THIOPHANATE-METHYL (077)/CARBENDAZIM (072)

The first draft was prepared by Professor M Lee, Andong National University, Republic of Korea

EXPLANATION

Thiophanate-methyl, its related compounds benomyl and carbendazim, are systemic benzimidazole fungicides with protective and curative action against a wide range of disease on cereals, fruits and vegetables. Those three compounds were first evaluated in 1973 (T, R) by JMPR and re-evaluated within the periodic review programme of CCPR in 1995 (T) and in 1998 (R). Since then, thiophanate-methyl was further evaluated in 1998 and 2006 for toxicology and in 2003 for residues. Carbendazim was also further evaluated in 2003 (R), 2005 (T) and 2010 (residues in spices). Benomyl was not evaluated by JMPR since the 1998 periodic review.

Current ADIs established by JMPR are 0–0.08 mg/kg bw for thiophanate-methyl and 0–0.03 mg/kg bw for carbendazim and 0–0.1 mg/kg bw for benomyl. ARfDs are established as unnecessary for thiophanate-methyl and for carbendazim, as 0.1 mg/kg bw for women of child-bearing age and 0.5 mg/kg bw for the general population and children. For benomyl, only an ADI has been established.

In 1998, JMPR defined residues for compliance with MRLs and for the estimation of dietary intake as follows:

Benomyl: the sum of benomyl and carbendazim, expressed as carbendazim

Carbendazim: carbendazim

Thiophanate-methyl: the sum of thiophanate-methyl and carbendazim, expressed as carbendazim.

At the 34th Session of the CCPR (2002), the Committee agreed to change the JMPR residue definition into "the sum of benomyl, carbendazim and thiophanate-methyl, expressed as carbendazim".

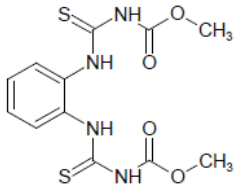
A number of CXLs for benomyl, carbendazim and thiophanate-methyl are established on various plant and animal commodities. The all CXLs are listed only under carbendazim, indicating the source (s) of the data on which the MRL is based. Thiophanate-methyl and benomyl were withdrawn by CAC in 2003 and listed as pesticides of which MRLs (CXLs) or GLs have been deleted by the CAC and for which no MRLs have been proposed.

Thiophanate-methyl/carbendazim was scheduled at the 48th session of the CCPR (2016) for periodic re-evaluation of residues by the 2017 JMPR. The Meeting received on physical and chemical properties, metabolism and environmental fate, residue analysis, use patterns, supervised trials, processing and animal feeding studies from manufacturer. Thailand submitted residue data on mango arising from use of carbendazim.

IDENTITY

ISO common name	Thiophanate-methyl
Chemical name (IUPAC)	Dimethyl 4,4'-(o-phenylene)bis(3-thioallophanate)
Chemical name (CA)	Dimethyl [1,2-phenylenebis (iminocarbonothioyl)] biscarbamate
Company code	NF-44
CAS No.	23564-05-8
CIPAC No.	262

Structural formula



Molecular formula $C_{12}H_{14}N_4O_4S_2$

Molecular weight 342.40 g/mol

Specifications

FAO specifications for thiophanate-methyl (262/WP/S/P, 1993; 262/SC/SP, 1993), carbendazim (263/WP/S, 1991; 263/WG/S, 1991) and benomyl (206/WP/S/F, 1992; 206/WG/S/F, 1992) were published in 1995, 1992 and 1995, respectively.

PHYSICAL AND CHEMICAL PROPERTIES (thiophanate-methyl (TM))

Test or study	Guideline and method	Test material, purity and specification	Findings	Reference
Appearance	EPA guideline 63-2/3/4	Technical purity 97.0%	Pale brown powder with faint sulfuric odour	Nakayama, K., 1990a, 1990b, 1990c ; RD-9024, RD-9023, RD-9025 (all, GLP)
	EPA guideline 63-2/3/4	Pure purity 99.88%	White powder with no odour	Nakayama, K., 1992c, 1992d, 1992e; RD-9213, RD-9215, RD-9214 (all, GLP)
Melting point	CIPAC MT 3	Purity 99.88%	Not determinable; decomposes at 165 °C	Nakayama, K., 1992a; RD-9216 (GLP)
Boiling point			Not required, test substance decomposes before melting	
Relative density	CIPAC MT 3	Purity 99.88%	1.45 at 20 °C	Nakayama, K., 1992b; RD-9217 (GLP)
Vapour pressure	OECD 104 OPPTS 830.7950 JMAFF 9-Nousan-5089	Purity > 99.9%,	Determined by gas saturation method: <9.4 x 10^{-6} Pa (9.5 °C) <8.8 x 10^{-6} Pa (19.6 °C) <9.5 x 10^{-6} Pa (29.8 °C)	Higashida, S. and Kobayashi, H., 1999; RD-IIM001 (GLP)
Henry's law constant	Calculated using water solubility and vapour pressure data	Not applicable	Henry's law H = p × Mw/C H = 1.67 × 10^{-5} Pa × m^3 × mol^{-1} (20 °C) Calculation Vapour pressure: 9 × 10^{-6} Pa (20 °C, 99.9%) Water solubility: 18.5 mg/L (= g/m³) at 20 °C (pH 7, phosphate buffer) (98.23%) MW of TM: 342.40 g/mol	Higashida, S., Kobayashi, H., 1999; RD-IIM001 (GLP). Gomyo, T., 1996a; RD-9629 (GLP)
Water solubility of purified active substance	EC A6 Flask Method, Quantification by HPLC	Pure purity 98.23%	in buffer solutions (20 °C) pH 4: 0.0224 g/L (phthalate buffer) pH 5: 0.0211 g/L (phthalate buffer) pH 6: 0.0207 g/L (phosphate buffer) pH 7: 0.0185 g/L (phosphate buffer) pH 7.5: 0.0168 g/L (phosphate buffer) pH > 8: unstable	Gomyo, T., 1996a; RD-9629 (GLP)
	US EPA 63-8 Flask Method Quantification by	Pure purity 99.88%	40 mg/kg in distilled water (25 °C)	Nakayama, K., 1992f; RD-9219 (GLP)

Test or study	Guideline and method	Test material, purity and specification	Findings	Reference
	HPLC			
	US EPA CG-1500 Flask Method, Quantification by HPLC	Purity >99%	24.6 mg/kg in distilled water (25 °C, pH 6.3)	Nomura, O. and Nakashima, N., 1987; RD-8775 (GLP)
	OECD 105 Flask Method Quantification by HPLC	Purity 99%	21.8 mg/kg in distilled water (25 °C, pH 5.1)	Soeda, Y. and Shiotani, H., 1986a; RD-8659 (GLP)
Solubility in organic solvents	US EPA 63-8 Quantification by HPLC	Purity >99%	At 25 °C, n-Hexane: 0.00047 g/L Xylene: 0.11 g/L Dichloromethane: 0.73 g/L Methanol: 7.8 g/L n-Octanol: 0.18 g/L Acetone: 29.0 g/L Ethyl Acetate: 8.4 g/L	Ishihara, K., 1990a; RD-9014 (GLP)
n-Octanol/ water partition coefficient	OECD 107, Shake Flask Method HPLC measurements	Purity 99.88%	log Pow = 1.40 at 25 °C (distilled water, pH was not reported)	Shiotani, H., 1992; RD-9212 (GLP)
	OECD 107 Shake Flask Method HPLC measurements	Purity 99%	log Pow = 1.40 (distilled water, pH was not reported) log Pow = 1.50 (pH 5) log Pow = 1.52 (pH 6) log Pow = 1.57 (pH 7)	Soeda, Y. and Shiotani, H., 1986b; RD-8660 (GLP)
	EC A.8 Shake Flask Method HPLC measurements	Purity 98.23%	log Pow at 25 °C 1.41 at pH 4 (phthalate buffer) 1.45 at pH 5 (phthalate buffer) 1.47 at pH 6 (phthalate buffer)	Gomyo, T., 1996b; RD-9630 (GLP)
Hydrolysis rate	US EPA Guideline 161-1; BBA Merkblatt No. 55 Part 1	Purity 99.6%	The DT_{50} of TM obtained by interpolation at 25 °C was 867, 36, and 0.7 days at pH 5, 7, and 9, respectively. The major hydrolysis products (22 °C, pH 7 and pH 9) were carbendazim (up to 33% on molar basis, pH 9) and AV-1951 (up to 22% on molar basis, pH 9).	Soeda, Y. and Nomura, O., 1986; RD-8679 (non-GLP)
Dissociation in water of purified active substance	OECD 112 Conductometric method was used.	Purity >99%	pKa = 7.28 at 25 °C	Ishihara, K., 1990b; RD-9016, RD-9857 (all, GLP)
Photo-degradation in water Quantum yield	US EPA FIFRA Guideline No. 161-2	[Phenyl-^{14}C] TM 15 mCi/mmol 99%	The DT_{50} of TM, 2.17 days (in sterilised aq. solutions, at pH 5, at 10 mg/L, outdoor in Japan). The DT_{50} at 40°N latitude, 0.53 days in summer and 2.48 days in winter. The quantum yield was determined to be 5.97×10^{-3}.	Soeda, Y. and Shiotani, H., 1987; RD-8701 (non-GLP)
	US EPA Guidelines Subdivision N No. 161 2 and CG 6000, OPPTS 835.2210	[Phenyl-^{14}C] TM 15 mCi/mmol 99%	The half-life of TM, 2.17 days (in sterilised aq. solutions, at pH 5, at 10 mg/L, in Japan, at 35°N latitude and 139°E longitude in December 1986). The DT_{50} value at 40°N latitude, 0.99 days in summer and 5.044 days in winter. The quantum yield was determined to be 3.84×10^{-3}.	Shiotani, H., 2003; RD-03185 (non-GLP)
Dissociation in water of purified active substance	OECD 112 Conductometric method was used.	Pure purity >99%	pKa = 7.28 at 25 °C	Ishihara, K., 1990b; RD-9016, RD-9857 (all, GLP)

Test or study	Guideline and method	Test material, purity and specification	Findings	Reference
Flammability	EC A.10	Purity, 98.23%	Not highly flammable; in the burning test the flames extinguished immediately	Krips, H.J., 1996a; RD-9657 (GLP)
Self-ignition	EC A.16	Purity 98.23%, technical	No self-ignition of the test substance; melted and changed into a black residue	Krips, H.J., 1996b; RD-9658
Explosive Properties	EC A.14	97.9% technical	Not explosive with respect to thermal sensitivity, shock and friction.	Pointer, C., 2014; RD-02837 (GLP)

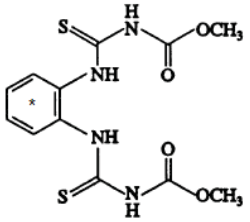
Formulations

Thiophanate-methyl is primarily available in suspension concentrate (SC), wettable powder (WP) and water dispersible granule (WG) formulations.

Formulations	Active ingredient content
Topsin M SC	500 g/L
Topsin M WP	700 g/kg
Topsin M WG	700 g/kg

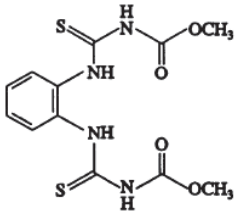
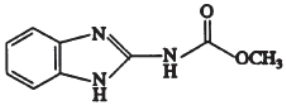
METABOLISM AND ENVIRONMENTAL FATE

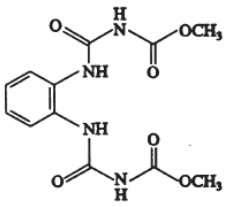
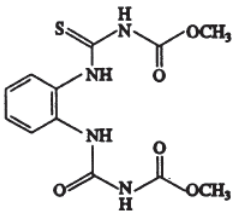
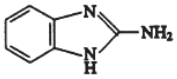
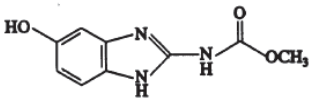
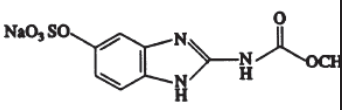
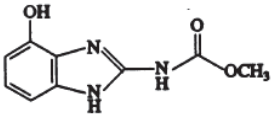
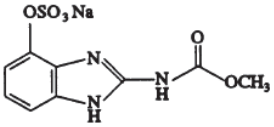
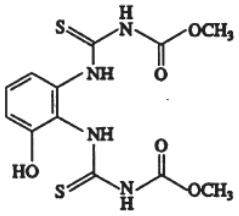
The metabolism of thiophanate-methyl was investigated using the following [^{14}C] labeled test materials:

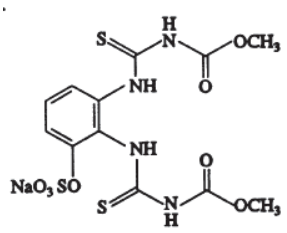
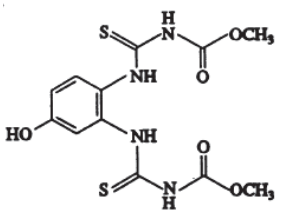
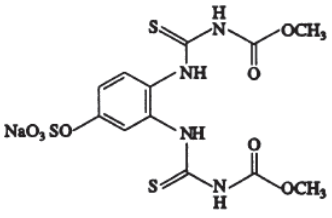
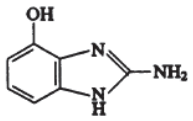
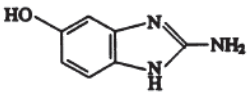
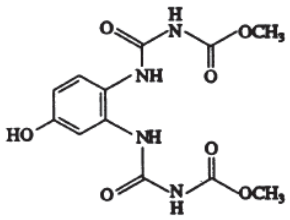
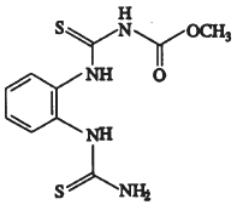


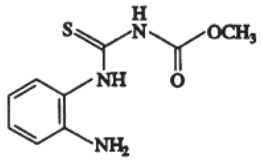
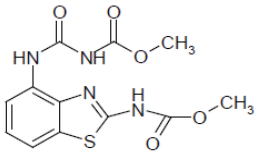
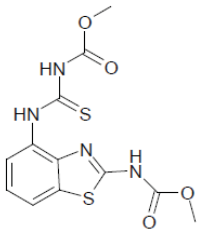
The chemical names and structures of the major degradation compounds arising from the metabolism of thiophanate-methyl are presented in Table 1.

Table 1 Degradation compounds from metabolism of thiophanate-methyl in plants, animals and environment

Chemical name	Abbreviation	Structure	Found in:
Dimethyl 4,4'-(o-phenylene)bis(3-thioallophanate)	TM		Soya bean, green bean, sugar beet, apple, grape, hens
Methyl benzimidazol-2-ylcarbamate	MBC		Soya bean, wheat, green bean, lima bean, sugar beet, grape, carrot (rotational), hen, soil (aerobic, photolysis), water (hydrolysis)

Chemical name	Abbreviation	Structure	Found in:
dimethyl[(1,2-phenylene) bis(iminocarbonyl)]bis(carbamate)	FH-432; allophanate		Soya bean, green bean, sugar beet, apple, grape, carrot (rotational), wheat (rotational), lettuce (rotational), soil (aerobic)
methyl N-[2-(N'-methoxycarbonylthioureido) phenyl aminocarbonyl]-carbamate	DX-105		Soya bean, green bean, apple, grape, soil (aerobic)
2-Aminobenzimidazole	2-AB		Apple, tomato, wheat (rotational)
	5-OH-MBC		Apple, grape, hens
	5-OH-MBC-S		hens
	4-OH-MBC		apple
	4-OH-MBC-S		
	3-OH-TM		

Chemical name	Abbreviation	Structure	Found in:
	3-OH-TM-S		hens
	4-OH-TM		Apple, hens
	4-OH-TM-S		hens
	4-OH-2-AB		Apple, hens
	5-OH-2-AB		Apple, wheat (rotational), hens
	4-OH-FH-432		hens
methyl-N-[2-(thioureido)phenylaminocarbonothioyl] carbamate	AV-1951		Apple, water (hydrolysis),

Chemical name	Abbreviation	Structure	Found in:
	FH-73		Apple, hens
Methoxy-N-{4-[(methoxycarbonylamino)carbonyl amino]-benzothiazol-2-yl}carboxamide	CM-0237		Soil (aerobic)
{4-(3-methoxycarbonyl-2-thioureido)benzothiazol-2-yl} carbamic acid methyl ester	CM-0238		Soil (aerobic)

Plant metabolism

Metabolism data on soya bean, snap bean, sugar beet, wheat, lima bean, apple, tomato and grape were provided by manufacturer. The soya been and green bean studies were performed prior to the implementation of GLP.

Guava

Soya bean

The fate of ^{14}C-thiophanate-methyl (label position not given) in soya bean plants (variety, *Toyosuzu*) was studied under two different conditions (non-GLP; Anonymous, 1977a; Report No. RD-8970). In experiment A., soya bean plants with 3.5–4.5 cm pods were treated once, until run-off, with 700 mg ai/L suspension of ^{14}C-TM (14.3 µCi/mg) mixed with 70% TM wettable powder. The treated plants were placed outdoors during the day but kept inside at night. In experiment B, soybean plants (3–4 cm pods) were treated once, until run-off, with solutions of 50 or 70 mg ai/L of TM technical in acetone-water (1:1). The treated plants were divided into two groups: for group 1, kept as experiment A; for group 2, kept in a greenhouse. Pods and leaves were collected one hour (only experiment B), one week and two weeks after treatment.

Plant samples (pods and leaves) were dipped in 20 mL methanol for ten minutes to remove surface residue. The plant sample after methanol stripping was extracted with methanol by homogenization. Radioactivity in the methanol stripping solution and extracts was measured by LSC.

The methanol stripping solution and the extracts each were partitioned with n-hexane, subsequently, dichloromethane. The water-methanol fraction was partitioned with ethyl acetate and for the dichloromethane fraction (50 mL), 1 N hydrochloric acid (20 mL) was added and shaken for five minutes and then partitioned. The resulting final fractions (CH_2Cl_2 fraction, water fraction, ethyl acetate fraction and hexane fraction, see Table 2) from the methanol stripping solution and the extracts were combined. The combined water fraction was further partitioned with dichloromethane after neutralization. In experiment A, radioactivity was determined by LSC and HPLC-UV/FD was used for characterisation of metabolites. In non-labelled experiment A, HPLC-UV/FD was used for

determination of metabolites. As reference compounds, TH, MBC, FH-432, DX-105 and 2-AB were used. The results are shown in Tables 2–4.

Table 2 Extraction of radioactivity in soya bean following application of ^{14}C-TM (700 mg ai/L)

Experiment A	TRR(mg eq/kg)[a]	% TRR								
		Water-Methanol					Hexane*	Total	Ext.[b]	Residue
		Dichloromethane [c]			Water-Methanol					
		Dichloro-methane*	Water*		Ethyl acetate*	Water				
			Dichloro-methane	Water						
Leaves (7 days)	1.26 (258 ppm)	83.8	11.1	2.6	0.9	na	1.6	100	91.6	8.4
Leaves (14 days)	0.685 (156 ppm)	78.2	14.8	3.8	1.0	na	2.2	100	91.7	8.3
Pods (14 days)	0.230 (53 ppm)	86.0	9.5	2.7	0.4	na	1.4	100	91.7	8.3

[a] TM equivalent

[b] Total radioactivity was counted from the methanol stripping solution and soya bean extract. Of 92% extracted, 90-95% was counted in the methanol stripping solution.

[c] Partitioned after addition of 1 N HCl solution

* Fractions of methanol stripping solution and soya bean extract were combined

na: not analysed

Table 3 Metabolites in soya bean following application of ^{14}C-TM (700 mg ai/L): Exp. A

Experiment A: Metabolites	Leaves (7 DAT) (1.26 mg eq/kg)		Leaves (14 DAT) (0.685 mg eq/kg)		Pods (14 DAT) (0.230 mg eq/kg)	
	%[a]	mg eq/kg [b]	%	mg eq/kg	%	mg eq/kg
CH_2Cl_2 fr.	83.8		78.2		86.0	
TM	81.8	1.03	73.1	0.501	86.1	0.198
DX-105	0.8	0.010	1.0	0.007		nd
FH-432	1.3	0.016	3.9	0.027		nd
CH_2Cl_2 fr.[c]	11.1		14.8		9.5	
MBC	11.0	0.138	15.0	0.103	9.4	0.022
EtOAc fr	0.9		1.0		0.4	
2-AB		nd		nd		nd

[a] Percentage (%) over total detection analysed by HPLC-UV/FD

[b] TM equivalent

[c] Fraction obtained from partitioning after addition of 1 N HCl solution

nd: not detected

In experiment A (outdoor, sprayed with ^{14}C-TM mixed with a 70% TM WP), total radioactivity comprised of 92% extracted radioactivity and 8% remaining in unextracted residue. Majority (90–95%) of 92% extractability was counted in in methanol stripping solution, and. Total radioactive residues (TRRs) in soybean leaves decreased from 1.26 mg eq/kg (7 DAT) to 0.685 mg eq/kg (14 DAT) over time. TRR in pods (14 DAT) was 0.230 mg eq/kg.

In pods (14 DAT), parent compound was present at 86.1% (0.198 mg/kg) of the total detection (%, ratio over total HPLC detection). MBC was found at 9.4% (0.022 mg eq/kg) of the total detection.

In leaves, parent TM decreased from 81.8% (1.027 mg/kg) at 7 DAT to 73.1% (0.501 mg/kg) at 14 DAT, of the total detection. MBC was detected at 11.0% (0.138 mg eq/kg) at 7 DAT and 15.0% (0.103 mg eq/kg) at 14 DAT. DX-105 and FH-432 were detected only in leaves and the amounts were very small, less than 1.0% (0.007 mg eq/kg) and 3.9% of the total detection, respectively. 2-AB was not detected in soya bean pods and leaves.

In non-labelled experiment B (outdoor and indoor experiments with TM technical in 50% aqueous acetone), the residues were analysed by HPLC-UV/FD. Percentage value represented ratio over total HPLC detection.

In the indoor pods (14 DAT; spray conc. of 50, 700 mg ai/L), the parent was determined at 0.5 mg/g (31.2%; 50 mg ai/L) to 12.3 mg/kg (69.5%, 700 mg ai/L) and MBC determined at 1.1 mg eq/kg (68.8%; 50 mg ai/L) and 4.5 mg eq/kg (25.4%, 700 mg ai/L). In the 14 DAT indoor pods, residue levels of FH-432 and DX-105 detected only in higher spray concentration were 0.6 mg eq/kg (3.4%) and 0.3 mg eq/kg (1.7%), respectively.

In indoor leaves (14 DAT; spray conc. of 50, 700 mg ai/L), the parent was determined at 3.6 mg/kg (32.1%; 50 mg ai/L) and 120 mg/kg (75.0%; 700 mg ai/ha) and MBC determined at 7.0 mg eq/kg (62.5%; 50 mg ai/L) and 33.8 mg eq/kg (21.1%; 700 mg ai/l). In the 14 DAT indoor leaves, DX-105 was detected at 0.6 mg eq/kg (5.4%, 50 mg ai/L) and 1.3 mg eq/kg (50.8%, 700 mg ai/L). FH-432 was detected only in higher spray concentration, 5.0 mg eq/kg (3.1%).

The detected residue level of total or parent compound was higher in indoor pods. At a spray concentration of 700 mg ai/L, the total detection was 17.7 mg eq/kg in indoor pods and 5.4 mg eq/kg in outdoor pods and residue value of parent compound was 12.3 mg/kg in indoor pods and 3.1 mg/kg in outdoor pods. This indicated a faster degradation of the parent compound under outdoor conditions. For leaves, however, such difference in residue levels was not shown.

Table 4 Metabolites in soya bean following application of TM technical in aq. acetone: Exp. B

Experiment B: Metabolites	Group I (outdoor)				Group II (indoor)					
	DAT 7		DAT 14		DAT 0		DAT 7		DAT 14	
	%	mg eq/kg	%	mg eq/kg	%	mg eq/kg	%	mg eq/kg	%	mg eq/kg
Pods										
50 mg ai/L										
TM		nd[c]		nd	95.0	3.8	43.5	1.0	31.2	0.5
DX-105		nd		nd		nd		nd		nd
FH-432		nd		nd		nd		nd		nd
MBC		nd		nd	5.0	0.2	56.5	1.3	68.8	1.1
2-AB		nd		nd		nd		nd		nd
Total					100	4.0	100	2.3	100	1.6
700 mg ai/L										
TM	73.6	17.6	57.4	3.1	95.2	15.9	87.4	39.4	69.5	12.3
DX-105		nd		nd		nd		nd	1.7	0.3
FH-432	1.7	0.4	5.6	0.3		nd	0.7	0.3	3.4	0.6
MBC	24.7	5.9	37.0	2.0	4.8	0.8	12.0	5.4	25.4	4.5
2-AB		nd		nd		nd		nd		nd
Total	100	23.9	100	5.4	100	16.7	100	45.1	100	17.7
Leaves										
50 mg ai/L										
TM	8.9	1.0	2.3	0.3	97.6	66.0	40.0	4.8	32.1	3.6
DX-105		nd		nd		nd		nd	5.4	0.6
FH-432	18.8	2.1	18.6	2.4		nd		nd		nd
MBC		8.1	79.1	10.2	2.4	1.6	60.0	7.2	62.5	7.0
2-AB		nd		nd		nd		nd		nd
Total	100	11.2	100	12.9	100	67.6	100	12.0	100	11.2
700 mg ai/L										
TM	71.9	267	54.4	189	98.8	500	82.3	163	75.0	120
DX-105	6.3	23.5	6.4	22.1		nd	2.9	5.8	0.8	1.3
FH-432	3.1	11.4	8.7	30.3		nd	2.1	4.2	3.1	5.0
MBC	18.7	69.4	30.5	106	1.2	5.9	12.6	25.0	21.1	33.8
2-AB		nd		nd		nd		nd		nd
Total	100	371	100	347	100	506	100	198	100	160

Percentage (%) over total detection analysed by HPLC-UV/FD

Green bean

Green snap beans (variety, Spartan arrow) were planted in pots in greenhouse when pods were growing 3–4 cm long (Anonymous, 1977b; Report No. RD-8969). At that time, the plants were treated with ^{14}C-thiophanate-methyl (label position not given) in 1:1 acetone/water. Each plant was sprayed with 20 mL containing *ca.* 1 mg TM (14.3 μCi/mg) equivalent to 50 mg ai/L. In addition, 70% TM WP formulation (non-labelled TM) was sprayed at a concentration of 1,680 mg ai/L on the soya bean plants under the same conditions. Samples were collected two weeks after treatment and stored frozen until analysis for *ca.* one year.

Pods (*ca.* 20 g) or leaves (*ca.* 5 g) was dipped in 50 mL methanol for 10 minutes and then washed with 10 mL of water. The methanol solution was combined. Analytical procedures were the same with the soybean study described above. LSC was used for determination of radioactivity. TLC radio scanner was used for characterisation. For non-labelled TM experiment, HPLC-UV was used for determination of TM, MBC, DX-105, FH-432 and 2-AB. The results are shown in Tables 5–7.

Table 5 Extraction of radioactivity in green beans following application of ^{14}C-TM (50 mg ai/L of 50% aqueous acetone)

Sample	TRR (mg eq/kg)[a]	% TRR								
		Water-Methanol					Hexane	Total	Ext.[b]	Residue
		Dichloromethane[c]			Water-Methanol					
		Dichloro-methane[*]	Water[*]		Ethyl acetate[*]	Water				
			Dichloro-methane	Water						
Pods	0.47	29.4	52.8	9.4	4.8	na	3.6	100	91.0	9.0
Leaves	23.4	27.5	60.3	4.3	4.5	na	3.4	100	94.2	5.8
Stems	0.96	33.6	49.3	8.9	5.3	na	2.9	100	92.4	7.6

[a] TM equivalent

[b] Total radioactivity was counted from the methanol stripping solution and green bean extract. Of *ca.* 93% extracted, 70-80% was counted in the methanol stripping solution.

[c] Partitioned after addition of 1 N HCl solution

[*] Fractions of methanol stripping solution and green bean extract were combined

In the green beans (pods, leaves and stem at 14 DAT), radioactivity comprised of extracted *ca.* 93% and *ca.* 7% remained in unextracted residue. Of extracted 93%, 70–80% was counted in the methanol stripping solution. The TRRs in pods, leaves and stems were 0.47 mg eq/kg, 23.4 mg eq/kg and 0.96 mg eq/kg, respectively.

The parent TM (including DX-105 of < 10%) was present at 18.2% TRR (0.086 mg eq/kg) in pods, 10.0% TRR (2.34 mg eq/kg) in leaves and 18.1% TRR (0.174 mg eq/kg) in stems. MBC was found at 48.0% TRR (0.226 mg eq/kg) in pods, 56.9% TRR (13.3 mg eq/kg) in leaves and 45.3% TRR (0.435 mg eq/kg) in stems. FH-432 was detected 6.7–9.2% TRRs in the three parts of green beans. 2-AB was not detected in any parts of bean.

Table 6 Metabolite components in green beans following application of ^{14}C-TM (50 mg ai/L of aq. acetone solution)

Metabolites	Pods (14 DAT) (0.47 mg eq/kg)		Leaves (14 DAT) (23.4 mg eq/kg)		Stems (14 DAT) (0.96 mg eq/kg)	
	% TRR	mg eq/kg[a]	% TRR	mg eq/kg	% TRR	mg eq/kg
n-Hexane fr.	3.4		3.4		2.9	
CH_2Cl_2 fr.	29.4		27.5		33.6	
TM (+DX-105)[b]	18.2	0.086	10.0	2.34	18.1	0.174
FH-432	6.7	0.031	8.1	1.90	9.2	0.088
Others	4.5		9.4		6.3	
CH_2Cl_2 fr.[c]	52.8		60.3		49.3	
MBC	48.0	0.226	56.9	13.3	45.3	0.435

Metabolites	Pods (14 DAT) (0.47 mg eq/kg)		Leaves (14 DAT) (23.4 mg eq/kg)		Stems (14 DAT) (0.96 mg eq/kg)	
	% TRR	mg eq/kg[a]	% TRR	mg eq/kg	% TRR	mg eq/kg
Others	4.8		3.4		4.0	
EtOAc fr.	4.8		4.5		5.3	
Aq. fr	9.4		4.3		8.9	
Total	100		100		100	

[a] TM equivalent

[b] In additional non-labelled TM experiment, included in the report, DX-105 was determined by HPLC-UV at < 10% of TM fraction.

[c] Fraction obtained from partitioning after addition of 1 N HCl solution

Table 7 Metabolites in green beans following application of non-labelled TM 70% WP (1,680 mg ai/L)

Metabolites	Pods (14 DAT)		Leaves (14 DAT)		Stems (14 DAT)	
	%[a]	mg eq/kg[b]	%	mg eq/kg	%	mg eq/kg
TM	58.0	4.7	91.2	440	81.1	43.8
DX-105	9.9	0.8	0.5	2.2	1.7	0.9
FH-432	nd	nd	0.2	1.1	0.5	0.3
MBC	32.1	2.6	8.1	39	16.7	9.0
2-AB	nd		nd[c]	nd	nd	nd
Total residue as TM	100	8.1	100	482.3	100	54.0

[a] Percentage (%) over total detection analysed by HPLC-UV

[b] TM equivalent

[c] not detected, < 0.04 mg eq/kg

In an additional experiment (outdoor and indoor), conducted with non-labelled TM 70% WP (1,680 mg ai/L), TM, MBC, DX-105, FH-432 and 2-AB in pods, leaves and stems (14 DAT) were analysed by HPLC-UV. Percentage value represented a ratio over total HPLC detection.

The concentrations of parent compound were 4.7 mg/kg (58.0%) in pods, 440 mg/kg (91.2%) in leaves and 43.8 mg/kg (81.1%) in stems. MBC was determined at 2.6 mg eq/kg (32.1%), 39 mg eq/kg (8.1%) in leaves, 9.0 mg eq/kg (16.7%) in stems. DX-105 was present at levels of 0.8–2.2 mg eq/kg (0.5–9.9%) in the three parts of beans. FH-432 was detected 0.3–1.1 mg eq/kg (0.2–0.5%) in stems and leaves. 2-AB was not detected in any parts of the bean plants (< 0.04 mg eq/kg).

Sugar beet

^{14}C-Thiophanate-methyl (phenyl ring label) was applied to sugar beets (variety, SS-NBZ) as a 70% WP formulation with three foliar sprays (21-days intervals) at a rate of 0.39 kg ai/ha (Malik, N.S.A and Wright, M.C., 1992a; Report No. RD-II01232). The foliage and roots were collected separately on 21 days after final application (DALA). In addition, a few plants were sampled immediately before and after each application. The foliage samples were immediately frozen after harvest and kept frozen until arrival at an analytical laboratory. The root samples were refrigerated after harvest and shipped on blue ice to an analytical laboratory (for two weeks, under refrigeration conditions). At the analytical laboratory, the roots were rinsed with water and the stem portion was separated from the roots. All samples were then frozen, pulverized with liquid nitrogen and stored frozen until analytical analysis.

Plant samples were extracted by blending with a solvent mixture of methanol:Tris buffer:chloroform (11:5:5, v/v/v). The chloroform fraction from each sample was concentrated and then partitioned with a mixture of hexane and acetonitrile (1:1, v/v). Non-extracted residues in the

PES (post extraction solids) from the root and foliage were subjected to cellulase enzyme digestion, followed by 1 N and 6 N HCl hydrolysis and 1 N sodium hydroxide hydrolysis. The aqueous fraction obtained from the 1 N NaOH hydrolysate was partitioned with ethyl acetate. The stem was subjected only to the step of cellulase treatment. Radioactivity was determined by combustion analysis and LSC. For characterization, HPLC and TLC were used. Results are shown in Tables 8-12.

Table 8 Total radioactive residues in sugar beet samples

Sample at application time	TRR (mg eq/kg)		Sample at harvest (21 DALA)	TRR (mg eq/kg)
	Pre-application	Post-application		
Foliage			Root	0.116
Application 1	0.002	7.16	Root rinse [a]	0.026
Application 2	0.969	19.2	Stem	2.82
Application 3	4.71	28.8	Foliage	3.29

[a] For root rinses, further analysis was not performed.

In sugar beets foliarly treated with ^{14}C-TM (phenyl ring label), TRRs were present at 0.116 mg eq/kg in root, 0.026 mg eq/kg in root rinse, 2.82 mg eq/kg in stem and 3.29 mg eq/kg in foliage. The 42.7–67.2% of the TRRs in root, stem and foliage samples was extracted in chloroform fraction and most of which was transferred to acetonitrile fraction. 4.1–10.8% of the TRRs distributed into the MeOH/Tris buffer fraction, and 22.0–51.1% of the TRRs remained in post extraction solids.

In root, foliage and stem, 5.2–7.5% TRR was released from the post extraction solids by cellulase digestion. In root and foliage, acid and base hydrolyses with 1 N HCl, 6 N HCl and 1 N NaOH further released 9.5–19.1% TRR and 0.8–2.2% TRR, and 0.8–5.3% TRR, respectively. Radioactive residues remained in the final PESs were 4.1–16.6% TRRs.

Table 9 Extraction of radioactivity in sugar beet following application of ^{14}C-TM

Fraction	Root		Foliage		Stem	
	% TRR [a]	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
$CHCl_3$	42.7		67.2		44.9	1.26
ACN	42.3	0.049	66.5	2.19	44.7	1.26
Hexane	0.4	0.001	0.7	0.023	0.2	0.006
MeOH/Tris	6.7	0.008	10.8	0.354	4.1	0.115
PES (cellulase)	50.6		22.0		51.1	1.44
Aqueous	7.5	0.009	5.2	0.171	6.7	0.189
PES (1 N HCl) (for stem, final PES)	43.1		16.5		44.4	1.25
Aqueous	19.1	0.022	9.5	0.313		
PES (6 N HCl)	24.0		7.3			
Aqueous	2.2	0.002	0.8	0.027		
PES (1 N NaOH)	21. 9		6.5			
PES[a] (for root, final PES)	16.6	0.019				
Aqueous	5.3		0.8			
EtOAc	2.4	0.003	0.4	0.014		
Aqueous	2.9	0.003	0.4	0.012		
PES[b]						
PES[a] and PES[b,] combined			5.7			
Aqueous			1.6	0.053		
PES (for foliage, final PES)			4.1	0.134		
Total	100	0.116	100	3.29	100	2.818

[a] All values were normalized as a total recovery of 100%. Total recovery of radioactivity was actually measured as 111% in root, 107% in foliage and 123% in stem.

Table 10 Metabolites in sugar beet root following application of ^{14}C-TM

Fraction	TM		MBC		2-AB		Not anal.		Total	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
MeOH/Tris							6.7	0.008	6.7	0.008
ACN	26.9	0.031	15.4	0.018					42.3	0.049
Hexane							0.44	0.001	0.4	0.001
Aq. of cellulase hydrolysate							7.5	0.009	7.5	0.009
Aq.of 1 N HCl hydrolysate					19.1	0.022			19.1	0.022
Aq. of 6 N HCl hydrolysate							2.2	0.002	2.2	0.002
EtOAc from part. of 1 N NaOH aq.							2.4	0.003	2.4	0.003
Aq. from part. of 1 N NaOH aq.							2.9	0.003	2.91	0.003
Final PES							16.6	0.019	16.6	0.019
Total	26.9	0.031	15.4	0.018	19.1	0.022	38.7	0.045	100	0.116

Table 11 Metabolites in sugar beet foliage following application of ^{14}C-TM

Fraction	TM		MBC		FH-432		2-AB		Total[a]	
	% TRR	mg /kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
MeOH/Tris					7.8	0.258			10.8	0.354
ACN	41.1	1.35	25.5	0.838					66.5	2.19
Hexane			0.7	0.023					0.7	0.023
Aq.of cellulase hydrolysate					5.2	0.171			5.2	0.171
Aq. of 1 N HCl hydrolysate							9.5	0.313	9.5	0.313
Aq. of 6 N HCl hydrolysate							0.8	0.026	0.8	0.028
EtOAc from part. of 1 N NaOH									0.4	0.012
Aq. from part. of 1 N NaOH aq.							0.4	0.014	0.4	0.014
Aq. of combined PES									1.6	0.053
Final PES									4.1	0.134
Total	41.1	1.35	26.2	0.861	13.0	0.428	10.7	0.353	100[b]	3.29[b]

[a] Total included: In MeOH/Tris fraction: metabolite A, 2.9% TRR (0.096 mg eq/kg)

In AQ from 6 N HCl hydrolysate: 5-OH-2-AB, 0.02% TRR (0.001 mg eq/kg); metabolite E, 0.03% TRR (0.001 mg eq/kg)

IN EtOAC fraction, partitioning 1 N NaOH AQ: metabolite E, 0.4% TRR (0.012 mg eq/kg)

[b] Sum of radioactivity in the fractions

Table 12 Metabolites in sugar beet stem following application of ^{14}C-TM

Fraction	TM		MBC		FH-432		Not anal.		Total	
	% TRR	mg /kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
MeOH/Tris					4.1	0.115			4.1	0.115
ACN	21.1	0.593	23.6	0.665					44.7	1.26
Hexane							0.2	0.006	0.2	0.006
Aq. of cellulase hydrolysate					6.7	0.189			6.7	0.189
Final PES							44.4	1.26	44.4	1.26
Total	21. 1	0.593	23.6	0.665	10.8	0.304	44.6	1.26	100	2.82

The parent compound was present at levels of 26.9% TRR (0.031 mg/kg) in root, 41.1% (1.35 mg/kg) in foliage and 21.1% TRR (0.593 mg/kg) in stem. MBC was found as a major metabolite in the all samples, representing 15.4% TRR (0.018 mg eq/kg) in root, 25.5% TRR (0.838 mg eq/kg) and 23.6% TRR (0.665 mg eq/kg) in stem. Both parent and MBC compounds were found in acetonitrile extraction fraction.

Allophanate (FH-432) metabolite was found in foliage (13.0% TRR, 0.428 mg eq/kg) and stem (10.8% TRR, 0.304 mg eq/kg). In HPLC and TLC analysis, it was shown that allophanate could be easily converted to MBC during concentration prior to TLC analysis even under inert (argon environment) conditions. Another metabolite 2-AB was found in acid and base hydroylsates, representing 19.1% TRR (0.022 mg eq/kg) in root and 10.7% TRR (0.353 mg eq/kg) in foliage However, it was noted that a significant amount of 2-AB could be artefacts as it occurred only in acid/base hydrolysis conditions. Other metabolites, 5-OH-2-AB, metabolite A and E, were found in foliage, but present at a very small amount of 0.02–2.9% TRR.

Identified parent and metabolite residues amounted to 61.4% TRR in root, 91.0% TRR in foliage and 55.5% TRR in stem. Of the unidentified TRR in root (38.6%), bio-unavailable residues (base hydrolysis residues plus non-hydrolysed) were found to be 21.2% TRR of the root TRR.

To evaluate the stability of the acetonitrile extract for foliage sample, the extract was stored at different conditions for 4 weeks. Extract stored at 0–4 °C resulted in *ca.* 26% degradation of the parent compound. However, degradation of parent compound in the extract stored at -10 °C was negligible. Standard solution was stable under the same conditions. Thus this implies that catalysing factors seem to be present in plant tissues that impact the breakdown of the parent chemical.

This study showed that enzyme and acid/base digestion of PES released 2-AB and 5-OH-2-AB. A significant amount of those compounds could be artefacts of acid/base hydrolysis conditions. MBC can be readily formed from the parent compound, suggesting that its presence, in part, be due to the sample analytical processed employed.

From the results, metabolic pathway of TM was suggested as follows:

TM can be oxidized to form allophanate (FH-432), followed by subsequent association with cellulose and starch. Allophanate can further undergo degradative cyclization to form MBC and finally conjugation with monosaccharide and other endogenous plant biomolecules. The third major pathway involves decarbamilation of either MBC or hydroxylated MBC, which is conjugated with endogenous matrices, such as cellulose, hemicellulose, or lignin.

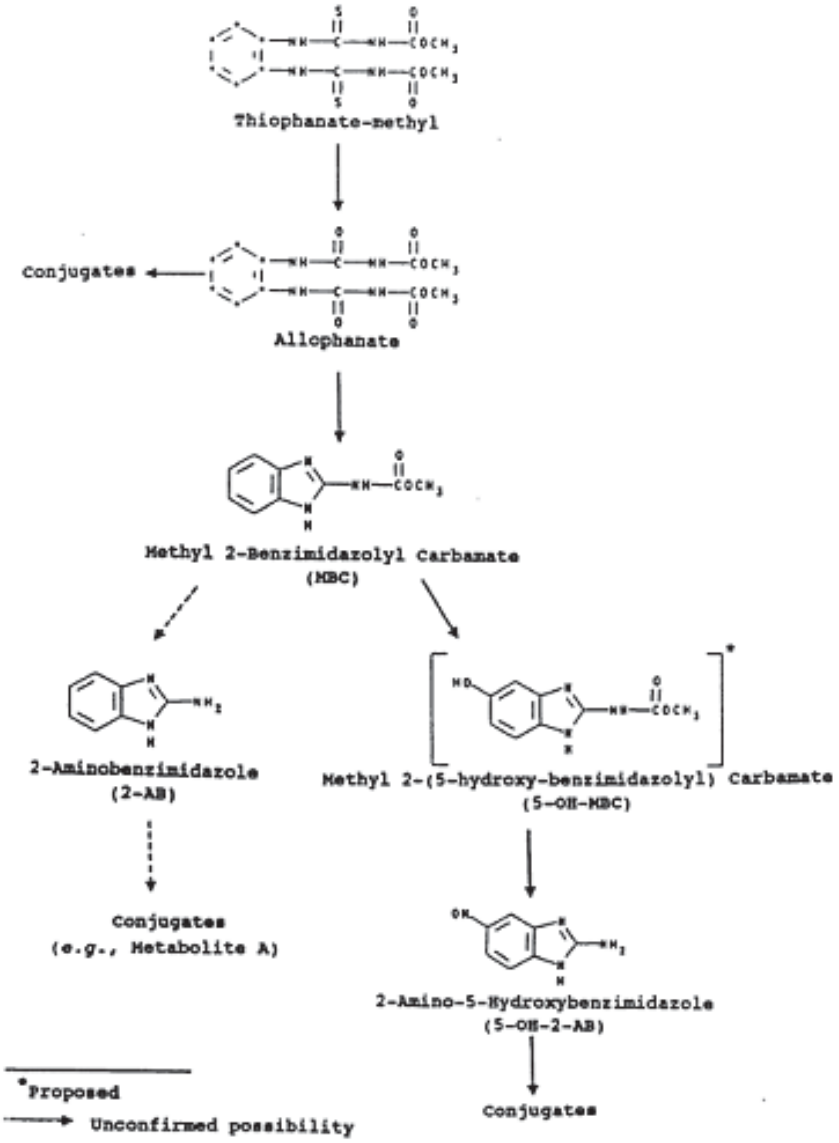


Figure 1 Proposed metabolic pathway of thiophanate-methyl in sugar beet

Wheat

A single-spray application of ^{14}C-thiophanate-methyl (phenyl ring label, formulated as 70% WP) was made to spring wheat plants (variety, *wheaton*) growing in a field plot (Davis, M.L., *et al*., 1992; Report No. RD-II01231). A rate of 0.75 kg ai/ha was applied to wheat plants just before the stem elongation stage and wheat samples were taken after 0 day, 28 days (foliage) and 69 days (straw, grain) of application of test substance. Wheat plant sample (0 days) frozen on dry ice was received at an analytical laboratory. Foliage and straw/grain samples refrigerated were received at an analytical laboratory (refrigerated for 2-3 days after harvest until receipt). Foliage and straw samples were rinsed with a solution of 1 N HCl:acetone (1:1, v/v) and 0.7 N HCl:acetone (1:1, v/v), respectively. The rinsed samples were air-dried. All samples were frozen, homogenized cryogenically with a liquid nitrogen slurry and kept at -20 °C for storage during the course of the study. Radioactivity was determined by LSC and combustion analysis. HPLC and TLC were used for characterization.

Grain sample was not extracted due to an insignificant amount of radioactive residues. Foliage and straw samples were extracted with a mixture of methanol: Tris buffer (pH 6.0) (11:5, v/v) and chloroform by shaking in a shaking water bath of 4 °C. The extract was centrifuged and separated to methanol/aqueous, organic (chloroform) phase and pellet (post extraction solids). The chloroform fraction was separated with methanol soluble and methanol non-soluble fraction. The methanol/aqueous fraction was partitioned with ethyl acetate and the resulting aqueous fraction was further purified and fractionized using C18 SPE. Those fractions were subjected to sequential acid hydrolyses with 2 N HCl and 6 N HCl.

To release radioactive residues from the PES, enzyme (with running control) and chemical treatments were applied. PES was extracted with Tris buffer at pH 7 to release soluble proteins, nucleic acids and oligosaccharides and then treated with α-amylase and further enzyme mixture (cellulase, hemicellulose, xylanase, proteinase, cellobiase, β-glucosidase, amyloglucosidase, etc.). The hydrolysate fraction (containing cellulosic materials) was further subjected to partition with ethyl acetate, acid/base hydrolyses and again partition with ethyl acetate. The remained PES was treated with 2 N HCl at 80 °C for 2 hours, and then extracted with dioxane: water (9:1, v/v). For straw, extracted again with dixoane:2 N HCl (9:1, v/v). Lignin precipitation was derived by adding water to the dioxane extract.

To verify extraction efficiency, ^{14}C-TM was fortified in foliage and straw control samples at comparable levels of total radioactivity in the treated samples. Chloroform fraction recovered > 97% in foliage and > 92% in straw, of the total radioactivity. The chloroform fraction was concentrated and mixed with methanol, and precipitation of non-polar materials was caused. The methanol soluble fraction contained most of the extracted radioactivity.

TRRs in wheat samples and the distribution of radioactive residues in each extraction fraction are shown in Tables 13 and 14.

Table 13 Total radioactive residues in spring wheat samples

Sample	TRR (mg eq/kg)
Whole plant (0 days)	9.91
Whole plant (28 days, foliage)	0.359
Whole plant rinsate (28 days, foliage)	0.007 (1.9% TRR)
Grain (69 days)	0.004
Straw (69 days)	1.15
Straw rinsate (69 days)	0.006 (0.5% TRR)

TRRs in spring wheat samples were 9.91 mg eq/kg in whole plant, 0.359 mg eq/kg in foliage and 1.15 mg eq/kg in straw. In wheat grain, the level of TRR was very low (0.004 mg eq/kg). Further analysis was not done for grain. In the rinsate of foliage and straw, 1.9% and 0.5% of the total radioactivity were present, respectively.

In foliage, 5.7% TRR and 14.8% TRR were contained in chloroform fraction and aqueous methanol fraction, respectively. In straw, 8.0% TRR and 10.1% TRR were contained in chloroform fraction and aqueous methanol fraction, respectively. Radioactivity in unextracted residues was 69.5% in foliage and 79.0% in straw.

The aqueous methanol fraction was subjected to exhaustive digestion with strong acid, where radioactive residues in the fraction did not exit as free metabolites or simple conjugates

Table 14 Extraction of radioactivity in wheat plant following application of ^{14}C-TM

Fraction	Foliage (28 DAT) (0.359 mg eq/kg)		Straw (69 DAT) (1.15 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg
Chloroform	5.7		8.0	
Methanol insoluble	2.6	0.009	1.1	0.013
Methanol soluble	3.1 (0.8)[a]	0.011	6.9 (3.8)[a]	0.079
Methanol/Aqueous	14.8		10.1	
Ethyl acetate soluble	2.2	0.010	1.5	0.017
Aqueous soluble	12.6	0.045	8.6	0.099
PES (Tris buffer)	69.5		79.0	
Aqueous (proteins, nucleic acids, oligosaccharides)	2.2	0.008	4.4	0.050
PES (α-amylase)				
Aqueous (starch)	6.1	0.022	10.1	0.116
PES (mixed enzyme)				
Aqueous (incl. cellulosic materials)	11.7*	0.042	14.1*	0.162
PES (2 N HCl)				
Aqueous (cellulosic materials)	10.8* (2.5)[a]	0.039	6.6 (0.2)*	0.076
PES (dioxane)				
Aq.[b], precipitated in water (lignin)	22.9*	0.082	29.4*	0.337
Aq.[b], water soluble (cellulosic)	11.4*	0.041	5.4*	0.062
Final PES	4.4*	0.016	9.0*	0.103
Total recovery	90.0	0.323	97.1	1.12

[a] Value in parenthesis means % TRR of MBC detected.

[b] Dioxane:water (9:1) was used. For straw, extraction was repeated with dioxane:2 N HCl (9:1).

* Ligno-cellulose materials; in total, 61.2% TRR in foliage and 64.5% TRR in straw

Lingo-cellulose materials in wheat foliage and straw were 61.2% TRR (0.220 mg eq/kg) and 64.5% TRR (0.739 mg eq/kg), respectively, indicating that the radioactive residues released by enzymatic and chemical analyses were intrinsically incorporated into cellulosic and lignin type components of the cell wall fraction.

In wheat grain, the TRR was insignificant (< 0.01 mg eq/kg). The parent compound was not found in any analytical fraction. MBC was found in foliage and straw. For foliage, 0.8% TRR was contained in chloroform fraction and 2.5% TRR was in PES. For straw, 3.8% TRR (0.043 mg eq/kg) was contained in chloroform fraction and 0.2% TRR was in PES.

Lima bean

^{14}C-Thiophanate-methyl (phenyl ring label) formulated as 70% WP was applied to lima bean plants (variety, Fordhook 242) in a field plot (Malik, N.S.A. and Wright, M.C., 1992b; RD-II01230). Twice foliar applications were made at a rate of 1.18 kg ai/ha, the first at 30% bloom and the second 7 days later at 100% bloom. The pods were harvested 28 days after the last application (DALA) and the foliage were taken 35 DALA. A few plants were taken immediately before and after each application. Samples were kept frozen after harvest until analysis.

Lima bean pods were rinsed with a mixture of acetone and water (1:1) and then homogenized in liquid nitrogen. Foliage was not rinsed, cut into small pieces and then homogenized in liquid nitrogen.

Pod and foliage samples were extracted with a solvent mixture of methanol:Tris buffer:chloroform (11:5:5, v/v/v) at ice bath. The chloroform fraction was concentrated and then partitioned with a mixture of hexane and acetonitrile (1:1, v/v). The PES from pod and foliage were

subjected to cellulase enzyme digestion and the resulting aqueous fraction was partitioned with ethyl acetate. Aqueous fraction from the partition was further fractionized to aqueous fraction and methanol fraction by using XAD-2 column. For foliage, the PES remained after cellulase digestion was subjected to 1 N HCl hydrolysis, followed by 6 N HCl and 1 N sodium hydroxide hydrolyses. The aqueous fractions from 1 N HCl hydrolysis and 1 N NaOH hydrolysis were partitioned with ethyl acetate. Radioactivity was determined by combustion analysis and LSC. For characterization, TLC and HPLC were used. For identification of a specific metabolite (metabolite A), MS was used. The results are shown in Tables 15-17.

In a fortification experiment of control pods (^{14}C-TM, 0.066 and 2.67 mg/kg) and foliage (^{14}C-TM, 5.39 mg/kg), 94–97% of the fortified radioactivity was partitioned into acetonitrile fraction. The faction was analysed by HPLC, which showed the stability of TM compound under HPLC conditions.

Total residues were present at 0.047 mg eq/kg and 1.36 mg eq/kg in pods (28 DALA) and foliage (35 DALA), respectively. In pods rinsate, the TRR was 0.001 mg eq/kg.

In pods, 11.0%, 45.8% and 43.2% of the TRR were contained in chloroform fraction (most in ACN fraction), MeOH/Tris fraction and PES, respectively. From the PES, 21.4% (0.010 mg eq/kg) was released by cellulase enzyme digestion.

The parent compound and MBC were not found in the pods. The methanol/Tris fraction (45.8% TRR) containing two major HPLC peaks (metabolite C and D) stayed at origin on TLC. From the metabolite C, D fraction treated with cellulase (C, D fraction was obtained from the foliage sample, due to a small amount of pod sample), 5-OH-MBC was released. The metabolite C, D fraction was also treated with 1N and 6N HCl. In the hydrolysates, only 2-AB was detected.

For foliage, 28.4% TRR, 36.4% TRR and 35.2% TRR were contained in chloroform fraction (most in ACN fraction), MeOH/Tris fraction and PES, respectively. From the PES, 4.2% (0.055 mg eq/kg) and 27.6% (0.376 mg eq/kg) of the TRR in foliage were released by cellulase enzyme digestion and by acid/base hydrolyses, respectively. At the end, 3.4% of the total radioactivity was remained in the final PES.

Parent compound was not detected in the foliage. MBC was found at 25.5% TRR (0.348 mg eq/kg), representing 16.2% TRR (0.220 mg eq/kg) in the acetonitrile fraction. MBC was also found in the fractions of hexane, cellulase hydrolysate and acid hydrolysate at levels of 0.6–6% TRRs. Metabolite A (non-conclusive by MS analysis) was found at a high level of 49.6% TRR (0.678 mg eq/kg), most (36.4% TRR) of which was present in the MeOH/Tris fraction. 2-AB was present at 2–8% TRRs only in the fractions after acid and base hydrolyses. For metabolite A, it was very unstable and was converted into 2-AB during the chromatographic workup and/or acid hydrolysis of the extract. For the reason, 2-AB could be artefact of acid and base hydrolyses conditions. Metabolite C, D and 5-OH-MBC were present at very minor levels of 1–3% TRRs in chemical hydrolysates.

Table 15 Total radioactive residues in lima bean samples

Sample at application time	TRR (mg eq/kg)		Sample at harvest	TRR (mg eq/kg)
	Pre-application	Post-application		
Foliage application 1	0.001	5.53	Foliage 35 DALA	1.36
Foliage application 2	4.79	43.5	Pods 28 DALA	0.047
			Pods rinsate	0.001

Table 16 Extraction of radioactivity in lima bean following application of ^{14}C-TM

Fraction	Foliage (1.36 mg eq/kg)		Pods (0.048 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg
$CHCl_3$	28.4		11.0	
ACN	23.5	0.321	9.5	0.004
Hexane	4.8	0.065	1.5	0.001
MeOH/Tris	36.4	0.497	45.8	0.022
PES (cellulase)	35.2		43.2	
Aqueous	4.2		21.4	
EtOAc	0. 8	0.011	1.1	0.001
Aqueous	4.3		20.1	
MeOH	1.8	0.025	5.7	0.003
Aqueous	1.6	0.022	14.6	0.007
PES (1 N HCl, for only foliage)	31.0		21.7 (final PES)	0.010
Aqueous	12.9			
EtOAc	2.3	0.031		
Aqueous	10.6	0.145		
PES (6 N HCl, for only foliage))	18.1			
Aqueous	3.9	0.053		
PES (1 N NaOH, for only foliage))	14.2			
Aqueous				
EtOAc	3.1	0.042		
Aqueous	7.7	0.105		
PES				
PES				
PES and PES	3.4 (final PES)	0.046		
Total, summed	100		100	
Total recovery	98.2		114	

Table 17 Metabolites in lima bean foliage following application of ^{14}C-TM

Fraction	MBC		5-OH-MBC		2-AB		Metabolite A		Metabolite C, D		Total [a]	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
MeOH/Tris							36.4	0.497			36.4	0.497
ACN	16.2	0.220					7.4	0.101			23.5	0.321
Hexane	0.68	0.009					3.8	0.052			4.8	0.066
EtOAC of cellulase hydrolysate	0.58	0.008					0.2	0.003			0.78	0.011
MeOH of cellulase hydrolysate							1.8	0.025			1.8	0.025
Aq. of cellulase hydrolysate											1.6	0.022
EtOAc of 1 N HCl hydrolysate	0.9	0.013							1.4	0.018	2.3	0.031
Aq. of 1 N HCl hydrolysate	5.9	0.081			4.7	0.064					10.6	0.145
Aq. of 6 N HCl hydrolysate	1.2	0.017	1.03	0.014	1.7	0.023					3.9	0.054
EtOAc of 1 N NaOH hydrolysate									1.7	0.023	3.1	0.042
Aq. of 1 N NaOH hydrolysate					7.7	0.105					7.7	0.105
Final PES											3.4	0.046
Total	25.5	0.348	1.03	0.014	14.1	0.192	49.6	0.678	3.1	0.041	100	1.37

The parent compound was not found in any fraction.

2-AB: a possible artefact derived during acid and base hydrolyses

[a] Total included the following TRR values: metabolite B (0.3% TRR, 0.005 mg eq/kg) was present in hexane fraction. As non-analysed TRR values, there are 1.6% TRR (0.022 mg eq/kg) in cellulase hydrolysate aqueous fraction, 1.4% TRR (0.019 mg eq/kg) in 1 N NaOH hydrolysate EtOAc fraction, and 3.4% TRR (0.046 mg eq/kg) in final PES.

In this study, parent compound was not found in both pods and foliage. MBC was found only in foliage as a major metabolite. The most major component, metabolite A (polar and unstable compound), C and D were not identified. Considerable part of 2-AB found could be derived at acid and base hydrolyses conditions. For 5-OH-MBC or possibly MBC, it was considered that some could be present as conjugates.

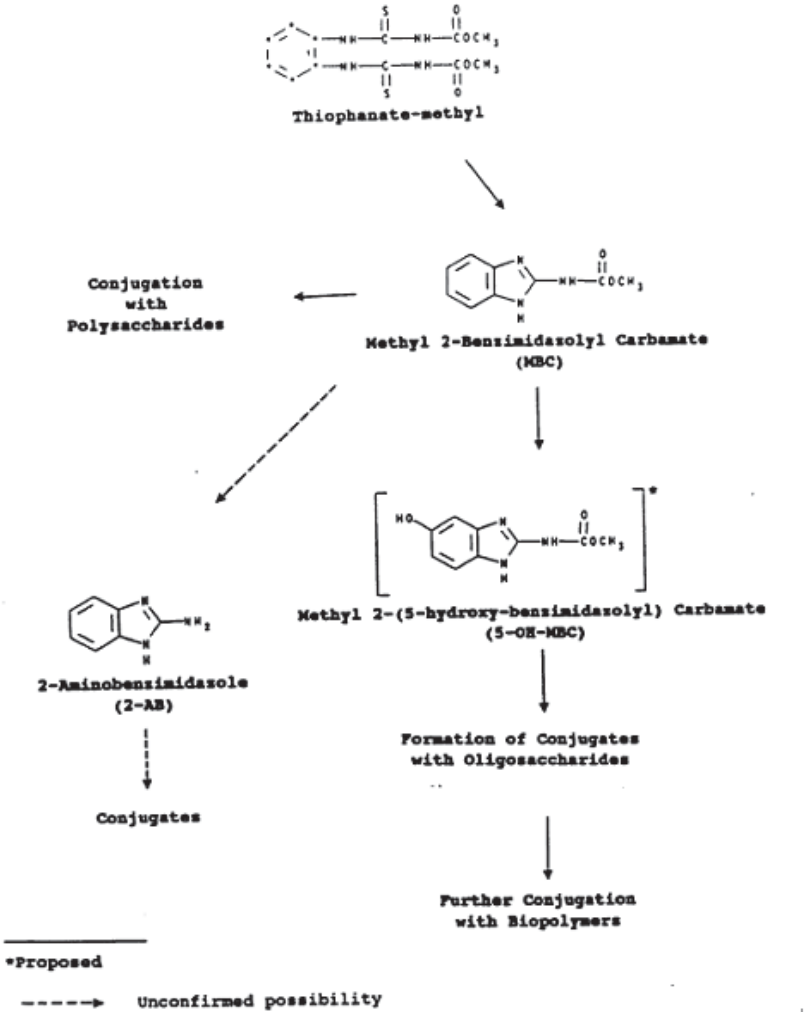


Figure 2 Proposed metabolic pathway of thiophanate-methyl in lima beans

Apple

^{14}C-Thiophanate-methyl (phenyl ring label) formulated as a 64% WP was applied to outdoor apple trees (variety, Granny Smith) in the maturation stage (Alam, F., *et al*., 1994; Report No. RD-II01233). Three foliar applications were made at a rate of 3.9 kg ai/ha. Apple samples were harvested one day and 7 days after the final application.

On the day of collection, samples were shipped on wet ice and kept frozen until arrival at an analytical laboratory. Apples were briefly rinsed twice, each time with 50% aqueous methanol. Each apple was then placed on a glass funnel and rinsed quickly with the same solvent from a wash bottle. The apples were peeled with sharp knives soon after the surface was dry. The pulp was further cut into smaller pieces. Both peel and pulp were stored frozen at *ca.* -20 °C. Stored samples were mixed with dry ice and homogenized and stored frozen until analysis. Combustion analysis (peel, pulp, PES) and LSC (rinsate, extracts) were used for the determination of radioactivity.

The rinsate was centrifuged, and separated to supernatant and pellet. The rinsate supernatant was subjected to HPLC and TLC analyses, and MS used for identification. A polar fraction stayed at the origin in TLC was purified by using C18 SPE and Sephadex LH20, A25 and C25. The rinsate pellet was extracted with acetonitrile and subsequently methanol and then subjected to acid hydrolysis.

The pulp and peel samples were extracted with methanol:Tris buffer:$CHCl_3$ (11:5:5, v/v/v) and again with a mixture solution of Tris buffer:$CHCl_3$ (1:1, v/v). During the extraction procedure, the sample containers were covered with aluminium foil, kept in ice water baths and flushed with nitrogen to minimize oxidative degradation. For peel, further purifications were done. Namely, methanol was added to the chloroform fraction and the resulting methanol soluble fraction was partitioned with water and hexane. The peel methanol/Tris fraction was partitioned with ethyl acetate. LSC, HPLC and TLC were used for analysis. Results are shown in Tables 18–20.

HPLC analysis of dosing solution, stored for 21 days at -20 °C, showed a significant break down (18.3%) of TM to MBC in the aqueous dosing solution during storage in freezer. In this study, applications were done within a short time (less than 2 hours) after preparation.

Stability of TM metabolites in peel samples was investigated by reanalysing 7 days sample after storage in the freezer at -20 °C for approximately 3 months. The analysis showed that the composition of metabolites was unchanged during storage.

In a fortification experiment of ^{14}C-TM in control apple peel, it was shown that nearly all of spiked radioactivity (100%) went into the organic chloroform fraction.

Table 18 Total radioactive residues in apple samples

Apple sample	1 DALA			7 DALA		
	% TRR	TRR (mg eq/kg whole apple)	TRR (mg eq/kg)	% TRR	TRR (mg eq/kg whole apple)	TRR (mg eq/kg)
Peel	2.6	0.134	0.761	7.0	0.151	0.712
Pulp	0.1	0.006	0.007	0.4	0.009	0.011
Rinsate	97.3	5.02		92.6	1.99	
Whole apple	100	5.16	5.16	100	2.15	2.15

Combustion analysis for peel and pulp and LSC for rinsate were used.

Weight ratio of peel: pulp was approximately 2:8.

Table 19 Distribution of radioactivity in apple extracts following application of ^{14}C-TM

Apple sample		TRR (mg eq/kg)	% TRR			
DALA	Compartment		Organic fraction (CHCl3)	Aqueous fraction (MeOH/Tris)	PES	Total
1	Peel	0.761	67.4	19.2	13.4	105
	Pulp	0.007	58.5	36.6	5.0	94.3
7	Peel	0.712	69.7	15.7	14.6	98.8
	Pulp	0.011	52.8	35.3	11.9	104

Total residues in whole apple decreased over time from 5.16 mg eq/kg at 1 DALA to 2.15 mg eq/kg at 7 DALA. Total residues were present at 2.6–7.0% TRR (0.712–0.761 mg eq/kg) in peel and 0.1–0.4% TRR (0.007–0.011 mg eq/kg) in pulp, with 92.6–97.3% of the total residues were present in the rinsate, representing 91.8–96.5% TRR in the supernatant and 0.8% TRR in the pellet.

In extraction of radioactivity from the peel and pulp, 52.8–69.7% of the TRR was contained in the organic fraction and 15.7–36.6% of the TRR was contained in the aqueous fraction. In the PES, 5.0–14.6% of the TRR remained.

In whole apple (1 and 7 DALA), the parent TM was most major component, accounting for 44.5–64.5% TRR (0.957–3.33 mg/kg) and MBC compound was found at 22.2–33.4% TRR (0.719–1.15 mg eq/kg). FH-432 and DX-105 were found, but present at 3.5–5.1% TRR (0.110-0.181) and 1.3–2.1% TRR (0.046-0.068 mg eq/kg), respectively. 4-OH-TM, 4-OH-MBC, 5-OH-MBC, FH-432, FH-73, AV-1951, 2-AB, 4-OH-2-AB, 5-OH-2-AB were also detected, but at very low levels of 0.1–0.6% TRR.

In peel, parent was detected at 0.1–0.3% TRR (0.004–0.006 mg/kg whole apple; 0.02–0.03 mg/kg peel). MBC was found at 1.5–4.1% TRR (0.081–0.088 mg eq/kg whole apple; 0.405–0.440 mg eq/kg peel). Metabolites, FH-432 and DX-105, were detected at 0.1–0.2% TRR and < 0.1–0.2% TRR, respectively but other metabolites were not detected. For pulp, analyses for component compounds including TM were not performed.

In this apple study, nearly all residues (>99% TRR) were present at the surface. TM and MBC were major components, accounting for up to 64.5% TRR or 3.33 mg/kg and 33.4% TRR or 1.15 mg eq/kg, respectively. FH-432 and DX-105 metabolites were found at up to 5.1% or 0.181 mg eq/kg and 2.1% or 0.068 mg eq/kg, respectively. Other various metabolites were detected, but at very minor levels.

Formation of MBC from TM might be a direct process involving cyclization through NH-C bond formation resulting in a side chain elimination. MBC might have also been formed by a similar mechanism via DX-105 or FH-432, both of which were generally present in almost all rinsates and peel fractions. DX-105 and FH-432 were formed from TM through successive displacement of sulphur by oxygen atoms. Another group of compounds observed in the rinsates were the products of successive hydrolysis of one side chain of TM. AV-1951 originated by hydrolysis of one of the amide bonds, while FH-73 was produced by hydrolysis of one of the thiocarbamide linkages. Both FH-432 and AV-1951 might have acted as precursors of MBC. The simpler metabolite 2-AB which was found in various fractions of apple was most likely formed from MBC via hydrolysis of the amide bond.

A number of compounds containing an oxidized aromatic ring were also identified in rinsate fractions. These included hydroxyl derivatives of TM, MBC and 2-AB. It is not clear whether oxidation occurred first in the parent compound (TM) and then the hydroxylated MBC and 2-AB were formed from it, or the oxidation of the aromatic ring processed after the formation of the non-hydroxylated metabolites. Bothe processes, on the other hand, might have equally contributed to the formation of the oxidation products.

Table 20 Distribution of metabolites in apple following application of ^{14}C-TM

Component	% TRR in upper part, mg eq/kg whole apple in lower part							
	1 DALA (5.16 mg eq/kg whole apple)				7 DALA (2.15 mg eq/kg whole apple)			
	Rinsate	Peel	Pulp	Total	Rinsate	Peel	Pulp	Total
TM	64.4 3.32	0.1 0.004	Na [a]	64.5 3.33	44.2 0.951	0.3 0.006	na	44.5 0.957
4-OH-TM	0.2 0.013		na	0.2 0.013			na	
MBC	20.7 1.07	1.5 0.081	na	22.2 1.15	29.3 0.631	4.1 0.088	na	33.4 0.719
4-OH-MBC	0.1 0.007		na	0.1 0.007			na	
5-OH-MBC	0.3 0.017		na	0.3 0.017	0.2 0.004		na	0.2 0.004
FH-432	3.4	0.1	na	3.5	4.9	0.2	na	5.1

Component	% TRR in upper part, mg eq/kg whole apple in lower part							
	1 DALA (5.16 mg eq/kg whole apple)				7 DALA (2.15 mg eq/kg whole apple)			
	Rinsate	Peel	Pulp	Total	Rinsate	Peel	Pulp	Total
	0.175	0.006		0.181	0.106	0.004		0.110
FH-73	0.3 0.017		na	0.3 0.017	0.5 0.011		na	0.5 0.011
AV-1951	0.2 0.012		na	0.2 0.012	1.2 0.026		na	1.2 0.026
DX-105	1.3 0.066	< 0.1 0.002	na	1.3 0.068	1.9 0.041	0.2 0.005	na	2.1 0.046
2-AB	0.6 0.032		na	0.6 0.032	1.2 0.025		na	1.2 0.025
4-OH-2-AB	0.4 0.019		na	0.4 0.019	1.5 0.032		na	1.5 0.032
5-OH-2-AB	0.1 0.006		na	0.1 0.006			na	
Total ident.	92.1 4.75	1.7 0.093	na	93.8 4.85	84.8 1.83	4.9 0.103	na	89.7 1.93
Unks	0.9 0.047	0.9 0.047	0.1 0.006	1.9 0.100	0.4 0.008	2.1 0.046	0.4 0.009	2.9 0.063
Artefacts[b]	4.3 0.224		na	4.3 0.224	7.3 0.159		na	7.3 0.159
Total	97.3[c] 5.02	2.6 0.140	0.1 0.006	100 5.17	92.6[c] 1.99	7.0 0.149	0.4 0.009	100 2.15

Metabolites were found as follows; in one DALA peel, TM, MBC (1.3% TRR), FH-432, DX-105 were found in the chloroform fraction. In 7 DALA peel, TM, MBC (3.7% TRR), FH-432, DX-105 were found in the chloroform fraction.

[a] Analysis was not done.

[b] Polar artefacts, a mixture of components that continuously elute during the entire HPLC run and become distributed in various solvent and chromatographic fractions.

[c] Total residues in rinsate included residues in supernatant (96.5% TRR in one DALA and 91.8% TRR in 7 DALA) and pellet (0.8% TRR in both DALAs). In pellet, TM, MBC and 2-AB were detected.

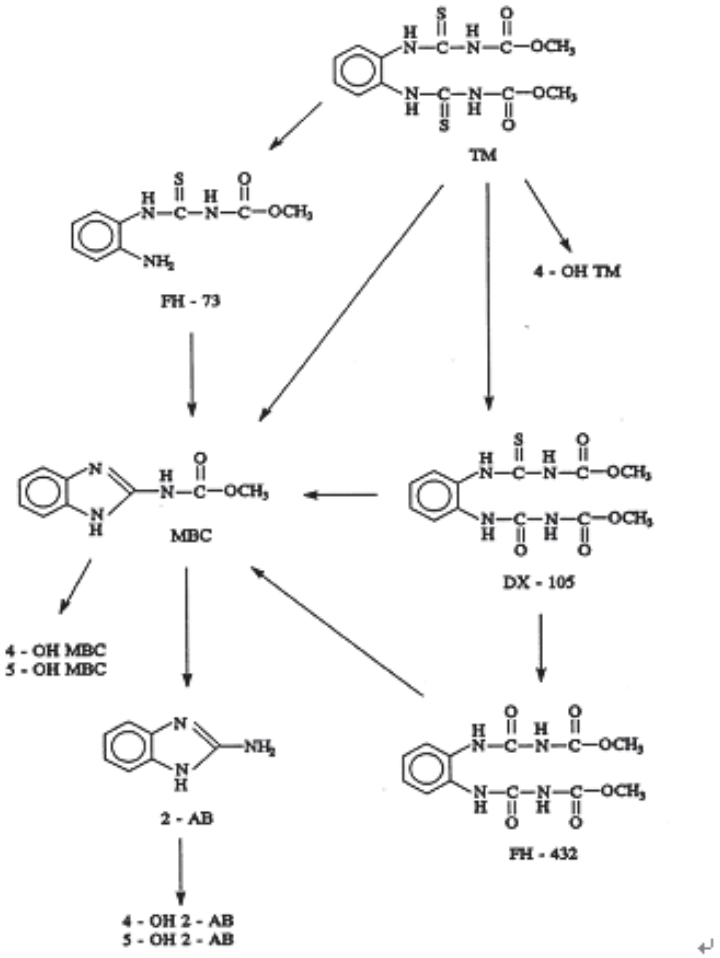


Figure 3 Proposed metabolic pathway of thiophanate-methyl in apple

Tomato

Labelled ^{14}C-Thiophanate-methyl (phenyl ring label) was applied to tomato (F1 hybrid variety *Phantasia*) planted in a sandy loam soil and kept outdoors throughout the study (Irmer, A., 2012; Report No. RD-02379). A SC formulation of ^{14}C-TM (500 g/L) was applied three times on the soil simulating drip irrigation. At 15 days after planting of the tomato plants, first application was made at a rate of 0.70 kg ai/ha. Second and third applications were done at a rate of 1.39 kg ai/ha at 45 days and 2.31 kg ai/ha at 75 days. The plants were kept under a plastic roof and were irrigated according to their needs. Mature tomatoes were harvested 7 days after the last application.

Before tomatoes were deep-frozen, a surface of tomato was rinsed by dipping and gently agitating in acetonitrile:water (1:4). Washed fruits were stored at -20 °C. The rinsed, frozen fruits were homogenized with a blender and the juice was separated from the pomace by centrifugation. Pomace was extracted with acetonitrile:water (4:1, v/v) and again acetonitrile. Radioactivity in fruits and pomace PES was determined by combustion analysis. For rinsate, LSC was used for determination of radioactivity. For juice and pomace extract, LSC and TLC were used. All samples were stored frozen at -20 °C except for short-term storage at 4–6 °C during work up and analysis. All samples were analysed within 6 months from harvest.

Total residue in mature tomato was 0.012 mg eq/kg both in combustion analysis of fruit and sum of TRRs in the rinsate, juice and pomace. TRRs in tomato comprised 0.5% TRR from rinsate, 60.8% TRR from juice and 38.7% TRR (extracted, 15.3% TRR; non-extracted, 23.4% TRR) from pomace, all below 0.01 mg eq/kg. In TLC analysis for juice and pomace extract, the parent compound was not detected and four metabolites were present, one of which was characterized as 2-AB (< 0.01 mg eq/kg; 5.9% TRR in juice, 1.7% TRR in pomace).

This study showed TM was not taken up by the tomato plants in significant amounts or was rapidly decomposed and mineralised.

Grape

Labelled ^{14}C-Thiophanate-methyl (phenyl ring label) was applied to grape vines (white table grape; variety *Lilla*) potted in a sandy loam soil and the plants were kept outdoors throughout the study (Walther, D., 2014; Report No. RD-02804). A single foliar application of ^{14}C-TM formulated as SC 500 g/L was performed at a target rate of 1.1 kg ai/ha and harvested 35 days (mature grape) after the application. All samples were stored at -20 °C before and between sample processing and analysis. Storage stability was verified by repeated analysis of stored sample: size of HPLC fractions from pomace extract and leaf extract was stable for 8–9 months.

The surface of the grape berries attached to the stem was rinsed by dipping and gently agitating the grape sequentially in acetonitrile:water (1:4) and acetonitrile:water (1:1). Thereafter the wet grape was rinsed off with acetonitrile:water (1:1) over a glass jar. The rinsed grapes (berries on stem) were homogenized with a blender and the juice was separated from the pomace by centrifugation. Pomace was extracted twice with acetonitrile:water (4:1, v/v), twice with acetonitrile:water (1:1) and once with acetone. The PES was combusted and also subjected to the following sequence of reflux treatments under acidic and alkaline conditions: 1st, 0.1 N HCl:acetonitrile (1:1); 2nd, 1 N HCl:acetonitrile (1:1); 3rd, 1 N NaOH:acetonitrile (1:1); 4th, 2 N NaOH:methanol (1:1); 5th, 10 N NaOH. The aliquot of solid residue after reflux treatments was combusted, except for solid residue from the 5th reflux.

Frozen leaves were homogenized with dry ice. Extraction and reflux treatments for the PES were the same with the processes as described for pomace.

For the determination of radioactivity, combustion analysis and LSC were used. HPLC and TLC were used for characterization and identification. LC-MS was used for identification of some metabolites. The results were shown in Tables 21–23.

Total residues were 1.27 mg eq/kg in grape berries and 19.7 mg eq/kg in leaves. The TRR in grape berries comprised 22.4% TRR in rinsate, 36.5% TRR (1.16 mg eq/kg) in juice and 41.1% TRR in pomace. Extraction with aqueous acetonitrile and acetone recovered 25.8% TRR from the pomace and 87.0% TRR from the leaves. By acidic and alkaline treatments on the pomace PES (15.3% TRR), 13.3% TRR was more released.

Table 21 Distribution of radioactivity in mature grapes following foliar single application of ^{14}C-TM

Sample	Compartment	TRR	
		%	mg eq/kg whole grape or leaves
Grape berries	Rinsate	22.4	0.284
	Juice	36.5	0.464 (1.16 mg eq/kg of juice)
	Pomace	41.1	0.522
	Extracted	25.8	0.328
	Unextracted (PES)	15.3	0.194
	Total	100	1.27
Leaves	Extracted	87.0	17.1
	Unextracted	13.0	2.56
	Total	100	19.7

Yield of juice was considered as 40%.

In grape berries, the parent compound was present at 3.7% TRR (0.047 mg/kg), all of which was found in the rinsate. MBC was found at 53.5% TRR (0.679 mg eq/kg), distributed in rinsate (16.8% TRR), juice (16.2% TRR, 0.515 mg eq/kg) and pomace (20.4% TRR).

5-OH-MBC was found at 12.8% TRR (0.163 mg eq/kg), distributed in juice (7.5% TRR) and pomace extract (5.4% TRR). FH-432 was present at 4.1% TRR (0.052 mg eq/kg), distributed in rinsate (1.2–1.5% TRR), juice and pomace. DX-105 was found at 0.5% TRR (< 0.01 mg eq/kg) in rinsate. Other metabolites (8 metabolites, not identified) in juice, were at 0.7–4.0% TRR (total, 11.3% TRR), each less than 4% TRR.

Table 22 Distribution of radioactive residues in grape berries following application of ^{14}C-TM

Components	Rinsate		Juice		Pomace, ext.		Pomace, unext.		Total	
	% TRR	mg eq/kg[a]	% TRR	mg eq/kg[a]	% TRR	mg eq/kg[a]	% TRR	mg eq/kg[a]	% TRR	mg eq/kg[a]
TM	3.7	0.047							3.7	0.047
DX-105	0.5	0.006							0.5	0.006
FH-432	1.4	0.017	1.5	0.019/ 0.048[b]	1.0	0.013	0.2[b]	0.002	4.1	0.052
MBC	16.8	0.214	16.2	0.206/ 0.515[b]	19.0	0.242	1.4[b]	0.018	53.5	0.679
5-OH-MBC			7.5	0.095/ 0.238[b]	5.4	0.068	-		12.8	0.163
M4			-		0.4	0.005	-		0.4	0.005
M7			0.7	0.009					0.7	0.009
M8			0.8	0.010					0.8	0.010
M9			1.0	0.013					1.0	0.013
M10			0.4	0.005					0.4	0.005
M11			2.9	0.037					2.9	0.037
M12			0.7	0.009					0.7	0.009
M13			0.8	0.010					0.8	0.010
M14			4.0	0.051					4.0	0.051
Total identified	22.4	0.284	25.2	0.320	25.4	0.323	1.6[c]	0.020	74.6	0.947
Total of all fractions	22.4	0.284	36.5	0.464	25.8	0.328	1.6	0.020	86.3	0.110
TRR berries	22.4	0.284	36.5	0.464	25.8	0.328	15.3	0.194	100	1.27

[a] mg eq/kg of whole grape

[b] mg eq/kg of juice; yield of juice was considered as 40%.

[c] released by acid and base refluxes

Table 23 Distribution of radioactive residues in grape leaves following application of ^{14}C-TM

Components	Extracted		Unextracted, released by reflux		Total	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
FH-432	7.6	1.49			7.6	1.49
MBC	68.6	13.5	3.4	0.665	72.0	14.2
5-OH-MBC	5.7	1.13			5.7	1.13
2-AB	-		1.2	0.242	1.2	0.242
M13	1.7	0.327			1.7	0.327
M15	3.5	0.687			3.5	0.687
Total of all identified metabolites	81.9	16.1	3.4	0.665	85.2	16.8
Total of all fractions	87.0	17.1	4.6	0.907	91.6	18.1
TRR leaves [1]	87.0	17.1	13.0	2.56	100	19.7

TM was not found.

MBC was detected at 0.1-2.0% TRRs in each 1st-4th reflux (acid and base)

2-AB: 0.1-0.3% TRRs in 1st-5th reflux each; this compound was not verified in a secondary method (HPLC).

In leaves, the parent TM was not present. MBC was found at 72.0% TRR (3.4% TRR from acid/base hydrolysate of the PES). FH-432 and 5-OH-MBC were found at 7.6% TRR (1.49 mg eq/kg) and 5.7% TRR (1.13 mg eq/kg), respectively. Two unknowns were present at each less than 1.7–3.5% TRR (0.327–0.687 mg eq/kg).

This study showed that the metabolism of TM in grape vine proceeds by replacement of the thio groups on both side chains by keto groups to form metabolites DX-105 and FH-432 followed by cyclization to form MBC. MBC is hydroxylated to form 5-OH-MBC and other metabolites as well as via residue incorporation into plant constituents.

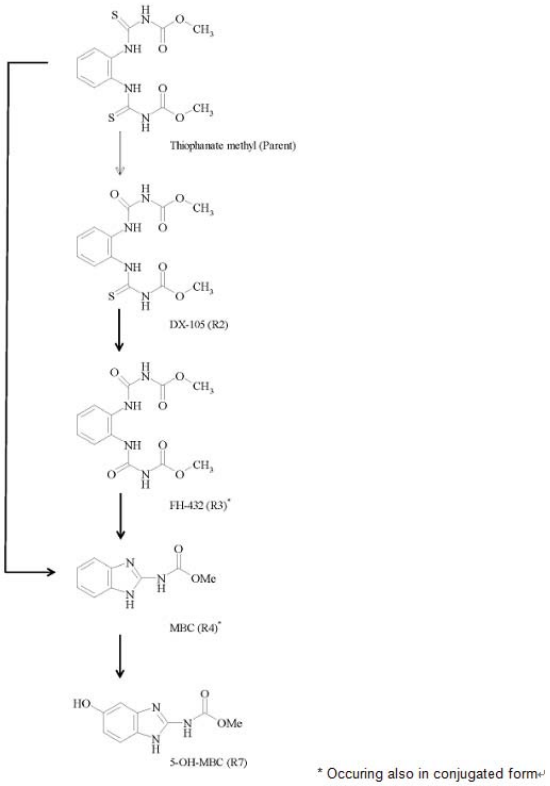


Figure 4 Proposed metabolic pathway of thiophanate-methyl in grapes

Summary in plant metabolism

The nature of the residues was essentially the same in apple, grape, sugar beet, soya bean and green bean. TM and the metabolite MBC were found as major components in apple, grape, sugar beet (root), soya bean (pods) and green bean (pods). TM accounted for up to 65% TRR (3.3 mg/kg in apple) and 86% TRR (0.20 mg/kg in green bean pods). MBC accounted for up to 48% TRR (0.23 mg eq/kg in green bean pods) and 54% TRR (0.68 mg eq/kg in grape). Amount of TM was 2-9 times greater than that of MBC in apple, sugar beet root and soya bean pods. On the contrary, amount of MBC was 2.6-15 times higher than that of TM in grape and green bean pods. In conclusion, both TM and MBC are principal residues resulted from application of TM on crop. Metabolites DX-105 and FH-432 were also found but very minor. FH-432 was found up to 6.7% TRR (0.031 mg eq/kg) in green bean pods.

For wheat grain, lima bean pods and tomato (soil treatment), both TM and MBC were not found.

Metabolism of TM forming MBC might be a direct process involving cyclization resulting in side chain elimination. MBC might be also formed by cyclization via DX-105 or FH-432. Another path way, products (FH-73, AV-1951) resulting from hydrolysis of one side chain of TM might be precursors of MBC. Either MBC or hydroxylated MBC can be involved in forming 2-AB or 5-OH-2AB. MBC and other metabolites can be present as conjugates with endogenous plant materials.

Residues in succeeding or rotational corps

Confined rotational crop study

^{14}C-Thiophanate-methyl of 70% WP formulation applied once to bare soil (sandy loam) at a rate of 1.6 kg ai/ha (Malik, N.S.A. and Wright, M.C., 1993; Report No. RD-99123) (Kim-Kang, H., 1997; Report No. RD-99124). After 30, 120 and 365 days after treatment (plant back interval, PBI), lettuce (*Lactuca sativa*), carrot(*Dacus carota*), and wheat (*Triticum aestivum*) were seeded and the plants were grown outdoor. Lettuce and carrots were harvested at full maturity and wheat was harvested at half-maturity and full maturity (straw/chaff and grain). Soil samples were also taken on the same dates. The harvest samples were frozen (for lettuce and carrots, within 1 hour after harvest) and shipped frozen to places for analysis, except 30 PBI and 120 PBI carrot root samples, which were refrigerated during storage (3–13 days) and shipped on blue ice. Homogenization of samples was performed with liquid nitrogen or dry ice, and kept frozen until TRR determination and further analysis. Soil samples were first air-dried, and then mixed in plastic bags by hand. TRR was determined by combustion and LSC.

Lettuce (30-day PBI and 365-day PBI) and soil samples were extracted with a mixture of methanol:Tris buffer:chloroform (11:5:5, v/v/v) at 0–4 °C. For lettuce, the resulting chloroform fraction was further fractionized into methanol soluble fraction and pellet.

Wheat sample (30-day PBI and 365-day PBI) was extracted with a mixture of methanol:Tris buffer:chloroform (11:5:5, v/v/v) at room temperature and resulted in chloroform fraction, MeOH/Tris fraction and PES. The chloroform fraction, solubilized in methanol, was concentrated and then partitioned with methanol, water and hexane. The MeOH/Tris fraction was subjected to hydrolysis with 2 N HCl and before and after the hydrolysis, partitioned with ethyl acetate. The PES was treated with 2 N HCl, and then further treated with 6 N HCl or the 2 N HCl. The 2 N HCl soluble hydrolysate (separated from insoluble residue) was partitioned with ethyl acetate under acid and neutral conditions.

For carrot top and root, TRRs were only determined at initial analytical work. After *ca.* 6.6–6.7 years, characterization and identification of metabolic components were performed. For testing of storage stability, TRRs for lettuce (30-day PBI), wheat straw (30-day PBI), carrot top and root (30-day PBI, 365-day PBI) were re-determined. These samples were extracted using modified procedure, namely, chloroform fraction was partitioned with hexane and acetonitrile.

As results, the earlier (initial work) and new TRR values (after 6.6–6.7 years) were very similar. TRR distribution in re-determined extracted and non-extracted fractions was similar to earlier reported values in the lettuce wheat straw samples. In analysis by HPLC, there was no significant difference in the percentage distribution of metabolites in lettuce and wheat straw samples when compared to the values determined previously except metabolite FH-432. FH-432 value was higher in the new work. Based on the results, this study regarded TM metabolites in the rotational crops samples as stable during frozen storage. Analysis of metabolites was performed as below.

Carrot tops and roots (30-day PBI and 365-day PBI) were extracted with a mixture of methanol: Tris buffer: chloroform (11:5:5, v/v/v) at ice bath. The resulting chloroform faction was partitioned with a mixture of hexane and acetonitrile. The PES from 30-day PBI top and root was subjected to cellulase enzyme treatment and then acid hydrolysis (1 N HCl). For 30-day PBI top, the aqueous fraction after the acid hydrolysis was partitioned with ethyl acetate under acid and base

conditions. The PES after acid hydrolysis was subjected to a base hydrolysis (1 N NaOH). The resulting aqueous fraction was partitioned with ethyl acetate.

Results from this study are summarized in Tables 24–28.

Table 24 Total radioactivity in rotational crops

Crop	TRR (mg eq/kg)		
	30-day PBI	120-day PBI	365-day PBI
Carrot tops	0.069, 0.065[a]	0.060	0.048, 0.045[a]
Carrot roots	0.031, 0.026[a]	0.015	0.023, 0.022[a]
Lettuce	0.263	0.070	0.042
Wheat forage (half-mature)	0.474, 0.501[a]	0.154	0.557, 0.546[a]
Wheat straw	1.253, 1.32[a]	0.194	2.02, 2.11[a]
Wheat grain	0.064, 0.066[a]	0.014	0.067, 0.089[a]

[a] Replicate in an analytical phase

TRR levels in rotational crops, carrot and lettuce, were generally decreased with prolonged PBIs. For wheat rotational crop (forage, straw and grain), the 120-day PBI TRR levels were significantly declined, however, 365-day PBI TRRs increased. Such an high TRR level in straw (365-day PBI) was explained from higher harvest crop weight of 120-day PBI straw, but for grain and forage, no factors could be explained. However, the TRR levels between 30- and 365-day PBI were not significantly different in grain and forage, which indicated no-bioaccumulation for this interval. Solvent extraction recovered 44.3-64.4% of the total radioactivity in lettuce and carrot and 26.4–42.6% TRR in wheat samples (26.4% TRR in grain). Unextracted residue portion was very large in all matrices, 30.8–73.5% TRR (highest in wheat grain).

Table 25 Extraction and distribution of radioactivity in rotational crop samples

Sample	PBI (days)	TRR (mg eq/kg)	% TRR in fraction				
			$CHCl_3$	MeOH / H_2O	Extr.	PES	Total
Lettuce	30	0.263	16.9	45.2	62.1	30.8	92.9
	120	0.070	31.0	44.3	64.4	35.6	111
	365	0.042	24.1	33.1	57.2	43.0	100
Carrot top	30	0.065	18.6	32.7	51.3	48.7	101
	365	0.045	15.0	30.4	45.0	54.6	110
Carrot root	30	0.026	11.3	33.0	44.3	55.7	108
	365	0.022	11.5	40.2	51.7	48.3	101
Wheat forage (half-mature)	30	0.501	10.8	24.2	35.0	65.0	95.7
	365	0.546	7.4	26.4	33.8	66.2	95.4
Wheat straw	30	1.32	7.4	29.8	37.2	62.8	105
	365	2.11	9.4	33.2	42.6	57.4	95.2
Wheat grain	30	0.066	5.2	21.2	26.4	73.5	95.3
	365	0.089	5.6	23.3	28.9	71.1	84.9

Table 26 Metabolite residues in rotational crop lettuce soil and plant

Metabolite	Lettuce soil								Lettuce plant					
	Post application		30-day PBI pre-plant		120-day PBI pre-plant		365-day PBI pre-plant		30-day PBI (0.263 mg eq/kg)		120-day PBI (0.070 mg eq/kg)		365-day PBI (0.042 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Organosoluble fraction														
TM	54.0	0.551	1.3	0.003	1.9	0.032	0.5	0.003	-	< 0.001	-	< 0.001	-	< 0.001
MBC	38.8	0.396	40.3	0.084	45.2	0.747	36.0	0.222	9.3	0.024	18.4	0.013	6.6	0.003
FH-432	-	< 0.001	1.3	0.003	-	< 0.001	-	< 0.001	5.1	0.014	10.8	0.008	12.9	0.005
2-AB	-	< 0.001	-	< 0.001	1.6	0.026	1.8	0.011	-	< 0.001	-	< 0.001	-	< 0.001
DX-105	1.3	0.014	-	< 0.001	0.5	0.008	0.2	0.001	-	< 0.001	-	< 0.001	-	< 0.001
Unk	0.8	0.008	-	< 0.001	0.8	0.014	1.2	0.008	2.5	0.006	1.9	0.001	4.7	0.002
Methanol/aqueous fraction														
Unk (s)	3.7	0.038	6.3	0.013	4.8	0.079	5.0	0.031	45.2	0.119	44.2		33.1	0.014

Metabolite	Lettuce soil								Lettuce plant					
	Post application		30-day PBI pre-plant		120-day PBI pre-plant		365-day PBI pre-plant		30-day PBI (0.263 mg eq/kg)		120-day PBI (0.070 mg eq/kg)		365-day PBI (0.042 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Unext.res.	11.3	0.115	42.7	0.089	35.7	0.59	50.8	0.313	30.8	0.081	35.6	0.025	43.0	0.018
Total	110	1.12	91.9	0.192	90.5	1.50	95.5	0.589	92.9	0.244	111	0.078	100	0.042

Table 27 Metabolite residues in rotational crop carrot

Metabolite	Tops				Roots			
	30-day PBI (0.065 mg eq/kg)		365-day PBI (0.045 mg eq/kg)		30-day PBI (0.026 mg eq/kg)		365-day PBI (0.022 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TM		nd		nd		nd	3.2	0.001
DX-105		nd		nd		nd	2.0	0.001
FH-432	8.3	0.005	6.7	0.003	7.2	0.002	4.6	0.001
MBC	5.2	0.003	6.7	0.003		nd		nd
Unks	0.8-16.3 (6)[a]	0.001-0.010	1.5-9.6 (6)	0.001-0.004	2.1-18.3 (4)	0.001-0.005	1.8-17.2 (5)	< 0.001 -0.004
Not analysed	45.5	0.030	55.2	0.025	57.7	0.015	48.3	0.011
Total	100	0.065	100	0.046	100	0.027	100	0.024

This analysis was performed after *ca.* 6.6-6.7 years after harvest.

nd, not detected

[a] Number of found metabolites

Table 28 Metabolite residues in rotational crop wheat

Metabolite	Wheat forage and chaff (half-mature)				Wheat straw				Wheat grain			
	30-day PBI (0.501 mg eq/kg)		365-day PBI (0.546 mg eq/kg)		30-day PBI (1.32 mg eq/kg)		365-day PBI (2.11 mg eq/kg)		30-day PBI (0.066 mg eq/kg)		365-day PBI (0.089 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Extracted residue												
MBC	5.2	0.025	2.3	0.012	1.6	0.021	2.6	0.053	0.1	< 0.001	0.4	< 0.001
FH-432	4.2	0.020	4.7	0.025	4.6	0.064	5.6	0.111	0.1	< 0.001	0.3	< 0.001
2-AB	5.0	0.024	3.3	0.018	1.5	0.020	2.6	0.052	0.7	< 0.001	0.1	< 0.001
5-OH-2AB	0.2	0.001	0.2	0.001	-		-		0.1	< 0.001	0.2	< 0.001
Unknown	20.4	0.098	23.3	0.121	29.5	0.411	31.8	0.640	25.4	0.016	27.9	0.021
Total extracted residue	35.0	0.168	33.8	0.177	37.2	0.516	42.6	0.856	26.4	0.016	28.9	0.022
Bound residue: acid hydrolysis (2 N HCl)												
MBC	-		1.5	0.008	-		0.5	0.009	-		-	
2-AB	-		0.1	0.001	-		0.5	0.010	-		-	
5-OH-2AB	-		0.2	0.001	-		-		-		-	
Unknown	-		7.9	0.041	-		7.1	0.145	-		45.6	0.034
Total, AHBR	-		9.7	0.051	-		8.1	0.164	-		45.6	0.034
Total, PHIR	-		56.5	0.294	-		49.3	0.991	-		25.5	0.019
Total bound residue	65.0	0.312	66.2	0.345	62.8	0.871	57.4	1.16	73.5	0.046	71.1	0.053

AHBR: acid hydrolysable bound residue

PHIR: post-hydrolysis insoluble residue

The parent compound was not detected in any matrices except a negligible detection (3.2% TRR, 0.001 mg/kg) in carrot root (365-day PBI). Major residues found in rotational crops were MBC and FH-432 metabolites.

MBC was detected at 6.6–18.4% TRR (0.003–0.024 mg eq/kg) in lettuce, 5.2–6.7% TRR (0.003 mg eq/kg) in carrot top, 3.8–5.2% TRR (0.020–0.025 mg eq/kg) in wheat forage, 1.6–3.1%

TRR (0.021–0.062 mg eq/kg) in wheat straw and 0.1–0.4% TRR (< 0.001 mg eq/kg) in wheat grain. In carrot root, MBC was not detected.

FH-432 was detected at 5.1–12.9% TRR (0.005–0.014 mg eq/kg) in lettuce, 4.6–7.2% TRR (0.001–0.002 mg eq/kg) in carrot root, 6.7–8.3% TRR (0.003–0.005 mg eq/kg) in carrot top, 4.2–4.7% TRR (0.020–0.025 mg eq/kg) in wheat forage, 4.6–5.6% TRR (0.064–0.111 mg eq/kg) in wheat straw and 0.1–0.3% TRR(< 0.001 mg eq/kg) in wheat grain.

2-AB and 5-OH-2-AB were detected only in wheat matrices. 2-AB was present at 3.4–5.0% TRR (0.019–0.024 mg eq/kg) in forage, 1.5–3.1% TRR (0.020–0.062 mg eq/kg) in straw and 0.1–0.7% TRR (< 0.001 mg eq/kg) in grain. 5-OH-2-AB was present at 0.2–0.4% TRR (0.001–0.002 mg eq/kg) in forage and 0.1–0.2% TRR (< 0.001 mg eq/kg) in grain. In straw, 5-OH-2-AB was not detected.

In food rotational crops (lettuce, carrot root and top, wheat grain), parent was not detected, except a negligible detection in carrot root (0.001 mg/kg). Any metabolite found was not present at above approximately 0.01 mg eq/kg, except MBC in lettuce (0.024 mg eq/kg at 30-day PBI and 0.013 mg eq/kg at 120-day PBI). In feed rotational crops (wheat forage and straw, carrot culls), residue level of metabolite found was less than approximately 0.1 mg eq/kg.

This study showed that there is no accumulation to be expected after application of TM and that metabolism in primary and rotational crops is comparable. Most of the radioactive residue was either incorporated in the plant matrix or soluble in aqueous methanol. All metabolites found are well known from plant metabolism studies and present in rotational crops only in small amounts.

Field rotational crop study

A single application of thiophanate-methyl (500 g/L SC) was done to bare soil during 2011–2012 in the UK and Spain (Wilson, A., 2014; Report No., RD-02975). At nominal intervals of 30, 70, 120 and 365 days after the application, both carrot and spinach were planted in UK and Spain, and spring barley was planted in the UK and spring wheat in Spain. Crop samples were taken on the following occasions:

Spinach: sufficient plant material available (BBCH 15); earliest commercial harvest (BBCH 44–46; commercial harvest (BBCH 47–49)

Carrot: sufficient plant material available (BBCH 14–16); earliest commercial harvest (BBCH 44–45; commercial harvest (BBCH 47–49)

Spring cereals: sufficient plant material available (BBCH 15–16); hay (BBCH 75); commercial harvest (BBCH 89)

Hay samples were field dried to a moisture content of 10–20%. The samples were placed into freezer storage within 3 hours after harvest, shipped and kept under frozen conditions until analytical analysis.

Analysis for TM and MBC was performed using an analytical method (P 2435 G). Crop samples were homogenised and extracted with acetonitrile:water. The samples were then cleaned up using dispersive solid phase extraction (dSPE) with centrifugation followed by partition into acetonitrile. The final extract was diluted with water (50:50, v/v) and quantification was performed using LC-MS/MS. The LOQ was 0.01 mg/kg for all matrices. The procedural recoveries were in the range of 70–110% (RSD, ≤ 20%).

The analytical analyses showed that no residues of TM and MBC were detected above < 0.01 mg/kg for any rotational crop samples.

Animal metabolism

Lactating goats

^{14}C-Thiophanate-methyl was administered to lactating goats for five consecutive days (Hanlon, C.M. and Norris, K.J., 1992; Report No. RD-9517, RD-9518) (Eldeib, M., 1995, Report No. RD-9519). Two goats were dosed orally in capsules twice daily at 52.4 and 57.3 mg/kg feed, corresponding to 1.15 mg/kg bw and 1.19 mg/kg bw, respectively. Milk, urine and faeces were collected during the dosing period. Approximately 14 hours after the last dose, goat was sacrificed with subsequent collection of organs and tissues. All samples were stored frozen and transported on dry ice to an analytical laboratory. All tissues were partially thawed before processing, cleaned of extraneous material and homogenized. Radioactivity was determined by direct radioassay, combustion and LSC. TLC and HPLC were used for characterization and identification.

Muscle sample was extracted with a mixture of water:methanol:chloroform (5:11:5, v/v/v) and the extract was centrifuged. The aqueous methanol fraction was partitioned with chloroform. Chloroform fractions were combined, concentrated and partitioned with acetonitrile:hexane (1:1). The PES was rinsed with water and treated with protease enzyme.

Liver sample was extracted in the same process with muscle. Additionally, the remaining solid after protease treatment was subjected to 1 N HCl, 6 N HCl and 1 N NaOH hydrolyses. One metabolic fraction, found in methanol aqueous fraction, was treated with glusulase enzyme containing sulfatase and β-glucuronidase. Further, the metabolic fraction was subjected to ion-exchange chromatography in order to fractionate it into neutrals, acids, weak bases, ampholytes, and bases using AG-50 and AG-1 resins. Another metabolic fraction, found in protease supernatant, was treated with β-glucuronidase enzyme.

Kidney sample was extracted in the same process with muscle. Additionally, the remaining solid after protease treatment was subjected to 1 N HCl, 6 N HCl and 1 N NaOH hydrolyses. After TLC and HPLC analysis of the methanol aqueous fraction, it was subjected to glusulase enzyme treatment to confirm a sulphate conjugation.

Fat sample was extracted with hexane, centrifuged and again extracted with methanol. The methanol fraction was partitioned with hexane, and hexane fractions were combined, partitioned with hexane:acetonitrile (1:1).

Milk sample was extracted with acetonitrile, and the supernatant of the extract (acetonitrile fraction) was concentrated, partitioned with hexane. The resulting aqueous fraction was partitioned with ethyl acetate. The PES was rinsed with water and treated with protease enzyme. After TLC and HPLC analysis of the aqueous fraction obtained from the ethyl acetate partition, the fraction was treated with glusulase to confirm a sulphate conjugation. The results are shown in Tables 29–32.

Excretion in urine (56.4% of the total dose) was a major route of elimination. In faeces, 14.1% of the total dose was excreted. Of the total dose, 1.5% (0.918 mg eq/kg) was excreted in milk.

Table 29 Total radioactivity in goat administered with ^{14}C-TM

Goat samples	TRR [a] (mg eq/kg)	% of dose
Faeces	49.5	14.1
Urine	262.5	56.4
Milk	0.918	1.5
Liver	4.56	1.1
Kidney	1.29	0.06
Muscle	0.116	0.9
Fat	0.186	0.09
Blood	0.188	0.3
Stomach content	0.676	0.6
Small intestine content	3.94	0.4
Large intestine content	8.05	3.5
Total	343	78.8

[a] Average TRR values for two goats

Table 30 Total radioactivity in goat milk by day

Samples	TRR (mg eq/kg)		
	Goat 1	Goat 2	Average
Day 1 (pm)	0.415	0.475	0.445
Day 2 (am)	0.715	1.04	0.878
Day 2 (pm)	0.810	1.01	0.910
Day 3 (am)	0.784	0.969	0.877
Day 3 (pm)	0.830	1.03	0.930
Day 4 (am)	0.848	1.30	1.07
Day 4 (pm)	0.863	1.59	1.23
Day 5 (am)	0.855	1.41	1.13
Day 5 (pm)	0.861	0.971	0.916
Day 6 (am)	0.780	0.793	0.787
Mean			0.846

The mean residue concentration in milk was 0.846 mg eq/kg (maximum: 1.59 mg eq/kg). The radioactive residues in edible tissues were 0.116 mg eq/kg in muscle, 0.186 mg eq/kg in fat, 4.56 mg eq/kg in liver and 1.29 mg eq/kg in kidney. Extraction of radioactivity in the milk and tissue by using different solvent systems was in the range of 57.9–84.3% of the TRR. For liver with most less extraction, enzymatic and acid/base hydrolyses for the PES further released 42.6% TRR, remaining 2.5% TRR as bound residue.

In muscle, parent compound and MBC were present at 24.0% TRR (0.02 mg eq/kg) and 26.3% TRR (0.03 mg eq/kg), respectively. Metabolites, 3-OH-TM, 4-OH-TM and 5-OH-MBC-S, were found but at below 0.01 mg eq/kg (each, at < 7% TRR).

In fat, the parent was present at 6.2% TRR (0.011 mg eq/kg). MBC was a predominant component, accounting for 45.0% TRR (0.083 mg eq/kg). 3-OH-TM was found at 2.8% TRR (< 0.01 mg eq/kg).

In liver, the parent was present at 0.8% TRR (0.04 mg eq/kg). MBC was found at 9.4% TRR (0.43 mg eq/kg). Other metabolites, 4-OH-MBC and 5-OH-MBC were present at 5.8% TRR (0.27 mg eq/kg) and 7.2% TRR (0.32 mg eq/kg), respectively. 3-OH-TM was detected at a very low level of 0.5% TRR (0.02 mg eq/kg). Another major component found in liver was a water-soluble unknown fraction (52.9% TRR, 2.41 mg eq/kg).

Table 31 Extraction and distribution of radioactivity in goat administered with ^{14}C-TM

Fraction	Muscle	Fat	Liver	Kidney	Milk
Aqueous methanol	31.3		46.5	57.2	
Acetonitrile	41.9	45.9	10.0	26.1	
Hexane	2.4	7.0	1.5	1.0	
Methanol		8.0			
Ethyl acetate					15.3
Aqueous					68.7
PES	21.5	1.7	45.0	9.6	14.5
Pellet wash	1.0		2.1	1.1	9.5
Protease	3.1		21.3	4.9	5.0
1 N HCl			6.6	1.4	
6 N HCl			2.9	0.6	
1 N NaOH			9.6		
Bound	17.4		2.5	1.6	1.2
Total	97.1	62.7	103	93.9	?

Milk: acetonitrile extract supernatant was partitioned with hexane, and then the resultant aqueous fraction was partitioned with ethyl acetate.

Fat: first, partitioned into hexane phase and methanol phase, and then the hexane fraction was partitioned with acetonitrile.

The unknown fraction, found both in aqueous methanol fraction (31.6% TRR) and protease supernatant fraction (21.3% TRR), were treated with ß-glucuronidase and glusulase, respectively. As a result, they were not changed, namely not glucuronide or sulphate conjugates. The unknown fraction found in aqueous methanol fraction was further analysed by using gel permeation chromatography (GPC, Sephadex G15), ion-exchange TLC analysis and SDS (sodium dodecyl sulphate) gel electrophoresis. In conclusion, basic unknown two compounds from the GPC zone 3 were isolated. It was proposed that the unknown fraction may contain several different forms of the two basic unknown compounds, either as polymeric materials (proteins) of various configurations or as various conjugates to other endogenous materials. LC-MS/MS analysis showed that MBC was not present in the GPC zone 3.

In kidney, parent was found at 1.6% TRR (0.01 mg eq/kg). Metabolite, 5-OH-MBC-S, was identified (confirmed by glusulase treatment) as a major component, accounting for 34.8% TRR (0.45 mg eq/kg). MBC was found at 20.5% TRR (0.27 mg eq/kg) and 4-OH-MBC at 17.4% TRR (0.23 mg eq/kg). 4-OH-TM and 5-OH-MBC were present at 3.1% TRR (0.04 mg eq/kg) and 1.8% TRR (0.02 mg eq/kg), respectively.

In milk, parent was present at 0.3% TRR (< 0.01 mg eq/kg). Metabolite, 5-OH-MBC-S (confirmed by glusulase treatment) was a major component, accounting for 73.3% TRR (0.623 mg eq/kg). MBC was found at 10.0% TRR (0.085 mg eq/kg). Other metabolites, 3-OH-TM-S, 4-OH-TM, 5-OH-MBC and 2-AB were found at each below 2.7% TRR (0.023 mg eq/kg).

Major components found were TM and MBC in muscle, MBC in fat, MBC, 5-OH-MBC and 4-OH-MBC in liver, MBC, 5-OH-MBC-S and 4-OH-MBC in kidney, MBC and 5-OH-MBC-S in milk. Metabolites, 3-OH-TM, 3-OH-TM-S, 4-OH-TM and 2-AB, were also found in tissue and milk, but at very minor levels of each below 3.5% TRR.

In lactating goats, TM was rapidly metabolised to MBC, which was then hydroxylated at various positions and subsequently conjugated.

Table 32 Metabolic residues in goat administered with ^{14}C-TM

Sample fraction	Muscle (0.116 mg eq/kg)		Fat (0.186 mg eq/kg)		Liver (4.56 mg eq/kg)		Kidney (1.29 mg eq/kg)		Milk (0.918 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TM	24.0	0.02	6.2	0.011	0.8	0.04	1.6	0.01	0.3	0.003
3-OH-TM	3.5	< 0.01	2.8	0.005	0.5	0.02				
3-OH-TM-S									1.2	0.010
4-OH-TM	1.9	< 0.01					3.1	0.04	1.0	0.008
MBC	26.3	0.03	45.0	0.083	9.4	0.43	20.5	0.27	10.0	0.085
4-OH-MBC					5.8	0.27	17.4	0.23		
5-OH-MBC					7.2	0.32	1.8	0.02	2.7	0.023
5-OH-MBC-S	7.0	< 0.01					34.8	0.45	73.3	0.623
2-AB									0.7	0.006
Unknown										
3'12"					1.5	0.07				
3'30"					1.0	0.05				
3'36"	2.3	< 0.01			0.4	0.02				
4'00"									1.2	0.010
18'00"					52.9[b]	2.41				
18'48"							4.9[a]	0.07		
22'00"							0.6	< 0.01		
27'36"	6.8	< 0.01								
27'48"							3.6	0.05		
31'00"	1.4	< 0.01								
Hexane	2.4	< 0.01	7.0	0.013			1.0	0.01		
Pellet wash	1.0	< 0.01			2.1	0.10	1.1	0.01		
Protease	3.1	< 0.01							5.0	0.042
1 N HCl					6.7	0.31	1.4	0.02		
6 N HCl					2.9	0.13	0.6			
1 N NaOH					9.6	0.44		0.01		
Bound	17.4	0.02	1.7	0.003	2.5	0.11	1.6	0.02	1.2	

Sample fraction	Muscle (0.116 mg eq/kg)		Fat (0.186 mg eq/kg)		Liver (4.56 mg eq/kg)		Kidney (1.29 mg eq/kg)		Milk (0.918 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Total	97.1	0.07	62.7	0.115	103.3	4.72	94.0	1.21	96.6	0.821

Milk samples from day 5 (pm) and day 6 (am) of goat 1 and day 5 (pm) and day 6 (am) of goat 2

[a] Released from protease treatment

[b] 31.6% TRR in aqueous methanol fraction and 21.3% TRR in protease supernatant fraction; Non-determination of MBC was confirmed. Further it was considered as containing basic two compounds of several different forms, either as polymeric materials of various configurations or as various conjugates to other endogenous materials.

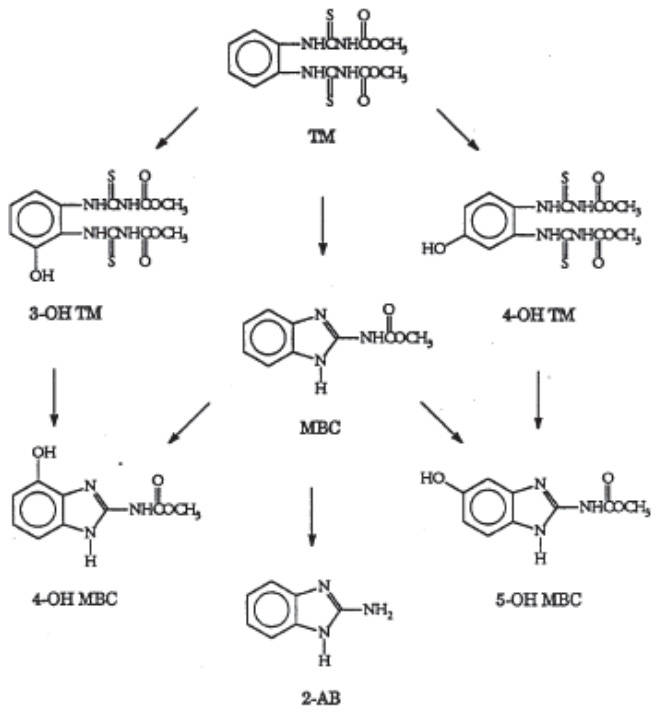


Figure 5 Proposed metabolic pathway for thiophanate-methyl in goats

Note: The sulphate conjugates of the hydroxylated metabolites 3-OH-TM and 5-OH-MBC were also found.

Laying hens

^{14}C-Thiophanate-methyl (phenyl ring label) was administered to a total of 30 laying hens (2 groups of 15 hens) (Wright, M.C., 1992; Report No. RD-9516). Hens were fed in capsules orally once daily for 10 days at a dose level of 48 mg/kg feed. Within 25 hours of the last dose, hens were sacrificed. Collected samples were frozen and homogenised by macerating partially thawed samples or by using dry ice. The samples were shipped on dry ice to an analytical laboratory. TRRs were determined by combustion or solubilisation of the radioactivity tissue residues and determination of the radioactive residues by LSC. Data on TRR compared very well between Group 1 and Group 2 samples and then group 2 samples were used for the analytical characterization.

Samples were extracted when just thawed, but still cold and using liquid nitrogen. Muscle, liver and kidney samples were extracted with a solvent mixture of methanol: water: chloroform (11:5:5, v/v/v) and again chloroform. The filtrates were separated into a chloroform fraction and a

MeOH/H_2O fraction. MeOH/H_2O fractions were analysed by HPLC and TLC. The chloroform fraction was evaporated and partitioned with a mixture of acetonitrile: hexane (1:1, v/v). The MeOH/H_2O fraction from the muscle sample was not further fractionized. The MeOH/H_2O fractions from the liver and kidney samples were further processed through partitions with ethyl acetate at acid and base conditions before and after 1 N HCl hydrolysis. The combined ethyl acetate fraction and final aqueous fraction were analysed by HPLC and TLC. The final aqueous fraction was further hydrolysed with 6 N HCl.

The PES fraction from the muscle sample was subjected to protease digestion and resulted in aqueous fraction and PES fraction. The protease aqueous fraction was partitioned with ethyl acetate at acid and base conditions before and after 1 N HCl hydrolysis. The ethyl acetate fractions were combined.

The PES fractions from the liver and kidney samples were subjected to protease digestion. The resulting protease aqueous fraction was hydrolysed with 6 N HCl followed by partitions with ethyl acetate at acid, neutral and base conditions. All ethyl acetate fractions were combined. The PES from protease treatment was hydrolysed with 1 N HCl followed by ethyl acetate partitions at acid and base conditions. All ethyl acetate fractions were combined.

For fat and skin samples, the samples were extracted with hexane and again methanol and resulted in methanol, hexane and PES fractions. The hexane fraction was concentrated and partitioned with acetonitrile. The skin PES fraction was further subjected to protease digestion. The protease aqueous fraction was fractionized using XAD-2 resin and resulted in methanol fraction and water fraction. The methanol fraction was analysed by HPLC and further treated with 6 N HCl and acid and base ethyl acetate partitions before and after the hydrolysis.

Egg yolk and egg white samples were extracted with a solvent mixture of acetonitrile:hexane (1:1, v/v) and resulted in ACN/aqueous, hexane and PES fractions. The ACN/aqueous fraction was evaporated and partitioned with ethyl acetate. The PES from yolk was further treated with protease and then the protease aqueous fraction was fractionized into methanol fraction and water fraction using XAD-2 resin.

Liver, kidney, muscle, egg yolk and egg white control samples were fortified with ^{14}C-TM. HPLC analysis of extract fractions, stored in a refrigerator for 2–3 weeks, showed substantial degradation of the parent compound to MBC. When extract sample was analysed by HPLC immediately after concentration (on the same day of fortification), litter degradation of TM was observed. Therefore, the parent-containing fractions were analysed immediately after concentration.

Metabolism study results on laying hens are shown in Tables 33–41.

Most (92.8%) of administered radioactivity was excreted. Liver (1.67 mg eq/kg), kidney (1.23 mg eq/kg) and egg yolk (0.537 mg eq/kg) were target tissues. Other tissues contained substantially lower residues as follows: breast muscle (0.069 mg eq/kg), fat (0.061 mg eq/kg), skin (0.145 mg eq/kg) and egg white (0.128 mg eq/kg). Egg white and yolk residues plateaued by day 5 and day 9 of dosing, respectively. Extraction using different solvent systems recovered 64.3% TRR in breast muscle, 85.2% TRR in fat, 57.5% TRR in skin, 36.2% TRR in liver, 44.8% TRR in kidney, 70.1% TRR in egg yolk and 95.1% TRR in egg white.

Table 33 Total radioactive residues in laying hens administered with ^{14} C-TM

Sample	TRR (mg eq/kg)	[%] of total dose
Excreta, day-7	42.5	92.8
Egg yolk, day-10	0.537	0.11
Egg white, day-10	0.128	0.091
Liver	1.67	0.10
Kidney	1.23	0.020
Breast muscle	0.069	0.008
Thigh muscle	na	0.008
Fat	0.061	0.001
Skin	0.145	0.004
Gizzard	na	0.042

Sample	TRR (mg eq/kg)	[%] of total dose
Blood	na	0.019
Heart	na	0.003
Total	na	93.2

na, not available

Table 34 Metabolites in breast muscle of laying hens administered with ^{14}C-TM

Metabolite	Total radioactivity in fraction										
	$CHCl_3$			MeOH/H_2O		PES				Total	
	ACN		Hexane			Protease-Aq.[a]			PES	(0.069 mg eq/kg)	
						EtOAc		Aq.			
%TRR	36.0		3.8	24.5		11.9		13.6	10.3	100	
	% TRR	mg eq/kg	% TRR	% TRR	mg eq/kg	% TRR	mg eq/kg			% TRR	mg eq/kg
5-OH-MBC	13.7	0.009		24.5	0.017					38.1	0.026
5-OH-MBC-S	1.4	0.001								1.4	0.001
MBC	12.0	0.008								12.0	0.008
TM	8.9	0.006								8.9	0.006
5-OH-2-AB						2.6	0.002			2.6	0.002
4-OH-FH-432						4.6	0.003			4.6	0.003
Unk (1)						4.7	0.003			4.7	0.003
Total	36.0	0.024		24.5	0.017	11.9	0.008			72.4	0.049

[a] Acid hydrolysed and partitioned with ethyl acetate

Table 35 Metabolites in fat of laying hens administered with ^{14}C-TM

Metabolite	Total radioactivity in fraction							
	MeOH/Aq.		PES	Hexane			Total	
				ACN		Hexane	(0.061 mg eq/kg)	
%TRR	18.0		14.8	36.7		30.5	100	
	% TRR	mg eq/kg		% TRR	mg eq/kg		% TRR	mg eq/kg
5-OH-MBC	0.6	0.000		5.3	0.003		5.9	0.003
5-OH-MBC-S	0.8	0.001					0.8	0.001
MBC	9.0	0.005		15.2	0.009		24.2	0.014
4-OH-TM conj.[a]	2.5	0.001					2.5	0.001
TM	1.0	0.001		6.1	0.004		7.1	0.005
Unk 1 (polar)	2.2	0.001		10.1	0.006		12.3	0.007
Unk 2	0.8	0.000					0.8	0.000
Unk 3	1.1	0.001					1.1	0.001
Total	18.0	0.010		36.7	0.022		54.7	0.033

[a] Tentatively identified

Table 36 Metabolites in skin of laying hens administered with ^{14}C-TM

Metabolite	Total radioactivity in fraction										
	MeOH/Aq.		PES				Hexane			Total	
			Protease-Aq.[a]			PES	ACN		Hexane	(0.145 mg eq/kg)	
			H_2O	MeOH[b]							
				EtOAc	Aq						
%TRR	53.5		3.6	8.2	19.0	11.7	3.2		0.8	100	
	% TRR	mg eq/kg		% TRR	mg eq/kg		% TRR	mg eq/kg		% TRR	mg eq/kg
5-OH-MBC	20.4	0.030		1.8	0.003		0.12	0.00		22.3	0.033
MBC				0.7	0.001		1.6	0.002		2.3	0.003
4-OH-TM conj[c]	22.6	0.033								22.6	0.033
4-OH-TM	4.2	0.006								4.2	0.006
TM	3.2	0.005					1.6	0.002		4.8	0.007
4-OH-2-AB				3.9	0.006					3.9	0.006
Unk 1	3.1	0.004								3.1	0.004
Unk 2				1.8	0.003					1.8	0.003

Metabolite	Total radioactivity in fraction											
	MeOH/Aq.		PES					Hexane			Total (0.145 mg eq/kg)	
			Protease-Aq. [a]				PES	ACN		Hexane		
			H_2O	MeOH [b]								
				EtOAc		Aq						
Total	53.5	0.078		8.2	0.013			3.3	0.004		65.0	0.095

[a] Protease-aqueous fraction was fractionized into water and methanol fractions by XAD-2 resin

[b] Acid hydrolysed (6 N HCl) and partitioned with ethyl acetate (acid, base), before and after the hydrolysis

[c] Tentatively identified

In breast muscle, parent TM was present at 8.9% TRR (0.006 mg/kg). Metabolite 5-OH-MBC was a major component, accounting for 38.1% TRR (0.026 mg eq/kg). MBC was found at 12.0% TRR (0.008 mg eq/kg). 5-OH-MBC-S, 5-OH-2-AB and 4-OH-FH-432 were found at each below 5% TRR.

In fat of hens, parent was present at 7.1% TRR (0.005 mg/kg). MBC was a major metabolite found at 24.2% TRR (0.014 mg eq/kg). 5-OH-MBC was found at 5.9% TRR (0.003 mg eq/kg). 5-OH-MBC-S was detected at 0.8% TRR (0.001 mg eq/kg). 4-OH-TM conjugate (tentatively identified), was at 2.5% TRR (0.001 mg eq/kg). 30.5% TRR (0.019 mg eq/kg) in hexane fraction and PES were further analysed.

In skin, the parent was present at 4.8% TRR (0.007 mg/kg). 5-OH-MBC was a major component, accounting for 22.3% TRR (0.033 mg eq/kg). The highest residue, however, was an unknown (22.6% TRR, 0.033 mg eq/kg), tentatively identified as 4-OH-TM conjugate because of showing a very similar chromatographic behaviour as the 4-OH-TM-S and/or 4-OH-TM conjugate isolated from liver and kidney. MBC, 4-OH-TM and 4-OH-2-AB were found, but each at < 5% TRR.

In liver, parent was present at 6.4% TRR (0.106 mg/kg). 5-OH-MBC was found at 6.3% TRR (0.105 mg eq/kg). MBC and 4-OH-TM were found at 1.7% TRR and 1.6% TRR, respectively. 4-OH-TM conjugated (tentatively identified) was present at 3.2% TRR (0.053 mg eq/kg). From the PES, various metabolites of 5-OH-MBC, 3-OH-TM-S, FH-73, MBC, 5-OH-MBC and polar metabolites were released by protease digestion and acid hydrolyses.

In kidney, parent was present at 3.7% TRR (0.045 mg/kg). The major metabolites were found as 5-OH-MBC (14.5% TRR, 0.179 mg eq/kg) and 5-OH-MBC-S (11.6% TRR, 0.143 mg eq/kg). MBC was found at 5.9% TRR (0.073 mg eq/kg). 4-OH-TM-S, 4-OH-TM conjugate (tentative), 2-AB and 5-OH-2-AB were detected at below 5% TRR. Like liver, various metabolites of 3-OH-TM-S, FH-73, MBC, 4-OH-FH-432 and polar metabolites were released from the PES by protease digestion and acid hydrolyses.

Table 37 Distribution of radioactivity in liver and kidney of laying hens administered with ^{14}C-TM

Sample	TRR (mg eq/kg)	% Total radioactivity in fraction								
		$CHCl_3$		$MeOH/H_2O$ [a]		PES				Total
		ACN	Hexane	EtOAc	Aq.	Protease-Aq. [b]		PES [c]		
						EtOAc	Aq.	EtOAc	Aq.	
Liver	1.67	10.9	0.6	11.3	13.4	2.8	40.1	3.7	17.1	100
Kidney	1.23	10.3	2.1	18.6	13.8	4.6	38.9	3.4	8.3	100

[a] Acid hydrolysed (6 N HCl) and partitioned with ethyl acetate

[b] Acid hydrolysed (1 N HCl) and partitioned with ethyl acetate

[c] Acid hydrolysed (1 N HCl) and partitioned with ethyl acetate

Table 38 Metabolites in liver and kidney of laying hens administered with ^{14}C-TM

Metabolite or fraction	Liver		Kidney	
	% TRR	mg eq/kg	% TRR	mg eq/kg
Organic and $MeOH/H_2O$				

Metabolite or fraction	Liver		Kidney	
	% TRR	mg eq/kg	% TRR	mg eq/kg
TM	6.4	0.106	3.7	0.045
4-OH-TM	1.6	0.026	-	
4-OH-TM-S	-		1.0	0.012
4-OH-TM conj.(tentatively identified)	3.2	0.053	1.1	0.014
MBC	1.7	0.028	5. 9	0.073
5-OH-MBC	6.3	0.105	14.5	0.179
5-OH-MBC-S	-		11.6	0.143
2-AB	-		0.1	0.001
5-OH-2-AB	-		4.6	0.057
Unks (M16-26)	16.5 (0.25-3.12)	0.276 (0.004-0.052)	-	
Unk (M27 polar)	-		0.2	0.002
Hexane soluble	0.6		2.1	
PES				
Protease-Aq. fraction[a]				
EtOAc[*]	2.8	0.047	4.6	0.057
Aqueous[**]	40.1	0.669	38.9	0.480
PES[b]				
EtOAc	3.7	0.063	3.4	0.042
Aqueous	17.1	0.285	8.3	0.103
Total	100	1.67	100	1.23

[a] Acid hydrolysed (6 N HCl) and partitioned with ethyl acetate; In the EtOAc fractions[*] of liver and kideny, 5-OH-MBC and unknown metabolites were detected. In the aqueous fractions[**] of liver and kidney, 5-OH-MBC and polar metabolites were detected.

[b] Acid hydrolysed (1 N HCl) and partitioned with ethyl acetate. In the EtOAC fractions of liver and kidney, 3-OH-TM-S, FH-73, MBC, 5-OH-MBC (liver), 4-OH-FH-432 (kidney) and polar metabolites were detected.

Table 39 Metabolites in egg yolk of hens administered with ^{14}C-TM

Metabolite	Total radioactivity in fraction										
	Acetonitrile/Aq.				PES			Hexane	Total (0.537 mg eq/kg)		
	EtOAc		Aq.		Protease-Aq.[a]		PES				
					EtOAc		Aq.				
%TRR	62.1		3.8		19.1		6.9	3.9	4.2	100	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg				%TRR	mg eq/kg
2-AB			2.7							2.7	0.015
5-OH-MBC	4.9		0.4		5.2					10.4	0.056
5-OH-MBC-S	2.4		0.3							2.7	0.014
MBC	7.5		0.4		2.2					10.0	0.054
4-OH-TM	2.2									2.2	0.012
TM	45.2									45.2	0.243
Unks (8)					0.3-5.3					11.8	0.063
Total	62.1		3.8		19.1					85.0	0.456

[a] Acid hydrolysed and partitioned with ethyl acetate

Table 40 Metabolites in egg white of hens administered with ^{14}C-TM

Metabolite	Total radioactivity in fraction									
	Acetonitrile/Aq.				PES		Hexane		Total (0.128 mg eq/kg)	
	EtOAc		Aq.							
%TRR	91.3		3.7		5.0		0.1		100	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
5-OH-MBC	16.9	0.022							16.9	0.022
5-OH-MBC-S	5.8	0.007							5.8	0.007
MBC	21.1	0.027							21.1	0.027
4-OH-TM	2.2	0.003							2.2	0.003
TM	45.3	0.058							45.3	0.058
Total	91.2	0.117							91.2	0.117

In egg yolk, parent was a major component, accounting for 45.2% TRR (0.243 mg/kg). 5-OH-MBC and MBC were found at 10.4% TRR (0.056 mg eq/kg) and 10.0% TRR (0.054 mg eq/kg), respectively. Metabolites, 5-OH-MBC-S, 4-OH-TM and 2-AB were detected at 2.2–2.7% TRRs. Other eight unknowns were detected at totally 11.8% TRR (0.063 mg eq/kg), each 0.3–5.3% TRR.

In egg white, parent was a major component, accounting for 45.3% TRR (0.058 mg/kg). MBC and 5-OH-MBC were found at 21.1% TRR (0.027 mg eq/kg) and 16.9% TRR (0.022 mg eq/kg), respectively. 5-OH-MBC-S and 4-OH-TM were detected at 5.8% TRR (0.007 mg eq/kg) and 2.2% TRR (0.003 mg eq/kg), respectively.

Table 41 Summary of identified metabolites in laying hens administered with ^{14}C-TM

Metabolite	Breast muscle (0.069 mg eq/kg)		Fat (0.061 mg eq/kg)		Skin (0.145 mg eq/kg)		Liver (1.67 mg eq/kg)		Kidney (1.24 mg eq/kg)		Egg yolk (0.537 mg eq/kg)		Egg white (0.128 mg eq/kg)	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
TM	8.9	0.006	7.1	0.005	4.8	0.007	6.4	0.106	3.7	0.045	45.2	0.243	45.3	0.058
4-OH-TM		nd		nd	4.1	0.006	1.6	0.026		nd	2.2	0.012	2.2	0.003
4-OH-TM-S		nd		nd		nd		nd	1.0	0.012		nd		nd
4-OH-FH-432	4.6	0.003		nd		nd		nd		nd		nd		nd
MBC	12.0	0.008	24.2	0.014	2.1	0.003	1.7	0.028	5.9	0.073	10.0	0.054	21.1	0.027
5-OH-MBC	38.1	0.026	5.9	0.003	22.8	0.033	6.3	0.105	14.5	0.179	10.4	0.056	16.9	0.022
5-OH-MBC-S	1.4	0.001	0.8	0.001		nd		nd	11.6	0.143	2.7	0.014	5.8	0.007
2-AB		nd		nd		nd		nd	0.1	0.001	2.7	0.015		nd
4-OH-2-AB		nd		nd	4.1	0.006		nd		nd		nd		nd
5-OH-2-AB	2.6	0.002		nd		nd		nd	4.6	0.057		nd		nd
Identified metabolites	68	0.046	38	0.023	38	0.055	16	0.265	41	0.510	73	0.394	91	0.117

Major components in tissue and eggs were as follows:

- Muscle: 5-OH-MBC
- Fat: MBC
- Skin: 5-OH-MBC
- Liver: TM, MBC and 5-OH-MBC
- Kidney: TM, MBC, 5-OH-MBC and 5-OH-MBC-S
- Egg (yolk, white): TM, MBC and 5-OH-MBC

Other components in tissue and eggs were also found at below 5% TRR.

- Muscle: 5-OH-MBC-S, 5-OH-2-AB, 4-OH-FH-432
- Fat: TM, 5-OH-MBC, 5-OH-MBC-S, 4-OH-TM conjugate (tentative)
- Skin: TM, 5-OH-MBC, 4-OH-TM, 4-OH-2-AB, 4-OH-TM conjugate (tentative)
- Liver: 4-OH-TM, 3-OH-TM-S, FH-73, 4-OH-TM conjugate (tentative)
- Kidney: 4-OH-TM, 4-OH-TM-S, 2-AB, 5-OH-2-AB, 3-OH-TM-S, FH-73, 4-OH-FH-432, 4-OH-TM conjugate (tentative)
- Egg (yolk, white): 2-AB, 5-OH-MBC-S, 4-OH-TM

This study indicated that TM is primarily metabolized in laying hens via the hydroxylation of the TM phenyl ring at the 3 or 4 position (presumably activated by microsomal mixed function oxidases, MFO), followed by oxidation, cleavage and cyclization of the thioamine side chains to form 4- or 5-OH-MBC. Another degradative pathway involves the chemical hydrolysis and cyclization of TM to MBC followed by formation of 5-OH-MBC by action of MFO. Further chemical and/or metabolic conversion of MBC to 2-AB (further 5-OH-2-AB) and 5-OH-MBC to 5-OH-2-AB is also

considered. Conjugates of OH-TM, OH-MBC and 5-OH-2-AB with a sulphate moiety are observed. A significant portion of the metabolites is tightly bound to endogenous solid matrices.

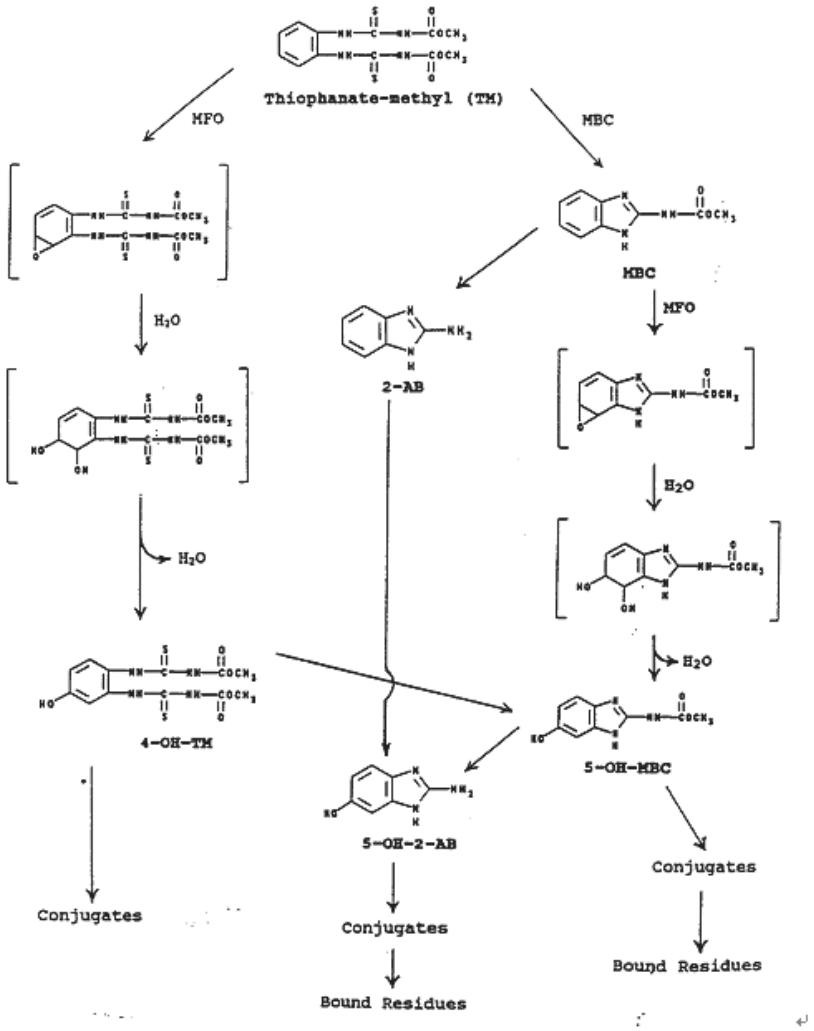


Figure 6 Proposed metabolic pathway of thiophanate-methyl in laying hens

Environmental fate in soil

Hydrolysis

The hydrolysis of TM (10 ppm) in buffer solutions was studied at pH 5, 7, and 9 and at 22, 45 and 65 °C (Soeda, Y., and Nomura, O., 1986; Report No. RD-8679). Half-life of TM obtained by interpolation at 25 °C was 867, 36 and 0.7 days at pH 5, 7 and 9, respectively. The major hydrolysis products at 22 °C and pH 7 and 9 were MBC (up to 33% on molar basis at pH 9) and AV-1951 (up to 22% on molar basis at pH 9).

Photolysis

The photodegradation of ^{14}C-TM was investigated in a silt loam soil for a period of 17 days of continuous irradiation which is equivalent to 31.6 days of natural summer sunlight at latitudes 30 °N

to 50 °N, respectively (Adam, D., 2014; Report No. RD-02996). Control samples were also incubated for 17 days under the same conditions except being kept in the dark. The soil surface (moisture content, pF2) was uniformly treated at a dose rate of 1.45 kg/ha. The total mean recovery of the applied dose was > 96%. Up to 18 degradation products were detected in irradiated samples and 13 in dark controls. MBC was the most predominant metabolite accounting on DAT 7 to maximum mean amounts of 67% and 74% in irradiated and dark control samples, respectively. All other metabolites, including the ones identified, did not exceed a mean amount of 3% AR at any time during entire incubation period. TM degraded by soil photolysis with a calculated DT_{50} of 0.75 days of artificial light, which corresponds to 1.4 days natural summer sunlight at 30 °N to 50 °N.

Aerobic degradation in soil

Two non-GLP studies and two GLP studies were provided by manufacturer.

Study 1

The metabolism of ^{14}C-thiophanate-methyl was studied in clay loam and light clay soils obtained from laboratory fields in Japan (non-GLP; Anonymous, 1981; Report No. RD-8194N). Acetone solution (0.25 mL) of ^{14}C-TM (phenyl ring label; 250 µg, 6.6×10^5 dpm) was treated to soil surface of 50% MWH. The treated soils were kept in the dark at 15 °C and 25 °C for 28 days and observed at time points of 0, 7, 14, 21 and 28 days. An analysis of metabolites was performed with soil taken at 0, 7, and 21 days.

The total recovery of radioactivity exceeded 95% of the applied radioactivity. Throughout the study period, carbon dioxide of 0.1–1.0% of the AR was generated in all cases. Extraction of radioactivity using aqueous methanol decreased consistenly, representing 25.0–57.7% of the AR at the end of study in all cases.

TM degraded instantly. The main product, in all cases, was MBC, which increased consistently and reached a maximum level of 29.3–68.3% of the AR at day 28. In all cases, DX-105 (max., 7.2% AR) and FH-432 (max., 2.4% AR) were found and other several unknown metabolites were also detected at each less than 2.5% of the AR.

Half-life of TM in light clay soil was about one day at both temperatures and in clay loam about 4 days at 25 °C and 7 days at 15 °C.

Study 2

^{14}C-Thiophanate-methyl was applied to sandy loam, clay loam and light clay soils (non-GLP; Anonymous, 1984; Report No. RD-8498N). Acetone solution of ^{14}C-TM (0.5 mg in 500 µL; 4.29×10^6 dpm) was treated to soil surface of 40% MWH and incubated at 22 °C in the dark for 64 days. Radioactivity ($^{14}CO_2$) evolved from soils was observed at 1, 2, 4, 8, 16, 32 and 64 days. Day 64 soil was subjected to analysis for metabolite.

More than 90% of the AR was recovered from the three soils. At day 64, the cumulative $^{14}CO_2$ was 20.3% in sandy loam, 26.3% in clay loam and 6.5% in light clay of the AR. Of the total radioactivity, 28.2–51.9% in the three soils (day 64) was extracted using aqueous methanol and subsequently 2 N HCl:methanol (2:8, v/v). In the unextracted soil residue, humin, humic acid and fulvic acid fractions were 33.2–39.0%, 0.3–4.4% and 1.0–3.9% of the AR, respectively.

At day 64, in the three soils, TM accounted for max. 0.9% of the AR and MBC accounted for maximum 37.0% of the AR. As other identified metabolites, DX-105 and FH-432 were found at maximum 2.0% (sandy loam) and 6.0% (sandy loam) of the AR, respectively. Unknown metabolites were detected at each less than 2% of the AR.

Study 3

^{14}C-Thiophanate-methyl was applied to three soils under aerobic conditions for a period of up to 120 days (Voelkl, S., 2002; Report No., RD-II02149). Silt loam (France), clay loam (France) and sandy loam (Germany) soils of 46% MWC were treated at 1.48 mg ai/kg soil dry weight and incubated at

20 °C in the dark. After 0, 1, 3, 7, 14, 28, 56 and 120 days of incubation, each soil samples were taken for analysis.

The total recoveries were 93.3–103% of the AR. The amount of CO_2 reached maximum values of silt loam 25.7%, clay loam 7.6% and sandy loam 7.3% of the AR at the end of incubation (day 120). Other volatile radioactivity did not exceed 0.1% of the AR.

In extraction with acetonitrile:water (8:2, v/v) followed by Soxhlet extraction (acetonitrile:water, 9:1, v/v), the amount of extracted radioactivity decreased continuously, representing silt lome 31.2%, clay loam 15.3% and sandy loam 23.3% of the AR at day 120. Organic matter fractionation of unextracted radioactivity (day 120) indicated that the major part of the radioactivity was incorporated into the humic acids and humin fraction (three soils, 15.6–58.6% of the AR) and the minor part of the bound radioactivity was associated with fulvic acids (three soils, 7.7–10.1% of the AR).

TM was present in the three soils at levels of 15.3–31.2% of the AR at day 120. Metabolites, MBC, CM-0237, DX-105 and 2-AB were found in the three soils. MBC was a major metabolite, showing a high peak of three soils, 62.8–75.8% of the AR at day 3 or 7. CM-0237 (idenfied by LC-MS) was present at maximum 9.8% of the AR in sandy loam soil at 3 day. DX-105 was detected at maximum 4.3% of the AR in silt loam soil at day 1. 2-AB was present at maximum 6.1% of the AR in clay loam at day 14. Several unknowns were detected, each less than *ca.* 5% of the AR.

DT_{50} and DT_{90} values calculated are shown in Table 42.

Table 42 DT_{50} and DT_{90} values for TM and MBC in soils

Metabolite	DT_{50} (days)			DT_{90} (days)		
	Silt loam	Clay loam	Sandy loam	Silt loam	Clay loam	Sandy loam
TM	0.5	0.7	0.6	1.6	2.4	2.1
MBC	58	50	39	192	164	128
CM-0237	5	86	45	15	284	149

Study 4

The degradation of ^{14}C-thiophanate-methyl (phenyl ring label) was investigated in sandy loam soil (Speyer 5M) under aerobic conditions (Adam, D., 2014; Report No. RD-02985). The soils (moisture content, pF 2) were treated at a rate of 1.42 mg ai/kg of dry soil and incubated at 20.9±0.1 °C for up to 120 days under dark conditions. The treatment rate corresponded to a field application rate of 1.1 kg ai/ha, assuming an even distribution of the test item on the top 5 cm soil layer and a soil bulk density of 1.5 g/cm^3. After treatment, soils were taken at 0, 1. 3. 7, 14, 28, 55, 90 and 120 days for analysis.

Total recovery of radioactivity was 98.4-108% of the applied radioactivity. Mineralisation of ^{14}C-TM was moderate with $^{14}CO_2$ reaching maximum 7.6% of the AR at study end. Extraction of radioactivity, using acetonitrile:water (4:1, v/v) followed by Soxhlet extraction with acetonitrile, decreased throughout the study reaching 15.9% at the end of incubation. In the unextracted soil residue, 13.9%, 14.4% and 36.1% of the AR were assoicated with fulvic acid, humic acid and humin fractions, respectively.

^{14}C-TM degraded instantly due to cleavage of the ester chains, representing 7.3% of the AR at day 1. MBC was a major metabolite, reaching maximum 48.3% of the AR at day 3 decreasing to 7.1% of the AR by day 120. Metabolites, DX-105, CM-0237, AV-1951, 2-AB and CM-0238, were also found, but each at less than 6.8% of the AR at any time. Other unknown six metabolites were also detected but very minor.

DT_{50}, DT_{75} and DT_{90} values for TM were 0.29 days, 057 days and 0.96 days, respectively. DT_{50}, DT_{75} and DT_{90} values for MBC were 40 days, 103 days and 133 days, respectively.

The main degradation pathway of TM in soil proceeded through formation of the major metabolite MBC and various minor metabolites with ultimate formation of bound residues and carbon dioxide.

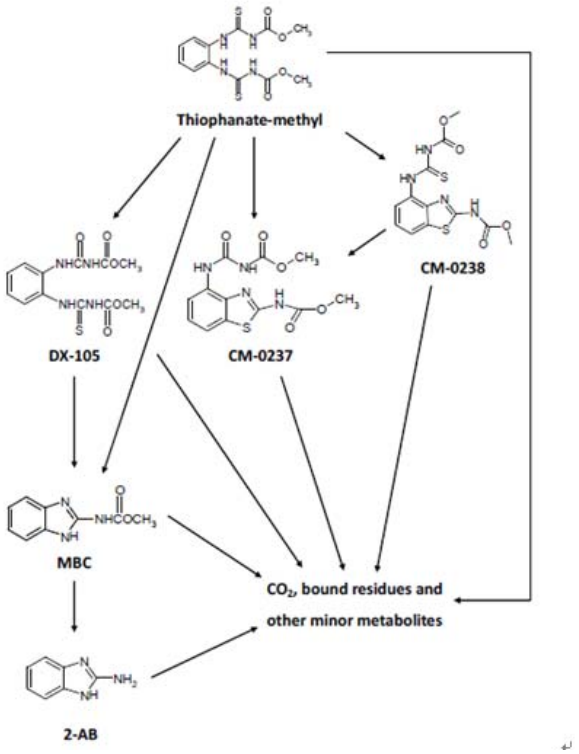


Figure 7 Proposed route of degradation of thiophanate-methyl in Speyer 5M soil

RESIDUE ANALYSIS

Analytical methods

Method ERV/005

Development and validation of methodology for the determination of TM and MBC residues in melon whole fruit and flesh was performed (2001; Report No., RD-II01024). Melon whole and flesh samples were extracted with methanol. Extract was partitioned with hexane, hexane phase discarded, and partitioned with dichloromethane. TM and MBC were determine by LC-MS/MS (TM, m/z 343>118; MBC, m/z 192>160).

Standard calibration for TM and MBC by LC-MS/MS was linear at 0.2 to 50 ppb (r^2=0.9987) and 0.2 to 40 ppb (r^2=0.9987), respectively. No interference (<20% of the LOQ) was in the chromatogram region of analyte in any of the matrices. LOQ for TM and MBC was 0.01 mg /kg in both matrices. Recoveries of TM and MBC in whole fruit and flesh were in the range of 70–110% (RSD, < 12%) and 73–111% (RSD, <9%), respectively at fortification levels of 0.01–1.0 mg/kg.

Table 43 Recovery of TM and MBC using method ERV/005

Compound	Matrix	Fortification level (mg/kg)	n	% Recovery		
				Range	Mean	RSD (%)
TM	Melon, whole	0.01	5	84-110	97	12
		0.1	5	87-95	91	4
		1.0	5	84-100	92	8
	Melon flesh	0.01	5	98-100	101	5
		0.1	5	70-99	89	12
		1.0	5	85-93	90	4
MBC	Melon, whole	0.01	5	74-93	82	9
		0.1	5	82-92	89	5
		1.0	5	97-104	100	3
	Melon flesh	0.01	5	73-77	75	2
		0.1	5	76-96	90	9
		1.0	5	99-111	105	5

LOQ, < 0.01 mg/kg for TM and MBC

In residue trials for plum, melon and grape, method ERV/005 was used as a reference method for residue analysis. The procedural recovery results were acceptable.

Table 44 Procedural recovery of TM and MBC in residue trials using method ERV/005

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Plum	TM	0.05	2	100, 104			RD-II01199
	MBC	0.05	2	71, 107			
	TM	0.05	1	87			RD-II02124
		0.1	3	73, 86, 88			
		0.5	5	77, 79, 98, 100, 103			
	MBC	0.05	1	104,95, 102, 109			
		0.1	3	80, 93, 96, 103, 108			
		0.5	5				
	TM	0.5	1	106			RD-03008
	MBC	0.5	1	109			
Melon	TM	0.1	2	891-85	83	3	RD-II01204
	MBC	0.05	1				
		0.1	2	73-82	78	8	
Melon, whole	TM	0.1	3	78-95	88	10	RD-II02128
	MBC	0.1	3	92-110	99	10	
Melon, flesh	TM	0.5	2	78-95	87	14	
	MBC	0.5	2	101-109	105	5	
Melon, whole	TM	05	1	110			RD-II02129
	MBC	0.5	1	90			
Melon, flesh	TM	0.1	1	73			
	MBC	0.1	1	92			
Grape	TM	0.05	2	75			RD-II01196
	MBC	0.05	2	71-95	83	20	
	TM	0.1	3	70-72	71	2	RD-II02143
		0.5	7	78-90	84	6	

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
		2.0	1	82			
	MBC	0.1	3	78-98	85	13	
		0.5	7	77-106	96	11	
		2.0	1	99			
	TM	0.5	2	73-76	75	3	RD-03042
	MBC	0.5	2	91-101	96	7	

Method ERV/006 and Method ERV/007

ERV/006 and ERV/007 involve separation of TM and MBC, conversion of TM to MBC and determination of MBC by LC-MS. These two are the same methods, only validating different matrices.

Development and validation of methodology for the determination of TM and MBC residues in winter wheat (ERV/006; 2001; RD-II01023) and oilseed rape (ERV/007; 2001; RD-II01025) were performed. Samples (whole wheat, grain, straw; whole rape, rape pod, rape seed) were extracted with cold (stored in a freezer) methanol:water:acetic acid (90:10:1, v/v/v). MBC was separated by use of SCX SPE cartridge, first eluting fraction containing TM with water and methanol and then eluting fraction containing MBC with 1% ammonia in methanol. MBC was determined by LC-MS (m/z, 192). TM fraction was partitioned with hexane, hexane phase discarded, and again partitioned with dichloromethane. Dichloromethane phase was concentrated and solubilized in pH 6.6 buffer solution prior to conversion to MBC by heating at 100 °C for 1 hour. The solution was partitioned with ethyl acetate and the ethyl acetate phase was cleaned up using SCX SPE cartridge. MBC was eluted with 1% ammonia in water.

Response of LC-MS system to MBC was linear in the range of 0.2–40 ppb (r^2=0.9998). No apparent interference was (< 20% of the LOQ) in the chromatogram region of analyte in any of the matrices. LOQ for MBC was 0.01 mg /kg in all matrices. Recoveries of TM (70–105%; RSD < 11%) and MBC (70–96%; RSD, < 14%) fortified at 0.01–1.0 mg/kg were satisfactory in all matrices.

Table 45 Recovery of TM and MBC using method ERV/006 and ERV/007

Analyte	Matrix	Fortification (mg/kg)	n	% Recovery		
				Range	Mean	RSD (%)
TM	Winter wheat grain	0.01	5	78-99	87	11
		0.1	5	70-77	75	5
		1.0	5	81-88	84	4
	Winter wheat straw	0.01	5	94-105	99	4
		0.1	5	71-73	72	1
		1.0	5	70-74	72	2
	Winter wheat whole plant	0.01	5	72-85	77	7
		0.1	5	70-78	74	4
		1.0	5	92-105	99	6
MBC	Winter wheat grain	0.01	5	70-76	73	3
		0.1	5	70-75	71	3
		1.0	5	77-90	83	6
		0.01	5	81-87	83	3
		0.1	5	77-85	81	4
		1.0	5	81-90	87	4
	Winter wheat whole plant	0.01	5	71-96	77	14
		0.1	5	76-83	79	3
		1.0	5	82-94	89	5
TM	Rape seed	0.01	5	76-90	85	7
		0.1	5	72-83	77	6
		1.0	5	75-85	80	5
	Rape pods	0.01	5	86-102	95	6
		0.1	5	72-98	85	13

Analyte	Matrix	Fortification (mg/kg)	n	% Recovery		
				Range	Mean	RSD (%)
		1.0	5	77-83	81	3
	Rape whole plant	0.01	5			
		0.1	5			
		1.0	5			
MBC	Rape seed	0.01	5	72-80	74	5
		0.1	5	72-81	75	6
		1.0	5	71-79	75	4
	Rape pods	0.01	5	102-110	106	4
4		0.1	5	84-91	89	4
		1.0	5	83-95	89	5
	Rape whole plant	0.01	5	93-103	96	5
		0.1	5	83-95	90	5
		1.0	5	91-97	93	3

LOQ, < 0.01 mg/kg for TM and MBC

In residue trials for barley and wheat using method ERV/006, 007 as a reference method for residue analysis, the procedural recovery results were acceptable.

Table 46 Procedural recovery of TM and MBC in residue trials using method ERV/006, 007

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Barely grain	TM	0.05	1	74			RD-II01194
	MBC	0.05	1	98			
Barley straw	TM	0.05	1	103			
	MBC	0.05	1	94			
Barely whole plant	TM	0.05	2	72-73	73		
		10.0	1	92			
	MBC	0.05	2	92-96	94		
		10.0	1	97			
Barley grain	TM	0.05	3	70-107	91	21	RD-II02144
		0.1	1	89			
		0.5	2	87-97	92		
	MBC	0.05	3	83-94	88	6	
		0.1	1	93			
		0.5	2	88-106	97		
Barley straw	TM	0.1	1	107			
		0.5	1	81			
	MBC	0.1	1	85			
		0.5	1	86			
Barley whole plant	TM	0.5	4	77-104	88	13	
		20.0	2	82-83	83		
	MBC	0.5	3	100-108	4		
		20.0	2	95-97	96		
Barley grain	TM	0.5	1	97			RD-03006
	MBC	0.5	1	79			
Barley whole plant	TM	1.0	1	75			
		10.0	1	70			
	MBC	1.0	1	84			
Wheat grain	TM	0.05	1	95			RD-II01193
	MBC	0.05	1	89			
Wheat straw	TM	0.05	1	93			
	MBC	0.05	1	82			
Wheat ears	TM	0.05	1	87			
	MBC	0.05	1	102			
Wheat whole plant	TM	0.05	2	87			
		10.0	1	87			
	MBC	0.05	2	91			
		10.0	1	92			
Wheat grain	TM	0.05	1	76			RD-II02132

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
		0.1	3	78-99	88	12	
	MBC	0.05	1	81			
		0.1	3	78-99	87		
Wheat straw	TM	0.5	5	70-102	85	17	
	MBC	0.5	5	81-110	88	14	
Wheat ears	TM	0.05	1	110			
		0.1	2	84-110	97		
	MBC	0.05	1	80			
		0.1	2	76-91	84		
Wheat whole plant	TM	0.5	8	71-106	92	17	
		20	1	74			
	MBC	0.5	8	78-102	87	9	
		20	1	99			
Wheat grain	TM	0.1	1	96			RD-03007
		0.5	2	73-80	77		
	MBC	0.1	1	73			
		0.5	2	92-93	93		
Wheat ears	TM	1.0	1	72			
	MBC	1.0	92				
Wheat whole plant	TM	1.0	2	74-83	79		
		10.0	1	72			
	MBC	1.0	1	96			
		10.0	1	103			

Method BR-011-03 (modified), Method BR-011-05, Method KP-024-01, Method KP-021-00

Methodology of these methods is basically the same. Sample is extracted with acidified methanol (MeOH:3 N H_3PO_4, 1:1, v/v) in the presence of L-(+)cysteine (antioxidant). Extract is neutralised with ammonium hydroxide and then partitioned with dichloromethane. HPLC is used for determination of analytes: TM and MBC in BR-011-05, KP-024-01 and KP-021-00 methods and TM, MBC, allophanate and DX-105 in method BR-011-03 (modified). In the all methods and matrices, LOQs are < 0.05 mg/kg. In method KP-024-01, 1', 2' amino SPE (PSA-SPE) procedure is optionally used after partitioning with dichloromethane for dry matrices such as hay and straw.

For analysis of TM, cautionary analysis is needed. For this, the following notes are included:

In the BR-011-05 (1996), chilled extraction solution is used. Processing small sets of samples to insure that samples are quickly extracted and partitioned into dichloromethane helps prevent conversion of TM to MBC. It is imperative that processing of the samples through the entire method should be completed in one day to obtain consistently good recoveries of TM. In BR-011-03 (1995) and KP-024-01 (2001) methods, rapid processing is essential to the success of this analysis due to the labile nature of TM. All flasks containing sample should be stored under refrigeration when not in use.

For the four methods, full data set for method validation were not provided. However, residue analysis in many residue trials was performed using one of those methods. Some residue trial studies included acceptable recovery results conducted before analysis of trial sample with small number of analyses (n=1 or 2 at each fortification level): peanut, soybean (two studies), sugar beet (processing), snap bean, dry bean. For watermelon, recoveries were not acceptable.

In many residue trials, procedural recoveries were acceptable. In some residue trials, procedural recoveries were not acceptable.

In residue trial studies using method BR-011-03 (modified), procedural recoveries in snap bean studies were acceptable, but for dry bean not acceptable.

In residue trial studies on rape using method KP-024-01, the procedural recoveries were acceptable.

In residue trial studies using method BR-011-05, procedural recoveries on strawberry, cucumber, soy bean, peanut and snap bean (storage stability test) were acceptable, but not for pecan.

In residue trial studies using method KP-021-00, procedural recoveries in almond were acceptable.

Table 47 Procedural recovery of TM and MBC in residue trials using method BR-011-03 (modified)

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Snap bean*	TM	0.05	1	62			RD-II02090
		0.1	1	91			
		0.5	1	89			
		1.0	1	99			
	MBC	0.05	1	94			
		0.1	1	86			
		0.5	1	97			
		1.0	1	91			
Snap bean vines*	TM	0.05	1	62			
		0.1	1	62			
		0.5	1	79			
		1.0	1	98			
	MBC	0.05	1	68			
		0.1	1	74			
		0.5	1	82			
		1.0	1	87			
Snap bean	TM	0.05	1	86			
		0.1	1	85			
		0.5	2	87-90			
		2.0	1	96			
		5.0	1	85			
		10.0	1	98			
	MBC	0.05	1	82			
		0.1	1	84			
		0.5	2	87-89			
		2.0	1	85			
		5.0	1	83			
		10.0	1	80			
Snap bean vine	TM	0.05	1	90			
		0.1	1	78			
		0.5	2	66-76			
		2.0	2	82-94			
		5.0	1	94			
		10.0	1	97			
	MBC	0.05	1	112			
		0.1	1	100			
		0.5	2	71-88			
		2.0	2	91-124			
		5.0	1	85			
		10.0	1	91			
Snap bean	FH-432	0.05	1	66			
		0.1	1	84			
		0.5	2	84-89			
		2.0	1	89			
		5.0	1	81			
		10.0	1	76			
	DX-105	0.05	1	120			
		0.1	1	107			
		0.5	2	94-94			
		2.0	1	95			
		5.0	1	85			
		10.0	1	100			
Snap bean vine	FH-432	0.05	1	84			
		0.1	1	86			

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
		0.5	2	74-81			
		2.0	2	88-89			
		5.0	1	83			
		10.0	1	90			
	DX-105	0.05	1	124			
		0.1	1	96			
		0.5	2	78-80			
		2.0	2	90-100			
		5.0	1	92			
		10.0	1	99			
Dry bean*	TM	0.05	1	82			RD-II02166**
		0.1	1	75			
		0.5	1	87			
		1.0	1	83			
	MBC	0.05	1	80			
		0.1	1	68			
		0.5	1	85			
		1.0	1	76			
	FH-432	0.05	1	90			
		0.1	1	73			
		0.5	1	83			
		1.0	1	71			
	DX-105	0.05	1	68			
		0.1	1	73			
		0.5	1	94			
		1.0	1	84			
Dry bean vines*	TM	0.05	1	80			
		0.1	1	80			
		0.5	1	76			
		1.0	1	77			
	MBC	0.05	1	100			
		0.1	1	95			
		0.5	1	85			
		1.0	1	74			
	FH-432	0.05	1	66			
		0.1	1	86			
		0.5	1	81			
		1.0	1	69			
	DX-105	0.05	1	68			
		0.1	1	78			
		0.5	1	84			
		1.0	1	80			
Dry bean	TM	0.05	2	70-86			
		0.1	2	69-106			
		0.5	2	73-78			
		1.0	3	81-98			
		5.0	1	85			
		10.0	1	80			
	MBC	0.05	2	58-66			
		0.1	2	56-97			
		0.5	2	50-65			
		1.0	3	84-96			
		5.0	1	75			
		10.0	1	61			
	FH-432	0.05	2	52-66			
		0.1	2	51-105			
		0.5	2	47-64			
		1.0	3	82-104			
		5.0	1	74			
		10.0	1	60			
	DX-105	0.05	2	54-66			
		0.1	2	65-109			

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
		0.5	2	67-74			
		1.0	3	85-100			
		5.0	1	87			
		10.0	1	77			
Dry bean vines	TM	0.05	1	90			
		0.1	2	76-98			
		0.5	1	88			
		1.0	1	75			
		3.0	1	78			
		5.0	1	68			
		10.0	2	37-97			
	MBC	0.05	1	54			
		0.1	2	57-68			
		0.5	1	73			
		1.0	1	61			
		3.0	1	68			
		5.0	1	76			
		10.0	2	34-83			
	FH-432	0.05	1	64			
		0.1	2	61-87			
		0.5	1	78			
		1.0	1	56			
		3.0	1	56			
		5.0	1	91			
		10.0	2	33-71			
	DX-105	0.05	1	84			
		0.1	2	72-84			
		0.5	1	87			
		1.0	1	65			
		3.0	1	75			
		5.0	1	72			
		10.0	2	30-93			

* Analysed before analysis of residue trial sample

* Recovery results, not acceptable

Table 48 Procedural recovery of TM and MBC in residue trials using method BR-011-05

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Cucumber	TM	0.05	1	68			RD-II02171
		0.1	1	66			
		0.5	1	86			
		1.0	1	93			
	MBC	0.05	1	100			
		0.1	1	111			
		0.5	1	99			
		1.0	1	122			
Peanut nutmeat	TM	0.05	2	86-87	87		RD-II02094
		0.1	2	86-88	87		
		0.5	2	75-91	83		
	MBC	0.05	2	78-81	80		
		0.1	2	87-97	92		
		0.5	2	95-98	97		
Peanut hay	TM	0.5	2	99-105	102		
		1.0	2	75-84	80		
		5.0	2	74-76	75		
	MBC	0.5	2	98-107	103		
		1.0	2	72-85	79		

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
		5.0	2	77-81	79		
Peanut nutmeat [d]	TM	0.05	1	78			RD-03607
		0.1	1	63			
		0.5	1	78			
		1.0	1	72			
	MBC	0.05	1	98			
		0.1	1	81			
		0.5	1	94			
		1.0	1	95			
Peanut meal [d]	TM	0.05	1	116			
		0.1	1	106			
		0.5	1	94			
		1.0	1	98			
	MBC	0.05	1	88			
		0.1	1	76			
		0.5	1	100			
		1.0	1	103			
Peanut oil [d]	TM	0.05	1	86			
		0.1	1	77			
		0.5	1	76			
		1.0	1	78			
	MBC	0.05	1	106			
		0.1	1	112			
		0.5	1	98			
		1.0	1	96			
Peanut nutmeat	TM	0.05	1	64			
		1.0	1	74			
	MBC	0.05	1	94			
		1.0	1	98			
Peanut meal	TM	0.05	1	88			
		1.0	1	97			
	MBC	0.05	1	92			
		1.0	1	98			
Peanut oil	TM	0.05	1	100			
		1.0	1	91			
	MBC	0.05	1	112			
		1.0	1	99			
Pecan	TM	0.05	2	62-64	63		RD-II02173[*]
		0.06	1	68			
		0.1	1	49			
		0.5	2	61-75	68		
	MBC	0.05	2	88-118	103		
		0.06	1	76			
		0.5	3	61-90	77	19	
Snap bean (storage stability)	TM	1.0	19	61-105	82	13	RD-03167
	MBC	1.0	2	105-106	106		
Soya bean seed[d]	TM	0.05	1	108			RD-II02091
		0.1	1	99			
		0.5	1	98			
		1.0	1	101			
	MBC	0.05	1	86			
		0.1	1	105			
		0.5	1	71			
		1.0	1	99			
Soya bean straw[d]	TM	0.2	1	78			
		0.5	1	73			
		1.0	1	69			

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
		2.0	1	82			
	MBC	0.2	1	101			
		0.5	1	102			
		1.0	1	97			
		2.0	1	107			
Soya bean seed	TM	0.05	2	88-100			RD-II02091
		0.1	2	73-94			
		0.5	1	80			
	MBC	0.05	2	66-88			
		0.1	2	81-88			
		0.5	1	85			
Soya bean straw	TM	0.2	2	81-89			
		0.5	1	81			
		1.0	1	77			
		5.0	1	74			
	MBC	0.2	2	93-121			
		0.5	1	102			
		1.0	1	106			
		5.0	1	99			
Soya bean seed[d]	TM	0.05	1	108			RD-II01045
		0.1	1	99			
		0.5	1	89			
		1.0	1	101			
	MBC	0.05	1	86			
		0.1	1	105			
		0.5	1	71			
		1.0	1	99			
Soya bean oil[d]	TM[e]	0.05	2	94, 100			
		0.1	1	110			
		0.5	1	95			
		1.0	1	92			
	MBC	0.05	2	100, 102			
		0.1	1	102			
		0.5	1	101			
		1.0	1	103			
Soya bean hull[d]	TM	0.05	1	98			
		0.1	1	105			
		0.5	1	90			
		1.0	1	92			
		5.0	1	84			
	MBC[e]	0.05	1	90			
		0.1	1	96			
		0.5	1	102			
		1.0	1	103			
		5.0	1	89			
Soya bean seed	TM	0.1	1	97			
		1.0	1	91			
	MBC	0.1	1	83			
		1.0	1	94			
Soya bean meal	TM[e]	0.05	1	242			
		5.0	1	73			
	MBC[e]	0.05	1	88			
		5.0	1	88			
Soya bean SRAC (seed raw agricultural commodity)	TM[e]	5.0	1	87			

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
	MBC	5.0	1	91			
Soya bean hull	TM	50.0	1	90			
	MBC[e]	50.0	1	85			
Strawberry	TM	0.05	2	79-87	83		RD-03544
		0.1	2	88-93	91		
		0.5	2	80-86	83		
	MBC	0.05	2	118-124	121		
		0.1	2	106-110	108		
		0.5	2	106-114	110		
Sugar beet sugar[d]	TM	0.05	2	106-109			RD-II02164
		0.5	2	93-95			
	MBC	0.05	2	94-98			
		0.5	2	93-94			
Sugar beet dry pulp[d]	TM	0.05	2	57-67			
		0.5	2	67-78			
	MBC	0.05	2	90-90			
		0.5	2	89-91			
Sugar beet molasses[d]	TM	0.05	2	82-106			
		0.5	2	87-88			
	MBC	0.05	2	98-105			
		0.5	2	110-113			
Sugar beet raw	TM	0.05	2	76-90			
	MBC	0.05	2	87-97			
Sugar beet sugar	TM	0.05	2	80-96			
	MBC	0.05	2	90-93			
Sugar beet dry pulp	TM	0.05	2	82-87			
	MBC	0.05	2	102-103			
Sugar beet molasses	TM	0.05	2	64-69			
	MBC	0.05	2	100-103			
Watermelon [d]	TM	0.05	2	34-52	43		RD-II02162[*]
		0.1	2	57-82	70		
		0.5	2	71-80	76		
	MBC	0.05	2	101-106	104		
		0.1	2	100-113	107		
		0.5	2	110-114	112		

na, Not available

[a] Storage stability test

[b] Analysed before analysis of storage sample; LOQ, < 0.01 mg/kg for TM and MBC

[c] Procedural recoveries

[d] Analysed before analysis of residue trial sample

[e] Corrected with control residue

[*] Recovery results, not acceptable

Table 49 Procedural recovery of TM and MBC in residue trials using method KP-024-01 (rape) and KP-21-00 (almond)

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Rape seed	TM	0.05	1	90			RD-00484
		0.5	1	72			
	MBC	0.05	1	108			
		0.5	1	93			
Rape seed	TM	0.05	2	79-82			RD-00496
		0.5	1	71			
		1.0	1	92			
	MBC	0.05	3	67, 85, 109			
		0.5	2	70-93			
		1.0	1	80			

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Almond nutmeat	TM	0.05	3	70, 86, 90			RD-01079
		0.1	2	78, 108			
		0.25	1	101			
		0.5	1	98			
		1.0	1	88			
	MBC	0.05	3	97, 107, 111			
		0.1	2	110-111			
		0.25	1	111			
		0.5	1	107			
		1.0	1	93			
Almond hull	TM	0.05	2	76-82			
		0.25	1	74			
		0.5	2	73-81			
		1.0	1	95			
		2.5	1	91			
		5.0	2	78-83			
		10.0	1	91			
	MBC	0.05	2	78-82			
		0.25	1	109			
		0.5	2	76-85			
		1.0	1	79			
		2.5	1	91			
		5.0	2	79-92			
		10.0	1	71			

KP-201R1 and KP-201R2

These two methods are basically the same. Sample is extracted with acidified methanol (50% methanol in 3 N H_3PO_4) after adding L-cysteine. Extract is neutralised with ammonium hydroxide and then cleaned up using SPE cartridge. For determination of TM and MBC, LC-MS/MS was used. LOQs are 0.01 mg/kg in various matrices.

Full validation data was not provided. In residue trials of apricot, spring onion, peanut, sugar beet, pistachio (KP-201R1) and snap bean (storage stability study; KP-201R1) using the methods, procedural recovery results for TM and MBC were acceptable.

Table 50 Procedural recovery of TM and MBC in residue trials using method KP-201R1 and KP201R2

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Apricot	TM	0.01	7	73-110	95	14	RD-01118
		0.1	6	98-118	108	8	
		1.0	1	86			
		2.0	2	81-89			
	MBC	0.01	7	78-97	86		
		0.1	6	91-102	96		
		1.0	1	101			
		2.0	2	87-87			
Peanut	TM	0.01	1	103			
		1.0	1	108			
	MBC	0.01	1	98			
		1.0	1	87			
Pistachio	TM*	0.01	3	101, 104, 113			RD-01074
		0.5	3	93, 93, 97			
		5.0	3	98, 99, 111			

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
	MBC*	0.01	3	80,89, 101			
		0.5	3	85, 102, 102			
		5.0	3	100, 100, 101			
	TM	0.01	6	75, 76, 83, 98, 100, 114			
		0.1	1	78			
		1.0	1	80			
	MBC	0.01	6	71, 73, 89, 94, 98, 99			
		0.1	1	100			
		1.0	1	92			
Snap bean (storage stability test)	TM	1.0	2	105-113			RD-03167
	MBC	1.0	2	105-106			
Spring onion	TM	0.01	2	82-103	93		RD-01116
		0.1	2	74-101	88		
	MBC	0.01	2	73-88	81		
		0.1	2	81-97	89		
Sugar beet	TM	0.01	2	107-109	108		
		0.1	2	106-108	107		
		5.0	1	91			
	MBC	0.01	2	75-83	79		
		0.1	2	99-115	107		
		5.0	1	102			

Method used in post-harvest treated orange and mandarin

Samples were extracted with acetonitrile:water (1:1, v/v) and filtered prior to analysis by LC-MS/MS. The detector responses for TM and MBC were linear within the range from 0.5 to 75 ppb ($r^2 > 0.99$). No peak interference occurred at the retention times of TM and MBC. LOQs are 0.05 mg/kg in all orange and mandarin matrices (orange peel and pulp, juice, pomace, marmalade, oil/water, orange water; mandarin peel and pulp, canned mandarin). Procedural recoveries in each matrix fortified several levels (including LOQ level; n=2-8 at each level) were in the range of 70-120% (RSD, <20%). The recoveries for peel and pulp of orange and mandarin are shown in the Table 51.

Table 51 Procedural recovery of TM and MBC in post-harvest treated orange and mandarin trials

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Orange peel	TM	0.05	5	93-102	98	4	RD-01293
		0.5	3	86-87	87	1	
		20	3	95-102	99	4	
	MBC	0.05	5	88-114	97	11	
		0.5	3	97-103	101	3	
		20	3	87-99	95	7	
Orange pulp	TM	0.05	6	89-96	93	3	
		0.5	3	91-96	93	3	
		2	3	97-106	100	5	
	MBC	0.05	6	76-101	90	13	
		0.5	3	94-95	94	1	
Mandarin peel	TM	0.05	5	85-102	93	7	
		0.5	3	103-106	105	1	
		20	3	87-96	93	5	
		100	3	96-113	105	8	
	MBC	0.05	8	89-102	94	5	
		0.5	3	84-91	88	4	
		20	3	89-96	94	4	

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No.
				Range	Mean	RSD (%)	
Mandarin pulp	TM	0.05	4	77-95	90	10	
		0.5	3	75-85	80	6	
		2	3	89-93	81	2	
	MBC	0.05	4	85-93	90	4	
		0.5	3	90-92	91	1	

Analysis of MBC

In one study (storage stability study: RD-03034, 1996), MBC was analysed for snap beans, apples, wheat grain, spinach, sugar beet root and tomato. Samples were extracted with acetone. Then the extract was partitioned with chloroform (use of sodium acetate and at pH 6.8), partitioned with hexane (addition of 1.0 N HCl solution), partitioned with chloroform, and then partitioned with chloroform (use of sodium acetate and at pH 6.8). HPLC was used for analysis of MBC and the LOQ was 0.05 mg/kg in all matrices. Recovery of MBC was tested at fortification levels of 0.5 (n=2) and 2.0 mg/kg (n=2) in each matrix. Recoveries were in the range of 70–104%.

Analysis of TM and MBC in some residue trials

For analytical methods used in some residue trials, the validation data set was not provided. Furthermore, procedural recoveries in the analysis of residues were not satisfactory. For the reason, residue values from such residue trials (apple, RD-01098; pear RD-03546; peach, RD-00078; cherry RD-1102093; summer squash, RD-II02092; sugar beet, RD-II02089; melon, RD-00427) are considered as not valid.

[NB: The unsatisfactory recovery data were as follows:

Apple (RD-01098): TM, 59–76% (mean 65%) at 0.1 mg/kg; MBC, 58–94% (RSD, 25%) at 0.05 mg/kg

Pear (RD-03546): TM, 148% (n=1) at 0.05 mg/kg; MBC, 126% (n=1) at 0.05 mg/kg

Peach (RD-00078): TM, 52–158% at 0.05 mg/kg, 67–94% (RSD, 21%) at 0.1 mg/kg; MBC, 64–96% (RSD, 24%) at 0.05 mg/kg

Cherry (RD-1102093): MBC, 60% (n=1) at 10 mg/kg and 67% (n=1) in 16 mg/kg

Summer squash (RD-II02092): TM, 58–97% (RSD, 22%) at 0.05 mg/kg; MBC, 57–138% (RSD, 22%) at 0.05 mg/kg

Sugar beet (RD-II02089): MBC, 54–96% (RSD, 22%)

Melon (RD-00427): recovery test was conducted before the study. Procedural recovery test was not done.]

Methods used for animal commodities

In feeding studies for lactating goat (including storage stability data) and laying hens (including storage stability data), TM and the metabolites were analysed as below.

Goat study (RD-9819, 1998a)

Muscle, TM analysis: Sample was extracted with acidified methanol, cleaned up by a reverse-phase cartridge and analysed by HPLC.

Muscle, MBC analysis: Sample was extracted with acidified methanol, partitioned with chloroform (pH, 6.8–7.0) and analysed by HPLC.

Liver, MBC and 5-OH-MBC: Liver sample was extracted with acidified methanol, partitioned with ethyl acetate (pH, 6.8–7.0) and analysed by HPLC

Whole milk, MBC and 5-OH-MBC-S: Well-mixed milk sample was acidified and incubated at approximately 100 °C for one hour (hydrolysis of 5-OH-MBC-sulfate to 5-OH-MBC). MBC and 5-OH-MBC were then extracted with ethyl acetate (pH, 6.8–7.0). The organic phase was filtered, acidified and concentrated. The acid extract was washed with hexane and analysed by HPLC.

The limit of quantification (LOQ) was 0.05 mg/kg for all analytes in all matrices. Overall recoveries for the matrices and analytes were in the range of 70–116% at fortification levels including the LOQ level.

Table 52 Recovery of TM and the metabolites from the goat samples

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No./Year
				Range	Mean	RSD (%)	
Fat	MBC	0.05	3	82, 93, 103			RD-9819/1998
		0.25	1	93			
		0.5	1	82			
		1.0	1	96			
Liver	5-OH-MBC	0.05	3	77, 86, 116			
		0.25	1	72			
		0.5	1	73			
		1.0	3	74, 76, 81			
	MBC	0.05	3	105, 108, 109			
		0.25	1	111			
		0.5	1	74			
		1.0	3	86, 90, 96			
Muscle	MBC	0.05	3	83, 86, 93			
		0.25	1	90			
		0.5	2	73, 87			
		1.0	2	86, 91			
	TM	0.05	3	76, 89, 103			
		0.2	1	81			
		0.5	1	99			
		1.0	3	86, 87, 94			
Whole milk	5-OH-MBC-S	0.05	3	79, 95, 102			
		0.2	1	80			
		0.25	1	94			
		0.5	1	88			
		1	3	74, 77, 92			
		2	1	91			
	MBC	0.05	3	94, 88, 105			
		0.2	1	93			
		0.25	1	93			
		0.5	1	98			
		1	3	80, 89, 89			
		2	1	94			
Skim milk	5-OH-MBC-S	0.05	2	73, 95			
		2	1	96			
	MBC	0.05	2	86, 103			
		2	1	102			
Cream	5-OH-MBC-S	0.05	2	70, 77			
		2	1	81			
	MBC	0.05	2	76, 87			
		2	1	97			
Kidney	4-OH-MBC	0.05	3	72, 78, 110			
		0.25	1	100			
		0.5	1	84			
		1	1	82			
		2	1	84			

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No./Year
				Range	Mean	RSD (%)	
		3	1	83			
	5-OH-MBC-S	0.05	3	74, 76, 82			
		0.25	1	109			
		0.5	1	87			
		1	1	79			
		2	1	78			
		3	1	83			
	MBC	0.05	3	74, 86, 101			
		0.25	1	91			
		0.5	1	89			
		1	1	88			
		2	1	91			
		3	1	88			

Laying hens (RD-9820, 1998b)

Muscle, MBC and 5-OH-MBC: Sample was extracted with acidified methanol, extracted with ethyl acetate (pH 6.8-7.0) and analysed by HPLC.

Liver, TM and 5-OH-MBC: Liver samples were extracted with acidified methanol or acetonitrile. TM was extracted from the liquid phase by SPE. For the analysis of 5-OH-MBC, the pH of the extract was adjusted and extracted with ethyl acetate. For the determination of both analytes, HPLC was used.

Eggs, TM: Well-mixed whole egg was extracted with acidified acetonitrile. TM was trapped on a reverse-phase cartridge, eluted with acetonitrile and analysed by HPLC.

Eggs, MBC and 5-OH-MBC: Well-mixed egg was diluted with water and washed with hexane. The extract was partitioned with ethyl acetate, which was evaporated. The extract was diluted with aqueous acid which was washed once more with hexane. HPLC was used for the determination of the analytes.

The limit of quantification (LOQ) was 0.05 mg/kg for all analytes in all matrices. Overall recoveries for the matrices and analytes were in the range of 72–111% at fortification levels including the LOQ level.

Table 53 Recovery of TM and the metabolites from hens and egg samples

Matrix	Analyte	Fortification (mg/kg)	n	% Recovery			Report No./Year
				Range	Mean	RSD (%)	
Fat	MBC	0.05	1	111			RD-9820/1998
		0.5	1	84			
Liver	TM	0.05	1	72			
		0.5	1	76			
	5-OH-MBC	0.05	1	78			
		0.5	1	80			
Muscle	MBC	0.05	1	98			
		0.5	1	94			
	5-OH-MBC	0.05	1	82			
		0.5	1	85			
Eggs	5-OH-MBC	0.05	3	72, 73, 85			
		0.1	2	70, 72			
	MBC	0.05	3	85, 99, 104			
		0.1	2	91, 109			
	TM	0.05	3	80, 87, 93			
		0.1	2	81, 81			

Enforcement methods

Multi-residue methods for the analysis of TM and the metabolites were developed: P/B 1407 G, P/B 1471 G, P 2014 G and P 2435 G for plant commodities and P/B 1674 G, P 3130 G and P 3131 G for animal commodities.

In the methods, residues were extracted using QuEChERS method and the extract was acidified with formic acid to stabilize base-sensitive analytes (such as TM). Determination of analytes was performed by LC-MS/MS with transition ions as follows: for TM, 343>151 m/z for quantification and 343>192 m/z for confirmation (further confirmation, 343>118 m/z); for MBC, 192>160 m/z for quantification and 192>132 for confirmation (further confirmation, 192>105); for 5-OH-MBC (P 3131 G only), 208>176 m/z for quantification and 208>148 for confirmation.

In most methods, matrix-matched standard were used. In the all studies, stability for standard solutions and sample extract stability, when kept in refrigerator or freezer throughout the study period (several days-weeks), were verified (insignificant degradation levels of TM to MBC, e.g., less than 5%). In one report (RD-01392), stability of fortified TM in fruit homogenates (apple) stored at room temperature, in the refrigerator and in the freezer was investigated. The apple homogenate for 4 hours in the laboratory at room temperature before extraction lead to *ca.* 50% loss of TM. One day refrigerated storage of the fortified homogenate apple sample resulted in about 90% loss of TM. TM was stable when stored as solution in acetonitrile in the freezer for *ca.* 4 weeks.

The all methods developed were well validated. No interferences were at the retention time of the analytes. The LC-MS/MS techniques were highly specific to analytes by monitoring such mass transitions per analyte. Linearity of detector response was well demonstrated (r^2, > 0.99), using matrix-matched standard solutions or solvent standard solutions. The recovery at each fortification level for TM and MBC (or 5-OH-MBC) was in the range of 70–110% (RSD, < 20%). In the all methods, LOQs were 0.01 mg/kg in all matrices tested. Thus the methods were considered valid and acceptable for determination of residues of TM and MBC for plant commodities (high water, high acid, high oil, dry crops) and TM, MBC and 5-OH-MBC for animal commodities (meat, liver, kidney, fat, milk, egg). Independent laboratory validation studies (methods, P/B 1407 G, P 3130 G, P 3131 G) were also conducted and the results demonstrated well validity for the original method.

Table 54 Enforcement methods (QuEChERS/LC-MS/MS) for TM and MBC residues in plant and animal commodities

Method	Matrix	Analyte	Fortification level (mg/kg)	Report No./Year
Plant commodity				
P/B 1407 G	Apple; apricot	TM	0.01, 0.5 or 2.0	RD-01392/2008
	Apple; apricot; peach	MBC	0.01, 0.2 (for peach, 0.01 only)	
P/B 1407 G -ILV	Tomato, orange, sunflower seed, oat	TM	0.01, 0.1	RD-03350/2009
		MBC	0.01, 0.1	
P/B 1471 G	High water (tomato), high oil (hazelnut, sunflower seed), dry crop (oat grain)	TM	0.01, one of 0.1, 0.2, 0.3, 2.0	RD-01391/2008
		MBC	0.01, one of 0.1, 0.5, 2.0	
P 2014 G	Acidic matrix (strawberry)	TM	0.01, 1	RD-02096/2010
		MBC	0.01, 1	
P 2435 G	High water (carrot root and leaf, spinach), dry crop (cereal straw, hay, forage)	TM	0.01, 0.1	RD-02381/2012
		MBC	0.01, 0.1	
Animal commodity				
P/B 1674 G	Milk, egg, meat	TM	0.01, 0.1	RD-01846/2009
		MBC	0.01, 0.1	
P 3130 G	Liver, fat	TM	0.01, 0.1	RD-02969/2014a
		MBC	0.01, 0.1	
P 3130 G - ILV	Meat, liver	TM	0.01, 0.1	RD-03273/2015
		MBC	0.01, 0.1	

Method	Matrix	Analyte	Fortification level (mg/kg)	Report No./Year
P 3131 G	Milk, egg, muscle, kidney, fat	5-OH-MBC	0.01, 0.1	RD-02981/2014b
P 3131 G - ILV	Meat, egg	5-OH-MBC	0.01, 0.1	RD-03316/2015

Stability of pesticide residues in stored analytical samples

Study 1

Storage stability test of TM and MBC on rape seed, dry peas, grapes and wheat grain were conducted (Brewin, S., 2002; Report No., RD-II02426). Fresh homogenised samples were fortified with TM and MBC separately at 1 mg/kg and kept in a frozen condition below -18 °C. Further, non-homogenised samples were also fortified and frozen in the same way. TM and MBC were analysed using the method ERV-005 (grape) and ERV-006 (other matrices). The results showed that TM and MBC were stable in non-homogenised (whole) crops when stored frozen for a period of up to 12 months. An apparent degradation of TM in all of the homogenised crops was observed when placed in freezer storage. For grape, recovery of TM was only 58% after 10 days storage.

Table 55 Storage stability of TM and MBC in homogenised commodities, stored at -18 °C (RD-II02426)

Commodity	Storage period (days)	% Recovery, fortified with TM or MBC at 1 mg/kg			
		TM*		MBC	
		Fortified control	Storage sample	Fortified control	Storage sample
Rape seed	0		80		106
	10	75	66	103	76
	14	85	68	93	67
Dry peas	0		81		102
	10	85	83	104	94
	14	70	84	95	84
Wheat gain	0		80		99
	10	87	85	85	87
	14	75	79	97	88
Grapes	0		82		101
	10	75	58	76	83
	14	74	53	95	86

Commodity sample was homogenized and then fortified with TM or MBC. * Degradation product of TM was not analysed.

Table 56 Storage stability of TM and MBC in non-homogenised commodities, stored at -18 °C (RD-II02426)

Commodity	Storage period (month)	% Recovery, fortified at 1 mg/kg			
		TM*		MBC	
		Fortified control	Storage sample	Fortified control	Storage sample
Rape seed	0 day		90		82
	1	86	83	93	94
	3	90	87	93	80
	6	71	74	94	82
	12	99	90	74	73
Dry peas	0 day		77		104
	1	89	86	103	97
	3	93	90	98	98
	6	73	73	110	110
	12	90	99	101	94
Wheat grain	0 day		88		93
	1	94	92	81	95
	3	82	82	84	98

Commodity	Storage period (month)	% Recovery, fortified at 1 mg/kg			
		TM*		MBC	
		Fortified control	Storage sample	Fortified control	Storage sample
	6	74	72	88	90
	12	92	93	106	110
Grapes	0 day		75		76
	1	71	75	89	84
	3	76	77	73	102
	6	77	86	95	84
	12	96	71	94	100

Non-homogenized (whole) sample was fortified with TM or MBC. * Degradation product, MBC, of TM was not analysed.

Study 2 (apple)

Storage stability test of TM on apple was conducted (Lucas, L.T., 2000; Report No., RD-00076). Apple sample was cut into halves (30-35 g each) and then frozen. The frozen sample was fortified either on the peel or on the pulp side of the apple segment at 0.17 mg/kg of TM (70 WP formulation, 0.25 mg/kg). The fortified apples samples were stored at -20 to -15 °C. TM and the metabolites (MBC, DX-105, FH-432) were analysed using the method BR-011-05. Fresh fortification control (whole apple) and storage samples were ground with dry ice prior to extraction procedure. After storage, the metabolites in apple samples were detected at most, < 0.05 mg/kg and the highest, 0.1 mg/kg. TM in non-homogenised apples was stable for storage periods of at least 1099 days (36.6 month) at -15 °C.

Table 57 Storage stability of TM in non-homogenised apple stored at -15 °C (RD-00076)

Storage period (days)	% Recovery of TM, fortified at 0.17 mg/kg		
	Fortified control (whole apple)	Storage sample	
		Pulp	Peel
0	101, 106	86, 98	90, 100
14	89, 103	94, 95	78, 86
30	104, 117	not reported	94, 97
42	102, 106	89, 93	not reported
62	106, 109	75, 92	71, 84
98	87, 95	79, 82	78, 78
196	77, 81	82, 84	74, 84
434	102, 120	98, 98	102, 103
731	93, 97	82, 84	69, 76
1099	84, 85	78, 78	74, 84

Study 3 (Strawberry)

Storage stability test of TM and MBC on strawberry was conducted (Class, T. and Senciuc, M., 2014; Report No., RD-02947). TM and MBC were dosed separately, each at 0.10 mg/kg to the intact whole specimens which were frozen at below -15 °C until analysis. At each storage time point, freshly fortified samples (one at 0.01 mg/kg and 3 replicates at 0.10 mg/kg) were analysed concurrently with the storage samples. TM and MBC were analysed using the method P 2014 G. After storage, TM and MBC in strawberry were stable for storage periods of at least 12 months at -15 °C.

Table 58 Storage stability of TM and MBC in whole strawberry, stored at -15 °C (RD-02947)

Storage period (month)	% Recovery, fortified at 0.1 mg/kg			
	TM		MBC	
	Fortified control	Storage sample	Fortified control	Storage sample
0 day	87, 99, 103	99, 98, 87	81, 79, 86	79, 84, 79
1	109, 100, 103	93, 85, 76	82, 75, 77	72, 66, 56
3	89, 83, 96	60, 79, 64	74, 75, 85	63, 77, 72
4.5	108, 110, 107	64, 78, 94	100, 103, 88	93, 109, 111
6	89, 103, 110	65, 73, 78	98, 90, 78	98, 117, 107
9	97, 96, 78	85, 60, 73	89, 89, 75	79, 97, 90
12	110, 113, 110	65, 87, 68	104, 104, 110	87, 92, 99

% Recovery of TM and MBC in freshly control samples, fortified at 0.01 mg/kg, were 82-122% (mean, 100%; RSD, 14%; n=7) and 70-114% (mean, 92%; RSD, 19%; n=7), respectively.

Study 4 (Snap beans)

Storage stability test of TM on snap beans was conducted (Fenn, L., 2003; Report No., RD-03167). Surface of snap bean was fortified with TM (70 WP formulation) at 1 mg/kg and the fortified samples were stored frozen at below -10 °C pending analysis. TM and the metabolite MBC were analysed by the method BR-011-05 and KP-201R1 (70 months only). MBC was detected at < 0.05 mg/kg or < 0.01 mg/kg (70 months only). Results showed TM in snap beans was stable for storage periods of at least 70 months at below -10 °C. MBC

Table 59 Storage stability of TM in snap beans stored at -10 °C (RD-03167)

Storage period (month)	% Recovery of TM, fortified at 1 mg/kg	
	Fortified control	Storage sample
0 day		90, 95
0.9	81, 91	93, 94
1.9	73, 78	77, 89
2.9	61, 78	83, 93
6.2	84, 85	72, 73
12.1	93, 105	80, 80
18.4	63, 79	76, 99
24.2	82, 88	93, 93
36.2	71, 83	80, 95
49.2	75, 81	77, 86
70.6	105, 103	115, 120

Study 5 (Cucumber)

Storage stability test of TM on cucumber was conducted (Ampofo, S.A., 2002; Report No., RD-03110). Fresh cucumber were cut into equal portions (*ca.* 10 g each) and frozen prior to fortification. Frozen samples removed from the freezer were kept on dry ice until extraction solution was added and during the fortification procedure. TM (70% WP formulation) was added drop wise onto the frozen cucumber skin at 1 mg/kg. The cucumber segments, with the outer skin up, were stored frozen at -20 to -15 °C until analysis. TM and the metabolite MBC were analysed by the method BR-011-05. MBC was detected at < 0.05–0.06 mg/kg. Results showed TM in cucumber was stable for storage periods of at least 60 months at -20 to -15 °C.

Table 60 Storage stability of TM in cucumber stored at -15 °C (RD-03110)

Storage period (month)	% Recovery of TM, fortified at 1 mg/kg	
	Fortified control	Storage sample
0 day	80, 84	65, 68
1	83, 87	71, 75
2	88, 96	80, 84
3	99, 100	84, 91
6	87, 92	77, 84
12	97, 101	84, 93
18	98, 102	91, 92
24	91, 97	78, 79
36	86, 93	77, 84
48	82, 86	79, 81
60	89, 93	79, 84

Study 6

Storage stability test of MBC on snap beans, apples, wheat grain, spinach, sugar beet roots and tomatoes was conducted (Wright, M.C., 1996; Report No., RD-03034). Samples were chopped, blended or ground (wheat grain) and then frozen. The frozen sample was fortified with MBC at 0.5 mg/kg and stored frozen at <-15 ± 5 °C pending analysis. MBC was analysed by the method described under the analytical method section. Results showed MBC in apple, snap bean, tomato, sugar beet root, spinach and wheat grain was stable for storage periods of at least 24 months at frozen conditions, below -15 ± 5 °C.

Table 61 Storage stability of MBC in plant commodities stored at -15 °C (RD-03034)

Commodity	Storage period (month)	% Recovery of MBC, fortified at 1 mg/kg	
		Fortified control	Storage sample
Wheat	0 day	97	
	3	97	95, 96
	12	96	73, 96
	24	85	90, 92
Apple	0	88	
	2	100	77, 79
	12	85	91, 91
	24	90	81, 87
Snap bean	0	90	
	2	91	91, 97
	12	90	66, 72
	24	78	81, 81
Tomato	0	97	
	2	96	99, 113
	12	89	85, 92
	24	86	87, 89
Sugar beet root	0	102	
	2	108	100, 100
	12	91	90, 95
	24	82	76, 83
Spinach	0		

Commodity	Storage period (month)	% Recovery of MBC, fortified at 1 mg/kg	
		Fortified control	Storage sample
	2	82	90, 97
	12	88	92, 97
	24	92	79, 85

Study 7 (cattle)

Storage stability test of TM and the metabolites on cattle muscle, cattle liver and whole milk was performed (Castro, L., 1998a; RD-9819). This storage stability test was done as a part of animal feeding study. Each sample was fortified at 1.0 mg/kg and with the appropriate analytes as follows: TM and MBC for muscle, MBC and 5-OH-MBC for liver and MBC and 5-OH-MBC-S for whole milk. The fortified samples were stored at about -20 ± 10 °C. Analyses were performed by the method described under the analytical method section. From this study, it was shown that these analytes were stable for at least 229–265 days in those matrices, when stored at -20 ± 10 °C.

Table 62 Storage stability of TM and the metabolites in cattle muscle, liver and milk, stored at -15 °C (RD-9819)

Matrix	Analyte	Storage period (days)	% Recovery, fortified at 1.0 mg/kg	
			Fortified control	Storage sample
Liver	MBC	0		86, 87
		229	100, 104	99, 99
	5-OH-MBC	0		73, 81
		229	92, 95	97, 98
Muscle	TM	0		91, 97
		265	88, 89	77, 79
	MBC	0		86, 90
		264	93, 96	96, 102
Whole milk	MBC	0		90, 10.
		258	85, 87	84, 85
	5-OH-MBC-S	0		77, 92
		258	94, 100	94, 103

Study 8 (hens)

Storage stability test of TM and the metabolites on muscle and liver of laying hens and eggs was performed (Castro, L., 1998b; RD-9820). This storage stability test was done as a part of animal feeding study. Each sample was fortified at 1.0 mg/kg and with the appropriate analytes as follows: MBC and 5-OH-MBC for muscle, TM and 5-OH-MBC for liver and TM, MBC and 5-OH-MBC for eggs. The fortified samples were stored at about -25 °C. Analyses were performed by the method described under the analytical method section. From this study, it was shown that these analytes were stable for at least 261–306 days in those matrices, when stored at -25 °C.

Table 63 Storage stability of TM and the metabolites in muscle and liver of laying hens and eggs stored at -25 °C (RD-9820)

Matrix	Analyte	Storage period (days)	% Recovery, fortified at 1.0 mg/kg	
			Fortified control	Storage sample
Liver	TM	0	90, 97	89, 109
		261	78, 79	66, 72
	5-OH-MBC	0	74, 75	75, 87

Matrix	Analyte	Storage period (days)	% Recovery, fortified at 1.0 mg/kg	
			Fortified control	Storage sample
		265	80, 81	79, 87
Muscle	5-OH-MBC	0	95, 97	94, 98
		265	82, 82	71, 75
	MBC	0	102, 104	101, 105
		265	91, 91	94, 98
Egg	TM	0	74, 80	86, 92
		295	84, 87	82, 82
	MBC	0	105, 106	105, 106
		306	92, 99	93, 94
	5-OH-MBC	0	80, 96	81, 106
		306	75, 85	84, 87

Table 64 Summary for storage stability periods of TM and MBC in plant commodities

Commodity category	Commodities	Storage stability period (months)	
		TM	MBC
Water content	Apples	36[a]	24[f]
	Snap beans	70[b]	24[f]
	Cucumber	60[c]	-
	Tomatoes	-	24[f]
	Spinach	-	24[f]
Starch content	Wheat grain	12[d]	12[d], 24[f]
	Sugar beet root	-	24[f]
Protein content	Dry peas	12[d]	12[d]
Acid content	Grapes	12[d]	12[d]
	Strawberries	12[d]	12[e]
Oil content	Oilseed rape seed	12[d]	12[d]

The same upper class letter indicates that the data came from the same storage stability test.

Based on the study results, when plant commodities are stored frozen at about -15 to -20 °C, storage stability period of TM or MBC is considered as follows: for TM, as at least 70 months for high water commodity and at least 12 months for high starch, high protein, high acid, high oil content commodities; for MBC, at least 24 months for high water and high starch content commodities and at least 12 months for high protein, high acid, high oil content commodities. It should be noted that TM is significantly degraded when TM is in homogenised plant sample at room temperature, as shown in grape.

Table 65 Summary for storage stability periods of TM and the metabolites in animal products

Animal products	Storage stability period (days)			
	TM	MBC	5-OH-MBC	5-OH-MBC-S
Ruminants				
Muscle	265	264		
Liver		229	229	
Milk		258		258
Poultry				
Muscle		265	265	
Liver	261	-	265	
Eggs	295	306	306	

In animal products, it is considered that TM and the metabolites are stable for the periods of at least 229–265 days in cattle matrices (muscle, liver, whole milk) and at least 261–306 days in hens matrices (muscle, liver, egg).

USE PATTERN

Thiophanate-methyl is a benzimidazole fungicide with protective and curative action against a wide range of disease on cereals, fruits and vegetables. It is registered in many countries for foliar use or soil treatment. Table 66 represents a summary of GAPs from the labels submitted and relevant to the uses of thiophanate-methyl and carbendazim proposed in this submission.

Table 66 Registered uses of thiophanate-methyl

Crop	Country	Form. (g/kg, g/L)	Appl. method	Growth stage	No. of Appl.	Appl. Int. (day)	Rate (kg ai/ha)	PHI (day)
Almond	France				1		0.070 kg ai/hL	30
Almond	France			Winter treatment of at time of planting	1		0.12 kg ai/hL	na
Almond	USA	WP, WSB 700		As needed between pink bud and petal fall			0.79-1.18 (2.35 kg ai/ha/yr)	-
Apple	Belgium	SC 500		Max one treatment within a 6-week period before harvest; max two treatments after 30% of leaf fall and at the end of leaf fall (BBCH 93-97)	1 & 2		0.5; 0.6 (BBCH 93-97)	14
Apple	Italy	WG 700					0.7	7
Apple	Spain	SC 450		Budding to flowering	1		0.68	na
Apple	USA	SC 539		From green tip		5-10; 7-14	0.59- 0.79; (1.18 in CA) (3.14 kg ai/ha/yr)	1
Apple, quince, nashi, loquot, aerole	France	WG 700		Early fruit disease, before blooming	1		0.07 kg ai/hL	14
Apricot	Italy	SC 500		Between pre-blossom and pre-harvest			0.7	3
Apricot	Italy	WG 700					0.70	3
Apricot	Spain	SC 450		Budding to flowering	1		0.68	na
Barley	Belgium	SC 500		BBCH 30-37	1		0.3-0.4	
Barley	CZ	SC 500		BBCH 61-65	1		0.75	
Barley	Italy	SC 500		Post-harvest treatment until pre-blossom or between pre-blossom and complete petal fall			0.63	35
Barley	Spain	SC 450		At flowering (BBCH 61-65)	1		0.68	42
Barley, winter	CZ	SC 500		Beginning of stem elongation	1		0.35	
Bean	Italy	WG 700					0.77	28
Beans (fresh and grains)	Italy	SC 500					0.75	14 (fresh) 28 (grain)
Beans and sweet lupins (freshly harvested without pod, dry beans), dry harvested beans, common bean	Belgium	SC 500		BBCH 60-69	1-2	14	0.8	14; 15 day (beans and sweet lupins)

Crop	Country	Form. (g/kg, g/L)	Appl. method	Growth stage	No. of Appl.	Appl. Int. (day)	Rate (kg ai/ha)	PHI (day)
outdoor								
Beans, dry	Spain	SC 450			2	14	0.68	29
Beans, dry and succulent [a]	USA	SC 539		For one application, when 100% of plants have at least one open bloom. For multiple applications, when 10-30% of plants have at least one open bloom, sequentially on a 4-7 days interval	single or multiple	4-7	1.18-1.58 (single); 0.79-1.18 (multiple) (3.14 kg ai/ha)	14 or 28[b]
Cherry	France				1		0.070	14
Cherry	Italy	SC 500		Between pre-blossom and pre-harvest			0.7	15
Cherry	Italy	WG 700					0.70	15
Citrus fruits	Spain	SC 500	Post-harvest	Post-harvest treatment: using a shower (drencher system) for 25-30 seconds			0.18 kg ai/hL	
Cucurbits (cantaloupe, casaba, cucumber, melon, pumpkin, squash, watermelon)	USA	SC 539	Drip irrigation	In-furrow, on top of the seeds at planting; apply through buried drip irrigation (chemigation) to the root zone; when disease first appears		7-14	0.39 (2.35 kg ai/ha/yr)	1
Egg plant (Aubergine)	Italy	WG 700					0.84	3
Eggplant	France	WG 700	Soil treatment	Soil treatment: winter treatment of at time of planting	1		0.07 kg ai/hL	na
Eggplant	France	WG 700	Foliar	Foliar treatment: during bloom	2		0.7	3
Eggplant (Aubergine)	Italy	SC 500	Foliar	Foliar spray		10-14	0.85	3
Eggplant (Aubergine)	Italy	SC 500	Drip irrigation	1st, at post-transplantation; 2nd, after 10-14 days; 3rd, until pre-harvest		10-14	0.85	3
Eggplant (Aubergine)	Spain	SC 450			3	7	0.99	3
Garlic (clove treatment)	USA	WG 850	Immersing	Immersing for at least 5 min. Dry cloves after treatment and prior to planting			0.81 g/L	
Garlic (clove treatment)	USA	SC 539	Immersing	Immersing for at least 5 min. Dry cloves after treatment and prior to planting			0.84 g/L	
Garlic (clove treatment)	USA	WP, WSB 700	Immersing	Immersing for at least 5 min. Dry cloves after treatment and prior to planting			0.84 g/L	
Grape	USA	WG 850		At first bloom and make additional applications		14-21	0.57-1.53 (3.14 kg ai/ha/yr)	14
Grape	USA	WP, WSB 700		At first bloom and make additional applications		14-21	0.59-1.17 (4.71 kg ai/ha/yr)	7
Grape (wine)	France	WG 700	Not use on table grapes	.	1		1.12	35
Grape vines (wine)	Spain	SC 450			1		0.99	35
Grapevine	Italy	WG 700					1.1	35

Crop	Country	Form. (g/kg, g/L)	Appl. method	Growth stage	No. of Appl.	Appl. Int. (day)	Rate (kg ai/ha)	PHI (day)
Hazelnut	Italy	SC 500		Fruit enlargement			0.75-0.88	
Leak	Belgium	SC 500	Soaking, watering	Soaking seedlings during 5-10 min before planting in 10 mL/L of water; through watering after planting, 6 mL/10 L/100 plants	1		0.005 kg ai/hL	
Leek	France		Soil treatment	At planting time	1		1.75-4.2	na
Melon	France	WG 700	Soil treatment	Winter treatment of at time of planting	1		0.07 kg ai/hL	na
Melon	France	WG 700	Foliar	During bloom	2		0.7	3
Melon	Italy	SC 500	Indoor and outdoor; foliar				0.7	3
Melon	Italy	SC 500	Indoor and outdoor; drip irrigation	1st, at post-transplantation; 2nd, after 10-14 days; 3rd, until pre-harvest		10-14	0.85	3
Melon	Italy	WG 700	Drip irrigation	1st, as post-transplantation treatment; 2nd, after 10-14 days; 3rd, one until pre-harvest	3		1.2?	3
Melon	Italy	WG 700	Foliar				0.7	3
Melon	Spain	SC 450	Outdoor		2	14	0.84	3
Melon	Spain	SC 450	Greenhouse; drip irrigation and spray	One drip irrigation during initial stage of fruit formation and twice spray application	3	14 in spray	2.7 (drip) 0.84 (spray)	3
Nectarine	Italy	WG 700					0.7	3
Nectarine	Spain	SC 450		Budding to flowering	1		0.68	na
Nectarine and similar hybrids	Italy	SC 500		Before leaf fall until blossom or between pre-blossom and pre-harvest			0.70	3
Oat	Belgium	SC 500		BBCH 30-37	1		0.3-0.4	
Oat	CZ	SC 500		BBCH 61-65	1		0.75	-
Oat	Spain	SC 450		At flowering	1		0.68	42
Onions (not for this use in CA) Garlic	USA	SC 539	Broadcast and spray	In furrow (broadcast); spray directly into the open furrow at the time of planting seed, sets or bulbs. Not for this use through any type of irrigation system			1.58 (1.58 kg ai/ha/yr)	
Peach	France			During the blooming season	1		0.070	3
Peach	France			Winter treatment	1		0.12 kg ai/hL	na
Peach	Italy	SC 500 L		Before leaf fall until blossom or between pre-blossom and pre-harvest			0.70	3
Peach	Italy	WG 700					0.7	3
Peach	Spain	SC 450		Budding to flowering	1		0.68	na
Peanut	USA	SC 539		When disease first appears		14	0.39 (1.58 kg ai/ha/yr)	14
Pear	Belgium	SC 500		Max one treatment within a 6-week period before harvest; mad two treatments after 30% of leaf	2		0.5; 0.6 (BBCH 93-97)	14

Crop	Country	Form. (g/kg, g/L)	Appl. method	Growth stage	No. of Appl.	Appl. Int. (day)	Rate (kg ai/ha)	PHI (day)
				fall and at the end of leaf fall (BBCH 93-97)				
Pear	France	WG 700		Early fruit disease, before blooming	1		0.07 kg ai/hL	14
Pear	Italy	SC 500		Post-harvest treatment until pre-blossom or between pre-blossom and complete petal fall			0.70	7
Pear	Spain	SC 450		Budding to flowering	1		0.68	na
Pear	USA	WP, WSB 700 g/kg		From green tip		5-10; 7-14	0.79 (3.14 kg ai/ha/yr)	1
Peas (fresh and grains)	Italy	SC 500, WG 700					0.75-0.77	14 (fresh) 28 (grain)
Peas (without pod) outdoor	Belgium	SC 500		BBCH 60-69	1-2	14	0.8	15
Pecan	USA	SC 539		From when first leaves are showing until shuck split. “Do not apply after shuck split.”		3-4 wks	0.79 (2.35 kg ai/ha)	-
Pistachio	USA	SC 539		At bloom			1.18-1.58 (1.58 kg ai/ha/yr)	
Plum	France	WG 700		During the blooming season	1		0.070 kg ai/hL	14
Plum	Italy	SC 500		Between pre-blossom and pre-harvest			0.7	15
Plum	Spain	SC 450		Budding to flowering			0.68	na
Potato	Italy	SC 500	Drip irrigation	1st, at post-transplantation; 2nd, after 10-14 days; 3rd, until pre-harvest		10-14	0.85	3
Potato	USA	SC 539		First application at row closure		7-14	0.79-1.18 (3.14 kg ai/ha/yr)	21
Pumpkin	France	WG 700	Soil treatment	Winter treatment of at time of planting	1		0.07 kg ai/hL	na
Pumpkin	France	WG 700	Foliar	During bloom	2		0.7	3
Pumpkin	Spain	SC 450	Outdoor		2	14	0.84	3
Pumpkin	Spain	SC 450	Greenhouse; drip irrigation and spray	One drip irrigation during initial stage of fruit formation and twice spray application	3	14 in spray	2.7 (drip) 0.84 (spray)	3
Rape (Canola, Crambe)	USA	WG 850		At 20-50% flowering for single application; at 20-30% and 40-50% flowering for twice applications	1 or 2		0.76-1.53 (single); 0.76 (twice) (1.57 kg ai/ha/yr)	40
Rape oil seed	CZ	SC 500		BBCH 55-69, no later than BBCH 71			0.7	
Rape oil seed, winter	CZ	SC 500		BBCH 14-16, in autumn			0.6	
Rape seed	Italy	SC 500					0.63	30
Rapeseed	Italy	WG 700					0.63	30, 35
Rye	Belgium	SC 500		BBCH 30-37	1		0.3-0.4	

Crop	Country	Form. (g/kg, g/L)	Appl. method	Growth stage	No. of Appl.	Appl. Int. (day)	Rate (kg ai/ha)	PHI (day)
Rye	CZ	SC 500		BBCH 61-65	1		0.75	
Rye	Spain	SC 450		At flowering	1		0.68	42
Soya bean[c]	USA	WP, WSB 700		From early or full bloom	Single for seed beans	14-21	0.39-0.78 (1.57 kg ai/ha/yr)); for seed beans, 0.78 kg ai/ha[d]	21
Spelt	Belgium	SC 500		BBCH 30-37	1		0.3-0.4	
Stone fruits	Italy	SC 500		Post-harvest before leaf fall or fruit formation-growing			0.88	
Stone fruits	Italy	WG 700					0.7-0.88	not req.
Stone fruits (apricot, cherry, nectarine, peach, plum and prune)	USA	SC 539, WP, WSB 700		At early, full bloom and additional applications		10-14	0.79-1.18 (3.14 kg ai/ha/yr)	1
Strawberry	Belgium	SC 500		Apply 0.35 mL/250 mL water on each plant which is equal to 35 mL/25 L water bucket/100 plants; BBCH 03	1-2		0.0007 kg ai/hL	
Strawberry	USA	SC 539		After establishment of the transplants and continue through first bloom		7-10	0.59-0.79 (3.14 kg ai/ha/yr)	1
Sugar beet	USA	SC 539					0.39-0.79 (2.35 kg ai/ha/yr)	21
Sugar beet, fodder beet	CZ	SC 500					0.3-0.35	21
Sunflower	CZ	SC 500		BBCH 15-19 or BBCH 51-61, no later than BBCH 61	1		0.75-0.9	
Tomato	France	WG 700	Soil treatment	Winter treatment of at time of planting	1		0.07 kg ai/hL	na
Tomato	France	WG 700	Foliar	During bloom	2		0.7	3
Tomato	Italy	SC 500	Indoor and outdoor; foliar			10-14	0.85	3
Tomato	Italy	SC 500	Indoor and outdoor; drip irrigation	1st, at post-transplantation; 2nd, after 10-14 days; 3rd, until pre-harvest		10-14	0.85	3
Tomato	Spain	SC 450	Outdoor		3	7	0.99	14
Tomato	Spain	SC 450	Greenhouse	Before flowering	1		0.99	na
Triticale	Belgium	SC 500		BBCH 30-37			0.3-0.4	
Triticale	CZ	SC 500		BBCH 61-65	1		0.75	
Triticale	Spain	SC 450		At flowering	1		0.68	42
Watermelon	France	WG 700	Soil treatment	Winter treatment of at time of planting	1		0.07 kg ai/hL	na
Watermelon	France	WG 700	Foliar	During bloom	2		0.7	3
Watermelon	Italy	SC 500	Drip irrigation	1st, at post-transplantation; 2nd, after 10-14 days; 3rd, until pre-harvest		10-14	0.85	3
Watermelon	Italy	SC 500	Indoor and				0.7	3

Crop	Country	Form. (g/kg, g/L)	Appl. method	Growth stage	No. of Appl.	Appl. Int. (day)	Rate (kg ai/ha)	PHI (day)
			outdoor; foliar					
Watermelon	Italy	WG 700	Drip irrigation	1st, as post-transplantation treatment; 2nd, after 10-14 days; 3rd, one until pre-harvest	3		0.84	3
Watermelon	Italy	WG 700	Foliar				0.70	3
Wheat	Belgium	SC 500		BBCH 30-37, 65	1		0.3-0.4 (BBCH 30-37); 0.75 (BBCH 65)	
Wheat	CZ	SC 500		BBCH 61-65	1		0.75	
Wheat, winter	CZ	SC 500		Beginning of stem elongation	1		0.35	
Wheat	Italy	SC 500		Post-harvest treatment until pre-blossom or between pre-blossom and complete petal fall			0.63	40
Wheat	Italy	WG 700					0.63	40
Wheat	Spain	SC 450		At flowering	1		0.68	42
Wheat (fall-seeded), triticale[e]	USA	SC 539	A or G	After tillering but before stem elongations has begun.	1		0.79 (0.79 kg ai/ha/yr)	-

na: not applicable

In USA, WP (700 g/kg) formulation is not allowed to be used aerially or through chemigation equipment to any food crops.

In California, USA, chemigation only can be used for beans, cucurbits, peanuts, soybeans, strawberries, and sugar beets.

In USA, for crops without labeled uses of TM, observe a 30-day plant back restriction (SC, WP, WSB).

[a] Including lima bean, snap bean, kidney bean, mung bean, navy bean, pinto bean, wax bean, broad bean, fava bean, asparagus bean, blackeyed pea, cowpea, sweet lupine, white lupine, white sweet lupine, grain lupine, chick pea and garbenzo bean

[b] 14 day PHI for succulent beans and lima beans and 28 day PHI for dry beans; California only, 28 day PHI for lima bean

[c] Do not graze or feed treated vines or hay to livestock.

[d] For seed beans only: for seed quality, make a single application at the high rate (0.78 kg ai/ha) when beans form in the pod.

[e] Do not cut for hay within 90 days of application. Do not allow livestock to graze in treated areas before harvest.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

Supervised trials have been conducted to support MRLs for various crops. The results of these supervised trials are summarised in the following tables:

Crop group	Commodity	Table No.
Citrus fruits	Orange, mandarin	67, 68
Pome fruits	Apple, pear	69, 70
Stone fruits	Cherry, plum, apricot, nectarine, peach	71, 72, 73, 74, 75
Berries and other small fruits	Grape, strawberry	76, 77
Assorted tropical and sub-tropical fruits	Mango	78
Bulb vegetables	Spring onion	79
Fruiting vegetables, Cucurbits	Cucumber, summer squash	80, 81
	Melon, watermelon	82, 83
Fruiting vegetables, other than Cucurbits	Tomato	84

Crop group	Commodity	Table No.
Legume vegetables	Snap bean (common bean)	85
Pulses	Dry bean, soya bean	86, 87
Root and tuber vegetables	Sugar beet	88
Cereal grains	Barely, oat, wheat	89, 90, 91
Tree nuts	Almond, hazelnut, pecan, pistachio	92, 93, 94, 95
Oilseeds	Peanut, rape seed	96, 97

Citrus fruits

Orange, mandarin

Orange and mandarin from each four field trials were post-harvest treated with SC formulation (500 g/L) of thiophanate-methyl during 2006 and 2007 in Spain [Report No., RD-01293]. On the latest one day after harvesting in the orchards, the fruits were treated for 25-35 seconds using a drencher system (dipping) in one place (Alcacér, Valencia), a spray liquid at a concentration of 0.18 kg ai/hL (SC formulation, 500 g/L; 41%, w/w). After drying for 2-6 hrs, on the same day of post-harvest treatment, the fruits were transported to a commercial storehouse at Iberica Brodex, Valencia and stored at 3–9 °C. On 0, 1, 3 and 7 days after treatment, twelve fruits were sampled and then immediately (fresh condition) divided into peel and pulp. Juice (if any) was collected and added to the pulp sample. Samples were deep frozen within 10 hrs after sampling, and until shipment to an analytical laboratory.

For processing studies, five additional studies (orange, 4 trials; mandarin, 1 trial) were conducted. Dipping was made in a concentration of 1.8 kg ai/hL. The treated fruits were stored in a storehouse and after a three-days storage, shipped (12–18 °C during transportation) and arrived to a processing place on the same day or the next day. Processing started on the arrival day (mandarin) or within two days after ambient storage. The products were deep frozen until transportation to an analytical laboratory.

During transportation to an analytical laboratory, all samples were stored frozen. Frozen samples were homogenized with addition of solid carbon dioxide in a large-scale mixer. An aliquot (300–500 g) of the homogenized sample was stored deep-frozen (below -18 °C) in polyethylene bags until analysis.

TM and MBC in orange, mandarin and their processed products were analysed. The method was described under residue analysis section. Concurrent recovery results for TM and MBC were acceptable. TM and MBC in orange (peel and pulp) and mandarin (peel and pulp) were stable for 15 days of a storage stability test period. Sample storage period was a maximum of 74 days and for citrus products, 98 days.

Table 67 Residues in orange post-harvest treated with TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (d)	Portion analysed	Residues (mg/kg)		Study/Trial
	No.	RTI (days)	Conc. (kg ai/L)	GS			TM	MBC	
GAP: Spain			**0.18** using drencher, 25-30 sec						
Sollana, Spain 2007 (Navel Foyos)	1	-	0.18	BBCH 89 11 Dec 06	0	Peel	7.3	0.14	RD-01293/ R06ESP010-1
					1		16	0.17	
					3		9.2	0.14	
					7		13	0.23	

Location, Country, Year (Variety)	Application				DALT (d)	Portion analysed	Residues (mg/kg)		Study/Trial
	No.	RTI (days)	Conc. (kg ai/L)	GS			TM	MBC	
					0	Pulp	< 0.05	< 0.05	
					1		< 0.05	< 0.05	
					3		< 0.05	< 0.05	
					7		< 0.05	< 0.05	
					0	Whole fruit*	1.6	0.07	
					1		**3.3**	0.08	
					3		2.2	0.07	
					7		3	**0.09**	
Quart de Poblet , Spain 2007 (Valencia)	1	-	0.18	BBCH 89 11 Dec 06	0	Peel	9.2	0.12	RD-01293/ R06ESP010-2
					1		13	0.15	
					3		11	0.14	
					7		10	0.18	
					0	Pulp	< 0.05	< 0.05	
					1		< 0.05	< 0.05	
					3		< 0.05	< 0.05	
					7		< 0.05	< 0.05	
					0	Whole fruit*	2.4	0.07	
					1		**2.9**	0.07	
					3		2.5	0.07	
					7		2.6	**0.08**	
Alzira, Spain 2007 (Valencia)	1	-	0.18	BBCH 89 05 Mar 07	0	Peel	8.5	0.14	RD-01293/ R06ESP010-5
					1		6.8	0.11	
					3		5.6	0.09	
					7		1.9	< 0.05	
					0	Pulp	< 0.05	< 0.05	
					1		< 0.05	< 0.05	
					3		< 0.05	< 0.05	
					7		< 0.05	< 0.05	
					0	Whole fruit*	2.3	0.07	
					1		**1.6**	0.06	
					3		1.4	**0.06**	
					7		0.48	< 0.05	
Quart de Poblet, Spain 2007 (Navel Lane-Late)	1	-	0.18	BBCH 89 05 Mar 07	0	Peel	8.4	0.12	RD-01293/ R06ESP010-6
					1		6.8	0.08	
					3		7.5	0.08	
					7		6.9	0.08	
					0	Pulp	< 0.05	< 0.05	
					1		< 0.05	< 0.05	
					3		< 0.05	< 0.05	
					7		< 0.05	< 0.05	
					0	Whole fruit*	1.7	0.06	
					1		1.4	0.06	
					3		**1.6**	**0.06**	
					7		1.6	0.06	

Post-harvest treatment in all trials: using a shower (drencher system) with a spray liquid (0.18 kg ai/hL , SC 500 g/L)

* Residue values in whole fruit were calculated from peel and pulp data.

Table 68 Residues in mandarin post-harvest treated with TM

Location, Country, Year (Variety)	Application				DALT (d)	Portion analysed	Residues (mg/kg)		Study/Trial
	No.	RTI (days)	Conc. (kg ai/La)	GS			TM	MBC	
GAP: Spain			**0.18** using drencher, 25-30 sec						
Albuixtech, Spain 2007 (Clemenoles)	1		0.18	BBCH 89 11 Dec 06	0	Peel	9.1	0.09	RD-01293/ R06ESP010-3
					1		9.5	0.10	
					3		9.2	0.10	
					7		10	0.16	
					0	Pulp	0.19	< 0.05	
					1		0.22	< 0.05	
					3		0.14	< 0.05	
					7		0.26	< 0.05	
					0	Whole fruit*	2.3	0.06	
					1		**2.5**	0.06	
					3		2.3	0.06	
					7		2.5	**0.08**	
Quart de Poblet, Spain 2007 (Satsuma)	1		0.18	BBCH 89 11 Dec 06	0	Peel	13	0.15	RD-01293/ R06ESP010-4
					1		10	0.13	
					3		9.4	0.12	
					7		9.4	0.14	
					0	Pulp	0.5	< 0.05	
					1		0.34	< 0.05	
					3		0.48	< 0.05	
					7		0.25	< 0.05	
					0	Whole fruit*	4.0	0.08	
					1		**3.2**	0.07	
					3		3.1	0.07	
					7		2.8	**0.08**	
Quart de Poblet, Spain 2007 (Hernandia)	1		0.18	BBCH 89 26 Feb 07	0	Peel	13	0.12	RD-01293/ R06ESP010-7
					1		11	0.13	
					3		11	0.12	
					7		13	0.17	
					0	Pulp	< 0.05	< 0.05	
					1		< 0.05	< 0.05	
					3		< 0.05	< 0.05	
					7		< 0.05	< 0.05	
					0	Whole fruit*	4.2	0.07	
					1		3.6	0.08	
					3		3.7	0.07	
					7		**4.3**	**0.09**	
Albuixtech, Spain 2007 (Ortanique)	1		0.18	BBCH 89 26 Feb 07	0	Peel	8.8	0.11	RD-01293/ R06ESP010-8
					1		4.5	0.10	
					3		8.6	0.15	
					7		5.1	0.16	
					0	Pulp	0.5	< 0.05	
					1		0.4	< 0.05	
					3		< 0.05	< 0.05	
					7		< 0.05	< 0.05	

Location, Country, Year (Variety)	Application				DALT (d)	Portion analysed	Residues (mg/kg)		Study/Trial
	No.	RTI (days)	Conc. (kg ai/La)	GS			TM	MBC	
					0	Whole fruit*	2.5	0.06	
					1		1.3	0.06	
					3		**2.0**	0.07	
					7		1.4	**0.08**	

Post-harvest treatment in all trials: using a shower (drencher system) with a spray liquid (0.18 kg ai/hL , SC 500 g/L)
* Residue values in whole fruit were calculated from peel and pulp data.

Pome fruits

Apple, pear

Residue trials on apple (11 trials) and pear (10 trials) were conducted in 1992 in the USA. A foliar application was made 8–9 times with TM (WG 850 g/kg) at rates of 0.74–0.83 kg ai/ha in apple and 0.77–0.80 kg ai/ha in pear. Harvest samples were frozen within several hours and frozen until analysis. Extraction was done in ice bath. In analysis of residues, procedural recovery results were not acceptable. A maximum storage period of samples was 285 days in apple and 812 days in pear.

Table 69 Residues in apple following application of TM (WG 850 g/kg)

Location, Country, Year (Variety)	Application				DALT (days)	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment		TM	MBC	FH-432	DX-105	
GAP: USA		**5-10, 7-14**	**0.79 (3.14 kg ai/ha/yr) 1.18 in CA**		**PHI, 1 day**					
Watsonville, CA, USA 1994 (Pippin)	8	11-32	0.79 (6.28)*	7.6-8.3 cm diameter fruit 06 Aug 92	1	0.32	0.15	< 0.05	< 0.05	RD-01098/ 27A-92
					7	0.19	0.1	< 0.05	< 0.05	
					14	0.28	0.1	< 0.05	< 0.05	
Cottonwood, CA, USA 1994 (Gayla)	8	7-36	0.77 (6.18) Aerial	Cover spray 11 Aug 92	1	0.065	< 0.05	< 0.05	< 0.05	RD-01098/ 27B-92
					7	0.069	< 0.05	< 0.05	< 0.05	
					14	0.11	< 0.05	< 0.05	< 0.05	
Cottonwood, CA, USA 1994 (Criterion)	8	6-35	0.74-0.75 (5.96)	Cover spray 11 Aug 92	1	0.33	0.097	< 0.05	< 0.05	RD-01098/ 27C-92
					7	0.21	0.072	< 0.05	< 0.05	
					14	0.19	0.072	< 0.05	< 0.05	
Fennville, MI,USA1994 (Red Delicious)	8	7-34	0.79 (6.28)	Mature fruits 16 Sep 92	1	0.069	0.10	< 0.05	< 0.05	RD-01098/ 27D-92
					7	< 0.05	0.093	< 0.05	< 0.05	
					14	< 0.05	0.065	< 0.05	< 0.05	
Knightdale, NC, USA 1994 (Lody)	8	6-28	0.77-0.81 (6.32)	Fruit developme nt mature 10 Jul 92	1	1.0	0.12	< 0.05	< 0.05	RD-01098/ 27E-92
					7	1.4	0.14	< 0.05	< 0.05	
					14	0.36	0.092	< 0.05	< 0.05	

Location, Country, Year (Variety)	Application				DALT (days)	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment		TM	MBC	FH-432	DX-105	
North Rose, NY, USA1994(Rhode Island Greening	8	7-34	0.79 (6.28)	Fruit 6.4 cm in diameter 09 Sep 92	1	0.10	< 0.05	< 0.05	< 0.05	RD-01098/ 27F-92
					7	0.13	0.052	< 0.05	< 0.05	
					14	0.069	< 0.05	< 0.05	< 0.05	
Alton, NY,USA1994(Monroe)	8	7-32	0.79 (6.28)	Fruit 6.7 cm in diameter 15 Sep 92	1	0.21	0.14	< 0.05	< 0.05	RD-01098/ 27G-92
					7	0.10	0.097	< 0.05	< 0.05	
					14	0.12	0.115	< 0.05	< 0.05	
Hood River, OR, USA1994 (Criterion)	8	10-35	0.79 (6.28)	6.4 cm fruit diameter 25 Aug 92	1	0.32	0.098	< 0.05	< 0.05	RD-01098/ 27H-92
					7	0.25	0.078	< 0.05	< 0.05	
					14	0.29	0.087	< 0.05	< 0.05	
Upper Black Eddy, PA, USA 1994 (Jersey Mac)	8	7-21	0.77-0.79 (6.23)	Fourth cover 21 Jul 92	1	0.29	0.077	< 0.05	< 0.05	RD-01098/ 27I-92
					7	0.089	< 0.05	< 0.05	< 0.05	
					14	0.11	< 0.05	< 0.05	< 0.05	
Yakima, WA, USA1994 (Red Delicious)	8	10-35	0.79-0.83 (6.46)	Post bloom 31 Aug 92	1	0.51	0.15	< 0.05	< 0.05	RD-01098/ 27J-92
					7	0.58	0.11	< 0.05	< 0.05	
					14	0.47	0.11	< 0.05	< 0.05	
Snelling, CA,USA 1994 (Golden Delicious)	9	6-37	0.79 (7.07)	5th cover – fruit mature 25 Aug 92	1	0.32	< 0.05	< 0.05	< 0.05	RD-01098/ 27K-92
					7	0.42	< 0.05	< 0.05	< 0.05	
					14	< 0.05	< 0.05	< 0.05	< 0.05	

* Value in parenthesis means a total application rate per year (kg ai/ha/year).

Table 70 Residues in pear following application of TM (WG 850 g/kg)

Location, Country, Year (Variety)	Application				DALT (days)	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment		TM	MBC	FH-432	DX-105	
GAP: USA										
Watsonville, CA, USA 1995 (Bosc)	8	10-35	0.79 (6.28)*	6.4-7.6 cm diameter fruit 29 Jul 92	1	**0.49**	0.10	0.06	< 0.05	RD-03546; RD-03547/ 28A-92
					7	0.33	**0.21**	< 0.05	< 0.05	

Location, Country, Year (Variety)	Application				DALT (days)	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment		TM	MBC	FH-432	DX-105	
					14	0.22	0.21	< 0.05	< 0.05	
Chico, CA, USA1995 (Shinseki & Hosui)	8	4-39	0.80 (6.37) Aerial	Cover spray 09 Jul 92	1	**0.37**	**0.09**	0.06	< 0.05	RD-03546; RD-03547/ 28B-92
					7	0.20	0.09	< 0.05	< 0.05	
					14	0.13	0.06	< 0.05	< 0.05	
Fairfield, CA,USA 1995(Bartlett)	8	7-28	0.79 (6.28)	Full sized fruit 08 Jul 92	1	**0.09**	< 0.05	< 0.05	< 0.05	RD-03546; RD-03547/ 28C-92
					7	0.05	**0.10**	< 0.05	< 0.05	
					14	0.05	0.07	< 0.05	< 0.05	
Eckert, CO,USA1995 (Bartlett)	8	9-31	0.79 (6.28)	Fruits ready to pick 18 Aug 92	1	**0.30**	0.12	< 0.05	< 0.05	RD-03546; RD-03547/ 28D-92
					7	0.12	**0.19**	< 0.05	< 0.05	
					14	< 0.05	0.14	< 0.05	< 0.05	
Fenneville, MI, USA 1995 (Bartlett)	8	7-28	0.77 – 0.79 (6.23)	5.1 cm fruit 12 Aug 92	1	**0.12**	0.11	0.06	< 0.05	RD-03546; RD-03547/ 28E-92
					7	0.08	**0.23**	< 0.05	< 0.05	
					14	0.07	0.18	< 0.05	< 0.05	
Wilkesboro, NC, USA1995 (Stark Delicious)	8	7-35	0.79 (6.28)	Fruit maturing 04 Aug 92	1	**0.60**	**0.12**	0.05	< 0.05	RD-03546; RD-03547/ 28F-92
					7	0.14	0.12	< 0.05	< 0.05	
					14	< 0.05	0.09	< 0.05	< 0.05	
Alton, NY,USA1995 (Bartlett)	8	7-28	0.79 (6.28)	Fruit 5-5.2 cm in diameter 18 Aug 92	1	**0.24**	0.06	0.07	< 0.05	RD-03546; RD-03547/ 28G-92
					7	< 0.05	**0.28**	< 0.05	< 0.05	
					14	< 0.05	0.20	< 0.05	< 0.05	
Salem, OR,USA 1995 (Bosc)	8	7-86	0.79 (6.28)	Fruit fully developed 27 Aug 92	1	**4.3**	**0.48**	0.20	0.08	RD-03546; RD-03547/ 28H-92
					7	1.28	0.45	0.11	< 0.05	
					14	0.80	0.45	0.12	< 0.05	
Spokane, WA,USA 1995 (Bartlett)	8	7-85	0.79 (6.28)	Coloring 05 Aug 92	1	**0.63**	0.15	< 0.05	< 0.05	RD-03546; RD-03547/ 28I-92
					7	0.44	**0.28**	< 0.05	< 0.05	
					14	0.45	0.23	< 0.05	< 0.05	
Spokane, WA,USA 1995 (Bartlett)	8	7-85	0.79	Coloring 05 Aug 92	1	**0.46**	0.18	< 0.05	< 0.05	RD-03546; RD-03547/ 28J-92
					7	0.35	**0.27**	< 0.05	< 0.05	
					14	0.41	0.20	< 0.05	< 0.05	

* Value in parenthesis means a total application rate per year (kg ai/ha/year).

Stone fruits

Cherry

Residue trials in cherry were conducted 1991 in the USA (Report No., RD-II02090, 1996a). A foliar application (ground or aerial) was made 3 or 5 times with TM (WP 700 g/kg, SC 539 g/L or WG 850 g/kg) at rates of 1.13–1.19 kg ai/ha. Harvest samples were frozen within 8 hours, pitted still frozen and homogenised with dry ice. In analysis of residues, procedural recovery results were not acceptable. A maximum storage period of samples was 1352 days.

Table 71 Residues in cherry following application of TM (WP 700, SC 539 or WG 850)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA		**10-14**	**1.18** (3.14 kg ai/ha/yr)		**PHI, 1 d**						
Conklin, MI, USA 1996a (Montmorency)	3	5	1.18 (3.53)	Petal fall 08 Mar 91	47	Fruit without stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02093/ 23A-91[a]
	5	5-42	1.8 (5.90)	Mature fruit 24 Jun 91	0		1.8	0.18	< 0.05	< 0.05	
					1		1.0	0.25	< 0.05	< 0.05	
Conklin, MI USA 1996a (Montmorency)	3	5	1.8 (3.53)	Petal fall 08 Mar 91	47	Fruit without stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02093/ 23B-91[a]
	5	5-42 Aerial	1.8 (5.89)	Mature fruit 24 Jun 91	0		0.58	< 0.05	< 0.05	< 0.05	
					1		0.49	0.11	< 0.05	< 0.05	
Sodus, NY USA 1996a (Montmorency)	3	5-6	1.18 (3.53)	Early petal fall 08 Mar 91	69	Fruit without stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02093/ 23C-91[b]
	5	5-63	1.18 (5.89)	Normal harvest 15 Jul 91	0		2.3	0.39	0.09	< 0.05	
					1		1.9	0.40	0.12	< 0.05	
Sodus, NY USA 1996a (Montmorency)	3	5-6	1.8 (3.53)	Early petal fall 08 Mar 91	69	Fruit without stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02093/ 23D-91[b]
	5	5-63	1.18-1.19 (5.91)	Normal harvest 15 Jul 91	0		5.8	0.51	0.12	< 0.05	
					1		3.3	0.53	0.13	< 0.05	
Salomon, WA USA 1996a (Lambert)	3	5 Aerial	1.14 – 1.19 (3.50)	Bloom to 35% petal fall 27 Apr 91	72	Fruit without stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02093/ 23E-91[c]
	5	5-67 Aerial	1.13 – 1.19 (5.80)	Red fruit 08 Jul 91	0		1.0	0.09	< 0.05	< 0.05	
					1		0.83	0.14	< 0.05	< 0.05	
Salomon, WA USA 1991a (Lambert)	3	5	1.18 (3.53)	Bloom to 35% petal fall 27 Apr 91	72	Fruit without stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02093/ 23F-91[c]
	5	5-67	1.18 (5.89)	Red fruit 08 Jul 91	0		1.3	< 0.05	< 0.05	< 0.05	
					1		0.71	0.13	< 0.05	< 0.05	
Cornelius, OR USA 1996a (Beds Sweet)	3	4-5	1.18 (3.53)	25% petal fall, 75% bloom 18 Apr 91	66	Fruit without stone	0.37	0.09	< 0.05	< 0.05	RD-II02093/ 23G-91[d]

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
	5	4-61	1.18 (5.89)	Red fruit 23 Jun 91	0		6.0	0.62	0.08	0.06	
					1		3.7	0.64	0.12	0.08	
Gaston, OR USA 1996a (Montmorency)	3	5	1.18 (3.53)	25% petal fall, 75% bloom 23 Apr 91	78	Fruit without stone	0.10	0.06	< 0.05	< 0.05	RD-II02093/ 23H-91[d]
	5	5-73	1.18 (5.89)	Red fruit 10 Jul 91	0		19[*]	0.67[*]	< 0.05	0.10	
					1		15[*]	0.80[*]	< 0.05	< 0.05	

[*] In spray application, hand-held gun was used. In the report, this was considered as use of non-commercial equipment and invalid data.

[a] Not independent trials (the sample site)

[b] Not independent trials (the same site)

[c] Not independent trials (close location)

[d] Not independent trials (close location)

Plums

Residue trials on plums were conducted in 2000 and 2001 in Northern France and Germany (Report No, RD-II01199, 2001; RD-I2124, 2002; RD-03008, 2003). A spray application was made 2 times with TM (SC 500 g/L) at rates of 0.65–0.71 kg ai/ha or 0.045–0.068 kg ai/hL. The first application was 84–127 days before the second application. Harvest samples were frozen within 10 hours and during shipment to an analytical laboratory. In laboratory, whole plum was homogenised with dry ice. In analysis of residues (method ERV/005), procedural recovery results were acceptable. A maximum storage period of samples was 124 days.

Table 72 Residues in plum following application of TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP		**10-14**	**1.18** (3.14 kg ai/ha/yr)		**PHI, 1 d**						
Thillot-sous-les-Cotes, France (NE) 2001a(Mirabelle de Nancy)	2	91	0.675 0.676 (1.351)	BBCH 85 02 Aug 00	0	Whole fruit	0.46	0.02			RD-II01199/ EA000152 FR01
					3		0.31	0.04			
					7		0.20	0.05			
					14		**0.11**	0.04			
	2	84	0.676 0.675 (1.351)	BBCH 85 26 Jul 00	21		0.09	**0.10**			
Thillot-sous-les-Cotes, France (NE).2002a (Mirabelle de Nancy)	2	91	0.675 0.676 (1.351)	BBCH 81 02 Aug 01	0	Whole fruit	0.55	0.03			RD-II02124/EA0 10143 FR01
					3		0.26	0.06			
					7		0.13	0.04			
					14		**0.23**	**0.10**			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					0	**Flesh**	0.58	0.03			
					3		0.27	0.06			
					7		0.14	0.04			
					14		0.24	0.11			
Vieville sous les cotes, France (NE), 2002a (Quetsche)	2	110	0.676 0.676 (1.352)	BBCH 85 21 Aug 01	0	Whole fruit	0.22	0.03			RD-II02124/EA010143 FR02
					3		0.06	< 0.01			
					7		0.11	0.04			
					14		**0.06**	**0.03**			
					0	Flesh	0.23	0.03			
					3		0.06	< 0.01			
					7		0.11	0.04			
					14		0.06	0.03			
Billy sous les cotes, France (NE) 002a (Mirabelle de Nancy)	2	91	0.677 0.685 (1.362)	BBCH 81 02 Aug 01	14	Whole fruit	**0.06**	**0.05**			RD-II02124/EA010143 FR03
						Flesh	0.06	0.05			
Schellerten, Germany (NE) 2002a, Meschenmoser (Quetsche)	2	127	0.654 0.660 (1.314)	BBCH 81 30 Aug 01	0	Whole fruit	0.14	< 0.01			RD-II02124/EA010143 GE01
					3		0.09	0.02			
					7		0.04	< 0.01			
					14		**< 0.01**	**0.02**			
					0	Flesh	0.15	< 0.01			
					3		0.09	0.02			
					7		0.04	< 0.01			
					14		< 0.01	0.02			
Naumburg, Germany (NE) 2002a (Stanley)	2	112	0.704 0.705 (1.409)	BBCH 85 13 Aug 01	14	Whole fruit	**0.02**	**0.02**			RD-II02124/EA010143 GE02
					14	Flesh	0.02	0.02			
Jork, Germany (NE) 2002a (Quetsche)	2	100	0.657 0.682 (1.339)	BBCH 85 10 Aug 01	13	Whole fruit	**< 0.01**	**< 0.01**			RD-II02124/EA010143 GE03
					13	Flesh	< 0.01	< 0.01			
Saintt Paul d'Espies, France (SE) 2002a (D'Ente)	2	132	0.676 0.666 (1.342)	BBCH 81 06 Aug 01	15	Whole fruit	**0.03**	**0.02**			RD-II02124/EA010143 FR05
					15	Flesh	0.03	0.02			
Moissac, France (SE) 2002a (D'Ente)	2	132	0.678 0.678 (1.356)	BBCH 81 06 Aug 01	0	Whole fruit	0.08	< 0.01			RD-II02124/EA010143 FR06
					3		0.05	< 0.01			
					7		0.04	0.01			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					15		**0.02**	**0.01**			
					0	Flesh	0.08	< 0.01			
					3		0.05	< 0.01			
					7		0.04	0.01			
					15		0.02	0.01			
Gensac, France (SE) 2002a (D'Ente)	2	133	0.642 0.664 (1.306)	BBCH 81 06 Aug 01	14	Whole fruit	**0.02**	**0.02**			RD-II02124/EA010143 FR07
					14	Flesh	0.02	0.02			
Platani, Greece (SE) 2002a (Back Diamond)	2	93	0.668 0.666 (1.334)	BBCH 82 05 Jul 01	0	Whole fruit	0.04	< 0.01			RD-II02124/EA010143 GR01
					3		0.04	< 0.01			
					7		0.04	0.02			
					14		**0.03**	**< 0.01**			
					0	Flesh	0.04	< 0.01			
					3		0.04	< 0.01			
					7		0.04	0.02			
					14		0.03	< 0.01			
Corropoli, Italy (SE) 2002a (Diamond)	2	94	0.662 0.675 (1.337)	BBCH 82 22 Jun 01	0	Whole fruit	0.15	0.02			RD-II02124/EA010143 IT01
					3		0.09	0.02			
					7		0.07	0.02			
					14		**0.07**	**0.02**			
					0	Flesh	0.15	0.02			
					3		0.09	0.02			
					7		0.07	0.02			
					14		0.07	0.02			
Corropoli, Italy (SE) 2002a (Stanley)	2	123	0.688 0.683 (1.371)	BBCH 82 27 Jul 01	14	Whole fruit	**0.03**	**0.01**			RD-II02124/EA010143 IT02
					14	Flesh	0.03	0.01			
Alcira, Spain (SE) 2002a (Black Star)	2	73	0.690 0.648 (1.338)	BBCH 79-81 29 May 01	0	Whole fruit	0.23	0.03			RD-II02124/EA010143 SP01
					3		0.22	0.03			
					7		0.04	< 0.01			
					13		**0.02**	**0.01**			
					0	Flesh	0.24	0.03			
					3		0.23	0.03			
					7		0.04	< 0.01			
					13		0.02	0.01			
Villena, Spain (SE) 2002a (Pruna gigante)	2	125	0.651 0.678 (1.329)	BBCH 81 25 Jul 01	14	Whole fruit	**0.09**	**0.06**			RD-II02124/EA010143 SP02
					14	Flesh	0.09	0.06			
Algemesi, Spain (SE) 2003a (Black Gold)	2	68	0.668 0.683 (1.351)	BBCH 81 28 May 02	0	Whole fruit	0.36	0.05			RD-03008/EA020153 SP01
					3		0.19	0.05			
					7		0.19	0.06			
					14		**0.13**	**0.06**			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					0	Flesh	0.37	0.05			
					3		0.20	0.05			
					7		0.19	0.06			
					14		0.13	0.06			

Residue concentration in flesh was calculated from weight ratio of stone and flesh.

Apricot

Residue trials on apricot were conducted in 2006 in the USA (Report No., RD-01118, 2006a). A spray application was made 3 times with TM (WP 700 g/kg or SC 539 g/L) at rates of 1.17–1.20 kg ai/ha. Harvest samples were frozen within 1.5 hours and kept frozen during shipment to analytical laboratory. Samples were thawed for approximately 15–20 min. Fruits were cut in halves using a knife and pit removed prior to processing with dry ice. In analysis of residues (method KP-201R2), procedural recovery results were acceptable. A maximum storage period of samples was 192 days.

Table 73 Residues in apricot following application of TM (WP 700 or SC 539)

Location, Country, Year (Variety)	Application				Portion analysed	DALT (days)	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA		**10-14**	**1.18** (3.14 kg ai/ha/yr)			**PHI, 1 d**					
Tulare, CA, USA 2006a (Castlebright)	3	26, 57	1.18 (3.54)	Mature fruit 06 Jun 06	Fruit without stone	1	0.50 / 0.72 (0.61)	0.051 / 0.015 (0.033)			RD-01118/ 2006-06-CA-01
	3	26, 57	1.17-1.18 (3.54)	Mature fruit 06 Jun 06	Fruit without stone	1	0.57 / 0.79 (0.68)	0.018 / 0.017 (0.018)			
Tulare, CA, USA 2006a (Lorena)	3	10, 63	1.18 (3.54)	Mature fruit 26 May 06	Fruit without stone	1	0.43 / 0.31 (0.37)	0.019 / 0.015 (0.017)			RD-01118/ 2006-06-CA-02
	3	10, 63	1.17 1.20 (3.55)	Mature fruit 26 May 06	Fruit without stone	1	0.50 / 0.18 (0.34)	0.021 / 0.015 (0.018)			
Tulare, CA, USA 2006a (Poppy)	3	9, 66	1.18-1.19 (3.58)	Mature fruit 18 May 06	Fruit without stone	1	0.15 / 0.042 (0.097)	< 0.01 / < 0.01 (< 0.01)			RD-01118/ 2006-06-CA-03
	3	9, 66	1.188 (3.56)	Mature fruit 18 May 06	Fruit without stone	1	0.35 / 0.12 (0.24)	< 0.01 / 0.11 (0.058)			
Quincy, WA, USA 2006a (Perfection)\	3	20, 97	1.19 (3.56)	Mature fruit 10 Jul 06	Fruit without stone	1	1.4 / 1.1 (1.3)	0.092 / 0.060 (0.076)			RD-01118/ 2006-06-WA-01
	3	20, 97	1.18-1.19 (3.55)	Mature fruit 10 Jul 06	Fruit without stone	1	0.90 / 1.6 (1.2)	0.067 / 0.077 (0.072)			
Madera, CA, USA 2006a (Poppy)	3	9, 66	1.18-1.19 (3.54)	Mature fruit 18 May 06	Fruit without stone	0	0.44 / 0.72 (0.58)	0.019 / 0.027 (0.023)			RD-01118/ 2006-06-CA-04
						1	0.32 / 0.51 (0.42)	0.016 / 0.041 (0.029)			

Location, Country, Year (Variety)	Application				Portion analysed	DALT (days)	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
						3	0.16 / 0.17 (0.17)	0.014 / 0.015 (0.015)			
						7	0.10 / 0.082 (0.093)	0.018 / 0.024 (0.021)			
						10	0.075 / 0.087 (0.081)	0.016 / 0.016 (0.016)			
						14	0.13 / 0.012 (0.073)	0.024 / < 0.01 (0.017)			
	3	9,66	1.18 (3.56)	Mature fruit 18 May 06	Fruit without stone	1	0.54 / 0.44 (0.49)	0.034 / 0.027 (0.031)			

Nectarine and peach

Residue trials on nectarine and peach were conducted in the USA in 1990 (Report No., RD-00078, 1996). A foliar application was made 3 or 5 times with TM (WP 700 g/kg) at rates of 1.17–1.19 kg ai/ha. For peach, spray application was done 3 or 5 times with TM (WP 700 g/kg or WG 850 g/kg) at rates of 0.93–1.27 kg ai/ha. Harvest samples were frozen within 2-3 hours. In an analytical laboratory, the fruits were pitted and ground with dry ice. In analysis of residues, procedural recovery results were not acceptable. A maximum storage period of nectarine and peach samples stored frozen was 1472 days (4 years) and 1531 days (4.2 years).

Table 74 Residues in nectarine following application of TM (WP 700)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA		**10-14**	**1.18** (3.14 kg ay/ha/yr)		**PHI, 1 d**						
Hughson, CA USA 1996 (May Grand)	3	8-14	1.17 – 1.18 (3.51)	Petal fall 28 Mar 90	75	Fruit without stone	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	RD-00078/ 07A-90
	5	5-70	1.17 – 1.19 (5.89)	0 days pre-harvest 11 Jun 90	0		1.6 / 2.1 / 1.8 / 1.3 (1.7)	0.11 / 0.12 / 0.13 / 0.11 (0.12)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	
					1		1.9 / 1.4 / 1.4 / 1.3 **(1.5)**	0.08 / 0.06 / 0.06 / 0.05 **(0.06)**	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	
					7		0.99 / 1.0 / 0.93 / 0.97 (0.98)	< 0.05 / 0.05 / 0.06 / 0.06 (0.06)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	

Fowler, CA USA 1996 (Summer Diamond)	3	5-8	1.18 (3.53)	Petal fall 20 Mar 90	120	Fruit without stone	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	RD-00078/ 07B-90
	5	5-108 (aerial appl.)	1.18 (5.89)	5.7-7.6 cm diameter 11 Jul 90	0		0.09 / 0.12 / 0.17 (0.13)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	
					1		0.08 / 0.10 / 0.11 / 0.13 **(0.11)**	< 0.05 / < 0.05 / < 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	
					7		< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	

Table 75 Residues in peach following application of TM (WP 700 or WG 850)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA		**10-14**	**1.18** (3.14 kg ay/ha/yr)		**PHI, 1 d**						
Farmersville, CA, USA 1996b (Queen Crest)	3	4-5	1.18 (3.538)	Petal fall 26 Mar 90	51	Fruit w/o stone	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	RD-00078/ 07C-90
	5	4-39 (aerial appl.)	1.18 (5.89)	Maturing fruit 09 May 90	0	Fruit w/o stone	0.25 / 0.41 / 0.24 / 0.14 (0.26)	< 0.05 / 0.09 / < 0.05 / < 0.05 (0.06)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / 0.06 / < 0.05 (0.05)	
					1		0.10 / 0.37 / 0.13 / 0.25 (0.21)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	
					7		< 0.05 / < 0.05 / 0.05 / < 0.05 (0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 / < 0.05 / < 0.05 (< 0.05)	
Winterville, GA, USA 1996b (Redskins)	3	5-7	1.20 – 1.23 (3.70)	Petal fall 12 Mar 90	126	Fruit w/o stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-00078/ 07D-90
	5	5-114	1.18 – 1.27 (6.11)	7-14 days pre-harvest 09 Jul 90	0	Fruit w/o stone	0.44	0.08	< 0.05	0.06	
					1		0.16	< 0.05	< 0.05	< 0.05	
					7		0.08	0.06	< 0.05	< 0.05	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Honor, MI, USA 1996b (Red Haven)	3	5-9	1.8 (3.53)	Petal fall 13 May 90	93	Fruit w/o stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-00078/ 07E-90
	5	5-85	1.18 (5.89)	3-5 days pre-harvest 11 Aug 90	0	Fruit w/o stone	3.4	0.18	< 0.05	< 0.05	
					1		1.9	0.19	< 0.05	< 0.05	
					7		1.2	0.23	< 0.05	< 0.05	
Belvidere, NJ , USA 1996b (Red Haven)	3	7-9	1.19 (3.56)	Petal fall 30 Apr 90	98	Fruit w/o stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-00078/ 07F-90
	5	7-84	1.19 (5.94)	Preharvest 30 Jul 90	0	Fruit w/o stone	2.9	0.31	0.08	< 0.05	
					1		1. 9	0.30	< 0.05	< 0.05	
					7		0.58	0.24	< 0.05	< 0.05	
Upper Black Eddy, PA, USA 1996b (Glohaven)	3	7-11	1.18 (3.53)	Petal fall 27 Apr 90	104	Fruit w/o stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-00078/ 07G-90
	5	7-90	1.18 (5.89)	Preharvest 02 Aug 90	0	Fruit w/o stone	0.79	0.11	< 0.05	< 0.05	
					1		0.73	0.13	0.06	< 0.05	
					7		0.18	0.09	< 0.05	< 0.05	
Hondo, TX, USA 1996b (Bicentennial)	3	5-7	0.96 – 1.1 (2.96)	80% petal fall 10 Mar 90	94	Fruit w/o stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-00078/ 07H-90
	5	5-94	0.93 – 1.01 (4.85)	Mature fruit 18 Jun 90	0	Fruit w/o stone	0.60	0.13	< 0.05	< 0.05	
					7		0.28	0.09	< 0.05	< 0.05	
Allendale, SC, USA 1996b (Winblo)	3	5-15 (aerial appl.)	1.8 (3.53)	Petal fall 20 Mar 90	88	Fruit w/o stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-00078/ 07J-90
	5	5-85	1.18 (5.89)	Mature fruit 16 Jun 90	0	Fruit w/o stone	0.25	0.06	< 0.05	< 0.05	
					1		0.13	0.06	< 0.05	< 0.05	
					7		0.06	< 0.05	< 0.05	< 0.05	
Romney, WV, USA 1996b (Loring)	3	5-26	1.15 (3.46)	Petal fall 21 Apr 90	103	Fruit w/o stone	< 0.05	< 0.05	< 0.05	< 0.05	RD-00078/ 07K-90
	5	5-90	1.15 (5.77)	Preharvest 26 Jul 90	0	Fruit w/o stone	1.2	0.19	< 0.05	< 0.05	
					1		2.0	0.29	0.07	< 0.05	
					7		0.58	0.18	< 0.05	< 0.05	

Berries and other small fruits

Grapes

Residue trials on grape vines were conducted in Northern France and Germany in 2000, 2001 and 2013. A foliar application was made once with TM (SC 500 g/L) at rates of 1.04–1.18 kg ai/ha.

Harvest samples were frozen within 7 hours and maintained frozen until analysis. Frozen whole fruits were homogenized with dry ice and analysed using the method ERV/005 and P 2014 G (RD-02825). The procedural recovery results were acceptable. A maximum storage period of grape samples stored frozen was 101 days.

Table 76 Residues in grape following application of TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: France	1		1.12		PHI, 35 days						
Vouvray, France (NE) 2001b (Chenin, white grape)	1	-	1.18	BBCH 83 28 Aug 00	0	Whole fruit	0.85	0.03	-	-	RD-II01196/ EA000160 FR01
					7		0.13	0.07	-	-	
					14		0.11	0.07	-	-	
					21		0.1	0.09	-	-	
					35		**< 0.01**	**0.08**	-	-	
Le Coudray Macouard, France (NE) 2002c (Chenin, white grape)	1	-	1.15	BBCH 85 28 Aug 01	0		0.12	< 0.01	-	-	RD-II02143/ EA010145 FR01
					7		0.07	0.03	-	-	
					14		0.09	0.08	-	-	
					21		0.07	0.03	-	-	
					35		**0.05**	**0.1**	-	-	
Merfy, France (NE) 2002c (Pinot Noir, red grapt)	1	-	1.04	BBCH 81 20 Aug 01	35		**0.02**	**0.15**	-	-	RD-II02143/ EA010145 FR02
Nogent l'Abesse, France (NE) 2002c (Chardonnay, white grape)	1	-	1.3	BBCH 81 22 Aug 01	35		**0.06**	**0.18**	-	-	RD-II02143/ EA010145 FR04
Montreuil Bellay, France (NE) 2002c (Cabernet, red grape)	1	-	1.18	BBCH 85 27 Aug 01	35		**0.04**	**0.09**	-	-	RD-II02143/ EA010145 FR05
Montreuil Bellay, France (NE) 2002c (Cabernet Franc, red grape)	1	-	1.15	BBCH 83 07 Sep 01	0		0.23	0.05	-	-	RD-II02143/ EA010145 FR06
					7		0.12	0.07	-	-	
					13		0.15	0.1	-	-	
					20		0.17	0.09	-	-	
					33		**0.04**	**0.05**	-	-	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Freyburg, Germany, 2002c (Müller-Thurgau, whit grape)	1	-	1.11	BBCH 81 31 Aug 01	0		0.29	0.04	-	-	RD-II02143/ EA010145 GE01
					7		0.04	0.05	-	-	
					14		0.03	0.1	-	-	
					22		0.02	0.08	-	-	
					37		**0.02**	**0.08**	-	-	
Hammelburg, Germany, 2002c (Müller-Thurgau, white grape)	1	-	1.05	BBCH 81 08 Aug 01	35		**0.01**	**0.05**	-	-	RD-II02143/ EA010145 GE02
Randersacker, Germany, 2002c (Müller-Thurgau, white grape)	1	-	1.12	BBCH 81 27 Aug 01	35		**0.04**	**0.1**	-	-	RD-II02143/ EA010145 GE03
Cernay les Reims, Germany 2014 (Chardonnay, white grape)	1	-	1.16	BBCH 81 20 Aug 13	35		**0.53**	**0.56**	-	-	RD-02825/ GBU-13-16020 FR01
Ilsfeld, Germany, 2014 (Weißriesling, white grape)	1	-	1.10	BBCH 81 27 Aug 13	35		**1.1**	**0.53**	-	-	RD-02825/ GBU-13-16020 DE02
Pompignac, France (SE) 2001b (Merlot, red grape)	1	-	1.16	BBCH 85 16 Aug 00	0		1.31	0.04	-	-	RD-II01196/ EA000160 FR02
					7		1.05	0.14	-	-	
					14		0.6	0.16	-	-	
					21		0.3	0.15	-	-	
					34		**0.27**	**0.14**	-	-	
Saint Jean de Blaignac, France (SE) 2002c (Semillon, white grape)	1	-	1.14	BBCH 81 08 Aug 01	0		0.36	0.02	-	-	RD-II02143/ EA010145 FR07
					6		0.23	0.07	-	-	
					13		0.09	0.14	-	-	
					20		0.13	0.11	-	-	
					34		**0.08**	**0.15**	-	-	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Bouillé Loretz, France (SE) 2002c (Cabernet franc, red grape)	1	-	1.08	BBCH 81 27 Aug 01	35		**0.02**	**0.1**	-	-	RD-II02143/ EA010145 FR10
Lakoma, Greece 2002c (Xinomavro, red grape)	1	-	1.08	BBCH 82 13 Aug 01	35		**0.21**	**0.25**	-	-	RD-II02143/ EA010145 GR01
Ziano Piacentino, Italy, 2002c (Malvasia, white grape)	1	-	1.12	BBCH 83 10 Aug 01	0		1.25	0.05	-	-	RD-II02143/ EA010145 IT01
					7		0.37	0.09	-	-	
					14		0.46	0.15	-	-	
					21		0.23	0.1	-	-	
					34		**0.13**	**0.11**	-	-	
Caltagirone, Italy, 2002c (Italia, table grape)	1	-	1.11	BBCH 83 08MOCT 01	35		**2.1**	**0.29**	-	-	RD-II02143/ EA010145 IT02
Turis, Spain, 2002c (Cencibel, red grape)	1	-	1.08	BBCH 81 03 Aug 01	0		0.2	0.08	-	-	RD-II02143/ EA010145 SP01
					7		0.11	0.08	-	-	
					14		0.06	0.19	-	-	
					21		0.05	0.21	-	-	
					35		**0.03**	**0.13**	-	-	
Ciaza, Spain, 2002c (A superior, table grape)	1	-	1.10	BBCH 81 12 Jun 01	36		**1.1**	**0.29**	-	-	RD-II02143/ EA010145 SP02
Chateauneuf de Gadagne, Southern France, 2003b (Carignan, red grape)	1	-	1.10	BBCH 81 06 Aug 02	37		**0.06**	**0.08**	-	-	RD-03042/ EA020154 FR01

Strawberry

Residue trials on strawberries were conducted in the USA in 1991. A spray application (ground or aerial) was made 4–5 times with TM (WP 700 g/kg, SC 539 g/L, WG or 850g/kg) at rates of 0.77–0.86 kg ai/ha. Harvest samples were frozen with 2 hours and kept frozen until analysis. The samples were homogenized with dry ice. In analysis of residues, extraction was done in ice chunk. The method BR-011-05 was used for analysis and the procedural recovery results were acceptable. A storage period of strawberry samples stored frozen was 1589-1809 days (max., 4.9 year).

Table 77 Residues in strawberry following application of TM (WP 700, WG 850 or SC 539)

Location, Country, Year (Variety)	Application				DALT (days	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA		**7-10**	**079** (3.14 kg ai/ha/yr)		**PHI, 1 day**						
Salinas, CA, USA, 1997 (Selva)	4	10-11	0.80 (3.81)	12 Oct 91	1		0.94	0.3			RD-03544/ 03A-91[a]
Salinas, CA, USA, 1997 (Fern)	5	7	0.80 (3.98)	09 Oct 91	1		1.6	0.41			RD-03544/ 03B-91[a]
Watsonville, CA, USA, 1997 (Selva)	4	7	0.77-0.86 (3.25)	16 May 91	1		1.7	0.6			RD-03544/ 03C-91
Riverview, FL USA, 1997 (Dover)	4	7	0.79 (3.14)	13 Jan 91	1		5.3	0.91			RD-03544/ 03D-91
Grand Rapids, MI, USA, 1997 (Allstar)	4	7-10 (Aerial)	0.79 (3.14)	07 Jun 91	1		0.44	0.21			RD-03544/ 03E-91
Phelps, NY, USA, 1997 (Late Grow)	4	7-10	0.79 (3.14)	10 Jun 91	1		1.6	0.27			RD-03544/ 03F-91
Circleville, OH, USA, 1997 (Kent)	4	7-13	0.77-0.79 (3.12)	May 30 91	1		1.3	0.74			RD-03544/ 03G-91
Hillsboro, OR, USA, 1997 (Benton)	5	7-10	0.79 (3.93)	05 Jun 91	1		0.81	0.38			RD-03544/ 03H-91[b]
Hillsboro, OR, USA, 1997 (Benton)	5	7-10 (Aerial)	0.77-0.81 (3.95)	05 Jun 91	1		0.33	0.16			RD-03544/ 03I-91[b]
Vancouver, WA, USA, 1997 (Hood)	5	7-12	0.79 (3.93)	13 Jun 91	1		0.27	0.75			RD-03544/ 03J-91

[a] Not independent

[b] Not independent

Mango

Residue trials (five trials) on mango were conducted in Thailand in 2001 and 2002. A spray application was made five or six times with carbendazim (EC 500 g/L) at a rate of 1.5 kg ai/ha. Mango samples were analysed on the day of harvest. Before analysis, seed was removed. Residue analysis was conducted by extraction with acetone, partition with dichloromethane and petroleum either, and partition with dichloromethane of extract aqueous layer and determination by HPLC-DAD. Residue concentration was expressed as carbendazim. This method was tested for recovery of carbendazim where 98–102% was recovered at fortification levels of 0.2–1.0 mg/kg (LOQ, 0.01 mg/kg). However, in

one trial (RT 44 13 FCBZ-I), RSD values in replicate analyses for each DALT sample were more than 20%. In other trials, only mean residue value was provided.

Table 78 Residues in mango following application of MBC

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	Interval days	Rate (kg ai/ha)	GS at last treatment			MBC				
Nakornchaisri, Nakormpathom, Thailand 2001 (NamDokMai)	6	10-14	1.5	Mature	0	Whole fruit	0.85				RT 44 13 FCBZ-I
					2		0.90				
					4		1.1				
					6		1.1				
					9		0.80				
					13		0.46				
					20		0.23				
Kanchanaburi, Thailand 2001 (NamDokMai)	6	10-14	1.5	Mature	0	Whole fruit	0.75				RT 44 13 FCBZ-II
					2		1.2				
					4		1.0				
					6		0.72				
					9		0.61				
					13		0.38				
					20		0.16				
Suphanburi, Thailand 2002 (NamDokMai)	5	10-14	1.5	Mature	0	Whole fruit	0.87				RT 44 13 FCBZ-III
					3		1.3				
					7		0.70				
					10		0.37				
Banglene, Thailand 2002 (NamDokMai)	5	10-14	1.5	Mature	0	Whole fruit	0.84				RT 44 13 FCBZ-IV
					3		1.2				
					7		0.72				
					10		0.54				
Bangpae, Rachaburi, Thailand 2002 (NamDokMai)	5	10-14	1.5	Mature	0	Whole fruit	0.76				RT 44 13 FCBZ-V
					3		1.2				
					7		0.71				
					10		0.37				

Bulb vegetables

Spring onion

Residue trials on spring onion were conducted in the USA in 2005. A foliar application was made once with TM (WP 700 g/kg) at rates of 1.59–1.63 kg ai/ha. Harvest samples were frozen with 2 hours

and kept frozen until analysis. The samples were homogenized with dry ice. In analysis of residues using the method KP-201R2, procedural recovery results were acceptable. A storage period of spring onion samples stored frozen was 244–282 days.

Table 79 Residues in green onion following application of TM (WP 700)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**1.58** (1.58 kg ai/ha/yr)								
Willacy, TX, USA 2006 (Gramex hybrid)	1		1.63 (1.63)	Mature plants, whole w/ roots clipped 27 Oct 05	75		< 0.01 / < 0.01 **(< 0.01)**	0.034 / 0.042 **(0.038)**			RD-01116 /KP-2005-40-TX-01
Fresno, CA, USA 2006 (Unknown)	1		1.6 (1.6)	Mature plants, whole w/ roots clipped 20 Oct 05	102		< 0.01 / < 0.01 **(< 0.01)**	< 0.01 / < 0.01 **(< 0.01)**			RD-01116/ KP-2005-40 -CA-02[a]
Fresno, CA, USA 2006 (Unknown)	1		1.59 (1.59)	Mature plants, whole w/ roots clipped 21 Oct 05	102		< 0.01 / < 0.01 **(< 0.01)**	0.039 / 0.031 **(0.035)**			RD-01116/ KP-2005-40 -CA-03[a]

[a] Not independent trials, conducted under the same weather conditions

Fruiting vegetables, Cucurbits

Cucumber

Residue trials on cucumber (outdoor) were conducted in the USA in 1991 and 1992. A broadcast application (ground or aerial) was made 8 times with TM at rates of 0.39-0.43 kg ai/ha. Harvest samples were frozen with 4 hours and kept frozen until analysis. The samples were homogenized with dry ice while frozen.. Extraction procedure was done in ice bath. The method BR-011-05 was used for residue analysis and the procedural recovery results were acceptable. A storage period of cucumber samples stored frozen was 1679-2043 days (4.6-5.6 years).

Table 80 Residues in cucumber (outdoor) following application of TM (WP 700, SC 539 or WG 850)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**0.39** (2.35 kg ai/ha/yr)	In-furrow, on the top of seeds; buried drip irrigation							
Thermal, CA, USA,1998a (Lucky Strike)	8	7-10	0.39 (3.14)	Harvest 28 May 932	1	fruit	0.08	< 0.05	< 0.05	< 0.05	RD-II02171/ 26A-91
					6	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Madera, CA, USA,1998a (Ashley)	8	7-10 Aerial	0.39-0.41 (3.16)	Fruiting 21 Aug 91	1	fruit	0.19	< 0.05	< 0.05	< 0.05	RD-II02171/ 26B-91
					5	fruit	0.08	< 0.05	< 0.05	< 0.05	
Jupiter, FL, USA,1998a (Poinsett)	8	6-8 Aerial	0.39-0.43 (3.18)	Mature Fruit 12 Dec 91	1	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26C-91

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Conklin, MI, USA,1998a (Marketmore 76)	8	6-8	0.39 (3.14)	Mature Fruit 09 Aug 91	1	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26D-91[a]
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Conklin, MI, USA,1998a (Marketmore 76)	8	6-8	0.39 (3.14)	Mature Fruit 09 Aug 91	1	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26E-91[a]
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Gaston, NC, USA,1998a (Marketmore 80)	8	7	0.40 (3.22)	Fruiting 11 Aug 91	1	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26F-91[b]
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Gaston, NC, USA,1998a (Marketmore 80)	8	7	0.39 (3.14)	Fruiting 11 Aug 91	1	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26G-91[b]
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
New Holland, OH, USA,1998a (Straight Eight)	8	6-8	0.39 (3.14)	Blooming / Fruiting 21 Aug 91	1	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26H-91
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Elko, SC, USA,1998a (Ashley)	8	7-9	0.39 (3.14)	Fruit-Mature 22 Jun 91	1	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26I-91
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Donna, TX, USA,1998a (Poinsett 76)	8	4-10	0.39-0.40 (3.20)	61-183 cm runners 10 Jun 91	1	fruit	0.12	< 0.05	< 0.05	< 0.05	RD-II02171/ 26J-91
					5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	
Hager City, WI, USA,1998a (not known)	8	5-10	0.39-0.40 (3.18)	Fruit Maturing 7.6-12.7 cm 30 Sep 91	5	fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02171/ 26K-91

[a] Not independent [b] Not independent

Summer squash

Residue trials on summer squash (outdoor) were conducted in the USA in 1991. A spray application (ground or aerial) was made 8 times with TM (WP 700 g/kg, SC 539 g/L or WG 850g/kg) at rates of 0.35–0.40 kg ai/ha. Frozen samples were homogenised with dry ice. Extraction procedure was done in ice bath. The analytical method used was KP-021-01 and the procedural recovery results were not acceptable. A storage period of summer squash samples stored frozen was 2034–2216 days (5.6–6.1 years).

Table Residues in summer squash (outdoor) following application of TM (WP 700, SC 539 or WG 850)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**0.39** (2.35 kg ai/ha/yr)	In-furrow, on the top of seeds; buried drip irrigation							
Fresno, CA, USA,1997 (Ambassador-Zucchini)	8	7-10	0.35 (2.78)	03 July 91	1	fruit	**0.16**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27A-91
Madera, CA, USA,1997 (Ambassador)	8	7-10 (Aerial)	0.39 (3.14)	21 Aug 91	1	fruit	**0.083**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27B-01
Jupiter, FL, USA,1997 (Goldie)	8	7-10 (Aerial)	0.39 (3.14)	12 Dec 91	1	fruit	**< 0.05**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27C-91
Luxahatchee, FL,USA,1997 (Dixie)	8	7-10	0.40 (3.22)	13 Jun 91	1	fruit	**0.12**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27D-91
Winterville, GA, USA,1997 (Summer Yellow Crookneck)	8	7-10	0.38 (3.05)	11 Jul 91	1	fruit	**0.34**	**0.13**	< 0.05	< 0.05	RD-II02092/ 27E-91
Conklin, MI, USA,1997 (Lemondrop L)	8	7-10	0.39 (3.14)	22 Jul 91	1	fruit	**< 0.05**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27F-91
Gaston, NC, USA,1997 (Early Golden Summer Crookneck)	8	7-10	0.40 (3.22)	28 Jul 91	1	fruit	**0.055**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27G-91
Phelps, NY, USA,1997 (President)	8	7-10	0.39 (3.14)	26 Aug 91	1	fruit	**0.12**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27H-91
Hillsoboro, OR, USA,1997 (Elete)	8	4-5	0.39 (3.14)	03 Aug 91	1	fruit	**0.057**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27I-91
Donna, TX, USA,1997 (Early Profile Straightneck)	8	4-5	0.39 (3.14)	10 Jun 91	1	fruit	**0.068**	**< 0.05**	< 0.05	< 0.05	RD-II02092/ 27J-91

Melon

Residue trials on melons (outdoor and indoor) were conducted in Spain, Southern France and Italy in 1999 and 2001. In the trials (outdoor) of one report (RD-00427), drip irrigation (TM, WG 700 g/kg) was done three times at rates of 0.87–1.39 kg ai/ha. In the other trials, TM (SC 500 g/L) was applied to melon once by drip irrigation at rates of 2.19 and 2.23 kg ai/ha followed by two spray applications in the range between 0.68 and 0.70 kg ai/ha (outdoor application in RD-II02129; indoor application in RD-II01204 and RD-III02128).

For melon samples from the three times drip applications (RD-00427), a total of MBC was analysed after converting TM into MBC, where TM was not separately analysed. In the analysis, procedural recoveries of TM or MBC were not acceptable. For the other trials, samples were frozen within several hours after harvest and kept frozen until analysis, homogenised with dry ice. The method ERV/005 was used and the procedural recoveries were acceptable. A storage period of melon samples stored frozen was 46–200 days.

Table 82 Residues in melon (indoor and outdoor) following foliar application of TM (WG 700 or SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Outdoor application											
Murcia, Spain (SE) 2000 (Ajax)	3	15-17	Drip: 0.87-1.37 (3.28)	BBCH 82 (22 Jun 99)	0	fruit		0.029 *			RD-00427/ 99558A1[a]
					7	fruit		0.020 *			
					14	fruit		0.016 *			
					21	peel		< 0.011*			
					21	flesh		< 0.011 [b]			
Murcia, Spain (SE) 2000 (Eros)	3	14-27 (drip)[a]	Drip: 0.87-1.39 (3.30)	BBCH 82 (13 Jul 99)	0	fruit		0.024 *			RD-00427/ 99558A2[a]
					7	fruit		0.034 *			
					14	fruit		0.016 *			
					21	peel		< 0.011*			
					21	flesh		< 0.011*			
Sevilla, Spain (SE) 2000 (Sancho)	3	14 (drip) [a]	Drip: 0.87-1.40 (3.31)	BBCH 72/73 (05 Jul 99)	0	fruit		0.014 *			RD-00427/ 99558SE1[b]
					7	fruit		0.017 *			
					14	fruit		0.014 *			
					21	peel		0.012 *			
					21	flesh		< 0.011*			
Sevilla, Spain (SE) 2000 (Rochet)	3	15 (drip) [a]	Drip: 0.87-1.39 (3.29)	BBCH 76/77 (28 Jul 99)	0	fruit		< 0.011 *			RD-00427/ 99558SE2[b]
					7	fruit		< 0.011[b]			
					13	fruit		< 0.011 *			
					21	peel		0.011 *			
					21	flesh		< 0.011*			
Lagarde-Fimarcon, France (SE) 2002c (Escripto)	3	14-22	Soil: 2.19 Foliar: 0.69 0.70 (3.58)	BBCH 75 (03 Aug 01)	3	Whole fruit	**0.02**	**0.04**			RD-II02129/EA0 10150 FR01
					3	Flesh	< 0.01	0.02			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Ramacca, Italy (SE) 2002c (na)	3	14-33	Soil: 2.23 Foliar: 0.69 0.8 (3.60)	BBCH 88 (27 Aug 01)	3	Whole fruit	**0.19**	**0.06**			RD-II02129/EA010150 IT01
					3	Flesh	0.08	0.02			
Indoor application											
Senas, France (SE) 2001b (Luna Star)	3	13-19	Soil: 0.26 Foliar: 0.74 0.75 (3.73)	BBCH 87 (29 May 00)	0	Whole fruit	0.05	0.02			RD-II01204/EA000156 FR01
					1		0.05	0.03			
					3		**0.02**	**< 0.01**			
					0	Flesh	< 0.01	< 0.01			
					1		< 0.01	< 0.01			
					3		< 0.01	< 0.01			
Pernes les Fontaines, France (SE) 2001b (Luna Star)	3	14-18	Soil: 2.15 Foliar: 0.68 0.71 (3.53) \	BBCH 89 (30 May 00)	0	Whole fruit	0.06	0.01			RD-II01204/EA000156 FR02
					1		0.05	0.02			
					3		**0.07**	**0.02**			
					0	Flesh	< 0.01	< 0.01			
					1		< 0.01	< 0.01			
					3		< 0.01	< 0.01			
Pernes les Fontaines, (SE) 2002b (Luna Star)	3	13-22	Soil: 2.18 Foliar: 0.9 0.68 (3.55)	BBCH 87 (15 May 01)	0	Whole fruit	0.08	0.03			RD-II02128/EA010149 FR01[c]
					1		0.04	0.03			
					3		0.05	0.04			
					7		0.03	0.03			
					0	Flesh	< 0.01	0.02			
					1		< 0.01	0.02			
					3		< 0.01	0.03			
					7		< 0.01	0.02			
Pernes les Fontaines, France (SE) 2002b (Luna Star)	3	14-21	Soil: 2.21 Foliar 0.70 0.66 (3.58)	BBCH 87 (18 May 01)	3	Whole fruit	0.04	0.01			RD-II02128/EA010149 FR03[c]
					3	Flesh	< 0.01	< 0.01			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Pernes les Fontaines, (S E) 2002b (Luna Belle)	3	14	Soil: 2.30 Foliar 0.69 0.71 (3.71)	BBCH 87 (11 Jun 01)	3	Whole fruit	**0.06**	**0.02**			RD-II02128/ EA010149 FR04[c]
					3	Flesh	< 0.01	< 0.01			
Pernes les Fontaines, France (SE) 2002b (Luna Star)	3	14-24	Soil: 2.25 Foliar: 0.65 0.68 (3.57)	BBCH 87 (25 May 01)	3	Whole fruit	0.05	0.02			RD-II02128/ EA010149 FR05[c]
					3	Flesh	< 0.01	0.01			
Pozuelo, Spain (SE) 2002b (Verdor)	3	14-22	Soil: 2.25 Foliar 0.66 0.646 (3.55)	BBCH 87-88(03 Jul 01)	0	Whole fruit	0.3	0.07			RD-II02128/ EA010149 SP01
					1		0.27	0.05			
					3		**0.22**	**0.06**			
					7		0.19	0.02			
					0	Flesh	< 0.01	< 0.01			
					1		0.02	< 0.01			
					3		0.02	< 0.01			
					7		0.03	< 0.01			
Adra, Spain (SE) 2002b (Cantagrillo)	3	13-14	Soil: 2.24 Foliar: 0.68 0.65 (3.57)	BBCH 81(BBCH 81)	3	Whole fruit	**0.02**	**0.04**			RD-II02128/ EA010149 SP02
					3	Flesh	< 0.01	0.02			

Drip irrigation was done with WG 700 formulation. Soil single treatment plus two foliar applications were done with SC 500 formulation.

[*] Determined as a total of MBC, including TM

[a] Not independent (field sites, not sufficiently far)

[b] Not independent (field sites in the same place)

[c] Not independent (field sites, not sufficiently far)

Watermelon

Residue trials on watermelon were conducted in the USA in 1991. A broadcast spray application was made 8 times with TM (WP, 700 g/kg, SC 539 g/L or WG 850g/kg) at rates of 0.39–0.42 kg ai/ha. Harvest samples were frozen within 1.5 hours and whole fruit was kept frozen until analysis. Watermelons were quartered and quarters were homogenised with dry ice. In the residue analysis using the method BR-011-05, procedural recovery result was satisfactory, however, method validation recovery result (before analysis of the study sample) was not acceptable (see residue analysis section). A storage period of watermelon samples stored frozen was 1800–1994 days (4.9–5.5 years).

Table 83 Residues in watermelon (outdoor) following application of TM (WP 700, WG 850, or SC 539)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**0.39** (2.35 kg ai/ha/yr)	In-furrow, on the top of seeds; buried drip irrigation							
Hughson, CA, USA, 1998b (Crimson Sweet)	8	7-8	0.39-0.42 (3.25)	Fruit 15 Aug 91	1	Fruit	0.09	0.06	< 0.05	< 0.05	RD-II02162/ 25A-91
					5		0.1	0.07	< 0.05	< 0.05	
Porterville, CA, USA, 1998b (Cal Sweet)	8	7-9 (Aerial)	0.39 (3.14)	Near maturity 19 Aug 91	1	Fruit	0.19	0.05	< 0.05	< 0.05	RD-II02162/ 25B-91
					5		< 0.05	< 0.05	< 0.05	< 0.05	
Jupiter, FL, USA, 1998b (Crimson Sweet)	8	6-8	0.39 (3.14)	Mature fruit 12 Dec 91	1	Fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02162/ 25C-91[a]
					5		< 0.05	< 0.05	< 0.05	< 0.05	
Jupiter, FL, USA, 1998b (Crimson Sweet)	8	6-8 (Aerial)	0.39 (3.14)	Not recorded 12 Dec 91	1	Fruit	0.27	< 0.05	< 0.05	< 0.05	RD-II02162/ 25D-91[a]
					5		< 0.05	< 0.05	< 0.05	< 0.05	
Meigs, GA, USA, 1998b (Jubilee)	8	7-10	0.39 (3.14)	Mature 02 Jul 91	1	Fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02162/ 25E-91
					5		< 0.05	< 0.05	< 0.05	< 0.05	
Gaston, NC, USA,1998b (Crimson Sweet)	8	7	0.39 (3.14)	Fruiting 04 Aug 91	1	Fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02162/ 25F-91
					5		< 0.05	< 0.05	< 0.05	< 0.05	
Elko, SC, USA,1998b (Crimson Sweet)	8	7-10	0.39 (3.14)	Fruit 11 Jul 91	1	Fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02162/ 25G-91
					5		< 0.05	< 0.05	< 0.05	< 0.05	
Donna, TX, USA,1998b (Jubilee)	8	6-11	0.39-0.40 (3.14)	Mature 28 Jun 91	1	Fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02162/ 25I-91[b]
					5		< 0.05	< 0.05	< 0.05	< 0.05	
Donna, TX, USA,1998b (Jubilee)	8	6-11	0.39-0.40 (3.14)	Mature 28 Jun 91	1	Fruit	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02162/ 25J-91[b]
					5		< 0.05	< 0.05	< 0.05	< 0.05	

[a] Not independent (field sites, not sufficiently far)

[b] Not independent

Fruiting vegetables, other than Cucurbits

Tomato

Residue trials on tomatoes (greenhouse) were conducted in The Netherlands, Greece, Italy and Spain in 2008 and 2009. A foliar application was made twice with TM (SC 500 g/L) at rates of 0.81 and 0.89 kg ai/ha. Harvest samples were frozen within 7 hours and whole fruit was kept frozen until analysis. Homogenisation was done only just before analysis. In analysis of residues using the method P 1471 G, procedural recovery result was acceptable. A storage period of tomato samples stored frozen was 16–236 days.

Table 84 Residues in tomato (indoor) following application of TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP											
JJ 6851 Huissen, The Netherlands, 2009a (Tourance)	2	7	0.89 (1.79)	BBCH 60-89 22 Aug 08	28		0.28	0.071			RD-01847/ GGU-08-3839 NL01
			0.88 (1.76)	BBCH 60-89 29 Aug 08	21		0.58	**0.11**			
			0.85-0.86 (1.72)	BBCH 60-89 16 Sep 08	14		0.18	0.025			
					7		**0.65**	0.075			
					3		0.35	0.021			
					1		0.40	0.021			
					0		0.74	0.037			
58300 Akrolimni, Greece, 2009a (Elpida)	2	7	0.85 (1.70)	BBCH 82 03 Oct 08	28		0.16	0.093			RD-01847/ GGU-08-3839 GR01
			0.85 (1.70)	BBCH 83 10 Oct 08	21		0.22	**0.12**			
			0.84-0.85 (1.69)	BBCH 85 29 Oct 08	13		0.42	0.091			
					6		0.30	0.073			
					3		**0.59**	0.052			
					1		0.56	0.044			
					0		0.91	0.064			
20090 Settala, Italy, 2009a (Intense-One)	2	6-8	0.84-0.88 (1.72)	BBCH 75 11 Sep 08	28		0.16	0.069			RD-01847/ GGU-08-3839 IT01
			0.89 (1.78)	BBCH 77 19 Sep 08	20		0.38	**0.10**			
			0.84-0.87 (1.71)	BBCH 83-85 06 Oct 08	14		**0.80**	0.062			
					7		0.58	0.034			
					3		0.36	0.021			
					1		1.0	0.031			
					0		0.68	0.017			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
04811 La Canada, Spain, 2009a (Fideltiy)	2	7	0.85 (1.69)	BBCH 86 28 Apr 08	28		0.36	0.12			RD-01847/ GGU–08-3839 SP01
			0.84-0.85 (1.68)	BBCH 86 05 May 08	21		0.47	0.11			
			0.83-0.84 (1.67)	BBCH 88 23 May 08	14		0.93	**0.24**			
					7		1.3	0.22			
					3		**1.6**	0.19			
					1		1.1	0.095			
					0		1.5	0.11			
JJ 6851 Huissen, The Netherlands, 2010a (Tourance)	2	6-8	0.84-0.85 (1.68)	BBCH 60-87 21 Aug 09	28		0.07	0.02			RD-02033/ GGU-09-5291 NL01
			0.84 (1.69)	BBCH 60-87 28 Aug 09	21		0.18	0.03			
			0.82-0.82 (1.66)	BBCH 60-87 15 Sep 09	14		0.26	**0.09**			
					7		**0.60**	0.06			
					3		0.43	0.03			
					1		0.84	0.05			
					0		1.0	0.04			
57007 Chalkidona, Greece, 2010a (Formula)	2	7	0.85-0.86 (1.70)\ Indoor	BBCH 71 02 Jul 09	28		0.11	0.03			RD-02033/ GGU-09-5291 GR01
			0.86 (1.72)	BBCH 81 09 Jul 09	21		0.23	0.05			
			0.85 (1.70)	BBCH 85 27 Jul 09	14		0.18	**0.08**			
					7		0.19	0.04			
					3		**0.26**	0.04			
					1		0.20	0.03			
					0		0.17	0.02			
04120 La Canada, Spain, 2010a (Shiren, cherry tomato)	2	7	0.84 (1.68)	BBCH 86 04 May 09	28		0.24	**0.24**			RD-02033/ GGU-009-5291 SP01
			0.84 0.85 (1.69)	BBCH 87 11 May 09	21		0.13	0.11			
			0.83-0.84 (1.68)	BBCH 87 29 May 09	14		0.43	0.10			
					7		0.71	0.14			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					3		**1.01**	0.20			
					1		2.04	0.20			
					0		2.18	0.20			
04100 Nijar, Spain, 2010a (Realeza)	2	6-8	0.85 (1.68)	BBCH 82 15 Oct 09	28		0.14	0.10			RD-02033/ GGU-09-5291 SP02
			0.81-0.84 (1.65)	BBCH 82 21 Oct 09	21		0.14	**0.13**			
			0.84-0.85 (1.68)	BBCH 83 10 Nov 09	14		0.18	0.06			
					7		0.33	0.08			
					3		**0.38**	0.06			
					1		0.38	0.05			
					0		0.65	0.04			

Legume vegetables

Snap bean

Residue trials on snap beans (outdoor) were conducted in the USA in 1990. A broadcast spray (ground or aerial) was made twice with TM (WG 850 g/kg or SC 539 g/L) at rates of 1.56 and 1.59 kg ai/ha. Harvest samples were frozen within 2 hours. In an analytical laboratory, pods and vines were ground frozen with dry ice. Extraction procedure was done in ice bath. The method BR-011-03 (modified version) was used for residue analysis. Recovery test results (before analysis of trial samples and procedural recovery) were acceptable. A storage period of snap bean samples stored frozen was 1654–1793 days (4.5–4.9 year).

Table 85 Residues in snap bean (outdoor) following application of TM (SC 539 or WG 850)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Loxahatchee, FL,USA 1996a (Triumph)	2	5 (Aerial)	1.58 (3.16)	Pods 1.3-5.1 cm long 23 Apr 90	14	beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02090/ 08A-90
					14	vines	< 0.05	< 0.05	< 0.05	< 0.05	
Theilman, MN,USA 1996a (HYSTYLE)	2	5	1.58 (3.14)	Late blossom 31 Aug 90	14	beans	0.07	< 0.05	< 0.05	< 0.05	RD-II02090/ 08B-90
					14	vines	3.51	2.01	0.10	< 0.05	
Marcellus, MI ,USA 1996a (Tendercrop)	2	5	1.59 (3.18)	Early blossom 18 Jul 90	14	beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02090/ 08C-90
					14	vines	0.10	0.55	0.06	< 0.05	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
	2	5	1.57 (3.14)	Flowering, pins 01 Jul 90	14	beans	0.13	0.15	< 0.05	< 0.05	RD-II02090/ 08D-90
					14	vines	7.88	2.91	0.61	0.06	
Bridgeton, NJ,USA 1996a (Provider)	2	5 (Aerial)	1.57 (3.14)	Bean pods 2.5-10 cm 30 Jul 90	14	beans	0.07	0.10	< 0.05	< 0.05	RD-II02090/ 08E-90
					14	vines	2.77	1.05	0.23	< 0.05	
Sodus, NY,USA 1996a (Improved Tendergreen)	2	5	1.57-1.59 (3.14)	Beans 2.5-10 cm 30 Jul 90	14	beans	0.70	0.41	< 0.05	< 0.05	RD-II02090/ 08F-90
					14	vines	12.91 / 13.15 (12.98)	3.27 / 3.65 (3.46)	0.44 / 0.52 (0.48)	0.08 / 0.11 (0.10)	
Hillsboro, OR,USA 1996a (OSU 91)	2	5	1.56 (3.12)	20% bloom, beans 2.5 cm 05 Aug 90	14	beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02090/ 08G-90
					14	vines	0.93	1.46	0.06	< 0.05	
Northampton, PA,USA 1996a (Burpee Stringless)	2	5	1.57-1.58 (3.15)	Bloom to small pods 17 Jul 90	14	beans	< 0.05	0.06	< 0.05	< 0.05	RD-II02090 /08H-90
					14	vines	2.44	1.38	0.27	< 0.05	
Toone, TN,USA 1996a (Contender)	2	5	1.57 (3.14)	Full bloom Bloom with 10% beans 0.6-1.2 cm 04 Jul 90	14	beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02090 /08I-90
					14	vines	0.42	0.42	0.12	< 0.05	
Jenesville, WI,USA 1996a (Hy-Style)	2	5 (Aerial)	1.57 (3.14)	Full bloom 05 Sep 90	14	beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02090 /08J-90[a]
					14	vines	2.17	1.95	0.11	< 0.05	
Delavan, WI,USA 1996a (Peak)	2	5	1.57-1.58 (3.16)	Full bloom 21 Aug 90	14	beans	0.06	0.13	< 0.05	< 0.05	D-II02090/ 08K-90[a]
	2	5			14	vines	5.18	5.18	0.16	< 0.05	

[a] Not independent (field sites, not sufficiently far)

Pulses

Dry bean

Residue trials on dry beans were conducted in the USA in 1990. A spray application was made twice with TM (WG 850 g/kg or SC 539 g/L) at rates of 1.51–1.68 kg ai/ha. Harvest samples were frozen within 2 hours and kept frozen until analysis. Frozen samples were homogenised with dry ice. Extraction was done at ice bath. In analysis of residues using the method BR-011-03 (modified version), procedural recovery results were not acceptable. A storage period of soya bean samples stored frozen was 1626–1725 days (4.5–4.7 years).

Table 86 Residues in dry bean following application of TM (SC 539 or WG 850)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Salinas, CA, USA 1996b (L.A. Hearne)	2	7	1.58 (3.16)	Flowering (12 Sep 90)	83	dry beans	< 0.05/ < 0.05/ < 0.05/ < 0.05 (< 0.05)	< 0.05/ < 0.05/ < 0.05/ < 0.05 (< 0.05)	< 0.05/< 0.05/ < 0.05/< 0.05 (< 0.05)	< 0.05/ < 0.05/ < 0.05/ < 0.05 (< 0.05)	RD-II02166/ 10A-90
					83	vines	0.07/ 0.06/ 0.09/ < 0.05 (0.07)	0.24/ 0.54/ 0.82/ 0.26 (0.30)	< 0.05/ < 0.05/ < 0.05/ < 0.05 (< 0.05)	< 0.05/ < 0.05/ < 0.05/ < 0.05 (< 0.05)	
Delta, CO, USA 1996b (Othello)	2	8	1.51-1.68 (3.19)	Full pod (16 Aug 90)	27	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10B-90
					27	vines	5.77	2.1	0.15	0.15	
Jerone, ID, USA 1996b (UI 126)	2	7	1.579 (3.14)	100% bloom, 1.3 cm pin beans (09 Aug 90)	39	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10C-90
					39	vines	2.46	2.96	0.07	0.07	
Conklin, MI, USA 1996b (Albion)	2	7 (Aerial)	1.57 (3.14)	Late bloom, early pod set (30 Jul 90)	38	dry beans	< 0.05	0.08	< 0.05	< 0.05	RD-II02166/ 10D-90
					38	vines	0.07	0.05	< 0.05	< 0.05	
Marcellus, MI, USA 1996b (Sea Farer)	2	7	1.58 (3.16)	Pod set (20 Jul 90)	55	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10E-90
					55	vines	< 0.05	< 0.05	0.05	< 0.05 [b]	
Theilman, MN, USA 1996b (Montcalm Red)	2	10	1.57 (3.14)	Mid-bloom to mid-pod (28 Jul 90)	51	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10F-90
					51	vines	< 0.05	< 0.05	< 0.05	< 0.05	
Northwood, ND, USA 1996b (Upland Navy)	2	7 (Aerial)	1.57-1.58 (3.15)	7 days post 1st (100% bloom) (25 Jul 90)	48	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10G-90[a]
					48	vines	< 0.05	< 0.05	< 0.05	< 0.05	
Northwood, ND, USA 1996b (Upland Navy #7333)	2	7	1.57 (3.14)	7 days post 1st (100% bloom) (18 Jul 90)	55	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10H-90[a]
					55	vines	< 0.05	< 0.05	< 0.05	< 0.05	
York, NE, USA 1996b (Navy small white Lot #7333)	2	7	1.59-1.60 (3.19)	Full bloom (30 Jul 90)	42	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10I-90

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					42	vines	0.1	0.15	< 0.05	< 0.05	
Phelps, NY, USA 1996b (Red Kloud)	2	7 (Aerial)	1.57 (3.14)	Flowering – 5.1-7.6 cm pods (25 Jul 90)	62	dry beans	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02166/ 10J-90
					62	vines	< 0.05	< 0.05	< 0.05	< 0.05	

[a] Not independent (field sites, not sufficiently far)

Soya bean

Residue trials on soya beans (outdoor) were conducted in the USA in 1990. A broadcast spray was made twice with TM (SC 850 g/kg or WG 539 g/L) at rates of 0.64–0.85 kg ai/ha. Harvest samples were frozen within 4 hours and kept frozen until analysis. Frozen samples were homogenised with dry ice. In analysis of residues using the method BR-011-05, procedural recovery results were acceptable. A storage period of soya bean samples stored frozen was 2359–2666 days (6.5–7.3 years).

Table 87 Residues in soya bean following application of TM (WG 850 or SC 539)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA (Not graze or feed)			**0.78** (1.57 kg ai/ha/yr)		**PHI, 21 days**						
Scott, AR, USA1998c (Asgrow 6242)	3	10	0.79 (2.35)	R6 (28 Sep 90)	14	seed	< 0.05	< 0.05			RD-II02091/ 03A-90
					14	straw	< 0.20	< 0.20			
Meigs, GA, USA 1998c (Coker 488)	3	10 (Aerial)	0.82-0.85 (2.47)	Maturing (18 Oct 90)	14	seed	0.09	0.06			RD-II02091/ 03B-90
					14	straw	0.74	1.05			
Muscatine, IA, USA 1998c (Pioneer 9272)	3	10-13 (Aerial)	0.79 (2.35)	R7 (27 Sep 90)	16	seed	< 0.05	< 0.05			RD-II02091/ 03C-90[a]
					16	straw	< 0.20	0.98			
Muscatine, IA, USA1998c (Pioneer 9272)	3	10-13	0.79-0.80 (2.37)	R7 (27 Sep 90)	16	seed	< 0.05	< 0.05			RD-II02091/ 03D-90[a]
					16	straw	< 0.20	1.31			
Carlyle, IL, USA1998c (Unions)	3	10	0.66-0.79 (2.23)	R6-R7 (05 Oct 90)	14	seed	< 0.05	< 0.05			RD-II02091/ 03E-90
					14	straw	< 0.20	0.24			
Hebron, IN, USA1998c (Century 84)	3	10	0.80 (2.39)	80% leaf drop (06 Oct 90)	15	seed	< 0.05	< 0.05			RD-II02091/ 03G-90
					15	straw	< 0.20	0.77			
Rosa, LA, USA1998c (Hartz 5370)	3	10	0.79 (2.35)	R7 (20 Sep 90)	14	seed	< 0.05	0.09			RD-II02091/ 03H-90
					14	straw	0.24	1.63			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Theitman, MN, USA 1998c (Pioneer 9161)	3	10	0.79 (2.35)	pods full (15 Sep 90)	14	seed	< 0.05	< 0.05			RD-II02091/ 03I-90
					14	straw	1	2.77			
Leonard, MO, USA 1998c (Williams 82)	3	9-11	0.64-0.79 (2.26)	R8 (10 Oct 90)	14	seed	< 0.05	< 0.05			RD-II02091/ 03J-90
					14	straw	< 0.20	1.44			
Hernando, MS,USA, 1998c (Centennial)	3	10	0.79 (2.35)	R7 (beginning maturity) (11 Oct 90)	14	seed	< 0.05	< 0.05			RD-II02091/ 03K-90
					14	straw	< 0.20	0.26			
York, NE, USA 1998c (Hack)	3	10-11	0.79 (2.35)	leaves yellowing (17 Sep 90)	14	seed	< 0.05	< 0.05			RD-II02091/ 03L-90
					14	straw	< 0.20	< 0.20			
New Holland, OH, USA 1998c (Madison Seed GL-3610)	3	10	0.79 (2.35)	R7 (27 Sep 90)	14	seed	< 0.05	< 0.05			RD-II02091/ 03M-90
					14	straw	< 0.20	0.63			

[a] Not independent (field sites, not sufficiently far)

Root and tuber vegetables

Sugar beet

Residue trials on sugar beet were conducted in the USA in 1997 and 2005. A spray application was made 3 times with TM (WP 700 g/kg) at rates of 0.77 and 0.83 kg ai/ha. In a study (RD-II02089, 11 trials), sugar beet seeds had TM treatment, using WP 700 g/kg at a rate of 4.0 oz ai/cwt of raw seed (0.11 kg ai/45.4 kg seed), prior to foliar application. Harvest samples were frozen within 4 hours and kept frozen until arrival at an analytical laboratory, where roots were either halved or quartered. Root or top was homogenised with dry ice. Extraction was done at ice bath. For RD-II02089, procedural recovery results were not acceptable. In RD-0114 using the method KP-201R2, procedural recovery results were acceptable. A storage period of sugar beet samples stored frozen was 54–107 days in RD-II02089 and 326 days in RD-01114.

Table 88 Residues in sugar beet following application of TM (WP 700)*

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**0.79** (2.35 kg ai/ha)		**PHI, 21 days**						
Moorhead, MN, USA 1998a (HM-Valley)	3	14	0.796 0.807 0.807 (2.41)	50.8 cm tall and 11.4 cm in diameter (11 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-1

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
						tops	< 0.05 / 0.05 (0.05)	< 0.05 / 0.086 (0.068)			
East Grand Forks, ND, USA 1998a (HM-Valley)	3	14	0.785 0.796 0.785 (2.365)	48.3 cm tall and 11.4 cm in diameter (10 Sep 97)	15	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-2
					18	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
					21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
					24	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
					27	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
					15	tops	0.070 / 0.14 (0.11)	0.23 / 0.38 (0.31)			
					18	tops	0.11 / 0.080 (0.095)	0.48 / 0.36 (0.42)			
					21	tops	< 0.05 / 0.055 (0.053)	0.093 / 0.38 (0.24)			
					24	tops	0.060 / 0.070 (0.065)	0.30 / 0.30 (0.30)			
					27	tops	0.070 / 0.055 (0.063)	0.21 / 0.27 (0.24)			
Grand Forks, ND, USA 1998a (HM-Valley)	3	13-15	0.785 0.785 0.773 (2.343)	45.7 cm tall with root diameter of 12.7 cm (09 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-3
						tops	0.26 / 0.14 (0.20)	0.44 / 0.37 (0.41)			
Wahpeton, ND, USA 1998a (HM-Valley)	3	14	0.785 0.785 0.785 (2.354)	15.2 cm root diameter (10 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-4
						tops	0.095 / 0.11 (0.10)	0.17 / 0.15 (0.16)			
Conklin, MI, USA 1998a (HM-Valley)	3	14	0.785 0.796 0.785 (2.365)	40.6-55.9 cm tall (19 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-5
						tops	< 0.05 / 0.055 (0.053)	0.25 / 0.30 (0.28)			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Velva, ND, USA 1998a (HM-Valley)	3	14	0.785 0.785 0.773 (2.343)	tall of 63.5 cm tall; beet diameter of 20.3-22.9 cm (12 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-6
						tops	0.32 / 0.29 (0.31)	0.51 / 0.52 (0.52)			
Levelland, TX, USA 1998a (Ranger)	3	14	0.818 0.830 0.785 (2.433)	40.6-45.7 cm in height (25 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-7
						tops	0.61 / 0.59 (0.60)	0.47 / 0.53 (0.50)			
Eaton, CO, USA 1998a (HM-9155)	3	14	0.807 0.807 0.796 (2.41)	61.0-76.2 cm in height; crown diameter 6.4-10.2 cm (09 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-8
						tops	0.24 / 0.22 (0.23)	0.68 / 0.50 (0.59)			
Porterville, CA, USA 1998a (Spreckles 781R Variety C)	3	14	0.785 0.785 0.785 (2.354)	tuber elongation (02 Oct 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-10
						tops	3.1 / 1.8 (2.45)	0.88 / 0.72 (0.80)			
Rupert, ID, USA 1998a (HM-9155)	3	14	0.796 0.773 0.796 (2.364)	roots of 10.2-17.8 cm in diameter (20 Aug 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-11
						tops	0.077 / 0.040 (0.059)	0.19 / 0.06 (0.125)			
Jerome, ID USA, 1998a (B HM-9155)	3	14	0.796 0.796 0.796 (2.388)	root diameter 10.2-15.2 cm (03 Sep 97)	21	roots	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-II02089/ 97284-12
						tops	0.080 / 0.16 (0.12)	0.149 / 0.19 (0.17)			
Fresno, CA, USA 2006c (SS NB7R)	3	14	0.795 0.785 0.791 (2.371)	not available (06 Oct 05)	21	roots	0.017 / 0.042 (0.030)	0.014 / < 0.01 (0.012)			RD-01114/ KP-2005-28-CA-01
						tops	4.9/ 6.7 (5.8)	5.3/ 5.1 (5.2)			

[*] In RD-II02089, sugar beet seeds were treated with TM, using WP 700 g/kg at a rate of 0.11 kg ai/45.4 kg seed, prior to foliar application.

Cereal grains

Barley

Residue trials on barley were conducted in Northern France, Belgium and Germany in 2000 and 2001. A spray application was made once with TM (SC 500 g/kg) at rates of 0.60 and 0.65 kg ai/ha. Harvest samples were frozen within 9 hours and kept frozen until arrival at an analytical laboratory. Samples were homogenised with dry ice. Extraction was done with cold solvent. In analysis of residues using the method ERV-006, procedural recovery results were acceptable. A storage period of barley samples stored frozen was 30–201 days.

Table 89 Residues in barley following application of TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Taissy, France (ND) 2001c (Esterel, winter)	1	-	0.622 (0.622)	BBCH 59 (26 May 00)	0	Whole	10	0.68			RD-II01194/ EA000159 FR01
					7	Whole	0.65	0.95			
					14	Whole	0.01	0.45			
					27	Ears	0.26	0.5			
					42	Straw	**0.31**	**0.36**			
					42	Grain	**0.16**	**0.23**			
Gravenvoern, Belgium 2002e (Nikel, winter)	1	-	0.603 (0.603)	BBCH 59-61 (23 May 01)	0	Whole	5.8	0.36			RD-II02144/ EA010156 BE01
					7	Whole	3.2	0.64			
					14	Whole	0.57	0.39			
					28	Ears	0.11	0.11			
					42	Straw	**0.12**	**0.12**			
					42	Grain	**0.13**	**0.08**			
Maarseik, Belgium 2002e (Carolette, winter)	1	-	0.632 (0.632)	BBCH 71 (29 Jun 01)	42	Straw	0.19	0.29			RD-II02144/ EA010156 BE02
					42	Grain	**< 0.01**	**0.1**			
Puisieulx, France (NE) 2002e (Estere, winter)	1	-	0.631 (0.631)	BBCH 59 (25 May 01)	0	Whole	20	1.4			RD-II02144/ EA010156 FR01[a]
					7	Whole	0.1	2.3			
					14	Whole	0.02	1.5			
					27	Ears	< 0.01	0.76			
					40	Straw	< 0.01	0.44			
					40	Grain	< 0.01	0.12			
Chanceaux sur Choisille, France (NE) 2002e (Aspenl, spring barley)	1	-	0.652 (0.652)	BBCH 57 (11 Jun 01)	43	Straw	**< 0.01**	**0.32**			RD-II02144/ EA010156 FR02
					43	Grain	**< 0.01**	**0.02**			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
St Brice la Neuvilette, France (NE) 2002e (Esterel, winter)	1	-	0.624 (0.624)	BBCH 59 (25 May 01)	40	Straw	**0.33**	**0.46**			RD-II02144/ EA010156 FR03[a]
					40	Grain	**0.02**	**0.12**			
Liethe, Germany 2002e (Theresa, winter)	1	-	0.65 (0.65)	BBCH 59 (30 May 01)	0	Whole	12	0.28			RD-II02144/ EA010156 GE01
					7	Whole	0.11	0.09			
					14	Whole	0.13	0.07			
					28	Ears	0.02	0.01			
					42	Straw	**0.05**	**0.04**			
					42	Grain	**< 0.01**	**< 0.01**			
Hondelage, Germany 2002e (Tiffani, winter)	1	-	0.63 (0.63)	BBCH 71 (01 Jun 01)	46	Straw	**0.12**	**0.04**			RD-II02144/ EA010156 GE02
					46	Grain	**< 0.01**	**< 0.01**			
Monblanc, Southern France 2001c (Nikel, winter)	1	-	0.621 (0.621)	BBCH 71 (18 May 00)	0	Whole	7.2	0.89			RD-II01194/ EA000159 FR02
					7	Whole	1.4	1.7			
					14	Whole	0.08	0.12			
					28	Ears	0.02	0.02			
					42	Straw	**0.02**	**0.03**			
					42	Grain	**< 0.01**	**< 0.01**			
St Jean de Blaingac, France (SE) 2002e (Majestic, winter)	1	-	0.6 (0.6)	BBCH 77 (25 May 01)	0	Whole	10	0.81			RD-II02144/ EA010156 FR05[b]
					6	Whole	11	1.8			
					14	Whole	3.1	2.6			
					27	Ears	0.13	1.6			
					45	Straw	0.17	0.25			
					45	Grain	0.02	0.21			
Aurade, France (SE) 2002e (Volga, spring barley)	1	-	0.641 / 0.638 (0.640)[a] (0.64)	BBCH 49 (21 May 01)	53	Straw	0.19	0.39			RD-II02144/ EA010156 FR06
					53	Grain	< 0.01	< 0.01			
Martres, France (SE) 2002e (Platine, winter)	1	-	0.604 (0.604)	BBCH 77 (25 May 01)	39	Straw	**0.97**	**0.76**			RD-II02144/ EA010156 FR07[b]
					39	Grain	**0.13**	**0.71**			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Corropoli, Italy 2002e (Otis, winter)	1	-	0.622 (0.622)	BBCH 59 (05 Jun 01)	0	Whole	11.1	0.76			RD-II02144/ EA010156 IT01
					7	Whole	7.2	2.4			
					14	Whole	0.95	1.3			
					28	Ears	1.6	2.8			
					42	Straw	**0.41**	**0.6**			
					42	Grain	**0.02**	**0.12**			
Mosciano Sant'Angelo, Italy 2002e (F. Giord, winter)	1	-	0.65 (0.65)	BBCH 59 (09 May 01)	43	Straw	**0.71**	**1.5**			RD-II02144/ EA010156 IT02[c]
	1	-			43	Grain	0.11	0.56			
Sant' Omero, Italy 2002e (Otis, winter)			0.632 (0.632)	BBCH 59 (09 May 01)	43	Straw	0.11	0.72			RD-II02144/ EA010156 IT03[c]
					43	Grain	**0.1**	**1.2**			
Pompiac, France (SE) 2003c (Nikel, winter)	1	-	0.613 (0.613)	BBCH 71 (14 May 02)	0	Whole	7.54	0.63			RD-03006/ EA020160 FR01[d]
					7	Whole	0.43	0.37			
					14	Whole	0.08	0.9			
					28	Ears	0.03	0.12			
					42	Straw	0.03	**0.04**			
					42	Grain	< 0.01	< 0.01			
Rieumes, France (SE) 2003c (Gaelic, winter)	1	-	0.631 (0.631)	BBCH 71 (14 May 02)	43	Straw	**0.03**	0.03			RD-03006/ EA020160 FR02[d]
					43	Grain	**< 0.01**	**< 0.01**			

[a] Not independent (field sites, not sufficiently far)

[b] Not independent (field sites, not sufficiently far)

[c] Not independent (field sites, not sufficiently far)

[d] Not independent (field sites, not sufficiently far)

Oat

Residue trials on oat were conducted in Germany, the United Kingdom, Czech Republic and Poland in 2008 and 2009. A spray application was made once with TM (SC 500 g/kg) at rates of 0.73–0.79 kg ai/ha. Harvest samples were frozen within 11 hours and kept frozen until arrival at an analytical laboratory. In analysis of residues using the method P/B 1471 G, procedural recovery results were acceptable. A storage period of oat samples stored frozen was 55–125 days.

Table 90 Residues in oat following application of TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Herrentierbach, Germany 2009b (Dominik)	1	-	0.76	BBCH 65 (01 Jul 08)	36	Grain	**< 0.01**	**0.018**			RD-01797/ GGU-08-3845 GE01
					36	Straw	**0.27**	**0.27**			
Wicken, UK 2009b (Gerald)	1	-	0.76	BBCH 65 (26 Jun 08)	48	Grain	**< 0.01**	**< 0.01**			RD-01797/ GGU-08-3845 UK01
					48	Straw	**0.052**	**0.095**			
Uherskyi, CZ 2010b (Expander)	1	-	0.79	BBCH 65 (22 Jun 09)	0	Whole	17	0.27			RD-02037/ GGU-09-5287 CZ01
					25	Panicles	0.01	0.01			
					56	Grain	**< 0.01**	**< 0.01**			
					56	Straw	**< 0.01**	**< 0.01**			
Bornhain, Germany 2010b (Dominik)	1	-	0.73	BBCH 65 (01 Jul 09)	0	Whole	8.2	0.2			RD-02037/ GGU-09-5287 GE01
					28	Panicles	0.02	0.02			
					46	Grain	**< 0.01**	**< 0.01**			
					46	Straw	**0.07**	**0.06**			
Kottmannsweiler, Germany 2010b (Dominik)	1	-	0.78	BBCH 65 (30 Jun 09)	49	Grain	**< 0.01**	**< 0.01**			RD-02037/ GGU-09-5287 GE02
					49	Straw	**0.02**	**0.08**			
Kslaz-Wielkploska, Poland 2010b (Furman)	1	-	0.75	BBCH 65 (18 Jun 09)	0	Whole	9.0	0.27			RD-02037/ GGU-09-5287 PL01
					25	Panicles	0.02	0.04			
					43	Grain	**< 0.01**	**< 0.01**			
					43	Straw	**0.02**	**0.02**			
Westbury UK 2010b (Gerald)	1	-	0.75	BBCH 65 (24 Jun 09)	0	Whole	15	0.19			RD-02037/ GGU-09-5287 UK01
					26	Panicles	0.11	0.18			
					40	Grain	**< 0.01**	**< 0.01**			
					40	Straw	**1.1**	**0.85**			
Basingstoke, UK 2010b (Gerald)	1	-	0.74	BBCH 65 (25 Jun 09)	36	Grain	**< 0.01**	**0.02**			RD-02037/ GGU-09-5287 UK02
					36	Straw	**2.0**	**1.0**			

Wheat

Residue trials on wheat were conducted in Northern France, Belgium, Germany, Hungary and Austria in 2000-2002 and 2013. A spray application was made once with TM (SC 500 g/kg) at rates of 0.61 and 0.77 kg ai/ha. Harvest samples were frozen within 7 hours and kept frozen until arrival at an

analytical laboratory. Samples were homogenised with dry ice. As analytical methods, a study, RD-02755 used the P/B 1471 G and the other studies used the method ERV-006. Procedural recovery results were acceptable in all studies. A storage period of wheat samples stored frozen was 20–168 days.

Table 91 Residues in wheat following application of TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Northern Europe											
Brimont, France 2001d (Shango, winter)	1	-	0.61	BBCH 73 (14 Jun 00)	0	Whole plant	5.8	0.52			RD-II01193/ EA000158 FR01
					7	Whole	3.98	1.6			
					15	Whole	3.3	0.9			
					27	Ears	< 0.01	0.09			
					43	Straw	0.96	0.4			
					43	Grain	**< 0.01**	**< 0.01**			
Kinrooi, Belgium 2002f (Record, winter)	1	-	0.65	BBCH 69 (19 Jun 01)	0	Whole	16	0.13			RD-II02132/ EA010157 BE01
					7	Whole	10	0.82			
					14	Whole	3.7	0.74			
					28	Ears	0.2	0.18			
					42	Straw	1.6	0.74			
					42	Grain	**< 0.01**	**< 0.01**			
Linter Neerherspen, Belgium 2002f (Rialto, winter)	1	-	0.64	BBCH 75 (02 Jul 01)	42	Straw	0.17	0.14			RD-II02132/ EA010157 BE02
					42	Grain	**< 0.01**	**< 0.01**			
Morand, France 2002f (Isengrain, winter)	1	-	0.63	BBCH 59 (29 May 01)	0	Whole	8.2	0.29			RD-II02132/ EA010157 FR01[a]
					7	Whole	5.6	0.91			
					14	Whole	1.8	0.71			
					29	Ears	0.16	0.16			
					42	Straw	< 0.01	0.3			
					42	Grain	< 0.01	< 0.01			
Rouziers de Touraine, France 2002f (Apache, winter)	1	-	0.63	BBCH 59 (29 May 01)	56	Straw	1.0	0.36			RD-II02132/ EA010157 FR02[a]
					56	Grain	**< 0.01**	**< 0.01**			
Brimont, France 2002f (Buccaneer, winter)	1	-	0.64	BBCH 59 (08 Jun 01)	46	Straw	< 0.01	< 0.01			RD-II02132/ EA010157 FR03
					46	Grain	**< 0.01**	**< 0.01**			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Wunstorf, Germany 2002f (Bandit, winter)	1	-	0.65	BBCH 69 (21 Jun 01)	0	Whole	19	0.19			RD-II02132/ EA010157 GE01
					7	Whole	3.4	0.49			
					14	Whole	0.38	0.19			
					27	Ears	0.05	0.04			
					42	Straw	0.31	0.16			
					42	Grain	**< 0.01**	**< 0.01**			
Oberboyen, Germany 2002f (Ritmo, winter)	1	-	0.65	BBCH 71 (26 Jun 01)	43	Straw	0.36	0.07			RD-II02132/ EA010157 GE02
					43	Grain	**< 0.01**	**0.01**			
Charentilly, France 2003d (Charger, winter)	1	-	0.64	BBCH 69 (29 May 01)	43	Straw	0.20	0.27			RD-03007/ EA020161 FR01
					43	Grain	**< 0.01**	**< 0.01**			
Saint Cyr du Gault, France 2013 (Pescadou, hard wheat)	1	-	0.75	BBCH 69 (20 Jun 13)	0	Whole	17	0.53			RD-02755/ JCB-13-15494 FR01
					7	Whole	5.3	2.3			
					14	Whole	0.79	1.7			
					28	Ears	0.43	1.7			
					28	Whole w/o ears	1.8	2			
					47	Grain	**< 0.01**	**0.033**			
					47	Straw	0.37	0.92			
Mohács, Hungary, 2013 (Mv TD 33-08, hard wheat)	1	-	0.77	BBCH 69 (03 Jun 13)	36	Grain	**< 0.01**	**< 0.01**			RD-02755/ JCB-13-15494 HU02
					36	Straw	0.021	0.040			
Gerhaus, Austria, 2013 (Floradur, hard wheat)	1	-	0.74	BBCH 69 (20 Jun 13)	35	Grain	**0.011**	**< 0.01**			RD-02755/ JCB-13-15494 AT03
					35	Straw	0.92	0.82			
Southern Europe											
Noilhan, France 2001d (Soissons, winter)	1	-	0.61	BBCH 77 (30 May 00)	0	Whole t	5.8	0.59			RD-II01193/ EA000158 FR02
					7	Whole	0.19	0.51			
					14	Whole	0.03	0.11			
					29	Ears	< 0.01	0.11			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					43	Straw	0.04	0.03			
					43	Grain	**< 0.01**	**< 0.01**			
Merville, France 2002f (Isengrain, winter)	1	-	0.64	BBCH 73 (01 Jun 01)	0	Whole	5.6	0.24			RD-II02132/ EA010157 FR04[b]
					7	Whole	5.2	1.6			
					14	Whole	0.21	0.26			
					28	Ears	0.28	0.2			
					55	Straw	< 0.01	0.07			
					55	Grain	**< 0.01**	**< 0.01**			
Martres, France 2002f (Sideral, winter)	1	-	0.63	BBCH 77 (31 May 01)	0	Whole	15	0.49			RD-II02132/ EA010157 FR05
					6	Whole	9.2	1.3			
					13	Whole	5.6	2.0			
					27	Ears	0.27	0.4			
					33	Straw	< 0.01	1.4			
					33	Grain	**< 0.01**	**0.03**			
Castillon Saves, France 2002f (Apache, winter)	1	-	0.63	BBCH 69 (01 Jun 01)	53	Straw	< 0.01	0.03			RD-II02132/ EA010157 FR06[b]
					53	Grain	< 0.01	< 0.01			
Marignac, France 2002f (Isengrain, winter)	1	-	0.61	BBCH 71 (06 Jun 01)	47	Straw	0.26	0.27			RD-II02132/ EA010157 FR07
					47	Grain	**< 0.01**	**< 0.01**			
Corropoli, Italy 2002f (Duilio, winter)	1	-	0.65	BBCH 69 (16 May 01)	41	Straw	0.24	0.5			RD-II02132/ EA010157 IT02[c]
					41	Grain	**0.01**	**0.03**			
Tortoreto, Italy 2002f (Ciccio, winter)	1	-	0.65	BBCH 69 (16 May 01)	42	Straw	0.14	0.42			RD-II02132/ EA010157 IT03[c]
					42	Grain	< 0.01	0.03			
Aurade, France 2003d (Apache, winter)	1	-	0.63	BBCH 75 (28 May 02)	0	Whole	9.2	0.64			RD-03007/ EA020161 FR02
					7	Whole	0.29	1.3			
					14	Whole	0.03	0.2			
					28	Ears	0.01	0.06			
					42	Straw	0.03	0.06			
					42	Grain	**< 0.01**	**< 0.01**			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Poucharramet, France 2003d (Soissons, winter)	1	-	0.63	BBCH 71 (28 May 02)	44	Straw	0.02	0.03			RD-03007/ EA020161 FR03
					44	Grain	**< 0.01**	**< 0.01**			
Colonella, Italy 2003d (Grazia, winter)	1	-	0.64	BBCH 60 (16 May 02)	0	Whole	10	0.39			RD-03007/ EA020161 IT01
					6	Whole	0.56	0.74			
					14	Whole	0.07	0.19			
					27	Ears	0.03	0.21			
					42	Straw	0.08	0.32			
					42	Grain	**0.02**	**< 0.01**			
Poggio Renatico, Italy 2013 (San Carlo, hard wheat)	1	-	0.75	BBCH 69 (21 May 13)	0	Whole	26	1.2			RD-02755/ JCB-13-15494 IT04
					7	Whole	1.5	1.7			
					14	Whole	0.70	0.95			
					28	Ears	0.13	0.54			
					28	Whole w/o ears	0.14	0.56			
					36	Grain	**< 0.01**	**0.027**			
					36	Straw	0.34	0.94			

[a] Not independent (field sites, not sufficiently far)

[b] Not independent (field sites, not sufficiently far)

[c] Not independent (field sites, not sufficiently far)

Tree nuts

Almond

Residue trials on almonds were conducted in the USA in 1998. A spray application was made 4 times with TM (WSB 700 g/kg) at rates of 1.14 and 1.27 kg ai/ha. After harvest, almond samples were separated to hulls and nutmeats using a mechanical huller in a processing site (shells, discarded), and shipped frozen to an analytical laboratory. Hull and nutmeat samples were ground with dry ice. Extraction was done at ice bath. In analysis of residues using the methods KP-21-00, procedural recoveries were acceptable. A storage period of almond samples stored frozen was 69–168 days.

Table 92 Residues in almond following application of TM (WP 700)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**1.18** (2.35 kg ai/ha/hr)	As needed b/w pink bud and petal fall							
Earlimart, CA, USA1999 (Carmel, long)	4	30-96	1.14-1.19 (4.68)	Hull Split (29 Jul 98)	43	hulls	2.2 / 1.9 (2.1)	0.71 / 0.63 (0.67)			RD-01079/ P-98-02-CA01[a]

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
					50	hulls	3.8 / 4.0 (3.9)	0.73 / 0.73 (0.73)			
					57	hulls	4.5 / 6.8 (5.7)	1.1 / 1.2 (1.2)			
					64	hulls	5.4 / 5.9 (5.7)	1.2 / 1.4 (1.3)			
					43	Nutmeat	< 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 **(< 0.05)**			
					50	Nutmeat	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
					57	Nutmeat	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
					64	Nutmeat	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
Terra Bella, CA, USA1999 (Carmel, long)	4	27-104	1.17-1.20 (4.73)	Hull Split (03 Aug 98)	30	hulls	7.0 / 6.3 (6.7)	0.70 / 0.78 (0.74)			RD-01079/ KP-98-02-CA02[a]
					30	Nutmeat	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			
McFarland, CA, USA1999 (Non Pareil, short)	4	27-99	1.14-1.18 (4.66)	Hull Split (29 Jul 98)	29	hulls	3.7 / 3.4 (3.6)	1.0 / 1.2 (1.1)			RD-01079/ KP-98-02-CA03
					29	Nutmeat	< 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 **(< 0.05)**			
Porterville, CA, USA1999 (Mission, long)	4	27-122	1.16 -1.20 (4.73)	Hull Split (03 Sep 98)	20	hulls	4.3 / 6.5 (5.4)	0.80 / 1.1 (0.95)			RD-01079/ KP-98-02-CA04
					20	Nutmeat	< 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 **(< 0.05)**			
Hughson, CA, USA1999 (Merced, long)	4	28-115	1.21-1.27 (4.96)	Hull Split (14 Aug 98)	55	hulls	5.6 / 4.2 (4.9)	0.64 / 0.68 (0.66)			RD-01079/ KP-98-02-CA05
					55	Nutmeat	< 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 **(< 0.05)**			

[a] Not independent (field sites, not sufficiently far)

Hazelnut

Residue trials on hazelnut were conducted in the Greece and Italy in 2008 and 2009. A spray application was made once with TM (SC 500 g/L) at rates of 1.01 and 1.03 kg ai/ha. Harvest hazelnut shells were removed at the test site (Greece trials) or in the field (Italy trials). Shells were discarded and flesh samples were frozen within 9 hours after harvest. Flesh samples were kept frozen until arrival to an analytical laboratory. The non-homogenised samples stored frozen were homogenised only just before analysis. In analysis of residues using the method P/B 1471 G, procedural recoveries were acceptable. A storage period of hazelnut samples stored frozen was 10–170 days.

Table 93 Residues in hazelnut following application of TM (SC 500)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: Italy			**0.88**	Fruit enlargement							
Katerini, Greece (SE) 2009C (Sivri-Giagli)	1		1.02	BBCH 69 (28 Mar 08)	130	Hazelnut flesh	**< 0.01**	**< 0.01**			RD-01796/ GGU-08-3843 GR01
Avli, Greece (SE) 2009C (Palace)	1		1.03	BBCH 69 (01 Apr 08)	127	Hazelnut flesh	**< 0.01**	**< 0.01**			RD-01796/ GGU-08-3843 GR02
Mombarruzo, Italy (SE) 2009c (Tonda Gentile delle Langhe)	1		1.03	BBCH 69 (16 Apr 08)	184	Hazelnut flesh	**< 0.01**	**< 0.01**			RD-01796/ GGU-08-3843 IT01
Carru, Italy (SE) 2010c (Nutella)	1		1.01	BBCH 69 (07 Apr 09)	189	Hazelnut flesh	**< 0.01**	**< 0.01**			RD-02034/ GGU-09-4890 IT01

Pecan

Residue trials on pecans were conducted in the USA in 1991. A spray application was made 8–9 times with TM (WG 850 g/kg or SC 539 g/L) at rates of 0.77–0.91 kg ai/ha. Harvest samples were homogenised with dry ice. Extraction was done with chilled solvent. In residue analysis, procedural recovery results were not acceptable. A storage period of pecan samples stored frozen was 2125–2247 (5.8–6.2 years).

Table 94 Residues in pecan following application of TM (SC 539 or WG 850)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**0.79** (2.35 kg ai/ha/yr)	Not apply after shuck split							
Proterville, CA,USA1998b (Wichita)	8	14-21	0.79 (6.28)	na (14 Sep 91)	66	Pecans	< 0.05	< 0.05			RD-II02173/ 06B-91
Melrose, FL, USA1998b (Desirable)	9	14-21	0.79 (7.07))	na (13 Sep 91)	25	Pecans	< 0.05	< 0.05			RD-II02173/ 06C-91
Hawkinsville, GA, USA 1998b (Stuart)	8	14-21 (Aerial)	0.79 (6.28)	na (11 Sep 91)	65	Pecans	< 0.05	< 0.05			RD-II02173/ 06D-91[a]
Hawkinsville, GA, USA 1998b (Stuart)	8	14-21	0.79 (6.28)	na (11 Sep 91)	65	Pecans	< 0.05	< 0.05			RD-II02173/ 06E-91[a]
Alexandria, LA, USA 1998b (Caddo)	8	14-21	0.91 (7.26))	na (28 Aug 91)	36	Pecans	< 0.05	< 0.05			RD-II02173/ 06F-91
Binger, OK, USA1998b (Merramac)	8	14-21	0.79 (6.28)	na (21 Sep 91)	48	Pecans	< 0.05	< 0.05			RD-II02173/ 06H-91
Uvalde, TX, USA1998b (Shoshone, TX)	8	14-21 (Aerial)	0.77 (6.18)	na (12 Aug 91)	53	Pecans	< 0.05	< 0.05			RD-II02173/ 06I-91[b]

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
Uvalde, TX, USA1998b (Shoshone, TX)	8	14-21	0.81 (6.46)	na (13 Aug 91)	52	Pecans	< 0.05	< 0.05			RD-II02173/ 06J-91[b]

[a] Not independent (field sites, not sufficiently far)

[b] Not independent (field sites, not sufficiently far)

Pistachio

Residue trials in pistachios were conducted 2002 in the USA (3 at harvest trials). A spray application was made 6 times with TM (WSB 700 g/kg; wettable powder) at application rates of 1.56–1.60 kg ai/ha. Harvest pistachio nuts were shelled and the nutmeat (shells, discarded) were frozen within 7 hours. The samples were kept frozen until arrival at an analytical laboratory. Homogenisation was done with dry ice. In analysis of residues using the method KP-201R1, procedural recoveries were acceptable. A storage period of pistachio samples stored frozen was 126–140 days.

Table 95 Residues in pistachio following application of TM (WSB 700)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA			**1.58** (1.58 kg ai/ha)	At bloom							
Parlier, CA,USA 2006 (Kerman)	6	14-15	1.57-1.58 (9.46)	Hull Split (06 Sep 02)	14	nutmeat	0.34 / 0.41 (0.37)	< 0.01 / < 0.01 (< 0.01)			RD-01074/ 02-CA56
Orland, CA, USA 2006 (Kerman)	6	14-15	1.56 -1.58 (9.42)	Nut development (29 Aug 02)	14	nutmeat	0.44	0.010			RD-01074/ 02-CA57
					15		0.70	0.011			
Madera, CA, USA 2006 (Kerman)	6	10-11	1.57 -1.60 (9.50)	Colouring pistachio(30 Aug 02)	14	nutmeat	0.32 / 0.50 (0.41)	< 0.01 / < 0.01 (< 0.01)			RD-01074/ 02-CA58

Oilseeds

Peanut

Residue trials on peanuts were conducted in the USA in 1991 and 2005. A broadcast spray (ground or aerial) was made 4–6 times with TM (WG, 850 g/kg, WSB 700 g/kg or SC 539 g/L) at rates of 0.35 and 0.42 kg ai/ha. In a study (RD-II02094), harvest peanut was allowed to dry for several days in the field, then separate in-shell nuts and hay samples were taken and frozen immediately. The samples were shipped under frozen conditions to an analytical laboratory. The entire portion of each frozen sample was homogenised with dry ice. In another study (RD-01115), peanut samples were frozen within 70 min after harvest and maintained frozen until arrival at an analytical laboratory. The peanuts were shelled and the nutmeat samples were homogenised with dry ice. For residue analysis, BR-011-05 (RD-II02094) and KP-201R2 (RD-01115) were used and the procedural recoveries were acceptable. A storage period of peanut samples stored frozen was 84 days (RD-01115) and 1835-2151 days (5.0–5.9 years; RD-II02094).

Table 96 Residues in peanut following application of TM (WG 850, SC 539 or WSB 700)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA		**14**	**0.39** (1.58 kg ai/ha/yr)		**PHI, 14 days**						
Grangerburg, AL,USA1998 (Florunner)	6	14	0.35 (2.09)	na (26 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01A-91[a]
					14	Hay	< 0.5	< 0.5	-	-	
Grangerburg, AL,USA1998 (Florunner)	6	14 (Aerial)	0.42 (2.50)	na (26 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01B-91[a]
					14	Hay	< 0.5	< 0.5	-	-	
Meigs, GA, USA1998 (Florunner)	6	12-14	0.40 (2.42)	na (04 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01C-91
					14	Hay	< 0.5	0.63	-	-	
Meigs, GA, USA1998 (Florunner)	6	14-21 (Aerial)	0.40 (2.42)	na (03 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01D-91
					14	Hay	< 0.5	< 0.5	-	-	
Meigs, GA, USA1998 (Florunner)	6	12-14	0.39 (2.35)	na (04 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01E-91
					14	Hay	< 0.5	< 0.5	-	-	
Whitakers, NC, USA1998 (NC 11)	6	10-14	0.39 (2.35)	na (11 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01F-91
					14	Hay	< 0.5	1.3	-	-	
Whitakers, NC, USA1998 (NC 11)	6	10-14	0.39 (2.35)	na (11 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01G-91
					14	Hay	< 0.5	0.84	-	-	
Pattison, TX, USA1998 (Spanish)	6	8-10 (Aerial)	0.39 (2.35)	na (03 Sep 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01H-91[b]
					14	Hay	< 0.5	< 0.5	-	-	
Pattison, TX, USA1998 (Spanish)	6	10-11	0.38 (2.29)	na (30 Aug 91)	14	Nutmeat	< 0.05	< 0.05	< 0.05	< 0.05	RD-II02094/ 01I-91[b]
					14	Hay	< 0.5	< 0.5	-	-	
Emporia, VA, USA1998 (NC 6)	6	14	0.39 (2.35)	na (22 Sep 91)	14	Nutmeat	< 0.05	< 0.05	0.074	< 0.05	RD-II02094/ 01J-91
					14	Hay	< 0.5	1.8	-	-	
Tift, GA,USA 2006 (Georgia Green)	4	6-7	0.39-0.40 (1.57)	na (20 Sep 05)	14	Nutmeat	**< 0.01**	**< 0.01**	-	-	RD-01115/ KP-2005-29-GA-01
	4	6-7	1.08 -1.10 (4.38)	20 Sep 05	14	Nutmeat	< 0.01	< 0.01	-	-	

[a] Not independent, conducted under the same weather conditions

[b] Not independent, conducted under the same weather conditions

Rape seed

Residue trials on rape seeds were conducted in the USA in 2001. A broadcast spray application was made once with TM (WSB 700 g/kg) at rates of 1.56–1.59 kg ai/ha. Collected samples were frozen with 4 hours and kept frozen until arrival at an analytical laboratory. Samples were homogenised with dry ice. In analysis of residues using the method KP-024-01, procedural recovery results were acceptable. A storage period of rape seed samples stored frozen was 22–44 days.

Table 97 Residues in rape seed following application of TM (WSB 700)

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)				Study/ Trial
	No.	RTI (days)	Rate (kg ai/ha)	GS at last treatment			TM	MBC	FH-432	DX-105	
GAP: USA	**1 or 2**		**1.57** (1.57 kg ai/ha/hr) **or 0.79** (1.57 kg ai/ha/yr)		**PHI, 40 days**						
McHenry, ND, USA 2001a (Hyola 357)	1	-	1.56	20% flowering (06 Jul 01)	39	Seeds	< 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 **(< 0.05)**			RD-00484/ 01ND101[a]
Foster, ND, USA 2001a (Top Score)	1	-	1.59	30% flowering (13 Jul 01)	41	Seeds	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-00484/ 01ND102[a]
Barnes, ND, USA 2001a (RR 357)	1	-	1.59	50% flowering (10 Jul 01)	57	Seeds	< 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 **(< 0.05)**			RD-00484/ 01ND103
Ward, ND, USA 2001b (Hyclass)	1	-	0.79	50% flowering (06 Jul 01)	38	Seeds	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			RD-00496/ 01ND101
	1	-	1.58	50% flowering (06 Jul 01)	38	Seeds	< 0.05 / < 0.05 **(< 0.05)**	< 0.05 / < 0.05 **(< 0.05)**			RD-00496/ 01ND104
	1	-	7.91	50% flowering (06 Jul 01)	38	Seeds	< 0.05 / < 0.05 (< 0.05)	< 0.05 / < 0.05 (< 0.05)			

[a] Not independent (field sites, not sufficiently far)

FATE OF RESIDUES IN STORAGE AND PROCESSING

Nature of the residue during processing

High-temperature hydrolysis

A high-temperature hydrolysis study was conducted to determine the nature of the residues generated under processing conditions (van der Gaauw, A., 2002; Report No., RD-II02134). [^{14}C]-TM (phenyl ring label) was dissolved in sterilised 0.01 M citrate-phosphate buffer at pH 4, 5 and 6. The samples were incubated to simulate pasteurisation (90 °C for 20 min at pH 4), baking, brewing and boiling (100 °C for 60 min at pH 5) and sterilisation (120 °C for 20 min at pH 6). LSC and HPLC were used for analysis.

The recoveries of the applied radioactivity were 99–108%. Under pasteurisation condition, TM was stable and little hydrolysed. Under baking, brewing and boiling conditions, TM accounted for 85.4% of the AR and major hydrolysis product was MBC, accounting for 14.2% of the AR. In the

condition of sterilisation, TM was not detected. MBC accounted for 92.0% of the AR. 2-AB was found at 10.3% of the AR.

In conclusion, TM was stable at pH 4 for 20 minutes at 90 °C. At pH 5 and 6 at elevated temperatures, TM was hydrolysed mainly to MBC and at much less extent to 2-AB. As other hydrolysis products, AV-1951 and two unknowns were detected, but at less than 4.1% of the AR.

Table 98 Hydrolysis of TM under simulated processing conditions

Component	% Applied radioactivity and concentration, mg/L					
	pH 4, 90 °C		pH 5, 100 °C		pH 6, 120 °C	
	0 min	20 min	0 min	60 min	0 min	20 min
TM	98.3 (2.10)	101(2.16)	98.2 (2.08)	85.4 (1.81)	98.1 (2.12)	-
MBC	-	-	-	14.2 (0.30)	-	92.0 (1.99)
2-AB	-	-	-	-	-	10.3 (0.22)
Unk1	-	-	-	-	-	4.1 (0.089)
AV-1951	-	-	-	1.4 (0.031)	-	-
Unk 2	1.7 (0.036)	1.0 (0.021)	1.8 (0.038)	2.1 (0.045)	1.9 (0.041)	0.6 (0.014)

AV-1951: [2-(N-Methoxy carbonyl thioureido) phenylene] thiourea

Residues after processing

Orange and mandarin (juice, marmalade, canned mandarin and pomace)

A processing study on orange and mandarin was conducted as a part of post-harvest treatment residue study (Pollmann, B., 2007; RD-01293). For processing study, orange and mandarin were treated with TM at a rate of 1.8 kg ai/hL of liquid of drencher system. Analytical method used for analysis of residues (TM and MBC) in the product matrices (juice, marmalade and pomace) was the same with that used for residue trial sample. Procedural recoveries on the product matrices were acceptable. Processed samples were stored frozen until analysis for 63–98 days.

Canned mandarins

Unwashed mandarins were peeled by hand and separated manually into segments. The segments were bathed in HCl solution (0.5–0.9% v/v HCl-deionised water). After bathing, the segments were washed three times with deionised water, bathed in a NaOH solution (0.3–0.5% v/v NaOH-deionised water) and again washed three times with deionised water. Subsequently, the segments were put into suitable recipients, which were filled with a sugar solution (25% sugar, 75% water). The recipients were closed airtight and pasteurized at 80–90 °C for 25 minutes.

Juice

Unwashed RAC samples were washed with water, pressed and extracted in a FMC machine (type 391 with 5 cups) and a water flow rate of 100 L/h. After juice extraction, three fractions (raw juice, wet pomace and oil/water emulsion) were obtained. The pomace fraction was dried until a constant weight was obtained to get dry pomace. The raw juice was pasteurised at 80–89 °C for 25–26 minutes.

Orange marmalade

Unwashed RAC samples were washed with water, peeled manually and the pulp cut into small pieces. For the marmalade preparation, extra fine peel and pulp was prepared. Thereafter, pulp (85%) and extra fine peel (15%, cut into small strips) were mixed in a thermomixer with sugar and pectin. After mixing, the paste was heated to 95–96 °C until the paste had jelled. After heating, acidifier was added. The final pH was 3, the sugar content was between 59 and 64° Brix. The hot marmalade was placed in suitable glass containers and cooled.

Table 99 Residues in processing products of orange and mandarin post-harvest treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/hL)	GS			TM	MBC	TM	MBC	
Orange											
Alzira, Spain 2007 (Valencia)	1		1.8	BBCH 89 (22 Feb 07)	na	fruit not washed	28 16*	0.6 16.6*			RD-01293/ R06ESP0110
						fruit washed	19	0.36			
						washing water	10	0.64			
						peel	23	0.22			
						pulp	1. 7	< 0.05			
						marmalade	26 15	0.37 15.4	0.93	0.62	
						fruit not washed	37 21	0.94 21.9			
						fruit washed	18	0.47			
						washing water	5.5	1.3			
						raw juice	1 0.6	< 0.05 < 0.65	0.03	< 0.05	
						wet pomace	46 26	1.2 27.2	1.2	1.3	
						dry pomace	28 16	23 39	0.76	24.5	
						oil/water susp.	246 137	6.4 143	8.8	10.7	
						pasteurized juice	1 0.6	< 0.05 < 0.65	0.04	< 0.08	
Quart de Poblet, Spain 2007 (Navel Lane-Late)	1		1.8	BBCH 89 (22 Mar 07)	na	fruit not washed	33 18	0.66 18.7			RD-01293/ R06ESP0111
						marmalade	7.6 4.2	0.27 4.47	0.23	0.41	
						fruit not washed	23 13	0.66 13.7			
						pasteurised juice	0.8 0.4	< 0.05 < 0.45	0.03	< 0.08	
						dry pomace	37 21	16.6. 37.6	1.1	25.2	
Catadau , Spain 2007 (Valencia)	1		1.8	BBCH 89 (26 Mar 07)	na	fruit not washed	28 16	0.63 16.6			RD-01293/ R06ESP0112
						marmalade	7.4 4.1	0.25 4.35	0.26	0.40	
						fruit not washed	28 16	0.59 16.6			
						pasteurised juice	0.8 0.4	< 0.05 < 0.45	0.03	< 0.08	
						dry pomace	42 23	16 39	1.5	27.1	
Catadau , Spain 2007 (Navel Lane-Late)	1		1.8	BBCH 89 (22 Feb 07)	na	fruit not washed	18 10	0.4 10.4			RD-01293/ R06ESP0113
						marmalade	13 7	0.25 7.25	0.72	0.63	
						fruit not washed	21 12	0.55 12.6			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/hL)	GS			TM	MBC	TM	MBC	
						pasteurised juice	0.6 0.3	< 0.05 < 0.35	0.03	< 0.09	
						dry pomace	32 18	24 42	1.5	43.6	
Mandarin											
Quart de Poblet, Spain 2007 (Hernandia)	1		1.8	BBCH 89 (22 Feb 07)		fruit not washed	39 22	0.73 22.7			RD-01293/ R06ESP0109
						peel	103	1.2			
						peeled fruits	2	< 0.05			
						canned mandarin	< 0.05 < 0.03	< 0.05 < 0.08	< 0.00 1	< 0.07	

Post-harvest treatment in all trials: using a shower (drencher system) with a spray liquid (0.18 kg ai/hL , SC 500 g/L)

* Calculated as MBC equivalent

Apple (puree, canned apple, juice and pomace)

Three processing studies on apple were conducted (Grolleau, G., 2002g; Report No., RD-II02140) (Grolleau, G., 2003e; Report No, RD-03029) (Pitt, J.L., 1995b; RD-99126). TM (SC 500) was applied twice to apple trees at rates of 0.64–0.69 kg ai/ha. Apples were harvested 3 days after the last application and processed to juice, puree and canned apples. In analysis of residues using the method ERV/005 (RD-II02140; RD-03029), procedural recoveries on the product matrices were acceptable. In the study RD-99126, the method ERV/007 was used, however, procedural recovery results were not acceptable. Processed samples were stored frozen until analysis for 14–15 days.

Juice

Unwashed apples were crushed with an electric crusher and then pressed. The apple juice was collected in a stainless steel tank and the wet pomace was weighed. The pomace dried for two or three days at approximately 60 °C in an oven to obtain dry pomace. Pectolytic enzymes were added to the raw apple juice for depectinisation and rested for 12 hours. The juice was decanted and the cleaned juice filtered. The juice was pasteurised by heating to approximately 80 °C for at least one minute and subsequently placed in sterilised glass bottles with screw cap.

Apple puree

Unwashed apples were blanched in boiling water for 2 minutes to avoid enzymatic browning. The blanched apples were crushed with an electric crusher and sieved to obtain puree. After addition of sugar, the puree was reduced by heating to obtain a degree Brix of 24%, filled in glass bottles with screw cap and sterilised at 115–120 °C for 10 minutes.

Canned apples

Unwashed apples were weighed and peeled using an apple peeler-knife. Peeled apples were blanched in boiling water for 2 minutes to avoid enzymatic browning. The cores were removed with an apple peeler-knife. According to the size, apples were cut in two or four pieces. A syrup of water and sugar was prepared (concentration: 200 g sugar in 800 g water). The pH was corrected with citric acid to obtain approximately a pH of 3. About 500 g of apple pieces were filled in sterilised glass jars and filled up with 250 g syrup. The jars were closed with a protective lid and pasteurised at 90–95 °C for 1 minute.

Table 100 Residues in processing products of apple treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Voeren, Belgium 2002g (Jonagold)	2	140	0.64-0.65 (1.29)	BBCH 85-87 (28 Sep 01)	3	Raw apple	0.06 0.03	0.05 0.08			RD-II02140/ EA010140 BE01
						Washed apple	0.05	0.06			
						Wet pomace	0.03 0.02	0.15 0.17	0.50	3.0	
						Dry pomace	< 0.01 < 0.006	0.59 0.60	< 0.17	11.8	
						Juice	< 0.01 < 0.006	0.03 0.04	< 0.17	0.60	
						Puree	0.01 0.006	0.05 0.056	0.17	1.0	
						Canned apple	< 0.01 < 0.006	< 0.01 < 0.02	< 0.17	< 0.20	
Caumont, France 2002g (Golden delicious)	2	164	0.67-0.69 (1.36)	BBCH 87 (14 Sep 01)	3	Raw apple	0.11 0.06	0.03 0.09			RD-II02140/ EA010140 FR07
						Washed apple	0.09	0.04			
						Wet pomace	0.04 0.02	0.11 0.13	0.44	3.7	
						Dry pomace	< 0.01 < 0.006	0.3 0.31	< 0.09	10.0	
						Juice	0.04 0.02	0.09 0.11	0.36	3.0	
						Blanching water	< 0.01	0.08			
						Seeds / peel	< 0.01	0.02			
						Puree	< 0.01 < 0.006	0.01 0.02	< 0.09	0.33	
						Peeled apple	< 0.01	0.01			
						Blanched apple	< 0.01	< 0.01			
						Cores	< 0.01	< 0.01			
						Canned apple	< 0.01 < 0.006	< 0.01 < 0.02	< 0.09	< 0.33	
Sommacampagna, Italy 2002g (Golden delicious)	2	150	0.68-0.67 (1.35)	BBCH 87 (10 Sep 01)	3	Raw apple	0.16 0.09	0.03 0.12			RD-II02140/ EA010140 IT01
						Washed apple	0.05	0.03			
						Wet pomace	0.03 0.02	0.2 0.22	0.19	6.7	
						Dry pomace	< 0.01 < 0.006	0.49 0.52	< 0.06	16.3	
						Juice	0.01 0.006	< 0.01 < 0.02	0.06	< 0.33	
						Puree	0.01 0.006	0.01 0.016	0.06	0.33	
						Canned apple	0.02 0.01	0.05 0.06	0.13	1.7	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Allonnes, France 2003e (Golden)	2	135	0.66-0.66 (1.35)	BBCH 85-87 (25 Aug 02)	3	Raw apple	0.03 0.02	0.03 0.05			RD-03029 EA020150 FR02
						Washed apple	0.02	0.03			
						Wet pomace	0.02 0.01	0.1 0.11	0.67	3.3	
						Dry pomace	< 0.01 < 0.006	0.27 0.28	< 0.33	9.0	
						Juice	0.01 0.006	0.03 0.04	0.33	1.0	
						Puree	< 0.01 < 0.006	< 0.01 < 0.02	< 0.33	< 0.33	
						Peels	0.06	0.31			
						Peeled apple	< 0.01	0.01			
						Blanching water	< 0.01	< 0.01			
						Blanched apple	0.01	< 0.01			
						Cores	< 0.01	< 0.01			
						Canned apple	< 0.01 < 0.006	< 0.01 < 0.02	< 0.33	< 0.33	
Watsonville, CA, USA 1995b (Newton Pippin)	10	7-28 d	7.83 – 8.07 (78-80)	Immature fruit (08 Aug 90)	30	Raw apple	4.7 2.6	1.32 3.92			RD-99126/ 02A-90
						Juice	0.2	0.76	*	*	
						Wet pomace	2.8	2.34	*	*	

* Pf was not estimated due to lack of validity of analytical data.

Cherry (canned cherries, jam, juice and pomace)

Two processing studies on cherry were conducted following application of TM (Grolleau, G., 2001e; Report No, RD-II01202) (Grolleau, G., 2002i; Report No., RD-II02125). TM (SC 500) was applied (foliar) twice to cherry trees at rates of 0.66–0.67 kg ai/ha. In analysis of residues using the method ERV/005 or ERV/006, procedural recoveries on the product matrices were acceptable. Processed samples were stored frozen until analysis for 38–134 days.

Canned cherries

Cherries (without stems) were blanched in boiling water for one minute to avoid enzymatic browning, then plunged in cold water. Syrup of water and sugar was prepared (concentration: 200 g sugar in 800 g water). About 500 g of cherries were filled in sterilised glass jars and filled up with 250 g syrup. The jars were closed with a protective lid and sterilised at 115 °C for 10 minutes (Grolleau G. 2001e) or pasteurised at 90–95 °C for 1 minute (Grolleau, G. 2002h).

Jam

Cherries (without stems) were stoned and crushed and sugar was added. The mix was reduced by heating to reach 62% Brix and filled in glass jars. The jars were closed with a protective lid and sterilised at 115–120 °C for 10 minutes.

Juice

Cherries (without stem) were stoned and pressed in a water press. The pH of the juice was corrected with citric acid to 3.5. The juice was pasteurised at 82–85 °C for 1 minute and filled in glass jars, closed with a lid.

Table 101 Residues in processing products of cherry treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Jussy, France 2001e (Montmorency)	2	81	0.67 (1.35)	BBCH 85 (30 Jun 00)	0	Whole fruit	2.0 1.1	0.13 1.23			RD-II01202/ EA000150 FR01
					3	Whole fruit	0.41	0.3			
					7	Whole fruit	0.25	0.15			
					12	Whole fruit	< 0.01	0.05			
						Washed cherries	< 0.01	0.04			
						Canned cherries	< 0.01 < 0.006	0.02 0.03	< 0.00 5	0.15	
						Jam	< 0.01 < 0.006	0.03 0.04	< 0.00 5	0.23	
Gargas, France 2001e (Napoleon)	2	56	0.66-0.67 (1.33)	BBCH 81 (25 May 00)	0	Whole fruit	1.3 0.7	0.06 0.76			RD-II01202/ EA000150 FR02
					3	Whole fruit	0.21	0.17			
					7	Whole fruit	0.28	0.14			
					14	Whole fruit	0.16	0.13			
						Washed cherries	< 0.01	0.04			
						Canned cherries	< 0.01 < 0.006	0.02 0.03	< 0.00 8	0.33	
						Jam	< 0.01 < 0.006	0.05 0.06	< 0.00 8	0.83	
Bonieux, France, 2002i (Summit)	2	55	0.66 (1.33)	BBCH 85 (28 May 01)	15	Raw cherries	< 0.01 < 0.006	0.03 0.036			RD-II02125/ EA010144 FR02
						Flesh	< 0.01	0.03			
						Washed cherries	< 0.01	0.04			
						Flesh	< 0.01	0.04			
						Waste (juice)	< 0.01	0.02			
						Wet pomace	< 0.01 < 0.006	0.05 0.056		1.7	
						Cherry juice	< 0.01 < 0.006	0.03 0.036		1.0	
						Blanching water	< 0.01	< 0.01			
						Canned cherries	< 0.01 < 0.006	0.02 0.026		0.67	
						Stoned cherries	< 0.01	0.05			
						Waste (jam)	< 0.01	0.02			
						Cherry jam	< 0.01 < 0.006	0.03 0.036		1.0	

Plum (juice, canned, puree, jam, puree, dried and pomace)

A processing study on plum was conducted as a part of residue trial study (Grolleau, G., 2002a; Report No., RD-II02124). In analysis of residues using the method ERV/005, procedural recoveries on the product matrices were acceptable. Processed samples were stored frozen until analysis for 14–26 days.

Juice

Fruits were stoned, crushed and sieved. After sieving, wet pomace was collected. Juice was pasteurised at 82–85 °C for 1 minute and put in sterilised glass jars and closed with a lid.

Canned plums

Fruits were blanched in boiling water for 1–2 minutes. Syrup of water and sugar was prepared (concentration: 200 g sugar in 800 g water). About 500 g of plums were filled in sterilised glass jars and filled up with 250 g syrup. The jars were closed with a protective lid and pasteurised at 90–95 °C for 1 minute.

Jam

Fruits were stoned and crushed. The degree Brix was measured and white sugar was added. The puree was reduced by heating to reach 60–62% Brix. The pH was corrected with citric acid to 3.5 and filled in glass jars. The jars were closed with a protective lid and sterilised at 115–120 °C for 10 minutes.

Puree

Fruits were stoned and crushed. The crushed plums were put into an automatic sieve to separate the raw puree from peels. Sugar was added to reach 24% degree Brix. The puree was put in glass bottles. Bottles were closed with a protective lid and sterilised at 115–120 °C for 10 minutes.

Prune (dried plum)

Plums were stoned and put (without contact between plums) in an oven on shelves covered with siliconised baking paper. Plums were dried at 60 °C.

Table 102 Residues in processing products of plum treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Billy sous les cotes, France 2002a (Mirabelle de Nancy)	2	91	0.68-0.69 (1.36)	BBCH 81 (02 Aug 01)	15	Raw mirabelles	0.03 0.02	0.06 0.08			RD-II02124/ EA010143 FR03
						Washed mirabelles	0.02	0.07			
						Washing water	< 0.01	< 0.01			
						Waste (juice)	0.01	0.04			
						Wet pomace	< 0.01 0.006	0.04 0.046	< 0.33	0.67	
						Mirabelles juice	0.02 0.01	0.14 0.15	0.67	2.3	
						Blanching water	< 0.01	0.03			
						Canned mirabelles	< 0.01 < 0.006	< 0.01 < 0.016	< 0.33	< 0.17	
						Stoned mirabelles	0.04	0.08			
						Waste (jam)	0.01	0.03			
						Puree	0.03 0.02	0.05 0.07	1.0	0.83	
						Mirabelles jam	0.02 0.01	0.08 0.09	0.67	1.3	
						Blanched mirabelles	< 0.01	0.01			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Saintt Paul, France 2002a (d'Espies D'Ente)	2	132	0.67 (1.34)	BBCH 81 (06 Aug 01)	15	Whole plum	< 0.01 < 0.006	0.02 0.026			RD-II02124/ EA010143 FR05
						Washed plum	< 0.01	0.01			
						Washing water	0.01	0.01			
						Stoned plum (juice)	0.01	0.04			
						Wet pomace	0.01 0.0056	0.06 0.066		3.0	
						Juice	0.01 0.0056	0.17 0.18		8.5	
						Blanched plum	< 0.01	0.02			
						Canned plum	< 0.01 < 0.006	0.02 0.026		1.0	
						Plum jam	0.01 0.006	0.03 0.036		1.5	
						Waste (puree)	< 0.01	0.04			
						Plum puree	0.01 0.006	0.05 0.056		2.5	
						Prune (dried plum)	< 0.01 < 0.006	0.12 0.13		6.0	
Moissac France 2002a (D'Ente)	2	132	0.68 (1.356)	BBCH 81 (06 Aug 01)	15	Whole plum	0.02 0.01	0.05 0.06			RD-II02124/ EA010143 FR06
						Washed plum	< 0.01	0.02			
						Juice	0.01 0.006	0.03 0.036	0.50	0.60	
						Canned plum	< 0.01 < 0.006	< 0.01 < 0.016	< 0.50	< 0.20	
						Plum jam	< 0.01 < 0.006	0.03 0.036	< 0.50	0.60	
						Plum puree	0.01 0.006	0.03 0.036	0.50	0.60	
						Prune (dried plum)	< 0.01 < 0.006	0.09 0.096	< 0.50	1.8	
Gensac, France 2002a (D'Ente)	2	133	0.64-0.66 (1.31)	BBCH 81 (06 Aug 01)	14	Whole plum	< 0.01 < 0.006	0.04 0.046			RD-II02124/ EA010143 FR07
						Washed plum	< 0.01	0.03			
						Juice	< 0.01 < 0.006	0.03 0.036		0.75	
						Canned plum	< 0.01 < 0.006	0.01 0.016		0.25	
						Plum jam	< 0.01 < 0.006	0.04 0.046		1.0	
						Plum puree	0.01	0.04		1.0	
						Prune (dried plum)	< 0.01 < 0.006	0.09 0.096		2.3	

Peach (juice, canned, jam, puree and pomace)

Two processing studies on peach were conducted following application of TM (Grolleau, G., 2002h; Report No, RD-II02123) (Grolleau, G., 2003f; Report No., RD-03030). TM (SC 500) was applied (foliar) twice to peach trees at rates of 0.66–0.69 kg ai/ha. In analysis of residues using the method ERV/005, procedural recovery results on the product matrices were acceptable. Processed samples were stored frozen until analysis for 14–46 days.

Juice

Peaches were stoned and crushed in a crusher. Crushed peaches were put into an automatic sieve to separate the juice from peels (=wet pomace). The juice was pasteurised at 82–85 °C for 1 minute and filled in sterilised glass jars.

Puree

Fruits were stoned and crushed. The crushed peaches were put into an automatic sieve to separate the raw puree from peels (=pomace). Sugar was added to reach 24% degree Brix. The puree was put in glass bottles. Bottles were closed with a protective lid and sterilised at 115–120 °C for 10 minutes.

Jam

Peaches were peeled, stoned and crushed. Sugar was added to the crushed peaches. The mix was reduced by heating to reach 60–62% Brix. The pH was corrected with citric acid to 3.5 and filled in glass jars. The jars were closed with a protective lid and sterilised at 115–120 °C for 10 minutes.

Canned peaches

Peaches were plunged into boiling water for two minutes maximum and then immediately plunged into cold water to crack the peels. Peaches were peeled, cut in two parts and stoned. A syrup of water and sugar was prepared (concentration: 200 g sugar in 800 g water). About 500 g of peach halves were filled in sterilised glass jars and filled up with 250 g syrup. The jars were closed with a protective lid and pasteurised at 90–95 °C for 1 minute.

Table 103 Residues in processing products of peach treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Noves, France 2002h (Blandine)	2	148	0.67-0.69 (1.36)	BBCH 87 (17 Aug 01)	3	Whole peach	0.08 0.04	0.02 0.06			RD-II02123/ EA010142 FR02
						Juice	0.26 0.15	0.13 0.28	3.3	6.5	
						Blanching water	0.03	0.24			
						Cold water	0.01	0.02			
						Peeled & stoned peaches (canned)	< 0.01	0.01			
						Canned peaches	< 0.01 < 0.006	< 0.01 < 0.016	< 0.13	< 0.50	
						Peeled & stoned peaches (jam)	0.03	0.02			
						Peach jam	0.03 0.02	0.03 0.05	0.38	1.5	
						Stoned peaches (puree)	0.14	0.08			

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
						Wet pomace	0.19 0.11	0.17 0.28	2.4	8.5	
						Peach puree	0.17 0.09	0.23 0.32	2.1	11.5	
Valeggio, Italy 2002h (Red Haven)	2	98	0.68 (1.36)	BBCH 85 (09 Jul 01)	3	Whole peach	0.05 0.03	0.02 0.05			RD-II02123/ EA010142 IT02
						Washed peach	0.04	0.02			
						Juice	0.13 0.07	0.07 0.14	2.6	3.5	
						Canned peaches	< 0.01 < 0.006	< 0.01 < 0.016	< 0.2	< 0.5	
						Peach jam	< 0.01 < 0.006	0.03 0.036	< 0.2	1.5	
						Peach puree	0.03 0.02	0.05 0.07	0.6	2.5	
Turis,Spain 2003f (Spring Crest)	2	87	0.66-0.68 (1.33)	BBCH84-85 (24 May 02)	3	Whole peach	0.18 0.10	0.08 0.18			RD-03030/ EA020152 SP01
						Washed peach	0.19	0.12			
						Juice	0.24 0.13	0.22 0.35	1.3	2.8	
						Canned peaches	0.04 0.02	0.03 0.05	0.22	0.38	
						Peels & stones	0.84	0.39			
						Peeled & stoned peaches (jam)	0.04	0.06			
						Peach jam	0.02	0.03	0.11	0.38	
						Peach puree	0.09	0.32	0.50	4.0	

Grape (juice, raisins, wine and pomace)

Processing studies on grape were conducted as a part of residue trial study (Grolleau, G., 2002c; Report No., RD-II02143) (Grolleau, G., 2003b; Report No., RD-03042) (Boileau, G., 2014; Report No., RD-02825). In analysis of residues using the method ERV/005 (RD-II02143, RD-03042) and P 2014 G (RD-02825), procedural recoveries on the product matrices were acceptable. Product samples were stored frozen until analysis for 8–162 days.

Grape juice

Grapes were crushed and stemmed. The crushed grapes were weighed and, after addition of pectolytic enzymes, placed into glass jars. The depectinisation was performed at 45–60 °C for two hours. The content of the glass jars was pressed in a water press. The recovered juice was analysed (degree Brix, total acidity, pH) and put back in glass jars for clarification. The clarification took place for 5 minutes at 85 °C, followed by a cold storage at 5–10 °C for at least 12 hours. Thereafter, juice was filtered, pasteurised at 85 °C for 1 minute and collected in sterilised glass bottles with screw cap.

Wine

White wine processing: Grapes were pressed with a press and the must recovered in a stainless steel tank. The remaining wet pomace was dried at approximately 60 °C in an oven. The must was decanted for at least 12 hours with the addition of pectolytic enzymes at 0.02 g/L and potassium metabisulphite at 0.10–0.14 g/L, according to the health status of the harvest. After decanting, dry active yeast at 10 g/L was added to the must. The progress of alcoholic fermentation was followed

each day by measuring density, temperature and pH. Sugar was added to the must during alcoholic fermentation to increase the probable alcohol content to reach 11–11.5%. The alcoholic fermentation was considered complete when the density of the must felt below 1000. Then, 0.10 g/L potassium metabisulphite was added to the wine and bottled. The wine was racked fourteen days after completion of the alcoholic fermentation. To improve the clarification of the wine, 0.10 g/L of dry gelatin and 0.04 g/L of potassium metabisulphite were added. The wine was kept in demijohns and stored at 5–10 °C. After clarification, the wine was filtered using a stainless steel filtration unit with a 10 L capacity under pressure using nitrogen (max 3 bar) and cellulose plates. During filtration, 0.10 g/L potassium metabisulphite was added to protect wine from oxidation. After filtration, the wine was filled in glass bottles.

Red wine processing

Grapes were crushed and stemmed with an electric crusher/stemmer. The crushed grapes were recovered in a stainless steel tank. Potassium metabisulphite was added to the crushed grapes according to the health status (0.06–0.08 g/L). Dry active yeast (0.10 g/L) was added to the must. The progress of alcoholic fermentation was followed each day by measuring density, temperature and pH. Sugar was added to the must during alcoholic fermentation to increase the probable alcohol content to reach 10% (RD-03042) or 11.5% (RD-II02143). The alcoholic fermentation was considered complete when the density of the must felt below 1000. The wine was run off to the tank (free-run win) and the solid part was pressed with a water press to recover the maximum quantity of wine. The pressed wine was added to the free-run wine in demijohns. The remaining wet pomace was dried at approximately 60 °C in an oven. The malolactic fermentation (MLF) was carried out in the absence of air, at ambient temperatures with a direct inoculation of lactic bacteria (*Leuconostoc oenos*, 0.01 g/L) after pressing to accelerate this process. When the MLF was completed, 0.10 g/L potassium metabisulphite was added. Natural clarification lasted between 7 and 35 days. Thereafter, 0.10 g/L of dry gelatin and 0.04 g/L potassium metabisulphite were added to the wine to improve clarification. The wine was kept in demijohns and stored at 5–10 °C. After clarification, the wine was filtered using a stainless steel filtration unit with a 10 L capacity under pressure using nitrogen (max 3 bar). Filtration was carried out over cellulose filter plates. During filtration, 0.10 g/L potassium metabisulphite was added to protect wine from oxidation. After filtration, the wine was filled in glass bottles.

Raisins

In studies of RD-II02143 and RD-03042, before drying, grapes were stored at 5–10 °C for 3–16 days. The grapes were put on shelves with siliconised paper in an oven at 60 °C. When the drying was considered visually as complete, the grapes were stemmed manually. In a study of RD-02825, grapes were stemmed by hand. A soaking solution (50 g/L Potassium Bicarbonate) was prepared. Berries were soaked in the same amount of soaking solution for 1 minute. The soaked berries were put in an oven at 60 °C on shelves with baking paper. Drying was deemed complete, when the weight of dried grapes was lower than 65% of the initial weight.

Table 104 Residues in processing products of grape treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Merfy, France 2002c (Pinot Noir (red grape)	1	-	1.04	BBCH 81 (20 Aug 01)	35	Grapes	0.02 0.01	0.15 0.16			RD-II02143/ EA010145 FR02
						Raisins	0.01 0.006	0.46 0.47	0.50	3.1	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Montreuil Bellay, France 2002c (Cabernet, red grape)	1	-	1.175	BBCH 85 (27 Aug 01)	35	Grapes	0.02 0.01	0.09 0.10			RD-II02143/ EA010145 FR05
						Must	0.03	0.15			
						Wet pomace	0.01 0.006	0.22 0.23	0.50	2.4	
						Wine	0.03 0.02	0.06 0.07	1.5	0.67	
						Grape juice	0.02 0.01	0.07 0.08	1.0	0.78	
Saint Jean de Blaignac, France 2002c (Semillon, white grape)	1	-	1.137	BBCH 81 (08 Aug 01)	34	Grapes	0.08 0.04	0.15 0.19			RD-II02143/ EA010145 FR07
						Raisins	0.02 0.01	0.38 0.39	0.25	2.5	
Bouillé Loretz, France 2002c (Cabernet franc, red grape)	1	-	1.075	BBCH 81 (27 Aug 01)	35	Grapes	0.02 0.01	0.1 0.11			RD-II02143/ EA010145 FR10
						Must	0.05	0.19			
						Wet pomace	0.02 0.01	0.49 0.50	1.0	4.9	
						Wine (red)	0.03 0.02	0.12 0.14	1.5	1.2	
						Grape juice	0.01 0.006	0.13 0.14	0.5	1.3	
Ziano Piacentino, Italy2002c (Malvasia, white grape)	1	-	1.121	BBCH 83 (10 Aug 01)	34	Grapes	0.12 0.07	0.13 0.20			RD-II02143/ EA010145 IT01
						Must	0.02	0.19			
						Wet pomace (wine)	0.05 0.03	0.19 0.22	0.42	1.5	
						Dry pomace	< 0.01 < 0.006	0.49 0.50	< 0.08	3.8	
						Must deposit	0.31	0.25			
						Alcoholic fermentation wine	0.1	0.21			
						Sediment	0.12	0.17			
						Wine (white)	0.15 0.08	0.19 0.27	1.3	1.5	
						Wet pomace (juice)	0.03 0.02	0.11 0.13	0.25	0.85	
						Sediment (juice)	0.06	0.26			
						Grape juice (before filtration)	0.03	0.17			
						Grape juice	0.02 0.01	0.18 0.19	0.17	1.4	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Chateauneuf de Gadagne, France 2003b (Carignan, red grape)	1	-	1.103	BBCH 81 (06 Aug 02)	37	Whole bunches	0.02 0.01	0.11 0.12			RD-03042/ EA020154 FR01
						Must	0.06	0.17			
						Wet pomace (wine)	0.03 0.02	0.29 0.31	1.5	2.6	
						Dry pomace	< 0.01 < 0.006	0.79 0.80	< 0.5	7.2	
						Alcoholic fermentation wine	0.02	0.1			
						Lees	0.06	0.14			
						MLF Wine	0.05	0.12			
						Sediment	0.04	0.09			
						Wine (red)	0.04 0.02	0.11 0.13	2.0	1.0	
						Wet pomace (juice)	0.02 0.01	0.15 0.16	1.0	1.4	
						Sediment	0.04	0.15			
						Grape juice (before filtration)	0.03	0.13			
						Grape juice	< 0.01 < 0.006	0.14 0.15	< 0.5	1.3	
						Raisins	0.02 0.01	0.4 0.41	1.0	3.6	
Cernay les Reims, France 2014 (Chardonnay , white grape)	1	-	1.155	BBCH 81 (20 Aug 13)	42	Whole bunches	0.12 0.07	0.2 0.3			RD-02825/ GBU-13-16020 FR01
						Raisins	< 0.01 < 0.006	0.4 0.41	< 0.08	2.0	
						Grape juice	< 0.01 < 0.006	0.35 0.36	< 0.08	1.8	
						Wet pomace	0.021 0.012	0.11 0.12	0.18	0.55	
						Dry pomace	< 0.01 < 0.006	0.63 0.64	< 0.08	3.2	
						White wine at bottling	0.15 0.08	0.18 0.26	1.3	0.90	
Ilsfeld, Germany 2014 (Weißriesling, white grape)	1	-	1.101	BBCH 81 (27 Aug 13)	42	Whole bunches	0.075 0.042	0.19 0.23			RD-02825/ GBU-13-16020 DE02
						Raisins	0.014 0.008	0.61 0.62	0.19	3.2	
						Grape juice	< 0.01 < 0.006	0.31 0.32	< 0.13	1.6	
						Wet pomace	0.053 0.029	0.28 0.31	0.71	1.5	
						Dry pomace	0.037 0.021	1.03 1.05	0.49	5.4	
						White wine at bottling	0.055 0.031	0.46 0.49	0.73	2.4	

Tomato (juce, puree, canned, ketchup, puree and pomace)

Two processing studies were conducted (Grolleau, G., 2002j; Report No., RD-II02126) (Grolleau, G., 2002k; Report No., RD-II02127). TM (SC 500) was applied three times to tomatoes at rates of 0.82–0.89 kg ai/ha. In analysis of residues using the method ERV/005, procedural recoveries on the product matrices were acceptable. Processed samples were stored frozen until analysis for 3–26 days.

Juice

Tomatoes were crushed in the crusher, the put onto an automatic sieve to separate the juice from the peels and seeds (= pomace). The pomace was dried at approximately 60 °C in an oven. The degree Brix of the juice was measured and some cooking salt was added to the juice at a level of 7 g/kg. The juice was pasteurised at 82–85 °C for 1 minute, put in sterilised glass jars and closed with a protective lid.

Puree

Tomatoes were crushed in the crusher and reduced by heating until a degree Brix of 12–13% is reached. After reduction, the puree was put onto an automatic sieve to remove peels and seeds. Cooking salt was added at a level of 4 g/kg and the puree was put in glass jars. The glass jars were closed with a protective lid and sterilised at 115–120 °C for 10 minutes.

Canned tomatoes

Tomatoes were peeled in the following way: tomatoes were put in boiling water for one minute maximum and then plunged in cold water to crack the peel. Afterwards, the peel was removed with a knife. The portions of canned tomatoes were two thirds of peeled whole tomatoes and one third of juice (see above, with the addition of citric acid to lower the pH of 3.0–3.5). The peeled whole tomatoes and juice were put in glass jars, closed with a protective lid and sterilised at 115 °C for 10 minutes.

Ketchup

Tomatoes were crushed in the crusher and reduced by heating until a degree Brix of 14–15% is reached. After reduction, the puree was put onto an automatic sieve to remove peels and seeds. Ketchup was prepared using the following composition: 72% tomato puree, 19% brown sugar, 7% cider vinegar and 2% salt. The ketchup was put in glass jars, closed with a protective lid and sterilised at 115 °C for 10 minutes.

Table 105 Residues in processing products of tomato treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
St Remy de Provence, France 2002j (Brenda)	3	7	0.82 -0.85 (2.51)	BBCH77-83 (13 Aug 01)	3	Whole tomato	0.13 0.07	0.06 0.13			RD-II02126/ EA010147 FR04
						Washed tomato	0.05	0.05			
						Washing water	0.04	0.13			
						Wet pomace	0.22 0.12	0.09 0.21	1.7	1.5	
						Dry pomace	0.22 0.12	1.23 1.35	1.7	20.5	
						Juice	0.33 0.18	0.09 0.27	2.5	1.5	
						Waste (puree)	0.76	0.2			
						Puree	0.31 0.17	0.12 0.29	2.4	2.0	

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
						Blanching water	0.13	0.15			
						Cold water	< 0.01	< 0.01			
						Peels (skin)	0.12	0.08			
						Peeled tomatoes	< 0.01	0.02			
						Canned tomatoes	0.09 0.05	0.04 0.09	0.69	0.67	
						Crushed tomatoes	0.27	0.2			
						Waste (ketchup)	0.48	0.16			
						Ketchup	0.23 0.13	0.12 0.25	1.8	2.0	
Raldon, Italy, 2002j (Petula)	3	7	0.83-0.86 (2.55)	BBCH 76 (23 Jul 01)	3	Whole tomato	0.35 0.2	0.17 0.37			RD-II02126/ EA010147 IT01
						Washed tomato	0.15	0.07			
						Juice	0.85 0.47	0.72 1.19	2.4	4.2	
						Puree	1.6 0.9	1.4 2.3	4.6	8.2	
						Peeled tomatoes	0.02	0.03			
						Canned tomatoes	0.2 0.1	0.11 0.21	0.57	0.65	
						Ketchup	1.4 0.8	1.3 2.9	4.0	7.6	
Tarascon, France 2002k (Camery Row)	3	7	0.84-0.89 (2.60)	BBCH 87 (10 Aug 01)	3	Whole tomato	0.1 0.06	0.02 0.08			RD-II02127/ EA010148 FR02
						Washed tomato	0.07	0.01			
						Juice	0.19 0.11	0.03 0.14	1.9	1.5	
						Puree	0.18 0.1	0.15 0.25	1.8	7.5	
						Peeled tomatoes	< 0.01	< 0.01			
						Canned tomatoes	0.07 0.04	0.02 0.06	0.70	1.0	
						Ketchup	0.11 0.06	0.13 0.19	1.1	6.5	
Borgotrebbia, Italy 2002k (121)	3	6-8	0.83-0.85 (2.52)	BBCH 85 (06 Aug 01)	3	Whole tomato	0.1 0.06	0.05 0.11			RD-II02127/ EA010148 IT02
						Washed tomato	0.06	0.04			
						Juice	0.26 0.15	0.1 0.25	2.6	2.0	
						Puree	0.23 0.13	0.23 0.36	2.3	4.6	
						Peeled tomatoes	< 0.01	< 0.01			
						Canned tomatoes	0.11 0.06	0.05 0.11	1.1	1.0	
						Ketchup	0.19 0.11	0.22 0.33	1.9	4.4	

Soya bean (meal, oil and hulls)

One processing study on soya bean was conducted (Castro, L., 1998d; Report No., RD-II01045). Soya beans were treated three times with TM (SC 539) at exaggerated rates of 8.35–15.5 kg ai/ha. In

analysis of residues using the method BR-011-05, procedural recoveries on the product matrices were acceptable. Processed samples were stored frozen until analysis for 114 days.

Soybean hulls, meal and oil processing:

The whole soybean sample was dried in an oven at 54–71 °C until a moisture content of 11–15% was reached. After removing of impurities with a Kice aspirator and with a Vac-Away two screen cleaner, whole soybeans were fed into a Bauer disc mill or Ferrell Ross cracking roll to crack the hull and liberate the kernels. The kernels were heated to 71–79 °C, flaked and fed into an expander/extruder and steam injected onto the product. Exiting temperature of the material (collets) was 82–113 °C. After expansion, collets were dried in an oven for 30–40 minutes at 54–71 °C and taken to solvent extraction. The collets were extracted in hexane at 49–60 °C for 30 minutes. Hexane was drained and fresh hexane added to repeat the extraction two more times for 15 minutes. Following the final draining, warm air was forced through the spent collets to remove residual hexane from the soybean meal. The miscella (crude oil and hexane) was passed through a Precision Scientific Recovery unit to separate the crude oil and hexane. Crude oil was then heated to 73–90 °C for hexane removal. The crude oil was refined according to AOCS Method Ca 9b-52. After refining, the refined oil and soapstock were separated.

Table 106 Residues in processing products of soya bean treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Meigs, GA, 1998d (Coker 488)	3	10	8.35-15.5	Maturing (18 Oct 90)	14	Soybean seed	3.8 2.1	1.6 3.7			RD-II01045/ 03A-90
					14	Hulls	23	12			
						Meal	1.3 0.7	1 1.7	0.34	0.63	
						Oil	0.07 0.04	< 0.05 < 0.09	0.02	< 0.03	

Sugar beet (sugar, molasses and dry pulp)

One processing study on sugar beet was conducted (Carr, B.L., 1998c; Report No., RD-II02164). TM (5% granular formation) was applied once to sugar beets at a rate of 0.318 kg ai/1000 feet of sugar beet. The applications were made in furrow at the time of planting prior to furrow closure. The processing was done in July of 1997. In analysis of residues using the method BR-011-05, procedural recoveries on the product matrices were acceptable. Processed samples were stored frozen for a maximum of 78 days.

Sugar

Sugar beets were washed for 90 seconds with jets of cold water in a rotary drum beet washer and then cut into small slices (cossettes) in a pilot-scale beet slicer. The sugar in the cossettes was extracted by counter-current diffusion with hot tap water (75 °C) in a stainless steel pilot-scale diffusor. After the diffusion process, the sugar-containing extract was transferred to a stainless steel carbonation tank. The extracted cossettes (i.e. spent pulp) were collected in stainless steel pails and mixed with hot tap water for about 10 minutes to extract additional sugar. The pulp was then de-watered by passage through a pulp press. The sugar-containing press water was added to the carbonation tank and the pressed pulp taken to dryness in a fluid-bed dryer. The content in the carbonation tank was heated to 80 °C and approx. 15 kg of hot slaked lime solution (2 kg CaO + 13.3 kg hot tap water) was added, stirred for 15 minutes and sparged with carbon dioxide. When the pH of the juice had been reduced to 10, two litres of aqueous settling aid (0.025% polyacrylamide) were added and stirred for 30 seconds.

The sludge was allowed to settle overnight and separated from the thin juice by decantation. The sludge was concentrated 15–18 fold by means of a climbing-film evaporator to yield a syrupy, sugar-rich thick juice which served as feedstock for the sugar end extraction process.

The thin juice was transferred to a vacuum evaporator and water was removed under vaccum at 62.5 °C. When the juice was saturated with respect to sugar, it was seeded with 200 g sucrose. Additional water was removed over the next 6–10 hours while sugar crystals formed and deposited. Sugar crystals were harvested by centrifugation, briefly washed with hot water, then recovered and stored at -20 °C. The liquid fraction from the centrifugation step was recovered, returned to the evaporator and concentrated to the saturation point and again seeded with sucrose. Sugar crystals were harvested as described above and the process repeated a third time. The final mother liquor comprised the molasses fraction. The molasses was stored at room temperature for 24–48 hours to allow any excess sugar to crystallise, which was removed by filtration. The three sugar crystals fractions were combined and dissolved in hot tap water and crystallised under vacuum to obtain the final white refined sugar.

Table 107 Residues in processing products of sugar beet treated with TM

Location, Country, Year (Variety)	Application				DALT (days)	Portion analysed	Residues (mg/kg)		Pf		Study/ Trial
	No.	RTI (days)	Rate (kg ai/kg)	GS at last treatment			TM	MBC	TM	MBC	
Jerome, ID 1998c (MH WS88)	1	-	0.7 lbs ai/ 1000 ft	at planting prior to furrow closure (17 Apr 91)	180	Sugar beet	0.69 0.39	0.094 0.48			RD-II02164/ 22A-91
						Sugar	< 0.05 < 0.03	< 0.05 < 0.08	< 0.07	< 0.53	
						Dry pulp	< 0.05 < 0.03	0.070 0.10	< 0.07	0.74	
						Molasses	< 0.05 < 0.03	< 0.05 < 0.08	< 0.07	< 0.53	

Spring barley (beer)

Processing studies on barley were conducted as a part of residue trial (Grolleau, G., 2002e; Report No., RD-II02114). In analysis of residues using the method ERV-006, procedural recoveries on the product matrices were acceptable. Processed samples were stored frozen until analysis for 106–203 days. Concentrations of TM and MBC in graded barley were < 0.01 mg/kg and 0.04 mg/kg, respectively. Residue values of TM and MBC were < 0.01 mg/kg in beer processing products (brewing malt, malt sprouts and beer, etc.).

Peanut (oil and meal)

One processing study on peanut was conducted (Carr, B.L., 1999; Report No., RD-03607). Peanuts were treated six times with TM (SC 539)) at exaggerated rates of 3.95 to 5.58 kg ai/ha. In analysis of residues using the method BR-011-05, procedural recoveries were acceptable in the product matrices. A storage period of the processing products was a maximum of 115 days. Concentrations of TM and MBC in nutmeat were < 0.05 mg/kg and not concentrated in the oil (< 0.05 mg/kg). In peanut meal, residue values of TM and MBC were 0.064 mg/kg and 0.055 mg/kg, respectively.

Table 108 Summary of processing factors

Commodity	Processed products	TM		MBC equivalent	
		Pfs	Pf, best estimate	Pfs	Pf, best estimate
Orange	Juice	0.03(p), 0.03(p), 0.03(p), 0.03/0.04(p)	0.03		

Commodity	Processed products	TM		MBC equivalent	
		Pfs	Pf, best estimate	Pfs	Pf, best estimate
	Marmalade	0.23, 0.26, 0.72, 0.93,	0.49		
	Oil/water suspension	8.8	8.8		
	Wet pomace	1.2	1.2		
	Dry pomace	0.76, 1.1, 1.5, 1.5	1.3		
Mandarin	Canned	< 0.001	< 0.01		
Apple	Juice	0.06, < 0.17, 0.33, 0.36	0.25		
	Puree	0.06, < 0.09, 0.17, < 0.33	0.13		
	Canned	< 0.09, 0.13, < 0.17, < 0.33	0.15		
	Wet pomace	0.19, 0.44, 0.50, 0.67	0.47		
	Dry pomace	< 0.06, < 0.09, < 0.17, < 0.33	< 0.13		
Cherry	Juice				
	Jam	< 0.005, < 0.008	< 0.01		
	Canned	< 0.005, < 0.008	< 0.01		
	Wet pomace				
Plum	Prune (dried plum)	< 0.50	< 0.5		
	Juice	0.50, 0.67	0.59		
	Jam	< 0.50, 0.67	0.59		
	Puree	0.50, 1.0	0.75		
	Canned	< 0.33, < 0.50	< 0.42		
	Wet pomace	< 0.33	< 0.33		
Peach	Juice	1.3, 2.6, 3.3	2.6		
	Jam	0.11, < 0.20, 0.38	0.23		
	Puree	0.50, 0.60, 2.1	0.60		
	Canned	< 0.13, < 0.20, 0.22	0.18		
	Wet pomace	2.4	2.4		
Grape	Raisins	< 0.08, 0.19, 0.25, 0.50, 1.0	0.25		
	Juice	< 0.08, < 0.13, 0.17, < 0.50, 0.50, 1.0	0.34		
	Wine	0.73, 1.3, 1.3, 1.5, 1.5, 2.0	1.4		
	Wet pomace	0.18, 0.42(w)/0.25(j), 0.50, 0.71, 1.0, 1.5(w)/1.0(j)	0.61		
	Dry pomace	< 0.08, < 0.08, 0.49, < 0.50	0.29		
Tomato	Juice	1.9, 2.4, 2.5, 2.6	2.5		
	Ketchup	1.1, 1.8, 1.9, 4.0	1.9		
	Puree	1.8, 2.3, 2.4, 4.6	2.4		
	Canned	0.57, 0.69, 0.70, 1.1	0.70		
	Wet pomace	1.7	1.7		
	Dry pomace	1.7	1.7		
Soya bean	Oil	0.02	0.02		
	Meal	0.34	0.34		
Sugar beet	Sugar	< 0.07	< 0.07		
	Dry pulp	< 0.07	< 0.07		
	Molasses	< 0.07	< 0.07		

RESIDUES IN ANIMAL COMMODITIES

Livestock feeding studies

Lactating ruminants

Holstein cows were orally dosed with capsules containing TM of 67, 205 and 839 mg/kg feed (Castro, L. 1998a; RD-9819 and RD-02854). Three cows per dose level (2.6, 7.3 and 24.0 mg/kg bw/day) were fed daily for 28 days. The cows were sacrificed within 24 hours after the final dose and samples of edible tissues (muscle, kidney, liver and fat) were taken. Composite milk samples were collected on 1, 3, 7, 10, 14, 17, 21, 24 and 28 days. Samples were frozen, homogenised and shipped on dry ice

shortly to an analytical laboratory. Extraction was done with chilled solvent. Analysed compounds were MBC and 5-OH-MBC-S in milk, TM and MBC in muscle, MBC in fat, MBC and 5-OH-MBC in liver and MBC, 4-OH-MBC and 5-OH-MBC-S in kidney. The method used was described under residue analysis section. Procedural recoveries on whole milk, muscle and liver matrices were acceptable. The samples were stored frozen until analysis for a maximum of 249 days for whole milk and 224 days for tissues.

The residues were detected, as TM equivalent, at < 0.05-0.95 mg eq/kg in muscle, < 0.05–0.42 mg eq/kg in fat, 0.20–2.7 mg eq/kg in liver, 0.38–4.6 mg eq/kg in kidney and 0.23–2.4 mg eq/kg in whole milk. The plateau in milk was approximately after 14–17 days of dosing. Residue concentration level in cream was 1.4–2.1 times higher than that in skim milk.

Table 109 Maximum residues in lactating cows fed with TM

Dose (ppm)	Maximum residues (mg eq/kg as TM)						
	Liver	Muscle	Fat	Kidney	Whole milk	Skim milk	Cream
Control	0.06	nd	nd	0.01	0.02	nd	nd
67.1	0.20	< 0.05	< 0.05	0.38	0.23	0.08	0.17
205	0.39	0.12	0.13	0.78	0.44	0.47	0.70
839	2.7	0.95	0.42	4.6	2.4	2.5	3.4

nd: not detected

Table 110 Residues in whole milk from cows fed with TM (average of three cows)

Day	67.1 ppm (1 x)			205 ppm (3 x)			839 ppm (10 x)		
	MBC (mg/kg)	5-OH-MBC-S (mg/kg)	Total TM eq. (mg/kg)	MBC (mg/kg)	5-OH-MBC-S (mg/kg)	Total TM eq. (mg/kg)	MBC (mg/kg)	5-OH-MBC-S (mg/kg)	Total TM eq. (mg/kg)
1	< 0.05	< 0.05	< 0.05	0.09	0.11	0.28	0.34	0.44	1.10
3	0.06	0.06	0.12	0.07	0.14	0.29	0.37	0.63	1.37
7	< 0.05	< 0.05	< 0.05	0.09	0.14	0.32	0.43	0.71	1.57
10	na	na	na	na	na	na	0.43	0.80	1.67
14	0.06	0.06	0.12	0.11	0.16	0.37	0.56	0.88	1.97
17	na	na	na	na	na	na	0.57	0.98	2.10
21	< 0.05	0.07	0.08	0.10	0.17	0.37	0.51	0.88	1.90
24	na	na	na	na	na	na	0.55	1.01	2.10
28	0.05	0.07	0.11	0.10	0.18	0.38	0.46	0.97	1.90
Mean	0.05	0.060	0.088	0.093	0.15	0.34	0.47	0.81	1.74

na, not analysed

Table 111 Residues in selected samples of skim milk and cream from cows fed with TM

Samples			Residues in cream (mg/kg)			Residues in skim milk (mg/kg)		
Dose	Cow #	Time point	MBC	5-OH-MBC-S	Total TM eq.	MBC	5-OH-MBC-S	Total TM eq.
67.1 ppm (1×)	178	14	0.07	< 0.05	0.13	< 0.05	0.06	0.07
		28	0.10	< 0.05	0.17	< 0.05	0.07	0.06
205 ppm (3×)	14	28	0.20	0.11	0.48	0.12	0.20	0.44
	945	14	0.31	0.13	0.70	0.15	0.18	0.47
839 ppm (10×)	98	17	1.4	0.38	2.9	0.49	1.1	2.1
		24	1.5	0.62	3.4	0.52	1.3	2.6
	971	21	0.96	0.38	2.1	0.49	0.91	1.9
		28	0.70	0.79	2.1	0.46	0.99	1.9
	253	14	1.6	0.41	3.3	0.81	0.93	2.5
		28	1.3	0.41	2.8	0.58	0.83	2.0

Table 112 Residues in cows fed with TM (average of three cows)

Dose (ppm)	Compound	Muscle (mg/kg)	Fat (mg/kg)	Liver (mg/kg)	Kidney (mg/kg)
67.1 (1×)	TM	< 0.05	na	na	na
	MBC	< 0.05	< 0.05	0.07	0.06
	4-OH-MBC	na	na	na	< 0.05
	5-OH-MBC	na	na	< 0.05	na
	5-OH-MBC-S	na	na	NA	0.17
	Total TM eq.	< 0.05	< 0.05	0.12	0.28
205 (3×)	TM	0.08	na	na	na
	MBC	< 0.05	0.06	0.15	0.16
	4-OH-MBC	na	na	na	< 0.05
	5-OH-MBC	na	na	< 0.05	na
	5-OH-MBC-S	na	na	na	0.30
	Total TM eq.	0.08	0.09	0.27	0.61
839 (10×)	TM	0.64	na	na	na
	MBC	0.09	0.23	1.21	0.92
	4-OH-MBC	na	na	na	0.06
	5-OH-MBC	na	na	< 0.05	na
	5-OH-MBC-S	na	na	na	2.00
	Total TM eq.	0.81	0.40	2.17	3.93

na, not analysed

The mean residue value of MBC in whole milk was 0.05, 0.093 and 0.47 mg/kg at low, medium and high dose level, respectively. The mean residue value of 5-OH-MBC in whole milk was 0.06, 0.15 and 0.81 mg/kg at each dose level. Residue concentration levels of MBC in cream were higher than in skim milk and 5-OH-MBC-S levels were lower in cream.

In muscle, TM, at low, medium and high dose level, was detected at < 0.05, 0.08 and 0.64 mg/kg, respectively. MBC was detected at < 0.05, < 0.05 and 0.69 mg/kg at each dose level, respectively.

In fat, residue value of MBC was < 0.05, 0.06 and 0.23 mg/kg at each dose level, respectively.

In liver, MBC was detected at 0.07, 0.15 and 1.2 mg/kg at each dose level, respectively. 5-OH-MBC was not detected in all dose levels.

In kidney, MBC was detected at 0.06, 0.16 and 0.92 mg/kg at each dose level, respectively. For 4-OH-MBC, value of above LOQ (0.05 mg/kg) was shown only in high dose level. 5-OH-MBC-S was detected at 0.17, 0.30, 2.0 mg/kg at each dose level, respectively.

Laying hens

Laying hens were orally dosed with capsules containing TM at 0.40, 1.3 and 4.3 mg/kg feed (Castro, L., 1998b; Report No., RD-9820 and RD03269). Four hens per dose level (0.033, 0.11, 0.36 mg/kg bw) were fed daily at for 28 days. The hens were sacrificed within 24 hours after the final dose and samples of edible tissues were taken. Samples were frozen and shipped on dry ice to an analytical laboratory. For analysis of residues, frozen samples were homogenised with dry ice. Extraction was done with chilled or non-chilled solvent. Analysed compounds were TM, MBC and 5-OH-MBC in egg, MBC and 5-OH-MBC in muscle, MBC in fat and TM and 5-OH-MBC in liver. The method used was described under residue analysis section. Procedural recoveries on hen matrices were acceptable. The samples were stored frozen until analysis for a maximum of 288 days for egg and 261 days for tissues.

No residues were detected in any tissue form the treated hens (< 0.05 mg/kg).

APPRAISAL

The meeting did not receive any information on the toxicology of carbendazim. The meeting was unable to complete its evaluation for residues.

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RD-02755	Boissinot, J.-C.	2013	Magnitude of the Residue of Thiophanate-methyl (including its metabolite Carbendazim) in Hard Wheat Raw Agricultural Commodity after a foliar application Northern and Southern Europe – 2013 Report No.: RD-02755 JCB-13-15494 (634-4011) STAPHYT, France GLP, unpublished
RD-02804	Walther, D.	2014	[^{14}C]Thiophanate methyl: Plant Metabolism in Grapes Report No.: RD-02804 D33520 (611-006) Harlan Laboratories Ltd. (former RCC Ltd.), Switzerland GLP, unpublished
RD-02825	Boileau, G.	2014	Magnitude of the Residue of Thiophanate-methyl and its metabolite Carbendazim in Grapevine Raw Agricultural Commodity and processed fractions following one foliar Application of Thiophanate-Methyl 500 SC – Northern Europe – 2013 Report No.: RD-02825 GBU-13-16020 P 2885 G (638-009) Staphyt, France GLP, unpublished
RD-02837	Pointer, C.	2014	Thiophanate-methyl: Explosive Properties and Oxidising Properties Report No.: RD-02837 LGG0100 (141-002) Huntingdon Life Sciences, Eye Research Centre, United Kingdom GLP, unpublished
RD-02947	Class, T. and Senciuc, M.	2014	Stability of Thiophanate-methyl and Carbendazim in/on Intact Strawberries Stored Frozen Report No.: RD-02947 P 2878 G (645-012) PTRL Europe, Germany GLP, unpublished
RD-02969	Senciuc, M.	2014a	Thiophanate-methyl and Carbendazim: Validation of an Enforcement Method for Foodstuffs of Animal Origin (Liver or Kidney and Fat) Report No.: RD-02969 P 3130 G (433-011) PTRL Europe, Germany GLP, unpublished
RD-02975	Wilson, A.	2014	Field rotational crop study (spring cereal, spinach and carrots) with an SC formulation containing 500 g/L Thiophanate-methyl applied to bare soil at 365, 120, 70 and 30 days prior to planting the rotational crops in UK and Spain, 2011/2012 Report No.: RD-02975 ACI11-013 (637-002) AgroChemex International Ltd, United Kingdom GLP, unpublished

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RD-02981	Senciuc, M.	2014b	5-Hydroxy-Carbendazim: Validation of an Enforcement Method for Foodstuffs of Animal Origin Report No.: RD-02981 P 3131 G (433-012) PTRL Europe, Germany GLP, unpublished
RD-02985	Adam, D.	2014	^{14}C-Thiophanate-methyl – Route and Rate of Degradation in One Soil under Aerobic Conditions Report No.: RD-02985 20110080 (722-001) Innovative Environmental Services (IES) Ltd., Switzerland GLP, unpublished
RD-02996	Adam, D.	2014	^{14}C-Thiophanate-methyl – Photodegradation on Soil Surface Innovative Environmental Services (IES) Ltd., Switzerland GLP, unpublished
RD-03006	Grolleau, G.	2003c	Magnitude of the residue of Thiophanate-methyl in winter barley raw agricultural commodity – Southern Europe – 2002 Report No.: RD-03006 EA020160 (634-4303) European Agricultural Services, France GLP, unpublished
RD-03007	Grolleau, G.	2003d	Magnitude of the residue of Thiophanate-methyl in winter wheat raw agricultural commodity –Northern and Southern Europe – 2002 Report No.: RD-03007 EA020161 (634-4006) European Agricultural Services, France GLP, unpublished
RD-03008	Grolleau, G.	2003a	Magnitude of the residue of Thiophanate-methyl in plum raw Agricultural Commodity – Spain – 2002 Report No.: RD-03008 EA020153 (632-3303) European Agricultural Services, France GLP, unpublished
RD-03029	Grolleau, G.	2003e	Magnitude of the Residue of Thiophanate-methyl in Apple Raw Agricultural Commodity and Processed Fractions – Northern Europe – 2002 Report No.: RD-03029 EA020150 (632-2004) European Agricultural Services, France GLP, unpublished
RD-03030	Grolleau, G.	2003f	Magnitude of the Residue of Thiophanate-methyl in Peach Raw Agricultural Commodity and Processed Fractions – Southern Europe – 2002 Report No.: RD-03030 EA020152 (632-3203) European Agricultural Services, France GLP, unpublished
RD-03034	Wright, M.C.	1996	Residue Stability Study of MBC (Methyl-2-Benzimidazole Carbamate) in Snap Beans, Apples, Wheat Grain, Spinach, Sugar Beet Roots, and Tomatoes Report No.: RD-03034 BR-87-6 80502 (formerly 88023) (645-008) Elf Atochem North America, USA GLP, unpublished

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RD-03042	Grolleau, G.	2003b	Magnitude of the residue of Thiophanate-methyl in wine grapes raw agricultural commodity and processed fractions – Southern Europe – 2002 Report No.: EA020154 ERV/043 RD-03042 (632-4004) European Agricultural Services, France GLP, unpublished
RD-03110	Ampofo, S.A.	2002	Stability of Thiophanate-Methyl in Cucumbers During Frozen Storage Pending Analysis Report No.: RD-03110 43512 KP-96-10 BR-011-05 (645-009) ABC Laboratories, USA GLP, unpublished
RD-03167	Fenn, L.	2003	Stability of Thiophanate Methyl in Snap Beans During Frozen Storage Pending Analysis Report No.: RD-03167 KP-96-11 (645-010) Exygen Research, USA GLP, unpublished
RD-03185	Shiotani, H.	2003	Photodegradation of Thiophanate-methyl Report No.: RD-03185 EC-74-1 (712-002) Nippon Soda Co. Ltd., Japan Not GLP, unpublished
RD-03273	Schernikau, N.	2015	Thiophanate-methyl and Carbendazim: Independent Laboratory Validation of an Enforcement Method for Foodstuffs of Animal Origin Report No.: RD-03273 S14-04472 (433-013) Eurofins Agroscience Services Chem GmbH, Germany GLP, unpublished
RD-03316	Witte, A.	2015	Independent Laboratory Validation of an Analytical Method for the Determination of Residues of 5-Hydroxy-Carbendazim in Food Stuff of Animal Origin Report No.: RD-03316 15N07153-01-VMAT (433-014) CIP Chemisches Institut Pforzheim GmbH, Germany GLP, unpublished
RD-03350	Weber, H.	2009	Independent Laboratory Validation of an Analytical Method for the Determination of Residues of Thiophanate-methyl and Carbendazim in Plant Material Report No.: RD-03350 NIP-0901V (432-024) Eurofins Analytik GmbH, Germany GLP, unpublished
RD-03544	Churchill, G.M. and Carey Jr., D.O.	1997	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Strawberry Report No.: RD-03544 BR-91-19 (632-4104) Elf Atochem North America, USA GLP, unpublished

Report No.	Author(s)	Year	Title, Report No. (Doc. No.), Source (where different from company) GLP or GEP status, Published or not
RD-03546	Pitt, J.L.	1995a	Thiophanate Methyl and its Metabolites: Magnitude of the Residue in Pears Report No.: RD-03546 BR-92-17 (632-2103) Elf Atochem North America, USA GLP, unpublished
RD-03547	Wright M.C.	1995	Thiophanate Methyl and its Metabolites: Magnitude of the Residue in Pears – Addendum 1 Report No.: RD-03547 BR-92-17 (632-2104) Elf Atochem North America, USA GLP, unpublished
RD-03607	Carr, B.L.	1999	Thiophanate Methyl and Its Metabolites: Magnitude of the Residue in Peanut Processed Fractions Report No.: RD-03607 BR-91-21 (638-011) Elf Atochem North America, USA GLP, unpublished
RD-73073	Noguchi, T.	1970	Studies on the biotransformation of Thiophanate-methyl in animal and plant (Part I) Report No.: RD-73073 (512-006) Nisso chemical Analysis Service Co., Ltd. Not GLP, unpublished
RD-73074	Noguchi, T. and Kosaka, S.	1971	Studies on the biotransformation of Thiophanate-methyl in animal, plant and soil (Part II) Report No.: RD-73074 (512-007) Nisso chemical Analysis Service Co., Ltd. Not GLP, unpublished
RD-73075	Noguchi, T. and Kosaka, S.	1971	Studies on the biotransformation of Thiophanate-methyl in animal and plant (Part III) Report No.: RD-73075 (512-008) Nisso chemical Analysis Service Co., Ltd. Not GLP, unpublished
RD-8194N	Anonymous	1981	Fate of Thiophanate-methyl in soil Report No.: RD-8194N (721-001) Nippon Soda Co. Ltd., Japan Not GLP, unpublished
RD-8498N	Anonymous	1984	Biodegradation of Thiophanate-methyl in soil Report No.: RD-8498N (721-002) Nippon Soda Co. Ltd., Japan Not GLP, unpublished
RD-8659	Soeda, Y. and Shiotani, H.	1986a	Thiophanate-methyl – Solubility in water Report No.: RD-8659 EC-62 (114-007) Nippon Soda, Japan GLP, unpublished
RD-8660	Soeda, Y. and Shiotani, H.	1986b	Thiophanate-methyl – Octanol/ water partition coefficient Report No.: RD-8660 EC-63 (114-006) Nippon Soda, Japan GLP, unpublished

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RD-8679	Soeda, Y. and Nomura, O.	1986	Thiophanate-methyl – Hydrolysis Report No.: EC-67 RD-8679 (711-001) Nippon Soda Co. Ltd., Japan Not GLP, unpublished
RD-8701	Soeda, Y. and Shiotani, H.	1987	Thiophanate-methyl – Photodegradation in water Report No.: EC-74 RD-8701 (712-001) Nippon Soda Co. Ltd., Japan Not GLP, unpublished
RD-8775	Nomura, O. and Nakashima, N.	1987	Thiophanate-methyl – Water solubility Report No.: RD-8775 EC-107 (114-004) Nippon Soda, Japan GLP, unpublished
RD-8969	Anonymous	1977b	Metabolism of ^{14}C-Thiophanate-methyl in/on green bean plants Report No.: RD-8969 (611-001) Nippon Soda Co., Ltd., Gohsei Gohensol Not GLP, unpublished
RD-8970	Anonymous	1977a	Metabolism of ^{14}C-Thiophanate-methyl in/on soybean plants Report No.: RD-8970 (611-002) Nippon Soda Co., Ltd., Gohsei Gohensol Not GLP, unpublished
RD-9014	Ishihara, K.	1990a	Thiophanate-methyl – Solubility in Organic Solvents Report No.: RD-9014 EC-223 (114-001) Nippon Soda, Japan GLP, unpublished
RD-9016 RD-9857	Ishihara, K.	1990b	Thiophanate-methyl – Dissociation constant Report No.: RD-9016 RD-9857 EC-225 (115-003) Nippon Soda, Japan Not GLP, unpublished
RD-9023	Nakayama, K.	1990b	Thiophanate-methyl – Color Report No.: RD-9023 TR-896302 (111-002) Nippon Soda, Japan GLP, unpublished
RD-9024	Nakayama, K.	1990a	Thiophanate-methyl – Physical state Report No.: RD-9024 TR-896303 (111-001) Nippon Soda, Japan GLP, unpublished
RD-9025	Nakayama, K.	1990c	Thiophanate-methyl – Odor Report No.: RD-9025 TR-896304 (111-003) Nippon Soda, Japan GLP, unpublished
RD-9212	Shiotani, H.	1992	Thiophanate-methyl, pure - Octanol/ water partition coefficient Report No.: RD-9212 EC-374 (114-005) Nippon Soda, Japan GLP, unpublished

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RD-9213	Nakayama, K.	1992c	Thiophanate-methyl, pure – Color Report No.: RD-9213 TR-2B9203 (111-004) Nippon Soda, Japan GLP, unpublished
RD-9214	Nakayama, K.	1992e	Thiophanate-methyl, pure – Physical state Report No.: RD-9214 TR-2B9205 (111-006) Nippon Soda, Japan GLP, unpublished
RD-9215	Nakayama, K.	1992d	Thiophanate-methyl, pure – Odor Report No.: RD-9215 TR-2B9204 (111-005) Nippon Soda, Japan GLP, unpublished
RD-9216	Nakayama, K.	1992a	Thiophanate-methyl, pure – Melting point Report No.: RD-9216 TR-2B9207 (112-001) Nippon Soda, Japan GLP, unpublished
RD-9217	Nakayama, K.	1992b	Thiophanate-methyl, pure – Specific gravity Report No.: RD-9217 TR-2B9206 (113-001) GLP, unpublished
RD-9219	Nakayama, K.	1992f	Thiophanate-methyl, pure – Solubility Report No.: RD-9219 TR-2B9209 (114-003) Nippon Soda, Japan GLP, unpublished
RD-9516	Wright, M.C.	1992	[^{14}C]-Thiophanate-methyl nature of the residue in laying hens Report No.: BR-90-15 RD-9516 (612-003) ABC Laboratories, USA GLP, unpublished
RD-9517 RD-9518	Hanlon, C.M. and Norris, K.J.	1992	Metabolism of the fungicide ^{14}C-Thiophanate-methyl in lactating goats (including Addendum 1) Report No.: BR-90-16 RD-9517 RD-9518 (612-002) Analytical Development Corporation, USA GLP, unpublished
RD-9519	Eldeib, D. *et al.*	1995	Isolation, characterization and identification of unknown metabolite(s) for goat liver treated with ^{14}C-Thiophanate-methyl Report No.: BR-93-34; 40875; 40875A; 40875B RD-9519 (612-001) ABC Laboratories, USA GLP, unpublished
RD-9629	Gomyo, T.	1996a	Thiophanate-methyl – Solubility in water Report No.: RD-9629 NCAS 95-168; EC-784 (114-002) Nisso Chemical Analysis Service Co., Ltd., Japan GLP, unpublished

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RD-9630	Gomyo, T.	1996b	Thiophanate-methyl – Partition coefficient Report No.: RD-9630 NCAS 95-167; EC-782 (114-008) Nisso Chemical Analysis Service Co., Ltd., Japan GLP, unpublished
RD-9657	Krips, H.J.	1996a	Determination of the flammability of Thiophanate-methyl Report No.: RD-9657 168323 (142-001) NOTOX B.V., The Netherlands GLP, unpublished
RD-9658	Krips, H.J.	1996b	Determination of the relative self-ignition temperature of Thiophanate-methyl Report No.: RD-9658 168334 (142-002) NOTOX B.V., The Netherlands GLP, unpublished
RD-9819 RD-02854	Castro, L.	1998a	Magnitude of the residue of Thiophanate-methyl in milk and tissue of lactating dairy cattle (including Addendum No. 1) Report No.: RD-9819 KP-96-04 43285 EPA MRID 44232401 RD-02854 – Addendum No. 1 (631-003) Elf Atochem North America, USA GLP, unpublished
RD-9820 RD-03269	Castro, L.	1998b	Residues of Thiophanate-methyl and its major metabolites in the eggs and tissue of laying hens following daily oral dosing with Thiophanate-methyl (including Addendum No. 1) Report No.: RD-9820 KP-96-05 RD-03269 – Addendum No. 1 MRID: 44287501 (631-004) Elf Atochem North America, USA GLP, unpublished
RD-99123 RD-99124	Malik, N.S.A. and Wright, M.C.	1993	[^{14}C]-Thiophanate-methyl nature of the residues in rotational crops (including the Addendum Report) Report No.: BR-90-14 RD-99123 RD-99124 (637-001) Elf Atochem North America, USA GLP, unpublished
RD-99126	Pitt, J.L.	1995b	Thiophanate-methyl and its metabolites: Magnitude of the residue in processed apple fractions Report No.: RD-99126 BR-90-05 (638-005) Elf Atochem North America, USA GLP, unpublished
RD-II00076	Lucas, L.T.	2000	Thiophanate-methyl – Frozen storage stability of residues in/on whole apples Report No.: BR-95-09 RD-II00076 (645-001) ABC Laboratories, Columbia, USA GLP, unpublished

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RD-II01023	Brewin, S.	2001b	Thiophanate-methyl and Carbendazim – Development and validation of methodology for the determination of residues in winter wheat (whole plant, grain and straw) Report No.: ERV 006/004489 RD-II01023 (432-008) Huntingdon Life Sciences GLP, unpublished
RD-II01024	Brewin, S.	2001a	Thiophanate-methyl and Carbendazim – Development and validation of methodology for the determination of residues in melon whole fruit and flesh Report No.: ERV 005/004237 RD-II01024 (432-009) Huntingdon Life Sciences GLP, unpublished
RD-II01025	Brewin, S.	2001c	Thiophanate-methyl and Carbendazim – Development and validation of methodology for the determination of residues in oilseed rape (whole plant, whole pod and seed) Report No.: ERV 007/004490 RD-II01025 (432-010) Huntingdon Life Sciences GLP, unpublished
RD-II01045	Castro, L.	1998d	Thiophanate Methyl and Its Metabolites: Magnitude of the Residue in Soybean Processed Commodities Report No.: RD-II01045 BR-90-07 (638-012) Elf Atochem North America, USA GLP, unpublished
RD-II01193	Grolleau, G.	2001d	Magnitude of the residue of Thiophanate-methyl in winter wheat raw agricultural commodity – Northern and Southern France – 2000 Report No.: EA000158 RD-II 01193 (634-4003) European Agricultural Services, France GLP, unpublished
RD-II01194	Grolleau, G.	2001c	Magnitude of the residue of Thiophanate-methyl in winter barley raw agricultural commodity– Northern and Southern France – 2000 Report No.: RD-II01194 EA000159 (634-4302) European Agricultural Services, France GLP, unpublished
RD-II01196	Grolleau, G.	2001b	Magnitude of the residue of Thiophanate-methyl in grapevines raw agricultural commodity – Northern and Southern France – 2000 Report No.: EA000160 RD-II01196 (632-4002) European Agricultural Services, France GLP, unpublished
RD-II01199	Grolleau, G.	2001a	Magnitude of the residue of Thiophanate-methyl in plum raw agricultural commodity – Northern and Southern France – 2000 Report No.: RD-II01199 EA000152 (632-3301) European Agricultural Services, France GLP, unpublished

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RD-II01202	Grolleau, G.	2001e	Magnitude of the residue of Thiophanate-methyl in cherry raw agricultural commodity and processed fractions – Northern and Southern France – 2000 Report No.: RD-II01202 EA000150 (632-3102) European Agricultural Services, France GLP, unpublished
RD-II01204	Grolleau, G.	2001b	Magnitude of the residue of Thiophanate-methyl in protected melon raw agricultural commodity – Southern France – 2000 Report No.: RD-II01204 EA000156 (633-2501) European Agricultural Services, France GLP, unpublished
RD-II01230	Malik, N.S.A. and Wright, M.C.	1992b	[^{14}C]-Thiophanate-methyl nature of the residue in spray treated lima beans Report No.: BR-90-19 RD-II01230 (611-003) Pan-Agricultural Laboratories GLP, unpublished
RD-II01231	Davis, M.L. *et al.*	1992	Metabolism of the fungicide Thiophanate-Methyl in spray-treated spring wheat Report No.: SC900053 RD-II01231 (611-004) Battelle Columbus Operations, OH GLP, unpublished
RD-II01232	Malik, N.S.A. and Wright, M.C.	1992a	[^{14}C]-Thiophanate-methyl nature of the residue in spray treated sugar beets Report No.: BR-90-18 RD-II01232 (633-0001) Pan-Agricultural Laboratories GLP, unpublished
RD-II01233	Alam, F. *et al.*	1994	Nature of the residues of ^{14}C-Thiophanate-Methyl in spray treated apples Report No.: 93292 RD-II01233 (632-2003) Pan-Agricultural Laboratories GLP, unpublished
RD-II02089	Carr, B.L.	1998a	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Sugar Beet from the application of TOPSIN® M Report No.: RD-II02089 KP-97-05 (633-0003) Elf Atochem North America, USA GLP, unpublished
RD-II02090	Leppert, B.C. and Churchill, G.M.	1996a	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Snap Bean Report No.: RD-II02090 BR-90-41 (633-5104) Elf Atochem North America, USA GLP, unpublished
RD-II02091	Castro, L.	1998c	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Soybean Report No.: RD-II02091 BR-90-42 (633-5105) Elf Atochem North America, USA GLP, unpublished

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RD-II02092	Carr, B.L.	1997	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Summer Squash Report No.: RD-II02092 BR-91-31 (633-2506) Elf Atochem North America, USA GLP, unpublished
RD-II02093	Leppert, B.C. and Castro, L.	1996a	Thiophanate Methyl and its Metabolites: Magnitude of the Residue in Cherry Report No.: RD-II02093 BR-91-27 (632-3106) Elf Atochem North America, USA GLP, unpublished
RD-II02094	Bradway, D.E. and Carr, B.L.	1998	Thiophanate-methyl and its Metabolites: Magnitude of the Residue in Peanut Report No.: RD-II02094 BR-91-14 (634-0101) Elf Atochem North America, USA GLP, unpublished
RD-II02123	Grolleau, G.	2002h	Magnitude of the residue of Thiophanate-methyl in peach raw agricultural commodity and processed fractions – Southern Europe – 2001 Report No.: RD-II02123 EA010142 (632-3202) European Agricultural Services, France GLP, unpublished
RD-II02124	Grolleau, G.	2002a	Magnitude of the Thiophanate-methyl in plum raw agricultural commodity and processed fractions – Northern and Southern Europe – 2001 Report No.: RD-II02124 EA010143 (632-3302) European Agricultural Services, France GLP, unpublished
RD-II02125	Grolleau, G.	2002i	Magnitude of Thiophanate-methyl in cherry raw agricultural commodity and processed fractions – Northern and Southern Europe – 2001 Report No.: RD-II02125 EA010144 (632-3104) European Agricultural Services, France GLP, unpublished
RD-II02126	Grolleau, G.	2002j	Magnitude of the residue of Thiophanate-methyl in protected tomato raw agricultural commodity and processed fractions – Northern and Southern Europe – 2001 Report No.: RD-II02126 EA010147 (633-2003) European Agricultural Services, France GLP, unpublished
RD-II02127	Grolleau, G.	2002k	Magnitude of the residue of Thiophanate-methyl in open field tomato raw agricultural commodity and processed fractions – Northern Europe – 2002 Report No.: RD-II02127 EA010148 (633-2004) European Agricultural Services, France GLP, unpublished
RD-II02128	Grolleau, G.	2002b	Magnitude of the residue of Thiophanate-methyl in protected melon raw agricultural commodity – Southern Europe – 2001 Report No.: RD-II02128 EA010149 (633-2503) European Agricultural Services, France GLP, unpublished

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RD-II02129	Grolleau, G.	2002d	Magnitude of the residue of Thiophanate-methyl in open field melon raw agricultural commodity – Southern Europe – 2001 Report No.: RD-II02129 EA010150 (633-2502) European Agricultural Services, France GLP, unpublished
RD-II02132	Grolleau, G.	2002f	Magnitude of the residue of Thiophanate-methyl in winter wheat raw agricultural commodity – Northern and Southern Europe – 2001 Report No.: EA010157 RD-II02132 (634-4005) European Agricultural Services, France GLP, unpublished
RD-II02134	van der Gaauw, A.	2002	[^{14}C]-Thiophanate-methyl: Simulated processing Report No.: RD-II02134 839621 (638-006) Research and Consulting Company, Switzerland GLP, unpublished
RD-II02140	Grolleau, G.	2002g	Magnitude of the residue of Thiophanate-methyl in apple raw agricultural commodity and processed fractions – Northern and Southern Europe – 2001 Report No.: RD-II02140 EA010140 (632-2005) European Agricultural Services, France GLP, unpublished
RD-II02143	Grolleau, G.	2002c	Magnitude of the residue of Thiophanate-methyl in wine and table grapes raw agricultural commodity and processed fractions – Northern and Southern Europe – 2001 Report No.: EA010145 RD-II02143 (632-4003) European Agricultural Services, France GLP, unpublished
RD-II02144	Grolleau, G.	2002e	Magnitude of the residue of Thiophanate-methyl in spring and winter barley raw agricultural commodity and processed fractions – Northern and Southern Europe – 2001 Report No.: RD-II02144 EA010156 (634-4304) European Agricultural Services, France GLP, unpublished
RD-II02149	Völkl, S.	2002	[^{14}C]-Thiophanate-methyl – Degradation and metabolism in three soils incubated under aerobic conditions Report No.: 815051 RD-II02149 (721-004) Research and Consulting Company, Switzerland GLP, unpublished
RD-II02162	Bennett, R. and Castro, L.	1998b	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Watermelon Report No.: RD-II02162 BR-91-29 (633-2507) Elf Atochem North America, USA GLP, unpublished
RD-II02164	Carr, B.L.	1998c	Thiophanate Methyl and Its Metabolites: Magnitude of the Residue in Sugar Beet Processed Fractions Report No.: RD-II02164 BR-91-24 (638-013) Elf Atochem North America, USA GLP, unpublished

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RD-II02166	Leppert, B.C. and Churchill, G.M.	1996b	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Dry Bean Report No.: RD-II02166 BR-90-39 (633-8003) Elf Atochem North America, USA GLP, unpublished
RD-II02171	Bennett, R. and Castro, L.	1998a	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Cucumber Report No.: RD-II02171 BR-91-30 (633-2303) Elf Atochem North America, USA GLP, unpublished
RD-II02173	Carr, B.L.	1998b	Thiophanate-Methyl and its Metabolites: Magnitude of Residue in Pecans Report No.: RD-II02173 BR-91-16 (632-1101) Elf Atochem North America, USA GLP, unpublished
RD-II02426	Brewin, S.	2002	Thiophanate-methyl and Carbendazim – The determination of Storage Stability in Rape Seed, Dry Peas, Grapes and Wheat Grain over a 12 Month Period Stored at approximately -18 °C Report No.: NOD 181/023745 NOD/181 RD-II02426 (645-003) Huntingdon Life Sciences GLP, unpublished
RD-IIM001	Higashida, S. and Kobayashi, H.	1999	Thiophanate-methyl – Vapor pressure Report No.: RD-IIM001 NCAS 99-145 (115-005) Nisso Chemical Analysis Service Co., Ltd., Japan GLP, unpublished