European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

EU Proficiency Test on the Analysis of Incurred and Spiked Pesticides Requiring Single Residue Methods in Maize Flour

EUPT–SRM10

May/June 2015

Final Report

Chemisches und
Veterinäruntersuchungsamt
Stuttgart

cvua STUTTGART

EURL-SRM, CVUA Stuttgart, Schaflandstr. 3/2, 70736 Fellbach, Germany

Fellbach, 08/08/2016

Additional Information on EUPT-SRM10:
Purity of standards of „N-acetyl glufosinate“ provided by LGC (= Dr. Ehrenstorfer) and Toronto Research Chemicals Inc.

Dear participants on the EUPT-SRM10,

As mentioned in the Final Report of EUPT-SRM10 (Section 4.3. p. 29) there was a very strong deviation between the assigned value of N-acetyl glufosinate (NAG) (0.319 mg/kg) and the mean values of the stability and homogeneity tests (0.186 mg/kg). The distribution of the participants' results was quite narrow (CV*=11.8%). It was therefore decided to ask all participants reporting numerical results for NAG to report the source, the Lot-number and its declared purity of the NAG standards used for quantification. Out of 13 participants replying to the survey 11 purchased their standard from LGC (= Dr. Ehrenstorfer) and the other two laboratories from Toronto Research Chemicals Inc. (TRC). The standard used by the organizers for spiking the PT-material and for the tests on homogeneity and stability was kindly provided by Bayer CropScience. All standards (LGC, TRC and Bayer) had a stated purity of approximately 98% indicated on the certificates.

The standard materials used by the participants (LGC: Art. No. C14031500, Lot: 40429 and Art. No. DRE-L14031500ME, Lot: 50429ME ; TRC: Art. No. A178235, Lot: 3-PKB-63-3) were purchased and tested against the standard by Bayer using LC-MS/MS, LC-ToF and NMR. Based on these tests it was concluded that the purity indicated by both commercial standard providers is much lower than indicated. Assuming that the purity of the standard from Bayer is correct, the purity of the commercial standards from LGC and TRC was estimated in the range between 51 and 60%. The suppliers of the standards were thus contacted and asked to provide explanations. LGC confirmed on 08.08.2016 our findings. According to LGC the standard of „N-acetyl glufosinate“(C14031500) Lot: 40429 and the standard solution prepared therefrom (DRE-L14031500ME) contained byproducts in the range of at least 40-45%. LGC has already taken extensive QM relevant measures, this includes the intention of informing the customers and improving the quality control procedures. A response from Toronto Research Chemicals Inc. is still pending.

We herewith kindly ask you to take any QM-relevant measures in your laboratory concerning the standards of „N-acetyl glufosinate“ provided by LGC (= Dr. Ehrenstorfer) and Toronto Research Chemicals Inc.

Best regards,
Your EURL-SRM Team

EU PROFICIENCY TEST
EUPT-SRM10, 2015

Residues of Pesticides Requiring Single Residue Methods

Test Item: Maize Flour

Final Report

Michelangelo Anastassiades
Pat Schreiter
Hubert Zipper

May 2016

The EURL-SRM is accredited by the DAkkS according to EN ISO/IEC 17043.
The accreditation is valid for the proficiency testing programs listed in the certificate.

DAkkS
Deutsche
Akkreditierungsstelle
D-EP-18585-01-00

Publication of parts of this EUPT-SRM10 final report by individuals or organizations shall always refer to the original document that can be found under:
http://www.eurl-pesticides.eu/library/docs/srm/EUPT_SRM10_FinalReport.pdf

Picture on the book cover: Irina Bart, www.123rf.com, 8041119

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FOREWORD

Regulation 882/2004/EC [1] defines the general tasks and duties of the EU Reference Laboratories (EURLs) for Food, Feed and Animal Health[1] including the organisation of comparative tests (proficiency tests = PTs). These PTs are carried out on an annual basis and aim to improve the quality, accuracy and comparability of the analytical results generated by EU Member States within the framework of the EU coordinated control programs as well as national monitoring programs. By participating in PTs laboratories can assess and at the same time demonstrate their analytical performance. The attention to details paid by laboratories during PT-analysis, together with the need to identify errors and to take corrective actions in cases of underperformance, typically lead to improvements in the quality of analytical results.

According to Article 28 of Regulation 396/2005/EC on maximum residue levels of pesticides in or on food and feed of plant and animal origin [2], all laboratories analysing for pesticide residues within the framework of official controls shall participate in the European Union Comparative Proficiency Tests (EUPTs) for pesticide residues. Each Official Laboratory (OfL) must participate in EUPTs concerning the commodities included in its area of competence.

Since 2006 the EURL for pesticide residues requiring the use of Single Residue Methods, EURL-SRM, has annually conducted one scheduled Proficiency Test. Two of these ten EUPT-SRMs, the EUPT-SRM7 (2012) based on milled dry lentils and the EUPT-SRM9 (2014) based on cow's milk, were organized by the EURL-SRM unilaterally. The EUPT-SRM9 was the only one within EUPT-SRMs so far, in which a commodity of animal origin was used. Four other EUPT-SRMs were conducted in collaboration with the EURL for pesticide residues in Fruits and Vegetables (EURL-FV) with apple juice (EUPT-SRM1, 2006), carrot homogenate (EUPT-SRM3, 2008), apple purée (EUPT-SRM5, 2010) and potato homogenate (EUPT-SRM8, 2013) as test items and the remaining four EUPT-SRMs were conducted in collaboration with the EURL for pesticide residues in Cereals and Feeding Stuff (EURL-CF) with wheat flour (EUPT-C1/SRM2, 2007), oat flour (EUPT-C3/SRM4, 2009), rice flour (EUPT-C5/SRM6, 2011) and the present EUPT-C9/SRM10 with maize flour as test items.

Participation in the respective EUPTs is mandatory for all NRLs for pesticides requiring Single Residue Methods (NRL-SRMs) and for all OfLs analysing pesticide residues within the framework of national or EU control programs in commodities represented by the respective test item of an EUPT. Laboratories in EU Member States analysing pesticide residues within the frame of import controls according to Reg. 669/2009/EC are also considered as performing official controls in the sense of Reg. 882/2005/EC and 396/2005/EC and are thus also obliged to take part in EUPTs. OfLs from EFTA countries (Iceland, Norway and Switzerland) which are also contributing data to the EU-coordinated community control programs, as well as OfLs from EU-acceding or -candidate countries (FYROM, Montenegro, Serbia and Turkey) are also invited to take part. A limited number of laboratories from third countries are allowed to take part in this exercise, too. However, only results submitted by labs from EU and EFTA countries are included in the calculation of the Assigned Values.

Based on information about the commodity scope and labs' NRL-status a tentative list of EU-labs considered as being obliged to participate in the EUPTs is published at the beginning of each year. The pesticide scope is not taken into account in these lists. NRLs and OfLs listed as being obliged to participate in an EUPT exercise in a given year but deciding not to take part, are always asked to state the reason(s) for their non-participation. The same applies to laboratories originally registering to participate in a certain EUPT but finally not submitting results.

DG-SANTE has full access to all data of EUPTs including the lab-code/lab-name key. The same applies to all NRLs as far as laboratories belonging to their own country networks are concerned. Results for this EUPT or a series of EUPTs, evaluated on a country by country basis, may be further presented to the European Commission Standing Committee on Plants, Animals, Food and Feed-Section Pesticides Residues (PAFF) or during EURL-Workshops.

[1] Formerly known as Community Reference Laboratories (CRLs)

CONTENT

EUPT-SRM10 - Supplementary Information on Analytical Methods

http://www.eurl-pesticides.eu/library/docs/srm/EUPT-SRM10_Supplementary_Information.pdf

EUROPEAN COMMISSION –
EU-PROFICIENCY TEST ON RESIDUES OF PESTICIDES
REQUIRING SINGLE RESIDUE METHODS
TEST ITEM: MAIZE FLOUR
EUPT-SRM10, 2015

INTRODUCTION

On 20 February, 2015 all relevant National Reference Laboratories (NRLs) of the 27 EU-Member States (MS), as well as all relevant EU-Official Laboratories (OfLs) whose contact details were available to the organisers (EURL-SRM), were invited to participate in the 10th European Commission's Proficiency Test Requiring Single Residue Methods (EUPT-SRM10). The EUPT-SRM10-Website contained links to the Announcement/Invitation Letter, the Calendar, as well as to the Target Pesticides List (**Appendix 11**). The Target Pesticides List contained 21 compounds potentially being present in the test item and requiring single residue methods for their analysis. 11 of them were compulsory compounds and were thus considered in Category A/B classification (based on scope). The compounds of the Target Pesticides List were selected based on a number of criteria and following consultation with the EUPT-Scientific Committee. For each compound a residue definition valid for the PT and the minimum required reporting level (MRRL) were stipulated. A link to the latest version of the "General Protocol" (**Appendix 9**) containing information common to all EUPTs, and to the "Specific Protocol" (**Appendix 10**) valid for the current PT, was also provided. The laboratories were able to register on-line from 25 March to 17 April, 2015.

Based on their commodity scope (food or feed based on cereals or dry pulses) and their NRL-status (NRL-SRMs) a tentative list of the laboratories considered as being obliged to participate in the EUPT-SRM10 was published on the EURL-Website as well as on the CIRCA-platform. To ensure that all relevant official laboratories were informed about this EUPT, the NRLs were asked to forward the invitation to all relevant official laboratories within their countries. It was made clear that the list of obliged laboratories prepared by the EURLs was only tentative and the real obligation to participate was based on Reg. 396/2005 and Reg. 882/2004 EC. Obliged labs that did not intend to participate were asked to provide an explanation.

In total 110 laboratories from EU and EFTA countries agreed to participate in the test with 6 of them failing to submit results. There were no participations from EU-Candidate countries in this EUPT. 6 laboratories from third countries have also registered for the present EUPT, and all of them have submitted results.

To produce maize containing incurred (field-sprayed) SRM pesticides as well as blank maize (lacking of SRM pesticides on the Target Pesticides List), the organisers subcontracted the EURL-CF. In order to obtain test item with 8 mandatory and 5 optional analytes at adequate levels, the incurred maize was additionally spiked with required analytes at the facilities of the EURL-SRM. Since the quantity of blank maize provided (45 kg) was not sufficient for the complete PT, additional 10 kg of maize from organic farming of German origin was purchased to supplement the blank material. More details are given in **Chapter 1 "Test Materials"**.

1. TEST ITEM AND BLANK MATERIAL

1.1 Selection of PT-Commodity and of Compounds for the Target Pesticides List

In agreement with the EUPT- Scientific Committee maize flour was chosen as commodity for the EUPT-SRM10.

The compounds to be included in the Target Pesticides List (**Appendix 11**) were selected by the organiser and the EUPT-Scientific Committee (Advisory Group and Quality Control Group) taking the following points into account: 1) the present and upcoming scope of the EU-coordinated control program; 2) a pesticide priority, ranking the pesticides according to their risk potential; 3) the relevance of pesticides to the specific commodity (maize and cereals in general); 4) the overall scope and capability of the OfLs as assessed in previous PTs or surveys; 5) the need of data to be able to evaluate the analytical proficiency of labs that offer analytical services via the SRM-PinBoard Service of the EURL-SRM. ***Phosphonic acid*** was selected as this compound sparked the attention of many laboratories due to residue findings in various commodities and its illegal use in organic agriculture.

The minimum required reporting levels (MRRLs) were set at 0.01 mg/kg for ***2,4-D***, ***chlormequat***, ***MCPA***, ***mepiquat***, ***propamocarb***, ***bentazone***, ***bromoxynil***, *dichlorprop*, *fluroxypyr*, *ioxynil* and *mecoprop*; at 0.02 mg/kg for ***ethephon***, *fenbutatin oxide*, *dicamba*, *glufosinate*, ***N-acetyl glufosinate***, *MPP*, *TFNA*, and ***TFNG***, and at 0.05 mg/kg for ***dithiocarbamates***, ***glyphosate***, *paraquat* and ***phosphonic acid***.

1.2 Preparation and Bottling of the Blank Material

Approximately 45 kg maize provided by the EURL-CF and 10 kg maize from organic farming of German origin, both not containing any detectable levels of the SRM pesticides, were mixed with a drum-hoop mixer for 10 h and milled in portions with a rotor beater mill (Retsch Rotor Beater Mill SR 300) equipped with a 0.5 µm sieve. In order to avoid overheating and process milling continuously approximately 750 ml maize was manually pre-mixed with 250 ml dry ice pellets (3 mm) prior to milling. The first 2 kg portion of the milled material was discarded. The milled material was re-mixed with a drum-hoop mixer over 10 h and weighed out in ca. 350 g portions into screw-capped polyethylene plastic bottles. The bottles were numbered, sealed and stored in a walk-in freezer at about -20 °C until packaging and distribution to the participants. A randomly chosen bottle was analyzed for the pesticides to verify that there was no cross-contamination during test item preparation.

1.3 Preparation and Bottling of Test Item

Before preparing the test item, the present target analytes and their suitable, approximate target residue levels for the study were selected by the organiser in coordination with the EUPT-QC-Group. The maize provided by the EURL-CF contained incurred ***glyphosate*** and ***chlormequat*** at a suitable level for the current exercise. For each of other analytes to be spiked to the material, a stock solution of 1 µg/ml was prepared (**Table 1-1**). Based on the solvent used the stock solutions were divided into four groups: analytes in acidified acetonitrile, methanol, toluene and water. For each solvent group, the necessary volumes of stock solution of each analyte were combined and added to separate portions (ca. 500 g each) of intact maize previously placed in a stainless steel pan. The spiked maize samples were shaken using an orbital shaker until the solvent was dried out. The four spiked portions were added to approximately 64.5 kg maize containing incurred ***glyphosate*** and ***chlormequat*** and mixed with a drum-hoop mixer over 10 h. The following treatment steps of milling, re-mixing, bottling and storage were conducted in exactly the same way as for the blank material described above.

Table 1-1: Composition of the spiking solution (of 150 ml) used in its entirety to prepare ca. 67 kg of the test item. (The losses onto the walls of the stainless steel pan were tolerated).

Stock Solution 1 µg/ml in									
Acetonitrile		Methanol		Methanol (acidified)		Toluene		Water	
Compound	Volume [ml]	Compound	Volume [ml]	Compound	Volume [ml]	Compound	Volume [ml]	Compound	Volume [ml]
2,4-D	6.8	N-Acetyl glufosinate	16.2	Ethephon	11.3	Thiram	82.9	Phosphonic acid	60
Bentazone	7.5	Mepiquat	8.9						
Bromoxynil	9.0	Propamocarb	6.0						
MCPA	6.0								
TFNG	13.5								

1.4 Packaging and Delivery of PT Materials to Participants

Three days prior to the sample delivery, one bottle of test item and one of Blank Material, both deep frozen, as well as a bottle containing 1 ml of $^{18}O_3$-***phosphonic acid*** were packed into thermo-insulated polystyrene boxes, filled with three cooling elements and stored at –20 °C for three days, so that at the day of delivery the cooling elements were deep frozen.

Among the 110 packages sent to destinations within Europe, 101 (92 %) reached the participating labs within 24 hours and 7 packages within 48 hours. Due to the remote location of certain laboratories, the remaining 2 packages took more than 2 days to arrive. Therefore, the organiser prepared for these two laboratories a second parcel using bigger polystyrene boxes and containing only the test item together with sufficient cooling elements. The packages were deep frozen at –80 °C for two days until shortly before shipment. In both cases the second shipment arrived to its destination within 48 hours, and the test item was in an acceptable condition. The delivery to countries outside the EU and EFTA zones was accomplished within 48 hours in 2 cases, within 72 hours in 1 case, within 4 days in 2 cases, and within 10 days in one case. The latter was, however, due to delays at the customs, and the parcel was kept in a freezer while waiting for customs clearance. Details on the shipments and the condition of the test items upon arrival are shown in **Appendix 2**.

Overall, the EUPT-materials arrived at the laboratories in good condition.

1.5 Analytical Methods

The analytical methods used by the organisers to check the homogeneity and storage-stability of the target analytes contained in the test item as well as the absence of target analytes in the blank material are summarized in **Table 1-2**. For more details on the methods used, please refer to the EURL-SRM website: http://www.eurl-pesticides.eu (EURL-SRM-website → Services → Methods).

1.6 Homogeneity Test

Following the filling of the test item bottles, approximately 14 bottles were randomly chosen, 10 of them were used for the homogeneity test and the remaining 4 for the transport simulation test. The analyses were performed on two analytical portions taken from each bottle. Before the analytical portions were taken, the entire content of each bottle was remixed manually by shaking the bottle. Both the order of sample preparation and the order of extract injection into the analytical instruments were random. Matrix-matched calibration standards, prepared using blank extracts, were used for quantification. Analytical portions of 25 g for ***dithiocarbamates*** and 5 g for all other compounds were applied.

Table 1-2: Analytical methods used by the organisers to check for the homogeneity and storage-/transport-stability of the pesticides present in the test item as well as for the absence of other pesticides in the blank material.

Compound	Extraction	IS	Determinative analysis		Notes
2,4-D (free acid)	**Modified QuEChERS-method** [3] involving: weighing of 5 g maize homogenate into a sealable vessel, addition of water (10 g) and IS / ILISs, extraction with ACN + 1 % formic acid (15 min) addition of partitioning salts (4 g $MgSO_4$, 1 g NaCl), 1 min shaking, centrifugation (twice with interval of 30 min), and direct determination by LC-MS/MS in the ESI (neg.) mode.	**BNPU / 2,4-D D_3**	**LC-MS/MS**	**ESI (neg)**	
Bentazone		**BNPU**	**LC-MS/MS**	**ESI (neg)**	
Bromoxynil		**BNPU**	**LC-MS/MS**	**ESI (neg)**	
MCPA		**BNPU / MCPA D_6**	**LC-MS/MS**	**ESI (neg)**	
TFNG		**BNPU**	**LC-MS/MS**	**ESI (neg)**	
*2,4-DP**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*Dicamba**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*Fenbutatin oxide**		*Chlorpyrifos D10*	*LC-MS/MS*	*ESI (pos)*	
*Fluroxypyr**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*Ioxynil**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*MCPP**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
*TFNA**		*BNPU*	*LC-MS/MS*	*ESI (neg)*	
Chlormequat	**QuPPe-PO method** [5] involving: weighing of 5 g maize homogenate into a sealable vessel, addition of water (10 g) and ILISs, addition of methanol containing 1 % formic acid, shaking, centrifugation, filtration and direct determination by LC-MS/MS in the ESI (neg.) or ESI (pos.) mode.	**Chlormequat D_4**	**LC-MS/MS**	**ESI (pos)**	**QuPPe M4.2**
Ethephon		**Ethephon D_4**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
Glyphosate		**Glyphosate $^{13}C_2$ ^{15}N**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
Mepiquat		**Mepiquat D_3**	**LC-MS/MS**	**ESI (pos)**	**QuPPe M4.2**
N-Acetyl glufosinate		**N-Acetyl glufosinate D_3**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
Phosphonic acid		**Phosphonic acid $^{18}O_3$**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.4**
Propamocarb		**Propamocarb D_7**	**LC-MS/MS**	**ESI (pos)**	**QuPPe M4.2**
*Glufosinate**		*Glufosinate D_3*	*LC-MS/MS*	*ESI (neg)*	*QuPPe M1.3*
*MPP**		*MPP D_3*	*LC-MS/MS*	*ESI (neg)*	*QuPPe M1.3*
*Paraquat**		*Paraquat D_6*	*LC-MS/MS*	*ESI (pos)*	*QuPPe M4.1*
CS_2	**Dithiocarbamate method** involving: weighing of 25 g maize homogenate into a sealable vessel, addition of chloroform (as IS) and 25 ml iso-octane and $SnCl_2$/HCl, followed by cleavage to CS_2 in a shaking water bath for 2 h at 80°C. Cleanup of an iso-octane extract aliquot with a silica column followed by GC-ECD analysis.	**Chloroform**	**GC-ECD**	–	

* : To check for absence in Blank Material

The statistical evaluation of the homogeneity test data was performed according to the International Harmonized Protocols published by IUPAC, ISO and AOAC [4]. An overview of the statistical evaluations of the homogeneity test is shown in **Table 1-3**. The individual residue data of the homogeneity test is given in **Appendix 3**.

The acceptance criterion for the test item to be sufficiently homogenous for the Proficiency Test was that s_{sam}^2 is smaller than c with s_{sam} being the between-bottle sampling standard deviation and $c = F_1 \times \sigma_{all}^2 + F_2 \times s_{an}^2$, F_1 and F_2 being constants with values of 1.88 and 1.01, respectively, and applying when duplicate samples are taken from 10 bottles. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD (25 %) $\times$ the analytical sampling mean of the analyte, and s_{an} is the estimate of the analytical standard deviation.

As all target compounds passed the homogeneity test, the test item was considered to be sufficiently homogenous and suitable for the EUPT-SRM10. In the Specific Protocol laboratories were strongly recommended thoroughly mixing the received test items before taking any analytical portions in order to ensure good homogeneity.

Table 1-3: Statistical evaluation of homogeneity test data (n = 20 analyses), details please see **Appendix 3**.

COMPULSORY COMPOUNDS								
	2,4-D	Chlormequat	Dithiocarbamates	Ethephon	Glyphosate	MCPA	Mepiquat	Propamocarb
Analytical portion size [g]	5	5	25	5	5	5	5	5
Mean [mg/kg]	0.099	0.143	0.782	0.161	0.575	0.091	0.103	0.073
s_{sam}^2	5.49×10^{-5}	1.16×10^{-4}	3.44×10^{-3}	1.46×10^{-4}	1.86×10^{-3}	4.62×10^{-5}	5.93×10^{-5}	3.01×10^{-5}
c	1.06×10^{-4}	2.25×10^{-4}	1.55×10^{-2}	3.20×10^{-4}	4.43×10^{-3}	1.19×10^{-4}	1.20×10^{-4}	6.18×10^{-5}
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed
OPTIONAL COMPOUNDS								
	Bentazone	Bromoxynil	N-Acetyl glufosinate	Phosphonic acid	TFNG			
Analytical portion size [g]	5	5	5	5	5			
Mean [mg/kg]	0.104	0.129	0.186	0.695	0.168			
s_{sam}^2	6.13×10^{-5}	9.38×10^{-5}	1.94×10^{-4}	2.72×10^{-3}	1.58×10^{-4}			
c	1.28×10^{-4}	1.94×10^{-4}	5.42×10^{-4}	7.06×10^{-3}	3.38×10^{-4}			
Passed/Failed	passed	passed	passed	passed	passed			

s_{sam}^2 : sampling variance; c: critical value

1.7 Storage Stability Test

The vast majority of laboratories received their test items still within 48 hours in cool or very cool condition. In the Specific Protocol laboratories were recommended storing the samples in the freezer until analysis. Possible losses during the transport to the participants were studied separately in the transport stability test (see below). For the storage stability test two analytical portions from three randomly chosen test item bottles were withdrawn on three dates, with the first and last one enclosing the period of the test, and analysed as described in **Section 1.5 (p. 2)**:

Stability test 1 (directly after test item preparation, 10 days prior to shipment):
08 May 2015 (all analytes but ***dithiocarbamates***)
24 June 2015 (***dithiocarbamates****)

Stability test 2 (three weeks after shipment):
16 June 2015 (all analytes but ***dithiocarbamates***)
25 August 2015 (***dithiocarbamates****)

Stability test 3 (three weeks after deadline for results submission):
07 July 2015 (all analytes but ***dithiocarbamates***)
07 September 2015 (***dithiocarbamates****)

* The analysis of ***dithiocarbamates*** had to be postponed due to technical problems.

Table 1-4: Results of storage stability test (storage at -18 °C), see also **Appendix 4**.

COMPULSORY COMPOUNDS								
	2,4-D	Chlormequat	Dithiocarbamates*	Ethephon	Glyphosate	MCPA	Mepiquat	Propamocarb
Storage at –18 °C (mean values in mg/kg)								
Analysis 1 08 May 2015/24 June 2015*	0.097	0.141	0.763	0.176	0.576	0.083	0.102	0.073
Analysis 2 16 June 2015/25 Aug. 2015*	0.099	0.139	0.780	0.163	0.555	0.088	0.097	0.071
Analysis 3 07 July 2015/07 Sept. 2015*	0.102	0.144	0.782	0.173	0.566	0.087	0.099	0.070
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.005 (5.07 %)	0.002 (1.66 %)	0.018 (2.40 %)	-0.003 (-1.66 %)	-0.011 (-1.87 %)	0.003 (4.19 %)	-0.003 (-2.96 %)	-0.002 (-3.10 %)
Critical value [mg/kg]	0.007	0.011	0.057	0.013	0.043	0.006	0.008	0.005
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed
* The analysis of dithiocarbamates had to be postponed due to technical problems.								

OPTIONAL COMPOUNDS								
	Bentazone	Bromoxynil	N-Acetyl glufosinate	Phosphonic acid	TFNG			
Storage at –18 °C (mean values in mg/kg)								
Analysis 1 08 May 2015	0.099	0.126	0.189	0.715	0.167			
Analysis 2 16 June 2015	0.105	0.130	0.178	0.725	0.164			
Analysis 3 07 July 2015	0.106	0.130	0.201	0.731	0.156			
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.007 (6.84 %)	0.004 (3.53 %)	0.012 (6.09 %)	0.016 (2.25 %)	-0.011 (-6.34 %)			
Critical value [mg/kg]	0.007	0.009	0.014	0.054	0.012			
Passed/Failed	passed	passed	passed	passed	passed			

A target compound is considered to be adequately stable if $|x_i - x_1| \leq 0.3 \times \sigma$, where x_1 is the mean value of the first stability test, x_i the mean value of the last stability test, and σ the standard deviation used for proficiency assessment (here x_1 was derived by multiplying 0.25, the fixed relative standard deviation using the fit-for-purpose RSD-approach of 25 %). None of the target compounds present in the test item showed any significant degradation under the recommended storage conditions (–18 °C) even during a storage period exceeding the duration of the exercise. It is thus assumed that if the recommended storage conditions were followed, the influence of sample storage on the results of the laboratories and the assigned value was negligible. The results of all analyses conducted within the framework of the stability test are shown in **Table 1-4** (p. 56) and **Appendix 4**.

1.8 Transport Stability Test

To complement the storage stability test, the stability at conditions simulating shipment was also studied. For this, 4 randomly chosen bottles of the test item were taken out of the freezer on July 19 and their content was poured in a larger container and thoroughly mixed, reportioned again into four bottles and put in a freezer at –18 °C over the weekend. Three of the bottles were packed into boxes in the same way as the boxes that were shipped to the participants. One bottle was kept in the freezer at –18 °C over the entire period of the test and the material contained was used as reference (= day 0). Assuming that the average temperatures during shipment would not exceed the average room temperature, the three boxes were left standing in the laboratory at ambient temperature from 22 June onwards. One of the boxes was opened on 24 June (= 2 days "shipment") and the test item bottle was placed in the freezer to conserve its condition. The same was done with the second sample on 26 June (= 4 days "shipment") and with the third one on 2 July (= 10 days "shipment"). This duration covers the shipping time of the packages to the laboratories. On 2 July six analytical portions from each of the 4 bottles were withdrawn and analysed.

At day-0 the test item had the core temperature of approx. –5 °C. At day-2 the temperature of the material increased to 16 °C, and at day-4 it reached ambient temperature.

All compounds remained sufficiently stable over 2 days shipment time, a period covering 100 % of the participating labs in the EU and EFTA countries. At longer shipping times moderate drops in concentration were observed for ***ethephon***, ***dithiocarbamates***, ***propamocarb***, ***bentazone*** and ***TFNG***. These were expected to have influenced those labs having received the samples late. The results of the transport stability test are shown in **Table 1-5**.

1.9 Organisational Aspects

1.9.1 Preparation and Distribution of a Tentative List of Obliged Laboratories

A tentative list of laboratories (NRLs and OfLs) obliged to participate in the current EUPT was compiled based on available information on NRL-status and commodity scope as recorded in the EURL-DataPool. The available data on the information on the pesticide scope of the laboratories was not considered when drafting this list due to concerns that it was not up-to-date and/or not applicable to the present commodity (maize). The draft list was distributed to the OfLs and the NRLs so that all laboratories could check their status and contact information and report any errors. The errors were corrected and a new list was released. NRLs were then prompted to carefully check the status, commodity scope and contact data of the OfLs within their network and asked to amend and complement the list, if necessary, and to further ensure that all obliged OfLs within their network were informed of this EUPT. The NRLs were reminded that they are ultimately responsible for their network, and it was made clear to all NRLs and OfLs that the list of obliged labs was tentative and the real obligation for participation is derived from Art. 28 of Reg. 396/2005/EU (for OfLs) and from Art. 33 of Reg. 882/2005/EC (for NRL-SRMs). Following DG-SANTE instructions, obliged labs that were not intending to participate in the EUPT-SRM10 were instructed to provide explanations for their non-participation.

1.9.2 Announcement / Invitation and EUPT-SRM10-Website

Within the EURL-Web-Portal an EUPT-SRM10-Website was constructed with links to all documents relevant to this EUPT (i.e., Announcement/Invitation Letter, Calendar, Target Pesticides List, Specific Protocol and General EUPT Protocol). These documents were uploaded to the EURL-Web-Portal and the CIRCA/FIS-VL platform.

Table 1-5: Transport stability test. Delivery units, deep frozen, packed with dry ice in thermo-insulated polystyrene boxes and left in the laboratory at room temperature

COMPULSORY COMPOUNDS								
	2,4-D	Chlormequat	Dithiocarbamates	Ethephon	Glyphosate	MCPA	Mepiquat	Propamocarb
Day-0 (~–5 °C)	0.103	0.153	0.706	0.164	0.581	0.089	0.103	0.079
Day-2 (~ 16 °C)	0.098	0.146	0.771	0.154	0.584	0.088	0.100	0.073
Day-4 (ambient temperature)	0.095	0.143	0.715	0.151	0.562	0.081	0.102	0.070
Day-10 (ambient temperature)	0.095	0.145	0.581	0.148	0.594	0.085	0.099	0.067
Deviation [%] Day-2 vs. Day-0	-5.2 %	-4.3 %	9.2 %	-6.2 %	0.6 %	-1.5 %	-2.7 %	-7.5 %
Deviation [%] Day-4 vs. Day-0	-7.5 %	-6.4 %	1.2 %	-7.9 %	-3.2 %	-9.0 %	-0.8 %	-11.5 %
Deviation [%] Day-10 vs. Day-0	-7.4 %	-5.2 %	-17.8 %	-9.8 %	2.2 %	-4.3 %	-4.1 %	-14.7 %
OPTIONAL COMPOUNDS								
	Bentazone	Bromoxynil	N-Acetyl glufosinate	Phosphonic acid	TFNG			
Day-0 (~–5 °C)	0.110	0.134	0.193	0.718	0.169			
Day-2 (~ 16 °C)	0.102	0.130	0.184	0.752	0.165			
Day-4 (ambient temperature)	0.100	0.129	0.183	0.725	0.160			
Day-10 (ambient temperature)	0.095	0.122	0.192	0.725	0.144			
Deviation [%] Day-2 vs. Day-0	-6.9 %	-2.7 %	-5.0 %	4.7 %	-2.4 %			
Deviation [%] Day-4 vs. Day-0	-8.9 %	-3.3 %	-5.1 %	1.1 %	-5.5 %			
Deviation [%] Day-10 vs. Day-0	-13.4 %	-8.7 %	-0.5 %	1.0 %	-14.7 %			

The Announcement/Invitation Letter for the EUPT-SRM10 was published on the EUPT-SRM10-Website in February 2015 and sent to all NRL-SRMs, all OfLs analysing pesticide residues in food and feeding stuff within the framework of official controls, and all laboratories performing import controls according to Reg. 669/2009/EC. The latter labs were considered eligible but not obliged to participate. It was indicated to the OfLs that their obligation to participate in EUPTs arises from Reg. 396/2005/EC, irrespective of the content of the tentative list of obliged laboratories. OfLs from EFTA and EU-candidate countries were also invited if their contact data was available.

1.9.3 Registration and Confidentiality

An EUPT-SRM10 registration website was constructed in collaboration with the EURL-CF. All laboratories listed in the tentative list as being obliged to participate in the current EUPT, regardless of whether they were intending to participate in this exercise or not, were requested to either register or to state their reasons for non-participation using the same website.

Upon registration, the labs received an electronic confirmation about their participation or non-participation in the current PT. On the day of sample shipment, participating labs were provided via e-mail with a unique laboratory code as well as with unique, automatically generated login data to access the online Result-Submission-Website. This ensured confidentiality throughout the entire duration of the PT.

For further information on confidentiality please refer to the General EUPT Protocol (**Appendix 9**).

1.9.4 Distribution of the Test Items and the Blank Material

One bottle of test item (approx. 350 g) and one bottle of blank material (approx. 350 g) were shipped on 18 May 2015 to each participant in thermo-insulated polystyrene boxes combined with three cooling elements. A small bottle containing 1 ml of ***phosphonic acid*** ILIS was also included in each package. Five days prior to the shipment, a short instruction sheet on handling the sample and application of ILIS was sent to the participant by e-mail.

Laboratories were asked to check the integrity and condition of the PT-materials upon receipt and to report to the organisers via the website any observations or complaints and whether the PT-materials are accepted. Detailed instructions on how to treat the test item and blank material upon receipt were provided to the participating laboratories in the Specific Protocol (**Appendix 10**) that was dispatched one month prior to the shipment date.

1.9.5 Submission of Results and Additional Information

An online submission tool allowed participants to submit their results via the Internet. Using their individual login data, all participants had access to the Result-Submission-Website from a week after the sample shipment until the result submission deadline (19 June 2015). Participants were asked not only to report their analytical results but also to state whether the compounds on the Target Pesticides List were part of their routine scope and to indicate their experience with the analysis of these compounds. In addition, laboratories had to provide details about the methods applied and to state their own reporting limits (RLs) for each target compound they had analysed.

Where information on analytical methods or results was inconsistent, laboratories were contacted. Laboratories having submitted false negative results were also contacted and asked to provide information on the methods used for analysing those compounds.

2. EVALUATION RULES

2.1 False Positives and Negatives

2.1.1 False Positives (FPs)

Any reported result with a concentration at, or above, the Minimum Required Reporting Level (MRRL) of an analyte in the Target Pesticides List which was (a) not detected by the organiser, even following repetitive analysis, and/or (b) not detected by the overwhelming majority (e.g. > 95 %) of the participants that tested for this compound, is treated as a false positive result. Results of an analyte absent in the test item but with a value lower than the MRRL are ignored by the organiser and not considered as false positives. No z-scores are calculated for false positive results.

2.1.2 False Negatives (FNs)

These are results of target analytes reported as "analysed" but without reporting numerical values, although they were used by the organiser to prepare the test item and were detected, at or above the MRRL, by the organiser and the overwhelming majority of the participating laboratories. In accordance with the General Protocol z-scores for false negatives are calculated using the MRRL as the result, or using the lab's reporting-limits (RLs), whichever is lower. Any RLs that are higher than the MRRL are not taken into account. Following the General Protocol results reported as "< RL" without providing a numerical value are also judged as false negatives if the RL exceeds the MRRL.

2.2 Establishment of the Assigned Values (x_{pt}) and Calculation of the Respective Uncertainties ($u(x_{pt})$)

The assigned values x_{pt} of each pesticide in the PT is established using the mean value of robust statistics (x^*) of all reported results from EU and EFTA countries. Results associated with obvious mistakes and gross errors may be excluded from the population for the establishment of the assigned values.

The uncertainty of the assigned values of each analyte is calculated according to ISO 13528:2009-1 [6] according to the following equation:

$$u(x_{pt}) = 1.25 \times [(s^*)/\sqrt{p}]$$

Where $u(x_{pt})$ is the uncertainty of the assigned value in mg/kg, s^* is the robust standard deviation estimate in mg/kg and p is the number of datapoints considered (= the number of results used to calculate the assigned value).

The tolerance for the uncertainty of the assigned value of each pesticide is calculated as $0.3 \times FFP\text{-}\sigma_{pt}$, where $FFP\text{-}\sigma_{pt}$ is the target standard deviation of the assigned value derived using a fixed standard deviation of 25 % (see below). If $u(x_{pt}) < 0.3 \times FFP\text{-}\sigma_{pt}$, is met, then the uncertainty of the assigned value is considered to be negligible and not needed to be considered in the interpretation of the proficiency test results.

2.3 Fixed Target Standard Deviation using FFP-approach ($FFP\text{-}\sigma_{pt}$)

Based on experience from previous EU Proficiency Tests on fruit and vegetables and cereals, the EUPT-Scientific Committee agreed to apply a fixed fit-for-purpose relative standard deviation (FFP-RSD) of 25 % for calculating the z-scores. The fixed target standard deviation using the fit-for-purpose approach ($FFP\text{-}\sigma_{pt}$), for each individual target analyte is calculated by multiplying the assigned value by the FFP-RSD of 25 %. In addition, the robust relative standard deviation of the assigned value (CV^*) is calculated for informative purposes.

2.4 z-Scores

For each combination of laboratory and target analyte a z-score is calculated according to the following equation:

$$z_i = (x_i - x_{pt}) / FFP\text{-}\sigma_{pt}$$

Where

- x_i is the result for the target analyte (i) as reported by the participant
  (For results considred as false negatives, x_i is set as equal to the respective minimum required reporting level (MRRL) or the laboratory reporting level (RL), if RL < MRRL.)
- x_{pt} is the assigned value for the target analyte (i)
- $FFP\text{-}\sigma_{pt}$ is the standard deviation for proficiency assessment using the fit-for-purpose approach (see above).

  Any z-scores > 5 are set at 5 in calculations of combined z-scores (see **2.5.2**).

The z-scores are classified as follows:

$\|z\| \leq 2$	acceptable
$2 < \|z\| < 3$	questionable
$\|z\| \geq 3$	unacceptable

For results considered as false negatives, z-scores are calculated using the MRRL or the RL, if RL < MRRL. No z-scores are allocated to false positive results.

2.5 Laboratory Classification

2.5.1 Category A and B classification

Based on the scope of target analytes covered by the laboratories in this exercise, laboratories are subdivided into Categories (A and B) in accordance with the rules in the General Protocol (**Appendix 9**). To be classified into Category A a laboratory should

a) have correctly reported concentration values for at least 90 % of the compulsory pesticides present in the test item,
b) not have reported any false positive results.

2.5.2 Combined z-Scores

For informative purposes and to allow comparison of the overall performance of the laboratories the Average of the Absolute z-Scores (AAZ) are calculated for laboratories with 5 or more z-scores. **Combined z-scores are, however, considered to be of lesser importance than the individual z-scores**.

Average of the Absolute z-Scores (AAZ)

The AAZ is calculated using the following formula:

$$AAZ = \frac{\sum_{i=1}^{n} |z_i|}{n}$$

where "n" is the number of each laboratory's z-scores that are considered in this formula. This includes z-scores assigned for false negative results.
For the calculation, any z-score > 5 is set at 5.

3. PARTICIPATION

116 laboratories from 34 countries (27 EU-Member States, 2 EFTA-States and 5 third countries) registered for participation in the EUPT-SRM10. Out of those laboratories 110 submitted at least one result; those were 102 laboratories from EU-Member States, 2 laboratories from EFTA-States and 6 laboratories from third countries. An overview of the participating laboratories and countries is given in **Table 3-1**.

A list of all individual laboratories that registered for this EUPT is presented in **Appendix 1**. For the first time OfLs from Croatia have participated in an EUPT-SRM. Croatia and Romania were the only EU-countries not represented by an NRL-SRM. Croatia had not yet designated an NRL-SRM, whereas the Romanian NRL-SRM indicated that the commodity as well as the target pesticides were out of its analytical scope. Malta was represented by its proxy-NRL-SRM based in the United Kingdom.

All 8 laboratories from non-EU countries submitted results (2 from EFTA Countries and 6 from third countries). The results submitted by the 6 laboratories form third countries were not taken into account when calculating the Assigned Values.

In total, 128 EU-OfLs (including NRL-SRMs) were originally considered as being obliged to participate in the present EUPT and were included on a tentative list of obliged labs that was distributed to the labs of the network prior to the registration period for this EUPT. The list included all NRL-SRMs, regardless of their commodity scope, and all EU-OfLs analysing for pesticide residues in cereals or feed.

All labs tentatively considered as obliged to participate had to either participate or to provide an explanation for their non-participation. Out of 28 obliged laboratories that did not register for this PT, 8 (from 6 EU countries) provided explanations for their non-participation. All of them explained their non-participation with the fact that the matrix (maize) or the SRM10 target pesticides or both were out of their routine scope, partly due to lacking of required instruments. Excluding those 8 laboratories that provided sufficient explanations, the number of EU-laboratories considered as being obliged decreased to 120, out of which 20 did neither register for the PT nor provided any explanation for non-participation. Out of the 100 obliged laboratories that have registered for this PT only 94 laboratories finally submitted result.

Table 3-2 gives an overview of the participation and non-participation of EU-labs obliged to take part in the EUPT-SRM10. The 6 laboratories that did not submit results were also requested to provide explanations. One of those laboratories reported a technical problem during the period of this PT. Another laboratory reported that the required standards did not arrive on time. The remaining 4 laboratories did not provide any explanations despite repetitive contact.

Table 3-1: Number of laboratories listed as being obliged to participate in the EUPT-SRM10, labs that registered to participate, and labs that finally submitted results (grouped by contracting country)

Contracting Country [1]	No. of obliged labs [2]	Registered for Participation		Submitted Results		Provided Explanations for non-participation		Notes
		All [3]	NRL-SRMs	All [3]	NRL-SRMs	All	NRL-SRMs	
Austria	2	2	1	2	1			
Belgium	4	4+[1]	1	2+[1]	1			
Belgium / Germany [4]	1	1		1				
Belgium / France / Luxemburg [4]	1	1		1				
Bulgaria	3	3	1	2	1			
Croatia	3	1+[1]		1+[1]		1		HR has not yet established an NRL-SRM.
Cyprus	1	1	1	1	1			
Czech Republic	4	3	1	3	1			
France	9	8	1	8	1			
Germany	22	22	1	22	1			
Denmark	2	2	1	2	1			
Estonia	2	2	1	2	1			
Finland	1	1	1‡	1	1‡	1	1‡	‡ The two NRL-SRMs in FI have divided responsibilities. The NRL-SRM responsible for products of animal origin was considered as non-obliged to participate in the present PT.
Greece	2	2	2	2	2			GR has appointed two NRL-SRMs.
Hungary	4	4	1	4	1			
Ireland	1	1	1	1	1			
Italy	17	11	1	8	1	2		
Lithuania	1	1+[1]	1	1+[1]	1			
Luxemburg	1	1	1	1	1			
Latvia	1	1	1	1	1			
Malta*	1	1	*	1	*			*MT-NRL-SRM represented by the UK-NRL-SRM which acts as proxy NRL
The Netherlands	2	2	1	2	1			
Poland	8	4+[3]	1	4+[3]	1			
Portugal	2	2	1	2	1	1		
Romania	3	[1]		[1]		1		
Spain	13	10+[1]	2	10+[1]	2	2		ES has appointed two NRL-SRMs
Spain / Malta [4]	1	1		1				
Sweden	2	2	1	2	1			
Slovenia	3	3	1	3	1			
Slovakia	1	1	1	1	1			
United Kingdom / Malta [4]	2	2	1	2	1			UK-NRL-SRM represents also MT-NRL-SRM; the UK-OfL was subcontracted also by MT.
EU Total	**120**	100+[8]	27 [5]	94+[8]	27 [5]			

1) Country on behalf of which a laboratory is acting NRL-SRM or is analysing official samples for pesticide residues. In case of laboratories from 3rd countries: location of the laboratories
2) Laboratories tentatively considered as obliged to participate in the EUPT-SRM10 minus those giving sufficient explanations that they are not obliged (e.g. "commodity maize or pesticides in the target list are out of scope")
3) Labs participating on voluntary basis are shown in squared brackets.
4) One lab was subcontracted by three countries; three labs were subcontracted by two countries. Such laboratories were listed separately.
5) The NRL-SRM of UK was counted only once, although it represents both UK and MT.

Table 3-1 (cont.): Number of laboratories listed as being obliged to participate in the EUPT-SRM10, labs that registered to participate, and labs that finally submitted results (grouped by contracting country)

Contracting Country [1]	No. of obliged labs [2]	Registered for Participation		Submitted Results		Provided Explanations for non-participation		Notes
		All [3]	NRL-SRMs	All [3]	NRL-SRMs	All	NRL-SRMs	
Norway		1	1	1	1			
Switzerland		1	–	1	–			
EU+EFTA Total	**120**	102+[8]	28 [5]	96+[8]	28 [5]			
Australia		2	–	2	–			
Egypt		1	–	1	–			
India		1	–	1	–			
Singapore		1	–	1	–			
Canada		1	–	1	–			
Third Countries		6		6				
Overall Sum	**120**	116		110				

1) Country on behalf of which a laboratory is acting NRL-SRM or is analysing official samples for pesticide residues. In case of laboratories from 3rd countries: location of the laboratories
2) Laboratories tentatively considered as obliged to participate in the EUPT-SRM10 minus those giving sufficient explanations that they are not obliged (e.g. "commodity maize or pesticides in the target list are out of scope")
3) Labs participating on voluntary basis are shown in squared brackets.
4) One lab was subcontracted by three countries; three labs were subcontracted by two countries. Such laboratories were listed separately.
5) The NRL-SRM of UK was counted only once, although it represents both UK and MT.

Table 3-2: Overview of EU-OfLs and NRLs considered as being obliged to participate in the EUPT-SRM10

	Number	Percent
Obliged EU-Labs [1]	**120**	**100 %**
Thereof...		
- Registered for participation (obliged / [on voluntary basis])	100 / [8]	83 %
- Submitting results (obliged / [on voluntary basis])	**94 / [8]**	**78 %**
- Not submitting results (providing explanation for non-submission)	6 (2)	5 % (1.7 %)
- Obliged to participate but non-participating	20	16 %
- Sum of obliged laboratories not participating (20) or registered for participating but not submitting results and not providing explanations (4)	**24**	**20 %**

1) Laboratories tentatively considered as obliged to participate in the EUPT-SRM10 minus those giving sufficient explanations that they are not obliged (e.g. commodity group or pesticides in target list are out of scope)

4. RESULTS

4.1 Overview of Results

An overview of the percentage of laboratories having targeted each of the analytes present in the Target Pesticides List is shown in **Table 4-1**.

Table 4-2 (p. 18) gives an overview of all results submitted by each laboratory. The individual numerical results reported by the laboratories are shown in **Table 4-7 (p. 34)** and **Table 4-8 (p. 40)**. Detailed information about the analytical methods used by the laboratories is shown in the web under "EUPT-SRM10 - Supplementary Information" accessible via the following link:
http://www.eurl-pesticides.eu/library/docs/srm/EUPT-SRM10_Supplementary_Information.pdf

Table 4-1: Percentage of EU and EFTA laboratories that have analysed for the compounds in the Target Pesticides List

Compounds		Present in test item	Labs analysed for the compound			
			EU [1]- and EFTA-Labs		EU obliged Labs only	
			No. [2]	% (based on *n* = 104 [3])	No. [2]	% (based on *n* = 120 [4])
Compulsory Compounds	**2,4-D**	**yes**	82	79 %	75	63 %
	Chlormequat	**yes**	75	72 %	69	58 %
	Dithiocarbamates	**yes**	86	83 %	77	64 %
	Ethephon	**yes**	61	59 %	55	46 %
	Fenbutatin oxide	no	56	54 %	51	43 %
	Glyphosate	**yes**	64	62 %	58	48 %
	MCPA	**yes**	80	77 %	73	61 %
	Mepiquat	**yes**	76	73 %	70	58 %
	Propamocarb	**yes**	87	84 %	80	67 %
Optional Compounds	**2,4-DP**	no	71	68 %	64	53 %
	Bentazone	**yes**	69	66 %	62	52 %
	Bromoxynil	**yes**	65	63 %	60	50 %
	Dicamba	no	41	39 %	35	29 %
	Fluroxypyr	no	62	60 %	56	47 %
	Glufosinate	no	33	32 %	29	24 %
	N-Acetyl glufosinate	**yes**	16	15 %	15	13 %
	MPP	no	14	13 %	13	11 %
	Ioxynil	no	66	63 %	59	49 %
	MCPP	no	69	66 %	63	53 %
	Paraquat	no	16	15 %	14	12 %
	Phosphonic acid	**yes**	25	24 %	21	18 %
	TFNA	no	30	29 %	25	21 %
	TFNG	**yes**	30	29 %	26	22 %

1) Including official laboratories participating on voluntary basis
2) Laboratories representing more than one country were counted only once.
3) 104 is the number of participating OfLs from EU and EFTA countries (including NRLs and official laboratories participating on voluntary basis) having registered for the present PT and submitted at least one result.
4) 120 is the number of OfLs (including NRLs) from EU countries, which were finally considered as obliged to participate in the EUPT-SRM10 (taking into account any explanations for non-participation).

Table 4-2: Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds												
Compulsory Compound listed in Target List			2,4-D	Chlormequat	Dithiocarbamates	Ethephon	Fenbutatin Oxide	Glyphosate	MCPA	Mepiquat	Propamocarb	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 9 / 8)
within MACP [1]			WD	Reg.	Reg.	Reg.	Reg.	Reg.	WD	Reg.	Reg.	
present in Test Item			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
evaluated in this PT			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
Lab-Code SRM10-	NRL-SRM	Cat. [2]										
1		B	V	V	V		ND	V	**FN**	V	V	8 / 6
2		A	V	V	V	V	ND	V	V	V	V	9 / 8
3		A	V	V	V	V	ND	V	V	V	V	9 / 8
4	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
5		A	V	V	V	V	ND	V	V	V	V	9 / 8
6	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
7		B			V							1 / 1
8		B [#]	V	V	V	V		V	V	V	V	8 / 8
9		B	V	V	V					V	V	5 / 5
10		A	V	V	V	V	ND	V	V	V	V	9 / 8
11		A	V	V	V	V	ND	V	V	V	V	9 / 8
12	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
13		B						**FN**				1 / 0
14		B		V		V		V		V		4 / 4
15		A	V	V	V	V	ND	V	V	V	V	9 / 8
16		A	V	V	V	V	ND	V	V	V	V	9 / 8
18		B	V	V				V	V	V	V	6 / 6
19		B	V	V	V				V	V	V	6 / 6
20		A	V	V	V	V	ND	V	V	V	V	9 / 8
21		A	V	V	V	V	ND	V	V	V	V	9 / 8
22		B	V		V	V	ND	V	V		V	7 / 6
23	x	A	V	V	V	V		V	V	V	V	8 / 8
24	x	B	V				ND		V		V	4 / 3
25		A	V	V	V	V	ND	V	V	V	V	9 / 8
26	x	A	V	V	V	V	ND	**FN**	V	V	V	9 / 7
27		A	V	V	V	V	ND	V	V	V	V	9 / 8

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

[#] Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total	
Optional Compound listed in Target List			Bentazone	Bromoxynil	Dicamba	2,4-DP	Fluroxypyr	Glufosinate	N-Acetyl glufosinate	MPP	Ioxynil	MCPP	Paraquat	Phosphonic acid	TFNA	TFNG	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 14/ 5)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 23 / 13)
within MACP [1]			–	–	–	–	–	WD	WD	WD	WD	–	WD	WD	WD	WD		
present in Test Item			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
evaluated in this PT			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
Lab-Code SRM10-	NRL-SRM	Cat. [2]																
1		B		V							ND						2 / 1	10 / 7
2		A	V	V		ND	ND	ND	V	ND	ND	ND					9 / 3	18 / 11
3		A	V	V	ND	ND	ND				ND	ND			ND	V	9 / 3	18 / 11
4	x	A	V	V	ND	ND	ND	ND	V	ND	ND	ND	ND	V	ND	V	14 / 5	23 / 13
5		A	V	V	ND	ND	ND	ND			ND	ND		V	ND	V	11 / 4	20 / 12
6	x	A	V	V	ND	ND	ND	ND	V	ND	ND	ND	ND	V	ND	V	14 / 5	23 / 13
7		B															0 / 0	1 / 1
8		B #	V	V				**FP**		**FP**				V			5 / 3	13 / 11
9		B		V													1 / 1	6 / 6
10		A	V	V	ND	ND	ND				ND	ND		V		V	9 / 4	18 / 12
11		A	V	V		ND	ND				ND	ND					6 / 2	15 / 10
12	x	A	V	V	ND	ND	ND	ND	V	ND	ND	ND	ND		ND	V	13 / 4	22 / 12
13		B															0 / 0	1 / 0
14		B						ND	V	ND				**FN**			4 / 1	8 / 5
15		A	V	V		ND	ND		V		ND	ND					7 / 3	16 / 11
16		A	V		ND	ND	ND				ND	ND					6 / 1	15 / 9
18		B	V	V		ND		ND	V		ND	ND					7 / 3	13 / 9
19		B	V	V	ND	ND	ND			ND	ND	ND					8 / 2	14 / 8
20		A	V	V	ND	ND	ND	ND	V	ND	ND	ND	ND	V	ND	V	14 / 5	23 / 13
21		A	V	V	ND	ND	ND	ND	V	ND	ND	ND	ND	V	ND	V	14 / 5	23 / 13
22		B		V		ND	ND				ND	ND					5 / 1	12 / 7
23	x	A		V		ND	ND				ND	ND					5 / 1	13 / 9
24	x	B	V	V	ND	ND	ND				ND	ND					7 / 2	11 / 5
25		A	V	V	ND	ND	ND	ND	V	ND	ND	ND		V	ND	V	13 / 5	22 / 13
26	x	A	V	V	ND	ND	ND				ND	ND	ND				8 / 2	17 / 9
27		A	V	V	ND	ND	ND	ND			ND	ND		V	ND	V	11 / 4	20 / 12

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds												
Compulsory Compound listed in Target List			2,4-D	Chlormequat	Dithiocarbamates	Ethephon	Fenbutatin Oxide	Glyphosate	MCPA	Mepiquat	Propamocarb	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 9 / 8)
within MACP [1]			WD	Reg.	Reg.	Reg.	Reg.	Reg.	WD	Reg.	Reg.	
present in Test Item			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
evaluated in this PT			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
Lab-Code SRM10-	NRL-SRM	Cat. [2]										
28		B	V		V	V		V	V			5 / 5
29	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
30		A	V	V	V	V	ND	V	V	V	V	9 / 8
31		A	V	V	V	V	ND		V	V	V	8 / 7
32		A	V	V	V		ND	V	V	V	V	8 / 7
33		A	V	V	V	V	ND	V	V	V	V	9 / 8
34		A	V	V	V	V	ND	V	V	V	V	9 / 8
35		A	V	V	V	V	ND	V	V	V	V	9 / 8
36		A	V	V		V	ND	V	V	V	V	8 / 7
37	x	B	V		V				V		V	4 / 4
38		A	V	V	V	V	ND	V	V	V	V	9 / 8
40		A	V	V	V	V	ND	V	V	V	V	9 / 8
41	x	B			V						V	2 / 2
42												0 / 0
43		A	V	V	V	V		V	V	V	V	8 / 8
44	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
45		A	V	V	V	V	ND	V	V	V	V	9 / 8
46		A	V	V	V	V		V	V	V	V	8 / 8
47	x	A	V	V	V	V	ND		V	V	V	8 / 7
48		B			V			V				2 / 2
49	x	B		V	V					V	V	4 / 4
50		B			V							1 / 1
51	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
52		B						V				1 / 1
53		B	V		V				V		V	4 / 4

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total	
Optional Compound listed in Target List			Bentazone	Bromoxynil	Dicamba	2,4-DP	Fluroxypyr	Glufosinate	N-Acetyl glufosinate	MPP	Ioxynil	MCPP	Paraquat	Phosphonic acid	TFNA	TFNG	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 14/ 5)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 23 / 13)
within MACP [1]			–	–	–	–	–	WD	WD	WD	WD	–	WD	WD	WD	WD		
present in Test Item			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
evaluated in this PT			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
Lab-Code SRM10-	NRL-SRM	Cat. [2]																
28		B	V	V		ND	ND				ND	ND					6 / 2	11 / 7
29	x	A		V		ND	ND	ND				ND			ND	V	7 / 2	16 / 10
30		A	V	V	ND	ND	ND	ND			ND	ND		V	ND	V	11 / 4	20 / 12
31		A	V	V		ND					ND	ND					5 / 2	13 / 9
32		A	V	V		ND	ND					ND					5 / 2	13 / 9
33		A	V	V	ND	ND	ND	ND			ND	ND	ND	V	ND	V	12 / 4	21 / 12
34		A	V	V		ND	ND	ND			ND	ND			ND	V	9 / 3	18 / 11
35		A											ND				1 / 0	10 / 8
36		A	V	V		ND	ND				ND	ND					6 / 2	14 / 9
37	x	B				ND											1 / 0	5 / 4
38		A	V		ND	ND						ND					4 / 1	13 / 9
40		A	V	V	ND	ND	ND				ND	ND					7 / 2	16 / 10
41	x	B									ND						1 / 0	3 / 2
42																	0 / 0	0 / 0
43		A	V	V	ND	ND	ND					ND					6 / 2	14 / 10
44	x	A	V				ND				ND	ND					4 / 1	13 / 9
45		A	V	V	ND	ND	ND				ND	ND			ND	V	9 / 3	18 / 11
46		A	V	V	ND	ND	ND	ND				ND		V			8 / 3	16 / 11
47	x	A				ND	ND	ND			ND	ND					5 / 0	13 / 7
48		B															0 / 0	2 / 2
49	x	B															0 / 0	4 / 4
50		B															0 / 0	1 / 1
51	x	A	V	V	ND	ND	ND		V		ND	ND			ND	V	10 / 4	19 / 12
52		B															0 / 0	1 / 1
53		B	V	V		ND	ND				ND	ND		V	ND	V	9 / 4	13 / 8

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds												
Compulsory Compound listed in Target List			2,4-D	Chlormequat	Dithiocarbamates	Ethephon	Fenbutatin Oxide	Glyphosate	MCPA	Mepiquat	Propamocarb	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 9 / 8)
within MACP [1]			WD	Reg.	Reg.	Reg.	Reg.	Reg.	WD	Reg.	Reg.	
present in Test Item			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
evaluated in this PT			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
Lab-Code SRM10-	NRL-SRM	Cat. [2]										
54	x	A	V	V	V		ND	V	V	V	V	8 / 7
55		A	V	V	V	V		V	V	V	V	8 / 8
56		B	V	V	V				V	V	V	6 / 6
57		A	V	V	V	V	ND	V	V	V	V	9 / 8
58		A	V	V	V	V	ND	V	V	V	V	9 / 8
59	x	B	V	V	V				V	V		5 / 5
60	x	A	V	V		V	ND	V	V	V	V	8 / 7
61		A	V	V	V	V	ND	V	V	V	V	9 / 8
62		B									V	1 / 1
63		A	V	V	V	V	ND	V	V	V	V	9 / 8
64	x	A	V	V	V	V		V	V	V	V	8 / 8
65	x	A	V	V		V	ND	V	V	V	V	8 / 7
66		B	V	V			ND		V	V	V	6 / 5
67	x	A	V	V	V	V	ND		V	V	V	8 / 7
68		B			V							1 / 1
69												0 / 0
70	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
71		B	V				ND				V	3 / 2
72		B	V		V	V	ND	V	V		V	7 / 6
73		B	V		V				V		V	4 / 4
74	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
75		A	V	V	V	V	ND	V	V	V	V	9 / 8
76		B	V		V				V	V	V	5 / 5
77		B	V	V		V	ND		V	V	V	7 / 6
78		A	V	V	V	V	ND	V	V	V	V	9 / 8
79		B	V						V		V	3 / 3

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																Total	
Optional Compound listed in Target List			Bentazone	Bromoxynil	Dicamba	2,4-DP	Fluroxypyr	Glufosinate	N-Acetyl glufosinate	MPP	Ioxynil	MCPP	Paraquat	Phosphonic acid	TFNA	TFNG	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 14/ 5)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 23 / 13)
within MACP [1]			–	–	–	–	–	WD	WD	WD	WD	–	WD	WD	WD	WD		
present in Test Item			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
evaluated in this PT			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
Lab-Code SRM10-	NRL-SRM	Cat. [2]																
54	x	A	V		ND	ND	ND	ND			ND	ND					7 / 1	15 / 8
55		A	V	V	ND	ND	ND	ND			ND	ND			ND	V	10 / 3	18 / 11
56		B	V	V		ND	ND				ND	ND					6 / 2	12 / 8
57		A	V	V		ND	ND	ND			ND	ND	ND	V			9 / 3	18 / 11
58		A	V	V	ND	ND	ND	ND	V	ND	ND	ND		V	ND	V	13 / 5	22 / 13
59	x	B															0 / 0	5 / 5
60	x	A	V	V				ND	**FN**		ND	ND		V			7 / 3	15 / 10
61		A	V	V	ND	ND	ND	ND	V	ND	ND	ND	ND	V	ND	V	14 / 5	23 / 13
62		B															0 / 0	1 / 1
63		A	V	V		ND	ND				ND			V			6 / 3	15 / 11
64	x	A	V	V		ND		ND			ND	ND	ND				7 / 2	15 / 10
65	x	A	V			ND						ND					3 / 1	11 / 8
66		B	V	V	ND	ND	ND				ND	ND					7 / 2	13 / 7
67	x	A	V	V		ND	ND				ND	ND	ND		ND	V	9 / 3	17 / 10
68		B															0 / 0	1 / 1
69																	0 / 0	0 / 0
70	x	A	V	V	ND	ND					ND	ND		V			7 / 3	16 / 11
71		B	V								ND						2 / 1	5 / 3
72		B	V	V	ND	ND	ND	**FP**			ND	ND			ND	V	10 / 3	17 / 9
73		B	V	V	ND	ND	ND				ND	ND			ND	V	9 / 3	13 / 7
74	x	A	V	V	ND	ND	ND	ND	V		ND	ND					9 / 3	18 / 11
75		A	V	V		ND	ND				ND	ND					6 / 2	15 / 10
76		B															0 / 0	5 / 5
77		B	V	V											ND	V	4 / 3	11 / 9
78		A	V	V	ND	ND	ND	ND			ND	ND	ND	V			10 / 3	19 / 11
79		B	V			ND					ND						3 / 1	6 / 4

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds												
Compulsory Compound listed in Target List			2,4-D	Chlormequat	Dithiocarbamates	Ethephon	Fenbutatin Oxide	Glyphosate	MCPA	Mepiquat	Propamocarb	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 9 / 8)
within MACP [1]			WD	Reg.	Reg.	Reg.	Reg.	Reg.	WD	Reg.	Reg.	
present in Test Item			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
evaluated in this PT			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	
Lab-Code SRM10-	NRL-SRM	Cat. [2]										
80		B	V	V					V	V	V	5 / 5
81	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
82		A	V	V	V	V		V	V	V	V	8 / 8
83		B	V	V				V	V	V	V	6 / 6
84	x	A	V	V	V	V		V	V	V	V	8 / 8
85		A	V	V	V	V	ND		V	V	V	8 / 7
86		B			V							1 / 1
87		A	V	V	V	V	ND		V	V	V	8 / 7
88		B			V							1 / 1
89		A	V	V	V	V		V	V	V	V	8 / 8
90		B	V	V	V				V	V	V	6 / 6
91	x	B #	V	V	V	V	ND	V	V	V	V	9 / 8
92												0 / 0
93		B			V							1 / 1
94	x	A	V	V	V	V	ND	V	V	V	V	9 / 8
95		B		V	**FN**	V		V		V	V	6 / 5
96												0 / 0
97	x	B	V	V			ND		V	V	V	6 / 5
98	x	B	V	V	V				V	V	V	6 / 6
99		B			V							1 / 1
100		A	V	V	V	V	ND	V	V	V	V	9 / 8
101												0 / 0
102		B			V							1 / 1
103		B	V		V	V			V		V	5 / 5
104		B			V							1 / 1

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total	
Optional Compound listed in Target List			Bentazone	Bromoxynil	Dicamba	2,4-DP	Fluroxypyr	Glufosinate	N-Acetyl glufosinate	MPP	Ioxynil	MCPP	Paraquat	Phosphonic acid	TFNA	TFNG	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 14/ 5)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 23 / 13)
within MACP [1]			–	–	–	–	–	WD	WD	WD	WD	–	WD	WD	WD	WD		
present in Test Item			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
evaluated in this PT			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
Lab-Code SRM10-	NRL-SRM	Cat. [2]																
80		B	V	V	ND	ND	ND				ND	ND	ND				8 / 2	13 / 7
81	x	A		V		ND	ND		V	ND	ND			V	ND	V	9 / 4	18 / 12
82		A	V	V		ND		ND				ND		V	ND	V	8 / 4	16 / 12
83		B	V	V	ND	ND	ND				ND	ND					7 / 2	13 / 8
84	x	A	V	V		ND					ND	ND					5 / 2	13 / 10
85		A	V	V			ND	ND									4 / 2	12 / 9
86		B															0 / 0	1 / 1
87		A	V	V	ND	ND	ND				ND	ND		V	ND	V	10 / 4	18 / 11
88		B															0 / 0	1 / 1
89		A	V	V	ND	ND	ND				ND	ND			ND		8 / 2	16 / 10
90		B				ND	ND					ND					3 / 0	9 / 6
91	x	B #	V	V	ND	ND	ND	**FP**			ND	ND			ND	V	10 / 3	19 / 11
92																	0 / 0	0 / 0
93		B															0 / 0	1 / 1
94	x	A			ND	ND	ND				ND	ND					5 / 0	14 / 8
95		B	V				ND										2 / 1	8 / 6
96																	0 / 0	0 / 0
97	x	B				ND	ND					ND					3 / 0	9 / 5
98	x	B	V			ND	ND				ND	ND					5 / 1	11 / 7
99		B															0 / 0	1 / 1
100		A	V	V	ND	ND	ND	ND			ND	ND	ND	V	ND	V	12 / 4	21 / 12
101																	0 / 0	0 / 0
102		B															0 / 0	1 / 1
103		B	V	V	ND	ND					ND	ND			ND	V	8 / 3	13 / 8
104		B															0 / 0	1 / 1

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

Compulsory Compounds													
Compulsory Compound listed in Target List			2,4-D	Chlormequat	Dithiocarbamates	Ethephon	Fenbutatin Oxide	Glyphosate	MCPA	Mepiquat	Propamocarb	Analysed / correctly found among COMPULSORY compounds within the EUPT-Target Pesticides List (max. 9 / 8)	
within MACP [1]			WD	Reg.	Reg.	Reg.	Reg.	Reg.	WD	Reg.	Reg.		
present in Test Item			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes		
evaluated in this PT			Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes		
Lab-Code SRM10-	NRL-SRM	Cat. [2]											
105		B									V	1 / 1	
106		A	V	V	V		ND	V	V	V	V	8 / 7	
107		B	V	V	V				V	V	V	6 / 6	
108		B			V							1 / 1	
109		B			V						V	2 / 2	
110												0 / 0	
111		B		V				V		V	V	4 / 4	
112		B			V							1 / 1	
3rd-113		B	V	V	V	V	ND	V	V	V	V	9 / 8	
3rd-114		B	V		V		ND	V	V	V	V	7 / 6	
3rd-115		B	V	V	V	**FN**		**FN**	V			6 / 4	
3rd-116		A	V	V	V	V	ND	V	V	V	V	9 / 8	
3rd-117		B	V		V	V						3 / 3	
3rd-118		A	V	V	V	V	ND	**FN**	V	V	V	9 / 7	

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

[#] Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories and laboratories that have not submitted results)

	Optional Compounds																	Total
Optional Compound listed in Target List			Bentazone	Bromoxynil	Dicamba	2,4-DP	Fluroxypyr	Glufosinate	N-Acetyl glufosinate	MPP	Ioxynil	MCPP	Paraquat	Phosphonic acid	TFNA	TFNG	Analysed / correctly found among OPTIONAL compounds within the EUPT-Target Pesticides List (max. 14/ 5)	analysed / correctly found among all compounds within the EUPT-Target Pesticides List (max. 23 / 13)
within MACP [1]			–	–	–	–	–	WD	WD	WD	WD	–	WD	WD	WD	WD		
present in Test Item			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
evaluated in this PT			Yes	Yes	No	No	No	No	Yes	No	No	No	No	Yes	No	Yes		
Lab-Code SRM10-	NRL-SRM	Cat. [2]																
105		B															0 / 0	1 / 1
106		A	V	V		ND					ND	ND					5 / 2	13 / 9
107		B	V		ND	ND	ND			ND	ND	ND					7 / 1	13 / 7
108		B															0 / 0	1 / 1
109		B															0 / 0	2 / 2
110																	0 / 0	0 / 0
111		B						ND					ND				2 / 0	6 / 4
112		B															0 / 0	1 / 1
3rd-113		B	V	**FN**	(FP)	ND	ND	ND			ND	ND	ND		ND	V	11 / 2	20 / 10
3rd-114		B	V	V	ND		ND	ND			ND	ND	ND				8 / 2	15 / 8
3rd-115		B	V	**FN**	ND			ND					ND				5 / 1	11 / 5
3rd-116		A	V		ND	ND											3 / 1	12 / 9
3rd-117		B	V	V													2 / 2	5 / 5
3rd-118		A	V	V													2 / 2	11 / 9

1) MACP = EU Multiannual Control Program; Reg.: MACP Regulation; WD: MACP Working Document ("Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin")

2) Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds present in the test item and that have not reported any false positive result, see section 4.4.4, p. 32)

V = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected";

Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result

Laboratories having reported a sufficient number of results from the compounds present in the test item, but being still classified into Category B due to the submission of false positive results

(FP): Result reported as "< MRRL" and, therefore, not regarded as FP

4.2 Analysis of Blank Material

Detection of analytes on the target pesticides list in the blank material was reported in very few cases. ***Dithiocarbamates*** was reported twice at or below the MRRL of 0.05 mg/kg and twice above the MRRL (SRM10-104: 0.0275 mg/kg; SRM10-40: 0.05 mg/kg; SRM10-59: 0.21 mg/kg and SRM10-93: 0.222 mg/kg). ***Glyphosate*** (MRRL = 0.05 mg/kg) was reported by SRM10-38 at 0.051 mg/kg and ***chlormequat*** (MRRL = 0.01 mg/kg) by SRM10-38 at 0.043 mg/kg. Since the organisers and all other laboratories having analysed for these compounds did not detect them in the blank material, these findings were regarded as analytical errors.

4.3 Assigned Values and Target Standard Deviations

To establish the assigned value (x_{pt}) of each analyte present in the test item, the mean of robust statistics (x^*) of all results submitted by laboratories from EU and EFTA countries was used. Results from third country laboratories were not taken into account. Based on these assigned values, z-scores were calculated for all submitted results using the FFP-approach (see **Section 4.4.3, p. 32)**, and a preliminary report was released on 30 June, 2015. The assigned values and their uncertainties ($u(x_{pt})$) were calculated as described under **Section 2.2 (p. 9)**. In all cases the uncertainties were within the tolerance (see results **Table 4-3**).

The relative standard deviations of the assigned value based on robust statistics (CV^*) were 36.9 % for ***dithiocarbamates*** and 30.8 % for ***ethephon***, which were both much higher than the FFP-RSD value of 25 %. The CV^*-values of all other compulsory analytes were lower than 25 %. Among the optional analytes only the

Table 4-3: Assigned values, uncertainties of assigned values and CV^* values calculated for all compounds present in the test item

	Compound	No. of FNs	No. of numerical results (EU+EFTA)	Assigned Value [1] [mg/kg]	$u(x_{pt})$ [2] [mg/kg]	$u(x_{pt})$ Tolerance [mg/kg]	Judgement for UAV-test	CV^* [3] [%]
Compulsory Compounds	2,4-D		82	0.092	+/-0.0023	0.0069	passed	18.2
	Chlormequat		75	0.167	+/-0.0044	0.0126	passed	18.2
	Dithiocarbamates	1	85	0.559	+/-0.0280	0.0419	passed	36.9
	Ethephon		61	0.162	+/-0.0080	0.0121	passed	30.8
	Glyphosate	2	62	0.568	+/-0.0206	0.0426	passed	22.8
	MCPA	1	79	0.081	+/-0.0022	0.0061	passed	18.9
	Mepiquat		76	0.114	+/-0.0030	0.0085	passed	18.5
	Propamocarb		87	0.067	+/-0.0021	0.0050	passed	23.3
	Average [4] CV^*							**23.5**
Optional Compounds	Bentazone		69	0.098	+/-0.0027	0.0073	passed	18.5
	Bromoxynil		65	0.125	+/-0.0033	0.0094	passed	17.0
	N-Acetyl glufosinate	1	15	0.319	+/-0.0121	0.0239	passed	11.8
	Phosphonic acid	1	24	0.584	+/-0.0406	0.0438	passed	27.3
	TFNG		30	0.168	+/-0.0071	0.0126	passed	18.6
	Average [4] CV^*							**18.6**
	Overall Average [4] CV^*							**21.6**

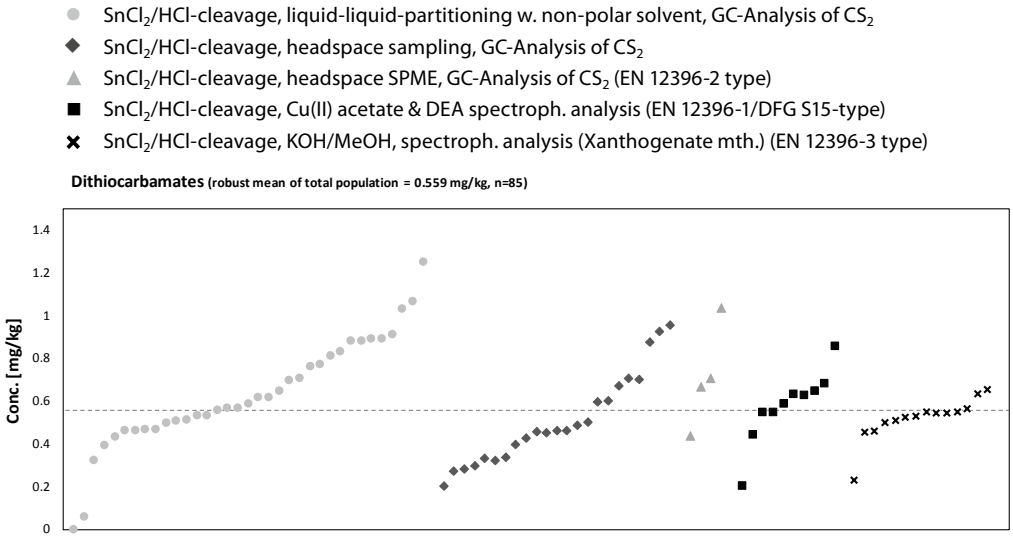
1: Robust mean based on the entire population of results from EU and EFTA laboratories
2: $u(x_{pt})$: Uncertainty of assigned value based on robust estimate of participant mean, calculated as shown under **Section 2.2 (p. 9)**
3: CV^*: Relative standard deviation based on robust statistics
4: The average CV^* is given for information purpose only. CV^*s of individual compounds or average CV^*s of individual compounds or related compounds over many PTs are more meaningfull and conclusive.

CV^* of ***phosphonic acid*** (27.3 %) was slightly higher than the FFP-RSD of 25 %. Although only 15 results were submitted for ***N-acetyl glufosinate***, that was for the first time tested in an EUPT-SRM, its CV^* was with 11.8 % the lowest in this PT. Such trends have been also observed in the past and can be explained by the fact that the few laboratories submitting results for newly introduced compounds are typically the very experienced ones.

The average CV^*s of compulsory and optional analytes were 23.5 % and 18.6 %, respectively. The latter is clearly lower than the FFP-RSD of 25 %. The overall average CV^* of this PT was 21.6 %. These average values are given for information only and are less conclusive compared to CV^*s or average CV^*s of individual or related compounds over one or many PTs.

A very strong deviation between the assigned value of ***N-acetyl glufosinate*** (0.319 mg/kg) and the mean values of the stability and homogeneity tests (0.186 mg/kg) was detected. To investigate this issue all participants having submitted results for ***N-acetyl glufosinate*** were asked to name the commercial providers and batch numbers of the standards they have used for the present PT. These standards were then purchased by the organisers and checked against a standard kindly provided by a manufacturer of plant protection products (PPPs). For the preparation of the standard solutions all relevant convertion factors (e.g. from salt to pure substance and purity) were taken into account. Quantitative analysis of the standard solutions by LC-MS/MS revealed that the ***N-acetyl glufosinate*** concentrations of the standards obtained from commercial providers only contained ca. 51, 55 and 60 % of the concentration of the PPP-manufacturer, which was set at 100 %. Analysis by LC-ToF and NMR revealed by far more impurities in the commercial standards compared to the standard by the PPP-manufacturer. Applying the factor obtained for the standard which was most frequently used by the participants, the assigned value of participants' results shift from 0.319 to 0.186 mg/kg, which exactly matches the mean value of the homogeneity test. As the concentrations of the standards used by all participants were relatively close together, the assigned value was considered suitable for the calculation of z-scores.

As can be seen in **Appendix 5** the kernel density estimate of the ***dithiocarbamates*** results using a default band-width (calculated according to The Royal Society of Chemistry, AMC technical brief, No. 4, 2001) visually shows possible evidence of bimodality with a second maximum being visible at the z-score of 2.2 using the overall robust mean as assigned value. This z-score corresponds to a concentration of 0.87 mg/kg. **Figure 4-1 (p. 30)** shows the populations of the various method types together with their robust mean values and CV^*s. The methods involving head-space showed the broadest results distribution (44.1 %) followed by methods involving liquid-liquid partitioning (34.9 %). The spectrophotometric methods showed the narrowest distribution with a CV^* of 21.1 % for the method employing Cu(II) acetate and diethanolamine, and a CV^* of 12.4 % for the method using xanthogenate. Overall the spectrophotometric methods showed a CV^* of 16.7 %. It was checked whether this trend was due to the differences in the sample size used by the laboratories employing the different methods (headspace methods 8.7 g on average, liquid-liquid partitioning-methods 26 g, and spectrophotometric methods 62 g), but no clear trend could be seen. As far as the robust means of the different methods were concerned, the results of the laboratories employing methods involving liquid-liquid partitioning showed a robust mean value of 0.649 mg/kg, which is 16 % higher than the assigned value of 0.559 mg/kg derived from the entire population (this corresponds to a z-score-shift of 0.64). The results obtained using methods employing headspace analysis showed a robust mean value of 0.525 mg/kg, which is just 6 % lower than the assigned value. Finally the results obtained using methods employing headspace analyses showed a robust mean value of 0.552 mg/kg, which is only 1 % lower than the assigned value. In any case, due to the inability to define which of the methods was biased and given that ***dithiocarbamates*** passed the UAV-test (see **Table 4-3, p. 28**), it was decided to still use the results of the entire population to calculate the assigned value. Given the consistently high CV^* values obtained for ***dithiocarbamates*** (**Table 4-3**), z-scores were additionally calculated using FFP-RSDs of 30 % and 35 % for informative purposes only (**Appendix 7**). Furthermore, also for information only, the results of



No. of Numerical Results	33	23	4	10	14
No. of FNs	1	0	0	0	0
Robust Mean [mg/kg]	0.649	0.492	0.708	0.593	0.527
CV^*	34.9 %	42.9 %	39.3 %	21.1 %	12.4 %

	Grouped Methods		
	involving Liquid-Liquid Partitioning	involving Head-Space	Spectrophotometric
No. of Numerical Results	33	27	24
No. of FNs	1	0	0
Robust Mean [mg/kg]	0.649	0.525	0.552
CV^*	34.9 %	44.1 %	16.7 %

Figure 4-1: Comparison of the dithiocarbamates results generated by various method-types. Only results of laboratories from EU and EFTA countries were considered. The dotted line represents the assigned value (robust mean) of the entire population.

the laboratories employing the liquid-liquid partitioning involving methods were evaluated based on the robust mean of this particular population and using the FFP-RSD of 25 %. In the upper range this resulted in a shift of 2 unacceptable values to questionable and of 5 questionable values to acceptable. In the lower range there was no changes in the classification of performance (**Appendix 7**).

In the case of ***ethephon*** the high CV^* was surely due to a couple of factors (see also the discussion in **Section 4.5.5, p. 64**). As can be seen in **Appendix 5** there were several labs reporting results in the lower range (z-scores < -2). Looking at the methodological information it becomes clear that several laboratories have used inappropriate methodologies; in two cases QuEChERS method was used and in further two cases the labs used inappropriate isotopically labelled internal standards (IL-glyphosate and IL-perchlorate). Nevertheless, it was still decided to use the results of the entire population for the calculation of the assigned value.

4.4 Assessment of Laboratory Performance

4.4.1 False Positives

Three laboratories reported in four cases (3× *glufosinate* and 1× *MPP*) numerical results for analytes in the Target Pesticides List which were neither spiked to the sample material, nor detected by the organisers and the overwhelming majority of the participants (**Table 4-4**). All these results exceeded both the laboratories'

Table 4-4: Overview of false positive and potentially false positive results reported by participating laboratories

Compound	PT-Code	Analysed	Reported Result [mg/kg]	RL [mg/kg]	MRRL [mg/kg]	Judgement
Dicamba	SRM10-3rd-113	yes	0.01	0.01	0.02	–
Glufosinate	SRM10-8	yes	0.105	0.05	0.02	FP
	SRM10-72	yes	0.209	0.02	0.02	FP
	SRM10-91	yes	0.167	0.02	0.02	FP
MPP	SRM10-8	yes	0.058	0.01	0.02	FP

reporting limits for these compounds and the respective MRRLs in the Target Pesticides List and were therefore judged as false positives. All these four false positive results concerned optional analytes.

One laboratory reported a numerical result for *dicamba* at the concentration of its own RL. As the RL of the lab was lower than the MRRL, this result was not judged as a false positive.

4.4.2 False Negatives

Among the compulsory compounds there were 7 cases (4× ***glyphosate***, 1× ***dithiocarbamates***, 1× ***ethephon***, and 1× ***MCPA***) where the participants reported "analysed, but not detected" for target compounds spiked to the test item and detected by the majority of the laboratories targeting them (**Table 4-5**). Four of these cases concerned laboratories from EU and EFTA countries and the other three two laboratories from third countries. As the assigned values for these four analytes were sufficiently distant from the MRRLs, these results were judged as false negatives. These 7 false negative results represented 1.1 % of the 650 results reported from all participating laboratories for compulsory target compounds present in the test item. Among EU/EFTA labs the FN-rate for COMPULSORY compounds was 0.6 % (4 out of 611 results).

Among the optional compounds there were 4 cases (2× ***bromoxynil***, 1× ***N-acetyl glufosinate*** and 1× ***phosphonic acid***) where the participants reported "analysed, but not detected" for target compounds that were spiked to the test item and detected by the majority of the laboratories targeting them (**Table 4-5**). Two of

Table 4-5: Overview of false negative results reported by participating laboratories (including 3rd country laboratories)

Compound		PT-Code	Analysed	Detected	RL [mg/kg]	MRRL [mg/kg]	Assigned Value [mg/kg]	Judgement
Compulsory Compounds	Dithiocarbamates	SRM10-95	yes	no	0.05	0.05	0.559	False Negative
	Ethephon	SRM10-3rd-115	yes	no	0.5	0.02	0.162	False Negative
	Glyphosate	SRM10-13	yes	no	0.01	0.05	0.568	False Negative
	Glyphosate	SRM10-26	yes	no	0.5	0.05	0.568	False Negative
	Glyphosate	SRM10-3rd-115	yes	no	0.01	0.05	0.568	False Negative
	Glyphosate	SRM10-3rd-118	yes	no	not reported	0.05	0.568	False Negative
	MCPA	SRM10-1	yes	no	0.01	0.01	0.081	False Negative
Optional Compounds	Bromoxynil	SRM10-3rd-113	yes	no	not reported	0.01	0.125	False Negative
	Bromoxynil	SRM10-3rd-115	yes	no	0.01	0.01	0.125	False Negative
	N-Acetyl glufosinate	SRM10-60	yes	no	0.04	0.02	0.319	False Negative
	Phosphonic acid	SRM10-14	yes	no	0.05	0.05	0.584	False Negative

them were reported by two laboratories from third countries, the other two by participants from EU and EFTA laboratories. These 4 false negative results accounted for 1.8 % of the 217 results reported from all participating laboratories for optional target compounds present in the test item. Among EU/EFTA labs the FN-rate for OPTIONAL compounds was 1.0 % (2 out of 205 results).

4.4.3 Laboratory Performance Based on z-Scores

All individual z-scores were calculated using the FFP-RSD of 25 %. **Table 4-6** shows the overall classification of z-scores achieved by all laboratories for compulsory and optional compounds. The respective rules are shown in **Section 2.4 (p. 10)**. Among results submitted by laboratories from EU and EFTA countries "Acceptable" z-scores were achieved by 78 – 96 % (89 % on average) of the labs in the case of compulsory compounds and by 80 – 95 % (92 % on average) in the case of optional compounds. Overall 90 % of the results submitted by EU- and EFTA-countries were acceptable, 7 % questionable and 4 % unacceptable (including false negatives). The respective overall figures of 3rd country labs were 57 %, 18 % and 25 %. Deviations of the sum from 100% are due to rounding. False positive results were not counted.

A compilation of all individual results and z-scores for each laboratory is shown in **Table 4-7 (p. 34)** and **Table 4-8 (p. 40)** for compulsory and optional compounds, respectively. The corresponding kernel density histograms showing the distribution of the reported results are shown in **Appendix 5**. A graphic representation of the z-score distribution of each target analyte present in the test item can be seen in **Appendix 6**.

4.4.4 Laboratory Classification Based on Scope

All participating laboratories having reported results were classified into categories A or B based on their "scope", as reflected by the number of target analytes correctly detected among the total number of COMPULSORY pesticides present in the test item. Following the rules defined in the General Protocol (5th Edition, see **Appendix 9**), a laboratory had to fulfill the following conditions in order to be classified into Category A in the present PT: a) correct detection of at least seven out of the eight compulsory pesticides present in the test item, and b) no false positive results. Two laboratories (SRM10-8 and SRM10-91) had submitted results for 7 of the 8 compulsory compounds, but were still classified into Category B due to the submission of false positive result(s).

A total of 55 EU and EFTA laboratories (53 %) were classified into Category A and 49 (47 %) into Category B. Three of the six third-country laboratories were classified into Category A, and the other ones into Category B. Considering only the compulsory compounds the laboratories from EU and EFTA countries classified into Category A achieved an overall AAZ of 0.8 (n = 440), whereas those classified into Category B achieved an overall AAZ[1] of 0.9 (n = 392).

Table 4-9 (p. 46) and **Table 4-10 (p. 47)** show the details of laboratories classified into Category A and B, respectively. For informative purposes, the AAZ was calculated for laboratories with 5 or more individual z-scores. For the AAZ calculation any z-scores > 5 were set at 5.

(Text is continued on page 49 after **Table 4-10**)

1 Overall AAZ was calculated based on the overall population of z-scores of all EU and EFTA laboratories.

Table 4-6: Overall classification of z-scores

EU and EFTA laboratories						
	Compound	No. of results	Acceptable No. (%)	Questionable No. (%)	Unacceptable [1] No. (%)	FNs No.
Compulsory Compounds	2,4-D	82	79 (96 %)	2 (2 %)	1 (1 %)	
	Chlormequat	75	68 (91 %)	5 (7 %)	2 (3 %)	
	Dithiocarbamates	86	67 (78 %)	13 (15 %)	6 (7 %)	1
	Ethephon	61	52 (85 %)	5 (8 %)	4 (7 %)	
	Glyphosate	64	56 (88 %)	5 (8 %)	3 (5 %)	2
	MCPA	80	74 (93 %)	4 (5 %)	2 (3 %)	1
	Mepiquat	76	69 (91 %)	3 (4 %)	4 (5 %)	
	Propamocarb	87	78 (90 %)	7 (8 %)	2 (2 %)	
	Subtotal	**611**	**543 (89 %)**	**44 (7 %)**	**24 (4 %)**	**4**
Optional Compounds	Bentazone	69	64 (93 %)	4 (6 %)	1 (1 %)	
	Bromoxynil	65	62 (95 %)	3 (5 %)	0 (0 %)	
	N-Acetyl glufosinate	16	15 (94 %)	0 (0 %)	1 (6 %)	1
	Phosphonic acid	25	20 (80 %)	3 (12 %)	2 (8 %)	1
	TFNG	30	28 (93 %)	0 (0 %)	2 (7 %)	
	Subtotal	**205**	**189 (92 %)**	**10 (5 %)**	**6 (3 %)**	**2**
Overall EU/EFTA (Average)		**816**	**732 (90 %)**	54 (7 %)	**30 (4 %)**	**6**

3rd country laboratories						
	Compound	No. of results	Acceptable	Questionable	Unacceptable [1]	FNs
Compulsory Compounds	2,4-D	6	4 (67 %)	2 (33 %)	0 (0 %)	
	Chlormequat	4	2 (50 %)	0 (0 %)	2 (50 %)	
	Dithiocarbamates	6	5 (83 %)	1 (17 %)	0 (0 %)	
	Ethephon	5	2 (40 %)	1 (20 %)	2 (40 %)	1
	Glyphosate	5	2 (40 %)	0 (0 %)	3 (60 %)	2
	MCPA	5	3 (60 %)	1 (20 %)	1 (20 %)	
	Mepiquat	4	3 (75 %)	0 (0 %)	1 (25 %)	
	Propamocarb	4	3 (75 %)	0 (0 %)	1 (25 %)	
	Subtotal	**39**	**24 (62 %)**	**5 (13 %)**	**10 (26 %)**	**3**
Optional Compounds	Bentazone	6	3 (50 %)	2 (33 %)	1 (17 %)	
	Bromoxynil	5	1 (20 %)	2 (40 %)	2 (40 %)	2
	N-Acetyl glufosinate	0	0 (0 %)	0 (0 %)	0 (0 %)	
	Phosphonic acid	0	0 (0 %)	0 (0 %)	0 (0 %)	
	TFNG	1	1 (100 %)	0 (0 %)	0 (0 %)	
	Subtotal	**12**	**5 (42 %)**	**4 (33 %)**	**3 (25 %)**	**2**
Overall 3rd country (Average)		**51**	**29 (57 %)**	9 (18 %)	**13 (25 %)**	**5**

1) including false negatives (FNs)

Table 4-7: Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				2,4-D (free acid)		Chlormequat		Dithiocarbamates		Ethephon	
Assigned Value [mg/kg]				0.092		0.167		0.559		0.162	
MRRL [mg/kg]				0.010		0.010		0.050		0.020	
*CV**				18.2 %		18.2 %		36.9 %		30.8 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found, max. 9 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1		8 / 6	B	0.095	0.1	0.208	1	0.590	0.2		
2		9 / 8	A	0.082	-0.4	0.155	-0.3	0.635	0.5	0.151	-0.3
3		9 / 8	A	0.098	0.3	0.137	-0.7	0.698	1	0.148	-0.3
4	x	9 / 8	A	0.127	1.5	0.159	-0.2	0.950	2.8	0.215	1.3
5		9 / 8	A	0.095	0.1	0.200	0.8	0.320	-1.7	0.130	-0.8
6	x	9 / 8	A	0.098	0.3	0.136	-0.8	0.458	-0.7	0.157	-0.1
7		1 / 1	B					0.532	-0.2		
8		8 / 8	B#	0.090	-0.1	0.226	1.4	0.450	-0.8	0.025	-3.4
9		5 / 5	B	0.092	0	0.167	0	0.774	1.5		
10		9 / 8	A	0.106	0.6	0.212	1.1	0.462	-0.7	0.185	0.6
11		9 / 8	A	0.096	0.2	0.159	-0.2	0.547	-0.1	0.162	0
12	x	9 / 8	A	0.098	0.3	0.168	0	0.392	-1.2	0.169	0.2
13		1 / 0	B								
14		4 / 4	B			0.152	-0.4			0.162	0
15		9 / 8	A	0.092	0	0.158	-0.2	0.435	-0.9	0.193	0.8
16		9 / 8	A	0.065	-1.2	0.136	-0.8	0.832	2	0.139	-0.6
18		6 / 6	B	0.068	-1	0.154	-0.3				
19		6 / 6	B	0.110	0.8	0.130	-0.9	0.650	0.6		
20		9 / 8	A	0.077	-0.7	0.172	0.1	0.500	-0.4	0.178	0.4
21		9 / 8	A	0.088	-0.2	0.171	0.1	0.883	2.3	0.159	-0.1
22		7 / 6	B	0.103	0.5			0.704	1	0.193	0.8
23	x	8 / 8	A	0.118	1.1	0.171	0.1	0.210	-2.5	0.158	-0.1
24	x	4 / 3	B	0.013	-3.4						
25		9 / 8	A	0.106	0.6	0.214	1.1	0.648	0.6	0.139	-0.6
26	x	9 / 7	A	0.092	0	0.183	0.4	0.325	-1.7	0.388	5.6
27		9 / 8	A	0.111	0.8	0.170	0.1	0.270	-2.1	0.153	-0.2
28		5 / 5	B	0.078	-0.6			0.498	-0.4	0.164	0.1
29	x	9 / 8	A	0.094	0.1	0.154	-0.3	0.558	0	0.218	1.4
30		9 / 8	A	0.105	0.6	0.179	0.3	0.228	-2.4	0.141	-0.5
31		8 / 7	A	0.062	-1.3	0.280	2.7	0.460	-0.7	0.047	-2.8
32		8 / 7	A	0.082	-0.4	0.240	1.7	0.860	2.2		
33		9 / 8	A	0.135	1.9	0.154	-0.3	0.484	-0.5	0.210	1.2
34		9 / 8	A	0.026	-2.9	0.120	-1.1	0.688	0.9	0.137	-0.6
35		9 / 8	A	0.071	-0.9	0.161	-0.2	0.568	0.1	0.240	1.9
36		8 / 7	A	0.109	0.7	0.080	-2.1			0.411	6.2
37	x	4 / 4	B	0.095	0.1			0.280	-2		
38		9 / 8	A	0.083	-0.4	0.162	-0.1	0.696	1	0.224	1.5
40		9 / 8	A	0.092	0	0.134	-0.8	0.541	-0.1	0.128	-0.8

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-7 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

	COMPULSORY Compound			Glyphosate		MCPA		Mepiquat		Propamocarb	
	Assigned Value [mg/kg]			0.568		0.081		0.114		0.067	
	MRRL [mg/kg]			0.050		0.010		0.010		0.010	
	*CV**			22.8 %		18.9 %		18.5 %		23.3 %	
	Lab code SRM10-	NRL-SRM	Analysed / corr. found, max. 9 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
	1		8 / 6	B	0.697	0.9	FN	-3.5	0.112	-0.1	0.081	0.9
	2		9 / 8	A	0.616	0.3	0.061	-1	0.122	0.3	0.053	-0.8
	3		9 / 8	A	0.506	-0.4	0.090	0.4	0.101	-0.4	0.098	1.9
	4	x	9 / 8	A	0.527	-0.3	0.125	2.2	0.124	0.4	0.053	-0.8
	5		9 / 8	A	0.550	-0.1	0.095	0.7	0.110	-0.1	0.075	0.5
	6	x	9 / 8	A	0.568	0	0.095	0.7	0.115	0	0.076	0.6
	7		1 / 1	B								
	8		8 / 8	B#	0.262	-2.2	0.081	0	0.093	-0.7	0.096	1.8
	9		5 / 5	B					0.114	0	0.087	1.2
	10		9 / 8	A	0.639	0.5	0.096	0.7	0.139	0.9	0.079	0.7
	11		9 / 8	A	0.421	-1	0.082	0	0.100	-0.5	0.060	-0.4
	12	x	9 / 8	A	0.582	0.1	0.091	0.5	0.106	-0.3	0.068	0.1
	13		1 / 0	B	FN	-3.6						
	14		4 / 4	B	0.775	1.5			0.101	-0.4		
	15		9 / 8	A	0.640	0.5	0.080	0	0.116	0.1	0.071	0.3
	16		9 / 8	A	0.576	0.1	0.061	-1	0.115	0	0.055	-0.7
	18		6 / 6	B	0.620	0.4	0.058	-1.1	0.090	-0.8	0.081	0.9
	19		6 / 6	B			0.090	0.4	0.076	-1.3	0.068	0.1
	20		9 / 8	A	0.550	-0.1	0.082	0	0.105	-0.3	0.082	0.9
	21		9 / 8	A	0.453	-0.8	0.082	0	0.114	0	0.074	0.4
	22		7 / 6	B	0.607	0.3	0.089	0.4			0.089	1.4
	23	x	8 / 8	A	0.788	1.6	0.100	0.9	0.120	0.2	0.057	-0.6
	24	x	4 / 3	B			0.029	-2.6			0.025	-2.5
	25		9 / 8	A	0.623	0.4	0.087	0.3	0.146	1.1	0.064	-0.2
	26	x	9 / 7	A	FN	-3.6	0.080	-0.1	0.120	0.2	0.086	1.2
	27		9 / 8	A	0.670	0.7	0.115	1.7	0.100	-0.5	0.072	0.3
	28		5 / 5	B	0.651	0.6	0.068	-0.6				
	29	x	9 / 8	A	0.619	0.4	0.081	0	0.105	-0.3	0.055	-0.7
	30		9 / 8	A	0.564	0	0.075	-0.3	0.135	0.8	0.077	0.6
	31		8 / 7	A			0.075	-0.3	0.160	1.6	0.067	0
	32		8 / 7	A	0.340	-1.6	0.068	-0.6	0.140	0.9	0.056	-0.6
	33		9 / 8	A	0.620	0.4	0.085	0.2	0.157	1.5	0.062	-0.3
	34		9 / 8	A	2.850	16.1	0.016	-3.2	0.110	-0.1	0.020	-2.8
	35		9 / 8	A	0.598	0.2	0.069	-0.6	0.114	0	0.056	-0.6
	36		8 / 7	A	0.676	0.8	0.096	0.8	0.095	-0.7	0.052	-0.9
	37	x	4 / 4	B			0.079	-0.1			0.034	-2
	38		9 / 8	A	0.495	-0.5	0.081	0	0.107	-0.2	0.071	0.3
	40		9 / 8	A	0.593	0.2	0.074	-0.4	0.102	-0.4	0.070	0.2

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-7 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				2,4-D (free acid)		Chlormequat		Dithiocarbamates		Ethephon	
Assigned Value [mg/kg]				0.092		0.167		0.559		0.162	
MRRL [mg/kg]				0.010		0.010		0.050		0.020	
*CV**				18.2 %		18.2 %		36.9 %		30.8 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found, max. 9 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
41	x	2 / 2	B					0.334	-1.6		
42		0 / 0									
43		8 / 8	A	0.081	-0.5	0.155	-0.3	0.870	2.2	0.150	-0.3
44	x	9 / 8	A	0.100	0.3	0.198	0.7	0.393	-1.2	0.351	4.7
45		9 / 8	A	0.099	0.3	0.150	-0.4	0.661	0.7	0.148	-0.3
46		8 / 8	A	0.108	0.7	0.178	0.3	0.496	-0.5	0.168	0.2
47	x	8 / 7	A	0.123	1.3	0.168	0	0.544	-0.1	0.155	-0.2
48		2 / 2	B					0.881	2.3		
49	x	4 / 4	B			1.350	28.3	0.530	-0.2		
50		1 / 1	B					0.465	-0.7		
51	x	9 / 8	A	0.088	-0.2	0.169	0	0.706	1.1	0.185	0.6
52		1 / 1	B								
53		4 / 4	B	0.100	0.3			0.920	2.6		
54	x	8 / 7	A	0.092	0	0.153	-0.3	0.432	-0.9		
55		8 / 8	A	0.092	0	0.258	2.2	0.568	0.1	0.270	2.7
56		6 / 6	B	0.085	-0.3	0.156	-0.3	0.451	-0.8		
57		9 / 8	A	0.092	0	0.117	-1.2	0.452	-0.8	0.221	1.5
58		9 / 8	A	0.049	-1.9	0.194	0.6	0.328	-1.7	0.146	-0.4
59	x	5 / 5	B	0.072	-0.9	0.163	-0.1	1.064	3.6		
60	x	8 / 7	A	0.083	-0.4	0.166	0			0.068	-2.3
61		9 / 8	A	0.090	-0.1	0.150	-0.4	0.700	1	0.150	-0.3
62		1 / 1	B								
63		9 / 8	A	0.130	1.6	0.194	0.6	1.030	3.4	0.150	-0.3
64	x	8 / 8	A	0.083	-0.4	0.168	0	1.030	3.4	0.196	0.8
65	x	8 / 7	A	0.074	-0.8	0.249	1.9			0.215	1.3
66		6 / 5	B	0.100	0.3	0.185	0.4				
67	x	8 / 7	A	0.111	0.8	0.154	-0.3	0.894	2.4	0.124	-0.9
68		1 / 1	B					0.630	0.5		
69		0 / 0									
70	x	9 / 8	A	0.091	-0.1	0.167	0	0.589	0.2	0.152	-0.2
71		3 / 2	B	0.133	1.8						
72		7 / 6	B	0.098	0.3			0.653	0.7	0.146	-0.4
73		4 / 4	B	0.085	-0.3			0.599	0.3		
74	x	9 / 8	A	0.076	-0.7	0.170	0.1	0.910	2.5	0.241	2
75		9 / 8	A	0.104	0.5	0.170	0.1	0.459	-0.7	0.082	-2
76		5 / 5	B	0.080	-0.5			0.890	2.4		
77		7 / 6	B	0.086	-0.3	0.245	1.9			0.059	-2.5
78		9 / 8	A	0.058	-1.5	0.100	-1.6	0.810	1.8	0.083	-1.9
79		3 / 3	B	0.055	-1.6						

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
# Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-7 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				Glyphosate		MCPA		Mepiquat		Propamocarb	
Assigned Value [mg/kg]				0.568		0.081		0.114		0.067	
MRRL [mg/kg]				0.050		0.010		0.010		0.010	
*CV**				22.8 %		18.9 %		18.5 %		23.3 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found, max. 9 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
41	x	2 / 2	B							0.077	0.6
42		0 / 0									
43		8 / 8	A	0.229	-2.4	0.080	-0.1	0.109	-0.2	0.067	0
44	x	9 / 8	A	0.592	0.2	0.102	1	0.142	1	0.072	0.3
45		9 / 8	A	0.241	-2.3	0.080	-0.1	0.109	-0.2	0.070	0.2
46		8 / 8	A	0.592	0.2	0.095	0.7	0.115	0	0.070	0.2
47	x	8 / 7	A			0.084	0.1	0.106	-0.3	0.057	-0.6
48		2 / 2	B	0.406	-1.1						
49	x	4 / 4	B					1.730	56.9	0.061	-0.3
50		1 / 1	B								
51	x	9 / 8	A	0.526	-0.3	0.091	0.5	0.117	0.1	0.058	-0.5
52		1 / 1	B	0.602	0.2						
53		4 / 4	B			0.081	0			0.030	-2.2
54	x	8 / 7	A	0.469	-0.7	0.073	-0.4	0.120	0.2	0.073	0.4
55		8 / 8	A	0.530	-0.3	0.110	1.4	0.126	0.4	0.050	-1
56		6 / 6	B			0.074	-0.3	0.122	0.3	0.072	0.3
57		9 / 8	A	0.584	0.1	0.072	-0.4	0.100	-0.5	0.049	-1.1
58		9 / 8	A	0.653	0.6	0.061	-1	0.127	0.5	0.012	-3.3
59	x	5 / 5	B			0.071	-0.5	0.087	-0.9		
60	x	8 / 7	A	0.484	-0.6	0.096	0.7	0.110	-0.1	0.058	-0.5
61		9 / 8	A	0.300	-1.9	0.100	0.9	0.110	-0.1	0.080	0.8
62		1 / 1	B							0.062	-0.3
63		9 / 8	A	0.391	-1.2	0.122	2	0.173	2.1	0.064	-0.2
64	x	8 / 8	A	0.746	1.3	0.038	-2.1	0.116	0.1	0.024	-2.6
65	x	8 / 7	A	0.612	0.3	0.066	-0.8	0.154	1.4	0.046	-1.2
66		6 / 5	B			0.091	0.5	0.122	0.3	0.101	2.1
67	x	8 / 7	A			0.108	1.3	0.176	2.2	0.124	3.4
68		1 / 1	B								
69		0 / 0									
70	x	9 / 8	A	0.772	1.4	0.077	-0.2	0.108	-0.2	0.076	0.5
71		3 / 2	B							0.115	2.9
72		7 / 6	B	0.264	-2.1	0.080	-0.1			0.072	0.3
73		4 / 4	B			0.091	0.5			0.078	0.7
74	x	9 / 8	A	0.550	-0.1	0.066	-0.7	0.100	-0.5	0.058	-0.5
75		9 / 8	A	0.517	-0.4	0.064	-0.8	0.103	-0.4	0.077	0.6
76		5 / 5	B			0.073	-0.4	0.172	2.1	0.060	-0.4
77		7 / 6	B			0.135	2.7	0.120	0.2	0.071	0.3
78		9 / 8	A	0.420	-1	0.047	-1.7	0.071	-1.5	0.065	-0.1
79		3 / 3	B			0.096	0.7			0.092	1.5

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-7 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

COMPULSORY Compound				2,4-D (free acid)		Chlormequat		Dithiocarbamates		Ethephon	
Assigned Value [mg/kg]				0.092		0.167		0.559		0.162	
MRRL [mg/kg]				0.010		0.010		0.050		0.020	
*CV**				18.2 %		18.2 %		36.9 %		30.8 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found, max. 9 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
80		5 / 5	B	0.105	0.6	0.197	0.7				
81	x	9 / 8	A	0.084	-0.4	0.171	0.1	0.616	0.4	0.137	-0.6
82		8 / 8	A	0.112	0.9	0.167	0	0.526	-0.2	0.200	0.9
83		6 / 6	B	0.086	-0.3	0.158	-0.2				
84	x	8 / 8	A	0.087	-0.2	0.163	-0.1	0.762	1.5	0.212	1.2
85		8 / 7	A	0.076	-0.7	0.065	-2.4	1.250	4.9	0.156	-0.1
86		1 / 1	B					0.617	0.4		
87		8 / 7	A	0.095	0.1	0.172	0.1	0.563	0	0.133	-0.7
88		1 / 1	B					0.547	-0.1		
89		8 / 8	A	0.104	0.5	0.197	0.7	0.520	-0.3	0.194	0.8
90		6 / 6	B	0.088	-0.2	0.165	-0.1	0.423	-1		
91	x	9 / 8	B#	0.083	-0.4	0.183	0.4	0.665	0.8	0.187	0.6
92		0 / 0									
93		1 / 1	B					0.450	-0.8		
94	x	9 / 8	A	0.111	0.8	0.166	0	0.292	-1.9	0.133	-0.7
95		6 / 5	B			0.180	0.3	FN	-3.6	0.070	-2.3
96		0 / 0									
97	x	6 / 5	B	0.060	-1.4	0.090	-1.8				
98	x	6 / 6	B	0.102	0.4	0.172	0.1	0.509	-0.4		
99		1 / 1	B					0.590	0.2		
100		9 / 8	A	0.144	2.2	0.601	10.4	0.056	-3.6	0.231	1.7
101		0 / 0									
102		1 / 1	B					0.550	-0.1		
103		5 / 5	B	0.093	0			0.550	-0.1	0.124	-0.9
104		1 / 1	B					0.508	-0.4		
105		1 / 1	B								
106		8 / 7	A	0.110	0.8	0.210	1	0.630	0.5		
107		6 / 6	B	0.082	-0.4	0.061	-2.5	0.510	-0.4		
108		1 / 1	B					0.470	-0.6		
109		2 / 2	B					0.196	-2.6		
110		0 / 0									
111		4 / 4	B			0.162	-0.1				
112		1 / 1	B					0.470	-0.6		
3rd-113		9 / 8	A	0.125	1.4	0.192	0.6	0.650	0.6	0.083	-1.9
3rd-114		7 / 6	B	0.028	-2.8			0.840	2		
3rd-115		6 / 4	B	0.030	-2.7	0.020	-3.5	0.660	0.7	FN	-3.5
3rd-116		9 / 8	A	0.110	0.8	0.120	-1.1	0.880	2.3	0.280	2.9
3rd-117		3 / 3	B	0.104	0.5			0.392	-1.2	0.114	-1.2
3rd-118		9 / 7	A	0.085	-0.3	0.0009	-4	0.721	1.2	0.003	-3.9

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-7 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for COMPULSORY compounds

	COMPULSORY Compound			Glyphosate		MCPA		Mepiquat		Propamocarb	
	Assigned Value [mg/kg]			0.568		0.081		0.114		0.067	
	MRRL [mg/kg]			0.050		0.010		0.010		0.010	
	*CV**			22.8 %		18.9 %		18.5 %		23.3 %	
	Lab code SRM10-	NRL-SRM	Analysed / corr. found, max. 9 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
	80		5 / 5	B			0.083	0.1	0.142	1	0.082	0.9
	81	x	9 / 8	A	0.603	0.2	0.074	-0.3	0.137	0.8	0.066	0
	82		8 / 8	A	0.462	-0.7	0.078	-0.2	0.136	0.8	0.072	0.3
	83		6 / 6	B	0.707	1	0.078	-0.2	0.110	-0.1	0.085	1.1
	84	x	8 / 8	A	0.652	0.6	0.079	-0.1	0.106	-0.3	0.055	-0.7
	85		8 / 7	A			0.070	-0.5	0.026	-3.1	0.067	0
	86		1 / 1	B								
	87		8 / 7	A			0.086	0.2	0.126	0.4	0.077	0.6
	88		1 / 1	B								
	89		8 / 8	A	0.442	-0.9	0.057	-1.2	0.100	-0.5	0.052	-0.9
	90		6 / 6	B			0.081	0	0.088	-0.9	0.041	-1.5
	91	x	9 / 8	B#	0.242	-2.3	0.075	-0.3	0.110	-0.1	0.076	0.5
	92		0 / 0									
	93		1 / 1	B								
	94	x	9 / 8	A	0.472	-0.7	0.096	0.7	0.130	0.6	0.058	-0.5
	95		6 / 5	B	0.536	-0.2			0.214	3.5	0.039	-1.7
	96		0 / 0									
	97	x	6 / 5	B			0.053	-1.4	0.065	-1.7	0.025	-2.5
	98	x	6 / 6	B			0.087	0.3	0.095	-0.7	0.056	-0.6
	99		1 / 1	B								
	100		9 / 8	A	0.844	1.9	0.114	1.6	0.485	13.1	0.084	1
	101		0 / 0									
	102		1 / 1	B								
	103		5 / 5	B			0.087	0.3			0.080	0.8
	104		1 / 1	B								
	105		1 / 1	B							0.058	-0.5
	106		8 / 7	A	0.670	0.7	0.079	-0.1	0.110	-0.1	0.069	0.1
	107		6 / 6	B			0.079	-0.1	0.104	-0.3	0.057	-0.6
	108		1 / 1	B								
	109		2 / 2	B							0.060	-0.4
	110		0 / 0									
	111		4 / 4	B	0.597	0.2			0.090	-0.8	0.060	-0.4
	112		1 / 1	B								
	3rd-113		9 / 8	A	2.494	13.6	0.104	1.1	0.089	-0.9	0.055	-0.7
	3rd-114		7 / 6	B	0.580	0.1	0.029	-2.6	0.100	-0.5	0.027	0.4
	3rd-115		6 / 4	B	FN	-3.6	0.020	-3				
	3rd-116		9 / 8	A	0.520	-0.3	0.090	0.4	0.130	0.6	0.150	5
	3rd-117		3 / 3	B								
	3rd-118		9 / 7	A	FN	-3.6	0.067	-0.7	0.015	-3.5	0.088	1.3

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-8: Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

		OPTIONAL Compound		Bentazone		Bromoxynil		N-Acetyl glufosinate	
		Assigned Value [mg/kg]		0.098		0.125		0.319	
		MRRL [mg/kg]		0.010		0.010		0.020	
		*CV**		18.5 %		17.0 %		11.8 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found max. 14 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1		2 / 1	B			0.155	1		
2		9 / 3	A	0.100	0.1	0.114	-0.4	0.329	0.1
3		9 / 3	A	0.104	0.3	0.125	0		
4	x	14 / 5	A	0.092	-0.2	0.133	0.2	0.337	0.2
5		11 / 4	A	0.120	0.9	0.147	0.7		
6	x	14 / 5	A	0.094	-0.2	0.139	0.4	0.305	-0.2
7		0 / 0	B						
8		5 / 3	B#	0.082	-0.6	0.111	-0.5		
9		1 / 1	B			0.137	0.4		
10		9 / 4	A	0.100	0.1	0.133	0.2		
11		6 / 2	A	0.099	0.1	0.121	-0.1		
12	x	13 / 4	A	0.118	0.8	0.130	0.2	0.279	-0.5
13		0 / 0	B						
14		4 / 1	B					0.278	-0.5
15		7 / 3	A	0.096	-0.1	0.123	-0.1	0.321	0
16		6 / 1	A	0.071	-1.1				
18		7 / 3	B	0.073	-1	0.083	-1.3	0.350	0.4
19		8 / 2	B	0.100	0.1	0.150	0.8		
20		14 / 5	A	0.075	-0.9	0.081	-1.4	0.318	0
21		14 / 5	A	0.110	0.5	0.127	0.1	0.335	0.2
22		5 / 1	B			0.129	0.1		
23	x	5 / 1	A			0.146	0.7		
24	x	7 / 2	B	0.034	-2.6	0.058	-2.2		
25		13 / 5	A	0.103	0.2	0.151	0.8	0.306	-0.2
26	x	8 / 2	A	0.101	0.1	0.147	0.7		
27		11 / 4	A	0.160	2.5	0.148	0.7		
28		6 / 2	B	0.100	0.1	0.146	0.7		
29	x	7 / 2	A			0.130	0.2		
30		11 / 4	A	0.084	-0.6	0.100	-0.8		
31		5 / 2	A	0.070	-1.1	0.140	0.5		
32		5 / 2	A	0.101	0.1	0.105	-0.6		
33		12 / 4	A	0.126	1.2	0.154	0.9		
34		9 / 3	A	0.049	-2	0.039	-2.8		
35		1 / 0	A						
36		6 / 2	A	0.075	-0.9	0.064	-2		
37	x	1 / 0	B						
38		4 / 1	A	0.092	-0.2				
40		7 / 2	A	0.093	-0.2	0.118	-0.2		

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
# Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

	OPTIONAL Compound			Phosphonic acid		TFNG	
	Assigned Value [mg/kg]			0.584		0.168	
	MRRL [mg/kg]			0.050		0.020	
	*CV**			27.3 %		18.6 %	
	Lab code SRM10-	NRL-SRM	Analysed / corr. found max. 14 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score ‡ (FFP-RSD = 25 %)
	1		2 / 1	B				
	2		9 / 3	A				
	3		9 / 3	A			0.174	0.2
	4	x	14 / 5	A	0.615	0.2	0.197	0.7
	5		11 / 4	A	0.971	2.6	0.217	1.2
	6	x	14 / 5	A	0.598	0.1	0.208	1
	7		0 / 0	B				
	8		5 / 3	B#	0.553	-0.2		
	9		1 / 1	B				
	10		9 / 4	A	0.617	0.2	0.159	-0.2
	11		6 / 2	A				
	12	x	13 / 4	A			0.132	-0.8
	13		0 / 0	B				
	14		4 / 1	B	FN	-3.7		
	15		7 / 3	A				
	16		6 / 1	A				
	18		7 / 3	B				
	19		8 / 2	B				
	20		14 / 5	A	0.585	0	0.170	0.1
	21		14 / 5	A	0.559	-0.2	0.164	-0.1
	22		5 / 1	B				
	23	x	5 / 1	A				
	24	x	7 / 2	B				
	25		13 / 5	A	0.334	-1.7	0.174	0.2
	26	x	8 / 2	A				
	27		11 / 4	A	0.606	0.1	0.186	0.4
	28		6 / 2	B				
	29	x	7 / 2	A			0.165	-0.1
	30		11 / 4	A	0.591	0	0.140	-0.7
	31		5 / 2	A				
	32		5 / 2	A				
	33		12 / 4	A	0.774	1.3	0.180	0.3
	34		9 / 3	A			0.029	-3.3
	35		1 / 0	A				
	36		6 / 2	A				
	37	x	1 / 0	B				
	38		4 / 1	A				
	40		7 / 2	A				

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

		OPTIONAL Compound		Bentazone		Bromoxynil		N-Acetyl glufosinate	
		Assigned Value [mg/kg]		0.098		0.125		0.319	
		MRRL [mg/kg]		0.010		0.010		0.020	
			*CV**	18.5 %		17.0 %		11.8 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found max. 14 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
41	x	1 / 0	B						
42		0 / 0							
43		6 / 2	A	0.109	0.5	0.132	0.2		
44	x	4 / 1	A	0.115	0.7				
45		9 / 3	A	0.107	0.4	0.127	0.1		
46		8 / 3	A	0.112	0.6	0.127	0.1		
47	x	5 / 0	A						
48		0 / 0	B						
49	x	0 / 0	B						
50		0 / 0	B						
51	x	10 / 4	A	0.105	0.3	0.127	0.1	0.416	1.2
52		0 / 0	B						
53		9 / 4	B	0.100	0.1	0.118	-0.2		
54	x	7 / 1	A	0.105	0.3				
55		10 / 3	A	0.102	0.2	0.138	0.4		
56		6 / 2	B	0.095	-0.1	0.120	-0.2		
57		9 / 3	A	0.116	0.7	0.116	-0.3		
58		13 / 5	A	0.068	-1.2	0.091	-1.1	0.356	0.5
59	x	0 / 0	B						
60	x	7 / 3	A	0.134	1.5	0.173	1.5	FN	-3.7
61		14 / 5	A	0.097	0	0.100	-0.8	0.350	0.4
62		0 / 0	B						
63		6 / 3	A	0.140	1.7	0.130	0.2		
64	x	7 / 2	A	0.038	-2.4	0.062	-2		
65	x	3 / 1	A	0.090	-0.3				
66		7 / 2	B	0.089	-0.3	0.126	0		
67	x	9 / 3	A	0.083	-0.6	0.116	-0.3		
68		0 / 0	B						
69		0 / 0							
70	x	7 / 3	A	0.081	-0.7	0.124	0		
71		2 / 1	B	0.083	-0.6				
72		10 / 3	B	0.105	0.3	0.135	0.3		
73		9 / 3	B	0.099	0	0.116	-0.3		
74	x	9 / 3	A	0.103	0.2	0.146	0.7	0.260	-0.7
75		6 / 2	A	0.120	0.9	0.120	-0.2		
76		0 / 0	B						
77		4 / 3	B	0.125	1.1	0.128	0.1		
78		10 / 3	A	0.092	-0.2	0.099	-0.8		
79		3 / 1	B	0.096	-0.1				

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
# Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

	OPTIONAL Compound				Phosphonic acid		TFNG	
	Assigned Value [mg/kg]				0.584		0.168	
	MRRL [mg/kg]				0.050		0.020	
	*CV**				27.3 %		18.6 %	
	Lab code SRM10-	NRL-SRM	Analysed / corr. found max. 14 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score # (FFP-RSD = 25 %)
	41	x	1 / 0	B				
	42		0 / 0					
	43		6 / 2	A				
	44	x	4 / 1	A				
	45		9 / 3	A			0.162	-0.1
	46		8 / 3	A	0.550	-0.2		
	47	x	5 / 0	A				
	48		0 / 0	B				
	49	x	0 / 0	B				
	50		0 / 0	B				
	51	x	10 / 4	A			0.164	-0.1
	52		0 / 0	B				
	53		9 / 4	B	0.469	-0.8	0.212	1.1
	54	x	7 / 1	A				
	55		10 / 3	A			0.180	0.3
	56		6 / 2	B				
	57		9 / 3	A	0.276	-2.1		
	58		13 / 5	A	0.592	0.1	0.014	-3.7
	59	x	0 / 0	B				
	60	x	7 / 3	A	0.226	-2.5		
	61		14 / 5	A	0.560	-0.2	0.200	0.8
	62		0 / 0	B				
	63		6 / 3	A	1.106	3.6		
	64	x	7 / 2	A				
	65	x	3 / 1	A				
	66		7 / 2	B				
	67	x	9 / 3	A			0.160	-0.2
	68		0 / 0	B				
	69		0 / 0					
	70	x	7 / 3	A	0.672	0.6		
	71		2 / 1	B				
	72		10 / 3	B			0.165	-0.1
	73		9 / 3	B			0.140	-0.7
	74	x	9 / 3	A				
	75		6 / 2	A				
	76		0 / 0	B				
	77		4 / 3	B			0.160	-0.2
	78		10 / 3	A	0.760	1.2		
	79		3 / 1	B				

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

OPTIONAL Compound				Bentazone		Bromoxynil		N-Acetyl glufosinate	
Assigned Value [mg/kg]				0.098		0.125		0.319	
MRRL [mg/kg]				0.010		0.010		0.020	
*CV**				18.5 %		17.0 %		11.8 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found max. 14 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
80		8 / 2	B	0.103	0.2	0.113	-0.4		
81	x	9 / 4	A			0.120	-0.2	0.282	-0.5
82		8 / 4	A	0.116	0.7	0.153	0.9		
83		7 / 2	B	0.102	0.2	0.132	0.2		
84	x	5 / 2	A	0.093	-0.2	0.122	-0.1		
85		4 / 2	A	0.044	-2.2	0.080	-1.4		
86		0 / 0	B						
87		10 / 4	A	0.090	-0.3	0.108	-0.6		
88		0 / 0	B						
89		8 / 2	A	0.094	-0.2	0.115	-0.3		
90		3 / 0	B						
91	x	10 / 3	B#	0.092	-0.2	0.124	0		
92		0 / 0							
93		0 / 0	B						
94	x	5 / 0	A						
95		2 / 1	B	0.106	0.3				
96		0 / 0							
97	x	3 / 0	B						
98	x	5 / 1	B	0.068	-1.2				
99		0 / 0	B						
100		12 / 4	A	0.175	3.1	0.210	2.7		
101		0 / 0							
102		0 / 0	B						
103		8 / 3	B	0.081	-0.7	0.104	-0.7		
104		0 / 0	B						
105		0 / 0	B						
106		5 / 2	A	0.110	0.5	0.140	0.5		
107		7 / 1	B	0.101	0.1				
108		0 / 0	B						
109		0 / 0	B						
110		0 / 0							
111		2 / 0	B						
112		0 / 0	B						
3rd-113		11 / 2	A	0.116	0.7	FN	-3.7		
3rd-114		8 / 2	B	0.029	-2.8	0.043	-2.6		
3rd-115		5 / 1	B	0.020	-3.2	FN	-3.7		
3rd-116		3 / 1	A	0.090	-0.3				
3rd-117		2 / 2	B	0.097	0	0.108	-0.6		
3rd-118		2 / 2	A	0.031	-2.7	0.052	-2.3		

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-8 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

	OPTIONAL Compound			Phosphonic acid		TFNG	
	Assigned Value [mg/kg]			0.584		0.168	
	MRRL [mg/kg]			0.050		0.020	
	*CV**			27.3 %		18.6 %	
	Lab code SRM10-	NRL-SRM	Analysed / corr. found max. 14 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score ‡ (FFP-RSD = 25 %)
	80		8 / 2	B				
	81	x	9 / 4	A	0.717	0.9	0.134	-0.8
	82		8 / 4	A	0.566	-0.1	0.210	1
	83		7 / 2	B				
	84	x	5 / 2	A				
	85		4 / 2	A				
	86		0 / 0	B				
	87		10 / 4	A	0.534	-0.3	0.102	-1.6
	88		0 / 0	B				
	89		8 / 2	A				
	90		3 / 0	B				
	91	x	10 / 3	B#			0.188	0.5
	92		0 / 0					
	93		0 / 0	B				
	94	x	5 / 0	A				
	95		2 / 1	B				
	96		0 / 0					
	97	x	3 / 0	B				
	98	x	5 / 1	B				
	99		0 / 0	B				
	100		12 / 4	A	0.355	-1.6	0.191	0.6
	101		0 / 0					
	102		0 / 0	B				
	103		8 / 3	B			0.156	-0.3
	104		0 / 0	B				
	105		0 / 0	B				
	106		5 / 2	A				
	107		7 / 1	B				
	108		0 / 0	B				
	109		0 / 0	B				
	110		0 / 0					
	111		2 / 0	B				
	112		0 / 0	B				
	3rd-113		11 / 2	A			0.134	-0.8
	3rd-114		8 / 2	B				
	3rd-115		5 / 1	B				
	3rd-116		3 / 1	A				
	3rd-117		2 / 2	B				
	3rd-118		2 / 2	A				

* Category A/B classification (Cat A was assigned to laboratories that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)

Laboratories had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-9: Category A laboratories ordered by lab-codes

COMPULSORY Compounds			2,4-D (free acid)	Chlormequat	Dithiocarbamates	Ethephon	Glyphosate	MCPA	Mepiquat	Propamocarb	
Assigned Value [mg/kg]			0.092	0.167	0.559	0.162	0.568	0.081	0.114	0.067	
MRRL [mg/kg]			0.010	0.010	0.050	0.020	0.050	0.010	0.010	0.010	
*CV**			18.2 %	18.2 %	36.9 %	30.8 %	22.8 %	18.9 %	18.5 %	23.3 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found [1]	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	AAZ [2]
2		9 / 8	-0.4	-0.3	0.5	-0.3	0.3	-1.0	0.3	-0.8	0.5
3		9 / 8	0.3	-0.7	1.0	-0.3	-0.4	0.4	-0.4	1.9	0.7
4	x	9 / 8	1.5	-0.2	2.8	1.3	-0.3	2.2	0.4	-0.8	1.2
5		9 / 8	0.1	0.8	-1.7	-0.8	-0.1	0.7	-0.1	0.5	0.6
6	x	9 / 8	0.3	-0.8	-0.7	-0.1	0.0	0.7	0.0	0.6	0.4
10		9 / 8	0.6	1.1	-0.7	0.6	0.5	0.7	0.9	0.7	0.7
11		9 / 8	0.2	-0.2	-0.1	0.0	-1.0	0.0	-0.5	-0.4	0.3
12	x	9 / 8	0.3	0.0	-1.2	0.2	0.1	0.5	-0.3	0.1	0.3
15		9 / 8	0.0	-0.2	-0.9	0.8	0.5	0.0	0.1	0.3	0.4
16		9 / 8	-1.2	-0.8	2.0	-0.6	0.1	-1.0	0.0	-0.7	0.8
20		9 / 8	-0.7	0.1	-0.4	0.4	-0.1	0.0	-0.3	0.9	0.4
21		9 / 8	-0.2	0.1	2.3	-0.1	-0.8	0.0	0.0	0.4	0.5
23	x	8 / 8	1.1	0.1	-2.5	-0.1	1.6	0.9	0.2	-0.6	0.9
25		9 / 8	0.6	1.1	0.6	-0.6	0.4	0.3	1.1	-0.2	0.6
26	x	9 / 7	0.0	0.4	-1.7	5.6	-3.6 FN	-0.1	0.2	1.2	1.5
27		9 / 8	0.8	0.1	-2.1	-0.2	0.7	1.7	-0.5	0.3	0.8
29	x	9 / 8	0.1	-0.3	0.0	1.4	0.4	0.0	-0.3	-0.7	0.4
30		9 / 8	0.6	0.3	-2.4	-0.5	0.0	-0.3	0.8	0.6	0.7
31		8 / 7	-1.3	2.7	-0.7	-2.8		-0.3	1.6	0.0	1.3
32		8 / 7	-0.4	1.7	2.2		-1.6	-0.6	0.9	-0.6	1.1
33		9 / 8	1.9	-0.3	-0.5	1.2	0.4	0.2	1.5	-0.3	0.8
34		9 / 8	-2.9	-1.1	0.9	-0.6	[16.1]	-3.2	-0.1	-2.8	2.1
35		9 / 8	-0.9	-0.2	0.1	1.9	0.2	-0.6	0.0	-0.6	0.6
36		8 / 7	0.7	-2.1		[6.2]	0.8	0.8	-0.7	-0.9	1.6
38		9 / 8	-0.4	-0.1	1.0	1.5	-0.5	0.0	-0.2	0.3	0.5
40		9 / 8	0.0	-0.8	-0.1	-0.8	0.2	-0.4	-0.4	0.2	0.4
43		8 / 8	-0.5	-0.3	2.2	-0.3	-2.4	-0.1	-0.2	0.0	0.8
44	x	9 / 8	0.3	0.7	-1.2	4.7	0.2	1.0	1.0	0.3	1.2
45		9 / 8	0.3	-0.4	0.7	-0.3	-2.3	-0.1	-0.2	0.2	0.6
46		8 / 8	0.7	0.3	-0.5	0.2	0.2	0.7	0.0	0.2	0.4
47	x	8 / 7	1.3	0.0	-0.1	-0.2		0.1	-0.3	-0.6	0.4
51	x	9 / 8	-0.2	0.0	1.1	0.6	-0.3	0.5	0.1	-0.5	0.4
54	x	8 / 7	0.0	-0.3	-0.9		-0.7	-0.4	0.2	0.4	0.4
55		8 / 8	0.0	2.2	0.1	2.7	-0.3	1.4	0.4	-1.0	1.0
57		9 / 8	0.0	-1.2	-0.8	1.5	0.1	-0.4	-0.5	-1.1	0.7
58		9 / 8	-1.9	0.6	-1.7	-0.4	0.6	-1.0	0.5	-3.3	1.3
60	x	8 / 7	-0.4	0.0		-2.3	-0.6	0.7	-0.1	-0.5	0.7
61		9 / 8	-0.1	-0.4	1.0	-0.3	-1.9	0.9	-0.1	0.8	0.7
63		9 / 8	1.6	0.6	3.4	-0.3	-1.2	2.0	2.1	-0.2	1.4
64	x	8 / 8	-0.4	0.0	3.4	0.8	1.3	-2.1	0.1	-2.6	1.3
65	x	8 / 7	-0.8	1.9		1.3	0.3	-0.8	1.4	-1.2	1.1
67	x	8 / 7	0.8	-0.3	2.4	-0.9		1.3	2.2	3.4	1.6

1) Referring to compulsory compounds only (max. 9/8)
2) AAZ: Average of Absolute z-scores, is given for informative purposes. It was calculated using all z-scores of each lab.
For the calculation of the AAZ the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
FN = false negative results;

Table 4-9 (cont.): Category A laboratories ordered by lab-codes

COMPULSORY Compounds			2,4-D (free acid)	Chlormequat	Dithiocarbamates	Ethephon	Glyphosate	MCPA	Mepiquat	Propamocarb	
Assigned Value [mg/kg]			0.092	0.167	0.559	0.162	0.568	0.081	0.114	0.067	
MRRL [mg/kg]			0.010	0.010	0.050	0.020	0.050	0.010	0.010	0.010	
*CV**			18.2 %	18.2 %	36.9 %	30.8 %	22.8 %	18.9 %	18.5 %	23.3 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found [1]	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	AAZ [2]
70	x	9 / 8	-0.1	0.0	0.2	-0.2	1.4	-0.2	-0.2	0.5	0.4
74	x	9 / 8	-0.7	0.1	2.5	2.0	-0.1	-0.7	-0.5	-0.5	0.9
75		9 / 8	0.5	0.1	-0.7	-2.0	-0.4	-0.8	-0.4	0.6	0.7
78		9 / 8	-1.5	-1.6	1.8	-1.9	-1.0	-1.7	-1.5	-0.1	1.4
81	x	9 / 8	-0.4	0.1	0.4	-0.6	0.2	-0.3	0.8	0.0	0.4
82		8 / 8	0.9	0.0	-0.2	0.9	-0.7	-0.2	0.8	0.3	0.5
84	x	8 / 8	-0.2	-0.1	1.5	1.2	0.6	-0.1	-0.3	-0.7	0.6
85		8 / 7	-0.7	-2.4	4.9	-0.1		-0.5	-3.1	0.0	1.7
87		8 / 7	0.1	0.1	0.0	-0.7		0.2	0.4	0.6	0.3
89		8 / 8	0.5	0.7	-0.3	0.8	-0.9	-1.2	-0.5	-0.9	0.7
94	x	9 / 8	0.8	0.0	-1.9	-0.7	-0.7	0.7	0.6	-0.5	0.7
100		9 / 8	2.2	[10.4]	-3.6	1.7	1.9	1.6	[13.1]	1.0	2.8
106		8 / 7	0.8	1.0	0.5		0.7	-0.1	-0.1	0.1	0.5
3rd-113		9 / 8	1.4	0.6	0.6	-1.9	13.6	1.1	-0.9	-0.7	1.5
3rd-116		9 / 8	0.8	-1.1	2.3	2.9	-0.3	0.4	0.6	5.0	1.7
3rd-118		9 / 7	-0.3	-4.0	1.2	-3.9	-3.6[FN]	-0.7	-3.5	1.3	2.3

1) Referring to compulsory compounds only (max. 9/8)
2) AAZ: Average of Absolute z-scores, is given for informative purposes. It was calculated using all z-scores of each lab. For the calculation of the AAZ the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
[FN] = false negative results;

Table 4-10: Category B laboratories ordered by lab-codes

COMPULSORY Compounds			2,4-D (free acid)	Chlormequat	Dithiocarbamates	Ethephon	Glyphosate	MCPA	Mepiquat	Propamocarb	
Assigned Value [mg/kg]			0.092	0.167	0.559	0.162	0.568	0.081	0.114	0.067	
MRRL [mg/kg]			0.010	0.010	0.050	0.020	0.050	0.010	0.010	0.010	
*CV**			18.2 %	18.2 %	36.9 %	30.8 %	22.8 %	18.9 %	18.5 %	23.3 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found [1]	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	AAZ [2]
1		8 / 6	0.1	1.0	0.2		0.9	-3.5[FN]	-0.1	0.9	1.0
7		1 / 1			-0.2						
8[#]		8 / 8	-0.1	1.4	-0.8	-3.4	-2.2	0.0	-0.7	1.8	1.3
9		5 / 5	0.0	0.0	1.5				0.0	1.2	0.5
13		1 / 0					-3.6[FN]				
14		4 / 4		-0.4		0.0	1.5		-0.4		
18		6 / 6	-1.0	-0.3			0.4	-1.1	-0.8	0.9	0.8
19		6 / 6	0.8	-0.9	0.6			0.4	-1.3	0.1	0.7
22		7 / 6	0.5		1.0	0.8	0.3	0.4		1.4	0.7
24	x	4 / 3	-3.4					-2.6		-2.5	
28		5 / 5	-0.6		-0.4	0.1	0.6	-0.6			0.5

1) Referring to compulsory compounds only (max. 9/8).
2) AAZ: Average of Absolute z-scores, is given for informative purposes for participants having reported at least 5 results for compulsory compounds. The AAZ was calculated using all z-scores of each lab. For the calculation of the AAZ the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
[#] = Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
[FN] = false negative results

Table 4-10 (cont.): Category B laboratories ordered by lab-codes

COMPULSORY Compounds			2,4-D (free acid)	Chlormequat	Dithiocarbamates	Ethephon	Glyphosate	MCPA	Mepiquat	Propamocarb	
Assigned Value [mg/kg]			0.092	0.167	0.559	0.162	0.568	0.081	0.114	0.067	
MRRL [mg/kg]			0.010	0.010	0.050	0.020	0.050	0.010	0.010	0.010	
*CV**			18.2 %	18.2 %	36.9 %	30.8 %	22.8 %	18.9 %	18.5 %	23.3 %	
Lab code SRM10-	NRL-SRM	Analysed / corr. found [1]	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	AAZ [2]
37	x	4 / 4	0.1		-2.0			-0.1		-2.0	
41	x	2 / 2			-1.6					0.6	
48		2 / 2			2.3		-1.1				
49	x	4 / 4		[28.3]	-0.2				[56.9]	-0.3	
50		1 / 1			-0.7						
52		1 / 1					0.2				
53		4 / 4	0.3		2.6			0.0		-2.2	
56		6 / 6	-0.3	-0.3	-0.8			-0.3	0.3	0.3	0.4
59	x	5 / 5	-0.9	-0.1	3.6			-0.5	-0.9		1.2
62		1 / 1								-0.3	
66		6 / 5	0.3	0.4				0.5	0.3	2.1	0.7
68		1 / 1			0.5						
71		3 / 2	1.8							2.9	
72		7 / 6	0.3		0.7	-0.4	-2.1	-0.1		0.3	0.7
73		4 / 4	-0.3		0.3			0.5		0.7	
76		5 / 5	-0.5		2.4			-0.4	2.1	-0.4	1.2
77		7 / 6	-0.3	1.9		-2.5		2.7	0.2	0.3	1.3
79		3 / 3	-1.6					0.7		1.5	
80		5 / 5	0.6	0.7				0.1	1.0	0.9	0.7
83		6 / 6	-0.3	-0.2			1.0	-0.2	-0.1	1.1	0.5
86		1 / 1			0.4						
88		1 / 1			-0.1						
90		6 / 6	-0.2	-0.1	-1.0			0.0	-0.9	-1.5	0.6
91#	x	9 / 8	-0.4	0.4	0.8	0.6	-2.3	-0.3	-0.1	0.5	0.7
93		1 / 1			-0.8						
95		6 / 5		0.3	-3.6[FN]	-2.3	-0.2		3.5	-1.7	1.9
97	x	6 / 5	-1.4	-1.8				-1.4	-1.7	-2.5	1.8
98	x	6 / 6	0.4	0.1	-0.4			0.3	-0.7	-0.6	0.4
99		1 / 1			0.2						
102		1 / 1			-0.1						
103		5 / 5	0.0		-0.1	-0.9		0.3		0.8	0.4
104		1 / 1			-0.4						
105		1 / 1								-0.5	
107		6 / 6	-0.4	-2.5	-0.4			-0.1	-0.3	-0.6	0.7
108		1 / 1			-0.6						
109		2 / 2			-2.6					-0.4	
111		4 / 4		-0.1			0.2		-0.8	-0.4	
112		1 / 1			-0.6						
3rd-114		7 / 6	-2.8		2.0		0.1	-2.6	-0.5	0.4	1.4
3rd-115		6 / 4	-2.7	-3.5	0.7	-3.5[FN]	-3.6[FN]	-3.0			2.8
3rd-117		3 / 3	0.5		-1.2	-1.2					

1) Referring to compulsory compounds only (max. 9/8).
2) AAZ: Average of Absolute z-scores, is given for informative purposes for participants having reported at least 5 results for compulsory compounds. The AAZ was calculated using all z-scores of each lab. For the calculation of the AAZ the value "5" was applied where the z-score was higher than 5 (shown in square brackets).

[#] = Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
[FN] = false negative results

4.4.5 Laboratory Feedback in Case of Poor Results

As a follow-up measure to this EUPT, all participating laboratories that had achieved questionable ($2 < |z\text{-score}| < 3$) or unacceptable ($|z\text{-score}| \geq 3$) results were asked to investigate the reasons for their poor performance and to report them to the organisers. This was done in order to sensibilize the laboratories to investigate the sources of errors. A compilation of the feedback received by the laboratories is given in **Appendix 8**. The main aim of this compilation is to inform all participants of possible error sources that should be avoided in the future. This information also provides input to NRLs on how to better assist laboratories in improving their performance.

In the current PT, in total, 106 results reported by 48 laboratories were evaluated with $|z| > 2$, thereof 43 results reported by 23 laboratories being evaluated with $|z| \geq 3$ (see **Table 4-6, p. 33**). As regards EU and EFTA laboratories $|z| > 2$ was assigned to 84 results with 36 of them being evaluated with $|z| \geq 3$. Overall, 37 laboratories responded to the organisers with (possible) reasons for their poor performance in 78 cases. In 9 of those case the real reasons could not be clarified, inspite of intensive investigation. Two laboratories stated internal transcription errors resulting in their false positive results. The most frequently reported error source (23 cases) was the lack of experience either with the commodity or the analytes. Several laboratories stated that the analysis of those analytes was just an exercise on the way to establish the method in routine work. "Application of inappropiate procedures" (15 cases), "error in the calibration solution or analytical standards" (12 cases) and "matrix effect not properly compensated" (11 cases) were further frequently reported error sources, followed by "procedure not properly conducted" (9 cases), "technical problem with the analytical instruments" (6 cases), "misinterpretation of the chromatogram" (4 cases), "results not corrected for low recovery" or "detection signal strongly interferred by matrix component" (3 cases each), "inappropiate calibration" or "inappropiate storage or pre-treatment of sample" (2 cases each) and "transcription error" (1 case).

One laboratory observed strong differences in the results of ***dithiocarbamates*** depending on the sample pretreatment (duration and temperature) to extraction. The organisers repeated the experiment in triplicate and could not confirm this observation (**Figure 4-2**). The results of the transport simulation stability test also do not support the laboratory's observations.

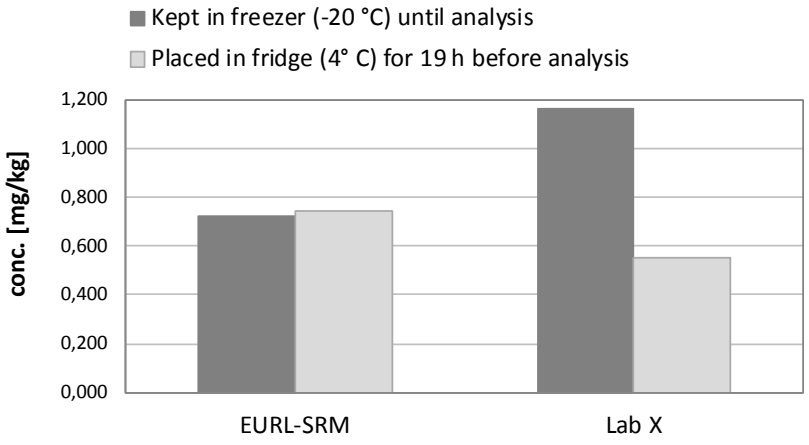


Figure 4-2: Influence of sample pretreatment prior to extraction on the concentration of dithiocarbamates. Results are the mean values of 3 experimental replicates from one analytical unit.

The 3 laboratories that have reported false positive results were also asked to provide feedback, with two of them doing so. In the case of false positive results of *glufosinate*, two laboratories performed the derivatisation step with trimethyl-orthoacetate (methylation) and acetic acid (acetylation). This method converts both *glufosinate* and ***N-acetyl glufosinate*** into the same target analyte and is not able to distinguish these two analytes in a sample. While ***N-acetyl glufosinate*** was present in the test item, *glufosinate* was not, thus using this analytical method led to the false positive results for *glufosinate* in the current PT.

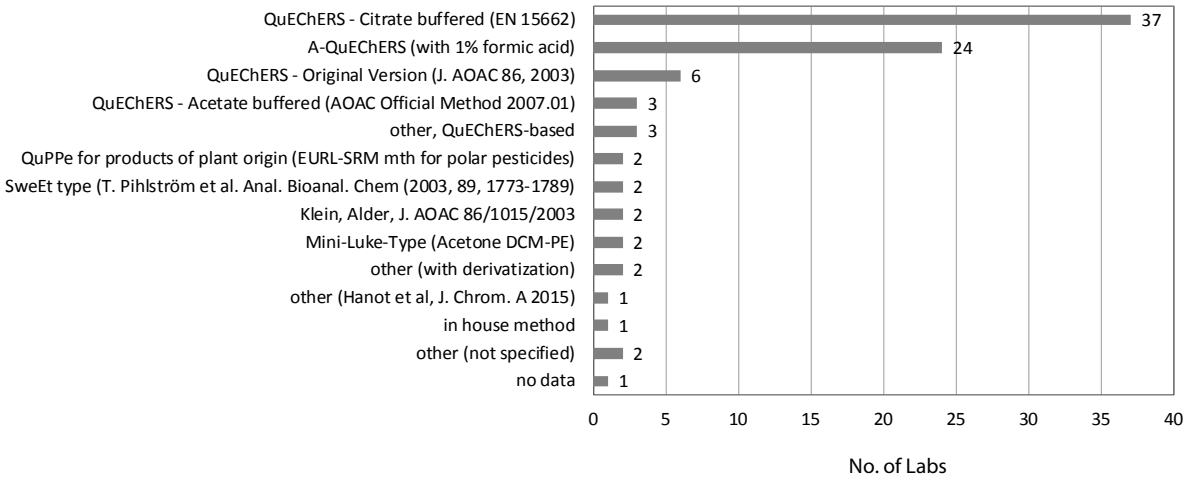
4.5 Methodological Information

Detailed information about the analytical methods used by the laboratories can be found on-line under **"EUPT-SRM10 - Supplementary Information"** that can be accessed using the following link: http://www.eurl-pesticides.eu/library/docs/srm/EUPT-SRM10_Supplementary_Information.pdf

4.5.1 Analytical methods used

An overview of the methods used by the participating labs for sample preparation and determination for each analyte present in the test item can be seen in **Figure 4-3**. As a support, a compilation of links to the methods provided by the EURL-SRM on the website concerning the target pesticides was sent to the participants. No specific recommendations on the analytical procedure to be used were made by the organiser, as the laboratories were prompted to use the procedures employed or intended to be employed for official controls in their laboratories.

2,4-D (free acid): Sample preparation



2,4-D (free acid): Determinative analysis

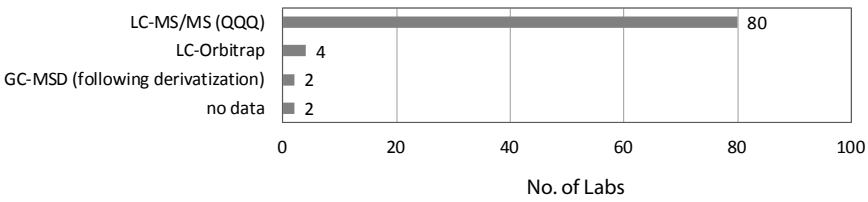
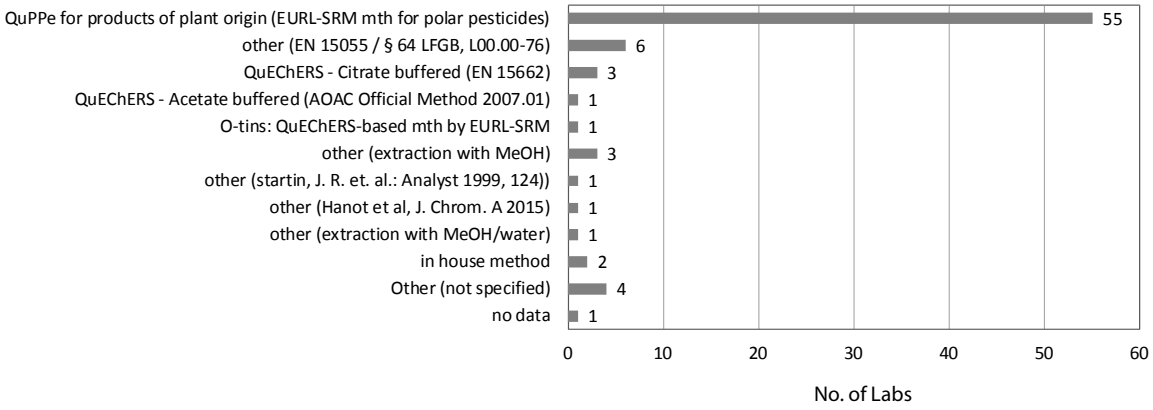
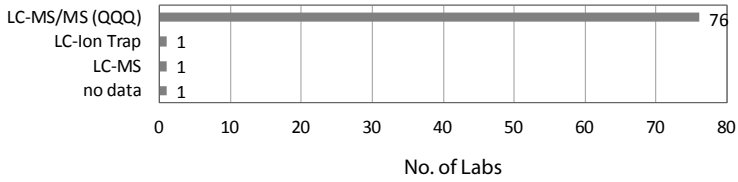


Figure 4-3: Methods applied for sample preparation and determinative analysis as reported by laboratories (all laboratories)

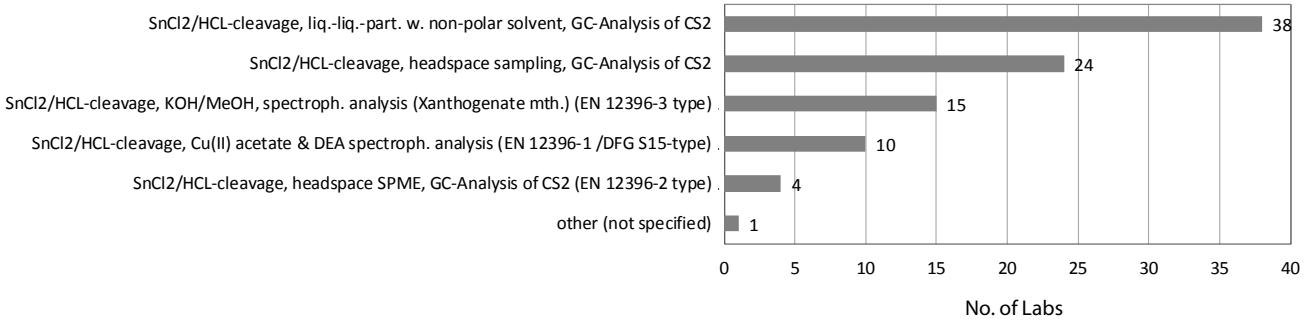
Chlormequat: Sample preparation



Chlormequat: Determinative analysis



Dithiocarbamates: Sample preparation



Dithiocarbamates: Determinative analysis

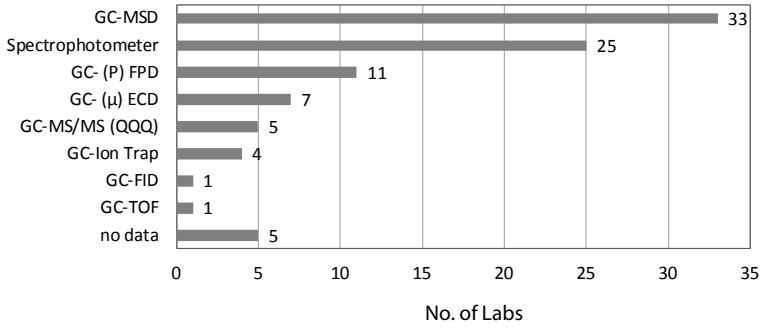
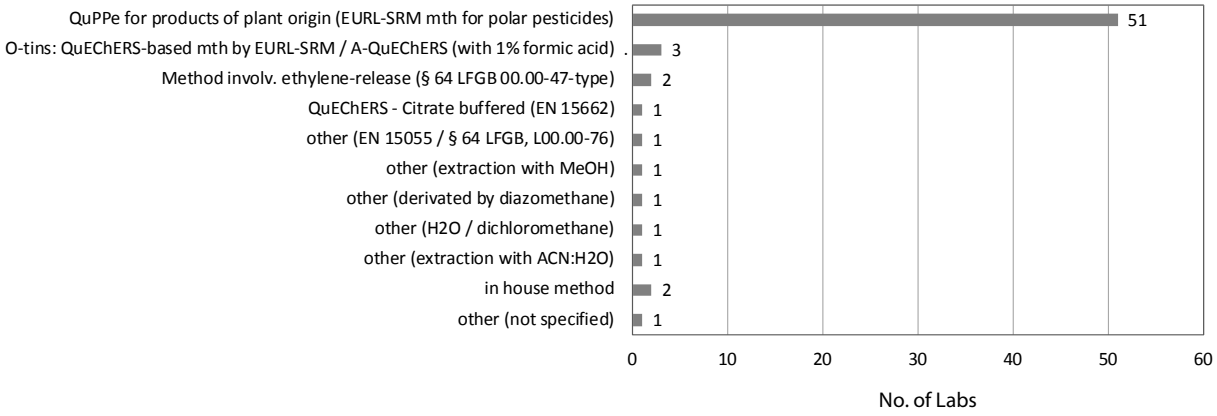
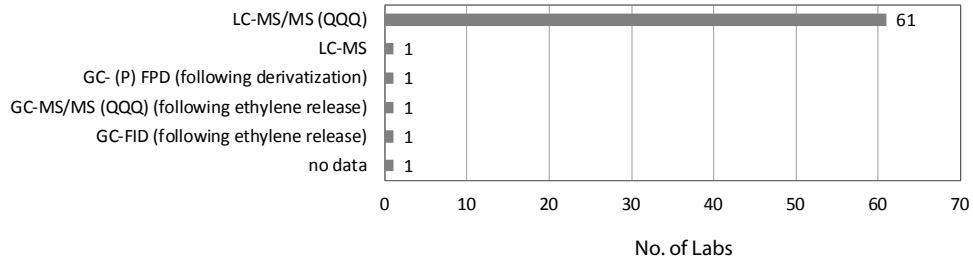


Figure 4-3 (cont.): Methods applied for sample preparation and determinative analysis as reported by laboratories (all laboratories)

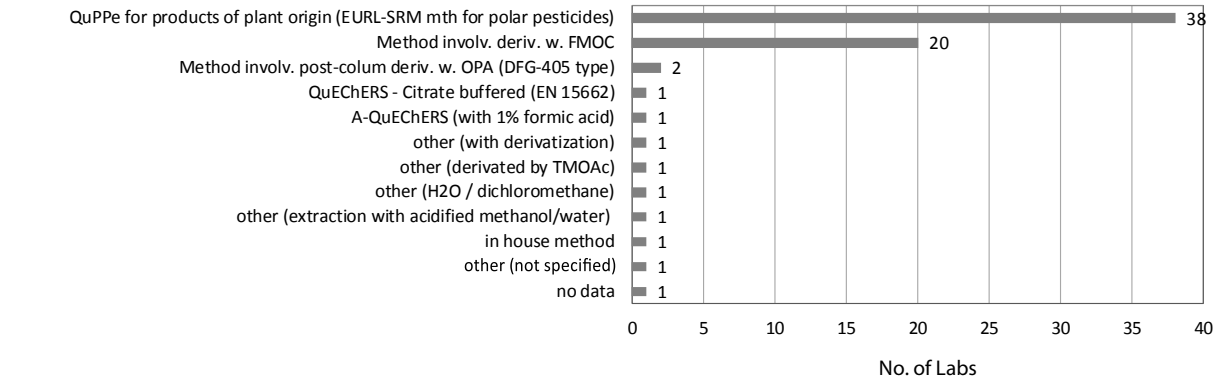
Ethephon: Sample preparation



Ethephon: Determinative analysis



Glyphosate: Sample preparation



Glyphosate: Determinative analysis

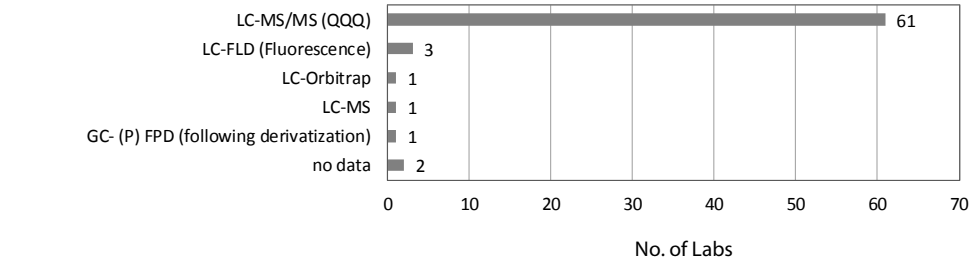
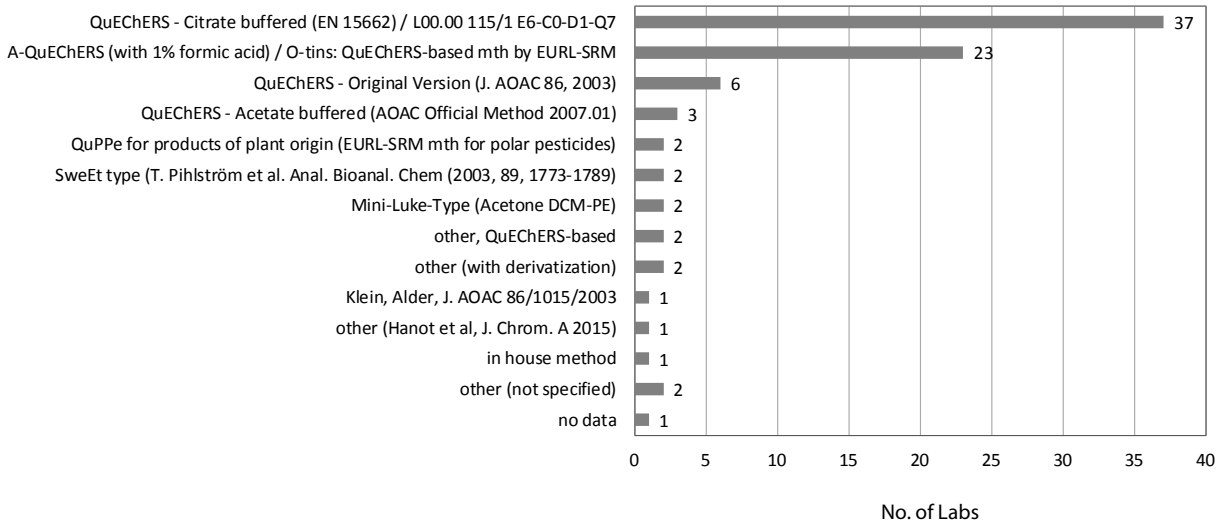
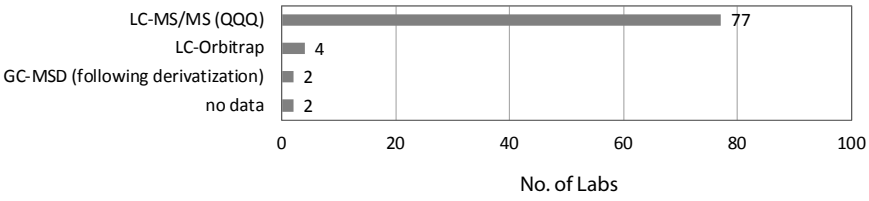


Figure 4-3 (cont.): Methods applied for sample preparation and determinative analysis as reported by laboratories (all laboratories)

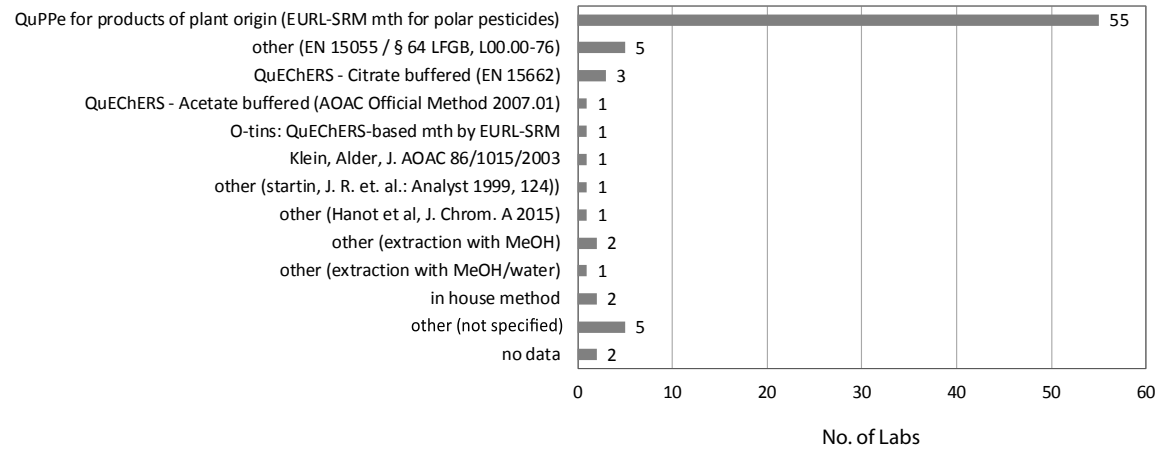
MCPA Sample preparation



MCPA: Determinative analysis



Mepiquat: Sample preparation



Mepiquat: Determinative analysis

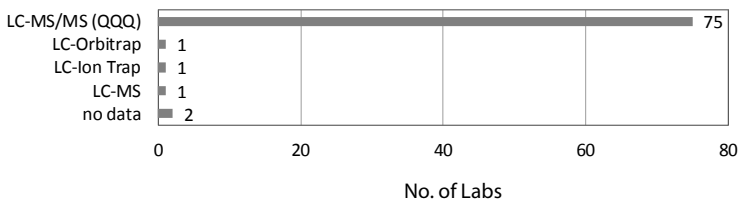
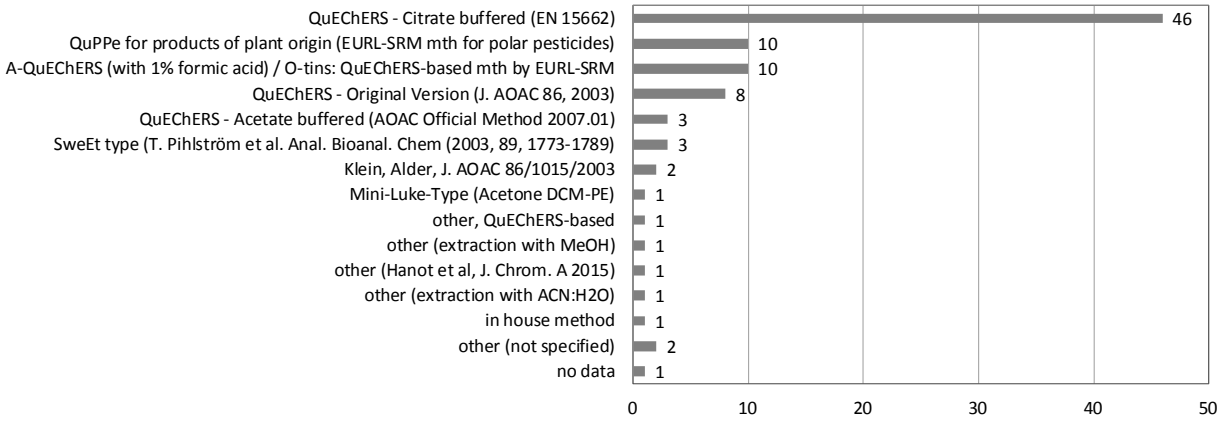
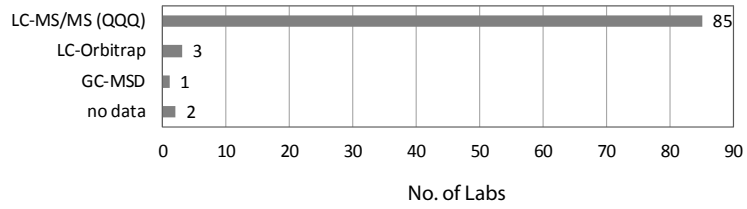


Figure 4-3 (cont.): Methods applied for sample preparation and determinative analysis as reported by laboratories (all laboratories)

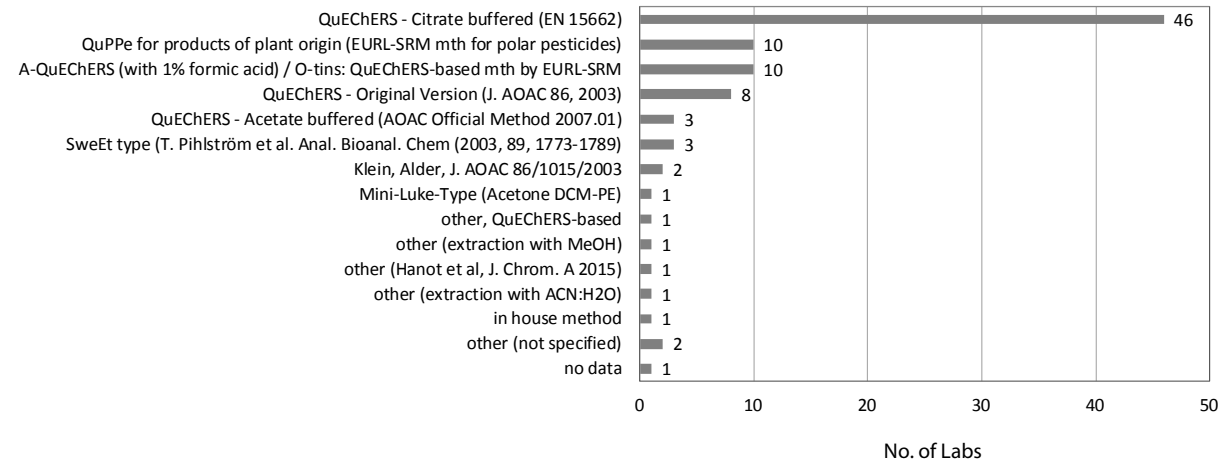
Propamocarb: Sample preparation



Propamocarb: Determinative analysis



Bentazone: Sample preparation



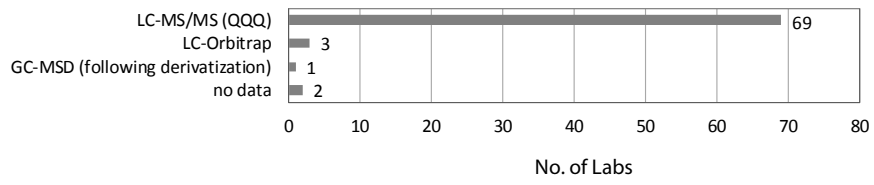
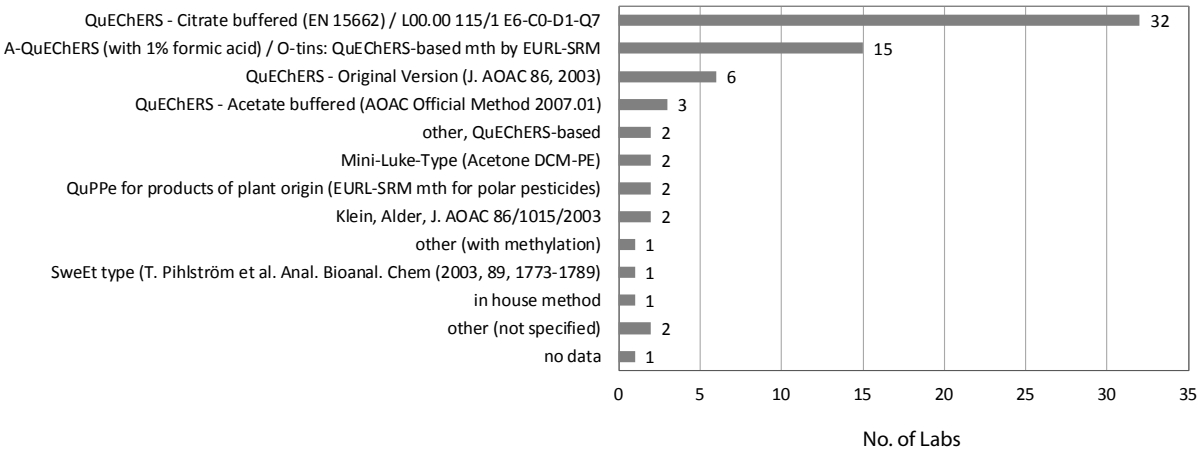
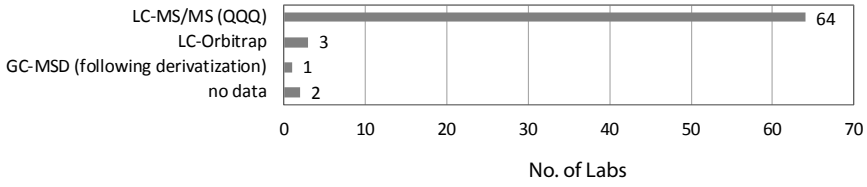


Figure 4-3 (cont.): Methods applied for sample preparation and determinative analysis as reported by laboratories (all laboratories)

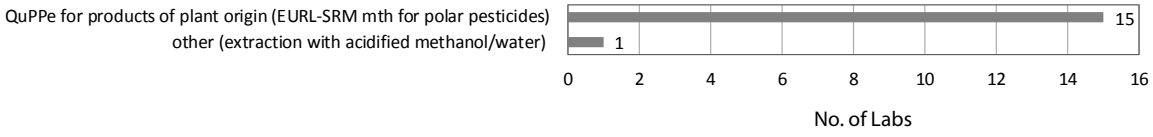
Bromoxynil: Sample preparation



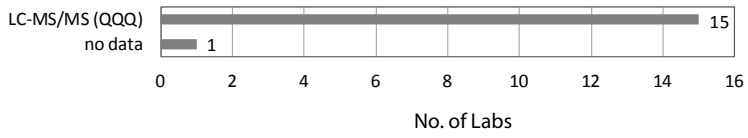
Bromoxynil: Determinative analysis



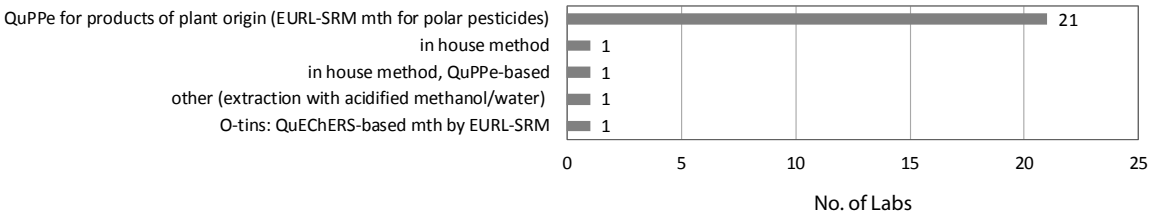
N-Acetyl glufosinate: Sample preparation



N-Acetyl glufosinate: Determinative analysis



Phosphonic acid: Sample preparation



Phosphonic acid: Determinative analysis

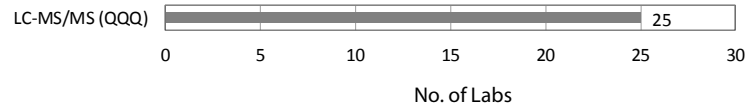
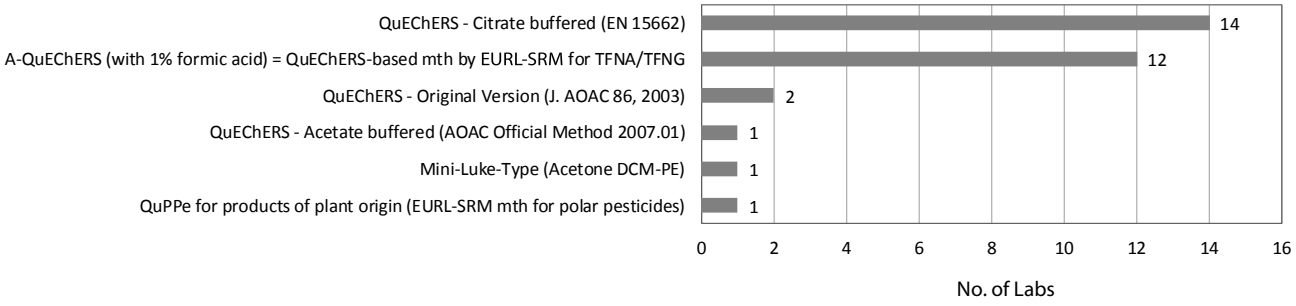


Figure 4-3 (cont.): Methods applied for sample preparation and determinative analysis as reported by laboratories (all laboratories)

TFNG: Sample preparation



TFNG: Determinative analysis

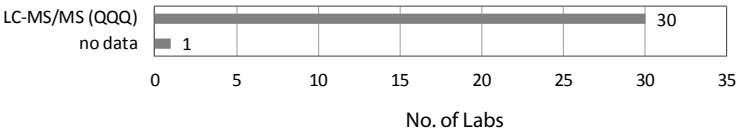


Figure 4-3 (cont.): Methods applied for sample preparation and determinative analysis as reported by laboratories (all laboratories)

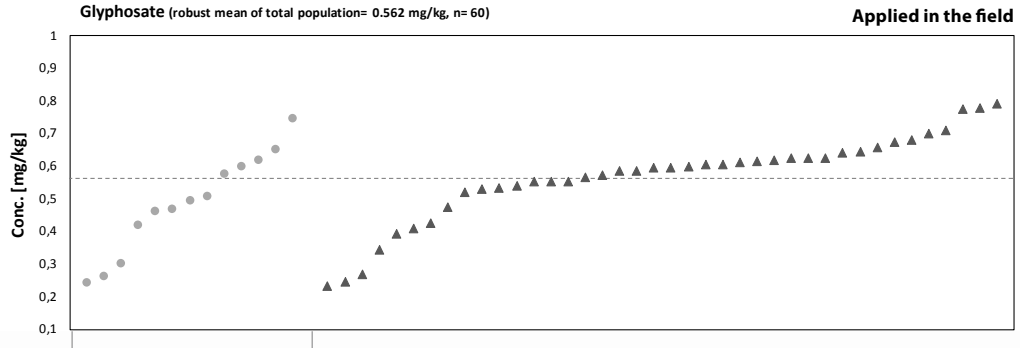
4.5.2 Initial Sample Temperature and Extraction Time

Since both temperature and soaking/extraction time can in some cases influence the stability or the extractability of pesticides, the participants were asked to indicate the initial temperature as well as the soaking and extraction times entailed in their procedure. For laboratories using QuEChERS and QuPPe methods this information is compiled in **Table 4-11**. As can be seen in this table, a considerable number of laboratories has extracted the samples after they have reached room temperature. The shipment simulation stability tests demonstrated that this is not expected to have influenced the results significantly, at least if the material was not left standing for days.

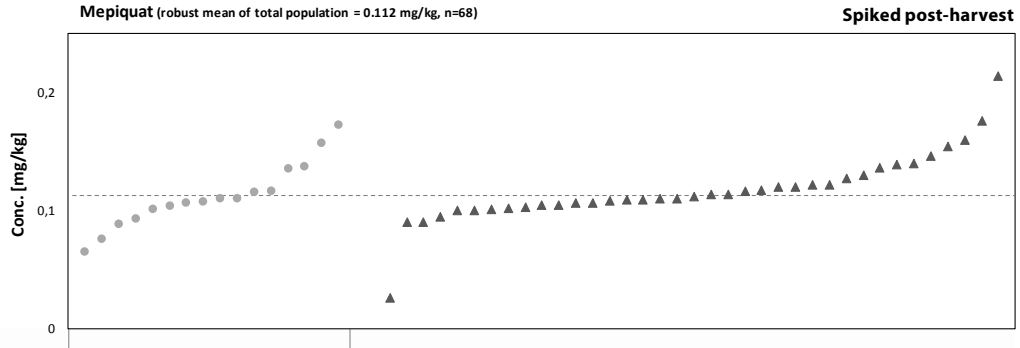
Soaking/extraction time plays a significant role in the extraction yields of incurred polar pesticides from cereals. In the case of ***glyphosate***, an incurred analyte in the current PT, the robust mean concentrations of the population applying cumulative soaking/extraction times ≤ 10 min and ≥ 15 min were 0.497 mg/kg and 0.584 mg/kg, respectively. This corresponds to an increase of 17.5 % (**Figure 4-4, p. 58**). Experiments by the EURL-SRM using the QuPPe method have shown extraction yields of ***glyphosate*** rising by 28 % when extracting the EUPT material (at the same milling grade as the material sent to the participants) for 15 min rather than 1 min. Prior to the start of the PT the organisers thus emphasized the need for extending QuPPe extraction time to at least 15 min. In the case of ***chlormequat***, which was also incurred, the impact of extraction time on the extraction yields was by far less pronounced (robust mean increased from 0.163 mg/kg when employing soaking/extraction times ≤ 10 min to 0.168 mg/kg at ≥ 15 min, see **Figure 4-4**). In experiments by the EURL-SRM, ***chlormequat*** did not show any significant increase in its extraction yields when comparing 1 min and 15 min extraction times. Only if the material was less intensively ground (with a knife mill), ***chlormequat*** yields rose by 25 % and ***glyphosate*** yields doubled when comparing 1 and 15 min extractions. The clearly smaller impact of particle size and extraction time in the case of ***chlormequat*** may be due to the fact that ***chlormequat*** tends to concentrate in the bran fraction than in the endosperm [7, 8]. In the case of ***mepiquat***, which was spiked after harvest, no impact of extraction time on extraction yields was observed (see **Figure 4-4**).

Table 4-11: Initial temperature, soaking and extraction time for sample preparation using QuEChERS and QuPPe methods

Soaking Step	Extraction time OR Soaking + Extraction time	Initial sample temperature											
		QuCEhERS						QuPPe					
		deep frozen (- 18 °C)	slightly frozen (- 8 °C – 0 °C)	just thawed	cold (4 °C – 10 °C)	ambient (20 °C – 24 °C)	no data	deep frozen (- 18 °C)	slightly frozen (- 8 °C – 0 °C)	just thawed	cold (4 °C – 10 °C)	ambient (20 °C – 24 °C)	no data
No	1 min										2		
	2 min	4	6		11	15			2			3	
	5 min		6			2			3			4	
	10 min				9						2	4	
	15 min		6	5		11		2	6			3	
	20 min	12						6				5	
	30 min					5		2		6	3	6	
	60 min											2	
Yes, after addition of water	1 min				1								
	6 min - 10 min	5		5	6	16	2	4				9	
	11 min - 15 min			5	4	17				3	5	7	
	16 min - 20 min	5			7	34		3	10		3	10	
	21 min - 25 min	6			9	18		6			6	18	
	30 min		6		5						2	3	
	31 min - 35 min				5	15	9				3	16	1
	40 min	8	4			5		1	1	1			
	45 min	4	5			6		2				14	
	50 min							2					
	> 60 min					4		6				6	
	no data			4									
Yes, after addition of water and organic solvent	2 min											1	
	5 min					12							
	6 min - 10 min	6			6	4		2			4	1	
	11 min - 15 min				5	5					8		
	16 min - 20 min					5						6	
	21 min - 25 min									3	5	1	
	30 min											2	
	35 min				4	6		5					
	50 min											2	
	60 min				1								
no data	1 min							1					
	2 min	5											
	10 min					5					5		
	15 min							2					
	20 min	6										2	
	25 min											4	
	30 min										1		
	45 min								2				
	no data					5	6					4	1
Total		61	33	19	73	190	17	44	24	13	49	133	2

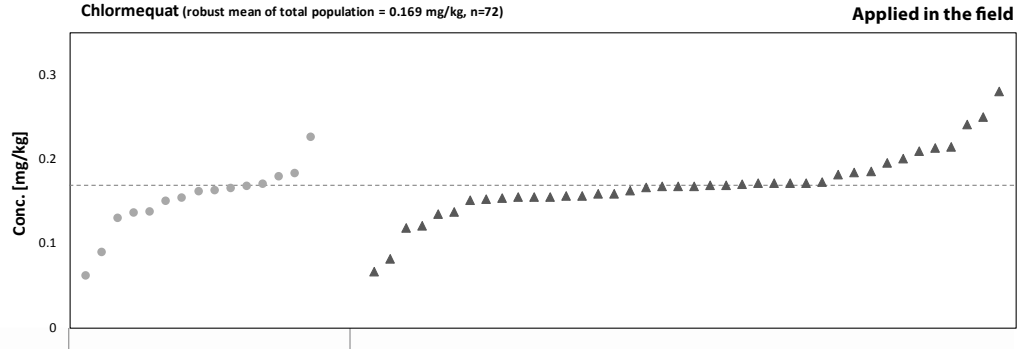


Soaking + Extraction Time	● ≤ 10 min	▲ > 15 min
No. of Numerical Results	13	41
No. of FNs	0	1
Robust Mean [mg/kg]	0.497	0.584



Soaking + Extraction Time	● ≤ 10 min	▲ > 15 min
No. of Numerical Results	17*	37
No. of FNs	0	0
Robust Mean [mg/kg]	0.112	0.113

* one result (1.73 mg/kg) not shown



Soaking + Extraction Time	● ≤ 10 min	▲ > 15 min
No. of Numerical Results	17*	41
No. of FNs	0	0
Robust Mean [mg/kg]	0.163	0.168

* two results (0.6009 mg/kg and 1.35 mg/kg) not shown

Figure 4-4: Influence of soaking/extraction time on the results of analytes extracted by QuPPe-based methods. Only results of laboratories from EU and EFTA countries were considered. The dotted lines represent the assigned values (robust means) of the entire population).

4.5.3 Calibration Approaches

Table 4-12 gives an overview of the calibration types as well as the use or non-use of internal standards by the participants within this PT. The standard additions approach was employed in 14 % of the cases (4 % with additions to the sample portions at the beginning of extraction and 10 % with addition to the extract aliquots). Ca. 74 % of the results were generated using matrix-matched calibration (including ca. 14 % that have employed standard additions approach). Ca. 19 % of the results were generated using solvent-based calibrations. For ca. 8 % of the results, no information was provided regarding the type of calibration. Among the 517 cases where matrix-matched calibrations were employed the blank matrix provided by the organisers was used to obtain the recovery figures in 85 % of the cases. Also among these 517 cases multiple level calibration was employed in 484 cases (94 %) and single level calibrations in 33 cases (6 %). Among the 160 cases where calibration solutions were prepared in pure solvent ILISs were applied in approximately 33 % of the cases (52 out of 160 cases). Approximately 50 % of the results were generated without the use of internal standards.

Table 4-12: Calibration approaches employed for the analysis of the target compounds combined with the internal standards used in the EUPT-SRM10

	Internal Standard used?																	
	COMPULSORY COMPOUNDS						OPTIONAL COMPOUNDS						Overall					
Calibration type	Yes, Isotope labelled analogue of target analyte (ILIS)	Yes, generic IS w. good extr., chr/phy, measurem. behaviour	Yes, other compound with similar behavior to target analyte	None	no data	sum	Yes, Isotope labelled analogue of target analyte (ILIS)	Yes, generic IS w. good extr., chr/phy, measurem. behaviour	Yes, other compound with similar behavior to target analyte	None	no data	sum	Yes, Isotope labelled analogue of target analyte (ILIS)*	Yes, generic IS w. good extr., chr/phy, measurem. behaviour*	Yes, other compound with similar behavior to target analyte*	None*	no data*	sum*
Matrix matched																		
Multiple level [and use of PT-Blank]	90 [80]	38 [36]	26 [26]	194 [162]	2 [0]	**350 [304]**	21 [20]	24 [21]	11 [11]	76 [60]	2 [0]	**134 [112]**	111 (13 %)	62 (7 %)	37 (4 %)	270 (31 %)	4 (0.5 %)	**484 (56 %)**
Single level [and use of PT-Blank]	2 [2]	3 [3]	4 [3]	15 [12]	1 [0]	**25 [20]**	0 [0]	0 [0]	0 [0]	8 [6]	0 [0]	**8 [6]**	2 (0.2 %)	3 (0.3 %)	4 (0.5 %)	23 (2.7 %)	1 (0.1 %)	**33 (3.8 %)**
Pure solvent																		
Multiple level	47	17	11	54	4	**133**	3	6	1	8	1	**19**	50 (6 %)	23 (3 %)	12 (1 %)	62 (7 %)	5 (1 %)	**152 (18 %)**
Single level	2	0	1	3	0	**6**	0	0	0	2	0	**2**	2 (0.2 %)	0 (0 %)	1 (0.1 %)	5 (1 %)	0 (0 %)	**8 (1 %)**
Standard addition																		
to sample portions	5	1	0	19	0	**25**	0	0	1	9	0	**10**	5 (1 %)	1 (0.1 %)	1 (0 %)	28 (3 %)	0 (0 %)	**35 (4 %)**
to extract aliquots	25	10	8	17	0	**60**	6	14	3	3	0	**26**	31 (4 %)	24 (3 %)	11 (1 %)	20 (2 %)	0 (0 %)	**86 (10 %)**
no data	20	1	8	20	1	**51**	6	2	2	7	1	**18**	26 (3 %)	3 (0.3 %)	11 (1 %)	28 (3 %)	2 (0.2 %)	**69 (8 %)**
Overall	**191 (29 %)**	**71 (11 %)**	**58 (9 %)**	**322 (50 %)**	**8 (1 %)**	**650 (100%)**	**36 (17 %)**	**46 (21 %)**	**18 (8 %)**	**113 (52 %)**	**4 (2 %)**	**217 (100%)**	**228 (26 %)**	**118 (14 %)**	**74 (9 %)**	**435 (50 %)**	**12 (1 %)**	**867 (100%)**

* Percentages in parentheses based on total number of results = 867

4.5.4 Use of Internal standards (ISs)

ISs are typically applied to correct for recovery, volume deviations and/or to compensate for the influence of matrix on measurement or derivatisation. An overview of the ISs used by the participants in the present PT is shown in **Table 4-13**. Approximately 50 % of the results were generated using ISs. ILISs were empoloyed in 26 % of the cases overall, this is roughly half of the cases where ISs were employed. In the case of compulsory compounds 29 % of the results were generated using ILIS with ***glyphosate*** (64 %), ***chlormequat*** (61 %) and ***mepiquat*** (55 %) showing the highest figures. In the case of ***dithiocarbamates*** 2 laboratories used $^{13}CS_2$ as ILIS. In the case of optional compounds ILISs were employed in only 17 % of the cases with ***phosphonic acid*** (72 %) and ***N-acetyl glufosinate*** (38 %) leading the list. ILISs offer the highest accuracy and are recommended for both recovery correction and matrix-effect correction. In order to assist the laboratories in the analysis of ***phosphonic acid***, the Organisers provided the participants with a solution of $^{18}O_3$ ***phosphonic acid***, together with short instructions on how to use. As can be seen in **Table 4-13** the percentage of laboratories using ILIS for the analysis of ***phosphonic acid*** was the highest among all analytes in the current PT.

The generic ISs nicarbazin (46 cases) and triphenyl phosphate (27 cases), which are often used in the QuEChERS procedure, were the most frequently used ISs. In the case of ***dithiocarbamates***, laboratories used dichlormethane, thiophene, chloroform and iodoethane. Generic ISs mainly correct for volumetric errors, spills, and to some extend also for sensitivity drifts of instruments. Showing very high recoveries, the recovery-based correction through such ISs is typically minor. In case of significant matrix effects specifically on

Table 4-13: Use of internal standards for the analysis of the compounds in the EUPT-SRM10

COMPULSORY COMPOUNDS											
Q: was IS used?	**ISs were added to...**	**2,4-D**	**Chlormequat**	**Dithiocarbamates**	**Ethephon**	**Glyphosate**	**MCPA**	**Mepiquat**	**Propamocarb**	**Sum**	
Yes, Isotope labelled analogue of target analyte (ILIS)	**Sum**	**6 (7 %)**	**48 (61 %)**	**2 (2 %)**	**31 (47 %)**	**44 (64 %)**	**7 (8 %)**	**44 (55 %)**	**9 (10 %)**	**191 (29 %)**	
	1) at the beginning of procedure	4 (5 %)	40 (51 %)	2 (2 %)	23 (35 %)	37 (54 %)	6 (7 %)	35 (44 %)	8 (9 %)	155 (24 %)	
	2) to an aliquot of the final extract	2 (2 %)	6 (8 %)	–	6 (9 %)	4 (6 %)	1 (1 %)	7 (9 %)	1 (1 %)	27 (4 %)	
	3) at an intermediate stage (between 1 and 2)	–	2 (3 %)	–	1 (2 %)	2 (3 %)	–	2 (3 %)	–	6 (1 %)	
	no data	–	–	–	1 (2 %)	1 (1 %)	–	–	–	2 (0 %)	
Yes, generic IS w. good extr. and chr/phy, measurement behaviour OR Yes, other compound with similar behavior to target analyte	**Sum**	**31 (35 %)**	**4 (5 %)**	**14 (15 %)**	**9 (14 %)**	**(0 %)**	**31 (36 %)**	**7 (9 %)**	**32 (35 %)**	**128 (20 %)**	
	1) at the beginning of procedure	22 (25 %)	3 (4 %)	12 (13 %)	8 (12 %)		21 (25 %)	7 (9 %)	24 (26 %)	97 (15 %)	
	2) to an aliquot of the final extract	8 (9 %)	1 (1 %)	2 (2 %)	1 (2 %)		9 (11 %)		6 (7 %)	27 (4 %)	
	3) at an intermediate stage (between 1 and 2)	1 (1 %)	–	–	–	–	1 (1 %)	–	2 (2 %)	4 (1 %)	
no	–	51 (58 %)	27 (34 %)	74 (80 %)	25 (38 %)	21 (30 %)	46 (54 %)	29 (36 %)	50 (55 %)	323 (50 %)	
no data	–	–	–	2 (2 %)	1 (2 %)	4 (6 %)	1 (1 %)	–	–	8 (1 %)	
Overall		**88**	**79**	**92**	**66**	**69**	**85**	**80**	**91**	**650**	

the IS (e.g. in LC-analysis) a bias is, however, added to all analytes. Among the 419 cases where ISs were used the IS was added at the beginning of the procedure in 329 cases (79 %), to an aliquot of the final extract in 73 cases (17 %) and at an intermediate stage in 10 cases (4 %).

4.5.5 Correction of Results for Recovery

The various approaches employed by the laboratories to correct their results for recovery are compiled in **Table 4-14 (p. 62)**. Recovery corrections can be accomplished by using ILISs or other approaches. In many cases other approaches were combined with the use of ILISs for better accuracy. Among the compulsory compounds ILISs were used as the only means of recovery correction in 75 cases (12 % overall) and in combination with other means of recovery correction in 74 cases (11 %). Among compulsory compounds recovery correction approaches other than ILISs included procedural calibrations (95 cases, 15 %), standard additions to sample portions (95 cases, 15 %), standard additions to extraction aliquots (47 cases, 7 %) and the use of recovery factors (16 cases, 3 %). Therein ILISs were combined with procedural calibrations in 27 cases (4 % overall) and with standard additions to sample portions in 37 cases (6 %). ILISs were furthermore combined with standard additions to extract aliquots in 10 cases (2 %). Standard additions to aliquots alone only compensate for matrix influences during measurement or derivatizations but not for recovery losses or volumetric errors during extraction. The use of matrix-matched calibrations also helps to compensate matrix effects especially when the same matrix is used. The use of recovery factors was very limited (3 % of the cases for compulsory compounds).

	OPTIONAL COMPOUNDS								ALL COMPOUNDS
	Q: was IS used?	ISs were added to...	Bentazone	Bromoxynil	N-Acetyl glufosinate	Phosphonic acid	TFNG	Sum	Overall
	Yes, Isotope labelled analogue of target analyte (ILIS)	**Sum**	**7 (9 %)**	**4 (6 %)**	**6 (38 %)**	**18 (72 %)**	**1 (3 %)**	**36 (17 %)**	**227 (26 %)**
		1) at the beginning of procedure	5 (7 %)	3 (4 %)	4 (25 %)	14 (56 %)	1 (3 %)	27 (12 %)	182 (21 %)
		2) to an aliquot of the final extract	2 (3 %)	1 (1 %)	2 (13 %)	2 (8 %)	–	7 (3 %)	34 (4 %)
		3) at an intermediate stage (between 1 and 2)	–	–	–	1 (4 %)	–	1 (0 %)	8 (1 %)
		no data	–	–	–	1 (4 %)	–	1 (0 %)	3 (0 %)
	Yes, generic IS w. good extr. and chr/phy, measurement behaviour OR Yes, other compound with similar behavior to target analyte	**Sum**	**23 (31 %)**	**26 (37 %)**	**2 (13 %)**	**–**	**13 (42 %)**	**64 (29 %)**	**192 (22 %)**
		1) at the beginning of procedure	17 (23 %)	20 (29 %)	2 (13 %)		11 (35 %)	50 (23 %)	147 (17 %)
		2) to an aliquot of the final extract	5 (7 %)	5 (7 %)			2 (6 %)	12 (6 %)	39 (4 %)
		3) at an intermediate stage (between 1 and 2)	1 (1 %)	1 (1 %)	–	–	–	2 (1 %)	6 (1 %)
	no	–	45 (60 %)	38 (54 %)	7 (44 %)	6 (24 %)	17 (55 %)	113 (52 %)	436 (50 %)
	no data	–	–	2 (3 %)	1 (6 %)	1 (4 %)	–	4 (2 %)	12 (1 %)
	Overall		**75**	**70**	**16**	**25**	**31**	**217**	**867**

Table 4-14: Overview of other means of correcting for recovery or matrix-effects used by the laboratory

	COMPULSORY COMPOUNDS								
Q: Other means of correcting for recovery or matrix-effects used?	**2,4-D**	**Chlormequat**	**Dithiocarbamates**	**Ethephon**	**Glyphosate**	**MCPA**	**Mepiquat**	**Propamocarb**	**Overall**
Yes,	42 (48 %)	48 (61 %)	19 (21 %)	44 (67 %)	57 (83 %)	40 (47 %)	49 (61 %)	48 (53 %)	347 (53 %)
1): using procedural calibration [combined with ILIS]	12 [1]	12 [5]	7	12 [4]	14 [9]	11 [1]	12 [5]	15 [2]	95 (15 %) [27 (4 %)]
2): via std. additions to sample portions [combined with ILIS]	11 [1]	13 [8]	10	11 [8]	12 [9]	11 [1]	14 [8]	13 [2]	95 (15 %) [37 (6 %)]
3): via std. additions to extract aliquots [combined with ILIS]	9	6 [2]		5 [1]	5 [3]	8 [1]	6 [2]	8 [1]	47 (7 %) [10 (2 %)]
4): use a recovery factor [combined with ILIS]	3	1 [1]	1	1 [1]	3 [1]	3	1 [1]	3	16 (3 %) [4 (0.6 %)]
5): other [combined with ILIS]	5 [1]	1 [1]	1	2 [1]	2 [2]	4 [1]	1 [1]	4 [1]	20 (3 %) [8 (1 %)]
Correcting via ILIS only	41 (47 %) [3]	35 (44 %) [22]	59 (64 %) [2]	27 (41 %) [11]	23 (33 %) [15]	40 (47 %) [3]	34 (43 %) [17]	38 (42 %) [2]	297 (46 %) [75 (12 %)]
not answering this question **[but correcting via ILIS]**	7	11 [9]	14	8 [5]	10 [5]	8	12 [10]	10 [1]	80 (12 %) [30 (5 %)]
Overall SUM	**88**	**79**	**92**	**66**	**69**	**85**	**80**	**91**	**650**

	OPTIONAL COMPOUNDS					
Q: Other means of correcting for recovery or matrix-effects used?	**Bentazone**	**Bromoxynil**	**N-Acetyl glufosinate**	**Phosphonic acid**	**TFNG**	**Overall**
Yes,	**38 (51 %)**	**36 (51 %)**	**16 (100 %)**	**24 (96 %)**	**17 (55 %)**	**131 (60 %)**
1): using procedural calibration [combined with ILIS]	11 [2]	12 [1]	3	8 [5]	5	39 (18 %) [8 (4 %)]
2): via std. additions to sample portions [combined with ILIS]	10	9	3 [3]	5 [3]	6	33 (15 %) [6 (3 %)]
3): via std. additions to extract aliquots [combined with ILIS]	9 [1]	8	4 [1]	1	2	24 (11 %) [2 (1 %)]
4): use a recovery factor	1	2	1		2	6 (3 %) [0 (0 %)]
5): other [combined with ILIS]	4 [1]	4 [1]	1	2 [2]	2	13 (6 %) [4 (2 %)]
Correcting via ILIS only	**32 (43 %) [3]**	**27 (39 %) [2]**	**1 (6 %) [1]**	**7 (28 %) [7]**	**11 (35 %) [1]**	**78 (36 %) [14 (7 %)]**
not answering this question **[but correcting via ILIS]**	8	8	3 [1]	2 [1]	3	24 (11 %) [2 (1%)]
Overall SUM	**75**	**70**	**16**	**25**	**31**	**217**

The distribution of the recovery figures are shown in **Figure 4-5**. None of the reported recovery figures exceeded 100 %. In 6 (27 %) of the total 22 cases where results were corrected based on recovery figures the recoveries reported were within the 70 to 100 % range and in 5 (23 %) of the cases the recovery figures were below 50 %. In 19 out of the 22 cases the respective experiments for establishing the recovery figures were conducted within the same batch, using the blank material provided by the organiser. In the other three cases the recovery figures were derived from the same batch using other matrices (1×) or from QC validation data (2×). In 4, 1, 7, 5 and 5 cases the recovery figures used were based on only one, two, three, four or more than five recovery experimental replicates, respectively (**Table 4-15**). Compared with the previous EUPT-SRMs the use of recovery figures for the correction of results has dropped from 67 cases in EUPT-SRM8 to 52 cases in EUPT-SRM9 and to 22 cases in EUPT-SRM10. In addition, the percentage of cases in which the recovery figures were obtained from only one experiment reduced significantly: 28 % (19 out of 67) for EUPT-SRM8, 56 % (29 out of 52) for EUPT-SRM9 and 18 % (4 out of 22) in the current EUPT-SRM10.

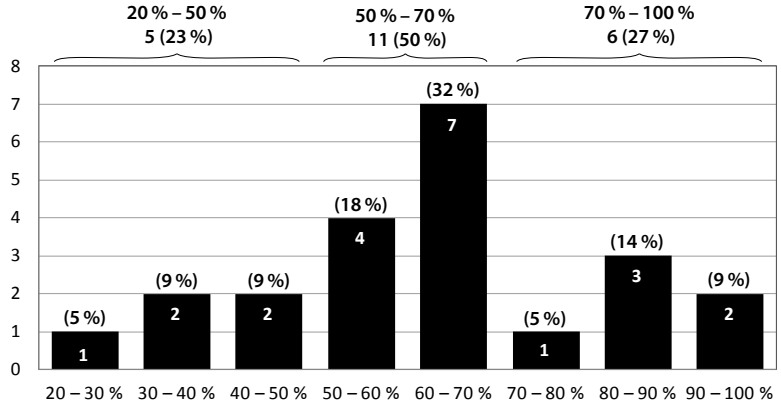


Figure 4-5: Distribution of recovery figures used for results correction for the recovery

Table 4-15: Compilation of results where RECOVERY-BASED CORRECTION OF RESULTS was applied and influence on the AAZ-scores (average bias)

Compounds	LabCode SRM10-	Submitted Recovery figure [%]	Recovery Replicates considered	Submitted Result [mg/kg]	z-score derived from submitted result	z-score (if non-corrected results were submitted)*
2,4-D (free acid) | AV = 0.092 mg/kg	36	61	> 5	0.109	0.7	-1.1
	70	62	> 5	0.0906	-0.1	-1.6
	103	69	1	0.093	0.0	-1.2
Chlormequat | AV = 0.167 mg/kg	15	84	3	0.158	-0.2	-0.8
Dithiocarbamates | AV = 0.559 mg/kg	112	85	4	0.47	-0.6	-1.1
Ethephon | AV = 0.162 mg/kg	15	90	3	0.193	0.8	0.3
Glyphosate | AV = 0.568 mg/kg	15	96	3	0.64	0.5	0.3
	72	53	3	0.264	-2.1	-3.0
	83	50	3	0.707	1.0	-1.5
MCPA | AV = 0.081 mg/kg	36	68	> 5	0.0964	0.8	-0.8
	70	60	> 5	0.0767	-0.2	-1.7
	103	68	1	0.087	0.3	-1.1
Mepiquat | AV = 0.114 mg/kg	15	79	3	0.116	0.1	-0.8
Propamocarb | AV = 0.067 mg/kg	71	61.2	2	0.115	2.9	0.2
	82	29	4	0.072	0.3	-2.8
	103	31	1	0.08	0.8	-2.5
Bentazone | AV = 0.098 mg/kg	82	59	4	0.116	0.7	-1.2
Bromoxynil | AV = 0.125 mg/kg	70	60	> 5	0.124	0.0	-1.6
	82	66	4	0.153	0.9	-0.8
N-Acetyl glufosinate | AV = 0.319 mg/kg	15	93	3	0.321	0.0	-0.3
TFNG | AV = 0.168 mg/kg	82	40	4	0.21	1.0	-2.0
	103	50	1	0.156	-0.3	-2.1
Overall	**9 labs**	**22 cases**	1 repl. (4×) 2 repl. (1×) 3 repl. (7×) 4 repl. (5×) > 5 repl. (5×)		**AAZ = 0.7** 20× Acceptable 2× Questionable 0× Unacceptable	**AAZ = 1.3** 18× Acceptable 4× Questionable 0× Unacceptable

* Calculated using the current Assigned Values
AV = assigned value; AAZ = average of absolute z-score indicating average bias

This trend is surely related to the fact that the EURL-SRM has repeatedly emphasized in the EUPT-reports and at the EURL-Workshops that using a single recovery figure may be critical due to the higher risk of spurious errors. On the other hand the use of historical QC-data from basic and routine validations is also risky especially if there is differences from matrix to matrix and if variability is high.

Correction using a recovery factor will typically lead to a result that is closer to the assigned value compared to the result that would have been reported if no recovery correction had been applied (provided that the assigned value is not strongly biased from the real value itself). As in previous EUPT-SRMs the submitted data support this trend. In 18 cases the absolute z-scores resulted from results with recovery correction were smaller than if the recovery correction was not applied. Only in 4 cases the opposite happened. In one case the z-score paradoxically shifted from "acceptable" even to "unacceptable" following the correction for recovery. When comparing the AAZ of the recovery-corrected results with the AAZ of the results that would have been submitted if no recovery-based correction had been applied, a significant decline from 1.3 to 0.7 is observed. In previous EUPT-SRMs similar trends were observed. Despite this trend, recovery correction based on recovery figures should be the last remedy as this approach is tricky and less accurate compared to other types of result correction such as the use of ILISs or standard addition to sample portions (see below).

As in previous EUPT-SRMs the results generated using ILISs were compared to the results generated not using them. Both the bias (reflected by the deviation of the robust means) and the variability (reflected by the AAZ and the robust relative standard deviation CV^*) of the two populations were compared (see **Table 4-16**). In the case of ***chlormequat*** the robust means of the two populations were very close. The distribution of the results of the laboratories using ILIs was, however, clearly narrower (CV^* = 14.5 %, AAZ = 0.70) compared to that of laboratories not using ILIS (CV^* = 23 %, AAZ = 0.96). In the case of ***glyphosate*** the effect was equally impressive with the distribution of the results being much narrower when ILIS was used (CV^* = 17 %) than if no ILIs was used (CV^* = 42 %). The difference in the robust means was again moderate.

In the case of ***phosphonic acid*** the number of results obtained without ILIS was too small (n = 7) thus not allowing proper statistical evaluation. However, when excluding these results from the overall population the CV^* of the remaining population impressively dropped from 27 % to 14 %. The robust mean concentration of the remaining population (not using ILIS) was relatively far apart (ca. 18 %) from the population using ILIS. But the population not using ILIS was small and, furthermore, the individual results within this population were broadly distributed above and below the assigned value. The EUPT-Scientific committee decided not to disregard them from the total population used to establishing the assigned value.

In the case of ***ethephon***, the population of results submitted by laboratories using ILIS (n = 31) was similar to that of those not using ILIS (n = 30). Robust mean values, CV^*s and AAZs were comparable indicating that for this compound the impact of ILIS was rather minor. The non-improvement in precision when using ILIS in the present EUPT may be related to various effects such as a) differences in the degradation rate of ***ethephon***-ILIS between the undiluted and the diluted working solutions used for spiking analytical portions and calibration standards, respectively; b) the weak matrix effects of maize on ***ethephon*** (e.g using QuPPe 1.3, which was employed by the majority of the laboratories reducing the risk of matrix-effect-related errors) and c) the more careful choice of non-ILIS-related recovery correction approaches by the laboratories, as reflected by an increase in the percentage of participants correcting results for recovery and a decrease of the laboratories correcting results based on recovery figures (which is tricky). Among the 30 laboratories not using ILIS of ethephon, other means were applied to correct for recovery (procedural calibration: 8 laboratories; standard additions to sample portions: 3 laboratories) or to correct for matrix effects (standard additions to extract aliquots: 3 laboratories; matrix matched calibrations: 26 laboratories).

In the case of ***mepiquat*** a paradox effect was observed with the population using ILIS having a higher CV^* and AAZ than the population not using. Excluding two strangely high results with z-scores of 56.9 and 13.1 from the population using ILIS the CV^* and AAZ drops to 18.8 % and 0.65, respectively, which is close but still slightly higher than the respective figures of the laboratories not using ILIS.

Similar observations as regards the positive impact of ILISs on the quality of the results were made in the previous EUPT-SRMs (6 – 9).

Table 4-16: Impact of ILISs on the distribution of results and the average bias (only results from EU and EFTA laboratories were taken into account)

	Phosphonic acid			Chlormequat		
	All Results	Results Obtained Using ILIS	Results Obtained without ILIS	All Results	Results Obtained Using ILIS	Results Obtained without ILIS
Robust Mean [mg/kg]	0.584	0.620	0.514	0.167	0.173	0.164
*CV**	27.3 %	**13.9 %**	41.3 %	18.2 %	**14.5 %**	23.2 %
AAZ [1] (average bias)	0.98	**0.80**	1.41	0.73	**0.70**	0.96
No. of results [2]	25	18	7	75	45	30
No. (%) of acceptable results	20 (80 %)	16 (89 %)	6 (86 %)	68 (91 %)	41 (91 %)	27 (90 %)
No. (%) of questionable results	3 (12 %)	1 (6 %)	0 (0 %)	5 (7 %)	2 (4 %)	3 (10 %)
No. (%) of unacceptable [2] results	2 (8 %)	1 (6 %)	1 (14 %)	2 (3 %)	2 (4 %)	0 (0 %)
	Glyphosate					
	All Results	Results Obtained Using ILIS	Results Obtained without ILIS			
Robust Mean [mg/kg]	0.568	0.582	0.489			
*CV**	22.8 %	**17.0 %**	42.1 %			
AAZ [1] (average bias)	0.89	**0.54**	1.57			
No. of results [2]	64	43	21			
No. (%) of acceptable results	56 (88 %)	42 (98 %)	16 (76 %)			
No. (%) of questionable results	5 (8 %)	1 (2 %)	2 (10 %)			
No. (%) of unacceptable [2] results	3 (5 %)	0 (0 %)	3 (14 %)			
	Ethephon			Mepiquat		
	All Results	Results Obtained Using ILIS	Results Obtained without ILIS	All Results	Results Obtained Using ILIS	Results Obtained without ILIS
Robust Mean [mg/kg]	0.162	0.182	0.149	0.114	0.120	0.112
*CV**	30.8 %	**28.6 %**	30.9 %	18.5 %	**20.8 %**	15.2 %
AAZ [1] (average bias)	1.11	**1.09**	0.96	0.74	**0.86**	0.60
No. of results [2]	61	31	30	76	44	32
No. (%) of acceptable results	52 (85 %)	27 (87 %)	25 (83 %)	69 (91 %)	41 (93 %)	30 (94 %)
No. (%) of questionable results	5 (8 %)	1 (3 %)	4 (13 %)	3 (4 %)	0 (0 %)	1 (3 %)
No. (%) of unacceptable [2] results	4 (7 %)	3 (10 %)	1 (3 %)	4 (5 %)	3 (7 %)	1 (3 %)

1) z-scores calculated using the robust mean in the corresponding population, "5" was used in case of the z-score was higher than 5
2) including false negative results

4.5.6 Coverage of Compounds in Routine Scope and Analytical Experience of Laboratories

As can be seen in **Figure 4-6 (p. 66)** the percentage of participating laboratories from EU- and EFTA-countries (n = 104) that covered the various compounds in the EUPT-SRM10 Target Pesticides List varied greatly ranging from 54 % (*fenbutatin oxide*) to 84 % (***propamocarb***) in the case of compulsory compounds and between 13 % (*MPP*) and 68 % (*2,4-DP*) for the optional ones. Calculating based on the full number of laboratories that were finally considered as being obliged to take part in this test (n = 120, see **Chapter 3**), the percentages lower further (see Figure 4-3). Although introduced several years ago, *fenbutatin oxide*, ***ethephon*** and ***glyphosate*** are still analysed by a comparably small percentage of laboratories on a routine basis (37, 39 and 45 %, respectively).

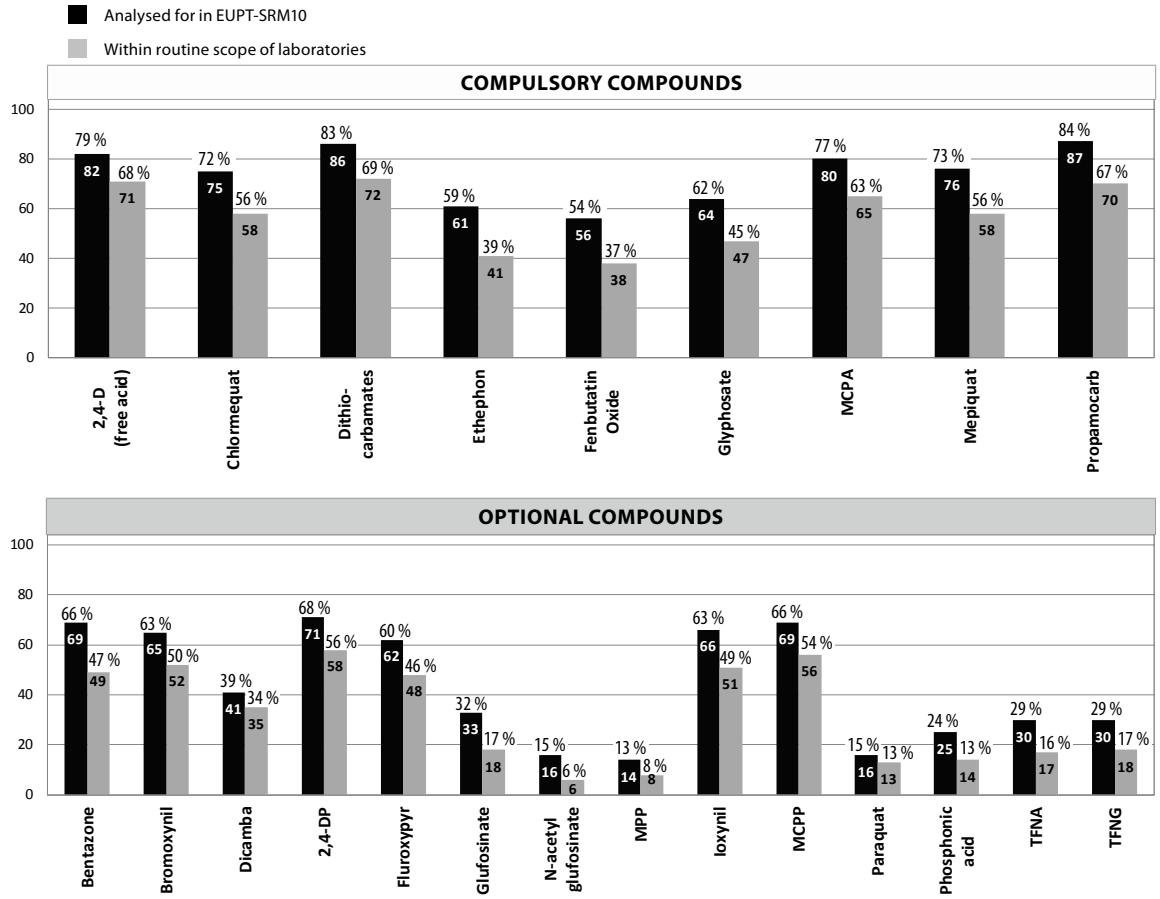


Figure 4-6: Number of laboratories targeting compounds within the framework of the EUPT-SRM10 and within their routine scope. Percentages are based on the total number of participating laboratories from EU- and EFTA-countries having submitted at least one result (n = 104).

Compounds reported as belonging to the routine scope of laboratories were all targeted by most laboratories with very few exceptions for which the organisers asked for explanations. Among the COMPULSORY compounds, one laboratory not covering ***ethephon*** reported that this compound is part of the routine scope but not routinely covered in this specific commodity (maize). *Fenbutatin oxide* was not covered by two laboratories, one of them informing about technical problems and the other one not giving any explanation. OPTIONAL compounds included in the routine scope of participating laboratories were in 97 % of the cases also targeted by those laboratories in this exercise (**Table 4-17**). In 7 out of the 12 cases, where the laboratories did not target the analytes belonging to the their routine scope, no reason was reported. In three cases (1× *paraquat*, 1× *dicamba* and 1× MCPP) the laboratories reported about technical problems and in the remaining two cases (1× *paraquat* and 1× ***bromoxynil***) the laboratories could not perform the analysis due to personnel shortage.

In 356 cases the participating laboratories even analysed compounds not yet included in their routine scope, among them 165 cases concerning compulsory compounds and 191 cases concerning optional compounds. This indicates that many laboratories are in the position or even in the process of expanding

Table 4-17: Inclusion of EUPT-SRM10 compounds in the laboratories' routine scope (including data of laboratories from EU-candidate and third countries)

		within routine scope of lab		NOT within routine scope of lab	
		analysed for in this EUPT	not analysed for	analysed for in this EUPT	not analysed for
COMPULSORY COMPOUNDS	**2,4-D**	75 (100 %)		13 (37 %)	22
	Chlormequat	61 (100 %)		18 (37 %)	31
	Dithiocarbamates	77 (100 %)		15 (45 %)	18
	Ethephon	44 (98 %)	1	22 (34 %)	43
	Fenbutatin oxide	37 (95 %)	2	23 (32 %)	48
	Glyphosate	51 (100 %)		18 (31 %)	41
	MCPA	67 (100 %)		18 (42 %)	25
	Mepiquat	61 (100 %)		19 (39 %)	30
	Propamocarb	72 (100 %)		19 (50 %)	19
	Sum	**545 (99 %)**	**3 (0.5 %)**	**165 (37 %)**	**277 (63 %)**
OPTIONAL COMPOUNDS	**Bentazone**	52 (100 %)		23 (40 %)	35
	Bromoxynil	54 (98 %)	1	16 (29 %)	39
	Dicamba	35 (97 %)	1	10 (14 %)	64
	2,4-DP	57 (98 %)	1	16 (31 %)	36
	Fluroxypyr	47 (98 %)	1	17 (27 %)	45
	Glufosinate	21 (100 %)		15 (17 %)	74
	N-Acetyl glufosinate	6 (100 %)		10 (10 %)	94
	MPP	8 (100 %)		6 (6 %)	96
	Ioxynil	51 (98 %)	1	17 (29 %)	41
	MCPP	54 (96 %)	2	17 (31 %)	37
	Paraquat	13 (81 %)	3	6 (6 %)	88
	Phosphonic acid	14 (100 %)		11 (11 %)	85
	TFNA	17 (94 %)	1	14 (15 %)	78
	TFNG	18 (95 %)	1	13 (14 %)	78
	Sum	**447 (97 %)**	**12 (2.6 %)**	**191 (18 %)**	**890 (82 %)**

their scope with additional SRM-compounds. The compounds most frequently analysed by laboratories but not yet included in their routine scope were *fenbutatin oxide* and ***bentazone*** (23 laboratories each).

Regarding compulsory compounds in 76 % of the cases laboratories indicated more than two years of analytical experience with the compounds that they reported results for (**Figure 4-7, p. 68**). In 10 % of the cases laboratories reported short experience (1 – 2 years), in 6 % of the cases they reported experience of less than one year and in another 6 % of the cases laboratories reported that there was no experience. Regarding optional compounds in 49 % of the cases laboratories indicated more than two years of analytical experience, in 20 % of the cases laboratories reported short experience (1 – 2 years), in 12 % of the cases they reported experience of less than one year and in 16 % of the cases no experience.

Laboratories with at least one year experience with the analytes seem to achieve on average better z-scores than those having less experience (**Figure 4-8, p. 68**). This mainly applies for the compulsory compounds. In the case of optional compounds the differences were moderate. In general differences could also result from different frequency with which compounds of varying analytical difficulty are represented in each group.

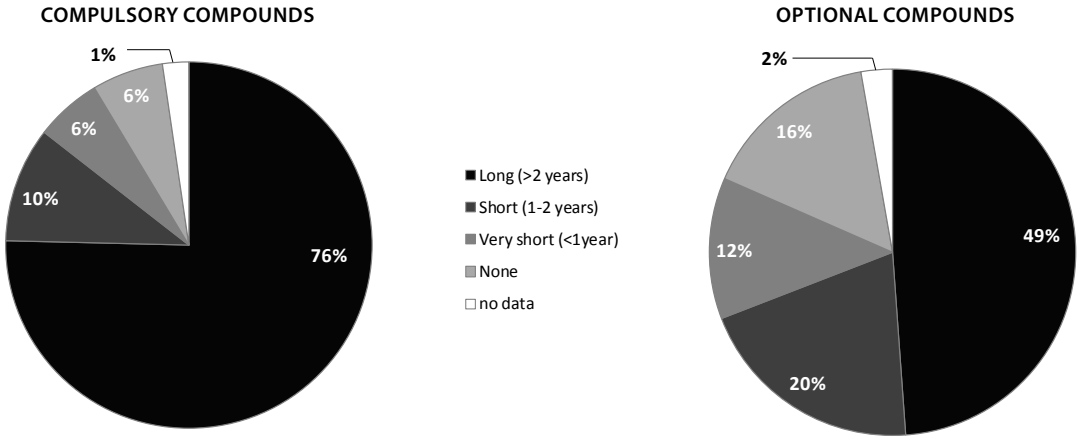


Figure 4-7: Experience of laboratories with the analysis of pesticides present in the test item (overall)

Table 4-18 gives an overview of laboratories' experience with the analysis of the various compounds in the Target Pesticides List. Among the compulsory compounds present in the test item laboratories had the most experience with the analysis of ***dithiocarbamates***. 80 laboratories (88 %) indicated more than two years of experience with analysing ***dithiocarbamates***. ***Propamocarb*** (87 %) follows. The compulsory compounds with which the laboratories had the least experience are ***ethephon*** with 25 % and ***glyphosate*** with 10 % of the laboratories reporting less than one year or no experience. This shows that the number of laboratories including these compounds in their portfolio is increasing.

For optional compounds the laboratories reported having overall less analytical experience compared to the compulsory ones. ***Bromoxynil*** (79 %) and ***bentazone*** (66 %) were the optional compounds with which the laboratories had the most experience. ***N-Acetyl glufosinate*** was the compound with which the participating laboratories had the least experience with more than 30 % of the laboratories submitting results reporting no experience with its analysis. Furthermore, almost half of the laboratories analysing for phosphinoic acid stated analytical experience of less than 1 year.

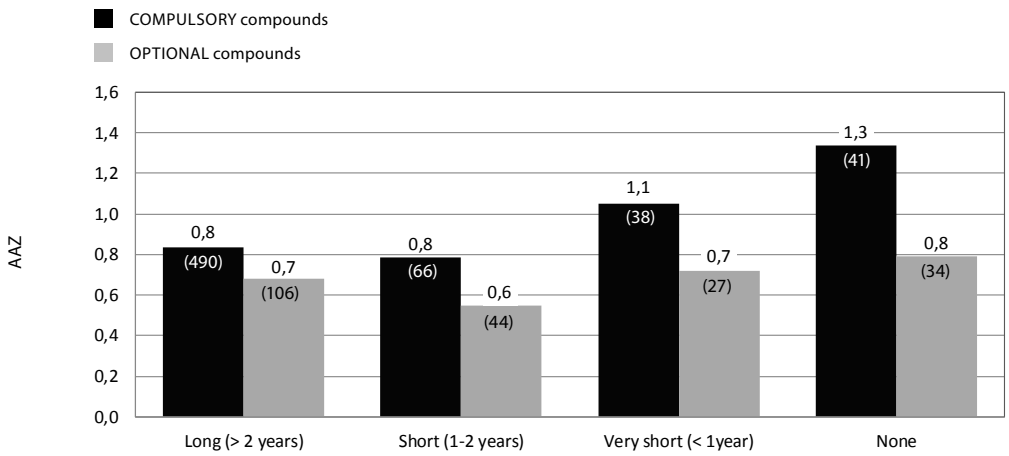


Figure 4-8: Correlation between the labs' experience with the analytes and the AAZ. (No. of data in each case in parentheses)

Table 4-18: Laboratories' experience with the analysis of individual compounds present in the test item and correlation with AAZ reflecting the average deviation from the assigned value. AAZs were calculated for population with at least 5 laboratories, CV^* were calculated for population with at least 10 laboratories. All participants, including laboratories from 3rd countries, were considered.

COMPULSORY COMPOUNDS				OPTIONAL COMPOUNDS			
Pesticides	**Experience**	**No. of Labs (%)**	**AAZ/CV^***	**Pesticides**	**Experience**	**No. of Labs (%)**	**AAZ/CV^***
2,4-D (free acid) AAZ: 0.7 CV^*: 19.5 %	> 2 years	69 (79 %)	0.6/17.0 %	**Bentazone** AAZ: 0.7 CV^*: 20.1 %	> 2 years	44 (79 %)	0.7/19.6 %
	1 – 2 years	10 (11 %)	0.8/19.5 %		1 – 2 years	11 (35 %)	0.6/17.7 %
	< 1 year	3 (3 %)			< 1 year	8 (26 %)	
	None	5 (6 %)	1.3/–		None	11 (35 %)	0.9/–
	no data	1 (1 %)			no data	1 (3 %)	
Chlormequat AAZ: 0.8 CV^*: 19.8 %	> 2 years	62 (78 %)	0.7/17.7 %	**Bromoxynil** AAZ: 0.8 CV^*: 18.7 %	> 2 years	46 (66 %)	0.7/19.7 %
	1 – 2 years	6 (8 %)	0.7/21.0 %		1 – 2 years	13 (19 %)	0.5/13.9 %
	< 1 year	6 (8 %)			< 1 year	2 (3 %)	
	None	4 (5 %)			None	6 (9 %)	0.7/–
	no data	1 (1 %)			no data	3 (4 %)	
Dithiocarbamates AAZ: 1.2 CV^*: 35.6 %	> 2 years	80 (88 %)	1.1/33.9 %	**N-Acetyl glufosinate** AAZ: 0.6 CV^*: 11.8 %	> 2 years	3 (19 %)	
	1 – 2 years	3 (3 %)	1.3/–		1 – 2 years	4 (25 %)	0.4/–
	< 1 year	2 (2 %)			< 1 year	3 (19 %)	
	None	5 (5 %)	1.4/–		None	5 (31 %)	0.4/–
	no data	2 (3 %)			no data	1 (6 %)	
Ethephon AAZ: 1.2 CV^*: 34.3 %	> 2 years	39 (67 %)	1.2/33.6 %	**Phosphonic acid** AAZ: 1.0 CV^*: 27.4 %	> 2 years	4 (17 %)	
	1 – 2 years	10 (17 %)	1.3/41.5 %		1 – 2 years	9 (38 %)	0.9/32.9 %
	< 1 year	7 (12 %)			< 1 year	6 (25 %)	
	None	9 (13 %)	1.1/–		None	5 (21 %)	0.4/–
	no data	1 (1 %)			no data	1 (4 %)	
Glyphosate AAZ: 1.0 CV^*: 23.4 %	> 2 years	43 (61 %)	0.9/22.4 %	**TNFG** AAZ: 0.7 CV^*: 19.1 %	> 2 years	9 (38 %)	0.5/–
	1 – 2 years	14 (20 %)	0.8/29.9 %		1 – 2 years	7 (29 %)	0.6/16.3 %
	< 1 year	4 (6 %)			< 1 year	8 (33 %)	
	None	3 (4 %)			None	7 (29 %)	1.4/–
	no data	5 (6 %)	2.9/–				
MCPA AAZ: 0.7 CV^*: 20.1 %	> 2 years	63 (74 %)	0.7/19.5 %				
	1 – 2 years	10 (12 %)	0.7/12.7 %				
	< 1 year	4 (5 %)					
	None	6 (7 %)	1.1/–				
	no data	2 (2 %)					
Mepiquat AAZ: 0.8 CV^*: 18.7 %	> 2 years	61 (73 %)	0.7/16.8 %				
	1 – 2 years	7 (8 %)	1.1/34.3 %				
	< 1 year	7 (8 %)					
	None	3 (4 %)					
	no data	2 (2 %)					
Propamocarb AAZ: 0.9 CV^*: 24.8 %	> 2 years	73 (87 %)	0.9/23.8 %				
	1 – 2 years	6 (7 %)	0.6/21.2 %				
	< 1 year	5 (9 %)					
	None	6 (11 %)	1.2/–				
	no data	1 (2 %)					

4.5.7 Size of Analytical Portions

The size of the analytical portions employed by the participants were in a range from 1 g to 200 g for ***dithiocarbamates***; from 2 g to 20 g for ***2,4-D***, ***MCPA***, ***bentazone***, and ***bromoxynil***; from 1 to 25 g for ***glyphosate***; from 2 to 25 g for ***chlormequat*** and ***mepiquat***; from 2 to 15 g for ***propamocarb*** and from 1, 2 or 3 g to 10 g for ***phosphonic acid***, ***TFNG*** and ***N-acetyl glufosinate*** respectively (**Figure 4-9**). The majority of the laboratories (90 %) employed analytical portions equal or larger than 5 g (the analytical portion size used by the organisers in the homogeneity test of all compounds except ***dithiocarbamates*** where 25 g were used). In the case of ***dithiocarbamates*** 54 % laboratories used analytical portions of 25 g (the sample weight used in the homogeneity test) or higher.

Where the analytical portions employed were significantly smaller than those used in the homogeneity test, sufficient homogeneity cannot be guaranteed. The participating laboratories were also informed via the Specific Protocol about the sample sizes (5 g and 25 g) used in the homogeneity tests and that sufficient homogeneity cannot be guaranteed when smaller analytical portions were used. In any case, the organisers recommended the participants in the Specific Protocol and in a short instruction accompanying the PT-materials thoroughly re-homogenising the entire sample at low temperatures before any analytical portions were taken. If performed, this step might have improved homogeneity.

4.5.8 Comparison of Reporting Limits, Assigned Values and MRRLs

Table 4-18 (p. 69) shows a compilation of the reporting limits (RLs) reported by the laboratories for each of the compounds present in the test item. In the case of ***dithiocarbamates*** three participants reported RLs of 0.5 mg/kg, which is close to the assigned value of 0.559 mg/kg. All other reported RLs were clearly lower than the corresponding assigned values.

In the case of compulsory compounds present in the test item, the respective MRRLs were not met in 12 % of the cases by the participating laboratories on average, in detail, the MRRLs were not met by 8 laboratories (9 %) in the case of ***2,4-D***, by 6 laboratories (8 %) in the case of ***chlormequat***, by 12 laboratories (13 %) in the case of ***dithiocarbamates***, by 19 laboratories (29 %) in the case of ***ethephon***, by 10 laboratories (14 %) in the case of ***glyphosate***, by 10 laboratories (12 %) in the case of ***MCPA***, by 7 laboratories (9 %) in the case of ***mepiquat***, and by 6 laboratories (7 %) in the case of ***propamocarb***. Among the optional compounds present in the test item, on average there were also 12 % of the participating laboratories not meeting the MRRL, namely 5 laboratories (7 %) in the case of ***bentazone***, 6 laboratories (9 %) in the case of ***bromoxynil***, 5 laboratories (31 %) in the case of ***N-acetyl glufosinate***, 8 laboratories (32 %) in the case of ***phosphonic acid*** and 3 laboratories (10 %) in the case of ***TFNG***.

4.5.9 Hydrolysis Step

For some acidic pesticides in the Target Pesticides List the legal residue definition includes esters and conjugates. The organizers still decided to only ask for the analysis of the free acids to keep the PT more simple and avoid mixed populations of results. The impact of alkaline hydrolysis on the release of conjugated residues of acidic pesticides will be studied in future EUPTs and collaborative method validation tests. Still, in total in 47 cases laboratories have performed hydrolysis step for these analytes: 7 cases for ***2,4-D***, 6 cases for ***MCPA***, 4 cases for ***bentazol***, 6 cases for ***bromoxynil*** and 5 cases for each of *2,4-DP*, *fluroxypyr*, *ioxynil* and *MCPP*. Since these analytes were either not present in the test material or spiked post harvest in form of free acid or free phenol (not incurred). For the compounds present in the Test Item no significant influence of hydrolysis on the results was observed by the organizers. However, the participants should keep in mind, that hydrolysis step does influence the analytical results in the real samples with incurred pesticides.

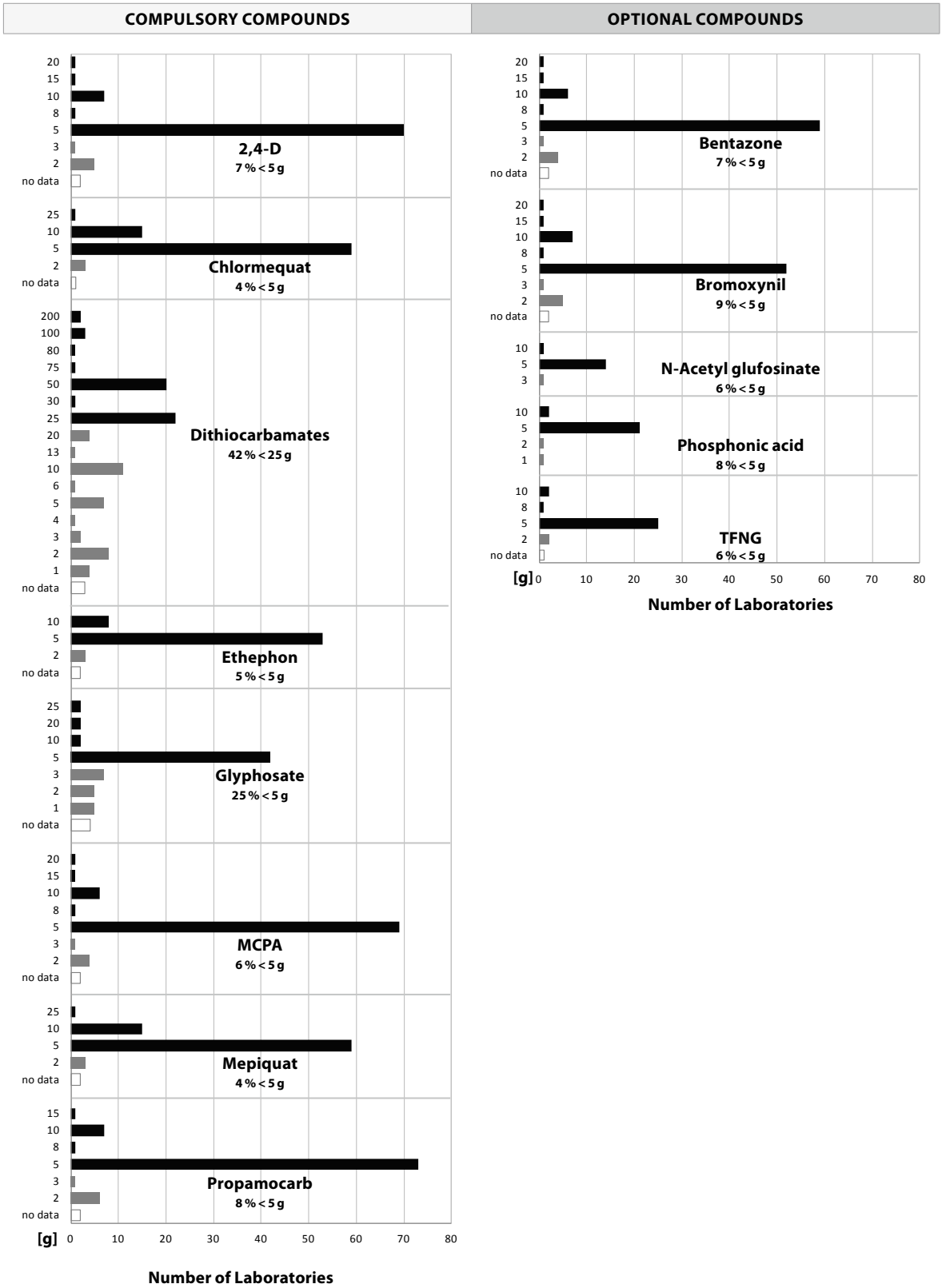


Figure 4-9: Size of analytical portions [g] employed by labs and percentage of analytical portions smaller than those used to test homogeneity by the organiser.

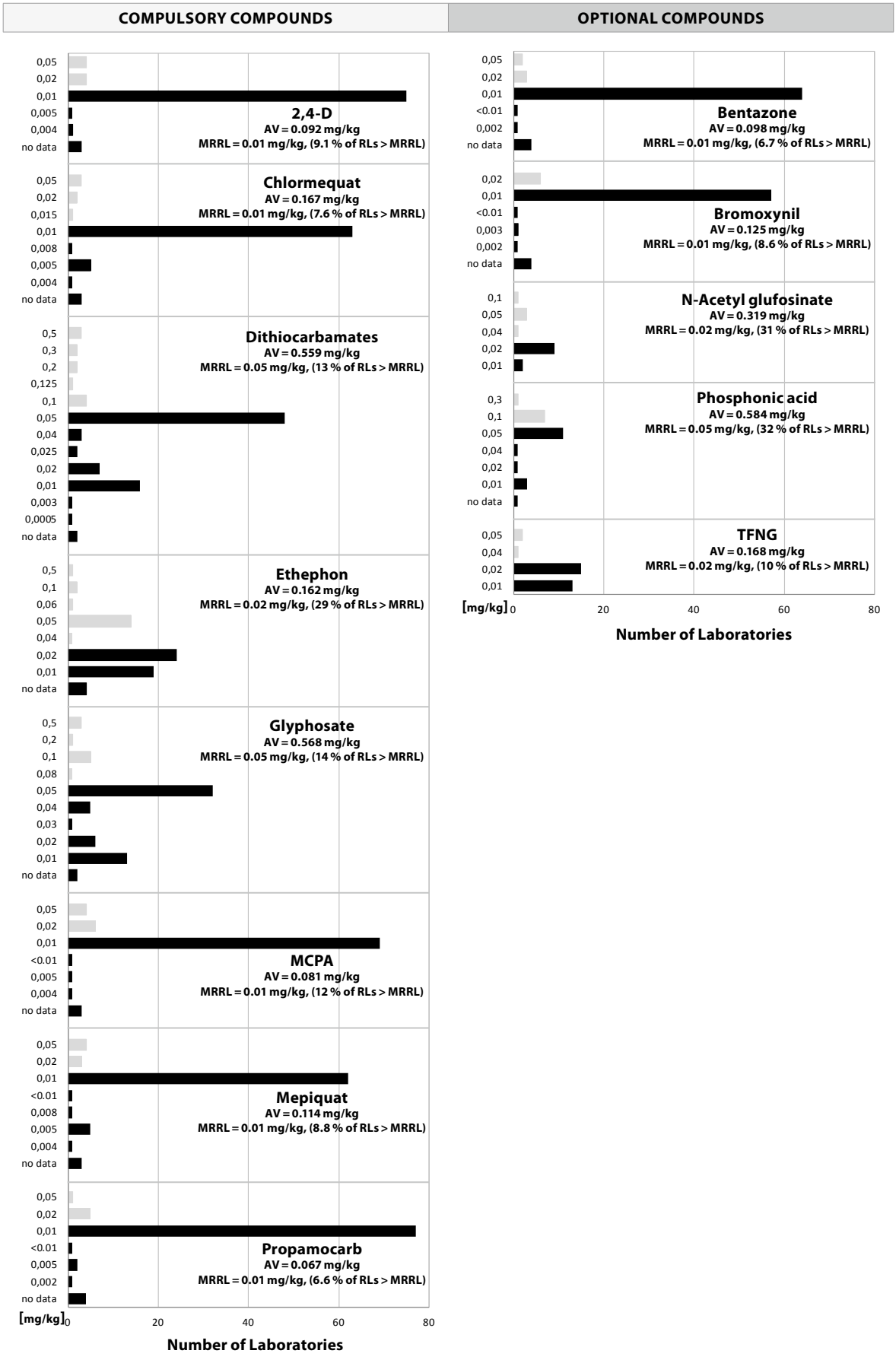


Figure 4-10: Distribution of laboratories' Reporting Limits (RLs) and comparison with the MRRLs and the assigned values (AV), all in [mg/kg]

4.6 Critical Points in this PT and Post-PT Advices to Participants

- Make sure that the analytical portion is not too small as this increases portion-to-portion variability.
- Consider reducing the portion size of homogenized samples for ***dithiocarbamate*** analysis.
- To avoid bias it is important to compensate for strongly deviating recovery rates and matrix effects:
  - ◊ Strongly deviating recovery rates: Employ procedures that adjust for recovery (e.g. ILIS added at the beginning of the procedure, standard addition to sample portions, procedural calibration); these approaches also correct for matrix effects.
  - ◊ Significant matrix effects: Use either the above mentioned procedures that also correct for recovery or procedures that compensate for matrix effects only (e.g. matrix-matched calibrations, ILISs added to the sample extract, standard addition to extract aliquots, analyte protectants in GC)
- Be careful with derivatizations leading to products not specific to the target analyte (e.g. acetylation of ***glyphosate***/*N-acetyl glyphosate*, *glufosinate* and ***N-acetyl glufosinate***)
- If you analyse cereals for highly polar pesticides using QuPPe or similar methods, extend the sample extration time to at least 15 min to ensure quantitative extraction.
- Be careful with the purity of commercially available analytical standards of ***N-acetyl glufosinate***. The ***N-acetyl glufosinate*** content of the standards of two providers was found being 1.7-fold lower than that of a standard provided by the applicant. The commercial providers were informed about the deviation in the concentration.
- Always refer to the analyte definition stated on the Target Pesticides List. If "free acid"/"free phenol" without hydrolysis are asked for acidic/phenolic compounds, no hydrolysis step should be performed.
- Always submit all methodological data requested and check their correctness and plausibility. Posterior corrections of missing or contradictory input is time consuming and delays the publication of the final report.
- Follow the instruction and details in the invoice for payment und indicate the complete invoice number as payee identification text. Otherwise it is not possible to identify the payer and the payment cannot be allocated.

4.7 Summary, Conclusions, Retrospect and Prospect

The EUPT-SRM10 was the 10th scheduled EUPT focusing on pesticides requiring the use of "single" residue methods.

A total of 110 laboratories representing 27 EU and 2 EFTA countries registered for the EUPT-SRM10, and 104 thereof submitted results. In addition, 6 laboratories from third countries registered for participation with all of them reporting results. Regarding NRL-SRMs two EU-countries (Croatia and Romania) were not represented in the EUPT-SRM10. The NRL-SRM in Croatia has not yet been designated, whereas the NRL-SRM in Romania reported that the commodity of the current PT is not part of its analytical scope. Malta was represented by the UK NRL-SRM acting as proxy-NRL-SRM for Malta and three additional laboratories, one in Germany, one in Spain and one in the UK, that were both subcontracted for the analysis of Maltese official controls samples.

Compared to most of the previous EUPT-SRMs using cereals as commodity the number of laboratories that participated in this EUPT has increased significantly (**Table 4-19, p. 74**). It should be noted that participation in EUPTs largely depends on the compounds included in the Target Pesticides List as well as the matrices concerned. The number of participants in EUPT-SRMs based on fruit or vegetables is generally higher compared to PTs based on cereals or feeding stuff. EUPTs entailing target compounds which are included in the scope of many laboratories, such as ***dithiocarbamates***, also tend to show an increased number of

participants (**Table 4-20, p. 76**). The organisers would like to appeal to all laboratories to gradually expand their scope so that more SRM compounds are covered. Where possible and reasonable, specialized laboratories may be established to cover SRM compounds on a subcontract basis, both in commodities of animal and plant origin.

Judging from the number of participants, the average of absolute z-scores (AAZ) and the number of laboratories classified into Category A the EUPT-SRM10 was the most successful one so far using cereals as matrix. (**Table 4-19**).

The Target Pesticides List of EUPT-SRM10 (**Appendix 11**) contained in total 23 SRM-compounds. 9 of them were compulsory and the rest optional for the laboratories in terms of scope. All of the compulsory compounds were relevant to the EU multiannual coordinated control program (MACP) for maize. Two of them, ***2,4-D*** and ***MCPA***, were included in the MACP working document, whereas the other seven (***chlormequat***, ***dithiocarbamates***, ***ethephon***, *fenbutatin oxide*, ***glyphosate***, ***mepiquat*** and ***propamocarb***) where included in

Table 4-19: Retrospective comparison of EUPT-SRMs (Statistical evaluation based on data from laboratories in EU and EFTA countries)

EUPT-	SRM1 (2006)	SRM2 (2007)	SRM3 (2008)	SRM4 (2009)	SRM5 (2010)
Test Item (Commodity)	Apple juice	Wheat flour	Carrot homogenate	Oat flour	Apple purée
Participants submitting results (EU/EFTA)	24	30	66	48	81
Participants submitting results (3rd and Candidate Countries)	–	–	–	–	2
Compounds in Target Pesticides List Compulsory / Optional	15 / –	8 / 3	8 / –	13 / 8	11 / –
Compounds in test item Compulsory / Optional	3 [1] / –	3 / 2	5 / –	5 [2] / 2	5 [3] / –
No. of results without false positives Compulsory / Optional	38 / –	56 / 22	193 / –	95 / 47	239 / –
No. of false negative results Compulsory / Optional	0 / –	1 / 0	0 / –	3 / 2	5 / –
Mean no. of results per lab Compulsory / Optional	1.58 / –	1.87 / 0.73	2.92 / –	1.97 / 0.98	2.95 / –
Average of absolute z-scores (AAZ) Compulsory / Optional	0.57 / –	1.13 / 0.67	1.04 / –	0.98	1.11 / –
Acceptable z-scores Compulsory / Optional	97 % / –	81 % / 100 %	87 % / –	89 % / 88 %	92 % / –
Questionable z-scores Compulsory / Optional	– / –	9 % / 0 %	7 % / –	5 % / 6 %	3 % / –
Unacceptable z-scores Compulsory / Optional (thereof false negatives)	3 % / –	10 % / 0 % (1.8 % / 0 %)	6 % / –	6 % / 6 % (3.7 % / 4 %)	5 % / – (0.6 % / –)
Number of false positives Compulsory / Optional	0 / –	1 / –	0 / –	0 / –	3 / 3
Category A laboratories [6]	–	–	–	31 %	19 %
CV^* (average) [7] Compulsory / Optional	25 % / –	37 % / 22 %	28 % / 24 %	27 %	22 % / –

1) One compound (fenbutatin oxide) was evaluated for information only due to insufficient number of participants.
2) Two compounds (ethephon and glyphosate) were evaluated for information only due to insufficient number of participants.
3) One compound (dithiocarbamates as CS_2) was evaluated for information only due to uncertain assigned value.
4) Three compounds (chlorothalonil, cyromazine and fenbutatin oxide) were evaluated for information only due to uncertain assigned value.
5) Two compounds (4-OH-chlorothalonil and trimesium) were evaluated for information only due to uncertain assigned value.
6) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRM6 – 10.
7) CV^* = robust relative standard dieviation, known as Qn-RSD in EUPT-SRM1 – 9 (calculated for informative purpose)

the MACP regulation. In addition eight pesticides (*glufosinate*, ***N-acetyl glufosinate***, *MPP*, *ioxynil*, *paraquat*, ***phosphonic acid***, *TFNA*, and ***TFNG***) of the 14 optional compounds were included in the MACP working document.

9 of total 23 compounds in the Target Pesticides List were included for the first time in the EUPT-SRM with 5 of them being present in the test item: ***bentazone***, ***bromoxynil***, ***N-acetyl glufosinate*** and ***TFNG***. All these new compounds were analysed by a sufficient number of laboratories to allow proper statistical evaluation. Although only 15 laboratories reported a result for ***N-acetyl glufosinate***, the CV^* of 11.8 % indicates the high analytical quality of these laboratories. Similar observations with compounds analyzed by only a few, but obviously well performing, laboratories were also made in past PTs.

Phosphonic acid became an issue of high interest some months before the launch of the EUPT-SRM10. The EURL-SRM had developed an analytical method which was distributed to the laboratories via the website. To enable simple and still accurate quantitative analysis the EURL-SRM synthesized an isotope labelled in-

EUPT-	SRM6 (2011)	SRM7 (2012)	SRM8 (2013)	SRM9 (2014)	SRM10 (2015)
Matrix of test item	Rice flour	Lentil flour	Potato homogenate	Cow's whole milk	Maize flour
Participants submitting results (EU/EFTA)	77	110	110	62	104
Participants submitting results (3rd and Candidate Countries)	2	4	6	5	6
Compounds in Target Pesticide List Compulsory / Optional	13 / –	16 / –	13 / 10	12 / 7	9 / 14
Compounds in test item Compulsory / Optional	7 / –	8 [4] / –	8 [5] / 7	8 [5] / 6	8 / 5
No. of results without false positives Compulsory / Optional	291 / –	439 / –	604 / 212	361 / 132	461 / 135
No. of false negative results Compulsory / Optional	5 / –	11 / –	14 / 8	3 / 4	4 / 2
Mean no. of results per lab Compulsory / Optional	3.79 / –	4.12 / –	5.49 / 1.93	5.87 / 2.19	4.43 / 1.29
Average of absolute z-scores (AAZ) Compulsory / Optional	0.83 / –	0.97 / –	0.98 / 1.06	0.75 / 0.80	0.9 / 0.7
Acceptable z-scores Compulsory / Optional	91 % / –	90 % / –	88 % / 85 %	92 % / 71 %	87 % / 89 %
Questionable z-scores Compulsory / Optional	6 % / –	3 % / –	6 % / 5 %	4 % / 5 %	8 % / 6 %
Unacceptable z-scores Compulsory / Optional (thereof false negatives)	4 % / – (1.7 % / –)	7 % / – (2.1 % / –)	6 % / 10 % (2.2 % / 3.6 %)	4 % / 3.5 % (0.8 % / 2.7 %)	5 % / 4 % (0.8 % / 2.9 %)
Number of false positives Compulsory / Optional	0 / –	0 / –	2 / 0	6 / 0	0 / 4
Category A laboratories [6]	25 %	28 %	47 %	52 %	53 %
CV^* (average) Compulsory / Optional	23 % / –	27 % / –	26 % / 26 %	20 % / 19 %	24 % / 19 %

1) One compound (fenbutatin oxide) was evaluated for information only due to insufficient number of participants.
2) Two compounds (ethephon and glyphosate) were evaluated for information only due to insufficient number of participants.
3) One compound (dithiocarbamates as CS_2) was evaluated for information only due to uncertain assigned value.
4) Three compounds (chlorothalonil, cyromazine and fenbutatin oxide) were evaluated for information only due to uncertain assigned value.
5) Two compounds (4-OH-chlorothalonil and trimesium) were evaluated for information only due to uncertain assigned value.
6) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRM6 – 10.
7) CV^* = robust relative standard dieviation, known as Qn-RSD in EUPT-SRM1 – 9 (calculated for informative purpose)

Table 4-20: Overview of selected pesticides tested in the EUPT-SRMs 1 – 10 and analysed by the participating laboratories. ***n***: Number of laboratories having analysed selected pesticides present in the test items. The figures in brackets show the percentage of laboratories submitting numerical results for a compound out of the total number of laboratories submitting results (only EU and EFTA labs considered; CV^*, formerly known as Qn, was calculated for populations with at least 10 laboratories). Only CV^*s based on 15 or more labs were used to calculated the average CV^*s at the bottom.

				Acidic pesticides					Requiring individual methods		Polar pesticides				Other
EUPT	No. of laboratories	Commodity type [1]		2,4-D	MCPA	Bentazone	Haloxyfop	Fluazifop	Bromide	Dithio-carbamates	Chlormequat	Mepiquate	Ethephon	Glyphosate	Fenbutatin oxide
SRM1	24	FV	*n*		10 (42 %)						23 (96 %)				5 (21 %)
		HW	CV^*		27.1 %						**13.8 %**				–
SRM2	30	CF	*n*		13 (43 %)						25 (83 %)				
		D	CV^*		45.8 %						**29.1 %**				
SRM3	66	FV	*n*		38 (58 %)			35 (55 %)		59 (89 %)					
		HW	CV^*		**27.0 %**			**26.6 %**		**38.4 %**					
SRM4	48	CF	*n*	32 (66 %)							38 (83 %)		4 (8.3 %)	6 (13 %)	
		D	CV^*	**27.5 %**							**25.8 %**		–	–	
SRM5	81	FV	*n*					51 (64 %)		70 (86 %)			28 (35 %)		35 (43 %)
		HW	CV^*					**19.8 %**		**58.9 %**			**23.0 %**		**24.3 %**
SRM6	77	CF	*n*	57 (74 %)			49 (64 %)		34 (44 %)	64 (83 %)			28 (36 %)	34 (44 %)	
		D	CV^*	**22.1 %**			**17.7 %**		**8.6 %**	**24.2 %**			**29.7 %**	**40.6 %**	
SRM7	110	CF	*n*	70 (64 %)					44 (40 %)	83 (75 %)			32 (29 %)	39 (35 %)	
		D	CV^*	**27.9 %**					**18.0 %**	**23.1 %**			**25.2 %**	**34.5 %**	
SRM8	110	FV	*n*				81 (74 %)					71 (65 %)		45 (41 %)	59 (54 %)
		HW	CV^*				**20.2 %**					**22.2 %**		**24.5 %**	**31.4 %**
SRM9	62	AO	*n*	50 (81 %)				50 (81 %)			50 (81 %)	49(79 %)			
		HW	CV^*	**18.7 %**				**26.0 %**			**29.8 %**	**19.6 %**			
SRM10	104	CF	*n*	82 (79 %)	79 (76 %)	69 (66 %)				85 (82 %)	75 (72 %)	76 (67 %)	61 (59 %)	62 (60 %)	
		D	CV^*	**18.2 %**	**18.9 %**	**18.5 %**				**36.9 %**	**18.2 %**	**18.5 %**	**30.8 %**	**22.8 %**	
Average CV^* EUPT-SRMs 1 – 10				**22.9 %**	**23.0 %**	**18,5 %**	**19.0 %**	**24.1 %**	**13.3 %**	**36.3 %**	**23.3 %**	**20.1 %**	**27.2 %**	**30.6 %**	**27.9 %**

Average CV^* of Group EUPT-SRMs 1 – 10	Acidic pesticides	Br^-	DTCs	Chlormequat + Mepiquat	Ethephon + Glyphosate	FBO
	22.2 %	13.3 %	36.3 %	22.1 %	28.9 %	27.9 %

1) Commodity type:
HW: High water content; D: dry = high strach or high protein content and low water content

ternal standard (ILIS) of this compound and provided it to all participants. 24 laboratories reported results for ***phosphonic acid*** allowing analytical evaluation with a relative statistical certainty. The CV^* of 27 % was satisfactory but it improves further to 14 % if the 6 laboratories not using the ILIS are excluded from the population.

The robust relative standard deviation (CV^*) reflects the width of the result-distribution and was calculated for each target analyte. The average CV^*, which is calculated for informative purposes, was 23.5 % and 18.6 % for compulsory and optional compounds, respectively, and was thus clearly lower than the FFP-RSD of 25 % used to calculate the z-scores. The individual CV^* values of the compulsory compounds were as follows: ***2,4-D*** 18.2 %, ***chlormequat*** 18.2 %, ***dithiocarbamates*** 36.9 %, ***ethephon*** 30.8 %, ***glyphosate*** 22.8 %, ***MCPA*** 18.9 %, ***mepiquat*** 18.5 %, and ***propamocarb*** 23.3 %. The CV^* values of the optional compounds were as follows: ***Bentazone*** 18.5 %, ***bromoxynil*** 17.0 %, ***N-acetyl glufosinate*** 11.8 %, ***phosphonic acid*** 27.3 %, and ***TFNG*** 18.6 %.

Looking at the long-term CV^*s of selected individual compounds or compound groups (**Table 4-20**) we can see for acidic pesticides (***2,4-D***, ***MCPA***, ***bentazone***, haloxyfop, fluazifop) an average CV^* of 22.2 %, for ***chlormequat*** and ***mepiquat*** an average CV^* of 22.1 %, for ***glyphosate***, and ***ethephon*** an average CV^* of 28.9 %, for fenbutatin oxide an average CV^* of 27.9 % and for bromide an average CV^* of 13.3 %. Most critical is the CV^*s of ***dithiocarbamates*** with an average value of 36.3 %.

In accordance with the definition in the General EUPT Protocol, z-scores based on the FFP-RSD of 25 % were calculated and classified into "acceptable", "questionable", and "unacceptable" for each laboratory/target-analyte combination. Overall, the quality of the results was high. In the case of compulsory compounds 83 out of 88 laboratories (94 %) reported results within the acceptable z-score-range for ***2,4-D***, 70 out of 79 (89 %) for ***chlormequat***, 72 out of 92 (78 %) for ***dithiocarbamates***, 54 out of 66 (82 %) for ***ethephon***, 58 out of 69 (84 %) for ***glyphosate***, 77 out of 85 (91 %) for ***MCPA***, 72 out of 80 (90 %) for ***mepiquat***, and 81 out of 91 (89 %) for ***propamocarb***. In the case of optional compounds 67 out of 75 laboratories (89 %) submitted results within the acceptable z-score-range for ***bentazone***, 63 out of 70 (90 %) for ***bromoxynil***, 15 out of 16 (94 %) for ***N-acetyl glufosinate***, 20 out of 25 (80 %) for ***phosphonic acid***, and 29 out of 31 (94 %) for ***TFNG***.

As ***dithiocarbamates*** showed broad result distributions over several EUPT-SRMs, z-scores were additionally calculated using a "FFP-RSD" of 30 % and 35 %. The percentages of acceptable, questionable and unacceptable z-scores shifted from 78 %, 15 % and 7 % using the FFP-RSD of 25 % to 87 %, 8 % and 5 % using the FFP-RSD of 30 % and to 93 %, 6 % and 1 % using the FFP-RSD of 35 %.

Considering results reported by all participating laboratories, among the compulsory compounds false negative results were reported in 7 cases for ***glyphosate*** (4×) and ***ethephon***, ***MCPA*** and ***dithiocarbamates*** (each 1×). Among the optional compounds false negative results were reported in four cases for ***bromoxynil*** (2×), ***phosphonic acid*** (1×), and ***N-acetyl glufosinate*** (1×). False positive results were reported in 4 cases: 3× *glufosinate* and 1× *MPP*, both optional compounds.

All participating laboratories were classified according to the number of compulsory pesticides detected following the rules of the General EUPT Protocol. Laboratories correctly detecting at least seven of the eight compulsory pesticides present in the test item without reporting any false positive result were classified into Category A. A total of 55 EU/EFTA-laboratories (53 %) were classified into Category A and the remaining 49 (47 %) laboratories into Category B. Among the 6 participating laboratories from third countries, three were classified into Category A and the other 3 into Category B.

8 of the 108 EU laboratories that registered for participation in this EUPT participated on a voluntary basis. The other 100 laboratories represent 83 % of the 120 laboratories that were finally considered as being obliged to participate in this exercise based on their function (NRL-SRM) or scope (routinely analysing official samples for pesticide residues in cereals or feed). Several laboratories originally considered as obliged to take part in the current PT provided explanations for their non-participation. Most of them stated that the matrix (maize) or the SRM10 target pesticides or both were out of their routine scope. Some laboratories indicated the lack of required instruments or technical problems as reasons.

Post-PT measures and assistance to the laboratories: Following the distribution of the preliminary results all laboratories achieving questionable or unacceptable z-scores as well as false positive results were asked to investigate the reasons and report them to the organisers, as far as possible. 37 laboratories responded to the organisers with (possible) reasons for their poor performance in 79 cases. In 9 cases the real reasons could not be clarified, in spite of intensive investigation. In a few cases, the real reasons were not yet clear and the laboratories were going to continue the investigation. The most frequently reported error source (23 cases) was lack of experience either with the commodity or the analytes, and the participating laboratories stated taking the PT as an opportunity to test their methods, which will be eventually employed

for routine testing. “Application of inappropiate procedures” (15 cases), “error in the calibration solution or analytical standards” (12 cases) and “matrix effect not properly compensated” (11 cases) were further frequently reported error sources, followed by, “procedure not properly conducted” (9 cases), “technical problem with the analytical instruments” (6 cases), “misinterpretation of the chromatogram” (4 cases), “results not corrected for low recovery” or “detection signal strongly interfered by matrix component” (3 cases each), “inappropiate calibration” or “inappropiate storage or pre-treatment of sample” (2 cases each) and “transcription error” (1 case). Even if in many cases the laboratories did not give any feedback to the organiser for their poor performance, the organisers hope that every participating laboratory has tried to find out the reason, as this will reduce errors in the future and improve analytical quality.

Expanding the scope and improving the overall performance of NRLs and OfLs in the area of pesticides and metabolites not amenable to multiresidue methods is one of the main aims of the EURL-SRM. The EURL-SRM is thus pleased to assist the laboratories via bilateral discussions, workshops and trainings and will continue developing, validating and distributing easy-to-use, fast and cost-efficient methodologies for such compounds. In future PTs, the selection of target analytes will continue to focus on those included in the scope of the EU coordinated control programs as well as on additional pesticides and metabolites of high relevance. Specific requests by NRLs and OfLs will be also taken into account.

5. ACKNOWLEDGEMENTS

The organisers wish to thank the members of the EUPT Scientific Committee (Quality Control Group and Advisory Group) for their valuable advice. Special thanks also go to Jens-Ole Frimann for his support in establishing the online registration and result submission tool.

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7. APPENDICES

Appendix 1 List of laboratories registered to participate in the EUPT-SRM10

(a): participating labs of EU and EFTA Member States

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Austria	AT	Austrian Agency for Health and Food Safety, Institute for Food Safety Innsbruck - Department for Pesticide and Food Analytics	Innsbruck	x	Yes
Austria	AT	MA 38 - LUA	Vienna		Yes
Belgium	BE	Scientific Institute of Public Health	Brussels	x	Yes
Belgium	BE / FR / LU	Fytolab - Belgium, Gent (Zwijnaarde)	Gent-Zwijnaarde		Yes
Bulgaria	BG	Central Laboratory for Chemical Testing and Control, Sofia	Sofia	x	Yes
Bulgaria	BG	Fytolab - Bulgaria, Plovdiv	Plovdiv		No [3)]
Bulgaria	BG	SGS - Bulgaria Ltd., Varna	Varna		Yes
Croatia	HR	Euroinspekt - Croatiakontrola d.o.o.	Zagreb		Yes
Croatia	HR	Institute of Public Health, Dr. Andrija štampar	Zagreb		Yes
Cyprus	CY	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	x	Yes
Czech Republic	CZ	Central Institute for Supervising and Testing in Agriculture1)	Brno		Yes
Czech Republic	CZ	Czech Agriculture and Food Inspection Authority	Praha	x	Yes
Czech Republic	CZ	University of Chemical Technology, Dept. of Food Chemistry and Analysis - Prague	Praha		Yes
Denmark	DK	Danish Veterinary and Food Administration, Department of Residues, Ringsted	Ringsted		Yes
Denmark	DK	National Food Institute, Technical University of Denmark	Søborg	x	Yes
Estonia	EE	Agricultural Research Centre, Saku, Lab for Residues and Contaminants	Saku		Yes
Estonia	EE	Health Board - Tartu Laboratory	Tartu	x	Yes
Finland	FI	Finnish Customs Laboratory	Espoo	x	Yes
France	FR	Analysis Center Mediterranean Pyrenees	perpignan		Yes
France	FR	ANSES Laboratoire de Maisons-Alfort (Pesticides)	MAISONS-ALFORT	x	Yes
France	FR	Capinov	Landerneau		Yes
France	FR	CERECO SUD	GARONS		Yes
France	FR	GIRPA - Groupement Interrégional Recherche Produits Agropharma	BEAUCOUZE		Yes
France	FR	INOVALYS Le Mans	Le Mans		Yes
France	FR	Service Commun des Laboratoires / Laboratoire de Montpellier	Montpellier		Yes
France	FR	Service Commun des Laboratoires / Laboratoire Ile de France - Massy	Massy		Yes
Germany	DE	Amt für Verbraucherschutz Düsseldorf - 39/2 Chemische und Lebensmitteluntersuchung	Düsseldorf		Yes
Germany	DE	Bavarian Health and Food Safety Authority Office Erlangen	Erlangen		Yes
Germany	DE	Berlin-Brandenburg State Laboratory, Potsdam	Potsdam		Yes
Germany	DE	Chemical and Veterinary Analytical Institute Muensterland-Emscher Lippe	Münster		Yes
Germany	DE	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld		Yes
Germany	DE	Chemisches Labor Dr. Mang	Frankfurt		Yes
Germany	DE	Chemisches und Veterinäruntersuchungsamt Ostwestfalen-Lippe, Detmold	Detmold		Yes
Germany	DE	Chemisches und Veterinäruntersuchungsamt Rheinland, Standort Bonn	Bonn		Yes
Germany	DE	Chemisches- und Veterinäruntersuchungsamt Westfalen (AöR) - Standort Bochum	Bochum		Yes

* only for EU-member states; [1)]: no reference material received in time; [2)] Technical problems; [3)]: no reason reported to the organisers

Appendix 1-a (cont.): participating labs of EU and EFTA member states

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Germany	DE	Federal Office of Consumer Protection and Food Safety, NRL for Pesticide Residues	Berlin	x	Yes
Germany	DE	Food and Veterinary Institute Oldenburg	Oldenburg		Yes
Germany	DE	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei Mecklenburg-Vorpommern	Rostock		Yes
Germany	DE	Landesamt für Verbraucherschutz - Sachsen-Anhalt	Halle/Saale		Yes
Germany	DE	Landesanstalt für Landwirtschaft, Forsten und Gartenbau, Halle	Halle/Saale		Yes
Germany	DE	Landesbetrieb Hessisches Landeslabor, Kassel	Kassel		Yes
Germany	DE	Landesuntersuchungsamt Institut für Lebensmittelchemie Speyer	Speyer		Yes
Germany	DE	Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer	Speyer		Yes
Germany	DE	Landwirtschaftliches Technologiezentrum Augustenberg, Karlsruhe	Karlsruhe		Yes
Germany	DE	State Department of Environmental and Agricultural Operations in Saxony	Nossen		Yes
Germany	DE	State Investigation Institute of Health and Veterinary Saxony	Dresden		Yes
Germany	DE	State Laboratory Schleswig-Holstein	Neumünster		Yes
Germany	DE	Thuringian Institute of Agriculture	Jena		Yes
Germany	BE / DE	LUFA-ITL GmbH	Kiel		Yes
Germany	LT	GALAB Laboratories GmbH - Germany, Hamburg	Hamburg		Yes
Germany	MT	Eurofins - Dr. Specht Laboratorien GmbH	Hamburg		Yes
Greece	GR	Benaki Phytopathological Institute, Pesticide Residues Laboratory	Kifissia	x	Yes
Greece	GR	General Chemical State Laboratory, D Division, Pesticide Residues Laboratory	Athens	x	Yes
Hungary	HU	National Food Chain Safety Office Directorate of Plant Protection, Soil Conservation and Agri-environment, Pesticide Residue Analytical Laboratory, Szolnok	Szolnok		Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-environment - Pesticide Analytical Laboratory, Velence	Velence		Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Hódmezovásárhely	Hódmezovásárhely		Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Miskolc	Miskolc	x	Yes
Ireland	IE	Pesticide Control Laboratory, Department of Agriculture, Fisheries and Food	Co. Kildare	x	Yes
Italy	IT	APPA Bolzano	Bolzano		Yes
Italy	IT	ARPA Ferrara Eccellenza Fitofarmaci	Ferrara		Yes
Italy	IT	ARPA Puglia - Dipartimento di Bari	Bari		Yes
Italy	IT	ARPA VENETO DIP.REG.LAB. S.L. VERONA	Verona		Yes
Italy	IT	ARPALAZIO SEZIONE P.LE DI LATINA - SERVIZIO LABORATORIO AMBIENTE E SALUTE, UNITA` DI CHIMICA INORGANICA	Latina		No [3)]
Italy	IT	Istituto Superiore di Sanità, Pesticide Section	Roma	x	Yes
Italy	IT	Istituto Zooprofilattico Sperimentale Abruzzo e Molise	Teramo		Yes
Italy	IT	Istituto Zooprofilattico Sperimentale Lombardia ed Emilia Romagna	Brescia		Yes
Italy	IT	Istituto Zooprofilattico Sperimentale Sicilia	Palermo		No [3)]
Italy	IT	Istituto Zooprofilattico Sperimentale Umbria e Marche, PERUGIA	Perugia		Yes
Italy	IT	IZS LT	San Martino alla Palma Scandic		No [1)]
Latvia	LV	Institute of Food Safety, Animal Health and Environment (BIOR) - Riga	Riga	x	Yes
Lithuania	LT	National Food and Veterinary Risk Assessment Institute (Lithuania, Vilnius)	Vilnius	x	Yes
Luxembourg	LU	National Health Laboratory Luxembourg (Food Laboratory)	Dudelange	x	Yes

* only for EU-member states; [1)]: no reference material received in time; [2)] Technical problems; [3)]: no reason reported to the organisers

Appendix 1-a (cont.): participating labs of EU and EFTA member states

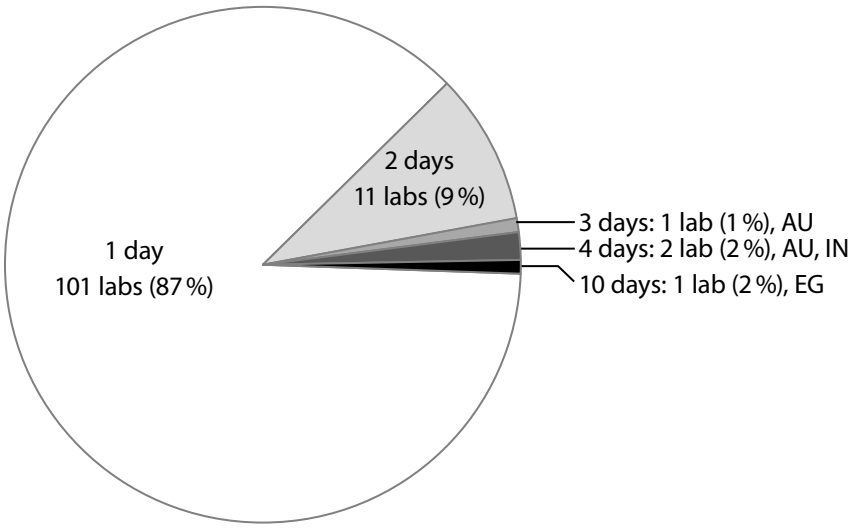
Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Netherlands	NL	NVWA - Netherlands Food and Consumer Product Safety Authority (Wageningen, The Netherlands)	Wageningen	x	Yes
Netherlands	NL	RIKILT Institute of Food Safety (Natural Toxins & Pesticides)	Wageningen		Yes
Netherlands	BE	Eurofins Lab Zeeuws-Vlaanderen (LZV) B.V.	Graauw		Yes
Netherlands	BE	Groen Agro Control	Delfgauw		Yes
Netherlands	BE	Handelslaboratorium Dr. Verwey	Rotterdam		No [3)]
Netherlands	BE	NofaLab	Schiedam		No [2)]
Norway	NO	Norwegian Institute for Agricultural and Environmental Research, Plant Health and Plant Protection Division, Pesticide Chemistry Section	Aas		Yes
Poland	PL	Institute of Horticulture, Food Safety Laboratory (Skierniewice)	Skierniewice		Yes
Poland	PL	Institute of Plant Protection - National Research Institute, Branch Sosnicowice	Sosnicowice		Yes
Poland	PL	Institute of Plant Protection Pesticide Residue Laboratory, Bialystok	Bialystok		Yes
Poland	PL	UO-Technologia	Grójec		Yes
Poland	PL	Voievodship Sanitary - Epidemiological Station in Rzeszow	Rzeszow		Yes
Poland	PL	Voievodship Sanitary - Epidemiological Station in Warszaw	Warszaw	x	Yes
Poland	PL	Wojewódzka Stacja Sanitarno-Epidemiologiczna w Opolu, Oddzial Laboratoryjny w Kluczborku	Kluczbork		Yes
Portugal	PT	INIAV- Pesticide Residues Laboratory Oeiras	Oeiras		Yes
Portugal	PT	Regional Laboratory of Veterinary and Food Safety - Madeira Island	Funchal - Madeira Island	x	Yes
Romania	RO	Central Laboratory for Pesticides Residues Control in Plants and Vegetable Products - Bucharest	Bucharest		Yes
Slovakia	SK	State Veterinary and Food Institute - Veterinary and Food Institute in Bratislava	Bratislava	x	Yes
Slovenia	SI	Agricultural Institute of Slovenia, Central Laboratories	Ljubljana		Yes
Slovenia	SI	National Laboratory for Health, Environment and Food - Maribor	Maribor	x	Yes
Slovenia	SI	National Laboratory for Health, Environment and Food - Maribor (Location Ljubljana)	Ljubljana		Yes
Spain	ES	Analytica Alimentaria GmbH Sucursal España	Almeria		Yes
Spain	ES	CNTA (National Centre for Technology and Food Safety - Laborytory of Ebro)	San Adrián (Navarra)		Yes
Spain	ES	Laboratorio Agrario Regional - Junta de Castilla y Leon	Burgos		Yes
Spain	ES	Laboratorio Agroalimentario de Extremadura (Cáceres)	Cáceres		Yes
Spain	ES	Laboratorio Agroalimentario de Zaragoza	Zaragoza		Yes
Spain	ES	Laboratorio Arbitral Agroalimentario, Madrid	Madrid	x	Yes
Spain	ES	Laboratorio de Producción y Sanidad Vegetal de Jaén	Mengibar (Jaén)		Yes
Spain	ES	Laboratorio KUDAM S.L.	Pilar de la Horadada		Yes
Spain	ES	Laboratorios Ecosur, S.A.	Lorquí (Murcia)		Yes
Spain	ES	Laboratory of Barcelona Public Health Agency	Barcelona		Yes
Spain	ES	National Centre for Food - Spain, Majadahonda	Majada-honda	x	Yes
Spain	ES / MT	Agrofood Laboratory of the Comunidad Valenciana	Burjassot-Valencia		Yes
Sweden	SE	Eurofins - Food&Agro Sweden, Lidköping	Lidköping		Yes
Sweden	SE	National Food Agency, Science Department, Chemistry Division 1	Uppsala	x	Yes
Switzerland	CH	Kantonales Laboratorium Zürich	Zürich		Yes
United Kingdom	MT / UK	Laboratory of the Government Chemist - Teddington	Teddington		Yes
United Kingdom	MT / UK	The Food and Environment Research Agency - York	York	x	Yes

* only for EU-member states; [1)]: no reference material received in time; [2)] Technical problems; [3)]: no reason reported to the organisers

Appendix 1-b: participating labs from EU Candidate countries and third countries

Country	Institution	City	Reported results
India	TUV-SUD SOUTH ASIA Pvt Ltd.	Bangalore	Yes
Australia	Advanced Analytical Australia	North Ryde	Yes
Australia	Australian Superintendence Company	East Brisbane, Queensland	Yes
Singapore	Agri-Food & Veterinary Authority of Singapore	Singapore	Yes
Egypt	Central Lab of Residue Analysis of Pesticides and Heavy Metals in Foods	Giza	Yes
Canada	ISURA	Burnaby	Yes

Appendix 2 Shipment evaluation: Compilation of duration of shipment



Appendix 3 Data of homogeneity test

COMPULSORY COMPOUNDS								
	2,4-D		Chlormequat		Dithiocarbamates		Ethephon	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 007	0.101	0.101	0.142	0.138	0.877	0.693	0.158	0.180
No. 011	0.099	0.099	0.149	0.145	0.672	0.761	0.162	0.164
No. 019	0.102	0.101	0.144	0.146	0.686	0.748	0.151	0.156
No. 025	0.098	0.100	0.145	0.142	0.778	0.748	0.167	0.162
No. 032	0.101	0.100	0.142	0.145	0.948	0.813	0.163	0.161
No. 040	0.102	0.099	0.147	0.140	0.773	0.834	0.161	0.168
No. 058	0.092	0.095	0.146	0.146	0.755	0.831	0.159	0.154
No. 069	0.103	0.097	0.145	0.146	0.671	0.801	0.156	0.165
No. 074	0.100	0.101	0.143	0.136	0.925	0.782	0.162	0.147
No. 097	0.093	0.091	0.140	0.140	0.900	0.639	0.165	0.166
mean / AV*	0.099 / 0.092		0.143 / 0.167		0.782 / 0.559		0.161 / 0.162	
	Glyphosate		MCPA		Mepiquat		Propamocarb	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 007	0.540	0.542	0.095	0.097	0.103	0.099	0.078	0.073
No. 011	0.559	0.627	0.098	0.088	0.107	0.105	0.072	0.073
No. 019	0.585	0.560	0.096	0.086	0.105	0.103	0.070	0.072
No. 025	0.604	0.549	0.094	0.087	0.108	0.109	0.074	0.071
No. 032	0.603	0.583	0.099	0.082	0.099	0.096	0.075	0.070
No. 040	0.590	0.551	0.094	0.088	0.104	0.098	0.076	0.072
No. 058	0.554	0.603	0.088	0.092	0.103	0.102	0.071	0.074
No. 069	0.581	0.534	0.090	0.084	0.100	0.105	0.074	0.074
No. 074	0.566	0.609	0.089	0.088	0.098	0.106	0.070	0.073
No. 097	0.607	0.566	0.092	0.088	0.101	0.102	0.074	0.074
mean / AV*	0.575 / 0.568		0.091 / 0.081		0.103 / 0.114		0.073 / 0.067	

OPTIONAL COMPOUNDS								
	Bentazone		Bromoxynil		N-Acetyl glufosinate		Phosphonic acid	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 007	0.113	0.104	0.136	0.125	0.175	0.192	0.666	0.716
No. 011	0.099	0.100	0.123	0.123	0.185	0.184	0.636	0.706
No. 019	0.115	0.113	0.138	0.138	0.183	0.184	0.701	0.644
No. 025	0.102	0.106	0.125	0.133	0.177	0.198	0.671	0.724
No. 032	0.103	0.106	0.127	0.134	0.200	0.162	0.691	0.695
No. 040	0.108	0.100	0.136	0.126	0.186	0.195	0.674	0.665
No. 058	0.104	0.104	0.127	0.127	0.181	0.191	0.702	0.772
No. 069	0.101	0.100	0.125	0.129	0.167	0.186	0.766	0.660
No. 074	0.101	0.105	0.130	0.127	0.178	0.204	0.729	0.640
No. 097	0.097	0.105	0.125	0.127	0.198	0.190	0.711	0.737
mean / AV*	0.104 / 0.098		0.129 / 0.125		0.186 / 0.319 #		0.695 / 0.584	

	TFNG	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 007	0.176	0.176
No. 011	0.162	0.153
No. 019	0.178	0.174
No. 025	0.163	0.173
No. 032	0.162	0.176
No. 040	0.171	0.154
No. 058	0.159	0.164
No. 069	0.166	0.161
No. 074	0.168	0.173
No. 097	0.174	0.169
mean / AV*	0.168 / 0.168	

* mean / AV =
Average value of the homogeneity test data [mg/kg] / Assigned value of PT [mg/kg]

The strong deviation between the assigned value and the mean value of the homogeneity test was found to be due to the lower concentration of N-acetyl-glufosinate in commercial standards (please see discussion under **Section 4.3: „Assigned Values and Target Standard Deviations" p. 29**).

Appendix 4 Data of stability test

COMPULSORY COMPOUNDS												
	2,4-D			Chlormequat			Dithiocarbamates			Ethephon		
	08.05.2015	16.06.2015	07.07.2015	08.05.2015	16.06.2015	07.07.2015	24.06.2015	25.08.2015	08.09.2015	08.05.2015	16.06.2015	07.07.2015
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 047	0.097	0.100	0.106	0.139	0.133	0.147	0.717	0.776	0.783	0.178	0.165	0.170
No. 093	0.099	0.100	0.103	0.138	0.145	0.148	0.804	0.761	0.779	0.176	0.165	0.175
No. 152	0.096	0.098	0.098	0.147	0.138	0.135	0.770	0.804	0.782	0.173	0.159	0.174
Mean [mg/kg]	**0.097**	**0.099**	**0.102**	**0.141**	**0.139**	**0.144**	**0.763**	**0.780**	**0.782**	**0.176**	**0.163**	**0.173**
RSD* [%]	**1.51 %**	**1.34 %**	**3.62 %**	**3.64 %**	**4.59 %**	**4.98 %**	**5.74 %**	**2.82 %**	**0.28 %**	**1.67 %**	**2.34 %**	**1.57 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**2.22 %**	**5.07 %**	**—**	**-1.71 %**	**1.66 %**	**—**	**2.25 %**	**2.40 %**	**—**	**-7.16 %**	**-1.66 %**
	Glyphosate			**MCPA**			**Mepiquat**			**Propamocarb**		
	08.05.2015	16.06.2015	07.07.2015	08.05.2015	16.06.2015	07.07.2015	08.05.2015	16.06.2015	07.07.2015	08.05.2015	16.06.2015	07.07.2015
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 047	0.573	0.569	0.570	0.085	0.090	0.089	0.104	0.100	0.102	0.070	0.068	0.065
No. 093	0.570	0.560	0.556	0.085	0.087	0.085	0.101	0.096	0.098	0.073	0.075	0.067
No. 152	0.586	0.537	0.570	0.081	0.086	0.087	0.101	0.096	0.098	0.075	0.071	0.079
Mean [mg/kg]	**0.576**	**0.555**	**0.566**	**0.083**	**0.088**	**0.087**	**0.102**	**0.097**	**0.099**	**0.073**	**0.071**	**0.070**
RSD* [%]	**1.49 %**	**2.92 %**	**1.44 %**	**2.29 %**	**2.47 %**	**2.21 %**	**1.47 %**	**2.58 %**	**2.40 %**	**2.90 %**	**4.94 %**	**11.01 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**-3.63 %**	**-1.87 %**	**—**	**4.91 %**	**4.19 %**	**—**	**-4.80 %**	**-2.96 %**	**—**	**-2.17 %**	**-3.10 %**

OPTIONAL COMPOUNDS												
	Bentazone			Bromoxynil			N-Acetyl glufosinate			Phosphonic acid		
	08.05.2015	16.06.2015	07.07.2015	08.05.2015	16.06.2015	07.07.2015	08.05.2015	16.06.2015	07.07.2015	08.05.2015	16.06.2015	07.07.2015
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 047	0.100	0.103	0.108	0.126	0.126	0.132	0.183	0.183	0.202	0.721	0.719	0.722
No. 093	0.100	0.107	0.106	0.125	0.131	0.130	0.191	0.181	0.196	0.693	0.727	0.736
No. 152	0.098	0.103	0.104	0.127	0.133	0.129	0.194	0.171	0.204	0.731	0.730	0.736
Mean [mg/kg]	**0.099**	**0.105**	**0.106**	**0.126**	**0.130**	**0.130**	**0.189**	**0.178**	**0.201**	**0.715**	**0.725**	**0.731**
RSD* [%]	**1.07 %**	**2.24 %**	**1.64 %**	**0.85 %**	**2.73 %**	**1.26 %**	**2.86 %**	**3.63 %**	**2.16 %**	**2.79 %**	**0.81 %**	**1.10 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**5.36 %**	**6.84 %**	**—**	**3.20 %**	**3.53 %**	**—**	**-5.82 %**	**6.09 %**	**—**	**1.44 %**	**2.25 %**

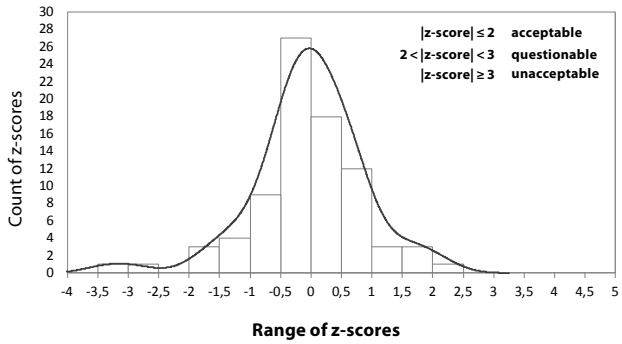
	TFNG		
	08.05.2015	16.06.2015	07.07.2015
Sample	[mg/kg]	[mg/kg]	[mg/kg]
No. 047	0.167	0.164	0.157
No. 093	0.167	0.165	0.162
No. 152	0.166	0.162	0.149
Mean [mg/kg]	**0.167**	**0.164**	**0.156**
RSD* [%]	**0.55 %**	**0.82 %**	**4.14 %**
Diviation [%] (ref. 1st Anaylsis)	**—**	**-1.80 %**	**-6.34 %**

* RSD = relative standard diviation

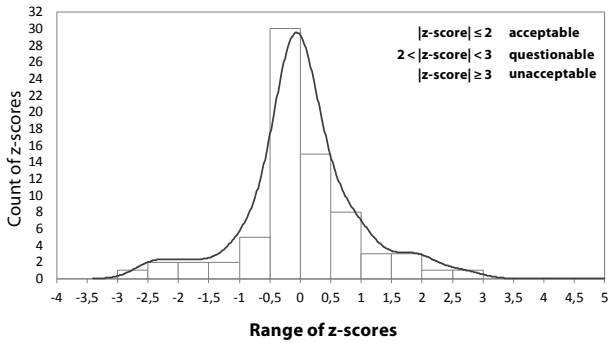
Appendix 5 Histograms and kernel density estimates of z-scores* distributions

Compulsory compounds

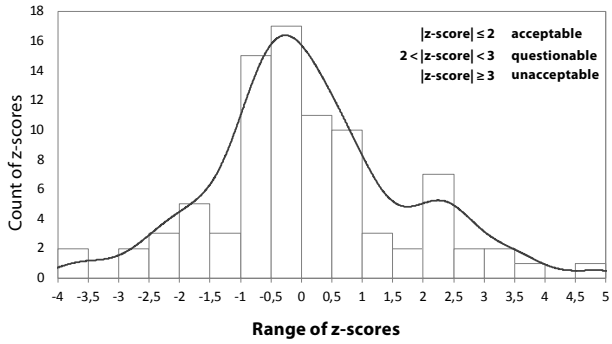
2,4-D



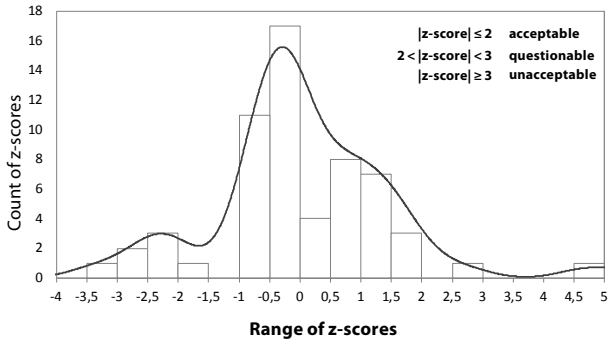
Chlormequat



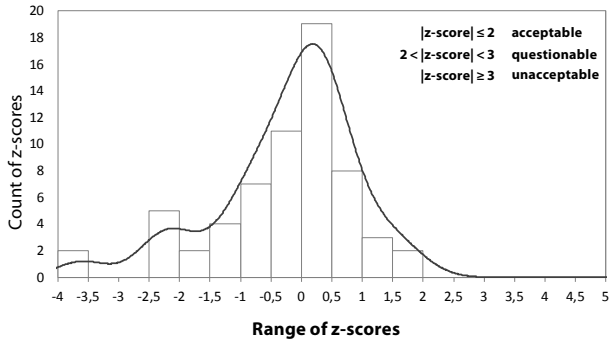
Dithiocarbamates



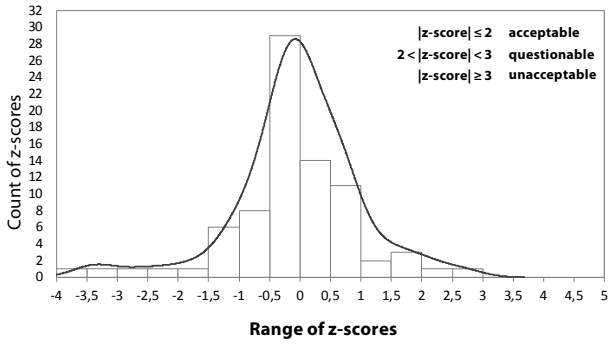
Ethephon



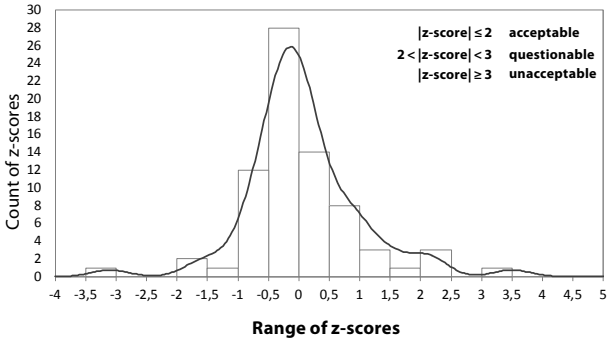
Glyphosate



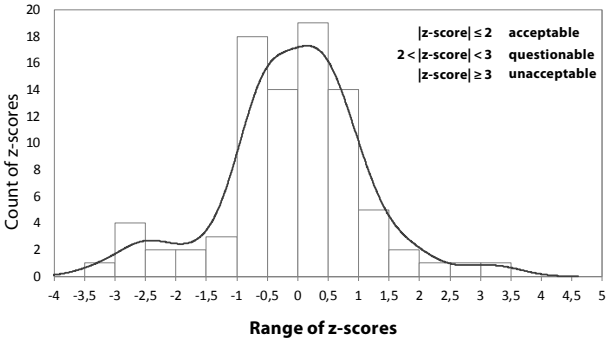
MCPA



Mepiquat



Propamocarb

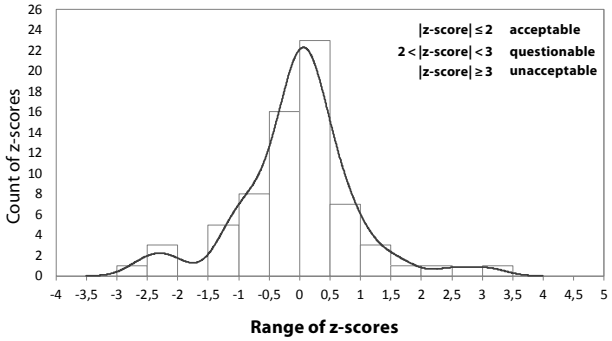


* Cut-off at z-score = 5

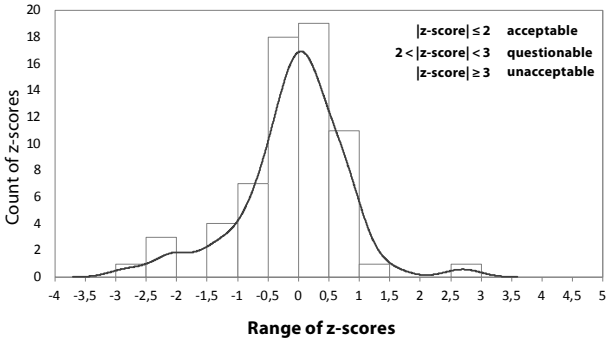
Appendix 5 (cont.) Histograms and kernel density estimates of z-scores* distributions

Optional compounds

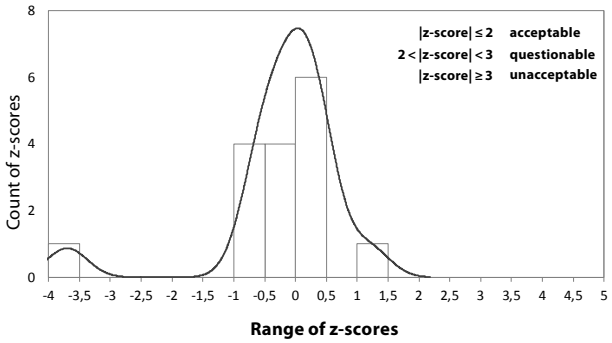
Bentazone



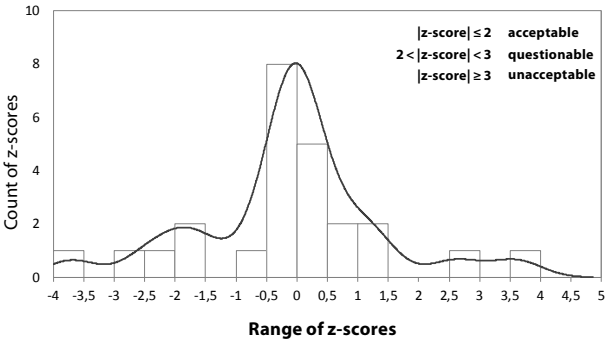
Bromoxynil



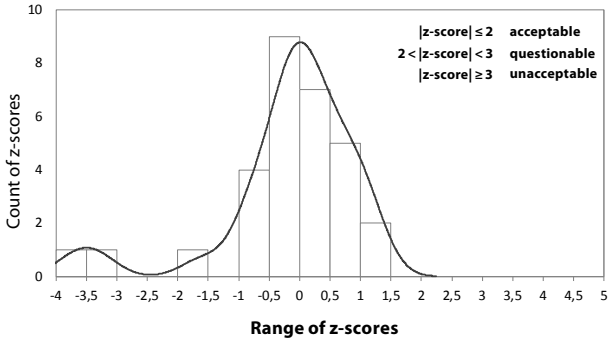
N-Acetyl glufosinate



Phosphonic acid

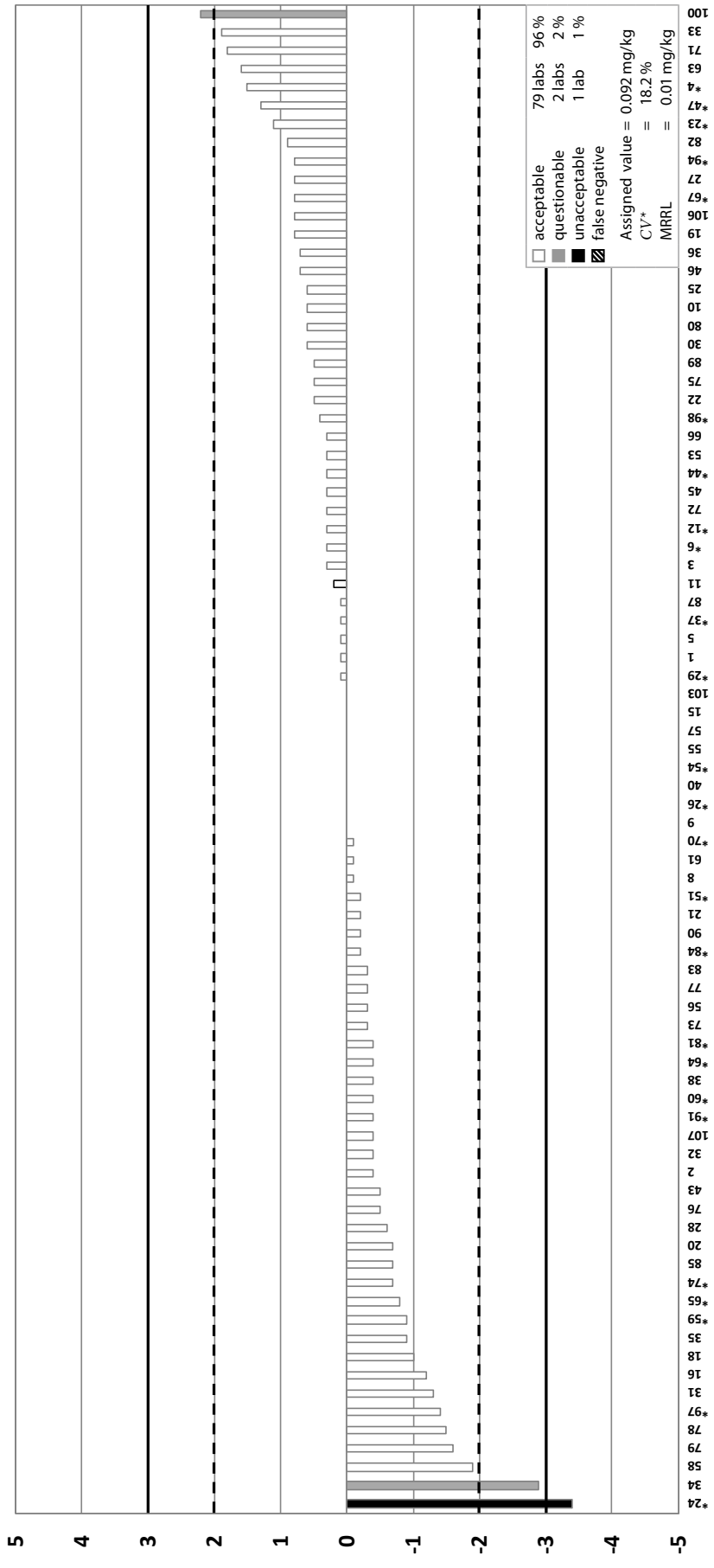


TNFG

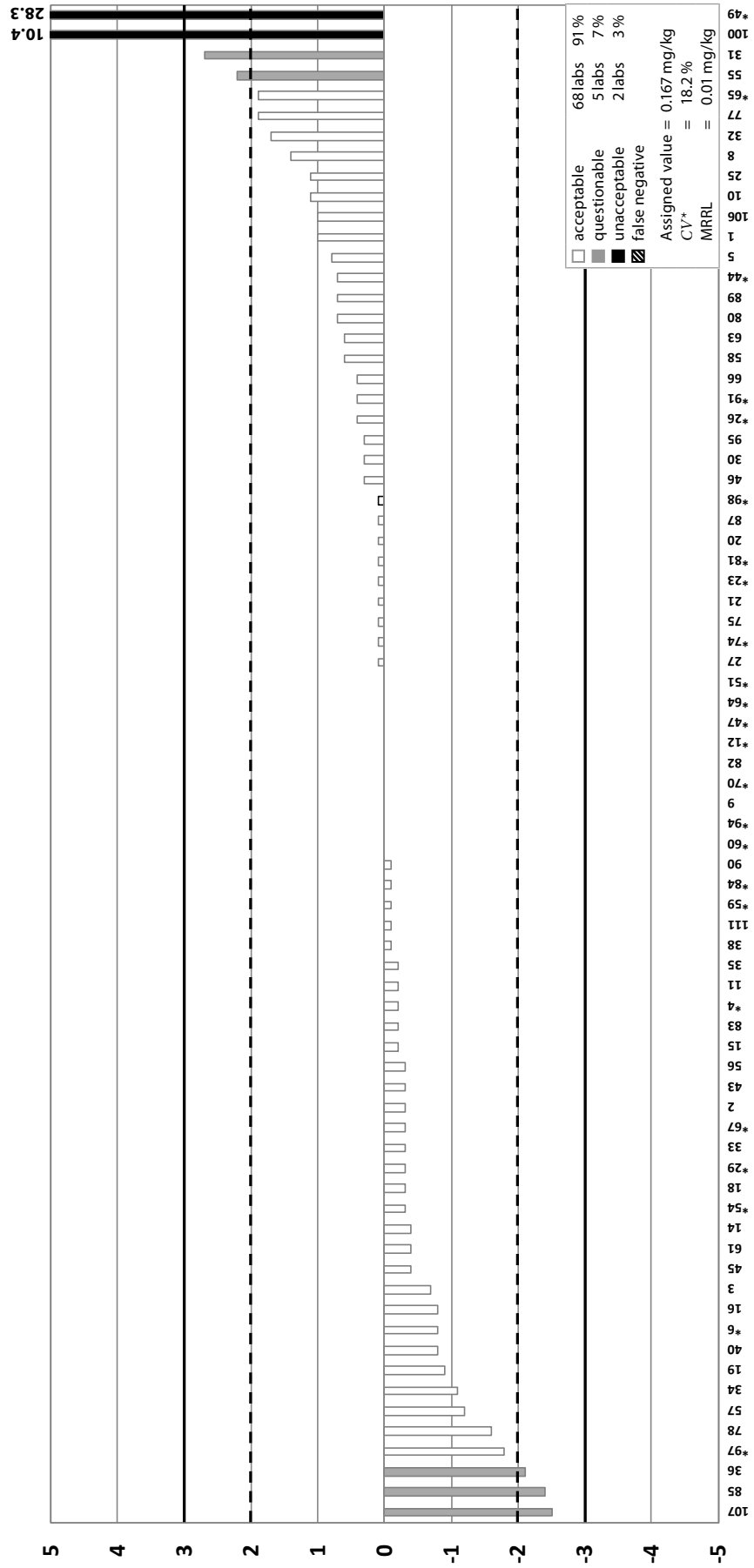


* Cut-off at z-score = 5

Appendix 6 Graphic presentation of z-scores: Compulsory compounds

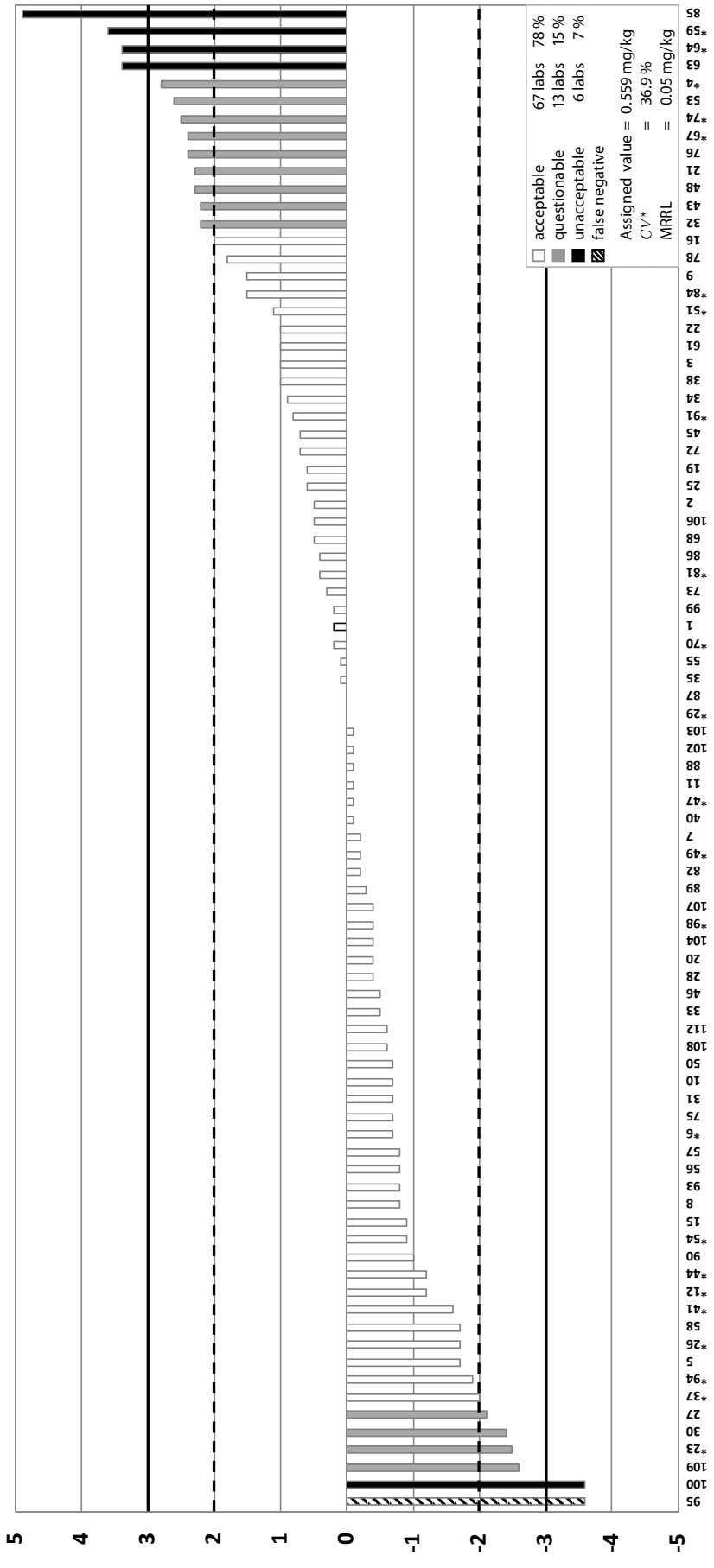


Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds

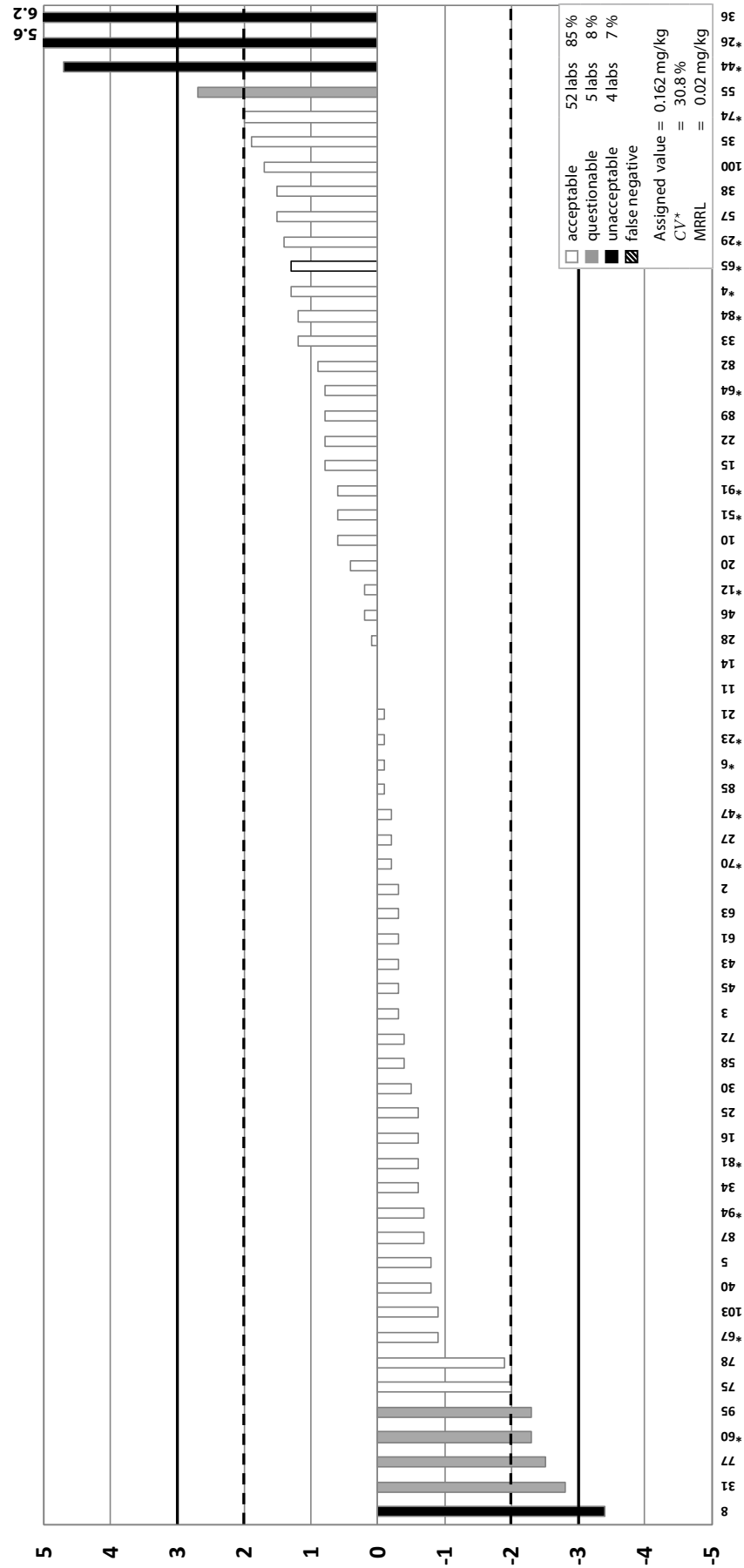


Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds

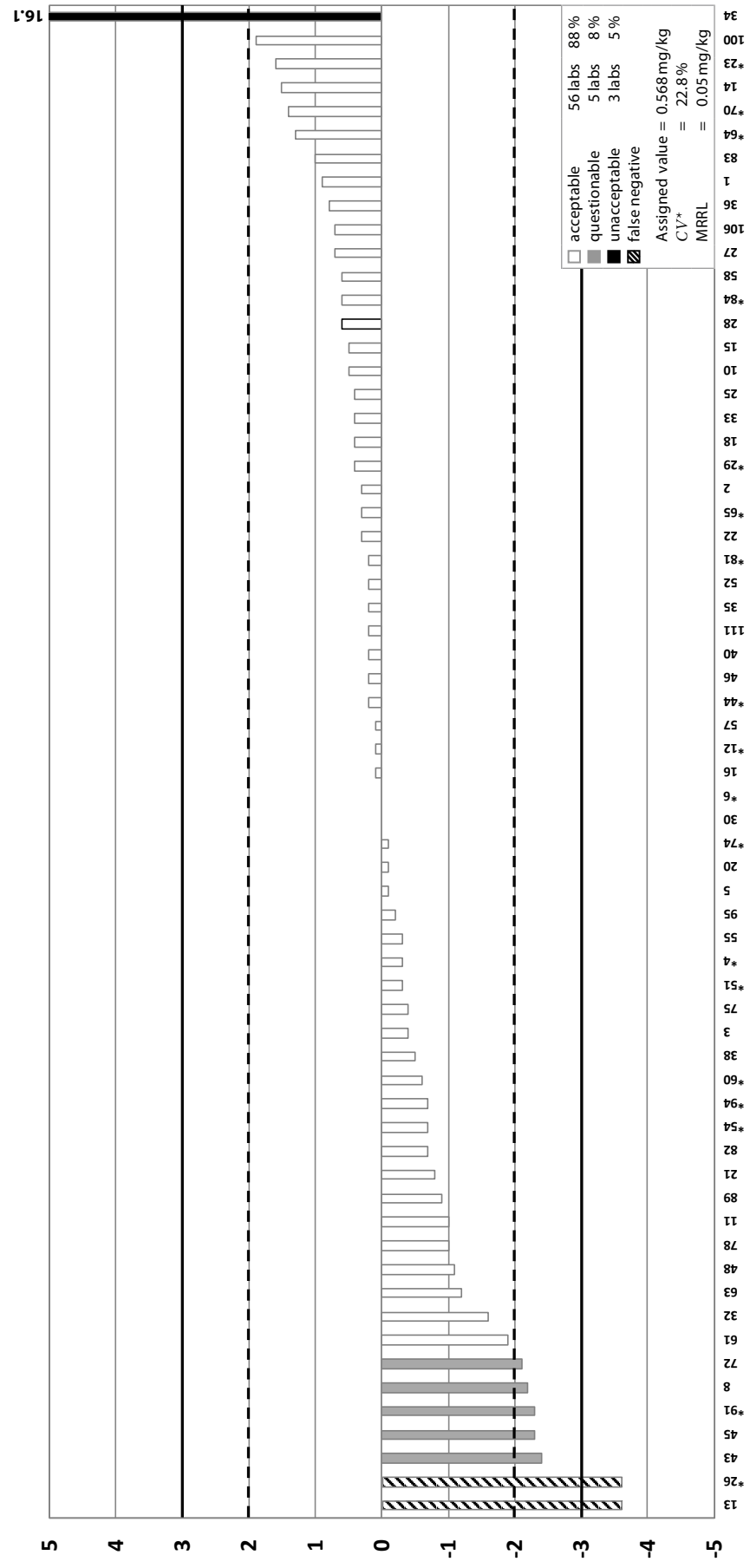
Dithiocarbamates



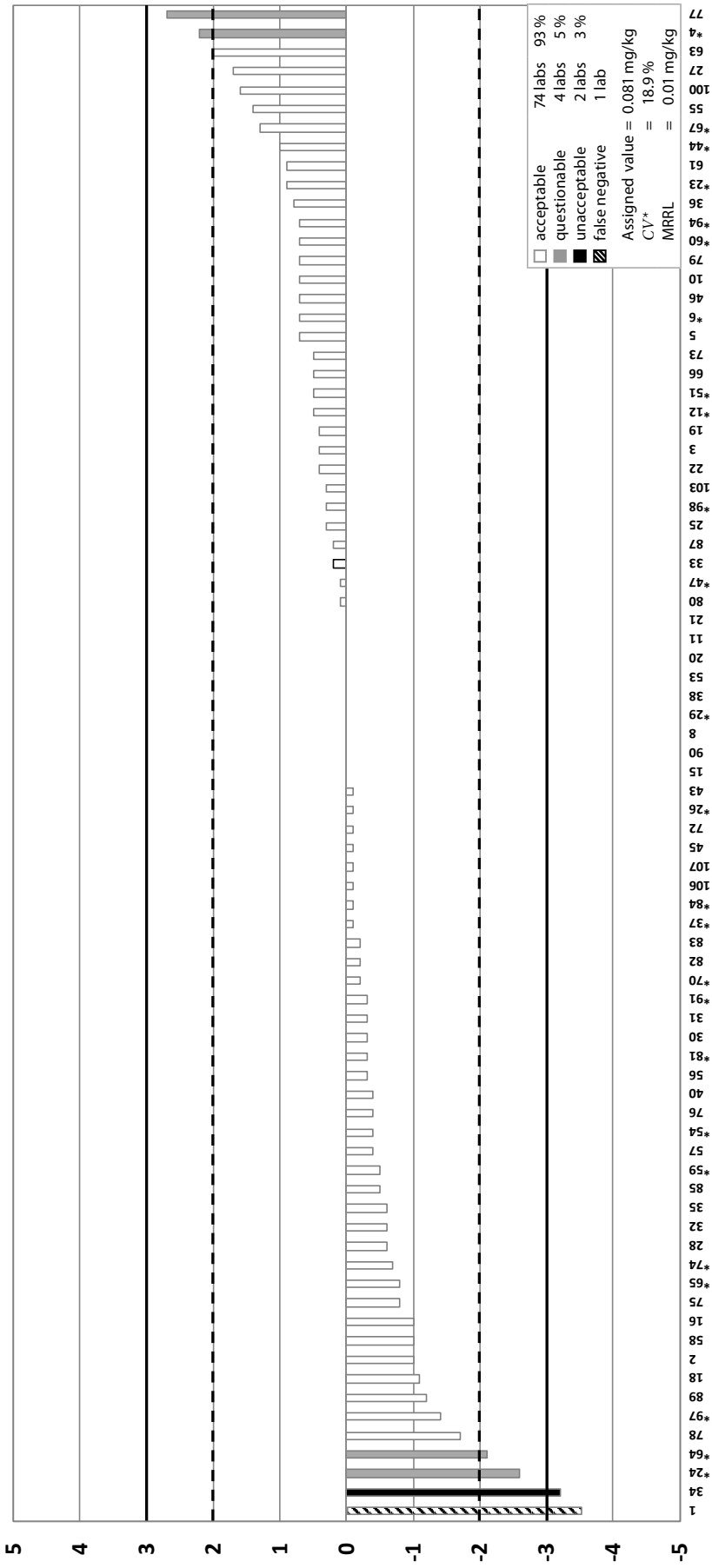
Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds



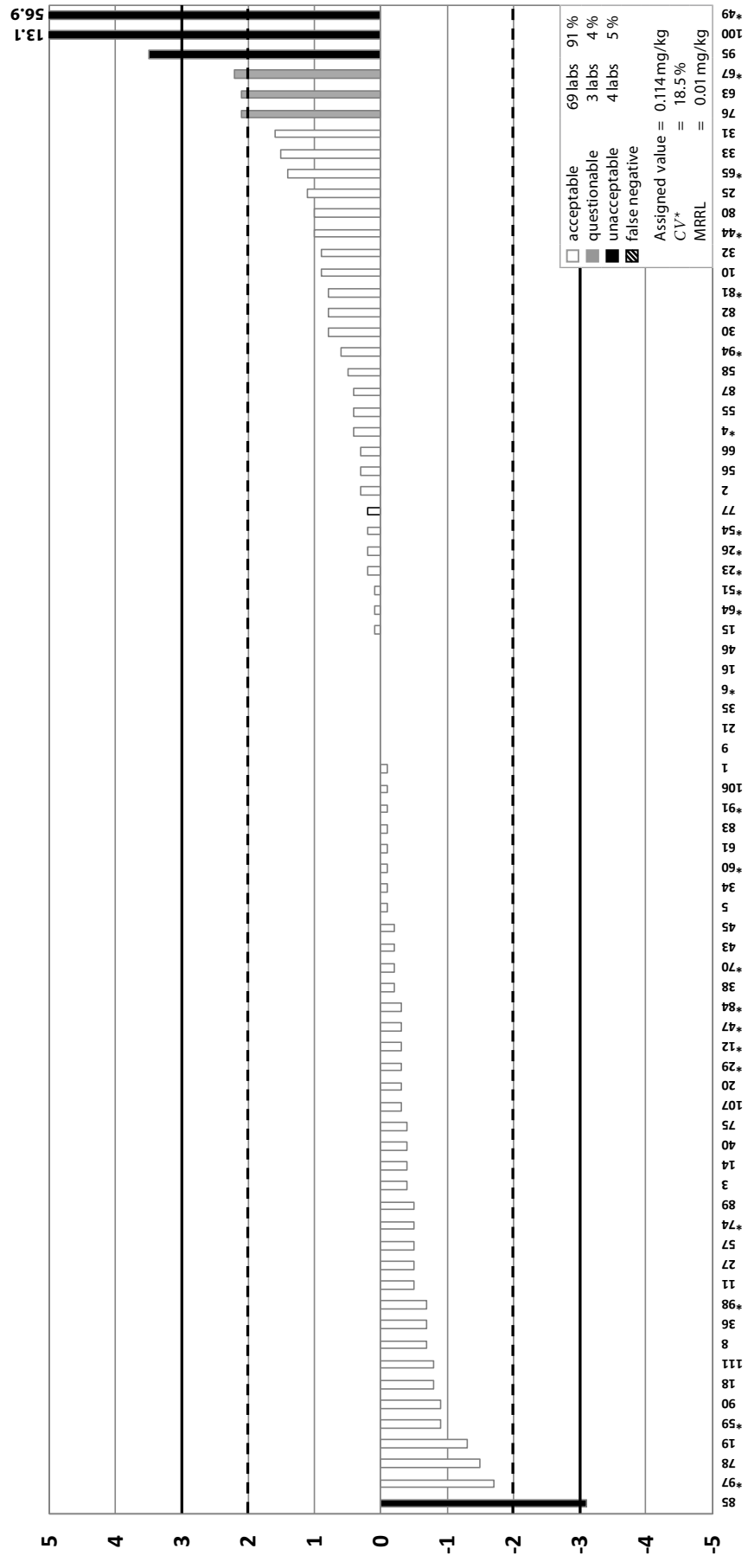
Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds



Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds

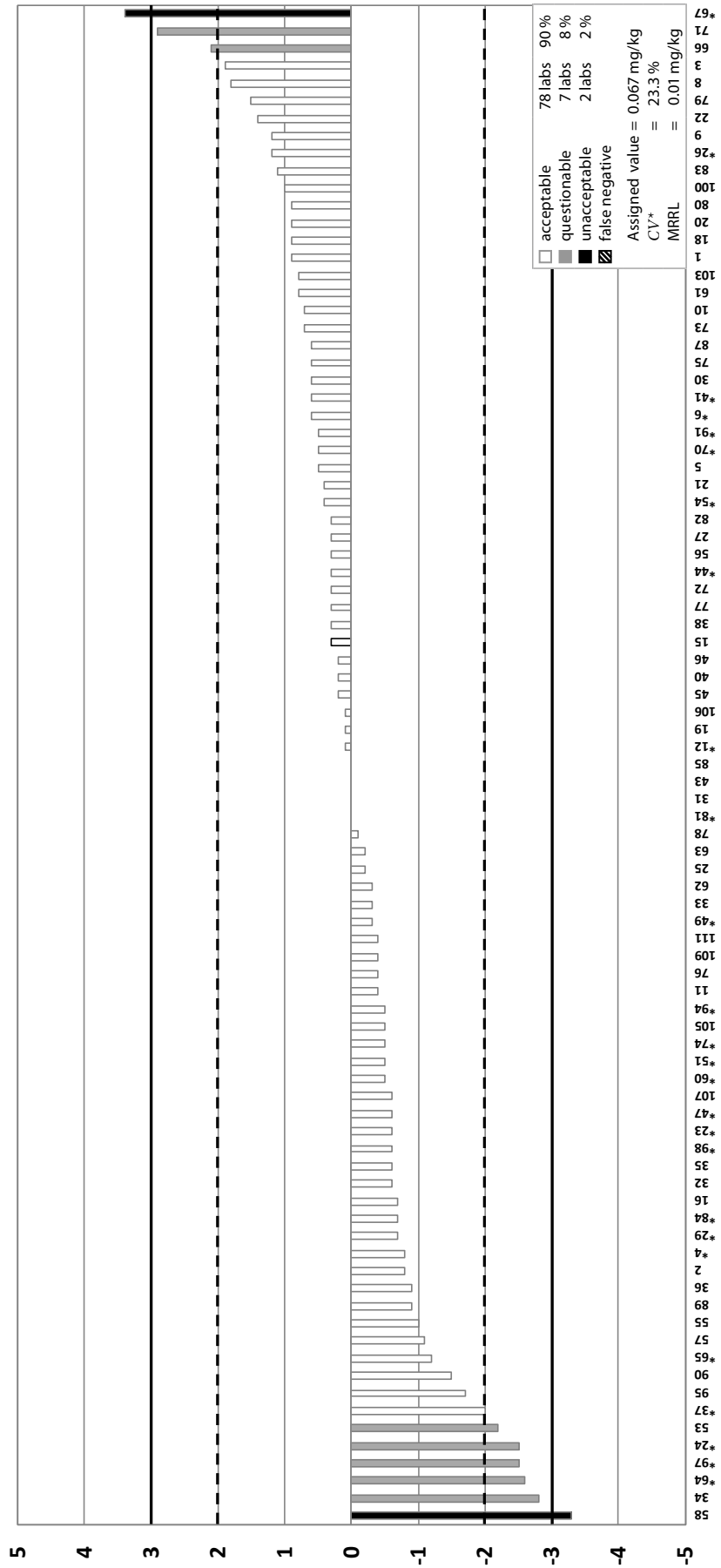


Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds



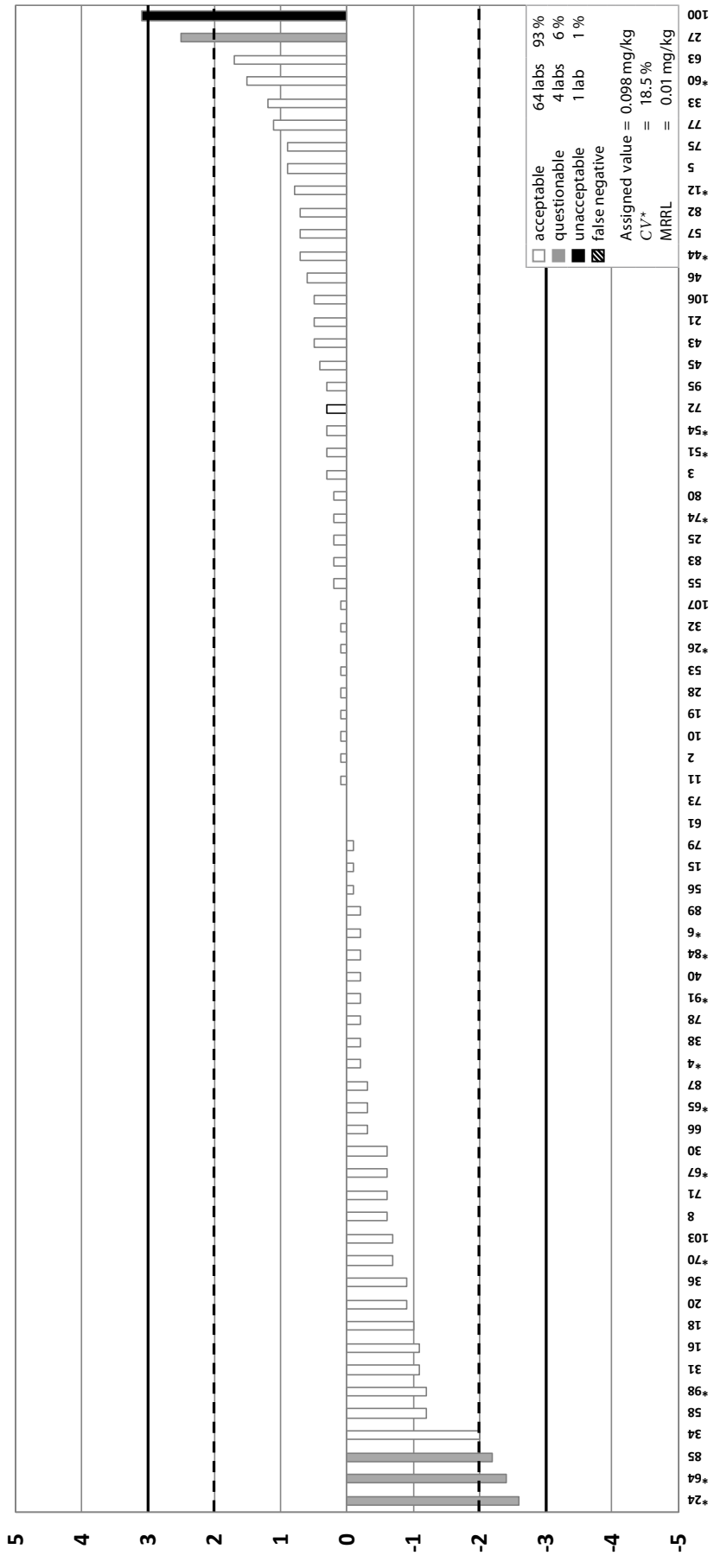
Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds

Propamocarb



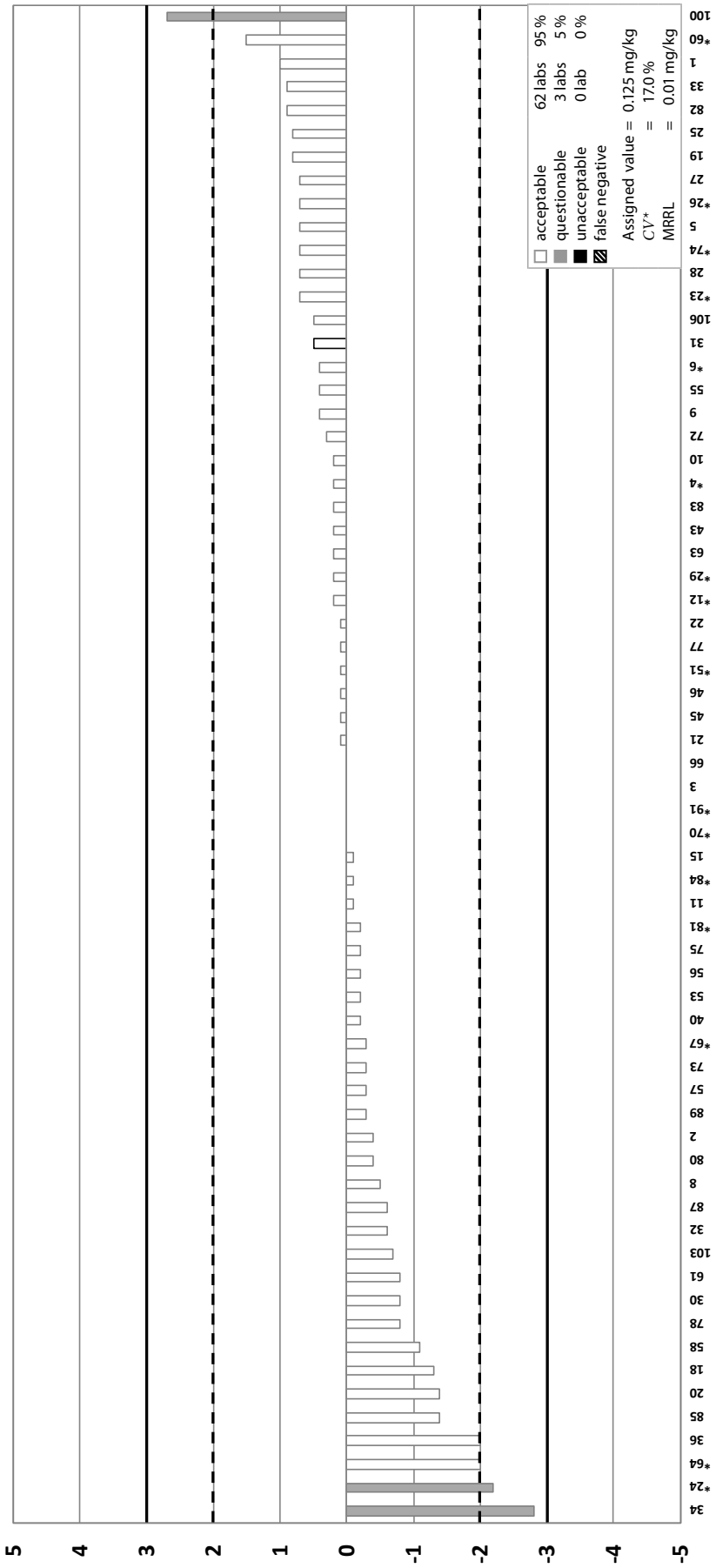
Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds

Bentazone



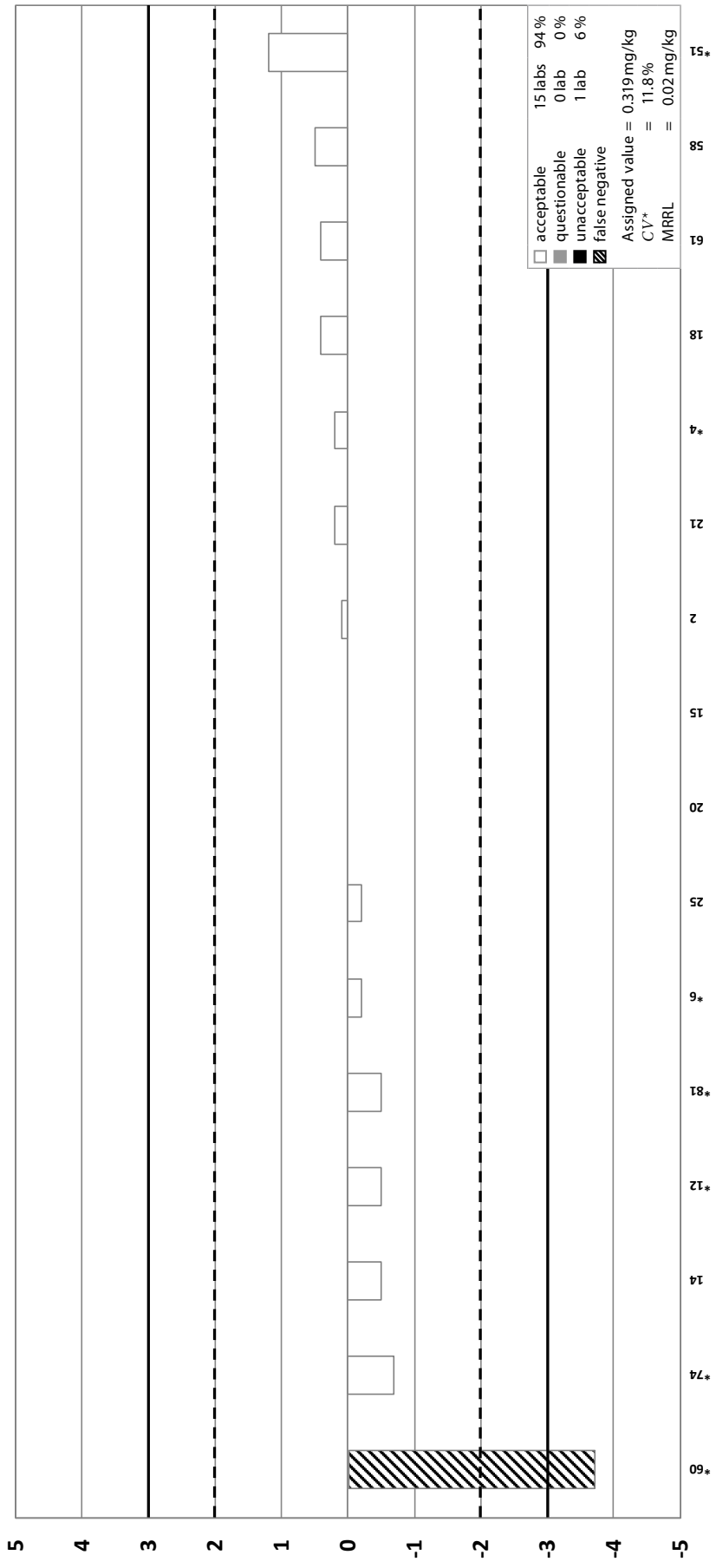
Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds

Bromoxynil

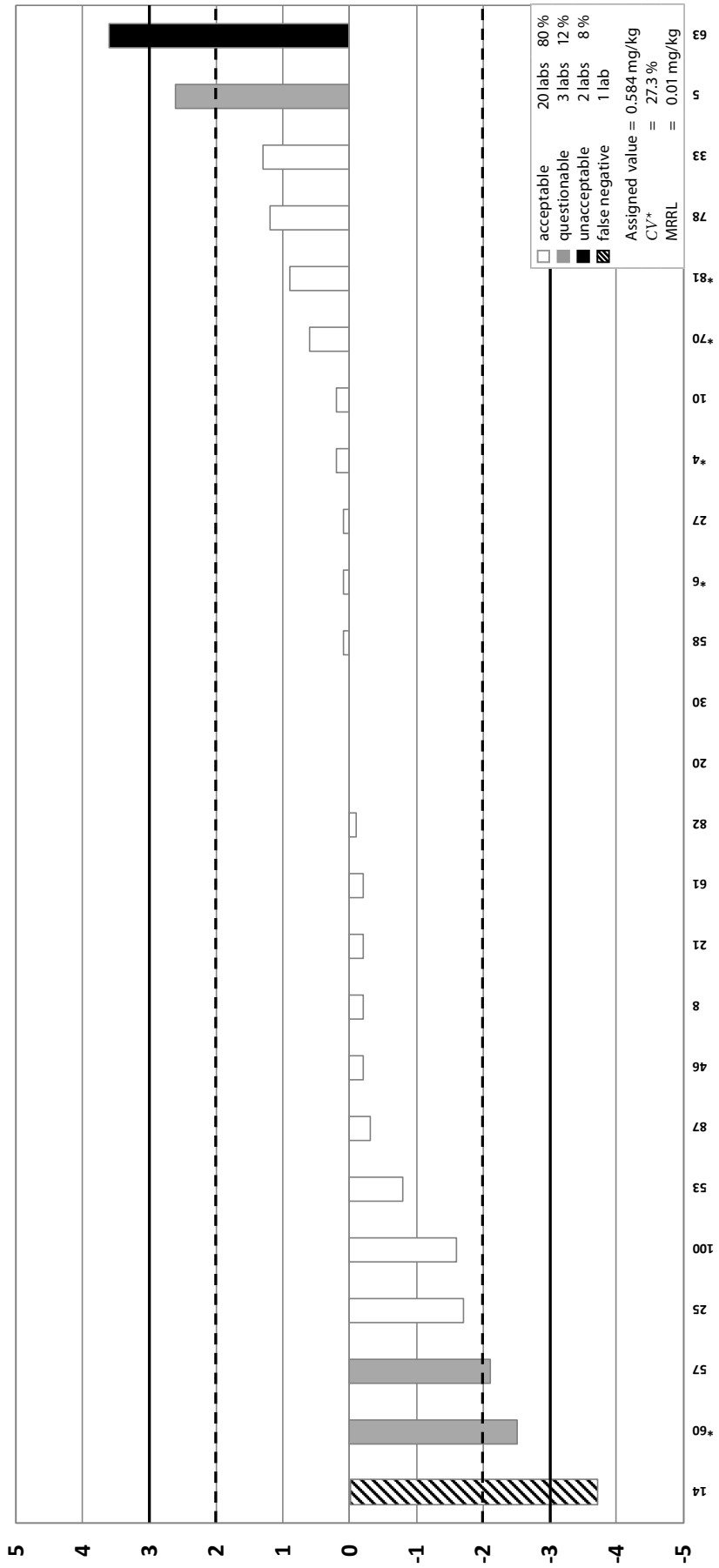


Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds

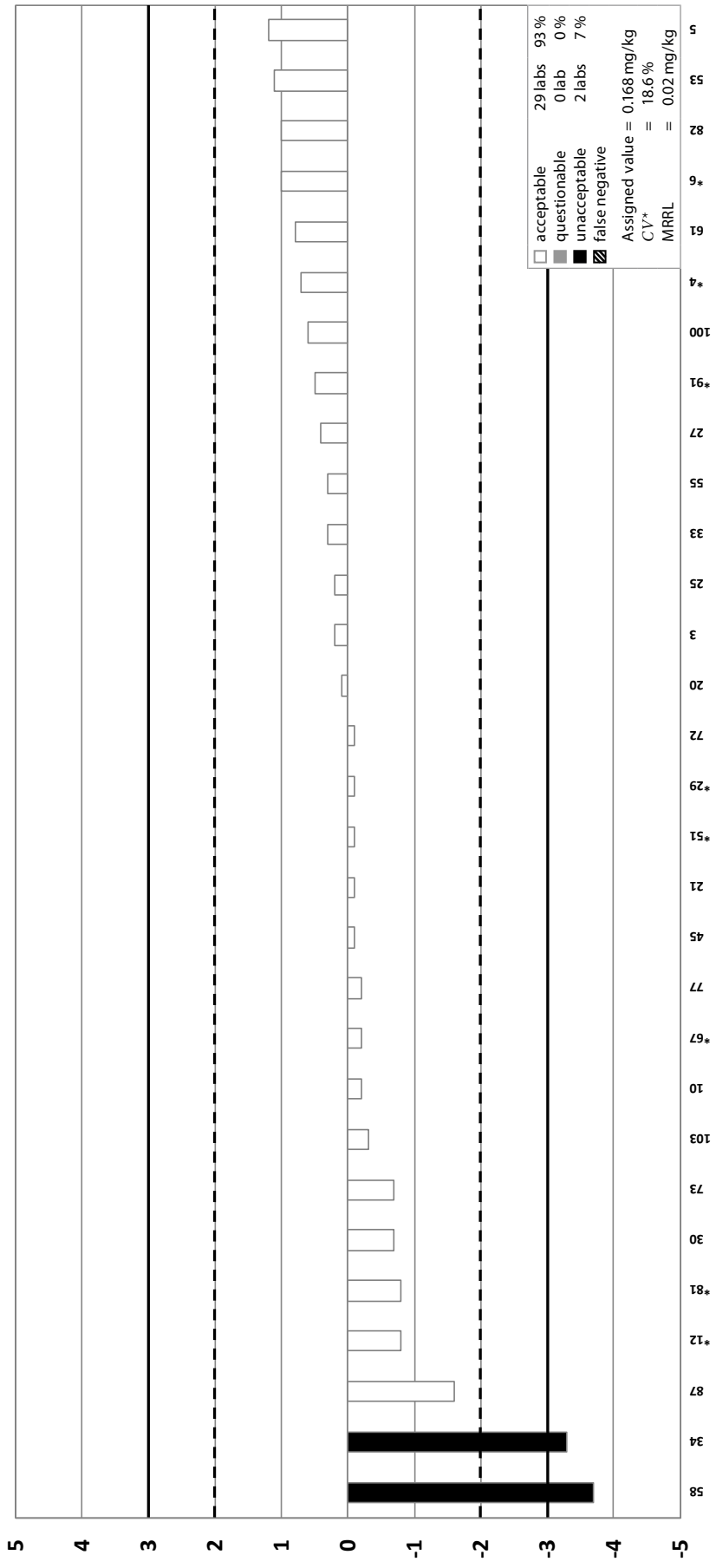
N-acetyl glufosinate



Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds



Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds



Appendix 7 Special z-scores evaluation for dithiocabamates (for information only)

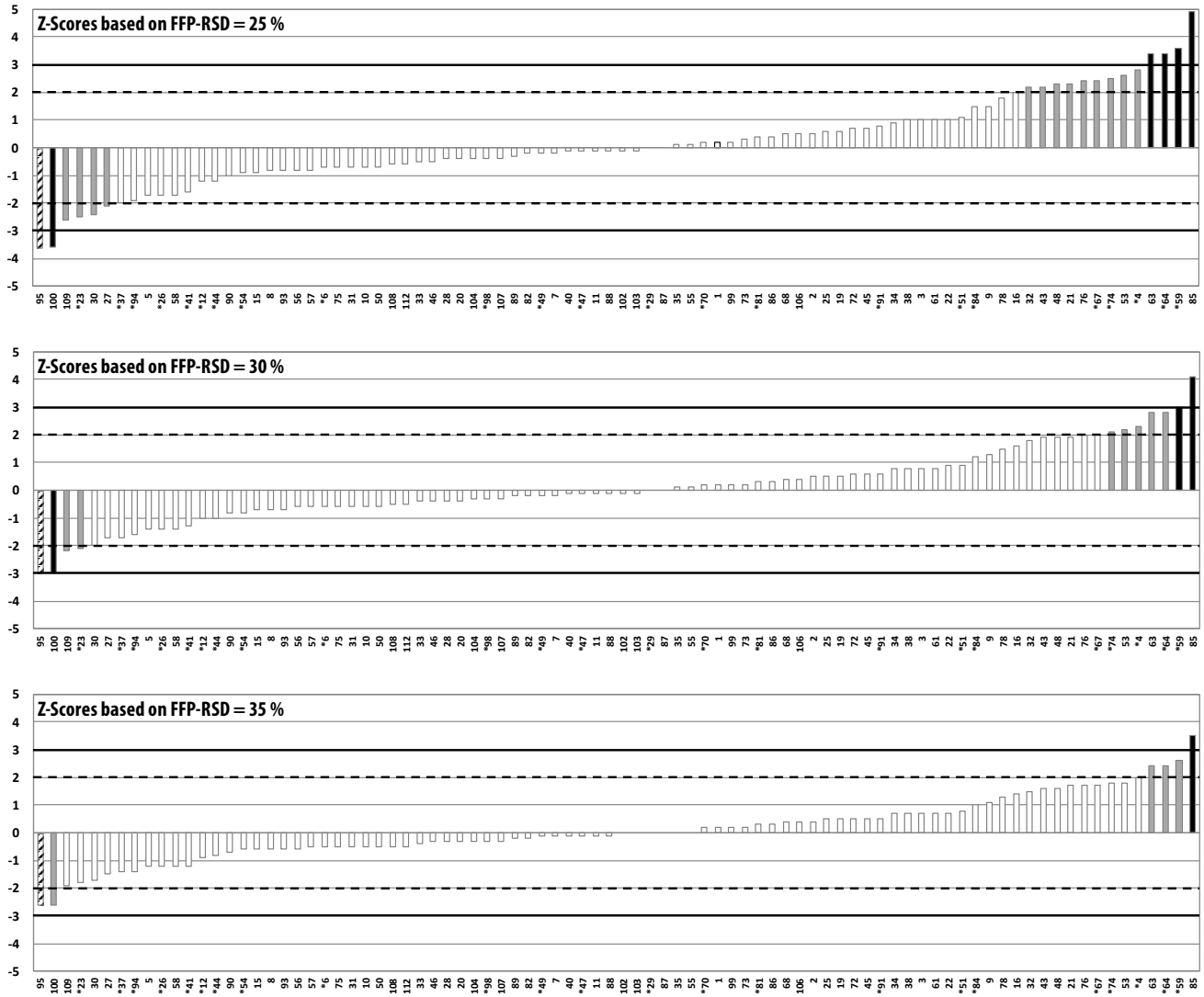
Robust Mean [mg/kg] [1]		0.559	0.559	0.559	0.649
Lab code SRM10-	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	z-score (FFP-RSD = 30 %)	z-score (FFP-RSD = 35 %)	z-score [2] (FFP-RSD = 25 %)
1	0.590	0.2	0.2	0.2	–
2	0.635	0.5	0.5	0.4	–
3	0.698	1.0	0.8	0.7	–
4	0.950	***2.8***	***2.3***	2.0	–
5	0.320	-1.7	-1.4	-1.2	–
6	0.458	-0.7	-0.6	-0.5	–
7	0.532	-0.2	-0.2	-0.1	-0.7
8	0.450	-0.8	-0.7	-0.6	–
9	0.774	1.5	1.3	1.1	0.8
10	0.462	-0.7	-0.6	-0.5	-1.2
11	0.547	-0.1	-0.1	-0.1	–
12	0.392	-1.2	-1.0	-0.9	–
15	0.435	-0.9	-0.7	-0.6	–
16	0.832	2.0	1.6	1.4	1.1
19	0.650	0.6	0.5	0.5	–
20	0.500	-0.4	-0.4	-0.3	–
21	0.883	***2.3***	1.9	1.7	1.4
22	0.704	1.0	0.9	0.7	–
23	0.210	***-2.5***	***-2.1***	-1.8	–
25	0.648	0.6	0.5	0.5	0.0
26	0.325	-1.7	-1.4	-1.2	-2.0
27	0.270	***-2.1***	-1.7	-1.5	–
28	0.498	-0.4	-0.4	-0.3	–
29	0.558	0.0	0.0	0.0	-0.6
30	0.228	***-2.4***	-2.0	-1.7	–
31	0.460	-0.7	-0.6	-0.5	–
32	0.860	***2.2***	1.8	1.5	–
33	0.484	-0.5	-0.4	-0.4	–
34	0.688	0.9	0.8	0.7	–
35	0.568	0.1	0.1	0.0	-0.5
37	0.280	-2.0	-1.7	-1.4	–
38	0.696	1.0	0.8	0.7	0.3
40	0.541	-0.1	-0.1	-0.1	–
41	0.334	-1.6	-1.3	-1.2	–
43	0.870	***2.2***	1.9	1.6	–
44	0.393	-1.2	-1.0	-0.8	-1.6
45	0.661	0.7	0.6	0.5	–
46	0.496	-0.5	-0.4	-0.3	-0.9
47	0.544	-0.1	-0.1	-0.1	–
48	0.881	***2.3***	1.9	1.6	1.4
49	0.530	-0.2	-0.2	-0.1	-0.7
50	0.465	-0.7	-0.6	-0.5	-1.1
51	0.706	1.1	0.9	0.8	0.3
53	0.920	***2.6***	***2.2***	1.8	–
54	0.432	-0.9	-0.8	-0.6	-1.3
55	0.568	0.1	0.1	0.0	-0.5

Robust Mean [mg/kg] [1]		0.559	0.559	0.559	0.649
Lab code SRM10-	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	z-score (FFP-RSD = 30 %)	z-score (FFP-RSD = 35 %)	z-score [2] (FFP-RSD = 25 %)
56	0.451	-0.8	-0.6	-0.6	–
57	0.452	-0.8	-0.6	-0.5	–
58	0.328	-1.7	-1.4	-1.2	–
59	1.064	***3.6***	***3.0***	***2.6***	***2.6***
61	0.700	1.0	0.8	0.7	–
63	1.030	***3.4***	***2.8***	***2.4***	–
64	1.030	***3.4***	***2.8***	***2.4***	***2.3***
67	0.894	2.4	2.0	1.7	1.5
68	0.630	0.5	0.4	0.4	–
70	0.589	0.2	0.2	0.2	-0.4
72	0.653	0.7	0.6	0.5	–
73	0.599	0.3	0.2	0.2	–
74	0.910	***2.5***	***2.1***	1.8	1.6
75	0.459	-0.7	-0.6	-0.5	–
76	0.890	2.4	2.0	1.7	1.5
78	0.810	1.8	1.5	1.3	1.0
81	0.616	0.4	0.3	0.3	-0.2
82	0.526	-0.2	-0.2	-0.2	–
84	0.762	1.5	1.2	1.0	0.7
85	1.250	***4.9***	***4.1***	***3.5***	***3.7***
86	0.617	0.4	0.3	0.3	-0.2
87	0.563	0.0	0.0	0.0	–
88	0.547	-0.1	-0.1	-0.1	–
89	0.520	-0.3	-0.2	-0.2	–
90	0.423	-1.0	-0.8	-0.7	–
91	0.665	0.8	0.6	0.5	–
93	0.450	-0.8	-0.7	-0.6	–
94	0.292	-1.9	-1.6	-1.4	–
95	FN	***-3.6***	***-3.0***	***-2.6***	***-3.7***
98	0.509	-0.4	-0.3	-0.3	-0.9
99	0.590	0.2	0.2	0.2	–
100	0.05662	***-3.6***	***-3.0***	***-2.6***	***-3.7***
102	0.550	-0.1	-0.1	0.0	–
103	0.550	-0.1	-0.1	0.0	–
104	0.508	-0.4	-0.3	-0.3	–
106	0.630	0.5	0.4	0.4	–
107	0.510	-0.4	-0.3	-0.3	-0.9
108	0.470	-0.6	-0.5	-0.5	-1.1
109	0.196	***-2.6***	***-2.2***	-1.9	–
112	0.470	-0.6	-0.5	-0.5	-1.1
113	0.650	0.6	0.5	0.5	0.0
114	0.840	2.0	1.7	1.4	–
115	0.660	0.7	0.6	0.5	0.1
116	0.880	***2.3***	1.9	1.6	1.4
117	0.392	-1.2	-1.0	-0.9	-1.6
118	0.721	1.2	1.0	0.8	–

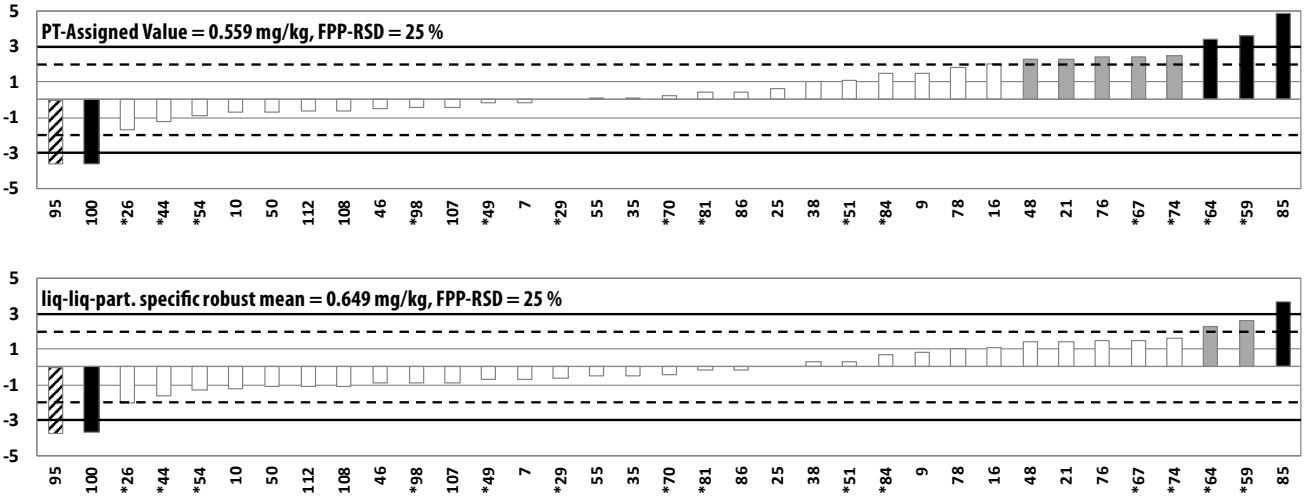
1: 0.559 mg/kg: robust mean based on the entire population of EU/EFTA-laboratories(= assigned value in the PT);
0.649 mg/kg: robust mean based on the population of EU/EFTA-laboratories employing liquid-liquid partitioning involving methods
2: This evaluation was calculated only for results driven from methods involving liquid-liquid partitioning

Appendix 7 (cont.) Special z-scores evaluation for dithiocabamates (for information only)

Distribution of z-scores based on different FFP-RSDs and PT assigned value 0.559 mg/kg



Distribution of z-scores for results derived from methods involving liquid-liquid partitioning



Appendix 8 Possible reasons reported for poor performance (ordered by z-scores)

A: Technical problems with measurement instrumentation
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of analytical standard
F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level too close to assigned value
I: Inappropriate storage or pre-treatment of sample
J: Transcription error
K: Result not corrected for low recovery
L: Inappropriate calibration
M: Detection signals strongly interferred by matrix components

2,4-D (free acid) Assigned value: 0.092 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
24	-3.4	yes	The reason for bad the performance was unfortunally because I forgot to acidify the solvent before extraction.	B, G
34	-2.9	yes	Problem with calibration solution	E
114	-2.8	yes	In house method is not validated on this type of matrices and not accredited for maize flour. No experience with commodities with low water content. No hydratation was undertaken. After repeating the prcedure with hydratation the result was acceptable.	D, G
100	2.2	yes	High matrix effect of maize flour extractions on LC -MS. The matrix effect was minimized by diluting the extract. That resulted in small signal and big uncertainty.	C

Chlormequat Assigned value: 0.167 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
118	-4	yes	no experience with the analyte and method not yet fully established. It was for information only.	D
107	-2.5	yes	misuse of the chromatographic column	B
85	-2.4	yes	technical problem with detector and another type of detector that was not validated was used for the PT result	A
100	10.4	yes	High matrix effect of maize flour extractions on LC -MS. The matrix effect was minimized by diluting the samples from this source that resulted in small signal and big uncertainty	C
55	2.2	no	So far the error source could not be found and no correction measures were undertaken.	–
49	28.3	yes	false concentration of stock solution for calibration (factor 10)	E

Dithiocarbamates Assigned value: 0.559 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
100	-3.6	yes	Degradation of the sample in the laboratory	I
109	-2.6	no	So far no concret error cause was found.	–
23	-2.5	yes	Probably: 1) result not recovery corrected; 2) problem with spectrophotometrical measurement	A, K
30	-2.4	no	so far the error source could not be found and no correction measures were undertaken.	–

Appendix 8 (cont.) Possible reasons for poor performance (ordered by z-scores)

A: Technical problems with measurement instrumentation
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of analytical standard
F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level too close to assigned value
I: Inappropriate storage or pre-treatment of sample
J: Transcription error
K: Result not corrected for low recovery
L: Inappropriate calibration
M: Detection signals strongly interferred by matrix components

Dithiocarbamates Assigned value: 0.559 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
32	2.2	yes	During the "cooking process" (cleavage with $SnCl_2$/HCl etc.) part of the sample was burnt resulting in an increased colour of the solution being measured finally with the UV-spectromete	B, M
43	2.2	yes	Head-space approach (without CS_2 reextraction into solvent) was used for sample preparation. Calibration on processed standard (Thiram addition to a sample matrix) might be a reason for higher results	M
21	2.3	no	at the moment we can not find any answer for our high concentration. We have the right concentration of the standard solution. We prepared a new standard solution with new standard and make a comparison with the old one. We get the same amount. When we analyzed the PT sample again we got the right result (0.568 mg/kg), but our recovery was not so good (68 %). GC System: no changes, we only analyze Dithiocarbamate with this GC.	–
48	2.3	no	So far the error source could not be found and no correction measures were undertaken.	–
76	2.4	yes	"Out of lab's routine scope and method not validated matrix effects not compensated (solved by matrix-matched calibration)"	C, D
74	2.5	yes	degradation of the standard solutions	E
53	2.6	yes	Probably 1) due to matrix effects. Our investigation shown, results based on matrix-matched calibration led to much higher concentration and high z-score. For this matrix, it seems that no calibration by matrix-matched standard solutions is necessary; 2) The assigned valued is distorted because of the matrix effect if other laboratories performed only calibration in solvent"	C
4	2.8	yes	It was the first time we analized dithiocarbamates (CS_2), and we don't carry out any official controls for this molecule. We need more practise and optimisation (both for extraction and GC-MS analysis) in order to obtain reliable results. The development/validation of this method is not planned at our NRL programme for the moment, but we will submit this proposition at our next Steering Committee meeting at the end of the year.	D
64	3.4	no	So far the error source could not be found and no correction measures were undertaken.	–
59	3.6	no	So far the error source could not be found. Investigation is continued.	–
85	4.9	yes	Analyzing the frozen sample (-20) data obtained are similar to the initial (Rep1 Rep2 1.22 ppm and 1.10 ppm 1.28 ppm-O_3). Analyzing previous thawing in the refrigerator (+4 °C) the data have been Rep1 0.54ppm and 0.55 ppm Rep2-O_3 0.63. ppm. Remark from the organisers: The same expreiment was repeated in tripel replicates by the organisers, but the impact mentioned could not be observed (s. **Section 4.3.5, p. 49**).	I

Appendix 8 (cont.) Possible reasons for poor performance

Ethephon Assigned value: 0.162 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
118	-3.9	yes	no experience with the analyte and method not yet fully established. It was for information only.	D
77	-2.5	yes	1) no experience with dry commodities 2) maybe the rehydratation was not appropiate	D, (G)
60	-2.3	yes	QuPPe not validated and accreded in your laboratory. In addition maybe errors in our standard mixture or stock solutions that will be investigated.	D, (E)
55	2.7	yes	Concentration of commercially provided standard solution was wrong (ethephon 100,00 µg/mL in toluene)	E
44	4.7	(yes)	Maybe due to expired standard substance. A new batch was ordered and ib to be used to check.	–
26	5.6	yes	Signals could not be correctly calculated due to strong variation and lacking of ILIS.	C

Glyphosate Assigned value: 0.568 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
13	-3.6 (FN)	yes	Glyphosate not within laboratorie's routine scope. It was for information only!	D
26	-3.6 (FN)	yes	Method 1.3 of QuPPe-Method protocol, Version 8.1, in combination with our LC-MSMS (Varian 1200L) system was not selective/sensitive enough to determine glyphosate at the concentration levels in the sample The determination using a derivatization step is proposed in order to optimize and to improve the LOQ levels. The "new" method with the derivatization step with FMOC, is going to be fully validated in various matrices and will be the method for analysis of samples for the compound glyphosate.	A, G
118	-3.6 (FN)	yes	no experience with the analyte and method not yet fully established. It was for information only.	D
43	-2.4	yes	Two approaches to quantification of results were used – Matrix match calibration and Standard addition to the sample provided different sets of results. We sent lower result (0.229 mg/kg) from Matrix match calibration. The higher result (0.452 mg/kg) from Standard addition would be quite satisfactory	C, L
45	-2.3	yes	Probably due to usage of glass vials. Unfortunately we run out of plastic vials that time, and we tried to use plastic equipments but the final extracts were placed in regular glass vials	B
91	-2.3	yes	Analysis was carried out by derivatization after extraction and clean-up. Poor perfomance could be caused by the complexity of such sample preparation approach. Additionally, we choose that kind of anlysis because of recent negative experinces of QUPPE method using Dionex AS columns (the HPLC column we have): low sensitivity, unstable retention, etc…	G
72	-2.1	yes	recovery was low: 53.2%, and the result submitted was not corrected recovery	K
113	13.6	yes	High level of glyphosate found in the blank which led to inappropiate external calibration without correction of matrix effect	C
34	16.1	yes	Maybe the method used currently with FMOC-Cl derivatization was not appropiate. We are going to adapting QuPPe-Method	G

MCPA Assigned value: 0.081 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
1	-3.5 (FN)	yes	"For the analyte MCPA we submitted the result "not detected". Actually we determined a mean value of 0.081 mg/kg MCPA in the sample. Due to an individual mistake during the data transcription and a misinterpretation of our internal result table the result for MCPA was mistakably considered to be "not detectable"."	F, J
34	-3.2	yes	Problem with calibration solution	E

Appendix 8 (cont.) Possible reasons for poor performance (ordered by z-scores)

A: Technical problems with measurement instrumentation
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of analytical standard
F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level too close to assigned value
I: Inappropriate storage or pre-treatment of sample
J: Transcription error
K: Result not corrected for low recovery
L: Inappropriate calibration
M: Detection signals strongly interferred by matrix components

MCPA Assigned value: 0.081 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
24	-2.6	yes	The reason for bad the performance was unfortunally because I forgot to acidify the solvent before extraction.	B, G
114	-2.6	yes	In house method is not validated on this type of matrices and not accredited for maize flour. No experience with commodities with low water content. No hydratation was undertaken. After repeating the prcedure with hydratation the result was acceptable.	D
64	-2.1	yes	no experience with the maize flour as matrix and problem with extration.	D
4	2.2	yes	It was the first time we analized MCPA, and we don't carry out any official controls for this molecule. The error comes form the presence of an interference at the retention time of MCPA on the quantification transition (most intense transition: 199 > 141). This punctual interference was not present in the first analysis we made. For our second (confirmatory) analysis, this interference was only visible in our reagent blank, but not in our matrix blank: we chose to take into account the matrix blank, more representative of the sample. We would have obtained a satisfactory z-score if we had substracted the value quantified in the reagent blank, or if we had used the second transition for quantifying the sample (201 > 143). Our follow-up actions will consist in using the second transition for quantification and in raising awareness among the analysts of our lab.	D, F
77	2.7	yes	1) no experience with dry commodities 2) maybe the rehydratation was not appropiate	D, (G)

Mepiquat Assigned value: 0.114 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
118	-3.5	yes	no experience with the analyte and method not yet fully established. It was for information only.	D
85	-3.1	yes	technical problem with detector and another type of detector that was not validated was used for the PT result	A
76	2.1	yes	Out of lab's routine scope and method not validated matrix effects not compensated (solved by matrix-matched calibration)	C, D
100	13.1	yes	High matrix effect of maize flour extractions on LC -MS. The matrix effect was minimized by diluting the extract that resulted in small signal and big uncertainty.	C
49	56.9	yes	false concentration of stock solution for calibration (factor 10)	E

Appendix 8 (cont.) Possible reasons for poor performance

Propamobarb Assigned value: 0.067 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
58	-3.3	yes	Standard addition with 3 levels were applied. It seemed, that the extraction with ACN for the "polar" propamocarb will result in higher concentration and better z-score.	G
34	-2.8	yes	Problem with calibration solution	E
64	-2.6	yes	no experience with the maize flour as matrix and problem with extration.	D
24	-2.5	yes	The reason for bad the performance was unfortunally because I forgot to acidify the solvent before extraction.	B, G
97	-2.5	yes	I perform the preliminary analysis to check if the propamocarb was present in the sample but I cannot perform the correct quantification because the instrument was out of work the day after, so I perform the calcultation with the available results, it was an approximate results.	A
53	-2.2	yes	Extration solution was not acidified and led to underestimation	B
71	2.9	no	So far the error source could not be found and no correction measures were undertaken.	–

Bentazone Assigned value: 0.098 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
114	-2.8	yes	In house method is not validated on this type of matrices and not accredited for maize flour. No experience with commodities with low water content. No hydratation was undertaken. After repeating the prcedure with hydratation the result was acceptable.	D
118	-2.7	yes	no experience with the analyte and method not yet fully established. It was for information only.	D
24	-2.6	yes	The reason for bad the performance was unfortunally because I forgot to acidify the solvent before extraction.	B, G
64	-2.4	yes	no experience with the maize flour as matrix and problem with extration.	D
85	-2.2	yes	The recovery was low (54 %) but the residue data was not adjustaed with recovery data, because we thought it was a punctual failure in the analysis of the recovery	K
100	3.1	yes	High matrix effect of maize flour extractions on LC -MS. The matrix effect was minimized by diluting the extract that resulted in small signal and big uncertainty	C

Bromoxynil Assigned value: 0.125 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
113	-3.7 (FN)	yes	detected but not quantified	A
34	-2.8	yes	Problem with calibration solution	E
114	-2.6	yes	In house method is not validated on this type of matrices and not accredited for maize flour. No experience with commodities with low water content. No hydratation was undertaken. After repeating the prcedure with hydratation the result was acceptable.	D
118	-2.3	yes	no experience with the analyte and method not yet fully established. It was for information only.	D
24	-2.2	yes	The reason for bad the performance was unfortunally because I forgot to acidify the solvent before extraction.	B, G
100	2.7	yes	High matrix effect of maize flour extractions on LC -MS. The matrix effect was minimized by diluting the samples from this source that resulted in small signal and big uncertainty	C

Appendix 8 (cont.) Possible reasons for poor performance (ordered by z-scores)

A: Technical problems with measurement instrumentation
B: Procedure not properly conducted
C: Matrix effect not properly compensated
D: Lack of experience
E: Error in concentration of analytical standard
F: Error in the evaluation/interpretation of measurement data
G: Use of inappropriate procedure
H: Reporting level too close to assigned value
I: Inappropriate storage or pre-treatment of sample
J: Transcription error
K: Result not corrected for low recovery
L: Inappropriate calibration
M: Detection signals strongly interferred by matrix components

N-Acetyl glufosinate Assigned value: 0.319 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
60	-3.7 (FN)	yes	QuPPe not validated and accreded in your laboratory. In addition maybe errors in our standard mixture or stock solutions that will be investigated.	D, (E)

Phosphonic acid Assigned value: 0.584 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
60	-2.5	yes	QuPPe not validated and accreded in your laboratory. In addition maybe errors in our standard mixture or stock solutions that will be investigated.	D, (E)
57	-2.1	yes	Interference in the chromatogramm resulting in missinterpretation and integration of the peaks.	M
5	2.6	yes	Error in the calibration function applied with a factor of 1.66	L

TFNG Assigned value: 0.168 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
58	-3.7	yes	Standard addition with 3 levels were applied. It seemed, that the extration with unbuffered EE would lead to better result than with unbuffered ACN.	G
34	-3.3	yes	Problem with calibration solution	E

Glufosinate (false positive results)

LabCode	Source of error localized?	Reason / Remarks	
72 and 91	yes	Analysis was carried out by derivatisation with trimethyl-orthoacetate (methylation) and acetic acid (acetylation) leading to the same derivative product in case of glufosinate and N-acetyl glufosinate. It means that with this analytical method these two components can not be distinguished from each other.	F, G

GENERAL PROTOCOL

for EU Proficiency Tests on Pesticide Residues in Food and Feed

Introduction

This protocol contains general procedures valid for all European Union Proficiency Tests (EUPTs) organised on behalf of the European Commission, DG-SANTÉ[1] by the four European Union Reference Laboratories (EURLs) responsible for pesticide residues in food and feed. These EUPTs are directed at laboratories belonging to the Network[2] of National Reference Laboratories (NRLs) and Official Laboratories (OfLs) of the EU Member States. OfLs from EFTA countries and EU-Candidate countries are also welcome to participate in the EUPTs. OfLs from Third countries may be permitted to participate on a case-by-case basis.

The following four EURLs for pesticide residues were appointed by DG-SANTÉ based on regulation 882/2004/EC[3]:

- EURL for Fruits and Vegetables (EURL-FV),
- EURL for Cereals and Feedingstuffs (EURL-CF),
- EURL for Food of Animal Origin and Commodities with High Fat Content (EURL-AO) and
- EURL for pesticides requiring Single Residue Methods (EURL-SRM).

The aim of these EUPTs is to obtain information regarding the quality, accuracy and comparability of pesticide residue data in food and feed reported to the European Union within the framework of the national control programmes and the EU multiannual co-ordinated control programme[4]. Participating laboratories will be provided with an assessment of their analytical performance that

[1] DG-SANTÉ = European Commission, Health and Consumer Protection Directorate-General

[2] For more information about the EURL/NRL/OfL-Network please refer to the EURL-Web-portal under: http://www.eurl-pesticides.eu

[3] Regulation (EC) No 882/2004 of the European Parliament and of the Council on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Published at OJ of the EU L191 of 28.05.2004

[4] European Commission Proficiency Tests for Pesticide Residues in Fruits and Vegetables, Trends in Analytical Chemistry, 2010, 29 (1), 70 – 83.

they can use to demonstrate their analytical performance and compare themselves with other participating laboratories.

EUPT-Organisers and Scientific Committee

EUPTs are organised by individual EURLs, or by more than one EURL, in joint collaboration.

An **Organising Team** is appointed by the EURL(s) in charge. This team is responsible for all administrative and technical matters concerning the organisation of the PT, e.g. the PT-announcement, production of Test Item and Blank Material, the undertaking of homogeneity and stability tests, packing and shipment of the Test Item and Blank Material, handling and evaluation of the results and method information submitted by the participants and the drafting of the preliminary and final reports.

To complement the internal expertise of the EURLs, a group of external consultants that form the **EUPT-Scientific Committee** (EUPT-SC)[5] has been established and approved by DG-SANTÉ. The EUPT-SC consists of expert scientists with many years of experience in PTs and/or pesticide residue analysis. The actual composition of the EUPT-SC, the affiliation of each member is shown on the EURL-Website. The members of the EUPT-SC will also be listed in the Specific Protocol and the Final Report of each EUPT.

The EUPT-SC is made up of the following two subgroups:

a) An independent **Quality Control Group** (EUPT-QCG) and

b) An **Advisory Group** (EUPT-AG).

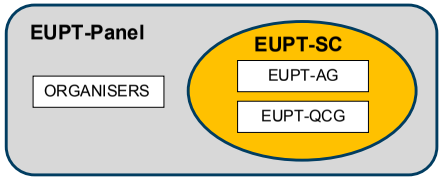
The EUPT-SC's role is to help the Organisers make decisions regarding the EUPT design: the selection of the commodity, the selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the statistical treatment and evaluation of participants results (in anonymous form), and the drafting and updating of documents such as the General and Specific PT Protocols and the Final EUPT-Reports.

The EUPT-QCG has the additional function of supervising the quality of EUPTs and of assisting the EURLs in confidential aspects such as the choice of the pesticides to be present in the Test Item and the concentrations at which they should be present.

[5] Link to the List of current members of the EUPT Scientific Committee: http://www.eurl-pesticides.eu/library/docs/allcrl/EUPT-SC.pdf

The EUPT-SC typically meets once a year, after the EUPTs of all four pesticide EURLs have been conducted, to discuss the evaluation of the EUPT-results and to consult with the EURLs in their decision making. Upcoming EUPTs are also planned during these meetings.

The EUPT-Organising Team and the EUPT-SC together form the **EUPT-Panel**.



The decisions of the EUPT-Panel will be documented.

This present EUPT General Protocol was jointly drafted by the EUPT-SC and the EURLs and was approved by DG-SANTÉ.

EUPT Participants

Within the European Union all NRLs operating in the same area as the organising EURL, as well as all OfLs whose scope overlaps with that of the EUPT, are legally obliged to participate in EUPTs. The legal obligation of NRLs and OfLs to participate in EUPTs arises from:

- Art. 28 of Reg. 396/2005/EC[6] (for all OfLs analysing for pesticide residues within the framework of official controls[7] of food or feed)
- Art. 33 of Reg. 882/2004/EC (for all NRLs)

The four EURLs will annually issue and distribute, via the EURL-website, a joint list of all OfLs that must participate in each of the EUPTs to be conducted within a given year. The list of obliged labs

[6] Regulation (EC) No 396/2005, published at OJ of the EU L70 of 16.03.2005, as last amended by Regulation 839/2008 published at OJ of the EU L234 of 30.08.2008.

[7] Official controls in the sense of Reg. 882/2004/EC This includes labs involved in controls within the framework of national and/or EU-controlled programmes as well as labs involved in import controls according to Regulation 669/2009/EC.

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will be updated every year to take account of any changes in the lab profiles. Interim updates will be issued to eliminate any possible errors.

NRLs are responsible for checking whether all relevant OfLs within their network are included in the list of obligated laboratories and whether the contact information and commodity-scopes are correct.

OfLs are furthermore urged to keep their own profiles within the EURL-DataPool up-to-date, especially their commodity and pesticide scopes and their contact information.

Labs that are obliged to participate in a given EUPT, and that are not able to participate, must provide the reasons for their non-participation without prejudice of any legal action taken against them for not participating. This also applies to any participating laboratories that then fail to report results.

Confidentiality and Communication

The proprietor of all EUPT data is DG-SANTÉ and as such has access to all information.

For each EUPT, the laboratories are given a unique code (lab code), initially only known to themselves and the Organisers. In the final EUPT-Report, the names of participating laboratories will not be linked to their laboratory codes. It should be noted, however, that the Organisers, at the request by DG-SANTÉ, may present the EUPT-results on a country-by-country basis. It may therefore be possible that a link between codes and laboratories could be made, especially for those countries where only one laboratory has participated. Furthermore, the EURLs reserve the right to share EUPT results and codes amongst themselves: for example, for the purpose of evaluating overall lab or country performance as requested by DG-SANTÉ.

As laid down in Regulation 882/2004, NRLs are responsible for evaluating and improving their own OfL-Network. On request from the NRLs, the EURLs will provide them with the PT-codes of the participating OfLs belonging to their OfL-Network. This will allow NRLs to follow the participation and performance of the laboratories within their network.

Communication between participating laboratories during the test on matters concerning a PT exercise is not permitted from the start of the PT exercise until the distribution of the preliminary report.

For each EUPT the organising EURL prepares a specific EUPT-Website where all relevant documents in their latest version are linked.

The official language used in all EUPTs is English.

www.eurl-pesticides.eu

Announcement / Invitation Letter

At least 3 months before the Test Item of a given EUPT is distributed to the laboratories the EURLs will publish an Announcement/Invitation letter on the EURL-web-portal and distribute it via e-mail to the NRL/OfL mailing list available to the EURLs. This letter will inform about the commodity to be used as Test Item, as well as links to the tentative EUPT-Target Pesticide List and the tentative EUPT-Calendar.

Target Pesticide List

This list contains all analytes (pesticides and metabolites) to be sought, along with the Minimum Required Reporting Levels (MRRLs) valid for the specific EUPT. The MRRLs are typically based upon the lowest MRLs found either in Regulation 396/2005/EC or Commission Directive 2006/125/EC (Baby Food Directive).

Labs must express their results as stated in the Target Pesticides List.

Specific Protocol

For each EUPT the organizing EURL will publish a Specific Protocol at least 2 weeks before the Test Item is distributed to the participating laboratories. The Specific Protocol will contain all the information previously included in the Invitation Letter but in its final version, information on payment and delivery, instructions on how to handle the Test Item upon receipt and on how to submit results, as well as any other relevant information.

Homogeneity of the Test Item

The Test Item will be tested for homogeneity typically before distribution to participants. The homogeneity tests involve the analysis of two replicate analytical portions, taken from at least ten randomly chosen units of treated Test Item. Both, sample preparation and measurements should be conducted in random order.

The homogeneity test data are statistically evaluated according to the International Harmonized Protocols published by ISO and IUPAC. The acceptance criterion for the Test Items to be sufficiently homogeneous for the Proficiency Test is that s_{sam}^2 is less than c with s_{sam} being the between-bottle sampling standard deviation and $c = F_1 \times \sigma_{all}^2 + F_2 \times s_{an}^2$. F_1 and F_2 are constants,

with values of 1.88 and 1.01, respectively, if 10 samples are used. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD[8] (25 %) × the analytical sampling mean for all pesticides, and s_{an} is the estimate of the analytical standard deviation.

The results of all homogeneity tests are presented to the EUPT-SC. In special cases where the above homogeneity test criteria are not met, the EUPT-SC considering all relevant aspects (e.g. the homogeneity results of other pesticides spiked at the same time, the overall distribution the participants' results, the analytical difficulties faced during the test, knowledge of the analytical behaviour of the pesticide question) may decide to overrule the test. The reasons of this overruling have to be transparently explained in the Final EUPT-Report.

Stability of the analytes contained in the Test Item

The Test Items will also be tested for stability - according to ISO 13528, Annex B. The time delay between the first and the last stability test must exceed the period of the EUPT-exercise. Typically the first analysis is carried out shortly before the shipment of the Test Items and the last one shortly after the deadline for submission of results. To better recognise trends and gain additional certainty one or more additional tests may be conducted by the Organisers. At least 6 sub-samples (analytical portions) should be analysed on each test day (e.g. 2 analytical portions withdrawn from three randomly chosen containers OR 6 portions withdrawn from a single container). In principle all pesticides contained in the Test Item should be checked for stability. However, in individual cases, where sufficient knowledge exists that the stability of a certain analyte is very unlikely to be significantly affected during storage (e.g. based on experience from past stability tests or knowledge of its physicochemical properties), the Organisers, after consultation with the EUPT-QCG, may decide to omit a specific stability test. The EUPT-SC will finally decide whether analytes for which the stability test was not undertaken will be included in the final report, considering all relevant aspects such as the distribution of the participant's results (CVs*).

A pesticide is considered to be adequately stable if $| x_1 - y_1 | \leq 0.3 \times \sigma$, where x_1 is the mean value of the first stability test, y_1 the mean value of the last stability test and σ the standard deviation used for proficiency assessment (typically 25% of the assigned value).

The results of all stability tests are presented to the EUPT-SC. In special cases where the above stability test criteria are not met, the EUPT-SC considering all relevant aspects (e.g. the past experience with the stability of the compound, the overall distribution the participants' results, the

[8] FFP-RSD = fit for purpose relative standard deviation, see also p. 11.

analytical difficulties faced during the test, knowledge about the analytical behaviour of the pesticide question) may decide to overrule the test. The reasons of this overruling will be transparently explained in the Final EUPT-Report.

The Organisers may also decide to conduct additional stability tests at different storage conditions than those recommended to the participants e.g. at ambient temperature.

Considering knowledge about the expected susceptibility of pesticides in the Test Item to possible losses, the Organisers will chose the shipment conditions to be such that pesticide losses are minimised (e.g. shipment of frozen samples, addition of dry ice). As shipment time can differ between labs/countries it is recommended that the Organisers conduct additional stability tests at conditions simulating shipment. Should critical losses be detected for certain pesticides the EUPT-SC will be informed (or the EUPT-QCG before or during the test). Case-by-case decisions may be taken considering all relevant aspects including the shipment time of the samples to each laboratory.

Methodologies to be used by the participants

Participating laboratories are instructed to use the analytical procedure(s) that they would routinely employ in official control activities (monitoring etc.). Where an analytical method has not yet been established routinely this should be stated.

General procedures for reporting results

Participating laboratories are responsible for reporting their own quantitative results to the Organiser within the stipulated deadline. Any pesticide that was targeted by a participating laboratory should be reported as "analysed". Each laboratory will be able to report only one result for each analyte detected in the Test Item. The concentrations of the pesticides detected should be expressed in 'mg/ kg' unless indicated otherwise in the specific protocol.

The Test Item is intentionally treated with pesticides whereas the Blank Material is analysed to ensure that it does not contain any of the pesticides in the Target Pesticides List, at or above, the specified MRRLs. Both the Test Item and Blank Material have to be analysed by the participating laboratories and any pesticide detected in them must be reported.

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Correction of results for recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed[9], it is common practice that pesticide analysis results are not corrected for recovery, but may be corrected if the average recovery is significantly different from 100 % (typically if outside the 70 – 120 % range, but also exhibiting good precision). Other approaches for recovery correction explicitly allowed in the SANCO document are the use of stable isotope labelled analogues of the target analytes used as Internal Standards (ISTDs), the 'procedural calibration' approach as well as the approach of 'standard addition' with additions of analyte(s) being made to analytical portions. Where reported residue data have been automatically adjusted for recovery by the method, or have subsequently been adjusted using a recovery factor, this must be indicated on the specific field of the 'Result Submission Form'. Results may be corrected for recovery only in cases where this correction is applied in routine practice (including cases of MRL-violations). Laboratories are required to report whether their results were adjusted for recovery and, if a recovery factor was used, the recovery (in percentage) must also be reported. No recovery data are required where correction for recovery is automatic by using the 'standard addition approach, or isotopically-labelled internal standards (in both cases with spiking of the Test Item at the beginning of the extraction procedures). In these cases, the laboratories should report the actual approach that was followed.

Methodology information

All laboratories are requested to provide information on the analytical method(s) they have used. A compilation of the methodology information submitted by all participants is presented in an Annex of the final report or in a separate report. Where necessary the methods are evaluated and discussed, especially in those cases where the result distribution is not unimodal or very broad (e.g. CVs* > 35 %). If no sufficient information on the methodology used is provided, the Organiser reserves the right not to accept the analytical results reported by the participants concerned.

[9] Document N° SANCO/12571/2013; Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed

www.eurl-pesticides.eu

Results evaluation

The procedures used for the treatment and assessment of results are described below.

– ***False Positive results***

These are results of pesticides from the Target Pesticides List, that are reported, at or above, their respective MRRL although they were: (i) not detected by the Organiser, even after repeated analyses, and/or (ii) not detected by the overwhelming majority (e.g. > 95 %) of the participating laboratories that had targeted the specific pesticides. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary.

Any results reported lower than the MRRL will not be considered as false positives, even though these results should not have been reported.

– ***False Negative results***

These are results for pesticides reported by the laboratories as 'analysed' but without reporting numerical values although they were: a) used by the Organiser to treat the Test Item and b) detected by the Organiser as well as the majority of the participants that had targeted these specific pesticides at or above the respective MRRLs. Results reported as '< RL' (RL= Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary.

In cases of the assigned value being less than a factor of 4 times the MRRL, false negatives will typically not be assigned. The EUPT-Panel may decide to take case-by-case decisions in this respect after considering all relevant factors such as the result distribution and the reporting limits of the affected labs.

– ***Estimation of the assigned value (x*)***

In order to minimise the influence of out-lying results on the statistical evaluation, the assigned value (= consensus concentration) will typically be estimated using robust statistics as described in ISO 13528:2009-01[10]. In special justifiable cases, the EUPT-Panel may decide to eliminate certain

[10] DIN ISO 13528:2009-01, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization. Therein a specific robust method for determination of the consensus mean and standard deviation without the need for removal of deviating results is described (Algorithm A in Annex C).

results traceably associated with gross errors (see "Omission or Exclusion of results" below) or to use only the results of a subgroup consisting of laboratories that have repeatedly demonstrated good performance for the specific compound in the past.

– ***Omission or Exclusion of results***

Before estimating the assigned value results associated with obvious mistakes have to be examined to decide whether they should be removed from the population. Such gross errors may include incorrect recording (e.g. due to transcription errors by the participant, decimal point faults or transposed digits, incorrect unit), calculation errors (e.g. missing factors), analysis of a wrong sample/extract (e.g. a spiked blank), use of wrong concentrations of standard solutions, incorrect data processing (e.g. integration of wrong peak), major deviations from the analytical procedure, inappropriate storage or transport conditions (in case of susceptible compounds), and the use of inappropriate procedures that demonstrably lead to significantly biased results (e.g. due to degradation or incomplete extraction). Where the Organisers (e.g. after the publication of the preliminary report) receive information of such gross errors, having a significant impact on a generated result, the affected results will be examined on a case-by-case basis to decide whether, or not, they should be excluded from the population used for robust statistics. Even results that cannot be specifically identified as outliers might be excluded. All decisions to omit/exclude results will be discussed with the EUPT-SC and the reasoning for the omission of each result clearly stated in the final EUPT-Report. However, z-scores will be calculated for all results irrespective of the fact that they were omitted from the calculation of the assigned value.

Omitted results might be interesting as they might give indications about possible source(s) of errors. The Organisers will thus ask the relevant lab(s) to provide feedback on possible sources of errors (see also "follow-up activities").

Any exclusion of results from the population is to be discussed within the EUPT-SC and the reasoning behind is to be revealed in the EUPT-final report.

Uncertainty of the assigned value

The uncertainty of the assigned values x_i is calculated according to ISO 13528:2009-01 as:

$$x_i = 1.25 \cdot \frac{s^*}{\sqrt{n}}$$

where s* is the robust standard deviation and n is the number of results.

In certain cases and considering all relevant factors (e.g. the result distribution, multimodality), the number of submitted results, information regarding analyte homogeneity/stability, information regarding the use of methodologies that might produce a bias that were used by the participants), the EUPT-Panel may consider the assigned value of a specific analyte to be too uncertain and decide that the results should not be evaluated, or only evaluated for informative purposes. The provisions of ISO 13528:2009-01 concerning the uncertainty of the assigned value will be taken into account.

– ***Standard deviation of the assigned value (target standard deviation)***

The target standard deviation (FFP-s) of the assigned value will be calculated using a Fit-For-Purpose Relative Standard Deviation (FFP-RSD) approach, as follows:

$$\textbf{FFP-s}_i = \textbf{b} \cdot \textbf{x*}_i \qquad \text{with } \textbf{b = 0.25 (25 \% FFP-RSD)}$$

The percentage FFP-RSD is set at 25% based on experience from results of previous EUPTs[11]. The EUPT-Panel reserves the right to also employ other approaches on a case-by-case basis considering analytical difficulties and experience gained from previous proficiency tests.

For informative purposes the robust relative standard deviation (CVs*) is calculated according to ISO 13528:2009-01; Chapter 5.6 (Consensus value from participants) following Algorithm A in Annex C.

– ***z-scores***

This parameter is calculated using the following formula:

$$z_i = (x_i - x^*_i) \,/\, \text{FFP-s}_i$$

where $\mathbf{x}_i$ is the value reported by the laboratory, $\mathbf{x^*}_i$ the assigned value, and $\mathbf{FFP\text{-}s}_i$ the standard deviation for each pesticide (i). Z-scores will be rounded to one decimal place. For the calculation of combined z-scores (see below) the original z-scores will be used and rounded to one decimal place after calculation.

[11] Comparative Study of the Main Top-down Approaches for the Estimation of Measurement Uncertainty in Multiresidue Analysis of Pesticides in Fruits and Vegetables. J. Agric. Food Chem., 2011, 59(14), 7609-7619.

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Any z-scores > 5 will be typically reported as '> 5' and a value of '5' will be used to calculate combined z-scores (see below).

Z-scores will be interpreted in the following way, as is set in the ISO 17043:2010[12]:

$\lvert z\rvert \leq 2.0$	Acceptable
$2.0 < \lvert z\rvert < 3.0$	Questionable
$\lvert z\rvert \geq 3.0$	Unacceptable

For results considered as false negatives, z-scores will be calculated using the MRRL or RL (the laboratory's Reporting Limit) if the RL < MRRL. The EUPT-Panel will decide whether, or not, these values should appear in the z-score histograms.

– ***Category A and B classification***

The EUPT-Panel will decide if and how to classify the laboratories into two categories - A or B. Currently, laboratories that have detected and quantified a sufficiently high percentage of the pesticides present in the Test Item (e.g. at least 90 %) and reported no false positives will have demonstrated 'sufficient scope' and can therefore be classified into Category A. The 90 % criterion will be applied following Table 1.

Table 1. No. of pesticides needed to be detected to have sufficient scope.

No. of Pesticides Present in the Test Item (N)	90 %	No. of Pesticides needed to be reported to have sufficient scope (n)	n
3	2.7	3	N
4	3.6	4	
5	4.5	4	N - 1
6	5.4	5	
7	6.3	6	
8	7.2	7	
9	8.1	8	
10	9.0	9	
11	9.9	10	
12	10.8	11	
13	11.7	12	
14	12.6	13	

[12] ISO/IEC 17043:2010. Conformity assessment -- General requirements for proficiency testing

No. of Pesticides Present in the Test Item (N)	90 %	No. of Pesticides needed to be reported to have sufficient scope (n)	n
15	13.5	13	N - 2
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	
20	18	18	
21	18.9	19	
22	19.8	20	
23	20.7	21	
24	21.6	22	
25	22.5	22	N - 3
26	23.4	23	

– ***Overall performance of laboratories - combined z-scores***

For evaluation of the overall performance of laboratories within Category A, the Average of the Squared z-Score (AZ^2)[13,14] (see below) will be used. The AZ^2 is calculated as follows:

$$AZ^2 = \frac{\sum_{i=1}^{n} Z_i^2}{n}$$

Where n is the number of z-scores to be considered in the calculation. In the calculation of the AZ^2, z-scores higher than 5 will be classified as 5. Based on the AZ^2 achieved, the laboratories are classified as follows:

$AZ^2 \leq 2.0$	Good
$2.0 < AZ^2 < 3.0$	Satisfactory
$AZ^2 \geq 3.0$	Unsatisfactory

Combined z-scores are considered to be of lesser importance than the individual z-scores. The EUPT-Panel retains the right not to calculate AZ^2 if it is considered as not being useful or if the number of results reported by any participant is considered to be too low.

[13] Formerly named "Sum of squared z-scores (SZ^2)"

[14] Laboratory assessment by combined z-score values in proficiency tests: experience gained through the EUPT for pesticide residues in fruits and vegetables. Anal. Bioanal. Chem., 2010, 397, 3061–3070.

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In the case of EUPT-SRMs, where only a few results per lab may be available, the Average of the Absolute z-scores (AAZ) may be calculated for informative purposes, but only for labs that have reported enough results to obtain 5 or more z-scores. For the calculation of the AAZ, z-scores higher than 5 will also be classified as 5.

Laboratories within Category B will be ranked according to the total number of pesticides that they correctly reported to be present in the Test Item. The number of acceptable z-scores achieved will be presented, too. The EURL-Panel retains the right to calculate combined z-scores (see above) also for labs within Category B, e.g. for informative purposes, provided that a minimum number of results (z-scores) are have been reported.

Publication of results

The EURLs will publish a preliminary report, containing tentative medians and z-score values for all pesticides present in the Test Item, within 2 months of the deadline for result submission.

The Final EUPT Report will be published after the EUPT-Panel has discussed the results. Taking into account that the EUPT-Panel meets normally only once a year (typically in late summer or autumn) to discuss the results of all EUPTs organised annually by the EURLs in the following year, the final report may be published up to 10 months after the deadline for results submission.

Certificates of participation

Together with the Final EUPT-Report, the EURL Organiser will deliver a Certificate of Participation to each participating laboratory showing the z-scores achieved for each individual pesticide, the combined z-scores calculated (if any), and the classification into Category A or B.

Feedback

At any time before, during or after the PT participants have the possibility to contact the Organisers and make suggestions or indicate errors. After the distribution of the Final EUPT-Report, participating laboratories will be given the opportunity to give their feedback to the Organisers and make suggestions for future improvements.

Correction of errors

Should errors be discovered in any of the documents issued prior to the EUPT (Calendar, Target Pesticides List, Specific Protocol, General Protocol) the corrected documents will be uploaded onto the website and in the case of substantial errors the participants will be informed. **Before starting the exercise participants should make sure to download the latest version of these documents.**

If substantial errors are discovered in the Preliminary EUPT-Report the Organisers will distribute a new corrected version, where it will be stated that the previous version is no longer valid.

Where substantial errors are discovered in the Final EUPT-Report the EUPT-Panel will decide whether a corrigendum will be issued and how this should look. The online version of the final report will be replaced by the new one and all affected labs will be contacted.

Where errors are discovered in EUPT-Certificates the relevant laboratories will be sent new corrected ones. Where necessary the laboratories will be asked to return the old ones.

Follow-up activities

Laboratories are expected to undertake follow-up activities to trace back the sources of erroneous or strongly deviating results (typically those with with $|z| > 2.0$) - including all false positives and false negatives. Even results within $|z| \leq 2.0$ may have to be checked if there is indications of a significant positive or negative bias.

Upon request, the laboratory's corresponding NRL and EURL are to be informed of the outcome of any investigative activities for false positives, false negatives and for results with $|z| \geq 3.0$. Concerning z-scores between 2.0 and 3.0 the communication of the outcome of traceability activities is optional but highly encouraged where the source of deviation could be identified and could be of interest to other labs.

According to instructions from DG-SANTÉ, the "Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with EU Reference Laboratories (EURLs) activities" is to be followed.

Disclaimer

The EUPT-Panel retains the right to change any parts of this EUPT – General Protocol based on new scientific or technical information. Any changes will be communicated in due course.

SPECIFIC PROTOCOL

for the 10th EU Proficiency Test
on Pesticides requiring Single Residue Methods
EUPT – SRM10 (2015)
(last update 15 May, 2015)

Introduction

This protocol is complementary to the "**General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed**[1]" covering all EUPTs.
The EUPT-SRM10 is organised by the EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL–SRM) in cooperation with the EU Reference Laboratory for pesticide residues in Cereals and Feeding stuff (EURL-CF). Both EURLs are **accredited according to ISO 17043** as a provider of proficiency tests.
The EUPT-SRM10 deals with the analysis of SRM-pesticides in maize flour and is to be performed by all National Reference Laboratories for Single Residue Methods (NRL-SRMs) as well as by all official EU laboratories (OfLs) involved in official pesticide residue controls as far as their scope overlaps with that of the EUPT-SRM10. This includes laboratories involved in import control within the frame of Reg. 669/2009/EC. A special **EUPT-SRM10-Website** containing links to the most important documents of relevance was constructed.

Considering only the commodity scope (not the pesticide scope) of OfLs a **Tentative List of obliged labs for EUPTs in 2015** has been prepared by the EURLs and published on the CIRCA-Platform. As far as the EUPT-SRM10 is concerned all laboratories analysing for cereals or feeding stuffs were considered as obliged. The comprehensiveness and correctness of this list was checked by the OfLs and reviewed by the NRL-SRMs and any change requests were considered in a new version. OfLs listed as "obliged to participate in the EUPT-SRM10" but having decided not to participate have to state their reasons of non-participation in a special online form within the EUPT-SRM10 registration website, which was accessible from 23 March till 17 April, 2015.

Test Item and Blank Material

This EUPT deals with the analysis of pesticide residues in **Maize Flour**.

Participants will receive two bottles containing:

1) ca. 350 g **Test Item (with incurred or spiked analytes)**, containing pesticides from the **Target Pesticides List.**
2) ca. 350 g **Blank Material**, that can be used for recovery experiments as well as for the preparation of matrix-matched calibration standards

[1] Please refer to the latest version (Edition 5)

Using randomly chosen bottles, the Organizers will check the Test Item for sufficient homogeneity and for the stability of the pesticides contained in the Test Item over the period of the exercise. The Blank Material will be also checked to prove that none of the pesticides on the Target pesticides List is contained at relevant levels.

Target Analytes and MRRLs

The Test Item will contain several pesticides from the **EUPT-SRM10 Target Pesticides List.** Laboratories should read this list carefully, as it shows how the residues are expected to be reported as well as the **Minimum Required Reporting Levels (MRRLs)**. The MRRL values will be used to help identify false positive and false negative results and for the calculation of z-scores for false negatives.
It should not be assumed that only pesticides registered for use in maize are present in the Test Item.

Shipment of Test Item

Test item and Blank Material are planned to be shipped on 18 May, 2015.
Frozen Test Item and Blank Material will be packed in thermo-boxes together with freeze gel packs and shipped to the participants. Prior to shipment a reminder will be sent to the participating laboratories by e-mail.

Laboratories must make their own arrangements for the receipt of the package. They should **inform the Organiser of any public holidays in their country/city during the week of the shipment, and must make the necessary arrangements to receive the shipment, even if the laboratory is closed.**
Should any complications during shipment, delivery or the customs be expected, the participating laboratories should provide the Organizers with contact information of possible contact persons of the lab (e.g. mobile phone numbers) as well as instructions in local language explaining the need to keep the package in freezer during delay in transit. This information will be attached to the package.

Instructions on handling the Test Item

Once received, the Test Item should be stored deep frozen (at -18°C or lower) until analysis in order to avoid any possible deterioration/spoilage and to minimize pesticide degradation.

Before analytical portions are taken for analysis the Test Item should be mixed thoroughly in its entirety. During mixing, try to keep temperatures low to avoid losses of susceptible pesticides.

Participating laboratories should use their routine standard operating procedures for extraction, clean-up and analytical measurement as well as their own reference standards for identification and quantification purposes. Laboratories may also employ methods not yet implemented routinely for example if they are in the test-phase of implementing them. In this case the limited experience and the non-inclusion of the analyte in the routine scope should be indicated in the **result submission website**.

The homogeneity tests will be conducted using 5 g analytical portions of Test Item for all analytes except for dithiocarbamates where expectedly 25 g will be used. Please note: Sub-sampling variability increases with decreasing analytical portion size, and sufficient homogeneity can only be guaranteed for sample portions ≤ 10 g.

Results submission website

Sample receipt acknowledgement, analytical results and method information are to be submitted via the following website: **EUPT-SRM10 result submission website.**

- **Sub-Page 0 (Sample receipt acknowledgement), accessible from 19 May, 2015**
- **Sub-Pages 1-3 (analytical results and method information) accessible from 26 May till 19 June, 2015.**

To access the data-submission forms participants must use their unique login data (username and password) that will be provided to them before sample shipment. The unique EUPT-SRM10 lab-codes will be provided in a separate e-mail.

The deadline for result submission is 19 June 2015 at 16 h (CEST).

- Sample Receipt and Acceptance (Sub-Page 0)

Once the laboratory has received the Test Items it must report to the organiser, via the **EUPT-SRM10 Result Submission Website** (sub-page 0) the date of receipt, the condition of the Test Item, and its acceptance. The deadline for acceptance is the 22 May 2015. If a laboratory does not respond by this deadline, the Organisers will assume that Test Item and Blank Material have been received and accepted.
If any participants have not received the Test Items by the 21 May in the afternoon, they must inform the Organiser by e-mail (EURL-SRM@cvuas.bwl.de). The Organiser will localize the package and decide on further action including new shipment, if necessary.
Selected participants might be asked to provide information on the condition of the Test Item upon receipt (e.g. core temperature of Test Item etc.).

- Reporting qualitative and quantitative Results (Sub-Page 1 and 2)

To report their results, laboratories must access the **EUPT-SRM10 Result Submission Website.**
All results must be reported on the above website by 19 June 2015 at 16 h (CEST). The website will not be accessible after this deadline, and all results submitted afterwards will not be accepted.

Before entering the results, please study the **Target Pesticide List** carefully, in particular the residue definitions, which are not given on the **Result Submission Website.**

The following fields will be available for reporting the quantitative results:

- "**Concentration in mg/kg":** the pesticide concentrations that would be reported in routine work. Recovery-corrected results should be reported only where this reflects the routine lab's procedure; otherwise the non-recovery-corrected result should be reported. Results should not be reported where a pesticide was not detected, or was detected below the RL (Reporting Limit) of the laboratory or the MRRL. Results reported as "< RL" or "< #,# mg/kg" will be considered as „Not Detected".

  The residue levels of the pesticides must be reported in mg/kg using the following **significant figures**:
  - Levels <0.010 mg/kg to be expressed to 2 significant figures, e.g. 0.0058 mg/kg;
  - Levels ≥ 0.010 mg/kg to be expressed to 3 significant figures, e.g. 0.156, 1.64, 10.3 mg/kg.

- **"Conc. in blank in mg/kg":** concentration values of any pesticides from the Target Pesticides List determined in the Blank Material (even at levels below the MRRL).

- **"Experience with this compound":** Use the dropdown-menu to indicate for how many years you have been analysing for each compound using the method applied in this EUPT.

- **Did you use an Internal standard (IS):** Please only choose one of the three **"Yes" options if the IS was used for calculation of the result** of the target analyte (not merely for quality control purposes).
  Please choose …
  - **"Yes, *Isotope labelled analogue of* target analyte *(ILIS)*"** if you have employed a real ILIS as defined in the SANCO document (e.g. Ethephon D4 for Ethephon)
  - "**Yes, *Other compound with similar behaviour to target analyte***" if you have employed a compound that you expect to behave similar to your analyte during extraction and possibly contribute towards the correction of the result for recovery (e.g. MCPA for 2,4-D or MCPA D3 for 2,4-D)
  - "**Yes, *Other comp. w. good extr., chr/phy and measurem. properties***" if you have used a generic IS the main function of which is to correct for volume deviations during the entire procedure (e.g. TPP; Chlorpyrifos D10, Nicarbazin).

- **At what stage of the procedure did you employ the IS:**
  Please choose…
  - "**at the beginning**" if the IS was added to the sample portion directly or shortly following extraction solvent addition
  - "**to an aliquot of the final extract**" if the IS was added to an isolated aliquot of the final extract
  - "**at an intermediate stage**" if the IS was added at any stage in-between the above two

- **Other means of recovery or matrix-effect correction used**
  Please choose one of the following:
  - None
  - Procedural calibration
  - Standard addition to sample portions
  - Standard addition to extract aliquots
  - Matrix-matched calibration
  - Use of a recovery factor (please indicate recovery figure)
  - Other

- **"Recovery figure (in %)":** Here labs can report any recovery figures (in %) obtained for the analyte in question. If a recovery factor was used to correct the result for recovery, the recovery figure (in %) used for the calculation MUST be reported.

- **Recovery Details:** Please indicate here concisely how the recovery experiment(s) was/were conducted, e.g. spiking level, spiked compound.

  Additional information will be asked in separate fields.

- Reporting Information on Analytical Methodology (Sub-Page 3)

In **sub-page 3 of** the "**EUPT-SRM10 Result Submission Website**" the participating laboratories must provide complete information on the analytical method(s) applied to **all pesticides which were analysed, irrespective if they were detected or not**.

The participating laboratories are urged to thoroughly fill-in all requested information in order to minimize the administrative burden of collecting it a posteriori.

If no sufficient information on the methodology used is provided, the Organisers reserve the right not to accept the analytical results reported by the participant.

Subcontracting

The following tasks were subcontracted to the EURL-CF, Soeborg, Denmark:

a) dried maize grain with and without incurred analytes relevant to the EUPR-SRM10

b) administration of EUPT-SRM10 Registration and Result Submission Website

Follow-up actions

After the distribution of the Preliminary Report on EUPT-SRM10 laboratories with poor performance (high absolute z-scores, false negatives or false positives) will be asked to provide information concerning the reasons for poor performance and possible corrective actions. This information will be forwarded to the corresponding NRL-SRMs upon request.
All EUPT-SRM10-participants are welcome to ask the EURL-SRM for technical assistance.
According to instructions by DG-SANCO, the "**Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with Community reference laboratories (CRLs) activities**" will be followed for NRLs.

Documents

All documents related to the EUPT–SRM10 can be found in the **EURL-Document Repository (CIRCA/FIS-VL).** Links to the documents can also be found in the **EUPT-SRM10 Website.**
For further information please contact the organizers **EURL-SRM@cvuas.bwl.de**
Please check the **EUPT-SRM10 Website** before starting with the analysis to **make sure that you have the latest version of all documents available**. In case of major changes the participants will be informed via e-mail.

Participation fees and payment details

To cover the costs of production, handling and shipment of the PT-Materials the following fees will be charged for one unit of the PT-Material to the participating laboratories:

- OfLs (including NRLs) from EU countries, EU-candidate countries and EFTA countries: 175 €
- Labs based in third countries: 350 €

An invoice issued for the "invoice address" stated in the registration form will be sent to the e-mail address(es) responsible for the PT. Participants must forwarded the invoice to their financial department for the remittance, especially if the invoice address differs from the address of the participating laboratory. Details of payment will be given in the invoices.

Payment is expected to be made within 30 days upon the date of shipment.
If for any reason payment cannot be carried out before this date, please contact the Organizer to give explanations.
If no payment or no proof of payment is received and no explanation is given to the Organizers, the Organizers reserve the right not to accept the results from those labs or not to include them in the Final EUPT-Report.

Bank details for remittance will be given in the invoices.

To facilitate tracking of money transfer the special **payee identification text (= invoice number) as shown in the invoice MUST be indicated in the remittance.**

Please note:
The bank account of EURL-SRM has been changed since the end of October 2013! Please ask your financial department to update the bank account of EURL-SRM!

NEW Bank Details:

Bank account holder:	**Landesoberkasse Baden Wuerttemberg**
Bank Name :	**Baden Wuerttembergische Bank**
IBAN:	**DE 02 6005 0101 7495 5301 02**
BIC/SWIFT:	**SOLADESTXXX**
Payee identification text:	***See invoice (important and MUST be indicated!)***
VAT of CVUA Stuttgart	**DE 811 600 510**

Calendar of EUPT-SRM10

(see under **http://www.eurl-pesticides.eu/library/docs/srm/EUPT_SRM10_Calendar.pdf**)

Target Pesticides List of EUPT-SRM10

(see under **http://www.eurl-pesticides.eu/library/docs/srm/EUPT_SRM10_TargetPesticideList.pdf**)

Contact information

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CALENDAR for the EUPT – SRM10

Maize flour

(update: 23 March, 2015)

Activity	Who ?	Dates
Opening of the **EUPT-SRM10 Website** with links to all relevant documents (**List of obliged labs**, **Calendar**, **Target Pesticides List**, **General Protocol**)	EURL-SRM	Jan. – Feb. 2015
Registration via "**EUPT-Registration Website**" (Note: obliged OfLs MUST enter this Website and either register or give **explanations for non-participation**)	**- Obliged OfLs from EU-MSs** **- OfLs from EFTA Countries** **- OfLs from EU-candidate C.** **- Labs from 3rd Countries**	**25 Mar. - 17 Apr. 2015**
Dispatch of **EUPT-SRM10-Specific Protocol**	EURL-SRM	Apr. 2015
Preparation of EUPT-SRM10-Test Item (preliminary tests Spiking / Homogenization)	EURL-SRM	Jan. – May 2015
Homogeneity Tests	EURL-SRM	May 2015
Stability Tests	EURL-SRM	May – June 2015
Shipment of EUPT-SRM10 Test Item (+reminder of upcoming parcel arrival)	EURL-SRM	**18 May 2015**
Confirmation of sample Receipt and acceptance via "**EUPT-SRM10 Result Submission Website**", (Sub-Page 0)	**Participating Labs**	**within 48 h of receipt**
Result Submission **(Pesticide scope, Results, Method Info)** in "**EUPT-SRM10 Result Submission Website**", (Sub-Pages 1 – 3)	**Participating Labs**	**26 May – 19 June**
Preliminary Report (only compilation of results)	EURL-SRM	July 2015
EUPT Evaluation Meeting	EUPT-SC, DG-SANCO	July 2015
Survey to collect reasons for underperformance and missing information on methods	EURL-SRM / **Participating Labs**	July 2015
Final Report	EURL-SRM	Dec. 2015

REMARK: Please note that the dates mentioned above may be subject to minor **changes**. In the case of changes the participants will be informed via e-mail. But still **please check periodically our website for possible updates** in case the email does not get through to you.
Contact: **eurl-srm@cvuas.bwl.de**

The EUPT-SRM Team

EU Reference Laboratory Requiring Single Residue Methods (EURL-SRM)
CVUA Stuttgart, Schaflandstr. 3/2, DE-70736 Fellbach, Germany
Website: www.eurl-pesticides.eu, E-Mail: EURL-SRM@cvuas.bwl.de

TARGET PESTICIDE LIST

for the EUPT – SRM10 2015

Maize Flour

last update on 03.03.2015

Compounds Potentially Present in Test Item	In MACP	MRRL (mg/kg)
Compulsory Compounds (will be considered in Category A/B classification)		
2,4-D (free acid*)	MACP-WD	0.01
Chlormequat (cation)	MACP-Reg.	0.01
Dithiocarbamates (including maneb, mancozeb, metiram, propineb, thiram and ziram) expressed as CS_2	MACP-Reg.	0.05
Ethephon	MACP-Reg.	0.02
Fenbutatin Oxide	MACP-Reg.	0.02
Glyphosate	MACP-Reg.	0.05
MCPA (free acid*)	MACP-WD	0.01
Mepiquat (cation)	MACP-Reg.	0.01
Propamocarb	MACP-Reg.	0.01
Optional Compounds (will NOT be considered in Category A/B classification)		
Bentazone (parent*)		0.01
Bromoxynil (free phenol*)		0.01
Dicamba (free acid*)		0.02
Dichlorprop (2,4-DP) including Dichlorprop-P (free acid*)		0.01
Fluroxypyr (free acid*)		0.01
Glufosinate (parent)	MACP-WD	0.02
- N-Acetyl Glufosinate	MACP-WD	0.02
- MPP (3-(hydroxymethylphosphinyl)propionic acid)	MACP-WD	0.02
Ioxynil (free phenol*)	MACP-WD	0.01
Mecoprop (MCPP) including Mecoprop-P (free acid*)		0.01
Paraquat (dication)	MACP-WD	0.05
Phosphonic acid (metabolite of Fosetyl)	MACP-WD	0.05
TFNA (metabolite of flonicamid)	MACP-WD	0.02
TFNG (metabolite of flonicamid)	MACP-WD	0.02

MACP = EU Multi-Annual Coordinated Control Program;
MACP-Reg.: MACP Regulation; MACP-WD: MACP Working Document
* no hydrolysis

Note: This document may be subject to minor changes. In case of significant changes the organizers will send e-mails. In any case please check our website periodically to make sure you are using the latest available version.

For any further clarification don't hesitate to contact us under **eurl-srm@cvuas.bwl.de**

The EUPT-SRM10 Organising Team

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