European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

EU Proficiency Test on the Analysis of Spiked Pesticides in Potato Homogenates

EUPT–SRM8

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Final Report

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EU PROFICIENCY TEST
EUPT-SRM8, 2013

Residues of Pesticides requiring Single Residue Methods

Test Item:
Potato Homogenates

Final Report

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April/May 2013

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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. These Proficiency Tests 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 programmes as well as national monitoring programmes. By participating in PTs laboratories can assess and at the same time demonstrate their analytical performance. The competitive nature of EUPTs and the attention to detail paid when laboratories conduct PT-analyses, together with the need to identify errors and take corrective actions in cases of underperformance, typically lead to improvements in the quality of data generated by participating laboratories.

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 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. Four of these 8 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 selected test items; three other EUPT-SRMs were conducted in collaboration with the EURL for Pesticide Residues in Cereals and Feeding Stuff (EURL-CF) with wheat flour (EURL-C1/SRM2, 2007), oat flour (EURL-C3/SRM4, 2009) and rice flour (EURL-C5/SRM6, 2011) as the test items. The EUPT-SRM7 (2012) based on milled dry lentils was organized by the EURL-SRM alone.

Participation in the EUPT-SRM8 was mandatory for all NRLs for pesticides requiring Single Residue Methods (NRL-SRMs) and for all OfLs analysing pesticide residues in fruit and vegetables, or feed within the framework of national and EU official control programmes. OfLs from EFTA countries (Iceland, Norway and Switzerland) also contributing data to the EU-coordinated community control programmes, as well as OfLs from EU-acceding or -candidate countries (Croatia, FYROM and Turkey) were also invited to take part in this EUPT. Following approval by DG-SANCO selected laboratories from Third Countries were allowed to take part in this exercise, too. However, only results submitted by labs from EU and EFTA countries were included in the calculation of the Assigned Values. Based on information about the commodity scope and NRL-status of the labs a tentative list of EU-labs considered as being obliged to participate in the EUPT-SRM8 was published at the beginning of 2013. The pesticide scope of those labs could not be considered since the data available in the EUPT-DataPool was not up-to-date. NRLs and OfLs listed as being obliged to participate in this exercise but having decided not to take part, were asked to state the reason(s) for their non-participation. The same applied to laboratories that originally had registered to participate in this PT but did not submit results.

DG-SANCO will have 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 for Animal Health and the Food Chain or during EURL-Workshops.

[1] Former Community Reference Laboratories (CRLs)

CONTENT

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EU-Proficiency Test on Residues of Pesticides Requiring Single Residue Methods
Test Item: Potato Homogenates
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INTRODUCTION

On 8 January, 2013 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 Organizers (EURL-SRM), were invited to participate in the 8th European Commission's Proficiency Test on Residues of Pesticides Requiring Single Residue Methods (EUPT-SRM8). The EUPT-SRM8-Website contained links to the Announcement, the Calendar, as well as to the Target Pesticides List of the EUPT-SRM8 (Appendix 9 and Appendix 10). The Target Pesticides List contained 23 compounds potentially being present in the Test Item and requiring single residue methods for their analysis. 13 were compulsory compounds and were thus considered in Category A/B classification (based on scope). The pesticides of the Target Pesticides List were selected based on a number of criteria and following consultation with the EUPT-Advisory Group. For each compound a residue definition valid for the PT was given and the minimum required reporting level (MRRL) was stipulated. A link to the "General Protocol" containing information common to all EUPTs was also provided. The laboratories were able to register on-line from 18 February to 12 March, 2013.

Based on their commodity scope and NRL-status a tentative list of laboratories considered as being obliged to participate in the EUPT-SRM8 was constructed and 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 laboratories within their countries. It was made clear that the list of obliged laboratories 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 117 laboratories from EU and EFTA countries agreed to participate in the test with 7 of them failing to submit any results. 7 laboratories from EU candidate countries and Third Countries have also registered for the present EUPT with 6 of them submitting results.

To prepare the Test Items, organically produced potatoes (variety Merlin) of Spanish origin were purchased. The potatoes were first checked for the absence of the pesticides in the Target Pesticides List and then spiked post-harvest with 15 compounds (captan, cyromazine, dicofol, fenbutatin oxide, folpet, glyphosate, haloxyfop, mepiquat, diquat, fentin, fosetyl aluminium, glufosinate, maleic hydrazide, BAC-C12 and DDAC-C10) using standard solutions. More details are given in the Section "Test Item".

1. TEST ITEM

1.1 Analytical methods

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

Table 1-1: Analytical methods used 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 pesticide in the Blank Material.

Compound	Extraction	ISTD	Cleanup	Determination	Detector	Notes
BAC-C12	**Modified QuEChERS-method [3]** involving: addition of internal standard, extraction with acetonitrile containing 0.4 % acetic acid, liquid-liquid partitioning following addition of salts (without citrate salts) and determinative analysis by GC-MS or LC-MS/MS	**Chlorpyrifos-D10/ BAC-C10-D7 (for transport-stability test only)**	**none**	**LC-MS/MS**	**ESI (pos)**	
Captan		**Captan-D6**	**none**	**GC-MS/MS**	**EI (pos)**	
DDAC-C10		**Chlorpyrifos-D10/ DDAC-C10-D6 (for transport-stability test only)**	**none**	**LC-MS/MS**	**ESI (pos)**	
Dicofol		**Dicofol-D8**	**none**	**GC-MS/MS**	**EI (pos)**	
Fenbutatin oxide		**Chlorpyrifos-D10**	**none**	**LC-MS/MS**	**ESI (pos)**	
Fentin		**Triphenyl-D15 tin**	**none**	**LC-MS/MS**	**ESI (pos)**	
Folpet		**Folpet-D4**	**none**	**GC-MS/MS**	**EI (pos)**	
Haloxyfop		**Chlorpyrifos-D10**	**none**	**LC-MS/MS**	**ESI (pos)**	
*2,4-D**		*Nicarbacin*	*none*	*LC-MS/MS*	*ESI (neg)*	
*BAC-C10**		*Chlorpyrifos-D10*	*none*	*LC-MS/MS*	*ESI (pos)*	
*BAC-C14**		*Chlorpyrifos-D10*	*none*	*LC-MS/MS*	*ESI (pos)*	
*BAC-C16**		*Chlorpyrifos-D10*	*none*	*LC-MS/MS*	*ESI (pos)*	
*Chlorothalonil**		*PCB 138*	*none*	*GC-MS*	*CI (neg)*	
*Fluazifop**		*Nicarbacin*	*none*	*LC-MS/MS*	*ESI (neg)*	
Cyromazine	**QuPPe method [5]** involving: addition of ISTDs, addition of methanol containing 1 % formic acid, centrifugation, filtration and direct determination by LC-MS/MS in the ESI (neg). mode using ion-pac AS1-HC column (QuPPe-M1.3)	**Cyromazine-D4**	**filtration**	**LC-MS/MS**	**ESI (pos)**	**QuPPE M4**
Diquat		**Diquat-D4**	**filtration**	**LC-MS/MS**	**ESI (pos)**	**QuPPE M4**
Fosetyl		**Fosetyl-D5**	**filtration**	**LC-MS/MS**	**ESI (neg)**	**QuPPE M1.3**
Glyphosate		**Glyphosate-$^{13}C_2{}^{15}N$**	**filtration**	**LC-MS/MS**	**ESI (neg)**	**QuPPE M1.3**
Glufosinate		**Glufosinate-D3**	**filtration**	**LC-MS/MS**	**ESI (neg)**	**QuPPE M1.3**
Maleic hydrazide		**Maleic hydrazide-D2**	**filtration**	**LC-MS/MS**	**ESI (neg)**	**QuPPE M1.3**
Mepiquat		**Mepiquat-D3**	**filtration**	**LC-MS/MS**	**ESI (pos)**	**QuPPE M4**
*Chlormequat**		*Chlormequat-D4*	*filtration*	*LC-MS/MS*	*ESI (pos)*	*QuPPE M4*
*Ethephon**		*Ethephon-D4*	*filtration*	*LC-MS/MS*	*ESI (neg)*	*QuPPE M1.3*

*: To check for absence in Blank Material

1.2 Selection of pesticides for the Target Pesticides List

The pesticides 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 six points into account: 1) the present and upcoming scope of the EU-coordinated control programme; 2) a pesticide priority list ranking the pesticides according to their risk potential; 3) the relevance of pesticides to the specific commodity group (potatoes); 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; and 6) OfL needs as expressed via surveys or e-mail communications.

In some cases it was decided that the residue definitions valid for the EUPT should differ from those in the legislation (e.g., for 2,4-D and fluazifop only free acid). The minimum required reporting levels (MRRLs) were set at 0.01 mg/kg for ***captan***, ***cyromazine***, ***dicofol***, ***fenbutatin oxide***, ***folpet***, ***haloxyfop***, ***mepiquat*** and ***fentin***, 0.05 mg/kg for ***glyphosate***, and at 0.1 mg/kg for ***BAC-C12*** and ***DDAC-C10***.

1.3 Preparation and bottling of the Blank Material by EURL-FV

The potatoes (variety Merlin) used for preparation of the Blank Material were purchased from an organic farmer in Spain and checked by the EURL-SRM for the absence of the pesticides included in the Target Pesticides List. Following cut in small pieces, freezing of the pieces with liquid nitrogen and thorough homogenization ca. 350 g of Blank Material was weighed out into leak-proof screw-capped polyethylene plastic bottles, sealed, and stored in a freezer at about –20 °C until the distribution to participants or transport to EURL-SRM.

1.4 Preparation and bottling of the Potato Test Item by EURL-FV

Before preparing this Test Item, the pesticides and their suitable, approximate target residue levels for the study were selected by the Organizer in coordination with the EUPT-QC-Group. The Test Item was spiked with 15 different pesticides in total (see **Table 1-2**).

For the spiking 80 kg of potato were spread on the floor and sprayed with an acidic solution prepared with 50 g citric acid and 5 g ascorbic acid dissolved in 100 ml acetone plus 60 ml water. This spraying was done to protect potatoes from getting dark and preventing base-sensitive pesticides from degradation. When the potatoes were dry, they were spiked with 500 ml of a solution (acetone : water = 1 : 2) containing ***BAC-C12*** chloride salt (83.6 mg), ***DDAC-C10*** chloride salt (50.8 mg), ***fentin***-hydroxide (42.4 mg), ***haloxyfop***

Table 1-2: Compounds employed for the preparation of the Test Item.

Compulsory Pesticide	Spiking in laboratory	Treatment Form	Optional Pesticide	Spiking in laboratory	Treatment Form
Captan	x	Standard solution	Diquat-dibromide hydrate	x	Standard solution
Cyromazine	x	Standard solution	Fentin-hydroxide	x	Standard solution
Dicofol	x	Standard solution	Fosetyl aluminium	x	Standard solution
Fenbutatin oxide	x	Standard solution	Glufosinate (ammonium salt)	x	Standard solution
Folpet	x	Standard solution	Maleic hydrazide	x	Standard solution
Glyphosate	x	Standard solution	BAC-C12 chloride salt	x	Standard solution
Haloxyfop	x	Standard solution	DDAC-C10 chloride salt	x	Standard solution
Mepiquat chloride	x	Standard solution			

(87.6 mg), ***fenbutatin oxide*** (26.6 mg), ***maleic hydrazide*** (140.9 mg), ***glyphosate*** (73.9 mg), ammonium ***glufosinate*** (65.2 mg), ***diquat***-dibromide monohydrate (81.2 mg), ***mepiquat*** chloride (25.7 mg), and ***cyromazine*** (20.1 mg). After drying, they were treated with additional 125 ml of a solution (methanol with 2 % formic acid) containing ***captan*** (160.8 mg), ***folpet*** (159.8 mg), ***dicofol*** (94 mg), and ***fosetyl*** aluminium (235.1 mg). Both solutions were applied to the potatoes using a Pasteur pipette.

After all the pesticides had been spiked, the potatoes were cut in pieces, frozen with liquid nitrogen and processed using additional liquid nitrogen in a mincer with approx. 50 ml of a solution containing 50 g citric acid and 5 g ascorbic acid dissolved in 160 ml double deionized water. The frozen minced potatoes were mixed in a constantly-spinning container until a homogeneous material was obtained.

Approximately 350 g portions of the well-mixed homogenate were weighed out into leak-proof screw-capped polyethylene plastic bottles, sealed and stored in a freezer at about –20 °C until distribution to participants or transport to EURL-SRM.

1.5 Packaging and delivery of Test Items and Blank Materials to Participants

Following preparation and bottling 25 randomly chosen bottles of each Test Item and Blank Material were put aside in a freezer. On the day of shipment a bottle of the Test Item and Blank Material were packed into thick-walled polystyrene boxes together with cooling elements, to maintain them in frozen state during transport, and shipped directly from Almería to laboratories located in Spain. All other bottled materials were firstly deep frozen using dry ice and then shipped together with dry ice to the EURL-SRM wherefrom they were distributed to the rest of the participating laboratories. Upon arrival at EURL-SRM they were immediately placed in a walk-in freezer at –18 °C. On the day of shipment two frozen bottles, one with Test Item and one with Blank Material, were packed into thick-walled thermo-insulated polystyrene boxes and filled-up with dry ice pellets (approx. 2 kg in each box).

Among the shipments to destinations within Europe all but 6 packages arrived at the participating labs within 24 hours. Due to remote location of some laboratories or the closure of the laboratory reception area the remaining 6 packages arrived to the participants within 48 hours. In two cases the participants were informed about delayed delivery. In two cases the reason for the delay was unknown. The delivery to countries outside the EU and EFTA zones was accomplished within 72 hours in 1 case, and within 8 or 17 days in two other cases with complications at the customs. It should be noted that the results of these laboratories were not considered in the calculation of the Assigned Values. A compilation of the shipment duration is shown in **Appendix 2**.

25 participating laboratories from Europe and from Third Countries were asked to give detailed information on the condition of the EUPT materials upon receipt, and 19 of them gave feedback. 12 of those laboratories received their packages within 24 hours. All these labs reported that there was still dry ice within the package and that the core temperature for the material was in all cases well below –18 °C. In two cases where packages arrived within 48 hours the participating labs reported that there was no dry ice left but the material was still frozen with a temperature of about –2 °C. Where the shipment took more than 2 days, the sample condition depended on various factors, e.g., whether the package was put in a freezer during the delivery or at the customs station. A compilation of the answers from laboratories regarding the condition of the received materials is given in **Appendix 2**.

Overall, the EUPT-materials arrived at the laboratories in good condition with three exceptions of Third Country laboratories, where the samples could not be sent using dry ice and/or was held up at the customs for several days.

1.6 Homogeneity test

As soon as the shipment with the EUPT-SRM8 materials arrived at the EURL-SRM premises 10 bottles containing Test Items were randomly chosen for the homogeneity test. The analyses were performed on duplicate analytical portions taken from each bottle. Before withdrawing the analytical portions, the contents of each bottle was quickly remixed with a high speed mixer. Both the order of sample preparation and the order of extract injection into the analytical instruments were random. For quantification matrix-matched calibration standards, prepared using blank extracts were used. Analytical sub-sample portions of 10 g were used for all compounds.

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 analyses of the homogeneity test is shown in **Table 1-3**. The individual residue data from the homogeneity tests, as well as the results of the statistical analyses, are 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, when duplicate samples are taken from 10 bottles. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD (25 %) $\times$ the analytical sampling mean for all pesticides, and s_{an} is the estimate of the analytical standard deviation.

As all pesticides passed the homogeneity test, the Test Item was considered to be sufficiently homogenous and suitable for the EUPT-SRM8.

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

COMPULSORY COMPOUNDS								
	Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate	Haloxyfop	Mepiquat
Analytical portion size [g]	10	10	10	10	10	10	10	10
Mean [mg/kg]	1.079	0.085	1.129	0.072	1.560	0.311	0.495	0.091
s_{sam}^2	4.79×10^{-3}	3.20×10^{-5}	9.86×10^{-3}	6.74×10^{-5}	1.48×10^{-2}	2.08×10^{-4}	1.78×10^{-3}	3.49×10^{-6}
c	6.55×10^{-3}	8.92×10^{-5}	1.53×10^{-2}	6.74×10^{-5}	2.76×10^{-2}	1.31×10^{-3}	2.82×10^{-3}	9.12×10^{-5}
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed
OPTIONAL COMPOUNDS								
	Diquat	Fentin	Fosetyl	Glufosinate	Maleic hydrazide	BAC-C12	DDAC-C10	
Analytical portion size [g]	10	10	10	10	10	10	10	
Mean [mg/kg]	0.079	0.176	0.941	0.233	0.667	0.554	0.421	
s_{sam}^2	1.96×10^{-5}	3.08×10^{-4}	7.32×10^{-4}	2.97×10^{-4}	1.49×10^{-3}	2.08×10^{-4}	1.34×10^{-3}	
c	8.01×10^{-5}	3.59×10^{-4}	9.54×10^{-3}	6.26×10^{-4}	5.54×10^{-3}	1.31×10^{-3}	2.42×10^{-3}	
Passed/Failed	passed	passed	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 in a frozen condition. We thus assumed that the influence of the transport on the stability of pesticides contained in the Test Items received by these laboratories must have been minor and approximately equal. For this reason the Test Items used for the stability test were stored at –18 °C (the storage temperature recommended to the participants in the Specific Protocol). Possible losses during transport were studied separately (see below). Two analytical portions from each Test Item bottle were analysed on three occasions as follows:

Stability test 1 (shortly before shipment):
12 April 2013

Stability test 2 (two weeks after shipment):
30 April 2013

Stability test 3 (shortly after deadline for results submission):
21 May 2013

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

COMPULSORY COMPOUNDS								
	Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate	Haloxyfop	Mepiquat
Storage at -18 °C (mean values in mg/kg)								
Analysis 1 12.04.2013	1.039	0.078	1.025	0.065	1.42	0.271	0.465	0.081
Analysis 2 30.04.2013	0.961	0.079	0.973	0.06	—	0.271	0.43	0.085
Analysis 3 21.05.2013	0.966	0.078	0.952	0.062	1.326	0.256	0.455	0.085
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	-0.073 (-7.04 %)	0.000 (-0.43 %)	-0.073 (-7.12 %)	-0.003 (-4.54 %)	-0.094 (-6.64 %)	-0.015 (-5.42 %)	-0.010 (-2.08 %)	0.004 (5.42 %)
Critical value [mg/kg]	0.078	0.006	0.077	0.005	0.106	0.02	0.035	0.006
Passed/Failed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
OPTIONAL COMPOUNDS								
	Diquat	Fentin	Fosetyl	Glufosinate	Maleic hydrazide	BAC-C12	DDAC-C10	
Storage at -18 °C (mean values in mg/kg)								
Analysis 1 12.04.2013	0.082	0.162	0.901	0.214	0.605	0.582	0.417	
Analysis 2 30.04.2013	0.076	0.150	0.843	0.221	0.577	0.538	0.398	
Analysis 3 21.05.2013	0.079	0.154	0.772	0.229	0.592	0.577	0.421	
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.004 (-4.44 %)	0.007 (-4.64 %)	0.139 (-15.23 %)	0.015 (7.17 %)	0.013 (-2.07 %)	0.005 (-0.86 %)	0.004 (1.04 %)	
Critical value [mg/kg]	0.006	0.012	0.068	0.016	0.045	0.044	0.031	
Passed/Failed	Passed	Passed	**Failed**	Passed	Passed	Passed	Passed	

A pesticide is considered to be adequately stable if $|x_1 - y_i| \leq 0.3 \times \sigma$, where x_1 is the mean value of the first stability test, y_i 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 analyses conducted within the framework of the stability test are shown in **Table 1-4** and **Appendix 4**. With the exception of ***fosetyl***, that did not fulfil the stability-test criteria, all other pesticides present in the Test Item did not show any significant degradation during the test period and under the recommended storage conditions (–18 °C).

Considering that a) significant ***fosetyl*** losses were observed in the transport stability test (see **Chapter 1.8**, **Figure 1-1**) and in the storage stability test (even when stored at –18 °C), and b) the wide distribution of results submitted by the participants and the high uncertainty of its Assigned Value driven therefrom (see **Section 4.2**), the Scientific Committee decided to evaluate ***fosetyl*** for information only.

1.8 Transport stability test

To complement the storage stability test the stability at conditions simulating shipment was also studied. Three randomly chosen bottles containing Test Item were mixed thoroughly with dry ice re-portioned again into three bottles and put in a freezer at –18 °C for 48 h. One of the Test Items was analysed immediately (day-0 of transport stability test), whereas the other 2 bottles were packed into 2 boxes exactly as the units delivered to the participants, i.e., one bottle of test item plus one bottle of Blank Material plus dry ice in each box. Assuming that the average temperatures during shipment would not exceed room temperature, the boxes were left standing in the laboratory at room temperature to simulate the shipment conditions. One of the boxes was opened for analysis after 48 hours (day-2), and the other one after 72 hours (day-3). All analyses were conducted in 6 replicates.

The results of the transport stability test are shown in **Table 1-5**. All compounds remained sufficiently stable up to 2 days, a period covering 94 % of the participation labs in the EU and EFTA countries. Again, ***fosetyl*** was the least stable compound with a high degradation rate in the thawed material. On day-1 phosphonic acid, a main degradation product of ***fosetyl***, was additionally analysed. A concentration of 0.58 mg/kg was determined which is higher than the concentration of its parent ***fosetyl***.

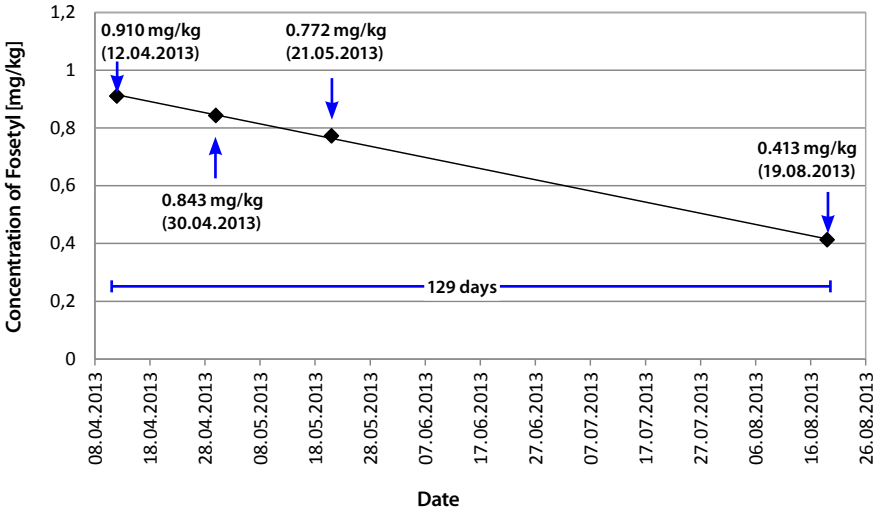

Figure 1-1: Decline of fosetyl content in the Test Item during storage in a freezer.

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

COMPULSORY COMPOUNDS								
	Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate	Haloxyfop	Mepiquat
Day-0	1.634	0.097	1.139	0.077	1.634	0.301	0.513	0.098
Day-2 (< –1 °C)	1.665	0.092	1.163	0.081	1.665	0.296	0.512	0.096
Day-3 (~ 12 °C)	1.527	0.089	1.167	0.079	1.527	0.296	0.530	0.099
Deviation [%] Day-2 vs. Day-0	6.70 %	-4.72 %	2.11 %	5.37 %	1.90 %	-1.66 %	-0.28 %	-2.06 %
Deviation [%] Day-3 vs. Day-1	-3.23 %	-7.98 %	2.47 %	3.37 %	-6.59 %	-1.66 %	3.22 %	0.53 %
OPTIONAL COMPOUNDS								
	Diquat	Fentin	Fosetyl	Glufosinate	Maleic hydrazide	BAC-C12	DDAC-C10	
Day-0	0.084	0.174	0.446[1]	0.250	0.645	0.520	0.381	
Day-2 (< –1 °C)	0.81	0.183	0.446	0.262	0.585	0.524	0.390	
Day-3 (~ 12°C)	0.83	0.178	0.389	0.269	0.611	0.499	0.391	
Deviation [%] Day-2 vs. Day-0	-2.87 %	5.17 %	-0.00 %	4.86 %	-9.35 %	0.82 %	2.43 %	
Deviation [%] Day-3 vs. Day-1	-0.60 %	2.06 %	-12.78 %	7.40 %	-5.32 %	-3.91 %	2.76 %	

1) 0.58 mg/kg phosphonic acid, the metabolite of fosetyl, was determined.

1.9 Organisational aspects

1.9.1 Preparation and distribution of a tentative list of obliged labs

A tentative list of laboratories (NRLs and OfLs) obliged to participate in the current EUPT was constructed based on information on NRL-status and commodity scope as recorded in the EURL-DataPool. The pesticide scope of the laboratories was not considered when drafting this list due to concerns that the available data is not up-to-date and/or not applicable to the present commodity (potatoes). 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-SANCO instructions, obliged labs that were not intending to participate in the EUPT-SRM8 were instructed to provide explanations for their non-participation.

1.9.2 Announcement / Invitation and EUPT-SRM8-Website

An Announcement/Invitation Letter for the EUPT-SRM8 was published on the EUPT-SRM8-Website in February 2013 and sent to all NRL-SRMs as well as any other OfLs analysing pesticide residues in fruit and vegetables or feeding stuff within the framework of official controls. The invitation letter was also sent to all OfLs for which no information regarding scope was available. OfLs from EFTA countries and EU-candidate states were also invited if their contact data was available.

An EUPT-SRM8-Website was constructed within the EURL-Web-Portal with links to all documents relevant to this EUPT (i.e. 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.

1.9.3 Registration and confidentiality

An EUPT-SRM8 registration website was constructed in collaboration with the EURL-CF. All laboratories 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 participating labs were provided via e-mail with a unique laboratory code as well as unique, automatically generated login data to be used 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 (ca. 350 g) and one bottle of Blank Material (ca. 350 g) were shipped on 16 April 2013 to each participant in thermo-insulated polystyrene boxes covered with approx. 2 kg dry ice. A short instruction sheet on handling the sample was also included in the package.

Laboratories were asked to check the integrity and condition of the materials upon receipt and to report to the Organizers via the website any observations or complaints and whether they are accepted. A number of labs geographically widespread throughout Europe and in Third Countries were asked to give detailed information on the whereabouts of the package between receipt and opening, on whether there was still dry ice in the box upon opening and on the core temperature of the Blank Material.

Detailed Instructions on how to treat the Test Items and Blank Material upon receipt were provided to the participating laboratories in the Specific Protocol (**Appendix 10**).

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 (17 May 2013). Participants were asked not only to report their analytical results but also to state whether the compounds on the Target Pesticides List are part of their routine scope and to indicate the experience with the analysis of these compounds. In addition, labo-

ratories had to provide details about the methods they had used and to state their own reporting limits (RLs) for each pesticide they have analysed.

Where information on analytical methods, that is important for the evaluation, was missing or 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)

In principle, any result indicating the presence of a pesticide listed in the Target Pesticides List, which was (a) not used in the preparation of the Test Item; (b) not detected by the Organizer, even following repetitive analysis; and (c) not detected by the overwhelming majority (e.g. > 95 %) of the participants that tested for this compound, is treated as a false positive, if it is reported at a concentration at, or above, the Minimum Required Reporting Level (MRRL). Results lower than the MRRL are ignored by the Organizer and are not considered as false positives. No z-scores are calculated for false positive results.

2.1.2 False negatives (FNs)

These are results of pesticides reported as "analysed" but where no numerical values are reported, 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 majority of the participating laboratories. Z-scores for false negatives are calculated using the MRRL as the result. Any reporting-limits (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

To establish the Assigned Values (consensus values), the median levels of all reported results from EU and EFTA countries, excluding outliers, are used.

2.3 Fixed target standard deviation (FFP-approach)

Based on experience from previous EU Proficiency Tests on fruit and vegetables and cereals, a fixed fit-for-purpose relative standard deviation (FFP-RSD) of 25 % is applied. The target standard deviation (σ) for each individual pesticide is calculated by multiplying the Assigned Value by the FFP-RSD. In addition, the robust relative standard deviation (Qn-RSD) is calculated for informative purposes.

2.4 z-Scores

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

$$z_i = (x_i - \mu_i) / \delta_i$$

Where

- x_i is the result for the pesticide (i) as reported by the participant
  (For results considered 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.)
- μ_i is the Assigned Value for the pesticide (i)
- δ_i is the target standard deviation for the pesticide (i), which equals 25 % of the Assigned Value (FFP-approach)
  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
$2 < \|z\| \leq 3$	questionable
$\|z\| > 3$	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 Lab ranking and classification

2.5.1 Category A and B classification

Based on the scope of pesticides covered by the labs, 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 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 as measure of the overall performance the Average of the Absolute z-Score (AAZ) is 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.

The AAZ-scores were classified as follows:

$AAZ \leq 2$	good
$2 < AAZ \leq 3$	satisfactory
$AAZ > 3$	unsatisfactory

3. PARTICIPATION

124 laboratories from 35 countries (26 EU Member States, 2 EFTA countries, 1 EU Candidate country and 6 Third Countries) registered for participation in the EUPT-SRM8. Out of those laboratories 116 (108 from EU-Member States, 2 from EFTA countries, 1 from EU Candidate countries and 5 from Third Countries) submitted at least one result. An overview of the participating labs and countries is given in **Table 3-1**.

A list of all individual laboratories that registered for this EUPT is presented in **Appendix 1**. Out of the EU Member States only Romania was not represented among the participating labs. Regarding NRL-SRMs Romania and Portugal were not represented whereas Malta was represented by its proxy-NRL based in the United Kingdom.

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

In total, 189 EU-OfLs (including NRL-SRMs) were considered as being obliged to participate in the present EUPT and thus included on a tentative list of obliged labs distributed 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 fruit and vegetables or feed.

All labs that were listed as obliged to participate had to either participate or to provide an explanation for their non-participation. Out of 74 obliged laboratories that did not register for this PT, 33 (from 10 EU countries) provided explanations for their non-participation. The most frequent reasons stated by the laboratories to explain their non-participation in the EUPT-SRM8 was that all target pesticides or the matrix or their combination were out of their routine scope. **Table 3-2** gives an overview of the participating and non-participating EU-labs that were obliged to participate in the EUPT-SRM8.

Upon request, all 7 EU-laboratories (1× BE, 1× DE, 1× FR, 1× PL and 3× ES) that had originally registered for the EUPT-SRM8, but then failed to submit results, provided explanations for their non-submission of results.

Table 3-1: Number of laboratories listed as being obliged to participate in the EUPT-SRM8, 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 [3]		Notes
		Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	
Austria	**2**	2	1	2	1			
Belgium	**9**	9	1	8	1	**1**		One lab based in NL was subcontracted by BE and NL but is only listed here
Bulgaria	**9**	1	1	1	1			
Cyprus	**1**	2	1	2	1			
Czech Republic	**3**	3	1	3	1			
Denmark	**2**	2	1	2	1			
Estonia	**2**	2	1	2	1			
Finland	**3**	2	2	2	2			
France	**10***	8+2 [4]	1	8+1 [4]	1			One of the two non-obliged labs did not submit results
Germany	**21**	20+1 [4]	1	19+1 [4]	1	**4**		CVUA Stuttgart hosting the EURL-SRM (organizing this PT) was not considered being an obliged lab.
Greece	**10**	2	2	2	2	**6**		GR has appointed two NRL-SRMs.
Hungary	**4**	4	1	4	1			
Ireland	**1**	1	1	1	1			
Italy	**31**	13	1	13	1	**5**		
Latvia	**2**	1	1	1	1	**1**		
Lithuania	**2**	1	1	2	1			
Luxembourg	**1**	1	1	1	1			
Malta	**5**	2	1	2	1			MT-NRL-SRM represented by the UK-NRL-SRM which acts as proxy NRL. Official controls are (subcontracted to a lab in Germany
Netherlands	**1**	1	1	1	1			
Poland	**11**	6	1	5	1	**5**		
Portugal	**4**	1	–	1	–	**3**	**1**	
Romania	**5**	–	–	–	–	**1**	**1**	
Slovakia	**1**	1	1	1	1			One of the two participating labs wasn't obliged to participate.
Slovenia	**4**	2	1	2	1	**1**		
Spain	**39**	20	2	17	2	**6**		Spain has appointed two NRL-SRMs.
Sweden	**2**	2	1	2	1			
UK	**4**	4	1	4	1			
EU Total	**189**	115 [5]	27 [5]	108 [5]	27 [5]			

1) Country on behalf of which a laboratory is analysing official samples for pesticide residues .
2) The obliged labs were tentatively defined based on their function (NRL-SRMs) and the commodity-scope covered (vegetables, cereals or feed). Obliged labs that did not participate were requested to provide an explanation.
3) Explanation for non-participation or for non-submission of results
4) additional labs participating on voluntary basis
5) The NRL-SRM of UK was counted twice as it also represents MT.

Table 3-1 (cont.): Number of laboratories listed as being obliged to participate in the EUPT-SRM8, 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 [3]		Notes
		Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	
Norway		1	1	1	1			
Switzerland		1	–	1	–			
EU+EFTA Total		117	28	110	28			
Brazil		1	–	1	–			
Egypt		1	–	1	–			
Peru		1	–	–	–			
Serbia		1	–	1	–			
Singapore		1	–	1	–			
Thailand		1	–	1	–			
USA		1	–	1	–			
EU Candidate countries and Third Countries		7		6				
Overall Sum	**189**	124		116				

Table 3-2: Overview of EU-labs with a obligation to participate in the EUPT-SRM8

	Number	Percent
Obliged EU-labs	**189** [1]	**100 %**
Thereof		
- Registered for Participation	**115** [2]	**61** [2] **%**
- Submitting results	**108** [2]	**57** [2] **%**
- Not submitting results / providing explanation for non-submission	7 / 7	4 % / 4 %
- Not Registered for Participation	**74**	**39 %**
- Providing explanations for non-participation	33	17 %
- No feedback	41	22 %

1) Number of OfLs (including NRLs) of EU-Member States that were on the tentative list of labs obliged to participate in the EUPT-SRM8 (see Section 1.7.1)
2) Including laboratories participating on voluntary basis

4. RESULTS

4.1 Overview of results

An overview of the results reported for the pesticides present in the Test Item is shown in **Table 4-1**.

Table 4-2 gives an overview of scope of compounds covered by each laboratory. For the individual results reported by the laboratories see **Table 4-7** and **Table 4-8**. The detailed information about the analytical methods used by the laboratories is shown in **Appendix 7**.

4.2 Assigned values, target standard deviations and outliers

To establish the Assigned Values for each pesticide the medians of all results submitted by labs from EU and EFTA countries were used. Results from Third Country laboratories were not taken into account. Prior to the calculation of the median values outliers were excluded. Results with z-scores > 5 were a priori eliminated as outliers. The results of the remaining population were then subjected to the Grubbs' test (alpha = 0.01) to identify and eliminate further outliers. The Assigned Values and their uncertainties are shown in **Table 4-3**.

For ***diquat***, the number of submitted results (10 numerical and 4 false negative results) was insufficient for statistical evaluation. For ***fosetyl*** the number of results was sufficient, but their distribution was very broad (Qn-RSD = 45 %) with the Assigned Value not fulfilling the stipulated criteria of statistical certainty. The instability of ***fosetyl*** (it did not pass the stability test) was almost certainly the most important factor contributing to this broad distribution of results. Therefore, the Assigned Values for ***diquat*** and ***fosetyl*** were evaluated for information only. In the case of ***fentin*** the uncertainty of its Assigned Value was marginally higher than the statistical tolerance, however, the Qn-RSD of 37 % was lower than the acceptable limit of 37.5 % [4]. Furthermore, no laboratory would have been changed to another z-score classification, if the lower or upper limit of the Assigned Value was applied. Therefore, ***fentin*** was considered in the evaluation.

Table 4-1: Percentage of EU[1)] and EFTA labs that have analysed for the compounds present in the Test Item.

Pesticides present in Test Item		Labs analysed for the compound		
		No.	% (based on *n* = 110 [2)])	% (based on *n* = 189 [3)])
Compulsory Compounds	**Captan**	94	85 %	50 %
	Cyromazine	77	70 %	41 %
	Dicofol *(p,p´-isomer)*	92	84 %	49 %
	Fenbutatin oxide	59	54 %	31 %
	Folpet	94	85 %	50 %
	Glyphosate	49	45 %	26 %
	Haloxyfop *(free acid)*	81	74 %	43 %
	Mepiquat *(cation)*	72	65 %	38 %
Optional Compounds	**Diquat** *(dication)*	14	13 %	7 %
	Fentin *(expr. as triphenyltin cation)*	28	25 %	15 %
	Fosetyl aluminium *(expr. as fosetyl)*	25	23 %	13 %
	Glufosinate *(parent only)*	25	23 %	13 %
	Maleic hydrazide	24	22 %	13 %
	BAC-C12 *(expr. as chloride salt)*	51	46 %	27 %
	DDAC-C10 *(expr. as chloride salt)*	53	48 %	28 %

1) Including official laboratories participating on voluntary basis
2) based on 110 laboratories from EU and EFTA countries having submitted at least one result
3) 189 EU-laboratories were concidered as obliged to participate in the EUPT-SRM8

Table 4-2: Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

Compulsory Compounds																
Compulsory Compound listed in Target List			2.4-D (free acid)	Captan	Chlormequat (cation)	Chlorothalonil	Cyromazine	Dicofol (p, p´ isomer)	Ethephon	Fenbutatin oxide	Fluazifop (free acid)	Folpet	Glyphosate	Haloxyfop (free acid)	Mepiquat (cation)	analysed / correctly found among compulsory compounds within the EUPT-Target Pesticides List (max. 13 / 8)
within MACP			√	√	√	√	√	√	√	√	√	√	√	√	√	
present in Test Item				√			√	√		√		√	√	√	√	
Evaluated within this PT				√			√	√		√		√	√	√	√	
Lab-Code SRM8-	NRL-SRM	Cat.*														
1	x	A	ND	V	ND	ND	V‡	V	ND		ND	V	V	V	V	12 / 7
2	x	B	ND	FN	ND	ND	V	V	ND	V	ND	V		V	FN	12 / 5
3		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
4		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
5		A	ND	V	ND	ND	V	V		V	ND	V		V	V	11 / 7
6	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
7		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
8		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
9		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
10	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
11	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
12	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
13		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
14		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
15																
16		B	ND		ND		V	V	ND		ND		V	V	V	9 / 5
17																
18		B		V		ND						V				3 / 2
19		A	ND	V	ND	ND	V	V	ND	V	ND	V		V	V	12 / 7
21	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
22		B		V	ND	ND	V	V				V			V	7 / 5
23		B	ND		ND		V		ND	V	ND		V	V	V	9 / 5
24		A	ND	V	ND	ND	V	V		V	ND	V		V	V	11 / 7
25		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
26		A	ND	V	ND	ND	V	V		V	ND	V		V	V	11 / 7
27		B	ND	V		ND		V				V		V		6 / 4
28		B		V		ND		V				V				4 / 3
30		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
31	x	A	ND	V	ND	ND	V	V		V	ND	V	V	V	V	12 / 8
32		A	ND	V	ND	ND	V	V	ND	V#	ND	V	V	V	V	13 / 8
33	x	B	ND	V		ND	V	V		V	ND	V		V		9 / 6

MACP = EU Mutiannual Community Control Program (2012-14)
V = analysed for and submitted concentration Value > MRRL; **ND** = analysed for and correctly Not Detected;
Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result
V# : Outlier according to the General Protocol (z-score > 5); **V‡**: Outlier according to Grubbs' test, alpha = 0.01;
* : Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)
** : detected, but was not able to submit result due to technical problem. Judged as ND in accordance with the General Protocol

Table 4-2 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

			Optional Compounds											Total
Optional Compound listed in Target List			Diquat (dication)	Fentin (expr. as triphenyltin cation)	Fosetyl aluminium (expr. as fosetyl)	Glufosinate (parent only)	Maleic hydrazide	BAC-C10 (expr. as chloride salt)	BAC-C12 (expr. as chloride salt)	BAC-C14 (expr. as chloride salt)	BAC-C16 (expr. as chloride salt)	DDAC-C10 (expr. as chloride salt)	analysed / correctly found among optional compounds within the EUPT-Target Pesticides List (max. 10 / 7)	analysed / correctly found amoung all compounds within the EUPT-Target Pes-ticides List (max. 23 / 15)
within MACP								ad hoc	ad hoc	ad hoc	ad hoc	ad hoc		
present in Test Item			√	√	√	√	√		√			√		
Evaluated within this PT			√§	√§		√§	√§		√§			√§		
Lab-Code SRM8-	NRL-SRM	Cat.*												
1	x	A											0 / 0	12 / 7
2	x	B		V				ND	V	ND	ND	V	6 / 3	18 / 8
3		A		V	V			ND	V	ND	ND	V	7 / 4	20 / 12
4		A											0 / 0	13 / 8
5		A										V	1 / 1	12 / 8
6	x	A	FN	V	V	V	V	ND	V	ND	ND	V	10 / 6	23 / 14
7		A	FN		V	V	V	ND	V	ND	ND	V	9 / 5	22 / 13
8		A		V	V		V	ND	V	ND	ND	V	8 / 5	21 / 13
9		A	FN	V	V	V	V	ND	V	ND	ND	V	10 / 6	23 / 14
10	x	A			V		V						2 / 2	15 / 10
11	x	A				V							1 / 1	14 / 9
12	x	A											0 / 0	13 / 8
13		A	V	V#	V	V	V		V		ND	V	8 / 7	21 / 15
14		A		V	V	V	V	ND	V	ND	ND	V	9 / 6	22 / 14
15														
16		B											0 / 0	9 / 5
17														
18		B											0 / 0	3 / 2
19		A						ND	V	ND	ND	V	5 / 2	17 / 9
21	x	A		V				ND	V	ND	ND	V	6 / 3	19 / 11
22		B											0 / 0	7 / 5
23		B	V	V	V	FN		ND	V	ND	ND	V	9 / 5	18 / 10
24		A						ND	V	ND	ND	V	5 / 2	16 / 9
25		A		V	V	V	V	ND	V	ND	ND	V	9 / 6	22 / 14
26		A						ND	V	ND	ND	FN	5 / 1	16 / 8
27		B						ND	V	ND	ND	V	5 / 2	11 / 6
28		B						ND			ND	V	3 / 1	7 / 4
30		A		V	V	V	V	ND	V	ND	ND	V	9 / 6	22 / 14
31	x	A				V		ND	V	ND	ND	V	6 / 3	18 / 11
32		A	V	V	V	V	V	ND	V	ND	ND	V	10 / 7	23 / 15
33	x	B						ND	V	ND	ND	V	5 / 2	14 / 8

MACP = EU Mutiannual Community Control Program (2012-14)
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Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result
V# : Outlier according to the General Protocol (z-score > 5); **V‡**: Outlier according to Grubbs' test, alpha = 0.01;
√§ : evaluated only in terms of performance (z-score), not in terms of scope
***** : Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)

Table 4-2 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

Compulsory Compounds																
Compulsory Compound listed in Target List			2.4-D (free acid)	Captan	Chlormequat (cation)	Chlorothalonil	Cyromazine	Dicofol (p, p´ isomer)	Ethephon	Fenbutatin oxide	Fluazifop (free acid)	Folpet	Glyphosate	Haloxyfop (free acid)	Mepiquat (cation)	analysed / correctly found among compulsory compounds within the EUPT-Target Pesticides List (max. 13 / 8)
within MACP			√	√	√	√	√	√	√	√	√	√	√	√	√	
present in Test Item				√			√	√		√		√	√	√	√	
Evaluated within this PT				√			√	√		√		√	√	√	√	
Lab-Code SRM8-	NRL-SRM	Cat.*														
34		B				ND	V									2 / 1
35						ND										1 / 0
36		B	ND	V	ND	ND	V	V			ND	V		V	V	10 / 6
37		B				ND		V				V				3 / 2
38		A	ND	V	ND	ND	V	V		V	ND	V		V	V	11 / 7
39																
40	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
41		A	ND	V	ND	ND	V	V	ND		ND	V	V	V	V	12 / 7
42		B	ND					V			ND			V		4 / 2
43		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
44		B		V		ND		V				V				4 / 3
46		A	ND	V	ND	ND	V	V	ND	V	ND	V		V	V	12 / 7
47		B	ND	V	ND	ND	V			V#	ND	V		V	V	10 / 6
48		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
49	x	A	ND	V	ND	ND	V	V	ND	V	ND	V		V	V	12 / 7
51		B	ND	V	FP	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
53	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
55	x	B	ND	V	ND	ND				V	ND	V		V	V	9 / 5
56		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
57	x	B		V	ND	ND	V	V				V			V	7 / 5
59		A	ND	V	ND	ND	V	V	ND	V	ND	V		V	V	12 / 7
60																0 / 0
63		B	ND			FP		FN								3 / 0
64		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
65		B		V		ND		V		V		V				5 / 4
66																
67		B	ND	FN**	ND	ND	V	V	ND	V		V			V	10 / 5
68		B		V	ND	ND	V				ND	V		V		7 / 4
69		A	ND	V	ND	ND	V	V	ND		ND	V	V	V	V	12 / 7
70	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
71		B	ND	V		ND		V			ND	V		V		7 / 4

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Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result
V# : Outlier according to the General Protocol (z-score > 5); **V‡**: Outlier according to Grubbs' test, alpha = 0.01;
***** : Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)
****** : detected, but was not able to submit result due to technical problem. Judged as ND in accordance with the General Protocol

Table 4-2 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

			Optional Compounds											Total
Optional Compound listed in Target List			Diquat (dication)	Fentin (expr. as triphenyltin cation)	Fosetyl aluminium (expr. as fosetyl)	Glufosinate (parent only)	Maleic hydrazide	BAC-C10 (expr. as chloride salt)	BAC-C12 (expr. as chloride salt)	BAC-C14 (expr. as chloride salt)	BAC-C16 (expr. as chloride salt)	DDAC-C10 (expr. as chloride salt)	analysed / correctly found among optional compounds within the EUPT-Target Pesticides List (max. 10 / 7)	analysed / correctly found amoung all compounds within the EUPT-Target Pes-ticides List (max. 23 / 15)
within MACP								ad hoc	ad hoc	ad hoc	ad hoc	ad hoc		
present in Test Item			√	√	√	√	√		√			√		
Evaluated within this PT			√§	√§		√§	√§		√§			√§		
Lab-Code SRM8-	NRL-SRM	Cat.*												
34		B						ND	V	ND	ND	V	5 / 2	7 / 3
35													0 / 0	1 / 0
36		B											0 / 0	10 / 6
37		B											0 / 0	3 / 2
38		A											0 / 0	11 / 7
39														
40	x	A	FN			V	V	ND	V	ND	ND	V	8 / 4	21 / 12
41		A						ND	V	ND	ND	V	5 / 2	17 / 9
42		B						ND	V	ND	ND	V	5 / 2	9 / 4
43		A	V	V			V		V	ND	ND	V	7 / 5	20 / 13
44		B											0 / 0	4 / 3
46		A											0 / 0	12 / 7
47		B		V				ND	V	ND	ND	V	6 / 3	16 / 9
48		A			FN								1 / 0	14 / 8
49	x	A					V						1 / 1	13 / 8
51		B		V	FN		V	ND	V	ND	ND	V	8 / 4	21 / 12
53	x	A											0 / 0	13 / 8
55	x	B						ND	V	ND	ND	V	5 / 2	14 / 7
56		A											0 / 0	13 / 8
57	x	B											0 / 0	7 / 5
59		A	V					ND	V	ND	ND	V	6 / 3	18 / 10
60								ND	V	ND	ND	V	5 / 2	5 / 2
63		B											0 / 0	3 / 0
64		A											0 / 0	13 / 8
65		B											0 / 0	5 / 4
66														
67		B					V	ND	V	ND	ND	V	6 / 3	16 / 8
68		B		V	V			ND	V	ND	ND	V	7 / 4	14 / 8
69		A				V							1 / 1	13 / 8
70	x	A											0 / 0	13 / 8
71		B											0 / 0	7 / 4

MACP = EU Mutiannual Community Control Program (2012-14)
V = analysed for and submitted concentration Value > MRRL; **ND** = analysed for and correctly Not Detected;
Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result
V#: Outlier according to the General Protocol (z-score > 5); **V+**: Outlier according to Grubbs' test, alpha = 0.01;
√§: evaluated only in terms of performance (z-score), not in terms of scope
*: Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)

Table 4-2 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

Compulsory Compounds																
Compulsory Compound listed in Target List			2.4-D (free acid)	Captan	Chlormequat (cation)	Chlorothalonil	Cyromazine	Dicofol (p, p´ isomer)	Ethephon	Fenbutatin oxide	Fluazifop (free acid)	Folpet	Glyphosate	Haloxyfop (free acid)	Mepiquat (cation)	analysed / correctly found among compulsory compounds within the EUPT-Target Pesticides List (max. 13 / 8)
within MACP			√	√	√	√	√	√	√	√	√	√	√	√	√	
present in Test Item				√			√	√		√		√	√	√	√	
Evaluated within this PT				√			√	√		√		√	√	√	√	
Lab-Code SRM8-	NRL-SRM	Cat.*														
72		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
73	x	B		V		ND		V				V				4 / 3
75		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
76		B	ND	V							ND			V		4 / 2
77		B	ND	V		ND		V	ND		ND	V	V	V		9 / 5
78		B	ND	V		ND		V			ND	V				6 / 3
79		B		V				V				V				3 / 3
80		A	ND	V	ND	ND	V	V	ND	V	ND	V		V	V	12 / 7
81	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	FN	V	V	13 / 7
82	x	A	ND	V	ND	ND	V	V	ND		ND	V	V	V	V	12 / 7
83		A	ND	V	ND	ND	V	V	ND	V	ND	V		V	V	12 / 7
84		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
85																
86		B		V		ND						V				3 / 2
87		B											V			1 / 1
88		A	ND	V		ND	V	V		V	ND	V	V	V		10 / 7
89		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
91		B				ND					ND			V		3 / 1
92		B						V								1 / 1
93		B				ND							V			2 / 1
96		B		FN				V				V				3 / 2
97		B		V		ND		V				V				4 / 3
98		B	ND	V	ND	ND	V	V	ND		ND	V	FN	V	V	12 / 6
99	x	A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
100																
101		B		V		ND		V			ND	V	FN	V		7 / 4
102		B	ND	V	ND	ND	V	V	ND		ND	V		V	V	11 / 6
103		A	ND	V	ND	ND	V		ND	V	ND	V	V	V	V	12 / 7
104	x	A	ND	V	ND	ND	V	V		V	ND	V		V	V	11 / 7
105		B	ND	V	ND	ND		V			ND		V		V	8 / 4
107		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8

MACP = EU Mutiannual Community Control Program (2012-14)
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V# : Outlier according to the General Protocol (z-score > 5); **V‡**: Outlier according to Grubbs' test, alpha = 0.01;
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Table 4-2 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

			Optional Compounds											Total
Optional Compound listed in Target List			Diquat (dication)	Fentin (expr. as triphenyltin cation)	Fosetyl aluminium (expr. as fosetyl)	Glufosinate (parent only)	Maleic hydrazide	BAC-C10 (expr. as chloride salt)	BAC-C12 (expr. as chloride salt)	BAC-C14 (expr. as chloride salt)	BAC-C16 (expr. as chloride salt)	DDAC-C10 (expr. as chloride salt)	analysed / correctly found among optional compounds within the EUPT-Target Pesticides List (max. 10 / 7)	analysed / correctly found amoung all compounds within the EUPT-Target Pes-ticides List (max. 23 / 15)
within MACP								ad hoc	ad hoc	ad hoc	ad hoc	ad hoc		
present in Test Item			√	√	√	√	√		√			√		
Evaluated within this PT			√§	√§		√§	√§		√§			√§		
Lab-Code SRM8-	NRL-SRM	Cat.*												
72		A	V	V		V		ND	V	ND	ND	V	8 / 5	21 / 13
73	x	B							V	ND	ND	V	4 / 2	8 / 5
75		A	V	V	V	V	V	ND	V	ND	ND	V	10 / 7	23 / 15
76		B						ND	V	ND	ND	V	5 / 2	9 / 4
77		B				V							1 / 1	10 / 6
78		B											0 / 0	6 / 3
79		B											0 / 0	3 / 3
80		A			V		V						2 / 2	14 / 9
81	x	A	V	V	V	V	V	ND	V	ND	ND	V	10 / 7	23 / 14
82	x	A	V			V		ND	V	ND	ND	V	7 / 4	19 / 11
83		A		V	V		V	ND	V	ND	ND	V	8 / 5	20 / 12
84		A		V	V	V	V	ND	V	ND	ND	V	9 / 6	22 / 14
85														
86		B											0 / 0	3 / 2
87		B							V	ND	ND	V#	4 / 2	5 / 3
88		A						ND	V	ND	ND	V	5 / 2	15 / 9
89		A						ND	V	ND	ND	V	5 / 2	18 / 10
91		B											0 / 0	3 / 1
92		B											0 / 0	1 / 1
93		B				V							1 / 1	3 / 2
96		B						ND	V	ND	ND	V	5 / 2	8 / 4
97		B											0 / 0	4 / 3
98		B	V		V	V	V	ND	V	ND	ND	V	9 / 6	21 / 12
99	x	A		V			V	ND	V	ND	ND	V	7 / 4	20 / 12
100														
101		B											0 / 0	7 / 4
102		B			V		V						2 / 2	13 / 8
103		A					V		V	ND		V	4 / 3	16 / 10
104	x	A											0 / 0	11 / 7
105		B				V							1 / 1	9 / 5
107		A		V	V	V							3 / 3	16 / 11

MACP = EU Mutiannual Community Control Program (2012-14)
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V# : Outlier according to the General Protocol (z-score > 5); **V+**: Outlier according to Grubbs' test, alpha = 0.01;
√§ : evaluated only in terms of performance (z-score), not in terms of scope
***** : Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)

Table 4-2 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

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within MACP			√	√	√	√	√	√	√	√	√	√	√	√	√	
present in Test Item				√			√	√		√		√	√	√	√	
Evaluated within this PT				√			√	√		√		√	√	√	√	
Lab-Code SRM8-	NRL-SRM	Cat.*														
108		B				ND	V	V		V	ND	V		V		7 / 5
109	x	B	ND	V	ND	ND		V			ND	V		V	V	9 / 5
110	x	B	ND	V							ND	V		V		5 / 3
112		B	ND	V		ND	V	V			ND	V				7 / 4
115		B	ND	V		ND		V	ND		ND	V	FN	V		9 / 4
117	x	A	ND	V	ND	ND	V	V		V	ND	V		V	V	11 / 7
118	x	B			ND										V	2 / 1
119	x	B	ND	V	ND	ND	FN	V		V	ND	V		V	V	11 / 6
120		A	ND	V	ND	ND	V	V			ND	V	V	V	V	11 / 7
121		B		V		ND	FN	V			ND	V	V			7 / 4
122		B		FN	ND	ND	V#	FN			ND	FN		V	V	9 / 3
124		B		V		ND		V				V				4 / 3
125																
126		B	ND	V	ND	ND	V	V			ND	V		V	V	10 / 6
127		B		V		ND		V				V				4 / 3
128		B		V		ND	V	V#				V				5 / 4
129	x	A	ND	V	ND	ND	V	V	ND	V#	ND	V	V	V	V	13 / 8
130		B	ND	V	ND	ND	V	V			ND	V		V	V	10 / 6
131		B			ND	ND	V	V#						V	V	6 / 4
132		B	ND	V		ND	V		ND	V	ND	V		V		9 / 5
133		A	ND	V#	ND	ND	V	V		V	ND	V		V	V	11 / 7
134		B	ND		ND	ND	V			V	ND			V	V	8 / 4
136		A	ND	V	ND	ND	V	V		V	ND	V		V	V	11 / 7
137		B	ND	V		ND		V				V				5 / 3
45																
50		B	ND		ND	ND	V								V	5 / 2
52		A	ND	V	ND	ND	V	V	ND	V	ND	V	V		V	12 / 7
54		B							ND				V			2 / 1
61		A	ND	V	ND	ND	V	V	ND	V	ND	V	V	V	V	13 / 8
94		B		FN		ND		V				V	V			5 / 3
95		B	ND			ND	V							V		4 / 2

MACP = EU Mutiannual Community Control Program (2012-14)
V = analysed for and submitted concentration Value > MRRL; **ND** = analysed for and correctly Not Detected;
Empty cells: not analysed; **FN** = analysed for but falsely not detected (False Negative result); **FP** = false positive result
V# : Outlier according to the General Protocol (z-score > 5); **V‡**: Outlier according to Grubbs' test, alpha = 0.01;
***** : Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)
****** : detected, but was not able to submit result due to technical problem. Judged as ND in accordance with the General Protocol

Table 4-2 (cont.): Scope and categorization of participating labs (including Third Country labs and labs that have not submitted results).

			Optional Compounds											Total
Optional Compound listed in Target List			Diquat (dication)	Fentin (expr. as triphenyltin cation)	Fosetyl aluminium (expr. as fosetyl)	Glufosinate (parent only)	Maleic hydrazide	BAC-C10 (expr. as chloride salt)	BAC-C12 (expr. as chloride salt)	BAC-C14 (expr. as chloride salt)	BAC-C16 (expr. as chloride salt)	DDAC-C10 (expr. as chloride salt)	analysed / correctly found among optional compounds within the EUPT-Target Pesticides List (max. 10 / 7)	analysed / correctly found amoung all compounds within the EUPT-Target Pes-ticides List (max. 23 / 15)
within MACP								ad hoc	ad hoc	ad hoc	ad hoc	ad hoc		
present in Test Item			√	√	√	√	√		√			√		
Evaluated within this PT			√§	√§		√§	√§		√§			√§		
Lab-Code SRM8-	NRL-SRM	Cat.*												
108		B											0 / 0	7 / 5
109	x	B											0 / 0	9 / 5
110	x	B											0 / 0	5 / 3
112		B			V								1 / 1	8 / 5
115		B				V							1 / 1	10 / 5
117	x	A		V				ND	V	ND	ND	V	6 / 3	17 / 10
118	x	B						ND	V	ND	ND	V	5 / 2	7 / 3
119	x	B											0 / 0	11 / 6
120		A											0 / 0	11 / 7
121		B											0 / 0	7 / 4
122		B		V				ND	V	ND	ND	V	6 / 3	15 / 6
124		B											0 / 0	4 / 3
125														
126		B											0 / 0	10 / 6
127		B											0 / 0	4 / 3
128		B											0 / 0	5 / 4
129	x	A		V		V							2 / 2	15 / 10
130		B											0 / 0	10 / 6
131		B											0 / 0	6 / 4
132		B			V								1 / 1	10 / 6
133		A		V									1 / 1	12 / 8
134		B		V				ND	V	ND	ND	V	6 / 3	14 / 7
136		A						ND	V	ND	ND	V	5 / 2	16 / 9
137		B											0 / 0	5 / 3
45														
50		B											0 / 0	5 / 2
52		A	V			V		ND	V	ND	ND	V	7 / 4	19 / 11
54		B											0 / 0	2 / 1
61		A	FN										1 / 0	14 / 8
94		B											0 / 0	5 / 3
95		B						ND	V	ND	ND	V	5 / 2	9 / 4

MACP = EU Mutiannual Community Control Program (2012-14)
V = analysed for and submitted concentration Value > MRRL; **ND** = analysed for and correctly Not Detected;
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***** : Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)

Table 4-3: Assigned Values, uncertainties of assigned values and Qn-RSDs calculated for all pesticides present in the Test Item

	Compound	No. of NDs	No. of Outliers	Assigned Value [mg/kg]	No. of numerical results (EU+EFTA)	UAV [$] [mg/kg]	UAV-Tolerance [mg/kg]	Judgement for UAV-test	Qn-RSD [%]
Compulsory Compounds	Captan	3+1[¶]	1[#]	1.010	90	+/- 0.0345	0.0758	passed	26.0
	Cyromazine	2	1[#] + 1[‡]	0.102	75	+/- 0.0040	0.0077	passed	27.2
	Dicofol	2	2[#]	1.030	90	+/- 0.0374	0.0776	passed	27.6
	Fenbutatin oxide	0	3[#]	0.065	59	+/- 0.0036	0.0049	passed	31.4
	Folpet	1	0	1.320	93	+/- 0.0519	0.0990	passed	29.6
	Glyphosate	4	0	0.340	45	+/- 0.0151	0.0255	passed	24.5
	Haloxyfop	0	0	0.508	81	+/- 0.0140	0.0381	passed	20.1
	Mepiquat	1	0	0.096	71	+/- 0.0033	0.0072	passed	22.7
	Average								**26.1**
Optional Compounds	Diquat	***4***	***0***	***(0.107)****	***10***	***+/- 0.0127***	***0.0080***	***failed***	***28.6***
	Fentin	0	1[#]	(0.167)	28	+/- 0.0147	0.0125	***(failed)***	37.1
	Fosetyl	***2***	***1[#]***	***(0.798)****	***23***	***+/- 0.0985***	***0.0599***	***failed***	***45.2***
	Glufosinate	1	0	0.271	24	+/- 0.0120	0.0203	passed	16.9
	Maleic hydrazide	0	0	0.689	24	+/- 0.0467	0.0517	passed	27.7
	BAC-C12	0	0	0.568	51	+/- 0.0236	0.0426	passed	24.1
	DDAC-C10	1	0	0.380	52	+/- 0.0156	0.0285	passed	22.9
	Average								**25.7[§]**

¶: detected, but was not able to submit result due to technical problem. Judged as FN in accordance with the General Protocol
#: Outliers due to z-score > 5
‡: Outliers according to Grubbs' test, alpha value = 0.01
*: Median of all reported results excluding outliers (too uncertain to be defined as assigned value), for information only, not for calculation of z-score
§: Diquat and fosetyl were not considered.
$: **UAV:** Uncertainty of Assigned Value (μ_i) is calculated according to ISO 13528:2009-01 as
$\mu_i = 1.25 * [(Qn\text{-}SD)/\sqrt{n}]$, where *Qn-SD* is the robust standard deviation and *n* is the number of results

The average Qn-RSD of all compulsory compounds was 26.1 %. Excluding ***diquat*** and ***fosetyl*** the average Qn-RSD of optional compounds was 25.7 %. Both values are close to the FFP-RSD of 25 %.

4.3 Assessment of laboratory performance

4.3.1 False Positives

Lab SRM8-51 reported 0.025 mg/kg *chlormequat* and Lab SRM8-63 reported 0.065 mg/kg *chlorothalonil* in the Test Item. Both results were above the MRRL and were, therefore, judged as false positive results (FPs). Furthermore, Lab SRM8-101 reported 0.001 mg/kg *fluazifop* in the Test Item. Although it exceeded its own reporting limit of 0.0005 mg/kg, it is lower than the MRRL (0.01 mg/kg) and thus was not judged to be a false positive result.

Laboratories from EU Candidate countries and Third Countries did not report any false positive result.

Table 4-4: Overview of potential false positive results reported by participating labs from EU and EFTA countries

Compound	PT-Code	Analysed	Reported Result [mg/kg]	RL [mg/kg]	MRRL [mg/kg]	Judgement
Chlormequat	SRM8-51	yes	0.025	0.01	0.01	False Positive
Chlorothalonil	SRM8-63	yes	0.65	0.005	0.01	False Positive
Fluazifop	SRM8-101	yes	0.001	0.0005	0.01	

4.3.2 False Negatives

Among the compulsory compounds there were 14 cases (4× ***captan***, 2× ***cyromazine***, 2× ***dicofol***, 1× ***folpet***, 4× ***glyphosate*** and 1× ***mepiquat***) where the participants from EU and EFTA labs reported "analysed, but not detected" for pesticides spiked to the Test Item (**Table 4-5**). In all these cases the Assigned Values were sufficiently distant from the MRRLs and the individual RLs of the labs, they were therefore judged to be false negative results. In addition, Lab SRM8-67 reported that they detected ***captan*** in the Test Item, however, they could not provide a quantitative result due to a technical problem. Following the rules of the General Protocol and a decision of the Scientific Committee this result was also judged as a false negative result. These 14 false negative results represented 2.3 % of all 618 reported results covering compulsory pesticides present in the Test Item.

Among the optional compounds there were 8 cases (4× ***diquat***, 2× ***fosetyl***, 1× ***glufosinate*** and 1× ***DDAC-C10***) where the participants from EU and EFTA labs reported "analysed, but not detected" for pesticides spiked to the Test Item (**Table 4-5**). For the same reasons as described for the compulsory compounds these results were also judged as false negative results. These false negative results made 3.6 % of the 220 results reported for optional pesticides (including ***fosetyl*** and ***diquat***). Among the 49 unacceptable results (|z-score| > 3) 16 (= 33 %) concerned FNs (***fosetyl*** and ***diquat*** were not considered).

Labs from EU Candidate countries and Third Countries reported false negative results in 2 cases: one concerning ***captan*** (Lab 94) and the other one ***diquat*** (Lab 61). The long transport might have played a role here as this lab has also reported a very low concentration for ***folpet*** which has similar properties as ***captan***.

Table 4-5: Overview of false negative results reported by participating labs from EU and EFTA countries

	Compound	PT-Code	Analysed	Detected	Reported Result [mg/kg]	RL [mg/kg]	MRRL [mg/kg]	Assigned Value [mg/kg]	Judgement
Compulsory Compounds	Captan	SRM8-2	yes	no	–	0.1	0.01	1.010	False Negative
		SRM8-67	yes	yes	–	0.01			False Negative
		SRM8-96	yes	no	–	0.05			False Negative
		SRM8-122	yes	no	–	0.01			False Negative
	Cyromazine	SRM8-119	yes	no	–	0.01	0.01	0.102	False Negative
		SRM8-121	yes	no	–	0.01			False Negative
	Dicofol	SRM8-63	yes	no	–	0.005	0.01	1.030	False Negative
		SRM8-122	yes	no	–	0.01			False Negative
	Folpet	SRM8-122	yes	no	–	0.01	0.01	1.320	False Negative
	Glyphosate	SRM8-81	yes	no	–	0.05	0.05	0.340	False Negative
		SRM8-98	yes	no	–	0.1			False Negative
		SRM8-101	yes	no	–	0.05			False Negative
		SRM8-115	yes	no	–	0.05			False Negative
	Mepiquat	SRM8-2	yes	no	–	0.01	0.01	0.096	False Negative
Optional Compounds	Diquat	SRM8-6	yes	no	–	0.02	0.02	*(0.107)* [1]	False Negative
		SRM8-7	yes	no	–	0.02			False Negative
		SRM8-9	yes	no	–	0.01			False Negative
		SRM8-40	yes	no	–	0.02			False Negative
	Fosetyl	SRM8-48	yes	no	–	0.05	0.05	*(0.798)* [1]	False Negative
		SRM8-51	yes	no	–	0.5			False Negative
	Glufosinate	SRM8-23	yes	no	–	0.005	0.05	0.750	False Negative
	DDAC-C10	SRM8-26	yes	no	–	0.02	0.1	0.380	False Negative

1) Due to statistical uncertainty no assigned value could be established for fosetyl and diquat. The median value (see Table 4-3), even considering the uncertainty, was, however, sufficiently distant from the MRRL and allowed safe judgement of false negatives.

Table 4-6: Overall classification of z-scores achieved by EU and EFTA laboratories

	Compound	No. of results	Acceptable No. (%)	Questionable No. (%)	Unacceptable [1] No. (%)	FNs No.
Compulsory Compounds	Captan	94	83 (88 %)	4 (4 %)	7 (7 %)	3 + 1[2]
	Cyromazine	77	66 (86 %)	6 (8 %)	5 (6 %)	2
	Dicofol	92	80 (87 %)	4 (4 %)	8 (9 %)	2
	Fenbutatin oxide	59	50 (85 %)	3 (5 %)	6 (10 %)	0
	Folpet	94	84 (89 %)	6 (6 %)	4 (4 %)	1
	Glyphosate	49	42 (86 %)	3 (6 %)	4 (8 %)	4
	Haloxyfop	81	74 (91 %)	4 (5 %)	3 (4 %)	0
	Mepiquat	72	66 (92 %)	4 (6 %)	2 (3 %)	1
	Sum	**618**	**545 (88 %)**	**34 (6 %)**	**39 (6 %)**	**14**
Optional Compounds	Fentin	28	23 (82 %)	3 (11 %)	2 (7 %)	0
	Glufosinate	25	22 (88 %)	2 (8 %)	1 (4 %)	1
	Maleic hydrazide	24	22 (92 %)	1 (4 %)	1 (4 %)	0
	BAC-C12	51	45 (88 %)	4 (8 %)	2 (4 %)	0
	DDAC-C10	53	46 (87 %)	3 (6 %)	4 (8 %)	1
	Sum	**181**	**158 (87 %)**	**13 (7 %)**	**10 (6 %)**	**2**
	Overall Sum	**799**	**703 (88 %)**	47 **(6 %)**	**49 (6 %)**	**16**

1) including false negatives (FNs)
2) detected, but was not able to submit result due to technical problem and was judged as FN in accordance with the General Protocol

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				Captan		Cyromazine		Dicofol		Fenbutatin oxide	
Assigned Value [mg/kg]				1.010		0.102		1.030		0.065	
MRRL [mg/kg]				0.01		0.01		0.01		0.01	
Qn-RSD				26.0 %		27.2 %		27.6 %		31.4 %	
Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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	x	12 / 7	A	0.876	-0.53	0.229	4.98	1.060	0.12		
2	x	12 / 5	B	FN	-3.96	0.049	-2.08	0.818	-0.82	0.038	-1.66
3		13 / 8	A	0.970	-0.16	0.055	-1.84	1.000	-0.12	0.047	-1.11
4		13 / 8	A	1.066	0.22	0.099	-0.12	0.740	-1.13	0.069	0.25
5		11 / 7	A	0.995	-0.06	0.084	-0.71	0.845	-0.72	0.051	-0.84
6	x	13 / 8	A	0.716	-1.16	0.107	0.20	0.893	-0.53	0.082	1.05
7		13 / 8	A	1.050	0.16	0.140	1.49	1.240	0.82	0.043	-1.35
8		13 / 8	A	1.283	1.08	0.100	-0.08	1.005	-0.10	0.082	1.05
9		13 / 8	A	0.705	-1.21	0.101	-0.04	1.050	0.08	0.065	0.01
10	x	13 / 8	A	1.110	0.40	0.105	0.12	0.913	-0.45	0.064	-0.06
11	x	13 / 8	A	1.150	0.55	0.142	1.57	1.880	3.30	0.063	-0.13
12	x	13 / 8	A	0.781	-0.91	0.139	1.45	0.888	-0.55	0.138	4.49
13		13 / 8	A	1.120	0.44	0.082	-0.78	0.923	-0.42	0.064	-0.06
14		13 / 8	A	1.289	1.10	0.127	0.98	1.248	0.85	0.098	2.03
15											
16		9 / 5	B			0.093	-0.35	1.180	0.58		

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)
** detected, but was not able to submit a result due to technical problem. Judged as FN in accordance with the General Protocol

4.3.3 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, respectively. The respective classification rules are shown in **Section 2.4**. In the case of compulsory compounds "acceptable" z-scores were achieved by 85 – 92 % (88 % on average) of the labs. Disregarding ***diquat*** and ***fosetyl***, where no trustworthy Assigned Values could be established, "acceptable" z-scores of optional compounds were achieved by 82 – 92 % (87 % on average) of the labs.

A compilation of all individual results and z-scores of each laboratory is shown in **Table 4-7** (compulsory compounds) and **Table 4-8** (optional compounds). The corresponding kernel density histograms showing the distribution of the reported results can be found in **Appendix 5**. A graphic representation of the z-score distribution of each pesticide present in the Test Item can be seen in **Appendix 6**.

In **Table 4-9** all laboratories are ranked based on the individual z-scores obtained for each of the analytes present in the Test Item.

		COMPULSORY Compound		Folpet		Glyphosate		Haloxyfop		Mepiquat	
		Assigned Value [mg/kg]		1.320		0.340		0.508		0.096	
		MRRL [mg/kg]		0.01		0.05		0.01		0.01	
		Qn-RSD		29.6 %		24.5 %		20.1 %		22.7 %	
Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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	x	12 / 7	A	1.270	-0.15	0.380	0.47	0.518	0.08	0.089	-0.31
2	x	12 / 5	B	0.587	-2.22			0.484	-0.19	FN	-3.58
3		13 / 8	A	1.500	0.55	0.340	0.00	0.530	0.17	0.094	-0.08
4		13 / 8	A	1.661	1.03	0.474	1.58	0.462	-0.36	0.080	-0.67
5		11 / 7	A	1.420	0.30			0.355	-1.20	0.070	-1.10
6	x	13 / 8	A	1.015	-0.92	0.355	0.18	0.555	0.37	0.085	-0.46
7		13 / 8	A	1.800	1.45	0.227	-1.33	0.503	-0.04	0.134	1.58
8		13 / 8	A	1.829	1.54	0.410	0.82	0.535	0.21	0.134	1.58
9		13 / 8	A	1.190	-0.39	0.333	-0.08	0.412	-0.76	0.085	-0.45
10	x	13 / 8	A	1.590	0.82	0.415	0.88	0.517	0.07	0.077	-0.81
11	x	13 / 8	A	1.290	-0.09	0.266	-0.87	0.221	-2.26	0.103	0.29
12	x	13 / 8	A	1.380	0.18	0.271	-0.81	0.789	2.21	0.116	0.83
13		13 / 8	A	2.080	2.30	0.184	-1.84	0.113	-3.11	0.077	-0.79
14		13 / 8	A	1.897	1.75	0.292	-0.56	0.518	0.08	0.121	1.04
15											
16		9 / 5	B			0.379	0.46	0.394	-0.90	0.120	1.00

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

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				Captan		Cyromazine		Dicofol		Fenbutatin oxide	
Assigned Value [mg/kg]				1.010		0.102		1.030		0.065	
MRRL [mg/kg]				0.01		0.01		0.01		0.01	
Qn-RSD				26.0 %		27.2 %		27.6 %		31.4 %	
Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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 %)
17											
18		3 / 2	B	1.210	0.79						
19		12 / 7	A	0.404	-2.40	0.096	-0.24	0.965	-0.25	0.062	-0.18
21	x	13 / 8	A	1.160	0.59	0.126	0.94	1.100	0.27	0.071	0.37
22		7 / 5	B	1.210	0.79	0.069	-1.29	1.350	1.24		
23		9 / 5	B			0.127	0.98			0.069	0.26
24		11 / 7	A	1.280	1.07	0.067	-1.37	0.633	-1.54	0.050	-0.92
25		13 / 8	A	0.845	-0.65	0.098	-0.16	1.300	1.05	0.047	-1.11
26		11 / 7	A	1.040	0.12	0.093	-0.35	1.280	0.97	0.102	2.28
27		6 / 4	B	0.870	-0.55			0.660	-1.44		
28		4 / 3	B	1.160	0.59			1.030	0.00		
30		13 / 8	A	1.130	0.48	0.132	1.18	1.080	0.19	0.077	0.74
31	x	12 / 8	A	0.647	-1.44	0.092	-0.39	0.884	-0.57	0.065	0.00
32		13 / 8	A	1.070	0.24	0.090	-0.47	1.080	0.19	0.147	5.05
33	x	9 / 6	B	0.890	-0.48	0.114	0.47	1.100	0.27	0.061	-0.27
34		2 / 1	B			0.085	-0.66				
35		1 / 0									
36		10 / 6	B	1.080	0.28	0.120	0.71	1.010	-0.08		
37		3 / 2	B					0.889	-0.55		
38		11 / 7	A	1.170	0.63	0.104	0.08	0.766	-1.03	0.088	1.42
39											
40	x	13 / 8	A	1.140	0.51	0.104	0.08	1.480	1.75	0.071	0.34
41		12 / 7	A	1.340	1.31	0.100	-0.08	1.110	0.31		
42		4 / 2	B					0.783	-0.96		
43		13 / 8	A	0.978	-0.13	0.081	-0.82	1.050	0.08	0.051	-0.89
44		4 / 3	B	1.620	2.42			0.910	-0.47		
46		12 / 7	A	0.720	-1.15	0.121	0.75	0.601	-1.67	0.046	-1.14
47		10 / 6	B	1.010	0.00	0.115	0.51			0.200	8.31
48		13 / 8	A	0.645	-1.45	0.085	-0.65	0.694	-1.30	0.051	-0.87
49	x	12 / 7	A	0.916	-0.37	0.101	-0.04	1.575	2.12	0.061	-0.25
51		13 / 8	B	1.550	2.14	0.160	2.27	1.190	0.62	0.091	1.60
53	x	13 / 8	A	1.029	0.08	0.108	0.24	1.100	0.27	0.077	0.74
55	x	9 / 5	B	1.150	0.55					0.061	-0.25
56		13 / 8	A	0.797	-0.84	0.080	-0.87	0.006	-3.98	0.057	-0.52
57	x	7 / 5	B	1.050	0.16	0.010	-3.59	1.780	2.91		
59		12 / 7	A	0.700	-1.23	0.170	2.67	1.200	0.66	0.085	1.23
60		0 / 0									

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)
** detected, but was not able to submit a result due to technical problem. Judged as FN in accordance with the General Protocol

				COMPULSORY Compound	Folpet		Glyphosate		Haloxyfop		Mepiquat	
				Assigned Value [mg/kg]	1.320		0.340		0.508		0.096	
				MRRL [mg/kg]	0.01		0.05		0.01		0.01	
				Qn-RSD	29.6 %		24.5 %		20.1 %		22.7 %	
	Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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 %)
	17											
	18		3 / 2	B	1.410	0.27						
	19		12 / 7	A	1.120	-0.61			0.700	1.51	0.080	-0.67
	21	x	13 / 8	A	1.350	0.09	0.356	0.19	0.578	0.55	0.090	-0.25
	22		7 / 5	B	1.820	1.52					0.096	0.00
	23		9 / 5	B			0.373	0.39	0.694	1.46	0.108	0.50
	24		11 / 7	A	1.670	1.06			0.582	0.58	0.097	0.04
	25		13 / 8	A	1.160	-0.48	0.239	-1.19	0.415	-0.73	0.085	-0.46
	26		11 / 7	A	1.790	1.42			0.533	0.20	0.081	-0.63
	27		6 / 4	B	1.140	-0.55			0.480	-0.22		
	28		4 / 3	B	1.480	0.48						
	30		13 / 8	A	1.800	1.45	0.369	0.34	1.000	3.87	0.114	0.75
	31	x	12 / 8	A	0.949	-1.12	0.579	2.81	0.463	-0.35	0.079	-0.71
	32		13 / 8	A	1.540	0.67	0.370	0.35	0.699	1.50	0.091	-0.21
	33	x	9 / 6	B	1.890	1.73			0.490	-0.14		
	34		2 / 1	B								
	35		1 / 0									
	36		10 / 6	B	1.340	0.06			0.615	0.84	0.078	-0.75
	37		3 / 2	B	1.182	-0.42						
	38		11 / 7	A	1.510	0.58			0.550	0.33	0.072	-1.00
	39											
	40	x	13 / 8	A	1.200	-0.36	0.358	0.21	0.445	-0.50	0.088	-0.34
	41		12 / 7	A	1.640	0.97	0.280	-0.71	0.450	-0.46	0.127	1.29
	42		4 / 2	B					0.373	-1.06		
	43		13 / 8	A	1.500	0.55	0.376	0.42	0.513	0.04	0.090	-0.23
	44		4 / 3	B	2.900	4.79						
	46		12 / 7	A	0.939	-1.15			0.335	-1.36	0.097	0.03
	47		10 / 6	B	1.300	-0.06			0.618	0.87	0.125	1.21
	48		13 / 8	A	1.010	-0.94	0.291	-0.58	0.333	-1.38	0.105	0.38
	49	x	12 / 7	A	1.496	0.53			0.470	-0.30	0.089	-0.29
	51		13 / 8	B	1.040	-0.85	0.452	1.32	0.692	1.45	0.030	-2.75
	53	x	13 / 8	A	1.622	0.92	0.315	-0.29	0.508	0.00	0.102	0.25
	55	x	9 / 5	B	1.530	0.64			0.471	-0.29	0.023	-3.04
	56		13 / 8	A	0.663	-1.99	0.462	1.44	0.013	-3.90	0.132	1.50
	57	x	7 / 5	B	1.320	0.00					0.113	0.71
	59		12 / 7	A	0.600	-2.18			0.530	0.17	0.136	1.67
	60		0 / 0									

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

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				Captan		Cyromazine		Dicofol		Fenbutatin oxide	
Assigned Value [mg/kg]				1.010		0.102		1.030		0.065	
MRRL [mg/kg]				0.01		0.01		0.01		0.01	
Qn-RSD				26.0 %		27.2 %		27.6 %		31.4 %	
Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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 %)
63		3 / 0	B					FN	-3.98		
64		13 / 8	A	1.330	1.27	0.120	0.71	1.200	0.66	0.071	0.35
65		5 / 4	B	1.210	0.79			1.160	0.50	0.053	-0.73
66											
67		10 / 5	B	FN**	-3.96	0.060	-1.65	1.150	0.47	0.034	-1.91
68		7 / 4	B	0.461	-2.17	0.057	-1.76				
69		12 / 7	A	1.110	0.40	0.119	0.67	1.290	1.01		
70	x	13 / 8	A	0.809	-0.80	0.044	-2.29	0.954	-0.30	0.084	1.15
71		7 / 4	B	0.777	-0.92			1.280	0.97		
72		13 / 8	A	0.828	-0.72	0.084	-0.71	0.737	-1.14	0.089	1.48
73	x	4 / 3	B	0.548	-1.83			1.010	-0.08		
75		13 / 8	A	1.220	0.83	0.111	0.35	1.350	1.24	0.063	-0.12
76		4 / 2	B	1.170	0.63						
77		9 / 5	B	0.769	-0.95			1.030	0.00		
78		6 / 3	B	1.490	1.90			1.130	0.39		
79		3 / 3	B	1.300	1.15			1.070	0.16		
80		12 / 7	A	1.460	1.78	0.086	-0.64	0.980	-0.19	0.100	2.15
81	x	13 / 7	A	1.010	0.00	0.108	0.24	1.340	1.20	0.048	-1.07
82	x	12 / 7	A	0.797	-0.84	0.115	0.51	0.892	-0.54		
83		12 / 7	A	1.250	0.95	0.119	0.67	1.350	1.24	0.088	1.42
84		13 / 8	A	1.145	0.53	0.104	0.08	1.346	1.23	0.072	0.43
85											
86		3 / 2	B	0.976	-0.13						
87		1 / 1	B								
88		10 / 7	A	0.934	-0.30	0.106	0.16	0.462	-2.21	0.056	-0.55
89		13 / 8	A	1.220	0.83	0.139	1.45	0.645	-1.50	0.121	3.45
91		3 / 1	B								
92		1 / 1	B					1.073	0.17		
93		2 / 1	B								
96		3 / 2	B	FN	-3.96			0.888	-0.55		
97		4 / 3	B	1.220	0.83			1.890	3.34		
98		12 / 6	B	1.000	-0.04	0.095	-0.26	1.230	0.78		
99	x	13 / 8	A	0.932	-0.31	0.068	-1.33	1.060	0.12	0.068	0.18
100											
101		7 / 4	B	0.220	-3.13			0.645	-1.50		
102		11 / 6	B	0.830	-0.71	0.040	-2.43	1.370	1.32		
103		12 / 7	A	0.847	-0.65	0.127	0.98			0.120	3.38

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)
** detected, but was not able to submit a result due to technical problem. Judged as FN in accordance with the General Protocol

		COMPULSORY Compound		Folpet		Glyphosate		Haloxyfop		Mepiquat	
		Assigned Value [mg/kg]		1.320		0.340		0.508		0.096	
		MRRL [mg/kg]		0.01		0.05		0.01		0.01	
		Qn-RSD		29.6 %		24.5 %		20.1 %		22.7 %	
Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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 %)
63		3 / 0	B								
64		13 / 8	A	1.090	-0.70	0.160	-2.12	0.591	0.65	0.106	0.42
65		5 / 4	B	1.940	1.88						
66											
67		10 / 5	B	1.500	0.55					0.084	-0.50
68		7 / 4	B	1.030	-0.88			0.450	-0.46		
69		12 / 7	A	1.400	0.24	0.291	-0.58	0.499	-0.07	0.092	-0.17
70	x	13 / 8	A	0.919	-1.22	0.138	-2.38	0.523	0.12	0.070	-1.07
71		7 / 4	B	0.705	-1.86			0.496	-0.09		
72		13 / 8	A	1.110	-0.64	0.315	-0.29	0.431	-0.61	0.068	-1.17
73	x	4 / 3	B	0.830	-1.48						
75		13 / 8	A	1.240	-0.24	0.301	-0.46	0.555	0.37	0.105	0.38
76		4 / 2	B					0.434	-0.58		
77		9 / 5	B	1.080	-0.73	0.217	-1.45	0.195	-2.46		
78		6 / 3	B	1.940	1.88						
79		3 / 3	B	1.770	1.36						
80		12 / 7	A	2.030	2.15			0.570	0.49	0.082	-0.58
81	x	13 / 7	A	1.280	-0.12	FN	-3.88	0.481	-0.21	0.086	-0.40
82	x	12 / 7	A	1.250	-0.21	0.327	-0.15	0.553	0.35	0.098	0.08
83		12 / 7	A	1.930	1.85			0.512	0.03	0.090	-0.26
84		13 / 8	A	1.468	0.45	0.379	0.46	0.456	-0.41	0.150	2.25
85											
86		3 / 2	B	1.260	-0.18						
87		1 / 1	B			0.359	0.22				
88		10 / 7	A	1.320	0.00	0.370	0.35	0.547	0.31		
89		13 / 8	A	1.330	0.03	0.401	0.72	0.701	1.52	0.120	1.00
91		3 / 1	B					0.603	0.75		
92		1 / 1	B								
93		2 / 1	B			0.195	-1.71				
96		3 / 2	B	1.920	1.82						
97		4 / 3	B	1.630	0.94						
98		12 / 6	B	0.827	-1.49	FN	-3.88	0.581	0.57	0.103	0.29
99	x	13 / 8	A	1.300	-0.06	0.400	0.71	0.434	-0.58	0.120	1.00
100											
101		7 / 4	B	0.523	-2.42	FN	-3.88	0.423	-0.67		
102		11 / 6	B	1.290	-0.09			0.430	-0.61	0.100	0.17
103		12 / 7	A	1.120	-0.61	0.359	0.22	0.520	0.09	0.092	-0.17

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

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		Captan		Cyromazine		Dicofol		Fenbutatin oxide	
		Assigned Value [mg/kg]		1.010		0.102		1.030		0.065	
		MRRL [mg/kg]		0.01		0.01		0.01		0.01	
		Qn-RSD		26.0 %		27.2 %		27.6 %		31.4 %	
Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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 %)
104	x	11 / 7	A	1.350	1.35	0.075	-1.05	1.112	0.32	0.058	-0.43
105		8 / 4	B	0.148	-3.41			0.568	-1.79		
107		13 / 8	A	0.825	-0.73	0.121	0.75	0.897	-0.52	0.051	-0.86
108		7 / 5	B			0.065	-1.45	0.701	-1.28	0.040	-1.54
109	x	9 / 5	B	1.480	1.86			1.350	1.24		
110	x	5 / 3	B	0.770	-0.95						
112		7 / 4	B	1.427	1.65	0.070	-1.25	1.020	-0.04		
115		9 / 4	B	0.926	-0.33			1.120	0.35		
117	x	11 / 7	A	1.150	0.55	0.102	0.00	1.320	1.13	0.063	-0.12
118	x	2 / 1	B								
119	x	11 / 6	B	0.738	-1.08	FN	-3.61	0.686	-1.34	0.065	0.00
120		11 / 7	A	0.841	-0.67	0.161	2.31	0.791	-0.93		
121		7 / 4	B	0.924	-0.34	FN	-3.61	0.368	-2.57		
122		9 / 3	B	FN	-3.96	0.303	7.88	FN	-3.96		
124		4 / 3	B	0.920	-0.36			0.860	-0.66		
125											
126		10 / 6	B	1.120	0.44	0.124	0.86	0.876	-0.60		
127		4 / 3	B	0.866	-0.57			0.803	-0.88		
128		5 / 4	B	1.100	0.36	0.120	0.71	3.640	10.14		
129	x	13 / 8	A	0.844	-0.66	0.126	0.94	1.080	0.19	0.150	5.23
130		10 / 6	B	0.796	-0.85	0.093	-0.35	0.111	-3.57		
131		6 / 4	B			0.088	-0.56	3.750	10.56		
132		9 / 5	B	0.580	-1.70	0.120	0.71			0.080	0.92
133		11 / 7	A	2.850	7.29	0.125	0.90	1.020	-0.04	0.082	1.05
134		8 / 4	B			0.111	0.35			0.091	1.60
136		11 / 7	A	0.762	-0.98	0.083	-0.75	0.734	-1.15	0.046	-1.17
137		5 / 3	B	1.190	0.71			1.290	1.01		
45											
50		5 / 2	B			0.092	-0.39				
52		12 / 7	A	0.543	-1.85	0.064	-1.49	0.208	-3.19	0.420	21.85
54		2 / 1	B								
61		13 / 8	A	0.327	-2.70	0.427	12.75	0.276	-2.93	0.111	2.83
94		5 / 3	B	FN	-3.96			0.570	-1.79		
95		4 / 2	B			0.138	1.41				

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result, see 4.3.4, p. 50.)
** detected, but was not able to submit a result due to technical problem. Judged as FN in accordance with the General Protocol

				COMPULSORY Compound	Folpet		Glyphosate		Haloxyfop		Mepiquat	
				Assigned Value [mg/kg]	1.320		0.340		0.508		0.096	
				MRRL [mg/kg]	0.01		0.05		0.01		0.01	
				Qn-RSD	29.6 %		24.5 %		20.1 %		22.7 %	
	Lab code SRM8-	NRL-SRM	Analysed / Correctly Found	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 %)
	104	x	11 / 7	A	2.567	3.78			0.500	-0.06	0.057	-1.61
	105		8 / 4	B			0.345	0.06			0.099	0.11
	107		13 / 8	A	1.310	-0.03	0.303	-0.44	0.372	-1.07	0.096	0.00
	108		7 / 5	B	0.752	-1.72			0.490	-0.14		
	109	x	9 / 5	B	1.720	1.21			0.590	0.65	0.130	1.42
	110	x	5 / 3	B	1.000	-0.97			0.250	-2.03		
	112		7 / 4	B	1.024	-0.90						
	115		9 / 4	B	1.100	-0.67	FN	-3.88	0.475	-0.26		
	117	x	11 / 7	A	1.410	0.27			0.436	-0.57	0.127	1.29
	118	x	2 / 1	B							0.088	-0.33
	119	x	11 / 6	B	0.383	-2.84			0.509	0.01	0.095	-0.04
	120		11 / 7	A	1.160	-0.48	0.337	-0.04	0.585	0.61	0.096	0.00
	121		7 / 4	B	0.709	-1.85	0.186	-1.81				
	122		9 / 3	B	FN	-3.97			0.536	0.22	0.038	-2.42
	124		4 / 3	B	1.350	0.09						
	125											
	126		10 / 6	B	1.550	0.70			0.422	-0.68	0.164	2.83
	127		4 / 3	B	1.390	0.21						
	128		5 / 4	B	1.300	-0.06						
	129	x	13 / 8	A	1.270	-0.15	0.336	-0.05	0.608	0.79	0.104	0.33
	130		10 / 6	B	1.260	-0.18			0.658	1.18	0.114	0.75
	131		6 / 4	B					0.495	-0.10	0.078	-0.74
	132		9 / 5	B	0.890	-1.30			0.370	-1.09		
	133		11 / 7	A	2.880	4.73			0.655	1.16	0.130	1.42
	134		8 / 4	B					0.511	0.02	0.085	-0.46
	136		11 / 7	A	1.110	-0.64			0.515	0.06	0.096	0.00
	137		5 / 3	B	1.640	0.97						
	45											
	50		5 / 2	B							0.110	0.58
	52		12 / 7	A	0.751	-1.72	0.348	0.09			0.080	-0.67
	54		2 / 1	B			0.263	-0.91				
	61		13 / 8	A	0.442	-2.66	0.365	0.29	0.394	-0.90	0.104	0.33
	94		5 / 3	B	0.073	-3.78	0.310	-0.35				
	95		4 / 2	B					0.154	-2.79		

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

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		Fentin		Glufosinate		Maleic hydrazide	
		Assigned Value [mg/kg]		0.167		0.271		0.689	
		MRRL [mg/kg]		0.01		0.05		0.05	
		Qn-RSD		37.1 %		16.9 %		27.7 %	
Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	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	x	0 / 0	A						
2	x	6 / 3	B	0.066	-2.42				
3		7 / 4	A	0.069	-2.35				
4		0 / 0	A						
5		1 / 1	A						
6	x	10 / 6	A	0.194	0.65	0.255	-0.23	0.700	0.07
7		9 / 5	A			0.235	-0.52	0.388	-1.75
8		8 / 5	A	0.194	0.65			0.694	0.03
9		10 / 6	A	0.064	-2.46	0.401	1.93	0.554	-0.78
10	x	2 / 2	A					0.802	0.66
11	x	1 / 1	A			0.318	0.70		
12	x	0 / 0	A						
13		8 / 7	A	0.493	7.81	0.324	0.79	0.160	-3.07
14		9 / 6	A	0.225	1.39	0.276	0.08	0.720	0.18
15									
16		0 / 0	B						
17									
18		0 / 0	B						
19		5 / 2	A						
21	x	6 / 3	A	0.211	1.05				
22		0 / 0	B						
23		9 / 5	B	0.219	1.25	FN	-3.70		
24		5 / 2	A						
25		9 / 6	A	0.095	-1.72	0.253	-0.26	0.890	1.17
26		5 / 1	A						
27		5 / 2	B						
28		3 / 1	B						
30		9 / 6	A	0.104	-1.51	0.256	-0.21	0.763	0.43
31	x	6 / 3	A			0.272	0.02		
32		10 / 7	A	0.166	-0.02	0.424	2.27	0.639	-0.29
33	x	5 / 2	B						
34		5 / 2	B						
35		0 / 0							
36		0 / 0	B						
37		0 / 0	B						
38		0 / 0	A						
39									
40	x	8 / 4	A			0.269	-0.02	0.886	1.15
41		5 / 2	A						
42		5 / 2	B						

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

			OPTIONAL Compound	BAC-C12		DDAC-C10		Diquat	Fosetyl	
			Assigned Value [mg/kg]	0.568		0.380		0.107‡	0.798‡	
			MRRL [mg/kg]	0.1		0.1		0.02	0.05	
			Qn-RSD	24.1 %		22.9 %		28.6 %‡	45.2 %	
Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score‡ (FFP-RSD = 25 %)
1	x	0 / 0	A							
2	x	6 / 3	B	0.518	-0.35	0.338	-0.44			
3		7 / 4	A	0.560	-0.06	0.480	1.05		0.483	-1.58
4		0 / 0	A							
5		1 / 1	A			0.364	-0.17			
6	x	10 / 6	A	0.629	0.43	0.343	-0.39	FN	0.741	-0.28
7		9 / 5	A	0.440	-0.90	0.408	0.29	FN	0.750	-0.24
8		8 / 5	A	0.613	0.32	0.454	0.78		1.558	3.81
9		10 / 6	A	0.371	-1.39	0.305	-0.79	FN	0.199	-3.00
10	x	2 / 2	A						1.128	1.65
11	x	1 / 1	A							
12	x	0 / 0	A							
13		8 / 7	A	0.273	-2.08	0.306	-0.78	0.109	0.766	-0.16
14		9 / 6	A	0.997	3.02	0.552	1.81		0.742	-0.26
15										
16		0 / 0	B							
17										
18		0 / 0	B							
19		5 / 2	A	0.316	-1.77	0.277	-1.08			
21	x	6 / 3	A	0.533	-0.25	0.397	0.18			
22		0 / 0	B							
23		9 / 5	B	0.554	-0.10	0.351	-0.31	0.087	0.184	-3.08
24		5 / 2	A	0.438	-0.92	0.323	-0.60			
25		9 / 6	A	0.630	0.44	0.740	3.79		1.929	5.67
26		5 / 1	A	0.467	-0.71	FN	-3.79			
27		5 / 2	B	0.610	0.30	0.380	0.00			
28		3 / 1	B			0.310	-0.74			
30		9 / 6	A	0.660	0.65	0.617	2.49		1.010	1.06
31	x	6 / 3	A	0.573	0.04	0.383	0.03			
32		10 / 7	A	0.685	0.82	0.446	0.69	0.105	0.993	0.98
33	x	5 / 2	B	0.401	-1.18	0.229	-1.59			
34		5 / 2	B	0.646	0.55	0.445	0.68			
35		0 / 0								
36		0 / 0	B							
37		0 / 0	B							
38		0 / 0	A							
39										
40	x	8 / 4	A	0.669	0.71	0.412	0.34	FN		
41		5 / 2	A	0.480	-0.62	0.320	-0.63			
42		5 / 2	B	0.645	0.54	0.424	0.46			

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

‡ Assigned Value is too uncertain, therefore, z-scores are for information only

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		Fentin		Glufosinate		Maleic hydrazide	
		Assigned Value [mg/kg]		0.167		0.271		0.689	
		MRRL [mg/kg]		0.01		0.05		0.05	
		Qn-RSD		37.1 %		16.9 %		27.7 %	
Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	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 %)
43		7 / 5	A	0.197	0.72			0.772	0.49
44		0 / 0	B						
46		0 / 0	A						
47		6 / 3	B	0.157	-0.24				
48		1 / 0	A						
49	x	1 / 1	A					0.557	-0.76
51		8 / 4	B	0.140	-0.65			0.854	0.96
53	x	0 / 0	A						
55	x	5 / 2	B						
56		0 / 0	A						
57	x	0 / 0	B						
59		6 / 3	A						
60		5 / 2							
63		0 / 0	B						
64		0 / 0	A						
65		0 / 0	B						
66									
67		6 / 3	B					0.440	-1.44
68		7 / 4	B	0.140	-0.65				
69		1 / 1	A			0.293	0.33		
70	x	0 / 0	A						
71		0 / 0	B						
72		8 / 5	A	0.143	-0.57	0.226	-0.66		
73	x	4 / 2	B						
75		10 / 7	A	0.173	0.14	0.281	0.16	0.730	0.24
76		5 / 2	B						
77		1 / 1	B			0.132	-2.05		
78		0 / 0	B						
79		0 / 0	B						
80		2 / 2	A					0.653	-0.21
81	x	10 / 7	A	0.099	-1.63	0.244	-0.39	0.559	-0.75
82	x	7 / 4	A			0.242	-0.42		
83		8 / 5	A	0.370	4.86			0.717	0.17
84		9 / 6	A	0.179	0.29	0.343	1.07	0.391	-1.73
85									
86		0 / 0	B						
87		4 / 2	B						
88		5 / 2	A						
89		5 / 2	A						

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

			OPTIONAL Compound	BAC-C12		DDAC-C10		Diquat	Fosetyl	
			Assigned Value [mg/kg]	0.568		0.380		0.107‡	0.798‡	
			MRRL [mg/kg]	0.1		0.1		0.02	0.05	
			Qn-RSD	24.1 %		22.9 %		28.6 %‡	45.2 %	
	Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score‡ (FFP-RSD = 25 %)
	43		7 / 5	A	0.558	-0.07	0.405	0.26	0.115		
	44		0 / 0	B							
	46		0 / 0	A							
	47		6 / 3	B	0.619	0.36	0.456	0.80			
	48		1 / 0	A						FN	-3.75
	49	x	1 / 1	A							
	51		8 / 4	B	0.334	-1.65	0.333	-0.49		FN	-3.75
	53	x	0 / 0	A							
	55	x	5 / 2	B	0.477	-0.64	0.355	-0.26			
	56		0 / 0	A							
	57	x	0 / 0	B							
	59		6 / 3	A	0.920	2.48	0.537	1.65	0.150		
	60		5 / 2		0.730	1.14	0.350	-0.32			
	63		0 / 0	B							
	64		0 / 0	A							
	65		0 / 0	B							
	66										
	67		6 / 3	B	0.050	-3.65	0.060	-3.37			
	68		7 / 4	B	0.292	-1.94	0.313	-0.71		0.492	-1.53
	69		1 / 1	A							
	70	x	0 / 0	A							
	71		0 / 0	B							
	72		8 / 5	A	0.454	-0.80	0.294	-0.91	0.103		
	73	x	4 / 2	B	0.568	0.00	0.465	0.89			
	75		10 / 7	A	0.446	-0.86	0.347	-0.35	0.157	0.458	-1.70
	76		5 / 2	B	0.601	0.23	0.355	-0.26			
	77		1 / 1	B							
	78		0 / 0	B							
	79		0 / 0	B							
	80		2 / 2	A						1.080	1.42
	81	x	10 / 7	A	0.608	0.28	0.390	0.11	0.081	0.575	-1.12
	82	x	7 / 4	A	0.421	-1.04	0.251	-1.36	0.137		
	83		8 / 5	A	0.568	0.00	0.363	-0.18		1.080	1.42
	84		9 / 6	A	0.511	-0.40	0.370	-0.11		0.914	0.58
	85										
	86		0 / 0	B							
	87		4 / 2	B	0.691	0.87	1.005	6.58			
	88		5 / 2	A	0.698	0.92	0.464	0.88			
	89		5 / 2	A	0.868	2.11	0.616	2.48			

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

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				Fentin		Glufosinate		Maleic hydrazide	
Assigned Value [mg/kg]				0.167		0.271		0.689	
MRRL [mg/kg]				0.01		0.05		0.05	
Qn-RSD				37.1 %		16.9 %		27.7 %	
Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	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 %)
91		0 / 0	B						
92		0 / 0	B						
93		1 / 1	B			0.238	-0.48		
96		5 / 2	B						
97		0 / 0	B						
98		9 / 6	B			0.269	-0.02	0.683	-0.03
99	x	7 / 4	A	0.131	-0.86			0.524	-0.96
100									
101		0 / 0	B						
102		2 / 2	B					0.610	-0.46
103		4 / 3	A					1.040	2.04
104	x	0 / 0	A						
105		1 / 1	B			0.305	0.51		
107		3 / 3	A	0.167	0.00	0.236	-0.51		
108		0 / 0	B						
109	x	0 / 0	B						
110	x	0 / 0	B						
112		1 / 1	B						
115		1 / 1	B			0.314	0.64		
117	x	6 / 3	A	0.167	0.00				
118	x	5 / 2	B						
119	x	0 / 0	B						
120		0 / 0	A						
121		0 / 0	B						
122		6 / 3	B	0.246	1.89				
124		0 / 0	B						
125									
126		0 / 0	B						
127		0 / 0	B						
128		0 / 0	B						
129	x	2 / 2	A	0.214	1.13	0.321	0.75		
130		0 / 0	B						
131		0 / 0	B						
132		1 / 1	B						
133		1 / 1	A	0.201	0.81				
134		6 / 3	B	0.180	0.31				
136		5 / 2	A						
137		0 / 0	B						
45									

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

			OPTIONAL Compound	BAC-C12		DDAC-C10		Diquat	Fosetyl	
			Assigned Value [mg/kg]	0.568		0.380		0.107‡	0.798‡	
			MRRL [mg/kg]	0.1		0.1		0.02	0.05	
			Qn-RSD	24.1 %		22.9 %		28.6 %‡	45.2 %	
Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score‡ (FFP-RSD = 25 %)
91		0 / 0	B							
92		0 / 0	B							
93		1 / 1	B							
96		5 / 2	B	0.615	0.33	0.407	0.28			
97		0 / 0	B							
98		9 / 6	B	0.687	0.84	0.476	1.01	0.078	0.588	-1.05
99	x	7 / 4	A	0.525	-0.30	0.347	-0.35			
100										
101		0 / 0	B							
102		2 / 2	B						1.584	3.94
103		4 / 3	A	0.495	-0.51	0.366	-0.15			
104	x	0 / 0	A							
105		1 / 1	B							
107		3 / 3	A						0.894	0.48
108		0 / 0	B							
109	x	0 / 0	B							
110	x	0 / 0	B							
112		1 / 1	B						0.979	0.91
115		1 / 1	B							
117	x	6 / 3	A	0.518	-0.35	0.380	0.00			
118	x	5 / 2	B	0.639	0.50	0.414	0.36			
119	x	0 / 0	B							
120		0 / 0	A							
121		0 / 0	B							
122		6 / 3	B	0.904	2.37	0.707	3.44			
124		0 / 0	B							
125										
126		0 / 0	B							
127		0 / 0	B							
128		0 / 0	B							
129	x	2 / 2	A							
130		0 / 0	B							
131		0 / 0	B							
132		1 / 1	B						0.829	0.16
133		1 / 1	A							
134		6 / 3	B	0.636	0.48	0.351	-0.31			
136		5 / 2	A	0.518	-0.35	0.499	1.25			
137		0 / 0	B							
45										

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

‡ Assigned Value is too uncertain, therefore, z-scores are for information only

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				Fentin		Glufosinate		Maleic hydrazide	
Assigned Value [mg/kg]				0.167		0.271		0.689	
MRRL [mg/kg]				0.01		0.05		0.05	
Qn-RSD				37.1 %		16.9 %		27.7 %	
Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	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 %)
50		0 / 0	B						
52		7 / 4	A			0.235	-0.52		
54		0 / 0	B						
61		1 / 0	A						
94		0 / 0	B						
95		5 / 2	B						

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

Table 4-9: Laboratories ranked by the absolute z-scores achieved for each compound (where $2 < |z| \leq 3$ the ranking position is shown in bold, and where $|z| > 3$ in bold and italics)

				COMPULSORY Compounds					
				Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate
Assigned Value [mg/kg]				1.010	0.102	1.030	0.065	1.320	0.340
MRRL [mg/kg]				0.01	0.01	0.01	0.01	0.01	0.05
Qn-RSD				26.0 %	27.2 %	27.6 %	31.4 %	29.6 %	24.5 %
No. of Labs reporting results (incl. Third Country Laboratories)				97	81	95	61	97	53
Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
1	x	12 / 7	A	29	***79***	10		14	26
2	x	12 / 5	B	***92(FN)***	**70**	48	49	**88**	
3		13 / 8	A	9	69	10	36	34	1
4		13 / 8	A	12	9	60	11	60	43
5		11 / 7	A	4	35	46	26	25	
6	x	13 / 8	A	70	13	34	32	53	8
7		13 / 8	A	9	64	48	42	69	40
8		13 / 8	A	65	4	9	32	74	34
9		13 / 8	A	71	2	5	3	27	5
10	x	13 / 8	A	22	9	29	4	49	36
11	x	13 / 8	A	31	66	***88***	8	9	35
12	x	13 / 8	A	58	61	36	***57***	16	33
13		13 / 8	A	24	44	28	4	**89**	46
14		13 / 8	A	67	51	50	51	78	27
15									
16		9 / 5	B		18	40			23

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

			OPTIONAL Compound	BAC-C12		DDAC-C10		Diquat	Fosetyl	
			Assigned Value [mg/kg]	0.568		0.380		0.107‡	0.798‡	
			MRRL [mg/kg]	0.1		0.1		0.02	0.05	
			Qn-RSD	24.1 %		22.9 %		28.6 %‡	45.2 %	
Lab code SRM8-	NRL-SRM	No. Compounds Analysed / Correctly Found	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score‡ (FFP-RSD = 25 %)
50		0 / 0	B							
52		7 / 4	A	0.500	-0.48	0.350	-0.32	0.160		
54		0 / 0	B							
61		1 / 0	A					FN		
94		0 / 0	B							
95		5 / 2	B	0.186	-2.69	0.168	-2.23			

* Category A/B classification (Cat A was assigned to labs that have correctly detected 7 or more out of the 8 compulsory compounds and that have not reported any false positive result)
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

			COMPULSORY		OPTIONAL Compounds				
			Haloxyfop	Mepiquat	Fentin	Glu-fosinate	Maleic hydrazide	BAC 12	DDAC 10
		Assigned Value [mg/kg]	0.508	0.096	0.167	0.271	0.689	0.568	0.380
		MRRL [mg/kg]	0.01	0.01	0.01	0.05	0.05	0.1	0.1
		Qn-RSD	20.1 %	22.7 %	37.1 %	16.9 %	27.7 %	24.1 %	22.9 %
		No. of Labs reporting results (incl. Third Country Laboratories)	83	75	28	26	24	53	55
Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
1	x	12 / 7	A	11	22					
2	x	12 / 5	B	21	***75(FN)***	**25**			14	24
3		13 / 8	A	19	8	**24**			4	41
4		13 / 8	A	34	40					
5		11 / 7	A	68	58					7
6	x	13 / 8	A	35	32	9	7	3	19	23
7		13 / 8	A	5	66		15	22	37	14
8		13 / 8	A	23	66	9		1	12	33
9		13 / 8	A	57	31	**26**	23	15	43	35
10	x	13 / 8	A	9	50			12		
11	x	13 / 8	A	**78**	19		19			
12	x	13 / 8	A	**77**	51					
13		13 / 8	A	***81***	49	***28***	21	***24***	***47***	33
14		13 / 8	A	11	56	19	4	5	***52***	47
15										
16		9 / 5	B	61	52					

‡ Only compulsory compounds were considered.
(FN) = false negative results;
(FN)# = detected, but was not able to submit result due to technical problem. Judged as FN in accordance with the General Protocol

Table 4-9 (cont.): Laboratories ranked by the absolute z-scores achieved for each compound (where 2 < |z| ≤ 3 the ranking position is shown in bold, and where |z| > 3 in bold and italics)

				COMPULSORY Compounds					
				Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate
Assigned Value [mg/kg]				1.010	0.102	1.030	0.065	1.320	0.340
MRRL [mg/kg]				0.01	0.01	0.01	0.01	0.01	0.05
Qn-RSD				26.0 %	27.2 %	27.6 %	31.4 %	29.6 %	24.5 %
No. of Labs reporting results (incl. Third Country Laboratories)				97	81	95	61	97	53
Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
17									
18		3 / 2	B	48				23	
19		12 / 7	A	**87**	14	19	9	39	
21	x	13 / 8	A	36	49	20	18	9	9
22		7 / 5	B	48	57	66		73	
23		9 / 5	B		51		14		20
24		11 / 7	A	64	59	77	30	61	
25		13 / 8	A	40	11	59	36	30	38
26		11 / 7	A	6	18	54	**53**	68	
27		6 / 4	B	31		74		34	
28		4 / 3	B	36		1		30	
30		13 / 8	A	26	55	15	24	69	16
31	x	12 / 8	A	76	23	39	1	62	**49**
32		13 / 8	A	13	25	15	***58***	44	17
33	x	9 / 6	B	26	25	20	15	77	
34		2 / 1	B		32				
35		1 / 0							
36		10 / 6	B	14	35	5		5	
37		3 / 2	B			36		28	
38		11 / 7	A	38	4	58	43	38	
39									
40	x	13 / 8	A	28	4	79	16	26	10
41		12 / 7	A	74	4	24		57	30
42		4 / 2	B			53			
43		13 / 8	A	7	45	5	29	34	21
44		4 / 3	B	**88**		30		***97***	
46		12 / 7	A	68	41	78	38	63	
47		10 / 6	B	1	27		***60***	5	
48		13 / 8	A	77	31	71	28	55	28
49	x	12 / 7	A	21	2	**82**	11	33	
51		13 / 8	B	**85**	**71**	42	47	50	39
53	x	13 / 8	A	5	14	20	24	53	13
55	x	9 / 5	B	31			11	41	
56		13 / 8	A	55	47	***92***	21	85	41
57	x	7 / 5	B	9	***76***	**85**		1	

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

				COMPULSORY		OPTIONAL Compounds				
				Haloxyfop	Mepiquat	Fentin	Glu-fosinate	Maleic hydrazide	BAC 12	DDAC 10
	Assigned Value [mg/kg]			0.508	0.096	0.167	0.271	0.689	0.568	0.380
	MRRL [mg/kg]			0.01	0.01	0.01	0.05	0.05	0.1	0.1
	Qn-RSD			20.1 %	22.7 %	37.1 %	16.9 %	27.7 %	24.1 %	22.9 %
	No. of Labs reporting results (incl. Third Country Laboratories)			83	75	28	26	24	53	55
	Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
	17										
	18		3 / 2	B							
	19		12 / 7	A	74	40				45	42
	21	x	13 / 8	A	42	16	16			8	8
	22		7 / 5	B		1					
	23		9 / 5	B	72	35	18	***26 (FN)***		6	15
	24		11 / 7	A	45	6				38	27
	25		13 / 8	A	55	32	22	8	19	20	***53***
	26		11 / 7	A	22	39				30	***53 (FN)***
	27		6 / 4	B	25					10	1
	28		4 / 3	B							32
	30		13 / 8	A	***82***	46	20	6	9	29	50
	31	x	12 / 8	A	32	43		1		3	3
	32		13 / 8	A	73	14	3	25	8	33	30
	33	x	9 / 6	B	17					42	45
	34		2 / 1	B						26	29
	35		1 / 0								
	36		10 / 6	B	59	46					
	37		3 / 2	B							
	38		11 / 7	A	31	52					
	39										
	40	x	13 / 8	A	41	26		1	18	30	19
	41		12 / 7	A	38	61				27	28
	42		4 / 2	B	63					25	25
	43		13 / 8	A	5	15	13		11	5	10
	44		4 / 3	B							
	46		12 / 7	A	69	5					
	47		10 / 6	B	60	60	5			17	36
	48		13 / 8	A	70	27					
	49	x	12 / 7	A	29	19			14		
	51		13 / 8	B	71	**72**	9		16	44	26
	53	x	13 / 8	A	1	16					
	55	x	9 / 5	B	28	***74***				28	10
	56		13 / 8	A	***83***	65					
	57	x	7 / 5	B		43					

‡ Only compulsory compounds were considered.
(FN) = false negative results;
(FN)# = detected, but was not able to submit result due to technical problem. Judged as FN in accordance with the General Protocol

Table 4-9 (cont.): Laboratories ranked by the absolute z-scores achieved for each compound (where 2 < |z| ≤ 3 the ranking position is shown in bold, and where |z| > 3 in bold and italics)

				COMPULSORY Compounds					
				Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate
Assigned Value [mg/kg]				1.010	0.102	1.030	0.065	1.320	0.340
MRRL [mg/kg]				0.01	0.01	0.01	0.01	0.01	0.05
Qn-RSD				26.0 %	27.2 %	27.6 %	31.4 %	29.6 %	24.5 %
No. of Labs reporting results (incl. Third Country Laboratories)				97	81	95	61	97	53
Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
59		12 / 7	A	72	**75**	43	41	**87**	
60		0 / 0							
63		3 / 0	B			***92(FN)***			
64		13 / 8	A	73	35	43	17	46	**47**
65		5 / 4	B	48		32	23	83	
66									
67		10 / 5	B	***92(FN#)***	67	30	50	34	
68		7 / 4	B	**86**	68			51	
69		12 / 7	A	22	33	56		21	28
70	x	13 / 8	A	51	**72**	23	39	65	**48**
71		7 / 4	B	59		54		82	
72		13 / 8	A	46	35	62	45	41	13
73	x	4 / 3	B	81		5		71	
75		13 / 8	A	52	18	66	6	21	23
76		4 / 2	B	38					
77		9 / 5	B	60		1		48	42
78		6 / 3	B	84		27		83	
79		3 / 3	B	68		13		67	
80		12 / 7	A	80	30	15	**52**	**86**	
81	x	13 / 7	A	1	14	64	35	13	***50 (FN)***
82	x	12 / 7	A	55	27	35		19	7
83		12 / 7	A	60	33	66	43	80	
84		13 / 8	A	29	4	65	19	29	23
85									
86		3 / 2	B	7				16	
87		1 / 1	B						11
88		10 / 7	A	15	11	**83**	22	1	17
89		13 / 8	A	52	61	75	***56***	3	32
91		3 / 1	B						
92		1 / 1	B			14			
93		2 / 1	B						44
96		3 / 2	B	***92(FN)***		36		79	
97		4 / 3	B	52		***89***		55	
98		12 / 6	B	3	17	47		72	***50 (FN)***
99	x	13 / 8	A	16	58	10	9	5	30
100									

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

				COMPULSORY		OPTIONAL Compounds				
				Haloxyfop	Mepiquat	Fentin	Glu-fosinate	Maleic hydrazide	BAC 12	DDAC 10
			Assigned Value [mg/kg]	0.508	0.096	0.167	0.271	0.689	0.568	0.380
			MRRL [mg/kg]	0.01	0.01	0.01	0.05	0.05	0.1	0.1
			Qn-RSD	20.1 %	22.7 %	37.1 %	16.9 %	27.7 %	24.1 %	22.9 %
			No. of Labs reporting results (incl. Third Country Laboratories)	83	75	28	26	24	53	55
	Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
	59		12 / 7	A	19	69				**50**	46
	60		0 / 0							41	17
	63		3 / 0	B							
	64		13 / 8	A	51	30					
	65		5 / 4	B							
	66										
	67		10 / 5	B		35			20	***53***	***51***
	68		7 / 4	B	38		9			46	31
	69		12 / 7	A	9	11		9			
	70	x	13 / 8	A	16	57					
	71		7 / 4	B	13						
	72		13 / 8	A	48	59	8	18		32	39
	73	x	4 / 3	B						1	38
	75		13 / 8	A	35	27	4	5	7	35	20
	76		4 / 2	B	45					7	10
	77		9 / 5	B	**79**			**24**			
	78		6 / 3	B							
	79		3 / 3	B							
	80		12 / 7	A	40	37			6		
	81	x	13 / 7	A	23	29	21	10	13	9	4
	82	x	12 / 7	A	32	8		11		40	44
	83		12 / 7	A	4	18	***27***		4	1	8
	84		13 / 8	A	37	**70**	6	22	21	18	4
	85										
	86		3 / 2	B							
	87		1 / 1	B						36	***55***
	88		10 / 7	A	30					38	37
	89		13 / 8	A	75	52				**48**	**49**
	91		3 / 1	B	56						
	92		1 / 1	B							
	93		2 / 1	B				12			
	96		3 / 2	B						13	13
	97		4 / 3	B							
	98		12 / 6	B	43	19		1	1	34	40
	99	x	13 / 8	A	45	52	15		16	10	20
	100										

‡ Only compulsory compounds were considered.
(FN) = false negative results;
(FN)# = detected, but was not able to submit result due to technical problem. Judged as FN in accordance with the General Protocol

Table 4-9 (cont.): Laboratories ranked by the absolute z-scores achieved for each compound (where 2 < |z| ≤ 3 the ranking position is shown in bold, and where |z| > 3 in bold and italics)

				COMPULSORY Compounds					
				Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate
Assigned Value [mg/kg]				1.010	0.102	1.030	0.065	1.320	0.340
MRRL [mg/kg]				0.01	0.01	0.01	0.01	0.01	0.05
Qn-RSD				26.0 %	27.2 %	27.6 %	31.4 %	29.6 %	24.5 %
No. of Labs reporting results (incl. Third Country Laboratories)				97	81	95	61	97	53
Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
101		7 / 4	B	***90***		75		**90**	***50 (FN)***
102		11 / 6	B	44	**74**	72		9	
103		12 / 7	A	40	51		***55***	39	11
104	x	11 / 7	A	75	54	25	19	***93***	
105		8 / 4	B	***91***		80			4
107		13 / 8	A	47	41	33	27	3	22
108		7 / 5	B		61	70	46	75	
109	x	9 / 5	B	83		66		64	
110	x	5 / 3	B	60				57	
112		7 / 4	B	78	56	3		52	
115		9 / 4	B	17		26		44	***50(FN)***
117	x	11 / 7	A	31	1	60	6	23	
118	x	2 / 1	B						
119	x	11 / 6	B	65	***77(FN)***	73	1	**92**	
120		11 / 7	A	43	**73**	52		30	2
121		7 / 4	B	18	***77(FN)***	**84**		80	45
122		9 / 3	B	***92(FN)***	***80***	***91(FN)***		***95(FN)***	
124		4 / 3	B	19		43		9	
125									
126		10 / 6	B	24	46	41		46	
127		4 / 3	B	35		51		19	
128		5 / 4	B	19	35	***94***		5	
129	x	13 / 8	A	42	49	15	***59***	14	3
130		10 / 6	B	57	18	***90***		16	
131		6 / 4	B		29	***95***			
132		9 / 5	B	79	35		30	66	
133		11 / 7	A	***97***	48	3	32	***96***	
134		8 / 4	B		18		47		
136		11 / 7	A	63	41	63	40	41	
137		5 / 3	B	44		56		57	
45									
50		5 / 2	B		23				
52		12 / 7	A	82	64	***87***	***61***	75	6
54		2 / 1	B						37
61		13 / 8	A	89	***81***	**86**	54	**91**	13
94		5 / 3	B	***92(FN)***		80		***93***	17
95		4 / 2	B		60				

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

				COMPULSORY		OPTIONAL Compounds				
				Haloxyfop	Mepiquat	Fentin	Glu-fosinate	Maleic hydrazide	BAC 12	DDAC 10
			Assigned Value [mg/kg]	0.508	0.096	0.167	0.271	0.689	0.568	0.380
			MRRL [mg/kg]	0.01	0.01	0.01	0.05	0.05	0.1	0.1
			Qn-RSD	20.1 %	22.7 %	37.1 %	16.9 %	27.7 %	24.1 %	22.9 %
			No. of Labs reporting results (incl. Third Country Laboratories)	83	75	28	26	24	53	55
Lab code SRM8-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
101		7 / 4	B	53						
102		11 / 6	B	48	11			10		
103		12 / 7	A	13	11			**23**	24	6
104	x	11 / 7	A	7	68					
105		8 / 4	B		10		13			
107		13 / 8	A	64	1	1	13			
108		7 / 5	B	17						
109	x	9 / 5	B	51	63					
110	x	5 / 3	B	**76**						
112		7 / 4	B							
115		9 / 4	B	27			17			
117	x	11 / 7	A	43	61	1			14	1
118	x	2 / 1	B		23				23	22
119	x	11 / 6	B	2	6					
120		11 / 7	A	48	1					
121		7 / 4	B							
122		9 / 3	B	25	**71**	23			**49**	***52***
124		4 / 3	B							
125										
126		10 / 6	B	54	**73**					
127		4 / 3	B							
128		5 / 4	B							
129	x	13 / 8	A	58	23	17	20			
130		10 / 6	B	67	46					
131		6 / 4	B	15	45					
132		9 / 5	B	65						
133		11 / 7	A	66	63	14				
134		8 / 4	B	3	32	7			21	15
136		11 / 7	A	7	1				14	43
137		5 / 3	B							
45										
50		5 / 2	B		37					
52		12 / 7	A		40		15		21	17
54		2 / 1	B							
61		13 / 8	A	61	23					
94		5 / 3	B							
95		4 / 2	B	**80**					**51**	**48**

‡ Only compulsory compounds were considered.
(FN) = false negative results;
(FN)# = detected, but was not able to submit result due to technical problem. Judged as FN in accordance with the General Protocol

4.3.4 Laboratory classification based on scope

All participating laboratories that reported results were classified into categories A or B, based on their "scope" as reflected by the number of pesticides they correctly detected among the total number of compulsory pesticides present in the Test Item. Following the rules defined in the General Protocol (3rd Edition, see **Appendix 9**), in order to be classified into Category A a laboratory should have: a) correctly detected at least seven out of the eight compulsory pesticides present in the Test Item, and b) not reported any false positive results.

A total of 52 EU and EFTA labs (47 %) were classified into Category A (**Table 4-10**) and 58 (53 %) into Category B (**Table 4-11**). Two of the six Third Country and EU Candidate country labs were classified into Category A, and the other into Category B.

For informative purposes, the AAZ was calculated for all Category A labs. For the AAZ calculation any z-scores > 5 were set at 5. An AAZ of 1 indicates a 25 % deviation from the assigned value on average.

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

Lab-code SRM8-	NRL-SRM	Analysed / correctly found [1]	z-scores								AAZ [2]
			Captan	Cyroma-zine	Dicofol	Fenbutatin oxide	Folpet	Glypho-sate	Haloxyfop	Mepiquat	
1	x	12 / 7	-0.53	4.98	0.12		-0.15	0.47	0.08	-0.31	0.95
3		13 / 8	-0.16	-1.84	-0.12	-1.11	0.55	0.00	0.17	-0.08	0.50
4		13 / 8	0.22	-0.12	-1.13	0.25	1.03	1.58	-0.36	-0.67	0.67
5		11 / 7	-0.06	-0.71	-0.72	-0.84	0.30		-1.20	-1.10	0.71
6	x	13 / 8	-1.16	0.20	-0.53	1.05	-0.92	0.18	0.37	-0.46	0.61
7		13 / 8	0.16	1.49	0.82	-1.35	1.45	-1.33	-0.04	1.58	1.03
8		13 / 8	1.08	-0.08	-0.10	1.05	1.54	0.82	0.21	1.58	0.81
9		13 / 8	-1.21	-0.04	0.08	0.01	-0.39	-0.08	-0.76	-0.45	0.38
10	x	13 / 8	0.40	0.12	-0.45	-0.06	0.82	0.88	0.07	-0.81	0.45
11	x	13 / 8	0.55	1.57	3.30	-0.13	-0.09	-0.87	-2.26	0.29	1.13
12	x	13 / 8	-0.91	1.45	-0.55	4.49	0.18	-0.81	2.21	0.83	1.43
13		13 / 8	0.44	-0.78	-0.42	-0.06	2.30	-1.84	-3.11	-0.79	1.22
14		13 / 8	1.10	0.98	0.85	2.03	1.75	-0.56	0.08	1.04	1.05
19		12 / 7	-2.40	-0.24	-0.25	-0.18	-0.61		1.51	-0.67	0.84
21	x	13 / 8	0.59	0.94	0.27	0.37	0.09	0.19	0.55	-0.25	0.41
24		11 / 7	1.07	-1.37	-1.54	-0.92	1.06		0.58	0.04	0.94
25		13 / 8	-0.65	-0.16	1.05	-1.11	-0.48	-1.19	-0.73	-0.46	0.73
26		11 / 7	0.12	-0.35	0.97	2.28	1.42		0.20	-0.63	0.85
30		13 / 8	0.48	1.18	0.19	0.74	1.45	0.34	3.87	0.75	1.13
31	x	12 / 8	-1.44	-0.39	-0.57	0.00	-1.12	2.81	-0.35	-0.71	0.92
32		13 / 8	0.24	-0.47	0.19	5.05	0.67	0.35	1.50	-0.21	1.08
38		11 / 7	0.63	0.08	-1.03	1.42	0.58		0.33	-1.00	0.72
40	x	13 / 8	0.51	0.08	1.75	0.34	-0.36	0.21	-0.50	-0.34	0.51
41		12 / 7	1.31	-0.08	0.31		0.97	-0.71	-0.46	1.29	0.73

1) Only compulsory compounds were considered.
2) AAZ: Average of Absolute z-scores, calculated for informative purposes only for the labs in Category A.
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;
(FN)# = detected, but was not able to submit result due to technical problem. Judged as FN in accordance with the General Protocol

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

Lab-code SRM8-	NRL-SRM	Analysed / correctly found [1]	z-scores								AAZ [2]
			Captan	Cyroma-zine	Dicofol	Fenbutatin oxide	Folpet	Glypho-sate	Haloxyfop	Mepiquat	
43		13 / 8	-0.13	-0.82	0.08	-0.89	0.55	0.42	0.04	-0.23	0.39
46		12 / 7	-1.15	0.75	-1.67	-1.14	-1.15		-1.36	0.03	1.04
48		13 / 8	-1.45	-0.65	-1.30	-0.87	-0.94	-0.58	-1.38	0.38	0.94
49	x	12 / 7	-0.37	-0.04	2.12	-0.25	0.53		-0.30	-0.29	0.56
53	x	13 / 8	0.08	0.24	0.27	0.74	0.92	-0.29	0.00	0.25	0.35
56		13 / 8	-0.84	-0.87	-3.98	-0.52	-1.99	1.44	-3.90	1.50	1.88
59		12 / 7	-1.23	2.67	0.66	1.23	-2.18		0.17	1.67	1.40
64		13 / 8	1.27	0.71	0.66	0.35	-0.70	-2.12	0.65	0.42	0.86
69		12 / 7	0.40	0.67	1.01		0.24	-0.58	-0.07	-0.17	0.45
70	x	13 / 8	-0.80	-2.29	-0.30	1.15	-1.22	-2.38	0.12	-1.07	1.16
72		13 / 8	-0.72	-0.71	-1.14	1.48	-0.64	-0.29	-0.61	-1.17	0.84
75		13 / 8	0.83	0.35	1.24	-0.12	-0.24	-0.46	0.37	0.38	0.50
80		12 / 7	1.78	-0.64	-0.19	2.15	2.15		0.49	-0.58	1.14
81	x	13 / 7	0.00	0.24	1.20	-1.07	-0.12	-3.88 (FN)	-0.21	-0.40	0.89
82	x	12 / 7	-0.84	0.51	-0.54		-0.21	-0.15	0.35	0.08	0.38
83		12 / 7	0.95	0.67	1.24	1.42	1.85		0.03	-0.26	0.92
84		13 / 8	0.53	0.08	1.23	0.43	0.45	0.46	-0.41	2.25	0.73
88		10 / 7	-0.30	0.16	-2.21	-0.55	0.00	0.35	0.31		0.55
89		13 / 8	0.83	1.45	-1.50	3.45	0.03	0.72	1.52	1.00	1.31
99	x	13 / 8	-0.31	-1.33	0.12	0.18	-0.06	0.71	-0.58	1.00	0.54
103		12 / 7	-0.65	0.98		3.38	-0.61	0.22	0.09	-0.17	0.87
104	x	11 / 7	1.35	-1.05	0.32	-0.43	3.78		-0.06	-1.61	1.23
107		13 / 8	-0.73	0.75	-0.52	-0.86	-0.03	-0.44	-1.07	0.00	0.55
117		11 / 7	0.55	0.00	1.13	-0.12	0.27		-0.57	1.29	0.56
120		11 / 7	-0.67	2.31	-0.93		-0.48	-0.04	0.61	0.00	0.72
129	x	13 / 8	-0.66	0.94	0.19	[5.23]	-0.15	-0.05	0.79	0.33	1.01
133		11 / 7	7.29	0.90	-0.04	1.05	4.73		1.16	1.42	2.04
136		11 / 7	-0.98	-0.75	-1.15	-1.17	-0.64		0.06	0.00	0.68
52		12 / 7	-1.85	-1.49	-3.19	[21.85]	-1.72	0.09		-0.67	2.00
61		13 / 8	-2.70	[12.75]	-2.93	2.83	-2.66	0.29	-0.90	0.33	2.21
		AAZ [2]	**0.88**	**0.92**	**0.95**	**1.28**	**0.95**	**0.78**	**0.75**	**0.67**	
										Overall AAZ	**0.90**

1) Only compulsory compounds were considered.
2) AAZ: Average of Absolute z-scores, calculated for informative purposes only for the labs in Category A.
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;
(FN)# = detected, but was not able to submit result due to technical problem. Judged as FN in accordance with the General Protocol

Table 4-11: Category B laboratories ordered by lab-codes

Lab-code SRM8-	NRL-SRM	Analysed / correctly found [1)]	z-scores							
			Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate	Haloxyfop	Mepiquat
2	x	12 / 5	-3.96 (FN)	-2.08	-0.82	-1.66	-2.22		-0.19	-3.58 (FN)
16		9 / 5		-0.35	0.58			0.46	-0.90	1.00
18		3 / 2	0.79				0.27			
22		7 / 5	0.79	-1.29	1.24		1.52			0.00
23		9 / 5		0.98		0.26		0.39	1.46	0.50
27		6 / 4	-0.55		-1.44		-0.55		-0.22	
28		4 / 3	0.59		0.00		0.48			
33	x	9 / 6	-0.48	0.47	0.27	-0.27	1.73		-0.14	
34		2 / 1		-0.66						
35		1 / 0								
36		10 / 6	0.28	0.71	-0.08		0.06		0.84	-0.75
37		3 / 2			-0.55		-0.42			
42		4 / 2			-0.96				-1.06	
44		4 / 3	2.42		-0.47		4.79			
47		10 / 6	0.00	0.51		[8.31]	-0.06		0.87	1.21
51		13 / 8	2.14	2.27	0.62	1.60	-0.85	1.32	1.45	-2.75
55	x	9 / 5	0.55			-0.25	0.64		-0.29	-3.04
57	x	7 / 5	0.16	-3.59	2.91		0.00			0.71
60		0 / 0								
63		3 / 0			-3.98 (FN)					
65		5 / 4	0.79		0.50	-0.73	1.88			
67		10 / 5	-3.96 (FN)#	-1.65	0.47	-1.91	0.55			-0.50
68		7 / 4	-2.17	-1.76			-0.88		-0.46	
71		7 / 4	-0.92		0.97		-1.86		-0.09	
73	x	4 / 3	-1.83		-0.08		-1.48			
76		4 / 2	0.63						-0.58	
77		9 / 5	-0.95		0.00		-0.73	-1.45	-2.46	
78		6 / 3	1.90		0.39		1.88			
79		3 / 3	1.15		0.16		1.36			
86		3 / 2	-0.13				-0.18			
87		1 / 1						0.22		
91		3 / 1							0.75	
92		1 / 1			0.17					
93		2 / 1						-1.71		
96		3 / 2	-3.96 (FN)		-0.55		1.82			
97		4 / 3	0.83		3.34		0.94			
98		12 / 6	-0.04	-0.26	0.78		-1.49	-3.88 (FN)	0.57	0.29
101		7 / 4	-3.13		-1.50		-2.42	-3.88 (FN)	-0.67	
102		11 / 6	-0.71	-2.43	1.32		-0.09		-0.61	0.17
105		8 / 4	-3.41		-1.79			0.06		0.11
108		7 / 5		-1.45	-1.28	-1.54	-1.72		-0.14	
109	x	9 / 5	1.86		1.24		1.21		0.65	1.42
110	x	5 / 3	-0.95				-0.97		-2.03	
112		7 / 4	1.65	-1.25	-0.04		-0.90			
115		9 / 4	-0.33		0.35		-0.67	-3.88 (FN)	-0.26	

1) Only compulsory compouns were considered.
2) AAZ: Average of Absolute z-scores. 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;
(FN)# = detected, but was not able to submit result due to technical problem and was judged as ND according to the General Protocol

Table 4-11 (cont.): Category B laboratories ordered by lab-codes

Lab-code SRM8-	NRL-SRM	Analysed / correctly found [1]	z-scores							
			Captan	Cyromazine	Dicofol	Fenbutatin oxide	Folpet	Glyphosate	Haloxyfop	Mepiquat
118	x	2 / 1								-0.33
119	x	11 / 6	-1.08	-3.61 (FN)	-1.34	0.00	-2.84		0.01	-0.04
121		7 / 4	-0.34	-3.61 (FN)	-2.57		-1.85	-1.81		
122		9 / 3	-3.96 (FN)	[7.88]	-3.96 (FN)		-3.97 (FN)		0.22	-2.42
124		4 / 3	-0.36		-0.66		0.09			
126		10 / 6	0.44	0.86	-0.60		0.70		-0.68	2.83
127		4 / 3	-0.57		-0.88		0.21			
128		5 / 4	0.36	0.71	[10.14]		-0.06			
130		10 / 6	-0.85	-0.35	-3.57		-0.18		1.18	0.75
131		6 / 4		-0.56	[10.56]				-0.10	-0.74
132		9 / 5	-1.70	0.71		0.92	-1.30		-1.09	
134		8 / 4		0.35		1.60			0.02	-0.46
137		5 / 3	0.71		1.01		0.97			
50		5 / 2		-0.39						0.58
54		2 / 1						-0.91		
94		5 / 3	-3.96		-1.79		-3.78	-0.35		
95		4 / 2		1.41					-2.79	
		AAZ [2]	**1.36**	**1.46**	**1.31**	**1.31**	**1.22**	**1.56**	**0.76**	**1.10**
									Overall AAZ [2]	**1.24**

1) Only compulsory compouns were considered.
2) AAZ: Average of Absolute z-scores. 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;
(FN)# = detected, but was not able to submit result due to technical problem and was judged as ND according to the General Protocol

4.3.5 Laboratory feedback in case of poor performance

As a follow-up measure to this EUPT, participating laboratories that had achieved questionable or unacceptable z-scores were asked to give, where possible, reasons for their poor performance. A compilation of the feedback received by the laboratories is given in **Appendix 8**. By asking labs to provide this information, the organizer aimed to emphasize the importance of tracing potential sources of errors so that they can be avoided in the future. This information also provides input to NRLs on how to better assist labs in improving their performance.

In many cases the laboratories were not able to fully clarify the reasons for their poor performance. The most common explanations given concerned: a) problematic calibration (e.g., no use of IL-IS, no measure for the elimination of matrix effects for ***glufosinate***, ***dicofol***, ***cyromazine***, ***fenbutatin oxide*** and ***mepiquat***); b) degradation of standard solutions (for ***captan***, ***folpet***, ***fosetyl***, ***DDAC-C10*** and ***glyphosate***); c) inappropriate cleanup approach (for ***haloxyfop***); d) inappropriate method (for ***fenbutatin oxide*** and ***glyphosate***); e) technical problems; and f) calculation errors.

4.4 Methodological Information

Detailed information about the analytical methods used by the laboratories can be found in **Appendix 7**.

4.4.1 Initial temperature, soaking and extraction time for sample preparation

In order to ensure good homogeneity, the Organizer strongly recommended the laboratories mixing the received Test Items thoroughly before withdrawing any analytical portions. To reduce any losses of pesticides, it was further recommended keeping the temperature low, where possible by adding dry ice. Specific recommendations on the analytical procedure to be used were not made as the labs were prompted to use the procedures employed or intended to be employed routinely in their labs. As both temperature and soaking/extraction time can in some cases influence the stability or the extractability of pesticides, the participants were asked for the first time to indicate the initial temperature as well as the soaking and extraction times entailed in their procedure. This information for labs using QuEChERS or QuPPe is compiled in (**Table 4-12**). No clear trends regarding the impact of soaking time, extraction time or initial sample temperature on the results of pesticides could be seen.

Table 4-12: Initial temperature, soaking and extraction time for sample preparation using QuChERS and QuPPe methods

Soaking time	Extr. time	Initial sample temperature											
		QuEhERS						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
1 min	1 min	6	16	4	7	11		2				7	
	2 min			10		7				3			
	3 min		7			6			1			1	
	5 min			2									
	10 min				1								
	15 min		1	5		8				1		4	
	20 min	1											
	30 min					13							
2 min	1 min	6	1					10			1		
	2 min	9	3	10	6			6		1	4		
	3 min									5			
	5 min	2		4	12	2		1		1	5	6	
	10 min				3	5			4			3	
	15 min	8		8						7			
	30 min	5	5	2	4						2		
5 min	1 min	3	8		8				6		5		
	2 min		8			2			3			2	
	5 min		10	7	5	3				1	2		
	15 min											6	
	20 min	1						2					
	30 min					2							
	60 min				1								

Table 4-12 (cont.): Initial temperature, soaking and extraction time for sample preparation using QuChERS and QuPPe methods

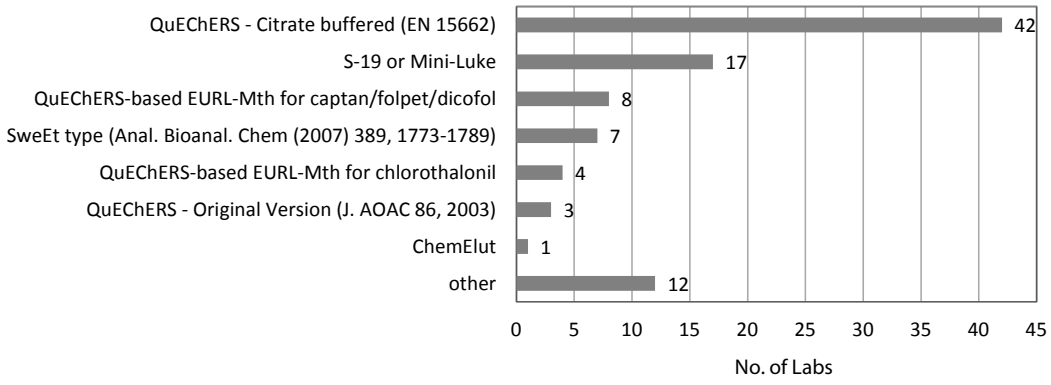
Soaking time	Extr. time	Initial sample temperature											
		QuEhERS						QuPPe					
		deep frozen (-18 °C)	slightly frozen (-8 °C - 0 °C)	just thawed	cold (4 °C -10 °C)	ambient (20 °C -24 °C)	no data	deep frozen (-18 °C)	slightly frozen (-8 °C - 0 °C)	just thawed	cold (4 °C -10 °C)	ambient (20 °C -24 °C)	no data
10 min	1 min	6			9	5					3	3	
	2 min			5						1			
	5 min					13							
	10 min				4	11							
	15 min	1	4					3				1	
	20 min	6											
	30 min											5	
15 min	1 min								4				
	10 min				5								
20 min	5 min									2	4		
	15 min											3	
	20 min				6								
	60 min			2									
	> 60 min				5								
30 min	1 min	1											
	2 min				1								
	5 min					1							
	10 min		4										
	15 min					4						1	
	30 min	1											
	60 min							2					
> 30 min	2 min				2						1	2	
	5 min					2							
	10 min	7						1					
no data	1 min	7	7	3	4	6	6	2				2	1
	2 min	3		8		1			1		4		
	3 min		2						2				
	5 min			3									
	10 min						4						1
	15 min			1					1				
	20 min	3											
	30 min					2							
	Sum	**76**	**76**	**74**	**83**	**104**	**10**	**29**	**22**	**22**	**31**	**46**	**2**

4.4.2 Analytical methods used

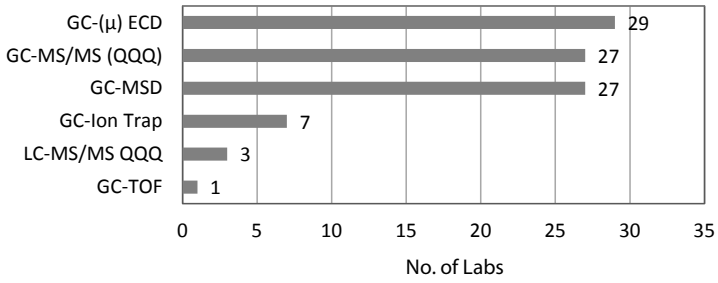
The distribution of methods used by the participating labs for the analysis of each analyte present in the Test Item can be seen in **Figure 4-1**.

Figure 4-1: Methods applied for sample preparation and determinative analysis as reported by labs[#]

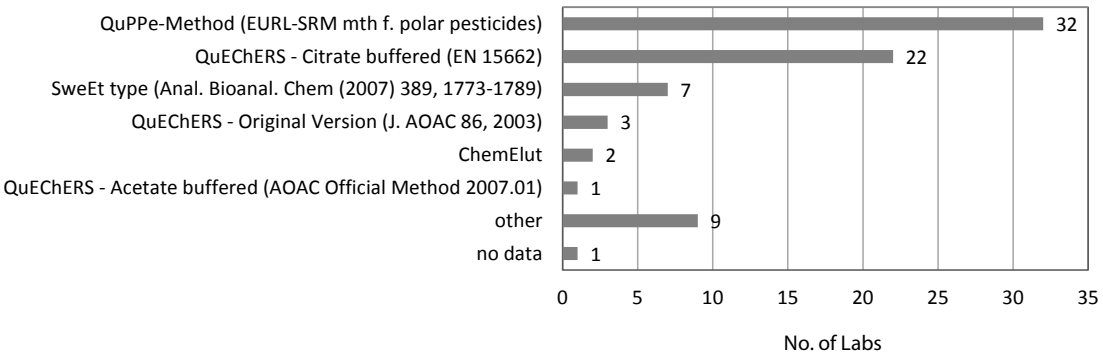
Captan: Sample preparation



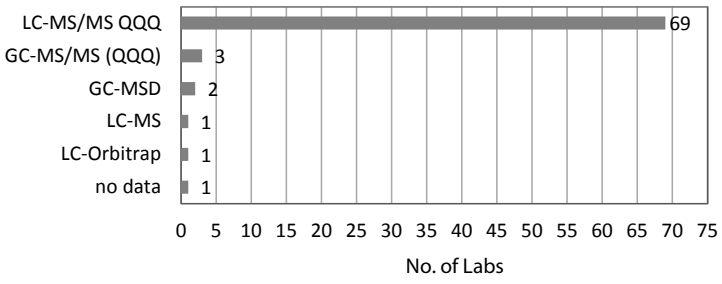
Captan: Determinative analysis



Cyromazine: Sample preparation



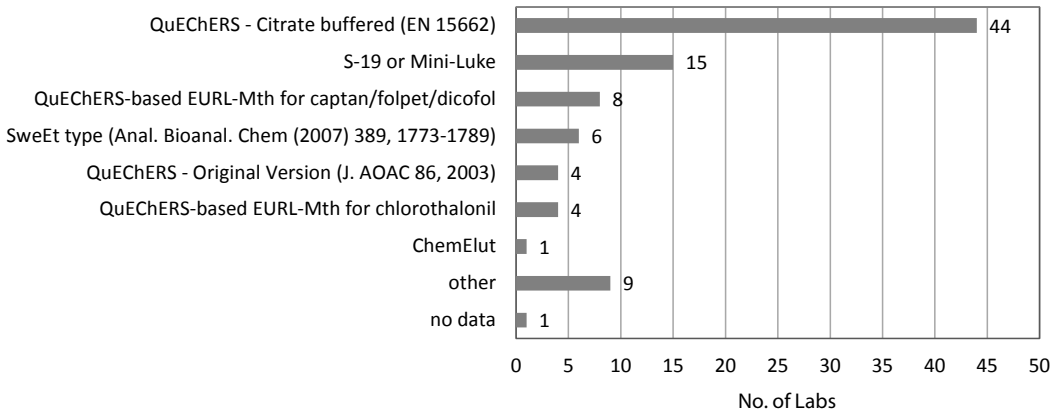
Cyromazine: Determinative analysis



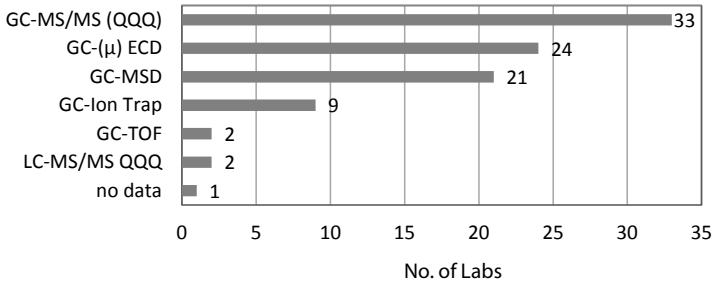
[#]: In case of non-conclusive information on methods labs were asked to check. However, some labs did not react to this request.

Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs[#]

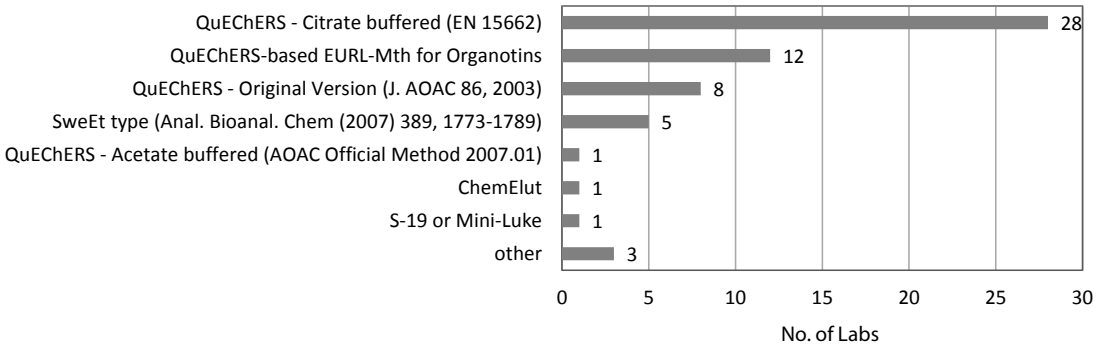
Dicofol: Sample preparation



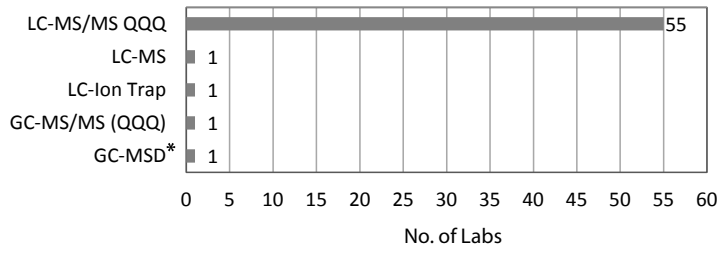
Dicofol: Determinative analysis



Fenbutatin oxide: Sample preparation



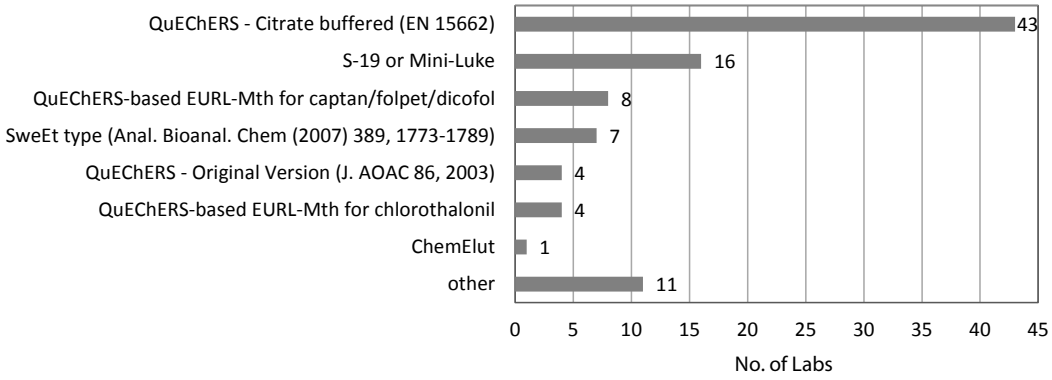
Fenbutatin oxide: Determinative analysis



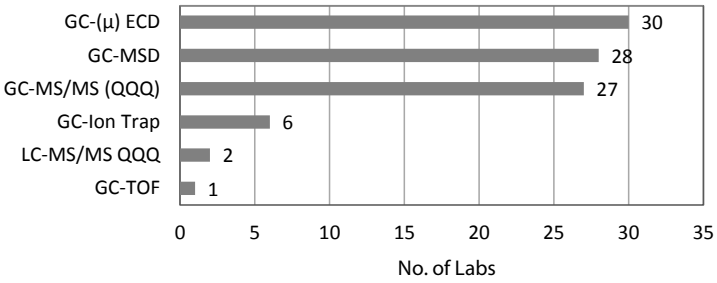
[#]: In case of non-conclusive information on methods labs were asked to check. However, some labs did not react to this request.
*: Methylation with tert-butylmethylether/methylmagnesiumchloride

Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs[#]

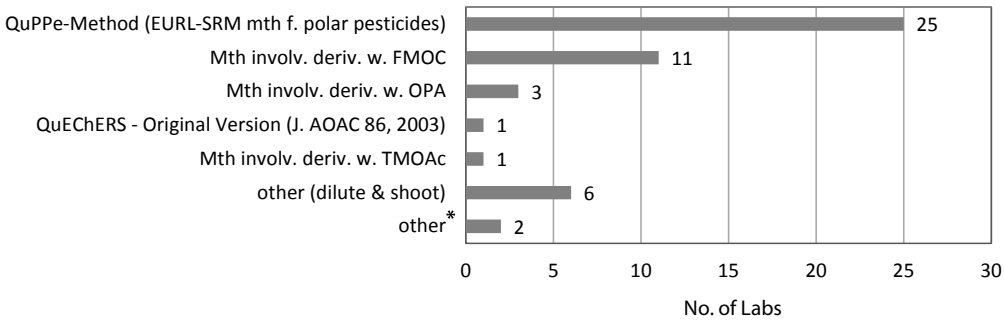
Folpet: Sample preparation



Folpet: Determinative analysis

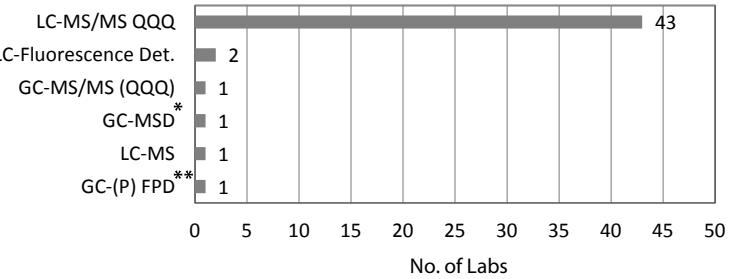


Glyphosate: Sample preparation



*: Derivatisation, one with (9-Fluorenylmethyl)-chlorformiat; the other with heptaflourobutanol & trifluroacetic anhydride

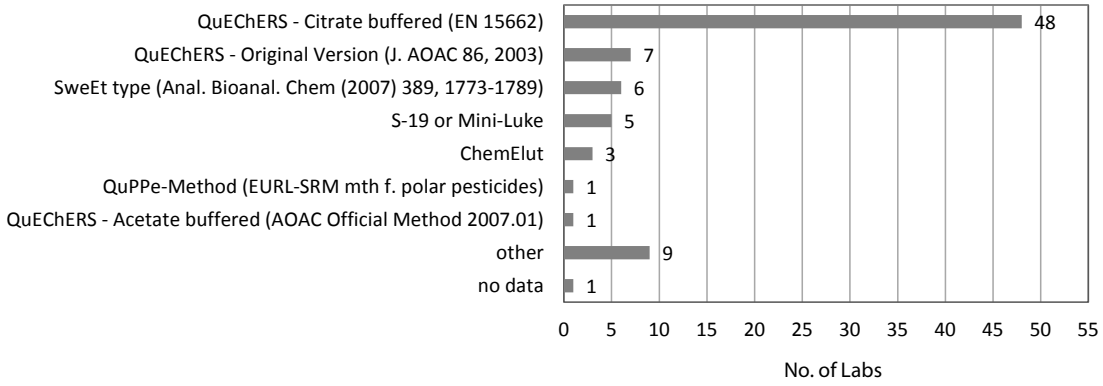
Glyphosate: Determinative analysis



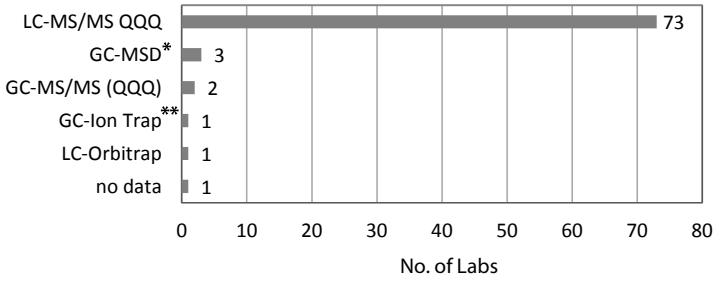
[#]: In case of non-conclusive information on methods labs were asked to check. However, some labs did not react to this request.
*: following derivatisation with heptaflourobutanol & trifluroacetic anhydride; **: following derivatisation with TMOAc

Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs[#]

Haloxyfop: Sample preparation



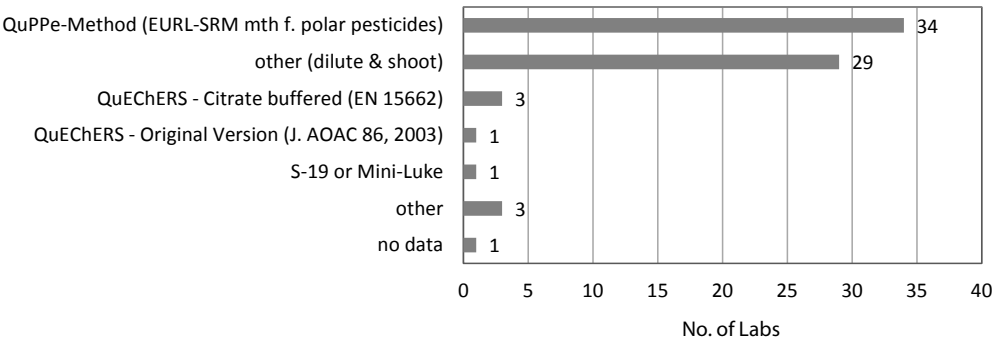
Haloxyfop: Determinative analysis



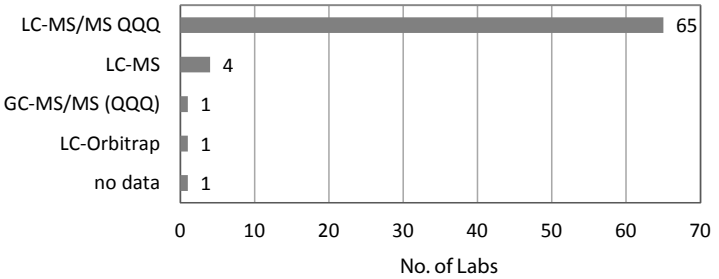
*: following derivatisation, one with tetrabutyl-ammoniumhydroxide/iosomethane, one with trimethylsulfonium hydroxide and the othe one with PFBBr

**: following derivatisation with TMS-diazomethane

Mepiquat: Sample preparation



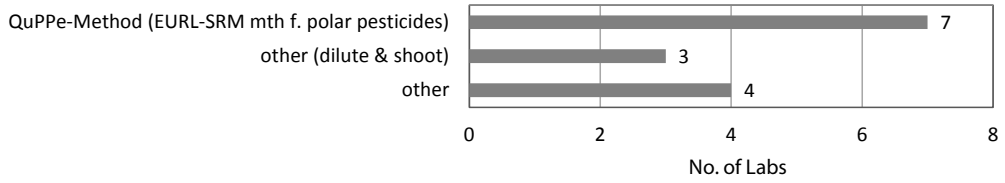
Mepiquat: Determinative analysis



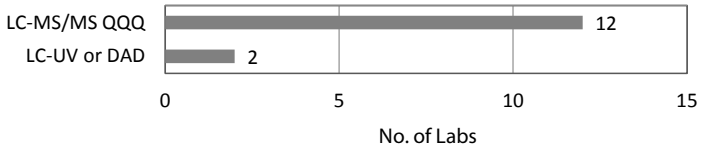
[#]: In case of non-conclusive information on methods labs were asked to check. However, some labs did not react to this request.

Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs[#]

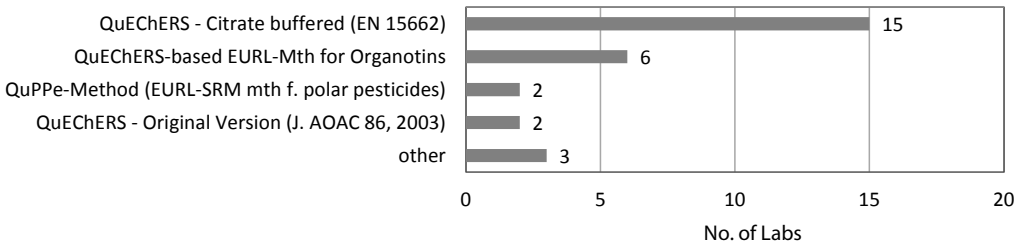
Diqaut: Sample preparation



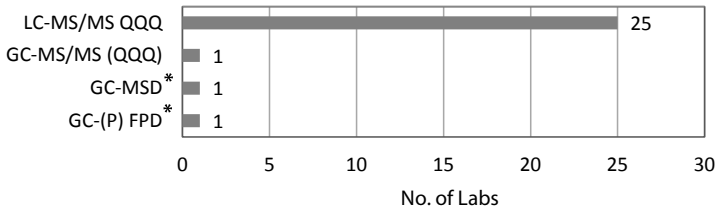
Diquat: Determinative analysis



Fentin: Sample preparation

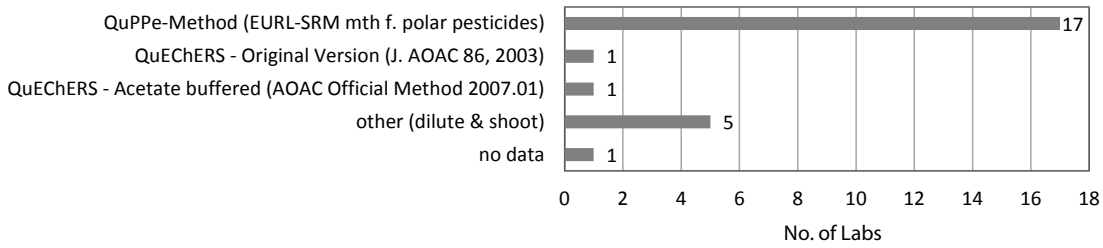


Fentin: Determinative analysis



*: Following methylation with tert-butylmethylether/methylmagnesiumchloride

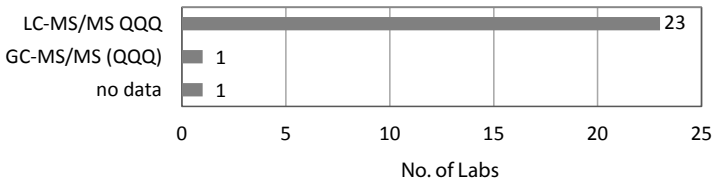
Fosetyl Sample preparation



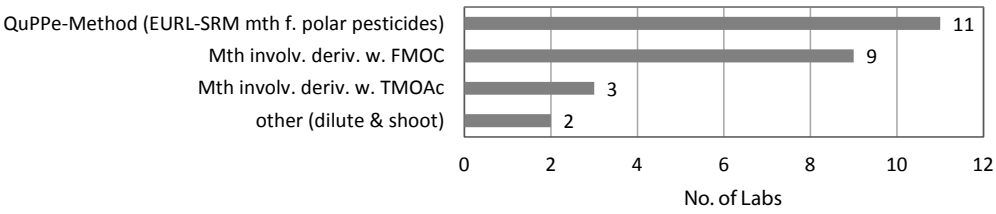
[#]: In case of non-conclusive information on methods labs were asked to check. However, some labs did not react to this request.

Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs[#]

Fosetyl: Determinative analysis



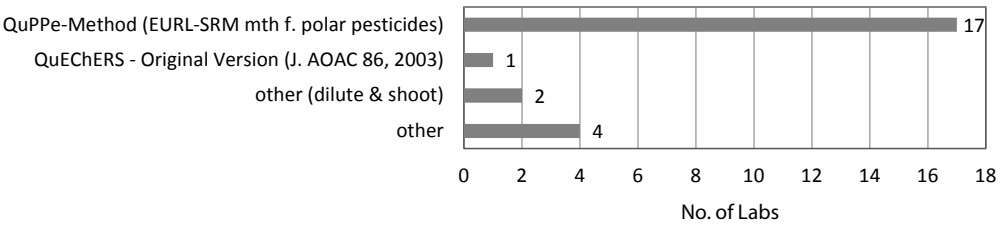
Glufosinate: Sample preparation



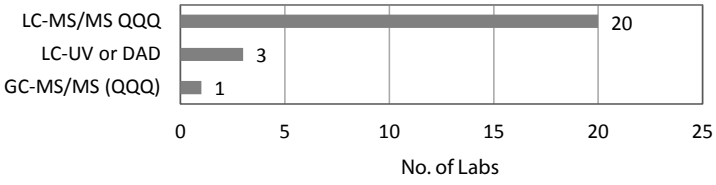
Glufosinate: Determinative analysis

*: following derivatisation with TMOAc

Maleic hydrazide: Sample preparation



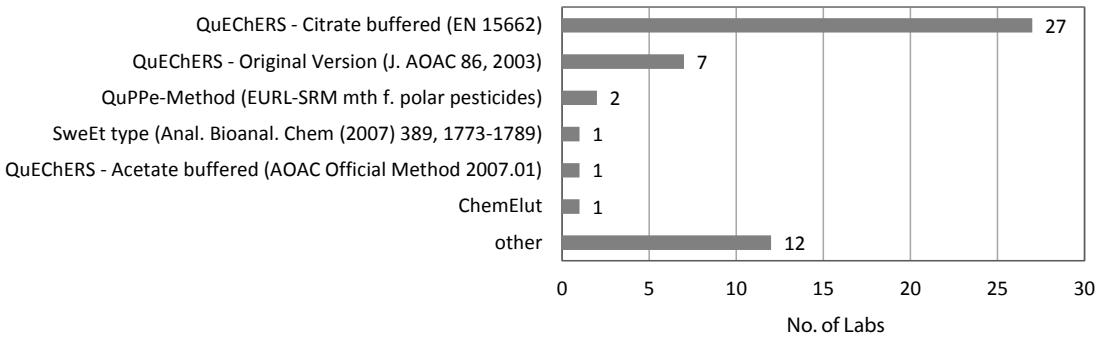
Maleic hydrazide: Determinative analysis



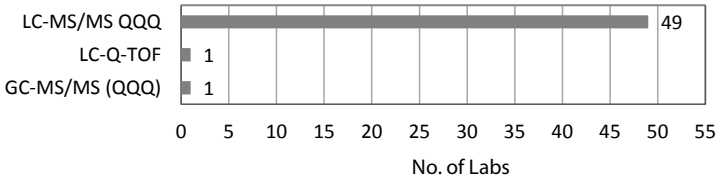
[#]: In case of non-conclusive information on methods labs were asked to check. However, some labs did not react to this request.

Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs[#]

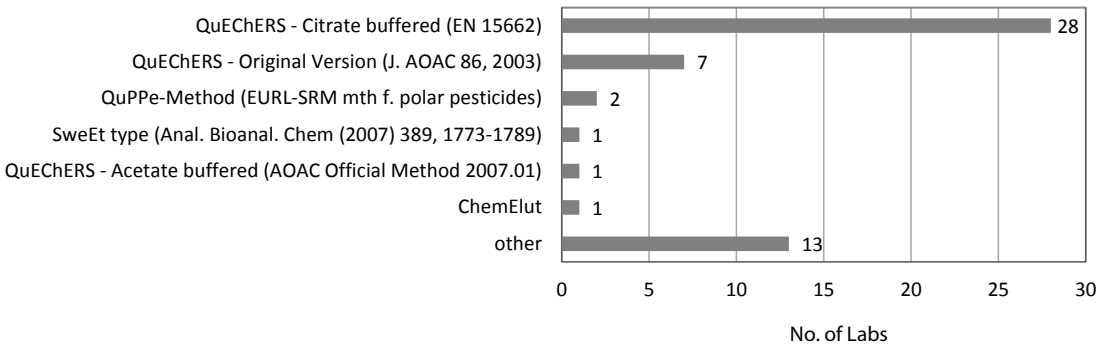
BAC-C12: Sample preparation



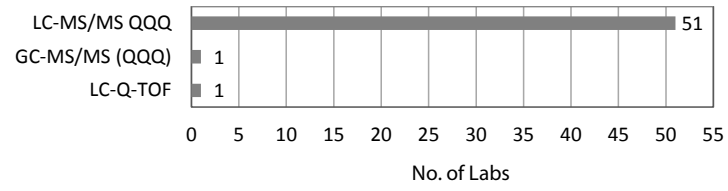
BAC-C12: Detection



DDAC-C10: Sample preparation



DDAC-C10: Detection



[#]: In case of non-conclusive information on methods labs were asked to check. However, some labs did not react to this request.

Table 4-13: Calibration approaches employed for the analysis of the pesticides in the EUPT-SRM8

Calibration type	COMPULSORY COMPOUNDS	Optional compounds
Matrix matched	**466 (75 %)**	**156 (71 %)**
Multiple level	412 (67 %)	141 (64 %)
Single level	54 (8.7 %)	15 (6.8 %)
Pure solvent	**78 (13 %)**	**47 (21 %)**
Multiple level	67 (11 %)	45 (21 %)
Single level	11 (1,8 %)	2 (0.9 %)
Standard addition to…	**69 (11 %)**	**16 (7.3 %)**
Sample portions	48 (7,8 %)	11 (5.0 %)
Extract aliquots	21 (3,4 %)	5 (2.3 %)
no data	5 (0.8 %)	1 (0.5 %)
Sum	**618 (100 %)**	**220 (100 %)**

4.4.3 Calibration approaches

Calibration types employed in the current PT are shown in **Table 4-13**.

4.4.4 Use of Internal standards (ISTDs)

ISTDs applied in this PT to correct for recovery and/or to compensate for the influence of matrix on measurement or during derivatisation are shown in **Table 4-14**.

Table 4-14: Use of internal standards for the analysis of the pesticides in the EUPT-SRM8

	COMPULSORY COMPOUNDS								OPTIONAL COMPOUNDS							
ISTD used	**Captan**	**Cyromazine**	**Dicofol**	**Fenbutatin oxide**	**Folpet**	**Glyphosate**	**Haloxyfop**	**Mepiquat**	**Diquat**	**Fentin**	**Fosetyl**	**Glufosinate**	**Maleic hydrazide**	**BAC-C12**	**DDAC-C10**	**Sum**
Yes, isotop. labelled target pesticide	7	10	5		8	**31**	1	**33**	**7**	1	8	7	8	1	1	128
Yes, isotop. labelled other substance	6	11	8	9	7	2	11	9	1	4	2	7		4	5	86
Yes, other	**41**	16	**38**	22	**40**		26	6		10		1	1	15	16	232
No	**40**	**39**	**40**	**28**	**39**	16	**42**	23	6	**13**	**14**	**10**	**15**	**31**	**31**	387
no data		1	1				1	1			1					5
Sum	**94**	**77**	**92**	**59**	**94**	**49**	**81**	**72**	**14**	**28**	**25**	**25**	**24**	**51**	**53**	**838**

4.4.5 Correction of results for recovery

The various approaches employed by the labs to correct their results for recovery are compiled in **Table 4-15**.

In all 73 cases where recovery correction was applied using a recovery figure the respective experiments were conducted within the same batch, using the blank material provided by the Organizer. 19 labs used

Table 4-15: Overview of approaches followed by laboratories for the correction of results for recovery

	COMPULSORY COMPOUNDS								
Are results recovery corrected?	**Captan**	**Cyromazine**	**Dicofol**	**Fenbutatin oxide**	**Folpet**	**Glyphosate**	**Haloxyfop**	**Mepiquat**	**Sum**
Yes	**20 (21 %)**	**33 (43 %)**	**23 (39 %)**	**21 (22 %)**	**24 (49 %)**	**28 (30 %)**	**18 (22 %)**	**36 (50 %)**	**203 (33 %)**
1): using **recovery figure** (as indicated)	4	**13**	**6**	8	6	3	5	6	51 (8 %)
2): autom. via **std. add.** to sample portions	**9**	9	**11**	**8**	12	**4**	8	6	67 (11 %)
3): autom. via **IL-IS**	3	5	3	2	**3**	14		**19**	49 (8 %)
4): autom. via **combination of 2) + 3)**	1	3				3		3	10 (2 %)
5): autom. via **procedural calibration**	3	3	3	3	3	4	5	2	26 (4 %)
No [thereof using **Matrix-Matched calibration**]	**70** [61]	**42** [33]	**68** [60]	**38** [29]	**69** [60]	**17** [12]	**63** [49]	**35** [24]	**402 (65 %)**
no data	4	2	1		1	4		1	13 (2 %)
Overall SUM	**94**	**77**	**59**	**94**	**49**	**92**	**81**	**72**	**618**
	OPTIONAL COMPOUNDS								
Are results recovery corrected?	**Diquat**	**Fentin**	**Fosetyl**	**Glufosinate**	**Maleic hydrazide**	**BAC-C12**	**DDAC-C10**	**Sum**	
Yes	**10 (71 %)**	**11 (39 %)**	**12 (48 %)**	**14 (56 %)**	**13 (54 %)**	**14 (27 %)**	**14 (26 %)**	**88 (40 %)**	
1): using **recovery figure** (as indicated)	**3**	**4**	2	1	2	**5**	**5**	22 (10 %)	
2): autom. via **std. add.** to sample portions	1	3	**3**	**4**	**4**	**5**	**5**	25 (11 %)	
3): autom. via **IL-IS**	5	2	**5**	**5**	**6**	2	2	27 (12 %)	
4): autom. via **combination of 2) + 3)**				1				1 (0 %)	
5): autom. via **procedural calibration**	1	2	2	3	1	2	2	13 (6 %)	
No [thereof using **Matrix-Matched calibration**]	**2** [1]	**17** [12]	**11** [7]	**10** [8]	**11** [5]	**37** [27]	**38** [28]	**126 (57 %)**	
no data	2		2	1			1	6 (3 %)	
Overall SUM	**14**	**28**	**25**	**25**	**24**	**51**	**53**	**220**	

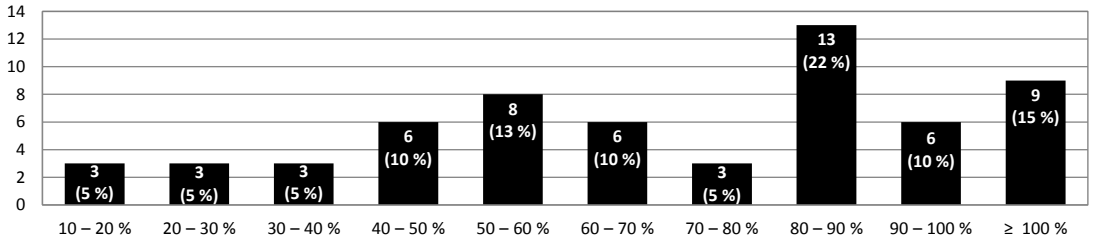


Figure 4-2: Distribution of recovery figures used for results correction for the recovery

recovery figures based on only one recovery experiment, 18 labs based on two replicate recovery experiments; 3 labs used recovery figures based on three, four, or five replicate recovery experiments; 11 labs used recovery figures obtained from more than 5 replicate recovery experiments. 10 labs did not give information this concerning. The distribution of the recovery figures are shown in **Figure 4-2**.

Regardless one false negative result and the results reported for ***diquat*** and ***fosetyl***, for which the z-scores are evaluated for information only due to insufficient number of reported result for statistical evaluation or high statistical uncertainty of the Assigned Value, the remaining 67 cases concerned ***cyromazine*** (13 cases), ***fenbutatin oxide*** (8 cases), ***folpet*** and ***mepiquat*** (each 6 cases), ***dicofol***, ***haloxyfop***, ***BAC-C12*** and ***DDAC-C10*** (each 5 cases), ***captan*** and ***fentin*** (each 4 cases) ***glyphosate*** (3 cases), ***maleic hydrazide*** (2 cases) as well as ***glufosinate*** (1 case). Recovery correction using a recovery factor typically leads to a result closer to the Assigned Value than when no recovery correction had been applied. As shown in **Table 4-16**, laboratories applying a recovery factor were able to "shift" their z-scores from unacceptable to acceptable levels in 6 cases, from questionable to acceptable in 14 cases and from unacceptable to questionable in 2 cases. In 35

Table 4-16: Compilation of results where correction of results for recovery using a recovery figure was applied

Pesticide	LabCode	Submitted Recovery figure [%]	Recovery Replicates considered	Submitted Result [mg/kg]	z-score derived from submitted result	z-score (if non-corrected results were used)*
Captan	3	115	no data	0.970	-0.16	0,42
	51	90	> 5	1.550	2.14	1,52
	71	64.3	1	0.777	-0.92	-2,02
	120	90	4	0.841	-0.67	-1,00
Cyromazine	1	24	1	0.229	4.98	-1,84
	3	53	no data	0.055	-1.84	-2,86
	13	50.7	1	0.082	-0.78	-2,37
	19	46.5	1	0.096	-0.24	-2,25
	31	50.1	3	0.092	-0.39	-2,19
	36	52	> 5	0.120	0.71	-1,55
	38	46	1	0.104	0.08	-2,12
	51	90	> 5	0.160	2.27	1,65
	57	30	2	0.0104	-3.59	-3,88
	107	35	2	0.121	0.75	-2,34
	120	64.8	5	0.161	2.31	0,09
	130	23	2	0.093	-0.35	-3,16
	133	50.2	> 5	0.125	0.90	-1,54
Dicofol	3	90	no data	1.000	-0.12	-0,50
	37	114	2	0.889	-0.55	-0,06

* Calculated using the current Assigned Values

Table 4-16 (cont.): Compilation of results where correction of results for recovery using a recovery figure was applied

Pesticide	LabCode	Submitted Recovery figure [%]	Recovery Replicates considered	Submitted Result [mg/kg]	z-score derived from submitted result	z-score (if non-corrected results were used)*
Dicofol	51	90	> 5	1.190	0.62	0,16
	81	122.8	1	1.340	1.20	-1,92
	120	82	4	0.791	-0.93	-1,48
Fenbutatin oxide	2	50	2	0.038	-1.66	-2,83
	3	91	no data	0.047	-1.11	-1,37
	8	83	2	0.082	1.05	0,19
	13	84.6	1	0.064	-0.06	-0,67
	19	51.8	1	0.062	-0.18	-2,02
	31	72.3	1	0.065	0.00	-1,11
	38	47	1	0.088	1.42	-1,45
	51	90	> 5	0.091	1.60	1,04
Folpet	3	118	no data	1.500	0.55	1,36
	37	50	2	1.182	-0.42	-2,21
	51	90	> 5	1.040	-0.85	-1,16
	64	147	2	1.090	-0.70	0,86
	71	75.5	1	0.705	-1.86	-2,39
	120	80	4	1.160	-0.48	-1,19
Glyphosate	3	98	no data	0.340	0.00	-0,08
	13	130	2	0.184	-1.84	-1,19
	51	90	1	0.452	1.32	0,79
Haloxyfop	3	93	no data	0.530	0.17	-0,12
	13	66	1	0.113	-3.11	-3,41
	51	90	> 5	0.692	1.45	0,90
	71	115	1	0.496	-0.09	0,49
	110	16	1	0.250	-2.03	-3,69
Mepiquat	3	97	no data	0.094	-0.08	-0,20
	13	90	2	0.077	-0.79	-1,11
	51	90	1	0.030	-2.75	-2,88
	119	48	2	0.095	-0.04	-2,10
	130	40	2	0.114	0.75	-2,10
	133	62.1	> 5	0.130	1.42	-0,64
Fentin	3	106	no data	0.069	-2.35	-3,71
	8	90	2	0.194	0.65	-3,31
	51	90	> 5	0.140	-0.65	-3,50
	107	62	2	0.167	0.00	-3,59
Glufosinate	13	88	2	0.324	0.79	0,21
Maleic hydrazide	13	40	2	0.160	-3.07	-3,63
	51	90	1	0.854	0.96	4,09
BAC-C12	3	92	no data	0.560	-0.06	-0,37
	13	84	1	0.273	-2.08	-2,39
	23	41	2	0.554	-0.10	-2,40
	51	90	5	0.334	-1.65	-1,88
	87	113.7	3	0.691	0.87	1,53
DDAC-C10	3	89	no data	0.480	1.05	0,50
	13	80.6	1	0.306	-0.78	-1,40
	23	16	2	0.351	-0.31	-3,41
	51	90	5	0.333	-0.49	-0,85
	87	56.7	3	1.005	6.58	2,00

* Calculated using the current Assigned Values

Table 4-16 (cont.): Compilation of results where correction of results for recovery using a recovery figure was applied

Pesticide	LabCode	Submitted Recovery figure [%]	Recovery Replicates considered	Submitted Result [mg/kg]	z-score derived from submitted result	z-score (if non-corrected results were used)*
Overall	**23 labs**	**67 cases**	1 repl. (19×) 2 repl. (18×) 3 repl. (3×) 4 repl. (3×) 5 repl. (3×) > 5 repl. (10×) no data (11×)		**AAZ = 1.12** 55× Acceptable 7× Questionable 5× Unacceptable	**AAZ = 1.72** 40× Acceptable 16× Questionable 11× Unacceptable
* Calculated using the current Assigned Values						

cases z-scores remained within the acceptable range, in 2 cases within the questionable range and in three cases within the unacceptable range. There were also 3 cases where the z-score paradoxically shifted from acceptable to questionable and 2 cases even from acceptable to unacceptable. When comparing the AAZ of the submitted results recovery corrected with the AAZ of the results that would have been submitted if no recovery correction had been applied, a significant decline from 1.72 to 1.12 is observed. Similar observations were made in EUPT-C5/SRM6 and EUPT-SRM7.

4.4.6 Frequent errors and critical points in this PT

The following aspects were considered concerning the analysis of certain pesticides and are thus highlighted below:

Dicofol: ***Dicofol*** is extensively and sometimes even completely, degraded during sample preparation and GC analysis. This results in poor recoveries and poor analytical precision. However, only 5 of 96 laboratories in this PT have used the isotopically labelled ***dicofol*** (e.g. ***dicofol***-D8). The use of isotopically labelled internal standards is, in general, the most efficient and convenient way to eliminate most sources of errors. If added to the final extract the ISTD can match for any decomposition and signal fluctuations in GC. If added at the beginning of the procedure it will also match for any losses during extraction. Of high importance is, however, that a measurable signal is obtained for both ***dicofol*** and ***dicofol***-D8. Thus, measures should be taken to minimize ***dicofol*** degradation during entire procedure. Skipping dispersive SPE with PSA and the use of calibration standards on blank extracts or analyte protectants (APs) is strongly recommended. Degradation of the standard solutions is another critical aspect to be considered. Acidification with acetic acid (e.g., 0.4 % in acetonitrile) can help to minimize degradation of ***dicofol*** to p,p'-dichlorobenzophenone, which is not part of the residue definition. For further information please see: http://www.eurl-pesticides.eu/library/docs/srm/EurlSrm_Observations_***dicofol***.pdf

Fosetyl: The EUPT-SRM8 was the first PT in which ***fosetyl*** was spiked to the test material. The commercially available reference substance is ***fosetyl***-aluminium (aluminium tris(O-ethylphosphonate) with the molecular weight of 354.14 g/mol. Each ***fosetyl***-aluminium contains one aluminium cation and three ***fosetyl*** anion moieties. ***Fosetyl*** (ethyl hydrogen phosphonate) has a molecular weight of 110.03 g/mol. If ***fosetyl***-aluminium is used for the preparation of calibration solution, a factor not of 0.311 (= 110.3/354.14) but of 0.932 (= (110.3 x 3)/354.14) must be applied to convert the concentration of ***fosetyl***-aluminium to ***fosetyl***.

Haloxyfop and other acidic pesticides: Eight of 81 laboratories that have tested for ***haloxyfop*** used PSA during dispersive SPE clean up. As shown in **Figure 4-3** seven out of those eight laboratories had a negative z-score, including 3 between -2 and -3 and one false negative. In the case using PSA but with a positive z-score the respective laboratory had corrected its result via procedural calibration. As already mentioned in the reports and at the workshops of previous EUPT-SRMs, PSA has a tendency to remove organic acids from

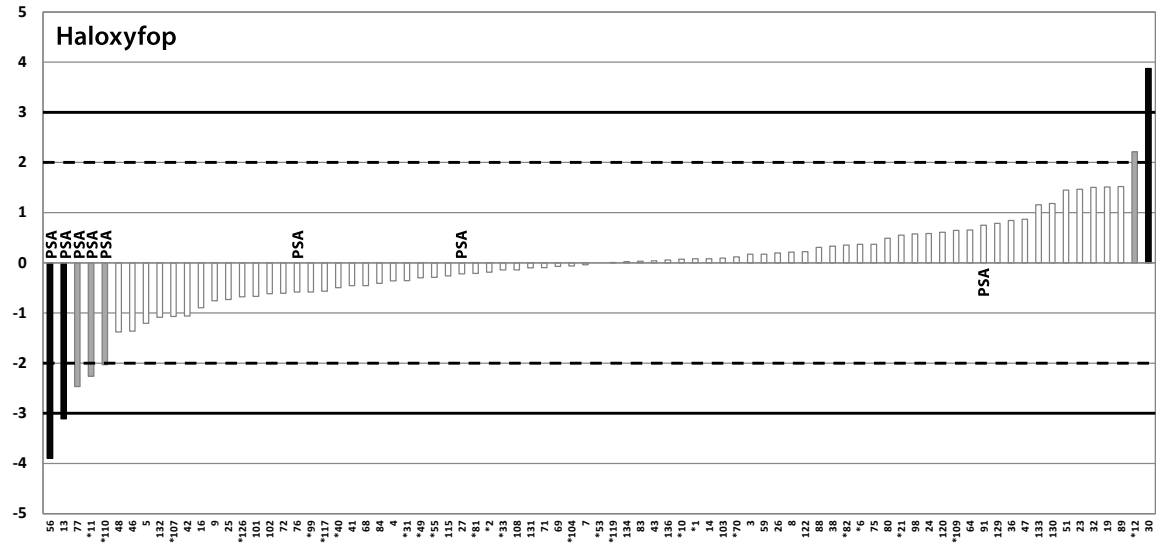


Figure 4-3: Z-scores achieved by the participating labs for haloxyfop; PSA: using PSA during dSPE cleanup

extracts and it is, therefore, not recommended to be used in the cleanup step for acidic pesticides (e.g. ***2,4-D***, ***haloxyfop*** and ***quinclorac***).

Furthermore, 10 out of 81 laboratories that analysed for ***haloxyfop*** employed a hydrolysis step: 9 of them employed alkaline hydrolysis, one of them acidic hydrolysis. Although our own experiments have shown that alkaline hydrolysis had practically no impact on ***haloxyfop*** levels determined, the use of a hydrolysis step should have been avoided as only the concentration of the free acid was requested in the Target Pesticides List. As the impact of hydrolysis was negligible, the 10 results submitted by labs employing hydrolysis were not eliminated from the population for establishment of the Assigned Values.

Use of isotopically labelled internal standards (IL-IS): The use of an IL-IS is generally considered as the most effective approach for eliminating all kinds of errors in pesticide residue analysis. It can compensate for variations in sample extraction and the influence of matrix on the LC-MS/MS analysis due to its nearly identical chemical and physical properties to the unlabelled analyte. As demonstrated in **Table 4-17** in the case of ***glyphosate*** and ***mepiquat*** laboratories using IL-IS reported results with clearly lower Qn-RSDs and AAZs. Wherever possible, it is strongly recommended using IL-ISs during sample preparation.

Table 4-17: Impact of using isotopically labelled target pesticide as internal standard (IL-IS) on the results

	Glyphosate			Mepiquat		
	all results	results obtained using IL-ISs	results obtained without IL-ISs	all results	results obtained using IL-ISs	results obtained without IL-ISs
Assigned Value ([mg/kg])	0.340	0.350	0.291	0.096	0.097	0.092
Qn-RSD	24.5 %	**16.4 %**	38.6 %	22.7 %	**18.8 %**	27.7 %
AAZ	1.02	0.70	1.53	0.80	0.58	0.98
No. of results [1)]	49	31	18	72	32	40
No. (%) of acceptable results	42 (86 %)	28 (90 %)	14 (78 %)	66 (92 %)	32 (100 %)	34 (85 %)
No. (%) of questionable results	3 (6 %)	2 (6 %)	1 (6 %)	4 (6 %)	0 (0 %)	4 (10 %)
No. (%) of unacceptable [1)] results	4 (8 %)	1 (3 %)	3 (17 %)	2 (3 %)	0 (0 %)	2 (5 %)
No. (%) of false negative results	4 (8 %)	1 (3 %)	3 (17 %)	1 (1 %)	0 (0 %)	1 (3 %)

1) including false negative results

Influence of pH value on the extraction of organotins: Generally, using citrate-buffered QuEChERS organotin compounds tend to give low recoveries in various types of commodities. Commodities with high pH values are typically the most affected. Recovery improvements can be achieved by lowering the pH (e.g., with sulfuric or acetic acid). For detailed information please see: http://www.eurl-pesticides.eu/library/docs/srm/EURL_observations_Organotins.pdf.

4.4.7 Coverage of compounds in routine scope and analytical experience of labs

As can be seen in **Figure 4-4** the percentage of participating labs that covered the various compounds in the EUPT-SRM8 Target Pesticides List varied greatly ranging from 45 % (***glyphosate***) to 90 % (*chlorothalonil*) in the case of compulsory compounds and between 13 % (***diquat***) and 48 % (***DDAC-C10***) for the optional ones. If calculated based on the full number of labs that were considered as being obliged to take part

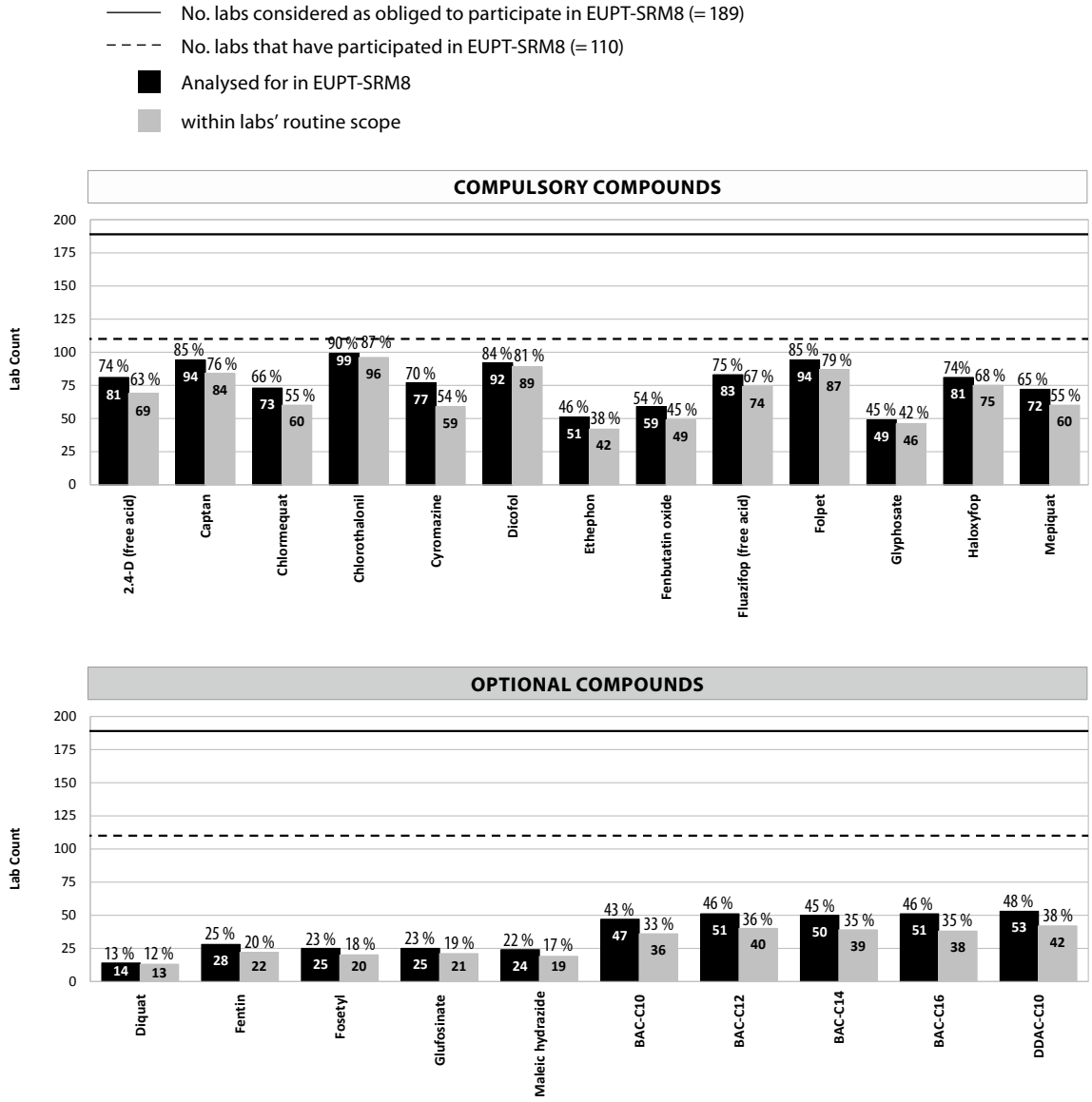


Figure 4-4: Number of laboratories targeting pesticides within their routine scope and within the framework of the EUPT-SRM8

in this test ($n = 189$), the percentages become considerably smaller. Nevertheless, it is interesting to see that in all cases the number of laboratories targeting a pesticide in this EUPT was always higher than the number of laboratories routinely analysing for it, i.e., some labs have targeted certain pesticides in the PT even though these compounds were not within their routine scope. This suggests that there is an obvious capacity and intention for substantial progress in the official controls of SRM-pesticides.

96 % of all cases in the compulsory compounds covered routinely by labs participating in this EUPT were also targeted by those labs in this exercise (**Table 4-18**). Many participating labs (on average 29 %) analysed compounds even although they are not yet included in their routine scope (155 cases overall and 96 cases concerning compulsory compounds contained in the Test Item). This indicates that many labs are in the process of expanding their scope with additional SRM-compounds. The compounds most frequently analysed by labs but not yet included in their routine scope were ***cyromazine*** (20 labs), *chlormequat* (16 labs), ***mepiquat*** (15 labs) and *2,4-D* (14 labs). Like in EUPT-SRM7 ***glyphosate*** and *ethephon* were the compounds most frequently not covered by participating labs, despite being part of their routine scope (6 of 46 and 4 of 42 cases, respectively). The reasons given were: out of scope for this commodity, shortage of personnel and technical problems for ***glyphosate*** and the non-coverage in potatoes for *ethephon*.

Table 4-18: Inclusion of EUPT-SRM8 compounds in the laboratories' routine scope

		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 (free acid)**	67 (97 %)	2	14 (34 %)	27
	Captan	82 (98 %)	2	12 (46 %)	14
	Chlormequat	57 (95 %)	3	16 (32 %)	34
	Chlorothalonil	94 (98 %)	2	5 (36 %)	9
	Cyromazine	57 (97 %)	2	20 (39 %)	31
	Dicofol	84 (94 %)	5	8 (38 %)	13
	Ethephon	38 (90 %)	4	13 (19 %)	55
	Fenbutatin oxide	46 (94 %)	3	13 (21 %)	48
	Fluazifop (free acid)	72 (97 %)	2	11 (31 %)	25
	Folpet	84 (97 %)	3	10 (43 %)	13
	Glyphosate	40 (87 %)	6	9 (14 %)	55
	Haloxyfop (free acid)	72 (96 %)	3	9 (26 %)	26
	Mepiquat	57 (95 %)	3	15 (30 %)	35
	Sum	**850 (96 %)**	**40 (4 %)**	**155 (29 %)**	**385 (71 %)**
OPTIONAL COMPOUNDS	**Diquat**	8 (62 %)	5	6 (6 %)	91
	Fentin	18 (82 %)	4	10 (11 %)	78
	Fosetyl	16 (80 %)	4	9 (10 %)	81
	Glufosinate	15 (71 %)	6	10 (11 %)	79
	Maleic hydrazide	15 (79 %)	4	9 (10 %)	82
	BAC-C10	33 (92 %)	3	14 (19 %)	60
	BAC-C12	37 (93 %)	3	14 (20 %)	56
	BAC-C14	36 (92 %)	3	14 (20 %)	57
	BAC-C16	35 (92 %)	3	16 (22 %)	56
	DDAC-C10	38 (90 %)	4	15 (22 %)	53
	Sum	**251 (87 %)**	**39 (13 %)**	**117 (14 %)**	**693 (86 %)**

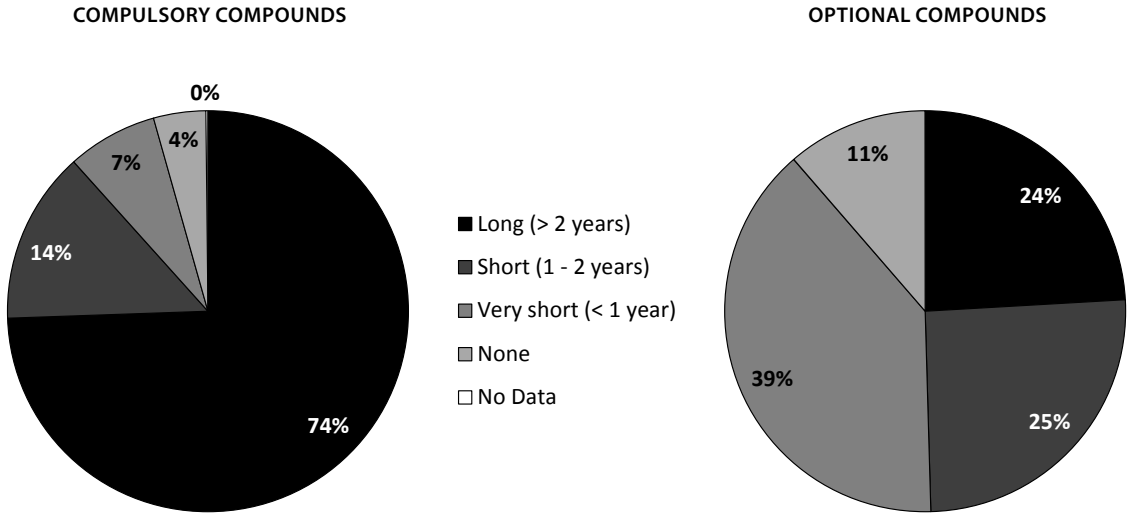


Figure 4-5: Experience of labs with the analysis of pesticides present in the Test Item (overall)

Optional compounds covered routinely by labs participating in this EUPT were in 87 % of all cases also targeted by those labs in this exercise (**Table 4-18**). Also here the number of participating labs that have analysed certain compounds that are not yet part of their routine scope is encouraging (117 cases overall and 73 cases concerning optional compounds contained in the Test Item). The compounds most frequently analysed by labs but not yet within their routine scope were *BAC-C16* (16 labs), ***DDAC-C10*** (15 labs), *BAC-C10*, BAC-C-12, *BAC-C14* (14 labs each), ***glufosinate*** and ***fentin*** (10 labs each) and ***fosetyl*** (9 labs).

Regarding compulsory compounds in 74 % of the cases labs indicated more than two years of analytical experience with the compounds that they reported results for (**Figure 4-5**). In 14 % of the cases labs reported short experience (1 – 2 years), in 7 % of the cases they reported experience of less than one year, and in 4 % of the cases no experience. In the case of optional compounds an average of 50 % of the labs had only very short experience or even no experience with analysis of the concerned pesticides. Concerning compulsory compounds, there seems to be little correction between AAZ and the experience of the labs with the analysis of the compounds (**Figure 4-6**). The small differences observed could also be due to the number of data involved and the compounds represented mostly or least frequently in each group.

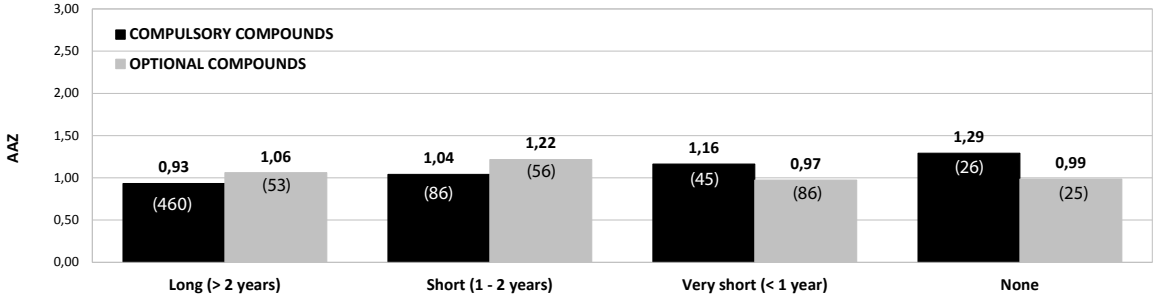


Figure 4-6: Correlation between the labs' experience with the analytes and the AAZ. (No. of data in each case in parentheses)

Table 4-19: Labs' experience with the analysis of individual compounds present in the Test Item

COMPULSORY COMPOUNDS				OPTIONAL COMPOUNDS			
Pesticides	**Experience**	**No. of Labs (%)**	**AAZ**	**Pesticides**	**Experience**	**No. of Labs (%)**	**AAZ**
	> 2 years	85 (90 %)	1.02		> 2 years	8 (57 %)	
Captan	1 – 2 years	2 (2 %)		**Diquat**	1 – 2 years	3 (21 %)	
AAZ: 1.03	< 1 year	3 (3 %)		AAZ: 1.05	< 1 year	1 (7 %)	
	None	4 (4 %)			None	2 (14 %)	
	> 2 years	39 (51 %)	1.18		> 2 years	12 (43 %)	
Cyromazine	1 – 2 years	22 (29 %)	1.06	**Fentin**	1 – 2 years	8 (29 %)	
AAZ: 1.06	< 1 year	11 (14 %)		AAZ: 1.26	< 1 year	5 (18 %)	
	None	5 (6 %)			None	3 (11 %)	
	> 2 years	82 (89 %)	0.94		> 2 years	11 (44 %)	
Dicofol	1 – 2 years	4 (4 %)		**Fosetyl**	1 – 2 years	6 (24 %)	
AAZ: 1.20	< 1 year	1 (1 %)		AAZ: 1.72	< 1 year	5 (20 %)	
	None	5 (5 %)			None	3 (12 %)	
	> 2 years	29 (49 %)	0.95		> 2 years	6 (24 %)	
Fenbutatin oxide	1 – 2 years	22 (37 %)	1.33	**Glufosinate**	1 – 2 years	3 (12 %)	
AAZ: 1.02	< 1 year	6 (10 %)		AAZ: 0.75	< 1 year	11 (44 %)	
	None	2 (3 %)			None	5 (20 %)	
	> 2 years	82 (87 %)	0.99		> 2 years	10 (42 %)	
Folpet	1 – 2 years	3 (3 %)		**Maleic hydrazide**	1 – 2 years	6 (25 %)	
AAZ: 1.02	< 1 year	5 (5 %)		AAZ: 0.83	< 1 year	6 (25 %)	
	None	4 (4 %)			None	2 (8 %)	
	> 2 years	25 (51 %)	0.85		> 2 years	3 (6 %)	
	1 – 2 years	11 (22 %)			1 – 2 years	15 (29 %)	
Glyphosate	< 1 year	10 (20 %)		**BAC-C12**	< 1 year	28 (55 %)	0.86
AAZ: 1.03	None	2 (4 %)		AAZ: 0.85	None	5 (10 %)	
	No Data	1 (2 %)					
	> 2 years	60 (74 %)	0.72		> 2 years	3 (6 %)	
Haloxyfop	1 – 2 years	15 (19 %)		**DDAC-C10**	1 – 2 years	15 (29 %)	
AAZ: 0.73	< 1 year	4 (5 %)		AAZ: 0.97	< 1 year	30 (59 %)	0.90
	None	2 (2 %)			None	5 (10 %)	
	> 2 years	58 (81 %)	0.80				
Mepiquat	1 – 2 years	7 (10 %)					
AAZ: 0.80	< 1 year	5 (7 %)					
		2 (3 %)					

Table 4-19 gives an overview of the labs' experience with the analysis of the various compounds on the Target Pesticides List. Among the compulsory compounds present in the Test Item ***captan*** is the compound with which labs had the most experience. Eighty-five labs (90 %) indicated more than two years of experience analysing this compound. ***Dicofol*** (89 %) and ***folpet*** (87 %) follow. The compounds with which the participating labs had the least experience are ***cyromazine*** (51 % more than 2 years of experience and 20 % less than 1 year of experience) and ***fenbutatin oxide*** (49 % more than 2 years of experience and 13 % less than 1 year of experience). Among the optional compounds ***BAC-C12*** and ***DDAC-C10*** were the pesticides, with which the participating labs had the least experience. More than 50 % of the labs analysing for these compounds indicated less than 1 year of experience.

4.4.8 Size of analytical portions

Concerning the compulsory compounds, the size of the analytical portions employed by the participants ranged between 2 g and 25 g for ***cyromazine***, ***glyphosate***, ***haloxyfop*** and ***mepiquat***; 2 g and 50 g for ***captan***, ***dicofol*** and ***folpet*** as well as 5 g and 50 g for ***fenbutatin oxide*** (**Figure 4-7**). Concerning optional compounds, the size of the analytical portions employed by the participants ranged between 2 g and 25 g for ***fentin***, ***glufosinate*** and ***BAC-C12***; 3 g and 25 g for ***diquat***, 4 g and 25 g for ***DDAC-C10*** as well as 4 g and 25 g for ***fosetyl*** and ***maleic hydrazide*** (**Figure 4-7**).

There were several cases where the sample portions employed by the laboratories were smaller than those used by the Organizer in the homogeneity test, i.e., 10 g for all compounds (**Figure 4-7**). Sub-sampling (= portion by portion) variability increases as the weight of the analytical portions decreases. Where the analytical portions employed were significantly smaller than those used in the homogeneity test, sufficient homogeneity cannot be guaranteed. In any case, prior to arrival of samples the Organizer provided an instruction on how to properly handle the Test Item, which included a recommendation to homogenise the entire sample in frozen state and, if available, with dry ice. If performed, this step might have improved the homogeneity of the sub-samples without affecting the stability of the pesticides contained. Nevertheless, the participating labs were informed about the sample size of 10 g employed for the homogeneity test and that no sufficient homogeneity can be guaranteed when analytical portions used were significantly smaller than 10 g.

4.4.9 Comparison of Reporting Limits, Assigned Values and MRRLs

Figure 4-8 shows a compilation of the reporting limits (RLs) reported by the labs for each of the compounds present in the Test Item. In all cases the RLs were clearly lower than the Assigned Values.

In the majority of cases the laboratories were also able to reach the stipulated MRRLs. In the case of compulsory compounds present in the Test Item, the respective MRRLs were not met by 16 % participating laboratories on average and more specifically by 22 labs (23 %) in the case of ***captan***, by 16 labs (21 %) in the case of ***cyromazine***, by 12 labs (13 %) in the case of ***dicofol***, by 11 labs (19 %) in the case of ***fenbutatin oxide***, by 20 labs (21 %) in the case of ***folpet***, by 8 labs (10 %) in the case of ***haloxyfop***, and by 9 labs (13 %) in the case of ***mepiquat***. In all these cases the MRRL was set at 0.01 mg/kg. The MRRL of ***glyphosate*** (0.05 mg/kg) could not be met by only 4 labs (8 %). Among the optional pesticides present in the Test Item, all participating laboratories were able to meet the MRRLs for ***BAC-C12***, ***DDAC-C10*** (0.1 mg/kg) and ***glufosinate*** (0.05 mg/kg). The MRRLs of ***fentin*** (0.01 mg/kg), ***fosetyl*** (0.05 mg/kg), ***diquat*** (0.02 mg/kg) and ***maleic hydrazide*** (0.05 mg/kg) were not met by 3 labs (33 %), 3 labs (16 %), 4 labs (29 %) and 8 labs (33 %), respectively.

4.5 Post-PT advice to participants

- When analysing acidic pesticides (e.g. ***haloxyfop***) dispersive SPE cleanup should be performed without amino-sorbents (e.g. PSA). Amino-sorbents tend to remove acidic pesticides from the extracts leading to low recoveries.
- Where for acidic pesticides only the concentration of free acid is requested, do not perform any hydrolysis step.
- When analysing organotin pesticides (e.g. ***fenbutatin oxide, fentin***) the samples should be acidified prior to or during extraction.
- Wherever possible, use an appropriate isotopically labelled internal standard (IL-IS) to compensate for recovery and matrix effects. If an IL-IS is not available/affordable use other approaches to

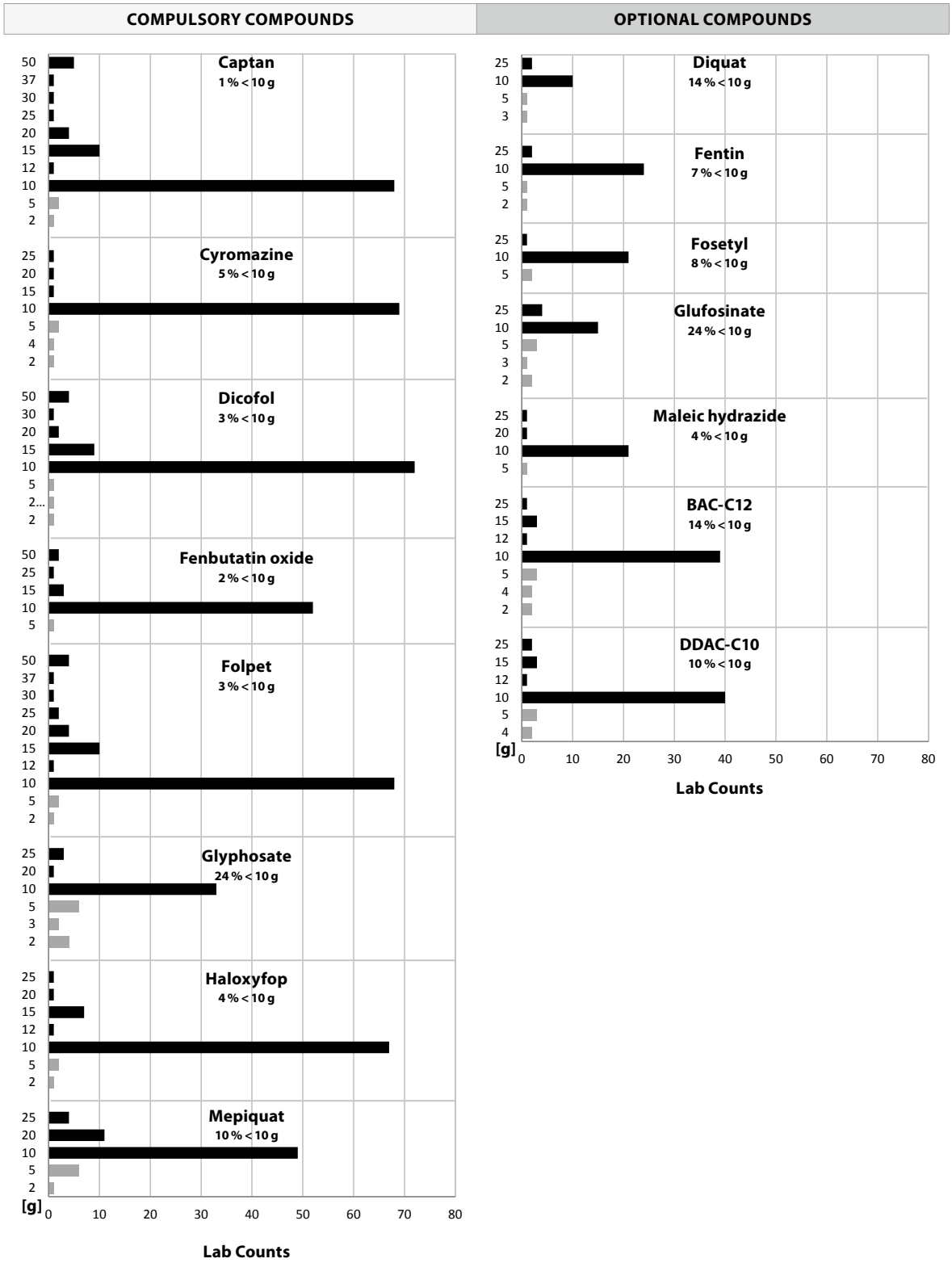


Figure 4-7: Size of analytical portions [g] employed by labs and percentage of analytical portions smaller than those used to test homogeneity by the Organizer

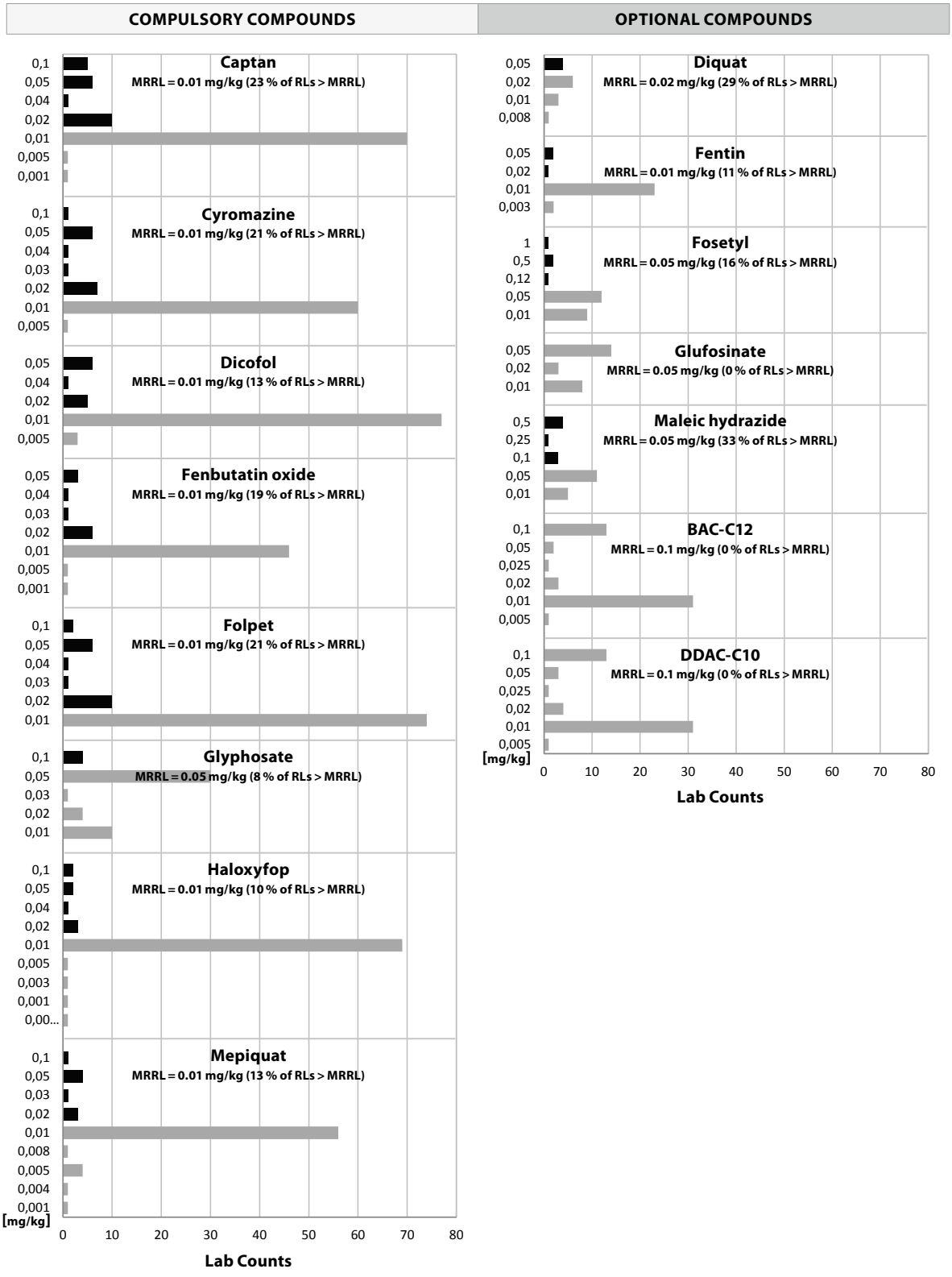


Figure 4-8: Distribution of labs' Reporting Limits [mg/kg] and comparison with the MRRLs set by the Organizer.

compensate for recovery and/or matrix effects such as the standard additions approach and the matrix-matched calibration.

- Avoid using very small analytical portions sizes (e.g. < 3 g) because sub-sampling variability increases as sample size is reduced. Keep in mind that the Organizer typically does not use analytical portions < 5 g in their homogeneity tests.
- Please fill-in the method information table comprehensively during results submission as this information is crucial for the detection of error sources and can be very helpful in the interpretation of the results distribution profiles.
- Follow the advices in the Specific EUPT Protocol as regards the storage and further processing of Test Items
- Try to localise the reasons for results with questionable or unacceptable z-scores and/or false positive or negative results and take corrective measures where appropriate. Also report any localised error-sources to the Organizer so that they can be communicated to the other participants on anonymous basis.

4.6 Summary, conclusions and prospects for the SRM pesticides

The EUPT-SRM8 was the 8th scheduled EUPT focusing on pesticides requiring the use of "single" residue methods and the first with a wide range of optional compounds.

A total of 114 laboratories representing 26 EU and 2 EFTA countries registered for the EUPT-SRM8 and 110 thereof submitted results. In addition, six of the seven participating laboratories from Third Countries and EU Candidate countries reported results. The only EU Member State from which no laboratory participated in EUPT-SRM8 was Romania. Malta was represented by the UK NRL-SRM acting as proxy-NRL-SRM for Malta and a lab in Germany that is subcontracted for the analysis of official controls samples. As shown in **Table 4-20** the participation in EUPT-SRMs has clearly increased over the years. The number of participants analysing pesticides present in the Test Items in EUPT-SRM1– 8 is shown in **Table 4-21**.

The clearly positive trend observed over the course of the EUPT-SRMs did not concern only the quantity of participants and their results, but also the scope of pesticides analysed by many individual labs. The quality of the results as reflected by the average Qn-RSDs and the overall average of absolute z-scores (AAZ) remained at acceptable levels for the majority of the compounds. 13 out of total 23 pesticides were included for the first time on the Target Pesticides List of an EUPT-SRM with 10 of them being present in the Test Item of EUPT-SRM8 (***captan***, ***dicofol***, ***fentin***, ***folpet***, ***maleic hydrazide***, ***diquat***, ***fosetyl***, ***glufosinate***, ***DDAC-C10*** and *BAC-C10*). With the exception of ***diquat*** all these new compounds were analysed by a sufficient number of labs. ***Diquat*** was analysed by only 14 laboratories with 4 false negative results so that a reliable statistical evaluation was not possible. Although 25 laboratories have reported results for ***fosetyl***, a reliable estimation of the Assigned Value for further statistical evaluation was not possible due to the broad distribution of the results that is partly a result of the instability of this compound in the Test Item, which was demonstrated in the stability tests conducted by the Organizer.

The positive trend regarding scope and participation is based on many factors such as the increased use of LC-MS/MS instrumentation by the laboratories, the implementation of simple methodologies including those developed and distributed by the EURL-SRM, as well as the strengthening of the network of official laboratories within the EU and the information flow within it. Another important factor contributing to this positive trend lies in the fact that participation in the EUPTs has been compulsory for EU official laboratories since 2009. Nevertheless, it should be noted that participation in EUPTs also largely depends on the pesticides included in the Target Pesticides List. For example, the inclusion of dithiocarbamates in the

Table 4-20: Comparison of EUPT-SRMs

EUPT-	SRM1 (2006)	SRM2 (2007)	SRM3 (2008)	SRM4 (2009)	SRM5 (2010)	SRM6 (2011)	SRM7 (2012)	SRM8 (2013)
Test Item	Apple juice	Wheat flour	Carrot homogenate	Oat flour	Apple purée	Rice flour	Lentil flour	Potato homogenate
Participants submitting results (EU/EFTA)	24	30	66	48	81	77	110	110
SRM pesticides in Target Pesticide List / in the Test Item	15 / 3 [1]	8 [3] / 5 [3]	8 / 5	21 [3] / 7 [3]	11 / 5 [4]	13 / 7	16 / 8 [5]	23 / (8 + 7 [8]) [9]
No. of results for SRM pesticides (without false positives)	38	73	193	138 [2]	239	291	439	604 + 212 [9]
No. of false negative results	0	7	0	5 [2]	5	5	11	14 + 8 [9]
Mean no. of results per lab	1.58	2.50	2.92	2.88	2.95	3.79	4.12	5.49 / 1.93 [9]
Average of absolute z-scores	0.57	1.04	1.04	0.98	1.11	0.83	0.97 [7]	0.98 / 1.06 [9]
Acceptable z-scores	97 %	86 %	87 %	88 %	92 % [7]	91 %	90 % [7]	88 % / 85 % [9]
Questionable z-scores	–	7 %	7 %	6 %	3 % [7]	6 %	3 % [7]	6 % / 5 % [9]
Unacceptable z-scores (thereof false negatives) [3]	3 %	8 % [3] (1.3 %) [3]	6 %	7 % [3] (3.6 %) [3]	5 % [7] (0.6 %) [7]	4 % (1.7 %)	7 % [7] (2.1 %) [7]	6 % / 10 % [9] (2.2 % / 3.6 %) [9]
Number of false positives	0	1	0	0	6	0	0	2
Category A laboratories [6]	–	–	–	31 %	19 %	25 %	28 %	47 % [10]
Qn-RSD (average)	25 %	25 %	29 %	27 %	22 % [7]	23 %	27 % [7]	26 % / 26 % [9,11]

1) One compound was evaluated for information only due to insufficient number of participants.
2) Two compounds were excluded from evaluation due to insufficient number of participants.
3) Including optional analytes
4) One of the 5 compounds was not included in the evaluation due to uncertain assigned value.
5) 3 of the 8 pesticides were not included in the evaluation.
6) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRM6, -SRM7 and SRM8.
7) Pesticides that were evaluated for information only were excluded.
8) One compound was excluded due to insufficient number of results and the other one due to failed uncertainty of Assigned Value
9) 8 compulsory and 7 optional compounds
10) based on compulsory compounds only
11) Diquat and fosetyl were excluded

Table 4-21: Number of labs having analysed selected pesticides present in the Test Items of the EUPT-SRMs 1 – 8

EUPT	Acidic pesticides					Requiring individual methods		Polar pesticides			Other
	2,4-D	MCPA	MCPP	Haloxyfop	Fluazifop	Bromide	Dithiocarbamates	Chlormequat	Ethephon	Glyphosate	Fenbutatin Oxide
SRM1		10						23			10
SRM2		23	28					25			
SRM3		38			35		59		7	9	
SRM4	33							38			
SRM5					51		70		28	35	35
SRM6	57			49		34	64		29		
SRM7	70					44	83		32	39	44
SRM8				81						49	59

Target Pesticides List usually positively impacts participation, like in the EUPT-SRMs 5-7, as the analysis of dithiocarbamates is routinely conducted by the majority of the OfLs.

The Target Pesticide List of EUPT-SRM8, which was distributed to the laboratories well in advance of the test, contained a total of 23 SRM-compounds. 13 of which belonged to the EU co-ordinated control program and were declared as compulsory in terms of scope. The other 10 pesticides not included in the EU co-ordinated control program were optional; among them 4 quaternary ammonium compounds which were introduced in an *ad hoc* monitoring program of the EU. The Test Item itself contained eight compulsory compounds, namely: ***captan***, ***cyromazine***, ***dicofol***, ***fenbutatin oxide***, ***folpet***, ***glyphosate***, ***haloxyfop*** and ***mepiquat***, and seven optional compounds: ***diquat***, ***fentin***, ***fosetyl***, ***glufosinate***, ***maleic hydrazide***, ***BAC-C12*** and ***DDAC-C10***. Spiking, homogenization and bottling of the Test Item was subcontracted to the EURL-FV.

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/pesticide combination. Overall, the quality of the results was good. In the case of compulsory compounds 83 out of 94 laboratories (88 %) reported results within the acceptable z-score-range for ***captan***, 66 out of 77 (86 %) for ***cyromazine***, 80 out of 92 (87 %) for ***dicofol***, 50 out of 59 (85 %) for ***fenbutatin oxide***, 84 out of 94 (89 %) for ***folpet***, 42 out of 49 (86 %) for ***glyphosate***, 74 out of 81 (91 %) for ***haloxyfop*** and 66 out of 72 (96 %) for ***mepiquat***. In the case of optional compounds 23 out of 28 laboratories (82 %) submitted results within the acceptable z-score-range for ***fentin***, 22 out of 24 (88 %) for ***glufosinate***, 22 out of 24 (92 %) for ***maleic hydrazide***, 45 out of 51 (88 %) for ***BAC-C12*** and 46 out of 53 (87 %) for ***DDAC-C10***.

The robust relative standard deviation (Qn-RSD), reflecting the result-distribution, was calculated for each pesticide. Excluding the two above-mentioned problematic compounds, ***diquat*** and ***fosetyl***, the average Qn-RSD was 26.1 % and 25.7 % for compulsory and optional compounds, respectively. These values are quite close to the FFP-RSD of 25 % used to calculate the z-scores. The individual Qn-RSDs of the compulsory compounds were: ***captan*** 26.0 %, ***cyromazine*** 27.2 %, ***dicofol*** 27.6 %, ***fenbutatin oxide*** 31.4 %, ***folpet*** 29.6 %, ***glyphosate*** 24.5 %, ***haloxyfop*** 20.1 %, and ***mepiquat*** 22.7 %. Although the Qn-RSD of ***fenbutatin oxide*** was relatively high, it is much lower than that in the previous EUPT-SRM7 where its Qn-RSD was 58.0 %. In addition to the clear improvement in precision a progress was also noticed in the number of submitted results which increased from 44 in EUPT-SRM7 to 59 in EUPT-SRM8. Looking back even further, only 5 laboratories covered ***fenbutatin oxide*** in the EUPT-SRM1 and 35 labs in the EUPT-SRM5. The Qn-RSDs of the optional compounds were: ***fentin*** 37.1 %, ***glufosinate*** 16.9 %, ***maleic hydrazide*** 27.7 %, ***BAC-C12*** 24.1 %, and ***DDAC-C10*** 22.9 %. For ***fosetyl*** and ***diquat*** the Qn-RSDs were 45.2 % and 28.6 %, respectively.

Among the compulsory compounds false negative results were presented for ***captan*** (4×), ***cyromazine*** (2×), ***dicofol*** (2×), ***folpet*** (1×), ***glyphosate*** (4×) and ***mepiquat*** (1×). In the case of ***captan*** one laboratory reported "detected in the Test Item", however, without submitting a numerical result due to technical problem. This result was still judged as a false negative result following the rules in the General EUPT Protocol. Eight false negative results were reported for the optional compounds, they were ***diquat*** (4×), ***fosetyl*** (2×), ***glufosinate*** (1×), and ***DDAC-C10*** (1×).

Laboratories were classified into category A and B according to the scope of pesticides detected in the Test Item, as defined in the General EUPT Protocol. Correctly detecting at least seven of the eight compulsory pesticides present in the Test Item without reporting any false positive result qualified for Category A. A total of 52 laboratories (47 %) were classified into Category A; the remaining 58 (53 %) laboratories were classified into Category B.

The 108 EU labs that finally participated in this EUPT represent 57 % of all 189 labs that were considered as being obliged to participate in this exercise based on their function (NRL-SRM) or scope (routinely analysing for pesticide residues in vegetables, cereals or feeding stuff). The most frequent reason given by labs to explain their non-participation was the pesticides in the SRM target list are out of the lab's scope.

Improving the scope and overall performance of NRLs and OfLs in the area of pesticides not amenable to multiresidue methods is one of the main aims of the EURL-SRM. The EURL-SRM is thus pleased to assist the labs via bilateral discussions, workshops and training and will continue developing, validating and distributing easy-to-use, fast and cost-effective methodologies for such compounds. In future PTs, the selection of pesticides will continue to focus on those included in the scope of the EU co-ordinated control programmes as well as on additional pesticides of high relevance. Lab requests will also be taken into account.

The Organizer would like to emphasize that any laboratories having received questionable or unacceptable z-scores in EUPTs should aim to find the reasons for this underperformance and try eliminating the sources of error. Following the distribution of the preliminary results all laboratories achieving questionable or unacceptable z-scores were asked to provide the reasons for questionable or unacceptable results, as far as possible. In many cases the reasons for poor performance could not be traced by the laboratories. The most prominent among the clarified sources of errors were the use of calibration solutions with incorrect concentration, the use of inappropriate procedures, the influence of matrix in calibration as well as calculation errors.

5. ACKNOWLEDGEMENTS

The Organizer wishes to thank the members of the EUPT Scientific Committee (Quality Control Group and Advisory Group) for their valuable advice. Special thanks also go to Arne Bent Jensen for his support in establishing the online registration and result submission tool as well as the Team of EURL-FV for preparation the EUPT-materials and shipment within Spain.

6. REFERENCES

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[3] EN 15662: Determination of Pesticide Residues Using GC-MS and/or LC-MS(/MS) following Acetonitrile Extraction/Partitioning and Clean-up by Dispersive SPE-QuEChERS method. In European Committee for Standardization, Technical Committee CEN/TC 275; „Food Analysis – Horizontal Methods"; Brussels, Belgium, 2008.

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[5] http://quppe.eu/

7. APPENDICES

Appendix 1 List of Laboratories registered to participate in the EUPT-SRM8

(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 (PLMA)	Innsbruck	x	Yes
Austria	AT	MA 38 - LUA	Vienna		Yes
Belgium	BE	Fytolab	Gent - Zwijnaarde		Yes
Belgium	BE	LOVAP (Laboratorium voor Onderzoek Van levensmiddelen en Aanverwante Produkten) NV	Geel		Yes
Belgium	BE	Scientific Institute of Public Health	Brussels	x	Yes
Bulgaria	BG	Central Laboratory for Chemical Testing and Control, Sofia	Sofia	x	Yes
Cyprus	CY	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	x	Yes
Czech Republic	CZ	Central Institute for Supervising and Testing in Agriculture	Brno		Yes
Czech Republic	CZ	Czech Agriculture and Food Inspection Authority	Praha	x	Yes
Czech Republic	CZ	Institute 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
Finland	FI	Finnish Food Safety Authority	Helsinki	x	Yes
France	FR	Analysis Center Mediterranean Pyrenees	perpignan		Yes
France	FR	ANSES Laboratoire de Maisons-Alfort (Pesticides)	MAISONS-ALFORT Cedex	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	Laboratoire Départemental d`Analyses de la Sarthe, Département de Chimie	Le Mans		Yes
France	FR	Laboratoire Départemental d`Analyses des Cotes d`Armor	Ploufragan		Yes
France	FR	Laboratoire Départemental d`Analyses des LANDES	Mont de Marsan		No [1)]
France	FR	Service Commun des Laboratoires / Laboratoire de Montpellier	Montpellier		Yes
France	FR	Service Commun des Laboratoires / Laboratoire Ile de France - Massy	Massy Cedex		Yes
France	BE	Agro-Analyses Laboratoire	Metz		Yes
Germany	BE	LUFA-ITL GmbH	Kiel		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	Bavarian Health and Food Safety Authority Office Oberschleißheim Feed Analytics (Feedingstuff)	Oberschleißheim		No [2)]
Germany	DE	Berlin-Brandenburg State Laboratory, Frankfurt (Oder)	Frankfurt (Oder)		Yes
Germany	DE	Chemical and Veterinary Analytical Institute Muensterland-Emscher Lippe	Münster		Yes

* only for EU-member states; [1)]: target pesticides and/or matrix out of scope; [2)]: technical problem

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	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld		Yes
Germany	DE	Chemisches und Lebensmitteluntersuchungsamt Dortmund	Bochum		Yes
Germany	DE	Chemisches und Veterinäruntersuchungsamt Ostwestfalen-Lippe	Detmold		Yes
Germany	DE	Chemisches und Veterinäruntersuchungsamt Rheinland, Standort Bonn	Bonn		Yes
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	Institut für Hygiene und Umwelt Hamburg	Hamburg		Yes
Germany	DE	Labor Friedle GmbH	Regensburg		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	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 Investigation Institute of Health and Veterinary Saxony	Dresden		Yes
Germany	DE	State Laboratory Schleswig-Holstein	Neumünster		Yes
Germany	LT, LV, CY, EE	GALAB Laboratories GmbH	Geesthacht		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	CY	Wessling Groupe - Hungary, Budapest	Budapest		Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Pesticide Residue Analytical Laboratory of Hódmezovásárhely	Hódmezovásárhely		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 Residue Analytical Laboratory, Miskolc	Miskolc	x	Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Velence	Velence		Yes
Ireland	IE	Pesticide Control Laboratory, Department of Agriculture, Fisheries and Food	Co. Kildare	x	Yes
Italy	IT	APPA Bolzano	Bolzano		Yes
Italy	IT	APPA Trento Settore Laboratorio e Controlli	Trento		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 INORGAN	Latina		Yes
Italy	IT	ARPAM Dipartimento di Macerata	Macerata		Yes
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	Laboratorio di Prevenzione - ASL Provincia di Milano	Milano		Yes

* only for EU-member states; [1]: target pesticides and/or matrix out of scope; [2]: technical problem

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

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Italy	IT	Laboratorio di Sanità Pubblica ASL BERGAMO	Bergamo		Yes
Italy	IT	Public Health Laboratory - Florence	FLORENCE		Yes
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
Luxem-bourg	LU	National Health Laboratory Luxembourg (Food Laboratory)	Luxembourg	x	Yes
Netherlands	BE	Groen Agro Control	Delfgauw		Yes
Netherlands	BE	Grond-, Gewas- en Milieulaboratorium Zeeuws-Vlaanderen b.v.	Graauw		Yes
Netherlands	BE	Handelslaboratorium Dr. Verwey	Rotterdam		No [2)]
Netherlands	BE	NofaLab	Schiedam		Yes
Netherlands	NL	Netherlands Food and Consumer Products Safety Authority	Wageningen	x	Yes
Norway	NO	Norwegian Institute for Agricultural and Environmental Research, Plant Health and Plant Protection D	Aas		Yes
Poland	PL	Institute of Horticulture, Food Safety Laboratory (Skierniewice)	Skierniewice		Yes
Poland	PL	Institute of Plant Protection Pesticide Residue Laboratory, Bialystok	Bialystok		Yes
Poland	PL	Institute of Plant Protection, Department of Pesticide Residue Research - Poznan	Poznan		Yes
Poland	PL	National Research Institute Regional Experimental Station in Trzebnica	Trzebnica		No [2)]
Poland	PL	Voievodship Sanitary - Epidemiological Station in Lodz	Lodz		Yes
Poland	PL	Voievodship Sanitary - Epidemiological Station in Warszaw	Warszaw	x	Yes
Portugal	PT	Regional Laboratory of Veterinary and Food Safety - Madeira Island	Funchal - Madeira Island		Yes
Slovakia	SK	State Veterinary and Food Institute Bratislava	Bratislava	x	Yes
Slovenia	SI	Institute of Public Health, Maribor	Maribor	x	Yes
Slovenia	SI	Institute of Public Health, Maribor	Ljubljana		Yes
Spain	ES	Agricultural and Phytopathological Laboratory of Galicia	Abegondo. A Coruña		Yes
Spain	ES	Agrofood Laboratory of the Comunidad Valenciana	Burjassot-Valencia		Yes
Spain	ES	Analytica Alimentaria GmbH Sucursal España	Almeria		Yes
Spain	ES	Instituto Tecnologico de Canarias, División de Investigación y Desarrollo Tecnológico - Laboratorio	Agüimes, Gran Canaria		Yes
Spain	ES	Laboratori Agroalimentari de la Generalitat de Catalunya	Cabrils		Yes
Spain	ES	Laboratorio Agrario Regional - Junta de Castilla y Leon	Burgos		Yes
Spain	ES	Laboratorio Agrario Regional de Castilla La Mancha	Albacete		No [1)]
Spain	ES	Laboratorio Agroalimentario de Extremadura	Cáceres		Yes
Spain	ES	Laboratorio Agroalimentario de Zaragoza	Zaragoza		Yes
Spain	ES	Laboratorio Agroalimentario y de Sanidad Animal de Murcia	El Palmar-Murcia		Yes
Spain	ES	Laboratorio Arbitral Agroalimentario, Madrid	Madrid	x	Yes
Spain	ES	Laboratorio de Producción y Sanidad Vegetal de Almería, Ministry of Agriculture	La Mojonera (Almería)		No [2)]
Spain	ES	Laboratorio de Producción y Sanidad Vegetal de Jaén	Mengibar (Jaén)		Yes
Spain	ES	Laboratorio de Salud Pública de Badajoz	Badajoz		Yes
Spain	ES	Laboratorio de Salud Pública de Cuenca	Cuenca		Yes
Spain	ES	Laboratorios Ecosur, S.A.L.	Lorquí (Murcia)		Yes
Spain	ES	Laboratory of Barcelona Public Health Agency	Barcelona		No [1)]
Spain	ES	Labs & Technological Services AGQ, S.L.	Burguillos (Sevilla)		Yes

* only for EU-member states; [1)]: target pesticides and/or matrix out of scope; [2)]: technical problem

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

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Spain	ES	National Centre for Food - Spain, Majadahonda	Majadahonda	x	Yes
Spain	ES	National Centre for Technology and Food Safety - Laborytory of Ebro	San Adrián (Navarra)		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	UK, MT	The Food and Environment Research Agency - York	York	x	Yes
United Kingdom	UK	Eurofins - United Kingdom, Wolverhampton	Wolverhampton		Yes
United Kingdom	UK	Laboratory of the Government Chemist - Teddington	Teddington		Yes
United Kingdom	UK	Science and Advice for Scottish Agriculture	Edinburgh		Yes

* only for EU-member states; [1)]: target pesticides and/or matrix out of scope; [2)]: technical problem

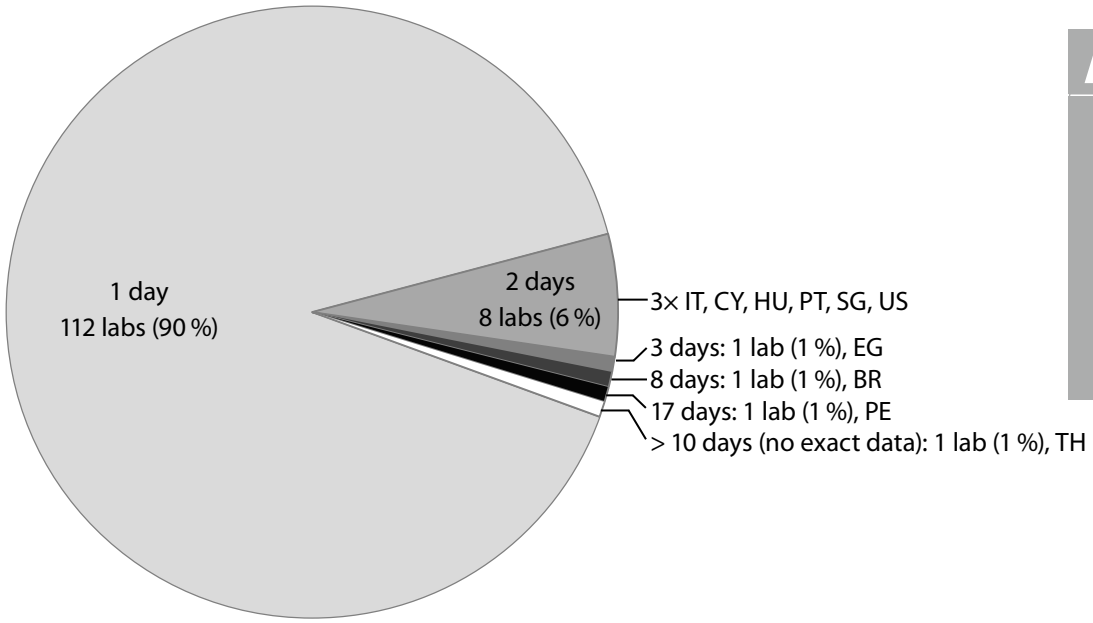
(b): participating labs from EU Candidate countries and Third Countries

Country	Institution	City	Reported results
Brazil	AgroSafety Monitoramento Agrícola Ltda	Piracicaba/SP	Yes
Egypt	Central Lab of Residue Analysis of Pesticides and Heavy Metals in Foods	Giza	Yes
Peru	CENTRO DE CONTROL DE INSUMOS Y RESIDUOS TOXICOS	Lima	No [2)]
Serbia	SP LABORATORIJA	Becej	Yes
Singapore	Veterinary Public Health Laboratory-Chem Dept	Singapore	Yes
Thailand	APSRDO, Dept of Agriculture	Bangkok	Yes
USA	Eurofins Central Analytical Laboratories	Metairie	Yes

[2)]: technical problem

Appendix 2 Shipment evaluation

(a): Compilation of duration of shipment



Appendix 2 (cont.) Shipment evaluation

(b): Condition of packages on arrival

Questions:

1: **At what day and time did you OPEN the package with the material?**
(NOT the time at which the material arrived to your institution but at the time you opened the package)

2: **Was the box with the material stored in a freezer within your institution before you opened it?**

3: **If Yes, for how many hours was it stored in the freezer approximately?**

4: **Was there still some dry ice in the package when you opened it?**

5: **Did you observe any substantial melting of the material?**

6: **If yes, please estimate how much of the material (in %) was defrosted!**

7: **What was the temperature of the material)**
(in °C , preferably use the Blank for temperature measurements and measure soon after opening the box. If the material is still well frozen please do not measure superficially, dig a small hole (ca. 2 cm) on the top with a screw driver and measure with a normal thermometer. If considerable material has defrosted then measure the temperature of the defrosted material)

Country	Answer to questions (s. above)						
	1 (Date; hh:mm CET)	2	3	4	5	6	7
Austria	16.04.2013; 14:30	No		No	No		–27 °C
Bulgaria	18.04.2013; 13:30	Yes	4,5 h	Yes	No		–20 °C
Cyprus	17.04.2013; 09:30	No		No	No		–4 °C
Egypt	06.05.2013	Yes	430 h	Not sure	No		–10 °C
Estonia							
France	16.04.2013; 12:00	No		Yes	No		–41 °C
France	16.04.2013; 12:00	No		Yes	No		–35 °C
Germany	16.04.2013; 09:00	No		Yes	Yes		Sorry, we did not measure
Germany	16.04.2013; 13:30	Yes	4.5 h	Yes	No		–22 °C
Germany	16.04.2013; 10:00	No		Yes	No		below –18 °C (limit of the thermometer). All material was frozen.
Greece	16.04.2013; 15:15	No		Yes	No		–24 °C
Lithuania	16.04.2013; 14:40	No		Yes	No		–18 °C
Norway	16.04.2013; 12:25	No		Yes	No		–45 °C
Poland	16.04.2013	No		Yes	No		Sorry, we have not checked
Portugal	17.04.2013; 14:00	No		No	No		Blank: (-2.0 ± 0.5) °C, appearance: Solid, as sand, with grains with ± 3 – 5 mm diameter Sample:(-2.0 ± 0.5) °C), appearance: Solid, one block.
Singapore	17.04.2013, 15:50	No		No	No		–2 °C
Slovenia	16.04.2013; 12:45	No		Yes	No		< –20 °C
Spain	16.04.2013; 10:00	No		Yes	No		As we did not read the email on time we did not measure the test material temperature but in any case it was frozen.
USA		Yes	in the freezer for a day, then stored in the refrigerator for a day				

Appendix 3 Data of homogeneity test

COMPULSORY COMPOUNDS								
	Captan		Cyromazine		Dicofol		Fenbutatin oxide	
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. 004	1.095	1.046	0.089	0.078	1.005	1.065	0.064	0.073
No. 017	1.053	0.987	0.082	0.076	1.003	1.008	0.064	0.062
No. 027	1.171	1.088	0.085	0.091	1.275	1.144	0.072	0.069
No. 055	0.977	1.042	0.092	0.087	1.038	1.019	0.063	0.062
No. 067	1.038	1.014	0.072	0.078	1.026	1.046	0.063	0.068
No. 091	1.017	1.038	0.084	0.082	1.174	1.064	0.079	0.075
No. 102	1.047	1.054	0.082	0.084	1.078	1.093	0.072	0.070
No. 104	1.265	1.266	0.097	0.098	1.386	1.385	0.089	0.094
No. 156	1.052	1.076	0.088	0.087	1.133	1.109	0.075	0.069
No. 170	1.102	1.022	0.086	0.086	1.122	1.166	0.073	0.079
	Folpet		Glyphosate		Haloxyfop		Mepiquat	
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. 004	1.369	1.437	0.303	0.293	0.470	0.492	0.088	0.091
No. 017	1.405	1.402	0.290	0.297	0.463	0.451	0.086	0.086
No. 027	1.730	1.686	0.321	0.300	0.533	0.511	0.096	0.097
No. 055	1.414	1.475	0.315	0.334	0.444	0.462	0.089	0.092
No. 067	1.452	1.454	0.311	0.271	0.463	0.490	0.085	0.083
No. 091	1.613	1.545	0.321	0.283	0.531	0.501	0.093	0.088
No. 102	1.476	1.468	0.299	0.299	0.475	0.461	0.088	0.085
No. 104	1.802	1.888	0.365	0.338	0.590	0.613	0.107	0.103
No. 156	1.538	1.560	0.328	0.309	0.499	0.477	0.091	0.092
No. 170	1.526	1.555	0.337	0.312	0.477	0.498	0.091	0.092

OPTIONAL COMPOUNDS								
	Diquat		Fentin		Fosetyl		Glufosinate	
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. 004	0.081	0.073	0.165	0.177	0.953	0.934	0.231	0.234
No. 017	0.076	0.076	0.160	0.161	0.918	0.916	0.213	0.211
No. 027	0.088	0.084	0.187	0.185	0.971	0.961	0.257	0.252
No. 055	0.084	0.079	0.151	0.159	0.901	0.933	0.233	0.232
No. 067	0.076	0.075	0.167	0.165	0.891	0.924	0.222	0.214
No. 091	0.078	0.077	0.188	0.171	0.943	0.940	0.231	0.227
No. 102	0.079	0.070	0.167	0.165	0.903	0.910	0.214	0.209
No. 104	0.093	0.088	0.217	0.221	0.989	0.996	0.279	0.255
No. 156	0.079	0.078	0.181	0.177	0.964	0.959	0.237	0.222
No. 170	0.082	0.075	0.178	0.185	0.940	0.971	0.249	0.240
	Maleic hydrazide		BAC-C12		DDAC-C10			
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]		
No. 004	0.662	0.628	0.564	0.619	0.416	0.473		
No. 017	0.646	0.614	0.595	0.563	0.445	0.420		
No. 027	0.708	0.685	0.638	0.604	0.486	0.447		
No. 055	0.663	0.692	0.557	0.565	0.417	0.420		
No. 067	0.626	0.619	0.594	0.642	0.429	0.479		
No. 091	0.672	0.649	0.660	0.624	0.506	0.477		
No. 102	0.628	0.600	0.600	0.603	0.447	0.456		
No. 104	0.803	0.723	0.729	0.745	0.563	0.596		
No. 156	0.708	0.655	0.633	0.584	0.487	0.449		
No. 170	0.700	0.650	0.605	0.644	0.441	0.485		

Appendix 4 Data of stability test

COMPULSORY COMPOUNDS												
	Captan			Cyromazine			Dicofol			Fenbutatin oxide		
	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013
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. 004	1.071	1.013	1.034	0.084	0.081	0.080	1.035	1.005	1.016	0.066	0.067	0.067
No. 017	1.020	0.912	0.905	0.074	0.081	0.077	1.006	0.927	0.927	0.064	0.057	0.057
No. 067	1.026	0.960	0.958	0.077	0.074	0.077	1.036	0.986	0.914	0.064	0.057	0.062
Mean [mg/kg]	**1.039**	**0.961**	**0.966**	**0.078**	**0.079**	**0.078**	**1.025**	**0.973**	**0.952**	**0.065**	**0.060**	**0.062**
RSD* [%]	**2.66 %**	**5.28 %**	**6.72 %**	**6.22 %**	**5.13 %**	**1.87 %**	**1.68 %**	**4.21 %**	**5.84 %**	**1.89 %**	**9.48 %**	**8.23 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**-7.45 %**	**-7.04 %**	**—**	**0.32 %**	**-0.43 %**	**—**	**-5.16 %**	**-7.12 %**	**—**	**-7.12 %**	**-4.54 %**
	Folpet			**Glyphosate**			**Haloxyfop**			**Mepiquat**		
	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013
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. 004	1.403	1.479	1.371	0.276	0.281	0.266	0.471	0.456	0.478	0.081	0.084	0.083
No. 017	1.403	1.311	1.303	0.278	0.270	0.256	0.454	0.420	0.451	0.081	0.088	0.087
No. 067	1.453	1.408	1.304	0.259	0.262	0.247	0.471	0.416	0.438	0.079	0.083	0.084
Mean [mg/kg]	**1.420**	**1.399**	**1.326**	**0.271**	**0.271**	**0.256**	**0.465**	**0.430**	**0.455**	**0.081**	**0.085**	**0.085**
RSD* [%]	**2.03 %**	**6.03 %**	**2.93 %**	**3.81 %**	**3.61 %**	**3.81 %**	**2.14 %**	**5.12 %**	**4.47 %**	**1.67 %**	**3.04 %**	**2.47 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**-1.45 %**	**-6.64 %**	**—**	**0.00 %**	**-5.42 %**	**—**	**-7.49 %**	**-2.08 %**	**—**	**5.32 %**	**5.42 %**

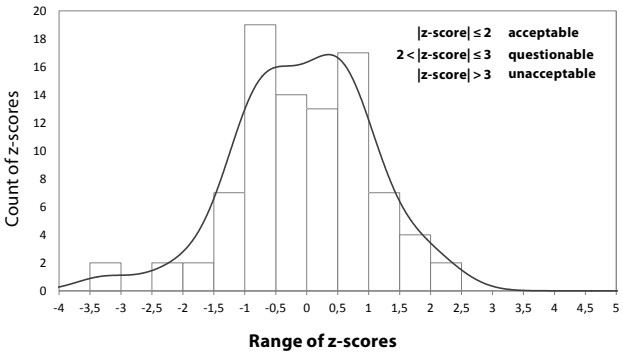
OPTIONAL COMPOUNDS												
	Diquat			Fentin			Fosetyl			Glufosinate		
	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 004	0.086	0.081	0.082	0.164	0.161	0.167	0.914	0.879	0.786	0.225	0.224	0.235
No. 017	0.081	0.076	0.078	0.158	0.145	0.145	0.928	0.855	0.778	0.208	0.221	0.235
No. 067	0.079	0.071	0.075	0.164	0.145	0.151	0.889	0.794	0.751	0.210	0.217	0.219
Mean [mg/kg]	**0.082**	**0.076**	**0.079**	**0.162**	**0.150**	**0.154**	**0.910**	**0.843**	**0.772**	**0.214**	**0.221**	**0.229**
RSD* [%]	**4.55 %**	**6.55 %**	**4.97 %**	**2.24 %**	**6.06 %**	**7.51 %**	**2.13 %**	**5.18 %**	**2.33 %**	**4.29 %**	**1.71 %**	**3.90 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**-7.14 %**	**-4.44 %**	**—**	**-7.22 %**	**-4.64 %**	**—**	**-7.40 %**	**-15.23 %**	**—**	**3.04 %**	**7.17 %**
	Maleic hydrazide			**BAC-C12**			**DDAC-C10**					
	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013	12.04.2013	30.04.2013	21.05.2013			
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]			
No. 004	0.627	0.586	0.608	0.578	0.564	0.602	0.420	0.424	0.444			
No. 017	0.590	0.584	0.590	0.574	0.520	0.566	0.411	0.379	0.415			
No. 067	0.598	0.561	0.579	0.593	0.531	0.562	0.421	0.392	0.406			
Mean [mg/kg]	**0.605**	**0.577**	**0.592**	**0.582**	**0.538**	**0.577**	**0.417**	**0.398**	**0.422**			
RSD* [%]	**3.21 %**	**2.44 %**	**2.48 %**	**1.72 %**	**4.25 %**	**3.82 %**	**1.32 %**	**5.81 %**	**4.71 %**			
Diviation [%] (ref. 1. Anaylsis)	**—**	**-4.63 %**	**-2.07 %**	**—**	**-7.45 %**	**-0.86 %**	**—**	**-4.55 %**	**1.04 %**			

***** RSD = relative standard diviation

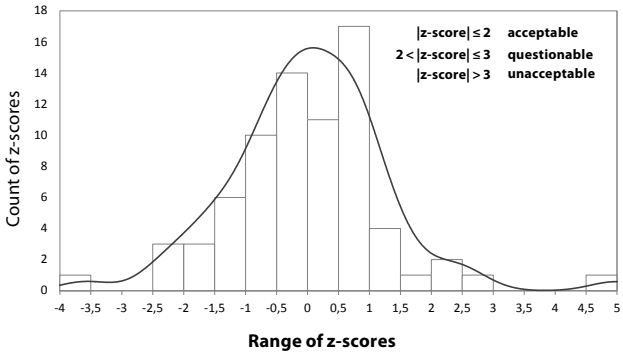
Appendix 5 Histograms and kernel density estimates of z-scores* distribution

Compulsory compounds

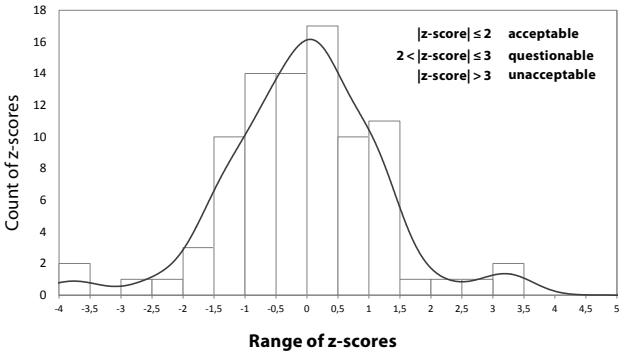
Captan



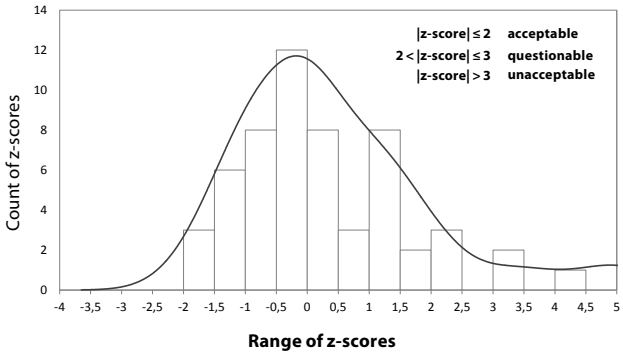
Cyromazine



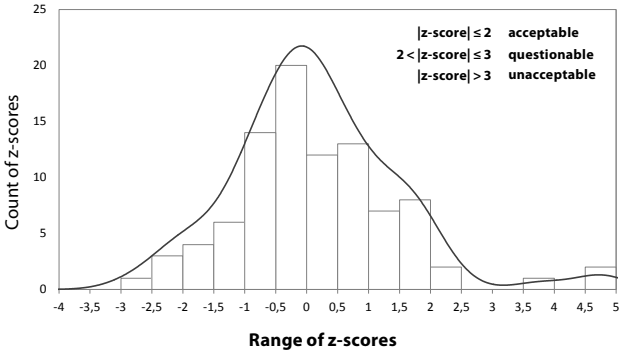
Dicofol



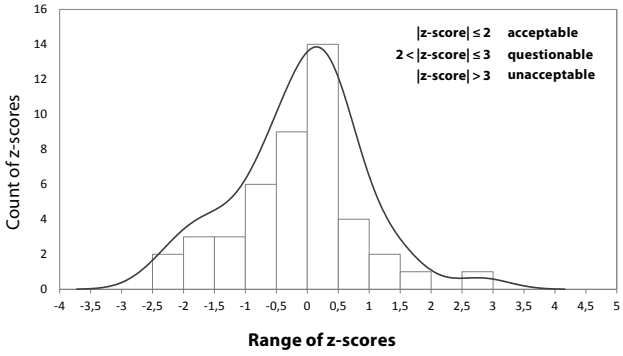
Fenbutatin oxide



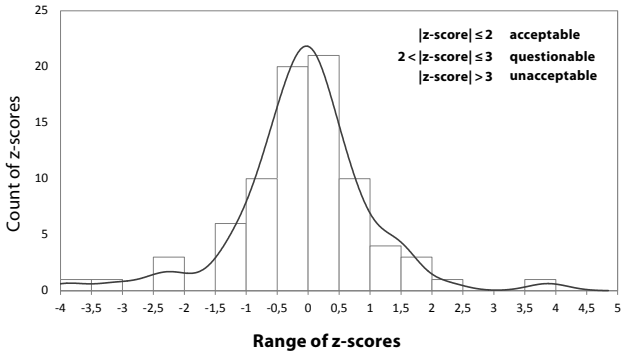
Folpet



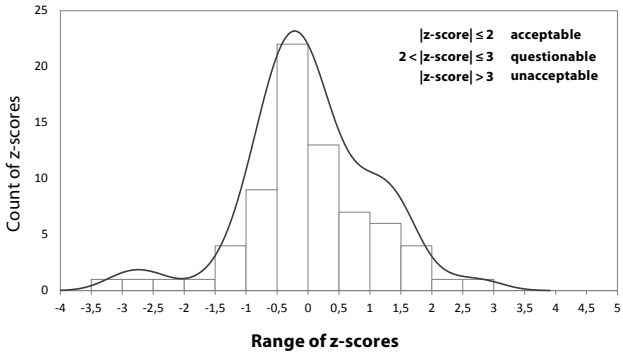
Glyphosate



Haloxyfop



Mepiquat

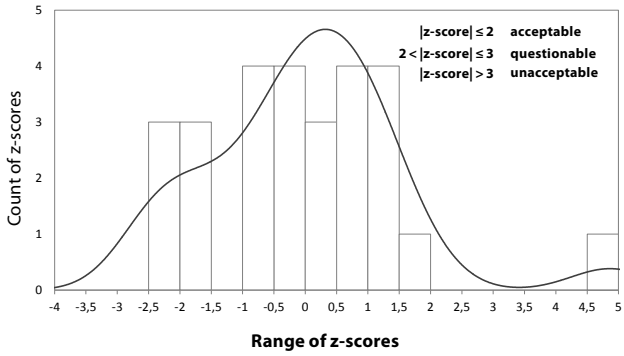


* Cut-off at z-score = 5

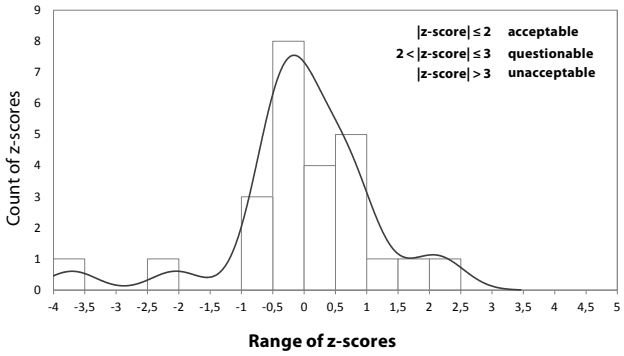
Appendix 5 (cont.) Histograms and kernel density estimates of z-scores* distribution

Optional compounds

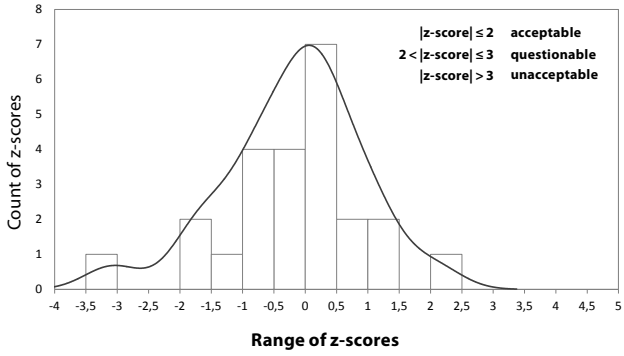
Fentin



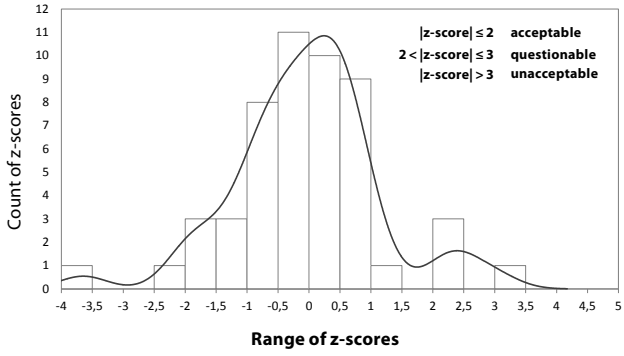
Glufosinate



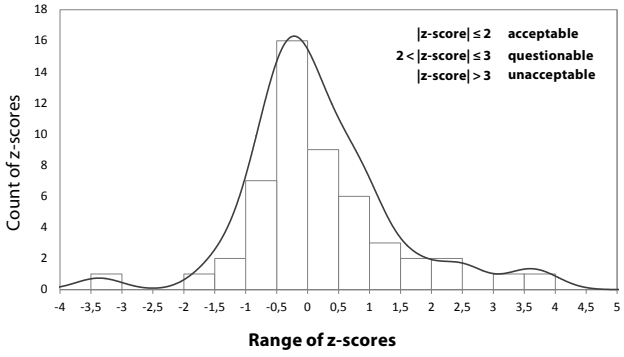
Maleic hydrazide



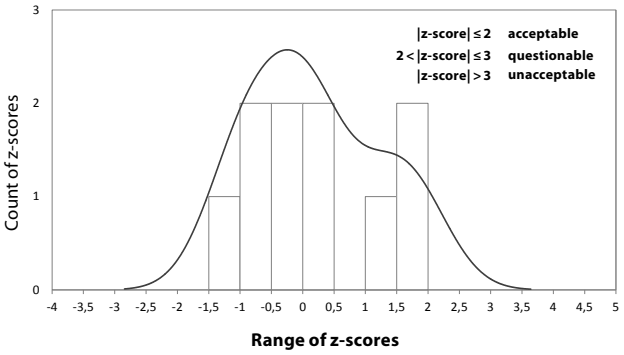
BAC-C12



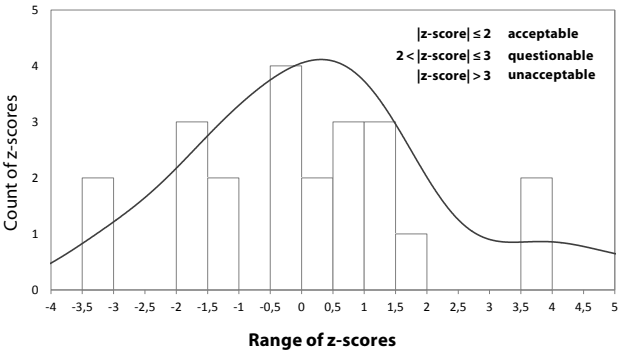
DDAC-C10



Diquat

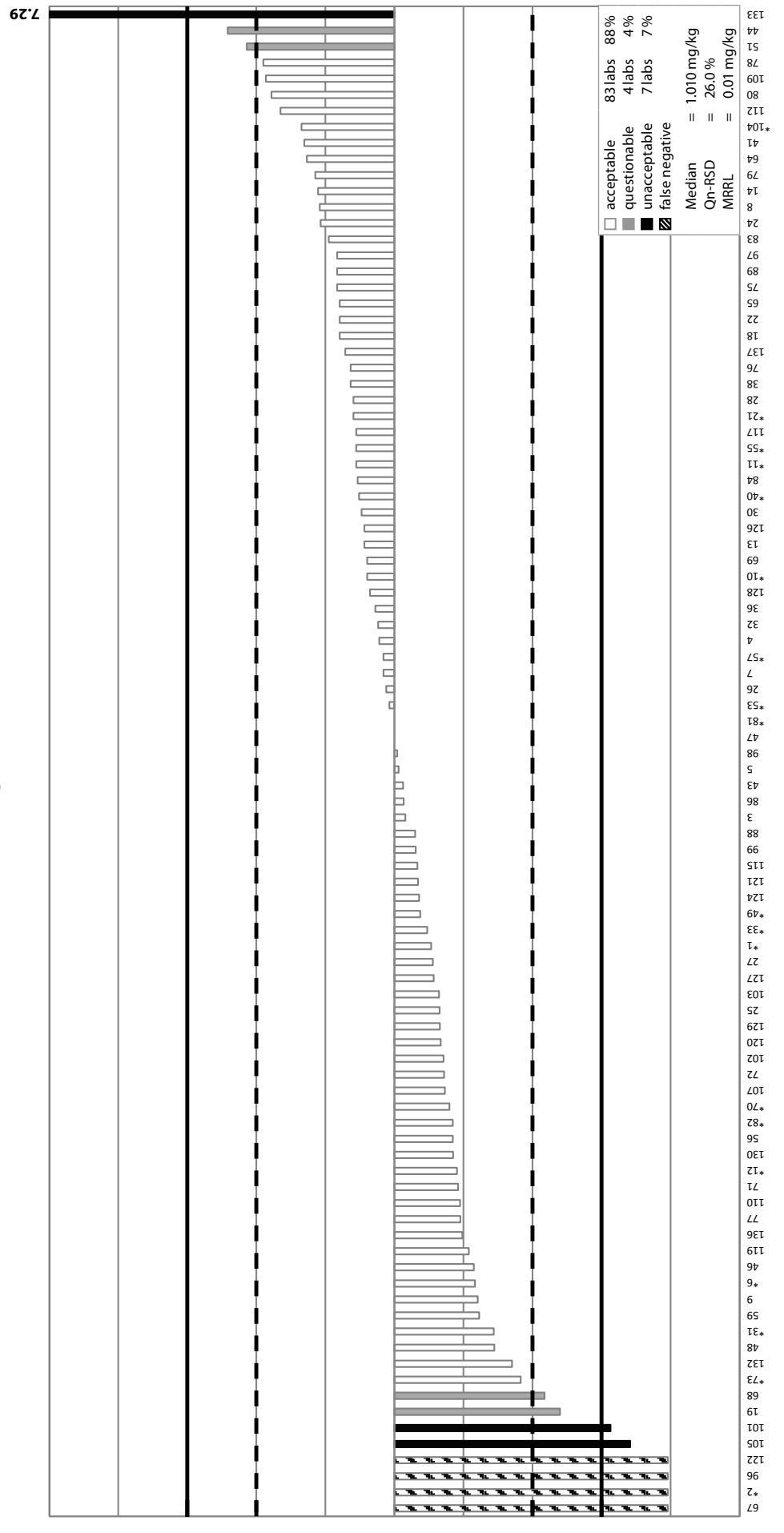


Fosetyl

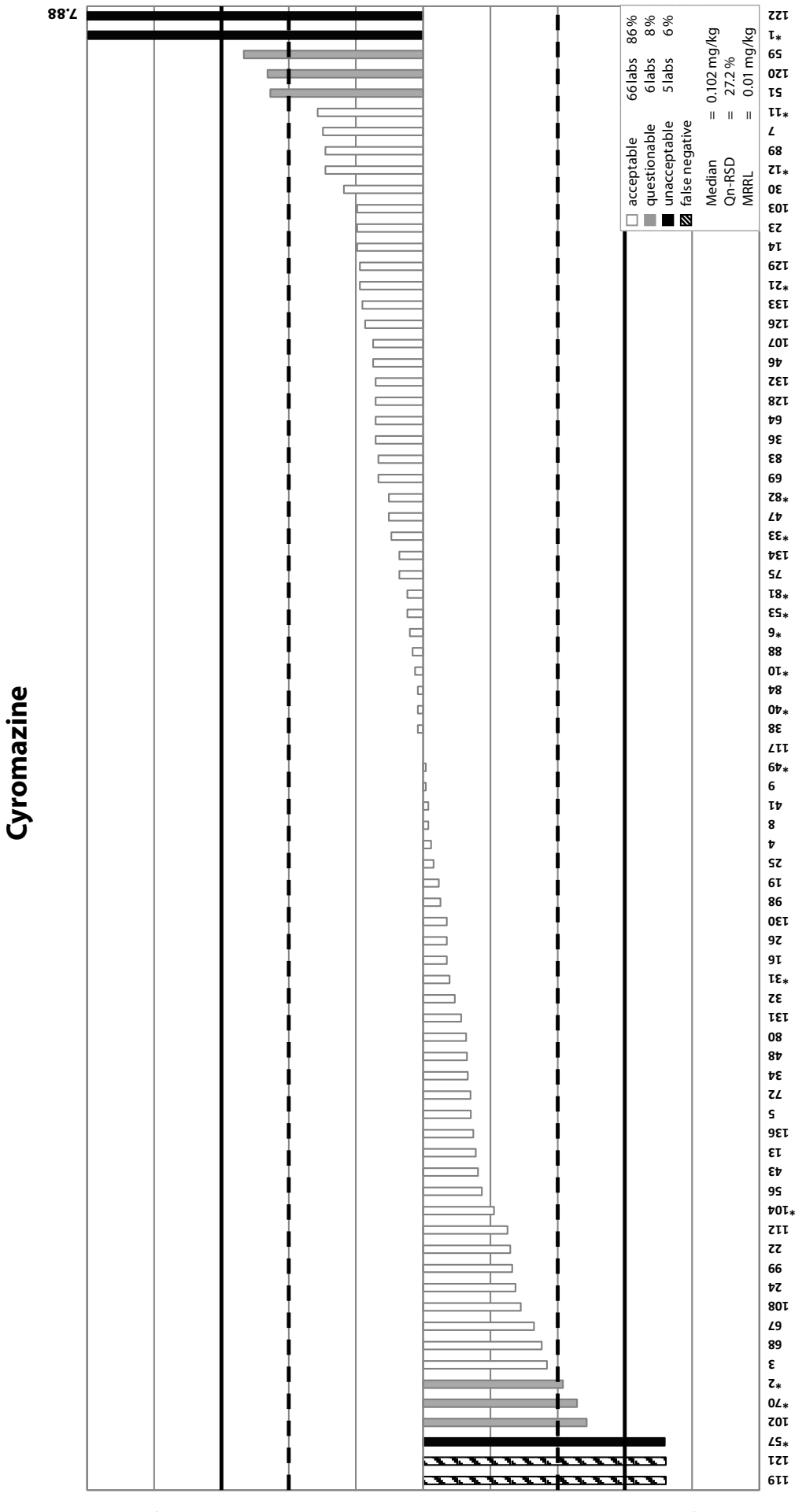


* Cut-off at z-score = 5

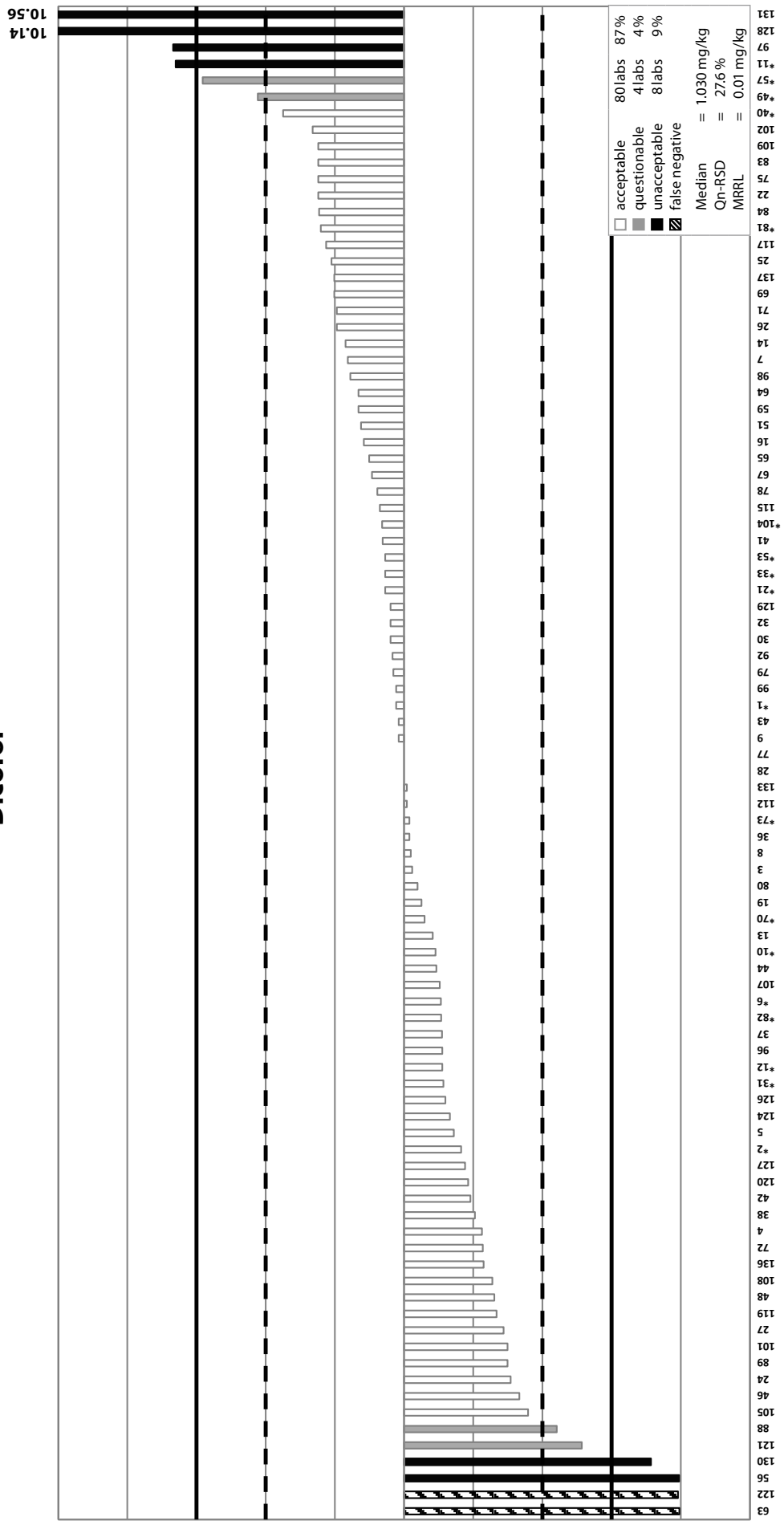
Appendix 6 Graphic presentation of z-scores: Compulsory compounds



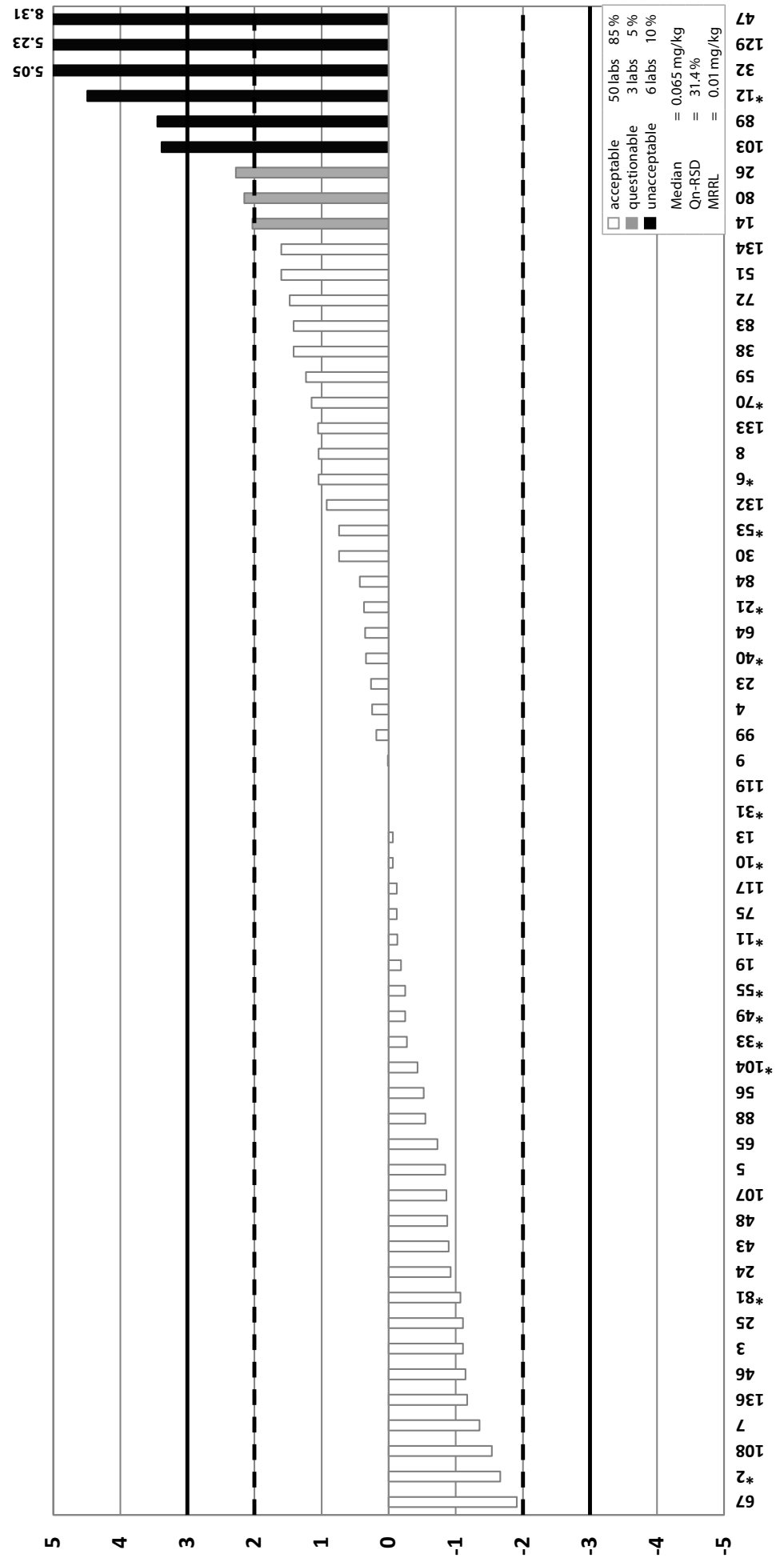
Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds



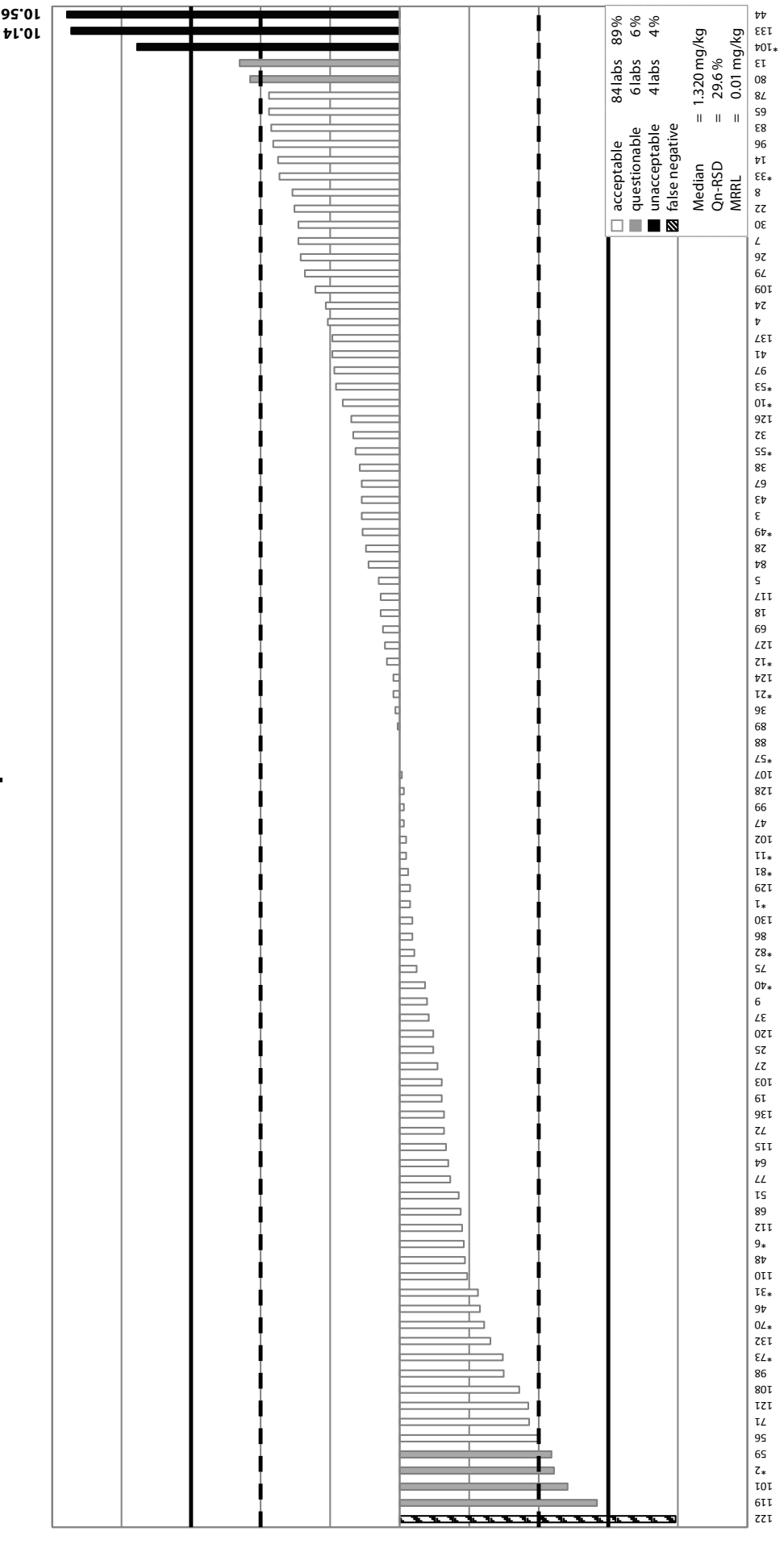
Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds



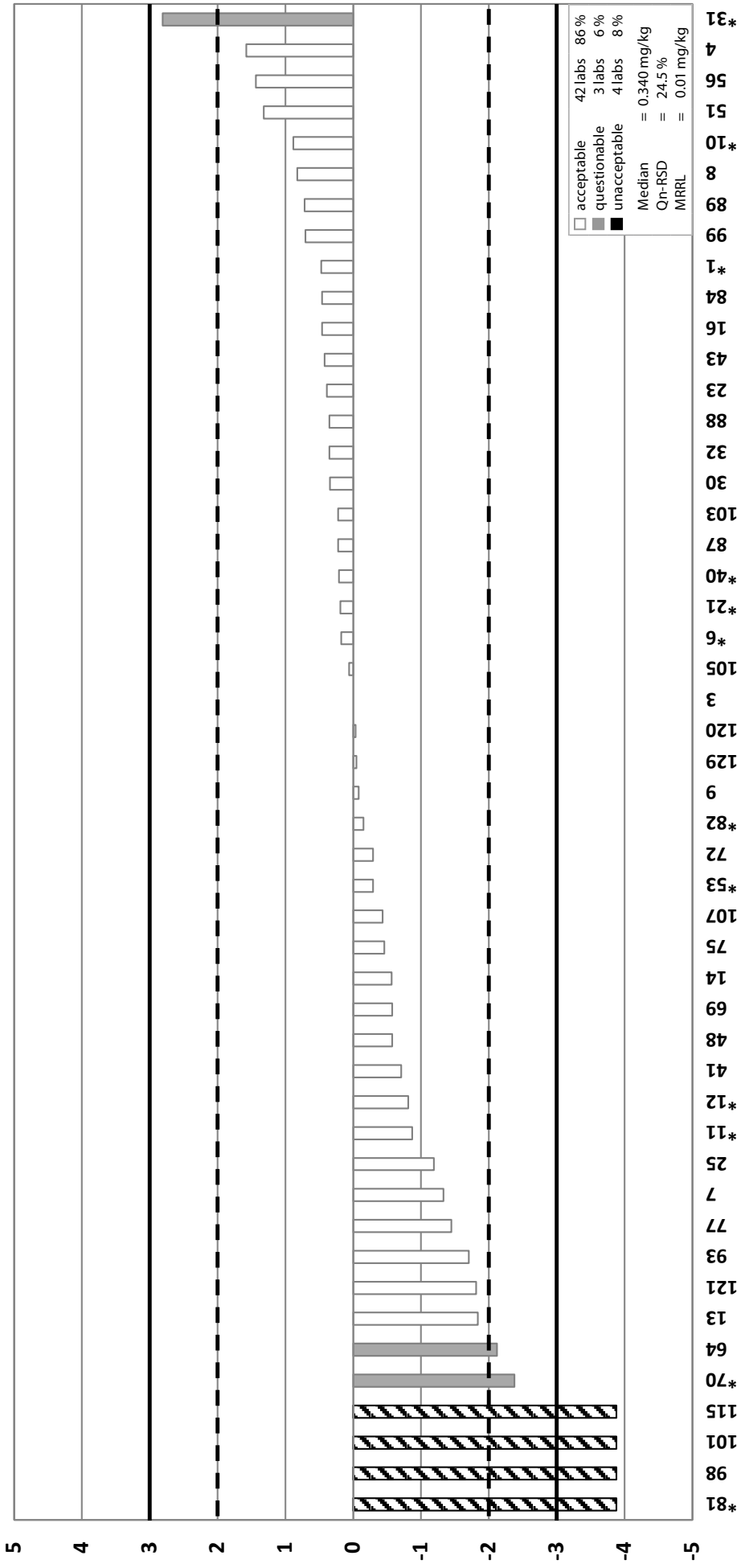
Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds



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

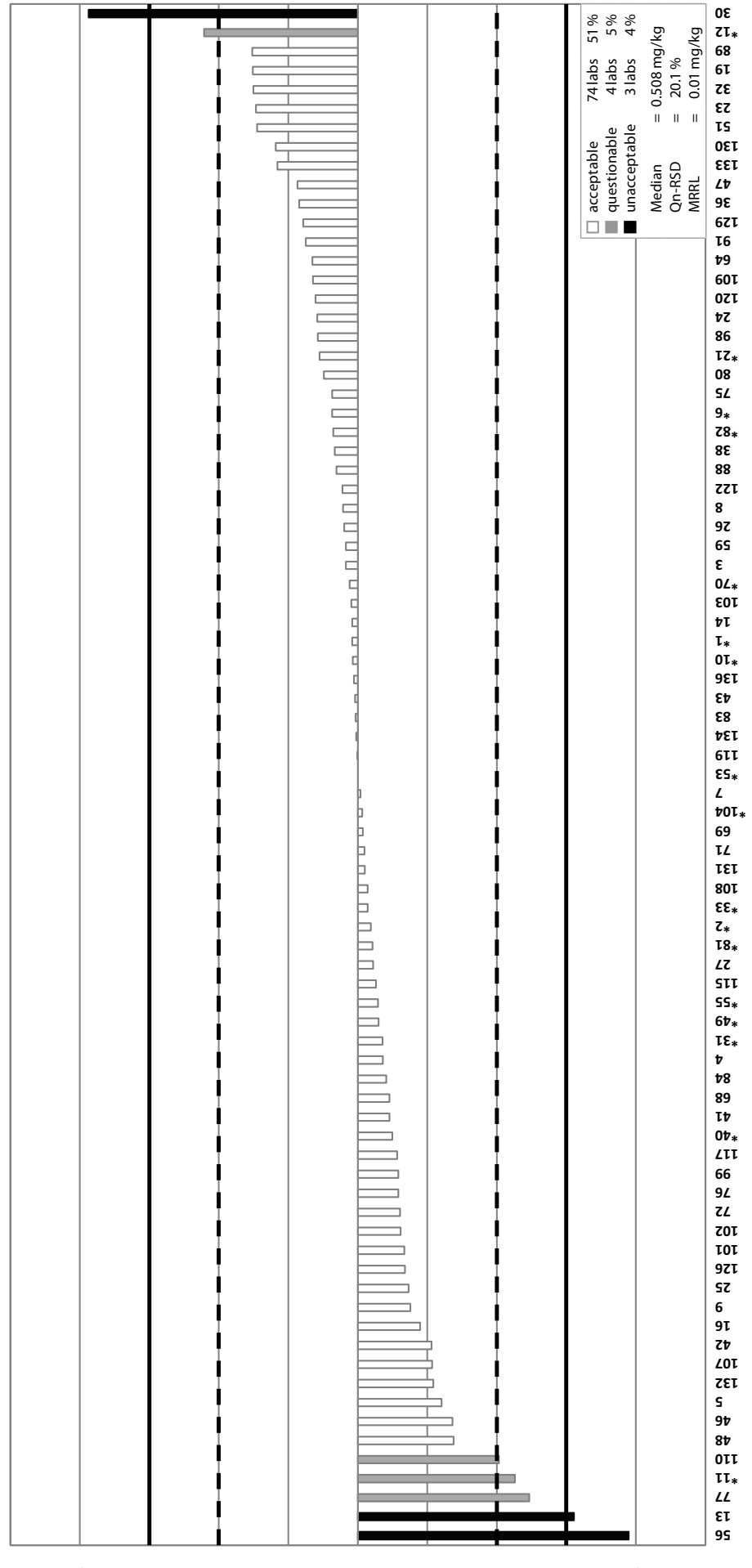


Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds



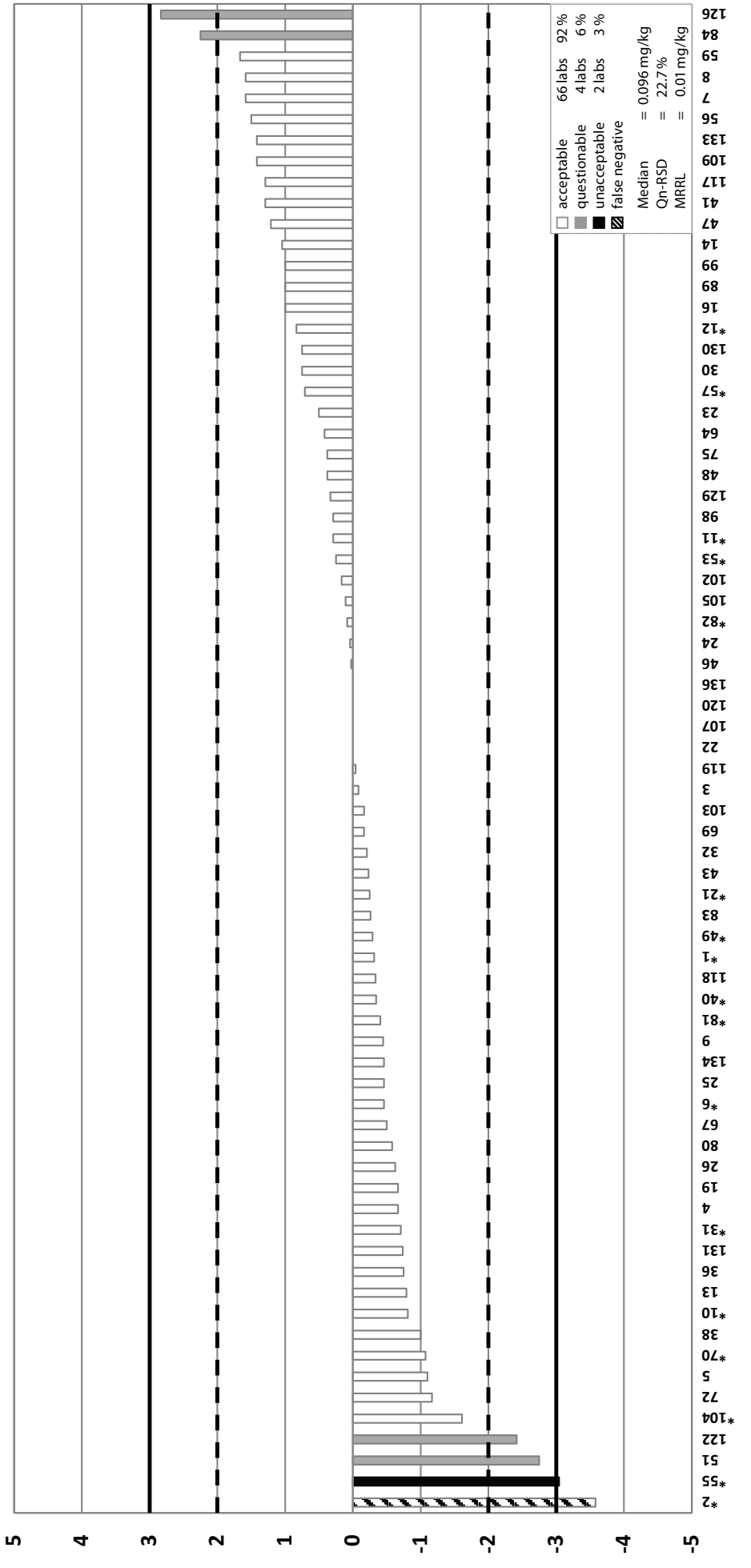
Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds

Haloxyfop

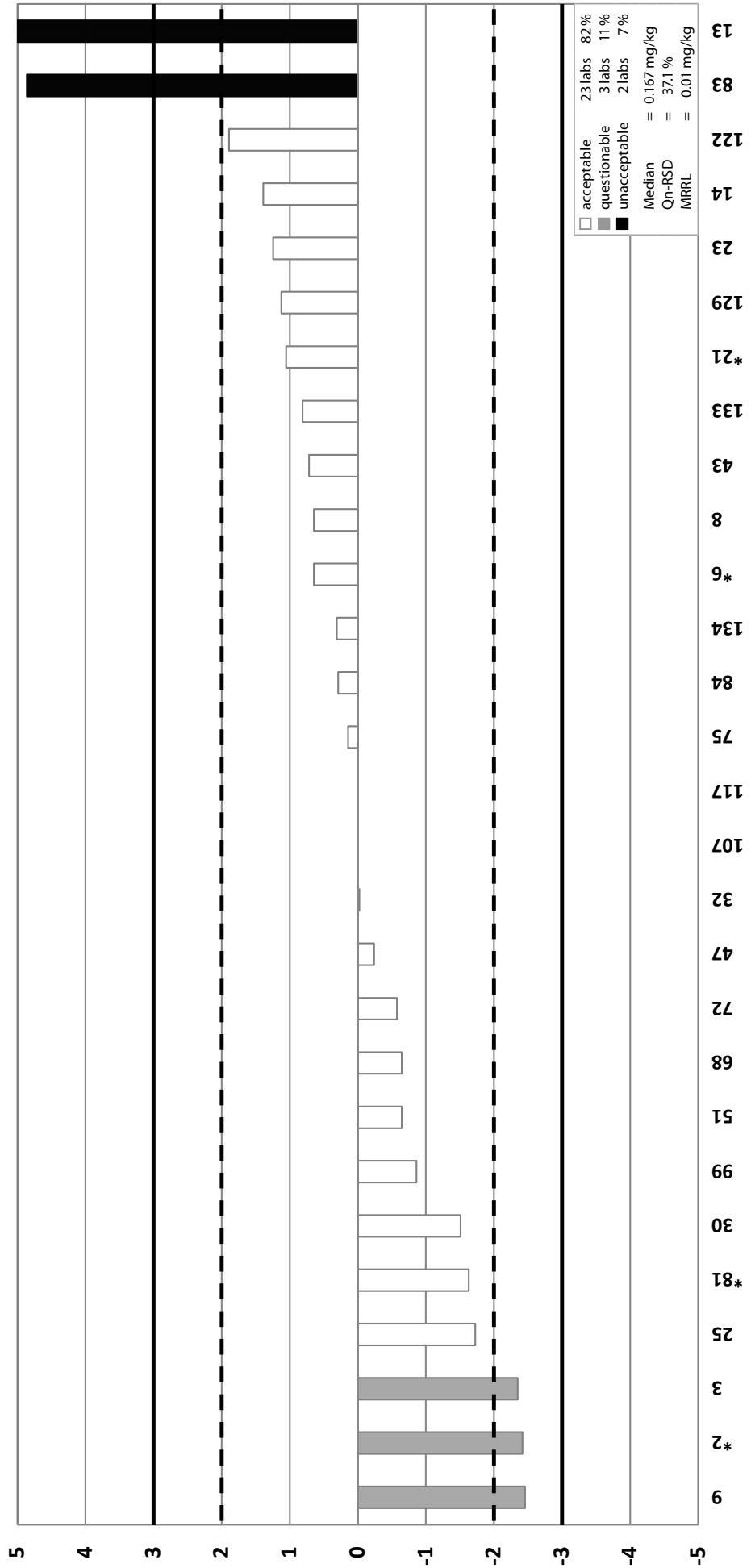


Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds

Mepiquat

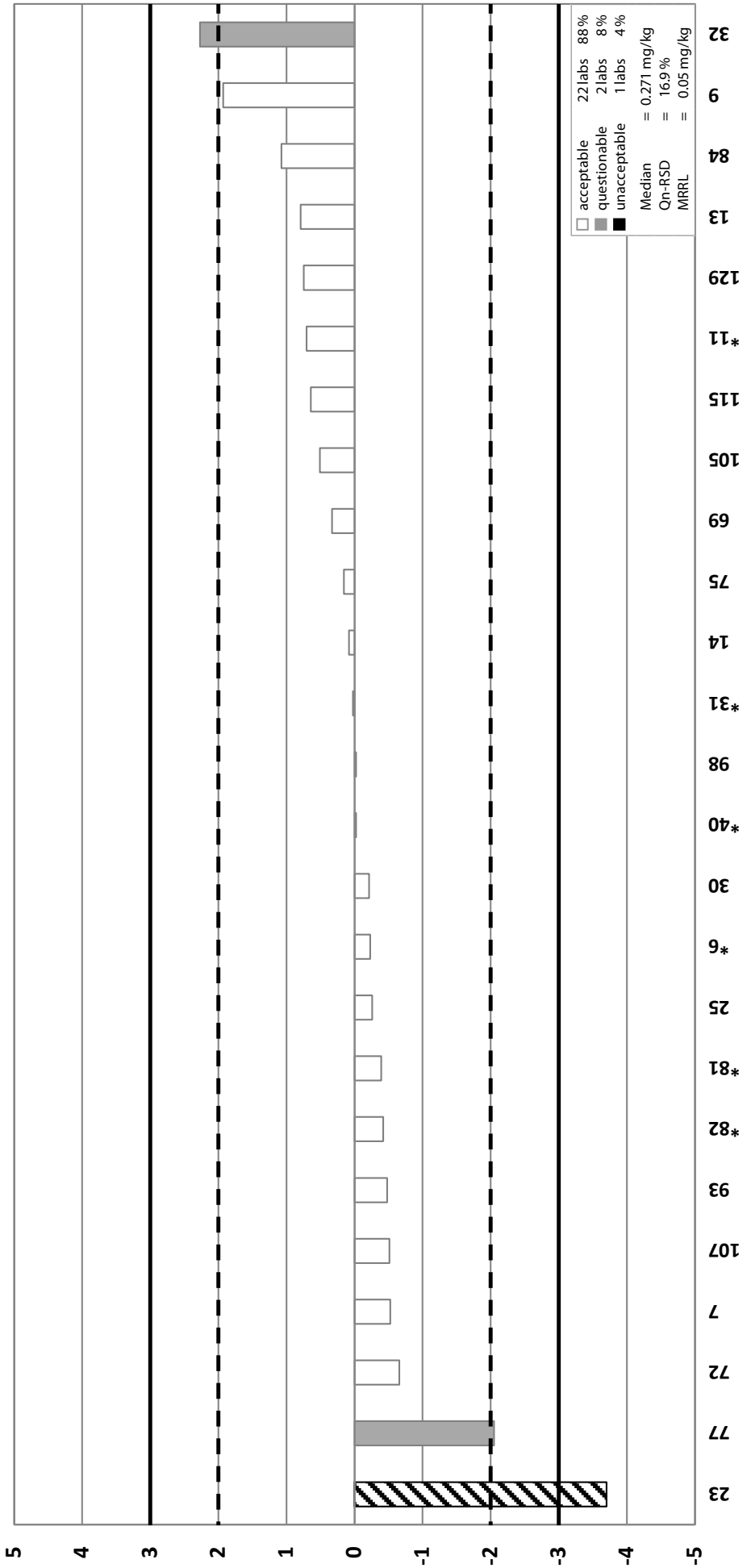


Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds



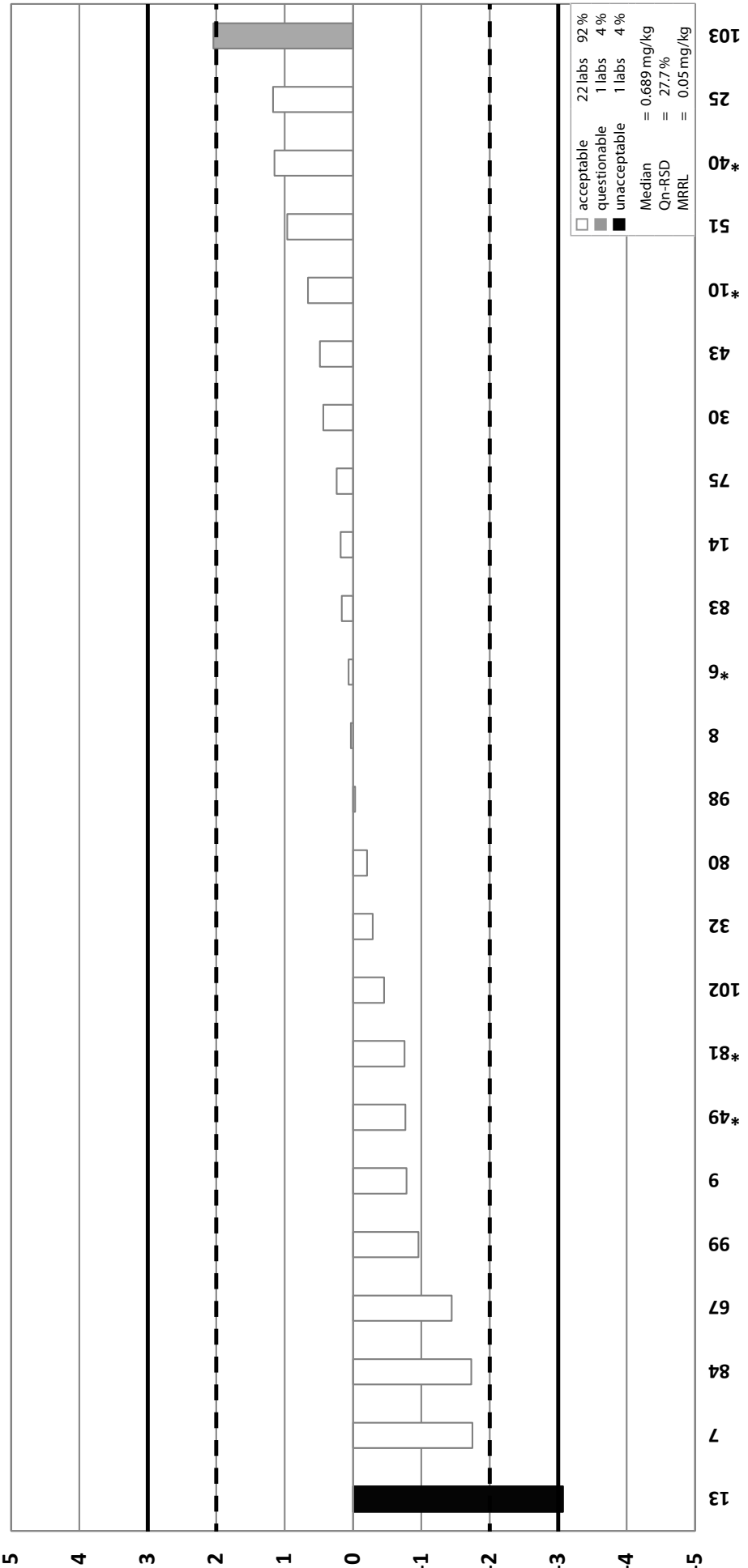
Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds

Glufosinate

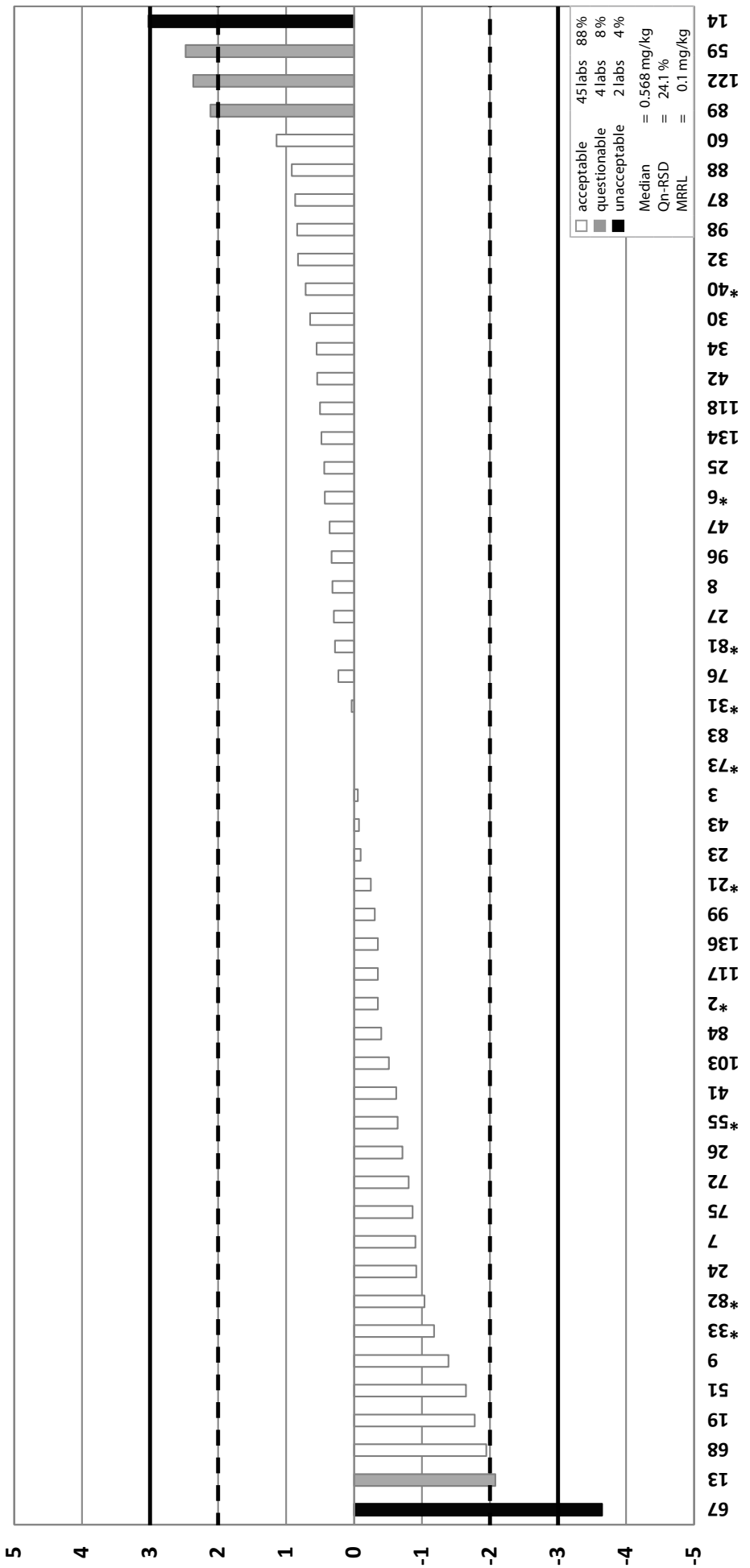


Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds

Maleic hydrazide

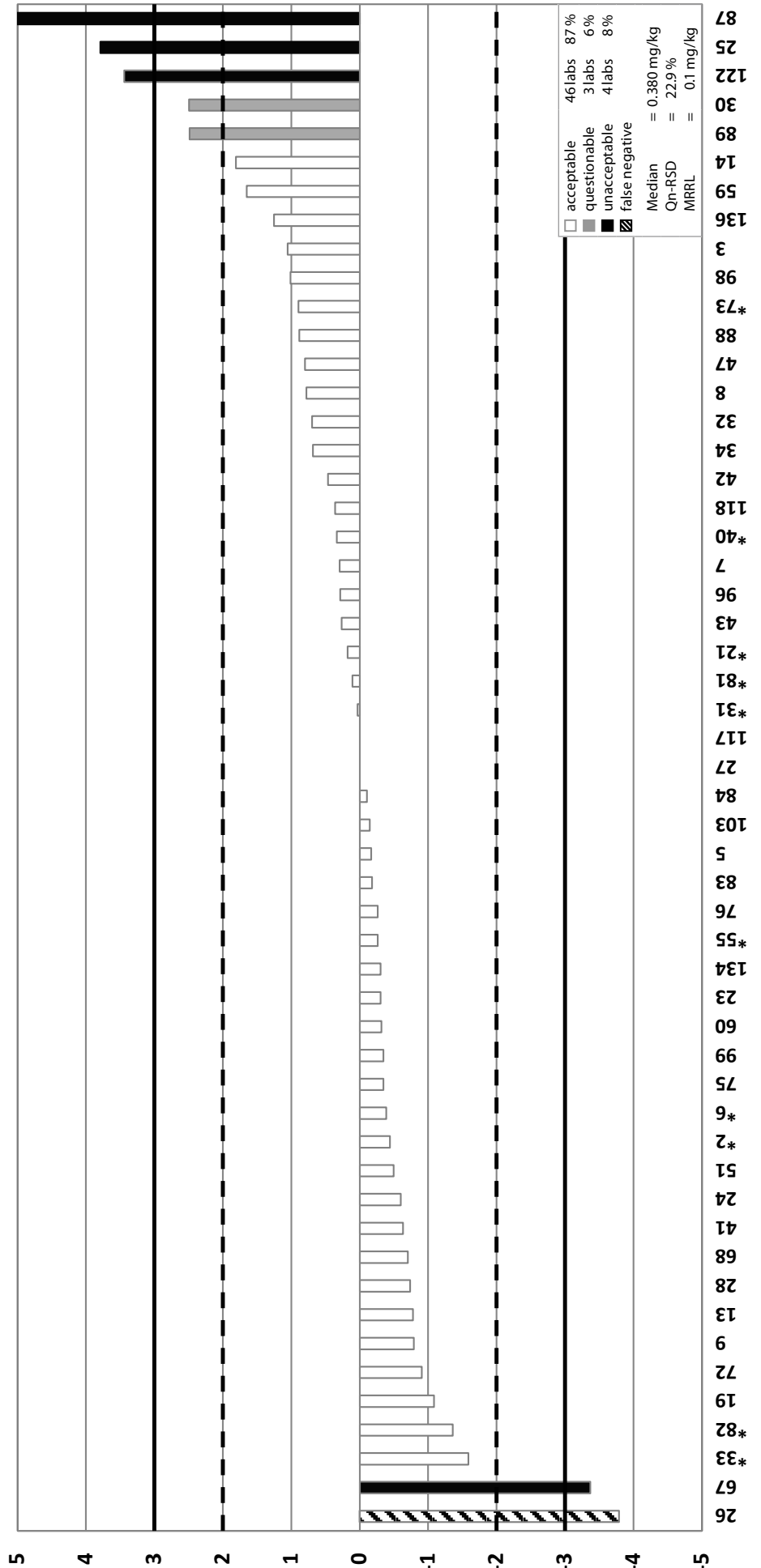


Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds

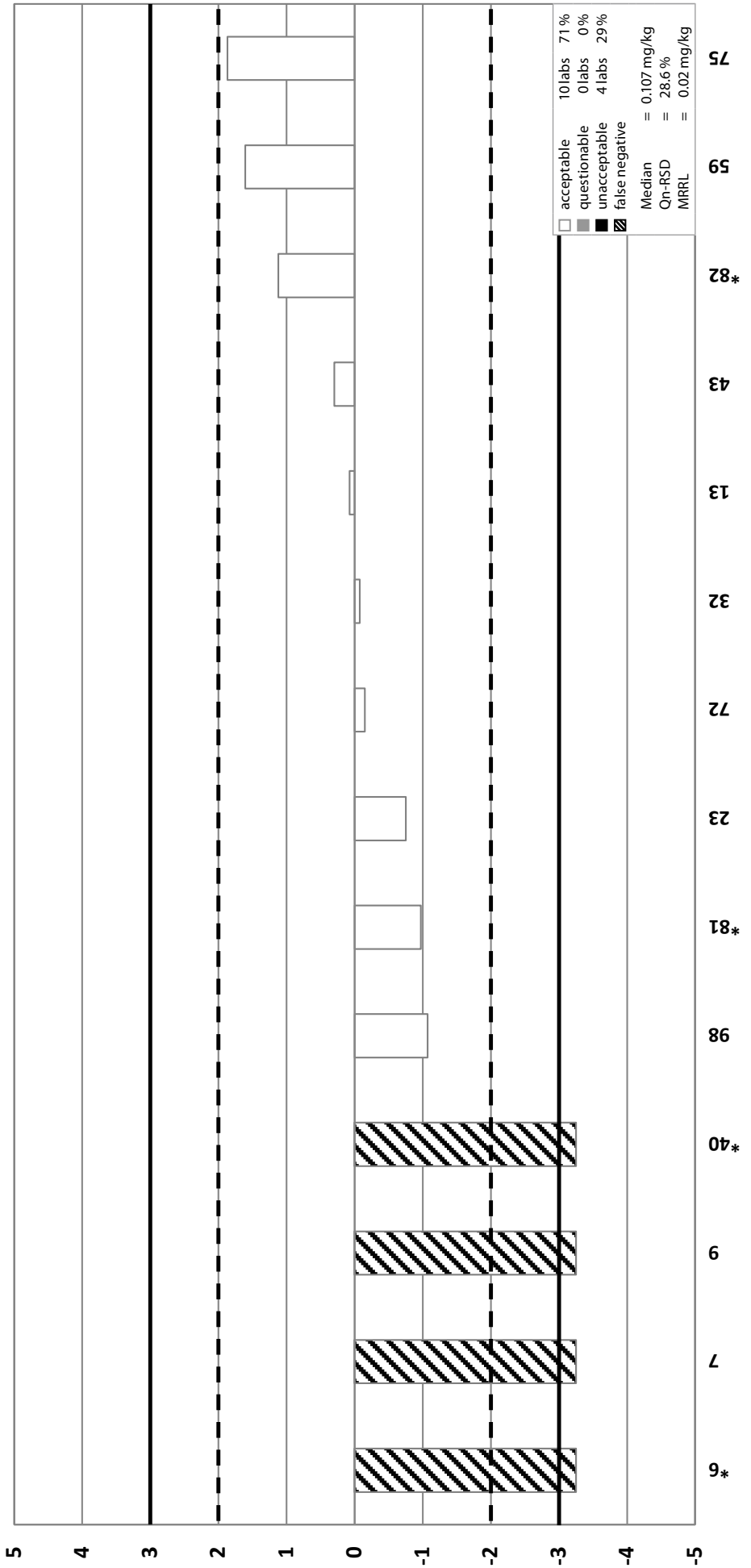


Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds

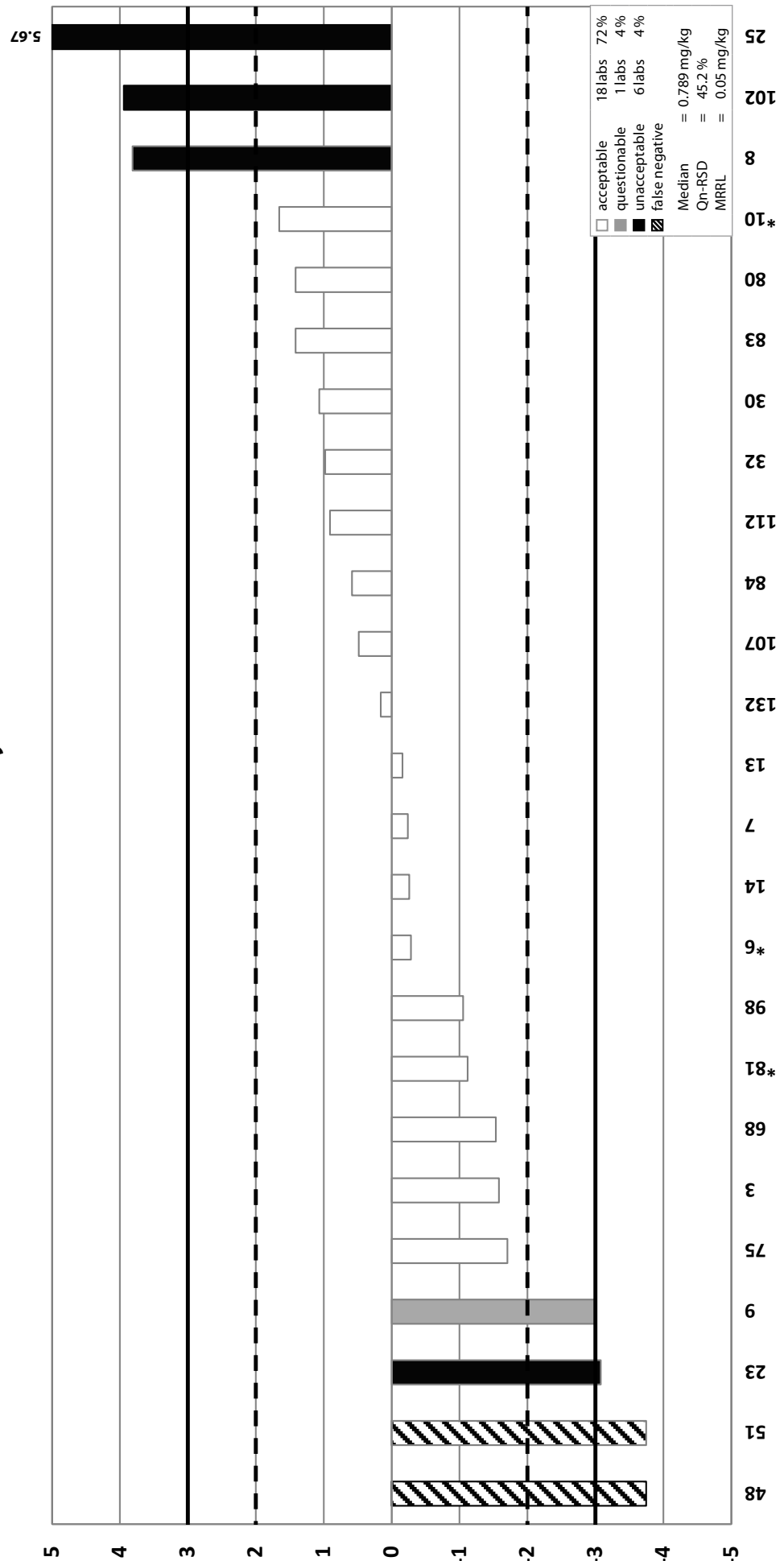
DDAC-C10



Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds and FOR INFORMATION ONLY



Appendix 6 (cont.) Graphic presentation of z-scores: Optional compounds and FOR INFORMATION ONLY



Appendix 7 Methods used by the participating laboratories (ordered by z-scores)

Captan

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
2	x	Yes	> 2 y	FN	-3.96	0.1	10	ambient	1	No	No	3	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
67		Yes	> 2 y	FN*	-3.96	0.01	10	just thawed	5			5	ACN		
96		No	None	FN	-3.96	0.05	10	ambient	1	No	No	2	ACN; 100%	No	Dispersive-SPE (PSA/ $MgSO_4$)
122		Yes	> 2 y	FN	-3.96	0.01	2	cold	10	Yes	No	1	10ml ACN 9 ml H_2O	No	None
94		Yes	> 2 y	FN	-3.96	0.01	10	cold		No	No	2	ACN		Dispersive-SPE (ODS/ $MgSO_4$)
105		Yes	> 2 y	0.148	-3.41	0.01	10	cold	30	No	No	5	EtOAc	No	SPE-column, Carbon black
101		Yes	> 2 y	0.22	-3.13	0.001	5	cold	10	Yes, 5 mL	No	10	ACN	No	Filtration
61		No	1 – 2 y	0.327	-2.7	0.01	10	ambient	1	No	No	1	ACN	No	None
19		Yes	> 2 y	0.404	-2.4	0.01	15	slightly frozen	5	No	No	1	ACN	No	None
68		Yes	> 2 y	0.461	-2.17	0.01	10	just thawed	2	No	No	2	ACN	No	None
52		Yes	> 2 y	0.543	-1.85	0.02	5	ambient	1	No	No	15	1% HOAc in ACN; shaken and centrifuged	No	$MgSO_4$/C18/ PSA
73	x	No	1 – 2 y	0.548	-1.83	0.02	10	ambient	5	No	No	30	Acetone; DMC; PE	Yes, pH = 6.5	None
132		No	< 1 y	0.58	-1.7	0.01	10	cold	20	Yes, 2 mL	No	> 60	ACN	Yes, 5-5.5	Dispersive-SPE (PSA/ $MgSO_4$)
48		Yes	> 2 y	0.645	-1.45	0.05	10	deep frozen	5	No	No	20	EtOAc	No	Centrifugation; Dilution
31	x	Yes	> 2 y	0.647	-1.44	0.02	37	just thawed	2	No	No	1	EtOAc	No	GPC, Gel-Permeation Chr/phy
59		Yes	> 2 y	0.7	-1.23	0.01	10	ambient	30	Yes	No	2	MeOH; DMC	No	Dispersive-SPE, other, PSA

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	Different Column, DB-5 & DB-17 columns	MM-SL	No					QuEChERS - Citrate buffered (EN 15662)
		GC-MS/MS (QQQ)		MM-ML	No					QuEChERS - Citrate buffered (EN 15662), / Unable to quantify - Problems with the standards.
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No					QuEChERS - Citrate buffered (EN 15662), extraction and DSPE purification
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate					QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD, ion ratio	MM-SL	No					QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, TBP	No	64 % (0.25mg/kg)	SB-EUPT	1	other, Blending, SPE, GC-MSMS
	No	LC-MS/MS QQQ	GC-NPD, detection	MM-ML	No	No				QuEChERS - Original Version (J. AOAC 86, 2003)
	No	GC-(μ) ECD		MM-ML	No	No	87 %		1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-SL	No	No	71.7 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	70 % Compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), without clean-up
	No	GC-MS/MS (QQQ)		PS-ML	No	Yes-1	99 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), Modified Quechers
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	80 %	SB-EUPT	2	S-19 or Mini-Luke
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	Yes-5	63 % 0.05 mg/kg			QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		Std add. to sample portions	No	Yes-2		see comments	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	GC-(μ) ECD	GC-MSD, NCI	MM-ML	No	No	90 % (1 mg/kg)	SB-EUPT	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), extraction ethylacetate, GPC cleaning, Isooctane sample analyzed
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	Yes-5	40 %	QC	> 5	ChemElut

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Captan

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
9		Yes	> 2 y	0.705	-1.21	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
6	x	Yes	> 2 y	0.716	-1.16	0.01	10	cold	5	Yes, 2.2 ml	No	1	EtOAc	No	None
46		Yes	> 2 y	0.72	-1.15	0.02	20	cold	1	No	No	1	Acetone; DMC; PE	No	Centrifugation
119	x	Yes	> 2 y	0.738	-1.08	0.01	10	cold	> 30	No	No	25	EtOAc	No	GPC, Gel-Permeation Chr/phy
136		Yes	> 2 y	0.762	-0.98	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
77		Yes	> 2 y	0.769	-0.95	0.01	10	ambient		No	No	1	ACN	Yes, 5	Dispersive-SPE (PSA/ $MgSO_4$)
110	x	No	> 2 y	0.77	-0.95	0.1	12	just thawed		No	No	1	ACN	Yes, citrate buffer	Dispersive-SPE (PSA/ $MgSO_4$)
71		Yes	> 2 y	0.777	-0.92	0.01	15	ambient	10	No	No	5	ACN	Yes	None
12	x	Yes	None	0.781	-0.91	0.01	10	cold		No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
130		No	> 2 y	0.796	-0.85	0.01	10	just thawed	15	No	No	60	DMC; with diatomaceous earths	Yes, acido citrico	None
56		Yes	> 2 y	0.797	-0.84	0.01	10	just thawed	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
82	x	Yes	> 2 y	0.797	-0.84	0.01	15	just thawed	1	No	No	5	Acetone; DMC; PE	No	None
70	x	Yes	> 2 y	0.809	-0.8	0.01	10			No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
107	x	No	> 2 y	0.825	-0.73	0.01	10	just thawed	1	No	No	2	ACN	Yes, H2SO4	None
72		Yes	> 2 y	0.828	-0.72	0.01	10	deep frozen	10	Yes	No	30	Acetone; DMC; PE	No	Dessication with Na_2SO_4
102		Yes	> 2 y	0.83	-0.71	0.01	10	slightly frozen	2	No	No	5	EtOAc	No	Dispersive-SPE (PSA/ $MgSO_4$)
120		Yes	> 2 y	0.841	-0.67	0.01	10	ambient	1	Yes, ca. 10:1 (H_2O :acetone)	No	> 60	Acetone	No	Filtration; SPE-column, EnviChromP

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MS/MS (QQQ)		MM-ML	Yes, PCB 31	No	73 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	No	89 %	SB-EUPT	2	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	89.0 % (0.05 and 0.1mg/ kg)	SB-EUPT	2	S-19 or Mini-Luke
	No	GC-MSD	GC-MSD	MM-ML	No	No	85 %	SB-EUPT	2	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MS/MS (QQQ)		MM-ML	Yes, IL-target pesticide	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap	GC-Ion Trap	MM-ML	Yes, TPP	No	124 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD		MM-ML	No	No	82 % (0.1 mg/ kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-Ion Trap	MM-SL	No	Yes-1	64.3 % (0.2 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MSD	GC-MSD, 2 SIM	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD, 3 sim ions	PS-ML	Yes, Bromophos methyl	No	73 % 1.5 mg/ kg (twice)	SB-EUPT	2	other, Rapporti Istisan n° 1997/23 - met. B4, with analyte protectant
	No	GC-MSD	GC-MSD, 2 columns with different polarities	MM-ML	Yes, Bromophos methyl	No	125 % compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MSD	MM-ML	No	No	87.5 % (0.1mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MSD	GC-MSD	MM-ML	No	No	77 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), Two transistions	MM-ML	Yes, C6-captan	Yes-3	96 %	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-(μ) ECD	GC-ECD	MM-ML	Yes, nitrofen	No	95 %	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-ECD	PS-ML	No	No	96 %	QC	1	other, QUECHERS ETHYL ACETATE
	No	GC-MSD		MM-ML	Yes, TPP to extract aliquots	Yes-1	90 % (0.01, 0.10, 0.25 and 1.0 mg/kg)	SB-EUPT	4	other, extraction acetone, filtration, dilution with H_2O, SPE (EnviChrom P), elution with acetone

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Captan

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
129		Yes	> 2 y	0.844	-0.66	0.01	10	ambient	30	No	No	15	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
25		Yes	> 2 y	0.845	-0.65	0.01	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	Dispersive-SPE (PSA/ $MgSO_4$)
103		Yes	> 2 y	0.847	-0.65	0.02	15	cold	2	No	No	2	ACN; H_2OH_2O from sample	No	Dispersive-SPE (PSA/ $MgSO_4$)
127		Yes	> 2 y	0.866	-0.57	0.05	20	ambient	1	No	No	3	Acetone; DMC	No	Liquid/liquid Partitioning
27		Yes	> 2 y	0.87	-0.55	0.01	10	deep frozen	10	No	Yes, 200 µl 5m NaOH	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
1	x	Yes	> 2 y	0.876	-0.53	0.01	10	cold	5	No	No	3	ACN	Yes, phosphoric acid, pH=2	LicHrolut EN/ DEA columns
33	x	Yes	> 2 y	0.89	-0.48	0.01	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration
49	x	Yes	> 2 y	0.916	-0.37	0.02	50	ambient	1	No	No	1	Acetone	No	Liquid-liquid partitioning; isopropyl-ether
124		Yes	> 2 y	0.92	-0.36	0.01	10		30	No	No	> 60	ACN	No	None
121		Yes	> 2 y	0.924	-0.34	0.01	10	ambient		No	No	10	Acetone	No	None
115		Yes	> 2 y	0.926	-0.33	0.01	10	cold	2	No	No	5	ACN	No	None
99	x	Yes	> 2 y	0.932	-0.31	0.01	30			No	No	1	EtOAc	Yes $NaHCO_3$	GPC, Gel-Permeation Chr/phy
88		Yes	> 2 y	0.934	-0.3	0.01	10	deep frozen	> 30	No	No	10	ACN; citrate buffer	Yes, extraction and partitioning	Centrifugation; Dispersive-SPE (PSA/ $MgSO_4$)
3		Yes	> 2 y	0.97	-0.16	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	Dispersive-SPE (PSA/ $MgSO_4$)
86		No	1 – 2 y	0.976	-0.13	0.01	20	ambient	2	No	No	3	EtOAc	No	Dessication with Na_2SO_4
43		Yes	> 2 y	0.978	-0.13	0.05	10	ambient		No	No	3	EtOAc	Yes, $NaHCO_3$	Filtration

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	99 % (1mg/kg)	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003), / Normal Quechers
	No	GC-MS/MS (QQQ)	GC-Ion Trap	MM-ML	Yes, Bromophos methyl	No	85 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD		MM-ML	No	No	98 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-NPD	MM-ML	No	No	101.2 %	SB-EUPT	3	S-19 or Mini-Luke, acetone extraction, partition to DMC (with H_2O addition)
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	95 % compound spiked			QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MSD	GC-MSD	MM-ML	Yes, phenathrene-D10	No	94 %	SB-EUPT	1	other, ACN extraction, column RP-SPE+NP-SPE cleanup
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), EI	MM-ML	No	No				SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MS/MS (QQQ)	GC-ECD	MM-ML	No	No	90 % (100ng/g)	SB-other	1	S-19 or Mini-Luke
	No	GC-(μ) ECD		MM-ML	No	No	70 %	SB-EUPT	5	other, MSPD
	No	GC-MS/MS (QQQ)		MM-ML	No	Yes-5	89 %	QC	1	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	98.2 % (1ppm)	SB-EUPT	3	QuEChERS-based EURL-Mth for captan/folpet/dicofol, / evaluated by multilevel matrix calibration
	No	GC-MSD	GC-MSD	MM-ML	Yes, Tetraphenylethylene	No	90 % (0.02 mg/kg)		1	other, in house / Used in house potato blank for recovery.
	No	GC-MSD		MM-ML	Yes, TPP, not for calculation	No	88 % (1 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662), / rel. standard deviation 2.8 % with 5 individuals
	No	GC-MSD		Std add. to sample portions	Yes, IL-target pesticide	Yes-1	115 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	No	No	108 %	SB-other	1	other, solid-liquid extraction
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-SL	Yes, Parathion-D10	No	89 % (1.13 mg/kg)	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Captan

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
5		Yes	> 2 y	0.995	-0.06	0.01	10	deep frozen	1	No	No	2	EtOAc	Yes; $NaHCO_3$ added at extraction stage	SPE-column, SampliQ Carbon	
98		Yes	> 2 y	1	-0.04	0.01	10	cold	20	No	No	20	ACN	No	Centrifugation; Dispersive-SPE (PSA/ $MgSO_4$)	
47		Yes	> 2 y	1.01	0	0.01	10	deep frozen		No	No	1	ACN	Yes, citrate buffer	Dispersive-SPE (PSA/ $MgSO_4$)	
81	x	Yes	> 2 y	1.01	0	0.01	10	cold	2	No	No	5	ACN	No	None	
53	x	Yes	> 2 y	1.029	0.08	0.01	10	ambient	2	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
26		Yes	> 2 y	1.04	0.12	0.01	50	slightly frozen	10	Yes	No	3	Acetone; CyHn; EtOAc; Cyclohexan/ Ethylacetat 1:1	No	GPC, Gel-Permeation Chr/phy; Silica Column; mini-silicacolumn, fraktion 1-3 together	
7		Yes	> 2 y	1.05	0.16	0.01	10	deep frozen	2	No	No	30	ACN	No	None	
57	x	Yes	> 2 y	1.05	0.16	0.01	15	slightly frozen		No	No	1	Acetone	No	None	
4		Yes	> 2 y	1.066	0.22	0.01	10	deep frozen	2	No	No	1	ACN	No	None	
32		Yes	> 2 y	1.07	0.24	0.01	10	deep frozen	2	No	No	15	ACN	No	None	
36		Yes	> 2 y	1.08	0.28	0.01	10	slightly frozen		No	No	1	ACN	Yes, pH 5.5	Dispersive-SPE (PSA/ $MgSO_4$)	
128		Yes	> 2 y	1.1	0.36	0.01	10	slightly frozen	10	No		15	ACN	Yes, 5.5	Dispersive-SPE (PSA/ $MgSO_4$)	
10	x	Yes	> 2 y	1.11	0.4	0.05	50	ambient	1	No	No	1	EtOAc	Yes, extraction	GPC, Gel-Permeation Chr/phy	
69		Yes	> 2 y	1.11	0.4	0.05	10	slightly frozen	30	No	No	10	ACN	Yes, after add. of salt	Dispersive-SPE (PSA/ $MgSO_4$)	
13		No	> 2 y	1.12	0.44	0.01	10	slightly frozen	5	No	No	5	ACN	Yes, H_2SO_4	None	
126	x	No	None	1.12	0.44	0.1	10	cold	2	No	No	30	ACN	No	None	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MSD	GC-MS/MS (QQQ), MSMS transition	MM-ML	Yes, trifluralin D14	No	83 % (0.02 mg/kg)	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-(μ) ECD	GC-Ion Trap	PS-ML	Yes, Tris-(1.3-dichlor-isopropyl)-phosphat	No	77.6 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	Yes, PCB 52	No	85 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), +analyte protectant
	No	GC-Ion Trap	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	No	100.0 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-MSD	GC-MSD	MM-ML	No	Yes-2		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-TOF	MM-ML	No	No	72.8 %	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to extract aliquots	Yes, TPP	Yes-2		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	No	No	87 %	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MSD	MM-SL	No	No	78.9 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	Std add. to extract aliquots	Yes, Chlorpyrifos D10	Yes-2	99 %	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)		MM-ML	Yes, D4 Folpet	No	98 %	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		MM-ML	No	No	72 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-Ion Trap	MM-ML	No	No	79 %	SB-EUPT	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MSD		MM-ML	Yes, TDCPP	No	121 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Analyte Protectans
	No	GC-MS/MS (QQQ)		MM-ML	Yes, Tris-(2-chloro-1(chloro-methyl) ethyl) phosphate	No	109.5 % spiked level 0.04 mg/kg	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-Ion Trap	GC-Ion Trap	MM-ML	No	No	75 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Captan

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
30		Yes	> 2 y	1.13	0.48	0.005	50	ambient	5	Yes, 60 mL	No	2	Acetone; CyHn; EtOAc	No	GPC, Gel-Permeation Chr/phy; Silica Column
40	x	Yes	> 2 y	1.14	0.51	0.02	10	cold	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
84		Yes	> 2 y	1.145	0.53	0.01	15	cold	> 30	No	No	2	Acetone; DMC; PE	No	Centrifugation; Filtration
11	x	No	None	1.15	0.55	0.01	10	deep frozen	10	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
55	x	Yes	< 1 y	1.15	0.55	0.01	25	deep frozen		No	No	5	EtOAc	No	None
117	x	Yes	> 2 y	1.15	0.55	0.01	15	ambient	1	No	No	1	Acetone; DMC; PE	No	None
21	x	Yes	> 2 y	1.16	0.59	0.01	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$
28		Yes	> 2 y	1.16	0.59	0.02	15	cold	1	No	No	20	Acetone; DMC; Other; PE	No	Centrifugation
38		Yes	> 2 y	1.17	0.63	0.01	10	slightly frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
76		Yes	> 2 y	1.17	0.63	0.1	50	just thawed	5	No	No	45	MeOH; DMC; EtOAc	No	GPC, Gel-Permeation Chr/phy
137		Yes	> 2 y	1.19	0.71	0.01	10	slightly frozen	2	No	No	2	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
18		Yes	> 2 y	1.21	0.79	0.01	10	slightly frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
22		Yes	> 2 y	1.21	0.79	0.01	10	deep frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
65		No	< 1 y	1.21	0.79	0.01	10	slightly frozen	5	No	No	25	EtOAc; EtOAc acidified 1% HOAc	No	None
75		Yes	> 2 y	1.22	0.83	0.01	15	ambient	1	No	No	5	Acetone; DMC; PE	No	None
89		Yes	> 2 y	1.22	0.83	0.01	10	ambient	1	No	No	1	ACN	No	Freezing-out

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, not for calculation, only to check extraction efficiency	No	89 % (1 mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, aldrin	No	91 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-ECD	MM-ML	Yes, PCB	Yes-2	70 % (0.1 mg/kg)	SB-EUPT	2	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)		PS-ML	No	No	120 % (0.010 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		MM-SL	Yes, TPP	No	85 % (0.1 mg/kg)	SB-EUPT	3	other, Ethyl acetate extraction
	No	GC-MSD	LC-MS/MS QQQ, Ion ratio	MM-ML	No	No	84 % (40 ug/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-TOF		MM-ML	Yes, TPP	No	93 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-(μ) ECD	GC-Ion Trap, ITD MS/MS	MM-ML	Yes, TPP	No	126 %)0.02 mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-ECD	MM-SL	No	No	102 % Spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, Mirex	No	100 % (0.1 mg/kg)	SB-other	1	S-19 or Mini-Luke, / No
	No	GC-Ion Trap	GC-MSD	MM-ML	Yes, TPP	No	115 % (1 mg/kg)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, Etion	No	101 % compound spiked	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	Yes, TPP	No	105 %	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap	GC-Ion Trap	Std add. to sample portions	No	No	81 % (0.1, 0.2, 0.5 mg/kg)	SB-EUPT	3	other, Ethyl acetate acidified 1% HOAc / recovery calculated by slope ratio: 3 levels
	No	GC-(μ) ECD	GC-MSD	MM-ML	Yes anthracen	No	80 % (0.5, 1.0, 2.0 and 3.0 mg/kg)	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-TOF, additional standard addition to extract portions	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3	98 %	QC	> 5	QuEChERS-based EURL-Mth for captan/folpet/dicofol

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Captan

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
97		Yes	> 2 y	1.22	0.83	0.02	10	ambient	2	No	No	20	DMC	No	Others; diatomaceus earth
83		Yes	> 2 y	1.25	0.95	0.01	5	slightly frozen	1	No	No	3	ACN	No	None
24		Yes	> 2 y	1.28	1.07	0.01	10	just thawed	1	No	No	15	ACN	No	Dispersive-SPE (PSA/$MgSO_4$); Centrifugation; 13 mm Acrodisc syringe filter
8		Yes	> 2 y	1.283	1.08	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, Citrate Buffer pH 5.5	Dispersive-SPE (PSA/$MgSO_4$)
14		Yes	> 2 y	1.289	1.1	0.01	10	ambient	1	No	No	15	ACN	Yes, HCl, pH 5	None
79		Yes	> 2 y	1.3	1.15	0.01	15	cold		No	No	60	Acetone; DMC; PE	No	Centrifugation
64		Yes	> 2 y	1.33	1.27	0.01	10	ambient	10	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
41		Yes	> 2 y	1.34	1.31	0.01	10	deep frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
104	x	Yes	> 2 y	1.35	1.35	0.02	10	just thawed	10	No	No	2	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
112		No	> 2 y	1.427	1.65	0.1	10	deep frozen	1	No	No	5	Acetone	No	None
80		Yes	> 2 y	1.46	1.78	0.01	20	deep frozen	30	Yes	No	3	Acetone	No	solid-supported liquid/liquid partition (Chem Elut - DMC)
109	x	Yes	> 2 y	1.48	1.86	0.01	10	just thawed	2	No	No	5	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
78		Yes	> 2 y	1.49	1.9	0.02	10	deep frozen		No	No	20	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
51		Yes	> 2 y	1.55	2.14	0.01	10	ambient	1	No	No	30	ACN	No	Centrifugation
44		Yes	> 2 y	1.62	2.42	0.01	10	deep frozen	5	No	No	1	ACN	Yes, after extraction	Dispersive-SPE (PSA/$MgSO_4$)
133		Yes	> 2 y	2.85	7.29	0.04	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, endosulfan lactone	No	80 %	QC	5	other, mix in diatomaceus earth extraction dichloromethane
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), 2 MRM	MM-SL	Yes Captan D6	Yes-2	92.7 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MSD	MM-ML	Yes, Pirimicarb-D6, TPP	No	95 %	SB-EUPT	2	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MSD		Std add. to sample portions	Yes, Tris-(1.3-dichlor-isopropyl)-phosphat	Yes-2	81 % (1.5 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Analyte Protectants added prior GC-NCI
	No	GC-MSD		MM-ML	Yes, Captan (D6)	Yes-4	79 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-Ion Trap	GC-MSD	MM-ML	No	No	88 % standard addition	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, PCB 209	No	120 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MS/MS (QQQ)	MM-SL	Yes, TPP	No	93 % (0.1 mg/kg & 0.01 mg/kg)	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	Yes, TRIS	No	88 % (0.1mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap		MM-SL	No	No	70 % (0.1 mg/kg)	SB-EUPT	1	other, extraction, dilution
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, IL- other substance	No	93 % (2 mg/kg)	SB-other	2	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	98.6 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-Ion Trap	MM-SL	No	No	91 % (1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	> 5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to sample portions	Yes, TRISCP	Yes-2	113 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	Different Column, HP-5 and SPB-1 (30 x 0.53 μm) both	MM-ML	No	No	99.6 % (0.16 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), 10g+ACN:10mL; Citrate mixt.: 6.5g; evaporation of 6 mL ACN phase; redissol.2 mL Isooct:tol(90:10) / Recovery RSD= 7.8%

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
119	x	Yes	> 2 y	FN	-3.61	0.01	10	cold	> 30	No	No	25	EtOAc	No	GPC, Gel-Permeation Chr/phy
121		No	< 1 y	FN	-3.61	0.01	10	ambient		Yes, 1.5ml	No	2	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
57	x	Yes	> 2 y	0.0104	-3.59	0.01	10	slightly frozen		No	No	1	ACN	No	Centrifugation; Dispersive-SPE (PSA/$MgSO_4$)
102		Yes	> 2 y	0.04	-2.43	0.01	10	slightly frozen	2	No	No	10	QuPPe solvent	No	None
70	x	Yes	1 – 2 y	0.0436	-2.29	0.01	10			No	No	10	MeOH	No	Centrifugation
2	x	Yes	> 2 y	0.049	-2.08	0.01	10	ambient	1	No	No	3	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
3		Yes	> 2 y	0.055	-1.84	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	None
68		Yes	1 – 2 y	0.057	-1.76	0.01	10	just thawed	2	No	No	2	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
67		Yes	> 2 y	0.06	-1.65	0.01	10	just thawed				5	ACN		
52		Yes	> 2 y	0.064	-1.49	0.02	5	ambient	1	No	No	15	1% HOAc in ACN; shaken and centrifuged	No	Others; $MgSO_4$/C18/PSA
108		Yes	1 – 2 y	0.065	-1.45	0.05	10	cold	15	No	No	10	ACN	No	Filtration
24		Yes	1 – 2 y	0.067	-1.37	0.01	10	just thawed	1	Yes, 2 mL	No	15	MeOH	No	Centrifugation; Filtration; 13 mm Acrodisc syringe filter
99	x	Yes	> 2 y	0.0682	-1.33	0.01	10			No	No	1	ACN	Yes, acetate buffer	Centrifugation
22		No	< 1 y	0.069	-1.29	0.01	10	deep frozen	1	No	No	1	MeOH	No	None
112		No	1 – 2 y	0.07	-1.25	0.01	10	deep frozen	1	No	No	10	H_2O; MeOH two different extractions: solvent A then B	No	None
104	x	No	> 2 y	0.0751	-1.05	0.02	10	just thawed	10	No	No	2	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
56		Yes	> 2 y	0.0797	-0.87	0.03	10	just thawed	5	No	No	5	EtOAc	No	Filtration

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MSD	GC-MSD	MM-ML	No					SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ		MM-ML	No					QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	30 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	No	No	60 %	QC	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, chlormequat D4	No	103 %	SB-EUPT	2	other, LST EN 15055
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	51.6 % (0.05 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), / from QC data Recoveries 70-80%
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Isoproturond8	Yes-1	53 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	70 % Compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), with clean up
	No	LC-MS/MS QQQ		MM-ML	No	No	60 % (0.025mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		PS-ML	No	Yes-1	78 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), Modified Quechers
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, d3-Carbendazim	Yes-2				QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Pirimicarb-D6, TPP	No	60 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	MM-ML	No	No	74 % (0.02 mg/kg)		1	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), / Used in house potato blank for recovery.
	No	LC-Orbitrap	LC-Orbitrap	PS-ML	Yes, TPP	No	71 %	SB-EUPT	3	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, chlorpyriphos D10	No	71 % (0.1 mg/kg)	SB-EUPT	1	other, extraction and concentration
	No	GC-MSD	GC-MSD	MM-ML	Yes, TRIS	No	90 % (0.1mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-Ion Trap	MM-ML	Yes, TPP	No	129 % compound spiked	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
43		Yes	> 2 y	0.0812	-0.82	0.05	10	ambient		No	No	3	EtOAc	YesHCO_3	Filtration
13		Yes	> 2 y	0.082	-0.78	0.01	10	slightly frozen	5	No	No	5	ACN	No	SPE-column, PSA/C18
136		Yes	> 2 y	0.083	-0.75	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
5		Yes	1 – 2 y	0.0839	-0.71	0.01	10	deep frozen	1	No	No	2	EtOAc	Yes $NaHCO_3$ added at extraction stage	None
72		Yes	> 2 y	0.084	-0.71	0.02	5	deep frozen	1	No	No	5	ACN	Yes, with FA	Dessication with Na_2SO_4
34		Yes	> 2 y	0.0851	-0.66	0.01	10	deep frozen	2	No	No	5	QuPPe solvent (MeOH/1% FA)	No	None
48		Yes	> 2 y	0.0854	-0.65	0.01	10	deep frozen	5	No	No	20	EtOAc	No	Centrifugation; Dilution
80		Yes	> 2 y	0.0857	-0.64	0.01	10	deep frozen	30	Yes	No	3	EtOAc	No	None
131		Yes	> 2 y	0.0876	-0.56	0.01									
32		Yes	1 – 2 y	0.09	-0.47	0.01	10	deep frozen	2	No	No	1	QuPPe solvent	No	Filtration
31	x	No	< 1 y	0.092	-0.39	0.02	10	slightly frozen	2	No	No	30	ACN	No	None
50		No	None	0.092	-0.39	0.01	10	ambient	1	No	No	1	1% FA in ACN	No	None
16		Yes	> 2 y	0.093	-0.35	0.04	10	cold	1	No	No	30	MeOH	No	Centrifugation; Filtration; 4.1.6 Mini uniprep polypropylen filter vials
26		Yes	1 – 2 y	0.093	-0.35	0.02	20	slightly frozen	10	Yes	No	2	MeOH	No	None
130		No	> 2 y	0.093	-0.35	0.01	10	just thawed	2	Yes, up to 10 g of H_2O	No	2	ACN	Yes, citrate buffer	None
98		No	> 2 y	0.0954	-0.26	0.01	10	cold	20	No	No	5	QuPPe solvent	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-SL	Yes, Pirimicarb-D6	No	74 % (0.0925 mg/kg)	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	50.7 % (0.10 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Nicarbazin	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second MSMS transition	MM-ML	Yes, methomyl D3, carbendazim D4, pendimethalin D5	No	67 % (0.02 mg/kg)	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), solvent exchange into MeOH
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide to extract aliquots	No	91 %	SB-EUPT	1	other, in house method
	No	LC-MS/MS QQQ		PS-ML	No	No	108 % spikyng level	SB-EUPT	5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to sample portions	No	Yes-2		see comments	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL- other substance	No	99 % (0.1mg/kg)	SB-other	2	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No					No	54 %	SB-other		
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, chlormequat-D3	Yes-3	111 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 167-125, 167-108	MM-ML	No	Yes-1	50.1 % (0.1 mg/kg)	SB-EUPT	3	QuEChERS - Original Version (J. AOAC 86, 2003), extraction in ACN, cenfrituge, analyze with LC MSMS
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	Yes-5	87 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-ML	No	No	86 % Compound spiked in blank, wait 30, then extraction	SB-EUPT	2	other, Methanolic extraction, published by Kit Granby et al.
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	93.3 %	SB-EUPT	1	other, §64 LFGB L00.00-76
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, TPP	Yes-1	23 % 0.05mg/kg (twice)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	78.3 % (0.1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
19		Yes	> 2 y	0.096	-0.24	0.01	15	slightly frozen	5	No	No	1	ACN	No	None
25		Yes	1 – 2 y	0.098	-0.16	0.01	10	deep frozen	2	No	No	2	QuPPe solvent	No	None
4		No	< 1 y	0.099	-0.12	0.01	10	deep frozen	2	No	No	2	MeOH	No	None
8		Yes	> 2 y	0.1	-0.08	0.01	10	just thawed	2	Yes, added to 10 g	No	3	MeOH	Yes, 1% FA in MeOH	None
41		No	None	0.1	-0.08	0.01	10	deep frozen	2	Yes, 2 mL	No	1	QuPPe solvent	No	Centrifugation; Filtration
9		Yes	> 2 y	0.101	-0.04	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
49	x	Yes	> 2 y	0.101	-0.04	0.05	10	ambient	5	No	No	1	90% MeOH, 10% H_2O, 0.5mM NH_4CH_3COO	No	Filtration
117	x	Yes	> 2 y	0.102	0	0.01	10	ambient	1	No	No	1	MeOH	No	None
38		No	< 1 y	0.104	0.08	0.01	10	slightly frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
40	x	No	None	0.104	0.08	0.01	10	cold	10	No	No	1	QuPPe solvent	No	Filtration
84		Yes	> 2 y	0.104	0.08	0.05	25	ambient	> 30	No	No	2	MeOH	No	Centrifugation; Filtration
10	x	No	< 1 y	0.105	0.12	0.01	10	ambient	1	No	No	1	QuPPe solvent	No	Filtration
88		Yes	> 2 y	0.106	0.16	0.005	10	deep frozen	> 30	No	No	10	QuPPe solvent	No	Centrifugation; Filtration; Polyester filters 0.45 µm pore size
6	x	Yes	> 2 y	0.107	0.2	0.01	10	cold	5	Yes, 2.2 ml	No	1	QuPPe solvent	No	None
53	x	Yes	None	0.108	0.24	0.01	10	ambient	2	No	No	10	MeOH	No	None
81	x	No	< 1 y	0.108	0.24	0.02	10	cold	2	No	No	5	ACN; 1 v/v % FA in ACN	No	None
75		Yes	> 2 y	0.111	0.35	0.05	10	ambient	2	No	No	5	MeOH	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-SL	No	Yes-1	46.5 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	100 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS	LC-MS	MM-ML	No	No	101.3 %	SB-EUPT	3	other, Analysis of Chlormequat and mepiquat residues in Food of Plant origin, EURL-SRM, ver.2, 2009
	No	LC-MS/MS QQQ		MM-ML	Yes, Mepiquat-D3	No	87 % (0.1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	104 % (0.01 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, Sulfotep	No	81 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Oxfendazole	No	73 % (100ng/g)	SB-EUPT	1	other, in house method (ISTD was used to correct the injection, but not the recovery!)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	MM-ML	No	No	116 % (50 ug/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	Yes-1	46 % Spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	84 % (0.05 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/ MS QQQ, Mini-Luke extraction	PS-ML	No	Yes-2	84.4 %	SB-EUPT	2	other, MeOH-extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	98 %	SB-EUPT	3	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, Pirimicarb-D6, not for calculation	No	91 % (0.0625 mg/kg)	SB-EUPT	3	QuPPe-Method (EURL-SRM mth f. polar pesticides), / rel standard deviation 2.2 % with 3 individuals
	No	LC-MS/MS QQQ		MM-ML	No	Yes-5	100 % Blank matrix spiked before extraction	SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-2		SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	No	85.0 % (0.05 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), final extract was adjusted to 20 ml
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	Yes-2	100 % (0.05 and 0.1 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
134		No	< 1 y	0.111	0.35	0.01	10	cold	5	No	No	5	QuPPe solvent	No	Freezing out
33	x	Yes	> 2 y	0.114	0.47	0.01	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration
47		No	< 1 y	0.115	0.51	0.01	10	deep frozen		No	No	1	QuPPe solvent	Yes, FA	None
82	x	Yes	1 – 2 y	0.115	0.51	0.01	10	just thawed	15	No	No	60	MeOH	Yes, extraction	None
69		Yes	1 – 2 y	0.119	0.67	0.01	10	slightly frozen	15	Yes	No	1	QuPPe solvent	No	None
83		Yes	> 2 y	0.119	0.67	0.01	5	slightly frozen	1	No	No	3	ACN	No	None
36		No	1 – 2 y	0.12	0.71	0.01	10	slightly frozen		No	No	1	ACN	Yes, pH = 5.5	Filtration
64		Yes	1 – 2 y	0.12	0.71	0.01	10	ambient	10	Yes, 2 mL	No	1	MeOH; 1% FA	Yes	None
128		Yes	1 – 2 y	0.12	0.71	0.01	10	slightly frozen	10	No		15	ACN	Yes, pH = 5.5	Dispersive-SPE (PSA/ $MgSO_4$)
132		Yes	1 – 2 y	0.12	0.71	0.01	10	cold	20	Yes, 2 mL	No	> 60	ACN	Yes, 5 – 5.5	Dispersive-SPE (PSA/ $MgSO_4$)
46		Yes	> 2 y	0.121	0.75	0.01	10	cold	2	No	No	1	QuPPe solvent	No	None; centrifugation and filtration
107	x	No	1 – 2 y	0.121	0.75	0.02	10	just thawed	1	No	No	2	ACN	No	Filtration
126	x	No	None	0.124	0.86	0.1	10	cold	2	Yes, 2ml	No	30	QuPPe solvent	No	None
133		Yes	None	0.125	0.9	0.01	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None
21	x	Yes	> 2 y	0.126	0.94	0.01	10	slightly frozen	5	Yes, 4mL to 10g sample	No	2	QuPPe solvent	No	None
129		Yes	1 – 2 y	0.126	0.94	0.01	10	ambient	20	No	No	15	MeOH	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	No	95 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, ES+	MM-ML	No	Yes-2		QC		SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	100 %	QC		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second transition	MM-ML	Yes, D4-cyromazine	Yes-3	101.8 % (0.1mg/kg)	SB-EUPT	1	other, acidified MeOH extraction
	No	LC-MS/MS QQQ		Std add. to sample portions	No	No	106 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	Different Column, Poroshell 120 and Zorbax Eclipseplus C18	MM-SL	No	Yes-2	64.1 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	52 %	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	70 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	GC-MS/MS (QQQ)		MM-ML	No	No	70 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	Yes-5	61 % 0.05 m/kg			QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	111.2 % (0.02 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-carbaryl	Yes-1	35 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Without PSA clean-up
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	70 %	SB-other	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ), Note: Normaly we use the column Obelisc R	Std add. to extract aliquots	No	Yes-1	50.2 % (0.05 mg/kg; n=6)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662), 10g+ACN:10mL; Citrate mixture buffer (6.5g); no-cleanup; Column: Phenomenex Synergi 4u Hydro RP 80A / Recovery RSD= 17.5%
	No	LC-MS/MS QQQ		MM-ML	Yes, chlormequat D4	No	77 % (0.05 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-5	97 % (0.25 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), / Polar Quechers: extraction with MeOH

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Cyromazine

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
14		Yes	> 2 y	0.127	0.98	0.01	10	ambient	1	No	No	15	QuPPe solvent	No	None
23		No	< 1 y	0.127	0.98	0.01	10	ambient	5	Yes, 2 mL	No	2	QuPPe solvent	Yes, addition of FA to MeOH	Filtration
103		No	1 – 2 y	0.127	0.98	0.01	10	cold	2	No	No	2	MeOH; H_2O from sample	No	None
30		Yes	> 2 y	0.132	1.18	0.05	4	ambient	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
95		Yes	> 2 y	0.138	1.41	0.01	10	cold		No	No		ACN	No	Dispersive-SPE (C18/ $MgSO_4$)
12	x	Yes	< 1 y	0.139	1.45	0.01	10	cold		No	No	2	QuPPe solvent	No	Filtration
89		Yes	1 – 2 y	0.139	1.45	0.01	10	ambient	1	No	No	1	QuPPe solvent	No	Centrifugation; 5min > 2500 g
7		Yes	1 – 2 y	0.14	1.49	0.02	10	just thawed	2	No	No	15	QuPPe solvent	No	None
11	x	Yes	1 – 2 y	0.142	1.57	0.01	10	deep frozen	10	No	No	15	QuPPe solvent	No	None
51		Yes	> 2 y	0.16	2.27	0.01	10	ambient	1	No	No	30	ACN	No	Centrifugation
120		Yes	1 – 2 y	0.161	2.31	0.01	10	ambient	20	Yes, 2ml	No	60	H_2O; MeOH = 33 : 67	Yes, pH6 – 7	Filtration; SPE-column, Extrelut columns
59		Yes	> 2 y	0.17	2.67	0.01	10	ambient	30	Yes	No	2	MeOH; DMC	Yes, pH 4.5 buffered	None
1	x	Yes	> 2 y	0.229	4.98	0.01	10	ambient	1	No	No	1	ACN	No	None
122		Yes	> 2 y	0.303	7.88	0.01	2	cold	10	Yes	No	1	10ml ACN; 9 ml H_2O	No	None
61		Yes	> 2 y	0.427	12.75	0.01	2	ambient	1	Yes	Yes	1	0.1% FA in H_2O	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	Different Column, Phenyl column	MM-ML	Yes, Cyromazine (D4)	Yes-4	82 % Extraction recovery vs MMC	SB-EUPT	5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	Different Method, QuEChERS after correction to recovery	MM-ML	Yes, TPP	No	115 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	No	100 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, not for calculation, only to check extraction efficiency	Yes-2	87 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	Yes, PCB 31	No	80 % (0.2, 0.5 and 0.7mg/kg)	SB-EUPT	5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2MRM	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3		SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	No	73 %	QC	4	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-4		QC		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Cyromazine D4	Yes-4	105 % (0.010 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), QuPPe EURL-SRM method for polar pesticides v.6
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	> 5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	64.8 % spiked blank sample on diff. cali. levels; covering linear range	SB-EUPT	5	ChemElut, extraction MeOH/H_2O; pH adjustment; cleaning Extrelut columns, modif. mobile phase
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	Yes-5	30 %	QC	> 5	ChemElut
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-1	24 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate	No	84 %	QC	4	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	No	109 %		1	other

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dicofol

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
63		Yes	> 2 y	FN	-3.98	0.005	2.5	cold	5	No		60	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
56		Yes	> 2 y	0.006	-3.96	0.01	10	just thawed	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
122		Yes	< 1 y	FN	-3.96	0.01	2	cold	10	Yes	No	1	10ml ACN; 9 ml H_2O	No	None	
130		No	> 2 y	0.111	-3.57	0.01	10	just thawed	15	No	No	60	DMC; with diatomaceous earths	Yes, acido citrico	None	
52		Yes	> 2 y	0.208	-3.19	0.02	5	ambient	1	No	No	15	1% HOAc in ACN; shaken and centrifuged	No	Others; $MgSO_4$/C18/ PSA	
61		No	1 – 2 y	0.276	-2.93	0.01	10	ambient	1	No	No	1	ACN	No	None	
121		Yes	> 2 y	0.368	-2.57	0.01	10	ambient		No	No	10	Acetone	No	None	
88		Yes	> 2 y	0.462	-2.21	0.01	10	deep frozen	> 30	No	No	10	ACN; citrate buffer	Yes, extraction and partitioning	Centrifugation; Dispersive-SPE (PSA/ $MgSO_4$)	
105		Yes	> 2 y	0.568	-1.79	0.01	10	cold	30	No	No	5	EtOAc	No	SPE-column, Carbon black	
94		Yes	> 2 y	0.57	-1.79	0.01	10	cold		No	No	2	ACN		Dispersive-SPE (ODS/ $MgSO_4$)	
46		Yes	> 2 y	0.601	-1.67	0.01	10	cold	2	No	No	10	ACN	No	None; centrifugation	
24		Yes	> 2 y	0.633	-1.54	0.01	10	just thawed	1	No	No	15	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); Centrifugation; 13 mm Acrodisc syringe filter	
89		Yes	> 2 y	0.645	-1.5	0.01	10	ambient	1	No	No	1	ACN	No	Freezing-out	
101		Yes	> 2 y	0.645	-1.5	0.005	10	cold	10	No	No	10	ACN	No	Filtration	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MS/MS (QQQ)			Yes, differents PCB's	Yes-1	40 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	GC-MSD	GC-MSD, 2 columns with different polarities	MM-ML	Yes, Bromophos methyl	No	90 % compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate					QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD, 3 sim ions	PS-ML	Yes, Bromophos methyl	No	112 % 0.20mg/kg	SB-EUPT	2	other, Rapporti Istisan n° 1997/23 - met. B4, with analyte protectant
	No	GC-MS/MS (QQQ)		PS-ML	No	Yes-1	82 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), Modified Quechers
	No	GC-(μ) ECD		MM-ML	No	No	92 %		1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		MM-ML	No	Yes-5	92 %	QC	1	S-19 or Mini-Luke
	No	GC-MSD		MM-ML	Yes, TPP, not for calculation	No	104 % (0.375 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662), / rel. standard deviation 8.6 % with 5 individuals
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, TBP	No	71 % (0.25mg/kg)	SB-EUPT	1	other, Blending, SPE, GC-MSMS
	No	GC-MSD	GC-MSD, ion ratio	Std. add. to sample portion	No	Yes-1	90 %	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	Yes-5		SB-other	4	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MSD	MM-ML	Yes, Pirimicarb-D6, TPP	No	88 %	SB-EUPT	2	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)	GC-TOF, additional standard addition to extract portions	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3	82 %	QC	5	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-(μ) ECD	GC-NPD, detection	MM-ML	No	Yes-2	89.28 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dicofol

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
27		Yes	> 2 y	0.66	-1.44	0.01	10	deep frozen	10	No	Yes, 200 µl 5m NaOH	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
119	x	Yes	> 2 y	0.686	-1.34	0.01	10	cold	> 30	No	No	25	EtOAc	No	GPC, Gel-Permeation Chr/phy
48		Yes	> 2 y	0.694	-1.3	0.01	10	deep frozen	5	No	No	20	EtOAc	No	Centrifugation; Dilution
108		Yes	1 – 2 y	0.701	-1.28	0.01	10	cold	15	No	No	10	ACN	No	None
136		Yes	> 2 y	0.734	-1.15	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
72		Yes	> 2 y	0.737	-1.14	0.01	10	deep frozen	10	Yes	No	30	Acetone; DMC; PE	No	Dessication with Na_2SO_4
4		Yes	> 2 y	0.74	-1.13	0.01	10	deep frozen	2	No	No	1	ACN	No	None
38		Yes	> 2 y	0.766	-1.03	0.01	10	slightly frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
42		No	> 2 y	0.783	-0.96	0.01	10	just thawed	1	No	No	1	ACN	Yes, Citrate Buffered	Dessication with $MgSO_4$; Dispersive-SPE (PSA/ $MgSO_4$)
120		Yes	> 2 y	0.791	-0.93	0.01	10	ambient	1	Yes, ca. 10:1 (H_2O : acetone)	No	> 60	Acetone	No	Filtration; SPE-column, EnviChromP
127		Yes	> 2 y	0.803	-0.88	0.02	20	ambient	1	No	No	3	Acetone; DMC	No	Liquid/liquid Partitioning
2	x	Yes	> 2 y	0.818	-0.82	0.05	10	ambient	1	No	No	3	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
5		Yes	> 2 y	0.845	-0.72	0.01	10	deep frozen	1	No	No	2	EtOAc	Yes $NaHCO_3$ added at extraction stage	SPE-column, SampliQ Carbon
124		Yes	> 2 y	0.86	-0.66	0.01	10		> 30	No	No	> 60	ACN	No	None
126	x	No	1 – 2 y	0.876	-0.6	0.01	10	cold	2	No	No	30	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	99 % compound spiked			QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MSD	GC-MSD	MM-ML	No	No	87 %	SB-EUPT	2	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MS/MS (QQQ)		Std add. to sample portions	No	Yes-2		see comments	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to sample portions	Yes, d6-Parathion	Yes-2				QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		Std add. to sample portions	Yes, TDCP	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	No	106 %	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MSD	MM-SL	No	No	101.0 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-ECD	MM-SL	No	No	101 % Spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-ECD	MM-ML	No	No				QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD		MM-ML	Yes, TPP to extract aliquots	Yes-1	82 % (0.01, 0.10, 0.25 and 1.0 mg/kg)	SB-EUPT	4	other, extraction acetone, filtration, dilution with H_2O, SPE (EnviChrom P), elution with acetone
	No	GC-(μ) ECD	GC-NPD	MM-ML	No	No	93.2 %	SB-EUPT	3	S-19 or Mini-Luke, acetone extraction, partition to DMC (with H_2O addition)
	No	GC-(μ) ECD	Different Column, DB-5 & DB-17 columns	MM-SL	No	No	113 % (0.5 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), second MSMS transition	MM-ML	Yes, trifluralin D14, ppDDE D8	No	85 % (0.02 mg/kg)	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-(μ) ECD		MM-ML	No	No	86 %	SB-EUPT	5	other, MSPD
	No	GC-Ion Trap	GC-Ion Trap	MM-ML	No	No	80 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dicofol

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
31	x	Yes	> 2 y	0.884	-0.57	0.02	10	slightly frozen	2	No	No	1	ACN; ACN acidified with H_2SO_4	Yes, ACN prepared with 100µl conc. H_2SO_4 for 10 ml ACN	None
12	x	Yes	None	0.888	-0.55	0.01	10	cold		No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
96		Yes	1 – 2 y	0.888	-0.55	0.01	10	ambient	1	No	No	2	ACN; 100%	No	Dispersive-SPE (PSA/ $MgSO_4$)
37		Yes	> 2 y	0.889	-0.55	0.01	10	just thawed	20	No	No	60	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
82	x	Yes	> 2 y	0.892	-0.54	0.01	15	just thawed	1	No	No	5	Acetone; DMC; PE	No	None
6	x	Yes	> 2 y	0.893	-0.53	0.01	10	cold	5	Yes, 2.2 ml	No	1	EtOAc	No	None
107	x	No	> 2 y	0.897	-0.52	0.01	10	just thawed	1	No	No	2	ACN	Yes, H_2SO_4	None
44		Yes	> 2 y	0.91	-0.47	0.01	10	deep frozen	5	No	No	1	ACN	Yes, after extraction	Dispersive-SPE (PSA/ $MgSO_4$)
10	x	Yes	> 2 y	0.913	-0.45	0.01	50	ambient	1	No	No	1	EtOAc	Yes, extraction	GPC, Gel-Permeation Chr/phy
13		Yes	> 2 y	0.923	-0.42	0.01	10	slightly frozen	5	No	No	5	ACN	No	PSA/C18
70	x	Yes	> 2 y	0.954	-0.3	0.01	10			No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
19		Yes	> 2 y	0.965	-0.25	0.01	15	slightly frozen	5	No	No	1	ACN	No	Dispersive-SPE, PSA/C18
80		Yes	> 2 y	0.98	-0.19	0.01	20	deep frozen	30	Yes	No	3	Acetone	No	Others; solid-supported liquid/liquid partition (Chem Elut - DCM)
3		Yes	> 2 y	1	-0.12	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	Dispersive-SPE (PSA/ $MgSO_4$)
8		Yes	> 2 y	1.005	-0.1	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, Citrate Buffer pH 5.5	Dispersive-SPE (PSA/ $MgSO_4$)

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	GC-MSD, NCI	MM-ML	No	No	100 % (1 mg/kg)	SB-EUPT	3	QuEChERS-based EURL-Mth for chlorothalonil, extraction acidified ACN with H_2SO_4, no cleanup
	No	GC-MSD	GC-MSD, 2 SIM	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	70 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), extraction and DSPE purification
	No	GC-MSD	GC-Ion Trap	MM-ML	Yes, ALFA HCH D6	Yes-1	114 % 0.5	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003), / dicofol degradacion
	No	GC-MS/MS (QQQ)	GC-MSD	MM-ML	No	No	95.1 % (0.1mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	No	106 %	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), Two transistions	MM-ML	No	No	91 %	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to sample portions	Yes, TRISCP	Yes-2	120 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-Ion Trap	MM-ML	No	No	85 %	SB-EUPT	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MS/MS (QQQ)		MM-ML	Yes, Tris-(2-chloro-1(chloro-methyl) ethyl) phosphate	No	85.3 % (0.04 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	No	No	91 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD, 3 ions	MM-SL	Yes, TDCPP	No	99.0 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, IL- other substance	No	102 % (1mg/kg)	SB-other	2	S-19 or Mini-Luke
	No	GC-MSD		Std add. to sample portions	Yes, IL-target pesticide	Yes-1	90 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD		MM-ML	Yes, Triphenylmethan	No	76 % (1.0 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Analyte Protectants added prior GC-MSD

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dicofol

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
36		No	None	1.01	-0.08	0.01	10	slightly frozen		No	No	1	ACN	Yes, pH 5.5	Dispersive-SPE (PSA/ $MgSO_4$)	
73	x	Yes	> 2 y	1.01	-0.08	0.02	10	ambient	5	No	No	30	Acetone; DMC; PE	Yes, 6.5	None	
112		Yes	> 2 y	1.02	-0.04	0.01	10	deep frozen	1	No	No	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
133		Yes	> 2 y	1.02	-0.04	0.01	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None	
28		Yes	> 2 y	1.03	0	0.01	15	cold	1	No	No	20	Acetone; DMC; PE	No	Centrifugation	
77		Yes	> 2 y	1.03	0	0.01	10	ambient		No	No	1	ACN	Yes, 5	Dispersive-SPE (PSA/ $MgSO_4$)	
9		Yes	> 2 y	1.05	0.08	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
43		Yes	> 2 y	1.05	0.08	0.05	10	ambient		No	No	3	EtOAc	Yes $NaHCO_3$	Filtration	
1	x	Yes	> 2 y	1.06	0.12	0.01	10	cold	5	No	No	3	ACN	Yes, H_3PO_4, pH=2	LiChrolut EN/ DEA columns	
99	x	Yes	> 2 y	1.06	0.12	0.01	30			No	No	1	EtOAc	Yes; $NaHCO_3$	GPC, Gel-Permeation Chr/phy	
79		Yes	> 2 y	1.07	0.16	0.01	15	cold		No	No	60	Acetone; DMC; PE	No	Centrifugation	
92		Yes	> 2 y	1.073	0.17	0.01	10	deep frozen	10	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
30		Yes	> 2 y	1.08	0.19	0.005	50	ambient	5	Yes, 60 mL	No	2	Acetone; CyHn; EtOAc	No	GPC, Gel-Permeation Chr/phy; Silica Column	
32		Yes	> 2 y	1.08	0.19	0.01	10	deep frozen	2	No	No	15	ACN	No	None	
129		Yes	> 2 y	1.08	0.19	0.01	10	ambient	30	No	No	15	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
21	x	Yes	> 2 y	1.1	0.27	0.01	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$	
33	x	Yes	> 2 y	1.1	0.27	0.05	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MS/MS (QQQ)		MM-ML	Yes, D10 Chlorpyrifos	No	97 %	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	80 %	SB-EUPT	2	S-19 or Mini-Luke
	No	GC-Ion Trap		MM-SL	No	No	66 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), extraction then purification by liquid/liquid partitions
	No	GC-(μ) ECD	Different Column, HP-5 and SPB-1(30 x 0.53 μm) both	MM-ML	No	No	99.3 % (0.04 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), 10g+ACN:10mL; Citrate mixt.: 6.5g; evaporation of 6 mL ACN phase; redissol.2 mL Isooct:tol(90:10) / Recovery RSD= 4.9%
	No	GC-Ion Trap	GC-Ion Trap, ITD MS/MS	MM-ML	Yes, TPP	No	122 % (0.01 mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-Ion Trap	GC-Ion Trap	MM-ML	Yes, TPP	No	128 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), / DIcofol ppÂ´+ dicofol deg
	No	GC-MS/MS (QQQ)		MM-ML	Yes, PCB 31	No	75 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-SL	Yes, Parathi-on-D10	No	92 % (1.00 mg/kg)	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MSD	GC-MSD	MM-ML	Yes, phen-athrene-D10	No	90 %	SB-EUPT	1	other, ACN extraction, column RP-SPE+NP-SPE cleanup
	No	GC-MSD	GC-MSD	MM-ML	Yes, Tetrap-henylethyl-ene	No	88 % (0.02 mg/kg)		1	other, in house / Used in house potato blank for recovery.
	No	GC-Ion Trap	GC-MSD	MM-ML	No	No	95 % stand-ard addition	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	103.39 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, not for calcula-tion, only to check extraction efficiency	No	86 % (1 mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MSD	GC-MSD	Std add. to ex-tract aliquots	Yes, Dicofol D8	Yes-2	110 %	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	136 % (1 mg/kg)	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003), / Normal Quechers
	No	GC-TOF		MM-ML	Yes, TPP	No	111 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), EI	MM-ML	No	No	88 % 0.05 mg/kg	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dicofol

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
53	x	Yes	> 2 y	1.1	0.27	0.01	10	ambient	2	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
41		Yes	1 – 2 y	1.11	0.31	0.01	10	deep frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
104	x	Yes	> 2 y	1.112	0.32	0.02	10	just thawed	10	No	No	2	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
115		Yes	> 2 y	1.12	0.35	0.01	10	cold	2	No	No	5	ACN	No	None	
78		Yes	> 2 y	1.13	0.39	0.02	10	deep frozen		No	No	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
67		Yes	> 2 y	1.15	0.47	0.01	10	just thawed				5	ACN			
65		Yes	> 2 y	1.16	0.5	0.01	10	slightly frozen	5	No	No	25	EtOAc; EtOAc acidified 1% HOAc	No	None	
16		Yes	> 2 y	1.18	0.58	0.01	10	cold	1	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); Centrifugation	
51		Yes	> 2 y	1.19	0.62	0.01	10	ambient	1	No	No	30	ACN	No	Centrifugation	
59		Yes	> 2 y	1.2	0.66	0.01	10	ambient	30	Yes	No	2	MeOH; DMC	No	Dispersive-SPE, PSA	
64		Yes	> 2 y	1.2	0.66	0.01	10	ambient	10	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
98		Yes	> 2 y	1.23	0.78	0.01	10	cold	20	No	No	20	ACN	No	Centrifugation; Dispersive-SPE (PSA/ $MgSO_4$)	
7		Yes	> 2 y	1.24	0.82	0.01	10	deep frozen	2	No	No	30	ACN	No	None	
14		Yes	> 2 y	1.248	0.85	0.01	10	ambient	1	No	No	15	ACN	Yes, HCl, pH 5	None	
26		Yes	> 2 y	1.28	0.97	0.04	50	slightly frozen	10	Yes	No	3	Acetone; CyHn; EtOAc; Cyclohexan/ Ethylacetat 1:1	No	GPC, Gel-Permeation Chr/phy; Silica Column; mini-silicacolumn, fraktion 1-3 together	
71		Yes	> 2 y	1.28	0.97	0.01	15	ambient	10	No	No	5	ACN	Yes	None	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MSD	GC-MSD	MM-ML	No	Yes-2		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MS/MS (QQQ)	MM-SL	Yes, TPP	No	95 % (0.1 mg/kg & 0.01 mg/kg)	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	Yes, TRIS	No	92 % (0.1mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	99.8 % (2ppm)	SB-EUPT	3	QuEChERS-based EURL-Mth for captan/folpet/dicofol, / evaluated by multilevel matrix calibration
	No	GC-(μ) ECD	GC-Ion Trap	MM-SL	No	No	93 % (2 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		MM-ML	No	No	98 % (0.025mg/kg)	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap	GC-Ion Trap	Std add. to sample portions	No	No	96 % (0.1, 0.2, 0.5 mg/kg)	SB-EUPT	3	other, Ethyl acetate acidified 1% HOAc / recovery calculated by slope ratio: 3 levels
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), 2 transitions	MM-ML	Yes, coffein	No	100 % Compound spiked in blank, wait 30, then extraction	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	> 5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	GC-TOF	GC-TOF	MM-ML	Yes, TPP	Yes-5	93 %	QC	> 5	ChemElut
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, PCB 209	No	116 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap	GC-ECD	MM-ML	No	No	115.0 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to extract aliquots	Yes, TPP	Yes-2		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD		MM-ML	Yes, Captan (D6)	Yes-2	81 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-TOF	MM-ML	No	No	76.1 %	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-Ion Trap	MM-SL	No	No	98.8 % (0.2 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Dicofol

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
69		Yes	> 2 y	1.29	1.01	0.05	10	slightly frozen	30	No	No	10	ACN	Yes, after add.of salt	Dispersive-SPE (PSA/ $MgSO_4$)	
137		Yes	> 2 y	1.29	1.01	0.01	10	slightly frozen	2	No	No	2	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
25		Yes	> 2 y	1.3	1.05	0.01	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	Dispersive-SPE (PSA/ $MgSO_4$)	
117	x	Yes	> 2 y	1.32	1.13	0.01	15	ambient	1	No	No	1	Acetone; DMC; PE	No	None	
81	x	Yes	> 2 y	1.34	1.2	0.01	10	cold	2	No	No	5	ACN	No	None	
84		Yes	> 2 y	1.346	1.23	0.01	15	cold	> 30	No	No	2	Acetone; DMC; PE	No	Centrifugation; Filtration	
22		No	> 2 y	1.35	1.24	0.01	10	deep frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
75		Yes	> 2 y	1.35	1.24	0.01	15	ambient	1	No	No	5	Acetone; DMC; PE	No	None	
83		Yes	> 2 y	1.35	1.24	0.01	5	slightly frozen	1	No	No	3	ACN	No	None	
109	x	Yes	> 2 y	1.35	1.24	0.01	10	just thawed	2	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
102		Yes	> 2 y	1.37	1.32	0.01	10	slightly frozen	2	No	No	5	EtOAc	No	Dispersive-SPE (PSA/ $MgSO_4$)	
40	x	Yes	> 2 y	1.48	1.75	0.01	10	cold	1	No	No	1	ACN	No	Others; QuEChERS without PSA	
49	x	Yes	> 2 y	1.575	2.12	0.01	50	ambient	1	No	No	1	Acetone	No	Liquid-liquid partitioning; isopropyl-ether	
57	x	Yes	> 2 y	1.78	2.91	0.01	15	slightly frozen		No	No	1	Acetone	No	None	
11	x	No	None	1.88	3.3	0.01	10	deep frozen	10	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
97		Yes	> 2 y	1.89	3.34	0.05	10	ambient	2	No	No	20	DMC	No	Others; diatomaceus earth	
128		No	None	3.64	10.14	0.01	10	slightly frozen	10	No		15	ACN	Yes, pH = 5.5	Dispersive-SPE (PSA/ $MgSO_4$)	
131		Yes	None	3.75	10.56	0.05										

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MSD		MM-ML	No	No	99 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Analyte Protectans
	No	GC-Ion Trap	GC-MSD	MM-ML	Yes, TPP	No	87 % (1 mg/kg)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-Ion Trap	MM-ML	Yes, Bromophos methyl	No	90 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	MM-ML	No	No	79 % (40 ug/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-Ion Trap	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	Yes-1	122.8 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-(μ) ECD	GC-ECD	MM-ML	Yes, PCB	Yes-2	91 % (0.1 mg/kg)	SB-EUPT	2	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	Yes, TPP	No	90 %	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	Yes, anthracen	No	99 % (0.5, 1.0, 2.0 and 3.0 mg/kg)	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), 2 MRM	MM-SL	Yes, PCB-31	Yes-2	94.1 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	100.8 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	Yes, TPP	No	100 %	SB-EUPT	1	other, QUECHERS ETHYL ACETATE
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, D8-dicofol	Yes-3	98 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)	GC-ECD	MM-SL	No	No	86 % (100ng/g)	SB-other	1	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	No	No	81 %	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	PS-SL	No	No	120 % (0.010 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, endosulfan lactone	No	82 %	QC	5	other, mix in diatomaceus earth extraction dichloromethane
	No	GC-MS/MS (QQQ)		MM-ML	No	No	120 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No					No	110 %	SB-other		

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fenbutatin oxide

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
67		Yes	1 – 2 y	0.034	-1.91	0.01	10	just thawed				5	ACN		
2	x	No	1 – 2 y	0.038	-1.66	0.01	10	ambient	1	No	No	3	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
108		Yes	< 1 y	0.04	-1.54	0.02	10	cold	15	No	No	10	ACN	No	Filtration
7		Yes	> 2 y	0.043	-1.35	0.01	10	deep frozen	2	No	No	30	ACN	No	None
136		No	> 2 y	0.046	-1.17	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
46		Yes	> 2 y	0.0464	-1.14	0.01	10	cold	2	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); centrifugation and filtration
3		Yes	1 – 2 y	0.047	-1.11	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	None
25		Yes	1 – 2 y	0.047	-1.11	0.02	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	None
81	x	No	< 1 y	0.0476	-1.07	0.01	10	cold	2	No	No	5	ACN	No	None
24		Yes	1 – 2 y	0.05	-0.92	0.01	10	just thawed	1	No	No	15	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); Centrifugation; 13 mm Acrodisc syringe filter
43		Yes	1 – 2 y	0.0505	-0.89	0.05	10	ambient		No	No	3	EtOAc	Yes, $NaHCO_3$	Filtration
48		Yes	> 2 y	0.0508	-0.87	0.01	10	deep frozen	5	No	No	20	EtOAc	No	Centrifugation; Dilution
107	x	No	None	0.051	-0.86	0.01	10	just thawed	1	Yes	No	2	ACN	No	Filtration
5		Yes	> 2 y	0.0513	-0.84	0.01	10	deep frozen	1	No	No	2	EtOAc	Yes, $NaHCO_3$ added at extraction stage	None
65		Yes	> 2 y	0.0532	-0.73	0.01	15	slightly frozen	5	No	No	5	ACN acidified with 1% HOAc	No	Dispersive-SPE (PSA/ $MgSO_4$)

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	No	No	61 % (0.025mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	Yes-1	50 % (0.05 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), different mobile phase
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, d3-Carbendazim	Yes-2				QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, TPP	Yes-2		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Nicarbazin	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	82.4 % (0.02 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Isoproturond8	Yes-1	91 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	110 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	72.2 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Pirimicarb-D6, TPP	No	68 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-SL	Yes, Pirimicarb-D6	No	92 % (0.0727 mg/kg)	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ		Std add. to sample portions	No	Yes-2		see comments	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-carbaryl	No	74 %	SB-EUPT	1	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second MSMS transition	MM-ML	Yes, methomyl D3, carbendazim D4, pendimethalin D5	No	70 % (0.02 mg/kg)	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), solvent exchange into MeOH
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 confirmation ions	MM-ML	No	No	89 % spiking level 0.01 mg/kg	SB-EUPT	1	QuEChERS - Acetate buffered (AOAC Official Method 2007.01)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fenbutatin oxide

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
88		Yes	> 2 y	0.0561	-0.55	0.005	10	deep frozen	> 30	No	No	10	ACN; citrate buffer	Yes, extraction and partitioning	Centrifugation	
56		Yes	> 2 y	0.0565	-0.52	0.01	10	just thawed	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
104	x	No	> 2 y	0.058	-0.43	0.03	10	just thawed	10	No	No	2	ACN	No	None	
33	x	Yes	> 2 y	0.0606	-0.27	0.05	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration	
49	x	Yes	1 – 2 y	0.061	-0.25	0.02	10	ambient	5	No	No	1	90% MeOH 10% H_2O 0.5mM NH_4CH_3COO	No	Filtration	
55	x	Yes	> 2 y	0.061	-0.25	0.01	10	deep frozen		No	No	2	ACN	Yes, 100 µL FA	Others; $MgSO_4Cl$	
19		No	< 1 y	0.062	-0.18	0.01	15	slightly frozen	5	No	No	1	ACN	No	None	
11	x	No	None	0.0629	-0.13	0.01	10	deep frozen	10	No	No	1	ACN	No	None	
75		Yes	1 – 2 y	0.063	-0.12	0.01	10	ambient	2	No	No	5	ACN	No	None	
117	x	Yes	1 – 2 y	0.063	-0.12	0.01	10	ambient	1	No	No	1	ACN	No	None	
10	x	Yes	1 – 2 y	0.064	-0.06	0.01	50	ambient	1	No	No	1	EtOAc	Yes, extraction	GPC, Gel-Permeation Chr/phy	
13		Yes	> 2 y	0.064	-0.06	0.01	10	slightly frozen	5	No	No	5	ACN	No	SPE-column, PSA/C18	
31	x	Yes	1 – 2 y	0.065	0	0.02	10	slightly frozen	2	No	No	30	ACN	No	None	
119	x	No	> 2 y	0.065	0	0.01	10	cold	> 30	No	No	2	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
9		Yes	> 2 y	0.0652	0.01	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
99	x	Yes	> 2 y	0.068	0.18	0.01	10			No	No	1	ACN	Yes, 400 µl HOAc	Centrifugation	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	Yes, Pirimicarb-D6, not for calculation	No	62 % (0.0625 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662), / rel. standard deviation 1.7 % with 5 individuals
	No	LC-MS/MS QQQ	LC-Ion Trap	MM-ML	Yes, TPP	No	104 % compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-Ion Trap	LC-Ion Trap	MM-ML	No	No	71 % (0.1mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, ES+	MM-ML	No	No	85 % 0.06 mg/kg	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, Oxfendazole	Yes-2		SB-EUPT		other, in house method (ISTD was used to correct the injection, but not the recovery!)
	No	LC-MS/MS QQQ		MM-SL	Yes, TPP	No	70 % (0.1 mg/kg)	SB-EUPT	3	QuEChERS-based EURL-Mth for Organotins, Acetonitrle extraction after purification and acidification
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-SL	No	Yes-1	51.8 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	108 % (0.010 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	90 % (0.02, 0.05, 0.1 and 0.25 mg/kg)	SB-EUPT	4	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	MM-ML	No	No	81 % (50 ug/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	92 %	SB-EUPT	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	84.6 % (0.10 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 519-197; 519-91;517-91	MM-SL	No	Yes-1	72.3 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003), extraction in ACN, cenfrituge, analyze with LC MSMS
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	63 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, Sulfotep	No	81 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	72 % (0.02 mg/kg)		1	QuEChERS - Citrate buffered (EN 15662), modified as recommended in EURL observations / Used in house potato blank for recovery.

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fenbutatin oxide

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
4		Yes	> 2 y	0.069	0.25	0.01	10	deep frozen	2	No	No	1	ACN	No	Centrifugation
23		Yes	1 – 2 y	0.0693	0.26	0.001	10	ambient	5	No	No	2	H_2O; ACN	Yes, addition of FA to acetonitrile	None
40	x	Yes	1 – 2 y	0.0705	0.34	0.01	10	cold	1	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
64		No	1 – 2 y	0.0707	0.35	0.01	10	ambient	10	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
21	x	Yes	> 2 y	0.071	0.37	0.01	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$
84		Yes	> 2 y	0.072	0.43	0.01	10	ambient	> 30	No	No	5	ACN	No	Centrifugation; Filtration
30		Yes	> 2 y	0.077	0.74	0.02	25	ambient	5	No	No	2	H_2SO_4, H_2O, Aceton	No	Liquid-liquid partitioning; with ethylacetat/ cyclohexan
53	x	Yes	1 – 2 y	0.077	0.74	0.01	10	ambient	2	No	No	10	ACN	No	None
132		Yes	1 – 2 y	0.08	0.92	0.01	10	cold	20	Yes, 2 mL	No	> 60	ACN	Yes, 5 – 5.5	Dispersive-SPE (PSA/$MgSO_4$)
6	x	Yes	> 2 y	0.082	1.05	0.01	10	cold	5	Yes, 2.2 ml	No	1	ACN	No	None
8		Yes	> 2 y	0.082	1.05	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, 100 µL FA	Dispersive-SPE (PSA/$MgSO_4$)
133		Yes	1 – 2 y	0.0821	1.05	0.01	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None
70	x	Yes	> 2 y	0.0837	1.15	0.01	10			No	No	10	MeOH	Yes, FA	Centrifugation
59		Yes	> 2 y	0.085	1.23	0.01	10	ambient	30	Yes	No	2	MeOH; DMC	Yes, pH 4.5 buffered	None
38		No	> 2 y	0.088	1.42	0.01	10	slightly frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS	LC-MS	MM-ML	No	No	80.2 %	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	78 %	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003), 1% FA in ACN
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	91 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	Yes, TPP	No	99.4 %	SB-EUPT	2	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	103 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Quechers without PSA
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-3	98.9 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	Yes, Methylation with tert..butylmethylether/methylmagnesiumchloride	GC-MSD	GC-MSD, via second m/z	PS-SL	No	No	125 % (0.1 mg/kg)	SB-EUPT	1	other, extraction, derivatisation, methylation, GC-MSD-detectio
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-2		SB-EUPT		QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	Yes-5	62 % 0.05 m/kg			QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-5	100 % Blank matrix spiked before extraction	SB-EUPT		QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ		MM-ML	Yes, Linuron-D6	Yes-1	83 % (0.05 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Citrate salts replaced by 100 µL FA
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	Std add. to extract aliquots	No	No	95.9 % (0.05 mg/kg; n=6)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662), 10g+ACN:10mL; Citrate mixture tampon (6.5g); no-cleanup; Column:Zorbax Eclipse XDB C18 / Recovery RSD= 4.0%
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Nicarbazin	No	56 %	SB-EUPT	2	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	Yes-5	23 %	QC	> 5	ChemElut
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	Yes-1	47 % Spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fenbutatin oxide

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
83		Yes	1 – 2 y	0.088	1.42	0.01	5	slightly frozen	1	No	No	3	ACN	Yes, acetic with H_2SO_4	None
72		Yes	1 – 2 y	0.089	1.48	0.01	10	deep frozen	1	No	No	30	MeOH	Yes	None
51		Yes	> 2 y	0.091	1.6	0.05	10	ambient	1	No	No	30	ACN	No	Centrifugation
134		No	< 1 y	0.091	1.6	0.01	10	cold	5	No	No	5	ACN	No	Freezing out
14		Yes	> 2 y	0.098	2.03	0.01	10	ambient	1	No	No	15	ACN	No	None
80		Yes	> 2 y	0.1	2.15	0.01	10	deep frozen	30	Yes	No	30	ACN	Yes	Dispersive-SPE (PSA/ $MgSO_4$)
26		Yes	> 2 y	0.102	2.28	0.04	50	slightly frozen	10	Yes	No	3	Acetone; CyHn; EtOAc; Cyclohexan/ Ethylacetat 1:1	No	GPC, Gel-Permeation Chr/phy
61		No	1 – 2 y	0.111	2.83	0.01	2	ambient	1	No	No	1	ACN	No	None
103		No	< 1 y	0.12	3.38	0.02	15	cold	2	No	No	2	ACN; H_2O (H_2O from sample)	No	None
89		Yes	> 2 y	0.121	3.45	0.01	10	ambient	1	No	No	1	ACN	No	Freezing-out
12	x	Yes	1 – 2 y	0.138	4.49	0.01	10	cold		No	No	1	acidified ACN	No	Dessication with $MgSO_4$
32		Yes	1 – 2 y	0.147	5.05	0.01	10	deep frozen	2	No	No	15	ACN	Yes, 100 µl FA instead of citrate buffer	Filtration
129		Yes	1 – 2 y	0.15	5.23	0.01	10	ambient	30	No	No	15	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
47		No	< 1 y	0.2	8.31	0.01	10	deep frozen		No	No	1	ACN	Yes, H_2SO_4	Dispersive-SPE (PSA/ $MgSO_4$)
52		Yes	> 2 y	0.42	21.85	0.05	1	ambient	1	Yes, add to dilute extract to volume	No	45	H_2O_2 and HNO_3	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 MRM	MM-SL	No	Yes-2	100.0 %	QC	1	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, TPP	No	98 %	SB-EUPT	1	other, in house method
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	> 5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	92 %	SB-EUPT	2	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-2	85 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL- other substance	No	91 % (0.2 mg/kg)	SB-other	2	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	88.6 %	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	100 %		1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	No	114 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), / Carry-over from sample to sample in HPLC-system
	No	LC-MS/MS QQQ		MM-ML	No	No	105 %	QC	5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2MRM	Std add. to extract aliquots	Yes, TPP	No	97.3 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for Organotins, QuEChERS without C18 and PSA, extraction with acidified ACN
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Pirimicarb D6	Yes-3	78 %	SB-EUPT	1	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	72 % (0.25 mg/kg)	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003), / Normal Quechers
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	101 %	QC		QuEChERS-based EURL-Mth for Organotins
	No	ICP-MS		PS-ML	Yes, Indium	No	98 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	other, AOAC 986.15 Modified

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Folpet

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
122		Yes	< 1 y	FN	-3.97	0.01	2	cold	10	Yes	No	1	10ml ACN 9 ml H_2O	No	None
94		Yes	> 2 y	0.073	-3.78	0.01	10	cold		No	No	2	ACN		Dispersive-SPE (ODS/ $MgSO_4$)
119	x	Yes	> 2 y	0.383	-2.84	0.01	10	cold	> 30	No	No	25	EtOAc	No	GPC, Gel-Permeation Chr/phy
61		No	1 – 2 y	0.442	-2.66	0.01	10	ambient	1	No	No	1	ACN	No	None
101		Yes	> 2 y	0.523	-2.42	0.01	5	cold	10	Yes, 5 mL	No	10	ACN	No	Filtration
2	x	Yes	> 2 y	0.587	-2.22	0.05	10	ambient	1	No	No	3	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
59		Yes	> 2 y	0.6	-2.18	0.01	10	ambient	30	Yes	No	2	MeOH; DMC	No	Dispersive-SPE, other, PSA
56		Yes	> 2 y	0.663	-1.99	0.01	10	just thawed	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
71		Yes	> 2 y	0.705	-1.86	0.01	15	ambient	10	No	No	5	ACN	Yes	None
121		Yes	> 2 y	0.709	-1.85	0.01	10	ambient		No	No	10	Acetone	No	None
52		Yes	> 2 y	0.751	-1.72	0.01	5	ambient	1	No	No	15	1% HOAc in ACN; shaken and centrifuged	No	$MgSO_4$/C18/ PSA
108		Yes	< 1 y	0.752	-1.72	0.03	10	cold	15	No	No	10	ACN	No	None
98		Yes	> 2 y	0.827	-1.49	0.01	10	cold	20	No	No	20	ACN	No	Centrifugation; Dispersive-SPE (PSA/ $MgSO_4$)
73	x	No	1 – 2 y	0.83	-1.48	0.02	10	ambient	5	No	No	30	Acetone; DMC; PE	Yes, 6.5	None
132		No	< 1 y	0.89	-1.3	0.01	10	cold	20	Yes, 2 mL	No	> 60	ACN	Yes, 5 – 5.5	Dispersive-SPE (PSA/ $MgSO_4$)
70	x	Yes	> 2 y	0.919	-1.22	0.01	10			No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
46		Yes	> 2 y	0.939	-1.15	0.02	20	cold	1	No	No	1	Acetone; DMC; PE	No	Centrifugation

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate					QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD, ion ratio	Std. add. to sample portion	No	Yes-1	116 %	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MSD	GC-MSD	MM-ML	No	No	84 %	SB-EUPT	2	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-(μ) ECD		MM-ML	No	No	88 %		1?	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	GC-ECD, detection	MM-ML	No	Yes-2	15.46 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	GC-(μ) ECD	Different Column, DB-5 & DB-17 columns	MM-SL	No	No	115 % (0.5 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-TOF	MM-ML	Yes, TPP	Yes-5	10 %	QC	> 5	ChemElut
	No	GC-MSD	GC-MSD, 2 columns with different polarities	MM-ML	Yes, Bromophos methyl	No	95 % compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-Ion Trap	MM-SL	No	Yes-1	75.5 % (0.2 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)		MM-ML	No	Yes-5	76 %	QC	1	S-19 or Mini-Luke
	No	LC-MS/MS QQQ	Different Method, Transitions MS/MS	PS-ML	No	Yes-1	91 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), Modified Quechers
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to sample portions	Yes, d6-Parathion	Yes-2				QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-Ion Trap	PS-ML	Yes, Tris-(1.3-dichlor-isopropyl)-phosphat	No	79.3 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	80 %	SB-EUPT	2	S-19 or Mini-Luke
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	Yes-5	80 % 0.05 mg/kg			QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	No	No	65 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	85.5 % (0.05 and 0.1 mg/kg)	SB-EUPT	2	S-19 or Mini-Luke

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Folpet

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
31	x	Yes	> 2 y	0.949	-1.12	0.02	37	just thawed	2	No	No	1	EtOAc	No	GPC, Gel-Permeation Chr/phy
110	x	Yes	> 2 y	1	-0.97	0.1	12	just thawed		No	No	1	ACN	Yes, citrate buffer	Dispersive-SPE (PSA/ $MgSO_4$)
48		Yes	> 2 y	1.01	-0.94	0.01	10	deep frozen	5	No	No	20	EtOAc	No	Centrifugation; Dilution
6	x	Yes	> 2 y	1.015	-0.92	0.01	10	cold	5	Yes, 2.2 ml	No	1	EtOAc	No	None
112		No	> 2 y	1.024	-0.9	0.01	25	deep frozen	1	No	No	10	EtOAc; ACN/ H_3PO_4	No	Liquid-liquid partitioning; SPE-column, L/L partition, solid/liqui partition and L/L parti
68		Yes	> 2 y	1.03	-0.88	0.01	10	just thawed	2	No	No	2	ACN	No	None
51		Yes	> 2 y	1.04	-0.85	0.01	10	ambient	1	No	No	30	ACN	No	Centrifugation
77		Yes	> 2 y	1.08	-0.73	0.01	10	ambient		No	No	1	ACN	Yes, pH = 5	Dispersive-SPE (PSA/ $MgSO_4$)
64		Yes	> 2 y	1.09	-0.7	0.01	10	ambient	10	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
115		Yes	> 2 y	1.1	-0.67	0.01	10	cold	2	No	No	5	ACN	No	None
72		Yes	> 2 y	1.11	-0.64	0.02	10	deep frozen	10	Yes	No	30	Acetone; DMC; PE	No	Dessication with Na_2SO_4
136		Yes	> 2 y	1.11	-0.64	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
19		Yes	> 2 y	1.12	-0.61	0.01	15	slightly frozen	5	No	No	1	ACN	No	Dispersive-SPE, PSA/C18
103		Yes	> 2 y	1.12	-0.61	0.01	15	cold	2	No	No	2	ACN; H_2O (H_2O from sample)	No	Dispersive-SPE (PSA/ $MgSO_4$)
27		Yes	> 2 y	1.14	-0.55	0.01	10	deep frozen	10	No	Yes, 200 µl 5m NaOH	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
25		Yes	> 2 y	1.16	-0.48	0.01	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	Dispersive-SPE (PSA/ $MgSO_4$)

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	GC-MSD, NCI	MM-ML	No	No	96 % (1 mg/kg)	SB-EUPT	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), extraction ethylacetate, GPC cleaning, Isooctane sample analyzed
	No	GC-MSD		MM-ML	No	No	117 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		Std add. to sample portions	No	Yes-2		see comments	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	No	87 %	SB-EUPT	2	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-(μ) ECD		MM-ML	No	No	85 % (0.1 mg/kg)	SB-EUPT	1	other, extraction then purification by liquid/liquid partitions,
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	100 % Compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), without clean-up
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	> 5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	GC-Ion Trap	GC-Ion Trap	MM-ML	Yes, TPP	No	101 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, PCB 209	Yes-1	147 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	100.9 % (2ppm)	SB-EUPT	3	QuEChERS-based EURL-Mth for captan/folpet/dicofol, / evaluated by multilevel matrix calibration
	No	GC-(μ) ECD	GC-ECD	MM-ML	Yes, nitrofen	No	82 %	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)		MM-ML	Yes, Captan-d5	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD, 3 ions	MM-SL	Yes, TDCPP	No	85.0 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD		MM-ML	No	No	89 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	90 % compound spiked			QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)	GC-Ion Trap	MM-ML	Yes, Bromophos methyl	No	80 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Folpet

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
120		Yes	> 2 y	1.16	-0.48	0.01	10	ambient	1	Yes, cca. 10:1 (H_2O :acetone)	No	> 60	Acetone	No	Filtration; SPE-column, EnviChromP
37		Yes	> 2 y	1.182	-0.42	0.01	10	just thawed	20	No	No	60	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
9		Yes	> 2 y	1.19	-0.39	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
40	x	Yes	> 2 y	1.2	-0.36	0.02	10	cold	1	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
75		Yes	> 2 y	1.24	-0.24	0.01	15	ambient	1	No	No	5	Acetone; DMC; PE	No	None
82	x	Yes	> 2 y	1.25	-0.21	0.01	15	just thawed	1	No	No	5	Acetone; DMC; PE	No	None
86		No	1 – 2 y	1.26	-0.18	0.01	20	ambient	2	No	No	3	EtOAc	No	Dessication with Na_2SO_4
130		No	> 2 y	1.26	-0.18	0.01	10	just thawed	15	No	No	60	DMC; with diatomaceous earths	Yes, acido citrico	None
1	x	Yes	> 2 y	1.27	-0.15	0.01	10	cold	5	No	No	3	ACN	Yes, phosphoric acid, pH=2	LicHrolut EN/ DEA columns
129		Yes	> 2 y	1.27	-0.15	0.01	10	ambient	30	No	No	15	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
81	x	Yes	> 2 y	1.28	-0.12	0.01	10	cold	2	No	No	5	ACN	No	None
11	x	No	None	1.29	-0.09	0.01	10	deep frozen	10	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
102		Yes	> 2 y	1.29	-0.09	0.01	10	slightly frozen	2	No	No	5	EtOAc	No	Dispersive-SPE (PSA/$MgSO_4$)
47		Yes	> 2 y	1.3	-0.06	0.01	10	deep frozen		No	No	1	ACN	Yes, citrate buffer	Dispersive-SPE (PSA/$MgSO_4$)
99	x	Yes	> 2 y	1.3	-0.06	0.01	30			No	No	1	EtOAc	YesHCO_3	GPC, Gel-Permeation Chr/phy
128		Yes	> 2 y	1.3	-0.06	0.01	10	slightly frozen	10	No		15	ACN	Yes, 5.5	Dispersive-SPE (PSA/$MgSO_4$)
107	x	No	> 2 y	1.31	-0.03	0.01	10	just thawed	1	No	No	2	ACN	Yes, H_2SO_4	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-MSD		MM-ML	Yes, TPP to extract aliquots	Yes-1	80 % (0.01, 0.10, 0.25 and 1.0 mg/kg)	SB-EUPT	4	other, extraction acetone, filtration, dilution with H_2O, SPE (EnviChrom P), elution with acetone
	No	GC-MSD	GC-Ion Trap	MM-ML	Yes, ALFA HCH D6	Yes-1	50 % 0.5	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	GC-MS/MS (QQQ)		MM-ML	Yes, PCB 31	No	85 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	Yes, aldrin	No	80 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	MM-ML	Yes, anthracen	No	85 % (1.0, 2.0, 3.0 and 4.0 mg/kg)	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-MSD	MM-ML	No	No	88.0 % (0.1mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MSD	GC-MSD	MM-ML	No	No	60 %	SB-other	1	other, solid-liquid extraction
	No	GC-(μ) ECD	GC-MSD, 3 sim ions	PS-ML	Yes, Bromophos methyl	No	97 % 1.50mg/kg	SB-EUPT	2	other, Rapporti Istisan n° 1997/23 - met. B4, with analyte protectant
	No	GC-MSD	GC-MSD	MM-ML	Yes, phenathrene-D10	No	93 %	SB-EUPT	1	other, ACN extraction, column RP-SPE+NP-SPE cleanup
	No	GC-MSD	GC-MSD	MM-ML	Yes, TPP	No	107 % (1.5 mg/kg)	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003), / Normal Quechers
	No	GC-Ion Trap	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	No	88.3 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-MS/MS (QQQ)		PS-ML	No	No	120 % (0.010 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-ECD	PS-ML	No	No	90 %	QC	1	other, QUECHERS ETHYL ACETATE
	No	GC-MSD	GC-MSD	MM-ML	Yes, PCB 52	No	71 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), +analyte protectant
	No	GC-MSD	GC-MSD	MM-ML	Yes, Tetraphenylethylene	No	90 % (0.02 mg/kg)		1	other, in house / Used in house potato blank for recovery.
	No	GC-MS/MS (QQQ)		MM-ML	No	No	114 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), Two transistions	MM-ML	Yes, C4-folpet	Yes-3	101 %	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Folpet

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
57	x	Yes	> 2 y	1.32	0	0.01	15	slightly frozen		No	No	1	Acetone	No	None
88		Yes	> 2 y	1.32	0	0.01	10	deep frozen	> 30	No	No	10	ACN; citrate buffer	Yes, extraction and partitioning	Centrifugation; Dispersive-SPE (PSA/$MgSO_4$)
89		Yes	> 2 y	1.33	0.03	0.01	10	ambient	1	No	No	1	ACN	No	Freezing-out
36		Yes	> 2 y	1.34	0.06	0.01	10	slightly frozen		No	No	1	ACN	Yes, pH 5.5	Dispersive-SPE (PSA/$MgSO_4$)
21	x	Yes	> 2 y	1.35	0.09	0.01	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$
124		Yes	> 2 y	1.35	0.09	0.01	10		> 30	No	No	> 60	ACN	No	None
12	x	Yes	None	1.38	0.18	0.01	10	cold		No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
127		Yes	> 2 y	1.39	0.21	0.05	20	ambient	1	No	No	3	Acetone; DMC	No	Liquid/liquid Partitioning
69		Yes	> 2 y	1.4	0.24	0.05	10	slightly frozen	30	No	No	10	ACN	Yesch Salzzugabe	Dispersive-SPE (PSA/$MgSO_4$)
18		Yes	> 2 y	1.41	0.27	0.01	10	slightly frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
117	x	Yes	> 2 y	1.41	0.27	0.01	15	ambient	1	No	No	1	Acetone; DMC; PE	No	None
5		Yes	> 2 y	1.42	0.3	0.01	10	deep frozen	1	No	No	2	EtOAc	YesHCO_3 added at extraction stage	SPE-column, SampliQ Carbon
84		Yes	> 2 y	1.468	0.45	0.01	15	cold	> 30	No	No	2	Acetone; DMC; PE	No	Centrifugation; Filtration
28		Yes	> 2 y	1.48	0.48	0.02	15	cold	1	No	No	20	Acetone; DMC; PE	No	Centrifugation
49	x	Yes	> 2 y	1.496	0.53	0.02	50	ambient	1	No	No	1	Acetone	No	Liquid-liquid partitioning; isopropyl-ether
3		Yes	> 2 y	1.5	0.55	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	Dispersive-SPE (PSA/$MgSO_4$)

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-ML	No	No	78 %	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-MSD		MM-ML	Yes, TPP, not for calculation	No	86 % (1.5 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662), / rel. standard deviation 2.8 % with 5 individuals
	No	GC-MS/MS (QQQ)	GC-TOF, additional standard addition to extract portions	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3	79 %	QC	5	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)		MM-ML	Yes, D4 Folpet	No	95 %	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-TOF		MM-ML	Yes, TPP	No	106 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-(μ) ECD		MM-ML	No	No	75 %	SB-EUPT	5	other, MSPD
	No	GC-MSD	GC-MSD, 2 SIM	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-NPD	MM-ML	No	No	103.9 %	SB-EUPT	3	S-19 or Mini-Luke, acetone extraction, partition to DMC (with H_2O addition)
	No	GC-MSD		MM-ML	Yes, TDCPP	No	103 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Analyte Protectans
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, Etion	No	95 % compound spiked	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	LC-MS/MS QQQ, Ion ratio	MM-ML	No	No	86 % (40 ug/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MSD	GC-MS/MS (QQQ), MSMS transition	MM-ML	Yes, trifluralin D14	No	80 % (0.02 mg/kg)	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-(μ) ECD	GC-ECD	MM-ML	Yes, PCB	Yes-2	79 % (0.1 mg/kg)	SB-EUPT	2	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-Ion Trap, ITD MS/MS	MM-ML	Yes, TPP	No	137 %)0.02 mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-ECD	MM-ML	No	No	97 % (100ng/g)	SB-other	1	S-19 or Mini-Luke
	No	GC-MSD		Std add. to sample portions	Yes, IL-target pesticide	Yes-1	118 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Folpet

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
43		Yes	> 2 y	1.5	0.55	0.05	10	ambient		No	No	3	EtOAc	YesHCO_3	Filtration
67		Yes	> 2 y	1.5	0.55	0.01	10	just thawed	5			5	ACN		
38		Yes	> 2 y	1.51	0.58	0.01	10	slightly frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
55	x	Yes	< 1 y	1.53	0.64	0.01	25	deep frozen		No	No	5	EtOAc	No	None
32		Yes	> 2 y	1.54	0.67	0.01	10	deep frozen	2	No	No	15	ACN	No	None
126	x	No	None	1.55	0.7	0.1	10	cold	2	No	No	30	ACN	No	None
10	x	Yes	> 2 y	1.59	0.82	0.05	50	ambient	1	No	No	1	EtOAc	Yes, extraction	GPC, Gel-Permeation Chr/phy
53	x	Yes	> 2 y	1.622	0.92	0.01	10	ambient	2	No	No	10	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
97		Yes	> 2 y	1.63	0.94	0.02	10	ambient	2	No	No	20	DMC	No	Others; diatomaceus earth
41		Yes	1 – 2 y	1.64	0.97	0.01	10	deep frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
137		Yes	> 2 y	1.64	0.97	0.01	10	slightly frozen	2	No	No	2	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
4		Yes	> 2 y	1.661	1.03	0.01	10	deep frozen	2	No	No	1	ACN	No	None
24		Yes	> 2 y	1.67	1.06	0.01	10	just thawed	1	No	No	15	ACN	No	Dispersive-SPE (PSA/$MgSO_4$); Centrifugation; 13 mm Acrodisc syringe filter
109	x	Yes	> 2 y	1.72	1.21	0.01	10	just thawed	2	No	No	5	ACN	No	Dispersive-SPE (PSA/$MgSO_4$)
79		Yes	> 2 y	1.77	1.36	0.01	15	cold		No	No	60	Acetone; DMC; Other; petroleum ether	No	Centrifugation
26		Yes	> 2 y	1.79	1.42	0.01	50	slightly frozen	10	Yes	No	3	Acetone; CyHn; EtOAc; Cyclohexan/ Ethylacetat 1:1	No	GPC, Gel-Permeation Chr/phy; Silica Column; mini-silicacolumn, fraktion 1-3 together
7		Yes	> 2 y	1.8	1.45	0.01	10	deep frozen	2	No	No	30	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	GC-MS/MS (QQQ)	MM-SL	Yes, Parathion-D10	No	88 % (1.59 mg/kg)	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MS/MS (QQQ)		MM-ML	No	No	112 % (0.025mg/kg)	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-ECD	MM-SL	No	No	97 % Spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)		MM-SL	Yes, TPP	No	80 % (0.1 mg/kg)	SB-EUPT	3	other, Ethyl acetate extraction
	No	GC-MSD	GC-MSD	Std add. to extract aliquots	Yes, Chlorpyrifos D10	Yes-2	101 %	SB-EUPT	1	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-Ion Trap	GC-Ion Trap	MM-ML	No	No	84 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-Ion Trap	MM-ML	No	No	85 %	SB-EUPT	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MSD	GC-MSD	MM-ML	No	Yes-2		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, endosulfan lactone	No	85 %	QC	5	other, mix in diatomaceus earth extraction dichloromethane
	No	GC-MSD	GC-MS/MS (QQQ)	MM-SL	Yes, TPP	No	101 % (0.1 mg/kg & 0.01 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap	GC-MSD	MM-ML	Yes, TPP	No	94 % (1 mg/kg)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	GC-MSD	MM-SL	No	No	80.5 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MSD	MM-ML	Yes, Pirimicarb-D6, TPP	No	93 %	SB-EUPT	2	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-(μ) ECD	GC-MSD	MM-ML	No	No	95.2 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap	GC-MSD	MM-ML	No	No	86 % standard addition	SB-EUPT	4	S-19 or Mini-Luke
	No	GC-(μ) ECD	GC-TOF	MM-ML	No	No	76.1 %	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to extract aliquots	Yes, TPP	Yes-2		SB-EUPT		QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Folpet

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
30		Yes	> 2 y	1.8	1.45	0.01	50	ambient	5	Yes, 60 mL	No	2	Acetone; CyHn; EtOAc	No	GPC, Gel-Permeation Chr/phy; Silica Column
22		Yes	> 2 y	1.82	1.52	0.01	10	deep frozen	1	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
8		Yes	> 2 y	1.829	1.54	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, Citrate Buffer pH 5.5	Dispersive-SPE (PSA/ $MgSO_4$)
33	x	Yes	> 2 y	1.89	1.73	0.01	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration
14		Yes	> 2 y	1.897	1.75	0.01	10	ambient	1	No	No	15	ACN	Yes, HCl, pH 5	None
96		No	None	1.92	1.82	0.05	10	ambient	1	No	No	2	EtOAc; 100%	No	Dispersive-SPE (PSA/ $MgSO_4$)
83		Yes	> 2 y	1.93	1.85	0.01	5	slightly frozen	1	No	No	3	ACN	No	None
65		No	< 1 y	1.94	1.88	0.01	10	slightly frozen	5	No	No	25	EtOAc; EtOAc acidified with 1% HOAc	No	None
78		Yes	> 2 y	1.94	1.88	0.02	10	deep frozen		No	No	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
80		Yes	> 2 y	2.03	2.15	0.01	20	deep frozen	30	Yes	No	3	Acetone	No	Others; solid-supported liquid/liquid partition (Chem Elut - DMC)
13		Yes	> 2 y	2.08	2.3	0.01	10	slightly frozen	5	No	No	5	ACN	Yes, H_2SO_4	None
104	x	Yes	> 2 y	2.567	3.78	0.02	10	just thawed	10	No	No	2	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
133		Yes	> 2 y	2.88	4.73	0.04	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None
44		Yes	> 2 y	2.9	4.79	0.01	10	deep frozen	5	No	No	1	ACN	Yes, after extraction	Dispersive-SPE (PSA/ $MgSO_4$)

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	GC-(μ) ECD	GC-MSD	PS-SL	Yes, not for calculation, only to check extraction efficiency	No	88 % (1.8 mg/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	Yes, TPP	No	96 %	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MSD		Std add. to sample portions	Yes, Tris-(1.3-dichlor-isopropyl)-phosphat	Yes-2	78 % (1.5 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Analyte Protectants added prior GC-NCI
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), EI	MM-ML	No	No	88 % 0.05 mg/kg	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	GC-MSD		MM-ML	Yes, Captan (D6)	Yes-2	78 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS-based EURL-Mth for captan/folpet/dicofol
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	103 % (0.01 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), extraction and DSPE purification
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ), 2 MRM	MM-SL	Yes, Folpet D4	Yes-2	89.5 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-Ion Trap	GC-Ion Trap	Std add. to sample portions	No	No	80 % (0.1, 0.2, 0.5 mg/kg)	SB-EUPT	3	other, Ethyl acetate acidified 1% HOAc / recovery calculated by slope ratio: 3 levels
	No	GC-(μ) ECD	GC-Ion Trap	MM-SL	No	No	87 % (2.4 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, IL- other substance	No	88 % (2 mg/kg)	SB-other	2	S-19 or Mini-Luke
	No	GC-MS/MS (QQQ)		MM-ML	Yes, Tris-(2-chloro-1(chloro-methyl) ethyl) phosphate	No	103.7 % (0.04 mg/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for chlorothalonil
	No	GC-MSD	GC-MSD	MM-ML	Yes, TRIS	No	80 % (0.1mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-(μ) ECD	Different Column, HP-5 and SPB-1(30 x 0.53 μm) both	MM-ML	No	No	100.4 % (0.16 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), 10g+ACN:10mL; Citrate mixt.: 6.5g; evaporation of 6 mL ACN phase; redissol.2 mL Isooct:tol(90:10) / Recovery RSD = 3.4%
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	Std add. to sample portions	Yes, TRISCP	Yes-2	125 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glyphosate

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Wateraddition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
81	x	No	> 2 y	FN	-3.88	0.05	10	cold	2	No	No	5	QuPPe solvent	No	None
98		No	> 2 y	FN	-3.88	0.1	10	cold	20	No	No	5	QuPPe solvent	No	None
101		Yes		FN	-3.88	0.05	10	cold	10	No	No	10	MeOH : H_2O =10 : 9	No	Centrifugation
115		Yes	1 – 2 y	FN	-3.88	0.05	25	cold	2	No	No	60	H_2O	No	Silica Column
70	x	Yes	> 2 y	0.138	-2.38	0.05	10			No	No	10	MeOH	No	Centrifugation
64		No	1 – 2 y	0.16	-2.12	0.01	2	ambient	10	Yes, 8.5 ml	No	1	MeOH; 1% FA	Yes	None
13		No	< 1 y	0.184	-1.84	0.05	10	slightly frozen	5	Yes, + 1.5 ml H_2O	No	1	QuPPe solvent	No	None
121		Yes	< 1 y	0.186	-1.81	0.05	10	ambient		Yes, 1.5ml	No	5	MeOH	No	Filtration
93		Yes	< 1 y	0.195	-1.71	0.01	10	deep frozen	2	Yes, 40 mL (H_2O 1% FA)	No	20	H_2O; DMC	Yes, pH = 9	Centrifugation; SPE-column, 4°C - SEP C18
77		Yes	< 1 y	0.217	-1.45	0.05	10	ambient		No	No	1	QuPPe solvent	No	None
7		Yes	> 2 y	0.227	-1.33	0.02	10	just thawed	2	No	No	15	QuPPe solvent	No	None
25		Yes	1 – 2 y	0.239	-1.19	0.05	10	deep frozen	2	No	No	2	QuPPe solvent	No	None
54		Yes	1 – 2 y	0.263	-0.91	0.05	10	just thawed	2	Yes	No	2	H_2O	No	None
11	x	Yes	1 – 2 y	0.266	-0.87	0.05	10	deep frozen	10	No	No	15	QuPPe solvent	No	None
12	x	Yes	1 – 2 y	0.271	-0.81	0.05	10	cold		No	No	2	QuPPe solvent	No	Filtration
41		No	None	0.28	-0.71	0.03	10	deep frozen	2	Yes, 2 mL	No	1	QuPPe solvent	No	Centrifugation; Filtration
48		No	< 1 y	0.291	-0.58	0.1	5	deep frozen	5	Yes	No	20	QuPPe solvent	No	Centrifugation
69		Yes	< 1 y	0.291	-0.58	0.05	10	slightly frozen	15	Yes	No	1	QuPPe solvent	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide					QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	No					QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	No					other (dilute & shoot), simple extraction with MeOH-H_2O
	Yes, TMOAc	GC-(P) FPD	GC-NPD	MM-ML	No					other (involv. deriv. w. TMOAc), extraction with H_2O,evaporation to dry,1ml HOAc+20ml TMOAc,evaporation
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Ethephon D4	No	96 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	Yes, IL-target pesticide	No	71 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	130 % (0.050 and 0.50 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-5	90 %	QC	1	other (dilute & shoot)
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	No	100 % 25 µg/kg	SB-EUPT	1	Mth involv. deriv. w. FMOC
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No				QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	93 % (0.1 mg/kg)	QC	> 5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	102 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	82 % (0.05mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), extraction with H_2O in presence of DCM
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Glyphosate 13C2 15N	Yes-4	85 % (0.050 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), QuPPe EURL-SRM method for polar pesticides v.6
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2MRM	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3		SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	No	100 % (0.1 mg/kg & 0.05 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to sample portions	No	Yes-2		see comments	3	QuPPe-Method (EURL-SRM mth f. polar pesticides), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	LC-MS/MS QQQ		Std add. to sample portions	No	No	96 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glyphosate

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Wateraddition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
14		Yes	> 2 y	0.292	-0.56	0.01	2	ambient	1	Yes, 10 ml	No	60	H_2O	Yes, Borate, pH 9.5	Liquid-liquid partitioning; LLE Acetonitrile
75		Yes	1 – 2 y	0.301	-0.46	0.05	10	ambient	2	No	No	5	MeOH	No	None
107	x	No	> 2 y	0.303	-0.44	0.05	10	just thawed	1	Yes, 2 mL	No	2	ACN	No	Filtration
94		Yes	> 2 y	0.31	-0.35	0.05	12.5	cold		No	No	60	H_2O		Ion-Exchange; AG1-X8 Acetate Form Resin
53	x	Yes	None	0.315	-0.29	0.05	10	ambient	2	No	No	10	MeOH	No	None
72		Yes	> 2 y	0.315	-0.29	0.05	5	deep frozen	10	No	No	15	MeOH; H_2O	No	None
82	x	Yes	1 – 2 y	0.327	-0.15	0.05	10	just thawed	1	No	No	5	H_2O	Yes, extraction	None
9		No	< 1 y	0.333	-0.08	0.01	10	ambient	10	No	No	30	QuPPe solvent	No	None
129		No	< 1 y	0.336	-0.05	0.05	10	ambient	30	No	No	15	MeOH	No	None
120		Yes	1 – 2 y	0.337	-0.04	0.1	10	ambient	20	No	No	60	H_2O : MeOH = 50 : 50	Yes, acidification, alkaline condition before derivatization	Filtration; SPE-column, SPE ENVICARB supelco
3		Yes	> 2 y	0.34	0	0.01	5	ambient	10	No	No	15	H_2O; DMC	No	None
105		Yes	> 2 y	0.345	0.06	0.05	5	cold	30	No	No	10	H_2O; DMC	No	SPE-column, Oasis HLB cartridge
52		Yes	> 2 y	0.348	0.09	0.01	2	ambient	1	Yes, Extacted with H_2O	No	20	H_2O, acetone; shaken and centrifuged	Yes, pH at 7	Dowex column; HLB column

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	Yes, FMOC-Cl	LC-MS/MS QQQ		MM-ML	Yes, Glyphosate (13C2 15N)	Yes-4	81 % Extraction recovery vs MMC	SB-EUPT	5	Mth involv. deriv. w. OPA, GALAB SOP-232
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, glyphosate 13C15N	Yes-2	100 % (0.5 and 1.0 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-glyphosate	No	84 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), method 1.1
	Yes, TMOAc	GC-MSD	GC-MSD, ion ratio	Std. add. to sample portion	No	Yes-1	86 %	SB-EUPT	1	other (involv. deriv. w. TMOAc), derivatization of the functional groups with HOAc and trimethyl orthoacetate
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-2		SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide to extract aliquots	No	101 %	SB-EUPT	1	Mth involv. deriv. w. OPA, in house method
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second transition	MM-ML	Yes, C13-glyphosate	Yes-3	94.8 % (0.1mg/kg)	SB-EUPT	1	other (dilute & shoot), H_2O/2%FM
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	No	75 %	QC	> 5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, FMOC-Cl	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Glyphosate-13C2.15N	Yes-5	93 % (0.25 mg/kg)	SB-EUPT	1	Mth involv. deriv. w. FMOC, / Polar Quechers: extraction with MeOH and derivatis
	Yes, FMOC-chloride	LC-MS/MS QQQ		Std add. to sample portions	No	Yes-2		SB-EUPT		Mth involv. deriv. w. FMOC, extraction MeOH/H_2O / standard addition; calculation via extrapolation
	Yes, FMOC	LC-MS/MS QQQ		Std add. to sample portions	Yes, IL-target pesticide	Yes-1	98 %	SB-EUPT		Mth involv. deriv. w. FMOC
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	110 % (0.10mg/kg)	SB-EUPT	1	Mth involv. deriv. w. FMOC
	Yes, Added FMOC-Cl and let derivitize overnight.	LC-MS/MS QQQ	Different Method, Transitions MS/MS	PS-ML	Yes, Glyphosate IS	No	100 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	Mth involv. deriv. w. FMOC, Extraced with H_2O twice, cleaned up with Dowex column and HLB column.

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glyphosate

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Wateraddition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
6	x	Yes	> 2 y	0.355	0.18	0.05	5	cold	5	Yes, 10 ml	No	15	MeOH; DMC	No	Liquid-liquid partitioning; DMC	
21	x	Yes	> 2 y	0.356	0.19	0.02	10	slightly frozen	5	Yes, 4 mL to 10 g sample	No	2	QuPPe solvent	No	None	
40	x	Yes	> 2 y	0.358	0.21	0.01	3	cold	1	Yes, used for extraction	No	20	H_2O	No	Liquid-liquid partitioning	
87		Yes	> 2 y	0.359	0.22	0.05	20	ambient		No	No	30	35ml DMC; H_2O/HCl (100ml 0.1m)	Yes, pH=1.5 - 2.5	Others; 1) Chelex 100; 2) AG1-X8	
103		Yes	> 2 y	0.359	0.22	0.05	10	cold	2	No	No	2	MeOH; H_2O from sample	No	Liquid-liquid partitioning	
61		No	1 – 2 y	0.365	0.29	0.05	10	ambient	1	Yes	Yes	1	H_2O	No	None	
30		Yes	> 2 y	0.369	0.34	0.01	2	ambient	5	No	No	30	H_2O/HCl	Yes	SPE-column, C8	
32		Yes	> 2 y	0.37	0.35	0.05	10	deep frozen	2	No	No	1	QuPPe solvent	No	Filtration	
88		Yes	> 2 y	0.37	0.35	0.05	5	deep frozen	> 30	No	No	20	DMC partitioning with 20 ml HCl, 10 ml DMC	Yes, neutralisation with NaOH to pH 6 – 8	Centrifugation; ion-exchange	
23		Yes	> 2 y	0.373	0.39	0.02	10	ambient	5	Yes, 1.5 ml	No	15	QuPPe solvent	Yes, addition of FA to MeOH	Centrifugation; Filtration	
43		Yes	1 – 2 y	0.376	0.42	0.02	10	cold		No	No	2	QuPPe solvent	No	Filtration	
16		Yes	> 2 y	0.379	0.46	0.05	3	cold	1	No	No	30	H_2O	No	Centrifugation; Filtration; Filter 0.20 µm hydrophile	
84		Yes	< 1 y	0.379	0.46	0.01	25	ambient	> 30	No	No	2	H_2O; QuPPe solvent	No	Centrifugation; Filtration	
1	x	Yes	> 2 y	0.38	0.47	0.01	10	ambient	1	No	No	3	QuPPe solvent	No	None	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	Yes, FMOC-Cl	LC-MS/MS QQQ	Different Method, QuPPE-method	MM-ML	Yes, IL-target pesticide	Yes-5	100 % Blank matrix spiked before extraction	SB-EUPT		Mth involv. deriv. w. FMOC
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	No	96 % (0.1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes 1.2-$^{13}C_2$ ^{15}N-glyphosate	Yes-5		SB-EUPT		Mth involv. deriv. w. FMOC
	No	LC-Fluorescence Det.		PS-ML	No	No	89.9 % (0.5 mg/kg)	SB-EUPT	1	Mth involv. deriv. w. OPA
	Yes, FMOC-Cl	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	110 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	90 %		1	Mth involv. deriv. w. FMOC
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	Yes-3	93 % (0.3 mg/kg)	SB-EUPT	1	Mth involv. deriv. w. FMOC, extraction with hydrochloric acid, online-derivatisation, online-SPE
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	53 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, FMOC	LC-Fluorescence Det.		MM-ML	No	No	99 % (0.4 mg/kg)	SB-EUPT	2	Mth involv. deriv. w. FMOC, acid extraction,neutralisation,ion-exchange,LC-Fluorescense-Detection after derivatisation with FMOC / rel. standard deviation 3.0 % with 3 individuals
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	86 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides), 1% FA in MeOH
	No	LC-MS/MS QQQ		PS-ML	Yes, IL-target pesticide	Yes-3	94 % (0.35 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-ML	Yes, Glyphosate-13C2 15N	Yes-3	95 % Compound spiked in blank	SB-EUPT	1	other (dilute & shoot), Internal developed method from 2007, using a hypercarb column
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	85.9 %	SB-EUPT	2	other (dilute & shoot), acid MeOH/H2O extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, etephone-D4	No	105 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glyphosate

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Wateraddition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
99	x	Yes	> 2 y	0.4	0.71	0.05	25			Yes, extracted with H_2O	No	1	H_2O; MeOH; conc HCl	Yes, acidified H_2O/ MeOH	Liquid-liquid partitioning; Ion-Exchange	
89		Yes	> 2 y	0.401	0.72	0.05	2	ambient	1	No	No	30	A: H_2O-MeOH-borat-buffer; B: EtOAc, after derivation	Yes, after SPE-elution to pH 9 with NH_3	SPE-column, Oasis MAX, 30 Ã‚Âµm; elution with ACN/HCl	
8		Yes	> 2 y	0.41	0.82	0.05	10	just thawed	2	Yes, added to 10 g	No	3	MeOH	Yes, 1% FA in MeOH	None	
10	x	Yes	1 – 2 y	0.415	0.88	0.1	10	ambient	1	No	No	1	QuPPe solvent	No	Filtration	
51		Yes	> 2 y	0.452	1.32	0.05	10	ambient	1	No	No	30	ACN	No	Centrifugation	
56		Yes	1 – 2 y	0.462	1.44	0.05	10	just thawed	5	No	No	5	H_2O	No	Others; Filtration; cleaning up with ethyl acetate (3 times)	
4		Yes	> 2 y	0.474	1.58	0.05	10	deep frozen	2	No	No	2	DMC; MeOH; FA	No	Centrifugation	
31	x	Yes	< 1 y	0.579	2.81	0.01	10	slightly frozen	2	No	No	2	H_2O; $DMCH_2O$ acidified with FA	No	SPE-column, HLB Oasis	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	Yes, heptaflouro-butanol & triflouro-ace-tic anhydride	GC-MSD	GC-MSD	MM-ML	Yes, glypho-sate (13C, 15N)	No	87 % (0.1 mg/ kg)		1	other, Alferness PL & Iwata Y, J. Agric. Food Chem, 1994, 42, 2751-2759 / Used in house potato blank for recovery.
	Yes, with (9-fluorenyl-methyl)-chlor-formiat	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-4	103 %	QC	> 5	other
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3				QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	98 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003)
	Yes, FMOC derivatiza-tion	LC-MS/MS QQQ	LC-Ion Trap	MM-ML	No	No	91 % com-pound spiked	SB-EUPT	1	Mth involv. deriv. w. FMOC
	No	LC-MS	LC-MS	MM-ML	No	No	76.0 %	SB-EUPT	2	other (dilute & shoot), PA 048, EPRW 2010, Czech, CAFIA
	Yes, FMOC, 30, addition FA for stop derivatiza-tion	LC-MS/MS QQQ	LC-MS/MS QQQ, 392-214; 392-179; 392- 88	MM-ML	Yes, glypho-sate 13C2, 15N	Yes-3	(Leer)	SB-EUPT	1	Mth involv. deriv. w. FMOC, extrac-tion to dichloromethan-H_2O FA, derivatization FMOC, annalyze on LC MSMS

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combina-tion of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Haloxyfop

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
56		Yes	> 2 y	0.0129	-3.9	0.01	10	just thawed	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
13		No	1 – 2 y	0.113	-3.11	0.05	10	slightly frozen	5	No	No	5	ACN	No	SPE-column, PSA/C18
95		Yes	> 2 y	0.154	-2.79	0.01	10	cold		No	No		ACN	No	Dispersive-SPE (C18/ $MgSO_4$)
77		Yes	> 2 y	0.195	-2.46	0.01	10	ambient		No	No	1	ACN	Yes, pH = 5	Dispersive-SPE (PSA/ $MgSO_4$)
11	x	No	None	0.221	-2.26	0.01	10	deep frozen	10	No	No	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
110	x	No	1 – 2 y	0.25	-2.03	0.1	12	just thawed		No	No	1	ACN	Yes, citrate buffer	Dispersive-SPE (PSA/ $MgSO_4$)
48		Yes	> 2 y	0.333	-1.38	0.01	10	deep frozen	5	No	No	20	EtOAc	No	Centrifugation; Dilution
46		Yes	> 2 y	0.335	-1.36	0.01	10	cold	2	No	No	10	ACN	No	None; centrifugation and filtration
5		Yes	> 2 y	0.355	-1.2	0.01	10	deep frozen	1	No	No	2	EtOAc	Yes HCO_3 added at extraction stage	None
132		Yes	1 – 2 y	0.37	-1.09	0.01	10	cold	20	Yes, 2 mL	No	> 60	ACN	Yes, 5 – 5.5	Dispersive-SPE (PSA/ $MgSO_4$)
107	x	No	1 – 2 y	0.372	-1.07	0.01	10	just thawed	1	No	No	2	ACN	No	Filtration
42		Yes	> 2 y	0.373	-1.06	0.01	10	just thawed	1	No	No	1	ACN	Yes, Citrate Buffered	Dessication with $MgSO_4$
16		Yes	> 2 y	0.394	-0.9	0.04	10	cold	1	No	No	30	MeOH	No	Centrifugation; Filtration; 4.1.6 Mini uniprep polypropylen filter vials
61		No	1 – 2 y	0.394	-0.9	0.01	2	ambient	1	No	No	1	ACN	No	None
9		Yes	> 2 y	0.412	-0.76	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-Ion Trap	MM-ML	Yes, TPP	No	108 % compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	66 % (0.10 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	78 % (0.1mg/kg)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	Yes, TPP	No	48 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	81 % (0.010 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-1	16 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), / result only qualitative (always poor recovery)
	No	LC-MS/MS QQQ		Std add. to sample portions	No	Yes-2		see comments	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	103.9 % (0.02 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second MSMS transition	MM-ML	Yes, methomyl D3, carbendazim D4, pendimethalin D5	No	72 % (0.02 mg/kg)	SB-other	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789), solvent exchange into MeOH
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	Yes-5	57 % 0.05 mg/kg			QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-carbaryl	No	76 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Without PSA clean-up
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No				QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-ML	No	No	97 % Compound spiked in blank, wait 30, then extraction	SB-EUPT	2	other, Methanolic extraction, published by Kit Granby et al.
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	86 %		1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, Sulfotep	No	95 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Haloxyfop

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
25		Yes	1 – 2 y	0.415	-0.73	0.01	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	None
126	x	Yes	> 2 y	0.422	-0.68	0.01	10	cold	2	No	No	30	ACN	No	None
101		Yes	> 2 y	0.423	-0.67	0.0006	10	cold	10	No	No	10	ACN	No	Filtration
102		Yes	1 – 2 y	0.43	-0.61	0.01	10	slightly frozen	2	No	No	5	EtOAc	No	None
72		Yes	> 2 y	0.431	-0.61	0.003	10	deep frozen	10	Yes	No	30	Acetone; DMC; PE	No	Dessication with Na_2SO_4
76		Yes	> 2 y	0.434	-0.58	0.01	10	just thawed	1	No	No	2	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
99	x	Yes	> 2 y	0.434	-0.58	0.01	10			No	No	1	ACN	Yes, acetate buffer	Centrifugation
117	x	Yes	> 2 y	0.436	-0.57	0.01	15	ambient	1	No	No	1	Acetone; DMC; PE	No	None
40	x	Yes	> 2 y	0.445	-0.5	0.01	10	cold	1	No	No	1	ACN	No	Filtration
41		No	None	0.45	-0.46	0.01	10	deep frozen	30	No	Yes, alkaline hydrolysis: NaOH & neutralization: H_2SO_4	1	ACN	No	Centrifugation; Filtration
68		No	1 – 2 y	0.45	-0.46	0.01	10	just thawed	2	No	No	2	ACN	No	None
84		Yes	1 – 2 y	0.456	-0.41	0.01	15	ambient	> 30	No	No	2	Acetone; DMC; PE	No	Centrifugation; Filtration
4		Yes	> 2 y	0.462	-0.36	0.01	10	deep frozen	2	No	No	2	ACN	No	None
31	x	Yes	> 2 y	0.463	-0.35	0.01	10	slightly frozen	2	No	No	30	ACN	No	None
49	x	Yes	> 2 y	0.47	-0.3	0.02	10	ambient	5	No	No	1	90% MeOH, 10% H_2O, 0.5mM NH_4CH_3COO	No	Filtration
55	x	Yes	> 2 y	0.471	-0.29	0.05	10	deep frozen		No	No	1	ACN	Yes, addition 100 µl H_3PO_4	None
115		Yes	1 – 2 y	0.475	-0.26	0.01	10	cold	2	No	No	5	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	87 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	75 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	Yes-2	19.30 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, CARBO-FURAN D3	No	97 %	SB-EUPT	1	other, QUECHERS ETHYL ACETATE
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, TPP	No	87 %	SB-EUPT	1	S-19 or Mini-Luke
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	71.2 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), / No
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	MM-ML	No	No	89 % (0.02 mg/kg)		1	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), / Used in house potato blank for recovery.
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	MM-ML	No	No	108 % (50 ug/kg)	SB-EUPT	1	S-19 or Mini-Luke
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	108 % (0.01 mg/kg)	SB-EUPT	1	other, QuEChERS without cleanup
	No	LC-MS/MS QQQ		MM-ML	No	No	100 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	110 % Compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), without clean-up
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, MeOH-extraction	PS-ML	No	No	114 %	SB-EUPT	2	S-19 or Mini-Luke
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	85.6 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 360-288; 360- 252	MM-ML	No	No	89 % (0.3 mg/kg)	SB-EUPT	3	QuEChERS - Original Version (J. AOAC 86, 2003), extraction in ACN, cenfrituge, analyze with LC MSMS
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Oxfendazole	No	77 % (100ng/g)	SB-EUPT	1	other, in house method (ISTD was used to correct the injection, but not the recovery!)
	No	LC-MS/MS QQQ		MM-SL	No	No	80 % (0.05 and 0.5 mg/kg)	QC	5	other, J. of Environ Science and Health, Part B, (2009), 44, 584-590
	Yes, PFBBr	GC-MSD	GC-ECD	MM-ML	No	No	94.0 % (0.5ppm)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662), 100ul HOAc was added to 10ml AcN. / evaluated by multilevel matrix calibration

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Haloxyfop

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
27		Yes	> 2 y	0.48	-0.22	0.01	10	deep frozen	10	No	Yes, 200 µl 5 m NaOH	20	ACN	No	Dispersive-SPE ($PSA/MgSO_4$)
81	x	Yes	> 2 y	0.481	-0.21	0.01	10	cold	2	No	No	5	ACN	No	None
2	x	Yes	1 – 2 y	0.484	-0.19	0.01	10	ambient	30	No	Yes, with NaOH	5	ACN	Yes, 12	Dispersive-SPE, $MgSO_4Cl$, citrates
33	x	Yes	> 2 y	0.49	-0.14	0.01	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration
108		Yes	< 1 y	0.49	-0.14	0.01	10	cold	15	No	No	10	ACN	No	Filtration
131		Yes	> 2 y	0.495	-0.1	0.01									
71		No	< 1 y	0.496	-0.09	0.01	15	ambient	10	No	No	5	ACN	Yes	None
69		Yes	> 2 y	0.499	-0.07	0.01	10	slightly frozen	30	No	No	10	ACN	Yes after add. of salt	None
104	x	No	> 2 y	0.5	-0.06	0.02	10	just thawed	10	No	Yes, with NaOH	2	ACN	Yes, H_2SO_4	Others; $C18/MgSO_4$
7		Yes	> 2 y	0.503	-0.04	0.01	10	deep frozen	2	No	No	30	ACN	No	None
53	x	Yes	> 2 y	0.508	0	0.01	10	ambient	2	No	No	10	ACN	No	None
119	x	Yes	1 – 2 y	0.509	0.01	0.01	10	cold	> 30	No	No	2	ACN	No	None
134		No	< 1 y	0.511	0.02	0.01	10	cold	5	No	No	5	ACN	No	Freezing out
83		Yes	> 2 y	0.512	0.03	0.01	5	slightly frozen	1	No	No	3	ACN	No	None
43		Yes	> 2 y	0.513	0.04	0.01	10	ambient		No	No	3	EtOAc	YesHCO_3	Filtration
136		Yes	> 2 y	0.515	0.06	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
10	x	Yes	> 2 y	0.517	0.07	0.01	10	ambient	1	No	Yes	1	EtOAc	Yes	Centrifugation
1	x	Yes	1 – 2 y	0.518	0.08	0.01	10	ambient	1	No	No	1	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Nicarbazin	No	55 % compound spiked			QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	96.5 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	102 % (0.3 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), alkaline hydrolysis with NaOH and addition of H_2SO_4
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, ES+	MM-ML	No	No	81 % (0.5 mg/kg)	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, d3-Carbendazim	Yes-2				QuEChERS - Original Version (J. AOAC 86, 2003)
	No					No	87 %	SB-other		
	Yes, TMS-diazomethane	GC-Ion Trap	GC-Ion Trap	MM-ML	No	Yes-1	115 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-Orbitrap		MM-ML	Yes, Mecoprop D3	No	83 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	Yes, trimethylsulfonium hydroxide	GC-MSD	GC-MSD	MM-ML	No	No	98 % (0.1mg/kg)	SB-EUPT	2	other, Hydrolyses, extraction and clean-up.,
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, Nicarbazin	Yes-2		QC		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-2		SB-EUPT		QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	69 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	102 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	Different Column, Poroshell 120 and Zorbax Eclipseplus C18	MM-SL	No	Yes-2	101.5 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-SL	Yes, Pirimicarb-D6	No	73 % (0.429 mg/kg)	SB-EUPT	1	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Nicarbazin	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	87 %	SB-EUPT	3	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	50 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

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Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
14		Yes	> 2 y	0.518	0.08	0.01	10	ambient	1	No	No	15	ACN	No	None
103		Yes	> 2 y	0.52	0.09	0.01	15	cold	2	No	No	2	ACN; H_2O (H_2O from sample)	No	None
70	x	Yes	> 2 y	0.523	0.12	0.01	10			No	Yes, H_2SO_4	10	ACN	Yes	Freezing-out
3		Yes	> 2 y	0.53	0.17	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	None
59		Yes	> 2 y	0.53	0.17	0.01	10	ambient	30	Yes	No	2	MeOH; DMC	Yes, pH 4.5 buffered	None
26		Yes	> 2 y	0.533	0.2	0.005	5	slightly frozen	10	Yes	No	2	MeOH	Yes, pH 4	Liquid-liquid partitioning; ChemElut
8		Yes	> 2 y	0.535	0.21	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, Citrate Buffer pH 5.5	None
122		Yes	> 2 y	0.536	0.22	0.01	2	cold	10	Yes	No	1	ACN : H_2O = 10 : 9	No	None
88		Yes	> 2 y	0.547	0.31	0.01	10	deep frozen	> 30	No	No	10	ACN; citrate buffer	Yes, extraction and partitioning	Centrifugation
38		Yes	> 2 y	0.55	0.33	0.01	10	slightly frozen	1	No	No	1	ACN	No	None
82	x	Yes	> 2 y	0.553	0.35	0.02	15	just thawed	1	No	No	5	Acetone; DMC; PE	No	None
6	x	Yes	> 2 y	0.555	0.37	0.01	10	cold	5	Yes, 2.2 ml	No	1	ACN	No	None
75		Yes	> 2 y	0.555	0.37	0.01	15	ambient	1	No	No	5	Acetone; DMC; petroleum ether	No	None
80		Yes	< 1 y	0.57	0.49	0.01	20	deep frozen	30	Yes	No	3	ACN	No	None
21	x	Yes	> 2 y	0.578	0.55	0.01	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$
98		Yes	> 2 y	0.581	0.57	0.01	10	cold	20	No	No	20	ACN	No	Centrifugation

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	GC-MSD, GC-NCI-MSD of PFBr derivative	MM-ML	Yes, 2.4-D (D3)	Yes-2	80 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	No	105 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Nicarbazin	No	86 %	SB-EUPT	2	other, EN 15162 modified
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Isoproturon-D8	Yes-1	93 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Nicarbazin	Yes-5	93 %	QC	> 5	ChemElut
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	96.4 %	SB-EUPT	1	ChemElut
	No	LC-MS/MS QQQ		MM-ML	Yes, Linuron-D6	No	99 % (0.3 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate	No	103 %	QC	4	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, Pirimicarb-D6, not for calculation	No	108 % (0.725 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), / rel. standard deviation 1.6 % with 5 individuals
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	104 % Spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	91.8 % (0.05 mg/kg	SB-EUPT	1	S-19 or Mini-Luke
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-5	100 % Blank matrix spiked before extraction	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	101 % (0.1, 0.25, 0.5 and 1.0 mg/kg)	SB-EUPT	4	S-19 or Mini-Luke
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL- other substance	No	102 % (0.5 mg/kg)	SB-other	2	SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	98 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Quechers without PSA
	No	LC-MS/MS QQQ		PS-ML	No	No	107.0 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Haloxyfop

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
24		Yes	> 2 y	0.582	0.58	0.01	10	just thawed	1	No	Yes, 300 µl 5 N NaOH, 30 min hydrolysis, then neutralization	15	ACN	Yes, pH ~ 12 for hydrolysis	Centrifugation
120		Yes	> 2 y	0.585	0.61	0.01	10	ambient	20	Yes, 2ml	Yes NaOH	60	H_2O : MeOH = 33 : 67	Yes, pH 3 – 4	Filtration; SPE-column, Extrelut columns
109	x	Yes	1 – 2 y	0.59	0.65	0.01	10	just thawed	2	No	No	5	ACN	No	None
64		Yes	1 – 2 y	0.591	0.65	0.01	10	ambient	10	No	No	1	ACN	No	None
91		Yes	> 2 y	0.603	0.75	0.1	10	slightly frozen		No	No	1	ACN		Dispersive-SPE (PSA/ $MgSO_4$)
129		Yes	1 – 2 y	0.608	0.79	0.01	10	ambient	20	No	No	15	MeOH	No	None
36		Yes	> 2 y	0.615	0.84	0.01	10	slightly frozen		No	No	1	ACN	Yes, pH 5.5	Filtration
47		Yes	> 2 y	0.618	0.87	0.01	10	deep frozen		No	Yes NaOH	1	ACN	Yes, H_2SO_4	None
133		Yes	> 2 y	0.655	1.16	0.01	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None
130		Yes	> 2 y	0.658	1.18	0.01	10	just thawed	2	Yes, up to 10 g of H_2O	No	2	ACN	Yes, citrate buffer	None
51		Yes	> 2 y	0.692	1.45	0.01	10	ambient	1	No	No	30	ACN	No	Centrifugation
23		Yes	> 2 y	0.694	1.46	0.001	10	ambient	5	No	No	2	H_2O; ACN	Yes, addition of FA to acetonitrile	None
32		Yes	> 2 y	0.699	1.5	0.01	10	deep frozen	2	No	No	15	ACN	No	Filtration
19		Yes	> 2 y	0.7	1.51	0.01	15	slightly frozen	5	No	No	1	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Nicarbazin, 2.4-D-D3	No	95 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	No	No	105 % spiked blank sample on diff. cali. levels; covering linear range	SB-EUPT	4	ChemElut, extraction MeOH/H_2O; hidrolysis; pH adjustment; cleaning Extrelut columns
	No	LC-MS/MS QQQ		MM-ML	No	No	92.2 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	Yes, TPP	No	105 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), without PSA
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-5				QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-5	99 % (0.25 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), / Polar Quechers: extraction with MeOH
	No	LC-MS/MS QQQ		MM-ML	No	No	99 %	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No				other, QuEChERS 1 Step
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	Std add. to extract aliquots	No	No	100.3 % (0.05 mg/kg; n=6)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662), 10 g + ACN : 10 mL; Citrate mixture buffer (6.5 g); no-cleanup; Column: Waters Atlantis T3 / Recovery RSD = 4.5 %
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, TPP	No	108 % 0.05mg/kg (twice)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	> 5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-3	93 %	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003), 1% FA in ACN
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Nicarbazin	Yes-5	103 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-SL	No	No	87.9 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Haloxyfop

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
89		Yes	> 2 y	0.701	1.52	0.01	10	ambient	1	No	No	1	ACN	No	Freezing-out
12	x	Yes	> 2 y	0.789	2.21	0.01	10	just thawed		No	No	15	ACN	Yes	Liquid-liquid partitioning
30		Yes	> 2 y	1	3.87	0.01	25	ambient	2	Yes	Yes, alkine with NaOH	2	Acetone; CyHn; EtOAc	Yes	Gel-Permeation Chr/phy & acid/base distribution

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

Mepiquat

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
2	x	Yes	> 2 y	FN	-3.58	0.01	10	ambient	1	No	No	1	MeOH	No	None
55	x	Yes	> 2 y	0.023	-3.04	0.01	25	deep frozen		No	No	5	EtOAc	No	None
51		Yes	> 2 y	0.03	-2.75	0.05	10	ambient	1	No	No	30	ACN	No	Centrifugation
122		Yes	> 2 y	0.038	-2.42	0.01	2	cold	10	Yes	No	1	ACN : H_2O = 10 : 9	No	None
104	x	No	> 2 y	0.0573	-1.61	0.02	20	just thawed	10	Yes, 4 ml	No	2	MeOH	No	None
72		Yes	> 2 y	0.068	-1.17	0.01	10	deep frozen	10	Yes	No	30	MeOH	No	Dessication with Na_2SO_4
5		Yes	> 2 y	0.0696	-1.1	0.01	25	deep frozen	1	No	No	2	ACN	No	None
70	x	Yes	> 2 y	0.0703	-1.07	0.01	10			No	No	10	MeOH	No	Centrifugation

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	No	No	112 %	QC	5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2MRM	MM-ML	Yes, Nicarbazin	No	114 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	Yes, Methylation with tetrabutylammonium-hydroxide/ iosomethane	GC-MSD	GC-MSD, via second m/z	PS-SL	Yes, Mercoprop-D3, no calculation; only to check extr.e	No	85 % (1 mg/kg)	SB-EUPT	1	other, alkine hydrlysis extraction, GPC, acid/base distribution, methylation, GC-MSD detection

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-SL	No					other (dilute & shoot), extraction with MeOH
	No	LC-MS/MS QQQ		MM-SL	Yes, TPP	No	95 % (0.05 mg/kg)	SB-EUPT	5	other (dilute & shoot), Ethyl acetate extraction
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate	No	58 %	QC	4	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS	LC-MS	MM-ML	No	No	110 % (0.4mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	GC-ECD	MM-ML	Yes, nitrofen	No	89 %	SB-EUPT	1	other (Dilute & Shoot), in house method
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second MSMS transition	MM-ML	Yes, methomyl D3, carbendazim D4, pendimethalin D5	No	70 % (0.02 mg/kg)	SB-other	1	other (dilute & shoot), ACN extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, chlormequat D4	No	94 %	SB-EUPT	2	other (dilute & shoot), LST EN 15055

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Mepiquat

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
38		Yes	> 2 y	0.072	-1	0.01	10	slightly frozen	1	No	No	1	MeOH	No	None
10	x	Yes	> 2 y	0.0765	-0.81	0.01	10	ambient	1	No	No	1	QuPPe solvent	No	Filtration
13		No	1 – 2 y	0.077	-0.79	0.01	10	slightly frozen	5	Yes, + 1.5 ml	No	1	QuPPe solvent	No	None
36		Yes	1 – 2 y	0.078	-0.75	0.008	10	slightly frozen		Yes	No	15	QuPPe solvent	Yes, 1% FA	Filtration
131		Yes	> 2 y	0.0783	-0.74	0.01									
31	x	Yes	> 2 y	0.079	-0.71	0.01	10	slightly frozen	2	No	No	45	H_2O; MeOH (H_2O acidified with FA)	No	None
4		Yes	> 2 y	0.08	-0.67	0.01	10	deep frozen	2	No	No	2	MeOH	No	None
19		No	> 2 y	0.08	-0.67	0.01	10	ambient	5	No	No	1	MeOH	No	None
52		Yes	> 2 y	0.08	-0.67	0.01	3	ambient	1	No	No	15	1% FA in MeOH; shaken and centrifuged	No	None
26		Yes	> 2 y	0.081	-0.63	0.01	20	slightly frozen	10	Yes	No	2	MeOH	No	None
80		Yes	> 2 y	0.0821	-0.58	0.01	10	deep frozen	30	No	No	60	HCl; MeOH, H_2O	No	Dispersive-SPE, other
67		Yes	> 2 y	0.084	-0.5	0.05	5	just thawed	1			1	MeOH		
6	x	Yes	> 2 y	0.085	-0.46	0.01	10	cold	5	Yes, 2.2 ml	No	1	QuPPe solvent	No	None
25		Yes	> 2 y	0.085	-0.46	0.01	10	deep frozen	2	No	No	2	QuPPe solvent	No	None
134		No	< 1 y	0.085	-0.46	0.01	10	cold	5	No	No	5	QuPPe solvent	No	None
9		Yes	> 2 y	0.0853	-0.45	0.01	10	ambient	10	No	No	30	QuPPe solvent	No	None
81	x	No	> 2 y	0.0863	-0.4	0.01	10	cold	2	No	No	5	ACN; 1 v/v % FA in ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	66 % Spiked	SB-EUPT	1	other (dilute & shoot), §64 LFGB ASU L00.00-76
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	94 %	SB-EUPT	3	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	90 % (0.050 and 0.50 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	Yes, D3 Mepiquat	No	103 %	SB-EUPT	4	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No					No	117 %	SB-EUPT		
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 114-98; 114 - 58	MM-ML	Yes, chlormequat D4	Yes-3	83 % (0.08 mg/kg)	SB-EUPT	3	other (dilute & shoot), extraction - acidif H_2O- MeOH; centrifuge, filter, analyze
	No	LC-MS	LC-MS	MM-ML	No	No	104.2 %	SB-EUPT	3	other (dilute & shoot), Analysis of Chlormequat and mepiquat residues in Food of Plant origin, EURL-SRM, ver.2, 2009
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	Std add. to sample portions	Yes, IL-target pesticide	Yes-2		SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides), SRM:"Quick method for the analysis of residues of highly polar pesticides" version 4 may 2010
	No	LC-MS/MS QQQ	Different Method, Transitions MS/MS	PS-ML	No	Yes-1	79 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	other (dilute & shoot), EU ref. version 5; Extracted with MeOH
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	96.5 %	SB-EUPT	1	other (dilute & shoot), §64 LFGB L00.00-76
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	No	103 % (0.1mg/kg)	SB-other	2	other
	No	LC-MS/MS QQQ		MM-ML	No	No	77 % (0.5mg/kg)	SB-EUPT		other, MeOH extraction
	No	LC-MS/MS QQQ		MM-ML	No	Yes-5	100 % Blank matrix spiked before extraction	SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	95 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	No	98 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	No	99 %	QC	> 5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	No	94.6 % (0.05 mg/kg	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), final extract was adjusted to 20 ml

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Mepiquat

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
40	x	Yes	> 2 y	0.0878	-0.34	0.01	25	ambient		No	No	2	MeOH	No	Filtration
118	x	Yes	> 2 y	0.088	-0.33	0.05	10	cold	10	Yes	No	20	H_2O; MeOH	No	None
1	x	Yes	> 2 y	0.0885	-0.31	0.01	20	ambient	1	No	No	2	MeOH	No	None
49	x	Yes	> 2 y	0.089	-0.29	0.01	10	ambient	5	No	No	1	90% MeOH, 10% H_2O, 0.5mM NH_4CH_3COO	No	Filtration
83		Yes	> 2 y	0.0897	-0.26	0.001	5	slightly frozen	1	No	No	3	QuPPe solvent	No	None
21	x	Yes	> 2 y	0.09	-0.25	0.01	10	slightly frozen	5	Yes, 4mL to 10g sample	No	2	QuPPe solvent	No	None
43		Yes	> 2 y	0.0904	-0.23	0.005	20	ambient		Yes	No	15	H_2O; MeOH	No	Filtration
32		Yes	> 2 y	0.091	-0.21	0.01	10	deep frozen	2	No	No	1	QuPPe solvent	No	Filtration
69		Yes	> 2 y	0.092	-0.17	0.01	10	slightly frozen	15	Yes	No	1	QuPPe solvent	No	None
103		Yes	> 2 y	0.092	-0.17	0.01	10	cold	2	No	No	2	MeOH; H_2O from sample	No	None
3		Yes	> 2 y	0.094	-0.08	0.005	20	ambient	10	No	No	60	MeOH; H_2O	No	None
119	x	Yes	1 – 2 y	0.095	-0.04	0.01	10	cold	> 30	No	No	2	QuPPe solvent	No	None
22		No	< 1 y	0.096	0	0.01	10	deep frozen	1	No	No	1	MeOH	No	None
107	x	No	> 2 y	0.096	0	0.01	10	just thawed	1	No	No	10	H_2O; MeOH; HOAc	No	Filtration
120		Yes	> 2 y	0.096	0	0.01	10	ambient	20	Yes, 2ml	No	60	H_2O : MeOH = 33 : 67	No	Filtration
136		No	> 2 y	0.096	0	0.01	20	just thawed		No	No	2	MeOH	No	Centrifugation; Filtration
46		Yes	> 2 y	0.0966	0.03	0.02	20	cold	1	Yes, 4.4 mL	No	1	MeOH	No	Centrifugation; Filtration

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, D3-mepiquat to extract aliquots	Yes-3		SB-EUPT		other (dilute & shoot), MeOH extraction
	No	LC-MS		Std add. to sample portions	No	Yes-2		SB-EUPT		other (dilute & shoot), H_2O/MeOH extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, chlormequat-D4	No	120 %	SB-EUPT	1	other (dilute & shoot), EN 15055
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	No	Yes-2		SB-EUPT		other (dilute & shoot), EN 15055
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 MRM	MM-SL	Yes, mepiquat D3	Yes-2	100.0 %	QC	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	No	86 % (0.05 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	Yes, IL-target pesticide	Yes-3	101 % (0.082 mg/kg)	SB-EUPT	1	other (dilute & shoot), Homogenized sample is extracted with H_2O/MeOH and filtered with polypropylene filter
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	103 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to sample portions	No	No	114 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	112 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, IL-target pesticide	Yes-1	97 %	SB-EUPT		other (dilute & shoot), MeOH/H_2O 4/1
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-1	48 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-Orbitrap	LC-Orbitrap	PS-ML	Yes, TPP	No	83 %	SB-EUPT	3	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-chlormequat	No	98 %	SB-EUPT	1	other (dilute & shoot), FP081-2.
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	105 % spiked blank sample on diff. cali. levels; covering linear range	SB-EUPT	4	other (dilute & shoot), modif SIST EN 15055:2006; modification is mobile phase
	No	LC-MS/MS QQQ		Std add. to extract aliquots	Yes, IL-target pesticide	Yes-4	100 %	SB-EUPT	1	other (dilute & shoot), L 00.00-76
	No	LC-MS	LC-MS	PS-ML	No	No	112.5 % (0.05 mg/kg)	SB-other	1	other (dilute & shoot), EN 15054

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Mepiquat

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
24		Yes	> 2 y	0.097	0.04	0.01	20	just thawed	2	Yes, max 20 ml	No	10	MeOH	No	Centrifugation; Filtration; 13 mm Acrodisc syringe filter
82	x	Yes	> 2 y	0.098	0.08	0.01	10	just thawed	15	No	No	60	MeOH	Yes, extraction	None
105		Yes	> 2 y	0.0986	0.11	0.01	5	cold	30	No	No	2	H_2O; QuPPe solvent	No	None
102		No	< 1 y	0.1	0.17	0.01	10	slightly frozen	2	No	No	10	QuPPe solvent	No	None
53	x	Yes	> 2 y	0.102	0.25	0.01	10	ambient	2	No	No	10	MeOH	No	None
11	x	Yes	1 – 2 y	0.103	0.29	0.01	10	deep frozen	10	No	No	15	QuPPe solvent	No	None
98		Yes	> 2 y	0.103	0.29	0.01	20	cold	30	Yes, 4 ml	No	2	MeOH; ultra-turrax	No	Centrifugation
129		Yes	< 1 y	0.104	0.33	0.01	10	ambient	30	No	No	15	MeOH	No	None
61		No	1 – 2 y	0.104	0.33	0.01	2	ambient	1	No	No	1	FA : MeOH : H_2O = 5 : 30 : 65	No	None
48		Yes	> 2 y	0.105	0.38	0.01	5	deep frozen	5	Yes	No	20	QuPPe solvent	No	Centrifugation; Dilution
75		Yes	> 2 y	0.105	0.38	0.03	10	ambient	2	No	No	5	MeOH	No	None
64		No	1 – 2 y	0.106	0.42	0.01	10	ambient	10	Yes, 2 mL	No	1	MeOH; 1% FA	Yes	None
23		Yes	> 2 y	0.108	0.5	0.004	5	ambient	5	No	No	45	MeOH; H_2O	Yes, addition of FA to extraction solvent	Centrifugation; Filtration
50		No	None	0.11	0.58	0.01	10	ambient	1	No	No	1	1% FA in ACN	No	None
57	x	No	> 2 y	0.113	0.71	0.01	10	slightly frozen		No	No	2	QuPPe solvent	No	Centrifugation; Filtration
30		Yes	> 2 y	0.114	0.75	0.005	10	ambient	10	Yes, 10 ml	No	2	MeOH	No	Centrifugation; Filtration
130		No	> 2 y	0.114	0.75	0.01	10	just thawed	2	Yes, up to 10 g of H_2O	No	2	ACN	Yes, citrate buffer	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	No	97 %	SB-EUPT	4	other (dilute & shoot), §64 LFGB L 00.00-76
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second transition	MM-ML	Yes, D3-mepiquat	Yes-3	107.0 % (0.1mg/kg)	SB-EUPT	1	other (dilute & shoot), acidified MeOH extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, chlormequat	No	113 % (0.05mg/kg)	SB-EUPT	1	other (dilute & shoot), Quechers based
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	No	117 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-2		SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to extract aliquots	No	Yes-4	78 % (0.010 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), V6
	No	LC-MS/MS QQQ		PS-ML	No	No	93.7 % (0.1 mg/kg)	SB-EUPT	2	other (dilute & shoot), EN 15055:2006
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-5	97 % (0.25 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), / Polar Quechers: extraction with MeOH
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	114 %		1	other (dilute & shoot)
	No	LC-MS/MS QQQ		Std add. to sample portions	No	Yes-2		see comments	3	QuPPe-Method (EURL-SRM mth f. polar pesticides), / recovery obtained by standard add. to EUPT-sample (not blank) portions
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, mepiquat D3	No	101 % (0.05, 0.1, 0.25 and 0.5 mg/kg)	SB-EUPT	4	other (dilute & shoot), MeOH extraction
	No	LC-MS/MS QQQ		PS-ML	No	No	60 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	No	93 %	SB-EUPT	2	other (dilute & shoot), extraction with mixture of H_2O and MeOH (acidified with FA)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, Mepiquat-D3	Yes-3	95 % (0.1 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	Yes, IL-target pesticide	Yes-3	95 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	Yes-3	93 % (0.1 mg/kg)	SB-EUPT	1	other (dilute & shoot), DIN EN 15055, 2006-08
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, TPP	Yes-1	40 % 0.05mg/kg	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Mepiquat

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
12	x	Yes	< 1 y	0.116	0.83	0.01	10	cold		No	No	2	QuPPe solvent	No	Filtration
16		Yes	> 2 y	0.12	1	0.005	5	cold	1	No	No	30	MeOH :H_2O = 2:1	No	Centrifugation; Filtration; 0.2 µ filter, minisart SRP 25 no. 17575
89		Yes	> 2 y	0.12	1	0.01	20	ambient	1	No	No	2	MeOH	No	Centrifugation; 14 000 U/min
99	x	Yes	> 2 y	0.12	1	0.01	20			Yes, 2 ml H_2O added prior to extraction	No	1	MeOH	No	Centrifugation
14		Yes	> 2 y	0.121	1.04	0.01	10	ambient	1	No	No	15	QuPPe solvent	No	None
47		No	> 2 y	0.125	1.21	0.01	10	deep frozen		No	No	1	QuPPe solvent	Yes, FA	None
41		No	None	0.127	1.29	0.01	10	deep frozen	2	Yes, 2 mL	No	1	QuPPe solvent	No	Centrifugation; Filtration
117	x	Yes	> 2 y	0.127	1.29	0.01	10	ambient	1	No	No	1	MeOH	No	None
109	x	Yes	1 – 2 y	0.13	1.42	0.05	10	just thawed	2	No	No	5	MeOH	No	None
133		Yes	> 2 y	0.13	1.42	0.01	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None
56		Yes	> 2 y	0.132	1.5	0.01	10	just thawed	5	No	No	5	QuPPe solvent	No	Filtration
7		Yes	1 – 2 y	0.134	1.58	0.02	10	just thawed	2	No	No	15	QuPPe solvent	No	None
8		Yes	> 2 y	0.134	1.58	0.01	10	just thawed	2	Yes, added to 10 g	No	3	MeOH	Yes, 1% FA in MeOH	None
59		Yes	> 2 y	0.136	1.67	0.01	10	ambient	10	Yes, 8 ml	No	1	ACN	No	SPE-column
84		Yes	> 2 y	0.15	2.25	0.01	25	ambient	> 30	No	No	2	MeOH	No	Centrifugation; Filtration
126	x	No	None	0.164	2.83	0.1	10	cold	2	Yes, 2ml	No	30	QuPPe solvent	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2MRM	Std add. to extract aliquots	Yes, IL-target pesticide	Yes-3		SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-ML	Yes, D3-mepiquat	Yes-3	100 % Compound spiked in blank	SB-EUPT	1	other (dilute & shoot), EN 15054
	No	LC-MS/MS QQQ		PS-ML	Yes, IL-target pesticide	Yes-3	104 %	QC	5	other (dilute & shoot), L 00.0076 von 12/2008 der ASU § 64 LFGB
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	MM-ML	Yes, d4-chlormequat chloride	No	103 % (0.02 mg/kg)		1	QuPPe-Method (EURL-SRM mth f. polar pesticides), / Used in house potato blank for recovery.
	No	LC-MS/MS QQQ		MM-ML	Yes, Mepiquat (D3)	Yes-4	83 % Extraction recovery vs MMC	SB-EUPT	5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	100 %	QC		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	110 % (0.01 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	MM-ML	Yes, IL-target pesticide	Yes-3	101 % (50 ug/kg)	SB-EUPT	2	other (dilute & shoot), MeOH extraction
	No	LC-MS/MS QQQ		MM-ML	No	No	118.5 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ), Note: Normaly we use the column Obelisc R	Std add. to extract aliquots	No	Yes-1	62.1 % (0.05 mg/kg; n=6)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662), 10g+ACN:10mL; Citrate mixture buffer (6.5g); no-cleanup; Column: Phenomenex Synergi 4u Hydro RP 80A / Recovery RSD= 7.4%
	No	LC-MS/MS QQQ	LC-Ion Trap	MM-ML	No	No	74 % compound spiked	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-4		QC		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	103 % (0.1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	Yes-3	103 %	SB-EUPT	2	other, Waters Appl. Note
	No	LC-MS/MS QQQ		MM-ML	Yes, CCC	Yes-3	93.5 %	SB-EUPT	2	other (dilute & shoot), MeOH-extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	70 %	SB-other	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Diquat

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
6	x	No	1 – 2 y	FN	-3.25	0.02	10	cold	5	Yes, 2.2 ml	No	1	QuPPe solvent	No	None
7		Yes	1 – 2 y	FN	-3.25	0.02	10	just thawed	2	No	No	15	QuPPe solvent	No	None
9		No	> 2 y	FN	-3.25	0.01	10	ambient	10	No	No	30	QuPPe solvent (MeOH/1% FA)	No	None
40	x	No	None	FN	-3.25	0.02	10	cold	10	No	No	1	QuPPe solvent	No	Filtration
61		No	1 – 2 y	FN	-3.25	0.02	2	ambient	1	No	No	1	Other	No	None
98		Yes	> 2 y	0.0783	-1.07	0.02	25	cold	30	No	No	> 60	H_2O; 450 ml H_2O + 30 ml conc. H_2SO_4, 5 hours reflux	No	Ion-Exchange; elution with 50 ml saturated NH_4Cl
81	x	No	> 2 y	0.081	-0.97	0.05	25	cold	> 30	Yes	No	> 60	H_2O 475ml + 10ml conc. sulfuric acid + 1ml n-octanole	No	Ion-Exchange; using DOWEX 50 WX8
23		Yes	> 2 y	0.0869	-0.75	0.008	5	ambient	5	No	No	45	MeOH; H_2O	Yes, addition of FA to extraction solvent	Centrifugation; Filtration
72		Yes	> 2 y	0.103	-0.15	0.01	10	deep frozen	10	No	No	30	MeOH	Yes, with FA	Dessication with Na_2SO_4
32		No	None	0.105	-0.07	0.02	10	deep frozen	2	No	No	1	QuPPe solvent	No	Filtration
13		No	< 1 y	0.109	0.07	0.05	10	slightly frozen	5	Yes, + 1.5 ml H_2O	No	1	QuPPe solvent	No	None
43		Yes	> 2 y	0.115	0.3	0.01	3	ambient		No	No	30	0.01 M $NaHCO_3$	No	SPE-column, OASIS WCX-SPE
82	x	Yes	> 2 y	0.137	1.12	0.05	10	just thawed	15	No	No	60	MeOH	Yes, extraction	None
59		Yes	> 2 y	0.15	1.61	0.02	10	ambient	10	Yes, 8 ml	No	1	ACN	No	SPE-column
75		Yes	1 – 2 y	0.157	1.87	0.05	10	ambient	2	No	No	5	MeOH	No	None
52		Yes	> 2 y	0.16	1.98	0.01	3	ambient	1	No	No	15	1% FA in MeOH; shaken and centrifuged	No	None

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtOAc: ethyl acetate; HOAc: HOAc; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	No	Yes-5	100 % Blank matrix spiked before extraction	SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3				QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL- other substance					QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No					QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ			No					other (dilute & shoot)
	No	LC-UV or DAD		PS-ML	No	Yes-1	60.1 % (0.025 and 0.05 mg/kg)	SB-EUPT	2	other, R036FEJ1 validated in house method, acetic extraction
	No	LC-UV or DAD		PS-ML	No	Yes-1	58.0 % (0.1 mg/kg)	SB-EUPT	1	other, see note
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	86 %	SB-EUPT	2	other (dilute & shoot), extraction with mixture of H_2O and MeOH (acidified with FA)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	No	80 %	SB-EUPT	1	other (Dilute & Shoot), in house method
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	81 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	20 % (0.050 and 0.50 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	Yes, IL-target pesticide	Yes-3	94 % (0.11 mg/kg)	SB-EUPT	1	other, M.S. Young, K.M. Jenkins; Oasis WCX: A Novel Mixed-Mode SPE Sorbent for LC-MS Detection of Paraquat
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second transition	MM-ML	Yes, D4-diquat	Yes-3	104.1 % (0.1mg/kg)	SB-EUPT	1	other (dilute & shoot), acidified MeOH extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	Yes-3	102 %	SB-EUPT	2	other, Waters Appl. Note
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, diquat D4	Yes-2	100 % (0.20 and 0.50 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	Different Method, Transitions MS/MS	PS-ML	Yes, Diquat d6	Yes-1	77 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	other (dilute & shoot), EU ref. version 5; Extracted with MeOH

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fentin

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
9		Yes	> 2 y	0.0644	-2.46	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
2	x	No	1 – 2 y	0.0661	-2.42	0.01	10	ambient	1	No	No	3	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
3		Yes	> 2 y	0.069	-2.35	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	None
25		Yes	< 1 y	0.095	-1.72	0.01	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	None
81	x	Yes	> 2 y	0.099	-1.63	0.01	10	cold	2	No	No	5	ACN	No	None
30		Yes	> 2 y	0.104	-1.51	0.02	25	ambient	5	No	No	2	Other; solvent A H_2SO_4, H_2O,Aceton	No	Liquid-liquid partitioning; with EtOAc/ cyclohexan
99	x	Yes	> 2 y	0.131	-0.86	0.01	10			No	No	1	ACN	Yes, 400 µl HOAc	Centrifugation
51		Yes	> 2 y	0.14	-0.65	0.003	10	ambient	1	No	No	30	ACN	No	Centrifugation
68		No	< 1 y	0.14	-0.65	0.01	10	just thawed	2	No	No	2	ACN	No	None
72		Yes	1 – 2 y	0.143	-0.57	0.003	10	deep frozen	1	No	No	30	MeOH	Yes	None
47		No	< 1 y	0.157	-0.24	0.01	10	deep frozen		No	No	1	ACN	Yes, H_2SO_4	Dispersive-SPE (PSA/ $MgSO_4$)
32		Yes	1 – 2 y	0.166	-0.02	0.01	10	deep frozen	2	No	No	15	ACN	Yes, 100 µl FA instead of citrate buffer	Filtration
107	x	No	None	0.167	0	0.01	10	just thawed	1	Yes	No	2	ACN	No	Filtration
117	x	No	1 – 2 y	0.167	0	0.01	10	ambient	1	No	No	1	ACN	No	None
75		Yes	1 – 2 y	0.173	0.14	0.01	10	ambient	2	No	No	5	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	Yes,	No	79 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	53.2 % (0.05 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), different mobile phase
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Isoproturond8	Yes-1	106 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	89 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	65.5 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	Yes, Methylation with tert..butylmethylether/ methylmagnesiumchloride	GC-MSD	GC-MSD, via second m/z	PS-SL	No	No	125 % (0.1 mg/kg)	SB-EUPT	1	other, extraction, derivatisation, methylation, GC-MSD-detectio
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	76 % (0.04 mg/kg)		1	QuEChERS - Citrate buffered (EN 15662), modified as recommended in EURL observations / Used in house potato blank for recovery.
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	> 5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	60 % Compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), without clean-up
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, TPP	Yes-2		SB-EUPT		other, in house method
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	99 %			QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Pirimicarb D6	Yes-3	98 %	SB-EUPT	1	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-carbaryl	Yes-1	62 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	MM-ML	No	No	87 % (50 ug/kg)	SB-EUPT	1	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	93 % (0.1, 0.25, 0.5 and 1.0 mg/kg)	SB-EUPT	4	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fentin

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
84		No	> 2 y	0.179	0.29	0.01	10	ambient	> 30	No	No	5	ACN	No	Centrifugation; Filtration
134		No	< 1 y	0.18	0.31	0.01	10	cold	5	No	No	5	ACN	No	Freezing out
6	x	No	> 2 y	0.194	0.65	0.01	10	cold	5	Yes, 2.2 ml	No	1	ACN	No	None
8		Yes	1 – 2 y	0.194	0.65	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, 100 µL FA	Dispersive-SPE (PSA/$MgSO_4$)
43		Yes	> 2 y	0.197	0.72	0.05	25	ambient		No	No	2	Isooctane H_2O:HOAc 4:1	No	Florisil Column
133		Yes	None	0.201	0.81	0.01	10	slightly frozen	1	No	No	1	ACN; ACN was acidified with 0.1% HOAc	No	None
21	x	Yes	> 2 y	0.211	1.05	0.01	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$
129		No	1 – 2 y	0.214	1.13	0.01	10	ambient	20	No	No	15	MeOH	No	None
23		No	None	0.219	1.25	0.05	10	ambient	5	Yes, 1.5 ml	No	15	QuPPe solvent	Yes, addition of FA to MeOH	Centrifugation; Filtration
14		Yes	> 2 y	0.225	1.39	0.01	10	ambient	1	No	No	15	ACN	No	None
122		Yes	> 2 y	0.246	1.89	0.01	2	cold	10	Yes	No	1	10ml ACN; 9 ml H_2O	No	None
83		Yes	1 – 2 y	0.37	4.86	0.01	5	slightly frozen	1	No	No	3	ACN	Yes, acetic with H_2SO_4	None
13		Yes	< 1 y	0.493	7.81	0.01	10	slightly frozen	5	No	No	5	ACN	No	SPE-column, PSA/C18

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-3	99.4 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	94 %	SB-EUPT	2	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-5	100 % Blank matrix spiked before extraction	SB-EUPT		QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ		MM-ML	Yes, Linuron-D6	Yes-1	90 % (0.15 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), Citrate salts replaced by 100 µL FA
	Yes, Methyl-magnesium-chloride	GC-(P) FPD		PS-SL	No	No	99 % (0.15 mg/kg)	SB-EUPT	1	other, The sample is extracted with isooctane and H_2O:HOAc (4:1). Clean up with Florisil column.
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	Std add. to extract aliquots	No	No	77.1 % (0.05 mg/kg; n=6)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662), 10g+ACN:10mL; Citrate mixture tampon (6.5g); no-cleanup; Column:Zorbax Eclipse XDB C18 / Recovery RSD= 18.5%
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	115 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Quechers without PSA
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-5	95 % (0.25 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), / Polar Quechers: extraction with MeOH
	No	LC-MS/MS QQQ		MM-ML	No	No	84 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides), 1% FA in MeOH
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-2	81 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate	No	86 %	QC	4	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 MRM	MM-SL	No	Yes-2	100.0 %	QC	1	QuEChERS-based EURL-Mth for Organotins
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-5	100 % (0.10 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fosetyl

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	H_2O addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
48		Yes	1 – 2 y	FN	-3.75	0.05	10	deep frozen	5	No	No	20	ACN	No	Centrifugation; Dilution
51		Yes	> 2 y	FN	-3.75	0.5	10	ambient	1	No	No	30	ACN	No	Centrifugation
23		No	None	0.184	-3.08	0.05	10	ambient	5	Yes, 1.5 ml	No	15	QuPPe solvent	Yes, addition of FA to MeOH	Centrifugation; Filtration
9		Yes	> 2 y	0.199	-3	0.01	10	ambient	10	No	No	30	Other	No	None
75		Yes	1 – 2 y	0.458	-1.7	0.05	10	ambient	2	No	No	5	MeOH	No	None
3		Yes	> 2 y	0.483	-1.58	0.01	5	ambient	10	No	No	15	QuPPe solvent; H_2O	No	None
68		Yes	> 2 y	0.492	-1.53	0.01	10	just thawed	2	No	No	2	QuPPe solvent	No	None
81	x	No	< 1 y	0.575	-1.12	0.05	10	cold	2	No	No	5	ACN; 1 v/v % FA in ACN	No	None
98		No	> 2 y	0.588	-1.05	0.05	10	cold	20	No	No	5	QuPPe solvent	No	None
6	x	No	< 1 y	0.741	-0.28	0.05	10	cold	5	Yes, 2.2 ml	No	1	QuPPe solvent	No	None
14		Yes	> 2 y	0.742	-0.26	0.01	10	ambient	1	No	No	15	QuPPe solvent	No	None
7		Yes	< 1 y	0.75	-0.24	0.01	10	just thawed	2	No	No	15	QuPPe solvent	No	None
13		No	< 1 y	0.766	-0.16	0.05	10	slightly frozen	5	Yes, + 1.5 ml H2O	No	1	QuPPe solvent	No	None
132		No	1 – 2 y	0.829	0.16	0.05									
107	x	No	None	0.894	0.48	0.01	10	just thawed	1	Yes	No	2	ACN	No	Filtration
84		Yes	> 2 y	0.914	0.58	0.5	25	ambient	> 30	No	No	2	MeOH	No	Centrifugation; Filtration
112		No	> 2 y	0.979	0.91	0.12	10	deep frozen	1	No	No	10	ACN : H_2O = 50 : 50	No	None

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtOAc: ethyl acetate; HOAc: HOAc; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		PS-ML	No					QuEChERS - Acetate buffered (AOAC Official Method 2007.01), / Reporting limit determined by matrix-mached calibration in EUPT-blank material
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No					QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	No	No	102 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides), 1% FA in MeOH
	No	LC-MS/MS QQQ		MM-ML	Yes, IL- other substance	No	101 %	QC	> 5	other (dilute & shoot)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-2	100 % (1.0 and 2.0 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, IL-target pesticide	Yes-1	89 %	SB-EUPT		other (dilute & shoot), acetic extraction MeOH/H_2O 1/1
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	82 % Compound spiked	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), Column: Atlantis t3
	No	LC-MS/MS QQQ		MM-ML	No	No	82.3 % (0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), final extract was adjusted to 20 ml
	No	LC-MS/MS QQQ		PS-ML	No	No	76.6 % (0.1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-5	100 % matrix spiked before extraction	SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-2	83 % Extraction recovery vs MMC	SB-EUPT	5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	114 % (0.1 mg/kg)	QC	> 5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	94.4 % (0.050 and 0.50 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No					Yes-5	74 % 0.092 mg/kg			
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-glyphosate	No	100 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), Method 1.3
	No	LC-MS/MS QQQ		PS-ML	No	No	102 %	SB-EUPT	2	other (dilute & shoot), MeOH-extraction / Fosetyl-aluminium=0.98
	No	LC-MS/MS QQQ		MM-SL	No	No	104 % (0.05 and 0.1 mg/kg)	SB-EUPT	2	other (dilute & shoot), extraction, dilution

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Fosetyl

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	H_2O addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
32		Yes	1 – 2 y	0.993	0.98	0.05	10	deep frozen	2	No	No	1	QuPPe solvent	No	Filtration	
30		Yes	> 2 y	1.01	1.06	0.01	10	ambient	15	No	No	15	MeOH	No	Centrifugation; Filtration	
80		Yes	1 – 2 y	1.08	1.42	1	10	deep frozen	30	Yes	No	60	QuPPe solvent (MeOH/1% FA)	No	Dispersive-SPE	
83		Yes	> 2 y	1.08	1.42	0.01	5	slightly frozen		No	No	3	QuPPe solvent	No	None	
10	x	No	None	1.128	1.65	0.05	10	ambient	1	No	No	1	QuPPe solvent	No	Filtration	
8		Yes	> 2 y	1.558	3.81	0.05	10	just thawed	2	Yes, added to 10 g	No	3	MeOH	Yes, 1% FA in MeOH	None	
102		Yes	1 – 2 y	1.584	3.94	0.01	10	slightly frozen	2	No	No	10	QuPPe solvent	No	None	
25		Yes	< 1 y	1.929	5.67	0.05	10	deep frozen	2	No	No	2	QuPPe solvent	No	None	

Abb. of solvent: ACN: acetonitrile; DCM:dichlormethan; EtOAc: ethyl acetate; HOAc: HOAc; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	112 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	Yes-3	102 % (1 mg/kg)	SB-EUPT	1	other (dilute & shoot), exctration with H_2O/MeOH, centrifugated
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	No	117 % fosetyl-al 1mg/kg + phosphonic acid 1 mg/kg	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-SL	No	Yes-2	95.0 %	QC	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	100 %	SB-EUPT	3	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	84 % (1.6 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	No	117 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	115 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glufosinate

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
23		No	< 1 y	FN	-3.7	0.02	10	ambient	5	Yes, 1.5 ml	No	15	QuPPe solvent	Yes, addition of FA to MeOH	Centrifugation; Filtration
77		Yes	< 1 y	0.132	-2.05	0.05	10	ambient		No	No	1	QuPPe solvent	No	None
72		Yes	> 2 y	0.226	-0.66	0.05	5	deep frozen	10	No	No	15	MeOH; H_2O	No	None
7		Yes	< 1 y	0.235	-0.52	0.02	10	just thawed	2	No	No	15	QuPPe solvent	No	None
52		Yes	> 2 y	0.235	-0.52	0.01	2	ambient	1	No, extracted with H_2O	No	20	H_2O; Acetone; shaken with the solvent; centrifuged	Yes, pH = 7	Dowex column;HLB column
107	x	No	None	0.236	-0.51	0.05	10	just thawed	1	Yes	No	2	ACN	No	Filtration
93		Yes	< 1 y	0.238	-0.48	0.01	10	deep frozen	2	Yes, 40 mL (H2O 1% FA)	No	20	H_2O; DMC	Yes, pH = 9	Centrifugation; SPE-column, 4°C - SEP C18
82	x	Yes	1 – 2 y	0.242	-0.42	0.05	10	just thawed	1	No	No	5	H_2O	Yes, extraction	None
81	x	No	> 2 y	0.244	-0.39	0.02	25	cold	5	No	No	15	H_2O; Turax with 200 ml distilled H_2O	No	Others; elution with methanol on 3%desact. silicagel column
25		Yes	< 1 y	0.253	-0.26	0.05	10	deep frozen	2	No	No	2	QuPPe solvent	No	None
6	x	Yes	> 2 y	0.255	-0.23	0.05	5	cold	5	Yes 10 ml	No	15	MeOH; DMC	No	Liquid-liquid partitioning
30		Yes	> 2 y	0.256	-0.21	0.01	2	ambient	5	No	No	30	H_2O/HCl	Yes	SPE-column, C8
40	x	No	None	0.269	-0.02	0.01	3	cold	1	Yes	No	20	H_2O	No	Liquid-liquid partitioning
98		Yes	> 2 y	0.269	-0.02	0.05	25	cold	30	No	No	15	H_2O; ultra-turrax, centrifugation, evaporation	No	Silica Column; washed 15ml EtOAc, eluated 3ml methanol

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	No					QuPPe-Method (EURL-SRM mth f. polar pesticides), 1% FA in MeOH
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No				QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	Yes-2		SB-EUPT		Mth involv. deriv. w. FMOC, in house method
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	111 % (0.1 mg/kg)	QC	> 5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, Added FMOC-Cl and let derivitize overnight.	LC-MS/MS QQQ	Different Method, Transitions MS/MS	PS-ML	Yes, Glyphosate IS	No	95 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	Mth involv. deriv. w. FMOC, extraced with H_2O twice, cleaned up with Dowex column and HLB column
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Two transistions	MM-ML	Yes, C13-glyphosate	No	97 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), Method 1.3
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	No	97 % 25 µg/kg	SB-EUPT	1	Mth involv. deriv. w. FMOC
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second transition	MM-ML	Yes, D4	No	78.6 % (0.1mg/kg)	SB-EUPT	1	other(dilute & Shoot), H_2O/2%FM
	Yes, trimethyl orthoacetate with HOAc and then reflux	GC-(P) FPD		MM-ML	Yes, TPP	No	128.7 % (0.1 mg/kg)	SB-EUPT	1	other (involv. deriv. w. TMOAc), derivatization and then clean up with silicagel
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	97 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, FMOC-Cl	LC-MS/MS QQQ	Different Method, QuPPE-method	MM-ML	Yes, IL-target pesticide	Yes-5	100 % matrix spiked before extraction	SB-EUPT		Mth involv. deriv. w. FMOC
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to extract aliquots	No	Yes-2	60 % (0.3 mg/kg)	SB-EUPT	1	Mth involv. deriv. w. FMOC, extraction with hydrochloric acid, online-derivatisation, online-SPE
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to sample portions	Yes, 1.2-$^{13}C_2{}^{15}N$-glyphosate	Yes-5		SB-EUPT		Mth involv. deriv. w. FMOC
	Yes, 20 ml trimethyl orthoacetate, 4 hours reflux	GC-(P) FPD	LC-MS/MS QQQ	PS-ML	No	No	67.2 % (0.1 mg/kg)	SB-EUPT	2	other (involv. deriv. w. TMOAc), R486FEJ1 validated in house method, H_2O extraction

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Glufosinate

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
31	x	No	None	0.272	0.02	0.01	10	slightly frozen	2	No	No	2	H_2O; DMC; H_2O acidified with FA	No	SPE-column, HLB Oasis
14		Yes	> 2 y	0.276	0.08	0.01	2	ambient	1	Yes, 10 ml	No	60	H_2O	Yes, Borate, pH 9.5	Liquid-liquid partitioning; LLE Acetonitrile
75		Yes	1 – 2 y	0.281	0.16	0.05	10	ambient	2	No	No	5	MeOH	No	None
69		No	None	0.293	0.33	0.01	10	slightly frozen	15	Yes	No	1	QuPPe solvent	No	None
105		Yes	< 1 y	0.305	0.51	0.05	5	cold	30	No	No	10	H_2O; DMC	No	SPE-column, Oasis HLB cartridge
115		Yes	1 – 2 y	0.314	0.64	0.05	25	cold	2	No	No	60	H_2O	No	Silica Column
11	x	Yes	< 1 y	0.318	0.7	0.05	10	deep frozen	10	Yes, 2 mL	No	15	QuPPe solvent	No	None
129		No	< 1 y	0.321	0.75	0.05	10	ambient	30	No	No	15	MeOH	No	None
13		No	< 1 y	0.324	0.79	0.05	10	slightly frozen	5	Yes, + 1.5 ml H2O	No	1	QuPPe solvent	No	None
84		Yes	< 1 y	0.343	1.07	0.01	25	ambient	> 30	No	No	2	H_2O; QuPPe solvent	No	Centrifugation; Filtration
9		No	< 1 y	0.401	1.93	0.01	10	ambient	10	No	No	30	QuPPe solvent (MeOH/1% FA)	No	None
32		No	None	0.424	2.27	0.05	10	deep frozen	2	No	No	1	QuPPe solvent	No	Filtration

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	Yes, FMOC, 30, addition FA for stop derivatization	LC-MS/MS QQQ	LC-MS/MS QQQ, 404-208; 404- 179; 404 -136	MM-ML	Yes, glyphosate 13C2, 15N	Yes-3		SB-EUPT	1	Mth involv. deriv. w. FMOC, extraction to dichloromethan-H_2O FA, derivatization FMOC, annalyze on LC MSMS
	Yes, FMOC-Cl	LC-MS/MS QQQ		MM-ML	Yes, Glufosinate (D3)	Yes-4	79 % Extraction recovery vs MMC	SB-EUPT	5	Mth involv. deriv. w. FMOC, GALAB SOP-232
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, glyphosate 13C15N	Yes-2	100 % (0.5 and 1.0 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		Std add. to sample portions	No	No	103 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	Yes, FMOC	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Glyphosate	Yes-3	115 % (0.10mg/kg)	SB-EUPT	1	Mth involv. deriv. w. FMOC
	Yes, TMOAc	GC-(P) FPD	GC-NPD	MM-ML	No	No	120.0 % (0.5ppm)	SB-EUPT	3	other (involv. deriv. w. TMOAc), extraction with H_2O,evaporation to dry,1ml HOAc+20ml TMOAc,evaporation / evaluated by multilevel matrix calibration
	No	LC-MS/MS QQQ		Std add. to sample portions	No	Yes-2	90 % (0.050 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), QuPPe EURL-SRM method for polar pesticides v.6
	Yes, FMOC-Cl	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, Glyphosate-13C2.15N	Yes-5	127 % (0.25 mg/kg)	SB-EUPT	1	Mth involv. deriv. w. FMOC, / Polar Quechers: extraction with MeOH and derivatis
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, two transitions	MM-ML	No	Yes-1	88 % (0.050 and 0.50 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, Glyphosate	Yes-3	83.5 %	SB-EUPT	2	other(dilute & Shoot), acid MeOH-H2O extr
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	No	79 %	QC	> 5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	89 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Maleic hydrazie

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	H_2O addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
13		No	1 – 2 y	0.16	-3.07	0.1	10	slightly frozen	5	Yes, + 1.5ml H2O	No	1	QuPPe solvent	No	None
7		Yes	< 1 y	0.388	-1.75	0.01	10	just thawed	2	No	No	15	QuPPe solvent	No	None
84		Yes	> 2 y	0.391	-1.73	0.5	25	ambient	> 30	No	No	2	MeOH	No	Centrifugation; Filtration
67		Yes	> 2 y	0.44	-1.44	0.5	10	just thawed	> 30			10	MeOH		SPE-column, SCX
99	x	Yes	> 2 y	0.524	-0.96	0.05	10			No	No	1	MeOH	No	SPE-column, SAX/PSA mixed mode
9		No	1 – 2 y	0.554	-0.78	0.01	10	ambient	10	No	No	30	QuPPe solvent (MeOH/1% FA)	No	None
49	x	No	< 1 y	0.557	-0.76	0.1	10	ambient	5	No	No	2	QuPPe solvent	No	Centrifugation
81	x	No	< 1 y	0.559	-0.75	0.1	10	cold	2	No	No	5	ACN; 1 v/v % FA in ACN	No	None
102		No	< 1 y	0.61	-0.46	0.01	10	slightly frozen	2	No	No	10	QuPPe solvent	No	None
32		Yes	1 – 2 y	0.639	-0.29	0.05	10	deep frozen	2	No	No	1	QuPPe solvent	No	Filtration
80		Yes	> 2 y	0.653	-0.21	0.05	10	deep frozen	30	Yes	No	60	QuPPe solvent (MeOH/1% FA)	Yes	Dispersive-SPE
98		No	> 2 y	0.683	-0.03	0.05	10	cold	20	No	No	5	QuPPe solvent	No	None
8		Yes	> 2 y	0.694	0.03	0.05	10	just thawed	2	Yes, added to 10 g	No	3	MeOH	Yes, 1% FA in MeOH	None
6	x	No	< 1 y	0.7	0.07	0.05	10	cold	5	Yes, 2.2 ml	No	1	QuPPe solvent	No	None
83		Yes	1 – 2 y	0.717	0.17	0.01	5	slightly frozen		No	No	3	QuPPe solvent	No	None
14		Yes	1 – 2 y	0.72	0.18	0.01	10	ambient	1	No	No	15	QuPPe solvent	No	None
75		Yes	1 – 2 y	0.73	0.24	0.05	10	ambient	2	No	No	5	MeOH	No	None
30		Yes	> 2 y	0.763	0.43	0.05	10	ambient	> 30	No	No	1	MeOH	No	SPE-column, SCX
43		Yes	> 2 y	0.772	0.49	0.5	20	cold		Yes	No	1	MeOH; H_2O	No	SPE-column LiChrolut SCX

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-UV or DAD	LC-UV or DAD, UV spectrum	MM-ML	No	Yes-1	40 % (0.050 and 0.50 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3				QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	No	No	87.4 %	SB-EUPT	2	other (dilute & shoot), MeOH-extraction
	No	LC-UV or DAD		PS-ML	No	No	77 % (2.5mg/kg)	SB-other	1	other, MeOH extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	76 % (0.1 mg/kg)		1	other, in house / Used in house potato blank for recovery.
	No	LC-MS/MS QQQ		MM-ML	No	No	81 %	QC	> 5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, maleic hydrazide D2	Yes-3		SB-EUPT		other (Dilute & shoot), in house MeOH extraction (1% a formic)
	No	LC-MS/MS QQQ		MM-ML	No	No	94.8 % (0.5 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), final extract was adjusted to 20 ml
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, IL-target pesticide	No	120 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	115 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	Yes, IL-target pesticide	No	102 % (0.1 mg/kg)	SB-other	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		PS-ML	No	No	71.5 % (0.1 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	81 % (0.8 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-5	100 % matrix spiked before extraction	SB-EUPT		QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-SL	No	Yes-2	90.0 %	QC	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-2	80 % Extraction recovery vs MMC	SB-EUPT	5	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	Yes-2	100 % (0.5 and 1.0 mg/kg)	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to extract aliquots	No	Yes-2	83 % (0.5 mg/kg)	SB-other	1	other, extraction with MeOH, clean-up on SCX-column
	No	LC-UV or DAD		PS-ML	No	No	94 % (1.01 mg/kg)	SB-EUPT	1	other, The sample is extracted with MeOH and H_2O. Clean up with SPE

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

Maleic hydrazie

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	H_2O addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
10	x	No	None	0.802	0.66	0.05	10	ambient	1	No	No	1	QuPPe solvent	No	Filtration
51		Yes	> 2 y	0.854	0.96	0.5	10	ambient	1	No	No	30	ACN	No	Centrifugation
40	x	No	None	0.886	1.15	0.25	10	cold	10	No	No	1	QuPPe solvent	No	Filtration
25		Yes	< 1 y	0.89	1.17	0.05	10	deep frozen	2	No	No	2	QuPPe solvent	No	None
103		Yes	> 2 y	1.04	2.04	0.05	10	cold	2	No	No	2	MeOH; H_2O from sample	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

BAC-C12

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
67		Yes	< 1 y	0.05	-3.65	0.01	10	just thawed	20			5	ACN		
95		No	< 1 y	0.186	-2.69	0.1	10	cold		No	No		ACN	No	Dispersive-SPE (C18/ $MgSO_4$)
13		No	< 1 y	0.273	-2.08	0.01	10	slightly frozen	5	No	No	5	ACN	No	None
68		Yes	< 1 y	0.292	-1.94	0.01	10	just thawed	2	No	No	2	ACN	No	None
19		No	1 – 2 y	0.316	-1.77	0.01	15	slightly frozen	5	No	No	1	ACN	No	None
51		Yes	> 2 y	0.334	-1.65	0.01	10	ambient	1	No	No	30	ACN	No	Centrifugation

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	103 %	SB-EUPT	3	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	97 % (1.0 mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	103 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)
	No	LC-MS/MS QQQ		MM-ML	Yes, IL-target pesticide	Yes-3	116 %	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		PS-ML	No	No	82 % (0.02mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), Quechers without buffers / Background levels detected in all samples
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, tris-(1.3-dichlor isopropyl)-phosphate	No	85 % (0.1mg/kg)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 3 transitions	MM-ML	No	Yes-1	84 % (0.10 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	96 % Compound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), without clean-up
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transitions	MM-SL	No	No	86.1 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	5	QuEChERS - Original Version (J. AOAC 86, 2003)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

BAC-C12

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
9		Yes	1 – 2 y	0.371	-1.39	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
33	x	No	1 – 2 y	0.401	-1.18	0.1	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration
82	x	No	< 1 y	0.421	-1.04	0.1	15	just thawed	1	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
24		Yes	< 1 y	0.438	-0.92	0.1	10	just thawed	1	No	No	15	ACN	No	Centrifugation; Filtration; 13 mm Acrodisc syringe filter
7		Yes	1 – 2 y	0.44	-0.9	0.01	10	just thawed	2	No	No	30	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
75		Yes	1 – 2 y	0.446	-0.86	0.01	10	ambient	1	No	No	3	ACN	No	None
72		Yes	< 1 y	0.454	-0.8	0.01	10	deep frozen	10	No	No	10	ACN; H_2O	No	Centrifugation
26		Yes	1 – 2 y	0.467	-0.71	0.01	5	slightly frozen	10	Yes	No	2	MeOH	Yes, pH 4	Liquid-liquid partitioning; ChemElut
55	x	Yes	< 1 y	0.477	-0.64	0.01	10	deep frozen		No	No	2	ACN	No	Others; $MgSO_4$ClCitrate, Citric acid
41		No	None	0.48	-0.62	0.01	10	deep frozen	2	No	YesOH	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); Filtration
103		Yes	< 1 y	0.495	-0.51	0.02	15	cold	2	No	No	2	ACN; H_2O (H_2O from sample)	No	Dispersive-SPE (PSA/ $MgSO_4$)
52		Yes	< 1 y	0.5	-0.48	0.01	2	ambient	1	Yes, vortexed and shaken for 20utes	No	20	ACN; shaken, centrifuged, filtered	No	None
84		Yes	1 – 2 y	0.511	-0.4	0.01	25	ambient	> 30	No	No	2	MeOH	No	Centrifugation; Filtration
2	x	No	None	0.518	-0.35	0.1	10	ambient	1	No	No	2	ACN	No	None
117	x	Yes	> 2 y	0.518	-0.35	0.1	4	ambient	1	No	No	3	H_2O-ACN-TFA (300-700-0.8)	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	Yes	No	98 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, ES+	MM-ML	No	Yes-2		SB-EUPT		SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second transition	MM-ML	No	No	54.8 % (0.05 mg/kg	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, D6-DDAI, Pirimicarb-D6	No	76 %	SB-EUPT	2	other, EURL CVUA Stuttgart, SRM QAV
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to extract aliquots	Yes, TPP	Yes-2		QC		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	102 % (0.25, 0.5, 1.0 and 2.0 mg/kg)	SB-EUPT	4	other, ACN
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	95 %	SB-EUPT	1	other, in house method
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	93.8 %	SB-EUPT	1	ChemElut
	No	LC-MS/MS QQQ		MM-SL	No	No	87 % (0.1 mg/kg)	SB-EUPT	3	QuEChERS - Original Version (J. AOAC 86, 2003), QuEChERS extraction withou purification (CRL SRM method)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	111 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	No	No	101 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	Different Method, Transitions MS/MS	PS-ML	No	No	130 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	other, www.eurl-pesticides-datapool.eu
	No	LC-MS/MS QQQ		PS-ML	No	No	120 %	SB-EUPT	2	other, MeOH-extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	105 % (0.1 mg/kg)	SB-EUPT	1	other, QAC-QuEChERS METHOD BASED ON METHOD BY EURL-SRM
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	PS-ML	Yes, Tetrahexylammonium-bromide	Yes-5		SB-EUPT		other, Extraction with H_2O-ACN-TFA (300-700-0.8)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

BAC-C12

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
136		No	< 1 y	0.518	-0.35	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
99	x	Yes	< 1 y	0.525	-0.3	0.1	10			No	No	1	ACN	Yes, acetate buffer	Centrifugation
21	x	Yes	1 – 2 y	0.533	-0.25	0.05	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$
23		No	None	0.554	-0.1	0.01	10	ambient	5	Yes, 1.5 ml	No	15	QuPPe solvent	Yes, addition of FA to MeOH	Centrifugation; Filtration
43		Yes	< 1 y	0.558	-0.07	0.01	10	ambient		No	No	1	ACN	No	Dessication with $MgSO_4$; PSA
3		Yes	1 – 2 y	0.56	-0.06	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	None
73	x	Yes	< 1 y	0.568	0	0.01	12	ambient	5	No	No	30	ACN; QuPPe solvent	No	None
83		Yes	> 2 y	0.568	0	0.01	5	slightly frozen		No	No	3	ACN	No	None
31	x	Yes	< 1 y	0.573	0.04	0.02	10	slightly frozen	2	No	No	30	ACN	No	None
76		Yes	< 1 y	0.601	0.23	0.01	10	just thawed	1	No	No	2	ACN	No	None
81	x	No	< 1 y	0.608	0.28	0.1	10	cold	2	No	No	5	ACN	No	None
27		Yes	1 – 2 y	0.61	0.3	0.02	10	deep frozen	10	No	No, 200 µl 5m NaOH	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
8		Yes	1 – 2 y	0.613	0.32	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, Citrate Buffer pH 5.5	None
96		Yes	< 1 y	0.615	0.33	0.01	10	ambient	1	No	No	2	ACN; 100%	No	None
47		No	< 1 y	0.619	0.36	0.1	10	deep frozen		No	No	1	ACN	No	None
6	x	Yes	< 1 y	0.629	0.43	0.1	10	cold	5	Yes, 2.2 ml	No	1	ACN	No	None
25		Yes	< 1 y	0.63	0.44	0.05	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Nicarbazin	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	MM-ML	No	No	97 % (0.1 mg/kg)		1	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), / Used in house potato blank for recovery.
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	105 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Quechers without PSA
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	41 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides), 1% FA in MeOH
	No	LC-MS/MS QQQ		MM-SL	No	No	107 % (0.30 mg/kg)	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Isoproturond8	Yes-1	92 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	MM-ML	No	No	91 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-SL	No	Yes-2	80.0 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 304-91; 304-212	MM-ML	No	No	89 % (0.5 mg/kg)	SB-EUPT	3	QuEChERS - Original Version (J. AOAC 86, 2003), extraction to ACN, no purifying, filter into vials, measurement LC MSMS
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	86.4 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), without cleanup / No
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	115.5 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	95 % compound spiked			QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	Yes, Linuron-D6	No	89 % (0.5 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	70 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Extraction and diluition
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No				other, QuEChERS 1 Step
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-5	100 % matrix spiked before extraction	SB-EUPT		other, QAC (DDAC, BAC) V4: QuEChERS-based, by EURL-SRM
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	86 %	QC	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

BAC-C12

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
134		No	None	0.636	0.48	0.1	10	cold	5	No	No	5	ACN	No	None
118	x	No	< 1 y	0.639	0.5	0.01	5	cold	15	No	No	1	0.1% FA ACN; Saturated NaCl	No	None
42		Yes	< 1 y	0.645	0.54	0.01	10	just thawed	1	No	No	1	ACN	Yes, Citrate Buffered	Dessication with $MgSO_4$; Dispersive-SPE (PSA/ $MgSO_4$)
34		Yes	< 1 y	0.646	0.55	0.01	10	deep frozen	2	No	No	5	ACN	No	None
30		Yes	1 – 2 y	0.66	0.65	0.01	4	ambient	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); Centrifugation
40	x	Yes	< 1 y	0.669	0.71	0.025	10	cold	1	No	No	1	ACN	No	Filtration
32		Yes	< 1 y	0.685	0.82	0.1	10	deep frozen	2	No	No	15	ACN	No	Filtration
98		No	1 – 2 y	0.687	0.84	0.1	10	cold	20	No	No	20	ACN	No	Centrifugation
87		No	None	0.691	0.87	0.01	10	ambient		No	No	30	ACN	Yes, buffer-saltmixture	Freezing-out; Dispersive-SPE (PSA/ $MgSO_4$); multiple Centrifugation
88		Yes	< 1 y	0.698	0.92	0.005	10	deep frozen	> 30	No	No	10	ACN; citrate buffer	Yes, extraction and partitioning	Centrifugation
60		Yes	< 1 y	0.73	1.14	0.01	10	cold	5	No	No	1	ACN	No	None
89		Yes	< 1 y	0.868	2.11	0.01	10	ambient	1	No	No	1	ACN	No	Freezing-out
122		Yes	< 1 y	0.904	2.37	0.01	2	cold	10	Yes	No	1	10ml ACN, 9 ml H_2O	No	None
59		Yes	1 – 2 y	0.92	2.48	0.1	2	ambient	10	Yes, 9.6 ml	No	10	ACN	No	None
14		Yes	1 – 2 y	0.997	3.02	0.01	10	ambient	1	No	No	15	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	103 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-Q-TOF		Std add. to sample portions	No	No	70 %	SB-EUPT	3	other, 0.1%FA/ACN extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No				QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	80 % spikyng level	SB-EUPT	5	other, QuEChERS without cleanup
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, not for calculation, only to check extraction efficiency	No	93 % (0.4 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	96 % (0.1 mg/kg)	SB-EUPT	1	other, QuEChERS without cleanup
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	108 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	99.1 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	113.7 % (0.1 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, Pirimicarb-D6, not for calculation	No	107 % (0.75 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662), / rel. standard deviation 1.7 % with 5 individuals
	No	LC-MS/MS QQQ		MM-ML	No	No	105 % Spiked samples	SB-EUPT	4	other, EURL (QAC) version 14.09.2012
	No	LC-MS/MS QQQ		MM-ML	No	No	101 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate	No	104 %	QC	4	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, D6-BAJ C12	Yes-3	105 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-2	85 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

DDAC-C10

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
26		Yes	1 – 2 y	FN	-3.79	0.02	5	slightly frozen	10	Yes	No	2	MeOH	Yes, pH 4	Liquid-liquid partitioning; ChemElut
67		Yes	< 1 y	0.06	-3.37	0.01	10	just thawed	20			5	ACN		
95		No	< 1 y	0.168	-2.23	0.1	10	cold		No	No		ACN	No	Dispersive-SPE (C18/ $MgSO_4$)
33	x	No	1 – 2 y	0.229	-1.59	0.1	10	deep frozen	1	No	No	15	EtOAc	Yes, Buffered with $NaHCO_3$	Dessication with Na_2SO_4; Filtration
82	x	No	< 1 y	0.251	-1.36	0.1	15	just thawed	1	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
19		No	1 – 2 y	0.277	-1.08	0.01	15	slightly frozen	5	No	No	1	ACN	No	None
72		Yes	< 1 y	0.294	-0.91	0.01	10	deep frozen	10	No	No	10	ACN; H_2O	No	Centrifugation
9		Yes	1 – 2 y	0.305	-0.79	0.01	10	ambient	10	No	No	10	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
13		No	< 1 y	0.306	-0.78	0.01	10	slightly frozen	5	No	No	5	ACN	No	None
28		No	< 1 y	0.31	-0.74	0.01	10	slightly frozen	1	No	No	15	ACN	No	Centrifugation
68		Yes	< 1 y	0.313	-0.71	0.01	10	just thawed	2	No	No	2	ACN	No	None
41		No	None	0.32	-0.63	0.01	10	deep frozen	2	No	Yes, NaOH	1	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); Filtration
24		Yes	< 1 y	0.323	-0.6	0.1	10	just thawed	1	No	No	15	ACN	No	Centrifugation; Filtration; 13 mm Acrodisc syringe filter
51		Yes	> 2 y	0.333	-0.49	0.01	10	ambient	1	No	No	30	ACN	No	Centrifugation
2	x	No	None	0.338	-0.44	0.1	10	ambient	1	No	No	2	ACN	No	None
6	x	Yes	< 1 y	0.343	-0.39	0.1	10	cold	5	Yes, 2.2 ml	No	1	ACN	No	None
75		Yes	1 – 2 y	0.347	-0.35	0.01	10	ambient	1	No	No	3	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No					ChemElut
	No	LC-MS/MS QQQ		PS-ML	No	No	76 % (0.02mg/kg)	SB-EUPT	1	QuPPe-Method (EURL-SRM mth f. polar pesticides), Quechers without buffers
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, tris-(1.3-dichlor-isopropyl)-phosphate	No	82 % (0.1mg/kg)	SB-EUPT	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, ES+	MM-ML	No	Yes-2		SB-EUPT		SweEt type (Anal. Bioanal. Chem (2007) 389, 1773-1789)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second transition	MM-ML	No	No	57.5 % (0.05 mg/kg	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 2 transi-tions	MM-SL	No	No	83.7 % (0.05 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	100 %	SB-EUPT	1	other, in house method
	No	LC-MS/MS QQQ		MM-ML	Yes,	No	97 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	80.6 % (0.10 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	98 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	88 % Com-pound spiked	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), without clean-up
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	110 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, D6-DDAI, Pirimicarb-D6	No	84 %	SB-EUPT	2	other, EURL CVUA Stuttgart, SRM QAV
	No	GC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	Yes-1	90 %	SB-EUPT	5	QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-SL	No	No	98.6 % (0.1 mg/kg)	SB-EUPT	1	other, QAC-QuEChERS METHOD BASED ON METHOD BY EURL-SRM
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-5	100 % matrix spiked before extraction	SB-EUPT		other, QAC (DDAC, BAC) V4: QuEChERS-based, by EURL-SRM
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	95 % (0.1, 0.25, 0.5 and 1.0 mg/kg)	SB-EUPT	4	other, ACN

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

DDAC-C10

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
99	x	Yes	< 1 y	0.347	-0.35	0.1	10			No	No	1	ACN	Yes, acetate buffer	Centrifugation	
60		Yes	< 1 y	0.35	-0.32	0.01	10	cold	5	No	No	1	ACN	No	None	
52		Yes	< 1 y	0.35	-0.32	0.01	2	ambient	1	Yes, vortexed and shaken for 20 min	No	20	ACN; Other; Other; shaken, centrifuged, filtered	No	None	
23		No	None	0.351	-0.31	0.02	10	ambient	5	Yes, 1.5 ml	No	15	QuPPe solvent	Yes, addition of FA to MeOH	Centrifugation; Filtration	
134		No	None	0.351	-0.31	0.1	10	cold	5	No	No	5	ACN	No	None	
55	x	Yes	< 1 y	0.355	-0.26	0.01	10	deep frozen		No	No	2	ACN	No	Others; $MgSO_4$ClCitrate, Citric acid	
76		Yes	< 1 y	0.355	-0.26	0.01	10	just thawed	1	No	No	2	ACN	No	None	
83		Yes	> 2 y	0.363	-0.18	0.01	5	slightly frozen		No	No	3	ACN	No	None	
5		Yes	< 1 y	0.364	-0.17	0.01	25	deep frozen	1	No	No	2	ACN	No	None	
103		Yes	< 1 y	0.366	-0.15	0.02	15	cold	2	No	No	2	ACN; H_2OH_2O from sample	No	Dispersive-SPE (PSA/ $MgSO_4$)	
84		Yes	1 – 2 y	0.37	-0.11	0.01	25	ambient	> 30	No	No	2	MeOH	No	Centrifugation; Filtration	
27		Yes	1 – 2 y	0.38	0	0.02	10	deep frozen	10	No	No, 200 µl 5m NaOH	20	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)	
117	x	Yes	> 2 y	0.38	0	0.1	4	ambient	1	No	No	3	H_2O; ACN; Other; H_2O-ACN-TFA (300-700-0.8)	No	None	
31	x	Yes	< 1 y	0.383	0.03	0.01	10	slightly frozen	2	No	No	30	ACN	No	None	
81	x	No	< 1 y	0.39	0.11	0.1	10	cold	2	No	No	5	ACN	No	None	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	MM-ML	No	No	98 % (0.1 mg/kg)		1	QuEChERS - Acetate buffered (AOAC Official Method 2007.01), / Used in house potato blank for recovery.
	No	LC-MS/MS QQQ		MM-ML	No	No	100 % spiked samples	SB-EUPT	4	other, EURL (QAC) version 14.09.2012
	No	LC-MS/MS QQQ	Different Method, Transitions MS/MS	PS-ML	No	No	120 % Blank sample spiked with known concentration of analyte	SB-EUPT	2	other, www.eurl-pesticides-data-pool.eu
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	16 %	SB-EUPT	2	QuPPe-Method (EURL-SRM mth f. polar pesticides), 1% FA in MeOH
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	103 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-SL	No	No	91 % (0.1 mg/kg)	SB-EUPT	3	QuEChERS - Original Version (J. AOAC 86, 2003), QuEChERS extraction withou purification (CRL SRM method)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	88.6 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662), without cleanup / No
	No	LC-MS/MS QQQ		MM-SL	No	Yes-2	85.5 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, second MSMS transition	MM-ML	Yes, methomyl D3, carbendazim D4, pendimethalin D5	No	71 % (0.02 mg/kg)	SB-other	1	other, ACN extraction
	No	LC-MS/MS QQQ		MM-ML	No	No	112 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	101 %	SB-EUPT	2	other, MeOH-extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, TPP	No	95 % compound spiked			QuEChERS - Original Version (J. AOAC 86, 2003)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, Ion ratio	PS-ML	Yes, Tetrahexylammoniumbromide	Yes-5		SB-EUPT		other, Extraction with H_2O-ACN-TFA (300-700-0.8)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ, 326-186; 326- 58	MM-ML	No	No	83.5 % (0.5 mg/kg)	SB-EUPT	3	QuEChERS - Original Version (J. AOAC 86, 2003), extraction to ACN, no purifying, filter into vials, measurement LC MSMS
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	106.5 % (0.5 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration

4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

DDAC-C10

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup
21	x	Yes	1 – 2 y	0.397	0.18	0.05	10	slightly frozen	5	Yes, 2mL to 10g sample	No	2	ACN	No	Dessication with $MgSO_4$
43		Yes	< 1 y	0.405	0.26	0.01	10	ambient		No	No	1	ACN	No	Dessication with $MgSO_4$; PSA
96		Yes	< 1 y	0.407	0.28	0.01	10	ambient	1	No	No	2	ACN; 100%	No	None
7		Yes	1 – 2 y	0.408	0.29	0.01	10	just thawed	2	No	No	30	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$)
40	x	Yes	< 1 y	0.412	0.34	0.025	10	cold	1	No	No	1	ACN	No	Filtration
118	x	No	< 1 y	0.414	0.36	0.01	5	cold	15	No	No	1	Other; Other0.1% FA ACN; Saturated NaCl	No	None
42		Yes	< 1 y	0.424	0.46	0.01	10	just thawed	1	No	No	1	ACN	Yes, Citrate Buffered	Dessication with $MgSO_4$; Dispersive-SPE (PSA/ $MgSO_4$)
34		Yes	< 1 y	0.445	0.68	0.01	10	deep frozen	2	No	No	5	ACN	No	None
32		Yes	< 1 y	0.446	0.69	0.1	10	deep frozen	2	No	No	15	ACN	No	Filtration
8		Yes	1 – 2 y	0.454	0.78	0.01	10	just thawed	2	Yes, added to 10 g	No	15	ACN	Yes, Citrate Buffer pH 5.5	None
47		No	< 1 y	0.456	0.8	0.1	10	deep frozen		No	No	1	ACN	No	None
88		Yes	< 1 y	0.464	0.88	0.005	10	deep frozen	> 30	No	No	10	ACN; Othersolvent B: citrate buffer	Yes, extraction and partitioning	Centrifugation
73	x	Yes	< 1 y	0.465	0.89	0.01	12	ambient	5	No	No	30	ACN; QuPPe solvent	No	None
98		No	1 – 2 y	0.476	1.01	0.1	10	cold	20	No	No	20	ACN	No	Centrifugation
3		Yes	1 – 2 y	0.48	1.05	0.01	10	ambient	10	No	No	5	ACN; H_2O	No	None
136		No	< 1 y	0.499	1.25	0.01	10	just thawed		No	No	2	ACN	No	Centrifugation; Filtration; without PSA
59		Yes	1 – 2 y	0.537	1.65	0.1	2	ambient	10	Yes, 9.6 ml	No	10	ACN	No	None

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	No	103 % (0.1 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Quechers without PSA
	No	LC-MS/MS QQQ		MM-SL	No	No	103 % (0.30 mg/kg)	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	70 % (0.01 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662), Extraction and diluition
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	Std add. to extract aliquots	Yes, TPP	Yes-2		QC		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No	96 % (0.1 mg/kg)	SB-EUPT	1	other, QuEChERS without cleanup
	No	LC-Q-TOF		Std add. to sample portions	No	No	76 %	SB-EUPT	3	other, 0.1%FA/ACN extraction
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No				QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	88 % spikyng level	SB-EUPT	5	other, QuEChERS without cleanup
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, IL-target pesticide	Yes-3	111 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	Yes, Linuron-D6	No	75 % (0.3 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	No	No				other, QuEChERS 1 Step
	No	LC-MS/MS QQQ		MM-ML	Yes, Pirimicarb-D6, not for calculation	No	106 % (0.575 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662), / rel. standard deviation 1.3 % with 5 individuals
	No	LC-MS/MS QQQ	GC-MS/MS (QQQ)	MM-ML	No	No	90 %	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		PS-ML	No	No	106.0 % (0.1 mg/kg)	SB-EUPT	2	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Isoproturond8	Yes-1	89 %	SB-EUPT		QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		Std add. to sample portions	Yes, Nicarbazin	Yes-2	100 %	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, D6-BAJ C12	Yes-3	104 %	SB-EUPT	2	QuEChERS - Original Version (J. AOAC 86, 2003)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 7 (cont.) Methods used by the participating laboratories (ordered by z-scores)

DDAC-C10

Lab-Code SRM8-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Initial sample temperature	Soaking time [min]	Water addition	Hydrolysis / Cleavage	Extraction time [min]	Extraction- and/or partitioning solvents	pH-adj. during Extraction / Partitioning	Cleanup	
14		Yes	1 – 2 y	0.552	1.81	0.01	10	ambient	1	No	No	15	ACN	No	None	
89		Yes	< 1 y	0.616	2.48	0.01	10	ambient	1	No	No	1	ACN	No	Freezing-out	
30		Yes	1 – 2 y	0.617	2.49	0.01	4	ambient	5	No	No	5	ACN	No	Dispersive-SPE (PSA/ $MgSO_4$); Centrifugation	
122		Yes	< 1 y	0.707	3.44	0.01	2	cold	10	Yes	No	1	ACN; H_2O10ml ACN 9 ml H_2O	No	None	
25		Yes	< 1 y	0.74	3.79	0.05	10	deep frozen	2	No	No	2	ACN	Yes, according to NF EN 15662	None	
87		No	None	1.005	6.58	0.05	10	ambient		No	No	30	ACN	Yes, buffer-saltmixture	Freezing-out; Dispersive-SPE (PSA/ $MgSO_4$); multiple Centrifugation	

Abb. of solvent: ACN: acetonitrile; CyHn: cyclohexane; DCM:dichlormethan; FA: formic acid; EtOAc: ethyl acetate; HOAc: acetic acid; MeOH: methanol; PE: petroleum ether
1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection	Confirmation	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details / Comments
	No	LC-MS/MS QQQ		MM-ML	Yes, TPP	Yes-2	82 % Extraction recovery vs MMC	SB-EUPT	5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	No	95 %	QC	> 5	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	Yes, not for calculation, only to check extraction efficiency	No	100 % (0.4 mg/kg)	SB-EUPT	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	PS-ML	Yes, atrazine d5, chlorpyrifos-methyl d6, dimethoate	No	97 %	QC	4	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ	LC-MS/MS QQQ	MM-ML	No	No	99 %	QC	1	QuEChERS - Citrate buffered (EN 15662)
	No	LC-MS/MS QQQ		MM-ML	No	Yes-1	56.7 % (0.1 mg/kg)	SB-EUPT	3	QuEChERS - Citrate buffered (EN 15662)

3) Yes-1: using recovery figure (as indicated); Yes-2: Yes, aut. via standard add. to sample portions; Yes-3: Yes, aut. via isotope labelled ISTD; Yes 4: Yes, aut. via combination of 2) + 3); Yes-5: Yes, aut. via procedural calibration
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 8 Reported 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: No or inappropriate correction for recovery
J: Inappropriate storage or pre-treatment of sample
K: Transcription error
L: Cross contamination

Captan Assigned value: 1.010 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
96	-3.96 (FN)	yes	The Method for Captan and Folpet aren't validated because the GC-QQQ (EI) method is not OK, and the EUPT has confirmed this problem.	G
66	-3.96 (FN)	yes	detected but quantification was not possible due to failure of the calibration standards" as the reason for this FN.	E
133	7.29	no	due to degradation of the intermediate standard solution? Human error?	–

Cyromazine Assigned value: 0.102 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
119	-3.61 (FN)	no	Degradation of these compounds during melting up the sample was observed. As our result of cyromazine in EUPT-SRM7 was quite good, this small peak remained was not regardesd as a cyromazine peak. Maybe the method was also not very suitable altough recoveries of fortified samples were quite acceptable, even for cyromazine.	G, J
70	-2.29	yes	effect of matrix on the signals (Analysis was performed without using the internal standard, therefore matrix effect was not evaluated. Also the calibration curve was made in solvent but not in matrix)"	C

Dicofol Assigned value: 1.030 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
52	-3.19	no	No transcription or calculation error post review of original data. The matrix spike recovery for the analyte was within the acceptance criteria for the test method (82%). All other quality control checks in the sample batch were within QC specifications	
49	2.12	yes	During the injection step, a degradation product is formed. We knew that the ratio degradation product/dicofol is different in solvent and in matrix. Unfortunately these ratios were not the same in the PT sample and in the matrix match calibration. The degradation is the calibration is more pronounced than in the PT sample leading to an overestimation of the concentration.	C
11	3.30	no	No experience with these compounds in vegetables, maybe due to lack of isotopically labbled internal standards	C, D

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

Fenbutatin oxide Assigned value: 0.065 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
89	3.45	no	all steps controlled, no error source could be found.	–
12	4.49	(yes)	Extraction with acidified acetonitrile and extended extraction of 15 min was probably the reasons for our poor performance	
32	5.05	yes	short of time to verification the result via standard addition approach	C
52	21.85	yes	An inappropriate method was utilized to quantify fenbutatin oxide. ICP-MS method was used for screening; however, positive result of fenbutatin oxide was not confirmed by LC-MS/MS as the method is still in development.	G

Folpet Assignedvalue: 1.320 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
119	-2.84	no	Degradation of these compounds during melting up the sample was observed. Maybe the method was also not very suitable altough recoveries of fortified samples were quite acceptable, even for cyromazine.	G, J
104	3.78	yes	degradation of the calibration solution	E
133	4.73	no	due to degradation of the intermediate standard solution? Human error?	–

Glyphosate Assigned value: 0.340 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
98	-3.88		The glyphosate analysis was done by the QuPPe-method version 7. Using the Dionex IonPack AS-11 column and smaller ion concentration than the method recommended (because the citrate buffer pollute the MS). Unfortunately under these conditions the glyphosate compound was not detected in the test sample.	G
70	-2.38	yes	calculation error	F
31	2.81	yes	degradation of the calibration solution	E

Haloxyfop Assigned value: 0.508 mg/kg;				
LabCode	z-score	Source of error localized?	Reason / Remarks	
11	-2.26	yes	no analytical experience; due to improper cleanup step appyling PSA which interacts with acidic pesticides and partly removes them from the extracts.	D, G
110	-2.03	yes	due to improper cleanup step appyling PSA which interacts with acidic pesticides and partly removes them from the extracts.	G
12	2.21	(yes)	The extended extraction time of 15 min was probably the reasons for our poor performance	

Mepiquat Assigned value: 0.096 mg/kg				
LabCode	z-score	Source of error localized?	Reason / Remarks	
55	-3.04	yes	Error in calculation (correctly calculated = 0,099 mg/kg, z-score = 0,13)	F
126	2.83	(yes)	no analytical experience; using external matrix-matched calibration	D, 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: No or inappropriate correction for recovery
J: Inappropriate storage or pre-treatment of sample
K: Transcription error
L: Cross contamination

Fosetyl Assigned value: 0.798 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
8	3,81	yes	degradation of the calibration solution (several years old!)	E
25	5,67	yes	Low solubility in methanol used for preparation of stock solution and decomposition therein. Using water as solvent for preparation of stock solution led to a good results of 0.760 mg/kg	E

Glufosinate Assigned value: 0.271 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
32	2.27	yes	no experience with Glufosinate, not in our scope, no internal standard (Glufosinate D3) available in our laboratory	C, D

BAC-C12 Assigned value: 0.568 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
89	2.11	no	all steps controlled, no error source could be found.	–

DDAC-C12 Assigned value: 0.380 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
89	2,48	(no)	all steps controlled, no error source could be found.	–
25	3,79	yes	"Problem with calibration solution (With a new solution, our result is divided with a factor 2, near by the reference.)"	E
87	6,58	yes	Error in calculation	F

3rd Edition

Approved: January 2012

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-SANCO[1] by the four European Union Reference Laboratories (EURLs) for pesticide residues in food and feed. These EUPTs are directed at all National Reference Laboratories (NRLs) and Official Laboratories (OfLs) within the EU Member States. Laboratories outside of this EURL/NRL/OfL-Network[2] may be permitted to participate on a case-by-case basis after consultation with DG-SANCO.

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

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

NRLs are appointed by Member State based on the provisions of Regulation 882/2004/EC, whereas OfLs are laboratories that are actively involved in official controls following Article 26 of Regulation 396/2004/EC (e.g. by conducting pesticide residue analyses within the framework of national and/or EU-controlled programmes).

[1] DG-SANCO = 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

3rd Edition

Approved: January 2012

According to Article 28 (3) of Regulation 396/2005/EC[4], all laboratories analysing samples for the official control of pesticide residues shall participate in the European Union Proficiency Test(s) organised by the European Union. The aim of these EUPTs is to obtain information regarding the quality, accuracy and comparability of the pesticide residue data in food and feed sent to the European Union within the framework of the national control programmes and the co-ordinated multiannual community control programme[5]. Participating laboratories will be provided with an assessment of their analytical performance and the reliability of their data – compared to the other participating laboratories.

EUPT-Panel

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

An **Organising Team** is appointed from the EURL(s) in charge. This team is responsible for all administrative and technical matters concerning the organisation of the PT, e.g. PT-announcement; Test Item production; undertaking the homogeneity and stability tests; packing and shipment of Test Item, as well as the handling and first assessment of participants' results.

Approved by DG SANCO, expert scientists with long-term experience in pesticide residue analysis will be chosen as members of a joint **EUPT-Scientific Committee** (SC). This Committee is made up of the following two subgroups:

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

b) An **Advisory Group** (AG)

The SC's role is to help the organisers make decisions regarding the EUPT design: the selection of pesticides to be included in the Target Pesticide List (see below); the establishment of the Minimum Required Reporting Levels (MRRLs); the evaluation and statistical treatment of the results and the drafting of the protocol and final report. The

[4] 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.

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

Appendix 9. General EUPT Protocol (3rd Ed.)

QCG has the additional function of supervising the quality of the EUPT and to assist the EURL in confidential aspects such as the choice of the pesticides to be present in the Test Item and the concentration levels at which they should be present in the Test Item.

The EUPT-Organising Team and the EUPT-Scientific Committee (the AG and the QCG) together form the **EUPT-Panel**.

The present EUPT General Protocol was drafted by the EUPT-Panel and was approved by DG-SANCO.

EUPT Participants

All NRLs operating in the same area as the organising EURL are legally obliged to participate in EUPTs - as well as all OfLs whose scope overlaps with that of the EUPT. The four EURLs will be annually issuing and distributing via the EURL website, a joint list of all OfLs that shall participate in all EUPTs to be conducted within a given year. The "list of obliged labs" is to be considered as tentative as it will be only based on information submitted by OfLs concerning their commodity scope and status. The legal obligation of NRLs and OfLs to participate in EUPTs arises from:

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

If necessary the "list of obliged labs" will be updated within the same year to take account of any changes in the lab profiles.

NRLs are responsible for checking whether all relevant OfLs within their network are included in the list of obliged laboratories and whether the contact information is correct.

The NRLs should further make arrangements to urge all relevant OfLs within their network to participate in all EUPT relevant to them.

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

Any OfL not intending to participate in a given EUPT will have to explain to the EURL its reasons for non-participation without prejudice of any legal action taken against it for not

participating. This also applies to initially participating laboratories that do not deliver results.

Official labs from EFTA countries and EU-candidate countries are also welcome to participate in the EUPTs. In special cases, the Organisers, upon consultation with DG-SANCO, will also allow laboratories outside of the EURL/NRL/OfL-Network to participate in EUPTs.

Confidentiality

The proprietor of all EUPT data is DG-SANCO and thus has access to all information.

In each EUPT, the laboratories are given a unique code, initially only known to themselves and the Organisers. In the final EUPT-Report, the list of participating laboratories will not be linked to their laboratory codes. It should be noted that the organisers, at the request of DG-SANCO, may present the EUPT-results to the Standing Committee on the Food Chain and Animal Health on a country-by-country basis. It is therefore possible that a link between codes and laboratories could be made, especially for those countries where only one laboratory has participated.

As laid down in Regulation 882/2004, NRLs are responsible for evaluating and improving their own OfL network. For this reason, the EURLs will provide the OfL laboratory codes to their NRLs together with the final report. This will allow NRLs to correlate the laboratories within their network and their performance. Furthermore, the EURLs reserve the right to share EUPT results and codes among themselves: for example, for the purpose of evaluating overall lab performance as requested by DG-SANCO.

Communication

The official language used in all EUPTs is English.

Communication between participating laboratories during the test on matters concerning this PT exercise is not permitted.

Announcement / Invitation Letter

The announcement of the individual EUPT will be issued at least 3 months before the Test Item is distributed to the laboratories. The announcement will be published on the EURL portal and additionally distributed via e-mail to the NRL/OfL mailing list available to the EURLs. The announcement will contain an invitation letter, details on how to register and where to find additionally-related documents, as well as some preliminary information on the specific protocol such as the tentative calendar, the name of the commodity expected to be used, and the tentative Target Pesticide List.

Target Pesticide List

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

In some cases, that will be clearly marked, results calculated according to the pesticide residue definition may be requested with those residue definitions differing from the legal ones in certain cases.

Specific Protocol

For each EUPT a Specific Protocol will be published at least 2 weeks before the Test Item is distributed to the laboratories. This protocol will contain all the information previously included in the Invitation Letter but in its final version, in addition to information on payment for delivery service and/or participation. It will furthermore include instructions on how to handle the Test Item upon receipt, on how to submit results, and any other relevant information.

General procedures for reporting results

Laboratories are responsible for reporting their results to the Organiser within the stipulated deadlines. Any pesticide that was targeted by a participating laboratory should be reported as "analysed". Each laboratory must report only one result for each of the analytes detected in the Test Items, using the analytical procedure(s) that they

would routinely use for each compound for monitoring purposes. The residue levels of the pesticides detected should be expressed in mg/kg and in some cases for products of animal origin in µg/kg fat.

One Test Item is intentionally treated with pesticides and one is not. Both Test Items have to be analysed by the laboratories and any pesticide detected in them shall be reported.

Correction of results for recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed, (Document SANCO), 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 with good precision), therefore, if residue data are adjusted for recovery, then this must be indicated on the specific field of the 'reporting result form'. Laboratories are required to report whether their results were adjusted for recovery and, if this was the case, the recovery (as percentage) used should be also reported. No recovery data are required where correction for recovery results automatically from using the 'standard addition(s)' 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 calculation technique used for the results instead of the recovery data.

Methodology information

All laboratories are requested to provide information on the analytical method(s) they have used. 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.

Results evaluation

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

– ***False Positives***

These are results reported above the MRRLs that suggest the presence of pesticides that were listed in the Target Pesticide List, but which 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 pesticide. However, in certain instances, case-by-case decisions by the EUPT-Panel may be necessary.

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

– ***False Negatives***

These are results for pesticides reported by the laboratories as "analysed" but without reporting numerical values although they were used by the Organiser to treat the Test Item and were detected by the Organiser and the majority of the participants that had targeted these specific pesticides, at or above the MRRL. Results reported as <RL (RL= Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives. However, 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 not be assigned as this is not statistically justifiable.

– ***Estimation of the true concentration (μ)***

The "true" concentration (assigned value) will be typically estimated using the median of all the results. In special justifiable cases, the EUPT-Panel may decide to use only part of the population of results to establish the median (e.g. only results with z-scores ≤ 5.0, or by excluding results generated by a method that demonstrably generates significantly biased results, e.g. due to incomplete extraction).

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Approved: January 2012

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

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

$$\delta = b_i * \mu_i \qquad \text{with } b_i = 0.25 \text{ (25\% FFP-RSD)}$$

The percentage FFP-RSD is set at 25% based on experience from previous EUPTs[6]. 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.

– ***z-scores***

This parameter is calculated using the following formula:

$$z_i = (x_i - \mu_i) / \delta_i$$

Where: x_i is the value reported by the laboratory, μ_i the assigned value, and δ_i the standard deviation at that level for each pesticide (i).

Any z-scores of > 5 will be reported as >5 and where combined z-scores are calculated a value of "5" will be used.

z-Scores will be interpreted in the following way:

$\|z\| \leq 2$	Acceptable
$2 < \|z\| \leq 3$	Questionable
$\|z\| > 3$	Unacceptable

[6] 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.

For results that are considered to be 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 consider whether, or not, these values should appear in the z-score histograms.

z-Scores will not be calculated for any false positive result.

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

The EUPT-Panel will decide whether to classify the laboratories into two groups - A or B. Laboratories that detect 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 will 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 Sample (N)	90%	No. of Pesticides needed to be detected 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	
15	13.5	13	N - 2
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	
20	18.0	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	

For evaluation of the overall performance of laboratories within Category A, the Average of the Squared z-Score (AZ^2)[7,8] will be used.

Laboratories within Category B will be ranked according to the total number of pesticides present in the sample. The number of acceptable z-scores achieved will be presented too. The EURL-Panel retains the right to calculate combined z-scores (see below) also for Category B labs, e.g. for informative purposes, provided that a minimum number of results (z-scores) is available.

– ***Combined z-scores***

For evaluation of the overall performance, the Average of the Squared z-Score (AZ^2) will be used. The AZ^2 is calculated as follows:

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

This formula multiplies each z-score by itself and not by an arbitrary number. Based on the AZ^2 achieved, the laboratories are classified as follows:

Formula	Good	Satisfactory	Unsatisfactory
AZ^2	≤ 2	$2 < AZ^2 \leq 3$	$AZ^2 > 3$

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. In the case of EUPT-SRMs, where only few results per lab are available,

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

[8] 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.

the Average of the Absolute z-scores (AAZ) will be calculated for informative purposes, but only for labs within Category A and as long as 5 or more z-scores are available.

Publication of results

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

The Final 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 to discuss the results of all EUPTs organised annually by the EURLs in the running year, the final report may be published up to 8 months after the deadline for results submission.

Certificates of participation

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

Feedback

After the distribution of the final report of an EUPT, participating laboratories will be given the opportunity to give their feedback to the Organiser and make suggestions for future improvements.

Follow-up activities

Laboratories are expected to undertake follow-up activities to trace back to the source of any erroneous or (strongly) deviating results - including all false positives and false negatives, along with results with |z|>2.

Upon request, the laboratory's corresponding NRL, or EURL, are to be informed of the outcome of these traceability activities.

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3rd Edition

Approved: January 2012

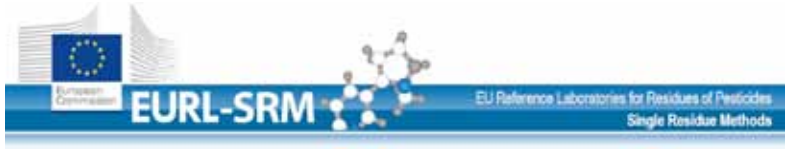
According to instructions by DG-SANCO, the "Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with EU Reference Laboratories (EURLs) activities" will be followed for NRLs.

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.

Laboratory Rights

After the Final Report has been sent, the laboratories will have the right to communicate the nonconformity of their result evaluation in written form. Any detected errors in the preliminary report should also be reported to the Organiser. The Organiser, assisted by the Scientific Committee, will decide upon any re-evaluation and will give a corresponding explanation.



SPECIFIC PROTOCOL

for the 8th EU Proficiency Test on Pesticides requiring Single Residue Methods
EUPT – SRM8 (2013)
(last updated: 02.04.2013)

Introduction

This protocol is complementary to the **"General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed"** covering all EUPTs.
The EUPT-SRM8 is organised by the EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL–SRM) and deals with the analysis of SRM-pesticides in potato homogenate. This EUPT is to be performed by all National Reference Laboratories for Single Residue Methods (NRL-SRMs) as well as by all official EU laboratories (OLs) involved in official pesticide residue controls as far as their scope overlaps with that of the EUPT-SRM8. The commodity "potatoes" is considered to represent commodities with high water content (see **SANCO document 12495/2011**). Considering only the commodity scope (not the pesticide scope) a **Tentative List of obliged labs for EUPTs in 2013** has been prepared by the EURLs and published on the CIRCA-Platform. Labs listed as "Obliged to participate in the EUPT-SRM8" that have decided not to participate, for whatever reasons, were requested to state their reasons in a special online form.

Test Item and Blank Material

This EUPT deals with the analysis of pesticide residues in **potato homogenate**.

Participants will receive two bottles containing:

1) ca. 350 g **Test Item (spiked)**, containing pesticides from the **Target Pesticide 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

Using randomly chosen bottles, the Organizers will check the Test Item for sufficient homogeneity and for the stability of the pesticides over the period of the exercise. The Blank Material will be also checked to prove that none of the pesticides of the Target pesticides List is contained at relevant levels. All these tests will be conducted by the EURL-SRM that is ISO 17025 accredited.

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

Analytical parameters

The Test Item contains several pesticides from the **Target Pesticide List.** Laboratories should read the Target Pesticides List carefully, as it contains the residue definition valid for the PT as well as the **Minimum Required Reporting Levels (MRRLs)**. For practical reasons, the residue definitions in the Target Pesticides List do not always fully match with the legal ones.

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 on potatoes are present in the Test Item.

Shipment of Test Item

Test item and Blank Material are planned to be shipped on 15 April, 2013.
Frozen Test Item and Blank Material will be packed in thermo-boxes together with dry ice and shipped to the participants. The organisers will aim to ensure that all participating laboratories will receive their shipments on the same day.
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.

Instructions on handling the Test Item

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

Before portions are taken for analysis the Test Item should be mixed thoroughly in its entirety. During mixing, try to keep temperatures low (e.g. frozen or semi-frozen condition) to avoid degradation of susceptible pesticides. To avoid frequent thawing of the test item it is further suggested to prepare all analytical portions that you intend to use for all EUPT-related experiments.

All participants should use their own routine standard operating procedures for extraction, clean-up and analytical measurement as well as their own reference standards for identification and quantification purposes. Considering that the amount of Test Item that the Organizers can provide is limited, laboratories are advised to consider scaling down their analytical procedures to avoid shortage of Test Item.

The homogeneity tests will be conducted using 10 g analytical portions of Test Item for all analytes. Sufficient homogeneity can only be guaranteed for sample portions ≥10g. Please note that sub-sampling variability increases with decreasing analytical portion size.

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Website: www.eurl-pesticides.eu, E-Mail: EURL-SRM@cvuas.bwl.de

Appendix 10. Specific Protocol of EUPT-SRM8

Results submission website

Sample receipt acknowledgement, analytical results and method information are to be submitted via the following website: **EUPT-SRM8 Result Submission Website** (**http://thor.dfvf.dk/eupt-srm8**).
Sub-page 0 (Sample receipt acknowledgement) will be accessible from 16 April 2013 and Sub-pages 1-3 (analytical results and method information) from 22 April till 17 May 2013.

This website also contains a link to specific instructions on how to enter the required data in the various submission forms (sub-pages).

To access the data submission forms participants must use their unique login data (username and password) provided to them with the confirmation e-mails sent upon registration.

The deadline for result submission is 17 May 2013 at 14.00 h CET.

- Sample Receipt and Acceptance (Sub-Page 0)

Once the laboratory has received the Test Items it must report to the organiser, via the **EUPT-SRM8 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 19 April 2013. If a laboratory does not respond by this deadline, the Organisers will assume that the Test Items have been received and accepted. If any participants have not received the Test Items by the 19 April at noon, they must inform the Organiser immediately by e-mail (**EURL-SRM@cvuas.bwl.de**), so that a new shipment can be initiated.

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

To report their results, laboratories must access the **EUPT-SRM8 Result Submission Website**.

All results must be reported on the above website by 17 May 2013 at 14:00 h CET. The website will not be accessible after this deadline and all results submitted afterwards will not be included in the statistical treatment or in the final report.

Before entering the results, please study the **Target Pesticides List** carefully. The residue definitions 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 normal 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" 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 (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.

- **"Is your result recovery-corrected?":** Please specify, via dropdown-menu, whether the reported result was recovery-corrected and the recovery-correction approach used.

- **"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 for recovery, the recovery figure (in %) used for the calculation MUST be reported.

Additional information on how each recovery figure was derived will be asked in separate fields.

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

In **sub-page 3 within of** the "**EUPT-SRM8 Result Submission Website"** the participating laboratories must provide information on the analytical method(s) applied to the all pesticides which were analysed, irrespective if they were detected or not.

The laboratories are urged to thoroughly fill-in this important information in order to minimize the administrative burden of collecting this information 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 will be subcontracted to other partners:

a) Preparation of Test Item and Blank Material (to EURL-FV, Almería/Valencia, Spain)

b) The administration of **EUPT-SRM8 Result Submission Website** (to EURL-CF, Soeborg, Denmark)

Follow-up actions

After the distribution of the Preliminary EUPT-Report laboratories with poor performance (high z-scores, false negatives or false positives) will be asked to provide information concerning the reasons for poor performance and possible corrective actions. The EUPT-SRM8-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 relating to EUPT–SRM8 can be found in the **EURL-Document Repository (CIRCA/FIS-VL)**.
Links to the documents can be found in the **EUPT-SRM8 Website**.
For further information please contact the organizers **EURL-SRM@cvuas.bwl.de**

Participation fees and payment details

To cover the costs of production, handling and shipment of the Test Materials the following participation fees will be charged to the participating laboratories:

- OLs (including NRLs) from EU countries, EU-candidate countries and EFTA countries: 175 €
- Labs based in third countries: 250 €

All laboratories that have been accepted to participate will be sent an invoice to the "invoice address" stated in the registration form.

Payment is expected to be made prior to the scheduled shipment date. **If for any reason payment cannot be carried out before shipment, 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 proceed with sample shipment.**
Details of payment will be given in the invoices.

To facilitate tracking of money transfer mind to include your special payee identification text (= invoice number) as shown in the invoice.

Bank Details:

Bank account holder:	**CVUA Stuttgart**
Bank Name :	**Baden Wuerttembergische Bank**
IBAN:	**DE 72 6005 0101 7469 5341 03**
BIC/SWIFT:	**SOLADEST**
Payee identification text:	**See invoice (VERY IMPORTANT!)**
VAT of CVUA Stuttgart	**DE 811 600 510**

Calendar of EUPT-SRM8

(see also **http://www.crl-pesticides.eu/library/docs/srm/EUPT_SRM8_Calendar.pdf**)

Target Pesticides List of EUPT-SRM8

(see also **http://www.eurl-pesticides.eu/library/docs/srm/EUPT_SRM8_TargetPesticideList.pdf**)

Contact information

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Dr. Miguel Gamón	Pesticide Residue Laboratory, Valencia, ES
Dr. Magnus Jezussek	Bavarian Health and Food Safety Authority (LGL), Erlangen, DE
Ralf Lippold	CVUA, Freiburg, DE
Dr. André de Kok	Food and Consumer Product Safety Authority, Amsterdam, NL
Dr. Sonja Masselter	Austrian Agency for Health and Food Safety, Innsbruck, AT
Dr. Tuija Pihlström	National Food Agency of Sweden, Uppsala, SE
Dr. Mette E. Poulsen	National Food Institute, DTU, Soeborg , DK
Dr. Darinka Stajnbaher	Institute of Public Health, Maribor, SI

Quality Control Group

Prof. Antonio Valverde	University of Almería, ES
Stewart Reynolds	Food and Environmental Research Agency, York, UK

CALENDAR for the EUPT – SRM8

(last update 02.04.2013)

Activity	Who ?	Dates
Opening of the **EUPT-SRM8 Website** with links to all relevant documents and to the **EUPT-General Protocol**	EURL-SRM	Jan. 2013
Dispatch of "**Calendar**"	EURL-SRM	Jan. 2013
Dispatch of "**Target Pesticides List**",	EURL-SRM	Jan. 2013
Dispatch "**Announcement/Invitation-Letter**"	EURL-SRM	Jan. 2013
Registration (use "**EUPT-Registration Website**") (Note: obliged OLs MUST enter this Website and either register or give **explanations for non-participation**) Labs from **THIRD COUNTRIES** please contact us by 12 March for further instructions. (**eurl-srm@cvuas.bwl.de**)	**- Obliged OLs from EU-MSs** **- OLs from EFTA Countries** **- OLs from EU-candidate C.** **- Third country Labs**	**18 Feb. – 12 Mar. 2013**
Dispatch of **EUPT-SRM8-Specific Protocol**	EURL-SRM	Apr. 2013
Preparation of EUPT-SRM8-Test Item (preliminary tests Spiking / Homogenization)	EURL-FV / –SRM in collaboration	Feb. 2012 – Mar. 2013
Homogeneity tests	EURL-SRM	Mar.-Apr. 2013
Stability tests	EURL-SRM	Apr.-May 2013
Shipment of EUPT-SRM8 Test Item (+reminder of upcoming parcel arrival)	EURL-SRM	**15 Apr. 2013**
Confirmation of sample Receipt and acceptance via "**EUPT-SRM8 Result Submission Website**", (sub-page 0)	**Participating Labs**	**within 48 h of receipt**
Result Submission (Pesticide scope, Results, Method Info) in "**EUPT-SRM8 Result Submission Website**", (sub-pages 1 – 3)	**Participating Labs**	**22 Apr.-17 May 2013, (14:00 h CET),** NO DEADLINE EXTENSION!
Preliminary Report (only compilation of results)	EURL-SRM	June 2013
Survey to collect reasons for underperformance	EURL-SRM / **Participating Labs**	June 2013
EUPT Evaluation Meeting	EUPT-SC, DG-SANCO	26-28 June 2013
Final Report	EURL-SRM	Nov. 2013

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)
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TARGET PESTICIDE LIST

for the EUPT – SRM8 2013
(last update on 02.04.2013)

Compounds Potentially Present in Test Item	In MACP 2013 for FV	MRRL (mg/kg)
1) Compulsory Compounds (will be considered in Category A/B classification)		
2.4-D (free acid)	**Yes**	0.01
Captan	**Yes**	0.01
Chlormequat (cation)	**Yes**	0.01
Chlorothalonil	**Yes**	0.01
Cyromazine	**Yes**	0.01
Dicofol (p,p´ isomer)	**Yes**	0.01
Ethephon	**Yes**	0.02
Fenbutatin oxide	**Yes**	0.01
Fluazifop (free acid)	**Yes**	0.01
Folpet	**Yes**	0.01
Glyphosate	**Yes**	0.05
Haloxyfop (free acid)	**Yes**	0.01
Mepiquat (cation)	**Yes**	0.01
2) Optional Compounds (will NOT be considered in Category A/B classification)		
Diquat (dication)	No	0.02
Fentin (expressed as triphenyltin cation)	No	0.01
Fosetyl aluminium (expressed as fosetyl)	No	0.05
Glufosinate (parent only)	No	0.05
Maleic hydrazide	No	0.05
BAC-C10 (expressed as chloride salt)	**Adhoc program**	0.1
BAC-C12 (expressed as chloride salt)	**Adhoc program**	0.1
BAC-C14 (expressed as chloride salt)	**Adhoc program**	0.1
BAC-C16 (expressed as chloride salt)	**Adhoc program**	0.1
DDAC-C10 (expressed as chloride salt)	**Adhoc program**	0.1

MACP= EU Multi-Annual Coordinated Control Program

Notes:

- For analytical and practical reasons the residue definitions applying in this EUPT do not always correspond to those in the legislation.
- 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-SRM8 Team

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