European Union Reference Laboratories

for Pesticide Residues in Cereals & Feeding Stuff
and for Pesticides Requiring Single Residue Methods

Report on Proficiency Test on Incurred and Spiked Pesticides in Rice

EUPT–C5/SRM6, 2011

Final Report

December 2011

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EU PROFICIENCY TEST
EUPT-C5/SRM6, 2011

Pesticide Residues in Rice Flour using Multi- and Single Residue Methods

Final Report

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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 and national monitoring programmes. Participating laboratories can assess their analytical performance and scope relative to others, hopefully resulting in additional efforts towards improvement.

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 samples for the official controls of pesticide residues shall participate in the European Union Proficiency Tests (EUPTs) for pesticide residues. Each official laboratory has to participate in EUPTs concerning commodities included in its competence area.

The current EUPT (EUPT-C5/SRM6 based on rice flour) was the fifth to be organized with cereals as Test Material. The first (EUPT-C1/SRM2 in 2007 using wheat flour), and the third (EUPT-C3/SRM4 in 2009 using oat flour) were co-organised by the EURL for pesticide residues in Cereals and Feedingstuff[2] (EURL-CF) and the EURL for pesticides requiring Single Residue Methods (EURL-SRM). The current EUPT contained incurred and laboratory-spiked pesticides requiring the application of both multi residue methods (MRMs) and single residue methods (SRMs). The second (EUPT-C2 in 2008 using wheat flour) and the fourth (EUPT-C4 in 2010 using rye flour) were organized solely by the EURL-CF and contained mostly MRM pesticides as well as a few SRM pesticides (chlormequat and glyphosate in 2008 as well as glyphosate and 2,4-D in 2010). The EURL-SRM organized 3 additional EUPTs on fruits and vegetables focusing purely on SRM pesticides (EUPT-SRM1 in 2006 using apple juice, EUPT-SRM3 in 2008 using carrot homogenate and EUPT-SRM5 in 2010 using apple sauce).

Participation in the EUPT-C5/SRM6 was compulsory for all EU-Official Laboratories (OfLs) (including National Reference Laboratories (NRLs)) involved in pesticide residue control in cereals. As far as the SRM part of this EUPT is concerned the exercise was also compulsory for all NRLs responsible for pesticides requiring single residue methods (NRL-SRMs) regardless of the commodity scope covered. Although rice is not typically used as animal feed it was considered to be representative of cereals employed as feeds, so this EUPT was also compulsory for laboratories controlling pesticide residues in feed. Official laboratories from EFTA countries (Iceland, Norway and Switzerland), also contributing data to the EU-coordinated community control programme as well as official laboratories from EU-candidate states (Croatia, FYROM and Turkey) were also invited to take part in this EUPT. Selected laboratories from Third Countries were also allowed to take part in this exercise, but thier results, together with the EU-candidate state laboratories, were not used when establishing the Assigned Values. All NRLs and OfLs that were supposed to participate in this exercise, but decided not to take part, were asked to state the reasons for their non-participation. Laboratories that had registered to participate in this exercise but then did not submit results, either in the SRM or the MRM part, were also asked to provide explanations.

DG-SANCO will have full access to all data of EUPTs including the lab-code/lab-name key. The same will apply to all NRLs regarding data from laboratories belonging to their own country network. The results of this EUPT may be further presented to the European Commission Standing Committee for Animal Health and the Food Chain.

[1] Former Community Reference Laboratories (CRLs)

[2] Accredited by DANAK under registration number 516 for proficiency testing

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EUROPEAN COMMISSION –
EU-PROFICIENCY TEST ON PESTICIDE RESIDUES
IN RICE FLOUR USING MULTI- AND SINGLE RESIDUE METHODS

EUPT-C5/SRM6, 2011

INTRODUCTION

In December 2010 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 made available to the Organizers by the NRLs, were sent an invitation to participate in this 5th European Commission's Proficiency Test on Cereals using Multi- and Single Residue Methods (EUPT-C5/SRM6). A list of labs obliged to take part in the EUPT-C5/SRM6 was published on the EURL-Website and the CIRCA-platform. To make sure that all relevant official laboratories were informed of this EUPT, the NRLs were asked to forward the invitation to all relevant laboratories within their countries. Also included in the invitation were the Specific Protocol and the Schedule for the EUPT-C5/SRM6, as well as a Target Pesticides List showing the compounds that could potentially be present in the Test Material (**Appendix 15** and **Appendix 16**). The Target Pesticides List included 112 compounds (pesticides, metabolites etc.) requiring the use of multi-residue methods (MRMs) and an additional 13 compounds requiring single residue methods (SRMs), along with the minimum required reporting level (MRRL) stipulated for each compound. A link to the "General Protocol" containing information common to all EUPTs was also provided to the laboratories. The laboratories were able to register on-line from the 1st to the 21st of February 2011. In total 133 laboratories (86 in the SRM part) from EU and EFTA countries agreed to participate in the test with 3 of them failing to submit results in the MRM part and 9 in the SRM part. 22 laboratories (2 in the SRM part of the test) from Third Countries (including EU-Candidate States) also agreed to participate in the MRM part. Numerous EU-laboratories provided explanations for their non-participation as requested by DG-SANCO.

To produce rice containing incurred (field-sprayed) MRM and SRM pesticides as well as blank (non-treated) rice, the Organizers subcontracted the Federal University of Santa Maria, Brazil and the Universidade Estadual de Ponta Grossa, Brazil. Unfortunately, the quantity of rice material provided was only sufficient for the MRM part of the test. For the SRM part a separate material had to be produced by spiking blank rice with SRM pesticides in the laboratory. The material for the MRM part also had to be treated post-harvest at the facilities of the EURL-CF. The MRM Test Material finally contained 18 compounds and the SRM Test Material 7 compounds in total. More details are given in the Section "Test Materials".

1. TEST MATERIALS

1.1 Analytical methods

The analytical methods described briefly below were used by the organisers to check the homogeneity and the storage-stability of the pesticides contained in the Test Material:

- For MRM pesticides: QuEChERS method [3] using GC-MS/MS and LC-MS/MS.

- For SRM pesticides:

  2,4-D, haloxyfop and **quinclorac** (acidic pesticides): QuEChERS-method [3] involving extraction after addition of acetonitrile, partitioning after addition of salts, and direct determination by LC-MS/MS in the ESI-neg. mode.

  Ethephon and **glyphosate**: QuPPe method involving extraction following addition of methanol containing 1 % formic acid, centrifugation, filtration and direct determination by LC-MS/MS in the ESI-neg. mode using ion-exchange chromatography.

  Dithiocarbamates: 1) method involving cleavage with HCl/$SnCl_2$, partitioning into isooctane and determination by GC-ECD; and 2) for confirmation of the quantitative results, a method according to EN12396-3 involving cleavage with HCl/$SnCl_2$ to release carbon disulfide, which is separated and purified by distillation and collected in a methanol/potassium hydroxide solution where potassium xanthogenate is formed and spectrophotometrically determined.

  Bromide ion (bromine containing fumigants): derivatization with propylene oxide in an acidified aqueous solution, partitioning of the derivative into ethyl acetate, and direct determination by GC-ECD.

  For more details on the above methods used, see http://www.EURL-pesticides.eu.

1.2 Selection of pesticides for the Target Pesticide List

The Proficiency Test covered both MRM and SRM pesticides. The pesticides to be included in the Target Pesticides List (**Appendix 16**) were selected by the Organiser and the Scientific Committee taking into account the present and upcoming scope of the EU-coordinated control programme, a pesticide priority list ranking the pesticides according to their risk-potential, as well as a list of pesticides relevant to the specific commodity (rice). The overall scope and capability of the laboratories within the EU, as determined by previous PTs and surveys, was also taken into account. In some cases the residue definitions valid for the test were slightly different from those in the legislation in order to overcome specific analytical difficulties (e.g. in the case of prochloraz, vinclozolin and acidic pesticides). The minimum required reporting levels (MRRLs) were set at 0.01 mg/kg for the MRM compounds and at 0.02 mg/kg for all SRM compounds except for dithiocarbamates and glyphosate, which were set at 0.05 mg/kg, and for bromide set at 5 mg/kg.

1.3 Preparation of the rice Test Material

Before preparing the Test Material, the pesticides and suitable approximate target residue levels for the study were selected by the Organizers. The application rates and harvest intervals for the pesticides used

for treatment in the field were chosen based on local usage in Brazil. The field-spraying with selected MRM and SRM pesticides was performed by the Universidade Estadual de Ponta Grossa, Brazil, in collaboration with the Federal University of Santa Maria, Brazil. 15 kilograms of treated and 65 kilograms of untreated rice grain were delivered. A much smaller quantity than expected of field-treated rice was received and, it was found to contain only MRM pesticides and no SRM pesticides at detectable levels. The MRM pesticides contained in the harvested corp were in most cases at levels too low to allow for any dilution with non-treated rice. As a consequence it was decided to use this 15 kg of field-treated rice to prepare the MRM Test Material and then to additionally spike it in the laboratory with those pesticides where the residue level was too low. Following several incidences of isoprothiolane residues in rice of Indian origin distributed in the EU, it was decided to also spike the rice with this compound (see **Table 1-1**). As the total amount of MRM Test Material was limited it was decided to restrict the amount delivered to the participants to 50 g per lab.

Table 1-1: Pesticides used for application in the field and/or spiked in the laboratory for the pesticide residues present in the MRM Test Material

Pesticide	Application in the field	Spiking in laboratory	Treatment Form in Field / in Lab	Name of Formulation
Azoxystrobin	x	x	Formulation / Standard solution	Priori
Carbendazim	x		Formulation / -	Derosal
Chlorpyrifos	x		Formulation / -	Nufós
Deltamethrin	x	x	Formulation / Standard solution	Decis
Difenoconazole	x		Formulation / -	Score
Diflubenzuron	x		Formulation / -	Dimilin
Epoxyconazole	x		Formulation / -	Brio
Fipronil	x	x	Formulation / Standard solution	Klap
Isoprothiolane		x	- / Standard solution	Standard
Kresoxim-methyl	x	x	Formulation / Standard solution	Brio
Lambda-cyhalothrin	x		Formulation / -	Engeo Pleno
Malathion	x		Formulation / -	Malathion
Propiconazole	x		Formulation / -	Tilt
Pirimiphos-methyl	x		Formulation / -	Actellic
Tebuconazole	x		Formulation / -	Nativo
Thiametoxam	x	x	Formulation / Standard solution	Engeo Pleno
Tricyclazole	x		Formulation / -	Bim
Trifloxystrobin	x	x	Formulation / Standard solution	Nativo

Table 1-2: Pesticides spiked in the laboratory for the pesticide residues present in the SRM Test Material.

Pesticide	Application in the field	Spiking in laboratory	Treatment Form in Lab	Name of Formulation
2,4-D		x	Formulation	2,4-D (AH Marks)
Ethephon		x	Standard solution	
Glyphosate		x	Formulation	Glyphomax
Potassium bromide (Bromide ion)		x	Standard solution	
Quinclorac		x	Standard solution	
Thiram		x	Standard solution	
Haloxyfop		x	Standard solution	

Spiking in the laboratory was performed using pesticide formulations except in the case of isoprothiolane where a standard solution was used. One kilogram of field treated rice was spiked with the pesticides, then mixed with 14 kg of field-treated rice and homogenised thoroughly. The 15 kg of mixed rice grains were milled in 4 kg portions. To ensure that a well-homogenised bulk with respect to both incurred and spiked residues was obtained, the 4 portions were initially stirred individually, then doubled and mixed again and finally mixed all together. Subsequently, 50 g portions were weighed out into screw-capped polyethylene plastic bottles, sealed, numbered, and stored in a freezer at about -20 °C prior to homogeneity testing and distribution to participants.

The SRM Test Material was spiked with 7 different pesticides (see **Table 1-2**). As several analytical methods had to be applied to this material, it was decided to prepare 35 kg of SRM Test Material.

Spiking in the laboratory was performed using both pesticide formulations and standard solutions. One kilogram of untreated rice was spiked with the pesticides and was mixed with 34 kg of untreated rice and homogenised thoroughly. The 35 kg of mixed rice grain were milled in 4 kg portions. To ensure that a well-homogenised bulk with respect to both incurred and spiked residues was obtained, the portions were initially stirred individually, then doubled and mixed again and again until all portions were combined. Subsequently 250 g portions were weighed out into screw-capped polyethylene plastic bottles, sealed, numbered, and stored in a freezer at about -20 °C prior to homogeneity testing and distribution to participants.

1.4 Preparation of the blank Test Materials

The rice flour used for the blank Test Material was also prepared from grain grown in Brazil under growing conditions similar to the treated crop but without any pesticide treatment either in the field or in the laboratory. The blank Test Material was weighed out into screw-capped polyethylene plastic bottles (50 g for MRM and 250 g for SRM), sealed, and stored in a freezer at about -20 °C prior to distribution to participants.

1.5 Homogeneity Test

Eleven bottles of treated Test Material were randomly chosen and analyses were performed on duplicate portions taken from each bottle. The sequences of analysis and injections were both randomly chosen. Quantification was performed using a 5-point (for MRM pesticides) or 3-point (for SRM pesticides) calibration curve constructed from matrix-matched standards. A sample portion of 5 g was used for analysis of MRM compounds. The portion size of 5 g was employed for the analysis of glyphosate and ethephon; 3 g for 2,4-D, haloxyfop and quinclorac; 1 g for bromide and 20 g for dithiocarbamates.

The statistical evaluation of the homogeneity-test data was performed according to the International Harmonized Protocols published by IUPAC, ISO and AOAC [4]. An overview of the statistical analyses of the homogeneity test is shown in **Table 1-3** and **Table 1-4**. The individual residue data from the homogeneity tests, as well as the results of the statistical analyses, are given **Appendix 2**, **Appendix 3**, **Appendix 8** and **Appendix 9**.

The acceptance criterion for the Test Material 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 are constants, with values of 1.83 and 0.93, respectively, if using 11 samples; and 1.88 and 1.01, respectively, if using 10 samples. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD (25 %) $\times$ the analytical sampling mean for all pesticides, and s_{an} is the estimate of the analytical standard deviation.

As all pesticides passed the homogeneity test, the Test Material was considered to be sufficiently homogenous and suitable for the EUPT-C5/SRM6.

Table 1-3: Statistical evaluation of the homogeneity test data of MRM analytes (n = 22 analyses using a sample portion of 5 g in each case). See Appendix 2 for individual results

	Azoxystrobin	Carbendazim	Chlorpyrifos	Deltamethrin (cis)	Difenoconazole	Diflubenzuron	Epoxiconazole	Fipronil
Analytical portion size [g]	5	5	5	5	5	5	5	5
Mean, mg/kg	0.145	0.122	0.265	0.331	0.210	0.147	0.110	0.173
s_{sam}^2	0	0.00008	0	0	0.00002	0	0	0
c	0.0003	0.0003	0.0013	0.0088	0.0006	0.0004	0.0002	0.0004
Passed/Failed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
	Isoprothiolane	**Kresoxim-methyl**	**Pirimiphos-methyl**	**Propiconazole**	**Tebuconazole**	**Thiamethoxam**	**Tricyclazole**	**Trifloxystrobin**
Analytical portion size [g]	5	5	5	5	5	5	5	5
Mean, mg/kg	0.184	0.183	0.084	1.249	1.168	0.174	0.366	0.246
s_{sam}^2	0.00009	0	0.00001	0	0	0	0	0
c	0.0005	0.0005	0.0001	0.0190	0.0374	0.0021	0.002	0.0010
Passed/Failed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed

s_{sam}^2 : Between Sampling Standard Deviation; *c*: critical value

Table 1-4: Statistical evaluation of homogeneity test data of SRM analytes (n = 20 analyses), See Appendix 8 .

	2,4-D	Brominde	Dithiocarbamates	Ethephon	Glyphosate	Haloxyfop	Quinclorac
Analytical portion size [g]	3	1	20	5	5	3	3
Mean, mg/kg	0.262	57.0	0.611	0.295	0.390	0.122	0,288
s_{sam}^2	0	6.276	0.00003	0.00002	0.00016	0.00003	0.00005
c	0.00125	41.937	0.00444	0.00104	0.00228	0.00025	0.00096
Passed/Failed	passed	passed	passed	passed	passed	passed	passed

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

1.6 Stability test

The analytical methods described briefly above (**Caption 1.1**) were also used for the stability tests.

In the case of MRM compounds two different storage temperatures were used; room temperature and -18 °C. In the case of SRM compounds the samples were stored only at -18 °C, as recommended in the Specific Protocol. The analyses were performed on 5 randomly chosen samples. In each case one test was performed shortly after the start of the PT-exercise and one after the completion date.

For the MRM compounds the tests were performed on five occasions at a storage temperature of -18 °C and on three occasions at room temperature (day 2, 8 and 28):

For MRM compounds:

Day 2: 15 March 2011 (shortly after the first shipment)
Day 8: 21 March 2011
Day 15: 28 March 2011
Day 21: 4 April 2011
Day 28: 11 April 2011

For the SRM compounds the tests were carried out on three occasions.

For SRM compounds:

Day 1: 14 March 2011 (shortly after the first shipment)
Day 21: 4 April 2011
Day 43: 26 April 2011

The average results from each stability test for the MRM pesticides are given in **Table 1-5**. A graphic presentation of the stability test results is shown in **Appendix 3**. The tests did not show any significant decrease in the pesticide levels at -18 °C, indicating that at these storage conditions the pesticides present in the Test Material remained stable for the entire duration of the Proficiency Test. Even after storage at r room temperature there were no significant decreases in the pesticide levels.

The results of the stability test of the SRM pesticides are shown in **Table 1-6** and **Appendix 8**. The tests did not show any significant decrease in the pesticide levels at -18 °C (the recommended storage temperature), indicating that under these storage conditions the pesticides present in the Test Material remained sufficiently stable for the entire duration of the EUPT.

1.7 Organisational details

1.7.1 Announcement / Invitation and EUPT-C5/SRM6-Website

An Announcement/Invitation Letter was sent in December 2010 to all NRL-CFs and NRL-SRMs as well as to any other OfLs analyzing cereal or feed for pesticide residues within the framework of official controls. A list of laboratories that are obliged to participate in this EUPT according to Art. 28 of Reg. 396/2005/EU and Art 33 of Reg. 882/2005/EC was constructed based on information submitted by the NRLs and the official laboratories themselves. The invitation was also sent to all official laboratories for which no information regarding the scope they cover was available. NRLs were additionally prompted to carefully check the list of those laboratories within their network and asked to amend and complement it, as necessary, and to ensure that all laboratories obliged to participate within their network were informed of this EUPT.

Table 1-5: Stability test results of MRM pesticides stored at room temperature and -18 °C, please see also Appendix 3

	Azoxystrobin	Carbendazim	Chlorpyrifos	Deltamethrin (cis)	Difenoconazole	Diflubenzuron	Epoxiconazole	Fipronil
Day 2	0.161	0.088	0.246	0.301	0.220	0.112	0.096	0.175
Storage at -18 °C (mean values in mg/kg)								
Day 8	0.174	0.090	0.264	0.420	0.243	0.142	0.103	0.197
Day 15	0.167	0.089	0.246	0.349	0.222	0.120	0.096	0.177
Day 21	0.164	0.091	0.237	0.251	0.220	0.136	0.096	0.167
Day 28	0.164	0.090	0.244	0.322	0.237	0.140	0.100	0.171
Passed/Failed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
Storage at Room Temperature (mean values in mg/kg) – informative purpose only								
Day 8	0.168	0.087	0.239	0.506	0.232	0.141	0.094	0.182
Day 28	0.186	0.090	0.278	0.513	0.272	0.145	0.115	0.188

	Isoprothiolane	Kresoxim-methyl	Pirimiphos-methyl	Propiconazole	Tebuconazole	Thiamethoxam	Tricyclazole	Trifloxystrobin
Day 2	0.148	0.184	0.074	1.03	1.01	0.231	0.341	0.236
Storage at -18 °C (mean values in mg/kg)								
Day 8	0.146	0.199	0.082	1.11	1.06	0.330	0.384	0.246
Day 15	0.148	0.185	0.073	1.03	0.98	0.266	0.363	0.239
Day 21	0.151	0.179	0.072	1.04	0.98	0.235	0.347	0.230
Day 28	0.149	0.186	0.077	1.08	1.01	0.262	0.351	0.228
Passed/Failed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
Storage at Room Temperature (mean values in mg/kg) – informative purpose only								
Day 8	0.141	0.189	0.078	1.02	0.96	0.304	0.374	0.230
Day 28	0.146	0.180	0.078	1.20	1.11	0.310	0.431	0.261

Table 1-6: Stability test results of SRM analytes (storage at -18 °C), see also Appendix 8

	2,4-D	Brominde	Dithiocarbamates	Ethephon	Glyphosate	Haloxyfop	Quinclorac
Storage at -18 °C (mean values in mg/kg)							
Day 1: 14 March 2011	0.275	57.5	0.622	0.287	0.378	0.123	0.288
Day 21: 04 April 2011	0.279	60.2	0.609	0.281	0.371	0.129	0.286
Day 43: 26 April 2011	0.269	61.2	0.591	0.273	0.380	0.128	0.281
Deviation [%] Day 43 vs. Day 1	**-2.20 %**	**6.49 %**	**-4.86 %**	**-4.88 %**	**0.74 %**	**4.06 %**	**-2.70 %**
Passed/Failed	Passed	Passed	Passed	Passed	Passed	Passed	Passed

NRLs and OfLs from EFTA countries, as well as of EU-candidate states, were also invited if their contact data was available.

All documents relevant to this EUPT (Calendar, Target Pesticides List, Specific Protocol, General Protocol) were uploaded to the EURL-web-portal and the CIRCA/FIS-VL platform. A joint EUPT-C5/SRM6-Website containing links to all these documents was constructed within the EURL-web-portal.

1.7.2 Registration and confidentiality

All laboratories obliged to participate in the current PT, regardless of whether they were intending to participate in this exercise or not, were required to register within the EUPT-registration-website. Laboratories that did not intent to participate were asked to state the reasons for their non-participation.

The participating labs were provided with a unique laboratory code, as well as a unique login information to be used to enter 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 Protocol for EUPTs (**Appendix 14**).

1.7.3 Distribution of the Test Material

One bottle of treated Test Material (50 g for MRM analytes and 250 g for SRM analytes) and one bottle of 'blank' material (50 g for MRM analytes and 250 g for SRM analytes) were shipped on 14 March 2011 to each participant in thermo-insulated polystyrene boxes containing a cryobag. Laboratories were asked to check the integrity and condition of the sample upon receipt and to report to the Organizer via the website any observations or complaints and whether they would accept the Test Material.

Instructions on how to treat the Test Materials upon receipt were provided to the participating laboratories within the Specific Protocol (**Appendix 15**) released on 09 March 2011.

1.7.4 Submission of results

An online submission tool allowed participants to submit their results via the Internet. All participants had access to the result-submission-website from a week after the sample shipment until the result submission deadline (11 April 2011). Participants were asked not only to report their analytical results, but also to state their experience with the analysis of all pesticides on the Target Pesticides List. In addition, laboratories had to provide details about the methods they had used and to provide their own reporting limits (RLs) for each of the pesticides.

2. EVALUATION RULES

2.1 False positives and negatives

2.1.1 False positives (FP)

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

2.1.2 False negatives (FN)

These are results of pesticides reported as "Analyzed" but where no numerical values were reported, although they were used by the Organiser to prepare the Test Material and were detected, at or above the MRRL, by the Organiser and the majority of the participating laboratories. Z-Scores for false negatives were calculated using the MRRL as the result. Any reporting-limits (RLs) that were higher than the MRRL were not taken into account.

2.2 Establishment of the assigned (consensus) values

To establish the Assigned Values, the median levels of all reported results from EU and EFTA countries, excluding outliers, were used.

2.3 Fixed target standard deviation (FFP-approach)

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

2.4 z-Scores

A z-score for each combination of laboratory and pesticide was calculated according to the following equation:

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

Where

- x_i is the result for the pesticide (i) as reported by the participant
  (For results considered as false negatives, x_i was set as equal to the respective minimum required reporting level (MRRL) or the laboratory reporting level (RL), if RL< MRRL.)
- μ_i is the Assigned Value for the pesticide (i)
- δ_i is the target standard deviation for the pesticide (i), which equals 25 % of the Assigned Value (FFP-approach)

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

The z-scores were classified as follows:

$\|z\| \leq 2$	acceptable
$2 < \|z\| \leq 3$	questionnable
$\|z\| > 3$	unacceptable

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

2.5 Lab ranking and classification

2.5.1 Category A and B classification

Based on the scope covered by the labs, laboratories were subdivided into Categories (A and B) in accordance with the rules in the General Protocol (**Appendix 14**). To be classified into Category A a laboratory should

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

2.5.2 Combined z-scores

In order to evaluate the overall performance of each laboratory combined z-scores (SWZ and SZ^2) were calculated in the case of MRM pesticides. Both combined z-scores are considered to be of lesser importance than the individual z-scores.

Sum of Weighted z-scores (SWZ)

The SWZ[1] is calculated only for laboratories within Category A using the following formula:

$$SWZ = \frac{\sum_{|Z_i|=0}^{|Z_i|\leq 2} |z_i| \cdot 1 + \sum_{|Z_i|>2}^{|Z_i|\leq 3} |z_i| \cdot 3 + \sum_{|Z_i|>3}^{\infty} |z_i| \cdot 5}{n}$$

where "n" is the number of each laboratory's z-scores that were considered in this formula. For the calculation, any z-score > 5 was set at "5".

The SWZ-scores were classified as follows:

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

[1] The SWZ and SZ^2 formulas actually describe the **average** of the weighted absolute z-scores and squared z-scores respectively. The term "sum" is still used in this report for the sake of consistency with previous reports and to avoid confusion, but the Advisory Group may decide to change the nomenclature in future EUPT-reports.

Sum of Squared z-Scores (SZ^2)

The sum of squared z-scores (SZ^2) formula multiplies each z-score by itself and not by an arbitrary number, using the following formula:

$$SZ^2 = \frac{\sum_{|Z_i|=0}^{\infty} z_i^{\,2}}{n}$$

where "n" is the number of each laboratory's z-scores that were considered in this formula. For the calculation, any z-score > 5 was set at "5".

The SZ^2-scores were classified as follows:

$SZ^2 \leq 2$	good
$2 < SZ^2 \leq 3$	satisfactory
$SZ^2 > 3$	unsatisfactory

3. RESULTS – MRM PESTICIDES

3.1 Participation

In total, 133 laboratories representing 29 EU and EFTA countries agreed to participate in this Proficiency Test, and 130 of the laboratories submitted results for MRM pesticides before 11 April 2011. An additional 22 laboratories from Third Countries registered for the PT and 21 submitted results. The participating laboratories are listed in **Appendix 1**.

3.2 Overview of results

All reported analytical results can be seen in **Table 3-7** and the methods used are shown in **Appendix 6**. However, only results submitted by laboratories from EU and EFTA countries are included in **Tables 3-1** to **3-6**.

An overview of the results submitted by laboratories from the EU and EFTA can be seen in **Table 3-4**. It was not possible to perform a reliable statistical evaluation of the results for malathion and lambda-cyhalothrin because the median values were too close to the MRRL (Median < 4 × MRRL). Although the laboratories were asked to submit results for both individual compounds and summed residue definitions, the EUPT-Scientific Committee decided that only the individual compound should be statistically evaluated. Consequently, thiamethoxam (sum) is not included in **Table 3-4**. Three laboratories only reported results for "thiamethoxam sum", and not for the individual compounds. For these laboratories the "summed results" have been used to calculate z-scores for thiamethoxam.

Azoxystrobin, chlorpyrifos, deltamethrin (cis), pirimiphos-methyl and tebuconazole were the most frequently analysed compounds with 80 % or more of the labs submitting results for these compounds. All other pesticides were targeted by less than 80 % of the laboratories.

3.2.1 False positives

Nine laboratories reported ten results above the MRRL for additional pesticides that had not been used to treat the Test Material (see **Table 3-1**). In all cases the compounds were not detected either by the Organizer or by the overwhelming majority of the other participating laboratories. The reported results were therefore considered to be false positives.

Four laboratories reported twelve results below the MRRL for additional pesticides (see **Table 3-2**). These results were not considered to be false positives. However, the laboratories should be more careful when reporting results, as they were not only lower than the respective MRRLs, but most of them (eight) were also lower than the reporting limits (RLs) given by the respective laboratory.

3.2.2 False negatives

Missing results for pesticides actually present in the Test Material, were judged as false negatives. **Table 3-3** summarizes the number of reported false negatives for each pesticide. For the MRM pesticides, 41 results were judged as false negatives, which represents 2.7 % of the total number of MRM pesticide results. More than 20 % of the participants (26 laboratories) had false negative results. One laboratory submitted a result as < 0.01 (pirimiphos-methyl). This value is not in accordance with the protocol and therefore considered

Table 3-1: False positive results at or above 0.01 mg/kg, the concentration level detected in mg/kg, determination technique, reporting level and MRRL in mg/kg.

Laboratory code	Pesticide	Concentration [mg/kg]	Determination Technique	RL [mg/kg]	MRRL [mg/kg]
19	Prothioconazole	0.203	LC-MS/MS (QQQ)		0.01
22	Isoproturon	0.142	LC-MS/MS (QQQ)	0.01	0.01
38	Endosulfan sulfate	0.036	GC-ECD	0.01	0.01
41	Permethrin	0.0244	GC-MS/MS (QQQ)	0.01	0.01
49	Chlorpyrifos-methyl	0.156	GC-Ion Trap	0.042	0.01
95	Chlorpyrifos-methyl	0.0667	GC-MSD	0.02	0.01
101	DDT (sum)	0.027		0.001	0.01
117	DDT (sum)	0.091	GC-ECD	0.01	0.01
117	Endosulfan sulfate	0.078	GC-ECD	0.01	0.01
131	Imazalil	0.282	GC-MS/MS (QQQ)	0.282	0.01

Table 3-2: Submitted results below 0.01 mg/kg, the concentration level detected in mg/kg, determination technique, reporting level and MRRL in mg/kg.

Laboratory code	Pesticide	Concentration [mg/kg]	Determination Technique	RL [mg/kg]	MRRL [mg/kg]
41	Cypermethrin (sum)	0.0045	GC-MS/MS (QQQ)	0.01	0.01
41	Cyproconazole	0.0044	LC-MS/MS QQQ	0.05	0.01
41	Dimethoate (sum)	0.0013	LC-MS/MS QQQ	0.01	0.01
41	Isoproturon	0.0017	LC-MS/MS QQQ	0.01	0.01
41	Linuron	0.0009	LC-MS/MS QQQ	0.01	0.01
41	Tebufenozide	0.0017	LC-MS/MS QQQ	0.01	0.01
44	- Endosulfan, alpha	0.00008	GC-MSD	0.00005	0.01
44	- Endosulfan, beta	0.0001	GC-MSD	0.0001	0.01
44	- Endosulfan sulfate	0.0002	GC-MSD	0.0001	0.01
44	Endosulfan (sum)	0.0004	GC-MSD	0.00025	0.01
101	Cypermethrin (sum)	0.008		0.005	0.01
121	Cyproconazole	0.00141		0.01	

Table 3-3: False negative results.

Lab Code	Azoxystrobin	Carbendazim	Chlorpyrifos	Deltamethrin (cis)	Difenoconazole	Diflubenzuron	Epoxiconazole	Fipronil	Isoprothiolane	Kresoxim-methyl	Pirimiphos-methyl	Propiconazole	Tebuconazole	Thiamethoxam	Tricyclazole	Trifloxystrobin
5															ND	
9																ND
16														ND		
20				ND												
22									ND			ND				
36										ND						
43												ND				
46								ND								
49			ND													

Tabel 3-3 (cont.): False negative results.

Lab Code	Azoxystrobin	Carbendazim	Chlorpyrifos	Deltamethrin (cis)	Difenoconazole	Diflubenzuron	Epoxiconazole	Fipronil	Isoprothiolane	Kresoxim-methyl	Pirimiphos-methyl	Propiconazole	Tebuconazole	Thiamethoxam	Tricyclazole	Trifloxystrobin
53							ND			ND						
54											ND					
58															ND	
64									ND							
66					ND											
72				ND										ND		
75															ND	
79												ND				
95			ND													
97																ND
98									ND							
106	ND	ND		ND	ND		ND	ND					ND	ND	ND	ND
110											ND					
121												ND				
126						ND									ND	
131															ND	
135												ND				
145						ND										

Table 3-4: Overview of number of results, number of not analysed (NA), number of not detected (ND = false negatives) and the percentage of laboratories that reported results for the pesticides in the Test Material.

Pesticides	No. of results	No. of NA [1)]	No. of ND [2)]	% results [3)]
Azoxystrobin	107	26	1	80
Carbendazim	87	46	1	65
Chlorpyrifos	126	7	2	95
Deltamethrin (cis)	112	21	3	84
Difenoconazole	98	35	2	74
Diflubenzuron	72	61	2	54
Epoxiconazole	93	40	2	70
Fipronil	89	44	2	67
Isoprothiolane	54	79	4	41
Kresoxim-methyl	105	28	2	79
Pirimiphos-methyl	124	9	1	93
Propiconazole	105	28	5	79
Tebuconazole	108	25	1	81
Thiamethoxam	82	51	3	62
Tricyclazole	57	76	6	43
Trifloxystrobin	102	31	3	77

1) NA = not analysed
2) ND = not detected (false negatives)
3) '% results' has been calculated using the number of laboratories that reported results for that particular compound and the total number of EU laboratories submitting results (n = 133). False negatives are included in reported results.

to be a false negative. Several of the laboratories stated after the deadline for submitting results that they hadn't actually analysed for the pesticides. Nevertheless, these results, which in this case were due to administrative rather than analytical errors, have still been evaluated as false negative results.

3.3 Assigned Values, target standard deviations and outliers

To establish the Assigned Values, the median levels of all the reported results submitted by laboratories from EU and EFTA countries, excluding outliers, were used. Twenty results were regarded as outliers (z-score ≥ 5); azoxystrobin (0.981 and 14.233 mg/kg), carbendazim (0.383 mg/kg), difenoconazole (0.666 mg/kg), diflubenzuron (0.26, 0.261, 0.284, 0.317, 0.337 and 0.448 mg/kg), fipronil (1.178 mg/kg), kresoxim-methyl (0.393 and 0.515 mg/kg), pirimiphos-methyl (0.17, 0.195 and 0.215 mg/kg), propiconazole (1.11 mg/kg), thiamethoxam (0.675 and 0.786 mg/kg) and tricyclazole (1.6235 mg/kg).

All Assigned Values for the pesticides can be seen in **Table 3-5**. The target standard deviation was obtained using a fixed FFP-RSD value of 25 %. In parallel, the robust standard deviation (Qn-RSD) was calculated for informative purposes only. The range of Qn-RSD values was from 16 to 29 % but on average the Qn-RSD was 22 %, and thus very close to the 25 % FFP-RSD used for the calculations.

3.4 Assessment of laboratory performance

3.4.1 z-Scores

Z-scores were calculated for the quantified pesticides using the FFP-RSD of 25 %. **Table 3-6** shows an overview of the results and **Tables 3-7** to **3-11** show the individual results and z-scores for each laboratory and pesticide together with the Assigned Value. A graphic representation of the z-scores can be seen in **Appendix 5**, and the histograms showing the distribution of the results are in **Appendix 4**.

Acceptable results were obtained for carbendazim, chlorpyrifos, epoxiconazole, fipronil, kresoxim-methyl, pirimiphos-methyl and tebuconazole by 90 – 94 % of the laboratories. For azoxystrobin, deltamethrin (cis), difenoconazole, isoprothiolane, propiconazole, thiamethoxam and trifloxystrobin, acceptable results were obtained by 81 – 89 % of the laboratories. Finally, for diflubenzuron and tricyclazole acceptable z-scores were obtained by only 72 – 75 % of the laboratories

Table 3-5: Assigned Values in mg/kg and Fit For Purpose Relative Standard Deviation (FFP-RSD) and Robust Relative Standard Deviation (Qn-RSD) for the pesticides present in the Test Material.

Pesticides	MRRL [mg/kg]	Assigned Value [mg/kg]	FFP-RSD [%]	Qn-RSD [%]
Azoxystrobin	0.01	0.164	25	24
Carbendazim	0.01	0.122	25	23
Chlorpyrifos	0.01	0.199	25	18
Deltamethrin (cis)	0.01	0.154	25	29
Difenoconazole	0.01	0.100	25	27
Diflubenzuron	0.01	0.113	25	26
Epoxiconazole	0.01	0.097	25	25
Fipronil	0.01	0.153	25	20
Isoprothiolane	0.01	0.170	25	16
Kresoxim-methyl	0.01	0.168	25	20
Lambda-cyhalothrin[*)]	0.01	0.025	25	20
Malathion[*)]	0.01	0.012	25	20
Pirimiphos-methyl	0.01	0.074	25	21
Propiconazole	0.01	0.442	25	28
Tebuconazole	0.01	0.813	25	23
Thiamethoxam	0.01	0.217	25	19
Tricyclazole	0.01	0.295	25	21
Trifloxystrobin	0.01	0.216	25	21

*) Lambda-cyhalothrin and malation were not evaluated because the median values were less than 4 times MRRL.

Table 3-6: Number of acceptable, questionable, unacceptable z-scores and false negatives. The unacceptable z-scores includes the false negatives.

Pesticides	Acceptable z-scores	Questionable z-scores	Unacceptable z-scores	False negatives
Azoxystrobin	94	9	4	1
Carbendazim	79	3	5	1
Chlorpyrifos	119	2	5	2
Deltamethrin (cis)	97	6	9	3
Difenoconazole	83	6	9	2
Diflubenzuron	52	9	11	2
Epoxiconazole	87	2	4	2
Fipronil	80	4	5	2
Isoprothiolane	44	2	8	4
Kresoxim-methyl	98	2	5	2
Pirimiphos-methyl	113	2	9	1
Propiconazole	85	5	15	5
Tebuconazole	100	3	5	1
Thiamethoxam	70	6	6	3
Tricyclazole	43	1	13	6
Trifloxystrobin	91	3	8	3

Table 3-7: Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores for laboratorie with labcodes 1 – 41. (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Azoxystrobin	Z-scores (FFP-RSD (25 %)	Carbendazim	Z-scores (FFP-RSD (25 %)	Chlorpyrifos	Z-scores (FFP-RSD (25 %)	Deltamethrin (cis)	Z-scores (FFP-RSD (25 %)	Difenoconazole	Z-scores (FFP-RSD (25 %)	Diflubenzuron	Z-scores (FFP-RSD (25 %)	Epoxiconazole	Z-scores (FFP-RSD (25 %)	Fipronil	Z-scores (FFP-RSD (25 %)	Isoprothiolane	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.164		0.122		0.199		0.154		0.100		0.113		0.097		0.153		0.170	
1	0.16	-0.1	0.131	0.3	0.199	0.0	0.192	1.0	0.093	-0.3	0.26	5.2	0.098	0.1	0.163	0.3	0.179	0.2
2	0.194	0.7	0.146	0.8	0.207	0.2	0.196	1.1	0.119	0.8	0.125	0.4	0.107	0.4	0.177	0.6	0.19	0.5
3	0.172	0.2	0.168	1.5	0.169	-0.6	0.147	-0.2	0.108	0.3	0.123	0.4	0.073	-1.0	0.145	-0.2	0.188	0.4
4	0.198	0.8	0.183	2.0	0.295	1.9	0.179	0.6	0.22	4.8	0.317	7.2	0.132	1.5	0.152	0.0	0.19	0.5
5	0.164	0.0	0.143	0.7	0.163	-0.7	0.156	0.1	0.118	0.7	0.448	11.9	0.107	0.4	0.166	0.4	0.171	0.0
6	0.159	-0.1	0.13	0.3	0.203	0.1	0.176	0.6	0.105	0.2	0.138	0.9	0.103	0.3	0.138	-0.4	0.169	0.0
7	0.172	0.2	0.133	0.4	0.187	-0.2	0.21	1.5	0.12	0.8			0.109	0.5	0.195	1.1		
8	0.177	0.3	0.108	-0.5	0.209	0.2	0.127	-0.7	0.128	1.1	0.105	-0.3	0.127	1.3	0.165	0.3	0.152	-0.4
9	0.223	1.4	0.123	0.0	0.275	1.5	0.198	1.1	0.143	1.7	0.113	0.0	0.123	1.1	0.147	-0.1		
10	0.16	-0.1	0.13	0.3	0.172	-0.5	0.162	0.2	0.091	-0.4	0.119	0.2	0.099	0.1	0.133	-0.5		
11	0.127	-0.9	0.118	-0.1	0.152	-0.9	0.144	-0.3	0.109	0.4	0.261	5.2	0.0744	-0.9	0.156	0.1	0.196	0.6
12					0.11	-1.8	0.216	1.6							0.265	3.0		
13	0.266	2.5	0.177	1.8	0.25	1.0	0.267	2.9	0.224	5.0	0.105	-0.3	0.157	2.5	0.232	2.1		
14	0.143	-0.5	0.118	-0.1	0.182	-0.3	0.143	-0.3	0.0963	-0.1	0.107	-0.2	0.0913	-0.2	0.149	-0.1	0.166	-0.1
15	0.18	0.4	0.1	-0.7	0.228	0.6	0.129	-0.6	0.1	0.0	0.106	-0.2	0.104	0.3	0.146	-0.2	0.181	0.3
16	0.116	-1.2	0.119	-0.1	0.201	0.1	0.152	-0.1	0.08	-0.8			0.091	-0.2				
17	0.204	1.0	0.118	-0.1	0.238	0.8	0.134	-0.5	0.099	0.0	0.107	-0.2	0.154	2.4	0.14	-0.3	0.142	-0.7
18	0.177	0.3	0.154	1.0	0.219	0.4	0.155	0.0	0.087	-0.5	0.111	-0.1	0.077	-0.8	0.141	-0.3		
19	0.117	-1.1	0.145	0.8	0.253	1.1	0.165	0.3	0.0625	-1.5	0.194	2.9	0.0589	-1.6	0.195	1.1		
20					0.152	-0.9	ND	-3.7										
21	0.095	-1.7	0.078	-1.4	0.18	-0.4	0.129	-0.6	0.055	-1.8	0.082	-1.1	0.051	-1.9	0.109	-1.1		
22	0.122	-1.0	0.108	-0.5	0.189	-0.2	0.192	1.0	0.0684	-1.3	0.0877	-0.9	0.0669	-1.2	0.109	-1.1	ND	-3.8
24	0.199	0.9	0.138	0.5	0.189	-0.2	0.149	-0.1	0.127	1.1	0.284	6.1	0.123	1.1	0.175	0.6	0.188	0.4
25	0.126	-0.9	0.128	0.2	0.249	1.0	0.211	1.5	0.0867	-0.5			0.0798	-0.7	0.213	1.6		
28	0.182	0.4	0.13	0.3	0.175	-0.5	0.181	0.7	0.155	2.2			0.118	0.9	0.154	0.0		
29	0.23	1.6	0.15	0.9	0.21	0.2	0.16	0.2	0.11	0.4	0.22	3.8	0.11	0.6	0.21	1.5	0.21	0.9
30	0.2	0.9	0.13	0.3	0.18	-0.4	0.08	-1.9	0.09	-0.4	0.18	2.4	0.11	0.6	0.13	-0.6	0.14	-0.7
31	0.178	0.3	0.11	-0.4	0.186	-0.3	0.142	-0.3	0.0896	-0.4	0.12	0.2	0.101	0.2	0.148	-0.1	0.168	0.0
32					0.233	0.7	0.08	-1.9										
33	0.187	0.6	0.122	0.0	0.204	0.1	0.15	-0.1	0.117	0.7	0.176	2.2	0.112	0.6	0.132	-0.5	0.187	0.4
34	0.17	0.1	0.118	-0.1	0.216	0.4			0.103	0.1	0.123	0.4	0.0955	0.0	0.158	0.1	0.17	0.0
35	0.159	-0.1	0.106	-0.5	0.189	-0.2	0.178	0.6	0.096	-0.2								
36	0.288	3.0			0.203	0.1	0.264	2.9	0.173	2.9					0.203	1.3		
37	0.185	0.5	0.08	-1.4	0.2	0.0	0.179	0.6	0.11	0.4	0.148	1.2	0.112	0.6	0.186	0.9	0.193	0.5
38	14.233	343.1			0.203	0.1	0.236	2.1										
39	0.184	0.5	0.167	1.5	0.258	1.2	0.198	1.1	0.138	1.5	0.241	4.5	0.108	0.5	0.171	0.5		
40	0.155	-0.2	0.107	-0.5	0.205	0.1	0.152	-0.1	0.094	-0.2	0.119	0.2	0.093	-0.1	0.141	-0.3	0.187	0.4
41	0.187	0.6	0.0942	-0.9	0.348	3.0	0.195	1.1	0.0441	-2.2	0.102	-0.4	0.107	0.4	0.177	0.6	0.198	0.7

Table 3-7 (cont.): Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores (labcodes 1 – 41). (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Kresoxim-methyl	Z-scores (FFP-RSD (25 %)	Lambda-cyhalothrin	Z-scores (FFP-RSD (25 %)	Pirimiphos-methyl	Z-scores (FFP-RSD (25 %)	Malathion	Z-scores (FFP-RSD (25 %)	Propiconazole	Z-scores (FFP-RSD (25 %)	Tebuconazole	Z-scores (FFP-RSD (25 %)	Thiamethoxam	Z-scores (FFP-RSD (25 %)	Tricyclazole	Z-scores (FFP-RSD (25 %)	Trifloxystrobin	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.168		0.025		0.074		0.012		0.442		0.813		0.217		0.295		0.216	
1	0.175	0.2	0.028		0.085	0.6	0.011		0.74	0.3	0.817	0.0	0.215	0.0	0.277	-0.2	0.226	0.2
2	0.178	0.2			0.08	0.4	0.01		0.535	0.8	0.938	0.6	0.227	0.2	0.291	-0.1	0.247	0.6
3	0.15	-0.4	0.02		0.07	-0.2			0.335	-1.0	0.935	0.6	0.239	0.4	0.438	1.9	0.18	-0.7
4	0.168	0.0	0.032		0.117	2.4	0.017		0.54	0.9	1.02	1.0	0.332	2.1	0.41	1.6	0.272	1.0
5	0.128	-1.0	0.02		0.057	-0.9			0.251	-1.7	0.925	0.6	0.261	0.8	ND	-3.9	0.16	-1.0
6	0.161	-0.2	0.023		0.069	-0.2	0.012		0.485	0.4	0.76	-0.3	0.219	0.0	0.319	0.3	0.222	0.1
7	0.156	-0.3	0.029		0.084	0.6	0.01		0.442	0.0	0.755	-0.3	0.265	0.9			0.2	-0.3
8	0.186	0.4	0.027		0.08	0.4	0.014		0.442	0.0	0.814	0.0	0.204	-0.2	0.263	-0.4	0.218	0.0
9	0.213	1.1	0.0213		0.0823	0.5	0.0133		0.56	1.1	1.11	1.5	0.273	1.0	0.363	0.9	ND	-3.8
10	0.184	0.4	0.029		0.1	1.4	0.011		0.498	0.5	0.91	0.5	0.213	-0.1			0.195	-0.4
11	0.148	-0.5	0.0225		0.051	-1.2			0.408	-0.3	0.735	-0.4			0.296	0.0	0.202	-0.3
12	0.17	0.0	0.032		0.057	-0.9			0.678	2.1	1.624	4.0			0.307	0.2	0.256	0.7
13	0.211	1.0	0.057		0.089	0.8			0.513	0.6	0.984	0.8	0.253	0.7			0.307	1.7
14	0.169	0.0	0.024		0.0803	0.4	0.0088		0.431	-0.1	0.765	-0.2	0.183	-0.6	0.287	-0.1	0.203	-0.2
15	0.189	0.5	0.0266		0.0929	1.1	0.0119		0.486	0.4	0.876	0.3	0.207	-0.2	0.321	0.4	0.188	-0.5
16	0.156	-0.3			0.061	-0.7			0.405	-0.3	0.73	-0.4	ND	-3.8			0.216	0.0
17	0.202	0.8	0.026		0.096	1.2	0.026		0.426	-0.1	1.03	1.1	0.187	-0.6	0.254	-0.6	0.222	0.1
18	0.176	0.2	0.032		0.09	0.9	0.014		0.435	-0.1	0.806	0.0	0.171	-0.8			0.201	-0.3
19	0.125	-1.0	0.0269		0.102	1.6			0.552	1.0	0.509	-1.5	0.135	-1.5			0.185	-0.6
20																		
21	0.14	-0.7	0.018		0.058	-0.8			0.31	-1.2	0.5	-1.5	0.165	-1.0			0.17	-0.9
22	0.143	-0.6	0.0218		0.0648	-0.5			ND	-3.9	0.571	-1.2	0.195	-0.4	0.234	-0.8	0.181	-0.6
24	0.191	0.5	0.019		0.093	1.1	0.01		0.515	0.7	1.02	1.0	0.22	0.1	0.464	2.3	0.245	0.5
25	0.167	0.0	0.0302		0.0936	1.1			0.432	-0.1	0.729	-0.4	0.195	-0.4			0.244	0.5
28	0.174	0.1	0.02		0.061	-0.7			0.589	1.3	1.07	1.3	0.197	-0.4			0.213	-0.1
29	0.13	-0.9	0.02		0.07	-0.2	0.05				0.66	-0.8	0.27	1.0	0.31	0.2	0.24	0.4
30	0.16	-0.2	0.02		0.17	5.3	0.01		0.38	-0.6	0.6	-1.0	0.24	0.4	0.38	1.2	0.26	0.8
31	0.178	0.2	0.0244		0.0919	1.0	0.0116		0.592	1.4	0.975	0.8	0.208	-0.2	0.29	-0.1	0.232	0.3
32			0.023		0.064	-0.5	0.007											
33	0.185	0.4	0.0422		0.078	0.2	0.014		0.535	0.8	0.685	-0.6	0.23	0.2	0.36	0.9	0.243	0.5
34	0.187	0.5			0.0808	0.4			0.474	0.3	0.877	0.3	0.21	-0.1			0.225	0.2
35	0.202	0.8	0.022		0.077	0.2					0.983	0.8						
36	ND	-3.8	0.046		0.162	4.8			0.582	1.3	1.1	1.4					0.308	1.7
37	0.221	1.3			0.077	0.2	0.015		0.576	1.2	0.895	0.4	0.22	0.1	0.35	0.7	0.125	-1.7
38			0.023		0.07	-0.2	0.012		0.875	3.9	1.416	3.0	0.281	1.2				
39	0.143	-0.6	0.03		0.101	1.5			0.419	-0.2	0.856	0.2	0.325	2.0			0.22	0.1
40	0.177	0.2	0.028		0.075	0.1			0.51	0.6	0.802	-0.1	0.159	-1.1	0.241	-0.7	0.175	-0.8
41	0.198	0.7	0.0241		0.088	0.8	0.0128		0.3803	-0.6	1.068	1.3	0.786	10.5	1.6235	18.0	0.337	2.2

Table 3-8: Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores for laboratorie with labcodes 42 – 81. (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Azoxystrobin	Z-scores (FFP-RSD (25 %)	Carbendazim	Z-scores (FFP-RSD (25 %)	Chlorpyrifos	Z-scores (FFP-RSD (25 %)	Deltamethrin (cis)	Z-scores (FFP-RSD (25 %)	Difenoconazole	Z-scores (FFP-RSD (25 %)	Diflubenzuron	Z-scores (FFP-RSD (25 %)	Epoxiconazole	Z-scores (FFP-RSD (25 %)	Fipronil	Z-scores (FFP-RSD (25 %)	Isoprothiolane	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.164		0.122		0.199		0.154		0.100		0.113		0.097		0.153		0.170	
42	0.146	-0.4	0.275	5.0	0.16	-0.8	0.141	-0.3										
43	0.143	-0.5	0.112	-0.3	0.198	0.0	0.175	0.5	0.094	-0.2	0.102	-0.4	0.073	-1.0	0.161	0.2	0.155	-0.4
44																		
45	0.16	-0.1			0.218	0.4	0.215	1.6	0.102	0.1			0.093	-0.1	0.173	0.5		
46	0.172	0.2			0.188	-0.2	0.175	0.5	0.132	1.3	0.337	7.9	0.102	0.2	ND	-3.7		
47	0.175	0.3	0.115	-0.2	0.192	-0.1	0.181	0.7	0.11	0.4			0.106	0.4	0.151	0.0	0.159	-0.3
48	0.15	-0.3	0.115	-0.2	0.215	0.3	0.245	2.4	0.12	0.8	0.12	0.2	0.117	0.8	0.169	0.4	0.13	-0.9
49	0.086	-1.9	0.132	0.3	ND	-3.8	0.151	-0.1					0.079	-0.7				
50	0.143	-0.5	0.118	-0.1	0.201	0.1	0.126	-0.7	0.0928	-0.3	0.107	-0.2	0.11	0.6	0.157	0.1	0.168	0.0
51	0.195	0.8	0.119	-0.1	0.259	1.2	0.216	1.6	0.112	0.5	0.107	-0.2	0.103	0.3	0.174	0.6	0.183	0.3
52	0.2	0.9			0.156	-0.9	0.084	-1.8	0.094	-0.2								
53	0.125	-1.0	0.14	0.6	0.203	0.1	0.189	0.9	0.0776	-0.9	0.0728	-1.4	ND	-3.6	0.12	-0.9	0.138	-0.8
54					0.24	0.8	0.272	3.1										
55	0.164	0.0	0.139	0.6	0.214	0.3	0.156	0.1	0.0981	-0.1	0.111	-0.1	0.112	0.6	0.162	0.2		
57	0.191	0.7	0.125	0.1	0.19	-0.2	0.116	-1.0	0.121	0.8	0.121	0.3	0.11	0.6	0.181	0.7	0.171	0.0
58	0.28	2.8			0.234	0.7	0.225	1.8					0.113	0.7	0.169	0.4	0.284	2.7
60	0.136	-0.7	0.133	0.4	0.172	-0.5	0.219	1.7	0.0875	-0.5			0.083	-0.6	0.144	-0.2		
61					0.223	0.5												
62	0.12	-1.1			0.18	-0.4	0.18	0.7	0.12	0.8			0.08	-0.7	0.14	-0.3		
63	0.143	-0.5	0.383	8.6	0.164	-0.7	0.182	0.7	0.031	-2.8			0.129	1.3	0.138	-0.4		
64	0.17	0.1	0.128	0.2	0.23	0.6	0.1	-1.4	0.052	-1.9	0.103	-0.4	0.0528	-1.8	0.158	0.1	ND	-3.8
65	0.164	0.0	0.248	4.1	0.198	0.0	0.168	0.4	0.0562	-1.8	0.178	2.3	0.0484	-2.0	0.24	2.3		
66	0.136	-0.7	0.09	-1.0	0.175	-0.5	0.18	0.7	ND	-3.6	0.133	0.7	0.09	-0.3	0.1	-1.4		
67	0.168	0.1	0.138	0.5	0.199	0.0	0.142	-0.3	0.117	0.7			0.122	1.1				
68	0.148	-0.4			0.207	0.2	0.222	1.8			0.087	-0.9						
69																		
70	0.135	-0.7			0.195	-0.1	0.13	-0.6	0.0851	-0.6			0.0781	-0.8				
71	0.058	-2.6			0.13	-1.4	0.147	-0.2										
72	0.074	-2.2	0.07	-1.7	0.295	1.9	ND	-3.7	0.666	22.6	0.035	-2.8			0.214	1.6		
73	0.175	0.3	0.101	-0.7	0.21	0.2	0.202	1.2	0.101	0.0	0.103	-0.4	0.083	-0.6	0.153	0.0	0.153	-0.4
74	0.16	-0.1			0.19	-0.2	0.15	-0.1	0.09	-0.4			0.075	-0.9	0.13	-0.6		
75	0.261	2.4	0.188	2.2	0.196	-0.1	0.154	0.0	0.12	0.8	0.186	2.6	0.092	-0.2	0.125	-0.7		
76	0.166	0.0	0.132	0.3	0.199	0.0	0.133	-0.5	0.0792	-0.8	0.0777	-1.2	0.0529	-1.8	0.109	-1.1	0.175	0.1
77					0.21	0.2												
78	0.219	1.3	0.153	1.0	0.189	-0.2	0.134	-0.5	0.118	0.7	0.105	-0.3	0.104	0.3	0.12	-0.9	0.195	0.6
79	0.11	-1.3	0.07	-1.7	0.204	0.1	0.203	1.3	0.0779	-0.9	0.0987	-0.5	0.0526	-1.8				
80					0.202	0.1												
81					0.202	0.1												

Table 3-8 (cont.): Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores (labcodes 42 – 81). (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Kresoxim-methyl	Z-scores (FFP-RSD (25 %)	Lambda-cyhalothrin	Z-scores (FFP-RSD (25 %)	Pirimiphos-methyl	Z-scores (FFP-RSD (25 %)	Malathion	Z-scores (FFP-RSD (25 %)	Propiconazole	Z-scores (FFP-RSD (25 %)	Tebuconazole	Z-scores (FFP-RSD (25 %)	Thiamethoxam	Z-scores (FFP-RSD (25 %)	Tricyclazole	Z-scores (FFP-RSD (25 %)	Trifloxystrobin	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.168		0.025		0.074		0.012		0.442		0.813		0.217		0.295		0.216	
42	0.262	2.2			0.065	-0.5			0.379	-0.6	0.951	0.7						
43	0.188	0.5	0.026		0.078	0.2	0.011		ND	-3.9	0.786	-0.1	0.225	0.1	0.272	-0.3	0.207	-0.2
44																		
45	0.168	0.0	0.0275		0.0735	0.0			0.455	0.1	0.789	-0.1					0.199	-0.3
46	0.257	2.1			0.065	-0.5			0.355	-0.8	0.63	-0.9	0.166	-0.9			0.4	3.4
47	0.157	-0.3	0.022		0.08	0.4			0.495	0.5	0.971	0.8	0.192	-0.5	0.21	-1.2	0.261	0.8
48	0.172	0.1	0.043		0.065	-0.5	0.012		0.401	-0.4	0.942	0.6	0.228	0.2	0.273	-0.3	0.209	-0.1
49	0.143	-0.6			0.078	0.2			0.356	-0.8	0.494	-1.6					0.175	-0.8
50	0.174	0.1	0.018		0.068	-0.3	0.01		0.466	0.2	0.87	0.3	0.201	-0.3	0.291	-0.1	0.212	-0.1
51	0.153	-0.4	0.028		0.106	1.8	0.016		0.457	0.1	0.846	0.2	0.187	-0.6	0.314	0.3	0.202	-0.3
52	0.13	-0.9	0.02		0.064	-0.5			0.182	-2.4	0.141	-3.3					0.252	0.7
53	ND	-3.8	0.0271		0.0692	-0.2			0.353	-0.8	0.648	-0.8	0.206	-0.2	0.237	-0.8	0.191	-0.5
54					ND	-3.5												
55	0.169	0.0	0.0231		0.088	0.8			0.474	0.3	0.831	0.1					0.292	1.4
57	0.225	1.4	0.032		0.094	1.1	0.013		0.536	0.9	0.932	0.6	0.24	0.4	0.361	0.9	0.258	0.8
58	0.184	0.4	0.026		0.0928	1.1	0.0121		1.11	6.0	1.56	3.7			ND	-3.9	0.343	2.4
60	0.15	-0.4	0.0125		0.0645	-0.5			0.375	-0.6	0.641	-0.8	0.195	-0.4			0.18	-0.7
61					0.0705	-0.2												
62	0.12	-1.1			0.14	3.6			0.11	-3.0	0.65	-0.8					0.16	-1.0
63	0.101	-1.6	0.0291		0.0579	-0.8					0.778	-0.2	0.675	8.4			0.285	1.3
64	0.17	0.0	0.022		0.071	-0.1	0.014		0.63	1.7	0.58	-1.1	0.217	0.0	0.291	-0.1	0.205	-0.2
65	0.172	0.1	0.0259		0.0651	-0.5			0.631	1.7	0.815	0.0	0.135	-1.5			0.189	-0.5
66	0.141	-0.6			0.075	0.1			0.18	-2.4	0.632	-0.9	0.22	0.1	0.302	0.1	0.196	-0.4
67	0.18	0.3	0.03		0.071	-0.1	0.012		0.556	1.0	0.852	0.2	0.214	-0.1			0.238	0.4
68	0.183	0.4	0.021		0.081	0.4	0.013		0.869	3.9	1.43	3.0						
69																		
70	0.14	-0.7	0.0231		0.065	-0.5			0.36	-0.7	0.78	-0.2					0.265	0.9
71					0.034	-2.1					0.418	-1.9						
72	0.515	8.3			0.14	3.6	0.028		0.87	3.9	1.164	1.7	ND	-3.8			0.404	3.5
73	0.165	-0.1	0.031		0.084	0.6	0.014		0.164	-2.5	0.784	-0.1	0.187	-0.6	0.262	-0.4	0.205	-0.2
74	0.15	-0.4	0.035		0.08	0.4			0.35	-0.8	0.7	-0.6					0.19	-0.5
75	0.252	2.0	0.023		0.076	0.1	0.013		0.395	-0.4	0.698	-0.6	0.241	0.4	ND	-3.9	0.323	2.0
76	0.124	-1.0	0.021		0.0493	-1.3			0.319	-1.1	0.459	-1.7	0.0802	-2.5	0.281	-0.2	0.189	-0.5
77					0.0732	0.0	0.0124											
78	0.195	0.6	0.021		0.079	0.3	0.011		0.368	-0.7	0.695	-0.6	0.192	-0.5	0.21	-1.2	0.235	0.4
79	0.393	5.4	0.0303		0.0663	-0.4			ND	-3.9	0.453	-1.8	0.27	1.0			0.174	-0.8
80					0.073	0.0	0.012											
81					0.07	-0.2	0.011											

Table 3-9: Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores for laboratorie with labcodes 82 – 123. (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Azoxystrobin	Z-scores (FFP-RSD (25 %)	Carbendazim	Z-scores (FFP-RSD (25 %)	Chlorpyrifos	Z-scores (FFP-RSD (25 %)	Deltamethrin (cis)	Z-scores (FFP-RSD (25 %)	Difenoconazole	Z-scores (FFP-RSD (25 %)	Diflubenzuron	Z-scores (FFP-RSD (25 %)	Epoxiconazole	Z-scores (FFP-RSD (25 %)	Fipronil	Z-scores (FFP-RSD (25 %)	Isoprothiolane	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.164		0.122		0.199		0.154		0.100		0.113		0.097		0.153		0.170	
82					0.2	0.0												
84	0.168	0.1	0.109	-0.4	0.181	-0.4	0.135	-0.5	0.0973	-0.1	0.0942	-0.7	0.0885	-0.3	0.138	-0.4	0.163	-0.2
85	0.127	-0.9			0.156	-0.9	0.13	-0.6	0.0711	-1.2					0.0861	-1.7		
86	0.18	0.4	0.14	0.6	0.229	0.6	0.139	-0.4	0.106	0.2	0.112	0.0	0.092	-0.2	0.142	-0.3	0.164	-0.1
87					0.204	0.1												
88	0.17	0.1	0.131	0.3	0.196	-0.1	0.118	-0.9	0.093	-0.3	0.113	0.0	0.074	-0.9	0.161	0.2	0.133	-0.9
89	0.179	0.4	0.124	0.1	0.21	0.2	0.171	0.4	0.118	0.7	0.118	0.2	0.101	0.2	0.17	0.5	0.171	0.0
90	0.157	-0.2	0.115	-0.2	0.222	0.5	0.208	1.4	0.109	0.4	0.124	0.4	0.098	0.1	0.15	-0.1	0.165	-0.1
91					0.194	-0.1												
92					0.17	-0.6												
93	0.15	-0.3	0.11	-0.4	0.2	0.0	0.14	-0.4	0.11	0.4	0.1	-0.5	0.1	0.1	0.16	0.2	0.17	0.0
94	0.144	-0.5	0.115	-0.2	0.175	-0.5	0.151	-0.1	0.083	-0.7	0.083	-1.1	0.078	-0.8	0.144	-0.2	0.123	-1.1
95	0.111	-1.3			ND	-3.8	0.125	-0.8	0.0798	-0.8			0.0794	-0.7				
96	0.148	-0.4	0.114	-0.3	0.165	-0.7	0.123	-0.8	0.093	-0.3	0.092	-0.7	0.086	-0.4	0.19	1.0	0.144	-0.6
97	0.981	19.9			0.157	-0.8	0.0872	-1.7	0.0352	-2.6			0.0554	-1.7	1.178	26.9		
98	0.0545	-2.7	0.039	-2.7	0.132	-1.3	0.126	-0.7	0.021	-3.2	0.136	0.8			0.235	2.2	ND	-3.8
100	0.144	-0.5	0.085	-1.2	0.175	-0.5	0.149	-0.1										
101					0.237	0.8	0.141	-0.3										
102	0.183	0.5			0.141	-1.2	0.123	-0.8										
103	0.1	-1.6	0.0901	-1.0	0.162	-0.7	0.144	-0.3	0.0507	-2.0	0.0891	-0.8	0.0562	-1.7	0.0987	-1.4	0.117	-1.2
104	0.263	2.4	0.126	0.1	0.286	1.8	0.243	2.3	0.133	1.3	0.176	2.2	0.11	0.6	0.2	1.2	0.189	0.4
105					0.19	-0.2	0.178	0.6										
106	ND	-3.8	ND	-3.7	0.06	-2.8	ND	-3.7	ND	-3.6			ND	-3.6	ND	-3.7		
107	0.176	0.3	0.096	-0.9	0.218	0.4	0.121	-0.9	0.114	0.6	0.113	0.0			0.127	-0.7		
108	0.151	-0.3	0.118	-0.1	0.31	2.2			0.134	1.4			0.088	-0.4				
109			0.151	1.0					0.043	-2.3			0.12	1.0				
110					0.19	-0.2												
111	0.203	1.0	0.137	0.5	0.292	1.9	0.274	3.1	0.096	-0.2	0.117	0.1	0.144	2.0				
113	0.156	-0.2	0.12	-0.1	0.168	-0.6	0.118	-0.9	0.099	0.0	0.106	-0.2	0.07	-1.1	0.111	-1.1	0.116	-1.3
114	0.228	1.6	0.14	0.6	0.22	0.4	0.176	0.6	0.146	1.8	0.098	-0.5	0.053	-1.8	0.15	-0.1	0.169	0.0
115					0.21	0.2												
116	0.12	-1.1	0.103	-0.6	0.138	-1.2	0.089	-1.7	0.056	-1.8	0.078	-1.2	0.058	-1.6	0.113	-1.0	0.14	-0.7
117					0.148	-1.0	0.122	-0.8										
118	0.15	-0.3			0.231	0.7	0.14	-0.4							0.159	0.2		
119																		
120	0.054	-2.7	0.065	-1.9	0.134	-1.3	0.138	-0.4	0.0774	-0.9			0.056	-1.7				
121	0.165	0.0	0.122	0.0	0.195	-0.1	0.133	-0.5	0.122	0.9	0.181	2.4	0.109	0.5	0.126	-0.7	0.208	0.9
123	0.184	0.5	0.119	-0.1	0.2	0.0	0.14	-0.4	0.121	0.8	0.218	3.7	0.117	0.8	0.164	0.3	0.18	0.2

Table 3-9 (cont.): Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores (labcodes 82 – 123). (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Kresoxim-methyl	Z-scores (FFP-RSD (25 %)	Lambda-cyhalothrin	Z-scores (FFP-RSD (25 %)	Pirimiphos-methyl	Z-scores (FFP-RSD (25 %)	Malathion	Z-scores (FFP-RSD (25 %)	Propiconazole	Z-scores (FFP-RSD (25 %)	Tebuconazole	Z-scores (FFP-RSD (25 %)	Thiamethoxam	Z-scores (FFP-RSD (25 %)	Tricyclazole	Z-scores (FFP-RSD (25 %)	Trifloxystrobin	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.168		0.025		0.074		0.012		0.442		0.813		0.217		0.295		0.216	
82					0.067	-0.4	0.012											
84	0.169	0.0	0.0247		0.07	-0.2	0.0099		0.429	-0.1	0.813	0.0	0.211	-0.1	0.291	-0.1	0.217	0.0
85	0.134	-0.8	0.0232		0.0521	-1.2			0.225	-2.0	0.599	-1.1					0.317	1.9
86	0.16	-0.2	0.0253		0.0845	0.6	0.0152		0.427	-0.1	0.858	0.2	0.198	-0.4	0.296	0.0	0.22	0.1
87					0.0705	-0.2	0.012											
88	0.19	0.5	0.022		0.068	-0.3	0.0076		0.422	-0.2	0.722	-0.4	0.244	0.5	0.294	0.0	0.243	0.5
89	0.2	0.8	0.0305		0.0863	0.7			0.501	0.5	0.8	-0.1	0.228	0.2	0.287	-0.1	0.238	0.4
90	0.165	-0.1	0.025		0.063	-0.6	0.012		0.498	0.5	0.882	0.3	0.186	-0.6	0.3	0.1	0.196	-0.4
91					0.068	-0.3	0.013											
92							0.014											
93	0.18	0.3	0.03		0.08	0.4	0.02		0.48	0.3	0.84	0.1	0.23	0.2	0.33	0.5	0.24	0.4
94	0.143	-0.6	0.038		0.085	0.6			0.362	-0.7	0.696	-0.6	0.196	-0.4	0.23	-0.9	0.206	-0.2
95	0.15	-0.4	0.0161		0.195	6.6			0.509	0.6	0.667	-0.7					0.205	-0.2
96	0.138	-0.7	0.014		0.067	-0.4	0.011		0.399	-0.4	0.772	-0.2	0.174	-0.8	0.269	-0.4	0.187	-0.5
97	0.117	-1.2			0.0689	-0.3			0.606	1.5	0.21	-3.0					ND	-3.8
98	0.143	-0.6	0.0185		0.0535	-1.1			0.41	-0.3	0.272	-2.7	0.0225	-3.6			0.188	-0.5
100	0.133	-0.8	0.018		0.073	0.0	0.012				0.823	0.0					0.17	-0.9
101					0.104	1.7	0.014											
102					0.0975	1.3			0.417	-0.2	0.673	-0.7						
103	0.118	-1.2	0.0195		0.0491	-1.3			0.274	-1.5	0.515	-1.5	0.183	-0.6	0.169	-1.7	0.159	-1.1
104	0.223	1.3	0.049		0.095	1.2	0.0143		0.611	1.5	1.074	1.3	0.231	0.3			0.304	1.6
105			0.019		0.068	-0.3	0.011											
106	0.12	-1.1			0.06	-0.7			0.16	-2.6	ND	-4.0	ND	-3.8	ND	-3.9	ND	-3.8
107	0.182	0.3			0.092	1.0			0.516	0.7	0.85	0.2	0.216	0.0			0.216	0.0
108	0.238	1.7			0.215	7.7			0.557	1.0	0.914	0.5	0.227	0.2			0.134	-1.5
109					0.084	0.6	0.0114		0.465	0.2	0.789	-0.1	0.207	-0.2				
110					ND	-3.5												
111	0.237	1.6	0.025		0.09	0.9			0.441	0.0	0.815	0.0					0.21	-0.1
113	0.128	-1.0	0.016		0.067	-0.4	0.01		0.261	-1.6	0.732	-0.4	0.352	2.5	0.243	-0.7	0.141	-1.4
114	0.166	0.0	0.021		0.09	0.9	0.019		0.353	-0.8	1.04	1.1	0.213	-0.1	0.393	1.3	0.242	0.5
115					0.069	-0.2	0.014											
116	0.133	-0.8	0.021		0.09	0.9	0.015		0.23	-1.9	0.484	-1.6	0.1	-2.2	0.18	-1.6	0.168	-0.9
117			0.018		0.045	-1.6	0.018											
118	0.195	0.6	0.021		0.092	1.0			0.41	-0.3	0.752	-0.3					0.25	0.6
119																		
120	0.137	-0.7	0.0262		0.071	-0.1			0.36	-0.7	0.608	-1.0					0.174	-0.8
121	0.172	0.1	0.025		0.094	1.1	0.0124		ND	-3.9	0.925	0.6	0.228	0.2	0.329	0.5	0.265	0.9
123	0.188	0.5	0.056		0.09	0.9	0.013		0.557	1.0	0.868	0.3	0.221	0.1	0.355	0.8	0.23	0.3

Table 3-10: Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores for laboratorie with labcodes 124 – 163. (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Azoxystrobin	Z-scores (FFP-RSD (25 %)	Carbendazim	Z-scores (FFP-RSD (25 %)	Chlorpyrifos	Z-scores (FFP-RSD (25 %)	Deltamethrin (cis)	Z-scores (FFP-RSD (25 %)	Difenoconazole	Z-scores (FFP-RSD (25 %)	Diflubenzuron	Z-scores (FFP-RSD (25 %)	Epoxiconazole	Z-scores (FFP-RSD (25 %)	Fipronil	Z-scores (FFP-RSD (25 %)	Isoprothiolane	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.164		0.122		0.199		0.154		0.100		0.113		0.097		0.153		0.170	
124	0.185	0.5	0.122	0.0	0.233	0.7	0.172	0.5	0.126	1.0	0.129	0.6	0.1	0.1	0.209	1.5		
125	0.191	0.7	0.136	0.5	0.203	0.1	0.179	0.6	0.129	1.2	0.148	1.2	0.0956	0.0	0.196	1.1	0.201	0.7
126	0.196	0.8	0.048	-2.4	0.16	-0.8	0.135	-0.5	0.061	-1.6	ND	-3.6	0.051	-1.9	0.194	1.1		
127	0.129	-0.9			0.236	0.8	0.132	-0.6	0.0797	-0.8			0.0966	0.0	0.143	-0.2	0.145	-0.6
128	0.082	-2.0			0.158	-0.8	0.103	-1.3										
129					0.187	-0.2	0.176	0.6										
130																		
131	0.146	-0.4	0.109	-0.4	0.191	-0.2	0.04	-3.0	0.108	0.3	0.195	2.9	0.083	-0.6	0.156	0.1		
133																		
135	0.144	-0.5			0.164	-0.7	0.172	0.5	0.086	-0.6			0.068	-1.2	0.131	-0.6		
136					0.141	-1.2												
138					0.216	0.4			0.107	0.3			0.1	0.1				
139	0.18	0.4	0.141	0.6	0.179	-0.4	0.194	1.0	0.09	-0.4	0.105	-0.3	0.092	-0.2	0.134	-0.5		
140	0.177	0.3	0.177	1.8	0.186	-0.3	0.146	-0.2	0.105	0.2			0.12	1.0	0.145	-0.2		
141	0.182	0.4	0.134	0.4	0.103	-1.9	0.197	1.1	0.116	0.6	0.118	0.2	0.119	0.9	0.172	0.5	0.191	0.5
142					0.142	-1.1												
143	0.122	-1.0			0.18	-0.4	0.172	0.5										
144					0.255	1.1	0.296	3.7										
145	0.1	-1.6	0.1	-0.7					0.2	4.0	ND	-3.6	0.12	1.0	0.12	-0.9		
146	0.114	-1.2			0.205	0.1			0.106	0.2			0.0817	-0.6	0.149	-0.1		
147	0.061	-2.5	0.092	-1.0	0.127	-1.4	0.104	-1.3	0.078	-0.9	0.104	-0.3	0.049	-2.0	0.1	-1.4	0.07	-2.4
148	0.136	-0.7	0.065	-1.9	0.159	-0.8	0.145	-0.2	0.093	-0.3	0.172	2.1			0.133	-0.5		
149	0.14	-0.6	0.05	-2.4	0.19	-0.2	0.1	-1.4	0.09	-0.4	0.09	-0.8	0.07	-1.1	0.12	-0.9		
150																		
151																	0.0934	-1.8
152	0.171	0.2	0.245	4.0	0.202	0.1	0.198	1.1	0.089	-0.4	0.14	1.0	0.089	-0.3	0.16	0.2	0.185	0.4
153					0.443	4.9							0.172	3.1				
154					0.22	0.4	0.231	2.0										
155	0.159	-0.1	0.103	-0.6	0.152	-0.9	0.17	0.4	0.152	2.1			0.133	1.5	0.169	0.4	0.173	0.1
156	0.15	-0.3	ND	-3.7	0.220	0.4	0.1	-1.4	0.08	-0.8	ND	-3.6	0.1	0.1				
157	0.155	-0.2	0.129	0.2	0.171	-0.6			0.109	0.4	0.117	0.1			ND	-3.7	0.172	0.0
158	0.175	0.3	0.174	1.7	0.216	0.4	0.0379	-3.0	0.1	0.0	ND	-3.6			0.18	0.7	0.158	-0.3
159					0.214	0.3	0.0982	-1.4										
161					ND	-3.8	ND	-3.7										
162	0.156	-0.2	0.11	-0.4	0.175	-0.5	0.176	0.6	0.094	-0.2	0.12	0.2	0.085	-0.5	0.147	-0.1	0.159	-0.3
163	0.00081	-4.0	0.0065	-3.8					ND	-3.6			ND	-3.6				

Table 3-10 (cont.): Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores (labcodes 124 – 163). (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Kresoxim-methyl	Z-scores (FFP-RSD (25 %)	Lambda-cyhalothrin	Z-scores (FFP-RSD (25 %)	Pirimiphos-methyl	Z-scores (FFP-RSD (25 %)	Malathion	Z-scores (FFP-RSD (25 %)	Propiconazole	Z-scores (FFP-RSD (25 %)	Tebuconazole	Z-scores (FFP-RSD (25 %)	Thiamethoxam	Z-scores (FFP-RSD (25 %)	Tricyclazole	Z-scores (FFP-RSD (25 %)	Trifloxystrobin	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.168		0.025		0.074		0.012		0.442		0.813		0.217		0.295		0.216	
124	0.222	1.3	0.032		0.082	0.5	0.016		0.528	0.8	0.669	-0.7	0.254	0.7			0.221	0.1
125	0.197	0.7	0.024		0.0643	-0.5	0.011		0.589	1.3	0.937	0.6	0.275	1.1	0.347	0.7	0.25	0.6
126	0.109	-1.4	0.045		0.052	-1.2			0.284	-1.4	0.667	-0.7	0.226	0.2	ND	-3.9	0.149	-1.2
127	0.182	0.3	0.0212		0.0791	0.3	0.0124		0.467	0.2	0.876	0.3			0.332	0.5	0.216	0.0
128	0.125	-1.0							0.264	-1.6							0.143	-1.4
129			0.021		0.061	-0.7												
130																		
131	0.162	-0.1	0.034		0.076	0.1	0.011		0.508	0.6	0.832	0.1	0.243	0.5	ND	-3.9	0.199	-0.3
133																		
135	0.144	-0.6	0.02		0.062	-0.6	0.011		ND	-3.9	0.61	-1.0					0.178	-0.7
136					0.0755	0.1												
138					0.073	0.0			0.479	0.3	0.816	0.0	0.232	0.1			0.173	-0.8
139	0.138	-0.7	0.04		0.063	-0.6	0.006		0.294	-1.3	0.617	-1.0	0.333	2.1	0.389	1.3	0.23	0.3
140	0.134	-0.8	0.027		0.068	-0.3			0.499	0.5	0.842	0.1	0.261	0.8			0.224	0.1
141	0.189	0.5	0.025		0.071	-0.1			0.498	0.5	0.903	0.4	0.223	0.1	0.37	1.0	0.218	0.0
142					0.068	-0.3												
143	0.128	-1.0			0.0468	-1.5			0.391	-0.5								
144			0.0307		0.0834	0.5	0.0244											
145	0.14	-0.7							0.65	1.9	1	0.9					0.37	2.9
146	0.143	-0.6	0.0586		0.0827	0.5			0.388	-0.5	0.908	0.5	0.237	0.4			0.225	0.2
147	0.178	0.2	0.021		0.052	-1.2			0.303	-1.3	0.571	-1.2	0.067	-2.8			0.187	-0.5
148	0.137	-0.7	0.0215		0.066	-0.4			0.37	-0.7	0.719	-0.5	0.177	-0.7			0.133	-1.5
149	0.13	-0.9			0.06	-0.7			0.38	-0.6	0.54	-1.3	0.12	-1.8	0.18	-1.6	0.14	-1.4
150																		
151																		
152	0.187	0.5	0.032		0.077	0.2			0.436	-0.1	0.771	-0.2	0.235	0.3	0.293	0.0	0.259	0.8
153																		
154			0.0306		0.0946	1.1												
155	0.167	0.0	0.057		0.083	0.5	0.01		0.476	0.3	0.95	0.7	0.202	-0.3	0.372	1.0	0.237	0.4
156	0.13	-0.9	0.02		0.07	-0.2	0.03		0.41	-0.3	0.84	0.1	0.2	-0.3			ND	-3.8
157	0.187	0.5			0.095	1.2			0.375	-0.6	0.78	-0.2	0.196	-0.4	0.282	-0.2	0.193	-0.4
158	0.167	0.0	0.0183		0.0777	0.2			0.434	-0.1	0.823	0.0	0.263	0.7	0.344	0.7		
159			0.0287		0.0774	0.2												
161					0.074	0.0												
162	0.182	0.3	0.036		0.061	-0.7			0.503	0.6	0.832	0.1	0.19	-0.5	0.289	-0.1	0.21	-0.1
163	0.00013	-4.0									ND	-4.0						

Table 3-11: Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores for laboratorie with labcodes 164 – 168. (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Azoxystrobin	Z-scores (FFP-RSD (25 %)	Carbendazim	Z-scores (FFP-RSD (25 %)	Chlorpyrifos	Z-scores (FFP-RSD (25 %)	Deltamethrin (cis)	Z-scores (FFP-RSD (25 %)	Difenoconazole	Z-scores (FFP-RSD (25 %)	Diflubenzuron	Z-scores (FFP-RSD (25 %)	Epoxiconazole	Z-scores (FFP-RSD (25 %)	Fipronil	Z-scores (FFP-RSD (25 %)	Isoprothiolane	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.164		0.122		0.199		0.154		0.100		0.113		0.097		0.153		0.170	
164	0.12	-1.1	0.102	-0.7	0.223	0.5	0.185	0.8	0.058	-1.7	0.101	-0.4			0.153	0.0	0.141	-0.7
165					0.11043	-1.8												
166	0.149	-0.4			0.198	0.0	0.123	-0.8	0.119	0.8			0.11	0.6	0.148	-0.1		
167			0.101	-0.7													0.11	-1.4
168					0.163	-0.7									0.195	1.1		

Table 3-11 (cont.): Results for MRM pesticides in mg/kg as well as the corresponding Assigned Values and z-scores (labcodes 164 – 168). (Assigned Values for lambda-cyhalothrin and malathion are for informative purposes only and no z-scores were calculated.)

Laboratory code	Kresoxim-methyl	Z-scores (FFP-RSD (25 %)	Lambda-cyhalothrin	Z-scores (FFP-RSD (25 %)	Pirimiphos-methyl	Z-scores (FFP-RSD (25 %)	Malathion	Z-scores (FFP-RSD (25 %)	Propiconazole	Z-scores (FFP-RSD (25 %)	Tebuconazole	Z-scores (FFP-RSD (25 %)	Thiamethoxam	Z-scores (FFP-RSD (25 %)	Tricyclazole	Z-scores (FFP-RSD (25 %)	Trifloxystrobin	Z-scores (FFP-RSD (25 %)
MRRL	0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01		0.01	
Assigned value	0.168		0.025		0.074		0.012		0.442		0.813		0.217		0.295		0.216	
164	0.148	-0.5	0.024		0.059	-0.8			0.361	-0.7	0.702	-0.5	0.311	1.7	0.333	0.5	0.237	0.4
165					0.03564	-2.1												
166	0.19	0.5			0.073	0.0	0.037		0.404	-0.3	0.743	-0.3					0.22	0.1
167																		
168					0.039	-1.9												

3.4.2 Sum of Weighted z-Scores (SWZ) and Sum of Squared z-Scores (SZ^2) – Category A and B

For the laboratories in Category A, the MRM results were additionally evaluated by calculating the Sum of Weighted z-Scores (SWZ) and the Sum of Squared z-Scores (SZ^2). To be classified into Category A the labs had to submit results for at least 90 % of the pesticide present in the Test Material and report no false positives. Consequently, 59 laboratories that detected ≥ 14 pesticide residues in the Test Material and reported no false positives were classified into Category A. For these laboratories SWZ and SZ^2 were calculated. SZ^2

In total, 44 EU participants (75 %) obtained SWZ scores at or below 2 (good); 10 EU participants (17 %) obtained SWZ scores above 2 but below or at 3 (satisfactory); and 5 participants (8 %) obtained SWZ scores above 3 (unsatisfactory). The SWZ scores achieved by the labs can be seen in **Table 3-12**. The SZ^2 scores are given for information purposes for this PT. However, the classification in future EUPTs will be based on SZ^2 scores.

For the laboratories in Category B, the number of results reported as well as the number of acceptable z-scores can be seen in **Table 3-13**. The table also includes information on false negative and false positive results.

Table 3-12: Sum of Weighted z-Scores (SWZ), sum of Squared z-Scores (SZ^2), the number of pesticide analysed by the laboratory, false negatives reported, Classification and NRL status for laboratories in Category A

Lab code	No. of evaluated detected pesticides	SZ^2	SWZ	False negative	Classification based on SWZ	NRL-CF / -C / -F
1	16	1.7	1.8		Good	
2	16	0.3	0.5		Good	
3	16	0.6	0.6		Good	
4	16	4.7	4.6		Unsatisfactory	
5	15	3.2	3.3	Yes	Unsatisfactory	NRL
6	16	0.1	0.3		Good	
8	16	0.3	0.4		Good	NRL
9	14	2.2	2.1	Yes	Satisfactory	NRL
10	14	0.3	0.4		Good	NRL
11	15	2.0	2.1		Satisfactory	NRL
13	14	4.3	4.5		Unsatisfactory	
14	16	0.1	0.2		Good	
15	16	0.2	0.4		Good	
17	16	0.8	1.0		Good	
18	14	0.3	0.4		Good	NRL
21	14	1.5	1.2		Good	NRL
24	16	2.3	2.5		Satisfactory	NRL
29	15	1.6	1.9		Good	
30	16	2.5	2.6		Satisfactory	
31	16	0.3	0.4		Good	
33	16	0.6	0.8		Good	
34	14	0.1	0.2		Good	
37	16	0.8	0.7		Good	NRL
39	14	2.5	2.4		Satisfactory	
40	16	0.2	0.4		Good	
43	15	1.2	1.5	Yes	Good	NRL
47	15	0.3	0.4		Good	
48	16	0.6	0.8		Good	NRL
50	16	0.1	0.3		Good	NRL

Table 3-12 (cont.): Sum of Weighted z-Scores (SWZ) for laboratories in Category A, number of evaluated pesticides detected by the laboratory, false negatives reported and Classification as good, satisfactory and unsatisfactory.

Lab code	No. of evaluated detected pesticides	SZ²	SWZ	False negative	Classification based on SWZ	NRL-CF / -C / -F
51	16	0.6	0.6		Good	
53	14	2.5	2.9	Yes	Satisfactory	
57	16	0.6	0.6		Good	
64	15	1.9	1.8	Yes	Good	
65	14	2.9	3.1		Unsatisfactory	NRL
66	14	1.8	2.2	Yes	Satisfactory	
73	16	0.6	0.8		Good	
75	14	3.0	3.2	Yes	Unsatisfactory	
76	16	1.3	1.2		Good	
78	16	0.5	0.6		Good	
84	16	0.1	0.2		Good	
86	16	0.1	0.3		Good	NRL
88	16	0.2	0.4		Good	NRL
89	16	0.2	0.3		Good	
90	16	0.2	0.4		Good	NRL
93	16	0.1	0.3		Good	
94	16	0.4	0.6		Good	
96	16	0.3	0.5		Good	
103	16	1.7	1.2		Good	NRL
104	15	2.2	2.2		Satisfactory	NRL
113	16	1.1	1.2		Good	
114	16	0.9	0.8		Good	
116	16	1.9	1.6		Good	
121	15	1.8	2.1	Yes	Satisfactory	
123	16	1.2	1.6		Good	
124	14	0.6	0.6		Good	NRL
125	16	0.7	0.7		Good	NRL
139	15	0.8	1.0		Good	
141	16	0.6	0.6		Good	
147	15	2.4	2.4		Satisfactory	
149	15	1.5	1.4		Good	
152	16	1.3	1.6		Good	
155	15	0.7	0.9		Good	
162	16	0.1	0.3		Good	
164	15	0.7	0.7		Good	

Table 3-13: Number of evaluated pesticides detected, number of acceptable z-scores, false negatives and positives for the laboratories in Catagory B.

Lab code	No. of evaluated pesticides detected	No. of acceptable z-scores	False negatives	False positives	NRL-CF / -C / -F
7	13	13	0	0	NRL
12	9	6	0	0	NRL
16	11	11	1	0	
19	14	13	0	1	

Table 3-13 (cont.): Number of evaluated pesticides detected, number of acceptable z-scores, false negatives and positives for the laboratories in Catagory B.

Lab code	No. of evaluated pesticides detected	No. of acceptable z-scores	False negatives	False positives	NRL-CF / -C / -F
20	1	1	1	0	
22	14	14	2	1	NRL
25	13	13	0	0	NRL
28	13	12	0	0	NRL
32	3	3	0	0	
35	8	8	0	0	
36	9	5	1	0	
38	7	3	0	1	
41	16	11	0	1	
42	8	6	0	0	
44	0	0	0	0	
45	11	11	0	0	
46	12	9	1	0	
49	9	9	1	1	
52	9	7	0	0	
54	2	1	1	0	NRL
55	13	13	0	0	
58	11	6	1	0	
60	13	13	0	0	
61	2	2	0	0	
62	11	9	0	0	
63	12	9	0	0	
67	12	12	0	0	
68	8	6	0	0	
69	0	0	0	0	
70	10	10	0	0	
71	5	3	0	0	
72	11	4	2	0	
74	11	11	0	0	
77	2	2	0	0	
79	12	11	1	0	
80	2	2	0	0	
81	2	2	0	0	
82	2	2	0	0	
85	10	10	0	0	
87	2	2	0	0	
91	2	2	0	0	
92	1	1	0	0	
95	9	8	1	1	
97	10	6	1	0	
98	13	7	1	0	
100	8	8	0	0	
101	3	3	0	1	NRL
102	6	6	0	0	

Table 3-13 (cont.): Number of evaluated pesticides detected, number of acceptable z-scores, false negatives and positives for the laboratories in Catagory B.

Lab code	No. of evaluated pesticides detected	No. of acceptable z-scores	False negatives	False positives	NRL-CF / -C / -F
105	3	3	0	0	
106	4	2	10	0	
107	13	13	0	0	
108	11	9	0	0	NRL
109	7	6	0	0	
110	1	1	1	0	
111	12	11	0	0	
115	2	2	0	0	
117	3	3	0	2	
118	9	9	0	0	
119	0	0	0	0	
120	11	10	0	0	NRL
126	13	12	2	0	
127	13	13	0	0	NRL
128	6	6	0	0	NRL
129	3	3	0	0	
130	0	0	0	0	
131	14	12	1	1	
133	0	0	0	0	
135	10	10	1	0	NRL
136	2	2	0	0	NRL
138	8	8	0	0	
140	13	13	0	0	
142	2	2	0	0	
143	6	6	0	0	
144	3	2	0	0	
145	9	7	1	0	
146	11	11	0	0	
148	13	12	0	0	
150	0	0	0	0	
151	1	1	0	0	
153	2	0	0	1	
154	3	3	0	0	
156	10	10	3	1	
157	13	13	1	0	
158	13	12	1	0	
159	3	3	0	0	
160	0	0	0	0	
161	1	1	2	0	
163	3	0	3	0	
165	2	1	0	4	
166	11	11	0	0	
167	2	2	0	0	
168	3	3	0	0	

3.5 Trends in the number of participating laboratories and their performance

The number of laboratories participating in the EUPTs with cereals as the Test Material and focusing on MRM pesticides increased from 62 in EUPT-C1 (2007), 72 in EUPT-C2 (2008), 102 in EUPT-C3 (2009) and 115 in EUPT-C4 (2010) to 133 in EUPT-C5 (2011) (see **Table 3-14**). The Target Pesticide List was expanded from 34 to 86 MRM pesticides and the number of spiked or incurred pesticides contained in the Test Material has increased from 7 to 16, the same number as in EUPT-C4.

The analyte scope of pesticides covered is still rather narrow for many laboratories, with 29 % of them submitting results for less than 10 out of the 16 pesticides present in the Test Material. No significant improvement in performance has been observed when looking at the percentage of acceptable, questionable, unacceptable z-scores and false negative results. The percentage of Category A laboratories decreased from 60 to 44 % between the EUPT-C2 and EUPT-C5. Nevertheless, it is difficult to assess any improvement/deterioration in laboratory performance between the different Proficiency Tests, because the pesticides in the Test Materials and the laboratories participating in the PTs have signifcantly increased. However, azoxystrobin and carbendazim, which were included in all three Test Materials, can be good indicators of the developments in laboratory performance over the years.

The percentage of acceptable z-scores for azoxystrobin has increased from 62 % in the EUPT-C1 to 89 % in the current EUPT-C5. This is probably due to the recommendation to add water to the Test Material before extraction, as the percentage of laboratories adding water also increased from 65 % to 92 %. For carbendazim, the percentage of acceptable z-scores also increased, from 79 % to 89 %. Focusing only on the results from laboratories that have participated in all PTs, the laboratory performance has improved for both compounds. For azoxystrobin, the percentage of acceptable results increased from 66 % to 95 %, with no unacceptable results. For carbendazim, the percentage of acceptable results rose from 79 % to 100 %. It is therefore reasonable to conclude that the analytical accuracy for these particular pesticides has notably improved over the years, with the EUPTs playing an important role in this process.

Table 3-14: Overall participation and performance of laboratories in the 5 cereal-based EUPTs focusing on MRM pesticides

	EUPT-C1 (2007)	EUPT-C2 (2008)	EUPT-C3 (2009)	EUPT-C4 (2010)	EUPT-C5 (2011)
Type of Test Material	Wheat flour	Wheat flour	Oat flour	Rye flour	Rice flour
Participants submitting results (EU/EFTA)	63	72	102	115	133
MRM pesticides in Target Pesticide List [1)]	34	43	51	64	86
MRM pesticides in the Test Material	7	13	14	16	16
No. of results for MRM pesticides	323	830	981	1624	1521
Range of 'reported results', % [2)]	63 – 95	60 – 96	48 – 95	55 – 95	41–95
Acceptable z-scores, %	87	85	87	87	87
Questionable z-scores, %	7	12	8	6	4
Unacceptable z-scores, %	6	3	5	7	9
False negatives, %	2	3	3	4	3
Number of false positives	1	2	3	17	16
Catagory A, % of participating laboratories		60	46		46
Good SWZ, %		70	72		77
Satisfactory SWZ, %		9	15		8
Unsatisfactory SWZ, %		21	13		15

1) Number of pesticides, excluding isomers and degradation products
2) The "reported results" were calculated as the ratio of laboratories that reported results to the total number of laboratories submitting results (minimum and maximum values are given, see also Table 3-4)

3.6 Summary, conclusions and future plans for EUPTs on pesticide residues in cereals

EUPT-C5 was the fifth EUPT focusing on cereal-based Test Materials. A homogenous Test Material of rice flour, including both incurred and spiked pesticides, was successfully prepared. The rice was sprayed in the field, and also spiked in the laboratory following harvest with commercially available pesticide formulations or pesticide standards of the following pesticides: Azoxystrobin, carbendazim, chlorpyrifos, deltamethrin (cis), difenoconazole, diflubenzuron, epoxiconazole, fipronil, isoprothiolane, kresoxim-methyl, pirimiphos-methyl, propiconazole, tebuconazole, thiamethoxam, tricyclazole and trifloxystrobin. One hundred and thirthy three laboratories, representing 29 EU and EFTA countries, agreed to participate in the Proficiency Test, but three laboratories failed to submit results. All Member States and NRLs participated, with Malta delegating its obligations to laboratories in Germany, Italy and UK. An additional 22 laboratories from Third Countries registered for the PT and 21 submitted results. The Target Pesticide List distributed to the laboratories prior to the test contained 86 MRM pesticides, excluding isomers and degradation products.

Both the number of false positives and false negatives decreased comparison to EUPT-C4. The 10 false positive results concerned chlorpyrifos-methyl (2), DDT (sum) (2), endosulfan sulfate (2), imazalil, isoproturon, permethrin and prothioconazole. The 41 false negative results concerned azoxystrobin, carbendazim, chlorpyrifos (2), deltamethrin (cis) (3), difenoconazole (2), diflubenzuron (2), epoxiconazole (2), fipronil (2), isoprothiolane (4), kresoxim-methyl (2), pirimiphos-methyl (2), propiconazole (5), tebuconazole, thiamethoxam (3), tricyclazole (6) and trifloxystrobin (3). The average Qn-RSD (robust RSD) was at 22 %, close to the FFP-RSD of 25 % with a range from 16 to 29 % for the individual compounds.

For each laboratory/pesticide combination, z-scores based on the FFP-RSD of 25 % were calculated and classified as either 'acceptable', 'questionable' or 'unacceptable'. For carbendazim, chlorpyrifos, epoxiconazole, fipronil, kresoxim-methyl, pirimiphos-methyl and tebuconazole, acceptable results were obtained by 90 – 94 % of the laboratories. For azoxystrobin, deltamethrin (cis), difenoconazole, isoprothiolane, propiconazole, thiamethoxam and trifloxystrobin, acceptable results were obtained by 81– 89 % of the laboratories. Finally, for diflubenzuron and tricyclazole acceptable z-scores were obtained by only 72 – 75 % of the laboratories.

Overall, the performance of the laboratories appears not to have significantly improved compared to the previous PTs on cereals. The percentage of acceptable z-scores remained at high levels, whereas the percentage of laboratories achieving Category A classification reduced slightly to 44 %. However, when focusing on azoxystrobin and carbendazim (that were also included in all previous PTs), and only looking at results from laboratories participating in all the PTs, then a significant improvement in performance can be seen.

In future PTs, the selection of pesticides will continue to focus on pesticides included in the scope of the EU coordinated control programme as well as additional pesticides of relevance for cereal production in Europe and in other parts of the world from where significant quantities of cereals are imported. The pesticide residues will be incurred wherever practical and the commodites will alternate among the most important commodities. In 2012 the Test Material will be barley.

To encourage the laboratories to lower their LOQs so that they are able to fully enforce EU Regulations (e.g. MRLs for baby foods), the MRRL for all pesticides in the next PT will remain fixed at 0.01 mg/kg. The goal is that laboratories continue to increase their scope of analytes and to improve their overall performance, both in terms of correctly detecting the pesticides present and also determining the residue levels accurately.

Online registration and data submission will continue and be expanded to cover all EUPTs for pesticide residues, if possible.

4. RESULTS – SRM PESTICIDES

4.1 Participation

88 laboratories from 29 countries (25 EU-Member States, 2 EFTA-States and 2 Third Countries) registered for participation in the SRM part of this EUPT. Out of those laboratories 79 (75 from EU-Member States, 2 from EFTA-States and 2 from Third Countries), representing all 29 countries, submitted at least one result from an SRM compound. An overview of the participating labs and countries is given in **Table 4-1**.

A list of all individual laboratories that registered for this EUPT is presented in **Appendix 1**. Out of the EU Member States only the labs from Malta and Romania did not participate in the EUPT-SRM6. Regarding the NRL-SRMs, no results were received from France, Malta, Poland or Romania. Short explanations for the non-participation of some NRLs are shown in **Table 4-1**.

In total 4 laboratories from non-EU countries submitted results (2 from EFTA Countries and 2 from Third Countries). The results submitted by the 2 laboratories from the Third Countries were not taken into account when calculating the Assigned Values.

In total, 181 EU-OfLs (including NRL-SRMs) were considered as having an obligation to participate in the present EUPT and were included in a list distributed by the Organizers prior to the registration period for this EUPT. The list included all the NRL-SRMs, regardless of their commodity scope, and all EU-OfLs handling cereals or feed (regardless of their pesticide scope). The commodity rice was considered to be representative of both food and feed cereals. An additional 13 OfLs were considered as possibly obliged to participate as it was not clear whether cereals or feed were within their scope. It was further emphasized that the list of labs with an obligation to participate was only for orientation. The real obligation is stipulated in the legislation and is based on the scope and function of the laboratories analyzing for pesticide residues in food and feed within the framework of official controls.

All labs that were obliged to participate had to either participate or to provide an explanation for their non-participation. Out of 99 obliged laboratories that did not participate in this exercise, 58 (from 15 EU countries) provided explanations for their non-participation in the EUPT-SRM6. Upon request, 4 (1× IT, 1× FR, 1× UK, and 1× BG) of the 8 EU-laboratories (4× IT, 1× FR, 1× HR, 1× UK, 1× BG) that had originally registered for the EUPT-SRM6, but then failed to submit results, provided explanations for their non-delivery of results. The most frequent reasons stated by the laboratories to explain their non-participation in the EUPT-SRM6 was that the pesticides to be targeted in this EUPT were outside their scope. Other reasons concerned limitations in capacity (time, personnel, and instrument availability). All statements provided by the labs to explain their non-participation were forwarded to DG-SANCO as requested. **Table 4-2** gives an overview on the participating and non-participation of EU-labs that were obliged to participate in EUPT-SRM6.

Table 4-1: Number of laboratories obliged to participate in the EUPT-SRM6, labs that registered, and labs that finally submitted results (grouped by country)

Contracting Country	No. of obliged labs [1]	Registered for Participation		Submitted Results		Provided Explanations [3]		Notes
		Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	
Austria	**3**	1	1	1	1	**2**	**0**	
Belgium	**8**	5	1	5	1	**1**	**0**	5 of the 8 obliged labs are subcontraced commercial labs based in Belgium (2) Germany (1) and The Netherlands (2).
Bulgaria	**10**	2	1	1	1	**3 + 1** [4]	**0**	
Cyprus	**2**	1	1	1	1	**0**	**0**	
Czech Republic	**4**	2	1	2	1	**1**	**0**	
Denmark	**3**	2	0	2	0	**1**	**1**	The NRL-SRM of DK, being a co-organizer of this EUPT, was thus not obliged to participate.
Estonia	**2**	2	1	2	1	**0**	**0**	
Finland	**2**	2	1	2	1	**0**	**0**	
France	**13**	5	0	4	0	**5 + 1** [4]	**1**	The NRL-SRM was not yet officially established and fully operational when the test started
Germany	**26**	16	1	16	1	**9**	**0**	CVUA Stuttgart,hosting the Organizing EURL was not considered as an obliged lab
Greece	**4**	2	2	2	2	**2**	**0**	Greece has appointed two NRL-SRMs
Hungary	**8**	5	1	4	1	**3**	**0**	
Ireland	**1**	1	1	1	1	**0**	**0**	
Italy	**26**	7 + 1 [2]	1	4	1	**11 + 1** [4]	**0**	One non-obliged official lab registered but did not submit any results.
Latvia	**1**	1	1	1	1	**0**	**0**	
Lithuania	**2**	1	1	1	1	**1**	**0**	
Luxembourg	**1**	1	1	1	1	**0**	**0**	
Malta	**3**	1	0	0	0	**1**	**1**	Two of the obliged labs were subcontracted commercial labs based in Germany (1) and Italy (1) with the subcontracting term of the latter being discontinued.
Netherlands	**2**	2	1	2	1	**0**	**0**	
Poland	**25**	7	0	7	0	**8**	**1**	NRL-SRM had resigned prior to the test. The OfL designated as its successor participated in this test.
Portugal	**4**	3	1	3	1	**0**	**0**	
Romania	**6**	0	0	0	0	**3**	**0**	
Slovakia	**2**	1	1	1	1	**1**	**0**	
Slovenia	**3**	3	1	3	1	**0**	**0**	
Spain	**14**	5	1	5	1	**6**	**0**	Spain has appointed 2 NRL-SRMs, one of which participated
Sweden	**2**	2	1	2	1	**0**	**0**	
United Kingdom	**4**	3	1	2	1	**1** [4]	**0**	
EU Total	**181**	83 + 1 [2]	23	75	23	**58 + 4** [4]	**4**	

1) Labs that had a mandatory obligdation to participate were defined based on their function (NRL-SRMs) and the commodity-scope covered (cereals or feed)
2) One lab not among the obliged EU-Labs registered for participation in the EUPT-SRM6 but did not submit results.
3) Explanations for non-participation or for non-submission of results
4) Explanation for non-submission of results

Table 4-1 (cont.): Number of laboratories obliged to participate in the EUPT-SRM6, labs that registered, and labs that finally submitted results (grouped by country)

Contracting Country	No. of obliged labs [1]	Registered for Participation		Submitted Results		Provided Explanations [3]		Notes
		Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	Labs Total	NRL-SRMs	
Norway	**(2)**	1	1	1	1	**(1)**	**–**	
Switzerland	**(4)**	1	–	1	–	**–**	**–**	
EU+EFTA Total	**181 + (6)**	86	24	77	24	**62 + (1)**	**4**	
Egypt		1	–	1	–	**–**	**–**	
Taiwan		1	–	1	–	**–**	**–**	
3rd Countries		2	–	2	–	**–**	**–**	
Overall Sum	**181 + (6)**	88	24	79	24	**62 + (1)**	**4**	

1) Labs that had a mandatory obligdation to participate were defined based on their function (NRL-SRMs) and the commodity-scope covered (cereals or feed)
2) One lab not among the obliged EU-Labs registered for participation in the EUPT-SRM6 but did not submit results.
3) Explanations for non-participation or for non-submission of results
4) Explanation for non-submission of results

Table 4-2: Overview of EU-labs with a mandatory obligation to participate in the EUPT-SRM6

Total obliged EU-labs [1]	181	100 %
Thereof		
- Registered for Participation	**82**	**45 %**
- Submitting results *	74	**41 %**
- Not submitting results / providing explanation for non-submission	8 / 4	4 % / 2 %
- non-Participation	**99**	**55 %**
- Providing explanations for non-participation	58	32 %
- No feedback	41	23 %

1) Official labs (including NRLs) of EU-member states officially analyzing for cereals and feedingstuff plus any NRL-SRMs (regardless of commodity scope).

4.2 Overview of results

An overview of the results reported for the pesticides present in the sample is shown in **Table 4-3**.

Table 4-4 gives an overview of all results submitted by each laboratory. For the individual results reported by the laboratories see **Table 4-8**. The detailed information about the analytical methods used by the laboratories is shown **Appendix 12**.

Table 4-3: Overview of results with laboratory scope

Pesticides present in Test Material	MRRL [mg/kg]	Labs reporting results [1]			No. of reported NDs [4]
		No.	% (based on N = 77 [2])	% (based on N = 181 [3])	
2,4-D	0.02	57	74 %	31 %	0
Bromide	5.0	34	44 %	19 %	0
Dithiocarbamates	0.05	64	83 %	35 %	1
Ethephon	0.02	29	38 %	16 %	1
Glyphosate	0.05	35	45 %	19 %	1 [5]
Haloxyfop	0.02	50	65 %	28 %	1[6]
Quinclorac	0.02	22	29 %	12 %	1

1) including NDs (Not-detected)
2) based on 77 laboratories having submitted at least one result
3) 181 EU-laboratories were obliged to participate in the EUPT-SRM6
4) ND = Not detected (i.e. possibly false negative)
5) One lab (SRM6-9) reported that it had analysed, but not detected glyphosate (= ND) giving a Reporting Limit (RL) much higher than the MRRL. Following the General Protocol (Appendix 14) the MRRL was used for z-score calculation.
6) According to the respective lab (SRM6-108), haloxyfop was sought for in the EUPT-C6 Test Material (not containing haloxyfop) rather than in the EUPT-SRM6-Test-Material. If this is the case, "not detected" was actually not a "false negative"!

Table 4-4: Overview of results with laboratory scope Assigned Values and RSDs for all SRM pesticides present in the Test Material

Compound listed in Target List			2,4-D (free acid)	Bromide	Chlormequat Cation	2,4-DP (free acid)	Dithiocarbamates	Ethephon	Fluazifop (free acid)	Glyphosate	Haloxyfop (free acid)	MCPA (free acid)	MCPP (free acid)	Mepiquat cation	Quinclorac (free acid)	Compounds Analyzed / Correctly found out of those...		
Compound within EU-CCP			√	√	√		√	√	√	√	√			√		... listed in EUPT-Pesticide Target List	... present in EUPT-Test-Material	... included in EU-CPP
Compound present in Test Sample			√	√			√	√		√	√				√			
Lab-Code SRM6-	NRL-SRM	Cat.																
1	x	A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6
2		B	V			ND	V		ND	V	V	ND	ND			8 / 4	4 / 4	5 / 4
3		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6
4		B	V	V	ND				ND		V	ND	ND	ND		8 / 3	3 / 3	6 / 3

EU-CCP = EU Coordinated Community Control Programme (former monitoring programme)
V = analyzed for and submitted concentration **V**alue > MRRL
ND = analysed and correctly **N**ot **D**etected
Empty cells: not analyzed
FN = analyzed for but falsely not detected (**F**alse **N**egative result)
V# = Outlier (z-score > 5)

Table 4-4 (cont.): Overview of results with laboratory scope

Compound listed in Target List			2,4-D (free acid)	Bromide	Chlormequat Cation	2,4-DP (free acid)	Dithiocarbamates	Ethephon	Fluazifop (free acid)	Glyphosate	Haloxyfop (free acid)	MCPA (free acid)	MCPP (free acid)	Mepiquat cation	Quinclorac (free acid)	Compounds Analyzed / Correctly found out of those...		
Compound within EU-CCP			√	√	√		√	√	√	√	√			√		... listed in EUPT-Pesticide Target List	... present in EUPT-Test-Material	... included in EU-CPP
Compound present in Test Sample			√	√			√	√		√	√				√			
Lab-Code SRM6-	NRL-SRM	Cat.																
5	x	A	V	V	ND	ND	V		ND	V	V	ND	ND	ND	V	12 / 6	6 / 6	8 / 5
6		A	V		ND	ND	V	V	ND	V	V	ND	ND	ND	V	12 / 6	6 / 6	8 / 5
7		B		V	ND		V		ND		V			ND		6 / 3	3 / 3	6 / 3
8		A	V		ND	ND	V	V	ND	V	V	ND	ND	ND	V	12 / 6	6 / 6	8 / 5
9	x	B	V	V	ND	ND	V	V	ND	**FN**	V	ND	ND	ND		12 / 5	6 / 5	9 / 5
10	x	B	V		ND	ND	**FN**		ND		V	ND	ND	ND		9 / 2	3 / 2	6 / 2
11	x	B	V	V	ND	ND	V		ND		V	ND	ND	ND	V	11 / 5	5 / 5	7 / 4
13		B	V	V		ND	V	**FN**	ND		V	ND	ND			9 / 4	5 / 4	6 / 4
14		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6
15	x	B	V		ND	ND	V			V		ND	ND	ND		8 / 3	3 / 3	5 / 3
16		B	V		ND		V					ND		ND		5 / 2	2 / 2	4 / 2
17		B	V			ND	V	V	ND	V	V	ND	ND			9 / 5	5 / 5	6 / 5
18		B					V									1 / 1	1 / 1	1 / 1
21	x	B	V		ND	ND	V		ND		V	ND	ND	ND		9 / 3	3 / 3	6 / 3
22	x	B	V			ND			ND		V	ND	ND		**FN**	7 / 2	3 / 2	3 / 2
24	x	B	V		ND	ND		V	ND	V	V	ND	ND	ND	V	11 / 5	5 / 5	7 / 4
25		B			ND		V							ND		3 / 1	1 / 1	3 / 1
28	x	B	V			ND			ND		V	ND	ND			6 / 2	2 / 2	3 / 2
29		B		V			V	V		V						4 / 4	4 / 4	4 / 4
30		B	V	V			V									3 / 3	3 / 3	3 / 3
34		B	V	V	ND	ND	V		ND		V	ND	ND	ND		10 / 4	4 / 4	7 / 4
35		B					V									1 / 1	1 / 1	1 / 1
37		B	V		ND	ND				V		ND	ND	ND		7 / 2	2 / 2	4 / 2
39		B	V	V	ND	ND	V		ND		V	ND	ND	ND		10 / 4	4 / 4	7 / 4
40		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND		12 / 6	6 / 6	9 / 6
41		B					V			V						2 / 2	2 / 2	2 / 2
42		B					V									1 / 1	1 / 1	1 / 1
43	x	B			ND		V	V		V				ND		5 / 3	3 / 3	5 / 3
45		B					V									1 / 1	1 / 1	1 / 1
47	x	A	V	V	ND	ND	V		ND	V	V	ND	ND	ND	V	12 / 6	6 / 6	8 / 5
48		B	V			ND		V	ND	V		ND	ND			9 / 3	3 / 3	4 / 3
49		B	V	V	ND	ND			ND	V		ND	ND	ND		9 / 3	3 / 3	6 / 3
50	x	A	V	V	ND	ND	V	V	ND	V#	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6

EU-CCP = EU Coordinated Community Control Programme (former monitoring programme)
V = analyzed for and submitted concentration **V**alue > MRRL
ND = analysed and correctly **N**ot **D**etected
Empty cells: not analyzed
FN = analyzed for but falsely not detected (**F**alse **N**egative result)
V# = Outlier (z-score > 5)

Table 4-4 (cont.): Overview of results with laboratory scope

Compound listed in Target List			2,4-D (free acid)	Bromide	Chlormequat Cation	2,4-DP (free acid)	Dithiocarbamates	Ethephon	Fluazifop (free acid)	Glyphosate	Haloxyfop (free acid)	MCPA (free acid)	MCPP (free acid)	Mepiquat cation	Quinclorac (free acid)	Compounds Analyzed / Correctly found out of those...		
Compound within EU-CCP			√	√	√		√	√	√	√	√			√		... listed in EUPT-Pesticide Target List	... present in EUPT-Test-Material	... included in EU-CPP
Compound present in Test Sample			√	√			√	√		√	√				√			
Lab-Code SRM6-	NRL-SRM	Cat.																
51		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6
53		B	V	V	ND	ND	V		ND		V	ND	ND	ND	V	11 / 5	5 / 5	7 / 4
57		B	V		ND	ND	V		ND		V	ND	ND	ND	V	10 / 4	4 / 4	6 / 3
59	x	B	V		ND	ND			ND		V	ND	ND	ND		8 / 2	2 / 2	5 / 2
62		B					V									1 / 1	1 / 1	1 / 1
64		B	V	V	ND	ND	V		ND		V	ND	ND	ND		10 / 4	4 / 4	7 / 4
66		B	V	V	ND	ND	V		ND		V	ND	ND	ND	V	11 / 5	5 / 5	7 / 4
71		B					V									1 / 1	1 / 1	1 / 1
73		B	V		ND	ND	V		ND		V	ND	ND	ND		9 / 3	3 / 3	6 / 3
74		B					V									1 / 1	1 / 1	1 / 1
75		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND		12 / 6	6 / 6	9 / 6
76		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND		12 / 6	6 / 6	9 / 6
84	x	A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13/ 7	7 / 7	9 / 6
86		A	V		ND	ND	V	V	ND	V	V	ND	ND	ND	V	12 / 6	6 / 6	8 / 5
89		B	V		ND	ND	V		ND	V	V	ND	ND	ND	V	11 / 7	5 / 5	7 / 4
90	x	A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6
93		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6
94		B	V	V	ND	ND	V	V	ND		V	ND	ND	ND		11 / 5	5 / 5	8 / 5
98		B					V		ND			ND				3 / 1	1 / 1	2 / 1
100		B		V			V									2 / 2	2 / 2	2 / 2
103	x	B	V	V	ND		V	V	ND		V			ND		8 / 5	5 / 5	8 / 5
104	x	B	V		ND	ND	V	V	ND	V	V	ND	ND	ND		11 / 5	5 / 5	8 / 5
106		B			ND											1 / 0	0 / 0	1 / 0
107		B	V		ND	ND	V				V	ND	ND	ND		8 / 3	3 / 3	5 / 3
108	x	B	V			ND	V		ND		FN		ND			6 / 2	3 / 2	4 / 2
112	x	B	V	V		ND	V		ND		V	ND	ND			8 / 4	4 / 4	5 / 4
113		B					V									1 / 1	1 / 1	1 / 1
116		B					V									1 / 1	1 / 1	1 / 1
120	x	B					V									1 / 1	1 / 1	1 / 1
123		B	V			ND			ND	V	V	ND	ND		V	8 / 4	4 / 4	4 / 3
124	x	A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND		12 / 6	6 / 6	9 / 6
125	x	A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND		12 / 6	6 / 6	9 / 6
126	x	B	V		ND	ND	V		ND		V	ND	ND	ND		9 / 3	3 / 3	6 / 3

EU-CCP = EU Coordinated Community Control Programme (former monitoring programme)
V = analyzed for and submitted concentration **V**alue > MRRL
ND = analysed and correctly **N**ot **D**etected
Empty cells: not analyzed
FN = analyzed for but falsely not detected (**F**alse **N**egative result)
V# = Outlier (z-score > 5)

Table 4-4 (cont.): Overview of results with laboratory scope

Compound listed in Target List			2,4-D (free acid)	Bromide	Chlormequat Cation	2,4-DP (free acid)	Dithiocarbamates	Ethephon	Fluazifop (free acid)	Glyphosate	Haloxyfop (free acid)	MCPA (free acid)	MCPP (free acid)	Mepiquat cation	Quinclorac (free acid)	Compounds Analyzed / Correctly found out of those...		
Compound within EU-CCP			√	√	√		√	√	√	√	√			√		... listed in EUPT-Pesticide Target List	... present in EUPT-Test-Material	... included in EU-CPP
Compound present in Test Sample			√	√			√	√		√	√				√			
Lab-Code SRM6-	NRL-SRM	Cat.																
129		B			ND									ND		2 / 0	0 / 0	2 / 0
132		B			ND					V				ND		3 / 1	1 / 1	3 / 1
139		B	V	V	ND	ND	V	V	ND		V	ND	ND	ND		11 / 5	5 / 5	8 / 5
140		B	V		ND		V		ND		V	ND		ND		7 / 3	3 / 3	6 / 3
141		A	V	V	ND	ND	V	V	ND	V	V	ND	ND	ND	V	13 / 7	7 / 7	9 / 6
145		B	V			ND						ND	ND			4 / 1	1 / 1	1 / 1
147		B	V		ND	ND	V	V		V		ND	ND			8 / 4	4 / 4	5/ 4

EU-CCP = EU Coordinated Community Control Programme (former monitoring programme)
V = analyzed for and submitted concentration **V**alue > MRRL
ND = analysed and correctly **N**ot **D**etected
Empty cells: not analyzed
FN = analyzed for but falsely not detected (**F**alse **N**egative result)
V# = Outlier (z-score > 5)

4.3 Assigned Values, target standard deviations and outliers

All Assigned Values are shown in **Table 4-5**. To establish the Assigned Values, the medians of all results submitted by labs from EU and EFTA countries excluding one outlier (with z-scores > 5) were calculated and used. The results of the two participating Third Country laboratories were not taken into account. In the case of 2,4-D, glyphosate and ethephon, a certain bimodality of the result-distribution was noticed that could be linked to the use of certain methodologies considered to be associated with a systematic bias. Nevertheless, considering the small population of results within each sub-population and other aspects, the EUPT-Scientific Committee decided to still use the entire population of results for the establishment of the Assigned Values (see discussion under **4.5.2**).

Table 4-5: Assigned Values and RSDs for all SRM pesticides present in the Test Material

Compound	MRRL [mg/kg]	Assigned Value [mg/kg]	FFP-RSD [%]	Qn-RSD [%]
2,4-D (free acid)	0.02	0.269	25	22.1
Bromide	5.0	53.3	25	8.6
Dithiocarbamates	0.05	0.603	25	24.2
Ethephon	0.02	0.235	25	29.7
Glyphosate	0.05	0.294	25	40.6
Haloxyfop (free acid)	0.02	0.124	25	17.7
Quinclorac (free acid)	0.02	0.267	25	19.4
Average				**23.2**

The target standard deviation used for the calculation of z-scores was obtained using a fixed "fit-for-purpose" value of 25 % (FFP-RSD). The robust relative standard deviation (Qn-RSD) was calculated in order to allow comparison with the FFP-RSD (see **Table 4-5**).

On average, the robust relative standard deviation (Qn-RSD) fits well with the FFP-RSD (23.2 % versus 25 %, see **Table 4-5**). Ethephon (Qn-RSD = 29.7 %) and glyphosate (Qn = 40.6 %) showed the highest Qn-RSD-values as a result of a non-unimodal result distribution (see kernel density estimate curves in **Appendix 10**).

A certain bimodality was also detected in the case of 2,4-D (Qn-RSD = 22.1 %). This bimodality was, however, not visible in the kernel-density estimate curve due to the small distance between the means of the two sub-populations and the relatively small number of labs that submitted biased results (see discussion in **Chapter 4.5.2**).

Also remarkable was the very narrow distribution (Qn-RSD = 8.6 %) of the bromide results despite the fact that this analyte was included for the very first time in an EUPT-SRM and that different analytical approaches were employed by the various participants (see **Chapter 4.5**). Using the FFP-RSD of 25 % all results were well within the acceptable range (absolute z-score ≤ 2).

4.4 Assessment of laboratory performance

4.4.1 False Positives

No false positives were submitted in the EUPT-SRM6.

4.4.2 False Negatives

In 5 cases (1× dithiocabamates, 1× ethephon, 1× glyphosate, 1× haloxyfop, and 1× quinclorac) participating labs reported "analyzed, but not detected" (**Table 4-6**). This represents less than 2 % of all reported results concerning the pesticides present in the Test Sample (n = 291). In all cases the Assigned Values were sufficiently distant from the MRRLs stipulated in the Specific Protocol.

In the case of glyphosate the participating laboratory (SRM6-9) indicated a very high reporting limit (RL = 2 mg/kg) which greatly exceeded both the Assigned Value (0.294 mg/kg) as well as the MRL for glyphosate in rice (0.1 mg/kg). Following the rules of the General Protocol (**Appendix 14**) this result was still judged as a false negative, and the MRRL was used for the calculation of the z-score. In the case of haloxyfop the participating laboratory (SRM6-108) indicated that it had accidentally analyzed the wrong Test Material (C5 instead of SRM6). Although this information was deemed as trustworthy by the Organizers, the result had to be judged as a false negative as this information was received after the distribution of the preliminary EUPT results to the participants.

Table 4-6: Overview of False Negative results

Compound	PT-Code	Analyzed	Reported Result [mg/kg]	RL [mg/kg]	MRRL [mg/kg]	Assigned Value [mg/kg]	Judgement
Dithiocarbamates	SRM6-10	yes	–	0.05	0.05	0.603	False Negative
Ethephon	SRM6-13	yes	–	0.05	0.02	0.235	False Negative
Glyphosate	SRM6-9	yes	–	2	0.05	0.294	False Negative [1)]
Haloxyfop	SRM6-108	yes	–	0.02	0.02	0.124	False Negative [2)]
Quinclorac	SRM6-22	yes	–	0.01	0.02	0.267	False Negative

1) This lab (SRM6-9) reported that it had analysed, but not detected (= ND) glyphosate. The Reporting Limit (RL) submitted by this lab is much higher than the MRRL. Following the General Protocol (Appendix 14) the result was still judged as a "false negative" using the MRRL for the calculation of the z-scores.
2) According to the laboratory (SRM6-108), haloxyfop was sought for in the EUPT-C5 Test Material (not containing haloxyfop).

4.4.3 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. "Acceptable" z-scores (see classification rules in **Chapter 2.4**) were achieved in 80 – 100 % of the cases (90 % on average).

A compilation of all individual results and z-scores for each laboratory is shown in **Table 4-8**. A graphical representation of the z-score distribution of each pesticide present in the Test Material can be seen in **Appendix 11**. The corresponding histograms showing the distribution of the reported results are shown in **Appendix 10**.

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

Table 4-7: Overall classification of z-scores

Compound	No of results	Acceptable		Questionable		Unacceptable [1)]		FNs
		No.	(%)	No.	(%)	No.	(%)	No.
2,4-D (free acid)	57	51	(89 %)	6	(11 %)	0	(0 %)	0
Bromide	34	34	(100 %)	0	(0 %)	0	(0 %)	0
Dithiocarbamates	64	57	(89 %)	5	(8 %)	2	(3 %)	[1)]
Ethephon	29	26	(90 %)	2	(7 %)	1	(3 %)	[1)]
Glyphosate	35	**28**	(**80** %)	2	(6 %)	5	(14 %)	1 [2)]
Haloxyfop (free acid)	50	48	(96 %)	1	(2 %)	1	(2 %)	1 [3)]
Quinclorac (free acid)	22	20	(91 %)	0	(0 %)	2	(9 %)	1
Overall	**291**	**264**	(**90** %)	**16**	(**5** %)	**11**	(**4** %)	

1) Including false negatives (FN)
2) This lab (SRM6-9) reported that it had analysed, but not detected (= ND) glyphosate. The Reporting Limit (RL) submitted by this lab is much higher than the MRRL. Following the General Protocol (Appendix 14) the result was still judged as a "false negative" using the MRRL for the calculation of the z-scores
3) According to the laboratory (SRM6-108), haloxyfop was sought for in the EUPT-C5 test material (not containing haloxyfop). If this is the case, "not detected" was technically not a "false negative"!

Table 4-8: SRM Results reported by the laboratories and the respective z-scores calculated using the FFP-RSD of 25 %

Compound				2,4-D (free acid)		Bromide ion		Dithiocarbamates (sum) expr. as CS_2	
Assigned Value [mg/kg]				0.269		53.3		0.603	
MRRL [mg/kg]				0.02		5.0		0.05	
Qn-RSD				22.1 %		8.6 %		24.2 %	
Lab code SRM6-	NRL-SRM	No. Compounds Analysed / Corr. Found	Cat.	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1	x	13 / 7	A	0.25	-0.283	53	-0.021	0.549	-0.358
2		8 / 4	B	0.264	-0.074			0.302	-1.997
3		13 / 7	A	0.333	0.952	53.6	0.024	0.662	0.391
4		8 / 3	B	0.29	0.312	50	-0.247		
5	x	12 / 6	A	0.267	-0.030	56.7	0.256	0.492	-0.736
6		12 / 6	A	0.318	0.729			0.906	2.010
7		6 / 3	B			56.9	0.271	0.917	2.083
8		12 / 6	A	0.272	0.045			0.772	1.121
9	x	12 / 5	B	0.273	0.059	50.6	-0.202	0.694	0.604
10	x	9 / 2	B	0.353	1.249			FN	-3.668
11	x	11 / 5	B	0.291	0.327	53.4	0.009	0.494	-0.723
13		9 / 4	B	0.27	0.015	55	0.129	0.55	-0.352
14		13 / 7	A	0.223	-0.684	61	0.579	0.645	0.279
15	x	8 / 3	B	0.256	-0.193			0.477	-0.836
16		5 / 2	B	0.316	0.699			0.474	-0.856
17		9 / 5	B	0.247	-0.327			0.626	0.153
18		1 / 1	B					0.75	0.975
21	x	9 / 3	B	0.311	0.625			0.343	-1.725
22	x	7 / 2	B	0.249	-0.297				
24	x	11 / 5	B	0.245	-0.357				
25		3 / 1	B					0.617	0.093
28	x	6 / 2	B	0.268	-0.015				
29		4 / 4	B			56.83	0.266	0.5	-0.683
30		3 / 3	B	0.306	0.550	53.17	-0.009	0.96	2.368
34		10 / 4	B	0.246	-0.342	42.9	-0.780	0.305	-1.977
35		1 / 1	B					0.481	-0.809
37		7 / 2	B	0.33	0.907				
39		10 / 4	B	0.099	-2.528	54	0.054	0.8	1.307
40		12 / 6	A	0.247	-0.327	50	-0.247	0.447	-1.035
41		2 / 2	B					0.313	-1.924
42		1 / 1	B					0.59	-0.086
43	x	5 / 3	B					0.72	0.776
45		1 / 1	B					0.67	0.444
47	x	12 / 6	A	0.195	-1.100	60.5	0.542	0.62	0.113
48		9 / 3	B	0.38	1.651				
49		9 / 3	B	0.11	-2.364	48.3	-0.374		
50	x	13 / 7	A	0.278	0.134	59	0.429	0.707	0.690
51		13 / 7	A	0.284	0.223	49.5	-0.284	0.632	0.192

			Compound	Ethephon		Glyphosate		Haloxyfop (free acid)		Quinclorac (free acid)	
			Assigned Value [mg/kg]	0.235		0.294		0.124		0.267	
			MRRL [mg/kg]	0.02		0.05		0.02		0.02	
			Qn-RSD	29.7 %		40.6 %		17.7 %		26.7 %	
Lab code SRM6-	NRL-SRM	No. Compounds Analysed / Corr. Found	Cat.	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
1	x	13 / 7	A	0.169	-1.123	0.366	0.980	0.117	-0.226	0.256	-0.165
2		8 / 4	B			0.35	0.762	0.137	0.419		
3		13 / 7	A	0.163	-1.226	0.575	3.823	0.172	1.548	0.236	-0.464
4		8 / 3	B					0.12	-0.129		
5	x	12 / 6	A			0.417	1.673	0.124	0.000	0.267	0.000
6		12 / 6	A	0.103	-2.247	0.179	-1.565	0.126	0.065	0.307	0.599
7		6 / 3	B					0.131	0.226		
8		12 / 6	A	0.194	-0.698	0.265	-0.395	0.129	0.161	0.22	-0.704
9	x	12 / 5	B	0.23	-0.085	FN [1)]	-3.320	0.157	1.065		
10	x	9 / 2	B					0.129	0.161		
11	x	11 / 5	B					0.145	0.677	0.273	0.090
13		9 / 4	B	FN	-3.660			0.103	-0.677		
14		13 / 7	A	0.24	0.085	0.331	0.503	0.109	-0.484	0.541	4.105
15	x	8 / 3	B			0.377	1.129				
16		5 / 2	B								
17		9 / 5	B	0.148	-1.481	0.179	-1.565	0.161	1.194		
18		1 / 1	B								
21	x	9 / 3	B					0.172	1.548		
22	x	7 / 2	B					0.124	0.000	FN	-3.700
24	x	11 / 5	B	0.265	0.511	0.356	0.844	0.137	0.419	0.344	1.154
25		3 / 1	B								
28	x	6 / 2	B					0.165	1.323		
29		4 / 4	B	0.283	0.817	0.028	-3.619				
30		3 / 3	B								
34		10 / 4	B					0.114	-0.323		
35		1 / 1	B								
37		7 / 2	B			0.31	0.218				
39		10 / 4	B					0.099	-0.806		
40		12 / 6	A	0.283	0.817	0.289	-0.068	0.104	-0.645		
41		2 / 2	B			0.333	0.531				
42		1 / 1	B								
43	x	5 / 3	B	0.256	0.357	0.345	0.694				
45		1 / 1	B								
47	x	12 / 6	A			0.239	-0.748	0.137	0.419	0.216	-0.764
48		9 / 3	B	0.297	1.055	0.428	1.823				
49		9 / 3	B			0.294	0.000				
50	x	13 / 7	A	0.195	-0.681	1.13	**11.374** [2)]	0.109	-0.484	0.213	-0.809
51		13 / 7	A	0.1	-2.298	0.184	-1.497	0.098	-0.839	0.21	-0.854

1) The participating lab was not able to detect this compound due to its high RL (2 mg/kg)
2) Upon the preliminary report, Lab SRM6-50 reported to the Organizer, that it noticed an error in the calculation for glyphosate. A factor of 3 to compensate the sample weighting was not applied to its original calculation. Taking this into account, the z-score of glyphosate for this lab should be 1.129, instead of 11.37.

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

Compound				2,4-D (free acid)		Bromide ion		Dithiocarbamates (sum) expr. as CS_2	
Assigned Value [mg/kg]				0.269		53.3		0.603	
MRRL [mg/kg]				0.02		5.0		0.05	
Qn-RSD				22.1 %		8.6 %		24.2 %	
Lab code SRM6-	NRL-SRM	No. Compounds Analysed / Corr. Found	Cat.	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
53		11 / 5	B	0.245	-0.357	58.8	0.414	0.642	0.259
57		10 / 4	B	0.384	1.710			0.811	1.380
59	x	8 / 2	B	0.313	0.654				
62		1 / 1	B					0.59	-0.086
64		10 / 4	B	0.269	0.000	53	-0.021	0.56	-0.285
66		11 / 5	B	0.097	-2.558	52	-0.096	0.527	-0.504
71		1 / 1	B					0.544	-0.391
73		9 / 3	B	0.191	-1.160			0.65	0.312
74		1 / 1	B					0.55	-0.352
75		12 / 6	A	0.29	0.312	47	-0.472	0.632	0.192
76		12 / 6	A	0.265	-0.059	54.7	0.106	0.597	-0.040
84	x	13 / 7	A	0.291	0.327	51.7	-0.119	0.75	0.975
86		12 / 6	A	0.281	0.178			0.663	0.398
89		11 / 5	B	0.315	0.684			0.45	-1.015
90	x	13 / 7	A	0.231	-0.565	54	0.054	0.619	0.106
93		13 / 7	A	0.31	0.610	51.3	-0.149	0.602	-0.007
94		11 / 5	B	0.207	-0.922	46.9	-0.479	0.53	-0.484
98		3 / 1	B					0.415	-1.247
100		2 / 2	B			38.92	-1.078	0.436	-1.108
103	x	8 / 5	B	0.162	-1.591	56.1	0.211	0.639	0.239
104	x	11 / 5	B	0.354	1.264			0.71	0.710
106		1 / 0	B						
107		8 / 3	B	0.306	0.550			0.715	0.743
108	x	6 / 2	B	0.26	-0.134			0.17	-2.872
112	x	8 / 4	B	0.243	-0.387	56.5	0.241	0.603	0.000
113		1 / 1	B					0.525	-0.517
116		1 / 1	B					0.56	-0.285
120	x	1 / 1	B					0.648	0.299
123		8 / 4	B	0.381	1.665				
124	x	12 / 6	A	0.314	0.669	48.9	-0.329	0.883	1.857
125	x	12 / 6	A	0.191	-1.160	66.2	0.970	0.647	0.292
126	x	9 / 3	B	0.441	2.558			1.12	3.430
129		2 / 0	B						
132		3 / 1	B						
139		11 / 5	B	0.276	0.104	55	0.129	0.643	0.265
140		7 / 3	B	0.249	-0.297			0.249	-2.348
141		13 / 7	A	0.217	-0.773	53	-0.021	0.54	-0.418
145		4 / 1	B	0.1	-2.513				
147		8 / 4	B	0.12	-2.216			0.45	-1.015

Compound				Ethephon		Glyphosate		Haloxyfop (free acid)		Quinclorac (free acid)	
Assigned Value [mg/kg]				0.235		0.294		0.124		0.267	
MRRL [mg/kg]				0.02		0.05		0.02		0.02	
Qn-RSD				29.7 %		40.6 %		17.7 %		26.7 %	
Lab code SRM6-	NRL-SRM	No. Compounds Analysed / Corr. Found	Cat.	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)	Conc. [mg/kg]	z-score (FFP-RSD = 25 %)
53		11 / 5	B					0.123	-0.032	0.194	-1.094
57		10 / 4	B					0.144	0.645	0.254	-0.195
59	x	8 / 2	B					0.119	-0.161		
62		1 / 1	B								
64		10 / 4	B					0.12	-0.129		
66		11 / 5	B					0.05	-2.387	0.343	1.139
71		1 / 1	B								
73		9 / 3	B					0.097	-0.871		
74		1 / 1	B								
75		12 / 6	A	0.305	1.191	0.415	1.646	0.13	0.194		
76		12 / 6	A	0.174	-1.038	0.18	-1.551	0.109	-0.484		
84	x	13 / 7	A	0.177	-0.987	0.132	-2.204	0.124	0.000	0.257	-0.150
86		12 / 6	A	0.168	-1.140	0.184	-1.497	0.141	0.548	0.228	-0.584
89		11 / 5	B			0.207	-1.184	0.143	0.613	0.295	0.419
90	x	13 / 7	A	0.25	0.255	0.452	2.150	0.108	-0.516	0.298	0.464
93		13 / 7	A	0.156	-1.345	0.38	1.170	0.15	0.839	0.31	0.644
94		11 / 5	B	0.285	0.851			0.079	-1.452		
98		3 / 1	B								
100		2 / 2	B								
103	x	8 / 5	B	0.279	0.749			0.083	-1.323		
104	x	11 / 5	B	0.244	0.153	0.293	-0.014	0.142	0.581		
106		1 / 0	B								
107		8 / 3	B					0.138	0.452		
108	x	6 / 2	B					FN	-3.355		
112	x	8 / 4	B					0.103	-0.677		
113		1 / 1	B								
116		1 / 1	B								
120	x	1 / 1	B								
123		8 / 4	B			0.199	-1.293	0.157	1.065	0.275	0.120
124	x	12 / 6	A	0.149	-1.464	0.17	-1.687	0.13	0.194		
125	x	12 / 6	A	0.289	0.919	0.304	0.136	0.119	-0.161		
126	x	9 / 3	B					0.107	-0.548		
129		2 / 0	B								
132		3 / 1	B			0.367	0.993				
139		11 / 5	B	0.23	-0.085			0.122	-0.065		
140		7 / 3	B					0.109	-0.484		
141		13 / 7	A	0.24	0.085	0.27	-0.327	0.122	-0.065	0.291	0.360
145		4 / 1	B								
147		8 / 4	B	0.29	0.936	0.055	-3.252				

Table 4-9: 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 it is shown in bold and italics)

Compound				2.4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate	Haloxyfop (free acid)	Quinclorac (free acid)
Assigned Value [mg/kg]				0.269	53.3	0.603	0.235	0.294	0.124	0.267
Qn-RSD				22.1 %	8.6 %	24.2 %	29.7 %	40.6 %	17.7 %	26.7 %
No. Labs reporting results				57	34	64	29	35	50	22
Lab code SRM6-	NRL-SRM	No. Compounds Analysed / Corr. Found	Cat.	ranking position	ranking position	ranking position	ranking position	ranking position	ranking position	ranking position
1	x	13 / 7	A	15	3	23	20	14	16	5
2		8 / 4	B	8		57		12	19	
3		13 / 7	A	42	6	25	23	***34***	47	10
4		8 / 3	B	18	18				8	
5	x	12 / 6	A	4	20	37		26	1	1
6		12 / 6	A	38		58	**27**	23	5	12
7		6 / 3	B		22	59			16	
8		12 / 6	A	5		49	10	7	10	14
9	x	12 / 5	B	6	15	32	1	***32 (FN)***	41	
10	x	9 / 2	B	46		***64 (FN)***			10	
11	x	11 / 5	B	20	2	36			34	2
13		9 / 4	B	2	12	21	***29 (FN)***		35	
14		13 / 7	A	35	31	15	3	8	23	***22***
15	x	8 / 3	B	13		41		16		
16		5 / 2	B	37		42				
17		9 / 5	B	22		9	26	23	43	
18		1 / 1	B			43				
21	x	9 / 3	B	32		53			47	
22	x	7 / 2	B	16					1	***21 (FN)***
24	x	11 / 5	B	25			8	13	19	20
25		3 / 1	B			6				
28	x	6 / 2	B	2					44	
29		4 / 4	B		21	33	12	***33***		
30		3 / 3	B	28	1	61				
34		10 / 4	B	24	32	56			18	
35		1 / 1	B			40				
37		7 / 2	B	40				5		
39		10 / 4	B	**55**	7	51			37	
40		12 / 6	A	22	18	47	12	3	33	
41		2 / 2	B			55		9		
42		1 / 1	B			4				
43	x	5 / 3	B			39	7	10		
45		1 / 1	B			**28**				
47	x	12 / 6	A	43	30	8		11	19	15
48		9 / 3	B	49			19	28		
49		9 / 3	B	**53**	25			1		
50	x	13 / 7	A	10	27	34	9	***35*** [1)]	23	16
51		13 / 7	A	14	23	10	**28**	20	38	17
53		11 / 5	B	25	26	13			4	18

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

Compound				2.4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate	Haloxyfop (free acid)	Quinclorac (free acid)
Assigned Value [mg/kg]				0.269	53.3	0.603	0.235	0.294	0.124	0.267
Qn-RSD				22.1 %	8.6 %	24.2 %	29.7 %	40.6 %	17.7 %	26.7 %
No. Labs reporting results				57	34	64	29	35	50	22
Lab code SRM6-	NRL-SRM	No. Compounds Analysed / Corr. Found	Cat.	ranking position	ranking position	ranking position	ranking position	ranking position	ranking position	ranking position
57		10 / 4	B	51		52			32	6
59	x	8 / 2	B	33					10	
62		1 / 1	B			4				
64		10 / 4	B	1	3	16			8	
66		11 / 5	B	**56**	9	30			**49**	19
71		1 / 1	B			24				
73		9 / 3	B	44		20			40	
74		1 / 1	B			21				
75		12 / 6	A	18	28	10	22	25	14	
76		12 / 6	A	6	10	3	18	22	23	
84	x	13 / 7	A	20	11	43	17	**30**	1	4
86		12 / 6	A	12		26	21	20	28	11
89		11 / 5	B	35		45		18	31	8
90	x	13 / 7	A	30	7	7	6	**29**	27	9
93		13 / 7	A	31	14	2	24	17	38	13
94		11 / 5	B	41	29	29	14		46	
98		3 / 1	B			50				
100		2 / 2	B		34	48				
103	x	8 / 5	B	48	16	12	11		44	
104	x	11 / 5	B	47		35	5	2	30	
106		1 / 0	B							
107		8 / 3	B	28		38			22	
108	x	6 / 2	B	10		62			***50 (FN)***	
112	x	8 / 4	B	27	17	1			35	
113		1 / 1	B			31				
116		1 / 1	B			16				
120	x	1 / 1	B			19				
123		8 / 4	B	50				19	41	3
124	x	12 / 6	A	34	24	54	25	27	14	
125	x	12 / 6	A	44	33	18	15	4	10	
126	x	9 / 3	B	**56**		63			29	
129		2 / 0	B							
132		3 / 1	B					15		
139		11 / 5	B	9	12	14	1		5	
140		7 / 3	B	16		60			23	
141		13 / 7	A	39	3	27	3	6	5	7
145		4 / 1	B	**54**						
147		8 / 4	B	**52**		45	16	***31***		

1) Following the preliminary report, Lab SRM6-50 reported to the Organizer, that it noticed an error in the calculation for glyphosate due to the falure to apply a factor 3 in the calculation to account for the sample weigh. Taking this into account, the z-score of glyphosate for this lab should have been at 1.129 with a ranking position at 16.

4.4.4 Laboratory performance based on scope

All participating laboratories were classified into Category A and B based on their scope, following the rules stated in the General Protocol (2nd Edition, see **Appendix 14**). To be included in Category A a laboratory should have: a) analysed at least 6 of the 7 pesticides present in the Test Material, and b) have not reported any false positive results.

Table 4-10 and **Table 4-11** show the laboratories classified into Category A and B, respectively.

Table 4-10: Category A laboratories [1] ordered by lab-codes

Lab-code SRM6-	NRL-SRM	No. Compounds analysed / corr. found	z-Score							AAZ [3]
			2.4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate	Haloxyfop (free acid)	Quinclorac (free acid)	
1	x	13 / 7	-0.283	-0.021	-0.358	-1.123	0.980	-0.226	-0.165	0.45
3		13 / 7	0.952	0.024	0.391	-1.226	3.823	1.548	-0.464	1.20
5	x	12 / 6	-0.030	0.256	-0.736		1.673	0.000	0.000	0.45
6		12 / 6	0.729		2.010	-2.247	-1.565	0.065	0.599	1.20
8		12 / 6	0.045		1.121	-0.698	-0.395	0.161	-0.704	0.52
9	x	12 / 5	0.059	-0.202	0.604	-0.085	**-3.320 (FN)**	1.065		0.89
14		13 / 7	-0.684	0.579	0.279	0.085	0.503	-0.484	4.105	0.96
40		12 / 6	-0.327	-0.247	-1.035	0.817	-0.068	-0.645		0.52
47	x	12 / 6	-1.100	0.542	0.113		-0.748	0.419	-0.764	0.61
50	x	13 / 7	0.134	0.429	0.690	-0.681	11.374 [2]	-0.484	-0.809	1.18
51		13 / 7	0.223	-0.284	0.192	-2.298	-1.497	-0.839	-0.854	0.88
75		12 / 6	0.312	-0.472	0.192	1.191	1.646	0.194		0.67
76		12 / 6	-0.059	0.106	-0.040	-1.038	-1.551	-0.484		0.55
84	x	13 / 7	0.327	-0.119	0.975	-0.987	-2.204	0.000	-0.150	0.68
86		12 / 6	0.178		0.398	-1.140	-1.497	0.548	-0.584	0.72
90	x	13 / 7	-0.565	0.054	0.106	0.255	2.150	-0.516	0.464	0.59
93		13 / 7	0.610	-0.149	-0.007	-1.345	1.170	0.839	0.644	0.68
124	x	12 / 6	0.669	-0.329	1.857	-1.464	-1.687	0.194		1.03
125	x	12 / 6	-1.160	0.970	0.292	0.919	0.136	-0.161		0.61
141		13 / 7	-0.773	-0.021	-0.418	0.085	-0.327	-0.065	0.360	0.29

1) This table includes only laboratories that: a) have analysed and reported results for at least 6 of the 7 pesticides present in the Test Materials; and b) have not reported any false positive results.
2) Based upon the preliminary report, Lab SRM6-50 reported to the Organizer that it noticed an error in the calculation for glyphosate. A factor of 3 to compensate for the sample weight was missing in its original calculation. Taking this into account, the z-score of glyphosate for this lab would have been 1.129, instead of 11.37. This z-score was set at 5 in the calculation of the AAZ.
3) AAZ: Average of Absolute z-scores, calculated for informative purposes only for the labs in Category A

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

Lab code SRM6-	NRL-SRM	No. Compounds analysed / corr. found	z-Score						
			2.4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate	Haloxyfop (free acid)	Quinclorac (free acid)
2		8 / 4	-0.074		-1.997		0.762	0.419	
4		8 / 3	0.312	-0.247				-0.129	
7		6 / 3		0.271	2.083			0.226	
10	x	9 / 2	1.249		**-3.668 (FN)**			0.161	
11	x	11 / 5	0.327	0.009	-0.723			0.677	0.090
13		9 / 4	0.015	0.129	-0.352	**-3.660 (FN)**		-0.677	
15	x	8 / 3	-0.193		-0.836		1.129		
16		5 / 2	0.699		-0.856				

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

Lab code SRM6-	NRL-SRM	No. Compounds analysed / corr. found	z-Score						
			2.4-D (free acid)	Bromide ion	Dithiocarbamates (sum) expr. as CS_2	Ethephon	Glyphosate	Haloxyfop (free acid)	Quinclorac (free acid)
17		9 / 5	-0.327		0.153	-1.481	-1.565	1.194	
18		1 / 1			0.975				
21	x	9 / 3	0.625		-1.725			1.548	
22	x	7 / 2	-0.297					0.000	**-3.700 (FN)**
24	x	11 / 5	-0.357			0.511	0.844	0.419	1.154
25		3 / 1			0.093				
28	x	6 / 2	-0.015					1.323	
29		4 / 4		0.266	-0.683	0.817	-3.619		
30		3 / 3	0.550	-0.009	2.368				
34		10 / 4	-0.342	-0.780	-1.977			-0.323	
35		1 / 1			-0.809				
37		7 / 2	0.907				0.218		
39		10 / 4	-2.528	0.054	1.307			-0.806	
41		2 / 2			-1.924		0.531		
42		1 / 1			-0.086				
43	x	5 / 3			0.776	0.357	0.694		
45		1 / 1			0.444				
48		9 / 3	1.651			1.055	1.823		
49		9 / 3	-2.364	-0.374			0.000		
53		11 / 5	-0.357	0.414	0.259			-0.032	-1.094
57		10 / 4	1.710		1.380			0.645	-0.195
59	x	8 / 2	0.654					-0.161	
62		1 / 1			-0.086				
64		10 / 4	0.000	-0.021	-0.285			-0.129	
66		11 / 5	-2.558	-0.096	-0.504			-2.387	1.139
71		1 / 1			-0.391				
73		9 / 3	-1.160		0.312			-0.871	
74		1 / 1			-0.352				
89		11 / 5	0.684		-1.015		-1.184	0.613	0.419
94		11 / 5	-0.922	-0.479	-0.484	0.851		-1.452	
98		3 / 1			-1.247				
100		2 / 2		-1.078	-1.108				
103	x	8 / 5	-1.591	0.211	0.239	0.749		-1.323	
104	x	11 / 5	1.264		0.710	0.153	-0.014	0.581	
106		1 / 0							
107		8 / 3	0.550		0.743			0.452	
108	x	6 / 2	-0.134		-2.872			**-3.355 (FN)**	
112	x	8 / 4	-0.387	0.241	0.000			-0.677	
113		1 / 1			-0.517				
116		1 / 1			-0.285				
120	x	1 / 1			0.299				
123		8 / 4	1.665				-1.293	1.065	0.120
126	x	9 / 3	2.558		3.430			-0.548	
129		2 / 0							
132		3 / 1					0.993		
139		11 / 5	0.104	0.129	0.265	-0.085		-0.065	
140		7 / 3	-0.297		-2.348			-0.484	
145		4 / 1	-2.513						
147		8 / 4	-2.216		-1.015	0.936	-3.252		

4.4.5 Laboratory feedback in the case of poor results

As a follow-up measure to this EUPT, participating laboratories that had achieved questionable or unacceptable z-scores were asked to give, where possible, explanations for their poor performance. With this information the Organizers hope to help other labs recognize potential sources of errors so that they can be avoided in the future. Furthermore, the information collected should give hints to the EURLs on how to assist the labs in order to help improve their future performance. A compilation of this information is given in **Appendix 13**. In many cases the laboratories were not able to fully clarify the reasons for their bad performance. The most common reasons for poor performance given by the labs concerned errors in the concentrations of their standard solutions, as a result of degradation or incorrect dilution.

4.5 Analytical methods used

Detailed information about the analytical methods used by the laboratories can be found in **Appendix 12**.

4.5.1 Extraction and determinative analysis

2,4-D analysis was undertaken by 57 laboratories with none of them reporting any false negative results. All laboratories provided information about the method-type used. Of these labs, 46 (81 %) employed methods involving an acetonitrile extraction, with 43 labs (75 % overall) employing QuEChERS-type methodologies 3 labs (10 %) employing methods involving extraction with methanol (1 lab used the ChemElut method); 4 labs (7 %) using ethyl acetate-based methods, 1 lab (2 %) using a method involving extraction after addition of acetone followed by partitioning into dichloromethane (S19 / Luke type) and 1 lab (2 %) using a method involving extraction using ethanol followed by partitioning into dichloromethane. 5 labs in total employed methods not involving liquid-liquid partitioning with 2 of them employing methanol for extraction, 2 of them acetonitrile, and 1 of them water.

Although only the free acid was included in the Pesticides Target List, implying that no cleavage step was necessary, 8 labs employed alkaline hydrolysis. According to experiments performed by the Organizers, 2,4-D, which was spiked post-harvest, formed some amounts of conjugated residues resulting in an increase in the residue concentration of approx. 23 % when alkaline hydrolysis was performed. Furthermore, 2 labs employed dispersive SPE cleanup using PSA, which is not recommended as PSA has a tendency to remove organic acids from the extracts.

52 labs (91 % overall) indicated the use of LC-MS/MS and 1 lab the use of LC-ITD. 4 labs (7 %) employed GC-techniques following derivatization with PFB-Br (2×), diazomethane (1x) or trimethylsulfonium hydroxide (1x).

Bromide was analyzed by 34 laboratories with none of them reporting any false negative results. All laboratories provided information about the method-type used. Out of these labs 24 (71 %) employed methods involving derivatization, partitioning into a non-polar solvent (23× ethylacetate and 1× hexane) and gas chromatographic analysis (20× GC-ECD and 4× GC-MSD). 21 of these labs (62 % overall) employed 1,2-propylene oxide and 3 labs ethylene oxide for derivatization. 8 labs employed methods involving extraction with water (in 2 cases water/methanol mixtures) followed by liquid chromatographic separation (mostly using ion-chromatography columns) and detection by conductivity detectors (4 cases) or LC-UV/DAD (4 cases). In one case a lab employed ICP-MS to analyze bromide from the water extract, and in one further case analysis was performed directly from the homogenate using x-ray fluorescence measurement.

Dithiocarbamates were analyzed by 64 laboratories with one of them reporting a false negative result All 64 labs provided information about the methodology they used. Out of these labs 25 (39 % overall) employed methods involving reduction/cleavage to CS_2 followed by its derivatization and spectrophotometric detection. Out of this group 14 labs indicated derivatization with MeOH/KOH to xanthogenate (EN-12396-3-type methods) and 11 derivatization with copper-(II)-acetate in diethanolamine / ethanol (EN-12396-1-type methods). 25 laboratories (39 % overall) indicated the use of methods involving reduction/ cleavage to CS_2 and partitioning into isooctane followed by GC-analysis in combination with MSD (9 cases), FPD/PFPD (11 cases) or ECD (5 cases) detectors. 14 laboratories (22 % overal) employed methods involving reduction/cleavage to CS_2, headspace sampling and GC-analysis (EN-12396-2-type methods). Four of these labs employed SPME for headspace sampling.

Out of the 64 labs 25 (39 % overall) employed spectrophotometers, 16 labs (25%) GC-MSD, 15 labs (23%) GC-FPD, 7 labs (11%) GC-ECD and 1 GC-ITD.

In contrast to the EUPT-SRM5 with apple purée as Test Material there was no clear trend towards reporting poor or biased results when using any of the analytical approaches with the exception of methods using headspace sampling that showed a trend for underestimated results. All laboratories using spectrophotometric approaches (EN-12396-1- and EN-12396-3-type) reported acceptable results ($|z| \leq 2$).

Ethephon was analyzed by 29 laboratories with one of them reporting a false negative result. All 29 laboratories provided information about the method-type used. Out of these labs 20 (69 % overall) employed QuPPe-type methods involving extraction/dilution with a water-miscible solvent followed by LC-MS/MS (18 labs), LC-MS (1 lab) or LC-ITD (1 lab) determination. 15 of those labs using QuPPe-type methods (52 % overall) followed the protocol published by the EURL-SRM. 4 labs (14 %) employed methods involving cleavage to ethylene under alkaline conditions followed by headspace sampling and GC-FID analysis. 2 labs employed methods involving derivatization of ethephon (with MSTFA in one case, and diazomethane in the other) followed by GC-analysis.

20 of the 29 labs (69 %) indicated the use of LC with mass spectrometric detection and 8 (28 % overall) the use of GC-techniques, thereof 6 (21 % overall) in combination with headspace sampling.

Out of the 20 labs (N) employing methods involving extraction/dilution with a water-miscible solvent followed LC separation and mass spectrometric detection 11 labs (55 % of N) indicated the use of isotopically labelled ethephon as ISTD. The other 9 (45 % of N) did not use such as ISTD. Out of these 9 labs not employing an ISTD 6 employed matrix-matched calibrations using the blank Test Material provided by the Organizers, 2 labs employed the standard additions approach to sample portions and 1 lab calibration standards based on pure solvent.

Glyphosate was analyzed by 35 laboratories with one of them reporting a false negative result. Out of these labs 20 (57 % overall) employed methods involving extraction/dilution with a water-miscible solvent followed by LC-MS/MS (18 labs), LC-MS (1 lab) or LC-ITD (1 lab) determination. Most of these labs followed the QuPPe-method published in the EURL-website or modifications thereof. 9 labs (26 %) employed methods involving derivatization with FMOC and determination by LC-MS/MS (7) or LC-FLD (2). 3 labs employed methods involving post column derivatization. 2 labs employed methods involving LC-separation and post-column oxidation to glycine and further derivatization with OPA/ 2-mercaptoethanol (2×) or with OPA/ thiofluor (1×). Further 2 labs employed methods involving derivatization with MSTFA (2×) or with trifluoroacetanhydrite (TFAA) / heptafluorobutanol (HFB) (2×) followed by GC-analysis.

27 of the 35 labs (74 %) indicated the use of LC with mass spectrometric detection (including MS/MS, MS and ITD), and 5 labs (14%) the use of LC-FLD and 3 labs (9 %) the use of GC-techniques.

Out of the 20 labs (N) employing methods involving extraction/dilution with a water-miscible solvent followed by direct LC separation and mass spectrometric detection 11 labs (55 % of N) indicated the use of isotopically labelled glyphosate as ISTD, whereas the other 9 labs (45 % of N) did not. Out of these 9 labs not employing an ISTD 6 labs employed matrix-matched calibrations using the blank Test Material provided by the Organizer, 1 lab employed the standard additions approach to sample portions, 1 lab employed the standard additions approach to extract aliquots and 1 lab calibration standards based on pure solvent. Isotope labelled glyphosate was also employed by 5 out of the 7 labs that employed derivatization with FMOC followed by LC-MS/MS analysis as well as by the two labs that derivatized with TFAA/HFB followed by GC-MS analysis.

Haloxyfop was analyzed by 50 laboratories with one of them reporting a false negative result. All laboratories provided information about the method-type used. Out of these labs 41 (82 %) employed methods involving acetonitrile extraction with 40 labs (80 % overall) employing a QuEChERS-type methodology. 3 labs (6 %) employed methods involving extraction with methanol (2 of them the ChemElut method); 3 labs (6 %) employed ethyl acetate-based methods and 2 labs (4 %) methods based on acetone (S19 / Luke type).

Although only the free acid was included in the Pesticides Target List, implying that no cleavage step was necessary, 7 labs employed alkaline hydrolysis. According to experiments performed by the Organizers haloxyfop, which was spiked post-harvest, formed small amounts of conjugated residues resulting in an increase in the residue concentration of ca. 20 % when alkaline hydrolysis was performed. Further 2 labs employed dispersive SPE cleanup using PSA, which is not recommended as PSA has a tendency to remove organic acids from the extracts.

46 labs (92 % overall) indicated the use of LC-MS/MS and 1 lab the use of LC-ITD. 3 labs (6 %) employed GC-techniques following derivatization with diazomethane (1x), PFB-Br (1x) or trimethylsulfonium hydroxide (1x).

Quinclorac was analyzed by 22 laboratories with one of them reporting a false negative result. Out of these 22 labs 17 (77 %) employed methods involving acetonitrile extraction, with 16 labs (73 % overall) employing a QuEChERS-type methodology. 2 labs (9 %) employed methods involving extraction with methanol; 2 labs (9 %) employed ethyl acetate-based methods and 1 labs (5 %) a method involving extraction with acetone (S19 / Luke type).

Although only the free acid was included in the Pesticides Target List, implying that no cleavage step was necessary, 3 labs employed alkaline hydrolysis. According to experiments performed by the Organizers quinclorac, which was spiked post-harvest, formed very small amounts of conjugated residues causing an increase in the residue concentration of just ca. 10 % when alkaline hydrolysis was performed. Furthermore 2 labs employed dispersive SPE cleanup using PSA, which is not recommended as PSA has a tendency to remove organic acids from the extracts.

20 labs (91 % overall) indicated the use of LC-MS/MS and 1 lab the use of LC-ITD. 1 lab (5 %) employed GC-MSD following derivatization with diazomethane.

4.5.2 Methodology-related bias and bimodal distribution of results

As mentioned in **Chapter 4.3** a relatively broad distribution and a visible bimodality in the kernel-density-curves was observed in the case of glyphosate and ethephon (see also **Appendix 11**). Looking at the methodology information submitted by the labs, this bimodality could be linked to the use/non-use, of isotopically labeled ethephon and glyphosate as ISTDs. The non-use of isotope-labelled ISTDs resulted in

both cases in a clear trend towards lower values. A certain bimodality in the distribution of results was also observed in the case of 2,4-D allthough not visible in the kernel-density estimate curve and not reflected by a high Qn-RSD. Despite the fact that only the free acid had to be determined in this EUPT 8 laboratories still performed alkaline hydrolysis prior to extraction. Most of the labs reported tentatively overestimated results (**Appendix 10**).

In the case of **ethephon** (Assigned Value 0.235 mg/kg) 20 labs employed approaches involving extraction with water-miscible solvents followed by direct determination by LC-MS/MS (QuPPe-type or "dilute and shoot" methods). Out of these 20 labs 11 employed isotope-labelled ethephon as ISTD and 9 labs (2 of them employing standard addition to sample portions) did not. Looking at the median values of the two sub-populations, and excluding the results of the two labs correcting for recovery via standard additions, we see a clear median shift from 0.256 mg/kg in the first case to 0.177 mg/kg in the latter (see Appendix 10). The median of the remaining 8 results, obtained using other methods ("ethylene-approach"and derivatization followed by GC-analysis), is at 0,245 and thus closer to the value of the first sub-population (employing "dilute and shoot" methods with the use of an isotope labelled ISTD). Excluding from the total population the 7 results of the second sub-population (employing "dilute and shoot" methods without the use of an isotope labelled ISTD) a new median at 0,250 mg/kg is derived (+6% shift compared with the current Assigned Value). Taking this new median as the Assigned Value would result in a minor shift of the z-scores, but not to a different result classification (acceptable/questionable/unacceptable). Due to the small shift of the median, and the small population of the different sub-groups the EUPT-Scientific Committee decided to still use the entire population of results for the establishment of the Assigned Values.

In the case of **glyphosate** (Assigned Value 0.294 mg/kg) the situation was similar. 19 labs employed approaches involving extraction with water-miscible solvents followed by LC-MS/MS determination (QuPPe-type or "dilute and shoot" methods). Out of these 20 labs 11 employed isotope-labelled glyphosate as ISTD and 8 labs (thereof 1 employing standard addition to sample portions) did not. Looking at the median values of the two sub-populations, and excluding the result of the lab which corrected for recovery via standard additions, we see a clear median shift from 0.320 mg/kg in the first sub-population to 0.184 mg/kg in the latter (see **Appendix 10**). The median of the remaining 15 results, obtained using other methods (employing derivatization followed by LC-analysis, derivatization followed by GC-analysis or LC-analysis followed post-column derivatization), is then at 0,333 and thus closer to the value of the first sub-population (11 labs employing "dilute and shoot" methods with the use of an isotope-labelled ISTD). Excluding the 7 results of the second sub-population from the total population (employing "dilute and shoot" methods without the use of an isotope labelled ISTD) a new median at 0.321 mg/kg is derived (+9 % shift compared with the Assigned Value). Taking 0.321 mg/kg as the Assigned Value would result in a moderate shift of the z-scores and in 1 case even in a different result classification (Lab 90 from „questionable" to „acceptable")

Out of the mentioned 15 labs using other types of methods 7 also employed isotope-labelled glyphosate as ISTD (5 employing derivatization with FMOC followed by LC-MS/MS analysis and 2 employing derivatization with TFAA/HCB followed by GC-MS analysis). If these 7 labs are merged with the other 11 labs employing isotope labelled glyphosate as ISTD, then the median of all 18 labs that employed isotope-labelled ISTDs is at 0.331 mg/kg (+13 % shift compared with the Assigned Value). Taking 0.331 mg/kg as the Assigned Value would result in a moderate shift of the z-scores and in 2 cases in a different result classification (Lab SRM6-90 from „questionable" to „acceptable" and Lab SRM6-3 from „unacceptable" to „questionable").

Due to the rather moderate shift of the median, and the small population of the different sub-groups the EUPT-Scientific Committee decided to still use the entire population of results for the establishment of the Assigned Value in the case of glyphosate.

As can be seen in **Appendix 10** the 8 laboratories employing alkaline hydrolysis in the case of **2,4-D** (assigned concentration 0.269 mg/kg) in their majority reported overestimated results with the median of this sub-population at 0.335 mg/kg. Excluding this sub-population from the total population would result in a very minor shift of the median to 0.267 mg/kg. Comparing the median of the two sub-populations we see a shift of ca. 24 %, which correlates very well with the observations of the Organizers who determined a shift of ca. 23 %. Due to the very minor shift of the median, and the small population of the subgroups employing alkaline hydrolysis the EUPT-Scientific Committee decided to use the entire population of results for the establishment of the Assigned Value in the case of 2,4-D.

The impact of alkaline hydrolysis on the medians of the other two acidic pesticides haloxyfop and quinclorac was also minor.

4.5.3 Coverage of compounds by the labs in routine analysis and their experience

As can be seen in **Figure 4-1** only a fraction (29 – 83 %) of the labs that participated in the EUPT-SRM6 have analyzed for the compounds in the EUPT-SRM6 Target Pesticide List. The fraction of the labs that actually include those compounds in their routine scope is even lower (8 – 66 %). These percentage figures become even smaller when compared to the 181 labs that were obliged to participate in this EUPT (Note: the non-inclusion of the target pesticides of this PT in the scope of the labs was the most frequent reason provided by labs to explain their non-participation in this PT).

Nevertheless, in 99 % of all cases, compounds covered routinely by labs participating in this EUPT were also targeted by these labs within this exercize (**Table 4-12**). Many labs have even analyzed for compounds in this exercise although they are not, or not yet, part of their routine scope.

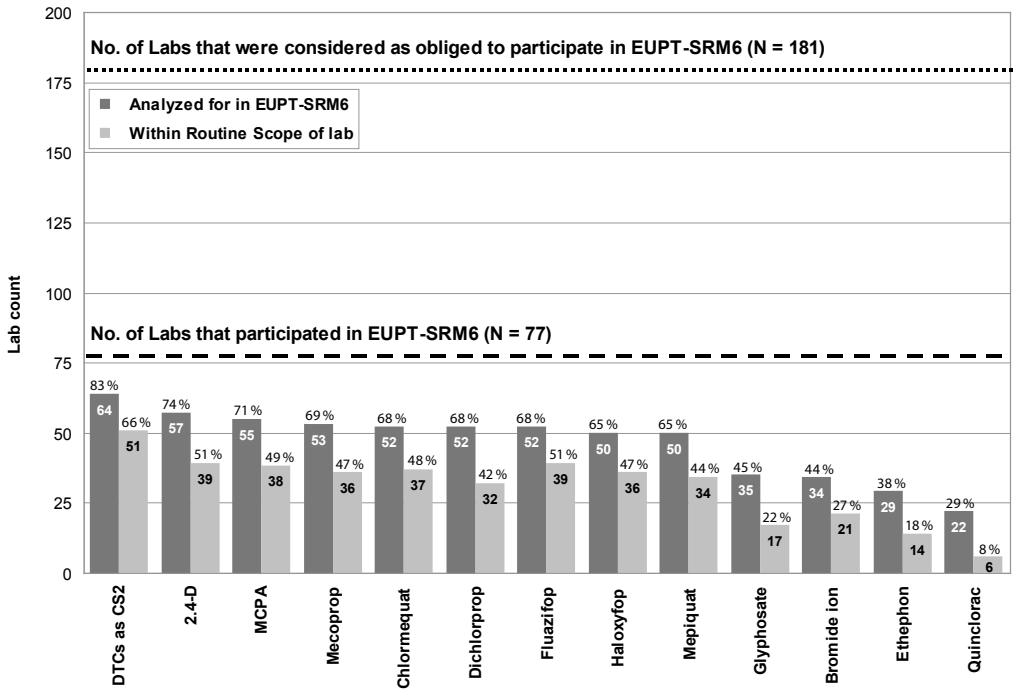

Figure 4-1: Inclusion of analytes in the routine scope of labs

Table 4-12: Coverage of EUPT-SRM6 compounds within routine scope of laboratories

Pesticides	Compound is within routine scope of lab		Compound is NOT within routine scope of lab	
	analysed for in this EUPT	not analysed for	analysed for in this EUPT	not analysed for
2.4-D (free acid)	39 (100 %)		18 (47 %)	20
Bromide ion	21 (100 %)		13 (23 %)	43
Chlormequat cation	35 (95 %)	2	17 (43 %)	23
Dichlorprop (2,4-DP) incl. Dichlorprop-P (free acids)	32 (100 %)		20 (44 %)	25
Dithiocarbamates (sum) expr. as CS_2	51 (100 %)		13 (50 %)	13
Ethephon	14 (100 %)		15 (24 %)	48
Fluazifop incl. Fluazifop-P (free acids)	39 (100 %)		13 (34 %)	25
Glyphosate	17 (100 %)		18 (30 %)	42
Haloxyfop incl. Haloxyfop-R (free acids)	35 (97 %)	1	15 (37 %)	26
MCPA (free acid)	38 (100 %)		17 (44 %)	22
Mecoprop (MCPP) incl. Mecoprop-P (free acids)	36 (100 %)		17 (41 %)	24
Mepiquat cation	33 (97 %)	1	17 (40 %)	26
Quinclorac (free acid)	5 (83 %)	1	17 (24 %)	54
	395 (99 %)	**5 (1 %)**	**210 (35 %)**	**391**

Of all the compounds included in the EUPT-SRM6 Target Pesticide List, dithiocarbamates were the group of compounds most frequently included in the routine scope of the labs. All laboratories indicating that they include dithiocarbamates in their routine scope plus 13 labs that do not include them in their routine scope targeted this compound group within this exercise. In the case of glyphosate, ethephon and quinclorac, the ones least frequently analyzed in routine, more than double as many labs covered these analytes in this EUPT compared those routinely analyzing for them.

In 58 % of the cases labs indicated that they have more than 2 years experience with the analysis of the respective compounds they have reported results for (**Figure 4-2**). 17 % of the labs indicated that they had 1 – 2 years experience, 15 % < 1 year experience and 9 % no experience. As far as the individual compounds are concerned (see **Table 4-13**), dithiocarbamates are the compounds with which labs have the most experience. 57 labs (89 %) indicated that they have > 2 years experience with analysing this compound group. 2,4-D (67 %) and bromide and haloxyfop (62 %) follow. The compounds where labs have the least overall experience, are ethephon (31 % experience > 2 years), glyphosate (29 %) and quinclorac (14 %). For quinclorac, ethephon and glyphosate 73 %, 44 % and 40 % of the labs respectively even indicated that they have < 1 year experience. In the case of dithiocarbamates not a single lab indicated "no experience" and 2 labs < 1 year experience.

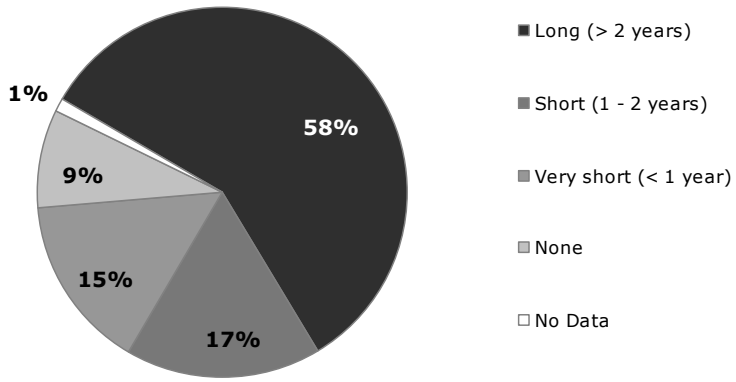

Figure 4-2: Experience of labs with the analysis of pesticides presend in the Test Material (overall)

Table 4-13: Experience of labs with the analysis of individual compounds

Pesticides	Experience	No of Labs	% of Labs
2.4-D (free acid)	> 2 years	38	67 %
	1 – 2 years	11	19 %
	< 1 year	6	11 %
	None	2	4 %
Bromide ion	> 2 years	21	62 %
	1 – 2 years	6	18 %
	< 1 year	4	12 %
	None	3	9 %
Dithiocarbamates (sum) expr. as CS_2	> 2 years	57	89 %
	1 – 2 years	4	6 %
	< 1 year	2	3 %
	No Data	1	2 %
Ethephon	> 2 years	9	31 %
	1 – 2 years	7	24 %
	< 1 year	10	34 %
	None	3	10 %
Glyphosate	> 2 years	10	29 %
	1 – 2 years	10	29 %
	< 1 year	9	26 %
	None	5	14 %
	No Data	1	3 %
Haloxyfop incl. Haloxyfop-R (free acids)	> 2 years	31	62 %
	1 – 2 years	9	18 %
	< 1 year	7	14 %
	None	3	6 %
Quinclorac (free acid)	> 2 years	3	9 %
	1 – 2 years	2	6 %
	< 1 year	7	20 %
	None	9	26 %
	No Data	1	3 %

4.5.4 Size of analytical portions

The size of the analytical portions employed by the participants ranged between 1 g and 5 g for quinclorac; between 1 g and 15 g for 2,4-D, bromide and haloxyfop; between 1 g and 25 g for glyphosate and ethephon; and between 1 g and 75 g for dithiocarbamates (see **Figure 4-3**). There were several cases where the sample portions employed by the laboratories were smaller than those used by the Organizer to check for the homogeneity of the Test Material (i.e.: 1 g for bromide; 3 g for 2,4-D, haloxyfop and quinclorac; 5g for glyphosate and ethephon and 20 g for dithiocarbamates). Where significantly smaller test portions were employed than those used in the homogeneity test, sufficient homogeneity cannot be guaranteed. Smaller portions than those tested by the Organizers were employed by 50 labs (78 %) in the case of dithiocarbamates; 16 labs (29 %) in the case of glyphosate; 7 labs (24 %) in the case of ethephon; 9 labs (16 %) in the case of 2,4-D; 5 labs (10 %) in the case of haloxyfop and 3 labs (5 %) in the case of quinclorac. No such cases were noticed in the case of bromide.

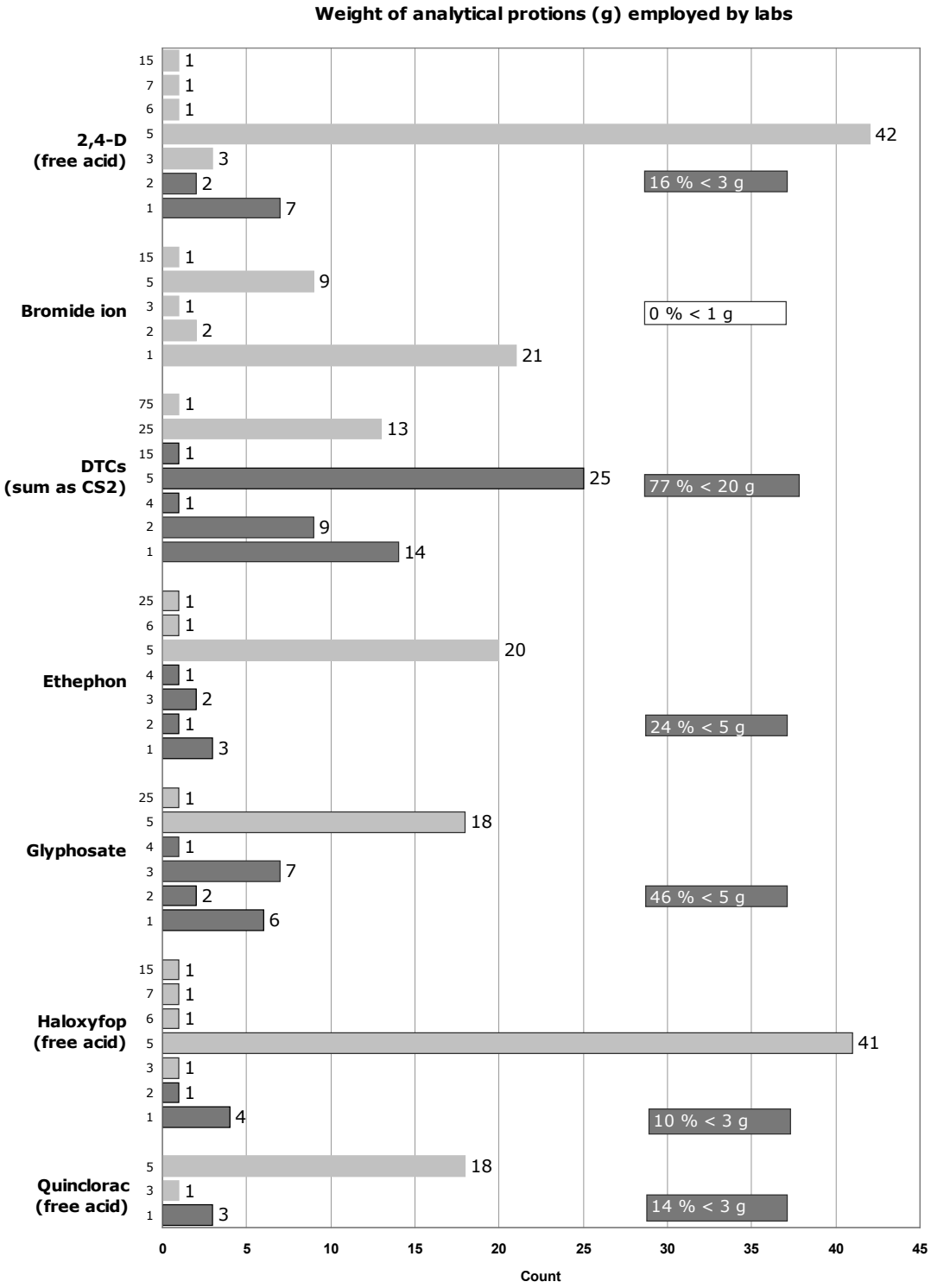

Figure 4-3: Size of analytical portions employed by labs

4.5.5 Reporting Limits (RLs)

The RLs submitted reported by the labs were in all but two cases lower than the assigned concentrations of the compounds in the Test Material (**Figure 4-4**). These two cases concerned the same laboratory that reported RLs of 2 mg/kg for glyphosate and ethephon.

In the majority of the cases the laboratories were also able to reach the required MRRLs. The MRRLs were not met by 12 labs (45 %) in the case of ethephon (MRRL = 0.02 mg/kg); by 9 labs (26 %) in the case of glyphosate (MRRL = 0.05 mg/kg); by 9 labs (14 %) in the case of dithiocarbamates (MRRL = 0.05 mg/kg); by 4 labs (18 %) in the case of quiclorac (MRRL = 0.02 mg/kg); by 4 labs (8 %) in the case of haloxyfop (MRRL = 0.02 mg/kg); by 3 labs (5 %) in the case of 2,4-D (MRRL = 0.02 mg/kg) and by 3 labs (9 %) in the case of bromide (MRRL = 5 mg/kg). In all other cases the RLs reported by the labs were lower than the Assigned Values.

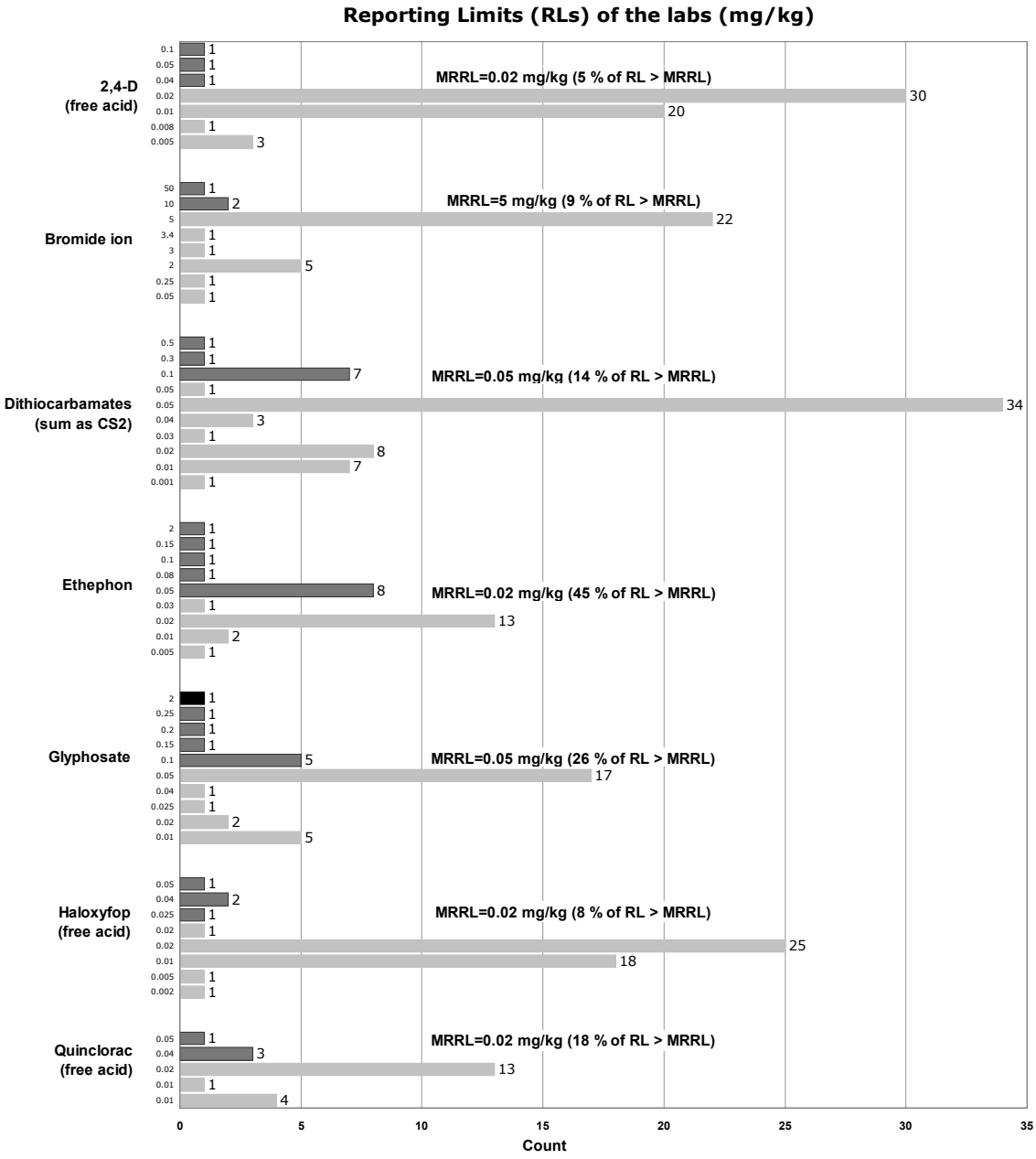

Figure 4-4: Labs' Reporting Limits and comparison with the MRRLs defined by the Organizers

4.5.6 Calibration approaches

Matrix-matched calibrations were employed in 69 % of the cases (including 11 % of the cases where a standard additions approaches were used). In 31 % of the cases solvent-based calibration solutions were employed by the participants. Among the 30 cases where standard additions approaches were employed 24 concerned standard additions to sample portions (where recovery correction is included) and 6 to aliqots of sample extracts.

Furthermore, 90 % of the reported results were generated using multi-level calibrations (including the cases where a standard additions approaches were used).

4.5.7 Recovery correction

As shown in **Table 4-14** recovery correction was applied in 23 % of all cases (68 results). In most cases recovery was corrected through the whole procedure, i.e. standard additions approach to sample portions (27 reported cases = 9 % overall); the use of isotopically labelled ISTDs (24 reported cases = 8 %); or a combination of both (3 cases = 1 %). In 14 cases recovery correction was accomplished using a recovery figure with the respective recovery experiments being conducted in all cases within the same batch using the blank material provided by the Organizers. **Table 4-15** shows detailed information concerning the cases where a recovery factor was used to correct the results. In 9 of these 14 cases, the recovery figures employed were below 70 %. Although 10 of the 14 recovery figures were derived from just 1 or 2 replicate experiments, in all cases recovery correction shifted results closer to the Assigned Value with the overall average of absolute z-scores (AAZ) of these 14 labs, impressively declining from 2.08 to 1.06. In 6 cases the non-corrected results would have been classified worse than the corrected ones (5× "questionable" and 1× "questionable" instead of "acceptable"). **Figure 4-5** shows the distribution of the overall recovery figures reported by the labs. 88 % of the reported recoveries were between 70 and 120 % and 10 % below.

Table 4-14: Overview concerning recovery correction applied by labs on their submitted results

Question: Are results recovery corrected?		2,4-D (free acid)	Bromide ion	Dithiocarbamates	Ethephon	Glyphosate	Haloxyfop (free acid)	Quinclorac (free acid)	Sum
Yes		**9**	**2**	**9**	**13**	**20**	**60**	**7**	**68 (23 %)**
Yes, automatically…	…via isotope-labelled ISTD				9	15			**24 (8 %)**
	…via standard additions	6	2	2	3	2	5	4	**24 (8 %)**
	…via combination of isotope-labelled ISTD and standard additions				1	2			**3 (1 %)**
Yes, using the submitted recov. figure		3		4	2	1	1	3	**14 (5 %)**
No		48	32	58	13	14	44	14	**223 (77 %)**
No data			1	1		1			**3 (1 %)**

Table 4-15: Compilation of results where recovery correction using a recovery figure was applied

Pesticide	LabCode	Submitted Recovery figure[%]	Recovery replicates considered	Submitted result [mg/kg]	z-score derived from submitted result	z-scores (if non-corrected results were used)*
2.4-D (free acid)	47	33	1	0.195	-1.10	-3.04
	21	33.8	1	0.311	0.62	-2.44
	145	85	5	0.1	-2.51	-2.74
Dithiocarbamates (as CS_2)	41	59	1	0.313	-1.92	-2.77
	103	62.1	3	0.639	0.24	-1.37
	74	75.5	2	0.55	-0.35	-1.25
	100	86.6	2	0.436	-1.11	-1.50
Ethephon	9	82	1	0.23	-0.09	-0.79
	6	74	3	0.103	-2.25	-2.70
Glyphosate	6	60	3	0.179	-1.56	-2.54
Haloxyfop (free acid)	21	33.6	1	0.172	1.55	-2.14
Quinclorac (free acid)	47	37	1	0.216	-0.76	-2.80
	90	51	2	0.298	0.46	-1.72
	141	61	2	0.291	0.36	-1.34
Overall	**11 labs**	**14 cases**	1 repl. (6×) 2 repl. (4×) 3 repl. (3×) 5 repl. (1×)		**AAZ = 1.06** 12× Acceptable 2× Questionable	**AAZ = 2,08** 6× Acceptable 7× Questionable 1× Unacceptable

* Calculated using the current Assigned Values

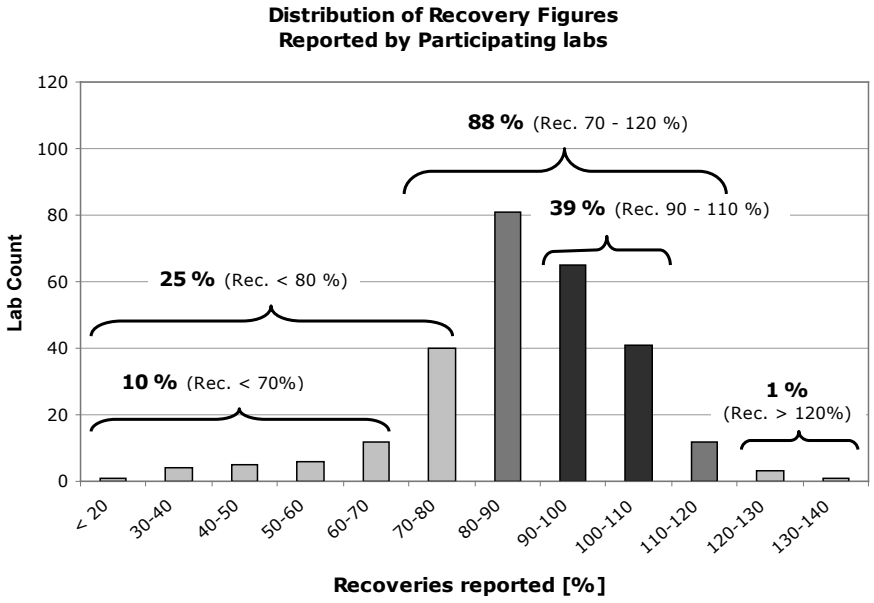

Figure 4-5: Distribution of recovery figures reported by labs

4.6 Summary, conclusions and prospects for the SRM pesticides

The EUPT-SRM6 was the 6th scheduled EUPT focusing on compounds requiring the use of 'single' residue methods and the 3rd organized collaboratively by the EURL-SRM and the EURL-CF.

In total 88 laboratories registered for the EUPT-SRM6 and 79, representing 27 EU and EFTA coutries and 2 Third Countries submitted results. Compared to previous EUPTs organized by the EURL-SRM the participation clearly increased (**Table 4-16**). In the previous two EUPT-SRMs focusing on cereals (EUPT-SRM2 in 2007 and -SRM4 in 2009) the laboratories submitting results were 30 from 18 countries (16 EU-MSs) and 48 from 25 countries (23 EU-MSs) respectively. The number of participants analyzing for 2,4-D (free acid), ethephon and glyphosate has increased from 31, 7 and 9 in EUPT-SRM4 to 57, 28 and 34 in EUPT-SRM6, respectively. A positive trend was noticed not only in the quantity of participants and submitted results, but also in the quality of the results as reflected by the increased percentage of acceptable z-scores (**Table 4-16**) as well as the average of absolute z-scores (AAZ) of all results submitted, which declined to 0.83 from 1.04 in EUPT-SRM2 and 0.98 in EUPT-SRM4.

This positive trend is surely based upon many factors such as the increased use of LC-MS/MS instrumentation by the laboratories, the implementation of simple methodologies including those developed and distributed by the EURL-SRM, as well as the strengthening of the network of official laboratories within the EU and the information flow within it. Another important factor contributing to this positive trend lies in the fact that participation in the EUPTs became compulsory for official laboratories within the EU from 2009 and onwards. Neverthless, it should be noted, that the increased participation in the EUPT-SRM6 was partly due to the inclusion of dithiocarbamates in the scope, which are routinely analysed by the vast majority of laboratories. This analysis can be performed by non-specific spectrophotometric methods that are available for decades and doesn't require sophisticated and expensive LC-MS/MS or even GC technology.

EU-member states from which no laboratory participated in EUPT-SRM6 were Romania and Malta. Malta subcontracted two laboratories, based in Italy and Germany to analyse official samples. None of them participated in the SRM part of this PT. However, Malta has apointed a UK-laboratory, not analysing official samples, as proxy-NRL. The EU-member states where NRL-SRMs did not submit any results were Romania, Poland and France. The latter had not officially appointed any NRL-SRM at the time the PT was undertaken. The current Polish NRL-SRM is planed to be replaced by another lab, which did participate in the exercise.

Table 4-16: Comparison of EUPT-SRMs focusing on cereal and feedingstuffs

	EUPT-SRM2 (2007)	EUPT-SRM4 (2009)	EUPT-SRM6 (2011)
Type of Test Material	Wheat flour	Oat flour	Rice flour
Participants submitting results (EU/EFTA)	30	48	77
SRM pesticides in Target Pesticide List / in the Test Material	8 [1] / 5 [1]	21 [1] / 7 [1]	13 / 7
No. of results for SRM pesticides (without false positive)	73	138	291
Mean of results per lab	2.50	2.88	3.79
Average of absolute z-scores (AAZ)	1.04	0.98	0.83
Acceptable z-scores	86 %	88 %	91 %
Questionable z-scores	7 %	6 %	6 %
Unacceptable z-scores (therein false negatives [1])	8 % (1.3 %)	7 % (3.6 %)	4 % (1.7 %)
Number of false positives	1	0	0
Category A laboratories [2]	–	31 %	25 %
Qn-RSD (average)	25 %	27 %	23 %

1) including optional analytes
2) The criteria applied to define Category A and B in EUPT-SRM4 and -SRM6 were different.

The Target Pesticide List, distributed to the laboratories well in advance to the test, contained in total 13 SRM-compounds with 9 of them belonging to the EU co-ordinated control program. The test material itself contained 7 pesticides namely; 2,4-D, bromide ion, dithiocarbamates (thiram), ethephon, glyphosate, haloxyfop, and quinclorac. All pesticides contained in the sample were spiked by the Organizer.

For each laboratory/pesticide combination, z-scores based on the FFP-RSD of 25 % were calculated and classified into "acceptable", "questionable" and "unacceptable" according to the rules in the General Protocol. Overall, the quality of the results was good with 51 out of 58 laboratories (89 %) reporting results within the acceptable z-score-range for 2,4-D, 34 out of 34 (100 %) for bromide ion, 57 out of 65 (89 %) for dithioscarbamates, 26 out of 30 (90 %) for ethephone, 48 out of 52 (94 %) for haloxyfop, and 20 out of 24 (87 %) for quinclorac. For glyphosate, however, only 28 out of 36 laboratories (80 %) achieved acceptable z-scores.

The robust standard deviation (Qn-RSD), reflecting the result-distribution, was also calculated for each pesticide. Qn-RSD-levels were very satisfactory for 2,4-D (22.1 %), bromide ion (8.6 %), dithiocarbamates (24.2 %), haloxyfop (17.7 %), and quinclorac (19.4 %). For ethephon and glyphosate, where bimodal distributions were noticed, the Qn-RSDs were 29.7 % and 40.6 %, respectively. This bimodality in the case of glyphosate and ethephon could be traced back to the use, or non-use, of isotope-labelled ISTDs, with the laboratories not using the isotope-labelled ISTDs reporting tentatively underestimating results. The Organizers thus strongly recommend the use of isotopically labelled internal ISTDs when analyzing for these compounds. Nevertheless, the EUPT-Panel decided to still consider the entire population of results for the determination of the median that were used as the Assigned Values.

False negative results concerned dithiocarbamates (1×), ethephon (1×), haloxyfop (1×), quinclorac (1×) and glyphosate (1×). In the latter case the result was reported as < RL but it was still judged as a false negative result following the rules in the General Protocol.

Laboratories were classified based on their scope according to the criteria in the General Protocol with laboratories that have targeted at least 6 of the 7 present pesticides being classified into Category A. In total 19 laboratories (24.7 %) were classified into Category A. The other 58 laboratories were included in Category B.

The 77 EU labs that finally participated in this EUPT represent only 43 % of all 181 labs that were obligated to participate in this exercise based on their function (NRL-SRM) or their scope (routinely analyzing for pesticide residues in cereals and feedingstuff). This figure needs to be further increased in the future. Among the most frequent reasons given by labs to explain their non-participation were that "the pesticides in the SRM target list are out of the lab's scope" and that "there is a shortage of instruments and staff". To encourage laboratories to further increase their scope and decrease their reporting levels the EUPT-Scientific Committee strongly recommends laboratories to equip themselves with LC-MS/MS, as most of the SRM pesticides can only be analysed, with the efficiency required for routine analyses, by utilising liquid chromatographic techniques. The EURL-SRM is pleased to assist the labs via bilateral discussions, exercises, workshops and training. The goal is that laboratories continue to increase their scope of analytes in order to be able to fully enforce EU legislation and to improve their overall performance, both in terms of correctly detecting the pesticides present in the samples, as well as being able to accurately determine the residue levels. To promote the expansion of the scope of official labs by SRM Analytes, the EURL-SRM will further continue developing, validating and distributing simple-to-use, fast and cheap methodologies for compounds not amenable to multiresidue methods. In future PTs, the selection of pesticides will continue to focus on those included in the scope of the EU co-ordinated control programmes as well as on additional pesticides of high relevance.

The Organizers emphasize that any laboratories that received questionable or unacceptable z-scores in this PT should aim to find the reasons for this underperformance. 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 of poor performance could not be traced by the laboratories. The most prominent among the clarified sources of errors were false concentration of standard solutions due to degradation or incorrect dilution as well as calculation errors.

NRL-SRMs will receive, upon request, the results as well as the explanations of non-participation or poor performance of all OfLs within their network and are expected to work towards addressing any sources of underperformance. NRLs or countries subcontracting official analyses and the conduction of EUPTs to other labs are urged to regularly check their performance and to take actions where necessary.

5. ACKNOWLEDGEMENTS

The Organisers wishes to thank the members of the Scientific Committee (Quality Control Group and Advisory Group) for their valuable advice.

6. REFERENCES

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[2] 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.

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

[4] Thompson M. Ellison S.L.R. and Wood R., The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories (IUPAC Technical Report). Pure Appl. Chem., Vol.78, No. 1, pp. 145 – 196, 2006

7. APPENDICES

Appendix 1 List of Laboratories registered to participate in the EUPT-C5/SRM6

(a): participating labs of EU and EFTA member states

Country (Location)	Analyzed on behalf of	Institution	City	NRL*-CF	NRL*-SRM	Reported results	
						C5	SRM6
Austria	Austria	Austrian Agency for Health and Food Safety - Competence Center for Residues of Plant Protection Products	Innsbruck		x	Yes	Yes
Austria	Austria	Austrian Agency for Health and Food Safety, Competence Center for Residue Analysis	Vienna	x		Yes	No
Belgium	Belgium	Scientific Institute of Public Health	Brussels	x	x	Yes	Yes
Belgium	Belgium	Laboratorium voor Onderzoek Van levensmiddelen en Aanverwante Produkten	Geel			Yes	Yes
Belgium	Belgium	Fytolab	Gent - Zwijnaarde			Yes	Yes
Belgium	Belgium	Federal Laboratory for Safety of Food Chain, Tervuren	Tervuren			Yes	No
Bulgaria	Bulgaria	Plant Protection Institute, Department on Toxicology	Kostinbrod	x		Yes	No
Bulgaria	Bulgaria	Laboratory Analysis Directorate, Regional Inspectorate for Public Health Protection and Control - Pleven	Pleven			Yes	No
Bulgaria	Bulgaria	Central Laboratory for Chemical Testing and Control, Sofia	Sofia		x	Yes	Yes
Cyprus	Cyprus	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	x	x	Yes	Yes
Cyprus	Cyprus	Animal Feeds and Feed Additives Laboratory of the Analytical Laboratories of the Department of Agriculture	Nicosia	x		Yes	No
Czech Republic	Czech Republic	Central Institute for Supervising and Testing in Agriculture	Brno	x		Yes	No
Czech Republic	Czech Republic	Institute of Chemical Technology, Prague	Praha			Yes	Yes
Czech Republic	Czech Republic	Czech Agriculture and Food Inspection Authority	Praha	x	x	Yes	Yes
Denmark	Denmark	Danish Plant Directorate, Laboratory for Feed and Fertilizers	Lyngby	x		Yes	Yes
Denmark	Denmark	Danish Veterinary and Food Administration, Region East	Ringsted			Yes	Yes
Estonia	Estonia	Agricultural Research Centre, Lab for Residues and Contaminants	Saku	x		Yes	Yes
Estonia	Estonia	Health Board - Tartu Laboratory	Tartu		x	Yes	Yes
Finland	Finland	Customs Laboratory	Espoo	x	x	Yes	Yes
Finland	Finland	Finnish Food Safety Authority	Helsinki			Yes	Yes
France	France	CERECO SUD	GARONS			Yes	Yes
France	France	Laboratoire Départemental d`Analyses de la Sarthe, Département de Chimie	Le Mans			Yes	No
France	France	ANSES Laboratoire de Maisons-Alfort	MAISONS-ALFORT		x	No	No
France	France	Service Commun des Laboratoires / Laboratoire Ile de France - Massy	Massy	x		Yes	No
France	France	Laboratoire Départemental d`Analyses des LANDES	Mont de Marsan			Yes	No
France	France	Service Commun des Laboratoires / Laboratoire de Montpellier	Montpellier			Yes	Yes

* only for EU-member states

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

Country (Location)	Analyzed on behalf of	Institution	City	NRL*-CF	NRL*-SRM	Reported results	
						C5	SRM6
France	France	Analysis Center Mediterranean Pyrenees	Perpignan			Yes	No
France	France	Laboratoire Départemental d`Analyses des Cotes d`Armor	Ploufragan			Yes	Yes
France	France	Service Commun des Laboratoires / Laboratoire de Rennes	Rennes			Yes	No
France	France	Laboratoire Départemental d`Analyses du MORBIHAN	Saint Ave			Yes	Yes
Germany	Germany	Federal Office of Consumer Protection and Food Safety, NRL for Pesticide Residues	Berlin	x		Yes	Yes
Germany	Germany	CVUA Rheinland, Standort Bonn	Bonn			Yes	Yes
Germany	Germany	Chemisches und Lebensmitteluntersuchungsamt der Stadt Dortmund	Dortmund			Yes	Yes
Germany	Germany	Landesuntersuchungsanstalt für das Gesundheits- und Veterinärwesen Sachsen	Dresden			Yes	Yes
Germany	Germany	Bavarian Health and Food Safety Authority Office Erlangen	Erlangen			Yes	Yes
Germany	Germany	Arbeitsgemeinschaft Chemisches und Veterinäruntersuchungsamt Rhein-Ruhr-Wupper, Essen	Essen			Yes	Yes
Germany	Germany	Landesamt für Verbraucherschutz - Sachsen-Anhalt	Halle/Saale			Yes	Yes
Germany	Germany	Landesanstalt für Landwirtschaft, Forsten und Gartenbau, Halle	Halle/Saale			Yes	No
Germany	Germany	Institut für Hygiene und Umwelt	Hamburg			Yes	Yes
Germany	Malta	Eurofins, Dr. Specht Laboratorien GmbH	Hamburg			Yes	No
Germany	Germany	Thuringian Institute of Agriculture	Jena			Yes	No
Germany	Germany	Landwirtschaftliche Technologiezentrum Augustenberg	Karlsruhe			Yes	Yes
Germany	Belgium	LUFA-ITL GmbH	Kiel			Yes	Yes
Germany	Germany	STAATLICHE BETRIEBSGESELLSCHAFT FÜR UMWELT UND LANDWIRTSCHAFT	Leipzig			Yes	Yes
Germany	Germany	Chemical and Veterinary Analytical Institute Muensterland-Emscher Lippe	Münster			Yes	Yes
Germany	Germany	State laboratory Schleswig-Holstein	Neumünster			Yes	Yes
Germany	Germany	Lower Saxony State Office for Consumer Protection and Food Safety, Food Institute Oldenburg	Oldenburg			Yes	Yes
Germany	Germany	Berlin-Brandenburg State Laboratory, Berlin	Potsdam			Yes	No
Germany	Germany	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei Mecklenburg-Vorpommern	Rostock			Yes	Yes
Germany	Germany	Landesuntersuchungsamt Institut für Lebensmittelchemie Speyer	Speyer			Yes	Yes
Germany	Germany	Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer	Speyer			Yes	Yes
Greece	Greece	General Chemical State Laboratory, D Division, Pesticide Residues Laboratory	Athens	x	X	Yes	Yes
Greece	Greece	Regional Center of Plant Protection and Quality Control of Piraeus, Pesticide Residues Laboratory	Athens			Yes	No
Greece	Greece	Regional Center of Plant Protection and Quality Control of Ioannina, Pesticide Residues Laboratory	Ioannina			Yes	No
Greece	Greece	Benaki Phytopathological Institute, Pesticide Residues Laboratory	Kifissia	x	X	Yes	Yes
Hungary	Hungary	Central Agricultural Office, Feed Investigation National Reference Laboratory	Budapest			No	No
Hungary	Hungary	Agricultural Office Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Hódmezovásárhely	Hódmezovásárhely			Yes	Yes
Hungary	Hungary	Agricultural Office Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Kaposvár	Kaposvár			Yes	Yes

* only for EU-member states

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

Country (Location)	Analyzed on behalf of	Institution	City	NRL*-CF	NRL*-SRM	Reported results	
						C5	SRM6
Hungary	Hungary	Agricultural Office Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Miskolc	Miskolc		x	Yes	Yes
Hungary	Hungary	Agricultural Office Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Szolnok	Szolnok			Yes	No
Hungary	Hungary	Agricultural Office Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Tanakajd	Tanakajd			Yes	No
Hungary	Hungary	Agricultural Office Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Velence	Velence	x		Yes	Yes
Ireland	Ireland	Pesticide Control Laboratory, Department of Agriculture, Fisheries and Food	Co. Kildare	x	x	Yes	Yes
Italy	Italy	ARPA TOSCANA Dipartimento di Arezzo	Arezzo			Yes	No
Italy	Malta	Laboratorio CEFIT	Avola - Siracusa			Yes	No
Italy	Italy	ARPA Puglia - Dipartimento di Bari	Bari			Yes	No
Italy	Italy	Laboratorio di Sanità Pubblica ASL BERGAMO	Beragmo			Yes	No
Italy	Italy	APPA Bolzano	Bolzano			Yes	Yes
Italy	Italy	Istituto Zooprofilattico Sperimentale Lombardia ed Emilia Romagna	Brescia			Yes	No
Italy	Italy	ARPA Ferrara Eccellenza Fitofarmaci	Ferrara			Yes	No
Italy	Italy	Centro di referenza nazionale per la sorveglianza ed il controllo degli alimenti per animali	Genova	x		Yes	No
Italy	Italy	ARPALAZIO SEZIONE P.LE DI LATINA - SERVIZIO LABORATORIO AMBIENTE E SALUTE, UNITA` DI CHIMICA INORGANICA	Latina			Yes	No
Italy	Italy	Istituto Zooprofilattico Sperimentale delle Venezie	Legnaro (Padova)			Yes	No
Italy	Italy	ARPAM Dipartimento di Macerata	Macerata			Yes	No
Italy	Italy	Istituto Zooprofilattico Sperimentale Umbria e Marche	Perugia			Yes	No
Italy	Italy	Environmental Regional Protection Agency - Laboratory of Pordenone	Pordenone			Yes	No
Italy	Italy	Istituto Zooprofilattico Sperimentale Lazio e Toscana	Roma			Yes	No
Italy	Italy	Istituto Superiore di Sanità	Roma		x	Yes	Yes
Italy	Italy	ARPA LAZIO Servizio Ambiente e Salute Sez. di Roma	Roma			Yes	Yes
Italy	Italy	Istituto Zooprofilattico Sperimentale Sardegna	Sassari			No	No
Italy	Italy	Istituto Zooprofilattico Sperimentale Abruzzo e Molise	Teramo			Yes	No
Italy	Italy	APPA Trento Settore Laboratorio e Controlli	Trento			Yes	No
Italy	Italy	ARPA VENETO DIP.REG.LAB. S.L. VERONA	Verona			Yes	Yes
Latvia	Latvia	Institute of Food Safety, Animal Health and Environment (BIOR) - Riga	Riga	x	x	Yes	Yes
Lithuania	Lithuania	National Food and Veterinary Risk Assessment Institute	Vilnius	x	x	Yes	Yes
Luxembourg	Luxembourg	National Health Laboratory Luxembourg (Food Laboratory)	Luxembourg	x	x	Yes	Yes
Netherlands	Netherlands	Food and Consumer Product Safety Authority Region Northwest, Pesticides & Mycotoxins Analysis Group	Amsterdam	x		Yes	Yes
Netherlands	Belgium	Grond-, Gewas- en Milieulaboratorium Zeeuws-Vlaanderen b.v.	Graauw			Yes	Yes

* only for EU-member states

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

Country (Location)	Analyzed on behalf of	Institution	City	NRL*-CF	NRL*-SRM	Reported results	
						C5	SRM6
Netherlands	Netherlands	RIKILT Institute of Food Safety (Natural Toxins & Pesticides)	Wageningen	x		Yes	Yes
Norway	Norway	Norwegian Institute for Agricultural and Environmental Research, Plant Health and Plant Protection Division, Pesticide Chemistry Section	Aas		x	Yes	Yes
Norway	Norway	National Institute of Nutrition and Seafood Research	Bergen			Yes	No
Poland	Poland	Institute of Plant Protection Pesticide Residue Laboratory, Bialystok	Bialystok			Yes	Yes
Poland	Poland	Zaklad Higieny Weterynaryjnej w Bialystoku	Bialystok			Yes	No
Poland	Poland	Zaklad Higieny Weterynaryjnej w Gdansku (Kartuska)	Gdansk			Yes	No
Poland	Poland	Zaklad Higieny Weterynaryjnej w Katowicach, Pracownia Badania Pasz	Katowice			Yes	No
Poland	Poland	Zaklad Higieny Weterynaryjnej w Opolu	Opole			Yes	No
Poland	Poland	Voievodship Sanitary - Epidemiological Station in Opole	Opole			Yes	Yes
Poland	Poland	Institute of Plant Protection, Department of Pesticide Residue Research - Poznan	Poznan	x		Yes	Yes
Poland	Poland	Provincial Veterinary Inspectorate Establishment of Veterinary Hygiene	Poznan			Yes	No
Poland	Poland	Institute of Plant Protection - National Research Institute, Regional Experimental Station in Rzeszo	Rzeszow			Yes	Yes
Poland	Poland	Institute of Horticulture, Food Safety Laboratory (Skierniewice)	Skierniewice			Yes	Yes
Poland	Poland	Institute of Plant Protection - National Research Institute, Branch Sosnicowice	Sosnicowice			Yes	Yes
Poland	Poland	Zaklad Higieny Weterynaryjnej w Szczecinie, Pracownia Analityki Chemicznej	Szczecin			Yes	No
Poland	Poland	Voievodship Sanitary - Epidemiological Station in Warszaw	Warszaw			Yes	Yes
Poland	Poland	Wojewodzki Inspektorat Weterynarii z/s w Siedlcach, Zaklad Higieny Weterynaryjnej w Warszawie	Warszawa			Yes	No
Poland	Poland	Regional Veterinary Laboratory Wroclaw	Wroclaw			Yes	No
Portugal	Portugal	Regional Laboratory of Veterinary and Food Safety - Madeira Island	Funchal - Madeira Island			Yes	Yes
Portugal	Portugal	INIA - Pesticides Residues Laboratory	Oeiras	x	x	Yes	Yes
Portugal	Portugal	Direcção Regional de Agricultura e Pescas do Norte- DEQAL	Senhora da Hora, Matosinhos			Yes	Yes
Romania	Romania	Central Laboratory for Pesticides Residues Control in Plants and Vegetable Products - Bucharest	Bucharest	x		Yes	No
Romania	Romania	Institute for Hygiene and Veterinary Public Health - Bucharest	Bucharest	x		Yes	No
Romania	Romania	Sanitary Veterinary and Food Safety Laboratory Bucharest	Bucharest			Yes	No
Romania	Romania	Sanitary Veterinary and Food Safety Directorate Cluj, Gas-Chromatography Laboratory	Cluj Napoca			Yes	No
Romania	Romania	Sanitary Veterinary and Food Safety Laboratory - IASI	Iasi			Yes	No
Slovakia	Slovakia	State Veterinary and Food Institute Bratislava	Bratislava	x	x	Yes	Yes
Slovakia	Slovakia	Public Health Authority of Slovak Republic	Bratislava			Yes	No
Slovenia	Slovenia	Institute of Public Health, Ljubljana	Ljubljana	x		Yes	Yes
Slovenia	Slovenia	Agricultural Institute of Slovenia, Central Laboratories	Ljubljana	x		Yes	Yes

* only for EU-member states

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

Country (Location)	Analyzed on behalf of	Institution	City	NRL*-CF	NRL*-SRM	Reported results	
						C5	SRM6
Slovenia	Slovenia	Institute of Public Health, Maribor	Maribor		x	Yes	Yes
Spain	Spain	Agricultural and Phytopathological Laboratory of Galicia	Abegondo. A Coruña			Yes	No
Spain	Spain	Laboratorio Agrario Regional de Castilla La Mancha	Albacete			Yes	No
Spain	Spain	Laboratorio Agrario Regional - Junta de Castilla y Leon	Burgos			Yes	Yes
Spain	Spain	Agrofood Laboratory of the Comunidad Valenciana	Burjassot-Valencia			Yes	Yes
Spain	Spain	Laboratori Agroalimentari de la Generalitat de Catalunya	Cabrils			Yes	No
Spain	Spain	Laboratorio de Producción y Sanidad Vegetal de Jaén	Jaen			Yes	Yes
Spain	Spain	Laboratorio Arbitral Agroalimentario, Madrid	Madrid		x	Yes	Yes
Spain	Spain	Laboratorio de Salud Pública Madrid Salud Ayuntamiento de Madrid	Madrid			Yes	No
Spain	Spain	National Centre for Food - Spain, Majadahonda	Majadahonda	x		Yes	No
Spain	Spain	Navarra de Servicios S.A.	Villava			Yes	No
Spain	Spain	Laboratorio Agroalimentario de Zaragoza	Zaragoza			Yes	Yes
Sweden	Sweden	Eurofins - Sweden, Lidköping	Lidköping			Yes	Yes
Sweden	Sweden	Chemistry Division 1, National Food Administration	Uppsala	x	x	Yes	Yes
Switzerland	Switzerland	Kantonales Laboratorium Zürich	Zürich			Yes	Yes
United Kingdom	United Kingdom	Agri-Food and Biosciences Institute	Belfast			Yes	No
United Kingdom	United Kingdom	Eurofins - United Kingdom, Wolverhampton	Wolverhampton			Yes	Yes
United Kingdom	United Kingdom	The Food and Environment Research Agency - York	York	x	x	Yes	Yes

* only for EU-member states

(b): participating labs from EU candidate state and the 3rd countries

Country	Institution	City	Reported results	
			C5	SRM
Brazil	Laboratorio Nacional Agropecuário - LANGRO/MG, Ministério da Agriultura	Pedro Leopoldo/MG	Yes	No
Brazil	Bioensaios Análises e Consultoria Ambiental Ltda, Ministry of Agriculture of Brazil	Viamão	Yes	No
Brazil	Laboratório Nacional Agropecuário em Goiás, Ministry of Agriculture of Brazil	Goiânia - Goiás	No	No
Burkina Faso	Laboratoire natiolan de santé publique	Ouagadougou	Yes	No
Croatia	Institute of public health Split	Split	Yes	No
Croatia	Faculty of Food Technology and Biotechnology - Food Control Center	Zagreb	Yes	No
Costa Rica	Centro de Investigación en Contaminación Ambiental (CICA)	Montes de Oca, San José	Yes	No
Egypt	Central Lab of Residue Analysis of Pesticides and Heavy Metals in Foods	Giza	Yes	Yes
India	Multi Laboratory , SGS India Pvt.Ltd.	Chennai, Tamilnadu State	Yes	No
India	Export Inspection Agency-Chennai (Laboratory), Ministry of Commerce & Industry, Govt. of India	Chennai	Yes	No
India	Export Inspection Council of India, Ministry of Commerce & Industry	Mumbai	Yes	No
India	Geo-Chem Laboratories (P) Ltd.	Mumbai, Maharashtra	Yes	No
Malaysia	National Public Health Laboratory	Selangor	Yes	No
Philippines	Jefcor Laboratories, Inc.	Dasmarinas, Cavite	Yes	No
Republic of KOREA	Experiment & Research Institute , National Agricultural Products Quality Management Service (NAQS)	Seoul	Yes	No
Singapore	Veterinary Public Health Laboratory	Singapore	Yes	No
Taiwan	Division of Taiwan Agricultural Chemicals and Toxic Substances Research Institute, Council of Agriculture (TACTRI/COA)	Taichung	Yes	Yes
Thailand	Central laboratory (Thailand) Co., Ltd.	Bangkok	Yes	No
Thailand	Central laboratory (Thailand) Co., Ltd.	Chiangmai	Yes	No
Thailand	Department of Medical Sciences, Bureau of Quality and Safety of Food	Nonthaburi	Yes	No
Turkey	MSM Food Control Laboratory	Mersin	Yes	No
Uruguay	Facultad de Quimica, Farmacognosia y Productos Naturales	Montevideo	Yes	No

Appendix 2 Data of homogeneity test – MRM pesticides

Azoxystrobin [mg/kg]			Carbendazim [mg/kg]			Chlorpyrifos [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
5	0.144	0.136	5	0.124	0.104	5	0.266	0.253
30	0.136	0.142	30	0.095	0.122	30	0.239	0.256
34	0.157	0.135	34	0.117	0.108	34	0.310	0.249
54	0.134	0.141	54	0.117	0.128	54	0.243	0.245
126	0.132	0.147	126	0.125	0.110	126	0.239	0.293
130	0.145	0.144	130	0.126	0.134	130	0.264	0.260
178	0.162	0.152	178	0.126	0.094	178	0.291	0.288
189	0.139	0.150	189	0.115	0.115	189	0.253	0.290
243	0.142	0.160	243	0.127	0.139	243	0.243	0.294
261	0.154	0.143	261	0.153	0.141	261	0.295	0.250
282	0.152	0.135	282	0.129	0.134	282	0.262	0.243

Deltamethrin [mg/kg]			Difenoconazole [mg/kg]			Diflubenzuron [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
5	0.139	0.183	5	0.103	0.107	5	0.133	0.156
30	0.140	0.156	30	0.099	0.104	30	0.125	0.161
34	0.195	0.126	34	0.112	0.101	34	0.154	0.132
54	0.093	0.208	54	0.096	0.103	54	0.140	0.127
126	0.211	0.213	126	0.093	0.100	126	0.158	0.130
130	0.168	0.179	130	0.102	0.113	130	0.142	0.156
178	0.145	0.170	178	0.109	0.117	178	0.164	0.143
189	0.196	0.166	189	0.100	0.105	189	0.149	0.141
243	0.128	0.153	243	0.109	0.113	243	0.137	0.166
261	0.169	0.203	261	0.101	0.115	261	0.160	0.166
282	0.188	0.166	282	0.113	0.100	282	0.154	0.135

Epoxyconazole [mg/kg]			Fipronil [mg/kg]			Isoprothiolane [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
5	0.107	0.101	5	0.172	0.174	5	0.191	0.167
30	0.103	0.113	30	0.170	0.170	30	0.159	0.181
34	0.123	0.106	34	0.184	0.171	34	0.155	0.161
54	0.106	0.100	54	0.169	0.174	54	0.196	0.189
126	0.095	0.115	126	0.160	0.182	126	0.187	0.176
130	0.105	0.107	130	0.168	0.174	130	0.182	0.209
178	0.120	0.116	178	0.181	0.183	178	0.191	0.156
189	0.103	0.120	189	0.169	0.178	189	0.185	0.176
243	0.111	0.121	243	0.166	0.186	243	0.180	0.207
261	0.120	0.111	261	0.177	0.173	261	0.195	0.204
282	0.116	0.107	282	0.174	0.160	282	0.196	0.204

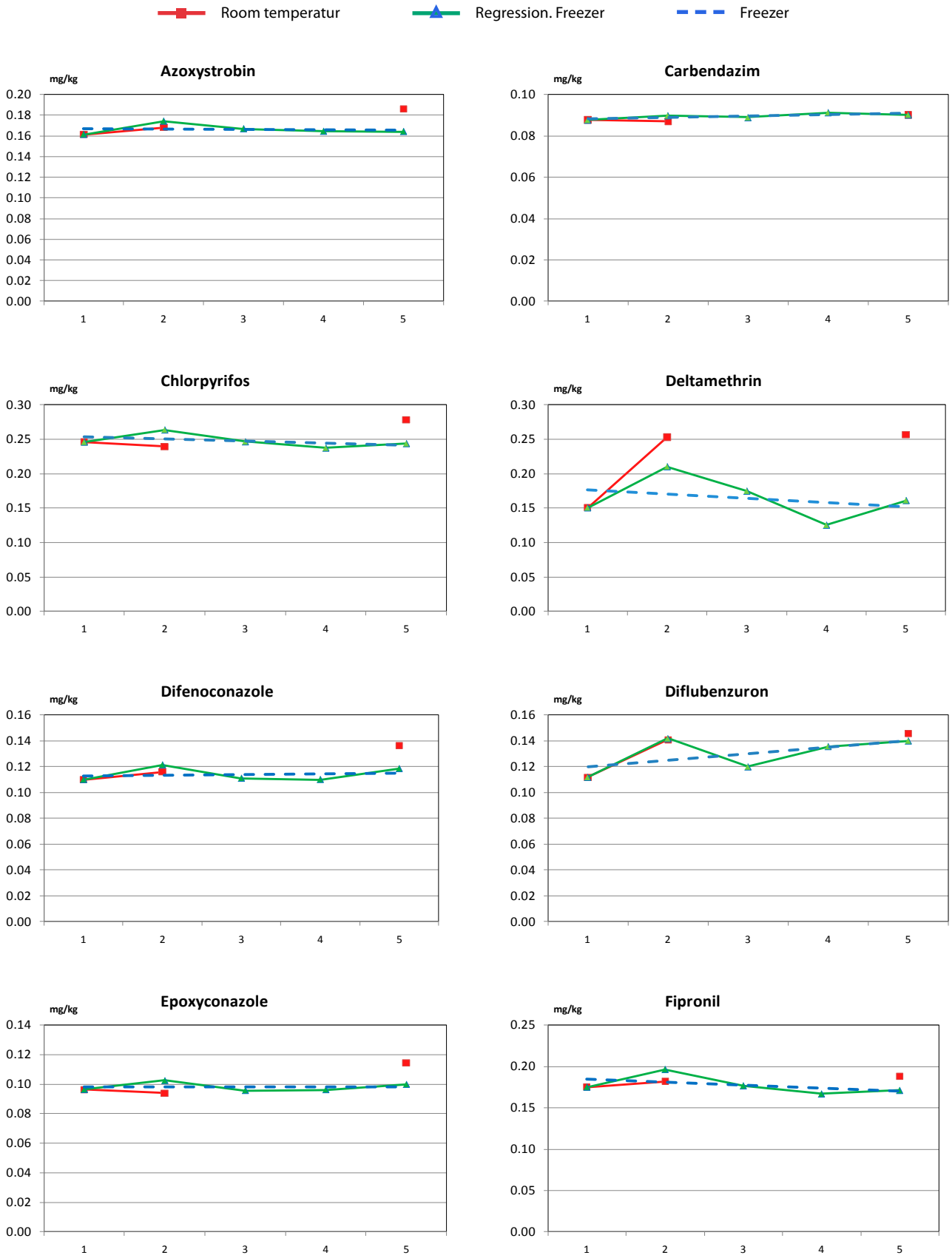
Appendix 2 (cont.) Data of homogeneity test – MRM pesticides

Kresoxim-methhyl [mg/kg]			Pirimiphos-methyl [mg/kg]			Propiconazole [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
5	0.185	0.181	5	0.089	0.085	5	0.613	0.605
30	0.171	0.174	30	0.080	0.081	30	0.596	0.655
34	0.199	0.167	34	0.086	0.077	34	0.672	0.625
54	0.163	0.179	54	0.073	0.087	54	0.641	0.582
126	0.168	0.196	126	0.082	0.083	126	0.568	0.614
130	0.188	0.179	130	0.087	0.088	130	0.603	0.628
178	0.208	0.204	178	0.092	0.096	178	0.653	0.614
189	0.175	0.201	189	0.084	0.086	189	0.598	0.655
243	0.174	0.199	243	0.083	0.085	243	0.641	0.661
261	0.198	0.174	261	0.081	0.084	261	0.640	0.639
282	0.191	0.164	282	0.087	0.081	282	0.614	0.624

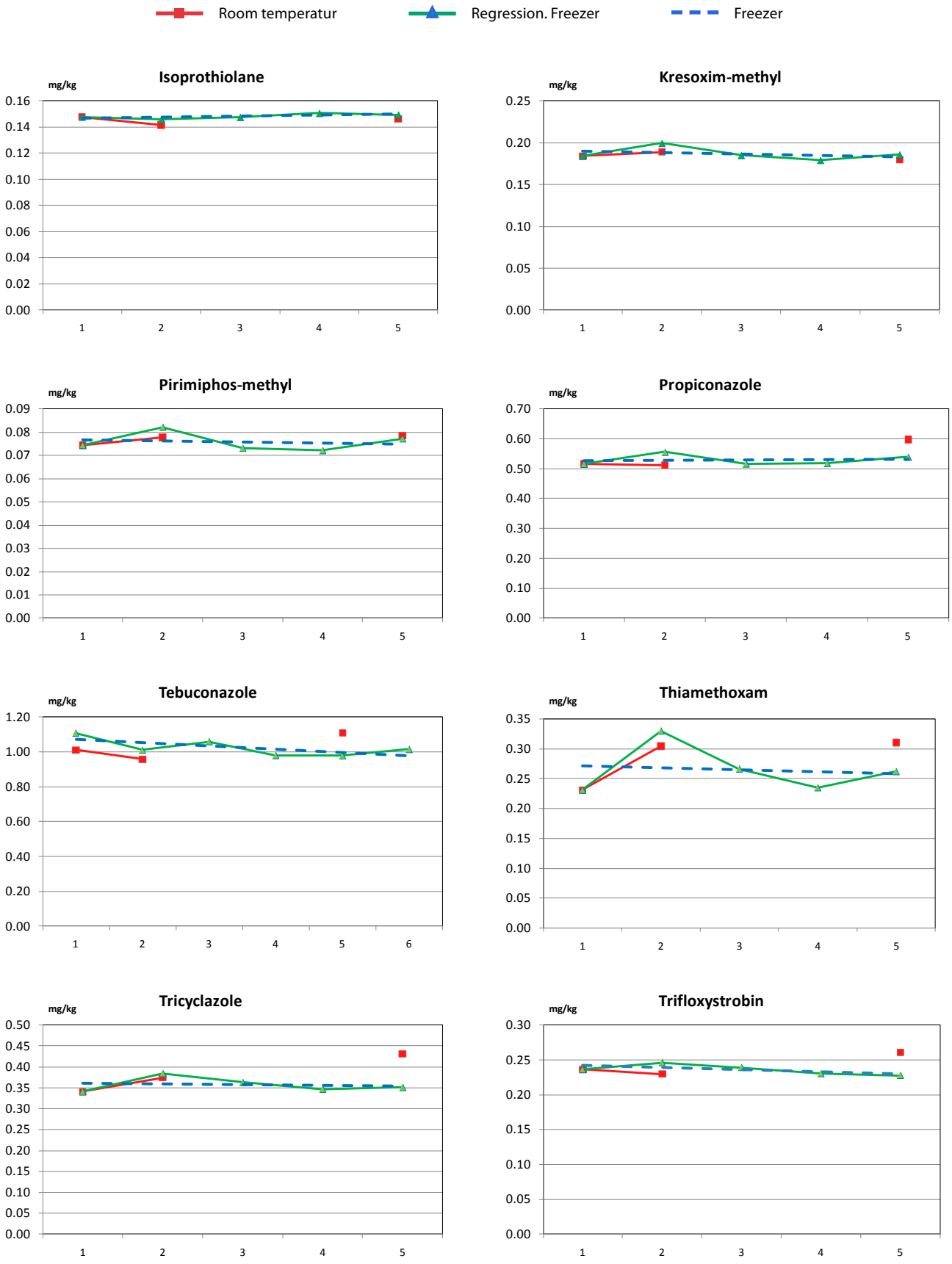
Tebuconazole [mg/kg]			Thiamethoxam [mg/kg]			Tricyclazole [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
5	1.166	1.076	5	0.182	0.155	5	0.317	0.373
30	1.039	1.202	30	0.131	0.135	30	0.323	0.401
34	1.373	1.093	34	0.226	0.132	34	0.343	0.359
54	1.154	1.008	54	0.121	0.156	54	0.381	0.342
126	0.996	1.337	126	0.141	0.235	126	0.354	0.325
130	1.120	1.069	130	0.189	0.148	130	0.332	0.402
178	1.304	1.149	178	0.227	0.233	178	0.385	0.352
189	1.054	1.382	189	0.150	0.227	189	0.346	0.356
243	1.101	1.361	243	0.131	0.209	243	0.354	0.376
261	1.389	1.088	261	0.218	0.154	261	0.388	0.410
282	1.167	1.068	282	0.200	0.125	282	0.503	0.440

Trifloxystrobin [mg/kg]		
Sample No.	Portion 1	Portion 2
5	0.246	0.239
30	0.230	0.238
34	0.277	0.231
54	0.235	0.236
126	0.220	0.275
130	0.250	0.239
178	0.264	0.253
189	0.237	0.267
243	0.227	0.272
261	0.268	0.238
282	0.251	0.224

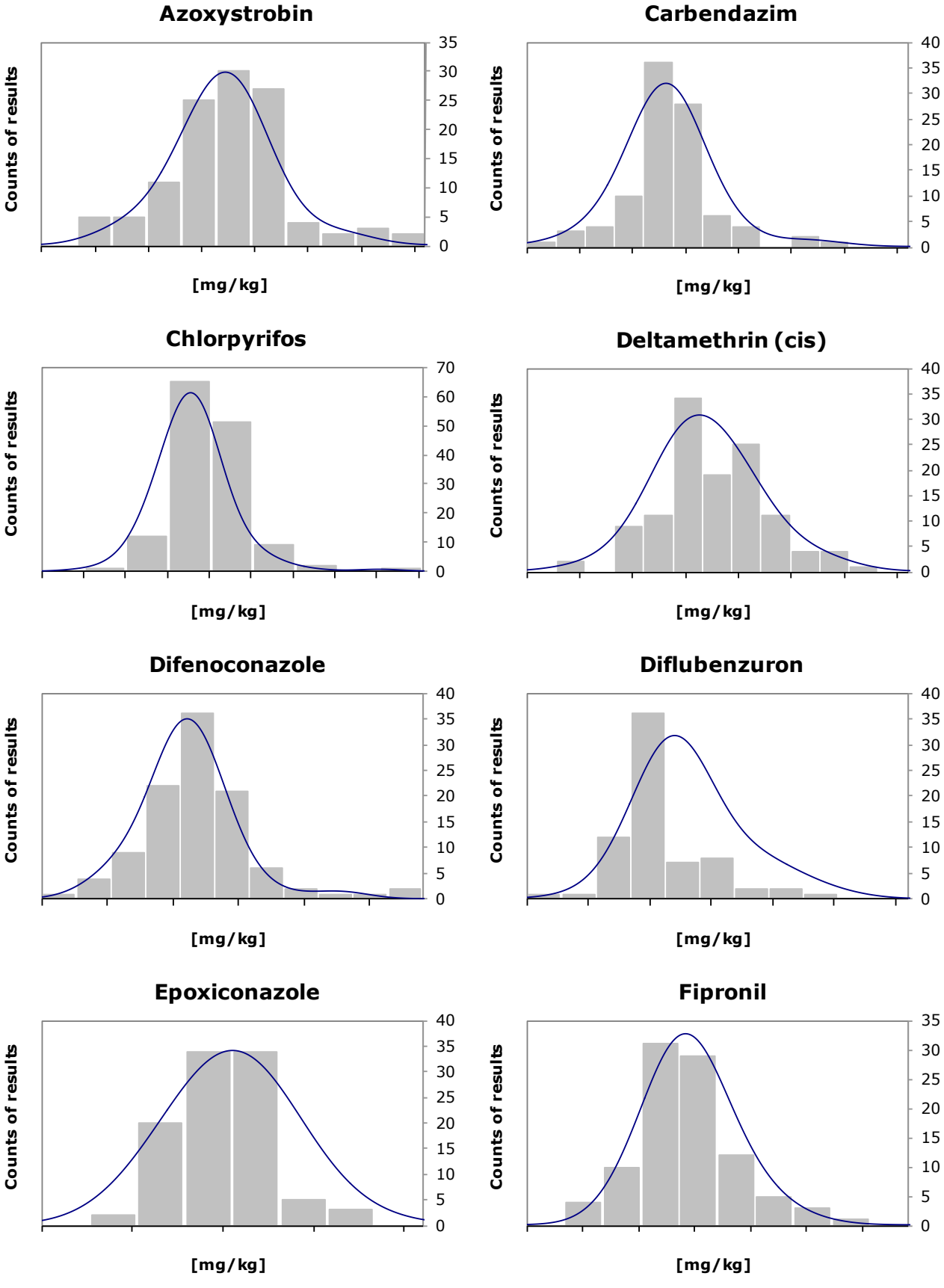
Appendix 3 Data of stability tests – MRM pesticides



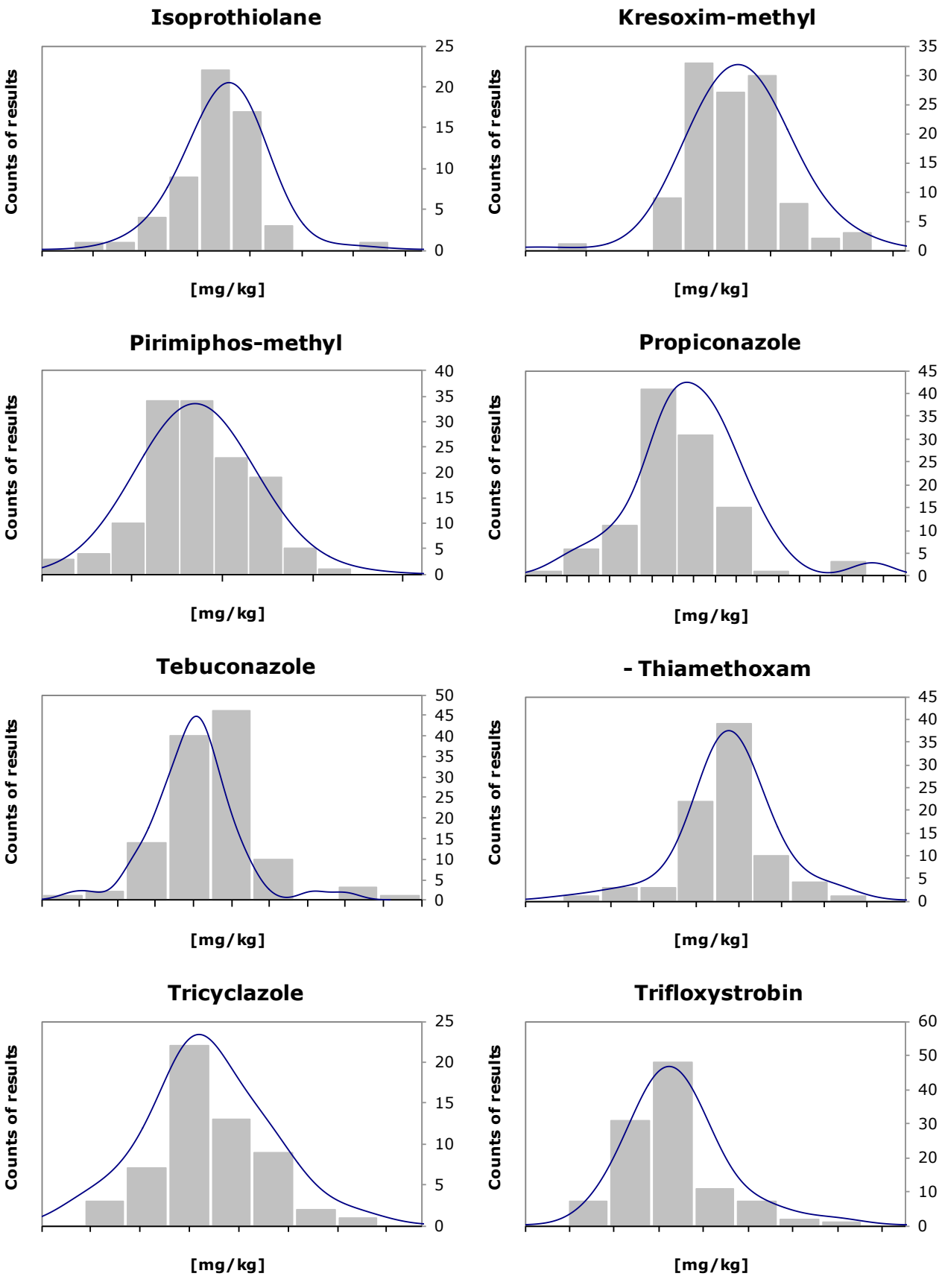
Appendix 3 (cont.) Data of stability tests – MRM pesticides



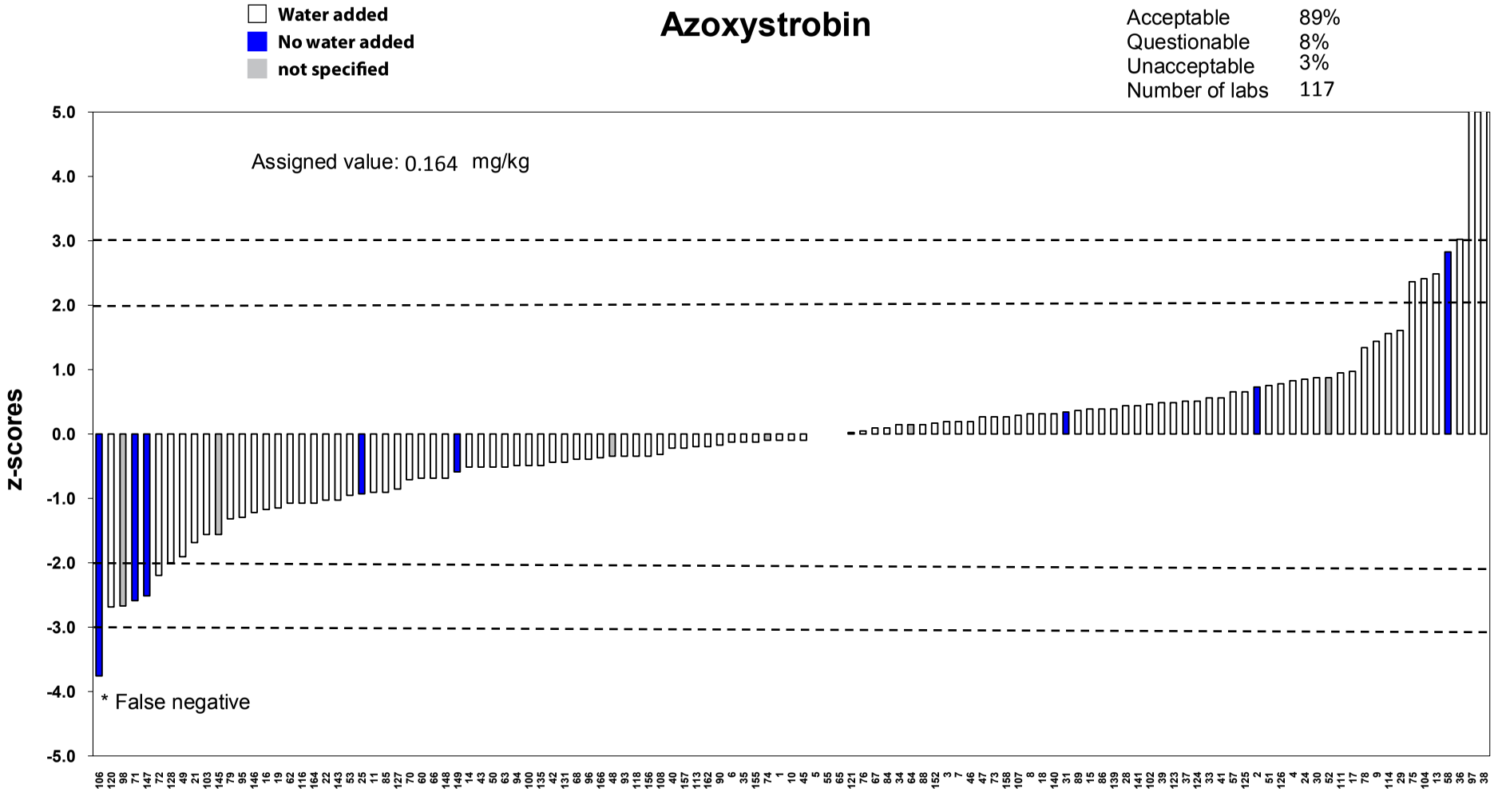
Appendix 4 Result distribution histograms – MRM pesticides



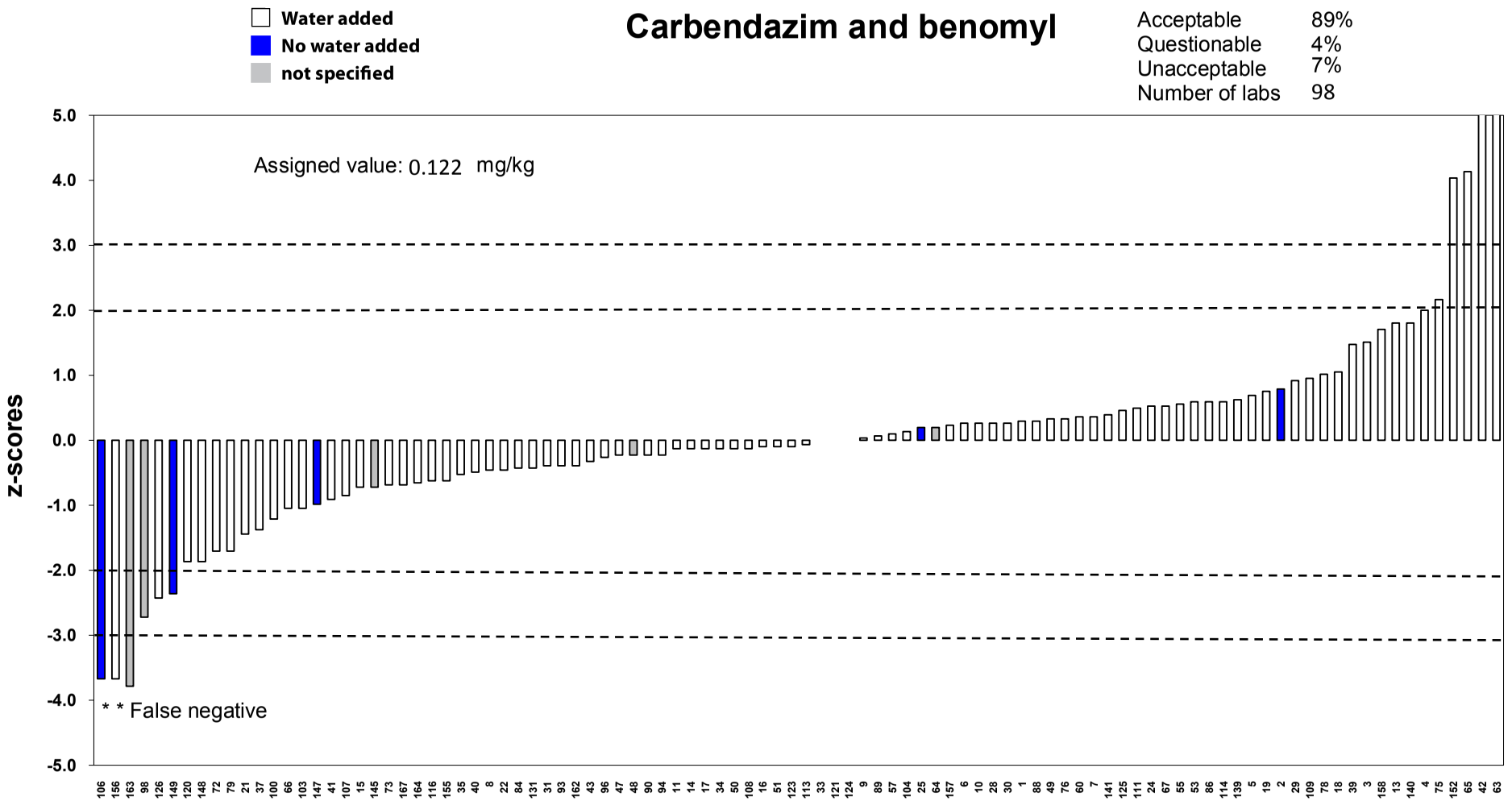
Appendix 4 (cont.) Histograms of residue data – MRM pesticides



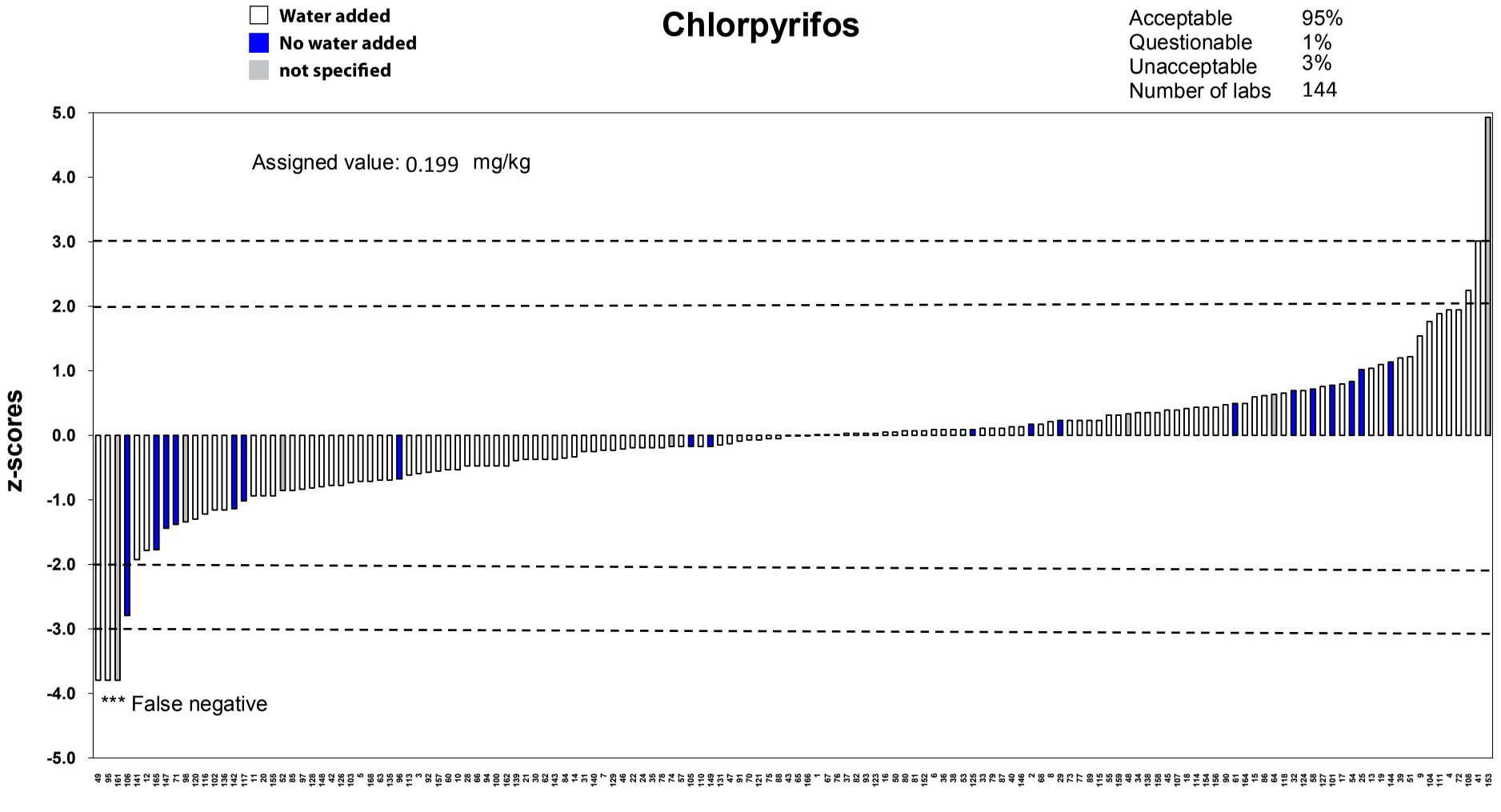
Appendix 5 Graphic presentation of z-Scores – MRM pesticides



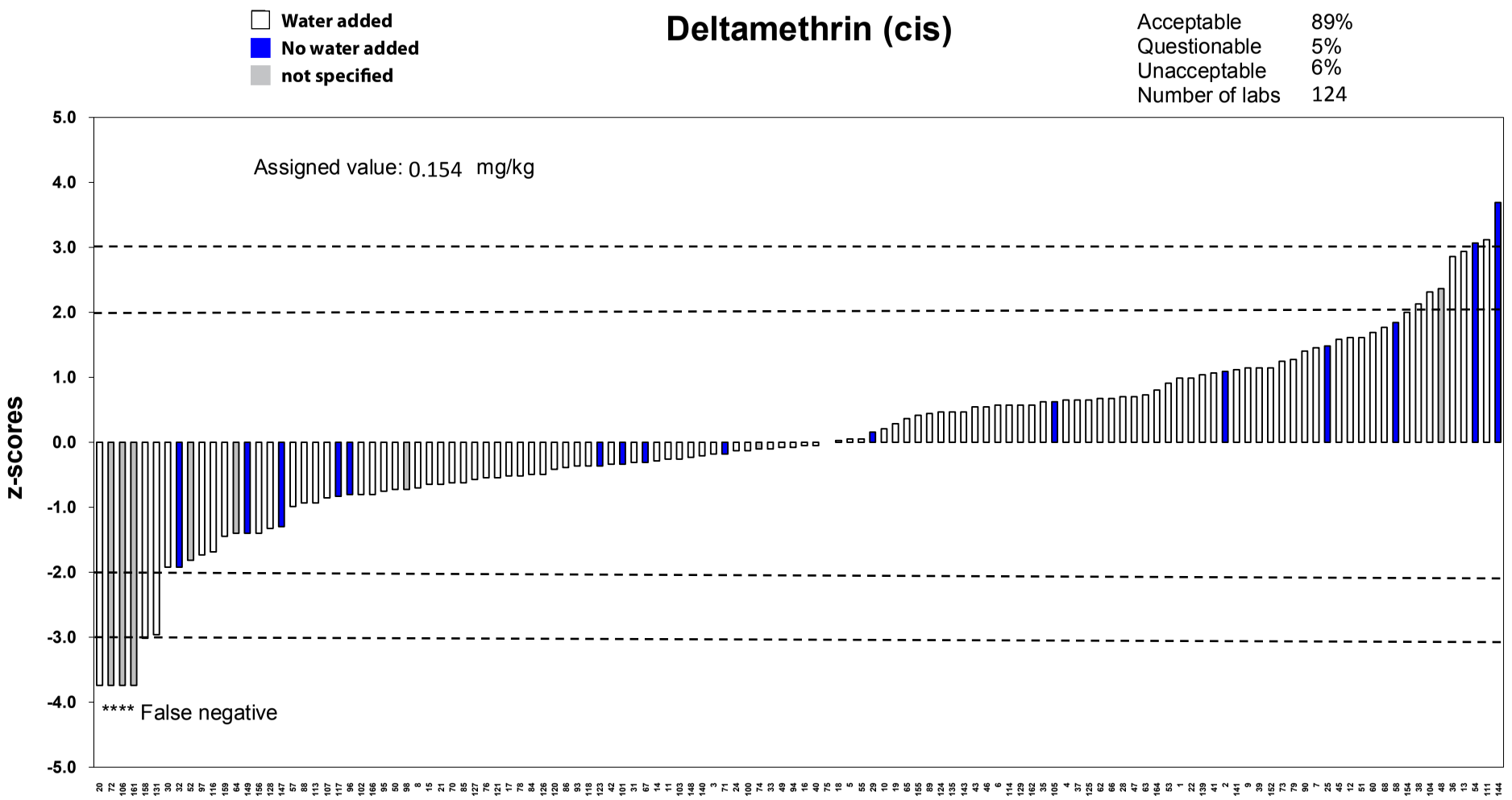
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



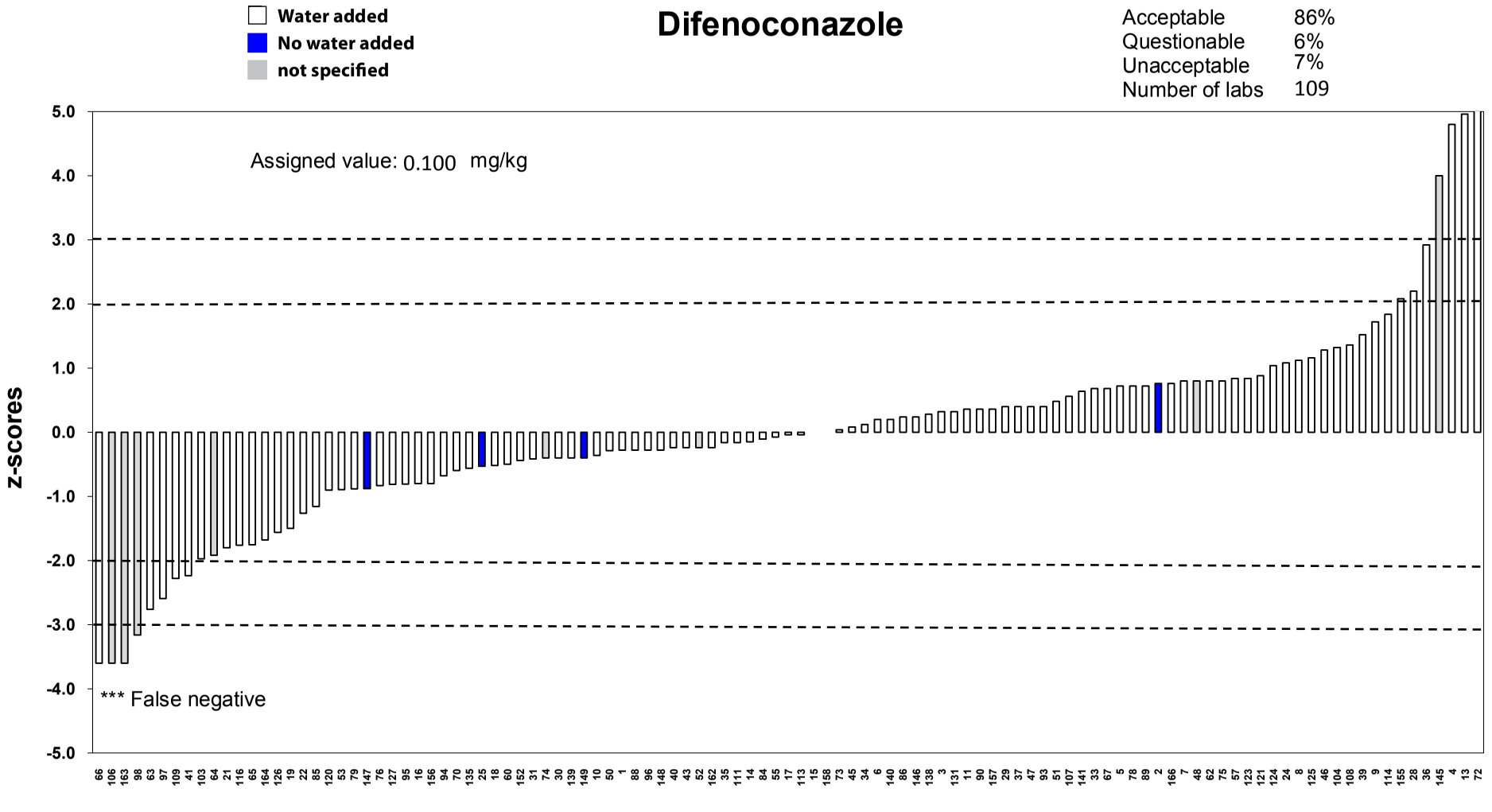
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



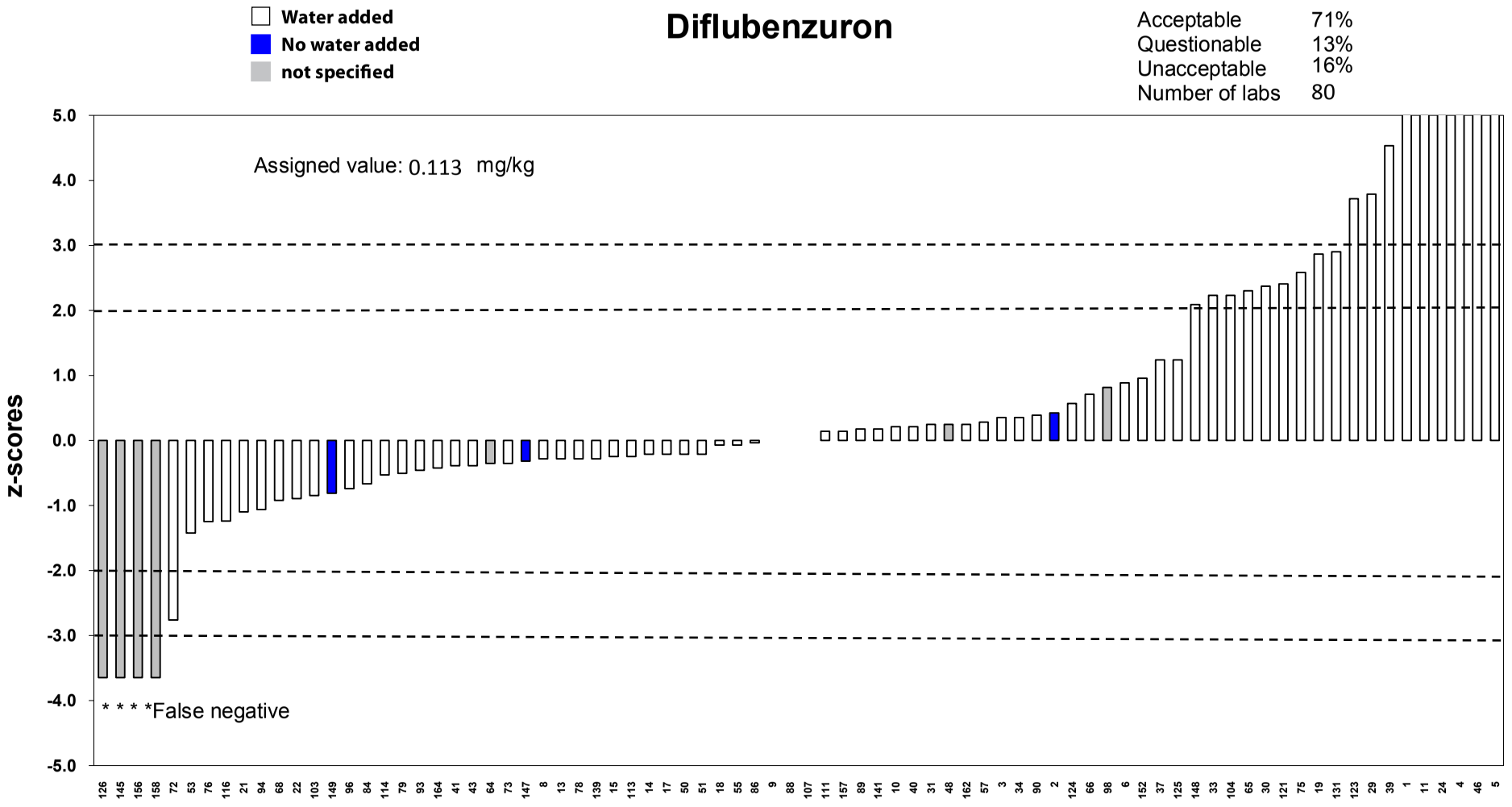
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



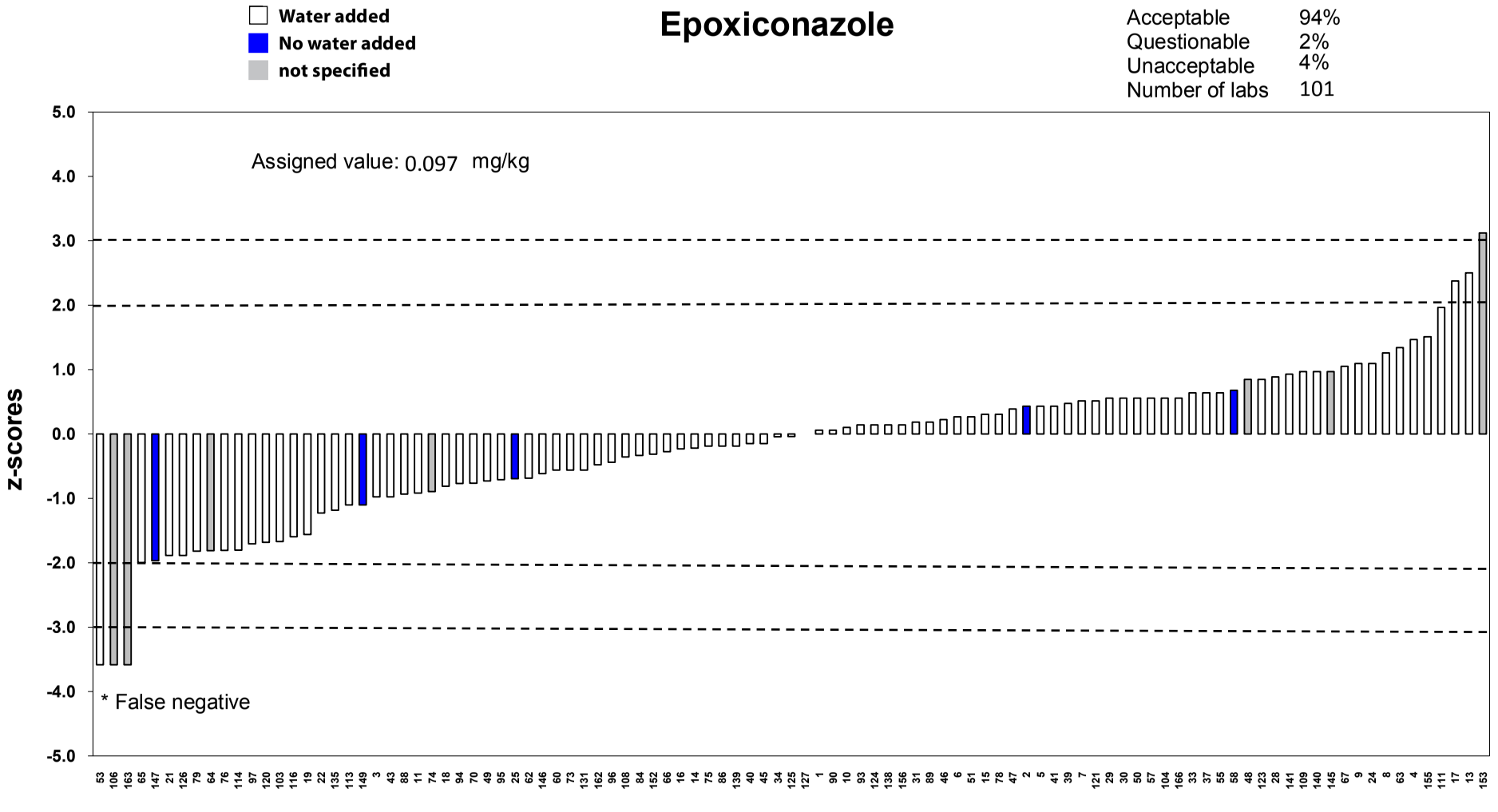
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



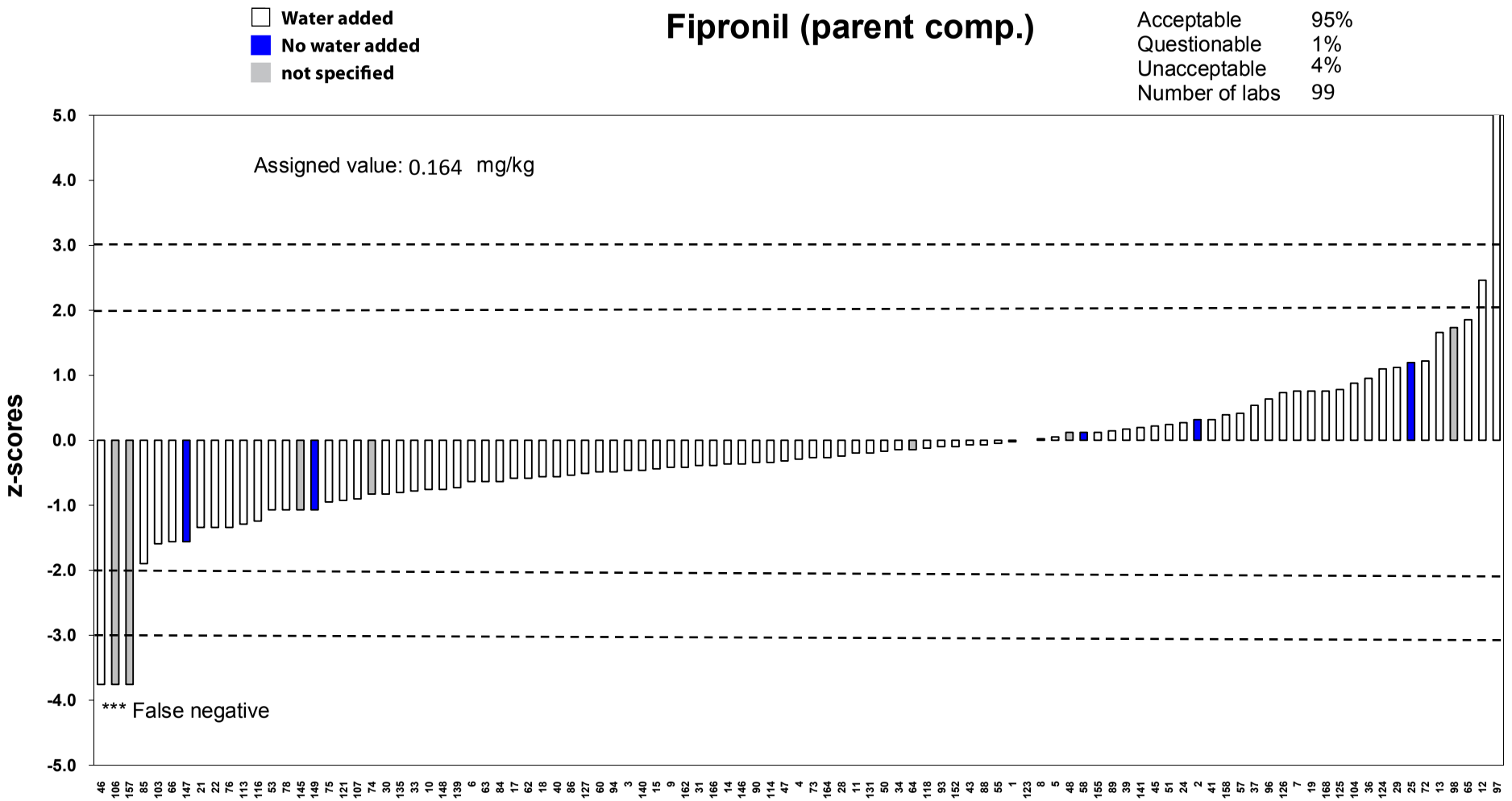
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



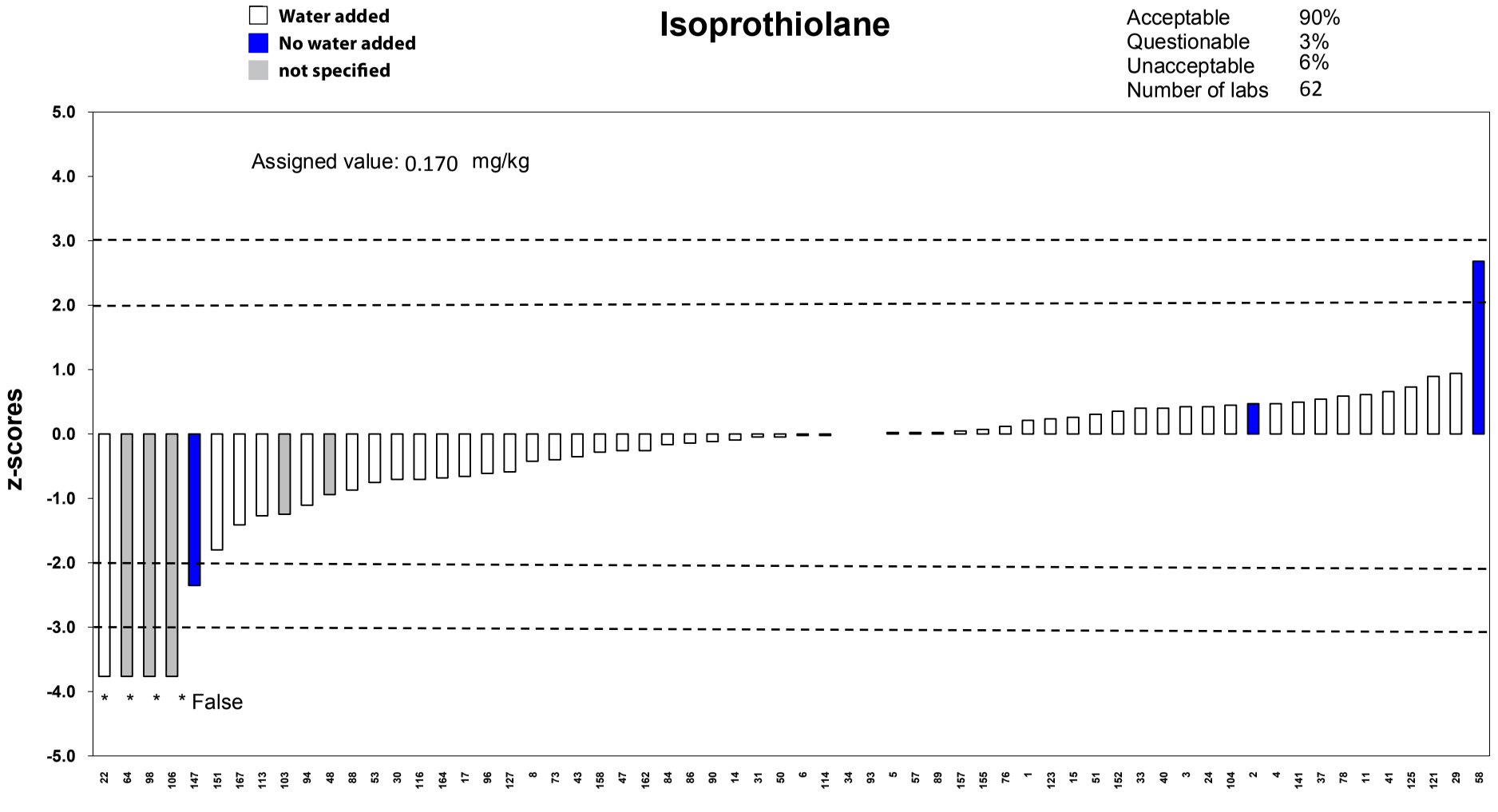
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



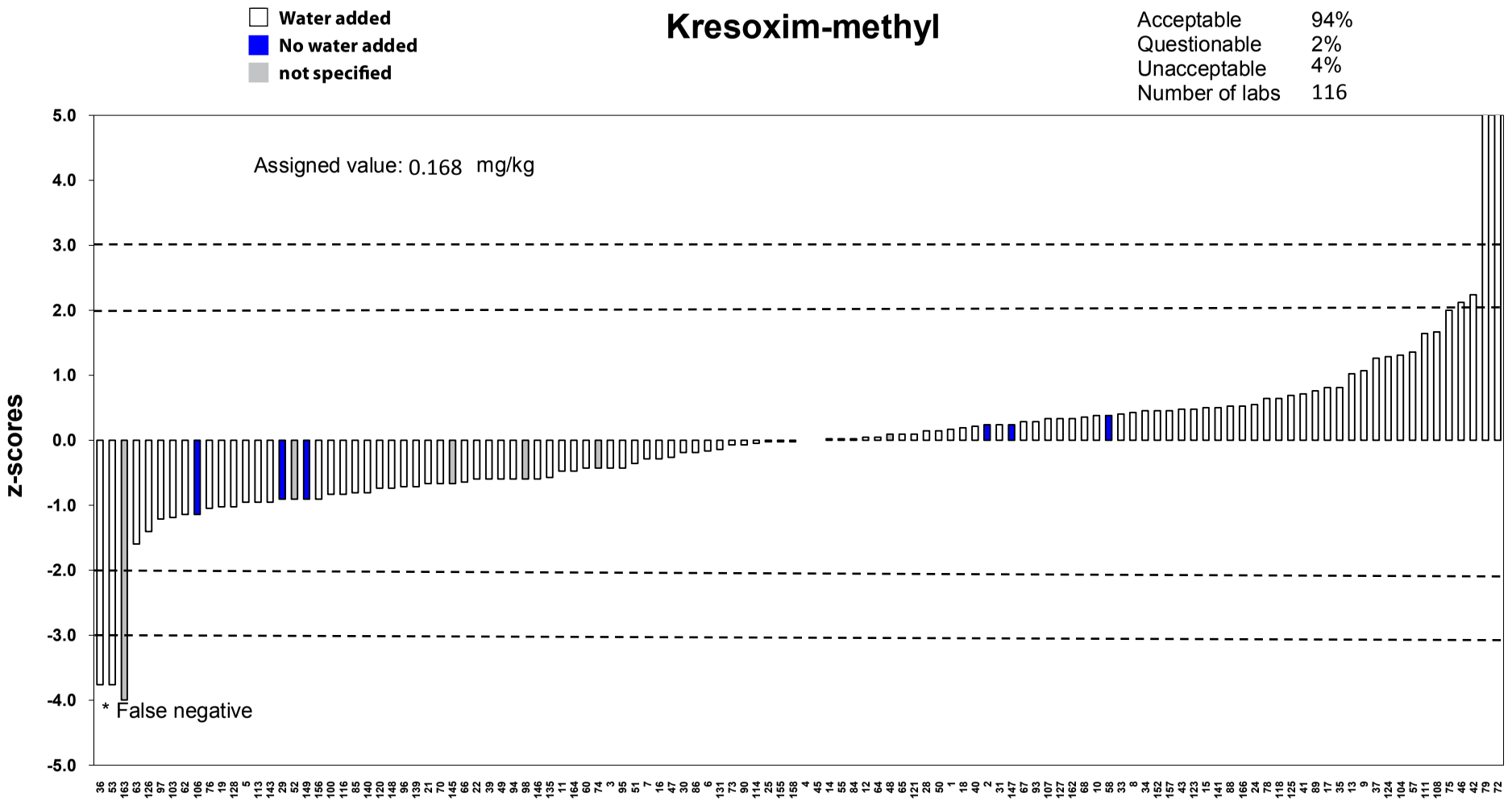
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



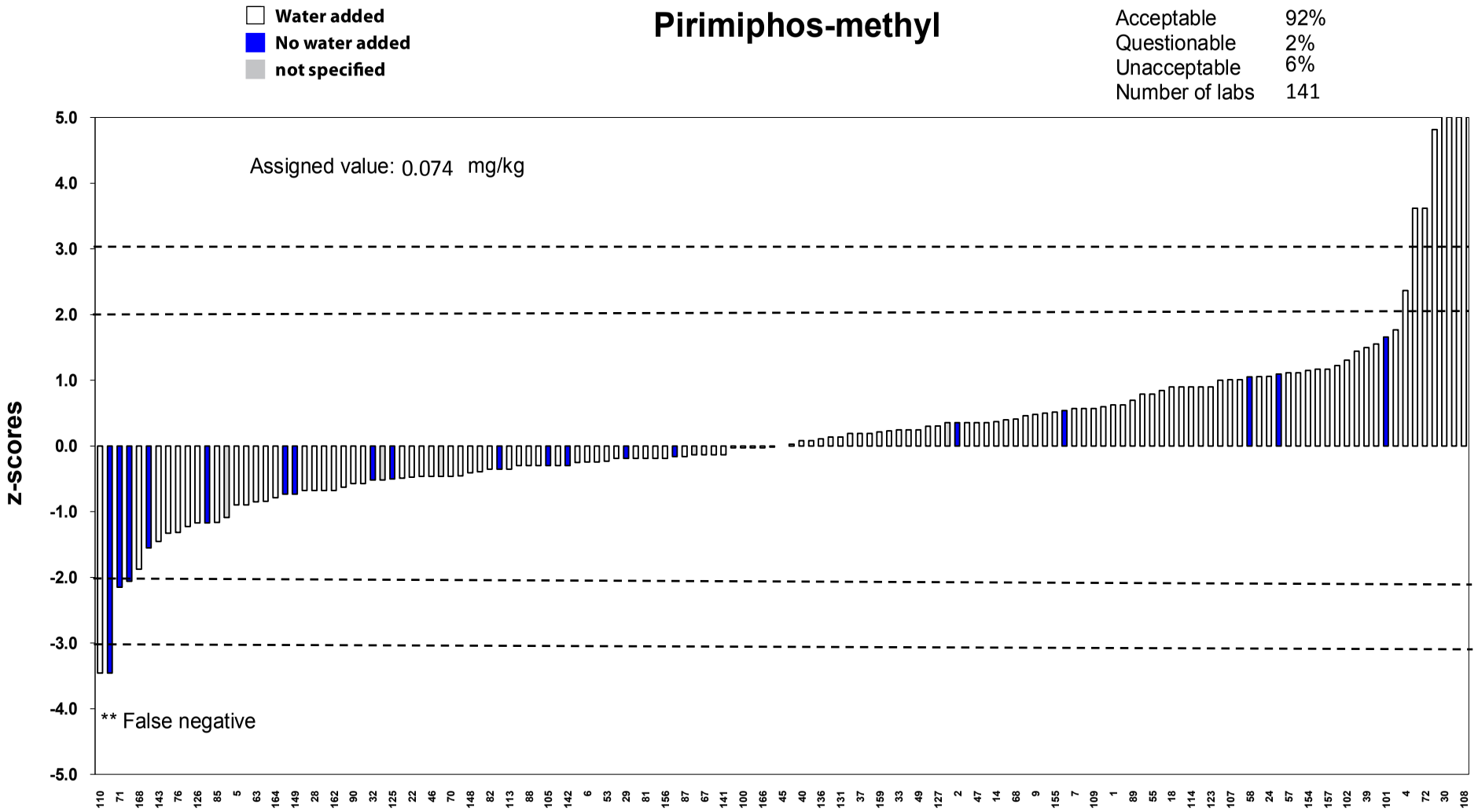
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



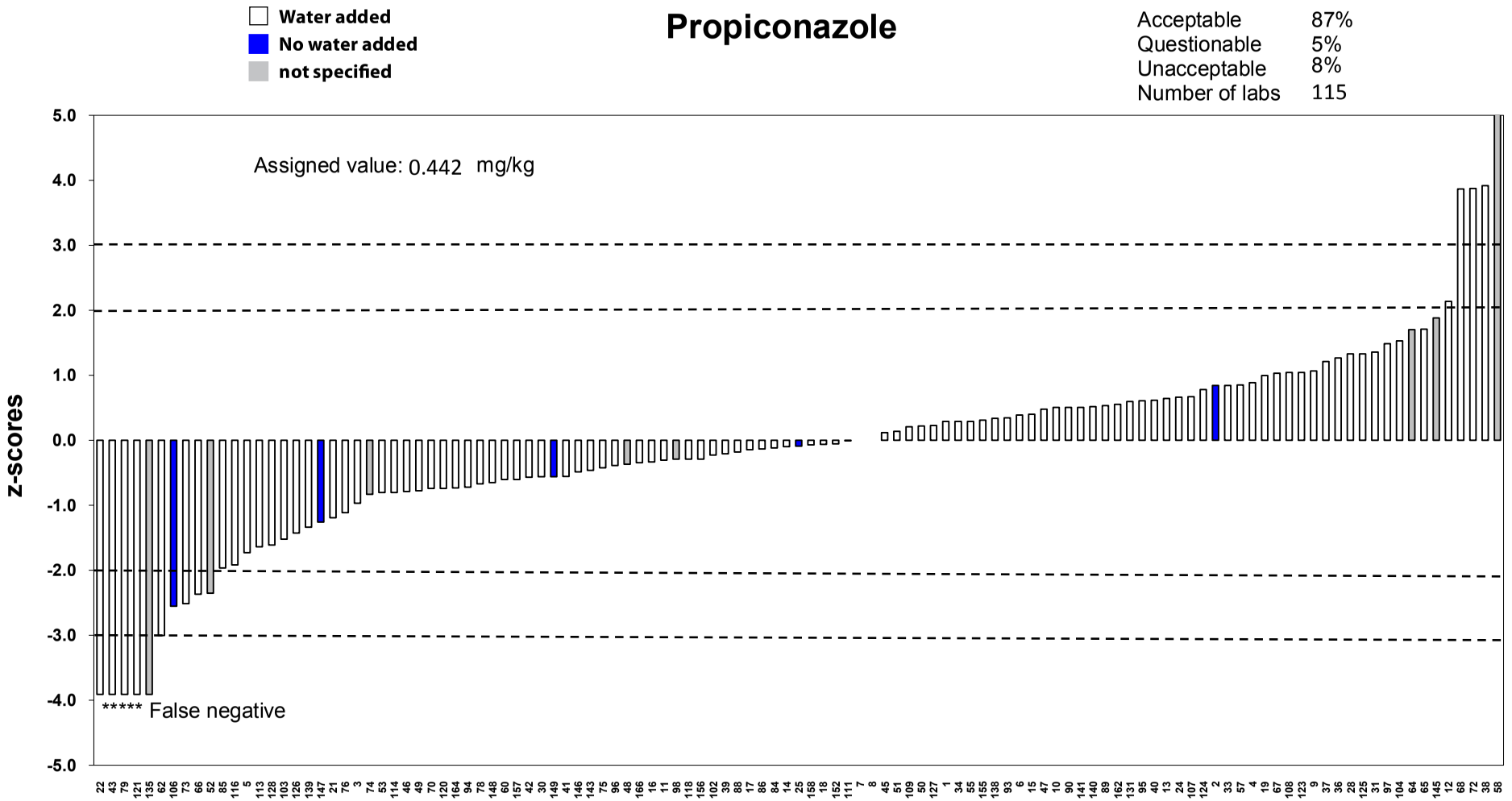
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



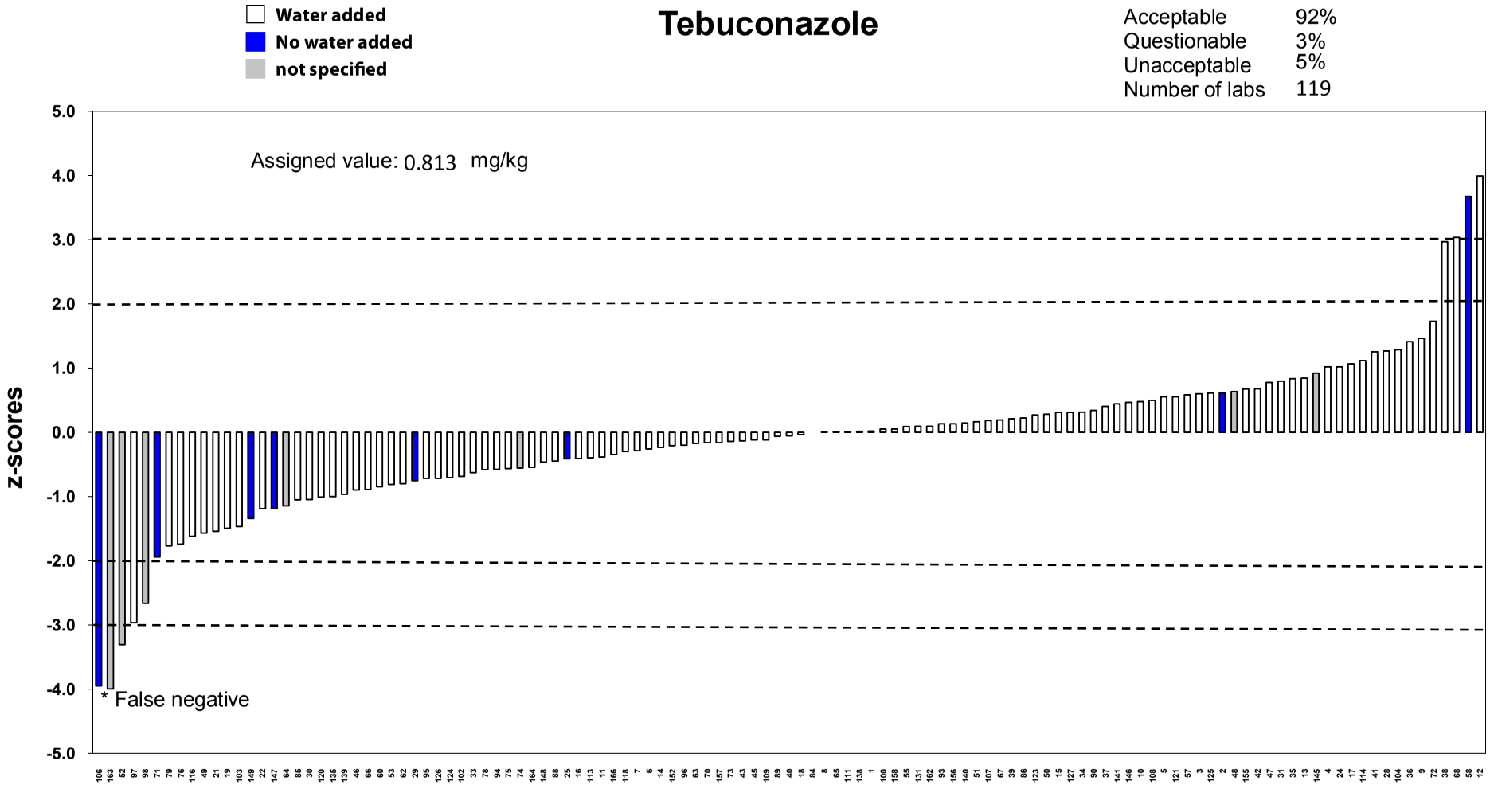
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



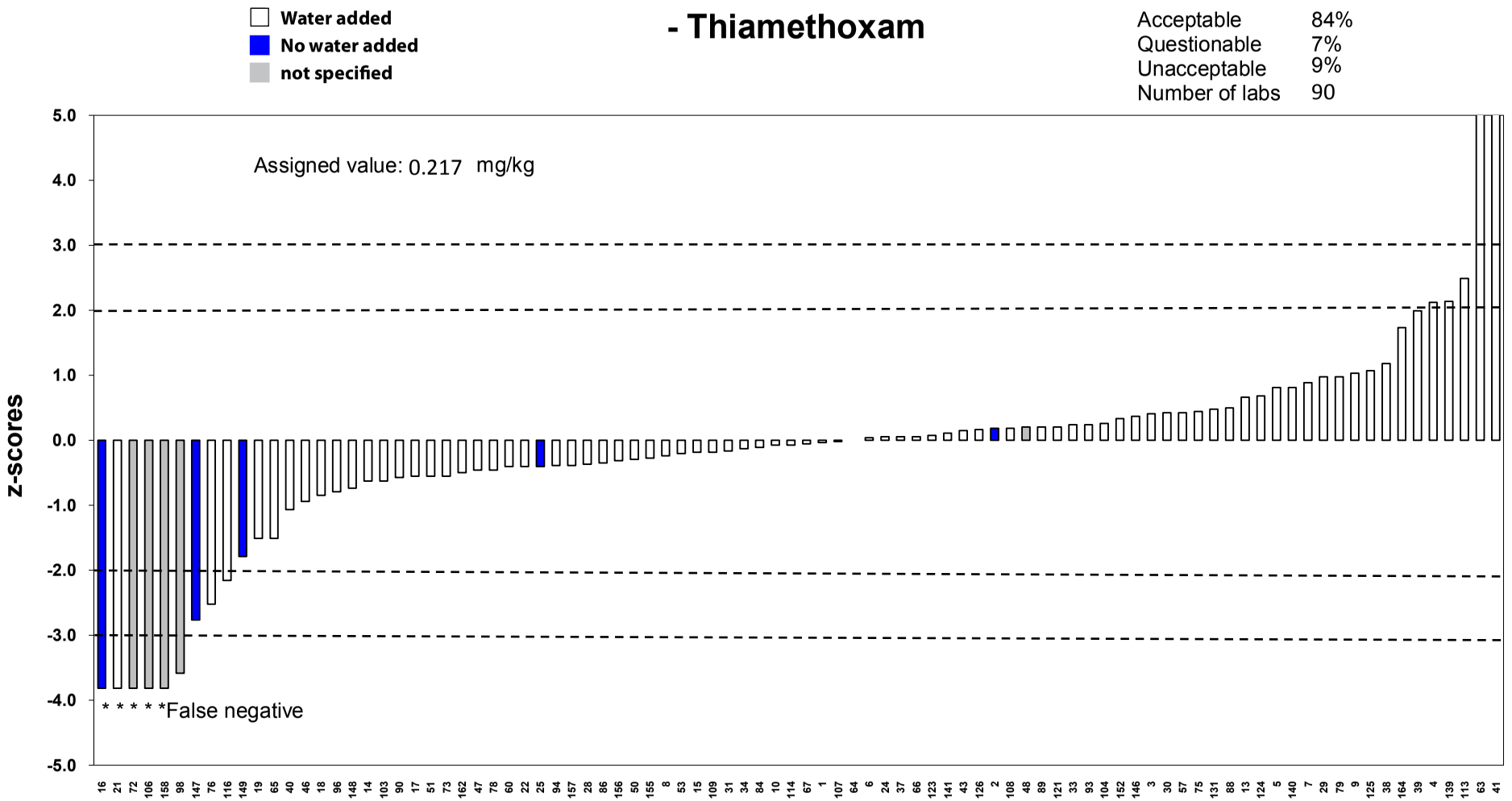
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



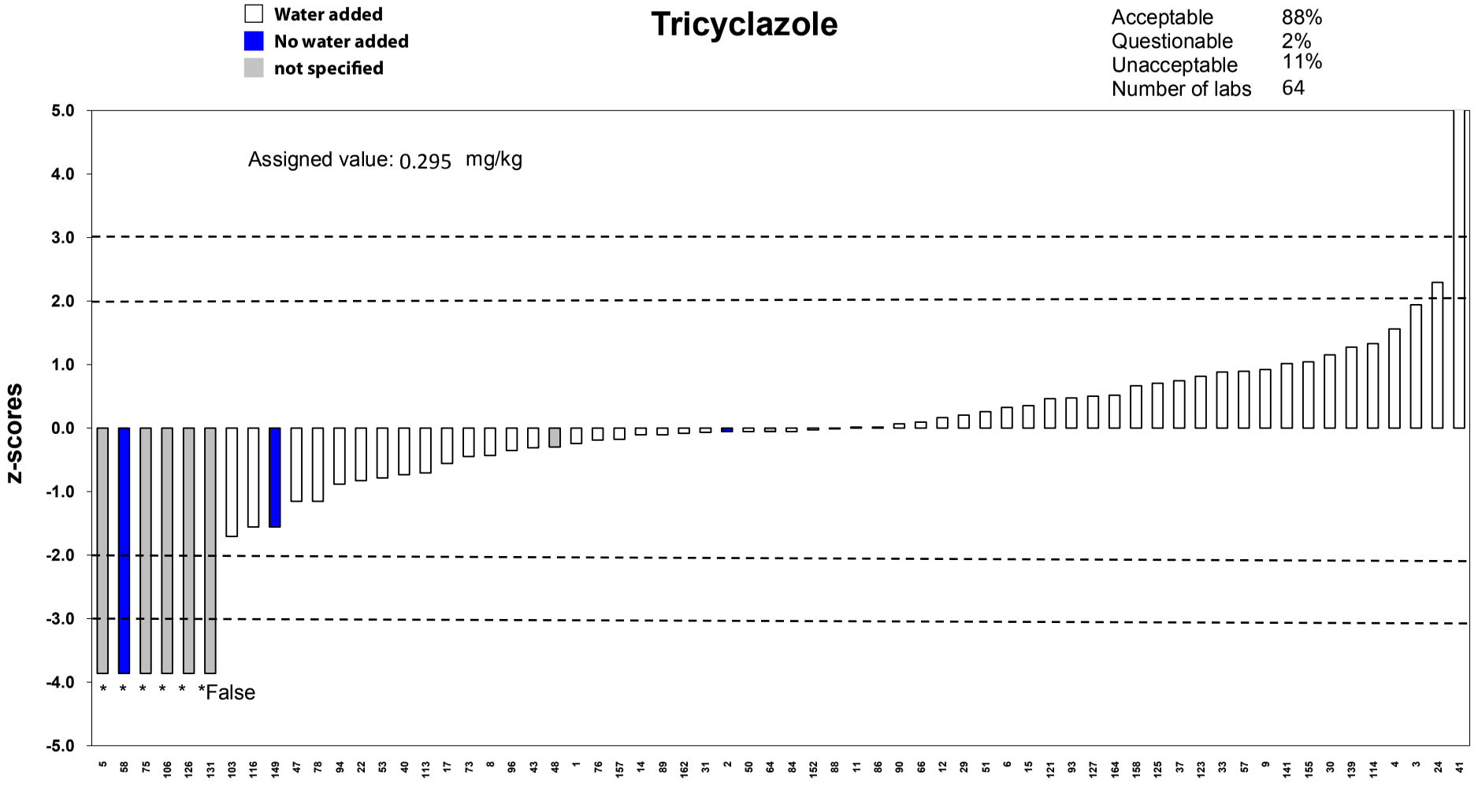
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



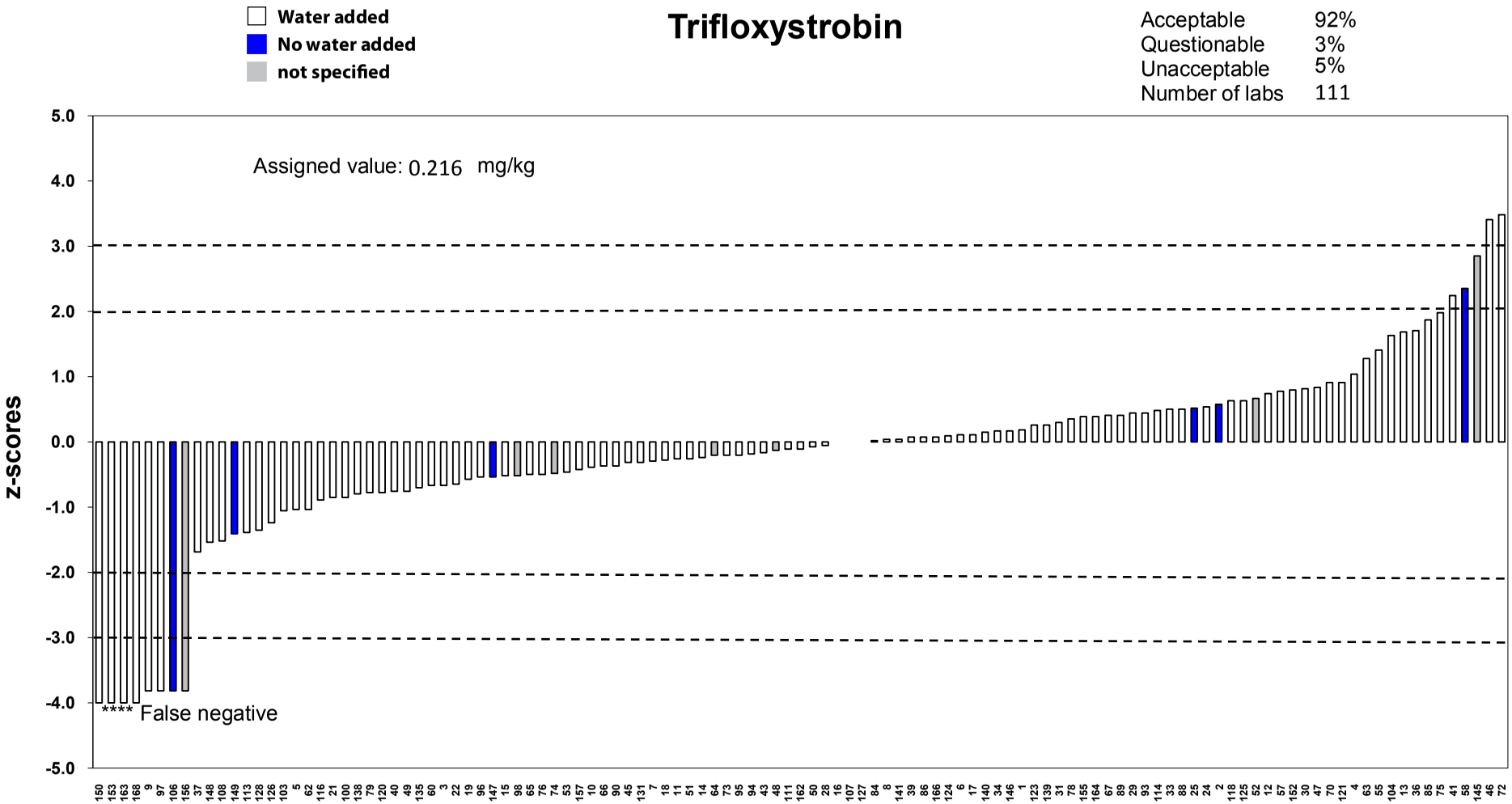
Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides



Appendix 5 (cont.) Graphic presentation of z-Scores – MRM pesticides (Trifloxystrobin)



Appendix 6 Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
1	Azoxystrobin	0.16	Yes, automatic		Std add.	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Carbendazim and benomyl	0.131	No	84	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
1	Chlorpyrifos	0.199	No	94	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Deltamethrin (cis)	0.192	Yes, automatic		Std add.	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Difenoconazole	0.093	No	96	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Diflubenzuron	0.26	No	93	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
1	Epoxiconazole	0.098	No	102	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
1	Fipronil (parent comp.)	0.163	No	101	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
1	Isoprothiolane	0.179	No	98	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Kresoxim-methyl	0.175	No	92	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	- Malathion	0.011	No	100	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
1	Pirimiphos-methyl	0.085	No	99	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Propiconazole	0.474	No	104	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Tebuconazole	0.817	No	120	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
1	Thiamethoxam	0.215	No	90	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
1	Tricyclazole	0.277	No	89	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
1	Trifloxystrobin	0.226	No	100	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
2	Azoxystrobin	0.194	No	105	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Carbendazim and benomyl	0.146	No	89	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Chlorpyrifos	0.207	No	84	Same batch	10	ACN	Toluen			No	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
2	Deltamethrin (cis)	0.196	No	94	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Difenoconazole	0.119	No	100	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Diflubenzuron	0.125	No	105	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Epoxiconazole	0.107	No	105	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
2	Fipronil (parent comp.)	0.177	No	104	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Isoprothiolane	0.19	No	99	Same batch	10	ACN	Toluen			No	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
2	Kresoxim-methyl	0.178	No	102	Same batch	10	ACN	Toluen			No	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
2	Malathion	0.01	No	87	Same batch	10	ACN	Toluen			No	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
2	Pirimiphos-methyl	0.08	No	103	Same batch	10	ACN	Toluen			No	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
2	Propiconazole	0.535	No	102	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Tebuconazole	0.938	No	104	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Thiamethoxam	0.227	No	98	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Clothianidin	0.01	No	103	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
2	Tricyclazole	0.291	No	86	Same batch	10	ACN	Toluen			No	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
2	Trifloxystrobin	0.247	No	104	Same batch	10	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
3	Azoxystrobin	0.172	Yes, automatic	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
3	Carbendazim and benomyl	0.168	Yes, automatic	109	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
3	Chlorpyrifos	0.169	Yes, automatic	127	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
3	Deltamethrin (cis)	0.147	Yes, automatic	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
3	Difenoconazole	0.108	Yes, automatic	109	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
3	Diflubenzuron	0.123	Yes, automatic	93	Same batch	5	ACN				Yes	None	MM-ML	Nicarbazin		Ion Trap	LC-Ion Trap	QuEChERS - Citrate buffered
3	Epoxiconazole	0.073	Yes, automatic	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
3	Fipronil (parent comp.)	0.145	Yes, automatic	123	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
3	Isoprothiolane	0.188	Yes, automatic	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
3	Kresoxim-methyl	0.15	Yes, automatic	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
3	Pirimiphos-methyl	0.07	Yes, automatic	91	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
3	Propiconazole	0.335	Yes, automatic	83	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
3	Tebuconazole	0.935	Yes, automatic	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
3	Thiamethoxam	0.239	Yes, automatic	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
3	Tricyclazole	0.438	Yes, automatic	121	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
3	Trifloxystrobin	0.18	Yes, automatic	123	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Pirimicarb D6, PCB 138	TOF		GC-MSD	QuEChERS - Citrate buffered
4	Azoxystrobin	0.198	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Carbendazim and benomyl	0.183	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Chlorpyrifos	0.295	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TDCP	MS/MS			QuEChERS - Citrate buffered
4	Deltamethrin (cis)	0.179	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TDCP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
4	Difenoconazole	0.22	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Diflubenzuron	0.317	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	Nicarbacin		MS/MS		QuEChERS - Citrate buffered
4	Epoxiconazole	0.132	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Fipronil (parent comp.)	0.152	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TDCP	MS/MS			QuEChERS - Citrate buffered
4	Isoprothiolane	0.19	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TDCP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
4	Kresoxim-methyl	0.168	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Malathion	0.017	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TDCP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
4	Pirimiphos-methyl	0.117	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Propiconazole	0.54	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Tebuconazole	1.02	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	- Thiamethoxam	0.332	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Tricyclazole	0.41	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS		QuEChERS - Citrate buffered
4	Trifloxystrobin	0.272	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TDCP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
5	Azoxystrobin	0.164	No	98	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Carbendazim and benomyl	0.143	No	105	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Chlorpyrifos	0.163	No	85	Same batch	10	EtOAc				Yes	DSPE (PSA/$MgSO_4$)/ C18	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
5	Deltamethrin (cis)	0.156	No	86	Same batch	10	EtOAc				Yes	DSPE (PSA/$MgSO_4$)/ C18	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 2 – 7: MRM – Pesticides

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
5	Difenoconazole	0.118	No	90	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Diflubenzuron	0.448	No	85	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Epoxiconazole	0.107	No	105	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Fipronil (parent comp.)	0.166	No	102	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Isoprothiolane	0.171	No	104	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Kresoxim-methyl	0.128	No	84	Same batch	10	EtOAc				Yes	DSPE ($PSA/MgSO_4$)/ C18	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
5	Pirimiphos-methyl	0.057	No	87	Same batch	10	EtOAc				Yes	DSPE ($PSA/MgSO_4$)/ C18	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
5	Propiconazole	0.251	No	78	Same batch	10	EtOAc				Yes	DSPE ($PSA/MgSO_4$)/ C18	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
5	Tebuconazole	0.925	No	96	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	- Thiamethoxam	0.261	No	109	Same batch	5	MeOH				Yes	None	MM-ML	Oxfendazole		MS/MS	LC-MS/MS	
5	Trifloxystrobin	0.16	No	87	Same batch	10	EtOAc				Yes	DSPE ($PSA/MgSO_4$)/ C18	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
6	Azoxystrobin	0.159	No	93	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS	GC-MSD	QuEChERS (original version)
6	Carbendazim and benomyl	0.13	No	77	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Chlorpyrifos	0.203	No	91	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS	GC-MSD	QuEChERS (original version)
6	Deltamethrin (cis)	0.176	No	90	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS	GC-MSD	QuEChERS (original version)
6	Difenoconazole	0.105	No	90	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS	GC-MSD	QuEChERS (original version)
6	Diflubenzuron	0.138	No	92	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Epoxiconazole	0.103	No	90	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Fipronil (parent comp.)	0.138	No	97	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Isoprothiolane	0.169	No	88	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Kresoxim-methyl	0.161	No	94	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS	GC-MSD	QuEChERS (original version)
6	- Malathion	0.012	No	92	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Pirimiphos-methyl	0.069	No	88	Same batch	7	EtOAc				Yes	GPC, PL gel	MM-ML	TPP	MSD		LC-MS/MS	Ethylacetate type
6	Propiconazole	0.485	No	93	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
6	Tebuconazole	0.76	No	89	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS	GC-MSD	QuEChERS (original version)
6	- Thiamethoxam	0.219	No	87	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	- Clothianidin	0.011	No	85	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Tricyclazole	0.319	No	89	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS		QuEChERS (original version)
6	Trifloxystrobin	0.222	No	92	Same batch	3	ACN				Yes	None	MM-ML	TPP		MS/MS	GC-MSD	QuEChERS (original version)
7	Azoxystrobin	0.172	No	97	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Carbendazim and benomyl	0.133	No	80	Same batch	5	MeOH				Yes	SPE (column)	MM-ML			MS/MS		Klein, Alder, J. AOAC 86/1015/2003
7	Chlorpyrifos	0.187	No	97	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Deltamethrin (cis)	0.21	No	99	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Difenoconazole	0.12	No	93	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Epoxiconazole	0.109	No	99	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Fipronil (parent comp.)	0.195	No	100	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Kresoxim-methyl	0.156	No	101	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	- Malathion	0.01	No	94	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Pirimiphos-methyl	0.084	No	101	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Propiconazole	0.442	No	101	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	Tebuconazole	0.755	No	97	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
7	- Thiamethoxam	0.265	No	113	Same batch	5	MeOH				Yes	SPE (column)	MM-ML			MS/MS		Klein, Alder, J. AOAC 86/1015/2003
7	- Clothianidin	0.009	No	111	Same batch	5	MeOH				Yes	SPE (column)	MM-ML			MS/MS		Klein, Alder, J. AOAC 86/1015/2003
7	Trifloxystrobin	0.2	No	100	Same batch	0	AC				Yes	SPE (column)	MM-ML	TPP	MSD			
8	Azoxystrobin	0.177	No	102	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Carbendazim and benomyl	0.108	No	90	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
8	Chlorpyrifos	0.209	No	93	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Deltamethrin (cis)	0.127	No	88	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 2 – 7: MRM – Pesticides

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
8	Difenoconazole	0.128	No	92	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Diflubenzuron	0.105	No	84	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
8	Epoxiconazole	0.127	No	88	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Fipronil (parent comp.)	0.165	No	93	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Isoprothiolane	0.152	No	84	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Kresoxim-methyl	0.186	No	85	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	- Malathion	0.014	No	90	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Pirimiphos-methyl	0.08	No	89	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Propiconazole	0.442	No	97	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	Tebuconazole	0.814	No	89	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
8	- Thiamethoxam	0.204	No	98	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
8	Tricyclazole	0.263	No	85	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
8	Trifloxystrobin	0.218	No	86	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
9	Azoxystrobin	0.223	No	107	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Carbendazim and benomyl	0.123	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Chlorpyrifos	0.275	No	85	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
9	Deltamethrin (cis)	0.198	No	72	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
9	Difenoconazole	0.143	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Diflubenzuron	0.113	No	114	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Epoxiconazole	0.123	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Fipronil (parent comp.)	0.147	No	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Kresoxim-methyl	0.213	No	111	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	- Malathion	0.013	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Pirimiphos-methyl	0.082	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
9	Propiconazole	0.56	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Tebuconazole	1.11	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	- Thiamethoxam	0.273	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	- Clothianidin	0.013	No	115	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
9	Tricyclazole	0.363	No	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Azoxystrobin	0.16	Yes, automatic	93	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Carbendazim and benomyl	0.13	Yes, automatic	98	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Chlorpyrifos	0.172	Yes, automatic	80	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.		MSD		GC-MSD	QuEChERS - Citrate buffered
10	Deltamethrin (cis)	0.162	Yes, automatic	130	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.		MSD		GC-MSD	QuEChERS - Citrate buffered
10	Difenoconazole	0.091	Yes, automatic	107	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Diflubenzuron	0.119	Yes, automatic	100	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Epoxiconazole	0.099	Yes, automatic	93	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Fipronil (parent comp.)	0.133	Yes, automatic	81	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.		MSD		GC-MSD	QuEChERS - Citrate buffered
10	Kresoxim-methyl	0.184	Yes, automatic	119	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	- Malathion	0.011	Yes, automatic	96	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Pirimiphos-methyl	0.1	Yes, automatic	130	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Propiconazole	0.498	Yes, automatic	74	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Tebuconazole	0.91	Yes, automatic	84	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	- Thiamethoxam	0.213	Yes, automatic	100	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	- Clothianidin	0.099	Yes, automatic	100	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
10	Trifloxystrobin	0.195	Yes, automatic	89	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
11	Azoxystrobin	0.127	No	87	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	ECD		GC-Ion Trap	QuEChERS (original version)
11	Carbendazim and benomyl	0.118	No	95	Same batch	5	ACN				Yes	Freeze-out	MM-ML			Ion Trap	LC-Ion Trap	QuEChERS (original version)
11	Chlorpyrifos	0.152	No	88	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	FPD		GC-Ion Trap	QuEChERS (original version)

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
11	Deltamethrin (cis)	0.144	No	92	Same batch	10	EtOAc				Yes	GPC	MM-ML		ECD		GC-MSD	Ethylacetate type
11	Difenoconazole	0.109	No	93	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	Ion Trap		GC-Ion Trap	QuEChERS (original version)
11	Diflubenzuron	0.261	No	94	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
11	Epoxiconazole	0.074	No	88	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	ECD		GC-Ion Trap	QuEChERS (original version)
11	Fipronil (parent comp.)	0.156	No	94	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD		LC-Ion Trap	QuEChERS (original version)
11	Isoprothiolane	0.196	No	100	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	ECD		GC-Ion Trap	QuEChERS (original version)
11	Kresoxim-methyl	0.148	No	95	Same batch	10	EtOAc				Yes	GPC	MM-ML		ECD		GC-MSD	Ethylacetate type
11	Pirimiphos-methyl	0.051	No	87	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	FPD		GC-Ion Trap	QuEChERS (original version)
11	Propiconazole	0.408	No	110	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	Ion Trap		GC-Ion Trap	QuEChERS (original version)
11	Tebuconazole	0.735	No	86	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	Ion Trap		GC-Ion Trap	QuEChERS (original version)
11	Tricyclazole	0.296	No	95	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
11	Trifloxystrobin	0.202	No	110	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	Ion Trap		GC-Ion Trap	QuEChERS (original version)
12	Chlorpyrifos	0.11	No	93	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Deltamethrin (cis)	0.216	No	89	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Fipronil (parent comp.)	0.265	No	104	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Kresoxim-methyl	0.17	No	98	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Pirimiphos-methyl	0.057	No	102	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Propiconazole	0.678	No	98	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Tebuconazole	1.624	No	92	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Tricyclazole	0.307	No	95	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
12	Trifloxystrobin	0.256	No	98	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	bromophos methyl	Ion Trap		Different Column	QuEChERS - Citrate buffered
13	Azoxystrobin	0.266	No	79	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	DCIP	MS/MS		GC-Ion Trap	QuEChERS - Citrate buffered
13	Carbendazim and benomyl	0.177	No	68	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	DCIP	MS/MS		GC-Ion Trap	QuEChERS - Citrate buffered
13	Chlorpyrifos	0.25	No	102	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-FPD	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
13	Deltamethrin (cis)	0.267	No	75	Same batch	0	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-ECD	QuEChERS - Citrate buffered
13	Difenoconazole	0.224	No	86	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	DCIP	MS/MS		GC-Ion Trap	QuEChERS - Citrate buffered
13	Diflubenzuron	0.105	No	72	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	DCIP	MS/MS		GC-Ion Trap	QuEChERS - Citrate buffered
13	Epoxiconazole	0.157	No	86	Same batch	0	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-ECD	QuEChERS - Citrate buffered
13	Fipronil (parent comp.)	0.232	No	66	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-FPD	QuEChERS - Citrate buffered
13	Kresoxim-methyl	0.211	No	70	Same batch	0	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-ECD	QuEChERS - Citrate buffered
13	Pirimiphos-methyl	0.089	No	93	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-FPD	QuEChERS - Citrate buffered
13	Propiconazole	0.513	No	80	Same batch	0	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-ECD	QuEChERS - Citrate buffered
13	Tebuconazole	0.984	No	86	Same batch	0	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-ECD	QuEChERS - Citrate buffered
13	- Thiamethoxam	0.253	No	84	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	DCIP	MS/MS		GC-Ion Trap	QuEChERS - Citrate buffered
13	Trifloxystrobin	0.307	No	71	Same batch	0	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	bromophos methyl	Ion Trap		GC-ECD	QuEChERS - Citrate buffered
14	Azoxystrobin	0.143	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	Carbendazim and benomyl	0.118	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS		QuEChERS - Citrate buffered
14	Chlorpyrifos	0.182	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Triphenylmethan	MSD		GC-MSD	QuEChERS - Citrate buffered
14	Deltamethrin (cis)	0.143	No	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Triphenylmethan	MSD		GC-MSD	QuEChERS - Citrate buffered
14	Difenoconazole	0.096	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	Diflubenzuron	0.107	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS		QuEChERS - Citrate buffered
14	Epoxiconazole	0.091	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS		QuEChERS - Citrate buffered
14	Fipronil (parent comp.)	0.149	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	Isoprothiolane	0.166	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	Kresoxim-methyl	0.169	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	- Malathion	0.009	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	Pirimiphos-methyl	0.08	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Triphenylmethan	MSD		GC-MSD	QuEChERS - Citrate buffered
14	Propiconazole	0.431	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
14	Tebuconazole	0.765	No	131	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	- Thiamethoxam	0.183	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	- Clothianidin	0.007	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	Tricyclazole	0.287	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
14	Trifloxystrobin	0.203	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Linuron-D6		MS/MS	GC-MSD	QuEChERS - Citrate buffered
15	Azoxystrobin	0.18	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Carbendazim and benomyl	0.1	No	69	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Chlorpyrifos	0.228	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
15	Deltamethrin (cis)	0.129	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
15	Difenoconazole	0.1	No	82	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Diflubenzuron	0.106	No	84	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Epoxiconazole	0.104	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Fipronil (parent comp.)	0.146	No	113	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Isoprothiolane	0.181	No	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Kresoxim-methyl	0.189	No	116	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	- Malathion	0.012	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Pirimiphos-methyl	0.093	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
15	Propiconazole	0.486	No	110	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Tebuconazole	0.876	No	115	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	- Thiamethoxam	0.207	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Tricyclazole	0.321	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
15	Trifloxystrobin	0.188	No	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
16	Azoxystrobin	0.116	No	103	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Carbendazim and benomyl	0.119	No	102	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-UV or DAD	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
16	Chlorpyrifos	0.201	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Deltamethrin (cis)	0.152	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Difenoconazole	0.08	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Epoxiconazole	0.091	No	103	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Kresoxim-methyl	0.156	No	110	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Pirimiphos-methyl	0.061	No	111	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Propiconazole	0.405	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Tebuconazole	0.73	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
16	Trifloxystrobin	0.216	No	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL	TPP	MSD			QuEChERS - Citrate buffered
17	Azoxystrobin	0.204	No	87	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Carbendazim and benomyl	0.118	No	79	Same batch	5	ACN				Yes	Freeze-out	MM-ML			UV or DAD	LC-UV or DAD	QuEChERS - Citrate buffered
17	Chlorpyrifos	0.238	No	104	Same batch	5	ACN				Yes	Freeze-out	MM-ML		FPD		GC-Ion Trap	QuEChERS - Citrate buffered
17	Deltamethrin (cis)	0.134	No	96	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Difenoconazole	0.099	No	95	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Diflubenzuron	0.107	No	101	Same batch	5	ACN				Yes	Freeze-out	MM-ML			UV or DAD	LC-UV or DAD	QuEChERS - Citrate buffered
17	Epoxiconazole	0.154	No	114	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Fipronil (parent comp.)	0.14	No	93	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Isoprothiolane	0.142	No	88	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Kresoxim-methyl	0.202	No	103	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	- Malathion	0.026	No	105	Same batch	5	ACN				Yes	Freeze-out	MM-ML		FPD		GC-Ion Trap	QuEChERS - Citrate buffered
17	Pirimiphos-methyl	0.096	No	100	Same batch	5	ACN				Yes	Freeze-out	MM-ML		FPD		GC-Ion Trap	QuEChERS - Citrate buffered
17	Propiconazole	0.426	No	117	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Tebuconazole	1.03	No	92	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	- Thiamethoxam	0.187	No	100	Same batch	5	ACN				Yes	Freeze-out	MM-ML			UV or DAD	LC-UV or DAD	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
17	Tricyclazole	0.254	No	124	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
17	Trifloxystrobin	0.222	No	99	Same batch	5	ACN				Yes	Freeze-out	MM-ML		Ion Trap		GC-ECD	QuEChERS - Citrate buffered
18	Azoxystrobin	0.177	No	100	Same batch	10	AC				Yes	Liq./liq. , SPE	MM-ML		ECD		GC-NPD	
18	Carbendazim and benomyl	0.154	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	isotop. Lab1	MS/MS		LC-MS/MS	
18	Chlorpyrifos	0.219	No	90	Same batch	10	AC				Yes	Liq./liq. , SPE	MM-ML		ECD		GC-NPD	
18	Deltamethrin (cis)	0.155	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
18	Difenoconazole	0.087	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
18	Diflubenzuron	0.111	No	111	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	isotop. Lab1	MS/MS		LC-MS/MS	
18	Epoxiconazole	0.077	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
18	Fipronil (parent comp.)	0.141	No	103	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
18	Kresoxim-methyl	0.176	No	82	Same batch	10	AC				Yes	Liq./liq. , SPE	MM-ML		ECD		GC-NPD	
18	- Malathion	0.014	No	92	Same batch	10	AC				Yes	Liq./liq. , SPE	MM-ML		ECD		GC-NPD	
18	Pirimiphos-methyl	0.09	No	92	Same batch	10	AC				Yes	Liq./liq. , SPE	MM-ML		NPD		Different Column	
18	Propiconazole	0.435	No	95	Same batch	10	AC				Yes	Liq./liq. , SPE	MM-ML		ECD		GC-NPD	
18	Tebuconazole	0.806	No	109	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	isotop. Lab1		MS/MS	LC-MS/MS	
18	- Thiamethoxam	0.171	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
18	Trifloxystrobin	0.201	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
19	Azoxystrobin	0.117	No	89	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP		MS/MS	GC-ECD	Mini-Luke-Type
19	Carbendazim and benomyl	0.145	No	123	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TFP		MS/MS		QuEChERS (original version)
19	Chlorpyrifos	0.253	No	102	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP	MS/MS			Mini-Luke-Type
19	Deltamethrin (cis)	0.165	No	92	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP/HCB	MS/MS		GC-ECD	Mini-Luke-Type
19	Difenoconazole	0.063	No	66	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP		MS/MS		Mini-Luke-Type
19	Diflubenzuron	0.194	No	114	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP		MS/MS		Mini-Luke-Type
19	Epoxiconazole	0.059	No	93	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP		MS/MS		Mini-Luke-Type

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
19	Fipronil (parent comp.)	0.195	No	79	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP/HCB		MS/MS		Mini-Luke-Type
19	Kresoxim-methyl	0.125	No	95	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP/HCB	MS/MS			Mini-Luke-Type
19	Pirimiphos-methyl	0.102	No	108	Same batch	5	AC	CH_2Cl_2	PE		Yes	Liq./liq.	PS-ML	TFP	MS/MS			Mini-Luke-Type
19	Propiconazole	0.552	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TFP		MS/MS		QuEChERS (original version)
19	Tebuconazole	0.509	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TFP		MS/MS		QuEChERS (original version)
19	- Thiamethoxam	0.135	No	123	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TFP		MS/MS		QuEChERS (original version)
19	Trifloxystrobin	0.185	No	68	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TFP		MS/MS		QuEChERS (original version)
20	Chlorpyrifos	0.152	No	119	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	PS-ML		Ion Trap			QuEChERS - Citrate buffered
21	Azoxystrobin	0.095	No	99	Same batch	20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Carbendazim and benomyl	0.078	No	93	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
21	Chlorpyrifos	0.18	No	94		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Deltamethrin (cis)	0.129	No	82		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Difenoconazole	0.055	No	83		15	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
21	Diflubenzuron	0.082	No	82		15	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
21	Epoxiconazole	0.051	No	93		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Fipronil (parent comp.)	0.109	No	110		15	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
21	Kresoxim-methyl	0.14	No	103		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Pirimiphos-methyl	0.058	No	88		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Propiconazole	0.31	No	95		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Tebuconazole	0.5	No	94		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
21	Trifloxystrobin	0.17	No	88		20	EtOAc				Yes	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
22	Azoxystrobin	0.122	No	92	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Carbendazim and benomyl	0.108	No	99	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Chlorpyrifos	0.189	No	84	Validation	5	EtOAc				Yes	None	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 2 – 7: MRM – Pesticides

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
22	Deltamethrin (cis)	0.192	No	86	Validation	5	EtOAc				Yes	None	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
22	Difenoconazole	0.068	No	87	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Diflubenzuron	0.088	No			5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Epoxiconazole	0.067	No	94	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Fipronil (parent comp.)	0.109	No	108	Validation	5	EtOAc				Yes	None	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
22	Kresoxim-methyl	0.143	No	87	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Pirimiphos-methyl	0.065	No	86	Validation	5	EtOAc				Yes	None	MM-ML		MS/MS		GC-MS/MS	Ethylacetate type
22	Tebuconazole	0.571	No	91	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	- Thiamethoxam	0.195	No	87	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Tricyclazole	0.234	No	93	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
22	Trifloxystrobin	0.181	No	108	Validation	5	EtOAc				Yes	None	MM-SL			MS/MS	LC-MS/MS	Ethylacetate type
24	Azoxystrobin	0.199	No	99	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Carbendazim and benomyl	0.138	No	95	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Chlorpyrifos	0.189	No	97	Same batch	2.5	EtOAc				Yes	GPC	MM-ML	PCB209	MSD		GC-MSD	Ethylacetate type
24	Deltamethrin (cis)	0.149	No	82	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Difenoconazole	0.127	No	86	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Diflubenzuron	0.284	No	91	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Epoxiconazole	0.123	No	88	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Fipronil (parent comp.)	0.175	No	101	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Isoprothiolane	0.188	No	98	Same batch	2.5	EtOAc				Yes	GPC	MM-ML	PCB209	MSD		GC-MSD	Ethylacetate type
24	Kresoxim-methyl	0.191	No	95	Same batch	2.5	EtOAc				Yes	GPC	MM-ML	PCB209	MSD		GC-MSD	Ethylacetate type
24	- Malathion	0.01	No	98	Same batch	2.5	EtOAc				Yes	GPC	MM-ML	PCB209	MSD		GC-MSD	Ethylacetate type
24	Pirimiphos-methyl	0.093	No	94	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Propiconazole	0.515	No	90	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
24	Tebuconazole	1.02	No	93	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	- Thiamethoxam	0.22	No	87	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
24	Tricyclazole	0.464	No	91	Same batch	2.5	EtOAc				Yes	GPC	MM-ML	PCB209	MSD		GC-MSD	Ethylacetate type
24	Trifloxystrobin	0.245	No	91	Same batch	5	ACN	ACN			Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TRIS		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
25	Azoxystrobin	0.126	No	103	Same batch	40	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML		MSD		GC-MSD	S-19
25	Carbendazim and benomyl	0.128	No	101	Same batch	20	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML			MS/MS	LC-MS/MS	S-19
25	Chlorpyrifos	0.249	No	101	Same batch	40	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML		MSD		GC-MSD	S-19
25	Deltamethrin (cis)	0.211	No	99	Same batch	40	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML		MSD		GC-MSD	S-19
25	Difenoconazole	0.087	No	98	Same batch	20	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML			MS/MS	LC-MS/MS	S-19
25	Epoxiconazole	0.080	No	96	Same batch	20	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML			MS/MS	LC-MS/MS	S-19
25	Fipronil (parent comp.)	0.213	No	95	Same batch	20	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML			MS/MS	LC-MS/MS	S-19
25	Kresoxim-methyl	0.167	No	102	Same batch	20	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML			MS/MS	LC-MS/MS	S-19
25	Pirimiphos-methyl	0.094	No	101	Same batch	40	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML		MSD		GC-MSD	S-19
25	Propiconazole	0.432	No	103	Same batch	20	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML			MS/MS	LC-MS/MS	S-19
25	Tebuconazole	0.729	No	100	Same batch	40	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML		MSD		GC-MSD	S-19
25	- Thiamethoxam	0.195	No	111	Same batch	20	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML			MS/MS	LC-MS/MS	S-19
25	Trifloxystrobin	0.244	No	102	Same batch	40	AC	CH_2Cl_2	PE		No	Liq./liq., GPC	MM-ML		MSD		GC-MSD	S-19
28	Azoxystrobin	0.182	No	76	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	Carbendazim and benomyl	0.13	No	80	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	Chlorpyrifos	0.175	No	101	Same batch	5	ACN				Yes	None	PS-ML		FPD		GC-Ion Trap	QuEChERS - Citrate buffered
28	Deltamethrin (cis)	0.181	No	79	Same batch	5	ACN				Yes	None	MM-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
28	Difenoconazole	0.155	No	83	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	Epoxiconazole	0.118	No	85	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	Fipronil (parent comp.)	0.154	No	83	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
28	Kresoxim-methyl	0.174	No	76	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	Pirimiphos-methyl	0.061	No	110	Same batch	5	ACN				Yes	None	PS-ML		FPD		GC-Ion Trap	QuEChERS - Citrate buffered
28	Propiconazole	0.589	No	70	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	Tebuconazole	1.07	No	110	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	- Thiamethoxam	0.197	No	78	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
28	Trifloxystrobin	0.213	No	90	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
29	Azoxystrobin	0.230	No	98	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Carbendazim and benomyl	0.150	No	85	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Chlorpyrifos	0.210	No	91	Same batch	10	Cy-He	EtOAc			No	GPC	MM-ML	TPP,TBP	MSD			S-19
29	Deltamethrin (cis)	0.160	No	90	Same batch	10	Cy-He	EtOAc			No	GPC, SPE	MM-ML	TPP,TBP	MS/MS			VDLUFA 3.3.7.1
29	Difenoconazole	0.110	No	95	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Diflubenzuron	0.220	No	107	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Epoxiconazole	0.110	No	118	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Fipronil (parent comp.)	0.210	No	104	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Isoprothiolane	0.210	No	97	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Kresoxim-methyl	0.130	No	81	Same batch	10	Cy-He	EtOAc			No	GPC, SPE	MM-ML	TPP,TBP	MS/MS			VDLUFA 3.3.7.1
29	- Malathion	0.050	No	87	Same batch	10	Cy-He	EtOAc			No	GPC, SPE	MM-ML	TPP,TBP	MS/MS			VDLUFA 3.3.7.1
29	Pirimiphos-methyl	0.070	No	82	Same batch	10	Cy-He	EtOAc			No	GPC	MM-ML	TPP,TBP	MSD			S-19
29	Tebuconazole	0.660	No	93	Same batch	10	Cy-He	EtOAc			No	GPC	MM-ML	TPP,TBP	MSD			S-19
29	- Thiamethoxam	0.270	No	93	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Tricyclazole	0.310	No	87	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
29	Trifloxystrobin	0.240	No	90	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$, ODS)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
30	Azoxystrobin	0.200	No	109	Same batch	10	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
30	Carbendazim and benomyl	0.130	No	100	Same batch	10	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
30	Chlorpyrifos	0.180	No	102	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	Deltamethrin (cis)	0.080	No	79	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	Difenoconazole	0.090	No	104	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	Diflubenzuron	0.180	No	153	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
30	Epoxiconazole	0.110	No	101	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
30	Fipronil (parent comp.)	0.130	No	106	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	Isoprothiolane	0.140	No	95	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	Kresoxim-methyl	0.160	No	101	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	- Malathion	0.010	No	101	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
30	Pirimiphos-methyl	0.170	No	111	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
30	Propiconazole	0.380	No	99	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	Tebuconazole	0.600	No	102	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
30	- Thiamethoxam	0.240	No	97	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
30	Tricyclazole	0.380	No	102	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
30	Trifloxystrobin	0.260	No	114	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
31	Azoxystrobin	0.178	No	114	Same batch	6	AC	CH_2Cl_2		+	No	GPC, SPE	MM-ML		MSD			
31	Carbendazim and benomyl	0.110	No	99	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		Â§64 LFGB, L00.00-115
31	Chlorpyrifos	0.186	No	89	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Deltamethrin (cis)	0.142	No	92	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Difenoconazole	0.090	No	112	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Diflubenzuron	0.120	No	76	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		Â§64 LFGB, L00.00-115
31	Epoxiconazole	0.101	No	114	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Fipronil (parent comp.)	0.148	No	99	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Isoprothiolane	0.168	No	93	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
31	Kresoxim-methyl	0.178	No	103	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	- Malathion	0.012	No	92	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Pirimiphos-methyl	0.092	No	104	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Propiconazole	0.592	No			5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	Tebuconazole	0.975	No	100	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
31	- Thiamethoxam	0.208	No	89	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		Â§64 LFGB, L00.00-115
31	Tricyclazole	0.290	No	100	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		Â§64 LFGB, L00.00-115
31	Trifloxystrobin	0.232	No	104	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS			Â§64 LFGB, L00.00-115
32	Chlorpyrifos	0.233	Yes, automatic		Std add.	1	Other	HEX			No	None	MM-ML	parathion ethyl d10	MS/MS		GC-MS/MS	
32	Deltamethrin (cis)	0.080	Yes, automatic		Std add.	1	Other	HEX			No	None	MM-ML	pp' DDT d8	MS/MS		GC-MS/MS	
32	- Malathion	0.007	Yes, automatic		Std add.	1	Other	HEX			No	None	MM-ML	parathion ethyl d10	MS/MS		GC-MS/MS	
32	Pirimiphos-methyl	0.064	Yes, automatic		Std add.	1	Other	HEX			No	None	MM-ML	parathion ethyl d10	MS/MS		GC-MS/MS	
33	Azoxystrobin	0.187	No	120	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
33	Carbendazim and benomyl	0.122	No	70	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
33	Chlorpyrifos	0.204	No	96	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
33	Deltamethrin (cis)	0.150	No	87	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
33	Difenoconazole	0.117	No	92	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered
33	Diflubenzuron	0.176	No	101	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
33	Epoxiconazole	0.112	No	93	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
33	Fipronil (parent comp.)	0.132	Recovery fig.	132	Same batch	20	AC				Yes	GPC, SPE	MM-ML		MS/MS		LC-MS/MS	S-19
33	Isoprothiolane	0.187	No	83	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
33	Kresoxim-methyl	0.185	No	100	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
33	- Malathion	0.014	No	98	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
33	Pirimiphos-methyl	0.078	No	88	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
33	Propiconazole	0.535	No	105	Same batch	20	AC				Yes	GPC, SPE	MM-ML			MS/MS	GC-MSD	S-19
33	Tebuconazole	0.685	No	118	Same batch	20	AC				Yes	GPC, SPE	MM-ML			MS/MS	GC-MSD	S-19
33	- Thiamethoxam	0.230	No	85	Same batch	20	AC				Yes	GPC, SPE	MM-ML		MSD		LC-MS/MS	S-19
33	- Clothianidin	0.010	No	108	Same batch	20	AC				Yes	GPC, SPE	MM-ML			MS/MS	GC-MSD	S-19
33	Tricyclazole	0.360	No	100	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MSD	QuEChERS - Citrate buffered
33	Trifloxystrobin	0.243	No	98	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
34	Azoxystrobin	0.170	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Carbendazim and benomyl	0.118	No	83	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Chlorpyrifos	0.216	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Difenoconazole	0.103	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Diflubenzuron	0.123	No	76	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Epoxiconazole	0.096	No	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Fipronil (parent comp.)	0.158	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Isoprothiolane	0.170	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Kresoxim-methyl	0.187	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Pirimiphos-methyl	0.081	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Propiconazole	0.474	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Tebuconazole	0.877	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	- Thiamethoxam	0.210	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
34	Trifloxystrobin	0.225	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS			QuEChERS - Citrate buffered
35	Azoxystrobin	0.159	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS (original version)
35	Carbendazim and benomyl	0.106	No			7	AC	CH_2Cl_2	Other		Yes	SPE (column)	PS-ML			UV or DAD	LC-UV or DAD	Mini-Luke-Type
35	Chlorpyrifos	0.189	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS (original version)
35	Deltamethrin (cis)	0.178	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS (original version)

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 2 – 7: MRM – Pesticides

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
35	Difenoconazole	0.096	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS (original version)
35	Kresoxim-methyl	0.202	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS (original version)
35	Pirimiphos-methyl	0.077	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS (original version)
35	Tebuconazole	0.983	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS (original version)
36	Azoxystrobin	0.288	No	111	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Chlorpyrifos	0.203	No	93	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Deltamethrin (cis)	0.264	No	111	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Difenoconazole	0.173	No	87	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Fipronil (parent comp.)	0.203	No	111	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Pirimiphos-methyl	0.162	No	97	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Propiconazole	0.582	No	109	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Tebuconazole	1.100	No	114	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
36	Trifloxystrobin	0.308	No	116	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
37	Azoxystrobin	0.185	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Carbendazim and benomyl	0.080	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Chlorpyrifos	0.200	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Deltamethrin (cis)	0.179	No	90	Validation	5	ACN				Yes	None	MM-ML		Ion Trap		GC-Ion Trap	QuEChERS - Citrate buffered
37	Difenoconazole	0.110	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Diflubenzuron	0.148	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Epoxiconazole	0.112	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Fipronil (parent comp.)	0.186	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Isoprothiolane	0.193	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Kresoxim-methyl	0.221	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	- Malathion	0.015	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
37	Pirimiphos-methyl	0.077	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Propiconazole	0.576	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Tebuconazole	0.895	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	- Thiamethoxam	0.220	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Tricyclazole	0.350	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
37	Trifloxystrobin	0.125	No	90	Validation	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
38	Azoxystrobin	14.233	No	114	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
38	Chlorpyrifos	0.203	Recovery fig.	129	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	Delta HCH	ECD		GC-ECD	QuEChERS - Citrate buffered
38	Deltamethrin (cis)	0.236	Recovery fig.	69	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	PCB 198	ECD		GC-ECD	QuEChERS - Citrate buffered
38	- Endosulfan sulfate	0.036	Recovery fig.	129	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	Delta HCH	ECD		GC-ECD	QuEChERS - Citrate buffered
38	- Malathion	0.012	Recovery fig.	135	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
38	Pirimiphos-methyl	0.070	No	104	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
38	Propiconazole	0.875	No	100	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
38	Tebuconazole	1.416	No	70	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
38	- Thiamethoxam	0.281	No	119	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
38	- Clothianidin	0.023	No	70	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
39	Azoxystrobin	0.184	No	105	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19
39	Carbendazim and benomyl	0.167	No	100	Same batch	1	MeOH	CH_2Cl_2			Yes	Liq./liq.	MM-ML			MS/MS	LC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
39	Chlorpyrifos	0.258	No	113	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		NPD		GC-Ion Trap	S-19
39	Deltamethrin (cis)	0.198	No	113	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19
39	Difenoconazole	0.138	No	102	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19
39	Diflubenzuron	0.241	No	98	Same batch	1	MeOH	CH_2Cl_2			Yes	Liq./liq.	MM-ML			MS/MS	LC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
39	Epoxiconazole	0.108	No	92	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19
39	Fipronil (parent comp.)	0.171	No	92	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 2 – 7: MRM – Pesticides

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
39	Kresoxim-methyl	0.143	No	94	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19
39	Pirimiphos-methyl	0.101	No	114	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		NPD		GC-Ion Trap	S-19
39	Propiconazole	0.419	No	96	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19
39	Tebuconazole	0.856	No	97	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		NPD		GC-Ion Trap	S-19
39	- Thiamethoxam	0.325	No	107	Same batch	1	MeOH	CH_2Cl_2			Yes	Liq./liq.	MM-ML			MS/MS	LC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
39	Trifloxystrobin	0.220	No	98	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML		ECD		GC-Ion Trap	S-19
40	Azoxystrobin	0.155	No	101	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Carbendazim and benomyl	0.107	No	92	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
40	Chlorpyrifos	0.205	No	105	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Deltamethrin (cis)	0.152	No	118	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Difenoconazole	0.094	Recovery fig.	132	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Diflubenzuron	0.119	No	104	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Epoxiconazole	0.093	No	99	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Fipronil (parent comp.)	0.141	Recovery fig.	144	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Isoprothiolane	0.187	No	95	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
40	Kresoxim-methyl	0.177	No	107	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
40	Pirimiphos-methyl	0.075	No	115	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Propiconazole	0.510	No	100	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	Tebuconazole	0.802	No	104	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD			QuEChERS - Citrate buffered
40	- Thiamethoxam	0.159	No	80	Same batch	0												
40	- Clothianidin	0.007	No	90	Same batch	7	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
40	Tricyclazole	0.241	No	95	Same batch	0												
40	Trifloxystrobin	0.175	No	117	Same batch	0												
41	Azoxystrobin	0.187	No	119	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
41	Carbendazim and benomyl	0.094	No	115	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Chlorpyrifos	0.348	No	104	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Deltamethrin (cis)	0.195	No	111	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Difenoconazole	0.044	No	112	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Diflubenzuron	0.102	No	85	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Epoxiconazole	0.107	No	116	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Fipronil (parent comp.)	0.177	No	118	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Isoprothiolane	0.198	No	99	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Kresoxim-methyl	0.198	No	111	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	- Malathion	0.013	No	108	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Pirimiphos-methyl	0.088	No	114	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Propiconazole	0.380	No	104	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Tebuconazole	1.068	No	93	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	- Thiamethoxam	0.786	No	98	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	- Clothianidin	0.011	No	116	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	
41	Tricyclazole	1.624	No	112	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
41	Trifloxystrobin	0.337	No	89	Same batch	10	AC	EtOAc	Cy-He		Yes	GPC	MM-ML			MS/MS	GC-MS/MS	VD LUFA MB VII 3.3.7.1
42	Azoxystrobin	0.146	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
42	Carbendazim and benomyl	0.275	No	113	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
42	Chlorpyrifos	0.160	No	77	Same batch	5	AC	CH_2Cl_2	PE		Yes	None	MM-ML	TPP	Ion Trap		GC-Ion Trap	Mini-Luke-Type
42	Deltamethrin (cis)	0.141	No	82	Same batch	5	AC	CH_2Cl_2	PE		Yes	None	MM-ML	TPP	Ion Trap		GC-Ion Trap	Mini-Luke-Type
42	Kresoxim-methyl	0.262	No	150	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
42	Pirimiphos-methyl	0.065	No	86	Same batch	5	AC	CH_2Cl_2	PE		Yes	None	MM-ML	TPP	Ion Trap		GC-Ion Trap	Mini-Luke-Type
42	Propiconazole	0.379	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
42	Tebuconazole	0.951	No	108	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
43	Azoxystrobin	0.143	No	80	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
43	Carbendazim and benomyl	0.112	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
43	Chlorpyrifos	0.198	No	88	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
43	Deltamethrin (cis)	0.175	No	87	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
43	Difenoconazole	0.094	No	96	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		LC-MS/MS	
43	Diflubenzuron	0.102	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
43	Epoxiconazole	0.073	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
43	Fipronil (parent comp.)	0.161	No	90	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
43	Isoprothiolane	0.155	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
43	Kresoxim-methyl	0.188	No	83	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
43	- Malathion	0.011	No	90	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
43	Pirimiphos-methyl	0.078	No	89	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
43	Tebuconazole	0.786	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
43	- Thiamethoxam	0.225	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
43	Tricyclazole	0.272	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
43	Trifloxystrobin	0.207	No	90	Same batch	15	AC	HEX	CH_2Cl_2		Yes	None	MM-ML		MSD		GC-MS/MS	
44	- Endosulfan, alpha	0.000	Yes, automatic		Isotop lab.	2	Other				No	SPE (column)	MM-ML	isotop. Lab1	MSD		GC-MSD	
44	- Endosulfan, beta	0.000	Yes, automatic		Isotop lab.	2	Other				No	SPE (column)	MM-ML	isotop. Lab1	MSD		GC-MSD	
44	- Endosulfan sulfate	0.000	Yes, automatic		Isotop lab.	2	Other				No	SPE (column)	MM-ML	Endosulfan alpha	MSD		GC-MSD	
45	Azoxystrobin	0.160	No	83	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
45	Chlorpyrifos	0.218	No	95	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
45	Deltamethrin (cis)	0.215	No	86	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		Different Column	Mini-Luke-Type
45	Difenoconazole	0.102	No	71	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
45	Epoxiconazole	0.093	No	91	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
45	Fipronil (parent comp.)	0.173	No	118	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
45	Kresoxim-methyl	0.168	No	90	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
45	Pirimiphos-methyl	0.074	No	86	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		NPD		Different Column	Mini-Luke-Type
45	Propiconazole	0.455	No	88	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
45	Tebuconazole	0.789	No	78	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
45	Trifloxystrobin	0.199	No	92	Validation	50	AC	CH_2Cl_2			Yes	florisil	MM-SL		ECD		GC-NPD	Mini-Luke-Type
46	Azoxystrobin	0.172	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Chlorpyrifos	0.188	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Deltamethrin (cis)	0.175	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Difenoconazole	0.132	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Diflubenzuron	0.337	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Epoxiconazole	0.102	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Kresoxim-methyl	0.257	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Pirimiphos-methyl	0.065	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Propiconazole	0.355	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Tebuconazole	0.630	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	- Thiamethoxam	0.166	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
46	Trifloxystrobin	0.400	Yes, automatic		Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
47	Azoxystrobin	0.175	No	83	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Carbendazim and benomyl	0.115	No	86	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
47	Chlorpyrifos	0.192	No	83	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Deltamethrin (cis)	0.181	No	82	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Difenoconazole	0.110	No	89	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
47	Epoxiconazole	0.106	No	89	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Fipronil (parent comp.)	0.151	No	87	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Isoprothiolane	0.159	No	92	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Kresoxim-methyl	0.157	No	88	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Pirimiphos-methyl	0.080	No	89	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Propiconazole	0.495	No	88	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Tebuconazole	0.971	No	82	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	- Thiamethoxam	0.192	No	92	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
47	Tricyclazole	0.210	No	65	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
47	Trifloxystrobin	0.261	No	109	Same batch	5	ACN				Yes	SPE (column)	MM-ML	phenanthrene-D10	MSD		GC-MSD	
48	Azoxystrobin	0.150	No	91	Same batch	3	ACN	Water				None	MM-ML			MS/MS	LC-MS/MS	
48	Carbendazim and benomyl	0.115	No	98	Same batch	3	ACN	Water				None	MM-ML			MS/MS	LC-MS/MS	
48	Chlorpyrifos	0.215	No	94	Same batch	3	ACN	Water				None	MM-ML			MS/MS	LC-MS/MS	
48	Deltamethrin (cis)	0.245	No	80	Same batch	3	ACN	Water				CaCl2, dSPE C18, PSA	MM-ML	PCB198	MS/MS		GC-TOF	
48	Difenoconazole	0.120	No	72	Same batch	3	ACN	Water				None	MM-ML			MS/MS	LC-MS/MS	
48	Diflubenzuron	0.120	No	94	Same batch	3	ACN	Water				None	MM-ML			MS/MS	LC-MS/MS	
48	Epoxiconazole	0.117	No	101	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Fipronil (parent comp.)	0.169	No			3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Isoprothiolane	0.130	No			3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Kresoxim-methyl	0.172	No	97	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	- Malathion	0.012	No	100	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Pirimiphos-methyl	0.065	No	89	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Propiconazole	0.401	No	110	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Tebuconazole	0.942	No	96	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
48	- Thiamethoxam	0.228	No	92	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Tricyclazole	0.273	No	92	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
48	Trifloxystrobin	0.209	No	101	Same batch	3	Other					None	MM-ML			MS/MS	LC-MS/MS	
49	Azoxystrobin	0.086	No	85	Same batch	5	EtOAc				Yes	GPC, Filter	MM-ML		ECD		Different Column	
49	Carbendazim and benomyl	0.132	No	112	Same batch	3	MeOH				Yes	Filter	MM-ML	C13-carbaryl		MS/MS	LC-MS/MS	
49	Deltamethrin (cis)	0.151	No	91	Same batch	5	EtOAc				Yes	GPC, Filter	MM-ML		ECD		Different Column	
49	Epoxiconazole	0.079	No	124	Same batch	3	MeOH				Yes	Filter	MM-ML	C13-carbaryl		MS/MS	LC-MS/MS	
49	Kresoxim-methyl	0.143	No	91	Same batch	5	EtOAc				Yes	GPC, Filter	MM-ML		Ion Trap		GC-Ion Trap	
49	Pirimiphos-methyl	0.078	No	101	Same batch	5	EtOAc				Yes	GPC, Filter	MM-ML		Ion Trap		GC-Ion Trap	
49	Propiconazole	0.356	No	110	Same batch	5	EtOAc				Yes	GPC, Filter	MM-ML		NPD		Different Column	
49	Tebuconazole	0.494	No	105	Same batch	5	EtOAc				Yes	GPC, Filter	MM-ML		Ion Trap		GC-Ion Trap	
49	Trifloxystrobin	0.175	No	94	Same batch	5	EtOAc				Yes	GPC, Filter	MM-ML		Ion Trap		GC-Ion Trap	
50	Azoxystrobin	0.143	No	118	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
50	Carbendazim and benomyl	0.118	No	92	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Chlorpyrifos	0.201	No	120	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
50	Deltamethrin (cis)	0.126	No	78	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Difenoconazole	0.093	No	118	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Diflubenzuron	0.107	No	97	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Epoxiconazole	0.110	No	99	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Fipronil (parent comp.)	0.157	No	103	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Isoprothiolane	0.168	No	85	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
50	Kresoxim-methyl	0.174	No	103	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
50	- Malathion	0.010	No	119	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Pirimiphos-methyl	0.068	No	123	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
50	Propiconazole	0.466	No	115	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Tebuconazole	0.870	No	103	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	- Thiamethoxam	0.201	No	101	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Tricyclazole	0.291	No	90	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
50	Trifloxystrobin	0.212	No	101	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
51	Azoxystrobin	0.195	No	111	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Carbendazim and benomyl	0.119	No	95	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Chlorpyrifos	0.259	No	109	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
51	Deltamethrin (cis)	0.216	No	103	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
51	Difenoconazole	0.112	No	95	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Diflubenzuron	0.107	No	97	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Epoxiconazole	0.103	No	96	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Fipronil (parent comp.)	0.174	No	100	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
51	Isoprothiolane	0.183	No	108	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Kresoxim-methyl	0.153	No	77	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	- Malathion	0.016	No	107	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
51	Pirimiphos-methyl	0.106	No	104	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
51	Propiconazole	0.457	No	97	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Tebuconazole	0.846	No	98	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	- Thiamethoxam	0.187	No	87	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Tricyclazole	0.314	No	92	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
51	Trifloxystrobin	0.202	No	103	Same batch	10	AC	CH_2Cl_2	Other		Yes	Na_2SO_4	PS-ML	TPP		MS/MS	LC-MS/MS	Mini-Luke-Type
52	Azoxystrobin	0.200	No	80	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	NPD		GC-MSD	QuEChERS - Citrate buffered
52	Chlorpyrifos	0.156	No	90	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	NPD		GC-MSD	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
52	Deltamethrin (cis)	0.084	No	75	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	ECD		GC-MSD	QuEChERS - Citrate buffered
52	Difenoconazole	0.094	No	80	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	ECD		GC-MSD	QuEChERS - Citrate buffered
52	Kresoxim-methyl	0.130	No	80	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	NPD		GC-MSD	QuEChERS - Citrate buffered
52	Pirimiphos-methyl	0.064	No	86	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	NPD		GC-MSD	QuEChERS - Citrate buffered
52	Propiconazole	0.182	No	90	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	ECD		GC-MSD	QuEChERS - Citrate buffered
52	Tebuconazole	0.141	No	85	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	NPD		GC-MSD	QuEChERS - Citrate buffered
52	Trifloxystrobin	0.252	No	88	Same batch	5	ACN					DSPE (PSA/$MgSO_4$)	PS-SL	TPP, ethion	NPD		GC-MSD	QuEChERS - Citrate buffered
53	Azoxystrobin	0.125	No	97	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Carbendazim and benomyl	0.140	No	98	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Chlorpyrifos	0.203	No	99	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6	MS/MS			Ethylacetate type
53	Deltamethrin (cis)	0.189	No	94	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6	MS/MS			Ethylacetate type
53	Difenoconazole	0.078	No	106	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Diflubenzuron	0.073	No	92	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Fipronil (parent comp.)	0.120	No	84	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6	MS/MS			Ethylacetate type
53	Isoprothiolane	0.138	No	94	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Pirimiphos-methyl	0.069	No	97	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6	MS/MS			Ethylacetate type
53	Propiconazole	0.353	No	98	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Tebuconazole	0.648	No	96	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	- Thiamethoxam	0.206	No	97	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Tricyclazole	0.237	No	84	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
53	Trifloxystrobin	0.191	No	101	Same batch	5	EtOAc				Yes	Filter	MM-SL	Pirimicarb-D6		MS/MS		Ethylacetate type
54	Chlorpyrifos	0.240	No	80	Validation	2	Other	ACN	ISO	+	No	SPE (column)	PS-ML	Ethion	NPD		GC-MSD	
54	Deltamethrin (cis)	0.272	No	80	Validation	2	Other	ACN	ISO	+	No	SPE (column)	PS-ML	Ethion	ECD		GC-MSD	
55	Azoxystrobin	0.164	No	103	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
55	Carbendazim and benomyl	0.139	No	86	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Chlorpyrifos	0.214	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Deltamethrin (cis)	0.156	No	116	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Difenoconazole	0.098	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Diflubenzuron	0.111	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Epoxiconazole	0.112	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
55	Fipronil (parent comp.)	0.162	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Kresoxim-methyl	0.169	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Pirimiphos-methyl	0.088	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
55	Propiconazole	0.474	No	114	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Tebuconazole	0.831	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
55	Trifloxystrobin	0.292	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
57	Azoxystrobin	0.191	No	126	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Carbendazim and benomyl	0.125	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	Different Method	QuEChERS - Citrate buffered
57	Chlorpyrifos	0.190	No	108	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Deltamethrin (cis)	0.116	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Difenoconazole	0.121	No	111	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Diflubenzuron	0.121	No	110	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	Different Method	QuEChERS - Citrate buffered
57	Epoxiconazole	0.110	No	114	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Fipronil (parent comp.)	0.181	No	109	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Isoprothiolane	0.171	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Kresoxim-methyl	0.225	No	116	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	- Malathion	0.013	No	117	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Pirimiphos-methyl	0.094	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
57	Propiconazole	0.536	No	112	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Tebuconazole	0.932	No	114	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	- Thiamethoxam	0.240	No	120	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Tricyclazole	0.361	No	111	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
57	Trifloxystrobin	0.258	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$, ODS)	MM-ML	several ISTD`s		MS/MS	GC-MSD	QuEChERS - Citrate buffered
58	Azoxystrobin	0.280	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Chlorpyrifos	0.234	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Deltamethrin (cis)	0.225	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Epoxiconazole	0.113	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Fipronil (parent comp.)	0.169	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Isoprothiolane	0.284	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Kresoxim-methyl	0.184	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	- Malathion	0.012	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Pirimiphos-methyl	0.093	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Propiconazole	1.110	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Tebuconazole	1.560	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
58	Trifloxystrobin	0.343	Yes, automatic		Same batch	5	ACN				No	DSPE (PSA/$MgSO_4$)	MM-ML	TCPP	MSD		GC-MSD	QuEChERS (original version)
60	Azoxystrobin	0.136	No	134	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Carbendazim and benomyl	0.133	No	111	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Chlorpyrifos	0.172	No	121	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Deltamethrin (cis)	0.219	No	92	Same batch	0	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			Modified QuEChERS method
60	Difenoconazole	0.088	No	120	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Epoxiconazole	0.083	No	135	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Fipronil (parent comp.)	0.144	No	75	Same batch	0	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			Modified QuEChERS method

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 2 – 7: MRM – Pesticides

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
60	Kresoxim-methyl	0.150	No	111	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Pirimiphos-methyl	0.065	No	116	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Propiconazole	0.375	No	119	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Tebuconazole	0.641	No	122	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	- Thiamethoxam	0.195	No	130	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
60	Trifloxystrobin	0.180	No	135	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		Modified QuEChERS method
61	Chlorpyrifos	0.223	No	101	Same batch	0	EtOAc				No	None			NPD		GC-NPD	
61	Pirimiphos-methyl	0.071	No	100	Same batch	0	EtOAc				No	None			NPD		GC-NPD	
62	Azoxystrobin	0.120	No	95	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		GC-NPD	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Chlorpyrifos	0.180	No	90	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		GC-NPD	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Deltamethrin (cis)	0.180	No	86	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		Different Column	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Difenoconazole	0.120	No	76	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		GC-NPD	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Epoxiconazole	0.080	No	81	Same batch	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		Different Column	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Fipronil (parent comp.)	0.140	No	72	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		Different Column	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Kresoxim-methyl	0.120	No	83	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		GC-NPD	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Pirimiphos-methyl	0.140	No	92	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		NPD		Different Column	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Propiconazole	0.110	No	83	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		GC-NPD	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Tebuconazole	0.650	No	72	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		NPD		Different Column	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
62	Trifloxystrobin	0.160	No	91	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-SL		ECD		GC-NPD	Kadenczki i wspÅ,. (1992)JOAOAC Int. 75: 53-63
63	Azoxystrobin	0.143	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$), SPE	MM-ML			MS/MS		QuEChERS (original version)
63	Carbendazim and benomyl	0.383	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$), SPE	MM-ML			MS/MS		QuEChERS (original version)
63	Chlorpyrifos	0.164	No	87	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	FPD		GC-MS/MS	QuEChERS (original version)
63	Deltamethrin (cis)	0.182	No	98	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD			QuEChERS (original version)
63	Difenoconazole	0.031	No	70	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD			QuEChERS (original version)

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
63	Epoxiconazole	0.129	No	107	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		ECD			QuEChERS (original version)
63	Fipronil (parent comp.)	0.138	No	78	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	Ion Trap			QuEChERS (original version)
63	Kresoxim-methyl	0.101	No	99	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	Ion Trap			QuEChERS (original version)
63	Pirimiphos-methyl	0.058	No	87	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	FPD		GC-MS/MS	QuEChERS (original version)
63	Tebuconazole	0.778	No	87	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	Ion Trap			QuEChERS (original version)
63	- Thiamethoxam	0.675	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$), SPE	MM-ML			MS/MS		QuEChERS (original version)
63	Trifloxystrobin	0.285	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$), SPE	MM-ML			MS/MS		QuEChERS (original version)
64	Azoxystrobin	0.170	Yes, automatic	118														S-19
64	Carbendazim and benomyl	0.128		100														
64	Chlorpyrifos	0.230	Yes, automatic	87														S-19
64	Deltamethrin (cis)	0.100	Yes, automatic	91														S-19
64	Difenoconazole	0.052	Yes, automatic	171														S-19
64	Diflubenzuron	0.103	Yes, automatic	108														
64	Epoxiconazole	0.053	Yes, automatic	114														S-19
64	Fipronil (parent comp.)	0.158	Yes, automatic	104														
64	Kresoxim-methyl	0.170	Yes, automatic	188														S-19
64	- Malathion	0.014	Yes, automatic	116														S-19
64	Pirimiphos-methyl	0.071	Yes, automatic	114														S-19
64	Propiconazole	0.630	Yes, automatic	87														S-19
64	Tebuconazole	0.580	Yes, automatic	121														S-19
64	- Thiamethoxam	0.217	Yes, automatic	117														
64	- Clothianidin	0.010	Yes, automatic	108														QuEChERS - Citrate buffered
64	Tricyclazole	0.291	Yes, automatic	101														
64	Trifloxystrobin	0.205	Yes, automatic	82														S-19

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
65	Azoxystrobin	0.164	No	91	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML			MS/MS	GC-TOF	
65	Carbendazim and benomyl	0.248	No	112	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML			MS/MS		
65	Chlorpyrifos	0.198	No	80	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML	HCB	Ion Trap		GC-TOF	
65	Deltamethrin (cis)	0.168	No	75	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML	HCB	TOF		GC-Ion Trap	
65	Difenoconazole	0.056	No	93	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML			MS/MS		
65	Diflubenzuron	0.178	No	75	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML	HCB	Ion Trap		GC-TOF	
65	Epoxiconazole	0.048	No	70	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML			MS/MS		
65	Fipronil (parent comp.)	0.240	No	74	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML	HCB	Ion Trap		GC-TOF	
65	Kresoxim-methyl	0.172	No	78	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML	HCB	Ion Trap		GC-TOF	
65	Pirimiphos-methyl	0.065	No	83	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML	HCB	Ion Trap		GC-TOF	
65	Propiconazole	0.631	No	110	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML			MS/MS	GC-TOF	
65	Tebuconazole	0.815	No	80	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML	HCB	Ion Trap		GC-TOF	
65	- Thiamethoxam	0.135	No	85	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML			MS/MS		
65	Trifloxystrobin	0.189	No	120	Same batch	7	AC	CH_2Cl_2	Other		Yes	None	MM-ML			MS/MS		
66	Azoxystrobin	0.136	No	109	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Carbendazim and benomyl	0.090	No	88	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Chlorpyrifos	0.175	No	91	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Deltamethrin (cis)	0.180	No	98	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Diflubenzuron	0.133	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Epoxiconazole	0.090	No	84	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Fipronil (parent comp.)	0.100	No	89	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Kresoxim-methyl	0.141	No	100	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Pirimiphos-methyl	0.075	No	87	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Propiconazole	0.180	No	81	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
66	Tebuconazole	0.632	No	85	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	- Thiamethoxam	0.220	No	98	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	- Clothianidin	0.008	No	86	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Tricyclazole	0.302	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
66	Trifloxystrobin	0.196	No	92	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
67	Azoxystrobin	0.168	No	120	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	Carbendazim and benomyl	0.138	No	100	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	Chlorpyrifos	0.199	No	91	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
67	Deltamethrin (cis)	0.142	No	104	Same batch	10	Other				No	GPC	MM-ML	TPP	MS/MS		LC-MS/MS	S-19
67	Difenoconazole	0.117	No	100	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	Epoxiconazole	0.122	No	120	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	Kresoxim-methyl	0.180	No	112	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	- Malathion	0.012	No	116	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	Pirimiphos-methyl	0.071	No	86	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
67	Propiconazole	0.556	No	84	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	Tebuconazole	0.852	No	100	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	- Thiamethoxam	0.214	No	104	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	- Clothianidin	0.010	No	102	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
67	Trifloxystrobin	0.238	No	120	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
68	Azoxystrobin	0.148	No	78	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
68	Chlorpyrifos	0.207	No	106	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
68	Deltamethrin (cis)	0.222	No	99	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
68	Diflubenzuron	0.087	No	74	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
68	Kresoxim-methyl	0.183	No	114	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
68	- Malathion	0.013	No	116	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
68	Pirimiphos-methyl	0.081	No	111	Same batch	5	ACN				Yes	DSPE	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
68	Propiconazole	0.869	No	80	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
68	Tebuconazole	1.430	No	86	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
70	Azoxystrobin	0.135	No	92	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Chlorpyrifos	0.195	No	95	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Deltamethrin (cis)	0.130	No	102	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Difenoconazole	0.085	No	91	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Epoxiconazole	0.078	No	96	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Kresoxim-methyl	0.140	No	104	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Pirimiphos-methyl	0.065	No	95	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Propiconazole	0.360	No	91	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Tebuconazole	0.780	No	101	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
70	Trifloxystrobin	0.265	No	93	Same batch	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TPP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
71	Azoxystrobin	0.058	No	79	Same batch	25	EtOAc	Cy-He			No	GPC	PS-ML		ECD		Different Column	
71	Chlorpyrifos	0.130	No	78	Same batch	25	EtOAc	Cy-He			No	GPC	PS-ML		NPD		Different Column	
71	Deltamethrin (cis)	0.147	No	100	Same batch	25	EtOAc	Cy-He			No	GPC	PS-ML		ECD		Different Column	
71	Pirimiphos-methyl	0.034	No	89	Same batch	25	EtOAc	Cy-He			No	GPC	PS-ML		NPD		Different Column	
71	Tebuconazole	0.418	No	81	Same batch	25	EtOAc	Cy-He			No	GPC	PS-ML		NPD		Different Column	
72	Azoxystrobin	0.074	No		Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Carbendazim and benomyl	0.070	No		Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	sudan 1		MS	LC-MS	QuEChERS - Citrate buffered
72	Chlorpyrifos	0.295	No		Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Difenoconazole	0.666	No		Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Diflubenzuron	0.035	No		Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	PS-ML	sudan 1		MS	LC-MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
72	Fipronil (parent comp.)	0.214	No		Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Kresoxim-methyl	0.515	No		Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	- Malathion	0.028	No		Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Pirimiphos-methyl	0.140	No		Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Propiconazole	0.870	No		Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Tebuconazole	1.164	No		Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
72	Trifloxystrobin	0.404	No		Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TDCP	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
73	Azoxystrobin	0.175	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered
73	Carbendazim and benomyl	0.101	No	80	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS		QuEChERS - Citrate buffered
73	Chlorpyrifos	0.210	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered
73	Deltamethrin (cis)	0.202	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered
73	Difenoconazole	0.101	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
73	Diflubenzuron	0.103	No	108	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS		QuEChERS - Citrate buffered
73	Epoxiconazole	0.083	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered
73	Fipronil (parent comp.)	0.153	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered
73	Isoprothiolane	0.153	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
73	Kresoxim-methyl	0.165	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered
73	- Malathion	0.014	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS			QuEChERS - Citrate buffered
73	Pirimiphos-methyl	0.084	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered
73	Propiconazole	0.164	No	79	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	GC-ECD	QuEChERS - Citrate buffered
73	Tebuconazole	0.784	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS		QuEChERS - Citrate buffered
73	- Thiamethoxam	0.187	No	85	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	GC-ECD	QuEChERS - Citrate buffered
73	Tricyclazole	0.262	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	GC-ECD	QuEChERS - Citrate buffered
73	Trifloxystrobin	0.205	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL		MS/MS		GC-MSD	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
74	Azoxystrobin	0.160	Recovery fig.	73	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-SL		ECD		GC-NPD	MSPD
74	Chlorpyrifos	0.190	Recovery fig.	95	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-SL		ECD		GC-NPD	MSPD
74	Deltamethrin (cis)	0.150	Recovery fig.	93	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-ML		NPD		GC-ECD	MSPD
74	Difenoconazole	0.090	Recovery fig.	77	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-ML		NPD		GC-ECD	MSPD
74	Epoxiconazole	0.075	Recovery fig.	76	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-SL		ECD		GC-NPD	MSPD
74	Fipronil (parent comp.)	0.130	Recovery fig.	91	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-SL		ECD		GC-NPD	MSPD
74	Kresoxim-methyl	0.150	Recovery fig.	95	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-SL		ECD		GC-NPD	MSPD
74	Pirimiphos-methyl	0.080	Recovery fig.	98	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-ML		NPD		GC-ECD	MSPD
74	Propiconazole	0.350	Recovery fig.	90	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-SL		ECD		GC-NPD	MSPD
74	Tebuconazole	0.700	Recovery fig.	84	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-ML		NPD		GC-ECD	MSPD
74	Trifloxystrobin	0.190	Recovery fig.	94	Same batch	2	MeOH	AC	ACN			SPE (column)	MM-SL		ECD		GC-NPD	MSPD
75	Azoxystrobin	0.261	No	89	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
75	Carbendazim and benomyl	0.188	No	94	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
75	Chlorpyrifos	0.196	No	95	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
75	Deltamethrin (cis)	0.154	No	96	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
75	Difenoconazole	0.120	No	108	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
75	Diflubenzuron	0.186	No	100	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
75	Epoxiconazole	0.092	No	79	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
75	Fipronil (parent comp.)	0.125	No	118	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
75	Kresoxim-methyl	0.252	No	107	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
75	- Malathion	0.013	No	120	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
75	Pirimiphos-methyl	0.076	No	98	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
75	Propiconazole	0.395	No	97	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
75	Tebuconazole	0.698	No	116	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
75	- Thiamethoxam	0.241	No	107	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
75	Trifloxystrobin	0.323	No	114	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
76	Azoxystrobin	0.166	No	105	Same batch	20	EtOAc	Cy-He			Yes	None	MM-ML			MS/MS	Different Method	S-19
76	Carbendazim and benomyl	0.132	No	97	Same batch	20	EtOAc	Cy-He			Yes	None	MM-ML			MS/MS	Different Method	S-19
76	Chlorpyrifos	0.199	No	84	Same batch	20	EtOAc	Cy-He			Yes	GPC, Silica gel	MM-ML		ECD		Different Method	S-19
76	Deltamethrin (cis)	0.133	No	87	Same batch	20	EtOAc	Cy-He			Yes	GPC, Silica gel	MM-ML		ECD		Different Method	S-19
76	Difenoconazole	0.079	No	114	Same batch	20	EtOAc	Cy-He			Yes	None	MM-ML			MS/MS	Different Method	S-19
76	Diflubenzuron	0.078	No	78	Same batch	20	EtOAc	Cy-He			Yes	None	MM-ML			MS/MS	Different Method	S-19
76	Epoxiconazole	0.053	No	65	Same batch	20	EtOAc	Cy-He			Yes	GPC	MM-ML		MSD		Different Method	S-19
76	Fipronil (parent comp.)	0.109	No	77	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		Different Method	QuEChERS - Citrate buffered
76	Isoprothiolane	0.175	No	105	Same batch	20	EtOAc	Cy-He			Yes	None	MM-ML			MS/MS	Different Method	S-19
76	Kresoxim-methyl	0.124	No	90	Same batch	20	EtOAc	Cy-He			Yes	GPC, Silica gel	MM-ML		ECD		Different Method	S-19
76	Pirimiphos-methyl	0.049	No	63	Same batch	20	EtOAc	Cy-He			Yes	GPC	MM-ML		MSD		Different Method	S-19
76	Propiconazole	0.319	No	92	Same batch	20	EtOAc	Cy-He			Yes	GPC, Silica gel	MM-ML		ECD		Different Method	S-19
76	Tebuconazole	0.459	No	53	Same batch	20	EtOAc	Cy-He			Yes	GPC	MM-ML		MSD		Different Method	S-19
76	- Thiamethoxam	0.080	No	80	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		Different Method	QuEChERS - Citrate buffered
76	Tricyclazole	0.281	No	129	Same batch	20	EtOAc	Cy-He			Yes	None	MM-ML			MS/MS	Different Method	S-19
76	Trifloxystrobin	0.189	No	106	Same batch	20	EtOAc	Cy-He			Yes	None	MM-ML			MS/MS	Different Method	S-19
77	Chlorpyrifos	0.210	No	86	Same batch	10	AC				Yes	Liq./liq. , SPE	PS-ML		NPD		Different Column	
77	- Malathion	0.012	No	84	Same batch	10	AC				Yes	Liq./liq. , SPE	PS-ML		NPD		Different Column	
77	Pirimiphos-methyl	0.073	No	84	Same batch	10	AC				Yes	Liq./liq. , SPE	PS-ML		NPD		Different Column	
78	Azoxystrobin	0.219	No	102	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Carbendazim and benomyl	0.153	No	96	Same batch	5	ACN				Yes	SPE (column)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS - Citrate buffered
78	Chlorpyrifos	0.189	No	93	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
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Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
78	Deltamethrin (cis)	0.134	No	89	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Difenoconazole	0.118	No	97	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Diflubenzuron	0.105	No	81	Same batch	5	ACN				Yes	SPE (column)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS - Citrate buffered
78	Epoxiconazole	0.104	No	94	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Fipronil (parent comp.)	0.120	No	96	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Isoprothiolane	0.195	No	87	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Kresoxim-methyl	0.195	No	88	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	- Malathion	0.011	No	91	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Pirimiphos-methyl	0.079	No	95	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Propiconazole	0.368	No	100	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
78	Tebuconazole	0.695	No	94	Same batch	5	ACN				Yes	None	PS-ML		FPD		GC-MSD	QuEChERS - Citrate buffered
78	- Thiamethoxam	0.192	No	97	Same batch	5	ACN				Yes	SPE (column)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS - Citrate buffered
78	Tricyclazole	0.210	No	87	Same batch	5	ACN				Yes	None	PS-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
78	Trifloxystrobin	0.235	No	100	Same batch	5	ACN				Yes	None	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
79	Azoxystrobin	0.110	No	110	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Terbutylazin D5		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	Carbendazim and benomyl	0.070	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Carbofuran D3		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	Chlorpyrifos	0.204	No	108	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	ChlorpyriphosMe-D6	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
79	Deltamethrin (cis)	0.203	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	ChlorpyriphosMe-D6	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
79	Difenoconazole	0.078	No	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Propiconazole D5		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	Diflubenzuron	0.099	No	122	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Propiconazole D5		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	Epoxiconazole	0.053	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Propiconazole D5		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	Kresoxim-methyl	0.393	No	114	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Propiconazole D5		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	Pirimiphos-methyl	0.066	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	ChlorpyriphosMe-D6	MS/MS		GC-MS/MS	QuEChERS - Citrate buffered
79	Tebuconazole	0.453	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Propiconazole D5		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
79	- Thiamethoxam	0.270	No	121	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Carbofuran D3		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	- Clothianidin	0.010	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Carbofuran D3		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
79	Trifloxystrobin	0.174	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	Carbofuran D3		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
80	Chlorpyrifos	0.202	No	86	Same batch	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		NPD		GC-MSD	extraction with AC, L:L extraction with CH_2Cl_2, SPE clean up
80	- Malathion	0.012	No	88	Same batch	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		NPD		GC-MSD	extraction with AC, L:L extraction with CH_2Cl_2, SPE clean up
80	Pirimiphos-methyl	0.073	No	87	Same batch	5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		NPD		GC-MSD	extraction with AC, L:L extraction with CH_2Cl_2, SPE clean up
81	Chlorpyrifos	0.202	No	96	Same batch	10	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD			PB-35/CHÅ» Edycja z dnia 25.02.2010 r.
81	- Malathion	0.011	No	90	Same batch	10	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD			PB-35/CHÅ» Edycja z dnia 25.02.2010 r.
81	Pirimiphos-methyl	0.070	No	88	Same batch	10	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD			PB-35/CHÅ» Edycja z dnia 25.02.2010 r.
82	Chlorpyrifos	0.200	No	80	Same batch	5	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD			
82	- Malathion	0.012	No	77	Same batch	5	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD			
82	Pirimiphos-methyl	0.067	No	78	Same batch	5	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD			
84	Azoxystrobin	0.168	No	103	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
84	Carbendazim and benomyl	0.109	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
84	Chlorpyrifos	0.181	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-FPD	QuEChERS - Citrate buffered
84	Deltamethrin (cis)	0.135	No	91	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	PCB 209	ECD		GC-MS/MS	QuEChERS - Citrate buffered
84	Difenoconazole	0.097	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
84	Diflubenzuron	0.094	No	112	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
84	Epoxiconazole	0.089	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
84	Fipronil (parent comp.)	0.138	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
84	Isoprothiolane	0.163	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
84	Kresoxim-methyl	0.169	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
84	- Malathion	0.010	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
84	Pirimiphos-methyl	0.070	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-FPD	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
84	Propiconazole	0.429	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
84	Tebuconazole	0.813	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
84	- Thiamethoxam	0.211	No	107	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
84	Tricyclazole	0.291	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS		QuEChERS - Citrate buffered
84	Trifloxystrobin	0.217	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
85	Azoxystrobin	0.127	No	110	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	endosulfan lactone	ECD		GC-MSD	
85	Chlorpyrifos	0.156	No	77	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	ethion	NPD		GC-MSD	
85	Deltamethrin (cis)	0.130	No	76	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	endosulfan lactone	ECD		GC-MSD	
85	Difenoconazole	0.071	No	109	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	ethion	MSD		GC-MSD	
85	Fipronil (parent comp.)	0.086	No	77	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	endosulfan lactone	ECD		GC-MSD	
85	Kresoxim-methyl	0.134	No	86	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	endosulfan lactone	ECD		GC-MSD	
85	Pirimiphos-methyl	0.052	No	77	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	ethion	NPD		GC-MSD	
85	Propiconazole	0.225	No	75	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	ethion	NPD		GC-MSD	
85	Tebuconazole	0.599	No	83	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	ethion	NPD		GC-MSD	
85	Trifloxystrobin	0.317	No	80	Same batch	5	ACN				Yes	Freeze-out, diato-maceous earth	PS-SL	endosulfan lactone	ECD		GC-MSD	
86	Azoxystrobin	0.180	No	104	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
86	Carbendazim and benomyl	0.140	No	78	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS		QuEChERS - Citrate buffered
86	Chlorpyrifos	0.229	No	96	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	TDCPP	NPD		GC-ECD	QuEChERS - Citrate buffered
86	Deltamethrin (cis)	0.139	No	98	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
86	Difenoconazole	0.106	No	101	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
86	Diflubenzuron	0.112	No	92	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS		QuEChERS - Citrate buffered
86	Epoxiconazole	0.092	No	98	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
86	Fipronil (parent comp.)	0.142	No	84	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-ECD	QuEChERS - Citrate buffered
86	Isoprothiolane	0.164	No	103	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS		QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
86	Kresoxim-methyl	0.160	No	86	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-ECD	QuEChERS - Citrate buffered
86	- Malathion	0.015	No	108	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	TDCPP	FPD		GC-ECD	QuEChERS - Citrate buffered
86	Pirimiphos-methyl	0.085	No	99	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	TDCPP	NPD		GC-MSD	QuEChERS - Citrate buffered
86	Propiconazole	0.427	No	92	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
86	Tebuconazole	0.858	No	106	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	GC-NPD	QuEChERS - Citrate buffered
86	- Thiamethoxam	0.198	No	97	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS		QuEChERS - Citrate buffered
86	Tricyclazole	0.296	No	85	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS		QuEChERS - Citrate buffered
86	Trifloxystrobin	0.220	No	100	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	GC-ECD	QuEChERS - Citrate buffered
87	Chlorpyrifos	0.204	Recovery fig.	110	Same batch	5	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD		GC-ECD	
87	- Malathion	0.012	Recovery fig.	110	Same batch	5	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD		GC-ECD	
87	Pirimiphos-methyl	0.071	Recovery fig.	120	Same batch	5	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD		GC-ECD	
88	Azoxystrobin	0.170	No	86	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
88	Carbendazim and benomyl	0.131	No	89	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
88	Chlorpyrifos	0.196	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TCP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
88	Deltamethrin (cis)	0.118	No	77	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TCP	MS/MS			QuEChERS - Citrate buffered
88	Difenoconazole	0.093	No	95	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
88	Diflubenzuron	0.113	No	90	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
88	Epoxiconazole	0.074	No	106	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TCP	MS/MS			QuEChERS - Citrate buffered
88	Fipronil (parent comp.)	0.161	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TCP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
88	Isoprothiolane	0.133	No	112	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
88	Kresoxim-methyl	0.190	No	93	Validation	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
88	- Malathion	0.008	No	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TCP	MS/MS		LC-MS/MS	QuEChERS - Citrate buffered
88	Pirimiphos-methyl	0.068	No	94	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
88	Propiconazole	0.422	No	91	Validation	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
88	Tebuconazole	0.722	No	116	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
88	- Thiamethoxam	0.244	No	104	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
88	Tricyclazole	0.294	No	90	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS		QuEChERS - Citrate buffered
88	Trifloxystrobin	0.243	No	84	Same batch	5	ACN				Yes	Freeze-out	MM-ML			MS/MS	GC-MS/MS	QuEChERS - Citrate buffered
89	Azoxystrobin	0.179	No	100	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Carbendazim and benomyl	0.124	No	89	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Chlorpyrifos	0.210	No	101	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Deltamethrin (cis)	0.171	No	100	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Difenoconazole	0.118	No	99	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Diflubenzuron	0.118	No	97	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Epoxiconazole	0.101	No	97	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Fipronil (parent comp.)	0.170	No	102	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Isoprothiolane	0.171	No	100	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Kresoxim-methyl	0.200	No	101	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Pirimiphos-methyl	0.086	No	100	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Propiconazole	0.501	No	97	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Tebuconazole	0.800	No	99	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	- Thiamethoxam	0.228	No	95	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Tricyclazole	0.287	No	66	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
89	Trifloxystrobin	0.238	No	99	Validation	5	ACN				Yes	DSPE ($PSA/MgSO_4$)	MM-ML	TDCPP		MS/MS		QuEChERS - Citrate buffered
90	Azoxystrobin	0.157	No	83	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Carbendazim and benomyl	0.115	No	81	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Chlorpyrifos	0.222	No	94	Same batch	5	ACN				Yes	None	MM-ML	bromophos-ethyl	MS/MS		GC-MS/MS	QuEChERS - Acetate buffered
90	Deltamethrin (cis)	0.208	No	96	Same batch	5	ACN				Yes	None	MM-ML	bromophos-ethyl	MS/MS		GC-MS/MS	QuEChERS - Acetate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
90	Difenoconazole	0.109	No	78	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Diflubenzuron	0.124	No	84	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Epoxiconazole	0.098	No	83	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Fipronil (parent comp.)	0.150	No	94	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Isoprothiolane	0.165	No	85	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Kresoxim-methyl	0.165	No	83	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	- Malathion	0.012	No	82	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Pirimiphos-methyl	0.063	No	80	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Propiconazole	0.498	No	76	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Tebuconazole	0.882	No	84	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	- Thiamethoxam	0.186	No	86	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	- Clothianidin	0.008	No	82	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Tricyclazole	0.300	No	80	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
90	Trifloxystrobin	0.196	No	82	Same batch	5	ACN				Yes	None	MM-ML	quinalphos		MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
91	Chlorpyrifos	0.194	No	99	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	PS-ML		NPD			
91	- Malathion	0.013	No	94	Validation	5	AC	CH_2Cl_2			Yes	SPE (column)	PS-ML		NPD			
91	Pirimiphos-methyl	0.068	No	96	Same batch	5	AC	CH_2Cl_2			Yes	SPE (column)	PS-ML		NPD			
92	Chlorpyrifos	0.170	Recovery fig.	72	Validation	10	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD		Different Column	
92	- Malathion	0.014	Recovery fig.	107		10	AC	CH_2Cl_2			Yes	Liq./liq. , SPE	PS-ML		NPD		Different Column	
93	Azoxystrobin	0.150	Yes, automatic	98	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	Carbendazim and benomyl	0.110	Yes, automatic	92	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
93	Chlorpyrifos	0.200	Yes, automatic	98	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	Deltamethrin (cis)	0.140	No	110	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		TOF		GC-MS/MS	QuEChERS - Citrate buffered
93	Difenoconazole	0.110	Yes, automatic	104	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
93	Diflubenzuron	0.100	Yes, automatic	103	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
93	Epoxiconazole	0.100	Yes, automatic	93	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	Fipronil (parent comp.)	0.160	Yes, automatic	105	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	Isoprothiolane	0.170	Yes, automatic	103	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	Kresoxim-methyl	0.180	Yes, automatic	102	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	- Malathion	0.020	No	115	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML		TOF		GC-MS/MS	QuEChERS - Citrate buffered
93	Pirimiphos-methyl	0.080	Yes, automatic	102	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	Propiconazole	0.480	Yes, automatic	101	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	Tebuconazole	0.840	Yes, automatic	99	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	- Thiamethoxam	0.230	Yes, automatic	94	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
93	- Clothianidin	0.008	Yes, automatic	95	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
93	Tricyclazole	0.330	Yes, automatic	99	Same batch	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
93	Trifloxystrobin	0.240	Yes, automatic	93	Validation	5	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	GC-TOF	QuEChERS - Citrate buffered
94	Azoxystrobin	0.144	No	100	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Carbendazim and benomyl	0.115	No	92	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Chlorpyrifos	0.175	No	99	Same batch	5	ACN				Yes	DSPE	MM-SL	TDCPP	MSD		GC-MSD	QuEChERS - Citrate buffered
94	Deltamethrin (cis)	0.151	No	118	Same batch	5	ACN				Yes	DSPE	MM-SL	TDCPP	MSD		GC-MSD	QuEChERS - Citrate buffered
94	Difenoconazole	0.083	No	101	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Diflubenzuron	0.083	No	101	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Epoxiconazole	0.078	No	107	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Fipronil (parent comp.)	0.144	No	106	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Isoprothiolane	0.123	No	97	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Kresoxim-methyl	0.143	No	107	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Pirimiphos-methyl	0.085	No	109	Same batch	5	ACN				Yes	DSPE	MM-SL	TDCPP	MSD		GC-MSD	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
94	Propiconazole	0.362	No	93	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Tebuconazole	0.696	No	100	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	- Thiamethoxam	0.196	No	96	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Tricyclazole	0.230	No	84	Same batch	5	ACN				Yes	None	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
94	Trifloxystrobin	0.206	No	105	Same batch	5	ACN				Yes	DSPE	MM-SL	TDCPP	MSD		GC-MSD	QuEChERS - Citrate buffered
95	Azoxystrobin	0.111	No	78	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Deltamethrin (cis)	0.125	No	68	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Difenoconazole	0.080	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Epoxiconazole	0.079	No	55	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Kresoxim-methyl	0.150	No	91	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Pirimiphos-methyl	0.195	No	83	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Propiconazole	0.509	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Tebuconazole	0.667	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
95	Trifloxystrobin	0.205	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
96	Azoxystrobin	0.148	No	83	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Carbendazim and benomyl	0.114	No	84	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Chlorpyrifos	0.165	No	83	Same batch	100	Cy-He	EtOAc			No	GPC	PS-SL	2,4,5-T-butylester	FPD		Different Column	S-19
96	Deltamethrin (cis)	0.123	No	87	Same batch	100	Cy-He	EtOAc			No	GPC	PS-SL	2,4,5-T-butylester	ECD		Different Column	S-19
96	Difenoconazole	0.093	No	91	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Diflubenzuron	0.092	No	87	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Epoxiconazole	0.086	No	89	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Fipronil (parent comp.)	0.190	No	85	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Isoprothiolane	0.144	No	83	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Kresoxim-methyl	0.138	No	96	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
96	- Malathion	0.011	No	85	Same batch	100	Cy-He	EtOAc			No	GPC	PS-SL	2,4,5-T-butylester	FPD		Different Column	S-19
96	Pirimiphos-methyl	0.067	No	88	Same batch	100	Cy-He	EtOAc			No	GPC	PS-SL	2,4,5-T-butylester	FPD		Different Column	S-19
96	Propiconazole	0.399	No	87	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Tebuconazole	0.772	No	90	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-SL			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	- Thiamethoxam	0.174	No	87	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Tricyclazole	0.269	No	87	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
96	Trifloxystrobin	0.187	No	90	Same batch	500	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
97	Azoxystrobin	0.981	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Chlorpyrifos	0.157	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Deltamethrin (cis)	0.087	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		ECD		GC-Ion Trap	QuEChERS - Acetate buffered
97	Difenoconazole	0.035	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Epoxiconazole	0.055	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Fipronil (parent comp.)	1.178	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Kresoxim-methyl	0.117	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Pirimiphos-methyl	0.069	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Propiconazole	0.606	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-Ion Trap	QuEChERS - Citrate buffered
97	Tebuconazole	0.210	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-Ion Trap	QuEChERS - Citrate buffered
98	Azoxystrobin	0.055				0												
98	Carbendazim and benomyl	0.039				0												
98	Chlorpyrifos	0.132				0												
98	Deltamethrin (cis)	0.126				0												
98	Difenoconazole	0.021				0												
98	Diflubenzuron	0.136				0												
98	Fipronil (parent comp.)	0.235				0												

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
98	Kresoxim-methyl	0.143				0												
98	Pirimiphos-methyl	0.054				0												
98	Propiconazole	0.410				0												
98	Tebuconazole	0.272				0												
98	- Thiamethoxam	0.023				0												
98	Trifloxystrobin	0.188				0												
100	Azoxystrobin	0.144	No	107	Validation	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		ECD			
100	Carbendazim and benomyl	0.085	No	80	Same batch	10	EtOAc	CH_2Cl_2	MeOH		Yes	Liq./liq.	PS-ML			Fluore-scence Det.		
100	Chlorpyrifos	0.175	No	93	Validation	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		ECD		GC-NPD	
100	Deltamethrin (cis)	0.149	No	119	Same batch	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		ECD			
100	Kresoxim-methyl	0.133	No	115	Same batch	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		ECD		GC-NPD	
100	- Malathion	0.012	No	109	Validation	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		ECD			
100	Pirimiphos-methyl	0.073	No	63	Same batch	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		NPD		GC-ECD	
100	Tebuconazole	0.823	No	83	Same batch	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		NPD			
100	Trifloxystrobin	0.170	No	108	Same batch	5	AC	CH_2Cl_2	EtOAc		Yes	GPC	MM-ML		ECD			
101	Chlorpyrifos	0.237	Yes, automatic	93	Validation	10	AC	CH_2Cl_2	Other		No	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
101	Deltamethrin (cis)	0.141	Yes, automatic	88	Validation	10	AC	CH_2Cl_2	Other		No	GPC	MM-ML	Mirex	MS/MS		GC-MS/MS	Mini-Luke-Type
101	- Malathion	0.014	Yes, automatic	105	Validation	10	AC	CH_2Cl_2	Other		No	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
101	Pirimiphos-methyl	0.104	Yes, automatic	85	Validation	10	AC	CH_2Cl_2	Other		No	GPC	MM-ML	TPP	MS/MS		GC-MS/MS	Mini-Luke-Type
102	Azoxystrobin	0.183	No	91	Same batch	10	AC	CH_2Cl_2	PE		Yes	centrifugation	MM-ML		Ion Trap		GC-MSD	Mini-Luke-Type
102	Chlorpyrifos	0.141	No	95	Same batch	10	AC	CH_2Cl_2	PE		Yes	centrifugation	MM-ML		Ion Trap		GC-MSD	Mini-Luke-Type
102	Deltamethrin (cis)	0.123	No	89	Same batch	10	AC	CH_2Cl_2	PE		Yes	centrifugation	MM-ML		Ion Trap		GC-MSD	Mini-Luke-Type
102	Pirimiphos-methyl	0.098	No	92	Same batch	10	AC	CH_2Cl_2	PE		Yes	centrifugation	MM-ML		Ion Trap		GC-MSD	Mini-Luke-Type
102	Propiconazole	0.417	No	85	Same batch	10	AC	CH_2Cl_2	PE		Yes	centrifugation	MM-ML		Ion Trap		GC-MSD	Mini-Luke-Type

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
102	Tebuconazole	0.673	No	82	Same batch	10	AC	CH_2Cl_2	PE		Yes	centrifugation	MM-ML		Ion Trap		GC-MSD	Mini-Luke-Type
103	Azoxystrobin	0.100	No	86	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	Carbendazim and benomyl	0.090	No	74	Same batch	10	EtOAc				Yes	None	MM-ML			MS/MS	LC-MS/MS	Ethylacetate type
103	Chlorpyrifos	0.162	No	92	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	Deltamethrin (cis)	0.144	No	95	Same batch	10	EtOAc				Yes	None	MM-ML		ECD		GC-Ion Trap	Ethylacetate type
103	Difenoconazole	0.051	No	85	Same batch	10	EtOAc				Yes	None	MM-ML			MS/MS	LC-MS/MS	Ethylacetate type
103	Diflubenzuron	0.089	No	99	Same batch	10	EtOAc				Yes	None	MM-ML			MS/MS	LC-MS/MS	Ethylacetate type
103	Epoxiconazole	0.056	No	86	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	Fipronil (parent comp.)	0.099	No	85	Same batch	10	EtOAc				Yes	None	MM-ML			MS/MS	LC-MS/MS	Ethylacetate type
103	Isoprothiolane	0.117	No	78	Same batch	0												
103	Kresoxim-methyl	0.118	No	83	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	Pirimiphos-methyl	0.049	No	91	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	Propiconazole	0.274	No	92	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	Tebuconazole	0.515	No	93	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	- Thiamethoxam	0.183	No	93	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
103	Tricyclazole	0.169	No	72	Same batch	10	EtOAc				Yes	None	MM-ML			MS/MS	LC-MS/MS	Ethylacetate type
103	Trifloxystrobin	0.159	No	94	Same batch	10	EtOAc				Yes	GPC	MM-ML			MS/MS	GC-Ion Trap	Ethylacetate type
104	Azoxystrobin	0.263	No	130	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Carbendazim and benomyl	0.126	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Chlorpyrifos	0.286	No	117	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Deltamethrin (cis)	0.243	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Difenoconazole	0.133	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Diflubenzuron	0.176	No	80	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Epoxiconazole	0.110	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
104	Fipronil (parent comp.)	0.200	No	137	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Isoprothiolane	0.189	No	104	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Kresoxim-methyl	0.223	No	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	- Malathion	0.014	No	109	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Pirimiphos-methyl	0.095	No	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Propiconazole	0.611	No	123	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Tebuconazole	1.074	No	117	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	- Thiamethoxam	0.231	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	- Clothianidin	0.010	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
104	Trifloxystrobin	0.304	No	139	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MS/MS		GC-MS/MS	
105	Chlorpyrifos	0.190	No	87	Same batch	3	AC	CH_2Cl_2	EtOAc		No	None	MM-ML	TPP	NPD			
105	Deltamethrin (cis)	0.178	No	91	Same batch	3	AC	CH_2Cl_2	EtOAc		No	None	MM-ML	Mirex	ECD			
105	- Malathion	0.011	No	85	Same batch	3	AC	CH_2Cl_2	EtOAc		No	None	MM-ML	TPP	NPD			
105	Pirimiphos-methyl	0.068	No	90	Same batch	3	AC	CH_2Cl_2	EtOAc		No	None	MM-ML	TPP	NPD			
106	Chlorpyrifos	0.060	No			0	EtOAc	EtOAc	EtOAc		No	diatomaceous earth	MM-ML	fenchlorfos	MS/MS		GC-MS/MS	ISTISAN 1997/23 1997/24
106	Kresoxim-methyl	0.120	No			6	EtOAc	EtOAc	EtOAc		No	diatomaceous earth	MM-ML	fenchlorfos	MS/MS		GC-MS/MS	ISTISAN 1997/23 1997/24
106	Pirimiphos-methyl	0.060	No			6	EtOAc	EtOAc	EtOAc		No	diatomaceous earth	MM-ML	fenchlorfos	MS/MS		GC-MS/MS	ISTISAN 1997/23 1997/24
106	Propiconazole	0.160	No			6	EtOAc	EtOAc	EtOAc		No	diatomaceous earth	MM-ML	fenchlorfos	MS/MS		GC-MS/MS	ISTISAN 1997/23 1997/24
107	Azoxystrobin	0.176	No	97	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Carbendazim and benomyl	0.096	No	75	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Chlorpyrifos	0.218	No	98	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Deltamethrin (cis)	0.121	No	72	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Difenoconazole	0.114	No	97	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Diflubenzuron	0.113	No	105	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
107	Fipronil (parent comp.)	0.127	No	98	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Kresoxim-methyl	0.182	No	94	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Pirimiphos-methyl	0.092	No	104	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Propiconazole	0.516	No	103	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Tebuconazole	0.850	No	96	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	- Thiamethoxam	0.216	No	85	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
107	Trifloxystrobin	0.216	No	100	Same batch	5	ACN				Yes	DSPE	PS-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
108	Azoxystrobin	0.151	No	122	Same batch	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
108	Carbendazim and benomyl	0.118	No	80		6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
108	Chlorpyrifos	0.310	No	98	Validation	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
108	Difenoconazole	0.134	No	98	Validation	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
108	Epoxiconazole	0.088	No	97	Same batch	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
108	Kresoxim-methyl	0.238	No	71	Validation	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
108	Pirimiphos-methyl	0.215	No	84	Validation	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
108	Propiconazole	0.557	No	101	Validation	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
108	Tebuconazole	0.914	No	105	Validation	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
108	- Thiamethoxam	0.227	No	124	Same batch	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
108	Trifloxystrobin	0.134	No	94	Validation	6	ACN				Yes	Freeze-out DSPE ($PSA/MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS - Citrate buffered
109	Carbendazim and benomyl	0.151	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
109	Difenoconazole	0.043	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
109	Epoxiconazole	0.120	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
109	- Malathion	0.011	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
109	Pirimiphos-methyl	0.084	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
109	Propiconazole	0.465	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
109	Tebuconazole	0.789	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
109	- Thiamethoxam	0.207	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
109	- Clothianidin	0.012	No			5	ACN				Yes	DSPE	MM-ML			MS/MS	LC-MS/MS	UNI EN 15662:2009
110	Chlorpyrifos	0.190	No	104	Same batch	10	ACN				Yes	Freeze-out DSPE (PSA/$MgSO_4$)	PS-ML	Triphenylmethane, TPP	MSD		GC-MSD	QuEChERS - Citrate buffered
111	Azoxystrobin	0.203	No	96	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	trichloronate	Ion Trap		LC-MS/MS	QuEChERS - Citrate buffered
111	Carbendazim and benomyl	0.137	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP		MS/MS		QuEChERS - Citrate buffered
111	Chlorpyrifos	0.292	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	trichloronate	Ion Trap			QuEChERS - Citrate buffered
111	Deltamethrin (cis)	0.274	No	84	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	trichloronate	Ion Trap			QuEChERS - Citrate buffered
111	Difenoconazole	0.096	No	73	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TPP		MS/MS	GC-Ion Trap	QuEChERS - Citrate buffered
111	Diflubenzuron	0.117	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	TPP		MS/MS		QuEChERS - Citrate buffered
111	Epoxiconazole	0.144	No	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	trichloronate	Ion Trap			QuEChERS - Citrate buffered
111	Kresoxim-methyl	0.237	No	117	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	trichloronate	Ion Trap		LC-MS/MS	QuEChERS - Citrate buffered
111	Pirimiphos-methyl	0.090	No	107	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	trichloronate	Ion Trap			QuEChERS - Citrate buffered
111	Propiconazole	0.441	Recovery fig.	137	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	trichloronate	Ion Trap		LC-MS/MS	QuEChERS - Citrate buffered
111	Tebuconazole	0.815	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML	trichloronate	Ion Trap		LC-MS/MS	QuEChERS - Citrate buffered
111	Trifloxystrobin	0.210	No	80	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	STD Add.	TPP		MS/MS	GC-Ion Trap	QuEChERS - Citrate buffered
113	Azoxystrobin	0.156	No	120	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-UV or DAD	QuEChERS (original version)
113	Carbendazim and benomyl	0.120	No	91	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS (original version)
113	Chlorpyrifos	0.168	No	93	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		NPD		GC-ECD	QuEChERS (original version)
113	Deltamethrin (cis)	0.118	No	87	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-ECD	QuEChERS (original version)
113	Difenoconazole	0.099	No	129	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-UV or DAD	QuEChERS (original version)
113	Diflubenzuron	0.106	No	91	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS (original version)
113	Epoxiconazole	0.070	No	115	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-UV or DAD	QuEChERS (original version)
113	Fipronil (parent comp.)	0.111	No	92	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-ECD	QuEChERS (original version)

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
113	Isoprothiolane	0.116	No	78	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-ECD	QuEChERS (original version)
113	Kresoxim-methyl	0.128	No	107	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-ECD	QuEChERS (original version)
113	- Malathion	0.010	No	98	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		NPD		GC-ECD	QuEChERS (original version)
113	Pirimiphos-methyl	0.067	No	94	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		NPD		GC-ECD	QuEChERS (original version)
113	Propiconazole	0.261	No	89	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-UV or DAD	QuEChERS (original version)
113	Tebuconazole	0.732	No	99	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS (original version)
113	- Thiamethoxam	0.352	No	96	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS (original version)
113	Tricyclazole	0.243	No	85	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			UV or DAD	LC-UV or DAD	QuEChERS (original version)
113	Trifloxystrobin	0.141	No	106	Same batch	15	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-UV or DAD	QuEChERS (original version)
114	Azoxystrobin	0.228	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-MS	QuEChERS - Citrate buffered
114	Carbendazim and benomyl	0.140	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS		QuEChERS - Citrate buffered
114	Chlorpyrifos	0.220	No	112	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		FPD		GC-NPD	QuEChERS - Citrate buffered
114	Deltamethrin (cis)	0.176	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-ECD	QuEChERS - Citrate buffered
114	Difenoconazole	0.146	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-MS	QuEChERS - Citrate buffered
114	Diflubenzuron	0.098	No	70	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS		QuEChERS - Citrate buffered
114	Epoxiconazole	0.053	No	102	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-MS	QuEChERS - Citrate buffered
114	Fipronil (parent comp.)	0.150	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
114	Isoprothiolane	0.169	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-MS	QuEChERS - Citrate buffered
114	Kresoxim-methyl	0.166	No	78	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-MSD	QuEChERS - Citrate buffered
114	- Malathion	0.019	No	85	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		FPD		GC-NPD	QuEChERS - Citrate buffered
114	Pirimiphos-methyl	0.090	No	114	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		FPD		GC-NPD	QuEChERS - Citrate buffered
114	Propiconazole	0.353	No	110	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-MS	QuEChERS - Citrate buffered
114	Tebuconazole	1.040	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		NPD		LC-MS	QuEChERS - Citrate buffered
114	- Thiamethoxam	0.213	No	70	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS		QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
114	Tricyclazole	0.393	No	70	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS		QuEChERS - Citrate buffered
114	Trifloxystrobin	0.242	No	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		LC-MS	QuEChERS - Citrate buffered
115	Chlorpyrifos	0.210	No	89	Same batch	10	Other	CH_2Cl_2			Yes	SPE (column)	PS-ML		NPD		GC-FPD	
115	- Malathion	0.014	No	89	Same batch	10	Other	CH_2Cl_2			Yes	SPE (column)	PS-ML		NPD		GC-FPD	
115	Pirimiphos-methyl	0.069	No	91	Same batch	10	Other	CH_2Cl_2			Yes	SPE (column)	PS-ML		NPD		GC-FPD	
116	Azoxystrobin	0.120	No	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Carbendazim and benomyl	0.103	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Chlorpyrifos	0.138	No	83	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	Deltamethrin (cis)	0.089	No	118	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	Difenoconazole	0.056	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Diflubenzuron	0.078	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Epoxiconazole	0.058	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Fipronil (parent comp.)	0.113	No	91	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	Isoprothiolane	0.140	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	Kresoxim-methyl	0.133	No	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	- Malathion	0.015	No	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Pirimiphos-methyl	0.090	No	79	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	Propiconazole	0.230	No	59	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	Tebuconazole	0.484	No	77	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
116	- Thiamethoxam	0.100	No	72	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Tricyclazole	0.180	No	86	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
116	Trifloxystrobin	0.168	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS (original version)
117	Chlorpyrifos	0.148	No	85	Same batch	7	AC	CH_2Cl_2			No	Liq./liq.	MM-ML	TPP	MSD		GC-MSD	Mini-Luke-Type
117	Deltamethrin (cis)	0.122	No	85	Same batch	7	AC	CH_2Cl_2			No	Liq./liq.	MM-ML	Mirex	ECD		GC-ECD	Mini-Luke-Type

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
117	- Endosulfan sulfate	0.078	No	82	Same batch	7	AC	CH_2Cl_2			No	Liq./liq.	MM-ML	Mirex	ECD		GC-ECD	Mini-Luke-Type
117	- Malathion	0.018	No	84	Same batch	7	AC	CH_2Cl_2			No	Liq./liq.	MM-ML	TPP	MSD		GC-MSD	Mini-Luke-Type
117	Pirimiphos-methyl	0.045	No	88	Same batch	7	AC	CH_2Cl_2			No	Liq./liq.	MM-ML	TPP	MSD		GC-MSD	Mini-Luke-Type
118	Azoxystrobin	0.150	No	98	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Chlorpyrifos	0.231	No	105	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Deltamethrin (cis)	0.140	No	86	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Fipronil (parent comp.)	0.159	No	103	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Kresoxim-methyl	0.195	No	108	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Pirimiphos-methyl	0.092	No	107	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Propiconazole	0.410	No	88	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Tebuconazole	0.752	No	94	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
118	Trifloxystrobin	0.250	No	96	Validation	5	ACN				Yes	Freeze-out DSPE(ODS/$MgSO_4$)	MM-ML	TDCPP	MSD		GC-MS/MS	QuEChERS - Citrate buffered
120	Azoxystrobin	0.054	No	77	Same batch	25	EtOAc				Yes	GPC	MM-ML		ECD		GC-TOF	EN 12393-2
120	Carbendazim and benomyl	0.065	No	74	Same batch	25	EtOAc				Yes	GPC	PS-ML			UV or DAD		Internal method based on EN 12393-2
120	Chlorpyrifos	0.134	No	83	Same batch	25	EtOAc				Yes	GPC	MM-ML	TPP	TOF			EN 12393-2
120	Deltamethrin (cis)	0.138	No	85	Same batch	25	EtOAc				Yes	GPC	MM-ML		ECD		GC-TOF	EN 12393-2
120	Difenoconazole	0.077	No	67	Same batch	25	EtOAc				Yes	GPC	MM-ML		ECD		GC-TOF	EN 12393-2
120	Epoxiconazole	0.056	No	74	Same batch	25	EtOAc				Yes	GPC	MM-ML		ECD		GC-TOF	EN 12393-2
120	Kresoxim-methyl	0.137	No	91	Same batch	25	EtOAc				Yes	GPC	MM-ML	TPP	TOF			EN 12393-2
120	Pirimiphos-methyl	0.071	No	81	Same batch	25	EtOAc				Yes	GPC	MM-ML	TPP	TOF			EN 12393-2
120	Propiconazole	0.360	No	66	Same batch	25	EtOAc				Yes	GPC	MM-ML	TPP	TOF			EN 12393-2
120	Tebuconazole	0.608	No	90	Same batch	25	EtOAc				Yes	GPC	MM-ML	TPP	TOF			EN 12393-2
120	Trifloxystrobin	0.174	No	90	Same batch	25	EtOAc				Yes	GPC	MM-ML	TPP	TOF			EN 12393-2
121	Azoxystrobin	0.165	Yes, automatic	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
121	Carbendazim and benomyl	0.122	Yes, automatic	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Chlorpyrifos	0.195	Yes, automatic	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Deltamethrin (cis)	0.133	Yes, automatic	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Difenoconazole	0.122	Yes, automatic	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Diflubenzuron	0.181	Yes, automatic	86	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Epoxiconazole	0.109	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Fipronil (parent comp.)	0.126	Yes, automatic	76	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Isoprothiolane	0.208	Yes, automatic	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Kresoxim-methyl	0.172	Yes, automatic	115	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	- Malathion	0.012	Yes, automatic	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Pirimiphos-methyl	0.094	Yes, automatic	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Tebuconazole	0.925	Yes, automatic	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	- Thiamethoxam	0.228	Yes, automatic	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	- Clothianidin	0.012	Yes, automatic	100	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Tricyclazole	0.329	Yes, automatic	89	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
121	Trifloxystrobin	0.265	Yes, automatic	108	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
123	Azoxystrobin	0.184	No	107	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Carbendazim and benomyl	0.119	No	91	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Chlorpyrifos	0.200	No	90	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Deltamethrin (cis)	0.140	No	81	Validation	10	ACN	AC			No	GPC, SPE	MM-ML	PCB 209	MSD		LC-MS/MS	VDLUFA MB VII (2008), 3.3.7.1
123	Difenoconazole	0.121	No	99	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Diflubenzuron	0.218	No	107	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Epoxiconazole	0.117	No	104	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Fipronil (parent comp.)	0.164	No	101	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
123	Isoprothiolane	0.180	No	104	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Kresoxim-methyl	0.188	No	105	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	- Malathion	0.013	No	107	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Pirimiphos-methyl	0.090	No	100	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Propiconazole	0.557	No	103	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Tebuconazole	0.868	No	101	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	- Thiamethoxam	0.221	No	96	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	- Clothianidin	0.011	No	110	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Tricyclazole	0.355	No	99	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
123	Trifloxystrobin	0.230	No	104	Same batch	5	ACN				Yes	DSPE	MM-ML			MS/MS		QuEChERS - Citrate buffered
124	Azoxystrobin	0.185	No	113	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Carbendazim and benomyl	0.122	No	106	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Chlorpyrifos	0.233	No	111	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Deltamethrin (cis)	0.172	No	105	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP	TOF		GC-TOF	QuEChERS - Citrate buffered
124	Difenoconazole	0.126	No	111	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Diflubenzuron	0.129	No	99	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	nicarbazin		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Epoxiconazole	0.100	No	109	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Fipronil (parent comp.)	0.209	No	98	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	nicarbazin		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Kresoxim-methyl	0.222	No	114	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	- Malathion	0.016	No	101	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Pirimiphos-methyl	0.082	No	117	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP	TOF		GC-TOF	QuEChERS - Citrate buffered
124	Propiconazole	0.528	No	112	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Tebuconazole	0.669	No	109	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	- Thiamethoxam	0.254	No	109	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
124	- Clothianidin	0.012	No	114	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
124	Trifloxystrobin	0.221	No	105	Same batch	5	ACN				Yes	Liq./liq.	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
125	Azoxystrobin	0.191	No	86	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Carbendazim and benomyl	0.136	No	83	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Chlorpyrifos	0.203	No	92	Same batch	10	AC	MeOH			No	GPC	MM-ML		MSD		GC-MSD	
125	Deltamethrin (cis)	0.179	No	90	Same batch	10	AC	MeOH			No	GPC	MM-ML		MSD		GC-MSD	
125	Difenoconazole	0.129	No	82	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Diflubenzuron	0.148	No	96	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Epoxiconazole	0.096	No	96	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Fipronil (parent comp.)	0.196	No	80	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Isoprothiolane	0.201	No	85	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Kresoxim-methyl	0.197	No	87	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	- Malathion	0.011	No	85	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Pirimiphos-methyl	0.064	No	92	Same batch	10	AC	MeOH			No	GPC	MM-ML		MSD		GC-MSD	
125	Propiconazole	0.589	No	86	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Tebuconazole	0.937	No	86	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	- Thiamethoxam	0.275	No	83	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Tricyclazole	0.347	No	83	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
125	Trifloxystrobin	0.250	No	95	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	GC-MS/MS	QuEChERS (original version)
126	Azoxystrobin	0.196	No	83	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Carbendazim and benomyl	0.048	No	75	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
126	Chlorpyrifos	0.160	No	91	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Deltamethrin (cis)	0.135	No	77	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Difenoconazole	0.061	No	91	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
126	Epoxiconazole	0.051	No	78	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Fipronil (parent comp.)	0.194	Recovery fig.	53	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Kresoxim-methyl	0.109	No	72	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Pirimiphos-methyl	0.052	No	87	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Propiconazole	0.284	No	92	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	Tebuconazole	0.667	Recovery fig.	66	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
126	- Thiamethoxam	0.226	No	72	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
126	- Clothianidin	0.009	No	81	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
126	Trifloxystrobin	0.149	No	82	Same batch	5	EtOAc				Yes	GPC	MM-ML		MSD		GC-MSD	Ethylacetate type
127	Azoxystrobin	0.129	No	88	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Chlorpyrifos	0.236	No	109	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Deltamethrin (cis)	0.132	No	87	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Difenoconazole	0.080	No	91	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Epoxiconazole	0.097	No	100	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Fipronil (parent comp.)	0.143	No	87	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Isoprothiolane	0.145	No	73	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Kresoxim-methyl	0.182	No	91	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	- Malathion	0.012	No	90	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Pirimiphos-methyl	0.079	No	105	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Propiconazole	0.467	No	106	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Tebuconazole	0.876	No	101	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Tricyclazole	0.332	No	85	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
127	Trifloxystrobin	0.216	No	90	Same batch	5	ACN				Yes	SPE (column)	MM-ML	TPP	MSD			QuEChERS - Citrate buffered
128	Azoxystrobin	0.082	No	99	Same batch	5	EtOAc				Yes	SPE (column)			ECD		GC-MSD	Ethylacetate type

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
128	Chlorpyrifos	0.158	No	99	Same batch	5	EtOAc				Yes	SPE (column)			ECD		GC-MSD	Ethylacetate type
128	Deltamethrin (cis)	0.103	No	88	Same batch	5	EtOAc				Yes	SPE (column)			ECD		GC-MSD	Ethylacetate type
128	Kresoxim-methyl	0.125	No	95	Same batch	5	EtOAc				Yes	SPE (column)			ECD		GC-MSD	Ethylacetate type
128	Propiconazole	0.264	No	93	Same batch	5	EtOAc				Yes	SPE (column)			ECD		GC-MSD	Ethylacetate type
128	Trifloxystrobin	0.143	No	101	Same batch	5	EtOAc				Yes	SPE (column)			ECD		GC-MSD	Ethylacetate type
129	Chlorpyrifos	0.187	No	82	Same batch	10	AC	CH_2Cl_2			Yes	Freeze-out, SPE (C18)	PS-ML	Ethion	NPD		Different Column	ISO 14182
129	Deltamethrin (cis)	0.176	No	104	Same batch	20	AC	CH_2Cl_2			Yes	Freeze-out, SPE (C18, florisil)	PS-ML	Transnonachlor	ECD		Different Column	ISO 14182
129	Pirimiphos-methyl	0.061	No	76	Same batch	10	AC	CH_2Cl_2			Yes	Freeze-out, SPE (C18)	PS-ML	Ethion	NPD		Different Column	ISO 14182
131	Azoxystrobin	0.146	No	82	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$), SPE (C18)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Carbendazim and benomyl	0.109	No	82	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$), SPE (C18)	PS-ML	isoproturon D6		MS/MS	LC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Chlorpyrifos	0.191	No	101	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Deltamethrin (cis)	0.040	No	86	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Difenoconazole	0.108	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Diflubenzuron	0.195	No	68	Same batch	5	MeOH				Yes		PS-ML	mcpp D3		MS/MS	LC-MS/MS	
131	Epoxiconazole	0.083	No	81	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Fipronil (parent comp.)	0.156	No	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Kresoxim-methyl	0.162	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	- Malathion	0.011	No	98	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Pirimiphos-methyl	0.076	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Propiconazole	0.508	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	Tebuconazole	0.832	No	83	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	- Thiamethoxam	0.243	No	95	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$), SPE (C18)	PS-ML	isoproturon D6		MS/MS	LC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003
131	- Clothianidin	0.009	No	100	Same batch	5	MeOH				Yes		PS-ML	isoproturon D6		MS/MS	LC-MS/MS	
131	Trifloxystrobin	0.199	No	91	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	anthracene	MS/MS		GC-MS/MS	Klein, Alder, J. AOAC 86/1015/2003

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
135	Azoxystrobin	0.144	No	80		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		ECD		GC-MSD	Mini-Luke-Type
135	Chlorpyrifos	0.164	No	75		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		FPD		GC-MSD	Mini-Luke-Type
135	Deltamethrin (cis)	0.172	No	85		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		ECD		GC-MSD	Mini-Luke-Type
135	Difenoconazole	0.086	No	75		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		MSD		GC-MSD	Mini-Luke-Type
135	Epoxiconazole	0.068	No	95		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		MSD		GC-MSD	Mini-Luke-Type
135	Fipronil (parent comp.)	0.131	No	85		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		ECD		GC-MSD	Mini-Luke-Type
135	Kresoxim-methyl	0.144	No	80		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		NPD		GC-MSD	Mini-Luke-Type
135	- Malathion	0.011	No	80		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		FPD		GC-MSD	Mini-Luke-Type
135	Pirimiphos-methyl	0.062	No	75		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		FPD		GC-MSD	Mini-Luke-Type
135	Tebuconazole	0.610	No	75		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		NPD		GC-MSD	Mini-Luke-Type
135	Trifloxystrobin	0.178	No	85		5	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		ECD		GC-MSD	Mini-Luke-Type
136	Chlorpyrifos	0.141	No	92	Same batch	5	AC	n-HEX			Yes	Liq./liq. , SPE	PS-ML	PCB97	ECD		Different Column	
136	Pirimiphos-methyl	0.076	No	99	Same batch	5	AC	n-HEX			Yes	Liq./liq. , SPE	PS-ML	TBP	NPD			
138	Chlorpyrifos	0.216	Yes, automatic	103	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
138	Difenoconazole	0.107	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
138	Epoxiconazole	0.100	Yes, automatic	103	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
138	Pirimiphos-methyl	0.073	Yes, automatic	100	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
138	Propiconazole	0.479	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
138	Tebuconazole	0.816	No			5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
138	Trifloxystrobin	0.173	Yes, automatic	103	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
139	Azoxystrobin	0.180	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	Carbendazim and benomyl	0.141	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	Chlorpyrifos	0.179	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.		MS/MS		GC-MS/MS	
139	Deltamethrin (cis)	0.194	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.		MS/MS		GC-MS/MS	

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
139	Difenoconazole	0.090	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.			MS/MS	LC-MS/MS	
139	Diflubenzuron	0.105	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.			MS/MS	LC-MS/MS	
139	Epoxiconazole	0.092	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.		MS/MS		GC-MS/MS	
139	Fipronil (parent comp.)	0.134	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	Kresoxim-methyl	0.138	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.		MS/MS		GC-MS/MS	
139	- Malathion	0.006	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.		MS/MS		GC-MS/MS	
139	Pirimiphos-methyl	0.063	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.		MS/MS		GC-MS/MS	
139	Propiconazole	0.294	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	Tebuconazole	0.617	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	- Thiamethoxam	0.333	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	- Clothianidin	0.009	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	Tricyclazole	0.389	Yes, automatic		Std add.	3	EtOAc				Yes	None	STD Add.			MS/MS	LC-MS/MS	Ethylacetate type
139	Trifloxystrobin	0.230	Yes, automatic		Std add.	2	Other			+	Yes	GPC	STD Add.		MS/MS		GC-MS/MS	
140	Azoxystrobin	0.177	No	102	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	GC-ECD	QuEChERS - Citrate buffered
140	Carbendazim and benomyl	0.177	No	87	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
140	Chlorpyrifos	0.186	No	72	Same batch	25	AC	CH_2Cl_2	Other		Yes	None	MM-ML		NPD		GC-TOF	Mini-Luke-Type
140	Deltamethrin (cis)	0.146	No	80	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	GC-ECD	QuEChERS - Citrate buffered
140	Difenoconazole	0.105	No	96	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
140	Epoxiconazole	0.12	No	91	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	GC-ECD	QuEChERS - Citrate buffered
140	Fipronil (parent comp.)	0.145	No	89	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	GC-ECD	QuEChERS - Citrate buffered
140	Kresoxim-methyl	0.134	No	70	Same batch	5	ACN				Yes	None	MM-ML		TOF		GC-ECD	QuEChERS - Citrate buffered
140	Pirimiphos-methyl	0.068	No	69	Same batch	25	AC	CH_2Cl_2	Other		Yes	None	MM-ML		NPD		GC-TOF	Mini-Luke-Type
140	Propiconazole	0.499	No	85	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
140	Tebuconazole	0.842	No	82	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
140	- Thiamethoxam	0.261	No	89	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
140	Trifloxystrobin	0.224	No	74	Same batch	5	ACN				Yes	None	MM-ML		TOF		GC-ECD	QuEChERS - Citrate buffered
141	Azoxystrobin	0.182	No	96	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Carbendazim and benomyl	0.134	No	111	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Chlorpyrifos	0.103	No	103	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML		MS/MS		GC-Ion Trap	Mini-Luke-Type
141	Deltamethrin (cis)	0.197	No	91	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML		MS/MS		GC-Ion Trap	Mini-Luke-Type
141	Difenoconazole	0.116	No	116	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Diflubenzuron	0.118	No	103	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Epoxiconazole	0.119	No	98	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Fipronil (parent comp.)	0.172	No	96	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML		MS/MS		GC-Ion Trap	Mini-Luke-Type
141	Isoprothiolane	0.191	No	105	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Kresoxim-methyl	0.189	No	101	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Pirimiphos-methyl	0.071	No	91	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML		MS/MS		GC-Ion Trap	Mini-Luke-Type
141	Propiconazole	0.498	No	94	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Tebuconazole	0.903	No	92	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	- Thiamethoxam	0.223	No	93	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	- Clothianidin	0.009	No	98	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Tricyclazole	0.370	No	102	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
141	Trifloxystrobin	0.218	No	92	Same batch	5	AC	CH_2Cl_2	Other		Yes	Filter	PS-ML			MS/MS	GC-MS/MS	Mini-Luke-Type
142	Chlorpyrifos	0.142	No			10	EtOAc				No	DSPE	MM-ML		MSD		GC-Ion Trap	Ethylacetate type
142	Pirimiphos-methyl	0.068	No			10	EtOAc				No	DSPE	MM-ML		MSD		GC-Ion Trap	Ethylacetate type
143	Azoxystrobin	0.122	No	107	Same batch	12	EtOAc				Yes		MM-ML		ECD		Different Column	
143	Chlorpyrifos	0.180	No	102	Same batch	12	EtOAc				Yes		MM-ML		NPD		Different Column	
143	Deltamethrin (cis)	0.172	No	98	Same batch	12	EtOAc				Yes		MM-ML		ECD		Different Column	

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
143	Kresoxim-methyl	0.128	No	96	Same batch	12	EtOAc				Yes		MM-ML		ECD		Different Column	
143	Pirimiphos-methyl	0.047	No	78	Same batch	12	EtOAc				Yes		MM-ML		NPD		Different Column	
143	Propiconazole	0.391	No	94	Same batch	12	EtOAc				Yes		MM-ML		NPD		Different Column	
144	Chlorpyrifos	0.255	No	106	Same batch	5	Other			+	No	GPC	MM-ML	PCB 209	MS/MS		GC-MS/MS	
144	Deltamethrin (cis)	0.296	No	92	Same batch	5	Other			+	No	GPC	MM-ML	PCB 209	MS/MS		GC-MS/MS	
144	- Malathion	0.024	No	95	Same batch	5	Other			+	No	GPC	MM-ML	PCB 209	MS/MS		GC-MS/MS	
144	Pirimiphos-methyl	0.083	No	86	Same batch	5	Other			+	No	GPC	MM-ML	PCB 209	MS/MS		GC-MS/MS	
145	Azoxystrobin	0.100	Recovery fig.	120	Same batch	10												QuEChERS
145	Carbendazim and benomyl	0.100	Recovery fig.	110	Same batch	10												
145	Difenoconazole	0.200	Recovery fig.	50	Same batch	10												
145	Epoxiconazole	0.120	Recovery fig.	65	Same batch	10												
145	Fipronil (parent comp.)	0.120	Recovery fig.	105	Same batch	10												
145	Kresoxim-methyl	0.140	Recovery fig.	95	Same batch	10												
145	Propiconazole	0.650	Recovery fig.	70	Same batch	10												
145	Tebuconazole	1	Recovery fig.	60	Same batch	10												
145	Trifloxystrobin	0.370	Recovery fig.	55	Same batch	10												
146	Azoxystrobin	0.114	No	82	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TDCP	MSD			QuEChERS - Citrate buffered
146	Chlorpyrifos	0.205	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TDCP	MSD			QuEChERS - Citrate buffered
146	Difenoconazole	0.106	No	115	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TDCP	MSD			QuEChERS - Citrate buffered
146	Epoxiconazole	0.082	No	112	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
146	Fipronil (parent comp.)	0.149	No	120	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
146	Kresoxim-methyl	0.143	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TDCP	MSD			QuEChERS - Citrate buffered
146	Pirimiphos-methyl	0.083	No	105	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TDCP	MSD			QuEChERS - Citrate buffered
146	Propiconazole	0.388	No	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
146	Tebuconazole	0.908	No	115	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TDCP	MSD			QuEChERS - Citrate buffered
146	- Thiamethoxam	0.237	No	106	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
146	- Clothianidin	0.017	No	118	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
146	Trifloxystrobin	0.225	No	114	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
147	Azoxystrobin	0.061	No	80	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Carbendazim and benomyl	0.092	No	80	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Chlorpyrifos	0.127	No	81	Same batch	10	EtOAc				No	None	MM-ML		MS/MS		GC-MS/MS	
147	Deltamethrin (cis)	0.104	Recovery fig.	68	Same batch	10	EtOAc				No	None	MM-ML		MS/MS		GC-MS/MS	
147	Difenoconazole	0.078	No	78	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Diflubenzuron	0.104	No	74	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Epoxiconazole	0.049	No	88	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Fipronil (parent comp.)	0.100	No	87	Same batch	10	EtOAc				No	None	MM-ML		MS/MS		GC-MS/MS	
147	Isoprothiolane	0.070	No	88	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Kresoxim-methyl	0.178	No	81	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Pirimiphos-methyl	0.052	No	88	Same batch	10	EtOAc				No	None	MM-ML		MS/MS		GC-MS/MS	
147	Propiconazole	0.303	No	81	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Tebuconazole	0.571	No	88	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	- Thiamethoxam	0.067	No	85	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
147	Trifloxystrobin	0.187	No	75	Same batch	10	EtOAc				No	None	MM-SL			MS/MS	LC-MS/MS	
148	Azoxystrobin	0.136	No	86	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Carbendazim and benomyl	0.065	No	83	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Chlorpyrifos	0.159	No	72	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Deltamethrin (cis)	0.145	No	92	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Difenoconazole	0.093	No	97	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
148	Diflubenzuron	0.172	No	99	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Fipronil (parent comp.)	0.133	No	106	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Kresoxim-methyl	0.137	No	91	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Pirimiphos-methyl	0.066	No	85	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Propiconazole	0.370	No	80	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Tebuconazole	0.719	No	85	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	- Thiamethoxam	0.177	No	86	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
148	Trifloxystrobin	0.133	No	94	Same batch	5	ACN				Yes	None	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
149	Azoxystrobin	0.140	No	73	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Carbendazim and benomyl	0.050	No	40	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Chlorpyrifos	0.190	No	79	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Deltamethrin (cis)	0.100	No	128	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Difenoconazole	0.090	No	67	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Diflubenzuron	0.090	No	64	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Epoxiconazole	0.070	No	115	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Fipronil (parent comp.)	0.120	No	39	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Kresoxim-methyl	0.130	No	49	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Pirimiphos-methyl	0.060	No	64	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Propiconazole	0.380	No	82	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Tebuconazole	0.540	No	63	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	- Thiamethoxam	0.120	No	69	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Tricyclazole	0.180	No	47	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
149	Trifloxystrobin	0.140	No	70	Same batch	5	ACN	MeOH			No	DSPE	PS-ML			MS/MS	LC-MS/MS	QuEChERS (original version), modified
151	Isoprothiolane	0.093	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MSD		GC-MSD	QuEChERS (original version)

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
152	Azoxystrobin	0.171	Recovery fig.	78	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Carbendazim and benomyl	0.245	Recovery fig.	94	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Chlorpyrifos	0.202	No	97	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS - Acetate buffered
152	Deltamethrin (cis)	0.198	Recovery fig.	92	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Difenoconazole	0.089	Recovery fig.	82	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Diflubenzuron	0.140	Recovery fig.	73	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Epoxiconazole	0.089	Recovery fig.	88	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Fipronil (parent comp.)	0.160	Recovery fig.	103	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS - Acetate buffered
152	Isoprothiolane	0.185	Recovery fig.	85	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Kresoxim-methyl	0.187	Recovery fig.	87	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Pirimiphos-methyl	0.077	No	103	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	MSD		GC-MSD	QuEChERS - Acetate buffered
152	Propiconazole	0.436	Recovery fig.	83	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Tebuconazole	0.771	Recovery fig.	80	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	- Thiamethoxam	0.235	Recovery fig.	78	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	- Clothianidin	0.005	Recovery fig.	80	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Tricyclazole	0.293	Recovery fig.	75	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
152	Trifloxystrobin	0.259	No	99	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Acetate buffered
154	Chlorpyrifos	0.220	No	90	Same batch	10	Other	Other			Yes	None	MM-SL		FPD		GC-MSD	
154	Deltamethrin (cis)	0.231	No	111	Same batch	10	Other	Other			Yes		PS-SL		ECD		GC-ECD	
154	Pirimiphos-methyl	0.095	No	119	Same batch	10	Other	Other			Yes	None	MM-SL		FPD		GC-MSD	
155	Azoxystrobin	0.159	No	95	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Carbendazim and benomyl	0.103	No	102	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Chlorpyrifos	0.152	No	122	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Deltamethrin (cis)	0.170	No	118	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS - Citrate buffered

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
155	Difenoconazole	0.152	No	73	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Epoxiconazole	0.133	No	72	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Fipronil (parent comp.)	0.169	No	107	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Isoprothiolane	0.173	No	109	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Kresoxim-methyl	0.167	No	96	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	- Malathion	0.010	No	104	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Pirimiphos-methyl	0.083	No	100	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Propiconazole	0.476	No	126	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Tebuconazole	0.950	No	108	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	- Thiamethoxam	0.202	No	88	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	- Clothianidin	0.010	No	102	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Tricyclazole	0.372	No	87	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
155	Trifloxystrobin	0.237	No	105	Same batch	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Azoxystrobin	0.150	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Chlorpyrifos	0.220	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Deltamethrin (cis)	0.100	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		GC-ECD	QuEChERS - Citrate buffered
156	Difenoconazole	0.080	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Epoxiconazole	0.100	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Kresoxim-methyl	0.130	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	- Malathion	0.030	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Pirimiphos-methyl	0.070	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Propiconazole	0.410	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	Tebuconazole	0.840	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
156	- Thiamethoxam	0.200	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
156	- Clothianidin	0.010	No	90	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Azoxystrobin	0.155	No	105	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Carbendazim and benomyl	0.129	No	97	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Chlorpyrifos	0.171	No	104	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Difenoconazole	0.109	No	89	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Diflubenzuron	0.117	No	96	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Isoprothiolane	0.172	No	106	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Kresoxim-methyl	0.187	No	96	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Pirimiphos-methyl	0.095	No	92	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Propiconazole	0.375	No	94	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Tebuconazole	0.780	No	108	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	- Thiamethoxam	0.196	No	100	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	- Clothianidin	0.008	No	92	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Tricyclazole	0.282	No	94	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
157	Trifloxystrobin	0.193	No	103	Same batch	5	ACN				Yes	None	STD Add.			MS/MS	LC-MS/MS	QuEChERS - Citrate buffered
158	Azoxystrobin	0.175	No	107	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
158	Carbendazim and benomyl	0.174	No	105	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML			MS	LC-MS	QuEChERS (original version)
158	Chlorpyrifos	0.216	No	96	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	FPD		GC-MSD	QuEChERS (original version)
158	Deltamethrin (cis)	0.038	No	64	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		Different Column	QuEChERS (original version)
158	Difenoconazole	0.100	No	87	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
158	Fipronil (parent comp.)	0.180	No	118	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	PS-ML		ECD		Different Column	QuEChERS (original version)
158	Isoprothiolane	0.158	No	100	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
158	Kresoxim-methyl	0.167	No	89	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
158	Pirimiphos-methyl	0.078	No	116	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP	FPD		GC-MSD	QuEChERS (original version)

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1)]	Extraction solvent 2 [1)]	Extraction solvent 3 [1)]	Accel. Solvent Extraction	Water addition	Clean up [2)]	Caibration [3)]	ISTD [4)]	GC detector	HPLC detector	Confirmation	Reference method
158	Propiconazole	0.434	No	91	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
158	Tebuconazole	0.823	No	93	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
158	Tricyclazole	0.344	No	97	Same batch	1	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML	TPP		MS/MS	LC-MS/MS	QuEChERS (original version)
159	Chlorpyrifos	0.214	No	83	Same batch	10	AC	CH_2Cl_2			Yes	None	MM-ML		FPD		Different Column	Steinwandter,H Universal 5 min On-line method Chemical Fresenius Z. Chem 1985 No 1155
159	Deltamethrin (cis)	0.098	No	78	Same batch	10	AC	CH_2Cl_2			Yes	SPE (column)	MM-ML		ECD		Different Column	Steinwandter,H Universal 5 min On-line method Chemical Fresenius Z. Chem 1985 No 1155
159	Pirimiphos-methyl	0.077	No	78	Same batch	10	AC	CH_2Cl_2			Yes	None	MM-ML		FPD		Different Column	Steinwandter,H Universal 5 min On-line method Chemical Fresenius Z. Chem 1985 No 1155
161	Pirimiphos-methyl	0.074	No	90	Same batch	20	ACN	Other	Other		No	SPE (column)	PS-ML		FPD		GC-MSD	
162	Azoxystrobin	0.156	No	99	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
162	Carbendazim and benomyl	0.110	No	90	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
162	Chlorpyrifos	0.175	No	104	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	Deltamethrin (cis)	0.176	No	101	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	Difenoconazole	0.094	No	80	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	Diflubenzuron	0.120	No	99	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
162	Epoxiconazole	0.085	No	103	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	Fipronil (parent comp.)	0.147	No	101	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
162	Isoprothiolane	0.159	No	100	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
162	Kresoxim-methyl	0.182	No	88	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	Pirimiphos-methyl	0.061	No	93	Same batch	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	Propiconazole	0.503	No	108	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	Tebuconazole	0.832	No	99	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS			QuEChERS - Citrate buffered
162	- Thiamethoxam	0.190	No	93	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
162	- Clothianidin	0.011	No	99	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
162	Tricyclazole	0.289	No	93	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 6 (cont.) Methods used by the participating laboratories – MRM pesticides

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
162	Trifloxystrobin	0.210	No	103	Validation	5	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS		QuEChERS - Citrate buffered
163	Azoxystrobin	0.001				0												
163	Carbendazim and benomyl	0.007				0												
163	Kresoxim-methyl	0.000				0												
163	Tebuconazole	0.001				0												
164	Azoxystrobin	0.120	Yes, automatic	85	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Carbendazim and benomyl	0.102	Yes, automatic	80	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Chlorpyrifos	0.223	Yes, automatic	90	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Deltamethrin (cis)	0.185	Yes, automatic	109	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML		MS/MS		GC-MS/MS	QuEChERS (original version)
164	Difenoconazole	0.058	Yes, automatic	90	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Diflubenzuron	0.101	Yes, automatic	98	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Fipronil (parent comp.)	0.153	Yes, automatic	102	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Isoprothiolane	0.141	Yes, automatic	111	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Kresoxim-methyl	0.148	Yes, automatic	108	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Pirimiphos-methyl	0.059	Yes, automatic	97	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Propiconazole	0.361	Yes, automatic	85	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Tebuconazole	0.702	Yes, automatic	82	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	- Thiamethoxam	0.311	Yes, automatic	110	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Tricyclazole	0.333	Yes, automatic	90	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
164	Trifloxystrobin	0.237	Yes, automatic	104	Validation	10	ACN				Yes	DSPE (PSA/$MgSO_4$)	MM-ML			MS/MS	LC-MS/MS	QuEChERS (original version)
165	Chlorpyrifos	0.110	No	119	Same batch	10	ACN	Other	Other		No	DSPE (PSA/$MgSO_4$)	PS-SL		ECD			IARI Manual
165	- Endosulfan, alpha	0.021	No	87	Same batch	0	ACN	Other	Other		No	DSPE (PSA/$MgSO_4$)	PS-SL		ECD			IARI Manual
165	- Endosulfan sulfate	0.086	No	89	Same batch	0	ACN	Other	Other		No	DSPE (PSA/$MgSO_4$)	PS-SL		ECD			IARI Manual
165	Pirimiphos-methyl	0.036	No	35	Same batch	10	ACN	Other	Other		No	DSPE (PSA/$MgSO_4$)	PS-SL		ECD			IARI Manual

Lab code	Pesticide	Reproted result [mg/kg]	Recovery corr.	Recovery [%]	Recovery approach	Sample weight [g]	Extraction solvent 1 [1]	Extraction solvent 2 [1]	Extraction solvent 3 [1]	Accel. Solvent Extraction	Water addition	Clean up [2]	Caibration [3]	ISTD [4]	GC detector	HPLC detector	Confirmation	Reference method
166	Azoxystrobin	0.149	No	115	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Chlorpyrifos	0.198	No	111	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Deltamethrin (cis)	0.123	Recovery fig.	132	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Difenoconazole	0.119	No	117	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Epoxiconazole	0.110	No	113	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Fipronil (parent comp.)	0.148	No	119	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Kresoxim-methyl	0.190	No	115	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	- Malathion	0.037	No	112	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Pirimiphos-methyl	0.073	No	113	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Propiconazole	0.404	No	122	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Tebuconazole	0.743	No	127	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
166	Trifloxystrobin	0.220	No	111	Same batch	5	ACN				Yes	PSA/$MGSO_4$/GCB	MM-ML		MSD		GC-MSD	QuEChERS (original version)
167	Carbendazim and benomyl	0.101	Recovery fig.	90	Same batch	10	EtOAc				Yes	PSA	PS-ML			MS/MS	LC-MS/MS	Modified QuEChERS method
167	Isoprothiolane	0.110	Recovery fig.	92	Same batch	10	EtOAc				Yes	PSA	PS-ML			MS/MS	LC-MS/MS	Modified QuEChERS method
168	Chlorpyrifos	0.163	Yes, automatic	96	Same batch	20	EtOAc				Yes	PSA and $MgSO_4$	MM-ML		NPD		Different Column	QuEChERS - Acetate buffered
168	Fipronil (parent comp.)	0.195	Yes, automatic	96	Same batch	20	EtOAc				Yes	PSA and $MgSO_4$	MM-ML		ECD		Different Column	QuEChERS - Acetate buffered
168	Pirimiphos-methyl	0.039	Recovery fig.	96	Same batch	20	EtOAc				Yes	PSA and $MgSO_4$	MM-ML		NPD		Different Column	QuEChERS - Acetate buffered
173	Azoxystrobin	0.220	Yes, automatic	66	Same batch	10	ACN				Yes							QuEChERS - Acetate buffered
196	Azoxystrobin	0.877	No	99	Same batch	5	ACN											QuEChERS (original version)
196	- Endosulfan sulfate	0.260			Same batch	25	AC	CH_2Cl_2			Yes			Yes, other				Mini-Luke-Type
196	Isoprothiolane	5			Same batch	25	AC	CH_2Cl_2			Yes			Yes, other				Mini-Luke-Type
198	Diflubenzuron	10				25	Other	Other	Other		Yes	DSPE	STD Add.	istd det		Fluores-cenc Det.	Different Column	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)

1) AC: Acetone; ACN: Acetonitile; Cy-He: Cyclohexane; CH_2Cl_2: Dichlormethane; EOH: Ethanol; EtOAc: Ethyl Acetate; HEX: Hexane; MeOH: Methanol; ISO: Isooctane: PE: Petroleum Ether
2) SPE: Solid Phase Extraction; DSPE: Dispersive Solid Phase Extraction; liq. / liq.: liquid/liquid partitioning; GPC: Gel Permeation Chromatography; Freez.: Freezing out
3) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition approach
4) isotop. Lab1: isotopically labeled target pesticide; isotop. lab2: isotopically labeled other substance

Appendix 2 – 7: MRM – Pesticides

Appendix 7 Possible reasons for poor performance – MRM pesticides

Azoxytrobin		
LabCode	z-score	Reason / Remarks
38	343,15	Wrong concentration in the standard solution sold by the vendor
97	19,93	Typing error during result submission (0.981 instead 0.0981)
36	3,02	Out of scope and standard solution used was not correct.
58	2,83	reason not yet clarified. Check of standard solution in progress.
13	2,49	reason inexplicable. acceptable result obtained after reanalysing, and good results in other PTs.
104	2,41	analytical instrument (GC-MS) contaminated. Problem solved by cleaning up.
72	-2,2	Problem with analytical instrument (LC-MS/MS, loss of sensitivity)
71	-2,59	reason not yet clarified.
98	-2,67	Problem with analytical instrument
120	-2,68	Problem with analytical instrument (GC-Tof/MS), accredited and standardly used in lab. For this PT the GC-ECD was used, a method not yet accredited but having achieved in the past good results.Investigation of GC-ECD with the aim of accreditation in progress.
147	-2,51	reason not yet clarified.
106	FN	Poor recovery in exctracion step. (few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)

Carbendazim		
LabCode	z-score	Reason / Remarks
63	8,56	short of time (EUPT-C5 and validation procedure for pesticides took place in the same time). For next EUPTs the validation will be completed.
42	5,02	Problem with standard solution, perhaps due to the low solubility of carbendazim in solvent methanol with the concentration of the stock solutionat 100mg/L.It would be appreciated if some other hints or methodology were provided.
65	4,13	methods not validated, analytes out of laboratory scope, this pesticide analyzed only for EUPT.
152	4,03	Carbendazin in the special mixture of standard solutions used only for this EUPT was not correct.
149	-2,36	Poor recovery of carbendazin at 49 % indicated loss of this analyte. This may have reflected in the sample results, for the concentration found by our lab was about 50 % of the Assigned Value. Carbendazin is not within the scope analyzed in rice by our lab. Verification of carbendazin in rice shown big variation of recovery from 46,8 % till 176 %, which not observed in matrices like fruit. To find the solution investigation is continued.
126	-2,43	probable losses during extraction and sample clean-up
98	-2,72	Problem with analytical instrument
163	-3,79	1) few experience with matrices with low content of water like cereals. In the routinary analysis, applying QuEChERS method, water addtion before extraction in not necessary for the majority of samples analyzed in our lab with high content of water, such as fruits and vegetables. However in the case of dry samples like soils and rice, water addition before extraction could be essential to open the rice pores and thus to increase the efficiency of the extraction. 2) Test Material was on the way for more then 3 weeks without cooling and any kind of control of the storage condition, which meight greatly impact the Test Material.

Chlorpyrifos		
LabCode	z-score	Reason / Remarks
41	3,01	different GC-MS and LC-MS values, only GC-MS would be better
108	2,25	reason inexplicable. No problems with this pesticide in other commodities, unknown matrix effect?
106	-2,79	Poor recovery in exctracion step.(few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
49	FN	submission error (By mistake chlorpyrifos-methyl was reported instead of chlorpyrifos)
95	FN	transcription error; true value = 0.195 mg/kg (z-score = 0.1)
161	FN	Mechanical problem with the analytical instrument (GC-MS) for results confiermation. (Vial gripper did not function correctly. Target analytes could be evaperated before being analysed.)

Appendix 7 (cont.) Possible reasons for poor performance – MRM pesticides

Chlorpyrifos-methyl		
LabCode	z-score	Reason / Remarks
49	FP	submission error (By mistake chlorpyrifos-methyl was reported instead of chlorpyrifos)
95	FP	submission error (true value= not detected)

DDT (sum)		
LabCode	z-score	Reason / Remarks
101	FP	due to an accidental intra-lab contamination of glassware. These all were noted during the quality assurance internal audit.
165	FP	probably due to co-elution of some other pesticides at the same retention time, and the laboratory didn't verify with the mass detector

Deltamethrin (cis)		
LabCode	z-score	Reason / Remarks
144	3,69	1) no experience with analysis of this pesticide (and the majority of the pesticides in the target list) in cereal products 2) We do have experience with this pesticide in products of animal origin and attempted all the pesticides included in our accreditation schedule for products of animal origin in the EUPT-C5 rice sample. This sample will be used as a reference material for future method development/validation purposes.
111	3,12	reason not yet clarified. (same method applied to a corn sample with additional clean-up with C18 and PSA resulted in good z-score in an other PT. For lack of material verification of this clean-up step in EUPT-C5 Test Material is not possible.)
13	2,94	Taking into account a second peak (just before standard) with the same ion scan for result submitted: (0.101 after reanalyse)
36	2,86	instead of only "sum of cis and trans" cis was erroneously reported
48	2,36	inconsistent GC-MS/MS response (re-analysis AUG2011: 152 µg/kg matrix-matched, 176 µg/kg standard addition)
104	2,31	analytical instrument (GC-MS) contaminated. Problem solved by cleaning up.
131	-2,96	reason not yet clarified.
158	-3,02	Under our GC condition there are two seperate peaks for Deltamethrin. Only one peak was taken into account for the calculation, and this resulted in the underestimation.
20	FN	Lab's reporting label too high (higher than Assigned Value)
72	FN	LC-MS/MS techniques: have not been identified
106	FN	Poor recovery in exctracion step. (few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
161	FN	Problem with analyticla instrument. Nitrogen gas supply to our GC- ECD became empty during the measurement sequence. The vial was left at room temperatur over 12 h till injection and the target analyte could be evaperated before injection.

Diazinon		
LabCode	z-score	Reason / Remarks
165	FP	probably due to co-elution of some other pesticides at the same retention time, and the laboratory didn't verify with the mass detector

Difenoconazole		
LabCode	z-score	Reason / Remarks
72	22,64	Calculation error. Did not take into account that the matrix was dried.
13	4,96	different GC_MS and LC-MS values, only GC-MS would be better
36	2,92	out of our scope; we have verified that expiry date of standard solution was not correct
28	2,20	reason inexplicable. RSD for Difenoconazle was 24%, for two other target pesticides analysed were over 20%, too, and for other target pesticides were 9 - 20 %. Absolute z-scores of all other target pesticides were unter 1.3.No significant difference was observed using an other freshly prepared stock solution of difenoconazole. Perhaps due to the homogeneity of the sample and/or of subsampling.
155	2,08	perhaps too higher recovery (114%) of this sequence.
41	-2,24	different GC_MS and LC-MS values, only GC-MS would be better

Appendix 7 (cont.) Possible reasons for poor performance – MRM pesticides

Difenoconazole		
LabCode	z-score	Reason / Remarks
109	-2,28	reason inexplicable.
97	-2,59	Effect of matrix (poor integration of the peak area, calibration curve is in pure solvent instead on matrix)
63	-2,76	short of time (EUPT-C5 and validation procedure for pesticides took place in the same time). For next EUPTs the validation will be completed.
98	-3,16	Problem with analyticla instrument.
106	FN	Poor recovery in exctracion step.(few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
163	FN	1) few experience with matrices with low content of water like cereals. In the routinary analysis, applying QuEChERS method, water addtion before extraction in not necessary for the majority of samples analyzed in our lab with high content of water, such as fruits and vegetables. However in the case of dry samples like soils and rice, water addition before extraction could be essential to open the rice pores and thus to increase the efficiency of the extraction. 2) Test Material was on the way for more then 3 weeks without cooling and any kind of control of the storage condition, which meight greatly impact the Test Material. 3) short of time (only three weeks remaining for the whole PT), quality control could not be completely down.

Diflubenzuron		
LabCode	z-score	Reason / Remarks
5	11,86	reason inexplicable.
46	7,93	method not validated for whole grain rice flour
24	6,05	Concentration of stock solution was not correct. (Diflubenzuron was not stable in ethanol. Diviation of the new Stock solution solved in acidic ACN vs. The old one in ethanl was 120 %)
11	5,24	Concentration of standard solution was not correct. (New analyte for the lab. Standard precipitated in the unsuitable solvent used and caused high results.)
1	5,20	Standard mix solution was not correct.Remark: standard stock solution in pure MeCN tends to precipitate at -20 °C, if not redissolved extensively in the ultrasonic bath, and results in a wrong concentration; a new standard stock solution was prepared in DMF/ACN (1:10 v/v)
39	4,53	reason inexplicable.
29	3,79	obviously problems with the standard solution, other pesticides in the same run were OK
123	3,72	solid standard of Diflubenzuron used for preparation of standard stock solution was approx. 6 month over expiry date (decomposition?)
131	2,90	Internal standard was not added
19	2,87	not validated, questionable concentration of standard
121	2,41	Perhaps due to few experience with this analyte, method not validated, for the calibration was performed on blank sample and the recovery at 100 ppb was 97 %.
30	2,37	Unaccredited active. Measurement uncertainty is significantly higher than typical. Questionable score not unexpected.
65	2,30	No experience with this analyte, no validation was carried out.
33	2,23	reason not yet fully clear. (different results from the same solution between LC MSMS and GC MSMS, recovery rate of the LC MSMS was better; the standard solution was not checked.)
104	2,23	analytical instrument (GC-MS) contaminated. Problem solved by cleaning up.
148	2,09	Concentration of standard solution was not correct. (diflubenzuron precipitated in the stock solution during storage in the freezer and caused high results.)
72	-2,76	Problem with analytical instrument (LC-MS/MS)
126	FN	submission error (actually not analysed!)
145	FN	submission error (actually not analysed!)
156	FN	Unable to detect as recovery was poor .
158	FN	error in reading the chromatogram on the monitor by eyes. (Diflubenzuron slipped through their fingers.)

Appendix 7 (cont.) Possible reasons for poor performance – MRM pesticides

- Endosulfan sulfate		
LabCode	z-score	Reason / Remarks
38	FP	No confirmation via MS-detecter
165	FP	co-eluation at the same retention time and no confirmation via MS-detecter

Epoxiconazole		
LabCode	z-score	Reason / Remarks
13	2,50	different GC_MS and LC-MS values, only GC-MS would be better
17	2,38	error in the first dilution step during preparation of calibration mixture.
53	FN	drift of retention time(For C5-Test the QC-Procedures using bracketing calibration was not followed, only the calibration at the beginning of the sequence was used, and Expoxiconazole-peak in the sample was thus out of the window refering to this standard.)
106	FN	Poor recovery in exctracion step.(few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
163	FN	1) few experience with matrices with low content of water like cereals. In the routinary analysis, applying QuEChERS method, water addtion before extraction in not necessary for the majority of samples analyzed in our lab with high content of water, such as fruits and vegetables. However in the case of dry samples like soils and rice, water addition before extraction could be essential to open the rice pores and thus to increase the efficiency of the extraction. 2) Test Material was on the way for more then 3 weeks without cooling and any kind of control of the storage condition, which meight greatly impact the Test Material. 3) short of time (only three weeks remaining for the whole PT), quality control could not be completely down.

Fipronil		
LabCode	z-score	Reason / Remarks
97	26,90	Effect of matrix (poor integration of the peak area, calibration curve is in pure solvent instead on matrix)
12	2,95	Analytical method (GC-MS) used for this PT was not applied in the routine work (LC-MS). Restults from LC-MS technique (reanalyzing after PT) was acceptable.
65	2,30	methods not validated, analytes out of laboratory scope, this pesticide analyzed only for EUPT.
98	2,16	Problem with analytical instrument
13	2,09	Problem with standard solution
46	FN	submission error (actually not analysed!)
106	FN	Poor recovery in exctracion step.(few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
157	FN	submission error due to misunderstanding of system and reporting (actually not analysed!)

Imazalil		
LabCode	z-score	Reason / Remarks
131	FP	Matrix effect

Isoprothiolane		
LabCode	z-score	Reason / Remarks
58	2,68	pesticide analyzed without internal standard
147	-2,35	reason not yet clarified.
22	FN	submisstion error (mixed up with isoproturon in reporting)
64	FN	submission error (actually not analysed!)
98	FN	submission error (actually not analysed!)

Isoproturon		
LabCode	z-score	Reason / Remarks
22	FP	submisstion error (mixed up with isoprothiolane in reporting)

Appendix 7 (cont.) Possible reasons for poor performance – MRM pesticides

Kresoxim-methyl		
LabCode	z-score	Reason / Remarks
72	8,26	Calculation error. Did not take into account that the matrix was dried.
79	5,36	Method developement in progress, not yet established.
42	2,24	Problem with chromatograficla technique (LC-MS/MS) z-score of Kresoxim-methyl in the previos PT using GC-MS/MS acceptable.
46	2,12	reason not yet clarified.
163	-4,00	1) few experience with matrices with low content of water like cereals. In the routinary analysis, applying QuEChERS method, water addtion before extraction in not necessary for the majority of samples analyzed in our lab with high content of water, such as fruits and vegetables. However in the case of dry samples like soils and rice, water addition before extraction could be essential to open the rice pores and thus to increase the efficiency of the extraction. 2) Test Material was on the way for more then 3 weeks without cooling and any kind of control of the storage condition, which meight greatly impact the Test Material. 3) short of time (only three weeks remaining for the whole PT), quality control could not be completely down.
36	FN	Out of scope and submisstion error (actually not analysed!)
53	FN	drift of retention time (For C5-Test the QC-Procedures using bracketing calibration was not followed, only the calibration at the beginning of the sequence was used, and Kresoxim-methyl-peak in the sample was thus out of the window refering to this standard.)

Permethrin		
LabCode	z-score	Reason / Remarks
41	FP	mass fragments assured, reason not clear

Pirimiphos-methyl		
LabCode	z-score	Reason / Remarks
108	7,70	transcription error in concentration of standard solution for calibration; true value=1.07 mg/Kg
95	6,61	submisstion error; true value=0,0667 mg/Kg (z-score = -0.4)
30	5,25	due to standard degredation in solution. Working standards to be made up from referance materials every three-four months
36	4,82	due to standard degredation in solution. (verified with standard freshly prepared from solid pure pirimiphos-methyl)
62	3,62	reason still not clear after several different approaches
72	3,62	Calculation error. Did not take into account that the matrix was dried.
165	-2,06	perhaps due to poor sensitivity of PFP-detecter to this compound
71	-2,15	reason not yet clarified after different approach
110	FN	Peak of pirimiphos-methyl was mistakenly rejected due to its presence in placebo and in the sample in the same amount.

Propiconazole		
LabCode	z-score	Reason / Remarks
58	6,05	error in calculation (concentration of the standard solution was not taken into account resulted in factor of 2 in the result!)
38	3,92	Verification of stability of the standard solution in progress
72	3,87	Calculation error. Did not take into account that the matrix was dried.
68	3,86	Perhaps due to matrix effect (Method not yet validated. Sample extraction must be diluted to get the signal within the current calibration range which had influence on the matrix effect. The results from non-diluted extract but out of the current calibration range would be better)
12	2,14	Analytical method (GC-MS) used for this PT was not applied in the routine work (LC-MS). Restults from LC-MS technique (reanalyzing after PT) was acceptable.
52	-2,35	standards was degraded (problem solved by using recovery obtained from a new standard)
66	-2,37	The preliminary result was not confirmed and checked, because it was initially not on the target list. Upon recognizing that propiconazole was on the list, there was no time to confirm the quantaty!

Appendix 7 (cont.) Possible reasons for poor performance – MRM pesticides

Propiconazole		
LabCode	z-score	Reason / Remarks
106	-2,55	Poor recovery in exctracion step. (few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
62	-3,00	reason still not clear after several different approaches
22	FN	submission error (not analysed, since it was missing from first published Target Pesticide List)
43	FN	submission error (actually not analysed)
79	FN	submission error (actually not analysed! Due to misunderstanding "ND" was shoosen.)
121	FN	submission error (not analysed, since it was missing from first published Target Pesticide List, reanalysed just after PT and before the report draft: 0.463 mg/kg = 0.2)
135	FN	submission error (actually analysed and detected with 0.383 mg/kg, z-score = -0.6)

Prothioconazole		
LabCode	z-score	Reason / Remarks
19	FP	method not validated; almost the same transitions as propiconazole

Tebuconazole		
LabCode	z-score	Reason / Remarks
12	3,99	Analytical method (GC-MS) used for this PT was not applied in the routine work (LC-MS). Restults from LC-MS technique (reanalyzing after PT) was acceptable.
58	3,68	reason still not clear, stability of standard solution still under investigation
68	3,04	Perhaps due to matrix effect (Method not yet validated. Sample extraction must be diluted to get the signal within the current calibration range which had influence on the matrix effect. The results from non-diluted extract but out of the current calibration range would be better)
38	2,97	Stability of standard solution still under investigation
98	-2,66	problem with analytical instrument
97	-2,97	Effect of matrix (poor integration of the peak area, calibration curve is in pure solvent instead on matrix)
52	-3,31	standards was degraded (problem solved by using recovery obtained from a new standard)
106	FN	Poor recovery in exctracion step. (few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
163	FN	1) few experience with matrices with low content of water like cereals. In the routinary analysis, applying QuEChERS method, water addtion before extraction in not necessary for the majority of samples analyzed in our lab with high content of water, such as fruits and vegetables. However in the case of dry samples like soils and rice, water addition before extraction could be essential to open the rice pores and thus to increase the efficiency of the extraction. 2) Test Material was on the way for more then 3 weeks without cooling and any kind of control of the storage condition, which meight greatly impact the Test Material. 3) short of time (only three weeks remaining for the whole PT), quality control could not be completely down. 4) Result 0.00056 ± 0.00004 mg/kg, not ND, was submitted!

- Thiamethoxam		
LabCode	z-score	Reason / Remarks
41	10,49	degradation of the standards
63	8,44	short of time (EUPT-C5 and validation procedure for pesticides took place in the same time). For next EUPTs the validation will be completed.
113	2,49	Difficult integration because of high interference on HPLC-DAD
139	2,14	Strong matrix effect of almost factor 2 was observed.
116	-2,16	result submitted was not recovery-corrected (recovery= 73.3%). Incl. Recovery-correction the result were acceptable.Remark: ASE (Accelerated Solvent Extraction) may be the better method for extraction of pesticeds from cereals than QuEChers, but we dont`t have an ASE.
76	-2,52	wrong delution factor (sampel weight for this PT was different from that for the routine analyses)
147	-2,76	reason still not clear

Appendix 7 (cont.) Possible reasons for poor performance – MRM pesticides

- Thiamethoxam		
LabCode	z-score	Reason / Remarks
98	-3,59	problem with analytical instrument
16	FN	submission error (actually analysed)
72	FN	Calculation error. Did not take into account that the matrix was dried.
106	FN	Poor recovery in exctracion step. (few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)

Thiamethoxam (sum)		
LabCode	z-score	Reason / Remarks
41	10,24	degradation of the standards
63	8,03	short of time (EUPT-C5 and validation procedure for pesticides took place in the same time). For next EUPTs the validation will be completed.
113	2,27	Difficult integration because of high interference on HPLC-DAD
139	2,13	Strong matrix effect of almost factor 2 was observed.
116	-2,22	result submitted was not recovery-corrected (recovery = 73.3 %). Incl. Recovery-correction the result were acceptable. Remark: ASE (Accelerated Solvent Extraction) may be the better method for extraction of pesticeds from cereals than QuEChers, but we dont`t have an ASE.
76	-2,57	wrong delution factor (sampel weight for this PT was different from that for the routine analyses)
147	-2,81	reason still not clear
5	FN	Forgotten to calculate the sum…
25	FN	1) no experience with rice as matrix 2) Extraction method used is different from QuEChers 3) Dynamic MRM was used for acquisition. The peak will be lost, if the retention time shifted for more than 1 minute.
72	FN	LC-MS/MS techniques: not yet been identified
98	FN	submission error (actually analysed)

Triazophos		
LabCode	z-score	Reason / Remarks
156	FP	Poor sensitivity at low levels and thus false identification

Tricyclazole		
LabCode	z-score	Reason / Remarks
41	18,01	degradation of the standards
24	2,29	perhaps due to problem with standard solution like degradation. Investigation will be continued, if the new standard solution arrived.
5	FN	submission error (actually analysed)
58	FN	pesticide analyzed without internal standard
106	FN	Poor recovery in exctracion step. (few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
126	FN	submission error (actually analysed)
131	FN	submission error (actually analysed)

Trifloxystrobin		
LabCode	z-score	Reason / Remarks
72	3,48	LC-MS/MS techniques: not yet been identified
46	3,41	reason still not clear
58	2,35	reason still not clear, stability of standard solution still under investigation
41	2,24	different GC-MS and LC-MS values, only GC-MS would be better

Appendix 7 (cont.) Possible reasons for poor performance – MRM pesticides

Trifloxystrobin		
LabCode	z-score	Reason / Remarks
9	FN	error in acquition and qunatification via software (a new peak in LC-MS/MS chromatogram, but not registerd by the software!)
97	FN	short experience. Optimization of method in progress
106	FN	Poor recovery in exctracion step. (few experience with matrices with low content of water like cereals. Extention of analytical spectrum to the field of cereals in progress)
156	FN	Unable to detect as recovery was poor .

Appendix 8 Data of homogeneity test – SRM pesticides

2,4-D (free acid) [mg/kg]			Bromide ion [mg/kg]			Dithiocarbamates [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
25	0.259	0.253	96	56.2	57.1	82	0.644	0.630
28	0.234	0.290	37	53.0	52.7	25	0.588	0.622
96	0.274	0.300	91	55.2	58.4	112	0.616	0.594
53	0.260	0.274	28	54.0	59.7	106	0.566	0.610
106	0.244	0.299	82	57.9	54.9	28	0.632	0.654
82	0.255	0.286	53	61.8	54.9	91	0.560	0.580
112	0.220	0.249	112	62.5	55.9	96	0.614	0.572
19	0.238	0.269	106	55.2	55.8	37	0.618	0.638
37	0.268	0.278	25	60.3	59.9	53	0.594	0.648
91	0.237	0.261	19	56.1	58.5	19	0.618	0.612

Ethephon [mg/kg]			Glyphosate [mg/kg]			Haloxyfop (free acid) [mg/kg]		
Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2	Sample No.	Portion 1	Portion 2
19	0.270	0.288	19	0.344	0.376	25	0.112	0.114
96	0.298	0.310	96	0.394	0.388	28	0.114	0.131
91	0.298	0.290	91	0.394	0.374	96	0.130	0.141
37	0.312	0.288	37	0.360	0.374	53	0.119	0.125
106	0.288	0.310	106	0.380	0.442	106	0.120	0.138
25	0.304	0.286	25	0.396	0.400	82	0.121	0.137
53	0.298	0.310	53	0.398	0.456	112	0.101	0.111
28	0.288	0.294	28	0.396	0.408	19	0.109	0.125
112	0.280	0.282	112	0.372	0.350	37	0.117	0.135
82	0.296	0.312	82	0.370	0.432	91	0.116	0.129

Quinclorac (free acid) [mg/kg]		
Sample No.	Portion 1	Portion 2
25	0.290	0.287
28	0.294	0.279
96	0.293	0.307
53	0.311	0.295
106	0.301	0.289
82	0.275	0.288
112	0.289	0.272
19	0.274	0.273
37	0.298	0.288
91	0.273	0.287

Appendix 9 Data of stability test – SRM pesticides

	2,4-D (free acid) [mg/kg]			Bromide ion [mg/kg]			Ethephon [mg/kg]		
Sample No.	14.03.'11	04.04.'11	26.04.'11	14.03.'11	04.04.'11	26.04.'11	14.03.'11	04.04.'11	26.04.'11
106	0.299	0.273	0.252	55.800	56.081	61.073	0.288	0.283	0.272
91	0.261	0.280	0.266	58.400	58.515	58.576	0.290	0.286	0.280
19	0.269	0.274	0.266	58.500	58.927	58.918	0.270	0.275	0.262
53	0.274	0.271	0.281	61.800	62.537	62.452	0.298	0.281	0.272
37	0.274	0.295	0.282	53.000	64.843	65.141	0.288	0.282	0.278
Mean [mg/kg]	**0.275**	**0.279**	**0.269**	**57.500**	**60.181**	**61.232**	**0.287**	**0.281**	**0.273**
RSD* [%]	**5.16 %**	**3.50 %**	**4.66 %**	**5.73 %**	**5.78 %**	**4.41 %**	**3.58 %**	**1.43 %**	**2.48 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**1.16 %**	**-2.20 %**	**—**	**4.66 %**	**6.49 %**	**—**	**-1.88 %**	**-4.88 %**

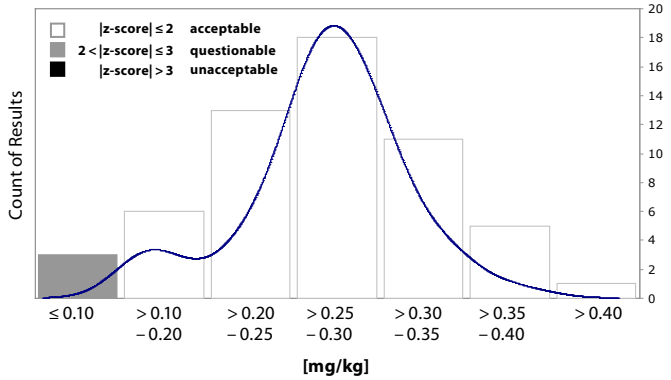
	Glyphosate [mg/kg]			Haloxyfop (free acid) [mg/kg]			Quinclorac (free acid) [mg/kg]		
Sample No.	14.03.'11	04.04.'11	26.04.'11	14.03.'11	04.04.'11	26.04.'11	14.03.'11	04.04.'11	26.04.'11
106	0.380	0.364	0.370	0.120	0.129	0.128	0.289	0.289	0.285
91	0.374	0.373	0.380	0.129	0.122	0.126	0.287	0.287	0.293
19	0.376	0.373	0.370	0.125	0.137	0.130	0.273	0.273	0.275
53	0.398	0.360	0.388	0.125	0.130	0.131	0.295	0.262	0.277
37	0.360	0.386	0.394	0.117	0.126	0.126	0.298	0.319	0.273
Mean [mg/kg]	**0.378**	**0.371**	**0.380**	**0.123**	**0.129**	**0.128**	**0.288**	**0.286**	**0.281**
RSD* [%]	**3.62 %**	**2.70 %**	**2.82 %**	**3.82 %**	**4.30 %**	**1.78 %**	**3.36 %**	**7.51 %**	**2.96 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**-1.69 %**	**0.74 %**	**—**	**4.55 %**	**4.06 %**	**—**	**-0.83 %**	**-2.70 %**

	Dithiocarmabates [mg/kg]		
Sample No.	14.03.'11	04.04.'11	26.04.'11
25	0.618	0.606	0.597
28	0.658	0.592	0.540
37	0.622	0.655	0.610
91	0.588	0.672	0.614
112	0.622	0.520	0.596
Mean [mg/kg]	**0.622**	**0.609**	**0.591**
RSD* [%]	**4.00 %**	**9.82 %**	**5.04 %**
Diviation [%] (ref. 1. Anaylsis)	**—**	**-2.03 %**	**-4.86 %**

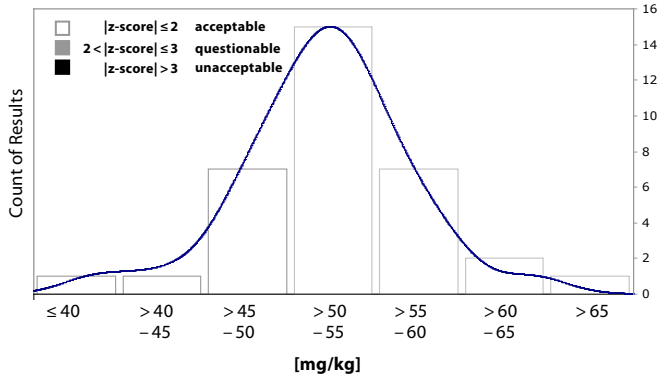
* RSD = relative standard diviation

Appendix 10 Result distribution histograms and kernel density estimates – SRM pesticides

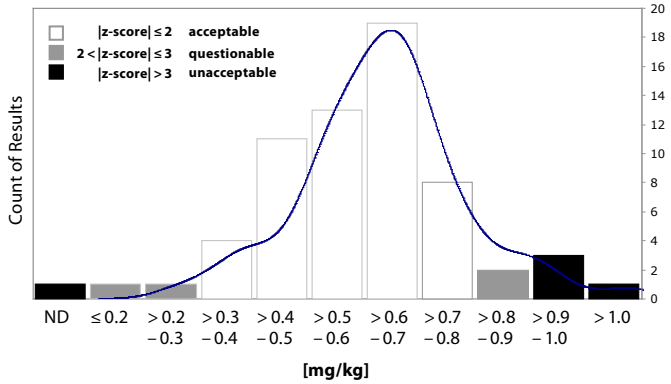
2,4-D (free acid)



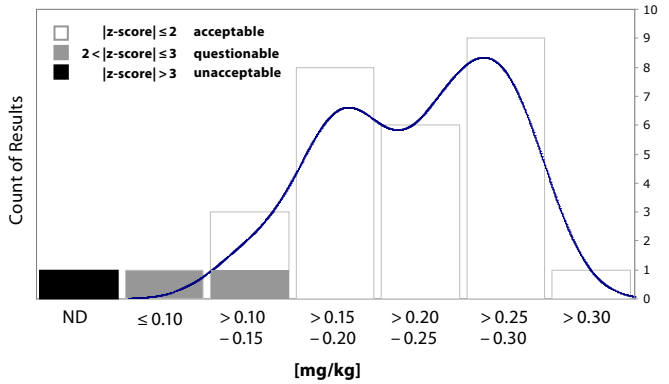
Bromide Ion



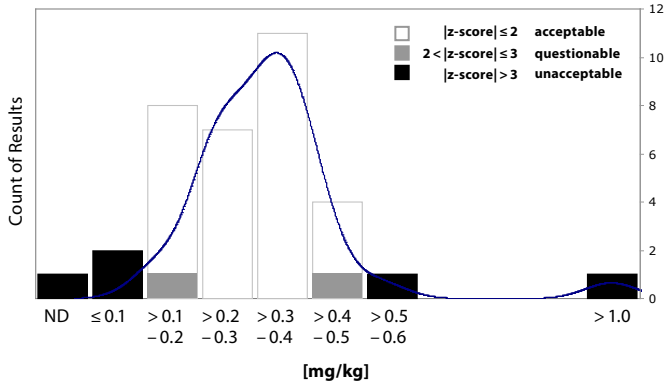
Dithiocarbamates (sum) expr. as CS_2



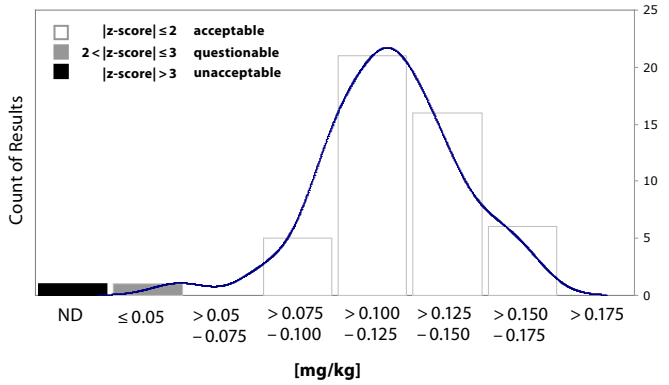
Ethephon



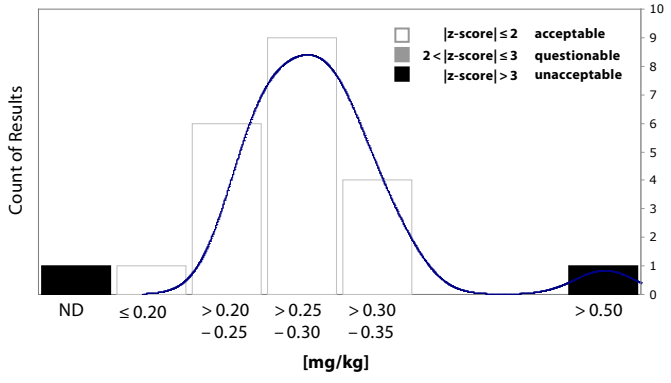
Glyphosate



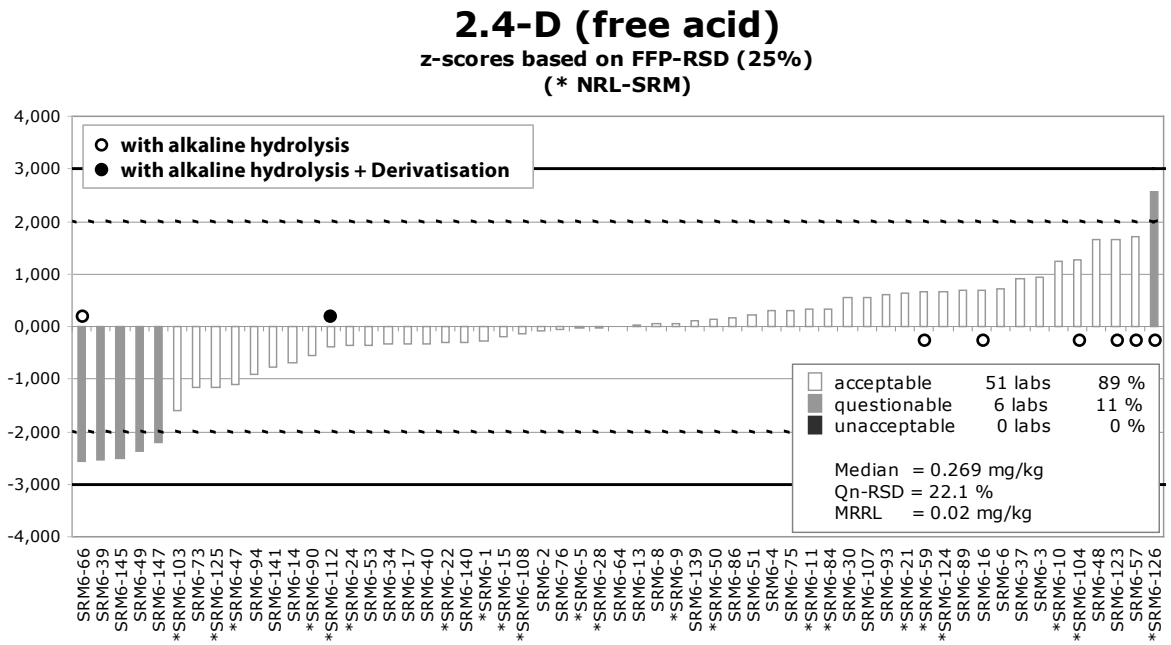
Haloxyfop (free acid)

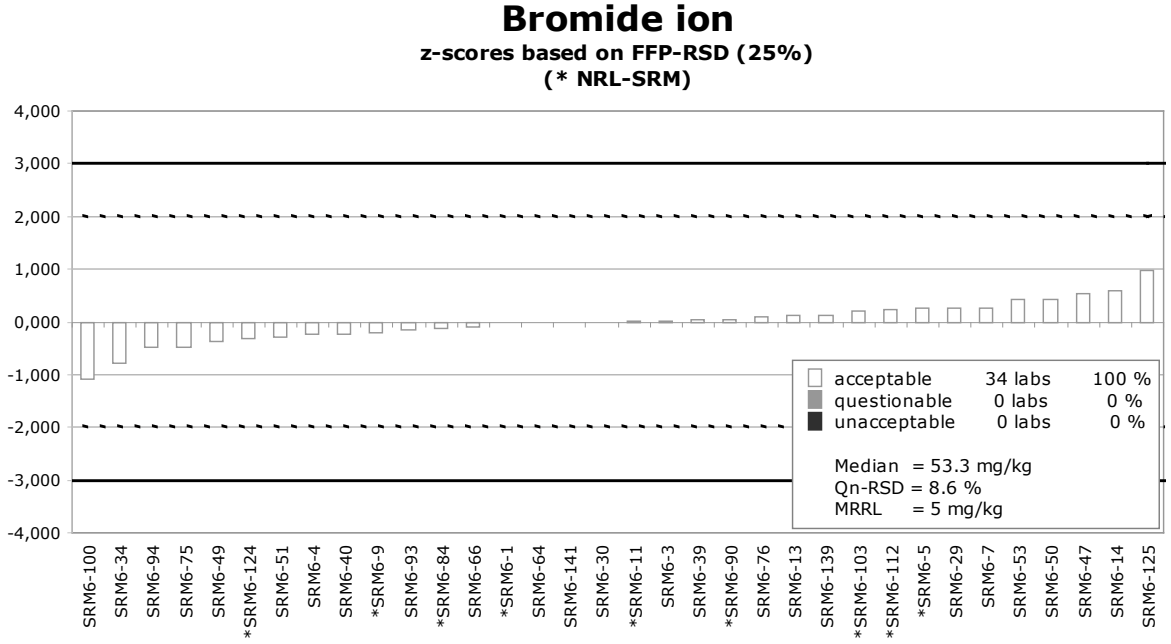


Quinclorac (free acid)

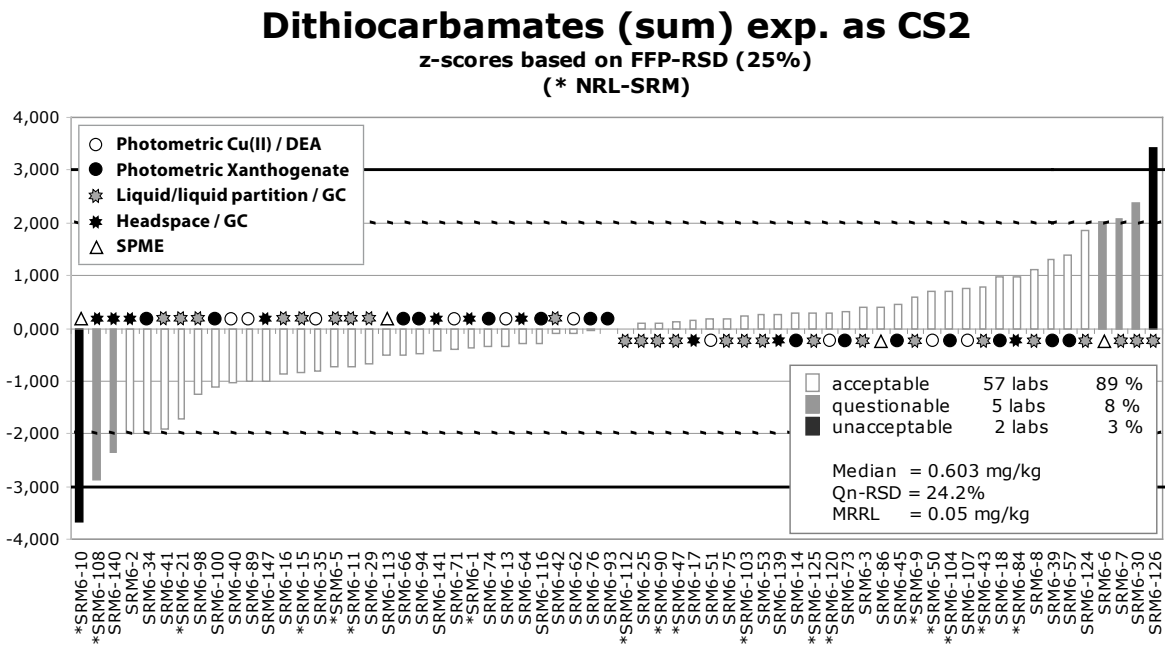


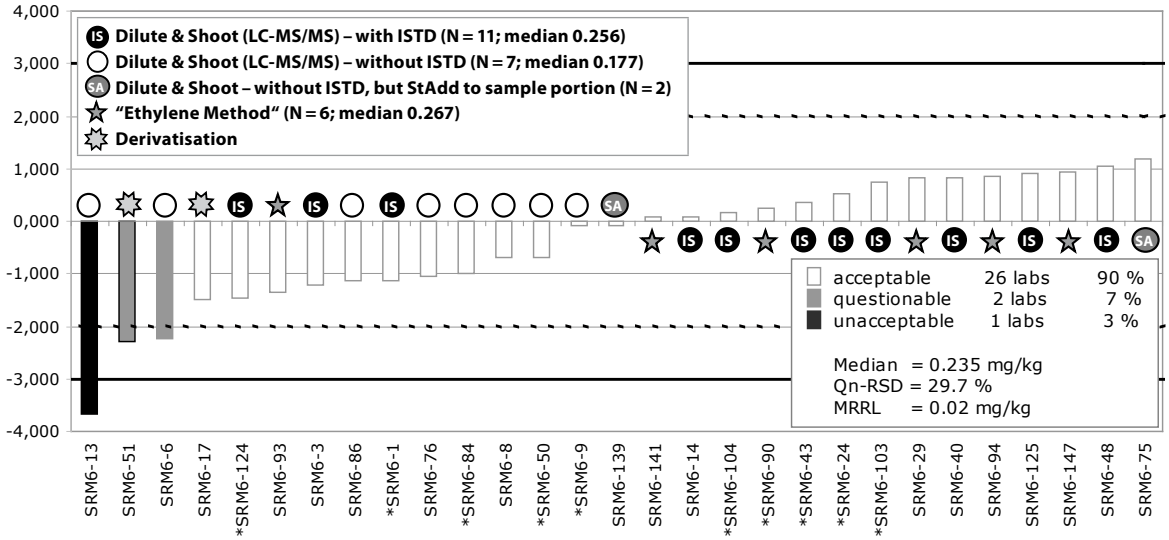
Appendix 11 Graphic presentation of z-scores – SRM pesticides



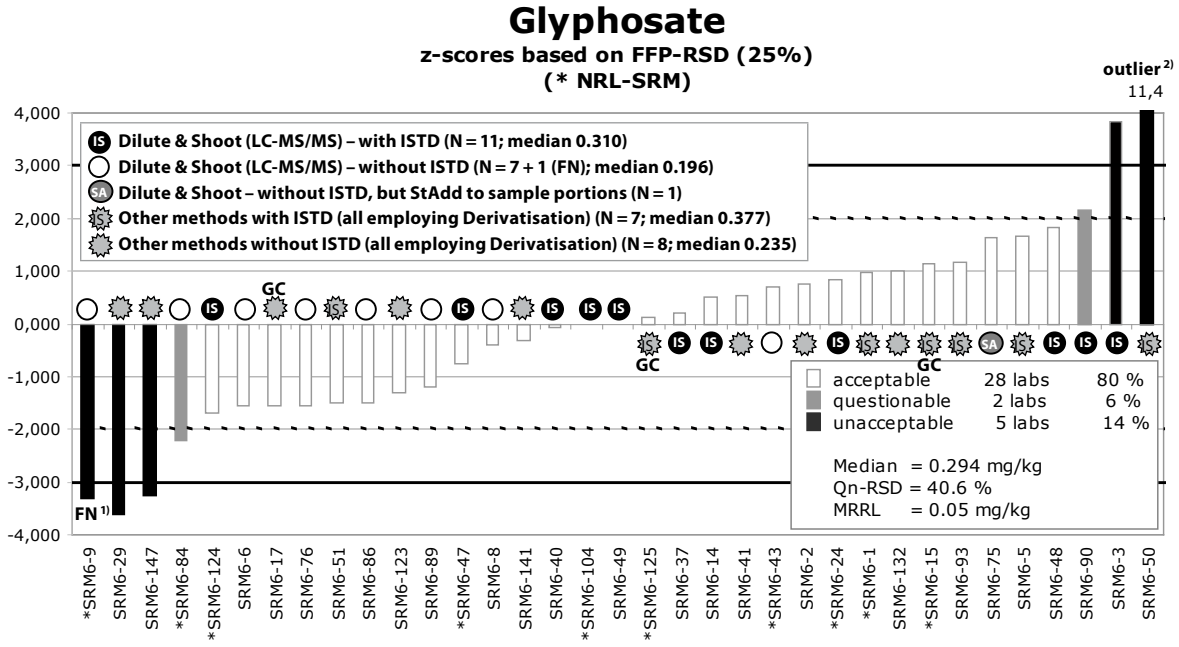


Appendix 11 (cont.) Graphic presentation of z-scores for each SRM pesticide

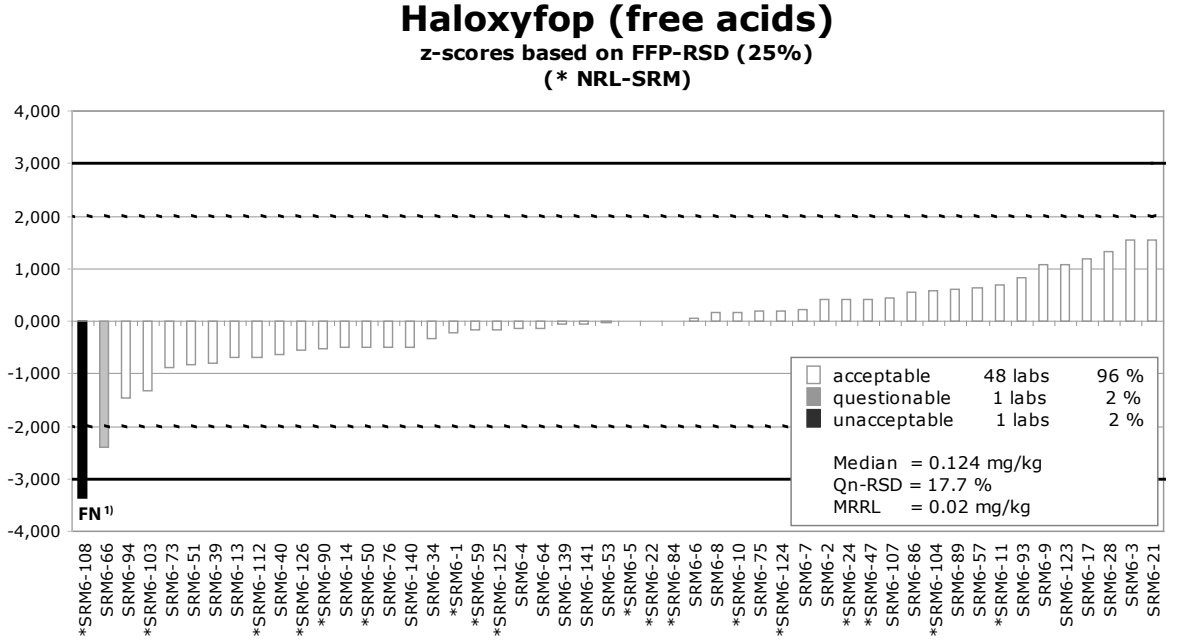




Appendix 11 (cont.) Graphic presentation of z-scores for each SRM pesticide

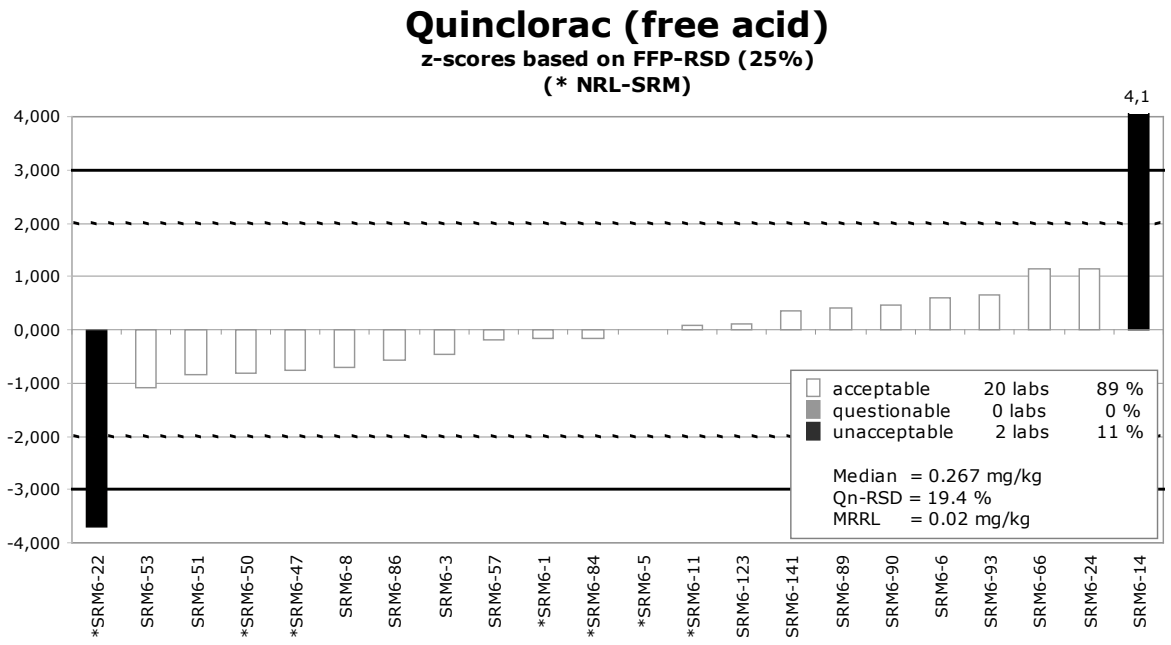


1) RL of this lab higher than the median
2) According to Lab 50, a calculation factor of 3 to account for the weight of the analytical portion was erroneously not applied. If this is the case, the z-score of this lab would have been at 1.129 instead of 11.37.



1) According to lab 108 haloxyfop was, by mistake, sought for in the EUPT-C5 Test Material (not containing haloxyfop) and not in the EUPT-SRM6 Test Material.

Appendix 11 (cont.) Graphic presentation of z-scores for each SRM pesticide



Appendix 12 Methods used by the participating laboratories – SRM pesticides

2,4-D (free acid)

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
66		no	1 - 2 y	0.097	-2,558	0.01	5	Yes	Yes	First alkaline hydrolysis, then neutralization then citrate buffer	None	ACN	No	
39		yes	> 2 y	0.099	-2,528	0.02	5	Yes	No	pH=4.5	Liquid-liquid partitioning	MeOH / DCM	No	
145		no	> 2 y	0.1	-2,513	0.01	1	Yes	No	Citrate-buffer	DSPE (PSA/ MgSO4/ Carbon)	ACN	No	
49		yes	> 2 y	0.110	-2,364	0.1	3	Yes	No	No	Filtration	MeOH	No	
147		no	< 1 y	0.120	-2,216	0.01	1	No	No	No	None	EtAc	No	
103	x	yes	< 1 y	0.162	-1,591	0.02	1	Yes	No	No	None	EtAc	No	
73		yes	1 - 2 y	0.191	-1,160	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
125	x	no	> 2 y	0.191	-1,160	0.02	5	Yes	No	Acetate Buffer	None	ACN	No	
47	x	no	1 - 2 y	0.195	-1,100	0.02	5	Yes	No	pH<2	None	ACN	Yes, with Diazomethane	
94		no	None	0.207	-0,922	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
141		yes	> 2 y	0.217	-0,773	0.01	5	Yes	No	No	Filtration	Acetone / DCM / Petroleumether	No	
14		yes	> 2 y	0.223	-0,684	0.005	5	Yes	No	Citrate-buffer	None	ACN	No	
90	x	yes	> 2 y	0.231	-0,565	0.01	5	Yes	No	Acetate Buffer	None	ACN	No	
112	x	yes	> 2 y	0.243	-0,387	0.05	5	Yes	Yes	First hydrolysis with 5N NaOH and then neutralization with 5N H_2SO_4, then Citrate buffer	DSPE (C18)	ACN	Yes, with Trimethylsulfonium hydroxide	
24	x	no	> 2 y	0.245	-0,357	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN / ACN	No	
53		yes	> 2 y	0.245	-0,357	0.01	5	Yes	No	1 % HAc	Filtration	EtAc	No	
34		yes	> 2 y	0.246	-0,342	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)		MM-SL	None	No	62	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662) / modified
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	67.0	SB-EUPT-Blank	1	Klein, Alder, J. AOAC 86/1015/2003
	LC-MS/MS (QQQ)		PS-ML	None	Yes-4	85	SB-EUPT-Blank	5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	Carbaryl-C13 (switching polarity within same run)	No	87 / 0.7 mk/kg	SB-Other	1	other / FP086
	LC-MS/MS (QQQ)	LC-MS/MS QQQ / ratio of two mrm	MM-SL	None	No	80.0 / 0.1 mg/kg	SB-EUPT-Blank	1	SweEt type
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	84.0	SB-EUPT-Blank	3	SweEt type
	LC-MS/MS (QQQ)		MM-SL	None	No	78 / 0.3 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662) / modified
	LC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	None	No	51	SB-EUPT-Blank	1	QuEChERS - Acetate buffered (AOAC Official Method 2007.01)
	GC-MSD	GC-MSD	MM-ML	None	Yes-4	33 / 0.20 mg/kg	SB-EUPT-Blank	1	other / SPE -preconcentration
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-SL	None	No	82 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	Different Column	PS-ML	None	No	77	SB-EUPT-Blank	2	Mini-Luke-Type (acetone/DCM-PE)
	LC-MS/MS (QQQ)		MM-ML	MCPA-D6	No	83 / 2,4-D at 0.2 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	71 / 0.01 and 0.05 mg/kg	SB-EUPT-Blank	2	QuEChERS - Acetate buffered (AOAC Official Method 2007.01)
	GC-MSD	GC-ITD / SIM	MM-ML	None	No	110 / 0.1 mg/kg	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662) / modified - Internal Laboratory method-Analysis of Acidic pesticides by GC-MS using the QuEChERS method
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	82.3 / 0.5 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-SL	Pirimicarb-D6 (from a separate run in pos-mode)	No	82 / 0.235 mg/kg	SB-EUPT-Blank	1	SweEt type / Ethyl acetate with 1% Acetic acid, National Food Administration Sweden (NFA-SE), Method 917
	LC-MS/MS (QQQ)		MM-ML	Nicarbazin	No	75.6 / 0.1 mg/kg	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

2,4-D (free acid)

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
17		yes	> 2 y	0.247	-0,327	0.02	5	No	No	yes with acetic acid to pH <5	None	ACN	Yes, with PFBBr	
40		no	< 1 y	0.247	-0,327	0.02	7	Yes	No	Citrate-buffer	None	ACN	No	
22	x	yes	> 2 y	0.249	-0,297	0.01	5	Yes	No	1 % HAc	None	EtAc	No	
140		yes	< 1 y	0.249	-0,297	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
1	x	yes	> 2 y	0.250	-0,283	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
15	x	yes	> 2 y	0.256	-0,193	0.01	1	No	No	Alkaline and acidic extraction with dichloromethane for clean-up	Liquid-liquid partitioning	EtOH 65 % / DCM	Yes, with PFBBr	
108	x	no	None	0.26	-0,134	0.02	6	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
2		yes	> 2 y	0.264	-0,074	0.005	1	Yes	No	Citrate-buffer	None	ACN	No	
76		yes	< 1 y	0.265	-0,059	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
5	x	no	> 2 y	0.267	-0,030	0.04	5	Yes	No	No	None	MeOH	No	
28	x	yes	> 2 y	0.268	-0,015	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
64		yes	> 2 y	0.269	0,000	0.01	2	Yes	No	Citrate-buffer	none	ACN	No	
13		no	1 - 2 y	0.270	0,015	0.01	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
8		yes	> 2 y	0.272	0,045	0.02	1	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
9	x	no	1 - 2 y	0.273	0,059	0.02	5	Yes	no	Citrate-buffer	DSPE (without PSA)	ACN	No	
139		no	> 2 y	0.276	0,104	0.02	5	Yes	No	No	None	Water	No	
50	x	yes	> 2 y	0.278	0,134	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
86		yes	> 2 y	0.281	0,178	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-ITD	GC-ECD	MM-ML	None	No	89	SB-EUPT-Blank	2	QuEChERS - Original version (J. AOAC 86 (2003)) / modified
	LC-MS/MS (QQQ)		MM-ML	None	No	105	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-SL	None	No	79 / 0.05 mg/kg	QC-Data	5	SweEt type
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	StAdd to extract aliquots	None	No	96.5	SB-EUPT-Blank	4	QuEChERS - Citrate buffered (EN 151662) / DAR-QuEChERS
	LC-MS/MS (QQQ)		MM-ML	None	No	83	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	GC-MSD	GC-MSD	PS-ML	FeNoneprop	No	87.0 / 0.05 mg/kg	SB-EUPT-Blank	2	other / in-house method
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	132	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	74.7	SB-EUPT-Blank	3	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	None	No	75 / 2.4-D at 0.1 mg/kg	SB-Other	>5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	Oxfendazole	No	85	SB-EUPT-Blank	1	other
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	70 / 0.02 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		StAdd to sample portions	None	Yes-2	101	SB-EUPT-Blank	5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	None	No	88	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	None	No	90	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-SL	None	No	100	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	StAdd to sample portions	None	Yes-2			3	other / Water extraction
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	109	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		PS-ML	None	No	109.0	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

2,4-D (free acid)

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
51		yes	> 2 y	0.284	0,223	0.01	1	Yes	No	No	Na_2SO_4	MeOH	No	
4		yes	> 2 y	0.290	0,312	0.02	5	Yes	No	Citrate-buffer	DSPE (without PSA)	ACN	No	
75		no	> 2 y	0.290	0,312	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
11	x	yes	1 - 2 y	0.291	0,327	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
84	x	yes	> 2 y	0.291	0,327	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
30		no	> 2 y	0.306	0,550	0.01	2	Yes	No	No	None	35%ACN/ water	No	
107		no	< 1 y	0.306	0,550	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
93		yes	> 2 y	0.31	0,610	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
21	x	yes	> 2 y	0.311	0,625	0.02	15	Yes	No	No	DSPE (PSA/ MgSO4)	ACN	No	
59	x	yes	1 - 2 y	0.313	0,654	0.02	5	Yes	Yes	No	Freezing-out	ACN	No	
124	x	yes	1 - 2 y	0.314	0,669	0.008	5	Yes	No	Citrate-buffer	Liquid-liquid partitioning	ACN	No	
89		yes	> 2 y	0.315	0,684	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
16		yes	1 - 2 y	0.316	0,699	0.005	5	Yes	Yes	Citrate-buffer	Freezing-out	ACN	No	
6		yes	> 2 y	0.318	0,729	0.01	3	Yes	No	water with 1% formic acid	None	ACN	No	
37		yes	> 2 y	0.330	0,907	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
3		yes	> 2 y	0.333	0,952	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
10	x	no	1 - 2 y	0.353	1,249	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	StAdd to sample portions	Nicarbazin	Yes-2				other
	LC-MS/MS (QQQ)		MM-SL	Nicarbazin	No	0	0	0	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	71 / 0.02 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	85 / 0.2 mg/kg	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	TPP (Triphenyl phosphate), using polarity switching within the same run	No	90.0 / 0.2 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		PS-ML	None	No	104 / 2,4-D at 0.4 mg/kg	SB-EUPT-Blank	1	other / 20g sample, extracted with 35%ACN/water
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	PS-ML	None	No	95	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	additional Std-Addition to extract aliquots	MM-ML	None	Yes-2	120	SB-Other	3	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ / second transition	MM-ML	None	Yes-4	33.8 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS - Original version (J. AOAC 86 (2003))
	LC-MS/MS (QQQ)		MM-SL	Nicarbazin	No	120 / 2,4-D at 0.02 mg/kg	SB-EUPT-Blank	5	QuEChERS - Citrate buffered (EN 151662) / 5g + 10 mL water + alkaline Hydrolysis + acetonitrile + salt addition + centrifugation + freezing out
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	nicarbazin	No	78 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	TRIS (Sodium tris-(1,3-dicloroisopropil)-Phosphate)	No	83 / spiked	QC-Data	5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	None	No	105	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	Nicarbazin	No	79	SB-EUPT-Blank	1	QuEChERS - Original version (J. AOAC 86 (2003))
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	90	QC-Data	>5	QuEChERS - Citrate buffered (EN 151662)
	LC-ITD	LC-ITD	MM-ML	Nicarbazin	Yes-2	88	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	StAdd to sample portions	None	Yes-2	100 / 0.02 mg/kg	QC-Data	5	QuEChERS - Citrate buffered (EN 151662)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

2,4-D (free acid)

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
104	x	yes	> 2 y	0.354	1,264	0.02	5	Yes	Yes	No	Centrifuga-tion	ACN	No	
48		yes	> 2 y	0.380	1,651	0.02	3	Yes	No	1% HCOOH	None	ACN/ water/ formic acid 75/25/1	No	
123		no	> 2 y	0.381	1,665	0.02	5	Yes	Yes	First alkaline hydrolysis, then neutralization with H_2SO_4 and then partitioning using citrate buffer	None	ACN	No	
57		yes	> 2 y	0.384	1,710	0.01	5	Yes	Yes	H_2SO_4	Freezing-out	ACN	No	
126	x	yes	1 - 2 y	0.441	2,558	0.02	5	Yes	Yes	Citrate-buffer	None	ACN	No	

Bromide Ion

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
100		yes	< 1 y	38.92	-1,08	5	1	No	–	H_2SO_4	None	Diisopropyl ether / EtAc	Yes, with Ethylene oxide	
34		yes	> 2 y	42.9	-0,78	3.4	5	No	–	H_2SO_4	None	EtAc	Yes, with Ethylene oxide	
94		yes	> 2 y	46.9	-0,48	5	5	Yes	–	No	None	Water	No	
75		no	> 2 y	47.0	-0,47	5	1	Yes	–	No	None	Water	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	nicarbazin	No	112 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS-modified / in-house method
	LC-MS/MS (QQQ)	LC-MS/MS QQQ / 2 transitions	MM-ML	None	No	103 / 0.05 mg/kg	SB-EUPT-Blank	1	other
	LC-MS/MS (QQQ)		MM-ML	None	No	109 / spiked	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662) / EURL-SRM Method with alkaline hydrolysis
	LC-MS/MS (QQQ)	Different Column / Acquity UPLC, BEH-C18; 2,1 x 50 mm; 1,7 mm	MM-ML	Nonet for calculation, several ISTD`s	No	103 / 0.1 and 0.5 mg/kg	SB-EUPT-Blank	4	QuEChERS - Citrate buffered (EN 151662) / Alkaline hydrolysis with NaOH before Extraction
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	None	No	84	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-ECD		MM-SL	No	No	72.9	QC-Data	5	PN-EN 13191-2:2002
	GC-MSD		PS-ML	No	No	86.8 / 0.05 mg/kg	SB-EUPT-Blank	1	DFG S18
	IC with conductivity detector		PS-ML	No	No	95 / ca. 40 mg/kg	SB-Other	1	other / ion chromatography
	LC-UV or DAD	Spectrophotometer	MM-ML	No	No	75 / 50 mg/kg	SB-EUPT-Blank	2	other / Water extraction

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Bromide Ion

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation
49		yes	< 1 y	48.3	-0,37	5	1	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
124	x	yes	> 2 y	48.9	-0,33	5	1	Yes	–	H_2SO_4	Liquid-liquid partitioning	EtAC	Yes, with 1,2 -propylene oxide, H_2SO_4
51		yes	> 2 y	49.5	-0,28	5	5	No	–	No	Filtration	Water / MeOH	No
4		no	> 2 y	50.0	-0,25	2	1	Yes	–	H_2SO_4	Liquid-liquid partitioning	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
40		no	> 2 y	50	-0,25	2	2	Yes	–	H_2SO_4	None	EtAc / Water / 9,5 ml water 0,5ml Propylene oxide, 2ml 3mol/l H_2SO_4; 50 ml EtAc and 4g NH_2SO_4	Yes, with 1,2 -propylene oxide, H_2SO_4
9	x	no	< 1 y	50.6	-0,20	5	1	No	–	H_2SO_4	SPE (column)	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
93		yes	> 2 y	51.3	-0,15	0.25	1	Yes	–		None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
84	x	no	None	51.7	-0,12	5	1	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
66		yes	1 - 2 y	52	-0,10	5	5	–	–	H_2SO_4	None	EtAc	yes, with 1,2 -propylene oxide, H_2SO_4
1	x	no	> 2 y	53.0	-0,02	5	1	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
64		no	> 2 y	53	-0,02	5	1	Yes	–	H_2SO_4	Liquid-liquid partitioning	H_2SO_4	Yes, with 1,2 -propylene oxide, H_2SO_4
141		yes	1 - 2 y	53	-0,02	50	5	Yes	–	No	Filtration	Water	No
30		no	> 2 y	53.17	-0,01	10	3	Yes	–	1g Ammonium Acetate	None	EtAc	Yes, with Ethylene oxide
11	x	yes	1 - 2 y	53.4	0,01	3	1	Yes	–	H_2SO_4	Liquid-liquid partitioning	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
3		yes	> 2 y	53.6	0,02	5	1	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4
39		yes	> 2 y	54.0	0,05	2	1	Yes	–	H_2SO_4 (3M), 2 ml	None	n-Hexane	Yes, with 1,2 -propylene oxide, H_2SO_4

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-ECD		PS-ML	3-bromo-1-propanol	No	96 / 12.5 and 100 mg/kg	SB-EUPT-Blank	2	EURL-SRM method
	GC-ECD	GC-ECD	PS-SL	No	No	104 / 50 mg/kg	SB-EUPT-Blank	2	other / reaction with propylenoxide in H_2SO_4
	LC-UV or DAD	LC-UV or DAD	PS-ML	No	No	89	SB-EUPT-Blank	1	other
	GC-ECD		PS-ML	No	No	105	SB-Other	2	§64 LFBG L 00.00-36/2
	GC-ECD		PS-ML	No	No	95	QC-Data	>5	other / water extraktion and derivatization
	GC-ECD	specific method	MM-SL	No	No	95	SB-EUPT-Blank	1	EURL-SRM method / modified
	GC-ECD		PS-ML	No	No	103	SB-Other	4	§64 LFBG L 00.00-36/2
	GC-ECD		PS-ML	3-bromo-1-propanol	No	95.2 / 50 mg/kg	SB-EUPT-Blank	3	Other
	GC-ECD		PS-ML	3-bromo-1-propanol	No	97.5	QC-Data	5	other
	GC-ECD		MM-ML	3-bromo-1-propanol	No	100	SB-EUPT-Blank	1	EURL-SRM method
	GC-MSD		MM-ML	No	Yes-2	90	SB-EUPT-Blank	2	§64 LFBG L 00.00-36/2
	LC-UV or DAD	Different Method	PS-ML	No	No	96	SB-EUPT-Blank	2	other / extraction with water, ion chromatography
	GC-MSD		MM-ML	No	No	114 / KBr at 100 mg/kg of Br ion	SB-EUPT-Blank	1	other / 3g sample, react with 5% aqueous ethylene oxide, extract with ethyl acetate, GC-MS analysis
	GC-ECD		PS-ML	3-bromo-1-propanol	No	99 / 0.025 mg/kg	SB-EUPT-Blank	2	EN ISO 13191-2
	GC-ECD	GC-ECD	PS-ML	No	No	94	SB-EUPT-Blank	1	§64 LFBG L 00.00-36/2
	GC-ECD	GC-MSD	MM-ML	No	No	109.3	SB-EUPT-Blank	1	§64 LFBG L 00.00-36/2

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Bromide Ion

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
90	x	no	None	54	0,05	5	5	Yes	–	No	None	water	No	
76		yes	> 2 y	54.7	0,11	5	1	Yes	–	H_2SO_4	None	EtAc / extraction after derivation	Yes, with 1,2 -propylene oxide, H_2SO_4	
13		no	1 - 2 y	55	0,13	10	5	No	–	No	None	Water / (hot)	No	
139		no	> 2 y	55	0,13	5	5	Yes	–	No	None	Water	No	
103	x	no	None	56.1	0,21	5	1	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4	
112	x	no	< 1 y	56.5	0,24	5	1	Yes	–	H_2SO_4 (3M)	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4	
5	x	yes	> 2 y	56.7	0,26	5	1	No	–	No	None	Water / MeOH	No	
29		yes	> 2 y	56.83	0,27	2	1	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4	
7		yes	1 - 2 y	56.9	0,27	5	1	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4	
53		yes	> 2 y	58.8	0,41	5	15	Yes	–	No	Filtration	Water	No	
50	x	yes	> 2 y	59.0	0,43	2	2	No	–	No	None	None	No	
47	x	yes	1 - 2 y	60.5	0,54	5	5	Yes	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4	
14		yes	> 2 y	61.0	0,58	0.05	1	–	–	H_2SO_4	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4	
125	x	yes	> 2 y	66.2	0,97	5	1	No	–	H_2SO_4 (3M)	None	EtAc	Yes, with 1,2 -propylene oxide, H_2SO_4	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	IC with conductivity detector		PS-ML	No	No	100 / 50 mg/kg	SB-EUPT-Blank	1	Other / Ion chromatography
	GC-ECD		MM-ML	No	No	106 / KBr at 50 mg Bromid/kg	SB-EUPT-Blank	4	§64 LFBG L 00.00-36/2
	IC with conductivity detector		PS-ML	No	No				other / Ion Chromatography
	IC with conductivity detector	Different Method / IC with conductivity detector	StAdd to sample portions	No	Yes-2			3	other / Water extraction
	GC-ECD		PS-ML		No	93.5	SB-EUPT-Blank	3	EURL-SRM method
	GC-ECD		PS-ML	TRIS (Sodium tris-(1,3-dicloro-isopropil)-Phosphate)	No	98 / 50 mg/kg	SB-EUPT-Blank	3	EURL-SRM method
	LC-UV or DAD		PS-ML		No	87	SB-EUPT-Blank	1	other
	GC-ECD		PS-ML	No	No	103 / 39.1 mg/kg	SB-Other	1	§64 LFBG L 00.00-36/2
	GC-ECD	Different Column	PS-ML	3-bromo-1-propanol	No	101	SB-EUPT-Blank	2	other / in house
	ICP-MS	0	PS-ML	No	No	123 / 53.5 mg/kg	SB-EUPT-Blank	1	other / Water extraction and ICP-MS determination of Bromide Ion, National Food Adminstration Sweden, M010
	X-ray fluorescence		MM-ML	No	No	110	SB-Other	1	other / XRF-analysis, direct measurement from rice powder
	GC-ECD		PS-ML	3-bromo-1-propanol	No	100 / 10 mg/kg	SB-EUPT-Blank	3	EURL-SRM method
	GC-ECD		PS-ML	No	No	106 / matrix with known content of 100 mg/kg bromide	SB-Other	2	other / derivatisation with propylenoxide
	GC-MSD	GC-MSD	MM-ML	No	No	120	SB-EUPT-Blank	1	Other / in house

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Dithiocarbamates (sum) expr. as CS_2

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
10	x	yes			-3,67	0.05	5	No	Yes	HCl	None	H_2O/ $SnCl_2$/HCl	No	
108	x	no	> 2 y	0.17	-2,87	0.02	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
140		yes	> 2 y	0.249	-2,35	0.01	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
2		yes	> 2 y	0.302	-2,00	0.01	4	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
34		yes	> 2 y	0.305	-1,98	0.04	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
41		yes	> 2 y	0.313	-1,92	0.01	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
21	x	yes	> 2 y	0.343	-1,72	0.1	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
98		no	> 2 y	0.415	-1,25	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	no	
100		yes	> 2 y	0.436	-1,11	0.05	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
40		yes	> 2 y	0.447	-1,03	0.1	25	Yes	Yes	HCl	KOH	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
89		yes	> 2 y	0.450	-1,01	0.1	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
147		no	> 2 y	0.450	-1,01	0.01	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
16		yes	> 2 y	0.474	-0,86	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
15	x	yes	1 - 2 y	0.477	-0,84	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
35		yes	> 2 y	0.481	-0,81	0.3	75	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
5	x	no	> 2 y	0.492	-0,74	0.04	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-ECD	GC-ECD	StAdd to sample portions	No	Yes-2	74 / 50µg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)
	GC-MSD	GC-MSD	PS-ML	No	No	81	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	GC-MSD	GC-ECD	PS-ML	No	No	107.8	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2 / IT.MP.DSLA.01.42
	GC-ECD	GC-ECD	MM-ML	No	No	110.4 / Sodium diethyl dithiocarbamate trihydrate	SB-EUPT-Blank	3	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	Spectrophotometer		PS-ML	No	No	92.9 / 0.19 mg/kg	QC-Data	3	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-MSD		PS-ML	No	Yes-4	59 / 0.062 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2 / GC-MS
	GC-MSD		MM-ML	No	No	76 / 1.8 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-FPD /-PFPD		PS-ML	No	No	82	SB-Other	3	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2 / Sample 5 gr.+ 15 ml HCl/$SnCl_2$ +5 ml Isooctane.1 hour in oven at 90 º C.cooling on ice. Collect isooctane layer. Injected into cormatografia
	Spectrophotometer		PS-SL	No	Yes-4	86.6	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	Spectrophotometer		PS-ML	No	No	90	QC-Data	>5	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer		PS-ML	No	No	95 / spiked	QC-Data	5	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	GC-MSD		MM-ML	Chloroform	No	101 / 0.25 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	GC-FPD /-PFPD	GC-MSD	PS-ML	No	No	79	SB-Other	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-MSD	GC-MSD	PS-ML	No	No	72.2 / 0.05 mg/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	not conducted			$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	GC-ECD		PS-ML	No	No	67	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Dithiocarbamates (sum) expr. as CS_2

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
11	x	yes	> 2 y	0.494	-0,72	0.05	25	Yes	Yes	HCl	Liquid-liquid partitioning	Water/ $SnCl_2$/HCl/ Isooctane	No	
29		yes	< 1 y	0.50	-0,68	0.05	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
113		yes	> 2 y	0.525	-0,52	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
66		yes	> 2 y	0.527	-0,50	0.02	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
94		yes	> 2 y	0.530	-0,48	0.04	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
141		yes	1 - 2 y	0.54	-0,42	0.05	2	Yes	Yes	HCl	Filtration	Water/ $SnCl_2$/HCl	No	
71		yes	> 2 y	0.544	-0,39	0.05	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
1	x	yes	> 2 y	0.549	-0,36	0.05	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
13		no	> 2 y	0.550	-0,35	0.01	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
74		no	> 2 y	0.55	-0,35	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/	Yes, to potassium xanthogenate	
64		no	> 2 y	0.56	-0,29	0.02	2	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	NO	
116		yes	> 2 y	0.56	-0,29	0.02	2	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
42		yes	> 2 y	0.59	-0,09	0.05	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
62		yes	> 2 y	0.59	-0,09	0.02	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ ethanol	Yes, with Cu(II) acetate-diethanolamine solution	
76		yes	> 2 y	0.597	-0,04	0.05	2	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ destillation	Yes, to potassium xanthogenate	
93		yes	> 2 y	0.602	-0,01	0.05	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
112	x	yes	1 - 2 y	0.603	0,00	0.05	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
25		yes	> 2 y	0.617	0,09	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-ECD		PS-ML	No	No	81 / 0.1 mg/l	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-ECD		PS-ML	No	No	85 / 0.516 mg/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-FPD /-PFPD		MM-ML	Thiophene	No	71 / 0.4 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)
	Spectrophotometer		PS-ML	No	No	78.2	QC-Data	5	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	Spectrophotometer		PS-ML	No	No	81 / 0.20 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-MSD	Different Method	PS-ML	No	No	80	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	Spectrophotometer		PS-ML	No	No	93	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	GC-MSD		MM-ML	Dichloromethane	No	108	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	Spectrophotometer		PS-ML	No	No	not performed			$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer	Spectrophotometer	PS-ML	No	Yes-4	75.5	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-MSD		MM-SL	No	Yes-2	81	SB-EUPT-Blank	4	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	Spectrophotometer		PS-ML	No	No	88.2	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-FPD /-PFPD	GC-MSD	PS-ML	No	No	92 / 0.05 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	Spectrophotometer		PS-ML	No	No	94	QC-Data	3	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer		PS-SL	No	No	81 / Thiram at 0.7 mg CS_2/kg	SB-Other	1	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	Spectrophotometer		PS-ML	No	No	91	SB-Other	3	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-ECD		PS-ML	No	No	85 / 0.2 mg/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-MSD	GC-MSD	PS-ML	No	No	100.8 / Thiram at 1 mg/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Dithiocarbamates (sum) expr. as CS_2

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
90	x	yes	> 2 y	0.619	0,11	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
47	x	yes	> 2 y	0.62	0,11	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	NO	
17		yes	> 2 y	0.626	0,15	0.02	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
51		yes	> 2 y	0.632	0,19	0.1	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
75		no	> 2 y	0.632	0,19	0.05	2	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
103	x	yes	> 2 y	0.639	0,24	0.1	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
53		yes	> 2 y	0.642	0,26	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
139		yes	> 2 y	0.643	0,27	0.05	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
14		yes	> 2 y	0.645	0,28	0.01	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ KOH/MeOH	Yes, to potassium xanthogenate	
125	x	no	> 2 y	0.647	0,29	0.05	5	Yes	Yes	HCl	Liquid-liquid partitioning	Water/ $SnCl_2$/HCl/ Isooctane	No	
120	x	yes	> 2 y	0.648	0,30	0.1	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
73		no	> 2 y	0.650	0,31	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
3		yes	> 2 y	0.662	0,39	0.01	2	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
86		yes	> 2 y	0.663	0,40	0.02	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
45		no	> 2 y	0.670	0,44	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ 60 ml	Yes, to potassium xanthogenate	
9	x	no	< 1 y	0.694	0,60	0.1	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	GC-FPD /-PFPD	GC-ITD	MM-ML	No	No	87 / 0.05 mg/kg and 0.25 mg/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-FPD /-PFPD		MM-SL	No	No	not performed			$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-FPD /-PFPD	GC-FPD	MM-ML	No	No	88	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	Spectrophotometer	Spectrophotometer	PS-ML	No	No	85	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	GC-FPD /-PFPD	GC-FPD	PS-ML	No	No	83 / 0.05 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-FPD /-PFPD		MM-ML	Thiophene	Yes-4	62.1	SB-EUPT-Blank	3	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-FPD /-PFPD		MM-SL	No	No	116 / 0.451 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-MSD	GC-MSD	StAdd to sample portions	Thiophene	Yes-2			3	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	Spectrophotometer		PS-ML	No	No	91 / Thiram at 0.25 mg CS_2/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-FPD /-PFPD	GC-MSD	MM-ML	No	No	89	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2 / (in house)
	Spectrophotometer		PS-ML	No	No	93.2	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	Spectrophotometer		MM-ML	No	No	74 / 0.127 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-MSD		PS-ML	No	No	90	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-FPD /-PFPD		StAdd to sample portions	No	Yes-2	100.7	SB-EUPT-Blank	4	$SnCl_2$/HCl-cleavage, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)
	Spectrophotometer		MM-ML	No	No	100 / 0.8 mg/kg	QC-Data	5	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-FPD /-PFPD	specific method	MM-SL	No	No	97	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Dithiocarbamates (sum) expr. as CS_2

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
50	x	yes	> 2 y	0.707	0,69	0.05	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
104	x	yes	> 2 y	0.71	0,71	0.05	1	Yes	Yes	HCl	Distillation	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
107		yes	> 2 y	0.715	0,74	0.5	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, with Cu(II) acetate-diethanolamine solution	
43	x	yes	> 2 y	0.720	0,78	0.05	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
18		yes	> 2 y	0.75	0,98	0.05	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
84	x	yes	> 2 y	0.750	0,98	0.02	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
8		yes	> 2 y	0.772	1,12	0.05	5	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
39		yes	> 2 y	0.800	1,31	0.05	5	Yes	Yes	HCl	1) NaOH, 2) H_2SO_4	Water/ $SnCl_2$/HCl	Yes, to potassium xanthogenate	
57		yes	> 2 y	0.811	1,38	0.05	2	Yes	Yes	HCl	H_2SO_4 and NaOH	Water/ $SnCl_2$/HCl/ MeOH / MeOH with 2 mol KOH	Yes, to potassium xanthogenate	
124	x	yes	1 - 2 y	0.883	1,86	0.03	15	Yes	Yes	HCl	Liquid-liquid partitioning	Water/ $SnCl_2$/HCl/ Isooctane	No	
6		yes	> 2 y	0.906	2,01	0.001	2	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl	No	
7		yes	> 2 y	0.917	2,08	0.05	2	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	NO	
30		no	> 2 y	0.96	2,37	0.05	25	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane	No	
126	x	yes	> 2 y	1.120	3,43	0.05	1	Yes	Yes	HCl	None	Water/ $SnCl_2$/HCl/ Isooctane / 80 °C 2h	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used.[2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	Spectro-photometer	GC-MSD	PS-ML	No	No	94	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	Spectro-photometer	Spectro-photometer	PS-ML	No	No	48 / spiked w. Maneb (low rec. maybe due to high N_2-flow)	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	Spectro-photometer		PS-ML	No	No	90 / Thiram	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, Cu(II) acetate & diethanolamine, spectroph. analysis (EN 12396-1 type)
	GC-FPD /-PFPD	GC-MSD	PS-ML	No	No	86	SB-EUPT-Blank	3	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	Spectro-photometer		PS-ML	No	No	104.2	SB-EUPT-Blank	4	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-FPD /-PFPD	"S" mode	MM-ML	Thiophene	No	64.9 / 1 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, headspace sampling, GC-analysis of CS_2
	GC-ECD	GC-MSD	MM-ML	No	No	102	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	Spectro-photometer	Spectro-photometer	PS-ML	No	No	97.5	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	Spectro-photometer	only Blank, Calibration curve and Recovery tests	PS-ML	No	No	90 / 0.8 mg/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, KOH/MeOH , spectroph. analysis (Xanthogenate mth.) (EN 12396-3 type)
	GC-MSD	GC-MSD	PS-ML	No	No	80 / 0.01 mg/kg	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-ITD	GC-TOF	StAdd to sample portions	No	Yes-2				$SnCl_2$/HCl-cleavage, headspace SPME, GC-Analysis of CS_2 (EN 12396-2 type)
	GC-MSD		PS-ML	No	No	95	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-MSD		PS-ML	No	No	123 / Thiram at 0.5 mg/kg	SB-EUPT-Blank	1	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2
	GC-MSD	GC-MSD	PS-ML	No	No	73	SB-EUPT-Blank	2	$SnCl_2$/HCl-cleavage, liquid-liquid-partitioning w. non-polar solvent, GC-analysis of CS_2

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Ethephon

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
13		no	< 1 y	FN	-3,66	0.05	5	Yes	No	1 % HCOOH	None	MeOH	No	
51		yes	> 2 y	0.100	-2,30	0.01	5	No	No	No	None	EtAc	Yes, with Diazomethane	
6		no	< 1 y	0.103	-2,25	0.02	5	Yes	No	1 % HCOOH	None	MeOH	No	
17		yes	> 2 y	0.148	-1,48	0.05	1	Yes	No	No	None	MeOH	Yes, with MSTFA	
124	x	yes	1 - 2 y	0.149	-1,46	0.05	1	No	No	1 % HCOOH	None	MeOH	No	
93		yes	> 2 y	0.156	-1,34	0.02	2	Yes	Yes	Yes, KOH	None	Acetone	No	
3		yes	> 2 y	0.163	-1,23	0.01	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
86		no	1 - 2 y	0.168	-1,14	0.02	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
1	x	yes	1 - 2 y	0.169	-1,12	0.05	5	Yes	No	1 % HCOOH	Freezing-out	MeOH / Water	No	
76		yes	< 1 y	0.174	-1,04	0.03	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
84	x	no	< 1 y	0.177	-0,99	0.02	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
8		yes	1 - 2 y	0.194	-0,70	0.02	3	No	No	No	None	Water	No	
50	x	no	< 1 y	0.195	-0,68	0.05	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
9	x	no	< 1 y	0.230	-0,09	2	5	Yes	No	1 % HCOOH	Freezing-out	MeOH / Water	No	
139		no	None	0.230	-0,09	0.02	5	Yes	No	No	None	Water	No	
14		yes	1 - 2 y	0.240	0,09	0.005	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
141		yes	> 2 y	0.24	0,09	0.05	5	Yes	Yes	Yes, NaOH	Filtration	Other	No	
104	x	yes	> 2 y	0.244	0,15	0.02	5	Yes	No	No	Centrifuga-tion	MeOH	No	
90	x	yes	1 - 2 y	0.250	0,26	0.02	25	Yes	Yes	Yes, KOH	Headspace sampling	30 % KOH in water	No	
43	x	no	< 1 y	0.256	0,36	0.02	5	Yes	No	1 % HCOOH	None	MeOH / Water / formic acid 1 %	No	
24	x	no	None	0.265	0,51	0.02	5	Yes	No	1 % HCOOH	Freezing-out	MeOH / Water	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)		MM-ML	No		0			QuPPe / EURL-SRM method for polar compounds
	GC-FPD /-PFPD	GC-FPD	StAdd to sample portions	No	Yes-2				Other
	LC-MS/MS (QQQ)		MM-ML	No	Yes-4	74	SB-EUPT-Blank	3	QuPPe / http://www.crl-pesticides.eu/library/docs/srm/meth_Polar-Pesticides_CrlSrm.pdf
	GC-ITD	GC-FPD	MM-ML	No	No	86	SB-EUPT-Blank	2	Other / in-house method
	LC-ITD	LC-ITD	MM-ML	Ethephon-D4	Yes-1	85 / 1.0 mg/kg	SB-EUPT-Blank	1	QuPPe / EURL-SRM method for polar pesticides (v.2)
	GC-FID		MM-ML	No	No	113	SB-EUPT-Blank	5	§64 LFBG L 00.00-47 / involving alkaline cleavage to ethen
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	Ethephon-D4	Yes-1	99	SB-EUPT-Blank	1	QuPPe / EURL-SRM method for polar pesticides
	LC-MS/MS (QQQ)		PS-ML	No	No	81.1	SB-EUPT-Blank	1	QuPPe / V5
	LC-MS/MS (QQQ)		MM-ML	Ethephon-D4	Yes-1	81 / also done with Standard addition	SB-EUPT-Blank	1	QuPPe / EURL-SRM method for polar pesticides (V5), different Chromatography
	LC-MS/MS (QQQ)		MM-ML	No	No	83 / Ethephon at 0.1 mg/kg	SB-EUPT-Blank	1	QuPPe / V5
	LC-MS/MS (QQQ)		MM-ML	No	No	47.2 / 0.2 mg/kg	SB-EUPT-Blank	1	QuPPe
	LC-MS	LC-MS	MM-ML	No	No	81	SB-EUPT-Blank	2	Other / JFood Additives and Contaminants, Vol 20, No 8.,pp 692-698
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	No	No	74	SB-EUPT-Blank	1	QuPPe / EURL-SRM method for polar pesticides
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-SL	No	Yes-4	82	SB-EUPT-Blank	1	QuPPe / EURL-SRM method for polar pesticides
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	StAdd to sample portions	No	Yes-2			3	Other / Water extraction
	LC-MS/MS (QQQ)		MM-ML	Ethephon-D4	Yes-1	98 / Ethephon at 0.2 mg/kg	SB-EUPT-Blank	3	QuPPe / EURL-SRM method for polar pesticides
	GC-FID	Different Method	PS-ML	No	No	82	SB-EUPT-Blank	2	Other / reaction with NaOH and heat GC-FID
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Ethephon-D4	No	84 / 0.05 mg/kg	SB-EUPT-Blank	1	Other / in-house method
	GC-FID	GC-FID	PS-ML	No	No	85 / 0.05 mg/kg	SB-EUPT-Blank	1	Other / Alkaline hydrolysis of ethephon to ethylene
	LC-MS/MS (QQQ)		MM-ML	Ethephon-D4	Yes-1	96	SB-EUPT-Blank	3	QuPPe / EURL-SRM method for polar pesticides
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	Ethephon-D4	Yes-3	105.6 / 0.1; 0.4 and 0.8 mg/kg	SB-EUPT-Blank	3	QuPPe / Quick Method for the Analysis of Residues of Highly Polar Pesticides using 10 mL acidified methanol

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Ethephon

Derivatisation	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
103	x	no	None	0.279	0,75	0.08	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
29		yes	> 2 y	0.283	0,82	0.15	1	Yes	Yes	Yes, KOH	None	Acetone / KOH (10mol/l)	No	
40		no	< 1 y	0.283	0,82	0.02	5	Yes	No	1 % HCOOH	None	MeOH / Water	No	
94		yes	> 2 y	0.285	0,85	0.05	4	Yes	Yes	Yes, alkaline	None	Water	No	
125	x	no	> 2 y	0.289	0,92	0.02	5	Yes	No	Acidified water/ metha-nol	None	Water/MeOH (7:1)	No	
147		no	< 1 y	0.290	0,94	0.1	6	Yes	Yes	Yes, alkaline	None	Other	No	
48		no	< 1 y	0.297	1,06	0.02	3	Yes	No	1 % HCOOH	None	Water	No	
75		no	1 - 2 y	0.305	1,19	0.05	5	Yes	No	No	None	MeOH / Water	No	

Glyphosate

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	
29		yes	< 1 y	0.028	-3,62	0.01	5	Yes	No	No	None	Water	
9	x	no		< RL	-3,32	2	5	Yes	No	1 % HCOOH	Freezing-out	MeOH	
147		no	< 1 y	0.055	-3,25	0.05	5	No	No	No	None	Water	
84	x	no	1 - 2 y	0.132	-2,20	0.05	5	Yes	No	1 % HCOOH	None	MeOH / Water	
124	x	yes	1 - 2 y	0.170	-1,69	0.05	1	No	No	1 % HCOOH	None	MeOH	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Detection	Confirmation	Calibration [1]	ISTD used. [2]	Result recovery corrected? [3]	Recovery % (compound. level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	Ethephon-D4	Yes-1	127	SB-EUPT-Blank	3	QuPPe
	GC-FID		MM-ML	No	No	108 / 0.25 mg/kg	QC-Data	>5	§64 LFBG L 00.00-47 / involving alkaline cleavage to ethen
	LC-MS/MS (QQQ)		MM-ML	Ethephon-D4	Yes-1	114	QC-Data	2	QuPPe / EURL-SRM method for polar pesticides
	GC-FID		MM-ML	No	No	96 / 3.0 mg/kg	SB-EUPT-Blank	1	Other / GC/FID Headspace
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	Ethephon-D4	Yes-1	87	SB-EUPT-Blank	1	Other / in house
	GC-FID		PS-ML	No	No	92.5 / 2 mg/kg	SB-EUPT-Blank	1	Other / Alkaline hydrolysis of ethephon to ethylene
	LC-MS/MS (QQQ)	LC-MS/MS QQQ / 2 transitions	MM-ML	Ethephon-D4	Yes-1	93 / 0.02 mg/kg and 0.1 mg/kg	SB-EUPT-Blank	2	QuPPe-modified / EURL-SRM polar pest Nov2010 5.6.1 method 1 using water instead of methanol as extraction solvent
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	StAdd to sample portions	No	Yes-2	100	0	4	Other / Water/metanol extraction

	Derivatisation	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	Yes, with FMOC-Chloride	LC-MS/MS (QQQ)		MM-ML	No	No	101	QC-Data	>5	other / In-house method
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No					QuPPe / from EURL-SRM site
	Yes, with FMOC-Chloride	LC-FLD		MM-ML	No	No	111 / 0.5 mg/kg	SB-EUPT-Blank	1	Other / polar extraction and fmoc-derivation
	No	LC-MS/MS (QQQ)		MM-ML	No	No	45.2 / 0.2 mg/kg	SB-EUPT-Blank	1	QuPPe
	No	LC-ITD	LC-ITD	MM-ML	IL-Glyphosate	Yes-1	79 / 1.0 mg/kg	SB-EUPT-Blank	1	QuPPe / CRL method for polar pesticides (v.2, MetOH extraction, Ion-LC)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Glyphosate

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	
6		no	< 1 y	0.179	-1,56	0.04	5	Yes	No	1 % HCOOH	None	MeOH	
17		yes	> 2 y	0.179	-1,56	0.05	1	Yes	No	No	None	Acetone	
76		no	None	0.180	-1,55	0.05	5	Yes	No	1 % HCOOH	None	MeOH / water	
51		yes	< 1 y	0.184	-1,50	0.1	5	No	No	No	None	MeOH / water	
86		no	1 - 2 y	0.184	-1,50	0.05	5	Yes	No	1 % HCOOH	None	MeOH / Water	
123		no	> 2 y	0.199	-1,29	0.05	3	No	No	pH = 1.6 - 2.4 with HCl	ion excange columns: Chelex 100 Resin, Fe-III-;+ AG 1-X8-Resin, Cl-form (for enrichment/ cleanup)	Water/HCl / DCM / 0.1M HCl	
89		no	None	0.207	-1,18	0.1	3	Yes	No	no	None	Water	
47	x	yes	1 - 2 y	0.239	-0,75	0.01	5	Yes	No	1 % HCOOH	None	MeOH	
8		yes	> 2 y	0.265	-0,39	0.05	3	No	No	No	None	Water	
141		no	< 1 y	0.27	-0,33	0.01	25	Yes	No	HCl	ion excange columns: Chelex 100 Resin, Fe-III-;+ AG 1-X8-Resin, Cl-form (for enrichment/ cleanup)	Water/HCl / DCM / 0.1M HCl	
40		no	< 1 y	0.289	-0,07	0.05	5	–	No	1 % HCOOH	None	MeOH	
104	x	yes	1 - 2 y	0.293	-0,01	0.05	5	Yes	No	No	Centrifugation	MeOH	
49		no	> 2 y	0.294	0,00	0.15	3	Yes	No	No	Filtration	Water	
125	x	yes	> 2 y	0.304	0,14	0.05	1	Yes	No	Acidified water/me-thanol	SPE (column)	Water/MeOH (7:1)	
37		yes	> 2 y	0.310	0,22	0.02	5	Yes	No	No	None	35% ACN/water / extration with water	
14		yes	1 - 2 y	0.331	0,50	0.01	5	Yes	No	1 % HCOOH	None	MeOH / Water	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	No	LC-MS/MS (QQQ)		MM-ML	No	Yes-4	60	SB-EUPT-Blank	3	QuPPe / http://www.crl-pesticides.eu/library/docs/srm/meth_PolarPesticides_CrlSrm.pdf
	Yes, with MSTFA	GC-ITD	GC-FPD	MM-ML	No	No	78	SB-EUPT-Blank	2	other / in house method
	No	LC-MS/MS (QQQ)		MM-ML	No	No	48 / Glyphosate at 0.1 mg/kg	SB-EUPT-Blank	1	QuPPe / V5
	Yes, with FMOC-Chloride	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-1	71	SB-EUPT-Blank	1	other
	No	LC-MS/MS (QQQ)		PS-ML	No	No	86.1	SB-EUPT-Blank	1	QuPPe / V5
	Yes, Post-column oxidation w. hypochloride to glycine then w. OPA/ 2-mercaptoethanol	LC-FLD		PS-ML	No	No	60 / spiked	SB-EUPT-Blank	1	other / DFG Method 405
	No	LC-MS/MS (QQQ)		StAdd to extract aliquots	No	No	93 / spiked	SB-Other	5	QuPPe (modified)
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	IL-Glyphosate	Yes-1	95	SB-EUPT-Blank	1	QuPPe / acidic methanol extraction
	No	LC-MS	LC-MS	MM-ML	No	No	85	SB-EUPT-Blank	2	other / JFood Additives and Contaminants, Vol 20, No 8.,pp 692-698
	Yes, Post-column oxidation w. hypochloride to glycine then w. OPA/ 2-mercaptoethanol	LC-FLD	Different Column	PS-ML	No	No	80	QC-Data	2	other / DFG 405: extraction with HCl and enriched and purified at ion excange columns HPLC with fluorescence detectio
	No	LC-MS/MS (QQQ)		MM-ML	IL-Glyphosate	Yes-1	96	QC-Data	2	QuPPe / EURL-SRM method for polar pesticides
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	IL-Glyphosate	No	85 / 0.05 mg/kg	SB-EUPT-Blank	1	other / in-house method
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ) / 2 transitions	MM-ML	IL-Glyphosate	Yes-1	70 / 0.33 mg/kg	SB-Other	1	other / FP054
	Yes, with TFAA + HFB (heptflourobutanol)	GC-MSD	GC-MSD	MM-ML	IL-Glyphosate	Yes-1	81	SB-EUPT-Blank	1	Other / Alferness PL & Iwata T, J. Agric. Food Chem, 1994, 42, 2751-2759
	no	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-1	100	QC-Data	>5	other / extraction with water
	No	LC-MS/MS (QQQ)		MM-ML	IL-Glyphosate	Yes-1	105 / Glyphosate at 0.4 mg/kg	SB-EUPT-Blank	3	QuPPe / EURL-SRM method for polar pesticides

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Glyphosate

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	
41		yes	1 - 2 y	0.333	0,53	0.05	2	No	No	pH=1,5 - 2,5	two resins; 1)Chelex 100; 2) AG1-X8	100 ml 0,1 M HCl; 35 ml CH_2Cl_2	
43	x	no	None	0.345	0,69	0.05	5	Yes	No	1 % HCOOH	None	MeOH / formic acid 1%	
2		yes	< 1 y	0.350	0,76	0.2	1	Yes	No	neutralisa-tion with NaOH to pH 6-7	ion-excange	DCM / extraction with HCl	
24	x	no	None	0.356	0,84	0.25	5	Yes	No	1 % HCOOH	Freezing-out	MeOH / Water	
1	x	yes	1 - 2 y	0.366	0,98	0.025	1	Yes	No	pH= 9	Liquid-liquid partitioning	DCM / MeOH	
132		no	> 2 y	0.367	0,99	0.1	5	Yes	No	No	None	Water	
15	x	yes	> 2 y	0.377	1,13	0.01	4	Yes	No	pH=2	Chelex100 and anion exchange	Water / DCM	
93		no	1 - 2 y	0.38	1,17	0.05	2	–	No	pH 9 with NH_3	SPE (column), Oasis MAX" 60 mg, 30 µm, 3 ml by Waters (Anion exchanger)	Water / MeOH / borat-buffer	
75		no	1 - 2 y	0.415	1,65	0.1	5	Yes	No	No	None	MeOH / water	
5	x	yes	< 1 y	0.417	1,67	0.02	1	No	No	No	Liquid-liquid partitioning	Water / MeOH / DCM	
48		no	< 1 y	0.428	1,82	0.05	3	Yes	No	1 % HCOOH	None	Water	
90	x	no	None	0.452	2,15	0.05	3	–	No	no	Centrifugation	water	
3		yes	> 2 y	0.575	3,82	0.1	5	Yes	No	No	None	MeOH	
50	x	yes	> 2 y	1.13	11,37	0.05	3	No	No	No	Liquid-liquid partitioning	Water	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled

	Derivatisation	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	Yes, Post-column oxidation w. hypochloride to glycine then w. OPA/ Thiofluor	LC-FLD	LC-FLD	PS-ML	No	No	99 / 0.5 mg/kg	SB-EUPT-Blank	2	other / method from LCTech GmbH; please see www.lctech.de/Nachsaeulenderivatisierung
	No	LC-MS/MS (QQQ)		MM-ML	No	No	78	SB-EUPT-Blank	4	QuPPe / EURL-SRM method for polar pesticides
	Yes, with FMOC-Chloride	LC-FLD	LC-FLD	MM-ML	No	No	85.0	SB-EUPT-Blank	1	other / LC-Fluorescense-Det. after derivatisation with FMOC
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	IL-Glyphosate	Yes-3	105.4 / 0.1; 0.4 and 0.8 mg/kg	SB-EUPT-Blank	3	QuPPe / Quick Method for the Analysis of Residues of Highly Polar Pesticides using 10 mL acidified methanol
	Yes, with FMOC-Chloride	LC-MS/MS (QQQ)		MM-ML	IL-Glyphosate	Yes-1				other / Precolumn derivatization with FMOC-Cl
	Yes, with FMOC-Chloride	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	Yes-2				other / extraction with water, FMOC derivatization
	Yes, with TFAA + HFB (heptflourobutanol)	GC-MSD	GC-MSD	PS-ML	IL-Glyphosate	Yes-1	90.1 / 0.025 mg/kg	SB-EUPT-Blank	2	other / Alferness PL & Iwata T, J. Agric. Food Chem, 1994, 42, 2751-2759
	Yes, with FMOC-Chloride	LC-MS/MS (QQQ)	additional Std-Addition to extract aliquots	MM-ML	IL-Glyphosate	Yes-3	103	QC-Data	>5	other / extr. with buffer, derivation with Fmoc-Cl, extr. with Ethylacetat, SPE, elution with ACN/HCl
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	StAdd to sample portions	No	Yes-2	100	0	4	other / Water/metanol extraction
	Yes, with FMOC-Chloride	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-1	105 / apparent recovery, corrected with labelled ISTD	SB-EUPT-Blank	1	other
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ) / 2 transitions	MM-ML	IL-Glyphosate	Yes-1	96 / 0.05 and 0.25 mg/kg	SB-EUPT-Blank	2	QuPPe-modified / EURL-SRM polar pest Nov 2010 5.6.1 method 1 using water instead of methanol as extraction solvent
	no	LC-MS/MS (QQQ)		MM-ML	IL-Glyphosate	Yes-1	95 / 0.05 and 0.25 mg/kg	SB-EUPT-Blank	2	"QuPPe-modified / in-house method (EURL-SRM polar pest Nov 2010 5.6.1 method 1, using water instead of methanol as extraction solvent.)"
	No	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	IL-Glyphosate	Yes-1	89	SB-EUPT-Blank	1	QuPPe / EURL-SRM method for polar pesticides
	Yes, with FMOC-Chloride	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	IL-Glyphosate	Yes-1	94	SB-EUPT-Blank	1	other / In-house method

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Haloxyfop (free acid)

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation
108	x	no	None	ND *	-3,35	0.02	6	Yes	No	Citrate-buffer	Freezing-out	ACN	No
66		no	< 1 y	0.05	-2,39	0.01	5	Yes	Yes	1) alkaline hydrolysis, 2) neutralization 3) citrate buffer	None	ACN	No
94		no	None	0.079	-1,45	0.01	5	Yes	No	Citrate-buffer	None	ACN	No
103	x	yes	< 1 y	0.0830	-1,32	0.02	1	Yes	No	No	None	EtAc	No
73		no	1 - 2 y	0.097	-0,87	0.02	5	Yes	No	Citrate-buffer	None	ACN	No
51		yes	> 2 y	0.0980	-0,84	0.01	1	Yes	No	No	Na_2SO_4	Acetone / DCM / PE	No
39		yes	> 2 y	0.099	-0,81	0.02	5	Yes	No	pH=4.5	Liquid-liquid partitioning	MeOH / DCM	No
13		no	< 1 y	0.103	-0,68	0.01	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No
112	x	yes	> 2 y	0.103	-0,68	0.05	5	Yes	Yes	1) hydrolysis with 5N NaOH 2) neutralization with 5N H_2SO_4, 3) Citrate buffer	DSPE (C18)	ACN	Yes, with Trimethyl-sulfonium hydroxide
40		no	< 1 y	0.104	-0,65	0.02	7	Yes	No	Citrate-buffer	None	ACN	No
126	x	yes	1 - 2 y	0.107	-0,55	0.02	5	Yes	Yes	Citrate-buffer	None	ACN	No
90	x	yes	> 2 y	0.108	-0,52	0.01	5	Yes	no	Acetate Buffer	None	ACN	No
14		yes	> 2 y	0.109	-0,48	0.005	5	Yes	No	Citrate-buffer	None	ACN	No
50	x	yes	> 2 y	0.109	-0,48	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No
76		yes	< 1 y	0.109	-0,48	0.02	5	Yes	No	Citrate-buffer	None	ACN	No
140		yes	1 - 2 y	0.109	-0,48	0.01	5	Yes	No	Citrate-buffer	None	ACN	No
34		yes	> 2 y	0.114	-0,32	0.025	5	Yes	No	Citrate-buffer	None	ACN	No
1	x	yes	> 2 y	0.117	-0,23	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
* Haloxyfop was sought for in Test Material for EUPT-C5 not containing Haloxyphop, therefore, this „not detected" is actually not false negative.

	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)		MM-ML	No	No	14	QC-Data	3	EN 151662 (QuEChERS - Citrate buffered)
	LC-MS/MS (QQQ)		MM-SL	No	No	97.2	SB-EUPT-Blank	3	QuEChERS - Citrate buffered (EN 151662) / modified
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	No	80 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	86.0	SB-EUPT-Blank	3	SweEt type
	LC-MS/MS (QQQ)		MM-SL	No	No	80 / 0.1 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662) / modified
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	TPP (Triphenyl phosphate), measured in pos. Mode	No	69	SB-EUPT-Blank	1	Mini-Luke-Type (acetone/DCM-PE)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	76.2	SB-EUPT-Blank	1	Klein, Alder, J. AOAC 86/1015/2003
	LC-MS/MS (QQQ)		MM-ML	No	No	93	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	GC-MSD	GC-ITD / SIM	MM-ML	No	No	90 / 0.1 mg/kg	SB-EUPT-Blank	2	QuEChERS-modified / Internal Laboratory method-Analysis of Acidic pesticides by GC-MS using the QuEChERS method
	LC-MS/MS (QQQ)		MM-ML	No	No	95	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	70	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	72 / 0.01 and 0.05 mg/kg	SB-EUPT-Blank	2	QuEChERS - Acetate buffered (AOAC Official Method 2007.01)
	LC-MS/MS (QQQ)		MM-ML	Linuron-D6	No	86 / Haloxyfop at 0.1 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	114	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	No	No	88 / Haloxyfop at 0.1 mg/kg	SB-Other	>5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	StAdd to extract aliquots	No	No	93.3	SB-EUPT-Blank	4	QuEChERS - Citrate buffered (EN 151662) / DAR-QuEChERS
	LC-MS/MS (QQQ)		MM-ML	TPP (Triphenyl phosphate)	No	89.9 / 0.1 mg/kg	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	No	No	88	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

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

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Haloxyfop (free acid)

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
59	x	yes	1 - 2 y	0.119	-0,16	0.02	5	Yes	Yes	No	Freezing-out	ACN	No	
125	x	no	> 2 y	0.119	-0,16	0.02	5	Yes	No	Acetate Buffer	None	ACN	No	
4		yes	> 2 y	0.120	-0,13	0.02	5	Yes	No	Citrate-buffer	DSPE (without PSA)	ACN	No	
64		yes	> 2 y	0.12	-0,13	0.01	2	Yes	No	Citrate-buffer	None	ACN	No	
139		no	> 2 y	0.122	-0,06	0.02	5	Yes	No	No	None	Water	No	
141		yes	< 1 y	0.122	-0,06	0.01	5	Yes	No	No	Filtration	Acetone / DCM / Petroleu-mether	No	
53		yes	> 2 y	0.123	-0,03	0.01	5	Yes	No	1 % HAc	Filtration	EtAc	No	
5	x	no	> 2 y	0.124	0,00	0.04	5	Yes	No	No	None	MeOH	No	
22	x	yes	> 2 y	0.124	0,00	0.01	5	Yes	No	1 % HAc	None	EtAc	No	
84	x	yes	> 2 y	0.124	0,00	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
6		yes	> 2 y	0.126	0,06	0.02	3	Yes	No	water with 1 % formic acid	None	ACN	No	
8		yes	> 2 y	0.129	0,16	0.02	1	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
10	x	yes	1 - 2 y	0.129	0,16	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
75		no	> 2 y	0.130	0,19	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
124	x	yes	1 - 2 y	0.130	0,19	0.002	5	Yes	No	Citrate-buffer	Liquid-liquid par-titioning	ACN	No	
7		no	None	0.131	0,23	0.01	5	Yes	No	pH=7	SPE (column)	MeOH / DCM	No	
2		yes	> 2 y	0.137	0,42	0.01	1	Yes	No	Citrate-buffer	None	ACN	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
* Haloxyfop was sought for in Test Material for EUPT-C5 not containing Haloxyphop, therefore, this „not detected" is actually not false negative.

	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)		MM-SL	Nicarbazin	No	85 / Haloxyfop + Haloxyfop-R at 0.02 mg/kg	SB-EUPT-Blank	5	QuEChERS - Citrate buffered (EN 151662) / 5g + 10 mL water + alkaline Hydrolysis + acetonitrile + salt addition+centrifugation + freezing out
	LC-MS/MS (QQQ)	GC-MS/MS (QQQ)	MM-ML	No	No	77	SB-EUPT-Blank	1	QuEChERS - Acetate buffered (AOAC Official Method 2007.01)
	LC-MS/MS (QQQ)		MM-SL	Nicarbazin	No	0	0	0	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-SL	No	Yes-2	98	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	StAdd to sample portions	No	Yes-2			3	other / Water extraction
	LC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	No	No	95	SB-EUPT-Blank	2	Mini-Luke-Type (acetone/DCM-PE)
	LC-MS/MS (QQQ)		MM-SL	Pirimicarb-D6 (from a separate run in pos-mode)	No	94 / 0.264 mg/kg	SB-EUPT-Blank	1	SweEt type / Ethyl acetate with 1% Acetic acid, National Food Administration Sweden (NFA-SE), Method 917
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	Oxfendazole	No	100	SB-EUPT-Blank	1	other
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	No	96 / 0.05 mg/kg	QC-Data	5	SweEt type
	LC-MS/MS (QQQ)		MM-ML	TPP (Triphenyl phosphate), using polarity switching within the same run	No	91.5 / 0.2 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	TPP (triphenylphosphate)	No	86	SB-EUPT-Blank	1	QuEChERS - Original version (J. AOAC 86 (2003))
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	94	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	StAdd to sample portions	No	Yes-2	100 / 0.02 mg/kg	QC-Data	5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	79 / 0.02 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	nicarbazin	No	81 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	No	No	117	SB-EUPT-Blank	4	Klein, Alder, J. AOAC 86/1015/2003
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	95.1	SB-EUPT-Blank	3	QuEChERS - Citrate buffered (EN 151662)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

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

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Haloxyfop (free acid)

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
24	x	no	> 2 y	0.137	0,42	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN / ACN	No	
47	x	no	1 - 2 y	0.137	0,42	0.02	5	Yes	No	pH<2	None	ACN	Yes, with Diazomethane	
107		yes	> 2 y	0.138	0,45	0.01	5	Yes	No	Citrate-buffer	DSPE (C18/PSA/$MgSO_4$)	ACN	No	
86		yes	> 2 y	0.141	0,55	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
104	x	yes	> 2 y	0.142	0,58	0.02	5	Yes	Yes	No	Centrifugation	ACN	No	
89		yes	1 - 2 y	0.143	0,61	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
57		yes	> 2 y	0.144	0,65	0.01	5	Yes	Yes	H_2SO_4	Freezing-out	ACN	No	
11	x	yes	1 - 2 y	0.145	0,68	0.04	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
93		yes	> 2 y	0.15	0,84	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
9	x	no	< 1 y	0.157	1,06	0.02	5	Yes	no	Citrate-buffer	DSPE (without PSA)	ACN	No	
123		no	> 2 y	0.157	1,06	0.02	5	Yes	Yes	First alkaline hydrolysis, then neutralization with H_2SO_4 and then partitioning using citrate buffer	None	ACN	No	
17		yes	> 2 y	0.161	1,19	0.01	5	No	No	yes with acetic acid to pH <5	None	ACN	Yes, with PFBBr	
28	x	yes	> 2 y	0.165	1,32	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
3		yes	> 2 y	0.172	1,55	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	
21	x	yes	> 2 y	0.172	1,55	0.02	15	Yes	No	No	DSPE (PSA/MgSO4)	ACN	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
* Haloxyfop was sought for in Test Material for EUPT-C5 not containing Haloxyphop, therefore, this „not detected" is actually not false negative.

	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	98.3 / 0.2 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	GC-MSD	GC-MSD	MM-ML	No	No	104 / 0.20 mg/kg	SB-EUPT-Blank	1	other / SPE preconcentration
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	PS-ML	TPP (Triphenyl phosphate)	No	99	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		PS-ML	No	No	108.8	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	nicarbazin	No	108 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS-modified / in-house method
	LC-MS/MS (QQQ)		MM-ML	TRIS (Sodium tris-(1,3-dicl-roisopropil)-Phosphate)	No	97 / spiked	QC-Data	5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	Different Column / Acquity UPLC, BEH-C18; 2,1 x 50 mm; 1,7 mm	MM-ML	not for calculation, several ISTD`s	No	91 / 0.1 and 0.5 mg/kg	SB-EUPT-Blank	>5	QuEChERS - Citrate buffered (EN 151662) / Alkaline hydrolysis with NaOH before Extraction
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	83 / 0.2 mg/kg	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	additional Std-Addition to extract aliquots	MM-ML	No	Yes-2	101	QC-Data	>5	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-SL	No	No	88	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	No	No	104 / spiked	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662) / EURL-SRM Method with alkaline hydrolysis
	GC-ITD	GC-ECD	MM-ML	No	No	81	SB-EUPT-Blank	2	QuEChERS - Original version (J. AOAC 86 (2003)) / modified
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	70 / 0.02 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-ITD	LC-ITD	MM-ML	Nicarbazin	Yes-2	75	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ) / second transition	MM-ML	No	Yes-4	33.6 / 0.05 mg/kg	SB-EUPT-Blank	1	QuEChERS - Original version (J. AOAC 86 (2003))

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Quinclorac (free acid)

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
22	x	yes		FN	-3,70	0.01	5	Yes	No	1 % HAc	None	EtAc	No	
53		no	None	0.194	-1,09	0.05	5	Yes	No	1 % HAc	Filtration	EtAc	No	
51		yes	> 2 y	0.210	-0,85	0.01	1	Yes	No	No	Na_2SO_4	MeOH	No	
50	x	no	None	0.213	-0,81	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
47	x	no	< 1 y	0.216	-0,76	0.02	5	Yes	No	pH<2	None	ACN	Yes, with Diazo-methane	
8		no	< 1 y	0.220	-0,70	0.02	1	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
86		no	1 - 2 y	0.228	-0,58	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
3		no	None	0.236	-0,46	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
57		yes	1 - 2 y	0.254	-0,19	0.02	5	Yes	Yes	H_2SO_4	Freezing-out	ACN	No	
1	x	yes	< 1 y	0.256	-0,16	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
84	x	no	None	0.257	-0,15	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	
5	x	no	None	0.267	0,00	0.04	5	Yes	No	No	None	MeOH	No	
11	x	no	None	0.273	0,09	0.04	5	Yes	No	Citrate-buffer	Freezing-out	ACN	No	
123		no	> 2 y	0.275	0,12	0.02	5	Yes	Yes	First alkaline hydrolysis, then neutralization with H_2SO_4 and then partitioning using citrate buffer	None	ACN	No	
141		yes	< 1 y	0.291	0,36	0.01	5	Yes	No	No	Filtration	Acetone / DCM / Petroleu-mether	No	
89		no	None	0.295	0,42	0.02	5	Yes	No	Citrate-buffer	None	ACN	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
* Haloxyfop was sought for in Test Material for EUPT-C5 not containing Haloxyphop, therefore, this „not detected" is actually not false negative.

	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-SL	No					SweEt type
	LC-MS/MS (QQQ)		MM-SL	Pirimicarb-D6 (from a separate run in pos-mode)	No	71 / 0.201 mg/kg	SB-EUPT-Blank	1	SweEt type / Ethyl acetate with 1% Acetic acid, National Food Administration Sweden (NFA-SE), Method 917
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	StAdd to sample portions	TPP (Triphenyl phosphate), measured in pos. Mode	Yes-2				other
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	No	No	103	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	GC-MSD	GC-MSD	MM-ML	No	Yes-4	37 / 0.20 mg/kg	SB-EUPT-Blank	1	other / SPE- preconcentration
	LC-MS/MS (QQQ)	LC-MS/MS (QQQ)	MM-ML	No	No	86	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		PS-ML	No	No	80.0	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-ITD	LC-ITD	MM-ML	Nicarbazin	Yes-2	81	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	Different Column / Acquity UPLC, BEH-C18; 2,1 x 50 mm; 1,7 mm	MM-ML	not for calculation, several ISTD`s	No	88 / 0.1 and 0.5 mg/kg	SB-EUPT-Blank	4	QuEChERS - Citrate buffered (EN 151662) / Alkaline hydrolysis with NaOH before Extraction
	LC-MS/MS (QQQ)		MM-ML	No	No	78	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	TPP (Triphenyl phosphate), using polarity switching within the same run	No	84.0 / 0.2 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	Oxfendazole	No	85	SB-EUPT-Blank	1	other
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	No	No	48 / 0.2 mg/kg	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		MM-ML	No	No	84 / spiked	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662) / EURL-SRM Method with alkaline hydrolysis
	LC-MS/MS (QQQ)	GC-MS/MS (QQQ)	PS-ML	No	Yes-4	61	SB-EUPT-Blank	2	Mini-Luke-Type (acetone/DCM-PE)
	LC-MS/MS (QQQ)		MM-ML	TRIS (Sodium tris-(1,3-dicloroisopropil)-Phosphate)	No	75 / spiked	SB-Other	5	QuEChERS - Citrate buffered (EN 151662)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)

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

Appendix 12 (cont.) Methods used by the participating laboratories – SRM pesticides

Quinclorac (free acid)

Lab-Code SRM6-	NRL	within routine scope	Experience w. analysis of compound	Reported result [mg/kg]	z-Score	RL [mg/kg]	Sample weight [g]	Water addition	Hydrolysis / Cleavage	pH-adj. during Extraction / Partitioning	Cleanup	Extraction- and/or Partitioning - solvents	Derivatisation	
90	x	no	None	0.298	0,46	0.01	5	Yes	No	Acetate Buffer	None	ACN	No	
6		no	< 1 y	0.307	0,60	0.04	3	Yes	No	water with 1% formic acid	None	ACN	No	
93		no	< 1 y	0.31	0,64	0.02	1	Yes	No	Sulfuric acid then Citrate-buffer	Freezing-out	ACN	No	
66		no	< 1 y	0.343	1,14	0.02	5	Yes	Yes	First alkaline hydrolysis, then neutralization then citrate buffer	None	ACN	No	
24	x	no	> 2 y	0.344	1,15	0.02	5	Yes	No	Citrate-buffer	Freezing-out	ACN / ACN	No	
14		no	None	0.541	4,10	0.01	5	Yes	No	Citrate-buffer	None	ACN	No	

1) MM – ML: Matrix matched – Multiple level; MM – SL: Matrix matched – Single level; PS – ML: Pure solvent – Multiple level; STD Add.: Standard addition
2) IL : isotropically labelled
* Haloxyfop was sought for in Test Material for EUPT-C5 not containing Haloxyphop, therefore, this „not detected" is actually not false negative.

	Detection technique	Confirmation technique	Calibration [1]	ISTD used [2]	Result recovery corrected? [3]	Recovery % (compound / spiking level)	Recovery obtained from [4]	Recovery replicates considered	Method details
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	No	Yes-4	51 / 0.01 and 0.05 mg/kg	SB-EUPT-Blank	2	QuEChERS - Acetate buffered (AOAC Official Method 2007.01)
	LC-MS/MS (QQQ)		MM-ML	TPP (triphenylphosphate)	No	70	SB-EUPT-Blank	1	QuEChERS - Original version (J. AOAC 86 (2003))
	LC-MS/MS (QQQ)		MM-ML	No	Yes-2	103	SB-Other	2	QuEChERS - Citrate buffered (EN 151662) / before adding acetonitril the sample was treated with a mixture of water and sulfuric acid
	LC-MS/MS (QQQ)	None	MM-SL	No	No	98.3	SB-EUPT-Blank	2	QuEChERS - Citrate buffered (EN 151662) / modified
	LC-MS/MS (QQQ)	LC-MS/MS QQQ	MM-ML	TRIS (Sodium tris-(1,3-dicloroisopropil)-Phosphate)	No	77.1 / 0.600 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)
	LC-MS/MS (QQQ)		StAdd to sample portions	Linuron-D6	Yes-2	55 / Quinclorac at 0.3 mg/kg	SB-EUPT-Blank	1	QuEChERS - Citrate buffered (EN 151662)

3) Yes-1: Yes, automatically via isotope labelled ISTD; Yes-2: Yes, automatically via standard additions; Yes-3: Yes, automatically via standard additions and ISTD; Yes-4: Yes, using recovery figure (as indicated)
4) SB-other: same batch using other matrix ; SB-EUPT: same batch using EUPT-blank matrix; QC: from QC validation data

Appendix 13 Possible reasons for poor performance – SRM pesticides

2.4-D (free acid)			
LabCode	z-score	Source of error localized?	Reason / Remarks
126	2,56	No	must have been some error with standard solutions
147	-2,22	Yes	Recovery not used in calculation (calculation error)
49	-2,36	Yes	Problem with concentration of standard solution
39	-2,53	No	we couldn't find the error sources
66	-2,56	No	No experience with analysis of 2,4-D. The most likely the hydrolysis did not go to completion becasue recoveries were not satisfactory.

Dithiocarbamates (sum) expr. as CS_2			
LabCode	z-score	Source of error localized?	Reason / Remarks
126	3,43	No	must have been some error with dilution or with sample homogeinity
30	2,37	No	Not unexpected due to the unstable nature of dithiocarbamates.
7	2,08	Yes	Our standard solution had the wrong concentration. The most probable reason is unstability of CS_2 stock solution.
6	2,01	No	Probably unproper sample handling (homogenization)
140	-2,35	No	1) Perhaps error during dilution of CS_2 solution 2) lack of material, analysis of duplicates was not possible. 3) Perhaps due to sample degradation during transport 4) to fit the normal-model, one result in 20 must fall in this region of the curve so, the result can happen.
108	-2,87	No	no problems with this pesticide in other commodities (unknown matrix effect?)
10	FN	No	All QC requirements fullfilled (injection with headspace conditions). Ditiocarbamates were detected when sample was reanalysed using partitioning into isooctane.

Ethephon			
LabCode	z-score	Source of error localized?	Reason / Remarks
6	-2,25	No	method not accredited, analyte not within routine scope
51	-2,30	No	Obtained same results via calibration curve and standard addtion. In future we will do research with a method that's not using derivatisation
13	FN	No	analyte not within routine scope

Glyphosate			
LabCode	z-score	Source of error localized?	Reason / Remarks
50	11,37	Yes	Calculation error (sample weight was not taken in to account.)
3	3,82	Yes	Our stock solution had the wrong concentration due to decomposition during storage (12 month old, only 46%)
90	2,15	No	Reason unknown (Re-analysis following same procedure resulted in adequate results)
147	-3,25	Yes	Calculation error (no recov. correction)
29	-3,62	Yes	obviously problems with the standard solution, the replicate was better
9	FN	Yes	This is not an actual false negative. We reported c<2mg/kg and this was correct. The problem is that by that time our RL was higher than the MRRL of 0,2 mg/kg.

Appendix 13 (cont.) Possible reasons for poor performance – SRM pesticides

Haloxyfop (free acids)			
LabCode	z-score	Source of error localized?	Reason / Remarks
66	-2,39	No	No experience with analysis of haloxyfop. Most likely the hydrolysis did not go to completion becasue recoveries were not satisfactory.
108	FN	Yes	We searched for Haloxyfop in the EUPT-C5 sample (by MRM). Retroactive analysis of SRM sample: Haloxyfop positive.

Quinclorac (free acids)			
LabCode	z-score	Source of error localized?	Reason / Remarks
14	4,10	Yes	Problem with the concentration of stock solution (compound not completely disolved!). Recognized by preparing a new, less concentrated stock solution and comparing new against old. The result of quinclorac was too high by factor of ca. 2.
22	FN	Yes	Problem with analytical instrument (poor sensitivity)

2nd Edition

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GENERAL PROTOCOL

for EU Proficiency Tests for Pesticide Residues in Food and Feed

Introduction

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

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

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

NRLs are appointed by the National Food or Feed Authorities based on the provisions of Regulation 882/2004/EC, whereas OfLs are laboratories that are actively involved in

[1] DG-SANCO = European Union, 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

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official controls in the sense of Article 26 of Regulation 396/2004/EC (e.g. by conducting pesticide residue analyses within the frame of national and/or EU control programmes).

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

EUPT-Panel

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

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

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

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

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

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

The OT and the SC (AG and QCG) together form the **EUPT-Panel**. The role of the SC is to help the OT in making decisions concerning the design of the EUPT: selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the evaluation and statistical treatment of the results and the drafting of the protocol and final report. The QCG has the additional function of supervising the quality of the EUPT and to assist the EURL in confidential aspects such as the choice of the pesticides to be present in the test material and the concentration levels at which they should be present in the test material.

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

EUPT Participants

Eligible, and at the same time legally obliged, to participate in EUPTs are all NRLs covering the same area as the organising EURL as well as all OfLs, the scope of which overlaps with that of the EUPT. The list of eligible labs will be generated using the Lab-Network Database within the EURL-Data Pool and based on the entries concerning the commodity scope of each lab. This list will be communicated to all relevant parties before each EUPT.

NRLs are responsible to check whether all relevant OfLs within their network are included in the list of eligible laboratories and whether the contact information is correct.

OfLs are responsible for keeping their profiles within the EURL-DataPool up-to-date, especially their commodity and pesticide scopes as well as their contact information.

DG-SANCO expects from each eligible lab not intending to participate in a given EUPT to explain the reasons of non-participation. This also applies to initially participating laboratories that do not deliver results.

In special cases the Organisers upon consultation with DG-SANCO will allow laboratories outside of the EURL/NRL/OfL-Network to participate in EUPTs.

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Confidentiality:

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

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

As laid down in Regulation 882/2004, NRLs are responsible for evaluating and improving their OfL network. For this reason, the EURLs will confide the laboratory codes of OfLs to their NRLs together with the final report. This will allow the NRLs to obtain the correlation between the laboratories within their network and their performance. The EURLs furthermore reserve the right to share the EUPT-results and codes among them, for example for the purpose of evaluating the overall lab-performance as requested by DG-SANCO.

Communication

The official language used in all EUPTs is English.

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

Announcement / Invitation Letter

The announcement of the individual EUPT will be issued at least 3 months before the test material is distributed to the laboratories. The announcement will be published on the EURL portal and additionally distributed via mail to the NRL/OfL mailing list available to the EURLs. The announcement will contain an invitation letter, details on how to register and where to find additional related documents, and some preliminary

information on the specific protocol such as the tentative calendar, the name of the commodity expected to be used, and the tentative Target Pesticide List.

Target Pesticide List

This list contains all pesticides, metabolites and residue definitions to be tested as well as the Minimum Required Reporting Levels (MRRLs) valid for the EUPT in question. The MRRLs are basically based upon the lowest MRLs of Regulation 396/2005/EC or the Commission Directive 2006/125/EC (Baby Food Directive).

The residue definitions listed in the Target Pesticide List of each EUPT are to be followed. In certain justified cases these residue definitions may differ from the legal ones.

Specific Protocol

For each EUPT a Specific Protocol will be published at least 2 weeks before the test material is distributed to the laboratories. This protocol will contain all the information included in the invitation in its final version, information on payment for delivery service and/or participation. Furthermore, it will also include instructions on how to handle the test material upon receipt, on how to submit results, and other relevant information.

General Procedures for Reporting Results

Laboratories are responsible for reporting their results to the Organiser within the stipulated deadlines. Each laboratory must only report one result for each of the analytes present in the test material, using the analytical procedure(s) that they would routinely use for each compound for monitoring purposes although more than one method may be used to cover all the compounds to be sought. The results (residue levels of the pesticides detected) are expressed in mg/kg and in some cases of food of animal origin in µg/kg. The laboratories will be requested to not only report individual pesticides and metabolites but also to express the residue as stated in the residue definition according to the Target Pesticide List.

Correction of Results for Recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed, (Document SANCO) it is common practice that pesticide analysis results are not corrected for recovery, but may be corrected if the average recovery is significantly different from 100% (typically if outside of the range 70-120%, with good precision). Therefore if residues data are adjusted for recovery, then this must be indicated on the specific field of the 'reporting result form'. Laboratories are required to report whether their results were adjusted for recovery and if this was the case, the recovery rate used. No recovery data is required where recovery adjustments resulted from using the 'standard additions' approach, or from the use of isotopically labelled internal standards (in both cases with spiking of the test material at the beginning of the extraction procedures). In these cases, the laboratories should report the technique used for calculation of the results instead of the recovery.

Evaluation of the Results

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

- ***False Positives***

These are the results above the MRRLs that show the apparent presence of pesticides that were listed in the Target Pesticide List, but which were: (i) not detected by the organiser, even after repeated analysis, and (ii) not detected by the overwhelming majority of the participating laboratories (e.g. 95% of the laboratories) that have targeted the specific pesticide. However, in certain instances case-by-case decisions by the EUPT-Panel will be necessary.

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

– ***False Negatives***

These are results for pesticides reported by the laboratories as "analysed" but without reporting numerical values, although they were used by the Organiser to treat the test material and were detected by the Organiser and the majority of the participants that have targeted this specific pesticide, at or above the MRRL. However, in certain instances case-by-case decisions by the EUPT-Panel will be necessary.

Where the assigned value is smaller than 4 times the MRRL, false negatives will not be assigned as this is statistically not justifiable.

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

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

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

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

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

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

– ***z-scores***

This parameter is calculated using the following formula:

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

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

Any z-scores of > 5 will be reported as "5" particularly where summed z-scores of many pesticides are calculated (see SWZ and SZ2 below).

z-Scores will be interpreted in the following way:

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

For results that are considered to be false negatives, z-scores will be calculated using the MRRL or RL (the laboratory's Reporting Limit) if the RL < MRRL.

The EUPT-Panel will consider whether, or not, these values should appear in the z-score histograms.

However, a z-score will not be calculated for any false positive result.

– ***Category A and B Classification***

The EUPT-Panel will decide in each EUPT whether to classify the laboratories in two groups, A and B. Laboratories that detect a sufficiently high percentage of the pesticides present in the test material (e.g. at least 90%) and reported no false positives will have

demonstrated 'sufficient scope' and will therefore be classified in Category A. The 90% criterion will be applied following Table 1.

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

No. of Pesticides Present in the Sample (N)	90%	Min. number of Pesticides needed to be detected to have sufficient scope (n)	n
3	2.7	3	N
4	3.6	4	
5	4.5	4	N - 1
6	5.4	5	
7	6.3	6	
8	7.2	7	
9	8.1	8	
10	9.0	9	
11	9.9	10	
12	10.8	11	
13	11.7	12	
14	12.6	13	
15	13.5	13	N - 2
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	
20	18.0	18	
21	18.9	19	
22	19.8	20	
23	20.7	21	
24	21.6	22	
25	22.5	22	N - 3
26	23.4	23	

– ***Combined z-scores***

❖ For evaluation of the overall performance of the laboratories within Category A, two formulas will be used.

i. Sum of Weighted z-Scores (SWZ)

The sum of weighted z-scores formula uses the z-scores with a fixed maximum value of 5 for individual z-scores, using the following formula:

$$|SWZ = \frac{\sum_{Zi=0}^{|Zi|\le 2}|z_i|\cdot 1+\sum_{|Zi|>2}^{|Zi|\le 3}|z_i|\cdot 3+\sum_{|Zi|>3}^{\infty}|z_i|\cdot 5}{n}$$

n = number of detected results

ii. Sum of Squared z-Scores (SZ^2)

The sum of squared z-scores formula multiplies each z-score by itself and not by an arbitrary number, using the following formula:

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

The SWZ and the SZ^2 have the following classification similar to the z-score:

Formula	Good	Satisfactory	Unsatisfactory
SWZ	≤ 2	$2 < SWZ \le 3$	$SWZ > 3$
SZ^2	≤ 2	$2 < SZ^2 \le 3$	$SZ^2 > 3$

Both, SWZ and SZ^2 are considered to be of lesser importance than the individual z-scores. The EUPT-Panel retains the right not to use them if they are considered not useful.

❖ Laboratories in Category B will be ranked according to the percentage of pesticides detected from the total number of pesticides present in the sample. The number of acceptable z-score achieved will be recall too.

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Publication of Results

The preliminary results from the EUPTs will be reported to the participants within 2 months from the deadline for result submission.

The final report will be published shortly after the EUPT-Panel has discussed the results. Taking into account that the EUPT-Panel meets normally only once a year to discuss the results of all EUPTs organised by the EURLs each year, the final report may be published up to 8 months after the deadline for results submission.

Follow-up activities

Laboratories are expected to undertake activities towards tracing back the sources of erroneous or strongly deviating results including all false positives and false negatives as well as results with |z|>2.

Upon request the corresponding NRL or EURL of a lab are to be informed about the outcome of these traceability activities.

Disclaimer

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

Laboratory Rights

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

SPECIFIC PROTOCOL

for the EU Proficiency Test for Pesticide Residues in Cereals using Multi- and Single-Residue Methods, EUPT-C5/SRM6 (2011)

(last updated: 08.03.2011)

Introduction

This protocol is complementary to the General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed[1]. The current proficiency test is collaboratively organized by the EURL-CF[2] and the EURL-SRM[3] and covers pesticides that are determined by both Multi-Residue Methods (MRMs) and Single-Residue Methods (SRMs). This EUPT is to be performed by all National Reference Laboratories for Cereals and Feeding stuffs (NRL-CFs), all NRLs for Single Residue Methods (NRL-SRMs) as well as by all official EU laboratories (OfLs) responsible for official pesticide residue controls on cereals and feeding stuff, as far as their scope overlaps with that of the EUPT-C5/SRM6. The commodity rice is to be considered as representative for commodities with "high starch and/or protein content and low water and fat content" **(see** SANCO document 10684/2009**)[4].**

Test Items (Test Materials)

This proficiency test concerns the analysis of pesticide residues in rice. The rice was grown in Brazil in 2010.

Two different spiked Test Items are available:

1) **MRM-Test Item**, with the contained pesticides having been partly applied in the field and partly spiked in the laboratory
2) **SRM-Test Item**, with all pesticides having been spiked in the laboratory

In addition, a blank Test Item is also provided, that can be used for recovery experiments as well as for the preparation of matrix-matched calibration standards for both MRM and SRM-pesticides.

The Organizers will check the spiked Test Items for sufficient homogeneity and for stability at conditions reproducing sample shipment and storage during the duration of the test. The blank Test Item will be also checked to prove that the target analytes are not contained at any relevant levels. All these test will be conducted by an ISO 17025 accredited laboratory.

Analytical Parameters

The Test Item contains several pesticides from the Target Pesticides List.

Laboratories should carefully read the Target Pesticides List, where important information about reporting of results, as well as the Minimum Required Reporting Levels (MRRLs) is given. The Target Pesticides List contains summed residue definitions, that should be calculated and reported as stated in the list, as well as individual components where these should be analyzed and reported separately. For practical reasons, the residue definitions listed in the Target Pesticides List, in some cases, do not fully match with the legal ones.

The MRRL values will be used to help to identify false positive and false negative results and for the calculation of z-scores for false negatives.

Amount of Test Item

For the analysis of the MRM-compounds the participants will receive:

- approximately 50 g of rice Test Item with incurred and spiked pesticides and
- approximately 50 g of blank rice Test Item.

For the analysis of the SRM-compounds the participants will receive:

- approximately 250 g of rice Test Item with spiked pesticides and
- approximately 250 g of blank rice Test Item.

All samples will be frozen and packed in thermo boxes together with a freeze gel pack.

As the amount of available material is limited, additional material can only be delivered to the laboratories in exceptional cases and only if sufficient explanations are given by the requesting laboratory. No additional material will be provided to be used for purposes not relevant to the current EUPT.

[1] http://www.crl-pesticides.eu/library/docs/allcrl/General%20Protocol%20for%20EUPTs-2ndEd-Nov2010.pdf

[2] EURL-CF= European Union Reference Laboratory for pesticides in Cereals and Feed

[3] EURL-SRM= European Union Reference Laboratory for pesticides requiring Single Residue Methods

[4] http://www.crl-pesticides.eu/library/docs/allcrl/AqcGuidance_Sanco_2009_10684.pdf

Shipment of Test Items

The Test Items are planned to be shipped on 14 March, 2011.

Test Items will be shipped frozen and packed in thermo-boxes together with a freeze gel pack. The organisers will aim to ensure that all participating laboratories will receive their shipments on the same day. Prior to shipment a reminder will be sent to the participating laboratories by e-mail.

Laboratories must make their own arrangements for the receipt of the package. They should inform the Organiser of any public holidays in their country/city during the week of the shipment, and must **make the necessary arrangements to receive the shipment, even if the laboratory is closed**.

Instructions on Test Item Handling

Once received, the Test Item should be stored deep frozen (at -18℃ or less) before analysis to avoid any possible deterioration/spoilage and to minimize pesticide losses. The Test Item should be mixed thoroughly, before taking the analytical portion(s).

All participants should use their own routine standard operating procedures for extraction, clean-up and analytical measurement and their own reference standards for identification and quantification purposes. Considering the available amount of Test Item, laboratories employing methods requiring large analytical portions are advised to scale them down. As the test material is already milled and sufficiently homogeneous, method sensitivity is the only major factor to consider when deciding about the size of the analytical portion.

The homogeneity tests will be conducted using 5 g of Test Item in all cases except for dithiocarbamates, where 20 g will be used. As sub-sampling variability increases with decreasing analytical portion size, sufficient homogeneity can only be guaranteed where participants employ sample portions that are equal or larger than the ones stated above.

Results Submission Website and Deadline

Sample receipt acknowledgement, analytical results and method information are to be submitted via the "EUPT-C5/SRM6 Result Submission Website" (http://thor.dfvf.dk/eupt-c5/srm6).

This website will be **accessible from 16 March onwards** and also contains a link to specific instructions on how to enter the data in the result submission website

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

The labs can fill-in the sub-pages at different stages/sessions. Remember to save the data of each page before leaving it.

Test Item Receipt and Acceptance - Subpage 0

Once the laboratory has received the Test Items it must report to the organiser, via t the EUPT-C5/SRM6 Result Submission Website (subpage 0), the date of receipt, the condition of the Test Item, and its acceptance. The deadline for acceptance is the 18 March 2011. If the laboratory does not respond by this deadline the Organisers will assume that the Test Items have been received and accepted. **If any participants have not received the Test Items by the 18th of March 2011, they must inform the Organiser immediately by e-mail** (crlcereal@food.dtu.dk).

Reporting Qualitative and Quantitative Results - Subpages 1 and 2

To report their results, laboratories must access the EUPT-C5/SRM6 Result Submission Website (subpages 1 and 2). **Before entering the results please carefully read the Target Pesticide List, since the residue definitions are not given on the Result Submission Website.**

It should not be assumed that only pesticides registered for use on rice are present in the Test Item.

Deadline: **All results must be reported on the online result submission website by 11 April 2011, at the latest.** The website will not be accessible after this date, and any results reported after the deadline will not be included in the statistical treatment, or in the final report.

Summed residue definitions: For pesticides where the residue definition is a sum of components, results for both the sum and the listed individual components must be reported.
- If all listed[5] components of a summed residue definition were targeted by a laboratory but only part of them were detected and quantified, the laboratory should calculate and report the result of the respective summed residue definition, considering only the quantified components.
- If none or only part of the listed components within a summed residue definition were targeted by a laboratory, the Organizers will consider the summed residue definition as non-analyzed and ignore any numerical results reported.

[5] separately listed in the Pesticide Target List

Results should not be reported where a pesticide was not detected, or was detected below the RL (Reporting Limit) of the laboratory, or below the MRRL. In these cases, it should be recorded as 'ND' (Not Detected). Results reported as <RL will be considered as „Not Detected".

The results (residue levels of the pesticides detected) must be expressed in mg/kg.
Significant Figures:

Residue levels <0.010 mg/kg;

- to be expressed to two significant figures (e.g. 0.0058 mg/kg).

Residue levels ≥ 0.010 mg/kg;

- to be expressed to three significant figures, e.g. 0.156, 1.64, 10.3 mg/kg.

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

- **"Concentration in mg/kg":** here the results should be filled-in, that you would report in your routine work. That means, the recovery-corrected result should be reported, if it reflects the normal procedure in your lab otherwise the non-recovery-corrected result should be reported.
- **"Conc. in blank in mg/kg":** any concentration values of pesticides from the Target Pesticides List you will determine in the blank (even at levels below the MRRL) you can enter here.
- **"Experience with this compound.** Use the dropdown-menu to indicate how many years you have analysed for this compound using the method applied in this EUPT.
- **"Is your result recovery-corrected?":** Please specify whether the result was recovery-corrected and the kind of recovery-correction via the dropdown-menu.
- **"Recovery figure (in %)":** Here labs can report any recovery figures (in %) obtained for the analyte in question. If a recovery factor was used to correct for recovery, the recovery figure (in %) used for the calculation MUST be reported.

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

Reporting Information on Analytical Methodology - Subpage 3

All laboratories are requested to provide information on the analytical method(s) they have used via the EUPT-C5/SRM6 Result Submission Website (subpage 3). The laboratories are asked to thoroughly fill-in this important information in order to minimize the administrative burden of collecting this information a posteriori.

Reporting missing information after result submission deadline – Subpage 4

In case of false negative results the affected laboratories will be asked to provide details on the methodology used after the deadline for result submission. This can be done by accessing subpage 4 within the EUPT-C5/SRM6 Result Submission Website. The dates this subpage will be accessible will be announced in due time. If the page is empty when you access subpage 4, no further information is needed from you and you can leave the page without any further actions.

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

Follow-up actions

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

Documents

All documents relating to EUPT–C5/SRM6 can be found in the EURL-Document Repository (CIRCA/FIS-VL). Links to the documents can be found in the EUPT–C5/SRM6 Website.

Calendar (see also http://www.crl-pesticides.eu/library/docs/cf/EUPT_C5_SRM6_Calendar.pdf)

Who?	Activity	Date / Period
Organizers	Release of "Specific PT-Protocol"	February 2011
Participants	Deadline for registration for the EUPT-C5/SRM6 (http://thor.dfvf.dk/eupt-signup)	Extended to 28 February 2011
Organizers	Test Item distribution and information to the laboratories regarding upcoming shipment	Starting 14 March 2011
Participants	Confirmation of Test Item receipt - **Subpage 0**	18 March 2011
Participants	Reporting of test results and method information **Subpages 1, 2 and 3**	11 April 2011
Participants	Reporting missing information - **Subpage 4**	To be announced in due time
Organizers	Dispatch of a preliminary report to all participants (only results, no statistical treatment)	June 2011
Organizers	Dispatch of the final report as pdf-file	November 2011

Participation Fees

For participating laboratories from the EU, EU-candidate states and EFTA states the participation fee will be

- 150 for all labs participating only in the MRM-partof this EUPT
- 150 for the labs participating only in the SRM part
- 200 for the labs participating in both parts.

The participation fees for laboratories from third countries:

- 300 for all labs participating only in the MRM-partof this EUPT
- 300 for the labs participating only in the SRM part
- 450 for the labs participating in both parts.

For further information visit the website www.eurl-pesticides.eu

Delays in Payment

The participants will receive an invoice from DTU-Dianova. The invoice will be sent by ordinary mail. The terms of payment are 30 days net. After this deadline reminders will be sent. From the second reminder onwards an administration fee of DKK 100.00 excluding VAT (ca. 13) will be charged per reminder.

Any question concerning invoices must be directed to DTU-Dianova at proficiencytest@food.dtu.dk

Contact information

***EURL-CF (MRM part of EUPT)**:*

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TARGET PESTICIDE LIST

for the EUPT – C5/SRM6 2011

(last updated: 23.02.2011)

Twenty one new MRM pesticides added to the Target Pesticide List from EUPT-C4 (2010) are marked in bold.

One new SRM pesticide is added to the list. Note that the SRM pesticides are listed in the table on page 5.

MRM-Compounds

Pesticides/Residue Definitions	MRRL (mg/kg)
Azoxystrobin	0.01
Acephate	0.01
Azinphos-methyl	0.01
Bifenthrin	0.01
Captan	0.01
Carbaryl	0.01
Carbendazim and benomyl (carbendazim + benomyl, expressed as carbendazim)	0.01
Carbofuran **(Sum of Carbofuran and 3-Hydroxycarbofuran expressed as Carbofuran)**	0.01
- Carbofuran	0.01
-3-Hydroxycarbofuran	0.01
Carboxin	0.01
Chlorfenvinphos	0.01
Chlorothanlonil	0.01
Chlorpropham (only parent compound)	0.01
Chlorpyrifos	0.01
Chlorpyrifos-methyl	0.01
Cyfluthrin **(cyfluthrin incl. other mixtures of constituent isomers (sum of isomers))**	**0.01**
Cypermethrin (cypermethrin incl. other mixtures of constituent isomers (sum of isomers))	0.01

Pesticides/Residue Definitions	MRRL (mg/kg)
Cyproconazole	0.01
Cyprodinil	0.01
DDT **(sum of p,p´-DDT, o,p´-DDT, p-p´-DDE and p,p´-TDE (DDD) expressed as DDT)**	0.01
Deltamethrin (cis-deltamethrin)	0.01
Diazinon	0.01
Dichlorvos	0.01
Difenoconazole	0.01
Diflubenzuron	0.01
Dimethoate (sum of dimethoate and omethoate expressed as dimethoate)	0.01
- Dimethoate	0.01
- Omethoate	0.01
Endosulfan (sum of alpha- and beta-isomers and endosulfan sulphate expressed as endosulfan)	0.01
- Endosulfan sulfate	0.01
- Endosulfan α	0.01
- Endosulfan β	0.01
Epoxiconazole	0.01
Ethion	0.01
Fenbuconazole	0.01
Fenhexamid	0.01
Fenitrothion	0.01
Fenpropimorph	0.01
Fenthion **(fenthion and its oxigen analogue, their sulfoxides and sulfone expressed as fenthion)**	0.01
- Fenthion	0.01
- Fenthion sulfoxide	0.01
- Fenthion sulfone	0.01
- Fenthion oxon	0.01
- Fenthion oxon sulfoxide	0.01
- Fenthion oxon sulfone	0.01
Fenvalerate and Esfenvalerate (Sum of RR/SS and RS/SR isomers)	0.01
Fipronil (parent compound)	0.01
Fludioxonil	0.01

Pesticides/Residue Definitions	MRRL (mg/kg)
Fluquinconazole	0.01
Flusilazole	0.01
Flutriafol	0.01
Hexachlorociclohexane (HCH) (sum of isomers, except the gamma isomer)	0.01
- HCH-alpha	0.01
- HCH-beta	0.01
Hexaconazole	0.01
Imazalil	0.01
Imidacloprid	0.01
Iprodione	0.01
Isoprothiolane	0.01
Isoproturon	0.01
Kresoxim-methyl	0.01
Lambda-cyhalothrin	0.01
Lindane (gamma- isomer of hexachlorocyclohexane (HCH))	0.01
Linuron	0.01
Malathion (Malathion + Malaoxon, expressed as Malathion)	0.01
- Malaoxon	0.01
- Malathion	0.01
Metconazole	0.01
Methacrifos	0.01
Methomyl and Thiodicarb (sum of methomyl and thiodicarb, expressed as methomyl)	0.01
- Methomyl	0.01
- Thiodicarb	0.01
Metribuzin	0.01
Oxydemeton-methyl (sum of oxydemeton-methyl and demeton-S-methylsulfone expressed as oxydemeton-methyl)	0.01
- Oxydemeton-methyl	0.01
- Demeton-S-methylsulfone	0.01
Paclobutrazol	0.01
Parathion	0.01
Penconazole	0.01
Pendimethalin	0.01

Pesticides/Residue Definitions	MRRL (mg/kg)
Permethrin (sum of isomers)	0.01
Phosphamidon	0.01
Pirimicarb (sum of pirimicarb and desmethyl pirimicarb, expressed as pirimicarb)	0.01
- Pirimicarb	0.01
- Desmethyl pirimicarb	0.01
Pirimiphos-methyl	0.01
Prochloraz (parent compound only)	0.01
Procymidone	0.01
Propiconazole	0.01
Prothioconazole (Prothioconazole-desthio)	0.01
Pyraclostrobin	0.01
Pyrimethanil	0.01
Quinoxyfen	0.01
Spiroxamine	0.01
Tebuconazole	0.01
Tebufenozide	0.01
Thiabendazole	0.01
Thiacloprid	0.01
Thiamethoxam (sum of thiamethoxam and clothianidin expressed as thiamethoxam)	0.01
- Thiamethoxam	0.01
- Clothianidin	0.01
Thiophanate-methyl	0.01
Triadimefon and triadimenol (sum of triadimefon and triadimenol)	0.01
- Triadimefon	0.01
- Triadimenol	0.01
Triazophos	0.01
Tricyclazole	0.01
Trifloxystrobin	0.01
Trifluralin	0.01
Triticonazole	0.01
Vinclozolin (only parent compound)	0.01

Appendix 16 (cont.) Target Pesticide List of EUPT-C5/SRM6

SRM-Compounds

Pesticides/Residue Definitions	MRRL (mg/kg)
*2.4-D (free acid)	0.02
*Bromide ion	5
*Chlormequat cation	0.02
Dichlorprop (2,4-DP) including Dichlorprop-P (free acids)	0.02
*Dithiocarbamates (including maneb, mancozeb, metiram, propineb, thiram and ziram) expressed as CS2	0.05
*Ethephon	0.02
*Fluazifop including Fluazifop-P (free acids)	0.02
*Glyphosate	0.05
*Haloxyfop including Haloxyfop-R (free acids)	0.02
MCPA (free acid)	0.02
Mecoprop (MCPP) including Mecoprop-P (free acids)	0.02
*Mepiquat cation	0.02
Quinclorac (free acid)	0.02

* The asterisk indicates that these SRM-compounds are part of the EU coordinated Community Control Program (CCP) and that they will be thus **considered in the overall performance-evaluation of the labs** as regards both their inclusion in the **lab-scope** and the results (**z-scores**) achieved for these compounds present in the test-sample. Chlormequat and mepiquat are not to be targeted in rice within the frame of the CCP but they were still marked with an asterisk as the commodity rice in this EUPT is to be considered as representative for cereals as a group.

Notes:

- For analytical and practical reasons the residue definitions applying in this EUPT do not always correspond to those in the legislation
- This document may be subject to minor changes, please thus check periodically, and especially after the start of the test to make sure you are using the latest version available

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