European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

EU Proficiency Test on the Analysis of Spiked Pesticides Requiring Single Residue Methods in Cow's Milk

EUPT–SRM9

April/May 2014

Final Report

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EU PROFICIENCY TEST
EUPT-SRM9, 2014

Residues of Pesticides Requiring Single Residue Methods

Test Item:

Whole Cow's Milk

Final Report

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April/May 2014

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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 9 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 and three further 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 Test Items. The remaining two EUPTs, namely the EUPT-SRM7 (2012) based on milled dry lentils and the EUPT-SRM9 (2014) based on cow's milk were organized by the EURL-SRM unilaterally. The EUPT-SRM9 was the first one in which a commodity of animal origin was used.

Participation in the respective EUPTs is mandatory for all NRLs for pesticides requiring Single Residue Methods (NRL-SRMs) and for all OfLs analysing pesticide residues in commodities represented by the respective commodity used as Test Item within the framework of national and EU official control programmes. Laboratories in EU member States analysing pesticide residues within the frame of import controls according to Reg. 669/2009/EC are also considered as performing official controls in the sense of Reg. 882/2005/EC and are thus also obliged to take part in EUPTs. 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 (FYROM, Montenegro, Serbia and Turkey) are also invited to take part. 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-SRM9, was published at the beginning of 2014. The pesticide scope of those labs could not be considered since the data available in the EUPT-DataPool was not always 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 has full access to all data of EUPTs including the lab-code/lab-name key. The same applies to all NRLs as far as laboratories belonging to their own country networks are concerned. Results for this EUPT, or a series of EUPTs, evaluated on a country by country basis, may be further presented to the European Commission Standing Committee for Animal Health and the Food Chain or during EURL-Workshops.

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

CONTENT

7. APPENDICES A-1

EUPT-SRM9 - Supplementary Information on Analytical Methods

http://www.eurl-pesticides.eu/library/docs/srm/EUPT-SRM9_Supplementary_Information.pdf

European Commission –
EU-Proficiency Test on Residues of Pesticides
Requiring Single Residue Methods
Test Item: Whole Cow's Milk
EUPT-SRM9, 2014

INTRODUCTION

On 30 January, 2014 all relevant National Reference Laboratories (NRLs) of the 27 EU-Member States (MS), as well as all relevant EU-Official Laboratories (OfLs) whose contact details were available to the Organisers (EURL-SRM), were invited to participate in the 9th European Commission's Proficiency Test Requiring Single Residue Methods (EUPT-SRM9). The EUPT-SRM9-Website contained links to the Announcement/Invitation letter, the Calendar of the EUPT-SRM9, as well as to the Target Pesticides List (**Appendix 9** and **Appendix 10**). The Target Pesticides List contained 19 compounds potentially being present in the Test Item and requiring single residue methods for their analysis. 12 of them were compulsory compounds and were thus considered in Category A/B classification (based on scope). The compounds of the Target Pesticides List were selected based on a number of criteria and following consultation with the EUPT-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 latest version of the "General Protocol", containing information common to all EUPTs, and to the "Specific Protocol", valid for the current PT, was also provided. The laboratories were able to register on-line from 25 February to 12 March, 2013.

Based on their commodity scope (food of animal origin) and their NRL-status (NRL-SRMs) a tentative list of the laboratories considered as being obliged to participate in the EUPT-SRM9 was published on the EURL-Website as well as on the CIRCA-platform. To ensure that all relevant official laboratories were informed about this EUPT, the NRLs were asked to forward the invitation to all relevant official laboratories within their countries. It was made clear that the list of obliged laboratories prepared by the EURLs was only tentative and the real obligation to participate was based on Reg. 396/2005 and Reg. 882/2004 EC. Obliged labs that did not intend to participate were asked to provide an explanation.

In total 62 laboratories from EU and EFTA countries agreed to participate in the test with 1 of them failing to submit results. 5 laboratories from EU candidate countries and third countries have also registered for the present EUPT, and all of them have submitted results.

To prepare the Test Item, UHT cow's milk from organic farming of German origin was purchased at a local supermarket. The milk was first checked for the absence of the compounds from the Target Pesticides List and then spiked with 14 compounds (2,4-D, BAC-C12, BAC-C14, chlormequat, DDAC-C10, fluazifop, maleic hydrazide, mepiquat, 4-OH-chlorothalonil, chlorate, cyromazine, melamine, perchlorate and trimethyl-sulfonium (trimesium)) using standard solutions. More details are given in 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 target analytes contained in the Test Item as well as the absence of target analytes in the Blank Material are summarized in **Table 1-1**. For more details on the 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	Determinative analysis		Notes
4-OH-chlorothalonil	**Modified QuEChERS-method** [3] involving: addition of water (1.2 g to 10 g milk) and internal standard, liquid-liquid partitioning following addition of citrate buffer salts and cleanup via freeze-out and filtration).	**Nicarbazine**	**LC-MS/MS**	**ESI (neg)**	
2,4-D		**Nicarbazine / 2,4-D D_3**	**LC-MS/MS**	**ESI (neg)**	
BAC-C12		**BAC-C12 D_6**	**LC-MS/MS**	**ESI (pos)**	
BAC-C14		**BAC 14 D_7**	**LC-MS/MS**	**ESI (pos)**	
DDAC-C10		**DDAC-C10 D_6**	**LC-MS/MS**	**ESI (pos)**	
Fluazifop		**Nicarbazine**	**LC-MS/MS**	**ESI (neg)**	
*BAC-C10**		*BAC-C10 D_7*	*LC-MS/MS*	*ESI (pos)*	
*BAC-C16**		*Chlorpyriphos D_{10}*	*LC-MS/MS*	*ESI (pos)*	
*Glyphosate**		*Glyphosate $^{13}C_2$,^{15}N*	*LC-MS/MS*	*ESI (neg)*	
*Haloxyfop**		*Nicarbazine*	*LC-MS/MS*	*ESI (neg)*	
Chlorate	**QuPPe-AO method** [5] involving: addition of water (1.2 g to 10 g milk) and ILISs, addition of methanol containing 1 % formic acid, shaking, centrifugation, dilution of extract 1:1 with ACN and dSPE-cleanup with C18 sorbent, centrifugation, filtration and direct determination by LC-MS/MS in the ESI (neg) + ESI (pos) mode.	**Chlorate $^{18}O_3$**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
Chlormequat		**Chlormequat D_4**	**LC-MS/MS**	**ESI (pos)**	**QuPPE M4**
Cyromazine		**Cyromazine D_4**	**LC-MS/MS**	**ESI (pos)**	**QuPPE M4**
Maleic hydrazide		**Maleic hydrazide D_2**	**LC-MS/MS**	**ESI (neg)**	**QuPPE M1.3**
Melamine		**Melamine triamine $^{15}N_3$**	**LC-MS/MS**	**ESI (pos)**	**QuPPe M4**
Mepiquat		**Mepiquat D_3**	**LC-MS/MS**	**ESI (pos)**	**QuPPE M4**
Perchlorate		**Perchlorate $^{18}O_4$**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
Trimesium		**Trimesium D_9**	**LC-MS/MS**	**ESI (pos)**	**QuPPE M4**
*Cyanuric acid**		*Cyanuric acid $^{13}C_3$*	*LC-MS/MS*	*ESI (neg)*	*QuPPe M1.3*

* : To check for absence in Blank Material

1.2 Selection of the commodity for the PT and the compounds for the Target Pesticides List

Following a request by DG-SANCO to conduct an EUPT-SRM on a commodity of animal origin three possible commodities were taken into consideration (milk, eggs and honey). Following a brief check on the relevance of SRM-pesticides in these three commodities, milk was considered being of highest interest followed by eggs, whereas honey was directly excluded due to the very small number of relevant SRM-pesticides. An exploratory survey was conducted in order to find out if milk would be a suitable commodity for the EUPT-SRM9 and which of the 15 preselected relevant pesticides would be of interest to the potential participants. A minimum number of interested laboratories were considered essential for an acceptable statistical evaluation and certainty of the assigned values. The survey was launched on 10 December, 2013 and was directed to all NRL-SRMs as well as all OfLs analysing for pesticides in food of animal origin. The laboratories were asked to indicate if they would participate in an EUPT-SRM with milk as commodity and if yes, which of the 15 preselected compounds they would foreseeable cover. They were also asked if there is any additional SRM-analytes that would be of interest for them in connection with milk. 50 of total 111 respondents indicated their intention to participate in a EUPT-SRM with milk as commodity. For 10 out of the 15 chosen potential target compounds there were more than 15 laboratories expressing interest of analysis. Based on this data the Organisers considered cow's milk as a suitable commodity for the EUPT-SRM9.

The compounds to be included in the Target Pesticides List (**Appendix 10**) were selected by the Organiser and the EUPT-Scientific Committee (Advisory Group and Quality Control Group) taking the following points into account: 1) the present and upcoming scope of the EU-coordinated control programme; 2) a pesticide priority list ranking the pesticides according to their risk potential; 3) the relevance of pesticides to the specific commodity (milk); 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) OfLs' needs or intentions as expressed via surveys or e-mail communications. Perchlorate, actually a contaminant, was selected following a request by labs as this compound is typically analyzed together with the pesticide chlorate. Both melamine and cyanuric acid are metabolites of cyromazine. Furthermore, melamine is formed in fertilizers by trimerization of cyanamide, and cyanuric acid is also formed from trichloroisocyanurate and dichloroisocyanurate which are added into chlorinated water to retard chlorine depleting. In the general context of the discussions on chlorination at that time, it was deemed appropriate to draw the attention to this compound.

The minimum required reporting levels (MRRLs) were set at 0.01 mg/kg for fluazifop, haloxyfop, 4-OH-chlorothalonil and cyromazine; at 0.02 mg/kg for 2,4-D, BAC-C10, BAC-C12, BAC-C14, BAC-C16, chlormequat, DDAC-C10 and mepiquat; and at 0.05 mg/kg for glyphosate, cyanuric acid, melamine and trimesium.

1.3 Preparation and bottling of the Blank Material

60 litres of UHT whole cow's milk of organic farming packaged in 1 litre packages and belonging to the same batch were purchased at a local supermarket for the purposes the EUPT-SRM9. The milk was checked by the EURL-SRM for the absence of any compounds included in the Target Pesticides List. 6 litres were used to clean the mixer and the containers in order to avoid any potential cross-contaminations. These 6 litres were disposed. From each remaining package roughly half was used for the preparation of the Blank Material, and the other half for the preparation of the Test Item. The total amount of milk for the Blank Material (approx. 27 litres) was placed in a 50 litre container and 150 ml of a solvent mixture were slowly added while gently stirring with a Silverson mixer. The solvent mixture consisted of 32.5 ml acetonitrile, 62.5 ml methanol and 55 ml water and corresponded both in volume and composition to the spiking solution (see below). Following the addition of the solvent the mixture was gently stirred for 30 min to ensure homogeneity. Approximately 350 g portions of the well-mixed blank milk 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.

Table 1-2: Composition of the spiking solution (of 150 ml) used in its entirety to prepare the Test Item.

Stock solution 1 µg/ml in acetonitrile		Stock solution 1 µg/ml in methanol		Purified water
Compound	Volume [ml]	Compound	Volume [ml]	Volume [ml]
2,4-D	2.5	Maleic hydrazide	10	55
Fluazifop	5	Chlorate	5	
4-OH-chlorothalonil	2.5	Perchlorate	5	
BAC-C12	7.5	Chlormequat	5	
BAC-C14	7.5	Mepiquat	10	
DDAC-C10	7.5	Cyromazine	7.5	
		Melamine	10	
		Trimesium	10	

1.4 Preparation and bottling of Test Item

Before preparing the Test Item, the target analytes and their suitable, approximate target residue levels for the study were selected by the Organiser in coordination with the EUPT-QC-Group. The Test Item was prepared exactly the same way as the Blank Material described above, but instead of adding 150 ml of pure solvent mixture 150 ml of an equally composed mixture containing the target analytes was added. The mixture contained 14 different compounds and was prepared as described in **Table 1-2**. Approximately 350 g portions of the well-mixed milk containing target analytes 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.

1.5 Packaging and delivery of PT Materials to Participants

On the day of shipment two frozen bottles, one with Test Item and the other one with Blank Material, as well as a bottle containing 1 ml of a solution of ILISs of chlorate and perchlorate were packed into thermo-insulated polystyrene boxes, filled-up with dry ice pellets (approx. 2 kg in each box) and shipped by DHL-Express to the laboratories. Where the dry ice transport, due to IATA regulations, was not allowed, bigger and thick-walled thermo-insulated polystyrene boxes were used. The materials were packed together with sufficient cooling elements, and the whole packages were deep frozen at –80°C for two days until shortly before shipment.

Among the 69 shipments to destinations within Europe 57 packages arrived at the participating labs within 24 hours and 8 packages within 48 hours. Due to the holiday on 1 May, 2014 or remote location of some laboratories the remaining 4 packages arrived to the participants within 4 days. In theses cases two participants asked for renewed shipment because of unsatisfactory situation of the packages on arrival. In both cases the second shipment arrived to its destination within 48 hours. The other two delivery units were accepted. The delivery to countries outside the EU and EFTA zones was accomplished within 48 hours in 2 cases, within 72 hours in 1 case, and within 4 days in one case. Details on the shipments and the condition of the Test Items upon arrival are shown in **Appendix 2**.

The participating laboratories were asked to give detailed information on the condition of the EUPT materials upon receipt, and 43 of them gave feedback. 34 of those laboratories that had received their packages within 24 hours with the materials being still embedded in dry ice and deep frozen. Six laboratories receiving the packages within 48 hours reported that there was no dry ice left but the material was in all

cases either still frozen or had a temperature below 4 °C. Even in one case where the shipment took more than 4 days the material was totally defrosted at arrival, but still at about 4 °C. The results submitted by this particular lab did not show any signs of significant losses. 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, even those sent without dry ice.

1.6 Homogeneity test

A week before material shipment 10 bottles containing Test Items were randomly chosen for the homogeneity test. The analyses were performed on two analytical portions taken from each bottle. Before the analytical portions were taken, the entire content of each bottle was thawed at approximately 0 – 2 °C and remixed manually. 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 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 evaluations of the homogeneity test is shown in **Table 1-3**. The individual residue data from the homogeneity test is given in **Appendix 3**.

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

COMPULSORY COMPOUNDS								
	2,4-D	BAC-C12	BAC-C14	Chlormequat	DDAC-C10	Fluazifop	Maleic hydrazide	Mepiquat
Analytical portion size [g]	10	10	10	10	10	10	10	10
Mean [mg/kg]	0.086	0.276	0.282	0.176	0.279	0.180	0.357	0.346
s_{sam}^2	4.13×10^{-5}	3.94×10^{-4}	1.15×10^{-4}	1.75×10^{-4}	2.25×10^{-4}	1.81×10^{-4}	1.88×10^{-4}	6.73×10^{-4}
c	1.54×10^{-4}	1.56×10^{-3}	1.61×10^{-3}	4.05×10^{-4}	1.74×10^{-3}	7.02×10^{-4}	7.18×10^{-3}	1.89×10^{-3}
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed
OPTIONAL COMPOUNDS								
	4-OH-chlorothalonil	Chlorate	Cyromazine	Melamine	Perchlorate	Trimesium		
Analytical portion size [g]	10	10	10	10	10	10		
Mean [mg/kg]	0.082	0.160	0.248	0.337	0.161	0.342		
s_{sam}^2	3.82×10^{-5}	1.44×10^{-4}	3.45×10^{-4}	6.38×10^{-4}	1.46×10^{-4}	6.59×10^{-4}		
c	1.41×10^{-4}	4.65×10^{-4}	9.61×10^{-4}	1.84×10^{-3}	4.21×10^{-4}	1.60×10^{-3}		
Passed/Failed	passed	passed	passed	passed	passed	passed		

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

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

As all target compounds passed the homogeneity test, the Test Item was considered to be sufficiently homogenous and suitable for the EUPT-SRM9.

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 the target compounds must have been minor and roughly equal for all these laboratories In the main stability test we thus focused on the stability of the compounds during storage at –18 °C (the storage temperature for the Test Items recommended to the participants in the Specific Protocol) disregarding the influence of transportation. Possible losses during transport were studied separately (see below). For the main stability test two analytical portions from three randomly chosen Test Item bottles were analysed on three occasions with the first and last one enclosing the period of the test:

Stability test 1 (shortly before shipment):
22 April 2014

Stability test 2 (two weeks after shipment):
14 May 2014

Stability test 3 (shortly after deadline for results submission):
16 June 2014

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

COMPULSORY COMPOUNDS								
	2,4-D	BAC-C12	BAC-C14	Chlormequat	DDAC-C10	Fluazifop	Maleic hydrazide	Mepiquat
Storage at –18 °C (mean values in mg/kg)								
Analysis 1 22 April 2014	0.081	0.258	0.263	0.182	0.251	0.170	0.322	0.355
Analysis 2 14 May 2014	0.084	0.276	0.265	0.181	0.266	0.174	0.330	0.354
Analysis 3 16 June 2014	0.078	0.259	0.244	0.169	0.263	0.170	0.326	0.343
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	-0.003 (-4.23 %)	0.002 (0.72 %)	-0.018 (-7.02 %)	-0.013 (-7.02 %)	0.012 (4.87 %)	0.000 (0.00%)	0.004 (1.14 %)	-0.012 (-3.33 %)
Critical value [mg/kg]	0.006	0.019	0.020	0.014	0.019	0.013	0.024	0.027
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed

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

OPTIONAL COMPOUNDS								
	4-OH-chlorothalonil	Chlorate	Cyromazine	Melamine	Perchlorate	Trimesium		
Storage at –18 °C (mean values in mg/kg)								
Analysis 1 22 April 2014	0.076	0.170	0.247	0.355	0.170	0.342		
Analysis 2 14 May 2014	0.081	0.181	0.264	0.362	0.181	0.363		
Analysis 3 16 June 2014	0.076	0.169	0.263	0.330	0.172	0.359		
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.000 (-0.00 %)	-0.001 (-0.59 %)	0.016 (6.63 %)	-0.025 (-7.14 %)	0.002 (1.18 %)	0.017 (4.92 %)		
Critical value [mg/kg]	0.006	0.013	0.018	0.027	0.013	0.026		
Passed/Failed	passed	passed	passed	passed	passed	passed		

A target compound 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 (here the default value of 25 % of the assigned value was used). None of the target compounds present in the Test Item showed any significant degradation under the recommended storage conditions (–18 °C) even during a storage period exceeding the duration of the exercise. It is thus assumed that if the recommended storage conditions were followed, analyte stability had no significant influence on the results of the laboratories. The results of all analyses conducted within the framework of the stability test are shown in **Table 1-4** and **Appendix 4**.

1.8 Transport stability test

To complement the storage stability test the stability at conditions simulating shipment was also studied. On 5 Sept. 2014 4 randomly chosen bottles containing Test Item were mixed thoroughly with dry ice re-portioned again into four bottles and put in a freezer at –18 °C over the weekend. One of the Test Items was analysed immediately on 8 Sept. 2014 (day-0 of transport stability test), whereas the other 3 bottles were packed into 3 boxes exactly as the units delivered to the participants, i.e., one bottle of test item plus one bottle of Blank Material embedded in 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), one after 72 hours (day-3) and the other one after 96 hours (day-4). This duration covers the shipping time of the packages to the laboratories. All analyses were conducted in 6 replicates.

At day-2 the sample was partly defrosted with the core temperature of the frozen part being approx. –1 °C. At day-3 the temperature of the material increased to 9 °C, and at day-4 it reached ambient temperature

Nevertheless, all compounds remained sufficiently stable even up to 4 days, a period covering 100 % of the participating labs in the EU and EFTA countries. The results of the transport stability test are shown in **Table 1-5**.

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								
	2,4-D	BAC-C12	BAC-C14	Chlormequat	DDAC-C10	Fluazifop	Maleic hydrazide	Mepiquat
Day-0 (< –20 °C)	0.077	0.276	0.275	0.197	0.275	0.173	0.349	0.364
Day-2 (< –1 °C)	0.078	0.270	0.265	0.180	0.275	0.173	0.344	0.340
Day-3 (~ 9 °C)	0.076	0.270	0.268	0.184	0.266	0.170	0.371	0.359
Day-4 (~ 22 °C)	0.077	0.253	0.261	0.185	0.261	0.170	0.346	0.348
Deviation [%] Day-2 vs. Day-0	1.5 %	-2.3 %	-3.8 %	-8.6 %	0.0 %	0.2 %	-1.4 %	-6.5 %
Deviation [%] Day-3 vs. Day-0	-1.0 %	-2.4 %	-2.7 %	-6.5 %	-3.4 %	-1.6 %	6.3 %	-1.2 %
Deviation [%] Day-4 vs. Day-0	0.2 %	-8.3 %	-5.1 %	-5.9 %	-5.0 %	-1.3 %	-0.7 %	-4.2 %
OPTIONAL COMPOUNDS								
	4-OH-chlorothalonil	Chlorate	Cyromazine	Melamine	Perchlorate	Trimesium		
Day-0 (< –20 °C)	0.082	0.183	0.283	0.392	0.167	0.369		
Day-2 (< –1 °C)	0.088	0.176	0.257	0.366	0.168	0.365		
Day-3 (~ 9 °C)	0.082	0.190	0.262	0.362	0.163	0.349		
Day-4 (~ 22 °C)	0.077	0.195	0.274	0.374	0.166	0.384		
Deviation [%] Day-2 vs. Day-0	6.9 %	-4.0 %	-9.0 %	-6.6 %	0.5 %	-1.2 %		
Deviation [%] Day-3 vs. Day-0	-0.1 %	3.8 %	-7.3 %	-7.6 %	-2.4 %	-5.6 %		
Deviation [%] Day-4 vs. Day-0	-5.9 %	6.4 %	-3.2 %	-4.7 %	-0.8 %	3.9 %		

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 (milk). 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-SRM9 were instructed to provide explanations for their non-participation.

1.9.2 Announcement / Invitation and EUPT-SRM9-Website

Within the EURL-Web-Portal an EUPT-SRM9-Website was constructed with links to all documents relevant to this EUPT (i.e., Announcement/Invitation Letter, Calendar, Target Pesticides List, Specific Protocol and General EUPT Protocol). These documents were uploaded to the EURL-Web-Portal and the CIRCA/FIS-VL platform.

The Announcement/Invitation Letter for the EUPT-SRM9 was published on the EUPT-SRM9-Website in February 2014 and sent to all NRL-SRMs as well as any other OfLs analysing pesticide residues in food of animal origin within the framework of official controls. Additionally, the letter was sent to all EU-OfLs including those for which no information regarding official commodity scope was available and those which according to the EURL-Network-database do not cover food of animal origin. These labs were considered eligible but not obliged to participate. It was indicated to the OfLs that their obligation to participate in EUPTs arises from Reg. 396/2005/EC, irrespective of the content of the tentative list of obliged laboratories. OfLs from EFTA and EU-candidate countries were also invited if their contact data was available.

1.9.3 Registration and confidentiality

An EUPT-SRM9 registration website was constructed in collaboration with the EURL-CF. All laboratories listed in the tentative list as being obliged to participate in the current EUPT, regardless of whether they were intending to participate in this exercise or not, were requested to either register or to state their reasons for non-participation using the same website.

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

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

1.9.4 Distribution of the Test Items and the Blank Material

One bottle of Test Item (approx. 350 g) and one bottle of Blank Material (approx. 350 g) were shipped on 28 April 2014 to each participant in thermo-insulated polystyrene boxes covered with approx. 2 kg dry ice. A short instruction sheet on how to handle the sample and a small bottle containing 1 ml of chlorate and perchlorate ILISs were also included in each package.

Laboratories were asked to check the integrity and condition of the PT-materials upon receipt and to report to the Organisers via the website any observations or complaints and whether the PT-materials are accepted. Furthermore, labs 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 Item and Blank Material upon receipt were provided to the participating laboratories in the Specific Protocol (**Appendix 9**) that was dispatched 14 days prior to the shipment date.

1.9.5 Submission of results and additional information

An online submission tool allowed participants to submit their results via the Internet. Using their individual login data all participants had access to the Result-Submission-Website from a week after the sample shipment until the result submission deadline (26 May 2014). Participants were asked not only to report their analytical results but also to state whether the compounds on the Target Pesticides List were part of their routine scope and to indicate their experience with the analysis of these compounds. In addition, laboratories had to provide details about the methods applied and to state their own reporting limits (RLs) for each target compound they 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 compound listed in the Target Pesticides List, which was (a) not used in the preparation of the Test Item; (b) not detected by the Organiser, 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 Organiser 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 target analytes 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, or using the lab's reporting-limits (RLs), if the RL < MRRL" (as stated in the general protocol). Any RLs that are higher than the MRRL are not taken into account. Following the General Protocol results reported as "< RL" without providing a numerical value are also judged as false negatives if the RL exceeds the MRRL.

2.2 Establishment of the assigned values

The Assigned Values were established using the mean value of robust statistics of all reported results from EU and EFTA countries excluding results associated with obvious mistakes and gross errors.

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 target analyte 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 target analyte 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 target analyte (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 target analyte (i)
- δ_i is the target standard deviation for the target analyte (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 classification and ranking

2.5.1 Category A and B classification

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

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

2.5.2 Combined z-scores

For informative purposes and to allow comparison of the overall performance of the laboratories the Average of the Absolute z-Score (AAZ) was 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

69 laboratories from 32 countries (25 EU-Member States, 2 EFTA-States, 1 EU candidate country and 4 third countries) registered for participation in the EUPT-SRM9. Out of those laboratories 67 submitted at least one result; those were 60 from EU-Member States, 2 from EFTA-States, 1 from EU candidate countries and 4 from third countries). 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 Croatia, Poland and Bulgaria were not represented. Regarding NRL-SRMs Poland, Bulgaria and Luxemburg were not represented. All of them indicated that milk or commodities of animal origin in general do not belong to their analytical scope. Malta was represented by its proxy-NRL-SRM based in the United Kingdom. The NRL-SRM in Romania participated for the first time in an EUPT-SRM as its scope entails products of animal origin but not fruits, vegetables and cereals that were subject of the previous 8 EUPT-SRMs. No NRL-SRM has been established yet in Croatia.

In total 7 laboratories from non-EU countries submitted results (2 from EFTA Countries and 5 from the EU candidate countries or third countries). The results submitted by the 5 laboratories form the EU candidate countries or third countries were not taken into account when calculating the Assigned Values.

In total, 132 EU-OfLs (including NRL-SRMs) were originally considered as being obliged to participate in the present EUPT and were included on a tentative list of obliged labs that was distributed to the network labs 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 commodities of animal origin.

All labs that were listed as obliged to participate had to either participate or to provide an explanation for their non-participation. Out of 75 obliged laboratories that did not register for this PT, 61 (from 16 EU countries) provided explanations for their non-participation. 41 of them explained their non-participation with the fact that the matrix (milk) or the SRM9 target pesticides or both were out of their routine scope. The other 20 labs provided other reasons such as lack of personnel and technical difficulties. That results in 91 obliged laboratories (including those 14 non-participating labs that did not provide any explanation). **Table 3-2** gives an overview of the participating and non-participating EU-labs that were obliged to participate in the EUPT-SRM9.

In this PT two EU-Laboratories that originally had registered for the EUPT-SRM9 failed to submit results. In one case the lab stated that milk did not belong to its commodity scope but it still liked to receive the Test Item as a reference material. In the other case no explanation was provided for the non-submission of results.

Table 3-1: Number of laboratories listed as being obliged to participate in the EUPT-SRM9, labs that registered to participate, and labs that finally submitted results (grouped by contracting country)

Contracting Country [1]	No. of obliged labs [2]	Registered for Participation		Submitted Results		Provided Explanations for non-participation		Notes
		All [3]	NRL-SRMs [3]	All [3]	NRL-SRMs [3]	All [3]	NRL-SRMs [3]	
Austria	1	1	1	1	1			
Belgium	4	3+[2]	1	3+[2]	1	2+[2]	1	One lab based in BE was subcontracted by BE, FR and LU and listed in all the three contracting countries.
Bulgaria	4	–	–	–	–	2	–	
Croatia	2	–	–	–	–	–	–	HR has not yet established an NRL-SRM.
Cyprus	1	1	1	1	1	–	–	
Czech Republic	3	2	1	2	1	–	–	
Denmark	2	2	1	2	1	–	–	
Estonia	1	1	1	1	1	1	–	
Finland	1	1	1	1	1	[1]	–	
France	12	4+[1]	1	3+[1]	1	8+[2]	–	One lab based in BE was subcontracted by BE, FR and LU and is thus listed in all the three contracting countries.
Germany	22	12+[1]	1	12+[1]	1	10	–	CVUA Stuttgart hosting the EURL-SRM (organizing this PT) was not considered as an obliged lab.
Greece	2	2	2	2	2	1+[1]	–	GR has appointed two NRL-SRMs.
Hungary	2	2	1	2	1	1	–	
Ireland	2	1	1	1	1	1	–	
Italy	21	7	1	6	1	8	–	
Latvia	1	1	1	1	1	–	–	
Lithuania	2	2	1	2	1	–	–	
Luxemburg	1	1	–	1	–	1	1	One lab based in BE was subcontracted by BE, FR and LU and listed in all the three contracting countries.
Malta	4	3	1	3	1	–	–	MT-NRL-SRM represented by the UK-NRL-SRM which acts as proxy NRL. Official controls are subcontracted to one lab in DE and one in UK.
Poland	12	–	–	–	–	11	1	
Portugal	3	1	1	1	1	2	–	
Romania	3	1	1	1	1	2	–	
Slovenia	1	1	1	1	1	[2]	–	
Slovakia	2	1	1	1	1	–	–	
Spain	18	5+[1]	1	5+[1]	1	10+[1]	1	Spain has appointed two NRL-SRMs
Sweden	2	2	1	2	1	–	–	
The Netherlands	2	2	1	2	1	–	–	
United Kingdom	3	2	1	2	1	1	–	UK-NRL-SRM represents also MT-NRL-SRM; the UK-OfL was subcontracted also by MT.
EU Total	**132** [2]	57 [4]+[5]	24 [5]	55 [4]+[5]	24 [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 (commodities of animal origin). Obliged labs that did not participate were requested to provide an explanation.
3) Labs participating on voluntary basis are shown in square brackets.
4) One lab was subcontracted by three countries; two labs represent both UK and MT. Such laboratories were counted only once independent of how many countries they represented.
5) The NRL-SRM of UK was counted only once, although it represents both UK and MT.

Table 3-1 (cont.): Number of laboratories listed as being obliged to participate in the EUPT-SRM9, labs that registered to participate, and labs that finally submitted results (grouped by contracting country)

Contracting Country [1]	No. of obliged labs [2]	Registered for Participation		Submitted Results		Provided Explanations for non-participation		Notes
		All [3]	NRL-SRMs [3]	All [3]	NRL-SRMs [3]	All [3]	NRL-SRMs [3]	
Norway		1	1	1	1			
Switzerland		1	–	1	–			
EU+EFTA Total		59 [4]+(5)	25 [5]	57 [4]+(5)	25 [5]			
Australia		1	–	1	–			
Egypt		1	–	1	–			
Serbia		1	–	1	–			
Singapore		1	–	1	–			
USA		1	–	1	–			
EU Candidate countries and third countries		5		5				
Overall Sum	**132** [2]	69 [4]		67 [4]				

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 (milk). Obliged labs that did not participate were requested to provide an explanation.
3) Labs participating on voluntary basis were shown in parentheses
4) One lab was subcontracted by three countries; two labs represent both UK and MT. Such laboratories were counted only once independent of how many countries they represent.
5) The NRL-SRM of UK was counted only once, although it represents both UK and MT.

Table 3-2: Overview of EU-OfLs and NRLs considered as being obliged to participate in the EUPT-SRM9

Obliged EU-labs		No. of Labs [1]	Percent of A)	Percent of B)
A)	Labs tentatively obliged to participate in the EUPT-SRM9 (Listed in "EURL-List of obliged labs 2014" compiled based on coarse commodity scope of labs) (see **"INTRODUCTION", p. ix**)	**132**	**100 %**	–
B)	**A** minus labs giving sufficient explanations that they are not obliged (e.g. "particular commodity, Milk is out of scope", "pesticides in the target list are out of scope") (see **Chapter 3, p. 13**)	**91**	–	**100 %**
Thereof				
- Registered for Participation (obliged / [on voluntary basis])		**57 [1] / [5]**	**43 [1] %**	**63 [1] %**
- Submitting results		**55 [1] / [5]**	**42 [1] %**	**40 [1] %**
- Not submitting results / providing explanation for non-submission		2 / 1	1.5 %	2.2 %
- Non-participating	out of A)	**75**	**57 %**	–
	out of B)	**34**	–	**37 %**
- Providing explanations for non-participation [2]	out of A)	61	46 %	–
	out of B)	20	–	22 %
- No feedback	out of A)	14	11 %	15 %

1) Laboratories subcontracted by more than one country were counted only once, independent of how many countries they represent.
2) Additionally 9 labs not listed in the provisional obliged list provided explanations for non-participation.

4. RESULTS

4.1 Overview of results

An overview of the results reported for the target analytes present in the sample is shown in **Table 4-1**.

Table 4-2 gives an overview of all results submitted by each laboratory and categorizes them. For the individual numerical results reported by the laboratories see **Table 4-8** (page 26) and **Table 4-9** (page 32). The detailed information about the analytical methods used by the laboratories is shown in the web under **"EUPT-SRM9 - Supplementary Information"** that can be accessed using the following link: http://www.eurl-pesticides.eu/library/docs/srm/EUPT-SRM9_Supplementary_Information.pdf

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

Compounds		present in Test Item	Labs analysed for the compound			
			No.	% (based on $n = 62$ [2)])	% (based on $n = 132$ [3)])	% (based on $n = 91$ [3)])
Compulsory Compounds	**Fluazifop**	yes	51	82 %	39 %	56 %
	2,4-D	yes	50	81 %	38 %	55 %
	Chlormequat	yes	50	81 %	38 %	55 %
	Mepiquat	yes	49	79 %	37 %	54 %
	BAC-C12	yes	45	73 %	34 %	49 %
	BAC-C14	yes	45	73 %	34 %	49 %
	DDAC-C10	yes	44	71 %	33 %	48 %
	Maleic hydrazide	yes	30	48 %	23 %	33 %
	Haloxyfop	no	51	82 %	39 %	56 %
	BAC-C16	no	45	73 %	34 %	49 %
	BAC-C10	no	43	69 %	33 %	47 %
	Glyphosate	no	36	58 %	27 %	40 %
Optional Compounds	**Cyromazine**	yes	38	61 %	29 %	42 %
	Perchlorate	yes	30	48 %	23 %	33 %
	Chlorate	yes	28	45 %	21 %	31 %
	Melamine	yes	19	31 %	14 %	21 %
	Trimesium	yes	14	23 %	11 %	15 %
	4-OH-chlorothalonil	yes	7	11 %	5 %	8 %
	Cyanuric acid	no	14	23 %	11 %	15 %

1) Including official laboratories participating on voluntary basis
2) Based on 62 laboratories from EU and EFTA countries having submitted at least one result. Laboratories representing more than one country were counted only once.
3) 132 EU-OfLs and NRLs were listed in the tentative list of labs considered as obliged to participate in the EUPT-SRM9, but finally 91 laboratories remained as obliged to participate in the EUPT-SRM9.

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	BAC-C10	BAC-C12	BAC-C14	BAC-C16	Chlormequat	DDAC-C10	Fluazifop	Glyphosate	Haloxyfop	Maleic hydrazide	Mepiquat	analysed / correctly found among compulsory compounds within the EUPT-Target Pesticides List (max. 12 / 8)
within MACP								x		x	x+	x	x	x+	
present in Test Item			x		x	x		x	x	x			x	x	
Evaluated in this PT			x		x	x		x	x	x			x	x	
Lab-Code SRM9-	NRL-SRM	Cat.*													
1		A	V	ND	V	V	ND	V	V	V	ND	ND	**FN**	V	12 / 7
2	x	A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
3		B	V	ND	V	V	ND		V	V	ND	ND			9 / 5
4		B	V					V		V		ND	V	V	6 / 5
5	x	A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
6		A	V	ND	V	V	ND	V	V	V	ND	ND		V	11 / 7
7	x	B		ND	V	V	ND	V	V		ND	ND		V	9 / 5
8		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
9	x	A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
10		A	V	ND	V	V	ND	V	V	**FN**		ND	V	V	11 / 7
11		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
12		A	V	ND	V	V	ND	V	V	V		ND	V	V	11 / 8
13		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
14															0 / 0
15		B										ND			1 / 0
16		A	V	ND	V	V	ND	V	V	V		ND		V	10 / 7
17		B								V					1 / 1
18	x	B	V					V		V		ND	V	V	6 / 5
20	x	B													0 / 0
21		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
22		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
23		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
24		A	V	ND	V	V	ND	V	V	V	ND	ND		V	11 / 7
25		A	V	ND	V	V	ND	V	V	V	ND	ND		V	11 / 7
26		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
27		A	V	ND	V	V	ND	V	V	V		ND		V	10 / 7
28		B	V					V			ND			V	4 / 3
30		B	V					V		V	ND	ND		V	6 / 4
31	x	A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
32		B#	V	**FP**	V	V	**FP**	V	V	V		ND	V		10 / 7

MACP = EU Multiannual Community Control Program (2013 – 2015)
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
*****: 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 section 4.3.4, p. 40.)
Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
+: not for milk

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			4-OH-chlorothalonil	Chlorate	Cyanuric acid	Cyromazine	Melamine	Perchlorate	Trimesium	analysed / correctly found among optional compounds within the EUPT-Target Pesticides List (max. 7/ 6)	analysed / correctly found amoung all compounds within the EUPT-Target Pesticides List (max. 19 / 14)
within MACP											
present in Test Item			x	x		x	x	x	x		
Evaluated in this PT				x		x	x	x			
Lab-Code SRM9-	NRL-SRM	Cat.*									
1		A		V	ND	V	V	V	V	6 / 5	18 / 12
2	x	A		V		V		V		3 / 3	15 / 11
3		B									9 / 5
4		B		V		V	V	V	V	5 / 5	11 / 10
5	x	A	V	V	ND	V	V	V	V	7 / 6	19 / 14
6		A		V		V		V		3 / 3	14 / 10
7	x	B		**FN**				V		2 / 1	11 / 6
8		A				V	V			2 / 2	14 / 10
9	x	A		V				V		2 / 2	14 / 10
10		A		V	ND	V	V	V		5 / 4	16 / 11
11		A		V		V	V	V	V	5 / 5	17 / 13
12		A		V		V		V		3 / 3	14 / 11
13		A	V	v	ND	V	V	V	V	7 / 6	19 / 14
14											0 / 0
15		B									1 / 0
16		A									10 / 7
17		B									1 / 1
18	x	B				V				1 / 1	7 / 6
20	x	B					V			1 / 1	1 / 1
21		A	V	V	ND	V	V	V	V	7 / 6	19 / 14
22		A								0 / 0	12 / 8
23		A		V		V		V		3 / 3	15 / 11
24		A				V				1 / 1	12 / 8
25		A									11 / 7
26		A		V				V	**FN**	3 / 2	15 / 10
27		A				V	**FN**			2 / 1	12 / 8
28		B				V				1 / 1	5 / 4
30		B		V		V		V		3 / 3	9 / 7
31	x	A		V		V		V		3 / 3	15 / 11
32		B#			ND	V		V		3 / 2	13 / 9

MACP = EU Multiannual Community Control Program (2013 – 2015)
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
*****: 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 section 4.3.4, p. 40.)
Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

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	BAC-C10	BAC-C12	BAC-C14	BAC-C16	Chlormequat	DDAC-C10	Fluazifop	Glyphosate	Haloxyfop	Maleic hydrazide	Mepiquat	analysed / correctly found among compulsory compounds within the EUPT-Target Pesticides List (max. 12 / 8)
within MACP								x		x	x[+]	x	x	x[+]	
present in Test Item			x		x	x		x	x	x			x	x	
Evaluated in this PT			x		x	x		x	x	x			x	x	
Lab-Code SRM9-	NRL-SRM	Cat.*													
34	x	B	V	ND	V	V	ND		V	V		ND			8 / 5
35		B		ND	V	V	ND	V	V					V	7 / 5
36	x	B			V	V	ND		V						4 / 3
37		A	V		V	V	ND	V	V	V	ND	ND	V	V	11 / 8
38	x	B	V					V		V		ND	V	V	6 / 5
39	x	B	V					V		V	ND	ND	V	V	7 / 5
40		B		ND	V	V	ND		V						5 / 3
41	x	A	V	ND	V	V	ND	V	V	V		ND		V	10 / 7
42		B									ND				1 / 0
43		B	V					V		V	ND	ND		V	6 / 4
44		A	V	ND	V	V	ND	V	V	V		ND		V	10 / 7
46		B	V					V		V	ND	ND	V	V	7 / 5
47	x	A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
48	x	A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
49	x	A	V	ND	V	V	ND	V	V	V	ND	ND	**FN**	V	12 / 7
50	x	B[#]	V	ND	V	V	ND	V	V	V	**FP**	ND		V	11 / 7
51	x	B	V					V		V	ND	ND		V	6 / 4
52	x	B	V					V		V	ND	ND	V	V	7 / 5
53	x	A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
54		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
55	x	B	V					V		V		ND	V	V	6 / 5
56		A	V	ND	V	V	ND	V	V	V	ND	ND		V	11 / 7
57		B		ND	V	V	ND		V						5 / 3
58	x	A	V	ND	V	V	ND	V	V	V		ND		V	10 / 7
59		B	V					V		V	ND			V	5 / 4
60	x	B	V	ND	V	V	ND		V	V		ND			8 / 5
61		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8
62		B						V		V		ND		V	4 / 3
63		A	V	ND	V	V	ND	V	V	V	ND	ND	V	V	12 / 8

MACP = EU Multiannual Community Control Program (2013 – 2015)
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
*****: 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 section 4.3.4, p. 40.)
[#] Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
[+]: not for milk

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			4-OH-chlorothalonil	Chlorate	Cyanuric acid	Cyromazine	Melamine	Perchlorate	Trimesium	analysed / correctly found among optional compounds within the EUPT-Target Pesticides List (max. 7/ 6)	analysed / correctly found amoung all compounds within the EUPT-Target Pesticides List (max. 19 / 14)
within MACP											
present in Test Item			x	x		x	x	x	x		
Evaluated in this PT				x		x	x	x			
Lab-Code SRM9-	NRL-SRM	Cat.*									
34	x	B				V				1 / 1	9 / 6
35		B		V				V		2 / 2	9 / 7
36	x	B						V		1 / 1	5 / 4
37		A		V				V		2 / 2	13 / 10
38	x	B				V			V	2 / 2	8 / 7
39	x	B									7 / 5
40		B									5 / 3
41	x	A				V				1 / 1	11 / 8
42		B									1 / 0
43		B									6 / 4
44		A		V	ND	V	V	V		5 / 4	15 / 11
46		B			ND	V	V			3 / 2	10 / 7
47	x	A	V	V	ND	V	V	V	V	7 / 6	19 / 14
48	x	A		V	ND	V	V	V	V	6 / 5	18 / 13
49	x	A				V				1 / 1	13 / 8
50	x	B#		V		V		V		3 / 3	14 / 10
51	x	B				V	V		V	3 / 3	9 / 7
52	x	B				V				1 / 1	8 / 6
53	x	A		V				V	V	3 / 3	15 / 11
54		A									12 / 8
55	x	B				V				1 / 1	7 / 6
56		A		V		V		V		3 / 3	14 / 10
57		B									5 / 3
58	x	A				V				1 / 1	11 / 8
59		B	V		ND		V			3 / 2	8 / 6
60	x	B									8 / 5
61		A	V	V	ND	V	V	V	V	7 / 6	19 / 14
62		B		**FN**		V		V		3 / 2	7 / 5
63		A	V	V	ND	V	V	V		6 / 5	18 / 13

MACP = EU Multiannual Community Control Program (2013 – 2015)
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
***** : 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 section 4.3.4, p. 40.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

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	BAC-C10	BAC-C12	BAC-C14	BAC-C16	Chlormequat	DDAC-C10	Fluazifop	Glyphosate	Haloxyfop	Maleic hydrazide	Mepiquat	analysed / correctly found among compulsory compounds within the EUPT-Target Pesticides List (max. 12 / 8)
within MACP								x		x	x+	x	x	x+	
present in Test Item			x		x	x		x	x	x			x	x	
Evaluated in this PT			x		x	x		x	x	x			x	x	
Lab-Code SRM9-	NRL-SRM	Cat.*													
64	x	A	V	ND	V	V	ND	V	V	V		ND		V	10 / 7
65		B		FP	V	V	FP		V						5 / 3
66	x	B	V	ND	V	V	ND	V		V		ND		V	9 / 6
68		B		ND	V	V	ND		V						5 / 3
70															0 / 0
3rd-33		B	V					V		V	ND	ND	V	V	7 / 5
3rd-67		B	V	ND								ND			6 / 3
3rd-69		B		ND	V	V	ND		V						5 / 3
3rd-71		A	V	ND	V	V	ND	V	V	V	ND			V	10 / 7
3rd-72		B	V							V					2 / 2

MACP = EU Multiannual Community Control Program (2013 – 2015)
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
*****: 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 section 4.3.4, p. 40.)
[#] Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
[+]: not for milk

4.2 Assigned values, target standard deviations and outliers

To establish the Assigned Value of each target analyte the mean of robust statistics of all results submitted by labs from EU and EFTA countries was used. Results from third country laboratories were not taken into account. Based on these Assigned Values z-scores were calculated for each of the results, and a preliminary report was released. Laboratories receiving questionable ($2 < |z\text{-score}| \leq 3$) or unacceptable ($|z\text{-score}| \geq 3$) results were asked to investigate the reasons and report them to the Organiser. If a questionable or unacceptable result resulted from gross errors, it was decided on a case by case basis to be omitted, and the corresponding Assigned Value was recalculated using the remaining population. The z-scores were calculated again using the new Assigned Value. The results excluded from the establishment of the Assigned Values are shown in **Table 4-3** and highlighted in the relevant tables. The Assigned Values and their uncertainties are shown in **Table 4-4**.

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			4-OH-chlorothalonil	Chlorate	Cyanuric acid	Cyromazine	Melamine	Perchlorate	Trimesium	analysed / correctly found among optional compounds within the EUPT-Target Pesticides List (max. 7/ 6)	analysed / correctly found amoung all compounds within the EUPT-Target Pesticides List (max. 19 / 14)
within MACP											
present in Test Item			x	x		x	x	x	x		
Evaluated in this PT				x		x	x	x			
Lab-Code SRM9-	NRL-SRM	Cat.*									
64	x	A		V	ND	V	V	V	V	6 / 5	16 / 12
65		B									5 / 3
66	x	B				V				1 / 1	10 / 7
68		B									5 / 3
70											0 / 0
3rd-33		B				V	V			2 / 2	9 / 7
3rd-67		B				V	V			2 / 2	8 / 5
3rd-69		B			ND		V			2 / 1	7 / 4
3rd-71		A									10 / 7
3rd-72		B					V			1 / 1	3 / 3

MACP = EU Multiannual Community Control Program (2013 – 2015)
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
***** : 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 section 4.3.4, p. 40.)
[#] Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-3: Results excluded from the population for the establishment of the Assigned Values due to gross errors

Compound	PT-Code	Reported Result [mg/kg]	Reason
2,4-D	SRM9-18	0.00366	Use of a wrong calculation factor due to sample weight differing from routine work.
2,4-D	SRM9-47	0.39	Unsuitable way of quantifying
Fluazifop	SRM9-18	0.0803	Use of a wrong calculation factor due to sample weight differing from routine work.
Perchlorate	SRM9-47	0.56	Quantification using a non-suitable standard
Trimesium	SRM9-5	0.914	Calculation factor for converting the salt into the cation (target analyte) was not used.

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

	Compound	No. of NDs	No. of Outliers	Assigned Value [1] [mg/kg]	No. of numerical results (EU+EFTA)	UAV [2] [mg/kg]	UAV-Tolerance [mg/kg]	Judgement for UAV-test	Qn-RSD [%]
Compulsory Compounds	2,4-D	0	2	0.088	50	+/- 0.00295	0.0066	passed	18.7
	BAC-C12	0	0	0.284	45	+/- 0.00932	0.0213	passed	17.6
	BAC-C14	0	0	0.279	45	+/- 0.00934	0.0210	passed	17.9
	Chlormequat	0	0	0.179	50	+/- 0.00628	0.0134	passed	19.8
	DDAC-C10	0	0	0.268	44	+/- 0.00953	0.0201	passed	18.9
	Fluazifop	1	1	0.170	50	+/- 0.00786	0.0127	passed	26.0
	Maleic hydrazide	2	0	0.342	28	+/- 0.01567	0.0256	passed	19.4
	Mepiquat	0	0	0.333	49	+/- 0.01166	0.0250	passed	19.6
	Average								**19.7**
Optional Compounds	4-OH-chlorothalonil	***0***	***0***	***0.100[3]***	***7***	***+/- 0.00804***	***0.0075***	***failed***	***17.0[3]***
	Chlorate	2	0	0.185	26	+/- 0.00773	0.0139	passed	17.0
	Cyromazine	0	0	0.230	38	+/- 0.01388	0.0172	passed	29.8
	Melamine	1	0	0.365	18	+/- 0.01031	0.0274	passed	9.6
	Perchlorate	0	1	0.180	30	+/- 0.00882	0.0135	passed	21.1
	Trimesium	***1***	***1***	***0.370[3]***	***13***	***+/- 0.04114***	***0.0277***	***failed***	***30.8[3]***
	Average								**19.4[4]**
	Overall Average								**19.6[4]**

1: Robust mean based on population excluding results with gross errors
2: **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
3: for information only, not for calculation of z-score
4: 4-OH-chlorothalonil and trimesium were not included.

For ***4-OH-chlorothalonil***, the number of submitted numerical results (n = 7) was not sufficient for statistical evaluation. For ***trimesium*** the number of results was sufficient, but their distribution was very broad (Qn-RSD = 30.8 %), so that the Assigned Value does not fulfill the stipulated criteria of statistical certainty. The Assigned Values and the z-scores for ***4-OH-chlorothalonil*** and ***trimesium*** were therefore calculated for information only.

The average Qn-RSD of all compulsory compounds was 19.7 %. Excluding ***4-OH-chlorothalonil*** and ***trimesium*** the average Qn-RSD of optional compounds was 19.4 %. Both of them are significantly under the FFP-RSD of 25 %.

4.3 Assessment of laboratory performance

4.3.1 False Positives

Three laboratories reported in 5 cases (2× BAC-C10, 2× BAC-C16 and 1× glyphosate) numerical results for compounds in the Target Pesticides List which were neither spiked to, nor detected by the Organisers and the overwhelming majority of the participants (**Table 4-5**). All results exceeded both the labs' reporting limits for these compounds and the respective MRRLs in the Target Pesticides List. Therefore, all of them were judged as false positives.

Table 4-5: Overview of false positive and 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
BAC-C10	SRM9-32	yes	0.139	0.01	0.02	False Positives
	SRM9-65	yes	0.308	0.02	0.02	False Positives
BAC-C16	SRM9-32	yes	0.095	0.01	0.02	False Positives
	SRM9-65	yes	0.229	0.02	0.02	False Positives
Glyphosate	SRM9-50	yes	0.298	0.05	0.05	False Positives

4.3.2 False Negatives

Among the compulsory compounds there were 3 cases (2× ***maleic hydrazide*** and 1× ***fluazifop***) where the participants from EU and EFTA labs reported "analysed, but not detected" for target compounds spiked to the Test Item and detected by the majority of the labs targeting them (**Table 4-6**). As the Assigned Values for ***maleic hydrazide*** and ***fluazifop*** were sufficiently distant from the MRRLs and the individual RLs of the labs, they were judged as false negatives. These 3 false negative results represented 0.9 % of the 364 results reported for compulsory target compounds present in the Test Item.

Among the optional compounds there were 4 cases (2× ***chlorate***, 1× ***melamine*** and 1× ***trimesium***) where the participants from EU and EFTA labs reported "analysed, but not detected" for target compounds that were spiked to the Test Item and detected by the majority of the labs targeting them (**Table 4-6**). In the case of ***trimesium*** the lab's RL was equal to the MRRL and much lower than the Assigned Value. This result was thus judged as a false negative. In both cases concerning ***chlorate***, the labs RLs were higher than the MRRL, however, much lower than the Assigned Value. These results were therefore also judged as false negatives. In the case of ***melamine*** the lab reported "< 1 mg/kg" which corresponds to its RL. However, this value was much higher than the MRRL (0.05 mg/kg) and the Assigned Value (0.364 mg/kg). This result was judged as a false negative in accordance with the provisions of the GP where the following is stated: "Results reported as "< RL" (RL = Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives.". These 4 false negative results made 2.9 % of the 136 results reported for optional target compounds (including ***4-OH-chlorothalonil*** and ***trimesium***).

Table 4-6: 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	Fluazifop	SRM9-10	yes	yes	< 0.01	0.01	0.01	0.170	False Negative
	Maleic hydrazide	SRM9-1	yes	no	–	0.05	0.05	0.342	False Negative
		SRM9-49	yes	no	–	0.05			False Negative
Optional Compounds	Chlorate	SRM9-7	yes	no	–	0.1	0.02	0.185	False Negative
		SRM9-62	yes	no	–	0.05			False Negative
	Melamin	SRM9-27	yes	yes	< 1	1	0.05	0.364	False Negative
	Trimesium	SRM9-26	yes	no [1)]	–	0.05	0.05	0.370 [2)]	False Negative

1) According to information provided by the laboratory the Test Item and Blank Material were swapped by mistake. Should this be the case the compound was actually correctly not found in the Blank Material. As the Organizers do not have the possibility to verify this information the result had to be judged as a false negative.
2) Due to statistical uncertainty no Assigned Value could be established for trimesium. The Assigned Value (see Table 3-5), even considering the uncertainty, is however sufficiently distant from the MRRL and the RL of the lab. Furthermore, this compound was detected by the majority of the labs targeting it. These facts allow a safe judgement of false negatives in this case.

Table 4-7: Overall classification of z-scores of EU and EFTA labs

	Compound	No. of results	Acceptable No. (%)	Questionable No. (%)	Unacceptable [1)] No. (%)	FNs No.
Compulsory Compounds	2,4-D	50	47 (94 %)	1 (2 %)	2 (4 %)	0
	BAC-C12	45	40 (89 %)	2 (4 %)	3 (7 %)	0
	BAC-C14	45	41 (91 %)	2 (4 %)	2 (4 %)	0
	Chlormequat	50	48 (96 %)	2 (4 %)	0 (0 %)	0
	DDAC-C10	44	41 (93 %)	3 (7 %)	0 (0 %)	0
	Fluazifop	51	44 (86 %)	4 (8 %)	3 (6 %)	1
	Maleic hydrazide	30	26 (87 %)	0 (0 %)	4 (13 %)	2
	Mepiquat	49	47 (96 %)	1 (2 %)	1 (2 %)	0
	Subtotal	**364**	**334 (92 %)**	**15 (4 %)**	**15 (4 %)**	**3**
Optional Compounds	Chlorate	28	26 (93 %)	0 (0 %)	2 (7 %)	2
	Cyromazine	38	34 (89 %)	4 (11 %)	0 (0 %)	0
	Melamine	19	18 (95 %)	0 (0 %)	1 (5 %)	1
	Perchlorate	30	27 (90 %)	2 (7 %)	1 (3 %)	0
	Subtotal	**115**	**105 (91 %)**	**6 (5 %)**	**4 (3 %)**	**3**
Overall Sum (average)		**479**	**439 (92 %)**	21 (4 %)	**19 (4 %)**	**6**

1) including false negatives (FNs)

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

COMPULSORY Compound				2,4-D (free acid)		BAC-C12		BAC-C14		Chlormequat	
Assigned Value [mg/kg]				0.088		0.284		0.279		0.179	
MRRL [mg/kg]				0.020		0.020		0.020		0.020	
Qn-RSD				18.7 %		17.6 %		17.9 %		19.8 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found, max. 12 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1		12 / 7	A	0.087	0.0	0.326	0.6	0.318	0.6	0.199	0.4
2	x	12 / 8	A	0.083	-0.2	0.543	3.7	0.330	0.7	0.158	-0.5
3		9 / 5	B	0.0957	0.4	0.291	0.1	0.291	0.2		
4		6 / 5	B	0.0875	0.0					0.118	-1.4
5	x	12 / 8	A	0.0931	0.3	0.333	0.7	0.308	0.4	0.180	0.0
6		11 / 7	A	0.070	-0.8	0.257	-0.4	0.281	0.0	0.168	-0.2
7	x	9 / 5	B			0.327	0.6	0.219	-0.9	0.179	0.0
8		12 / 8	A	0.107	0.9	0.277	-0.1	0.275	-0.1	0.175	-0.1
9	x	12 / 8	A	0.0967	0.4	0.244	-0.6	0.247	-0.5	0.138	-0.9
10		11 / 7	A	0.072	-0.7	0.244	-0.6	0.309	0.4	0.298	2.7
11		12 / 8	A	0.066	-1.0	0.231	-0.7	0.205	-1.1	0.179	0.0
12		11 / 8	A	0.103	0.7	0.354	1.0	0.315	0.5	0.199	0.4
13		12 / 8	A	0.095	0.3	0.325	0.6	0.320	0.6	0.205	0.6
14		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. 40.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

4.3.3 Laboratory performance based on z-scores

All individual z-scores were calculated using the FFP-RSD of 25 %. **Table 4-7** shows the overall classification of z-scores achieved by all laboratories for compulsory and optional compounds. The respective rules are shown in **Section 2.4** (page 11). In the case of compulsory compounds "Acceptable" z-scores were achieved by 86 – 94 % (92 % on average) of the labs. Disregarding ***4-OH-chlorothalonil*** and ***trimesium*** where no trustworthy Assigned Values could be established, "Acceptable" z-scores of optional compounds were achieved by 89 – 95 % (91 % on average) of the labs.

A compilation of all individual results and z-scores for each laboratory is shown in **Table 4-8** and **Table 4-9**. The corresponding kernel density histograms showing the distribution of the reported results are shown in **Appendix 5**. A graphic representation of the z-score distribution of each target analyte present in the Test Item can be seen in **Appendix 6**.

In **Table 4-10** all laboratories are ranked based on the individual z-scores obtained for each of the analytes present in the Test Item.

	COMPULSORY Compound			DDAC-C10		Fluazifop		Maleic hydrazide		Mepiquat	
	Assigned Value [mg/kg]			0.268		0.170		0.342		0.333	
	MRRL [mg/kg]			0.020		0.010		0.050		0.020	
	Qn-RSD			18.9 %		26.0 %		19.4 %		19.6 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found, max. 12 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1		12 / 7	A	0.320	0.8	0.094	-1.8	FN	-3.4	0.340	0.1
2	x	12 / 8	A	0.276	0.1	0.189	0.5	0.407	0.8	0.302	-0.4
3		9 / 5	B	0.305	0.6	0.187	0.4				
4		6 / 5	B			0.175	0.1	0.327	-0.2	0.306	-0.3
5	x	12 / 8	A	0.285	0.3	0.187	0.4	0.369	0.3	0.323	-0.1
6		11 / 7	A	0.215	-0.8	0.116	-1.3			0.301	-0.4
7	x	9 / 5	B	0.284	0.2					0.360	0.3
8		12 / 8	A	0.254	-0.2	0.154	-0.4	0.342	0.0	0.335	0.0
9	x	12 / 8	A	0.239	-0.4	0.188	0.4	0.374	0.4	0.248	-1.0
10		11 / 7	A	0.289	0.3	< 0.01	-3.8	0.343	0.0	0.472	1.7
11		12 / 8	A	0.217	-0.8	0.154	-0.4	0.381	0.5	0.357	0.3
12		11 / 8	A	0.339	1.1	0.270	2.4	0.316	-0.3	0.370	0.4
13		12 / 8	A	0.301	0.5	0.203	0.8	0.251	-1.1	0.361	0.3
14		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)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

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

COMPULSORY Compound				2,4-D (free acid)		BAC-C12		BAC-C14		Chlormequat	
Assigned Value [mg/kg]				0.088		0.284		0.279		0.179	
MRRL [mg/kg]				0.020		0.020		0.020		0.020	
Qn-RSD				18.7 %		17.6 %		17.9 %		19.8 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found, max. 12 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
15		1 / 0	B								
16		10 / 7	A	0.0821	-0.3	0.296	0.2	0.291	0.2	0.172	-0.2
17		1 / 1	B								
18	x	6 / 5	B	0.0366	-2.3					0.116	-1.4
20	x	0 / 0	B								
21		12 / 8	A	0.105	0.8	0.250	-0.5	0.250	-0.4	0.240	1.4
22		12 / 8	A	0.084	-0.2	0.274	-0.1	0.262	-0.3	0.137	-0.9
23		12 / 8	A	0.068	-0.9	0.110	-2.4	0.117	-2.3	0.131	-1.1
24		11 / 7	A	0.0781	-0.4	0.313	0.4	0.282	0.0	0.195	0.4
25		11 / 7	A	0.108	0.9	0.300	0.2	0.300	0.3	0.153	-0.6
26		12 / 8	A	0.091	0.2	0.295	0.2	0.296	0.2	0.146	-0.7
27		10 / 7	A	0.071	-0.8	0.239	-0.6	0.200	-1.1	0.279	2.2
28		4 / 3	B	0.083	-0.2					0.200	0.5
30		6 / 4	B	0.113	1.2					0.242	1.4
31	x	12 / 8	A	0.079	-0.4	0.220	-0.9	0.223	-0.8	0.197	0.4
32		10 / 7	B#	0.088	0.0	0.066	-3.1	0.075	-2.9	0.183	0.1
34	x	8 / 5	B	0.109	1.0	0.288	0.1	0.265	-0.2		
35		7 / 5	B			0.300	0.2	0.302	0.3	0.180	0.0
36	x	4 / 3	B			0.216	-1.0	0.240	-0.6		
37		11 / 8	A	0.078	-0.4	0.273	-0.2	0.298	0.3	0.186	0.2
38	x	6 / 5	B	0.0746	-0.6					0.164	-0.3
39	x	7 / 5	B	0.113	1.2					0.170	-0.2
40		5 / 3	B			0.265	-0.3	0.285	0.1		
41	x	10 / 7	A	0.065	-1.0	0.253	-0.4	0.192	-1.3	0.207	0.6
42		1 / 0	B								
43		6 / 4	B	0.0803	-0.3					0.229	1.1
44		10 / 7	A	0.101	0.6	0.324	0.6	0.300	0.3	0.180	0.0
46		7 / 5	B	0.0961	0.4					0.197	0.4
47	x	12 / 8	A	0.390	13.8	0.326	0.6	0.297	0.3	0.216	0.8
48	x	12 / 8	A	0.082	-0.3	0.211	-1	0.222	-0.8	0.178	0.0
49	x	12 / 7	A	0.088	0.0	0.360	1.1	0.350	1.0	0.170	-0.2
50	x	11 / 7	B#	0.0951	0.3	0.290	0.1	0.292	0.2	0.216	0.8
51	x	6 / 4	B	0.101	0.6					0.106	-1.6
52	x	7 / 5	B	0.0881	0.0					0.172	-0.2
53	x	12 / 8	A	0.0778	-0.4	0.304	0.3	0.335	0.8	0.144	-0.8
54		12 / 8	A	0.0880	0.0	0.309	0.4	0.286	0.1	0.170	-0.2

* 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. 40.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

	COMPULSORY Compound			DDAC-C10		Fluazifop		Maleic hydrazide		Mepiquat	
	Assigned Value [mg/kg]			0.268		0.170		0.342		0.333	
	MRRL [mg/kg]			0.020		0.010		0.050		0.020	
	Qn-RSD			18.9 %		26.0 %		19.4 %		19.6 %	
	Lab code SRM9-	NRL-SRM	Analysed / corr. found, max. 12 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
	15		1 / 0	B								
	16		10 / 7	A	0.301	0.5	0.190	0.5			0.349	0.2
	17		1 / 1	B			0.110	-1.4				
	18	x	6 / 5	B			0.0803	-2.1	0.192	-1.8	0.196	-1.6
	20	x	0 / 0	B								
	21		12 / 8	A	0.250	-0.3	0.160	-0.2	0.400	0.7	0.430	1.2
	22		12 / 8	A	0.278	0.1	0.175	0.1	0.918	6.7	0.255	-0.9
	23		12 / 8	A	0.118	-2.2	0.157	-0.3	0.606	3.1	0.290	-0.5
	24		11 / 7	A	0.321	0.8	0.194	0.6			0.368	0.4
	25		11 / 7	A	0.289	0.3	0.194	0.6			0.264	-0.8
	26		12 / 8	A	0.310	0.6	0.203	0.8	0.274	-0.8	0.292	-0.5
	27		10 / 7	A	0.234	-0.5	0.142	-0.6			0.708	4.5
	28		4 / 3	B							0.450	1.4
	30		6 / 4	B			0.218	1.1			0.429	1.2
	31	x	12 / 8	A	0.235	-0.5	0.150	-0.5	0.337	-0.1	0.375	0.5
	32		10 / 7	B#	0.097	-2.6	0.133	-0.9	0.250	-1.1		
	34	x	8 / 5	B	0.161	-1.6	0.137	-0.8				
	35		7 / 5	B	0.255	-0.2					0.362	0.3
	36	x	4 / 3	B	0.276	0.1						
	37		11 / 8	A	0.272	0.1	0.217	1.1	0.338	0.0	0.301	-0.4
	38	x	6 / 5	B			0.131	-0.9	0.309	-0.4	0.311	-0.3
	39	x	7 / 5	B			0.208	0.9	0.261	-0.9	0.388	0.7
	40		5 / 3	B	0.249	-0.3						
	41	x	10 / 7	A	0.129	-2.1	0.106	-1.5			0.467	1.6
	42		1 / 0	B								
	43		6 / 4	B			0.158	-0.3			0.466	1.6
	44		10 / 7	A	0.299	0.5	0.173	0.1			0.330	0
	46		7 / 5	B			0.0965	-1.7	0.361	0.2	0.342	0.1
	47	x	12 / 8	A	0.253	-0.2	0.184	0.3	0.346	0.0	0.359	0.3
	48	x	12 / 8	A	0.190	-1.2	0.152	-0.4	0.379	0.4	0.320	-0.2
	49	x	12 / 7	A	0.250	-0.3	0.200	0.7	FN	-3.4	0.280	-0.6
	50	x	11 / 7	B#	0.343	1.1	0.266	2.3			0.358	0.3
	51	x	6 / 4	B			0.202	0.8			0.219	-1.4
	52	x	7 / 5	B			0.133	-0.9	0.416	0.9	0.324	-0.1
	53	x	12 / 8	A	0.310	0.6	0.225	1.3	0.273	-0.8	0.294	-0.5
	54		12 / 8	A	0.189	-1.2	0.141	-0.7	0.346	0.0	0.326	-0.1

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

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

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

COMPULSORY Compound				2,4-D (free acid)		BAC-C12		BAC-C14		Chlormequat	
Assigned Value [mg/kg]				0.088		0.284		0.279		0.179	
MRRL [mg/kg]				0.020		0.020		0.020		0.020	
Qn-RSD				18.7 %		17.6 %		17.9 %		19.8 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found, max. 12 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
55	x	6 / 5	B	0.080	-0.3					0.170	-0.2
56		11 / 7	A	0.0744	-0.6	0.278	-0.1	0.278	0.0	0.179	0.0
57		5 / 3	B			0.282	0.0	0.280	0.0		
58	x	10 / 7	A	0.071	-0.8	0.290	0.1	0.340	0.9	0.160	-0.4
59		5 / 4	B	0.112	1.1					0.183	0.1
60	x	8 / 5	B	0.081	-0.3	0.362	1.1	0.358	1.1		
61		12 / 8	A	0.0899	0.1	0.279	-0.1	0.252	-0.4	0.211	0.7
62		4 / 3	B							0.150	-0.7
63		12 / 8	A	0.108	0.9	0.244	-0.6	0.233	-0.7	0.247	1.5
64	x	10 / 7	A	0.0726	-0.7	0.281	0.0	0.286	0.1	0.177	0.0
65		5 / 3	B			0.434	2.1	0.878	8.6		
66	x	9 / 6	B	0.189	4.6	0.295	0.2	0.277	0.0	0.090	-2.0
68		5 / 3	B			0.040	-3.4	0.046	-3.3		
70		0 / 0									
3rd-33		7 / 5	B	0.1	0.6					0.160	-0.4
3rd-67		6 / 3	B	0.077	-0.5	0.343	0.8	0.323	0.6		
3rd-69		5 / 3	B			0.310	0.4	0.330	0.7		
3rd-71		10 / 7	A	0.07	-0.8	0.320	0.5	0.300	0.3	0.340	3.6
3rd-72		2 / 2	B	0.07	-0.8						

* 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. 40.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

COMPULSORY Compound				DDAC-C10		Fluazifop		Maleic hydrazide		Mepiquat	
Assigned Value [mg/kg]				0.268		0.170		0.342		0.333	
MRRL [mg/kg]				0.020		0.010		0.050		0.020	
Qn-RSD				18.9 %		26.0 %		19.4 %		19.6 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found, max. 12 / 8	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
55	x	6 / 5	B			0.132	-0.9	0.344	0.0	0.307	-0.3
56		11 / 7	A	0.302	0.5	0.137	-0.8			0.343	0.1
57		5 / 3	B	0.264	-0.1						
58	x	10 / 7	A	0.240	-0.4	0.062	-2.5			0.300	-0.4
59		5 / 4	B			0.012	-3.7			0.273	-0.7
60	x	8 / 5	B	0.349	1.2	0.212	1.0				
61		12 / 8	A	0.267	0.0	0.175	0.1	0.363	0.2	0.400	0.8
62		4 / 3	B			0.190	0.5			0.300	-0.4
63		12 / 8	A	0.227	-0.6	0.191	0.5	0.229	-1.3	0.334	0.0
64	x	10 / 7	A	0.239	-0.4	0.154	-0.4			0.377	0.5
65		5 / 3	B	0.313	0.7						
66	x	9 / 6	B			0.332	3.8			0.102	-2.8
68		5 / 3	B	0.306	0.6						
70		0 / 0									
3rd-33		7 / 5	B			0.215	1.1	0.551	2.4	0.300	-0.4
3rd-67		6 / 3	B								
3rd-69		5 / 3	B	0.400	2.0						
3rd-71		10 / 7	A	0.270	0.0	0.290	2.8			0.360	0.3
3rd-72		2 / 2	B			0.202	0.8				

* 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)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.

Table 4-9: Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

		OPTIONAL Compound		Chlorate		Cyromazine		Melamine	
		Assigned Value [mg/kg]		0.185		0.230		0.365	
		MRRL [mg/kg]		0.020		0.030		0.050	
		Qn-RSD		17.0 %		29.8 %		9.6 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found max. 6 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1		6 / 5	A	0.175	-0.2	0.229	0.0	0.324	-0.5
2	x	3 / 3	A	0.202	0.4	0.361	2.3		
3		0 /	B						
4		5 / 5	B	0.178	-0.2	0.224	-0.1	0.351	-0.2
5	x	7 / 6	A	0.180	-0.1	0.252	0.4	0.349	-0.2
6		3 / 3	A	0.143	-0.9	0.151	-1.4		
7	x	2 / 1	B	FN	-3.6				
8		2 / 2	A			0.172	-1.0	0.347	-0.2
9	x	2 / 2	A	0.181	-0.1				
10		5 / 4	A	0.195	0.2	0.109	-2.1	0.394	0.3
11		5 / 5	A	0.210	0.5	0.278	0.8	0.364	0.0
12		3 / 3	A	0.276	2.0	0.254	0.4		
13		7 / 6	A	0.185	0.0	0.280	0.9	0.340	-0.3
14		0 / 0							
15		0 / 0	B						
16		0 / 0	A						
17		0 / 0	B						
18	x	1 / 1	B			0.145	-1.5		
20	x	1 / 1	B					0.396	0.3
21		7 / 6	A	0.180	-0.1	0.250	0.4	0.500	1.5
22		0 / 0	A						
23		3 / 3	A	0.159	-0.6	0.220	-0.2		
24		1 / 1	A			0.307	1.3		
25		0 / 0	A						
26		3 / 2	A	0.162	-0.5				
27		2 / 1	A			0.179	-0.9	< 1	-3.5
28		1 / 1	B			0.097	-2.3		
30		3 / 3	B	0.207	0.5	0.304	1.3		
31	x	3 / 3	A	0.209	0.5	0.355	2.2		
32		3 / 2	B#			0.287	1.0		
34	x	1 / 1	B			0.195	-0.6		
35		2 / 2	B	0.187	0.0				
36	x	1 / 1	B						
37		2 / 2	A	0.135	-1.1				
38	x	2 / 2	B			0.268	0.7		
39	x	0 / 0	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)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

			OPTIONAL Compound	Perchlorate		4-OH-chlorothalonil	Trimesium	
			Assigned Value [mg/kg]	0.180		0.100	0.370	
			MRRL [mg/kg]	0.020		0.010	0.050	
			Qn-RSD	21.1 %		17.0 %	30.8 %	
	Lab code SRM9-	NRL-SRM	Analysed / corr. found max. 6 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score ‡ (FFP-RSD = 25 %)
	1		6 / 5	A	0.265	1.9		0.569	2.2
	2	x	3 / 3	A	0.196	0.3			
	3		0 /	B					
	4		5 / 5	B	0.181	0.0		0.304	-0.7
	5	x	7 / 6	A	0.151	-0.7	0.0916	0.914	5.9
	6		3 / 3	A	0.127	-1.2			
	7	x	2 / 1	B	0.132	-1.1			
	8		2 / 2	A					
	9	x	2 / 2	A	0.184	0.1			
	10		5 / 4	A	0.250	1.5			
	11		5 / 5	A	0.204	0.5		0.378	0.1
	12		3 / 3	A	0.171	-0.2			
	13		7 / 6	A	0.210	0.7	0.085	0.320	-0.5
	14								
	15		0 / 0	B					
	16		0 / 0	A					
	17		0 / 0	B					
	18	x	1 / 1	B					
	20	x	1 / 1	B					
	21		7 / 6	A	0.170	-0.2	0.103	0.870	5.4
	22		0 / 0	A					
	23		3 / 3	A	0.126	-1.2			
	24		1 / 1	A					
	25		0 / 0	A					
	26		3 / 2	A	0.184	0.1		FN	-3.5
	27		2 / 1	A					
	28		1 / 1	B					
	30		3 / 3	B	0.199	0.4			
	31	x	3 / 3	A	0.217	0.8			
	32		3 / 2	B#	0.050	-2.9			
	34	x	1 / 1	B					
	35		2 / 2	B	0.193	0.3			
	36	x	1 / 1	B	0.076	-2.3			
	37		2 / 2	A	0.158	-0.5			
	38	x	2 / 2	B				0.350	-0.2
	39	x	0 / 0	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)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Assigned Values are too uncertain, therefore, z-scores are for information only.

Table 4-9 (cont.): Results reported by all participating laboratories and the respective z-scores calculated using the FFP-RSD of 25 % for OPTIONAL compounds

		OPTIONAL Compound		Chlorate		Cyromazine		Melamine	
		Assigned Value [mg/kg]		0.185		0.230		0.365	
		MRRL [mg/kg]		0.020		0.030		0.050	
		Qn-RSD		17.0 %		29.8 %		9.6 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found max. 6 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
40		0 / 0	B						
41	x	1 / 1	A			0.193	-0.6		
42		0 / 0	B						
43		0 / 0	B						
44		5 / 4	A	0.16	-0.5	0.121	-1.9	0.396	0.3
46		3 / 2	B			0.224	-0.1	0.399	0.4
47	x	7 / 6	A	0.172	-0.3	0.214	-0.3	0.375	0.1
48	x	6 / 5	A	0.203	0.4	0.196	-0.6	0.362	0.0
49	x	1 / 1	A			0.32	1.6		
50	x	3 / 3	B#	0.186	0.0	0.252	0.4		
51	x	3 / 3	B			0.138	-1.6	0.222	-1.6
52	x	1 / 1	B			0.285	1.0		
53	x	3 / 3	A	0.152	-0.7				
54		0 / 0	A						
55	x	1 / 1	B			0.221	-0.1		
56		3 / 3	A	0.235	1.1	0.305	1.3		
57		0 / 0	B						
58	x	1 / 1	A			0.17	-1.0		
59		3 / 2	B					0.360	-0.1
60	x	0 / 0	B						
61		7 / 6	A	0.236	1.1	0.248	0.3	0.305	-0.7
62		3 / 2	B	FN	-3.6	0.19	-0.7		
63		6 / 5	A	0.252	1.4	0.197	-0.6	0.394	0.3
64	x	6 / 5	A	0.178	-0.2	0.253	0.4	0.375	0.1
65		0 / 0	B						
66	x	1 / 1	B			0.275	0.8		
68		0 / 0	B						
70		0 / 0							
3rd-33		2 / 2	B			0.186	-0.8	0.362	0.0
3rd-67		2 / 2	B			0.163	-1.2	0.411	0.5
3rd-69		2 / 1	B					0.28	-0.9
3rd-71		0 / 0	A						
3rd-72		1 / 1	B					0.292	-0.8

* 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)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Assigned Value is too uncertain, therefore, z-scores are for information only

			OPTIONAL Compound		Perchlorate		4-OH-chlorothalonil	Trimesium	
			Assigned Value [mg/kg]		0.180		0.100	0.370	
			MRRL [mg/kg]		0.020		0.010	0.050	
			Qn-RSD		21.1 %		17.0 %	30.8 %	
	Lab code SRM9-	NRL-SRM	Analysed / corr. found max. 6 / 5	Cat.*	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	Conc. [mg/kg]	z-score ‡ (FFP-RSD = 25 %)
	40		0 / 0	B					
	41	x	1 / 1	A					
	42		0 / 0	B					
	43		0 / 0	B					
	44		5 / 4	A	0.18	0.0			
	46		3 / 2	B					
	47	x	7 / 6	A	0.560	8.4	0.111	0.387	0.2
	48	x	6 / 5	A	0.171	-0.2		0.387	0.2
	49	x	1 / 1	A					
	50	x	3 / 3	B#	0.198	0.4			
	51	x	3 / 3	B				0.210	-1.7
	52	x	1 / 1	B					
	53	x	3 / 3	A	0.156	-0.5		0.181	-0.1
	54		0 / 0	A					
	55	x	1 / 1	B					
	56		3 / 3	A	0.226	1.0			
	57		0 / 0	B					
	58	x	1 / 1	A					
	59		3 / 2	B			0.119		
	60	x	0 / 0	B					
	61		7 / 6	A	0.208	0.6	0.0780	0.480	1.2
	62		3 / 2	B	0.154	-0.6			
	63		6 / 5	A	0.197	0.4	0.109		
	64	x	6 / 5	A	0.177	-0.1		0.354	-0.2
	65		0 / 0	B					
	66	x	1 / 1	B					
	68		0 / 0	B					
	70		0 / 0						
	3rd-33		2 / 2	B					
	3rd-67		2 / 2	B					
	3rd-69		2 / 1	B					
	3rd-71		0 / 0	A					
	3rd-72		1 / 1	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)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Assigned Values are too uncertain, therefore, z-scores are for information only.

Table 4-10: 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					
				2.4-D (free acid)	BAC-C12	BAC-C14	Chlormequat	DDAC-C10	Fluazifop
Assigned Value [mg/kg]				0.088	0.284	0.279	0.179	0.268	0.170
MRRL [mg/kg]				0.020	0.020	0.020	0.020	0.020	0.010
Qn-RSD				18.7 %	17.6 %	17.9 %	19.8 %	18.9 %	26.0 %
No. of Labs reporting results (incl. third country Laboratories)				54	48	48	52	46	54
Lab code SRM9-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
1		12 / 7	A	1	26	28	21	33	46
2	x	12 / 8	A	8	***48***	32	28	3	16
3		9 / 5	B	20	3	10		27	9
4		6 / 5	B	1			43		1
5	x	12 / 8	A	12	35	22	1	12	9
6		11 / 7	A	36	19	1	12	33	41
7	x	9 / 5	B		26	38	1	8	
8		12 / 8	A	42	3	6	9	8	9
9	x	12 / 8	A	20	26	26	39	18	9
10		11 / 8	A	33	26	22	**51**	12	***53 (FN)***
11		12 / 7	A	46	35	41	1	33	9
12		11 / 8	A	33	39	26	21	37	**49**
13		12 / 8	A	12	26	28	30	21	26
14		0 / 0							
15		1 / 0	B						
16		10 / 7	A	12	11	10	12	21	16
17		1 / 1	B						43
18	x	6 / 5	B	**52**			43		47
20	x	0 / 0	B						
21		12 / 8	A	36	24	22	43	12	5
22		12 / 8	A	8	3	15	39	3	1
23		12 / 8	A	42	**45**	**45**	41	**45**	6
24		11 / 7	A	20	19	1	21	33	21
25		11 / 7	A	42	11	15	30	12	21
26		12 / 8	A	8	11	10	33	27	26
27		10 / 7	A	36	26	41	50	21	21
28		4 / 3	B	8			28		
30		6 / 4	B	50			43		38
31	x	12 / 8	A	20	38	35	21	21	16
32		10 / 7	B#	1	***46***	**46**	9	**46**	32
34	x	8 / 5	B	46	3	10		42	26
35		7 / 5	B		11	15	1	8	
36	x	4 / 3	B		39	28		3	
37		11 / 8	A	20	11	15	12	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 have not reported any false positive result.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Only compulsory compounds were considered, max. 12 / 8.
(FN) = false negative results;

				COMPULSORY		OPTIONAL Compounds			
				Maleic hydrazide	Mepiquat	Chlorate	Cyromazine	Melamine	Perchlorate
			Assigned Value [mg/kg]	0.342	0.333	0.185	0.230	0.365	0.180
			MRRL [mg/kg]	0.050	0.020	0.020	0.030	0.050	0.020
			Qn-RSD	19.4 %	19.6 %	17.0 %	29.8 %	9.6 %	21.1 %
			No. of Labs reporting results (incl. third country Laboratories)	31	51	28	40	23	30
	Lab code SRM9-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
	1		12 / 7	A	***29 (FN)***	4	7	1	16	27
	2	x	12 / 8	A	18	22	12	**39**		9
	3		9 / 5	B						
	4		6 / 5	B	8	12	7	2	7	1
	5	x	12 / 8	A	11	4	4	8	7	19
	6		11 / 7	A		22	21	32		24
	7	x	9 / 5	B		12	***27 (FN)***			23
	8		12 / 8	A	1	1		24	7	
	9	x	12 / 8	A	13	41	4			3
	10		11 / 8	A	1	49	7	**37**	10	26
	11		12 / 7	A	16	12	14	19	1	14
	12		11 / 8	A	11	22	26	8		6
	13		12 / 8	A	23	12	1	22	10	19
	14		0 / 0							
	15		1 / 0	B						
	16		10 / 7	A		10				
	17		1 / 1	B						
	18	x	6 / 5	B	26	46		33		
	20	x	0 / 0	B					10	
	21		12 / 8	A	17	42	4	8	21	6
	22		12 / 8	A	***31***	40				
	23		12 / 8	A	***28***	30	19	5		24
	24		11 / 7	A		22		29		
	25		11 / 7	A		38				
	26		12 / 8	A	18	30	14			3
	27		10 / 7	A		***51***		22	***23 (FN)***	
	28		4 / 3	B		44		**39**		
	30		6 / 4	B		42	14	29		11
	31	x	12 / 8	A	7	30	14	**38**		21
	32		10 / 7	B#	23			24		**29**
	34	x	8 / 5	B				13		
	35		7 / 5	B		12	1			9
	36	x	4 / 3	B						**28**
	37		11 / 8	A	1	22	22			14

* 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.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Only compulsory compounds were considered, max. 12 / 8.
(FN) = false negative results;

Table 4-10 (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					
				2.4-D (free acid)	BAC-C12	BAC-C14	Chlormequat	DDAC-C10	Fluazifop
Assigned Value [mg/kg]				0.088	0.284	0.279	0.179	0.268	0.170
MRRL [mg/kg]				0.020	0.020	0.020	0.020	0.020	0.010
Qn-RSD				18.7 %	17.6 %	17.9 %	19.8 %	18.9 %	26.0 %
No. of Labs reporting results (incl. third country Laboratories)				54	48	48	52	46	54
Lab code SRM9-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
38	x	6 / 5	B	28			20		32
39	x	7 / 5	B	50			12		32
40		5 / 3	B		17	6		12	
41	x	10 / 7	A	46	19	44	30	**44**	44
42		1 / 0	B						
43		6 / 4	B	12			41		6
44		10 / 7	A	28	26	15	1	21	1
46		7 / 5	B	20			21		45
47	x	12 / 8	A	***54***	26	15	36	8	6
48	x	12 / 8	A	12	39	35	1	39	9
49	x	12 / 7	A	1	42	40	12	12	24
50	x	11 / 7	B#	12	3	10	36	37	**48**
51	x	6 / 4	B	28			48		26
52	x	7 / 5	B	1			12		32
53	x	12 / 8	A	20	17	35	36	27	41
54		12 / 8	A	1	19	6	12	39	24
55	x	6 / 5	B	12			12		32
56		11 / 7	A	28	3	1	1	21	26
57		5 / 3	B		1	1		3	
58	x	10 / 7	A	36	3	38	21	18	**50**
59		5 / 4	B	49			9		***52***
60	x	8 / 5	B	12	42	41		39	37
61		12 / 8	A	7	3	22	33	1	1
62		4 / 3	B				33		16
63		12 / 8	A	42	26	32	47	27	16
64	x	10 / 7	A	33	1	6	1	18	9
65		5 / 3	B		**44**	***48***		32	
66	x	9 / 6	B	***53***	11	1	49		***53***
68		5 / 3	B		***47***	***47***		27	
70		0 / 0							
3rd-33		7 / 5	B	28			21		38
3rd-67		6 / 3	B	27	37	28			
3rd-69		5 / 3	B		19	32		43	
3rd-71		10 / 7	A	36	24	15	**52**	1	**51**
3rd-72		2 / 2	B	36					26

* 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.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Only compulsory compounds were considered, max. 12 / 8.
(FN) = false negative results;

				COMPULSORY		OPTIONAL Compounds			
				Maleic hydrazide	Mepiquat	Chlorate	Cyromazine	Melamine	Perchlorate
			Assigned Value [mg/kg]	0.342	0.333	0.185	0.230	0.365	0.180
			MRRL [mg/kg]	0.050	0.020	0.020	0.030	0.050	0.020
			Qn-RSD	19.4 %	19.6 %	17.0 %	29.8 %	9.6 %	21.1 %
			No. of Labs reporting results (incl. third country Laboratories)	31	51	28	40	23	30
	Lab code SRM9-	NRL-SRM	Analysed / corr. found‡	Cat.*	Ranking	Ranking	Ranking	Ranking	Ranking	Ranking
	38	x	6 / 5	B	13	12		17		
	39	x	7 / 5	B	21	36				
	40		5 / 3	B						
	41	x	10 / 7	A		46		13		
	42		1 / 0	B						
	43		6 / 4	B		46				
	44		10 / 7	A		1	14	36	10	1
	46		7 / 5	B	8	4		2	15	
	47	x	12 / 8	A	1	12	11	6	4	***30***
	48	x	12 / 8	A	13	10	12	13	1	6
	49	x	12 / 7	A	***29 (FN)***	35		34		
	50	x	11 / 7	B#		12	1	8		11
	51	x	6 / 4	B		44		34	22	
	52	x	7 / 5	B	21	4		24		
	53	x	12 / 8	A	18	30	20			14
	54		12 / 8	A	1	4				
	55	x	6 / 5	B	1	12		2		
	56		11 / 7	A		4	22	29		22
	57		5 / 3	B						
	58	x	10 / 7	A		22		24		
	59		5 / 4	B		36			4	
	60	x	8 / 5	B						
	61		12 / 8	A	8	38	22	6	18	17
	62		4 / 3	B		22	***27 (FN)***	17		17
	63		12 / 8	A	25	1	25	13	10	11
	64	x	10 / 7	A		30	7	8	4	3
	65		5 / 3	B						
	66	x	9 / 6	B		**50**		19		
	68		5 / 3	B						
	70		0 / 0							
	3rd-33		7 / 5	B	27	22		19	1	
	3rd-67		6 / 3	B				28	16	
	3rd-69		5 / 3	B					20	
	3rd-71		10 / 7	A		12				
	3rd-72		2 / 2	B					19	

* 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.)
# Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
‡ Only compulsory compounds were considered, max. 12 / 8.
(FN) = false negative results;

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 target analytes they correctly detected among the total number of COMPULSORY pesticides present in the Test Item. Following the rules defined in the General Protocol (4th Edition, see **Appendix 8**), 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. Two laboratories (SRM9-32 and SRM9-50) had submitted results for 7 of the 8 compulsory compounds, but had to be still classified into Category B due to the submission of false positive result(s).

A total of 32 EU and EFTA labs (52 %) were classified into Category A and 30 (48 %) into Category B. One of the five third-country labs was classified into Category A, and the other ones into Category B. Considering only the compulsory compounds laboratories classified into Category A achieved an overall AAZ of 0.7 (n = 263) whereas laboratories classified into Category B achieved an overall AAZ of 0.9 (n = 131).

Table 4-11 and **Table 4-12** show the details of laboratories classified into Category A and B, respectively. For informative purposes, the AAZ was calculated for labs with 5 or more individual z-scores. For the AAZ calculation any z-scores > 5 were set at 5.

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. By asking labs to provide this information, the Organisers aim to emphasize the importance of tracing back potential sources of errors so that they can be avoided in the future. A compilation of the feedback received by the laboratories is given in **Appendix 7**. The main aim of this compilation is to inform about possible error sources that should be avoided. This information also provides input to NRLs on how to better assist labs in improving their performance.

In the current PT, the most frequent reasons given for the poor performance were: a) wrong concentration of calibration solution; b) incorrect evaluation, calculation or interpretation of the measured data; c) no or inappropriate correction for recovery; d) lack of experience with the analyte or the matrix in question; e) use of inappropriate procedures. Additional reasons included non-consideration of matrix effects, transcription error and in one case the Test Item and Blank Material were swapped by mistake.

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

COMPULSORY Compounds			2,4-D (free acid)	BAC-C12	BAC-C14	Chlor-mequat	DDAC-C10	Fluazifop	Maleic hydrazide	Mepiquat	
Assigned Value [mg/kg]			0.088	0.284	0.279	0.179	0.268	0.170	0.342	0.333	
MRRL [mg/kg]			0.020	0.020	0.020	0.020	0.020	0.010	0.050	0.020	
Qn-RSD			18.7 %	17.6 %	17.9 %	19.8 %	18.9 %	26.0 %	19.4 %	19.6 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found [1]	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	AAZ [2]
1		12 / 7	0.0	0.6	0.6	0.4	0.8	-1.8	-3.4 (FN)	0.1	1.0
2	x	12 / 8	-0.2	3.7	0.7	-0.5	0.1	0.5	0.8	-0.4	0.9
5	x	12 / 8	0.3	0.7	0.4	0.0	0.3	0.4	0.3	-0.1	0.3
6		11 / 7	-0.8	-0.4	0.0	-0.2	-0.8	-1.3		-0.4	0.6
8		12 / 8	0.9	-0.1	-0.1	-0.1	-0.2	-0.4	0.0	0.0	0.2
9	x	12 / 8	0.4	-0.6	-0.5	-0.9	-0.4	0.4	0.4	-1.0	0.6
10		11 / 7	-0.7	-0.6	0.4	2.7	0.3	-3.8 (FN)	0.0	1.7	1.3
11		12 / 8	-1.0	-0.7	-1.1	0.0	-0.8	-0.4	0.5	0.3	0.6
12		11 / 8	0.7	1.0	0.5	0.4	1.1	2.4	-0.3	0.4	0.9
13		12 / 8	0.3	0.6	0.6	0.6	0.5	0.8	-1.1	0.3	0.6
16		10 / 7	-0.3	0.2	0.2	-0.2	0.5	0.5		0.2	0.3
21		12 / 8	0.8	-0.5	-0.4	1.4	-0.3	-0.2	0.7	1.2	0.7
22		12 / 8	-0.2	-0.1	-0.3	-0.9	0.1	0.1	6.7	-0.9	1.0
23		12 / 8	-0.9	-2.4	-2.3	-1.1	-2.2	-0.3	3.1	-0.5	1.6
24		11 / 7	-0.4	0.4	0.0	0.4	0.8	0.6		0.4	0.4
25		11 / 7	0.9	0.2	0.3	-0.6	0.3	0.6		-0.8	0.5
26		12 / 8	0.2	0.2	0.2	-0.7	0.6	0.8	-0.8	-0.5	0.5
27		10 / 7	-0.8	-0.6	-1.1	2.2	-0.5	-0.6		4.5	1.5
31	x	12 / 8	-0.4	-0.9	-0.8	0.4	-0.5	-0.5	-0.1	0.5	0.5
37		11 / 8	-0.4	-0.2	0.3	0.2	0.1	1.1	0.0	-0.4	0.3
41	x	10 / 7	-1.0	-0.4	-1.3	0.6	-2.1	-1.5		1.6	1.2
44		10 / 7	0.6	0.6	0.3	0.0	0.5	0.1		0.0	0.3
47	x	12 / 8	13.8	0.6	0.3	0.8	-0.2	0.3	0.0	0.3	0.9
48	x	12 / 8	-0.3	-1.0	-0.8	0.0	-1.2	-0.4	0.4	-0.2	0.5
49	x	12 / 7	0.0	1.1	1.0	-0.2	-0.3	0.7	-3.4 (FN)	-0.6	0.9
53	x	12 / 8	-0.4	0.3	0.8	-0.8	0.6	1.3	-0.8	-0.5	0.7
54		12 / 8	0.0	0.4	0.1	-0.2	-1.2	-0.7	0.0	-0.1	0.3
56		11 / 7	-0.6	-0.1	0.0	0.0	0.5	-0.8		0.1	0.3
58	x	10 / 7	-0.8	0.1	0.9	-0.4	-0.4	-2.5		-0.4	0.8
61		12 / 8	0.1	-0.1	-0.4	0.7	0.0	0.1	0.2	0.8	0.3
63		12 / 8	0.9	-0.6	-0.7	1.5	-0.6	0.5	-1.3	0.0	0.8
64	x	10 / 7	-0.7	0.0	0.1	0.0	-0.4	-0.4		0.5	0.3
3rd-71		10 / 7	-0.8	0.5	0.3	3.6	0.0	2.8		0.3	1.2

1) Only compulsory compounds were considered.
2) AAZ: Average of Absolute z-scores, is given for informative purposes.
For the calculation of the AAZ the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
(FN) = false negative results;

Table 4-12: Category B laboratories ordered by lab-codes

COMPULSORY Compounds			2,4-D (free acid)	BAC-C12	BAC-C14	Chlor-mequat	DDAC-C10	Fluazifop	Maleic hydrazide	Mepiquat	
Assigned Value [mg/kg]			0.088	0.284	0.279	0.179	0.268	0.170	0.342	0.333	
MRRL [mg/kg]			0.020	0.020	0.020	0.020	0.020	0.010	0.050	0.020	
Qn-RSD			18.7 %	17.6 %	17.9 %	19.8 %	18.9 %	26.0 %	19.4 %	19.6 %	
Lab code SRM9-	NRL-SRM	Analysed / corr. found [1]	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	z-scores	AAZ [2]
3		9 / 5	0.4	0.1	0.2		0.6	0.4			0.3
4		6 / 5	0			-1.4		0.1	-0.2	-0.3	0.4
7	x	9 / 5		0.6	-0.9	0	0.2			0.3	0.4
15		1 / 0									
17		1 / 1						-1.4			
18	x	6 / 5	-2.3			-1.4		-2.1	-1.8	-1.6	1.8
20	x	0 / 0									
28		4 / 3	-0.2			0.5				1.4	
30		6 / 4	1.2			1.4		1.1		1.2	
32 [3]		10 / 7 [3]	0	-3.1	-2.9	0.1	-2.6	-0.9	-1.1		1.5
34	x	8 / 5	1	0.1	-0.2		-1.6	-0.8			0.7
35		7 / 5		0.2	0.3	0	-0.2			0.3	0.2
36	x	4 / 3		-1	-0.6		0.1				
38	x	6 / 5	-0.6			-0.3		-0.9	-0.4	-0.3	0.5
39	x	7 / 5	1.2			-0.2		0.9	-0.9	0.7	0.8
40		5 / 3		-0.3	0.1		-0.3				
42		1 / 0									
43		6 / 4	-0.3			1.1		-0.3		1.6	
46		7 / 5	0.4			0.4		-1.7	0.2	0.1	0.6
50 [3]	x	11 / 7 [3]	0.3	0.1	0.2	0.8	1.1	2.3		0.3	0.7
51	x	6 / 4	0.6			-1.6		0.8		-1.4	
52	x	7 / 5	0			-0.2		-0.9	0.9	-0.1	0.4
55	x	6 / 5	-0.3			-0.2		-0.9	0	-0.3	0.3
57		5 / 3		0	0		-0.1				
59		5 / 4	1.1			0.1		-3.7		-0.7	
60	x	8 / 5	-0.3	1.1	1.1		1.2	1			0.9
62		4 / 3				-0.7		0.5		-0.4	
65		5 / 3		2.1	8.6		0.7				
66	x	9 / 6	4.6	0.2	0	-2		3.8		-2.8	2.3
68		5 / 3		-3.4	-3.3		0.6				
3rd-33		7 / 5	0.6			-0.4		1.1	2.4	-0.4	1.0
3rd-67		6 / 3	-0.5	0.8	0.6						
3rd-69		5 / 3		0.4	0.7		2				
3rd-72		2 / 2	-0.8					0.8			

1) Only compulsory compounds were considered.
2) AAZ: Average of Absolute z-scores, is given for informative purposes for participants having reported at least 5 results within compulsory compounds. For the calculation of the AAZ the value "5" was applied where the z-score was higher than 5 (shown in square brackets).
3) Labs had a sufficient scope but were classified into Category B due to the submission of false positive results.
(FN) = false negative results;

4.4 Methodological Information

Detailed information about the analytical methods used by the laboratories can be found in **"EUPT-SRM9 - Supplementary Information"** that can be accessed using the following link:
http://www.eurl-pesticides.eu/library/docs/srm/EUPT-SRM9_Supplementary_Information.pdf

4.4.1 Initial temperature and extraction time for sample preparation

In order to ensure good homogeneity the Organisers strongly recommended the laboratories to thoroughly mix the received Test Items before taking any analytical portions. To reduce any losses of target analytes it was further recommended keeping the temperature low. 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 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 to indicate the initial temperature as well as the soaking and extraction times entailed in their procedure. This information is compiled in (**Table 4-13**). No clear trend regarding the impact of extraction time or initial sample temperature could be observed for the studied compounds.

4.4.2 Analytical methods used

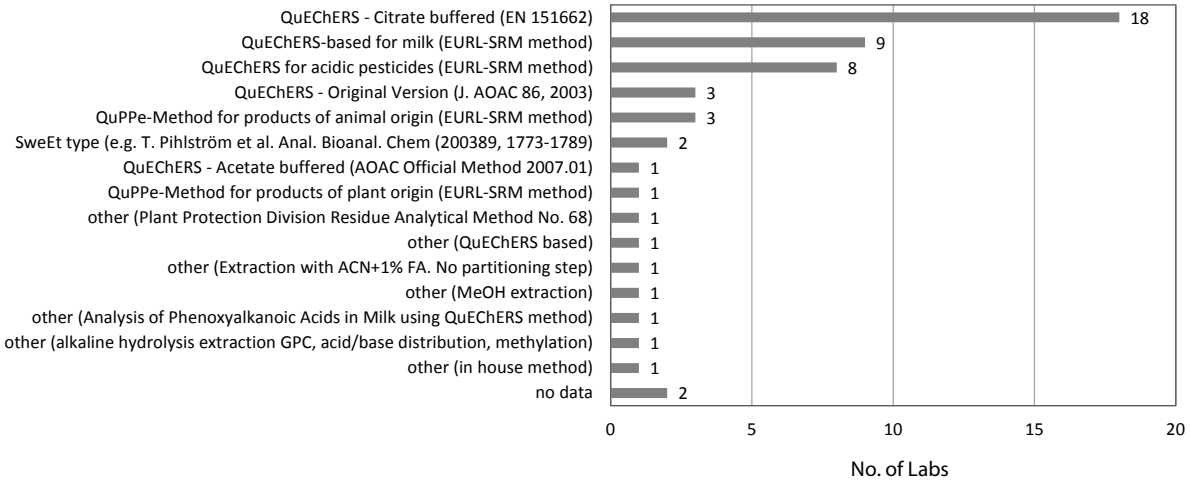
An overview of the methods used by the participating labs for sample preparation and determination for each analyte present in the Test Item can be seen in **Figure 4-1**.

Table 4-13: Number of results reported and AAZs achieved in correlation with the initial temperature and extraction time in sample preparation

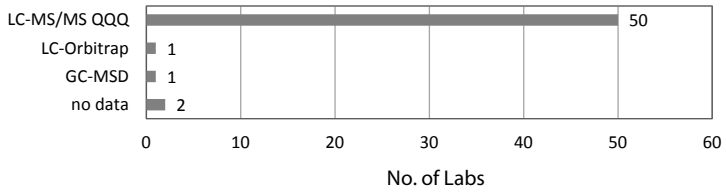
	Extraction time	1 min	2 min	3 min	5 min	10 min	15 min	20 min	30 min	45 min	> 60 min	no data	Sum
		No. of results (AAZ)											
Initial Sample Temperature	ambient (e.g. 20 °C – 24 °C)	49 (0.6)	10 (0.9)	2 (0.2)	20 (0.8)	22 (0.6)	30 (0.8)	24 (0.7)	27 (0.8)	10 (0.6)	2 (0.5)	3 (0.5)	199 (0.7)
	cold (e.g. 4 °C – 10 °C)	56 (0.7)	18 (1.6)	1 (0.8)	12 (0.9)	19 (0.9)	35 (0.7)	4 (1.9)	6 (0.8)				151 (0.9)
	just thawed (e.g. 0 °C – 3 °C)	43 (0.7)	3 (2.6)			2 (0.9)	28 (0.7)	12 (0.8)	1 (0.6)				89 (0.8)
	deep frozen (e.g. -18 °C)	25 (0.4)				5 (0.9)	7 (0.7)	4 (1.4)	1 (0.1)			14 (0.9)	56 (0.7)
	no data					3 (0.6)	2 (1.1)					26 (1)	31 (0.9)
	Overall	173 (0.7)	31 (1.5)	3 (0.4)	32 (0.8)	51 (0.8)	102 (0.7)	44 (0.9)	35 (0.8)	10 (0.6)	2 (0.5)	43 (0.9)	526 (0.8)

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

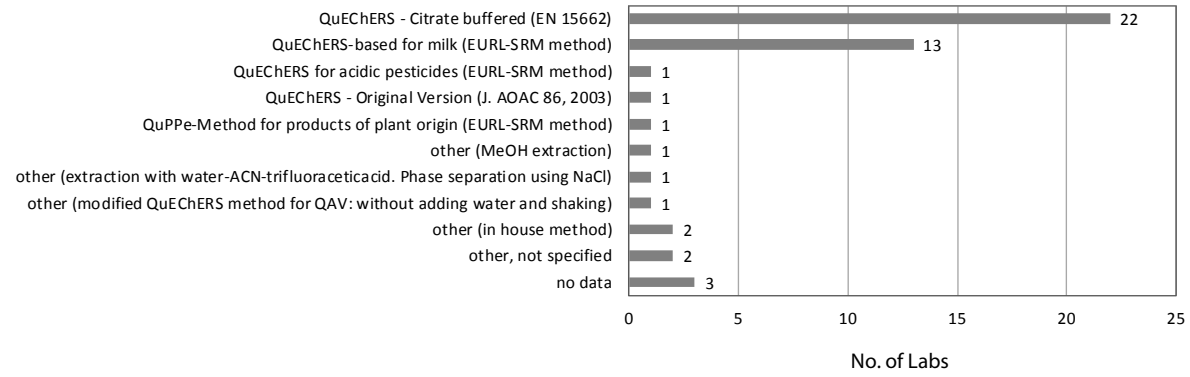
2,4-D: Sample preparation



2,4-D: Determinative analysis



BAC-C12: Sample preparation



BAC-C12: Determinative analysis

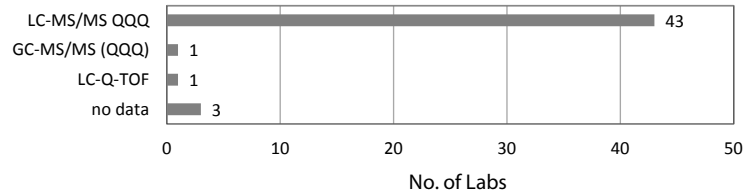
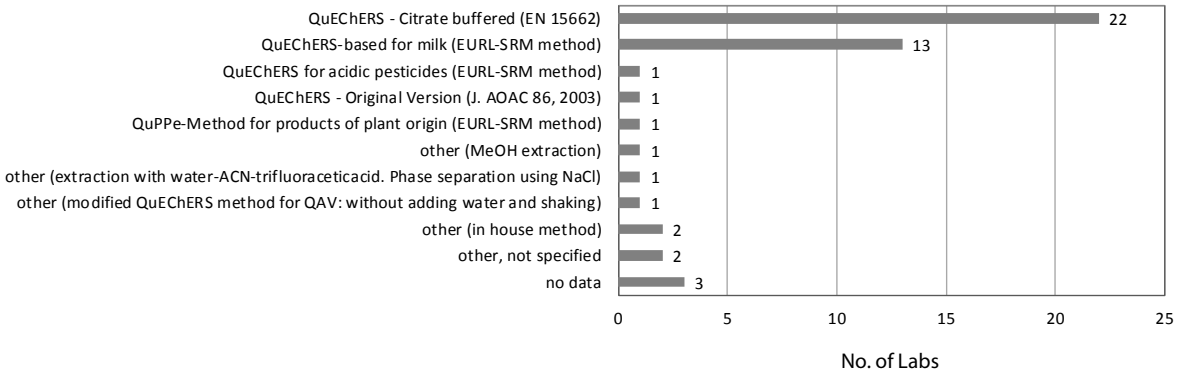
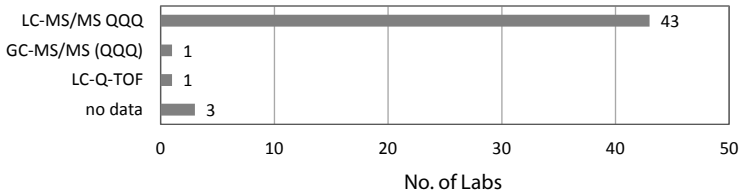


Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs

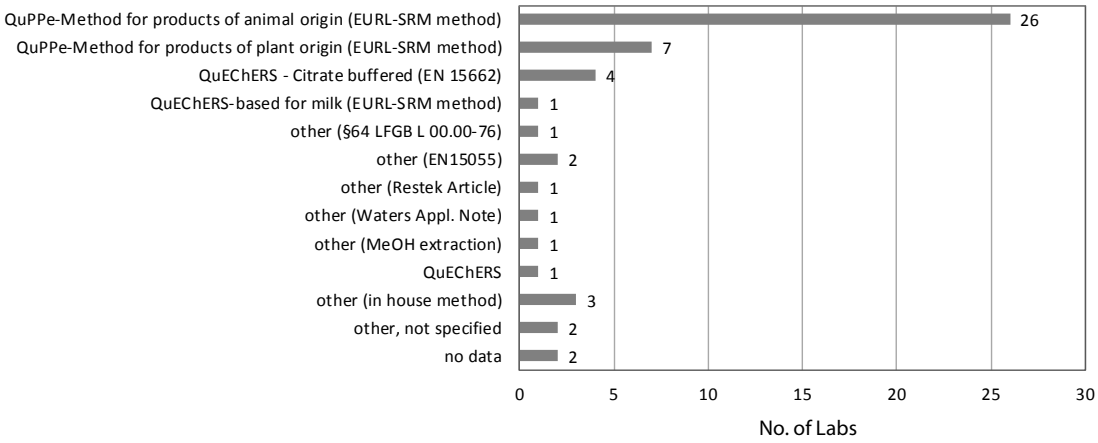
BAC-C14: Sample preparation



BAC-C14: Determinative analysis



Chlormequat: Sample preparation



Chlormequat: Determinative analysis

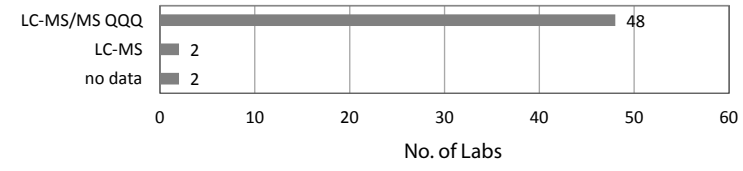
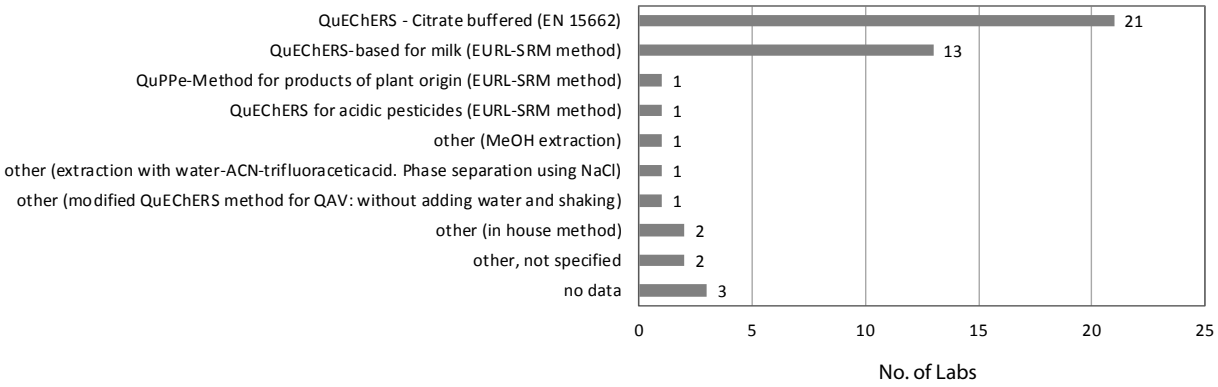


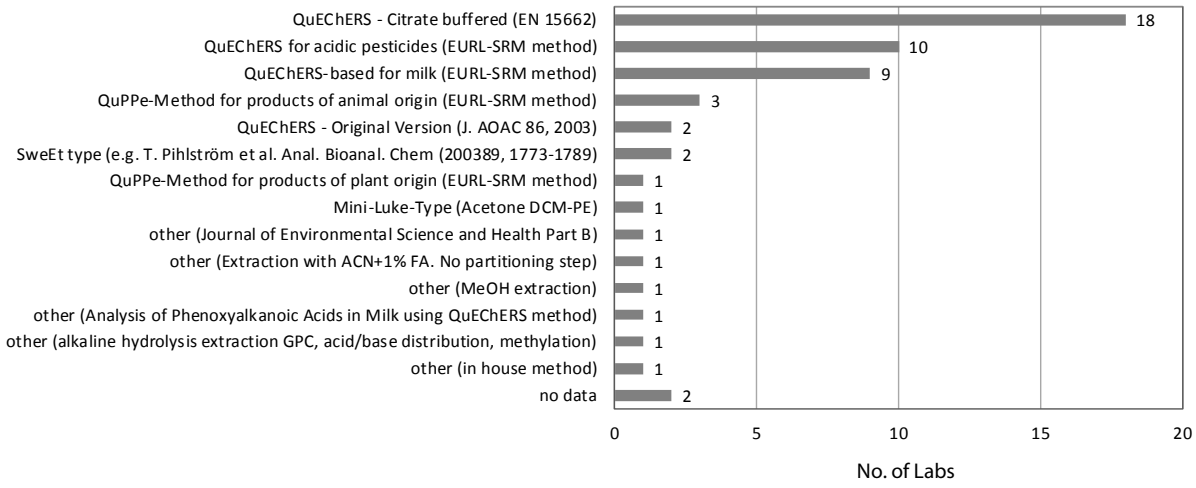
Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs

DDAC-C10: Sample preparation



DDAC-C10: Determinative analysis

Fluazifop: Sample preparation



Fluazifop: Determinative analysis

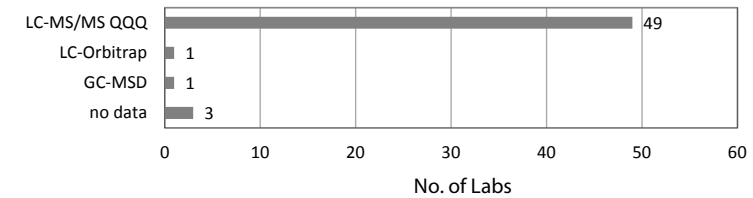
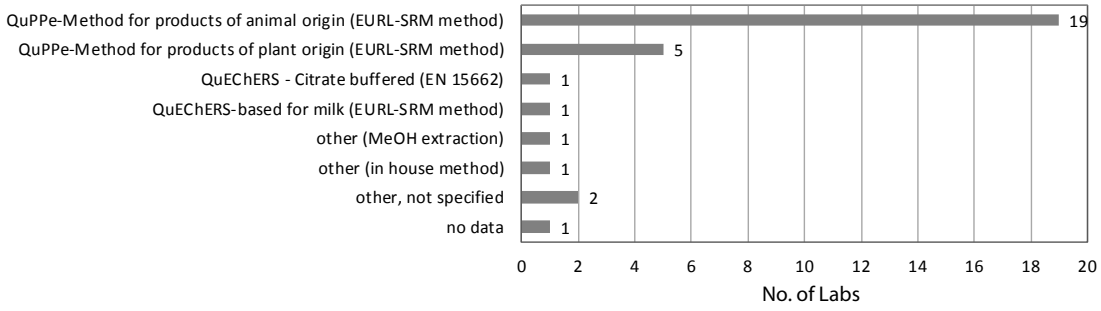
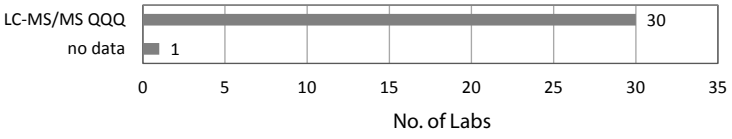


Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs

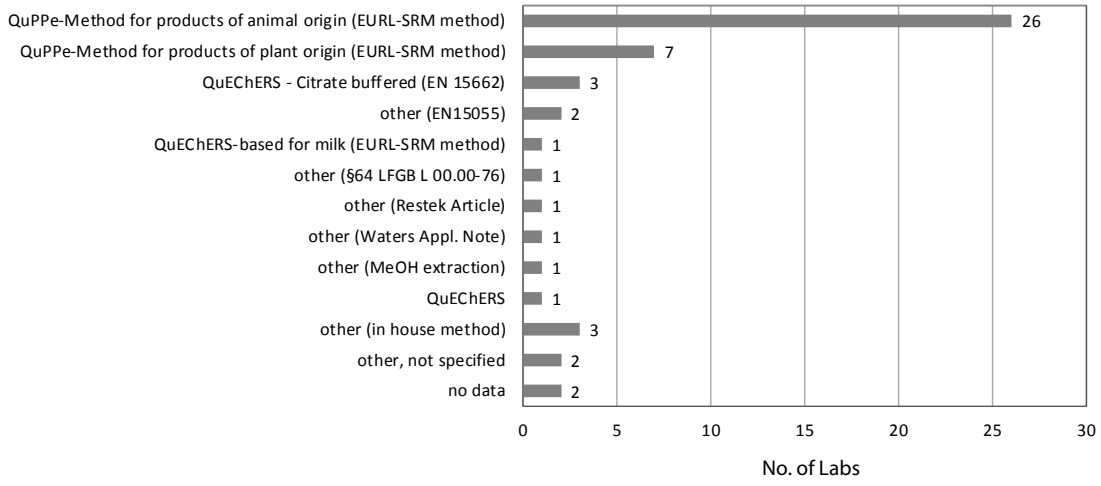
Maleic hydrazide: Sample preparation



Maleic hydrazide: Determinative analysis



Mepiquat: Sample preparation



Mepiquat: Determinative analysis

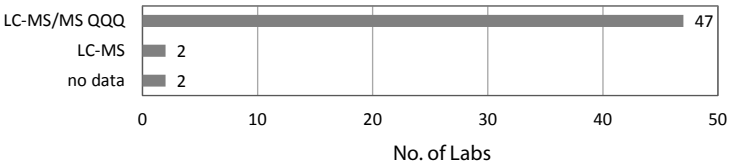
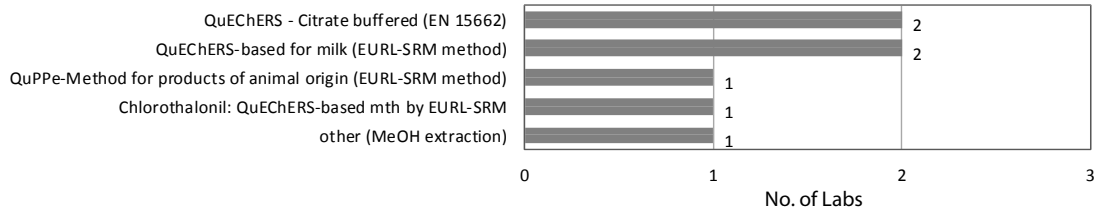


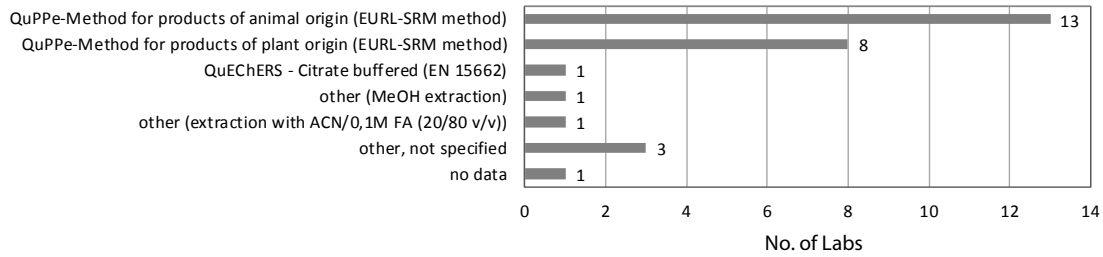
Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs

4-OH-chlorothalonil: Sample preparation

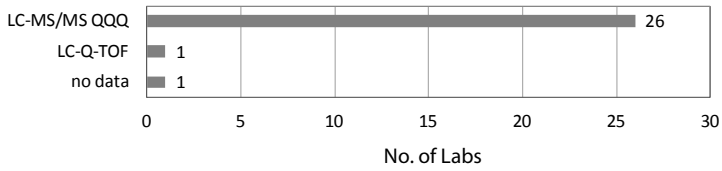


4-OH-chlorothalonil: Determinative analysis

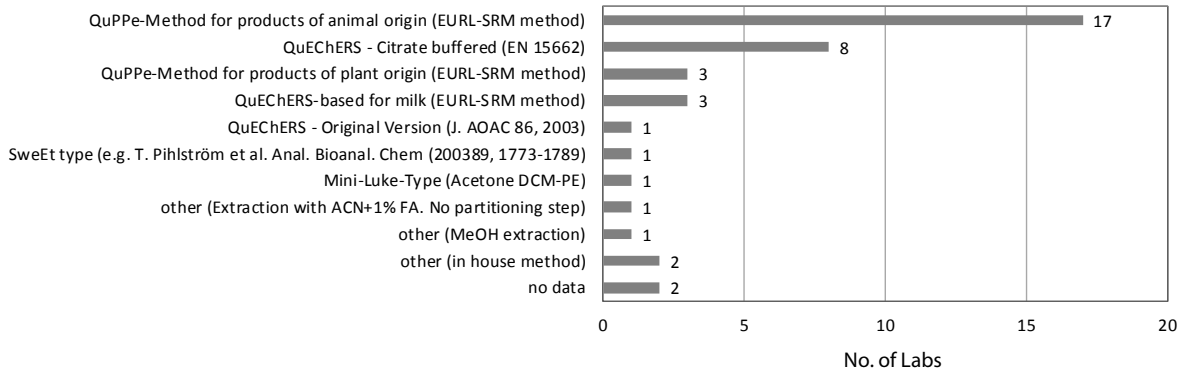
Chlorate: Sample preparation



Chlorate: Determinative analysis



Cyromazine: Sample preparation



Cyromazine: Determinative analysis

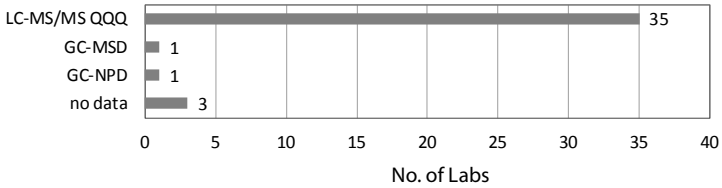
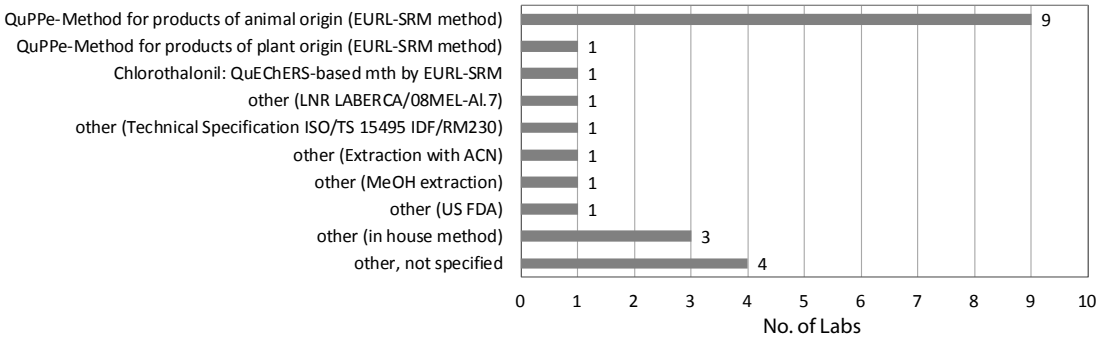
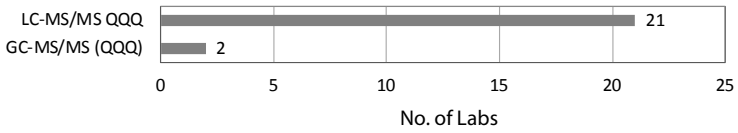


Figure 4-1 (cont.): Methods applied for sample preparation and determinative analysis as reported by labs

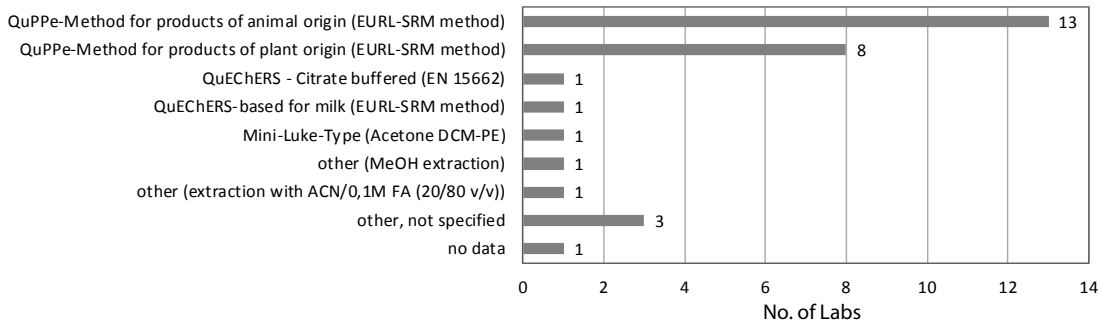
Melamine: Sample preparation



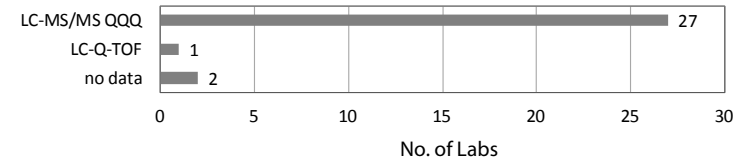
Melamine: Determinative analysis



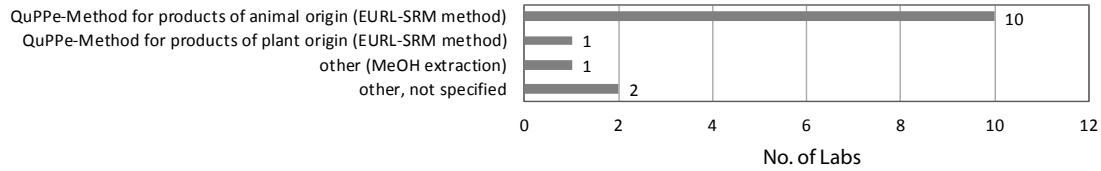
Perchlorate: Sample preparation



Perchlorate: Determinative analysis



Trimesium: Sample preparation



Trimesium: Determinative analysis

Table 4-14: Calibration approaches employed for the analysis of the target compounds of the EUPT-SRM9

Calibration type	COMPULSORY COMPOUNDS	OPTIONAL COMPOUNDS	Overall
Matrix matched	**196 (51 %)**	**72 (51 %)**	**268 (51 %)**
Multiple level	173 (45 %)	68 (48 %)	241 (46 %)
Single level	23 (6.0 %)	4 (2.8 %)	27 (5.1 %)
Pure solvent	**108[1] (28 %)**	**31[2] (22 %)**	**139[3] (26 %)**
Multiple level	100 (26 %)	28 (20 %)	128 (24 %)
Single level	8 (2.1 %)	3 (2.1 %)	11 (2.1 %)
Standard addition	**61 (16 %)**	**32 (23 %)**	**93 (18 %)**
to sample portions	38 (9.9 %)	25 (17.6 %)	63 (12 %)
to extract aliquots	23 (6.0 %)	7 (4.9 %)	30 (5.7 %)
no data	19 (4.9 %)	7 (4.9 %)	26 (4.9 %)
Overall	**384 (100 %)**	**142 (100 %)**	**526 (100 %)**

1) Thereof 27 (22 multiple levels, 5 single level) results obtained by using ILIS
2) Thereof 15 (15 multiple levels, none single level) results obtained by using ILIS
3) Thereof of 42 (37 multiple levels, 5 single level) results obtained by using ILIS

4.4.3 Calibration approaches

Calibration types employed by the various laboratories in this PT are shown in **Table 4-14**. In roughly half of the cases laboratories employed matrix-matched calibrations using the blank matrix provided by the Organisers. The standard additions approach was employed in 18 % of the cases. Calibrations using standard solutions in pure solvent were used in roughly 1 out of 4 cases with ILISs being employed in 27 % of the cases (37 out of 139 cases).

4.4.4 Use of Internal standards (ISs)

ISs are typically applied to correct for recovery, volume deviations and/or to compensate for the influence of matrix on measurement or derivatisation. An overview of the ISs used is shown in **Table 4-15**. In order

Table 4-15: Use of internal standards for the analysis of the compounds in the EUPT-SRM9

	COMPULSORY COMPOUNDS								OPTIONAL COMPOUNDS						
Q: was ISTD used?	**2,4-D**	**BAC-C12**	**BAC-C14**	**Chlormequat**	**DDAC-C10**	**Fluazifop**	**Maleic hydrazide**	**Mepiquat**	**4-OH-chlorothalonil**	**Chlorate**	**Cyromazine**	**Melamine**	**Perchlorate**	**Trimesium**	**Overall**
Yes, isotop. labelled other substance	3 (6 %)	1 (2 %)	2 (4 %)	2 (4 %)	1 (2 %)	5 (9 %)	2 (6 %)	6 (12 %)		2 (7 %)	3 (8 %)	–	1 (3 %)	1 (7 %)	29 (6 %)
Yes, isotop. labelled target pesticide	1 (2 %)	3 (6 %)	2 (4 %)	**28 (54 %)**	3 (7 %)	–	**15 (48 %)**	**24 (47 %)**	–	**15 (54 %)**	9 (23 %)	**12 (52 %)**	**16 (53 %)**	**7 (50 %)**	135 (26 %)
Yes, other	17 (31 %)	14 (29 %)	14 (29 %)	1 (2 %)	13 (28 %)	17 (31 %)	1 (3 %)	1 (2 %)	3 (43 %)	1 (4 %)	7 (18 %)	2 (9 %)	2 (7 %)	1 (7 %)	94 (18 %)
no	**30 (56 %)**	**25 (52 %)**	**25 (52 %)**	18 (35 %)	**24 (52 %)**	**28 (52 %)**	12 (39 %)	17 (33 %)	4 (57 %)	8 (29 %)	**17 (43 %)**	8 (35 %)	8 (27 %)	5 (36 %)	**229 (44 %)**
no data	3 (6 %)	5 (10 %)	5 (10 %)	3 (6 %)	5 (11 %)	4 (7 %)	1 (3 %)	3 (6 %)	–	2 (7 %)	4 (10 %)	1 (4 %)	3 (10 %)	–	39 (7 %)
Overall	**94**	**77**	**92**	**59**	**94**	**49**	**81**	**72**	**14**	**28**	**25**	**25**	**24**	**53**	**838**

to assist the laboratories in the analysis of ***chlorate*** and ***perchlorate***, a solution containing the ILISs of both compounds was provided by the Organiser to the participating laboratories together with short instructions on how to use. As can be seen in **Table 4-15** the percentage of laboratories using ILIS for the analysis of chlorate and perchlorate was the highest exceeding 50 % in both cases.

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 4-16** (**p. 52**).

In 35 % of the 53 cases where results were corrected based on recovery figures the recoveries reported were within the 80 to 120 % range. In more than half of the cases (53 %) the recoveries reported were < 80 %. In 49 out of the 53 cases the respective experiments were conducted within the same batch, using the blank material provided by the Organiser. In the other four cases the correction figures were derived from the same batch using other matrices (3×) or from QC validation data (1×). In 19, 16, 9, 6 and 1 cases the recovery figures used were based on only one, two, three, four or five recovery experiments, respectively. In two cases the recovery figures were obtained from more than 5 replicate recovery experiments. The distribution of the recovery figures are shown in **Figure 4-2**.

Disregarding ***4-OH-chlorothalonil***, for which the z-scores were evaluated for information only, the remaining 52 cases of recovery-based result corrections concerned ***cyromazine*** (9 cases), ***BAC-C12*** (6 cases), ***2,4-D***, ***chlormequat***, ***DDAC-C10*** and ***chlorate*** (each 5 cases), ***BAC-C12*** and ***mepiquat*** (each 4 cases), ***fluazifop*** (3 cases), as well as ***maleic hydrazide***, ***melamine*** and ***perchlorate*** (each 2 cases). In theory correction using a recovery factor will typically lead to a result that is closer to the Assigned Value compared to the results that would have been reported if no recovery correction had been applied. The submitted data support this trend. As shown in **Table 4-17**, laboratories applying a recovery factor were able to "shift" their z-scores from "unacceptable" to "acceptable" levels in 4 cases, from "questionable" to "acceptable" in 9 cases and from "unacceptable" to "questionable" in 1 case. In 36 cases z-scores remained within the "acceptable" range and in 6 cases within the "questionable" range. There were also 2 cases where the z-score paradoxically shifted from "acceptable" to "unacceptable" following the correction for recovery. When comparing the AAZ of

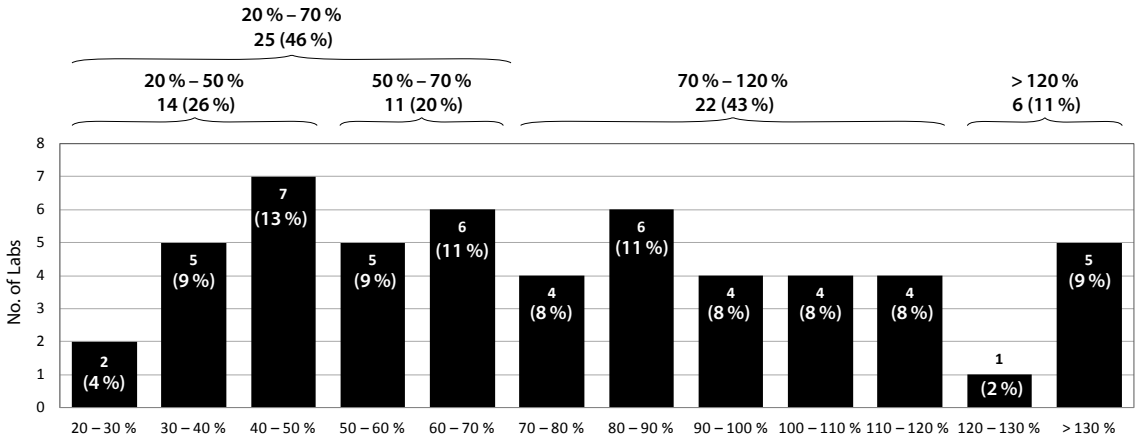


Figure 4-2: Distribution of recovery figures used for results correction for the recovery

Table 4-16: Overview of approaches followed by laboratories for the correction of results for recovery

	COMPULSORY COMPOUNDS								
Q: Are results recovery corrected?	**2,4-D**	**BAC-C12**	**BAC-C14**	**Chlormequat**	**DDAC-C10**	**Fluazifop**	**Maleic hydrazide**	**Mepiquat**	**Overall**
Yes	**19 (35 %)**	**13 (27 %)**	**15 (31 %)**	**30 (58 %)**	**14 (30 %)**	**17 (31 %)**	**17 (55 %)**	**30 (59 %)**	**155 (40 %)**
1): using **recovery figure** (as indicated)	5	**4**	**6**	5	5	3	2	4	34 (8.9 %)
2): autom. via **std. add.** to sample portions	**11**	5	**5**	**3**	5	**9**	1	5	44 (11 %)
3): automatically via **ILIS**		1	1	13	**1**	1	8	**13**	38 (10 %)
4): autom. via **combination of 2) + 3)**		2	2	5	2		4	4	19 (4.9 %)
5): autom. via **procedural calibration**	3	1	1	4	1	4	2	4	20 (5.2 %)
Result was NOT recovery corrected	**35 (65 %)**	**35 (73 %)**	**33 (69 %)**	**22 (42 %)**	**32 (70 %)**	**37 (69 %)**	**12 (39 %)**	**21 (41 %)**	**227 (59 %)**
no data							2		2 (0.5 %)
Overall SUM	**54**	**48**	**48**	**52**	**46**	**54**	**31**	**51**	**384**

	OPTIONAL COMPOUNDS						
Q: Are results recovery corrected?	**4-OH-chlorothalonil**	**Chlorate**	**Cyromazine**	**Melamine**	**Perchlorate**	**Trimesium**	**Sum**
Yes	**6 (86 %)**	**16 (57 %)**	**25 (63 %)**	**17 (74 %)**	**14 (47 %)**	**8 (57 %)**	**86 (61 %)**
1): using **recovery figure** (as indicated)	**1**	**5**	9	2	2		19 (13 %)
2): autom. via **std. add.** to sample portions	3	3	**5**	**3**	**4**	1	19 (13 %)
3): automatically via **ILIS**		3	**5**	**7**	**3**	3	21 (15 %)
4): autom. via **combination of 2) + 3)**		2	3	3	2	2	12 (8.5 %)
5): autom. via **procedural calibration**	2	3	3	2	3	2	15 (11 %)
Result was NOT recovery corrected	**1 (14 %)**	**10 (36 %)**	**15 (38 %)**	**6 (26 %)**	**16 (53 %)**	**5 (36 %)**	**53 (37 %)**
no data		2				1	3 (2.1 %)
Overall SUM	**7**	**28**	**40**	**23**	**30**	**14**	**142**

Table 4-17: Compilation of results where RECOVERY-BASED CORRECTION OF RESULTS was applied and influence on the AAZ-scores (average bias)

Compounds	LabCode SRM9-	Submitted Recovery figure [%]	Recovery Replicates considered	Submitted Result [mg/kg]	z-score derived from submitted result	z-score (if non-corrected results were used)*
2,4-D	18	88.2	4	0.0366	-2.3	-2.5
Assigned Value = 0.088 mg/kg	23	77.6	1	0.068	-0.9	-1.6
	50	198.2	1	0.0951	0.3	4.6
	54	59	1	0.088	0.0	-1.6
	58	23.7	1	0.071	-0.8	-3.2
* Calculated using the current Assigned Values						

Table 4-17 (cont.): Compilation of results where recovery-based correction of results was applied and influence on the AAZ-scores (average bias)

Compounds	LabCode SRM9-	Submitted Recovery figure [%]	Recovery Replicates considered	Submitted Result [mg/kg]	z-score derived from submitted result	z-score (if non-corrected results were used)*
BAC-C12	23	82.4	1	0.110	-2.4	-2.7
Assigned Value = 0.284 mg/kg	50	134.6	1	0.29	0.1	1.5
	60	48.4	3	0.362	1.1	-1.5
	3rd-69	112	2	0.310	0.4	0.9
BAC-C14	23	83.2	1	0.117	-2.3	-2.6
Assigned Value = 0.279 mg/kg	50	128.6	1	0.292	0.2	1.4
	56	75	3	0.278	0.0	-1.0
	60	45.8	3	0.358	1.1	-1.7
	61	66.9	2	0.252	-0.4	-1.6
	3rd-69	90	2	0.330	0.7	0.3
Chlormequat	18	107.5	4	0.116	-1.4	-1.2
Assigned Value = 0.179 mg/kg	23	33.6	1	0.131	-1.1	-3.0
	62	39	2	0.150	-0.7	-2.7
	66	59	3	0.090	-2.0	-2.8
	3rd-71	33	2	0.340	3.6	-1.5
DDAC-C10	23	77.8	1	0.118	-2.2	-2.6
Assigned Value = 0.268 mg/kg	37	107	2	0.272	0.1	0.3
	56	70	3	0.302	0.5	-0.8
	60	45.6	3	0.349	1.2	-1.6
	3rd-69	62	2	0.400	2.0	-0.3
Fluazifop	18	91.5	4	0.0803	-2.1	-2.3
Assigned Value = 0.170 mg/kg	23	87.9	1	0.157	-0.3	-0.7
	3rd-71	183	2	0.290	2.8	8.5
Maleic hydrazide	18	110.5	4	0.192	-1.8	-1.5
Assigned Value = 0.342 mg/kg	23	41.7	1	0.606	3.1	-1.0
Mepiquat	18	106.2	4	0.196	-1.6	-1.5
Assigned Value = 0.333 mg/kg	23	111.2	1	0.290	-0.5	-0.1
	62	52.5	2	0.300	-0.4	-2.1
	3rd-71	43	2	0.360	0.3	-2.1
Chlorate	6	95	>5	0.143	-0.9	1.4
Assigned Value = 0.185 mg/kg	12	59.6	1	0.276	2.0	2.6
	23	147.2	1	0.159	-0.6	5.4
	50	135.5	1	0.186	0.0	6.1
	61	62.6	2	0.236	1.1	1.9
Cyromazine	2	27	1	0.361	2.3	-2.3
Assigned Value = 0.230 mg/kg	18	101.4	4	0.145	-1.5	-1.4
	23	34.1	1	0.220	-0.2	-2.7
	52	43	2	0.285	1.0	-1.9
	56	120	3	0.305	1.3	2.4
	61	49.8	2	0.248	0.3	-1.8
	62	60.7	2	0.190	-0.7	-2.0
	66	56	3	0.275	0.8	-1.3
	3rd-67	36	>5	0.163	-1.2	-3.0
Melamine	20	93	5	0.396	0.3	0.0
Assigned Value = 0.365 mg/kg	3rd-69	84	2	0.280	-0.9	-1.4
Perchlorate	23	100	1	0.126	-1.2	-1.2
Assigned Value = 0.180 mg/kg	56	78	3	0.226	1.0	-0.1
Overall	**20 labs**	**52 cases**	1 repl. (29×) 2 repl. (15×) 3 repl. (9×) 4 repl. (6×) 5 repl. (1×) > 5 repl. (2×)		**AAZ = 1.1** 43× Acceptable 7× Questionable 2× Unacceptable	**AAZ = 1.9** 32× Acceptable 15× Questionable 5× Unacceptable

* Calculated using the current Assigned Values

the recovery-corrected results with the AAZ of the results that would have been submitted if no recovery-based correction had been applied, a significant decline from 1.9 to 1.1 is observed, which translates into a roughly 20 % reduction of the average bias (from approx. 48 % to approx. 28 %). This figure is still higher than the overall AAZ for compulsory compounds (AAZ = 0.75) confirming that result correction via recovery figure is less accurate compared to other types of result correction such as the use of ILISs or standard addition to sample portions (see also comparison of results with and without ILIS under **Table 4-18**). Similar observations were made in the previous EUPT-SRMs (6 – 8).

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

As can be seen in **Figure 4-3** the percentage of participating labs from EU- and EFTA-countries that covered the various compounds in the EUPT-SRM9 Target Pesticides List varied greatly ranging from 48 % (***maleic***

Table 4-18: Impact of ILISs on the distribution of results and the average bias

	Chlormequat			Mepiquat		
	all results	results obtained using ILISs	results obtained without ILISs	all results	results obtained using ILISs	results obtained without ILISs
Robust Mean [mg/kg]	0.179	0.176	0.180	0.333	0.337	0.330
Qn-RSD	19.8 %	**11.3 %**	25.0 %	19.6 %	**11.3 %**	24.8 %
AAZ	0.63	**0.45**	0.73	0.68	**0.60**	0.72
No. of results [1)]	50	18	32	49	17	32
No. (%) of acceptable results	48 (96 %)	17 (94 %)	31 (97 %)	66 (92 %)	16 (94 %)	47 (96 %)
No. (%) of questionable results	2 (4 %)	1 (6 %)	1 (3 %)	4 (6 %)	0 (0 %)	1 (2 %)
No. (%) of unacceptable [1)] results	0 (0 %)	0 (0 %)	0 (0 %)	2 (3 %)	1 (6 %)	1 (2 %)
	Maleic hydrazide					
	all results	results obtained using ILISs	results obtained without ILISs			
Robust Mean [mg/kg]	0.342	0.347	0.330			
Qn-RSD	19.4 %	**11.0 %**	31.8 %			
AAZ	0.94	**0.53**	1.34			
No. of results [1)]	30	15	15			
No. (%) of acceptable results	26 (87 %)	14 (93 %)	12 (80 %)			
No. (%) of questionable results	0 (0 %)	0 (0 %)	0 (0 %)			
No. (%) of unacceptable [1)] results	4 (13 %)	1 (7 %)	3 (20 %)			
	Chlorate			Perchlorate		
	all results	results obtained using ILISs	results obtained without ILISs	all results	results obtained using ILISs	results obtained without ILISs
Robust Mean [mg/kg]	0.185	0.182	0.195	0.180	0.188	0.169
Qn-RSD	17.0 %	**15.4 %**	18.5 %	21.1 %	**13.8 %**	39.6 %
AAZ	0.74	**0.48**	1.05	0.86	**0.50**	1.26
No. of results [1)]	28	15	13	30	16	14
No. (%) of acceptable results	26 (93 %)	15 (100 %)	11 (85 %)	27 (90 %)	16 (100 %)	11 (79 %)
No. (%) of questionable results	0 (0 %)	0 (0 %)	0 (0 %)	2 (7 %)	0 (0 %)	0 (0 %)
No. (%) of unacceptable [1)] results	2 (7 %)	0 (0 %)	2 (15 %)	1 (3 %)	0 (0 %)	3 (21 %)

1) including false negative results

hydrazide) to 82 % (***fluazifop*** and haloxyfop) in the case of compulsory compounds and between 11 % (***4-OH-chlorothalonil***) and 61 % (***cyromazine***) for the optional ones. Calculating based on the full number of labs that were tentatively (n = 132) or finally (n = 91, see **Chapter 3)** considered as being obliged to take part in this test, the percentages lower further.

COMPULSORY compounds included in the routine scope of participating labs were in all cases also targeted by those labs in this exercise (**Table 4-19**). OPTIONAL compounds included in the routine scope of participating labs were in 99 % of the cases also targeted by those labs in this exercise (**Table 4-19**). Only in one case (concerning ***cyromazine***) the compound was not analysed for due to personnel shortage.

In 331 cases the participating laboratories even analysed compounds not yet included in their routine scope, among them 242 cases concerning compulsory compounds and 89 cases concerning optional compounds. This indicates that many labs are in the position or even in the process of expanding their scope with additional SRM-compounds. The compounds most frequently analysed by labs but not yet included in their

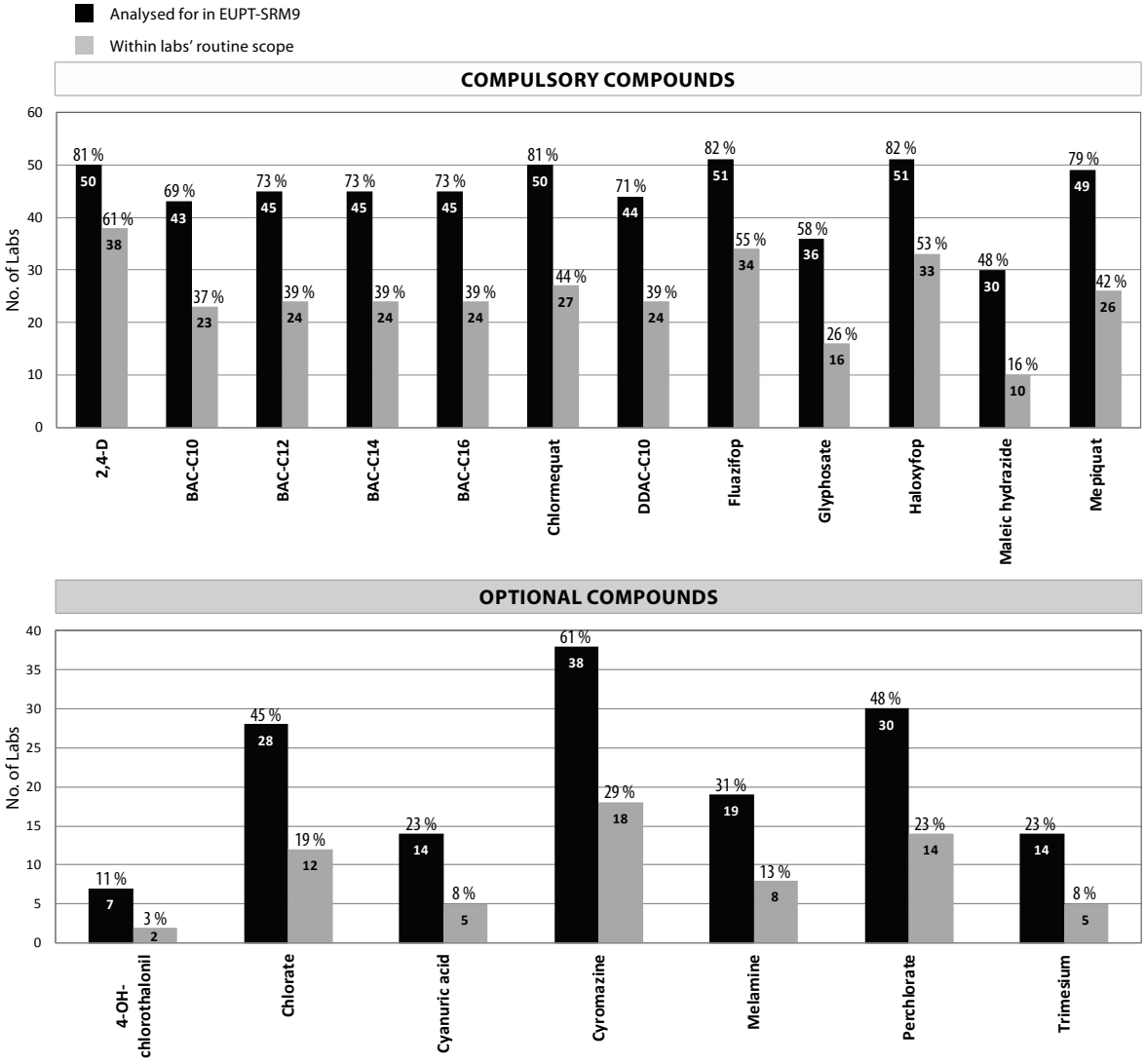


Figure 4-3: Number of laboratories targeting compounds within the framework of the EUPT-SRM9 and within their routine scope. Percentages are based on the total number of participating labs from EU- and EFTA-countries having submitted at least one result (n = 62).

Table 4-19: Inclusion of EUPT-SRM9 compounds in the laboratories' routine scope (including data of laboratories from EU-candidate and third countries)

		within routine scope of lab		NOT within routine scope of lab	
		analysed for in this EUPT	not analysed for	analysed for in this EUPT	not analysed for
COMPULSORY COMPOUNDS	**2,4-D**	42 (100 %)		12 (48 %)	13
	BAC-C10	25 (100 %)		21 (50 %)	21
	BAC-C12	26 (100 %)		22 (54 %)	19
	BAC-C14	26 (100 %)		22 (54 %)	19
	BAC-C16	26 (100 %)		22 (54 %)	19
	Chlormequat	29 (100 %)		23 (61 %)	15
	DDAC-C10	26 (100 %)		20 (49 %)	21
	Fluazifop	35 (100 %)		19 (59 %)	13
	Glyphosate	18 (100 %)		20 (41 %)	29
	Haloxyfop	35 (100 %)		18 (56 %)	14
	Maleic hydrazide	11 (100 %)		20 (36 %)	36
	Mepiquat	28 (100 %)		23 (59 %)	16
	Sum	**327 (100 %)**	**0 (0 %)**	**242 (51 %)**	**235 (49 %)**
OPTIONAL COMPOUNDS	**4-OH-chlorothalonil**	2 (100 %)		5 (8 %)	60
	Chlorate	12 (100 %)		16 (29 %)	39
	Cyanuric acid	5 (100 %)		10 (16 %)	52
	Cyromazine	19 (95 %)	1	21 (45 %)	26
	Melamine	11 (100 %)		12 (21 %)	44
	Perchlorate	14 (100 %)		16 (30 %)	37
	Trimesium	5 (100 %)		9 (15 %)	53
	Sum	**68 (99 %)**	**1 (1 %)**	**89 (22 %)**	**311 (78 %)**

routine scope were ***fluazifop*** and ***mepiquat*** (each 23 labs). On average more than 20 laboratories analysed for the newly introduced quaternary ammonium compounds ***BACs*** and ***DDACs***, even though they were still out of their analytical scope. ***Glyphosate*** and ***maleic hydrazide*** were the two compulsory compounds covered routinely by the least number of participating laboratories (18 and 11 laboratories, respectively). The optional compounds most frequently analysed by labs but not yet included in their routine scope were ***cyromazine*** (21 labs), ***chlorate*** and ***perchlorate*** (16 labs).

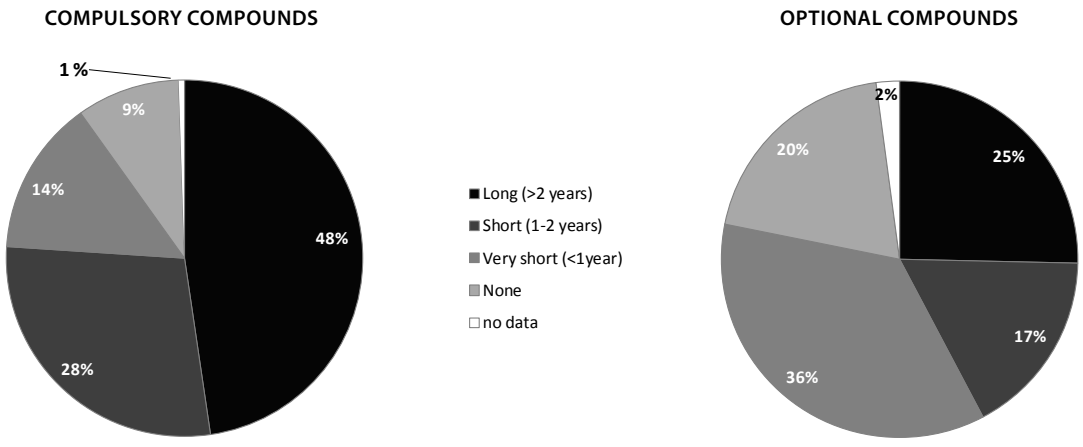


Figure 4-4: Experience of labs with the analysis of pesticides present in the Test Item (overall)

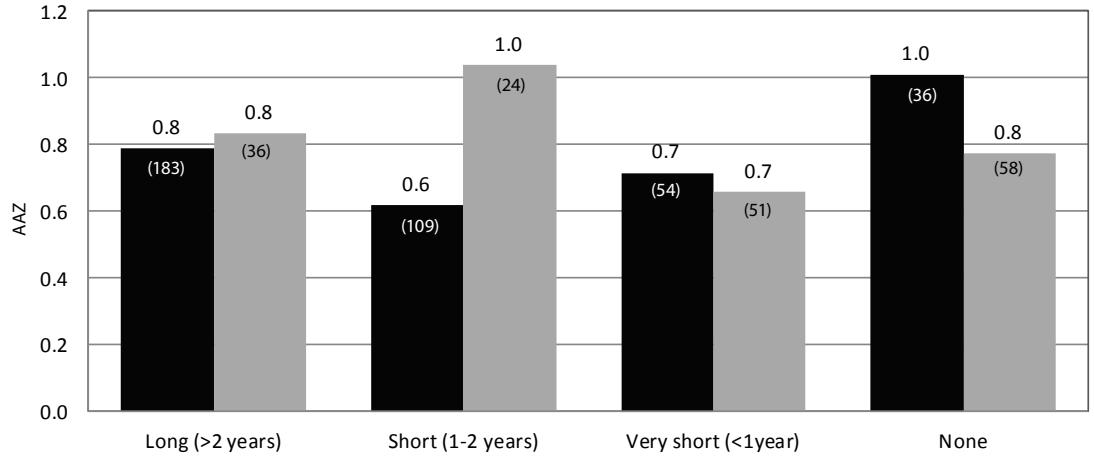


Figure 4-5: Correlation between the labs' experience with the analytes and the AAZ. (No. of data in each case in parentheses)

Regarding compulsory compounds in 48 % of the cases labs indicated more than two years of analytical experience with the compounds that they reported results for (**Figure 4-4**). In 28 % of the cases labs reported short experience (1 – 2 years), in 14 % of the cases they reported experience of less than one year and in 9 % of the cases no experience. Regarding compulsory compounds in 25 % of the cases labs indicated more than two years of analytical experience, in 17 % of the cases labs reported short experience (1 – 2 years), in 36 % of the cases they reported experience of less than one year and in 20 % of the cases no experience.

No clear correlation between AAZ and the experience of the labs with the analysis of the compounds could be observed. (**Figure 4-5**). The small differences observed could also be due to the small number of data involved, the analytical difficulties and the frequency with which the compounds are represented in each group.

Table 4-20 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 ***2,4-D*** is the compound with which labs had the most experience. 42 labs (78 %) indicated more than two years of experience analysing this compound. ***fluazifop*** (74 %) and ***mepiquat*** (67 %) follow. The compounds with which the least laboratories had long-term experience are quaternary ammonium compounds (BACs and DDAC.) Here only 15 % of the labs reported having experience of more than 2 years. But still 63 % of the labs indicated experience between 1 and 2 years for these compounds. This reflects the increased interest among laboratories in the analysis of this compound group and the implementation of an ad-hoc monitoring program specifically for these compounds roughly one-and-a-half years prior to the start of this exercise.

For optional compounds the laboratories reported having overall less analytical experience compared to compulsory compounds. ***Cyromazine*** and its metabolite ***melamine*** were the optional compounds with which the labs had the most experience. The latter is also considered as a contaminant plus a potential adulterant of milk. ***4-OH-chlorothalonil*** was the compound with which the participating labs had the least experience. More than half of the laboratories submitting a result for ***4-OH-chlorothalonil*** had no experience with its analysis. Furthermore, more than 50 % of the labs analysing for ***chlorate*** and ***perchlorate*** and ***trimesium*** indicated analytical experience of less than 1 year.

Table 4-20: Labs' experience with the analysis of individual compounds present in the Test Item and correlation with AAZ (reflecting the average bias from the Assigned Value)

COMPULSORY COMPOUNDS				OPTIONAL COMPOUNDS			
Pesticides	**Experience**	**No. of Labs (%)**	**AAZ**	**Pesticides**	**Experience**	**No. of Labs (%)**	**AAZ**
2,4-D AAZ: 0.7	> 2 years	42 (78 %)	0.7	**4-OH-chlorothalonil** AAZ: 0.5*	> 2 years	1 (14 %)	0.1*
	1 – 2 years	4 (7 %)	0.6		1 – 2 years	1 (14 %)	0.8*
	< 1 year	6 (11 %)	0.5		< 1 year	1 (14 %)	0.3*
	None	2 (4 %)	2.7		None	4 (57 %)	0.6*
BAC-C12 AAZ: 0.7	> 2 years	7 (15 %)	0.8	**Chlorate** AAZ: 0.7	1 – 2 years	5 (18 %)	0.6
	1 – 2 years	30 (63 %)	0.5		< 1 year	14 (50 %)	0.5
	< 1 year	6 (13 %)	0.8		None	7 (25 %)	0.4
	None	5 (10 %)	1.7		no data	2 (7 %)	3.6
BAC-C14 AAZ: 0.7	> 2 years	7 (15 %)	0.7	**Cyromazine** AAZ: 0.9	> 2 years	23 (58 %)	0.9
	1 – 2 years	30 (63 %)	0.5		1 – 2 years	9 (23 %)	1.3
	< 1 year	6 (13 %)	1.5		< 1 year	7 (18 %)	0.6
	None	5 (10 %)	1.1		None	1 (3 %)	1.0
Chlormequat AAZ: 0.7	> 2 years	36 (69 %)	0.8	**Melamine** AAZ: 0.6	> 2 years	10 (43 %)	0.7
	1 – 2 years	4 (8 %)	0.5		1 – 2 years	1 (4 %)	0.8
	< 1 year	8 (15 %)	0.5		< 1 year	7 (30 %)	0.4
	None	4 (8 %)	0.3		None	5 (22 %)	0.6
DDAC-C10 AAZ: 0.7	> 2 years	7 (15 %)	1.0	**Perchlorate** AAZ: 0.9	> 2 years	1 (3 %)	2.9
	1 – 2 years	29 (63 %)	0.6		1 – 2 years	7 (23 %)	0.9
	< 1 year	6 (13 %)	0.6		< 1 year	14 (47 %)	0.5
	None	4 (9 %)	0.8		None	8 (27 %)	1.3
Fluazifop AAZ: 1.0	> 2 years	40 (74 %)	1.0	**Trimesium** AAZ: 1.5*	> 2 years	1 (7 %)	0.1*
	1 – 2 years	5 (9 %)	1.4		1 – 2 years	1 (7 %)	2.2*
	< 1 year	6 (11 %)	1.0		< 1 year	8 (57 %)	1.6*
	None	3 (6 %)	0.7		None	3 (21 %)	0.8*
Maleic hydrazide AAZ: 1.0	> 2 years	10 (32 %)	0.5		no data	1 (7 %)	3.5*
	1 – 2 years	3 (10 %)	2.3				
	< 1 year	8 (26 %)	0.6				
	None	8 (26 %)	0.9				
	no data	2 (6 %)	3.4				
Mepiquat AAZ: 0.7	> 2 years	34 (67 %)	0.7				
	1 – 2 years	4 (8 %)	0.6				
	< 1 year	8 (16 %)	0.5				
	None	5 (10 %)	0.7				

* for informative purpose only

4.4.7 Size of analytical portions

Concerning the compulsory compounds, the size of the analytical portions employed by the participants were in a range from 1 to 25 g for ***2,4-D*** and ***fluazifop***; from 1 to 20 g for ***chlormequat***, and ***mepiquat*** and from 1 to 10 g for ***BAC-C12***, ***BAC-C14***, ***DDAC-C10*** and ***maleic hydrazide*** (**Figure 4-6**). Concerning optional compounds, the size of the analytical portions employed by the participants were in a range from 1 to 30 g for ***cyromazine*** and from 1 to 10 g for ***4-OH-chlorothalonil***, ***chlorate***, ***melamine***, ***perchlorate*** and ***trimesium*** (**Figure 4-6**). There were several cases where the sample portions employed by the laboratories were smaller than those used by the Organisers in the homogeneity test, i.e., 10 g for all compounds. Subsampling (= portion by portion) variability increases as the weight of the analytical portions decreases. Milk

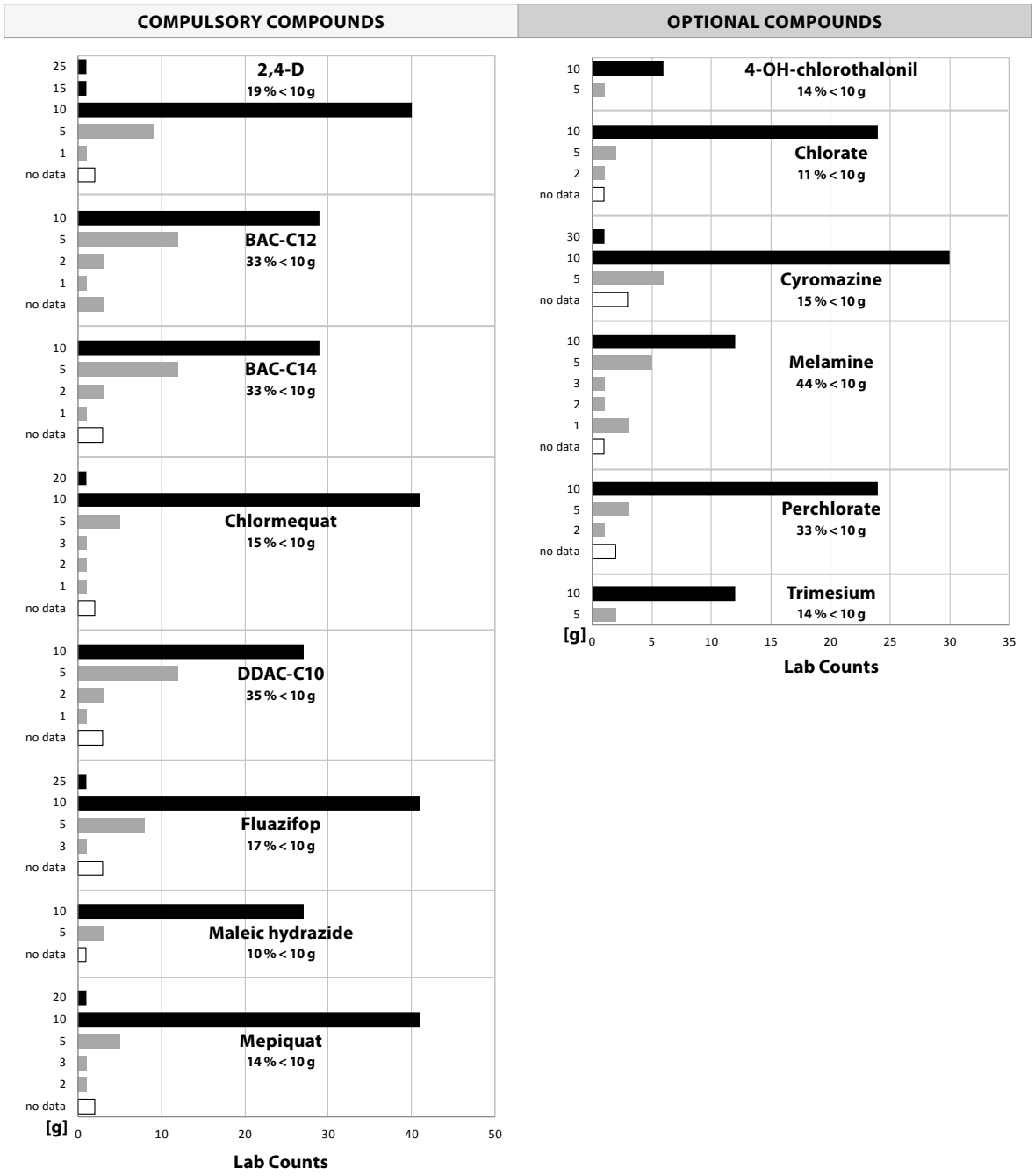


Figure 4-6: Size of analytical portions [g] employed by labs and percentage of analytical portions smaller than those used to test homogeneity by the Organiser.

as matrix can be regarded as very homogenous, however, where the analytical portions employed were significantly smaller than those used in the homogeneity test, sufficient homogeneity cannot be guaranteed. In any case, the Organisers recommended in the Specific Protocol and in a short instruction accompanying the PT-materials thoroughly re-homogenising the entire sample at low temperatures before any analytical portions were taken. If performed, this step might have improved the homogeneity of the subsamples. Nevertheless, the participating labs were informed via the Specific Protocol about the sample size of 10 g employed for the homogeneity test and that sufficient homogeneity cannot be guaranteed when smaller analytical portions were used.

4.4.8 Comparison of Reporting Limits, Assigned Values and MRRLs

Figure 4-7 shows a compilation of the reporting limits (RLs) reported by the labs for each of the compounds present in the Test Item. Except two cases in ***melamine*** all other RLs were clearly lower than the Assigned Values.

Considering only the cases where participants gave details about their reporting limits the laboratories were able to reach the stipulated MRRLs for ***2,4-D***, ***chlormequat*** and ***4-OH-chlorothalonil*** in all cases. In the

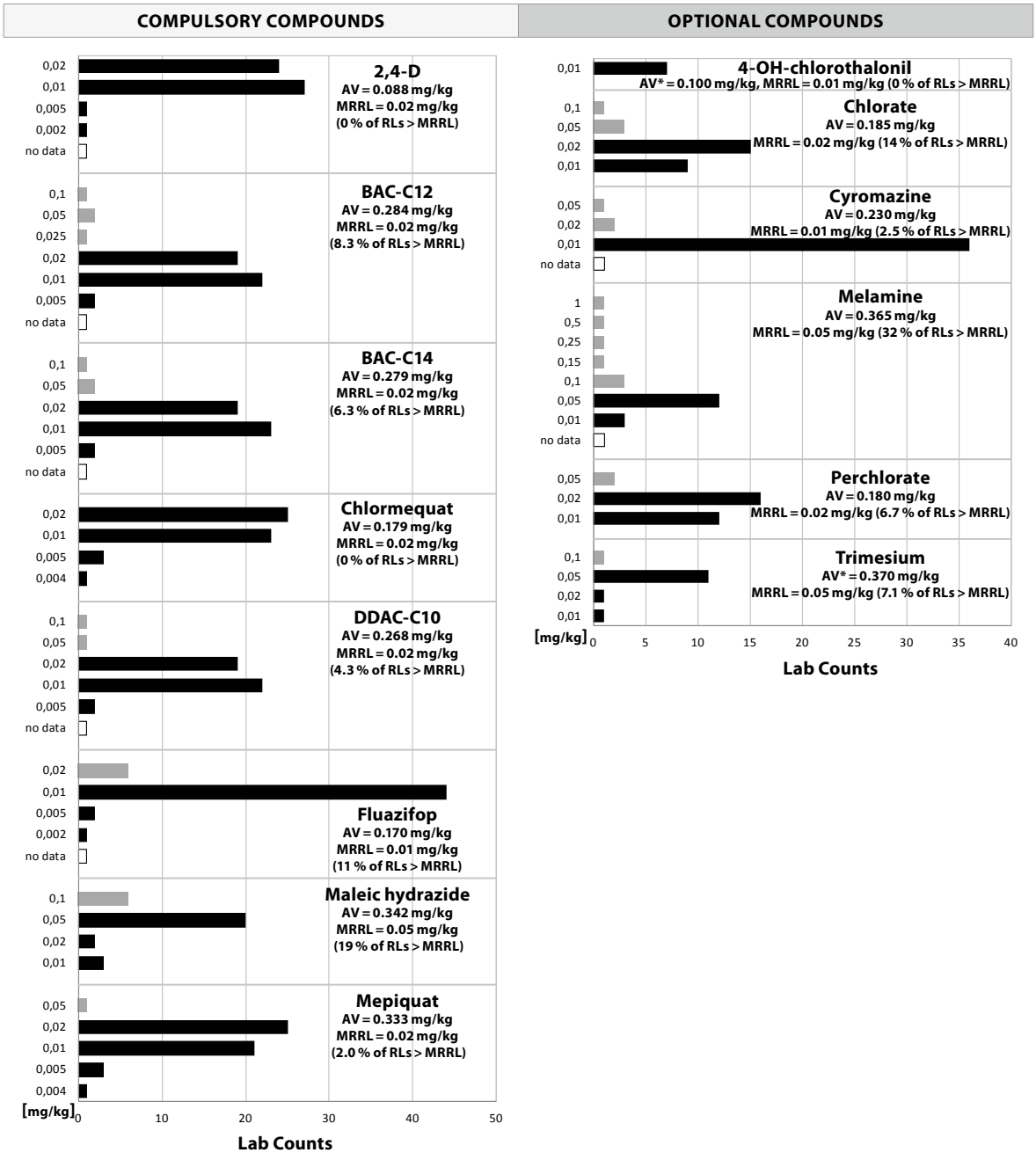


Figure 4-7: Distribution of labs' Reporting Limits [mg/kg] and comparison with the MRRLs and AVs (Assigned Values) set by the Organiser. AV*: Assigned Value for information only

case of compulsory compounds present in the Test Item, the respective MRRLs were not met by only 5.8 % participating laboratories on average and more specifically by 4 labs (8.5 %) in the case of ***BAC-C12***, by 3 labs (6.4 %) in the case of ***BAC-C14***, by 2 labs (4.4 %) in the case of ***DDAC-C10***, and by 1 lab (2 %) in the case of ***mepiquat***. In all these cases the MRRLs were set at 0.02 mg/kg. The MRRL of ***fluazifop*** (0.01 mg/kg) and of ***maleic hydrazide*** (0.05 mg/kg) could not be met by 6 labs each, corresponding to 11 % and 19 %, respectively. Among the optional compounds present in the Test Item, the MRRLs of ***chlorate*** and ***perchlorate*** (0.02 mg/kg) were not met by 4 labs (14 %) and 1 lab (6.7 %), respectively. The MRRLs of ***cyromazine*** (0.01 mg/kg) as well as ***melamine*** and ***trimesium*** (0.05 mg/kg) were not met by 3 labs (2.5 %), 7 labs (32 %) and 1 lab (7 %), respectively.

4.5 Frequent errors and critical points in this PT

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

Application of PSA during dispersive SPE clean up for acidic pesticides: In overall 8 cases laboratories analysing for the acidic pesticides ***2,4-D***, ***fluazifop*** and haloxyfop have employed PSA-sorbent during dispersive SPE clean-up. These were 3 out of 50 EU and EFTA laboratories and 1 of the 4 other laboratories having tested for 2,4-D, 2 out of 51 EU and EFTA laboratories having tested for fluazifop, and 1 out of 51 EU and EFTA laboratories as well as and 1 of the 2 other laboratories having tested for haloxyfop. Compared to previous EUPT-SRMs the number of labs employing PSA in dSPE cleanup has decreased significantly. Repeated communication by the EURL-SRM in EUPT-SRM-reports, EURL-workshops and trainings that PSA has a tendency to remove organic acids from sample extracts and leads to underestimated results for acidic pesticides has contributed to this trend. As the number of labs employing PSA was small, their results were not eliminated prior to calculating the robust means that were used as the Assigned Values.

Hydrolysis step: In overall 8 cases laboratories analysing for the acidic pesticides ***2,4-D***, ***fluazifop*** and haloxyfop conducted an alkaline hydrolysis step. These were 2 out of 50 EU and EFTA laboratories and 1 of the 4 other laboratories having tested for ***2,4-D***, 2 out of 50 EU and EFTA laboratories having tested for ***fluazifop***, and 1 out of 51 EU and EFTA laboratories having tested for haloxyfop. Tests by the Organisers using the EUPT Test Item have shown that alkaline hydrolysis had practically no impact neither in the recoveries of the three acids nor in on the determined haloxyfop, ***fluazifop*** and ***2,4-D*** levels in the Test Item (due to the absence of esters and conjugates). The use of a hydrolysis step was thus superfluous in this particular EUPT, especially as the Target Pesticides List requested only to report the levels of the free acid and it was additionally indicated in a footnote that no alkaline hydrolysis should be conducted. As the impact of hydrolysis on the results was negligible, the 4 results submitted by labs for ***2,4-D*** and ***fluazifop*** employing hydrolysis were not eliminated from the population for establishment of the Assigned Values.

Use of isotopically labelled internal standards (ILIS): The use of ILISs is generally considered as the most effective approach for eliminating all kinds of errors in pesticide residue analysis. Due to their nearly identical behaviour to the native analytes they can effectively compensate for variations in sample extraction and the influence of matrix in LC-MS/MS. As demonstrated in **Table 4-18** in the case of ***chlormequat***, ***mepiquat***, ***maleic hydrazide***, ***chlorate*** and ***perchlorate*** laboratories using ILISs reported results with clearly lower Qn-RSDs and AAZs. Comparing the results of labs having employed ILIS with those of the labs having not employed we see in the case of both ***chlormequat*** and ***mepiquat*** a decrease of the Qn-RSD from 25 % to 11 %, in the case of ***maleic hydrazide*** a decrease from 32 % to 11 %, in the case of ***chlorate*** a decrease from 19 % to 15 %, and in the case of ***perchlorate*** a significant decrease from 40 % to 14 %.

Using ILISs analytical procedures can be considerably simplified by reducing the efforts in cleanup. The analysis of multiple analytes simultaneously is also facilitated as there is less need for individual steps. This ultimately leads to a better efficiency. Wherever possible and feasible, it is thus strongly recommended using ILISs during sample preparation.

4.6 Summary, conclusions and prospects for the SRM pesticides

The EUPT-SRM9 was the 9th scheduled EUPT focusing on pesticides requiring the use of "single" residue methods and the first one using a commodity of animal origin as Test Item.

A total of 64 laboratories representing 25 EU and 2 EFTA countries registered for the EUPT-SRM9, and 62 thereof submitted results. In addition, 4 laboratories from third countries and one from an EU candidate country (Serbia) registered for participation with all of them reporting results. The EU-member states from which no laboratory participated in the EUPT-SRM9 were Bulgaria and Poland. Regarding NRL-SRMs 3 EU-

Table 4-21: Comparison of EUPT-SRMs (Statistical evaluation based on data from laboratories in EU and EFTA countries)

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

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) One compound was not included in the evaluation due to uncertain Assigned Value.
4) 3 of the 8 pesticides were not included in the evaluation.
5) Two compounds were excluded due to uncertain Assigned Value
6) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRM6 – 8.

countries (Poland, Bulgaria and Luxemburg) were not represented, and all of them indicated that commodities of animal origin (including milk) are not part of their analytical scope. The current EUPT-SRM was the first one in which the NRL-SRM from Romania participated. The reason provided to excuse its non-participation in previous EUPT-SRMs was that its scope covers commodities of animal origin only. Malta was represented by the UK NRL-SRM acting as proxy-NRL-SRM for Malta and two additional labs, one in Germany and one in the UK, that are both subcontracted for the analysis of Maltese official controls samples.

Compared to most of the previous EUPT-SRMs the number of labs that participated in this EUPT has declined (**Table 4-21**). It should be considered, however, that the present PT was the first EUPT-SRM with a commodity of animal origin and that both the number of laboratories covering the target analytes in milk was low. It should be noted that participating in EUPTs largely depends on the compounds included in the Target Pesticides List as well as the matrices concerned with the number of participants in EUPT-SRMs based on fruit or vegetables being higher than those based on cereals or feeding stuff. EUPTs entailing target compounds which are included in the scope of many labs, such as dithiocarbamates, also tend to show an increased number of participants (**Table 4-22**). The Organisers would like to appeal to all laboratories

EUPT-	SRM6 (2011)	SRM7 (2012)	SRM8 (2013)	SRM9 (2014)
Matrix of Test Item	Rice flour	Lentil flour	Potato homogenate	Cow's milk
Participants submitting results (EU/EFTA)	77	110	110	62
Participants submitting results (3rd and Candidate Countries)	2	4	6	5
Compounds in Target Pesticide List Compulsory / Optional	13 / –	16 / –	13 / 10	12 / 7
Compounds in Test Item Compulsory / Optional	7 / –	8 [4] / –	8 [5] / 7	8 [5] / 6
No. of results without false positives Compulsory / Optional	291 / –	439 / –	604 / 212	361 / 132
No. of false negative results Compulsory / Optional	5 / –	11 / –	14 / 8	3 / 4
Mean no. of results per lab Compulsory / Optional	3.79 / –	4.12 / –	5.49 / 1.93	5.87 / 2.19
Average of absolute z-scores (AAZ) Compulsory / Optional	0.83 / –	0.97 / –	0.98 / 1.06	0.75 / 0.80
Acceptable z-scores Compulsory / Optional	91 % / –	90 % / –	88 % / 85 %	92 % / 71 %
Questionable z-scores Compulsory / Optional	6 % / –	3 % / –	6 % / 5 %	4 % / 5 %
Unacceptable z-scores Compulsory / Optional (thereof false negatives)	4 % / – (1.7 % / –)	7 % / – (2.1 % / –)	6 % / 10 % (2.2 % / 3.6 %)	4 % / 3,5 % (0.8 % / 2.7 %)
Number of false positives Compulsory / Optional	0	0	2	6
Category A laboratories [6]	25 %	28 %	47 %	52 %
Qn-RSD (average) Compulsory / Optional	23 % / –	27 % / –	26 % / 26 %	19.7 % / 19.4 %

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) One compound was not included in the evaluation due to uncertain Assigned Value.
4) 3 of the 8 pesticides were not included in the evaluation.
5) Two compounds were excluded due to uncertain Assigned Value
6) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM5 were different from those in EUPT-SRMs 6 – 8.

performing official control of commodities of animal origin to gradually expand their scope so that more SRM compounds are covered. Where possible and reasonable, specialized laboratories may be established that cover SRM compounds on a subcontract basis both in commodities of animal and plant origin. Despite the lower number of participating laboratories, the EUPT-SRM9 was the best one since the EUPT-SRM1 as regards the quality of results, as reflected in the average of absolute z-scores (AAZ), the number of laboratories classified into Category A and the average Qn-RSDs (**Table 4-21**). The average of number of results submitted per laboratory was the highest of all EUPT-SRMs.

The Target Pesticide List of EUPT-SRM9 (**Appendix 10**) contained in total 19 SRM-compounds. 12 of them were compulsory and the rest optional for the laboratories in terms of scope. Among the compulsory compounds 6 compounds (***chlormequat***, ***fluazifop***, haloxyfop, ***maleic hydrazide***, glyphosate and ***mepiquat***) were part of the EU multiannual coordinated control program (MACP) for commodities of animal origin, with the latter two were not supposed to be analysed in milk. The compulsory compound ***2,4-D*** was included in the MACP but not for products of animal origin, whereas the 5 quaternary ammonium compounds (BACs and DDAC) were included in an ad-hoc monitoring program initiated by DG-SANCO. The 7 optional compounds (***4-OH-chlorothalonil***, ***chlorate***, cyanuric acid, ***cyromazine***, ***melamine***, ***perchlorate*** and ***trimesium***) were not included in the EU coordinated control program although ***chlorate*** and ***perchlorate*** were part of an ad-hoc monitoring program of the EU. The Test Item itself contained eight compulsory compounds (***2,4-D***, ***BAC-C12***, ***BAC-C14***, ***chlormequat***, ***DDAC-C10***, ***fluazifop***, ***maleic hydrazide*** and ***mepiquat***) and six of the seven optional compounds (***4-OH-chlorothalonil***, ***chlorate***, ***cyromazine***, ***melamine***, ***perchlorate***, and ***trimesium***), whereas ***cyromazine*** was part of the MACP for commodities of plant origin only.

Table 4-22: Number of labs having analysed selected pesticides present in the Test Items of the EUPT-SRMs 1 – 9. Figures in brackets concern the percentage of labs submitting results for a compound out of the total number of labs submitting results (only EU and EFTA labs considered)

EUPT	no. of lab	commodity type	Acidic pesticides					Requiring individual methods		Polar pesticides			Other
			2,4-D	MCPA	MCPP	Haloxyfop	Fluazifop	Bromide	Dithiocarbamates	Chlormequat	Ethephon	Glyphosate	Fenbutatin Oxide
SRM1	24	FV		10 (42 %)						23 (96 %)			5 (21 %)
SRM2	30	CF		23 (77 %)	28 (93 %)					25 (83 %)			
SRM3	66	FV		38 (58 %)			35 (53 %)		59 (89 %)		7 (11 %)		
SRM4	48	CF	33 (69 %)							38 (79 %)		9 (14 %)	
SRM5	81	FV					51 (63 %)		70 (86 %)		28 (35 %)		35 (43 %)
SRM6	77	CF	57 (74 %)			49 (64 %)		34 (44 %)	64 (83 %)		29 (38 %)	35 (43 %)	
SRM7	110	FV	70 (64 %)					44 (40 %)	83 (75 %)		32 (29 %)	39 (35 %)	44 (40 %)
SRM8	110	FV				81 (74 %)						49 (45 %)	59 (54 %)
SRM9	62	AO	50 (81 %)							50 (81 %)			

6 of total 19 compounds in the Target Pesticides List were included for the first time in the EUPT-SRM with 5 of them being present in the Test Item: ***4-OH-chlorothalonil***, ***chlorate***, ***melamine***, ***perchlorate*** and ***trimesium***. With the exception of ***4-OH-chlorothalonil*** all these new compounds were analysed by a sufficient number of labs to allow proper statistical evaluation. ***4-OH-chlorothalonil*** was analysed by only 7 laboratories, and thus not enough for achieving the necessary certainty of the Assigned Value. Assigned Value and z-scores for this compound were thus calculated for information only . Although 13 laboratories have reported results for ***trimesium*** with one false negative result, a reliable estimation of the Assigned Value for further statistical evaluation was still not possible due to the broad distribution of the results. Also here Assigned Value and z-scores were calculated for information only.

Quaternary ammonium compounds, which are, among others, used as disinfection reagents for containers and tubing in the dairy industry, were firstly introduced in EUPT-SRM8 as optional compounds, and in the EUPT-SRM9 as compulsory compounds. The percentage of participating laboratories reporting results for these compounds increased from 48 % in the EUPT-SRM8 to 73 % in EUPT-SRM9.

Chlorate and ***perchlorate*** became an issue of high interest some months before the launch of the EUPT-SRM9. The EURL-SRM had developed an analytical method for both food of animal and plant origin, which was distributed to the labs via the website. To enable simple quantitative analysis the EURL-SRM synthesized an isotope labelled internal standard (ILIS) of both compounds which was provided to the participants of the PT. Both for ***chlorate*** (26 results and 2 false negative results) and ***perchlorate*** (30 results) the results reported were sufficient for the analytical evaluation with good Qn-RSD (17 % and 21 % for ***chlorate*** and ***perchlorate***, respectively).

The robust relative standard deviation (Qn-RSD), reflecting the result-distribution, was calculated for each target analyte. Excluding ***4-OH-chlorothalonil*** and ***trimesium***, the average Qn-RSD was 19.7 % and 19.4 % for compulsory and optional compounds, respectively, and thus clearly lower than the FFP-RSD of 25 % used to calculate the z-scores. The Qn-RSDs of the compulsory compounds were: ***2,4-D*** 18.7 %, ***BAC-C12*** 17.6 %, ***BAC-C14*** 17.9 %, ***Chlormequat*** 19.8 %, ***DDAC-C10*** 18.9 %, ***fluazifop*** 26 %, ***maleic hydrazide*** 19.4 %, and ***mepiquat*** 19.6 %. The Qn-RSDs of the optional compounds were: ***chlorate*** 17.0 %, ***cyromazine*** 29.8 %, melamine 9.6 %, ***perchlorate*** 21.0 %, and ***trimesium*** 30.8 %. For ***4-OH-chlorothalonil*** and ***trimesium*** the Qn-RSD and the Assigned Values were calculated for information only due to not sufficient number of results for statistical evaluation or broad distribution of the results, respectively.

In accordance with the definition in the General EUPT Protocol, z-scores based on the FFP-RSD of 25 % were calculated and classified into “acceptable“, “questionable“, and “unacceptable” for each laboratory/target analyte combination. Overall, the quality of the results was high. Considering only the results reported by laboratories from EU-member states and EFTA countries, in the case of compulsory compounds 47 out of 50 laboratories (94 %) reported results within the acceptable z-score-range for ***2,4-D***, 40 out of 45 (89 %) for ***BAC-C12***, 41 out of 45 (91 %) for ***BAC-C14***, 48 out of 50 (96 %) for ***chlormequat***, 41 out of 44 (93 %) for ***DDAC-C10***, 42 out of 49 (86 %) for glyphosate, 44 out of 51 (86 %) for ***fluazifop***, 26 out of 30 (87 %) for ***maleic hydrazide*** and 47 out of 49 (96 %) for ***mepiquat***. In the case of optional compounds 26 out of 28 laboratories (93 %) submitted results within the acceptable z-score-range for ***chlorate***, 34 out of 38 (89 %) for ***cyromazine***, 18 out of 19 (95 %) for ***melamine***, 27 out of 30 (90 %) for ***perchlorate***.

Considering results reported by all participating laboratories, among the compulsory compounds false negative results were reported in 3 cases for ***maleic hydrazide*** (2×) and ***fluazifop*** (1×). Among the optional compounds false negative results were reported in four cases for ***chlorate*** (2×), ***melamine*** (1×), and ***trimesium*** (1×).

All participating laboratories were classified according to the scope of compulsory pesticides detected during the test following the rules of the General EUPT Protocol. Laboratories correctly detecting at least seven of the eight compulsory pesticides present in the Test Item without reporting any false positive result were qualified for Category A. A total of 32 EU/EFTA-laboratories (52 %) were classified into Category A; the remaining 30 (48 %) laboratories were designated into Category B. Among the participating laboratories from third countries and the EU candidate country, one was classified into Category A and the other 4 into Category B.

Five of the 62 EU labs that finally participated in this EUPT participated on the voluntary basis. The other 57 laboratories represent 43 % of all 132 labs that were tentatively considered as being obliged to participate in this exercise based on their function (NRL-SRM) or scope (routinely analysing official samples for pesticide residues in commodities of animal origin). The most frequent reasons given by labs to explain their non-participation were the following: In case of NRL-SRMs: "commodities of animal origin are not part of the lab's scope", in case a official labs routinely analysing pesticides "the commodity milk is not part of the lab's scope "; "the pesticides in the SRM target list are out of the lab's scope". Excluding those 41 laboratories 91 laboratories tentatively considered to be obliged to participate remained finally as obliged laboratories.

Post PT measures and assistance to the laboratories: Following the distribution of the preliminary results all laboratories achieving questionable or unacceptable z-scores were asked to provide the reasons for this, 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 or detection errors. In certain cases the Organisers have contacted laboratories, asked them for details about the methodology used and given them advice on how to improve in the future. Even if in many cases the laboratories did not give any feedback to the Organiser for their poor performance, the Organiser hopes that every participating laboratory has tried to find out the reason. Only in this way, we can learn from our errors and make improvement in the future.

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

5. ACKNOWLEDGEMENTS

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

6. REFERENCES

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7. APPENDICES

Appendix 1 List of Laboratories registered to participate in the EUPT-SRM9

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

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Austria	AT	Austrian Agency for Health and Food Safety, Institute for Food Safety Innsbruck - Department for Pesticide and Food Analytics	Innsbruck	x	Yes
Belgium	BE	Scientific Institute of Public Health	Brussels	x	Yes
Belgium	BE; FR; LU	Fytolab - Belgium, Gent (Zwijnaarde)	Gent - Zwijnaarde		Yes
Cyprus	CY	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	x	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	Health Board - Tartu Laboratory	Tartu	x	Yes
Finland	FI	Finnish Food Safety Authority	Helsinki	x	Yes
France	FR	ANSES Laboratoire de Maisons-Alfort (Pesticides)	MAISONS-ALFORT	x	Yes
France	FR	CERECO SUD	GARONS		Yes
France	FR	Laboratoire Départemental d`Analyses de la Sarthe, Département de Chimie (INOVALYS 72)	Le Mans		Yes
France	FR	Laboratoire Départemental d`Analyses des Cotes d`Armor	Ploufragan		No
Germany	BE	LUFA-ITL GmbH	Kiel		Yes
Germany	DE	Berlin-Brandenburg State Laboratory, Berlin	Berlin (Mitte)		Yes
Germany	DE	Chemical and Veterinary Analytical Institute Muensterland-Emscher Lippe	Münster		Yes
Germany	DE	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld		Yes
Germany	DE	Chemisches und Veterinäruntersuchungsamt Ostwestfalen-Lippe, Detmold	Detmold		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	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei Mecklenburg-Vorpommern	Rostock		Yes
Germany	DE	Landesuntersuchungsamt Institut für Lebensmittelchemie Speyer	Speyer		Yes
Germany	DE	Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer	Speyer		Yes
Germany	DE	State Institute for Chemical and Veterinary Analysis of Food, Freiburg	Freiburg		Yes
Germany	DE	State Investigation Institute of Health and Veterinary Saxony	Dresden		Yes
Germany	DE	State Laboratory Schleswig-Holstein	Neumünster		Yes
Germany	LT	GALAB Laboratories GmbH - Germany, Hamburg	Hamburg		Yes
Germany	MT	Eurofins - Dr. Specht Laboratorien GmbH	Hamburg		Yes
Greece	GR	Benaki Phytopathological Institute, Pesticide Residues Laboratory	Kifissia	x	Yes
Greece	GR	General Chemical State Laboratory, D Division, Pesticide Residues Laboratory	Athens	x	Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-environment - Pesticide Analytical Laboratory, Velence	Velence		Yes
Hungary	HU	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Miskolc	Miskolc	x	Yes

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

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

Country (Location)	Analysed on behalf of	Institution	City	NRL*-SRM	Reported results
Ireland	IE	Pesticide Control Laboratory, Department of Agriculture, Fisheries and Food	Co. Kildare	x	Yes
Italy	IT	APPA Bolzano	Bolzano		Yes
Italy	IT	ARPA EMILIA ROMAGNA, AREA FITOFARMACI	Ferrara		No [1)]
Italy	IT	ARPA VENETO DIP.REG.LAB. S.L. VERONA	Verona		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 Contaminanti Ambientali - Istituto Zooprofilattico Sperimentale Umbria e Marche	Perugia		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
Netherlands	BE	Groen Agro Control	Delfgauw		Yes
Netherlands	BE	Eurofins Lab Zeeuws-Vlaanderen (LZV) B.V.	Graauw		Yes
Netherlands	NL	NVWA - Netherlands Food and Consumer Product Safety Authority	Wageningen	x	Yes
Netherlands	NL	RIKILT Institute of Food Safety (Natural Toxins & Pesticides)	Wageningen		Yes
Norway	NO	Norwegian Institute for Agricultural and Environmental Research, Plant Health and Plant Protection Division, Pesticide Chemistry Section	Aas		Yes
Portugal	PT	Regional Laboratory of Veterinary and Food Safety - Madeira Island	Funchal - Madeira Island	x	Yes
Romania	RO	Institute for Hygiene and Veterinary Public Health - Bucharest	Bucharest	x	Yes
Slovakia	SK	State Veterinary and Food Institute Bratislava	Bratislava	x	Yes
Slovenia	SI	National Laboratory of Health, Environment and Foodstuffs - Maribor	Maribor	x	Yes
Spain	ES	Analytica Alimentaria GmbH Sucursal España	Almeria		Yes
Spain	ES	Laboratorio de Salud Pública de Cuenca	Cuenca		Yes
Spain	ES	Laboratorio de Salud Pública de Lugo	Lugo		Yes
Spain	ES	Laboratorios Ecosur, S.A.L.	Lorquí (Murcia)		Yes
Spain	ES	National Centre for Food - Spain, Majadahonda	Majada-honda	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	Laboratory of the Government Chemist - Teddington	Teddington		Yes
United Kingdom	UK; MT	The Food and Environment Research Agency - York	York	x	Yes

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

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

Country	Institution	City	Reported results
Australia	National Measurement Institute, Australia	Port Melbourne	Yes
Egypt	Central Lab of Residue Analysis of Pesticides and Heavy Metals in Foods	Giza	Yes
Serbia	SP LABORATORY	BECEJ	Yes
Singapore	Veterinary Public Health Laboratory	Singapore	Yes
United States of America	Eurofins Central Analytical Laboratories	New Orleans, Louisiana	Yes

Appendix 2 Shipment evaluation

(a): 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
AT	29.04.2014 10:30	No		Yes	No		
AU	02:05:2014 14:08	Yes	1 h	No	Yes	100 %	2 – 4 °C
BE	29.04.2014 10:30	No		Yes	No		
BE	29.04.2014 11:30	No		Yes	No		
CH	29.04.2014 12:15	No		Yes	No		
CY	30.04.2014 09:00	No		No	No		2 °C (approximately)
CZ	29.04.2014 13:00	No		Yes	No		
CZ	29.04.2014 10:50	No		Yes	No		
DE	29.04.2014 09:30	No		Yes	No		
DE	29.04.2014 08:30	No		Yes	No		
DE	29.04.2014 08:30	No		Yes	No		
DE	29.04.2014 13:20	No		Yes	No		
DE	29.04.2014 08:45	No		Yes	No		
DE	29.04.2014 09:15	Yes	30 min	Yes	No		
DE	29.04.2014 15:20	No		Yes	No		
DE	29.04.2014 12:00	No		Yes	No		
DE	29.04.2014 -	Yes	1 h	Yes	No		
DE	29.04.2014 11:00	No		Yes	No		
DE	29.04.2014 11:15	Yes	2 h	Yes	No		
DE	29.04.2014 09:40	No		Yes	No		
DK	29.04.2014 10:30	Yes	in refrigerator < 20 min	Yes	No		
DK	30.04.2014 14:45	Yes	28 h	No	No		
ES	30.04.2014 -			No			
FR	29.04.2014 10:30	No		Yes	No		
GR	29.04.2014 12:02	No		Yes	No		
HU	29.04.2014 11:31	No		Yes	No		
HU	29.04.2014 15:27	No		Yes	No		
IE	30.04.2014 10:30	No		No	No		
IT	07.05.2014 [1)]	No		No	Yes	1 %	
IT	29.04.2014 14:30	No		Yes	No		
IT	29.04.2014 16:30	Yes	1.5 h	No	No		
LT	29.04.2014 13:00	No		Yes	No		

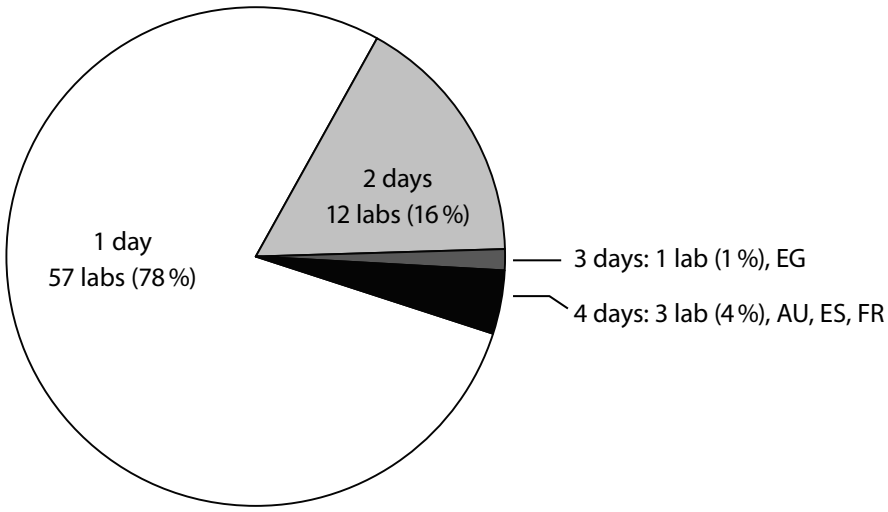
Appendix 2 (cont.) Shipment evaluation

(a) (cont.) : Condition of packages on arrival

Country	Answer to questions (s. above)						
	1 (Date; hh:mm CET)	2	3	4	5	6	7
LV	29.04.2014 16:00	No		Yes	No		
NL	29.04.2014 12:30	No		Yes	No		
NL	29.04.2014 -	No		Yes	No		
NL	29.04.2014 10:35	No		Yes	No		
NO	29.04.2014 12:50	Yes	in cool room 40 min	Yes	No		
PT	07.05.2014* 10:00	No		No [2)]	No		
RO	30.04.2014 15:00	No		No	No		
SE	29.04.2014 14:08	No		Yes	No		
SE	29.04.2014 -	No		Yes	No		
SG	02.05.2014	Yes	> 48 h		No		
SK	29.04.2014 12:50	No		Yes	No		
US	30.04.2014 17:00	No		No	Yes	90 %	4.3 °C

1) The first shipment took 4 days and arrived in unsatisfactory state, and the Organiser provided the second shipment .
2) Shipment without dry ice, but the samples arrived 100% deep frozen

(b): Compilation of duration of shipment



Appendix 3 Data of homogeneity test

COMPULSORY COMPOUNDS								
	2,4-D		BAC-C12		BAC-C14		Chlormequat	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 007	0.089	0.080	0.276	0.244	0.299	0.268	0.201	0.214
No. 011	0.087	0.094	0.292	0.307	0.312	0.295	0.173	0.173
No. 019	0.087	0.094	0.276	0.295	0.277	0.293	0.162	0.186
No. 025	0.081	0.103	0.269	0.340	0.275	0.320	0.166	0.174
No. 032	0.080	0.080	0.258	0.262	0.275	0.278	0.178	0.162
No. 040	0.088	0.080	0.282	0.267	0.293	0.291	0.178	0.178
No. 058	0.091	0.072	0.297	0.235	0.308	0.228	0.181	0.165
No. 069	0.094	0.075	0.301	0.248	0.297	0.273	0.161	0.168
No. 074	0.069	0.072	0.213	0.226	0.230	0.227	0.186	0.177
No. 097	0.095	0.104	0.298	0.335	0.271	0.339	0.172	0.170
mean / AV*	0.086 / 0.088		0.276 / 0.284		0.282 / 0.279		0.176 / 0.179	
	DDAC-C10		Fluazifop		Maleic hydrazide		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. 007	0.281	0.252	0.182	0.167	0.405	0.443	0.409	0.435
No. 011	0.296	0.329	0.188	0.196	0.358	0.336	0.349	0.341
No. 019	0.269	0.301	0.181	0.196	0.354	0.360	0.296	0.369
No. 025	0.263	0.317	0.174	0.215	0.344	0.355	0.345	0.337
No. 032	0.249	0.257	0.166	0.168	0.370	0.340	0.357	0.315
No. 040	0.284	0.273	0.180	0.166	0.379	0.376	0.349	0.342
No. 058	0.298	0.240	0.192	0.142	0.366	0.303	0.361	0.314
No. 069	0.316	0.241	0.206	0.160	0.317	0.342	0.301	0.340
No. 074	0.233	0.231	0.148	0.148	0.399	0.344	0.378	0.351
No. 097	0.292	0.349	0.201	0.215	0.332	0.323	0.317	0.311
mean / AV*	0.279 / 0.268		0.180 / 0.170		0.357 / 0.342		0.346 / 0.333	

OPTIONAL COMPOUNDS								
	4-OH-chlorothalonil		Chlorate		Cyromazine		Melamine	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
No. 007	0.088	0.077	0.185	0.197	0.289	0.297	0.399	0.410
No. 011	0.086	0.089	0.158	0.155	0.248	0.248	0.333	0.333
No. 019	0.083	0.088	0.135	0.178	0.215	0.239	0.289	0.367
No. 025	0.081	0.099	0.152	0.149	0.225	0.245	0.320	0.321
No. 032	0.078	0.078	0.161	0.138	0.247	0.202	0.350	0.297
No. 040	0.084	0.075	0.165	0.164	0.261	0.265	0.339	0.346
No. 058	0.088	0.067	0.165	0.155	0.262	0.238	0.349	0.322
No. 069	0.091	0.072	0.145	0.157	0.218	0.256	0.292	0.336
No. 074	0.069	0.069	0.185	0.154	0.273	0.240	0.352	0.332
No. 097	0.092	0.096	0.151	0.150	0.243	0.245	0.334	0.314
mean / AV*	0.082 / 0.100#		0.160 / 0.230		0.248 / 0.230		0.337 / 0.365	
	Perchlorate		Trimesium					
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]				
No. 007	0.174	0.191	0.394	0.403				
No. 011	0.162	0.155	0.344	0.336				
No. 019	0.141	0.182	0.313	0.373				
No. 025	0.148	0.152	0.312	0.319				
No. 032	0.165	0.152	0.345	0.324				
No. 040	0.168	0.166	0.360	0.348				
No. 058	0.161	0.150	0.342	0.325				
No. 069	0.145	0.160	0.314	0.351				
No. 074	0.177	0.158	0.367	0.336				
No. 097	0.160	0.154	0.322	0.316				
mean / AV*	0.161 / 0.180		0.342 / 0.370#					

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

for information only

Appendix 4 Data of stability test

COMPULSORY COMPOUNDS												
	2,4-D			BAC-C12			BAC-C14			Chlormequat		
	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014
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. 007	0.085	0.098	0.085	0.281	0.322	0.274	0.283	0.304	0.260	0.204	0.181	0.179
No. 032	0.087	0.079	0.077	0.264	0.262	0.264	0.277	0.260	0.247	0.164	0.157	0.172
No. 074	0.072	0.076	0.071	0.228	0.243	0.241	0.228	0.231	0.226	0.177	0.206	0.156
Mean [mg/kg]	**0.081**	**0.084**	**0.078**	**0.258**	**0.276**	**0.259**	**0.263**	**0.265**	**0.244**	**0.182**	**0.181**	**0.169**
RSD* [%]	**9.76 %**	**14.03 %**	**9.12 %**	**10.60 %**	**14.78 %**	**6.39 %**	**11.50 %**	**13.87 %**	**7.08 %**	**11.15 %**	**13.50 %**	**6.98 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**3.84 %**	**-4.23 %**	**—**	**7.08 %**	**0.72 %**	**—**	**0.98 %**	**-7.02 %**	**—**	**-0.40 %**	**-7.02 %**
	DDAC-C10			**Fluazifop**			**Maleic hydrazide**			**Mepiquat**		
	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014
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. 007	0.267	0.302	0.284	0.178	0.210	0.183	0.367	0.335	0.341	0.407	0.398	0.357
No. 032	0.253	0.257	0.264	0.172	0.169	0.172	0.263	0.303	0.330	0.309	0.315	0.346
No. 074	0.232	0.241	0.241	0.160	0.144	0.155	0.335	0.351	0.306	0.350	0.348	0.328
Mean [mg/kg]	**0.251**	**0.266**	**0.263**	**0.170**	**0.174**	**0.170**	**0.322**	**0.330**	**0.326**	**0.355**	**0.354**	**0.343**
RSD* [%]	**7.12 %**	**11.83 %**	**8.24 %**	**5.55 %**	**19.13 %**	**8.15 %**	**16.57 %**	**7.34 %**	**5.35 %**	**13.87 %**	**11.82 %**	**4.19 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**6.34 %**	**4.87 %**	**—**	**2.70 %**	**0.14 %**	**—**	**2.39 %**	**1.14 %**	**—**	**-0.42 %**	**-3.33 %**

OPTIONAL COMPOUNDS												
	4-OH-chlorothalonil			Chlorate			Cyromazine			Melamine		
	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014
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. 007	0.082	0.096	0.081	0.191	0.199	0.179	0.275	0.257	0.266	0.378	0.410	0.346
No. 032	0.078	0.078	0.077	0.150	0.160	0.168	0.227	0.226	0.275	0.311	0.303	0.333
No. 074	0.069	0.068	0.070	0.170	0.185	0.160	0.238	0.308	0.249	0.377	0.373	0.310
Mean [mg/kg]	**0.076**	**0.081**	**0.076**	**0.170**	**0.181**	**0.169**	**0.247**	**0.264**	**0.263**	**0.355**	**0.362**	**0.330**
RSD* [%]	**9.06 %**	**18.10 %**	**7.40 %**	**12.21 %**	**11.08 %**	**5.78 %**	**10.28 %**	**15.80 %**	**5.02 %**	**10.77 %**	**14.97 %**	**5.57 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**5.40 %**	**-0.27 %**	**—**	**6.66 %**	**-0.59 %**	**—**	**6.90 %**	**6.63 %**	**—**	**1.85 %**	**-7.18 %**

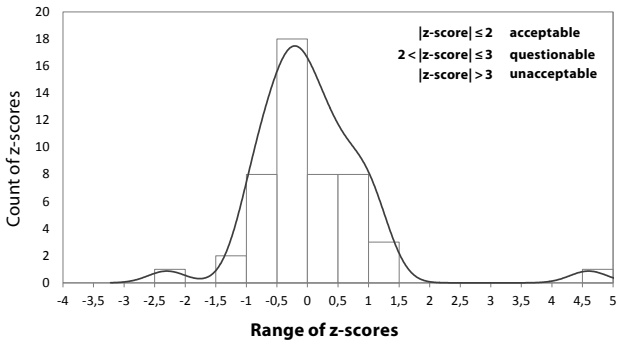
	Perchlorate			Trimesium		
	22.04.2014	14.05.2014	16.06.2014	22.04.2014	14.05.2014	16.06.2014
Sample	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
No. 007	0.183	0.194	0.182	0.359	0.396	0.375
No. 032	0.159	0.157	0.171	0.321	0.324	0.354
No. 074	0.168	0.192	0.162	0.347	0.370	0.348
Mean [mg/kg]	**0.170**	**0.181**	**0.172**	**0.342**	**0.363**	**0.359**
RSD* [%]	**7.15 %**	**11.58 %**	**5.65 %**	**5.60 %**	**9.98 %**	**3.87 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**6.77 %**	**1.18 %**	**—**	**6.19 %**	**4.92 %**

***** RSD = relative standard diviation

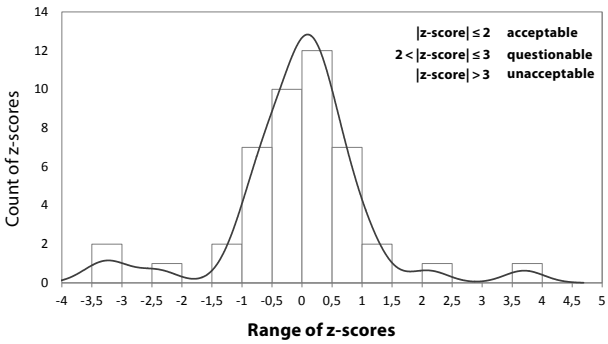
Appendix 5 Histograms and kernel density estimates of z-scores* distribution

Compulsory compounds

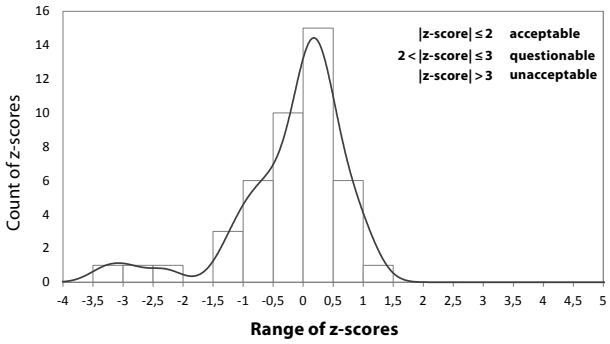
2,4-D



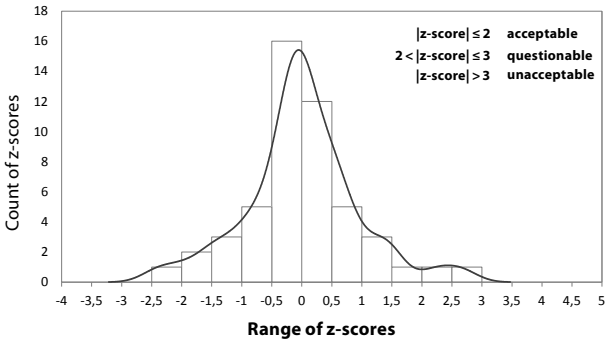
BAC-C12



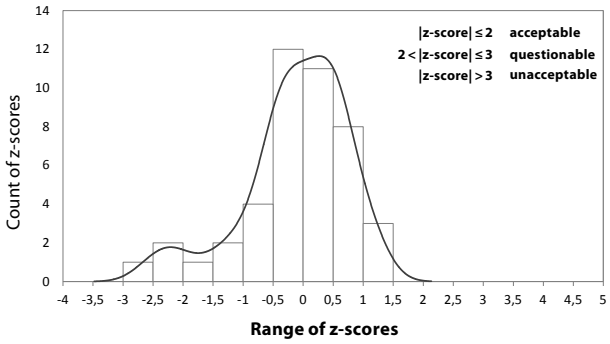
BAC-C14



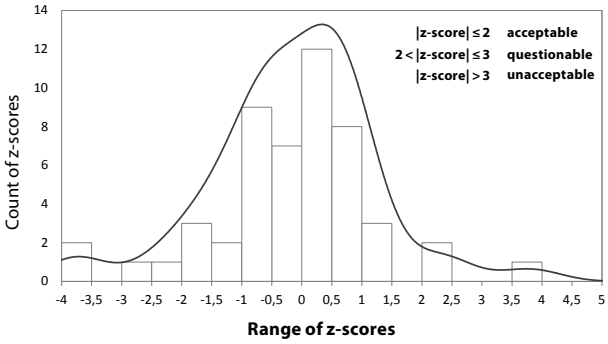
Chlormequat



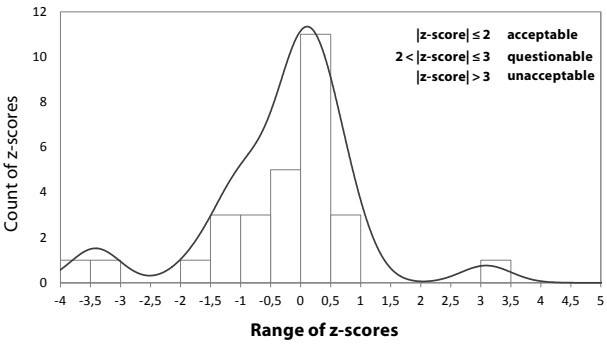
DDAC-C10



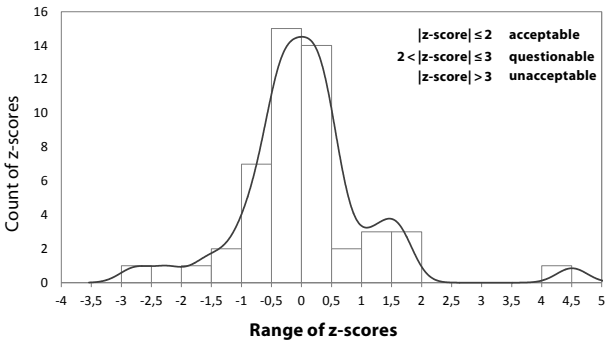
Fluazifop



Maleic hydrazide



Mepiquat

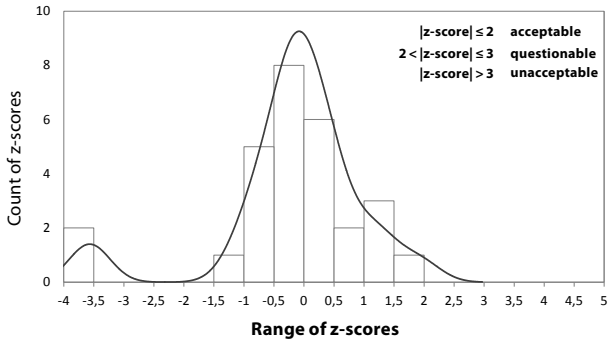


* Cut-off at z-score = 5

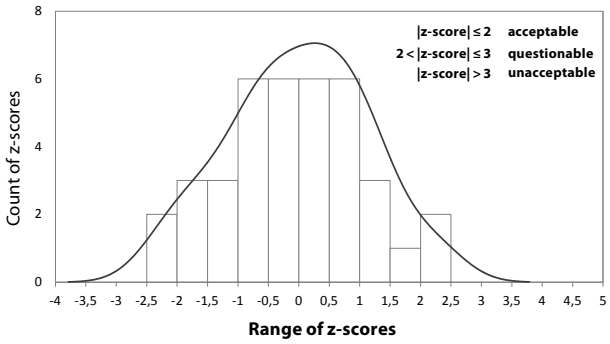
Appendix 5 (cont.) Histograms and kernel density estimates of z-scores* distribution

Optional compounds

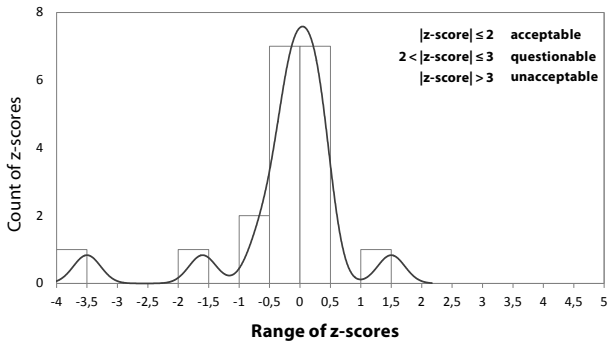
Chlorate



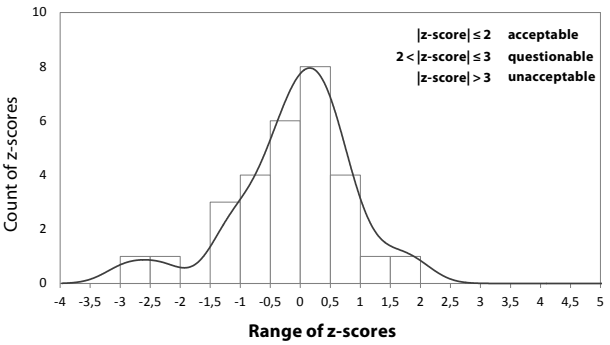
Cyromazine



Melamine

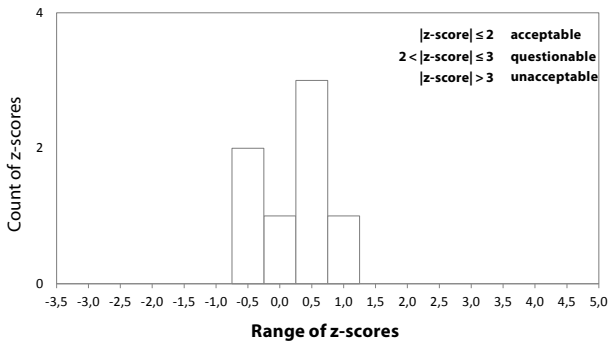


Perchlorate

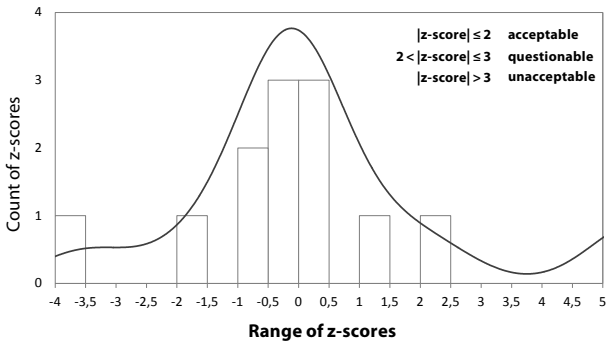


Optional compounds, informative only

4-OH-chlorothalonil



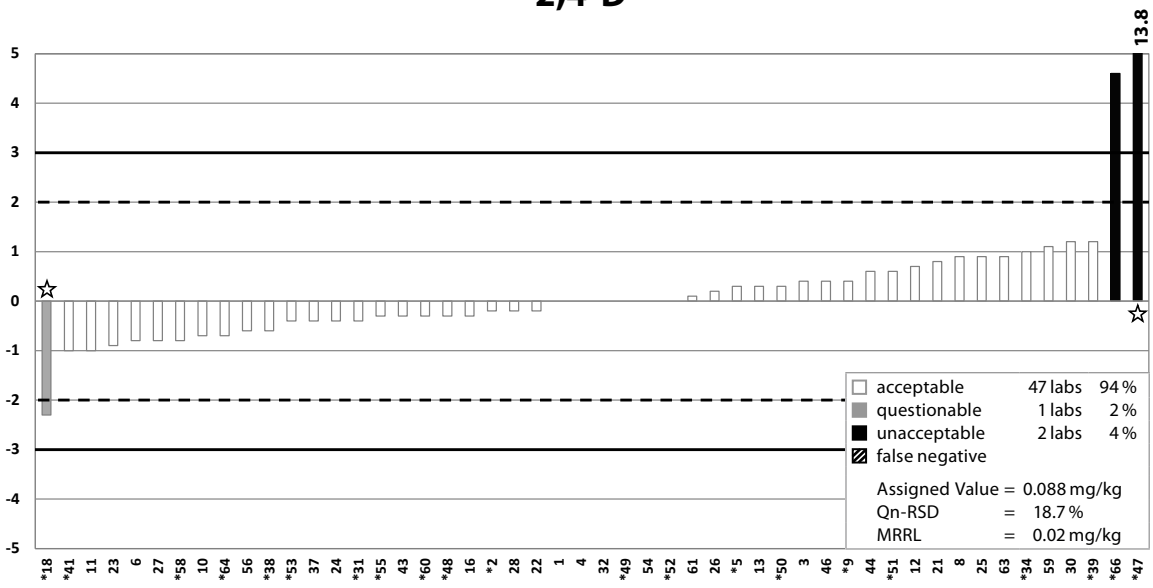
Trimesium



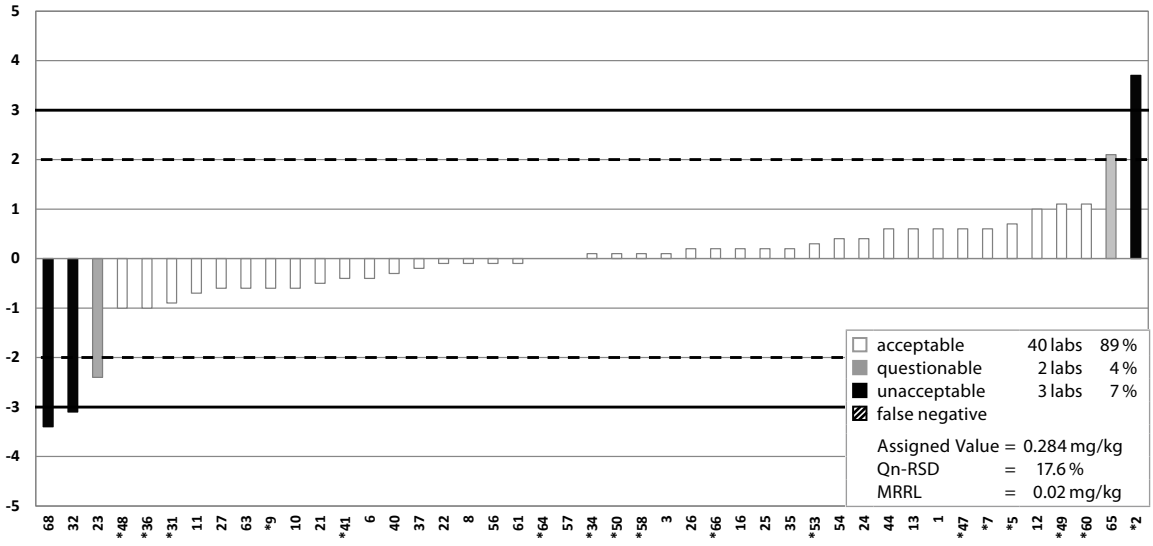
* Cut-off at z-score = 5

Appendix 6 Graphic presentation of z-scores: Compulsory compounds

2,4-D



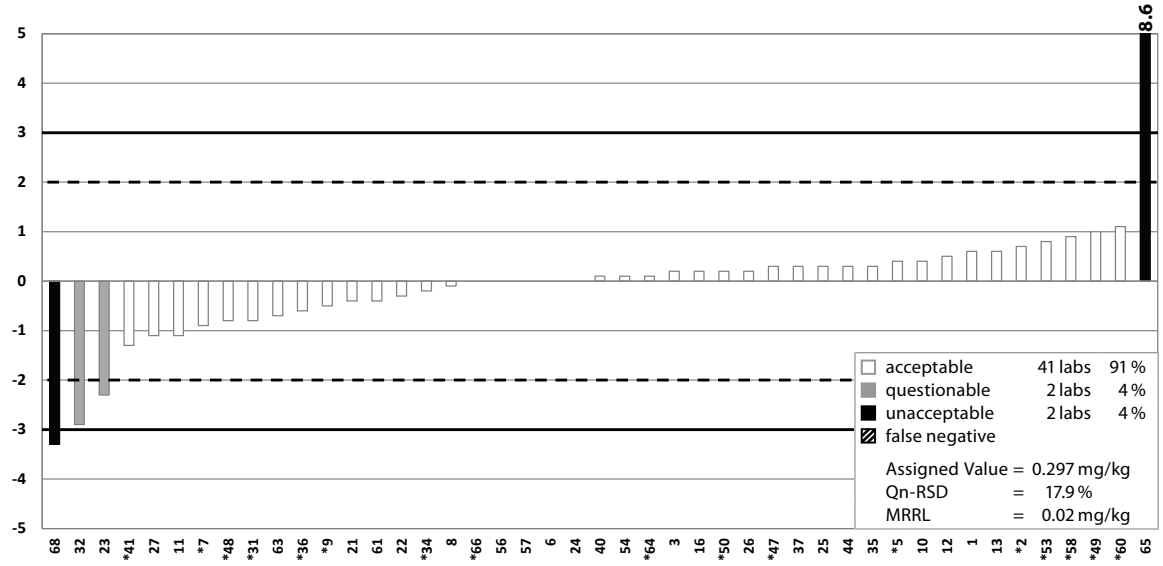
BAC-C12



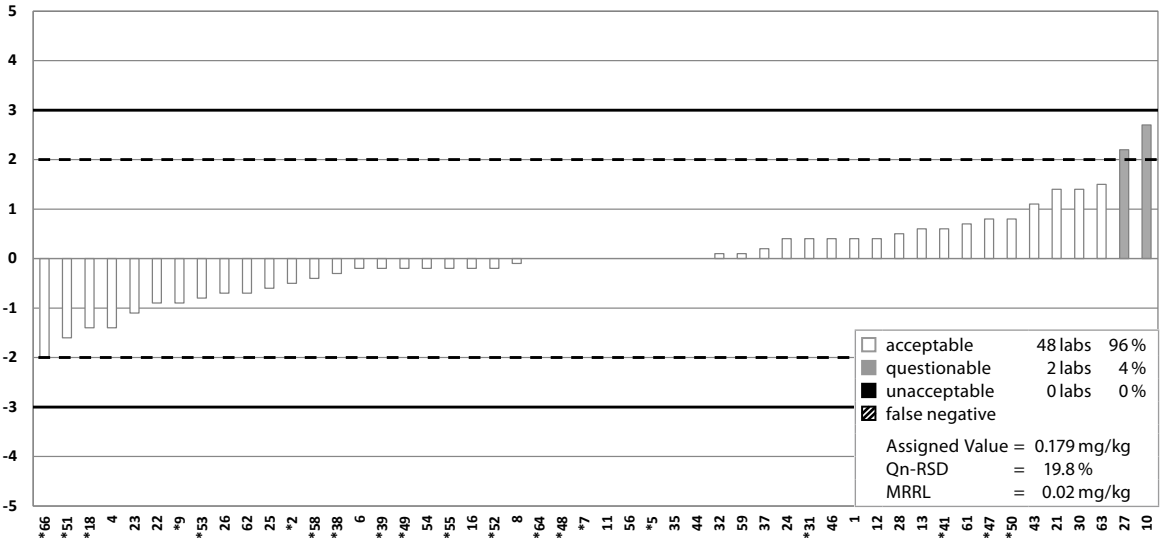
☆: not included in the establischment of Assigned Values due to gross errors

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

BAC-C14

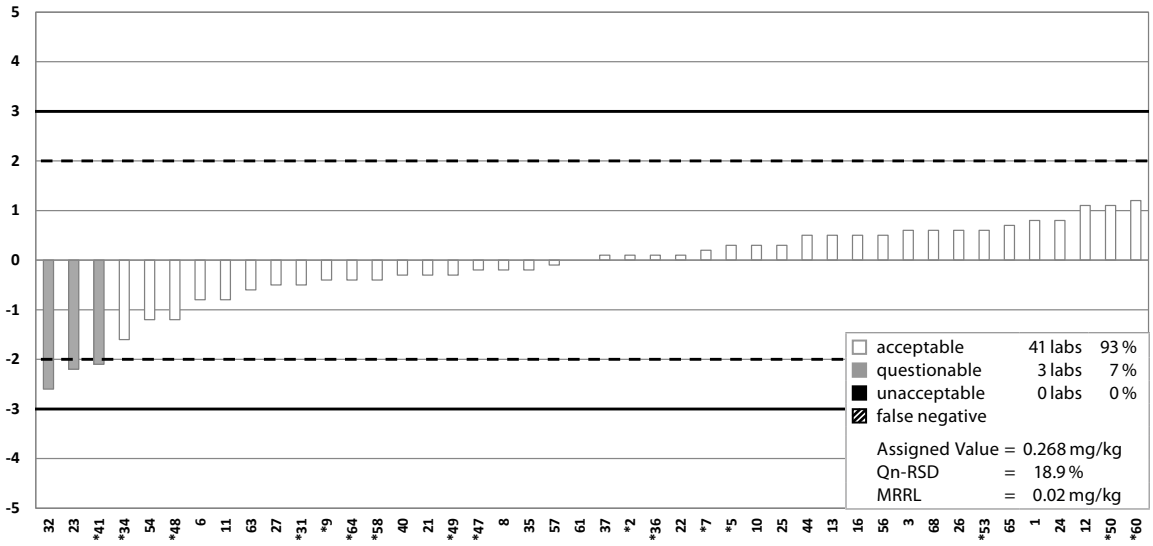


Chlormequat

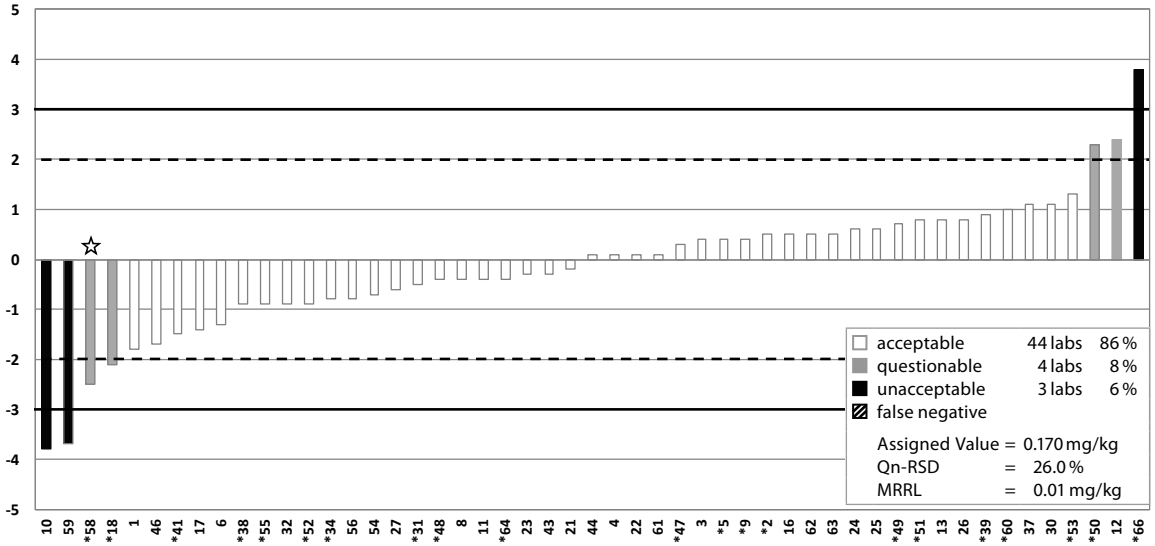


Appendix 6 (cont.) Graphic presentation of z-scores: Compulsory compounds

DDAC-C10



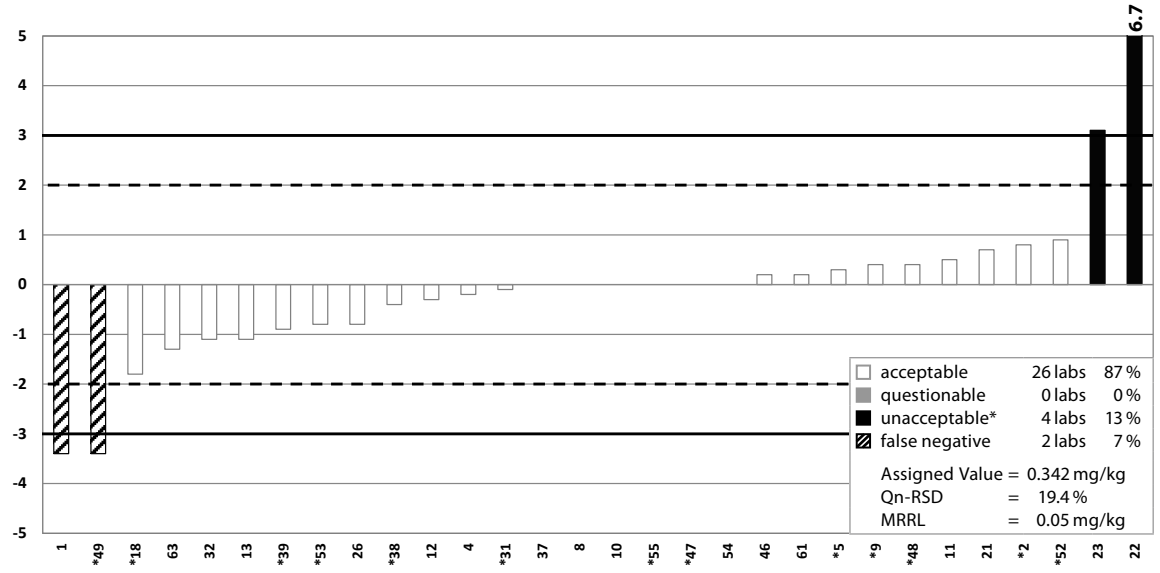
Fluazifop



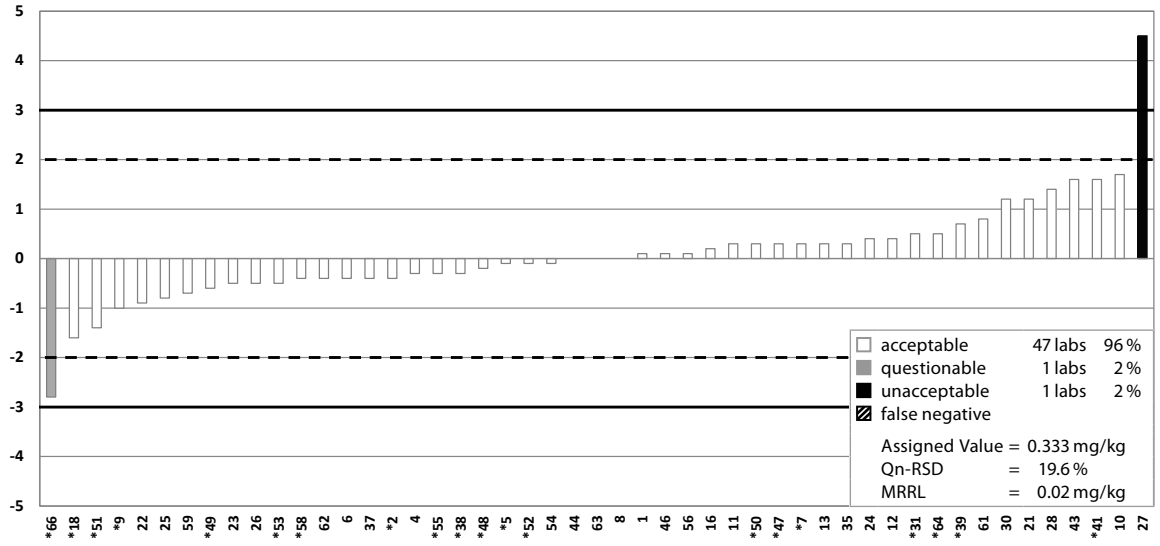
☆: not included in the establischment of Assigned Values due to gross errors

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

Maleic hydrazide



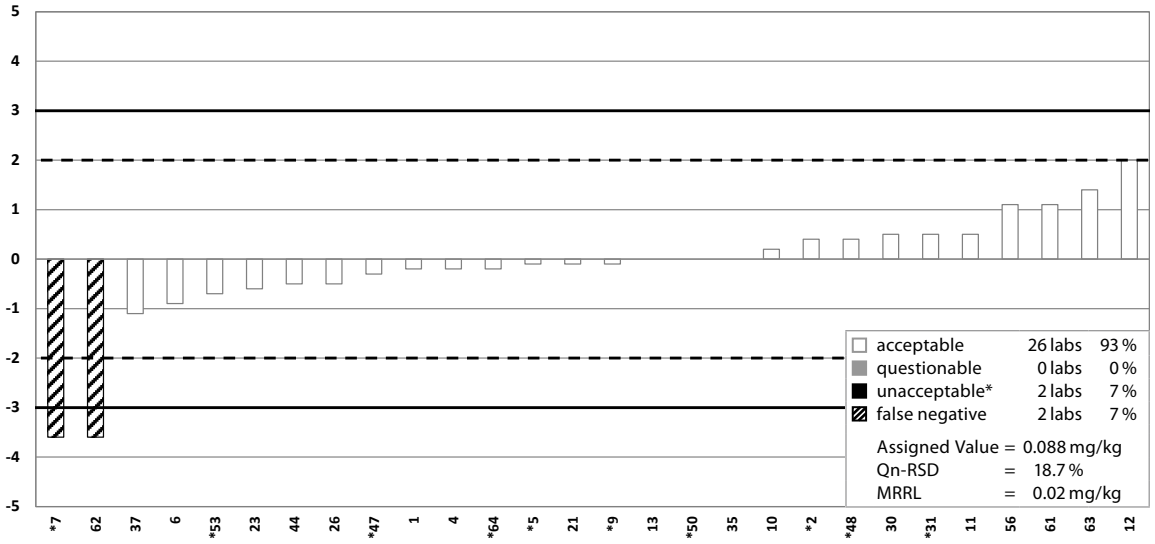
Mepiquat



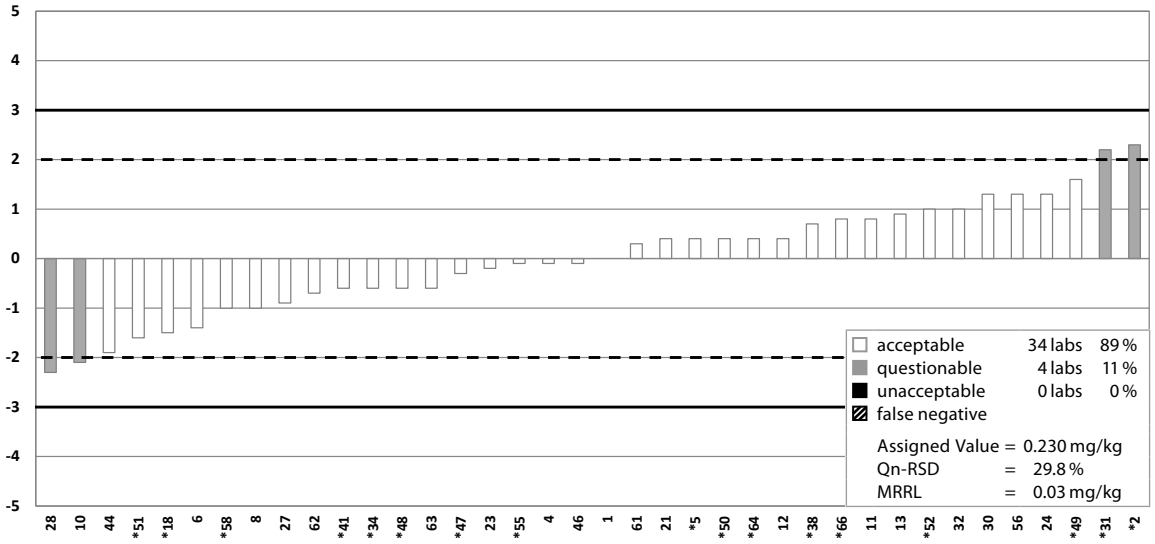
* including false negative results

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

Chlorate



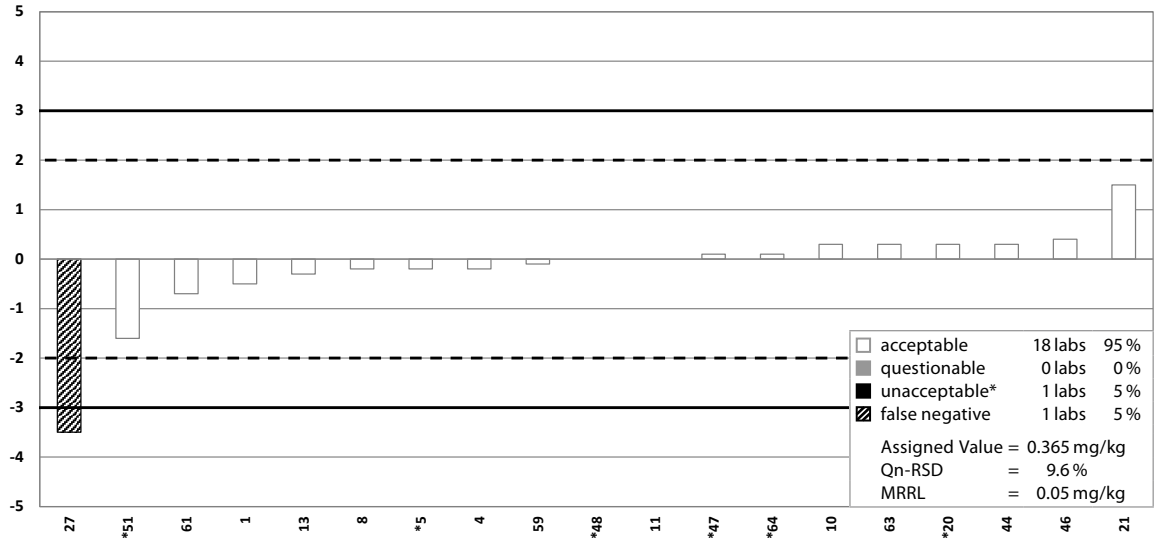
Cyromazine



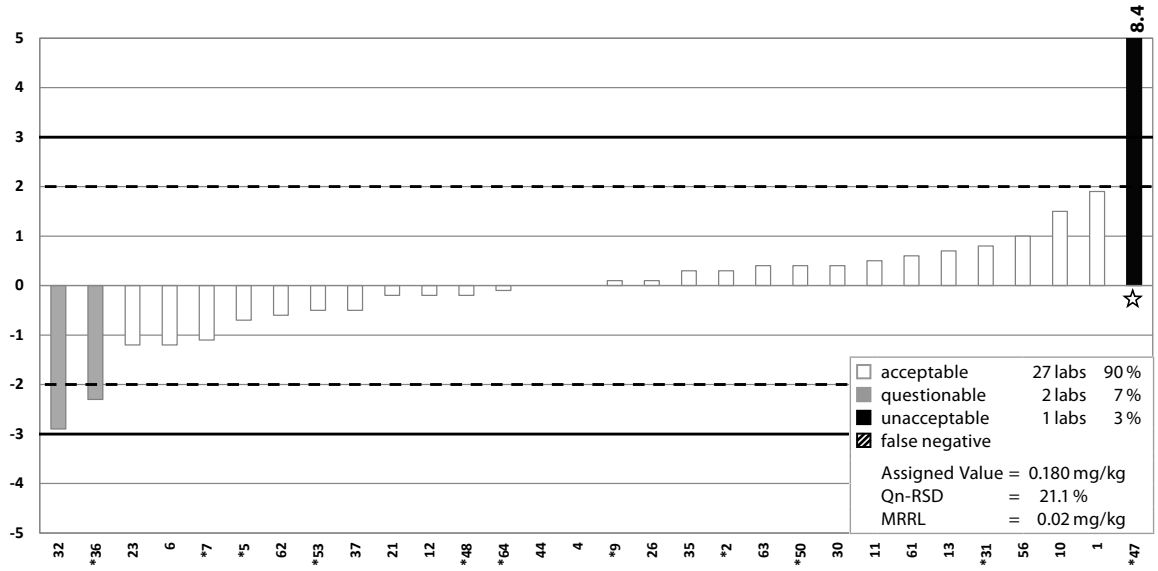
* including false negative results

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

Melamine



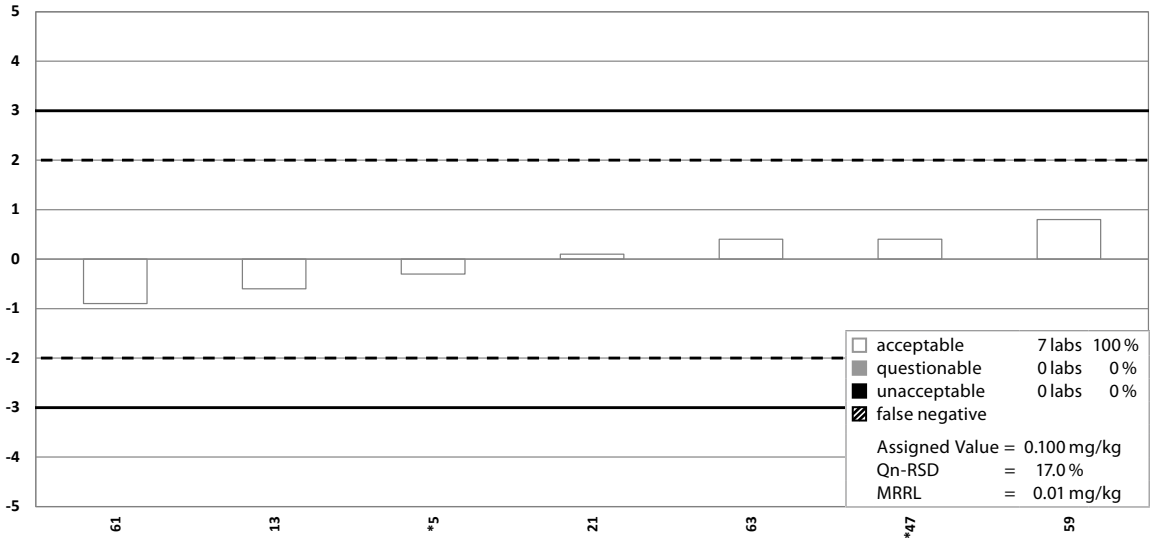
Perchlorate



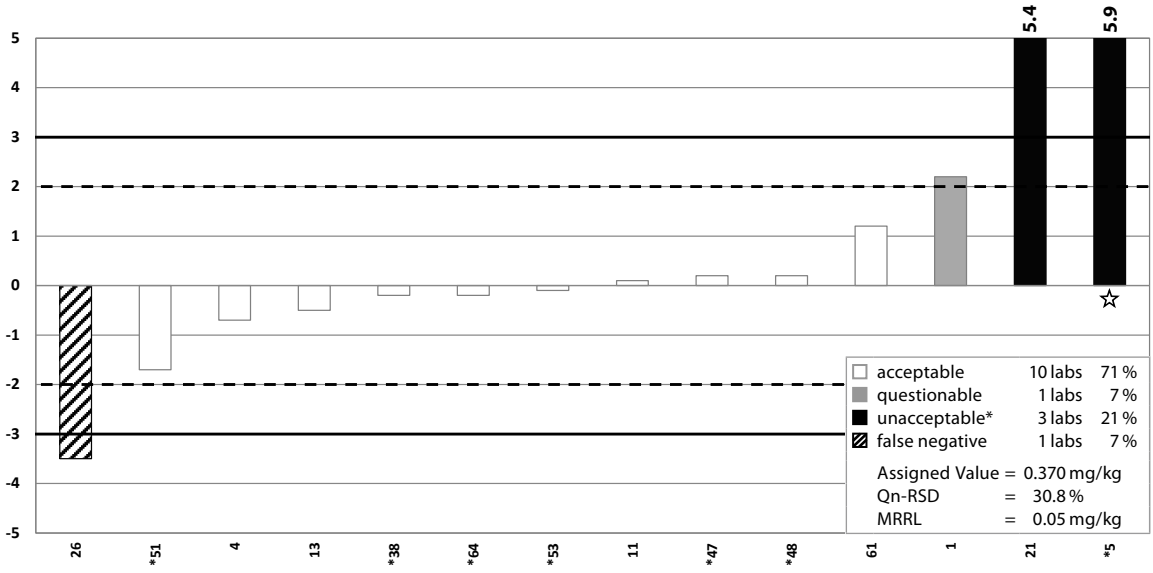
* including false negative results
☆: not included in the establischment of Assigned Values due to gross errors

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

4-OH-chlorothalonil



Trimesium



* including false negative results
☆: not included in the establischment of Assigned Values due to gross errors

Appendix 7 Possible reasons reported for poor performance

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

2,4-D Assigned value: 0.088 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
18	-2.3	yes	Sample weight differed from that in the routine work and that was not considered during calculation due to lack of communication	F
47	13.8	yes	1) no experience 2) Error in the concentration of analytical standards (The commercially purchaced standard solution at 100 ng/µl was not expired, but close to the expiry date 23.05.14. Using a new purchaced one, the z-score would have been 0.14)"	D, E

BAC-C12 Assigned value: 0.284 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
65	2.1	(yes)	Probably problem with the stability of the standards	E

BAC-C14 Assigned value: 0.279 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
65	8.6	(yes)	Probably problem with the stability of the standards	E

Chlormequat Assigned value: 0.197 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
10	2.7	no	We don´t know why we have given a high value. All our repetitions are so similiar. It is true that our working solution have more than one year but diquat is in the same solution and diquat´s value is ok.	–

Appendix 7 (cont.) Possible reasons for poor performance (ordered by z-scores)

DDAC-C10 Assigned value: 0.268 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
41	-2.1	yes	1) no experience. 2) error in the interpretation of noise backgrand resulting in overestimated intercept in the calibration curve	D, F

Fluazifop Assigned value: 0.170 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
10	-3.8	yes	We analysed Fluazifop butyl instead of fluazifop: 328 > 282.1 and 328 > 254. This is the reason why we have given a false negative.	F
59	-3.7	yes	Problem of the standard (out of the expiry date) which will be ordered rapidly. The analysis is done with the new standard from the Dr. Ehrenstorfer (the old one, from SIGMA-ALDRICH). The concentration obtained is 0.165 mg/kg for Fluazifop. So, the new standard will be used for the next EUPT SRM test.	E
58	-2.5	yes	Lack of correction (Recovery for Fluazifob was 41.4 %).	I
18	-2.1	yes	Sample weight differed from that in the routine work and that was not considered during calculation due to lack of communication	F
50	2.3	yes	lack of correction (Recoveries at different levels were between 112.5 % and 138 %).	I
12	2.4	yes	The recovery 125.0 % (obtained from same batch using EUPT-blank matrix) was not considered.	I

Maleic hydrazide Assigned value: 0.342 mg/kg;

LabCode	z-score	Source of error localized?	Reason / Remarks	
1	-3.4 (FN)	yes	Transcription error	K
22	6.7	yes	Calibration curve in matrix; wrong Internal standard addition	C, E

Chlorate Assigned value: 0.185 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
7	-3.6 (FN)	yes	wrong concentration in standard solution (re-analized and new concentration: 0.127 mg/kg)	E

Cyromazine Assigned value: 0.230 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
28	-2.3	yes	Recovery Rate was low (~ 60 %) and the result was not corrected for the recovery. If we had have corrected our result, it would have been 0,161 mg/kg and would have had a Z-score around -1.	I
10	-2.1	yes	We analysed Cyromacine using Citrate-Quechers method and our recovery for this pesticide is true that it is so low. We are going to try analyse Cyromacine with QuPPe method. Remark from the Organisers: If possible, use Cyromazine D4 as internal Standard and matrix matched calibration to compensate effects caused by the matrix.	G
31	2.2	yes	Cyromazine was calculated using matrix-matched calibration standards with chlormequat-D_4 as ISTD. It may be not an appropiate ISTD. Milk sample will be subsequently re-analysed and cyromazine will be calculated using standard addition approach and also matrix-matched cyromazine-D4 calibration standard (deuterated standard of cyromazine has been ordered however not yet received).	C

Appendix 7 (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

Perchlorate Assigned value: 0.180 mg/kg

LabCode	z-score	Source of error localized?	Reason / Remarks	
47	8.4	yes	1) no experience and we don't intend to include perchlorate in our Analyte scope. 2) The way of quantifying that we used was not suitable: Due to lack of perchlorate standard, we tried to use the standard of 18O4-perchlorate provided by the EURL for quantifying our extract (only 1 level) . The response factor of perchlorate 18O4 is apparently different from the one of perchlorate, that is why we obtained an unsatisfactory z-score.	D, F

Trimesium Assigned value: 0.370 mg/kg (informative only)

LabCode	z-score	Source of error localized?	Reason / Remarks	
26	-3.5 (FN)	(no)	Instead of the Test Item we have measured the Blank Sample!	B
5	5.9	yes	we missed to apply a conversion factor of 0.378 during result calculation	E

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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) responsible for pesticide residues in food and feed. These EUPTs are directed at laboratories belonging to the Network[2] of National Reference Laboratories (NRLs) and Official Laboratories (OfLs) of the EU Member States. OfLs from EFTA countries and EU-Candidate countries are also welcome to participate in the EUPTs. OfLs from Third countries may be permitted to participate on a case-by-case basis.

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

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

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

[1] DG-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

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

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

EUPT-Organisers and Scientific Committee

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

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

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

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

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

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

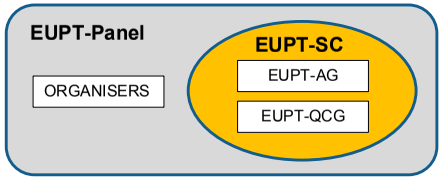
The EUPT-SC's role is to help the Organisers make decisions regarding the EUPT design: the selection of the commodity, the selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the statistical treatment and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

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

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

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

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



The decisions of the EUPT-Panel will be documented.

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

EUPT Participants

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

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

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

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

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

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

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

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

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

Confidentiality and Communication

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

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

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

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

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

The official language used in all EUPTs is English.

www.eurl-pesticides.eu

Announcement / Invitation Letter

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

Target Pesticide List

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

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

Specific Protocol

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

Homogeneity of the Test Item

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

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

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

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

Stability of the analytes contained in the Test Item

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

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

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

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

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

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

Methodologies to be used by the participants

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

General procedures for reporting results

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

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

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Correction of results for recovery

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

Methodology information

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

Results evaluation

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

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

www.eurl-pesticides.eu

– ***False Positive results***

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

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

– ***False Negative results***

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

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

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

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

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

use only the results of a subgroup consisting of laboratories that have repeatedly demonstrated good performance for the specific compound in the past.

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

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

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

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

Uncertainty of the assigned value

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

$$\mu_i = 1.25 * \frac{Qn\,SD}{\sqrt{n}}$$

where $Qn\,SD$ is the robust standard deviation and n is the number of results.

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

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

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

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

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

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

– ***z-scores***

This parameter is calculated using the following formula:

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

where x_i is the value reported by the laboratory, μ_i the assigned value, and δ_i the standard deviation for each pesticide (i). Z-scores will be rounded to one decimal place. For the calculation of combined z-scores (see below) the original z-scores will be used and rounded to one decimal place after calculation.

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

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

Z-scores will be interpreted in the following way:

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

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

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

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

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

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

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

For evaluation of the overall performance of laboratories within Category A, the Average of the Squared z-Score (AZ^2)[12,13] (see below) will be used. The AZ^2 is calculated as follows:

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

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

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

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

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

Laboratories within Category B will be ranked according to the total number of pesticides that they correctly reported to be present in the Test Item. The number of acceptable z-scores achieved will

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

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

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be presented, too. The EURL-Panel retains the right to calculate combined z-scores (see above) also for labs within Category B, e.g. for informative purposes, provided that a minimum number of results (z-scores) are have been reported.

Publication of results

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

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

Certificates of participation

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

Feedback

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

Correction of errors

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

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

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

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

Follow-up activities

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

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

According to instructions from DG-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" is to be followed.

Disclaimer

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

SPECIFIC PROTOCOL

for the 9th EU Proficiency Test
on Pesticides requiring Single Residue Methods
EUPT – SRM9 (2014)
(last update 24 April, 2014)

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-SRM9 is organised by the EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL–SRM) that is ISO 17043 accredited as a provider of proficiency tests. The EUPT-SRM9 deals with the analysis of SRM-pesticides in cow's milk with 3.5% - 4% fat and is to be performed by all National Reference Laboratories for Single Residue Methods (NRL-SRMs) as well as by all official EU laboratories (OfLs) involved in official pesticide residue controls, including imports control within the frame of Reg. 669/2009/EC, as far as their scope overlaps with that of the EUPT-SRM9. A special **EUPT-SRM9-Website** containing links to the most important documents of relevance was constructed.

Considering only the commodity scope (not the pesticide scope) of OfLs a **Tentative List of obliged labs for EUPTs in 2014** has been prepared by the EURLs and published on the CIRCA-Platform. As far as the EUPT-SRM9 is concerned all laboratories analysing for commodities of animal origin were considered as obliged. The comprehensiveness and correctness of this list was checked by the OfLs and reviewed by the NRL-SRM and any change requests were considered in a new version. OfLs listed as "obliged to participate in the EUPT-SRM9" that have decided not to participate had to state their reasons of non-participation in a special online form within the EUPT-SRM9 registration website which was accessible from 25 Feb. till 12 March, 2014.

Test Item and Blank Material

This EUPT deals with the analysis of pesticide residues in **cow's milk (3.5% – 4% fat)**.

Participants will receive two bottles containing:

1) ca. 250 ml **Test Item (spiked)**, containing pesticides from the **Target Pesticides List.**
2) ca. 250 ml **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 contained in the Test Item over the period of the exercise. The Blank Material will also be checked to prove that none of the pesticides on the Target pesticides List is contained at relevant levels.

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

Shipment of Test Item

Test item and Blank Material are planned to be shipped on 28 April, 2014.
Frozen Test Item and Blank Material will be packed in thermo-boxes together with dry ice and shipped to the participants. Prior to shipment a reminder will be sent to the participating laboratories by e-mail.

Laboratories must make their own arrangements for the receipt of the package. They should **inform the Organiser of any public holidays (except 1 May) in their country/city during the week of the shipment, and must make the necessary arrangements to receive the shipment, even if the laboratory is closed.**
Should any complications during shipment, delivery or the customs be expected, the participating laboratories should provide the Organizers with contact information of possible contact persons of the lab (e.g. mobile phone numbers) as well as instructions in local language explaining the need to keep the package in freezer during delay in transit. This information will be attached to the package.

Instructions on handling the Test Item

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

Before analytical portions are taken for analysis the Test Item should be mixed thoroughly in its entirety. During mixing, try to keep temperatures low (< 4°C or frozen) to avoid degradation of susceptible pesticides.
To avoid frequent thawing of the Test Item it is further recommended preparing all analytical portions that you intend to use for all EUPT-related experiments in the sample preparation tubes and store them at -18°C till use.

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. Where the procedure employed has not yet been implemented routinely, any other method can be used. The limited experience and the non-inclusion of the analyte in the routine scope should be indicated in the result submission website.

The homogeneity tests will be conducted using 10 g analytical portions of Test Item for all analytes. Please note: Subsampling variability increases with decreasing analytical portion size, and sufficient homogeneity can only be guaranteed for sample portions ≥ 10 g.

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

Appendix 9. Specific Protocol of EUPT-SRM9

Results submission website

Sample receipt acknowledgement, analytical results and method information are to be submitted via the following website: **EUPT-SRM9 Result Submission Website** (http://pesticides.food.dtu.dk/srm).

- **Sub-Page 0 (Sample receipt acknowledgement), accessible from 29 April, 2014**
- **Sub-Pages 1-3 (analytical results and method information) accessible from 6 May till 26 May, 2014.**

To access the data-submission forms participants must use their unique login data (username and password) that will be provided to them, together with their unique EUPT-SRM9 lab-code, in a separate e-mail before sample shipment.

The deadline for result submission is 26 May 2014 at 16 h (CEST).

- Sample Receipt and Acceptance (Sub-Page 0)

Once the laboratory has received the Test Items it must report to the organiser, via the **EUPT-SRM9 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 2 May 2014. If a laboratory does not respond by this deadline, the Organisers will assume that Test Item and Blank Material have been received and accepted.
If any participants have not received the Test Items by the 30 April in the afternoon, they must inform the Organiser by e-mail (EURL-SRM@cvuas.bwl.de**) to localize the package and decide on further action including new shipment if necessary**.
Selected participants might be asked to provide information on the condition of the Test Item upon receipt (e.g. existence of residual dry ice, core temperature of Test Item etc.).

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

To report their results, laboratories must access the **EUPT-SRM9 Result Submission Website**.
All results must be reported on the above website by 26 May 2014 at 16 h (CEST). 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 Pesticide List** carefully, in particular the residue definitions, which are not given on the Result Submission Website.

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

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

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

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

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

- **"Is your result recovery-corrected?":** Please specify via the dropdown-menu whether the reported result was corrected for recovery or not. Please note that in some cases recovery correction is performed automatically, e.g. when employing the standard additions approach with the additions being done to analytical portions prior to extraction or when an isotopically labelled analogue of the target analyte is used as internal standard. If an isotopically labelled compound not corresponding to the target analyte is used as internal standard (e.g. ethephon D4 for glyphosate), this question should be answered with "No". Where recovery correction was carried out using a recovery figure, this recovery figure should be stated (see below).

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

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

  Additional information will be asked in separate fields.

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

In **sub-page 3 of** the "**EUPT-SRM9 Result Submission Website**" the participating laboratories must provide complete information on the analytical method(s) applied to **all pesticides which were analysed, irrespective if they were detected or not**.

The participating laboratories are urged to thoroughly fill-in all requested information in order to minimize the administrative burden of collecting it 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 the EURL-CF, Soeborg, Denmark:

a) The administration of **EUPT-SRM9 Registration and Result Submission Website**

Follow-up actions

After the distribution of the Preliminary EUPT-Report laboratories with poor performance (high absolute z-scores, false negatives or false positives) will be asked to provide information concerning the reasons for poor performance and possible corrective actions. This information will be forwarded to the corresponding NRL-SRMs upon request. All EUPT-SRM9-participants are welcome to ask the EURL-SRM for technical assistance.
According to instructions by DG-SANCO, the "**Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with Community reference laboratories (CRLs) activities**" will be followed for NRLs.

Documents

All documents related to the EUPT–SRM9 can be found in the **EURL-Document Repository (CIRCA/FIS-VL).** Links to the documents can also be found in the **EUPT-SRM9 Website.**
For further information please contact the organizers **EURL-SRM@cvuas.bwl.de**
Please check the **EUPT-SRM9 Website** before starting with the analysis to **make sure that you have the latest version of all documents available**. In case of major changes the participants will be informed via e-mail.

Participation fees and payment details

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

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

Invoices, issued to the "invoice address" stated in the registration form, will be enclosed inside the package containing the PT-Materials.

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

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

Please note:

The bank account of EURL-SRM has been changed since the end of October 2013!

Please inform your financial department!

NEW Bank Details:

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

Calendar of EUPT-SRM9

(see under **http://www.eurl-pesticides.eu/library/docs/srm/EUPT_SRM9_Calendar.pdf**)

Target Pesticides List of EUPT-SRM9

(see under **http://www.eurl-pesticides.eu/library/docs/srm/EUPT_SRM9_TargetPesticideList.pdf**)

Contact information

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Ralf Lippold	CVUA, Freiburg, DE
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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 – SRM9

cow's milk, 3.5% – 4% fat

(last update: 24 April, 2014)

Activity	Who ?	Dates
Opening of the **EUPT-SRM9 Website** with links to all relevant documents (**List of obliged labs, calendar, target pesticides list, general protocol**)	EURL-SRM	Jan. 2014
Registration via "**EUPT-Registration Website**" (Note: obliged OfLs MUST enter this Website and either register or give **explanations for non-participation**)	**- Obliged OfLs from EU-MSs** **- OfLs from EFTA Countries** **- OfLs from EU-candidate C.** **- Labs from 3rd Countries**	**25 Feb. – 12 March 2014**
Dispatch of **EUPT-SRM9-Specific Protocol**	EURL-SRM	April 2014
Preparation of EUPT-SRM9-Test Item (preliminary tests Spiking / Homogenization)	EURL-SRM	Jan. – April 2014
Homogeneity tests	EURL-SRM	April 2014
Stability tests	EURL-SRM	April – May 2014
Shipment of EUPT-SRM9 Test Item (+reminder of upcoming parcel arrival)	EURL-SRM	**28 April 2014**
Confirmation of sample Receipt and acceptance via "**EUPT-SRM9 Result Submission Website**", (Sub-Page 0)	**Participating Labs**	**within 48 h on receipt**
Result Submission **(Pesticide scope, Results, Method Info)** in "**EUPT-SRM9 Result Submission Website**", (Sub-Pages 1 – 3)	**Participating Labs**	**6 May – 26 May 2014, (16:00 h CET)**
Preliminary Report (only compilation of results)	EURL-SRM	June 2014
Survey to collect reasons for underperformance **Collection of missing information on methods**	EURL-SRM / **Participating Labs**	June 2014
EUPT Evaluation Meeting	EUPT-SC, DG-SANCO	Sept. 2014
Final Report	EURL-SRM	Dez. 2014

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

The EUPT-SRM Team

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

TARGET PESTICIDE LIST

for the EUPT – SRM9 2014
cow's milk, 3.5% – 4% fat
last update on 31.03.2014

Compounds Potentially Present in Test Item	In MACP 2013-15 for AO-products (Reg. 788/2012/EC)	MRRL (mg/kg)
Compulsory Compounds (will be considered in Category A/B classification)		
2,4-D (free acid**)	No*	0.02
BAC-C10 (expressed as chloride salt)	No*	0.02
BAC-C12 (expressed as chloride salt)	No*	0.02
BAC-C14 (expressed as chloride salt)	No*	0.02
BAC-C16 (expressed as chloride salt)	No*	0.02
Chlormequat (cation)	Yes	0.02
DDAC-C10 (expressed as chloride salt)	No*	0.02
Fluazifop (free acid***)	Yes	0.01
Glyphosate	Yes (not for milk)	0.05
Haloxyfop (free acid***)	Yes	0.01
Maleic hydrazide (without conjugates)	Yes	0.05
Mepiquat (cation)	Yes (not for milk)	0.02
Optional Compounds (will NOT be considered in Category A/B classification)		
4-Hydroxy-chlorothalonil (= SDS-3701)	No	0.01
Chlorate (anion)	No*	0.02
Cyanuric acid	No	0.05
Cyromazine	No	0.01
Melamine	No	0.05
Perchlorate (anion)	No	0.02
Trimethyl-sulfonium (cation)	No	0.05

MACP = EU Multi-Annual Coordinated Control Program
* foreseen for the MACP Working Document for 2015 (in preparation)
** no alkaline hydrolysis
*** no alkaline hydrolysis, including R/S isomers which are part of the residue and cannot be distinguished by standard chromatographic applications

Notes:

- 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**

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