Rabbiteye)	490	0.11	4.2, 5.0, 5.5

Location	Crop (variety)	Application rate		Residues (mg/kg)
		Water (l/ha)	kg ai/hl	
MA, East Wareham	Cranberry (Early Black)	303	0.19	4.2, 3.8, 2.8
NY, Phelps	Grape (Catawba)	935	0.060	7.8, 7.7, 9.6
FL, Oviedo	Strawberry (Chandler)	281	0.20	3.0, 2.8, 2.4
OR , Weston	Strawberry (Benton)	220	0.26	3.1, 1.3, 2.6

Brassica vegetables. In eight trials on broccoli and cabbages in 1992/93 (Hattermann, 1994h,i) residues varied from 0.08 to 6.4 mg/kg. Cabbage heads with wrapper leaves had the highest residues (Table 30).

Table 30. Residues of piperonyl butoxide in broccoli and cabbages after 10-12 applications at 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate			Sample	Residues, mg/kg
		No.	Water (l/ha)	kg ai/hl		
AK, Newport	Broccoli (Sultan F1 hybrid)	10	187	0.30	Heads	1.7, 1.6, 1.7
CA, Poplar	Broccoli (Early green sprouting)	10	287	0.20	Heads	1.8, 2.3, 1.7
OR, Salem	Broccoli (Pirate)	12	196	0.29	Heads	0.63, 0.65, 0.69
CA, Poplar	Cabbage (Copenhagen market)	10	266	0.21	Heads with wrapper leaves	2.7, 0.79, 2.5
					Heads without wrapper leaves	0.23, 0.10, 0.17
FL, Oviedo	Cabbage (Tenacity)	11	280	0.20	Heads with wrapper leaves	3.4, 6.4, 4.5
					Heads without wrapper leaves	0.46, 0.28, 0.29
NY, Waterloo	Cabbage (Market prize)	10	234	0.24	Heads with wrapper leaves	0.92, 1.0, 1.1
					Heads without wrapper leaves	0.08, 0.09, <0.1

Fruiting vegetables, cucurbits. In eight trials on curcurbits in 1992/93 (Hattermann, 1996h) residues ranged from 0.07 to 0.83 mg/kg (Table 31).

Table 31. Residues of piperonyl butoxide in cantaloupes, cucumbers and squash after 10 applications of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate		Residues (mg/kg)
		Water (l/ha)	kg ai/hl	
AZ, Somerton	Cantaloupe (Topmark crowset)	236	0.24	0.42, 0.83, 0.73
CA, Porterville	Cantaloupe (Hales best jumbo)	289	0.19	0.60, 0.61, 0.39
MI, Mason	Cucumber (Dasher II)	236	0.24	0.07, 0.06, <0.1
NC, Lucama[1]	Cucumber (General Lee)	219	0.26	0.68, 0.58, 0.49
FL, Oviedo	Squash (Early summer crookneck)	275	0.20	0.23, 0.26, 0.27
GA, Montezuma	Squash (Ely yellow)	187	0. 30	0.05, 0.20, 0.11
NJ, Baptistown	Squash (Black beauty)	238	0.24	0.17, 0.08, 0.10
TX, Uvalde	Squash (Aztec)	154	0.37	0.19, 0.18, 0.25

[1]11 applications

Other fruiting vegetables. In six trials on peppers and tomatoes in 1992/1993 (Hattermann, 1995k), residues ranged from 0.25 to 1.4 mg/kg (Table 32).

Table 32. Residues of piperonyl butoxide in peppers and tomatoes after 10 applications at a rate of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate		Residues (mg/kg)
		Water (l/ha)	kg ai/hl	
CA, Porterville	Pepper (Yolo wonder)	295	0.19	0.76, 0.60, 1.4
NC, Lucama	Pepper (CA wonder bell)	208	0.27	0.17, 0.39, 0.25
TX, Uvalde	Pepper (Jupiter)	156	0.36	0.44, 0.56, 0.59
FL, Oviedo	Tomato (Heartland)	280	0.20	1.0, 0.90, 0.85
MI, Conklin	Tomato (Peto 118)	214	0.26	0.37, 0.23, 0.19
NJ, Baptistown	Tomato (Better boy)	252	0.22	0.48, 0.76, 0.61

Leafy vegetables. In nine trials in 1992/1993 (Hattermann, 1996f) residues in lettuce, radish leaves and spinach ranged from 0.35 to 39 mg/kg (Table 33).

Table 33. Residues of piperonyl butoxide in leafy vegetables after 10 applications of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (Variety)	Application rate		Sample	Residues (mg/kg)
		Water (l/ha)	kg ai/hl		
CA, Poplar	Head lettuce (Iceberg)	287	0.20	Heads with wrapper leaves	3.4, 3.2, 3.6
				Heads without wrapper leaves	0.21, 0.54, 0.21
FL, Oviedo	Head lettuce	280	0.20	Heads with wrapper leaves	5.0, 4.2, 5.0
				Heads without wrapper leaves	0.35, 0.09, <0.1
AZ, Somerton	Leaf lettuce (Walomanns Green)	241	0.23	Leaves	23, 23, 21
FL, Oviedo	Leaf lettuce (BSS)	280	0.20	Leaves	19, 16, 17
GA, Montezuma	Mustard greens (Florida Broadleaf)	191	0.29	Green leaves	34, 31, 37
TX , Uvalde	Mustard Greens (Giant Curled)	153	0.37	Green leaves	25, 31, 38
FL, Oviedo	Radish leaves (Early Scarlet)	275	0.20	Crowns with leaves attached	38, 35, 36
CO, Austin	Spinach (Polka)	234	0.24	Leaves	30, 32, 32
TX, Uvalde	Spinach (Fall Green)	157	0.36	Leaves	39, 31, 28

Legume vegetables. In two trials on succulent beans and two on succulent peas in 1992/1993 (Hattermann, 1994e,f), the residues in pods with seed ranged from 0.34 to 5.1 mg/kg (Table 34).

Table 34. Residues of piperonyl butoxide in the pods of succulent beans and peas after applications at 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate		Residues (mg/kg)
		Water (l/ha)	kg ai/hl	
FL, Oviedo	Succulent Bean (Green Crop)	275	0.20	1.6, 2.2, 1.5
WI, Delevan	Succulent Bean (Atlantic)	262	0.21	0.31, 0.28, 0.34
CA, Poplar	Succulent Pea (Wando Seed)	225	0.25	5.0, 5.1, 4.8
ND, Northwood	Succulent Pea (Wando Seed)	188	0.30	0.97, 1.9, 2.2

Pulses. In two trials on beans and two on peas in 1992/93 (Hattermann, 1994e,f) residues in the dry seeds ranged from 0.10 to 0.57 mg/kg. (Table 35).

Table 35. Residues of piperonyl butoxide in the dry seeds of peas and beans after 10 applications of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate		Residues (mg/kg)
		Water (l/ha)	kg ai/hl	
CO, Austin	Dry beans (Bill Z)	234	0.24	0.10, 0.10, <0.10
ND, Northwood	Dry beans (Upland Navy)	187	0.30	0.10, 0.11, 0.10
TX, Uvalde	Dry peas (CA Blackeye Pea #5)	157	0.36	0.50, 0.39, 0.57
WA, Walla Walla	Dry peas (Columbia)	228	0.25	0.24, 0.27,0.10

Celery .In a trial in Michigan and another in California in 1993 (Hattermann, 1996f) 10 applications of 0.56 kg ai/ha (0.21 or 0.23 kg ai/hl) with a 0 day PHI gave residues in untrimmed leaf stalk of 17, 7.2 and 6.1 mg/kg in Michigan and 23, 16 and 18 mg/kg in California. In the petiole, these values dropped to 0.98, 1.5 and 1.4 mg/kg, and 2.3, 2.0 and 3.7 mg/kg respectively.

Mustard seeds. In a trial in Georgia in 1993 after 10 applications of 0.56 kg ai/ha (0.30 kg ai/hl) (Hattermann, 1994h), residues were <0.10, 1.4 and 2.1 mg/kg.

Root and tuber vegetables. In a total of seven trials, one on carrots, 3 on potatoes, 1 on radishes and 2 on sugar beet (Hattermann, 1995d,e), the residues in the roots of all crops ranged from 0.10 to 0.34 mg/kg (Table 36).

Table 36. Residues of piperonyl butoxide in carrots, potatoes, radishes and sugar beet after 10 applications of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate		Sample	Residues (mg/kg)
		Water (l/ha)	kg ai/hl		
TX, Pearsall	Carrots (Imperator)	154	0.36	Roots with crowns removed, unwashed	0.36, 1.1, 1.1
CO, Austin	Potatoes	234	0.24	Tubers	<0.10, 0.11, <0.10
ID, Middleton	Potatoes	206	0.27	Tubers	<0.10, <0.10, ≤0.10
ME, Exeter	Potatoes	195	0.29	Tubers	<0.10, <0.10, ≤0.10
FL, Oviedo	Radishes (Early Scarlet)	275	0.20	Roots with crowns removed, washed	0.17, 0.27, 0.34
MN, Fisher	Sugar beet (ACH-192)	188	0.30	Roots with crowns removed, unwashed	<0.10, <0.10, ≤0.10
ND, Northwood	Sugar beet (ACH-192)	186	0.30	Roots with crowns removed, unwashed	<0.10, <0.10, ≤0.10

Sugar beet leaves. In a trial in Minnesota and another in North Dakota after 10 applications of 0.56 kg ai/ha (0.20 and 0.30 kg ai/hl), residues of piperonyl butoxide in crowns with leaves attached were 37, 35, and 36 mg/kg in Minnesota and 11, 8.4 and 12 mg/kg in North Dakota (Hattermann, 1995d).

Cotton. In trials on cotton residues were determined in the seed and forage (Hattermann, 1995g) (Table 37). Forage was collected from immature plants 14 days after the fourth application except in one trial when it was collected after the ninth application.

Table 37. Residues of piperonyl butoxide in cotton seed after 10 and in forage after 4 or 9 applications of 0.56 kg ai/ha, final 0-day PHI.

Location	Application rate		Sample	Residues (mg/kg)
	Water (l/ha)	kg ai/hl		
CA, Porteville	280	0.20	Seed	0.10, <0.10, <0.10
			Forage	18, 15, 20

Location	Application rate		Sample	Residues (mg/kg)
	Water (l/ha)	kg ai/hl		
MS, Greenville	194	0.29	Seed	0.21, 0.12, <0.10
			Forage	11, 11, 28
TX, Snook	95	0.59	Seed	0.10, 0.10, <0.1
			Forage	28, 30, 20
AZ, Yuma	234	0.24	Seed	≤0.1, 0.10, 0.11
			Forage	37, 36, 30
LA, Washington	185	0.30	Seed	≤0.1, <0.1, <0.1
			Forage	21, 29, 30

Legume animal feed. In trials on beans and peas forage was collected from immature plants, the bean hay samples were dried for 2 to 6 days in the open air, and the pea hay samples for up to 14 days in the field or glasshouse (Hattermann, 1994e) (Table 38).

Table 38. Residues of piperonyl butoxide in legume animal feed after 10 applications of 0.56 kg ai/ha, 0-day PHI.

Location	Crop (variety)	Application rate		Sample	Residues (mg/kg)
		Water (l/ha)	kg ai/hl		
FL, Oviedo	Succulent Bean (Green Crop)	275	0.20	Vine	19, 26, 28
				Hay	40, 31, 42
WI, Delevan	Succulent Bean (Atlantic)	262	0.21	Vine	14, 15, 16
				Hay	11, 7.4, 6.2
CO, Austin	Dry Beans (Bill Z)	234	0.24	Vine	16, 16, 11
				Hay	17, 21, 11
				Forage[1]	14, 10, 9.4
ND, Northwood	Dry Bean (Upland Navy)	187	0.30	Vine	24, 25, 26
				Hay	14, 13, 13
				Forage[1]	18, 17, 25
CA, Poplar	Succulent Pea (Wando Seed)	225	0.25	Vine	42, 47, 35
				Hay	153, 129, 116
ND, Northwood	Succulent Pea (Wando Seed)	188	0.30	Vine	23, 24, 26
				Hay	30, 25, 38
TX, Uvalde	Dry Pea (CA Blackeye Pea #5)	157	0.36	Vine	29, 29, 27
				Hay	1.2, 2.6, 3.7
				Forage[1]	30, 27, 31
WA, Walla Walla	Dry Pea (Columbia)	228	0.25	Vine	63, 96, 54
				Hay	40, 44, 48
				Forage[1]	42, <0.1, 25

[1] Sampled before maturity

Post-harvest treatments

Residues of piperonyl butoxide in beans, peanuts and prunes stored under simulated warehouse conditions were determined after two different methods of spraying (Meinen, 1991a,b).

Space spray. A pallet containing ten samples of each commodity was placed at the centre of a room 170 cubic m in volume, which was fogged twice a week for five weeks, using applications at the normal label rate of 0.25 kg/ai per 1000 cubic m.

Contact spray. A similar pallet was placed at the centre of a 3.05 m x 4.0 m room which was sprayed around its edges and around the pallet twice a week for five weeks at the normal label rate of 0.30 kg ai/100 square m.

Single samples of 0.9 kg of navy beans and 0.9 kg of Spanish peanuts in cotton cloth bags and 0.34 kg of dried prunes in a commercial foil bag were collected for analysis after each treatment. Each value is the result of a single analysis unless otherwise indicated (Table 39).

Table 39. PBO residues, mg/kg, in food commodities after space (SS) and contact (CS) sprayings under simulated warehouse conditions.

Commodity	No of applications									
	1	2	3	4	5	6	7	8	9	10
Beans (SS)	≤0.05	TR	≤0.05	0.10	TR	0.13	0.16	0.13	TR	0.17
(CS)	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05
Prunes (SS)	0.05[1]	≤0.05	≤0.05	0.11[1]	TR	≤0.05[1]	≤0.05	TR	TR	TR
(CS)	TR[1]	≤0.05	TR	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	TR	TR
Peanuts (SS)	TR	TR	TR	0.20	0.24	0.29	0.36	0.28	0.54	0.54
(CS)	≤0.05	0.15[1]	≤0.05	TR	≤0.05	TR[1]	TR[1]	TR	TR	0.12

TR: Trace, >0.05 mg/kg, <0.10 mg/kg
[1]Mean of duplicate analyses.

In trials in Germany, 1993-94, a 200 m^3 room was space-sprayed eight times with pyrethrum/piperonyl butoxide at 21.3 g PBO/1000 m^3 at 14-days intervals, or twice at 128 g PBO/1000m^3. Samples were taken from immediately after the last treatment until 90 days later (Nedvidek, 1994a,b). GAP for space spraying in Germany is 0.375 to 132 g ai/1000 m^3. The results are given in Table 40.

Table 40. Residues of piperonyl butoxide after space-spraying treatments in Germany.

Time (days)	Bulk wheat	Wheat flour in paper sacks	Cacao beans in jute sacks	Raisins in polythene/cardboard
8 x 21.3 g PBO/1000 m^3				
0	2.5	-	0.21	-
14	1.2	-	0.25	-
30	0.71	-	0.07	-
60	1.2	-	0.16	-
90	1.4	-	0.08	-
2 x 128 g PBO/1000 m^3				
0	2.2	0.16	0.52	≤0.01
14	2.0	0.12	0.53	<0.01
30	1.3	0.15	0.75	<0.01
60	1.5	0.46	0.58	<0.01
90	1.7	0.44	0.65	<0.01

Wheat. Post-harvest treatment of wheat is the most significant use for grain protectants containing piperonyl butoxide. In California, USA, Blinn *et al.* (1959) treated wheat at 13% moisture content with a wettable powder formulation containing 20% technical piperonyl butoxide at a rate of 15 mg ai/kg of grain. The grain was stored at 30ºC. Residues of PBO in the grain 1, 14, 30 and 90 days after application were 7.7, 6.2, 5.0 and 3.5 mg/kg. Each result is an average of 2 analyses, corrected for background (0.10 mg/kg) and for analytical recovery (98%). No full report of the study was provided.

Walkden and Nelson (1959) carried out concurrent trials with wheat using different formulations of pyrethrins/PBO in bins of 11276.5 hl in Kansas, from 1955 to 1957. Residues of PBO after the treatments are shown on Table 41. Formulations were applied to the wheat as it was transferred from the delivery truck to the bins.

Table 41. Residues of piperonyl butoxide in wheat, Kansas, 1955-57.

Dose (mg PBO/kg grain)	Piperonyl butoxide, mg/kg, range and (mean[1]) after months					
	3	13	16	19	22	25
15	2.6-4.4 (3.2)	7.5-12 (8.7)	5.2-10 (8.5)	4.3-7.2 (6.2)	4.6-11 (7.9)	9.4
20		8-12 (11)	9.4-13 (12)	6.8-10 (8.2)	9-11 (10)	9.4-11 (10)
25		9.5-13 (11)	6.6-17 (11)	7.7-11 (8.9)	8.6-12 (9.5)	9.4; 14 (12)
25[2]	16-30 (21)	13-16 (15)	17-20 (18)	4-14 (9.5)	17-25 (22)	13; 16 (14)
6.8	2.5-3.6 (3.2)	1.7-2.5 (2.2)	4.6-5.2 (4.7)	3.1-4.3 (3.7)	3.3-4.5 (3.9)	3.0-3.5 (3.3)

[1] Up to five bins
[2] piperonyl butoxide alone

Strong *et al.* (1961) treated wheat of 10% and 13% moisture content with 15 mg PBO/kg grain in emulsion, wettable powder and tetrachloroethylene formulations. The treated wheat was stored for 3 months at both 15.5ºC and 30ºC. Residues ranged from 4.1 to 11 mg/kg No full report of the study was provided.

In a trial by La Hue (1966) in the USA, small bins (0.14 m^3) were filled with wheat treated with an EC formulation at 21.4 mg piperonyl butoxide/kg/grain. Residues of PBO 0, 1, 3, 6, 9 and 12 months after treatment were 6.6, 11, 13, 8.4, 8.8 and 9.9 mg/kg respectively. No full report was provided.

A range of treatments with various insecticides synergised by piperonyl butoxide were tested in Australia. Five-tonne bins were used for liquid formulations and 200 kg drums for powder formulations (Ardley, 1978,1979). Residues were determined in the wheat after up to 9 months storage (Table 42).

Table 42. Residues of piperonyl butoxide in wheat stored up to 9 months.

Formulation	Dose, (mg PBO/kg grain)	Residues (mg/kg) after storage (months)				
		0.75	3	5.5	6	9
Permethrin/fenitrothion	4.0		2.9		3.0	3.3
			2.9		4.7	2.6
			2.6		2.5	3.2
	6.0		3.4		3.1	2.8
Bioresmethrin/fenitrothion (p)	10	6.9		8.0	5.5	4.0

Formulation	Dose, (mg PBO/kg grain)	Residues (mg/kg) after storage (months)				
		0.75	3	5.5	6	9
Bioresmethrin/fenitrothion	10	7.1		5.0	4.5	4.0
	4	3.6		3.4	3.5	3.5
			2.6		2.8	2.2
Pyrethrins/fenitrothion (p)	20	9.3		14	16	12
Pyrethrins/fenitrothion	20	12		13	14	12
	10	7.2		5.8	6.5	4.0
Permethrin	4	3.8		3.3	2.3	1.5
Deltamethrin/fenitrothion	10	6.2		5.8	2.5	2.0
Deltamethrin	10	5.8		9.1	5.6	5.0
Phenothrin/fenitrothion	10	4.7		3.0	7.5	5.5
Fenvalerate/fenitrothion	10	6.6		5.4	7.5	7.0
Fenvalerate	10	6.2		7.3	8.0	5.0
	2	2.4		1.4	1.3	0.8
	4	3.7		2.1	3.0	1.5

(p): powder formulations. The remainder are liquid.

Halls (1981) reported trials in which piperonyl butoxide was applied at 10 mg ai/kg in various formulations to wheat in Australia. Five tonnes of wheat were treated in a steel silo or a 200 kg metal drum. Samples were taken from the surface and at depths of 1-2 m in the silos and from the top, middle and bottom of the drums. Samples from the different levels were mixed and analysed during 8 months (Table 43). Ardley *et al.* (1982) carried out trials in Australia in 1980 on wheat stored in five-tonne bins and 200 kg drums, applying piperonyl butoxide in various EC formulations at 10 mg ai/kg grain; the results of these are also shown in Table 43.

Table 43. Piperonyl butoxide residues in wheat treated in Australia at 10 mg PBO/kg grain.

Formulation	Residues (mg/kg) after storage (months)						
	0	1	2	3	6	8	9
Halls (1981)							
permethrin/fenitrothion	3.9	4.5	4.4	5.0	5.7	3.8	
	7.9	4.6	4.1	5.5	6.7	4.0	
permethrin	4.2	3.4	3.0	4.0	4.0	3.5	
	5.6	7.3	6.9	6.6	6.4	5.9	
Ardley *et al.* (1982)							
bioresmethrin/fenitrothion	7.3	7.3	5.0	4.7	2.9	3.7	5.2
phenothrin/fenitrothion	4.5	4.5	5.3	4.5	5.3	4.6	3.5
fenvalerate/fenitrothion	4.5	4.2	3.4	4.8	5.0	4.3	3.8
	7.0	4.2	3.6	4.7	6.7	3.3	3.6

Formulation	Residues (mg/kg) after storage (months)						
	0	1	2	3	6	8	9
fenvalerate	3.9	4.1	4.5	4.5	4.1	3.5	4.3
	5.9	7.3	7.8	6.1	4.7	6.2	7.8
deltamethrin/fenitrothion	3.9	4.5	3.3	4.3	5.2	3.1	3.3
	3.1	3.0	4.5	3.9	4.8	2.9	4.1
deltamethrin susp conc	6.5	5.9	7.5	6.9	5.4	6.8	6.4
deltamethrin oil	6.5	7.8	7.2	8.1	5.5	6.9	5.2
permethrin/fenitrothion	3.9	4.5	4.4	5.0	5.7	3.8	3.0
	7.9	4.6	4.1	5.5	6.2	4.0	4.0
permethrin	4.2	3.4	3.0	4.0	4.0	3.5	2.7
	5.6	7.3	6.9	6.6	6.4	5.9	62
300H78	7.3	8.2	6.6	7.9	5.2	6.9	6.7
	5.3	5.9	4.2	6.4	5.1	4.2	10
	7.9	6.2	6.1	6.9	4.6	6.6	5.8
different sampling intervals	0	0.5	3.5	5.5	6.5	-	-
fenvalerate/fenitrothion	8.3	8.0	9.0	7.9	10		
	8.6	7.2	7.7	6.6	6.8		
fenvalerate	7.7	6.1	9.2	8.0	-		
	7.0	4.5	5.2	5.5	-		
	6.5	6.0	5.0	5.5	11		
fenvalerate/fenitrothion	7.5	7.4	8.0	-	5.7		
	8.8	7.6	9.4	-	8.2		
fenvalerate	7.4	5.8	7.8	6.0	6.4		
	7.2	6.1	8.3	6.2	10		
	17	30	6.5	9.3	14		

A long-term study was also conducted by Ardley *et al.* (1982) using different formulations of piperonyl butoxide at 10 mg PBO/kg grain (Table 44).

Table 44. Residues of piperonyl butoxide from trials conducted in Australia at 10 mg ai/kg grain.

Formulation	Residues of piperonyl butoxide (mg/kg) after storage (months)											
	10	11	12	13	16	18	19	25	26	27	28	31
deltamethrin/fenithrothion	7.3	6.5	4.7	7.0	5.5	5.3	5.0	-	-	-		-
deltamethrin oil	5.6	6.7	5.3	6.6	5.0	5.3	5.3	-	-	-		-
	4.5	3.6	1.9	3.5	4.7	2.4	2.5	2.8	2.8	3.1	5.9	4.5
deltamethrin flowable	5.9	3.6	4.5	8.1	4.0	5.3	4.8	-	-	-	-	-

Nicholls *et al.* (1984) evaluated further grain protectant combinations in EC formulations in Australia in 1978/80, storing the wheat in five-tonne bins and 200 kg drums. Residues were determined immediately after application and for up to 9 months afterwards (Table 45).

Table 45. Piperonyl butoxide residues in wheat stored for 9 months in Australia.

Formulation	Dose, (mg/kg PBO grain)	Piperonyl butoxide residues (mg/kg) after storage for (months)							
		0	1	2	3	4	6	7	9
phenothrin/fenvalerate/fenitrothion	5	-	2.2	2.2	3.1	3.3	3.6	4.2	4.5
	10	7.3	6.3	6.6	6.5	6.7	7.5	5.6	9.7
phenothrin/fenitrothion	10	5.4	6.3	6.4	-	6.3	8.6	6.0	6.5
		6.3	5.8	6.3	6.2	7.7	5.3	6.9	-
		5.6	5.2	5.3	7.9	5.6	9.2	8.5	8.7
deltamethrin/permethrin	3	1.4	2.3	1.5	-	1.8	1.2	1.8	1.6
deltamethrin/fenitrothion[1]	10	1.9	7.9	8.7	8.6	8.4	8.9	5.1	7.8
deltamethrin	10	3.5	9.3	6.5	5.1	8.1	6.2	7.3	9.3
		12	4.6	6.1	6.6	9.5	8.9	5.6	4.5
		7.6	8.4	8.5	8.7	7.4	7.3	5.2	10
		9.7	12	13	16	11	9.7	12	8.7
bioresmethrin/fenitrothion	10	5.8	3.5	4.9	5.0	5.7	6.4	4.4	7.3
fenvalerate/fenitrothion	10	4.7	7.9	8.1	7.7	8.4	7.0	5.8	8.3
cypermethrin	10	7.9	10	9.5	14	11	5.5	8.7	6.4
		4.5	8.6	8.2	8.2	8.1	7.8	10	6.3

[1] powder formulation

A series of trials were conducted in Australia from 1988 to 1998 at various sites using different formulations of piperonyl butoxide (Table 46). Except for Crampton *et al.* (1990), no full reports were provided.

Table 46. Residues of piperonyl butoxide in wheat from trials in Australia, 1988-98.

Site	Report	Formulation	PBO dose (mg ai/kg grain)	Residues of piperonyl butoxide (mg/kg)* after (months)					
				0	1.5	3	4.5	6	9
Bangalla, NSW	Crampton *et al.*, 1990	bioresmethrin/ chlorpyrifos-methyl	8.0	11	9.8	10	13		7.5
		bioresmethrin /fenitrothion	8.0	9.9	9.7	10	16		13
Wail, Vic		bioresmethrin/ chlorpyrifos-methyl	8.0	3.7	5.4	5.0	5.4		
			4.6	1.3	1.6	1.7			
Malu, Qld	Bengston, 1991a	methacrifos/ bioresmethrin	7.39	4.8	4.4	4.4	4.1	3.8	3.2
	Bengston, 1991b	methacrifos/ permethrin	9.5	7.5	5.7	6.2	5.5	5.3	4.5
Greenethorpe, NSW	Bengston, 1991a	methacrifos/ bioresmethrin	7.8	5.1	4.9	5.3	4.8	5.1	
	Bengston, 1991b	methacrifos/ permethrin	7.5	7.3	3.7	6.3	5.8	5.7	

Site	Report	Formulation	PBO dose (mg ai/kg grain)	Residues of piperonyl butoxide (mg/kg)* after (months)					
				0	1.5	3	4.5	6	9
Arkona, Vic	Bengston, 1991a	methacrifos/ bioresmethrin	8.2	3.6	3.8	3.4	3.3	4.4	
Vectis, Vic	Bengston, 1991b	methacrifos/ permethrin	10.7	7.6	7.9	7.3	6.2	5.6	
North Freemantle, WA	Bengston, 1991a	methacrifos/ bioresmethrin	5.8	5.3	4.8	3.9	3.8	4.3	3.4
	Bengston, 1991b	methacrifos/ permethrin	8.3	7.4	7.2	3.2	5.6	5.5	2.8
	Bengston, 1993c	chlorpyrifos-methyl/deltamethrin	8.0	3.0	3.8	4.3	3.7	4.8	
Thevenard	Bengston, 1991b	methacrifos/ permethrin	7.4	5.5	4.1	3.4	2.1	2.0	1.8
Cecil Plains, Qld	Crampton *et al.*, 1990	bioresmethrin/ chlorpyrifos-methyl	8.0	7.8	5.6	7.6	5.6	7.3	
	Bengston, 1993c	chlorpyrifos-methyl/deltamethrin	6.01	5.6	3.4	3.3	2.7	2.9	
	Bengston, 1993d	chlorpyrifos-methyl/deltamethrin**	7.8	6.4	8.9	7.4	8.2	8.3	
Premer, NSW	Bengston, 1993c	chlorpyrifos-methyl/deltamethrin	6.1	4.0	4.0	3.4	3.8	4.2#	
	Bengston, 1993d	chlorpyrifos-methyl/deltamethrin**	3.24	1.9	1.8	1.7	<1.1	2.4	
Ardrossan, SA	Bengston, 1993c	chlorpyrifos-methyl/deltamethrin	7.04	2.2	5.8	2.6	3.8	2.8	
Grenfell, NSW	Bengston, 1994b	chlorpyrifos-methyl/deltamethrin**	6.5	2.9	4.3	2.2			
Nyrang Creek, NSW	Bengston, 1996b	deltamethrin	8.0			5.2			
Bribbaree, NSW			4.0			1.5			
The Rock, NSW	Bengston, 1997	chlorpyrifos-methyl/deltamethrin**	4.5	2.1				1.5	
	Anon., 1999	bifenthrin/ chlorpyrifos methyl	8.3	5.6	5.4	6.1	3.9	5.0	5.8
	Daglish *et al.*, 1999		7.30	5.4		6.4	3.7	5.8	3.3
Millmerran Qld	Anon., 1999		8.0	11	6.4	6.7	6.8	6.1	
	Daglish *et al.*, 1999		6.98	6.2	4.9	5.1	4.2	4.0	7.5
Sutherland Vic	Anon., 1999		8.0	1.8		2.4	2.4	2.3	
Wychitella Vic	Daglish *et al.*, 1999		8.0	5.1	5.5	3.5	2.2	4.6	
Wirrabarra SA	Daglish *et al.*, 1999		8.0	5.2	4.4		4.9		4.3

*average of 2 or 3 laboratory results **7 months sample

Molinari (1987) in Italy applied 2 different deltamethrin/piperonyl butoxide products at 3 dosage levels to wheat stored either in vertical silos or warehouses for 3-12 months (Table 47).

Table 47. Trials on wheat in Italy, 1985/86.

Location	Dose (mg ai/kg grain)	Residue (mg/kg) after storage (months)				
		0	1.4	3	6	12
San Giorgio di Piano[1,2]	2.5	0.58	1.0	0.8	2.0	
	5	0.53	3.3	4.9	8.7	
	10	2.0	9.8	12	13	
Montepascali[1,2]	2.5	0.97	0.84	0.65	0.86	1.4
	5	0.89	2.3	0.21	0.98	3.0
	10	1.0	3.7	0.20	2.1	3.9
Ponte a Rigo[1,3]	2.5	1.0	1.2	0.89	1.8	0.98
	5	2.3	2.1	2.1	2.4	2.1
	10	0.14	2.7	4.6	5.2	3.7
La Spezia[1,2]	2.5	1.2	0.12	0.22	<0.10	
	5	2.5	0.80	0.65	0.99	
	10	4.2	1.6	1.7	2.6	
Lendinara [1,3]	2.5	0.34	0.24	0.18		
	5	1.0	0.70	0.88		
	10	3.4	2.1	3.9		
Lendinaria [3,4]	2.5	1.3	1.7	2.7		
	5	1.6	1.2	1.5		
	10	2.8	4.5	2.7		

[1] vertical silo
[2] hard wheat
[3] soft wheat
[4] warehouse

Barley. Post-harvest trials were conducted on barley in Australia at various sites from 1992 to 1996 using different PBO formulations (Table 48). Final, but not full, reports were provided.

Table 48. Residues of piperonyl butoxide in barley from trials in Australia 1992-96.

Site (trial size)	Report	Formulation	PBO dose (mg ai/kg grain)	Residues of piperonyl butoxide (mg/kg)[1] after (months)					
				0	1.5	3	4.5	6	6.5
Ardrossan, WA (pilot scale)	Bengston, 1993a	Methacrifos/ bioresmethrin	7.0	4.6	6.5	3.8	4.8	3.7	
(concrete silos)	Bengston, 1993b	fenitrothion/ bioresmethrin	3.52	1.8	2.0	2.6			
(pilot scale)	Bengston, 1994a	Methacrifos/ bioresmethrin	7.05	2.9	6.0	4.2	3.8	3.6	
Port Adelaide, SA (pilot scale)			6.76	3.9	6.4	6.7	3.3		
Jeparit, Vic (pilot scale)			6.78	6.6	6.4	5.6	6.6	5.4	4.4
Murray Bridge SA (field)	Bengston, 1996c	deltamethrin	6.33	7.2	4.3	4.3	4.6	4.2	
Brim, Victoria	Bengston, 1997c		8	0.9	0.8	-	<1.0		

[1]average of 2 or 3 laboratory results

Maize. In the USA Quinlan and Miller (1958) investigated residues of PBO after surface-layer treatment with pyrethrins synergised with piperonyl butoxide, applied half-weekly, weekly, and bi-weekly to maize in 1177 hl metal silos 5.5 m diameter. One litre of spray was applied to the surface of the grain and an additional half-litre was applied to the space above from the outside (Table 49).

Table 49. Residues of piperonyl butoxide in maize after surface application.

g PBO ai/100 m^2 (frequency of application)	Residue, as % of total applied	
	3 months after treatment	6 months after treatment
49.7 (half-weekly/weekly/bi-weekly)	26/27/27	12/11/12
99.3 (half-weekly/weekly/bi-weekly)	25/33/38	12/11/13
149 (half-weekly/weekly/bi-weekly)	41/30/31	11/13/12

Walkden and Nelson (1959) carried out trials using different pyrethrins/PBO formulations in bins of 11276.5 hl in Kansas, from 1952 to 1957. The formulations were applied to the maize as it was transferred from the delivery truck to the bins.

Residues of PBO after the treatments are shown on Tables 50-52. There is no approved use for dust formulation of PBO in the USA.

Table 50. Residues of piperonyl butoxide in maize (1952-1956).

Formulation (mg PBO/kg grain)	Piperonyl butoxide residue (mg/kg) after months			
	2	4	6	50
dust on talc (14.2)		6.0	3.0	
		6.0	3.0	
		8.0	7.0	

Formulation (mg PBO/kg grain)	Piperonyl butoxide residue (mg/kg) after months			
	2	4	6	50
dust on corncob flour (14.2)	2.5	2.0		10
(19.7)	12	2.0		
Solution spray (10.4)		8.0	1.0	
		7.0	2.0	
		1.0	-	
Emulsion spray (12.3)		4.0	3.0	
		21	1.5	3.3
		3.0	-	3.0

Table 51. Residues of piperonyl butoxide in maize. (1954-1957).

Formulation (mg PBO/kg grain)	Piperonyl butoxide residue (mg/kg) found after (months)										
	1	3	6	9	12	16	19	22	26	28	31
Spray (11.6)	3.0	5.5	5.0								
	7.0										
	8.0										
(17.4)	3.0										
(23.2)	11										
	4.0										
	8.0	8.0	8.0								
dust on corncob flour (14.7)	7.0										
	3.0	2.0	9.0								
	4.0										
		3.0	8.0								
	3.0	2.0	8.0								
	3.0										
(29.4)	8.0										15
	7.0										
	8.0	2.0	25	10	16	17	12	6.3	5.0	5.6	17
	6.0										
	4.0	2.0	9.0								
	6.0	2.0	13								8.9

Table 52. Residues of piperonyl butoxide in maize. (1954-1957).

Formulation	Piperonyl butoxide residue (mg/kg) found after (months)											
(mg PBO/kg grain)	2	5	7	11	13	16	22	26	28	31	34	35
Emulsion	15	10	1.7	6.0	9.6	7.5	5.0	10	7.8	7.4	7.0	6.6
Spray	16	9.0		2.0	8.8	8.3	9.0	10	8.4	7.8	7.5	6.6
(16.7)	14	13	3.5	2.0	8.0	6.4	10	9.5	8.2	7.8	6.5	6.6
	12	14	3.8	6.0	10	5.4	7.0	7.5	7.8	7.0	6.0	4.7
	10	11	4.3	6.0	6.4	6.9	10	8.5	6.2	7.4	6.0	5.5

In the USA La Hue (1966) treated 0.7 m^3 lots of maize with a piperonyl butoxide/pyrethrins EC at 28 mg piperonyl butoxide/g grain and moved them into small bins. Residues in samples taken after 1, 3, 6, 9 and 12 months were 10, 7.7, 6.7, 5.0 and 6.1 mg/kg. No full report was provided.

In Italy, Molinari (1991) carried out trials to determine residues in maize after the application of a deltamethrin/piperonyl butoxide EC formulation at two dosages of PBO. The residue levels up to 182 days are given in Table 53.

Table 53. Residues of piperonyl butoxide in treated maize in Italy.

Dose (mg ai/kg grain)	Days after treatment	Residue (mg/kg)[1]
2.43	0/42/91/182	1.3/1.2/1.2/0.72
11.14	0/42/91/182	4.1/2.8/2.2/2.7

[1] average of three samples

Sorghum. Trials were conducted in Australia (Tempone, 1979) using different PBO formulations at 3 to 20 mg ai/kg grain (Table 54).

Table 54. Post-harvest residue trials on sorghum in Australia

Formulation	PBO dose (mg ai/kg grain)	Months after treatment	Residue (mg/kg)
Fenitrothion/phenothrin	20	0/3	20/8.0
Fenitrothion/phenothrin	10	0/3	10/8.0
Pyrethrins.	3	0/3	0.5/<0.30
Pyrethrins	9	0/3	2.9/0.80

Bengston (1996a) carried out one silo-scale trial with sorghum in Australia during 1996, using a chlorpyrifos-methyl/deltamethrin/piperonyl butoxide formulation at 8.5 mg ai/kg grain of PBO. The residues of PBO determined at 0, 1.5, 3, 4.5 and 6 months were 9.3, 7.9, 9.7, 8.0 and 7.2 mg/kg respectively (average of 2 laboratory results). No full report was provided.

FATE OF RESIDUES IN STORAGE AND PROCESSING

Processing

A series of processing studies was conducted on oranges, grapes, tomatoes, beans, potatoes, sugar beet and cotton. Ten or more applications of an insecticide containing piperonyl butoxide were made by broadcast ground spray, following typical agricultural practices, to maturing crops at intervals of three to seven days, at a rate of 2.8 kg ai/ha per application, 5 times the intended maximum use rate. Mature raw commodities were collected as soon as the spray had dried after the last application, except for cotton which was collected 14 days after the last application. Bulk samples were processed into the required products using procedures that simulated commercial practice. Processing procedures are summarized below for each commodity.

Oranges. The fruit was sorted and extraneous material such as leaves and stems removed, before processing into juice, molasses, dry peel (dry pulp), and oil (Hattermann, 1995a,b). The fruit was washed on a Pennwalt/Decco Tiltbelt fruit washer-drier, a standard commercial foam detergent cleaner was applied in a brush washer and the washed fruit rinsed again to remove the detergent (Figure 11). Samples of unwashed oranges were also collected for analysis and stored at 23°C.

Juice. To extract juice a commercial FMC 391B In-Line-Juice Extractor (equipped with continuous water-spray nozzles for maximum recovery of peel oil) is used to produce juice, peel, and oil/water/peel-frit emulsion. Peel and oil/water/peel-frit emulsion then undergo further processing in separate steps. The extracted juice drains down a strainer tube to a manifold under the extractor where it is collected and passed continuously through a modified FMC Model 35 finisher that screens excess pulp from the juice (as in commercial practice). Juice is then collected in a 570 l stainless steel tank fitted with a motor, stirrer and volume-measuring device. At the end of the run, two cases (24 cans/case) of juice are canned and stored at 23°C.

Oil. The oil/water/peel-frit emulsion from the extractor is passed through an Automatic Machinery Co. finisher, Model TRF, with a 0.05 cm screen and variable clearance. The solids are collected and combined with peel from the extractor for further processing. The oil emulsion is passed over a Syntron Model SF 152 shaker screen feeder equipped with a double deck vibrating screening trough. The filtrate is collected in a 190 l stainless steel tank. After a minimum of 5 hours under ambient conditions, the lower unemulsified water phase is drained off. The remaining concentrated oil emulsion is kept at 0°C until processed (normally at least 16 hours).

After storage, any remaining water phase is siphoned off. The concentrated oil emulsion is centrifuged in a laboratory De Laval Gyro Tester continuous centrifuge. The oil fraction is stored at -18°C for at least 16 hours to freeze out any remaining water. The thawed cold-pressed oil is filtered to remove suspended solids. Anhydrous sodium sulfate is added to the oil to remove any remaining water and the mixture is again filtered. The resulting cold-pressed oil is stored at ambient temperature in sealed nitrogen-purged glass bottles.

Dried pulp. The peel-membrane-seed fraction from the FMC extractor and the solids from the oil/water/peel-frit emulsion finisher are combined and stored at ambient conditions (about 2-3 h). In processing, the peel is transferred to the hopper in the pilot plant feed mill. As peel leaves the hopper, a liquid lime slurry is added continuously at a rate of 0.3% lime per weight of peel. The peel is shredded to a more uniform particle size of approximately 12 mm, then passed down a reaction conveyor and up an elevator (~15 min) to the press. The limed-chopped-reacted peel is passed through a continuous press having 1 atmosphere back-pressure of air, that separates the peel into presscake and press liquor.

The presscake is fed to a triple pass direct-fired dryer adjusted to produce a dried citrus pulp of approximately 8-10% moisture with a minimum of charring. The temperature of the exhaust air

from the dryer is about 143°C, which is standard commercial practice. The dried pulp is stored at -23°C, and the press liquor at 0°C until processed into molasses.

Molasses. The press liquor is boiled under vacuum and concentrated in a Precision Scientific 3-l laboratory concentrator to approximately 50°Brix. Small amounts of Dow Corning antifoam B are added to inhibit foaming. The molasses is canned and stored at -23°C.

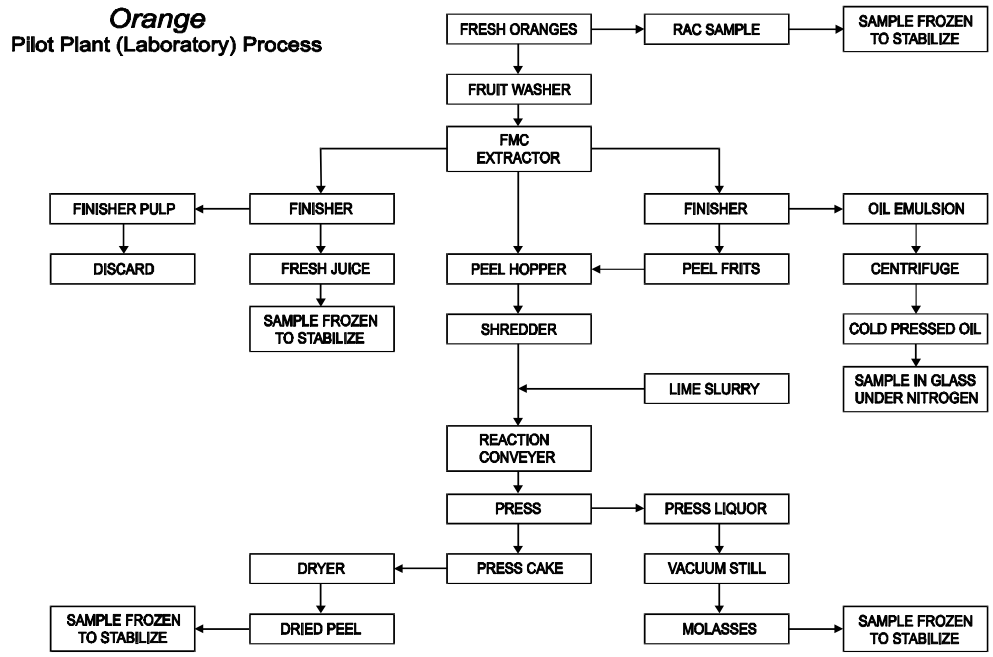


Figure 11. Flow chart for orange processing

Grapes. Grapes were processed into juice and wet and dry pomace by laboratory-scale procedures simulating commercial practice (Figure 12) (Hattermann, 1996a,b). The main differences between this procedure and commercial practice are shown in Table 55.

Table 55. Laboratory and commercial procedures for processing grapes.

Step	Laboratory	Commercial
Washing	High-pressure spray washer for 30 sec.	Powerful sprays of water.
Pressing	Suntech hydraulic fruit press for juice extraction. This method uses press racks and cloths to avoid crushing the stems and seeds. The grapes are pressed at least twice for maximum recoveries. After pressing the pulp (wet pomace), consisting of seeds, skins and stems, is packaged for the wet pomace sample. The remaining wet pomace is dried using a bin air drier, and when dry is packaged for the dry pomace sample. The fresh juice from the pressing operation is strained through a standard milk filter and a sample is packaged.	Rotary Grape Crusher where centrifugal force is applied to break up the grapes, separating juice and pulp from stems without crushing the stems or seeds. The stems are discharged and the juice and pulp gravitate to a large receiver beneath the machine. The grape mass then proceeds to either a hydraulic or continuous fruit juice pressing operation to remove the pulp from the juice

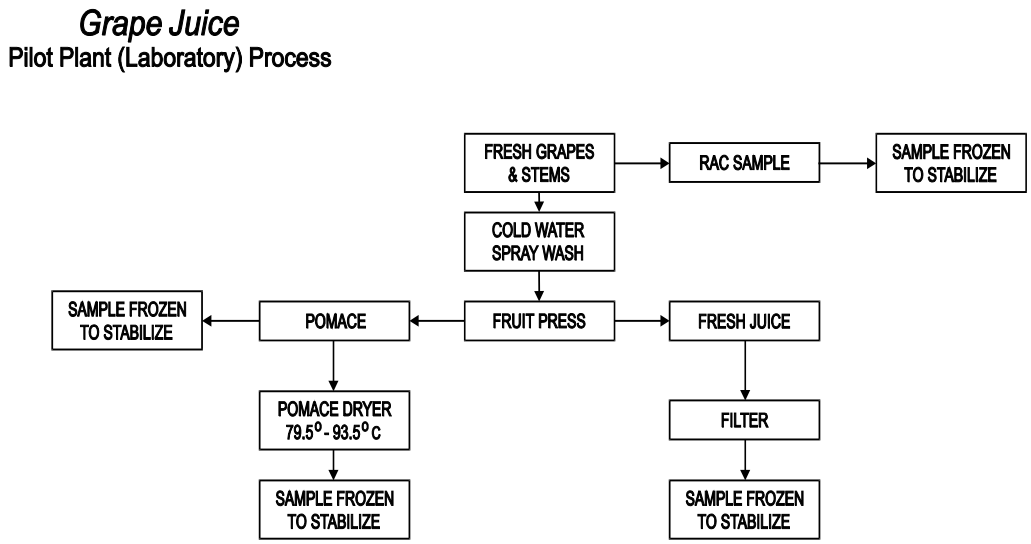


Figure 12. Flow chart for production of juice and pomace from grapes.

Raisins. Grapes were processed by sun-drying in greenhouses for 24 days. After drying, raisins were separated from raisin waste by screening. Figure 13 shows the procedures.

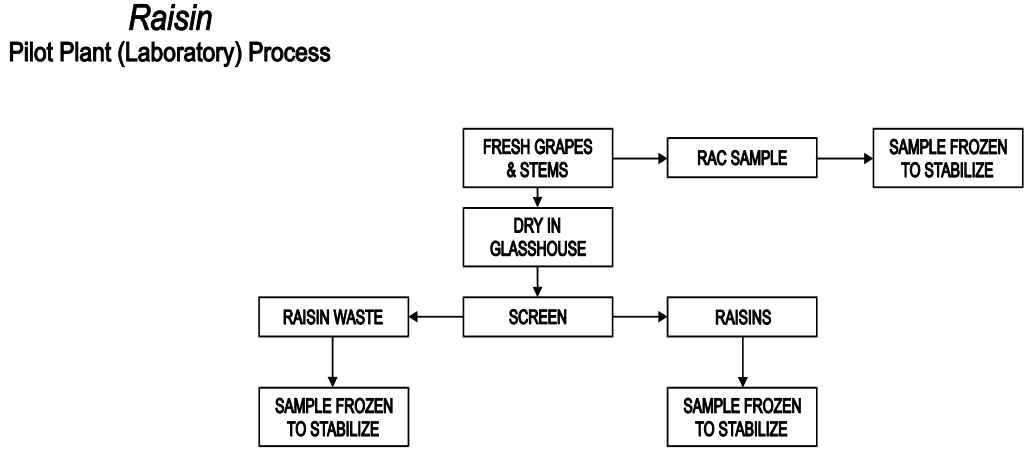


Figure 13. Flow chart for production of raisins from grapes.

Tomatoes. Simulating commercial operations, typical canning variety tomatoes were processed into wet and dry pomace, purée, and juice (Hattermann, 1995m, 1999) (Figure 14). Table 56 shows the main differences between the laboratory and commercial procedures.

Table 56. Laboratory and commercial procedures for tomato processing.

Step	Laboratory	Commercial
Inspection	Sorted by hand and discarded material retained as cannery waste. All material used.	Moving inspection belt to sort and remove stones, loose leaves, grossly contaminated and defective fruit (green, decomposed or unfit). Inspected tomatoes proceed to size grading machinery to sort different sizes according to their specified use
Washing and rising	Soak kettle with 0.5% lye solution for 3 min at 54°C and batch rinsed by high-pressure spray for 30 sec per batch.	Soak tank to aid in the removal of drosophila eggs and larvae and other contaminants. A lye (NaOH) solution at 0.5% is sometimes used. The tomatoes are soaked for 3 min at 54°C, and rinsed through a series of spray nozzles
Sorting and trimming	Fruit inspected and, if necessary, trimmed by hand. The sorting step was omitted as all available material was processed together.	Defective fruit or parts (rotten areas, mould portions, insect damage or sunscald) are removed. The fruit is then sorted so that large perfect fruit goes to the scalder, the rotten fruit to the dump and small and misshapen fruit to the pulping line.
Coring	Omitted because canned whole tomatoes are not a required fraction.	The tomatoes for canning proceed to a coring operation
Peeling	An atmospheric steam cabinet at 55-7 kg/cm^2 for 30 sec per batch.	Steam, lye or infrared peeling
Final inspection	Omitted as all material used.	Final inspection before canning to assess defects for grade classification
Crushing/ chopping	Tomatoes hand-fed into a pulper finisher and the pulp/pomace separated from the juice. The juice was then frozen for concentration at a later date. The wet pomace sample was packaged from the wet pomace recovered. The remaining wet pomace was then dried for the dry pomace sample. There is no commercial practice for drying wet pomace or cannery waste.	The tomatoes drop into the chopper at the end of the trimming belt. The chopped tomatoes proceed to either a screw or paddle type extractor for the extraction of juice.
Juice concen-tration	Groen vacuum pan batch concentrator. Purée packed, sealed, heated for 20 min at 98-100°C and then cooled under running cold tap water before packaging for purée sample.	Under reduced pressure and usually using double and multiple-effect evaporators (continuous machines, handling the juice and discharging the finished purée at 10.6 ± 1% solids and paste at approximately 30-32% solids). The purée is packed in cans, immediately sealed and the cans cooled before casing
Paste	Portion of the finished paste set aside for juice from concentrate manufacture. 1% salt added to a portion of the finished paste, the temperature raised to 88-91°C, and the paste canned and sealed. The sealed can is kept for 20 min at 98-100°C and then cooled under cold running tap water before packaging.	The finished paste is heated to approximately 90°C before being packed in cans, which are sealed immediately and cooled before casing
Juice	The finished paste is reconstituted with water, salt and ascorbic acid (vitamin C), heated to 88-91°C, packaged, sealed, heated to 98-100°C for 20 min, and cooled in cold running tap water before canning as the juice from concentrate sample fraction.	The tomato juice from concentrate must contain a minimum of 5.5% tomato solids. The paste is prepared as the previous step and then bulk-packaged in 208 l drums for products such as ketchup, juice from concentrate, and sauce

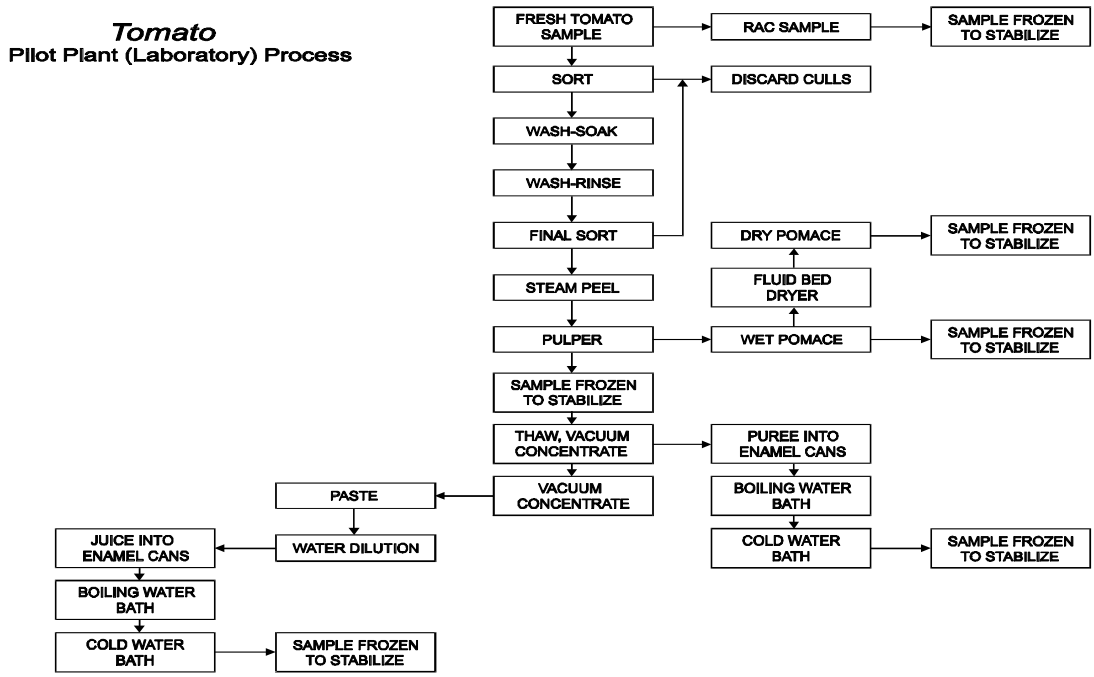


Figure 14**.** Flow chart for tomato processing.

Succulent beans. Pods and plants were processed into cannery waste (Hattermann 1995c, 1996c). Waste samples were made by collecting whole plants from at least 12 plot locations, stripping the leaves and pods, cutting approximately 2.5 cm off each end of some pods and discarding the middle section. A composite sample of leaves, whole pods, and pod tips was collected for the 2.2 kg cannery waste sample that consisted of 0.22 kg of leaves, 0.45 kg of whole pods and 1.6 kg of pod tips.

Potatoes. Potatoes were processed on a laboratory scale simulating commercial practices into chips, wet peel from the granule-making process, and granules, equivalent to flakes (Hattermann 1995f, 1996e).

Figure 15 shows the laboratory procedure for granules. The main differences between this procedure and commercial operations are shown in Table 57.

Table 57. Laboratory and commercial procedures for producing potato granules.

Step	Laboratory	Commercial
Washing	tub washing for 5-10 min	water flume and/or barrel washer and destoner machine
Peeling	continuous batch 13 k/cm^2 pressure steam peeler for ~10-20 sec	continuous batches using a pilot plant 5.5-6 kg/cm^2 pressure steam peeler for ~45-60 sec
Cutting	~1-1.3 cm slices using a restaurant-style food cutter	1.3 cm slices using a commercial model cutter
Starch removal	batch spray washing the slices for ~30 sec in cold water	continuous cold water spray washer

Step	Laboratory	Commercial
Pre-cooking	at 70-77°C while targeting 71-74°C for 20-22 min using a batch 150 l steam-jacketed kettle, cooled down to less than 32°C with cold running tap water	At 71-74°C continuous auger style pre-cooker for 20 min, proceed to a cold running tap water continuous auger style cooler to cool slices down to less than 32°C for 20 min
Cooking	At 94-100°C, for 40-42 min using a batch atmospheric steam cooker.	continuous auger steam cooker at 96-100°C for 35-45 min.
Ricing	mashed using a restaurant-style meat grinder without the grinding attachment.	auger containing a ricing/mashing grid
Add-back process	pre-weighed additives are added with the mashed potatoes and mixed for ~60 sec. Packaged in approximately 1 kg plastic containers and frozen for later dehydration	continuous primary mixer where additives are added. Dry potato granules (0.13 mm) are added to the wet mash at the rate of 1 kg of dry granules to 0.5 kg of wet mash
Drying	fluidized-bed dried	38-43°C conditioning belt for 30 min. Flash-dried at 260-304°C for ~30 sec to 13-17% moisture. Fluidized-bed dried to 8-10% moisture.
Granule	screened using a 30 and 60 mesh screen. The plus 60 mesh fraction is added to the added to the add-back supply. The minus 60 mesh product is packaged into the potato granule sample fraction.	sifted through a 32 mesh sieve, the <32 mesh product is cooled at 38°C to 7-7.5% moisture on an ambient fluid-bed cooler. The cooled product is sifted through a 105 mesh screen, the plus 105 mesh product is used for add-back “seed” supply and the minus 105 mesh product is packed.

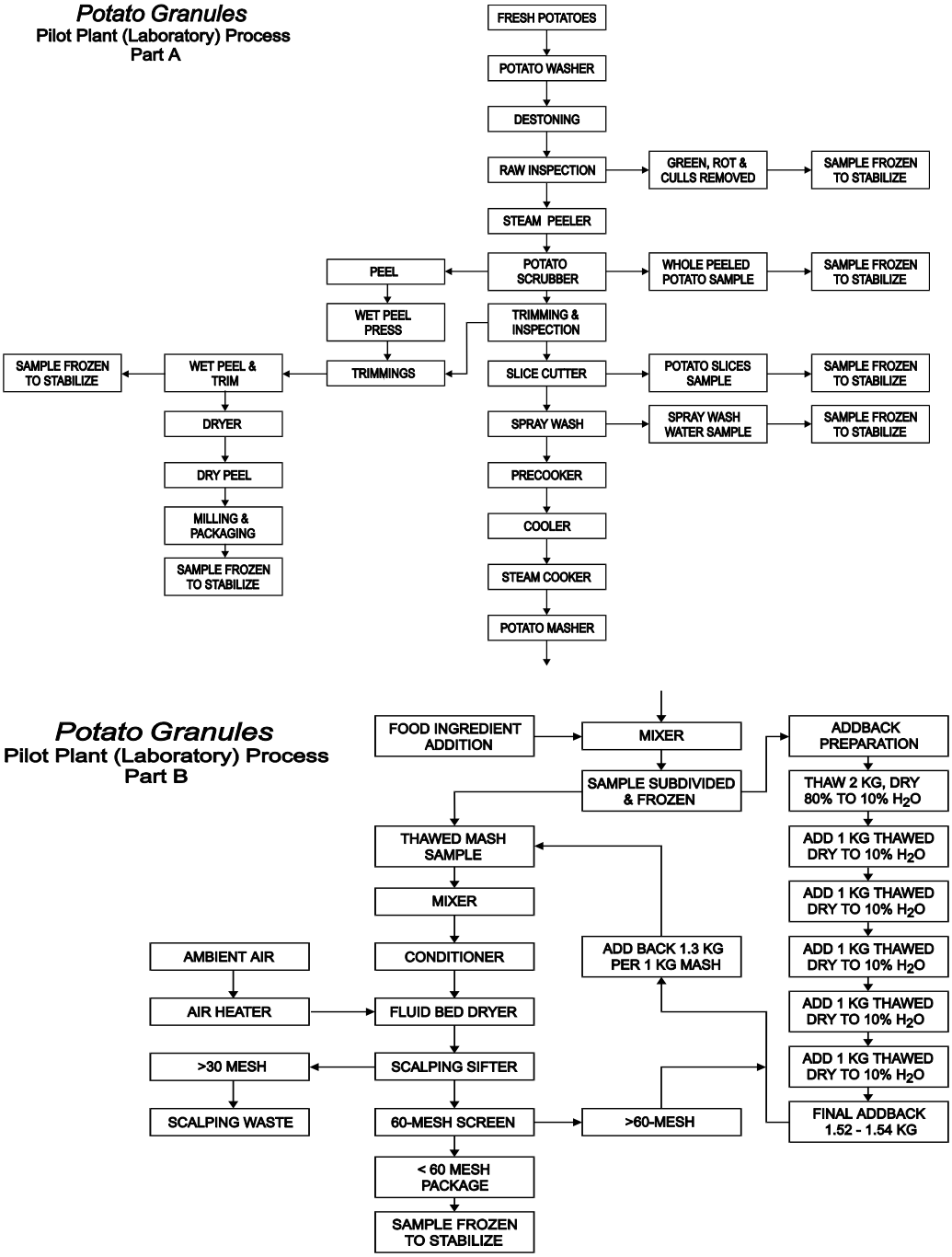


Figure 15. Flow chart for the production of granules.

Figure 16 shows the laboratory procedures for the production of potato chips. The main differences between this procedure and the commercial operation are shown in Table 58.

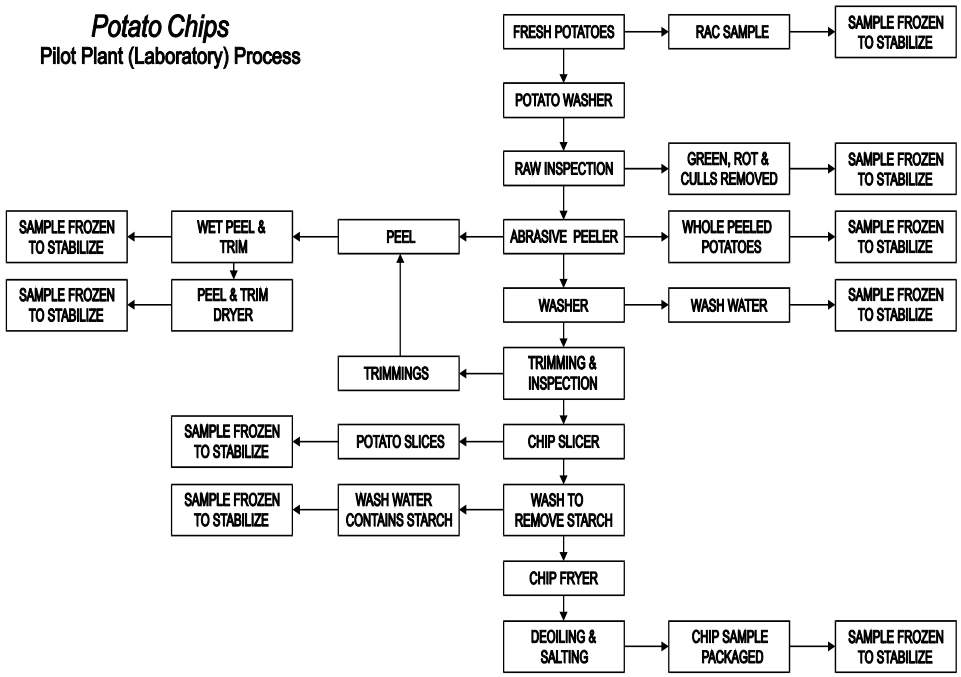


Figure 16**.** Flow chart for the production of potato chips.

Table 58. Laboratory and commercial procedures for processing potatoes to chips.

Step	Laboratory	Commercial
washing	tub washing for 5-10 min	water flume and/or barrel washer and destoner machine
peeling	peeled for 25-35 sec in batches using an abrasive peeler	continuous abrasive peeler
cutting	restaurant-style food cutter/slicer	Urschel Model CC cutter
frying	electrically heated restaurant-style deep fat fryer at ~163-191°C for 60-90 sec	continuous deep fat fryer and chain conveyer through hot oil at 185°C for ~60 sec
draining and packing	draining free oil in a restaurant-style draining tray and salting the chips by hand	chain conveyor to allow oil to drain, salting conveyor, inspection and then to packaging

Sugar beet. Beets were processed under simulated commercial conditions in a laboratory into dehydrated pulp, molasses, and refined sugar (Hattermann 1994g, 1995f). Although there are variations in the methods of producing beet sugar, all processes use essentially the same basic method.

The main differences between the laboratory procedures and commercial operations are shown in Table 59. Figure 17 is a flow chart of the laboratory processing of sugar beet.

Table 59. Laboratory and commercial procedures for processing sugar beet.

Step	Laboratory	Commercial
Sample	Beets stored frozen at 15 ± 8°C until processing.	Fresh or frozen outside in piles before processing
Washing	Washed in warm water in stainless steel tub	Water flume and a washing section where trash and field dirt are removed
Cutting	Into 1-3 mm thickness using a LanElec vegetable slicer	Into cossettes (strips) by large rotary wheels fitted with cutting knives having V-corrugated cutting edges. The thickness of cossettes produced depends partly on the type of diffuser used. The thickness could be as much as 4 mm
Diffusing	Batches of cossettes in stainless steel mesh baskets are moved by hand from cell to cell in one direction while diffusion liquid is transferred from cell to cell in the opposite direction. Temperature maintained at 70°C.	Continuous screw or chain, or a series of individual cells with means to transfer pulp and water from cell to cell
Pressing	Suntech fruit press removes free juice, which is then returned to the diffuser	Pressed to remove free juice which is then returned to the diffuser for thin juice recovery
Drying	Laboratory bin air dryer to <10% moisture	Heated rotary dryers to <10% moisture
First carbonation	Batch fashion using a 75 l steam jacketed stainless steel kettle. A milk of lime slurry containing about 11% CaO is added slowly while gassing with bottled CO_2. The pH is ~10 to keep alkalinity as close to 0.100% CaO/100 ml as possible. Alkalinity and CaO content are checked by titration.	Raw juice of 10-15% Brix is purified by the addition of lime and carbon dioxide gas, either continuously or batchwise. The first carbonation is done at 80-85°C. Lime addition may vary depending on beet quality from 1.4-2.0%.
Clarification	Settle in the 114 l stainless steel kettle. Supernatant liquor is decanted and the sludge filtered through Buchner funnels	Multi-tray clarifiers and rotary vacuum filters
Second carbonation	Batch fashion using a 75 l steam-jacketed stainless steel kettle at 90-95°C. Gassing is regulated by use of phenolphthalein and by laboratory titration.	Continuously in a large tank. The juice is gassed at 90-95°C to an optimum alkalinity, about 0.015 gm CaO/100 ml, to minimize lime salts
Filtering	Buchner funnels	Various types of industrial filters such as pressure leaf filters
Concentration	Groen steam-jacketed vacuum pan. Steam temperature automatically regulated at approximately 3°C. Vacuum is maintained at approximately 460 mm Hg	Multiple-effect evaporators of various designs
Increase Brix	Boiled directly to sugar in a small laboratory vacuum pan of a design similar to full scale vacuum pans. Vacuum is maintained at 10 cm Hg absolute	Addition of lower grade sugar such as intermediate and raw sugars from a three-boiling scheme. The enriched thick juice is called standard liquor and it is from this liquor that white sugar is made. Liquor is boiled to sugar in large vacuum pans of various designs and under conditions that cause the syrup to be supersaturated
Molasses	Massecuite (remaining materials) from the vacuum pan is centrifuged for white sugar recovery. It is washed and the initial spin-off syrup is molasses.	Large centrifuges to separate the white sugar from mother liquor. The sugar in the centrifuge basket is washed with hot clean water. The spin-off syrup is subjected to further processing for additional sugar recovery. The syrup after further sugar recovery is molasses

Step	Laboratory	Commercial
Sugar	Wet sugar is dried in a Kitchen Aid mixer. As the sugar is stirred in the mixing bowl warm air is blown against the bowl and into the stirred sugar.	Wet sugar from the centrifuge is dried in large rotary dryers, through which hot air is blown. As the sugar dries, the mixing in the heater and coolers prevents agglomeration and this results in white granulated sugar

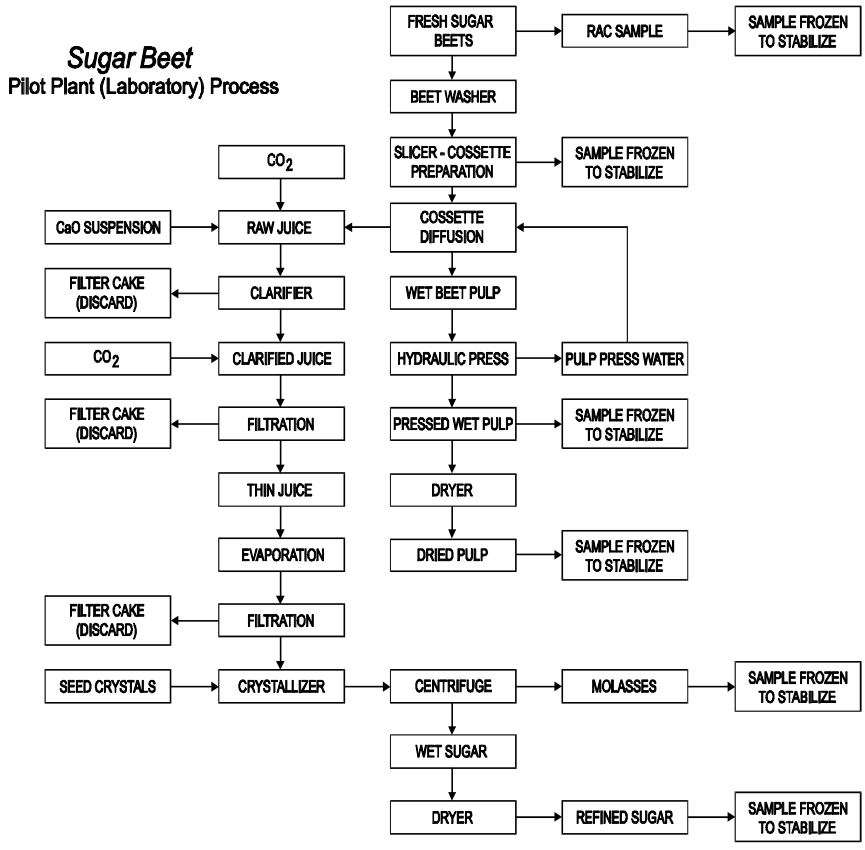


Figure 17. Flow chart for the processing of sugar beet.

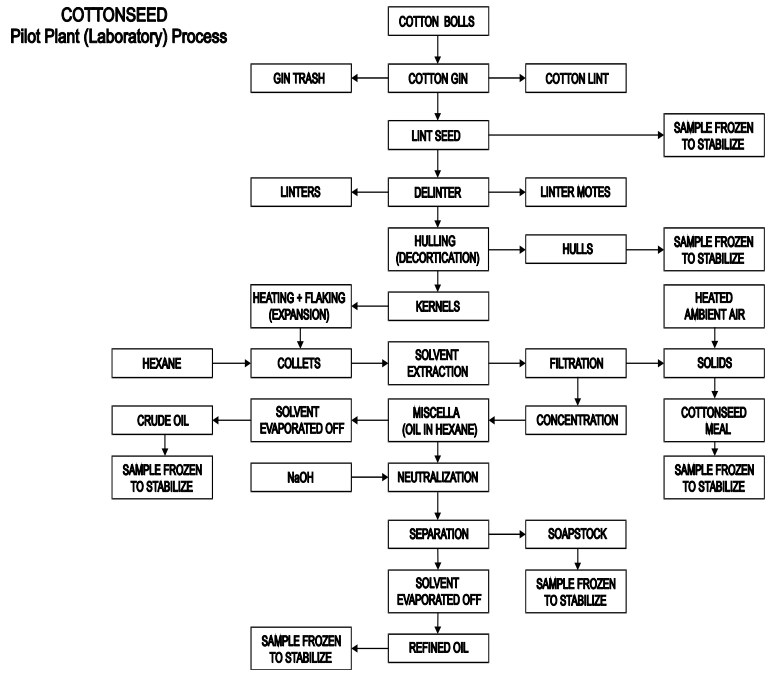


Figure 18. Flow chart for the processing of cotton.

Cotton. One control and three treated bulk samples of bolls were shipped at ambient temperature to the laboratory arriving on the day of collection (Hattermann, 1995i,j). The samples were processed into seeds, hulls, meal, crude and refined oil, and soapstock using procedures simulating industrial practice as closely as possible. Because of compliance monitoring requirements and sample size, however, the samples were processed in batches, as opposed to the continuous operations used commercially.

The bolls were ginned into gin trash, seed (lint seed), and fibre (lint). A portion of the ginned seed was frozen for analysis. After ginning, some of the lint cotton originally present remained attached to the seed as short fibres (linters), which were removed in a delinting machine (delinter) to produce two sizes of fibre, linters and linter motes. Decortication in the laboratory was by mechanical cracking and screening to remove most of the hull from the kernels. The hulls were frozen for analysis, and the kernels still containing a small amount of hull were warmed, flaked, expanded into collets, and then extracted with hexane to give a solution called the "miscella." Residual hexane was removed from the spent collets by warm forced air, and the resulting solids (cotton seed meal) frozen for analysis.

Hexane was evaporated from a portion of the miscella, a subsample was assayed for its free fatty acid content, and the remaining crude oil frozen for analysis.

The proportion of crude oil to hexane in the remaining miscella was adjusted to 60:40 oil:hexane by evaporation of hexane. NaOH was added to the miscella, the mixture was stirred, and the precipitated soapstock removed. Solvent was removed from the soapstock fraction by brief heating, and from the remaining miscella by heating under vacuum, producing refined oil. Soapstock and refined oil were frozen for analysis. Figure 18 shows the processing steps used in the laboratory.

All commodities were treated 10-11 times with 2.8 kg ai/ha, which represents about 4-5 times the GAP rate. Samples were collected on the day of treatment.

Table 60 shows the piperonyl butoxide residues in each raw commodity and processed product and the corresponding and mean processing factors.

Table 60. Processing factors for PBO residues in products of oranges, tomatoes, grapes, potatoes, sugar beet, succulent bean and cotton.

Raw commodity	Sample	Piperonyl butoxide (mg/kg)	Processing factor and (mean)
Orange[1]	Fruit	9.4	
	Dry pulp	54	5.7
	Oil	143	15
	Molasses	5.0	0.53
	Juice	<0.10	<0.01
Tomato[1]	Fruit	8.5	
	Wet pomace	50	5.9
	Dry pomace	293	34
	Purée	2.8	0.33
	Juice	1.3	0.15
Grape[2]	Fruit	14, 14, 11	
	Raisin	14, 14, 15	1.0, 1.0, 1.4 (1.1)
	Raisin waste	23, 31, 34	1.6, 2.2, 3.1 (2.3)
	Wet pomace	23, 31, 29	1.6, 2.2, 2.6 (2.1)
	Dry pomace	76, 81, 54	5.5, 5.8, 5.0 (5.5)
	Juice	0.22, 0.23, 0.24	0.02, 0.02, 0.02 (0.02)
Potato[2]	Tuber	<0.10, <0.10, <0.10	
	Granules	<0.10, <0.10, <0.10	
	Chips	<0.10, <0.10, <0.10	
	Wet peel	0.12, 0.16, 0.18	>1.2, >1.6, >1.8 (>1.5)
Sugar beet[3]	Root	0.08	
	Dry pulp	0.29	3.6
	Sugar	<0.10	<1.2
	Molasses	<0.10	<1.2
Succulent bean[1]	Pod	8.0	
	Cannery waste	51	6.4
Cotton[2]	Seed	0.10, 0.10, 0.10	
	Hulls	0.13, 0.11, 0.10	1.3, 1.1, 1.0 (1.1)
	Meal	<0.10, <0.10, <0.10	<1, <1, <1 (1)

Raw commodity	Sample	Piperonyl butoxide (mg/kg)	Processing factor and (mean)
	Crude oil	0.70, 0.54, 0.63	7.0, 5.4, 6.3 (6.2)
	Refined oil	2.7, 1.3, 1.9	27, 13, 19 (20)
	Soapstock	0.41, 0.23, 0.50	4.1, 2.3, 5.0 (3.8)

[1]Three trial plots were treated, only one bulk sample consisting of one-third from each treated plot was processed
[2] Three trial plots
[3] One trial plot

Wheat. Samples treated post-harvest with bioresmethrin/piperonyl butoxide or phenothrin/piperonyl butoxide formulations were taken for milling and baking approximately 5 weeks after treatment of the whole grains (Ardely, 1978). No information on processing or analytical methods was provided (Table 61).

Table 61. Residues of piperonyl butoxide in wheat, bran and bread.

	Sample	Residues (mg/kg)	Processing factor
bioresmethrin 4/PBO 20	Wheat	16	0.8[1]
	Bread	0.3	0.023
	Bran	57	4.45
phenothrin 4/PBO 20	Wheat	14	0.7[1]
	Bread	Negligible[2]	≤0.005 say
	Bran	30	3.1
phenothrin 4/PBO 20	Wheat	14	0.7[1]
	Bread	0.6	0.06
	Bran	40	4.1

[1] Reduced residues in raw wheat 5 weeks after treatment
[2] Limits of detection or determination not provided

Strong *et al.* (1961) treated wheat with piperonyl butoxide at 15 mg ai/kg grain in various formulations. The treated wheat was stored for 3 months and processed (Table 62). No full report was provided.

Table 62. Piperonyl butoxide residues in processed wheat.

Formulation	Sample	Residue	Processing factor
Emulsion	Whole grain	6.0	
	Cleaned	4.8	0.8
	Flour	1.7	0.28
	Bran	12	2.0
	Shorts	0.15	0.025
	Low grade middlings	2.5	0.42
	Whole grain	6.2	
	Cleaned	5.5	0.89
	Flour	3.3	0.53
	Bran	13	2.1
	Shorts	7.2	1.16

Formulation	Sample	Residue	Processing factor
	Low grade middlings	9.1	1.47
	Whole grain	6.1	
	Cleaned	3.9	0.64
	Flour	0.1	0.016
	Bran	11	1.80
	Shorts	2.3	0.38
	Low grade middlings	4.2	0.69
	Whole grain	7.3	
	Cleaned	8.6	1.18
	Flour	1.9	0.26
	Bran	11	1.51
	Shorts	4.8	0.66
	Low grade middlings	2.6	0.36
Wettable powder	Whole grain	12	
	Cleaned	3.6	0.3
	Flour	<0.5	<0.04
	Bran	11	0.92
	Shorts	<0.5	<0.04
	Low grade middlings	2.3	0.19
	Whole grain	5.4	
	Flour	3.2	0.59
	Bran	15	2.78
	Shorts	7.5	1.39
	Low grade middlings	1.0	0.18
	Whole grain	9.0	
	Cleaned	7.6	0.84
	Flour	2.9	0.32
	Bran	12	1.33
	Shorts	0.1	0.01
	Low grade middlings	5.3	0.59
	Whole grain	11	
	Cleaned	8.8	0.8
	Flour	4.3	0.39
	Bran	7.6	0.69
	Shorts	8.4	0.76
	Low grade middlings	4.2	0.38
Tetrachloro-ethylene solution	Whole grain	4.1	
	Cleaned	4.4	1.07
	Flour	3.2	0.78
	Bran	9.5	2.31
	Shorts	4.3	1.05
	Low grade middlings	3.3	0.80
	Whole grain	6.7	
	Cleaned	4.5	0.67
	Flour	4.6	0.69
	Bran	14	2.09
	Shorts	5.0	0.75
	Whole grain	7.9	
	Cleaned	8.6	1.09
	Flour	2.4	0.30
	Bran	7.2	0.91
	Shorts	1.4	0.18
	Low grade middlings	1.6	0.20
	Whole grain	5.4	
	Cleaned	4.2	0.78
	Flour	4.5	0.83
	Bran	11	2.04

Formulation	Sample	Residue	Processing factor
	Shorts	1.9	0.35
	Low grade middlings	1.1	0.20
	Cleaned	**Average processing factor**	0.82
	Flour		0.42
	Bran		1.71
	Shorts		0.56
	Low grade middlings		0.50

In trials in Italy Molinari (1987) applied two different deltamethrin/piperonyl butoxide products to wheat stored either in vertical silos or warehouses for 3-12 months at rates from 2.5 to 10 mg PBO/kg grain. Milling trials were carried out with a flour roller mill with at least 90 kg of hard or soft wheat. The dry treatment involved first cleaning the wheat by sifters and dust collectors, a wheat humidification followed by rest to balance humidity, and a second cleaning by rubbing to eliminate the particles attached to the caryopsis and the pericarp roughness. The wheat was ground in seven steps for bran and flour production. Residues in the grain and processed products are shown in Table 63**.**

Table 63. Processing factors (PF) for wheat products from trials conducted in Italy.

Location, mg PBO/kg grain	Sample	45 days storage		180 days storage		Average PF
		Residue (mg/kg)	PF	Residue (mg/kg)	PF	
S. Giorgio de Piano 5.0, 10	Grain	0.37, 1.8		0.29, 1.2		
	Cleaned	<0.10, 0.74	<0.27, 0.41	<0.10, 0.64	<0.34, 0.53	
	Decorticated	<0.10, 0.55	<0.27, 0.31	<0.10, 0.74	<0.34, 0.62	
	Bran	0.45, 2.0	1.2, 1.1	0.69, 2.4	2.4, 2.0	
	Flour	<0.10, 0.17	<0.27, 0.09	<0.10, <0.10	<0.34, <0.08	
Porto a Rigo 2.5, 10	Grain	0.64, 4.4		1.2, 4.4		
	Cleaned	0.32, 1.8	0.5, 0.41	0.49, 5.9	0.41, 1.34	
	Decorticated	0.30, 2.1	0.47, 0.48	0.80, 2.4	0.67, 0.54	
	Bran	2.0, 4.9	3.1, 1.1	1.8, 5.1	1.5, 1.16	
	Flour	0.40, 0.48	0.62, 0.11	0.14, <0.1	0.12, <0.02	
La Spezia 2.5, 10	Grain	<0.10, 2.4		<0.10, 2.4		
	Cleaned	<0.10, 0.96	-, 0.4	0.18, 1.5	>1.8, 0.63	
	Decorticated	<0.10, 0.59	-, 0.25	<0.10, 3.2	-, 1.33	
	Bran	<0.10, 4.6	-, 1.9	<0.10, 5.1	-, 2.13	
	Flour	<0.10, 0.86	-, 0.36	<0.10, 0.28	-, 0.12	
Landinara 2.5, 5.0, 10	Grain	0.67, - , 3.1		0.32, 0.82, 4.2		
	Cleaned	0.42, - , 0.28	0.63, - , 0.09	<0.10, 0.10, 0.60	0.31, 0.12, 0.14	0.535
	Decorticated	<0.10, - , 1.1	<0.15, - , 0.35	<0.10, <0.10, 1.6	<0.31, <0.12, 0.38	0.44
	Bran	<0.10, - , 5.7	<0.15, - , 1.84	<0.10, <0.10, <0.10	<0.31, <0.12, <0.02	1.3
	Flour	0.11, - , 0.24	0.16, - , 0.078	<0.10, <0.10, <0.10	<0.31, <0.12, <0.02	0.19

Turnbull and Ardley (1987) processed wheat treated with 8 mg/PBO/kg grain in an 800 tonne vertical silo in Australia. Flour extraction rates of 80% and 75% were used and 50:50 blends of the two were also used. Samples were examined after 1, 3 and 6 months (Turnbull, 1988). The residues and the processing factors (PF) are shown in Table 64.

Table 64. Residues of piperonyl butoxide in wheat and derived fractions.

Sample, extraction rate	1 month storage		3 months storage		6 months storage		Average
	Residue, mg/kg	PF	Residue, mg/kg	PF	Residue, mg/kg	PF	PF
Wheat	5.3		5.6		7.0		
Bran 80%	22	4.2	23	4.1	23	3.3	3.9
Bran 75%	19	3.6	28	5.0	21	3.0	3.9
Pollard 80%	-	-	-	-	15	2.1	2.1
Pollard 75%	10	1.9	-	-	16	2.3	2.1
Germ 80%	-	-	18	3.2	28	4.0	3.6
Germ 75%	-	-	16	2.9	29	4.1	3.5
Germ 50:50	11	2.1	-	-	-	-	2.1
Gluten 80%	-	-	-	-	10	1.4	1.4
Gluten 75%	-	-	-	-	11	1.6	1.6
Gluten 50:50	7.3	1.4	-	-	-	-	1.4
90:10 meal 80%	-	-	-	-	6.0	0.86	0.86
90:10 meal 75%	-	-	4.7	0.84	5.9	0.84	0.84
Flour 80%	1.6	0.30	2.0	0.36	2.4	0.34	0.33
Flour 75%	1.2	0.23	1.8	0.32	2.1	0.30	0.28
Wholemeal bread 80%	-	-	2.7	0.48	3.8	0.54	0.51
Wholemeal bread 50:50	2.7	0.51	-	-	-	-	0.51
White bread 80%	1.0	0.19	1.2	0.21	1.5	0.21	0.20
White bread 75%	0.9	0.17	1.2	0.21	1.5	0.21	0.20

Turnbull (1987) treated approximately 540 tonnes of wheat with two PBO formulations before milling. The output proportions were bran 18%, pollard 5% and flour 77%. The residues from the two treatments and the processing factors (PF) during 9 months storage are shown in Table 65.

Table 65. Piperonyl butoxide residues, mg/kg, in wheat fractions from treatments A and B, during 9 months storage.

Sample	Residues, mg/kg										Average PF
	1.5 months		3 months		4.5 months		6 months		9 months		
	A	PF	A, B	PF	A	PF	A, B	PF	A, B	PF	
Wheat	6.9		5.9, 7.1		6.5		6.5, 4.7		5.5, 5.4		
Bran	18	2.6	21, 21	3.6, 3.0	17	2.6	20, 17	3.1, 3.6	20, 16	3.6, 3.0	3.1
Pollard	8.1	1.2	6.3, 8.3	1.1, 1.2	10	1.5	13, 7.4	2.0, 1.6	14, 12	2.5, 2.2	1.7
90:10 meal	4.0	0.58	- , 7.0	- , 0.99	4.0	0.62	5.6, 5.7	0.86, 1.2	-		0.85
Flour	0.7	0.10	1.2, 1.0	0.20, 0.14	0.7	0.11	1.4, 1.6	0.22, 0.34	1.1, 1.3	0.20, 0.24	0.19
Wholemeal bread	2.9	0.42	3.1, 3.0	0.53, 0.42	2.4	0.37	4.2, 3.4	0.65, 0.72	4.9, 2.6	0.89, 0.48	0.56
White bread	0.6	0.09	0.4, <0.5	0.07 <0.07	0.4	0.06	0.4, <0.5	0.06, <0.11	0.4, <0.5	0.07, <0.09	<0.08

A: deltamethrin/PBO formulation
B: bioresmethrin/fenitrothion/PBO formulation

In a full-scale milling trial 500 tonnes of wheat in concrete silos were treated with two different formulations at two application rates and stored for 24 weeks (Australian Wheat Board, 1988). Samples were delivered to commercial mills A, B and C (50 t per sample) and to pilot mill D (1 t per sample) (Table 66).

Table 66. Residues of piperonyl butoxide, mg/kg, and processing factors in wheat fractions.

Rate mg/kg	Mill	Storage (weeks)	Wheat	Flour	Wholemeal	Bran	Germ	Pollard
Commercial milling								
10	A	10	4.7	1.8	7.3	26	12	
			PF	0.38	1.6	5.5	2.6	-
10	B	12	5.2	3.4	2.5	25	18	-
			PF	0.65	0.48	4.8	3.5	-
10	C	10	5.2	3.0	6.4	24	19	9.3
			PF	0.58	1.2	4.6	3.6	1.8
13.6	A	12	7.4	3.4	21	34	32	-
			PF	0.46	2.8	4.6	4.3	-
13.6	B	26	6.4	4.2	-	28	18	35
			PF	0.66	-	4.4	2.8	5.5
13.6	C	24	8.4	3.9	11	32	33	-
			PF	0.46	1.3	3.8	3.9	-

Rate mg/kg	Mill	Storage (weeks)	Wheat	Flour	Wholemeal	Bran	Germ	Pollard
Pilot milling								
10	D	8	6.8	3.4	10	21	24	12
			PF	0.50	1.5	3.1	3.5	1.8
10	D	20	9.4	4.3	8.8	29	20	21
			PF	0.46	0.94	3.1	2.1	2.2
13.6	D	15	11	4.4	9.5	36	36	21
			PF	0.40	0.86	3.3	3.3	1.9
13.6	D	23	11	3.0	11	42	28	36
			PF	0.27	1.0	3.8	2.5	3.3
			Average processing factor	0.48	1.3	4.1	3.2	2.8

Hong Nguyen (1988) determined residues in wheat grain sampled 2 and 4 hours after treatment with a nominal dose of 1 mg/kg deltamethrin plus 10 mg/kg piperonyl butoxide. Samples were milled and wheat fractions and bread analysed (Table 67).

Table 67. Residues of piperonyl butoxide in wheat milling fractions and bread.

Fraction	2 h sample		4 h sample		Average
	mg/kg	PF	mg/kg	PF	PF
Wheat	7.3		6.7		
Bran	26	3.6	27	4.0	3.8
Pollard	17	2.3	16	2.4	2.4
Germ	20	2.7	17	2.5	2.6
90:10 meal	5.5	0.75	5.5	0.82	0.78
Flour	1.4	0.19	1.6	0.24	0.22
Wholemeal bread	2.9	0.40	2.8	0.42	0.41
White bread	0.81	0.11	0.73	0.11	0.11

In a wheat admixture trial in Australia Webley (1994) treated 500 tonnes of wheat at the GAP rate and at twice the GAP rate. 50 tonne samples were delivered to two commercial mills and a pilot mill within 4 weeks and a second delivery was made to the pilot mill after 3 more months. Samples of wheat, straight run flour, bran and wheat germ were taken during milling for analysis by two independent laboratories. Wholemeal was prepared using 4.1 kg flour, 0.18 kg bran, and 0.27 kg pollard. The results are given in Table 68. A full report of the study was not provided.

Table 68. Residues of piperonyl butoxide in wheat and its processed products.

PBO dose (mg ai/kg grain)	Sample	Residue (mg/kg)	Processing factor	Average processing factor
9 (7 weeks storage)	Wheat	5.1		
	Bran	17	3.33	

PBO dose (mg ai/kg grain)	Sample	Residue (mg/kg)	Processing factor	Average processing factor
	Germ	6.8	1.33	
	Flour	2.1	0.41	
	Wholemeal	4.7	0.92	
	White pan bread	1.1	0.21	
	Wholemeal pan bread	2.7	0.53	
	Flat Arabic bread	1.4	0.27	
	Steamed bread	1.1	0.22	
	Yellow alkaline noodles	0.5	0.10	
	White noodles	1.1	0.22	
9 (26 weeks storage)	Wheat	4.5		
	Bran	16	3.56	
	Germ	13	2.89	
	Flour	2.3	0.51	
	Wholemeal	5.0	1.11	
	White pan bread	1.6	0.36	
	Wholemeal pan bread	2.9	0.64	
	Flat Arabic bread	2.2	0.49	
	Steamed bread	3.2	0.71	
	Yellow alkaline noodles	0.9	0.20	
	White noodles	1.7	0.38	
16 (7 weeks storage)	Wheat	6.6		
	Bran	31	4.7	
	Germ	14	2.12	
	Flour	2.9	0.44	
	Wholemeal	8.5	1.29	
	White pan bread	1.2	0.18	
	Wholemeal pan bread	5.5	0.83	
	Flat Arabic bread	4.5	0.68	
	Steamed bread	1.8	0.27	
	Yellow alkaline noodles	2.6	0.39	
	White noodles	2.3	0.35	
Not stated	Wheat	5.3		
	Flour	1.4	0.26	
	Gluten.	7.3	1.4	1.4
16 (26 weeks storage)	Wheat	6.1		
	Bran	22	3.61	3.8
	Germ	15	2.46	2.2

PBO dose (mg ai/kg grain)	Sample	Residue (mg/kg)	Processing factor	Average processing factor
	Flour	1.5	0.24	0.37
	Wholemeal	3.7	0.61	0.98
	White pan bread	-	-	0.25
	Wholemeal pan bread	3.5	0.57	0.64
	Flat Arabic bread	2.4	0.39	0.46
	Steamed bread	1.4	0.23	0.36
	Yellow alkaline noodles	1.6	0.26	0.24
	White noodles	1.0	0.16	0.28

Maize. In Italy maize was treated with deltamethrin/piperonyl butoxide EC formulation and processed in the laboratory under simulated commercial conditions by wet and dry procedures (Molinari, 1991). Under wet conditions, samples were sieved and the cleaned maize was placed in glass flasks with process water (1.6 degree Baume density, 2% dry weight solubility, 0.2% insolubility and pH 3.5) and sulfur dioxide. The flasks were placed in a water bath at 50°C for 30 hours, the maize then filtered and degermed by hand. Before oil extraction, moisture of the germ was reduced to approximately 5%. Under dry conditions, treated maize was sieved, the dust removed by an air stream and the maize subjected to various milling procedures to obtain the germ. The oil was extracted with hexane for 12 hours in a soxhlet extractor (Table 69).

Table 69. Piperonyl butoxide residues in maize and its processed products.

PBO dose (mg ai/kg grain)	Sample	Mean residue (mg/kg)	Processing factor	Average processing factor
	Dry process			
2.43, 11.14 (182 days storage)	Maize	0.67, 2.6		
	After cleaning	0.61[1], 1.2	0.91, 0.46	
	Degermed	0.58, 0.96	0.87, 0.37	
	Damaged degermed	0.58, 1.8	0.87, 0.69	
	Germ	0.53, 1.0	0.79, 0.38	
	Oil	4.6[2], 22	6.9, 8.5	
	Wet process			
2.43, 11.14 (42 days storage)	Maize	1.05, 3.7		
	After cleaning	0.96, 2.8	0.91, 0.76	
	Degermed	0.48, 1.3	0.46, 0.35	
	Damaged degermed	0.67, 1.4	0.64, 0.38	
	Germ	<0.1, <0.1	<0.1, <0.02	
	Oil	<0.1, <0.1	<0.1, <0.02	
2.43, 11.14 (182 days storage)	Maize	0.80, 2.2		
	After cleaning	0.78, 1.8	0.98, 0.82	0.81
	Degermed	0.32, 1.2	0.40, 0.55	0.50
	Damaged degermed	0.39, 1.2	0.49, 0.55	0.60
	Germ	0.13, 0.71	0.16, 0.32	<0.3
	Oil	<0.1, <0.1[3]	<0.12, <0.04	<2.7

[1] Outlier result of 4.2 mg, kg not included
[2] Outlier result of 36 mg/kg not included
[3] Outlier result of 9.0 mg/kg not included

Rice. Dath (1992) carried out trials in France using a ULV formulation of deltamethrin/piperonyl butoxide on dried and undried cargo rice at a rate of 4.2 l/100 tonnes to give 2.5 g ai PBO/tonne grain (Table 70). Only a short summary of the study was provided.

Table 70. Residues in rice before and after processing.

Sample	Residue[1] (mg/kg)	Processing factor[1]	Average processing factor
Cargo control	0.20/0.24		
Cargo treated	1.6, 1.8	8, 7.5	7.75
Cooked rice	1.0, 1.6	5.0, 6.7	5.85
Processed rice	0.13, 0.16	0.65, 0.67	0.66
Rice bran	20, 14	100, 58	79
Cooked processed rice	0.05, 0.06	0.25, 0.25	0.25

[1] First result for dried and second for undried rice

Cocoa and soya beans. The beans were treated with deltamethrin/piperonyl butoxide formulations at 7.5 and 10 mg ai/kg PBO and stored up to a year, before being processed and analysed (Table 71). Only a summary of the results was provided (Mestres, 1983a,b).

Table 71. Processing factors in cocoa and soya bean products.

Sample	Residues (mg/kg)	Processing factor	Average processing factor
Cocoa bean	1.3, 0.9, 0.65, 0.65, 1.5, 1.2, 0.7, 0.6, 1.0, 2.0		
Roasted bean	0.2, 0.5, 0.3, 0.4, 1.2, 0.4, 0.4, 0.4, 0.8, 1.7	0.15, 0.55, 0.46, 0.61, 0.80, 0.33, 0.57, 0.67, 0.80, 0.85	0.58
Chocolate paste	-, -, <0.1, <0.1, 0.2, -, -, <0.1, <0.1, 0.2	-, -, <0.15, <0.15, 0.13, -, -, <0.17, <0.1, 0.1	<0.13
Soya bean	0.7, 0.4, 1.2		
Oil	4.4, 8.8, 16	6.3, 22, 13	13.8
Cake	0.6, 0.3, 1.7	0.86, 0.75, 1.4	1.0

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ANIMAL FEEDING STUDIES

Ruminants

Four groups of three Holstein dairy cows were dosed orally once daily for 28 to 30 days with PBO in gelatine capsules at 100, 300, 900 and 3000 ppm PBO in the diet on a dry-weight basis. Based on mean body weights, these levels corresponded to 2.9, 10.3, 28.6 and 91.0 mg/PBO kg bw/day. A control group of three additional cows were given unfortified capsules. Proportionately composited milk samples were prepared from each cow from milk taken on days 0 (pre-dose) to 27 (Krautter *et al.*, 1995a). The results are shown in Table 72.

Table 72. Residues of PBO in milk from orally dosed cows (Krautter *et al.*, 1995).

Day	PBO, mg/kg and (mean)			
	100 ppm dose	300 ppm dose	900 ppm dose	3,000 ppm dose
1	0.01, 0.03, 0.01 (0.02)	0.04, 0.03, 0.03 (0.03)	0.12, 0.33, 0.42 (0.29)	3.2, 11, 3.8 (6.0)
3	<0.01, 0.02, 0.02 (0.01)	0.05, 0.03, 0.04 (0.04)	0.10, 0.44, 0.61 (0.38)	10, 10, 2.8 (7.6)
7	0.04, 0.02, <0.01 (0.02)	0.05, 0.09, 0.55[1] (0.07)	0.12, 12[1], 0.16 (0.14)	0.98, 12, 2.3 (5.1)
11	<0.01, 0.02, <0.01 (0.01)	0.03, 0.03, 0.03 (0.03)	0.19, 0.48, 0.34 (0.34)	8.8, 6.9, 1.5 (5.7)
14	<0.01, 0.02, 0.01 (0.01)	0.04, 0.04, 0.03 (0.04)	0.16, 0.72, 0.47 (0.45)	3.4, 10, 3.8 (5.7)
18	<0.01, <0.01, <0.01 (<0.01)	0.03, 0.03, 0.02 (0.03)	0.20, 0.78, 0.68 (0.55)	5.9, 8.8, 4.2 (6.3)
21	0.04, 0.01, 0.02 (0.02)	0.07, 0.07, 0.04 (0.06)	0.32, 0.70, 0.57 (0.53)	5.4, 5.7, 5.2 (5.4)
24	<0.01, 0.02, <0.01 (0.01)	0.02, 0.08, 0.03 (0.04)	0.18, 0.50, 0.63 (0.44)	5.1, 4.0, 3.1 (4.1)
27	<0.01, 0.01, <0.01 (0.01)	0.05, 0.06, 0.04 (0.05)	0.15, 0.56, 0.52 (0.41)	22[1], 3.8, 3.8 (3.8)
Mean of means	0.01	0.04	0.39	5.5

[1] Sample considered an outlier and not used in mean (no explanation)

After treatment the cows were slaughtered over 3 days within 16 to 24 hours of the last dose. No significant tissue abnormalities were noted in any of the cows. Liver, kidney, composite round and tenderloin muscle, and composite perineal and omental fat were collected, homogenized with dry ice and stored frozen. The residues are shown in Table 73.

Table 73. Residues of piperonyl butoxide in tissues of orally-dosed cows (Krautter *et al.*, 1995a).

Dose (group)	PBO, mg/kg and (mean) in			
	Liver	Kidney	Muscle	Fat
Low (100 ppm)	0.15; 0.15; 0.12 (0.14)	<0.05; <0.05; <0.05 (<0.05)	<0.05; <0.05; <0.05 (<0.05)	0.08; 0.42; 0.14 (0.21)
Medium low (300 ppm)	0.73; 0.33; 0.59 (0.55)	0.05; 0.14; 0.06 (0.08)	<0.05; 0.06; <0.05 (0.05)	0.95; 1.7; 0.99 (1.2)
Medium	1.4; 1.5; 1.2	0.61; 0.82; 0.28	<0.05; 0.67; 0.06	7.1; 15; 1.6

Dose (group)	PBO, mg/kg and (mean) in			
	Liver	Kidney	Muscle	Fat
(900 ppm)	(1.4)	(0.57)	(0.26)	(7.9)
High (3000 ppm)	13; 9.0; 13 (12)	4.8; 11; 15 (10)	1.7; 12; 9.0 (7.6)	86; 220; 132 (146)

In another study the backs of three Holstein dairy cows were sprayed with piperonyl butoxide twice daily for 28-30 days with a formulated product at 2.28 g piperonyl butoxide/day. Based on mean body weight, this corresponds to a dose of 3.78 mg piperonyl butoxide/kg bw/day. An additional three cows were sprayed twice daily with the mineral oil diluent as a control (Krautter *et al.*, 1995b).

Proportionately composited milk samples from each cow taken from days 0 (pre-dose) to 27 were analysed (Table 74).

Table 74. Residues of piperonyl butoxide in milk samples from cows treated dermally (Krautter *et al.*, 1995b).

Day	1	3	7	11	14	18	21	24	27
Residues, mg/l	0.07, 0.07, 0.03	0.17, 0.19, 0.07	0.14, 0.14, 0.08	0.14, 0.11, 0.07	0.14, 0.13, 0.07	0.16, 0.13, 0.17	0.18, 0.11, 0.09	0.24, 0.17, 0.11	0.20, 0.15, 0.13
(mean)	(0.06)	(0.14)	(0.12)	(0.11)	(0.11)	(0.15)	(0.13)	(0.17)	(0.16)

After the 28 to 30 days, cows were slaughtered 16 to 24 hours after the last dose. There were no significant tissue abnormalities in any of the control or treated cows. Liver, kidneys, composite round and loin muscle, and composite perineal and omental fat samples were analysed (Table 75).

Table 75. Residues of piperonyl butoxide in the tissues of cows after dermal application (Krautter *et al.*, 1995b).

Tissue	Liver	Kidney	Muscle	Fat
Residues, in mg/kg, and (mean)	0.02; 0.14; 0.03 (0.06)	0.21; 0.19; 0.21 (0.20)	0.16; 0.21; 0.16 (0.18)	2.6; 2.7; 2.3 (2.5)

Poultry. Groups of White Leghorn laying hens were dosed orally once daily for 28 to 30 days at three levels (10 hens/dose group) equivalent to 20.4, 61.2 or 198.8 ppm piperonyl butoxide in the diet (as-fed basis), corresponding to 1, 3, and 10 times the predicted maximum dietary burden (Krautter *et al.*, 1995c). Based on mean body weights, the doses corresponded to 1.58, 4.41 and 15.01 mg/kg piperonyl butoxide bw/day respectively. A control group of ten additional hens were given unfortified capsules. Hens within each dose group were divided into three subgroups (3 or 4 hens/subgroup), and eggs and tissues composited by subgroup. Egg samples taken on days 0 (pre-dose) to 27 were analysed with the results shown in Table 76.

Table 76. Residues of piperonyl butoxide in egg samples, mg/l, from orally-dosed laying hens (Krautter *et al.*, 1995c).

Day	PBO, mg/kg, and (mean)		
	Low (20.4 ppm)	Medium (61.2 ppm)	High (198.8 ppm)
1	<<0.01; <0.01; <0.01 (<0.01)	0.02; 0.01; 0.01 (0.01)	<0.01; 0.01; 0.02 (0.01)
3	0.01; <0.01; 0.03 (0.02)	0.08; 0.06; 0.13 (0.09)	0.48; 0.67; 0.68 (0.61)
7	0.02; 0.02; 0.02 (0.02)	0.14; 0.14; 0.23 (0.17)	1.4; 1.4; 1.6 (1.5)
11	0.03; 0.02; 0.02 (0.02)	0.13; 0.22; 0.14 (0.16)	1.2; 1.3; 1.5 (1.3)
14	0.03; 0.02; 0.03 (0.03)	0.13; 0.13; 0.25 (0.17)	1.35; 1.0; 1.6 (1.3)
18	0.03; 0.03; 0.02 (0.03)	0.16; 0.18; 0.28 (0.21)	1.2; 1.1; 1.4 (1.2)
21	0.02; 0.01; 0.03 (0.02)	0.15; 0.13; 0.23 (0.17)	1.3; 1.1; 1.0 (1.1)
24	0.02; 0.02; 0.03 (0.02)	0.12; 0.14; 0.14 (0.13)	1.2; 1.4; 1.4 (1.3)
27	0.03; 0.03; 0.04 (0.03)	0.19; 0.16; 0.35 (0.23)	1.9; 1.7; 1.7 (1.8)
Mean	0.02	0.15	1.4

After the 28 to 30 days, the hens were killed within three days, 16 to 24 hours after the last dose. Two hens in the low-dose group had gross abnormalities of the digestive and/or reproductive systems. Liver, composite breast and thigh muscle, and fat samples were composited by subgroup, frozen, homogenized with dry ice, and stored until analysis (Table 77).

Table 77. Residues of PBO in tissues of orally-dosed laying hens (Krautter *et al.*, 1995c).

Dose group	PBO, mg/kg, and (mean) in		
	Liver	Muscle	Fat
Low	-	<0.05; <0.05; <0.05 (<0.05)	0.25; 0.27; 0.38 (0.30)
Medium	<0.05; <0.05; <0.05 (<0.05)	<0.05; 0.10; 0.12 (0.09)	0.86; 1.7; 1.2 (1.3)
High	0.12; 0.15; 0.13	0.67; 0.88; 0.66	13; 10; 13

Dose group	PBO, mg/kg, and (mean) in		
	Liver	Muscle	Fat
	(0.13)	(0.74)	(12)

In another study 10 White Leghorn laying hens were exposed to a premise-spray of PBO once daily for 28 days (Krautter *et al.*, 1995d). The concentrate was sprayed with a mechanical cold fogger at a rate of 37.8 g per 1000 cubic m per day, the highest concentration of piperonyl butoxide that can be applied as a premise spray for any registered product. An additional control group of 10 hens was exposed once daily to a blank formulation at an equivalent application rate. The hens were divided into three groups of 3 or 4 birds, and tissue and egg samples were composited within each group.

During the acclimatization and treatment periods eggs were collected twice daily (in the mornings and evenings) and composited samples prepared from eggs taken on dose days 0 (pre-dose) to 27 (Table 78).

Table 78. Residues of PBO in eggs from laying hens treated dermally (Krautter *et al.*, 1995d).

Day	1	3	7	11	14	18	21	24	27
Residues, mg/l (mean)	<0.01, <0.01, <0.01 (<0.01)	0.02, 0.01, 0.02 (0.02)	0.09, 0.06, 0.03 (0.06)	0.14, 0.11, 0.04 (0.10)	0.21, 0.15, 0.05 (0.14)	0.33, 0.14, 0.06 (0.18)	0.41, 0.20, 0.11 (0.24)	0.58, 0.29, 0.21 (0.36)	0.79, 0.36, 0.23 (0.46)

The hens were killed 16 to 24 hours after the last dose and samples of liver, composite breast and thigh muscle, skin and fat were collected. No significant tissue abnormalities were detected in any of the control or treated hens. Tissue samples were composited by group, frozen, homogenized with dry ice, and stored until analysis (Table 79).

Table 79. Residues of piperonyl butoxide in the tissues of laying hens after dermal applications of PBO (Krautter *et al.*, 1995d).

Tissue	Liver	Skin	Muscle	Fat
Residues, mg/kg and (mean)	0.44, 0.26, 0.15 (0.28)	8.3, 3.8, 3.3 (5.1)	1.2, 1.0, 0.67 (0.96)	5.0, 2.0, 1.9 (3.0)

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Isshiki *et al.* (1978) in Japan analysed food samples from Japan, the USA, Canada, Indonesia, Thailand, Australia, New Zealand, Korea, Malaysia and unknown sources. No residues of piperonyl butoxide were detected in 56 maize samples, 121 samples of unhulled and 100 samples of hulled rice, or in samples of buckwheat, rye, oats, milo, soya beans and red beans. Of 39 barley samples examined three contained residues, of 0.3 and 1.4 mg/kg (Australia), and 0.8 mg/kg (USA), and of 65 wheat samples two contained 0.2 and one 1.4 mg/kg (all Australia). Earlier analysis of 33 samples of rice in Japan by Kawana *et al.* (1976) had also shown no piperonyl butoxide residues.

In 1997, a total of 1047 samples were analysed for residues of piperonyl butoxide in the USA (USDA 1999). 12 samples in all, one peach, eight sweet potato, one tomato, and two fresh winter squash, contained residues (Table 80).

Table 80. Residues of piperonyl butoxide in food in the USA, 1997.

Commodity	Total no. of samples	Samples with residues[1]	Range of residues, mg/kg
Peaches	115	1	0.12[2]
Sweet potatoes	179	8	0.067 to 0.18
Tomatoes	108	1	0.067[2]
Winter squash, fresh	55	2	0.067[2]

[1] Limit of detection 0.04 mg/kg
[2] Residue detected in only 1 of duplicate subsamples

In 1998, the United States Food and Drug Administration (FDA) analysed 271 domestic samples and two imported samples for residues of piperonyl butoxide (USFDA 1999). Two domestic samples contained piperonyl butoxide: apples, with 0.041 mg/kg, and cherries, with 0.017 mg/kg. The samples of imported beans, peas, dried corn, corn paste, and lentils from Australia contained <0.01 mg/kg, and vegetables and vegetable products from Canada 0.02 mg/kg.

In 1999, the most recent year for which data are available from the USDA, 1599 samples were analysed (USDA, 2000), and 21 samples had detectable residues of piperonyl butoxide (Table 81).

Table 81. Residues of piperonyl butoxide in food in the USA, 1999.

Commodity	Samples				Limit of detection, mg/kg
	No.	% with residues	No. with residues	Range of residues, mg/kg	
Cucumbers	180	0	0		0.050
Spinach frozen	353	1.9	7	0.067-4.0	0.040-0.050
Strawberries, fresh	338	0.6	2	0.058-0.067	0.040-0.050
Strawberries, frozen	12	0	0		0.050
Sweet bell pepper	356	0.6	2	0.067[1]	0.040-0.050
Tomatoes, canned	180	0	0	NA	0.040-0.050
Tomatoes, fresh	180	5.6	10	0.053-0.35	0.040-0.050
Total	1599	1.3	21	0.053-4.0	0.040-0.050

[1] Residue detected in only 1 of duplicate subsamples.

The results of the National Residue Survey (NRS) in Australia on stored grains, 1993-1999, are shown in Table 82. All samples analysed complied with Australian MRLs.

Table 82. PBO residues in National Residue Survey in Australia, 1993 to 1999.

Commodity	% of positive samples and (no. of samples analysed)						
	1993	1994	1995	1996	1997	1998	1999
Wheat	15.8 (63)	8.2 (243)	12.9 (726)	21.3 (1204)	0.46 (1495)	2.29 (1224)	1.87 (664)
Barley		6.72 (119)	9.3 (149)	37.3 (310)	11.4 (289)	2.80 (285)	6.8 (176)
Oats	19.4 (36)	0 (13)			0 (18)	0 (20)	5.0 (20)
Field peas		0 (26)	0 (89)		0 (34)	0 (33)	0 (11)
Lupins	-			7 (444)	0 (81)	0 (59)	0 (43)
Sorghum	-	-			0 (127)	3.22 (124)	6.38 (94)
Chickpeas	-	-	-		0 (38)	0 (12)	0 (1)
Canola	-	-	-		2.5 (39)	1.2 (78)	0 (84)
Bran	-	-	78.6 (42)	97.8 (45)	11.6 (43)	5 (40)	4.7 (21)
Flour	-	-	28.1 (42)	31.8 (44)	0 (43)	0 (40)	0 (21)

All PBO residues found from 1993 to 1996 were less than one-fifth of the MRL except one residue of 11 mg/kg in wheat in 1994, 3 in wheat and 8 in bran in 1995, and 9 in wheat, 6 in barley and 2 in sorghum in 1996.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported to the Meeting.

Country	Commodity	MRL mg/kg
Australia	Cattle milk; poultry meat (in the fat); poultry, edible offal of	0.05
	Edible offal (mammalian); eggs; meat (mammalian)	0.1
	Poultry meat (in the fat); poultry, edible offal	0.5
	Dried fruits; dried vegetables; fruits; oilseed; tree nuts; vegetables	8
	Cereal grains	20

Country	Commodity	MRL mg/kg
	Bran, unprocessed, of cereal grain	40
	Wheat germ	50
Austria	Cereals	10
	Fruit; oilseed; roasted coffee; spices; tea; tea like products; vegetables	3
	Other	0.5
Belgium	Cereals	10
	Nuts; oily seeds	8
	Other fruits; vegetables	3
	Others	0*(0.05)
Canada	Dried codfish	1
	Almonds; apples; beans; blackberries; blueberries; boysenberries; cherries; cocoa beans; copra; crab apples; currants; dewberries; figs; gooseberries; grapes; guavas; huckleberries; loganberries; mangoes; muskmelons; oranges; peaches; peanuts; pears; peas; pineapple; plums; raspberries; tomatoes; walnuts	8
	Raw cereals	20
Czech Republic	Pepper; potato; tomato; vegetables	0.1
	Fruits (apple, cherry, pear)	1
	Cereals; grain	10
Finland	Food products	10.00
France	Cereals	10
Germany	Other foods of plant origin	1
	Fruits; oilseeds; vegetables other than root and tuber veg.	3
	Cereal	10
Hungary	Corn; rape; sorghum; sugar beet; tobacco; unpeeled potato;	5
	Dried fruit; fruit; peanut; vegetables	8
	Barley grain; corn; oat grain; rice (brown); rye grain; triticale; wheat grain	20
Iceland	Bulbs; cane fruit; citrus fruit; cucurbits-edible skin; cucurbits-inedible skin; flowering Brassica; fruiting vegetables; fungi; grapes, table/wine; herbs; kohlrabi; leafy Brassica; legume vegetables; lettuce and similar; miscellaneous; oilseeds; other small fruit and berries; pome fruit; pulses; root and tuber vegetables; spinach; stem vegetables; stone fruit; strawberry; sweet corn; tree nuts; watercress; wild berries and wild fruit; witloof chicory	8
	Fish/fish products	20
Italy	Forage legumes; fruit; garden vegetables; potatoes; sugar beet; sunflower seeds; tobacco	3
	Cereals in bulk; legumes in bulk	20
Kenya	Dried fruits; dried vegetables; oilseeds, except peanut; peanut; tree nuts	8
	Cereal grains; dried fish	20
Korea	Almonds; chestnuts; dehydrated fruit; dehydrated vegetables; gingko nuts; peanuts; pecans; seedcrop plants; walnuts	8
	African millet; barley; buckwheat; corn (maize); oats; other grains; rye	20
Malaysia	Coffee; tea	3

Country	Commodity	MRL mg/kg
	Cocoa beans; copra; fresh and dried fruits; leafy vegetables (dried); non-leafy vegetables (dried)	8
	Cereal grains; milled products from raw grains	20
Netherlands	Tropical seed	1
	Other fruit; vegetables	3
	Nuts; oilseed	8
	Cereals	10
	Other	0*(0.05)
New Zealand	Fruit; vegetables	8
Romania	Dry fish; grain seeds	20
	Dry vegetables and fruits; nuts; peanuts	8
Singapore	Meat and meat products	0.1
	Dried fruits; dried vegetables; fruits; nuts; oilseeds; vegetables	8
	Cereal grains; dried fish	20
Slovak Republic	Rice	1
	Fruit; fruit (dried); nuts; oil seeds; peanuts; vegetables; vegetables (dried)	8
	Cereals in bulk	10
	Cereals in bulk	20
	Fish, dried	20
South Africa	Cotton seed; fruit (dried); groundnuts; nuts (dried); other oil seeds; sunflower seeds; vegetables (dried)	10
	Cereal grains	20
Spain	Berries and small fruit; bulb vegetables; cacao beans; citrus fruit; cola beans; dried products; fresh aromatic herbs and leaf vegetables; cucurbits and peppers; fungi; green vegetables (fresh); hay and forage crops; hops; other fruits; other infusions; other products for consumption (tobacco, sugar beet, sugar cane, other); root and tuber vegetables; seed fruit; stone fruit; vegetables of the genus Brassica; young stalks	0.5
	Coffee beans; fruit with or without shell; oilseeds; potatoes; spices; tea	5
	Grains; legumes	15
Switzerland	Milk	0.02
	Berries; unspecified foodstuffs; pip fruit; stone fruit; vegetables	0.5
	Cereal products	2
	Infusion plants; tea	3
	Dried fruits; dried vegetables; oil seeds; shell fruit	8
	Cereals	20
Sweden	All kinds of cabbages and lettuces; citrus fruits; fruiting vegetables with edible peel; fruiting vegetables without edible peel; legumes, fresh; misc. fruits, e.g. banana, kiwifruit, mango, etc; mushrooms; nuts; onions, all kinds; pome fruits; root vegetables; small fruits and berries, both cultivated and wild; solanaceae vegetables; spices; stem vegetables; stone fruits; sucker maize; table grapes	8

Country	Commodity	MRL mg/kg
USA[1]	Cattle, fat; cattle, meat; cattle, meat by-products; goat, fat; goat, meat; goat, meat by-products; hog, fat; hog, meat; hog, meat by-products; horse, fat; horse, meat; horse, meat by-products; sheep, fat; sheep, meat; sheep, meat by-products	0.1
	Milk fat	0.25[2]
	Potatoes; sweet potatoes	0.25
	Eggs	1
	Poultry, fat; poultry, meat; poultry, meat by-products	3
	Almonds; apples; beans; blackberries; blueberries (huckleberries); boysenberries; buckwheat; cherries; cocoa beans; copra; cotton seed; crab apples; currants; dewberries; figs; flaxseed; gooseberries; grain sorghum; grapes; guavas; loganberries; mangoes; muskmelons; oats; oranges; peaches; peanuts (with shell removed); pears; peas; pineapples; plums; raspberries; tomatoes; walnuts	8
	Barley; bird seed mixture; corn; rice; rye; wheat	20
Yugoslavia	Fruit; processed cereals; vegetables	8
	Cereals	20

[1] Post-harvest uses except animal products
[2] Reflecting negligible residues in milk

APPRAISAL

NOTE

As some incorrect figures were used in evaluating some of the data, the compound will be reconsidered at the 2002 Meeting.

This Appraisal is a reproduction of the "Residue and analytical aspects" section of the published report of the 2001 Meeting without amendment as the forthcoming re-evaluation is likely to result in changes to the current text.

Piperonyl butoxide is a synergist used to prolong the effects of insecticides. The compound was reviewed by the 1992 JMPR for both residues and toxicology. As some critical data were not submitted, in particular studies on metabolism in plants and animals, and as the studies of stability and processing that were received related only to commercially stored wheat and wheat products, withdrawal of all the MRLs was recommended. At its Twenty-sixth Session (1994), the CCPR decided to withdraw the CXLs for cereal grains and for all other commodities (ALINORM 95/24), except for wheat, which was advanced to step 5/8. The 1995 JMPR established an ADI of 0–0.2 mg/kg bw per day.

At its Twenty-ninth Session, the CCPR scheduled piperonyl butoxide for periodic review at the 1999 JMPR, but at its Thirtieth Session it re-scheduled the review for 2000 (ALINORM 99/24 App.VII). The compound was reviewed by the current Meeting within the CCPR periodic review programme.

The Meeting received information from the manufacturer on physical and chemical properties, metabolism and environmental fate, analytical methods, stability in freezer storage, registered uses, the results of supervised trials on pre- and post-harvest uses, studies of processing, studies of animal transfer, residues in food in commerce and national residue limits. The Australian Government provided information on registered uses and national residue limits.

Metabolism

Animals

Three studies were conducted on metabolism in rats. In the first study, rats were dosed with [^{14}C]piperonyl butoxide labelled in the glycol side-chain at a single dose of 50 or 500 mg/kg bw or repeated doses of 50 mg/kg bw per day. Seven days after treatment, 27–38% of the radiolabel had been excreted in urine, 55–66% in faeces and 0.89–1.5% in carcass and tissues, with no specific trends by sex or dose. The highest concentration of residue was found in the gastrointestinal tract (≤ 2.0 mg/kg). Piperonyl butoxide was detected only in urine from female rats dosed with 50 mg/kg bw, and eight metabolites were identified (representing 0.8–6.7% of the administered dose). Piperonyl butoxide can be metabolized at the propyl side-chain, the glycolate side-chain and the dioxole ring. A product of cyclization of the propyl and glycolate chain (lactone of 6-methoxy-1,3-benzodioxol-5-yl acetic acid) was the main compound in male rat urine (5.2–6.8%). In faeces, piperonyl butoxide accounted for 2.2–31% of the administered dose. Of the four metabolites detected, 4-{[[2-(hydroxymethoxy)ethoxy]ethoxy]methyl}-5-propyl-1,2-benzenediol, a catechol with an intact glycolate chain, was the main one, representing 9.4–26% of the administered dose.

In a second study, formulated [^{14}C]piperonyl butoxide applied to discs of skin excised from rats showed a potential for adsorption through skin. After 24 h, 31% of the radiolabel was recovered in the skin homogenate. In a third study, rats received a single dose of ring-labelled piperonyl butoxide at a dose of 50 or 500 mg/kg bw. Most of the radiolabel was eliminated within the first 48 h after dosing, primarily in the faeces. During the 7 days of collection, 11–23% of the administered dose was found in urine and 70–85% in faeces, with a mean of 97% in the excreta of animals at the high dose and 98% in the excreta of those at the low dose. The carcass accounted for 0.28–0.44% of the administered dose. The metabolite profiles in excreta were similar at the two doses, piperonyl butoxide being metabolized at the dioxole ring to produce either a catechol or a substituted anisole moiety, and at the glycolate side-chain. At the glycolate side-chain, metabolism occurred by hydroxylation at the terminal carbon, oxidation to acid, followed by successive losses of the acetate moiety to form alcohols and acids. At least 15 metabolites were identified in excreta of both male and female rats, the main metabolite being 4-{[[2-(hydroxymethoxy)ethoxy]ethoxy}-methyl-5-propyl-1,2-benzenediol, representing 19% of the administered dose.

One goat received a dermal application of a 10% solution of [^{14}C]piperonyl butoxide uniformly labelled in the benzene ring for 5 days, and two other goats were given feed containing 10 or 100 ppm for 5 days. The radiolabel was excreted rapidly by the orally dosed goats and more slowly by the dermally dosed goat. Within 22 h after administration of the last dose, most of the dose had been excreted in urine (73% and 79% after oral and 44% after dermal administration) and faeces (22% and 22% after oral and 8.9% after dermal administration). The amounts excreted in milk were similar throughout the study, with all dose regimens: 0.33% of the applied dose was found in milk of orally dosed goats and 0.53% in milk of the dermally dosed goat. Little radiolabel was found in muscle, and radiolabel was concentrated in the fat of dermally dosed animal (0.20 mg/kg) and in the liver of the orally dosed animals (0.36 and 2.0 mg/kg at the low and high doses, respectively). The same metabolite profiles were found in tissues and urine. Piperonyl butoxide was detected at > 0.02 mg/kg only in liver and fat from the animals given the high oral dose (0.12 and 0.13 mg/kg) and in fat from the dermally treated animal (0.16 mg/kg). It was metabolized primarily at the glycolate side-chain. Two metabolites were detected in milk, at concentrations of 0.001–0.016 mg/kg, which had a carboxylic acid moiety at C-2 or C-4 of the glycolate chain (1-(6-propyl-1,3-benzodioxol-5-yl)-2-oxabutan-4-oic acid and 2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}acetic acid). In kidney, the metabolites were found at concentrations of 0.001–0.045 mg/kg, and the alcohol precursor of the carboxylic acid at C-4 (2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}ethanol) was detected. In liver, a catechol of the latter metabolite (4-{[2-(hydroxymethoxy)ethoxy]methyl}-5-propyl-1,2-benzenediol) was detected at 0.14 mg/kg.

In two studies, laying hens received [^{14}C]piperonyl butoxide uniformly labelled in the benzene ring for 5 consecutive days by dermal application at a dose of 14 mg/g under an occluded patch of 2.5 x 530 cm or in the feed at 10 or 100 ppm. Excreta from hens dosed dermally contained 59% of the applied radiolabel, and those from the hens dosed orally at the low and high doses contained 89% and 94%, respectively. In eggs, the concentration of radiolabel was higher in the white during the first 48 h (up to 0.63 mg/kg) and then concentrated in the yolk (≤ 1.7 mg/kg at the higher oral dose). In tissues, the least radiolabel was found in muscle (0.002–0.124 mg/k) and the most in fat (0.13–4.8 mg/kg). The concentrations in kidney and liver were 0.11–1.6 mg/kg. At the end of the study, piperonyl butoxide was found in eggs and tissues at 0.006–1.2 mg/kg (the latter in egg yolk from hens given the high oral dose), but not in liver or kidney from hens given the low oral dose. No metabolites were found in egg white or fat. Of the four metabolites found in egg yolk, liver, kidney and thigh muscle (1-(6-propyl-1,3-benzodioxol-5-yl)-2-oxabutan-4-oic acid, 2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}ethanol, 2-{2-[(6-propyl-1,3-benzodioxol-5-yl)methoxy]ethoxy}acetic acid and 4-{[2-(hydroxymethoxy)ethoxy]methyl}-5-propyl-1,2-benzenediol), the last predominated, reaching 0.19 mg/kg in kidney from animals at the high oral dose.

Thus, in animals, piperonyl butoxide can be metabolized at the glycolate side-chain, through hydroxylation at the terminal carbon, oxidation to acid, followed by successive losses of the acetate moiety to form alcohols and acids, which can be conjugated; at the propyl side-chain, through cyclization with the hydrolysed glycolate chain; and through opening of the dioxole ring. The main residue in animal tissues, egg and milk is piperonyl butoxide.

Plants

The behavior of [^{14}C]piperonyl butoxide labelled in the glycolate chain was studied after foliar application to cotton, potato and lettuce, leaf at the maximum rate of 0.56 kg ai/ha. Only minimal uptake or translocation of parent or degradates occurred in cotton and potato. The concentration of TRR found in potato tubers was 0.076% of that found in the leaves (617 mg/kg) 8 days after the fourth and last application. Cotton leaves collected 5 weeks after the fifth application had 142 mg/kg of total radiolabel. Hulls, lint and seed from cotton bolls collected 16 days after the sixth and last application contained 5, 0.4 and 0.3% of the radiolabel found in leaves. Piperonyl butoxide was not detected in potato tubers. The concentrations in cotton products ranged from 0.047 in lint to 1.23 mg/kg TRR in hulls, corresponding to 0.2–5% of that found in leaves (26.3 mg/g). In lettuce leaves, piperonyl butoxide was responsible for 51% of TRR on the day of the fifth application, but the percentage dropped to 24.4% after 10 days.

The aqueous fraction of the lettuce extract at day 0 (24.2% of TRR) contained at least three conjugated metabolites, two of which were identified, and a small amount of piperonyl butoxide (1.5% TRR). An aqueous extract from plants on day 10 contained five identified metabolites at concentrations of 0.2–2.0 mg/kg (0.9–7.6% TRR), consisting of conjugated alcohols formed after hydrolysis and truncation of the glycosate side-chain, with an intact dioxole ring.

Potato leaves contained at least seven degradates of high to moderate polarity, none of which represented more than 3% TRR. About 82% of the TRR was extracted into organic solvent, and more than 30 degradates were present, each at < 0.02 mg/kg (4% TRR). The metabolite profile was different in potato leaves and tubers. The degradates in post-extraction solids of potato tubers were characterized as highly polar materials, probably the products of oxidation of one or both side-chains to benzyl alcohols or carboxylic acids and of opening of the dioxole ring to a catechol structure.

Cotton leaves contained 11 or more degradates soluble in organic solvents; the predominant one (7.5% TRR) was similar to compounds found in lettuce, with one to three oxygen atoms remaining in the glycolate side-chain. The metabolites observed in the leaves were not observed in hulls, seeds or lint. In cotton seed, parent piperonyl butoxide was the only residue soluble in organic solvents. Mild acid hydrolysis of the post-extraction solids released almost 50% of the TRR, which presented two minor peaks (< 0.05

mg/kg) on the HPLC and a third, comprising 45% TRR (0.12 mg/kg), with characteristics similar to those in potato tubers. Cotton lint extract also contained a highly polar material that eluted at the HPLC solvent front (80% TRR, 0.19 mg/kg), which may have been the same dioxole ring-opened metabolite found in potato tubers and cotton seed, except that it was not bound. Cotton hulls contained five degradates soluble in organic solvents (0.1% TRR). The predominant degradate released by mild acid hydrolysis of the post-extraction solids was 1-(6-propyl-1,3-benzodioxol-5-yl)-2-oxabutan-4-oic acid (5.1% TRR).

Thus, piperonyl butoxide is metabolized in plants in a manner similar to that in animals, except that more polar metabolites are formed, which are fully degraded molecules resulting from hydrolysis of the glycolate side-chain, oxidation of the propyl side-chain and opening of the dioxole ring. The main residue found in lettuce, potato and cotton leaves was piperonyl butoxide, and minimal translocation occurred to potato tubers and cotton products.

Environmental fate

Soil

A 2-mm layer of a sandy loam soil treated with [phenyl ring-^{14}C]piperonyl butoxide at a rate equivalent to 10 kg ai/ha was exposed to artificial sunlight for ≤ 15 days (corresponding to 41 days of natural sunlight) or kept in the dark. The half-time in both soils was 1–3 days. Four degradates were identified, resulting from loss of the glycolate side-chain and oxidation of the resulting benzyl alcohol to the corresponding aldehyde and acid. The concentration of hydroxymethyl dihydrosafrole, a benzyl alcohol, reached a peak at day 3 (63 and 44% of the applied radiolabel in unirradiated and irradiated soil, respectively) and fell to 1.9 and 3.1% after 15 days. Hydroxymethyl dihydrosafrole was oxidized to an acid (6-propyl-,3-benzodioxol-5-carboxylic acid) which accumulated in unexposed soil after 15 days (49% of applied radiolabel). More decomposition and oxidation of the phenyl ring, observed as formation of CO_2, occurred in irradiated soil (28%) than in the control dark soil (1.3%). In another experiment, piperonyl butoxide incubated in the dark for 242 days degraded with a half-time of approximately 14 days, in a pathway similar to that discussed above. Two additional metabolites with oxidized propyl side-chains were detected at 0.1–5.8% of the applied radiolabel during the incubation period. More than one-half the applied piperonyl butoxide had been mineralized to CO_2 by 242 days.

Terrestrial dissipation of piperonyl butoxide was studied in soil treated at rate of 5.2 kg ai/ha in the USA. The half-times were 4.3 in California and Georgia and 3.5 in Michigan. At 15 cm depth, the concentration of piperonyl butoxide after 14 days was 0.11–0.22 mg/kg and fell to < 0.10 mg/kg after 30 days of application. No parent compound was detected at any site in soil collected at depths below 15 cm.

Water–sediment systems

A solution of 1 mg/L radiolabelled piperonyl butoxide was stable when incubated at 25°C in the dark for 30 days at pH 5, 7 or 9 in sterile aqueous buffers (97–100 % of the applied radiolabel recovered). In another experiment, a 10 mg/L solution of [^{14}C]piperonyl butoxide (at pH 7) exposed to natural sunlight for 84 h degraded with a half-time of 8.4 h. Two main photoproducts were observed: hydroxymethyl dihydrosafrole (22% and 48% of the applied radiolabel after 4 and 84 h, respectively) and its aldehyde oxidation product (3,4-methylenedioxy-6-propylbenzyl aldehyde; 5.7–11% of the applied radiolabel). At least five other minor degradates were found, each representing < 10% of the applied radiolabel. Unexposed samples contained ≤ 2% of radiolabel associated with metabolites.

Radiolabelled piperonyl butoxide in a sandy loam soil water–sediment system incubated under aerobic conditions in the dark (10 mg/kg sediment or 3.2 μg/ml of water) degraded slowly, and 72% of the piperonyl butoxide remained after 30 days. Under anaerobic conditions, 91% of the parent compound was still present after 181 days. In both systems, it degraded to hydroxymethyl dihydrosafrole and further to 3,4-methylenedioxy-6-propylbenzyl aldehyde and acid, which represented ≤ 3.8% of the applied radiolabel.

The adsorption and desorption characteristics of piperonyl butoxide radiolabelled in the phenyl ring were assessed in sand, clay loam, sandy loam and silt loam soils at a concentration of 0.4, 2, 3 or 4 mg/l. The systems were equilibrated for 24 h at 25 °C in darkness at a soil:solution ratio of 1:10. Piperonyl butoxide showed low to moderate mobility in sandy loam, clay loam and silt loam (K_a, 8.4, 12 and 30, respectively) and high mobility in sandy soil (K_a, 0.98). The K_{oc} values ranged from 399 in sand to 830 in silt loam. A K_d value was not determined for sandy soil, but in the other soils it ranged from 8.2 to 42 after the first desorption step and from 6.3 to 95 after the second.

The leaching behaviour of [^{14}C]piperonyl butoxide was investigated in sand, silt loam, sandy loam and clay loam soils after application at a rate equivalent to 5 kg ai/ha to the top of 30-cm columns (1 mg/column) and eluted with 0.01 mol/L calcium chloride. Piperonyl butoxide did not leach readily into loam soils (0.2–1.3% of the applied radiolabel in the leachate), but it was highly mobile in sandy soil (74% in the leachate), with a distribution coefficient of 0.42 ml/g. When the experiment was conducted with a sandy loam soil aged for 18 days and treated with [^{14}C]piperonyl butoxide, 33% of the applied radiolabel remained in the top of the column (up to 5 cm) and 14% was recovered in the leachate. The three degradates found (hydroxymethyl dihydrosafrole, 3,4-methylenedioxy-6-propylbenzyl aldehyde and the acid) were more mobile than the parent compound, being detected at 20–25 cm of the column. An extract of the aged soil contained 45% of the applied radiolabel as piperonyl butoxide.

Methods of analysis

One method for determining residues of piperonyl butoxide and its metabolites in raw and processed plant commodities involves extraction with acetonitrile, partition of piperonyl butoxide into petroleum ether and analysis by HPLC with fluorescence detection. The more polar metabolites remain in the aqueous phase, which is subjected to mild acid hydrolysis to convert the metabolites quantitatively to hydroxymethyl dihydrosafrole, which is extracted and analysed by HPLC with fluorescence detection. The LOQ for piperonyl butoxide and for total metabolites was 0.10 mg/kg, with an average recovery of 91–94%. In grapes and cranberries, < 70% of metabolites were recovered. In another method, the extract containing piperonyl butoxide was brominated and cleaned up by liquid–solid partition, and the eluate was analysed by GC with ECD. The LOQ for piperonyl butoxide was 0.10 mg/kg, and average recovery was 56% in beans to 67% in peanuts. Other solvents can be used to extract piperonyl butoxide from wheat and the milled fraction, including methanol, hexane and ethyl acetate.

In the method used to determine residues of piperonyl butoxide in milk, eggs and tissues, samples were extracted with acetonitrile, the fat was removed, and piperonyl butoxide was partitioned into hexane. The hexane solution was cleaned up on silica gel with solid-phase extraction, and piperonyl butoxide was determined by GC–MS. The LOQ was validated at 0.05 mg/kg for tissues (liver, kidney, muscle and fat), with recovery of 70–108%. The recovery at 0.01 and 0.05 mg/kg from milk was 67–120%, and that from eggs was 71–104%.

Stability of residues in stored analytical samples

Piperonyl butoxide at 1.0 mg/kg was stable in samples stored frozen in the dark for up to 12 months. In potato tubers and chips, leaf lettuce, broccoli, cucumber, grapes, orange fruit, molasses, juice and dry pulp, tomato fruit, juice, puree, dry and wet pomace, succulent beans pod and vine, cotton seed, oil and soapstock and beans, 70–108% of the added piperonyl butoxide remained after a 12-month storage. In potato granules, potato wet peel and cotton meal, these values varied from 53 to 68%. When piperonyl butoxide was added to sweets, meat, bread, sugar and peanuts at a concentration of 0.2 mg/kg, 50–69% remained after 12 months of frozen storage.

Definition of the residue

On the day of application, piperonyl butoxide accounted for 51% of the TRR in lettuce, two metabolites being formed in approximately equal amounts and accounting for 24% of the radiolabel. After 10 days, the concentration of piperonyl butoxide had decreased by half, and at least 10 metabolites were formed, each representing < 10% of the TRR. Piperonyl butoxide was not translocated to potato tubers or cotton products when applied to the leaves of these plants. Some highly polar material was found in cotton seed and in lint, representing 44 and 80% TRR, respectively. Although these metabolites were not identified, they were highly degraded compounds and, owing to their high polarity, would probably not accumulate in animals if ingested. Although no studies of metabolism in stored plant commodities were conducted, the Meeting agreed that piperonyl butoxide is degraded mainly by photolysis and considered that such studies were not necessary, as the residues are very stable in cereal grains in storage. No major metabolite was found in edible animal commodities. The main compound in both plant and animal commodities is piperonyl butoxide.

The Meeting agreed that the residue definition for compliance with MRL and for estimating dietary intake in plant and animal commodities continues to be piperonyl butoxide.

Piperonyl butoxide has a log P_{ow} of 4.6 and is concentrated in the fat of animals dosed orally and dermally. The Meeting concluded that piperonyl butoxide is fat-soluble.

Results of supervised trials

Pre-harvest trials were conducted in crops in various regions of the USA between 1992 and 1996, with 10–12 applications of pyrethrins containing piperonyl butoxide, according to maximum GAP for piperonyl butoxide (0.56 kg/ha; no PHI).

Citrus

Seven supervised trials were conducted on citrus. The concentrations of residues of piperonyl butoxide in lemon were 3.1 and 1.7 mg/kg, those in oranges were 0.90, 0.98 and 1.0 mg/kg and those in grapefruit were 0.49 and 1.4 mg/kg. The concentrations in citrus were, in ranked order (median underlined): 0.49, 0.90, 0.98, 1.0, 1.4, 1.7 and 3.1 mg/kg. Although there were fewer trials on citrus fruits than would be required for a major crop, piperonyl butoxide is used to only a minor extent as a synergist in pre-harvest treatment in pyrethrin formulations. Recommendations for pyrethrins in citrus were made by the 2000 JMPR on the basis of trials conducted with a pyrethrin–piperonyl butoxide formulation. Therefore, the Meeting agreed to recommend a maximum residue level of 5 mg/kg and a STMR of 1.0 mg/kg for piperonyl butoxide in citrus.

Berries and small fruits

Seven supervised trials were conducted on berries and small fruits. The concentrations of residues of piperonyl butoxide were 2.8 mg/kg in blackberry, 5.0 and 5.0 mg/kg in blueberry, 4.2 mg/kg in cranberry, 9.6 mg/kg in grapes and 3.0 and 3.1 in strawberry. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in berries, strawberry and grapes. There is no current recommendation for pyrethrins in berries and small fruits.

Brassica vegetables

Three supervised trials were conducted on broccoli, giving rise to concentrations of residues of piperonyl butoxide of 0.69, 1.7 and 2.3 mg/kg. In three trials conducted on cabbage, the concentrations were 0.09, 0.23 and 0.46 mg/kg, while those in cabbage with wrapper leaves were 1.1, 6.4 and 2.7 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum

residue level for piperonyl butoxide in broccoli and cabbage. There is no current recommendation for pyrethrins in broccoli and cabbage.

Cucurbits

Eight supervised trials were conducted on cucurbits. The concentrations of residues of piperonyl butoxide were 0.83 and 0.61 mg/kg in cantaloupe, 0.07 and 0.68 mg/kg in cucumber and 0.10, 0.20, 0.25 and 0.27 mg/kg in squash. The Meeting agreed that the data on residues in cucurbits could be combined as 0.07, 0.10, 0.20, 0.25, 0.27 0.61, 0.68 and 0.83 mg/kg, and estimated a maximum residue level of 1 mg/kg and a STMR of 0.26 mg/kg for piperonyl butoxide in cucurbits.

Peppers and tomato

In three supervised trials conducted on peppers, the concentrations of residues of piperonyl butoxide were 0.39, 0.59 and 1.4 mg/kg. In three trials conducted in tomato, the values were 0.37, 0.76 and 1.0 mg/kg. Although there were fewer trials on peppers and tomato than required for these crops, the Meeting agreed to consider the data sufficient to recommend maximum residue levels, for the reasons outlined for citrus fruits. The data for peppers and tomato were combined, in ranked order, as 0.37, 0.39, 0.59, 0.76, 1.0 and 1.4 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg and a STMR of 0.675 mg/kg for piperonyl butoxide in peppers and tomato.

Leafy vegetables

Eleven supervised trials were conducted on leafy vegetables. In lettuce, head, the concentrations of residues of piperonyl butoxide were 0.54 and 0.35 mg/kg ; when the wrapper leaves were attached, the values were 5.0 and 3.6 mg/kg. Lettuce, leaf contained concentrations of 19 and 23 mg/kg, mustard greens contained 37 and 38 mg/kg, radish leaves (crowns with leaves) contained 38 mg/kg and spinach contained 32 and 39 mg/kg. The concentrations in mustard greens, radish leaves and spinach are within the same range and provide mutual support. They were, in ranked order: 32, 37, 38 (2) and 39 mg/kg. The Meeting recommended a maximum residue level of 50 mg/kg and a STMR of 38 mg/kg for piperonyl butoxide in mustard greens, radish leaves, leaf lettuce and spinach.

Legume vegetables

Two supervised trials were conducted on succulent beans, giving concentrations of piperonyl butoxide in pods of 0.34 and 2.2 mg/kg: In two trials conducted in succulent peas, the values were 2.2 and 5.5 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in succulent beans and peas.

Root and tuber vegetables

In one supervised trial conducted on carrot, the concentration of residues of piperonyl butoxide in roots was 1.1 mg/kg. Three trials conducted on potato gave values in tubers of < 0.10 (2) and 0.11 mg/kg, one trial on radish gave a value in roots of 0.34 mg/kg and two trials conducted on sugar beet gave concentrations in roots of < 0.10 mg/kg. In a study of metabolism conducted with labelled piperonyl butoxide on potato at maximum GAP, no residues were detected in tubers. Although there were fewer trials on root and tuber vegetables than would be required for this group, the Meeting agreed to consider the data sufficient to recommend residue levels, for the reasons outlined for citrus fruits. As only one trial was conducted on carrots, giving a much higher value than for the other commodities in the group, the Meeting agreed to combine the values for all commodities except carrots. Those are, in ranked order: < 0.10 (3), 0.11 and 0.34 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg and a STMR of 0.10 mg/kg for piperonyl butoxide in root and tuber vegetables, except carrots.

Pulses

In two supervised field trials on dry beans and two on dry peas at GAP rate, the concentrations of piperonyl butoxide residues in seed were 0.10 and 0.11 mg/kg in beans and 0.27 and 0.57 mg/kg in peas. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in pulses due to pre-harvest use.

Celery

In two supervised trials on celery, the concentrations of residues of piperonyl butoxide were 17 and 23 mg/kg in untrimmed leaf stalk and 0.98 and 2.3 mg/kg in the petiole. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in celery.

Mustard seed

One supervised trial was conducted on mustard seed, which gave a concentration of piperonyl butoxide residues of 2.1 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in mustard seeds.

Cotton seed

In five supervised trials conducted on cotton seed, the concentrations of residues of piperonyl butoxide were < 0.10 (2), 0.10 (2) and 0.21 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in cotton seed. There is no current recommendation for pyrethrins in cotton seed.

Animal feed

In four trials conducted on succulent or dry beans, the concentrations of residues in vine were 16 (2), 26 and 28 mg/kg. In hay samples dried for 2–6 days in the open air, the values were 11, 14, 21 and 42 mg/kg, and those in forage were 14 and 25 mg/kg. In four trials on succulent or dry pea, the concentrations in vine were 26, 29, 47 and 96 mg/kg. In hay samples dried for up to 14 days in the field or in a greenhouse, the values were 3.7, 38, 48 and 153 mg/kg, and those in forage were 31 and 42 mg/kg.

The Meeting agreed that the data on residues in bean vines represent the same population as those for pea vines and could be used to support a recommendation for pea vines. The concentrations were, in ranked order: 16 (2), 26 (2), 28, 29, 47 and 96 mg/kg. When the median (27 mg/kg) and the maximum values (96 mg/kg) were corrected for moisture content (75%, *FAO Manual*, p. 125), the values were 108 mg/kg and 384 mg/kg, respectively, in dry matter. The Meeting recommended a maximum residue level of 400 mg/kg and a STMR of 108 mg/kg for piperonyl butoxide in pea vines, green (dry basis).

The Meeting agreed that the data on residues in bean and pea hay represented a single population and could be combined, in ranked order, as 3.8, 11, 14, 21, 38, 42, 48 and 153 mg/kg. The median (17.5 mg/kg) and the maximum (153 mg/kg) values were corrected for the moisture content of pea hay (12%, *FAO Manual*, p. 125), and became 19.9 and 174 mg/kg, respectively, on a dried base. The Meeting estimated a maximum residue level of 200 mg/kg and a STMR of 19.9 mg/kg for piperonyl butoxide in bean hay and pea hay or fodder.

As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in pea and bean forage.

In five supervised trials conducted on cotton forage, the concentrations of residues of piperonyl butoxide were 20, 28, 30 (2) and 37 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in cotton forage.

In two trials conducted with sugar beet leaf, the concentrations of residues of piperonyl butoxide in crowns with leaves attached were 37 and 12 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not recommend a maximum residue level for piperonyl butoxide in sugar beet leaves.

Post-harvest treatment

Trials were conducted in which navy beans in cloth bags underwent treatment with up to 10 applications of piperonyl butoxide at the label rate in a warehouse by a space spray (0.25 kg ai/1000 m^3) and a contact spray (0.3 kg ai/100 m^2). One bag was collected for analysis after each application, for a total of 10 bags from each treatment. The concentrations of residues were < 0.05 (2) (LOD), < 0.10 (3) (LOQ), 0.10, 0.13 (2), 0.16 and 0.17 mg/kg in samples collected after the space spray treatment and < 0.05 (10) mg/kg in samples after the contact spray treatment. The concentrations of residues after post-harvest use were, in ranked order, < 0.05 (12), < 0.10 (3), 0.10, 0.13 (2), 0.16 and 0.17 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg, an STMR value of 0.05 and a highest residue of 0.17 mg/kg for piperonyl butoxide in pulses after post-harvest use.

Trials were conducted with harvested peanuts in cloth bags treated in a warehouse with 10 applications at the label rate by a space spray (0.25 kg ai/1000 m^3) and a contact spray (0.3 kg ai/100 m^2). One bag was collected for analysis after each application, for a total of 10 bags from each treatment. The concentrations of residues in samples collected after each space spray treatment were < 0.10 (3), 0.20, 0.24, 0.28, 0.29, 0.36 and 0.54 (2) mg/kg, while those after contact spray treatment were < 0.05 (6) and < 0.10 (4) mg/kg. The concentrations after post-harvest use were, in ranked order: < 0.05 (6), ≤ 0.10 (7), 0.20, 0.24, 0.28, 0.29, 0.36 and 0.54 (2) mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR value of 0.10 mg/kg for piperonyl butoxide in peanuts after post-harvest treatment.

Trials were conducted with prunes treated in a warehouse with 10 applications at the label rate by a space spray (0.25 kg ai/1000 m^3) or a contact spray (0.3 kg ai/100 m^2). One bag was collected for analysis after each application, for a total of 10 bags from each treatment. The concentrations of residues in samples collected after each space spray treatment were < 0.05 (5), < 0.10 (4) and 0.11 mg/kg, while those after contact spray were < 0.05 (6) and < 0.10 (4) mg/kg. The concentrations of residues after post-harvest use were, in ranked order, ≤ 0.05 (11), < 0.10 (8) and 0.11 mg/kg.

The Meeting agreed that the values for residues in prunes could be extended, and estimated a maximum residue level of 0.2 mg/kg and an STMR value of 0.05 mg/kg for piperonyl butoxide in dried fruits after post-harvest treatment.

Post-harvest trials were conducted on cacao beans, raisins and wheat flour in Germany during 1993–94 with eight space spray applications of pyrethrum–piperonyl butoxide formulation containing piperonyl butoxide at 21.3 g/1000 m^3 at 14-day intervals, or two applications of piperonyl butoxide at 128 g/1000 m^3. Samples were taken on days 0, 14, 30, 60 and 90 after treatment. In Germany, GAP for space spray treatment of stored products consists of 0.375–132 g ai/1000 m^3.

Two trials were conducted on cacao beans in jute sacks. At the lower rate, the concentrations of residues in beans 0 and 14 days after the last application were 0.21 and 0.25 mg/kg and then fell to 0.08 mg/kg at day 90. At the higher rate, the concentrations varied from 0.52 mg/kg on day 0 to 0.75 mg/kg on day 30. In one trial conducted at the higher rate (128 g ai/1000 m^3) on raisins in stored polythene and cardboard, the concentration was < 0.01 mg/kg at all sampling times. In one trial on wheat flour at the same rate, the concentrations ranged from 0.12 mg/kg at day 14 to 0.46 mg/kg at day 60.

As insufficient data from trials performed according to GAP were submitted, the Meeting agreed not to recommend a maximum residue level for piperonyl butoxide in cacao beans or wheat flour after post-harvest treatment. The maximum residue level, STMR value and highest residue for raisins are covered by the recommendations for dried fruits after post-harvest treatment.

Two trials were conducted on wheat in Germany. The concentrations in grain after the lower rate of treatment (21.3 g/1000 m^3) varied from 0.71 mg/kg after 30 days to 2.5 mg/kg on day 0. Samples taken after the higher rate of treatment (128 g/1000 m^3) contained concentrations of 1.3 mg/kg on day 30 and 2.2 mg/kg on day 0.

In the USA, there are two further approved post-harvest uses for piperonyl butoxide as a pyrethrin formulation on stored grains: direct treatment of grain as it is carried to a silo (11.1–26 mg ai/kg of grain) or application to grain in storage (0.12–0.24 kg ai/100 m^2). A series of trials was conducted in the USA in 1959 with various formulations of piperonyl butoxide applied to wheat at various rates as it was transferred to the bins. Up to five bins were treated at each application rate, and samples were taken 3–25 months after application. In three trials conducted at maximum GAP, the highest concentrations of piperonyl butoxide residues in all bins were 12, 17 and 25 mg/kg. One trial at lower rate gave similar results (maximum, 12 mg/kg), and the highest value in one trial conducted at a rate below GAP was 5.2 mg/kg.

Although trials were conducted on wheat in the USA according to GAP in 1959–61, full reports were not provided. The concentrations of piperonyl butoxide residues during storage for up to 12 months ranged from 4.1 to 13 mg/kg.

In Australia, piperonyl butoxide can be used on grain in various insecticide formulations for post-harvest treatment at a rate of 2.4–8.5 mg ai/kg of grain. In a series of trials conducted in 1978–79, treated wheat was sampled after up to 9 months of storage. In nine trials conducted at maximum GAP, the highest concentrations during sampling were 3.4, 8.0, 7.1, 7.2, 6.2, 9.1, 7.5 (2) and 8.0 mg/kg. In 10 trials conducted at a lower GAP rate or at a higher rate, the concentrations ranged from 2.4 to 16 mg/kg.

In 31 trials conducted in Australia in 1981–82, wheat treated with piperonyl butoxide at 10 mg/kg of grain in various formulations was sampled up to 9 months after treatment. The highest concentrations of residues found were 5.7 (2), 7.9 (3), 4.2 (2), 7.3 (3), 5.3, 5.0, 7.0 (2), 4.5, 7.8 (2), 5.2, 4.8, 7.5, 8.1, 8.2, 10 (3), 8.6, 9.2, 11, 8.0, 9.4 and 30 mg/kg. In four further trials conducted under the same conditions, treated wheat was sampled after 10–31 months of storage. The highest concentrations during this period were 7.3, 6.7 and 5.9 (2) mg/kg.

In a series of 13 trials conducted in Australia in 1979–80, wheat grain treated with various piperonyl butoxide formulations at 10 mg ai/kg of grain were sampled after up to 9 months of storage. The highest concentrations were 9.7 (2), 8.6, 7.7, 8.7, 8.9, 9.3, 9.5, 10 (2), 7.3, 8.4 and 14 mg/kg. In two other trials conducted at lower GAP the concentrations were 4.5 and 2.3 mg/kg.

In three trials conducted in Australia in 1998 at 8 mg ai/kg of grain in various formulations, the highest concentrations of piperonyl butoxide residues found during a 9-month storage period were 13, 16 and 5.4 mg/kg. In a trial conducted at a lower GAP, the concentration was 1.7 mg/kg. Although another 27 trials

were conducted between 1990 and 1998, at rates of 4–10.7 mg ai/kg of grain, full reports of the studies were not provided. The highest concentrations found in each trial ranged from 1.5 to 8.9 mg/kg.

In Italy, piperonyl butoxide can be used after harvest in various formulations at a rate of 2.3–12.5 mg ai/kg of grain. In 18 trials conducted at various locations in Italy at a rate of 2.5, 5.0 or 10 mg/kg, samples were taken after up to 12 months of storage. The concentrations of residues in the trial at the highest GAP rate were 13, 3.9, 5.2, 4.2, 3.9 and 4.5 mg/kg. The highest concentrations in trials conducted at lower rates were 0.37–8.7 mg/kg.

Six post-harvest trials were conducted on barley in Australia in 1992–96 according to maximum GAP (6.33–8 mg ai/kg of grain) in three formulations. The grain was stored for up to 6.5 months. The highest concentrations of piperonyl butoxide residues were, in ranked order, 0.9, 6.0, 6.4, 6.5, 6.6 and 7.2 mg/kg. One trial at a lower rate gave values within the same range, but a full report of the study was not provided.

In 30 trials on maize in the USA conducted in 1952–57 with dust and spray formulation at rates of 10.4–29.4 mg ai/kg of grain, samples were taken after 1–50 months of storage. The highest concentrations of piperonyl butoxide found during storage in samples from the 10 trials conducted according to maximum GAP were 12, 11, 4.0, 8.0, 7.0, 8.0, 25, 6.0, 9.0 and 13 mg/kg, while those in trials conducted at lower GAP rates were 1–21 mg/kg. In another study, for which a full report was not provided, conducted at maximum GAP, the highest concentration found during 12 months of storage was 10 mg/kg.

Trials were conducted in maize with three concentrations of piperonyl butoxide applied by surface spray (49.7–149 g ai/m^2) at various frequencies of application. Three months after treatment, 25–41% of the total applied remained in the maize; after 6 months, this value had dropped to 11–13%.

In Italy, two trials were conducted on maize at the lowest and highest GAP rates, and samples were taken for analysis after up to 6 months of storage. The highest concentrations of piperonyl butoxide found were 1.3 mg/kg at the lowest GAP rate and 4.1 mg/kg at the highest rate.

In two trials conducted on sorghum in Australia at maximum GAP, the concentrations of piperonyl butoxide residues on day 0 were 2.9 and 10 mg/kg; these were reduced after 3 months of storage. Two trials at lower and higher rates gave highest values of 0.50 and 20 mg/kg. In another trial conducted at maximum GAP, the highest concentration found during a 6-month storage period was 9.7 mg/kg. A full report of this trial was not provided.

GAP for post-harvest use of piperonyl butoxide on cereal grains is 10 mg/kg of grain in Australia, ≤ 12.5 mg/kg of grain in Italy and ≤ 26 mg/kg of grain in the USA. The Meeting agreed that the estimates should be derived from the critical GAP, that of the USA. The concentrations of residues in trials conducted according to GAP in the USA (10 trials on wheat, three on maize) were, in ranked order: 4.0, 6.0, 7.0, 8.0 (2), 11, 12 (2), 8.0, 9.0, 13 and 25 mg/kg. The Meeting estimated a maximum residue level of 30 mg/kg and a STMR value of 11 mg/kg for piperonyl butoxide in cereal grains after post-harvest treatment.

Fate of residues during processing

A series of studies was conducted on processing of orange, grapes, tomato, beans, potato, sugar beets and cotton that had been treated with at least 10 applications at five times the GAP rate. Samples were collected on the day of the last application, except for cotton, samples of which were collected after 14 days. Bulk samples were processed into the required products by procedures that simulated commercial practice.

Three orange plots were treated and one bulk sample consisting of one-third of each treated plot was processed. The concentration of piperonyl butoxide residues in orange was 9.4 mg/kg. The residues concentrated in orange dry pulp and orange oil, with processing factors of 5.7 and 15. In orange molasses, the

concentration of residues was reduced by a processing factor of 0.53, and no residue was found in orange juice (processing factor, < 0.01). On the basis of the recommended maximum residue level of 5 mg/kg and the STMR value of 1.0 mg/kg, the Meeting estimated an STMR-P value of 5.7 mg/kg and a maximum residue level of 0.05 mg/kg in orange dried pulp and an STMR-P value of 0.01 mg/kg in orange juice.

Three tomato plots were treated, and one bulk sample consisting of one-third of each treated plot was processed. The concentration of residues in tomato was 8.5 mg/kg, and was found in wet and dry pomace, with processing factors of 5.9 and 34, respectively. The concentrations of residues in tomato purée and juice were reduced, with processing factors of 0.33 and 0.15, respectively. On the basis of the recommended maximum residue level of 2 mg/kg and the STMR value of 0.675 mg/kg in tomato, the Meeting estimated a maximum residue level of 0.3 mg/kg and an STMR-P value of 0.10 mg/kg for tomato juice and a STMR-P of 0.223 mg/kg for tomato purée.

Three grape plots were treated, and samples were collected for processing. The concentrations of residues in fruit were 14 (2) and 11 mg/kg. In all samples, the concentration increased in raisin, raisin waste and wet and dry grape pomace, giving average processing factors of 1.1, 2.3, 2.1 and 5.5, respectively. The concentration in juice decreased to 0.22–0.24 mg/kg, giving a processing factor of 0.02. As no STMR value was recommended for grapes, the Meeting could not estimate a STMR-P value for grape products.

Samples from three treated potato plots contained no detectable residues (< 0.10 mg/kg), and no residues were found in granules or chips. The residues were concentrated in wet potato peel, giving an average processing factor > 1.5. On the basis of the STMR value of 0.10 mg/kg recommended for root and tuber vegetables, the Meeting estimated a STMR-P value for wet potato peel of 0.15 mg/kg.

The concentration of residues in sugar beet root in one treated plot was 0.08 mg/kg. The concentration increased after processing to dry pulp, with a processing factor of 3.44. No residues were detected in sugar or molasses (< 0.10 mg/kg), giving an estimated processing factor for both commodities of < 1.2.

In one treated plot of succulent bean, the concentration of residues in pods was 8.0 mg/kg. The residues concentrated in cannery waste, with a processing factor of 6.4.

Three treated cotton plots had concentrations of residues in seed of 0.10 mg/kg (3). Each sample was processed, and the residues were found mainly in hulls with an average processing factor of 1.1, in crude oil with an average processing factor of 6.3, in refined oil with an average processing factor of 20 and in soapstock with an average processing factor of 3.8. Residues were not detected in cotton meal (< 0.10 mg/kg). As no STMR value was recommended for cotton, the Meeting could not estimate a STMR-P value for cotton products.

Various studies were conducted on processing of wheat at various locations. In three studies conducted in Australia, wheat treated with piperonyl butoxide at 8.0 mg ai/kg of grain was processed into bread and bran. The concentrations of residues in grain were 16 and 14 (2) mg/kg and residues were found mainly in bran, giving processing factors of 2.85, 1.5 and 2 (average, 2.1); the values were reduced in bread, with average processing factors of 0.015 and 0.03 (average, 0.225). No residues were detected in one bread sample. No information of the processing or analytical method was provided.

In a series of 12 studies in Australia, wheat was treated at a 15 mg ai/kg of grain, stored for 3 months and processed to bran and flour. The concentration of residues decreased after cleaning in flour and short and low-grade middlings, with average processing factors of 0.82, 0.42, 0.56 and 0.56, respectively. In bran, the concentration increased, with an average processing factor of 1.7. A full report of the studies was not provided.

Eighteen processing studies were conducted in Italy with wheat treated at various rates and stored for 45 or 180 days. The processing factors of cleaned, decorticated grain ranged from 0.27 to > 1.8 (average, 0.549) and from < 0.27 to 1.33 (average, 0.506), respectively. On average, the concentrations of residues in bran increase, with an average processing factor of 1.3 (< 0.02–3.1). In all studies, the concentrations of residues in flour decreased, with an average processing factor of 0.285, ranging from < 0.24 to 0.78.

In one study conducted in Australia, treated wheat was processed to bran, pollard, germ, gluten, flour, wholemeal bread and white bread at various extraction rates. Piperonyl butoxide residues were determined 1 month after processing. The residues concentrated in bran with processing factors of 4.2 and 4.3, in pollard with a processing factor of 2.7, in germ with a processing factor of 2.6 and in gluten with a processing factor of 1.8. The concentration decreased in flour with processing factors of 0.30 and 0.23, in wholemeal bread with a processing factor of 0.51 and in white bread with processing factors of 0.19 and 0.20.

In one study conducted in Australia, wheat treated with piperonyl butoxide at 8 mg ai/kg of grain was stored for 1, 3 or 6 months and processed to bran, pollard, germ, gluten, meal, flour and bread. Two flour extraction rates and a 1:1 blend of the two were used. The concentrations of residues increased in bran, pollard, germ and gluten, with average processing factors of 3.95 (n = 6), 2.3 (n = 3), 3.3 (n = 5) and 1.57 (n = 3), respectively. In meal, flour and bread, the concentrations decreased with average processing factors of 0.85 (n = 3), 0.3 (n = 6) and 0.36 (n = 9), respectively, from wheat wholemeal to white bread.

Wheat treated with two formulations at application rates of 10 and 13 mg/kg of grain and stored for up to 24 weeks was processed in three commercial mills (50 t per sample) and a pilot mill (1 t per sample). The concentrations of residues increased in bran with processing factors of 3.1–4.8 (average, 4.1; n = 10), in germ with processing factors of 2.1–4.3 (average, 3.2; n = 10) and in pollard with processing factors of 1.8–5.5 (average, 2.8; n = 6). On average, the concentration increased in wholemeal, with processing factors of 0.48–2.8 (average, 1.3; n = 9), but decreased in flour, with processing factors of 0.27–1.1 (average, 0.53; n = 10).

Wheat treated with piperonyl butoxide at 10 mg/kg of grain was stored for 2 or 4 h and processed to bran, pollard, germ, meal, flour and bread. The concentration of residues increased in bran, pollard and germ, with average processing factors of 3.8, 2.6 and 2.6, respectively. The concentrations decreased in flour, meal, wholemeal bread and white bread, with processing factors of 0.22, 0.78, 0.41 and 0.11, respectively.

Five processing studies were conducted in Australia with wheat treated at the GAP rate or higher and stored for 1–26 weeks. The concentrations of residues increased in bran with an average processing factor of 3.8 (3.33–4.7, n = 4), in germ with an average processing factor of 2.2 (1.12–2.89, n = 4) and in gluten with a processing factor of 1.4. The concentrations decrease in flour with an average processing factor of 0.34 (0.24–0.51, n = 5), in bread (white pan, wholemeal, flat Arabic and steamed) with average processing factors of 0.19–0.36 (average, 0.47) and in noodles (yellow alkaline and white) with average processing factors of 0.24 and 0.28. On average, the concentrations of residues decreased in wheat wholemeal, with processing factors of 0.61–1.29 (n = 5; average, 0.98).

In summary, the concentrations of piperonyl butoxide residues increased in wheat bran, with an average processing factor of 3.5 (n = 42), in germ with an average processing factor of 2.8 (n = 20), in pollard with an average processing factor of 2.6 (n = 10) and in gluten with an average processing factor of 1.5 (n = 4). The concentrations decreased in wheat flour with an average processing factor of 0.32 (n = 42), in wheat wholemeal with an average processing factor of 0.98 (n = 18), in bread with an average processing factor of 0.32 (n = 18) and in noodles, with an average processing factor of 0.26 (n = 2).

On the basis of the processing factors derived and the recommended MRL of 30 mg/kg and the STMR value of 11 mg/kg for cereal grains, the Meeting estimated a maximum residue level of 100 mg/kg and an STMR-P value of 38.5 mg/kg for wheat bran; a maximum residue level of 10 mg/kg and an STMR-P value of 3.5 mg/kg for wheat flour; a maximum residue level of 30 mg/kg and an STMR-P value of 10.8

mg/kg for wheat wholemeal and a maximum residue level of 100 mg/kg and an STMR-P value of 30.8 mg/kg for piperonyl butoxide in wheat germ.

In Italy, six processing studies were conducted on maize treated with piperonyl butoxide at two rates and stored for 42 or 182 days. Degermination was conducted in the laboratory under conditions that matched the industrial procedure, by starch processing (wet conditions) and mill processing (dry conditions). The concentrations of residues in germ and oil decreased, with average processing factors of < 0.3 and < 2.7, respectively (n = 6). On the basis of the recommended MRL and the STMR value for cereal grains, the Meeting recommended a maximum residue level of 80 mg/kg and an STMR-P value of 29.7 mg/kg for maize oil, crude.

Two processing studies were conducted in France on dried and undried cargo rice treated with piperonyl butoxide at 2.5 mg/kg of grain, but only a short summary of the study was provided.

Cocoa beans and soya beans were treated with piperonyl butoxide formulations at 7.5 or 10 mg ai/kg and stored for up to 1 year. Samples were then processed and analysed. The processing factors were 0.15–0.85 (average, 0.58; n = 10) for roasted cocoa beans and < 0.15–0.53 (average, < 0.20; n = 6) for chocolate paste. The concentration of residues increased in soya oil, with processing factors of 6.18, 22 and 13 (average, 13.9), and decreased in soya cake, with processing factors of 0.86, 0.75 and 0.10 (average, 0.57). Only a summary of the studies was provided.

Residues in animal commodities

Dietary burden of farm animals

The Meeting estimated the dietary burden of piperonyl butoxide residues in cows and poultry on the basis of the diets listed in Appendix IX of the *FAO Manual* (FAO, 1997; pp. 121–127) and the maximum residue levels and STMR values estimated by the current Meeting.

Estimate of maximum dietary burden of farm animals

Commodity	Group	Residues (mg/kg)	Basis	Dry matter (%)	Residues, dry weight (mg/kg)	% of diet			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Citrus, dried pulp	AB	5.7	STMR-P	91	6.2	20	10	–	1.2	0.6	–
Potato peel, wet	AB	0.15	STMR-P	20	0.27			–			–
Sorghum	GC	30	MRL	86	34.2	5		20	1.7		27.4
Wheat	GC	30	MRL	89	33.3						
Wheat bran	GC	100	MRL	89	111	50	40	80	55.5	44.4	88.8
Rice	GC	30	MRL	88	33.6						
Maize	GC	30	MRL	88	33.6						
Pea vines	AL	400	MRL	–	400	25	50	–	100	200	–
Pea hay	AL	200	MRL	–	200						–
					Total	100	100	100	158	245	116

Estimated STMR value for dietary burden of farm animals

Commodity	Group	Residues (mg/kg)	Basis	Dry matter (%)	Residues, dry weight (mg/kg)	% of diet			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Citrus, dried pulp	AB	5.7	STMR-P	91	6.2	20	10	–	1.2	0.6	–
Potato peel, wet	AB	0.15	STMR-P	20	0.27			–			–
Sorghum	GC	11	STMR	86	12.5	5		20	0.6		2.5
Wheat	GC	11	STMR	89	12.2						
Wheat bran	GC	38.5	STMR	89	42.7	50	40	80	21.3	17.1	34.2
Rice	GC	11	STMR	88	12.3						
Maize	GC	11	STMR	88	12.3						
Pea vines	AL	108	STMR	–	108	25	50	–	27	54	–
Pea hay	AL	19.9	STMR	–	19.9			–			
					Total	100	100	100	50.1	71.7	36.7

Feeding and dermal application to animals

Cows were given diets containing piperonyl butoxide at a concentration of 100, 300, 900 or 3000 mg/kg (dry weight basis) once daily for 28–30 consecutive days. The average concentration of residues in milk from three cows at 100 and 300 ppm remained approximately constant throughout the dosing period within ranges of < 0.01–0.02 mg/kg and 0.03–0.07 mg/kg, respectively. The concentrations in milk reached a plateau rapidly at higher doses. The average concentration of piperonyl butoxide in milk from cows at 900 ppm was 0.41 mg/kg, and that in milk from cows at the highest dose was 6.2 mg/kg. The residues in all treated animals were concentrated in liver and fat, and none were detected in kidney or muscle at the lower dose. In liver, the mean concentration ranged from 0.14 mg/kg at 100 ppm to 12 mg/kg at 300 ppm. The concentrations in animals at 100 ppm and 3000 ppm were 0.21 and 146 mg/kg in fat, 0.08 and 10 mg/kg in kidney and 0.05 and 7.6 mg/kg in muscle.

In Costa Rica and the USA, piperonyl butoxide may be sprayed directly onto livestock and poultry at a rate of 0.42–8.9 g ai/animal. Three cows were treated dermally twice daily for 28 consecutive days at a maximum GAP dose of 2.28 g/day (3.78 mg/kg bw per day). The average concentration of residues in milk was 0.06 mg/kg on the first day and increased to 0.14 mg/kg on day 3, 0.12 mg/kg on day 7 and 0.16 mg/kg on day 27.

Laying hens were given diets containing 20.4, 61.2 or 196 ppm piperonyl butoxide equivalents. The concentrations of residues in eggs from hens at 61.2 ppm reached a plateau on day 7, at 0.16–0.21 mg/kg on days 7–21 and an increase on day 27. Residues were detected in liver only at the highest dietary level (at a concentration of 0.13 mg/kg). In muscle, residues were present in hens at the two higher dietary levels at mean concentrations of 0.09 and 0.74 mg/kg, respectively. The mean concentration in fat ranged was 0.30 mg/kg at the lowest dietary level and 12 mg/kg at the highest.

Laying hens exposed dermally for 28 consecutive days to piperonyl butoxide at a GAP application rate of 37.8 g/1000 m^3 had residues in their eggs from day 3, at a concentration of 0.02 mg/kg, which increased steadily up to day 27 (0.46 mg/kg) and did not reach a plateau. The average concentrations in tissues ranged from 0.96 mg/kg in muscle to 3.0 mg/kg in fat.

Maximum residue levels

The maximum calculated dietary burden of piperonyl butoxide for cattle was 158 mg/kg for beef cattle and 245 mg/kg for dairy cows. The highest dietary burden was used to estimate the maximum residue level in milk and tissues of cattle. The mean intake calculated for dairy cattle (71.7 mg/kg) was higher than that for beef cattle (50.1 mg/kg) and was used to estimate the STMR value for milk and cattle tissue. The calculated maximum and mean intakes of piperonyl butoxide for poultry, 116 mg/kg and 36.7 mg/kg, respectively, were used to estimate the maximum residue level and STMR value, respectively.

The highest concentrations of residues in tissues in the feeding studies and the mean value in milk after the plateau were used to estimate the maximum residue level. For eggs, the highest and the mean values at day 27 were used to calculate the maximum residue level and the STMR value, respectively. For cattle, the values at the calculated dietary burden (254 mg/kg) were estimated by interpolation of values for residues found at 100 and 300 ppm in feed. For poultry, these values (at a dietary burden of 116 mg/kg) were estimated by interpolation of concentrations found at 61.2 and 196 ppm. The mean concentrations of residues in tissues, milk and eggs were used to estimate the STMR value. For cattle, the concentration of residue at the calculated dietary burden (71.7 mg/kg) was estimated by 'proportioning' residues found at 100 ppm. For poultry, the concentration at 36.7 mg/kg was estimated by interpolation of data at 20.4 and 61.7 ppm.

The mean concentration of residue in milk after dermal treatment was used to estimate the maximum residue level and the STMR value for cattle milk. The highest and median concentrations of residues in eggs at day 27 (no plateau reached) were used to estimate the maximum residue level and the STMR value, respectively, in eggs, and the highest and median concentrations in tissues were used to estimate the maximum residue level and the STMR value, respectively, for both cattle and poultry.

Residues in cattle milk and tissues from animals treated orally

Dose (ppm) *Interpolated* / actual	Piperonyl butoxide concentration (mg/kg)								
	Milk (mean)	Liver		Kidney		Muscle		Fat	
		Highest	Mean	Highest	Mean	Highest	Mean	Highest	Mean
MRL									
245 /	*0.037* /	*0.71* /		*0.11* /		*0.0* /		*1.57* /	
100	0.01	0.15		< 0.05		< 0.05		0.42	
300	0.04	0.73		0.14		0.05		1.7	
STMR									
71.7 /	(0.007)		(0.10)		(<0.04)		(<0.04)		(0.15)
100	0.01		0.14		<0.05		<0.05		0.21

Residues in cattle milk and tissues from animals treated dermally

Piperonyl butoxide concentration (mg/kg)								
Milk (mean)	Liver		Kidney		Muscle		Fat	
	Highest	Median	Highest	Median	Highest	Median	Highest	Median
0.14	*0.14*	*0.03*	*0.21*	*0.21*	*0.21*	*0.16*	*2.7*	*2.6*

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR value of 0.10 mg/kg for piperonyl butoxide in cattle liver, on the basis of the data from the feeding study. The concentrations of residues in milk, kidney, muscle and fat after dermal treatment were higher than those in the feeding study and were used in the estimations. The Meeting estimated a maximum residue level for piperonyl butoxide of 0.2 mg/kg in cattle milk, 0.3 mg/kg in cattle kidney and 5 mg/kg in cattle meat (fat).

The STMR concept is designed for supervised field trials on crops to obtain a typical residue value when a pesticide is used at maximum GAP and is not applicable to a trial with a single direct treatment. The Meeting agreed that, in this case, a typical residue value can be derived from the median concentrations in tissues and in milk. The Meeting estimated values for typical piperonyl butoxide residues after direct use (at maximum label conditions) of 0.14 mg/kg in cattle milk, 0.21 mg/kg in cattle kidney and 0.16 mg/kg in cattle meat. These values can be used in the same way as STMR values for estimating the effect of long-term dietary intake on residue concentrations in tissues and of long-term and short-term intake on concentrations in milk.

Residues in poultry products from poultry treated orally

Dose (ppm) *Interpolated* / actual	Piperonyl butoxide (mg/kg)							
	Eggs		Liver		Muscle		Fat	
	Highest	Mean	Highest	Mean	Highest	Mean	Highest	Mean
MRL	*0.55* /		*< 0.02* /		*0.06* /		*1.14* /	
116 /	0.35		–		< 0.05		0.38	
61.2	1.0		< 0.05		0.12		1.7	
196								
STMR								
36.7 /		*0.18* /		< 0.045 /		*0.035* /		*0.90* /
20.4		0.03		–		< 0.05		0.30
61.2		0.23		< 0.05		0.09		1.3

Residues in poultry products from poultry treated dermally

Piperonyl butoxide (mg/kg)									
Eggs		Liver		Skin		Muscle		Fat	
Highest	Median	Highest	Median	Highest	Median	Highest	Median	Highest	Median
0.79	*0.36*	*0.44*	*0.26*	*8.3*	*3.8*	*1.2*	*1.0*	*5.0*	*2.0*

The concentrations of residues in eggs and tissues from poultry treated dermally are higher than those from poultry fed piperonyl butoxide and were used in the estimations. The Meeting estimated a maximum residue level of 1 mg/kg for piperonyl butoxide in eggs, 10 mg/kg in poultry edible offal (based on liver and skin) and 5 mg/kg for poultry meat (fat).

The Meeting estimated values for typical piperonyl butoxide residues after direct use (at maximum label concentration) of 0.36 mg/kg in eggs, 2.03 mg/kg in poultry edible offal (mean of 0.26 and 3.8 mg/kg) and of 1.0 mg/kg in poultry meat. These values can be used in the same way as STMR values for estimating long-term dietary intake of piperonyl butoxide.

RECOMMENDATIONS

On the basis of the results of the supervised trials, the Meeting concluded that the concentrations of residue shown below are suitable for establishing MRLs and for assessing dietary intake.

Definition of residue (for compliance with MRLs and for estimating dietary intake from plant and animal commodities): piperonyl butoxide.

The residue is fat-soluble.

CCN	Commodity	MRL (mg/kg)		STMR or STMR-P (mg/kg)
		New	Previous	
MO 1280	Cattle kidney	0.3 [a]		0.21 [b]
MO 1281	Cattle liver	1		0.10
MM 0812	Cattle meat	5 (fat) [a]		0.16 [b,c]
ML 0812	Cattle milk	0.2 [a]		0.14 [b]
GC 0080	Cereal grains	30 Po		11 Po
FC 0001	Citrus fruits	5		1.0
AB 0001	Citrus fruit, dry			5.7
JF 0001	Citrus juice	0.05		0.01
DM 0001	Citrus molasses			0.53
DF 0167	Dried fruits	0.2 Po		0.05 Po
PE 0112	Eggs	1 [a]		0.36 [b]
VC 0045	Fruiting vegetables, cucurbits	1		0.26
VL 0483	Lettuce, Leaf	50		38
OC 0645	Maize oil, crude	80 PoP		29.7
VL 0485	Mustard greens	50		38

CCN	Commodity	MRL (mg/kg)		STMR or STMR-P (mg/kg)
		New	Previous	
AL 0072	Pea hay or pea fodder	200 dry wt		19.9 dry wt
AL 0528	Pea vine (green)	400 dry wt		108 dry wt
SO 0703	Peanut, whole	1 Po		0.1 Po
VO 0051	Peppers	2		0.675
	Potato peel, wet			0.15
PO 0111	Poultry Edible offal of	10 [a]		2.03 [b]
PM 0110	Poultry meat	5 (fat) [a]		1.0 [b,c]
VD 0070	Pulses	0.2 Po		0.05 Po
VL 0494	Radish leaves	50		38
VR 0075	Root and tuber vegetables, except carrots	0.5		0.10
VL 0502	Spinach	50		38
VO 0448	Tomato	2		0.675
JF 0448	Tomato juice	0.3		0.10
	Tomato purée			0.22
GC 0654	Wheat	W	10 Po	
CM 0654	Wheat bran, unprocessed	100 PoP		38.5 PoP
CF 1211	Wheat flour	10 PoP		3.5 PoP
CF 1210	Wheat germ	100 PoP		30.8 PoP
CF 1212	Wheat wholemeal	30 PoP		10.8 PoP

[a] The MRL accommodates external animal treatment
[b] Not STMR value but median residue concentrations in animals in a treated group
[c] In meat

Dietary risk assessment

Long-term intake

Currently, the ADI for piperonyl butoxide is 0.2 mg/kg bw. IEDIs were calculated for commodities for human consumption for which STMR values had been estimated by the present Meeting. The results are shown in Annex 3`` (Report 2001).

The IEDIs for the five GEMS/Food regional diets, on the basis of the estimated STMRs, ranged from 20 to 40% of the ADI. The Meeting concluded that the intake of residues of piperonyl butoxide resulting from its uses that have been considered by the JMPR is unlikely to present a public heath concern.

Short-term intake

The 2001 JMPR concluded that an acute RfD for piperonyl butoxide was unnecessary. The Meeting therefore concluded that short-term dietary intake of piperonyl butoxide residues is unlikely to present a risk to consumers.

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SPINOSAD (203)

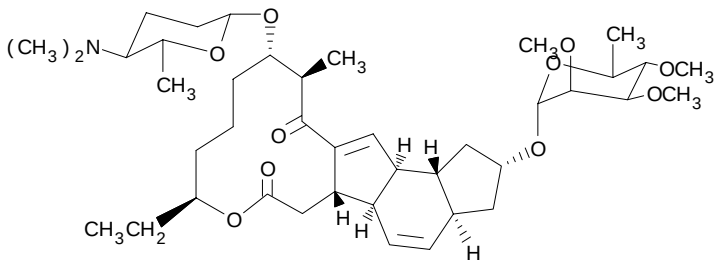
IDENTITY

Spinosad is a naturally derived fermentation product, which has demonstrated insect control activity against a large number of pests including members of the insect orders Lepidoptera, Coleoptera and Thysanoptera. The product is isolated from actinomycetes *Saccharopolyspora spinosa* and contains a mixture of two structurally similar molecules which are both active insecticidally and have been designated spinosyn A and spinosyn D.

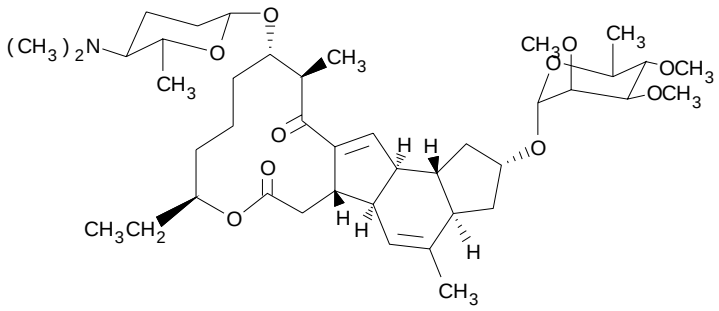
ISO common name:	spinosad. Spinosad is a mixture of spinosyn A and spinosyn D.
Chemical name IUPAC:	mixture of 50-95% of spinosyn A (2*R*,3a*S*,5a*R*,5b*S*,9*S*,13*S*,14*R*,16a*S*,16b*R*)-2-(6-deoxy-2,3,4-tri-*O*-methyl-α-L-mannopyranosyloxy)-13-(4-dimethylamino-2,3,4,6-tetradeoxy-β-D-erythropyranosyloxy)-9-ethyl-2,3,3a,5a,5b,6,7,9,10,11,12,13,14,15,16a,16b-hexadecahydro-14-methyl-1*H*-8-oxacyclododeca[*b*]*as*-indacene-7,15-dione and 50-5% spinosyn D (2*S*,3a*R*,5a*S*,5b*S*,9*S*,13*S*,14*R*,16a*S*,16b*R*)-2-(6-deoxy-2,3,4-tri-*O*-methyl-α-L-mannopyranosyloxy)-13-(4-dimethylamino-2,3,4,6-tetradeoxy-β-D-erythropyranosyloxy)-9-ethyl-2,3,3a,5a,5b,6,7,9,10,11,12,13,14,15,16a,16b-hexadecahydro-4,14-dimethyl-1*H*-8-oxacyclododeca[*b*]*as*-indacene-7,15-dione
CAS:	(2*R*,3a*S*,5a*R*,5b*S*,9*S*,13*S*,14*R*,16a*S*,16b*R*)-2-[(6-deoxy-2,3,4-tri-*O*-methyl-α-L-mannopyranosyl)oxy]-13-[[(2*R*,5*S*,6*R*)-5-(dimethylamino)tetrahydro-6-methyl-2*H*-pyran-2-yl]oxy]-9-ethyl-2,3,3a,5a,5b,6,9,10,11,12,13,14,16a,16b-tetradecahydro-14-methyl-1*H*-*as*-indaceno[3,2-*d*]oxacyclododecin-7,15-dione mixture with (2*S*,3a*R*,5a*S*,5b*S*,9*S*,13*S*,14*R*,16a*S*,16b*S*)-2-[(6-deoxy-2,3,4-tri-*O*-methyl-α-L-mannopyranosyl)oxy]-13-[[(2*R*,5*S*,6*R*)-5-(dimethylamino)tetrahydro-6-methyl-2*H*-pyran-2-yl]oxy]-9-ethyl-2,3,3a,5a,5b,6,9,10,11,12,13,14,16a,16b-tetradecahydro-4,14-dimethyl-1*H*-*as*-indaceno[3,2-*d*]oxacyclododecin-7,15-dione
CAS No.:	Spinosyn A: 131929-60-7 Spinosyn D: 131929-63-0
Synonyms	DE-105; XDE-105; DE-105 Factors A and D
Trade names:	Success, Tracer, Spintor, Spinoace, Boomerang, Laser, Extinosad

Structural formula:

Spinosyn A



Spinosyn D



Molecular formula: Spinosyn A: $C_{41}H_{65}NO_{10}$
Spinosyn D: $C_{42}H_{67}NO_{10}$

Molecular weight: Spinosyn A: 731.98
Spinosyn D: 745.99

Physical and chemical properties

Pure active ingredient

	Spinosyn A	Spinosyn D	Reference
Appearance	Light grey-white solid		
Vapour pressure, mPa (25°C)	3.0×10^{-5}	2.0×10^{-5}	Chakrabarti, 1991a,b
Melting point	84 to 99.5°C (98.3% purity)	161.5 to 170°C (98% purity)	Jones-Jefferson, 1994a
Octanol/water partition coefficient			Jones-Jefferson, 1994a
Log P_{ow} at 23°C (water)	3.9	4.4	Morrissey, 1994a,b
Log P_{ow} at 23°C (pH 5)	2.8	3.2	
Log P_{ow} at 23°C (pH 7)	4.0	4.5	
Log P_{ow} at 23°C (pH 9)	5.2	5.2	
Water solubility			Jones-Jefferson, 1994a,b
water, mg/l at 20°C	89	0.50	Heimerl, 1994
pH 5, mg/l at 20°C	290	29	
pH 7, mg/l at 20°C	235	0.33	
pH 9, mg/l at 20°C	16	0.053	Heimerl, 1993
Solvent solubility			Jones-Jefferson, 1994a,b
dichloromethane, g/l at 20°C	525	448	
methanol, g/l at 20°C	190	2.5	
acetone, g/l at 20°C	168	10	
acetonitrile, g/l at 20°C	134	2.6	
amyl acetate, g/l at 20°C	37	23	
hexane, g/l at 20°C	4.5	0.74	
1-octanol, g/l at 20°C	9.3	1.3	
toluene, g/l at 20°C	457	152	
isopropyl alcohol, g/l at 20°C	40	1.3	
ethyl acetate, g/l at 20°C	194	19	Richardson and Comb,
n-heptane, g/l at 20°C	12.4	0.3	1999a,b
xylene g/l at 20°C	>250	64	

	Spinosyn A	Spinosyn D	Reference
Hydrolysis at 25°C, sterile buffer, dark			Saunders *et al.*, 1994a
pH 5	not observed in 30-day test	not observed in 30-day test	
pH 7	not observed in 30-day test	not observed in 30-day test	
pH 9 half life	approx. 100-300 days	approx. 100-300 days	
Photolysis - half-life for degradation in dilute aqueous sterile buffer at pH 7, June-July, Indiana USA, 39.9°N.	22.3 h	19.7 h	Saunders and Powers, 1994b
Dissociation constant (determined by capillary electrophoresis)			
pKa (20°C)	8.10	7.87	Gluck, 1994a,b
Equivalent Ka	7.94×10^{-9}	1.35×10^{-8}	

Chakrabarti (1991a) measured the vapour pressure of spinosyn A (99.9% pure) over the range 33.1°C to 49.1°C by the Knudsen-effusion weight loss method. The vapour pressure at 25°C (2.4×10^{-10} mm Hg or 3.0×10^{-5} mPa) was obtained by extrapolation using the Clausius-Clapeyron equation. Chakrabarti (1991b) measured the vapour pressure of spinosyn B (99+%) in the same way over the range 38.9°C to 55.1°C and obtained a value of 1.6×10^{-10} mm Hg or 2.0×10^{-5} mPa at 25°C.

Saunders *et al.* (1994) measured the hydrolysis rates of [^{14}C]spinosyns A and D in sterile buffers of pH 5, 7 and 9 held at 25°C in the dark for 30 days. Spinosyns A and D were dissolved in 0.01M buffers at 2 mg/ml each, with 0.5% acetonitrile to maintain solubility, and solutions were analysed by HPLC at intervals, but hydrolysis was insufficient to be observed. It did occur at pH 9, but the estimation of accurate half-lives was difficult because the results were variable and measurements were made for only 30 days. Estimated half-lives were 100-300 days. Hydrolysis products, shown to result from loss of the amino sugar and water, were minor and not fully identified.

Technical material

Minimum purity: minimum 85% (w/w), mixture of spinosyn A and spinosyn D in a ratio between 95:5 and 50:50.

Melting point range: melting point minimum 112°C, maximum 123°C, determined as the endothermic peak by differential scanning calorimetry for 88% purity (spinosyn A + spinosyn B). Exothermic decomposition temperature 173°C. (Jones-Jefferson, 2000).

Formulations

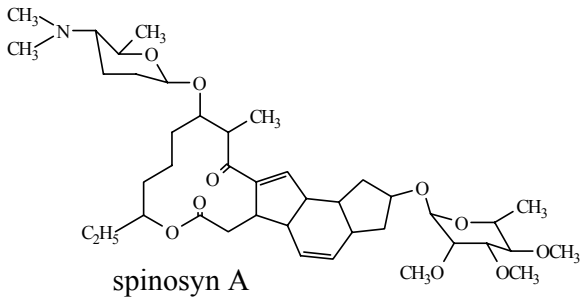
Spinosad is available as SC, WG and fly bait formulations:

- suspension concentrate (SC) formulations containing 25, 120, 240 or 480 g/l.
- water dispersible granule (WG) formulations containing 250, 780, or 800 g/kg.
- fly bait containing 0.008% spinosad.

METABOLISM AND ENVIRONMENTAL FATE

Radiolabelled spinosyns A and D were produced by fermentation using [1,2-^{14}C]acetate as a carbon source, which resulted in material reasonably uniformly labelled at 23 carbons in the aglycone ring system. The amino and rhamnose sugars do not contain the ^{14}C label.

Structures of compounds appearing during metabolism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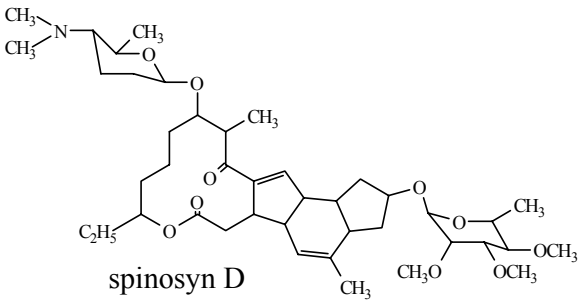
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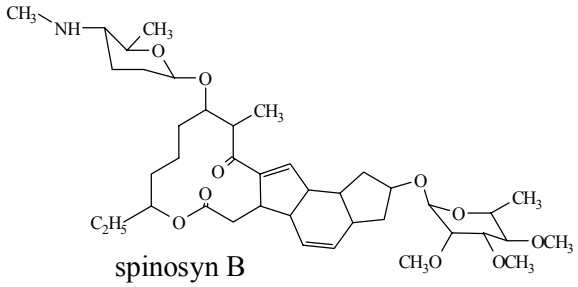
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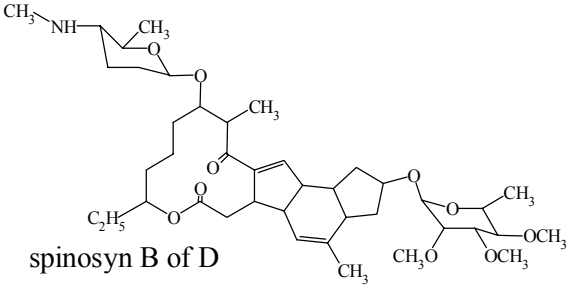
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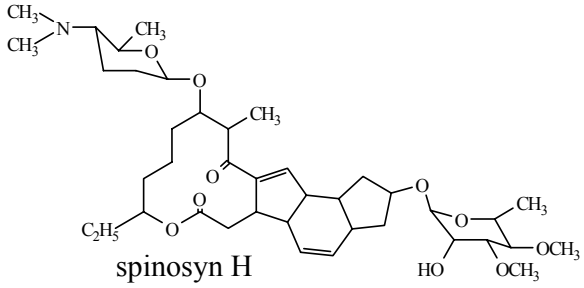
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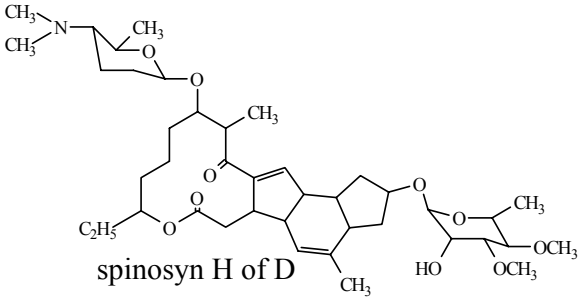
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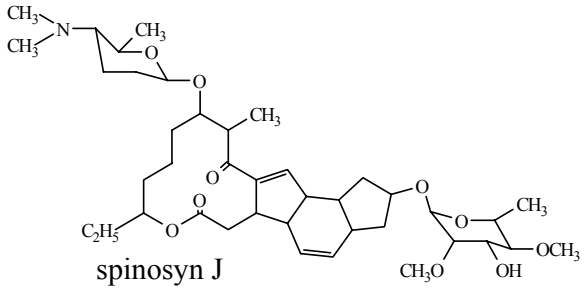
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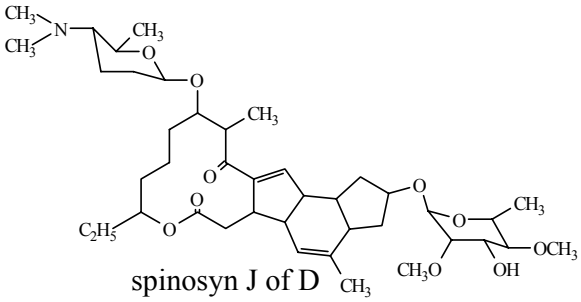
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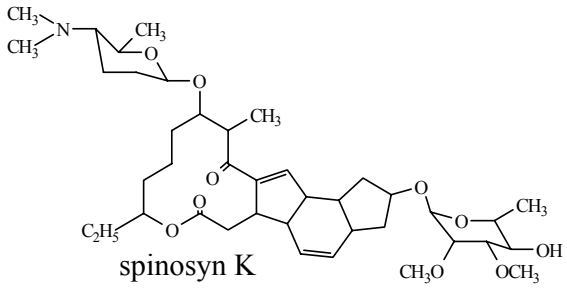

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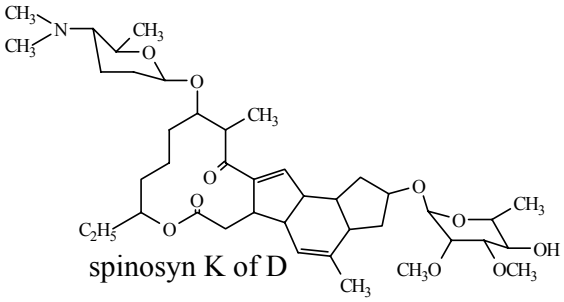

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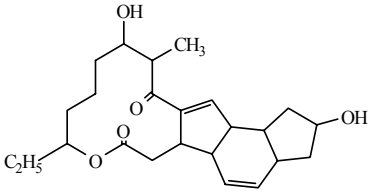
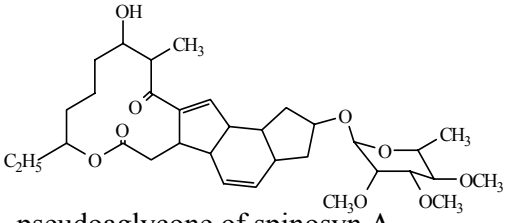
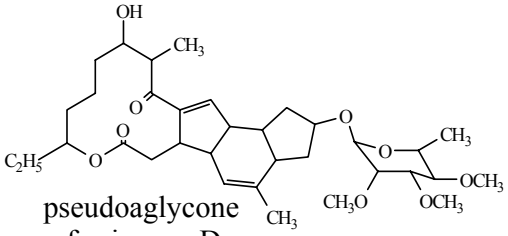


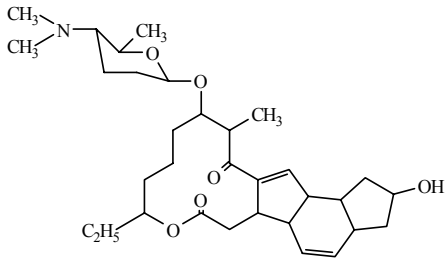
aglycone of spinosyn A



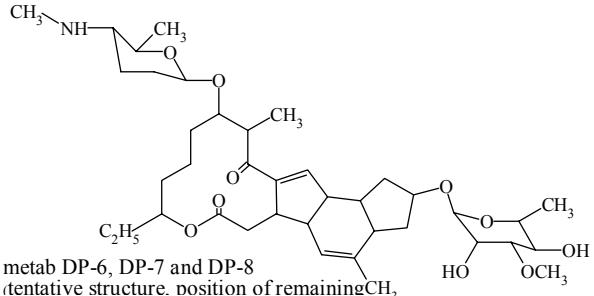
pseudoaglycone of spinosyn A



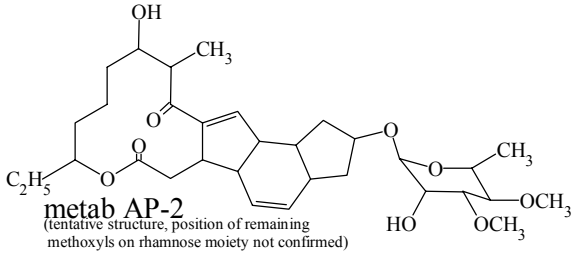
pseudoaglycone
of spinosyn D



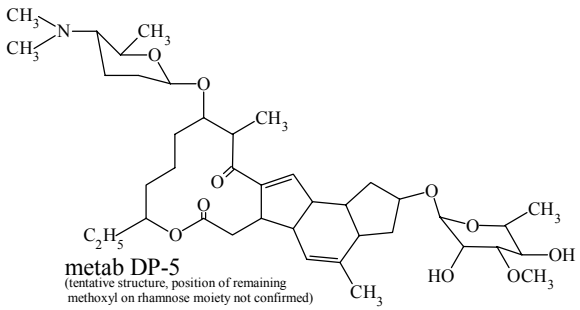
reverse pseudoaglycone
of spinosyn A



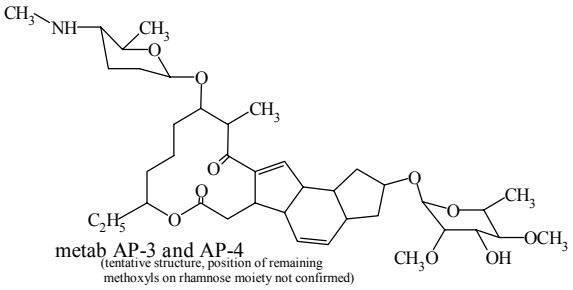
metab DP-6, DP-7 and DP-8
(tentative structure, position of remaining methoxyl on rhamnose moiety not confirmed)



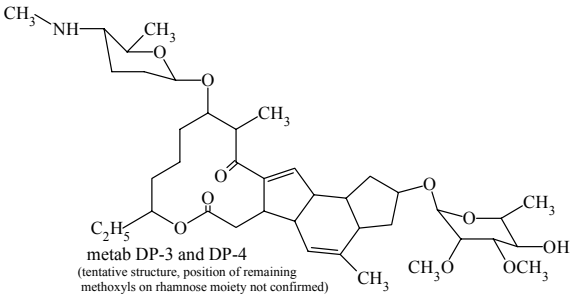
metab AP-2
(tentative structure, position of remaining methoxyls on rhamnose moiety not confirmed)



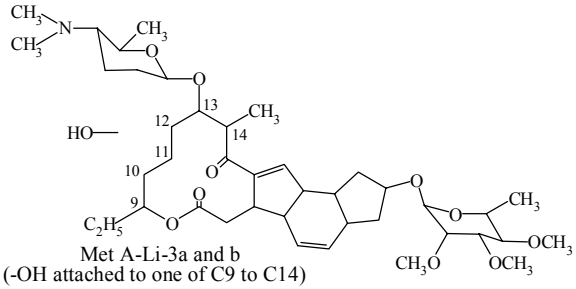
metab DP-5
(tentative structure, position of remaining methoxyl on rhamnose moiety not confirmed)



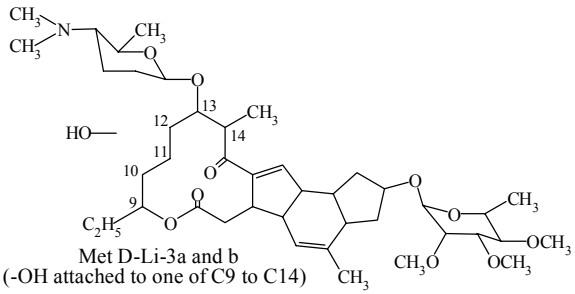
metab AP-3 and AP-4
(tentative structure, position of remaining methoxyls on rhamnose moiety not confirmed)



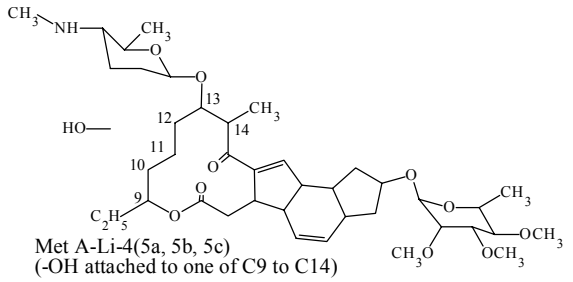
metab DP-3 and DP-4
(tentative structure, position of remaining methoxyls on rhamnose moiety not confirmed)



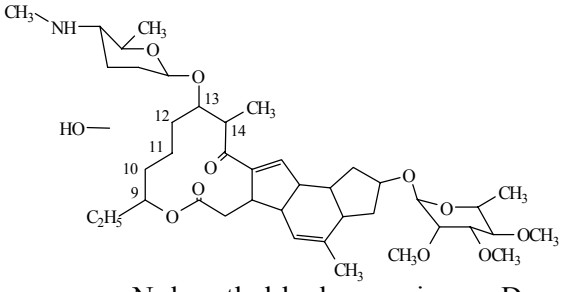
Met A-Li-3a and b
(-OH attached to one of C9 to C14)



Met D-Li-3a and b
(-OH attached to one of C9 to C14)



Met A-Li-4(5a, 5b, 5c)
(-OH attached to one of C9 to C14)



N-demethyl-hydroxy-spinosyn D
(-OH attached to one of C9 to C14)

Animal metabolism

The Meeting received information on the results of studies on lactating goats and laying hens given oral doses of spinosyns and on lactating goats treated dermally with spinosyns.

Goats. The tissues, milk and excreta of two lactating dairy goats, one dosed with spinosyn A, the other with spinosyn D, body weights 47 and 43 kg respectively were analysed for residues (Rainey, 1994a). The goats were dosed orally for 3 days by capsule with a nominal 25 mg/day [^{14}C]spinosyn equivalent to 10 ppm in the feed, The feed intake was 2.5-3.0 kg/animal/day, and the milk averages 0.98 and 1.36 kg per day. The milk and excreta were collected throughout the study and the goats slaughtered within 24 hours of the last dose. Tissue samples (composites of equal amounts of longissimus dorsi, semimembranosus and triceps muscles, and of omental and perirenal fat, and kidneys and liver) were analysed. The results are shown in Table 2.

A considerable proportion of the residues, 45% for spinosyn A and 20% for spinosyn D, was found in the tissues and milk - predominantly the fat (Table 1), and excretion of the ^{14}C was mainly via the faeces, 61% from A and 76% from D were found in excreta and intestine.

Spinosyns A and D were the main components of the residue in the tissues and milk, especially in the fat, and some of the metabolites were characterized without being fully identified. Metabolites Met A-Li-3, Met A-Li-4 and Met D-Li-3 were shown to be hydroxylated in the macrolide

ring between C9 and C14. Met A-Li-4 had also been *N*-demethylated. Other metabolites were investigated but insufficient information was available to propose structures.

Table 1. Disposition of ^{14}C in goats dosed with a nominal 25 mg/day [^{14}C]spinosyn (spinosyn A in one goat, spinosyn D in the other) for 3 days (Rainey, 1994a).

Sample	% of administered ^{14}C	
	spinosyn A dose	spinosyn D dose
Milk	1.8	0.69
Faeces	38	67
Urine	1.1	0.21
Composite fat	33	17
Composite muscle	8.7	2.7
Kidney	0.27	0.07
Liver	3.2	0.67
Rumen and contents	8.0	6.3
Intestine with contents	22	9.4
TOTAL	116	104

Table 2. Distribution of metabolites in the tissues and milk of lactating goats dosed orally for 3 days by capsule at a rate equivalent to 10 ppm spinosyn A or D in the feed (Rainey, 1994a). TRR is the total radioactive residue in the tissue or milk.

Compound or fraction	Fat		Muscle		Kidney		Liver		Milk	day 3
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
SPINOSYN A										
Spinosyn A	86	3.1	50	0.15	35	0.34	30	0.47	71	0.45
Spinosyn B	0.7	0.026	8.3	0.025	10	0.099	2.9	0.046	1.9	0.012
Met A-Li-3a	2.7	0.095	8.3	0.025	10	0.10	7.7	0.12	6.3	0.040
Met A-Li-3b	1.3	0.046	4.0	0.012	6.1	0.059	5.0	0.079	3.8	0.024
Met A-Li-4(5a)			13	0.040	16	0.15	3.0	0.047	1.6	0.010
Met A-Li-4(5b)			[1]	[1]	[1]	[1]	4.1	0.065	1.7	0.011
Met A-Li-4(5c)							4.1	0.064	1.4	0.009
Aq sol + extr tissue + misc	9.1	0.33	16	0.046	22	0.20	40	0.63	11	0.07
Total measured ^{14}C		3.6		0.30		0.97		1.6		0.63
SPINOSYN D										
Spinosyn D	85	1.5	57	0.063	40	0.12	20	0.10	81	0.13
Spinosyn B of D	1.1	0.020	12	0.013	15	0.046	4.4	0.022	2.5	0.004
Met D-Li-1	2.5	0.046	2.7	0.003			5.6	0.028		
Met D-Li-3a					3.0	0.009	2.2	0.011		
Met D-Li-3b	1.6	0.030	7.3	0.008	13	0.038	6.4	0.032	5.6	0.009
Aq sol + extr tissue + misc	11	0.19	24	0.026	29	0.087	57	0.28	9.4	0.015
Total measured ^{14}C		1.8		0.11		0.30		0.50		0.16

[1] Metabolite A-Li-4 (5b) in muscle and kidney is included with Met A-Li-4 (5a)

In a dermal application metabolism study Burnett *et al. (*1999) treated a lactating goat with [^{14}C]spinosyn A in a solution of isopropyl myristate and oleic acid at 18 mg ai/kg bw, and a second goat with [^{14}C]spinosyn D at 4.1 mg ai/kg bw. The dose was applied by pouring the weighed solution down the midline of the back from withers to tail. Milk and excreta were collected during the treatment period and for 4 days until the animals were slaughtered. Teats were cleaned before milking to prevent contamination of milk with spinosyns remaining on the animals' backs. The goats weighed 50 and 74 kg respectively. The distribution of ^{14}C among the samples is shown in Table 3 and among the identified compounds in Table 4.

Residues were higher in the liver and fat than in other tissues, and the parent compound was dominant, particularly in the fat and milk. Metabolites were produced by *N*-demethylation and hydroxylation of the macrolide ring, a process already identified in the oral dosing study.

Table 3. Levels of ^{14}C in the tissues and milk and percentages of the applied dose excreted by goats treated dermally with [^{14}C]spinosyn A or D at 18 or 4.1 mg ai/kg bw respectively and slaughtered 4 days later (Burnett *et al.,* 1999).

Sample	spinosyn A		spinosyn D	
	mg/kg	% of dose	mg/kg	% of dose
Liver	1.7		0.39	
Kidneys	0.86		0.17	
Muscle, loin	0.30		0.041	
Muscle, rump	0.27		0.043	
Muscle, shoulder	0.25		0.050	
Fat, abdominal	0.81		0.23	
Fat, perirenal	1.1		0.21	
Bile	5.5		1.9	
Faeces		2.3		2.6
Urine (3rd day only)		<0.1		<0.1
Milk total		0.05		0.05
Milk, 7 h	0.017		0.021	
Milk, 19 h	0.079		0.061	
Milk, 31 h	0.13		0.077	
Milk, 43 h	0.20		0.093	
Milk, 55 h	0.32		0.092	
Milk, 67 h	0.51		0.074	
Milk, 79 h	0.54		0.076	
Milk, 92 h	0.52		0.085	

mg/kg: ^{14}C expressed as spinosyn A or D

Table 4. Distribution of metabolites in the tissues and milk of goats treated dermally with [^{14}C]spinosyn A or D at 18 or 4.1 mg ai/kg bw respectively and slaughtered 4 days later (Burnett *et al.,* 1999).

Compound	Fat		Muscle		Kidney		Liver		Milk	92-h
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
SPINOSYN A										
Spinosyn A	77	0.74	57	0.16	35	0.30	46	0.78	68	0.35
Spinosyn B	5.0	0.047	8.7	0.024	14	0.12	9.4	0.16	5.6	0.029
hydroxy-spinosyn A [1]	9.5	0.090	8.7	0.024	14	0.12	10	0.17	7.3	0.038
N-demethyl-hydroxy-spinosyn A [2]	1.2	0.012	9.7	0.026	20	0.18	13	0.22	6.9	0.036
unidentified	7		16		18		21		13	
SPINOSYN D										
Spinosyn D	73	0.16	49	0.022	32	0.055	27	0.10	66	0.056
Spinosyn B of D	4.2	0.009	13	0.006	21	0.035	17	0.064	7.7	0.007
Hydroxy-spinosyn D [3]	7.9	0.017	9.6	0.004	13	0.022	12	0.046	6.8	0.006
N-demethyl hydroxy-spinosyn D	0.8	0.002	4.8	0.002	9.6	0.016	7.5	0.029	1.7	0.001
unidentified	13		22		23		36		16	

[1] Hydroxy-spinosyn A: same as Met A-Li-3a,b
[2] N-demethyl-hydroxy-spinosyn A : same as Met A-Li-4(5a,5b,5c)
[3] Hydroxy-spinosyn D: same as Met D-Li-3a,b

Metabolic pathways of spinosyn A in goats are shown in Figure 1.

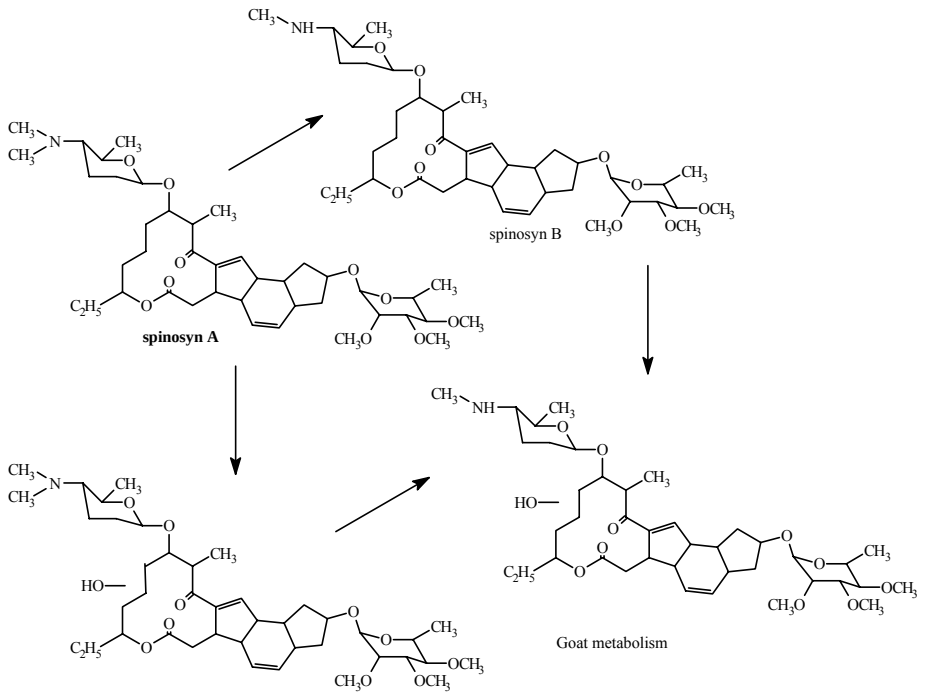


Figure 1. Metabolism of spinosyn A by goats. Spinosyn D metabolism parallels that of spinosyn A.

Hens. Residues were measured in the tissues, eggs and excreta of 10 Leghorn laying hens, each weighing 1.4 kg, dosed orally by capsule with 0.94 mg [^{14}C]spinosyn A, equivalent to 10 ppm spinosyn A in the feed, daily for 5 days (Magnussen and Castetter, 1994). The feed intake was 94 g/bird/day. Eggs and excreta were collected throughout, and the birds were slaughtered within 24 hours of the last dose. Another 10 laying hens were dosed with [^{14}C]spinosyn D in a parallel study.

For spinosyn A approximately 73% of the applied ^{14}C was accounted for (69% in the excreta, 0.77% in eggs, 1.4% in fat, 0.68% in liver, 0.53% in muscle and 0.12% in kidney), and for spinosyn D approximately 82% (78% in the excreta, 0.6% in eggs, 0.8% in fat, 1.2% in liver, 0.5% in muscle and 0.2% in kidney). ^{14}C residues in eggs were apparently still increasing at the end of the study, and from day 2 to 6 were 0.014, 0.082, 0.19, 0.32 and 0.38 mg/kg expressed as spinosyn A, and 0.019, 0.073, 0.14, 0.22 and 0.32 mg/kg as spinosyn D.

The highest residues occurred in the fat, most of which were accounted for by the parent compounds, and they were also major or important parts of the residue in muscle and eggs. Substantial metabolism occurred in the liver where metabolites were produced by *N*-demethylation, *O*-demethylation and loss of the furosamine sugar moiety (Table 5).

Table 5. Distribution of ^{14}C residues in the tissues and eggs of laying hens dosed orally for 5 days by capsule at a rate equivalent to 10 ppm spinosyn A or D in the feed (Magnussen and Castetter, 1994).

	Fat		Liver		Muscle		Eggs (day 6)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
SPINOSYN A								
Spinosyn A	81	1.8	14	0.12	55	0.064	34	0.13
Spinosyn B	2.0	0.044	11	0.10	12	0.014	11	0.041
Spinosyn J	1.5	0.033	0.9	0.008	2.3	0.003	3.3	0.012
Spinosyns H and K	4.1	0.090	9.3	0.082	5.1	0.006	9.7	0.037
Pseudoaglycone			4.6	0.041				
Metab AP-1			7.0	0.062				
Metab AP-2			4.1	0.036				

	Fat		Liver		Muscle		Eggs (day 6)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Metab AP-3			2.7	0.024	1.5	0.002	1.4	0.005
Metab AP-4			7.8	0.069	5.7	0.007	4.7	0.018
Metab AP-5			2.4	0.021			1.6	0.006
Metab AP-6			1.9	0.017			1.1	0.004
Aq sol + extr tissue + misc	12	0.26	34	0.30	20	0.024	33	0.12
Total measured ^{14}C		2.2		0.88		0.12		0.38
SPINOSYN D								
Spinosyn D	79	0.81	3.3	0.058	39	0.048	22	0.069
Spinosyn B of D	6.8	0.069	21	0.37	15	0.018	25	0.080
Spinosyn J of D	2.4	0.025						
Spinosyns H/K of D	6.0	0.061	12	0.21	6.1	0.007	8.0	0.026
Pseudoaglycone D			3.4	0.059	1.6	0.002		
Metab DP-1			5.2	0.091	2.7	0.003		
Metab DP-2			3.9	0.068				
Metab DP-3			6.7	0.12	1.5	0.002	5.4	0.017
Metab DP-4			17.7	0.31	6.0	0.007	12	0.037
Metab DP-5			2.2	0.038	2.0	0.002	2.6	0.008
Metab DP-6			2.4	0.042	1.2	0.001	1.7	0.005
Metab DP-7			2.5	0.044	0.9	0.001	1.5	0.005
Metab DP-8			2.5	0.044	0.8	0.001	1.4	0.004
Aq sol + extr tissue + misc			17	0.30	23	0.029	24	0.069
Total measured ^{14}C		1.0		1.7		0.12		0.32

mg/kg: ^{14}C expressed as spinosyn A or D

The metabolic pathways of spinosyn A in hens are shown in Figure 2.

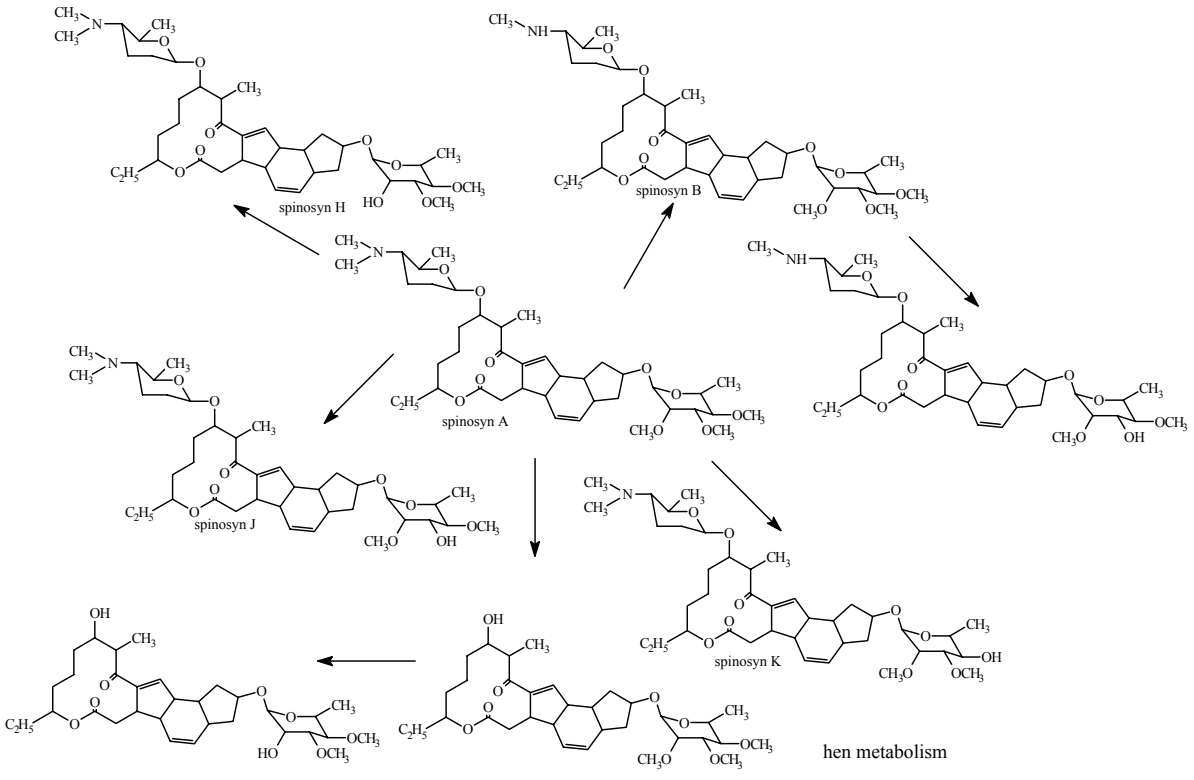


Figure 2. Metabolism of spinosyn A by hens. Spinosyn D metabolism parallels that of spinosyn A.

Plant metabolism

The Meeting received information on the fate of spinosyns in apples, cabbage, tomatoes, turnips, grapes and cotton after foliar applications.

Apples. Dwarf Red Delicious apple trees were sprayed with [^{14}C]spinosyn A at 0.089 kg ai/hl approximately one month before fruit maturity and fruit were sampled 0, 3, 7, 14, 28 and 42 days after treatment (Graper, 1996). Some apples were stored in the dark shortly after treatment to evaluate the influence of photolysis on the residue. Apples on one branch were protected from spray to assess translocation. Parallel experiments were run with [^{14}C]spinosyn D applied at 0.035 kg ai/hl. The results are shown in Table 6.

The total ^{14}C in the apples decreased by about 50% over the 42 days of sampling, probably owing to growth dilution. Solvent rinses removed much of the residue initially, but after 42 days 60% of the residue could still be rinsed from the surface. Some residue penetrated into the peel and a smaller amount into the pulp. About 10% of the remaining residue after 14 days was accounted for by parent spinosyn A which decreased quickly, and about 10% by spinosyn D after only 3 days. Spinosyns B and B of D were also identified. Spinosyns A and D were much more persistent on those apples kept from the light, demonstrating that photolysis is a dominant degradation process. ^{14}C in the protected apples on day 42 was only 1.3% of that in apples sprayed directly, showing that translocation was very minor.

The ^{14}C residues in the apples after day 0 were extensively analysed; they were mostly polar and multicomponent. Fractions from the day 14 spinosyn A apples had low sensitivity to the spinosyn immunoassay, suggesting they did not contain structures close to those for which the immunoassay is sensitive (spinosyns A, B, C, E, F, K and the pseudoaglycone of A).

Table 6. Distribution of ^{14}C in apples treated with [^{14}C]spinosyn A at 0.089 kg ai/hl or [^{14}C]spinosyn D at 0.035 kg ai/hl approximately one month before maturity (Graper, 1996).

Apple sample	^{14}C as spinosyn , mg/kg apple											
	spinosyn A						spinosyn D					
	day 0	day 3	day 7	day 14	day 28	day 42	day 0	day 3	day 7	day 14	day 28	day 42
total ^{14}C	2.7	3.2	2.3	1.8	1.6	1.3	0.98	1.2	1.2	0.84	0.74	0.51
rinses ^{14}C	2.6	2.8	1.9	1.5	0.85	0.80	0.91	0.88	0.89	0.59	0.44	0.30
peel ^{14}C	0.12	0.43	0.40	0.32	0.40	0.33	0.031	9.25	0.19	0.22	0.25	0.17
pulp ^{14}C	0.024	0.026	0.035	0.056	0.32	0.12	0.042	0.027	0.13	0.033	0.049	0.044
dark, total ^{14}C		1.8	1.8					0.84	0.83			
dark, rinses ^{14}C		1.7	1.7					0.81	0.75			
dark, peel ^{14}C		0.079	0.17					0.027	0.070			
dark, pulp ^{14}C		0.008	0.020					0.008	0.011			
protected, total ^{14}C	0.002					0.017						
protected, rinses ^{14}C	0.002					0.002						
protected, peel ^{14}C	0					0.004						
protected, pulp ^{14}C	0					0.011						
spinosyn A	2.3	1.1	0.39	0.19	0.080	0.025						
spinosyn B	0.064	0.24	0.14	0.088	0.014	0						
spinosyn D							0.77	0.12	0.062	0	0.019	0
spinosyn B of D							0.035	0.079	0.033	0.015	0.015	0
dark, spinosyn A		1.3	1.2									
dark, spinosyn B		0.11	0.11									
dark, spinosyn D								0.64	0.58			
dark, spinosyn B of D								0.05	0.06			

Berard and Satonin (1995) analysed the leaves from the apple trees treated by Graper (1996). Spinosyn A disappeared much more rapidly when exposed to sunlight, again suggesting that photolysis is the predominant mechanism of degradation (Table 7). Total ^{14}C levels in leaves protected from direct spraying were much lower than those directly sprayed but continued to increase over 28 days suggesting some translocation. The translocated materials were probably highly polar. ^{14}C was shown to be incorporated into structural carbohydrates in the treated leaves and the same pattern was found in the untreated leaves.

Table 7. Spinosyn A and D residues in leaves from apple trees treated with [^{14}C]spinosyn A at 0.089 kg ai/hl or [^{14}C]spinosyn D at 0.035 kg ai/hl approximately one month before maturity (Berard and Satonin, 1995).

Leaf sample	^{14}C expressed as spinosyn , mg/kg leaf									
	spinosyn A					spinosyn D				
	day 0	day 3	day 7	day 10	day 28	day 0	day 3	day 7	day 10	day 28
total ^{14}C	217	135	206	175	128	89	97	71	72	43
dark, total ^{14}C	217[1]	154	170			89[1]	90	126		
protected, total ^{14}C	0.023	0.13	0.31	0.56	0.85					
spinosyn A	183	21	20	8.6	0					
dark, spinosyn A	183[1]	119	132							
spinosyn D						79	2.7	0	0	0
dark, spinosyn D						79[1]	76	103		

[1] Apple leaves on day 0, same value for exposed and dark.

Cabbages. Wakamine variety plants were sprayed with [^{14}C]spinosyn A or D formulated as ECs and diluted to concentrations of 0.14 kg ai/hl (Berard, 1995). Samples of leaf were collected after 2.5 hours and 3, 10, 19 and 34 days. Levels of ^{14}C in the leaves decreased fairly rapidly, probably because of growth dilution and weathering. The parent compounds also disappeared quickly, probably mainly by photolysis, and accounted for only 10 and 13% of the residue after 3 days (Table 8). It was not possible to identify metabolites.

Table 8. Levels of ^{14}C in cabbage foliage at intervals after treatment with [^{14}C]spinosyn A or D at 0.14 kg ai/hl (Berard, 1995).

Days after treatment	Spinosyn A			Spinosyn D		
	^{14}C, mg/kg as spinosyn		^{14}C in spinosyn, % of total ^{14}C	^{14}C, mg/kg, as spinosyn		^{14}C in spinosyn, % of total ^{14}C
	Leaf rep 1	Leaf rep 2		Leaf rep 1	Leaf rep 2	
0	29	74	41	89	52	48
3	19	17	10	25	17	13
10	3.8	4.3	2.3	6.1	6.5	5.3
19	2.2	1.9	1.1	1.4	2.9	4.3
34	0.78	0.73	0.6	0.89	0.71	4.5

Copenhagen Market variety cabbages treated 4 times with [^{14}C]spinosyn A in an EC formulation at the equivalent of 2 x 0.10 + 2 x 0.15 kg ai/ha were harvested 3 days after the last application and leaves were also sampled 3 days after the first application (Satonin and Collins, 1996). Leaf samples contained 2.4 and 5.6 mg/kg ^{14}C (as spinosyn A) after the first and last applications respectively. Spinosyn A accounted for 15% and 12% of the ^{14}C at the two samplings, and spinosyns B and K for 2.3% and 7.7% respectively after harvest. The remainder of the ^{14}C was present either as numerous minor compounds in the extracts, as shown by TLC and HPLC, or very polar or incorporated into natural compounds. A likely pathway is an initial photodegradation to nonpolar

products such as spinosyns B and K followed by formation of polar products which are available for plant metabolism and incorporation.

Tomatoes. Early Girl hybrid tomatoes sprayed 4 times with [^{14}C]spinosyn A as an EC formulation at a rate equivalent to 2 x 0.10 + 2 x 0.15 kg ai/ha were harvested 3 days after the first and 0 and 3 days after the final application (Satonin and Collins, 1996). The tomatoes contained 0.037, 0.13 and 0.080 mg/kg ^{14}C (as spinosyn A) on days 0 after spray 1 and 0 and 3 after the last spray respectively. Spinosyn A accounted for 65% and 24% of the ^{14}C 0 and 3 days after the final spray. Numerous minor components of the residue were found by TLC and HPLC, with an increase in polar components at the longer interval after treatment. A portion of the tomatoes containing 0.080 mg/kg ^{14}C as spinosyn A was processed to juice and a seeds + peel fraction. Residues in the juice (0.048 mg/kg ^{14}C) and seeds + peel (0.28 mg/kg ^{14}C) suggested that most of the ^{14}C was on the surface.

Turnips. Seven Top variety plants were sprayed with [^{14}C]spinosyn A or D as EC formulations at spray concentrations of 0.098 and 0.051 kg ai/hl respectively (Satonin and Berard, 1995). Samples of leaf and root were collected 0, 10, 24 and 48 days after treatment. Additional 0-day samples were collected immediately after treatment while still wet to minimize exposure of the compounds to sunlight. By day 10 spinosyns A and D were minor components of the ^{14}C residue in the foliage. Residues of parent compounds that reached the root and were protected from sunlight were more persistent, and by day 24 were higher in the roots, and a higher proportion of the total ^{14}C, than in the foliage. Spinosyns B, K and B of D, which are products of photolysis, appeared as components of the residue in leaf and root from day 0. Polar metabolites could not be fully characterized. A proportion of the ^{14}C was shown to be incorporated into the cellulose of the leaves. The results are shown in Table 9.

Table 9. Levels of ^{14}C in turnip foliage and roots after treatment with [^{14}C]spinosyn A or D (Satonin and Berard, 1995).

Days after treatment	^{14}C, mg/kg as spinosyn A						^{14}C, mg/kg as spinosyn D					
	Leaf			Root			Leaf			Root		
	Total ^{14}C	A	B/K	Total ^{14}C	A	B/K	Total ^{14}C	D	B of D	Total ^{14}C	D	B of D
0	39	32	2.8	3.5	3.1	0.17	20	14	3.3	1.7	1.3	0.15
10	22	0.45	2.0	1.4	0.29	0.14	13	0.076	0.70	0.43	0.06	0.043
24	5.8	0.075	0.066	0.38	0.084	0.026	4.7	0.016	nd	0.21	0.036	0.010
48	0.33	0.001	0.003	0.18	0.047	0.013	0.30	0.001	nd	0.094	0.018	0.006

Grapes. Caley (1996) sprayed immature grapes at nominal concentrations of 500 mg ai/l with ^{14}C-labelled spinosyns A and D separately when the grapes were about half-grown, and another group with [^{14}C]spinosyn A which were immediately covered with black polythene to protect them from the light. The ^{14}C label was in the macrolide ring.

Grapes harvested at intervals after treatment up to maturity 49 days later were solvent-washed and extracted, and the washings and extracts were examined for ^{14}C content (Table 10) and the nature of the residue. A high percentage of the residue was always on the surface, even for aged residues. The percentage of the parent compound fell from 80-90% on day 0 to approximately 50% on day 21 for both spinosyns A and D. In the dark control it was still about 80-90% after 7 days. At mature harvest, spinosyn A accounted for approximately 35% of the residue and spinosyn D 22%.

Attempts to identify other components of the residue, which were polar and numerous, were unsuccessful. The decomposition products were probably products of photolysis.

Table 10. Distribution of ^{14}C between surface and internal residues from grapes treated with [^{14}C]spinosyns (Caley, 1996).

	^{14}C expressed as spinosyn A or D, mg/kg							
	Day 0	Day 1	Day 3	Day 7	Day 10	Day 14	Day 21	Maturity 49 days
Spinosyn A								
Washings	6.1	5.5	4.2	3.6	3.2	3.4	2.0	2.2
Washed fruit	0.005	0.14	0.091	0.18	0.20	0.15	0.13	0.20
Total	6.1	5.7	4.3	3.8	3.4	3.5	2.1	2.4
Spinosyn D								
Washings	7.5		5.7	4.3		3.1	2.0	1.5
Washed fruit	0.006		0.35	0.44		0.45	0.36	0.31
Total	7.5		6.0	4.8		3.5	2.4	1.8
Spinosyn A (dark control)								
Washings		2.9	1.6	1.4				
Washed fruit		0.11	0.11	0.089				
Total		3.0	1.7	1.5				

Best *et al. (*1997) further investigated degradation products from Caley's 1996 metabolism study using HPLC and MS. They tentatively proposed hydroxy-spinosyn A and D as consistent with observed spectra.

Cotton. One plot of DPL-90 plants was treated 5 times at 6-8 day intervals with [^{14}C]spinosyn A in an EC formulation at a rate equivalent to 0.39 kg ai/ha, and another with [^{14}C]spinosyn D at a rate equivalent to 0.2 kg ai/ha (Magnussen, 1994). Leaves were sampled at various intervals before harvest, and seed and fibre 48 or 49 days after the last treatment before being ginned to separate them.

Levels of ^{14}C expressed as spinosyn were 0.29 and 0.22 mg/kg for the spinosyn A treatment and 0.11 and 0.075 mg/kg for spinosyn D in seed and fibre respectively. Despite persistent attempts no spinosyn-related compounds were identified in the seed, but in the separated fractions some of the ^{14}C was incorporated into natural compounds (Table 11). Other residues were multicomponent and highly polar. The ^{14}C in the fibre was also shown to be incorporated into the cellulose. The leaves contained low levels of spinosyn A until just before harvest but none was translocated to the seed.

Table 11. Fate of spinosyn ^{14}C in cotton seed fractions harvested from plants treated with [^{14}C]spinosyn (Magnussen, 1994).

Fraction	spinosyn A		spinosyn D		Comments
	% of seed ^{14}C	^{14}C, mg/kg as spinosyn	% of seed ^{14}C	^{14}C, mg/kg as spinosyn	
Oil	32	0.091	37	0.041	incorporated into natural compounds
Water-soluble proteins	4.5	0.013	1.5	0.002	incorporation strongly suggested
Storage proteins	10.6	0.031	8.2	0.009	incorporation strongly suggested
Acid detergent fibre from extracted meal	8.6	0.025			incorporation strongly suggested
Extracted meal			21	0.024	possible incorporation, but spinosyn D fractions not extensively characterized
Various protein and hydrolysate fractions	40	0.12	30	0.033	no identifiable metabolite, but no proof that ^{14}C was incorporated into natural compounds

In another study DPL-90 plants were treated 5 times at 7-day intervals with [^{14}C]spinosyn A as an EC formulation at a rate equivalent to 0.42 kg ai/ha (Magnussen and Castetter, 1995). Seed and fibre were collected from the plots 28 days after the last treatment and ginned to separate seed from fibre.

Levels of residue (^{14}C expressed as spinosyn A) were 0.25 and 0.20 mg/kg for meal and lint plus hulls respectively. The level in the meal was quite similar to that in the seed (0.29 mg/kg) in Magnussen's 1994 study (see above) as was the nature of the ^{14}C residue in the seed which was shown to be incorporated into the fatty acids in the oil fraction, confirming the previous findings.

Environmental fate in soil

The Meeting received information on the volatilization, photolysis, aerobic degradation, adsorption-desorption, leaching behaviour, field dissipation and crop rotation carry-over of spinosad applied to soil.

Volatilization. Knoch (2000) measured the volatilization rate of spinosad from soil and dwarf runner bean foliage in a wind tunnel with air at 20°C flowing at 1-1.5 m/s. ^{14}C-labelled spinosad (labelled in spinosyn A or spinosyn D) as an SC formulation was applied to bean leaves or soil in petri dishes at a rate equivalent to 0.46 kg spinosyn A/ha or 0.081 kg spinosyn D/ha. Plant and soil samples were taken after 0, 1, 3, 6 and 24 hours for extraction and combustion analysis. Losses of spinosad by volatilization were too small to be observed (maxima of 1.6% from plant surface and 0.1% from soil).

photolysis. In a US study Saunders and Powers (1993) applied [^{14}C]spinosyn A and D at a rate equivalent to 1.015 kg ai/ha to a 1 mm layer of a silt loam soil (pH 7.8, sand 22%, silt 55%, clay 23%, organic carbon 0.72%) which was exposed to sunlight (August-September, latitude 39.8°N) at 25°C to observe rates of disappearance and production of photoproducts. Soil samples were periodically examined for ^{14}C and extracted for HPLC analysis. ^{14}C balances ranged from 89 to 96% for both irradiated and dark control samples: only 1-2% of the ^{14}C was volatilized. Little degradation occurred in the dark control samples. Both spinosyns were degraded quickly in the initial stages (initial half-lives of 17 and 7 days for A and D respectively), but subsequent degradation was slow with estimated half-lives exceeding 100 days, suggesting that residues become absorbed into the soil particles before UV exposure can take place. Spinosyn A produced 3 photoproducts accounting for 2-6.6% of the initial ^{14}C; the one in highest concentration was identified as spinosyn B. Spinosyn D produced 2 photoproducts accounting for 4-5.4% of the initial ^{14}C, the smaller of which was identified as N-demethyl spinosad D (B of D).

Saunders *et al.* (1995a) similarly exposed [^{14}C]spinosyn A applied at 1 kg ai/ha to the same silt loam soil and maintained the soil at 75% moisture capacity. Spinosyn A had a half-life of approximately 14 days. The photodegradation rate decreased during the 30 days; perhaps because part of the material was shaded or absorbed by the soil and therefore less available for photolysis. Spinosyn B was the primary photoproduct and the sum of spinosyns A and B disappeared with a half-life of approximately 20 days. In the dark control in 30 days 20% of spinosyn A disappeared and spinosyn B equivalent to 10% of the starting material was generated.

The photoproducts were examined by MS, but full characterization was not possible. Products A1 and A2 were shown to be parent compound with a hydroxyl attached to the macrolide ring, and product A0 was an *N*-demethyl derivative with a hydroxyl attached to the macrolide ring.

Table 12. Photolysis of [^{14}C]spinosyn A applied at 1 kg ai/ha to a silt loam soil and exposed to sunlight for 30 days at 25°C (Saunders *et al.,* 1995a).

Days	Spinosyn A and photoproducts, % of initial spinosyn A dose				
	Spinosyn A	Spinosyn B	Product A0	Product A1	Product A2
0	93	1.3	0	0	0
2	77	4.9	1.3	1.3	1.7
4	67	6.7	1.9	1.9	1.9
7	57	9.6	2.4	2.1	2.1
11	47	12	2.9	2.6	2.0

Days	Spinosyn A and photoproducts, % of initial spinosyn A dose				
	Spinosyn A	Spinosyn B	Product A0	Product A1	Product A2
18	31	15	5	2.4	2.1
24	23	14	4.3	3.2	2.5
30	21	12	4.4	2.9	2.3

Aerobic degradation. Osborne *et al. (*1993) incubated [^{14}C]spinosyn A at 1 mg/kg in a California sandy loam (59% sand, 35% silt, 6% clay, 1.4% organic matter, pH 6.8), a Mississippi sandy silt (23% sand, 65% silt, 12% clay, 1.1% organic matter, pH 7.7), a Georgia sandy loam (79% sand, 14% silt, 12% clay, 0.8% organic matter, pH 6.7) and an Oxfordshire clay loam (47% sand, 24% silt, 29% clay, 5.2% organic matter, pH 7.2) under aerobic conditions at 20°C for 237-359 days. Parallel experiments were run for spinosyn D at 1 mg/kg for 6 months. Mass balances for ^{14}C, including volatiles, were 78-101% for spinosyn A (mostly exceeding 90%), and 89-101% for spinosyn D. The results are shown in Table 13.

Estimated half-lives for spinosyn A ranged from 40 to 75 days and half-lives for spinosyns A + B were 340, 140, 99 and 96 days for the sandy silt, clay loam and 2 sandy loams respectively. Estimated half-lives for spinosyn D were 65-85 days and for spinosyns D + B of D 650, 150, 250 and 81 days respectively. Mineralisation was variable in the different soils, ranging for spinosyn A from 5.8% in 1 year in the sandy silt to 26% in 6 months in a sandy loam, and for spinosyn D from 4.8%-25% in 8 months. Numerous metabolites were observed on HPLC and TLC examination of soil extracts, but could not be identified.

Table 13. Aerobic soil degradation of spinosyns A and D in four soils (Osborne *et al.,* 1993).

Days	Sandy silt			Clay loam			Sandy loam			Sandy loam		
	Residues, expressed as % of dose											
SPINOSYN A												
	spin A	spin B	volatiles	spin A	spin B	volatiles	spin A	spin B	volatiles	spin A	spin B	volatiles
0	94	1.2		85	3.2		90	1.4		93	0	
14	84	11										
28	68	23										
36	65	24										
56	35	57		21	44		37	41		16	39	
80										10	29	1.0
84	21	63		12	43	0.48	22	46	0.45			
182	5.7	67	2.2						26			
246				5.7	21	8.6	8.1	9.6		5.9	9.0	18
359	4.2	43	5.8									
SPINOSYN D												
	spin D	spin B of D	volatiles	spin D	spin B of D	volatiles	spin D	spin B of D	volatiles	spin D	spin B of D	volatiles
0	71	8.1		69	7.8		69	7.8		71	8.4	
7	71	7.1	1.3	50	12	1.1	50	12	0.65	42	16	1.5
14	62	10	0.56	41	14	0.93	41	14	0.63	35	18	2.4
28	57	18	1.1	27	18	1.9	27	18	1.3	18	15	2.3
56	35	37	2.5	18	27	3.9	18	27	1.6	12	27	4.3
84	31	38	3.8	15	34	1.3	15	34	4.4	11	28	8.7
237	6.6	53	4.8	4.4	17	14	4.4	17	11	3.9	4.0	25

Hale (1994) incubated [^{14}C]spinosyn A in a sandy loam soil (56% sand, 34% silt, 10% clay, 1.0% organic matter, pH 7.5) and a silt loam (37% sand, 50% silt, 13% clay, 1.1% organic matter, pH 7.8) at 0.4 mg/kg under aerobic conditions at 25°C in the dark for 1 year. A parallel experiment was run for spinosyn D at 0.1 mg/kg in the silt loam for 6 months. Mass balances for ^{14}C, including

volatiles, ranged from 90-106% for spinosyn A, with the exception of days 182 and 365 where they fell to 87 and 79% respectively, and for spinosyn D from 93-103%.

Levels of spinosyns A and D and degradation products are shown in Table 14. The initial process was *N*-demethylation to form spinosyn B or spinosyn B of D. Spinosyn A had initial half-lives of 9 and 16 days in the two soils, spinosyn D approximately 16 days in the silt loam, spinosyns A+B 98 and 92 days in the sandy loam and silt loam respectively, and spinosyns D + B of D 157 days in the silt loam. Spinosyn A was mineralised to the extent of 15% and 21% in the sandy loam and silt loam respectively after one year, but Spinosyn D only 3% after 6 months. Half-lives in sterilized soils were 130-240 days demonstrating that microbial action was mainly responsible for the degradation. The products were not fully characterized, but Metabolite 5 appeared to be a hydroxy-spinosyn A and Metabolite 2 a hydroxy-spinosyn B.

Table 14. Aerobic metabolism of [^{14}C]spinosyns A and D in soil (Hale, 1994).

Incubation, days	Residues, expressed as % of ^{14}C dose							
	Spinosyn A	Spinosyn B	Met 2	Met 3	Met 4	Met 5	Met 6	Others
SANDY LOAM, SPINOSYN A								
0	85	2.2						
1	81	7.6						
3	67	22						
7	41	41	0.68				1.2	1.0
14	23	53	1.9					1.2
28	6.1	61	2.8		0.95		1.2	0.58
56	1.5	47	3.5	0.82	1.9		1.3	6.4
91	1.7	37	3.5	1.4	2.3	2.6	2.1	5.3
140	0.58	21	4.6	3.6	1.2	3.5	1.5	8.4
182	1.6	21	4.7	3.4	1.5	4.8	1.7	2.9
273	0.74	12	4.7	4.3	1.2	2.0	1.3	2.3
364	0.91	6.0	2.2	4.2	0.61	1.5	0.51	11
SILT LOAM, SPINOSYN A								
0	91	2.9						
1	91	4.4						
3	86	9.6						
7	75	18						
14	57	35					1.7	
28	23	51	0.91	0.41			1.2	5.9
56	8.9	56	2.1	0.92	0.61	0.92	2.1	4.4
91	2.7	36	6.4	2.9	2.8		2.0	3.8
140	2.5	34	5.8	2.3	0.51	1.5	3.3	6.9
182	1.9	17	8.1	2.6	1.4	1.2	2.5	2.8
273	1.6	22	6.3	2.8	1.2		2.8	8.4
364	1.6	2.8	3.4	3.2	1.6	0.64	0.54	2.7
SILT LOAM, SPINOSYN D								
	Spinosyn D	Spinosyn B of D						
0	92	3.1						
1	92	5.0						
7	70	26						
10	53	36						
14	45	48						
28	16	68						
56	7.2	60						
91	0	46						
182	0	49						

Adsorption-desorption. Saunders and Powers (1994c) measured the adsorption-desorption characteristics of [^{14}C]spinosyn A on a sand, loamy sand, sandy loam, silt loam and clay loam in 0.01 M $CaCl_2$ solutions of spinosyn A (initial concentrations 5.0, 1.0, 0.20 and 0.05 mg/l) equilibrated for 22 hours at 25°C in the dark (Table 15). K_{oc} values were not calculated because adsorption coefficients clearly were not correlated with organic matter content. The measured K_d values suggest that spinosyn A is unlikely to be leached in to ground water. Cohen *et al.* (1984) interpret K_d values below 1-5 as signifying a potential for leaching if other requirements, such as environmental persistence, are met.

Saunders and Powers (1994a) used the same procedure to measure the adsorption-desorption characteristics of [^{14}C]spinosyn B on four of the same soils. Spinosyn B is a demethylation product of spinosyn A, ($-N(CH_3)_2 \rightarrow -NHCH_3$). The results of both experiments are shown in Table 15.

Table 15. Soil properties and adsorption-desorption characteristics of spinosyns A and B (Saunders and Powers, 1994a,c).

Soil	Soil properties						Spinosyn A		Spinosyn B	
	sand, %	silt, %	clay, %	organic matter, %	pH	CEC, meq/100 g	Adsorp K_d	DesorpK_d	Adsorp K_d	DesorpK_d
Sand	89	5.6	5.2	0.5	7.7	3.5	8.3	8.8	6.2	6.4
Loamy sand	82	10	8	1.1	6.3	1.9	5.4	7.4	4.3	5.8
Sandy loam	56	34	10	1.0	7.5	6.9	25	29	17	20
Silt loam	22	55	23	0.4	7.8	12	320	320	180	180
Clay loam	24	44	32	2.0	6.9	21	280	290		

Column leaching. Magnussen and Meitl (1999) applied fresh [^{14}C]spinosyn A at 0.46 mg/kg to a loamy sand (85% sand, 8.0% silt, 7.2% clay, 2.8% organic matter, pH 6.5). Leaching solution (0.01M $CaCl_2$) was percolated through columns of the treated soil (5 cm i.d. × 30 cm) at 0.14 ml/min or 393 ml over 48 hours. Application rates were higher (1.4 mg/kg) for tests on microbially aged and photolytically aged residues. Parallel tests were run for spinosyn D. Recoveries of ^{14}C were 80-100% for fresh, 92-96% for microbially aged and 86-89% for photolytically aged residues.

Fresh residues were not leached at all (Table 16). Some products of microbial metabolism and photolytic decomposition were leached from the column. The ageing processes produced quite polar compounds which probably represented degradation fragments of the spinosyns. The compounds could not be fully identified but were substantially modified from the spinosyns.

Table 16. Distribution of ^{14}C after leaching tests on [^{14}C]spinosyns A and D on a sandy loam soil (Magnussen and Meitl, 1999). Each result is the mean of results from duplicate columns.

Sample	% of applied ^{14}C					
	spinosyn A residues			spinosyn D residues		
	fresh	microbial aged	photolysis aged	fresh	microbial aged	photolysis aged
0-5 cm segment	99.4	92.3	68.8	100	87.7	76.3
5-10 cm segment	0.6	2.2	7.7		6.5	6.8
10-15 segment		0.8	3.7		1.1	2.7
15-20 segment		0.7	3.4		0.6	1.8
20-25 segment		0.4	2.7		0.5	1.8
25-30 segment		0.3	1.7		0.3	1.6
0-24 h leachate		1.0	4.3		0.8	3.7
24-48 h leachate		0.9	7.1		1.0	4.4
48-68 h leachate						
NaOH traps		1.4			1.5	
exposure dish rinse			0.6			0.9

Field dissipation. Spinosyn A was applied to the soil surface at a nominal 0.5 kg ai/ha at 2 US sites, one in California (a sandy loam) and the other in Mississippi (a silty clay), after which soil samples down to 90 cm were taken at intervals up to 10 months later (Saunders *et al.,* 1995b). Spinosyn A disappeared very quickly (Table 17). Three products were formed at low levels and they too decreased within 2 months to undetectable levels. Very little of the residue penetrated below the top 15 cm layer of soil. The mineralization half-life was approximately 7 months at both sites.

Table 17. Field dissipation of spinosyn A (Saunders *et al.,* 1995b).

^{14}C, as g/ha (nd = not detected at 0.003 mg/kg, equiv to 7 g/ha)									
Silty clay					Sandy loam				
Days	Spin A	Metab A0	Metab A1	Metab A2	Days	Spin A	Metab A0	Metab A1	Metab A2
0	501	nd	8	14	0	375	nd	nd	8
1	142	34	63	111	1	34	57	73	74
3	16	31	47	60	3	nd	38	51	59
4	11	50	49	52	5	7	48	55	53
8	7	31	30	25	8	nd	23	30	22
14	nd	19	19	16	14	nd	20	28	21
24	nd	15	20	10	23	nd	11	15	8
38	nd	10	18	nd	40	nd	nd	8	nd
64	nd	nd	nd	nd	72	nd	nd	nd	nd
93	nd	nd	nd	nd	98	nd	nd	nd	nd
126	nd	nd	nd	nd	205	nd	nd	nd	nd
196	nd	nd	nd	nd	247	nd	nd	nd	nd
247	nd	nd	nd	nd	286	nd	nd	nd	nd
308	nd	nd	nd	nd	316	nd	nd	nd	nd

Residues in rotational crops. Rainey (1994b) treated sandy loam soil plots with [^{14}C]spinosyn A at a rate equivalent to 1.1 kg ai/ha and 30, 120 and 365 days after treatment sowed wheat, lettuce and radishes. Lettuce, radish root, radish foliage, wheat grain and wheat straw were harvested at maturity and analysed for ^{14}C content (Table 18). Immature wheat plants were also collected for analysis. The ^{14}C residues were characterized by HPLC and examination of natural products such as starch, lignin and protein. No spinosyns or closely related compounds were identified in the crops. At least some of the ^{14}C had been incorporated into natural compounds.

Table 18. Levels of ^{14}C in rotational crops sown in soil previously treated with [^{14}C]spinosyn A at 1.1 kg ai/ha (Rainey, 1994b).

Sowing interval, days after treatment	Total ^{14}C as spinosyn A, mg/kg					
	Lettuce	Radish root	Radish foliage	Immature wheat plant	Wheat grain	Wheat straw
30	0.009	0.016	0.008	0.022	0.023	0.079
120	0.020	0.014	0.030	0.048	0.29	0.50
365	0.006	0.004	0.004	0.010	0.009	0.027

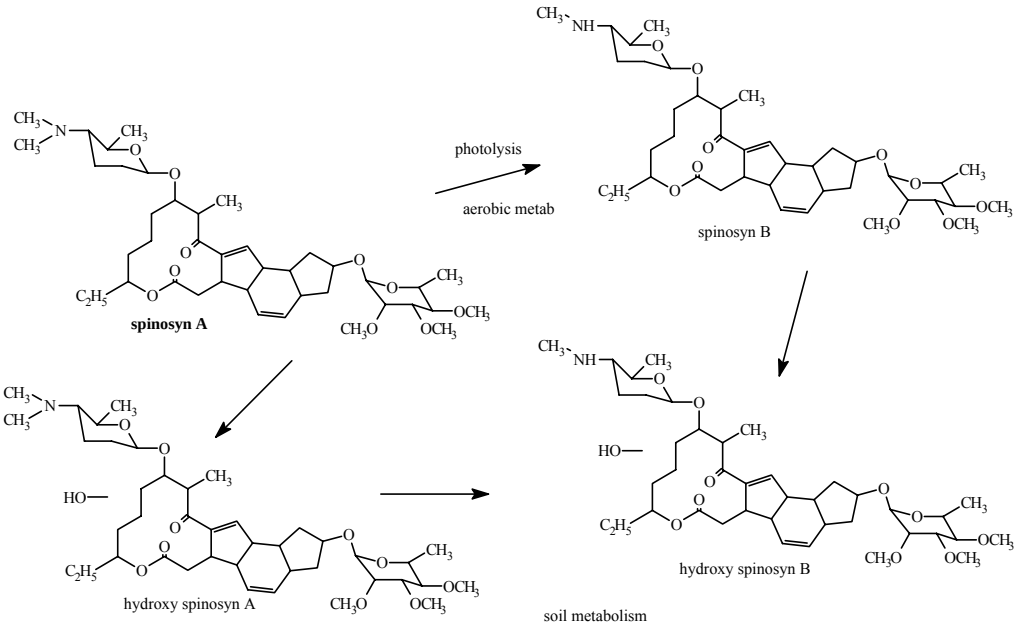


Figure 3. Degradation of spinosyn A in soil. Spinosyn D degradation parallels that of spinosyn A.

Environmental fate in water/sediment systems

The Meeting received information on photolysis in solution, anaerobic degradation and dissipation in an aquatic environment.

Photolysis. In a study in the USA, Saunders and Powers (1994b) exposed [^{14}C]spinosyns A and D dissolved in sterile pH 7 buffers at 2 mg/l in borosilicate glass tubes to natural sunlight at 25°C for 48 hours at 39.9°N latitude from June 26-28 and July 15-18, and samples were taken at various intervals for ^{14}C measurement and analysis by HPLC. Recoveries of ^{14}C ranged from 88.5-103%, and the half-lives of spinosyn A and D were 22.3 and 19.7 hours of sunlight respectively (Table 19).

Photoproduct A1 was identified by MS and NMR, after additional photolysis runs provided sufficient material, as the pseudoaglycone of spinosyn A with an additional 2 hydrogens saturating the double bond in the cyclopentane ring. Photoproduct A2 gave a molecular ion at m/z = 731, the same as spinosyn A, i.e. a rearrangement of spinosyn A, but the nature of the rearrangement was not determined. Photoproduct A3 gave a molecular ion at m/z = 749, equivalent to the addition of a water molecule to the parent. Photoproduct D1 had a molecular ion at m/z=606 consistent with the pseudoaglycone of spinosyn D plus 2 hydrogens; it is probably the analogue of A1 with the extra methyl group. Photoproducts D2 and D3 did not produce useful mass spectra. Photoproduct D4 gave a molecular ion at m/z = 763, equivalent to spinosyn D plus water.

Table 19. Photolysis of [^{14}C]spinosyns A and D dissolved in sterile pH 7 buffers at 2 mg/l in borosilicate glass tubes and exposed to natural sunlight for 48 hours (Saunders and Powers, 1994b).

	^{14}C, % of initial concentration				
SPINOSYN A					
Irradiation time, h	spinosyn A	product A1	product A2	product A3	
0	98				
6.0	83	3.3	4.8	3.7	
10.8	68	7.5	7.0	4.7	
14.2	59	14	4.1	7.5	

	^{14}C, % of initial concentration				
24.2	45	20	5.1	8.9	
31.7	37	24	6.0	8.3	
SPINOSYN D					
Irradiation time, h	spinosyn D	product D1	product D2	product D3	product D4
0	95				
5.5	76	5.8	4.1	2.7	3.3
11.0	61	12	5.3	4.1	3.4
19.0	47	18	7.1	5.7	3.7
28.3	33	16	3.5	6.0	3.0
39.8	24	19	3.1	5.2	3.4

Spinosyns A and D were subjected to photolysis in natural pond water at 25°C under sunlight for 2 days at 39.9°N latitude (USA) on 19-21 August to determine degradation rates (Yoder and Sanders, 1996). Spinosyn D has very low water solubility; the addition of 0.05% acetonitrile as a co-solvent raised the solubility to approximately 2.5 mg/l. Residual spinosyns in the solutions were measured periodically by an HPLC method. The half-lives for both were 4.3 hours (of sunlight). Concentrations in dark controls were substantially stable. Photodegradation products were identified as spinosyn B (from spinosyn A) and N-demethyl-spinosyn D or spinosyn B of D (from spinosyn D): their concentrations reached maximum levels about half way through the experiments and had begun to decrease by the end.

Anaerobic degradation. Reeves (1993) incubated pond water (100 ml) and sediment (50 g equiv dry weight) with [^{14}C]spinosyn A -at 0.85 µg/ml water in the dark at 25°C under anaerobic conditions for 1 year. The water had an alkalinity of 390 mg/l, expressed as $CaCO_3$ and the sediment contained 2.8% organic matter. The procedures were repeated for [^{14}C]spinosad D. Samples were taken at various intervals and sediment and water were separated by decanting and centrifuging. The sediment was then extracted with acetone-methanol and then acetone. ^{14}C balances for spinosyns A and D were 94-104% and 92-105% respectively. The distribution of ^{14}C in the spinosyns and degradation products in the water and sediment is shown in Table 20. The residue rapidly became attached to the sediment. Both compounds had initial half-lives of about 6 months, but were quite persistent in the second 6 months. Very small amounts (<2%) of volatile ^{14}C were produced. Major degradation products were identified as the *N*-demethyl compounds spinosyn B and spinosyn B of D. The others were not fully characterized.

Table 20. Anaerobic degradation of spinosyns A and D in pond water and sediment (Reeves, 1993). The distribution of the spinosyns and products are expressed as % of dose. Degradation products are identified by their retention times relative to the parent compound. Minor products (<5% of dose) are not included.

Days	^{14}C expressed as % of dose							
	Total ^{14}C		Spinosyn A		Degradation products			
	Water	Sediment	water	sediment	Rt 0.86	Rt 0.82	Rt 0.72	Rt 0.64
0	58	41	52	38		9.3		
3	14	89	13	85		6.0		
7	8.5	87	7	81	3.0	4.3		
14	4.3	91	4	79	6.5	5.8		
28	3.4	93	3	79	9.1	2.3	3.8	
56	2.6	96	2	71	12	3.7	7.5	3.8
84	2.1	92	1	56	14	2.5	11	3.8
170	2.3	92	1	49	13	7.3	12	6.2
365	2.1	92	1	38	9.2	2.1	18	18
Days	Total ^{14}C		Spinosyn D		Degradation products			
	Water	Sediment	water	sediment	Rt 0.84-7	Rt 0.82-4	Rt 0.75-6	
0	50	52	43	45	4.6	5.6		

3	14	91	11	84	3.4	2.3	0.1	
7	6.0	89	4.7	80	3.4	3.6	1.3	
14	4.3	89	3.6	76	3.8	3.2	2.8	
28	3.1	91	2.8	77	6.9	2.3	3.3	
56	2.5	92	1.6	74	10	3.2	3.9	
84	2.2	91	2.2	71	11	2.7	4.6	
170	2.0	90	0.9	56	12	8.0	6.4	
365	1.9	92	0.7	59	14	2.4	9.1	

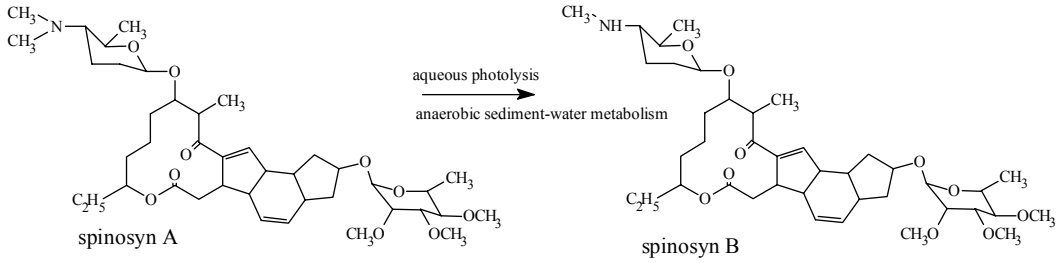
The fate of spinosad was investigated in an aquatic microcosm study using 3 open tanks 60 cm deep and 170 cm diameter holding 1100 l of pond water and a 6 cm layer of pond sediment exposed to sunlight and weather conditions (McGibbon *et al.,* 1995). Spinosad in a diluted SC formulation was applied to the surface at a nominal 0.10 kg ai/ha and samples were analysed by immunoassay and HPLC (Table 21). Spinosyn residues decreased rapidly in the water, with a half-life of about 1-2 days, and spinosyn A in the sediment generally accounted for only about 10-15% of that applied. The results suggest that spinosad dissipates principally by degradation (photolysis) then by adsorption to the sediment.

Table 21. Spinosyn residues in a water/sediment system treated with spinosad at 0.10 kg ai/ha (McGibbon *et al.,* 1995).

Hours	Spinosyn residues in water, mg/l (mean of 3 tanks)						Spinosyn residues in sediment, mg/kg (mean of 3 tanks)					
	A	D	B	B of D	Total		A	D	B	B of D	Total	
					HPLC	IA[1]					HPLC	IA[1]
0	0.028	0.0047	0.0011	0.0012	0.035	0.045						
1	0.018	0.0032	0.0014	0.0009	0.024	0.034						
2	0.015	0.0020	0.0011	0.0005	0.019	0.035						
4	0.014	0.0021	0.0017	0.0005	0.018	0.031						
8	0.011	0.0016	0.0022	0.0006	0.015	0.026						
24	0.0086	0.0008	0.0015	0.0004	0.011	0.020	0.01	<0.01	<0.01	<0.014	0.01	0.024
48	0.0049	0.0005	0.0015	<0.0001	0.0068	0.014	0.014	<0.01	<0.01	<0.014	0.014	0.029
96	0.0019	0.0008	0.0014	0.0005	0.0046	0.012	0.015	<0.01	<0.01	<0.014	0.019	0.031
192	0.0003	0.0001	0.0005	0.0005	0.0014	0.006	0.013	<0.01	<0.01	<0.014	0.018	0.041
360	<0.0001	0.0001	0.0002	<0.0001	0.0003	0.002	0.011	<0.01	<0.01	<0.014	0.019	0.039
840							0.014	<0.01	<0.01	<0.014	0.019	0.031

[1] IA: immunoassay

Figure 4. Water-sediment degradation of spinosyn A. Spinosyn D degradation parallels that of spinosyn A.



METHODS OF RESIDUE ANALYSIS

Analytical methods

Analytical methods for the determination of residues of the spinosyns fall into two main types after an extraction designed for the sample: HPLC and immunoassay. HPLC methods follow a reasonably standard clean-up with HPLC determination relying on UV or MS detection to measure the individual spinosyns, and in residue trials provide data on spinosyns A, D, K, B and B of D. Spinosyn A contributes most of the residue most of the time and some HPLC methods have concentrated on spinosyns A and D since national authorities have decided that spinosyns A and D should constitute the definition of the residue. Immunoassay methods may or may not require a clean-up before the final colorimetric determination. The method is specific and reports the sum of the spinosyns. The HPLC and immunoassay methods have been extensively validated with numerous recoveries on a wide range of substrates and when used side-by-side in trials agreement was usually good.

In an HPLC method for measuring residues in potatoes and tomatoes described by Balderrama Pinto and Matos (1996a) the residue is extracted from ground samples with an acetonitrile-water mixture which, after acidification with HCl, is washed with hexane. The aqueous phase is then made alkaline with NaOH and the residue extracted into hexane. The hexane extract is cleaned up on a solid-phase column and the eluate evaporated to dryness and taken up in acetonitrile-ammonium acetate solution for HPLC analysis with UV detection at 250 nm. Spinosyns A and D are measured separately as two peaks. Recoveries from potato samples were mean 99 and 101%, range 89-112%, n = 12 for spiking at 0.01 and 0.1 mg/kg, and from tomato samples mean 92 and 91%, range 73-106%, n = 12 at the same levels. The LOQ was 0.01 mg/kg for A and D.

In an HPLC method for measuring spinosad residues in almond nuts and hulls described by Duebelbeis *et al.* (1997) the residue is extracted with an acetonitrile-water mixture which, after filtration, is partitioned into 1-chlorobutane. The extract is cleaned up on silica and cyclohexyl solid-phase columns and analysed by reverse-phase HPLC with UV detection at 250 nm. Spinosyns A, D, B, K and N-demethyl-D are measured as 5 separate peaks. Identities are confirmed by reanalysis of the extracts by LC-MS. Recoveries from kernel samples were mean 85%, range 76-116%, n = 20, and from hulls mean 82%, range 72-94%, n=20 for spiking at 0.01, 0.02, 0.05, 0.25 and 1.0 mg/kg. The LOQ was 0.01 mg/kg for each spinosyn.

Turner *et al. (*1996a,b, GRM 95.15, GRM 95.15.R1) used a similar HPLC method for eggs and poultry tissues. Extracting solvents were tailored to the substrates as follows: acetonitrile-methanol 1:1 for eggs, acetonitrile-water 4:1 for meat and liver, and hexane-dichloromethane 3:2 for fat. Turner and West (1999) described modifications needed to improve recoveries from spoiled poultry fat.

Atkin and Dixon-White (1995) examined the GLC behaviour of spinosyns A and D to determine whether spinosad could be analysed by an FDA multi-residue method. It was concluded that spinosyns A and D could not be chromatographed after tests on a DB-1-phase capillary column at various temperatures and with FID and MS detection; spinosad was not amenable to analysis in the multiresidue methods. Satonin (1996) reached the same conclusion for spinosyns B, K and B of D.

In an LC-MS method for spinosyns A, D, K, B and N-demethyl-spinosyn D in crop samples with a high water content described by Hastings *et al.* (2000a) residues are extracted with an acetonitrile-water mixture and an aliquot of the extract is cleaned up on a cation-exchange solid-phase cartridge and eluted with a methanol-water-acetonitrile mixture containing ammonium acetate. HPLC with detection and quantification by APCI MS (scanning for 718.6, 732.6 and 746.6 amu). The LOQ was 0.01 mg/kg. Recoveries were consistent from apricots, banana peel and pulp, whole banana, green beans, broccoli, Brussels sprouts, cabbages, cauliflowers, celery, courgettes, cucumbers, leeks, lettuce, melon peel and pulp, whole melon, nectarines, onions, peach flesh, peas, potatoes, watermelon peel and pulp and whole watermelon (Table 22).

Table 22. Analytical recoveries of spinosyns from crop samples with high water content by an LC-MS method (Hastings *et al.*, 2000a).

	Spinosyn				
	A	D	B	B of D	K
Fortification at 0.01 mg/kg each analyte					
mean, %	96	94	94	93	98
range, %	71-110	81-106	79-108	72-107	84-108
n	50	50	50	50	50
Fortification at 0.1 mg/kg each analyte					
mean, %	95	94	95	93	96
range, %	82-109	81-107	79-106	79-104	80-106
n	50	50	50	50	50
Fortification at 1 mg/kg each analyte					
mean, %	95	95	94	94	96
range, %	83-107	82-108	73-109	70-106	85-109
n	50	50	50	50	50

Hastings and Clements (2000, GRM 00.04) applied essentially the same LC-MS method to a range of crop substrates with a low water content (Table 24): chick peas and forage, lucerne forage and hay, mung beans and forage, oat grain, sorghum grain and forage, wheat grain and forage and chick pea, oat, sorghum and wheat straw. The LOQ for grain and forage was 0.01 mg/kg and for straw 0.02 mg/kg.

Hastings *et al. (*2000b) applied a very similar method to pome fruit and grapes and their processed commodities, kiwifruit and avocados. Wine was extracted with dichloromethane after the addition of aqueous sodium chloride and the extract evaporated to leave a residue for clean-up in the same way as for other samples. Analytical recoveries are shown in Table 23 for apple juice, apple pomace, apples, avocados, grape juice and pomace, grapes, kiwifruit, pear juice and pomace, pears and wine. The LOQ was 0.01 mg/kg.

Van Acker and Hastings (2000, GRM 00.01) extracted brandy with methyl *tert*-butyl ether after the addition of sodium bicarbonate. The extract was evaporated to dryness and taken up in acetonitrile-methanol for LC-MS-MS analysis. The LOQ was 0.01 mg/l.

West (1995a) extracted residues from water samples with dichloromethane. Clean-up, if required, was by silica solid-phase extraction. The spinosyns were determined by HPLC with UV detection. LOQs were 0.001 mg/l.

Boothroyd *et al. (*1999) extracted spinosad residues from water with methyl *tert*-butyl ether after the addition of a sodium hydroxide solution. The extract was evaporated and reconstituted in water-methanol for analysis by LC-MS. The method was tested on drinking, surface and ground waters. LOQs were 0.0001 mg/l.

The HPLC method was also applied to soil and sediment over the concentration range 0.01-1.0 mg/kg by West (1995b). Residues were extracted with alkaline methanol containing sodium chloride. The method was later improved by adding clean-up steps to reduce interferences from some soils and the introduction of glycerol as a keeper solvent to reduce loss of analytes during concentration (West and Turner, 1999).

Table 23. Analytical recoveries of spinosyns from pome fruit, grapes, processed commodities, kiwifruit and avocados by an LC-MS method (Hastings *et al.*, 2000b).

	Spinosyn				
	A	D	B	B of D	K
Fortification at 0.01 mg/kg each analyte					
mean, %	100	102	101	98	103
range, %	81-113	79-115	86-115	75-108	78-117
n	26	26	24	26	26
Fortification at 0.1 mg/kg each analyte					
mean, %	102	102	100	100	102
range, %	83-123	92-117	76-122	85-116	91-115
n	26	26	26	26	26
Fortification at 1 mg/kg each analyte					
mean, %	96	94	93	93	97
range, %	75-113	74-116	72-111	71-109	79-116
n	25	25	26	24	26

Table 24. Summary of extensive testing of HPLC methods with UV or MS detection.

Commodity	Spike concn., mg/kg	n	Spinosyns recovery %										Ref.
			A		D		K		B		B of D		
			mean	range	mean	range	mean	range	mean	range	mean	range	
alfalfa forage	0.01-0.1	3	94		94		73		74		77		GRM95.17.S1
alfalfa hay	0.01-5.0	14	92	79-104	88	74-109	96	84-115	87	58-105	88	57-103	GRM 97.06
apple	0.01-5.0	28	91	78-102	91	82-102	90	74-101	91	74-102	91	75-108	ERC 97.18
apple	0.01-1.0	20	93	86-101	92	85-95	92	88-95	90	84-95	88	82-93	GRM 95.05
apple juice	0.01-5.0	28	93	80-114	91	82-109	93	81-104	89	78-97	89	71-102	ERC 97.18
apple juice	0.01-1.0	20	93	91-98	93	89-90	93	89-98	88	82-95	88	81-94	GRM 95.05
apple pomace	0.01-5.0	28	98	73-110	96	70-113	98	74-110	95	74-108	97	74-112	ERC 97.18
apple purée	0.01-5.0	28	97	80-111	97	79-109	98	84-110	96	81-109	95	81-109	ERC 97.18
apple wet pomace	0.02-2.0	20	89	86-95	88	81-93	90	88-93	88	81-92	86	79-97	GRM 95.05
beef fat	0.01-10.0	11	98	81-108	95	84-107			94	85-102	82	56-93	GRM 95.03
beef kidney	0.01-1.0	11	84	76-97	84	76-99			114	98-136	97	86-107	GRM 95.03
beef liver	0.01-1.0	11	106	97-120	92	83-110			107	88-125	94	71-109	GRM 95.03
brandy	0.01-0.5	34	105	83-116	105	81-118	103	84-112	96	81-108	97	84-112	GRM 00.01
broccoli	0.01-2.0	23	94	90-98	92	85-98	91	86-96	74	68-80	74	64-84	GRM 94.22
cabbage	0.01-2.0	23	84	76-91	79	64-90	80	69-90	75	70-79	74	68-79	GRM 94.22
celery	0.01-5.0	20	93	89-95	93	87-97	84	75-92	86	81-90	85	80-88	GRM 95.17.R1
cereal grain, forage	0.01-0.1	26	91	76-100	88	70-104	81	68-91	79	66-90	76	62-86	GRM95.17.S1
chicken fat	0.02-2.0	11	114	102-124	112	104-121			102	84-114	99	86-105	GRM 95.15.R1
chicken liver	0.01-1.0	11	94	85-113	84	77-97			93	83-100	93	88-99	GRM 95.15.R1
chicken meat	0.01-1.0	11	92	84-101	88	92-94			100	97-109	95	84-103	GRM 95.15.R1
chicken meat/skin/fat	0.01-1.0	11	86	76-95	77	71-83			96	88-105	92	76-99	GRM 95.15.R1
chilli peppers	0.01-1.0	20	96	92-102	94	89-99	96	90-100	88	84-92	87	83-90	GRM 95.04
citrus fruit, whole	0.01-2.0	20	104	97-111	101	94-110	99	84-109	98	89-113	95	85-111	GRM 96.09.R1
corn stover	0.01-5.0	7	93		93		88		77		82		GRM 97.06
cotton seed	0.01-0.10	22	93	68-107	89	55-113							GRM 93.02.R2
cotton seed	0.01-0.10	18	99	74-119	95	82-117							GRM 94.02
cotton seed hulls	0.01-0.10	10	100	89-116	100	87-110							GRM 94.02
cotton seed meal	0.01-0.10	10	90	81-100	85	73-96							GRM 94.02

Commodity	Spike concn., mg/kg	n	Spinosyns recovery %										Ref.
			A		D		K		B		B of D		
			mean	range	mean	range	mean	range	mean	range	mean	range	
cotton seed oil, crude	0.01-0.10	18	96	86-113	93	85-99							GRM 94.02
cotton seed oil, ref	0.01-0.10	10	92	70-98	86	68-103							GRM 94.02
cotton seed soapstock	0.01-0.10	18	99	93-104	102	98-110							GRM 94.02
cream	0.01-10.0	11	103	96-114	99	87-115			107	96-116	106	97-113	GRM 95.03
cucurbits	0.01-0.1	12	99	88-117	96	82-116	98	84-115	85	66-113	86	72-111	GRM95.17.S1
eggs	0.01-1.0	20	88	73-100	87	69-97			102	94-110	97	87-109	GRM 95.15.R1
grain and forage	0.01	22	100	89-119	99	87-114	93	80-111	93	79-103	95	77-117	GRM 00.04
grain and forage	0.1	22	90	74-108	90	72-105	86	73-101	89	76-102	87	72-100	GRM 00.04
grain and forage	1.0	22	89	76-102	89	73-101	87	77-94	91	81-99	89	73-99	GRM 00.04
grape	0.01-3	11	90	75-100	93	73-105							BRC 99.1
grape must	0.01-5.0	44	97	80-117	98	78-118	96	78-109	87	76-109	86	71-115	ERC 97.18
grape pomace	0.01-5.0	28	87	75-101	87	74-102	85	72-100	94	77-119	90	76-111	ERC 97.18
grapes	0.01-5.0	28	90	79-111	89	79-112	88	81-111	90	78-108	88	71-112	ERC 97.18
green peppers	0.01-1.0	20	95	92-99	93	89-98	94	90-98	85	78-92	84	78-90	GRM 95.04
head lettuce	0.01-5.0	20	88	84-96	88	82-95	85	80-93	78	72-86	77	71-86	GRM 95.17.R1
leaf lettuce	0.01-5.0	20	93	86-98	91	85-95	88	83-90	83	74-90	81	71-89	GRM 95.17.R1
lean beef tissue	0.01-1.0	11	95	81-107	87	82-93			101	91-107	98	92-107	GRM 95.03
lemon	0.01-0.1	11	94	90-102	94	88-101							GRM00.6
lemon oil	0.01-0.05	11	83	68-114	90	71-120							GRM00.6
maize	0.01-1	18	80	54-125	89	58-137							GRM00.6
milk, whole	0.01-1.0	20	104	99-116	101	90-114			101	94-109	101	92-112	GRM 95.03
mustard greens	0.01-2.0	23	92	88-102	90	83-95	87	82-91	82	78-89	81	75-86	GRM 94.22
nectarine	0.01-1	11	96	81-110	100	69-113							BRC 99.1
orange	0.01-1.0	23	85	64-108	80	69-96							GRM00.6
orange juice	0.01-20.0	20	102	92-110	94	83-101	104	95-112	94	80-102	90	75-98	GRM 96.09.R1
orange juice	0.01-1	12	96	71-113	82	74-89							GRM00.6
orange oil	0.02-10.0	20	88	76-98	87	74-101	88	79-98	77	65-86	77	70-85	GRM 96.09.R1
orange peel	0.01-10.0	20	97	75-110	95	79-107	99	87-108	90	79-108	90	79-107	GRM 96.09.R1
orange pulp, dried	0.02-10.0	20	113	106-23	110	105-19	110	105-18	99	87-116	97	85-112	GRM 96.09.R1
orange, edible portion	0.01-2.0	20	102	92-108	99	88-106	98	86-106	92	79-106	91	78-105	GRM 96.09.R1
peas, beans, soya beans	0.01-0.1	9	99	98-109	95	84-108	95	80-109	85	70-94	83	68-92	GRM95.17.S1
peppers	0.01-5.0	28	92	83-114	95	82-129	94	81-119	89	77-110	88	73-104	ERC 97.18
potato	0.01-0.1	3	93		86		88		74		92		GRM95.17.S1
soil, sediment	0.01-1.0	35	82	71-89	83	71-95			78	64-87	76	61-85	GRM 94.20
soil	0.01-1.0	15	88	81-91	83	74-90			85	66-98	77	63-90	GRM 94.20.R1
sorghum fodder	0.01-5.0	7	88		91		82		72		72		GRM 97.06
spinach	0.01-5.0	20	91	87-102	91	88-98	87	78-96	84	78-94	84	75-94	GRM 95.17.R1
stone fruits	0.01-0.1	12	100	87-122	97	72-126	85	64-105	84	78-95	81	64-94	GRM95.17.S1
straw	0.02	8	97	90-106	94	84-108	97	91-108	90	82-105	91	81-104	GRM 00.04
straw	0.1	8	92	86-97	90	83-95	90	85-97	86	81-91	88	82-93	GRM 00.04
straw	1.0	8	88	77-93	88	79-92	90	84-95	88	81-94	87	79-91	GRM 00.04
strawberries	0.01-5.0	28	95	74-110	96	86-109	94	83-108	95	82-110	96	86-108	ERC 97.18
tangerine	0.01-1	13	91	82-106	99	87-108							GRM00.6
tomato dry pomace	0.04-4.0	20	95	87-98	84	84-98	95	92-98	90	87-93	89	86-93	GRM 95.04

Commodity	Spike concn., mg/kg	n	Spinosyns recovery %										Ref.
			A		D		K		B		B of D		
			mean	range	mean	range	mean	range	mean	range	mean	range	
tomato juice	0.01-1.0	7	96	92-98	95	90-97	95	92-97	89	88-91	88	86-90	GRM 95.04
tomato paste	0.01-1.0	7	90	87-93	90	84-100	87	80-92	87	86-90	87	85-90	GRM 95.04
tomato purée	0.01-1.0	7	95	93-97	94	89-95	94	90-96	91	90-91	89	86-90	GRM 95.04
tomato wet pomace	0.02-2.0	20	92	89-97	92	88-96	91	88-96	78	75-84	76	74-79	GRM 95.04
tomatoes	0.01-5.0	28	101	81-120	101	81-127	99	90-113	95	85-110	97	74-110	ERC 97.18
tomatoes	0.01-1.0	20	96	88-104	93	87-98	91	85-96	85	78-90	84	78-90	GRM 95.04
tomatoes juice	0.01-5.0	28	98	91-109	97	89-104	88	68-107	96	87-105	96	86-108	ERC 97.18
tomatoes purée	0.01-5.0	28	98	85-118	97	85-113	90	76-111	94	71-114	97	80-118	ERC 97.18
tomatoes, tinned	0.01-5.0	26	97	88-116	98	91-114	94	85-112	96	89-110	96	91-111	ERC 97.18
water (pond well tap)	0.001-0.10	35	93	77-106	90	73-104			87	71-96	90	71-111	GRM 94.12
water (pond)[1]	0.001-0.10	11	81	71-105	81	71-87			82	73-117	78	72-97	GRM 94.12
water, drinking	0.1-5 ug/l	32	107	99-115	105	87-118	108	100-115	109	91-122	107	87-121	ERC 98.23
water, ground	0.1-5 ug/l	32	95	73-101	96	64-109	98	88-108	100	80-108	99	73-108	ERC 98.23
water, surface	0.1-5 ug/l	32	98	80-111	99	87-117	100	91-114	102	89-118	101	88-119	ERC 98.23
wheat hay	0.01-5.0	7	90		86		87		70		78		GRM 97.06
wheat straw	0.01-5.0	7	93		93		87		72		69		GRM 97.06
wine	0.01-5.0	28	98	87-112	97	74-109	99	79-112	99	87-119	98	86-115	ERC 97.18

[1] Method includes silica SPE clean-up step

Pinheiro *et al. (*2000a, GRM 00.6) used an HPLC method for determining residues of spinosyns A and D in citrus fruits, juice and oil and maize in supervised and processing trials in Brazil and Argentina. The method is essentially the same as that of Balderrama Pinto and Matos (1996a) with the initial extraction step modified to suit the substrate. The method was extensively tested for recoveries. The LOQ was 0.01 mg/kg. The method was also tested on nectarines and grapes (Pinheiro *et al.,* 1999a).

Tidswell and Cowles (1998a) extracted milled cotton seed with a hexane-acetone mixture. The extract was evaporated and the residue taken up in acidic aqueous methanol which was washed with hexane. The spinosyns were partitioned into hexane after the addition of sodium hydroxide and further cleaned up on a cyclohexyl solid-phase extraction column. Spinosyns A and D were then determined by HPLC with UV detection. Recoveries from spiked cotton seed (0.01 and 0.1 mg/kg, n = 17) were spinosyn A mean 78%, range 66-93%; spinosyn D mean 69%, range 60-76%. Tidswell and Cowles (1998b) further tested the method on cotton bracts and trash with recoveries (0.01-5.9 mg/kg, n = 17) of spinosyn A mean 83%, range 68-107%, and for spinosyn D mean 82%, range 67-111%.

Khoshab and Marshall (1998) described an immunoassay analytical method for grapes, pomace, must and wine that relies on the Strategic Diagnostics “Spinosad Rapid Assay” test kit. The antibody is sensitive to several spinosyns and measures the total residue of spinosad and its metabolites. Residues are extracted from the substrate with an acetonitrile-water mixture, except wine which is extracted with dichloromethane, and a portion of the extract cleaned up by cyclohexyl solid-phase extraction.

A portion of the diluted sample is incubated with enzyme-conjugated spinosad and magnetic particles coated with antibodies specific to spinosad. Spinosad in the sample and enzyme-conjugated spinosad compete for antibody sites on the magnetic particles. When a magnetic field is applied to the particles at the end of the incubation period, the spinosad and enzyme-conjugated spinosad bound to

the antibodies on the particles are held in the sample tube by the magnetic field while the unbound reagents are decanted. A coloured product, produced by incubating the antibody-bound enzyme conjugate with hydrogen peroxide and 3,3',5,5'-tetramethylbenzidine, is measured by its absorbance at 450 nm.

The assay is sensitive to spinosyn analogues with little or no modification of the trimethylpyranosyl ring, but relatively insensitive to analogues or degradation products if the ring has been modified or is missing. The method was tested for interference by 30 pesticides, 16 inorganic compounds and 8 organic compounds (most naturally occurring). Carbendazim was the only compound generating a response, but at a low sensitivity. Recoveries were satisfactory over the spiking range 0.01-5 mg/kg spinosyn A (Table 25). The LOQ was 0.01 mg/kg.

The I_{50} concentration is the concentration that results in a 50% inhibition of conjugate binding to the available antibodies and is a measure of the sensitivity of the method. The I_{50} for spinosyn A is approximately 0.0003 µg/ml (Redstone, 1998). Compounds with high sensitivity (I_{50} < 0.002 µg/ml) are spinosyns A, B, C, D, N-demethyl-D, E, F, K and A pseudoaglycone. Compounds with a low sensitivity (I_{50} > 0.05 µg/ml) are spinosyns H, J, L, A reverse pseudoaglycone and A aglycone. The I_{50} for carbendazim was 5 µg/ml.

The immunoassay method was applied to sediment over the concentration range 0.05-0.35 mg/kg (Young and Mihaliak, 1995). Spinosad was extracted from the sediment with alkaline methanol containing sodium chloride. Recoveries are shown in Table 25.

The immunoassay method was also shown to be suitable for spinosad residues in bovine tissues and milk (Young and Mihaliak, 1996). The residues are extracted from tissues with an acetonitrile-water mixture, and from milk with acetonitrile. The method was validated in the range 0.01-0.5 mg/kg (Table 25).

Table 25. Analytical recoveries of spiked spinosyn A from various substrates by an immunoassay method.

Sample	Spike concn., mg/kg	n	Mean recov., %	Range, %	Ref.
apples	0.01-1.0	18	102	92-119	GRM 95.20
bovine kidney	0.01-0.50	13	78	68-84	GRM 95.14
bovine liver	0.01-0.50	14	77	64-86	GRM 95.14
bovine milk	0.01-0.50	32	84	67-100	GRM 95.14
bovine muscle	0.01-0.50	22	77	68-86	GRM 95.14
broccoli	0.01-1.0	17	105	81-125	GRM 95.20
broccoli	0.01-3.0	26	85	71-107	PA-RM-97-07
Brussels sprouts	0.01-3.0	21	100	75-120	PA-RM-97-04
cabbage	0.01-1.0	18	110	83-128	GRM 95.20
cabbage	0.01-3.0	33	98	81-120	PA-RM-97-04
capsicum	0.01-5.0	16	101	86-112	PA-RM-97-04
cauliflower	0.01-2.0	15	90	76-109	PA-RM-97-07
celery	0.01-1.0	19	105	91-123	GRM 96.10
cherries	0.01-0.20	12	98	70-123	GRM 96.11.S1
Chinese cabbage	0.01-3.0	16	103	78-117	PA-RM-97-04
cucumber	0.01-0.10	10	93	70-110	GRM 96.10.S1
grape pomace	0.01-5.0	28	101	80-120	ERC 97.09
grapefruit, whole	0.01-1.0	17	96	77-118	GRM 96.11
grapes	0.01-5.0	28	104	86-118	ERC 97.09
head lettuce	0.01-1.0	17	94	81-104	GRM 96.10
kiwifruit	0.01-6.0	17	105	87-131	PA-RM-97-01
leaf lettuce	0.01-1.0	19	102	92-113	GRM 96.10
lemon, whole	0.01-1.0	17	101	87-124	GRM 96.11
lucerne pasture	0.01-10	21	87	70-111	PA-RM-97-07
maize	0.01-0.10	7	103	88-126	GRM 96.10.S1

Sample	Spike concn., mg/kg	n	Mean recov., %	Range, %	Ref.
muskmelon	0.01-0.25	10	94	73-125	GRM 96.10.S1
must	0.01-5.0	28	103	88-120	ERC 97.09
mustard greens	0.01-1.0	17	101	85-112	GRM 95.20
navy bean hay	0.01-1.0	10	110	92-119	PA-RM-98-01
navy bean whole plant	0.01-1.0	4	102	87-114	PA-RM-98-01
navy bean, dry bean	0.01-1.0	6	93	74-110	PA-RM-98-01
orange peel	0.01-1.0	19	100	74-127	GRM 96.11
orange, edible portion	0.01-1.0	17	97	79-116	GRM 96.11
orange, whole	0.01-1.0	17	98	75-122	GRM 96.11
peach	0.01-0.20	6	87	72-101	GRM 96.11.S1
pear	0.01-0.10	9	96	70-115	GRM 96.11.S1
peppers	0.01-5.0	28	92	75-114	ERC 97.17
peppers, green	0.01-1.0	17	102	82-115	GRM 95.20
plum	0.01-0.10	9	80	60-102	GRM 96.11.S1
potatoes	0.01-1.0	16	103	76-121	GRM 96.10.S1
prunes, dried plums	0.01-0.10	6	95	67-111	GRM 96.11.S1
sediment	0.05-0.35	39	77	66-98	GRM 94.21
snap beans	0.01-0.50	12	109	89-126	GRM 96.10.S1
snow peas	0.01-0.50	7	94	72-111	GRM 96.10.S1
sorghum fodder	0.01-1.0	17	98	67-117	GRM 97.05
sorghum forage	0.01-2.5	15	92	73-112	GRM 97.05.S1
sorghum grain and grain dust	0.01-2.5	29	102	75-123	GRM 97.05.S1
soya beans	0.01-0.50	10	112	91-137	GRM 96.10.S1
spinach	0.01-1.0	17	104	84-129	GRM 96.10
squash	0.01-0.10	6	89	70-112	GRM 96.10.S1
sweet corn forage	0.01-1.0	13	100	71-116	GRM 96.10.S1
sweet corn grain	0.01-1.0	16	98	64-126	GRM 96.10.S1
sweet corn stover	0.01-1.0	13	94	60-124	GRM 96.10.S1
tomato haulm	0.01-30	28	98	78-123	PA-RM-97-06
tomato juice	0.01-5.0	28	97	74-114	ERC 97.17
tomato purée	0.01-5.0	28	108	80-129	ERC 97.17
tomatoes	0.01-5.0	28	98	79-117	ERC 97.17
tomatoes	0.01-1.0	18	106	73-124	GRM 95.20
tomatoes	0.01-1.0	12	98	71-120	PA-RM-97-07
tomatoes, canned	0.01-5.0	28	99	81-117	ERC 97.17
water	0.0001-0.02	31	101	71-117	GRM 94.10
wheat	0.01-0.20	15	102	84-121	GRM 96.10.S1
wheat forage, hay and straw	0.01-1.0	29	93	66-119	GRM 96.10.S1
wine	0.01-5.0 mg/l	28	98	81-119	ERC 97.09

Stability of pesticide residues in stored analytical samples

The Meeting received information on the freezer storage stability of spinosyn residues in a range of commodities representing those in the supervised trials and feeding studies.

Fleeker *et al. (*1998) spiked blueberry homogenate with spinosad at 0.09 mg/kg and stored the samples at -20°C for 141 days. In the 4 separate tests 90%, 90%, 97% and 69% of the spiked spinosad remained.

Portions of untreated grape, pepper and strawberry samples in small polypropylene vessels were fortified with spinosyns A, D, K, B and N-demethyl-D at 0.1 mg/kg and stored at or below -18°C. Portions of wine in small glass vials were similarly fortified and stored (Khoshab, 2000a). Samples were analysed after various intervals up to approximately 18 months. On each occasion the method was tested with procedural recoveries but the results are unadjusted (Table 26). Residues were

generally stable. The calculated time for a 30% decrease in spinosyn D residues in wine was 12 months.

The rate of decrease and time for 30% loss of residue were calculated for each stability test by assuming a first-order rate (rate proportional to concentration). Where the calculated time for 30% decrease exceeded the duration of the test, the time is recorded as greater than the duration of the test, e.g. >18 months.

Table 26. Freezer storage stability of spinosyns in spiked grapes, peppers, strawberries and wine (Khoshab, 2000a).

Days	Spinosyn A		Spinosyn D		Spinosyn K		Spinosyn B		Spinosyn B of D	
	Conc, mg/kg [1]	Proc recov %	Conc, mg/kg	Proc recov %	Conc, mg/kg	Proc recov %	Conc, mg/kg	Proc recov %	Conc, mg/kg	Proc recov %
GRAPES										
0	0.087	93 92	0.084	92 81	0.086	92 82	0.104	97 92	0.103	95 89
98	0.096	88 87	0.090	91 85	0.098	86 88	0.099	83 84	0.097	82 82
202	0.095	87 88	0.087	87 85	0.092	85 85	0.093	88 86	0.092	85 85
571	0.085	86 82	0.060	85 83	0.085	85 81	0.082	92 91	0.070	95 94
Months for 30% decrease	>19		17		>19		>19		17	
PEPPERS										
0	0.094	94 93	0.094	94 94	0.095	94 94	0.096	99 97	0.095	96 96
101 [2]	0.12	93 159	0.12	89 156	0.12	98 156	0.12	103 162	0.12	97 159
205	0.099	90 93	0.094	89 94	0.094	87 89	0.092	86 89	0.092	85 87
574	0.092	88 91	0.069	85 88	0.095	94 93	0.085	87 86	0.082	86 85
Months for 30% decrease	>19		>19		>19		>19		>19	
STRAWBERRIES										
0	0.096	91 88	0.097	91 90	0.096	91 84	0.098	92 89	0.097	92 87
100	0.11	94 98	0.10	90 98	0.11	100 88	0.10	95 99	0.10	90 96
204	0.10	90 95	0.097	89 95	0.099	90 94	0.10	91 95	0.10	88 94
573	0.096	93 92	0.070	91 89	0.096	93 94	0.087	91 89	0.084	91 90
Months for 30% decrease	>19		>19		>19		>19		>19	
WINE										
0	0.11	107 103	0.11	107 107	0.11	106 104	0.11	111 110	0.11	109 108
99	0.14	115 107	0.14	114 106	0.15	117 110	0.15	119 107	0.15	115 108
203 [3]	0.12	106 115	0.11	101 115	0.11	100 114	0.028	27 37	0.029	27 38
572	0.097	98 98	0.072	94 92	0.10	100 99	0.10	104 103	0.10	105 103
Months for 30% decrease	>19		12		>19		>19		>19	

[1] The concentration at time 0 is the mean of 6 analyses and at later times the mean of 2.
[2] Results at 101 days for peppers are not included in the calculation because of an unacceptable procedural recovery.
[3] Results at 203 days for spinosyns B and B of D in wine are not included in the calculation because of unacceptable procedural recoveries.

Robb and Bormett (1996) tested the frozen storage stability of the spinosyns in spiked apples and juice stored at approximately -20°C. Spinosyns A and D were spiked together, and B, K and N-demethyl-D together. High-density polyethylene containers were used for apple samples and low density for the juice. Residues were stable for the periods tested. After 193 days apples were stored for one day at room temperature to simulate temperature conditions possible during shipping; no degradation of residues was observed. Robb and Rutherford (1996) tested the frozen storage stability of the residues in tomatoes using similar methods, and Phillips and Harris (1997) followed a similar procedure for almond kernels and hulls. Residues were stable for the periods tested. Phillips *et al.* (1996) tested stabilities in cabbages in the same way. Problems were experienced with low procedural recoveries on some occasions. The results of all the trials are shown in Table 27.

Table 27. Freezer storage stability of spinosyns in spiked apples, apple juice, tomatoes, almond kernels, almond hulls, cabbage and milk.

Days	Spinosyn A		Spinosyn D		Spinosyn K		Spinosyn B		Spinosyn B of D	
	Conc, mg/kg	Proc recov %	Conc, mg/kg	Proc recov %	Conc, mg/kg	Proc recov %	Conc, mg/kg	Proc recov %	Conc, mg/kg	Proc recov %
APPLES [1] Robb and Bormett, 1996										
0	0.091	90 93	0.089	89 90	0.098	86 88	0.080	85 78	0.080	82 78
28	0.085	90 87	0.084	89 86	0.096	90 87	0.076	87 87	0.073	84 84
90	0.087	87 88	0.086	92 93	0.096	92 85	0.079	80 84	0.075	78 82
194	0.091	90 92	0.087	86 88	0.097	92 93	0.086	77 82	0.083	78 83
Months for 30% decrease	>6		>6		>6		>6		>6	
APPLE JUICE [1]. Robb and Bormett, 1996										
0	0.082	85 83	0.081	84 81	0.081	86 82	0.068	72 66	0.072	75 70
41	0.086	89 87	0.083	87 84	0.085	86 88	0.081	82 84	0.079	80 83
71	0.081	93 92	0.079	91 80	0.079	88 87	0.074	77 69	0.072	76 69
92	0.092	85 90	0.088	82 88	0.087	89 89	0.081	79 78	0.079	80 78
Months for 30% decrease	>3		>3		>3		>3		>3	
TOMATOES (HDPE containers, -20°C) [2]. Robb and Rutherford, 1996										
0	0.092	93 91	0.093	95 91	0.087	84 91	0.081	87 82	0.081	85 82
34	0.092	92 95	0.091	91 94	0.076	82 82	0.081	79 84	0.080	80 85
99	0.088	90 90	0.087	90 88	0.082	80 79	0.066	73 70	0.068	73 73
183	0.092	108 109	0.088	106 106	0.092	92 94	0.075	78 75	0.074	77 74
336	0.098	105 105	0.091	104 104	0.094	101 100	0.087	81 86	0.081	80 83
Months for 30% decrease	>12		>12		>12		>12		>12	
ALMOND KERNELS (HDPE containers, -20°C) [2]. Phillips and Harris, 1997										
0	0.088	87 94	0.084	83 90	0.088	86 87	0.083	83 78	0.082	82 77
31	0.084	95 95	0.080	92 91	0.089	97 93	0.084	91 84	0.083	89 82
64	0.089	97 97	0.084	93 94	0.087	98 98	0.079	90 79	0.079	86 85
93	0.094	97 98	0.088	104 104	0.090	100 109	0.084	95 98	0.082	91 94
178	0.089	101 104	0.086	109 113	0.091	104 102	0.083	92 91	0.082	89 88
Months for 30% decrease	>6		>6		>6		>6		>6	
ALMOND HULLS (HDPE containers, -20°C) [2]. Phillips and Harris, 1997										
0 [3]	0.077	82 82	0.070	75 76	0.080	79 79	0.071	66 69	0.069	64 65
36 (16)	0.087	92 91	0.082	88 87	0.080	83 82	0.068	73 71	0.065	70 67
55 (35)	0.085	86 92	0.080	83 88	0.083	92 89	0.069	82 87	0.066	78 77
86 (66)	0.089	92 99	0.084	98 104	0.082	91 94	0.073	78 76	0.069	77 70
169 (149)	0.084	93 104	0.078	101 113	0.081	90 93	0.069	77 73	0.065	73 69
Months for 30% decrease	>6		>6		>5		>5		>5	
CABBAGE (HDPE containers, -20°C) [2]. Phillips et al., 1996, RES94098. [4]										
0	0.081	89	0.082	89	(0.071)	65 67	(0.068)	68 59	(0.067)	68 59
35	0.081	95 88	0.082	94 88	0.090	94 90	0.076	80 73	0.074	79 72
93	0.067	76 66	(0.065)	74 64	0.067	70 82	0.064	68 72	(0.061)	66 70
133	0.090	98 97	0.086	92 94	0.084	95	0.075	82 85	0.073	81 81
186	0.091	94 91	0.086	87 86	0.087	88 82	0.082	78 79	0.078	76 74
367	0.071	69 78	0.070	64 76	0.070	79 91	(0.067)	65 60	(0.062)	58 56
Months for 30% decrease	>12		>12		>12		>6		>6	
MILK (HDPE containers, -20°C) [2] Rutherford and Robb, 1996b, RES95126.										
0	0.097	104 104	0.093	101 100			0.103	102 103	0.100	99 101
41	0.089	100 97	0.086	97 93			0.093	93 90	0.089	92 89
136	0.080	97 101	0.076	94 96			0.082	90 97	0.076	90 95
Months for 30% decrease	>5		>5				>5		>5	

[1] The concentration at each time is the mean of 2 analyses
[2] The concentration at each time is the mean of 3 analyses

[3] Almond hulls: sampling times for spinosyns B, K and B of D are shown in parentheses
[4] Values in parentheses were not included in the estimate of storage stability because of poor procedural recoveries

Gardner and West (1994a) tested the storage stability of spinosyns A and D in spiked ground cotton seed at 0.1 mg/kg in polyethylene freezer cartons at -15°C to -20°C at intervals of 14-54 days, mainly about 50 days, in 17 separate tests without loss, and also showed that spinosyns A and D in cotton seed samples stored frozen in high-density polyethylene containers and in laminated cotton cloth bags were stable for the 9 months of the test (Table 28). Gardner *et al.* (1999) showed that the residues were still stable after 1 year.

Table 28. Freezer storage stability of spinosyns A and D in spiked cotton seed (Gardner and West, 1994a; Gardner *et al.,* 1999).

Days	Spinosyn A			Spinosyn D		
	HDPE [1]	PE-lam [2]		HDPE [1]	PE-lam [2]	
	Conc, mg/kg [3]	Conc, mg/kg [3]	Procedural recov %	Conc, mg/kg [3]	Conc, mg/kg [3]	Procedural recov %
0	0.075	0.073	77 85 80 76 74	0.072	0.064	78 80 71 72 72
36	0.075	0.079	82 79 90 90	0.066	0.073	70 67 81 83
98	0.074	0.079	91 89 94 86	0.065	0.077	81 81 86 78
212	0.094	0.081	97 97 88 89	0.085	0.075	88 92 82 84
283	0.096	0.092	102 98 96 96	0.098	0.095	105 99 97 97
366	0.092	0.091	98 98 93 97	0.088	0.088	91 94 88 94
Months for 30% decrease	>12	>12		>12	>12	

[1] HDPE (high-density polyethylene) freezer containers
[2] PE-laminated cotton cloth bags
[3] The concentration at each time is the mean of 2 analyses.

Phillips and Blakeslee (1997) fortified celery and spinach samples with a mixture of spinosyns A, D, B, K and B of D at a total spinosyn concentration of 0.5 mg/kg in HDPE bottles and stored them up to 202 days in a freezer at -20°C. Residues, measured by an immunoassay method, were stable (Table 29). Phillips *et al. (*1998a) fortified potato, and Robb *et al.* (1998) fortified maize grain and sweet corn forage and stover samples with 0.1 mg/kg spinosad (spinosyns A + D, 85 + 15) in HDPE containers for freezer storage at -20°C for 342 days. The residues, measured by an immunoassay method, were shown to be stable (Table 29).

Table 29. Freezer storage stability of spinosyns in potatoes, celery, spinach, maize grain, sweet corn forage and stover.

Days	Total spinosyns, mg/kg [1]	Proc recov %
POTATO, Phillips *et al*., 1998a		
0	0.108	112 119
28	0.082	105 117
31	0.075	96 98
55	0.075	100 101
97	0.075	104 102
191	0.076	109 123
342	0.072	98 112
Months for 30% decrease	>12	
CELERY, Phillips and Blakeslee, 1997		
0	0.33	63 69
1	0.34	68 66
4	0.32	63 59
7	0.32	62 72
14	0.35	75 74

Days	Total spinosyns, mg/kg [1]	Proc recov %
22	0.32	70 71
32	0.35	74 74
55	0.32	79
90	0.34	78 80
146	0.30	67 68
202	0.30	74 75
Months for 30% decrease	>7	
SPINACH, Phillips and Blakeslee, 1997		
0	0.34	70 71
1	0.33	66 67
4	0.33	68 66
7	0.33	69 70
14	0.33	69 64
22	0.34	67 68
32	0.37	81 76
55	0.32	72
90	0.36	80 74
146	0.31	72 74
202	0.32	78 73
Months for 30% decrease	>7	
MAIZE GRAIN, Robb *et al*., 1998		
0	0.103	108 106
28	0.099	102 100
97	0.090	107 99
191	0.094	101 110
342	0.091	99 95
Months for 30% decrease	>12	
SWEET CORN FORAGE, Robb *et al*., 1998		
0	0.099	97 99
28	0.080	77 88
97	0.085	84 88
191	0.103	112 114
342	0.099	105 97
Months for 30% decrease	>12	
SWEET CORN STOVER, Robb *et al*., 1998		
0	0.095	99 98
28	0.084 [2]	93 58
31	0.098	106 104
97	0.075	78 84
191	0.102	109 111
342	0.093	97 92
Months for 30% decrease	>12	

[1] The concentration at each time is the mean of 3 analyses, uncorrected for recoveries.
[2] This value disregarded because of problem with procedural recovery.

Spurlock-Brouwer *et al.* (2000) analysed 10 milk samples with incurred spinosad residues at approximately 0.1 mg/kg before and after freezer storage at intervals of 44 to 102 days and found an average loss of approximately 0.25% of the residue per day. They also tested 6 cream samples with incurred residues and found that spinosyn A residues were stable in freezer storage for the periods tested, 66 to 122 days.

Spurlock-Brouwer (1999) analysed samples of liver, kidney, muscle, subcutaneous and renal fat with incurred residues, then re-analysed them after storage at approximately -20°C for at least 6 months. The study was conducted with incurred residues because available fortification methods would denature the tissues. The residues were stable for the periods tested.

Table 30. Storage stability of incurred spinosad residues in animal tissues stored at -20°C (Spurlock-Brouwer, 1999). Each recorded value is the mean of 2 sample extractions.

Sample	Storage, months	Residue, mg/kg							
		spinosyn A		spinosyn D		spinosyn B		spinosyn B of D	
		initial	final	initial	final	initial	final	initial	final
Liver	7.5	0.455	0.442	0.066	0.068	0.099	0.099	0.030	0.030
Kidney	6.5	0.267	0.262	0.035	0.037	0.091	0.094	0.016	0.015
Muscle	6	0.082	0.095	0.013	0.015	<0.01	<0.01	<0.01	<0.01
SC fat	9	0.371	0.395	0.051	0.051	0.018	0.017	0.014	0.013
Renal fat	9	0.514	0.570	0.076	0.081	0.027	0.031	0.020	0.020

Definition of the residue

Spinosad is a mixture of spinosyns A and D. After it is used on crops the closely related compounds spinosyn B, spinosyn K and spinosyn B of D are formed, principally by photolysis. HPLC methods measure all these compounds separately. An immunoassay analytical method measures these spinosyns and some other metabolites also. Spinosyn A constitutes approximately 85% of the residue initially and in practice constitutes the main part of the spinosyn residue; in 482 of 624 cases (77%) in the residue trials spinosyn A constituted 70% or more of the measured residue. Spinosyn A is well correlated with the total residue (as measured by HPLC): total spinosyn residue = 1.206 × spinosyn A, $r^2 = 0.997$, n = 624, range = 0.01 to 5 mg/kg. Spinosyn D levels are typically only 10-20% of the spinosyn A levels but spinosyn A and spinosyn D together generally constitute more than 90% of the total spinosyn residue.

Spinosyns A and D were the main identifiable components of the residue in fat, muscle, kidney, liver and milk of goats dosed orally or treated dermally with spinosyns A and D.

In some trials the residue was measured by the immunoassay method; the residue so measured may be considered sufficiently close to the sum of spinosyn A and spinosyn D for the purpose of estimating maximum residue levels or dietary intakes.

The log P_{ow} values of 4 and 4.5 (pH 7) and the animal metabolism studies suggest that spinosyns A and D should be described as fat-soluble in body fat, but spinosad is incompletely partitioned into milk fat. In trials of the direct treatment of dairy cows described later, the residues in cream were 4.2 times those in milk (mean of 119 observations), and were 3-5 times those in the milk in the feeding study.

The Meeting was aware that national governments had already adopted the sum of spinosyn A and spinosyn D as a definition of the spinosad residue.

The Meeting recommended that the definition of the residue for compliance with MRLs and for the estimation of dietary intake should be the sum of spinosyn A and spinosyn D.

The Meeting recommended that spinosad should be described as fat-soluble for the determination of residues in meat, but not for residues in milk.

USE PATTERN

Information on registered uses made available to the Meeting is shown in Table **31**31 and 32.

Table 31. Registered uses of spinosad on crops.

Crop	Country	Form	Application				PHI, days
			Method[1]	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Alfalfa	Chile [12]	SC 480	foliar	0.060-0.072			7
Almonds	USA [12]	SC 240	foliar	0.070-0.18	0.0019-0.0047	[4]	14
Apple	Chile [12]	SC 480	foliar	0.060-0.072			14
Apple	Israel [12]	SC 480	foliar		0.0096		21
Apple	Japan [12]	SC 200	broadcast	0.60	0.010	3	3
Apple	USA [12]	SC 240	foliar	0.070-0.18	0.0025-0.0062	[4]	7
Avocado	Israel [12]	SC 480	foliar		0.0096		1
Avocado	Kenya [12]	SC 480	foliar		0.0096		21
Avocado	NZ [12]	SC 120	foliar		0.0048	4	3
Barley	USA [12]	SC 240	foliar	0.035-0.11		[9]	21 [10]
Barley	USA [12]	SC 480	foliar	0.050-0.11		[9]	21 [10]
Beans	Colombia [12]	SC 120	foliar	0.036-0.060			1
Beans	Kenya [12]	SC 480	foliar	0.12	0.012-0.024		1
Beans	Lebanon [12]	SC 480			0.036-0.048		1
Beans	Peru [12]	SC 120	foliar	0.012-0.024	0.003-0.006		1
Beans, dried	USA [12]	SC 240	foliar	0.053-0.11		[6]	28 [5]
Beans, succulent	USA [12]	SC 240	foliar	0.053-0.11		[4]	3 [5]
Brassica alboglabra	Malaysia	SC 25	broadcast	0.050	0.011	2	3
Brassica chinensis	Malaysia	SC 25	broadcast	0.025	0.055	2	3
Brassica oleracea	Malaysia	SC 25	broadcast	0.025	0.0055	2	3
Brassica rapa	Malaysia	SC 25	broadcast	0.025	0.055	2	3
Brassica vegetables	NZ [12]	SC 120	foliar	0.048			3
Brassicas	China	SC 25 ?	broadcast	0.025-0.13		2	1
Brassicas	Cyprus	SC 480	foliar	0.060-0.14	0.012-0.014		1
Broccoli	Australia [12]	SC 120	foliar (	0.048-0.096			3
Broccoli	Costa Rica [12]	SC 120	foliar	0.012-0.024		3	1
Broccoli	Guatemala [12]	SC 120	foliar	0.012-0.024		3	1
Broccoli	Honduras [12]	SC 120	foliar	0.012-0.024		3	1
Broccoli	Mexico	SC 480	foliar	0.012-0.024	0.0013-0.008	3	1
Broccoli	Paraguay [12]	SC 480	foliar	0.012-0.024			1
Brussels sprouts	Australia [12]	SC 120	foliar (	0.048-0.096			3
Buckwheat	USA [12]	SC 240	foliar	0.035-0.11		[9]	21 [10]
Buckwheat	USA [12]	SC 480	foliar	0.050-0.11		[9]	21 [10]
Cabbage	Australia [12]	SC 120	foliar (	0.048-0.096			3
Cabbage	Costa Rica [12]	SC 120	foliar	0.012-0.024		3	1
Cabbage	Guatemala [12]	SC 120	foliar	0.012-0.024		3	1
Cabbage	Honduras [12]	SC 120	foliar	0.012-0.024		3	1
Cabbage	Indonesia [12]	SC 25	broadcast	0.015-0.025	0.0014-0.0023		
Cabbage	Israel [12]	SC 480	foliar	0.072			7
Cabbage	Japan [12]	WG 250	broadcast	0.30	0.010	3	3
Cabbage	Kenya [12]	SC 480	foliar	0.12	0.012-0.024		3
Cabbage	Korea	SC 100	broadcast	0.038	0.0025	5	3
Cabbage	Peru	SC 240	foliar		0.006-0.0072	3	1

Crop	Country	Form	Application				PHI, days
			Method[1]	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Cabbage	Philippines	SC 25	broadcast	0.025	0.004	4	7
Cabbage	Uruguay [12]	SC 240	foliar		0.006-0.0072		1
Cabbage	Vietnam	SC 25	broadcast	0.020-0.025	0.006-0.0078	2	1
Cauliflower	Australia [12]	SC 120	foliar (	0.048-0.096			3
Cauliflower	Peru [12]	SC 120	foliar	0.012	0.003		1
Chard	Peru	SC 240	foliar		0.006-0.0072	3	1
Chard	Uruguay [12]	SC 240	foliar		0.006-0.0072		1
Chinese cabbage	Australia [12]	SC 120	foliar (	0.048-0.096			3
Chinese cabbage	Japan [12]	WG 250	broadcast	0.30	0.010	3	3
Chinese cabbage	Korea	WG 100	broadcast	0.038	0.0025	5	7
Chinese kale	Thailand	SC 120	broadcast	0.12-0.24	0.012-0.024	2	3
Citrus	Cyprus	SC 480	foliar	0.29-0.70	0.0096-0.014		
Citrus	Kenya [12]	SC 480	foliar		0.0096		21
Citrus	Korea	WG 100	broadcast		0.005	5	14
Citrus	Lebanon [12]	SC 480			0.006		7
Citrus	Peru [12]	SC 120	foliar		0.003-0.006		1
Citrus	UAE	SC 480	foliar		0.0072		7
Citrus	USA [12]	SC 240	foliar	0.070-0.18		[4]	1
Cole crops	USA [12]	SC 240	foliar	0.026-0.18		[4]	1
Corm vegetables	USA [12]	SC 240	foliar	0.053-0.11		[11]	7
Corm vegetables	USA [12]	SC 240	foliar	0.053-0.11		[11]	7
Cotton	Argentina [12]	SC 480	foliar	0.072-0.086	0.090-0.11	1	
Cotton	Argentina [12]	SC 480	foliar	0.019	0.024	3	
Cotton	Australia [12]	EO? 125	foliar (	0.075-0.10		3	28 [14]
Cotton	Bolivia	SC 480	foliar	0.072-0.086	0.090-0.11	1	
Cotton	Bolivia	SC 480	foliar	0.019	0.024	3	
Cotton	Brazil [12]	SC 480	foliar	0.012-0.072			7
Cotton	Cent Amer [12]	SC 480	foliar	0.012-0.072			7
Cotton	Colombia [12]	SC 120	foliar	0.012-0.036			28
Cotton	Costa Rica [12]	SC 480	foliar	0.036-0.060			0
Cotton	Guatemala [12]	SC 480	foliar	0.036-0.060			0
Cotton	Honduras [12]	SC 480	foliar	0.036-0.060			0
Cotton	Mexico	SC 480	foliar	0.036-0.060	0.009-0.030		28
Cotton	Nicaragua [12]	SC 480	foliar	0.036-0.060			0
Cotton	Paraguay [12]	SC 480	foliar	0.036-0.060			28
Cotton	Peru [12]	SC 120	foliar	0.006-0.024	0.0015-0.006		28
Cotton	USA [12]	SC 480	foliar	0.050-0.10		[4]	28
Cucumber	Israel [12]	SC 480	foliar		0.0096	3	7
Cucumber	Korea	WG 100	broadcast [3]	0.075	0.005	5	2
Cucumber	Lebanon [12]	SC 480			0.036-0.048		1
Cucumber	Mexico	SC 480	foliar	0.024-0.048			3
Cucumber	USA [12]	SC 240	foliar	0.070-0.14		[4]	1
Cucurbits	Peru [12]	SC 120	foliar	0.012-0.024	0.003-0.006		1
Cucurbits, except cucumbers	USA [12]	SC 240	foliar	0.070-0.14		[4]	3
Egg plant	Japan [12]	WG 250	broadcast [2]	0.30	0.010	2	1
Fruit, tropical	USA [12]	SC 240	foliar	0.070-0.18		[4]	1
Fruiting vegetables	USA [12]	SC 240	foliar	0.026-0.14		[4]	1

Crop	Country	Form	Application				PHI, days
			Method[1]	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Fruiting vegetables	USA [12]	SC 240	foliar	0.053-0.18		[4]	1
Grain Amaranth	USA [12]	SC 480	foliar	0.050-0.11		[4]	7 [8]
Grapes	Chile [12]	SC 480	foliar	0.060-0.072			14
Grapes	Cyprus	SC 480	foliar	0.036-0.072	0.0072		7
Grapes	Israel [12]	SC 480	foliar		0.0048-0.0096		7
Grapes	Lebanon [12]	SC 480			0.0036-0.0048		7
Grapes	UAE	SC 480	foliar		0.0048-0.0072		7
Japanese radish	Japan [12]	WG 250	broadcast	0.30	0.010	3	7
Kiwifruit	NZ [12]	SC 120	foliar		0.0048		120
Leafy vegetables	USA [12]	SC 240	foliar	0.026-0.18		[4]	1
Lettuce	Australia [12]	SC 120	foliar (	0.048-0.096			3
Lettuce	Japan [12]	WG 250	broadcast [2]		0.010	3	3
Lettuce	Kenya [12]	SC 480	foliar	0.12	0.012-0.024		3
Lettuce	Peru	SC 240	foliar		0.006-0.0072	3	1
Lettuce	Uruguay [12]	SC 240	foliar		0.006-0.0072		1
Maize	Bolivia	SC 480	foliar	0.029	0.036	1	
Maize	Brazil [12]	SC 480	foliar	0.018-0.048			7
Maize	Cent Amer [12]	SC 480	foliar	0.018-0.048			7
Maize	Israel [12]	SC 480	foliar	0.048-0.072			1
Maize	Paraguay	SC 480	foliar	0.029	0.036-0.048	2	
Maize	Peru [12]	SC 120	foliar	0.012	0.003		14
Maize	USA [12]	SC 240	foliar	0.050-0.11		[6]	28 [7]
Maize	USA [12]	SC 480	broadcast or directed spray	0.035-0.11		[6]	28 [7]
Maize	Venezuela [12]	SC 480		0.048-0.096			28
Mango	Kenya [12]	SC 480	foliar		0.0096		21
Melon	Costa Rica [12]	SC 480	foliar	0.031			1
Melon	Guatemala [12]	SC 480	foliar	0.031			1
Melon	Honduras [12]	SC 480	foliar	0.031			1
Melon	Israel [12]	SC 480	foliar	0.096			7
Melon	Mexico	SC 480	foliar	0.024-0.048			3
Millet, Pearl	USA [12]	SC 480	foliar	0.050-0.11		[4]	7 [8]
Millet, Proso	USA [12]	SC 480	foliar	0.050-0.11		[4]	7 [8]
Milo	USA [12]	SC 480	foliar	0.050-0.11		[4]	7 [8]
Nectarine	Chile [12]	SC 480	foliar	0.060-0.072	0.0072-0.0096		14
Nectarine	Israel [12]	SC 480	foliar		0.0072-0.0096		7
Oats	USA [12]	SC 240	foliar	0.035-0.11		[9]	21 [10]
Oats	USA [12]	SC 480	foliar	0.050-0.11		[9]	21 [10]
Onion	Israel [12]	SC 480	foliar	0.072-0.096			
Onion	Kenya [12]	SC 480	foliar	0.12	0.012-0.024		1
Passion fruit	Kenya [12]	SC 480	foliar	0.14	0.014		1
Peach	Chile [12]	SC 480	foliar	0.060-0.072	0.0072-0.0096		14
Peach	Japan [12]	SC 200	broadcast		0.010	3	3
Pear	Israel [12]	SC 480	foliar		0.0096		21
Peas	Kenya [12]	SC 480	foliar	0.12	0.012-0.024		1
Peas, dried	USA [12]	SC 240	foliar	0.053-0.11		[6]	28 [5]
Peas, succulent	USA [12]	SC 240	foliar	0.053-0.11		[4]	3 [5]
Peppers	Australia [12]	SC 120	foliar (	0.048-0.096			1
Peppers	Costa Rica [12]	SC 120	foliar	0.036-0.060			1

Crop	Country	Form	Application				PHI, days
			Method[1]	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Peppers	Guatemala [12]	SC 120	foliar	0.036-0.060			1
Peppers	Honduras [12]	SC 120	foliar	0.036-0.060			1
Peppers	Israel [12]	SC 480	foliar		0.0096		1
Peppers	Japan [12]	WG 250	broadcast [2]		0.010	2	1
Peppers	Kenya [12]	SC 480	foliar	0.19-0.24	0.019-0.048		3
Peppers	Mexico	SC 480	foliar	0.036-0.060			1
Peppers	Paraguay [12]	SC 480	foliar	0.036-0.060			1
Peppers	Peru	SC 240	foliar	0.012-0.024	0.0072	3	1
Peppers	Uruguay [12]	SC 240	foliar		0.0072		1
Pistachios	USA [12]	SC 240	foliar	0.070-0.18	0.0019-0.0047	[4]	14
Plums	Israel [12]	SC 480	foliar		0.0072-0.0096		7
Pome fruit	NZ [12]	SC 120	foliar		0.0048		3
Popcorn	USA [12]	SC 240	foliar	0.050-0.11		[6]	28 [7]
Popcorn	USA [12]	SC 480	broadcast or directed spray	0.035-0.11		[6]	28 [7]
Potato	Brazil [12]	SC 480	foliar	0.16-0.20			3
Potato	Cent Amer [12]	SC 480	foliar	0.16-0.20			3
Potato	Chile [12]	SC 480	foliar	0.048-0.072			7
Potato	Colombia [12]	SC 120	foliar	0.036-0.060			1
Potato	Cyprus	SC 480	foliar	0.12-0.36	0.024-0.036		0
Potato	Israel [12]	SC 480	foliar	0.048-0.096			14
Potato	Korea	WG 100	broadcast		0.005	5	7
Potato	Lebanon [12]	SC 480		0.24-0.34			0
Potato	Turkey [12]	SC 480	foliar		0.0048		1
Potato	UAE	SC 480	foliar		0.0048-0.024		1
Rye	USA [12]	SC 240	foliar	0.035-0.11		[9]	21 [10]
Rye	USA [12]	SC 480	foliar	0.050-0.11		[9]	21 [10]
Snowpeas	Kenya [12]	SC 480	foliar	0.12	0.012-0.024		3
Sorghum	USA [12]	SC 480	foliar	0.050-0.11		[4]	7 [8]
Soya beans	Argentina [12]	SC 480	foliar	0.024	0.030	1	
Soya beans	Bolivia	SC 480	foliar	0.024	0.030	1	
Soya beans	Brazil [12]	SC 480	foliar	0.006-0.024			9
Soya beans	Cent Amer [12]	SC 480	foliar	0.006-0.024			9
Soya beans	Paraguay	SC 480	foliar	0.036	0.045-0.060	2	
Soya beans	USA [12]	SC 480	foliar	0.035-0.070		[6]	28 [5]
Spinach	Australia [12]	SC 120	foliar (	0.048-0.096			3
Spinach	Peru	SC 240	foliar		0.006-0.0072	3	1
Spinach	Uruguay [12]	SC 240	foliar		0.006-0.0072		1
Stone fruit [13]	USA [12]	SC 240	foliar	0.070-0.14	0.0019-0.0037	[4]	7, 14
Strawberries	Kenya [12]	SC 480	foliar	0.072-0.14	0.0096-0.014		2
Strawberry	Israel [12]	SC 480	foliar	0.096			1
Strawberry	UAE	SC 480	foliar		0.014-0.019		1-2
Sweet corn	Australia [12]	SC 120	foliar (	0.048-0.096			
Sweet corn	USA [12]	SC 240	foliar	0.050-0.11		[4]	1
Tea	Japan [12]	SC 200	broadcast		0.010	2	7
Teosinte	USA [12]	SC 480	broadcast or directed spray	0.035-0.11		[6]	28 [7]
Tomato	Argentina [12]	SC 480	foliar	0.072-0.11	0.0072	3	3
Tomato	Australia [12]	SC 120	foliar (	0.048-0.096			1
Tomato	Brazil [12]	SC 480	foliar	0.048-0.060			3

Crop	Country	Form	Application				PHI, days
			Method[1]	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Tomato	Cent Amer [12]	SC 480	foliar	0.048-0.060			3
Tomato	Chile [12]	SC 480	foliar	0.058-0.072	0.0048-0.0072		1
Tomato	Costa Rica [12]	SC 120	foliar	0.036-0.060			1
Tomato	Cyprus	SC 480	foliar	0.060-0.17	0.012-0.017		1
Tomato	Guatemala [12]	SC 120	foliar	0.036-0.060			1
Tomato	Honduras [12]	SC 120	foliar	0.036-0.060			1
Tomato	Israel [12]	SC 480	foliar	0.096			3
Tomato	Japan [12]	WG 250	broadcast [2]		0.010	2	1
Tomato	Kenya [12]	SC 480	foliar	0.19-0.24	0.019-0.048		3
Tomato	Korea	WG 100	broadcast [3]	0.075	0.005	5	2
Tomato	Lebanon [12]	SC 480			0.036-0.048		1
Tomato	Mexico	SC 480	foliar	0.036-0.060			1
Tomato	NZ [12]	SC 120	foliar	0.048			3
Tomato	Paraguay [12]	SC 480	foliar	0.036-0.060			1
Tomato	Peru	SC 240	foliar	0.012-0.024	0.0072	3	1
Tomato	Peru [12]	SC 120	foliar	0.012-0.024	0.003-0.006		1
Tomato	UAE	SC 480	foliar		0.036-0.048		1
Tomato	Uruguay [12]	SC 240	foliar		0.0072		1
Triticale	USA [12]	SC 240	foliar	0.035-0.11		[9]	21 [10]
Triticale	USA [12]	SC 480	foliar	0.050-0.11		[9]	21 [10]
Tuber vegetables	USA [12]	SC 240	foliar	0.053-0.11		[11]	7
Vegetables	UAE	SC 480	foliar		0.012-0.036		1
Vegetables, leafy	Cyprus	SC 480	foliar	0.060-0.14	0.012-0.014		1
Watermelon	Korea	WG 100	broadcast		0.005	5	14
Watermelon	Mexico	SC 480	foliar	0.024-0.048			3
Wheat	USA [12]	SC 240	foliar	0.035-0.11		[9]	21 [10]
Wheat	USA [12]	SC 480	foliar	0.050-0.11		[9]	21 [10]
Zucchini	Mexico	SC 480	foliar	0.024-0.048			3

[1] (aerial application
[2] field or glasshouse use
[3] glasshouse use
[4] max total application 0.50 kg ai/ha
[5] do not feed forage or hay to meat or dairy animals
[6] max total application 0.21 kg ai/ha
[7] PHI 28 days for grain or fodder, 7 days for forage
[8] PHI 7 days for grain or fodder, 14 days for forage
[9] max total application 0.31 kg ai/ha
[10] PHI 21 days for grain or straw, 14 days for forage or hay
[11] Max. total application 0.37 kg ai/ha
[12] Label or label copy provided
[13] Stone fruit, USA. PHI 7 days for cherries, plums and prunes. PHI 14 days for peaches, nectarines and apricots.
[14] Cotton, Australia. Do not allow livestock to graze treated cotton crop, stubble or gin trash.

US labels for spinosad list the crops included in crop groups as follows.

Citrus: including but not limited to: grapefruit, lemons, limes, oranges and tangerines.

Cole crops: including but not limited to: broccoli, broccoli raab, Brussels sprouts, cabbage, cauliflower, cavalo, Chinese broccoli, Chinese cabbage (bok choy), Chinese cabbage (napa), Chinese mustard cabbage (gai choi), collards, kale, kohlrabi, mizuna, mustard greens, mustard spinach, rape greens and turnip greens.

Cucurbit crops: including but not limited to: cucumber, edible gourds, muskmelons (cantaloupe, honeydew, etc), pumpkin, summer squash, watermelon and winter squash.

Fruiting vegetable crops: egg plant, ground cherry, pepino, pepper, tomatillo and tomato.

Leafy vegetables: including but not limited to: arugula, celery, chervil, cilantro, corn salad, cress, dandelion, dock, edible chrysanthemum, endive, fennel, garden purslane, head lettuce, leaf lettuce, parsley, radicchio, rhubarb, spinach, Swiss chard, turnip greens and water cress.

Tuber and corm vegetables: including but not limited to: cassava, chayote root, Chinese artichoke, ginger, Jerusalem artichoke, potatoes, sweet potatoes, turmeric and yams.

Stone fruit: including but not limited to: apricots, cherries, nectarines, peaches, plums and prunes.

Succulent and dried beans and peas including but not limited to: Adzuki bean, blackeyed pea, chickpea, cowpea, crowder pea, edible-pod pea, English pea, fava bean, field bean, field pea, Garbanzo bean, garden pea, green pea, kidney bean, lentil, lima bean, lupins, mung bean, navy bean, pigeon pea, pinto bean, runner bean, snap bean, snow pea, sugar snap pea, tepary bean , wax bean and yardlong bean.

Tropical fruit: acerola, atemoya, avocado, biriba, black sapote, canistel, cherimoya, custard apple, feijoa, guava, ilama, jaboticaba, longan, lychee, mamey sapote, mango, papaya, passionfruit, pulasan, rambutan, sapodilla, soursop, Spanish lime, star apple, starfruit, sugar apple, wax jambu and white sapote.

Table 32. Registered uses of spinosad for external treatment of animals.

Animal	Country	Form	Application			whp slaughter, days	whp milk, days
			Method	Rate	Conc.		
Beef cattle	USA [1]	SC 25	pour-on	2 mg ai/kg bw	25 g ai/l		
Dairy cattle, non-lactating	USA [1]	SC 25	pour-on	2 mg ai/kg bw	25 g ai/l		
Dairy cattle, lactating	USA [1]	SC 25	pour-on	2 mg ai/kg bw	25 g ai/l		
Cattle, beef and dairy	USA [1]	SC 25	spray	0.38-0.76 g ai/animal	400 mg ai/l		
Sheep	Australia [1]	25	jetting	0.5 l fluid per month of wool growth	25 mg ai/l	0	[2]
Sheep	Australia [1]	25	wound dressing	Apply 1-2 l on wound	25 mg ai/l	0	[2]

whp: withholding period
[1] Label or label copy provided.
[2] Do not use on female sheep producing milk.

RESIDUES FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials of spinosad on the following crops.

Fruits	Table 34	citrus, Japan, USA
	Table 35	citrus, Argentina
	Table 36	apples, France, Italy, Japan, Spain, USA
	Table 37	stone fruit, USA
	Table 38	stone fruit, Chile, Japan
	Table 39	grapes, France, Italy, Spain
	Table 40	grapes, Chile
	Table 41	strawberries, Belgium, Greece, Italy, Spain, UK

	Table 42	blueberries, USA
	Table 43	kiwifruit, New Zealand
Vegetables	Table 44	Brassica vegetables, Australia, New Zealand
	Table 45	cabbage and Chinese cabbage, Japan
	Table 46	Brassica vegetables, USA
	Table 47	cucurbits, USA
	Table 48	tomatoes, Australia, New Zealand
	Table 49	tomatoes, Argentina, Brazil
	Table 50	tomatoes, Greece, Italy, Spain, UK
	Table 51	tomatoes, Mexico, USA
	Table 52	peppers, USA
	Table 53	sweet peppers, Australia, Greece, Italy, Mexico, Spain, UK
	Table 54	sweet corn, USA
	Table 55	egg plant, Japan
	Table 55	lettuce, Australia
	Table 57	leafy vegetables, USA
	Table 58	leafy vegetables, celery, USA
	Table 59	legume vegetables, USA
	Table 60	navy beans, Australia
	Table 61	soya beans, USA
	Table 62	soya beans, Argentina, Brazil
	Table 63	potatoes, Brazil, USA
	Table 64	Japanese radish, Japan
Cereals	Table 65	maize, sorghum, wheat, USA
	Table 66	maize, Argentina, Brazil
Tree nuts	Table 67	almonds, USA
Oilseeds	Table 68	cotton seed, Australia, USA
Animal feeds	Table 69	cereal forage and fodder, USA
	Table 70	cotton trash, Australia
	Table 71	navy bean forage, Australia
	Table 72	almond hulls, USA

Trials were generally well documented with full laboratory and field reports. Laboratory reports included method validation, with batch recoveries at spiking levels similar to those occurring in samples from the supervised trials. Dates of analyses were also provided. Field reports provided data on the sprayers used and their calibration, plot size, residue sample size and sampling dates.

Where residues were not detected, they are recorded in the Tables as below the limit of quantification (LOQ), e.g. <0.01 mg/kg. Residue data, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOQ, to 1 significant figure. Although trials included control plots, no control data are recorded except where residues in control samples exceeded the LOQ; these residues are prefixed with a "c". Residues are recorded uncorrected for percentage recoveries in most cases. In some trials, for example on peppers in Spain in 1997-98, there is no clear statement whether results are adjusted for recoveries or not.

The conditions of the supervised residue trials are shown in Table 33. Most trials were not replicated. US trials were generally on single plots with 2 independent random field samples per sampling, and European and Australian trials generally on single plots with a single random sample per sampling. South American trials were generally on 3 replicate plots with a sample from each plot per sampling.

Periods of freezer storage between sampling and analysis were recorded for all trials and were within the acceptable proven stability period of 1 year for many commodities except in a few cases. Excessive freezer storage periods are noted.

Supervised trials on the direct treatment of animals were reported from Australia and the USA. Trials on sheep and dairy cattle were well described with trial conditions comparable to GAP or proposed GAP.

Feeding studies were provided for dairy cows and laying hens.

Table 33. Sprayers, plot sizes and sample sizes in the spinosad supervised trials on crops.

Crop	Country	Year	Sprayer	Plot size	Sample size
almonds	USA	1996	airblast	220-390 m^2	3-10 kg
apple	France	1999	backpack, airblast	32-120 m^2	24 fruits
apple	Italy	1999	backpack, spraygun	68-94 m^2	24 fruits
apple	Spain	1998-9	knapsack, motorpump backpack	40-50 m^2	16-24 fruits
apple	USA	1995	tractor airblast, backpack mistblower	71-595 m^2	24-32 fruits
blueberries	USA	1998			1-1.5 kg
broccoli	Australia	1997	precision gas sprayer	12-48 m^2	
broccoli	USA	1995	backpack with boom, tractor mounted boom	45-204 m^2	12 heads
Brussels sprouts	Australia	1997	precision gas sprayer	50 m^2	
cabbage	USA	1995	backpack with boom, tractor mounted boom	45-124 m^2	12 heads
cauliflower	Australia and NZ	1996-7	precision gas sprayer	12-15 m^2	
celery	USA	1996	backpack	75-100 m^2	12 plants
cherries	USA	1997	airblast	160-270 m^2	1-2 kg
cotton	Argentina	1996-7	backpack	100-130 m^2	1-2 kg
cotton	Australia	1994,96	tractor mounted boom, precision sprayer, spinning disc	90-135 m^2	
cotton	Brazil	1994	CO_2 backpack	21-180 m^2	
cotton	USA	1993	tractor mounted compressed air, knapsack compressed air	70-680 m^2	1-6 kg
cucumber	USA	1997	backpack with boom, tractor mounted boom	80-340 m^2	0.6-5 kg
grapefruit	USA	1996	airblast	110-840 m^2	5-10 kg
grapes	France	1997-8	mistblower	80-230 m^2	0.6-1 kg
grapes	Italy	1997-8	motorpump backpack, plot sprayer	90-150 m^2	1-2 kg
grapes	Spain	1997-8	motorpump backpack	50-110 m^2	1 kg
head lettuce	USA	1996	backpack with boom	85-93 m^2	12 plants
kiwifruit	NZ	1996-9	airblast, handgun	15 m^2	
leaf lettuce	USA	1996	backpack sprayer with boom	75-100 m^2	12 plants
lemon	USA	1996-7	airblast	350-540 m^2	3-5 kg
lettuce	Australia	1998	precision sprayer	45-70 m^2	12 lettuce
lettuce	USA	1996	CO_2 backpack sprayer	74-93 m^2	12 heads
maize	Argentina	1999	CO_2 backpack sprayer	24 m^2	2 kg
maize	Brazil	1995	CO_2 backpack sprayer	72-108 m^2	
maize	USA	1997	backpack with boom, tractor mounted boom	90-150 m^2	12 areas
muskmelon	USA	1997	backpack with boom, tractor mounted boom	84-335 m^2	3-30 kg
mustard greens	USA	1995	backpack with boom	45-289 m^2	20-60 plants, 1.5-3 kg
navy beans	Australia	1995		22-30 m^2	
nectarine	Chile	1999	airblast	360-810 m^2	2 kg
orange	USA	1996-7	airblast	220-700 m^2	3-8 kg
peach	USA	1997	airblast	140-230 m^2	24 fruit
peppers	Australia	1997	precision gas sprayer	18-30 m^2	
peppers	Italy	1997-8	plot sprayer	16-40 m^2	1 kg, 12 fruit
peppers	Spain	1997-8	motorpump backpack	8-40 m^2	8-12 fruit
peppers	UK	1997-8	plot sprayer	13 m^2	12 fruit
peppers	USA	1995	backpack with boom, tractor mounted boom	41-120 m^2	1-3 kg
plum	USA	1997	airblast	140-250 m^2	24 fruit min
potato	Brazil	1995-6	CO_2 backpack	36-40 m^2	2 kg
potato	USA	1997	CO_2 backpack, tractor mounted CO_2 sprayer, tractor powered pump	30-124 m^2	2-5-3.5 kg

Crop	Country	Year	Sprayer	Plot size	Sample size
prune	USA	1997	airblast	160-210 m^2	24 fruit min
snap beans	USA	1997	backpack, tractor mounted	56-120 m^2	1.3 kg
snow peas	USA	1997	backpack, tractor mounted	90-120 m^2	1.3 kg
sorghum	USA	1997	backpack with boom, tractor mounted boom	93-1300 m^2	12 plants
soya beans	Argentina	1995-6	CO_2 backpack	16-42 m^2	1-2 kg
soya beans	Brazil	1994-5	CO_2 backpack	28-72 m^2	
soya beans	USA	1997	tractor mounted, backpack	48-93 m^2	1.3 kg
spinach	USA	1996	backpack with boom, tractor mounted boom, CO_2 backpack	56-120 m^2	12-24 plants
strawberry	Belgium	1998	boom spray	24 m^2	1.2 kg
strawberry	Italy	1999	spray gun, motorpump backpack, knapsack	20-63 m^2	1-2 kg
strawberry	Spain	1998-9	compressed air sprayer	10-22 m^2	0.5-1.5 kg
strawberry	UK	1999	compressed air sprayer	10 m^2	1 kg
summer squash	USA	1997	backpack with boom, tractor mounted boom	84-120 m^2	1.5-5 kg
sweet corn	USA	1997	tractor mounted boom , backpack with boom	75-250 m^2	12 ears, 12 stalks
tomato	Argentina	1996-7	CO_2 backpack	7-640 m^2	2 kg
tomato	Australia	1996-7	precision gas sprayer	10-60 m^2	20 fruit
tomato	Brazil	1995-6	CO_2 backpack	6-14 m^2	2 kg
tomato	Greece	1998	precision gas sprayer	14-16 m^2	2 kg
tomato	Italy	1997-8	spray gun	13-46 m^2	1 kg, 24 fruit
tomato	Spain	1997-8	motorpump backpack	8-44 m^2	1 kg, 12 fruit
tomato	UK	1997-8	plot sprayer	13-21 m^2	1.4 kg, 12 fruit
tomato	USA	1995-6	tractor mounted boom, backpack with boom, CO_2 backpack	41-200 m^2	12-24 fruit
wheat	USA	1997	tractor mounted boom	140-230 m^2	12 areas

Table 34. Spinosad residues in citrus fruits from supervised trials in Japan and the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Japan, 1995 (Mandarin)	WG 200	0.60	0.01	6000	g 2 [5]	21 28 21 28	p 0.09 p 0.05 f <0.01 f <0.01	p <0.01 p <0.01 f <0.01 f <0.01			GHF-P-1683
Japan, 1996 (Mandarin)	WG 200	0.60	0.01	6000	2	14 21 28 14 21 28	p <0.01 p <0.01 p <0.01 f <0.01 f <0.01 f <0.01	p <0.01 p <0.01 p <0.01 f <0.01 f <0.01 f <0.01			GHF-P-1682
USA (AZ), 1996 (Marsh Ruby grapefruit)	SC 480	0.070 +0.10 +0.15 +0.18		500	4	1 4				<u>0.021</u> 0.018	RES96023 AZ22

Country, year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
USA (CA), 1996 (Ruby Red grapefruit)	SC 480	0.070 +0.10 +0.15 +0.18		3700	4	1 4 7 14				0.013 0.012 <0.01 <0.01	RES96023 CA19
USA (FL), 1996 (Flame grapefruit)	SC 480	0.067 +0.10 +0.15 +0.18		3600 +3700 +3800 +4200	4	1 4				0.086 0.036	RES96023 FL11
USA (FL), 1996 (Ruby Red grapefruit)	SC 480	0.070 +0.10 +0.15 +0.18		190	4	1 4	0.16 0.072	0.025 0.011	0.19 0.091	0.13 0.094	RES96023 FL09
USA (FL), 1996 (White Marsh grapefruit)	SC 480	0.073 +0.10 +0.16 +0.19		490	4	1 4	0.051	0.01	0.061	0.063 0.044	RES96023 FL10
USA (TX), 1996 (Henderson Rio Red grapefruit)	SC 480	0.070 +0.10 +0.15 +0.18		3600	4	1 4				0.030 0.020	RES96023 TX13
USA (AZ), 1996 (Limonera lemons)	SC 480	0.14 +0.21 +0.30 +0.36		7400 +7500 +7200 +7200	4	1 4 7 14				0.048 0.01 0.01 <0.01	RES96023 AZ24
USA (AZ), 1996 (Lisbon lemons)	SC 480	0.070 +0.10 +0.15 +0.18		190	4	1 4				0.14 0.12	RES96023 AZ23
USA (CA), 1996 (Lisbon lemons)	SC 480	0.070 +0.10 +0.15 +0.18		460	4	1 4	0.021	<0.01	0.026	0.033 0.023	RES96023 CA20
USA (CA), 1996 (Lisbon lemons)	SC 480	0.070 +0.10 +0.15 +0.18		3800	4	1 4	0.037 0.023	<0.01 <0.01	0.051 0.029	0.056 0.046	RES96023 CA21
USA (FL), 1996 (Eureka lemons)	SC 480	0.075 +0.10 +0.15 +0.19		3900	4	1 4				0.056 0.035	RES96023 FL12

Country, year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
USA (CA), 1996 (Attwood oranges)	SC 480	0.070 +0.10 +0.15 +0.18		470	4	1 4 o [3] 1 4 p [4] 1 4				<u>0.046</u> 0.022 <0.01 <0.01 0.10 0.052	RES96023 CA17
USA (CA), 1996 (Cutter Valencia oranges)	SC 480	0.070 +0.10 +0.15 +0.18		3700	4	1 4 7 14				<u>0.01</u> <0.01 <0.01 <0.01	RES96023 CA16
USA (CA), 1996 (Navel oranges)	SC 480	0.070 +0.10 +0.15 +0.18		3700	4	1 4 o [3] 1 4 p [4] 1 4				<u>0.017</u> 0.01 <0.01 <0.01 0.021 0.035	RES96023 CA18
USA (CA), 1996 (Washington Navel oranges)	SC 480	0.070 +0.10 +0.15 +0.18		190	4	1 4				<u>0.11</u> 0.060	RES96023 CA15
USA (FL), 1996 (Ambersweet oranges)	SC 480	0.070 +0.10 +0.15 +0.18		190	4	1 4				<u>0.044</u> 0.033	RES96023 FL02
USA (FL), 1996 (Hamlin oranges)	SC 480	0.070 +0.10 +0.15 +0.18		480	4	1 4 o [3] 1 4 p [4] 1 4	<u>0.11</u> 0.05 <0.01 <0.01 0.35 0.18	<u>0.016</u> <0.01 <0.01 <0.01 0.050 0.020	0.14 0.06 0.01 <0.01 0.42 0.23	0.14 0.06 0.01 <0.01 0.64 0.30	RES96023 FL01
USA (FL), 1996 (Hamlin oranges)	SC 480	0.070 +0.10 +0.15 +0.18		3670 +3800 +4060 +3700	4	1 4 o [3] 1 4 p [4] 1 4	<u>0.12</u> 0.034	<u>0.019</u> <0.01	0.18 0.050	0.20 0.072 <0.01 <0.01 0.78 0.32	RES96023 FL03
USA (FL), 1996 (Hamlin oranges)	SC 480	0.075 +0.10 +0.15 +0.18		3800	4	1 4				<u>0.15</u> 0.10	RES96023 FL04

Country, year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
USA (FL), 1996 (Hamlin oranges)	SC 480	0.070 +0.10 +0.14 +0.17		450	4	1 4				0.070 0.032	RES96023 FL07
USA (FL), 1996 (Hamlin oranges)	SC 480	0.070 +0.10 +0.15 +0.19		3900	4	1 4	0.047 0.025	0.006 0.003	0.066 0.035	0.081 0.066	RES96023 FL08
USA (FL), 1996 (Navel oranges)	SC 480	0.070 +0.10 +0.15 +0.18		190	4	1 4 o [3] 1 4 p [4] 1 4				0.053 0.011 <0.01 <0.01 0.080 0.054	RES96023 FL06
USA (FL), 1996 (Pineapple oranges)	SC 480	0.076 +0.10 +0.15 +0.18		3800	4	1 4				0.14 0.084	RES96023 FL05
USA (TX), 1996 (Navel oranges)	SC 480	0.070 +0.10 +0.15 +0.18		200	4	1 4 o [3] 1 4 p [4] 1 4				0.031 0.016 <0.01 <0.01 0.046 0.11	RES96023 TX14

[1] Total includes spinosyns A, D, B, N-demethyl-D and K
[2] Immunoassay
[3] peeled orange
[4] orange peel
[5] g: glasshouse, p: peel, f: flesh.

Table 35. Spinosad residues in citrus from supervised trials in Argentina. Replicate residues represent samples from split or replicate plots.

Location, year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
Buenos Aires, 1999 (Frost Navel orange)	SC 480		0.0072	2060	2	0 3 7 10 15	0.05 0.11 0.06 0.01 0.01 0.01 0.02 0.01 0.01 <0.01 (3) <0.01 0.01 <0.01	<0.01 0.02 0.01 <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB-P 449
Buenos Aires, 1999 (Frost Navel orange)	SC 480		0.014	2060	2	0 3 7 10 15	0.11 0.14 0.10 0.11 0.03 0.02 0.02 0.06 0.04 <0.01 0.02 0.02 <0.01 <0.01 0.01	0.03 0.03 0.02 0.02 <0.01 <0.01 <0.01 (3) <0.01 (3) <0.01 (3)	GHB-P 449

Location, year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
Entre Rios, 1999 (Satsuma tangerine)	SC 480		0.007	5200	2	31	<0.01(3)	<0.01(3)	GHB-P 447
Entre Rios, 1999 (Satsuma tangerine)	SC 480		0.014	5200	2	31	<0.01(3)	<0.01(3)	GHB-P 447

Table 36. Spinosad residues in apples from supervised trials in France, Italy, Japan, Spain and the USA. US residues are the mean of 2 independent composite samples. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year, (variety)	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
France, 1998 (Golden)	SC 480	0.29	0.030	960	3 4	40 0 1 3 7 14	<0.01 0.18 0.14 0.09 0.09 0.02	<0.01 0.04 0.04 0.02 0.02 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 0.02 0.02 0.01 0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 0.25 0.21 0.13 0.12 0.03	GHE-P-8252
France, 1999 (Gloster)	SC 480	0.30 +0.27 +0.30 +0.35	0.029	1000 +920 +1000 +1200	4	7 14	0.03 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.04 <0.01	GHE-P-8527 R99-001C
France, 1999 (Golden)	SC 480	0.31	0.029	1100	3 4	38 0 1 3 7 14	<0.01 0.16 0.18 0.06 0.03 <0.01	<0.01 0.03 0.03 0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 0.20 0.21 0.08 0.04 <0.01	GHE-P-8527 R99-001B
France, 1999 (Golden)	SC 480	0.30	0.030	1000	3 4	49 0 1 3 7 14	<0.01 0.25 0.19 0.03 0.02 <0.01	<0.01 0.05 0.04 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 0.30 0.23 0.04 0.02 <0.01	GHE-P-8528 002A
France, 1999 (Jonagold)	SC 480	0.29	0.029	1000	3 4	33 0 1 3 7 14	<0.01 0.20 0.16 0.05 <0.01 <0.01	<0.01 0.04 0.03 0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 0.24 0.20 0.07 0.01 <0.01	GHE-P-8527 R99-001A
France, 1999 (Red Chief)	SC 480	0.29	0.040	730	4	7 14	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.01 <0.01	GHE-P-8528 002B
France, 1999 (Royal Gala)	SC 480	0.29 +0.30 +0.32 +0.31	0.029	1000 +1050 +1100 +1080	4	7 14	0.03 0.03	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.03 0.03	GHE-P-8527 R99-001D

Country, year, (variety)	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
Italy, 1999 (Golden Delicious)	SC 480	0.29	0.029 +0.019 +0.019 +0.019	980 +1500 +1500 +1500	4	7 14	0.05 0.01	<0.01 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.05 0.01	GHE-P-8531
Italy, 1999 (Red Delicious)	SC 480	0.29	0.024	1200	3 4	49 0 1 3 7 14	<0.01 0.13 0.11 0.09 0.04 <0.01	<0.01 0.02 0.02 0.02 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 0.16 0.13 0.11 0.05 <0.01	GHE-P-8529 003A
Italy, 1999 (Royal Gala)	SC 480	0.29	0.029	1000	3 4	30 0 1 3 7 14	0.03 0.23 0.18 0.15 0.11 0.02	<0.01 0.04 0.03 0.04 0.02 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	0.04 0.28 0.22 0.20 0.14 0.03	GHE-P-8529 003B
Japan, 1995 laboratory IET	SC 200		0.010	6000	3	3 7 14 21	0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.01 0.01 <0.01 <0.01	GHF-P-1489 Nagano
Japan, 1995 laboratory JCAC						3 7 14 21	0.03 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.03 <0.01 <0.01 <0.01	GHF-P-1489 Nagano
Japan, 1995 laboratory IET [1]	SC 200		0.010	6000	3	3 7 14 21	0.12 0.05 0.02 0.01	0.02 0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.14 0.06 0.02 0.01	GHF-P-1489 Miyagi
Japan, 1995 laboratory JCAC [2]						3 7 14 21	0.15 0.08 0.03 0.01	0.02 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.17 0.08 0.03 0.01	GHF-P-1489 Miyagi
Spain, 1998 (Golden 972)	SC 480	0.29	0.029	1010	4	7 14	0.08 0.11	0.06 0.10	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.15 0.21	GHE-P-8250
Spain, 1998 (Golden)	SC 480	0.29	0.025	1200	3 4	48 0 1 3 7 14	<0.01 0.07 0.05 0.08 0.08 0.01	<0.01 0.05 0.04 0.06 0.06 0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 0.12 0.09 0.14 0.14 0.02	GHE-P-8251
Spain, 1999 (Golden Smothee)	SC 480	0.33 +0.34 +0.28 +0.29	0.030	1080 +1100 +930 +950	4	7 14	0.05 0.01	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.07 0.02	GHE-P-8530

Country, year, (variety)	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
USA (CA), 1995 (Gala)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 1 7 14	0.054 0.042 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.059 0.046 <0.01 <0.01	RES950 14
USA (CA), 1995 (Gala)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 1 7 14	0.092 0.064 0.024 0.01	0.01 0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.10 0.072 0.026 0.01	RES950 14
USA (CA), 1995 (Granny Smith)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7 14	0.15 0.045 0.055	0.017 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.18 0.051 0.062	RES950 14
USA (CA), 1995 (Granny Smith)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7 14	0.071 0.041 0.035	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.081 0.046 0.040	RES950 14
USA (ID), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.13 0.079	0.01 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.15 0.092	RES950 14
USA (ID), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.12 0.077	0.014 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.13 0.090	RES950 14
USA (IL), 1995 (Jonathan)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.19 0.024	0.026 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.22 0.024	RES950 14
USA (IL), 1995 (Jonathan)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.10 0.016	0.018 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.12 0.016	RES950 14
USA (IN), 1995 (Golden Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.058 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.064 <0.01	RES950 14
USA (IN), 1995 (Golden Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.074 <0.01	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.086 <0.01	RES950 14
USA (MI), 1995 (Empire)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.10 <0.01	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.12 <0.01	RES950 14

Country, year, (variety)	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
USA (MI), 1995 (Empire)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.068 0.015	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.078 0.015	RES950 14
USA (MI), 1995 (Golden Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.15 0.01	0.019 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.17 0.01	RES950 14
USA (MI), 1995 (Golden Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.21 0.024	0.026 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.24 0.029	RES950 14
USA (NC), 1995 (Winesap)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7 14	0.13 0.017 0.016	0.014 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.15 0.017 0.016	RES950 14
USA (NC), 1995 (Winesap)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7 14	0.079 0.032 0.014	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.096 0.037 0.014	RES950 14
USA (NY), 1995 (Golden Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 3 7 10 14	0.10 0.019 0.014 <0.01 <0.01	0.013 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	0.11 0.020 0.014 <0.01 <0.01	RES950 14
USA (NY), 1995 (Golden Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 3 7 10 14	0.079 0.023 0.01 <0.01 <0.01	0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	0.095 0.025 0.01 <0.01 <0.01	RES950 14
USA (NY), 1995 (McIntosh)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.041 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.046 <0.01	RES950 14
USA (NY), 1995 (McIntosh)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.050 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.056 <0.01	RES950 14
USA (OR), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.061 0.025	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.068 0.029	RES950 14
USA (OR), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.090 0.028	0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.10 0.033	RES950 14

Country, year, (variety)	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
USA (OR), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.052 0.015	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.059 0.015	RES950 14
USA (OR), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.064 0.020	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.072 0.020	RES950 14
USA (PA), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.063 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.071 <0.01	RES950 14
USA (PA), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.095 <0.01	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.11 <0.01	RES950 14
USA (VA), 1995 (Red Yorking)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.049 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.055 0.01	RES950 14
USA (VA), 1995 (Red Yorking)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.075 0.01	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.084 0.01	RES950 14
USA (WA), 1995 (Basin Beauty)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 3 7 10 14	0.087 0.058 0.033 0.032 0.032	0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	0.098 0.064 0.040 0.037 0.036	RES950 14
USA (WA), 1995 (Basin Beauty)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 3 7 10 14	0.077 0.069 0.036 0.012 0.018	0.01 0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01	0.087 0.077 0.040 0.012 0.020	RES950 14
USA (WA), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		470	5	0 7	0.046 0.041	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.051 0.045	RES950 14
USA (WA), 1995 (Red Delicious)	WG 820	0.050 +0.070 +2x0.10 +0.18		1870	5	0 7	0.063 0.033	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.071 0.037	RES950 14

[1] IET: Institute of Environmental Toxicology
[2] JCAC: Japan Chemical Analysis Consultant

Table 37. Spinosad residues in stone fruit from supervised trials at 19 sites in the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Crop, location, year	Application					PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Cherry, CA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	0.083	RES97004
Cherry, CA, 1997	SC 240	0.07 +0.13 2×0.15		470	4	7	0.03	RES97004
Cherry, CA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	0.060	RES97004
Cherry, MI, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	0.040	RES97004
Cherry, NY, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	0.023	RES97004
Cherry, UT, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	0.11	RES97004
Cherry, WA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	0.11	RES97004
Cherry, WI, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	<0.02	RES97004
Peach, CA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	14	0.055	RES97004
Peach, CA, 1997	SC 240	0.07 +0.13 2×0.15		470	4	14	0.055	RES97004
Peach, CA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	14	0.050	RES97004
Peach, MI, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	14	<0.02	RES97004
Peach, NC, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	14	<0.02	RES97004

Crop, location, year	Application					PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Peach, PA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	14	<0.02	RES97004
Peach, SC, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	14	0.03	RES97004
Plum, CA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	<0.02	RES97004
Plum, CA, 1997	SC 240	0.07 +0.13 2×0.15		470	4	7	<0.02	RES97004
Plum, CA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	<0.02	RES97004
Plum, CA, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	<0.02	RES97004
Plum, MI, 1997	SC 240	0.07 +0.13 2×0.15		1900	4	7	<0.02	RES97004
Prune, dried, CA, 1997	SC 240	0.25 +0.46 2×0.53		1900	4	7	0.055	RES97004
Prune, dried, CA, 1997	SC 240	0.25 +0.46 2×0.53		1900	4	7	0.04	RES97004
Prune, fresh, CA, 1997	SC 240	0.25 +0.46 2×0.53		1900	4	7	0.065	RES97004
Prune, fresh, CA, 1997	SC 240	0.25 +0.46 2×0.53		1900	4	7	0.060	RES97004

Table 38. Spinosad residues in stone fruit from supervised trials in Chile and Japan.

Country, year (variety)	Application					PHI, days	Residues, mg/kg [1, 2]		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
Chile, 1999 nectarine (August red)	SC 480	0.17		2300	1	0 1 4 7 11 14 1 11 14	0.07 0.04 0.06 <0.01 (2) 0.10 0.03 0.04 0.04 <0.01(3) 0.03 0.02 0.02 0.02 0.02 0.01 c <0.01(3) c <0.01 (2) 0.02 c <0.01(3)	0.02 0.01 0.02 <0.01 (2) 0.02 <0.01(3) <0.01 (2) 0.01 0.01 0.01 0.01 0.01 0.01 <0.01 c 0.02 0.02 0.02 c <0.01(3) c <0.01 (2) 0.02	GHB-P 425
Chile, 1999 nectarine (August red)	SC 480	0.33		2300	1	0 1 4 7 11 14 1 11 14	0.10 0.12 0.09 0.23 0.14 0.11 <0.01 0.01 0.03 0.01 0.02 0.02 0.09 0.06 0.07 0.02 0.02 0.02 c <0.01(3) c <0.01 (2) 0.02 c <0.01(3)	0.03 0.04 0.04 0.06 0.04 0.04 <0.01(3) <0.01(3) 0.02 0.02 0.02 <0.01(3) c 0.02 0.02 0.02 c <0.01(3) c <0.01 (2) 0.02	GHB-P 425
Chile, 1999 nectarine (September red)	SC 480	0.14		2000	1	0 6 10 15 21 21	0.05 0.02 0.03 0.20 0.03 0.10 0.05 0.13 0.04 0.02 0.01 0.04 0.01 0.02 0.08 c <0.01 (2) 0.04	0.01 <0.01 0.01 0.06 <0.01 0.02 0.01 0.04 0.01 <0.01(3) <0.01 (2) 0.01 c <0.01 (2) 0.02	GHB-P 425
Chile, 1999 nectarine (September red)	SC 480	0.29		2000	1	0 6 10 15 21 21	0.49 0.28 0.37 0.08 0.16 0.27 0.12 0.10 0.08 0.02 0.03 <0.01 0.01 <0.01 (2) c <0.01 (2) 0.04	0.12 0.07 0.09 0.02 0.04 0.06 0.04 0.02 0.02 <0.01 (2) 0.02 0.01 <0.01 (2) c <0.01 (2) 0.02	GHB-P 425
Chile, 1999 nectarine (Sunrice late)	SC 480	0.14		2200	1	0 1 3 7 11 14 7 14	0.07 0.04 <0.01 0.01 0.01 0.03 0.04 <0.01 <0.01 0.02 0.04 <0.01(3) <0.01(3) c 0.02 <0.01 (2) c <0.01(3)	<0.01 (2) <0.01(3) <0.01(3) <0.01(3) <0.01(3) <0.01(3) c <0.01(3) c 0.02 <0.01 (2)	GHB-P 425
Chile, 1999 nectarine (Sunrice late)	SC 480	0.29		2200	1	0 1 3 7 11 14 7 14	0.05 0.04 0.05 0.03 0.02 0.03 0.05 <0.01 0.05 0.01 <0.01 (2) 0.02 0.03 <0.01 0.02 <0.01 (2) c 0.02 <0.01 (2) c <0.01(3)	<0.01(3) <0.01(3) <0.01(3) <0.01(3) <0.01(3) <0.01(3) c <0.01(3) c 0.02 <0.01 (2)	GHB-P 425

Country, year (variety)	Application					PHI, days	Residues, mg/kg [1, 2]		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
Japan, 1995 peach	SC 200	0.50	0.01	5000	2	3	p 0.38 f <0.01	p 0.04 f <0.01	GHB P-331
						7	p 0.08 f <0.01	p 0.01 f <0.01	
						14	p 0.03 f <0.01	p <0.01 f <0.01	
						21	p 0.02 f <0.01	p <0.01 f <0.01	
					3	3	p 0.06 f <0.01	p <0.01 f <0.01	

[1] p: peel, f: flesh
[2] c: samples from control plot

Table 39. Spinosad residues in grapes from supervised trials in France, Italy and Spain.

Country, year (variety)	Application [3]					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
France, 1997 (Chenin, Riparia Gloire)	SC 480	0.060	0.029	210	4	16	<0.01	<0.01	<0.01	<0.01	GHE-P-7575
					5	0	0.03	<0.01	0.05	0.08	
						5	0.01	<0.01	0.01	0.02	
						10	<0.01	<0.01	<0.01	<0.01	
						14	<0.01	<0.01	<0.01	<0.01	
France, 1997 (Gamay)	SC 480	0.060	0.032	190	4	17	<0.01	<0.01	<0.01	<0.01	GHE-P-7575
					5	0	0.08	0.02	0.10	0.09	
						5	0.02	<0.01	0.03	0.04	
						10	0.02	<0.01	0.03	0.02	
						15	0.01	<0.01	0.02	0.02	
France, 1997 (Negrette)	SC 480	0.060	0.024	260	5	15[6]	<0.01	<0.01	0.01	<0.01	GHE-P-7577
France, 1998 (Cabernet Franc)	SC 480	2×0.096 +3×0.048	2×0.036 +3×0.019	260	5	15	<0.01	<0.01	0.02		GHE-P-7853
France, 1998 (Chenin)	SC 480	2×0.096 +3×0.048	2×0.036 +3×0.019	260	5	15	<0.01	<0.01	<0.01		GHE-P-7850
						0	0.03	0.02	0.05		
						5	<0.01	<0.01	0.02		
						10	<0.01	<0.01	0.02		
						16	<0.01	<0.01	<0.01		
France, 1998 (Gamay)	SC 480	2×0.096 +3×0.048	2×0.042 +3×0.021	230	4	15	0.02	0.02	0.04		GHE-P-7851
					5	0	0.04	0.03	0.07		
						6	0.03	0.02	0.05		
						10	0.03	0.02	0.05		
						15	0.01	<0.01	0.02		
France, 1998 (Red wine grape, Cot)	SC 480	0.096 +0.096 +0.048 +0.048 +0.048	0.042 +0.042 +0.021 +0.021 +0.021	230	5	15	0.02	0.01	0.03		GHE-P-7856

Country, year (variety)	Application [3]					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Italy, 1997 (Tocai Verde)	SC 480	0.060	0.015	400	4 5	22 0 5 10 16	0.01 0.18 0.07 0.04 0.03	<0.01 0.04 0.02 0.01 0.01	0.02 0.24 0.09 0.06 0.04[4]	0.02 0.45 0.15 0.08 0.05[4]	GHE-P-7579
Italy, 1998 (Italia)	SC 480	0.099 +0.095 +0.041 +0.049 +0.048	0.014 +0.014 +0.0060 +0.0060 +0.0060	720 +690 +590 +710 +700	4 5	18 0 5 9 14	0.02 0.18 0.10 0.06 0.03	0.03 0.14 0.08 0.05 0.03	0.05 0.32 0.18 0.11 0.06		GHE-P-7852
Italy, 1998 (Trebiano)	SC 480	0.098 +0.091 +0.049 +0.046 +0.050	0.016 +0.016 +0.005 +0.005 +0.005	610 +570 +1010 +950 +1030	5	15	0.01	0.01	0.03		GHE-P-7855
Spain, 1997 (Italia Moscatel)	SC 480	0.060	2×0.0075 +3×0.0060	2×800 +3×995	5	15[7]	0.11	0.03	0.15	0.17	GHE-P-7576
Spain, 1997 (Italia)	SC 480	0.060	0.0075 +0.0075 +0.0060 +0.0060 +0.0060	780 +770 +960 +950 +1010	4 5	17 0 5 10 15	0.08 0.23 0.14 0.12 0.07	0.02 0.06 0.05 0.03 0.02	0.11 0.30 0.19 0.16 0.09[4]	0.12 0.40 0.24 0.17 0.12[4]	GHE-P-7578
Spain, 1998 (Cencibel)	SC 480	2×0.096 +3×0.048	0.019 +0.016 +0.0069 +2×0.006	500 +590 +700 +790 +795	5	15	0.04 c 0.01[5]	0.03 c <0.01	0.07 c 0.02		GHE-P-7854

[1] Total includes spinosyns A, D, B, N-demethyl-D and K
[2] Immunoassay
[3] Application rate, spray concentration and volume per ha were not identical for each application (variation generally within 20%). Single values are those for the last application.
[4] Samples analysed by IA method Nov-Dec 97 and by HPLC method Jan-Feb 99
[5] c: sample from control plot
[6] Samples in freezer storage approx. 17 months.
[7] Samples in freezer storage approx. 18 months.

Table 40. Spinosad residues in grapes from supervised trials in Chile.

Year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
1998 (Red Globe)[1]	SC 480	0.13		1800	2	0 18 38 66 86	1.4 1.5 1.5 0.02 0.02 0.01 <0.01(3) <0.01(3) <0.01(3)	0.50 0.61 0.61 <0.01 0.01 <0.01 <0.01(3) <0.01(3) <0.01(3)	GHB-P 419

Year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
1998 (Red Globe)[1]	SC 480	0.26		1800	2	0 18 38 66 86	3.2 3.1 3.9 0.06 0.02 0.04 <0.01(3) <0.01(3) <0.01(3)	1.3 1.2 1.4 0.03 <0.01 0.02 <0.01(3) <0.01(3) <0.01(3)	GHB-P 419

[1] Applications made when flowering commenced and 7 days later at full bloom. Grapes sampled shortly after flowering are unrelated to proper harvest.

Table 41. Spinosad residues in strawberries from supervised trials in Belgium, Greece, Italy, Spain and the UK.

Country, year, (variety)	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A	D	K	B	B of D	Total	
Belgium, 1998 (Elsanta) [1]	SC 480	0.074 +0.076 +0.081		760 +720 +800	g 2 g 3	14 0 1 2	0.01 0.05 0.04 0.03	<0.01 0.04 0.03 0.02	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.02 0.09 0.07 0.04	GHE-P-8056 Ittre
Belgium, 1998 (Elsanta) [1]	SC 480	0.077		800 +790 +860	g 2 g 3	14 0 1 2	0.01 0.05 0.04 0.03	<0.01 0.04 0.03 0.03	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.02 0.09 0.07 0.05	GHE-P-8056 Wepion
Greece, 1998 (Tulda)	SC 480	0.081	0.010	800	2 3	8 0 1 2	0.01 0.03 0.02 0.02	<0.01 0.02 0.02 0.02	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.02 0.05 0.04 0.04	GHE-P-8053
Italy, 1999 (Camarosa)	SC 480	0.080 +0.079 +0.081	0.013	590 +590 +600	2 3	7 0 1 2	0.01 0.09 0.07 0.07	<0.01 0.02 0.01 0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.01 0.11 0.09 0.09	GHE-P-8095 Catania
Italy, 1999 (Camarosa)	SC 480	0.079 +0.078 +0.079	0.011	700 +680 +700	3	1 2	0.06 0.07	0.01 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.08 0.09	GHE-P-8097
Italy, 1999 (Camarosa)	SC 480	0.081	0.013	600	3	1 2	0.12 0.09	0.03 0.02	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.15 0.10	GHE-P-8098
Italy, 1999 (Eddie)	SC 480	0.57 +0.079 +0.077	0.071 +0.010 +0.010	810	3	1 2	0.03 0.02	0.02 0.02	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.05 0.04	GHE-P-8054
Italy, 1999 (Marmolada)	SC 480	0.081 +0.076 +0.078	0.013	630 +600 +610	2 3	16 0 1 2	<0.01 0.10 0.04 0.01	<0.01 0.02 0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 0.12 0.05 0.02	GHE-P-8095 Forli
Italy, 1999 (Pajaro)	SC 480	0.077 +0.079 +0.079	0.011	670 +700 +700	g 3	1 2	0.19 0.12	0.04 0.02	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.24 0.14	GHE-P-7617

Country, year, (variety)	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A	D	K	B	B of D	Total	
Spain, 1998 (Camarosa)[2]	SC 480	0.54	0.054	1000	3	3 6	1.4 0.66	0.34 0.16	0.02 0.01	0.04 0.02	<0.01 <0.01	1.8 0.86	GHE-P-8055
Spain, 1998 (Camarosa)[2]	SC 480	0.54 +0.54 +0.52	0.054	1000 +1000 +960	g 3	3 6	1.0 0.72	0.25 0.18	0.02 0.01	0.03 0.02	<0.01 <0.01	1.4 0.94	GHE-P-8057
Spain, 1999 (Camarosa)	SC 480	0.069 +0.075 +0.075	0.0093	740 +800 +810	pt 2 pt 3	12 0 1 2	0.03 0.10 0.09 0.09	<0.01 0.03 0.02 0.02	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.04 0.12 0.11 0.10	GHE-P-6561
Spain, 1999 (Camarosa)	SC 480	0.076	0.0093	760 +810 +820	g 3	1 2	0.07 0.05	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.09 0.06	GHE-P-6582
Spain, 1999 (Camarosa)	SC 480	0.073 +0.075 +0.076	0.0093	790 +810 +820	2 3	12 0 1 2	<0.01 0.09 0.04 0.03	<0.01 0.02 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 0.12 0.05 0.03	GHE-P-7787
Spain, 1999 (Camarosa)	SC 480	0.076	0.0093	760 +820 +810	3	1 2	0.09 0.02	0.02 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.11 0.03	GHE-P-8096
UK, 1999 (Elsanta)	SC 480	0.080	0.013	590	g 2 g 3	11 0 1 2	0.02 0.06 0.06 0.07	<0.01 0.01 0.01 0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.03 0.07 0.07 0.08	GHE-P-6562 11A
UK, 1999 (Symphony)	SC 480	0.081 +0.080 +0.083	0.013	600 +600 +620	g 3	1 2	0.06 0.06	0.02 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.07 0.07	GHE-P-6562 11B

[1] Samples stored in a freezer for approx. 16 months
[2] Samples stored in a freezer for approx. 18 months
[3] g glasshouse. pt: plastic tunnel

Table 42. Spinosad residues in blueberries from supervised trials in the USA, 1998.

Location, year	Application, kg ai/ha	PHI, days	Spinosad, mg/kg	Ref.
ME	1.0	1	0.066 0.015	06850.98-ME02
MI	1.0	1	0.19 0.10	06850.98-MI32
MI	1.0	1	0.17 0.15	06850.98-MI33
MI	1.0	1	0.032 0.037	06850.98-MI34
NC	1.0	1	0.085 0.082	06850.98-NC15
NC	1.0	1	0.075 0.065	06850.98-NC16
OR	1.0	1	0.18 0.17	06850.98-OR14

Location, year	Application, kg ai/ha	PHI, days	Spinosad, mg/kg	Ref.
PA	1.0	1	0.13 0.084	06850.98-PA04

Table 43. Spinosad residues in kiwifruit from supervised trials in New Zealand. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total HPLC	IA	
1996	SC480	0.038		1500	8	0 3 7 14 45				0.22 0.13 0.08 0.09 0.03	GHF-P 1551
1996	SC480	0.075		1500	8	0 3 7 14 45				0.54 0.32 0.15 0.17 0.12	GHF-P 1551
1996	SC480	0.15		1500	8	0 3 7 14 45				0.78 0.54 0.27 0.36 0.34	GHF-P 1551
1996	SC480	0.30		1500	8	0 3 7 14 45				1.2 0.66 0.30 0.30 0.16	GHF-P 1551
1998 (Hayward)	SC120		0.0048		3	0 7 14 28				0.14 <0.05 0.06 <0.05	GHF-P 1798
1998 (Hayward)	SC120		0.0096		3	0 7 14 28				0.20 0.14 0.10 <0.05	GHF-P 1798
1998 (Hayward)	SC120		0.0048		3	134 156				<u><0.05</u> (2) <0.05 (2)	GHF-P 1798
1998 (Hayward)	SC120		0.0096		3	134 156				<0.05 0.11 0.07 0.08	GHF-P 1798
1998 (Hayward)	SC120		0.0048	2000	2	142				<u><0.05</u>	GHF-P 1799
1998 (Hayward)	SC120		0.0096	2000	2	142				<0.05	GHF-P 1799

Year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total HPLC	IA	
1999 (Hayward)	SC120		0.0048	2000	2	142	<0.01	<0.01	<0.01		GHF-P 1958 trial 98493-01
						143	<0.01	<0.01	<0.01		
						145	<0.01	<0.01	<0.01		
						149	<0.01	<0.01	<0.01		
						156	<0.01	<0.01	<0.01		
						170	<0.01	<0.01	<0.01		
					3	0	0.30	0.06	0.37		
						1	0.13	0.03	0.17		
						3	0.11	0.02	0.14		
						7	0.09	0.02	0.12		
						14	0.09	0.01	0.11		
						28	0.07	0.01	0.08		
1999 (Hayward)	SC120		0.0096	2000	2	142	<0.01	<0.01	<0.01		GHF-P 1958 trial 98493-01
						143	<0.01	<0.01	<0.01		
						145	<0.01	<0.01	<0.01		
						149	<0.01	<0.01	<0.01		
						156	<0.01	<0.01	<0.01		
						170	<0.01	<0.01	<0.01		
					3	0	0.46	0.09	0.57		
						1	0.20	0.04	0.26		
						3	0.15	0.03	0.19		
						7	0.19	0.03	0.24		
						14	0.11	0.02	0.14		
						28	0.07	0.01	0.09		
1999 (Hayward)	SC120		0.0048	2000	2	142	<0.01	<0.01	<0.01		GHF-P 1958 trial 98493-02
						143	<0.01	<0.01	<0.01		
						145	<0.01	<0.01	<0.01		
						149	<0.01	<0.01	<0.01		
						156	<0.01	<0.01	<0.01		
						170	<0.01	<0.01	<0.01		
					3	0	0.23	0.04	0.28		
						1	0.08	0.02	0.11		
						3	0.04	<0.01	0.05		
						7	0.04	<0.01	0.05		
						14	0.04	<0.01	0.05		
						28	0.02	<0.01	0.02		
1999 (Hayward)	SC120		0.0096	2000	2	142	<0.01	<0.01	<0.01		GHF-P 1958 trial 98493-02
						143	<0.01	<0.01	<0.01		
						145	<0.01	<0.01	<0.01		
						149	<0.01	<0.01	<0.01		
						156	<0.01	<0.01	<0.01		
						170	<0.01	<0.01	<0.01		
					3	0	0.45	0.09	0.56		
						1	0.16	0.03	0.21		
						3	0.11	0.02	0.14		
						7	0.08	0.01	0.10		
						14	0.08	0.02	0.10		
						28	0.05	<0.01	0.06		

Year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total HPLC	IA	
1999 (Hayward)	SC120		0.0048	2000	2	128	<0.01	<0.01	<0.01		GHF-P 1958 trial 98493-04
						129	<0.01	<0.01	<0.01		
						131	<0.01	<0.01	<0.01		
						135	<0.01	<0.01	<0.01		
						142	<0.01	<0.01	<0.01		
						156	<0.01	<0.01	<0.01		
					3	0	0.19	0.04	0.23		
						1	0.03	<0.01	0.04		
						3	0.03	<0.01	0.04		
						7	0.03	<0.01	0.03		
						14	0.02	<0.01	0.02		
						28	0.02	<0.01	0.02		
1999 (Hayward)	SC120		0.0096	2000	2	128	<0.01	<0.01	<0.01		GHF-P 1958 trial 98493-04
						129	<0.01	<0.01	<0.01		
						131	<0.01	<0.01	<0.01		
						135	<0.01	<0.01	<0.01		
						142	<0.01	<0.01	<0.01		
						156	<0.01	<0.01	<0.01		
					3	0	0.33	0.06	0.41		
						1	0.09	0.02	0.12		
						3	0.04	<0.01	0.05		
						7	0.05	0.01	0.07		
						14	0.03	<0.01	0.04		
						28	0.02	<0.01	0.02		
1999 (Hayward)	SC120		0.0048	2000	2	130	<0.01	<0.01	0.01		GHF-P 1958 trial 98493-05
						131	<0.01	<0.01	<0.01		
						133	<0.01	<0.01	0.01		
						137	<0.01	<0.01	<0.01		
						144	<0.01	<0.01	<0.01		
						158	<0.01	<0.01	<0.01		
					3	0	0.34	0.06	0.42		
						1	0.11	0.02	0.14		
						3	0.10	0.02	0.12		
						7	0.04	<0.01	0.05		
						14	0.02	<0.01	0.02		
						28	<0.01	<0.01	0.02		
1999 (Hayward)	SC120		0.0096	2000	2	130	0.12	0.02	0.15		GHF-P 1958 trial 98493-05
						131	<0.01	<0.01	0.01		
						133	<0.01	<0.01	0.01		
						137	<0.01	<0.01	<0.01		
						144	<0.01	<0.01	<0.01		
						158	<0.01	<0.01	<0.01		
					3	0	<0.01	<0.01	0.01		
						1	0.24	0.05	0.30		
						3	0.19	0.03	0.24		
						7	0.10	0.02	0.13		
						14	0.06	0.01	0.08		
						28	0.05	<0.01	0.06		

Year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total HPLC	IA	
1999 (Hayward)	SC120		0.0048	2000	2	111	0.01	0.01	0.02		GHF-P 1958 trial 98493-06
						112	<0.01	0.01	0.02		
						114	<0.01	0.01	0.02		
						118	0.01	0.01	0.02		
						125	<0.01	<0.01	0.01		
						139	<0.01	<0.01	0.01		
					3	0	0.33	0.07	0.40		
						1	0.23	0.05	0.29		
						3	0.20	0.05	0.24		
						7	0.17	0.04	0.22		
						14	0.09	0.02	0.11		
						28	0.03	<0.01	0.04		
1999 (Hayward)	SC120		0.0096	2000	2	111	0.01	0.01	0.02		GHF-P 1958 trial 98493-06
						112	0.01	0.01	0.03		
						114	0.01	0.01	0.03		
						118	<0.01	<0.01	0.02		
						125	0.01	<.01	0.02		
						139	0.01	<0.01	0.02		
					3	0	0.82	0.15	0.98		
						1	0.57	0.11	0.70		
						3	0.42	0.08	0.51		
						7	0.27	0.06	0.34		
						14	0.19	0.03	0.24		
						28	0.08	0.01	0.10		

Table 44. Spinosad residues in Brassica vegetables from supervised trials in Australia and New Zealand. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Crop, country, (location), year (variety)	Application					PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
BROCCOLI								
Australia (NSW), 1997	SC 120 +adjuvant	0.048			4	3	0.05	GHF-P 1585
						7	0.01	
Australia (NSW), 1997	SC 120 +adjuvant	0.096			4	3	0.08	GHF-P 1585
						7	0.01	
Australia (Vic), 1996	SC480	0.05		253	4	0	1.1	GHF-P 1539
						3	0.09	
						7	0.01	
						14	<0.01	
						21	<0.01	
Australia (Vic), 1996	SC480	0.10		253	4	0	2.3	GHF-P 1539
						3	0.39	
						7	0.03	
						14	<0.01	
						21	<0.01	

Crop, country, (location), year (variety)	Application					PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Australia (Vic), 1997 (Bushido)	SC 120	0.048		250	4	0 1 3 7 14	0.17 0.12 0.01 <0.01 <0.01	GHF-P 1586 96322.3
Australia (Vic), 1997 (Bushido)	SC 120	0.096		250	4	0 1 3 7 14	0.70 0.49 0.06 0.01 <0.01	GHF-P 1586 96322.3
CAULIFLOWER								
Australia (WA), 1996 (Freemont)	SC480	0.05		250	4	0 3 7 14 21	1.0 0.01 <0.01 <0.01 <0.01	GHF-P 1539
Australia (WA), 1996 (Freemont)	SC480	0.10		250	4	0 3 7 14 21	1.7 0.02 <0.01 <0.01 <0.01	GHF-P 1539
NZ, 1997 (All Year Hybrid)	SC 120	0.048		500	5	0 1 3 7 14	0.03 0.02 0.01 <0.01 <0.01	GHF-P 1570 211571
NZ, 1997 (All Year Hybrid)	SC 120	0.096		500	5	0 1 3 7 14	0.09 0.07 0.03 0.01 0.01	GHF-P 1570 211571
CHINESE CABBAGE								
Australia (Qld), 1996 (SPS Maltida)	SC 120 +adjuvant	0.048 +0.048 +0.072 +0.072		250 +250 +380 +760	4	3 7	0.10 0.01	GHF-P 1585
Australia (Qld), 1996 (SPS Maltida)	SC 120 +adjuvant	0.096 +0.096 +0.14 +0.14		250 +250 +380 +760	4	3 7	0.09 0.02	GHF-P 1585
CABBAGE								
Australia (Vic), 1997	SC 120	0.048		250	4	0 1 3 7 14	0.01 <0.01 <0.01 <0.01 <0.01	GHF-P 1586 96322.4

Crop, country, (location), year (variety)	Application					PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Australia (Vic), 1997	SC 120	0.096		250	4	0 1 3 7 14	0.01 0.01 <0.01 <0.01 <0.01	GHF-P 1586 96322.4
NZ, 1997 (Sovereign)	SC 120	0.048		500	5	0 1 3 7 14	0.02 0.01 <0.01 <0.01 <0.01	GHF-P 1570 211570
NZ, 1997 (Sovereign)	SC 120	0.096		500	5	0 1 3 7 14	0.03 0.03 0.01 <0.01 <0.01	GHF-P 1570 211570
BRUSSELS SPROUTS								
Australia (SA), 1997 (Oliver)	SC 120	0.048		912	4	0 1 3 7 14	0.05 0.02 0.02 0.01 0.01	GHF-P 1586 975001PN
Australia (SA), 1997 (Oliver)	SC 120	0.096		912	4	0 1 3 7 14	0.12 0.06 0.03 0.03 0.03	GHF-P 1586 975001PN
Australia (SA), 1997 (Oliver)	SC 120	0.048		912	4	0 1 3 7 14	0.04 0.03 0.01 0.01 0.01	GHF-P 1586 975002PN
Australia (SA), 1997 (Oliver)	SC 120	0.096		912	4	0 1 3 7 14	0.05 0.04 0.02 0.01 0.01	GHF-P 1586 975002PN

Table 45. Spinosad residues in cabbage and Chinese cabbage from supervised trials in Japan in 1995. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels. Residues were analysed by two laboratories.

Crop, Laboratory	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
CABBAGE													

Crop, Laboratory	Application					PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
DowElanco Japan	WG 250		0.01	3000	3	3 7 14	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	GHF-P-1486 Iwate
Institute of Environmental Toxicology						3 7 14	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	GHF-P-1486 Iwate
DowElanco Japan	WG 250		0.01	3000	3	3 7 14	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	GHF-P-1486 Gunma
Institute of Environmental Toxicology						3 7 14	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.01 <0.01 <0.01	GHF-P-1486 Gunma
CHINESE CABBAGE													
DowElanco Japan	WG 250		0.01	3000	3	3 6 14	0.08 <0.01 <0.01	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.09 <0.01 <0.01	GHF-P-1487 Miyagi
Institute of Environmental Toxicology						3 6 14	0.02 0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.02 0.01 <0.01	GHF-P-1487 Miyagi
DowElanco Japan	WG 250		0.01	3000	3	3 7 14	0.08 0.04 <0.01	0.01 0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.09 0.05 <0.01	GHF-P-1487 Nagano
Institute of Environmental Toxicology						3 7 14	0.08 0.04 0.01	0.02 0.01 <0.01	0.01 0.01 0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.11 0.06 0.02	GHF-P-1487 Nagano

Table 46. Spinosad residues in Brassica vegetables from supervised trials in the USA in 1995. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels. All WG 820 formulations.

Crop, Location (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
BROCCOLI												
AZ (Marathon)	2x0.10 +2x0.15		280	4	1 3	0.17 0.097	0.024 0.01	<0.01 <0.01	0.02 <0.01	<0.01 <0.01	0.22 0.12	RES95001
CA (Greenbelt)	2x0.10 +2x0.15		280	4	1 3	0.35 0.19	0.04 0.02	<0.01 <0.01	0.01 0.01	<0.01 <0.01	0.40 0.23	RES95001 CA1
CA (Marathont)	2x0.10 +2x0.15		280	4	1 3	0.14 0.097	0.02 0.01	<0.01 <0.01	0.01 <0.01	<0.01 <0.01	0.18 0.12	RES95001 CA2

Crop, Location (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
CA (Sultan)	2x0.10 +2x0.15		280	4	0 1 3 5 7 10	0.47 0.42 0.28 0.21 0.14 0.089	0.057 0.05 0.03 0.03 0.02 0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	0.03 0.02 0.02 0.01 0.01 0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	0.56 0.50 0.34 0.25 0.17 0.11	RES95001 CA3
CA (Green Valiant)	2x0.10 +2x0.15		280	4	1 3	0.32 0.20	0.04 0.02	<0.01 <0.01	0.03 0.02	<0.01 <0.01	0.39 0.25	RES95001 CA4
CA (Marathon)	2x0.10 +2x0.15		280	4	1 3	0.32 0.19	0.03 0.02	<0.01 <0.01	0.02 0.01	<0.01 <0.01	0.37 0.22	RES95001 CA5
OR (GEM)	2x0.10 +2x0.15		280	4	1 3	0.39 0.35	0.052 0.049	<0.01 <0.01	0.04 0.03	<0.01 <0.01	0.50 0.44	RES95001
TX (Green Comet)	2x0.10 +2x0.15		280	4	1 3	0.11 0.02	0.01 <0.01	<0.01 <0.01	0.01 <0.01	<0.01 <0.01	0.14 0.02	RES95001
CABBAGE												
CA (Charmant) include wrapper leaves	2x0.10 +2x0.15		290	4	1 3	0.078 0.03	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.01 <0.01	0.11 0.04	RES95001
CA (Charmant) wrapper leaves removed	2x0.10 +2x0.15		290	4	1 3	0.02 0.02	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.03 0.02	RES95001
FL (Savoy) include wrapper leaves	2x0.10 +2x0.15		280	4	1 3 5	0.93 0.04 0.03	0.16 <0.01 <0.01	<0.01 <0.01 <0.01	0.03 <0.01 <0.01	<0.01 <0.01 <0.01	1.1 0.052 0.04	RES95001
FL (Savoy) wrapper leaves removed	2x0.10 +2x0.15		280	4	1 3 5	0.15 <0.01 <0.01	0.02 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.18 <0.01 <0.01	RES95001
IN (Stonehead) include wrapper leaves	2x0.10 +2x0.15		290	4	1 3	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.01 0.01	RES95001 IN1
IN (Stonehead) wrapper leaves removed	2x0.10 +2x0.15		290	4	1 3	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	RES95001 IN1
IN (Golden Acre) include wrapper leaves	2x0.10 +2x0.15		280	4	1 3	0.053 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.064 0.01	RES95001 IN2
IN (Golden Acre) wrapper leaves removed	2x0.10 +2x0.15		280	4	1 3	0.02 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.03 0.01	RES95001 IN2
PA (Charmant) include wrapper leaves	2x0.10 +2x0.15		320	4	1 3	0.070 0.02	0.01 <0.01	<0.01 <0.01	0.01 <0.01	<0.01 <0.01	0.089 0.03	RES95001 PA1

Crop, Location (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
PA (Charmant) wrapper leaves removed	2x0.10 +2x0.15		320	4	1 3	0.01 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.01 0.01	RES95001 PA1
PA (Bravo) include wrapper leaves	2x0.10 +2x0.15		330	4	1 3	0.02 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.03 0.01	RES95001 PA2
PA (Bravo) wrapper leaves removed	2x0.10 +2x0.15		330	4	1 3	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	RES95001 PA2
TX (Early Cabbage) include wrapper leaves	2x0.10 +2x0.15		290	4	1 3 5	0.80 0.32 0.14	0.15 0.04 0.02	0.01 0.01 <0.01	0.077 0.04 0.02	0.01 <0.01 <0.01	1.0 0.41 0.20	RES95001
TX (Early Cabbage) wrapper leaves removed	2x0.10 +2x0.15		290	4	1 3 5	0.32 0.097 0.11	0.04 0.01 0.01	<0.01 <0.01 <0.01	0.03 0.01 0.01	<0.01 <0.01 <0.01	0.39 0.13 0.15	RES95001
VA (Market Prize) include wrapper leaves	2x0.10 +2x0.15		290	4	1 3	0.33 0.13	0.04 0.02	<0.01 <0.01	0.03 <0.01	<0.01 <0.01	0.40 0.16	RES95001
VA (Market Prize) wrapper leaves removed	2x0.10 +2x0.15		290	4	1 3	0.03 0.02	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.03 0.03	RES95001
MUSTARD GREENS												
AZ (So. Giant Curled)	2x0.10 +2x0.15		280	4	1 3	4.9 4.3	0.59 0.52	<0.01 0.01	0.28 0.29	0.03 0.04	5.8 5.2	RES95001
CA (Florida Broadleaf)	2x0.10 +2x0.15		280	4	1 3	5.1 3.0	0.64 0.37	0.01 <0.01	0.25 0.19	0.04 0.03	6.1 3.6	RES95001
IN (Florida Broadleaf)	2x0.10 +2x0.15		280	4	0 1 3 5 7 10	4.4 2.1 0.078 0.02 0.02 <0.01	0.55 0.30 0.01 <0.01 <0.01 <0.01	0.01 0.01 <0.01 <0.01 <0.01 <0.01	0.18 0.16 <0.01 <0.01 <0.01 <0.01	0.02 0.01 <0.01 <0.01 <0.01 <0.01	5.2 2.5 0.10 0.02 0.02 <0.01	RES95001
MS (Florida Broadleaf)	2x0.10 +2x0.15		280	4	1 3 5	3.6 0.14 0.02	0.40 0.02 <0.01	<0.01 <0.01 <0.01	0.21 0.01 <0.01	0.03 <0.01 <0.01	4.2 0.17 0.02	RES95001
TX (Florida Broadleaf)	2x0.10 +2x0.15		280	4	1 3	0.04 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.05 0.01	RES95001 TX1
TX (Florida Broadleaf)	2x0.10 +2x0.15		280	4	1 3	3.1 3.3	0.43 0.47	<0.01 <0.01	0.11 0.13	0.01 0.02	3.6 3.9	RES95001 TX2

Crop, Location (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
VA (Old Fashioned)	2x0.10 +2x0.15		280	4	1 3 5	0.83 0.41 0.17	0.12 0.060 0.02	<0.01 <0.01 <0.01	0.069 0.03 0.02	0.01 <0.01 <0.01	1.0 0.51 0.22	RES95001 VA1
VA (Old Fashioned)	2x0.10 +2x0.15		280	4	1 3	5.0 3.0	0.62 0.40	0.01 0.01	0.18 0.12	0.01 0.01	5.8 3.5	RES95001 VA2

Table 47. Spinosad residues in cucurbits from supervised trials in the USA in 1997. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location (variety)	Application					PHI, days	Spinosyn residues, mg/kg immunoassay	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
CUCUMBER								
FL (Sunre 3775)	SC 240	5×0.075 +1×0.15		450	6	1	0.046	RES97002 FL1
MI (Marketmore)	SC 240	5×0.075 +1×0.15		270	6	1	0.053	RES97002 MI
NC (Straight Eight)	SC 240	5×0.075 +1×0.15		240	6	1	0.01	RES97002 NC1
NC (Burpless)	SC 240	5×0.075 +1×0.15		230	6	1	0.059	RES97002 NC2
OH (General Lee)	SC 240	5×0.075 +1×0.15		230	6	1	0.052	RES97002 OH1
TX (Dasher II)	SC 240	5×0.075 +1×0.15		360	6	1	0.024	RES97002 TX5
MUSKMELON								
CA (Jumbo Hales Best)	SC 240	5×0.075 +1×0.15		270	6	3 3	0.12 f <0.01	RES97002 CA1
CA (Mission)	SC 240	5×0.075 +1×0.15		310	6	3	0.036	RES97002 CA2
CA (Primo cantaloupe)	SC 240	5×0.075 +1×0.15		320	6	3	0.045	RES97002 CA3
NC (Burpee Hybrid muskmelon)	SC 240	5×0.075 +1×0.15		220	6	3	0.054	RES97002 NC3
OH (Burpee Hybrid PMT Muskmelon)	SC 240	5×0.075 +1×0.15		220	6	3 3	0.16 f <0.01	RES97002 OH2

Location (variety)	Application					PHI, days	Spinosyn residues, mg/kg immunoassay	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
TX Hales Best #36)	SC 240	5×0.075 +1×0.15		350	6	3 3	0.092 f <0.01	RES97002 TX4
SUMMER SQUASH								
CA (Bennings Green tint)	SC 240	5×0.075 +1×0.15		290	6	3	0.038	RES97002 CA4
FL (Hurricane 9718)	SC 240	5×0.075 +1×0.15		450	6	3	0.024	RES97002 FL2
NC (Yellow Straightneck)	SC 240	5×0.075 +1×0.15		250	6	3	<0.01	RES97002 NC4

Table 48. Spinosad residues in tomatoes from supervised trials in Australia and New Zealand. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.			
Australia (NSW), 1996 (82B)	SC480	0.10	99	4	0 1 3 7 13	0.03 0.03 c 0.013 0.02 <0.01 <0.01	GHF-P 1535
Australia (NSW), 1996 (82B)	SC480	0.20	99	4	0 1 3 7 13	0.08 0.06 c 0.013 0.02 <0.01 0.01	GHF-P 1535
Australia (NSW), 1997 (Atlas)	SC 120	0.096	99	4	0 1 2 7	0.05 0.03 0.02 <0.01	GHF-P 1567
Australia (NSW), 1997 (Atlas)	SC 120	0.19	99	4	0 1 2 7	0.15 0.08 0.07 0.02	GHF-P 1567
Australia (NSW), 1997 (Pacesetter)	SC 120	0.096	99	4	0 1 2 7	0.05 0.02 0.03 <0.01	GHF-P 1567
Australia (NSW), 1997 (Pacesetter)	SC 120	0.19	99	4	0 1 2 7	0.13 0.09 0.06 0.02	GHF-P 1567

Country, year (variety)	Application				PHI, days	Residues, mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.			
Australia (Vic), 1996 (Arcadia)	SC480	0.10	250	4	0 1 3 7 15	0.07 <u>0.04</u> 0.02 <0.01 <0.01	GHF-P 1535
Australia (Vic), 1996 (Arcadia)	SC480	0.20	250	4	0 1 3 7 15	0.13 0.08 0.04 <0.01 <0.01	GHF-P 1535
Australia (Vic), 1997 (Red Gem)	SC 120	0.096	250	4	0 1 3 7	0.05 <u>0.03</u> 0.01 <0.01	GHF-P 1567
Australia (Vic), 1997 (Red Gem)	SC 120	0.19	250	4	0 1 3 7	0.17 0.07 0.08 0.01	GHF-P 1567
NZ, 1997 (H232)	SC 120	0.096	470	4	0 1 3 7 14	0.06 <u>0.04</u> <0.01 <0.01 <0.01	GHF-P 1568 10650
NZ, 1997 (H232)	SC 120	0.048	470	4	0 1 3 7 14	0.03 0.02 <0.01 <0.01 <0.01	GHF-P 1568 510650

c: sample from control plot

Table 49. Spinosad residues in tomatoes from supervised trials in Argentina and Brazil. Replicate residues represent samples from split or replicate plots. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country (location), year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	
Argentina (Buenos Aires), 1996 (Lerika)	SC 480	0.12	1000	5	0 3 7 14	0.35 0.32 0.39 <u>0.05</u> <0.01 0.01 <0.01 <0.01 0.01 0.02 0.01 0.04	0.05 0.05 0.06 <u>0.01</u> <0.01 <0.01 <0.01(3) <0.01(3)	GHB-P 370
Argentina (Buenos Aires), 1996 (Lerika)	SC 480	0.24	1000	5	0 3 7 14	0.72 0.76 0.33 0.11 0.19 0.18 0.02 0.01 0.02 0.02 0.01 0.05	0.11 0.12 0.05 0.02 0.03 0.03 <0.01(3) <0.01 <0.01 0.01	GHB-P 370
Argentina (Buenos Aires), 1997 (Lerika)	SC 480	0.12	1000	5	1 4 8	0.11 0.07 0.07 <u>0.18</u> 0.09 0.08 0.09 0.04 0.07	0.02 0.01 0.01 <u>0.03</u> 0.02 0.01 0.02 <0.01 0.01	GHB-P 370

Country (location), year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	
Argentina (Buenos Aires), 1997 (Lerika)	SC 480	0.24	1000	5	1 4 8	0.21 0.29 0.25 0.20 0.17 0.16 0.12 0.09 0.09	0.04 0.05 0.04 0.03 0.03 0.03 0.02 0.02 0.02	GHB-P 370
Argentina (Mendonza), 1996 (Presto)	SC 480	0.12	2600-3300	5	0 3 7 14	0.15 0.09 0.11 0.12 0.06 0.09 0.05 0.05 0.08 0.15 0.04 0.08	0.03 0.01 0.02 0.02 <0.01 0.01 <0.01 <0.01 0.01 0.02 <0.01 0.01	GHB-P 370
Argentina (Mendonza), 1996 (Presto)	SC 480	0.24	2600-3300	5	0 3 7 14	0.47 0.36 0.41 0.24 0.33 0.38 0.16 0.22 0.15 0.09 0.12 0.08	0.07 0.06 0.06 0.04 0.05 0.06 0.03 0.04 0.03 0.02 0.02 0.01	GHB-P 370
Argentina (Mendonza), 1997 (Misouri)	SC 480	0.12	300-600	5	0 3 7 14	0.14 0.22 0.18 0.04 0.06 0.06 <0.01(3) <0.01(3)	0.02 0.03 0.03 <0.01(3) <0.01(3) <0.01(3)	GHB-P 370
Argentina (Mendonza), 1997 (Misouri)	SC 480	0.24	300-600	5	0 3 7 14	0.15 0.14 0.19 0.15 0.13 0.12 <0.01 <0.01 0.01 <0.01(3)	0.02 0.02 0.03 0.02 0.02 0.02 0.01 <0.01 <0.01 <0.01(3)	GHB-P 370
Argentina (Santiago del Estero), 1996 (6002)	SC 480	0.12	1200	5	0 3 7 14	0.02 0.33 0.02 <0.01 0.01 <0.01 <0.01(3) <0.01(3)	<0.01 0.05 <0.01 <0.01(3) <0.01(3) <0.01(3)	GHB-P 370
Argentina (Santiago del Estero), 1996 (6002)	SC 480	0.24	1200	5	0 3 7 14	0.05 0.04 0.02 0.03 0.02 0.02 0.02 0.01 0.01 <0.01 <0.01 0.01	0.01 0.01 <0.01 <0.01(3) <0.01(3) <0.01(3)	GHB-P 370
Argentina (Santiago del Estero), 1997 (Rio Grande)	SC 480	0.12	1200	4	0 3 7 14	0.07 0.07 0.04 0.02 0.01 <0.01 <0.01 <0.01 0.01 0.01 0.01 <0.01	0.01 0.01 <0.01 <0.01(3) <0.01(3) <0.01(3)	GHB-P 370
Argentina (Santiago del Estero), 1997 (Rio Grande)	SC 480	0.24	1200	4	0 3 7 14	0.08 0.04 0.07 0.01 0.01 0.02 0.01 <0.01 0.01 <0.01 0.01 0.01	0.02 <0.01 0.01 <0.01(3) <0.01(3) <0.01(3)	GHB-P 370
Brazil (Paraná), 1995 (Grupo Santa Clara)	WG 800	0.20	1000	6	0 3 7 14 21	0.04 0.07 0.05 0.01 0.02 0.01 <0.01 (2) 0.02 <0.01 (2) 0.01 <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-331
Brazil (Paraná), 1995 (Grupo Santa Clara)	WG 800	0.40	1000	6	0 3 7 14 21	0.12 0.17 0.12 0.04 0.06 0.10 0.04 0.05 0.05 0.03 0.03 0.04 0.02 0.01 0.03	0.01 0.02 <0.01 <0.01 (2) 0.01 <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-331

Country (location), year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	
Brazil (São Paulo), 1995 (Angela 5200)	WG 800	0.20	1000	6	0 3 7 14 21	0.02 0.03 0.02 0.01 <0.01 (2) <0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-331
Brazil (São Paulo), 1995 (Angela 5200)	WG 800	0.40	1000	6	0 3 7 14 21	0.10 0.07 0.09 0.04 <0.01 (2) <0.01 (3) <0.01 (3) <0.01 (3)	0.01 <0.01 0.01 <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-331
Brazil (São Paulo), 1996 (Santa Clara)	SC 480	0.082	1000	6	0 1 3 7 14	0.02 0.01 0.02 0.01 0.01 <0.01 <0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-337
Brazil (São Paulo), 1996 (Santa Clara)	SC 480	0.16	1000	6	0 1 3 7 14	0.04 (3) 0.02 0.03 <0.01 0.03 0.02 0.02 <0.01 (2) 0.02 <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-337
Brazil (São Paulo), 1996 (Santa Clara)	SC 480	0.082	1000	6	0 1 3	0.03 (3) 0.01 (3) <0.01 (2) 0.02	<0.01 (3) <0.01 (3) <0.01 (3)	GHB P-337
Brazil (São Paulo), 1996 (Santa Clara)	SC 480	0.16	1000	6	0 1 3	0.06 0.07 0.05 0.01 (3) <0.01 (2) 0.02	<0.01 (3) <0.01 (3) <0.01 (3)	GHB P-337

Table 50. Spinosad residues in tomatoes from supervised trials in Greece, Italy, Spain and the UK.

Country, year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Greece, 1998 (Galli)	SC 480	0.58 +610 +620	0.094	620	2 3	14 0 2 3 6	0.01 0.10 0.04 0.02 0.02	<0.01 0.06 0.02 0.01 0.02	0.01 0.16 0.06 0.03 0.04		GHE-P-7858 R98-026B
Greece, 1998 (Noa F1)	SC 480	0.57 +0.58 +0.57	0.094	610 +610 +600	2 3	14 0 2 3 6	0.03 0.35 0.10 0.04 0.03	0.03 0.26 0.07 0.02 0.02	0.06 0.63 0.17 0.06 0.05		GHE-P-7858 R98-026A
Italy, 1997 (Erminia Peto Seed)	SC 480	0.54	0.067	800	5	3 [4]	0.30	0.08	0.40	0.38	GHE-P-7585

Country, year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Italy, 1997 (ES 200)	SC 480	0.53	0.067	790	g 4	11	0.20	0.05	0.26	0.34	GHE-P-7580
		+0.55		+810	g 5	0	0.61	0.13	0.75	1.1	
		+0.55		+810		2	0.38	0.09	0.47	0.70	
		+0.54		+800		3	0.45	0.10	0.57	0.68	
		+0.55		+820		6 [4]	0.30	0.06	0.37	0.42	
Italy, 1997 (UC 82)	SC 480	0.53	0.066	810	5	3	0.11	0.03	0.12	0.11	GHE-P-7589
						6	0.20	0.05	0.24	0.26	
Italy, 1997 (UC 82R Peto seed)	SC 480	0.54	0.067	800	4	11	0.11	0.03	0.15	0.21	GHE-P-7583
		+0.55		+810	5	0	0.54	0.12	0.66	0.76	
		+0.54		+800		2	0.08	0.03	0.10	0.11	
		+0.53		+790		3	0.04	0.01	0.05	0.06	
		+0.54		+810		6 [4]	0.03	<0.01	0.04	0.06	
Italy, 1998 (Cauda)	SC 480	0.55	0.057	970	g 2	19	0.07	0.05	0.12		GHE-P-7860
		+0.57		+1000	g 3	0	0.22	0.15	0.37		
		+0.57		+1000		2	0.19	0.13	0.32		
						3	0.21	0.15	0.36		
						7	0.08	0.06	0.14		
Italy, 1998 (ES 580)	SC 480	0.55	0.067	810	g 3	3	0.08	0.06	0.14		GHE-P-7865
						6	0.06	0.04	0.10		R98-033A
Italy, 1998 (EXH 98063)	SC 480	0.54	0.067	800	3	3	0.06	0.05	0.11		GHE-P-7861
						6	0.02	0.02	0.04		R98-029A
Spain, 1997 (Daniella)	SC 480	0.43	0.043	990	g 5	3	0.25	0.08	0.32	0.35	GHE-P-7587
		+0.42	+0.043	+980		6	0.29	0.08	0.36	0.41	
		+0.49	+0.054	+900							
		+0.53	+0.054	+980							
		+0.55	+0.054	+1010							
Spain, 1997 (Durinta)	SC 480	0.58	0.077	750	g 4	10	0.07	0.02	0.09	0.14	GHE-P-7581
		+0.54	+0.067	+810	g 5	0	0.15	0.05	0.21	0.36	
		+0.53	+0.060	+880		2	0.15	0.06	0.22	0.37	
		+0.52	+0.054	+970		3	0.17	0.05	0.23	0.36	
		+0.55	+0.049	+1120		6	0.26	0.08	0.35	0.54	
Spain, 1997 (Durinta)	SC 480	0.54	0.054	1000	4	12	0.02	<0.01	0.03	0.04	GHE-P-7584
		+0.53		+980	5	0	0.14	0.03	0.18	0.22	
		+0.54		+1000		2	0.17	0.04	0.21	0.26	
		+0.55		+1010		3	0.22	0.06	0.29	0.37	
		+0.55		+1020		6	0.10	0.03	0.12	0.18	
Spain, 1997 (Durinta)	SC 480	0.55	0.054	1030	5	3	0.07	0.02	0.09	0.10	GHE-P-7588
		+0.55		+1030		6	0.02	<0.01	0.03	0.04	
		+0.51		+950							
		+0.51		+950							
		+0.54		+1000							
Spain, 1998 (Durinta)	SC 480	0.52	0.090	580	2	14	0.04	0.04	0.08		GHE-P-7857
		+0.53	+0.067	+790	3	0	0.14	0.10	0.25		
		+0.57	+0.054	+1050		2	0.09	0.06	0.15		
						3	0.09	0.07	0.17		
						6	0.08	0.06	0.14		

Country, year (variety)	Application					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Spain, 1998 (Durinta)	SC 480	0.54	0.077 +0.060 +0.049	710 +890 +1110	g 3	3 6	0.07 0.05	0.05 0.03	0.12 0.08		GHE-P-7863
Spain, 1998 (Lustro)	SC 480	0.54 +0.56 +0.56	0.067 +0.054 +0.045	810 +1040 +1240	3	3 6	0.11 0.03	0.07 0.03	0.18 0.06		GHE-P-7862
UK, 1997 (Solairo F1)	SC 480	0.54	0.045	1200	g 4 g 5	10 0 2 3 6 [5]	0.10 0.19 0.13 0.12 0.14	0.05 0.08 0.04 0.04 0.04	0.15 0.27 0.17 0.17 0.19	0.25 0.32 0.19 0.19 0.22	GHE-P-7582 R97-057
UK, 1997 (Solairo F1)	SC 480	0.54	0.045	1200	g 5	3 6	0.23 0.20	0.06 0.05	0.30 0.25	0.42 0.38	GHE-P-7586 R97-061
UK, 1998 (Alicante)	SC 480	0.57 +0.56 +0.56	0.047	1210 +1190 +1190	g 3	3 6	0.16 0.17	0.11 0.11	0.27 0.28		GHE-P-7864
UK, 1998 (Solairo F1)	SC 480	0.57	0.045	1200	g 2 g 3	14 0 2 3 6	0.07 0.13 0.27 0.15 0.09	0.04 0.08 0.22 0.07 0.05	0.12 0.22 0.51 0.22 0.15		GHE-P-7859 R98-027

[1] Total includes spinosyns A, D, B, B of D and K
[2] Immunoassay
[3] g: glasshouse
[4] Samples stored in a freezer for approx. 16 months
[5] Samples stored in a freezer for approx. 18 months

Table 51. Spinosad residues in tomatoes from supervised trials in Mexico and the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
Mexico, 1995 (Pole, BR-84)	WG 820	0.050 +0.10 +0.10 +0.10 +0.15	280 +170 +250 +250 +240	5	0 1 3 7	0.046 0.066 0.026 0.014	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.063 0.091 0.034 0.015	RES95076 MEX9501
USA (CA), 1996 (Dimare 540)	SC 480	0.052 +0.057 +0.083 +0.083 +0.11 +0.16	510	6	1 3	<u>0.026</u> 0.011	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.030 0.011	RES96009/ RES96008 CA1

Country, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
USA (CA), 1996 (Dimare 540)	WG 800	0.060 +0.058 +0.089 +0.087 +0.12 +0.17	520	6	1 3	0.023 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.026 <0.01	RES96009/ RES96008 CA1
USA (CA), 1996 (Dimare 540)	SC 480	0.056 +0.055 +0.087 +0.085 +0.12 +0.16	490	6	1 3	0.013 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.013 0.01	RES96009/ RES96008 CA2
USA (CA), 1996 (Dimare 540)	WG 800	0.054 +0.053 +0.082 +0.083 +0.12 +0.17	530	6	1 3	0.024 0.018	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.027 0.020	RES96009/ RES96008 CA2
USA (FL), 1996 (Better Boy)	SC 480	0.050 +0.052 +0.075 +0.076 +0.10 +0.15	280	6	1 3	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	RES96009/ RES96008 FL
USA (FL), 1996 (Better Boy)	WG 800	0.048 +0.049 +0.074 +0.074 +0.10 +0.15	290	6	1 3	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	RES96009/ RES96008 FL
USA (CA), 1995 (Peelmech, processing)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.071 0.062 0.05	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.085 0.070 0.05	RES95016 CA1
USA (CA), 1995 (Halley 3155, processing)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.062 0.10 0.058	<0.01 0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.071 0.11 0.066	RES95016 CA2
USA (CA), 1995 (La Rossa, processing)	WG 800	0.050 +3x0.10 +0.15	280	5	0 1 3	0.057 0.04 0.03	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.069 0.05 0.03	RES95016 CA3
USA (CA), 1995 (Roma)	WG 800	0.050 +3x0.10 +0.15	280	5	0 1 3 7 10 14	0.03 0.02 0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	0.04 0.02 0.01 <0.01 <0.01 <0.01	RES95016 CA4

Country, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
USA (CA), 1995 (Shady Lady)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.059 0.03 0.02	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.067 0.04 0.03	RES95016 CA5
USA (CA), 1996 (Shady Lady)	WG 800	0.050 +3x0.10 +0.15	280	5	0 1 3	0.058 0.04 0.05	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.064 0.05 0.059	RES95016 CA6
USA (CA), 1995 (Shady Lady)	WG 800	0.050 +3x0.10 +0.15	280	5	0 1 3	<0.01 0.03 0.02	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 0.03 0.02	RES95016 CA7
USA (FL), 1995 (Fresh Market)	WG 800	0.050 +3x0.10 +0.15	280	5	0 1 3	0.04 0.03 0.02	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.05 0.04 0.02	RES95016 FL1
USA (FL), 1995 (Agriset)	WG 800	0.050 +3x0.10 +0.15	280	5	0 1 3	0.03 0.02 0.03	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.03 0.02 0.03	RES95016 FL2
USA (OH), 1995 (Heinz 8813, processing)	WG 800	0.050 +3x0.10 +0.15	180	5	0 1 3	0.060 0.076 0.02	<0.01 0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.067 0.091 0.03	RES95016
USA (PA), 1995 (La Roma, processing)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.01 0.02 0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.01 0.02 0.01	RES95016
USA (VA), 1995 (Mountain Pride)	WG 800	0.050 +3x0.10 +0.15	340	5	0 1 3	0.11 0.11 0.05	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.13 0.13 0.059	RES95016

Table 52. Spinosad residues in peppers from supervised trials in the USA . Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
AZ, 1995 (S414 Peppers, hot)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.13 0.15 0.083	0.01 0.02 0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.15 0.17 0.097	RES95016
CA, 1995 (Jupiter, bell)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.058 0.063 0.03	<0.01 0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.065 0.081 0.03	RES95016 CA8
CA, 1995 (Milta, hot)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.14 0.12 0.10	0.02 0.02 0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.16 0.14 0.12	RES95016 CA9

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
FL, 1995 (Jupiter, bell)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.093 <u>0.05</u> 0.05	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.11 0.054 0.060	RES95016
OH, 1995 (Cal Wonders, bell)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.075 <u>0.05</u> 0.03	0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.084 0.055 0.03	RES95016
TX, 1995 (Wonder Rio 66, bell)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.075 <u>0.062</u> 0.03	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.084 0.069 0.03	RES95016 TX1
TX, 1995 (Jalapeno, hot)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3	0.04 <u>0.03</u> 0.02	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	0.04 0.04 0.02	RES95016 TX2
VA, 1995 (Giant, bell)	WG 800	0.050 +3x0.10 +0.15	290	5	0 1 3 7 10 14	0.03 <u>0.02</u> 0.01 <0.01 0.01 0.02	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	0.04 0.02 0.01 <0.01 0.01 0.02	RES95016

Table 53. Spinosad residues in sweet peppers from supervised trials in Australia, Greece, Italy, Mexico, Spain and the UK. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year (variety)	Application [4]					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Australia (Qld), 1997 (Target capsicum)	SC 120	0.096		300 +450 +360 +360	4	0 1 3 7				0.05 <u>0.04</u> 0.03 0.03	GHF-P 1584
Australia (Qld), 1997 (Target capsicum)	SC 120	0.19		300 +450 +360 +360	4	0 1 3 7				0.24 0.14 0.09 0.06	GHF-P 1584
Australia (Vic), 1997 (Domino capsicum)	SC 120	0.096		250	4	0 1 3 7				0.12 <u>0.12</u> 0.06 0.02	GHF-P 1584
Australia (Vic), 1997 (Domino capsicum)	SC 120	0.19		250	4	0 1 3 7				0.20 0.23 0.23 0.10	GHF-P 1584

Country, year (variety)	Application [4]					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Greece, 1998 (Stamboli)	SC 480	0.44	0.055	800	2 3	13 0 2 3 6	<0.01 0.41 0.15 0.06 0.05	<0.01 0.13 0.04 0.02 0.02	<0.01 0.56 0.20 0.08 0.07		GHE-P-7873
Italy, 1997 (Magister)	SC 480	0.43	0.054	800	4 5	11 0 2 3 6	<0.01 0.31 0.01 0.01 0.01	<0.01 0.09 <0.01 <0.01 <0.01	<0.01 0.43 0.02 0.02 0.01	<0.01 0.39 <0.01 0.01 0.01	GHE-P-7751
Italy, 1997 (Magister)	SC 480	0.43	0.054	810	5	3 6	0.06 <0.01	0.02 <0.01	0.08 <0.01	0.10 0.01	GHE-P-7912 R97-053B
Italy, 1997 (Moutero)	SC 480	0.41	0.052	790	g 4 g 5	7 0 2 3 6 3	0.79 1.1 1.07 1.2 0.96 c <.01	0.20 0.27 0.28 0.32 0.23 c <0.01	1.1 1.5 1.4 1.7 1.3 c 0.02	1.1 1.2 1.1 2.0 0.88 c <0.01	GHE-P-7664
Italy, 1997 (Sanbor)	SC 480	0.37	0.052	700	5	3 6	0.13 0.07	0.04 0.02	0.16 0.10	0.19 0.14	GHE-P-7912 R97-053A
Italy, 1998 (Lipari)	SC 480	0.44	0.038	1160	3	3 6	0.08 0.03	0.07 0.04	0.15 0.08		GHE-P-7867
Italy, 1998 (Livor)	SC 480	0.43	0.054	790	g 3	3 6	0.35 0.28	0.25 0.19	0.63 0.49		GHE-P-7868R
Mexico, 1995 (Bell pepper, Galaxie)	WG 820	0.050 +0.11 +0.10 +0.092 +0.15		240 +360 +360 +350 +330	5	0 1 3 7	0.11 0.062 0.043 0.031	0.014 0.01 <0.01 <0.01	0.15 0.087 0.053 0.038		RES95076 MEX9502
Spain, 1997 (Carisma)	SC 480	0.43	0.33	1300	g 4 g 5	12 0 2 3 6	0.16 0.22 0.20 0.17 0.13	0.05 0.06 0.05 0.05 0.03	0.23 0.32 0.29 0.26 0.18	0.24 0.31 0.28 0.23 0.19	GHE-P-7685
Spain, 1997 (Lamuyo Largo)	SC 480	0.43	0.036	1200	4 5	11 0 2 3 6	0.04 0.12 0.10 0.17 0.06	0.01 0.03 0.03 0.05 0.02	0.05 0.17 0.13 0.23 0.09	0.04 0.25 0.17 0.35 0.10	GHE-P-7717
Spain, 1997 (Local)	SC 480	0.43	0.43	1000	5	3 6	0.18 0.11	0.05 0.03	0.24 0.14	0.32 0.18	GHE-P-7790
Spain, 1997 (Rosi)	SC 480	0.41	0.43	950	g 5	3 6	0.16 0.07	0.04 0.02	0.23 0.09	0.24 0.12	GHE-P-7784
Spain, 1998 (Atol)	SC 480	0.43	0.036	1180	g 3	3 6	0.20 0.16	0.05 0.04	0.25 0.20		GHE-P-7869R

Country, year (variety)	Application [4]					PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.[3]		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Spain, 1998 (Atol)	SC 480	0.43	0.036	1200	g 2 g 3	14 0 2 3 6 [5]	0.09 0.43 0.29 0.25 0.19	0.02 0.09 0.07 0.06 0.05	0.12 0.53 0.37 0.33 0.25		GHE-P-7872
Spain, 1998 (Dulce)	SC 480	0.45	0.045	1000	3	3 6	0.08 0.07	0.04 0.05	0.12 0.12		GHE-P-7866
Spain, 1998 (Lamuyo telier)	SC 480	0.44	0.045	980	2 3	13 0 2 3 6	0.02 <0.01 0.21 0.06 0.04	0.01 <0.01 0.08 0.04 0.02	0.03 <0.01 0.30 0.09 0.06		GHE-P-7870R R98-021B
Spain, 1998 (Lamuyo)	SC 480	0.47	0.038	1240	2 3	13 0 2 3 6	0.07 0.18 0.17 0.08 0.10	0.07 0.13 0.14 0.05 0.08	0.15 0.32 0.32 0.13 0.19		GHE-P-7870R R98-021A
UK, 1997 (Mazurka RZ)	SC 480	0.43	0.036	1190	g 4 g 5	10 0 2 3 6	0.35 0.45 0.35 0.38 0.41	0.10 0.12 0.09 0.10 0.10	0.50 0.65 0.49 0.54 0.59	0.67 0.78 0.55 0.73 0.80	GHE-P-7618
UK, 1997 (Mazurka RZ)	SC 480	0.44	0.036	1220	g 5	3 6	0.27 0.25	0.10 0.09	0.45 0.42	0.49 0.48	GHE-P-7626
UK, 1998 (Mazurka RZ)	SC 480	0.45	0.046	1000	g 2 g 3	14 1 2 3 6	0.08 0.24 0.19 0.17 0.18	0.06 0.16 0.13 0.13 0.14	0.15 0.42 0.34 0.31 0.33		GHE-P-7871

[1] Total includes spinosyns A, D, B, B of D and K
[2] Immunoassay
[3] g: glasshouse
[4] Application rate, spray concentration and volume per ha were not identical (variation mostly within 20%). The values reported are those for the final application.
[5] Samples stored frozen for approx. 15 months

Table 54. Residues of spinosad in sweet corn kernels and cob (with husk removed) from supervised trials in the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Residues, mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.			
CA, 1997 (Legend)	SC 240	0.10	190	5	1	<u><0.01</u>	RES97037
FL, 1997 (Silver Queen)	SC 240	0.10	280	5	1	<u><0.01</u>	RES97037

Location, year (variety)	Application				PHI, days	Residues, mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.			
MI, 1997 (Sweet Chorus)	SC 240	0.10	230	5	1	<0.01	RES97037
MN, 1997 (Quickie Hybrid)	SC 240	0.10	180	5	1	<0.01 <0.01 (HPLC)	RES97037
NC, 1997 (Silver Queen)	SC 240	0.10	240	5	1	<0.01	RES97037
NY, 1997 (Tuxedo)	SC 240	0.10	180	5	1	<0.01	RES97037
OR, 1997 (Jubilee)	SC 240	0.10	290	5	1	<0.01	RES97037
WA, 1997 (Silver Sweet Jubilee)	SC 240	0.10	290	5	1	<0.01	RES97037
WI, 1997 (Confection SH2 Bi-color)	SC 240	0.10	180	5	1	<0.01	RES97037

Table 55. Spinosad residues in egg plant from supervised glasshouse trials in Japan, in 1995[?].

Application				PHI, days	Spinosyn residues, mg/kg						Ref.
Form	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
WG 250	0.005	300	1	1	0.05	0.01	0.02	<0.01	<0.01	0.08	GHF-P-1485 N-NASU
				3	0.02	<0.01	0.01	<0.01	<0.01	0.03	
				7	0.01	<0.01	<0.01	<0.01	<0.01	0.01	
			3	1	0.14	0.02	0.01	<0.01	<0.01	0.17	
				3	0.15	0.02	0.01	<0.01	<0.01	0.18	
				7	0.07	0.01	0.01	<0.01	<0.01	0.09	
WG 250	0.005	300	1	1	0.08	0.01	<0.01	0.01	<0.01	0.10	GHF-P-1485 CHIKUYOU
WG 250	0.0025	300	1	1	0.06	0.01	0.01	0.01	<0.01	0.09	GHF-P-1485 CHIKUYOU
WG 250	0.0013	300	1	1	0.02	<0.01	<0.01	<0.01	<0.01	0.02	GHF-P-1485 CHIKUYOU

Table 56. Spinosad residues in lettuce from supervised trials in Australia. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Spinosad, mg/kg immunoassay	Ref.
	Form	kg ai/ha	water, l/ha	no.			
Qld, 1998 (Summertime)	SC120	0.096 +adjuvant	400	4	0 1 3 7 14	0.38 0.10 0.21 0.05 <0.01	GHF-P-1797 984008GW

Location, year (variety)	Application				PHI, days	Spinosad, mg/kg immunoassay	Ref.
	Form	kg ai/ha	water, l/ha	no.			
Qld, 1998 (Summertime)	SC120	0.19 +adjuvant	400	4	0 1 3 7 14	0.98 0.44 0.42 0.05 0.01	GHF-P-1797 984008GW
Qld, 1998 (Summertime)	SC120	0.096	400	4	0 3 7 14 21 28	2.2 <u>1.1</u> 0.04 <0.01 0.01 <0.01	GHF-P-1797 984016GW
Qld, 1998 (Summertime)	SC120	0.19	400	4	0 3 7 14 21 28	3.6 1.3 0.19 0.01 <0.01 <0.01	GHF-P-1797 984016GW
NSW, 1998 (Marksman)	SC120	0.096	250	4	0 1 3 7 14 21	3.5 3.4 <u>1.7</u> 0.50 0.01 <0.01	GHF-P-1797 97381.03
NSW, 1998 (Marksman)	SC120	0.19	250	4	0 1 3 7 14 21	8.3 7.7 3.8 0.61 0.10 <0.01	GHF-P-1797 97381.03

Table 57. Spinosad residues in leafy vegetables from supervised trials in the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
HEAD LETTUCE												
CA, 1996 (Pybas 251) include wrapper leaves	SC 480	0.049 +0.050 +0.073 +0.076 +0.099 +0.14	300	6	1 3	<u>0.094</u> 0.063	<u>0.015</u> 0.01	<0.01 <0.01	0.01 <0.01	<0.01 <0.01	0.12 0.081	RES96009/ RES96008 CA2

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
CA, 1996 (Pybas 251) wrapper leaves removed	SC 480	0.049 +0.050 +0.073 +0.076 +0.099 +0.14	300	6	1 3	0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.01 <0.01	RES96009/ RES96008 CA2
CA, 1996 (Pybas 251) include wrapper leaves	WG 800	0.050 +0.051 +0.075 +0.077 +0.098 +0.15	300	6	1 3	0.052 0.091	<0.01 0.015	<0.01 <0.01	<0.01 0.01	<0.01 <0.01	0.064 0.11	RES96009/ RES96008 CA2
CA, 1996 (Pybas 251) wrapper leaves removed	WG 800	0.050 +0.051 +0.075 +0.077 +0.098 +0.15	300	6	1 3	<0.01 0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 0.01	RES96009/ RES96008 CA2
CA, 1996 (Van May) include wrapper leaves	SC 480	0.048 +0.048 +0.078 +0.074 +0.099 +0.16	300	6	1 3	0.67 0.59	0.10 0.092	<0.01 <0.01	0.029 0.023	<0.01 <0.01	0.80 0.71	RES96009/ RES96008 CA1
CA, 1996 (Van May) wrapper leaves removed	SC 480	0.048 +0.048 +0.078 +0.074 +0.099 +0.16	300	6	1 3	0.019 0.018	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.019 0.021	RES96009/ RES96008 CA1
CA, 1996 (Van May) include wrapper leaves	WG 800	0.049 +0.048 +0.074 +0.076 +0.10 +0.15	300	6	1 3	0.59 0.37	0.082 0.055	<0.01 <0.01	0.024 0.016	<0.01 <0.01	0.70 0.44	RES96009/ RES96008 CA1
CA, 1996 (Van May) wrapper leaves removed	WG 800	0.049 +0.048 +0.074 +0.076 +0.10 +0.15	300	6	1 3	0.024 0.015	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	0.028 0.017	RES96009/ RES96008 CA1
FL, 1996 (Great Lakes) include wrapper leaves	SC 480	0.049 +0.050 +0.076 +0.077 +0.099 +0.15	280	6	1 3	0.63 0.25	0.10 0.041	<0.01 <0.01	0.048 0.034	<0.01 <0.01	0.79 0.33	RES96009/ RES96008 FL

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
FL, 1996 (Great Lakes) wrapper leaves removed	SC 480	0.049 +0.050 +0.076 +0.077 +0.099 +0.15	280	6	1 3	0.15 0.077	0.022 0.012	<0.01 <0.01	0.020 0.015	<0.01 <0.01	0.19 0.10	RES96009/ RES96008 FL
FL, 1996 (Great Lakes) include wrapper leaves	WG 800	0.051 +0.049 +0.075 +0.076 +0.098 +0.15	280	6	1 3	0.72 0.27	0.13 0.044	<0.01 <0.01	0.069 0.039	0.01 <0.01	0.94 0.35	RES96009/ RES96008 FL
FL, 1996 (Great Lakes) wrapper leaves removed	WG 800	0.051 +0.049 +0.075 +0.076 +0.098 +0.15	280	6	1 3	0.17 0.24	0.024 0.036	<0.01 <0.01	0.026 0.038	<0.01 <0.01	0.23 0.32	RES96009/ RES96008 FL
SPINACH												
CA, 1996 (St Helens)	SC 480	0.047 +0.050 +0.068 +0.074 +0.10 +0.15	290	6	1 3	2.5 0.97	0.37 0.14	0.01 <0.01	0.23 0.12	0.030 0.014	3.1 1.2	RES96009/ RES96008 CA1
CA, 1996 (St Helens)	WG 800	0.049 +0.050 +0.067 +0.074 +0.10 +0.15	290	6	1 3	2.6 1.4	0.37 0.19	<0.01 <0.01	0.22 0.14	0.022 0.018	3.3 1.7	RES96009/ RES96008 CA1
CA, 1996 (Bossa-nova)	SC 480	0.51 +0.48 +0.67 +0.74 +0.10 +0.15	300	6	1 3	2.4 0.48	0.37 0.079	<0.01 <0.01	0.17 0.060	0.024 <0.01	3.0 0.63	RES96009/ RES96008 CA2
CA, 1996 (Bossa-nova)	WG 800	0.052 +0.051 +0.077 +0.078 +0.10 +0.16	310	6	1 3	3.5 0.64	0.49 0.10	<0.01 <0.01	0.23 0.069	0.035 <0.01	4.3 0.82	RES96009/ RES96008 CA2
TX, 1996 (Skookum)	SC 480	0.050 +0.050 +0.075 +0.076 +0.10 +0.15	390	6	1 3	2.1 1.1	0.33 0.15	<0.01 <0.01	0.10 0.080	0.023 0.01	2.6 1.3	RES96009/ RES96008 TX

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
TX, 1996 (Skookum)	WG 800	0.051 +0.051 +0.075 +0.077 +0.10 +0.15	390	6	1 3	3.9 2.3	0.54 0.33	<0.01 <0.01	0.13 0.14	0.018 0.015	4.6 2.7	RES96009/ RES96008 TX

Table 58. Spinosad residues in leafy vegetables and celery from supervised trials in the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
HEAD LETTUCE										
AZ, 1996 (Diamond) include wrapper leaves	SC 480	0.053 +0.054 +0.079 +0.080 +0.11 +0.15	290	6	1 3	1.7	0.27	2.1	3.1 2.1	RES96008 AZ LV9606
AZ, 1996 (Diamond) wrapper leaves removed	SC 480	0.053 +0.054 +0.079 +0.080 +0.11 +0.15	290	6	1 3	1.6 0.40	0.25 0.069	1.9 0.50	2.3 0.61	RES96008 AZ LV9606
CA, 1996 (Jupiter) include wrapper leaves	SC 480	0.048 +0.051 +0.075 +0.077 +0.10 +0.15	320	6	0 1 3 5				0.93 0.92 0.097 0.13	RES96008 CA3 LV9605
CA, 1996 (Jupiter) wrapper leaves removed	SC 480	0.048 +0.051 +0.075 +0.077 +0.10 +0.15	320	6	0 1 3 5				0.073 0.052 0.09 0.01	RES96008 CA3 LV9605
NJ, 1996 (Ithaca) include wrapper leaves	SC 480	0.052 +0.051 +0.077 +0.077 +0.10 +0.15	290	6	1 3	<0.01	<0.01	0.01	0.12 0.012	RES96008 NJ LV9601
NJ, 1996 (Ithaca) wrapper leaves removed	SC 480	0.052 +0.051 +0.077 +0.077 +0.10 +0.15	290	6	1 3				<0.01 <0.01	RES96008 NJ LV9601
LEAF LETTUCE										
AZ, 1996 (Green Vision)	SC 480	0.052 +0.053 +0.081 +0.079 +0.10 +0.15	290	6	1 3	4.1	0.61	5.0	4.8 3.8	RES96008 AZ

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
CA, 1996 (Big Hoss)	SC 480	0.049 +0.050 +0.079 +0.076 +0.097 +0.15	280	6	1 3	0.35	0.062	0.45	2.0 0.53	RES96008 CA1
CA, 1996 (Deep Red)	SC 480	0.046 +0.050 +0.075 +0.077 +0.099 +0.15	370	6	1 3				5.2 2.8	RES96008 CA2
CA, 1996 (Romaine)	SC 480	0.051 +0.051 +0.076 +0.075 +0.10 +0.15	470	6	1 3				1.9 0.27	RES96008 CA3
FL, 1996 (Butter Crunch)	SC 480	0.051 +0.053 +0.074 +0.077 +0.10 +0.15	280	6	1 3	1.2 0.70	0.17 0.10	1.5 0.92	1.9 1.0	RES96008 FL
NJ, 1996 (Salad Bowl)	SC 480	0.049 +0.051 +0.077 +0.076 +0.10 +0.15	280	6	1 3				4.9 1.1	RES96008 NJ
SPINACH										
NJ, 1996 (Winter Bloomsdale)	SC 480	0.049 +0.051 +0.077 +0.077 +0.10 +0.15	280	6	1 3				1.5 0.31	RES96008 NJ
VA, 1996 (Long Standing Bloomsdale)	SC 480	0.051 +0.051 +0.075 +0.079 +0.10 +0.14	250	6	1 3	1.7 0.42	0.23 0.049	2.2 0.56	3.8 1.0	RES96008 VA
CO, 1996 (Melody F1 RS)	SC 480	0.049 +0.049 +0.075 +0.075 +0.10 +0.15	280	6	1 3	4.0 0.29	0.53 0.050	4.8 0.38	6.6 0.48	RES96008 CO

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
CELERY										
FL, 1996 (M68-29-5) untrimmed	SC 480	0.051 +0.051 +0.075 +0.074 +0.10 +0.15	280	6	0 1 3 5	1.3	0.19	1.5	1.7 1.1 0.89 0.30	RES96008 FL
FL, 1996 (M68-29-5) trimmed	SC 480	0.051 +0.051 +0.075 +0.074 +0.10 +0.15	280	6	0 1 3 5	0.15	0.02	0.19	0.21 0.18 0.083 0.084	RES96008 FL
MI, 1996 (Florida 683K) untrimmed	SC 480	0.050 +0.050 +0.076 +0.075 +0.10 +0.15	280	6	1 3				1.3 0.19	RES96008 MI
MI, 1996 (Florida 683K) trimmed	SC 480	0.050 +0.050 +0.076 +0.075 +0.10 +0.15	280	6	1 3				0.31 0.14	RES96008 MI
CA, 1996 (T&A Special #1) untrimmed	SC 480	0.051 +0.051 +0.078 +0.075 +0.10 +0.15	320	6	1 3	0.39 0.27	0.064 0.042	0.48 0.32	0.78 0.63	RES96008 CA1
CA, 1996 (T&A Special #1) trimmed	SC 480	0.051 +0.051 +0.078 +0.075 +0.10 +0.15	320	6	1 3	0.034 0.067	<0.01 0.01	0.04 0.08	0.056 0.089	RES96008 CA1
CA, 1996 (5270R) untrimmed	SC 480	0.050 +0.054 +0.079 +0.073 +0.10 +0.13	350 +370 +380 +370 +400 +470	6	1 3				0.84 0.59	RES96008 CA2
CA, 1996 (5270R) trimmed	SC 480	0.050 +0.054 +0.079 +0.073 +0.10 +0.13	350 +370 +380 +370 +400 +470	6	1 3				0.087 0.097	RES96008 CA2

Location, year (variety)	Application				PHI, days	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
CA, 1996 (Summit) untrimmed	SC 480	0.053 +0.049 +0.078 +0.075 +0.098 +0.14	450	6	1 3				0.40 0.18	RES96008 CA3
CA, 1996 (Summit) trimmed	SC 480	0.053 +0.049 +0.078 +0.075 +0.098 +0.14	450	6	1 3				0.11 0.096	RES96008 CA3
AZ, 1996 (Conquistador) untrimmed	SC 480	0.054 +0.055 +0.078 +0.079 +0.11 +0.16	290	6	1 3				1.7 1.2	RES96008 AZ
AZ, 1996 (Conquistador) trimmed	SC 480	0.054 +0.055 +0.078 +0.079 +0.11 +0.16	290	6	1 3				0.10 0.069	RES96008 AZ

[1] Total includes spinosyns A, D, B, N-demethyl-D and K. Results adjusted for procedural recoveries.
[2] HPLC only on selected samples as confirmation of immunoassay method. Results for HPLC are for single, and for immunoassay means of duplicate field samples.

Table 59. Spinosad residues in legume vegetables from supervised trials in the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	water, l/ha	no.			
SNAP BEANS (seed and pod)							
CA, 1997 (Strike)	SC 240	0.060 +4x0.080 +0.10	290	6	3	0.14	RES97034 CA1
CA, 1997 (Roma)	SC 240	5x0.080 +0.10	410	6	3	0.20	RES97034 CA2
FL, 1997 (Harvester)	SC 240	6x0.080	480	6	3	0.02	RES97034 FL1
FL, 1997 (Harvester)	SC 240	0.060 +4x0.080 +0.10	470	6	3	0.15	RES97034 FL2

Location, year (variety)	Application				PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	water, l/ha	no.			
IN, 1997 (Blue lake 274)	SC 240	2x0.062 +3x0.080 +0.10	130	6	3	0.02	RES97034
MI, 1997 (Envy)	SC 240	5x0.080 +0.10	190	6	3	0.042	RES97034
NJ, 1997 (Florence)	SC 240	0.080 +4x0.060 +0.10	300	6	3	0.085	RES97034
OH, 1997 (Bush Tenderpod)	SC 240	5x0.080 +0.10	200	6	3	0.077	RES97034
PA, 1997 (Roma II)	SC 240	3x0.080 +2x0.060 +0.080	180	6	3	<0.01	RES97034
WA, 1997 (Labrador)	SC 240	5x0.080 +0.10	280	6	3	0.02	RES97034
WI, 1997 (Florence)	SC 240	5x0.080 +0.10	180	6	3	<0.01	RES97034
SNOW PEA (seed and pod)							
MI, 1997 (Oregon Sugar)	SC 240	5x0.080 +0.10	190	6	3	0.20	RES97034
OH, 1997 (Oregon Sugar)	SC 240	3x0.060 +2x0.080 +0.10	210	6	3	0.21	RES97034
OR, 1997 (Green Arrow)	SC 240	3x0.060 +2x0.080 +0.10	190	6	3	0.063	RES97034
PA, 1997 (Dwarf White Sugar)	SC 240	5x0.080 +0.10	190	6	3	0.03	RES97034
WA, 1997 (Perfection)	SC 240	2x0.080 +3x0.060 +0.080	280	6	3	0.039	RES97034
WI, 1997 (Oregon Sugar Pod II)	SC 240	3x0.080 +2x0.060 +0.080	190	6	3	<0.01	RES97034
WI, 1997 (Super Sugar Mel)	SC 240	5x0.080 +0.10	180	6	3	0.01	RES97034

Table 60. Spinosad residues in navy beans stored in a freezer for approximately 28 months in supervised trials in Australia. .

Location, year (variety)	Application			PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	no.			
Qld, 1995 (Kerman)	SC480	0.096	2	14	<0.01	GHF-P 1672 Walkamin
Qld, 1995 (Kerman)	SC480	0.19	2	14	<0.01	GHF-P 1672 Walkamin
Qld, 1995 (Kerman)	SC480	0.096	2	14	<0.01	GHF-P 1672 Mareeba
Qld, 1995 (Kerman)	SC480	0.19	2	14	<0.01	GHF-P 1672 Mareeba

Table 61. Spinosad residues in soya beans from supervised trials in the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Residues, mg/kg spinosad	Ref.
	Form	kg ai/ha	water, l/ha	no.			
IA, 1997 (Pioneer 9294)	SC 480	0.38	190	3	28	<u><0.01</u>	RES97034
IL, 1997 (Asgrow AG4401)	SC 480	0.38	150	3	28	<u><0.01</u>	RES97034
IN, 1997 (Pioneer 9273)	SC 480	0.38	190	3	28	<u><0.01</u>	RES97034
MO, 1997 (Pioneer 9363)	SC 480	0.38	160	3	28	<u><0.01</u>	RES97034
MS, 1997 (DP3588)	SC 480	0.38	230	3	28	<u><0.01</u>	RES97034
NC, 1997 (Hartz H5566)	SC 480	0.38	330	3	28	<u><0.01</u>	RES97034
WI, 1997 (DeKalb CX 173)	SC 480	0.38	190	3	28	<u><0.01</u>	RES97034

Table 62. Spinosad residues in soya beans from supervised trials in Argentina and Brazil. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	
Argentina, 1995 (Asgrow 5308)	SC 480	0.050	100	1	75 [1]	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1995 (Asgrow 5308)	SC 480	0.10	100	1	75 [1]	<0.01 (3)	<0.01 (3)	GHB P-344

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	
Argentina, 1995 (Bataca 54)	SC 480	0.050	120	1	70 [1]	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1995 (Bataca 54)	SC 480	0.10	120	1	70 [1]	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1995 (DK 458)	SC 480	0.050	160	1	61 [1]	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1995 (DK 458)	SC 480	0.10	160	1	61 [1]	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1996 (Asgrow 4422)	SC 480	0.050	100	1	86	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1996 (Asgrow 4422)	SC 480	0.10	100	1	86	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1996 (Asgrow 4422)	SC 480	0.050	100	1	61	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1996 (Asgrow 4422)	SC 480	0.10	100	1	61	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1996 (Asgrow 5401)	SC 480	0.050	110	1	98	<0.01 (3)	<0.01 (3)	GHB P-344
Argentina, 1996 (Asgrow 5401)	SC 480	0.10	110	1	98	<0.01 (3)	<0.01 (3)	GHB P-344
Brazil (Paraná), 1995 (BR-4)	WG 800	0.048	100	2	19	<0.01 (3)	<0.01 (3)	GHB P-296
Brazil (Paraná), 1995 (BR-4)	WG 800	0.096	100	2	19	<0.01 (3)	<0.01 (3)	GHB P-296
Brazil (Paraná), 1995 (BR-4)	SC 480	0.048	100	2	19	<0.01 (3)	<0.01 (3)	GHB P-296
Brazil (Paraná), 1995 (BR-4)	SC 480	0.096	100	2	19	<0.01 (3)	<0.01 (3)	GHB P-296
Brazil (São Paulo), 1994 (Garimpo)	SC 480	0.048	100	2	0 9 20 [1]	<0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3)	GHB P-296
Brazil (São Paulo), 1994 (Garimpo)	SC 480	0.096	100	2	0 9 20 [1]	<0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3)	GHB P-296

[1] Samples stored in a freezer for 19-20 months.

Table 63. Spinosad residues in potatoes from supervised trials in Brazil and the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

country, year (variety)	Application				PHI, days	Residues, mg/kg			Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	IA [1]	
Brazil, 1995 (Achat)	WG 800	0.20	400	4	15	<0.01 (3)	<0.01 (3)		GHB P-295
Brazil, 1995 (Achat)	WG 800	0.40	400	4	15	<0.01 (3)	<0.01 (3)		GHB P-295
Brazil (São Paulo), 1996 (Achat)	SC 480	0.20	400	5	0 1 3 5 10	<0.01 <0.01 <u>0.01</u> <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01		GHB P-346
Brazil (São Paulo), 1996 (Achat)	SC 480	0.40	400	5	0 1 3 5 10	<0.01 <0.01 <u>0.01</u> <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01		GHB P-346
Brazil (Paraná), 1996 (Elvira)	SC 480	0.20	300	5	0 1 3 5 10	<0.01 <0.01 <u>0.01</u> <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01		GHB P-346
Brazil (Paraná), 1996 (Elvira)	SC 480	0.40	300	5	0 1 3 5 10	<0.01 <0.01 <u>0.01</u> <0.01 <0.01	<0.01 <0.01 <0.01 <0.01 <0.01		GHB P-346
USA (ME), 1997 (FL-1533)	SC 230	0.12	330	3	7			<u>0.005</u	IR-4 06653 97-ME03
USA (NJ), 1997 (Superior)	SC 230	0.12	410	3	7			<u>0.005</u	IR-4 06653 97-NJ29
USA (NJ), 1997 (Superior)	SC 230	0.62	410	3	7			<u>0.005</u	IR-4 06653 97-NJ29
USA (ID), 1997 (Russet Burbank)	SC 230	0.12	190	3	8			<u>0.005</u	IR-4 06653 97-ID13
USA (ID), 1997 (Russet Burbank)	SC 230	0.62	190	3	8			<u>0.005</u	IR-4 06653 97-ID13
USA (ID), 1997 (Russet Burbank)	SC 230	0.12	190	3	8			<u>0.005</u	IR-4 06653 97-ID14
USA (ID), 1997 (Russet Burbank)	SC 230	0.12	190	3	8			<u>0.005</u	IR-4 06653 97-ID15
USA (WI), 1997 (Superior)	SC 230	0.12	190	3	8			<u>0.005</u	IR-4 06653 97-WI18
USA (WI), 1997 (Russet Burbank)	SC 230	0.12	240	3	7			<u>0.005</u	IR-4 06653 97-WI19

country, year (variety)	Application				PHI, days	Residues, mg/kg			Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	IA [1]	
USA (WI), 1997 (Russet Noskotah)	SC 230	0.12	240	3	7			<0.005	IR-4 06653 97-WI20
USA (WI), 1997 (Norland Dark Red)	SC 230	0.12	200	3	8			<0.005	IR-4 06653 97-WI21
USA (FL), 1997 (Kennebec)	SC 230	0.12	280	3	6			<0.005	IR-4 06653 97-FL31
USA (GA), 1997 (Red La Soda)	SC 230	0.12	280	3	7			<0.005	IR-4 06653 97-GA15
USA (WA), 1997 (Russet Burbank)	SC 230	0.12	400	3	7			<0.005	IR-4 06653 97-WA41
USA (WA), 1997 (Russet Burbank)	SC 230	0.12	400	3	7			<0.005	IR-4 06653 97-WA42
USA (WA), 1997 (Russet Burbank)	SC 230	0.12	400	3	8			<0.005	IR-4 06653 97-WA43

[1] Immunoassay

Table 64. Spinosad residues in Japanese radish from supervised trials in Japan in 1995. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels. Note that residues in each trial were analysed by two laboratories.

Laboratory	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
Roots												
Institute of Environmental Toxicology	WG 250	0.01	3000	3	7 15 22 31	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	GHF-P-1488 Chiba
Japan Chemical Analysis Consultant					7 15 22 31	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	GHF-P-1488 Chiba
Institute of Environmental Toxicology	WG 250	0.01	3000	3	7 14 21 30	<0.01 0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.01 <0.01 <0.01 <0.01	0.01 <0.01 <0.01 <0.01	0.01 <0.01 <0.01 <0.01	0.03 0.01 <0.01 <0.01	GHF-P-1488 Niigata
Japan Chemical Analysis Consultant					7 14 21 30	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	GHF-P-1488 Niigata

Laboratory	Application				PHI, days	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
Leaves												
Institute of Environmental Toxicology	WG 250	0.01	3000	3	7 15 22 31	0.06 <0.01 <0.01 <0.01	0.01 <0.01 <0.01 <0.01	0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.08 <0.01 <0.01 <0.01	GHF-P-1488 Chiba
Japan Chemical Analysis Consultant					7 15 22 31	0.04 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.04 <0.01 <0.01 <0.01	GHF-P-1488 Chiba
Institute of Environmental Toxicology	WG 250	0.01	3000	3	7 14 21 30	0.20 0.02 <0.01 <0.01	0.03 <0.01 <0.01 <0.01	0.02 0.01 <0.01 <0.01	0.02 0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.27 0.04 <0.01 <0.01	GHF-P-1488 Niigata
Japan Chemical Analysis Consultant					7 14 21 30	0.12 0.02 <0.01 <0.01	0.02 <0.01 <0.01 <0.01	0.02 0.01 <0.01 <0.01	0.02 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.18 0.03 <0.01 <0.01	GHF-P-1488 Niigata

Table 65. Spinosad residues in cereals measured by an immunoassay method from supervised trials in the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	Residues, mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.			
MAIZE							
MN, 1997 (Pioneer 3751)	SC 480	0.50	200	2	27	<0.01	RES97037
NE, 1997 (Pioneer 3751)	SC 480	0.50	260	2	30	<0.01	RES97037
NC, 1997 (Pioneer 3394)	SC 480	0.50	190	2	30	<0.01	RES97037
OH, 1997 (GL 276)	SC 480	0.50	210	2	28	<0.01 <0.01 (HPLC)	RES97037
PA, 1997 (DK 385B)	SC 480	0.50	190	2	28	<0.01	RES97037
SORGHUM							
CO, 1997 (Cargill 577)	SC 480	0.10	250	5	7	0.68 0.62 (HPLC)	RES97037
KS, 1997 (DK 47)	SC 480	0.10	210	5	7	0.088	RES97037
MO, 1997 (Pioneer 8305)	SC 480	0.10	220	5	7	0.030	RES97037

Location, year (variety)	Application				PHI, days	Residues, mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.			
MS, 1997 (G-522DR, Mycogen Hybrid)	SC 480	0.10	270	5	0 9 14 21 0 9	0.85 0.086 0.099 0.037 c 0.90 [1] c 0.02	RES97037
NE, 1997 (Northrup King NK1210)	SC 480	0.10	190	5	7	0.47	RES97037 NE1
NE, 1997 (Northrup King NK1210)	SC 480	0.10	190	5	8	0.17	RES97037 NE2
OK, 1997 (T-E Eden)	SC 480	0.10	200	5	7	0.18	RES97037
TX, 1997 (DPol 1558)	SC 480	0.10	250	5	7	0.16	RES97037 TX1
TX, 1997 (Y363)	SC 480	0.10	190	5	7	0.12	RES97037 TX2
WHEAT							
IL, 1997 (Clemens 8530, winter wheat)	SC 480	0.50	190	3	21	0.01	RES97037
IN, 1997 (Pioneer 2571, winter wheat)	SC 480	0.50	190	3	21	<0.01	RES97037
ND, 1997 (2375 NDSU, spring wheat)	SC 480	0.50	290	3	21	0.051 0.05 (HPLC) 0.074 cleaned grain 0.57 grain trash	RES97037
OK, 1997 (Tam 200, winter wheat)	SC 480	0.50	240	3	21	0.061	RES97037
SD, 1997 (Hard Red 2375, spring wheat)	SC 480	0.50	190	3	21	0.054	RES97037
TX, 1997 (Thunderbird, winter wheat)	SC 480	0.50	250	3	21	0.084	RES97037

[1] Sample from control plot apparently swapped with a treated sample. Data from this trial are not included in the evaluation.

Table 66. Spinosad residues in maize from supervised trials in Argentina and Brazil. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	
Argentina (Buenos Aires), 1999 (DK752)	SC 480	0.029		1	137	<0.01 (3)	<0.01 (3)	GHB P-448

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	
Argentina (Buenos Aires), 1999 (DK752)	SC 480	0.058		1	137	<0.01 (3)	<0.01 (3)	GHB P-448
Argentina (Buenos Aires), 1999 (Tilcara)	SC 480	0.029		1	138	<0.01 (3)	<0.01 (3)	GHB P-448
Argentina (Buenos Aires), 1999 (Tilcara)	SC 480	0.058		1	138	<0.01 (3)	<0.01 (3)	GHB P-448
Argentina (La Virginia-Tucumán), 1999 (Hercules)	SC 480	0.029		1	122	<0.01 (2)	<0.01 (2)	GHB P-448
Argentina (La Virginia-Tucumán), 1999 (Hercules)	SC 480	0.058		1	122	<0.01 (3)	<0.01 (3)	GHB P-448
Brazil (Paraná), 1995 (G-85)	WG 800	0.060	250	3	0 7	<0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3)	GHB P-287
Brazil (Paraná), 1995 (G-85)	WG 800	0.12	250	3	0 7	<0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3)	GHB P-287
Brazil (Paraná), 1995 (G-85)	SC 480	0.048	250	3	0 7	<0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3)	GHB P-292
Brazil (Paraná), 1995 (G-85)	SC 480	0.096	250	3	0 7	<0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3)	GHB P-292
Brazil (São Paulo), 1995 (C-701)	WG 800	0.060	400	3	0 7 14 28 56	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-287
Brazil (São Paulo), 1995 (C-701)	WG 800	0.120	400	3	0 7 14 28 56	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-287
Brazil (São Paulo), 1995 (C-701)	SC 480	0.048	400	3	0 7 14 28 56	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-292
Brazil (São Paulo), 1995 (C-701)	SC 480	0.096	400	3	0 7 14 28 56	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	<0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3) <0.01 (3)	GHB P-292

Table 67. Spinosad residues in almonds from supervised trials in California, USA, in 1996. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Application				PHI,	Spinosyn residues, mg/kg						Ref.
Form	kg ai/ha	water, l/ha	no.	days	A	D	K	B	B of D	Total	
SC 450	0.070 +0.10 +0.15 +0.18	480	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA1
SC 450	0.070 +0.10 +0.15 +0.18	1800	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA1
SC 450	0.070 +0.10 +0.15 +0.18	490	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA2
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA2
SC 450	0.070 +0.10 +0.15 +0.18	470	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA3
SC 450	0.070 +0.10 +0.15 +0.18	2000	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA3
SC 450	0.070 +0.10 +0.15 +0.18	470	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA4
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA4
SC 450	0.070 +0.10 +0.15 +0.18	470	4	0 5 14 21	<0.01 <0.01 <u><0.01</u> <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	RES96004 CA5
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	0 5 14 21	<0.01 <0.01 <u><0.01</u> <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	RES96004 CA5
SC 450	0.070 +0.10 +0.15 +0.18	470	4	14	<u><0.01</u>	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA6

Application				PHI, days	Spinosyn residues, mg/kg						Ref.
Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	14	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	RES96004 CA6

Table 68. Spinosad residues in cotton seed from supervised trials in Argentina, Australia, Brazil and the USA. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Country, year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
Argentina (Salta), 1996 (Guazuncho 2)	SC 480	0.05		90	4	71	<0.01(3)	<0.01(3)	GHB-P 358
Argentina (Salta), 1996 (Guazuncho 2)	SC 480	0.10		90	4	71	<0.01(3)	<0.01(3)	GHB-P 358
Argentina (Salta), 1997 (Guazuncho 2)	SC 480	0.05		90	4	65	<0.01(3)	<0.01(3)	GHB-P 358
Argentina (Salta), 1997 (Guazuncho 2)	SC 480	0.10		90	4	65	<0.01(3)	<0.01(3)	GHB-P 358
Argentina (Santiago del Estero), 1996 (Guazuncho inta)	SC 480	0.05		108	4	41	<0.01(3)	<0.01(3)	GHB-P 358
Argentina (Santiago del Estero), 1996 (Guazuncho inta)	SC 480	0.10		108	4	41	<0.01(3)	<0.01(3)	GHB-P 358
Argentina (Santiago del Estero), 1997 (Guazuncho 2)	SC 480	0.05		190	4	41	<0.01(3)	<0.01(3)	GHB-P 358
Argentina (Santiago del Estero), 1997 (Guazuncho 2)	SC 480	0.10		190	4	41	<0.01(3)	<0.01(3)	GHB-P 358
Australia (NSW), 1994 (Deltapine 90)	UL 125	0.075		50	2	28	<0.01	<0.01	GHF-P 1371 93200
Australia (NSW), 1994 (Deltapine 90)	UL 125	0.15		50	2	28	<0.01	<0.01	GHF-P 1371 93200
Australia (NSW), 1994 (Deltapine 90)	UL 125	0.075	[1]	4	2	28	<0.01	<0.01	GHF-P 1371 93200
Australia (NSW), 1994 (Deltapine 90)	UL 125	0.15	[1]	4	2	28	<0.01	<0.01	GHF-P 1371 93200
Australia (NSW), 1996 (CS8S)	SC 125	0.10			3	28	<0.01	<0.01	GHF-P 1628

Country, year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
Australia (NSW), 1996 (CS8S)	SC 125	0.20			3	28	0.01	<0.01	GHF-P 1628
Australia (Qld), 1996 (65)	SC 125	0.10			3	28	0.01	<0.01	GHF-P 1628
Australia (Qld), 1996 (65)	SC 125	0.20			3	28	<0.01	<0.01	GHF-P 1628
Australia (Qld), 1996 (L22)	SC 480	0.10			3	28	<0.01 [2]	<0.01	GHF-P 1629 Emerald
Australia (Qld), 1996 (L22)	SC 125	0.10			3	28	<0.01 [2]	<0.01	GHF-P 1629 Emerald
Australia (Qld), 1996 (L22)	SC 125	0.20			3	28	<0.01 [2]	<0.01	GHF-P 1629 Emerald
Australia (Qld), 1996 (SK 1-4)	SC 480	0.10			3	28	<0.01	<0.01	GHF-P 1629 Gatton
Australia (Qld), 1996 (SK 1-4)	SC 125	0.10			3	28	<0.01	<0.01	GHF-P 1629 Gatton
Australia (Qld), 1996 (SK 1-4)	SC 125	0.20			3	28	<0.01	<0.01	GHF-P 1629 Gatton
Brazil (PR), 1994 (IAC-20)	SC 480	0.072		100	4	25	<0.01	<0.01	GHB-P 279
Brazil (PR), 1994 (IAC-20)	SC 480	0.14		100	4	25	<0.01	<0.01	GHB-P 279
Brazil (SP), 1994 (IAC-20)	SC 480	0.072		100	4	0 3 7 14 21 0	0.01 <0.01 <0.01 <0.01 <0.01 c 0.01	<0.01 <0.01 <0.01 <0.01 <0.01 c <0.01	GHB-P 279
Brazil (SP), 1994 (IAC-20)	SC 480	0.14		100	4	0 3 7 14 21 0	0.02 <0.01 <0.01 <0.01 <0.01 c 0.01	<0.01 <0.01 <0.01 <0.01 <0.01 c <0.01	GHB-P 279
USA (AR), 1993 (Deltapine 20)	SC 480	0.076 +0.097 +0.101 +0.101 +0.125		130 +140 +150 +110 +140	5	27	<0.01	<0.01	RES93026R/ RES92024R
USA (AR), 1993 (Stoneville 453)	SC 480	0.076 +0.101 +0.101 +0.101 +0.126		130 +140 +150 +110 +140	5	27	<0.01	<0.01	RES93026R/ RES92024R

Country, year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
USA (AZ), 1993 (Deltapine 20)	SC 480	0.074 +0.101 +0.102 +0.102 +0.125		140	5	23	<0.01	<0.01	RES93026R/ RES92024R
USA (AZ), 1993 (Deltapine 50)	SC 480	0.073 +0.099 +0.099 +0.097 +0.124		140	5	28	<0.01	<0.01	RES93026R/ RES92024R
USA (CA), 1992 (Acala SJ-2)	SC 480	0.20		280	5	14 28	<0.01 <0.01	<0.01 <0.01	RES93026R/ RES92024R
USA (CA), 1993 (Maxxa)	SC 480	0.079 +0.100 +0.099 +0.099 +0.127		200 +190 +190 +190 +190	5	28	<0.01	<0.01	RES93026R/ RES92024R
USA (CA), 1993 (Maxxa)	SC 480	0.47 +0.61 +0.60 +0.60 +0.76			5	28	<0.01	<0.01	RES93026R/ RES92024R
USA (CA), 1993 (Maxxa)	SC 480	0.076 +0.102 +0.101 +0.102 +0.126		190	5	28	<0.01	<0.01	RES93026R/ RES92024R
USA (CA), 1993 (Maxxa)	SC 480	0.076 +0.101 +0.100 +0.100 +0.124		190	5	28	<0.01	<0.01	RES93026R/ RES92024R
USA (GA), 1993 (DP 5415)	SC 480	0.076 +0.101 +0.101 +0.101 +0.126		190	5	28	<0.01	<0.01	RES93026R/ RES92024R
USA (LA), 1993 (Deltapine 20)	SC 480	0.076 +0.101 +0.102 +0.101 +0.12		150 +150 +150 +130 +120	5	27	<0.01	<0.01	RES93026R/ RES92024R
USA (MS), 1992 (Deltapine 50)	SC 480	0.20		120	5	14 28	<0.01 <0.01	<0.01 <0.01	RES93026R/ RES92024R
USA (MS), 1993 (Des119 Sure Grow)	SC 480	0.076 +0.099 +0.099 +0.099 +0.14		160 +100 +200 +200 +170	5	28	<0.01	<0.01	RES93026R/ RES92024R

Country, year (variety)	Application					PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		spinosyn A	spinosyn D	
USA (NC), 1993 (Deltapine 50)	SC 480	0.074 +0.100 +0.100 +0.100		190 +180 +180 +180	4	28	<u><0.01</u>	<0.01	RES93026R/ RES92024R
USA (OK), 1993 (Cascot C-13)	SC 480	0.075 +0.100 +0.100 +0.100 +0.125		140 +130 +140 +130 +150	5	28	<u><0.01</u>	<0.01	RES93026R/ RES92024R
USA (TX), 1993 (Deltapine 50)	SC 480	0.075 +0.100 +0.100 +0.101 +0.126		170	5	28	<u><0.01</u>	<0.01	RES93026R/ RES92024R
USA (TX), 1993 (Deltapine 51)	SC 480	0.075 +0.101 +0.099 +0.099 +0.127		170	5	28	<u><0.01</u>	<0.01	RES93026R/ RES92024R
USA (TX), 1993 (DP 5415)	SC 480	0.076 +0.099 +0.100 +0.097 +0.124		140	5	28	<u><0.01</u>	<0.01	RES93026R/ RES92024R
USA (TX), 1993 (HS-200)	SC 480	0.075 +0.101 +0.100 +0.101 +0.125		190	5	28	<u><0.01</u>	<0.01	RES93026R/ RES92024R
USA (TX), 1993 (Southland M1)	SC 480	0.075 +0.100 +0.100 +0.100 +0.125		190	5	28	<u><0.01</u>	<0.01	RES93026R/ RES92024R

[1] Spinning disc applicator; diluent was a crop oil, not water.
[2] Samples in stored in freezer for approx. 14 months

Table 69. Spinosad residues in cereal forage and fodder from supervised trials in the USA in 1997. Residues were measured by an immunoassay method. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application				PHI, days	% moisture	mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.				
SWEET CORN FORAGE								
CA (Legend)	SC 240	0.10	190	5	7	79	<u>0.48</u>	RES97037
FL (Silver Queen)	SC 240	0.10	280	5	7		<u>0.12</u> c 0.02	RES97037

Location, year (variety)	Application				PHI, days	% moisture	mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.				
IL (Sensor)	SC 240	0.10	280	5	7	80	0.099	RES97037
MI (Sweet Chorus)	SC 240	0.10	230	5	7	86	0.17	RES97037
MN (Quickie Hybrid)	SC 240	0.10	180	5	7	84	0.49	RES97037
NC (Silver Queen)	SC 240	0.10	240	5	7	75	0.18	RES97037
NY (Tuxedo)	SC 240	0.10	180	5	7	85	0.074	RES97037
OH (Silver Queen)	SC 240	0.10	220	5	7	72	0.36	RES97037
OR (Jubilee)	SC 240	0.10	290	5	7	87	0.087	RES97037
PA (Breeders Bi-Color)	SC 240	0.10	230	5	7	76	0.098	RES97037
WA (Silver Sweet Jubilee)	SC 240	0.10	290	5	7	70	0.16	RES97037
WI (Confection SH2 Bi-color)	SC 240	0.10	180	5	7	84	0.44	RES97037
SWEET CORN STOVER								
CA (Legend)	SC 240	0.10	190	5	28	68	0.68	RES97037
FL (Silver Queen)	SC 240	0.10	280	5	28	65	0.074	RES97037
IL (Sensor)	SC 240	0.10	280	5	28	76	0.099	RES97037
MI (Sweet Chorus)	SC 240	0.10	230	5	28	77	0.03	RES97037
MN (Quickie Hybrid)	SC 240	0.10	180	5	28	72	0.17	RES97037
NC (Silver Queen)	SC 240	0.10	240	5	28	77	0.12	RES97037
NY (Tuxedo)	SC 240	0.10	180	5	28	72	0.17	RES97037
OH (Silver Queen)	SC 240	0.10	220	5	28	75	0.23	RES97037
OR (Jubilee)	SC 240	0.10	290	5	28	65	0.053	RES97037
PA (Breeders Bi-Color)	SC 240	0.10	230	5	28	71	0.11	RES97037
WA (Silver Sweet Jubilee)	SC 240	0.10	290	5	28	43	0.46	RES97037
WI (Confection SH2 Bi-color)	SC 240	0.10	180	5	28	66	0.097	RES97037
SORGHUM FORAGE								
KS (DK 47)	SC 480	0.10	210	5	14	68	0.078	RES97037
MS (G-522DR, Mycogen Hybrid)	SC 480	0.10	270	5	0 3 7 14 14	66	0.68 1.1 0.11 0.084 c 0.04 [1]	RES97037

Location, year (variety)	Application				PHI, days	% moisture	mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.				
NE (Northrup King NK1210)	SC 480	0.10	190	5	14	66	0.095	RES97037 NE2
OK (T-E Eden)	SC 480	0.10	200	5	14	71	0.052	RES97037
TX (Y363)	SC 480	0.10	190	5	14	62	0.18	RES97037 TX2
SORGHUM STOVER								
KS (DK 47)	SC 480	0.10	210	5	15	64	0.060	RES97037
MS (G-522DR, Mycogen Hybrid)	SC 480	0.10	270	5	0 9 14 21	68	1.6 0.11 0.068 0.17	RES97037
NE (Northrup King NK1210)	SC 480	0.10	190	5	14	75	0.11	RES97037 NE2
OK (T-E Eden)	SC 480	0.10	200	5	14	67	0.27	RES97037
TX (Y363)	SC 480	0.10	190	5	14	67	0.097	RES97037 TX2
WHEAT FORAGE								
IL (Clemens 8530, winter wheat)	SC 480	0.10	190	1	14	76	0.054	RES97037
IN (Pioneer 2571, winter wheat)	SC 480	0.10	190	1	14	83	<0.01	RES97037
ND (2375 NDSU, spring wheat)	SC 480	0.10	290	1	14	83	<0.01	RES97037
OK (Tam 200, winter wheat)	SC 480	0.10	240	1	14	73	0.01	RES97037
SD (Hard Red 2375, spring wheat)	SC 480	0.10	190	1	14	82	0.01	RES97037
TX (Thunderbird, winter wheat)	SC 480	0.10	250	1	14	77	0.050	RES97037
WHEAT HAY								
IL (Clemens 8530, winter wheat)	SC 480	0.10	190	2	14	15	0.050	RES97037
IN (Pioneer 2571, winter wheat)	SC 480	0.10	190	2	14	53	<0.01	RES97037
ND (2375 NDSU, spring wheat)	SC 480	0.10	290	2	14	29	0.019	RES97037
OK (Tam 200, winter wheat)	SC 480	0.10	240	2	14	60	0.052	RES97037
SD (Hard Red 2375, spring wheat)	SC 480	0.10	190	2	14	30	0.15	RES97037
TX (Thunderbird, winter wheat)	SC 480	0.10	250	2	14	36	0.17	RES97037
WHEAT STRAW								
IL (Clemens 8530, winter wheat)	SC 480	0.10	190	3	21	15	0.19	RES97037

Location, year (variety)	Application				PHI, days	% moisture	mg/kg	Ref.
	Form	kg ai/ha	water, l/ha	no.				
IN (Pioneer 2571, winter wheat)	SC 480	0.10	190	3	21	48	<0.01	RES97037
ND (2375 NDSU, spring wheat)	SC 480	0.10	290	3	21	12	0.73	RES97037
OK (Tam 200, winter wheat)	SC 480	0.10	240	3	21	10	0.53	RES97037
SD (Hard Red 2375, spring wheat)	SC 480	0.10	190	3	21	13	0.56	RES97037
TX (Thunderbird, winter wheat)	SC 480	0.10	250	3	21	10	0.37	RES97037

[1] Contaminated control sample; data from this trial not included in the evaluation.

Table 70. Spinosad residues in cotton trash from supervised trials in Australia. [1]

Location, year (variety)	Application			PHI, days	Residues, mg/kg [2]			Ref.
	Form	kg ai/ha	no.		spinosyn A	spinosyn D	Total	
NSW, 1996 (CS8S)	SC 125	0.10	3	0 8 14 28	2.9 (11.2) 0.32 (1.2) 0.56 (2.0) 0.11 (0.13)	0.46 (1.8) 0.04 (0.13) 0.05 (0.18) 0.01 (0.01)	3.3 (13) 0.36 (1.3) 0.61 (2.2) 0.12 (0.14)	GHF-P 1628
NSW, 1996 (CS8S)	SC 125	0.20	3	0 8 14 28	6.2 (26) 0.99 (4.0) 1.2 (4.3) 0.37 (0.43)	0.90 (3.8) 0.10 (0.39) 0.11 (0.38) 0.04 (0.04)	7.1 (30) 1.1 (4.4) 1.3 (4.7) 0.41 (0.47)	GHF-P 1628
Qld, 1996 (65)	SC 125	0.10	3	0 7 14 28	12.8 (47) 2.0 (7.1) 0.95 (3.6) 0.59 (1.9)	2.6 (9.3) 0.31 (1.1) 0.09 (0.33) 0.04 (0.13)	15 (56) 2.3 (8.3) 1.0 (3.9) 0.63 (2.0)	GHF-P 1628
Qld, 1996 (65)	SC 125	0.20	3	0 7 14 28	27 (103) 4.0 (14) 1.7 (6.6) 1.6 (5.5)	4.3 (16) 0.61 (2.2) 0.14 (0.55) 0.08 (0.27)	32 (119) 4.6 (17) 1.8 (7.1) 1.6 (5.7)	GHF-P 1628
Qld, 1996 (L22)	SC 480	0.10	3	0 7 14 28	7.5 (32) 0.72 (3.1) 0.23 (0.99) 0.08 (0.09)	1.2 (5.0) 0.09 (0.39) 0.04 (0.17) 0.01 (0.01)	8.6 (37) 0.81 (3.5) 0.27 (1.2) 0.09 (0.11)	GHF-P 1629 Emerald
Qld, 1996 (SK 1-4)	SC 480	0.10	3	0 7 14 28	8.0 (29) 0.93 (3.1) 0.16 (0.57) 0.05 (0.07)	1.3 (4.7) 0.15 (0.51) 0.03 (0.09) 0.01 (0.01)	9.3 (34) 1.1 (3.6) 0.18 (0.66) 0.06 (0.08)	GHF-P 1629 Gatton
Qld, 1996 (L22)	SC 125	0.10	3	0 7 14 28	7.2 (32) 0.90 (3.9) 0.54 (2.3) 0.18 (0.21)	1.2 (5.3) 0.11 (0.47) 0.07 (0.30) 0.03 (0.04)	8.4 (37) 1.0 (4.4) 0.61 (2.6) 0.21 (0.24)	GHF-P 1629 Emerald

Location, year (variety)	Application			PHI, days	Residues, mg/kg [2]			Ref.
	Form	kg ai/ha	no.		spinosyn A	spinosyn D	Total	
Qld, 1996 (L22)	SC 125	0.20	3	0 7 14 28	16 (71) 1.1 (5.3) 0.50 (2.3) 0.21 (0.24)	2.5 (11) 0.13 (0.60) 0.05 (0.20) 0.04 (0.04)	18 (82) 1.3 (5.9) 0.55 (2.5) 0.24 (0.29)	GHF-P 1629 Emerald
Qld, 1996 (SK 1-4)	SC 125	0.10	3	0 7 14 28	7.2 (27) 1.2 (4.0) 0.71 (2.6) 0.04 (0.05)	1.3 (4.8) 0.19 (0.63) 0.11 (0.39) 0.01 (0.01)	8.5 (32) 1.4 (4.6) 0.81 (3.0) 0.05 (0.06)	GHF-P 1629 Gatton
Qld, 1996 (SK 1-4)	SC 125	0.20	3	0 7 14 28	11 (43) 1.6 (5.8) 1.4 (5.2) 0.08 (0.10)	2.0 (7.6) 0.27 (0.95) 0.18 (0.66) 0.01 (0.01)	13 (51) 1.9 (6.7) 1.6 (5.9) 0.09 (0.11)	GHF-P 1629 Gatton

[1] Gin trash is typically dried cotton foliage that has adhered to the lint during machine picking. For the 28-day samples, only dried leaves and cotton bracts that remained after the lint harvest were taken, and for earlier samples, green or partially green cotton leaves and bracts from the upper two-thirds of the plant were taken.

[2] Residues in parentheses are on a dry weight basis.

Table 71. Spinosad residues in navy bean forage and hay from supervised trials in Australia.

Location, year (variety)	Application				PHI, days	Commodity	Spinosad, mg/kg[1]	Ref.
	Form	kg ai/ha	water, l/ha	no.				
Qld, 1995 (Kerman)	SC480	0.096	230	1	14	whole plant	0.01 (0.02)	GHF-P 1672 Walkamin
Qld, 1995 (Kerman)	SC480	0.19	230	1	14	whole plant	0.02 (0.06)	GHF-P 1672 Walkamin
Qld, 1995 (Kerman)	SC480	0.096	?	1	14	whole plant	0.01 (0.05)	GHF-P 1672 Mareeba
Qld, 1995 (Kerman)	SC480	0.19	?	1	14	whole plant	0.03 (0.13)	GHF-P 1672 Mareeba
Qld, 1995 (Kerman)	SC480	0.096	230	2	14	hay	0.02 (0.02)	GHF-P 1672 Walkamin
Qld, 1995 (Kerman)	SC480	0.19	230	2	14	hay	0.6 (0.07)	GHF-P 1672 Walkamin
Qld, 1995 (Kerman)	SC480	0.096	?	2	14	hay	0.02 (0.02)	GHF-P 1672 Mareeba
Qld, 1995 (Kerman)	SC480	0.19	?	2	14	hay	0.04 (0.04)	GHF-P 1672 Mareeba

[1] Residues in parentheses are on a dry weight basis.

Table 72. Spinosad residues in almond hulls from supervised trials in California, USA, in 1996. Double-underlined residues are from treatments according to GAP and are valid for the estimation of maximum residue levels.

Application				PHI,	Spinosyn residues, mg/kg						Ref.
Form	kg ai/ha	water, l/ha	no.	days	A	D	K	B	B of D	Total	
SC 450	0.070 +0.10 +0.15 +0.18	480	4	14	0.59	0.080	<0.01	0.02	<0.01	0.70	RES96004 CA1
SC 450	0.070 +0.10 +0.15 +0.18	1800	4	14	0.64	0.087	<0.01	0.02	<0.01	0.75	RES96004 CA1
SC 450	0.070 +0.10 +0.15 +0.18	490	4	14	0.54	0.077	<0.01	0.02	<0.01	0.64	RES96004 CA2
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	14	0.98	0.14	<0.01	0.03	<0.01	1.2	RES96004 CA2
SC 450	0.070 +0.10 +0.15 +0.18	470	4	14	0.43	0.058	<0.01	0.02	<0.01	0.50	RES96004 CA3
SC 450	0.070 +0.10 +0.15 +0.18	2000	4	14	0.72	0.098	<0.01	0.030	<0.01	0.86	RES96004 CA3
SC 450	0.070 +0.10 +0.15 +0.18	470	4	14	0.25	0.03	<0.01	<0.01	<0.01	0.28	RES96004 CA4
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	14	0.33	0.04	<0.01	0.01	<0.01	0.38	RES96004 CA4
SC 450	0.070 +0.10 +0.15 +0.18	470	4	0 5 14 21	0.27 0.48 0.18 0.17	0.037 0.055 0.02 0.02	<0.01 <0.01 <0.01 <0.01	0.01 0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	0.32 0.56 0.21 0.20	RES96004 CA5
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	0 5 14 21	0.34 0.49 0.24 0.27	0.047 0.068 0.032 0.038	<0.01 <0.01 <0.01 <0.01	0.01 0.02 <0.01 0.01	<0.01 <0.01 <0.01 <0.01	0.40 0.58 0.28 0.32	RES96004 CA5
SC 450	0.070 +0.10 +0.15 +0.18	470	4	14	0.40	0.054	<0.01	0.02	<0.01	0.47	RES96004 CA6

Application				PHI, days	Spinosyn residues, mg/kg						Ref.
Form	kg ai/ha	water, l/ha	no.		A	D	K	B	B of D	Total	
SC 450	0.070 +0.10 +0.15 +0.18	1900	4	14	0.60	0.085	<0.01	0.02	<0.01	0.71	RES96004 CA6

Direct animal treatments

The Meeting received information on residues in the tissues and milk of sheep and cattle treated directly with spinosad.

Sheep. In two trials in Australia short-wool sheep were plunge-dipped in a solution of spinosad and long-wool sheep were sprayed with a jet (Ridley, 1999). At each withholding period (whp) 5 animals were slaughtered. Residues in the tissues are shown in Table 73. The short-wool sheep (wool length 1.6-2.6 cm) were one and a half years old and their live weight on the day of treatment was 36-46.5 kg, and the long-wool sheep (wool length 6.8-7.5 cm) were two and a half years old with live weights of 41-60 kg. The former sheep were shorn 45 days and the latter 9 months before treatment.

In the plunge dipping the sheeps' heads were immersed twice, each animal remaining in the fluid for 20 seconds, and on exit taking with them 12-15 l of fluid. Animals were weighed before dipping and again after 30-60 min when they had stopped dripping, demonstrating that the average weight of dipping fluid retained was 2.6 kg.

Similarly the long-wool sheep treated for 21 seconds with a hand-held jetting applicator supported by a motor driven diaphragm pump received 5.1 l each, retaining an average weight of fluid of 1.3 kg.

Tissue samples were analysed by the immunoassay method. Recoveries ranged from 59-149%, n=30, averaging 87%, 92%, 83% and 93% for kidney, liver, muscle and fat respectively.

In a further plunge-dipping trial on short-wool Dorset Horn ewes the sheep's heads were immersed twice, each animal remaining in the fluid for 30 seconds (Ridley, 2000). On exiting the sheep each removed approximately 12-15 l of fluid. The animals were shorn 42 days before treatment. On the day of treatment, wool length was 1.5-1.9 cm and live weight 36-67 kg. Residues in the tissues are shown in Table 73.

Table 73. Spinosad residues in the tissues of sheep from supervised trials in Australia in 1999 (analyses by immunoassay method).

Location (breed)	Application			Sample	whp days	Spinosad, mg/kg	Ref.
	Form	Method	Spray or dip conc, kg ai/hl				
NSW (Merino) short wool	aq susp 25 g ai/l	plunge dip	0.001	muscle	5 12 15	<0.01 (5) <0.01 (5) <0.01 (5)	ELANCO /GLP/980 9/1-1
				kidney	5 12 15	<0.01 0.013 0.01 <0.01 0.014 <0.01 (5) <0.01 (5)	

Location (breed)	Application			Sample	whp days	Spinosad, mg/kg	Ref.
	Form	Method	Spray or dip conc, kg ai/hl				
				liver	5 12 15	<0.01 (5) <0.01 (5) <0.01 (5)	
				back fat	5 12 15 21 39 56	0.020 0.029 0.014 <0.01 (2) 0.016 0.033 0.017 0.017 0.018 0.017 0.024 0.026 0.024 0.013 0.033 0.018 <0.01 0.011 <0.01 0.023 <0.01 (4) <0.01 (5)	
				perirenal fat	5 12 15 21 39 56	0.042 0.032 0.014 0.024 0.042 <0.01 0.011 0.021 0.040 0.017 0.027 0.021 0.030 0.029 0.024 0.032 0.021 0.025 0.020 0.024 <0.01 (5) <0.01 (5)	
NSW (Merino) long wool	aq susp 25 g ai/l	jetting, 5.1 l per sheep	0.0025	muscle	5 12 15	<0.01 (5) <0.01 (5) <0.01 (5)	ELANCO /GLP/980 9/1-1
				kidney	5 12 15	<0.01 (5) <0.01 (5) <0.01 (5)	
				liver	5 12 15	<0.01 (5) <0.01 (5) <0.01 (5)	
				back fat	5 12 15 21	<0.01 (5) <0.01 (5) <0.01 (5) <0.01 (5)	
				perirenal fat	5 12 15 21	<0.01 (5) <0.01 (5) <0.01 (5) <0.01 (5)	
NSW (Dorset Horn ewes) short wool	aq susp 25 g ai/l	plunge dip	0.001	muscle	5 15	<0.01 (5) <0.01 (5)	ELANCO /GLP/990 2a
				kidney	5 15	<0.01 (5) <0.01 (5)	
				liver	5 15	<0.01 (5) <0.01 (5)	
				back fat	5 15 21 56	<0.01 (3) 0.0100.017 <0.01 (5) <0.01 (5) <0.01 (5)	

Location (breed)	Application			Sample	whp days	Spinosad, mg/kg	Ref.
	Form	Method	Spray or dip conc, kg ai/hl				
				perirenal fat	5 15 21 56	0.01 <0.01 0.013 0.015 0.027 <0.01 (3) 0.01 0.011 <0.01 (5) <0.01 (5)	

Dairy cattle. In trials in the USA Holstein dairy cows were subjected to 3 kinds of direct treatment with spinosad and a premises treatment (Spurlock-Brouwer *et al.,* 2000). All treatments were applied 5 times.

1. Treatment every 7 days with 2 l of a 400 mg ai/l spray to cover the entire body (group of 9 cows). Lactating animals (groups of 3) were slaughtered 2, 7 and 14 days after the last treatment.
2. Treatment every 21 days with 5 l of a 400 mg ai/l spray to cover the entire body (group of 9 cows). Lactating animals (groups of 3) were slaughtered 2, 7 and 14 days after the last treatment.
3. Treatment every 14 days with 2 mg ai/kg bw, poured down the back from withers to tail (15 cows). Lactating animals (groups of 3) were slaughtered 2 and 14 days after the last treatment. The remaining (non-lactating) animals were slaughtered in groups of 3 21, 28 and 35 days after the last treatment.
4. Walls and ceiling of the premises were treated with a 800 mg ai/l spray every 7 days after the treated animals came in.

Milk was collected twice daily during the trial. Milk, muscle, kidney and liver were analysed by the immunoassay method and fat by HPLC. The results are shown in Table 74. Residues were higher in the fat than in other tissues, and the pour-on treatment produced the highest residues. Decline of the residues in fat was slow, with estimated half-lives of 20-40 days.

Spinosad residues were measured in 119 samples of milk and cream from the 3 treatments and followed the cycle of treatments with the level spiking the day after treatment and then falling over the next 3-5 days. Residues did not accumulate from one cycle to the next for the spray treatments, but did substantially for pour-on treatment. Spinosad does not partition totally into the fat fraction of milk. The mean quotient for concentration in cream divided by concentration in milk was 4.2, SD 1.6, max 9.0, min 1.2.

Table 74. Spinosad residues in the tissues of Holstein dairy cows from supervised trials in the USA in 1999. (Spurlock-Brouwer *et al.,* 2000). Muscle, kidney and liver were analysed by an immunoassay method and fat by an HPLC method (sum of spinosyns A, D, B and B of D).

Application				Sample	whp days	Spinosad, mg/kg	Ref.
Form	Method	Spray or dip conc, kg ai/hl	no				
aq susp 25 g ai/l	spray 2 l every 7 days	0.040	5	muscle	2 7 14	0.043 0.027 0.030 0.01 0.016 0.015 0.011 0.01 0.01	T9C739904
				kidney	2 7 14	0.083 0.13 0.13 0.036 0.045 0.037 0.021 0.018 0.030	

Application				Sample	whp days	Spinosad, mg/kg	Ref.
Form	Method	Spray or dip conc, kg ai/hl	no				
				liver	2 7 14	0.14 0.21 0.22 0.083 0.079 0.049 0.022 0.023 0.054	
				renal fat	2 7 14	0.37 0.47 0.30 0.27 0.32 0.25 0.21 0.19 0.20	
				sc fat	2 7 14	0.26 0.47 0.31 0.18 0.18 0.18 0.26 0.14 0.30	
aq susp 25 g ai/l	spray 5 l every 21 days	0.040	5	muscle	2 7 14	0.013 0.031 0.028 0.019 0.043 0.022 <0.01 <0.01 0.014	T9C739904
				kidney	2 7 14	0.075 0.11 0.089 0.049 0.058 0.055 0.011 0.022 0.030	
				liver	2 7 14	0.14 0.17 0.13 0.094 0.087 0.11 0.019 0.041 0.049	
				renal fat	2 7 14	0.19 0.21 0.26 0.36 0.33 0.30 0.056 0.17 0.25	
				sc fat	2 7 14	0.089 0.17 0.18 0.27 0.27 0.22 0.11 0.15 0.20	
aq susp 25 g ai/l	neat pour-on along backline at 2 mg/kg bw, every 21 days		5	muscle	2 14 21 28 35	0.28 0.074 0.070 0.078 0.13 <0.01 0.021 0.096 0.046 0.012 0.14 0.075 <0.01 0.075 0.018	T9C739904
				kidney	2 14 21 28 35	0.87 0.21 0.31 0.20 0.22 0.026 0.039 0.15 0.065 0.029 0.31 0.078 0.023 0.046 0.051	
				liver	2 14 21 28 35	1.2 0.38 0.66 0.23 0.35 0.040 0.052 0.080 0.17 0.059 0.38 0.075 0.031 0.077 0.065	
				renal fat	2 14 21 28 35	2.4 0.55 0.84 1.6 2.3 0.13 0.46 0.89 0.39 0.23 2.7 0.66 0.20 0.56 0.33	

Application				Sample	whp days	Spinosad, mg/kg	Ref.
Form	Method	Spray or dip conc, kg ai/hl	no				
				sc fat	2 14 21 28 35	1.7 0.22 0.50 1.6 2.2 0.12 0.57 0.94 0.50 0.26 0.27 0.79 0.26 0.79 0.58	

Table 75. Spinosad residues in the milk of groups of dairy cattle subject to 3 different treatments through 5 cycles of each treatment (Spurlock-Brouwer *et al.,* 2000). Treatment occurred on days marked 't'. Milk samples were analysed by an immunoassay method.

Days	Spinosad, mg/l milk		
	2-l spray each 7 days	5-l spray each 21 days	pour-on each 14 days
0	t 0.002	t 0.002	t 0.001
1	0.061	0.091	0.041
2	0.046	0.061	0.090
5	0.014	0.020	0.058
7	t 0.017		
8	0.061		
9	0.053		
12	0.017		
14	t 0.012		t 0.011
15	0.069		0.161
16	0.066		0.214
19	0.025		0.096
21	t 0.016	t 0.004	
22	0.060	0.083	
23	0.045	0.054	
26	0.017	0.015	
28	t 0.013		t 0.024
29	0.061		0.30
30	0.052		0.34
33	0.033		0.11
42		t 0.005	t 0.036
43		0.084	0.37
44		0.078	0.43
47		0.028	0.14
56		0.008	t 0.04
57		0.008	0.40
58		0.008	0.65
61		0.009	0.18
63		0.006	0.11
64		0.078	0.11
65		0.072	
68		0.029	
84		t 0.005	
85		0.064	
86		0.092	
89		0.035	

Farm animal feeding studies

Dairy cows. Groups of Holstein dairy cows (weighing 410-631 kg) were dosed orally daily with gelatine capsules at nominal levels of 1, 3 and 10 ppm technical spinosad equivalent in the diet for 28 days (Rutherford and Robb, 1996b). The technical spinosad was characterized as 76% spinosyn A and 12% spinosyn D. Doses were expressed as pure spinosad in dry feed matter. The cows ate 8 kg dairy ration, 16 kg alfalfa hay cubes and 2 kg baled hay each day. There were 3 cows in the lower dose groups and 7 in the 10 ppm group. Three animals from each group were slaughtered on day 29, and the four remaining animals on the 10 ppm diet were put on a residue-free diet and slaughtered on days 36, 43, 57 and 85. Milk was collected twice daily and the morning and evening milk was pooled to provide a daily sample for each cow.

Residues in the milk reached a plateau after 7-14 days. The residues in the milk of the cows eventually fed a residue-free diet decreased with a half-life of approximately 4 days. The results reported for residues in whole and skimmed milk and cream from day 14 and day 28 are shown in Table 78. The relationship between levels in cream and in whole milk seems anomalous for a fat-soluble compound. Levels of residue in cream were only 3-5 times the level in the whole milk (expect 20-25 times).

Spinosad residues were higher in the fat than in the other tissues, as in the metabolism studies, but residues were also found in the other tissues. Transfer factors were reasonably consistent for each tissue at all doses (Table 79), which adds confidence in interpolating to feeding levels that might occur in practice. Levels in fat decreased with an initial half-life of 14 days once dosing stopped, but decreased more slowly longer term.

Table 76. Spinosyn residues measured by immunoassay and HPLC in the tissues of dairy cows dosed with technical spinosad for 28 days at nominal levels of 1, 3 and 10 ppm in the diet (Rutherford and Robb, 1996b). Four animals from the highest dose group were given a residue-free diet after day 28 and slaughtered on days 36, 43, 57 and 85.

Tissue	Spinosyn, mg/kg						Day	Spinosyn, mg/kg	
	Dose – 1 ppm		Dose – 3 ppm		Dose – 10 ppm			Dose – 10 ppm	
	IA [1]	HPLC	IA	HPLC	IA	HPLC		IA	HPLC
Muscle	0.02 0.037 0.035	0.011 0.026 0.024	0.042 0.051 0.095	0.03 0.035 0.069	0.35 0.18 0.43	0.25 0.14 0.30	36	0.27	0.23
							43	0.028	0.022
							57	<0.01	<0.01
							85	0.03	0.022
Kidney	0.063 0.097 0.082	0.048 0.082 0.065	0.28 0.37 0.32	0.22 0.26 0.26	0.86 0.94 1.2	0.75 0.61 0.83	36	0.37	0.23
							43	0.074	0.038
							57	<0.01	<0.01
							85	0.051	0.034
Liver	0.14 0.22 0.20	0.089 0.15 0.15	0.51 0.80 0.52	0.32 0.44 0.29	1.9 2.1 3.2	0.99 1.0 1.7	36	0.84	0.34
							43	0.085	0.047
							57	0.013	<0.01
							85	0.026	0.01
Fat		0.62 0.66 0.66		0.81 0.78 1.7		6.1 3.6 7.5	36		3.7
							43		0.31
							57		0.026
							85		0.18

[1] IA: immunoassay method.

Table 77. Spinosyn residues in the milk of dairy cows dosed with technical spinosad for 28 days at nominal levels of 1, 3 and 10 ppm in the diet (Rutherford and Robb, 1996b). Four animals from the highest dose group were given a residue-free diet after day 28 and slaughtered on days 36, 43, 57 and 85.

Milk	Spinosyn, mg/kg					
	Dose - 1 ppm		Dose - 3 ppm		Dose - 10 ppm	
	IA [1]	HPLC	IA	HPLC	IA	HPLC
Day 1	<0.01 (3)	<0.01 (3)	<0.01 0.01 <0.01	<0.01 (3)	0.02 0.02 0.01 0.039 0.024 0.023 0.014	0.02 0.02 0.01 0.035 0.02 0.03 0.01
Day 2	0.031 0.02 0.02		0.062 0.079 0.067		0.21 0.26 0.18 0.32 0.23 0.20 0.18	
Day 3	0.037 0.031 0.034	0.035 0.037 0.035	0.095 0.13 0.090	0.074 0.12 0.090	0.32 0.47 0.32 0.42 0,40 0.32 0.35	0.33 0.48 0.26 0.41 0.36 0.31 0.37
Day 4	0.051 0.029 0.034		0.092 0.16 0.12		0.38 0.45 0.32 0.54 0.45 0.38 0.37	
Day 5	0.039 0.033 0.03	0.044 0.044 0.03	0.096 0.12 0.11	0.11 0.13 0.12	0.44 0.48 0.38 0.45 0.45 0.37 0.34	0.40 0.53 0.36 0.47 0.46 0.38 0.32
Day 6	0.049 0.044 0.031		0.094 0.18 0.14		0.46 0.58 0.46 0.60 0.52 0.41 0.42	
Day 7	0.047 0.039 0.045	0.039 0.051 0.03	0.096 0.15 0.14	0.13 0.15 0.14	0.47 0.69 0.52 0.68 0.55 0.41 0.42	0.42 0.61 0.39 0.57 0.47 0.36 0.35
Day 10	0.041 0.063 0.047	0.041 0.051 0.044	0.10 0.18 0.18	0.096 0.15 0.14	0.42 0.60 0.56 0.95 0.61 0.37 0.56	0.36 0.52 0.41 0.63 0.46 0.29 0.43
Day 12	0.071 0.066 0.046		0.13 0.21 0.16		0.46 0.28 0.67 0.46 0.56 0.42 0.40	
Day 14	0.076 0.071 0.065	0.042 0.036 0.044	0.19 0.21 0.14	0.13 0.16 0.13	0.79 0.61 0.99 1.3 0.76 0.55 1.2	0.44 0.58 0.82 1.3 0.63 0.43 1.1
Day 16	0.075 0.053 0.084		0.12 0.19 0.12		0.44 0.85 0.57 0.74 0.44 0.30 0.47	
Day 21	0.044 0.043 0.041	0.032 0.046 0.041	0.13 0.16 0.13	0.11 0.17 0.12	0.47 0.58 0.53 0.75 0.43 0.26 0.54	0.41 0.53 0.48 0.65 0.48 0.35 0.46
Day 28	0.052 0.054 0.041		0.15 0.20 0.13		0.39 0.55 0.58 0.70 0.43 0.31 0.50	
Day 29					0.82 0.57 0.28 0.51	
Day 30					0.54 0.29 0.15 0.42	
Day 31					0.41 0.26 0.14 0.35	
Day 32					0.34 0.17 0.071 0.30	
Day 33					0.32 0.15 0.062 0.25	
Day 34					0.26 0.11 0.038 0.20	
Day 35					0.24 0.11 0.042 0.20	
Day 36					0.074 0.031 0.17	
Day 37					0.059 0.027 0.17	
Day 38					0.060 0.02 0.15	
Day 39					0.064 0.02 0.12	
Day 40					0.051 0.02 0.12	
Day 41					0.040 0.01 0.093	
Day 42					0.034 0.01 0.098	
Day 49					<0.01 0.054	
Day 56					<0.01 0.032	
Day 70					0.01	
Day 84					<0.01	

[1] IA immunoassay method

Table 78. Spinosad residues in milk and cream from day 14 and day 28 milkings (Rutherford and Robb, 1996b).

	Spinosad residues, mg/kg												
	1 ppm feeding level			3 ppm feeding level			10 ppm feeding level						
Animal	15	11	1	9	6	4	3	14	8	12	2	5	16
Day 14 milk, HPLC	0.044	0.037	0.052	0.133	0.15	0.10	0.55	0.52	0.82	1.3	1.6	0.43	1.1
Day 14 milk	0.076	0.071	0.065	0.19	0.21	0.14	0.79	0.61	0.99	1.31	0.76	0.55	1.16
Day 14 cream	0.22	0.20	0.10	0.46	0.53	0.47	2.1	2.2	2.0	3.1	2.5	1.5	2.1
Day 14 skimmed milk	0.008	0.005	0.004	0.01	0.011	0.01	0.042	0.043	0.065	0.082	0.055	0.024	0.038
Day 28 milk	0.032	0.046	0.041	0.11	0.17	0.12	0.41	0.53	0.48	0.65	0.48	0.35	0.46
Day 28 milk, HPLC	0.052	0.054	0.041	0.15	0.20	0.13	0.39	0.55	0.58	0.70	0.43	0.31	0.50
Day 28 cream	0.15	0.22	0.17	0.48	0.71	0.58	1.4	2.2	2.1	2.9	2.1	1.6	1.1
Day 28 skimmed milk	0.005	0.004	0.003	0.009	0.021	0.013	0.064	0.059	0.13	0.11	0.067	0.058	0.083

Table 79. Transfer factors for spinosad residues from feed to tissues and milk of dairy cows (Rutherford and Robb, 1996b).

	Mean residue, mg/kg			Transfer factor = conc in tissue ÷ conc in feed			
Feeding level	1 ppm	3 ppm	10 ppm	1 ppm	3 ppm	10 ppm	Mean
Muscle	0.026	0.054	0.28	0.026	0.018	0.028	0.024
Kidney	0.073	0.29	0.87	0.073	0.095	0.087	0.085
Liver	0.16	0.48	1.8	0.16	0.16	0.18	0.17
Fat	0.65	1.1	5.7	0.65	0.37	0.57	0.53
Milk 28 days	0.044	0.15	0.49	0.044	0.048	0.049	0.047
Cream 28 days	0.18	0.59	1.9	0.18	0.20	0.19	0.19
Skimmed milk, 28 days	0.004	0.014	0.082	0.004	0.005	0.008	0.006

Laying hens. Groups of 12 White Leghorn laying hens each bird weighing c.1.5 kg were dosed by gelatine capsules at nominal levels of 0.1, 0.3, 1 and 5 ppm technical spinosad equivalent in the diet for 41 days (Gardner and Dolder, 1998). The technical spinosad was characterized as 76% spinosyn A and 12% spinosyn D. Birds ate an average 123 g of feed per day. Eggs were collected daily and were composited in groups of 3. On day 42, 4-9 hours after the last dose, hens from each group were killed. Samples were analysed by HPLC; the LOQ was 0.03 mg/kg for fat and 0.01 mg/kg for other tissues.

Residues were often below the LOQ at the lower feeding levels, so differences between tissues are clearer at the higher feeding level. At 5 ppm, spinosad residues were highest in the abdominal fat, 1.4 mg/kg, 1.0 mg/kg in subcutaneous fat, 0.18 mg/kg in whole body including fat and skin, 0.092 mg/kg in liver and 0.062 and 0.027 mg/kg in dark and light muscle meats respectively. Residues in fat from the 5 ppm dosing group were 8.7 and 7.0 times as high as levels from the 1 ppm group in abdominal and subcutaneous fat respectively, slightly more than the expected 5 times. Residues in eggs reached a plateau by day 13 in the highest dose group, and were generally below the LOQ (0.01 mg/kg) from the other groups.

Table 80. Spinosyn residues in the tissues and eggs of laying hens dosed with technical spinosad for 41 days at nominal levels of 0.1, 0.3, 1 and 5 ppm in the diet (Gardner and Dolder, 1998).

Sample	Residues, mg/kg							
	Dose – 0.1 ppm		Dose – 0.3 ppm		Dose – 1 ppm		Dose – 5 ppm	
	spinosyn A	spinosyn D	spinosyn A	spinosyn D	spinosyn A	spinosyn D	spinosyn A	spinosyn D
Whole body [1]	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	0.02 <0.01 0.01	<0.01 (3)	0.12 0.15 0.15	0.031 0.045 0.047
Light muscle	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	0.021 0.039 0.021	<0.01 (3)
Dark muscle	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	0.047 0.049 0.051	0.013 0.014 0.013
Fat, abdominal	<0.03 0.03 <0.03	<0.03 (3)	<0.03 0.047 <0.03	<0.03 (3)	0.13 0.12 0.11	0.049 0.040 0.040	1.0 1.2	0.30 0.35
Fat, SC	<0.03 (2) 0.04	<0.03 (3)	<0.03 0.05 <0.03	<0.03 (3)	0.12 0.12 0.095	0.04 0.04 0.03	0.66 1.2 0.55	0.18 0.32 0.19
Liver	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	0.01 <0.01 <0.01	<0.01 (3)	0.082 0.067 0.043	0.035 0.031 0.019
Eggs, day 1							<0.01 (3)	<0.01 (3)
Eggs, day 4							0.053 0.042 0.069	0.01 <0.01 0.01
Eggs, day 7							0.081 0.11	0.02 0.025
Eggs, day 10							0.14 0.14 0.16	0.035 0.036 0.041
Eggs, day 13							0.13 0.13 0.26	0.032 0.034 0.073
Eggs, day 20							0.13 0.14 0.18	0.037 0.036 0.030
Eggs, day 28	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	0.01 <0.01 0.01	<0.01 (3)	0.098 0.14 0.074	0.027 0.038 0.020
Eggs, day 35	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	0.01 0.01 <0.01	<0.01 (3)	0.16 0.11 0.13	0.042 0.029 0.037
Eggs, day 41	<0.01 (3)	<0.01 (3)	<0.01 (2) 0.02	<0.01 (3)	<0.01 0.01 <0.01	<0.01 (3)	0.12 0.14 0.15	0.036 0.040 0.044

[1] Whole body: the carcase was cut in half lengthways and bones removed. Whole body represents the whole commodity with overlying skin and fat, but with liver and abdominal fat removed.

Table 81. Transfer factors for spinosad residues from feed to tissues and eggs of laying hens (Gardner and Dolder, 1998).

	Mean residue, mg/kg		Transfer factor = conc in tissue ÷ conc in feed	
Feeding level	1 ppm	5 ppm	1 ppm	5 ppm
Whole body	0.010	0.18	0.01	0.04
Light muscle	<0.01	0.027	<0.01	0.01
Dark muscle	<0.01	0.062	<0.01	0.01
Fat, abdominal	0.16	1.43	0.16	0.29
Fat, SC	0.15	1.03	0.15	0.21
Liver	<0.01	0.092	<0.01	0.018
Eggs day 41	0.01	0.18	0.01	0.035

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

The Meeting received information on the fate of spinosad residues during the processing of apples, oranges, grapes, tomatoes and cotton seed.

Apples. In a supervised trial in France Khoshab and Hastings (1999c) treated apples with 4 applications of spinosad (Table 82). 20 kg were processed into juice and wet pomace, and 6 kg into purée (Figure). In the juicing operation spinosad residues were partitioned into the pomace rather than into the juice.

Bolles and Robb (1996) treated Red Chief apples on 5 occasions with an exaggerated spinosad application rate (×5) before harvesting the apples 7 days after the last application and processing them to juice and pomace (Table 82). An apple RAC sample was analysed as well as the bulk apple sample (30 kg) sent for processing.

Procedures simulated commercial practices. The apples were washed in cold water for 5 minutes and then leaves, stems and other debris were removed. Apples were crushed to pulp and heated with steam to raise the temperature of the pulp to 40-50°C. Pectic enzyme was mixed in. After standing for 2 hours, the pulp was pressed to produce juice and wet pomace. The juice was further screened through a standard milk filter to provide the final processed juice. Approximately 30% of the residue was removed in the washing step. Residues partitioned into pomace rather than to juice.

Oranges. Hamlin oranges were treated with an exaggerated spinosad application rate (×5) and harvested 4 days after the last application (approx. 400 kg) for processing to juice (Gardner and Phillips, 1997, RES96023 FL01). Much of the residue disappeared in the washing step. Residues were not detected in the juice, but were concentrated in the oil (Table 82).

Table 82. Spinosad residues in fruits and processed products.

CROP country, year, (variety)	Application					PHI, days, sample	Spinosyn residues, mg/kg						Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A	D	K	B	B of D	Total	
APPLES	SC 480	0.29	0.030	960	4	7							GHE-
France, 1998						apples	0.09	0.02	<0.01	0.01	<0.01	0.12	P-8252
(Golden)						pomace	0.17	0.06	<0.01	0.01	<0.01	0.23	
						purée	0.01	<0.01	<0.01	<0.01	<0.01	0.01	
						juice	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
ORANGES	SC 480	0.35		480	4	4							RES96
USA (FL),		+0.50				orange unw	0.065	0.010	<0.01	0.011	<0.01	0.088	023
1996 (Hamlin		+0.75				orange washed	0.014	<0.01	<0.01	<0.01	<0.01	0.020	FL01
oranges)		+0.90				juice	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
						dried pulp [1]	0.15	0.017	<0.01	0.024	<0.01	0.19	
						oil	0.80	0.14	<0.01	0.15	0.018	1.3	
APPLES	WG 820	0.25		1900	5	7							RES95
USA (WA),		+0.35				apples RAC	0.25	0.035	<0.01	<0.01	<0.01	0.30	041
1995 (Red		+0.50				apples unw	0.21	0.03	<0.01	<0.01	<0.01	0.25	
Chief)		+0.50				apples washed	0.15	0.02	<0.01	<0.01	<0.01	0.18	
		+0.90				juice	0.017	<0.01	<0.01	<0.01	<0.01	0.024	
						wet pomace	1.1	0.15	0.01	0.042	0.01	1.3	

[1] Dried citrus processing pulp: contains peel, membrane, rag and seeds that are chopped, limed and dried to 8-10% moisture.

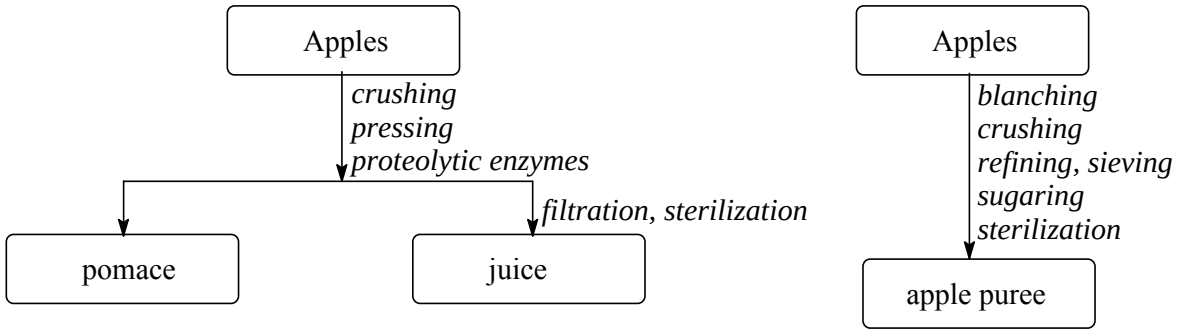


Figure 5. Apple processing (Khoshab and Hastings, 1999c).

Grapes. Khoshab and Volle (1999, report GHE-P-7575) treated grapes with spinosad before processing them into pomace, must and wine. Unfortunately residues in the white grapes (Chenin) were too low to provide useful information about the fate of spinosad during processing (Table 83). Residues in the red wine grapes (Gamay) were low, but provided evidence that residues tend to partition to the pomace rather than the wine.

Khoshab *et al. (*1999d, report GHE-P-7856) treated red wine grapes with spinosad before processing them into pomace, must and wine. Residues in the pomace were higher than in the grapes while residues in the must and wine were all below the LOQ of 0.01 mg/kg (Table 83).

Table 83. Spinosad residues in grapes, pomace, must and wine from supervised trials in France.

Year (variety)	Application [4]					PHI, days sample	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
1997 (Chenin, Riparia Gloire)	SC 480	0.060	0.029	210	5	14					GHE-P-7575
						grapes	<0.01	<0.01	<0.01	<0.01	
						pomace	<0.01	<0.01	<0.01	0.01	
						must	<0.01	<0.01	<0.01	<0.01	
						wine [3]	<0.01	<0.01	<0.01	<0.01	
						wine [4]	<0.01	<0.01	<0.01	<0.01	
						c pomace [5 6]	<0.01	<0.01	<0.01	0.01	
1997 (Gamay)	SC 480	0.060	0.032	190	5	15					GHE-P-7575
						grapes	0.01	<0.01	0.02	0.02	
						pomace	0.03	<0.01	0.05	0.06	
						must	0.02	<0.01	0.03	0.03	
						wine [3]	<0.01	<0.01	<0.01	<0.01	
						wine [4]	<0.01	<0.01	<0.01	<0.01	
1998 (Red wine grape, Cot)	SC 480	0.096	0.042	230	5	15					GHE-P-7856
		+0.096	+0.042			grapes	0.02	0.01	0.03		
		+0.048	+0.021			pomace	0.04	0.03	0.07		
		+0.048	+0.021			must	<0.01	<0.01	<0.01		
		+0.048	+0.021			wine [3]	<0.01	<0.01	<0.01		
						wine [4]	<0.01	<0.01	<0.01		

Year (variety)	Application [4]					PHI, days sample	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Italy, 1998 (Trebiano)	SC 480	0.098 +0.091 +0.049 +0.046 +0.050	0.016 +0.016 +0.005 +0.005 +0.005	610 +570 +1010 +950 +1030	5	15 grapes pomace must wine [3] wine [4]	 0.01 <0.01 0.01 <0.01 <0.01	 0.01 <0.01 <0.01 <0.01 <0.01	 0.03 0.01 0.02 <0.01 <0.01		GHE-P-7855

[1] Total includes spinosyns A, D, B, B of D and K
[2] Immunoassay
[3] wine at bottling
[4] wine after 4 months
[5] c pomace produced from control grapes

Tomatoes. Khoshab (1999v, report GHE-P-7585) treated tomatoes with spinosad and then produced canned tomatoes, juice and purée in a small-scale process (25 kg tomatoes available for the two processes). Residues in the processed commodities were much less than in the whole tomatoes (Table 84). The initial washing (Figure 6) probably removed much of the residue.

In a processing trial in the USA, tomatoes were treated with an exaggerated rate (×5) of spinosad and 350 kg harvested 1 day after the last treatment were converted into juice, purée, pomace and paste by a simulated commercial process (Rutherford and Robb, 1996d, RES95000). The tomatoes were washed with fresh water and then with chlorinated water, then passed through a grinder and heated to approximately 93°C before the peel and seeds were screened out as wet pomace. The wet pomace was dried in a food dehydrator to dry pomace containing approximately 92% dry matter. The juice was collected, canned, heated for at least 50 min at a minimum of 115°C, and concentrated in a vacuum evaporator to provide purée. A portion of purée was further condensed to paste in a vacuum kettle. The results are shown in Table 84. Washing removed much of the residue, which tended to concentrate in the pomace fractions.

The residue in the tomato RAC (0.53 mg/kg) taken directly for analysis was quite different from the residue found in the unwashed tomatoes (0.077 mg/kg) supplied for processing. It was found that the tomatoes plants had had very dense foliage and many of the fruit were on the ground sheltered from the spray. Visible fruit were picked for the RAC sample. For processing, whole plants were pulled from the ground and all pink or red tomatoes were picked. A higher proportion of sheltered fruit would have been collected for processing than for the RAC sample.

Table 84. Spinosad residues in tomatoes and their processed products from supervised trials in Italy and the USA.

Country, year (variety)	Application [4]					PHI, days sample	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
Italy, 1997 (Erminia Peto Seed)	SC 480	0.54	0.067	800	5	3 tomatoes juice purée canned tomatoes	 0.30 0.01 0.06 <0.01	 0.08 <0.01 0.01 <0.01	 0.40 0.01 0.07 <0.01	 0.38 0.02 0.11 0.02	GHE-P-7585

Country, year (variety)	Application [4]					PHI, days sample	Spinosyn residues, mg/kg				Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.		A HPLC	D HPLC	Total [1] HPLC	IA [2]	
USA (CA), 1995 (La Rossa)	WG 800	0.25		900	5	1					RES95000
		+0.50		+890		tomato RAC	0.41	0.053	0.53		
		+0.52		+960		tomato unwashed	0.062	0.01	0.077		
		+0.54		+980		tomato washed	0.021	<0.01	0.027		
		+0.83		+1000		juice	0.018	<0.01	0.024		
						wet pomace	0.55	0.070	0.66		
						dry pomace	0.91	0.11	1.1		
						purée	0.042	<0.01	0.054		
						paste	0.12	0.020	0.15		

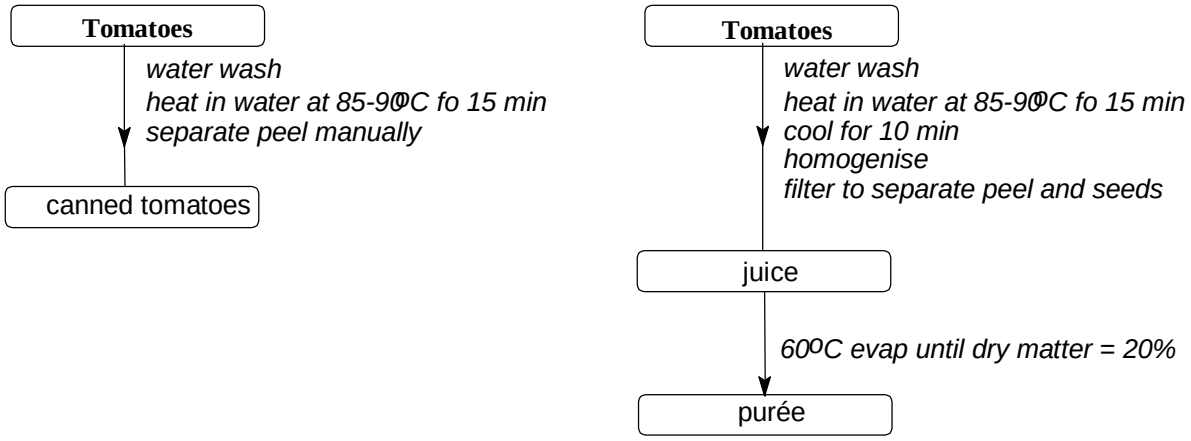


Figure 6. Tomato processing (Khoshab, 1999v, GHE-P-7585)

Cotton was treated at an exaggerated rate and approximately 18 kg of harvested seed was processed (Figure 7) to hulls, meal, oil and soapstock (Gardner and West, 1994b). Spinosad residues generally decreased during processing, but residues were apparent in the hulls and oil (Table 85).

Table 85. Spinosad residues in cotton seed and its processed products from supervised trials in the USA (Gardner and West, 1994b).

Location, year (variety)	Application				PHI, days sample	Residues, mg/kg			Ref.
	Form	kg ai/ha	water, l/ha	no.		spinosyn A	spinosyn D	total	
MS, 1993 (Des119 Sure Grow)	SC 480	0.54	560	5	28				RES93026.01
		+0.60	+560		cotton seed	0.060	<0.01	0.067	
		+0.60	+410		hulls	0.012	<0.01	0.014	
		+0.60	+560		meal	<0.01	<0.01	<0.01	
		+0.84	+510		crude oil	0.011	<0.01	0.011	
					refined oil	0.012	<0.01	0.013	
					soapstock	<0.01	<0.01	<0.01	

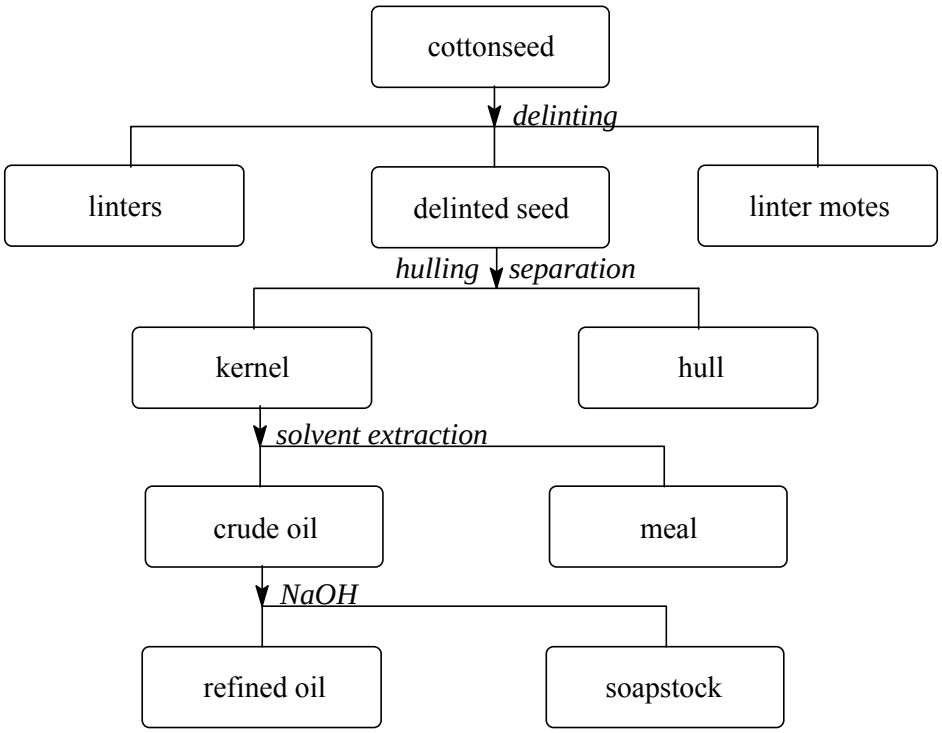


Figure 7. Cotton seed processing (Gardner and West, 1994b).

Processing factors were calculated from the residue data in the studies (Table 86) in three ways: spinosyn A residues, sum of spinosyns A and D by HPLC or immunoassay. Generally the results are similar except where residues are at or close to the 0.01 mg/kg LOQ, and they were lower in the processed commodity the calculated factor is shown with a "<" sign although the value of this is very limited when the residue in the raw commodity is close to the LOQ.

The residue is a surface one and washing removes some or most of it. In juicing operations the residue tends to attach itself to the solids, and in the production of oilseed it partitions to the oil rather than the meal.

Table 86. Calculated processing factors for apples, oranges, grapes, tomatoes and cotton seed.

Crop		Residues, mg/kg			Processing factors			Ref.
	Commodity	Spinosyn A	Sum (A+D)	IA	Spinosyn A	Sum (A+D)	IA	
Apples	apples	0.09	0.11					GHE-P-8252
	pomace	0.17	0.23		1.9	2.1		
	purée	0.01	0.01		0.11	0.09		
	juice	<0.01	<0.01		<0.11	<0.09		
Apples	apples unwashed	0.21	0.24					RES95041
	apples washed	0.15	0.17		0.71	0.71		
	juice	0.017	0.017		0.08	0.07		
	wet pomace	1.1	1.25		5.2	5.2		
Oranges	orange unwashed	0.065	0.075					RES96023 FL01
	orange washed	0.014	0.014		0.22	0.19		
	juice	<0.01	<0.01		<0.15	<0.13		
	dried pulp	0.15	0.167		2.3	2.2		
	oil	0.8	0.94		12	13		

Crop		Residues, mg/kg			Processing factors			Ref.
	Commodity	Spinosyn A	Sum (A+D)	IA	Spinosyn A	Sum (A+D)	IA	
Grapes	grapes	0.01	0.01	0.02				GHE-P-7575
	pomace	0.03	0.03	0.06	3	3.0	3	
	must	0.02	0.02	0.03	2	2.0	1.5	
	wine at bottling	<0.01	<0.01	<0.01	<1	<1	<0.5	
	wine after 4 months	<0.01	<0.01	<0.01	<1	<1	<0.5	
Grapes	grapes	0.02	0.03					GHE-P-7856
	pomace	0.04	0.07		2.0	2.3		
	must	<0.01	<0.01		<0.5	0.3		
	wine at bottling	<0.01	<0.01		<0.5	<0.3		
	wine after 4 months	<0.01	<0.01		<0.5	<0.3		
Grapes	grapes	0.01	0.02					GHE-P-7855
	pomace	<0.01	0.01		<1	<0.5		
	must	0.01	0.01		1	0.5		
	wine at bottling	<0.01	<0.01		<1	<0.5		
	wine after 4 months	<0.01	<0.01		<1	<0.5		
Tomato	tomatoes	0.3	0.38	0.38				GHE-P-7585
	juice	0.01	0.01	0.02	0.033	0.026	0.053	
	purée	0.06	0.07	0.11	0.20	0.18	0.29	
	canned tomatoes	<0.01	<0.01	0.02	<0.03	<0.03	0.053	
Tomato	tomato unwashed	0.062	0.072					RES95000
	tomato washed	0.021	0.021		0.34	0.29		
	juice	0.018	0.018		0.29	0.25		
	wet pomace	0.55	0.62		8.9	8.6		
	dry pomace	0.91	1.02		15	14		
	purée	0.042	0.042		0.68	0.58		
	paste	0.12	0.14		1.94	1.94		
Cotton seed	cotton seed	0.06	0.06					RES93026.01
	hulls	0.012	0.012		0.20	0.20		
	meal	<0.01	<0.01		<0.17	<0.17		
	crude oil	0.011	0.011		0.18	0.18		
	refined oil	0.012	0.012		0.20	0.20		
	soapstock	<0.01	<0.01		<0.17	<0.17		

Residues in the edible portion of food commodities

Information was reported on residues in head cabbages, head lettuce and celery from residue trials.

In a trial on mandarins in Japan (Table 34), residues of spinosyn A were 0.09 and 0.05 mg/kg in the peel, but none were found in the pulp.

In US trials the residue was essentially on the peel of oranges, and was undetectable in the pulp of muskmelons. Residues in head cabbages were reduced by averages of 78% in head cabbages, and of 77% in head lettuce when wrapper leaves were removed (calculations based on those cases where residues exceeded the LOQ). Residues in trimmed celery were approximately 15% of those in untrimmed celery.

Table 87. Spinosad residues in trade commodities and edible portions of citrus fruits, melons, cabbages, head lettuce and celery (Table 34, Table 46, Table 47, Table 57 and Table 58).

Sample	Trade commodity, mg/kg	Edible portion, mg/kg	Peel, mg/kg	Residue in edible portion ÷ residue in commodity	Ref.
	whole fruit	**peeled fruit**			
Mandarin		<0.01	0.09		GHF-P-1683
Orange	0.046	<0.01	0.10	<0.22	RES96023
Orange	0.022	<0.01	0.052	<0.45	RES96023

Sample	Trade commodity, mg/kg	Edible portion, mg/kg	Peel, mg/kg	Residue in edible portion ÷ residue in commodity	Ref.
Orange	0.017	<0.01	0.021	<0.59	RES96023
Orange	0.01	<0.01	0.035	<1.00	RES96023
Orange	0.14	0.01	0.64	0.07	RES96023
Orange	0.06	<0.01	0.30	<0.17	RES96023
Orange	0.20	<0.01	0.78	<0.05	RES96023
Orange	0.072	<0.01	0.32	<0.14	RES96023
Orange	0.053	<0.01	0.08	<0.19	RES96023
Orange	0.011	<0.01	0.054	<0.91	RES96023
Orange	0.031	<0.01	0.046	<0.32	RES96023
Orange	0.016	<0.01	0.11	<0.63	RES96023
Musk melon	0.16	<0.01		<0.063	RES97002
Musk melon	0.092	<0.01		<0.11	RES97002
	include wrapper leaves	**wrapper leaves removed**			
Head cabbage	0.089	0.02		0.22	RES95001 CA
Head cabbage	1.09	0.17		0.16	RES95001 FL
Head cabbage	0.01	<0.01		<1	RES95001 IN1
Head cabbage	0.053	0.02		0.38	RES95001 IN2
Head cabbage	0.08	0.01		0.13	RES95001 PA1
Head cabbage	0.02	<0.01		<0.5	RES95001PA2
Head cabbage	1.0	0.36		0.38	RES95001 TX
Head cabbage	0.37	0.03		0.08	RES95001 VA
Head lettuce	1.97	1.85		0.94	RES96008AZ LV9606
Head lettuce	0.93	0.073		0.08	RES96008CA3 LV9605
Head lettuce	0.12	<0.01		<0.08	RES96008NJ LV9601
Head lettuce	0.109	0.01		0.09	RES96009/RES96008CA2
Head lettuce	0.052	<0.01		<0.19	RES96009/RES96008CA2
Head lettuce	0.77	0.019		0.02	RES96009/RES96008CA1
Head lettuce	0.672	0.024		0.04	RES96009/RES96008CA1
Head lettuce	0.73	0.172		0.24	RES96009/RES96008FL
Head lettuce	0.85	0.194		0.23	RES96009/RES96008FL
	untrimmed	**trimmed**			
Celery	1.1	0.18		0.16	RES96008 FL
Celery	1.3	0.31		0.24	RES96008 MI
Celery	0.454	0.034		0.07	RES96008 CA1
Celery	0.84	0.087		0.10	RES96008 CA2
Celery	0.4	0.11		0.28	RES96008 CA3
Celery	1.7	0.1		0.06	RES96008 AZ

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was available on residue monitoring data for spinosad.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware that the following national MRLs had been established.

Country	MRL, mg/kg	Commodity
Argentina	0.03	Tomato
	<0.001*	Soya bean; cotton seed
Australia	5	Cabbage, Chinese; leafy vegetables (except Chinese cabbage); lettuce; spinach
	0.5	Brassica vegetables (cole or cabbage); broccoli; cabbage; cauliflower; flowerhead Brassica (broccoli, cauliflower)
	0.5 (T)	Strawberry
	0.2	Cattle, fat
	0.2 (T)	Melon

Country	MRL, mg/kg	Commodity
	0.2	Peppers; sheep fat; tomato
	0.1 (T)	Apple; citrus; egg plant; grapes; pome fruits (apples, pears)
	0.05	Edible mammalian offal
	0.02	Maize grain, sweet; milk of cattle, goats, and sheep
	0.01	Cotton seed
	0.01*	Egg; poultry offal, poultry meat
Brazil	0.1	Tomato
	0.01	Potato; soya bean
Japan	5	Japanese radish (leaf); lettuce
	2	Egg plant; peppers; tea; tomato
	1	Cabbage; Chinese cabbage
	0.5	Apple
	0.2	Japanese radish (root); peach
Mexico	2	Flowerhead Brassica (broccoli, cauliflower)
	0.4	Peppers; tomato
	0.02	Cotton seed
New Zealand	0.1	Apple; avocado; broccoli; Brussels sprouts; cabbage; cabbage, Chinese; cauliflower; Brassica vegetables (cole or cabbage); flowerhead Brassica (broccoli, cauliflower); kiwifruit; pome fruits (apples, pears); tomato
Philippines	2	Cabbage
Switzerland	1	Cabbage; pepper
	0.5	Tomato
	0.2	Cucumber
	0.1	Grapes
Taiwan	1	Cabbage
Thailand	0.05	Cabbage
USA	20	Aspirated grain fractions
	10	Ti palm; turnip greens; vegetables, leafy Brassica – crop group 5-b
	10 (T)	Beet, sugar (tops)
	8	Cilantro; vegetables, leafy (except Brassica) – crop group 4; watercress
	5	Milk, fat
	4 (T)	Alfalfa forage; alfalfa hay
	3.5	Cattle, fat; goats, fat; hogs, fat; horses, fat; sheep, fat
	3	Citrus oil
	2	Almond hulls; vegetables, head and stem Brassica- crop group 5-a
	1.5	Cotton gin by products
	1	Amaranth, grain; cattle, mbyp; corn, fodder; corn, forage; corn, hay; corn, stover; corn, straw; corn, sweet, forage; corn, sweet, stover; goats, mbyp; hogs, mbyp; horses, mbyp; pearl, millet; proso, millet; sheep, mbyp; sorghum, fodder; sorghum, forage; sorghum, grain; sorghum, hay; sorghum, stover; sorghum, straw; wheat, fodder; wheat, forage; wheat, hay; wheat, stover; wheat, straw
	1 (T)	Peanut hay
	0.5	Apple pomace, wet; citrus pulp, dried; milk, whole
	0.4	Vegetables, fruiting except cucurbits – crop group 8
	0.3	Acerola; atemoya; avocado; biriba; canistel; cherimoya; citrus fruits group; cucurbit vegetables group; custard apple; feijoa; guava; ilama; jaboticaba; legume vegetables, edible podded – crop subgroup 6-a; longan; lychee; mango; papaya; passionfruit; pulasan; rambutan; sapodilla; sapote, black; sapote, mamey; sapote, white; soursop; Spanish lime; star apple; starfruit; sugar apple; wax jambu
	0.2	Apples; poultry, fat; stone fruit group
	0.15	Cattle, meat; goats, meat; hogs, meat; horses, meat; sheep, meat; wheat, bran; wheat, flour; wheat, middlings; wheat, shorts
	0.02	Almond; animal feed, non-grass- crop group 18; barley, grain; buckwheat, grain; corn, field, grain; corn, grain; corn, pop, grain; corn, sweet, k+cwhr; cotton seed; grass, fodder, forage, hay –crop group 17; legume veg, dried shell pea and bean (except soya beans)– crop subgroup 6-c; legume vegetables, succulent shelled pea and bean – crop subgroup 6-b; oats, grain; pistachio; popcorn, grain; poultry, eggs; poultry, meat; poultry, mbyp; rye, grain; soya beans; teosinte, grain; tuberous and corm vegetables – crop group 1-c; wheat, grain
	0.02 (T)	Beet, sugar (root); grapes; kiwifruit; nectarines; peanuts; strawberries

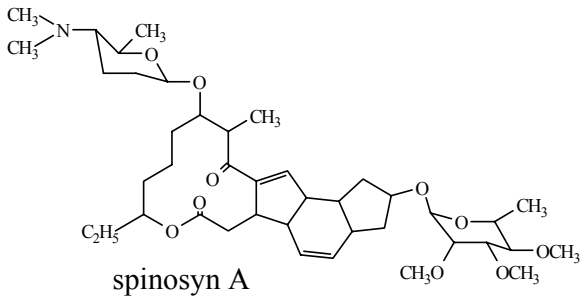
* indicates lower limit of determination (LOD) or MRL set at or about limit of analytical quantification.
T: temporary

The definition of the residue is spinosyn A + spinosyn D in Argentina, Australia, Brazil, Canada, EU, Malaysia, NZ, PRC, Taiwan and the USA.

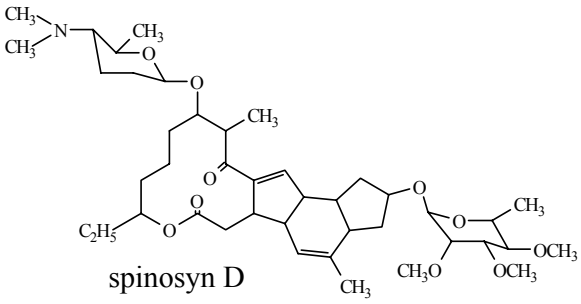
APPRAISAL

Residue and analytical aspects of spinosad were considered for the first time by the present Meeting.

Spinosad is a naturally derived fermentation product, which has demonstrated insect control activity against a large number of pests, including members of the insect orders Lepidoptera, Coleoptera and Thysanoptera. The product contains a mixture of two structurally similar molecules which are both active insecticidally and have been designated spinosyn A and spinosyn D. *N*-Demethyl-spinosyn A is called spinosyn B, and the analogous product from spinosyn D is called spinosyn B of D.



spinosyn A



spinosyn D

The Meeting received extensive information on the metabolism and environmental fate of spinosad, methods of analysis for residues, stability in freezer storage, national registered use patterns, the results of supervised trials, direct animal treatments, farm animal feeding studies, the fate of residues in processing and national MRLs.

Metabolism

Animals

Spinosyns A and D, reasonably uniformly radiolabelled at 23 carbons in the aglycone ring system, were used in studies of metabolism and environment fate. The amino and rhamnose sugars did not contain the ^{14}C label.

When lactating goats were dosed orally with [^{14}C]spinosyn A or [^{14}C]spinosyn D at the equivalent of 10 ppm in the feed for 3 consecutive days, a considerable portion of the residue (45% spinosyn A and 20% spinosyn D) transferred to tissues and milk. Excretion occurred mainly via the faeces. The parent compounds (spinosyns A and D) were major components of the residue in tissues and milk and constituted an especially high percentage of the total residue in fat (86 and 85%) and milk (71 and 81%). The concentrations of spinosyn A in fat and milk were 3.1 and 0.45 mg/kg, respectively. A number of metabolites were identified and were most prevalent in kidney and liver. The metabolites resulted from *N*-demethylation and hydroxylation of the macrolide ring.

Most of a dose of [^{14}C]spinosyn A (69%) or [^{14}C]spinosyn D (82%) appeared in the excreta of laying hens dosed at the equivalent of 10 ppm in feed for 5 consecutive days. The concentrations in eggs were apparently still increasing at the end of the study. The highest concentrations occurred in fat, parent compound constituting most of the residue; spinosyns A and D constituted 81% and 79%

of the fat residue, respectively, at concentrations of 1.8 and 0.81 mg/kg. The parent compounds were also the main or important constituents of the residue in muscle and eggs. Substantial metabolism occurred in liver, where the metabolites were identified as deriving from *N*-demethylation, *O*-demethylation and loss of the forosamine sugar moiety.

When goats were treated dermally once along the backline with [^{14}C]spinosyn A or [^{14}C]spinosyn D, more residue was found in liver and fat than in other tissues. The parent compound was the predominant component of the residue, particularly in fat and milk. The metabolites were produced by *N*-demethylation and hydroxylation of the macrolide ring, a process also identified after oral dosing. The concentrations of residues in milk reached a peak 40–70 h after treatment.

Plants

The Meeting received information on the fate of spinosyns after foliar application to apples, cabbage, tomatoes, turnips, grapes and cotton. The residues of spinosad on fruits, vegetables and other crops are usually at the surface, and the main primary degradation step is photolysis.

Apple trees were sprayed with [^{14}C]spinosyn A or [^{14}C]spinosyn D, one branch being protected from the spray and some apples being protected from light immediately after spraying. The total amount of radiolabel in the apples decreased by about half during the 42 days of sampling, most likely because of growth dilution. The residue occurred mostly on the surface; even after 42 days, about 60% of the remaining residue could be rinsed from the surface. The concentrations of parent spinosyns A and D declined quickly (more than 50% during the first 3 days). The only metabolites that were characterized were spinosyn B and spinosyn B of D, both resulting from *N*-demethylation of the parent compound. The nature of the radiolabelled residues was extensively investigated: they were shown to be polar and to have multiple components. Fractions taken on day 14 from apples sprayed with spinosyn A had low sensitivity in the spinosyn immunoassay, suggesting that the residues did not contain structures similar to those to which the immunoassay is sensitive (spinosyns A, B, C, E, F, K or pseudoaglycone of A).

Both spinosyns A and D were more persistent on apples kept from the light, indicating that photolysis is a major process of degradation. The radiolabelled residues in apples protected from spraying represented only 1.3% of those on apples that had been sprayed directly on day 42, indicating that translocation was minimal. The radiolabel was shown to be incorporated into structural carbohydrates in both treated and untreated leaves.

When grapes were treated separately with [^{14}C]spinosyn A and [^{14}C]spinosyn D, a high percentage of residue was found on the surface, even when aged. When the grapes reached maturity (49 days after treatment), spinosyn A accounted for about 35% of its residue and spinosyn D for 22%. Other components of the residue were polar and numerous and were probably products of photolysis. Hydroxy-spinosyn A and hydroxy-spinosyn D were tentatively identified in the residues.

After cabbage was treated with [^{14}C]spinosyn A and [^{14}C]spinosyn D, the parent compounds disappeared rapidly, most likely by photolysis, and accounted for only 10 and 13% of the residue 3 days after treatment. In a study in which cabbages were treated with [^{14}C]spinosyn A, spinosyns B and K were identified in the residue, which also comprised numerous polar compounds and some incorporation of radiolabel into natural compounds.

When tomato plants were treated four times with [^{14}C]spinosyn A 0 and 3 days before harvest, spinosyn A accounted for 65% and 24% of the radiolabel in the fruit. A portion of the tomatoes (TRR, 0.080 mg/kg as spinosyn A) was processed to juice and seeds plus peel. The concentrations of residue in the juice (TRR, 0.048 mg/kg as spinosyn A) and seeds plus peel (TRR, 0.28 mg/kg as spinosyn A) indicated that most of the radiolabelled residue was on the surface.

Turnip plants were treated with [^{14}C]spinosyn A and [^{14}C]spinosyn D, and the leaves and roots were subsequently sampled for analysis. By day 10, the parent compounds constituted a minor proportion of the radiolabelled residue in the foliage; however, the residues of parent compounds that reached the root and were protected from sunlight were more persistent. By day 24, the concentrations of parent compound were higher in the roots (A: leaf and root, 0.075 and 0.084 mg/kg; D: leaf and root, 0.016 and 0.036 mg/kg) than in the foliage and constituted a much higher percentage of the total radiolabel in the roots. Spinosyns B, K and B of D, which are products of photolysis, appeared as components of the residue in leaf and root from day 0.

Cotton plants were treated five times with [^{14}C]spinosyn A and [^{14}C]spinosyn D. Cotton seed and fibre were collected from the plots 48 or 49 days after the final treatment and were ginned to separate seed from fibre. The concentrations of radiolabel were 0.29 mg/kg in seed and 0.22 mg/kg in fibre after spinosyn A treatment and 0.11 and 0.075 mg/kg (seed and fibre) after spinosyn D treatment. Despite persistent attempts to identify spinosyn-related compounds, none were identified in cotton seed. Further attempts on separated fractions of the seeds showed that at least some of the radiolabel had become incorporated into natural compounds; the other residues had multiple components and were highly polar. The radiolabel in the fibre was incorporated into cellulose.

Environmental fate

Soil

The losses of spinosad by volatilization from soil and foliar surfaces were too small to be observed at 20 °C in a wind tunnel with air flowing at 1–1.5 m/s.

When [^{14}C]spinosyn A and [^{14}C]spinosyn D on a soil surface were exposed to sunlight in August–September at 39.8° N, the initial disappearance half-lives were 17 and 7 days, respectively. Subsequent disappearance was slow (estimated half-lives > 100 days), indicating that the residues had become absorbed into the soil particles and unavailable for exposure to UV radiation. Spinosyns B and B of D were identified as photoproducts. In another study, spinosyn B was shown to be the primary photoproduct of spinosyn A. Spinosyns A and B disappeared with a half-life of about 20 days. Other photoproducts were characterized as parent compound with a hydroxyl attached to the macrolide ring and an *N*-demethyl derivative, also hydroxylated on the macrolide ring.

Spinosyns A and D were quite persistent under aerobic soil conditions at 20 °C in the dark, with estimated half-lives of 40–75 days and 65–85 days, respectively, in four different soils. Spinosyn B and spinosyn B of D were the main degradation products and were more persistent than the parent compounds, with concentrations exceeding those of the parents after 56 days. The amount of mineralization of spinosyn A ranged from 5.8% within 1 year in a sandy silt to 26% within 6 months in a sandy loam, while that of spinosyn D ranged from 4.8% to 25% within 8 months. In another study of aerobic soil degradation, additional products of spinosyn A were characterized as a hydroxy-spinosyn A and a hydroxy-spinosyn B.

In a series of studies of soil adsorption and desorption, spinosyn A and its metabolite spinosyn B were rated as unlikely to leach in most agricultural soils.

The leaching behaviour of fresh, microbially aged and photolytically aged [^{14}C]spinosyn A and [^{14}C]spinosyn D in soil columns was tested on a loamy sand. The fresh residues were not leached at all. Some products of ageing were leached down the column and into the leachate. The compounds could not be fully identified but were substantially modified from the starting spinosyns.

In a study of confined rotational crops, lettuce, radish and wheat seed were sown into a soil that had been treated 30, 120 and 365 days previously with [^{14}C]spinosyn A at 1.1 kg ai/ha. Radiolabel was present in lettuce leaf, radish root and leaf and wheat forage from crops grown to

maturity. No spinosyns or closely related metabolites were identified in the crops. At least some of the radiolabel had been incorporated into natural compounds.

Spinosyn A residues disappeared very quickly (> 70% within 1 day) in field studies of dissipation on a silty clay and a sandy loam. Three metabolites were formed at low concentrations, which declined within 2 months to undetectable levels. Very little of the residue penetrated below the top 15 cm. The mineralization half-life was about 7 months at both sites.

Water–sediment systems

In a study of photolysis, [^{14}C]spinosyn A and [^{14}C]spinosyn D dissolved in sterile pH 7 buffers at 2 mg/l in borosilicate glass tubes were subjected to natural sunlight at 39.9° N in summer. The disappearance half-lives for spinosyns A and D were 22.3 and 19.7 h of sunlight, respectively. The photoproducts were characterized as parent compounds with changes such as saturation of a double-bond and addition of a water molecule. The disappearance half-life for spinosyns A and D in pond water was 4.3 h. The photodegradates were identified as spinosyn B and spinosyn B of D.

In a study of anaerobic sediment water, [^{14}C]spinosyn A and [^{14}C]spinosyn D rapidly became attached to the sediment and were relatively persistent (50% decrease within 6 months). Little mineralization occurred (< 2% within 1 year). The main metabolites were spinosyn B (from A) and spinosyn B of D (from D).

Spinosad in the form of a diluted suspension concentrate formulation was applied to the surface of an aquatic microcosm (1200-l open tank) at a nominal rate of 0.10 kg ai/ha. The concentrations of residues declined rapidly in the water, with a half-life of 1–2 days. Small amounts of spinosyn A reached the sediment, generally accounting for only about 10–15% of that applied. The results suggest that spinosad dissipates principally by degradation (photolysis) and then by adsorption to the sediment.

Methods of analysis

Methods for the analysis of residues of the spinosyns fall into two main categories: HPLC and immunoassay. The methods have been extensively validated on a wide range of substrates.

The HPLC methods, after an extraction specific to the matrix, follow a reasonably standard clean-up, with determination based on UV or MS detection. These methods allow measurement of the individual spinosyns and provide data on spinosyns A, D, K, B and B of D in residue trials. Spinosyn A usually contributes most of the residue, and some HPLC methods are designed to concentrate on spinosyns A and D. The LOQ for most substrates was 0.01 mg/kg.

Immunoassay methods, again after an extraction designed for the matrix, may or may not require clean-up before the final colorimetric determination. The method is specific and represents the sum of the spinosyns and their metabolites. When the HPLC and immunoassay methods were tested side-by-side, the agreement was usually good. The method is based on a commercially available test kit in which the antibody is sensitive to several spinosyns. A portion of a cleaned-up sample extract is incubated with enzyme-conjugated spinosad and magnetic particles coated with antibodies specific to spinosad. The spinosad in the sample and enzyme-conjugated spinosad compete for antibody sites on the magnetic particles. When a magnetic field is applied to the particles at the end of the incubation period, the spinosad and enzyme-conjugated spinosad bound to antibodies on the particles are held in the sample tube by the magnetic field, while the unbound reagents are decanted. A coloured product, produced by incubating the antibody-bound enzyme conjugate with hydrogen peroxide and 3,3′,5,5′-tetramethylbenzidine, is measured by its absorbance at 450 nm. The assay is sensitive to spinosyn analogues with little or no modification to the trimethylpyranosyl ring, but it is relatively insensitive

to analogues or degradates in which the trimethylpyranosyl ring has been modified or is missing. The LOQ for most substrates was 0.01 mg/kg.

Stability of residues in stored analytical samples

Stability in freezer storage was tested for a range of representative substrates. Residues of spinosyns A, D, K, B and B of D were generally stable for the intervals tested:

18 months: grapes, peppers, strawberries, wine (estimated 30% decrease in spinosyn D residues in wine within 12 months)

12 months: tomatoes, cabbage, cotton seed, potato, maize grain, sweet corn forage, sweet corn stover

6 months: apples, almond kernels, almond hulls, celery, spinach; incurred residues in liver, kidney, muscle and fat.

5 months: milk

3 months: apple juice

Definition of the residue

Spinosad is a mixture of spinosyn A and spinosyn D. After it has been applied to crops, the closely related compounds spinosyn B, spinosyn K and spinosyn B of D are formed, principally by photolysis. HPLC methods can be used to measure all these compounds separately, whereas immunoassay allows measurement of these spinosyns and also some other metabolites. Spinosyn A constitutes approximately 85% of the residue initially and in practice represents most of the spinosyn residue; in 482 of 624 (77%) measurements in the residue trials, spinosyn A constituted ≥ 70% of the measured residue. Spinosyn A and spinosyn D together generally constitute more than 90% of the total spinosyn residue.

Spinosyns A and D were major identifiable components of the residue in fat, muscle, kidney, liver and milk of goats dosed orally or treated dermally with spinosyns A and D.

In some trials the residue was measured by the immunoassay method; the residue so measured may be considered sufficiently close to the sum of spinosyn A and spinosyn D for the purpose of estimating maximum residues levels or dietary intake.

The log P_{ow} of 4 and 4.5 (pH 7) and the studies of animal metabolism indicate that spinosyns A and D should be described as soluble in body fat. However, spinosad residues are incompletely partitioned into the fat of milk. In the study with direct treatment of dairy cows, the ratio of residue in cream to that in milk was 4.2 (mean of 119 observations). In the feeding study in dairy cows, the concentrations of residue in cream were three to five times those in milk.

The Meeting recommended that spinosad be described as fat-soluble for the purposes of residues in meat but not for residues in milk.

The Meeting was aware that national governments had already adopted the sum of spinosyn A and spinosyn D as the residue definition for spinosad.

The Meeting recommended that the residue definition for compliance with MRLs and for estimation of dietary intake be the sum of spinosyn A and spinosyn D.

The proposed definition of the residue for compliance with MRLs and for estimation of dietary intake is the sum of spinosyn A and spinosyn D. The residue is fat-soluble, but residues in milk should be measured in whole milk.

Results of supervised trials

The results of supervised trials were available for use of spinosad on almonds, apples, blueberries, Brassica vegetables, celery, citrus, cotton, cucurbits, egg plant, grapes, Japanese radish, kiwifruit, leafy vegetables, legume vegetables, lettuce, maize, navy beans, peppers, potatoes, sorghum, soya beans, stone fruit, strawberries, sweet corn, tomatoes and wheat. No relevant GAP was available to evaluate the data for blueberries, egg plant, grapes, navy beans and strawberries, and only those trials with relevant GAP are discussed below.

The residue definition for spinosad requires addition of residues of spinosyns A and D. In this calculation, when the concentration of residue of spinosyn D was below the LOQ, it was assumed to be zero, except when the concentrations of residues of both spinosyns A and D were below the LOQ. In that case, the total was taken as below the LOQ, which is a reasonable assumption because the concentration of spinosyn D is usually much lower than that of spinosyn A. For example:

Spinosyn A	Spinosyn D	Sum of spinosyns A and D
0.59	0.082	0.67
0.052	< 0.01	0.052
< 0.01	< 0.01	< 0.01

When residues had been measured in a sample by both HPLC and immunoassay, the results from the HPLC method were preferentially chosen for evaluation.

Citrus

Spinosad is registered in the USA for use on citrus fruits at 0.18 kg ai/ha with a PHI of 1 day. The concentrations of residues resulting from trials in the USA in 1996 that met those conditions were grapefruit, 0.013, 0.021, 0.03, 0.061, 0.086 and 0.19 mg/kg; lemon, 0.021, 0.037, 0.056 and 0.14 mg/kg; and oranges, 0.01, 0.017, 0.031, 0.044, 0.046, 0.053, 0.053, 0.07, 0.11, 0.13, 0.14, 0.14 and 0.15 mg/kg. The residues in the three fruits appeared to be from the same population and were therefore evaluated together. The concentrations of spinosad residues in citrus in 23 trials that matched GAP in the USA, in ranked order (median underlined), were 0.01, 0.013, 0.017, 0.021, 0.021, 0.03, 0.031, 0.037, 0.044, 0.046, 0.053 (2), 0.056, 0.061, 0.07, 0.086, 0.11, 0.13, 0.14 (3), 0.15 and 0.19 mg/kg.

The Meeting estimated a maximum residue level of 0.3 mg/kg and an STMR value of 0.053 mg/kg for spinosad in citrus whole fruit.

Six samples of orange from the trials were peeled, and residues were measured in the peeled oranges. In five of the peeled oranges, the concentrations of residues were < 0.01 mg/kg (0.017, 0.031, 0.046, 0.053 and 0.20 mg/kg in the whole oranges). In one peeled orange (0.14 mg/kg in the whole orange), the concentration was 0.01 mg/kg, and this finding was taken as evidence that the concentrations in the edible portion were usually below the LOQ but occasionally reached 0.01 mg/kg.

The Meeting estimated an STMR value for spinosad in citrus edible portion of 0.01 mg/kg.

Apple

In Japan, spinosad is registered for use on apple at a spray concentration of 0.01 kg ai/hl and harvesting 3 days after the final application. In two trials in Japan that matched GAP, the concentrations of residues of spinosyn A were 0.03 and 0.17 mg/kg.

GAP in the USA permits application of spinosad at 0.18 kg ai/ha on apples with a PHI of 7 days. The concentrations of spinosad residues, in ranked order, in apples from 32 trials that matched GAP were < 0.01 (8), 0.01 (4), 0.014, 0.015 (2), 0.016, 0.017, 0.020, 0.024 (3), 0.025, 0.028, 0.032, 0.033 (2), 0.036, 0.041 (2), 0.045, 0.078 and 0.080 mg/kg.

The results of the Japanese trials were not included in the evaluation because they probably did not represent the same population as those from the USA. The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR value of 0.0165 mg/kg for spinosad in apples.

Stone fruits

The results of trials in Japan on peach could not be evaluated because the results were for peel and flesh rather than fruit. Trials on nectarine in Chile could not be evaluated because the conditions did not match GAP.

GAP in the USA permits application of spinosad at 0.14 kg ai/ha with harvesting 7 days after the final application for cherries, plums and prunes or 14 days for peach, nectarine and apricot. The concentrations of residues, in ranked order, from eight trials on cherry that met GAP in the USA were <0.02, 0.023, 0.03, 0.04, 0.06, 0.083 and 0.11 (2) mg/kg; those in seven trials on peach were < 0.02 (3), 0.03, 0.05 and 0.055 (2) mg/kg; and those in five trials on plum were < 0.02 (5) mg/kg.

The Meeting agreed that cherries, peaches and plums represent the stone fruit group and that cherries and peaches would usually have the highest concentrations of residues in the group. Therefore, a maximum residue level could be recommended for stone fruit. The concentrations in ranked order in the 20 trials (median underlined) were < 0.02 (9), 0.023, 0.03 (2), 0.04, 0.05, 0.055 (2), 0.06, 0.083 and 0.11 (2) mg/kg. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR value of 0.0265 mg/kg for spinosad in stone fruits.

Kiwifruit

GAP in New Zealand permits application of spinosad at a spray concentration of 0.0048 kg ai/hl and harvesting 120 days after the final application on kiwifruit. In seven trials in New Zealand in 1998–99 which matched the application rate and with PHIs of 118–142 days, the concentrations of spinosad residues, in ranked order, were < 0.01 (3) 0.02 (2) and < 0.05 (2) mg/kg.

The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR value of 0.02 mg/kg for spinosad in kiwifruit.

Brassica vegetables

Spinosad is registered in Australia for use on broccoli, cauliflower, cabbage and Brussels sprouts at 0.096 kg ai/ha with a PHI of 3 days. In trials in Australia that matched GAP conditions, the concentrations of spinosad residues were 0.06, 0.08 and 0.39 mg/kg in broccoli; 0.02 mg/kg in cauliflower; < 0.01 mg/kg in cabbage; and 0.02 and 0.03 mg/kg in Brussels sprouts.

Spinosad is registered in New Zealand for use on Brassica vegetables at 0.048 kg ai/ha with a PHI of 3 days. In trials in New Zealand that matched GAP, the concentrations were 0.02 mg/kg in cauliflower and < 0.01 mg/kg in cabbage.

Spinosad is registered in Japan for use on cabbage at a spray concentration of 0.01 kg ai/hl and a PHI of 3 days. In trials in Japan that matched GAP conditions, the concentrations of spinosad residues in cabbage were < 0.01 and 0.01 mg/kg.

In the USA, spinosad is registered for use on cole crops at 0.18 kg ai/ha with a 1-day PHI. In trials in the USA that matched GAP (0.15 kg ai/ha is sufficiently close to 0.18 kg ai/ha) for cole crops, the concentrations of spinosad residues were 0.12, 0.16, 0.19, 0.35, 0.36, 0.39, 0.44 and 0.53 mg/kg in broccoli and 0.01, 0.02, 0.053, 0.080, 0.088, 0.37, 0.95 and 1.1 mg/kg in cabbage.

The data from the USA appeared to represent a different population from those from Australia, Japan and New Zealand. The Meeting agreed that the data from the USA for cabbage and broccoli represented the same population and could be combined for Brassica vegetables. The concentrations of spinosad residues in Brassica vegetables from the 16 trials in the USA, in ranked order, were 0.01, 0.02, 0.053, 0.080, 0.088, 0.12, 0.16, 0.19, 0.35, 0.36, 0.37, 0.39, 0.44, 0.53, 0.95 and 1.1 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR value of 0.27 mg/kg for spinosad in Brassica vegetables.

Cucurbits

Spinosad is registered in the USA for use on cucumbers at 0.14 kg ai/ha with a 1-day PHI. In six trials that matched GAP, the concentrations of spinosad residues in cucumbers, in ranked order, were 0.01, 0.024, 0.046, 0.052, 0.053 and 0.059 mg/kg.

Spinosad is registered in the USA for use on cucurbit vegetables other than cucumbers at 0.14 kg ai/ha with a 3-day PHI. In six trials in the USA that matched GAP, the concentrations of spinosad residues in musk melons, in ranked order, were 0.036, 0.045, 0.054, 0.092, 0.12 and 0.16 mg/kg. In three trials in the USA that matched GAP, the concentrations of spinosad residues in summer squash were < 0.01, 0.024 and 0.038 mg/kg.

The Meeting agreed to pool the data to support an MRL for cucurbit vegetables, as follows (ranked order): < 0.01, 0.01, 0.024 (2), 0.036, 0.038, 0.045, 0.046, 0.052, 0.053, 0.054, 0.059, 0.092, 0.12 and 0.16 mg/kg. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR value of 0.046 mg/kg for spinosad in cucurbit vegetables.

Tomato

In Argentina, spinosad is registered for use on tomato at 0.11 kg ai/ha with harvesting permitted 3 days after the final application. In six trials in Argentina that matched GAP conditions, the concentrations of spinosad residues were 0.01, 0.02, 0.06 (2), 0.17 and 0.21 mg/kg.

In Australia, spinosad is registered for use on tomato at 0.096 kg ai/ha with harvesting permitted 1 day after the final application. In five trials in Australia that matched GAP conditions, the concentrations of spinosad residues were 0.02, 0.03 (3) and 0.04 mg/kg. In a trial in New Zealand that matched Australian GAP, the concentration of spinosad residues was 0.04 mg/kg.

GAP in New Zealand for use of spinosad on tomato requires a 3-day PHI after application at 0.048 kg ai/ha. The concentration of spinosad residues in a trial that matched GAP in New Zealand was < 0.01 mg/kg.

Spinosad is registered in the USA for use on fruiting vegetables, including tomato, at 0.18 kg ai/ha with harvesting permitted 1 day after the final application. The concentrations of spinosad residues in 18 trials that matched GAP (0.15 kg ai/ha is sufficiently close to 0.18 kg ai/ha), in ranked order, were < 0.01 (2), 0.013, 0.02 (3), 0.023, 0.024, 0.026, 0.03 (3), 0.04 (2), 0.062, 0.086 and 0.11 (2) mg/kg.

As the data on tomato appeared to represent the same population, except for that from New Zealand where the GAP application rate was lower, they may be combined for evaluation. The concentrations of spinosad residues in tomatoes in the 30 trials, in ranked order, were < 0.01 (2), 0.01, 0.013, 0.02 (5), 0.023, 0.024, 0.026, 0.03 (6), 0.04 (4), 0.06 (2), 0.062, 0.086, 0.11(2), 0.17 and 0.21 mg/kg. The Meeting estimated a maximum residue level of 0.3 mg/kg and an STMR value of 0.03 mg/kg for spinosad in tomato.

Peppers

In Australia, spinosad is registered for use on peppers at 0.096 kg ai/ha with harvesting permitted 1 day after the final application. In two trials in Australia that matched GAP conditions, the concentrations of spinosad residues on sweet peppers were 0.04 and 0.12 mg/kg.

Spinosad is registered in the USA for use on fruiting vegetables, including peppers, at 0.18 kg ai/ha with harvesting permitted 1 day after the final application. The concentrations of spinosad residues in eight trials that matched GAP (0.15 kg ai/ha is sufficiently close to 0.18 kg ai/ha) in hot and sweet peppers, in ranked order, were 0.02, 0.03, 0.05 (2), 0.062, 0.073, 0.14 and 0.17 mg/kg.

The Meeting agreed to combine the data on peppers from Australia and the USA, as follows: 0.02, 0.03, 0.04, 0.05 (2) 0.062, 0.073, 0.12, 0.14 and 0.17 mg/kg. The Meeting estimated a maximum residue level of 0.3 mg/kg and an STMR value of 0.056 mg/kg for spinosad in peppers.

Sweet corn

In the USA, spinosad is registered for use on sweet corn at 0.11 kg ai/ha with harvesting permitted 1 day after the final application. In nine trials in USA that matched GAP conditions, the concentrations of spinosad residues on sweet corn were below the LOQ (0.01 mg/kg). The Meeting estimated a maximum residue level of 0.01* and an STMR value of 0.01 mg/kg for spinosad in sweet corn.

Leafy vegetables

In the USA, spinosad is registered for use on cole crops, including mustard greens, at 0.18 kg ai/ha with a 1-day PHI. In trials in the USA that matched GAP (0.15 kg ai/ha is sufficiently close to 0.18 kg ai/ha) for cole crops, the concentrations of spinosad residues in mustard greens were 0.040, 1.0, 3.5, 4.0, 5.0, 5.5, 5.6 and 5.7 mg/kg.

Australian GAP permits an application rate of 0.096 kg ai/ha and a 3-day PHI for the use of spinosad on lettuce. In three trials in Australia that matched GAP conditions, the concentrations of spinosad residues in head lettuce were 0.21, 1.1 and 1.7 mg/kg.

Spinosad is registered in Australia for use on Chinese cabbage at 0.096 kg ai/ha with a PHI of 3 days. In a trial in Australia that matched GAP conditions, the concentration of spinosad residues in Chinese cabbage was 0.10 mg/kg.

Spinosad is registered in Japan for use on Chinese cabbage at a spray concentration of 0.01 kg ai/hl with a PHI of 3 days. In trials in Japan that matched GAP conditions, the concentration of spinosad residues in Chinese cabbage was 0.09 (2) mg/kg.

In the USA, spinosad is registered for use on leafy vegetables at 0.18 kg ai/ha with a 1-day PHI. In trials in the USA that matched GAP conditions (0.15 kg ai/ha is sufficiently close to 0.18 kg ai/ha), the concentrations of spinosad residues were 0.052, 0.11, 0.12, 0.67, 0.73, 0.77, 0.85, 0.93 and

2.0 mg/kg in head lettuce; 1.4, 1.9, 2.0, 4.7, 4.9 and 5.2 mg/kg in leaf lettuce; and 1.5, 1.9, 2.4, 2.8, 2.9, 3.0, 4.0, 4.4 and 4.5 mg/kg in spinach.

The range of residue concentrations was quite wide, but there was overlap among the different crops. The Meeting decided to pool the data to support an MRL for leafy vegetables, as follows (ranked order): 0.040, 0.052, 0.090 (2), 0.10, 0.11, 0.12, 0.21, 0.67, 0.73, 0.77, 0.85, 0.93, 1.0, 1.1, 1.4, 1.5, 1.7, 1.9 (2), 2.0 (2), 2.4, 2.8, 2.9, 3.0, 3.5, 4.0 (2), 4.4, 4.5, 4.7, 4.9, 5.0, 5.2, 5.5, 5.6 and 5.7 mg/kg. The Meeting estimated a maximum residue level of 10 mg/kg and an STMR value of 1.9 mg/kg for spinosad in leafy vegetables.

Celery

In the USA, spinosad is registered for use on leafy vegetables, including celery, at 0.18 kg ai/ha with a 1-day PHI. In trials in the USA that matched GAP (0.15 kg ai/ha is sufficiently close to 0.18 kg ai/ha), the concentrations of spinosad residues in celery were 0.40, 0.45, 0.84, 1.1, 1.3 and 1.7 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR value of 0.97 mg/kg for spinosad in celery.

Legume vegetables

Spinosad is registered in the USA for use on succulent beans at 0.11 kg ai/ha with harvesting permitted 3 days after the final application. In 11 trials that matched GAP, the concentrations of spinosad residues in snap beans seed and pod, in ranked order, were < 0.01 (2), 0.02 (3), 0.042, 0.077, 0.085, 0.14, 0.15 and 0.20 mg/kg. In seven trials that matched GAP, the concentrations of spinosad residues in snow peas seed and pod, in ranked order, were < 0.01, 0.01, 0.03, 0.039, 0.063, 0.20 and 0.21 mg/kg.

The Meeting agreed to pool the data for snap beans and snow peas to estimate an MRL for legume vegetables. The concentrations of residues, in ranked order, were < 0.01 (3), 0.01, 0.02 (3), 0.03, 0.039, 0.042, 0.063, 0.077, 0.085, 0.14, 0.15, 0.20 (2) and 0.21 mg/kg. The Meeting estimated a maximum residue level of 0.3 mg/kg and an STMR value of 0.041 mg/kg for spinosad in legume vegetables.

Soya bean (dry)

Spinosad is registered in Brazil for use on soya beans with application at 0.024 kg ai/ha and a 9-day PHI. In two trials in Brazil with a 9-day PHI but with application at 0.048 kg ai/ha, the concentration of spinosad residues was below the LOQ (0.01 mg/kg).

Spinosad is registered in the USA for use on soya beans at 0.070 kg ai/ha with harvesting permitted 28 days after the final application. The concentrations of spinosad residues were below the LOQ (0.01 mg/kg) in seven trials in which the application rate was 0.38 kg ai/ha and the PHI was 28 days.

The Meeting agreed that the residue in soya beans is effectively zero because application rates higher than that of GAP did not produce concentrations of residues exceeding the LOQ. The Meeting estimated a maximum residue level of 0.01* mg/kg and an STMR value of 0 mg/kg for spinosad in soya bean (dry).

Potato

In Brazil, spinosad is registered for use on potato at 0.20 kg ai/ha with harvesting permitted 3 days after the final application. In two trials that matched GAP and two trials at 0.40 kg ai/ha, the concentrations of spinosyn A residues were below the LOQ (0.01 mg/kg).

Spinosad is registered in the USA for use on tuber vegetables including potatoes at 0.11 kg ai/ha with harvesting permitted 7 days after the final application. In 14 trials that matched GAP, the concentrations of spinosad residues were below the LOQ (0.005 mg/kg). In two trials with an application rate of 0.62 kg ai/ha and harvesting 7 and 8 days after the third treatment, the concentrations of residues were also below the LOQ (0.005 mg/kg).

The Meeting agreed that, because higher application rates did not result in measurable residues, the concentration in potatoes was effectively zero. The practical LOQ for enforcement purposes is 0.01 mg/kg. The Meeting estimated a maximum residue level of 0.01* mg/kg and an STMR value of 0 mg/kg for spinosad in potato.

Radish, Japanese

GAP in Japan permits three spray applications of spinosad at a concentration of 0.01 kg ai/hl with harvesting 7 days after the final application. In two trials in which the conditions matched GAP, the concentrations of spinosad residues were < 0.01 and 0.01 mg/kg in Japanese radish roots and 0.07 and 0.23 mg/kg in the leaves.

The Meeting noted that the concentrations in the leaves would be included in the recommendations for leafy vegetables. Only two trials were available, and, even though Japanese radish is a minor crop, the Meeting agreed that the number of trials was insufficient to make a recommendation.

Cereals

Spinosad is registered in Brazil for use on maize at an application rate of 0.048 kg ai/ha and a 7-day PHI. In eight trials in Brazil, all with a 7-day PHI but with application rates of 0.048 kg ai/ha (two trials), 0.060 kg ai/ha (two trials), 0.096 kg ai/ha (two trials) and 0.12 kg ai/ha (two trials), the concentrations of spinosad residues were all below the LOQ (0.01 mg/kg).

Spinosad is registered in the USA for use on maize at 0.11 kg ai/ha with harvesting permitted 28 days after the final application. In five trials in which the application rate was 0.50 kg ai/ha and the PHI 27–30 days, the concentrations of residues were all below the LOQ (0.01 mg/kg).

The Meeting agreed that the concentration of residues in maize is effectively zero because rates higher than that in GAP did not produce concentrations exceeding the LOQ. The Meeting estimated a maximum residue level of 0.01* mg/kg and an STMR value of 0 mg/kg for spinosad in maize.

Spinosad is registered in the USA for use on sorghum at 0.11 kg ai/ha with harvesting permitted 7 days after the final application. In eight trials that matched GAP, the concentrations of spinosad residues in sorghum, in ranked order, were 0.03, 0.088, 0.12, 0.16, 0.17, 0.18, 0.47 and 0.68 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR value of 0.165 mg/kg for spinosad in sorghum.

Spinosad is registered in the USA for use on wheat at 0.11 kg ai/ha with harvesting permitted 21 days after the final application. The Meeting was unable to evaluate the trials on wheat in the USA, because spinosad was used at 0.50 kg ai/ha.

Almonds

Spinosad is registered in the USA for use on almonds at 0.18 kg ai/ha with harvesting permitted 14 days after the final application. The concentrations of spinosad residues in almond kernels were below the LOQ (0.01 mg/kg) in 12 trials that were in line with GAP conditions.

The Meeting estimated a maximum residue level of 0.01* mg/kg and an STMR value of 0.01 mg/kg for spinosad in almonds.

Cotton seed

In Australia, spinosad is registered for use on cotton at 0.10 kg ai/ha with harvesting permitted 28 days after the final application. In six trials in Australia that matched GAP conditions, the concentrations of spinosad residues in cotton seed were below the LOQ (0.01 mg/kg). In six trials at higher application rates (two trials at 0.15 kg ai/ha and four trials at 0.20 kg ai/ha) with harvesting 28 days after the final application, the concentrations of residues in cotton seed were all below the LOQ (0.01 mg/kg).

Spinosad is registered in Brazil for use on cotton, with application at 0.072 kg ai/ha and a 7-day PHI. In two trials in Brazil with a 7-day PHI and application rates of 0.072 and 0.14 kg ai/ha, the concentrations of spinosad residues in cotton seed were below the LOQ (0.01 mg/kg).

Spinosad is registered in the USA for use on cotton at 0.10 kg ai/ha with harvesting permitted 28 days after the final application. The concentrations of spinosad residues in cotton seed were below the LOQ (0.01 mg/kg) in 19 trials in which the PHI was 28 days but with various application rates (one trial at 0.10 mg/kg, one at 0.12 kg ai/ha, 14 at 0.125 kg ai/ha, one at 0.14 kg ai/ha and two at 0.20 kg ai/ha).

In summary, the concentrations of spinosad residues in cotton seed were below the LOQ (0.01 mg/kg) in 33 trials on cotton The Meeting noted that, as residues did reach cotton seed in a processing trial with an exaggerated application rate, the concentration could not be considered to be effectively zero.

The Meeting estimated a maximum residue level of 0.01* mg/kg and an STMR value of 0.01 mg/kg for spinosad in cotton seed.

Maize forage and fodder

In the USA, a 7-day PHI is required for use of spinosad on maize (field corn) for maize forage. In 12 trials on sweet corn that matched GAP requirements for maize forage, the concentrations of spinosad residues in sweet corn forage, in ranked order, were 0.12, 0.074, 0.087, 0.098, 0.099, 0.16, 0.17, 0.18, 0.36, 0.44, 0.48 and 0.49 mg/kg (fresh weight) and 0.12, 0.41, 0.49, 0.50, 0.53, 0.67, 0.72, 1.2, 1.3, 2.3, 2.8 and 3.1 mg/kg (dry weight).

The Meeting estimated a maximum residue level of 5 mg/kg and an STMR value of 0.70 mg/kg for spinosad in maize forage.

In the USA, a 28-day PHI is required for use of spinosad on maize (field corn) for maize fodder. In 12 trials on sweet corn that matched GAP requirements for maize fodder, the concentrations of spinosad residues in sweet corn stover, in ranked order, were 0.03, 0.053, 0.074, 0.097, 0.099, 0.11, 0.12, 0.17 (2), 0.23, 0.46 and 0.68 mg/kg (fresh weight) and 0.13, 0.15, 0.21, 0.29, 0.38, 0.41, 0.52, 0.61 (2), 0.81, 0.92 and 2.1 mg/kg (dry weight).

The Meeting estimated a maximum residue level of 5 mg/kg and an STMR value of 0.46 mg/kg for spinosad in maize fodder.

Sorghum forage

In the USA, a 7-day PHI is required for use of spinosad on sorghum for fodder and a 14-day PHI for forage. The concentrations of spinosad residues in sorghum forage in four trials that matched GAP were 0.052, 0.078, 0.095 and 0.18 mg/kg (fresh weight) and 0.18, 0.24, 0.28 and 0.47 mg/kg (dry weight).

The Meeting agreed that the number of supervised trials was insufficient to recommend a maximum residue level.

Wheat forage, hay and straw

In the USA, an application rate of 0.11 kg ai/ha is required for use of spinosad on wheat, with a 21-day PHI required for grain and straw and 14 days for forage and hay. The concentrations of spinosad residues in wheat forage in six trials that matched GAP were < 0.01 (2), 0.01 (2), 0.05 and 0.054 mg/kg (fresh weight) and 0.04, < 0.05 (2), 0.06, 0.22 and 0.23 mg/kg (dry weight). The Meeting noted that the concentration in forage was lower than that in straw and fodder.

The concentrations of spinosad residues in six trials in the USA that matched GAP were < 0.01, 0.019, 0.05, 0.052, 0.15 and 0.17 mg/kg (fresh weight) and < 0.02, 0.03, 0.06, 0.13, 0.21 and 0.27 mg/kg (dry weight) in wheat hay; and < 0.01, 0.19, 0.37, 0.53, 0.56 and 0.73 (fresh weight) and < 0.02, 0.22, 0.41, 0.59, 0.64 and 0.83 mg/kg (dry weight) in wheat straw. The combined data for wheat straw and hay were < 0.02 (2), 0.03, 0.06, 0.13, 0.21, 0.22, 0.27, 0.41, 0.59, 0.64 and 0.83 mg/kg (dry weight).

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR value of 0.215 mg/kg for spinosad in wheat straw and fodder.

Almond hulls

Spinosad is registered in the USA for use on almonds at 0.18 kg ai/ha with harvesting permitted 14 days after the final application. In 12 trials in line with GAP conditions, the concentrations of spinosad residues in almond hulls, in ranked order, were 0.20, 0.27, 0.28, 0.37, 0.45, 0.49, 0.62, 0.67, 0.69, 0.73, 0.82 and 1.1 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR value of 0.56 mg/kg for spinosad in almond hulls.

Fate of residues during processing

The Meeting received information on the fate of incurred residues of spinosad during the processing of apples, oranges, grapes, tomatoes and cotton seed. Processing factors were calculated for commodities derived from these raw agricultural commodities on the basis of the concentrations of residues of spinosyn A or spinosyns A and D measured by HPLC or of spinosad by immunoassay. The results for spinosyn A or the sum of spinosyns A and D were similar, except at low concentrations, where analytical errors and rounding of data influenced the results When the concentration of residues in a processed commodity was below the LOQ, the processing factor was calculated from the LOQ and was prefixed with a 'less than' symbol (<).

The processing factors for apples were 2.1 and 5.2 (mean, 3.9) for processing to wet pomace, < 0.09 and 0.07 (mean, 0.08) to juice and 0.09 to purée. Application of these factors to the STMR value for apples resulted in STMR-P values of 0.064 mg/kg for wet apple pomace, 0.0013 mg/kg for apple juice and 0.0015 mg/kg for apple purée.

The processing factors for oranges were < 0.13 to juice and 2.2 to dried pulp. Application of these factors to the STMR value for citrus whole fruit resulted in STMR-P values of 0.007 mg/kg for orange juice and 0.12 mg/kg for dried processed citrus pulp.

The processing factors for tomatoes to juice were 0.026 and 0.25; as the two values did not agree, the Meeting agreed to choose the higher value. The processing factors for tomatoes to purée were 0.18 and 0.58, and again the higher value was chosen. The processing factor for tomato to paste was 1.94. Application of these factors to the STMR value for tomatoes resulted in STMR-P values of 0.0075 mg/kg for tomato juice, 0.017 mg/kg for tomato purée and 0.059 mg/kg for tomato paste.

Application of the processing factors for cotton seed to hulls (0.20), meal (< 0.17), crude oil (0.18) and refined oil (0.20) to the STMR value for cotton seed resulted in STMR-P values of 0.0020 mg/kg for hulls, 0.0017 mg/kg for meal, 0.0018 mg/kg for crude oil and 0.0020 mg/kg for refined oil.

The Meeting recommended MRLs of 0.01* mg/kg for crude and edible cotton seed oils on the basis of the LOQ of the available analytical method.

Residues in animal commodities

Direct treatment of farm animals

Spinosad is registered for direct use on sheep in Australia, by jetting and wound dressing. The jetting mixture contains 25 mg ai/l and is applied at a rate of 0.5 l per month of wool growth.

In a trial in Australia that matched label instructions, long-wool sheep were treated with a hand-held jetting applicator delivering 5.1 l in a 21-s application time for each sheep. Five animals were slaughtered 5, 12, 15 and 21 days after treatment, and residues were measured in the tissues. The concentrations of spinosad residues were below the LOQ (0.01 mg/kg) in muscle, kidney, liver, back fat and perirenal fat in all samples.

The Meeting estimated a maximum residue level of 0.01* mg/kg for spinosad residues in sheep meat (fat) and sheep offal.

The STMR concept is designed for use in supervised field trials on crops to obtain the typical residue value when a pesticide is used at maximum GAP. The method is not directly applicable to a trial of single direct treatment of animals. However, the Meeting agreed that a typical residue value for a pesticide used directly on animals (at maximum label conditions) would be useful in estimating long-term dietary intake. The Meeting estimated a typical concentration of spinosad residues (from direct use at maximum label conditions) of 0.01 mg/kg in sheep meat and sheep offal.

In the USA, beef and dairy cattle may be treated directly with spinosad in an aqueous suspension formulation as a pour-on. The permitted application rate is 2 mg ai/kg bw, and no restrictions on milk or slaughter intervals are imposed. Animals may also be sprayed (at a concentration of 400 mg/l) at a rate of 0.76 g ai/animal. Spinosad is also approved for treatment of animal housing.

In trials in the USA, groups of Holstein dairy cows underwent five cycles of each of three treatments: (1) body spray with 2 l at 400 mg ai/l every 7 days; (2) body spray with 5 l at 400 mg ai/l every 21 days; or (3) pour-on at 2 mg ai/kg bw every 14 days. The housing was sprayed every 7 days. Residues were measured in milk throughout the study. The animals were slaughtered for tissue collection at intervals after a cycle of treatments. Muscle, kidney, liver and milk were analysed by

immunoassay and fat by HPLC; the values reported are for the sum of spinosyns A, D, B and B of D. The concentrations of residues arising from treatments 1 and 2 were similar, but both were much lower than that from treatment 3. The highest concentrations observed after treatment 3 were 0.28 mg/kg in muscle, 0.87 mg/kg, in kidney, 1.2 mg/kg in liver, 2.7 mg/kg in renal fat, 2.2 mg/kg in subcutaneous fat and 0.65 mg/kg in milk.

The Meeting estimated maximum residue levels of 3 mg/kg for cattle meat (fat), 1 mg/kg for cattle kidney, 2 mg/kg for cattle liver and 1 mg/kg for cattle milk.

As for the sheep treatments, the Meeting agreed that a typical residue value for a pesticide used directly on animals (at maximum label conditions) would be useful in estimating long-term dietary intake. In this case, the median concentration of residues in the tissues of the three animals slaughtered at the shortest interval after treatment (or later if the values were higher later) was taken to represent that typical value. For milk, the highest average concentration for the group on the day after treatment (or later if the values were higher later) was taken to represent the typical value.

The Meeting estimated typical concentrations of spinosad residues (from direct use at maximum label conditions) of 0.078 mg/kg for cattle meat, 0.31 mg/kg for kidney, 0.66 mg/kg for liver and 0.65 mg/kg for milk. These values can be used in the same way as STMR values for estimating long-term dietary intake.

Dietary burden of farm animals

The Meeting estimated the dietary burden of spinosad residues in farm animal on the basis of the diets listed in Appendix IX of the *FAO Manual*. Calculation from MRLs and STMR-P values provides the levels in feed suitable for estimating MRLs for animal commodities, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities. The percentage of dry matter is taken as 100% when MRLs and STMR values are already expressed as dry weight.

The concentrations of spinosad residues in milk reached a plateau after about 6 days, i.e. relatively rapidly. The maximum residue levels in animal commodities were derived from the MRLs, as stated by the 1997 JMPR.

Estimated maximum dietary burden of farm animals

Commodity	Group	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Apple pomace wet	AB	0.064	STMR-P	40	0.16	10			0.016		
Citrus pulp	AB	0.12	STMR-P	91	0.13						
Maize forage	AF	5	MRL	100	5.0	40	50		2.0	2.5	
Maize fodder	AS	5	MRL	100	5.0						
Wheat straw and fodder, dry	AS	1	MRL	100	1.0						

Commodity	Group	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Sorghum	GC	1	MRL	86	1.2	40	40	80	0.47	0.47	0.93
Almond hulls	AM	2	MRL	90	2.2	10	10		0.22	0.22	
Cotton seed hulls		0.0020	STMR-P	90	0.0022						
Cotton seed meal		0.0017	STMR-P	88	0.0019			20			0.0004
					Total	100	100	100	2.7	3.2	0.93

Estimated STMR dietary burden of farm animals

Commodity	Group	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Apple pomace wet	AB	0.064	STMR-P	40	0.16	10			0.016		
Citrus pulp	AB	0.12	STMR-P	91	0.13						
Maize forage	AF	0.70	STMR	100	0.70	40	50		0.28	0.35	
Maize fodder	AS	0.46	STMR	100	0.46						
Wheat straw and fodder, dry	AS	0.215	STMR	100	0.22						
Sorghum	GC	0.165	STMR	86	0.19	40	40	80	0.08	0.08	0.15
Almond hulls	AM	0.56	STMR	90	0.62	10	10		0.062	0.062	
Cotton seed hulls	SO	0.0020	STMR-P	90	0.0022						
Cotton seed meal	SO	0.0017	STMR-P	88	0.0019			20			0.00039
					Total	100	100	100	0.43	0.49	0.15

The dietary burdens of spinosad for estimating MRLs and STMR values for animal commodities (residue concentrations in animal feeds expressed as dry weight) are: 2.7 and 0.43 mg/kg for beef cattle, 3.2 and 0.49 mg/kg for dairy cattle and 0.93 and 0.15 mg/kg for poultry.

Feeding studies

The Meeting received information on the concentrations of residues arising in tissues and milk when dairy cows were dosed with spinosad in capsules at the equivalent of 1, 3 or 10 ppm in the diet for 28 days. The concentrations in fat were higher than those in other tissues. The transfer factors (concentration of residue in tissue ÷ concentration in feed) for tissues and milk were reasonably consistent at the three dietary levels: fat, 0.65, 0.37, 0.57, mean 0.53; muscle, 0.026, 0.018, 0.028, mean 0.024; kidney, 0.073, 0.095, 0.087, mean 0.085; liver, 0.16, 0.16, 0.18, mean 0.17, milk 28 days, 0.044, 0.048, 0.049, mean 0.047; cream 28 days, 0.18, 0.20, 0.19, mean 0.19.

The average concentration in milk (day 14, HPLC analysis) from the three animals at 1 ppm was 0.044 mg/kg, and that in milk from cows at 3 ppm was 0.13 mg/kg. The highest individual concentrations (HPLC analysis) at 3 ppm in the diet were 1.7 mg/kg in fat, 0.069 mg/kg in muscle, 0.44 mg/kg in liver and 0.26 mg/kg. in kidney. The mean concentrations (HPLC analysis) in the three animals at 1 ppm were 0.65 mg/kg in fat, 0.0.020 mg/kg in muscle, 0.13 mg/kg in liver and 0.065 mg/kg in kidney.

The Meeting received information on the concentrations of residues in tissues and eggs after laying hens were dosed with spinosad at the equivalent of 0.1, 0.3, 1 or 5 ppm in the diet for 41 days. At the lower feeding levels, the concentrations of residues were often below the LOQ of the analytical method. The values in fat were substantially higher than those in other tissues and eggs. The concentrations in fat from hens at 5 ppm were 8.7 and 7.0 times higher than those in hens at 1 ppm in abdominal and subcutaneous fat, respectively, slightly more than the five times that was expected. The concentrations of residues in eggs from hens at 5 ppm reached a plateau by day 13, but the values in eggs were generally below the LOQ (0.01 mg/kg) at lower dietary concentrations.

Maximum residue levels

As the maximum dietary burdens of beef and dairy cattle were 2.7 and 3.2 mg/kg, respectively, the concentrations of residues in tissues and milk were taken as those seen at the dietary concentration of 3 ppm, without interpolation. As the STMR dietary burdens (0.43 and 0.49 mg/kg) were lower than the lowest dietary concentration, 1 ppm, the resulting residues in tissues and milk were calculated by applying the transfer factors (concentration of residue in tissue or milk ÷ concentration in feed) found at the lowest dietary concentration to the STMR dietary burdens.

The highest individual tissue concentration of residue at the relevant dietary concentration was used in conjunction with the highest dietary burden of residue to calculate the likely highest residue in animal commodities. The mean concentration of residue in tissues from animals at the relevant dietary concentration was used in conjunction with the STMR dietary burden to estimate the STMR values for animal commodities. For milk, the mean concentration of residue at the plateau for the relevant dietary concentration was used to estimate both the highest residue and the STMR values. As the STMR burden of dairy cows exceeds that of beef cattle, it was used to estimate the STMR value in fat, muscle, liver and kidney.

Feeding level (ppm) *Interpolated* / actual	Residue concentration (mg/kg)								
	Milk (mean)	Fat		Muscle		Liver		Kidney	
		Highest	Mean	Highest	Mean	Highest	Mean	Highest	Mean
MRL beef cattle									
2.7 / 3									
MRL dairy cows	*0.13* /	*1.7* / 1.7		*0.069* /		*0.44* /		*0.26* /	

3.2 / 3	0.13	0.069	0.44	0.26	
STMR beef cattle					
0.43 / 1					
STMR dairy cows	*0.022* /	*0.32* /	*0.010* /	*0.064* /	*0.032* /
0.49 / 1	0.044	0.65	0.020	0.13	0.065

The maximum concentrations of residues expected in tissues are: 1.7 mg/kg in fat, 0.069 mg/kg in muscle, 0.26 mg/kg in kidney, 0.44 mg/kg in liver and 0.13 mg/kg in milk.

The Meeting estimated maximum residue levels of 2 mg/kg for cattle meat (fat), 0.5 mg/kg for cattle kidney, 0.5 mg/kg for cattle liver and 0.2 mg/kg for milk.

The STMR dietary burden for beef and dairy cattle is 0.5 mg/kg (the higher of the two values). As the transfer factors were reasonably consistent across dietary levels, the Meeting agreed that extrapolation below the lowest concentration (1 ppm) was appropriate. The Meeting estimated STMR values of 0.32 mg/kg for cattle fat, 0.010 mg/kg for cattle meat, 0.032 mg/kg for cattle kidney, 0.064 mg/kg for cattle liver and 0.022 mg/kg for cattle milk.

The concentrations of residues arising from direct treatment of animals were higher than those resulting from feed intake. The recommended MRLs are therefore based on the direct treatments. Similarly, the estimates for typical concentrations of spinosad residues (from direct use at maximum label conditions) should be used for estimating long-term intake in place of STMR values derived from the dietary burden of farm animals and animal feeding studies.

As the maximum dietary burden of poultry was 0.93 mg/kg, the concentrations of residues in tissues and eggs can be taken directly from the study in which hens were fed a diet containing 1 ppm, without interpolation, where the highest concentrations of residues were < 0.01 mg/kg in muscle, 0.16 mg/kg in fat, 0.01 mg/kg in liver and 0.01 mg/kg in eggs.

The Meeting estimated maximum residue levels of 0.2 mg/kg for poultry meat (fat) and 0.01 mg/kg for eggs. As the STMR dietary burden for poultry was 0.24 mg/kg, the concentrations of residues in tissues and eggs can be taken directly from the study in which hens were fed a diet containing 0.3 ppm, without interpolation. The Meeting estimated STMR values of 0.01 mg/kg for poultry meat, 0.05 mg/kg for poultry fat, 0.01 mg/kg for poultry liver and 0.01 mg/kg for eggs.

Recommendations

On the basis of the data from supervised trials, the Meeting concluded that the residue concentrations listed below are suitable for establishing MRLs and for assessing the IEDIs.

Definition of the residue (for compliance with MRL and for estimation of dietary intake): sum of spinosyn A and spinosyn D. The residue is fat-soluble, but residues in milk should be measured in whole milk.

Commodity		MRL (mg/kg)	STMR or STMR-P (mg/kg)
CCN	Name		
AM 0660	Almond hulls	2	0.56
TN 0660	Almonds	0.01*	0.01
JF 0226	Apple juice		0.0013
	Apple pomace, wet		0.064

Commodity		MRL (mg/kg)	STMR or STMR-P (mg/kg)
CCN	Name		
	Apple puree		0.0015
FP 0226	Apple	0.1	0.0165
VB 0040	Brassica vegetables, head cabbages, flowerhead Brassicas	2	0.27
MO 1280	Cattle kidney	1 [a]	0.31 [b]
MO 1281	Cattle liver	2 [a]	0.66 [b]
MM 0812	Cattle meat	3 (fat) [a]	0.078 [b]
ML 0812	Cattle milk	1 [a]	0.65
VS 0624	Celery	2	0.97
FC 0001	Citrus fruits	0.3	0.01
AB 0001	Citrus, dried processing pulp		0.12
SO 0691	Cotton seed	0.01*	0.01
	Cotton seed hulls		0.0020
	Cotton seed meal		0.0017
OC 0691	Cotton seed oil, crude	0.01*	0.0018
OR 0691	Cotton seed oil, edible	0.01*	0.0020
PE 0112	Eggs	0.01	0.01
VC 0045	Fruiting vegetables, cucurbits	0.2	0.046
FI 0341	Kiwifruit	0.05	0.02
VL 0053	Leafy vegetables	10	1.9
VP 0060	Legume vegetables	0.3	0.041
GC 0645	Maize	0.01*	0
AS 0645	Maize fodder (dry)	5	0.46
AF 0645	Maize forage (dry)	5	0.70
JF 0004	Orange juice		0.0072
VO 0051	Peppers	0.3	0.056
VR 0589	Potato	0.01*	0
PM 0110	Poultry meat	0.2 (fat)	0.01
MO 0822	Sheep, edible offal of	0.01* [a]	0.01
MM 0822	Sheep meat	0.01* (fat) [a]	0.01
GC 0651	Sorghum	1	0.165
VD 0541	Soya bean (dry)	0.01*	0
FS 0012	Stone fruits	0.2	0.0265
VO 0447	Sweet corn (corn-on-the-cob)	0.01*	0.01
VO 0448	Tomato	0.3	0.03
JF 0448	Tomato juice		0.0075
	Tomato paste		0.059
	Tomato puree		0.017
AS 0654	Wheat straw and fodder, dry	1	0.215

* The MRL is estimated at or about the LOQ.
[a] The MRL accommodates external animal treatment.
[b] Residues from direct animal treatment, not an STMR, but median concentration of residues from animals in a treatment group.

Dietary risk assessment

Chronic intake

The evaluation of spinosad resulted in recommendations for new MRLs and STMR values for raw and processed commodities. Data on consumption were available for 29 food commodities and were used to calculate dietary intake. The results are shown in Annex 3 (Report 2001).

The IEDIs in the five GEMS/Food regional diets, based on estimated STMRs were 2–30% of the ADI (0–0.02 mg/kg bw). The Meeting concluded that long-term intake of residues of spinosad from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The 2001 JMPR concluded that it was unnecessary to establish an acute RfD for spinosad. The Meeting therefore concluded that short-term dietary intake of spinosad residues is unlikely to present a risk to consumers.

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TEBUFENOZIDE (196)

EXPLANATION

Tebufenozide was first evaluated in 1996 for toxicology and residues and was subsequently reviewed to include a proposed MRL for kiwifruit in 1997 while data on grapes and pome fruit were re-evaluated in 1999. The manufacturer requested that tebufenozide be scheduled for evaluation by the 2001 JMPR to consider MRLs for other commodities to accommodate new registered uses in a number of countries.

The present Meeting received information requested by the 1996 JMPR on rotational crops, animal feeding studies, stability in stored samples and residues in raisins. Supervised trials on avocados, bush berries, Brassica vegetables, citrus, rape seed, cranberries, fruiting vegetables other than cucurbits, leafy vegetables, mint, stone fruit (excluding cherries), sugar cane, tree nuts and turnips were also reported as were various analytical methods. Information on current GAP was provided.

METABOLISM AND ENVIRONMENTAL FATE

Tebufenozide and its metabolites in this evaluation are generally designated by codes instead of chemical names (see below).

RH-5992	tebufenozide, *N-tert*-butyl-*N'*-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide
RH-9886	*N-tert*-butyl-*N'*-(4-ethylbenzoyl)-3-hydroxymethyl-5-methylbenzohydrazide
RH-1788	*N-tert*-butyl-*N'*-[4-(1-hydroxyethyl)benzoyl]-3,5-dimethylbenzohydrazide
RH-0282	*N-tert*-butyl-*N'*-[4-(1-hydroxyethyl)benzoyl]-3-hydroxymethyl-5-methylbenzohydrazide
RH-0126	*N-tert*-butyl-*N'*-[4-(1-hydroxyethyl)benzoyl]-3-carboxy-5-methylbenzohydrazide
RH-2703	*N-tert*-butyl-*N'*-(4-carboxymethylbenzoyl)-3,5-dimethylbenzohydrazide
RH-6595	*N-tert*-butyl-*N'*-(4-acetylbenzoyl)-3,5-dimethylbenzohydrazide
RH-9871	*N-tert*-butyl-*N'*-(4-acetylbenzoyl)-3-hydroxymethyl-5-methylbenzohydrazide
RH-2631	*N-tert*-butyl-*N'*-(4-acetylbenzoyl)-3-carboxy-5-methylbenzohydrazide
RH-0875	*N-tert*-butyl-*N'*-(4-ethylbenzoyl)-3,5-dicarboxybenzohydrazide
RH-9841 (RH-5992-olefin)	*N-tert*-butyl-*N'*-(4-vinylbenzoyl)-3,5-dimethylbenzohydrazide
RH-9526	Stearic acid conjugate of RH-9886

Note. The names of RH-0126, RH-2703, RH-2631 and RH-0875 are not strictly according to IUPAC usage, but have been used to show more clearly their relations to the other compounds

Animal metabolism

No additional information was provided.

Plant metabolism

No additional information was provided.

Environmental fate in soil

Residues in rotational crops. In a confined rotational crop study in 1991 in Madera, California, USA (Sharma and Bergin, 1996a) three separate plots were treated with four applications at 14-day intervals to bare ground, at the maximum US label rate of 0.28 kg ai/ha, of [^{14}C]tebufenozide labelled in the ethylphenyl ring (A), the dimethylphenyl ring (B), or the *tert*-butyl group (T). Wheat, collards and turnips were planted back in each plot 30, 90, 250 and 365 days (384 days for turnips) after the last applications. Samples of mature turnips, collards, grain and straw, and immature wheat forage were analysed by combustion to determine the total radioactive residue (TRR). Results with the three labels were comparable, except in wheat grain and straw at 30 days plant-back, in which some A values were higher and some T values lower than those for the B label. The average results are shown in Table 1.

Table 1. Total radioactive residues in rotational crops.

Crop	^{14}C, mg/kg as tebufenozide, mean of A, B and T labels			
	30 DAT	90 DAT	250 DAT	365/384 DAT
Wheat grain	0.4	0.06	0.07	0.07
Wheat straw	7.2	0.4	0.8	0.3
Wheat forage	2.6	0.3	0.1	0.1
Collards	0.1	0.03	0.08	0.006
Turnip top	0.5	0.06	0.08	0.03
Turnip root	0.08	0.007	0.008	0.007

DAT: days between last treatment and plant-back.

Extracts were analysed by a combination of HPLC and TLC. Wheat straw, which contained the highest residues, was analysed at each interval. Since the residues in wheat straw differed only in their magnitude and not the nature of the metabolites, only the 30- and 250-day samples of the remaining crop samples were analysed. Sample were stored for about 4 years before being analysed.

Wheat. Extraction of the residue with methanol and water containing acetic acid recovered 80% from wheat straw and forage and 52% from grain, but became less efficient at later samplings: about 60% from straw and forage and 15% from grain at 250 or 365 days plant-back. The major component in all samples was RH-1788, either as the free alcohol or conjugated with glucose or malonylglucose. In all the straw and in the 30-day plant-back grain samples, the amount of free RH-1788 was almost equal to the conjugated. Residues in forage were almost entirely conjugated, predominantly consisting of the malonylglucose conjugate of RH-1788. Low concentrations (<10%) of other metabolites, which could only be identified in wheat samples at 30 days plant-back, were the ketone RH-6595, the two alcohols RH-9886 and RH-0282 as well as their sugar conjugates, and RH-0126 and 9871. Less than 1% of the parent compound was present and only in 30 days plant-back straw and grain. The residues in 90, 250 and 365-day straw, forage and grain consisted mainly of RH-1788 and its sugar conjugates. The parent compound was not detected in any of these samples. In the 250-day grain samples the extracted residue amounted to only about 0.01 mg/kg. No quantifiable individual residues were detected in the 250-day grain. Residues as percentages of the TRR are shown in Table 2.

Table 2. Percentages of the TRR (mean of 3 labels) in wheat planted as a rotational crop.

Compound	Straw				Forage		Grain	
	DAT 30	DAT 90	DAT 250	DAT 365	DAT 30	DAT 250	DAT 30	DAT 250
Tebufenozide	1.2						1.2	
RH-1788	17	>29	>16	>9	<5	<1	11	
RH-1788-conj	>25	22	23	24	66	46	21	
RH-0282	8.1					<1	<4	
RH-0282-conj	2.0				7.4			
RH-6595	9.2				<5		1.4	
RH-9886	2.7	<6	<12	<6	<5	<1		
RH-9886-conj	<6							
RH-0126	1.4						<4	
RH-9871					<5		2.5	

[>] Metabolite also found in adjacent fraction(s) mainly containing other(s).
[<] Fraction contains other metabolites as well.

Additional extraction of the post-extraction solids from wheat forage and straw was by sequential incubation with the enzymes amylase and pronase, followed by extraction with EDTA, sodium chlorite, 20% KOH and 70% sulfuric acid to release the activity associated with large molecule natural products such as starch, proteins, pectin, lignins, hemicellulose and cellulose. Each step released 1-6% of the TRR from the straw and forage, indicating that the bound residue was either incorporated into natural complex molecules like starch and cellulose or tightly trapped in these natural biopolymers.

Since bound residue levels in grain were high, two samples of solvent-extracted grain were extracted by the sequential treatment with two different enzymes, followed by digestion with acid and base, each of which made 3-13% of the bound residue in the 30-day grain soluble. The extracted activity in each case contained too much substrate to allow any analysis. The remaining radioactivity was incorporated into natural grain constituents like starch and cellulose.

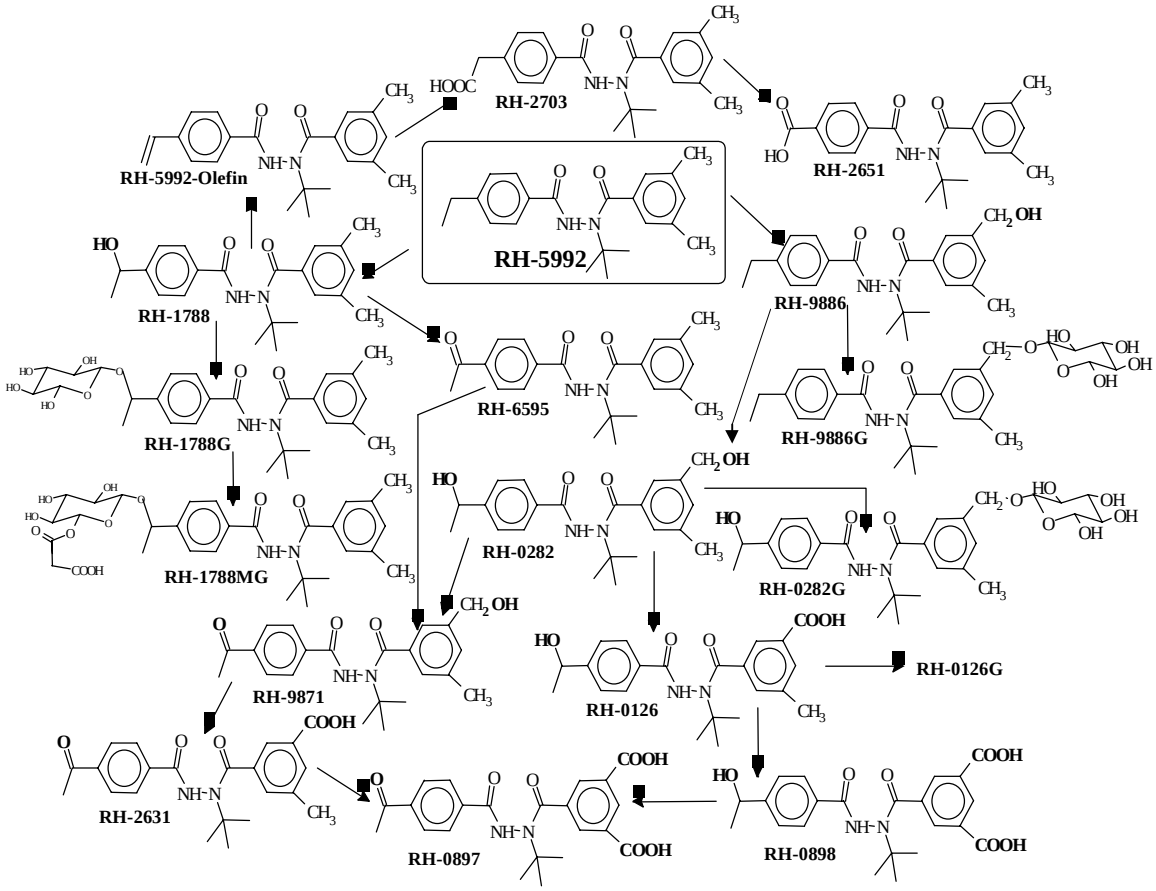
Collards. Residues in the collards planted back at 30 days were about 0.1 mg/kg as tebufenozide, of which 70% was extractable by solvents. The identified residues included the glucose conjugates of RH-1788 as well as small amounts of RH-9886 and 0282; altogether 42% of the TRR. The main individual component was the olefin RH-9841 (15%), in which the ethyl group on the A-ring had been converted into a vinyl substituent. Hydrolysis with cellulase enzyme liberated small quantities of several metabolites such as RH-1788, RH-6595, RH-9886, RH-2631 and RH-0282. The parent compound was undectable. Residues in 250-day collards were low and no single component was detected above 0.01 mg/kg.

Turnips. Residues were about 0.1 mg/kg in roots and 0.5 mg/kg in tops at 30 DAT plant-back, and had decreased to less than 0.01 mg/kg in the roots at the later intervals. In tops 89% and in roots 76% of the residue of 30-day plant-back samples was extractable by organic solvents, and was partitioned into CH_2Cl_2, EtOAc and MeOH before analysis. Low levels of a large number of metabolites were found, which resulted from the oxidation of tebufenozide. About 14% of the residues in both root and tops consisted of the sugar conjugates of RH-1788 that were also found in the wheat samples. The parent compound accounted for 6.7% of the TRR (0.03 mg/kg) in the tops, and was the main compound at 20% of the TRR (0.02 mg/kg) in the roots. RH-1788, RH-6595, RH-0282, RH-9886, RH-2703, RH-0875, RH-2631 and RH-9871 were also identified by a combination of HPLC and TLC and accounted for the remaining residue, each <5% of the TRR.

In summary, the main residues in the wheat samples were RH-1788 and its sugar conjugates. Only the turnip roots had a significant percentage of the residue as tebufenozide. The leafy crop

collards contained mainly sugar conjugates of RH-1788 and tebufenozide-olefin (RH-9841). On the basis of the results of the confined and field rotation studies, the significant residues were identified as tebufenozide, the alcohol metabolite RH-1788, and tebufenozide-olefin (RH-9841). Proposed metabolic pathways are shown in Figure 1.

Figure 1. Metabolic pathways of tebufenozide (RH-5992) in rotational crops.



Note: In the text, RH-5992-olefin is also referred to as RH-9841.

The metabolites found in rotational crops were similar to those identified in the crop metabolism studies reviewed by the 1996 JMPR, except that the parent compound was a minor component or undetectable, and large amounts of sugar conjugates were formed from the alcohol metabolites. Most of the metabolites found in rotational crops were also identified in rats, except the conjugates. In soil, the parent compound and RH-6595 were identified.

Two US field rotational crop studies each consisted of two trials, one in Tulare County, CA and the other in Willacy County, TX. One control and one treated plot were planted with leaf lettuce as a primary crop in each trial. Test plots were sprayed four times with a foliar-ground application of tebufenozide at 0.28 kg ai/ha ± 5%, 234 to 281 l/ha, per application at intervals of 9 to 12 days (Dong, 1998, 1999). The leaf lettuce was removed at maturity and the plots, divided into unequal subplots, were prepared for rotational planting according to normal agronomic practices. Rotational crops were then planted 30 and/or 120 ± 2 days after the last treatment (DAT) as shown in Table 3 below.

Table 3. Tebufenozide field rotation studies.

Both studies		Study A (34P-95-69)		Study B (34P-95-104)
Primary crop	Rotational crop group	30 DAT CA and TX	120 DAT CA and TX	30 DAT CA and TX
Leaf lettuce[1]	Leafy vegetables	Leaf lettuce	Leaf lettuce	Leaf lettuce
	Root crops	Radish	Radish	Radish
	Cereal Grains	Wheat	Wheat/sorghum	Sorghum
	Onion	Bulb onion	Green onion	Green onion
	Fruiting vegetables		Green pepper	Green pepper
	Cucurbits		Squash	Squash
	Legumes		Soya bean[2]	Soya bean

[1] 4 applications at 0.28 kg ai/ha.
[2] The soya beans at the TX site were replanted at 134 DAT.

One sample of each crop from the control plots and two from the treated plots were collected at normal harvest maturity, except forage, cereal grains and legume vegetables which were collected at appropriate growing stages.

The high-moisture samples, leaf lettuce, radish (tops and roots), squash, onions (green and bulb), and green peppers were processed and analysed for residues of tebufenozide and its olefin metabolite RH-9841 - the significant residues found in the confined study on rotational crops by Sharma and Bergin (1996a). Samples were analysed by the preliminary analytical method TR 34-97-91 (Deakyne, 1997) with LC-MS quantification. The LOQ was 0.01 mg/kg, the lower limit of detection (LOD) 0.003 mg/kg, and the sampling-to-analysis interval (SAI) 1-1.6 years (350 to 590 days).

No residues of tebufenozide or RH-9841 above the LOQ were observed in the 30-day plantings of any of these crops (Table 4).

Table 4. Residues in 30-day plant-back high-moisture rotational crops at sites in California and Texas, USA.

Group	Crop	Sample	No. of trials	Tebufenozide	RH-9841
Leafy vegetables	Leaf lettuce	Leaves	4	<LOQ	<LOD
Root crops	Radish	Top and root	4	<LOD	<LOD
Fruiting vegetables	Green bell pepper	Fruit	2	<LOD	<LOD
Cucurbit vegetables	Squash	Fruit	2	<LOD	<LOD
Onion	Green onion Bulb onion	Green onion Bulb onion	2 2	<LOQ <LOD	<LOD <LOD

For tebufenozide and RH-9841 LOQ is 0.01 mg/kg, and LOD 0.003 mg/kg.

Low-moisture crop samples (wheat, sorghum, and soya beans) were analysed for residues of tebufenozide and its alcohol metabolite RH-1788 using the preliminary analytical method TR 34-98-149 (Choo, 1998a) with LC-MS and/or LC-MS-MS quantification that measures residues of tebufenozide and RH-1788 in low-moisture crops with an LOQ of 0.02 mg/kg and an LOD of 0.006 mg/kg. Overall average recoveries from fortified crop samples (n=50) were 88.4% ± 8.1% for tebufenozide, and 79.2% ± 9.4% for RH-1788; the average recoveries at the LOQ level (0.02 mg/kg) at both sites in both studies (n=16) were 92.4% ± 9.7% for tebufenozide and 80.6% ± 11.7% for RH-1788. Samples were stored for 2-2.6 years before analysis (SAI of 718 to 954 days). The results are shown in Table 5.

No residues of tebufenozide above the 0.02 mg/kg LOQ were observed in any wheat, sorghum or soya bean components planted at 30 DAT, and none of RH-1788 above its 0.02 mg/kg LOQ in the grain or seed fractions, but residues of the latter were 0.28 mg/kg, 0.12 mg/kg, and 0.03 mg/kg in wheat straw and hay and soya bean forage respectively.

Table 5. Residues in 30-day plant-back low-moisture rotational crops.

Group	Crop	Sample	Site	No. of samples	Tebufenozide (mg/kg)	RH-1788 (mg/kg)	Total residue[1] (mg/kg)
Cereal Grain	Wheat	Grain	CA	2	<LOD	<LOD	<LOQ
			TX	2	<LOD	<LOD	<LOQ
		Forage	CA	2	<LOD	<LOD	<LOQ
			TX	2	<LOD	<LOD	<LOQ
		Hay	CA	2	<LOD	0.12	0.14
			TX	2	<LOD	0.034	0.053
		Straw	CA	2	<LOQ	0.28	0.30
			TX	2	<LOD	0.062	0.079
	Sorghum	Grain	CA	2	<LOD	<LOD	<LOQ
			TX	2	<LOD	<LOQ	<LOQ
		Forage	CA	2	<LOD	<LOD	<LOQ
			TX	2	<LOD	<LOD	<LOQ
		Hay	CA	2	<LOD	<LOD	<LOQ
			TX	2	<LOD	<LOD	<LOQ
		Straw	CA	2	<LOD	<LOD	<LOQ
			TX	2	<LOD	<LOD	<LOQ
Legume	Soya beans	Grain	TX	2	<LOD	<LOD	<LOQ
		Forage	CA	1	<LOD	0.033	0.052
			TX	2	<LOQ	<LOQ	<LOQ
		Hay	TX	2	<LOD	<LOD	<LOQ

[1] As parent equivalent, LOQ 0.02 mg/kg, LOD 0.006 mg/kg (tebufenozide and RH-1788)

Environmental fate in water/sediment systems

No additional information was provided

METHODS OF RESIDUE ANALYSIS

Analytical methods

Rotational crops. Tebufenozide and its metabolites RH-9841 and RH-1788 can be determined in rotational crops by the enforcement method TR 34-99-10 (Choo, 1999), based on the preliminary methods TR 34-97-91 (Deakyne, 1997) for high-moisture crops, and TR 34-98-149 (Choo, 1998a) for low-moisture crops.

For high-moisture crops such as root and leafy vegetables tebufenozide and RH-9841 are extracted by blending with acidic methanol. Sodium chloride solution is added and the extract is partitioned with hexane to remove oils. Residues are then partitioned into methylene chloride. The methylene chloride layer is evaporated to dryness and the residues are cleaned up on a basic alumina column. A carbon solid-phase extraction tube clean-up is also sometimes used as an optional additional step. For quantification an isocratic HPLC system with a C-18 column is used with negative ion MS detection of the 351 ion for tebufenozide and the sum of the 349 and 385 ions for RH-9841. The average recoveries were 95 ± 10% for tebufenozide and 88±12% for RH-9841, with a demonstrated LOQ of 0.01 mg/kg for both analytes.

For low-moisture rotation crops such as cereal grains tebufenozide and RH-1788 are extracted from the grain by refluxing, and the remaining non-grain fractions by blending or shaking, with acidic methanol. The sample extract is initially purified by the two liquid/liquid partitions described for high-moisture crops, then on a silica column. Soya beans and sorghum grain are cleaned up further by carbon SPE (solid-phase extraction) and non-grain fractions by phenyl SPE. Quantification of the residues is by gradient HPLC on a C-8 column. Negative ion MS detection is used to monitor the 351 ion for tebufenozide and the 367 ion for RH-1788. Average recoveries were 89 ± 10% for tebufenozide and 78 ± 11% for RH-1788, with a demonstrated LOQ of 0.02 mg/kg for both analytes. For confirmation of the residues, MS-MS can be used as an alternative detector, monitoring the 149 daughter ion of both analytes.

Citrus fruit. The method for the determination of tebufenozide in citrus fruits and their processed fractions, TR 34-00-09, is described by Choo (2000). It is derived from the preliminary methods TR 34-96-184 (Meng and Choo, 1996) for citrus and TR 34-97-119 (Choo, 1997) for processed fractions. Residues are extracted from whole fruit, juice and dry pulp by blending with methanol/0.1N HCl (90:10). A salt solution is added to the extract, which is then partitioned with hexane to remove wax, oil and hexane-soluble interferences. Citrus oil samples are partitioned directly with methanol/HCl/hexane. The methanol extract is then diluted with water and partitioned with dichloromethane. The dichloromethane layer is concentrated and further cleaned up successively on carbon and C-18 SPE columns. Analysis of the final extract is by HPLC with UV detection. The LOQ was 0.02 mg/kg, with average recoveries of 98 ± 7.3% for fruit, 98 ± 11% for juice, 90 ± 13% for dry pulp and 92 ± 9.1% for oil. A confirmatory method uses the same extraction and purification procedure with HPLC-MS for quantification of residues in whole fruit, juice and dry pulp and HPLC-MS-MS for oil.

Lettuce. The method TR 34-94-90 for the determination of tebufenozide residues in grapes by GLC (Mellet, 1993), which was evaluated by the 1996 JMPR , was validated for lettuce by Quintelas (2000). The average recovery was 96% ± 6% with an LOQ of 0.02 mg/kg.

Vegetables. The revised enforcement method for the determination of residues of tebufenozide in vegetable crops (TR 34-98-193) described by Chen *et al.* (1998) is similar to 34-93-119 reported by Deakyne (1993) and evaluated by the 1996 JMPR. It includes a new HPLC-MS confirmation of the residues detected and a revised calculation of fortification recoveries. These varied according to the sample but mean recoveries were above 80% from lettuce, cabbage, spinach, mustard greens, broccoli and celery, and overall 85 ± 9%. An LOQ of 0.01 mg/kg has been demonstrated for all samples except celery, which has an LOQ of 0.05 mg/kg. Residues determined by HPLC-UV were confirmed by HPLC-MS.

Sugar cane and its processed fractions. In method TR 34-97-115 (Filchner and Deakyne, 1997) residues of tebufenozide are extracted from stems and stalks, molasses, raw sugar and refined sugar by blending samples with acidic methanol/water (methanol/0.1 N aqueous HCl, 90:10). A salt solution is then added to the extract, which is partially purified by liquid-liquid partition, first with hexane (which is discarded), then with methylene chloride. The methylene chloride layer is concentrated and residues are further purified by carbon SPE followed by chromatography on basic alumina. HPLC on a C-18 column with UV detection is used for quantification. The LOQ was 0.01 mg/kg for all samples with average recoveries of 87 ± 8.4%. Confirmatory analysis is by HPLC-MS, with negative monitoring of the 351 ion.

Pecans. TR 34-96-198 (Cui, 1996) is an updated version of method TR 34-95-20 (Cui and Deakyne, 1994) evaluated by the 1996 JMPR, which describes several necessary precautions in the clean-up procedures. Before the Alumina-B open column clean-up, the extract must be completely dried before reconstitution. In the optional carbon solid-phase extraction the SPE tube must not be allowed to go

dry between the addition of eluents. Finally, the control correction factor was removed from the fortification recovery calculation. The LOQ of 0.01 mg/kg remained unchanged.

Oilseed and process fractions. Method TR 34-96-135 for cotton seed and processed fractions (Wu *et al.*, 1996) was used in supervised trials on rape and the processing studies with rape seed and mint. Residues of tebufenozide are extracted from whole cotton seed and its processed fractions by blending with methanol/0.1N HCl (90:10). A salt solution is added to the extract, which is then partitioned with hexane to remove wax, oil and hexane-soluble interferences. The methanol extract is diluted with water and partitioned with dichloromethane. The dichloromethane layer is concentrated and further cleaned up by chromatography on basic alumina. An additional silica column clean-up step is added for gin trash and a final clean-up by carbon SPE follows. Analysis of the final extract is by HPLC with UV detection. The LOQ was 0.01 mg/kg. Average recoveries were 98 ± 14% for whole cotton seed, 97 ± 11% for meal, 94 ± 11% for hulls, 94 ± 20% for refined oil and 88 ± 16% for gin trash. A confirmatory method uses the same extraction and purification procedure with HPLC-MS for quantification.

Animal commodities. The analytical method TR 34-96-109 (Burnett *et al.*, 1996) described below is based on the preliminary methods TR 34-95-98 for milk (Choo *et al.*, 1996b), TR 34-95-160 for muscle and kidney (Chen *et al.*, 1996), TR 34-95-159 for liver (Filchner *et al.*, 1995), and TR 34-95-161 for fat (Choo *et al.*, 1996a). Method TR 34-96-109 determines tebufenozide in all samples, and its metabolites RH-9886 in muscle and kidney, RH-0282 in milk, muscle and kidney, fatty acid conjugates of RH-9886 in milk and fat, and RH-2703 in liver. RH-9526, the stearic acid conjugate of RH-9886, was used to generate recovery data for the fatty acid conjugates through the method.

Milk samples are blended with methanol containing 10% water and filtered, and the filtrate divided into two equal portions. Residues of RH-9526 (and other fatty acid conjugates of RH-9886) are determined in the first portion after refluxing with hydrochloric acid for 2 hours to effect hydrolysis to the free alcohol. A hexane partition then removes fat contaminants. After adding aqueous sodium chloride, the residues of RH-9886 are partitioned into methylene chloride, which is evaporated to dryness and the residue cleaned up on a carbon SPE column. Residues of tebufenozide and RH-0282 are determined in the second portion of the milk filtrate, which is initially cleaned up by partitioning with hexane. The aqueous extract is then concentrated and the residues partitioned into methylene chloride. The methylene chloride layer is evaporated to dryness and the residue is cleaned up on a basic alumina column. The analytes in the two final extracts are determined by isocratic HPLC with a C-18 column and UV detection. Average recoveries were 84 ± 10% for RH-9526, 88 ± 12% for tebufenozide, and 90 ± 8.4% for RH-0282, with a demonstrated LOQ of 0.01 mg/kg for all three analytes.

Muscle and kidney samples are blended with methanol containing 10% 0.1 N hydrochloric acid and filtered. Sodium chloride solution is added and the extract partitioned with hexane to remove non-polar contaminants. After concentration and addition of additional sodium chloride, the residues are partitioned into methylene chloride. The methylene chloride layer is evaporated to dryness and the residue cleaned up on basic alumina and carbon SPE columns. The analytes in the final extract are determined by isocratic HPLC as before. Average recoveries were 87 ± 12% for tebufenozide, 93 ± 11 % for RH-9886 and 88 ± 11% for RH-0282, with a demonstrated LOQ of 0.02 mg/kg for all three analytes.

+ are homogenized with methanol/0.5 N hydrochloric acid (70:30) and centrifuged. After addition of aqueous sodium chloride solution, residues of tebufenozide and RH-2703 are partitioned into methylene chloride. RH-2703 is then partitioned into aqueous sodium bicarbonate solution. The methylene chloride fraction containing tebufenozide is concentrated to dryness and cleaned up on a basic alumina column. An optional carbon SPE step is also described for samples which require additional clean-up. The sodium bicarbonate fraction is acidified with 1 N hydrochloric acid and the free acid extracted into methylene chloride. This is evaporated to dryness and the residue cleaned up on a silica gel column. Analysis of the two final extracts is by HPLC as before. Average recoveries

were 93 ± 11% for tebufenozide, and 84 ± 11% for RH-2703, with a demonstrated LOQ of 0.02 mg/kg for both analytes.

Fat samples are blended with a mixture of methanol, water and concentrated hydrochloric acid (120:40:15). The mixture is then refluxed for two hours to hydrolyse the fatty acid conjugates of RH-9886 to the free alcohol. After cooling, the extract is filtered and partitioned with hexane to remove non-polar contaminants. The filtrate is treated with sodium chloride solution and residues of tebufenozide and RH-9886 are partitioned into methylene chloride. The methylene chloride fraction is washed with aqueous sodium bicarbonate solution, then concentrated to dryness. The residue is cleaned up on a carbon SPE column and the extract is chromatographed on basic alumina, separating tebufenozide from RH-9886. The eluates containing each analyte are concentrated to dryness and taken up in different mobile phase mixtures of acetonitrile and water. Quantification of the analytes in each final extract is by HPLC as before. Average recoveries were 89 ± 9.8% for tebufenozide and 78 ± 9.1% for RH-9526, with a demonstrated LOQ of 0.02 mg/kg for both analytes.

Confirmatory HPLC methods for all samples used modified mobile phases together with MS detection. In these methods, the negative ions monitored were 351, 367 and 383 for tebufenozide, RH-9886 and RH-0282 respectively. Detection of RH-2703 was by positive ion monitoring of the 383 ion.

Stability of pesticide residues in stored analytical samples

Wheat. Samples from the rotational crop study (Sharma and Bergin, 1996a) were stored for approximately 4 years, and the stability of residues during freezer storage was examined as part of the studycby comparing the TLC profile of a straw sample analysed after two years of storage with that of the same sample after 4 years' storage. The major components in straw were RH-6595, RH-1788 and its glucose conjugate. These represented respectively 14, 26 and 18% of the TRR after 2 years, and 11, 21 and 19% after 4 years.

The composition of the residue in extracts of forage stored for 4 years (which mainly contained the glucose and malonylglucose conjugates of RH-1788) was comparable to that of the same extracts stored for 4 years and 7 months.

Rice straw and grain. The storage stability of tebufenozide and its metabolites RH-1788, RH-6595 and RH-9886 in rice was examined by Sharma and Bergin (1996b). Samples of rice straw and grain from a rice metabolism study initiated in 1989 were analysed for the first time in 1991 i.e. after 2 years of storage (Randazzo, 1992). In 1996, these samples were re-analysed after another 5 years of frozen storage. Subsamples of each field sample were re-extracted and analysed by methods identical to those used in the metabolism study. It was found that tebufenozide was still the main compound, although its proportion of the TRR decreased slightly from 77.9 to 74.8% in rice straw and from 49.5 to 47.5% in rice grain. It was probably mainly converted to RH-9886, which approximately doubled from 1.0 to 1.9% of the TRR in straw and from 1.1 to 2.5% in grain. The proportion of the metabolites RH-1788 and RH-6595 decreased slightly too, in both straw and grain. A small amount of conjugated RH-1788 was identified in 1996 at the same level as in 1991, but then as one of the low level unknown components. The profile remained essentially the same in that by far the main component was tebufenozide, while the proportions of the metabolites were less than 5% each (except RH-1788 in rice grain, which was less than 10%). This stability study does not cover the first two years of storage.

Green onions (RH-9841). A study was conducted by Graves (2000b) to assess the frozen storage stability of RH-9841 in green onions to support the residue data for the rotational crop study (Doug, 1998). Green onion samples spiked with 1.0 mg/kg of RH-9841 on two dates 3 months apart and stored below -10ºC were analysed by the preliminary analytical method for rotational crops TR 34-97-91 (Deakyne, 1997). The sample to analysis intervals (SAIs) for all high-moisture crop samples in

the field rotational crop study (Dong, 1998) ranged from 350 to 590 days (less than 20 months). RH-9841 was stable during 24 months of frozen storage in green onion samples. There was a slight decrease (10%) in the corrected daily recovery over the 24 months of storage.

Citrus oil (Graves, 2000a). Commercial orange oil samples spiked with 1.0 mg/kg of tebufenozidewere stored at about -20ºC. Periodically one control, 2 fresh fortifications, and 3 aged fortifications were analysed by method TR 34-97-119 (Choo, 1997). There was no decrease in the recovery over the 15 months of storage.

Lettuce. 20 g samples of homogenized head lettuce were fortified with tebufenozide at a concentration of 1 mg/kg and stored in a freezer at -15 ± 10°C for 36 months (Choo, 1998b). Samples were analysed before storage and at various intervals by method TR 34-93-119 (Deakyne, 1993). Tebufenozide was found to be stable for the 36 months.

Animal commodities. Control samples of bovine milk, meat, liver and fat were fortified with tebufenozide and its relevant metabolites for each sample at a concentration of 1 mg/kg and stored in a freezer at -15 ± 10°C for 8 months (Choo, 1996). In addition to tebufenozide, milk was fortified with RH-0282 and RH-9526, meat with RH-9886 and RH-0282, liver with RH-2703, and fat with RH-9526. Samples were analysed before storage and then at various intervals by method TR 34-96-109 (Burnett, *et al.*, 1996). No analytes showed any signs of degradation. Residues were stable in the milk, liver, meat and fat samples for a minimum of 192, 203, 182 and 145 days respectively.

Blueberries, raspberries, cranberries, turnip roots and foliage, rape seed and processed fractions, mint and mint oil. Dorschner and Breuninger (1998a-f) conducted stability studies in conjunction with residue trials on these and the results are shown in Table 6. Recoveries are uncorrected for concurrent analytical recoveries, since these were not measured except in cranberries. For comparison, the (general) method recovery at approximately the same fortification level is shown as the 0-day SAI.

Table 6. Stability of residues in frozen storage (Dorschner and Breuninger, 1998).

Crop	Sample	Longest SAI in supervised trials	Fortification (mg/kg)	No.	SAI of sample (days)	Recovery (%)	Ref
Blueberry	fruit	186	1.07	1	0	97.2	1998d
			1.07	3	189	87.3	
Raspberry	fruit	305	0.99	4	0	101.6	1998c
			1.07	3	322	87.5	
Cranberry	fruit	127	2.2	2	0	85.3	1998a
			2.2	2	30	91	
			2.2	1	30 (fresh fort.)	91	
Turnip	roots	259	1.07	4	0	92.7	1998b
			1.07	3	279	89.5	
	tops	244	1.07	4	0	100.4	
			1.07	3	279	84.0	
Rape	seed	231	1.07	4	0	86.3	1998f
			1.07	3	236	77.9	
	meal	68	1.07	3	0	85.8	
			1.07	3	90	80.7	
	oil	68	1.07	3	0	90.7	
			1.02	3	83	83.1	
Mint	foliage	200	1.07	4	0	89.0	1998e
			1.07	3	279	70.2	
	oil	273	1.02	4	0	97.1	
			1.07	3	285	90.6	

USE PATTERN

The Meeting received updated information on the registered uses of tebufenozide. Table 7 shows only the approved GAP for the crops evaluated. Application intervals generally vary between 7 and 21 days.

Table 7. Registered uses of tebufenozide.

Crop	Country	Form	Application					PHI, days	Comments
			Method	Growth stage	Rate kg ai/ha	Spray conc kg ai/hl	Max no.		
Citrus fruits									
	Algeria	SC	high volume	ripening of fruits	0.19	0.019	4	21	
	Italy .	SC	high/low volume			0.017-0.019*	2	14	c2
	Morocco	SC	high volume	ripening of fruits	0.18	0.018	4	45	
	Portugal (.)	SC	high volume airblast	from young growing shoots		0.0144-0.018	2	7	c2
	Tunisia	SC	high volume	ripening of fruits	0.18	0.018	4	21	
	Spain .	SC	high volume			0.0144-0.018	2	14	c1
Stone fruits									
Stone fruits excl. cherries	New Zealand .	WP	high/low volume	from flowering	0.12		4	14	a, c4
Berries and small fruits									
Bush and cane berries (excl. cranberries)	USA	SC	Ground or aerial appl		0.07-0.28			14	a
Cranberries	USA	SC	Ground or aerial appl		0.28			30	a
Grapes	Algeria	SC	high volume	ripening of fruits	0.144	0.0144	3	21	
Grapes	Australia .	WP	high/low volume	from pre-flowering onwards		0.006*		21	a, c3
Grapes	France .	SC	airblast	ripening berries	0.144			21	
Grapes	Germany	SC	high volume	after blossom		0.012		28	c3
Grapes	Italy .	SC	high/low volume	from pre-flowering onwards		0.0144*		30	c3
Grapes	New Zealand .	WP	high/low volume	14-21 days and 1 day pre-bunch closure	0.12	0.006*	2	28	a
Grapes	Portugal (.)	SC	medium /high volume	beginning of ripening	0.144	0.0144*		14	
Grapes	Slovenia	SC	high volume	bunch closing	0.144	0.0144	2	21	
Grapes	Spain .	SC	high/low volume	ripening of fruits	0.144	0.012-0.0144*	4	21	
Grapes	Switzerland .	SC	high volume	after blossom	0.18	0.012	2	none	
Grapes	Tunesia	SC	high volume	ripening of fruits	0.144	0.0144	3		
Assorted tropical and sub-tropical fruits – inedible peel									

Crop	Country	Form	Application					PHI, days	Comments
			Method	Growth stage	Rate kg ai/ha	Spray conc kg ai/hl	Max no.		
Avocado	New Zealand .	WP	high/low volume	from pre-flowering	> 0.12	0.006*	4	21	a, c4
Brassica vegetables									
	Switzerland	SC	high volume			0.012	2	14	
	USA	SC	ground or aerial appl	from young crop/small plants	0.105-0.14			7	b
Cabbage	Slovenia	SC	high volume	directly after hatching	0.043-0.076	0.0096-0.017	1	14	
Fruiting vegetables other than cucurbits									
	USA	SC	ground or aerial appl.	from young crop/small plants	0.105-0.28			7	b, c2
Peppers, tomatoes and egg plant	Belgium .	SC	spraying		0.18	0.018-0.024	2	3	c1
Peppers and tomatoes	Spain .	SC	high volume			0.0144-0.018	3	3	
Tomatoes	Algeria	SC	high volume	ripening of fruits	0.144-0.19	0.0144-0.019	5	21	
Leafy vegetables including leafy brassica									
	USA	SC,	ground or aerial appl	from young crop/small plants	0.105-0.14			7	b
Lettuce, spinach	Switzerland	SC	high volume			0.012		14	
Root and tuber vegetables									
Turnips	USA	SC,	ground or aerial appl	from young crop/small plants	0.105-0.140			7	b
Stalk and stem vegetables									
Celery, celture, rhubarb, cardoon	USA	SC	ground or aerial appl	from young crop/small plants	0.105-0.140			7	b
Grasses for sugar or syup production									
Sugar cane	USA	SC	ground or aerial appl.		0.105-0.28			14	b, c2
Tree Nuts									
Tree nuts excl. pecans	USA	SC	ground or aerial appl		0.28-0.53			14	a, c2
Pecans	USA	SC	ground or aerial appl		0.14-0.28			14	a, c2
Walnuts	France .	SC	airblast	ripening of fruits		0.0144		21	
Walnuts	Spain	SC	high volume	ripening of fruits	0.29	0.0144		21	
Oilseed									
Rape seed (Canola)	USA	UL	ground or aerial appl	from young crop/small plants	0.14-0.28			14	b
Herbs									
Mint	USA	SC	ground or aerial appl.	from young crop/small plants	0.105-0.28			14	c2

. label available

(.) only a translation or summary of label in English available

* concentration for normal (high) volume application. For concentrate (low volume) spraying, adjust dilution rate accordingly (use same rate of product per hectare as in normal volume applications). In Australia do not use at rates greater than 5 times the dilute spraying rate

[1] maximum total application per season is 2.1 kg ai/ha

a) do not graze any treated area, do not feed treated crops to stock.

b) rotational crop restrictions: crops for which use of tebufenozide is registered no restrictions; all other crops 30 days re-cropping interval.

c) interval between applications: c1= 7 days, c2= 10 days, c3= 2 weeks, c4= 3 weeks

d) maximum total application per season 2.1 kg ai/ha

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received residue data from supervised field trials on citrus fruits, stone fruit, berry crops, cranberries, avocado, fruiting vegetables, turnip greens and roots, sugar cane, rape seed (canola) and mint, and supplementary data on residues in grapes, head lettuce, pecans, almonds and macademia nuts. Because of newly approved registered used previously reviewed trials on cabbage, broccoli, head and leaf lettuce, spinach, mustard greens, Chinese kale and celery were re-evaluated. Residues have not been corrected for analytical method recoveries except where indicated. Trials are listed in the following Tables, where residues resulting from trials according to GAP are underlined. All applications were with ground equipment.

Table 8	Oranges	Table 24	Head lettuce
Table 9	Lemons	Table 25	Head lettuce (JMPR 1996)
Table 10	Grapefruit	Table 26	Leaf lettuce (JMPR 1996)
Table 11	Mandarins	Table 27	Spinach (JMPR 1996)
Table 12	Peaches	Table 28	Mustard greens (JMPR 1996)
Table 13	Nectarines	Table 29	Chinese kale (JMPR 1996)
Table 14	Blueberries	Table 30	Turnip greens
Table 15	Raspberries	Table 31	Turnip roots
Table 16	Cranberries	Table 32	Celery (JMPR 1996)
Table 17	Grapes (JMPR 1996)	Table 33	Sugar cane
Table 18	Grapes	Table 34	Pecans (JMPR 1996)
Table 19	Avocado	Table 35	Pecans
Table 20	Cabbage (JMPR 1996)	Table 36	Almonds
Table 21	Broccoli (JMPR 1996)	Table 37	Macadamia nuts
Table 22	Tomatoes	Table 38	Rape
Table 23	Peppers	Table 39	Mint

Citrus fruits

Summer oil or other adjuvant with strong penetrating properties is mixed into the holding tank unless otherwise noted.

Oranges. The available data on whole oranges from Australia, Italy, Spain, and the USA are shown in Table 8. In field trials in Australia from 1994 to 1999 (Arlett, 2000) 2 to 3 applications of a WP formulation at the proposed GAP rate of 0.006 kg ai/hl and at exaggerated rates of 0.012 and 0.024 kg ai/hl were made to the foliage at approximately 14 day intervals (except in trial RTL 446/96, in which the intervals between applications were 45 and 21 days). Residues of tebufenozide were determined according to the method of Holzwarth and Schuld (1993a), modified so that the methylated derivative of tebufenozide was determined by GC-MS rather than GLC with an NPD with an LOQ of 0.02 mg/kg, except in trial DJR/171/00 for which the Agrifood Technology method TP/215/990201 (Bayer) was used (GLC/NPD; LOQ 0.05 mg/kg). The SAI ranged from 2 to 9 months.

In ten trials in Italy and Spain in 1996 and 1997 (Balluff, 1997a, 1999) two foliar applications of an SC formulation of tebufenozide at 0.018 kg ai/hl, which corresponds to approved GAP, were made , with an interval of 13-16 days. In each of the trials, oranges were collected on day 0 and 13 or 14 days after the second application. In addition in 3 of the 5 1996 trials, samples were also taken at days 3 and 7. Day 13/14 samples were peeled as part of the processing. In 1996 the peel, pulp and whole fruit samples were analysed by method TR 34-96-184 (HPLC-UV) (Meng and Choo, 1996) with an LOQ of 0.02 mg/kg for whole fruit and pulp, and 0.04 mg/kg for peel which was subjected to an additional alumina column clean-up. In the 1997 trials, whole fruit, peel and pulp samples were analysed by the GLC method AL 013/92-0 (Schuld and Holzwarth, 1994) with an LOQ of 0.02 mg/kg. The analytical laboratory made slight modifications to the method and used mass spectrometry for detection. Residues in whole fruit were calculated from the residues found in the peel and pulp samples and the weights of each. The SAI was up to 234 days.

In a further eleven field trials in geographically representative areas of the USA (Koals and Carpenter, 2000) 4 foliar applications of a WP formulation of tebufenozide were made at a rate of 0.34 kg ai/ha + 5%. The first was made in the early season, the second in mid-summer and the third and fourth 28 ± 2 and 14 ± 1 days before harvest. In all the trials, duplicate field samples of oranges were collected at maturity. All samples were analysed for tebufenozide by method TR 34-96-184. The LOQ was 0.02 mg/kg. The SAI ranged from 186 to 547 days.

Table 8. Residues of tebufenozide from supervised trials on oranges in Australia, Italy, Spain and the USA.

Country, year, location, variety	Application				PHI, days	Sample	Residue mg/kg	Ref, trial number
	Form	No	kg ai/ha	kg ai/hl				
Australia 1997, Ramco (SA) Washington Navel	WP	3	[3]	0.006	0 1 5 12	fruit fruit fruit fruit	0.42 0.38 0.42 0.42	Arlett, 2000 DJR 136/98[1]
Australia 1997, Leeton (NSW) Navel	WP	3	0.24	0.006	0 1 7 14	fruit fruit fruit fruit	0.35 0.41 0.37 0.42	Arlett, 2000 JES 542/98[1]
Australia 1994, Cobram (Vic) Valencia	WP	3	0.12	0.006	1 8 15 22	fruit fruit fruit fruit	0.20 0.16 0.20 0.20	Arlett, 2000 RTL 446/96 int: 45, 21 [2]
		3	0.24	0.012	1 8 15 22	fruit fruit fruit fruit	0.64 0.47 0.40 0.35	Arlett, 2000 RTL 446/96 int: 45, 21 [2]
		3	0.48	0.024	1 8 15 22	fruit fruit fruit fruit	0.68 0.63 0.62 0.77	Arlett, 2000 RTL 446/96 int: 45, 21[2]
		2	0.12	0.006	1 8 15 22	fruit fruit fruit fruit	0.17 0.17 0.12 0.07	Arlett, 2000 RTL 446/96 int.: 21 days [2]
		2	0.24	0.012	1 8 15 22	fruit fruit fruit fruit	0.18 0.46 0.32 0.36	Arlett, 2000 RTL 446/96 int.: 21 days[2]
Australia, 1999 Loxton North (SA) Valencia	WP	3	[3]	0.006	0 1 7 14	fruit fruit fruit fruit	0.12 0.14 0.15 0.09	Arlett, 2000 DJR 171/00[1]

Country, year, location, variety	Application				PHI, days	Sample	Residue mg/kg	Ref, trial number
	Form	No	kg ai/ha	kg ai/hl				
		3	[3]	0.012	0 1 7 14	fruit fruit fruit fruit	0.43 0.37 0.39 0.28	Arlett, 2000 DJR 171/00[1]
Italy 1996, Fondi Tarocco	SC	2	0.20, 0.21	0.018	0 14	fruit fruit* peel pulp	0.42 <u>0.25</u> 0.79 <u>0.053</u>	Balluff, 1997a 96I019R
Italy 1996, Catania Navelina	SC	2	0.52, 0.52	0.018	0 3 7 14	fruit fruit fruit fruit* peel pulp	0.48 0.24 0.43 <u>0.78</u> 2.69 <u>0.15</u>	Balluff, 1997a 96I020R
Italy 1996, Carlentini Navelina	SC	2	0.49, 0.48	0.018	0 3 7 14	fruit fruit fruit fruit* peel pulp	0.30 0.47 0.54 <u>0.60</u> 2.02 <u>0.11</u>	Balluff, 1997a 96I021R
Spain 1996, Palacios Navelina	SC	2	0.31, 0.30	0.018	0 3 7 14	fruit fruit fruit fruit* peel pulp	0.61 0.27 0.48 <u>0.43</u> 1.28 <u>0.13</u>	Balluff, 1997a 96S004R
Spain 1996, Lliria Navelina	SC	2	0.40, 0.39	0.018	0 14	fruit fruit* peel pulp	0.84 <u>0.39</u> 1.46 <u>0.021</u>	Balluff, 1997a 96S005R
Italy 1997, Catania Navelina	SC	2	0.54, 0.52	0.018	0 14	fruit fruit* peel pulp	0.29 <u>0.21</u> 0.75 <u>0.03</u>	Balluff, 1999 I97049R
Italy 1997, Lentini Navelina	SC	2	0.56, 0.55	0.018	0 14	fruit fruit* peel pulp	0.47 <u>0.56</u> 1.5 <u>0.13</u>	Balluff, 1999 I97050R
Spain 1997, Torrente Navelina	SC	2	0.62, 0.64	0.018	0 13	fruit fruit* peel pulp	0.56 <u>0.38</u> 1.2 <u>0.04</u>	Balluff, 1999 S97016R
Spain 1997, Anahuir Salustiana	SC	2	0.48, 0.47	0.018	0 14	fruit fruit* peel pulp	0.47 <u>0.48</u> 1.8 <u>0.05</u>	Balluff, 1999 S97017R
Spain 1997, Beniel Newhall	SC	2	0.47, 0.46	0.018	0 14	fruit fruit* peel pulp	0.37 <u>0.36</u> 1.1 <u>0.04</u>	Balluff, 1999 S97018R
USA 1995, LaBelle (FL), Hamlin	WP	4	0.34	0.037	7 14 21 28	fruit fruit fruit fruit	0.42, 0.43 mean 0.42 0.41[4], 0.42[5] 0.17, 0.28 mean 0.22 0.22, 0.28 mean 0.25	Koals 2000 95-0271 + 95-0274[2]
USA 1995, Alva (FL), Valencia	WP	4	0.34	0.037	14	fruit	0.52, 0.43 mean 0.47	Koals 2000, 95-0273[2]

Country, year, location, variety	Application				PHI, days	Sample	Residue mg/kg	Ref, trial number
	Form	No	kg ai/ha	kg ai/hl				
USA 1995, Raymondville (TX) Everhard Navel	WP	4	0.34	0.037	14	fruit	0.12, 0.14 mean 0.13	Koals 2000 95-0279[2]
USA 1996, Porterville (CA) Wahington Navel	WP	4	0.34	0.009	14	fruit	0.15, 0.12 mean 0.14	Koals 2000 96-0082[2]
USA 1996, Windermere (FL) Parson Brown	WP	4	0.34	0.037	14	fruit	0.16, 0.26 mean 0.21	Koals 2000 96-0241[2]
USA 1996, Raymondville (TX) Everhard Navel	WP	4	0.34	0.037	14	fruit	0.17, 0.23 mean 0.20	Koals 2000 96-0272[2]
USA 1996-1997, LaBelle (FL) Hamlin	WP	4	0.34	0.037	14 14 14	fruit peel pulp	0.47, 0.47 mean 0.47 1.04, 0.75 mean 0.88 0.069, 0.093 mean 0.081	Koals 2000 96-0304[2]
USA 1996, LaBelle (FL) Pineapple	WP	4	0.34	0.037	14 14 14	fruit peel pulp	0.29, 0.35 mean 0.32 0.68, 0.56 mean 0.62 0.098, 0.053 mean 0.075	Koals 2000 96-0306[2]
USA 1996, LaBelle (FL) Hamlin	WP	4	0.34	0.037	14	fruit	0.24, 0.46 mean 0.35	Koals 2000 96-0310[2]
USA 1996-1997, Porterville (CA) Navel	WP	4	0.34	0.009	14 14 14	fruit* peel pulp	0.25, 0.30 mean 0.28 0.56, 0.71 mean 0.64 0.082, 0.097 mean 0.089	Koals 2000 96-0336[2]
USA 1996-1997, Rich Grove (CA) Navel	WP	4	0.34	0.008	14 14 14	fruit* peel pulp	0.19, 0.24 mean 0.21 0.26, 0.38 mean 0.32 0.052, 0.11 mean 0.082	Koals 2000 96-0337[2]

* residue in whole fruit is calculated from peel and pulp samples and their respective weights
[1] 1 tree per plot, sampling is required from 4 individual trees. Sample size was about 1 kg instead of min 2 kg
[2] application in absence of a wetting agent or summer oil
[3] sprayed well in excess of run-off
[4] 0.41 is the mean of 2 field samples (0.36, 0.46)
[5] 0.42 is the mean of 2 field samples (0.45, 0.39)

Lemons. The lemon residue data from the USA and Australia are shown in Table 9.

In two field trials in Australia, one in 1997 and the other in 1999 (Arlett, 2000) 3 applications of a WP formulation of tebufenozide at the proposed GAP rate of 0.006 kg ai/hl, corresponding to 0.12 kg ai/ha per application, were made at approximately 14 day intervals to the leaves of the crop . Lemons were collected 0, 1, (3), 7 and 14 days after the last application. Analytical method AL013/92-0 (Holzwarth and Schuld, 1993a) with GC-MS instead of GLC and NPD was used in trial TAB 274/98 (LOQ=0.02 mg/kg), and the Agrifood Technology method TP/215/990201 (GC/NPD; LOQ=0.05 mg/kg) (Bayer) in trial DJR/173/00. Recoveries were low: 72% at 0.4 mg/kg in trial TAB 274/98 and 74% at 0.5 mg/kg in trial DJR/173/00. The SAI was 2 months.

In five field trials in the USA from 1995 to 1997 with a WP formulation of tebufenozide (Koals, 1999a) 4 foliar applications, each at 0.34 kg ai/ha ± 5%, were made by airblast sprayers. The interval between the third and fourth applications was 14 days, and between the first and second ranged from approximately 2 to 6 months. In 3 of the trials in California and the single trial in Florida, duplicate field samples of lemons were collected 13 or 14 days after the last application. In the fourth trial in California, samples were collected 7, 14, 21 and 28 days after the last application. Whole fruit, peel and pulp samples were analysed by method TR 34-96-184 (Meng and Choo, 1996) with an LOQ of 0.02 mg/kg. The SAI ranged from 220 to 520 days.

Table 9. Residues of tebufenozide from supervised trials on lemons in Australia and the USA. All WP formulations.

Country, year, location, variety	Application			PHI, days	Sample	Residue mg/kg	Ref, trial number
	No	kg ai/ha	kg ai/hl				
Australia 1997, Galston (NSW) Eureka Lemon	3	[1]	0.006	0 1 3 7 14	fruit fruit fruit fruit fruit	0.37 0.16 0.24 0.24 0.13	Arlett, 2000 TAB 274/98[2,3]
Australia 1999, Loxton North (SA) Lisbon	3	0.012	0.006	0 1 7 14	fruit fruit fruit fruit	0.48 0.52 0.38 0.41	Arlett, 2000 DJR 173/00[2,4]
USA 1995, Fallbrook (CA) Eureka	4	0.34	0.018-0.025	13	fruit	0.22, 0.21 mean 0.22	Koals, 1999a 95-0258[5]
USA 1995, Porterville (CA) Lisbon	4	0.34	0.008-0.009	14	fruit	0.23, 0.22 mean 0.22	Koals, 1999a 95-0278[5]
USA 1996, Clewiston (FL) Eureka	4	0.34	0.037	14	fruit	0.14, 0.12 mean 0.13	Koals, 1999a 96-0307[5]
USA 1996-1997, Porterville (CA) Lisbon	4	0.34	0.008-0.009	7 14 14 14 21 28	fruit fruit peel pulp fruit fruit	0.30 0.51, 0.32 mean 0.42 0.97, 0.50[6] mean 0.74 0.10, 0.11 mean 0.11 0.33 0.36	Koals, 1999a 96-0342[5]
USA 1996-1997, Porterville (CA) Lisbon	4	0.34	0.009	14 14 14	fruit peel pulp	0.24, 0.47 mean 0.35 0.49, 0.59 mean 0.54 0.070, 0.030 mean 0.050	Koals, 1999a 96-0344[5]

[1] sprayed well in excess of run-off
[2] recovery at the level of found residues was less than 80%. TAB 274/998: R=72% at 0.40 mg/kg (n=2), DJR 173/00: R=74% at 0.5 mg/kg (n=1)
[3] 2 trees per plot, sampling is required from 4 trees
[4] 1 tree per plot, sampling is required from 4 trees. Sample size was about 1 kg instead of min 2 kg
[5] application in absence of a wetting agent or summer oil
[6] average residue of 3 analytical samples (0.720, 0.330 and 0.459 mg/kg)

Grapefruit. The residue data from the USA are shown in Table 10. In six field trials in geographically representative areas of the USA in 1995, 1996 and 1997 (Koals, 1999b) 4 applications of a WP formulation of tebufenozide at 0.34 kg ai/ha ± 5% were made to the leaves of the crop at early season, mid-season and the third and fourth 28 ± 2 and 14 ± 1 days before harvest. In each of the trials, duplicate field samples of grapefruit were collected 13-14 days after the last application. All samples were analysed for tebufenozide by the method of Meng and Choo (1996) with an LOQ of 0.02 mg/kg. The SAI ranged from 277 to 673 days.

Table 10. Residues of tebufenozide from supervised trials on grapefruit in the USA. All 4 applications of a WP formulation.

Year, location, variety	Application		PHI, days	Sample	Residue mg/kg	Ref, trial number
	kg ai/ha	kg ai/hl				
1995, Porterville (CA) Mello Gold	0.34	0.009	14	fruit	0.15, 0.18 mean 0.17	Koals, 1999b 95-0249[1]
1995, Raymondville (TX), Rio Red	0.34	0.035- 0.037	7 14 21 28	fruit fruit fruit fruit	0.047, 0.098 mean 0.072 0.11, 0.095 mean 0.10 0.12, 0.12 mean 0.12 0.093, 0.12 mean 0.11	Koals, 1999b 95-0268[1]
1995, LaBelle (FL) White Marsh	0.34	0.037	14	fruit	0.30, 0.50 mean 0.40	Koals, 1999b 95-0272[1]
1996, Windermere (FL) Ruby Red	0.34	0.037	13	fruit	0.10, 0.075 mean 0.089	Koals, 1999b 96-0263[1]
1996, LaBelle (FL) White Marsh	0.34	0.037	14 14 14	fruit[2] peel pulp	0.27, 0.24 mean 0.25 0.68, 0.81 mean 0.74 0.15, 0.10 mean 0.12	Koals, 1999b 96-0308[1]
1996-1997, Porterville (CA) Mello Gold	0.34	0.009	14 14 14	fruit peel pulp	0.071, 0.065 mean 0.068 0.21, 0.22 mean 0.21 0.019, 0.026 mean 0.022	Koals, 1999b 96-0343[1]

[1] application in absence of a wetting agent or summer oil
[2] residue in whole fruit is calculated from peel/pulp samples and their respective weights

Mandarins. The results of trials in Australia, Spain and Italy are shown in Table 11.

In two trials in Australia in 1996 and 1997 (Arlett, 2000) one and three applications of a WP formulation of tebufenozide at the proposed GAP rate of 0.006 kg ai/hl and at 0.012 and 0.024 kg ai/hl were sprayed in excess to the point of run-off. Foliar applications were made to the crop at approximately 14-day intervals in trial JES 557/98 and at 23- and 19-day intervals in trial MJG 035/97. Single samples of mandarins were collected 1, 7, 14 and 21 days after the last application and residues were determined by the method of Holzwarth and Schuld (1993a) with GC-MS instead of GLC with an NPD. The LOQ was 0.02 mg/kg. The SAI was 5 to 6 months.

In trials in Spain in 1995 (Jousseaume, 1995) two foliar applications of an SC formulation of tebufenozide at the GAP rate of 0.018 kg ai/hl equivalent to 0.31 to 0.51 kg ai/ha were made to the crop at 14-15 day intervals. In most trials, single samples of treated mandarins were collected 0, 7, 14, 21 and 28 days after the last application, and 0, 7 and 14 days after the first. Samples were analysed for tebufenozide by HPLC method TR 34-96-184 (Meng and Choo, 1996). Peel samples were analysed by the same method with an additional clean-up before quantification. The LOQ was 0.02 mg/kg for pulp and fruit and 0.05 mg/kg for peel. The SAI ranged from 363 to 455 days.

In five trials in Italy and Spain in 1996 (Balluff, 1997b) 2 foliar applications of a SC formulation of tebufenozide at 0.017 kg ai/hl, corresponding to GAP, were made to the crop with an interval of 14 days. In each of the trials, treated samples of mandarins were collected 0 and 13 or 14 days after the last application. Day 13/14 samples were peeled as part of the processing. Peel, pulp and whole fruit were analysed by method TR 34-96-184 (Meng and Choo 1996). The LOQ was 0.02 mg/kg for all samples. The SAI ranged from 101 to 271 days.

Table 11. Residues of tebufenozide resulting from supervised trials on mandarins in Australia, Italy and Spain.

Country, year, location, variety	Application				PHI, days	Sample	Residue mg/kg	Ref, trial number
	Form	No	kg ai/ha	kg ai/hl				
Australia 1996, Bundaberg (Qld) Murcott	WP	1	0.18	0.006	1 7 14 21	fruit fruit fruit fruit	0.05 0.05 0.04 0.04	Arlett, 2000 MJG 035/97[1, 2, 3]
	WP	1	0.45	0.012	1 7 14 21	fruit fruit fruit fruit	0.09 0.10 0.09 0.09	Arlett, 2000 MJG 035/97[1, 2, 3]
	WP	1	0.91	0.024	1 7 14 21	fruit fruit fruit fruit	0.17 0.13 0.16 0.17	Arlett, 2000 MJG 035/97[1, 2, 3]
	WP	3	0.22, 0.28, 0.23	0.006	1 7 14 21	fruit fruit fruit fruit	0.08[4] 0.14 0.10 0.15	Arlett, 2000 MJG 035/97[1, 2, 3]
	WP	3	0.35, 0.34, 0.44	0.012	1 7 14 21	fruit fruit fruit fruit	0.14 0.35 0.33[4] 0.19	Arlett, 2000 MJG 035/97[1, 2, 3]
	WP	3	0.94, 0.91, 0.91	0.024	1 7 14 21	fruit fruit fruit fruit	0.34 0.46 0.34 0.17	Arlett, 2000 MJG 035/97[1, 2, 3]
Australia 1997, Leeton (NSW) Imperial	WP	3	0.24	0.006	0 1 7 14	fruit fruit fruit fruit	0.23 0.20 0.34[4] 0.25	Arlett, 2000 JES 557/98[2, 3]
Italy 1996, Belpasso Avana	SC	2	0.48, 0.49	0.017	0 14	fruit fruit[7] peel pulp	1.0[4] <u>0.59</u> 1.8 <u>0.082</u>	Balluff, 1997b 96I022R[5]
Italy 1996, Catania Avana	SC	2	0.49	0.017	0 14	fruit fruit[7] peel pulp	0.62[4] <u>0.30</u> 0.71 <u>0.14</u>[6]	Balluff, 1997b 96I023R[5]
Spain 1995, Sal Alcacer (Valentia) Clementine	SC	1	0.43	0.018	0 7 14	fruit fruit fruit	0.094 0.25 0.37	Jousseaume, 1995 96-0148
		2	0.43, 0.51	0.018	0 7 14 21 28	fruit fruit fruit fruit fruit	0.77 0.48 <u>0.95</u> 0.80 0.62	Jousseaume, 1995 96-0148
Spain 1995, Sal Turis (Valentia) Clementine	SC	1	0.35	0.018	0 7 14	fruit fruit fruit	0.41 0.50 0.45	Jousseaume, 1995 96-0149
		2	0.35, 0.40	0.018	0 7 14 21 28	fruit fruit fruit fruit fruit	0.83 0.79 0.48 <u>0.78</u> 0.42	Jousseaume, 1995 96-0149
Spain 1995, Sal Alcacer (Valentia) Clementine	SC	1	0.31	0.018	0 7 14	fruit fruit fruit	0.62 0.44 0.23	Jousseaume, 1995 96-0150

Country, year, location, variety	Application				PHI, days	Sample	Residue mg/kg	Ref, trial number
	Form	No	kg ai/ha	kg ai/hl				
		2	0.31, 0.35	0.018	0	fruit	0.94	Jousseaume, 1995 96-0150
					7	fruit	0.60	
					14	fruit	0.84	
					21	fruit	0.62	
					28	fruit	0.52	
Spain 1995, Sal Via (Valentia) Clementine	SC	1	0.41	0.018	0	fruit	0.41	Jousseaume, 1995 96-0189
					0	peel	0.97	
					0	pulp	0.12	
					7	fruit	0.37	
					7	peel	1.0	
					7	pulp	0.096	
					14	fruit	0.47	
					14	peel	0.76	
					14	pulp	0.071	
		2	0.41, 0.37	0.018	0	fruit	0.64	Jousseaume, 1995 96-0189
					0	peel	2.2	
					0	pulp	0.18	
					7	fruit	0.67	
					7	peel	2.0	
					7	pulp	0.18	
					14	fruit	0.52	
					14	peel	2.1	
					14	pulp	0.13	
					21	fruit	0.42	
					21	peel	1.4	
					21	pulp	0.18	
					28	fruit	0.60	
					28	peel	1.3	
					28	pulp	0.17	
Spain 1996, Alcala Clemenales	SC	2	0.33, 0.32	0.017	0	fruit	0.42[6]	Balluff, 1997b 96S006R[5]
					13	fruit[7]	0.30	
						peel	0.82	
						pulp	0.092	
Spain 1996, Alcala Oroval	SC	2	0.38, 0.37	0.017	0	fruit	0.74[4]	Balluff, 1997b 96S007R[5]
					13	fruit[7]	0.42	
						peel	1.3	
						pulp	0.076	
Spain 1996, Lliria Clemenales	SC	2	0.40, 0.41	0.017	0	fruit	1.2[4]	Balluff, 1997b 96S008R[5]
					14	fruit[7]	0.60	
						peel	1.9	
						pulp	0.069	

[1] application in absence of a wetting agent or summer oil
[2] recoveries of spiked samples at the level of found residues were <80%. MJG 035/97: 78, 70 and 69% at 0.040, 0.10 and 0.20 mg/kg respectively (n=1), JES 557/98: 67% at 0.20 mg/kg (n=2)
[3] 1 tree per plot, sampling is required from 4 trees. Sample size was about 0.5 - 1 kg, instead of min 2 kg
[4] average of 2 analytical samples
[5] recovery of peel samples spiked at 1.0 mg/kg was 77.4% (n=2)
[6] average of 3 analytical samples
[7] residue in whole fruit calculated from peel/pulp samples and their respective weights

Stone fruits

Peaches. In three field trials in 1996-1998 in New Zealand 3 or 6 applications of a WP formulation of tebufenozide at the GAP rate of 0.12 kg ai/ha and at an exaggerated rate of 0.24 kg ai/ha were made to the leaves of the crop at intervals of 17 to 35 days (Baynon, 1998a,b). From 3-4 days after the last application and every week thereafter single samples of peaches were collected and analysed by method TR 34-95-66 (HPLC-MS) with slight modifications (Deakyne *et al.*, 1995). In the 1996/97

trials the LOQ was 0.01 mg/kg, and in the 1997/1998 trial 0.03 mg/kg. The SAI was up to 4 months. The results in fruit without stone are shown in Table 12.

Table 12. Residues of tebufenozide in fruit without stone resulting from supervised trials on peaches in New Zealand.

Year, Location Variety	Application				PHI days	Residue, mg/kg	Reference/ Comments
	Form.	No.	kg ai/ha	kg ai/hl			
1996-1997, Hawkes Bay Golden Queen	WP	6	0.12	0.006	1 8 15 22	0.36 0.13 <u>0.10</u> 0.10	Baynon, 1998a FSLHBRE02[1]
		6	0.24	0.012	1 8 15 22	1.3 0.86 0.82 0.47	Baynon, 1998a FSLHBRE02[1]
1996/1997 Nelson Golden Queen	WP	6	0.12	0.006	1 8 15 22 29	0.20 0.15 <u>0.14</u> 0.10 0.06	Baynon, 1998a FSLNRE05[1]
		6	0.24	0.012	1 8 15 22 29	0.61 0.54 0.51 0.37 0.23	Baynon, 1998a FSLNRE05[1]
1997/1998 Hastings Elegant Lady	WP	3	0.12	0.006	3 10 17 25 31	0.28 0.13 0.08 <u>0.09</u> 0.03	Baynon, 1998b FSLH/08/98/R[1]
		3	0.24	0.012	10 17 25 31	0.44 0.31 0.28 0.14	Baynon, 1998b FSLH/08/98/R[1]

[1] No soil type or weather data available

<u>Nectarines</u>. The results of trials in New Zealand are shown in Table 13. In three field trials, 1996-1998, 3 or 4 applications of a WP formulation of tebufenozide at 0.12 kg ai/ha were sprayed on the leaves of the crop at 16-35-day intervals (Baynon, 1998a,b). Samples were collected and analysed as in the peach trials, with the same LOQs and an SAI of up to 4 months.

Table 13. Residues of tebufenozide in fruit without stone resulting from supervised trials on nectarines in New Zealand.

Year, location Variety	Application				PHI days	Residue, mg/kg	Reference/ Comments
	Form.	No.	kg ai/ha	kg ai/hl			
1996-1997, Hastings Tasty Gold	WP	4	0.12	0.006	0 7 14	0.19 0.13 <u>0.05</u>	Baynon, 1998a FSLHBR01[1]
		4	0.24	0.012	0 7 14	0.68 0.28 0.19	Baynon, 1998a FSLHBR01[1]

Year, location Variety	Application				PHI days	Residue, mg/kg	Reference/ Comments
	Form.	No.	kg ai/ha	kg ai/hl			
1997-1998, Hastings Fantasia	WP	3	0.12	0.006	3 10 17 25 31	0.34 0.33 <u>0.26</u> 0.09 0.07	Baynon, 1998b FSLH/07/98R[1, 2]
		3	0.24	0.012	3 10 17 25 31	0.58 0.27 0.22 0.17 0.15	Baynon, 1998b FSLH/07/98R[1, 2]
1997-1998, Nelson Red Gold	WP	4	0.12	0.006	0 7 14 21 28	0.32 0.15 <u>0.22</u> 0.14 0.21	Baynon, 1998b FSLH/06/98R[1]
		4	0.24	0.012	0 7 14 21 28	0.68 0.48 0.52 0.56 0.37	Baynon, 1998b FSLH/06/98R[1]

[1] No soil type or weather data available
[2] Residues in untreated samples were 0.12, 0.07, 0.07, 0.08, <0.03 mg/kg, at 3, 10, 17, 25, and 31 days, probably due to spray drift (decrease with time).

Berries and other small fruits

Blueberries. In eight field trials in geographically representative areas of the USA in 1996 (Dorschner and Breuninger, 1998d) (Table 14) 4 foliar applications of a WP formulation of tebufenozide were made to the crop at 0.29 kg ai/ha (maximum GAP) ± 5% at intervals of approximately 14 days (in the trial in Ohio each application was 15% less). Replicate samples were collected 12-15 days after the last application, and analysed by method TR 34-94-40 (Deakyne *et al.*, 1994). Slight modifications were made during analyses. The LOQ was 0.005 mg/kg. The SAI ranged from 121 to 186 days. The storage stability of tebufenozide was demonstrated in blueberries stored frozen for 189 days.

Table 14. Residues of tebufenozide resulting from supervised trials on blueberries in the USA in 1996 (Dorschner and Breuninger, 1998d).

Location variety	Application				PHI days	Residue, mg/kg	Report no.
	Form	No.	kg ai/ha	kg ai/hl			
Castle Hayne (NC) Blue Chip	WP	4	0.29	0.034	12	1.2, 1.1 mean <u>1.2</u>	96-NC12
Gainesville (FL) Choice	WP	4	0.29	0.021	13	1.3, 2.2 mean <u>1.7</u>	96-FL33
Wooster (OH) Early Blue	WP	4	0.25	0.056	15	0.35, 0.32 mean <u>0.34</u>	96-OH16
Aurora (OR) Blue Crop	WP	4	0.29	0.043	14	0.81, 1.4 mean <u>1.1</u>	96-OR22[1]
Chatsworth (NJ) Blue Crop	WP	4	0.29	0.077	14	0.75, 0.87 mean <u>0.81</u>	96-NJ19
Pennsylvania Furnace (PA) Blue Crop	WP	4	0.29	0.063	12	0.60, 0.53 mean <u>0.56</u>	96-PA01
Douglas (MI) Jersey	WP	4	0.29	0.062	14	0.32, 0.28 mean <u>0.30</u>	96-MI17

Location variety	Application				PHI days	Residue, mg/kg	Report no.
	Form	No.	kg ai/ha	kg ai/hl			
Douglas (MI) Jersey	WP	4	0.29	0.062	14	0.45, 0.55 mean 0.50	96-MI18

[1] no soil type data available

Raspberries. In five field trials in geographically representative areas of the USA in 1996 (Dorschner and Breuninger, 1998c) (Table 15) 4 applications of a WP formulation of tebufenozide at the maximum GAP rate of 0.29 kg ai/ha ± 5% were made to the leaves of the crop at approximately 14-day intervals. Sampling and analysis were as for blueberries. The LOQ was 0.01 mg/kg. The SAI ranged from 283 to 305 days, with demonstrated stability of tebufenozide in raspberries stored frozen for 322 days.

Table 15. Residues of tebufenozide resulting from supervised trials on raspberries in the USA, 1996 (Dorschner and Breuninger, 1998c).

Location Variety	Application				PHI days	Residue, mg/kg	Report no.
	Form.	No.	kg ai/ha	kg ai/hl			
Aurora (OR) Meeker	WP	4	0.30	0.032	14	0.56, 0.43 mean 0.50	96-OR21
Skagit County (WA) Meeker	WP	4	0.31	0.076	15	0.95, 0.78 mean 0.86	96-WA52
Burlington (WA) Meeker	WP	4	0.30	0.076	15	0.71, 0.94 mean 0.82	96-WA34
Greenwood (WI) Royalty	WP	4	0.30	0.25	13	0.32, 0.39 mean 0.36	96-WI15
Pennsylvania Furnace (PA) Titan	WP	4	0.29	0.063	12	0.55, 0.57 mean 0.56	96-PA02

Cranberries. In four field trials in geographically representative areas of the USA in 1996 (Dorschner and Breuninger, 1998a) (Table 16) 4 foliar applications of a WP formulation of tebufenozide at 0.29 kg ai/ha ± 5% were made at approximately 14-day intervals, except in the MA trial where each application was 31% lower. In a single trial in Canada 4 applications were made at the same rate but of an SP formulation. In all the trials 2 or 4 replicate samples of cranberries were collected 13-14 days and 25-29 days after the last application, and analysed for tebufenozide as before. The LOQ was 0.05 mg/kg. The SAI ranged from 109 to 127 days, with demonstrated storage stability in cranberries stored frozen for 30 days.

Table 16. Residues of tebufenozide resulting from supervised trials on cranberries in the USA and Canada, 1996 (Dorschner and Breuninger, 1998a).

Country, Location Crop variety	Application				PHI days	Residue, mg/kg	Report no.
	Form	No.	kg ai/ha	kg ai/hl			
US, Wisconsin Rapids (WI), Ben Lear	WP	4	0.29	0.14	14 27	0.19, <0.01 mean 0.10 0.040, 0.051 mean 0.046	96-WI01
US, Biron (WI) Ben Lear	WP	4	0.29	0.14	14 25	0.18, 0.10 mean 0.14 <0.01, <0.01 mean <0.01	96-WI02
US, Chatsworth (NJ) Early Black	WP	4	0.29	0.083	14 29	0.12, 0.072 mean 0.091 <0.01, 0.023 mean 0.016	96-NJ23
US, East Wareham (MA) Early Black	WP	4	0.20	0.040	13 27	0.074, 0.069 mean 0.072 0.034, 0.050 mean 0.042	96-MA01
Canada, Agassiz (BC) MacFarlin	SC	4	0.29	0.038	14 27	0.84, 0.61, 0.89, 0.42 mean 0.69 0.23, 0.21, 0.34, 0.32 mean 0.28	96-BC01/02

Grapes. French trials in 1990 and 1992 conducted according to GAP in Portugal were reported to the 1996 JMPR but could not be evaluated because Portugese GAP was pending. It is now confirmed. The data are shown in Table 17.

Table 17. Previously summarized data for residues of tebufenozide in grapes.

Country, year	Application				PHI days	Residue, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
France, 1990	SC	2	0.15	0.04	12	0.16	Gocha, 1995
France, 1992	SC	2	0.144	0.048	14	0.29	Gocha, 1995
France, 1992	SC	2	0.144	0.048	14	0.68 0.81	Gocha, 1995

In five field trials in Australia in 1995 and 1998 (Hamblin *et al.*, 2001) (Table 18) 2 or 3 applications of a WP formulation of tebufenozide at a rate of 0.006 kg/hl, 0.12 kg ai/ha were made to the leaves of the crop . The intervals were 14 or 15 days between the first and second applications and 14 to 63 days between the second and third in 1998, and 33 days between the two in 1995. In all the trials single samples of grapes were collected 21, 28 and 35 days after the last application and analysed for tebufenozide by method AL013/92-0 (Holzwarth and Schuld, 1993a) with GC-MS instead of NPD. The laboratory made slight modifications during analyses. The LOQ was 0.01 mg/kg. The SAI was up to 9 months.

Table 18. Residues of tebufenozide resulting from supervised trials on grapes in Australia (Hamblin *et al.*, 2001).

Year, location variety	Application				PHI days	Residue, mg/kg	Report no./ application interval, days
	Form	No.	kg ai/ha	kg ai/hl			
1995/1996 Irymple (Vic) M12 Sultana	WP	2	0.071	0.006	0 21 28 35	0.32 0.12 0.09, 0.13, 0.22, 0.18, 0.15 <0.01	SCM248/96 33
	WP	2	0.141	0.012	0 21 28 35	0.80 0.33 0.39 0.29	SCM248/96 33
1998/1999, Dixons Creek (Vic) Chardonnay	WP	2	[1]	0.06	83 90 97	0.24 0.11 0.09	RTL528/99 14
	WP	3	[1]	0.006	21 28 35	1.3 0.72 0.64	RTL528/99 14, 62
1998/1999, Herne Hill (WA) Table Grapes/Flame Seedless, Red Globe	WP	3	0.12	0.006	21 28 35	1.0 1.1 0.85	MWS427/99 14, 14
1998/1999, Young (NSW) Firmint, Harslevelo	WP	2	0.135	0.006	60 67 74	0.18 0.17 0.12	PJH285/99 14
	WP	3	0.135, 0.135 0.18	0.006	21 28 35	1.5 0.58 1.2	PJH285/99 14, 39
1998/1999, Coonawarra (SA) Shiraz	WP	2	0.094, 0.129	0.006	84 91 98	0.06 0.06 0.05	SCM296/99 15

Year, location variety	Application				PHI days	Residue, mg/kg	Report no./ application interval, days
	Form	No.	kg ai/ha	kg ai/hl			
	WP	3	0.094, 0.129 0.144	0.006	21 28 35	0.61 0.81 0.78	SCM296/99 15, 63

[1] 1st and 2nd application sprayed well in excess of run-off, 3rd application (where applicable) >0.18 kg ai/ha.

Avocados. In five field trials in Australia and New Zealand from 1998 to 2000 (Brookbanks *et al.*, 2001) 4 foliar applications of a WP formulation of tebufenozide at a rate of 0.006 kg ai/hl (New Zealand GAP), 0.012 kg ai/hl, and 0.060 kg ai/hl (a tenfold concentrate) were made at intervals of 20-22 days in New Zealand and 14-15 days in Australia. In most of the trials, replicate samples of avocados were collected 0, 7, 14 and 21 days after the last application. GAP in New Zealand specifies a PHI of 21 days and proposed GAP in Australia 14 days.

Samples in Australia were analysed by Agrifood Technology method TP/215/990201 (GLC with an NPD) (Bayer). In trial DCP015/99 corrected data are also shown because recoveries of samples were low (59 to 65% at 0.2 to 1.0 mg/kg). Samples from New Zealand were analysed by HPLC-MS method 34-94-66 (Deakyne *et al.*, 1995). The LOQ was 0.04-0.05 mg/kg. All samples were analysed without stone. Table 19 shows the results with and without adjustment for the weight of the stone. The SAI ranged from 4 to 12 months. In trial DCP 020/00 it rained after the last application and residues were considerably lower.

Table 19. Residues of tebufenozide from supervised trials on avocados in Australia and New Zealand (Brookbanks *et al.*, 2001).

Country, year, location variety	Application				PHI days	Residue in stoneless fruit, mg/kg	Calculated residue[1] mg/kg	Report no.
	Form	No.	kg ai/ha	kg ai/hl				
Australia, 1998, Toowoomba (Qld) Hass	WP	4	0.12	0.006	0 7 14 21	0.12 0.086 0.10 0.12	0.099 0.074 0.087 0.10	IMI 243/00 [2]
	WP	4	0.18	0.012	0 7 14 21	0.36 0.45 0.43 0.33	0.30 0.40 0.38 0.28	IMI 243/00 [2]
	WP	4	0.30	0.060[3]	0 7 14 21	0.16 0.18 0.13 0.091	0.13 0.15 0.11 0.075	IMI 243/00 [4]
Australia, 1999-2000, Walkamin (Qld) Sheppard	WP	4	0.050	0.006	0 7 14 21	0.044 0.042 0.044 <0.040	0.037 0.036 0.037 0.033	DCP 020/00) [4,5]
		4	0.10	0.012	0 7 14 21	0.13 0.083 0.10 0.080	0.11 0.069 0.082 0.066	DCP 020/00 [4,5]
Australia, 1999, Kairi (Qld) Hass	WP	4	0.042	0.006	0 7 14 21	0.20/0.31[6] 0.16/0.24[6] 0.18/0.28[6] 0.16/0.24[6]	0.18/0.27[6] 0.13/0.21[6] 0.16/0.25[6] 0.13/0.21[6]	DCP 015/99 [7,8]
		4	0.086	0.012	0 7 14 21	0.48/0.75[6] 0.37/0.58[6] 0.36/0.57[6] 0.33/0.52[6]	0.43/0.67[6] 0.33/0.51[6] 0.32/0.50[6] 0.28/0.45[6]	DCP 015/99 [7,8]

Country, year, location variety	Application				PHI days	Residue in stoneless fruit, mg/kg	Calculated residue[1] mg/kg	Report no.
	Form	No.	kg ai/ha	kg ai/hl				
		4	0.086	0.060[3]	0 7 14 21	0.51/0.80[6] 0.44/0.70[6] 0.48/0.76[6] 0.34/<u>0.53</u>[6]	0.46/0.72[6] 0.39 /0.61[6] 0.43/0.67[6] 0.30/<u>0.47</u>[6]	DCP 015/99 [7,8]
New Zealand, 1999-2000, Mangawhai Hass	WP	4	n.d.[9]	0.006	0 7 14 21 28	0.26 0.37 0.45 <u>0.21</u>[10] 0.32	0.22 0.31 0.38 <u>0.18</u>[10] 0.28	FSLA039 [11]
New Zealand, 1999-2000, Katikati Hass	WP	4	n.d. [9]	0.006	21	0.18, 0.20 mean <u>0.19</u>	0.16, 0.18 mean <u>0.17</u>	FSLA039 [11]

[1] in whole fruit with stone
[2] one tree per plot (sampling is required from 4 trees), duplicate plots, one analytical sample per treatment
[3] application by concentrate spraying (10x). Spray volume was 0.63 l/tree
[4] one tree per plot, unreplicated. Samples consisted of 5 fruit instead of min. 12. Duplicate analyses.
[5] it rained after the last application (35 mm)
[6] uncorrected/corrected for recovery (64%). Corrected results are given because recoveries from samples spiked at 0.2, 0.5 and 1.0 mg/kg were 65, 64 and 59% respectively
[7] one tree per plot, duplicate plots. The average value is taken because of small plot size
[8] recoveries from samples spiked at 0.2, 0.5 and 1.0 mg/kg were 65, 64 and 59% respectively
[9] n.d.: no data available, spray volume/tree 7.2 l (corresponds to 0.11 kg ai/ha if 250 trees/ha (average))
[10] mean of duplicate analyses
[11] samples stored for up to 6 months at –4°C, and then another 3 months at $\leq$ –10°C

<u>Brassica vegetables</u>

<u>Cabbage and broccoli</u>. Table 20 and Table 21 show residue data submitted to the 1996 JMPR on cabbages and broccoli from US trials which comply with currently approved US GAP. These data could not be evaluated in 1996 because US GAP was pending. The SAI ranged from 110 to 938 days.

Table 20. Previously submitted data for residues of tebufenozide in cabbage from trials in the USA.

Location, Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
OH, 1992	SC	7	0.14	0.048-0.054	0 8	0.004[1], 0.007 <0.01[1], <u>0.004</u>	Chen, 1994b
FL, 1992	SC	7	0.14	0.015	9	<0.01[1], <u>0.03</u>	Chen, 1994b
TX, 1993	SC	7	0.14	0.045-0.062	0 7 14	0.02[1], 0.05 <0.01[1], <u>0.30</u> <0.01[1], 0.06	Chen, 1994b
WI, 1993	SC	7	0.14	0.057-0.064	0 7	<0.01[1], 0.01 0.01[1], <u>0.04</u>	Chen, 1994b
VA, 1993	SC	7	0.14	0.037	7	<u>0.53</u>	Chen, 1994b
CA, 1991	SC	8	0.14	0.075	0 7	0.39 <u>0.17</u>	Chen, 1994b
NY, 1991	SC	8	0.14	0.026-0.028	0 7	1.5 <u>0.09</u>	Chen, 1994b
TX, 1991	SC	8	0.14	0.047	0 7	0.24[1], 1.1 0.01[1], <u>0.11</u>	Chen, 1994b
CA, 1993	SC	8	0.14	0.05	0 7 14	1.5 <u>1.0</u> 0.91	Chen, 1994b

Location, Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
GA, 1991	SC	9	0.14	0.075	0 7	0.07[1], 1.3 0.01[1], 0.38	Chen, 1994b
TX, 1994	SC	9	0.14	0.05-0.075	0 7	0.8 0.78	Dong, 1995b
TX, 1994	WP	9	0.14	0.05-0.075	0 7	1.2 1.3	Dong, 1995b
FL, 1994	SC	9	0.14	0.05	0 7	3.6 4.6	Dong, 1995b
FL, 1994	WP	9	0.14	0.05	0 7	5.2 4.3	Dong, 1995b

[1] Head without wrapper leaves

Table 21. Previously submitted data for residues of tebufenozide in broccoli from trials in the USA.

Location Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
VA, 1992	SC	7	0.14	0.038	7	0.33	Chen, 1994b
OR, 1991	SC	8	0.14	0.044-0.047	0 7	0.67 0.24	Chen, 1994b
TX, 1991	SC	8	0.14	0.047	0 7	0.45 0.11	Chen, 1994b
CA, 1991	SC	8	0.14	0.042	0 7	0.33 0.09	Chen, 1994b
TX, 1992	SC	8	0.14	0.047-0.050	6	0.01	Chen, 1994b
CA, 1993	SC	8	0.14	0.050	0 7 14	0.46 0.07 0.05	Chen, 1994b
OR, 1992	SC	9	0.14	0.030	7	0.12	Chen, 1994b
CA, 1994	SC	7	0.14	0.025	0 7	0.36 0.1	Dong, 1995b
CA, 1994	WP	7	0.14	0.025	0 7	0.32 0.11	Dong, 1995b
CA, 1994	SC	9	0.14	0.025	0 7	0.75 0.31	Dong, 1995b
CA, 1994	WP	9	0.14	0.025	0 7	0.94 0.34	Dong, 1995b

Fruiting vegetables

Tomatoes (including cherry tomatoes). The residue data from France, Greece, Italy, The Netherlands, Spain and the USA are shown in Table 22.

Field trials were conducted in France, Greece and Spain in 1995 (Bürstell *et al.*, 1996), and greenhouse trials in Italy, Greece, Spain and The Netherlands in 1996 (Sonder and Bürstell, 1997) and 1997 (Schreuder, 1998). 2-6 foliar applications of a SC formulation of tebufenozide at rates between 0.18 and 0.45 kg ai/ha were made at 7-12 day intervals. In The Netherlands, all trials were at the same location but were independent. Single samples of tomatoes were collected 0, 1, 3, 7, 10 and/or 14 days after the last application and analysed for tebufenozide by the GC-MS method AL 013/92-0 (Holzwarth and Schuld, 1993a-c). The LOQ was 0.02 mg/kg. The SAI ranged from 4 to 8 months.

In field trials in the USA in 1996 (Carpenter, 1997a) 4 foliar applications of a WP formulation of tebufenozide at 0.29 $\pm$ 5% kg ai/ha (maximum GAP rate) were made at 6-8 day intervals. Replicate field samples of tomatoes were collected in all trials at the 7-day PHI and in some trials also at 0, 3,

14 and 21 days. All tomato samples were analysed for tebufenozide by method TR 34-95-66 (Deakyne *et al.*, 1995). The LOQ was 0.02 mg/kg. The SAI ranged from 203 to 327 days.

Table 22. Residues of tebufenozide resulting from supervised trials on tomatoes.

Country, year, location variety	Site	Application				PHI days	Residue, mg/kg	Reference/ Report no.
		Form	No.	kg ai/ha	kg ai/hl			
Spain, 1995, Brenes/Sevilla (Andalucia) Red Hunter	F	SC	4	0.18	0.051	0 3 7 10 14	0.33 0.41 0.33 0.26 0.09	Bürstell, 1996 ESP 00 01
France, 1995, St.Sixte (Midi-Pyrénées) Cannery row	F	SC	6	0.18	0.030	0 3 7 10 14	0.24, 0.28 0.30, 0.34 0.17, 0.27 0.14, 0.12 0.16, 0.16	Bürstell, 1996 FRA 00 01/ FRA 00 02
Greece, 1995, Korifi (Macedonia) Rio Grande	F	SC	6	0.18	0.040	0 3 7 10 14	0.27 0.19 0.19 0.13 0.10	Bürstell, 1996 GRC 00 01
Spain, 1996, Ultera (Andalucia) Caruso	G	SC	4	0.38	0.018	0 3	0.42 0.34	Sonder, 1997 ESP 00 01[1]
Spain, 1996, Los Palacios (Andalucia) Genaro	G	SC	4	0.45	0.018	0 3	0.33 0.25	Sonder, 1997 ESP 00 02[1]
Greece, 1996, Esovalta (Macedonia) Arletta	G	SC	4	0.45	0.018	0 3	0.16 0.09	Sonder, 1997 GRC 00 01[1]
Italy, 1996, Zapponeta (Puglia) Maiorca	G	SC	4	0.27	0.018	0 3	0.28 0.19	Sonder, 1997 ITA 00 01[1]
Italy, 1996, Molfetta (Puglia) Granito	G	SC	4	0.27, 0.31	0.018	0 3	0.40 0.20	Sonder, 1997 ITA 00 02[1]
Netherlands, 1997, Haren (Gr) Aramato	G	SC	2	0.21	0.014 3	0 1 3 7	0.12 0.10 0.07 0.16	Schreuder, 1998 NLD 015 01[2]
Netherlands, 1997, Haren (Gr) Aramato	G	SC	2	0.21	0.014 3	0 1 3 7	0.12 0.09 0.11 0.11	Schreuder, 1998 NLD 015 02[2]
Netherlands, 1997, Haren (Gr) Aramato	G	SC	2	0.21	0.014 3	0 1 3 7	0.11 0.09 0.11 0.10	Schreuder, 1998 NLD 015 03[2]
Netherlands, 1997, Haren (Gr) Aramato	G	SC	2	0.21	0.014 3	0 1 3 7	0.09 0.09 0.08 0.10	Schreuder, 1998 NLD 015 04[2]
US, 1996, North Rose (NY) Floradade	F	WP	4	0.29	0.062	7	0.057, 0.060 mean 0.058	Carpenter, 1997a 96-0214 2079601
US, 1996, Lucama (NC) Campbell 1327	F	WP	4	0.29	0.10	7	0.28, 0.22 mean 0.25	Carpenter, 1997a 96-0229 2079602

Country, year, location variety	Site	Application				PHI days	Residue, mg/kg	Reference/ Report no.
		Form	No.	kg ai/ha	kg ai/hl			
US, 1996, Chipley (FL) Mountain Spring	F	WP	4	0.30	0.16	7	0.10, 0.15 mean 0.13	Carpenter, 1997a 96-0157 2079603
US, 1996, Sneads (FL) Mountain Spring	F	WP	4	0.30	0.16	0 3 7 14 21	0.12, 0.12 mean 0.12 0.088, 0.050 mean 0.069 0.060, 0.12 mean 0.089 0.058, 0.032 mean 0.045 0.063, 0.070 mean 0.068	Carpenter, 1997a 96-0158 2079604
US, 1996, Dow (IL) Mountain Fresh	F	WP	4	0.29	0.16	7	0.092, 0.098 mean 0.095	Carpenter, 1997a 96-0236 2079605
US, 1996, Maricopa (AZ) Romano	F	WP	4	0.29, 0.33	0.12	7	0.086, 0.084 mean 0.085	Carpenter, 1997a 96-0210
US, 1996, Arroyo Grande (CA) Shady Lady	F	WP	4	0.30	0.095, 0.19	7	0.018, 0.045 mean 0.031	Carpenter, 1997a 96-0211[3]
US, 1996, Porterville (CA) Celebrity	F	WP	4	0.29	0.10	7	0.11, 0.098 mean 0.11	Carpenter, 1997a 96-0280
US, 1996, Porterville (CA) 88-90	F	WP	4	0.29	0.10	0 3 7 14 21	0.44, 0.42 mean 0.43 0.47, 0.50 mean 0.49 0.41, 0.36 mean 0.38 0.52, 0.53 mean 0.53 0.21, 0.63 mean 0.42	Carpenter, 1997a 96-0227
US, 1996, Porterville (CA) 88-90	F	WP	4	0.29	0.094, 0.045	7	0.35, 0.28 mean 0.31	Carpenter, 1997a 96-0249[4]
US, 1996, Avila (CA) Cherry tomato Sweet Cherry	F	WP	4	0.29	0.045	7 14 21	0.14, 0.21 mean 0.17 0.15, 0.15 mean 0.15 0.12, 0.16 mean 0.14	Carpenter, 1997a 96-0173[3]
US, 1996, Nipomo (CA) Cherry tomato Sweet Cherry	F	WP	4	0.30	0.19	0 3 7 14 21	0.61, 0.76 mean 0.68 0.74, 0.64 mean 0.69 0.51, 0.52 mean 0.52 0.49, 0.54 mean 0.52 0.47, 0.33 mean 0.40	Carpenter, 1997a 96-0273[5]

F: field, G: greenhouse
[1] sand or sandy-clay soil, cold house
[2] rockwool soil
[3] fruit was picked only from the bottom of the vines because the upper, exposed vines had no ripe fruit
[4] 50% of tomato fruit sampled was green, 50% was red. Sufficient ripe samples were available.
[5] sample sizes were too small (0.5 to 0.8 kg instead of min 2 kg)

Peppers (bell and non-bell). Nine field trials were conducted in the USA in 1996 (Carpenter, 1997b) in which 4 foliar applications of a WP formulation of tebufenozide at the GAP rate of 0.29 + 5% kg ai/ha were made at 6-8 day intervals. Replicate field samples of peppers were collected in all trials at the 7-day PHI and in some trials also 0, 3, 14 and 21 days after the last application. All samples were analysed for tebufenozide by method TR 34-95-66 (Deakyne *et al.*, 1995). The LOQ was 0.02 mg/kg. Non-bell pepper samples received an additional Florisil column clean-up to remove interferences. The SAI ranged from 185 to 290 days. Results are shown in Table 23.

Table 23. Residues of tebufenozide resulting from supervised trials on peppers in the USA, 1996 (Carpenter, 1997b).

Location, variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form	No.	kg ai/ha	kg ai/hl			
Bell peppers							
Lucama (NC) Capistrano	WP	4	0.29	0.10	0 3 7 14 21	0.37, 0.21 mean 0.29 0.052, 0.058 mean 0.055 0.049, 0.054 mean 0.052 0.037, 0.018 mean 0.027 0.017, 0.016 mean 0.017	96-0223
Sneads (FL) Camelot	WP	4	0.29	0.16	7	0.11, 0.20 mean 0.16	96-0156
Columbia (IL) King Arshon	WP	4	0.29	0.16	7	0.056, 0.041 mean 0.048	96-0237[1]
Uvalde (TX) Grand Rio 66	WP	4	0.29	0.20	0 3 7 14 21	0.19, 0.082 mean 0.14 0.070, 0.072 mean 0.071 0.038, 0.090 mean 0.064 0.075, 0.030 mean 0.052 0.074, 0.044 mean 0.059	96-0168
Porterville (CA) California Wonder	WP	4	0.29	0.10	7	0.52, 0.76 mean 0.64	96-0245
San Arch (CA) California Wonder 300	WP	4	0.29	0.11	7	0.14, 0.21 mean 0.17	96-0244
Non-bell peppers							
Levelland (TX) Jalapeno	WP	4	0.29	0.16	7	0.046, 0.034 mean 0.040	96-0195
Lubbock (TX) Jalapeno	WP	4	0.29	0.16	7	0.030, 0.062 mean 0.046	96-0197
Porterville (CA) Mitla Chili	WP	4	0.29	0.11	7	0.11, 0.086 mean 0.097	96-0246

[1] recovery from a spiked sample at the level of found residues was 75%

Leafy vegetables

Lettuce, spinach and mustard greens. In eight trials on head lettuce in Europe 3 foliar applications of an SC formulation were made at 7-day intervals at 0.144 kg a.i./ha ± 5% (Heydkamp, 2000). Single samples of head lettuce were taken 3, 7, 14 and 21 days after the last application. The validated analytical method was GLC with specific thermoionic detection (Quintelas, 2000). The LOQ was 0.02 mg/kg. The SAI was up to 10 months. The results are shown in Table 24.

Table 24. Residues of tebufenozide resulting from supervised trials on head lettuce in Europe in 1999 (Heydkamp, 2000).

Country, location, variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form.	No.	kg ai/ha	kg ai/hl			
Italy, Callepio di Settala (MI), Batavia/Dublin	SC	3	0.144	0.0144	3 7 14 21	0.72 0.05 <0.02 <0.02	VP98-1-33I1
Italy, Triginto di Mediglia (MI), Iceberg/Camaro	SC	3	0.144	0.0144	3 7 14 19	1.9 1.8 0.06 0.05	VP98-1-33I2
France, Manziat Romana/Feuille de Chêne	SC	3	0.144	0.0144	3 7 14 21	1.0 0.17 0.06 <0.02	VP98-1-33F3

Country, location, variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form.	No.	kg ai/ha	kg ai/hl			
France, Lucenay Batavia	SC	3	0.144	0.0144	3 7 14 21	1.5 0.18 0.25 0.12	VP98-1-33F4
Spain, La Palma (Murcia) Iceberg/Lluma	SC	3	0.144	0.0144	3 7 14 21	2.1 0.59 0.34 0.15	VP98-1-33E5
Spain, Almusafes Batavia/Empire	SC	3	0.144	0.0144	3 7 14 21	1.8 0.92 0.59 0.37	VP98-1-33E6
Spain, Castellar (Val) Iceberg	SC	3	0.144	0.0144	3 7 14 21	4.2 2.4 0.67 0.21	VP98-1-33E7
Spain, Castellar (Val) Inverna	SC	3	0.144	0.0144	3 7 14 21	4.9 2.6 0.83 0.40	VP98-1-33E9

Tables 25 to 28 show previously submitted residue data (JMPR 1996) on head lettuce, leaf lettuce, spinach and mustard greens from US trials conducted according to currently approved US GAP. These results could not be evaluated in 1996 because US GAP was pending. The SAIs in head and leaf lettuce ranged from 264 to 1186 in trials by Chen, and from 178 to 344 days in trials by Dong. The SAI in spinach was about 750 days and in mustard greens ranged from 139 to 930 days.

Table 25. Previously submitted data for residues of tebufenozide in head lettuce in the USA.

Location Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
NJ, 1991	SC	7	0.14	0.043	0 7	0.03[1], 0.48 0.009[1], <u>0.092</u>	Chen, 1994a
CA, 1993	SC	7	0.14	0.042	0 7 14	0.41 <u>0.14</u> 0.009	Chen, 1994a
CA, 1991	SC	8	0.14	0.075	0 7	1.7[1], 5.1 0.053[1], <u>0.83</u>	Chen, 1994a
FL, 1991	SC	8	0.14	0.019-0.03	0 7 14	0.09[1], 1.0 0.018[1], <u>0.9</u> 0.006[1], 0.02	Chen, 1994a
TX, 1992	SC	9	0.14	0.044	0 7	1.5[1] <u>0.29</u>	Chen, 1994a
CA, 1994	SC	7	0.14	0.037	0 7	3.0 <u>2.3</u>	Dong, 1995a
CA, 1994	WP	7	0.14	0.037	0 7	3.8 <u>6.6</u>	Dong, 1995a
AZ, 1994	SC	7	0.14	0.05	0 7	3.5 <u>3.2</u>	Dong, 1995a
AZ, 1994	WP	7	0.14	0.050	0 7	4.4 <u>2.7</u>	Dong, 1995a

[1] Head without wrapper leaves

Table 26. Previously submitted data for residues of tebufenozide in leaf lettuce in the USA.

Location Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
NJ, 1991	SC	7	0.14	0.043	0 7	3.5 2.2	Chen, 1994a
CA, 1991	SC	8	0.14	0.042	0 6	5.7 1.7	Chen, 1994a
FL, 1991	SC	8	0.14	0.019	0 7	0.88 0.41	Chen, 1994a
TX, 1991	SC	9	0.14	0.044	0 7	2.7 0.69	Chen, 1994a
CA, 1994	SC	7	0.14	0.025	0 7	3.7 1.1	Dong, 1995a
CA, 1994	WP	7	0.14	0.025	0 7	3.5 2.5	Dong, 1995a
AZ, 1994	SC	7	0.14	0.050	0 7	3.3 3.2	Dong, 1995a
AZ, 1994	WP	7	0.14	0.05	0 7	3.6 2.6	Dong, 1995a

Table 27. Previously submitted data for residues of tebufenozide in spinach in the USA.

Location Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
VA, 1991	SC	6	0.14	0.05-0.058	0 7	10 7.1	Chen, 1994a
AZ, 1993	SC	7	0.14	0.074-0.076	0 7 14	4.4 0.99 0.13	Chen, 1994a
OK, 1993	SC	7	0.14	0.050-0.052	0 7	5.1 1.3	Chen, 1994a
CA, 1991	SC	8	0.14	0.075	0 7	5.5 8.1	Chen, 1994a
TX, 1992	SC	9	0.14	0.044	0 7	15 2.7	Chen, 1994a
CA, 1994	SC	7	0.14	0.025	0 7	7.0 3.9	Dong, 1995a
CA, 1994	WP	7	0.14	0.025	0 7	7.0 3.3	Dong, 1995a
TX, 1994	SC	7	0.14	0.05	0 7	8.3 3.8	Dong, 1995a
TX, 1994	WP	7	0.14	0.05	0 7	7.0 4.2	Dong, 1995a

Table 28. Previously submitted data for residues of tebufenozide in mustard greens in the USA.

Location Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
NJ, 1992	SC	7	0.14	0.043	7	5.6	Chen, 1994b
NJ, 1993	SC	7	0.14	0.043	0 7	4.1 1.6	Chen, 1994b
AZ) 1993/1994	SC	7	0.14	0.060	0 7 14	7.1 2.6 1.6	Chen, 1994b
CA, 1991	SC	8	0.14	0.075	0 7	8.2 3.9	Chen, 1994b
CA, 1991	SC	8	0.14	0.075	0 7	5.5 6.9	Chen, 1994b
CA, 1991	SC	8	0.14	0.075	0 7	5.6 4.4	Chen, 1994b

	Application						
CA, 1994	SC	7	0.14	0.025	0 7	4.3 0.65	Dong, 1995b
CA, 1994	WP	7	0.14	0.025	0 7	2.5 0.93	Dong, 1995b
TX, 1994	SC	8	0.14	0.050-0.075	0 7	5.1 1.9	Dong, 1995b
TX, 1994	WP	8	0.14	0.050-0.075	0 7	6.8 2.4	Dong, 1995b

The previously submitted residues from one trial on Chinese kale in Thailand are shown in Table 29. According to the manufacturers, this trial was in compliance with current GAP in Thailand (5 applications of 0.30 kg ai/ha, PHI 14 days), but no independent confirmation was reported to the JMPR.

Table 29. Previously submitted data for residues of tebufenozide in Chinese kale, Thailand, 1993.

Application				PHI	Residue,	Reference
Form.	No.	kg ai/ha	kg ai/hl	days	mg/kg	
SC	5	0.25	0.033-0.053	0 3 5 10 15	17.2 8.8 5.2 1.5 0.88	Ishii and Higuchi, 1993

Turnip greens and roots. In six new field trials on turnips in geographically representative areas of the USA in 1996 4 foliar applications of a WP formulation of tebufenozide were made at 0.295 ± 5% kg ai/ha at approximately 7-day intervals (Dorschner and Breuninger, 1998b). At three of the sites (GA, OH, TN), two separate plots were treated and root samples collected from one plot and foliage samples (turnip greens) from the other. At the TX site, plots were divided into two sub-plots, and tops and roots were harvested from different sub-plots. At the sites in CA and SC, both roots and tops were collected from the same plot but separated into two samples. In each of the trials, replicate samples of roots and tops were collected 6-8 days after the last application.

All root and foliage samples were analysed for tebufenozide by method TR 34-94-41 (Chen *et al.*, 1994c). The analytical laboratory made slight modifications during analyses. The LOQ was 0.01 mg/kg. The longest SAI was 244 days. Storage stability was demonstrated in turnip greens and roots stored frozen for 279 days. The results for turnip greens are given in Table 30 and for roots in Table 31.

Table 30. Residues of tebufenozide in turnip greens resulting from supervised trials in the USA, 1996 (Dorschner and Breuninger, 1998b).

Location, variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form.	No.	kg ai/ha	kg ai/hl			
Tifton (GA) Purple Top	WP	4	0.29	0.11	8	1.3, 1.3 mean 1.3	96-GA*04
Charleston (SC) Purple Top White Globe	WP	4	0.30	0.09	7	2.6, 1.5 mean 2.1	96-SC*01
Weslaco (TX) Purple Top White Globe	WP	4	0.31	0.11	6	8.3, 6.4 mean 7.4	96-TX*02
Celeryville (OH) Purple Top	WP	4	0.30	0.04	7	0.57, 0.31 mean 0.44	96-OH*03
Salinas (CA) Purple Top White Globe	WP	4	0.29	0.10, 0.08, 0.04, 0.04	8	0.34, 0.34 mean 0.34	96-CA*04

Location, variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form.	No.	kg ai/ha	kg ai/hl			
Crossville (TN) Purple Top White Globe	WP	4	0.29	0.12	7	2.1, 2.1 mean 2.1	96-TN02

Table 31. Residues of tebufenozide in turnip roots resulting from supervised trials in the USA, 1996 (Dorschner and Breuninger, 1998b).

Location variety	Application				PHI days	Residue, mg/kg	Report no.
	Form.	No.	kg ai/ha	kg ai/hl			
Tifton (GA) Purple Top	WP	4	0.29	0.11	8	0.18, 0.17 mean 0.18	96-GA*04
Charleston (SC) Purple Top White Globe	WP	4	0.30	0.09	7	0.09, 0.07 mean 0.08	96-SC*01
Weslaco (TX) Purple Top White Globe	WP	4	0.31	0.11	6	0.21, 0.23 mean 0.22	96-TX*02
Celeryville (OH) Purple Top	WP	4	0.30	0.040	7	0.02, 0.02 mean 0.02	96-OH*03
Salinas (CA) Purple Top White Globe	WP	4	0.29	0.10, 0.08, 0.04, 0.04	8	0.02, 0.03 mean 0.02	96-CA*04
Crossville (TN) Purple Top White Globe	WP	4	0.29	0.12	7	0.06, 0.12 mean 0.09	96-TN02

Celery. The previously submitted residue data (JMPR 1996) on celery from trials complying with currently approved US GAP are shown in Table 32. These data could not be evaluated in 1996 because US GAP was pending. In all except two trials only stalk samples were analysed. The SAI ranged from 71 to 525 days.

Table 32. Previously submitted data for residues of tebufenozide in celery in the USA.

Location Year	Application				PHI days	Residue, mg/kg	Reference
	Form.	No.	kg ai/ha	kg ai/hl			
MI, 1992	SC	7	0.14	0.045-0.047	0 6	1.4 0.47	Chen, 1994a
FL, 1992/1993	SC	7	0.14	0.015	9	0.1	Chen, 1994a
CA, 1993	SC	7	0.14	0.030	0 7	2.3[1], 0.29 1.3[1], 0.49	Chen, 1994a
CA, 1994	SC	7	0.14	0.025	0 7	0.38 0.64	Dong, 1995a
CA, 1994	WP	7	0.14	0.025	0 7	0.47 0.6	Dong, 1995a
MI, 1993	SC	8	0.14	0.050-0.055	0 6 13	1.2 1.2 0.64	Chen, 1994a
CA, 1993	SC	8	0.14	0.075	0 7	1.2[1], 0.15 0.41[1], 0.09	Chen, 1994a
MI, 1993	SC	8	0.14	0.100-0.111	0 6 13	4.5 3.2 1.5	Chen, 1994a
FL, 1995	SC	9	0.14	0.05	0 7	0.08 0.04	Dong, 1995a
FL, 1995	WP	9	0.14	0.05	0 7	0.08 0.05	Dong, 1995a

[1] stalk with foliage

Grasses

One field trial was conducted on sugar cane in the USA in 1994 with the SC formulation and seven in 1995 with the WP (Filchner, 1997a,b). In two further 1997 US field trials SC and WP formulations were compared (Bergin, 1998). Four foliar applications were made at the US GAP rate of 0.28 kg ai/ha at intervals of 14 to 21 days. Duplicate samples of sugar cane stems were collected 13-14 days after the last application. Residue decline was determined in 2 trials in 1995, and extra samples for processing were collected in the 1994 and 1997 trials.

Analyses were by method TR 34-94-41 (Chen *et al.*, 1994c) in 1994 and TR 34-95-66 (Deakyne *et al.*, 1995) in 1995. Both methods were adapted by the addition of a carbon solid phase clean-up to achieve an LOQ of 0.01 mg/kg. Samples from the 1997 trials were analysed by method TR 34-97-115 (Filchner and Deakyne, 1997), which has an LOQ of 0.01 mg/kg. The results are shown in Table 33. The SAI ranged from 115 to 404 days.

Table 33. Residues of tebufenozide in sugar cane stems resulting from supervised trials in the USA.

Year, location variety	Application				PHI days	Residue, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
1994, Washington (LA) 357	SC	4	0.28	0.20	14	0.31, 0.25 mean <u>0.28</u>	Filchner, 1997b 94-0168
1995, Church Point (LA) CP 70-321	WP	4	0.30	0.31	14	0.11, 0.14 mean <u>0.12</u>	Filchner, 1997a 95-0182
1995, Simmsport (LA) CP65-357	WP	4	0.29	0.31	13	0.10, 0.14 mean <u>0.12</u>	Filchner, 1997a 95-0192
1995, Cheneville (LA) CP65-357	WP	4	0.29	0.31	7 13 20 27	0.046, 0.066 mean 0.056 0.16, 0.16 mean <u>0.16</u> 0.10, 0.14 mean 0.12 0.068, 0.092 mean 0.080	Filchner, 1997a 95-0193
1995, Moorehaven (FL) CP-1133	WP	4	0.29	0.15	14	0.036, 0.034 mean <u>0.035</u>	Filchner, 1997a 95-0275
1995, Belleglade (FL) CP-1210	WP	4	0.29	0.15	14	0.032, 0.032 mean <u>0.032</u>	Filchner, 1997a 95-0276
1995, Belleglade (FL) CP-1210	WP	4	0.29	0.15	7 14 21 28	0.036, 0.023 mean 0.030 0.016, 0.010 mean <u>0.013</u> 0.000, 0.000 mean <0.01 0.006, 0.000 mean <0.01	Filchner, 1997a 95-0277
1995, Raymondville (TX) CP310	WP	4	0.29	0.31	14	0.055, 0.053 mean <u>0.054</u>	Filchner, 1997a 95-0280
1997, Port Allen (LA) CP-845	WP	4	0.29	0.24	13	0.63, 0.61 mean <u>0.62</u>	Bergin, 1998 97-0130
	SC	4	0.29	0.25	13	0.56, 0.52 mean <u>0.54</u>	Bergin, 1998 97-0130

<u>Tree nuts</u>

<u>Pecans</u>. Data on residues in pecans were submitted to the JMPR in 1996 but could not be evaluated since in 1996 the use of tebufenozide was not registered for any tree nuts except walnuts. US trials in 1993 on pecans that were within the range of the now-approved US GAP are shown in Table 34.

Table 34. Previously submitted US data on residues of tebufenozide in pecans (Cui and Desai, 1995b).

Location, Year	Application				PHI days	Residue, mg/kg
	Form.	No.	kg ai/ha	kg ai/hl		
TX, 1993	SC	6	0.28	0.035	0 14 28	<0.01 <0.01 <0.01
NM, 1993	SC	6	0.28	0.30	0 14 28	<0.01 <0.01 <0.01
AL, 1993	SC	6	0.28	0.019-0.031	0 14 28	<0.01 <0.01 <0.01
GA, 1993	SC	6	0.28	0.033	0 14 28	<0.01 <0.01 <0.01

In eight field trials on pecans in geographically representative areas of the USA in 1997 4 ground-applied foliar applications of either a WP or an SC formulation of tebufenozide were made at 0.54 kg/ha ± 5% (total application 2.1 kg ai/ha) at 14-83 day intervals (Bergin, 1999). Surfactant was tank-mixed with the WP formulation. Replicate samples of nuts were collected 14 days after the last application. The results are shown in Table 35.

All pecans were shelled and kernels were analysed for tebufenozide by the HPLC-UV method TR 34-95-20 (Cui and Desai, 1995a). The analytical laboratory made slight modifications during analyses. The LOQ was 0.01 mg/kg. The SAI ranged from 245 to 295 days.

Table 35. Residues of tebufenozide in pecan kernels resulting from supervised trials in the USA, 1997 (Bergin, 1999).

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Location, Variety	Application				PHI days	Residue, mg/kg	Trial no., appl. interval, days
	Form.	No.	kg ai/ha	kg ai/hl			
Cary (MS) Cape Fear	WP	4	0.54	0.10	14	<0.01, <0.01 mean <0.01	97-0114 17, 18, 42
Burr (TX) USDA 67-9-7	WP	4	0.54	0.10	14	<0.01, <0.01[1] mean <0.01	97-0115 14, 14, 53
Hawkinsville (GA) Stuart	WP	4	0.54	0.11	7 14 21 28	<0.01[1] <0.01, <0.01 mean <0.01 <0.01 <0.01	97-0110 $int^{7,14}$: 14, 48, 14 $int^{21, 28}$: 14, 34, 14
Silverton (TX), Western Sly	WP	4	0.54	0.10	14	<0.01, <0.01 mean <0.01	97-0129 14, 34, 14
Eastman (GA), Desirable	WP	4	0.54	0.09	14	<0.01, <0.01 mean <0.01	97-0113 21, 76, 20
	SC	4	0.54	0.09	14	<0.01, <0.01 mean <0.01	97-0113[2] 21, 62, 14
Hereford (TX), Wichita	WP	4	0.54	0.08	14	<0.01, <0.01 mean <0.01	97-0128 14, 19, 35
	SC	4	0.55	0.08	14	<0.01, <0.01 mean <0.01	97-0128 21, 14, 83

$int^{7,14}$: intervals for samples with PHIs of 7 and 14 days
$int^{21, 28}$: intervals for samples with PHIs of 21 and 28 days
[1] average of duplicate analyses
[2] surfactant was also inadvertently tank-mixed with the SC formulation

Almonds. In ten field trials in geographically representative areas of the USA in 1995/96 (Filchner, 1998) and 1998 (Yoshida, 1999) 4 foliar applications of either a WP or an SC formulation of tebufenozide at the maximum GAP rate of 0.54 kg/ha ± 5% (total application 2.1 kg ai/ha) were made with a first and second interval of 27-64 days and a third of 12-17 days in 1995/96, and 10-39-day intervals in 1998. Surfactant was tank-mixed. In all the trials, replicate samples of nuts were collected 14 days after the last application, and in all except one the hulls were removed in the field.

All kernel and hull samples were analysed by method TR 34-95-20 (Cui and Desai, 1994) with slight modifications. The LOQ was 0.01 mg/kg for the kernels. The SAI ranged from 174 to 330 days for the kernels and 164 to 549 days for hulls. The results are shown in Table 36.

Table 36. Residues of tebufenozide in almond kernels and hulls resulting from supervised trials in the USA.

Year, Location, Variety	Application				PHI days	Sample	Residue, mg/kg	Reference/appl. interval, days
	Form	No.	kg ai/ha	kg ai/hl				
1995, Arbuckle (CA) Non Pariel	WP	4	0.54	0.06	13	kernel hull	0.029, 0.040 mean 0.034 8.9, 7.9 mean 8.4	Filchner, 1998 95-0120 27, 35, 17
1995, Chico (CA) Non Pariel	WP	4	0.54	0.05	14	kernel hull	0.038, 0.052 mean 0.045 18, 16 mean 17	Filchner, 1998 95-0163 28, 48, 13
1995, Chico (CA) Non Pariel	WP	4	0.54	0.05	11	kernel hull	0.024, 0.034 mean 0.029 9.6, 9.5 mean 9.5	Filchner, 1998 95-0164 26, 45, 12
1995, Porterville (CA) Mission	WP	4	0.54	0.03	14	kernel	<0.01, <0.01 mean ≤0.01	Filchner, 1998 95-0165 33, 62, 14
1995 Sanger (CA) Butte	WP	4	0.54	0.03	14	kernel hull	0.023, <0.01 mean 0.017 12, 18 mean 15	Filchner, 1998 95-0174 29, 51, 12
1996, Madera (CA) Butte	WP	4	0.54[1]	0.06, 0.05, 2x 0.03	7 14 21 28	kernel hull kernel hull kernel hull kernel hull	0.050, 0.055 mean 0.052 22, 20 mean 21 0.036, 0.023 mean 0.029 10, 20 mean 15 0.038, 0.030 mean 0.034 12, 15 mean 14 0.030, 0.054 mean 0.042 21, 14 mean 17	Filchner, 1998 96-0184 28, 61, 15
1998, Terra Bella (CA) Non Pariel	WP	4	0.54	0.03	14	kernel hull	0.015, 0.032 mean 0.024 9.6, 12 mean 11	Yoshida, 1999 98-0319 [2] 14, 21, 14
	SC	4	0.54	0.03	14	kernel hull	<0.01, <0.01 mean ≤0.01 16, 16 mean 16	Yoshida, 1999 98-0319 [2] 14, 21, 14
1998, Brooks (CA) Carmel	WP	4	0.54	0.06	14	kernel hull	<0.01, 0.011 mean 0.010 23, 19 mean 21	Yoshida, 1999 98-0231 10, 39, 16
	SC	4	0.54	0.06	14	kernel hull	0.022, <0.01 mean 0.016 4.1, 16 mean 10	Yoshida, 1999 98-0231 10, 39, 16

[1] Second application was 17% low (0.49 kg ai/ha)
[2] Recovery from spiked kernel sample at 0.02 mg/kg was 61.1% (79.5% at 0.01 mg/kg)

Macadamia nuts. In six field trials in Australia from 1997 to 1999 5 foliar applications of a WP formulation of tebufenozide at a rate of 0.012 kg ai/hl, corresponding to 0.084 to 0.42 kg ai/ha, depending on the spray volumes used, were made to macadamia trees at intervals of 14 to 36 days

(14 to 111 days between the second and third). Single samples of nuts were collected 21, 28 and 35 days after the last application (Lewis and Vitelli, 2000).

All kernels samples were analysed for tebufenozide by method AL013/92-0 (Holzwarth and Schuld, 1993a) with GC-MS instead of GLC with NPD detection and slight modifications during analyses. The LOQ was 0.02 mg/kg. The SAI was up to 240 days (Table 37).

Table 37. Residues of tebufenozide in macadamia kernels resulting from supervised trials in Australia (Lewis and Vitelli, 2000).

Year, Location variety	Application				PHI days	Residue, mg/kg	Trial no/interval, days, between appl.
	Form.	No.	kg ai/ha	kg ai/hl			
1996/97, Kairi (Qld)	WP	5	hv[1]	0.006	21 28 35	<0.02 <0.02 <0.02	JME 231/97 [2-4] 15, 14, 14, 18
	WP	5	hv[1]	0.012	21 28 35	0.03 <0.02 0.03	JME 231/97 [2-4] 15, 14, 14, 18
1997/98, Wongabel (Qld) 344	WP	5	hv[1]	0.006	21 28 35	<0.02 <0.02 <0.02	JME 265/98 [4] 14, 111, 14, 14
	WP	5	hv[1]	0.009	21 28 35	<0.02 <0.02 <0.02	JME 265/98 [4] 14, 111, 14, 14
	WP	5	hv[1]	0.012	21 28 35	<0.02 <0.02 <0.02	JME 265/98 [4] 14, 111, 14, 14
1996/97, Bundaberg (Qld) A4	WP	5	hv[1]	0.006	21 28 32	<0.02 <0.02 <0.02	RAV 007/98 26, 31, 28, 36
	WP	5	hv[1]	0.012	21 28 32	0.02 <0.02 0.02	RAV 007/98 26, 31, 28, 36
1997/98, Bundaberg (Qld) 344	WP	5	0.21	0.006	21 28 35	0.03 <0.02 <0.02	RAV 051/98 28, 49, 19, 19
	WP	5	0.32	0.009	21 28 35	0.03 0.03 <0.02	RAV 051/98 28, 49, 19, 19
	WP	5	0.42	0.012	21 28 35	0.04 0.05 0.06	RAV 051/98 28, 49, 19, 19
1998/99, Bundaberg (Qld) 344	WP	5	0.13	0.006	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 28, 64, 20, 24
	WP	5	0.13	0.006	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 [2] 28, 64, 20, 24
	WP	5	0.13	0.030 (5x conc of 0.006)	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 28, 64, 20, 24
	WP	5	0.13	0.048 (8x conc of 0.006)	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 28, 64, 20, 24
	WP	5	0.26	0.012	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 28, 64, 20, 24
	WP	5	0.26	0.012	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 b 28, 64, 20, 24

Year, Location variety	Application				PHI days	Residue, mg/kg	Trial no/interval, days, between appl.
	Form.	No.	kg ai/ha	kg ai/hl			
	WP	5	0.26	0.060 (5x conc of 0.012)	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 28, 64, 20, 24
	WP	5	0.26	0.096 (8x conc of 0.012)	21 28 35	<0.02 <0.02 <0.02	RAV 073/99 28, 64, 20, 24
2000, Bundaberg (Qld) HAES 772	WP	5	0.17	0.012	0 14 21 28 35	0.03 <0.02 0.03 <0.02 0.03	RAV 113/00 14, 14, 13, 14
	WP	5	0.17	0.12 (as 10x conc of 0.012)	0 14 21 28 35	<0.02 <0.02 <0.02 <0.02 0.02	RAV 113/00 14, 14, 13, 14
	WP	5	0.25	0.18	0 14 21 28 35	0.08 0.05 0.06 0.05 0.03	RAV 113/00 14, 14, 13, 14

[1] high volume spray to the point of run-off, in trial RAV 007/98 spray volume was 2 l/tree
[2] a wetting adjuvant (BS 1000) was tank mixed
[3] tebufenozide was applied one day before 5th application, but heavy rain soon washed it off
[4] no weather data available

Rape (canola). In six field trials on rape in geographically representative areas of the USA and one in Canada in 1996 and 1997 four foliar applications of either the UL formulation (USA) or the SC formulation (Canada) of tebufenozide at the maximum US GAP rate of 0.28 kg/ha ± 5% were made at 12-15-day intervals. In all the trials, replicate samples of mature canola seed were collected 6-15 days after the last application. In addition, meal, soapstock and refined oil generated from canola were collected from two sites (Dorschner and Breuninger, 1998f).

All canola seed samples were analysed by the LC-MS method TR 34-96-135 (Wu *et al.*, 1996) with slight modifications. The LOQ was 0.01 mg/kg for the seed. The SAI ranged from 13 to 231 days. Storage stability was demonstrated for rape seed stored frozen for 236 days. The results are given in Table 38.

Table 38. Residues of tebufenozide in rape seed (canola) resulting from supervised trials in the USA and Canada (Dorschner and Breuninger, 1998f).

Country, year, location, variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form.	No.	kg ai/ha	kg ai/hl			
Canada, 1996, Minto (MB) 45A71	SC	4	0.29	0.14	6 (+8)[1]	0.29, 0.65 mean 0.47	96-MB04
US, 1996, Moxee (WA) Tobin	UL	4	0.28	0.074	9 9 9	0.95 1.6, 1.5 mean 1.6 1.1, 1.1 mean 1.1	96-WA*40/41/42[2, 3]
US, 1997, Tifton (GA) Bingo	UL	4	0.28	0.15	15	0.32, 0.30 mean 0.31	96-GA17 [4, 5]

Country, year, location, variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form.	No.	kg ai/ha	kg ai/hl			
US, 1996, Langdon (ND) Hyola 401	UL	4	0.27	0.15	14 (+7) [1]	0.49, 0.61, 0.47 mean 0.52	96-ND03
US, 1996, Carrington (ND) Hyola 401	UL	4	0.29	0.15	14	1.2, 1.1 mean 1.2	96-ND04

[1] After swathing, seed was left on the field to dry for several days. In ND, this mimics local commercial practice
[2] extremely hot and dry weather caused early crop maturation
[3] Silwet L-11 was added to each tank mix
[4] on the day of the last application it had rained 79 mm
[5] samples arrived thawed at the analytical laboratory 5 days after shipment

Mint. In five field trials in Wisconsin and Washington, USA, in 1996 (Table 39) 4 foliar applications of a WP formulation of tebufenozide at the maximum GAP rate of 0.295 kg ai/ha ± 5% were made at approximately 14-day intervals (Dorschner and Breuninger, 1998e). At the two Wisconsin sites an additional application was made because cool early season temperatures delayed maturity by approximately two weeks. In trial 96WI14, a frost killed the mint tops on the day of the first application. In all trials replicate samples of the foliage were collected 14 days after the last application. At two sites, additional foliage samples were collected for processing to oil. Foliage samples were analysed for tebufenozide by method TR 34-94-41 (HPLC-UV; Chen *et al.*, 1994c) with an additional clean up by Envi-Carbon solid-phase extraction and other slight modifications. The LOQ was 0.01 mg/kg. The SAI ranged from 155 to 200 days. Storage stability was demonstrated in mint foliage stored frozen for 279 days.

Table 39. Residues of tebufenozide in mint resulting from supervised trials in the USA, 1996 (Dorschner and Breuninger, 1998e).

Location variety	Application				PHI days	Residue, mg/kg	Trial no.
	Form.	No.	kg ai/ha	kg ai/hl			
Prosser (WA) Spearmint, Native	WP	4	0.29	0.10	14	8.2, 8.5 mean 8.4	96-WA*37
Mabton (WA) Spearmint, Native	WP	4	0.29	0.10, 0.08	14	8.0, 9.2 mean 8.6	96-WA*38
Mabton (WA) Pepermint	WP	4	0.29	0.08	14	8.2, 8.5 mean 8.3	96-WA*39
Marquette Co. (WI) Spearmint, Scotch	WP	5	0.30	0.15	14 (+1) [1]	6.0, 9.0 mean 7.5	96-WI13
Dalton (WI) Spearmint, Scotch	WP	5	0.30	0.15	14	2.9, 2.6 mean 2.8	96-WI14 [2]

[1] mint was collected after drying in field for 1 day
[2] frost killed the mint tops on day of first application

Animal feeding studies

Cows. Sixteen dairy cows, divided into groups of four, were dosed with tebufenozide (purity: 96.5%) with capsules at levels equivalent to 0, 6, 18 or 60 ppm ai in the diet for 28 consecutive days (Deakyne, 1996). Doses were based on the highest feed consumption over the previous 7 days: 25 kg (mean about 20 kg). One cow from each group was dosed for the 28 days before having a 3-day recovery period. Composited milk samples were taken from the morning and afternoon milkings. The sampling schedule was -1 day, 0 day and then at 3-day intervals to day 27 or day 30 (for the depurated

cows). No significant differences were noted in body weights between control and test animals during the quarantine and test periods. Autopsies showed no effects that appeared to be related to the test material.

Analytes for determination were selected from the significant residues found in the metabolism study in lactating dairy goats (JMPR 1996) and included tebufenozide, the free oxidation products RH-9886, RH-0282 and RH-2703, and fatty acid conjugates of RH-9886. In the metabolism study, multiple fatty acid conjugates of RH-9886 were identified. For residueanalysis the stearic acid conjugate (RH-9526) was synthesized for fortification purposes. Table 40 lists the analytes that were determined in each sample.

Table 40. Analytes determined in samples from cow feeding study.

Sample	Analyte				
	tebufenozide	RH-9886	RH-0282	RH-9526	RH-2703
Milk	X		X	X	
Meat	X	X	X		
Liver	X				X
Kidney	X	X	X		
Fat	X			X	

Samples were analysed by method TR 34-96-109 (Burnett *et al.*, 1996). The metabolite RH-9526 was, after hydrolysis, measured as RH-9886 and was used as a standard for all fatty acid conjugates of RH-9886. Milk samples were shaken vigorously by hand on the day of analysis; cream and skimmed milk were not analysed separately. For all analytes, the LOQ was 0.02 mg/kg in liver, kidney, muscle and fat, and 0.01 mg/kg in milk. SAIs were 183-250 days for milk, 151 days for liver, 240 days for meat and 274 days for fat. Table 41 shows the average residues of tebufenozide, RH-0282 and RH-9526 in milk in each dosed group and Table 42 the individual residues of tebufenozide and metabolites in the tissues.

Table 41. Average group residues (4 cows/group) by day in milk of cows fed tebufenozide.

Day	Tebufenozide, mg/kg	RH-0282, mg/kg	RH-9886[1], mg/kg
6 ppm feeding level			
-1	0[2]	0	0
0	0	0	0
3	0	0	0.004 (<LOQ)
6	0	0	0.005 (<LOQ)
9	0	0	0.003 (<LOQ)
13	0	0	0.002 (<LOQ)
16	0.002 (<LOQ)	0	0.003 (<LOQ)
20	0.002 (<LOQ)	0	0.004 (<LOQ)
23	0.003 (<LOQ)	0	0.004 (<LOQ)
27	0	0	0.002 (<LOQ)
30[3]	0	0	0
18 ppm feeding level			
-1	0	0	0
0	0.002 (<LOQ)	0.003 (<LOQ)	0
3	0.005 (<LOQ)	0	0.011
6	0.004 (<LOQ)	0	0.012
9	0.006 (<LOQ)	0.002 (<LOQ)	0.012
13	0.006 (<LOQ)	0.004 (<LOQ)	0.011
16	0.007 (<LOQ)	0	0.011
20	0.009 (<LOQ)	0	0.014
23	0.007 (<LOQ)	0	0.012
27	0.004 (<LOQ)	0	0.012
30[3]	0	0	0
60 ppm feeding level			

Day	Tebufenozide, mg/kg	RH-0282, mg/kg	RH-9886[1], mg/kg
-1	0	0	0.003 (<LOQ)
0	0.004 (<LOQ)	0	0.002 (<LOQ)
3	0.025	0.004 (<LOQ)	0.027
6	0.021	0.005 (<LOQ)	0.027
9	0.024	0.004 (<LOQ)	0.025
13	0.017	0.004 (<LOQ)	0.020
16	0.026	0.005 (<LOQ)	0.024
20	0.028	0.007 (<LOQ)	0.030
23	0.019	0.004 (<LOQ)	0.024
27	0.015	0.004 (<LOQ)	0.020
30[3]	0	0	0

[1] RH-9526 and all fatty acid conjugates of RH-9886 are reported as RH-9886
[2] A value of zero indicates that no peaks were detected and residues would be less than the LOD (<0.003 mg/l). All detected peaks were reported
[3] 3-day recovery

Table 42. Residues in tissue samples of 3 cows dosed with tebufenozide.

Sample	Dose (ppm)	Tebufenozide (mg/kg)	Metabolite A (mg/kg)	Metabolite B (mg/kg)
Fat			***RH-9526[1]***	
	6	0.029, 0.011 (2x)	0.005, 0.03, 0.02	
	18	0.109, <LOD, 0.063	0.007, 0.05, 0.02	
	60	0.063, 0.38, 0.23	0.15, 0.02, 0.012	
Muscle			***RH-9886***	***RH-0282***
	6	<LOD (3x)	<LOD (3x)	<LOD (3x)
	18	<LOD (2x), 0.022	<LOD (3x)	<LOD (3x)
	60	<LOD, 0.056, 0.028	0.003, 0.004, 0.005	0.008, 0.006 (2x)
Kidney			***RH-9886***	***RH-0282***
	6	<LOD (3x)	<LOD (3x)	<LOD (3x)
	18	<LOD (2x), 0.007	0.003 (2x), 0.004	0.005, 0.004, 0.009
	60	0.007, 0.006, 0.043	0.008, 0.007, 0.004	0.015, 0.014, 0.007
Liver			***RH-2703***	
	6	0.014, 0.008, 0.009	<LOD (3x)	
	18	0.041, 0.026, 0.014	<LOD (2x), 0.007	
	60	0.061, 0.101, 0.066	0.018, 0.066, 0.020	

LOQ for parent and metabolites 0.02 mg/kg, and LOD 0.006 mg/kg
[1] RH-9526 residues are reported as equivalent mg/kg of RH-9886, and represent all fatty acid conjugates of RH-9886.

Overall, residues of tebufenozide and the metabolites were at or below the LOQ in all samples except fat in the 2 lowest dose groups (6 and 18 ppm), and liver (mean 0.03 mg/kg) in the 18 ppm group. In fat both tebufenozide and RH-9526 were detected in all groups, the former at concentrations up to 0.03 mg/kg in the 6 ppm group and 0.1 mg/kg in the 18 ppm group. In the 60 ppm group tebufenozide levels were up to 0.03 mg/kg in milk, 0.04 mg/kg in kidney, 0.06 mg/kg in muscle, and 0.38 mg/kg in fat. No residues were detectable in milk, liver, muscle or kidney samples of any depurated cows, while in fat approximately 30% of the initial residue could still be detected.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Processing studies were carried out on citrus fruits, peaches, grapes, tomatoes, sugar cane, rape seed and mint.

Citrus fruits. In two US studies on oranges and grapefruit (Dong, 2000) the crops were field-treated with tebufenozide at the proposed GAP rate (Koals, 1999b, Koals and Carpenter, 2000). Samples of orange and grapefruit (about 375 kg) were harvested and stored cold for 3 days. RAC samples were first rinsed with water, then washed in a brush washer with a fruit-cleaning detergent. The washed fruit was stored under ambient conditions until the following day, when it was extracted in an extractor and continuously pumped into a finisher which removed the excess ruptured juice sacs. The resulting fresh juice was sampled for analysis.

The oil/water/peel emulsion from the juice extractor was passed through another finisher which removed peel frits. The remaining water/oil emulsion was stored for a minimum of 5 hours to separate the water which was removed from the concentrated oil emulsion. After further storage at 5°C and centrifugation, additional water was removed and the oil fraction frozen, thawed, filtered, treated with anhydrous sodium sulfate and then refiltered to remove any remaining water. The remaining cold-pressed oil was sampled for analysis.

The solid peel residue from the juice extractor was transferred to a peel hopper and chopped before a liquid lime slurry was added. A press separated the wet pulp into press cake and liquor. The press cake was dried with air at 143°C, resulting in dried pulp containing about 10% moisture with a minimum of charring which was sampled for analysis.

Processed samples were analysed by method TR 34-97-119 (Choo, 1997), with minor modifications for the oil fraction. Residues in the whole fruit, juice and dried pulp were quantified by HPLC-UV and in citrus oil by HPLC-MS. The LOQ was 0.02 mg/kg for all samples. The SAI ranged from 357 to 406 days. The results are shown in Table 43.

Table 43. Residues of tebufenozide in orange and grapefruit products, Windermere, Florida, USA, 1966.

Crop, variety	TTR kg ai/ha	PHI days	Sample	Residues mg/kg	Processing factor	Reference
Orange, Parson Brown	1.38	14	unwashed fruit	0.21[1]		Koals 2000
			washed fruit	0.030[2]	0.14	96-0241
			dried pulp	0.17[2]	0.82	Dong 2000
			juice	<0.02[2]	<0.10	
			oil	4.8[2]	23.1	
Grapefruit, Ruby Red	1.38	13	unwashed fruit	0.089[1]		Koals, 1999b
			washed fruit	0.023	0.26	96-0263, 24:Dong 2000
			dried pulp	0.070	0.79	
			juice	<0.02	<0.23	
			oil	2.6	29.2	

TTR: total treatment rate
[1] Mean of duplicate field samples
[2] Mean of duplicate analyses

Peaches. Peaches from two field trials in New Zealand (Baynon, 1998a) treated at 1 and 2 times the GAP rate were canned at a commercial cannery. The stone was removed, and the peeled and sliced fruit added to cans, followed by a fruit juice/water/sugar syrup. The cans were sealed and heated at temperatures approaching 100°C. Fresh and canned fruit and canned syrup were analysed by method TR 34-95-96 (Deakyne *et al.*, 1995), with an LOQ of 0.01 mg/kg. The SAI was 3 months. The results are shown in Table 44.

Table 44. Residues of tebufenozide in canned peaches, New Zealand, 1996-97 (Baynon, 1998a).

Location variety	TTR kg ai/ha	PHI days	Residue (mg/kg)			Processing factor for canned fruit	Trial no.
			fruit	canned fruit	canned syrup		
Hawkes Bay Golden Queen	0.72	15	0.10	<0.01	<0.01	<0.10	FSLHBRE 02
		22	0.10	<0.01	<0.01	<0.10	
	1.44	15	0.82	<0.01	<0.01	<0.01	
		22	0.47	<0.01	<0.01	<0.02	
Nelson Golden Queen	0.72	22	0.10	<0.01	<0.01	<0.10	FSLNRE05
	1.44	22	0.37	<0.01	<0.01	<0.03	

Grapes. Six processing trials were conducted on grapes harvested in Australia (Hamblin *et al.*, 2001) (Table 45). In Trial RTL 412, residues were found in juice but not in whole grapes, so processing factors could not be determined. No processing factors were calculated for the 0.22 kg ai/ha treatment in trial SCM296/99, since the residues in whole grapes (0.05-0.06 mg/kg) were too low to make accurate estimates.

In the trial with sultana grapes, berries treated at either 0.14 or 0.28 kg ai/ha were processed into raisins by first drying on commercial grape drying racks, then spraying on the rack with an emulsion of vegetable oil and potash (pH 9.5-11) which is used in Australian dried fruit production to facilitate drying by removing the grapes' waxy bloom. When the grapes had dried to 18% moisture they were removed from the rack and finish-dried for a day in direct sunlight. Bunch stems were removed by hand, leaving only raisins and their stems.

Wine and pomace samples were prepared by hand-crushing 1.5-2 kg of grapes from 4 trials. The mixture was inoculated with re-hydrated active wine yeast and fermented on the skins for 7 days at 20-25° C with daily mixing. The must was pressed twice, each time at 0.14 MPa for 3 minutes with mixing of the pomace between pressings. The wine (about 1-1.5 l) was fermented to dryness at 20-25°C. Except in trial PJH151, sulfur dioxide was added after fermentation at 0.1 g/kg and the must allowed to settle at 4°C until clear.

Juice was prepared by pressing of 600 g grapes twice at 0.14 MPa for 3 minutes with mixing of the pomace between pressings, yielding approximately 350 ml of juice.

Wine, pomace, juice and raisins were analysed for tebufenozide by method AL013/92-0 (Holzwarth and Schuld, 1993a) with GC-MS instead of GLC with an NPD; the LOQ was 0.01 mg/kg. The SAI was up to 9 months.

Table 45. Residues of tebufenozide in grapes and processed products, Australia, 1995-99 ((Hamblin *et al.*, 2001).

Year, Location, Variety	TTR kg ai/ha	PHI, days	Sample	Residues mg/kg	Processing factor	Trial no.
1995/96 Irymple (Vic) M12 Sultana	0.14	28	whole fruit dried fruit	0.15[1] 0.10[2]	- 0.62	SCM248/96[3]
	0.28	28	whole fruit dried fruit	0.39 0.34	- 0.87	SCM248/96[3]
1998/99 Dixons Cr. (Vic) Chardonnay	[4]	83, 90, 97	whole fruit pomace wine	0.24, 0.11, 0.09 1.2, 1.6, 0.57 0.04, 0.04, 0.01	- 5.0, 15[5], 6.3 0.17, 0.36, 0.11	RTL528/99
	[6]	21, 28, 35	whole fruit pomace wine	1.3, 0.72, 0.64 5.2, 3.9, 5.6 0.29, 0.14, 0.21	- 4.1, 5.5, 8.7 0.23, 0.19, 0.33	RTL528/99
1998/99Young (NSW) Firmint, Harslevelo	0.27	60, 67, 74	whole fruit pomace wine	0.18, 0.17, 0.12 0.44, 0.63, 0.74 0.03, 0.07, 0.04	- 2.4, 3.7, 6.2 0.17, 0.41, 0.33	PJH 285/99
	0.45	21, 28, 35	whole fruit pomace wine	1.5, 0.58, 1.2 2.5, 2.6, 3.2 0.24, 0.20, 0.24	- 1.6, 4.5, 2.7 0.16, 0.34, 0.20	PJH 285/99
1998/99 Coonawarra SA Shiraz	0.22	84, 91, 98	whole fruit pomace wine	0.06, 0.06, 0.05 0.49, 0.73, 0.61 0.06, 0.04, 0.04	- - -	SCM296/99
	0.37	21, 28, 35	whole fruit pomace wine	0.61, 0.81, 0.78 2.3, 1.8, 3.0 0.26, 0.20, 0.15	- 3.8, 2.3, 3.8 0.43, 0.25, 0.19	SCM296/99
	6 g/hl	0, 14, 28, 35	whole fruit juice pomace wine	1.3, 0.68, 0.27, 0.35 0.12, 0.07, 0.05, 0.08 4.05, -, -, 0.97 0.30, 0.21, 0.09, 0.04	- 0.09, 0.10, 0.19, 0.23 3.0, -, -, 2.8 0.22, 0.31, 0.33, 0.11	PJH151[7]
	12 g/hl	0, 14, 28, 35	whole fruit juice pomace wine	2.6, 2.2, 0.83, 0.71 0.19, 0.24, 0.13, 0.09 9.8, -, -, 2.6 0.50, 0.46, 0.19, 0.22	- 0.07, 0.11, 0.16, 0.13 3.8, -, -, 3.6 0.19, 0.21, 0.23, 0.31	PJH151[7]
	6 g/hl	0, 14, 28, 35	whole fruit juice	<0.01 <0.01, 0.06, 0.04, 0.03	- -	RTL412[7]
	12 g/hl	0, 14, 28, 35	whole fruit juice	<0.01 0.13, 0.09, 0.04, 0.12	- -	RTL412[7]

[1] mean of 0.09, 0.13, 0.22, 0.18 and 0.15
[2] mean of 0.06, 0.03, 0.13, 0.10 and 0.16
[3] in the control dried fruit samples, residues varied from <0.01 to 0.04 mg/kg
[4] 2 applications of 0.006 kg ai/hl, sprayed well in excess of run-off
[5] outlier according to Dixons test, not used to estimate the mean processing factor for pomace
[6] 3 applications of 0.006 kg ai/hl, 1st and 2nd sprayed well in excess of run-off, 3rd >0.18 kg ai/ha
[7] analytical data were included in the analytical report of trial SCM 248/96. No field reports available. Application rates were 0.006 and 0.012 kg ai/hl, number of treatments and interval(s) unknown.

Tomatoes. Residues in processed fractions of tomatoes treated with tebufenozide at the GAP rate in the USA, and at approximately twice the GAP rate in Europe are shown in Table 46.

In the US trial (Carpenter, 1997a), about 150 kg tomato fruit was first washed with water and chlorinated water and then crushed. The mash was heated to 99°C, then screened to remove the seed and peel fraction (wet pomace) and produce juice. The juice was condensed under vacuum to form purée (9% natural tomato soluble solids, NTSS) and then canned and heated to 94°C for 5 minutes. A sub-sample of the purée was further condensed under vacuum to form paste (25% NTSS), which was also canned and heated to 94°C for 5 minutes. Samples were analysed by method TR 34-95-66

(Deakyne *et al.*, 1995). The LOQ in tomatoes was 0.02 mg/kg; the method was not validated for processed commodities. The SAI was 242 ± 2 days.

Processed commodities were prepared from tomatoes collected from four supervised trials in France, Greece and Spain (Bürstell *et al.*, 1996). 5 kg of tomatoes were washed in water at 25°C with gentle motion for 1 minute. The ratio of tomatoes to water was 1:2. The tomatoes were then divided into 2 portions, one for canning, the second for processing into juice, purée and paste. The canning process was one which retained the peel, since this was expected to leave the highest residues in the processed fruit. Washed, unpeeled tomatoes were drained, the calyx was removed, and the peel pricked several times with a fork. The tomatoes in jars filled with 1% salt water were then sterilized at 115-120°C for 20 minutes. The fruit and preserving liquid were later separated for analysis.

The second portion of washed tomatoes was chopped and blanched. A tenfold volume of water was added to the chopped fruit in a saucepan and the mixture heated to 70°C for 2-5 minutes. After blanching, the mashed pulp was separated from the pomace fraction (skin, pith and seeds) by sieving. After separation, part of the pulp was used to produce paste, and part for juice. To prepare paste, the sieved pulp was rotary-evaporated at a pressure of 300-100 mbar and a maximum water bath temperature of 65°C until the volume had been reduced to about one fifth. The paste was then bottled and sterilized by heating in an oven at 115-120°C for 20 minutes. Tomato juice was prepared by heating the sieved pulp in an oven at 113-117°C for 15 minutes.

All tomato samples were analysed by the GC-MS method AL 013/92-0 (Holzwarth and Schuld, 1993a-c). The LOQ was 0.02 mg/kg for fruit and fractions from the processing except juice, wash water and canning liquid where the LOQ was 0.01 mg/kg. The SAI ranged from 185 to 252 days.

Table 46. Residues of tebufenozide in tomatoes and processed products.

Country, year, location, variety	TTR kg ai/ha	PHI days	Sample	Residues mg/kg	Processing factor	Reference
US, 1996, Porterville (CA) 88-90	1.16	7	unwashed fruit washed fruit purée paste	0.35 0.090[1] 0.11[1] 0.29[1]	- 0.26 0.31 0.83	Carpenter 1997b 96-0249 [2,3]
France, 1995, St.Sixte (Midi-Pyrénées) Cannery row	1.08	3	unwashed fruit washed fruit wash water juice, unsterilized juice, sterilized wet pomage fruit, preserved canning liquid paste	0.24, 0.27 0.08, 0.12 <0.01, <0.01 0.05, 0.05 0.05, 0.06 0.24, 0.29 0.07, 0.08 0.01, 0.02 0.18, 0.20	- 0.33, 0.44 0.21, 0.22 0.29, 0.30 0.75, 0.74	Bürstell, 1996 FRA 00 01/ FRA 00 02

Country, year, location, variety	TTR kg ai/ha	PHI days	Sample	Residues mg/kg	Processing factor	Reference
Greece, 1995, Korifi (Macedonia) Rio Grande	1.08	3	unwashed fruit	0.18	-	Bürstell, 1996 GRC 00 01
			washed fruit	0.07	0.39	
			wash water	<0.01		
			juice, unsterilized	0.03		
			juice, sterilized	0.03	0.17	
			wet pomage	0.25		
			fruit, preserved	0.06	0.33	
			canning liquid	0.01		
			paste	0.13	0.72	
Spain, 1995, Brenes/Sevilla (Andalucia) Red Hunter	0.72	3	unwashed fruit	0.25	-	Bürstell, 1996 ESP 00 01
			washed fruit	0.09	0.36	
			wash water	<0.01		
			juice, unsterilized	0.03		
			juice, sterilized	0.03	0.12	
			wet pomage	0.31		
			fruit, preserved	0.05	0.20	
			canning liquid	<0.01		
			paste	0.15	0.60	

[1] mean of two laboratory replicates
[2] almost all of the fruit used for processing came from the field sample which had a residue of 0.35 mg/kg. In the replicate field sample, approximately 95% of the tomatoes were green and unsuitable for processing.
[3] no validation data for analysis of processed commodities available for the method used

Sugar cane. Four processing studies were conducted with sugar cane harvested from supervised trials according to GAP, two (trials 94-0168 and 95-0291) in the state of Hawaii (Filchner, 1997a,b) and two (both from trials 97-0130) in Louisiana (Bergin, 1998).

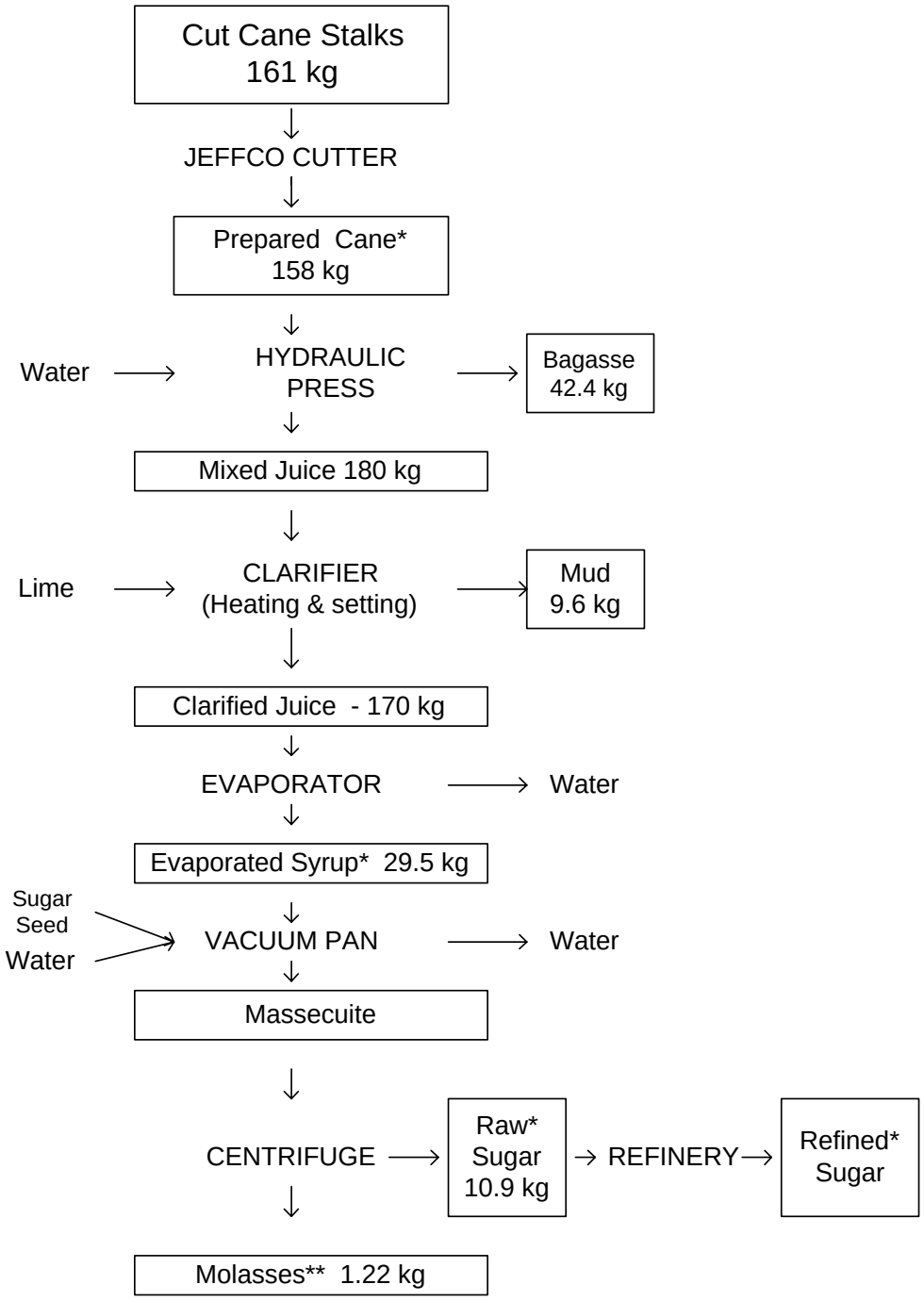
The processing procedures were the same in all the trials, although the samples analysed differed. The cane was processed into molasses and sugar by the procedure shown in Figure 2. The cane was chopped and, after water was added, pressed to produce juice and bagasse. The juice was mixed with lime, boiled for 3 minutes and then allowed to settle for 1 hour in the clarifier, yielding mud and clarified juice. In the evaporator the juice is concentrated to syrup, which is mixed with water and sugar seed in a vacuum pan and concentrated by boiling under vacuum to obtain A-strike massecuite. The massecuite is centrifuged to produce A-strike raw sugar and A-strike molasses (A-strike process). The A-strike molasses is blended with additional syrup, water and sugar seed and again concentrated in a vacuum pan to yield B-strike massecuite, which is centrifuged to produce B-strike raw sugar and B-strike molasses (B-strike process). The B-strike molasses and additional syrup, water and sugar seed are concentrated under vacuum to C-strike massecuite which is crystallized. The cured C-strike massecuite from the crystallizer is centrifuged to produce C-strike raw sugar and C-strike (final) molasses (C-strike process). Refined sugar was prepared from raw sugar dissolved in pure water. In trials 94-0168 and 95-0291 only the A-strike raw sugar was used for processing to refined sugar, whereas in trial 97-0130 A- and B-strike raw sugars were used. The raw sugar syrup was decolorized with activated charcoal, filtered and evaporated to crystallize the refined sugar, which was separated by centrifugation. Figure 2 shows the weights of the individual fractions isolated in the 1994 trial; the weight distribution was similar in the other 3 trials.

Method TR 34-95-66 (Deakyne *et al.*, 1995) was used in trial 95-0291, method TR 34-94-41 (Chen *et a.l*, 1994c) in trial 94-0168, and method TR 34-97-115 (Filchner and Deakyne, 1997) in trial 97-0130. The LOQ was 0.01 mg/kg in all methods. The SAI ranged from 115 to 169 days in trials 94-0168 and 97-0130 and was 397 days in trial 95-0291. The results are shown in Table 47.

Table 47. Residues of tebufenozide in sugar cane and processed products, USA.

Year, location variety	TTR kg ai/ha	PHI days	Sample	Residues, mg/kg	Processing factor	Reference
1994, Washington (LA), 357	1.12 (SC)	14	sugar cane	0.28[1]	-	Filchner, 1997b 94-0168
			raw sugar A	0.017[2]	0.06	
			raw sugar B	0.054	0.19	
			raw sugar C	0.060	0.21	
			refined sugar	<0.01[2]	<0.04	
			final molasses	0.32[2]	1.1	
			molasses A	0.49	1.75	
			molasses B	0.53	1.9	
			molasses blend	0.35	1.25	
			evaporated syrup	0.22	0.79	
1995, Waialua (HI), 73-6110	1.16 (WP)	14	sugar cane	-[3]	-	Filchner, 1997a 95-0291
			refined sugar	<0.01[2]	-	
			raw sugar	0.016[2]	-	
			final molasses	0.70[1]	-	
1997, Port Allen (LA), CP-845	1.16 (SC)	13	sugar cane	0.54[1]	-	Bergin, 1998 97-0130
			burned stems	0.27[1]	0.50	
			raw sugar A	0.26	0.48	
			raw sugar B	0.30	0.55	
			refined sugar	<0.01[2]	<0.019	
			final molasses	4.9[2]	9.0	
1997, Port Allen (LA), CP-845	1.16 (WP)	13	sugar cane	0.62[1]	-	Bergin, 1998 97-0130
			burned stems	0.29[1]	0.47	
			raw sugar A	0.24	0.39	
			raw sugar B	0.33	0.53	
			refined sugar	<0.01[2]	<0.016	
			final molasses	4.7[2]	7.6	

[1] mean of duplicate field samples
[2] mean of analytical duplicates
[3] no RAC sample was taken for analysis so processing factors cannot be calculated.



* Sampling points for analysis.
**Molasses returned to the vacuum pan to isolate one or more additional batches of raw sugar before the final molasses fraction is isolated; final molasses is subsampled for analysis.

Figure 2. Sugar cane processing scheme.

Rape seed (Canola). Treated and untreated canola seed was processed into refined oil (Dorschner and Breuninger, 1998f) by a small-scale process (Figure 3). Canola seeds were dried in an oven at 54-71°C to a moisture content of 7-10%. After aspiration and screening to separate foreign particles, whole cleaned seeds were flaked, heated to 82-99°C for 10-15 minutes, and then pressed in an expeller to liberate most of the crude oil. Residual crude oil remaining in the solid material

(presscake) was extracted by submerging three times in hexane at 43-52°C for 15-30 minutes and subsequent draining. After the final draining, warm air was forced through the extracted presscake to remove residual hexane. The final solvent-extracted presscake is the meal fraction. The drained crude oil/hexane mixture (miscella) was heated to 73-90°C to remove hexane.

Crude oil recovered from the expeller and from solvent extraction was combined and refined. It was first treated with phosphoric acid (40-45°C, 30 min, stirred at 70 rpm). After the addition of NaOH, the solution was mixed (40-45°C, 250 rpm; 20 min, and 60-65°C, 70 rpm, 10 min). The neutralized oil was allowed to settle for 1 hour at 60-65°C and then overnight in a refrigerator. The refined oil was decanted and filtered; the solid fraction is soapstock. All samples were analysed by method TR 34-96-135 (Wu *et al.*, 1996). The LOQ was 0.01 mg/kg for the seed and meal and 0.03 mg/kg for soapstock and oil. The longest SAI was 68 days for oil and meal fractions and 20 days for soapstock. Storage stability was demonstrated in oil stored frozen for 83 days, and meal for 90 days. The results are shown in Table 48.

Table 48. Residues of tebufenozide in processed rape (canola) seed products, USA, 1996 (Dorschner and Breuninger, 1998f).

Location, Variety	TTR kg ai/ha	PHI days	Sample	Residues, mg/kg	Processing factor	Trial no.
Moxee (WA) Tobin	1.12	9	seed meal soapstock refined oil	0.95 0.11 1.2 2.6	- 0.12 1.3 2.7	96-WA*40
Langdon (ND) Hyola 401	1.09	14 (+7) [1]	seed meal soapstock refined oil	0.52[2] 0.10 0.46 0.95	- 0.19 0.88 1.8	96-ND03

[1] After swathing, rape seed was left in the field to dry for 7 days. In ND, this mimics local commercial practice
[2] Mean of 3 replicate field samples (0.47, 0.61, 0.49)

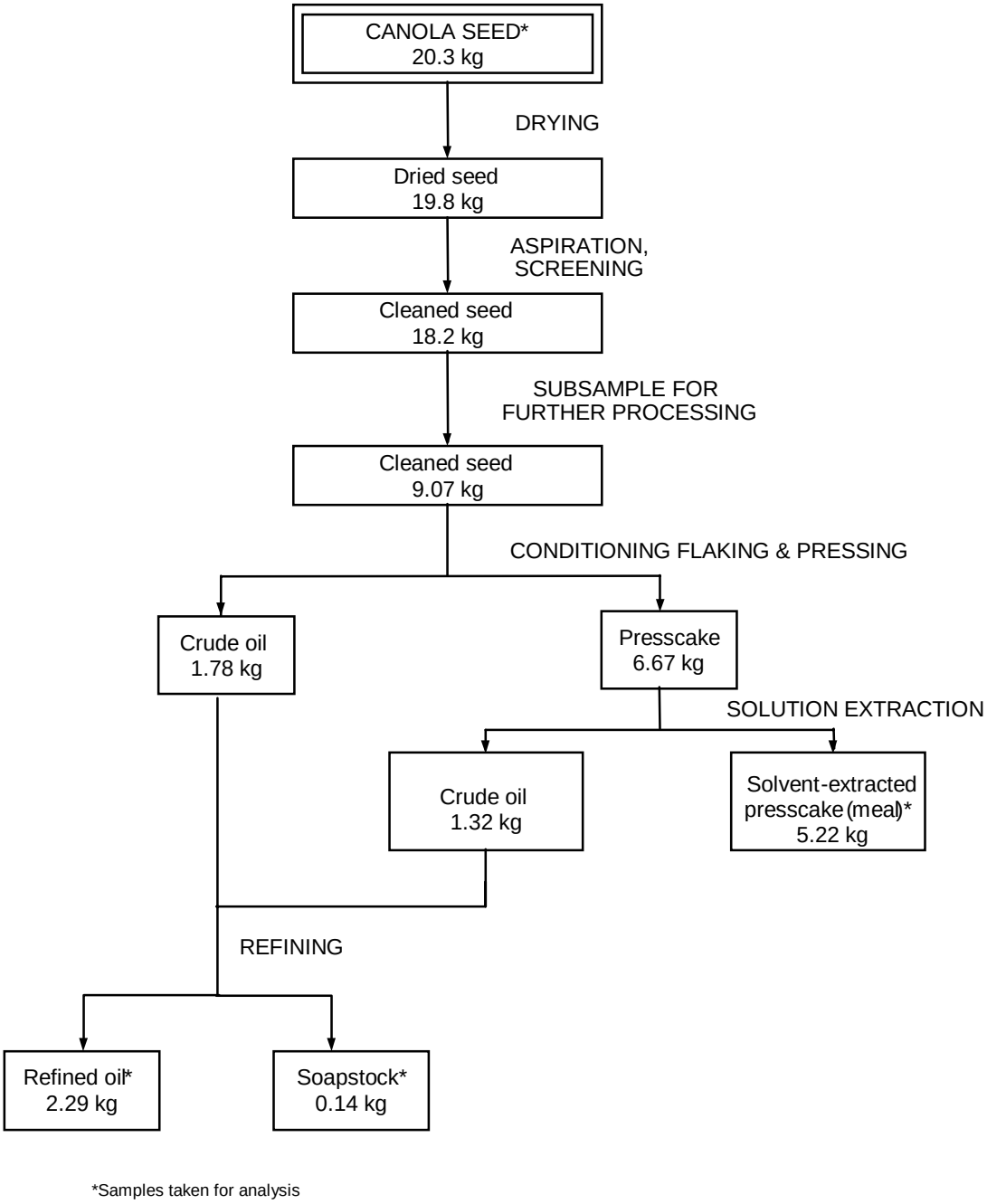


Figure 3. Rape seed processing.

Mint. Mint oil was producted from mint treated at the GAP rate in the USA in 1996 (Dorschner and Breuninger, 1998e) by steam distillation of the treated foliage according to a standard protocol. Approximately 3 kg of leaves in a cloth mesh bag were transferred to an electric boiler connected to a condenser and separator. The mint sample was tightly packed in the boiler to ensure that steam would pass through the sample. Steam was blown into the boiler and the distillate passed through the water-cooled condenser into a separatory funnel. After 1 hour the steam flow was disconnected and the water drained from the funnel. The oil was sampled and analysed by method TR 34-96-135 (Wu *et al.*, 1996), with an LOQ of 0.02 mg/kg. A Florisil clean-up to remove residual oil was added before basic alumina chromatography. The SAIs for mint oil were 225 and 273 days. Storage stability was demonstrated in mint oil stored frozen for 285 days.

Table 49. Residues of tebufenozide in mint and mint oil, USA, 1996 (Dorschner and Breuninger, 1998e).

Location, Variety	TTR kg ai/ha	PHI days	Sample	Residues, mg/kg	Processing factor	Trial no.
Prosser (WA) Spearmint, Native	1.16	14	leaves and stems oil	8.4[1] 0.33	- 0.04	96-WA*37
Marquette Co. (WI) Spearmint, Scotch	1.50	14 (+1) [2]	leaves and stems oil	7.5[1] 0.12	- 0.02	96-WI13

[1] mean of field duplicates
[2] the mint was collected after drying in the field for 1 day

Residues in the edible portion of food commodities

The available information is reported in the previous section.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported by the manufacturers.

Commodity	Country	MRL, mg/kg
Avocado	New Zealand	0.5
Bush berries, caneberries (excluding grapes and cranberries)	USA	3
Citrus	Brazil	0.5
Citrus	Greece	1
Citrus	Italy	1
Citrus	Morocco	0.5
Citrus	Portugal	1
Clementine, Mandarin	Spain	1
Citrus	Tunisia	0.5
Citrus	Uruguay	0.5
Cranberries	USA	1
Fruiting vegetables, other than cucurbits	USA	1
Eggplant	Belgium	0.2
Peppers	Belgium	0.2
Peppers	Mexico	1
Peppers	Spain	1
Tomato	Argentina	0.5
Tomato	Belgium	0.2
Tomato	Brazil	0.5
Tomato	Mexico	1
Tomato	Spain	1
Tomato	Uruguay	0.5
Grapes Dried grapes Grape pomace, dry	Australia	2 4 10
Head and stem Brassica Leafy Brassica vegetables	USA	5 10
Cabbage species	Switzerland	0.5
Kale	Brazil	2

Commodity	Country	MRL, mg/kg
Kale	Uruguay	2
Leafy green vegetables Leaf petioles (including celery)	USA	10 2
Lettuce	Switzerland	1
Spinach	Switzerland	1
Turnip, garden	USA	0.3 roots 9 greens
Mint	USA	10
Rape seed (Canola) Rape seed oil, edible	USA	2 4
Stone fruits excluding cherries	New Zealand	0.5
Sugar cane Sugar cane molasses	USA	1 3
Tree nuts including pistachio	USA	0.1 25 almond hulls
Walnut	France	0.5
Walnut	Mexico	0.1
Milk	USA	04**
Meat (from mammals other than marine mammas)	USA	08**
Edible offal (Mammalian)	USA	08**
Mammalian fats (except milk fats)	USA	0.1**

**includes residues of tebufenozide and its 3 metabolites

The Meeting was informed that the following MRLs for tebufenozide were pending.

Commodity name	Country	MRL, mg/kg
Avocado	Australia	1
Citrus	Australia	1
Citrus fruits	USA	0.8, oil 15
Lettuce	Spain	1.0
Macadamia nuts	Australia	0.05

APPRAISAL

The insecticide tebufenozide was first evaluated by the 1996 JMPR, which recommended MRLs for grapes, pome fruits, husked rice and walnuts. In 1997, an additional MRL for kiwifruit was recommended, and in 1999 data on pome fruits and grapes were re-evaluated. The present Meeting received information requested by the 1996 JMPR, including information about rotational crops, animal feeding studies, storage stability and data on residues on raisins. Furthermore, the results of new supervised trials and analytical methods for new and previously considered commodities were submitted, and information on currently registered GAP was provided.

The abbreviations used for metabolites are as follows:

RH-5992	tebufenozide, N-tert-butyl-N'-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide
RH-9886	N-tert-butyl-N'-(4-ethylbenzoyl)-3-hydroxymethyl-5-methylbenzohydrazide
RH-1788	N-tert-butyl-N'-[4-(1-hydroxyethyl)benzoyl]-3,5-dimethylbenzohydrazide
RH-0282	N-tert-butyl-N'-[4-(1-hydroxyethyl)benzoyl]-3-hydroxymethyl-5-methylbenzohydrazide

RH-0126	N-tert-butyl-N'-[4-(1-hydroxyethyl)benzoyl]-3-carboxy-5-methylbenzohydrazide
RH-2703	N-tert-butyl-N'-(4-carboxymethylbenzoyl)-3,5-dimethylbenzohydrazide
RH-6595	N-tert-butyl-N'-(4-acetylbenzoyl)-3,5-dimethylbenzohydrazide
RH-9871	N-tert-butyl-N'-(4-acetylbenzoyl)-3-hydroxymethyl-5-methylbenzohydrazide
RH-2631	N-tert-butyl-N'-(4-acetylbenzoyl)-3-carboxy-5-methylbenzohydrazide
RH-0875	N-tert-butyl-N'-(4-ethylbenzoyl)-3,5-dicarboxybenzohydrazide
RH-9841 (RH-5992-olefin)	N-tert-butyl-N'-(4-vinylbenzoyl)-3,5-dimethylbenzohydrazide
RH-9526	Stearic acid conjugate of RH-9886

Environmental fate

Soil

In 1996, the Meeting requested a detailed report of a completed study of uptake by rotational crops that the Meeting was informed was available. The current Meeting received the results of both confined and field studies of rotational crops.

In the study of confined rotational crops, tebufenozide labelled with ^{14}C in the ethylbenzoyl ring, the dimethylbenzoyl ring or the central carbon of the *tert*-butyl group was applied in four applications to bare ground, each at the maximum rate of use described on the label for crops in the USA that could be rotated. Rotational crops (wheat, collards and turnips) were planted back 30, 90, 250 and 365 days after last treatment of the initial crop.

High concentrations of residues were found in wheat at 30 days' plant-back: expressed as parent equivalents, 0.4 mg/kg TRR in grain, 7.2 mg/kg in straw and 2.6 mg/kg in forage. At 90 days plant-back, the TRR had fallen to 0.06 mg/kg in grain, 0.4 mg/kg in straw, and 0.3 mg/kg in forage. The concentrations at 250 and 365 days plant-back were comparable. The main component in all wheat samples was RH-1788, either as the free alcohol or conjugated to glucose or malonylglucose. The parent compound was present in only small amounts (1%) in samples of straw and grain at 30 days plant-back and was not detected in any of the wheat samples at longer plant-back intervals.

The concentration of residues in collards at 30 days plant-back was about 0.1 mg/kg. The residues included the glucose conjugates of RH-1788 and small amounts of glucose conjugates of RH-9886 and RH-0282; the conjugates constituted 42% of the TRR. The main individual component (15%) in collards was RH-5992-olefin (RH-9841). The parent compound was not found.

The concentrations of residues were about 0.1 mg/kg in turnip roots and 0.4 mg/kg in turnip tops at 30 days plant-back. The parent compound was the most prevalent component in turnip roots (20% of TRR, 0.02 mg/kg) and accounted for about 7% of the TRR (0.03 mg/kg) in turnip tops. Sugar conjugates of RH-1788 constituted 14% of the TRR in both turnip roots and tops.

Thus, the main residues in wheat samples were RH-1788 and its sugar conjugates. Only the turnip root crop had a significant percentage of tebufenozide. The leafy crop collard contained mainly sugar conjugates of RH-1788 and tebufenozide-olefin (RH-9841).

The metabolites found in rotational crops were similar to those identified previously in the studies of crop metabolism, except that the parent compound was either a minor component or undetectable and large amounts of sugar conjugates were formed from the metabolites. All the metabolites found in rotational crops, except the conjugated metabolites, have also been characterized in rats. In soil, the parent compound and RH-6595 were characterized.

In the field study of rotational crops, leaf lettuce was planted as the primary crop and tebufenozide was applied at maximum GAP rate in the USA. The lettuce was removed at maturity, and rotational crops were planted 30 and 120 days after the last application.

The high-moisture crops, including leaf lettuce, radish tops and roots, squash, green and bulb onion and green peppers, were analysed for residues of tebufenozide and its olefin metabolite RH-9841. These compounds were found at concentrations below the LOQ (0.01 mg/kg) in all crops tested.

The low-moisture crop samples (wheat, sorghum and soya beans), planted at 30 days plant-back, were analysed for residues of tebufenozide and its alcohol metabolite RH-1788. No residues of tebufenozide or RH-1788 were found in wheat or sorghum grain or soya bean seed, at concentrations above the LOQ (0.02 mg/kg). In the plant parts used for animal feed, residues of RH-1788 were found in wheat straw (0.28 mg/kg), wheat hay (0.12 mg/kg) and soya bean forage (0.03 mg/kg); no residues of RH-1788 were found in wheat forage, sorghum forage, fodder or stover or soya bean hay. No residues of the parent compound were found at concentrations above the LOQ (0.02 mg/kg) in any of the animal feed commodities from wheat, sorghum and soya bean.

Methods of analysis

Two analytical methods that had been evaluated by the 1996 JMPR were updated with respect to the methods used to measure residues of tebufenozide in six vegetable crops (lettuce, cabbage, spinach, mustard greens, broccoli and celery) and in pecans. The LOQs were unchanged. The GLC method for determining tebufenozide in grapes, evaluated by the 1996 JMPR, was validated for lettuce. The LOQ was 0.02 mg/kg.

An analytical method for determining tebufenozide in citrus fruit and its processed fractions includes the extraction and partitioning of whole citrus fruit, juice and dry pulp samples and direct partitioning of citrus oil samples. The samples are cleaned-up on a carbon and C-18 solid-phase extraction column and analysed by HPLC with UV detection. The LOQ was 0.02 mg/kg. A confirmatory method is based on the same extraction and purification procedure with HPLC–MS for quantification of residues in whole fruit, juice and dry pulp and HPLC–MS/MS for quantification of residues in oil.

A method for measuring residues of tebufenozide in sugar cane and sugar cane processed fractions and one for residues in cotton seed and cotton seed processed fractions were submitted. The method for cotton seed was used in trials on rape seed. After extraction, partitioning and further purification, HPLC–UV was used for quantification. The LOQ was 0.01 mg/kg for all matrices with both methods. The concentrations of residue obtained by HPLC–UV were confirmed by the HPLC–MS method.

A method was reported for the detection and quantification of residues of tebufenozide and its metabolites RH-9841 and RH-1788 in rotational crops. After extraction, partitioning and clean-up, residues were quantified by LC–MS. The LOQ was 0.01 mg/kg for tebufenozide and RH-9841 in high-moisture crops such as root and leafy vegetables, and 0.02 mg/kg for tebufenozide and RH-1788 in low-moisture crops such as grains.

In a method for enforcement of concentrations of residues of tebufenozide and its metabolites in animal commodities, tebufenozide was quantified in all matrices, RH-9886 in muscle and kidney, RH-0282 in milk, muscle and kidney, fatty acid conjugates of RH-9886 in milk and fat and RH-2703 in liver. Residues of fatty acid conjugates of RH-9886 were hydrolysed with hydrochloric acid, and the hydrolysed and normal extracts were partitioned, cleaned-up and then quantified by HPLC–UV. The LOQ was 0.01 mg/kg for all three analytes in milk and 0.02 mg/kg for all analytes in animal

tissues. The confirmatory HPLC methods for all matrices consisted of use of modified mobile phases with MS detection.

Stability of residues in stored analytical samples

As described by the 1996 JMPR, the stability of tebufenozide at –20°C has been demonstrated in apples (at least 33 months), apple juice (at least 6 months), grapes and wine (at least 12 months) and walnuts (at least 18 months). The 1996 JMPR requested representative data on the stability of residues on leafy vegetables for the full duration of the storage studies that the Meeting was informed were in progress, and on the stability of residues in analytical samples of rice stored for longer than the 20–21 days already reported. The present Meeting received reports on stability in storage for wheat, rice, green onion, citrus oil, lettuce and animal commodities.

The stability of RH-6595, RH-1788 and the RH-1788-glucose conjugate was tested in wheat straw derived from a study of rotational crops for only the last 2 years of a 4-year storage period. Although little or no degradation was observed, no information was available about a possible change in composition during the first 2 years of storage. Since degradation is usually not a linear process, extrapolation is not possible. The composition of the residue in extracts of wheat forage samples stored for 4 years, which contained mainly the glucose and malonylglucose conjugates of RH-1788, was comparable to that of the remainder of the extracts stored for 4 years and 7 months, but no information was available about stability during the first 4 years of storage.

The stability of tebufenozide and its metabolites RH-1788, RH-6595 and RH-9886 was examined in frozen stored samples of rice straw and grain from a study of metabolism. Samples were first analysed after 2 years and were re-analysed after another 5 years of frozen storage. The proportions of the metabolites remained essentially the same. Although this study did not cover the first 2 years of storage, it satisfied the request of the 1996 JMPR.

In support of the findings on the stability of tebufenozide residues in stored rotational crops, the metabolite RH-9841 was shown to be stable in green onion for at least 24 months at < –10 C. The interval between storage and analysis for high-moisture crop samples in the study of rotational crops was $\leq$ 20 months.

The stability of tebufenozide was demonstrated in orange oil frozen at –20ºC for at least 15 months, and in head lettuce stored at –15 ± 10 °C for up to 36 months.

In the supervised trials, the stability of tebufenozide was shown to be at least 189 days in blueberries, 322 days in raspberries, 30 days in cranberries, 279 days in turnip roots and foliage, 236 days in rape seed, 90 days in rape seed meal, 83 days in rape seed oil, 279 days in mint and 285 days in mint oil. The periods evaluated covered the interval between storage and analysis for the crops in the supervised trials.

The intervals between storage and analysis for leafy vegetables and tree nuts are covered by the data on the stability of head lettuce and walnuts, respectively. No studies of the stability of tebufenozide in storage were conducted with citrus fruit (interval between storage and analysis in supervised trials, $\leq$ 2 years), stone fruit (interval, $\leq$ 4 months), avocado (interval, $\leq$ 1 year), cabbage and broccoli (interval, $\leq$ 2.5 years), fruiting vegetables (interval, $\leq$ 11 months), celery (interval, $\leq$ 1.5 years) or sugar cane (interval, $\leq$ 14 months). The stability of tebufenozide in these commodities can be inferred from the stability of its residues in other crop matrices.

In animal commodities, the stability of tebufenozide and the metabolites of possible concern in each matrix during a certain duration at –15 ± 10 °C was tested. In milk (RH-0282 and RH-9526, 192 days), meat (RH-9886 and RH-0282, 203 days), liver (RH-2703, 182 days) and fat (RH-9526, 145 days), no decrease was found in the concentrations of tebufenozide and the metabolites measured.

Although these data do not cover the entire interval between storage and analysis of milk and fat samples in the feeding trial in cows (250 days for milk and 274 days for fat), as judged from the stability observed, there should be no concern that the measured concentrations of residues were influenced by the storage period.

Definition of the residue

In 1996, the Meeting agreed that the residue for compliance with MRLs and for estimating dietary intake should be defined as tebufenozide. The residue is fat-soluble.

The Meeting agreed that this residue definition would apply to both plant and animal commodities.

Results of supervised trials

Citrus fruit

Five trials in Spain and five trials in Italy on oranges were conducted according to Spanish and Italian GAP for citrus fruit (two applications at 0.018 or 0.019 kg ai/hl; PHI, 14 days). The concentrations of residues of tebufenozide in these trials were: 0.21, 0.25, 0.36, 0.38, 0.39, 0.43, 0.48, 0.56, 0.60 and 0.78 mg/kg in whole fruit and 0.021, 0.03, 0.04 (2), 0.05, 0.053, 0.11, 0.13 (2) and 0.15 mg/kg in pulp.

Five trials with oranges in Australia and nine in the USA, two trials on lemon in Australia and five in the USA, six trials with grapefruit in the USA and two trials with mandarin in Australia were conducted according to the respective pending national GAPs for citrus fruit. Trials based on pending GAP were not taken into consideration by the Meeting.

The concentrations of residues in mandarin in trials in Italy and Spain conducted according to approved GAP for citrus fruit, with a PHI of at least 14 days, were: 0.30 (2), 0.42, 0.59, 0.60 (2), 0.78, 0.84 and 0.95 mg/kg in whole fruit and 0.069, 0.076, 0.082, 0.092, 0.14 and 0.18 mg/kg in pulp.

As the concentrations of residues of tebufenozide were comparable in the whole commodity and in edible portions (pulp) of citrus fruits, the Meeting agreed to evaluate the combined data for oranges and mandarins to apply to citrus fruit. The concentrations of residues in citrus fruit were, in ranked order (median underlined): 0.21, 0.25, 0.30 (2), 0.36, 0.38, 0.39, 0.42, 0.43, 0.48, 0.56, 0.59, 0.60 (3), 0.78 (2), 0.84 and 0.95 mg/kg in whole fruit and 0.021, 0.03, 0.04 (2), 0.05, 0.053, 0.069, 0.076, 0.082, 0.092, 0.11, 0.13 (2), 0.14, 0.15 and 0.18 mg/kg in the edible portion (pulp).

The Meeting estimated a maximum residue level of 2 mg/kg for tebufenozide in citrus fruit, and an STMR value of 0.079 mg/kg and a highest residue of 0.18 mg/kg for tebufenozide in the edible part of citrus fruit (the pulp).

Stone fruit

The values for residues in peaches and nectarines were derived directly from measurements in fruit without stones, whereas the MRL for peaches and nectarines applies to residues measured in fruit without stones but calculated and expressed as the whole fruit. The weight of the stone is set at a default value of 10% of the total weight of the fruit (see table “Unit weights and edible %” prepared by GEMS/Food for the CCPR and JMPR; nectarines were assumed to resemble peaches). As correction for the weight of the stones resulted in only marginally different figures, the values for residues were used without correction.

Three trials on peach in New Zealand were conducted according to national GAP for stone fruit (four applications at 0.12 kg ai/ha; PHI, 14 days), yielding concentrations of residues of 0.09, 0.10 and 0.14 mg/kg; and three trials on nectarines conducted at GAP yielded concentrations of residues of 0.05, 0.22 and 0.26 mg/kg.

As the concentrations of residues in the trials on peach and nectarine were within the same range, the Meeting agreed to combine the data for mutual support. The concentrations of residues in peach and nectarine were, in ranked order: 0.05, 0.09, 0.10, 0.14, 0.22 and 0.26 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg, an STMR value of 0.11 mg/kg and a highest residue of 0.23 mg/kg for tebufenozide in peaches and nectarines.

Berries

Eight field trials were conducted in the USA on blueberry according to national GAP (four applications of 0.29 kg ai/ha; PHI, 14 days), resulting in concentrations of residues of 0.30, 0.34, 0.50, 0.56, 0.81, 1.1, 1.2 and 1.7 mg/kg.

The Meeting estimated a maximum residue level of 3 mg/kg, an STMR value of 0.685 mg/kg and a highest residue of 1.7 mg/kg for tebufenozide in blueberries.

Five trials on raspberries conducted in the USA according to GAP resulted in concentrations of residues of 0.36, 0.50, 0.56, 0.82 and 0.86 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg, an STMR value of 0.56 mg/kg and a highest residue of 0.86 mg/kg for tebufenozide in raspberries.

Five trials on cranberry (one in Canada, four in the USA) were conducted according to GAP in the USA (four applications of 0.29 kg ai/ha; PHI, 30 days). The concentrations of residues were < 0.01, 0.016, 0.042, 0.046 and 0.28 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg, an STMR value of 0.042 mg/kg and a highest residue of 0.28 mg/kg for tebufenozide in cranberries.

Residues of tebufenozide in grapes were evaluated by the 1996 and 1999 JMPR . The ranked order of concentrations of residues from 18 trials in France and Germany was 0.05, 0.06, 0.07, 0.08, 0.12, 0.18, 0.21, 0.22, 0.24, 0.26 (2), 0.27, 0.28 (3), 0.4, 0.42 and 0.5 mg/kg (see Annex 5, reference 87). Re-evaluation of data from four trials in France conducted according to current GAP in Portugal (three applications of 0.144 kg ai/ha; PHI, 14 days; GAP was pending in 1996) resulted in concentrations of residues of 0.16, 0.29, 0.68 and 0.81 mg/kg (Annex 5, reference 78). Trials on grapes conducted in Australia in 1995 and 1998 according to Australian GAP (0.006 kg ai/hl, ≤ 0.030 kg ai/hl for low volume spraying; PHI, 21 days) resulted in highest residues at least 21 days after the last treatment of 0.22, 0.39, 0.81, 1.1, 1.3 and 1.5 mg/kg. The four re-evaluated French trials and the Australian trials yielded higher concentrations and were considered to represent different data populations from the study in Germany and the previously considered French trials. Therefore the Meeting estimated the maximum residue level, the STMR value and the highest residue on the basis of the four re-evaluated French and six Australian trials.

The concentrations of residues in grapes in trials with Portuguese and Australian GAP were: 0.16, 0.22, 0.29, 0.39, 0.68, 0.81 (2), 1.1, 1.3 and 1.5 and mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg for tebufenozide in grapes to replace the previous recommendation of 1 mg/kg, an STMR value of 0.745 mg/kg and a highest residue of 1.5 mg/kg.

Avocado

Trials were conducted in Australia and New Zealand on avocado according the approved GAP of New Zealand (four applications of 0.006 kg ai/hl; PHI, 21 days). The results of one trial (Walkamin) were not used because there had been heavy rainfall after the last application and the values for residue in this trial were considerably lower than those in other trials. The concentrations of residues measured in stoneless fruit, but calculated for whole fruit, were: 0.08, 0.10, 0.17, 0.18, 0.28, 0.45 and 0.47 mg/kg. The concentrations in the edible portion of avocados (stoneless fruit) were: 0.09, 0.12, 0.19, 0.21, 0.33, 0.52 and 0.53 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg for tebufenozide in avocados and an STMR value of 0.21 mg/kg and a highest residue of 0.53 mg/kg for tebufenozide in the edible part of avocados (seeded avocados).

Cabbage

Trials on cabbage in the USA were summarized by the 1996 JMPR but, because there was no approved GAP at that time, no MRLs were proposed.

In 14 trials on cabbage conducted in the USA according to GAP for brassica (seven applications at 0.14 kg ai/ha; PHI, 7 days), the concentrations of residues were 0.004, 0.03, 0.04, 0.09, 0.11, 0.17, 0.30, 0.38, 0.53, 0.78, 1.0, 1.3, 4.3 and 4.6 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg, an STMR value of 0.34 mg/kg and a highest residue of 4.6 mg/kg for cabbage.

Broccoli

Trials on broccoli in the USA were summarized by the 1996 JMPR but, because there was no approved GAP at that time, no MRLs were proposed.

Eleven trials on broccoli conducted in compliance with GAP in the USA for brassica resulted in concentrations of residues of 0.01, 0.07, 0.09, 0.1, 0.11 (2), 0.12, 0.24, 0.31, 0.33 and 0.34 mg/kg.

The Meeting estimated a maximum residue level at 0.5 mg/kg, an STMR value of 0.11 mg/kg and a highest residue of 0.34 mg/kg for broccoli.

Tomato

Trials on tomato were performed in both greenhouses and the field. Five trials conducted in greenhouses in southern Europe in 1996 according to Spanish GAP (three applications of 0.018 kg ai/hl; PHI, 3 days) resulted in concentrations of residues of 0.09, 0.19, 0.20, 0.25 and 0.34 mg/kg. Four trials in greenhouses performed in The Netherlands according to Belgian GAP (two applications of 0.18 kg ai/ha; PHI, 3 days) resulted in concentrations of residues in tomatoes of 0.10, 0.11 (2) and 0.16 mg/kg. The concentrations in tomatoes from field trials in the USA that complied with GAP (four applications of 0.28 kg ai/ha; PHI, 7 days) were 0.031, 0.058, 0.085, 0.089, 0.095, 0.11, 0.13, 0.17, 0.25, 0.31, 0.52 and 0.53 mg/kg. As the results for tomatoes grown in the field and in greenhouses are comparable, the data can be combined. The concentrations of residues in trials conducted according to GAP, in ranked order, were: 0.031, 0.058, 0.085, 0.089, 0.09, 0.095, 0.10, 0.11 (3), 0.13, 0.16, 0.17, 0.19, 0.20, 0.25 (2), 0.31, 0.34, 0.52 and 0.53 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg, an STMR value of 0.13 mg/kg and a highest residue of 0.53 mg/kg for tomato.

Peppers

Trials on peppers conducted in the USA according to GAP (four applications at 0.29 kg ai/ha; PHI, 7 days) gave concentrations of residues of 0.048, 0.052, 0.064, 0.16, 0.17 and 0.64 in bell peppers and 0.040, 0.046 and 0.097 in other peppers.

The Meeting agreed to combine the data for the two types of peppers, resulting in concentrations, in ranked order, of: 0.040, 0.046, 0.048, 0.052, 0.064, 0.097, 0.16, 0.17 and 0.64 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg, an STMR value of 0.064 mg/kg and a highest residue of 0.64 mg/kg for tebufenozide in peppers.

Leafy vegetables

Eight newly submitted trials on lettuce, head were conducted in Europe according to pending GAP and were therefore not considered by the Meeting. Newly submitted trials on turnip greens in the USA were not performed according to GAP (application rate too high) and were also not taken into consideration.

The results of trials on head lettuce, leaf lettuce, spinach and mustard greens were reviewed by the 1996 JMPR, but, as there was no approved GAP at that time no MRLs were proposed. As GAP for leafy vegetables is now registered in the USA, these trials can be evaluated.

Trials on leafy vegetables conducted in the USA in compliance with current GAP (seven applications at 0.14 kg ai/ha; PHI, 7 days) resulted in concentrations of residues of: 0.092, 0.14, 0.29, 0.83, 0.9, 2.3, 2.7, 3.2 and 6.6 mg/kg in lettuce, head; 0.41, 0.69, 1.1, 1.7, 2.2, 2.5, 2.6 and 3.2 mg/kg in lettuce, leaf; 0.13 (2), 2.7, 3.3, 3.8, 3.9, 4.2, 7.1 and 8.1 mg/kg in spinach and 0.65, 0.93, 1.6, 1.9, 2.4, 2.6, 3.9, 4.4, 5.6 and 6.9 mg/kg in mustard greens.

As the use patterns of tebufenozide in leafy vegetables are similar and the concentrations of residues are in the same range, the Meeting concluded that the data for leafy vegetable crops could be combined. This resulted in concentrations of residues of tebufenozide, in ranked order, of: 0.092, 0.13, 0.14, 0.29, 0.41, 0.65, 0.69, 0.83, 0.9, 0.93, 1.1, 1.3, 1.6, 1.7, 1.9, 2.2, 2.3, 2.4, 2.5, 2.6 (2), 2.7 (2), 3.2 (2), 3.3, 3.8, 3.9 (2), 4.2, 4.4, 5.6, 6.6, 6.9, 7.1 and 8.1 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg, an STMR value of 2.45 mg/kg and a highest residue of 8.1 mg/kg for the crop group leafy vegetables.

Turnip roots

Trials on turnip roots in the USA were not conducted according to GAP (0.14 kg ai/ha; PHI, 7 days) and were therefore not considered The Meeting could not estimate a maximum residue level for tebufenozide residues in turnip roots.

Celery

The maximum residue level in celery applies to the whole commodity after removal of adhering soil and clearly decomposed or withered leaves. The data on residues in trials on celery submitted previously, which were conducted in compliance with currently approved GAP in the USA (seven applications at 0.14 kg ai/ha; PHI, 7 days), pertained mainly to celery stalks *without* foliage. In two samples of celery stalks with foliage, the concentrations of residues were 0.41 and 1.3 mg/kg. The concentrations of residues in the stalk were lower. Insufficient data were available to estimate a maximum residue level in celery.

Sugar cane

The concentrations of tebufenozide residues in sugar cane were derived from 10 trials in the USA that complied with GAP (four applications, 0.28 mg/kg; PHI, 14 days). The values were 0.013, 0.032, 0.035, 0.054, 0.12 (2), 0.16, 0.28, 0.54 and 0.62 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg, an STMR value of 0.12 mg/kg and a highest residue of 0.62 mg/kg for tebufenozide in sugar cane stems.

Tree nuts

Four trials on pecan previously submitted to the JMPR, which were conducted within currently approved GAP for pecans (0.28 kg ai/ha; PHI, 14 days), resulted in undetectable residues (< 0.01 mg/kg). Further trials on pecans were conducted in the USA in 1997. Although the total amount of tebufenozide applied was equal to the maximum allowed (2.1 kg ai/ha per season), the application rate per treatment was twice as high and the number of applications twice as low as the critical GAP. Residues were undetectable (< 0.01 mg/kg). Since these results confirm those obtained in 1993, the Meeting decided to include them in the evaluation. The concentration of residues in the 12 trials on pecans was < 0.01 mg/kg.

The Meeting estimated a maximum residue level of 0.01* mg/kg as a practical limit of quantification for tebufenozide in pecans. In addition, the Meeting estimated an STMR value of 0.01 mg/kg and a highest residue of 0.01 mg/kg.

Ten trials were conducted on almonds in the USA in 1995–98 in accordance with GAP for tree nuts excluding pecans (0.53 kg ai/ha; PHI, 14 days). The concentrations of residues were < 0.01 (2), 0.010, 0.016, 0.017, 0.024, 0.029, 0.034, 0.042 and 0.045 mg/kg in almond nut kernel.

The Meeting estimated a maximum residue level of 0.05 mg/kg, an STMR value of 0.0205 mg/kg and a highest residue of 0.045 mg/kg for tebufenozide in almond nut kernel.

Information on residues in macadamia nuts was generated in Australia, where the GAP for macadamia nuts (five applications of 0.009 kg ai/hl or concentrate spraying; PHI, 28 days) is still pending. The data were therefore not considered by the Meeting.

Rape seed

One trial on rape seed was performed in Canada and six in the USA. The approved GAP in the USA is four applications of 0.28 kg ai/ha and a PHI of at least 14 days. In one trial in the USA conducted according to GAP, the concentration of tebufenozide residue was 1.2 mg/kg. Each of the other trials involved either a deviation from the PHI or a special circumstance such as thawing of samples during transport. The residue values that were probably underestimates were 0.31, 0.47 and 0.52 mg/kg; and the values that were probably overestimates were 0.95, 1.1 and 1.6 mg/kg. However, since the values are more or less within the same range, the Meeting agreed to use all of them. In ranked order, the concentrations of tebufenozide residues in rape seed were 0.31, 0.47, 0.52, 0.95, 1.1, 1.2 and 1.6 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg, an STMR value of 0.95 mg/kg and a highest residue of 1.6 mg/kg for rape seed.

Mint

Five trials on mint were conducted in the USA according to GAP (0.28 kg ai/ha; PHI, 14 days). The concentrations of residues were much lower in mint foliage from one site (2.9 and 2.6 mg/kg) than in

that from the other sites, perhaps due to a frost that killed the mint tops on the day of the first application at the former site. The values from that trial were therefore not used to estimate the maximum residue level. The concentrations of residues in mint foliage in the remaining four trials were 7.5, 8.3, 8.4 and 8.6 mg/kg.

The Meeting estimated a maximum residue level of 20 mg/kg, an STMR value of 8.35 mg/kg and a highest residue of 8.6 mg/kg for tebufenozide in mint.

Almond hulls

Ten residue trials were conducted on almonds in the USA in 1995–98 in accordance with approved GAP for tree nuts excluding pecans (0.53 kg ai/ha; PHI, 14 days). The concentrations of residues measured in hulls (used as feed for livestock) in nine of these trials were 8.4, 9.5, 10, 11, 15, 16, 17 (2) and 21 mg/kg.

The Meeting estimated an maximum residue level of 30 mg/kg, an STMR value of 15 mg/kg and a highest residue of 21 mg/kg for tebufenozide in almond hulls.

Fate of residues during processing

The 1996 JMPR requested information on tebufenozide residues in raisins, raisin culls and rice hulls. The present Meeting received a report on two supervised trials with grapes in which raisins were generated. Furthermore, processing studies on citrus fruit, peaches, tomatoes, sugar cane and rape seed were supplied.

Washing, the first step in processing citrus fruit, removed most of the residue in oranges (86%) and grapefruit (74%). The calculated processing factors for industrial processing of citrus fruits were (mean of two trials, one in orange and one in grapefruit) 26.1 for oil, 0.80 for dried pulp and <0.016 for juice.

On the basis of the STMR value for citrus whole fruit of 0.48 mg/kg, the Meeting estimated STMR-P values of 12.5 mg/kg for citrus oil, 0.38 mg/kg for dried pulp and 0.0077 mg/kg for citrus juice.

During canning of peaches, all the residues of tebufenozide originally present were depleted, and no measurable residues (> 0.01 mg/kg) were found in either the fruit or the syrup of canned peaches. On the basis of the processing factor for canned peaches of < 0.06 (mean of six trials) and the STMR value for peaches of 0.11 mg/kg, the Meeting estimated an STMR-P value of 0.0066 mg/kg for canned peaches.

Processing of grapes yields wine, wet pomace, juice and raisins. Two trials with dried grapes resulted in a processing factor of 0.74 for raisins. Eight trials on grapes that were processed into juice resulted in a processing factor of 0.13 for juice. The 1996 JMPR determined processing factors of 2.7 (mean of 1.6, 2.8 and 3.7) for wet pomace and 0.36 for mature wine (0.07–0.69; n = 14). Additional data from 26 studies of wine processing conducted in Australia showed that the residues in pomace were concentrated by factors of 1.6–8.7 with an average of 4.1 (n = 18); the concentrations of residues in wine resulted in processing factors of 0.11–0.43 with an average of 0.25 (n = 23). Combining these processing factors with those of the 1996 JMPR resulted in processing factors of 3.9 for wet pomace (n = 21) and 0.29 for wine (n = 37).

On the basis of the highest residue in grapes of 1.5 mg/kg, the Meeting estimated a maximum residue level of 2.0 mg/kg for tebufenozide in raisins and a highest residue of 1.11 mg/kg. On the basis of the STMR value for grapes of 0.745 mg/kg, the Meeting estimated an STMR-P value for

tebufenozide of 0.551 mg/kg in raisins, 0.097 mg/kg in grape juice, 2.9 mg/kg in wet pomace to replace the STMR-P value of 0.36 mg/kg, and 0.216 mg/kg in wine to replace the STMR-P value of 0.03 mg/kg.

Tomatoes were processed differently in the four trials conducted in Europe and the one trial in the USA, but, to the extent that the processes yielded the same products, the data were comparable. About two-thirds of the residue in tomatoes was removed by washing in all five trials. The calculated processing factors were 0.31 for purée (n = 1), 0.73 for paste (n = 5), 0.18 for sterilized juice (n = 4) and 0.28 for preserved fruit (n = 4).

On the basis of the STMR value for tomatoes of 0.13 mg/kg, the Meeting estimated STMR-P values of 0.04 mg/kg for purée, 0.095 mg/kg for paste, 0.023 mg/kg for tomato juice and 0.036 mg/kg for preserved tomatoes.

During isolation of refined sugar from sugar cane, all the residues of tebufenozide originally present were depleted; no residues were present at a concentration > 0.01 mg/kg in the resulting refined sugar in four separate studies. The mean processing factor for refined sugar in three trials was < 0.025. Residues of tebufenozide concentrate in molasses; the processing factor for molasses was 5.9 (n = 3).

On the basis of the STMR value for sugar cane stems of 0.12 mg/kg, the Meeting estimated an STMR-P value of 0.003 mg/kg for refined sugar and 0.71 mg/kg for molasses.

Rape seed was processed in two trials into meal, soapstock and refined oil, resulting in processing factors of 0.15 for meal, 1.1 for soapstock and 2.3 for refined oil. On the basis of the STMR value for rape seed of 0.95 mg/kg, the Meeting estimated an STMR-P value of 0.14 mg/kg for meal, 1.0 mg/kg for soapstock and 2.2 mg/kg for refined rape seed oil.

Two studies on the processing of mint oil from mint resulted in a mean processing factor of 0.03 for mint oil. On the basis of the STMR value for mint foliage of 8.35 mg/kg, the Meeting estimated an STMR-P value of 0.25 mg/kg for mint oil.

Residues in animal commodities

Dietary burden of farm animals

The Meeting estimated the dietary burden of tebufenozide residues for farm animals from the diets listed in Appendix IX of the *FAO Manual*. Calculation from the HR values provides the concentrations in feed suitable for estimating MRLs for animal commodities, while calculation from the STMR values for feed is suitable for estimating STMR values for animal commodities. In the case of processed commodities, the STMR-P value is used for both intake calculations.

Estimated maximum intake

Commodity	Group	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Almond hulls	AM	30	MRL	90	33.3	10	10	–	3.3	3.3	–

Apple wet pomace	AB	0.4	STMR-P	40	1.0	40	20	–	0.4	0.2	–
Citrus dry pulp	AB	0.38	STMR-P	91	0.42	20	20	–	0.08	0.08	–
Rape seed meal	SO	0.14	STMR-P	88	0.16	10	15	15	0.02	0.02	0.02
Rice grain	GC	0.1	MRL	88	0.114	–	15	60	–	0.02	0.07
Rice straw[a]	AS	7.7	HR	90	8.6	10	10	–	0.86	0.86	–
Sugar cane molasses	DM	0.71	STMR-P	75	0.9	10	10	–	0.09	0.09	–
					Total	100	100	75	4.8	4.6	0.09

[a] 2.9, 3.9, 6.2 and 7.7 mg/kg (1996 JMPR); STMR = 5.05 mg/kg

Estimated mean intake

Commodity	Group	Residue (mg/kg)	Basis	Dry matter (%)	Residue, dry weight (mg/kg)	Choose diets (%)			Residue contribution (mg/kg)		
						Beef cattle	Dairy cows	Poultry	Beef cattle	Dairy cows	Poultry
Almond hulls	AM	15.5	STMR	90	17.2	10	10	–	1.7	1.7	
Apple wet pomace	AB	0.4	STMR-P value	40	1.0	40	20	–	0.4	0.2	
Citrus dry pulp	AB	0.38	STMR-P value	91	0.42	20	20	–	0.08	0.08	
Rape seed meal	SO	0.14	STMR-P value	88	0.16	10	15	15	0.02	0.02	0.02
Rice grain	GC	0.025	STMR	88	0.028	–	15	60	–	0.004	0.02
Rice straw[a]	AS	5.05	STMR	90	5.6	10	10	–	0.56	0.56	
Sugar cane molasses	DM	0.71	STMR-P value	75	0.95	10	10	–	0.10	0.10	
					Total	100	100	75	2.9	2.7	0.04

[a] 2.9, 3.9, 6.2, 7.7 mg/kg (1996 JMPR); STMR = 5.05 mg/kg

Feeding studies

The 1996 JMPR requested the results of a study in which cows were fed diets containing tebufenozide, which the Meeting was informed was in progress. The present Meeting received those results.

Four cows in each group were given a capsule containing tebufenozide at 0, 6, 18 or 60 ppm ai for 28 days. One cow from each group was observed for 3 days while on a normal diet after the end of the dosing period. Whole milk, fat, meat, kidney and liver samples were analysed. The analytes of interest included parent tebufenozide in all matrices, RH-9886 in muscle and kidney, RH-0282 in milk, muscle and kidney, fatty acid conjugates of RH-9886 in milk and fat and RH-2703 in liver.

In cows at the two lower concentrations, the values for residues were below the LOQ (0.01 mg/kg in milk and 0.02 mg/kg in other matrices) in milk, muscle and kidney, except for a residue at the LOQ in muscle of one cow at 18 ppm. The concentration of residue in milk reached a plateau within about 3 days. The concentration in cream was not reported. In milk, the highest average group concentration of residue was at the LOD of 0.003 mg/kg in cows at 6 ppm, 0.009 mg/kg at 18 ppm and 0.028 mg/kg at 60 ppm. The highest individual concentrations of residues at 6, 18 and 60 ppm were 0.029 mg/kg, 0.11 mg/kg and 0.38 mg/kg in fat, < 0.006 mg/kg, 0.02 mg/kg and 0.06 mg/kg in muscle, < 0.006 mg/kg, 0.009 mg/kg and 0.04 mg/kg in kidney and 0.014 mg/kg, 0.04 mg/kg and 0.10 mg/kg in liver.

No detectable residues of analytes were found in cows observed on a normal diet for 3 days after treatment, except in fat in which approximately 30% of the initial residue was still present.

The Meeting considered that a feeding study with poultry was not necessary, as the concentrations of residues in poultry feed do not exceed 0.1 mg/kg and residues are therefore not expected in poultry products.

Maximum residue levels

As the maximum dietary burden of beef and dairy cattle was 4.8 mg/kg, the concentrations of residues in tissues and milk can be taken directly from results of the feeding study with 6 ppm, without interpolation. The maximum concentrations expected in tissues at this level are: 0.029 mg/kg in fat, < 0.006 mg/kg in muscle and kidney, 0.014 mg/kg in liver and 0.003 mg/kg in milk.

The Meeting estimated maximum residue levels of 0.05 mg/kg for cattle meat (fat), 0.02* mg/kg for cattle kidney, 0.02* mg/kg for cattle liver and 0.01* mg/kg for milk.

The STMR dietary burden of beef and dairy cattle was 2.9 mg/kg, which is about one-half the lowest concentration used in the feeding studies. The Meeting estimated STMR and highest residue values of 0.006 mg/kg for cattle meat and kidney and 0.02 mg/kg for liver, and an STMR value of 0.003 mg/kg for cattle milk.

A study of metabolism in poultry treated orally, evaluated by the 1996 JMPR, showed that, when laying hens were treated at a concentration equivalent to 30 ppm in the feed for 7 days, the concentrations of parent compound were 0.005 mg/kg in eggs, 0.18 mg/kg in fat and undetectable in liver and muscle. The maximum dietary burden of poultry was calculated to be 0.09 mg/kg, which is 300 times lower than that used in the study of metabolism. Therefore, the Meeting agreed to recommend MRLs for poultry meat and eggs at the LOQ. The Meeting acknowledged that the analytical method for animal commodities had not been validated for eggs but accepted that the LOQ for cattle tissues could apply to poultry tissues. The Meeting estimated maximum residue levels for poultry meat (fat) and eggs of 0.02* mg/kg, an STMR value and a highest residue for poultry meat (fat) of 0.02 mg/kg and an STMR value and a highest residue for eggs of 0 mg/kg.

The Meeting was informed that a report on validation of the analytical method for residues of tebufenozide in chicken liver, muscle, fat and eggs was available and would be submitted to a future Meeting.

Further work or information

Desirable

1. Information on the level of residues in milk cream
2. A report on validation of the analytical method for animal commodities with respect to poultry meat and eggs that the Meeting was informed was available.

Dietary risk assessment

Long-term intake

STMR or STMR-P values for tebufenozide were estimated by the current Meeting for 43 plant commodities and animal products. STMR values for four additional plant commodities were estimated by the 1996, 1997 and 1999 Meetings. When data on consumption were available, these values were used in the estimates of dietary intake. The results are shown in Annex 3.

The International Estimated Daily Intakes for the five GEMS/Food regional diets, based on the estimated STMRs, were in the range of 1-20% of the ADI. The Meeting concluded that the chronic intake of residues of tebufenozide from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The international estimated short-term intake (IESTI) for tebufenozide was calculated for those plant commodities and animal products for which maximum residue levels and STMRs were estimated and for which consumption data were available. The results are shown in Annex 4. The IESTI represented 0-440% of the acute RfD for the general population and 0-1220% of the acute RfD for children. That representing 440% (general population) and 1220% (children) results from the consumption of leafy vegetables (spinach). The short-term intake of cabbage also exceeded the acute RfD in both groups, with 230% (general population) and 410% (children). For children, the estimated short-term intake of pomefruit (apple) and grapes exceeded the acute RfD with 210% and 190% respectively.

RECOMMENDATIONS

CCN	Commodity	MRL, mg/kg		STMR, STMR-P, mg/kg	HR, HR-P, mg/kg
		New	Previous		
TN 0660	Almonds	0.05	–	0.0205	0.045
AM 0660	Almond hulls	30		15	
FI 0326	Avocado	1	–	0.21	0.53
VB 0400	Broccoli	0.5	–	0.11	0.34
FB 0020	Blueberries	3	–	0.685	1.7
VB 0041	Cabbage, Head[1]	5	–	0.34	4.6
MO 1280	Cattle, kidney	0.02*		0.006	0.006
MO 1281	Cattle, liver	0.02*	–	0.02	0.02
MM 0812	Cattle meat (F)	0.05		0.006	0.006
ML 0812	Cattle milk	0.01*	–	0.003	
FC 0001	Citrus fruit Citrus oil Citrus dried pulp	2	–	0.079 12.5 0.38	0.18
JF 0001	Citrus juice			0.0077	
FB 0265	Cranberries	0.5	–	0.042	0.28
DF 0269	Dried grapes (currants, raisins and sultanas)	2	–	0.551	1.11
PE 0112	Eggs	0.02*		0	0
FB 0269	Grapes[1] Grape wet pomace Wine	2	1	0.745 2.9 0.216	1.5
JF 0269	Grape juice			0.097	
VL 0053	Leafy vegetables[1]	10	–	2.45	8.1
HH 0738	Mint Mint oil	20	–	8.35 0.25	8.6
FS 0245	Nectarines	0.5	–	0.11	0.23
FS 0247	Peaches Peaches, canned	0.5	–	0.11 0.0066	0.23

CCN	Commodity	MRL, mg/kg		STMR, STMR-P, mg/kg	HR, HR-P, mg/kg
		New	Previous		
TN 0672	Pecans	0.01*	–	0.01	0.01
VO 0051	Peppers	1		0.064	0.64
PM 0110	Poultry meat	0.02*	–	0.02	0.02
FB 0272	Raspberries	2		0.56	0.86
SO 0495	Rape seed Rape seed meal Rape seed soapstock	2	–	0.95 0.14 1.0	1.6
OC 0495	Rape seed oil			2.2	
GS 0659	Sugarcane stems Refined sugar Molasses	1	–	0.12 0.003 0.708	0.62
VO 0448	Tomato Tomato purée Tomato paste Tomatoes (preserved)	1	–	0.13 0.04 0.095 0.036	0.53
JF 0448	Tomato juice			0.023	

[1] The information provided to the JMPR precludes an estimate that the dietary intake would be below the acute RfD.Acute RfD: 0.05 mg/kg bw

Definition of the residue: for compliance with MRL and for estimation of dietary intake for plant and animal products*:* tebufenozide

The residue is fat-soluble

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THIODICARB (154)

EXPLANATION

Thiodicarb was reviewed for residues in 1985, and supervised field trial data for various crops were considered in 1987 and 1988. The 22nd Session of the CCPR decided to combine the MRLs for methomyl and thiodicarb into a single list (ALINORM 91/24 A, para. 126, p.21). The toxicology of thiodicarb was reviewed by the 2000 JMPR. The present review is a re-evaluation within the CCPR Periodic Review Programme.

The manufacturer submitted data on product chemistry, metabolism, environmental fate, analytical methods, storage stability, animal transfer and survey samples. The governments of Australia and Germany submitted label information.

IDENTITY

Chemical name

IUPAC: 3,7,9,13-tetramethyl-5,11-dioxa-2,8,14-trithia-4,7,9,12-tetra-azapentadeca-3,12-diene-6,10-dione

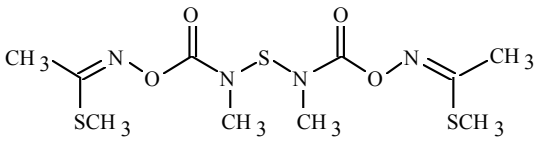
C.A. dimethyl *N*,*N*′-[thiobis[(methylimino)carbonyloxy]]bis(ethanimidothioate)

Chemical group: carbamates

BSI common name: thiodicarb

Chemical Abstracts registry No. (CAS No.): 59669-26-0

Structural formula



Thiodicarb

Empirical formula: $C_{10}H_{18}N_4O_4S_3$

Molecular weight: 354.5

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

		Reference
Appearance	White powder containing small aggregates	Robles and Bascou, 2000
Melting point:	172.6°C	Robles and Bascou, 2000
Decomposition point	184.7°C	Robles and Bascou, 2000
Octanol/water partition coefficient (shake-flask method)	log P_{OW} 1.62 at 25 °C	Cookinham, 1999a
Hydrolysis:		
PH 5 (buffered, 25°C)	DT_{50} = 78.4 days	Feung and Weisbach, 1991b
PH 7 (buffered, 25°C)	DT_{50} = 31.6 days	
PH 9 (buffered, 25°C)	DT_{50} = 0.48 days	
Photolysis:	DT_{50} = 7.6 days, (k=1.05 x 10^{-6} sec^{-1})	
	The UV/Vis spectrum showed that the molar absorption coefficient (ε) was below 10 $l.mol^{-1}.cm^{-1}$ when λ was ≥ 290nm. Quantum yield (Φ_{300}) study not conducted.	Feung and Blanton, 1987
Dissociation constant:	No dissociation observed	Cookinham, 1999b
Vapour pressure:	2.7 X 10^{-3} Pa at 25°C 2.7 X 10^{-3} Pa at 30°C 6.9 X 10^{-4} Pa at 35°C	Schweitzer, 1993
Henry's law constant	K = 4.31.10^{-2} $Pa.m^3.mol^{-1}$	Bascou, 1999
Solubility:		
Water		
deionised water (25°C)	22.19 µg/ml	
water buffered (pH 3, 25°C)	26.88 µg/ml	Cookinham, 1999c
water buffered (pH 5, 25°C)	29.83 µg/ml	
Water buffered (pH 7,25°C)	24.47 µg/ml	
Organic solvents		
dichloromethane	21 g/ml at 23°C	
hexane	0.000463 g/ml at 23°C	Lipscomb, 1987
methanol	0.32 g/ml at 23°C	
1,4 dioxane	0.65 g/ml at 25°C	
Relative density:	1.47 g/ml^{-1} at 20°C	Robles and Bascou, 2000

Technical material

Property	Results	Reference
Appearance	Off-white powder containing small aggregates	Robles and Bascou, 2000
Melting point:	167.1°C	Robles and Bascou, 2000
Decomposition point	171.6°C	
Purity		
Minimum purity	94.1%	Robles and Bascou, 2000
Main impurities	methomyl	
Relative density:	1.48 g/ml^{-1} at 20°C	Robles and Bascou, 2000
Surface tension	71.97 mN.m^{-1} at 20°C	Robles and Bascou, 2000
Stability:		
Thermal	Stable for 30 days at 25°C and 54°C	South and Pitts, 1993
Flammability	Not highly inflammable or autoflammable under the test conditions	Francois, 1999
Oxidising properties	The oxidising property test performed in air was positive, but no combustion was observed in an inert atmosphere.	Francois, 1999
Explosivity	No shock, friction or thermal sensibility to explosion	Francois, 1999
Estimated photochemical oxidative degradation	Thiodicarb was slightly degraded (<5%) after exposure to artificial sunlight (xenon lamp).	South and Pitts, 1993

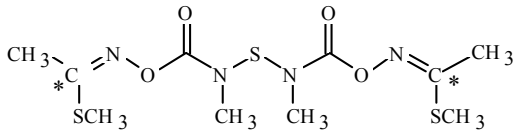
FORMULATIONS

The following list includes the major formulations developed for the use of thiodicarb on crops.

Formulation type	ai content	principal brand names
Suspension concentrate (SC)	300, 320, 375 g/l	Larvin®, Securex®, Souverain®
Flowable concentrated for seed treatment (FS)	350, 400, 500 g/l	Semevin®, Futur®
Water dispersible granule (WG)	800 g/kg	Larvin®, Relark®
Wettable powder (WP)	250, 750 g/kg	Larvin®
Granular bait (GB) and bait -ready to use- (RB)	20, 40 g/kg	Genesis®,Judge®, Skipper®
Ultra low volume liquid (UL)	350 g/l	Larvin®

METABOLISM AND ENVIRONMENTAL FATE

In all studies with [14C]thiodicarb the C=N carbons were labelled as shown below.



[^{14}C]thiodicarb.

* Denotes the ^{14}C carbons.

Animal metabolism

The metabolism of thiodicarb in laboratory rats and monkeys, and in domestic goats and chickens was reported.

Rats. Groups of 10 Sprague Dawley rats, 5 of each sex, were given single oral doses of 2 or 16 mg/kg bw thiodicarb (^{14}C, 87.5% purity, specific activity 23 mCi/mmol) by gavage (Hiles, 1987; Andrawes and Bailey, 1979; Huhtanen and Dorough, 1976).

Thiodicarb was rapidly and extensively absorbed. The time of maximum concentration (t_{max}) of ^{14}C in the blood was 1 to 4 hours after treatment at both doses and a high percentage of the applied dose was eliminated in the urine and respired gases. The results are shown in Table 1.

Table 1. Elimination of radioactivity in the respiratory gases, urine, and faeces of rats during 7 days after oral treatment at 2 and 16 mg/kg bw, average of 5 animals (Hiles, 1987).

Sample	Average cumulative % of applied dose			
	2 mg/kg bw		16 mg/kg bw	
	Male	Female	Male	Female
Urine	34	21	34	31
Faeces	5.3	9.2	4.4	4.2
Respired gases	38	50.5	42	43.1
Cage residue	0.35	0.88	0.46	3.6
Carcase	8.7	7.5	8.0	6.9
Total	86.3	89.0	89.7	88.6

Acetonitrile and carbon dioxide accounted for more than 99% of the radioactivity in the respired gases. Conversion of test material to CO_2 was rapid, with 58 to 74% eliminated in the first 6 hours and 89 to 95% within 24 hours. Elimination of acetonitrile was slower, 9 to 16% during the first 6 hours and 67 to 75% after 24 hours.

Residues in the carcase and tissues were 7-9% of the applied dose after seven days, and were highest in the red blood cells.

Acetonitrile was identified as a significant metabolite in urine. Minor amounts (1% or less of the urinary radioactivity) were identified in the involatile organosoluble fraction as methomyl, methomyl oxime, methomyl sulfoxide, and methomyl oxime sulfoxide. Water-soluble metabolites accounted for more than 86% of the radioactivity in the urine.

Monkeys. The absorption, distribution, metabolism and excretion of [^{14}C]thiodicarb (radiochemical purity >97%, specific activity 17.72 mCi/mM) were studied in four male cynomolgus monkeys aged 1 to 2.5 years placed in individual metabolic chambers immediately after being given single oral doses at a nominal rate of 5 mg/kg (Hawkins *et al.,* 1993). Urine was collected 6 and 24 hours after dosing and every 24 hours for 7 days (168 hours). Faeces, cage debris, and cage washings were collected

daily. Expired gases were trapped and analysed after 6, 24 and 48 hours. After one week the monkeys were killed and lungs, brain, gastrointestinal tract, liver, fat, muscle and skin sampled for the characterization and quantification of radiolabelled compounds. Approximately 60% of the radioactivity was excreted or expired during the first 24 hours. Over the 7-day period, an average of 31% of the administered dose was excreted in the urine (including cage wash), and only 4.6% in the faeces (Table 2).

4.7% of the dose was measured in the tissues. In the 48 hours after dosing when volatiles were collected an average of 28% of the administered dose was eliminated as $^{14}CO_2$, and 8.6% as [^{14}C]acetonitrile. The overall recovery of ^{14}C was 74-81%. Presumably the missing material could be attributed to volatiles exhaled after 48 hours.

Table 2. Distribution of radioactivity in monkeys given single oral doses of thiodicarb (5 mg/kg) expressed as a percentage of the administered dose (Hawkins *et al.*, 1993).

Sample, time after dosing (h)		Animal number				Mean ± SD
		Q168	R100	R69	R189	
Expired air, acetonitrile	0-6	2.0	1.9	1.7	2.1	1.9 ± 0.18
	6-24	3.8	3.0	3.4	6.0	4.0 ± 1.6
	24-48	2.9	1.7	1.5	4.2	2.6 ± 1.2
	Total	8.8	6.6	6.6	12	8.6 ± 2.7
Expired air, $^{14}CO_2$	0-6	14	23	16	17	17 ± 4.0
	6-24	12	5.9	6.9	10	8.6 ± 2.7
	24-48	2.2	1.1	2.5	1.2	1.8 ± 0.71
	Total	27	30	25	29	28 ± 2.1
Total expired air		36	37	32	41	36 ± 3.8
Urine	0-6	15	29	22	19	21 ± 5.8
	6-24	5.1	3.7	4.7	6.2	5.0 ± 1.0
	24-48	1.4	1.2	1.6	2.2	1.61 ± 0.44
	48-72	0.60	0.51	0.33	0.41	0.46 ± 0.12
	72-96	0.30	0.28	0.27	0.19	0.26 ± 0.05
	96-120	0.24	0.19	0.15	0.15	0.18 ± 0.04
	120-144	0.17	0.14	0.13	0.15	0.15 ± 0.02
	144-168	0.14	0.11	0.10	0.12	0.12 ± 0.02
	Total urine	23	35	29	28	29 ± 4.9
Cage washes		4.1	0.88	3.1	2.0	2.5 ± 1.4
Total faeces		4.8	4.5	5.4	3.8	4.6 ± 0.63
TOTAL		67.9	77.3	69.5	74.8	72

Metabolic degradation was extensive. At least 18 metabolites were found in the urine, none of which individually accounted for more than 5% of the applied dose; the metabolites identified using co-chromatography in two different systems were acetonitrile (1.2-2.9% of the dose), acetic acid (0.4-0.9%), and acetamide (0.8-1.0%).

No radioactive components in the urine corresponded to thiodicarb or its major degradation product methomyl. Chromatography also confirmed the absence of *syn*- and *anti*-forms of methomyl oxime (MHTA), methomyl sulfoxide, and methomyl oxime sulfoxide. Following treatment with *E.coli* ß-glucuronidase, radioactivity associated with the major polar component decreased from 11.9% of the applied dose to 4.2%, and that associated with eight components increased, including those corresponding to acetic acid (0.5-2.1% of the dose) and acetonitrile (3.2-3.8%).

Concentrations in the tissues were highest in the liver (0.8-1.5 µg thiodicarb equivalents/g) and fat (0.4-0.6 µg equivalents/g), and 0.1-0.3 µg equivalents/g in other tissues. Major polar metabolites were detected in extracts of whole blood (0.09-0.16 µg equivalents/g) and liver (0.5-1.1

µg equivalents/g). In liver, a component corresponding to acetic acid (0.12-0.1 µg equivalents/g) was confirmed by both reverse-phase and ion-exchange HPLC, but was not found in blood. No radioactive components in whole blood or liver corresponded to thiodicarb, the *syn*- or *anti*-forms of methomyl, methomyl oxime, methomyl oxime sulfoxide, acetonitrile, or acetamide.

Hens. The metabolic fate of [^{14}C]thiodicarb (21.35 mCi/mM, 1.37 x 10^5 dpm/ µg) was studied in laying hens. Groups consisting of 3 sub-groups of 3 hens (9 total per group) were dosed orally for 21 days at 15, 29, or 102 ppm in the diet (specific activity 1.37 x 10^5 dpm/µg, 9.15 x 10^4 dpm/µg, and 2.74 x 10^4 dpm/µg respectively) (Andrawes and Bailey, 1980) Faeces and eggs were analysed during the treatment period and for seven days afterwards. Tissue samples were taken for analysis 6 hours, 3 days and 7 days after the last dose (1 hen from each sub-group was killed at each interval).

The total radioactive residue (TRR) was measured by combustion and liquid scintillation counting (LSC). The level of detection was 0.01 mg/kg. Eggs and tissues were extracted with acetone-water and separated into volatile, organosoluble and water-soluble residue fractions. The volatile fraction was analysed by distillation and gas-liquid chromatography (GLC). Gel permeation was used to separate metabolites in the organosoluble and water-soluble fractions. The metabolites were identified and quantified by two-dimensional TLC, radio-autography and LSC.

Radioactivity reached a plateau within one day in the faeces, two days in egg whites and ten days in the yolks of the high-dose group. Levels of radioactivity declined during the withdrawal period. The results are shown in Tables 3 and 4.

Table 3. Distribution of radioactivity in the faeces and eggs of laying hens dosed with [^{14}C]thiodicarb for 21 days (Andrawes and Bailey, 1980).

Day	mg/kg [^{14}C]thiodicarb equivalents								
	15 ppm			29 ppm			102 ppm		
	Faeces	Yolk	White	Faeces	Yolk	White	Faeces	Yolk	White
1	1.6	--	--	3.2	--	--	14.	--	--
2	1.3	--	--	3.7	--	--	15	1.9	2.0
3	1.4	--	--	4.4	--	--	15	--	--
4	--	--	--	--	--	--	--	4.5	2.0
6	--	--	--	--	--	--	--	10.2	1.5
7	1.2	--	--	5.0	--	--	19	--	--
8	--	--	--	--	--	--	--	13	1.7
10	--	--	--	--	--	--	--	14	1.5
12	--	1.4	0.19	--	4.0	0.58	--	15	2.0
14	1.5	1.3	0.23	6.1	4.6	0.77	30	15.	2.0
21	1.4	1.5	0.21	4.5	4.6	0.59	13	13	1.6
Withdrawal									
1	0.36	--	--	2.0	--	--	10.	14	1.3
2	0.16	--	--	0.53	--	--	1.5	--	--
3	0.08	--	--	0.25	--	--	1.1	10.	0.21
5	--	--	--	--	--	--	--	6.5	0.11
7	0.06	--	--	0.18	--	--	0.37	2.2	0.05

Table 4. Distribution of radioactivity in the tissues of hens dosed with [^{14}C]thiodicarb in the feed for 21 days following a 6 hours, 3 days, or 7 days withdrawal period (Andrawes and Bailery, 1980).

Sample	mg/kg [^{14}C]thiodicarb equivalents at slaughter								
	15 ppm			29 ppm			102 ppm		
	6 h	3 days	7 days	6 h	3 days	7 days	6 h	3 days	7 days
Breast muscle	0.46	0.19	0.14	1.0	0.53	0.39	3.4	1.9	1.3
Thigh muscle	0.53	0.21	0.25	1.2	0.79	0.63	4.2	2.7	1.9
Leg muscle	0.53	0.30	0.24	1.2	0.76	0.59	4.2	2.9	1.6
Subcutaneous fat	0.97	0.94	0.52	2.5	1.89	1.8	5.8	8.0	5.7
Abdominal fat	1.3	0.77	0.58	2.9	1.89	1.6	6.6	7.5	6.1
Skin	0.57	0.38	0.26	1.6	1.05	0.71	4.3	4.0	1.6
Heart	0.71	0.25	0.21	1.6	0.82	0.61	3.7	3.0	1.5
Kidney	1.4	0.68	0.27	3.4	1.74	0.89	8.5	4.7	1.7
Gizzard	0.66	0.26	0.16	1.3	0.70	0.51	3.0	2.7	1.1
Liver	1.5	0.41	0.27	3.5	1.08	0.63	10.	4.6	1.6
Plasma	0.35	0.08	0.04	1.2	0.21	0.11	3.9	0.86	0.32
RBCs	2.3	1.4	0.67	7.5	4.45	2.7	20.	18.	8.4

The absence of thiodicarb and its potential metabolites methomyl, methomyl oxime, methomyl oxime sulfoxide and methomyl methylol (hydroxymethyl-methomyl, see Figure 2) was confirmed in all samples. Low levels of acetonitrile (volatile) and acetamide (water-soluble) were detected in eggs (Table 5). In addition, some radioactivity was associated with lipids and other natural products through incorporation of $^{14}CO_2$ (e.g. cholesterol and lecithin).

Table 5. Characterization of radioactivity in the eggs of hens dosed with [^{14}C]thiodicarb in the diet (Andrawes and Bailey, 1980).

Feeding level (ppm)	Metabolite/fraction	^{14}C (mg/kg as compound where applicable)			
		Day 14		Day 21	
		Yolk	White	Yolk	White
15	Acetonitrile	0.012	0.037	0.024	0.024
	Acetamide	NF	0.007	NF	0.006
	Lipids*	1.2	NA	1.2	NA
	Unextracted*	0.20	0.049	0.22	0.044
29	Acetonitrile	0.083	0.14	0.076	0.081
	Acetamide	NF	0.020	NF	0.022
	Lipids*	3.8	NA	3.5	NA
	Unextracted*	0.58	0.13	0.57	0.15
102	Acetonitrile	0.16	0.27	0.15	0.21
	Acetamide	NF	0.055	NF	0.029
	Lipids*	10. (68% of TRR)	NA	10. (77% of TRR)	NA
	Unextracted*	1.9	0.70	1.6	0.38

NF: not found
NA: not applicable
* ^{14}C as thiodicarb

Extractable radioactivity in the tissues accounted for about 50% of the total 6 hours after the last dose. Low levels of acetonitrile and acetamide were found in the liver and muscle but not in abdominal fat (Table 6).

Table 6. Characterization of radioactivity in the liver, muscle and fat of hens dosed with [^{14}C]thiodicarb (Andrawes and Bailey, 1980).

Metabolite or fraction	^{14}C (mg/kg as thiodicarb) at intervals after 21 days dosing								
	102 ppm dose			29 ppm dose			15 ppm dose		
	6 h	3 days	7 days	6 h	3 days	7 days	6 h	3 days	7 days
Liver									
Acetonitrile	0.44	0.076	0.018	0.134	0.017	0.005	0.047	0.007	0.003
Acetamide[1]	0.051	NC	NC	NA	NA	NA	NA	NA	NA
Unknown lipids	2.5	0.84	0.53	NA	NA	NA	NA	NA	NA
Unknown polar[2]	0.84	0.18	0.043	NA	NA	NA	NA	NA	NA
Involatile	NA	NA	NA	1.2	0.33	0.22	0.43	0.14	0.054
Unextractable	4.7	2.0	0.20	1.5	0.68	0.41	0.84	0.2	0.11
Recovery (% of TRR)	85%								
Breast muscle									
Acetonitrile	0.27	0.011	0.001	0.1	0.017	0.005	0.030	0.002	Trace
Acetamide[1]	0.009	NC	NC	NA	NA	NA	NA	NA	NA
Unknown lipids	0.44	0.45	0.22	NA	NA	NA	NA	NA	NA
Unknown polars[2]	0.062	0.052	0.034	NA	NA	NA	NA	NA	NA
Involatile	NA	NA	NA	1.257	0.33	0.220	0.082	0.047	0.035
Unextractable	1.3	1.4	1.00	0.52	0.40	0.23	0.21	0	0.11
Recovery (% of TRR)	61%								
Thigh muscle									
Acetonitrile	0.22	0.009	0.005	0.067	0.003	Trace	0.035	0.002	Trace
Acetamide[1]	0.006	NC	NC	NA	NA	NA	NA	NA	NA
Unknown lipids	2.5	0.84	0.53	NA	NA	NA	NA	NA	NA
Unknown polars[2]	0.84	0.048	0.042	NA	NA	NA	NA	NA	NA
Involatile	NA	NA	NA	0.36	0.22	0.21	0.15	0.084	0.099
Unextractable	1.2	1.1	0.95	0.64	0.43	0.35	0.24	0.16	0.16
Recovery (% of TRR)	113%								
Abdominal fat									
Acetonitrile	ND	ND	ND	NA	NA	NA	NA	NA	NA
Acetamide[1]	ND	ND	ND	NA	NA	NA	NA	NA	NA
Unknown lipids	5.6	12.	9.4	NA	NA	NA	NA	NA	NA
Unknown polars[2]	ND	ND	ND	NA	NA	NA	NA	NA	NA
Unextractable	0.16	0.26	0.31	NA	NA	NA	NA	NA	NA
Recovery (% of TRR)	87%								

[1] Only tissue samples at 6 h contained sufficient total water-soluble radioactivity to allow separation and confirmation of absolute acetamide levels
[2] Fraction containing any acetamide present in 3 and 7 day samples
NC: level not confirmed
NA: not analysed
ND: not detected

Goats. The metabolic fate of [^{14}C]thiodicarb (specific activity 17.72 mCi/mmol) was studied in two lactating goats after 7 days of dosing at levels equivalent to 200 and 300 ppm in the diet (Hanlon and Norris, 1991; Hanlon, 1994).

The goats were placed in indirect respiration chambers for the collection of volatiles for approximately 10 hours on the 6th day. Faeces, urine and milk were collected twice daily during the treatment period. Blood, gut content and tissue samples were taken for analysis within 18 hours of the last dose. The nominal level of detection of ^{14}C in combustion samples was 0.01 mg/kg as thiodicarb and for LSC measurement 0.002 μg.

Urine samples were analysed directly by HPLC and TLC. Milk samples were extracted with acetonitrile and hexane, stomach contents and faeces with methanol, and selected tissues by water and then by methanol. Extracted solids were treated with protease to liberate additional residues, and other

fractions were treated with various enzymes and/or base as appropriate. Extracts were analysed by a combination of chromatographic techniques including HPLC and TLC.

Trapped volatile compounds were acetonitrile and carbon dioxide. Volatile production during 10 hours was extrapolated to cover the entire dosing period, and the total ^{14}C residues associated with respiration were estimated to be 21 and 23% of the total dose for goats 1 and 2.

Table 7. Distribution of radioactivity in goats dosed with [^{14}C]thiodicarb for 7 days (Hanlon and Norris, 1991; Hanlon, 1994).

	^{14}C, % of total dose					
	Tissues[1]	Milk	Urine	Faeces	Volatiles[2]	Total
Goat 1	8.6	6.4	8.9	7.7	21.	52
Goat 2	14.	3.1	5.8	3.5	23.	50
Average	11.	4.7	7.3	5.6	22.	51

[1] including blood and gut contents
[2] Extrapolated from 10-h period.

Total radioactivity appeared to reach a plateau within three days in the faeces, urine and milk. The levels in the milk and tissues are shown in Table 8.

Table 8. Distribution of residues of [^{14}C]thiodicarb in goats dosed for 7 days (Hanlon and Norris, 1991; Hanlon, 1994).

Sample	Cumulative % of applied dose			^{14}C as thiodicarb (mg/kg)		
	Goat 1	Goat 2	Mean	Goat 1	Goat 2	Mean
Milk	6.4	3.1	4.7	15*	20*	17.*
Liver	0.93	1.1	1.0	25.	23.	24.
Kidney	0.08	0.11	0.10	13	14	13.
Muscle	3.3	3.9	3.6	4.3	4.2	4.3
Fat	0.66	0.26	0.46	1.4	0.45	0.91
Blood	1.6	2.0	1.8	10.	11	11

* Maximum level over the 7 days dosing

Gut contents contained acetonitrile (15 and 24% of the TRR), acetamide (5.8 and 7.1%), thiodicarb (6.3 and 5.5%) and methomyl (3.2 and 7.5%). Faeces from early and late periods were found to contain thiodicarb and methomyl as the main radioactive residues. In urine only acetonitrile and acetamide were identified.

Goat 2 became ill in the latter part of the study with resultant decline in urine, faeces and milk outputs. Because of this the tissues from goat 2 were used mainly for method development, and definitive work was done on tissues from goat 1. Between 70 and 91% of the radioactive residues were extractable from liver, kidney and muscle with water. No thiodicarb, methomyl, or methomyl metabolites were found in any of these tissues. Acetonitrile and acetamide were detected in liver, kidney and muscle; one of the radioactive components was an unknown water-soluble polar compound which was converted to acetic acid by alkaline hydrolysis (Table 9).

Table 9. Residues in the edible tissues of goat 1 (dosed at 200 ppm dietary equivalent) as a percentage of the total administered ^{14}C and mg/kg thiodicarb equivalents (Hanlon and Norris, 1991; Hanlon, 1994).

Metabolite	Liver		Kidney		Muscle	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Acetonitrile	32.	8.2	23	2.9	72	3.1
Acetamide	5.9	1.5	10.	1.3	14.	0.62
Acetic acid*	57.	14.	43.	5.4	11.	0.49
Total	95.	24.	76.	9.6	97.	4.2

*From alkaline hydrolysis of an unknown polar compound

Most of the TRR was extracted from fat and milk samples with acetonitrile and hexane. The acetonitrile extracts were analysed by HPLC and the ^{14}C residues in the hexane were characterized by saponification. Post-extraction solids were also examined further in both cases (Tables 10 and 11).

Table 10. Residues in the fat of two goats as a percentage of total ^{14}C-residues and mg/kg thiodicarb equivalents.

Metabolite	Goat 1		Goat 2	
	% of TRR	mg/kg	% of TRR	mg/kg
Acetonitrile	9.9	0.14	11.1	0.05
Acetamide*	6.0	0.08	25	0.11
Non-saponifiable fatty acids	1.3	0.02	1.0	0.01
Saponifiable fatty acids	46	0.63	15	0.07
Other saponifiable lipids	27	0.37	26	0.12
Total	90	1.2	79	0.36

*Acetamide may be due in part to hydrolysis of acetonitrile during concentration of extracts

Table 11. Residues in milk as % of total ^{14}C residues and mg/kg thiodicarb equivalents.

Metabolite	Goat 1		Goat 2	
	% of TRR	mg/kg	% of TRR	mg/kg
Acetonitrile	29	4.1	18	1.8
Acetamide	0.0	0.0	4.0	0.41
Lactose	11	1.6	23.	2.3
Acetic acid	0.0	0.0	4.0	0.41
Non-saponifiable fatty acids	0.6	0.09	0.3	0.03
Saponifiable fatty acids	18	2.6	8.2	0.84
Other saponifiable lipids	14	2.6	9.7	1.0
Losses*	8.4	1.2	7.8	0.80
Solids (bound)	1.0	0.14	2.5	0.25
Total	82	12	77	7.9

*Losses during transfers, etc., not volatility

In the supplementary report (Hanlon, 1994), saponifiable fatty acids in hexane extracts of the milk and fat were identified as [^{14}C]palmitic and [^{14}C]myristic acids and a water-soluble saponifiable lipid in milk yielded [^{14}C]glycerol. In addition, material retained on the column from HPLC of an aqueous fraction of liver and kidney was further characterized as amino acids or proteins, which release acetonitrile and acetic acid upon strong basic hydrolysis. The combined results of the original and supplementary reports show identification or characterization of acceptable percentages of the TRR in liver (>90%), kidney (>75%), muscle (>95%), fat (>63%) and milk (>69%).

An older study on lactating cows (Feung *et al.,* 1980) corroborates the results of the goat study.

In ruminants and poultry the transfer and distribution of radioactivity was the result of thiodicarb metabolism to acetonitrile and carbon dioxide followed by incorporation of ^{14}C fragments into natural pathways. No thiodicarb, methomyl, or intact methomyl metabolites were detected in any edible tissues, eggs, or milk, even after feeding at dietary concentrations as high as 100 ppm in poultry or 290 ppm in goats.

The results of animal metabolism studies are consistent with thiodicarb being extensively metabolized and almost no residual material was retained in any species. Thiodicarb is rapidly degraded to *syn*- and *anti*-methomyl, and subsequently to CO_2 and acetonitrile, which are primarily eliminated by respiration and in the urine. A portion of the CO_2 fraction can be incorporated to natural products. Acetonitrile which is not eliminated can be further converted to CO_2, acetic acid and acetamide, all of which can be subsequently incorporated into natural products. There is no evidence of direct transfer of carbamate residues to edible substrates in lactating goats, even when animals are administered exaggerated levels (200-300 ppm). The proposed metabolic pathways for thiodicarb in mammals and poultry are shown in Figure 1.

Plant metabolism

The metabolism in plants was studied using [^{14}C]thiodicarb in root crops (potato and carrot), a fruiting vegetable (tomato), cereal grains (wheat, maize and sweet corn) and oilseed crops (cotton, soya beans and peanuts).

Potatoes. The absorption, translocation and metabolism of thiodicarb in foliage and tubers following the application of radiolabelled material to the upper leaf surfaces was reported by Feung and Chancey (1979c). [^{14}C]Thiodicarb (specific activity about 41,000 dpm/µg) was spread on the top surfaces of leaves of 6 greenhouse-reared plants approximately 60 cm high at a rate approximating 1.12 kg ai/ha. The plants were watered daily and harvested when the tubers were of good size. The time from application to harvest was not specified. Harvested plants were separated into foliage and tubers and stored in a freezer until analysis.

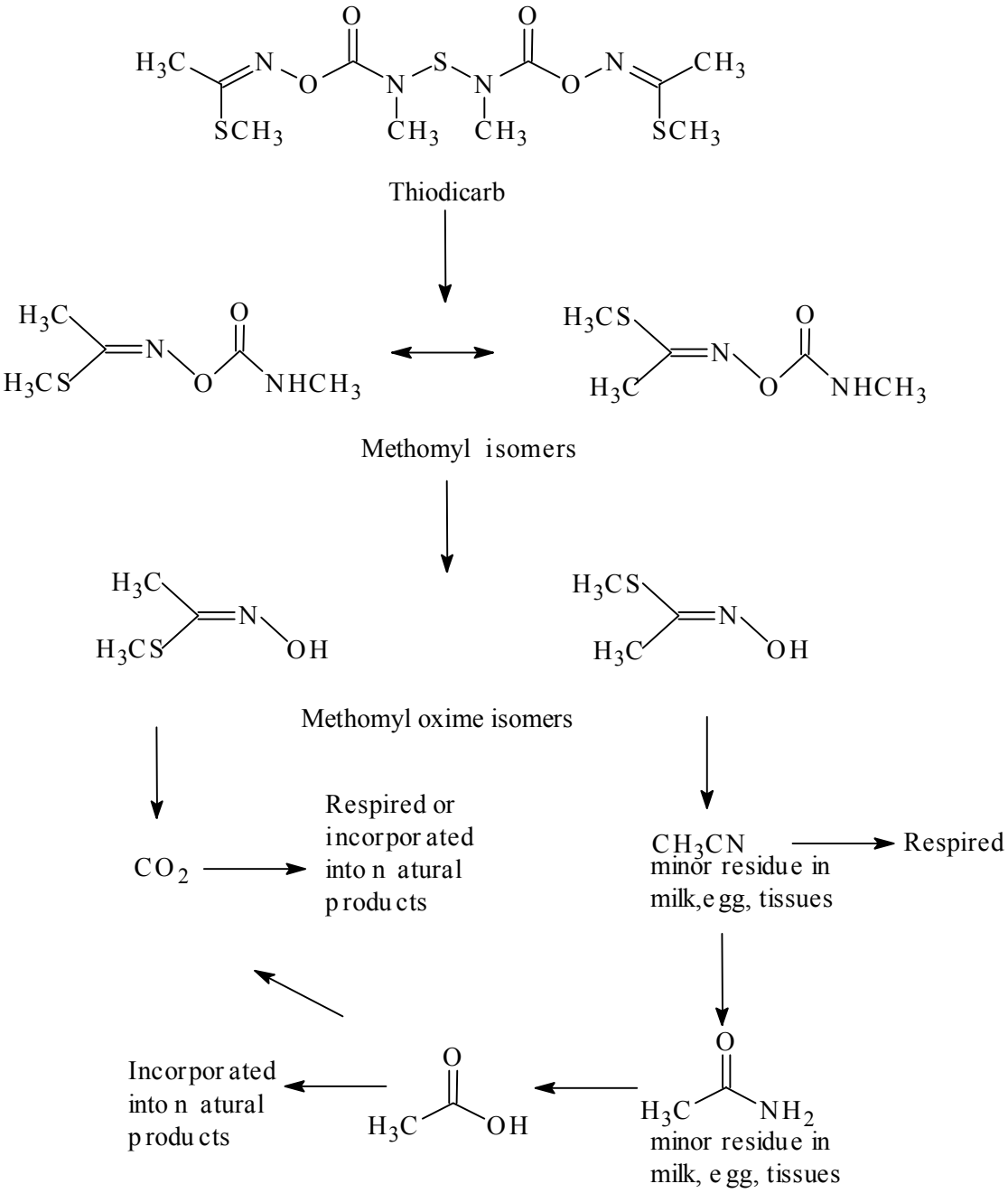
The radioactive residue in the foliage accounted for 59% of the applied dose, but in tubers for only 0.12%. The remaining radioactivity (approximately 40%) is presumed to represent the amount of volatile $^{14}CO_2$ and $^{14}CH_3CN$ lost from the leaf surface following thiodicarb degradation. Isolated metabolites were determined by two-dimensional thin-layer chromatography.

he very low level of ^{14}C found in the tubers was indicative of the very low potential for translocation of thiodicarb from leaves to tubers. The extractable radioactivity (approximately 0.024 mg/kg as thiodicarb, or 50% of the total radioactive residue in the tubers) was almost entirely water-soluble. A single polar metabolite was seen in the organosoluble fraction (representing less than 5% of the radioactivity in the tuber, <<0.01 mg/kg) that did not compare with any known standard on TLC.

Isolation of metabolites from the tuber was not possible owing to the extremely low level of radioactivity in the acetonitrile extract following enzymatic treatment of the water-soluble fraction. The low level of radioactivity arose from translocation from the leaves and/or incorporation of $^{14}CO_2$ released from the parent compound into naturally occurring plant components.

pproximately 53% of the radioactivity in foliage was organosoluble. Nine components were observed on TLC, four of which were identified as thiodicarb (major), methomyl and methomyl methylol (minor), and methomyl oxime (trace).

Figure 1. Metabolic fate of thiodicarb in animals.



Note: methomyl oxime was not observed in tissues, milk or eggs.

The remaining 5 components accounted for only 0.54% of the radioactivity in the fraction and did not match any of the standards on TLC. A small percentage of the foliage radioactivity (4%) was found in the water-soluble fraction. After enzymolysis, three aglycones, methomyl, methomyl oxime and methomyl methylol, were seen on TLC.

Carrots. Feung and Chancey (1978c) spread approximately 10 μCi of [^{14}C]thiodicarb on the top surface of the leaves of six-week old greenhouse plants with a microsyringe. The plants were manually watered daily and harvested 28 days later, separated into aerial portions and roots, and then stored in a freezer until analysis.

Appreciable activity was found in the aerial portions, but only traces in the root extracts. High recoveries (90.47% of the applied) indicated little volatilisation on the leaves. The low activity in the roots (0.06% of that applied) was attributed to poor translocation of thiodicarb or its metabolites from the leaves to the roots. It did not allow any isolation or determination of metabolites.

In the foliage, four of nine organosoluble metabolites were tentatively identified by two-dimensional co-chromatography on TLC as unchanged thiodicarb (79% of the applied radioactivity), methomyl (8.2%), *N*-hydroxymethyl methomyl (0.18%) and methomyl oxime (0.09%). The remaining metabolites did not match the authentic standards.

TLC of the water-soluble fraction before enzymolysis showed a single radioactive spot remaining at the origin. After enzymolysis, eight aglycones were resolvable. Three were identified by two-dimensional TLC as methomyl (0.29% of the applied radioactivity), *N*-hydroxymethyl-methomyl (0.02%) and methomyl oxime (0.01%). The remaining metabolites did not behave like any of the authentic standards on TLC in any of the solvents used. Methomyl and methomyl oxime were verified by mass spectrometry.

Tomatoes. The disposition and metabolism of [^{14}C]thiodicarb was investigated in foliage and fruit by Feung and Chancey (1979b).

A solution of [^{14}C]thiodicarb (about 6000 mg/kg, specific activity approximately 41,000 dpm/μg) was spread on the top surfaces of tomato leaves at the time of flower cluster initiation at a rate approximating 1.12 kg ai/ha. The plants were maintained in a greenhouse until mature, when the fruits were harvested, weighed and stored in the freezer until analysis. The foliage was also collected and frozen until analysis.

Frozen tissues from harvested plants were ground in a blender with acetonitrile/acetone/water. The homogenate was centrifuged and filtered and the plant residue washed several times with mixed solvent and air-dried at room temperature. The radioactivity of each fraction was determined by liquid scintillation counting. The filtrate was diluted with chloroform and partitioned into organosoluble and water-soluble fractions. The organosoluble fraction was concentrated in a rotary evaporator. The aqueous fraction was concentrated and a portion subjected to enzyme hydrolysis, extracted with acetonitrile/chloroform and separated into aglycone and aqueous fractions. The aqueous fraction was then refluxed with 1N HCl and partitioned into organic and aqueous fractions.

Approximately 50% of the radioactivity was lost from the leaf surface as volatiles, presumably CO_2 and CH_3CN. Appreciable radioactivity was detected in leaves (approximately 49% of the applied dose). Radioactivity measurements indicated very low activity in tomato fruit (0.45% of the applied dose), evidence of low absorption and translocation. Although metabolites in the fruit were fractionated and isolated characterization was not possible owing to the very low radioactivity. The low level of radioactivity in the fruit was thought to be the result of incorporation of $^{14}CO_2$, released from degraded metabolites, into naturally occurring plant components.

In total, organic and aqueous extracts of the foliage accounted for about 45% of the applied ^{14}C, with unextractable residues amounting to a further 4%. Identification of metabolites was by comparison against authentic standards using two-dimensional TLC. The results are shown in Table 12.

Table 12. Compounds identified in tomato leaves (Feung and Chancey, 1979b).

Compound	% of total recovered radioactivity in leaves fraction[1]
Organosoluble	
– thiodicarb	78.
– methomyl	5.9
– methomyl oxime	0.18
– others	<3
Water-soluble, conjugates of	
– methomyl	<1
– methomyl oxime	0.16
– methomyl methylol	<1
Unextractable	0.8

[1] Represents 49% of applied radioactivity

Four organosoluble compounds were identified (96% of organic fraction, 84% of the total radioactivity in the leaves): thiodicarb (major), methomyl (minor), methomyl oxime (very minor) and methomyl methylol (trace). The remaining 5 organosoluble metabolites accounted for approximately 4% of the fraction and did not match any of the standards on TLC. Three of the water-soluble components (12% of the fraction, 0.5% of the total radioactivity in leaves) were identified as conjugates of methomyl, methomyl oxime and methomyl methylol. The remaining unidentified water-soluble components accounted for 88% of the fraction but only 0.8% of the total radioactivity in the leaves.

Feung and Jeffs (1986) investigated the metabolism of [^{14}C]thiodicarb in tomato foliage and fruit following application of radiolabelled material to both tomatoes and foliage. Three experiments were conducted, each with two plants treated 6 times at 6-day intervals at a rate approximating 1.12 kg ai/ha/treatment.

In experiment 1, a solution of [^{14}C]thiodicarb was spread on the top surfaces of tomato leaves, equivalent to a season rate of 6.72 kg ai/ha. The plants were maintained in a greenhouse for 6 days after the last treatment, when the fruits and foliage were harvested, weighed, chopped and stored in the freezer until analysis.

In experiment 2, only the fruits were treated, harvested 6 days after the last treatment and washed with 70% methanol to remove surface compounds. The washed fruit were weighed, chopped and stored in the freezer until analysis. The methanol rinse was concentrated and analysed by TLC.

In experiment 3, both fruits and foliage were treated and harvested 6 days after the last treatment. The tomatoes were processed, stored and analysed in the same way as in experiment 2. The foliage was stored with the fruit in the freezer.

Samples of fruit and foliage from all experiments were blended with methanol and the homogenate filtered; this was repeated and the residue cake washed twice with methanol and dried. Radioactivity was measured in the fractions. Residues were extracted from fruit and foliage as in previous studies, separating organosoluble and water-soluble components.

Approximately 57-63% of the applied radioactivity was lost as volatiles in the three experiments (presumably as CO_2 and CH_3CN). The results are shown in Table 13. The foliar applications resulted in very little residue in the fruit and fruit applications resulted in very little residue in the foliage.

Table 13. Distribution of the applied radioactivity in tomato fruit and foliage (Feung and Jeffs, 1986).

Sample	^{14}C, % of applied					
	Experiment 1, foliage treated		Experiment 2, fruit treated		Experiment 3, both fruit and foliage treated	
	Extractable	Unextractable	Extractable	Unextractable	Extractable	Unextractable
Residues rinsed from fruit surface	NA	NA	29.7 25.1	NA	2.91 3.30	NA
Residues in foliage	33.3 34.8	8.61 8.12	0.35 0.33	0.10 0.45	26.6 23.1	6.28 7.17
Residues in fruit	0.35 0.12	0.33 0.55	8.47 6.81	1.96 1.83	1.06 1.63	0.66 0.57
Total involatile	42.6 43.6		40.6 34.5		37.5 35.7	

NA: not applicable

Residues rinsed from the surface of fruits in experiments 2 and 3 were identified by two-dimensional TLC of the concentrated rinse solutions; ten radioactive compounds were observed. Three were identified as thiodicarb (73 to 83% of the rinsed fraction), methomyl (3 to 5%) and methomyl methylol (<1 to 4%). The remaining 6 metabolites, representing 13 to 17% of the rinsed fraction, did not match authentic standards on TLC. No acetamide was found in the extracts rinsed from the fruit surface (limit of detection estimated to be 0.03 to 0.05 mg/kg).

Compounds in the bulk samples of fruit and foliage were identified by two-dimensional TLC and mass spectrometry. In the fruit extracts from experiment 2 (which contained the highest total radioactive residue in fruit), methomyl (1% of the applied dose) and methomyl oxime (0.43% of the applied dose) were identified in the organosoluble fraction. In the foliage from experiments 1 and 3, 11 radioactive compounds were found in the organosoluble fraction; three were identified as thiodicarb (major), methomyl (minor to major) and methomyl methylol (minor to trace). The remaining metabolites accounted for less than 16% of the radioactivity in the leaves and did not match any of the standards on TLC. In both fruit and foliage, the water-soluble metabolites were determined to be natural products resulting from the incorporation of radioactive thiodicarb fragments (e.g. CO_2). No acetamide was found in either fruit or foliage.

Sweet corn and wheat. Approximately 5 µCi of [^{14}C]thiodicarb in 30 µl of acetonitrile/acetone/water (0.5:1.5:1.0) was injected into the stems of 3-week-old greenhouse-grown sweet corn and wheat plants which were maintained in a greenhouse for 7 days, then harvested, weighed and stored in the freezer until analysis (Feung and Chancey, 1977b). Samples were extracted and analysed as previously described.

Approximately 26% and 53% of the radioactivity was lost from sweet corn and wheat respectively, presumably as volatiles such as CO_2 and CH_3CN. In sweet corn, organosoluble plus water-soluble fractions accounted for about 70% of the applied ^{14}C, with unextractable residues amounting to a further 4%. In wheat the extracts accounted for about 34%, and the unextractable residues for about 14%, of the applied dose.

Compounds were identified by comparison with authentic standards using two-dimensional TLC and mass spectrometry. Four organosoluble compounds were identified in both sweet corn and wheat (accounting for >95% of the fraction in each case): thiodicarb and methomyl (major in both), and methomyl oxime and methomyl sulfoxide (very minor in both). The remaining 5 organosoluble metabolites did not match any of the standards on TLC. Three of the water-soluble components were identified as conjugates of methomyl, methomyl oxime and methomyl sulfoxide (all <1% in both plants), with most of organo-insoluble radioactivity unchanged by enzymatic hydrolysis.

Feung and Blanton (1986a) investigated the metabolism of [^{14}C]thiodicarb in sweet corn following application of radiolabelled material to surfaces of the foliage, particularly to verify that acetamide is not a metabolite of thiodicarb in sweet corn. [^{14}C]thiodicarb (224 mg, 18 mCi) was painted onto the foliage of 8 plants. In experiment 1 the application was made to leaves and ears, including silks, and in experiment 2 to the leaves only. A total of 4 treatments were made at 7-day intervals, representing a seasonal use rate of 4.48 kg ai/ha.

The plants were maintained in a greenhouse for 7 days after the last treatment, when the ears (kernels and cobs) and the foliage, including ear sheath and silk, were harvested, weighed, chopped and stored in the freezer until analysis. Samples were blended twice with methanol and the homogenate filtered, and the residue cake washed twice with methanol and dried. Radioactivity was measured in the fractions. Residues were extracted by a procedure which separated organosoluble fractions, precipitates (presumed natural products), pigments (foliage only) and unextractable components.

Approximately 64-67% of the applied radioactivity was presumably lost as CO_2 and CH_3CN during the seven days after the last application. There was very little residue penetration through the foliage; only minute quantities of radioactivity were found in kernels and cobs (Table 14).

Table 14. Distribution of applied radioactivity in sweet corn foliage, kernels and cobs (Feung and Blanton, 1986)**.**

Sample	^{14}C, % of applied					
	Experiment 1 (leaves + ear)			Experiment 2 (leaves)		
	Organo-soluble	Natural products	Unextracted	Organo-soluble	Natural products	Unextracted
Foliage	27	3.4	3.5	27	3.2	0.73
Kernels	0.012	0.007	0.052	0.017	0.019	0.093
Cobs	0.018	0.004	0.012	0.014	0.005	0.013

Identification of residues was made by comparison with authentic standards using two-dimensional TLC. No acetamide was found in any sample.

The highest residues were observed in foliage, where 31 to 34% of the applied radioactivity was recovered. Approximately 85 to 89% of this fraction (27-28% of the applied) was organosoluble; 9 radiolabelled components were observed. The main compounds were identified as thiodicarb (68 to 76% of the foliage fraction, about 20% of the applied dose) and methomyl (19 to 21% of the fraction, about 6% of the applied dose). Methomyl oxime and methomyl methylol were identified at about 0.3% of the applied dose in experiment 1 and at trace levels in experiment 2. The additional unidentified organosolubles accounted for less than 10% of the radioactivity in the fraction (about 3 to 4% of the applied dose). Less than 5% of the applied radioactivity was water-soluble, postulated to be mainly natural constituents derived from the incorporation of labelled metabolites. Only about 1% of the radioactivity was recovered as free metabolites after enzymatic hydrolysis.

In the kernels, most of the radioactivity (72 to 74%) could not be extracted. Only 26 to 28% of the radioactive residue was organosoluble, with 13 to 17% as organosoluble metabolites and the rest precipitated or unextractable. Unextractable and precipitated residues were postulated to be natural kernel constituents resulting from the absorption of radiolabelled carbon dioxide or incorporation of other metabolites. The low residue in kernels precluded identification of any individual metabolites; 4 compounds were observed by TLC, none of which corresponded to any reference standard. Results in cobs were similar, with only about half in the organosoluble fraction but no component corresponding to known authentic standards.

Cotton. Two studies were reported on the metabolism of thiodicarb in cotton plants following stem injection and leaf application (Feung and Chancey, 1977a) .

In one [^{14}C]thiodicarb (50 µg, 4 x 10^6 dpm, 2 µCi, specific activity 8.1 X 10^4 dpm/µg) was injected into the stem of 4 to 5 week cotton plants which were maintained in a greenhouse and harvested 7, 14, 21 and 28 days after treatment. Samples were frozen until analysis (at least 8 hours). In the other [^{14}C]thiodicarb (160 µg, 13 X 10^6 dpm, 6 µCi) was applied by stem injection to some plants and by topical application to the top surfaces of leaves of other 4-week plants. Both groups of plants were maintained in enclosed glass containers and volatiles were collected in a series of traps at intervals of 1, 4 and 7 days after application. Samples were analysed as previously described and extracted by a procedure similar to that used for tomato leaves.

Carbon dioxide and acetonitrile accounted for most of the radioactivity determined as volatile components in the second experiment. The percentage of the total applied radioactivity released as $^{14}CO_2$ and $^{14}CH_3CN$ was greater from leaf treatment than stem injection, with a ratio of CO_2:CH_3CN of 2:1 for injected and 1:20 for leaf-treated plants.

In the first experiment apparent volatile compounds, presumed to be mostly carbon dioxide and acetonitrile, accounted for 70% of the applied radioactivity in the 28-day samples. The remaining extractable residues (28%) showed that thiodicarb was metabolized in cotton to at least 7 water-soluble and 6 organosoluble components (7 and 21% of the radioactivity respectively). It was observed that after short treatment times, the organosoluble metabolites were predominant, whereas longer times resulted in a decrease in organosoluble concentrations with a corresponding increase in water-soluble compound levels. Only a small proportion of the radioactivity (0.7 to 2.6%) remained in the plant tissues after extraction (Table 15).

Table 15. Recovery of the applied radioactivity from injected cotton plants measured at selected intervals (Feung and Chancey, 1977a)

Fraction	^{14}C, % of applied			
	7 DAT	14 DAT	21 DAT	28 DAT
Organosoluble	53.1	8.0	8.4	6.7
Water-soluble	11.6	25.2	21.7	21.2
Unextractable	0.7	2.6	1.7	1.5
Presumed volatiles	34.6	64.8	67.9	69.7

DAT: days after treatment
Presumed volatiles: radioactivity not accounted for by combined extractable and unextractable fractions

Compounds were identified or characterized by co-chromatography against authentic standards in one and two-dimensional TLC with mass spectrometry and nuclear magnetic resonance as appropriate.

Of the 6 organosoluble compounds (53 to 7% of the applied ^{14}C, declining over the duration of the 4-week growth period) three were identified, accounting for 50 to 98% of the fraction: thiodicarb (initially major), methomyl (finally major) and methomyl oxime (trace). The three unidentified compounds (2 to 50% of the fraction) accounted for between 1 and 4% of the total applied dosage.

Of the 7 water-soluble components (12 to 25% of the applied ^{14}C), 2 were identified as conjugates of methomyl and methomyl oxime (probably glycoside esters). The remaining 5 components, which accounted for over 80% of the radioactivity in the aglycone fraction, were thought to be naturally occurring products formed by incorporation of $^{14}CO_2$ from the absence of N-S and N-C bonds by NMR as well as their different behaviour from standards on TLC in all solvent systems used.

The absorption, translocation and metabolism of [^{14}C]thiodicarb (purity >98.5%) in or on cotton after a leaf surface application was also investigated by Feung and Chancey (1978a).

A solution of [^{14}C]thiodicarb (about 6000 ppm, specific activity 12,000 dpm/µg) was spread on the top surfaces of cotton leaves at the flower bud stage at a rate approximating 1.12 kg ai/ha. The plants were maintained in a greenhouse until the bolls were mature, when they were harvested and the seeds de-linted. The senescent leaves were also collected and all samples were frozen until analysis. Small branches were also taken from treated plants 14 days after application to investigate absorption and translocation. Frozen seed and leaves from the harvested plants were ground in a blender with acetonitrile/water. Previously described extraction and fractionation procedures were followed to separate organosoluble and water-soluble compounds.

In order to assess the extent of absorption and translocation, the branches removed after 14 days were pressed and dried and then exposed to X-ray film for 21 days. Absorption and translocation of radioactivity were both poor; most of the radioactivity still remained on the leaf surface. Radioactivity measurements in harvested seed and lint samples indicated very low activity in lint (0.05% of the applied dose) and seeds (0.09%), further evidence of low absorption and translocation.

Although seed samples were fractionated, the characterization of metabolites was not possible owing to the very low radioactivity. The low level of radioactivity found in seeds and lint was thought to be the result of incorporation of $^{14}CO_2$ released from the parent compound into naturally occurring plant components.

The identification of compounds in and on senescent leaves was by two-dimensional TLC, and infrared and mass spectrometry.

Table 16. Compounds isolated from senescent leaves of cotton (Feung and Chancey, 1978a).

Compounds	% of total radioactivity in leaves
Organosoluble	
– thiodicarb	21.85
– methomyl	12.42
– methomyl oxime	0.14
– methomyl methylol	0.51
– others	1.25
Water-soluble, conjugates of	
– methomyl	3.1
– methomyl oxime	0.84
– methomyl methylol	1.71
– others	4
Unextractable	20

Eleven organosoluble and nine water-soluble components were isolated. Four of the organosoluble components were identified, accounting for 95% of this fraction, 35% of the total radioactivity in the leaves: thiodicarb (major), methomyl (major), methomyl oxime (minor) and methomyl methylol (minor). The remaining organosoluble metabolites (about 5% of the fraction) did not match authentic standards on TLC. Three of the water-soluble components (about 60% of the fraction, 6% of the total radioactivity in the leaves) were identified as conjugates of methomyl, methomyl oxime and methomyl methylol. The remaining metabolites (40% of this fraction) did not correspond to any of the standards on TLC. Unextractable residues accounted for approximately 20% of the total radioactivity in the leaves.

Soya beans. The disposition and metabolism of thiodicarb in or on soya beans after a leaf surface application was investigated by Feung and Chancey (1979a).

A solution of [^{14}C]thiodicarb (purity >98.5%, about 6000 ppm, specific activity 12,000 dpm/µg) was spread on the top surfaces of soya bean leaves at the flower bud stage at a rate approximating 1.12 kg ai/ha, purity >98.5%. The plants were maintained in a greenhouse until the

pods were mature, when they were harvested and the seeds separated from the hulls. The senescent leaves were also collected and all samples frozen until analysis.

Radioactivity was very low in the seed (0.18% of the applied dose) and hulls (0.19%), evidence of low absorption and translocation. The radioactivity was too low for the characterization of metabolites. The radioactivity in the seeds and lint was thought to be the result of incorporation of $^{14}CO_2$, released from degraded metabolites, into naturally occurring plant components.

Residues were extracted from the leaves as from tomato leaves, separating organosoluble and water-soluble components. Identification was by two-dimensional TLC and mass spectrometry.

Table 17. Compounds isolated from soya bean leaves (Feung and Chancey, 1979a).

Compounds	% of applied radioactivity
Organosoluble	
– thiodicarb	85
– methomyl	5.7
– methomyl oxime	Trace
– others	<1
Water-soluble, conjugates of	
– methomyl	0.10
– methomyl oxime	0.03
– methomyl methylol	0.13
Unextractable	<5

Three organosoluble compounds (99% of the fraction, 91% of the total radioactivity in the leaves) were identified: thiodicarb (major), methomyl (minor) and methomyl oxime (trace). The remaining radioactivity (1% of the fraction) did not match any of the standards on TLC. Of seven water-soluble components, three (65% of the fraction, 0.3% of the total radioactivity in the leaves) were identified as conjugates of methomyl, methomyl oxime and methomyl methylol. Two other minor components were found to correspond to unidentified water-soluble compounds from cotton, indicating consistency of metabolism. The unextractable residues accounted for <5% of the total radioactivity in the leaves.

Peanuts. Feung and Blanton (1986b) investigated the potential for the formation of acetamide as a metabolite of thiodicarb in peanut foliage, roots, nuts and shells. The [^{14}C]thiodicarb (purity >98%, 18.0 mCi) was applied topically to the foliage four times at the rate of 1.1 kg ai/ha at 7-day intervals. Samples harvested 21 days after the last treatment were individually analysed.

Appreciable radioactivity was found in foliage (21.8% of the applied dose), while only 0.197%, 0.499% and 0.207% were detected in the roots, nuts and shells respectively. Approximately 77% of the applied radioactivity was unaccounted for, possibly owing to volatilization.

In foliage, almost 60% of the radioactive residue was organosoluble. It was analysed by two-dimensional TLC. In this fraction, thiodicarb (7.28% of the applied dose) and methomyl (1.70%) were respectively the major component and the major metabolite. The remaining 5 minor metabolites (all <1.5% of the applied dose) did not match any of the authentic standards on TLC. No acetamide was found as a metabolite of thiodicarb.

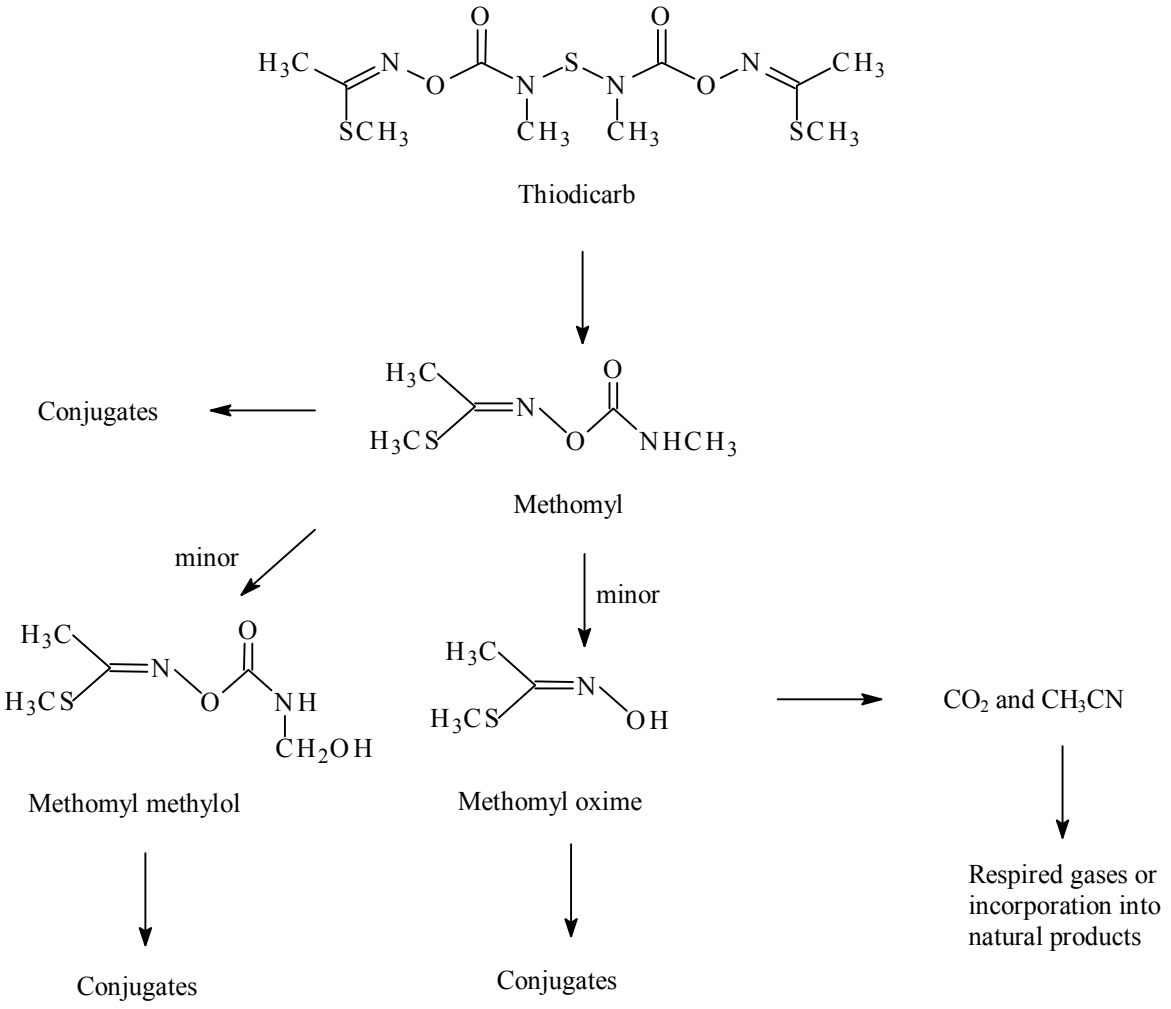
In roots, nuts and shells, most of the ^{14}C residues (53-68%) could not be extracted from the tissue. The organosoluble extract of roots represented 28% of the total radioactivity, while in nuts and shells 23 and 18% of the total radioactivity was organosoluble.

The organosoluble fractions isolated from nuts and shells were further analysed by two-dimensional co-chromatography. At least three radioactive spots were detected, none of which matched any of the authentic standards on TLC. In roots, five spots were detected; again, none

matched authentic standards. These organosoluble metabolites were believed to be natural constituents of roots, nuts and shells. Acetamide was not detected as a metabolite of thiodicarb in any of the samples.

The metabolism of thiodicarb has been found to be qualitatively similar among plant species. It is cleaved at an N-S bond to form methomyl, which is hydrolysed to methomyl oxime, thence further metabolized to CO_2 and acetonitrile. A small amount of methomyl can also be hydroxylated to methomyl methylol. Additional polar metabolites can be envisaged to result from conjugation or incorporation of ^{14}C fragments into natural products. The proposed metabolic pathways are shown in Figure 2.

Figure 2. Proposed metabolic pathways of thiodicarb in plants.



The volatile components $^{14}CO_2$ and [^{14}C]acetonitrile together generally accounted for the loss of 50% or more of the applied dose. In general thiodicarb was the major component recovered from plant foliage, with methomyl or conjugates thereof being major metabolites. Minor free metabolites such as methomyl oxime and methomyl methylol accounted for less than 2% of the extracted radioactivity, with apparent conjugates of these metabolites also present in varying amounts in mature plant foliage. Significant translocation of residues from foliage to seeds, fruits, grain or tubers does not occur**.** However, residues of methomyl were found in supervised field trials on maize in the corn + cob from the foliar application of methomyl.

Environmental fate in soil

Photolysis. Doble *et al.* (2000) incubated thiodicarb under aerobic conditions at 20 ± 2°C with a clay loam soil at a rate equivalent to 1 kg ai/hectare for a period of 21 days. Throughout the study, the moisture content of the soil was maintained at approximately 45% of the maximum water-holding capacity.

The photolysis units, fitted with quartz glass lids and connected to a series of trapping solutions to collect any volatile products evolved, were irradiated with xenon lamps. At each sampling duplicate irradiated and control samples were extracted and the components characterized and quantified by HPLC. Selected extracts were also analysed by TLC to provide confirmation of the compounds present. The associated trapping solutions were also taken for analysis. The traps were changed once during the study.

The overall recovery of radioactivity was 103% for irradiated samples and 99% for control samples. Volatile radioactivity reached a maximum of almost 50% of the applied dose in control and 45% in irradiated samples. It was determined to be associated with carbon dioxide.

Unextractable residues increased steadily and reached a maximum of about 30% of the applied radioactivity at 21 days in both irradiated and control soil. HPLC and TLC of extracts showed that thiodicarb was quickly degraded to the major product methomyl, which reached a maximum of 82% of the applied dose in the control soil and 92% in the irradiated soil at day 2. It then decreased to about 20% by the end of the study.

Methomyl oxime was detected only once in one of the duplicate samples at day 1 in the control soil at 0.5% of the applied radioactivity.

The DT_{50} and DT_{90} of thiodicarb, calculated using a kinetic modelling program, were 0.4 and 1.5 days in control soil and 0.9 and 3 days in irradiated soil.

Aerobic degradation. In two different studies sandy loam soil (pH 5.4, 0.49% organic matter, 70% sand, 17% silt, 13% clay, 9.24% water-holding capacity at 0.33 bar) in metabolism flasks was treated with 10 mg/kg of [^{14}C]thiodicarb (specific activity 20.05 mCi/mmole and radiochemical purity 99%) and maintained under aerobic conditions at 75% moisture content at 1/3 bar in an environmental chamber in the dark at 25 ± 1°C for up to 60 days (Feung and Weisbach, 1991a). Viability in the soil was verified at the beginning and end of the experiment. Volatile organic compounds were trapped in methanol, and CO_2 in 2-ethoxyethanol/ethanolamine, 2:1. Duplicate samples were taken at 0, 0.5, 1, 3, 7, 14, 21, 30 and 60 days, and extracted with methanol and acidified methanol; the extracts were concentrated and analysed by TLC.

Radioactivity in the soil decreased gradually to 42% of the applied dose at day 60 while volatiles increased to 53% over the same period. The volatile radioactive product retained in the methanol traps was identified as acetonitrile by HPLC and GC-MS, and that in the ethoxyethanol-ethanolamine traps was identified as carbon dioxide by re-trapping in NaOH and precipitating with barium chloride.

Thiodicarb steadily decreased as time progressed. It was rapidly degraded to methomyl which in turn was degraded, although more slowly than thiodicarb, to methomyl oxime which was further degraded to acetonitrile and carbon dioxide in a ratio of about 1:28. Methomyl oxime never exceeded 3.2% of the applied dose at any time and was generally less than 1%. A plot of thiodicarb against time followed apparent first-order kinetics. The half-life was calculated to be 1.5 days and the DT_{90} 5.1 days.

Methomyl increased rapidly to 80% of the applied radiocarbon at day 7 and then gradually decreased when most of the thiodicarb had been degraded. The linear portion of the degradation curve

(days 7, 14, 21, 30 and 60) was used to calculate the degradation rate. Methomyl had a half-life of 27 days and a DT_{90} of 90 days.

Three UK soils, a sandy loam (77% sand, 14% silt, 10% clay, 1.8% organic carbon, pH 6.0), a high-pH clay loam (20% sand, 52% silt, 28% clay, 4.6% organic carbon, pH 7.6) and a clay loam (24% sand, 53% silt, 23% clay, 1.9% organic carbon, pH 6.9), were treated with [^{14}C]thiodicarb at a rate equivalent to 1 kg ai/ha and incubated in the dark at a temperature of 20°C, the clay loam also at 10°C, for 56 days (Burr, 2000). After treatment the soil flasks were connected to a series of trapping solutions to collect volatile products, and flasks were removed for analysis at intervals.

Throughout the study, the moisture content of the soil was maintained at approximately 45% of the maximum water-holding capacity.

The soils were extracted and the components identified and quantified by HPLC. Selected extracts were analysed by LC-MS to confirm structural identity. At each sampling the radioactivity in the traps was quantified and the traps were replenished between samplings.

Volatile radioactivity was shown to be due to CO_2, produced rapidly in all the soils. After 56 days incubation the levels reached 61% in the high-pH clay loam, 66% in the sandy loam, 59% in the clay loam incubated at 20°C and 40% in the clay loam incubated at 10°C.

The levels of extractable ^{14}C decreased to <5% after 56 days in all the soils incubated at 20°C and <20% in the soil incubated at 10°C. The unextractable ^{14}C reached a maximum of about 34-35% after 28 days in the three soils incubated at 20°C, with some evidence of a decrease at 56 days, and a maximum of about 30% in the clay loam incubated at 10°C.

The levels of thiodicarb in the extracts decreased rapidly to form one major product, methomyl, which reached a maximum of 80% of the applied radioactivity in the high-pH clay loam, 63% in the sandy loam and 78% in the clay loam incubated at both 20°C and 10°C. The quantity of methomyl in the extracts decreased with time and no further major degradation products of methomyl were detected. There were low levels of minor products, including methomyl oxime, but none of these exceeded 4% of the applied radioactivity at any time.

The DT_{50} and DT_{90} of thiodicarb, calculated with a kinetic modelling program, are shown in Table 18.

Table 18. DT_{50} and DT_{90} of thiodicarb in aerobic conditions (Feung and Weisbach, 1991b).

Soil	DT_{50} (days)	DT_{90} (days)
High-pH clay loam at 20°C	0.01	0.23
Sandy Loam at 20°C	1.2	4.9
Clay Loam at 20°C	0.67	2.2
Clay Loam at 10°C	2.0	6.7

Anaerobic degradation. A clay loam soil was flooded with deionized water and purged with nitrogen for 42-43 days before treatment to establish anaerobic conditions. A solution of [^{14}C]thiodicarb (specific activity 3.96 MBq mg^{-1}; radio purity 98.0%) in a minimal volume of methanol was applied to the water surface at a nominal application rate equivalent to 1 kg ai/ ha, and the soil was incubated at 20°C in the dark (Clarke, 2000). During incubation the system was continually purged with nitrogen, which was then passed through two traps containing methanol, a further trap containing water and a final trap containing 2M aqueous potassium hydroxide to trap liberated volatile materials. Duplicate samples were removed from the system for analysis after 0, 16, 28, 74, 123 and 240 min incubation. At each sampling point the water phase was separated from the soil and the two phases analysed separately.

The radioactivity in the water phase was quantified by LSC of representative aliquots. The nature of the radioactive material present in the water phase was determined by HPLC and structural

confirmation of the species was obtained, where possible, by LC-MS-MS of representative water samples. Because of the rapid degradation of thiodicarb the amount of [^{14}C]thiodicarb present at time 0 was taken as the radio purity value. The results actually found in the duplicates at this time are shown in Table 19 as having incubation periods of 5 and 8 min owing to the inevitable delay between treatment and chromatographic analysis.

All soil samples were extracted with methanol by shaking at room temperature. The radioactivity present in the extracts was quantified by LSC of representative aliquots. The methanol extracts of each soil sample were combined and those containing >5% of the applied radioactivity were analysed by HPLC. The soil was then air-dried, ground to a fine powder and the residual radioactivity quantified by combustion of representative subsamples.

After 240 minutes incubation 78% of the applied radioactivity remained in the water phase. A further 12% was extracted from the soil, 3.5% remained unextracted and 1.4% was present as volatile material.

The mean total recovery of ^{14}C from each soil sample was 94%. All recoveries were within the range 90-98% except one of the 123 min samples, from which the recovery was 88%.

Under anaerobic conditions in water, thiodicarb was degraded extremely quickly through the transient intermediate *S*-methly *N*-[*N*-methyl-*N*-(methylaminothio)carbamoyloxy]thioacetamidate to form acetonitrile, methomyl and methomyl oxime (Table 19).

Table 19. Thiodicarb degradation in water under anaerobic condition (Clarke, 2000).

Incubation time (min)	^{14}C, % of applied							
	0	5	8	16	28	74	123	240
thiodicarb	98	61	32	0.9	0.7	nd	nd	nd
methomyl	nd	2.2	2.8	2.5	2.3	2.3	2.0	1.3
methomyl oxime	nd	nd	nd	nd	nd	0.3	0.2	0.8
acetonitrile	1.5	24.	35	69	69	78	73	75
S-methyl *N*-[*N*-methyl-*N*-(methylaminothio)carbamoyloxy]thioacetamidate	0.5	9.4	28.2	17.4	17.1	7.4	4.8	0.9
Minor products (total)*	nd	nd	nd	nd	nd	0.3	0.3	1.7

nd : not detected
* up to three were observed, each <1.2% of the applied radioactivity

HPLC analysis of soil extracts containing >5% of the applied radioactivity showed that no thiodicarb was present. The radioactivity detected was attributed to acetonitrile and methomyl oxime, which were present at 10% and 0.3% of the applied radioactivity respectively after 240 minutes.

The DT_{50} and DT_{90} values for thiodicarb degradation in the water phase were calculated as 6.0 and 12.6 minutes respectively, using a modelling program. Nearly all the applied radioactivity (about 90%) was present in the water phase during the first 28 minutes and <1% of this was present as thiodicarb at this time point, so the DT_{50} and DT_{90} values for thiodicarb degradation in the entire system are equivalent to those in the water phase.

Soil adsorption/desorption. Cranor (1991) determined the adsorption isotherms and Freundlich constants of four soils equilibrated with aqueous solutions of [^{14}C]thiodicarb (specific activity 23.0 mCi/mmole). The characteristics of the soils are shown in Table 20.

Table 20. Characteristics of soils used in adsorption/desorption study (Cranor, 1991).

Characteristic	Soil #21	Soil #36	Soil #79	Soil #92
Classification	Silt loam	Clay	Sandy loam	Sand
% Organic matter	2.4	2.4	0.8	0.5
% Sand	14	8	54	92
% Silt	68	34	36	4

Characteristic	Soil #21	Soil #36	Soil #79	Soil #92
Classification	Silt loam	Clay	Sandy loam	Sand
% Clay	18	58	10	4
CEC (meq/100 g)	10	26	4.7	0.3
pH	7.1	6.7	6.5	7.4
% Field moisture capacity at 1/3 bar	28	37	9.5	1.9
Bulk density (g/cm^3)	1.2	1.2	1.5	1.6

One-g portions of each sterilized soil were equilibrated with 5 ml aliquots of each [^{14}C]thiodicarb solution in 0.01 M $CaCl_2$ with nominal concentrations of 2.0, 1.0, 0.8 and 0.5 µg/ml. Equilibration was in darkness on a mechanical shaker in an environmental chamber at 25 ± 1^{o}C for 24 h. Each of the suspensions was then centrifuged and the supernatant removed by pipetting. The volume of the supernatant was measured and triplicate aliquots radioassayed.

For desorption, appropriate volumes of 0.01 M $CaCl_2$ solution were added to each sample tube according to the volume removed after the adsorption phase. The soil suspensions were shaken in darkness for 24 h as before, then centrifuged and the supernatants removed.

Table 21. Freundlich adsorption/desorption constants for thiodicarb in four soils (Cranor, 1991).

Soil	% organic carbon	Adsorption		Desorption	
		K_d	K_{oc}	K_d	K_{oc}
Silt loam	1.2	4.5	373	5.3	444
Clay	1.2	14	1167	6.2	518
Sandy loam	0.4	1.3	335	3.4	855
Sand	0.25	0.16	64	0.20	79

K_{oc} values above 5,000 denote immobility in soil, 2,000-5,000 slight mobility, 500-2,000 low mobility, 150-500 medium mobility and 50-150 high mobility. The results indicated that thiodicarb had low mobility in clay, medium mobility in silt loam and sandy loam, and high mobility in sand.

Residues in rotational crops. In a study with a confined sandy loam soil (Jordan and Wyatt, 1994) two plots were established in a Lexan-covered, open-air structure in Lucama, Wilson County, North Carolina, USA. [^{14}C]Thiodicarb (specific activity 20,362 dpm/µg, radiochemical purity 99.7%) was applied at the rate of 6.7 kg ai/ha. The confined soil was then planted with rotational crops, mustard greens, radishes and wheat, at 31, 125 and 364 days after treatment (DAT). Before planting, the soil was tilled 8-10 cm to prepare a suitable seedbed. Soil samples were taken for analysis immediately after treatment and at the times of planting and harvesting the rotational crops. Mature samples of all crops and the immature forage samples of wheat plants were taken for analysis.

Immediately after treatment, the soil residue averaged 2.13 mg/kg and decreased steadily to 0.12 mg/kg at 364 days. Most of the applied radioactivity was at the depth of 0-15 cm. 0-15 cm soil cores were extracted with methanol followed by acidified acetone, and the extracts analysed by TLC and HPLC. The remaining solid was extracted with 0.5 N NaOH, and the unextractable solid (humin) combusted. The NaOH extracts were adjusted to pH 1 and centrifuged. The supernatant (fulvic acid) and the precipitate (humic acid) were radioassayed.

The identification and characterization of ^{14}C residues in the soil are shown in Table 22. Thiodicarb was rapidly degraded in soil as only 5.4% of the radiocarbon in the 31 DAT soil was due to unchanged parent compound. Methomyl increased rapidly and accounted for 47% of the TRR in the 31 DAT soil. These results are consistent with previous studies of degradation in soil.

Table 22. Characterization of ^{14}C residues in soil (Jordan and Wyatt, 1994).

Fraction		0 DAT		31 DAT	
		% of TRR	mg/kg as thiodicarb	% of TRR	mg/kg as thiodicarb
Organic extracts	Thiodicarb	82	1.5	5.4	0.03
	Methomyl	0	0	47	0.20
	Unknown	0	0	0.2	<0.01
	Subtotal	82	1.5	53	0.23
Solid	Fulvic acid	--	--	13	0.05
	Humic acid	--	--	4.1	0.02
	Humin	--	--	18	0.07
	Subtotal	9.9	0.18	35	0.14
Total		92	1.7	88	0.37

The residue levels in the rotational crops are shown in Table 23.

Table 23. Total radioactive residues rotational crops (Jordan and Wyatt, 1994).

Time	^{14}C (mg/kg thiodicarb equivalents)					
	Wheat forage	Mustard greens	Radish tops	Radish roots	Wheat grain	Wheat straw
Day 0	--	--	--	--	--	--
31 DAT	2.1	1.3	1.2	1.6	0.48	2.4
125 DAT	0.28	0.28	0.24	0.11	0.21	0.81
364 DAT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

The identification and characterization of the residues from 31 and 125 DAT crop samples are shown in Tables 24 to 27. Methomyl was the major component identified in aqueous extracts before hydrolysis (up to 0.14 mg/kg, the level in radish tops from the 31-day plant-back interval), and acetic acid the main identified compound after either acid or base hydrolysis. Glucose was also identified in aqueous extracts of radish tops (up to 0.14 mg/kg) after hydrolysis with β-glucosidase. Unidentified polar residues (Unknowns 1 and 2) constituted up to 36% of the TRR in aqueous extracts. Analysis of the aqueous extracts after extensive hydrolysis suggested that these were likely to consist of natural products and conjugates. Insoluble bound final residues constituted up to 10% of the TRR.

In general, most of the radiocarbon residue consisted of natural products: fatty acids (1 to 11% of the TRR), water-soluble polysaccharides, proteins and lipids (5 to 20% of the TRR), starch, protein, pectin, lignin, hemicellulose and cellulose fractionated from cell walls (17 to 63% of the TRR). As in degradation in plants and soil, it was proposed that thiodicarb is quickly metabolized to

methomyl, thence via an assumed methomyl oxime intermediate to acetic acid and carbon dioxide, which are then incorporated into natural products.

Table 24. Characterization of ^{14}C residues in 31 DAT wheat (Jordan and Wyatt, 1994).

Fraction	Wheat forage		Wheat straw		Wheat grain	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Aqueous extract						
Unknown 1	21.9	0.45	17.2	0.42	5.4	0.03
Unknown 2	5.1	0.10				
Methomyl	3.6	0.07				
Aqueous extract- acid hydrolysed [1]						
Unknown 1	13.6	0.28	4.4	0.11		
Acetic acid	8.5	0.17	9.4	0.23	5.4	0.03
Bound to column	8.6	0.18	3.4	0.08		
Aqueous extract- base hydrolysed [1]						
Unknown 1	8.2	0.17	7.4	0.18		
Unknown 2	10.7	0.22				
Acetic acid	9.4	0.19	7.3	0.18		
Methomyl oxime	2.3	0.05				
Bound to column			2.5	0.06		
Hexane extract						
Fatty acids					1.6	<0.01
Fatty acid region #1	1.0	0.02	2.3	0.06		
Fatty acid region #2	0.7	0.02	2.5	0.06		
Fatty acid region #3	2.1	0.05				
Fatty acid region #4	1.3	0.03				
Fatty acid region #5	1.4	0.03				
Fatty acid region #6	4.3	0.09				
Bound residues - cell wall fractionation						
Phosphate - polysaccharide fraction						
Region #1 (TLC origin)	3.0	0.06	1.9	0.05	9.5	0.05
Region #2	0.1	<0.01	3.8	0.09		
Methomyl			2.4	0.06		
Bound to column			7.5	0.18		
MeOH/CH_2Cl_2 extract - protein fraction						
Region #1 (TLC origin)	0.6	0.01	2.5	0.06	8.6	0.04
Acetone/phosphate extract						
Lipid fraction					0.6	<0.01
Region #1 (TLC origin)	1.2	0.02	2.3	0.06		
Starch	0.7	0.01	2.7	0.07	9.1	0.04
Proteins	14.1	0.29	4.6	0.11	23.6	0.11
Pectins	10.6	0.22	2.8	0.07	9.5	0.05
Lignin	4.3	0.09	11.0	0.27	9.7	0.05
Hemicellulose	0.4	<0.01	12.2	0.30	6.7	0.03
Cellulose	1.0	0.02	2.2	0.05	0.8	<0.01
Unextractable solids	1.9	0.04	9.2	0.22	4.9	0.02
Total recoveries	79	1.6	87	2.1	90	0.42

[1] Not included in total.

Table 25. Characterization of ^{14}C residues in 31 DAT mustard greens and radishes (Jordan and Wyatt, 1994).

Fraction	Mustard greens		Radish tops		Radish roots	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	M/kg
Aqueous extract						
Unknown 1	17.	0.23	16.	0.19	11.	0.18
Unknown 2	6.3	0.08				
Methomyl	9.4	0.12	12.	0.14	5.5	0.09
Aqueous extract - acid hydrolysed [1]						
Unknown 1	11	0.14	17.	0.20	9.1	0.15

Fraction	Mustard greens		Radish tops		Radish roots	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	M/kg
Unknown 2	6.5	0.08				
Acetic acid	16.	0.21	10.9	0.13	7.6	0.12
Aqueous extract - base hydrolysed [1]						
Unknown 1	7.6	0.10	6.5	0.08		
Unknown 2	10.	0.13	4.3	0.05		
Acetic acid	8.6	0.11	9.5	0.11		
Methomyl oxime	6.8	0.09	7.8	0.09		
Aqueous extract - β-glucosidase treated [1]						
Glucose	--	--	12.1	0.14		
Hexane extract – fatty acids						
Fatty acid region #1	1.9	0.03	2.1	0.02	1.2	0.02
Fatty acid region #2	1.0	0.01	1.6	0.02	4.9	0.08
Fatty acid region #3	1.0	0.01	2.4	0.03	3.5	0.05
Fatty acid region #4	1.2	0.02	5.2	0.06		
Fatty acid region #5	0.8	0.01				
Bound residues – cell wall fractionation						
Phosphate - polysaccharide fraction						
Region #1 (TLC origin)	3.9	0.05	6.8	0.08	3.9	0.06
Region #2	0.5	<0.01	0.5	<0.01		
$MeOH/CH_2Cl_2$ extract - protein fraction	0.7	<0.01	1.0	0.01	2.0	0.03
Acetone/phosphate extract – lipid fraction						
Region #1 (TLC origin)	1.6	0.02	3.0	0.03	0.7	0.01
Starch	0.8	0.01	1.4	0.02	1.8	0.03
Proteins	7.7	0.10	10.8	0.13	6.2	0.10
Pectins	6.1	0.08	9.3	0.11	19.0	0.30
Lignin	1.2	0.02	1.9	0.02	6.1	0.10
Hemicellulose	0.4	<0.01	0.5	<0.01	3.4	0.05
Cellulose	0.1	<0.01	0.5	<0.01	2.3	0.04
Unextractable solids	0.4	<0.01	1.5	0.02	4.6	0.07
Total recoveries	62.	0.79	77	0.88	76.	1.2

[1] Not included in total.

Table 26. Characterization of ^{14}C residues in 125 DAT wheat (Jordan and Wyatt, 1994).

Fraction	Wheat forage		Wheat straw		Wheat grain	
	% of TRR	ppm	% of TRR	ppm	% of TRR	ppm
Aqueous extract					4.5	<0.01
Unknown 1	22	0.06	4.6	0.04		
Unknown 2	14	0.04	7.7	0.06		
Unknown 3			4.0	0.03		
Methomyl	7.0	0.02				
Aqueous extract - acid hydrolysed [1]						
Unknown 1	18	0.05	4.0	0.03		
Acetic acid	25	0.07	12.3	0.10		
Hexane extract						
Fatty acids					1.0	<0.01
Fatty acid region #1	2.3	<0.01	0.5	<0.01		
Fatty acid region #2	1.8	<0.01	1.6	0.02		
Fatty acid region #3	0.8	<0.01	0.8	<0.01		
Fatty acid region #4	1.9	<0.01	0.2	<0.01		
Bound residues - cell wall fractionation						
Phosphate- polysaccharide fraction						
Region #1 (TLC origin)	7.8	0.02	11.4	0.09	10.3	0.02
$MeOH/CH_2Cl_2$ extract						
Protein fraction	1.5	<0.01				
Region #1 (TLC origin)			3.8	0.03	8.5	0.02
Acetone/phosphate extract						

Fraction	Wheat forage		Wheat straw		Wheat grain	
	% of TRR	ppm	% of TRR	ppm	% of TRR	ppm
Lipid fraction	1.6	<0.01			1.0	<0.01
Region #1 (TLC origin)			2.7	0.02		
Starch	1.4	<0.01	6.4	0.05	9.8	0.02
Proteins	7.9	0.02	5.4	0.04	24.	0.05
Pectins	10.	0.03	4.2	0.03	13.	0.03
Lignin	4.4	0.01	7.4	0.06	8.9	0.02
Hemicellulose	6.6	0.02	12.2	0.10	6.5	0.01
Cellulose	1.5	<0.01	1.9	0.02	0.9	<0.01
Unextractable solids	2.0	<0.01	9.8	0.08	9.9	0.02
Total recoveries	94.	0.22	85	0.67	98.	0.19

[1] Not included in the total.

Table 27. Characterization of ^{14}C residues in 125 DAT mustard greens and radishes (Jordan and Wyatt, 1994).

Fraction	Mustard greens		Radish tops		Radish roots	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Aqueous extract						
Unknown 1	22.	0.06	34.	0.08	30.	0.03
Unknown 2	10.2	0.03				
Methomyl	14	0.04	14.	0.03	14	0.02
Thiodicarb[1]	16.	0.04	7.2	0.02		
Aqueous extract- acid hydrolysed [2]						
Unknown 1	7.8	0.02	25.	0.06		
Unknown 2	9.4	0.03				
Acetic acid	45.	0.12	30.	0.07		
Hexane extract						
Fatty acids					9.2	0.01
Fatty acid region #1	1.3	<0.01	5.1	0.01		
Fatty acid region #2	1.6	<0.01	1.4	<0.01		
Fatty acid region #3	2.5	<0.01	1.7	<0.01		
Fatty acid region #4	1.1	<0.01	2.5	<0.01		
Bound residues- cell wall fractionation						
Phosphate- polysaccharide fraction					3.5	<0.01
Region #1 (TLC origin)	6.8	0.02	9.0	0.02		
MeOH/CH_2Cl_2 extract						
Protein fraction	2.6	<0.01	5.7	0.01	2.9	<0.01
Acetone/phosphate extract						
Lipid fraction	0.8	<0.01	2.2	<0.01	1.1	<0.01
Starch	1.5	<0.01	2.0	<0.01	1.5	<0.01
Proteins	4.4	0.01	17.9	0.04	9.2	0.01
Pectins	17.	0.05	18.3	0.04	25.	0.03
Lignin	2.7	<0.01	5.2	0.01	5.2	<0.01
Hemicellulose	1.4	<0.01	2.4	<0.01	1.6	<0.01
Cellulose	0.3	<0.01	0.5	<0.01	1.2	<0.01
Unextractable solids	1.3	<0.01	2.6	<0.01	1.0	<0.01
Total recoveries	107.	0.25	130.	0.26	105.	0.10

[1] The thiodicarb may have been an artefact: it appears in the 125-day mustard greens and radish tops at levels up to 0.04 mg/kg but it was not present in the 31-day plants and only at very low levels in the soil. It may have been the result of contamination or analysis error.
[2] Not included in the total.

The results show that thiodicarb was rapidly metabolized to compounds such as methomyl, acetic acid (and glucose conjugates of related compounds). It was further metabolized to characterized natural product fractions, which account for a large percentage of the residues. At the high rate of 6.72 kg ai/ha in a worst-case system (confined soil), residues in rotational crops were significant at plant-

back intervals up to 125 days and negligible (TRR <0.01 mg/kg) in crops planted 1 year after application. Thiodicarb was not considered to be a measurable residue in any crop at any plant-back interval, whereas methomyl was observed in wheat forage, mustard greens and radishes (roots and tops) at the 31- and 125-day plant-back intervals, but only at low levels (31 days, 0.07 to 0.14 mg/kg; 125 days, 0.02 to 0.04 mg/kg).

Environmental fate in water and water/sediment systems

Hydrolysis. The rate of hydrolysis of radiolabelled thiodicarb (purity>99%, specific activity 20.05 mCi/mmol) at a concentration of 12 mg/l was determined at pH 5, 7 and 9 in sterile aqueous buffer solutions (acetate 0.01 M, phosphate 0.01 M and borate 0.1 M respectively) in the dark at 25 ± 1°C (Feung and Weisbach, 1991b).

Samples were taken at 0, 1, 3, 7, 14, 21 and 30 days at all pH levels, as well as 0.17 and 0.33 days at pH 9, for LSC and TLC. Products were identified by 2-dimensional TLC, HPLC and MS. Recovery of radioactivity during the incubation period ranged from 93-105% of the applied dose.

Five radioactive components were detected by TLC (Table 28). Thiodicarb, methomyl and methomyl oxime were identified by 2D-TLC co-chromatography, HPLC and MS. Unknown 0 at the TLC origin was scraped and separated into two components by HPLC. These both fragmented into methomyl and methomyl oxime partial structures on MS, but they could not be identified.

Table 28. Degradation products of thiodicarb hydrolysis (Feung and Weisbach, 1991b).

Products	^{14}C, % of applied dose at intervals (days)								
	0	0.17	0.33	1	3	7	14	21	30
pH 5									
Unknown 0*	1.0	-	-	0.38	0.31	0.68	1.6	2.5	4.4
Unknown 1	0.19	-	-	0.31	0.87	0.94	1.3	1.4	2.1
Thiodicarb	96	-	-	97	94	92	87	84	72
Methomyl	2.9	-	-	1.9	4.3	6.5	9.4	12	20
Methomyl oxime	0.00	-	-	0.22	0.29	0.29	0.37	0.46	0.92
pH 7									
Unknown 0*	0.58	-	-	0.59	1.5	2.2	4.9	6.3	10.
Unknown 1	0.20	-	-	0.22	0.41	0.42	0.42	0.73	0.77
Thiodicarb	97	-	-	96	92	85	72	65	49
Methomyl	1.8	-	-	3.0	5.8	11	21	26	36
Methomyl oxime	0.00	-	-	0.20	0.08	0.94	1.4	1.8	3.1
pH 9									
Unknown 0*	0.46	3.8	7.2	10	11	12	10	7.3	4.4
Unknown 1	0.0	2.5	6.1	7.2	5.3	1.6	0.01	0.00	0.00
Thiodicarb	96	66	39	8.7	1.1	0.56	0.37	0.00	0.00
Methomyl	2.9	25	43	66	66	54	40	29	19
Methomyl oxime	0.36	2.1	4.0	7.5	16	32	49	64	77

* 2 components

Thiodicarb is hydrolyzed to methomyl. Methomyl is more stable than thiodicarb, but is itself hydrolysed to methomyl oxime, particularly at pH 9.

Thiodicarb hydrolysis followed apparent first-order kinetics at a rate dependent on the pH. The calculated half-life of thiodicarb was 78 days at pH 5, 32 days at pH 7 and 0.48 day at pH 9. In pH 9 buffer, methomyl reached a maximum at 1 h, then steadily decreased with a half-life of 15 days.

Photolysis. Feung and Blanton (1987) exposed thiodicarb to outdoor natural sunlight in Research Triangle Park, North Carolina, USA, with a dark control. Weather conditions including sunlight intensity, cloud coverage and air temperature during the irradiation period were reported.

[^{14}C]thiodicarb (specific activity 23 mCi/mmol, radiochemical purity 99.3%) was dissolved in an aqueous 0.05 M phosphate buffer at pH 6 at a concentration of 10 mg/l (the water solubility of thiodicarb was 35 mg/l at 25°C). The temperature was maintained at 25 ± 1°C. Two organic traps each containing 90 ml acetone/dry ice and two CO_2 traps each containing 100 ml of 2-ethoxyethanol/ethanolamine (2:1) at ambient temperature were used to trap volatile components. Sampling intervals were 0, 1, 3, 7, 14, 21 and 23 days. Analyses were carried out by direct LSC and TLC.

Volatile radioactivity was detected as the radioactivity in the irradiated solution decreased, while in the dark control the radioactivity remained essentially unchanged (Table 29).

Table 29. ^{14}C balance of thiodicarb during natural sunlight photolysis (Feung and Blanton, 1987).

Time (days)	Treatment	% of initial radioactivity					
		Buffer solution	CO_2 traps		Acetonitrile traps	Rinse	Total recoveries
			1	2			
0	dark	100	-	-	-	-	100
	irradiated	100	-	-	-	-	100
1	dark	98	-	-	-	-	98
	irradiated	94	0.19	0.06	1.0	-	94
3	dark	98	-	-	-	-	98
	irradiated	92	0.46	0.12	2.9	-	95
7	dark	98	-	-	-	-	98
	irradiated	88	0.65	0.14	6.2	-	95
14	dark	98	-	-	-	-	98
	irradiated	77	2.9	0.32	12	-	92
21	dark	97	-	-	-	-	97
	irradiated	72	3.9	0.37	15	-	91
23	dark	98	-	-	-	-	98
	irradiated	72	4.4	0.43	15	0.17	92

Photolysis followed apparent first-order kinetics. After 23 days of exposure, only 12% of the initial [^{14}C]thiodicarb was present as such in the aqueous solution, while 67% remained in the dark control. The half-life of thiodicarb was calculated to be 7.6 days under natural sunlight and 37 days in the dark.

Methomyl was the major degradation product (Table 30). Methomyl methylol and methomyl oxime were also identified (≤2% of the applied radioactivity). Identification was based on two-dimensional TLC co-chromatography with authentic reference standards. The volatile compounds were identified as CO_2 when trapped in 2-ethoxyethanol/ethanolamine and as acetonitrile when trapped in acetone-dry ice. There were 9 other degradation products, each less than 6% (most 0.1-1%) of the initial dose.

Table 30. Photodecomposition products of thiodicarb in water at pH 6 under natural sunlight (North Carolina, USA).

Products	^{14}C, % of initial dose at intervals (days)						
	0	1	3	7	14	21	23
Irradiated							
Unknown 0	-	-	-	0.08	0.87	0.54	0.83
Unknown 1	-	-	0.38	-	-	-	-
Unknown 2	-	-	0.82	2.29	-	-	-
Unknown 3	-	0.91	1.8	3.9	5.2	5.1	5.0
Unknown 4	-	1.5	1.9	2.6	3.3	3.2	3.2
Methomyl methylol	-	0.54	1.5	2.0	1.9	2.0	2.0
Unknown 5a	-	-	-	-	0.40	-	-
Thiodicarb	-	83	70	51	26	14	12
Methomyl	-	6.6	14	24	38	46	47
Unknown 8	-	0.23	0.45	0.50	0.36	0.31	0.34
Unknown 9	-	-	0.12	-	-	-	-
Unknown 10	-	-	0.15	0.40	0.31	0.13	0.08
Methomyl oxime	-	0.38	0.63	0.92	1.2	1.6	1.7
Dark control							
Unknown 0	-	-	-	0.38	0.46	0.52	0.49
Unknown 1	0.54	0.47	-	0.28	-	-	-
Unknown 2	-	-	-	-	-	-	-
Unknown 3	0.27	0.24	-	1.3	1.8	2.2	2.3
Unknown 4	-	-	-	0.32	0.49	0.59	0.69
Methomyl methylol	-	-	-	1.1	1.0	1.1	1.1
Unknown 5a	-	-	-	-	0.33	-	-
Thiodicarb	97	96	-	82	75	68	67
Methomyl	1.71	1.91	-	11.2	17	22	24
Unknown 8	-	-	-	0.45	0.67	0.46	0.52
Unknown 9	-	-	-	-	-	-	-
Unknown 10	-	-	-	-	0.18	-	-
Methomyl oxime	-	-	-	0.83	1.1	1.3	1.5

The photodecomposition of thiodicarb in aqueous solution involved N-S cleavage to methomyl which was subsequently hydroxylated to methomyl methylol (minor) or hydrolyzed to methomyl oxime. Methomyl oxime was further degraded to acetonitrile and carbon dioxide.

Water sediment systems. The degradation of thiodicarb, applied at a rate of approximately 0.25 mg/kg water, was investigated in two systems over a period of 100 days at 20°C (Bieber, 1992).

Soil and water were collected from two areas northwest and north of Hamburg, Germany (referred to as “Krempe” and “Ohlau” systems). Incubation flasks were equipped with a device for the slow stirring of the water only and a trap for volatile components containing quartz wool impregnated with paraffin oil and soda-lime. The treated flasks were placed on an orbital shaker in the dark at 20°C. Thus aerobic conditions were achieved in the water and anaerobic conditions were found in parts of the sediment.

The recoveries of the applied radiocarbon at various sampling intervals were 86-99% from the Ohlau system (mean 91%) and 75-93% from the Krempe system (mean 86%).

Radioactivity in the water of both systems decreased slowly from 65% to <1% in the Krempe system and from 74% to <1% in the Ohlau system. The radioactivity retained in the sediment was approximately 10% at day 0 and increased slowly to approximately 50% (Ohlau system) and 30% (Krempe) on day 7, then decreased slowly again to about 15% on day 100.

Water and sediment samples were analysed by TLC. In both water and sediment, thiodicarb accounted for 1-2% of the ^{14}C at day 0 and was negligible in all further samples. Thiodicarb was degraded in both test systems to methomyl, which reached 50% and 17% of the applied dose in the

Ohlau and Krempe systems respectively, within one day. Methomyl levels decreased rapidly, becoming negligible by day 7. The levels of methomyl oxime were low (<5%) at all samplings. The final degradation product was carbon dioxide, which rose to represent more than 70% of the applied radioactivity by 100 days.

Some polar components which were present in water initially (about 20% and 14% of the applied dose in the Ohlau and Krempe systems respectively) decreased to negligible levels during the study, but approximately 15% of the applied radioactivity was retained in the sediment finally after having reached maxima at day 7 of about 50% and 30% of the applied dose in the Ohlau and Krempe systems respectively.

The degradation of methomyl from its maximum concentration was found to fit a square root first-order model in the Ohlau system and a first-order model in the Krempe system. The half-life was calculated to be 21 hours in the Ohlau system and 29 hours in the Krempe system, with a DT_{90} of 4 days in both systems. The half-life of thiodicarb was impossible to determine owing to the extremely rapid degradation.

The degradation of [^{14}C]methomyl was studied in two water/sediment systems, from Manningtree and Ongar, over a period of 44 days at 20°C (Oddy, 1999).

The Manningtree sediment had higher organic carbon, nitrogen and niomass contents, while the Ongar sediment had a much higher cation exchange capacity. The Manningtree sediment was classified as a sandy silt loam by the UK Agricultural Development and Advisory Service (ADAS) and as a loam by the USDA, and the Ongar sediment as a clay loam by ADAS and a sandy clay loam by USDA.

Incubation was in glass flasks, containing sediment to associated water in an average ratio of 1:7 in the Manningtree system and 1:5 in the Ongar system, maintained in the dark at 20°C ± 2°C. The water/sediment systems were equilibrated for approximately 4 weeks before adding 113 µg [14C]methomyl to the surface of the water, equivalent to a field application rate of 0.38 kg /ha.

Moist air was passed into the water layer in each flask at a constant rate and then through an ethylene glycol trap to capture organic volatiles and two potassium hydroxide traps to retain any evolved carbon dioxide.

Duplicate samples were taken at intervals for analysis. The water layer was decanted and the sediment layer extracted with methanol. Water and solvent extracts were analysed by HPLC, with certified reference standards for comparison.

Overall mean recoveries of ^{14}C were 87% and 90% from the Manningtree and Ongar systems respectively.

In both systems methomyl was rapidly degraded to CO_2 with levels reaching about 72% and 60% of the applied radioactivity after 31 and 41 days in the Manningtree and Ongar systems respectively. Dissolved carbon dioxide in the form of carbonate was also found in the water phases. Methomyl oxime reached 4% in the water phase and less than 1% in the sediment. It never exceeded 5% of the applied radioactivity in total.

Unextracted residues increased steadily to a maximum of about 16% and 19% of the applied radioactivity in the Manningtree and Ongar systems respectively, before declining to about 15% in both systems after 31 and 44 days.

Half-lives of methomyl calculated with a modelling program were 2.4 days in the Manningtree water and 5.7 days in the Ongar water. The DT_{90} values were 9 days and 11 days respectively.

In summary, in aerobic aquatic systems, thiodicarb is rapidly converted to methomyl which in turn is degraded to CO_2, with no other major products. Thiodicarb and methomyl are unlikely to persist in the aerobic aquatic environment. In or on soil, under aerobic or anaerobic conditions, thiodicarb is rapidly degraded to methomyl and then to acetonitrile and carbon dioxide.

Under sterile conditions in water, thiodicarb is more stable at lower than higher pH. It is hydrolysed to methomyl which is further degraded to methomyl oxime. Photolysis of aqueous solutions of thiodicarb yields methomyl and ultimately acetonitrile and carbon dioxide. The degradation of thiodicarb in the environment is shown in Figure 3.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Hunt (1996) validated an analytical method, HPLC 3-96, for the determination of thiodicarb and methomyl in animal substrates at a limit of quantification of 0.02 mg/kg.

Residues are extracted by shaking homogenized samples with acetone/water (90:10). The extracts are purified by coagulation with ammonium chloride and phosphoric acid, followed by liquid-liquid partitioning and silica gel column chromatography. Quantification is by HPLC on a Zorbax phenyl column with fluorescence detection after post-column conversion to methylamine and derivatization. Typical retention times are 3.5 minutes for methomyl and 8.8 minutes for thiodicarb.

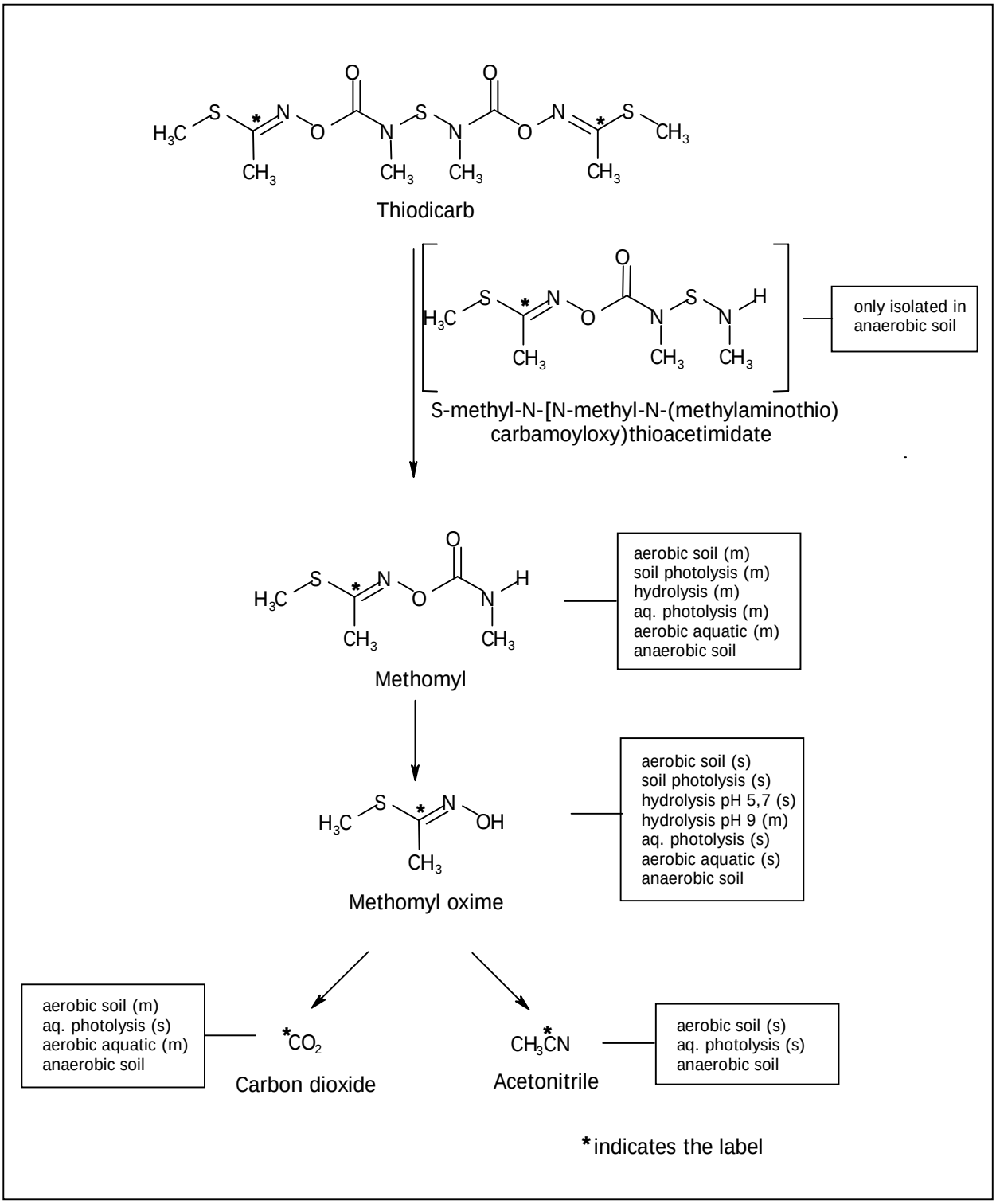
A total of 135 samples were analysed, 15 for each of the nine substrates milk, beef muscle, beef fat, beef liver, beef kidney, eggs, poultry muscle, poultry skin and fat and poultry liver. Control samples of each substrate were spiked at 0.02 and 0.10 mg/kg of thiodicarb or methomyl. The average recoveries are shown in Table 31.

Thiodicarb is very unstable in animal substrates, being degraded to methomyl during analysis. Residues of thiodicarb and methomyl were determined and reported as either total thiodicarb equivalents or total methomyl equivalents.

Table 31. Average recoveries of thiodicarb and methomyl from animal materials fortified at 0.02 and 0.10 mg/kg (Hunt, 1996).

Substrate (15 samples of each)	Thiodicarb recovery		Methomyl recovery	
	Mean %	SD %	Mean %	SD %
Milk	92	2	93	4
Beef muscle	96	9	94	3
Beef fat	82	6	99	2
Beef liver	68	5	88	11
Beef kidney	91	9	90	7
Eggs	85	6	86	2
Poultry muscle	92	2	95	3
Poultry skin and fat	80	5	98	11
Poultry liver	83	4	90	8

Figure 3. Degradation of thiodicarb in the environment.



s: minor product, <10% of the applied ^{14}C
m: major product, >10% of the applied ^{14}C
(note: although not indicated above, methomyl methylol was observed as a very minor product of aqueous photolysis)

Methods for plant commodities are similar to one another and rely upon base hydrolysis of thiodicarb and methomyl to methomyl oxime (MHTA) and determination of the MHTA by gas chromatography (Tew, 1992; Hunt and Langdon, 1982; US FDA, PAM II). These methods cannot distinguish between thiodicarb, methomyl and MHTA. In the general method SOP 90311 for thiodicarb determination developed in 1982 for a wide range of crops (Hunt and Langdon, 1982; Anon., 1982) the residues are extracted with a mixture of 9:1 acetone/water. A standard coagulation procedure is used to remove interfering co-extractives, and caustic hydrolysis converts thiodicarb and methomyl to methomyl oxime. The oxime is quantified by gas chromatography with a flame-photometric detector selective for sulfur-containing compounds.

The LOQ is 0.04 mg/kg for a 25 g sample. The average recoveries were 89% for thiodicarb and 93% for methomyl at several levels over a range of 0.04 to 10 mg/kg. The method was validated for almond hulls, almond kernels, apples, broccoli, cabbage, carrots, cauliflower, grapes, peanut hay, peanut hulls, peanut kernels, bell peppers, rice, soil (clay, clay loam, silt loam and sand), sorghum forage, sorghum grain, sorghum silage, spinach, tea, tobacco (flue-cured), wheat grain, wheat straw, cotton seed and cotton foliage.

A modification of the method, SOP 90321 (Tew, 1992), incorporates extraction of the parent and metabolites with acetone/methanol (90:10) or acetonitrile depending on the sample, and gel permeation chromatography (GPC) clean-up, before hydrolysis to methomyl oxime and quantification as above. The limit of quantification is about 0.02 mg/kg. Table 32 summarizes the recovery data.

Table 32. Recoveries from fortified samples by method SOP 90321 (Tew, 1992).

Sample	Fortification range (mg/kg)	No. of samples	Average recovery (%)	Standard deviation
Soya bean seed	0.02-1.0	35	89	11
Soya bean straw	2.8-60	11	83	8
Soya bean forage	4-60	14	74	5
Soya bean hay	12-60	14	90	17
Soya bean meal	0.04-1.0	15	99	10
Soya bean crude oil	0.04-1.0	15	90	8
Soya bean refined oil	0.04-1.0	15	86	9
Soya bean hulls	0.04-1.0	16	88	10
Soya bean soapstock	0.04-1.0	15	92	15
Soya bean grain dust	0.20	2	91	-
Cotton seed	0.02-1.2	26	89	11
Cotton straw	2.8-60	10	83	8
Cotton meal	0.04-1.0	16	93	18
Cotton crude oil	0.04-1.0	15	96	12
Cotton refined oil	0.04-1.0	15	90	12
Cotton soapstock	0.04-1.0	15	92	14
Sweet corn kernel	0.02-1.0	17	83	13
Sweet corn kernel + cob	0.02-1.0	16	102	12
Sweet corn cannery waste	0.02-1.0	16	103	7

This method was used with minor modifications for the analysis of tomatoes, sugar beet and Brussels sprouts (Moertl and Class, 1998). Mass spectrometric detection (GC-MS) was used for the determination of methomyl oxime instead of GLC with a flame photometric detector. Residues are extracted from the homogenized samples with acetone/water (9:1) and coagulation removes co-extractives. Residues in the aqueous extract are partitioned into methylene chloride, and after hydrolysis the methomyl oxime is again partitioned into methylene chloride. Methomyl oxime is quantified by measuring the sum of the characteristic ions m/e 58 + 88 + 105. The LOQ is 0.04 mg/kg. Recoveries from fortified samples of three different crops are shown in Table 33. A retention time shift problem was mentioned and thiodicarb recovery from Brussels sprouts was poor, 56%-66%.

Table 33. Recoveries from fortified control samples (Moertl and Class, 1998).

Crop	Fortification level (mg/kg)	thiodicarb		methomyl	
Tomato	0.04-0.20-0.4	73% ± 21%	n = 8	76% ± 22%	n = 8
Sugar beet	0.04-0.20-0.4	80% ± 12%	n = 7	72% ± 15%	n = 8
Brussels sprouts	0.04-0.4	60% ± 8%	n = 4	76% ± 11%	n = 4

An analytical method SOP-90318 was described for the determination of thiodicarb and methomyl in soils (Robinson, 1989). The residues are extracted with 50:50 acetone/water, then partitioned with methylene chloride. Quantification is by HPLC with post-column derivatization and fluorescence detection. The limit of quantification is 1 µg/kg (ppb) for a 50 g sample.

The method was validated with fortified soil samples over a range of 1 to 5000 µg/kg for methomyl and 1 to 2000 µg/kg for thiodicarb. The average recovery was 92% for both methomyl and thiodicarb.

In a comparison of conventional HPLC with LC-MS-MS in this method (Leonard, 1999) thiodicarb and methomyl were extracted from sandy loam and clay loam soil and partitioned as before, then analysed by HPLC with fluorescence detection. The samples were then analysed by LC-MS-MS.

Recoveries were determined with samples of sandy loam and clay loam soils from California and Iowa respectively fortified at 1 and 50 µg/kg. Recoveries by conventional HPLC were between 84% and 101% and averaged 91% ± 8% for methomyl and between 78% and 93% and averaged 86% ± 8% for thiodicarb. Very similar results were obtained from the same samples when analysed by LC-MS-MS. Recoveries of methomyl were between 82% and 91% and averaged 86% ± 5% and those of thiodicarb were between 81% and 95% and averaged 89% ± 7%.

Stability of residues in stored analytical samples

Field-treated samples of celery, head lettuce, leaf lettuce and spinach with quantifiable residues were re-analysed to determine the stability of thiodicarb during storage at -30°C (Hunt, 1988b). The results are given in Table 34.

Table 34. Stability of incurred residues of thiodicarb in leafy vegetables (Hunt, 1988b).

Crop	Celery				Head lettuce				Leaf lettuce				Spinach			
Days stored	0	152	0	235	0	176	0	499	0	100	0	202	0	162	0	486
mean residue (mg/kg)	17	17	5.1	4.6	16	14	1.4	1.1	3.2	3.1	17	14	22	16	1.9	0.99

The stability of thiodicarb in soya bean and its processed commodities during frozen storage was studied in North Carolina, USA (Lee, 1992a). Samples were fortified in duplicate and analysed for thiodicarb/methomyl after 1, 3, 6 and 12 months frozen storage at –15 ± 5°C by GLC with gel permeation clean-up. Analytical recoveries at 0.04 mg/kg were 95% for soya beans, 78% for hulls, 87% for meal, 90% for crude oil, 71% for refined oil and 76% for soapstock. The findings are shown in Table 35.

Table 35. Stability of thiodicarb/methomyl in soya beans and processed fractions stored frozen (Lee, 1992a).

Sample	Storage period (months)	% thiodicarb/methomyl remaining
Soya bean	0	91
	1	90
	3	92
	6	70
	12	56
Meal	0	100
	1	95
	3	86
	6	77
	12	60
Hulls	0	83
	1	77
	3	59
	6	79
	12	82
Crude oil	0	88
	1	75
	3	82
	6	92
	12	83
Refined oil	0	85
	1	69
	3	84
	6	83
	12	78
Soapstock	0	104

Sample	Storage period (months)	% thiodicarb/methomyl remaining
	1	95
	3	85
	6	44
	12	66

Samples of apples from field residue trials conducted in Virginia, USA in 1984 were first analysed 320 days after harvest by GLC with FPD, and again about 415 days later (Hunt, 1994). For 7-day PHI apples, the initial results were 1.5, 2.9 and 2.8 mg/kg, average 2.4 mg/kg. After the additional 415 days of storage, the corresponding values were 1.8, 3.0 and 2.8 mg/kg, average 2.5 mg/kg. For 14-day PHI apples, the initial results were 2.0, 2.0 and 1.3 mg/kg, average 1.8 mg/kg, and the corresponding final values 1.3, 1.9 and 0.89 mg/kg, average 1.4 mg/kg. The results were not corrected for concurrent analytical recoveries. It was concluded that residues of thiodicarb were stable in frozen apples for up to 14 months.

In a storage stability study on sorghum grain (Hunt, 1988e, 1989b) the field-treated grain was stored at -30°C and analysed 97, 166 and 473 days after harvest. The thiodicarb residue remained at 14 mg/kg during the 376 days between the first and third analyses.

In a companion study sorghum forage and stover were fortified at 40 and 45 mg/kg respectively and stored for approximately 6 months at -20°C (186 days for forage and 184 days for stover) (Hunt, 1989b). The results are shown in Table 36.

Table 36. Average thiodicarb residues remaining in fortified sorghum forage and stover after storage at -20°C (Hunt, 1989b).

Sample	Residue, mg/kg, after storage for				
	0 (initial sample)	1 month	2 months	3 months	6 months
Forage	40	39	33	30	33
Stover	44	44	39	38	37

The residues decreased during the 6 months of storage. The estimated half-life was calculated by first-order regression statistics to be 559 days in forage and 980 days in stover.

The stability of thiodicarb/methomyl in sweet corn and its processed commodities was determined by Lee (1991b). Samples fortified at 1 mg/kg were analysed after 0.5, 1, 3, 6, 9 and 12 months frozen storage at –15 ± 5°C by method SOP 90321, validated at 0.02 to 1.0 mg/kg for kernels, kernels plus cobs and cannery waste. The findings are shown in Table 37.

Table 37. Stability of thiodicarb/methomyl in sweet corn commodities (1 mg/kg fortification) during frozen storage (Lee, 1991b).

Sample	% of initial residue remaining after storage for (months)						
	0	0.5	1	3	6	9	12
Corn kernels	80	83	85	117	16, 57	8	56
Corn kernels + cobs	111	77	85	105	51	41	32
Cannery waste	101	94	82	113	61	66	75

A first-order kinetics model indicated half-lives of 86, 225 and 265 days for thiodicarb/methomyl in kernels, kernels plus cobs and cannery waste respectively.

In a similar study to determine the stability of thiodicarb on cotton seed and its processed commodities during storage at -15 ± 5°C (Lee, 1991a) samples were fortified with thiodicarb at a concentration of 1 mg/kg and analysed after 0, 1, 3, 6 and 12 months storage by method SOP 90321, validated at 0.04-1.0 mg/kg for all commodities. Results are shown in Table 38. Using a first-order model, the half-life of thiodicarb/methomyl was calculated to be 770 days in cotton seed, 386 days in meal and 828 days in hulls.

Table 38. Stability of thiodicarb/methomyl in fortified cotton seed commodities (1 mg/kg fortification) during frozen storage (Lee, 1991a).

Sample	% of initial residue remaining after storage for (months) [1]				
	0	1	3	6	12
Cotton seed	95	87	97	79	70
Meal	86	110	90	61	54
Hulls	94	104	106	83	76
Crude oil	90	106	91	102	87
Refined oil	98	104	106	83	76
Soapstock	87	88	88	80	98

[1] Average of duplicate samples

In a storage stability study on animal commodities (Davis *et al.*, 1996) control samples of milk, muscle, liver, kidney and fat were fortified with thiodicarb or methomyl at a level of 1 mg/kg and stored for up to 2 months at a nominal temperature of -20°C. Milk, muscle, kidney and fat samples were analysed at 0, 1 and 2 months; liver samples at 0 and 1 month and again in a separate experiment at 0 and 2 days. Analyses were by method HPLC 3-96. All control samples contained <0.1 mg/kg methomyl and thiodicarb. Results were not corrected for concurrent analytical recoveries.

Table 39. Stability of methomyl and thiodicarb in milk and tissues fortified at 1 mg/kg and stored frozen (Davis *et al.,* 1996).

Sample	Milk			Muscle			Kidney			Fat			Liver	
Storage (days)	0	31	62	0	31	60	0	43	69	0	32	63	0	2
% methomyl remaining	90	92	89	84	87	86	76	66	54	84	79	84	85, 86	0
% thiodicarb remaining	86	84	87	83	81	83	83	68	48	77	82	75	85, 63[1]	0

[1] As methomyl. No thiodicarb recovered.

Thiodicarb and methomyl appeared to be stable in milk, fat and muscle during 2 months of freezer storage. Both thiodicarb and methomyl decreased significantly in kidney, and in liver neither was detected after 2 days of storage.

Definition of the residue

The current definition is "sum of thiodicarb, methomyl and methyl hydroxythioacetimidate ('methomyl oxime'), expressed as thiodicarb". This definition is consistent with the analytes determined as methomyl oxime (MHTA) by the gas chromatography-based methods for thiodicarb. HPLC determines thiodicarb and methomyl separately and does not determine MHTA. This method has been used mainly for animal commodities to determine thiodicarb, but is the primary method for the analysis of plant commodities for methomyl.

Animal and plant metabolic studies have shown that thiodicarb is metabolized to methomyl, which is further degraded to carbon dioxide and acetonitrile. MHTA is a very minor metabolite, <0.5% in plants and absent in animals.

The recommended residue definition is "sum of thiodicarb and methomyl, expressed as methomyl". This recognizes that MHTA is a very minor metabolite and is not determined by some methods. Expressing the total residue as methomyl is consistent with combining the MRLs of thiodicarb and methomyl into a single list and recognizes that a significant proportion of the residue from the use of thiodicarb is methomyl. The practical effect is small, as the conversion factor from mg/kg thiodicarb to mg/kg methomyl is 0.92.

USE PATTERN

Tables 40-48 identify registered uses of thiodicarb. The Tables are based upon labels, and summaries and translations of labels, provided by the manufacturer. Formulation codes GB (granular bait) and RB (bait ready-to-use) are used interchangeably on labels, as are codes SG and WG.

Table 40. Registered uses on root and tuber vegetables.

Commodity	Country	Formulation	Application	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Beet	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	2	--
	Chile	WG 800 g/kg	Spraying	0.8	--	--	14
Potatoes	Chile	WG 800 g/kg	Spraying	0.6	--	--	14
	Colombia	SC 375 g/l	Ground spray	0.38	0.1-0.19	--	--
	Ireland	RB 40 g/kg	Soil broadcast	0.2	--	--	--
	Ecuador	SC 375 g/l	Foliar spray	0.51	0.01-0.13	1	10
	Central America	SG 800 g/kg	Spray	0.24	--	--	7
		SC 375 g/l	Spray	1.9	--	--	7
		SG 800 g/kg	Spray	0.24	--	--	7
	Japan	WP 750g/kg	Spraying	1000-1500 dilution	--	5	7
	UK	RB 40 g/kg	Soil broadcast	0.2	--	1-3	21
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	21
Radish	Japan	RB 20 g/kg	Spray to base stem	0.8	--	2	45
		SC 320 g/l	Spraying	1000 dilution	--	2	21
Sugar beet	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	2	--
	Japan	SC 320 g/l	Spray	750 dilution	--	3	30
		WP 750 g/kg	Spray	1000-1500 dilution	--	3	30

Sweet potatoes	Japan	SC 320 g/l	Spraying	750 dilution	--	3	3
		WP 750g/kg	Spraying	1500 dilution	--	3	3
All crops	France	GB 40 g/kg	Soil broadcast	0.2	Not relevant	--	7

Table 41. Registered uses on leafy vegetables

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Leafy vegetables	USA	SC 375 g/l	Spraying by air or by ground	0.84	0.225-1.87	([1])	14
Lettuce	Myanmar	SC 375 g/l	Foliar spraying	-0.93	0.23-2.07	--	14
	Japan	20 g/kg	Spraying to base stem	0.8	--	2	45
	Chile	WG 800 g/kg	Spraying	-0.8	--	--	14
Spinach	Chile	WG 800 g/kg	Spraying	0.8	--	--	14
Vegetables	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	3	21
	Norway	GB 40 g/kg	Soil broadcast	0.2	--	1	7
	Venezuela	SC 375 g/l	Spraying	0.56	--	--	15
	Western Africa	GB 40 g/kg	Soil broadcast	0.2	--	--	--
All crops	France	GB 40 g/kg	Soil broadcast	0.2	Not relevant	--	7

Table 42. Registered uses on Brassica vegetables.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Brassica crops	Australia	SC 375 g/l	Spray	0.75	--	--	7
		WG 800 g/kg	Spray	0.75	--	--	7
	Myanmar	SC 375 g/l	Foliar spray	0.93	--	--	7
Broccoli	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	3	21
	Chile	WG 800 g/kg	Spraying	0.8	--	--	7
	Central America	SG 800 g/kg	Spray	0.24	--	--	7
		SC 375 g/l	Spray	1.9	--	--	7
		SG 800 g/kg	Spray	0.24	--	--	7
	USA	SC 375 g/l	Air or ground spray	1.2	0.1-2.55(air) 0.225-0.575 (ground)	([1])	7
Brussels sprouts	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	6	21
	Chile	WG 800 g/kg	Spraying	0.8	--	--	7
Cabbage	China	WP 750 g/kg	Spray	0.75	0.17	--	--
	Central America	SG 800 g/kg	Spray	0.24	--	--	7
		SC 375 g/l	Spray	1.87	--	--	7

[1] Do not exceed 1.7 kg/ha per season

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
		SG 800 g/kg	Spray	0.24	--	--	7
	Chile	WG 800 g/kg	Spraying	0.8	--	--	7
	Ecuador	SC 375 g/l	Foliar	0.26	0.07	1	10
Cabbage	India	WP 750 g/kg	Spray	1	0.2	2-3([1])	7
	Japan	SC 320 g/l	Spraying	--	750-1000 dil.	4	7
		WP 750 g/kg	Spraying	--	100-1500 dil	4	7
	Pakistan	WG 800g/kg	Foliar	0.6	0.16-0.24	1	--
	Taiwan	WP 750 g/kg	Foliar spray	0.5	--	([2])	6
	USA	SC 375 g/l	air or ground Spray	1.2	0.1-2.55(air) 0.225-0.575 (ground)	([3])	7
Chinese cabbage	Japan	20 g/kg	Spraying to base stem	0.8	--	2	45
		SC 320 g/l	Spraying	--	750-1000 dil.	4	7
		WP 750 g/kg	Spraying	--	1000-1500 dil.	4	7
Cauliflower	Chile	WG 800 g/kg	Spraying	0.8	--	--	7
	Central America	SG 800 g/kg	spray	0.24	--	--	7
		SC 375 g/l	Spray	1.9	--	--	7
		SG 800 g/kg	Spray	0.24	--	--	7
	USA	SC 375 g/l	Air or ground spray	1.2	0.1-2.55(air) 0.225-0.575 (ground)	([4])	7
Vegetables	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	6	21
	Norway	GB 40 g/kg	Soil broadcast	0.2	--	1	7
	Western Africa	GB 40 g/kg	Soil broadcast	0.2	--	--	--
	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	6	21
All crops	France	GB 40 g/kg	Soil broadcast	0.2	Not relevant	--	7

Table 43. Registered uses on legume vegetables.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Beans	Brazil	FS 350 g/l	Seed treatment	0.52	--	1	--
	Ecuador	FS 350 g/l	Seed treatment	0.70	--	--	--
		SC 375 g/l	Foliar	0.23	0.05-0.08	1	15
	Central America	FS 350 g/l	Seed treatment	0.76	--	--	--
		FS 300 g/l	Seed treatment	0.3	--	--	--
	Paraguay	FS 350 g/l	Seed treatment	0.525	--	--	--

[1] 7 to 10 days interval depending on the pest intensity

[2] every 7 days

[3] Do not exceed 6.7 kg/ha per season

[4] Do not exceed 6.7 kg/ha per season

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
	Peru	FS 350 g/l	Seed treatment		--	--	28
		SC 375 g/l	Foliar		0.09-0.375	1	14
	Sri Lanka	SC 375 g/l	Spray	0.38	--	--	14
	Venezuela	FS 350 g/l	Seed treatment	0.7	--	--	--
Peas	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	1	--
Pigeon peas	Sri Lanka	SC 375 g/l	Spray	0.47	--	--	14
Pulses: Soya beans Mung beans, Chick-peas, Pigeon peas, Navy beans	Australia	SC 375 g/l	Aerial/ground	0.28	0.375-1.4	--	21
		WG 800 g/kg	Aerial/ground	0.28	0.375-1.4	--	21
	Myanmar	SC 375 g/l	Foliar application	0.46	0.08-0.5	--	21
Soya beans	Argentina	SC 375 g/l	Aerial/ ground	0.11	0.28-1.12 0.028-0.1125	1-2	20
		WG 800 g/kg	Aerial/ ground	0.092	0.2-0.95 0.02-0.095	1-2	20
		FS 350 g/l	Seed treatment	0.14	--	--	--
	Brazil	WG 800 g/kg	Aerial/ ground	0.056	0.56-1.12 (air) 0.028-0.056 (ground)	--	14
	Ecuador	FS 350 g/l	Seed treatment	0.70	--	--	--
		SC 375 g/l	Foliar	0.26	0.04-0.07	1	15
	Central America	SG 800 g/kg	spray	0.24	--	--	28
		SC 375 g/l	spray	1.9	--	--	28
		SG 800 g/kg	spray	0.24	--	--	28
		FS 350 g/l	Seed treatment	0.76	--	--	--
		FS 300 g/l	Seed treatment	0.3	--	--	--
	Indonesia	SC 375 g/l	Foliar spray	-0.3	0.02-0.08	--	14
		WP 750 g/kg	Spraying	1.4	0.15-0.22	2	14
	Japan	WP 750 g/kg	Spraying	750 dilution	--	2	14
Soya beans	Paraguay	WG 800 g/kg	Spray	0.12	--	--	14
	Mexico	SC 350 g/l	Seed treatment	0.88	--	--	--
	Thailand	SC 375 g/l	Foliar spray	0.21	0.11	1-2	28
	USA	SC 375 g/l	Spraying by air or by ground	0.84	0.6-8.4 (air) 0.14-0.42 (ground)	([1])	28
	Venezuela	SC 375 g/l	Spray	0.38	--	--	28
		FS 350 g/l	Seed treatment	0.7	--	--	--
All crops	France	GB 40 g/kg	Soil broadcast	0.2	Not relevant	--	7

[1] Do not exceed 3.4 kg/ha per season

Table 44. Registered uses on fruiting vegetables.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Sweet corn	USA	SC 375 g/l	Spraying by air or by ground	0.84	Max 2.94 (air) 0.4-3 (ground)	([1])	0
	Australia	SC 375 g/l	Spraying by air or by ground	0.75	1.12-1.5	--	7
		WG 800 g/kg	Spraying by air or by ground	0.75	1.12-3.75	--	7
		FS 500 g/l	Seed treatment	0.75	--	--	--
Tomato	Australia	SC 375 g/l	Spraying	0.52 (a)	0.13(a) 0.026 (b)	--	1
		WG 800 g/kg	Spraying	0.52 (a)	0.13 (a) 0.026 (b)	--	1
	Chile	WG 800 g/kg	Spraying	0.8	--	--	3
	Central America	SG 800 g/kg	Spray	0.24	--	--	7
		SC 375 g/l	Spray	1.9	--	--	7
		SG 800 g/kg	Spray	0.24	--	--	7
	Ecuador	FS 350 g/l	Seed treatment	2 l/q seeds	--	--	--
		SC 375 g/	Foliar	0.26	--	1	10
	Myanmar	SC 375 g/l	Foliar application	0.55	0.12-0.61	--	21
	Peru	SC 375 g/l	Spraying	0.75	--	1	14
	Spain	SC 375 g/l	Upward foliar spray	0.94	--	--	7
	Taiwan	SC 375 g/l	Foliar spray	0.56	--	([2])	3
		WP 750 g/kg	Foliar spray	0.25	--	--	3
	Thailand	SC 375 g/l	Foliar spray	--	0.11	NS	28

(a) low spray volume
(b) high spray volume
NS: not specified

Table 45. Registered uses on pome fruits.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Apple	Japan	SC 320 g/l	Spraying	750-1000 dil.	--	3	21
		WP 750 g/kg	Spraying	1000-1500 dil.	--	3	21
	South Korea	WP 750 g/kg	Foliar Spraying	3.4	0.075	3	21
	Romania	SC 375 g/l	Foliar spraying	0.56	0.038	--	15
Pear	Japan	SC 320 g/l	Spraying	750 dilution	--	3	7
		WP 750 g/kg	Spraying	1000-1500 dil.	--	3	7
Pome fruits	Chile	WG 800 g/kg	Spray	2	--	--	--
	Portugal	GB 40 g/kg	Soil broadcast	0.2	--	1	--

[1] Do not exceed 8.4 kg/ha per season, 1 to 7 day intervals.

[2] every 7 days

Table 46. Registered uses on small fruits and berries.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Grape	France	SC 375 g/l	Foliar spray	0.45	0.094-0.45	1-2	14
		SC 300 g/l	Upward foliar spray	0.45	0.094-0.45	1-2	45
	Greece	SC 375 g/l	Foliar spray	0.46	0.02-0.09	2-3	21
	Portugal	GB 40 g/kg	Soil broadcast	0.2	--	1	--
	Spain	SC 375 g/l	Foliar spray	0.75	--	--	21
	Taiwan	WP 750 g/kg	Foliar spray	0.5	0.01-0.02	([1])	14
	Myanmar	SC 375 g/l	Foliar application	0.93	0.2-1	--	7
	Romania	SC 375 g/l	Foliar spraying	0.38	0.038	--	15

Table 47. Registered uses on cereal grains.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI, days
Barley	Ireland	RB 40 g/kg	Soil broadcast	0.2	--	--	--
	Norway	GB 40 g/kg	Soil broadcast	0.2	--	1	7
	UK	RB 40 g/kg	Admixture	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Admixture with seed	0.2	--	1	--
Cereals	Portugal	GB 40 g/kg	Soil broadcast	0.2	--	1	--
	Netherlands	GB 40 g/kg	Strew on the soil	0.2	--	2	--
Cereals (All crops)	France	GB 40 g/kg	Soil broadcast or admixture with seed	0.2	Not relevant	--	7
Cereals (except maize)	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	2	--
Cereals (winter)	Germany	GB 40 g/kg	Soil broadcast	0.2	--	1-2	--
Maize	Argentina	FS 350 g/l	Seed treatment	0.70	--	1	--
	Ecuador	FS 350 g/l	Seed treatment	0.70	--	--	--
		SC 375 g/l	Foliar spraying	0.38	--	1-2	15
	Central America	SG 800 g/kg	Spray	0.24	--	--	0
		SC 375 g/l	Spray	1.9	--	--	0
		SG 800 g/kg	Spray	0.24	--	--	0
		GR 75 g/kg	Soil broadcast	0.52	--	--	10
		FS 350 g/l	Seed treatment	0.76	--	--	--
		FS 300 g/l	Seed treatment	0.3	--	--	--
	Paraguay	WG 800 g/kg	Spray	0.8	--	--	14
		FS 350 g/l	Seed treatment	0.70	--	--	--
		FS 300 g/l	Seed treatment	0.60	--	--	--

[1] every 7 days

	Mexico	SC 350 g/l	Seed treatment	1.4	--	-	--
		SC 375 g/l	Aerial/ground	0.47	--	--	--
		SC 300 g/l	Seed treatment	1.5	--	--	--
	Philippines	FS 350 g/l	Seed treatment	0.49	--	--	--
	Turkey	WG 800 g/kg	Foliar spraying	0.72	--	--	28
Maize	Australia	SC 375 g/l	Spraying by air or ground	0.75	1.12 (air) 1.5 (ground)	--	7
		WG 800 g/kg	Spraying by air or ground	0.75	1.12 (air) 3.75 (ground)	--	7
		FS 500 g/l	Seed treatment	0.75	--	--	--
	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	2	--
	Brazil	FS 350 g/l	Seed treatment	0.7	--	1	--
		WG 800g/kg	Aerial/ground	0.1	0.5-1 (air) 0.03-0.0 (ground)	--	30
		300 g/l	Seed treatment	0.6	--	1	--
	Chile	FS 350 g/l	Seed treatment	1.0	--	--	--
		WG 800 g/kg	Spray	0.6	--	--	14
	Indonesia	SC 375 g/l	Foliar spray	0.77	0.154	--	14
		WP 750 g/kg	Seed treatment	1.5	-	--	--
	Myanmar	SC 375 g/l	Foliar application	0.93	--	--	7
	Peru	FS 350 g/l	Seed treatment	0.35	--	--	28
		SC 375 g/l	Spraying	0.38	0.14-0.09	1	14
	South Africa	SC 375 g/l	Ground or aerial spray	0.3	--	--	21
	Spain	SC 375 g/l	Upward foliar spray	0.94	--	--	21
	Venezuela	FS 300 g/kg	Seed treatment	0.75	--	--	--
		SC 375 g/l	Spray	0.38	--	--	28
		FS 320 g/l	Seed treatment	0.64	--	--	--
Oats	Ireland	RB 40 g/kg	Soil broadcast	0.2	--	--	--
	UK	RB 40 g/kg	Admixture	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Admixture with seed	0.2	--	1	--
Rice	Brazil	FS 350 g/l	Seed treatment	0.52	--	1	--
		300 g/l	Seed treatment	0.45	--	1	--
	Ecuador	FS 350 g/l	Seed treatment	0.70	--	--	--
		SC 375 g/l	Foliar spraying	0.38	0.05-0.125	1	15
	Japan	DP 30 g/kg	Spraying	1.2	--	3	30
	Paraguay	FS 350 g/l	Seed treatment	0.52	--	--	--
		FS 300 g/l	Seed treatment	0.45	--	--	--
Rye	Norway	GB 40 g/kg	Soil broadcast	0.2	--	1	7
Sorghum	Australia	FS 500 g/l	Seed treatment	0.5	--	--	--
	Colombia	FS 350 g/l	Seed treatment	0.52	--	--	--
		SC 375 g/l	Foliar pray	0.38	0.94-1.25	--	--

	Ecuador	SC 375 g/l	Foliar pray	0.38	--	1-2	15
	Central America	GR 75 g/kg	Soil broadcast	0.52	--	--	10
		FS 350g/l	Seed treatment	0.76	--	1	--
		FS 300 g/l	Seed treatment	0.3	--	--	--
	Mexico	FS 350 g/l	Seed treatment	1.4	--	--	--
		SC 300 g/l	Seed treatment	1.5	--	--	--
	Thailand	SC 375 g/l	Foliar spray	--	0.094	--	28
	Venezuela	SC 375 g/l	Spray	0.38	--	--	14
		FS 320 g/l	Seed treatment	0.64	--	--	--
Sweet corn	USA	SC 375 g/l	Spraying by air or by ground	0.84	Max 2.94 (air) 0.4-3 (ground)	([1])	0
	Australia	SC 375 g/l	Spraying by air or by ground	0.75	1.12-1.5	--	7
		WG 800 g/kg	Spraying by air or by ground	0.75	1.12-3.75	--	7
		FS 500 g/l	Seed treatment	0.75	--	--	--
Triticale	UK	RB 40 g/kg	Admixture with seed	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Admixture with seed	0.2	--	1	--
Wheat	Argentina	FS 350 g/l	Seed treatment	0.14		1	--
	Chile	FS 350 g/l	Seed treatment	0.14	--	--	--
	Ecuador	FS 350 g/l	Seed treatment	0.70	--	--	--
	Central America	FS 350 g/l	Seed treatment	0.76	--	--	--
		FS 300 g/l	Seed treatment	0.3	--	--	--
	Ireland	RB 40 g/kg	Soil broadcast	0.2	--	--	--
	Norway	GB 40 g/kg	Soil broadcast	0.2	--	1	7
	UK	RB 40 g/kg	Admixture	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Admixture with seed	0.2	--	1	--
Wheat (durum)	UK	RB 40 g/kg	Admixture with seed	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Admixture with seed	0.2	--	1	--

Table 48. Registered uses on oilseed.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI , days
Cotton	Argentina	FS 350 g/l	Seed treatment	0.7	--	1	-
		SC 375 g/l	Aerial/ground	0.3	1.1-3 (air) 0.11-0.3 (ground)	1	20

[1] Do not exceed 8.4 kg/ha per season, 1 to 7 day intervals.

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI , days
		WG 800 g/kg	Aerial/ground	0.38	0.95-3.75 (air) 0.1-0.375 (ground)	1-2	20
	Australia	SC 375 g/l	Aerial/ground	0.94	3.75-4.7 (air) 1.5-1.9 (ground)	--	21
		WG 800 g/kg	Aerial/ground	0.96	3.75-4.8 (air) 1.5-1.9 (ground)	--	21
		FS 500 g/l	Seed treatment	0.5	--	--	--
		FS 400 g/l	Seed treatment	0.25	--	--	--
	China	SC 375 g/l	Spray	0.51	0.675-1.69	3	14
		WP 750 g/kg	Spray	0.51	0.675-1.69	3	14
	Colombia	FS 350 g/l	Seed treatment	0.70	--	--	--
		SC 375 g/l	Airway	0.56	0.7-1.86	--	--
	Ecuador	FS 350 g/l	Seed treatment	0.7	--	--	--
		SC 375 g/l	Foliar spraying	0.38	--	1	15
	Egypt	SC 375 g/l	Spraying	0.89	--	--	28
		WG 800 g/kg	Spraying	0.95	--	--	28
	Greece	WG 800 g/kg	Foliar spray	0.8	0.06-0.16	2-3	28
	Central America	SG 800 g/kg	Spray	-0.24	--	--	28
		SC 375 g/l	Spray	1.8	--	--	28
		SG 800 g/kg	Spray	0.24	--	--	28
		FS 300 g/l	Seed treatment	0.3	--	--	--
		FS 350 g/l	Seed treatment	0.76	--	--	--
	India	WP 750 g/kg	Spray	0.75	0.15	3 -4[1]	30
Cotton	Indonesia	SC 375 g/l	Foliar spray	0.38	0.04-0.08	--	14
		WP 750 g/kg	Foliar spray	1.5	0.19-0.5	--	14
	Iran	WG 800g/kg	Foliar spraying	-0.8	--	--	--
	Mexico	SC 350 g/l	Seed treatment	0.75	--	--	--
		SC 375 g/l	Foliar spraying	0.94	--	--	--
	Myanmar	SC 375 g/l	Foliar spraying	0.93	0.2-1	--	21
	Pakistan	WG 800g/kg	Spraying	0.9	0.27-0.36	1	--
	Paraguay	WG 800 g/kg	Spray	0.048	0.01-0.005	2-3	28
	Peru	FS 350 g/l	Seed treatment	0.35	--	--	28
		SC 375 g/l	Foliar spraying	0.094	0.01-0.02	1	14
	South Africa	SC 375 g/l	Ground or aerial spray	0.38	1.25 (air) 0.19 (ground)	--	21
	Spain	SC 375 g/l	Upward foliar spray	0.94	--	--	21
	Thailand	SC 375 g/l	Foliar spray	0.21	0.11	--	28
	Turkey	WG 800g/kg	Foliar spraying	0.72	--	--	28
	USA	SC 375 g/l	Spraying by air or by ground	1	0.1-5	--	28
	Zimbabwe	SC 375 g/l	Aerial/ground	0.41	1-8.2 (air) 0.14-0.41 (ground)	--	--
Oily crops	Portugal	GB 40 g/kg	Soil broadcast	0.2	--	1	--

[1] 10 to 15 days interval depending on the pest intensity

Commodity	Country	Formulation	Method	Rate kg ai/ha or /100 kg seed	Spray conc., kg ai/hl	No. of appl.	PHI , days
Oilseed rape	Ireland	GB 40 g/kg	Soil broadcast	0.2	--	--	--
	Belgium	GB 40 g/kg	Soil broadcast	0.2	--	2	--
	UK	RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
		RB 40 g/kg	Soil broadcast	0.2	--	1-3	--
Oilseed rape (winter)	Germany	GB 40 g/kg	Soil broadcast	0.2	--	1-2	--
	Netherlands	GB 40 g/kg	Soil broadcast	0.2	--	2	--
Oilseed rape (All crops)	France	GB 40 g/kg	Soil broadcast or admixture with seed	0.2	Not relevant	--	7

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised field trials were reported for numerous commodities. Where results were given as ND (not detected) and a substantiated value for ND was not supplied, the ND was assigned 50% of the limit of quantification. Unless indicated otherwise, residues are the sum of thiodicarb and methomyl. Trials are listed in the following Tables. Residues from trials according to GAP are underlined and were used in estimating maximum residue levels.

Table no.	Commodity
49	Apples (foliar)
50	Grape (foliar)
51	Potato (bait)
52	Potato (foliar)
53	Sugar beet (bait)
54	Lettuce (bait)
55	Lettuce (foliar)
56	Lettuce (aerial)
57	Spinach (foliar)
58	Collards
59	Broccoli (foliar)
60	Broccoli (aerial)
61	Brussels sprouts (bait)
62	Cabbage (foliar)
63	Cabbage (aerial)
64	Cauliflower (foliar)
65	Cauliflower (aerial)
66	Garden peas (foliar)
67	Pea hay (foliar)
68	Chick-peas (foliar)
69	Chick-pea forage (foliar)
70	Chick-pea straw
71	Soya bean (foliar)
72	Soya bean (aerial)
73	Soya bean (seed treatment)
74	Soya bean forage (foliar)
75	Soya bean forage (seed treatment)
76	Soya bean hay (foliar)
77	Soya bean straw (foliar)
78	Tomato (foliar)

Table no.	Commodity
79	Sweet corn (kernel + cob with husk removed)(foliar)
80	Sweet corn (aerial)
81	Sweet corn (seed treatment)
82	Barley and wheat grain (bait)
83	Wheat (seed treatment)
84	Maize (foliar)
85	Maize (seed treatment)
86	Rice
87	Rice (seed treatment)
88	Sorghum (foliar)
89	Sorghum (seed treatment)
90	Barley and wheat forage (bait)
91	Barley and wheat forage (bait)
92	Barley and wheat straw (bait)
93	Barley and wheat forage (foliar)
94	Rice straw (foliar)
95	Sorghum forage (foliar)
96	Sorghum forage (seed treatment)
97	Sorghum straw (foliar)
98	Sorghum stover (foliar)
99	Sorghum stover (seed treatment)
100	Sweet corn fodder (foliar)
101	Sweet corn forage (foliar)
102	Sweet corn forage (seed treatment)
103	Cotton seed (foliar)
104	Cotton seed delinted (foliar)
105	Cotton seed (aerial)
106	Cotton seed (seed treatment)
107	Cotton leaves (foliar)

Table no.	Commodity
108	Cotton forage (foliar)
109	Cotton forage (aerial)
110	Cotton forage (seed treatment)

Table no.	Commodity
111	Rape seed (bait)
112	Rape forage (green) (bait)
113	Rape straw (bait)

Pome fruit

Supervised trials were conducted on apples in Australia, USA, Italy, Greece and Japan (Table 49). GAP exists only in Japan.

The samples from Japan were analysed by a GLC method, with an LOQ of 0.02 mg/kg and a stated limit of detection of 0.005 mg/kg (Anon., 2001a).

Table 49. Residues in apples (foliar application, ground equipment).

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Fennville, Michigan USA 1982	SC, 375 g/l	8	1.1		7 14 21	0.78, 0.64 0.74, 0.74 0.15, 0.30	Hunt, 1989a, File 40674, Project 804R10
Fennville, Michigan USA 1982	SC, 375 g/l	8	2.2		7 14 21	1.6, 1.3 3.0, 2.2 0.73, 0.66	Hunt, 1989a, File 40674, Project 804R10
Clayton, North Carolina USA 1982	SC, 375 g/l	8	1.1	0.11	3 7 14	0.60, 0.74 0.36, 0.56 0.22, 0.27	Hunt, 1989a, File 40674, Project 804R10
Clayton, North Carolina USA 1982	SC, 375 g/l	8	2.2	0.11	3 7 14	2.7, 2.2 2.6, 2.0 1.6, 0.80	Hunt, 1989a, File 40674, Project 804R10
Sodus, New York USA 1982	SC, 375 g/l	8	1.1	0.20	3 7 14 21	1.1 0.95 0.53 0.28	Hunt, 1989a, File 40674, Project 804R10
Sodus, New York USA 1982	SC, 375 g/l	8	2.2	0.20	3 7 14 21	3.6 1.2 0.78 0.77	Hunt, 1989a, File 40674, Project 804R10
Fennville, Michigan USA 1985	SC, 375 g/l	8	1.1	0.29	7 14 21	1.9 1.1 0.48	Hunt, 1989a, File 40674, Project 804R10
Sodus, New York USA 1985	SC, 375 g/l	8	1.1	0.03	7 14 21	0.64 0.50 0.70	Hunt, 1989a, File 40674, Project 804R10
Winchester, Virginia USA 1985	SC, 375 g/l	8	1.1		6 16 21	1.5 1.3 1.1	Hunt, 1989a, File 40674, Project 804R10
Kearneysville, West Virginia 1985	SC, 375 g/l	8	1.1	0.12	7 14 21	0.89 0.35 0.17	Hunt, 1989a, File 40674, Project 804R10
El Dorado, California USA 1986	SC, 375 g/l	1	1.1	0.08	90	0.20, 0.14	Hunt, 1989a, File 40674, Project 804R10
Manteca, California USA 1986	SC, 375 g/l	1	1.1	0.12	88	0.44, 0.78	Hunt, 1989a, File 40674, Project 804R10
Yakama, Washington USA 1986	SC, 375 g/l	1	1.1	0.04	92	0.16, 0.14, 0.19, 0.09	Hunt, 1989a, File 40674, Project 804R10
Manteca, California USA 1987	SC, 375 g/l	1	1.1	0.08	91	0.88, 0.84	Hunt, 1989a, File 40674, Project 804R10

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Bathurst, New South Wales Australia, 1982	SC 375 g/l	8	--	0.05	0 7 14 22	3.2 1.9 3.0 4.4 2.6 1.5 3.1 4.0 3.6 2.2 1.7 3.0 2.5 2.2 2.6 4.0	Hunt, 1983 Project No.20566 File No.1451V
Bathurst, New South Wales Australia, 1982	SC 375 g/l	8	--	0.1	0 7 14 22	9.2 6.5 6.9 9.6 6.8 5.8 6.2 6.0 6.7 4.4 5.7 7.8 5.7 3.8 4.3 7.0	Hunt, 1983 Project 20566 File 1451V
Corticella, Bologna Italy, 1989	SC 375 g/l	1	0.51	0.15	0 7 14 21 28 35	0.87 0.44 0.42 0.27 0.30 0.17	Muller 1990a AG/CRLD/AN/9015940
Naoussa Macedonia Greece, 1994	WG 800 g/kg	2	1.6		42	0.16 0.23	Richard and Muller, 1995b Study 94-689
Naoussa Macedonia Greece, 1994	WG 800 g/kg	2	1.6		17	0.22 0.22	Richard and Muller, 1995b Study 94-689
Naoussa Macedonia Greece, 1994	WG 800 g/kg	2	1.6		32	0.57 0.40	Richard and Muller, 1995b Study 94-689
GAP, Japan	SC 320 g/l	3		0.032-0.042	21		
Japan, 1990	SC 375 g/l	3	2.5	0.05	14 21 28	0.562 <u>0.676</u> 0.392	Anon., AventisCrop Science, 2001a Iwate Prefecture Study No.Saku3p-2-69
Japan, 1990	SC 375 g/l	3	2.5	0.05	14 21 28	0.472 <u>0.305</u> 0.346	Anon., AventisCrop Science, 2001a Nagano Prefecture Study No.Saku3p-2-69
Japan, 1990	SC 375 g/l	3	2.5	0.05	14 21 28	0.720 <u>0.612</u> 0.406	Anon., AventisCrop Science, 2001a Iwate Prefecture Study No.Saku3p-2-69
Japan, 1990	SC 375 g/l	3	2.5	0.05	14 21 28	0.680 <u>0.317</u> 0.662	Anon., AventisCrop Science, 2001a Nagano Prefecture Study No.Saku3p-2-69

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, Japan	WP 750 g/kg	3		0.05-0.075	21		
Japan, 1985	WP 750 g/kg	3	2.5	0.05	21 28 44	0.676 0.724 0.322	Anon., AventisCrop Science, 2001a Nagano Prefecture Saku61p-4-106
Japan, 1985	WP 750 g/kg	3	3.75	0.075	21 28 44	1.46 1.76 0.159	Anon., AventisCrop Science, 2001a Nagano Prefecture Saku61p-4-106
Japan, 1985	WP 750 g/kg	3	2.5	0.05	21 28 44	0.370 0.839 0.410	Anon., AventisCrop Science, 2001a Toyama Prefecture Saku61p-4-106
Japan, 1985	WP 750 g/kg	3	3.75	0.075	21 28 44	0.682 1.52 0.472	Anon., AventisCrop Science, 2001a Toyama Prefecture Saku61p-4-106
Japan, 1985	WP 750 g/kg	3	2.5	0.05	21 28 44	0.390 0.176 0.165	Anon., AventisCrop Science, 2001a Nagano Prefecture Nissan Chemical Industry
Japan, 1985	WP 750 g/kg	3	3.75	0.075	21 28 44	0.481 0.177 0.235	Anon., AventisCrop Science, 2001a Nagano Prefecture Nissan Chemical Industry
Japan, 1985	WP 750 g/kg	3	2.5	0.05	21 28 45	0.375 0.170 0.069	Anon., AventisCrop Science, 2001a Toyama Prefecture Nissan Chemical Industry
Japan, 1985	WP 750 g/kg	3	3.75	0.075	21 28 45	0.430 0.234 0.054	Anon., AventisCrop Science, 2001a Toyama Prefecture Nissan Chemical Industry
Japan, 1982	WP 750 g/kg	3	3.75	0.075	7 14 21	17.1 1.28 0.91	Anon., AventisCrop Science, 2001a Aomori Prefecture Saku57p-8-121
Japan, 1982	WP 750 g/kg	3	3.75	0.075	7 14 21	25.5 1.71 0.91	Anon., AventisCrop Science, 2001a Nagano Prefecture Saku57p-8-121
Japan, 1982	WP 750 g/kg	3	3.75	0.075	7 14 21	1.55 1.30 1.56	Anon., AventisCrop Science, 2001a Aomori Prefecture Saku57p-8-1216
Japan, 1982	WP 750 g/kg	3	3.75	0.075	7 14 21	0.622 0.712 0.403	Anon., AventisCrop Science, 2001a Nagano Prefecture Saku57p-8-1216

Small fruits and berries

Results of supervised trials on grapes in France, Spain and Italy are shown in Table 50.

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Table 50. Residues in grapes from foliar applications.

Location, year	Application				Residues		Reference/Comments
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, France	SC 375 g/l SC 300 g/l	1-2	0.375-0.45	0.094-0.45	14 45		SC 300 g/l also contains bifenthrin
Languedoc France, 1983	SC 375 g/l	1	0.38	0.038	1 7 14 20	1.2 0.9 0.7 0.5	Barciet, 1990
Languedoc France, 1983	SC 375 g/l	1	0.38	0.038	6	0.65 1.3	Barciet, 1990
Languedoc France, 1983	SC 375 g/l	1	0.45	0.045	6	1.3 2.8	Barciet, 1990
Languedoc France, 1981	SC 375 g/l	1	0.45 calculated	0.045 and 1000/ha	84	<0.02	Cooper and Mestres, 1982 UC 51-702
Languedoc France, 1981	SC 375 g/l	2	0.45	0.045	38	0.15	Cooper and Mestres, 1982 UC 51-702
Bordeaux region Burgundy France, 1982	SC 375 g/l	2	0.45	0.045	22	<0.02	Cooper and Mestres, 1982 UC 51-702
France, 1982	SC 375 g/l	1	0.45	0.045	60	0.04	Cooper and Mestres, 1982 UC 51-702
Colombiers Languedoc France, 1982	SC 375 g/l	1	0.3		0 1 2 4 7 14 20	0.9 1.2 0.9 0.7 0.9 0.7 0.5	Cooper and Mestres, 1983
Colombiers France, 1988	SC 375 g/l	2	0.38	0.12	35	0.66	Lusson and Muller, 1989a AG/CRLD/AN/8916392
Pouzolles France, 1988	SC 375 g/l	2	0.38	0.12	35	0.22	Lusson and Muller, 1989a AG/CRLD/AN/8916392
Coustellet France, 1988	SC 375 g/l	2	0.38	0.25	54	<0.08	Lusson and Muller, 1989a AG/CRLD/AN/8916392
Mazan France, 1992	SC 375 g/l	3	0.38	0.14	49	<0.05	Richard and Muller, 1994a Study No.92-147
Mazan France, 1992	SC 375 g/l	3	0.56	0.14	49	0.16	Richard and Muller, 1994a Study No.92-147
Pouzolles France, 1992	SC 375 g/l	3	0.38	0.12	45	<0.05	Richard and Muller, 1994a Study No.92-147
Pouzolles France, 1992	SC 375 g/l	3	0.56	0.18	45	0.11	Richard and Muller, 1994a Study No.92-147
Bram France, 1995	SC 300 g/l	2	0.30	0.023 0.062	40	0.14 0.44	Maestracci, 1997a Study 95-541
Caromb France, 1995	SC 300 g/l	2	0.31	0.10	49	0.10	Maestracci, 1997b Study 95-540
Marignac France, 1995	SC 300 g/l	2	0.30	0.20	31	0.32	Maestracci, 1997c Study 95-539
Corticella, Bologna Italy, 1989	SC 375 g/l	1	0.51	0.051	0 7 14 21 28 35	1.29 0.96 0.59 0.64 0.30 0.27	Muller, 1990b Ref. AG/CRLD/AN/9015941
GAP, Spain	SC 375 g/l	--	0.375-0.75		21		
Camarena Spain, 1993	SC 375 g/l	2	0.56	0.17	26	0.60 2.21	Richard and Muller, 1994b Study No.93-624
Requena Spain, 1993	SC 375 g/l	2	0.55	0.071	64	1.08 1.01	Richard and Muller, 1994b Study No.93-624

Root and tuber vegetables

Supervised trials were conducted on potatoes in the UK (Table 51) and Japan (Table 52) and on sugar beet in the UK (Table 53).

Table 51. Residues in potatoes from trials in the UK (bait application).

Location, year	Application				Residues		Reference
	Formulation	No	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, UK	RB 40 g/kg	1-3	0.2	--	21	--	
Swillington, 1992	GB 40 g/kg	3	0.2		9 34	<0.04 <0.04 <0.04 <0.04 <0.04 <0.04	Maycey *et al.*, 1993. Study No.P92/218 Doc No.200163
Todcaster, 1992	GB 40 g/kg	3	0.2		9 38	<0.04 <0.04 <0.04 <0.04 <0.04 <0.04	Maycey *et al.*, 1993. Study No.P92/218 Doc No.200163
Driffield, 1992	GB 40 g/kg	3	0.2		8 28	<0.04 <0.04 <0.04 <0.04 <0.04 <0.04	Maycey *et al.*, 1993. Study No.P92/218 Doc No.200163
Helmsley, 1993	GB 40 g/kg	3	0.2		7	<0.040 <0.040 <0.040	Anderson-Taylor, 1996a Study No.RES/93/007 Doc No.201126
Swillington, 1993	GB 40 g/kg	3	0.2		7	<0.040 <0.040 <0.040	Anderson-Taylor, 1996a Study No.RES/93/007 Doc No.201126
Wistow, 1993	GB 40 g/kg	3	0.2		7	<0.040 <0.040 <0.040	Anderson-Taylor, 1996a Study No.RES/93/007 Doc No.201126
Goole, 1993	GB 40 g/kg	3	0.2		7	<0.040 <0.040 <0.040	Anderson-Taylor, 1996a Study No.RES/93/007 Doc No.201126
North Walsham UK, 1994	GB 40 g/kg	3	0.2		7	<0.040 <0.040 <0.040	Anderson-Taylor, 1996b Study No.RES/94/007 Doc No.201127
Bourne, 1994	GB 40 g/kg	3	0.2		7	<0.040 <0.040 <0.040	Anderson-Taylor, 1996b Study No.RES/94/007 Doc No.201127
Great Barford UK, 1994	GB 40 g/kg	3	0.2		7	<0.040 <0.040 <0.040	Anderson-Taylor, 1996b Study No.RES/94/007 Doc No.201127
North Walsham UK, 1994	GB 40 g/kg	3	0.2		8	<0.040 <0.040 <0.040	Anderson-Taylor, 1996b Study No.RES/94/007 Doc No.201127

In the Japanese trials, tubers were analysed by GLC with FPD in the sulfur mode (limit of detection 0.008, 0.007 mg/kg; LOQ not reported).

Table 52. Residues in potatoes from trials in Japan, 1985.

Application				Residues		Reference
Formulation	No	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP Japan WP 750 g/kg	5	--	0.05-0.075	7		
WP 750 g/kg	5		0.075	7 14	<0.008 <0.008	Imose, 1986
WP 750 g/kg	5		0.075	7 14	<0.008 <0.008	Imose, 1986

Application				Residues		Reference
Formulation	No	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
WP 750 g/kg	5		0.075	7 14	<0.007 <0.007	Hayashi *et al.*, 1986
WP 750 g/kg	5		0.075	7 14	<0.007 <0.007	Hayashi *et al.*, 1986

Sugar beet roots from trials with granular bait in the UK were analysed by GC-MS (LOQ 0.04 mg/kg).

Table 53. Residues in sugar beet from trials in the UK, 1997.

Location	Application				Residues		Reference
	Formulation	No	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, Belgium	GB 40 g/kg	--	0.2	--	--	--	--
Hertfordshire	RB 40 g/kg	3	0.195		98	<0.040	Maestracci, 1998a, Study 97-732
Norfolk	RB 40 g/kg	3	0.195		101	<0.040	Maestracci, 1998a, Study 97-32
Cambridgeshire	RB 40 g/kg	3	0.195		101	<0.040	Maestracci, 1998a, Study 97-732
Ely	RB 40 g/kg	3	0.195		101	<0.040	Maestracci, 1998a, Study 97-732

Leafy vegetables (except Brassica vegetables)

Supervised trials were conducted on lettuce with granular bait treatment in Italy and France and with aerial and ground foliar application in Spain and the USA. Supervised trials were also conducted on spinach with ground foliar application in the USA.

In the French trials, lettuce heads were analysed by GC-MS (LOQ 0.04 mg/kg). Duplicate samples were taken at each site.

Table 54. Residues in lettuce (granular bait application).

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Italy, 1992	GB 40 g/kg	1	0.8	--	7	<0.04	Anon., 1992 Report No.0026
GAP, France	GB 40 g/kg	1-3	0.4		7		
Ingre, France, 2000	GB 40 g/kg	2	0.413	--	0 8 14 22	0.17 14 <0.04 <0.04 0.14 <0.04 <0.04 0.13 0.047	Gateaud and Yslan, 2001a Study No.00-561
Le Meillard, France, 2000	GB 40 g/kg	2	0.413	--	0 8 14 21	0.13 0.19 <0.04 0.048 <0.04 <0.04 <0.04 <0.04	Gateaud and Yslan, 2001a Study No.00-561
Ingre, France, 2000	GB 40 g/kg	2	0.413	--	21	0.14 0.14	Gateaud and Yslan, 2001b, Study No.00-562. Control: 0.056 mg/kg
Le Meillard, France, 2000	GB 40 g/kg	2	0.413	--	22	0.053 0.043	Gateaud and Yslan, 2001b Study No.00-562

Trials with foliar application to lettuce were reported from Spain and the USA. Lettuce heads were analysed by GLC (nitrogen FPD, LOQ 0.04 mg/kg).

Table 55. Residues in head lettuce (foliar spray application with ground equipment).

Location, year	Application				Residues		Reference
	Form.	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Spain, 1999	SC 375 g/l	3	0.94	0.141	0 7	9.4 7.3 1.5 2.4	Gateaud and Yslan, 2000. Study No.99-568
Spain, 1999	SC 375 g/l	3	0.941	0.231	0 7 15 22	27 25 3.0 3.5 0.50 0.25 0.082 0.14	Gateaud and Yslan, 2000. Study No.99-568
Spain, 1999	SC 375 g/l	3	0.85	0.257	0 7 14 21	21 26 8.9 10 2.4 2.3 0.93 1.2	Gateaud and Yslan, 2000. Study No.99-568
Spain, 1999	SC 375 g/l	3	0.941	0.221	0 7 14 21	12 14 1.1 0.96 0.12 0.16 0.041 0.073	Gateaud and Yslan, 2000. Study No.99-568
GAP, USA	SC 375 g/l	--	0.45-0.84		14		Do not exceed 1.7 kg ai/ha per season
Santa Maria, CA USA, 1985	SC 375 g/l	2	0.84	--	14	0.34 0.64 <u>0.71</u>	Langdon, 1987 Project No.804R10; File No.34768
Salinas, CA USA, 1985	SC 375 g/l	2	0.84	--	14	<u>0.12</u> <0.04	Langdon, 1987 Project No.804R10; File No.34768
Manteca, CA USA, 1985	SC 375 g/l	2	0.84	--	14	<u>13</u> 7.2 12	Langdon, 1987 Project No.804R10; File No.34768
Sanford, FL USA, 1985	SC 375 g/l	2	0.84	--	14	6.1 <u>7.7</u> 5.8 3.8 2.8 3.0	Langdon, 1987 Project No.804R10; File No.34768
Newton, IA USA, 1985	SC 375 g/l	2	0.84	--	14	0.28 <u>0.49</u> 0.36	Langdon, 1987 Project No.804R10; File No.34768
Marcellus, MI USA, 1985	SC 375 g/l	2	0.84	--	14	<u><0.04</u> <0.04 <0.04	Langdon, 1987 Project No.804R10; File No.34768
Wayside, MS USA, 1985	SC 375 g/l	2	0.84	--	14	<u>10</u> 7.7 7.9	Langdon, 1987 Project No.804R10; File No.34768

Clayton, NC USA, 1985	SC 375 g/l	2	0.84	--	14	3.6 2.0 6.2	Langdon, 1987 Project No.804R10; File No.34768
Phelps, NY USA, 1985	SC 375 g/l	2	0.84	--	14	18 17 17	Langdon, 1987 Project No.804R10; File No.34768
Westlaco, TX USA, 1985	SC 375 g/l	2	0.84	--	14	5.5 5.5 6.3	Langdon, 1987 Project No.804R10; File No.34768
Glendale, AZ USA, 1983-84	SC 375 g/l	4	0.84		14	0.17 0.10 0.25	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		14	0.11 0.21 0.20	
Hollister, CA USA, 1983	SC 375 g/l	4	0.84		7 14	2.7 2.4 3.0 1.7 1.7	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		7 14	1.7 0.37 0.06 0.06 1.8	
El Centro, CA USA, 1983-84	SC 375 g/l	4	0.84		14	1.8 3.2 2.4	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		14	1.5 1.4 1.7	
Arlington, WI USA, 1983	SC 375 g/l	4	0.84		14	0.24 0.34 0.24 0.20	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		14	0.24 0.34 0.14 0.48	
Manteca, CA USA, 1984	SC 375 g/l	4	0.84		14	0.07 0.06 0.06	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		14	0.14 0.14 0.13	
Sanford, FL USA, 1984	SC 375 g/l	4	0.84		14	1.2 1.1 1.3	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		14	1.7 1.5	
Sodus, NY USA, 1984-85	SC 375 g/l	4	0.84		14	0.08 0.06 0.09	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		14	0.19 0.17 0.11	
Westlaco, TX USA, 1984-85	SC 375 g/l	4	0.84		14	0.29 0.42 0.28	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		14	0.26 0.34 0.44	

Dome Valley, AZ USA, 1984-85	SC 375 g/l	4	0.84		15	0.63 0.96 0.96	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	4	0.84		15	0.96 1.4 1.9	
Santa Maria, CA USA, 1985	SC 375 g/l	2	0.84		14	0.13 0.35 0.27	Hunt, 1986a Project No.804R11 File No.34501
Salinas, CA USA, 1985	SC 375 g/l	2	0.84		14	2.6 0.73	Hunt, 1986a Project No.804R11 File No.34501
Manteca, CA USA, 1985	SC 375 g/l	2	0.84		14	17 8.6 16	Hunt, 1986a Project No.804R11 File No.34501
Newton, IA USA, 1985	SC 375 g/l	2	0.84		14	0.09 0.08 0.06	Hunt, 1986a Project No.804R11 File No.34501
Marcellus, MI USA, 1985	SC 375 g/l	2	0.84		14	0.05 0.05 0.07	Hunt, 1986a Project No.804R11 File No.34501
Wayside, MS USA, 1985	SC 375 g/l	2	0.84		14	≤0.04 <0.04 <0.04	Hunt, 1986a Project No.804R11 File No.34501
Clayton, CA USA, 1985	SC 375 g/l	2	0.84		14	≤0.04 <0.04 <0.04	Hunt, 1986a Project No.804R11 File No.34501
Godus, NY USA, 1985	SC 375 g/l	2	0.84		14	0.33 0.36 0.17	Hunt, 1986a Project No.804R11 File No.34501

Table 56. Residues in lettuce (aerial application), USA.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, US	SC 375 g/l	--	0.45-0.84		14		Do not exceed 1.7 kg ai/ha per season
Hollister, CA, 1983	SC 375 g/l	4	0.84		7 14	2.8 2.2 2.0	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	4	0.84		7 14	1.3 0.27 ≤0.05 <0.05 <0.05	
Dome Valley, AZ, 1984-85	SC 375 g/l	4	0.84		15	1.1 1.0 1.5	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	4	0.84		15	0.65 1.1 0.78	

In spinach trials in the USA, analyses were by GLC (nitrogen FPD, LOQ 0.04 mg/kg).

Table 57. Residues in spinach (foliar spray application), USA.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.45-0.84		14		Do not exceed 1.7 kg ai/ha per season
Santa Maria, CA, 1985	SC 375 g/l	2	0.84	--	14	3.2 3.4 3.5	Langdon, 1987 ProjectNo.804R10;File No.34768
Salinas, CA, 1985	SC 375 g/l	2	0.84	--	14	<0.04 0.21	Langdon, 1987 ProjectNo.804R10;File No.34768
Manteca, CA, 1985	SC 375 g/l	2	0.84	--	14	20 20 23 21 21 25	Langdon, 1987 ProjectNo.804R10;File No.34768
	SC 375 g/l + oil	2	0.84	--	14	22 25 18	
Sanford, FL, 1985	SC 375 g/l	2	0.84	--	14	2.2 4.1 3.9 1.0 2.5 1.9	Langdon, 1987 ProjectNo.804R10;File No.34768
Newton, IA, 1985	SC 375 g/l	2	0.84	--	14	0.04 <0.04 <0.04	Langdon, 1987 ProjectNo.804R10;File No.34768
Marcellus, MI, 1985	SC 375 g/l	2	0.84	--	14	<0.04 <0.04 0.04	Langdon, 1987 ProjectNo.804R10;File No.34768
Clayton, NC, 1985	SC 375 g/l	2	0.84	--	14	2.2 1.7 3.2	Langdon, 1987 ProjectNo.804R10;File No.34768 (Spinach growth not vigorous)
	SC 375 g/l + oil	2	0.84	--		0.57 0.74 0.85	
Phelps, NY, 1985	SC 375 g/l	2	0.84	--	14	0.94 1.0 0.99 0.23 0.31 0.15	Langdon, 1987 ProjectNo.804R10;File No.34768
Westlaco, TX, 1985	SC 375 g/l	2	0.84	--	14	6.6 10 12	Langdon, 1987 ProjectNo.804R10;File No.34768

Supervised trials on collards were reported from the USA.

Table 58. Residues in collards (foliar spray application), USA.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Tifton, GA 1988	SC 375 g/l	5	0.84		7 11 14 	0.33 1.4 2.0 1.4 0.88 1.1 0.91 1.9 0.70 0.89 <u>1.5</u> 0.11	Hunt, 1988a File No.40458 Project No.804R10
Tifton, GA 1988	SC 375 g/l	5	1.7		7 11 14 	2.8 3.5 3.1 3.1 0.98 1.3 0.16 0.88 0.34 <u>1.8</u> 0.62 1.3	Study No.40458 Project No.804R10

<u>Brassica vegetables</u>

Supervised trials were conducted on broccoli, Brussels sprouts, cabbage and cauliflower in the USA, Australia, the UK and The Netherlands.

Samples were analysed by GLC with FPD in the sulfur mode (LOQ 0.04 mg/kg in the USA, 0.02 mg/kg in Australia).

Table 59. Residues in broccoli (foliar spray application; ground equipment).

Location, year	Application				Residues		Reference/Comment
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.45-1.15		7		Do not exceed 6.7 kg ai/ha per season
Manteca, CA USA, 1982	SC 375 g/l	6	0.56	0.200	1 3 7 14	3.2 3.4 3.0 4.8 2.6 2.5 0.61 0.46 0.44 0.32 0.36 0.20	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	0.56	0.200	1 3 7 14	3.5 2.0 3.4 4.2 4.2 3.9 0.20 0.25 0.21 0.22 0.35 0.20	
Manteca, CA USA, 1982	SC 375 g/l	6	1.1	0.399	1 3 7 14	6.9 8.8 9.2 5.1 7.6 6.4 1.2 1.3 1.2 1.0 0.91 0.71	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	1.1	0.399	1 3 7 14	7.1 6.4 7.3 4.9 5.5 4.9 0.77 1.1 1.1 0.62 0.54 0.59	

Location, year	Application				Residues		Reference/Comment
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Newton, IA USA, 1982	SC 375 g/l	6	0.56	0.15	1 3 14 	5.9 3.6 6.5 4.8 0.23 0.44 <0.02 <0.02 <0.02	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	0.56	0.15	1 3 14 	7.8 8.4 7.6 2.4 4.2 11 0.04 0.03 0.05	
Newton, IA USA, 1982	SC 375 g/l	6	1.1	0.300	1 3 14 	16 9.5 7.5 3.6 3.7 1.2 0.13 0.11 <0.02	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	1.121	0.300	1 3 14 	23 9.2 13 7.1 5.9 5.9 0.03 0.16 0.10	
Wayside, MS USA, 1982	SC 375 g/l	6	0.56	0.35	1 3 7 14 	2.3 2.1 2.1 1.3 2.1 2.3 0.29 0.51 0.54 <0.02 <0.02 <0.02	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	0.56	0.346	1 3 7 14 	2.3 3.1 2.5 1.6 1.1 2.1 0.69 1.2 0.32 0.05 0.04 0.04	

Location, year	Application				Residues		Reference/Comment
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Wayside, MS USA, 1982-85	SC 375 g/l	6	1.1	0.700	1 3 7 14	7.2 8.1 7.2 3.1 4.6 3.5 2.0 <u>2.6</u> 2.4 0.09 0.11 0.07	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	0.56	0.346	1 3 7 14	2.3 3.1 2.5 1.6 1.1 2.1 0.69 1.2 0.32 0.05 0.04 0.04	
San Benito, CA USA, 1983	SC 375 g/l	6	1.1	0.40	7 14	4.2 <u>5.0</u> 3.3 0.67 0.46 0.60	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	1.1	0.400	7 14	1.5 1.5 <u>1.6</u> 0.20 0.15 0.11	
Weslaco, TX USA, 1985	SC 375 g/l	6	1.1	1.19	14	0.27 0.15 0.23	Hunt, 1986a Project No.804R10 File No.34501
GAP, Australia	SC 375 g/l	--	0.375-0.75		7		
Cambooya Australia, 1989	SC 375 g/l	5	0.525		3 7 11[1] 14	2.1 <u>0.14</u> 0.09 <0.04	Keats, 1990 Report No.AK/TN/AK905
Cambooya Australia, 1989	SC 375 g/l	5	0.52		3 7 11[1] 14	4.2 <u>0.33</u> 0.20 0.08	Keats, 1990 Report No.AK/TN/AK905

[1] 11 days after 4th application and 2 h before 5th (final) application.

Table 60. Residues in broccoli (aerial application), USA.

Location, year	Application				Residues		Reference
	Formulation.	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.45-1.15		7		Do not exceed 6.7 kg ai/ha per season
San Benito, CA, 1982	SC 375 g/l	6	1.1	NR	7 14	3.3 5.6 4.9 0.57 0.33 0.60	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	1.1	NR	7 14	1.8 1.9 1.2 0.20 0.14 0.17	

Brussels sprouts were analysed by a GLC method (LOQ 0.05 mg/kg) in supervised field trials in The Netherlands.

Table 61. Residues in Brussels sprouts (granular bait application).

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP (Belgium)	GB 40g/kg	6	0.2	21		
Thorrington UK, 1997-98	RB 40 g/kg	5	0.2	7	<0.04 <0.04	Maestracci, 1998b Study No.97-733
Freiston UK, 1997	RB 40 g/kg	5	0.2	7	<0.04 <0.04	Maestracci, 1998b Study No.97-733
Boston UK, 1997	RB 40 g/kg	5	0.2	7	<0.04 <0.04	Maestracci, 1998b Study No.97-733
Biggleswad UK, 1997	RB 40 g/kg	5	0.2	7	<0.04 <0.04	Maestracci, 1998b Study No.97-733
Smitshoek Netherlands, 1997	GB 40 g/kg	6	0.2	21	0.059 <0.050	Richard and Muller, 1995a. Study No.92-304
Achterzeedijk Netherlands, 1997	GB 40 g/kg	6	0.2	21	<0.050 <0.050	Richard and Muller, 1995a. Study No.92-304
Noordeinde Netherlands, 1997	GB 40 g/kg	6	0.2	21	<0.050 <0.050	Richard and Muller, 1995a. Study No.92-304
Hoogeveenseweg Netherlands, 1997	GB 40 g/kg	6	0.2	21	<0.050 <0.050	Richard and Muller, 1995a. Study No.92-304
Netherlands, 1998	GB 40 g/kg	6	0.19	21	<0.004 <0.004	Yslan and Baudet, 1999 Study No.98-747 Limit of detection: 0.004 mg/kg
Netherlands, 1998	GB 40 g/kg	6	0.19	21	<0.004 <0.004	Yslan and Baudet, 1999 Study No.98-747
Netherlands, 1998	GB 40 g/kg	6	0.19	21	<0.004 <0.004	Yslan and Baudet, 1999 Study No.98-747
Netherlands, 1998	GB 40 g/kg	6	0.19	21	<0.004 <0.004	Yslan and Baudet, 1999 Study No.98-747

Supervised trials on cabbages were conducted in the USA and Australia. Samples were analysed by GLC with an FPD (LOQ 0.04 mg/kg in the USA, 0.02 mg/kg in Australia).

Table 62. Residues in cabbage (foliar spray application).

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	1.15	7		Do not exceed 6.7 kg ai/ha per season
Montgomery, AL USA, 1982	SC 375 g/l	6	1.1	3 5 7	0.19 0.22 0.18 0.22 0.19 0.11 0.08 0.09 <u>0.12</u>	Hunt, 1986a Project No.804R11 File No.34501
Teloxsira Farms, CA USA, 1982	SC 375 g/l	6	1.1	3 5 7	5.8 6.1 4.7 8.6 4.4 5.4 2.5 <u>3.0</u> 1.5	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1	3 5 7	9.6 5.4 6.9 3.9 7.3 11 1.9 <u>2.8</u> 2.3	
Sanford, FL USA, 1982	SC 375 g/l	6	1.1	3 5 7	1.4 2.4 1.8 2.1 2.7 3.0 2.0 1.8 <u>3.1</u>	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1	3 5 7	4.7 3.5 3.2 3.5 3.6 4.1 <u>2.1</u> 0.37 1.7	
Phelps, NY USA, 1982	SC 375 g/l	6	1.1	3 5 7	1.2 0.77 1.6 0.70 0.88 1.1 1.2 0.44 <u>1.3</u>	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1	3 5 7	1.2 1.7 2.1 2.0 2.0 1.8 <u>3.5</u> 1.0 1.2	

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Clayton, NC USA, 1982	SC 375 g/l	6	1.1	3 5 7	0.13 0.20 0.16 0.12 0.17 0.18 0.07 <0.05 0.08	Hunt, 1986a Project No.804R11 File No.34501
Wooster, OH USA, 1982	SC 375 g/l	5	1.1	3 5	1.1 2.8 3.0 0.56 1.7 5.0	Hunt, 1986a Project No.804R11 File No.34501
Rock Spring, PA USA, 1982	SC 375 g/l	6	1.1	3 5 7	4.0 1.5 1.4 0.45 0.15 0.09 0.08 0.04	Hunt, 1986a Project No.804R11 File No.34501
Arlington, WI USA, 1982	SC 375 g/l	6	1.1	3 5 7	0.74 0.51 0.23 1.1 0.61 0.18 0.20 0.53	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1	3 5 7	0.55 0.79 0.91 0.16 0.75 0.58 0.14 0.51 1.2	
San Benito, CA USA, 1983	SC 375 g/l	6	1.1	7 14	3.4 2.4 3.8 0.41 0.21 0.24	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1	7 14	1.9 1.7 2.7 0.13 0.07 0.10	
Wayside, MS USA, 1983	SC 375 g/l	6	1.1	7 14	0.76 0.75 0.73 0.22 0.28 0.32	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1	7 14	0.73 0.97 0.88 0.21 0.19 0.21	

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Clayton, NC	SC 375 g/l	6	1.1	7 14	3.2 3.4 <u>4.3</u> 1.0 1.0 1.9	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1	7 14	4.8 4.1 <u>5.3</u> 1.6 2.0 1.4	
Cleveland, Queensland Australia, 1989	SC 375 g/l	5	0.75	3 7 14	0.07 0.05 <0.04	Keats, 1989a AK/aw/ak89006
Cleveland, Queensland Australia, 1989	SC 375 g/l	5	1.5	3 7 14	0.13 0.07 0.05	Keats, 1989a AK/aw/ak89006

Table 63. Residues in cabbage (aerial application) from trials in the USA.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
US GAP	SC 375 g/l	--	0.45-1.15		7		Do not exceed 6.7 kg ai/ha per season
San Benito, CA, 1982	SC 375 g/l	6	1.1		7 14	4.9 2.3 <u>5.0</u> 0.37 0.28 0.47	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	6	1.1		7 14	<u>4.8</u> 1.9 1.1 0.10 0.22 0.13	

Supervised field trials on cauliflower were conducted in Australia and the USA. Samples were analysed by GLC with FPD (LOQ 0.04 mg/kg in the USA, 0.02 mg/kg in Australia).

Table 64. Residues in cauliflower (foliar spray application)

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.45-1.15		7		Do not exceed 6.7 kg ai/ha per season
Manteca, CA USA, 1982	SC 375 g/l	7	0.56	0.20	1 3 7 14	0.70 1.3 1.1 0.53 0.80 1.3 0.29 0.24 0.24 0.22 0.18 0.21	Hunt, 1986a Project No.804R11 File No.34501
	WG 800 g/kg	7	0.56	0.20	1 3 7 14	1.0 0.94 0.89 0.72 0.69 0.66 0.21 0.27 0.26 0.30 0.25 0.26	
Manteca, CA USA, 1982	SC 375 g/l	7	1.1	0.40	1 3 7 14	1.5 3.4 3.4 1.2 1.2 1.4 <u>0.64</u> 0.55 0.63 0.27 0.28 0.43	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	7	1.1	0.40	1 3 7 14	2.1 3.8 1.7 0.89 1.5 1.3 <u>0.71</u> 0.51 0.67 0.35 0.53 0.55	

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Wayside, MS USA, 1982	SC 375 g/l	6	0.56	0.346	1 3 7 14	2.2 2.6 2.0 2.6 1.8 1.3 1.3 1.3 1.3 0.16 0.15 0.14	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	0.56	0.346	1 3 7 14	3.4 2.3 3.7 3.4 2.3 2.8 1.5 1.7 1.7 0.38 0.29 0.23	
Wayside, MS USA, 1982	SC 375 g/l	6	1.1	0.69	1 3 7 14	3.8 5.4 4.9 5.5 4.5 3.2 <u>2.3</u> 2.2 1.8 0.64 0.70 0.34	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	1.1	0.69	1 3 7 14	4.1 5.3 5.0 3.3 3.0 4.2 1.4 1.7 <u>2.3</u> 0.51 0.49 0.45	
San Benito, CA USA, 1982	SC 375 g/l	6	1.1	0.400	7 14	0.36 <u>0.45</u> 0.33 <0.04 <0.04 ND	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	1.1	0.400	7 14	ND <u>0.09</u> 0.06 <0.04 ND ND	
Phelps, NY USA, 1982	SC 375 g/l	6	1.1	0.24	14	4.1 1.9 1.7	Hunt, 1986a Project No.804R10 File No.34501

Table 65. Residues in cauliflower (aerial application), USA.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.45-1.15		7		Do not exceed 6.7 kg ai/ha per season
San Benito, CA, 1982	SC 375 g/l	6	1.1		7 14	0.07 0.10 <u>0.16</u> <0.04 0.04 ND	Hunt, 1986a Project No.804R10 File No.34501
	WG 800 g/kg	6	1.1		7 14	0.10 <u>0.27</u> 0.06 ND <0.04 <0.04	

<u>Legume vegetables</u>

Supervised trials were conducted on peas and chick-peas in Australia and soya beans in Australia, Brazil and the USA.

In Australia, peas and hay from supervised field trials were analysed by GLC with an FPD (LOQ 0.02 mg/kg).

Table 66. Residues in peas (foliar spray application), Australia, 1990.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.188-0.28		21		
Redland Bay Research Station	SC 375 g/l	1	0.19	--	28	<0.02	Keats, 1991, Report No. AK/JG/AK002
Redland Bay Research Station	SC 375 g/l	1	0.28	--	28	<0.02	Keats, 1991, Report No. AK/JG/AK002
Redland Bay Research Station	SC 375 g/l	1	0.38	--	28	<0.02	Keats, 1991, Report No. AK/JG/AK002
Redland Bay Research Station	SC 375 g/l	1	0.56	--	28	<0.02	Keats, 1991, Report No. AK/JG/AK002
Redland Bay Research Station	SC 375 g/l	1	1.1	--	28	0.04	Keats, 1991, Report No. AK/JG/AK002

Table 67. Residues in peas (hay), Australia, 1990.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Redland Bay Research Station,	SC 375 g/l	1	0.19	--	0 7 14 28	3.48 0.08 <0.02 <0.02	Keats, 1991, Report No. AK/JG/AK002
Redland Bay Research Station	SC 375 g/l	1	0.28	--	0 7 14 28	5.21 0.20 0.04 0.02	Keats, 1991, Report No. AK/JG/AK002
Redland Bay Research Station,	SC 375 g/l	1	0.38	--	0 7 14 28	5.82 0.36 0.05 <0.02	Keats, 1991, Report No. AK/JG/AK002

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Redland Bay Research Station,	SC 375 g/l	1	0.56	--	0 7 14 28	9.3 0.92 0.13 0.02	Keats, 1991, Report No. AK/JG/AK002
Redland Bay Research Station	SC 375 g/l	1	1.1	--	0 7 14 28	16.4 2.17 0.29 0.05	Keats, 1991, Report No. AK/JG/AK002

In trials in Australia, chick-peas, straw, foliage, stems and immature pods were analysed by a GLC method (LOQ 0.05 mg/kg for straw and peas, 0.02 mg/kg for foliage).

Table 68. Residues in chick-peas (foliar spray application, ground), Australia, 1986.

Location	Application				Interval (days)	Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl		PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.188-0.28			21		
South East of Emerald Queensland	SC 375 g/l	2	0.56		15	38	<0.05	Clark and Shields, 1986, Ref. 1870/86/5
South East of Emerald Queensland	SC 375 g/l	2	1.1		15	38	<0.05	

Table 69. Residues in chick-pea foliage, stems and immature pods, Australia, 1986.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.188-0.28		21		
South East of Emerald Queensland	SC 375 g/l	1	0.56		0 7 14	19 6.0 2.5	Clark and Shields, 1986, Ref. 1870/86/5
South East of Emerald Queensland	SC 375 g/l	2	0.56		0 7 14	45 23 21	
South East of Emerald Queensland	SC 375 g/l	1	1.1		0 7 14	51 16 12	
South East of Emerald Queensland	SC 375 g/l	2	1.1		0 7 14	52 44 96	

Table 70. Residues in chick-peas (straw), Australia, 1986.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
South East of Emerald Queensland	SC 375 g/l	2	0.56		38	1.4	Clark and Shields, 1986, Ref. 1870/86/5
South East of Emerald Queensland	SC 375 g/l	2	1.1		38	2.7	

Supervised field trials on soya beans were reported from Australia, Brazil and the USA. Seeds, forage, hay and straw were analysed by GLC (FPD in sulfur mode, LOQ 0.04 mg/kg) in the USA. In Brazil, seeds were analysed by HPLC (LOQ 0.1 mg/kg and LOD 0.05 mg/kg). In Australia, seeds were analysed by GLC (sulfur FPD, LOQ 0.04 mg/kg).

Table 71. Residues in soya bean seed (foliar spray application; ground equipment).

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.84		28		Do not exceed 3.4 kg/ha per season
East Baton Rouge, Louisiana USA, 1991	SC 375 g/l	4	0.84	--	28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Lonoke, AR USA, 1991	SC 375 g/l	4	0.841	--	28	0.05 <u>0.06</u> 0.05	Bird and Coffey, 1992 Project No.USA91L30
Washington, MS USA, 1991	SC 375 g/l	4	0.84	--	27	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Sibley, MN USA, 1991	SC 375 g/l	4	0.84	--	28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992
Martin, NC USA, 1991	SC 375 g/l	4	0.84	--	28	<u>≤0.04</u> <0.04 <0.04	Project No.USA91L30
Clay, MN USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992
Lancaster, PA USA, 1991	SC 375 g/l	4	0.94		27	0.10 0.06 <u>0.15</u>	Project No.USA91L30
Landry, LA USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992
Washington, MS USA, 1991	SC 375 g/l	4	0.84		29	<u>≤0.04</u> <0.04 <0.04	Project No.USA91L30
Des Moines, IA USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992
Des Moines, IA USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Project No.USA91L30
Shelby, MO USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Shelby, MO USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Arkansas, AR USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Hamilton, IN USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Hamilton, IN USA, 1991	SC 375 g/l	4	0.84		31	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Henderson, IL USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Henry, IL USA, 1991	SC 375 g/l	4	0.89		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Richmond, VA USA, 1991	SC 375 g/l	4	0.84		28	<u>≤0.04</u> <0.04 <0.04	Bird and Coffey, 1992 Project No.USA91L30
Geneseo, IL USA, 1990	SC 375 g/l	4	4.2		29	0.04	Lee, 1991c Project No.USA90L01 File No.41003

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.188-0.28		21		
Patrick Estate, Lowood Australia, 1985	SC 375 g/l	1	0.75		35	ND (<0.02) ND ND ND	Hunt and Langdon, 1985
Patrick Estate, Lowood Australia, 1985	SC 375 g/l	1	1.9		35	ND (<0.02) ND ND ND	Hunt and Langdon, 1985
GAP, Brazil	WG 800 g/l	--	0.056		14		
Paulinia Brazil, 1996-1997	WG 800 g/kg	3	0.08		14	<0.05 <0.05 <0.05	Anon., 1997 CP-2480/97 Study No.006/97-PC
Paulinia Brazil, 1996-1997	WG 800 g/kg	3	0.16		14	<0.05 <0.05 <0.05	Anon., 1997 CP-2480/97 Study No.006/97-PC

Supervised field trials with aerial application were conducted in the USA. 2.3 l/ha of a commercially available emulsified vegetable oil was used in all cases.

Table 72. Residues in soya bean seed (aerial application), USA, 1987.

Location	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.84		28		Do not exceed 3.4 kg/ha per season
Proctor, AR	SC 375 g/l	2	0. 50		28	<0.04 <0.04 <0.04	Hunt, 1988d File No.40383 Project No.804R10
Midville, GA	SC 375 g/l	2	0. 50		31	<0.04 <0.04 <0.04	Hunt, 1988d File No.40383 Project No.804R10
Cohoama Country, MS	SC 375 g/l	2	0. 50		28	<0.04 <0.04 <0.04	Hunt, 1988d File No.40383 Project No.804R10
Leland, MS	SC 375 g/l	2	0. 50		27	<0.04 <0.04 <0.04	Hunt, 1988d File No.40383 Project No.804R10
Clarence, MO	SC 375 g/l	2	0. 50		31	ND (<0.02) ND ND	Hunt, 1988d File No.40383 Project No.804R10
Jamesville, NC	SC 375 g/l	2	0. 50		28	ND (<0.02) ND ND	Hunt, 1988d File No.40383 Project No.804R10
Plymouth, NC	SC 375 g/l	2	0. 50		28	<0.04 <0.04 <0.04	Hunt, 1988d File No.40383 Project No.804R10
Darlington Country, SC	SC 375 g/l	2	0. 50		28	0.05 <0.04 0.05	Hunt, 1988d File No.40383 Project No.804R10
Sulfolk, VA	SC 375 g/l	2	0. 50		28	<0.04 <0.04 <0.04	Hunt, 1988d File No.40383 Project No.804R10

Location	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Keller, VA	SC 375 g/l	2	0. 50		28	ND <0.04 <0.04	Hunt, 1988d File No.40383 Project No.804R10

Table 73. Residues in soya bean seed (seed treatment), USA, 1985.

Location	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Elberta, Al	900 g/kg	1	20	115	ND (<0.02)	Hunt, 1988c File No.40388 Project No.804R10
Buckley, IL	900 g/kg	1	20	155	ND ND	Hunt, 1988c File No.40388 Project No.804R10
Newton, IA	900 g/kg	1	20	149	ND ND ND ND	Hunt, 1988c File No.40388 Project No.804R10
Wayside, MS	900 g/kg	1	20	142	ND ND ND ND	Hunt, 1988c File No.40388 Project No.804R10
Clayton, NC	900 g/kg	1	20	206	ND ND ND ND	Hunt, 1988c File No.40388 Project No.804R10

Supervised field trials were conducted in the USA for residues in soya bean forage, hay and straw, but the labels forbid the use of these commodities as livestock feed.

Table 74. Residues in soya bean forage (foliar spray application), USA.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.28-0.84		--		Do not exceed 3.4 kg/ha per season
East Baton Rouge, LA	SC 375 g/l	4	0.84	--	0	16.0 8.6 11.9	Bird and Coffey, 1992 Project No.USA91L30
Lonoke, AR	SC 375 g/l	4	0.84	--	0	19.1 20.4 24.0	Bird and Coffey, 1992 Project No.USA91L30
Sibley, MN	SC 375 g/l	4	0.84	--	7	3.96 3.94 3.49	Bird and Coffey, 1992 Project No.USA91L30
Martin, NC	SC 375 g/l	4	0.84	--	0	16.2 13.4 22.0	Bird and Coffey, 1992 Project No.USA91L30
Richmond, VA	SC 375 g/l	4	0.84		0	10.6 23.2 23.0	Bird and Coffey, 1992 Project No.USA91L30
Clay, MN	SC 375 g/l	4	0.84		0	28.3 27.5 25.3	Bird and Coffey, 1992 Project No.USA91L30
Lancaster, PA	SC 375 g/l	4	0.94		0	35.7 19.8 25.8	Bird and Coffey, 1992 Project No.USA91L30
St Landry, LA	SC 375 g/l	4	0.84		0	26.7 32.2 29.6	Bird and Coffey, 1992 Project No.USA91L30

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Washington, MS	SC 375 g/l	4	0.84		0 29	26.4 27.4 22.2	Bird and Coffey, 1992 Project No.USA91L30
Des Moines, IA	SC 375 g/l	4	0.84		0	18.6 22.5 17.2	Bird and Coffey, 1992 Project No.USA91L30
Des Moines, IA	SC 375 g/l	4	0.84		0	25.6 14.0 11.9	Bird and Coffey, 1992 Project No.USA91L30
Shelby, MO	SC 375 g/l	4	0.84		0	22.0 19.5 22.5	Bird and Coffey, 1992 Project No.USA91L30
Shelby, MO	SC 375 g/l	4	0.84		0	29.6 16.3 20.7	Bird and Coffey, 1992 Project No.USA91L30
Arkansas, AR	SC 375 g/l	4	0.84		0	20.9 21.9 25.8	Bird and Coffey, 1992 Project No.USA91L30
Hamilton, IN	SC 375 g/l	4	0.84		0	17.5 15.8 21.8	Bird and Coffey, 1992 Project No.USA91L30
Hamilton, IN	SC 375 g/l	4	0.84		0	40.0 27.8 29.3	Bird and Coffey, 1992 Project No.USA91L30
Henderson, IL	SC 375 g/l	4	0.84		0	51.1 37.6 51.2	Bird and Coffey, 1992 Project No.USA91L30
Henry, IL	SC 375 g/l	4	0.8		0	23.1 23.0 24.3	Bird and Coffey, 1992 Project No.USA91L30
Richmond, VA	SC 375 g/l	4	0.84		3	8.36 20.5 15.5	Bird and Coffey, 1992 Project No.USA91L30

Table 75. Residues in soya bean forage (seed treatment), USA, 1985.

Location	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Clayton, NC	900 g/kg	1	20	14	21 22 31 25	Hunt, 1988c File No.40388 Project No.804R10
				21	7.6 6.9 3.9 2.1	
				35	0.70 0.78 0.76 0.76	
				68	ND ND ND ND	
				99	ND ND ND ND	

Table 76. Residues in soya bean hay (foliar spray application), USA, 1991.

Location	Application				Residues		Reference
	Form.	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.28-0.84	0.14-0.42	0-7		Do not exceed 3.4 kg/ha per season
East Baton Rouge, LA	SC 375 g/l	4	0.84		0	59.5 75.0 43.9	Bird and Coffey, 1992. Project No.USA91L30
Lonoke, AR	SC 375 g/l	4	0.84		5	85.0 50.2 64.7	Bird and Coffey, 1992. Project No.USA91L30
Sibley, MN	SC 375 g/l	4	0.84		11	7.19 7.18 4.73	Bird and Coffey, 1992. Project No.USA91L30
Martin, NC	SC 375 g/l	4	0.84		5	134.4 61.4 114.5	Bird and Coffey, 1992. Project No.USA91L30
Clay, MN	SC 375 g/l	4	0.84		0	21.2 30.4 37.6	Bird and Coffey, 1992. Project No.USA91L30
Lancaster, PA	SC 375 g/l	4	0.94		1	19.1 23.8 19.2	Bird and Coffey, 1992. Project No.USA91L30
St Landry, LA	SC 375 g/l	4	0.84		7	161.7 151.9 162.7	Bird and Coffey, 1992. Project No.USA91L30
Washington, MS	SC 375 g/l	4	0.84		2	47.2 45.2 50.8	Bird and Coffey, 1992. Project No.USA91L30
Des Moines, IA	SC 375 g/l	4	0.84		7	30.0 34.9 16.5	Bird and Coffey, 1992. Project No.USA91L30
Des Moines, IA	SC 375 g/l	4	0.84		7	35.6 20.3 78.9	Bird and Coffey, 1992. Project No.USA91L30
Shelby, MO	SC 375 g/l	4	0.84		4	17.7 25.7 12.3	Bird and Coffey, 1992. Project No.USA91L30
Shelby, MO	SC 375 g/l	4	0.84		4	17.6 10.5 22.6	Bird and Coffey, 1992. Project No.USA91L30

Location	Application				Residues		Reference
	Form.	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Arkansas, AR	SC 375 g/l	4	0.84		0	35.6 25.0 41.8	Bird and Coffey, 1992. Project No.USA91L30
Hamilton, IN	SC 375 g/l	4	0.84		0	65.9 31.9 63.5	Bird and Coffey, 1992. Project No.USA91L30
Hamilton, IN	SC 375 g/l	4	0.84		0	145.2 54.0 50.2	Bird and Coffey, 1992. Project No.USA91L30
Henderson, IL	SC 375 g/l	4	0.84		7	40.7 36.8 49.7	Bird and Coffey, 1992. Project No.USA91L30
Henry, IL	SC 375 g/l	4	0.89		3	31.1 27.2 27.7	Bird and Coffey, 1992. Project No.USA91L30
Richmond, VA	SC 375 g/l	4	0.84		3	13.1 25.3 17.7	Bird and Coffey, 1992. Project No.USA91L30

Table 77. Residues in soya bean straw (foliar spray application).

Location	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.28-0.84	0.14-0.42	28		Do not exceed 3.4 kg/ha per season
East Baton Rouge USA, 1991	SC 375 g/l	4	0.84	--	28	0.82 0.30 0.10	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Lonoke, AR USA, 1991	SC 375 g/l	4	0.84	--	28	0.71 0.65 1.61	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Washington, MS USA, 1991	SC 375 g/l	4	0.84	--	27	0.41 2.36 0.27	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Sibley, MN USA, 1991	SC 375 g/l	4	0.84	--	28	0.04 0.09 <0.04	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Martin, NC USA, 1991	SC 375 g/l	4	0.84	--	28	0.13 0.09 0.07	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Clay, MN USA, 1991	SC 375 g/l	4	0.84		28	0.51 0.19 0.28	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Lancaster, PA USA, 1991	SC 375 g/l	4	0.94		27	0.08 <0.04 0.05	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
St Landry, LA USA, 1991	SC 375 g/l	4	0.84		28	<0.04 0.04 0.04	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Washington, MS USA, 1991	SC 375 g/l	4	0.84		29	0.32 1.97 0.23	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Des Moines, IA USA, 1991	SC 375 g/l	4	0.84		28	0.28 0.20 0.24	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Des Moines, IA USA, 1991	SC 375 g/l	4	0.84		28	1.00 0.30 0.54	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Shelby, MO USA, 1991	SC 375 g/l	4	0.84		28	0.21 0.23 0.20	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Shelby, MO USA, 1991	SC 375 g/l	4	0.84		28	0.22 0.28 0.33	Bird and Coffey, 1992 File No.41215 Project No.USA91L30

Location	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Arkansas, AR USA, 1991	SC 375 g/l	4	0.84		28	<0.04 0.06 <0.04	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Hamilton, IN USA, 1991	SC 375 g/l	4	0.84		28	0.06 0.06 <0.04	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Hamilton, IN USA, 1991	SC 375 g/l	4	0.84		31	0.09 0.05 0.13	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Henderson, IL USA, 1991	SC 375 g/l	4	0.84		28	0.33 0.69 0.18	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Henry, IL USA, 1991	SC 375 g/l	4	0.89		28	0.20 0.27 0.42	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
Richmond, VA USA, 1991	SC 375 g/l	4	0.84		28	2.68 1.95 3.43	Bird and Coffey, 1992 File No.41215 Project No.USA91L30
GAP, Australia	SC 375 g/l	--	0.19-0.28		21		
Patrick Estate, Lowood Australia, 1985	SC 375 g/l	1	0.75		35	1.1 0.28 0.67 0.47	Hunt and Langdon, 1985
Patrick Estate, Lowood Australia, 1985	SC 375 g/l	1	1.9		35	0.11 0.11 0.26 0.09	Hunt and Langdon, 1985

Fruiting vegetables

Supervised trials were conducted in Australia, the USA and Spain on tomatoes. Samples in Australia were analysed by GLC with FPD (LOQ 0.04 mg/kg) and in Spain by GC-MS (LOQ 0.04 mg/kg).

Table 78. Residues in tomatoes and cherry tomatoes (foliar spray application).

Crop, Location, Year	Application				Interval (days)	Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl		PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.524			1		
TOMATO Carpendale, Queensland Australia, 1985	SC 375 g/l	6	0.52	0.32	--	0 7 14 28 	0.18 0.73 0.14 0.16 0.33 0.14 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04	Anon., 1986.
TOMATO Carpendale, Queensland Australia, 1985	SC 375 g/l	6	1.0	0.62	--	0 7 14 28 	1.6 0.42 0.47 0.70 050 0.32 0.05 <0.04 <0.04 <0.04 <0.04 <0.04	Anon., 1986.

Crop, Location, Year	Application				Interval (days)	Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl		PHI, days	mg/kg	
TOMATO Ma Ma Creek, Queensland Australia, 1985	SC 375 g/l	6	0.52	0.03	--	0 7 14 28 	<0.04 <u>0.09</u> <0.04 <0.04 0.09 0.04 0.13 <0.04 <0.04 <0.04 <0.04 <0.04	Anon., 1986.
TOMATO Ma Ma Creek, Queensland Australia, 1985	SC 375 g/l	6	1.0	0.05	--	7 14 28 	0.41 0.15 <0.04 <0.04 <0.04 <0.04 0.07 <0.04 <0.04	Anon., 1986.
TOMATO Clayton, NC USA, 1981	Larvin 500	6	1.1		7	1 3 7 14 	0.49 0.35 0.33 0.18 0.23 0.08 0.14 0.05 0.20 0.05 0.05 0.06	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Wayside, MS USA, 1981	Larvin 500	6	1.1		7	1 3 7 14 	0.10 0.06 0.09 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Manteca, CA USA, 1981	Larvin 500	6	1.1		7	1 3 7 14 	2.0 2.0 1.1 2.2 1.4 1.4 0.92 1.3 0.89 1.5 2.2 1.8	Hunt *et al.*, 1983 File No.32116 Project 804R11

Crop, Location, Year	Application				Interval (days)	Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl		PHI, days	mg/kg	
TOMATO Newton, Iowa USA, 1981	Larvin 500	6	1.1		7	1 3 7 14 	0.49 0.35 0.33 0.18 0.23 0.08 0.14 0.05 0.20 0.05 0.05 0.06	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Mendota, CA USA, 1981	SC 375 g/l	6	1.1			1 4 7 	0.06 0.04 0.04 0.05 0.04 0.06 0.11 0.07 0.06 0.09 0.04	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO California USA, 1981	SC 375 g/l	6	1.			1 3 7 	0.34 0.63 0.46 0.25 0.24 0.32 0.35 0.53 0.44	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Indiana USA, 1981	SC 375 g/l	6	1.1			1 4 7 	0.28 0.26 0.47 <0.02 0.24 0.20 0.17 0.12 0.10	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Montgomery, Al USA, 1981	SC 375 g/l	6	1.1			1 4 7 	0.24 0.24 0.24 0.07 0.08 0.06 0.07 0.07 0.08	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Pomona, CA USA, 1981	SC 375 g/l	6	1.1			1 4 7 	0.32 0.31 0.37 0.16 0.13 0.21 0.20 0.03 0.62	Hunt *et al.*, 1983 File No.32116 Project 804R11

Crop, Location, Year	Application				Interval (days)	Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl		PHI, days	mg/kg	
TOMATO Wooster, CA USA, 1981	SC 375 g/l	6	1.1			1 4 7 	0.30 0.49 0.64 0.52 0.52 0.39 0.28 0.35 1.0	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO California USA, 1981	SC 375 g/l	6	1.1			2	1.2 0.82 1.0 1.0	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO USA, 1981	SC 375 g/l	6	1.1			1 4 7 	0.02 0.03 <0.02 0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO USA, 1981	SC 375 g/l	6	1.1			1 4 7 	0.07 0.24 0.08 0.14 0.08 0.03 0.05 0.05 0.05	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO California USA, 1981	SC 375 g/l	6	1.1			1	0.13	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Mendota, CA USA, 1981	WG 800 g/kg	6	1.1		--	1 4 7 	0.06 0.04 0.04 0.04 0.04 0.04 0.04 0.06 0.08 0.04 0.09 0.07	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO California USA, 1981	WG 800 g/kg	6	1.1		--	0 3 7 	0.43 0.39 0.55 0.30 0.17 0.31 0.31 0.42 0.36	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Indiana USA, 1981	WG 800 g/kg	6	1.1		--	1 4 7 	0.16 0.34 0.37 0.04 0.21 0.13 0.09 0.12 0.12	Hunt *et al.*, 1983 File No.32116 Project 804R11

Crop, Location, Year	Application				Interval (days)	Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl		PHI, days	mg/kg	
TOMATO Pomona, CA USA, 1981	WG 800 g/kg	6	1.1		--	1 4 7	1.0 0.47 0.19 0.04 0.58 0.07 0.25 0.29 0.20	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO California USA, 1981	WG 800 g/kg	6	1.1		--	2	1.4 0.77 1.3 1.2	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO Florida USA, 1981	WG 800 g/kg	6	1.1		--	1 4 7	0.09 0.11 0.19 0.18 0.13 0.05 0.09 0.08 0.08	Hunt *et al.*, 1983 File No.32116 Project 804R11
TOMATO North Rose, NY USA, 1996	SC 375 g/l	6	1.1		7	1	<0.04 0.04	Kowite, 1998a File No.45559; Study No.96L10369
TOMATO San Juan Bautista, CA USA, 1996	SC 375 g/l	6	1.1		7	1	1.70 1.96	Kowite, 1998a File No.45559; Study No.96L10369
TOMATO Madera, CA USA, 1996	SC 375 g/l	6	1.1		7	1	0.26 0.18	Kowite, 1998a File No.45559; Study No.96L10369
CHERRY TOMATO Hickman, CA USA, 1996	SC 375 g/l	6	1.1		7	1	1.04 0.86	Kowite, 1998a File No.45559; Study No.96L10369
CHERRY TOMATO San Juan Bautista, CA USA, 1996	SC 375 g/l	6	1.1		7	1	2.36 2.48	Kowite, 1998a File No.45559; Study No.96L10369
CHERRY TOMATO Madera, CA USA, 1996	SC 375 g/l	6	1.1		7	1	0.99 0.89	Kowite, 1998a File No.45559; Study No.96L10369
TOMATO Hickman, CA USA, 1996	SC 375 g/l	6	1.1		7	1	0.88 0.80	Kowite, 1998a File No.45559; Study No.96L10369
GAP, Spain	SC 375 g/l	--	0.94			7		
TOMATO Roquetas, Almeria Spain, 1996-97 GLASSHOUSE	SC 375 g/l	3	0.94	0.070	15-22	7 14	<u>0.23</u> 0.21 0.38 0.30	Maestracci, 1998c Study No. 96-645
TOMATO Roquetas, Almeria Spain, 1996-97 GLASSHOUSE	SC 375 g/l	3	0.94	0.060	15-22	7 14	<u>0.18</u> 0.18 0.31 0.29	Maestracci, 1998c Study No. 96-645

Crop, Location, Year	Application				Interval (days)	Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl		PHI, days	mg/kg	
TOMATO Alginet, Valencia Spain, 1996-97 GLASSHOUSE	SC 375 g/l	2	0.94	0.064	21	7 14	0.06 0.05 0.06 0.05	Maestracci, 1998c Study No. 96-645
TOMATO La Canãda, Ameria Spain, 1996-97 GLASSHOUSE	SC 375 g/l	2	0.95	0.066	14	7 14	0.23 0.33 0.22 0.44	Maestracci, 1998d Study No. 97-680
TOMATO Alginet, Valencia Spain, 1996-97 GLASSHOUSE	SC 375 g/l	2	0.94	0.045	14	7 14	0.04 0.05 <0.04 <0.04	Maestracci, 1998d Study No. 97-680
TOMATO Ameria Spain, 1992-1993 GLASSHOUSE	SC 375 g/l	3	0.75	0.03	12-22	0 7 14 21 28	0.20 0.16 0.16 0.13 0.26	Richard and Muller, 1993 Study No. 91-242
TOMATO Ameria Spain, 1992-1993 GLASSHOUSE	SC 375 g/l	3	1.1	0.04	12-22	0 7 14 21 28	<0.05 0.13 0.23 0.16 0.18	Richard and Muller, 1993 Study No. 91-242
TOMATO Alginet Spain, 1992-1993 GLASSHOUSE	SC 375 g/l	3	0.75	0.11	10-11	0 7 14 21 28	0.15 0.08 <0.05 0.16 0.15	Richard and Muller, 1993 Study No. 91-242

Sweet corn. Supervised trials were conducted in the USA and Australia with ground foliar application, and in the USA with seed treatment application.

GAP in the USA for foliar application specifies 0.56-0.84 kg ai/ha, applied up to 8.4 kg ai/ha per season and a PHI of 0 days. Kernels, cobs and cannery waste were analysed by GLC with FPD (sulfur mode, LOQ 0.04 mg/kg). There is no GAP in the USA for seed treatment.

GAP in Australia for foliar application requires 0.56-0.75 kg ai/ha and a PHI of 7 days. Cobs and stalk were analysed by GLC with sulfur FPD (LOQ 0.02 mg/kg).

Table 79. Residues in sweet corn (kernel + cob with husk removed; foliar spray application).

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.75		7		
Cowra, New South Wales, Australia, 1989	SC 375 g/l	2	0.52		18	<0.02	Keats, 1989d ak/aw/ak89005
Cowra, New South Wales, Australia, 1989	SC 375 g/l	2	1.05		18	<0.02	Keats, 1989d ak/aw/ak89005
GAP, USA	SC 375 g/l	--	0.84	0.40	0		Do not exceed 8.4 kg/ha per season
Lamberton, MN, USA, 1992	SC 375 g/l	10	0.84	0.45	0	<0.02	Lee, 1993 92-030; Project No.USA92L01 File No.44128. Retreatment interval 1 day.
Waterville, AR, USA, 1992	SC 375 g/l	10	0.84	0.82	0	0.07	Lee, 1993 92-098; Project No.USA92L01 File No.44128 Retreatment interval 1 day.

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Edcough, TX USA, 1977	WP 750 g/kg	8	1		1	0.02	Hunt, 1982, File No. 31094, Project No. 06570
Clayton, NC USA, 1978	WP 750 g/kg	16	1		1 3 7	<0.02 0.09 0.11	Hunt, 1982, File No. 31094, Project No. 06570
Edcough, TX USA, 1978	WP 750 g/kg	15	1		1 3 7	0.28 0.09 0.06	Hunt, 1982, File No. 31094, Project No. 06570
Newton, IA USA, 1981	WP 750 g/kg	10	0.84		0	<0.03 <0.03 <0.03	Hunt, 1982, File No. 31094, Project No. 06570
	SC 500 g/l	10	0.84		0 1 2	<0.03 <0.03 <0.03 <0.03 <0.03 <0.03 <0.03 <0.03 <0.03	
Clayton, NC USA, 1981	WP 750 g/kg	10	0.84		0	0.04 0.06 0.05	Hunt, 1982, File No. 31094, Project No. 06570
	SC 500 g/l	10	0.84		0 1 2	0.04 <0.04 0.13 0.06 0.07 0.08 0.07 0.08 0.06	
Sanford, FL USA, 1978	SC 500 g/l	10	0.84		1	0.19 0.82 0.39 0.29	Hunt, 1982, File No. 31094, Project No. 06570
Geneseo, IL USA, 1981	SC 500 g/l	10	0.84		0	<0.03 <0.03 <0.03	Hunt, 1982, File No. 31094, Project No. 06570
Salisbury, MD USA, 1981	SC 500 g/l	10	0.84		0	0.21 0.54 0.16	Hunt, 1982, File No. 31094, Project No. 06570
Hollandale, MN USA, 1981	SC 500 g/l	10	0.84		0	0.08 <0.03 0.06	Hunt, 1982, File No. 31094, Project No. 06570
Phelps, NY USA, 1981	SC 500 g/l	10	0.84		0	<0.03 <0.03 <0.03	Hunt, 1982, File No. 31094, Project No. 06570
Sanford, FL USA, 1981	SC 500 g/l	12	0.84		0 3 7	0.15 0.26 0.43 0.47 0..37 0.26 0.20 0.38 0.25	Hunt, 1982, File No. 31094, Project No. 06570
Donna, TX USA, 1981	SC 500 g/l	10	0.84		0	0.31 1.3 1.5	Hunt, 1982, File No. 31094, Project No. 06570
Kimberly, ID USA, 1981	SC 500 g/l	10	0.84		0	<0.03	Hunt, 1982, File No. 31094, Project No. 06570
Prosser, WA USA, 1981	SC 500 g/l	10	0.84		0	0.03 0.04 0.04	Hunt, 1982, File No. 31094, Project No. 06570

Location, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Manteca, CA USA, 1981	SC 500 g/l	10	0.84		0 1 2 	0.17 0.04 <u>0.22</u> 0.08 0.05 0.05 0.09 0.06 0.06	Hunt, 1982, File No. 31094, Project No. 06570

Table 80. Residues in sweet corn (kernel + cob with husk removed; simulated aerial application), USA, 1981.

Location	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.56-0.84	0.40	0		Do not exceed 8.4 kg/ha per season
Newton, IA	SC 500 g/l	10	0.84		0	<u><0.03</u> <0.03 <0.03	Hunt, 1982, File No. 31094, Project No. 06570
Clayton, NC	SC 500 g/l	10	0.84		0	<0.04 <u>0.09</u> <0.04	Hunt, 1982, File No. 31094, Project No. 06570
Manteca, CA	SC 500 g/l	10	0.84		0	0.03 <u>0.07</u> 0.03	

Table 81. Residues in sweet corn (kernel + cob with husk removed; seed treatment), USA, 1988.

Location	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Manteca, CA	SC 375 g/l	1	10	85	ND (<0.02) ND ND ND	Hunt, 1988i Project No.804R10 File No.40389
Manteca, CA	SC 375 g/l	1	10	81	ND ND ND ND	Project No.804R10 File No.40389
Newton, IA	SC 375 g/l	1	10	77	ND ND ND ND	Project No.804R10 File No.40389
Clayton, NC	SC 375 g/l	1	10	103	ND ND ND ND	Project No.804R10 File No.40389
Redfield, IA	SC 375 g/l + vitavax	1	10	81	ND ND ND ND	Project No.804R10 File No.40389
Manteca, CA	900 g/kg	1	20	76	ND ND ND ND	Project No.804R10 File No.40389
Newton, IA	900 g/kg	1	20	90	ND ND ND ND	Project No.804R10 File No.40389

Location	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Wayside, MS	900 g/kg	1	20	68	ND ND ND ND	Project No.804R10 File No.40389
Clayton, NC	900 g/kg	1	20	76	ND ND ND ND	Project No.804R10 File No.40389
Rochester, NY	900 g/kg	1	20	83	ND ND ND ND	Project No.804R10 File No.40389
Rochester, NY	900 g/kg	1	20	95	ND ND ND ND	Project No.804R10 File No.40389

Cereal grains

Barley and wheat. Supervised trials were conducted in the UK and Germany with granular bait applications. Grain and leaves were harvested and analysed by GLC (sulfur FPD, LOQs 0.05 and 0.04 mg/kg). Two other supervised trials in Brazil were with seed treatment applications.

Table 82. Residues in barley and wheat grain (granular bait application).

CROP Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, UK	RB 40 g/kg	1-3	0.2	--		
WINTER BARLEY Thirsk, North Yorkshire, UK, 1988	GB 40 g/kg	4	0.3	162	<0.04	Brockelsby *et al.*, 1989 Report No. 1295
WINTER BARLEY Chelmsford, Essex, UK, 1988	GB 40 g/kg	4	0.3	105	<0.04 <0.04	Brockelsby *et al.*, 1989 Report No. 1295
WINTER BARLEY Chapeltown, Derbyshire, UK, 1988	GB 40 g/kg	4	0.3	158	<0.04 <0.04	Brockelsby *et al.*, 1989 Report No. 1295
WINTER BARLEY West Hayes, Bedfordshire, UK, 1990	GB 40 g/kg	3	0.2	133	0.04 0.06 0.04	Brockelsby *et al.*, 1990a Report No. 1535
WINTER Eastwell, Leicestershire, UK, 1989-90	GB 40 g/kg	3	0.2	224	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. 1535
WINTER BARLEY Abberley, Worcestershire, UK, 1989-90	GB 40 g/kg	3	0.2	175	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. 1535
WHEAT Reepham, Lincolnshire, UK, 1989-90	GB 40 g/kg	3	0.2	245	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. 1535
WHEAT Abberley, Worcestershire UK, 1989-90	GB 40 g/kg	3	0.2	182	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. 1535
WHEAT West Hayes, Bedfordshire, UK 1990	GB 40g/kg	3	0.2	133	0.04 0.06 0.04	Brockelsby *et al.*, 1990a Report No. 1535
WHEAT Yeovil, Somerset K, 1987-88	GB 40 g/kg	4	0.3	165	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1989 Report No. 1295
WHEAT Northallerton, North Yorkshire, UK, 1987-88	GB 40 g/kg	3	0.4	179	<0.04	Brockelsby *et al.*, 1989 Report No. 1295
WHEAT Haywards Heath, Sussex, UK, 1987-88	GB 40 g/kg	4	0.3	123	<0.04 <0.04	Brockelsby *et al.*, 1989 Report No. 1295

CROP Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
WHEAT Salzhemmendorf Niedersachsen Germany, 1987-88	GB 40 g/kg	2	0.2	281	ND	Anon., 1992d BBA report No.05148
WHEAT Salzhemmendorf Niedersachsen Germany, 1987-88	GB 40 g/kg	2	0.2	101	ND	Anon., 1992d BBA report No.05149
WHEAT Schwaighofen Bayern, Germany, 1987-88	GB 40 g/kg	2	0.2	136	ND	Anon., 1992d BBA report No.03675
WINTER BARLEY Gerolfingen Germany, 1987-88	GB 40 g/kg	2	0.2	239	ND	Anon., 1992b BBA report No. 03725
WINTER BARLEY Gerolfingen Germany, 1987-88	GB 40 g/kg	2	0.2	93	ND	Anon., 1992b BBA report No. 05132

Table 83. Residues in wheat grain (seed treatment), Brazil, 1997-98.

Location	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Paulinia, Soa Paulo	SC 300 g/l	1	3	NR	< 0.2 <0.2 <0.2	Anon., 1998a Study No.CP-2557/98
Paulinia, Soa Paulo	SC 300 g/l	1	6	NR	< 0.2 <0.2 <0.2	Anon., 1998a Study No.CP-2557/98
Ponta Grossa	SC 300 g/l	1	3	NR	<0.2 <0.2 <0.2	Anon., 1998b Study No.001/98-PC
Ponta Grossa	SC 300 g/l	1	6	NR	<0.2 <0.2 <0.2	Anon., 1998b Study No.001/98-PC

Maize. Four supervised trials were conducted in Brazil with ground foliar and seed treatment applications, and in Australia one trial with foliar application only. Samples were analysed by GLC (sulfur FPD, LOQ 0.02 mg/kg) or HPLC (LOQ 0.1 mg/kg).

Table 84. Residues in maize grain (foliar application), Paulinia, Brazil, 1995.

Application			Residues		Reference
Formulation	No.	kg ai/ha	PHI, days	mg/kg	
WG 800g/l	--	0.1	30		
SC 375 g/l	1	0.18	30	≤0.1 <0.1	Anon., 1996, CP-2344/96, Study No. 049/95-PC
SC 375 g/l	1	0.35	30	≤0.1 <0.1	Anon., 1996, CP-2344/96, Study No. 049/95-PC
WDG 800 g/l	1	0.2	30	≤0.1 <0.1	Anon., 1996, CP-2344/96, Study No. 049/95-PC
WDG 800 g/l	1	0.4	30	≤0.1 <0.1	Anon., 1996, CP-2344/96, Study No. 049/95-PC
WG 800 g/l	1	0.2	30	≤0.1 <0.1	Anon., 1996, CP-2344/96, Study No. 049/95-PC
WG 800 g/l	1	0.4	30	≤0.1 <0.1	Anon., 1996, CP-2344/96, Study No. 049/95-PC

Table 85. Residues in maize grain (seed treatment)

Location, year	Application			Residues		Reference
	Formulation	No.	kg/tonne seeds	PHI, days	mg/kg	
GAP, Brazil	SC 375 g/l	1	7			
Emerald, Queensland, Australia, 1988	SC 375 g/l	1	7.5	120	<0.02 <0.02	Keats, 1989b, ak/am/ak89010
Londrina, Brazil, 1999-2000	SC 375 g/l	1	7.5	99	<u>≤0.10</u>	Anon., 2000
Londrina, Brazil, 1999-2000	SC 375 g/l	1	14	99	<u>≤0.10</u>	Anon., 2000
Paulinia, Brazil, 1999-2000	SC 375 g/l	1	7.5	90	<u>≤0.10</u>	Anon., 2000
Paulinia, Brazil, 1999-2000	SC 375 g/l	1	14	90	<u>≤0.10</u>	Anon., 2000

<u>Rice</u>. Supervised trials were conducted in Japan with ground foliar application. Grain was analysed by GLC (sulfur FPD, LOQ 0.25 mg/kg or 0.4 mg/kg, limit of detection 0.008 mg/kg). In four supervised trials in Brazil with seed treatment, grain was analysed by HPLC with an LOQ of 0.10 mg/kg.

Table 86. Residues in brown rice grain (foliar spray application), Japan, 1985.

Application			Residues		Reference
Formulation	No.	kg ai/ha	PHI, days	mg/kg	
DP 30 g/kg	3	0.9-1.2	30		
DP 30 g/kg	3	1.2	21 28 45	<0.25 (0.086) <u>≤0.25</u> (0.024) <0.008	Anon., 2001b Aventis CropScience Saku61p-2-55; Ibaraki Tokyo Kenbikyo Foundation LOQ 0.25 mg/kg
DP 30 g/kg	3	1.2	21 28 45	<0.25 (0.080) <u>≤0.25</u> (0.010) <0.008	Anon., 2001b Aventis CropScience Saku61p-2-55; Kochi Tokyo Kenbikyo Foundation LOQ 0.25 mg/kg
DP 30 g/kg	3	1.2	21 28 45	<0.4 (0.12) <u>≤0.4</u> (0.040) <0.008	Anon., 2001b Aventis CropScience Ibaraki Hokko Chemical Industry LOQ 0.4 mg/kg
DP 30 g/kg	3	1.2	21 28 45	<0.4 (0.10) <u>≤0.4</u> (0.041) <0.008	Anon., 2001b Aventis CropScience Saku61p-2-55; Kochi Hokko Chemical Industry LOQ 0.4 mg/kg

Table 87. Residues in rice grain (seed treatment), Brazil, 1999-2000.

Location	Application			Residues		Reference
	Formulation	No	kg/tonne seeds	PHI, days	mg/kg	
GAP, Brazil	SC 350 g/l	1	5.25	--		
Paulinia	SC 375 g/l	1	5.25	148	<u>≤0.10</u>	Anon., 2000c, No.2971/00
Paulinia	SC 375 g/l	1	10.5	148	<0.10	Anon., 2000c, No.2971/00
Rio Verde	SC 375 g/l	1	7.5	148	<0.10	Anon., 2000c, No.2972/00
Rio Verde	SC 375 g/l	1	14	148	<0.10	Anon., 2000c, No.2972/00

<u>Sorghum</u>. Supervised trials were conducted in the USA and Australia with ground foliar application, and in the USA also with seed treatment application. There is no GAP in the USA for foliar or seed treatment application and no GAP in Australia for foliar application.

Table 88. Residues in sorghum grain (foliar spray application).

Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Manteca, CA USA, 1982	SC 375 g/l	3	0.28	14 21 28	0.22 0.47 0.26 0.39 0.68 0.49 0.13 0.27 0.16	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.56	14 21 28	1.6 1.5 1.5 1.4 2.0 1.3 0.46 0.79 0.55	
	SC 375 g/l	3	0.84	14 21 28	1.2 1.6 1.7 1.5 1.5 1.9 0.66 0.64 0.69	
Newton, IA USA, 1982	SC 375 g/l	3	0.28	14 21 28	0.18 0.24 0.44 0.15 0.06 <0.04 <0.04 0.06 <0.04 <0.04 <0.04 <0.04	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.56	14 21 28	0.87 1.2 0.75 0.73 0.05 0.05 0.43 0.16 <0.04 <0.04 <0.04 <0.04	
	SC 375 g/l	3	0.84	14 21 28	1.4 0.94 1.2 0.66 0.12 0.06 0.10 0.17 <0.04 <0.04 <0.04 <0.04	

Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Wayside, MS USA, 1982	SC 375 g/l	3	0.28	14 21 28 	0.64 0.33 0.31 0.32 0.13 0.12 0.34 0.32 <0.04 <0.04 <0.04 0.20	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.56	14 21 28 	0.58 0.57 2.0 0.96 0.38 0.30 0.81 0.88 <0.04 0.10 <0.04 <0.04	
	SC 375 g/l	3	0.84	14 21 28 	1.9 2.0 2.4 1.3 1.8 0.47 0.60 1.2 0.10 0.79 0.60 0.49	
Clayton, NC USA, 1982	SC 375 g/l	3	0.28	14 21 28 	ND (<0.02) ND ND ND ND ND ND ND ND	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.56	14 21 28 	ND ND ND ND ND ND ND ND ND	
	SC 375 g/l	3	0.84	14 21 28 	ND ND ND ND ND ND ND ND ND	

Manteca, CA USA, 1983	SC 375 g/l	3	0.84	14	1.3 0.97 0.75	Hunt, 1988f Project No.804R10 File No.35252
Newton, IA USA, 1983	SC 375 g/l	3	0.84	13	4.5 5.7 6.6 6.1	Hunt, 1988f Project No.804R10 File No.35252
Manhattan, KS USA, 1983	SC 375 g/l	3	0.84	14	5.4 19 8.5	Hunt, 1988f Project No.804R10 File No.35252
Wayside, MS USA, 1983	SC 375 g/l	3	0.84	14	ND ND ND ND	Hunt, 1988f Project No.804R10 File No.35252
Clayton, NC USA, 1983	SC 375 g/l	3	0.84	14	0.86 0.68 0.69 1.4	Hunt, 1988f Project No.804R10 File No.35252
York, NE USA, 1983	SC 375 g/l	3	0.84	14	0.55 2.6 0.51	Hunt, 1988f Project No.804R10 File No.35252
Brookings, SD USA, 1983	SC 375 g/l	3	0.84	14	ND ND ND	Hunt, 1988f Project No.804R10 File No.35252
Burleson County, TX USA, 1983	SC 375 g/l	3	0.84	14	4.4 2.7 6.4	Hunt, 1988f Project No.804R10 File No.35252
Nobby, Darling Downs Queensland Australia, 1989	SC 375 g/l	1	0.49	215	<0.02 <0.02	Keats, 1989c, ak/am/ak89008
Emerald, Queensland Australia, 1989	SC 375 g/l	1	0.49	103	<0.02 <0.02 <0.02 <0.02	Keats, 1989c ak/am/ak89008

Table 89. Residues in sorghum grain (seed treatment), USA.

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Wayside, MS 1984	SC 375 g/l	1	10	91	ND ND ND ND	Hunt, 1988g Project No.804R10 File No.40387
Newton, IA 1985	900 g/kg	1	10	145	ND ND ND ND	Hunt, 1988g Project No.804R10 File No.40387
Wayside, MS 1985	900 g/kg	1	20	99	ND <0.02 <0.02 ND	Hunt, 1988g Project No.804R10 File No.40387
Clayton, NC 1985	900 g/kg	1	20	113	ND ND ND ND	Hunt, 1988g Project No.804R10 File No.40387
Frisco, TX 1985	900 g/kg	1	20	170	<0.04	Hunt, 1988g Project No.804R10 File No.40387
Newton, IA 1985	900 g/kg + vitavax	1	20	145	ND ND ND ND	Hunt, 1988g Project No.804R10 File No.40387
Wayside, MS 1985	900 g/kg + vitavax	1	20	99	ND <0.02 <0.02 ND	Hunt, 1988g Project No.804R10 File No.40387

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Clayton, NC 1985	900 g/kg + vitavax	1	20	113	ND ND ND ND	Hunt, 1988g Project No.804R10 File No.40387

Crops used as animal feed

Barley and wheat. Residues in barley and wheat plant parts used as feed are shown in Tables 90-93.

Table. 90 Residues in the whole plant (forage) of barley and wheat (granular bait application), Germany, 1987-88.

Crop, Location	Application			Part	Residues		Reference
	Formulation	No.	kg ai/ha		PHI, days	mg/kg	
GAP, UK	GB 40 g/kg	1-3	0.2		--		
WHEAT Salzhemmendorf Niedersachsen	GB 40 g/kg	2	0.2	Plant	49 161 194	ND (<0.02) ND ND	Anon., 1992d BBA report No.05148, 1992 LOQ 0.05 mg/kg
WHEAT Salzhemmendorf Niedersachsen	GB 40 g/kg	2	0.2	Plant	7 19 42	ND ND ND	Anon., 1992d BBA report No.05149, 1992
WHEAT Schwaighofen Bayern	GB 40 g/kg	2	0.2	Green Plant	7 38 76	ND ND ND	Anon., 1992d BBA report No.03675,1992
WINTER BARLEY Gerolfingen	GB 40 g/kg	2	0.2	Plant	6 143 193	ND (<0.02) ND ND	Anon., 1992b BBA report No. 03725, 1992 LOQ 0.05 mg/kg
WINTER BARLEY Gerolfingen	GB 40 g/kg	2	0.2	Plant	7 36	ND ND	Anon., 1992b BBA report No. 05132, 1992

Table 91. Residues in barley and wheat leaves (forage; granular bait application), UK.

CROP Country, year	Application			Part	Residues		Reference
	Formulation	No.	kg ai/ha		PHI, days	mg/kg	
GAP, UK	RB 40 g/kg	1-3	0.2		--		
WINTER BARLEY Trent, Dorset, 1988	GB 40 g/kg	4	0.3	Leaves	46	0.25	Brockelsby *et al.*, 1989 Report No. D.Ag.1295
WINTER BARLEY Thirsk, North Yorkshire, 1988	GB 40 g/kg	4	0.3	Leaves	0	<0.04	Brockelsby *et al.*, 1989 Report No. D.Ag.1295
WINTER BARLEY Chelmsford, Essex, 1988	GB 40 g/kg	4	0.3	Leaves	0	0.04	Brockelsby *et al.*, 1989 Report No. D.Ag.1295
WINTER BARLEY West Hayes, Bedfordshire, 1990	GB 40 g/kg	3	0.2	Leaves	42	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. D.Ag.1535
WINTER BARLEY Eastwell, Leicestershire, 1989-90	GB 40 g/kg	3	0.2	Leaves	126	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. D.Ag.1535
WHEAT Brentwood, Essex 1989-90	GB 40 g/kg	3	0.2	Leaves	84	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No.D.Ag.1535
WHEAT Reepham, Lincolnshire, 1989-90	GB 40 g/kg	3	0.2	Leaves	133	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No.D.Ag.1535
WHEAT Abberley, Worcestershire, 1989-90	GB 40 g/kg	3	0.2	Leaves	14	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No.D.Ag.1535

CROP Country, year	Application			Part	Residues		Reference
	Formulation	No.	kg ai/ha		PHI, days	mg/kg	
WHEAT Northallerton, North Yorkshire, 1987-88	GB 40 g/kg	3	0.4	Leaves	0	<0.04	Brockelsby *et al.*, 1989 Report No.D.Ag.1295
WHEAT Haywards Heath, Sussex, 1987-88	GB 40 g/kg	4	0.3	Leaves	0	0.21	Brockelsby *et al.*, 1989 Report No.D.Ag.1295
WHEAT West Midlands, Worcestershire, 1986	RB 40 g/kg	2	0.2	Leaves at 2 leaf stage	60	< 0.03 <0.03	Blundstone *et al.*, 1987 U.C.Project No.I60/03/11/86
WHEAT West Midlands, Worcestershire, 1986	RB 40 g/kg	2	0.4	Leaves at 2 leaf stage	60	ND ND	Blundstone *et al.*, 1987 U.C.Project No.I60/03/11/86
WHEAT West Midlands, Worcestershire, 1986	RB 40 g/kg	3	0.2	Leaves at 2 leaf stage	3	0.06 0.05	Blundstone *et al.*, 1987 U.C.Project No.I60/03/11/86
WHEAT West Midlands, Worcestershire, 1986	RB 40 g/kg	3	0.4	Leaves at 2 leaf stage	3	<0.03 ND	Blundstone *et al.*, 1987 U.C.Project No.I60/03/11/86

Table 92. Residues in barley and wheat straw (granular bait application).

CROP Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, UK	RB 40 g/kg	1-3	0.2	--		
WINTER BARLEY Trent, Dorset, UK, 1988	GB 40 g/kg	4	0.3	138	<0.04	Brockelsby *et al.*, 1989 Report No. D.Ag.1295
WINTER BARLEY Thirsk, North Yorkshire, UK, 1988	GB 40 g/kg	4	0.3	162	<0.04	Brockelsby *et al.*, 1989 Report No. D.Ag.1295
WINTER BARLEY Chelmsford, Essex, UK, 1988	GB 40 g/kg	4	0.3	105	<0.04 <0.04	Brockelsby *et al.*, 1989 Report No. D.Ag.1295
WINTER BARLEY Chapeltown, Derbyshire, UK, 1988	GB 40 g/kg	4	0.3	158	<0.04 <0.04	Brockelsby *et al.*, 1989 Report No. D.Ag.1295
WINTER BARLEY West Hayes, Bedfordshire, UK, 1990	GB 40 g/kg	3	0.2	133	0.24 0.16 0.13	Brockelsby *et al.*, 1990a Report No. D.Ag.1535
WINTER BARLEY Eastwell, Leicestershire, UK, 1989-90	GB 40 g/kg	3	0.2	224	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. D.Ag.1535
WINTER BARLEY Abberley, Worcestershire, UK, 1989-90	GB 40 g/kg	3	0.2	175	<0.04 <0.04 <0.04	Brockelsby *et al.*, 1990a Report No. D.Ag.1535
WHEAT Salzhemmendorf, Niedersachsen Germany 1987-88	GB 40 g/kg	2	0.2	281	ND (<0.2)	Anon., 1992d BBA report No.05148, 1992. LOQ 0.5 mg/kg
WHEAT Salzhemmendorf, Niedersachsen Germany 1987-88	GB 40 g/kg	2	0.2	101	ND	Anon., 1992d BBA report No.05149, 1992
WHEAT Schwaighofen, Bayern Germany, 1987-88	GB 40 g/kg	2	0.2	136	ND	Anon., 1992d BBA report No.03675, 1992
WINTER BARLEY Gerolfingen Germany, 1987-88	GB 40 g/kg	2	0.2	239	ND (<0.2)	Anon., 1992b BBA report No. 03725, 1992 LOQ 0.5 mg/kg
WINTER BARLEY Gerolfingen, Germany, 1987-88	GB 40 g/kg	2	0.2	93	ND	Anon., 1992b BBA report No. 05132, 1992

Table 93. Residues in the whole plant of barley (forage; foliar application).

CROP Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
WINTER BARLEY Colombiers France, 1986	SC 375 g/l	1	0.25	7 15 45	<0.02 <0.02 <0.02	Mestre, 1986 ET/FB/AB/67

Rice. Four supervised trials were conducted in Japan with foliar application (see Table 86). GAP in Japan consists of a rate of 0.9-1.2 kg ai/ha, applied up to 3 times, and a PHI of 30 days. Straw was analysed by GLC (sulfur FPD, LOQ 0.5 to 1.0 mg/kg).

Table 94. Residues in rice straw (foliar application), Japan, 1985.

Application			Residues		Reference
Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, Japan, DP 30 g/kg	3	0.9-1.2	30		
DP 30 g/kg	3	1.2	21 28 45	0.76 0.62 0.19	Anon., 2001b Aventis CropScience 08-18 ASaku61p-2-55; Ibaraki Tokyo Kenbikyo Foundation LOQ 0.5 mg/kg
DP 30 g/kg	3	1.2	21 28 45	1.4 0.40 0.25	Anon., 2001b Aventis CropScience Saku61p-2-55; Kochi Tokyo Kenbikyo Foundation LOQ 0.5 mg/kg
DP 30 g/kg	3	1.2	21 28 45	1.0 0.69 0.25	Anon., 2001b Aventis CropScience Ibaraki Hokko Chemical Industry LOQ 1.0 mg/kg
DP 30 g/kg	3	1.2	21 28 45	1.6 0.50 0.36	Anon., 2001b Aventis CropScience Saku61p-2-55; Kochi Hokko Chemical Industry LOQ 1.0 mg/kg

Sorghum. Residues in plant parts used as animal feed are shown in Tables 95-99.

Table 95. Residues in sorghum forage (foliar application), USA.

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Manteca, CA 1982	SC 375 g/l	1	280	8	8.8 6.8 8.1	Hunt, 1988f Project No.804R10 File No.35252
Manteca, CA 1982	SC 375 g/l	1	560	8	18 6.0 26	Hunt, 1988f Project No.804R10 File No.35252
Manteca, CA 1982	SC 375 g/l	1	841	8	23 23 21	Hunt, 1988f Project No.804R10 File No.35252
Newton, IA 1982	SC 375 g/l	3	280	7	0.22 0.27 0.16 0.18	Hunt, 1988f Project No.804R10 File No.35252
Newton, IA 1982	SC 375 g/l	3	560	7	0.55 0.39 0.51 0.45	Hunt, 1988f Project No.804R10 File No.35252
Newton, IA 1982	SC 375 g/l	3	841	7	1.8 1.3 1.2 1.6	Hunt, 1988f Project No.804R10 File No.35252

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Wayside, MS 1982	SC 375 g/l	2	280	7	0.25 5.0 0.39 0.16	Hunt, 1988f Project No.804R10 File No.35252
Wayside, MS 1982	SC 375 g/l	2	560	7	0.59 0.62 0.35 0.68	Hunt, 1988f Project No.804R10 File No.35252
Wayside, MS 1982	SC 375 g/l	2	841	7	1.5 1.4 2.0 5.6	Hunt, 1988f Project No.804R10 File No.35252
Clayton, NC 1982	SC 375 g/l	3	280	7	0.12 0.03 0.03	Hunt, 1988f Project No.804R10 File No.35252
Clayton, NC 1982	SC 375 g/l	3	560	7	0.04 0.05 0.04	Hunt, 1988f Project No.804R10 File No.35252
Clayton, NC 1982	SC 375 g/l	3	841	7	0.05 0.09 0.15	Hunt, 1988f Project No.804R10 File No.35252
Manteca,CA 1983	SC 375 g/l	3	841	7	8.6 5.2 6.3	Hunt, 1988f Project No.804R10 File No.35252
Newton, IA 1983	SC 375 g/l	3	841	7	0.98 0.91 1.9 1.3	Hunt, 1988f Project No.804R10 File No.35252
Manhattan, KS 1983	SC 375 g/l	3	841	7	12 28 24	Hunt, 1988f Project No.804R10 File No.35252
Wayside, MS 1983	SC 375 g/l	1	841	7	0.52 0.46 0.41 0.45	Hunt, 1988f Project No.804R10 File No.35252
Clayton, NC 1983	SC 375 g/l	3	841	7	14 20 13 12	Hunt, 1988f Project No.804R10 File No.35252
York, NE 1983	SC 375 g/l	3	841	7	4.8 2.8 5.6	Hunt, 1988f Project No.804R10 File No.35252
Brookings, SD 1983	SC 375 g/l	3	841	7	ND ND ND	Hunt, 1099f Project No.804R10 File No.35252
Burleson County, TX 1983	SC 375 g/l	3	841	7	9.3 9.7 13	Hunt, 1988f Project No.804R10 File No.35252

Table 96. Residues in sorghum forage (seed treatment), USA.

Country, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Wayside, MS 1984	SC 375 g/l	1	10	29	0.08 0.11 0.09 0.02	Hunt, 1988g Project No.804R10 File No.40387
Newton, IA 1985	900 g/kg	1	10	27	0.04 0.03 0.07 0.11	Hunt, 1988g Project No.804R10 File No.40387

Country, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Clayton, NC 1985	900 g/kg	1	20	29	ND ND ND 0.03	Hunt, 1988g Project No.804R10 File No.40387
Frisco, TX 1985	900 g/kg	1	20	21	<0.04 <0.04	Hunt, 1988g Project No.804R10 File No.40387
Newton, IA 1985	900 g/kg + vitavax	1	20	27	0.02 0.04 0.05 0.04	Hunt, 1988g Project No.804R10 File No.40387
Clayton, NC 1985	900 g/kg + vitavax	1	20	29	ND ND <0.02 0.02	Hunt, 1988g Project No.804R10 File No.40387

Table 97. Residues in sorghum stubble straw (foliar application), Australia, 1989.

Location	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Emerald, Queensland	SC 375 g/l	1	0.49	103	<0.02 <0.02 <0.02 <0.02	Keats, 1989c ak/am/ak89008

Table 98. Residues in sorghum stover (foliar application), USA.

Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Manteca, CA 1982	SC 375 g/l	3	0.280	14 21 28 	6.7 8.0 6.7 11 6.7 8.6 8.8 5.4 5.1	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.560	14 21 28 	13 19 12 16 17 12 10 9.8 9.4	
	SC 375 g/l	3	0.841	14 21 28 	22 30 24 28 38 27 18 25 29	

Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Newton, IA 1982	SC 375 g/l	3	0.280	14 21 28 	0.30 0.33 0.21 0.10 0.05 0.07 <0.04 0.18 <0.04 <0.04 <0.04 <0.04	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.560	14 21 28 	0.80 0.71 0.47 0.85 0.14 0.12 0.07 0.11 <0.04 <0.04 <0.04 <0.04	
	SC 375 g/l	3	0.841	14 21 28 	0.50 1.3 1.2 0.95 0.11 0.28 0.17 0.14 <0.04 <0.04 0.17 0.11	
Wayside, MS 1982	SC 375 g/l	3	0.280	14 21 28 	0.82 0.29 0.47 0.43 0.12 0.07 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.560	14 21 28 	0.50 0.93 0.51 0.57 0.12 0.07 0.05 0.11 <0.04 <0.04 <0.04 <0.04	

Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
	SC 375 g/l	3	0.841	14 21 28	1.1 1.0 0.84 1.3 0.64 0.47 0.61 0.45 0.30 0.30 0.37 0.31	
Clayton, NC 1982	SC 375 g/l	3	0.280	14 21 28	ND (<0.02) ND ND ND ND ND ND ND ND	Hunt, 1988f Project No.804R10 File No.35252
	SC 375 g/l	3	0.560	14 21 28	ND ND ND ND ND ND ND ND ND	
	SC 375 g/l	3	0.841	14 21 28	ND ND ND ND ND ND ND ND ND	
Manteca, CA 1983	SC 375 g/l	3	0.841	14	4.7 4.9 3.0	Hunt, 1988f Project No.804R10 File No.35252
Newton, IA 1983	SC 375 g/l	3	0.841	13	7.2 7.3 6.3 5.1	Hunt, 1988f Project No.804R10 File No.35252
Manhattan, KS 1983	SC 375 g/l	3	0.841	14	5.4 2.5 4.0	Hunt, 1988f Project No.804R10 File No.35252
Wayside, MS 1983	SC 375 g/l	3	0.841	14	<0.10 <0.10 <0.10 <0.10	Hunt, 1988f Project No.804R10 File No.35252
Clayton, NC 1983	SC 375 g/l	3	0.841	14	0.12 0.40 0.54 0.36	Hunt, 1988f Project No.804R10 File No.35252
York, NE 1983	SC 375 g/l	3	0.841	14	1.0 1.0 0.8	Hunt, 1988f Project No.804R10 File No.35252
Brookings, SD 1983	SC 375 g/l	3	0.841	14	0.11 0.11 <0.10	Hunt, 1988f Project No.804R10 File No.35252

Country, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Burleson County,TX 1983	SC 375 g/l	3	0.841	14	9.5 2.9 2.3	Hunt, 1988f Project No.804R10 File No.35252

Table 99. Residues in sorghum stover (seed treatment), USA.

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Wayside, MS 1984	SC 375 g/l	1	10	91	ND (<0.01) ND ND ND	Hunt, 1988g, Project No.804R10 File No.40387
Newton, IA 1985	900 g/kg	1	10	145	ND ND ND ND	Hunt, 1988g, Project No.804R10 File No.40387
Wayside, MS 1985	900 g/kg	1	20	99	0.07 0.02 <0.02 <0.02	Hunt, 1988g, Project No.804R10 File No.40387
Clayton, NC 1985	900 g/kg	1	20	114	ND ND 0.03 <0.02	Hunt, 1988g, Project No.804R10 File No.40387
Frisco, TX 1985	900 g/kg	1	20	170	<0.04	Hunt, 1988g, Project No.804R10 File No.40387
Newton, IA 1985	900 g/kg + vitavax	1	20	145	ND ND ND ND	Hunt, 1988g, Project No.804R10 File No.40387
Wayside, MS 1985	900 g/kg + vitavax	1	20	99	<0.02 <0.02 <0.02 0.23	Hunt, 1988g, Project No.804R10 File No.40387
Clayton, NC 1985	900 g/kg + vitavax	1	20	114	ND 0.02 ND ND	Hunt, 1988g, Project No.804R10 File No.40387

Sweet corn. Residues in stalks and forage are shown in Tables 100-102.

Table 100. Residues in sweet corn fodder (stalk; foliar application), Australia, 1989.

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.56-0.75	7		
Cowra, New South Wales	SC 375 g/l	2	0.525	20	0.02	Keats, 1989d ak/aw/ak89005
Cowra, New South Wales	SC 375 g/l	2	1.050	20	0.04	Keats, 1989d ak/aw/ak89005

Table 101. Residues in sweet corn forage (foliar application), USA, 1985.

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.84	21		Do not exceed 3.36 kg/ha per season
Santa Maria, CA	SC 375 g/l	4	0.84	7 14 21	22 ND 11	Hunt and Schwehr, 1987 Project No.804R10 File No.35293
Manteca, CA	SC 375 g/l	4	0.84	7 14 21	<0.05 <0.05 <0.05 5.8 9.9 5.4 18 13 11	Hunt and Schwehr, 1987 Project No.804R10 File No.35293
Sanford, FL	SC 375 g/l	4	0.84	7 14 21	0.96 1.2 1.1 ND 0.24 0.12 ND ND ND	Hunt and Schwehr, 1987 Project No.804R10 File No.35293
Geneseo, IL	SC 375 g/l	4	0.84	7 14 21	14 29 23 3.6 3.3 4.4 4.7 2.9 6.9	Hunt and Schwehr, 1987 Project No.804R10 File No.35293
Newton, IA	SC 375 g/l	4	0.84	7 14 21	1.3 0.78 2.2 1.0 2.1 2.4 1.1 0.51 0.37	Hunt and Schwehr, 1987 Project No.804R10 File No.35293
Haslett, MI	SC 375 g/l	4	0.84	7 14 21	2.9 4.4 7.6 <0.05 1.1 <0.05 <0.05 <0.05 <0.05	Hunt and Schwehr, 1987 Project No.804R10 File No.35293
Lamberton, MN	SC 375 g/l	4	0.84	7 14 21	0.18 <0.05 0.07 <0.05 <0.05 0.05 <0.05 0.06 <0.05	Hunt and Schwehr, 1987 Project No.804R10 File No.35293

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Wayside, MS	SC 375 g/l	4	0.84	7	13	Hunt and Schwehr, 1987
					20	Project No.804R10
					12	File No.35293
				14	0.45	
					0.32	
					0.28	
				21	0.21	
					2.3	
					0.19	
Bridgetown, NJ	SC 375 g/l	4	0.84	7	0.18	Hunt and Schwehr, 1987
					0.29	Project No.804R10
					0.16	File No.35293
				14	0.11	
					0.05	
					0.07	
				21	0.06	
					0.21	
					ND	
Phelps, NY	SC 375 g/l	4	0.84	7	0.26	Hunt and Schwehr, 1987
					0.32	Project No.804R10
					0.59	File No.35293
				14	0.09	
					0.26	
					0.42	
				21	0.06	
					0.11	
					0.16	
Clayton, NC	SC 375 g/l	4	0.84	7	0.69	Hunt and Schwehr, 1987
					0.90	Project No.804R10
					0.64	File No.35293
				14	0.54	
					0.62	
					1.1	
				21	0.54	
					0.24	
					0.56	
Prosser, WA	SC 375 g/l	4	0.84	7	7.3	Hunt and Schwehr, 1987
					8.3	Project No.804R10
					5.4	File No.35293
				14	1.0	
					5.2	
					0.87	
				21	5.1	
					5.2	
					2.9	

Table 102. Residues in sweet corn forage (seed treatment), USA, 1988.

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Manteca, CA	SC 375 g/l	1	10	85	ND	Hunt, 1988i
					(<0.02)	Project No.804R10
					ND	File No.40389
					ND	
					0.05	
Redfield, IA	SC 375 g/l	1	10	81	ND	Hunt, 1988i
					ND	Project No.804R10
					ND	File No.40389
					ND	

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Newton, IA	SC 375 g/l	1	10	13	0.44	Hunt, 1988i
					0.29	Project No.804R10
					0.34	File No.40389
					0.36	
				20	0.32	
					1.2	
					0.30	
					0.21	
				33	ND	
					ND	
					ND	
					ND	
				69	ND	
					ND	
					ND	
					ND	
				77	ND	
					ND	
					ND	
					0.05	
Redfield, IA	SC 375 g/l	1	10	69	ND	Hunt, 1988i
					ND	Project No.804R10
					ND	File No.40389
					ND	
Clayton, NC	SC 375 g/l + vitavax	1	10	81	ND	Hunt, 1988i
					ND	Project No.804R10
					ND	File No.40389
					ND	
Manteca, CA	900 g/kg	1	20	76	<0.05	Hunt, 1988i
					ND	Project No.804R10
					ND	File No.40389
					ND	
Newton, IA	900 g/kg	1	20	14	11	Hunt, 1988i
					9.0	Project No.804R10
					11	File No.40389
					9.2	
				21	2.9	
					3.5	
					2.6	
					1.2	
				35	0.07	
					<0.05	
					<0.05	
					<0.05	
				68	0.08	
					0.06	
					<0.05	
					ND	
				90	ND	
					ND	
					ND	
					ND	
Wayside, MS,	900 g/kg	1	20	68	0.27	Hunt, 1988i
					0.45	Project No.804R10
					0.25	File No.40389
					0.34	
Clayton, NC	900 g/kg	1	20	107	ND	Hunt, 1988i
					ND	Project No.804R10
					ND	File No.40389
					ND	
Rochester, NY	900 g/kg	1	20	83	ND	Hunt, 1988i
					ND	Project No.804R10
					ND	File No.40389
					ND	

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Rochester, NY,	900 g/kg	1	20	95	ND ND ND ND	Hunt, 1988i Project No.804R10 File No.40389

Oilseed

Cotton. Supervised trials were conducted in Brazil, Australia, USA, Greece, Sudan and France with ground foliar application, and in the USA also some with aerial foliar application and others with seed treatment (no GAP). Grain, leaves, staple cotton and forage from the US trials were analysed by GLC (sulfur FPD, LOQ 0.04 mg/kg) and by CG-MS (limit of detection (LOD) 0.04 mg/kg). Cotton seeds from the Australian trials were analysed by GLC (sulfur FPD), and from the Greek trials by CG-MS (LOD 0.04 mg/kg and LOQ 0.10 mg/kg).

Table 103. Residues in cotton seed with linter (foliar application), Brazil, 1999-2000.

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Maracaju	WP 800 g/kg	1	0.24	7	<0.1	Anon., 2000 Study No.2988/00
Maracaju	WP 800 g/kg	1	0.48	7	<0.1	Anon., 2000 Study No.2988/00
Uberlândia,	WP 800 g/kg	1	0.24	7	<0.1	Anon., 2000 Study No.2988/00
Uberlândia	WP 800 g/kg	1	0.48	7	<0.1	Anon., 2000 Study No.2988/00

Table 104. Residues in cotton seed (foliar application).

Country, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
GAP, Australia	SC 375 g/l	--	0.75-0.84		21		
Wee Waa, North West New South Wales Australia, 1982	SC 375 g/l	6	0.84		0 7 14 21	0.30 0.15 0.08 0.05	Hunt and Langdon, 1983 Report No.1452V
Wee Waa, North West New South Wales Australia, 1982	SC 375 g/l	6	1.7		0 7 14 21	0.88 0.28 0.59 0.09	Hunt and Langdon, 1983 Report No.1452V
GAP, USA	SC 375 g/l	--	0.14-1.0		28		
El Centro, CA USA, 1988	SC 375 g/l	2	1.009		46	ND (<0.02) ND ND	Hunt, 1989c Project No.804R10 File No.40512
El Centro, CA USA, 1988	SC 375 g/l	2	1.009		46	ND ND ND	Hunt, 1989c Project No.804R10 File No.40512
Litchfield Park, AZ USA, 1988	SC 375 g/l	2	0.673		44	ND 0.04 <0.04	Hunt, 1989c Project No.804R10 File No.40512
Litchfield Park, AZ USA, 1988	SC 375 g/l	2	0.673		44	<0.04 <0.04 <0.04	Hunt, 1989c Project No.804R10 File No.40512
Fresno, CA USA, 1988	SC 375 g/l	2	1.009		33	0.10 0.06 0.04	Hunt, 1989c Project No.804R10 File No.40512
Poplar, CA USA, 1988	SC 375 g/l	2	1.009		45	<0.04 <0.04 <0.04	Hunt, 1989c Project No.804R10 File No.40512

Country, year	Application				Residues		Reference
	Formulation	No.	kg ai/ha	kg ai/hl	PHI, days	mg/kg	
Poplar, CA USA, 1988	SC 375 g/l	2	1.009		45	0.04 <0.04 <0.04	Hunt, 1989c Project No.804R10 File No.40512
El Campo, TX USA, 1998-99	SC 375 g/l	6	5.045		28	0.22	Lee, 1991d 90-047;, File No.40969 Study No.USA90L82
Caddo, OK USA, 1991	SC 375 g/l	6	1.022		28	<u>≤0.04</u> <0.04 <0.04	Lee, 1992b 91-005, Study No.USA91L82 File No.41198
Uvalde, TX USA, 1991	SC 375 g/l	6	1.026		28	<u>≤0.04</u> <0.04 <0.04	Lee, 1992b 91-007, Study No.USA91L82 File No.41198
Rapids, LA USA, 1991	SC 375 g/l	6	0.994		28	<u>≤0.04</u> <0.04 <0.04	Lee, 1992b 91-026, Study No.USA91L82 File No.41198
Lonoke, AR USA, 1991	SC 375 g/l	6	1.009		28	<u>≤0.04</u> <0.04 <0.04	Lee, 1992b 91-039, Study No.USA91L82 File No.41198
Hidalgo, TX USA, 1991	SC 375 g/l	6	1.007		28	<u>≤0.04</u> <0.04 <0.04	Lee, 1992b 91-071, Study No.USA91L82 File No.41198
Mitchell, GA USA, 1991	SC 375 g/l	6	1.035		28	0.08 0.07 <u>0.10</u>	Lee, 1992b 91-102, Study No.USA91L82 File No.41198
Washington, MS USA, 1991	SC 375 g/l	6	1.009		28	<u>≤0.04</u> <0.04 <0.04	Lee, 1992b 91-250, Study No.USA91L82 File No.41198
GAP, Greece	WG 800 g/kg	2-3	0.56-0.8		28		
Arma Viotas Greece, 1998	WG 800 g/kg	3	0.805		21 28	<0.04 <0.04 <0.04 <u>≤0.04</u>	Jendrzejczak and Yslan, 2000 99657, Study No.99-657
Thiva Viotia Greece, 1994	WG 800 g/kg	2	0.80	0.1	22	<u>≤0.05</u>	Richard and Muller, 1995c Study 94-692
Thiva Viotia Greece, 1994	WG 800 g/kg	1	0.80	0.1	42	<0.05	Richard and Muller, 1995c Study 94-692
GAP: Sudan (Egypt)	SC 375 g/l		0.89		28		
Arc Wad Me Sudan, 1998-99	WG 800 g/kg	3	0.571		61	0.59 0.33 0.23 <0.08	Lusson and Muller, 1989 b AG/CRLD/AN 8916381
GAP, Spain	SC 375 g/l		0.72		21		
Torre de la Reina, Seville Spain, 1993	SC 375 g/l	6	0.75		67	<0.05 <0.05	Richard and Muller, 1994c Study 93-625
Spain, 2000	WG 800 g/kg	1	0.24		7	<0.1	Anon., 2000d ESALQ/USP
Spain, 2000	WG 800 g/kg	1	0.48		7	<0.1	Anon., 2000e ESALQ/USP

Table 105. Residues in cotton seed (aerial application), USA, 1991.

Location	Application			Residues		Reference
	Form.	No.	kg ai/ha	PHI, days	mg/kg	
US GAP	SC 375 g/l	--	0.14-1.0	28		
Caddo, OK	SC 375 g/l	6	1.0	28	<0.04 <0.04 <0.04	Lee, 1992b 91-006, Study No.USA91L82 File No.41198
Uvalde, TX	SC 375 g/l	6	1.0	28	<0.04 <0.04 <0.04	Lee, 1992b 91-008, Study No.USA91L82 File No.41198
Rapids, LA	SC 375 g/l	6	1.0	28	<0.04 <0.04 <0.04	Lee, 1992b 91-027, Study No.USA91L82 File No.41198
Lonoke, AR	SC 375 g/l	6	1.0	28	0.05 0.04 0.10	Lee, 1992b 91-040, Study No.USA91L82 File No.41198
Hidalgo, TX	SC 375 g/l	6	1.0	28	<0.04 <0.04 0.09	Lee, 1992b 91-072, Study No.USA91L82 File No.41198
Mitchell, GA	SC 375 g/l	6	1.0	28	<0.04 <0.04 <0.04	Lee, 1992b 91-103, Study No.USA91L82 File No.41198
Washington, MS	SC 375 g/l	6	1.0	28	<0.04 <0.04 <0.04	Lee, 1992b 91-251, Study No.USA91L82 File No.41198

Table 106. Residues in cotton seed (seed treatment), USA.

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Manteca, CA 1984	WG 800g/kg	1	5	144	ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386
Wayside, MS 1984	WG 800g/kg	1	5	137	ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386
Clayton, NC 1984	WG 800g/kg	1	5	101	ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386
Manteca, CA 1985	900 g/kg	1	20	161	ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386
Wayside, MS 1985	900 g/kg	1	20	151	ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386
Clayton, NC 1985	900 g/kg	1	20	168	ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386
Clayton, NC 1985	900 g/kg	1	20	189	ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386

Table 107. Residues in cotton leaves (foliar application), Sudan, 1998-99.

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
Arc Wad Medani	WG 800 g/kg	3	0.571	61	42 61 81 0.26	Lusson and Muller, 1989b AG/CRLD/AN 8916381

Table 108. Residues in cotton forage (foliar application), USA, 1991.

Location	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.14-1.0	28		
Caddo, OK	SC 375 g/l	6	1.022	0	25.4 30.7 24.5	Lee, 1992b 91-005, Study No.USA91L82 File No.41198
Uvalde, TX	SC 375 g/l	6	1.026	0	47.9 53.9 97.5	Lee, 1992b 91-007, Study No.USA91L82 File No.41198
Rapids, LA	SC 375 g/l	6	0.994	0	47.1 32.5 46.6	Lee, 1992b 91-026, Study No.USA91L82 File No.41198
Lonoke, AR	SC 375 g/l	6	1.009	0	57.6 37.5 43.4	Lee, 1992b 91-039, Study No.USA91L82 File No.41198
Hidalgo, TX	SC 375 g/l	6	1.007	0	172.2 168.7 193.6	Lee, 1992b 91-071, Study No.USA91L82 File No.41198
Mitchell, GA	SC 375 g/l	6	1.035	0	98.2 27.1 65.1	Lee, 1992b 91-102, Study No.USA91L82 File No.41198
Washington, MS	SC 375 g/l	6	1.009	0	28.4 32.1 30.6	Lee, 1992b 91-250, Study No.USA91L82 File No.41198

Table 109. Residues in cotton forage (aerial application), USA, 1991.

Location	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, USA	SC 375 g/l	--	0.14-1.0	28		
Caddo, OK	SC 375 g/l		1.000	0	27.2 31.9 14.7	Lee, 1992b 91-006, Study No.USA91L82 File No.41198
Uvalde, TX	SC 375 g/l		1.009	0	26.2 22.3 21.7	Lee, 1992b 91-008, Study No.USA91L82 File No.41198
Rapids, LA	SC 375 g/l		1.043	0	126.5 86.2 73.1	Lee, 1992b 91-027, Study No.USA91L82 File No.41198
Lonoke, AR	SC 375 g/l		1.009	0	33.0 33.8 34.1	Lee, 1992b 91-040, Study No.USA91L82 File No.41198

Hidalgo, TX	SC 375 g/l		1.007	0	91.1 99.1 106.8	Lee, 1992b 91-072 Study No.USA91L82 File No.41198
Mitchell, GA	SC 375 g/l		1.009	0	23.2 28.8 23.8	Lee, 1992b 91-103, Study No.USA91L82 File No.41198
Washington, MS	SC 375 g/l		1.009	0	116.5 93.3 81.6	Lee, 1992b, 91-251, Study No.USA91L82 File No.41198

Table 110. Residues in cotton forage (seed treatment), USA.

Location, year	Application			Residues		Reference
	Formulation	No.	kg/ton, seeds	PHI, days	mg/kg	
Clayton, NC 1984	SC 375 g/l	1	5	17 24 38 70 101 	0.21 0.28 0.27 0.29 0.25 0.46 0.72 0.60 ND (<0.02) ND ND ND ND ND ND ND ND ND ND ND	Hunt, 1988h Project No.804R10 File No.40386
Wayside, MS 1985	900 g/kg	1	20	19 26 40 75 103 	3.2 3.1 3.4 6.4 1.0 0.98 0.5 0.93 ND ND ND ND ND ND ND ND <0.04 <0.04 <0.04 <0.04	Hunt, 1988h Project No.804R10 File No.40386

Oilseed rape. Supervised trials were conducted in the UK and Germany with granular bait application. GAP in the UK and Germany specifies a rate of 0.2 kg ai/ha, applied up to 3 times. Seed, forage and straw were analysed by GLC with sulfur FPD (LOQ 0.04 mg/kg seed and forage in the UK; 0.05 mg/kg forage, 0.2 mg/kg straw, 0.1 mg/kg seed in Germany).

Table 111. Residues in rape seed (granular bait application).

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, UK	RB 40 g/kg	1-3	0.2	--		
Melton Mowbray Leicestershire UK, 1987-88	GB 40 g/kg	4	0.3	154	<0.04 <0.04	Brockelsby *et al.*, 1990b Report No.D.Ag.1439
Ongar; Essex UK, 1987-88	GB 40 g/kg	4	0.3	98	<0.04 <0.04	Brockelsby *et al.*, 1990b Report No.D.Ag.1439
Chelmsford; Essex UK, 1987-88	GB 40 g/kg	4	0.3	105	0.04 <0.04	Brockelsby *et al.*, 1990b Report No.D.Ag.1439
Abberley Worcestershire UK, 1989-90	GB 40 g/kg	1	0.2	322	≤0.04 <0.04 <0.04	Brockelsby *et al.*, 1990c Report No.D.Ag.1562
Stoney Stanton Leicestershire UK, 1989-90	GB 40 g/kg	1	0.2	322	0.05 <0.04 <0.04	Brockelsby *et al.*, 1990c Report No.D.Ag.1562
Dry Doddington Lincolnshire UK, 1989-90	GB 40 g/kg	1	0.2	280	≤0.04 <0.04 <0.04	Brockelsby *et al.*, 1990c Report No.D.Ag.1562
GAP, Germany	RB 40 g/kg	1-3	0.2			
Winseldorf Schleswig-Holstein Germany, 1988-89	GB 40 g/kg	2	0.2	259	ND (<0.05)	Anon., 1992c 2214 ; BBA report No. 05128
Winseldorf Schleswig-Holstein Germany, 1988-89	GB 40 g/kg	2	0.2	125	ND	Anon., 1992c 2214 ; BBA report No. 05051
Mönchneversdorf Schleswig-Holstein Germany, 1987-88	GB 40 g/kg	2	0.2	117	ND	Anon., 1992c 2431; BBA report No. 05107
Mönchneversdorf Schleswig-Holstein Germany, 1987-88	GB 40 g/kg	2	0.2	276	ND	Anon., 1992c 2431; BBA report No. 05071
Mohnesee Theiningsen Germany, 1987-88	GB 40 g/kg	2	0.2	117	ND	Anon., 1992c 4773 ; BBA report No. 05103
Mohnesee Theiningsen Germany, 1987-88	GB 40 g/kg	2	0.2	262	ND	Anon., 1992c 4773 ; BBA report No. 05076
Lentersheim,Bayern Germany, 1987-88	GB 40 g/kg	2	0.2	239	ND	Anon., 1992c 8821; BBA report No. 03724
Lentersheim,Bayern Germany, 1987-88	GB 40 g/kg	2	0.2	93	ND	Anon., 1992c 8821; BBA report No. 05133

Table 112. Residues in oilseed rape forage (granular bait application).

Location	Application			Residues		Reference
	Form.	No.	kg ai/ha	PHI, days	mg/kg	
GAP, UK	RB 40 g/kg	1-3	0.2			
Melton Mowbray Leicestershire, UK, 1987-88	GB 40 g/kg	4	0.3	56	≤0.04	Brockelsby *et al.*, 1990b Report No.D.Ag.1439
Ongar; Essex, UK, 1987-88	GB 40 g/kg	4	0.3	0	≤0.04	Brockelsby *et al.*, 1990b Report No.D.Ag.1439
Chelmsford; Essex, UK, 1987-88	GB 40 g/kg	4	0.3	0	≤0.04	Brockelsby *et al.*, 1990b Report No.D.Ag.1439

Location	Application			Residues		Reference
	Form.	No.	kg ai/ha	PHI, days	mg/kg	
GAP, Germany	RB 40 g/kg	1-3	0.2			
Winseldorf Schleswig-Holstein Germany, 1988-89	GB 40 g/kg	2	0.2	07 42 142 168	ND (<0.02) ND ND ND	Anon., 1992c 2214 ; BBA report No. 05128
Winseldorf Schleswig-Holstein Germany, 1988-89	GB 40 g/kg	2	0.2	7 20 45	ND ND ND	Anon., 1992c 2214 ; BBA report No. 05051
Mönchneversdorf Schleswig-Holstein Germany, 1987-88	GB 40 g/kg	2	0.2	06 15 37	ND ND ND	Anon., 1992c 2431; BBA report No. 05107
Mönchneversdorf Schleswig-Holstein Germany, 1987-88	GB 40 g/kg	2	0.2	6 26 156 176	ND ND ND ND	Anon., 1992c 2431; BBA report No. 05071
Mohnesee Theiningsen Germany, 1987-88	GB 40 g/kg	2	0.2	07 27	ND ND	Anon., 1992c 4773 ; BBA report No. 05103
Mohnesee Theiningsen Germany, 1987-88	GB 40 g/kg	2	0.2	7 136 157	ND ND ND	Anon., 1992c 4773 BBA report No. 05076
Lentersheim, Bayern Germany, 1987-88	GB 40 g/kg	2	0.2	14 151 161	ND ND ND	Anon., 1992c 8821; BBA report No. 03724
Lentersheim, Bayern Germany, 1987-88	GB 40 g/kg	2	0.2	7 36	ND ND	Anon., 1992c 8821; BBA report No. 05133

Table 113. Residues in oilseed rape straw (granular bait application), Germany.

Location, year	Application			Residues		Reference
	Formulation	No.	kg ai/ha	PHI, days	mg/kg	
GAP, Germany	RB 40 g/kg	1-3	0.2			
Winseldorf Schleswig-Holstein, 1988-89	GB 40 g/kg	2	0.2	259	ND (<0.1)	Anon., 1992c 2214 ; BBA report No. 05128
Winseldorf Schleswig-Holstein, 1988-89	GB 40 g/kg	2	0.2	125	ND	Anon., 1992c 2214 ; BBA report No. 05051
Mönchneversdorf Schleswig-Holstein, 1987-88	GB 40 g/kg	2	0.2	117	ND	Anon., 1992c 2431; BBA report No. 05107
Mönchneversdorf Schleswig-Holstein, 1987-88	GB 40 g/kg	2	0.2	276	ND	Anon., 1992c 2431; BBA report No. 05071
Mohnesee Theiningsen, 1987-88	GB 40 g/kg	2	0.2	117	ND	Anon., 1992c 4773 ; BBA report No. 05103
Mohnesee Theiningsen, 1987-88	GB 40 g/kg	2	0.2	262	ND	Anon., 1992c 4773 ; BBA report No. 05076
Lentersheim, Bayern, 1987-88	GB 40 g/kg	2	0.2	239	ND	Anon., 1992c 8821; BBA report No. 03724
Lentersheim, Bayern, 1987-88	GB 40 g/kg	2	0.2	93	ND	Anon., 1992c 8821; BBA report No. 05133

Animal feeding studies

In a cattle feeding study (Davis and Wilkes, 1994) eight lactating dairy cattle were randomly assigned to one of three groups. Group I was the control group and contained 2 animals. Groups II and III each contained 3 cows and were administered thiodicarb at dose levels equivalent to 350 ppm and 1050 ppm in the diet respectively by bolus for a period of 28 days. The 1050 ppm cows were dosed once a day for 12 days, and twice a day at half the quantity per dose for the remainder of the study. The dosing was changed to twice daily when cholinesterase inhibition was observed.

The cows were milked twice daily throughout the study except on day 28 when the high-dose cows were only milked once. Samples were immediately frozen. Milk samples for a given study day were defined as those taken at the evening milking of that day and next morning's milking. They were composited by mixing equal volumes from the two milkings. All samples were stored at a nominal temperature of -20°C.

Animals were slaughtered within 3 hours after the final dose and samples of muscle, fat, liver and kidney were collected and stored frozen for 0.5-2 months before extraction and clean-up. The storage stability study reported above indicates adequate stability over this period in all substrates except liver.

Samples were analysed by the HPLC method, with coagulation as a clean-up step. No quantifiable thiodicarb (<0.1 mg/kg) and no methomyl (<0.1 mg/kg) were found in any milk or tissue sample from the 1050 mg/kg dosing, nor in several milk samples analysed from the 350 ppm feeding level. At least one milk sample from the 1050 ppm feeding level on days 1, 7 and 25 showed unquantifiable residues, estimated at 0.02-0.03 mg/kg. A fat sample showed a residue estimated at 0.04 mg/kg, muscle 0.03 mg/kg, kidney 0.01 mg/kg, and liver 0.06 mg/kg, all from the 1050 ppm feeding level. The corresponding liver control sample yielded 0.09 mg/kg.

A poultry feeding study was not reported.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Processing studies were conducted on soya beans, tomatoes, apples, sweet corn and cotton in the USA and grapes in France and Spain, as shown in the following Tables. The studies were conducted according to standard commercial practices in the respective countries and in all cases except one tomato study the residues were field-incurred. Processing factors are shown in Tables 114-119.

Table 114. Processing factors – soya beans.

Sample	Average residues (mg/kg)	Processing factors	Reference/Comments
Whole seed	0.04	1	Lee, 1991c Project USA90L01 File 41003 Illinois, USA Processing and analyses within 6 months of harvest. GLC method validated at 0.04 mg/kg for methomyl and thiodicarb in each sample.
Hulls	0.16	3.6	
Meal	<0.04	<1	
Refined oil	<0.04	<1	
Crude oil	<0.04	<1	
Soapstock	<0.04	<1	
Grain dust	1.24	29	

Table 115. Processing factors – tomatoes.

Processed fraction	Average residues (mg/kg)	Processing factors	Reference/Comment
Whole tomato	5.6	1	Hunt, 1986b Study No.804R11. File No.35032 Tomatoes sprayed in the laboratory with thiodicarb solution, allowed to dry for 24 h, then washed.
Whole tomato washed	0.62	0.11	
Wet pomace	1.5	0.27	

Dry pomace	3.9	0.70	
Juice	0.26	0.05	
Puree	<0.04	<0.01	
Paste	0.07	0.01	
Whole tomato	1.4		Kowite, 1998b Study No.96L10370. File No.45563 California, USA Tomatoes stored for 2 days at room temperature before processing. Maximum frozen storage 263 days.
Purée	<0.04	<0.03	
Paste	<0.04	<0.03	

Table 116. Processing factors – apples.

Sample	Residues (mg/kg) [1]	Processing factors	Reference/location
Apple	5.02, 7.2, 4.02 (5.4)	1	Avakian, 1991 Project No.S78AP01[2] North Carolina, USA
Fresh juice	0.67, 0.49, 0.59 (0.58)	0.11	
Canned juice	0.096, 0.055, 0.072 (0.074)	0.014	
Wet pomace	2.4, 1.4, 2.2 (2.0)	0.37	
Unwashed fruit	4.6	1	Hunt, 1989e Project No.804R10 File No.40657 Pennsylvania, USA
Washed fruit	1.4	0.30	
Juice	<0.02	<0.01	
Wet pomace	1.1	0.24	

[1] Replicate experiments. Average in parenthesis.
[2] Concurrent method recovery data (GLC) from 0.5 to 15 mg/kg fortifications. Apples stored for one week at 8-13°C before processing and one month at -20°C before analysis.

Table 117. Residues in grapes and wine.

Country, year	Application			Residues (mg/kg)				Reference
	Form.	No	kg ai/ha	PHI, days	Grapes	Wine	Processing factor	
France, 1988	SC 375 g/l	2	0.375	5	0.66	<0.08	0.12	Lusson and Muller, 1989a Study 8916392
France, 1988	SC 375 g/l	2	0.375	35	0.22	<0.08	0.36	
France, 1988	SC 375 g/l	2	0.375	54	<0.08	<0.08	-	
France, 1992	SC 375 g/l	3	0.563	49	0.16	<0.05	0.31	Richard and Muller, 1994a, Study 92-147
France, 1992	SC 375 g/l	3	0.563	45	0.11	<0.05	0.45	
France, 1995	SC 300 g/l	2	0.306	49	0.096	< 0.025 mg/l	0.31	Maestracci, 1997b Study 95-540
France, 1995	SC 300 g/l	2	0.30	31	0.32	0.15 mg/l	0.47	Maestracci, 1997c Study 95-539
Spain, 1993	SC 375 g/l	2	0.563	90	1.4	<0.05	0.036	Richard and Muller 1994b, Study 93-624; 9415899
Average							0.3	-

Table 118. Processing factors – sweet corn. [1]

Location	Kernels + Cob	Kernels	Cannery waste	Processing factor for waste	Reference
Minnesota, USA, 1992	<0.02	0.03	1.28	>64	Lee, 1993 Project No.USA92L01 File No.44128
Wisconsin, USA, 1992	0.07	0.06	5.46	78	

[1] Deviations from commercial practice: corn husked by hand; husked corn not washed.

Table 119. Processing factors – cotton.

Processed fraction	PHI (days)	Average residues (mg/kg)	Processing factors	Reference/Comment
Cotton seed (delinted)	28	0.184, 0.215 (0.20)	1	Lee, 1991d Study USA90L82. Texas. Seed held frozen for 3 months before processing. GLC method 90321 validated at 0.04 mg/kg. Processed fractions held frozen for up to 60 days before analysis.
Hulls	28	0.22	1.1	
Crude oil	28	<0.04	<0.2	
Refined oil	28	<0.04	<0.2	
Soapstock	28	0.06	0.31	
Meal	28	0.05	0.26	

Residues in the edible portion of food commodities

Table 120 Residues in lettuce (foliar application), USA.

Location. year	Application			Residues (mg/kg)			Reference
	Formulation	No	kg ai/ha	PHI, days	with wrapper leaves	without wrapper leaves	
GAP, USA	SC 375 g/l	--	0.45-0.84	14	Do not exceed 1.7 kg ai/ha per season		
Arizona, 1983-84	SC 375 g/l	4	0.841	14	0.17 0.10 0.25 mean 0.17	0.05 ND (<0.02) 0.04 mean 0.036 factor 0.21	Hunt, 1986a Project 804R10 File 34501
	WG 800 g/kg	4	0.841	14	0.11 0.21 0.20 mean 0.17	0.06 ND 0.06 0.047 factor 0.3	
California, 1983	SC 375 g/l	4	0.841	7 14	2.7 2.4 mean 2.6 3.0 1.7 1.7 mean 2.1	<0.05 0.07 0.06 mean 0.06 factor 0.02 <0.05 0.13 <0.05 0.077 factor 0.04	
	WG 800 g/kg	4	0.841	7 14	1.7 0.37 mean 1.0 0.06 0.06 1.8 mean 0.64	0.09 <0.05 <0.05 mean 0.063 factor 0.06 0.05 <0.05 <0.05 mean 0.05 factor 0.08	
California, 1983-84	SC 375 g/l	4	0.841	14	1.8 3.2 2.4 mean 2.5	0.04 0.04 0.04 mean 0.04 factor 0.02	
	WG 800 g/kg	4	0.841	14	1.5 1.4 1.7 mean 1.5	0.03 0.02 0.03 mean 0.027 factor 0.02	

Location. year	Application			Residues (mg/kg)			Reference
	Formulation	No	kg ai/ha	PHI, days	with wrapper leaves	without wrapper leaves	
Wisconsin, 1983	SC 375 g/l	4	0.841	14	0.24 0.34 0.24 0.20 mean 0.26	0.05 0.05 <0.05 mean 0.05 factor 0.2	
	WG 800 g/kg	4	0.841	14	0.24 0.34 0.14 0.48 mean 0.30	0.20 0.08 0.08 mean 0.12 factor 0.4	
California, 1984	SC 375 g/l	4	0.841	14	0.07 0.06 0.06 mean 0.063	<0.04 0.05 <0.04 mean 0.043 factor 0.7	
	WG 800 g/kg	4	0.841	14	0.14 0.14 0.13 mean 0.14	0.12 0.14 0.08 mean 0.11 factor 0.8	
Florida, 1984	SC 375 g/l	4	0.841	14	1.2 1.1 1.3 mean 1.2	0.08 0.06 0.11 mean 0.083 factor 0.07	
	WG 800 g/kg	4	0.841	14	1.7 1.5 mean 1.6	0.06 0.04 0.05 mean 0.05 factor 0.03	
New York, 1984-85	SC 375 g/l	4	0.841	14	0.08 0.06 0.09 mean 0.077	0.08 0.08 0.07 mean 0.077 factor 1	
	WG 800 g/kg	4	0.841	14	0.19 0.17 0.11 mean 0.16	0.06 0.08 0.08 mean 0.073 factor 0.4	
Texas, 1984-85	SC 375 g/l	4	0.841	14	0.29 0.42 0.28 mean 0.33	ND 0.04 0.04 mean 0.033 factor 0.1	
	WG 800 g/kg	4	0.841	14	0.26 0.34 0.44 mean 0.35	0.06 0.03 <0.04 mean 0.043 factor 0.1	
Arizona, 1984-85	SC 375 g/l	4	0.841	15	0.63 0.96 0.96 mean 0.85	ND ND ND mean <0.02 factor 0.02	
	WG 800 g/kg	4	0.841	15	0.96 1.4 1.9 mean 1.4	ND ND ND mean <0.02 factor 0.01	

The average factor for reduction of residue when removing the wrapper leaves from head lettuce is 0.2 (n = 20).

Table 121. Residues in lettuce (aerial application), USA.

Location , year	Application			Residues (mg/kg)			Reference
	Formulation	No	kg ai/ha	PHI, days	with wrapper leaves	without wrapper leaves	
GAP, USA	SC 375 g/l	--	0.45-0.84	14	Do not exceed 1.7 kg ai/ha per season		
California, 1983	SC 375 g/l	4	0.841	7 14	2.8 2.2 2.0	<0.05 0.05 0.06 0.15	Hunt, 1986a Project 804R10 File 34501
	WG 800 g/kg	4	0.841	7 14	1.3 0.27 <0.05 <0.05 <0.05	<0.05 <0.05 <0.05 <0.05	
Arizona, 1984-85	SC 375 g/l	4	0.841	15	1.1 1.0 1.5	ND ND ND	
	WG 800 g/kg	4	0.841	15	0.65 1.1 0.78	0.08 ND ND	

Table 122. Residues in cabbage (foliar application), USA.

Location, year	Application			Residues (mg/kg)			Reference
	Formulation	No	kg ai/ha	PHI, days	with wrapper leaves	without wrapper leaves	
GAP, USA	SC 375 g/l	--	0.45-1.15	7	Do not exceed 6.7 kg ai/ha per season		
Florida, 1982	SC 375 g/l	6	1.121	3	1.4 2.4 1.8 mean 1.9	0.34 0.22 0.50 mean 0.35 factor 0.2	Hunt, 1986a Project 804R10 File 34501
				5	2.1 2.7 3.0 mean 2.6	0.50 0.67 0.60 mean 0.59 factor 0.2	
				7	2.0 1.8 3.1 mean 2.3	0.37 0.23 0.54 mean 0.38 factor 0.2	
	WG 800 g/kg	6	1.121	3	4.7 3.5 3.2 mean 3.8	0.47 0.29 0.21 mean 0.32 factor 0.08	
				5	3.5 3.6 4.1 mean 3.7	0.93 1.0 1.2 mean 1.0	
				7	2.1 0.37 1.7 mean 1.4	0.54 2.9[1] 0.82 mean 0.68 factor 0.49	

Location, year	Application			Residues (mg/kg)			Reference
	Formulation	No	kg ai/ha	PHI, days	with wrapper leaves	without wrapper leaves	
New York, 1982	SC 375 g/l	6	1.121	3	1.2 0.77 1.6 mean 1.2	0.18 0.11 <0.03 mean 0.11 factor 0.1	
				5	0.70 0.88 1.1 mean 0.89	<0.03 0.04 <0.03 mean 0.033 factor 0.04	
				7	1.2 0.44 1.3 mean 0.98	<0.03 <0.03 <0.03 mean <0.03 factor 0.03	
	WG 800 g/kg	6	1.121	3	1.2 1.7 2.1 mean 2.0	0.05 <0.03 0.04 mean 0.04 factor 0.02	
				5	2.0 2.0 1.8 mean 1.9	<0.03 0.05 <0.03 mean 0.036 factor 0.02	
				7	3.5 1.0 1.2 mean 1.9	<0.03 ND <0.03 mean 0.04 factor 0.02	
Ohio, 1982	SC 375 g/l	5	1.121	3	1.1 2.8 3.0 mean 2.3	0.18 0.34 0.37 mean 0.30 factor 0.1	
				5	0.56 1.7 5.0 mean 2.4	0.25 0.21 0.22 mean 0.23 factor 0.09	
Pennsylvania, 1982	SC 375 g/l	6	1.121	3	4.0 1.5 1.4 mean 2.3	0.05 <0.03 ND mean 0.033 factor 0.01	
				5	0.45 0.15 0.09 mean 0.23	0.04 <0.03 ND mean 0.045 factor 0.2	
				7	0.08 0.04 mean 0.06	<0.03 <0.03 <0.03 mean <0.03 factor 0.5	

Location, year	Application			Residues (mg/kg)			Reference
	Formulation	No	kg ai/ha	PHI, days	with wrapper leaves	without wrapper leaves	
Wisconsin, 1982	SC 375 g/l	6	1.121	3	0.74 0.51 mean 0.62	0.19 0.05 mean 0.12 factor 0.2	
				5	0.23 1.1 0.61 mean 0.65	0.07 0.27 0.13 mean 0.16 factor 0.2	
				7	0.18 0.20 0.53 mean 0.30	0.17 0.07 0.09 0.07 mean 0.1 factor 0.3	
	WG 800 g/kg	6	1.121	3	0.55 0.79 0.91 mean 0.75	0.11 0.13 0.09 mean 0.11 factor 0.1	
				5	0.16 0.75 0.58 mean 0.50	0.11 0.25 0.18 mean 0.18 factor 0.4	
				7	0.14 0.51 1.2 mean 0.62	<0.05 0.18 mean 0.12 factor 0.2	
California, 1983	SC 375 g/l	6	1.121	7	3.4 2.4 3.8 mean 3.2	0.06 0.07 0.07 mean 0.67 factor 0.02	
				14	0.41 0.21 0.24 mean 0.29	0.06 0.12 0.07 mean 0.08 factor 0.3	
	WG 800 g/kg	6	1.121	7	1.9 1.7 2.7 mean 2.1	0.05 0.03 0.03 mean 0.037 factor 0.02	
				14	0.13 0.07 0.10 mean 0.10	0.11 0.08 ND mean 0.07 factor 0.7	

[1]Aberrant result. Excluded from calculation of mean.

Table 123. Residues in cabbage (aerial application), USA, 1982.

Location	Application			Residues (mg/kg)			Reference
	Formulation	No.	kg ai/ha	PHI, days	with wrapper leaves	without wrapper leaves	
California	SC 375 g/l	6	1.121	7	4.9	0.06	Hunt, 1986a Project 804R10 File 34501
					2.3	0.07	
					5.0	0.07	
				14	0.37	0.08	
					0.28	0.07	
					0.47	0.04	
	WG 800 g/kg	6	1.121	7	4.8	0.03	
					1.9	0.09	
					1.1	0.07	
				14	0.10	0.05	
					0.22	0.03	
					0.13	ND	

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The Carbamate Market Basket Survey Task Force (CMBSTF) sponsored a study to determine the level of certain *N*-methylcarbamate insecticide residues in single-serving samples of fresh fruits and vegetables available for consumption by the US population (Carringer, 2000). Thiodicarb was one of the insecticides of interest in this study. The commodities selected were head lettuce and broccoli.

The analytical method used to quantify residues was "Determination of Selected N-Methyl Carbamate Pesticides in Fruits and Vegetables", Morse Laboratories, Inc., SOP No. Meth-118 (Revision 2), December 22, 1998. The residues are extracted with a mixture of acetonitrile and water. The water and acetonitrile are partitioned by the addition of NaCl and an aliquot of the resulting acetonitrile phase is partitioned with hexane, followed by dichloromethane/salt water, then cleaned up on a Florisil solid phase extraction (SPE) cartridge. Broccoli samples require an additional carbon black SPE clean-up. The purified extract is concentrated and analysed by high-performance liquid chromatography with post-column derivatisation and fluorescence detection. The LOQ is 0.001 mg/kg. The method detection limit (MDL), confirmed by analysing samples fortified at one-third or one-half the LOQ, was 0.00033 mg/kg for thiodicarb in all commodities.

Sampling took place during 1999 and 2000, although most of the samples were gathered in 1999.

Table 124 summarizes the results. Of the approximately 400 samples analysed, 98%-100% have no residues above the LOQ of 0.001 mg/kg. The highest residue was 0.0022 mg/kg, in broccoli. Six samples were at or above the LOQ at the following levels: 0.0010 (1 sample), 0.0011 (2), 0.0012 (2), 0.0022 (1).

Table 124. Carbamate Market Basket Survey in the USA (1999-2000).

Analyte	Sample	No. of analyses	Residues <0.001 mg/kg		Residues ≥0.001 mg/kg		Range of residues (mg/kg)
			No.	%	No.	%	
Thiodicarb	Head Lettuce	399	399	100	0	0	ND - <0.001
	Broccoli	395	389	98	6	2	ND - 0.0022

NATIONAL MAXIMUM RESIDUE LIMITS

The following existing national MRLs were provided by the manufacturer.

Commodity	Country	MRL (mg/kg)
Beans	Brazil	0.1
Beans	Peru	0.1
Beans and peas	Taiwan	1
Beet leaves (Chard)	Europe	2
Beetroot	Europe	0.05
Brassica crops	Australia	1
Broccoli	USA	7
Brussels sprouts	Austria	0.2
Brussels sprouts	Belgium	1
Brussels sprouts	Europe	0.05*
Brussels sprouts	Germany	0.5
Cabbage	USA	7
Cauliflower	USA	7
Cereals	Europe	0.05
Corn	Argentina	-
Cotton	Argentina	0.4
Cotton	Brazil	0.1
Cotton	Europe	0.1
Cotton	Peru	0.4
Cotton seed	USA	0.4
Cotton seed oil	Australia	0.1
Cotton seed, hulls	USA	0.8
Grapes (table)	Europe	0.05*
Grapes (wine)	Europe	1
Leaf vegetables with small leaves	Taiwan	1
Leaf vegetables with wrapped leaves	Taiwan	1
Leafy vegetables	USA	35
Lettuce	Europe	2
Maize	Australia	0.1
Maize	Brazil	0.1
Maize	Europe	0.05
Maize	Peru	2
Melon vegetables	Taiwan	1
Oilseed rape	Europe	0.05*
Peach	Europe	0.2
Pome fruits	Europe	0.2
Potato	Europe	0.05*
Pulses	Europe	0.05*
Pulses (soya beans, Mung beans, chick-peas, pigeon peas, navy beans)	Australia	0.1
Radish	Europe	0.5
Rice	Brazil	0.1
Root vegetables	Taiwan	0.5
Small berries	Taiwan	0.5
Sorghum	Australia	0.5 (temporary)
Soya bean	Argentina	0.2
Soya bean	Brazil	0.1
Soya bean	Europe	0.1
Soya bean	USA	0.2
Soya bean hulls	USA	0.8
Spinach	Europe	2
Sunflower	Argentina	0.2
Sunflower	Australia	0.05
Sunflower	Europe	0.05

Sweet corn	USA	2
Sweet corn (corn-on-the-cob)	Australia	0.1
Tomato	Australia	2
Tomato	Europe	0.5
Tomato	Peru	0.2
Wheat	Argentina	-
Wheat	Brazil	0.2

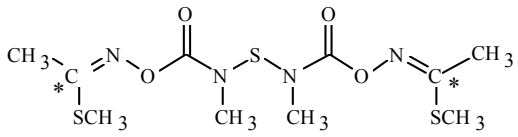
APPRAISAL

Thiodicarb is a carbamate insecticide and molluscicide. It is registered and used in agriculture and horticulture, against lepidoterous insects as a foliar treatment, as a molluscicide in the form of granular bait in various crops, and as a seed treatment.

Thiodicarb decomposes in plants and animals and in the environment to the insecticide methomyl. Currently, the MRLs for thiodicarb and methomyl are combined under methomyl.

Thiodicarb was evaluated by the FAO Panel of the JMPR in 1985, 1987 and 1988. The WHO Panel of the JMPR re-evaluated its toxicology in 2000.

Metabolism



[acetyl-1-^{14}C]Thiodicarb (designated [acetimide-^{14}C] thiodicarb in 2000 JMPR)
* Denotes ^{14}C carbons

The metabolism of thiodicarb in rats, monkeys, goats and chickens has been reported. Rats were given [acetyl-1-^{14}C]thiodicarb orally at 2 or 16 mg/kg bw in a single dose. More than 70% of the radiolabel was found in urine and respired gases over 7 days. The respired gases contained radiolabelled CO_2 and acetonitrile, and urine contained acetonitrile as a major metabolite and methomyl, methomyl oxime, methomyl sulfoxide and methomyl oxime sulfoxide as minor metabolites.

Cynomolgus monkeys were given a single oral dose of [acetyl-1-^{14}C]thiodicarb at 5 mg/kg bw. About 37% of the administered dose was eliminated in respired air over the first 48 h, consisting of 9% acetonitrile and 28% CO_2. Urine excreted over 168 h contained a combined total of 29% of the administered dose. Thiodicarb, methomyl and methomyl oxime were not detected in urine, blood or liver, while acetic acid was identified in liver.

The metabolic fate of [acetyl-1-^{14}C]thiodicarb in laying hens was studied after administration of a diet containing 15, 29 or 102 ppm for 21 days. The concentrations of residues achieved plateaux in egg white after 2 days and in egg yolk after 10 days. Thiodicarb and the potential metabolites methomyl, methomyl oxime, methomyl oxime sulfoxide and methomyl methylol were not detected in eggs, although low concentrations of acetonitrile (volatile) and acetamide (water-soluble) were found. In addition, considerable radiolabel was present as lipids (70% of the TRR) and other natural products due to incorporation of $^{14}CO_2$.

The concentrations of radiolabel in tissues of hens given 102 ppm were 4.2 mg/kg in muscle, 6.6 mg/kg in fat, 8.5 mg/kg in kidney and 10 mg/kg in liver. Acetonitrile and acetamide were identified in liver and muscle but not in abdominal fat. About 25% of the TRR in liver, 60% in muscle and 85% in fat was characterized as lipids. Methomyl, methomyl oxime, methomyl oxime sulfoxide and methomyl methylol were not found in any tissue.

The metabolic fate of [acetyl-1-^{14}C]thiodicarb was studied in two lactating goats after administration of 200 and 290 ppm per day for 7 days. The concentration of radiolabel reached maxima of 15 mg/kg and 20 mg/kg in the milk of the two goats on day 3. The goat at the higher dose became ill, and most of the results reported were for tissues from the goat at the lower dose.

After alkaline hydrolysis of water-soluble polar extracts, 32% of the TRR in liver was identified as acetonitrile, 6% as acetamide and 57% as acetic acid; 23% of the TRR in kidney was identified as acetonitrile, 10% as acetamide and 43% as acetic acid; and 72% of the TRR in muscle was acetonitrile, 14% was acetamide and 11% was acetic acid. No thiodicarb, methomyl or methomyl oxime was detected in any tissue.

The metabolites identified in fat were acetonitrile (10% of the TRR), acetamide (6% of the TRR) and saponifiable fatty acids and lipids (73% of the TRR). In milk, acetonitrile (29% of the TRR), lactose (11% of the TRR), saponifiable fatty acids and other lipids (32% of the TRR), palmitic and myristic acids and glycerol were identified. Some of the radiolabel in liver and kidney was also associated with amino acids and proteins.

The metabolism of [acetyl-1-^{14}C]thiodicarb in plants was studied in root crops (potato and carrot), in a fruiting vegetable (tomato), in cereal grain (wheat, maize and sweet corn) and in oilseed crops (cotton, soya bean and peanuts). When the radiolabelled compound was applied to the upper surface of the leaves of potato plants, < 0.2% of the administered dose migrated to the tubers, and 59% was found on the foliage. The constituents were thiodicarb (main), methomyl and methomyl oxime (trace).

[acetyl-1-^{14}C]Thiodicarb was applied to the upper surface of the leaves of 6-week-old carrot plants, and the carrots were harvested 28 days later. The aerial portions of the plants contained 90% of the applied radiolabel, and 0.06% was found in the roots. The following radiolabelled components were identified tentatively on the foliage: thiodicarb (79% of applied radiolabel), methomyl (8%), *N*-hydroxymethyl methomyl (0.18%) and methomyl oxime (0.09%).

[acetyl-1-^{14}C]Thiodicarb was also applied to the tops of tomato leaves at the time of flowering. The plants were maintained in a glasshouse, and the fruits were harvested at maturity. About 50% of the radiolabel was lost, perhaps as volatile compounds. About 49% was found on the foliage and about 0.45% on the tomatoes. The constituents on the foliage were identified as thiodicarb (78% of the TRR), methomyl (6%) and methomyl oxime (0.3%).

[acetyl-1-^{14}C]Thiodicarb was injected into the stems of 3-week-old sweet corn and wheat plants. The plants were maintained for 7 days and then harvested. The following metabolites were identified in both crops: thiodicarb (major), methomyl (major), methomyl oxime (very minor) and methomyl sulfoxide (very minor). About 30–50% of the radiolabel was unaccounted for.

A second study was performed with sweet corn, in which [acetyl-1-^{14}C]thiodicarb was painted onto leaves, ears and silk in one experiment and the leaves only in another. The plants were maintained for 7 days in a glasshouse and then harvested. Almost 70% of the applied radiolabel was unaccounted for. Only minute quantities were found in kernels plus cob. The concentrations on cobs and kernels were similar in the two experiments and were low (0.1–0.15% of the applied dose) in both cases. Over 70% of the radiolabel in the kernels could not be extracted. The metabolites identified on foliage (34% of the applied dose) were thiodicarb (20%), methomyl (6%) and methomyl oxime (trace to 0.3%).

In a study conducted with cotton plants, [^{14}C]thiodicarb was injected into the stem of 4–5-week-old cotton plants, which were maintained in a greenhouse and harvested 7, 14, 21 or 28 days after treatment. In a separate experiment, [^{14}C]thiodicarb was applied by stem injection and topical application to the tops of the leaves of 4-week-old cotton plants maintained in enclosed glass containers. Volatile compounds were collected in a series of traps at intervals of 1, 4 and 7 days after application and were identified as CO_2 and acetonitrile. In the injected plants (with no collection of volatile compounds), the percentage of the total applied radiolabel attributable to compounds soluble in organic solvents decreased from 53% on day 7 to 7% on day 28, whereas the percentage of water-soluble compounds increased from 12% to 21%. Throughout the experiment, 1–2% of the compounds could not be extracted. The compounds soluble in organic solvents were identified as thiodicarb, methomyl and methomyl oxime (trace). Methomyl was the major component on day 28.

The absorption, translocation and metabolism of thiodicarb in and on cotton after application to the leaf surface were investigated in a study in which a solution of [^{14}C]thiodicarb was spread onto the tops of the leaves of cotton plants at the flower bud stage at a rate equivalent to 1.1 kg ai/ha. The plants were maintained in a greenhouse until the bolls were mature, at which time they were harvested and the seeds de-linted. Senescent leaves were also collected for analysis. Lint and seed each contained < 0.1% of the applied dose, which was too little to allow adequate characterization. The senescent leaves were found to contain thiodicarb (22% of the TRR), methomyl (12% of the TRR), methomyl oxime (0.14% of the TRR) and methomyl methylol (0.5% of the TRR).

A similar experiment was performed with soya bean plants. A solution of [^{14}C]thiodicarb was spread onto the tops of the leaves of soya bean plants at the flower bud stage at a rate approximating 1.12 kg ai/ha. The plants were maintained in a greenhouse until the pods were mature, at which time they were harvested and the seeds separated from the hulls. Senescent leaves were also collected for analysis. Measurements of radiolabel in harvested seed and hull samples indicated activity representing 0.18–0.19% of the applied dose. The organic extract of soya bean leaves contained thiodicarb (85% of the applied radiolabel), methomyl (6%) and methomyl oxime (trace).

In a final study, [acetyl-1-^{14}C]thiodicarb was applied topically to peanut foliage four times at 7-day intervals at a rate of 1.1 kg ai/ha. The plants were harvested 21 days after the last treatment, and foliage, root, nut and shell were analysed separately. Of the applied radiolabel, 22% was in foliage, 0.2% in root, 0.5% in nut and 0.2% in nut shell. Almost 77% was unaccounted for and was presumably volatilized. The foliage contained thiodicarb and methomyl but no methomyl oxime or acetamide. Most (50–70%) of the radiolabelled residues in nut, shell and root could not be extracted. None of the components soluble in organic solvents could be identified.

The Meeting concluded that the metabolism of thiodicarb is adequately understood in both animals and plants. In animals, thiodicarb is converted to methomyl and, presumably via methomyl oxime, to CO_2, acetonitrile and acetamide. These may then be incorporated into natural products. Significantly, thiodicarb, methomyl and methomyl oxime are not found in tissues, eggs or milk. An analogous pathway exists in plants. Thiodicarb and its metabolites showed little tendency to translocate from the point of application. Thiodicarb is converted to methomyl and methomyl is metabolized to CO_2 and acetonitrile. At the point of application, e.g., foliage, the main soluble residue components are thiodicarb and methomyl. Volatile compounds often accounted for 50% or more of the residue. Traces of methomyl oxime, a potential intermediate to CO_2 and acetonitrile, were often found. The volatile compounds may be incorporated into natural products.

Environmental fate

Soil

A study of rotational crops was performed in sandy loam soil under confined conditions after application of [acetyl-1-^{14}C]thiodicarb at a rate of 6.7 kg ai/ha. After the soil had been tilled to a maximum depth of 10 cm, crops of mustard greens, radish and wheat were planted at intervals of 31,

125 and 364 days after treatment. Soil was analysed at the time of treatment and at the first plant-back interval (31 days). At day 0, 82% of the radiolabel was on thiodicarb; by day 31, thiodicarb accounted for 5% and methomyl for 47% of the radiolabel. Residues were found in crops planted 31 and 125 days after treatment but not in those with a 364-day plant-back (< 0.01 mg/kg). The concentrations of residues ranged from 0.11 mg/kg in radish root to 0.81 mg/kg in wheat straw at the 125-day plantback. At the 31-day plantback, the concentrations ranged from 0.48 mg/kg in wheat grain to 2.4 mg/kg in wheat straw.

When the crop matrices were extracted and analysed, the compounds identified included acetic acid released by acid hydrolysis, methomyl (maximum, 15% of the TRR), and methomyl oxime released by base hydrolysis (2–10% of the TRR). Most of the radiolabelled residues was not soluble in water or organic solvents and were found to be associated with natural products such as starch, proteins, pectins and lignin. At the 31-day plant-back, methomyl (from thiodicarb plus methomyl) was found at the following concentrations: wheat forage, 0.07 mg/kg; mustard greens, 0.12 mg/kg; radish tops, 0.14 mg/kg; and radish roots, 0.09 mg/kg. At the 125-day plant-back, the concentrations of methomyl were 0.02 mg/k in wheat forage, 0.04 mg/kg in mustard greens and 0.02 mg/kg in radish tops These values represented the LOQ of the analytical methods.

The Meeting concluded that thiodicarb and methomyl degradates persist in soil for at least 4 months and are taken up by plants and ultimately incorporated into natural products. The Meeting further concluded that, under typical GAP, ≥ 15% of the rate used in this study and field conditions, residues of methomyl and thiodicarb would not be quantifiable in rotational crops at intervals > 30 days.

Photolytic degradation of thiodicarb incubated under aerobic conditions at a temperature of 20 °C in a clay loam soil for 21 days was reported. In both irradiated and control soil, 50% of the radiolabelled material was lost as CO_2. Thiodicarb rapidly degraded to methomyl in both soils, the concentration of methomyl reaching a maximum of 80–90% of the applied dose on day 2. The concentration of thiodicarb declined slightly faster in the control than in the irradiated soil.

The Meeting concluded that sunlight has no net effect on the degradation of thiodicarb in soil.

In soil under aerobic conditions, thiodicarb degraded rapidly to methomyl, with a half-time based on first-order kinetics of 0.01–2.0 days, depending of soil type. The half-time of methomyl in sandy loam soil was 27 days. Methomyl oxime was found in the soil, at no more than about 3% of the applied dose. Over 60 days, the amount of radiolabel in sandy loam soil decreased to 42% of the applied dose, and the proportion of volatile compounds, identified as CO_2 and acetonitrile, increased to 53% of the applied dose. After 56 days, the radiolabel associated with volatile compounds represented 61% of the applied dose in clay loam with a high pH, 59% in clay loam at 20 °C and 40% in clay loam incubated at 10 °C. At the same time, the amount of unextractable radiolabel in the soils increased to a maximum of 35% of the applied dose.

The route and rate of degradation of [acetyl-1-^{14}C]thiodicarb under anaerobic conditions was studied in a soil–water mixture. The soil was flooded with deionized water and purged with nitrogen for 42–43 days before treatment to establish anaerobic conditions. A solution of [^{14}C]thiodicarb was applied to the water surface at a nominal application rate equivalent to 1 kg ai/ha. During incubation, the system was purged continuously with nitrogen to maintain anaerobic conditions. Within 16 min, the concentration of thiodicarb was < 1% of the applied dose. The concentration of methomyl was constant, at about 2% of the applied dose. An intermediate compound, *S*-methyl *N*-[*N*-methyl-*N*-(methylaminothio)-carbamoyloxy] thioacetamidate, was found at ≤ 17% of the applied dose. Acetonitrile was the ultimate degradate, accounting for 88% of the applied radiolabel after 4 h. No more than 16% of the applied radiolabel was associated with the soil at any time.

The adsorption and desorption properties of [acetyl-1-^{14}C]thiodicarb were characterized in four soil types. Thiodicarb had little mobility in clay soil, medium mobility in silt loam and sandy loam and high mobility in sandy soil.

The Meeting concluded that thiodicarb degrades within a few days to methomyl in soil under aerobic conditions and that methomyl degrades at a much slower rate. About 50% of methomyl is degraded to volatile compounds over 60 days in various soil types. Under anaerobic conditions in a water–soil mixture, thiodicarb degraded in < 4 h to acetonitrile. The Meeting further concluded that thiodicarb has little mobility in clay but is increasingly mobile in soils containing loam and sand. Some leaching of thiodicarb/methomyl can be expected in soil types other than clay.

Water–sediment systems

The hydrolysis of [acetyl-1-^{14}C]thiodicarb was determined at various pHs in sterile aqueous buffer solutions. After 7 days at pH 7 and pH 5, 92–94% of the applied radiolabel remained as thiodicarb. At pH 9, however, < 1% remained, with 54% methomyl and 32% methomyl oxime. The methomyl underwent degradation at pH 9, resulting in 77% methomyl oxime and 19% methomyl after 30 days.

The photodegradation of [acetyl-1-^{14}C]thiodicarb was tested in a buffered solution at pH 6 under natural sunlight. After 23 days, the solution of a control sample kept in the dark contained 98% of the applied radiolabel, consisting of 67% thiodicarb and 24% methomyl, whereas the irradiated solution contained only 72% of the applied radiolabel, consisting of 12% thiodicarb and 47% methomyl. CO_2 and acetonitrile accounted for 4.4% and 15%, respectively, of the applied radiolabel in the irradiated solution. No volatile compounds arose from the solution maintained in the dark. The time to 50% degradation was calculated to be 8 days in sunlight and 37 days in the dark.

The degradation of thiodicarb, applied at a rate of approximately 0.25 mg/kg of water, was investigated in two water–sediment systems under aerobic conditions over 100 days at 20 °C. The concentration of radiolabel in the water phase of both systems decreased slowly to < 1% of that applied, whereas that in the sediments increased from 10% on day 0 to 30–50% and then decreased to about 15%. Thiodicarb disappeared in both phases within < 1 day. Methomyl accounted for 50% and 17% of the applied dose in the two systems by day 2. Within 100 days, CO_2 accounted for 70% of the applied radiolabel in both systems. The half-time of methomyl was calculated as 20–30 h.

The Meeting concluded that thiodicarb is unstable at alkaline pH, decomposing to methomyl, which is converted to methomyl oxime. The Meeting further concluded that thiodicarb photodegrades in water, with a half-time of 8 days, and that it is rapidly converted to methomyl in water–sediment systems, with ultimate conversion to CO_2.

Methods of analysis

An HPLC method with post-column derivatization and a fluorescence detector has been validated for the determination of thiodicarb and methomyl in milk, muscle, kidney, liver and eggs, with an LOQ of 0.02 mg/kg for both thiodicarb and methomyl. Thiodicarb is unstable in animal matrices and degrades to methomyl.

GLC methods exist for the determination of thiodicarb, methomyl and methomyl oxime as methomyl oxime in plant commodities. The commodity is extracted with acetone and water and treated with a coagulation mixture to remove co-extractives. Caustic hydrolysis is used to convert both thiodicarb and methomyl to methomyl oxime, which is quantified by GLC with a flame photometric detector in the sulfur mode. Variations have been developed, including the use of GPC for extract clean-up, capillary GC columns and MS detectors. The LOD is either 0.02 or 0.04 mg/kg, depending on the exact procedure.

The Meeting concluded that adequate analytical methods exist for the determination of thiodicarb and methomyl in and on plant and animal commodities for the purposes of data collection and for monitoring and enforcing MRLs.

Stability of residues in stored analytical samples

Data were presented on the stability of thiodicarb and methomyl under frozen storage (–20 °C) in celery, head lettuce, leaf lettuce, spinach, soya bean, soya bean processed commodities (meal, hulls, oil, soapstock), apples, sorghum grain, sorghum forage, sweet corn, cotton seed, cotton seed processed commodities (meal, hulls, oil, soapstock), milk and ruminant muscle, kidney, fat and liver.

Thiodicarb plus methomyl was stable in celery, head lettuce and leaf lettuce for at least 7 months, but a significant proportion (30%) was lost in spinach after 5 months. Thiodicarb plus methomyl was stable in soya beans and cotton seed and its processed commodities, except cotton seed soapstock (50% loss) and cotton seed meal (40% loss), for 6 months. Thiodicarb and methomyl were stable in apples for at least 14 months and in sorghum grain for at least 13 months; however, thiodicarb plus methomyl showed a continuous decline on sorghum forage and stover, with a 20% loss over 6 months. Thiodicarb and methomyl were stable on frozen sweet corn (cob plus kernel) for 3 months but showed significant loss thereafter. Thiodicarb and methomyl were each stable in frozen milk, muscle and fat for 2 months but unstable in kidney (50% loss in 2 months, 20% in 1 month), disappearing from liver within 2 days.

The Meeting concluded that the stability of thiodicarb plus methomyl in frozen plant commodities is variable, 6 months generally being the longest desired storage interval. The Meeting further concluded that animal commodities, except liver and kidney, may be stored for 2 months, whereas kidney should be stored no more than 1 month, and liver is not amenable to standard frozen storage (see report item on methomyl).

Definition of the residue

The studies of animal and plant metabolism showed that thiodicarb is converted to methomyl and that methomyl is metabolized primarily to CO_2, acetonitrile and acetamide (animals only). The simpler metabolic products may then be incorporated into natural products, particularly in plants. Thiodicarb/methomyl showed no tendency to bioaccumulate in animal matrices. The P_{ow} of 1.6 indicates no tendency to accumulate in fat. Moreover, the studies of plant metabolism showed that thiodicarb/methomyl has a low tendency to migrate from the point of application, i.e. is not systemic. In both animals and plants, methomyl oxime appeared as a minor metabolite, representing < 1% in most cases, and is probably the intermediate in the metabolism of methomyl.

The analytical method for animal commodities allows determination of both thiodicarb and methomyl but not methomyl oxime. The method for plant commodities does not allow a distinction between thiodicarb and methomyl but reflects the sum of thiodicarb, methomyl and methomyl oxime as methomyl oxime.

The Meeting concluded that the residue definition for both plant and animal commodities should be the sum of thiodicarb and methomyl, expressed as methomyl. This definition takes into account the fact that methomyl oxime is a very minor metabolite and is not determined in some methods. Expression of the total residue as methomyl is consistent with the combination of the MRLs for thiodicarb and methomyl and reflects the fact that a significant portion of the residue found after use of thiodicarb is methomyl. The practical effect is small, as the conversion factor from mg/kg thiodicarb to mg/kg methomyl is 0.92.

Results of supervised field trials

The results of supervised field trial studies were presented for apple, grapes, potato, sugar beet roots, head lettuce, spinach, broccoli, Brussels sprouts, cabbage, cauliflower, collards, chick-peas, garden (green) peas, pea hay, soya beans, soya bean forage and hay and straw, tomato, barley grain, wheat grain, maize grain, sweet corn, rice grain, sorghum grain, barely forage and straw, wheat forage and straw, rice straw, sorghum forage and straw and stover, sweet corn forage, cotton seed, cotton forage, rape seed grain and rape seed forage (green) and straw.

As relevant GAP was not available for sorghum grain, this commodity was not considered further.

Generally, information on moisture content was not available for the forages, stovers and fodders, and the default values for per cent dry matter presented in Appendix IX of the *FAO Manual* were used.

Supervised trials on apple were conducted in Australia, Italy, Greece, Japan and the USA. The only relevant GAP is that of Japan, in which a wettable powder formulation of 750 g ai/kg may be applied three times at a maximum rate of 0.075 kg ai/hl, with a 21-day PHI, or a suspension concentrate formulation of 320 g/l may be applied three times at a rate of 0.043 kg ai/hl, with a 21-day PHI. In eight trials conducted at GAP with the wettable powder formulation, the ranked order of concentrations of residues was: 0.40, 0.43, 0.48, 0.68, 0.91 (2), 1.5 and 1.6 mg/kg. In four trials conducted at GAP with the suspension concentrate formulation, the ranked order of concentrations of residues was: 0.30, 0.32, 0.61 and 0.68. The data from the 12 trials may be combined, as they appear to represent the same population, as follows (ranked order, median underlined): 0.30, 0.32, 0.40, 0.43, 0.48, 0.61, 0.68 (2), 0.91 (2), 1.5 and 1.6 mg/kg (see report item on methomyl).

Supervised trials on grapes were conducted in France, Italy and Spain. The two trials in Spain were not conducted at the GAP of Spain (0.75 kg ai/ha; PHI, 21 days). The one trial in Italy and two in France were conducted at the GAP of France (0.45 kg ai/ha; PHI, 14 days), as no GAP was available for Italy. The ranked order of concentrations of residues was: 0.59 and 0.7 (2) mg/kg (see report item on methomyl).

Supervised trials on potato were presented from Japan and the UK. The trials in Japan involved five foliar applications at a GAP rate of 0.075 kg ai/hl and a 7-day PHI. In four trials conducted at GAP, no residues were detected: < 0.007 mg/kg (2) and < 0.008 mg/kg (2). The trials reported from the UK involved bait application to soil at 0.2 kg ai/ha and a PHI of 21 days. In the 11 trials at GAP, the concentrations of residues were: < 0.04 mg/kg (11) (see report item on methomyl).

Four supervised trials on sugar beet were reported from the UK. The GAP of Belgium requires application of a bait to soil at 0.2 kg ai/ha with no specified PHI. All the concentrations of residues in or on beet roots were < 0.040 mg/kg. The Meeting concluded that the number of trials was insufficient to permit estimation of a maximum residue level or an STMR value. The Meeting further agreed to withdraw the recommended MRL for sugar beet (0.1 mg/kg).

Supervised trials were conducted on lettuce, head, involving application of a granular bait to soil in Italy (no GAP) and France (0.8 kg ai/ha; PHI, 7 days) and aerial and ground foliar application in Spain (no GAP) and the USA (0.84 kg ai/ha; PHI, 14 days). In two trials in France at GAP, the concentrations of residues were 0.048 and 0.14 mg/kg. In 36 trials in the USA at GAP, the ranked order of concentrations of residues was: < 0.04 (3), 0.07 (2), 0.09 (2), 0.12, 0.14, 0.19, 0.21, 0.25, 0.34, 0.35, 0.36, 0.42, 0.44, 0.48, 0.49, 0.71, 0.96, 1.2, 1.7 (2), 1.8, 1.9, 2.6, 3.0, 3.2, 6.2, 6.3, 7.7, 10, 13, 17 and 18 mg/kg (see report item on methomyl).

Supervised field trials on spinach were conducted in the USA. In the nine trials at GAP (foliar spray at 0.84 kg ai/ha; PHI, 14 days), the ranked order of concentrations of residues was: 0.04 (2), 0.21, 1.0, 3.2, 3.5, 4.1, 12 and 25 mg/kg (see report item on methomyl).

Supervised field trials were conducted on collards in the USA (GAP: suspension concentrate, 0.84 kg ai/ha; PHI, 14 days). In two trials conducted under maximum conditions, the concentrations of residues were 1.5 and 1.8 mg/kg. The Meeting concluded that the number of trials was insufficient to permit estimation of a maximum residue level or STMR value but decided to combine the data with those for leafy vegetables treated with methomyl (see report item on methomyl).

Supervised field trials were conducted on broccoli in the USA. The GAP for foliar application (ground or aerial) is 1.2 kg ai/ha; with a 7-day PHI. The ranked order of concentrations of residues in the seven trials at GAP was: 1.1, 1.3, 1.6, 1.9, 2.6, 5.0 and 5.6 mg/kg. Two trials were reported from Australia, but they were not conducted at GAP (0.75 kg ai/ha; PHI, 7 days) (see report item on methomyl).

Supervised field trials were conducted on Brussels sprouts in The Netherlands and the UK (GAP of Belgium: bait application, 40 g ai/kg, 0.2 kg ai/ha; PHI, 21 days). In eight trials conducted at maximum GAP, the ranked order of concentrations of residues was < 0.04 (4), ≤ 0.05 (3) and 0.059 mg/kg. The Meeting decided to establish a group maximum residue level for Brassica vegetables based on foliar application, which results in higher concentrations of residues (see report item on methomyl).

Supervised trials were conducted on foliar application to cabbage in Australia (no GAP) and the USA (1.2 kg ai/ha; PHI, 7 days). In 19 trials at GAP, the ranked order of concentrations of residues was: 0.08 (2), 0.12, 0.53, 0.76, 0.97, 1.2, 1.3, 2.1, 2.7, 2.8, 3.0, 3.1, 3.5, 3.8, 4.3, 4.8, 5.0 and 5.3 mg/kg (see report item on methomyl).

Supervised field trials with foliar application to cauliflower were conducted in the USA (GAP: 1.2 kg ai/ha; PHI, 7 days). In eight trials at GAP, the ranked order of concentrations of residues was: 0.09, 0.16, 0.27, 0.45, 0.64, 0.71 and 2.3 (2) mg/kg (see report item on methomyl).

Supervised trials were conducted on garden peas in Australia. None of the trials met GAP (0.28 kg ai/h; PHI, 21 days), and the Meeting agreed to recommend withdrawal of the MRL for peas, shelled (succulent seeds) (0.5 mg/kg).

Supervised trials of foliar application to chick-pea were conducted in Australia. None of the trials met GAP (0.28 kg ai/ha; PHI, 21 day PHI).

Supervised field trials were conducted on foliar treatment of soya beans in Australia (0.28 kg ai/ha; PHI, 28 day), Brazil (0.06 kg ai/ha; PHI, 14 days) and the USA (0.84 kg ai/ha; PHI, 28 days). None of the trials in Australia and Brazil met GAP. In 19 trials with foliar ground application in the USA that were at GAP, the ranked order of concentrations of residues was: < 0.04 (17), 0.06 and 0.15 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg, an STMR value of 0.04 mg/kg and a highest residue of 0.15 mg/kg. The Meeting agreed to maintain the current recommended MRL for soya bean (dry) (0.2 mg/kg).

Supervised field trials on tomato were conducted in Australia (0.52 kg ai/ha; PHI, 1 day), Spain (0.94 kg ai/ha; PHI, 7 days) and the USA (no GAP). The trials in Spain were conducted in glasshouses. In two trials in Australia that met GAP, the concentrations of residues were 0.09 and 0.73 mg/kg. In nine trials in Spain at GAP, the ranked order of concentrations was: 0.05, 0.06, 0.08, 0.09, 0.13, 0.16, 0.18, 0.23 (2), 0.33 and 0.73 mg/kg (see report item on methomyl).

Supervised field trials were conducted on sweet corn in the USA (0.84 kg ai/ha; no PHI) and Australia (0.75 kg ai/ha; PHI, 7 days) with foliar application. None of the trials in Australia met GAP. In 22 trials in the USA at GAP, the ranked order of concentrations of residues was: < 0.02, 0.02, < 0.03 (6), < 0.04, 0.04, 0.06, 0.07 (2), 0.08, 0.11, 0.13, 0.22, 0.28, 0.43, 0.54, 0.82 and 1.5 mg/kg. Additional trials of seed treatment were presented, but there is no GAP for this application in the USA. Field trials were also conducted with methomyl, and the Meeting decided to combine the data sets (see report item on methomyl).

Supervised field trials of the application of granular bait to barley were conducted in Germany (0.2 kg ai/ha; PHI not specified) and the UK (at drilling and before the second node is detectable; 0.2 kg ai/ha; PHI not specified). In two trials in Germany and six in the UK at GAP, the ranked order of residues was: < 0.02 (2), ≤ 0.04 (5) and 0.06 mg/kg. Trials with foliar application of methomyl resulted in higher concentrations (see report item on methomyl).

Supervised field trials of the application of granular bait to wheat were conducted in Germany (0.2 kg ai/ha; PHI not specified) and the UK (at drilling and before the second node is detectable; 0.2 kg ai/ha; PHI not specified). In three trials in Germany and six in the UK at GAP, the ranked order of concentrations of residues was < 0.02 (3), < 0.04 (5) and 0.06 mg/kg. Supervised field trials conducted with methomyl yielded higher values (see report item on methomyl). Supervised field trials with seed treatment were provided from Brazil, but no GAP was reported and the LOQ was unacceptably high, at 0.2 mg/kg.

Supervised field trials on maize were conducted in Brazil with both foliar (0.1 kg ai/ha; PHI, 30 days) and seed treatment (7 kg/t of seeds). The trials with foliar application were conducted at an excessive rate (two to four times GAP), but the concentrations of residues were < 0.1 (6) mg/kg. In four trials of seed treatment at GAP the concentration was < 0.1 mg/kg. The Meeting concluded that data from the two uses could not be combined. The data for foliar treatment were combined with similar data in trials with methomyl (see the report item on methomyl).

Supervised trials on rice were conducted in Japan with foliar application (1.2 kg ai/ha; PHI, 30 days). In four trials at GAP, the ranked order of concentrations of residues was: < 0.25 (2) and < 0.4 (2) mg/kg. Supervised trials were conducted in Brazil with seed treatment of rice (5.3 kg/t of seed). The one trial at GAP and three trials at exaggerated rates (1.4–2.7 times GAP) yielded no quantifiable residues; the concentrations of residues were < 0.10 (4) mg/kg. The Meeting considered that the data from foliar and seed treatments could not be combined, and that the numbers of trials for the two treatments were insufficient to permit estimation of a maximum residue level or an STMR value. Furthermore, the LOQ of the analytical method for rice grain in Japan was unacceptably high.

Supervised field trials on barley forage were conducted in Germany (0.2 kg ai/ha) and the UK (early season, bait application; 0.2 kg ai/ha). In seven trials at GAP, the ranked order of concentrations of residues was: < 0.02 (2), ≤ 0.04 (3), 0.04 and 0.25 mg/kg. Barley forage is not a recognized animal feed commodity.

Supervised field trials were conducted on wheat forage in Germany (0.2 kg ai/ha) and the UK (0.2 kg ai/ha). In 12 trials at GAP, the ranked order of concentrations of residues was: < 0.02 (4), ≤ 0.04 (4), < 0.03 (2), 0.06 and 0.21 mg/kg. Trials conducted with methomyl by foliar application yielded higher concentrations (see report item on methomyl).

Supervised field trials on barley straw were conducted in Germany (0.2 kg ai/ha) and the UK (0.2 kg ai/ha). In nine trials at GAP, the ranked order of concentrations of residues was: ≤ 0.04 (6), < 0.2 (2) and 0.24 mg/kg (see report item on methomyl).

Supervised field trials on wheat straw were conducted in Germany (0.2 kg ai/ha). In three trials at GAP, the concentration of residues was < 0.2 mg/kg. The Meeting decided that the number of trials was insufficient to permit estimation of a maximum residue level or an STMR value (see report item on methomyl).

Supervised field trials were conducted on rice straw in Japan. In four trials at GAP (1.2 kg ai/ha; PHI, 30 days), the ranked order of concentrations of residues was: < 0.5, 0.62, and ≤ 1 (2) mg/kg. The Meeting decided to combine these data with those for cereal grain straw treated with methomyl (see report item on methomyl).

Supervised trials on sweet corn fodder were conducted in Australia, but none was at GAP (0.75 kg ai/ha; PHI, 7 days).

Supervised trials were conducted on foliar application to sweet corn forage in the USA. In 12 trials at GAP (0.84 kg ai/ha; PHI, 21 days), the ranked order of concentrations of residues was: < 0.02, < 0.05, 0.06, 0.16, 0.21, 0.56, 1.1, 2.3, 5.2, 6.9, 11 and 18 mg/kg. Trials were also conducted with methomyl, and the Meeting decided to combine the results (see report item on methomyl).

Supervised trials on cotton seed were conducted in Australia (GAP: 0.84 kg ai/ha; PHI, 21 days), Brazil (no GAP), Greece (GAP: 0.8 kg ai/ha; PHI, 28 days), Spain (0.94 kg ai/ha; PHI, 21 days), the Sudan (no GAP) and the USA (1 kg ai/ha; PHI, 28 days) by foliar application. None of the trials in Brazil corresponded to the GAP of Argentina (0.38 kg ai/ha; PHI, 20 days), and none of the trials in Spain was at GAP. One trial in Australia, two in Greece and 15 in the USA were at GAP; the ranked order of concentrations of residues was: ≤ 0.04 mg/kg (12), < 0.05, 0.05, 0.09 and 0.10 (3) mg/kg. Supervised trials were also conducted with methomyl, and the Meeting decided to combine the values (see report item on methomyl). Supervised field trials were presented on seed treatment in the USA, but there is no GAP for this application.

Many supervised field trials on cotton forage were conducted in the USA, but none was at GAP (1.0 kg ai/ha; PHI, 28 days), and cotton forage is not a recognized feed item, either in the USA or in the *FAO Manual*.

Supervised field trials on rape seed were conducted in Germany (0.2 kg ai/ha; no PHI) and the UK (soil broadcast up to and including stem extension stage; 0.2 kg ai/ha; no PHI) with granular bait. In 14 trials at GAP, the ranked order of concentrations of residues in rape seed was: < 0.04 (4), 0.04, ≤ 0.05 (8) and 0.05 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR value of 0.05 mg/kg.

Supervised field trials on rape seed forage (green) were conducted in Germany (winter rape, soil broadcast; 0.2 kg ai/ha; no PHI) and the UK (soil broadcast, up to an including stem extension stage; 0.2 kg ai/ha; no PHI) with granular bait. In 11 trials at GAP, the ranked order of concentrations of residues was: ≤ 0.02 (8) and < 0.04 (3) mg/kg. Applying the default value for dry matter of 30%, the Meeting estimated a maximum residue level of 0.2 mg/kg, an STMR value of 0.07 mg/kg and a highest residue of 0.13 mg/kg. Data were also presented for rape seed straw, but this is not a recognized feed commodity.

Fate of residues during processing

Studies were conducted on the processing of grapes in France and Spain and of soya, tomato, apple, sweet corn and cotton in the USA. The studies were conducted according to standard commercial practices. One study on tomato was rejected because samples in which residues had been incurred in the field were not used.

The processing factors and the maximum residue levels and STMR-P and HR-P values resulting from application of the factor to the estimated maximum residue levels and STMR values presented above and in the report item on methomyl are summarized in the latter.

Residues in animal commodities

No studies were provided on poultry, but the study of the nature of the residue in poultry was conducted after feeding concentrations ≤ 102 ppm for 21 days. The concentrations of residues reached a plateau in eggs within 10 days. Thiodicarb, methomyl and methomyl oxime were not detected in eggs or tissues, at an estimated LOD of about 0.005 mg/kg. As poultry diet contains a maximum of 2 ppm thiodicarb/methomyl (see report item on methomyl), quantifiable amounts of thiodicarb and/or methomyl in poultry commodities are unlikely. For methomyl plus thiodicarb, the Meeting estimated maximum residue levels of 0.02(*) mg/kg in meat, 0.02(*) mg/kg in eggs and 0.02(*) mg/kg in edible offal. Furthermore, the Meeting estimated STMR and highest residue values of 0.00 mg/kg for edible offal, meat and eggs (see report item on methomyl).

In a study in lactating dairy cattle in the USA, thiodicarb was administered orally for 28 consecutive days at 350 or 1050 ppm, as measured from actual feed consumption. Milk, liver, kidney, fat and muscle from cows at 1050 ppm contained no thiodicarb (LOQ 0.1 mg/kg) and no methomyl (LOQ 0.1 mg/kg). The vast majority of samples contained no detectable residues. Thiodicarb/methomyl was detected at 0.02 mg/kg in one milk sample on day 1 and at 0.02 mg/kg on day 25, in one muscle sample at about 0.03 mg/kg, in one liver sample at 0.06 mg/kg and in one kidney sample at 0.01 mg/kg from cows at 1050 ppm. A control sample of liver contained 0.09 mg/kg.

The Meeting estimated the dietary burden of thiodicarb for farm animals on the basis of the diets listed in Appendix IX of the *FAO Manual*. As the data for methomyl and thiodicarb were combined for estimating maximum residue levels and STMR values, a single diet applies to both. The dietary calculations are given in the report item on methomyl. The dietary burden of beef and dairy cattle was estimated to be 28 ppm. No residue (< 0.1 mg/kg) was found in meat, milk, fat, kidney or liver from cattle fed at 350 or 1050 ppm. Thiodicarb/methomyl was detected in a few samples at 0.02–0.03 mg/kg from cattle at 1050 ppm. Residues of thiodicarb/methomyl will therefore not be quantifiable in ruminant commodities. For methomyl plus thiodicarb, the Meeting estimated a maximum residue level of 0.02 (*) mg/kg for meat, 0.02 (*) mg/kg for milk and 0.02 (*) mg/kg for edible offal (see the report item on methomyl). The estimates for meat and milk confirm the existing values.

The average daily dietary burden of thiodicarb for ruminants is a fraction of the maximum daily burden. Thus, the STMR values for meat and milk were estimated to be 0.000 mg/kg. The highest residues for meat and milk were estimated to be 0.000 mg/kg, as there is no reasonable expectation of residues (see report item on methomyl).

RECOMMENDATIONS

On the basis of the data from supervised trials and studies of processing, the Meeting concluded that the concentrations of residues listed in the evaluation of methomyl are suitable for establishing MRLs and for assessing IEDIs and IESTIs.

Definition of residue (for compliance with MRLs and for estimation of dietary intake): sum of thiodicarb and methomyl, expressed as methomyl.

Dietary risk assessment

See evaluation of methomyl.

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[1] 7 to 10 days interval depending on the pest intensity

[1] every 7 days

[1] Do not exceed 6.7 kg/ha per season

[1] Do not exceed 6.7 kg/ha per season

[1] Do not exceed 3.4 kg/ha per season

[1] Do not exceed 8.4 kg/ha per season, 1 to 7 day intervals.

[1] every 7 days

[1] every 7 days

[1] Do not exceed 8.4 kg/ha per season, 1 to 7 day intervals.

[1] 10 to 15 days interval depending on the pest intensity

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ANNEX 1

ACUTE DIETARY INTAKES, ACUTE REFERENCE DOSES, RECOMMENDED MAXIMUM RESIDUE LIMITS AND SUPERVISED TRIALS MEDIAN RESIDUE VALUES RECORDED BY THE 2001 MEETING

The Meeting allocated acceptable daily intakes (ADIs) and acute reference doses (acute RfDs), estimated maximum residue levels which it recommended for use as maximum residue limits (MRLs) by the CCPR, and estimated supervised trials median residue (STMR) and highest residue (HR) values as a basis for estimating the dietary intakes of residues of the pesticides reviewed. The STMR is the expected residue concentration (in mg/kg) in the edible portion of a food commodity when a pesticide has been used according to maximum GAP conditions. The STMR is estimated as the median of the residue values (one from each trial) from supervised trials conducted according to maximum GAP conditions. The highest residue (HR) value is the highest concentration of residue found in the edible portion of a commodity in trials in which the maximum residue level was evaluated. The estimates are recorded in the table below.

As in recent years, the Meeting devoted particular attention to estimating the dietary intakes of the pesticides reviewed in relation to their ADIs. Those compounds for which estimated dietary intake might, on the basis of the available information, exceed their ADIs are marked with footnotes. The Meeting also estimated the acute dietary risk of some of the pesticides.

The table includes the Codex reference numbers of the compounds and the Codex classification numbers (CCNs) of the commodities, to facilitate reference to the Codex Maximum Residue Limits for Pesticides (*Codex Alimentarius*, Vol. 2B) and other documents and working documents of the Codex Alimentarius Commission.

The following qualifications are used in the Table.

* following recommended MRL	At or about the limit of determination
* following name of pesticide	New compound
** following name of pesticide	Reviewed within CCPR periodic review programme
Po	Recommendation accommodates post-harvest treatment of the commodity.
PoP	Recommendation accommodates post-harvest treatment of the primary food commodity (classes D and E in CODEX classification).
T	Temporary
W in place of a recommended MRL	Previous recommendation withdrawn, or withdrawal of recommended or existing Codex or draft MRL is recommended

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
Aldicarb (117)	0–0.003	FI 0327	Banana	0.2	W	0.01	0.10
		VR 0589	Potato	0.5	0.5	0.06	0.45
			Potato, microwaved			0.042	0.315
			Potato flakes			0.045	
			Potato chips			0.0228	
			Potato frozen fries			0.0174	
			Potato cooked fries			0.0234	
		Residue: for compliance with MRLs and estimation of dietary intake for plant commodities: sum of aldicarb, aldicarb sulfoxide and aldicarb sulfone, expressed as aldicarb. Acute RfD: 0.003 mg/kg bw					
Carbaryl (008)	0–0.008	Acute RfD: 0.2 mg/kg bw					
Chlorpropham* (201)	0–0.03	MM 0812	Cattle meat	0.1(fat)	–	0.004	0.004
		ML 0812	Cattle milk	0.0005*F	–	0.0003	
		MO 0812	Cattle, edible offal of	0.01*	–	0.005	0.007
		VR 0589	Potato	30 Po	–	11	23
			Potato chips with skin			4.6	
			Potato chips without skin			1.1	
			Potato dehydrated granules			0.845	
			Potato French fries with skin			1.6	
			Potato French fries without skin			0.2	
			Potato, cooked[1]			3.6	7.6
			Potato, peeled and cooked			0.098	0.2
		Residue: for compliance with MRLs and for estimation of dietary intake: chlorpropham. The residue is fat-soluble. [1]The information provided to the JMPR precludes an estimate that the dietary intake would be below the acute RfD. Acute RfD: 0.03 mg/kg bw					
Chlorpyrifos-methyl (090)	0–0.01	Acute RfD: Unnecessary					
2,4-D (020)	0.01	FC 0001	Citrus fruits	1 Po	–	0.3 [1]	
			Citrus juice			0.03[1]	
			Citrus oil			0.3 [1]	
		FC 0203	Grapefruit	W	0.1		
		FC 0004	Oranges, Sweet, Sour	W	0.1		
		Residue: for compliance with MRLs and for estimation of dietary intake: 2,4-D. [1]As no data for edible portion were available, STMR values are based on results for whole fruits. Acute RfD: Unnecessary					
Diazinon (022)	0–0.002	Acute RfD: 0.03 mg/kg bw					
Diflubenzuron (130)	0–0.02	Acute RfD: Unnecessary					
Dimethipin** (151)	0–0.02	SO 0691	Cotton seed	1	0.5	0.1	0.7
		OC 0691	Cotton seed oil, crude	0.1	0.1	0.02	
		OR 0691	Cotton seed oil, edible	0.1	0.02*	0.02	
		MO 0105	Edible offal (mammalian)	0.01*	0.02*	0	0
		PE 0112	Eggs	0.01*	0.02*	0	0
		SO 0693	Linseed	W	0.2		

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
		MM 0095	Meat (from mammals other than marine mammals)	0.01*	0.02*	0	0
		ML 0106	Milks	0.01*	0.02*	0	
		VR 0589	Potato	0.05*	0.05*	0.02	0.02
		PM 0110	Poultry meat	0.01*	0.02*	0	0
		PO 0111	Poultry, edible offal	0.01*	0.02*	0	0
		SO 0495	Rapeseed	0.2	–	0.1	0.1
		SO 0702	Sunflower seed	1	0.5	0.1	0.77
		OC 0702	Sunflower seed oil, crude	W	0.1		
		OR 0702	Sunflower seed oil, edible	W	0.02*		
		Residue: for compliance with MRL and for estimation of dietary intake: dimethipin. Acute RfD: 0 .02 mg/kg bw					
Dinocap (087)	0–0.008	FB0269	Grapes	0.5	1	0.05	0.35
		Residue: for compliance with MRLs and for estimation of dietary intake: sum of dinocap isomers and dinocap phenols, expressed as dinocap Acute RfD: 0.03 mg/kg bw (for the general population) 0.008 mg/kg bw (for women of childbearing age)					
Diphenylamine** (030)	0–0.08	FP 0226	Apple	10 Po	5 Po	4.45	
		JF 0226	Apple juice	0.5 PoP		0.23	
		AB 0226	Apple pomace (dry)	25 PoP		10.6	
			Apple pomace (wet)			21	
		MO 1280	Cattle, kidney	0.01*		0.0007	
		MO 1281	Cattle, liver	0.05		0.024	
		ML 0812	Cattle milk	0.0004* F[1]		0.00015	
		MM 0812	Cattle meat	0.01* (fat)		0.0005	
		FP 0230	Pear	5 Po		2.2	
		Residue: for compliance with the MRL and for estimation of dietary intake: diphenylamine. The residue is fat-soluble. [1] Equivalent to 0.01* mg/kg in the milk fat Acute RfD: Unnecessary					
Fenpropimorph (188)	0–0.003	Acute RfD: 1 mg/kg bw					
Fipronil* (202)	0–0.0002[1]	FI 0327	Banana	0.005	–	0.004	0.005
		GC 0640	Barley	0.002*	–	0.004	0.004
		VB 0041	Cabbages, Head	0.02	–	0.005	0.0215
		MO 1280	Cattle, kidney	0.02	–	0.014	0.018
		MO 1281	Cattle, liver	0.1	–	0.064	0.079
		MM 0812	Cattle meat	0.5 (fat)	–	0.015	0.019
		ML 0812	Cattle milk	0.02	–	0.011	
		PE 0112	Eggs	0.02	–	0.006	0.0078
		VB 0042	Flowerhead brassicas	0.02	–	0.005	0.0215
		GC 0645	Maize	0.01	–	0.005	0.02
		AF 0645	Maize forage	0.1[2]	–		
		AS 0645	Maize fodder	0.1[2]	–		
		GC 0647	Oats	0.002*	–	0.004	0.004
		VR 0589	Potato	0.02	–	0.004	0.028
			Potato chips			0.0009	
			Potato flakes			0.0011	
		PO 0110	Poultry, edible offal of	0.02	–	0.008	0.0084
		PM 0110	Poultry meat	0.01*	–	0.006	0.006
		GC 0649	Rice	0.01	–	0.006	0.013
		AS 0649	Rice straw and fodder, dry	0.2[2]	–		
		GC 0650	Rye	0.002*	–	0.004	0.004
		VR 0596	Sugar beet	0.2	–	0.0125	0.17
		AV 0596	Sugar beet leaves or tops	0.2[2]	–		
		SO 0702	Sunflower seed	0.002*	–	0.004	0.008

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
		GC 0653	Triticale	0.002*	–	0.004	0.004
		GC 0654	Wheat	0.002*	–	0.004	0.004
		Residues: for compliance with MRLs for plant commodities: fipronil. For compliance with MRLs for animal commodities: sum of fipronil and 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonylpyrazole (MB 46136), expressed as fipronil. For estimation of dietary intake for plant and animal commodities: sum of fipronil, 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonylpyrazole (MB 46136), 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthiopyrazole (MB 45950) and 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylpyrazole (MB 46513), expressed as fipronil. The residue is fat-soluble. [1]Group ADI for fipronil and fipronil-desulfinyl [5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethyl pyrazole (MB 46513)] [2]Expressed on dry weight basis. Acute RfD: 0.003 mg/kg bw (for fipronil and fipronyl-desulfinyl[5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethyl pyrazole (MB 46513)], alone or in combination)					
Haloxyfop (194)	0–0.0003	AL 1021	Alfalfa forage (green)	5.0[1]	W	2.33	–
		MM 0812	Cattle meat	0.05	W	0.02	0.03
		ML 0812	Cattle milk	0.3	W	0.22	–
		MO 0812	Cattle, edible offal of	–	W	–	–
		MO 1280	Cattle, kidney	1	–	0.73	0.95
		MO 1281	Cattle, liver	0.5	–	0.28	0.33
		PE 0840	Chicken eggs	0.01*	0.01*	0.002	0.003
		PM 0840	Chicken meat	0.01*[2]	0.01*	0.002	0.003
		PO 0840	Chicken, Edible offal of	0.05	0.1	0.009	0.030
		AV 1051	Fodder beet leaves or tops	0.3[1]	W	0.03	–
		AV 0596	Sugar beet leaves or tops	0.3[1]	W	0.03	–
		Residue: for compliance with MRLs and for estimation of dietary intake for products of animal origin: haloxyfop ester, haloxyfop and its conjugates expressed as haloxyfop (whole product basis). [1]Fresh weight basis [2]With adhering skin Acute RfD: may be necessary but has not yet been established Note: The information provided to the JMPR precludes an estimate that the dietary intake would be below the ADI.					
Imidacloprid*	0–0.06	Acute RfD: 0.4 mg/kg bw					
Imazalil (110)	0–0.03	Acute RfD: Unnecessary					
Iprodione (111)	0–0.06	VO 0448	Tomato	5	5	1.1	4.2
		JF 0448	Tomato juice			0.55	
			Tomato purée			0.55	
			Tomato ketchup			0.99	
		Residue: for compliance with MRLs and for estimation of the dietary intake: iprodione Acute RfD: may be necessary but has not been established					
Kresoxim-methyl (199)	0–0.4	FC 0203	Grapefruit	0.5	–		
			Grapefruit, edible portion of			0.01	
		FT 0305	Olives	0.2	–	0.05	
		OC 0305	Olive oil, virgin	0.7	–	0.22	
		FC 0004	Oranges, Sweet, Sour	0.5	–		
			Oranges, edible portion of			0.01	

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
		Residue: for compliance with MRLs and for estimation of the dietary intake for plant commodities: kresoxim-methyl. For compliance with MRLs and for estimation of the dietary intake for animal commodities: α-(*p*-hydroxy-*o*-tolyloxy)-*o*-tolyl(methoxyimino)acetic acid, expressed as kresoxim-methyl Acute RfD: Unnecessary					
Methomyl** (094)	0–0.02	AL 1021	Alfalfa forage (green)	25[1]	10 fresh wt		
		AL 1020	Alfalfa fodder (hay)	20[1]	–		
		FP 0226	Apple[4]	2[2]	–	0.41	1.6
		JF 0226	Apple juice	–	–	0.12	
		VS 0621	Asparagus	2[1]	2	0.33	1.1
		GC 0640	Barley	2[1]	0.5	0.14	1.3
		AS 0640	Barley straw and fodder,dry	W	5		
		VD 0071	Beans (dry)	0.05[1]	0.1	0.02	0.023
		AL 0061	Bean fodder (hay)	10[1]	–		
		VP 0061	Beans (except broad and soya)	1[1]	–	0.005	0.68
		VB 0040	Brassica (cole or cabbage) vegetables[4]	7[3]	–	1.3	5.6
		VB 0041	Cabbages, Head	W	5		
		VB 0404	Cauliflower	W	2		
		VS 0624	Celery[4]	3[1]	2	0.66	2
		AS 0161	Cereal grain, straw, fodder (dry), hay	10[3]	–		
		FC 0001	Citrus fruits	1[1]	1	0.034 flesh	0.18 flesh
		AB 0001	Citrus pulp, dry	3	–		
		JF 0001	Citrus juice	–		0.004	
		VP 0526	Common bean (pods and/or immature seeds)	1[1]	2	0.055	0.68
		SO 0691	Cotton seed	0.2[3]	0.5		
		OR 0691	Cotton seed, edible oil	0.04		0.006	
			Cotton seed, meal	0.05	–		
			Cotton seed, hulls	0.2	–		
		VC 0424	Cucumber	W	0.2		
		MO 0105	Edible offal (from mammals other than marine mammals)	0.02*[3]	–	0.00	0.00
		VO 0440	Egg plant	W	0.2		
		PE 0112	Eggs	0.02*[3]	–	0.00	0.00
		VC 0045	Fruiting vegetables, Cucurbits[5]	0.1[1]		0.02	0.07
		FB 0269	Grapes[4]	7[1]	5	0.86	5.2
		DH 1100	Hops, dry	W	10		
		VL 0480	Kale	W	5		
		VL 0482	Lettuce, Head	W	5		
		VL 0053	Leafy vegetables[4]	30[3]	–	1.4	25
		GC 0645	Maize	0.02*[1]	0.05*	0.02	0.02
		AS 0645	Maize fodder	W	50 fresh wt		
		AF 0645	Maize forage	50[3]	50 fresh wt		
		OR 0645	Maize, edible oil	0.02*	–	0.004	
		MM 0095	Meat (from mammals other than marine mammals)	0.02*[3]	0.02*	0.000	0.000
		VC 0046	Melons, except watermelon	W	0.2		
		ML 0106	Milks	0.02*[3]	0.02*	0.000	
		AM 0738	Mint hay	W	2		
		FS 0245	Nectarines	0.2[1]	5	0.05	0.10
		AS 0647	Oat straw and fodder, dry	W	5		

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
		GC 0647	Oats	0.02*[1]	0.5	0.02	0.02
		VA 0385	Onion, bulb	0.2[1]	0.2	0.068	0.14
		VA 0387	Onion, Welsh	W	0.5		
		AL 0528	Pea vines (green)	40[1]	10 fresh wt		
		FS 0247	Peach	0.2[1]	5	0.05	0.10
		SO 0697	Peanut	W	0.1		
		AL1270	Peanut forage (green)	W	5		
		FP 0230	Pear	0.3[1]	–	0.09	0.18
		VP 0063	Peas (pods and succulent = immature seeds)	5[1]	5	0.46	4.0
		VP 0064	Peas, shelled (succulent seeds)	W	0.5		
		VO 0051	Peppers	W	1		
		Fl 0353	Pineapple	W	0.2		
		FS 0014	Plums	1[1]	–	0.08	0.51
		FP 0009	Pome fruits	W	2		
		VR 0589	Potato	0.02*[3]	0.1	0.00	0.00
		PO 0110	Poultry meat	0.02*[3]	–	0.00	0.00
		PO 0111	Poultry, edible offal of	0.02*[3]	–	0.00	0.00
		SO 0495	Rapeseed	0.05[2]	–		
			Rapeseed forage	0.2	–		
		GC 0651	Sorghum	W	0.2		
		AF 0651	Sorghum forage (green)	1[1]	1		
		VD 0541	Soya bean (dry)	0.2[2]	0.2		
		VP 0541	Soya bean (immature seed)	W	0.1		
		AL 1265	Soya bean forage (green)	40[1]	10		
		AL 0541	Soya bean hay	0.2[1]	–		
			Soya bean hulls	1	–		
			Soya bean meal	0.2			
		VD 0541	Soya bean oil, crude	0.2	–	0.04	
		OR 0541	Soya bean oil, refined	0.2	–	0.04	
		VL 0502	Spinach	W	5		
		VC 0431	Squash, summer	W	0.2		
		VR 0596	Sugar beet	W	0.1		
		VO 0447	Sweet corn (corn-on-the-cob)[4]	2[2]	2	0.065	1.5
		VO 0448	Tomato[4]	1[2]	1	0.16	0.73
		VJ 0448	Tomato paste	–	–	0.007	
		VC 0432	Watermelon[4]	W	0.2		
		GC 0654	Wheat	2[1]	0.5	0.14	1.3
		CF 0121	Wheat flour	0.03	–	0.003	
		CF 0654	Wheat bran	3	–	0.27	
		CF 1210	Wheat germ	2	–	0.13	
		–	Wine, of grape	–	–	0.26	
		Residue: for compliance with MRLs and for the estimation of dietary intake: sum of thiodicarb and methomyl, expressed as methomyl. [1]Resulting from consideration of methomyl supervised field trial data. [2]Resulting from consideration of thiodicarb supervised field trial data. [3]Resulting from consideration of methomyl + thiodicarb supervised field trial data. [4]The information provided to the JMPR precludes an estimate that the dietary intake would be below the acute RfD. Acute RfD: 0.02 mg/kg bw					
Methoprene** (147)	0–0.09[1] 0–0.05[2]	[1]ADI for the *R,S* racemate [2]ADI for *S*-methoprene Acute RfD: Unnecessary					
Phosalone (060)	0–0.02	Acute RfD: 0.3 mg/kg bw					
Piperonyl butoxide** (062)	0–0.2	MO 1280	Cattle kidney	0.3[1]		0.21[2]	
		MO 1281	Cattle liver	1		0.10	

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
		MM 0812	Cattle meat	5 (fat)[1]		0.16[2,3]	
		ML 0812	Cattle milk	0.2[1]		0.14[2]	
		GC 0080	Cereal grains	30 Po		11	
		FC 0001	Citrus fruits	5		1	
		AB 0001	Citrus pulp, dry			5.7	
		JF 0001	Citrus juice	0.05		0.01	
		DM 0001	Citrus molasses			0.53	
		DF 0167	Dried fruits	0.2 Po		0.05	
		PE 0112	Eggs	1[1]		0.36[2]	
		VC 0045	Fruiting vegetables, Cucurbits	1		0.26	
		VL 0483	Lettuce, Leaf	50		38	
		OC 0645	Maize oil, crude	80 PoP		29.7	
		VL 0485	Mustard greens	50		38	
		AL 0072	Pea hay or pea fodder	200		19.9	
		AL 0528	Pea vine (green)	400		108	
		SO 0703	Peanut, whole	1 Po		0.1	
		VO 0051	Peppers	2		0.675	
		PM 0110	Poultry meat	5 (fat)[1]		1.0[2,3]	
		PO 0111	Poultry, Edible offal of	10[1]		2.03[2]	
		VD 0070	Pulses	0.2 Po		0.05	
		VL 0494	Radish leaves	50		38	
		VR 0075	Root and tuber vegetables, except carrots	0.5		0.10	
		VL 0502	Spinach	50		38	
		VO 0448	Tomato	2		0.675	
		JF 0448	Tomato juice	0.3		0.10	
			Tomato purée			0.22	
		GC 0654	Wheat	W	10 Po		
		CM 0654	Wheat bran, unprocessed	100 PoP		38.5	
		CF 1211	Wheat flour	10 PoP		3.5	
		CF 1210	Wheat germ	100 PoP		30.8	
		CF 1212	Wheat wholemeal	30 PoP		10.8	
		Residue: for compliance with MRLs and for estimation of the dietary intake for plant and animal commodities: piperoyl butoxide The residue is fat-soluble [1]The MRL accommodates external animal treatment [2]Not STMR but median residues from animals in a treated group [3]In muscle Acute RfD: Unnecessary					
Prochloraz** (142)	0–0.01	Acute RfD: 0.1 mg/kg bw					
Pyriproxyfen (200)	0–0.1	Safety of addition to drinking-water as a larvicide was evaluated Acute RfD: Unnecessary					
Spinosad* (203)	0–0.02	AM 0660	Almond hulls	2		0.56	
		TN 0660	Almonds	0.01*		0.01	
		JF 0226	Apple juice			0.0013	
			Apple pomace, wet			0.064	
			Apple purée			0.0015	
		FP 0226	Apples	0.1		0.0165	
		VB 0040	Brassica vegetables, Head cabbages, Flowerhead brassicas	2		0.27	
		MO 1280	Cattle kidney	1[1]		0.31[2]	
		MO 1281	Cattle liver	2[1]		0.66[2]	
		MM 0812	Cattle meat	3 (fat)[1]		0.078[2]	
		ML 0812	Cattle milk	1[1]		0.65	
		VS 0624	Celery	2		0.97	
		FC 0001	Citrus fruits	0.3		0.01	

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
		AB 0001	Citrus, dried processing pulp			0.12	
		SO 0691	Cotton seed	0.01*		0.01	
			Cotton seed hulls			0.0020	
			Cotton seed meal			0.0017	
		OC 0691	Cotton seed oil, crude	0.01*		0.0018	
		OR 0691	Cotton seed oil, edible	0.01*		0.0020	
		PE 0112	Eggs	0.01		0.01	
		VC 0045	Fruiting vegetables, Cucurbits	0.2		0.046	
		FI 0341	Kiwifruit	0.05		0.02	
		VL 0053	Leafy vegetables	10		1.9	
		VP 0060	Legume vegetables	0.3		0.041	
		GC 0645	Maize	0.01*		0	
		AS 0645	Maize fodder (dry)	5		0.46	
		AF 0645	Maize forage (dry)	5		0.70	
		JF 0004	Orange juice			0.007	
		VO 0051	Peppers	0.3		0.056	
		VR 0589	Potato	0.01*		0	
		PM 0110	Poultry meat	0.2 (fat)		0.01	
		MO 0822	Sheep, edible offal of	0.01*,[1]		0.01	
		MM 0822	Sheep meat	0.01* (fat)[1]		0.01	
		GC 0651	Sorghum	1		0.165	
		VD 0541	Soya bean (dry)	0.01*		0	
		FS 0012	Stone fruits	0.2		0.0265	
		VO 0447	Sweet corn (corn-on-the-cob)	0.01*		0.01	
		VO 0448	Tomato	0.3		0.03	
		JF 0448	Tomato juice			0.0075	
			Tomato paste			0.059	
			Tomato purée			0.017	
		AS 0654	Wheat straw and fodder, dry	1		0.215	
		Residue: for compliance with MRLs and for estimation of dietary intake : sum of spinosyn A and spinosyn D. The residue is fat-soluble, but residues in milk should be measured on the whole milk. [1]The MRL accommodates external animal treatment [2]Residues from direct animal treatment – not an STMR, but median of residues from animals in a treatment group Acute RfD: Unnecessary					
Tebufenozide (196)	0–0.02	TN 0660	Almonds	0.05	–	0.0205	0.045
		AM 0660	Almond hulls	30		15	
		FI 0326	Avocado	1	–	0.21	0.53
		VB 0400	Broccoli	0.5	–	0.11	0.34
		FB 0020	Blueberries	3	–	0.685	1.7
		VB 0041	Cabbages, Head[1]	5	–	0.34	4.6
		MO 1280	Cattle, kidney	0.02*		0.006	0.006
		MO 1281	Cattle, liver	0.02*	–	0.02	0.02
		MM 0812	Cattle meat	0.05 (fat)		0.006	0.006
		ML 0812	Cattle milk	0.01*	–	0.003	
		FC 0001	Citrus fruit	2	–	0.079	0.18
			Citrus oil			12.50.38	
			Citrus dried pulp				
		JF 0001	Citrus juice			0.0077	
		FB 0265	Cranberries	0.5	–	0.042	0.28
		DF 0269	Dried grapes (currants, raisins and sultanas)	2	–	0.551	1.11
		PE 0112	Eggs	0.02*		0	0
		FB 0269	Grapes[1]	2	1	0.745	1.5
			Grape wet pomace			2.9	
		JF 0269	Grape juice			0.097	

Pesticide (Codex reference number)	ADI (mg/kg bw)	CCN	Commodity name	Recommended MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR HR-P (mg/kg)
				New	Previous		
		VL 0053	Leafy vegetables[1]	10	–	2.45	8.1
		HH 0738	Mint	20	–	8.35	8.6
			Mint oil			0.25	
		FS 0245	Nectarines	0.5	–	0.11	0.23
		FS 0247	Peaches	0.5	–	0.11	0.23
			Peaches, canned			0.0066	
		TN 0672	Pecans	0.01*	–	0.01	0.01
		VO 0051	Peppers	1		0.064	0.64
		PM 0110	Poultry meat	0.02* (fat)	–	0.02	0.02
		FB 0272	Raspberries	2		0.56	0.86
		SO 0495	Rape seed	2	–	0.95	1.6
			Rape seed meal			0.14	
			Rape seed soapstock			1.0	
		OR 0495	Rape seed oil, refined			2.2	
		GS 0659	Sugar cane	1	–	0.12	0.62
			Sugar, refined			0.003	
			Molasses			0.708	
		VO 0448	Tomato	1	–	0.13	0.53
			Tomato purée			0.04	
			Tomato paste			0.095	
			Tomatoes (preserved)			0.036	
		JF 0448	Tomato juice			0.023	
			Wine			0.216	
		Residue: for compliance with MRLs and for estimation of dietary intake for plant and animal products: tebufenozide The residue is fat-soluble [1]The information provided to the JMPR precludes an estimate that the dietary intake would be below the acute RfD.Acute RfD: 0.05 mg/kg bw					
Thiodicarb** (154)	0–0.03	Residue for compliance with MRLs and for the estimation of dietary intake: sum of thiodicarb and methomyl, expressed as methomyl Acute RfD: 0.04 mg/kg bw.					

ANNEX 5

Reports and other documents resulting from previous Joint Meetings of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and WHO Expert Groups on Pesticide Residues

1. Principles governing consumer safety in relation to pesticide residues. Report of a meeting of a WHO Expert Committee on Pesticide Residues held jointly with the FAO Panel of Experts on the Use of Pesticides in Agriculture. FAO Plant Production and Protection Division Report, No. PL/1961/11; WHO Technical Report Series, No. 240, 1962.
2. Evaluation of the toxicity of pesticide residues in food. Report of a Joint Meeting of the FAO Committee on Pesticides in Agriculture and the WHO Expert Committee on Pesticide Residues. FAO Meeting Report, No. PL/1963/13; WHO/Food Add./23, 1964.
3. Evaluation of the toxicity of pesticide residues in food. Report of the Second Joint Meeting of the FAO Committee on Pesticides in Agriculture and the WHO Expert Committee on Pesticide Residues. FAO Meeting Report, No. PL/1965/10; WHO/Food Add./26.65, 1965.
4. Evaluation of the toxicity of pesticide residues in food. FAO Meeting Report, No. PL/1965/10/1; WHO/Food Add./27.65, 1965.
5. Evaluation of the hazards to consumers resulting from the use of fumigants in the protection of food. FAO Meeting Report, No. PL/1965/10/2; WHO/Food Add./28.65, 1965.
6. Pesticide residues in food. Joint report of the FAO Working Party on Pesticide Residues and the WHO Expert Committee on Pesticide Residues. FAO Agricultural Studies, No. 73; WHO Technical Report Series, No. 370, 1967.
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