Proficiency Test on pesticide residues in rye flour

EU Reference Laboratory on Cereals & Feeding stuff

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DTU Food
National Food Institute

EU PROFICIENCY TESTS
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Pesticide Residues in Rye Flour

Final Report

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PREFACE

Regulation (EC) No 882/2004 [1], defines the general tasks and duties of the European Union Reference Laboratories (EURLs) for Food, Feed and Animal Health including the organisation of comparative tests. These proficiency tests (PTs) are carried out on an annual basis, and aim to improve the quality, accuracy and comparability of the analytical results generated by EU Member States within the framework of the EU multi-annual co-ordinated control and national monitoring programmes. Participation in the proficiency test scheme "European Union Proficiency Tests (EUPTs) for pesticide residues" is mandatory according to Article 28 of Regulation (EC) No 396/2005 on maximum residue levels of pesticides in, or on, food and feed of plant and animal origin [2], as long as the analytical scope of the PT and the laboratory overlap.

The present EUPT was the tenth organized within the frame of the EURL activities with cereal or feed matrices as Test Items. The previous PTs were EUPT-C1/SRM2 on wheat, EUPT-C2 on wheat, EUPT-C3/SRM4 on oats, EUPT-C4 on rye, EUPT-C5/SRM6 on rice, EUPT-C6 on barley, EUPT-CF7 on animal feed, EUPT-CF8 on wheat and EUPT-CF9 on rye. The PTs in 2007, 2009 and 2011 were jointly organised by the EURL-CF and EURL-SRM using and focusing on both MRM and SRM pesticides, whereas the present EUPT-CF10 on rye was only focused on MRM-pesticides. The rye Test Item used for EUPT-CF10 was treated with formulations in the field and post-harvest in the laboratory.

Participation in EUPT-CF10 was compulsory for all National Reference Laboratories (NRLs) and Official Laboratories (OfLs) within the EU involved in the determination of pesticide residues in cereals for human or animal consumption using multiresidue methods for their national programmes. Official laboratories from EFTA countries (Iceland, Norway and Switzerland), as well as official laboratories from EU-candidate states, were invited to take part in this EUPT. Selected laboratories from Third Countries were also allowed to take part in this exercise, but their results, together with the EU-candidate state laboratories, were not used when establishing the Assigned Values for each pesticide.

DG-SANTE will have full access to all data from 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.

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1. INTRODUCTION

On 4 December 2015 the announcement of the 10th European Commission's Proficiency Test on cereals and feed (EUPT-CF10) was published on the EURL website, together with the Calendar and the Pesticide Target List including all compounds that could potentially be present in the Test Item. The Target Pesticides List included 134 individual compulsory compounds and 7 voluntary requiring the use of multiresidue methods (MRMs), along with a minimum required reporting level (MRRL) stipulated for each compound. Links to The General Protocol containing information (**Annex 1**) that is common to all EUPTs, the Specific protocol (**Annex 2**), as well as a list of labs that are obliged to take part in the EUPT-CF10, were provided via the homepage. Laboratories were able to register on-line from 10 February to 20 March 2016. In total 141 laboratories from EU and EFTA countries agreed to participate in the test as well as 22 laboratories from EU-Candidate States and Third Countries (**Appendix 1**).

The present proficiency test was performed using rye flour of Danish origin, which had been partly treated in the field, and partly spiked post-harvest at the facilities of the EURL-CF. The Test Item contained 18 compounds in total. Danish Centre for Food and Agriculture at Aarhus University grew the rye and performed the field treatments in 2015. The pesticides employed for the field treatment were selected by the EURL-CF and the EURL quality control group and the application rates and harvest intervals chosen were based on previous experience and data from supervised residue trials. The harvested rye grains were spiked with 18 pesticides post-harvest, and then checked for homogeneity before shipping to participants. Furthermore, the stabilities of the pesticides in the Treated Test Item were checked several times during the period of time allowed for laboratories to complete the PT exercise.

The participating laboratories were provided with 125 g portions of the Treated rye Test Item and 125 g of untreated Blank rye Test Item. Both Test Items were shipped to participants on 20 April 2016 and the deadline for submission of results to the Organiser was the 19 May 2016. The participants were asked to analyse the Treated Test Item as well as the Blank Test Item and report the concentrations of any pesticide residues found that were included in the Target Pesticide List (**Appendix 2**). Submission of results was performed online via the website.

1.1 Analytical methods

The QuEChERS method [3] was used by the organiser to test the homogeneity and stability of the Test Items. Determination was performed GC-MS/MS and LC-MS/MS.

- QuEChERS: Cold water was added to a milled portion of the test item and shaken. Acetonitrile was added immediately and the tube was shaken again. A salt and buffer mixture was then added together with ceramic homogenizers and the sample was shaken vigorously for 1 min. After centrifugation, an aliquot of the supernatant was cleaned by freezing out. After additional centrifugation of the cold extract the supernatant was transferred to a tube containing PSA and $MgSO_4$. After shaking and centrifugation the extract was ready for analysis by GC-MS/MS and LC-MS/MS.

1.2 Selection of Pesticides for the Target Pesticide List

The pesticides to be included in the target pesticides list were selected by the Organiser and the Quality Control Group taking into account the present and upcoming scope of the EU multi-annual coordinated control programme, a pesticide priority list ranking the pesticides according to their relevance and risk-potential, as well as a list of pesticides relevant to the specific commodity (rye). The overall capacity and capability of the laboratories within the EU, as assessed from previous PTs and surveys, was also taken into account. The minimum required reporting level (MRRL) for all pesticides in the target list was set at 0.01 mg/kg.

1.3 Preparation of the treated Test Item

Before preparing the Test Item, the pesticides and suitable target residue levels for the study were selected. The application rates and harvest intervals for the 14 pesticides used for treatment in the field were chosen based on experience from previous PTs and data from supervised residue trials. The field spraying was performed by the Danish Centre for Food and Agriculture at Aarhus University. Approximately, 70 kg of the harvested rye grain was delivered for preparation of the Test Item. Following a preliminary analysis of the material it was decided to additionally spike in the laboratory with an additional six pesticides, which were not included in the field treatments and over spike with one pesticide where the residue in the rye was too low (**Table 1)**. Spiking in the laboratory was performed using formulations or pure standards. One kilogram of the field treated rye was spiked and subsequently mixed with 44 kg of field treated rye and homogenised thoroughly. The resulting 45 kg of mixed rye grain was milled separately per approximately 4 kilograms portions. To ensure that a well-homogenised bulk was obtained, with respect to the spiked residues, the 4 kilogram portions were initially mixed individually by hand. Two 4 kilograms portions were then mixed together by hand and finally all the 8 kg portions were combined. One hundred twenty-five gram 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 Item

The rye used to prepare the blank Test Item was also produced by the Danish Centre for Food and Agriculture at Aarhus University under similar growing conditions as the treated crop but without any pesticide treatment in the field or spiking in the laboratory. One hundred and twenty-five gram portions were weighed out into screw-capped polyethylene plastic bottles, sealed, and stored in a freezer at about -20 °C prior to distribution to participants.

1.5 Homogeneity test

Ten bottles of the pesticide treated Test Items were randomly chosen and analyses were performed on duplicate portions taken from each bottle using the analytical methods described in section 1.1. The sequence of analyses and injections were also randomly chosen. Quantification was performed using a 5-point calibration curve constructed from matrix-matched standards.

The statistical evaluation 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 2**. The individual residues data from the homogeneity tests, as well as the results of the statistical analyses, are given in **Appendix 3**.

The homogeneity test is to show that the between bottle variance is not greater than the within bottle variance. The acceptance criteria to show that the Test Items were sufficiently homogeneous for the proficiency test was that: $S_s^2 < c$ where S_s is the between-bottle sample standard deviation and $c = F_1 \times \sigma_{all}^2 + F_{2\,x}\, s_{an}^2$; F1 and F2 being constants with values of 1.83 and 0.93, respectively, from the 11 samples taken, $\sigma_{all}^2 = 0.3 \times$ FFP RSD (25%) x 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 treated Test Item was considered to be sufficiently homogenous and suitable for the EUPT-CF10.

Table 1. Pesticides used for application in the field and/or spiked in the laboratory.

Pesticides [1]	Application in field	Spike in laboratory	Formulation/standard
Azoxystrobin	x		Amistar
Bixafen	x		Aviator
Boscalid	x		Viverda
Buprofezin		x	Analytical standard
Carbendazim	x		Benlate
Cypermethrin	x	x	Cyperb
Epoxiconazole	x		Viverda
Fenpropidin	x		Tern
Fluopyram	x		Propulse
Heptachlor		x	Analytical standard
Isocarbophos		x	Analytical standard
Metrafenone	x		Flexity
Pencycuron		x	Analytical standard
Pirimicarb-desmethyl		x	Analytical standard
Prothioconazole	x		Aviator and Propulse
Pyraclostrobin	x		Viverda
Tebuconazole	x		Folicur
Tetramethrin		x	Analytical standard

[1] Deltamethrin and lambda-cyhalothrin were also applied in the field, but too low residue levels were achieved.

1.6 Stability tests

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

The stability test was performed according to ISO 13528, Annex B [5]. Two different storage temperatures were used; room temperature and -18 °C. Six sub-samples (analytical portions) were analysed on each test day. A pesticide is considered to be adequately stable if $| x1 - yi | \leq 0.3 \times \sigma$, where x1 is the mean value of the first stability test, yi the mean value of the last stability test and σ the standard deviation used for proficiency assessment (25% of the assigned value):

The dates of testing were as follows:

Day 1: 7 March 2016

Day 2: 12 March 2016

Day 3: 11 April 2016

Table 2. Statistical evaluation of the homogeneity test data (n=22 analyses using a sub-sample of 5 g in each case). S_s: Between Sampling Standard Deviation

Pesticide	Mean, mg/kg	S_s^2	c	$S_s^2 < c$
Azoxystrobin	0.087	0.00000	0.0001	Pass
Bixafen	0.073	0.00000	0.0001	Pass
Boscalid	0.422	0.00030	0.0020	Pass
Buprofezin	0.048	0.00000	0.0000	Pass
Carbendazim	0.077	0.00000	0.0001	Pass
Cypermethrin	0.140	0.00011	0.0004	Pass
Epoxiconazole	0.173	0.00005	0.0004	Pass
Fenpropidin	0.313	0.00007	0.0012	Pass
Fluopyram	0.257	0.00006	0.0007	Pass
Heptachlor	0.031	0.00000	0.0000	Pass
Isocarbophos	0.048	0	0.0000	Pass
Metrafenone	0.086	0.00001	0.0001	Pass
Pencycuron	0.032	0.00000	0.0000	Pass
Pirimicarb-desmethyl	0.050	0.00000	0.0000	Pass
Prothioconazole-desthio	0.112	0	0.0002	Pass
Pyraclostrobin	0.098	0.00002	0.0001	Pass
Tebuconazole	0.099	0.00002	0.0001	Pass
Tetramethrin	0.096	0.00001	0.0001	Pass

Table 3. Statistical evaluation of the stability test data

Pesticide	Mean, mg/kg	$\lvert x1 - yi \rvert$	$0.3\times\sigma$	$\lvert x1 - yi \rvert \leq 0.3\times\sigma$
Azoxystrobin	0.088	0.001	0.007	Pass
Bixafen	0.077	0.002	0.006	Pass
Boscalid	0.436	0.029	0.031	Pass
Buprofezin	0.046	0.002	0.004	Pass
Carbendazim	0.078	0.003	0.006	Pass
Cypermethrin	0.110	0.000	0.010	Pass
Epoxiconazole	0.192	0.009	0.013	Pass
Fenpropidin	0.382	0.003	0.026	Pass
Fluopyram	0.265	0.014	0.019	Pass
Heptachlor	0.029	0.001	0.002	Pass
Isocarbophos	0.048	0.003	0.004	Pass
Metrafenone	0.092	0.003	0.007	Pass
Pencycuron	0.031	0.001	0.002	Pass
Pirimicarb-desmethyl	0.055	0.001	0.004	Pass
Prothioconazole-desthio	0.113	0.004	0.011	Pass
Pyraclostrobin	0.101	0.005	0.007	Pass
Tebuconazole	0.093	0.001	0.007	Pass
Tetramethrin	0.098	0.003	0.007	Pass

The results of the stability test for storage temperature -18 °C are given in Table 3. All pesticides passed the test at -18 °C. However, heptachlor, pencycuron and pirimicarb-desmethyl did not pass when stored for 4 weeks at room temperature and these compounds were clearly partially degraded. Additionally, isocarbophos showed signs of degradation but to a much lesser degree than the other compounds. See the individual stability figures for all pesticides in Appendix 4.

The laboratories were instructed to store the test item at -18 degree and the results for heptachlor, isocarbophos, pencycuron and pirimicarb-desmethyl were very good with robust RSDs at 21%, 16%, 16% and 15%, respectively. The stability of the test material was consequently acceptable for all pesticides.

1.7 Organisational details

1.7.1 Access to documents, registration and confidentiality

In the invitation letter, all NRLs and OfLs were requested to register using the online registration link from 11 January to 1 February 2016. All documents related to this EUPT (Calendar, Target Pesticides List, Specific Protocol, General Protocol) were uploaded to the EURL website and the CIRCA platform. Laboratories that were intending not to participate were given the opportunity to explain the reasons for their non-participation. Participants from third countries also had access to another online registration link after contacting the EURL. After registration, the participants were provided with username, password, laboratory code and link for the online result submission website. This ensured confidentiality throughout the entire duration of the PT.

1.7.2 Distribution of the Test Item

On 7 March 2016, one bottle of treated Test Item (125 g) and one bottle of blank Test Item (125 g) were shipped to all participants in insulated polystyrene boxes containing a freezer block. The laboratories were asked to check the state of the sample on receipt and to enter the website (see above) and report whether they accept/not accept the Test Items. Test Items for Third Countries were shipped one week earlier due the often very time-consuming customs procedures at the borders.

1.7.3 Submission of results

An online submission tool was developed that allowed participants to submit their results via the internet. All participants had access to the result-submission website (http://pesticide.food.dtu.dk) from a few days after shipment until the result-submission deadline (11 April 2016). Participants were asked not only to report their analytical results, but also to give information regarding accreditation, reporting limits and details regarding the methods they used to analyse the Test Items.

2. EVALUATION OF THE RESULTS

2.1 False positives and negatives

2.1.1 False positives

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

2.1.2 False negatives

These are results for pesticides reported by the laboratories as 'analysed' but without reporting numerical values although they were: a) used by the Organiser to treat the Test Item and b) detected by the Organiser as well as the majority of the participants that had targeted these specific pesticides at, or above the respective MRRLs. Results reported as '< RL' (RL= Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary. In cases of the assigned value being less than a factor of 4 times the MRRL, false negatives will typically not be assigned. The EUPT-Panel may decide to take case-by-case decisions in this respect after considering all relevant factors such as the result distribution and the reporting limits of the affected labs.

2.2 Estimation of the true concentration (μ)

In order to minimise the influence of out-lying results on the statistical evaluation, the assigned value (equal consensus concentration) will typically be estimated using robust statistics as described in ISO 13528:2009 [5]. The EUPT-Panel has decided that only results from laboratories that added water to the samples before extraction should be included in the calculation of the assigned values as this procedure has repeatedly demonstrated good performance in the past.

2.3 Uncertainty of the assigned value

The uncertainty of the assigned values μ_i is calculated according to ISO 13528:2009 [5] as:

$$u(x_{pt}) = 1.25 \frac{s*}{\sqrt{n}}$$

Where:

- $u(x_{pt})$ is the uncertainty in mg/kg
- s* is the robust standard deviation estimate
- n is the total number results

2.4 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:

$$FFP\text{-}\sigma_{pt} = 0.25 * x_{pt}$$

Where:

- FFP-σpt is the target fit-for-pourse standard deviation of the assigned value
- xpt is the assigned value

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

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

2.5 Z scores

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

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

Where:

- x_i is the value reported by the laboratory
- x_{pt} the assigned value
- FFP-σ_{pt} is the standard deviation using FFP approach

Z scores will be rounded to one decimal place. For the calculation of combined z score (see below) the original z scores will be used and rounded to one decimal place after calculation. Any z scores >5 will typically be reported as >5 and a value of '5' will be used to calculate combined z scores (see below).

Z scores will be interpreted in the following way as is set in the ISO 17043:2010 [6]:

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

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

2.6 Category A and B classification and combined z scores (AZ^2)

Laboratories that are able to analyse at least 90% of the compulsory pesticides in the target pesticides list, have correctly detected and quantified a sufficiently high percentage of the pesticides present in the Test Item (at least 90 %) and reported no false positives will have demonstrated 'sufficient scope' and can therefore be classified into Category A. For the 90% criterion the number of pesticides needed to be correctly analysed to have sufficient scope will be calculated by multiplying the number of compulsory pesticides from the Target Pesticides List by 0.9 and rounding to the nearest full number with 0.5 decimals being rounded downwards.

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

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

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".

Based on the AZ^2 achieved, the laboratories are classified as follows:

$AZ^2 \leq 2$	Good
$2 < AZ^2 < 3$	Satisfactory
$AZ^2 \geq 3$	Unsatisfactory

The AZ^2 is considered being of lesser importance than the individual z scores.

Laboratories within Category B are ranked according to the total number of pesticides that they correctly reported to be present in the Test Item. The number of acceptable z scores achieved is listed as well.

3. RESULTS

3.1 Summary of reported results

In total, 160 EU and EFTA laboratories, from 30 different countries (27 EU member states), agreed to participate in this proficiency test. Additionally, Malta was represented by UK NRL. Five EU/EFTA participants did not submit results among these was one NRL. Additionally, 18 Third Countries registered for the PT. Four of these laboratories did not submit results. The participating laboratories are listed in **Appendix 1.**

An overview of results submitted by laboratories from the EU and EFTA can be seen in **Table 4.** All reported analytical results for the pesticide residues are shown in **Table 8-13(a/b)** and in **Appendix 5**. The methods used are presented in **Appendix 6** but in a separate electronic file. However, only results submitted by laboratories from EU and EFTA countries are included in **Table 4-7, 15** and in the z scores histograms in **Appendix 5.**

Table 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 treated Test Item. Only results submitted by laboratories from the EU and EFTA are included in this table.

Pesticide	No. of reported results	No. of NA [1]	No. of false negatives	% of labs reporting results [2]
Azoxystrobin	135	19	2	88
Bixafen	89	65	3	58
Boscalid	137	17	0	89
Buprofezin	138	16	2	90
Carbendazim	116	38	1	75
Cypermethrin	136	18	4	88
Epoxiconazole	132	22	2	86
Fenpropidin	105	49	0	68
Fluopyram	99	55	1	64
Heptachlor	131	23	7	85
Isocarbophos	99	55	1	64
Metrafenone	97	57	0	63
Pencycuron	117	37	3	76
Pirimicarb-desmethyl	99	55	3	64
Prothioconazole-desthio	107	47	2	69
Pyraclostrobin	121	33	1	79
Tebuconazole	139	15	0	90
Tetramethrin	103	51	3	67

[1] NA = not analysed

[2] '% results' have been calculated using the number of laboratories that reported results for each particular compound and the total number of EU laboratories that submitted results (n = 154). False negatives are included in reported results.

Buprofezin and tebuconazole were the most frequently analysed compounds with 90 % of the labs submitting results for these compounds. Azoxystrobin, boscalid, carbendazim, cypermethrin, epoxiconazole, heptachlor, pencycuron and pyraclostrobin were analysed and reported by 75-89% of the participants and bixafen, fenpropidin, fluopyram, isocarbophos, metrafenone, pirimicarb-desmethyl, prothioconazole-desthio and tetramethrin were only analysed and reported by 57-69% of participants. The two pesticides, deltamethrin and lambda-cyhalothrin that were present in very low levels, were analysed by 135 and 137, respectively. Only 40 and 72 laboratories detected these residues, respectively.

3.1.1 False positives

No false positive results were reported.

3.1.2 False negatives

Not reported results for pesticides actually present in the treated Test Item were judged as false negatives. **Table 5** summarizes the number of reported false negatives for each pesticide. Twenty laboratories submitted 25 false negatives results for 12 different pesticides, which represents 1.2% of the total number of results. Around 15% of the participants (20 laboratories) reported false negative results. This is lower than for previous EUPTs on cereals where 20-30% of the labs reported false negative results. No false negatives results were reported for boscalid, fenpropidin, metrafenone and tebuconazole. Not reported results for heptachlor and pencycuron were not judged to be false negatives as the assigned values were less than 4 times the MRRL, see 3.2.

Table 5. False negative results (FN).

Lab code	Azoxystrobin	Bixafen	Buprofezin	Carbendazim	Cypermethrin	Epoxiconazole	Fluopyram	Isocarbophos	Pirimicarb-desmethyl	Prothioconazole-desthio	Pyraclostrobin	Tetramethrin
5		FN										
27									FN			
38												
45												
49						FN			FN			
85												FN
110		FN										
113					FN							
114												
116	FN				FN				FN			
125								FN				
129			FN									
134												FN
141										FN		
143			FN									
153		FN										
156	FN				FN						FN	
159												FN
168					FN		FN					
173				FN		FN				FN		

3.3 Assigned values and target standard deviations

The Assigned Values were calculated as the Algorithm A mean, including the reported results submitted by laboratories from EU and EFTA countries. However, because of earlier experience with significantly biased results from laboratories not adding water to the sample before extraction (or using a mixture of water and extraction solvent) these results were not included in the calculation of the Algorithm A mean. Also results from laboratories that did not provide information about their extraction method were excluded from the calculations.

All Assigned Values for the pesticides can be seen in **Table 6**. The assigned values for heptachlor and pencycuron was less than 4 times the MRRL (equal to 0.04 mg/kg). Consequently, the assigned values for these two compounds are given for informative purposes only. Deltamethrin and lambda-cyhalothrin were present in very low levels around 0.01 and are not included in the tables below.

The target standard deviation was obtained using a fixed FFP-RSD value of 25 %. In parallel, the Algorithm A standard deviation (Alg A-RSD) was calculated for informative purposes only. The range of Alg A-RSD values was 14-23 % but on average the Alg A-RSD was 16 %, and thus below the 25 % FFP-RSD used for the calculations.

The uncertainty of the assigned values is calculated according ISO 13528 [5] as:

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

Where s* is the robust standard deviation estimate and n is the number of datapoints equal to the number of results used to calculate the assigned value (number of results in **Table 7**)

Table 6. Assigned values and their uncertainty in mg/kg, Fit-For-Purpose Relative Standard Deviation (FFP RSD) and Robust Relative Standard Deviation (Alg A RSD) for the pesticides present in the Test Item.

Pesticides	MRRL, mg/kg	Assigned value, mg/kg	Uncertainty, mg/kg	FFP RSD, %	Alg A RSD, %
Azoxystrobin	0.01	0.088	0.002	25	17
Bixafen	0.01	0.074	0.002	25	15
Boscalid	0.01	0.414	0.006	25	14
Buprofezin	0.01	0.048	0.001	25	16
Carbendazim	0.01	0.086	0.002	25	23
Cypermethrin	0.01	0.134	0.003	25	23
Epoxiconazole	0.01	0.177	0.003	25	16
Fenpropidin	0.01	0.347	0.009	25	21
Fluopyram	0.01	0.250	0.005	25	17
Heptachlor [1]	0.01	0.032	0.001	25	21
Isocarbophos	0.01	0.048	0.001	25	16
Metrafenone	0.01	0.088	0.002	25	14
Pencycuron [1]	0.01	0.033	0.001	25	16
Pirimicarb-desmethyl	0.01	0.048	0.001	25	15
Prothioconazole-desthio	0.01	0.149	0.003	25	16
Pyraclostrobin	0.01	0.098	0.002	25	22
Tebuconazole	0.01	0.091	0.001	25	15
Tetramethrin	0.01	0.096	0.002	25	18

[1] The assigned values are less than 4 times the MRRL and consequently for informative purposes only.

3.4 Assessment of laboratory performance

3.4.1 Z scores

Z scores have been calculated for all the quantified pesticides using the FFP RSD of 25 %. **Table 7** shows an overview of the acceptable, questionable and unacceptable z scores and **Tables 8a/b-13a/b** show the individual results and z scores for each laboratory and pesticide together with the assigned values. A graphical representation of the z scores (for EU and EFTA countries) can be seen in **Appendix 4**.

Table 7. Number of acceptable, questionable, unacceptable z scores and false negatives.

Pesticide	No. of reported results	Assigned values	Acceptable	Questionable	Unacceptable[2]	False negatives[1]
Azoxystrobin	135	0.088	130	2	3	2
Bixafen	89	0.074	84	2	3	3
Boscalid	137	0.414	134	2	1	0
Buprofezin	138	0.048	133	2	3	2
Carbendazim	116	0.086	102	6	8	1
Cypermethrin	136	0.134	127	1	8	4
Epoxiconazole	132	0.177	128	2	2	2
Fenpropidin	105	0.347	98	5	2	0
Fluopyram	99	0.250	96	2	1	1
Heptachlor [1]	131	0.032	121	10	0	7
Isocarbophos	99	0.048	95	1	3	1
Metrafenone	97	0.088	97	0	0	0
Pencycuron [1]	117	0.033	108	8	1	3
Pirimicarb-desmethyl	99	0.048	93	2	4	3
Prothioconazole-desthio	107	0.149	101	1	5	2
Pyraclostrobin	121	0.098	116	3	2	1
Tebuconazole	139	0.091	137	1	1	0
Tetramethrin	103	0.096	99	0	4	3

[1] The assigned value is less than 4 times the MRRL (<0.04 mg/kg) and consequently for informative purposes only.
[2] Unacceptable z scores include those for false negative results.

For azoxystrobin, boscalid, buprofezin, epoxiconazole, fluopyram, metrafenone, pyraclostrobin and tebuconazole acceptable results were obtained by 96-99% of the laboratories. For bixafen, cypermethrin, fenpropidin, isocarbophos, pirimicarb-desmethyl, prothioconazole-desthio and tetramethrin acceptable results were obtained by 91-94% of the laboratories.

As seen in previous EUPTs on cereals some laboratories reported very high results for carbendazim. This is probably due to the low solubility of the compound in organic solvent, e.g. for ethyl acetate it is only 0.135 mg/ml. It is therefore crucial to check if the carbendazim in stock solution is completely dissolved. It is recommended to prepare stock solutions of carbendazim at a concentration no higher than 0.1 mg/ml.

The Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed, SANTE 11945/2015 [7] recommends the addition of water to the samples prior to extraction to improve the extraction efficiency of low moisture containing commodities like cereals (paragraph C7). For pesticides as cypermethrin and heptachlor, no correlation was seen between adding water and improved extraction efficiency. However, for most of the other incurred pesticides in this EUPT the now relatively few laboratories not adding water, reported results towards the low end of the range.

Several different analytical methods have been used by the laboratories. QuEChERS, Citrate buffered (EN 151662) was used for 60% of the reported results. However, variations in the clean-up procedures were reported by the labs, e.g. some used a freezing out step, some used PSA, others PSA/C18 or PSA/ODS or

PSA/GCB or $CaCl_2$. So it is not one specific method. Two other QuEChERS methods were used, the Original Version (J. AOAC 86, (2003) 412) and the Acetate buffered (AOAC Official Method 2007.01). These were used for 6% and 8% of the results, respectively. The SweEt method (NMKL 195, 2013) was used for 4%, Mini Luke 6%, the methanol extraction method (Klein, Alder, J. AOAC 86 (2003) 1015) 2% and the German S-19 method for 1% of the results. Finally 1% of the results were analysed by other methods and for 13% of the results no information on the reference method was given by the laboratories.

More than 92% of the reported results derived from a method where water was added before extraction and for 4% of the results no information was given. Likewise, no information was given concerning the use of an ISTD for 4% of the results, while 56% of the results were produced with the use of an ISTD and 40% without an ISTD. Finally, no information on the type of instruments used was reported for 1% of the reported results. GC instruments was used for 43% of the results, mainly GC-MS/MS and GC-MSD (27% and 8%), 1 % used GC-TOF instruments, and the rest used GC with specific detectors, ECD, NPD and FPD. LC instruments was used for 56% of the reported results, mainly LC-MS/MS (50%) but 5% used high resolution instrument like LC-Orbitrap or LC-Q-TOF. Only 3 results were analysed using specific detectors such as LC-Fluorescence, LC-UV or LC-DAD.

Table 8a. Results for azoxystrobin, bixafen, boscalid, buprofezin, carbendazim, cypermethrin, epoxiconazole, fenpropidin and fluopyram in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Buprofezin	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	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	**0.088**		**0.074**		**0.414**		**0.048**		**0.086**		**0.134**		**0.177**		**0.347**		**0.250**	
1	0.0947	0.3	0.072	-0.1	0.447	0.3	0.051	0.3	0.084	-0.1	0.158	0.7	0.176	0.0	0.382	0.4	0.205	-0.7
2	0.033	-2.5	0.031	-2.3	0.188	-2.2	0.042	-0.5	0.025	-2.8	0.141	0.2	0.072	-2.4	0.168	-2.1	0.103	-2.4
3	0.126	1.7			0.559	1.4	0.057	0.7	0.096	0.5	0.153	0.6	0.258	1.8	0.527	2.1		
4					0.424	0.1	0.056	0.7			0.119	-0.5						
5	0.123	1.6	FN	-3.5	0.461	0.5	0.053	0.4	0.084	-0.1	0.138	0.1	0.19	0.3	0.426	0.9	0.345	1.5
6	0.0839	-0.2	0.061	-0.7	0.381	-0.3	0.040	-0.6	0.083	-0.1	0.12	-0.4	0.18	0.1	0.233	-1.3	0.22	-0.5
7	0.0766	-0.5	0.060	-0.7	0.391	-0.2	0.046	-0.1	0.089	0.1	0.162	0.8	0.164	-0.3	0.413	0.8	0.212	-0.6
8	0.0913	0.2	0.066	-0.4	0.381	-0.3	0.042	-0.4	0.093	0.3	0.137	0.1	0.163	-0.3	0.301	-0.5	0.231	-0.3
9	0.0742	-0.6	0.066	-0.4	0.379	-0.3	0.042	-0.5	0.129	2.0	0.144	0.3	0.182	0.1	0.359	0.1	0.249	0.0
10	0.067	-0.9	0.064	-0.5	0.38	-0.3	0.034	-1.2	0.079	-0.3	0.1	-1.0	0.15	-0.6	0.34	-0.1	0.2	-0.8
11	0.067	-0.9			0.441	0.3	0.045	-0.3	0.067	-0.9	0.118	-0.5	0.124	-1.2	0.222	-1.4	0.246	-0.1
12																		
13	0.08	-0.4	0.075	0.1	0.39	-0.2	0.044	-0.3	0.08	-0.3	0.125	-0.3	0.188	0.2	0.34	-0.1	0.255	0.1
14	0.081	-0.3	0.062	-0.6	0.386	-0.3	0.046	-0.2	0.04	-2.1	0.107	-0.8	0.159	-0.4	0.299	-0.6	0.219	-0.5
15	0.106	0.8			0.594	1.7	0.073	2.1	0.1	0.6	0.165	0.9	0.207	0.7	0.255	-1.1	0.393	2.3
16	0.0907	0.1	0.075	0.1	0.502	0.9	0.052	0.3	0.143	2.6	0.15	0.5	0.195	0.4	0.262	-1.0		
17	0.1	0.6			0.437	0.2	0.05	0.2	0.08	-0.3	0.15	0.5	0.16	-0.4	0.3	-0.5		
18	0.0764	-0.5	0.063	-0.5	0.392	-0.2	0.056	0.7	0.054	-1.5	0.145	0.3	0.163	-0.3	0.34	-0.1	0.191	-0.9
19											0.084	-1.5						
20	0.0834	-0.2	0.076	0.2	0.402	-0.1	0.049	0.1	0.086	0.0	0.132	-0.1	0.18	0.1	0.399	0.6	0.283	0.5
21	0.1	0.6	0.08	0.3	0.488	0.7	0.052	0.4	0.098	0.6	0.124	-0.3	0.19	0.3	0.329	-0.2	0.285	0.6
22	0.0743	-0.6	0.054	-1.1	0.389	-0.2	0.058	0.8	0.099	0.6	0.139	0.1	0.159	-0.4	0.237	-1.3	0.224	-0.4
23	0.104	0.7	0.069	-0.2	0.475	0.6	0.057	0.7	0.089	0.2	0.204	2.1	0.191	0.3	0.307	-0.5	0.318	1.1
24	0.0828	-0.2			0.402	-0.1	0.048	0.0	0.15	3.0	0.335	>5	0.195	0.4			0.251	0.0
25	0.068	-0.9	0.064	-0.5	0.36	-0.5	0.051	0.2	0.075	-0.5	0.085	-1.5	0.154	-0.5	0.347	0.0	0.219	-0.5
26	0.115	1.2	0.086	0.7	0.451	0.4	0.058	0.8	0.101	0.7	0.131	-0.1	0.205	0.6	0.34	-0.1	0.286	0.6
27	0.1	0.6	0.071	-0.1	0.485	0.7	0.039	-0.8	0.171	3.9	0.1	-1.0	0.19	0.3	0.376	0.3	0.371	1.9
28	0.076	-0.5			0.36	-0.5	0.043	-0.4	0.061	-1.2	0.114	-0.6	0.171	-0.1	0.27	-0.9	0.21	-0.6
29	0.084	-0.2			0.625	2.0	0.047	-0.1	0.09	0.2	0.2	1.9	0.234	1.3	0.375	0.3		
30																		
31	0.0669	-1.0			0.244	-1.6	0.038	-0.8	0.063	-1.0	0.134	0.0	0.112	-1.5				
32	0.115	1.2	0.07	-0.2	0.361	-0.5	0.048	0.0	0.217	>5	0.108	-0.8	0.218	0.9	0.377	0.3	0.305	0.9
33	0.0895	0.1			0.438	0.2	0.055	0.6			0.132	-0.1	0.202	0.6				
34	0.0961	0.4			0.424	0.1	0.059	0.9			0.153	0.6	0.171	-0.1				
35	0.096	0.4	0.069	-0.2	0.433	0.2	0.051	0.2	0.089	0.2	0.141	0.2	0.199	0.5	0.418	0.8	0.2472	0.0
36	0.103	0.7	0.082	0.5	0.51	0.9	0.047	-0.1	0.082	-0.2	0.13	-0.1	0.193	0.4	0.338	-0.1	0.302	0.8
37	0.092	0.2	0.086	0.7	0.457	0.4	0.054	0.5	0.098	0.5	0.146	0.3	0.214	0.8	0.443	1.1	0.227	-0.4
38	0.05	-1.7			0.347	-0.6	0.034	-1.2	0.13	2.0			0.1	-1.7				
39	0.084	-0.2	0.074	0.1	0.405	-0.1	0.044	-0.3	0.076	-0.5	0.154	0.6	0.166	-0.3	0.317	-0.3	0.244	-0.1
40	0.078	-0.4			0.353	-0.6	0.036	-1.0			0.111	-0.7						
41	0.08	-0.4	0.072	-0.1	0.384	-0.3	0.043	-0.4	0.091	0.2	0.106	-0.8	0.162	-0.3	0.301	-0.5	0.234	-0.3

Table 8b. Results for isocarbophos, metrafenone, pirimicarb-desmethyl, prothioconazole-desthio, pyraclostrobin, tebuconazole and tetramethrin, in mg/kg, the corresponding z scores, MRRLs and the assigned values. Z scores, and assigned values for heptachlor and pencycuron are for information only.

Laboratory code	Isocarbophos	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Pirimicarb-desmethyl	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)	Tetramethrin	Z score (FFP RSD (25%)	Heptachlor	Z score (FFP RSD (25%)	Pencycuron	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.048**		**0.088**		**0.048**		**0.149**		**0.098**		**0.091**		**0.096**		***0.032***		***0.033***	
1	0.050	0.2	0.087	0.0	0.0479	0.0	0.157	0.2	0.096	-0.1	0.0875	-0.1	0.104	0.3	0.04	*1.0*	0.0324	*0.0*
2	0.032	-1.3	0.062	-1.2	0.039	-0.8	0.061	-2.4	0.051	-1.9	0.037	-2.4	0.065	-1.3	0.036	*0.5*	0.034	*0.2*
3					0.061	1.1	0.198	1.3	0.131	1.3	0.129	1.7	0.115	0.8	0.016	*-2.0*	0.04	*0.9*
4									0.127	1.2	0.105	0.6			0.0313	*0.0*		
5	0.052	0.3	0.098	0.5	0.055	0.6	0.156	0.2	0.123	1.0	0.097	0.3	0.106	0.4	0.0452	*1.7*	0.036	*0.4*
6	0.050	0.2	0.081	-0.3	0.0455	-0.2	0.131	-0.5	0.111	0.5	0.0823	-0.4	0.0841	-0.5	0.0236	*-1.0*	0.0307	*-0.2*
7	0.046	-0.2	0.083	-0.2	0.0551	0.6	0.159	0.3	0.129	1.3	0.0838	-0.3	0.0935	-0.1	0.034	*0.3*	0.058	*3.1*
8	0.041	-0.6	0.082	-0.2	0.0459	-0.2	0.139	-0.3	0.0892	-0.4	0.0853	-0.2	0.0903	-0.2	0.0252	*-0.8*	0.0285	*-0.5*
9	0.045	-0.2	0.082	-0.2	0.0479	0.0	0.177	0.7	0.0737	-1.0	0.0867	-0.2	0.0645	-1.3	0.035	*0.4*	0.0327	*0.0*
10	0.04	-0.7	0.052	-1.6	0.039	-0.8	0.13	-0.5	0.11	0.5	0.07	-0.9	0.078	-0.7	0.016	*-2.0*	0.023	*-1.2*
11	0.04	-0.7			0.037	-0.9			0.079	-0.8	0.073	-0.8			0.026	*-0.7*	0.024	*-1.1*
12															0.033	*0.2*		
13	0.041	-0.6	0.09	0.1	0.055	0.6	0.154	0.1	0.095	-0.1	0.091	0.0					0.038	*0.6*
14	0.049	0.1	0.074	-0.6	0.047	-0.1	0.132	-0.5	0.09	-0.3	0.09	0.0	0.066	-1.2	0.025	*-0.8*	0.027	*-0.7*
15	0.054	0.5			0.045	-0.3	0.192	1.2	0.108	0.4	0.115	1.1			0.03	*-0.2*	0.034	*0.2*
16	0.054	0.6											0.131	1.5	0.0396	*1.0*		
17	0.05	0.2	0.09	0.1	0.05	0.1	0.17	0.6	0.11	0.5	0.08	-0.5	0.11	0.6	0.03	*-0.2*	0.03	*-0.3*
18	0.061	1.1	0.085	-0.1	0.0523	0.3	0.136	-0.4	0.0756	-0.9	0.091	0.0	0.103	0.3	0.0325	*0.1*	0.0349	*0.3*
19											0.075	-0.7	0.081	-0.6	0.031	*-0.1*		
20	0.050	0.2	0.092	0.2	0.0518	0.3	0.169	0.5	0.108	0.4	0.0988	0.4	0.0931	-0.1	0.0295	*-0.3*	0.0324	*0.0*
21	0.052	0.4	0.092	0.2	0.0544	0.5	0.167	0.5	0.104	0.2	0.103	0.6	0.102	0.3	0.0375	*0.7*	0.033	*0.0*
22	0.045	-0.3	0.088	0.0	0.0395	-0.7	0.142	-0.2	0.086	-0.5	0.085	-0.2	0.092	-0.2	0.0225	*-1.2*	0.029	*-0.5*
23	0.055	0.6	0.104	0.8	0.0315	-1.4	0.176	0.7	0.124	1.1	0.0901	0.0	0.119	1.0	0.028	*-0.5*	0.0419	*1.1*
24					0.0445	-0.3			0.0948	-0.1	0.0883	-0.1	0.0964	0.0			0.0329	*0.0*
25	0.029	-1.6	0.101	0.6	0.047	-0.1	0.128	-0.6	0.099	0.0	0.083	-0.3	0.118	0.9	0.041	*1.2*	0.033	*0.0*
26	0.045	-0.3	0.103	0.7	0.045	-0.3	0.165	0.4	0.124	1.1	0.11	0.9	0.115	0.8	0.032	*0.0*	0.046	*1.6*
27	0.04	-0.7	0.103	0.7	FN	-3.2	0.182	0.9	0.118	0.8	0.091	0.0	0.086	-0.4	0.024	*-1.0*	0.039	*0.8*
28	0.047	-0.1					0.12	-0.8	0.091	-0.3	0.077	-0.6	0.081	-0.6	0.023	*-1.1*	0.0273	*-0.7*
29	FN	-3.2	0.09	0.1	FN	-3.2			0.084	-0.6	0.105	0.6	0.123	1.1	0.037	*0.7*	FN	*-2.8*
30																		
31					0.0482	0.0	0.118	-0.8	0.0743	-1.0	0.0618	-1.3			0.0223	*-1.2*		
32	FN	-3.2	0.065	-1.0	0.098	4.1	0.168	0.5	0.106	0.3	0.1	0.4	0.098	0.1	0.029	*-0.3*	0.013	*-2.4*
33							0.131	-0.5			0.0928	0.1			0.0343	*0.3*		
34							0.123	-0.7			0.0973	0.3			0.0359	*0.5*		
35	0.06	1.0	0.093	0.2	0.064	1.3	0.1682	0.5	0.142	1.8	0.099	0.4	0.1009	0.2	0.034	*0.3*	0.0315	*-0.2*
36	0.054	0.5	0.092	0.2	0.0552	0.6	0.154	0.1	0.114	0.7	0.0992	0.4	0.0957	0.0	0.0282	*-0.4*	0.036	*0.4*
37	0.045	-0.3	0.093	0.2	0.06	1.0	0.164	0.4	0.111	0.5	0.102	0.5	0.105	0.4	0.028	*-0.5*	0.035	*0.3*
38									0.06	-1.6	0.073	-0.8			FN	*-2.7*	0.047	*1.7*
39	0.045	-0.2	0.088	0.1	0.044	-0.4	0.134	-0.4	0.0962	-0.1	0.0777	-0.6	0.114	0.8	0.0356	*0.5*	0.0305	*-0.3*
40									0.114	0.7	0.112	0.9			0.018	*-1.7*		
41	0.05	0.2	0.077	-0.5	0.045	-0.3	0.14	-0.2	0.1	0.1	0.086	-0.2	0.09	-0.2	0.025	-0.8	0.027	-0.7

Table 9a. Results for azoxystrobin, bixafen, boscalid, buprofezin, carbendazim, cypermethrin, epoxiconazole, fenpropidin and fluopyram in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Buprofezin	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	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	**0.088**		**0.074**		**0.414**		**0.048**		**0.086**		**0.134**		**0.177**		**0.347**		**0.250**	
42	0.0848	-0.1	0.076	0.1	0.39	-0.2	0.043	-0.4			0.14	0.2	0.19	0.3	0.371	0.3	0.269	0.3
43	0.0819	-0.3	0.067	-0.3	0.43	0.2	0.05	0.2	0.105	0.9	0.164	0.9	0.174	-0.1	0.33	-0.2	0.232	-0.3
44							0.043	-0.4			0.005	-3.9	0.141	-0.8				
45	0.087	0.0	0.07	-0.2	0.34	-0.7	0.037	-0.9	0.079	-0.3	0.083	-1.5	0.175	0.0	0.369	0.3	0.253	0.1
46	0.074	-0.6	0.075	0.1	0.344	-0.7	0.041	-0.6	0.096	0.5	0.129	-0.2	0.151	-0.6	0.255	-1.1	0.234	-0.3
47	0.083	-0.2	0.078	0.2	0.427	0.1	0.038	-0.8	0.085	-0.1	0.105	-0.9	0.189	0.3	0.378	0.4	0.268	0.3
48																		
49	0.087	0.0	0.073	0.0	0.41	0.0	0.055	0.6	0.053	-1.5	0.14	0.2	FN	-3.8	0.38	0.4	0.15	-1.6
50	0.087	0.0	0.073	0.0	0.405	-0.1	0.044	-0.3	0.083	-0.1	0.13	-0.1	0.176	0.0	0.413	0.8	0.259	0.1
51	0.0859	-0.1			0.492	0.8	0.046	-0.1	0.070	-0.7	0.109	-0.8	0.218	0.9	0.424	0.9	0.26	0.2
52																		
53	0.069	-0.9			0.341	-0.7	0.038	-0.8	0.049	-1.7	0.089	-1.4						
54	0.0952	0.3	0.075	0.1	0.381	-0.3	0.037	-0.9	0.099	0.6	0.105	-0.9	0.136	-0.9	0.385	0.4	0.245	-0.1
55																		
56	0.085	-0.1	0.071	-0.1	0.388	-0.2	0.046	-0.2	0.08	-0.3	0.162	0.8	0.159	-0.4	0.411	0.7	0.271	0.3
57	0.093	0.2	0.081	0.4	0.443	0.3	0.050	0.2	0.086	0.0			0.204	0.6	0.365	0.2	0.273	0.4
58	0.1	0.6	0.082	0.5	0.439	0.2	0.05	0.2	0.079	-0.3	0.154	0.6	0.189	0.3	0.425	0.9	0.276	0.4
59	0.089	0.1	0.084	0.6	0.44	0.3	0.062	1.2	0.08	-0.3	0.149	0.4	0.176	0.0	0.35	0.0	0.29	0.6
60	0.086	-0.1	0.072	-0.1	0.419	0.1	0.059	0.9			0.137	0.1	0.174	-0.1	0.256	-1.0		
61																		
62	0.082	-0.3	0.094	1.1	0.447	0.3	0.044	-0.3	0.076	-0.5	0.158	0.7	0.215	0.9	0.37	0.3	0.29	0.6
63	0.0865	-0.1	0.082	0.5	0.403	-0.1	0.052	0.4	0.080	-0.3	0.146	0.3	0.222	1.0	0.304	-0.5		
64	0.088	0.0	0.069	-0.3	0.352	-0.6	0.051	0.2	0.08	-0.3	0.151	0.5	0.157	-0.5	0.414	0.8	0.241	-0.1
65	0.058	-1.4	0.056	-1.0	0.31	-1.0	0.042	-0.5	0.047	-1.8	0.079	-1.6	0.125	-1.2	0.235	-1.3	0.195	-0.9
66	0.0811	-0.3	0.074	0.0	0.373	-0.4	0.045	-0.2	0.099	0.6	0.164	0.9	0.195	0.4	0.312	-0.4	0.27	0.3
67	0.0836	-0.2			0.452	0.4	0.048	0.1	0.095	0.4			0.209	0.7	0.269	-0.9	0.265	0.2
68	0.095	0.3	0.09	0.9	0.496	0.8	0.058	0.8	0.109	1.1	0.0968	-1.1	0.249	1.6	0.451	1.2	0.303	0.9
69	0.078	-0.4	0.055	-1.0	0.38	-0.3	0.046	-0.2	0.082	-0.2	0.119	-0.5	0.12	-1.3	0.322	-0.3	0.171	-1.3
70	0.108	0.9	0.083	0.6	0.494	0.8	0.052	0.4	0.094	0.4	0.153	0.6	0.206	0.7	0.426	0.9	0.328	1.3
71	0.098	0.5	0.095	1.2	0.412	0.0	0.053	0.5	0.085	0.0	0.12	-0.4	0.185	0.2	0.856	>5	0.228	-0.3
72	0.0609	-1.2			0.466	0.5	0.062	1.2			0.19	1.7	0.257	1.8	0.626	3.2		
73	0.0868	0.0	0.074	0.1	0.419	0.1	0.046	-0.1	0.076	-0.5	0.147	0.4	0.178	0.0	0.355	0.1	0.249	0.0
74	0.097	0.4			0.45	0.4	0.054	0.5	0.099	0.6			0.196	0.4	0.417	0.8		
75	0.105	0.8			0.446	0.3	0.054	0.5	0.084	-0.1	0.1	-1.0	0.217	0.9	0.442	1.1	0.302	0.8
76	0.0925	0.2			0.406	-0.1	0.059	0.9			0.142	0.2	0.167	-0.2				
77	0.104	0.7			0.414	0.0	0.056	0.7			0.149	0.4	0.169	-0.2				
78	0.093	0.2	0.09	0.9	0.45	0.4	0.05	0.2	0.075	-0.5	0.17	1.1	0.19	0.3	0.3	-0.5	0.26	0.2
79	0.115	1.2	0.087	0.8	0.453	0.4	0.051	0.3	0.095	0.4	0.147	0.4	0.219	0.9	0.392	0.5	0.285	0.6
80	0.087	0.0	0.076	0.1	0.39	-0.2	0.049	0.1	0.108	1.0	0.12	-0.4	0.164	-0.3	0.394	0.5	0.237	-0.2
81																		
82	0.0578	-1.4	0.068	-0.3	0.286	-1.2	0.042	-0.5	0.079	-0.3	0.129	-0.2	0.122	-1.2	0.265	-0.9	0.269	0.3

Table 9b. Results for isocarbophos, metrafenone, pirimicarb-desmethyl, prothioconazole-desthio, pyraclostrobin, tebuconazole and tetramethrin, in mg/kg, the corresponding z scores, MRRLs and the assigned values. Z scores, and assigned values for heptachlor and pencycuron are for information only.

Laboratory code	Isocarbophos	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Pirimicarb-desmethyl	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)	Tetramethrin	Z score (FFP RSD (25%)	Heptachlor	Z score (FFP RSD (25%)	Pencycuron	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	**0.048**		**0.088**		**0.048**		**0.149**		**0.098**		**0.091**		**0.096**		***0.032***		***0.033***	
42	0.0523	0.4	0.090	0.1	0.042	-0.5	0.145	-0.1			0.078	-0.5					0.0358	*0.4*
43	0.0424	-0.5	0.083	-0.2	0.047	-0.1	0.161	0.3	0.0864	-0.5	0.092	0.1	0.102	0.3	0.0437	*1.5*	0.0323	*-0.1*
44	0.047	-0.1									0.068	-1.0						
45	0.035	-1.1	0.079	-0.4	0.044	-0.4	0.142	-0.2	0.095	-0.1	0.095	0.2	0.095	0.0	FN	*-2.7*	0.03	*-0.3*
46	0.031	-1.4	0.072	-0.7	0.034	-1.2	0.129	-0.5	0.084	-0.6	0.088	-0.1	0.074	-0.9	0.032	*0.0*	0.032	*-0.1*
47	0.034	-1.2	0.079	-0.4	0.048	0.0	0.156	0.2	0.103	0.2	0.097	0.3	0.107	0.5	0.03	*-0.2*	0.029	*-0.5*
48																		
49	0.039	-0.8			FN	-3.2			0.019	-3.2	0.09	0.0	0.096	0.0	0.025	*-0.8*	FN	*-2.8*
50			0.092	0.2	0.042	-0.5	0.155	0.2	0.0946	-0.1	0.089	-0.1	0.102	0.3	0.0295	*-0.3*	0.0386	*0.7*
51	FN	-3.2	0.078	-0.4					0.0945	-0.1	0.122	1.4			0.0225	*-1.2*	0.0327	*0.0*
52																		
53									0.08	-0.7	0.083	-0.3	0.057	-1.6				
54	0.0493	0.1	0.090	0.1	0.051	0.2	0.149	0.0	0.0942	-0.2	0.090	0.0	0.088	-0.3	0.0197	*-1.5*	0.0327	*0.0*
55															0.021	*-1.3*		
56	0.042	-0.5	0.075	-0.6	0.05	0.1	0.168	0.5	0.125	1.1	0.077	-0.6	0.085	-0.5	0.034	*0.3*	0.029	*-0.5*
57			0.094	0.3	0.056	0.7	0.169	0.5	0.106	0.3	0.099	0.4	0.0991	0.1			0.0306	*-0.3*
58	0.051	0.2	0.093	0.2	0.052	0.3	0.161	0.3	0.11	0.5	0.098	0.3			0.035	*0.4*	0.034	*0.2*
59	0.057	0.7	0.116	1.3	0.065	1.4	0.165	0.4	0.122	1.0	0.094	0.2	0.091	-0.2	0.037	*0.7*	0.035	*0.3*
60	0.0537	0.5	0.078	-0.4			0.153	0.1			0.091	0.0	0.085	-0.5	0.0257	*-0.8*	0.0536	*2.5*
61																		
62	0.05	0.2	0.089	0.1	0.035	-1.1	0.185	1.0	0.115	0.7	0.083	-0.3	0.084	-0.5	0.038	*0.8*	0.03	*-0.3*
63	0.0535	0.5	0.093	0.3	0.043	-0.4	0.148	0.0	0.098	0.0	0.097	0.3			0.027	*-0.6*	0.0325	*0.0*
64	0.053	0.4	0.083	-0.2	0.043	-0.4	0.146	-0.1	0.085	-0.5	0.08	-0.5	0.091	-0.2	0.031	*-0.1*	0.029	*-0.5*
65	0.041	-0.6	0.061	-1.2	0.036	-1.0	0.117	-0.9	0.075	-0.9	0.064	-1.2	0.075	-0.9	0.032	*0.0*	0.026	*-0.8*
66	0.0455	-0.2	0.094	0.3	0.032	-1.3	0.177	0.7	0.153	2.2	0.102	0.5	0.0951	0.0			0.029	*-0.5*
67	0.0477	0.0	0.079	-0.4	0.048	0.0	0.134	-0.4	0.102	0.2	0.093	0.1	0.0908	-0.2	0.0275	*-0.5*	0.0302	*-0.3*
68	0.0503	0.2	0.101	0.6	0.048	0.0	0.191	1.1	0.107	0.4	0.114	1.0	0.108	0.5	0.041	*1.2*	0.0367	*0.5*
69	0.044	-0.3	0.077	-0.5	0.043	-0.4	0.119	-0.8	0.066	-1.3	0.067	-1.0	0.09	-0.2	0.038	*0.8*	0.024	*-1.1*
70	0.0614	1.1	0.101	0.6	0.050	0.2	0.19	1.1	0.148	2.0	0.108	0.8	0.103	0.3	0.0347	*0.4*	0.0366	*0.5*
71	0.0427	-0.4	0.089	0.1	0.052	0.4	0.167	0.5	0.0814	-0.7	0.103	0.6	0.0729	-1.0	0.0293	*-0.3*	0.0301	*-0.3*
72	0.065	1.4	0.216	>5			0.247	2.6			0.116	1.1	0.2	4.3	0.0355	*0.5*		
73	0.0467	-0.1	0.088	0.0	0.047	-0.1	0.151	0.1	0.0934	-0.2	0.091	0.1	0.115	0.8	0.0352	*0.4*	0.0309	*-0.2*
74									0.105	0.3	0.095	0.2			0.032	*0.0*	0.039	*0.8*
75			0.093	0.2	0.056	0.6	0.17	0.6	0.123	1.0	0.086	-0.2	0.12	1.0	0.025	*-0.8*	0.034	*0.2*
76							0.127	-0.6			0.086	-0.2			0.0365	*0.6*		
77							0.125	-0.6			0.096	0.3			0.0367	*0.6*		
78	0.06	1.0	0.091	0.2	0.053	0.4	0.18	0.8	0.11	0.5	0.1	0.4	0.125	1.2	0.037	*0.7*	0.032	*-0.1*
79	0.052	0.3	0.1	0.6	0.051	0.3	0.168	0.5	0.114	0.7	0.108	0.8	0.102	0.3	0.0294	*-0.3*	0.0353	*0.3*
80	0.047	-0.1	0.085	-0.1	0.047	-0.1	0.121	-0.8	0.08	-0.7	0.093	0.1	0.103	0.3	0.034	*0.3*	0.029	*-0.5*
81																		
82	0.0411	-0.6	0.072	-0.7	0.043	-0.4	0.162	0.3	0.0752	-0.9	0.082	-0.4	0.0779	-0.8	0.0243	-0.9	0.0296	-0.4

Table 10a. Results for azoxystrobin, bixafen, boscalid, buprofezin, carbendazim, cypermethrin, epoxiconazole, fenpropidin and fluopyram in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Buprofezin	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	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	**0.088**		**0.074**		**0.414**		**0.048**		**0.086**		**0.134**		**0.177**		**0.347**		**0.250**	
83	0.0842	-0.2	0.074	0.0	0.412	0.0	0.049	0.1	0.078	-0.4	0.147	0.4	0.185	0.2	0.346	0.0	0.256	0.1
84	0.104	0.7	0.082	0.5	0.398	-0.2	0.055	0.6	0.098	0.5	0.2	1.9	0.171	-0.1	0.409	0.7	0.214	-0.6
85	0.0928	0.2	0.077	0.2	0.432	0.2	0.051	0.3	0.082	-0.2	0.101	-1.0	0.185	0.2	0.375	0.3	0.263	0.2
86	0.085	-0.1			0.334	-0.8	0.041	-0.6	0.051	-1.6	0.117	-0.5	0.13	-1.1				
87	0.096	0.4	0.077	0.2	0.425	0.1	0.049	0.1	0.079	-0.3	0.139	0.1	0.201	0.5	0.319	-0.3	0.279	0.5
88	0.084	-0.2	0.075	0.1	0.412	0.0	0.048	0.1	0.097	0.5	0.142	0.2	0.182	0.1	0.237	-1.3	0.249	0.0
89	0.09	0.1			0.36	-0.5	0.04	-0.7	0.04	-2.1	0.1	-1.0	0.17	-0.2				
90	0.132	2.0			0.425	0.1	0.049	0.1	0.185	4.6	0.14	0.2	0.156	-0.5	0.31	-0.4		
91	0.105	0.8	0.045	-1.6	0.32	-0.9	0.038	-0.8	0.112	1.2	0.13	-0.1	0.095	-1.9	0.2	-1.7	0.18	-1.1
92											0.14	0.2						
93	0.115	1.2			0.68	2.6	0.066	1.5	0.108	1.0	0.173	1.1	0.212	0.8				
94	0.084	-0.2			0.424	0.1	0.044	-0.3			0.079	-1.6	0.266	2.0	0.415	0.8	0.265	0.2
95	0.0983	0.5	0.071	-0.1	0.427	0.1	0.043	-0.4	0.076	-0.5	0.198	1.9	0.187	0.2	0.355	0.1	0.264	0.2
96	0.0871	0.0			0.39	-0.2	0.045	-0.3			0.14	0.2	0.187	0.2				
97											0.0943	-1.2						
98	0.0565	-1.4			0.323	-0.9	0.049	0.1			0.11	-0.7	0.146	-0.7	0.258	-1.0		
99																		
100	0.11	1.0									0.135	0.0	0.201	0.5				
101	0.094	0.3			0.395	-0.2	0.051	0.2			0.155	0.6	0.176	0.0				
102	0.0871	0.0			0.458	0.4	0.043	-0.4	0.1	0.6	0.0984	-1.1	0.169	-0.2	0.329	-0.2	0.357	1.7
103	0.089	0.1	0.08	0.3	0.434	0.2	0.05	0.2	0.081	-0.2	0.136	0.0	0.181	0.1	0.303	-0.5	0.281	0.5
104	0.095	0.3			0.42	0.1	0.045	-0.3	0.145	2.7	0.14	0.2	0.14	-0.8	0.466	1.4	1.19	>5
105	0.1	0.6	0.075	0.1	0.448	0.3	0.046	-0.2	0.07	-0.8	0.13	-0.1	0.199	0.5	0.297	-0.6	0.256	0.1
106	0.0815	-0.3	0.124	2.7	0.442	0.3	0.046	-0.1	0.152	3.1	0.0677	-2.0	0.184	0.2	0.162	-2.1	0.278	0.5
107	0.105	0.8			0.413	0.0	0.051	0.2			0.144	0.3	0.173	-0.1				
108	0.067	-0.9			0.345	-0.7	0.041	-0.6	0.082	-0.2	0.115	-0.6					0.208	-0.7
109	0.11	1.0	0.101	1.5	0.417	0.0	0.053	0.4	0.119	1.5	0.167	1.0	0.178	0.0	0.391	0.5	0.301	0.8
110	0.104	0.7	FN	-3.5	0.351	-0.6			0.153	3.1	0.18	1.4	0.231	1.2			0.236	-0.2
111	0.076	-0.5			0.366	-0.5	0.046	-0.2			0.144	0.3	0.168	-0.2				
112																		
113							0.059	0.9			FN	-3.7						
114	0.0873	0.0			0.319	-0.9	0.067	1.6	0.167	3.7	0.116	-0.5	0.165	-0.3	0.408	0.7	0.193	-0.9
115	0.09	0.1	0.083	0.5	0.411	0.0	0.052	0.3	0.087	0.0	0.169	1.0	0.184	0.2	0.388	0.5	0.247	0.0
116	FN	-3.5			0.42	0.1	0.04	-0.7	0.16	3.4	FN	-3.7	0.13	-1.1				
117	0.0828	-0.2	0.072	0.0	0.434	0.2	0.043	-0.4	0.084	-0.1	0.152	0.5	0.168	-0.2	0.371	0.3	0.248	0.0
118	0.093	0.2					0.036	-1.0			0.062	-2.2						
119																		
120	0.103	0.7	0.080	0.4	0.497	0.8	0.048	0.0	0.077	-0.4	0.11	-0.7	0.2	0.5	0.292	-0.6	0.277	0.4
121	0.0869	0.0			0.492	0.8	0.038	-0.8	0.082	-0.2	0.0853	-1.5	0.185	0.2				
122					0.367	-0.5	0.068	1.7			0.241	3.2						
123	0.045	-2.0	0.05	-1.3	0.357	-0.5	0.033	-1.3	0.185	4.6	0.085	-1.5	0.088	-2.0	0.337	-0.1	0.156	-1.5

Table 10b. Results for isocarbophos, metrafenone, pirimicarb-desmethyl, prothioconazole-desthio, pyraclostrobin, tebuconazole and tetramethrin, in mg/kg, the corresponding z scores, MRRLs and the assigned values. Z scores, and assigned values for heptachlor and pencycuron are for information only.

Laboratory code	Isocarbophos	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Pirimicarb-desmethyl	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)	Tetramethrin	Z score (FFP RSD (25%)	Heptachlor	Z score (FFP RSD (25%)	Pencycuron	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	**0.048**		**0.088**		**0.048**		**0.149**		**0.098**		**0.091**		**0.096**		***0.032***		***0.033***	
83	0.0487	0.1	0.089	0.1	0.396	>5	0.154	0.1	0.108	0.4	0.0922	0.1	0.113	0.7	0.0348	*0.4*	0.0307	*-0.2*
84	0.053	0.4	0.096	0.4	0.053	0.4	0.159	0.3	0.108	0.4	0.099	0.4	0.08	-0.7	0.038	*0.8*	0.03	*-0.3*
85	0.0442	-0.3	0.098	0.5	0.0503	0.2	0.143	-0.2	0.102	0.2	0.096	0.2	FN	-3.6	FN	*-2.7*	0.027	*-0.7*
86					0.059	0.9	0.149	0.0	0.115	0.7	0.091	0.0					0.053	*2.5*
87	0.051	0.2	0.09	0.1	0.052	0.3	0.152	0.1	0.11	0.5	0.089	-0.1	0.102	0.3	0.032	*0.0*	0.034	*0.2*
88	0.0502	0.2	0.085	-0.1	0.0584	0.8			0.107	0.4	0.0914	0.0	0.101	0.2	0.0318	*0.0*	0.0366	*0.5*
89			0.08	-0.3	0.04	-0.7	0.15	0.0	0.09	-0.3	0.09	0.0	0.05	-1.9	0.03	*-0.2*	0.03	*-0.3*
90			0.086	-0.1					0.131	1.3	0.085	-0.2			0.034	*0.3*	0.038	*0.6*
91	0.05	0.2	0.065	-1.0			0.11	-1.0	0.06	-1.6	0.078	-0.6			0.035	*0.4*	0.04	*0.9*
92															0.041	*1.2*		
93									0.129	1.3	0.095	0.2			0.035	*0.4*	0.041	*1.0*
94			0.106	0.8					0.099	0.0	0.125	1.5			0.029	*-0.3*	0.031	*-0.2*
95			0.091	0.2	0.0478	0.0	0.148	0.0	0.104	0.2	0.0892	-0.1	0.116	0.8	0.048	*2.1*	0.0321	*-0.1*
96									0.1	0.1	0.0831	-0.3	0.098	0.1	0.0251	*-0.8*		
97													0.12	1.0	0.0461	*1.8*		
98	0.05	0.2	0.07	-0.8			0.14	-0.2	0.115	0.7	0.083	-0.3	0.0785	-0.7	0.027	*-0.6*	0.03	*-0.3*
99															0.037	*0.7*		
100											0.078	-0.6			0.03	*-0.2*		
101											0.091	0.0			0.036	*0.5*		
102	0.0422	-0.5	0.071	-0.7	0.0493	0.1	0.149	0.0	0.0862	-0.5	0.077	-0.6	0.114	0.8	0.0333	*0.2*	0.0284	*-0.5*
103	0.051	0.2	0.088	0.0	0.056	0.6	0.161	0.3	0.106	0.3	0.094	0.2	0.092	-0.2	0.033	*0.2*	0.035	*0.3*
104	FN	-3.2			0.05	0.1	0.15	0.0	0.105	0.3	0.06	-1.3	0.09	-0.2	0.035	*0.4*	0.035	*0.3*
105	0.05	0.2	0.087	0.0	0.047	-0.1					0.095	0.2			0.029	*-0.3*		
106	0.045	-0.3	0.127	1.8	0.0434	-0.4	0.135	-0.4	0.0978	0.0	0.076	-0.6	0.0742	-0.9	0.0336	*0.2*	0.0282	*-0.6*
107							0.132	-0.5			0.089	-0.1			0.037	*0.7*		
108					0.048	0.0			0.078	-0.8	0.067	-1.0					0.026	*-0.8*
109	0.052	0.3	0.087	0.0	0.048	0.0	0.152	0.1	0.117	0.8	0.103	0.6	0.089	-0.3			0.039	*0.8*
110	0.043	-0.4							0.149	2.1	0.116	1.1					0.038	*0.6*
111							0.132	-0.5	0.096	-0.1	0.096	0.2			0.039	*0.9*		
112																		
113															FN	*-2.7*		
114	0.0765	2.4	0.092	0.2	0.0536	0.4	0.402	>5	0.0657	-1.3	0.0789	-0.5	0.084	-0.5	FN	*-2.7*	0.0211	*-1.4*
115	0.045	-0.3	0.11	1.0	0.042	-0.5	0.136	-0.4	0.095	-0.1	0.093	0.1	0.094	-0.1	0.04	*1.0*	0.032	*-0.1*
116					FN	-3.2					0.09	0.0						
117	0.0547	0.6	0.077	-0.5	0.0437	-0.4	0.136	-0.4	0.0903	-0.3	0.0892	-0.1	0.105	0.4	0.0278	*-0.5*	0.028	*-0.6*
118									0.072	-1.1	0.124	1.5			0.022	*-1.2*	0.032	*-0.1*
119															0.0404	*1.1*		
120	0.047	-0.1	0.103	0.7	0.054	0.5	0.16	0.3	0.109	0.5	0.0925	0.1	0.108	0.5	0.027	*-0.6*	0.0305	*-0.3*
121	0.0487	0.1							0.0946	-0.1	0.0868	-0.2			0.0206	*-1.4*	0.026	*-0.8*
122											0.062	-1.3			0.033	*0.2*		
123	0.031	-1.4	0.063	-1.1	0.023	-2.1	0.1	-1.3	0.053	-1.8	0.078	-0.6					0.019	-1.7

Table 11a. Results for azoxystrobin, bixafen, boscalid, buprofezin, carbendazim, cypermethrin, epoxiconazole, fenpropidin and fluopyram in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Buprofezin	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	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	**0.088**		**0.074**		**0.414**		**0.048**		**0.086**		**0.134**		**0.177**		**0.347**		**0.250**	
124	0.095	0.3					0.048	0.0			0.138	0.1	0.185	0.2				
125	0.0434	-2.0	0.040	-1.8	0.209	-2.0	0.024	-2.0			0.0926	-1.2	0.0885	-2.0			0.131	-1.9
126											0.139	0.1						
127																		
128	0.08	-0.4			0.464	0.5	0.047	-0.1	0.085	0.0	0.138	0.1	0.167	-0.2				
129							FN	-3.2										
130	0.082	-0.3			0.411	0.0	0.057	0.7			0.152	0.5	0.169	-0.2				
131											0.117	-0.5						
132			0.058	-0.8	0.355	-0.6	0.053	0.4	0.114	1.3	0.12	-0.4	0.154	-0.5	0.156	-2.2		
133	0.069	-0.9	0.054	-1.1	0.366	-0.5	0.043	-0.4	0.075	-0.5	0.116	-0.5	0.121	-1.3	0.243	-1.2	0.207	-0.7
134	0.089	0.1	0.069	-0.2	0.485	0.7	0.045	-0.2	0.061	-1.2	0.123	-0.3	0.184	0.2	0.329	-0.2	0.238	-0.2
135	0.107	0.9	0.090	0.9	0.451	0.4	0.049	0.1	0.089	0.1	0.145	0.3	0.214	0.8	0.547	2.3	0.321	1.1
136	0.0498	-1.7			0.229	-1.8	0.029	-1.6	0.041	-2.1	0.0749	-1.8	0.107	-1.6				
137	0.0727	-0.7	0.066	-0.4	0.339	-0.7	0.047	0.0	0.094	0.4	0.152	0.5	0.165	-0.3	0.335	-0.1	0.221	-0.5
138	0.0814	-0.3	0.076	0.2	0.413	0.0	0.041	-0.6	0.056	-1.4	0.186	1.5	0.149	-0.6	0.285	-0.7	0.218	-0.5
139	0.09	0.1	0.079	0.3	0.477	0.6	0.057	0.7	0.08	-0.3	0.144	0.3	0.196	0.4	0.397	0.6	0.267	0.3
140	0.0726	-0.7	0.059	-0.8	0.418	0.0	0.051	0.2	0.101	0.7	0.191	1.7	0.174	-0.1	0.334	-0.1	0.269	0.3
141	0.0693	-0.8			0.379	-0.3	0.047	-0.1	0.052	-1.6	0.16	0.8	0.177	0.0	0.337	-0.1	0.2	-0.8
142	0.0795	-0.4	0.071	-0.1	0.384	-0.3	0.047	-0.1	0.072	-0.7	0.133	0.0	0.176	0.0	0.345	0.0	0.24	-0.2
143	0.101	0.6	0.051	-1.2	0.45	0.4	FN	-3.2	0.105	0.9	0.162	0.8	0.228	1.2	0.488	1.6	0.277	0.4
144																		
145	0.098	0.5			0.459	0.4	0.047	-0.1			0.111	-0.7	0.194	0.4	0.68	3.8		
146	0.112	1.1			0.403	-0.1	0.055	0.6	0.213	>5			0.208	0.7				
147			0.086	0.7	0.586	1.7	0.047	-0.1	0.078	-0.4			0.239	1.4	0.489	1.6	0.288	0.6
148	0.0706	-0.8	0.07	-0.2	0.358	-0.5	0.039	-0.7	0.083	-0.1	0.0957	-1.2	0.16	-0.4	0.374	0.3	0.223	-0.4
149	0.1	0.6																
150	0.0936	0.3	0.075	0.1	0.422	0.1	0.059	1.0	0.080	-0.3	0.121	-0.4	0.173	-0.1	0.342	-0.1	0.274	0.4
151	0.079	-0.4			0.426	0.1	0.051	0.2	0.114	1.3	0.121	-0.4	0.136	-0.9	0.336	-0.1	0.303	0.9
152	0.093	0.2	0.065	-0.5	0.411	0.0	0.04	-0.7	0.078	-0.4	0.149	0.4	0.173	-0.1	0.339	-0.1	0.222	-0.4
153	0.114	1.2	FN	-3.5	0.444	0.3	0.052	0.3	0.091	0.2	0.141	0.2	0.188	0.2				
154	0.062	-1.2	0.072	-0.1	0.448	0.3	0.04	-0.7	0.065	-1.0	0.066	-2.0	0.134	-1.0	0.191	-1.8	0.227	-0.4
155	0.0952	0.3	0.084	0.6	0.36	-0.5	0.05	0.2	0.09	0.2	0.193	1.7	0.16	-0.4	0.358	0.1	0.248	0.0
156	FN	-3.5			0.3	-1.1	0.03	-1.5			FN	-3.7	0.11	-1.5	0.17	-2.0	0.15	-1.6
157	0.06	-1.3			0.29	-1.2	0.064	1.3	0.094	0.4	0.122	-0.4	0.0815	-2.2				
158	0.0878	0.0			0.4	-0.1	0.048	0.0	0.051	-1.6	0.172	1.1	0.156	-0.5	0.381	0.4		
159	0.0959	0.4	0.072	-0.1	0.47	0.5	0.052	0.4	0.071	-0.7	0.197	1.9	0.16	-0.4	0.255	-1.1	0.198	-0.8
160																		
161	0.0865	-0.1			0.444	0.3			0.094	0.4			0.182	0.1				
162																		
163	0.066	-1.0	0.06	-0.7	0.329	-0.8	0.043	-0.4	0.088	0.1	0.124	-0.3	0.125	-1.2	0.246	-1.2	0.196	-0.9

Table 11b. Results for isocarbophos, metrafenone, pirimicarb-desmethyl, prothioconazole-desthio, pyraclostrobin, tebuconazole and tetramethrin, in mg/kg, the corresponding z scores, MRRLs and the assigned values. Z scores, and assigned values for heptachlor and pencycuron are for information only.

Laboratory code	Isocarbophos	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Pirimicarb-desmethyl	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)	Tetramethrin	Z score (FFP RSD (25%)	Heptachlor	Z score (FFP RSD (25%)	Pencycuron	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	**0.048**		**0.088**		**0.048**		**0.149**		**0.098**		**0.091**		**0.096**		***0.032***		***0.033***	
124											0.09	0.0	0.117	0.9	0.033	*0.2*		
125	FN	-3.2					0.085	-1.7	0.0483	-2.0	0.0456	-2.0	0.0477	-2.0			0.0137	*-2.3*
126															0.0391	*0.9*		
127															0.0432	*1.5*		
128									0.0697	-1.2	0.0782	-0.5			0.026	*-0.7*	0.0396	*0.8*
129															0.0354	*0.5*		
130							0.126	-0.6			0.091	0.0			0.039	*0.9*		
131													0.108	0.5	0.0222	*-1.2*		
132					0.039	-0.8	0.0179	-3.5	0.12	0.9	0.0809	-0.4			0.0222	*-1.2*		
133	0.166	>5	0.081	-0.3	0.064	1.3	0.121	-0.8	0.075	-0.9	0.063	-1.2	0.094	-0.1	0.029	*-0.3*	0.032	*-0.1*
134	0.0491	0.1	0.094	0.3	0.0548	0.5	0.111	-1.0	0.094	-0.2	0.0874	-0.1	FN	-3.6			0.0292	*-0.4*
135	0.0557	0.6	0.123	1.6	0.039	-0.8	0.164	0.4	0.102	0.2	0.116	1.1	0.098	0.1	0.047	*1.9*	0.0345	*0.2*
136	0.03	-1.5	0.055	-1.5					0.0562	-1.7	0.0451	-2.0					0.0365	*0.5*
137	0.0455	-0.2	0.083	-0.2	0.051	0.2	0.159	0.3	0.0795	-0.8	0.0804	-0.4	0.102	0.3	0.0344	*0.3*	0.0322	*-0.1*
138	0.0483	0.0	0.059	-1.3	0.0422	-0.5	0.103	-1.2	0.0664	-1.3	0.0768	-0.6	0.117	0.9	0.0346	*0.4*	0.0323	*-0.1*
139	0.03	-1.5	0.101	0.6	0.032	-1.3	0.157	0.2	0.108	0.4	0.097	0.3	0.08	-0.7	0.037	*0.7*	0.028	*-0.6*
140	0.057	0.7	0.106	0.8	0.0553	0.6	0.149	0.0	0.0811	-0.7	0.0797	-0.5	0.102	0.3	0.04	*1.0*	0.0341	*0.2*
141			0.056	-1.4			FN	-3.7	0.0847	-0.5	0.11	0.9	0.11	0.6	0.019	*-1.6*	0.0305	*-0.3*
142	0.0465	-0.1	0.084	-0.1	0.0462	-0.2	0.145	-0.1	0.092	-0.2	0.0882	-0.1	0.0904	-0.2	0.0285	*-0.4*	0.0307	*-0.2*
143	0.067	1.6	0.097	0.4	0.06	1.0	0.166	0.5	0.12	0.9	0.117	1.2	0.092	-0.2	0.028	*-0.5*	0.019	*-1.7*
144																		
145					0.055	0.6	0.169	0.5	0.134	1.5	0.108	0.8			0.034	*0.3*	0.047	*1.7*
146									0.0851	-0.5	0.111	0.9			0.0315	*0.0*	0.0331	*0.0*
147	0.041	-0.6			0.044	-0.4	0.141	-0.2			0.106	0.7					0.045	*1.5*
148	0.0377	-0.9	0.072	-0.7	0.0441	-0.3	0.117	-0.9	0.0904	-0.3	0.0751	-0.7	0.0924	-0.1			0.0438	*1.4*
149											0.0943	0.2	0.082	-0.6	0.0498	*2.3*		
150	0.0469	-0.1	0.098	0.5	0.0533	0.4	0.157	0.2	0.108	0.4	0.101	0.5	0.092	-0.2	0.0371	*0.7*	0.0355	*0.3*
151	0.048	0.0	0.084	-0.2			2.04	>5	0.071	-1.1	0.102	0.5	0.112	0.7	0.038	*0.8*	0.038	*0.6*
152	0.047	-0.1	0.08	-0.3	0.046	-0.2	0.122	-0.7	0.103	0.2	0.085	-0.2	0.078	-0.7	0.033	*0.2*	0.036	*0.4*
153	0.052	0.3	0.094	0.3	0.042	-0.5	0.179	0.8	0.102	0.2	0.104	0.6	0.0996	0.2	0.0337	*0.3*	0.034	*0.2*
154	0.044	-0.3	0.068	-0.9	0.043	-0.4	0.138	-0.3	0.083	-0.6	0.081	-0.4	0.088	-0.3			0.028	*-0.6*
155	0.0578	0.8	0.08	-0.3	0.05	0.1	0.157	0.2	0.0971	0.0	0.0848	-0.3	0.116	0.8	0.0375	*0.7*	0.0353	*0.3*
156	0.04	-0.7							FN	-3.6	0.07	-0.9	0.05	-1.9	FN	*-2.7*	FN	*-2.8*
157											0.07	-0.9			0.0205	*-1.4*		
158	0.0665	1.5	0.097	0.4	0.0453	-0.2	0.116	-0.9	0.126	1.1	0.0783	-0.5	0.11	0.6	0.0398	*1.0*	0.0328	*0.0*
159	0.0558	0.6	0.102	0.7	0.0492	0.1			0.1	0.1	0.1	0.4	FN	-3.6	0.0391	*0.9*	FN	*-2.8*
160																		
161			0.089	0.1					0.105	0.3	0.0972	0.3					0.0287	*-0.5*
162															0.025	*-0.8*		
163	0.035	-1.1	0.076	-0.5	0.049	0.1	0.11	-1.0	0.069	-1.2	0.072	-0.8	0.074	-0.9	0.031	*-0.1*	0.029	*-0.5*

Table 12a. Results for azoxystrobin, bixafen, boscalid, buprofezin, carbendazim, cypermethrin, epoxiconazole, fenpropidin and fluopyram in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Buprofezin	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	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	**0.088**		**0.074**		**0.414**		**0.048**		**0.086**		**0.134**		**0.177**		**0.347**		**0.250**	
164																		
165	0.087	0.0			0.551	1.3	0.085	3.1										
166	0.094	0.3			0.44	0.3	0.05	0.2	0.039	-2.2	0.031	-3.1	0.17	-0.2	0.36	0.2		
167	0.102	0.6			0.518	1.0	0.036	-1.0			0.076	-1.7	0.239	1.4				
168	0.128	1.8			0.536	1.2	0.045	-0.3	0.06	-1.2	FN	-3.7	0.167	-0.2			FN	-3.8
169																		
170	0.0981	0.5	0.088	0.8	0.461	0.5	0.0514	0.3	0.0813	-0.2	0.166	0.9	0.205	0.6	0.433	1.0	0.287	0.6
171	0.068	-0.9			0.38	-0.3	0.04	-0.7	0.059	-1.3	0.122	-0.4	0.162	-0.3				
172	0.0793	-0.4	0.069	-0.2	0.394	-0.2	0.0356	-1.0	0.0731	-0.6	0.149	0.4	0.176	0.0	0.31	-0.4	0.19	-1.0
173	0.201	>5			1.17	>5	0.0372	-0.9	FN	-3.5	0.0851	-1.5	FN	-3.8				
174	0.085	-0.1	0.077	0.2	0.39	-0.2	0.056	0.7	0.081	-0.2	0.135	0.0	0.186	0.2	0.288	-0.7	0.215	-0.6
175																		
176	0.04	-2.2			0.5	0.8	0.025	-1.9	0.045	-1.9	0.079	-1.6	0.11	-1.5	0.18	-1.9	0.22	-0.5
177	0.085	-0.1	0.07	-0.2	0.43	0.2	0.049	0.1	0.076	-0.5	0.28	4.3	0.18	0.1	0.46	1.3	0.28	0.5
178																		

Table 12b. Results for isocarbophos, metrafenone, pirimicarb-desmethyl, prothioconazole-desthio, pyraclostrobin, tebuconazole and tetramethrin, in mg/kg, the corresponding z scores, MRRLs and the assigned values. Z scores, and assigned values for heptachlor and pencycuron are for information only.

Laboratory code	Isocarbophos	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Pirimicarb-desmethyl	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)	Tetramethrin	Z score (FFP RSD (25%)	Heptachlor	Z score (FFP RSD (25%)	Pencycuron	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	**0.048**		**0.088**		**0.048**		**0.149**		**0.098**		**0.091**		**0.096**		***0.032***		***0.033***	
164															0.038	*0.8*		
165											0.075	-0.7						
166									0.1	0.1	0.11	0.9	0.121	1.0			0.032	*-0.1*
167									0.109	0.5	0.126	1.6			0.014	*-2.2*		
168	0.134	>5					0.111	-1.0	0.072	-1.1	0.114	1.0	0.022	-3.1	FN	*-2.7*	0.048	*1.9*
169															0.0289	*-0.4*		
170	0.0606	1.0	0.088	0.0	0.075	2.3	0.136	-0.4	0.103	0.2	0.095	0.2	0.119	1.0	0.0383	*0.8*	0.032	*-0.1*
171			0.084	-0.2					0.065	-1.3	0.08	-0.5	0.074	-0.9			0.032	*-0.1*
172	0.0484	0.0	0.071	-0.7	0.039	-0.8	0.158	0.2	0.0942	-0.2	0.097	0.3	0.0993	0.1			0.0236	*-1.1*
173							FN	-3.7	0.168	2.9	0.306	>5			0.0402	*1.1*	0.0571	*3.0*
174	0.056	0.7	0.094	0.3	0.047	-0.1	0.159	0.3	0.12	0.9	0.088	-0.1	0.099	0.1	0.029	*-0.3*	0.032	*-0.1*
175																		
176	0.025	-1.9	0.047	-1.9	0.03	-1.5			0.07	-1.1	0.05	-1.8	0.049	-2.0	0.016	*-2.0*	0.01	*-2.8*
177	0.041	-0.6	0.093	0.2	0.047	-0.1	0.15	0.0	0.11	0.5	0.094	0.2	0.1	0.2	0.037	*0.7*	0.03	*-0.3*
178																		

3.4.2 Sum of Weighted Z scores (AZ^2) – Category A

To be classified into Category A, the laboratories had to submit quantitative results for at least 90 % of the compulsory pesticides present in the Test Item (≥14 pesticide residues, exclusive of any false negatives results), analyse for more than 90% of the compulsory pesticides on the target list and also report no false positive results. For the 82 EU and EFTA laboratories in Category A (53%), the results were additionally evaluated by calculating the Average of the Squared -Score (AZ^2). Of the 82 participants, 76 participants (93%) obtained AZ^2 values at or below 2 (good) and 4 participants (4.9%) obtained AZ^2 values between 2-3 (satisfactory) and 2 participants (2.4%) obtained AZ^2 values ≥3 (unsatisfactory). An additional three laboratories from Third Countries were evaluated and classified into Category A. The AZ^2 scores achieved by the labs can be seen in **Table 13.**

Table 13 Sum of Weighted z scores (AZ^2) for laboratories in Category A, the number of pesticide analysed by the laboratory, the number of false negatives reported and the classification as good, satisfactory and unsatisfactory. The table include data for both EU and non-EU participants

Lab code	No. of detected compulsory pesticides	No. of detected volutary pesticides	AZ^2	No. Of False negative	Classification	NRL
1	16	1	0.1	0	Good	NRL
2	16	1	3.8	0	Unsatisfactory	
5	15	1	1.3	1	Good	NRL
6	16	1	0.3	0	Good	
7	16	1	0.3	0	Good	NRL
8	16	1	0.1	0	Good	
9	16	1	0.5	0	Good	
10	16	1	0.7	0	Good	
14	16	1	0.6	0	Good	NRL
17	14	1	0.2	0	Good	
18	16	1	0.4	0	Good	
20	16	1	0.1	0	Good	
21	16	1	0.2	0	Good	
22	16	1	0.3	0	Good	
23	16	1	0.8	0	Good	NRL
25	16	1	0.5	0	Good	
26	16	1	0.5	0	Good	
27	15	1	2.3	1	Satisfactory	
32	15	1	3.9	1	Unsatisfactory	
35	16	1	0.5	0	Good	NRL
36	16	1	0.2	0	Good	
37	16	1	0.3	0	Good	
39	16	1	0.1	0	Good	
41	16	1	0.1	0	Good	
43	16	1	0.2	0	Good	
45	16	1	0.3	0	Good	NRL-EFTA
46	16	1	0.5	0	Good	

Lab code	No. of detected compulsory pesticides	No. of detected volutary pesticides	AZ[2]	No. Of False negative	Classification	NRL
47	16	1	0.2	0	Good	
50	15	1	0.1	0	Good	
54	16	1	0.2	0	Good	
56	16	1	0.3	0	Good	NRL
58	15	1	0.2	0	Good	
59	16	1	0.5	0	Good	
62	16	1	0.4	0	Good	NRL
63	14	1	0.2	0	Good	
64	16	1	0.2	0	Good	
65	16	1	1.3	0	Good	
66	16	0	0.6	0	Good	
67	14	1	0.2	0	Good	
68	16	1	0.8	0	Good	
69	16	1	0.6	0	Good	
70	16	1	0.8	0	Good	NRL
71	16	1	1.8	0	Good	NRL
73	16	1	0.1	0	Good	NRL
75	14	1	0.5	0	Good	
78	16	1	0.4	0	Good	NRL
79	16	1	0.4	0	Good	
80	16	1	0.2	0	Good	
82	16	1	0.6	0	Good	NRL
83	16	1	1.6	0	Good	
84	16	1	0.5	0	Good	NRL
85	15	1	1.0	1	Good	
87	16	1	0.1	0	Good	
88	15	1	0.2	0	Good	
95	15	1	0.3	0	Good	
102	15	1	0.5	0	Good	
103	16	1	0.1	0	Good	NRL
106	16	1	1.9	0	Good	NRL
109	16	0	0.5	0	Good	
114	15	1	3.5	0	Unsatisfactory	
115	16	1	0.2	0	Good	
117	16	1	0.1	0	Good	NRL
120	16	1	0.3	0	Good	
133	16	1	2.3	0	Satisfactory	NRL
134	15	0	1.1	1	Good	

Lab code	No. of detected compulsory pesticides	No. of detected volutary pesticides	AZ^2	No. Of False negative	Classification	NRL
135	16	1	0.9	0	Good	
137	16	1	0.2	0	Good	
138	16	1	0.8	0	Good	
139	16	1	0.4	0	Good	
140	16	1	0.4	0	Good	NRL
142	16	1	0.1	0	Good	
143	15	1	1.6	1	Good	
148	16	0	0.4	0	Good	NRL
150	16	1	0.1	0	Good	
151	14	1	2.2	0	Satisfactory	
152	16	1	0.2	0	Good	
154	16	0	0.8	0	Good	
155	16	1	0.3	0	Good	NRL
158	14	1	0.7	0	Good	
159	14	1	1.5	1	Good	
163	16	1	0.7	0	Good	NRL
170	16	1	0.7	0	Good	NRL
172	16	0	0.3	0	Good	
176	14	1	2.8	0	Satisfactory	
177	16	1	1.4	0	Good	

The laboratories that did not fulfil the requirements described above, were classified in Category B. The number of reported quantitative results, analysed compounds from the Target List and acceptable z scores as well as information on false negative and positive results are shown in **Table 14.** Five participants fulfilled the criteria of detecting 90 % of the compulsory pesticides in the Test Item but did not fulfil the criteria of analysing for 90 % of the compulsory pesticides on the Target List. The reverse was the case for seven participants. Forty participants (25%) analysed and detected less than 70% of the pesticides present in the Test Item.

Table 14 Number of pesticides analysed, number of compulsory and voluntary compounds analysed from the Target List, number of acceptable z scores, false negative and positive results for the laboratories in Category B.

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected, %	Analysed of compulsory pesticides on Target List	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
3	12	75%	92%	1	11	0	0	NRL
4	5	31%	48%	1	5	0	0	
11	12	75%	75%	1	12	0	0	
12	0	0%	9%	1	0	0	0	
13	15	94%	89%	0	15	0	0	NRL
15	13	81%	94%	1	11	0	0	
16	10	63%	78%	1	9	0	0	NRL
19	3	19%	29%	1	3	0	0	
24	11	69%	56%	0	9	0	0	
28	13	81%	78%	1	13	0	0	
29	11	69%	93%	1	10	2	0	
30	0	0%	0%	0	0	0	0	
31	10	63%	74%	1	10	0	0	
33	7	44%	46%	1	7	0	0	
34	7	44%	40%	1	7	0	0	
38	7	44%	65%	1	6	0	0	
40	6	38%	44%	1	6	0	0	
42	13	81%	69%	0	13	0	0	
44	5	31%	43%	0	4	0	0	
48	0	0%	2%	0	0	0	0	
49	12	75%	86%	1	11	2	0	
51	11	69%	90%	1	11	1	0	
52	0	0%	0%	0	0	0	0	
53	8	50%	60%	0	8	0	0	
55	0	0%	9%	1	0	0	0	
57	14	88%	68%	0	14	0	0	
60	12	75%	72%	1	12	0	0	
61	0	0%	0%	0	0	0	0	NRL
72	11	69%	60%	1	7	0	0	
74	8	50%	66%	1	8	0	0	

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected, %	Analysed of compulsory pesticides on Target List	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
76	7	44%	46%	1	7	0	0	
77	7	44%	46%	1	7	0	0	
81	0	0%	0%	0	0	0	0	
86	10	63%	76%	0	10	0	0	
89	12	75%	84%	1	11	0	0	
90	10	63%	88%	1	8	0	0	
91	14	88%	86%	1	14	0	0	NRL
92	1	6%	31%	1	1	0	0	
93	8	50%	66%	1	7	0	0	
94	10	63%	70%	1	9	0	0	
96	8	50%	60%	1	8	0	0	
97	2	13%	28%	1	2	0	0	
98	12	75%	79%	1	12	0	0	
99	0	0%	9%	1	0	0	0	
100	4	25%	40%	1	4	0	0	
101	6	38%	42%	1	6	0	0	
104	13	81%	90%	1	11	1	0	
105	13	81%	68%	1	13	0	0	
107	7	44%	46%	1	7	0	0	
108	9	56%	64%	0	9	0	0	
110	9	56%	70%	0	7	1	0	
111	8	50%	55%	1	8	0	0	
112	0	0%	0%	0	0	0	0	
113	1	6%	25%	1	1	1	0	
116	5	31%	63%	0	4	3	0	NRL
118	5	31%	65%	1	4	0	0	
119	0	0%	9%	1	0	0	0	
121	9	56%	74%	1	9	0	0	
122	4	25%	32%	1	3	0	0	
123	15	94%	75%	0	12	0	0	
124	6	38%	49%	1	6	0	0	
125	11	69%	77%	0	7	1	0	
126	1	6%	24%	1	1	0	0	
127	0	0%	9%	1	0	0	0	
128	8	50%	65%	1	8	0	0	
129	0	0%	20%	1	0	1	0	
130	7	44%	46%	1	7	0	0	
131	2	13%	25%	1	2	0	0	

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected, %	Analysed of compulsory pesticides on Target List	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
132	11	69%	60%	1	9	0	0	NRL
136	10	63%	61%	0	8	0	0	
141	12	75%	92%	1	12	1	0	
144	0	0%	0%	0	0	0	0	
145	10	63%	83%	1	9	0	0	
146	7	44%	60%	1	6	0	0	
147	11	69%	74%	0	11	0	0	NRL
149	3	19%	40%	1	3	0	0	
153	13	81%	95%	1	13	1	0	
156	8	50%	69%	1	7	3	0	
157	7	44%	55%	1	6	0	0	NRL
160	0	0%	0%	0	0	0	0	
161	7	44%	50%	0	7	0	0	
162	0	0%	9%	1	0	0	0	
164	0	0%	9%	1	0	0	0	
165	4	25%	37%	0	3	0	0	
166	10	63%	63%	0	8	0	0	
167	7	44%	46%	1	7	0	0	
168	10	63%	84%	1	8	2	0	NRL
169	0	0%	7%	1	0	0	0	
171	10	63%	72%	0	10	0	0	
173	6	38%	78%	1	2	3	0	
174	16	100%	87%	1	16	0	0	
175	0	0%	0%	0	0	0	0	
178	0	0%	0%	0	0	0	0	

3.5 Trends in numbers of participating laboratories and their performance

The number of EU and EFTA laboratories participating in the EUPTs on cereals has increased steadily over the years. In EUPT-C3 in 2009 102 labs participated and in the latest EUPT-CF10 143 labs participated (**Table 15**). The number of pesticides included in the Target Pesticide List has also increased during this 8-year period, from 43 to 117 individual compounds. The number of spiked or incurred pesticides contained in the Test Items has in the same period increased from 13 to 18 (two of them not evaluated in this EUPT-CF10). Thus, the demands put on the participating laboratories has increased every year. Many laboratories have a limited scope and are therefore not able to cover all pesticides in the PT. Of the laboratories submitting results, 25 % submitted results for less than 70% of pesticides present in the Test Item.

Table 15. Overall trends in participation of laboratories, pesticides in the target list and test item, and performance of laboratories in the 7 latest EUPTs cereals (excluding EUPT-CF7 on feed).

PT and type of test item	EUPT-C3 Oat flour	EUPT-C4 Rye flour	EUPT-C5 Rice flour	EUPT-C6 Barley flour	EUPT-CF8 Wheat flour	EUPT-CF9 Maize flour	EUPT-CF10 Rye flour
Participants submitting results (EU and EFTA)	102	115	133	127	142	143	160
MRM pesticides in the Target Pesticide List	51	64	103	107	111	117	134/7
MRM pesticides in the test material	14	16	16	18	17	18	16
No. of results for MRM pesticides	981	1624	1521	1741	1893	2012	2012
Average of 'reported results', %	69	88	71	76	78	78	79
Range of 'reported results', %	48 - 95	55 - 95	41-95	50-95	49-93	61-94	58-90
Acceptable z scores, %	87	87	87	90	90	89	95
Questionable z scores, %	8	6	4	5	6	2	2
Unacceptable z scores, %	5	7	9	4	4	3	2
False negatives, %	3	4	3	1	3	2	2
Number of false positives	3	17	16	2	4	9	0
Category A, % of participating laboratories	46	46	44	55	50	57	53
Good SWZ/AZ^2, %	72	77	80	79	85	96	93
Satisfactory SWZ/AZ^2, %	15	8	15	14	10	1	5
Unsatisfactory SWZ/AZ^2, %	13	15	5	7	4	3	2

As for previous years an improvement was seen in the overall analytical performance (accuracy of measurement) if looking at the percentage of acceptable, questionable, unacceptable z scores, while this was not the case for the analytical scope. The average % of reported results has in the last four EUPT-C/CF been between 76-79%. This was because a lot of participants analysed for less than 50% of the pesticide residues present in the test Item. The false negative results has been relatively low, for the last PT it was only 2% of the results and this year, for the first time, no false positive results were reported.

The percentage of Category A laboratories has only varied slightly and for the last 4 EUPTs no improvement can be seen. For Category A an improvement in AZ^2 was seen in EUPT-CF9 where 96% of the results were Good, and in EUPT-CF10 still 93% of the laboratories were evaluated as good. However, it is difficult to assess any improvement/deterioration in laboratory performance between the Proficiency Tests, because the numbers of pesticides in the Test item and the numbers of laboratories participating in the PTs have both significantly increased.

3.6 Summary, conclusions and prospects for the EUPTs on pesticide residues in cereals

The EUPT-CF10 Test Item consisted of rye flour containing incurred and spiked pesticides. The rye crop had been sprayed in the field with commercially available pesticide formulations. The final Test Item contained the following pesticides: azoxystrobin, bixafen, boscalid, buprofezin, carbendazim, cypermethrin, epoxiconazole, fenpropidin, fluopyram, heptachlor, isocarbophos, metrafenone, pencycuron, pirimicarb-desmethyl, prothioconazole-desthio, pyraclostrobin, tebuconazole and tetramethrin. One hundred fifty-five laboratories, representing 31 EU and EFTA countries submitted results. Five more laboratories registered, but did not submit any results. All NRLs, except one of the two Cypriot labs, participated in the PT. Malta was represented in the PT by the NRL for the UK. An additional 18 laboratories from EU candidate states and Third Countries registered for the PT and 14 submitted results. The Target Pesticide List distributed to the laboratories prior to the test contained 134 individual compulsory and 7 voluntary compounds..

The number of false positives and false negatives has varied between the EUPTs. For the first time during the 10 EUPT-CFs no false positive results were reported. The number of false negatives represented only 2% of the total number of results. This is very similar with the percentage of false negatives reported in the previous EUPTs. The average Alg A-RSD was at 17%, well below the FFP-RSD of 25% with a range from 14-23% for the individual compounds.

For azoxystrobin, boscalid, buprofezin, epoxiconazole, fluopyram, metrafenone, pyraclostrobin and tebuconazole acceptable results were obtained by 96-99% of the laboratories. For bixafen, cypermethrin, fenpropidin, isocarbophos, pirimicarb-desmethyl, prothioconazole-desthio and tetramethrin acceptable results were obtained by 91-94% of the laboratories..

The EUPT-CF11 will be with oat as test item, which will be shipped to the laboratories in April/May 2017. The selection of pesticides will continue to be focused on pesticides included in the scope of the EU multi-annual coordinated control programme, as well as additional pesticides of relevance to feed and/or cereal production in Europe and in other parts of the world from where significant quantities of feed and cereals are imported.

4. ACKNOWLEDGEMENTS

The Organisers wish to thank the members of the EURL Quality Control and Advisory Groups for their valuable advice.

5. 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] CEN EN 15662 - Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE - QuEChERS-method

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

[5] ISO 13528:2005 – Statistical methods for use in proficiency testing by interlaboratory comparison

[6] ISO 17043:2010 – Conformity assessment -- General requirements for proficiency testing-

[7] Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. SANTE 11945/2015.
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APPENDICES

Appendix 1 List of laboratories registered to participate in the EUPT-CF10

Participating labs from EU and EFTA member states

Country	Institution	City	NRL-CF	Report data
Austria	Austrian Agency for Health and Food Safety, Institute for Food Safety Innsbruck - Department for Pesticide and Food Analytics	Innsbruck	NRL	Yes
Austria	MA 38 - Lebensmitteluntersuchung Wien	Wien		Yes
Belgium	Scientific Institute of Public Health	Brussels	NRL	Yes
Belgium	Primoris Belgium - Belgium, Gent (Zwijnaarde)	Gent - Zwijnaarde		Yes
Belgium	Federal Laboratory for Safety of Food Chain, Tervuren	Tervuren		Yes
Bulgaria	Central Laboratory for Chemical Testing and Control, Sofia	Sofia	NRL	Yes
Bulgaria	Fytolab - Bulgaria, Plovdiv	Plovdiv		Yes
Croatia	Faculty of Food Technology and Biotechnology, Food Control Center - Croatia, Zagreb	Zagreb		Yes
Croatia	Institute of Public Health, Split	Dalmatia County, Split		Yes
Croatia	Euroinspekt - Croatiakontrola d.o.o.	Zagreb		Yes
Croatia	Institute of Public Health, Dr. Andrija štampar	Zagreb		Yes
Croatia	Croatian Veterinary Institute	Zagreb		Yes
Croatia	Croatian National Institute of Public Health	Zagreb	NRL	Yes
Croatia	Institute of Public Health, Primorje-Gorski	Kotar County, Rijeka		Yes
Cyprus	Animal Feeds and Feed Additives Laboratory of the Analytical Laboratories of the Department of Agriculture	Nicosia	NRL	No
Cyprus	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	NRL	Yes
Czech Republic	Czech Agriculture and Food Inspection Authority	Praha	NRL	Yes
Czech Republic	Central Institute for Supervising and Testing in Agriculture	Brno	NRL	Yes
Czech Republic	University of Chemical Technology, Dept. of Food Chemistry and Analysis - Prague	Praha		Yes
Denmark	Danish Veterinary and Food Administration, Department of Residues, Ringsted	Ringsted	NRL	Yes
Estonia	Agricultural Research Centre, Saku, Lab for Residues and Contaminants	Saku	NRL	Yes
Finland	Finnish Food Safety Authority	Helsinki	NRL	Yes
Finland	Finnish Customs Laboratory	Espoo	NRL	Yes
France	Capinov	Landerneau		Yes
France	Service Commun des Laboratoires / Laboratoire Ile de France - Massy	Massy Cedex	NRL	Yes
France	Service Commun des Laboratoires / Laboratoire de Montpellier	Montpellier		Yes
France	GIRPA - FREDON Pays de la Loire	Beaucouzé		Yes
France	INOVALYS Le Mans	Le Mans		Yes
France	CERECO SUD	GARONS		Yes
France	Analysis Center Mediterranean Pyrenees	perpignan		Yes
France	Phytocontrol - France, Nimes	nimes		Yes
Germany	Federal Office of Consumer Protection and Food Safety, NRL for Pesticide Residues	Berlin	NRL	Yes

Country	Institution	City	NRL-CF	Report data
Germany	Chemisches und Veterinäruntersuchungsamt Ostwestfalen-Lippe, Detmold	Detmold		Yes
Germany	Niedersächsisches Landesamt für Verbraucherschutz und Lebensmittelsicherheit, Stade	Stade		Yes
Germany	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld		Yes
Germany	Thuringian Institute of Agriculture	Jena		Yes
Germany	Chemisches und Veterinäruntersuchungsamt Rheinland, Standort Bonn	Bonn		Yes
Germany	Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer	Speyer		Yes
Germany	Food and Veterinary Institute Oldenburg	Oldenburg		Yes
Germany	Landesamt für Verbraucherschutz - Sachsen-Anhalt	Halle/Saale		Yes
Germany	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei Mecklenburg-Vorpommern	Rostock		Yes
Germany	Landesuntersuchungsamt Institut für Lebensmittelchemie Speyer	Speyer		Yes
Germany	Landesbetrieb Hessisches Landeslabor, Wiesbaden	Wiesbaden		Yes
Germany	State Laboratory Schleswig-Holstein	Neumünster		Yes
Germany	State Department of Environmental and Agricultural Operations in Saxony	Nossen		Yes
Germany	Berlin-Brandenburg State Laboratory, Potsdam	Potsdam		Yes
Germany	Bavarian Health and Food Safety Authority Office Erlangen	Erlangen		Yes
Germany	Chemical and Veterinary Investigations Office, Stuttgart (CVUAS), (Residues)	Fellbach		Yes
Germany	LUFA-ITL GmbH	Kiel		Yes
Germany	Landesanstalt für Landwirtschaft, Forsten und Gartenbau, Halle	Halle/Saale		Yes
Germany	Chemical and Veterinary Analytical Institute Muensterland-Emscher Lippe	Münster		Yes
Germany	Eurofins - Dr. Specht Laboratorien GmbH	Hamburg		Yes
Germany	Landesbetrieb Hessisches Landeslabor, Kassel	Kassel		Yes
Germany	Eurofins SOFIA GmbH - Germany, Berlin	Berlin		Yes
Germany	Landwirtschaftliches Technologiezentrum Augustenberg, Karlsruhe	Karlsruhe		Yes
Greece	General Chemical State Laboratory, D Division, Pesticide Residues Laboratory	Athens	NRL	Yes
Greece	Regional Center of Plant Protection and Quality Control of Ioannina, Pesticide Residues Laboratory	Ioannina		Yes
Greece	Benaki Phytopathological Institute, Pesticide Residues Laboratory	Kifissia	NRL	Yes
Hungary	National Food Chain Safety Office Directorate of Plant Protection, Soil Conservation and Agri-environment, Pesticide Residue Analytical Laboratory, Szolnok	Szolnok		Yes
Hungary	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-environment - Pesticide Analytical Laboratory, Velence	Velence	NRL	Yes
Hungary	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Miskolc	Miskolc		Yes
Hungary	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory, Hódmezovásárhely	Hódmezovásárhely		Yes
Iceland	Matís - Icelandic Food Research	Reykjavík		Yes
Ireland	Pesticide Control Laboratory, Department of Agriculture, Fisheries and Food	Co. Kildare	NRL	Yes

Country	Institution	City	NRL-CF	Report data
Italy	ARPA Puglia - Dipartimento di Bari	Bari		Yes
Italy	Laboratorio analisi acque e cromatografia	Bolzano		Yes
Italy	ARPALAZIO SEZIONE P.LE DI RIETI	Rieti		Yes
Italy	ARPAL Sez. di La Spezia	La Spezia		Yes
Italy	Istituto Zooprofilattico Sperimentale Umbria e Marche, PERUGIA	Perugia		Yes
Italy	Centro di referenza nazionale per la sorveglianza ed il controllo degli alimenti per animali	Genova	NRL	Yes
Italy	Istituto Zooprofilattico Sperimentale Abruzzo e Molise	Teramo		Yes
Italy	ARPA FVG Settore Laboratorio Unico - Laboratorio di Pordenone	Pordenone		Yes
Italy	Laboratorio Tematico Fitofarmaci ARPAE Emilia Romagna Sezione Provinciale di Ferrara	Ferrara		Yes
Italy	Laboratorio di Sanità Pubblica ASL BERGAMO	Bergamo		Yes
Italy	Environement protection regional agency Aosta Valley	Saint Christophe		No
Italy	Istituto Zooprofilattico Sperimentale Lombardia ed Emilia Romagna	Brescia		Yes
Italy	ATS Milano Città Metropolitana - Laboratorio di Prevenzione	Milano		Yes
Italy	APPA Trento Settore Laboratorio	Trento		Yes
Italy	ARPAM Dipartimento di Macerata	Macerata		Yes
Italy	Istituto Zooprofilattico Sperimentale Lazio e Toscana - Roma	Roma		Yes
Italy	IZS LT (sezione Firenze)	San Martino alla Palma Scandicci (FI)		Yes
Italy	Istituto Zooprofilattico Sperimentale Puglia e Basilicata	Foggia		No
Italy	Istituto Zooprofilattico Sperimentale Sardegna	Sassari		Yes
Italy	Istituto Zooprofilattico Sperimentale delle Venezie	Legnaro (Padova)		Yes
Italy	Public Health Laboratory - Florence	Firenze		Yes
Italy	Istituto Zooprofilattico Sperimentale Sicilia	Palermo		Yes
Italy	ARPA VENETO DIP.REG.LAB. S.L. VERONA	Verona		Yes
Italy	Istituto Superiore di Sanità, Pesticide Section	Roma		Yes
Italy	Agrobiolab S.R.L.	Rutigliano		Yes
Latvia	Institute of Food Safety, Animal Health and Environment (BIOR) - Riga	Riga	NRL	Yes
Lithuania	National Food and Veterinary Risk Assessment Institute (Lithuania, Vilnius)	Vilnius	NRL	Yes
Luxembourg	National Health Laboratory Luxembourg (Food Laboratory)	Dudelange	NRL	Yes
Netherlands	Eurofins Lab Zeeuws-Vlaanderen (LZV) B.V.	Graauw		Yes
Netherlands	Groen Agro Control	Delfgauw		Yes
Netherlands	NVWA - Netherlands Food and Consumer Product Safety Authority (Wageningen, The Netherlands)	Wageningen	NRL	Yes
Netherlands	RIKILT – Wageningen UR (Natural Toxins & Pesticides)	Wageningen		Yes
Netherlands	Handelslaboratorium Dr. Verwey	Rotterdam		Yes
Netherlands	NofaLab	Schiedam		Yes
Norway	Norwegian Institute of Bioeconomy Research, Biotechnology and Plant Health Division, Department og Pesticides and Natural Bioactive Compounds	Aas	NRL-EFTA	Yes
Norway	National Institute of Nutrition and Seafood Research - Norway, Bergen	Bergen		No

Country	Institution	City	NRL-CF	Report data
Poland	Institute of Plant Protection Pesticide Residue Laboratory, Bialystok	Bialystok		Yes
Poland	Reginal Veterinary Laboratory in Opole	Opole		Yes
Poland	Regional Veterinary Laboratory in Bialystok	Bialystok		Yes
Poland	Research Institute of Horticulture, Food Safety Laboratory (Skierniewice)	Skierniewice		Yes
POLAND	J.S. HAMILTON POLAND S.A.	Gdynia		Yes
Poland	Institute of Plant Protection - National Research Institute, Regional Experimental Station in Rzeszow	Rzeszow		Yes
Poland	Regional Veterinary Laboratory in Gdansk (Kartuska)	Gdansk		Yes
Poland	Regional Veterinary Laboratory in Szczecin	Szczecin		Yes
Poland	Voievodship Sanitary - Epidemiological Station in Warszaw	Warszaw	NRL	Yes
Poland	Institute of Plant Protection - National Research Institute, Branch Sosnicowice	Sosnicowice		Yes
Poland	Regional Veterinary Laboratory in Katowice	Katowice		Yes
Poland	Voievodship Sanitary - Epidemiological Station in Opole	Opole		Yes
Poland	Regional Veterinary Laboratory Wroclaw	Wroclaw		Yes
Poland	Regional Veterinary Laboratory in Poznan	Poznan		Yes
Poland	Regional Veterinary Laboratory in Warsaw	Warszaw		Yes
Poland	Institute of Plant Protection, Department of Pesticide Residue Research - Poznan	Poznan	NRL	Yes
Portugal	Regional Laboratory of Veterinary and Food Safety - Madeira Island	Funchal - Madeira Island		Yes
Portugal	INIAV- Pesticide Residues Laboratory	Oeiras	NRL	Yes
Romania	Regional Laboratory for Pesticide Residues Control in Plant and Plant Products Mures	Targu Mures		Yes
Romania	Central Laboratory for Pesticides Residues Control in Plants and Vegetable Products - Bucharest	Bucharest	NRL	Yes
Romania	Institute for Hygiene and Veterinary Public Health - Bucharest	Bucharest		Yes
Romania	Zonal Laboratory for pesticides Residues in feed - Dolj	Craiova		Yes
Romania	Zonal Laboratory for pesticides Residues in feed - Bistrita	Bistrita		Yes
Romania	Sanitary Veterinary and Food Safety Laboratory - IASI	Iasi		Yes
Romania	Sanitary Veterinary and Food Safety Directorate, Bucharest	Bucharest		Yes
Romania	Sanitary Veterinary and Food Safety Directorate Cluj, Gas-Chromatography Laboratory	Cluj Napoca		Yes
Romania	Zonal Laboratory for pesticides Residues in feed - Braila	Braila		Yes
Slovakia	Public Health Authority of the Slovak Republic	Bratislava		Yes
Slovakia	State Veterinary and Food Institute - Veterinary and Food Institute in Bratislava	Bratislava	NRL	Yes
Slovenia	National Laboratory of Health, Environment and Food - Maribor	Maribor	NRL	Yes
Slovenia	National Laboratory for Health, Environment and Food - Maribor (Location Ljubljana)	Ljubljana		Yes
Slovenia	Agricultural Institute of Slovenia, Central Laboratories	Ljubljana		No
Spain	Laboratori Agroalimentari de la Generalitat de Catalunya	Cabrils		Yes
Spain	Laboratorio Agroalimentario de Extremadura (Cáceres)	Cáceres		Yes
Spain	Analytica Alimentaria GmbH Sucursal España	Almeria		Yes
Spain	National Centre for Food - Spain, Majadahonda	Majadahonda	NRL	Yes

Country	Institution	City	NRL-CF	Report data
Spain	Navarra de Servicios y Tecnologias, S.A.	Villava		Yes
Spain	Agrofood Laboratory of the Comunidad Valenciana	Valencia		Yes
Spain	Laboratorio Regional CCAA La Rioja	Logroño		Yes
Spain	Laboratory of Barcelona Public Health Agency	Barcelona		Yes
Spain	Laboratorio de Salud Pública de Badajoz	Badajoz		Yes
Spain	Laboratorio KUDAM S.L.	Pilar de la Horadada (Alicante)		Yes
Spain	Laboratorio Agrario Regional - Junta de Castilla y Leon	Burgos		Yes
Spain	Laboratorio Agroalimentario de Zaragoza	Zaragoza		Yes
Spain	Laboratorio de Producción y Sanidad Vegetal de Jaén	Mengibar (Jaén)		Yes
Spain	Instituto Tecnologico de Canarias, División de Investigación y Desarrollo Tecnológico - Laboratorio de Residuos	Agüimes, Gran Canaria		Yes
Spain	National Centre for Technology and Food Safety (CNTA) - Spain, San Adrián	San Adrián (Navarra)		Yes
Spain	Laboratorio de Salud Pública de Galicia	Lugo		Yes
Spain	Agricultural and Phytopathological Laboratory of Galicia	Abegondo. A Coruña		Yes
Spain	Labs & Technological Services AGQ, S.L. - Spain, Burguillos	Burguillos		Yes
Spain	Laboratorio Arbitral Agroalimentario, Madrid	Madrid	NRL	Yes
Spain	Laboratorio Regional Agroalimentario y Ambiental de Castilla la Mancha (LARAGA), Toledo	Toledo		Yes
Spain	Servicio de Laboratorio y Control de Santander	Santander		Yes
Spain	Laboratorios Ecosur, S.A.L.	Lorquí (Murcia)		Yes
Sweden	Eurofins - Food&Feed Testing Sweden AB, Lidköping	Lidköping		Yes
Sweden	National Food Agency, Science Department, Chemistry Division 1	Uppsala	NRL	Yes
Switzerland	Kantonales Laboratorium Zürich	Zürich		Yes
United Kingdom	Fera Science Ltd	York	NRL	Yes
United Kingdom	Agri-Food and Biosciences Institute	Belfast		Yes
United Kingdom	Laboratory of the Government Chemist - Teddington	Teddington		Yes

Participating labs from EU candidate state and other non EU countries

Country	Institution	City	Report data
Albania	Pesticides Residues	Tirana	No
Argentina	BOLSA DE COMERCIO DE ROSARIO	Rosario	Yes
Australia	Symbio Laboratories	Eight Mile Plains, QLD	Yes
Brasil	Laboratório Nacional Agropecuário em Goiás / National Agricultural Laboratory at Goiás	Goiânia, Goiás	Yes
Brazil	Bioagri Análises de Alimentos Ltda	São Paulo	Yes
Brazil	Eurofins do Brasil Análises de Alimentos Ltda	Indaiatuba	Yes
China	Shanghai Municipal Center for Disease Control and Prevention	Shanghai	Yes
Egypt	Central Lab of Residue Analysis of Pesticides and Heavy Metals in Foods	Giza	Yes
India	SGS India PVT Limited	Chennai	Yes
India	Pesticide Management Division, National Institute of Plant Health Management	Hyderabad	Yes
India	Angler BiochemLab, PT	Surabaya	Yes
Israel	National Residue Control Laboratory	Bet Dagan	No
Serbia	Center for Food Analysis, Belgrade	Belgrade	Yes
Serbia	SP LABORATORIJA A.D.	BECEJ	Yes
Singapore	Agri-Food & Veterinary Authority of Singapore, Veterinary Public Health Center	Singapore	Yes
Tanzania	Tropical Pesticides Research Institute	Arusha	No
Tanzania	Government Chemist Laboratory Agency	Dar Es salaam	No
Thailand	Central Laboratory (Thailand) Co., Ltd. Bangkok branch	Bangkok	Yes

Appendix 2 Target Pesticide List

Pesticides	MRRL (mg/kg)
Compulsory Compounds considered in Category A/B classification)	
Acephate	0.01
Acetamiprid	0.01
Aldrin	0.01
Azinphos-methyl	0.01
Azoxystrobin	0.01
Bifenthrin	0.01
Bixafen	0.01
Boscalid	0.01
Bromuconazole	0.01
Buprofezin	0.01
Carbaryl	0.01
Carbendazim	0.01
Carbofuran	0.01
Carbofuran, 3-hydroxy	0.01
Carboxin	0.01
Chlorantraniliprole	0.01
Chlorfenvinphos	0.01
Chlorpropham (parent compound only)	0.01
Chlorpyrifos	0.01
Chlorpyrifos-methyl	0.01
Clothianidin	0.01
Cyfluthrin (sum of isomers)	0.01
Cymoxanil	0.01
Cypermethrin (sum of isomers)	0.01
Cyproconazole	0.01
Cyprodinil	0.01
DDD- p,p'	0.01
DDE- p,p'	0.01
DDT- o,p'	0.01
DDT- p,p'	0.01
Deltamethrin-cis	0.01
Demeton-S-methylsulfone	0.01
Diazinon	0.01
Dichlorvos	0.01
Dieldrin	0.01
Difenoconazole	0.01
Diflubenzuron	0.01

Pesticides	MRRL (mg/kg)
Dimethoate	0.01
Diniconazole	0.01
Endosulfan-alpha	0.01
Endosulfan-beta	0.01
Endosulfan-sulfate	0.01
Epoxiconazole	0.01
Ethion	0.01
Ethirimol	0.01
Famoxadone	0.01
Fenbuconazole	0.01
Fenhexamid	0.01
Fenitrothion	0.01
Fenpropidin	0.01
Fenpropimorph	0.01
Fenthion	0.01
Fenthion-oxon	0.01
Fenthion-oxon-sulfone	0.01
Fenthion-oxon-sulfoxide	0.01
Fenthion-sulfone	0.01
Fenthion-sulfoxide	0.01
Fenvalerate and Esfenvalerate (Sum of RR/SS and RS/SR isomers)	0.01
Fipronil (parent compound only)	0.01
Flonicamid	0.01
Fludioxonil	0.01
Fluopyram	0.01
Fluquinconazole	0.01
Flusilazole	0.01
Flutolanil	0.01
Flutriafol	0.01
Fluxapyroxad	0.01
Famoxadone	0.01
HCH-alpha	0.01
HCH-beta	0.01
Hexaconazole	0.01
Imazalil	0.01
Imidacloprid	0.01
Iprodione	0.01
Isocarbophos	0.01
Isoprothiolane	0.01

Pesticides	MRRL (mg/kg)
Isoproturon	0.01
Kresoxim-methyl	0.01
Lambda-cyhalothrin	0.01
Lindane	0.01
Linuron	0.01
Malaoxon	0.01
Malathion	0.01
Mandipropamid	0.01
Metconazole	0.01
Methacrifos	0.01
Methamidophos	0.01
Methomyl	0.01
Metolachlor	0.01
Metrafenone	0.01
Metribuzin	0.01
Omethoate	0.01
Oxydemeton-methyl	0.01
Paclobutrazol	0.01
Parathion	0.01
Penconazole	0.01
Pencycuron	0.01
Pendimethalin	0.01
Permethrin (sum of isomers)	0.01
Phenylphenol-ortho	0.01
Phosphamidon	0.01
Pirimicarb	0.01
Pirimicarb-desmethyl	0.01
Pirimiphos-methyl	0.01
Prochloraz (parent compound only)	0.01
Procymidone	0.01
Propamocarb	0.01
Propiconazole	0.01
Prothioconazole-desthio	0.01
Pyraclostrobin	0.01
Pyrimethanil	0.01
Quinoxyfen	0.01
Spiromesifen	0.01
Spiroxamine	0.01
Tau-Fluvalinate	0.01

Pesticides	MRRL (mg/kg)
Tebuconazole	0.01
Tebufenozide	0.01
Tefluthrin	0.01
Terbuthylazine	0.01
Tetraconazole	0.01
Tetramethrin	0.01
Thiabendazole	0.01
Thiacloprid	0.01
Thiamethoxam	0.01
Thiodicarb	0.01
Thiophanate-methyl	0.01
Triadimefon	0.01
Triadimenol	0.01
Triazophos	0.01
Tricyclazole	0.01
Trifloxystrobin	0.01
Trifluralin	0.01
Triticonazole	0.01
Vinclozolin (parent compound only)	0.01
Voluntary Compounds	
Chlordane, cis-	0.01
Chlordane, oxy	0.01
Chlordane, trans-	0.01
Endrin	0.01
Heptachlor	0.01
Heptachlorepoxid-cis	0.01
Heptachlorepoxid-trans	0.01

Only individual compounds are included in the pesticide target list. except for pyrethroids where the sum of isomers should be reported, unless other is specified in the list.

Appendix 3 Homogeneity data

	Azoxystrobin, mg/kg		Bixafen, mg/kg		Boscalid, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
3	0.079	0.091	0.063	0.077	0.413	0.443
33	0.087	0.090	0.076	0.070	0.426	0.427
72	0.083	0.082	0.065	0.068	0.400	0.398
90	0.085	0.085	0.076	0.077	0.436	0.412
101	0.083	0.086	0.077	0.070	0.448	0.417
137	0.090	0.080	0.066	0.075	0.411	0.412
152	0.088	0.092	0.070	0.084	0.436	0.434
198	0.082	0.083	0.078	0.069	0.426	0.396
217	0.094	0.092	0.072	0.063	0.396	0.373
298	0.076	0.086	0.080	0.078	0.435	0.441
301	0.103	0.086	0.078	0.080	0.459	0.453

	Buprofezin, mg/kg		Carbendazim, mg/kg		Cypermethrin, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
3	0.048	0.049	0.071	0.076	0.113	0.147
33	0.053	0.052	0.081	0.082	0.150	0.151
72	0.049	0.049	0.076	0.079	0.128	0.150
90	0.050	0.051	0.077	0.077	0.146	0.143
101	0.045	0.049	0.076	0.073	0.141	0.183
137	0.044	0.045	0.076	0.074	0.123	0.139
152	0.048	0.047	0.078	0.082	0.129	0.139
198	0.049	0.047	0.080	0.073	0.127	0.153
217	0.050	0.047	0.074	0.078	0.110	0.108
298	0.040	0.045	0.069	0.074	0.149	0.148
301	0.057	0.045	0.086	0.077	0.155	0.154

	Epoxiconazole, mg/kg		Fenpropidin, mg/kg		Fluopyram, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
3	0.162	0.178	0.300	0.321	0.244	0.263
33	0.173	0.173	0.310	0.320	0.251	0.256
72	0.156	0.166	0.288	0.300	0.241	0.248
90	0.181	0.165	0.334	0.318	0.265	0.254
101	0.175	0.166	0.327	0.316	0.261	0.247
137	0.164	0.179	0.298	0.305	0.247	0.261
152	0.180	0.188	0.326	0.330	0.265	0.268
198	0.180	0.169	0.319	0.300	0.263	0.245
217	0.160	0.152	0.298	0.294	0.251	0.243
298	0.184	0.177	0.342	0.296	0.263	0.256
301	0.183	0.185	0.324	0.329	0.278	0.281

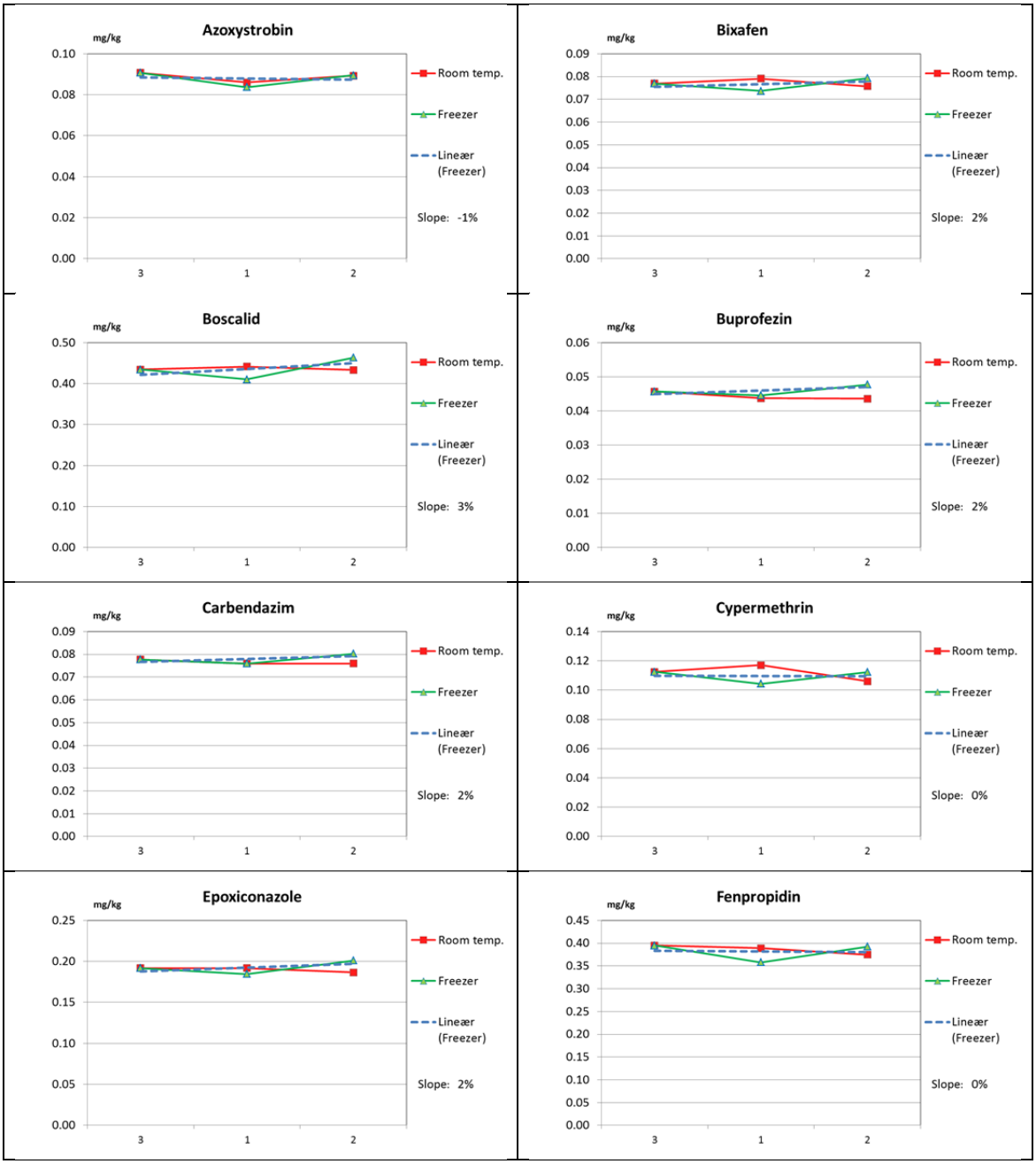
	Heptachlor, mg/kg		Isocarbophos, mg/kg		Metrafenone, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
3	0.033	0.035	0.049	0.054	0.088	0.090
33	0.034	0.032	0.050	0.050	0.087	0.090
72	0.030	0.032	0.047	0.052	0.082	0.083
90	0.035	0.032	0.053	0.048	0.085	0.083
101	0.033	0.023	0.050	0.045	0.082	0.088
137	0.030	0.030	0.044	0.052	0.077	0.086
152	0.032	0.032	0.045	0.050	0.089	0.086
198	0.030	0.030	0.045	0.052	0.084	0.086
217	0.033	0.030	0.046	0.038	0.081	0.079
298	0.031	0.030	0.048	0.048	0.086	0.088
301	0.032	0.031	0.048	0.050	0.097	0.094

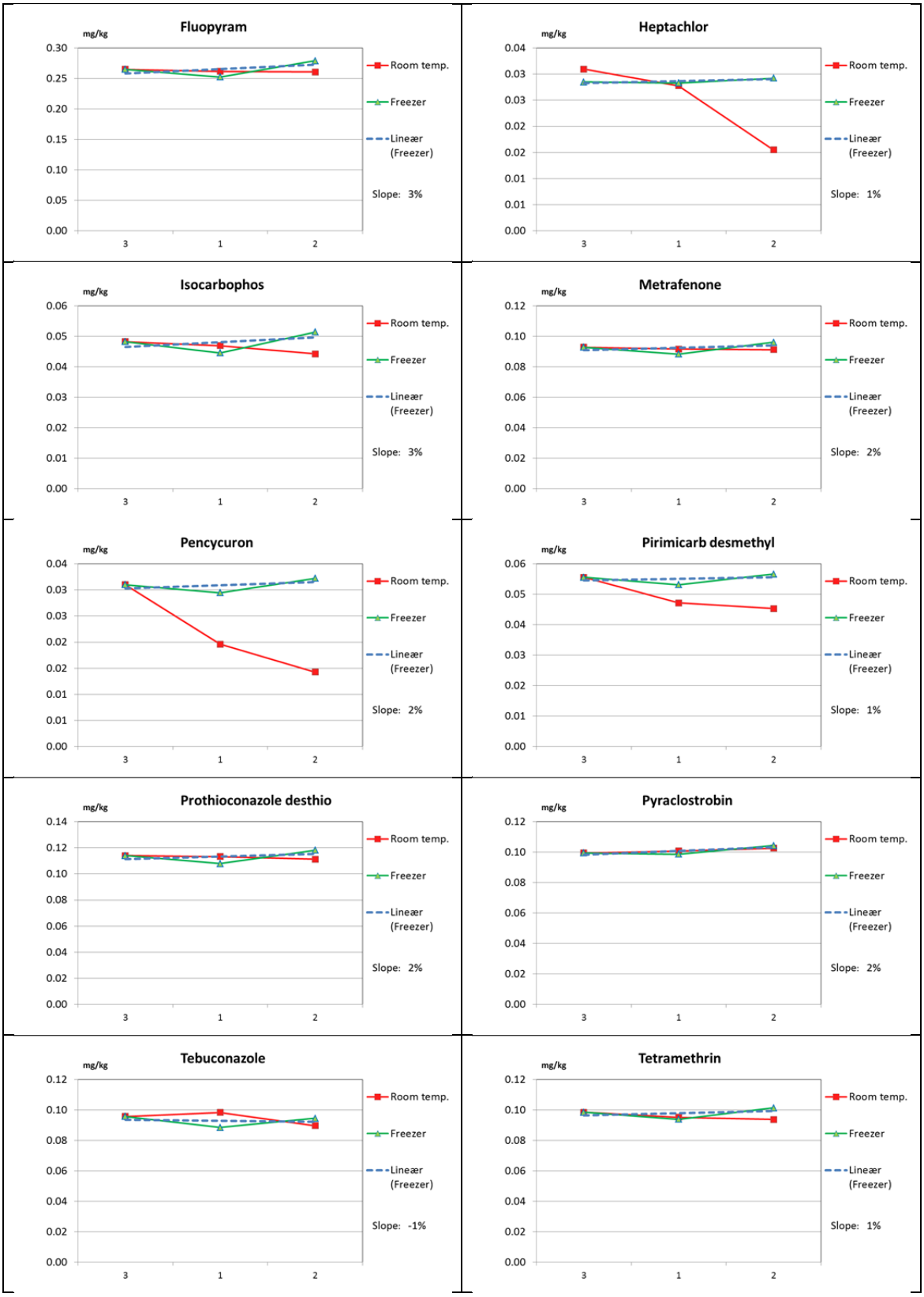
	Pencycuron, mg/kg		Pirimicarb-desmethyl, mg/kg		Prothioconazole-desthio, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
3	0.033	0.033	0.048	0.052	0.080	0.070
33	0.034	0.032	0.056	0.053	0.083	0.072
72	0.032	0.031	0.050	0.051	0.084	0.073
90	0.032	0.031	0.052	0.049	0.090	0.091
101	0.032	0.031	0.046	0.048	0.070	0.083
137	0.030	0.032	0.048	0.048	0.077	0.068
152	0.029	0.032	0.047	0.050	0.089	0.097
198	0.030	0.029	0.053	0.046	0.088	0.090
217	0.030	0.030	0.053	0.051	0.078	0.084
298	0.032	0.032	0.042	0.051	0.082	0.079
301	0.034	0.033	0.062	0.048	0.043	0.032

	Pyraclostrobin, mg/kg		Tebuconazole, mg/kg		Tetramethrin, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
3	0.093	0.095	0.095	0.099	0.096	0.108
33	0.105	0.102	0.098	0.099	0.099	0.098
72	0.092	0.097	0.087	0.097	0.092	0.098
90	0.103	0.099	0.102	0.092	0.106	0.091
101	0.098	0.100	0.103	0.097	0.090	0.103
137	0.092	0.092	0.093	0.102	0.079	0.098
152	0.102	0.107	0.102	0.107	0.094	0.095
198	0.101	0.092	0.101	0.094	0.095	0.106
217	0.099	0.099	0.089	0.090	0.088	0.078
298	0.085	0.094	0.104	0.106	0.100	0.094
301	0.115	0.100	0.104	0.108	0.106	0.107

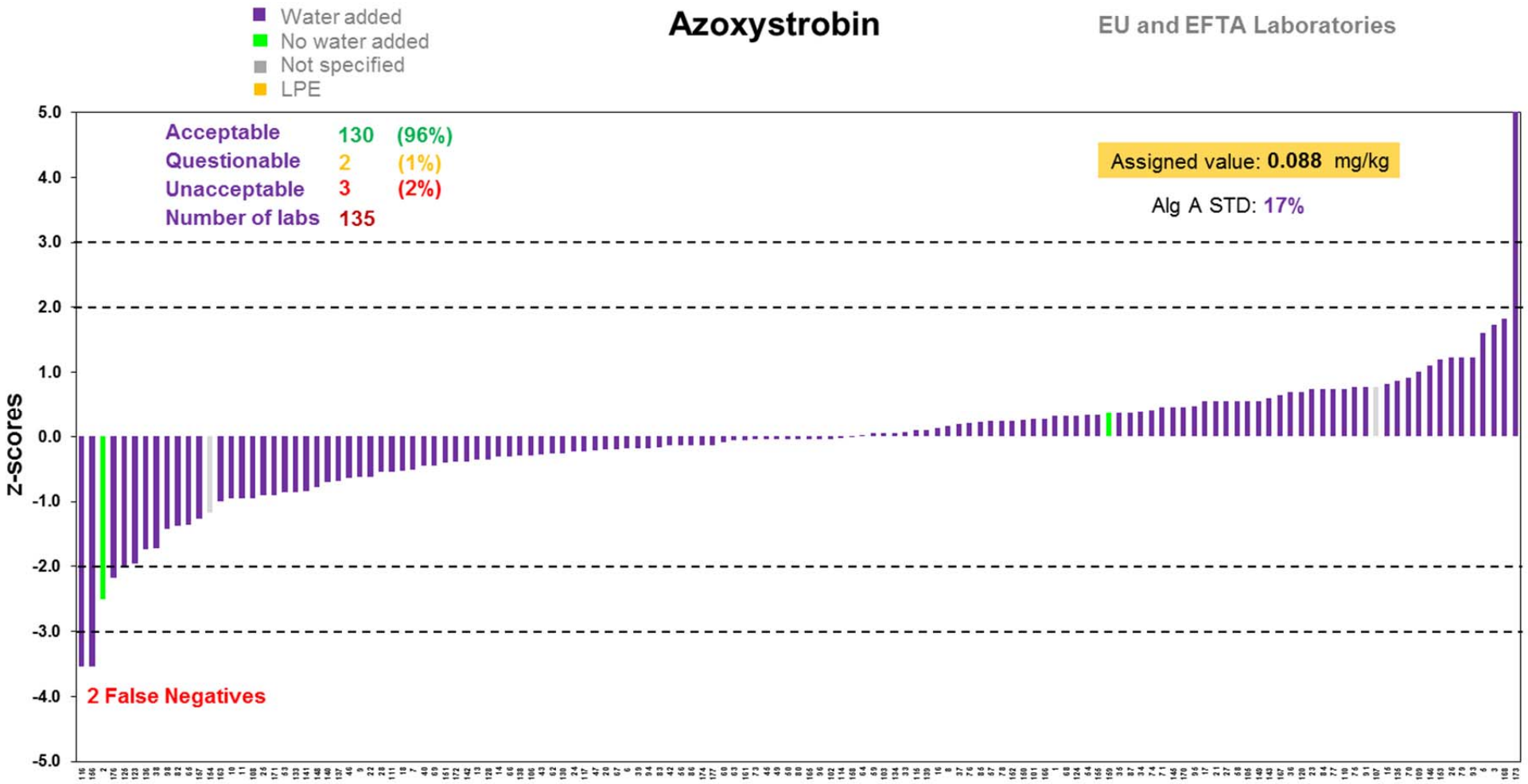
Appendix 4 Stability figures

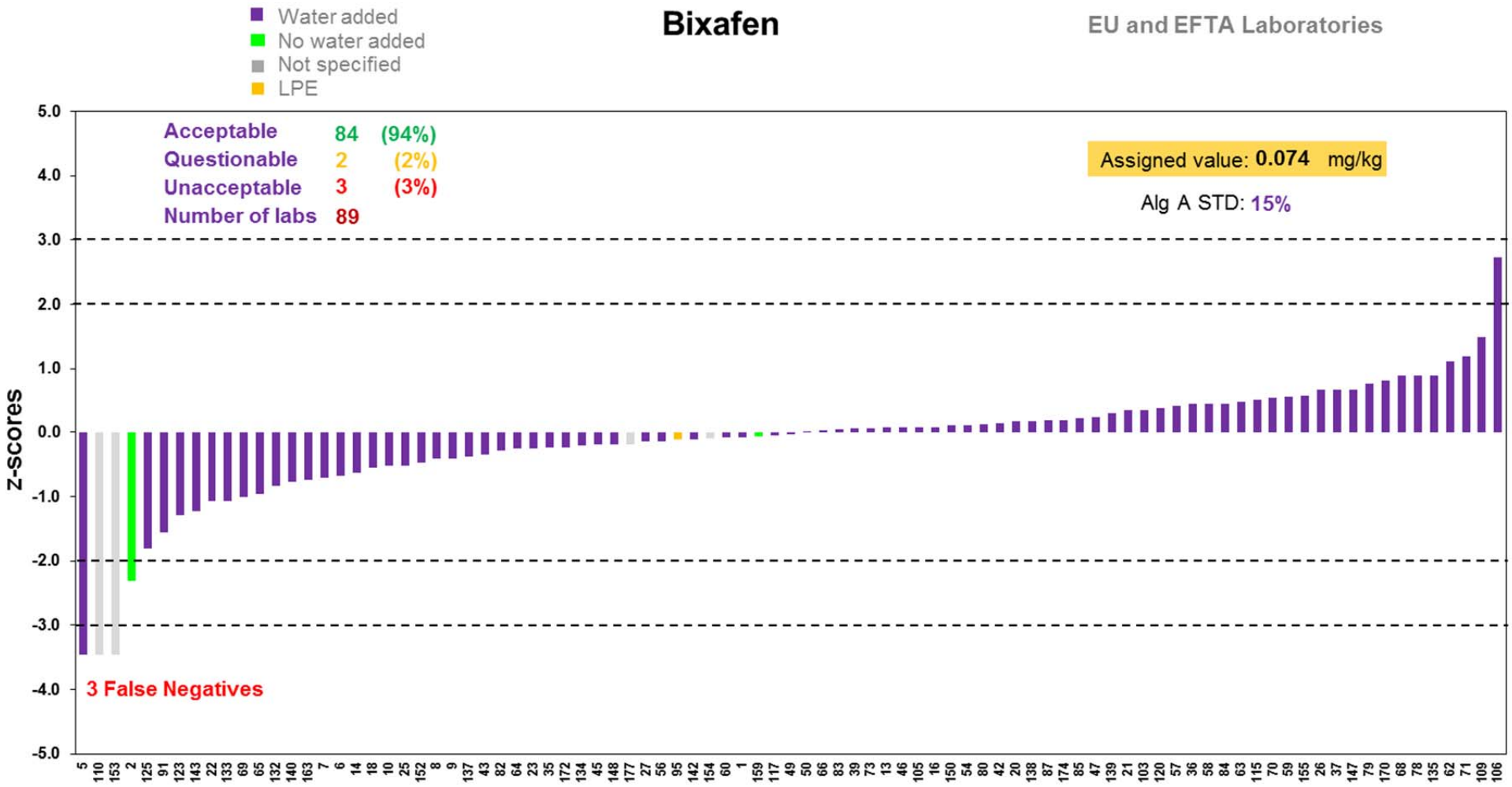
All pesticides passed the test at -18 °C. However, spiromefesin did not pass when stored 4 week at room temperature and this compound was clearly degraded. Additionally, carbendazim, fluopyram, lindane, metribuzin, pendimethalin and triticonazole did not pass the test. This, however, was evaluated not to be caused by degradation of the pesticides but changes the in maize matrix. During storage at room temperature the fatty acid peak eluting from 16-18 min increased dramatically, see Figure 1. All stability test was analysed in the same run and calculated from matrix matched calibration curve where the matrix was maize stored at -18 degree. Consequently, the differences in the coextracted compound has most likely caused the higher result measured after 4 weeks storage. See the statistical results in Table 3.

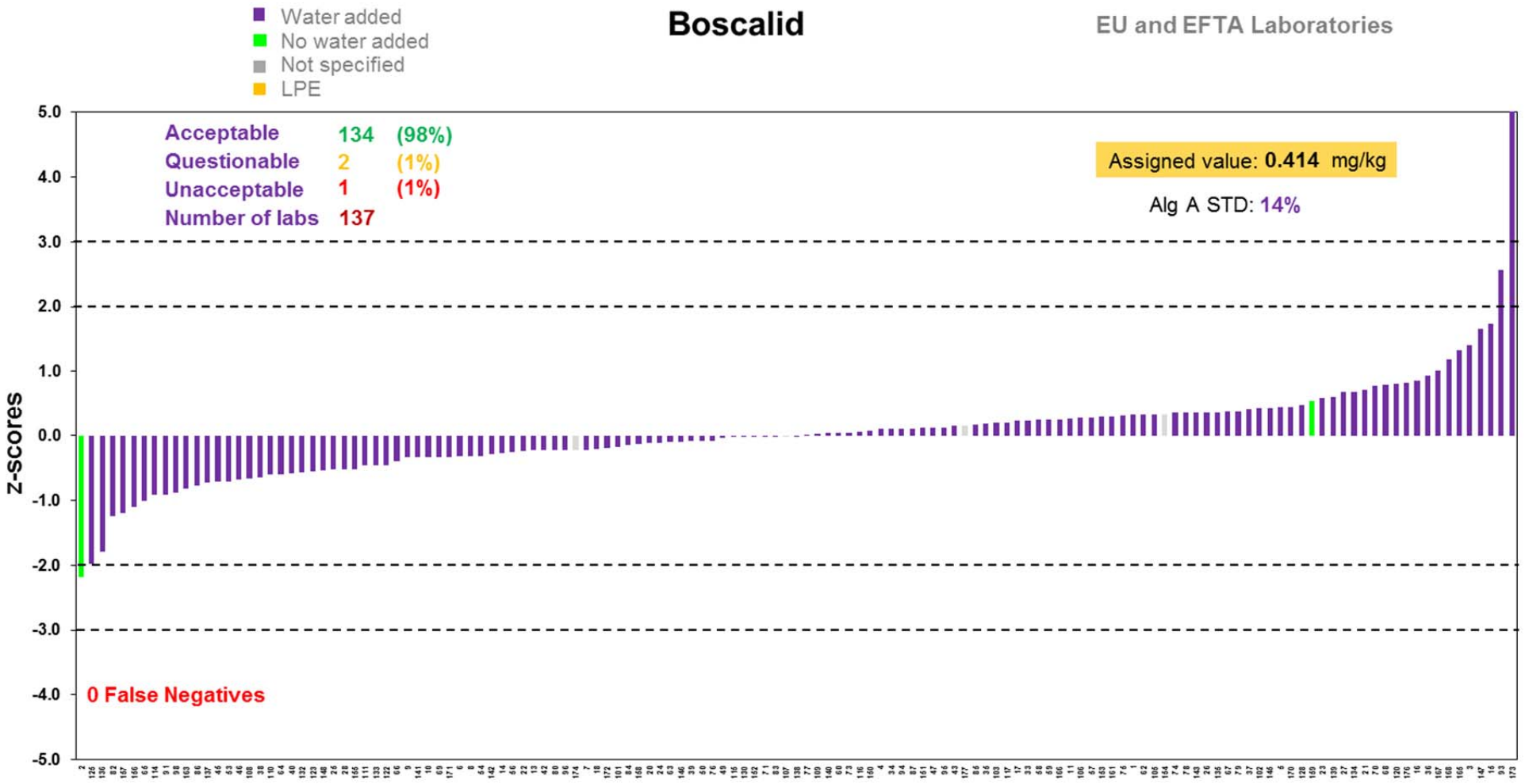


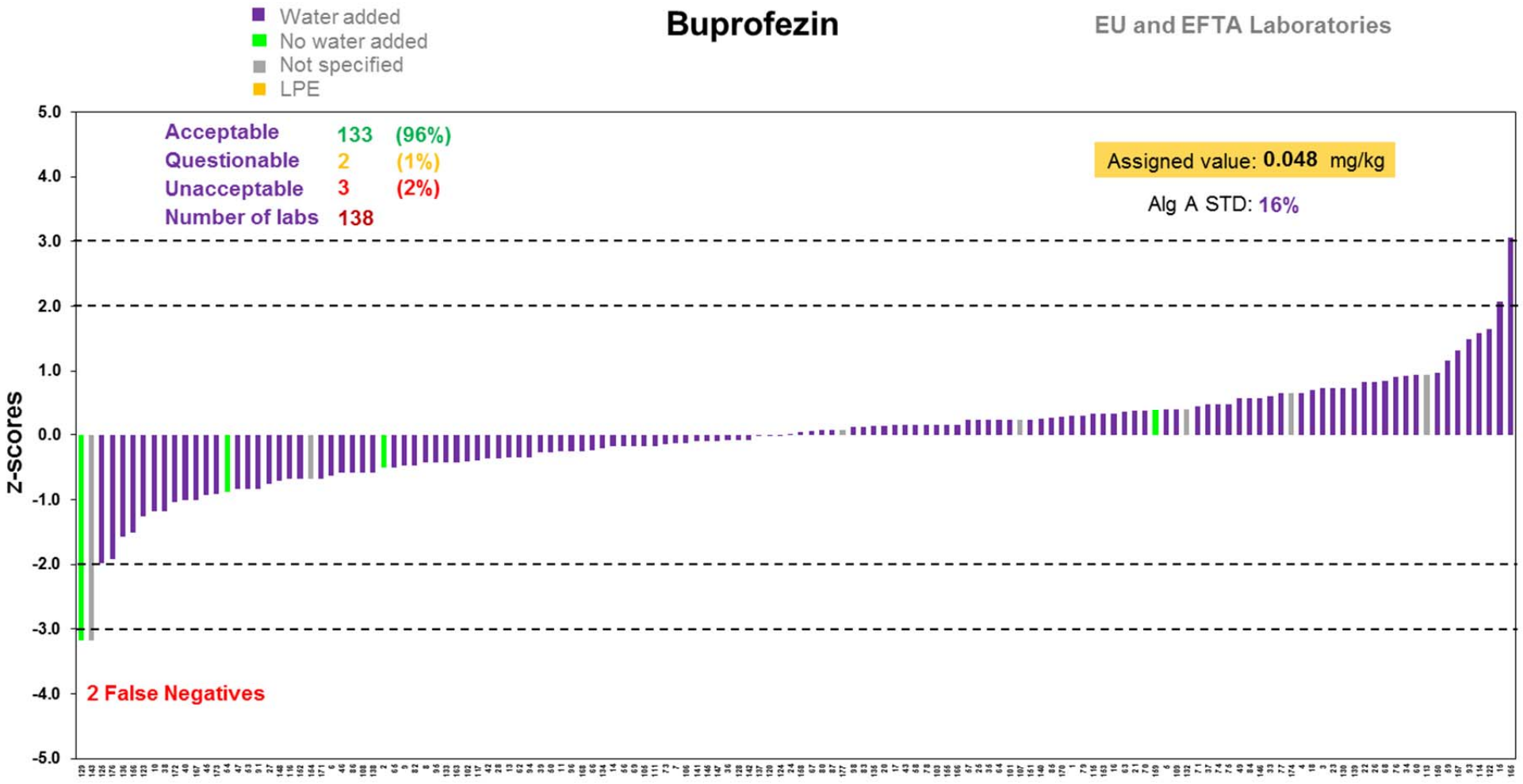

Fluopyram
mg/kg
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 3%
Heptachlor
mg/kg
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 1%
Isocarbophos
mg/kg
0.06
0.05
0.04
0.03
0.02
0.01
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 3%
Metrafenone
mg/kg
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 2%
Pencycuron
mg/kg
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 2%
Pirimicarb desmethyl
mg/kg
0.06
0.05
0.04
0.03
0.02
0.01
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 1%
Prothioconazole desthio
mg/kg
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 2%
Pyraclostrobin
mg/kg
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 2%
Tebuconazole
mg/kg
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: -1%
Tetramethrin
mg/kg
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3
1
2
Room temp.
Freezer
Lineær (Freezer)
Slope: 1%

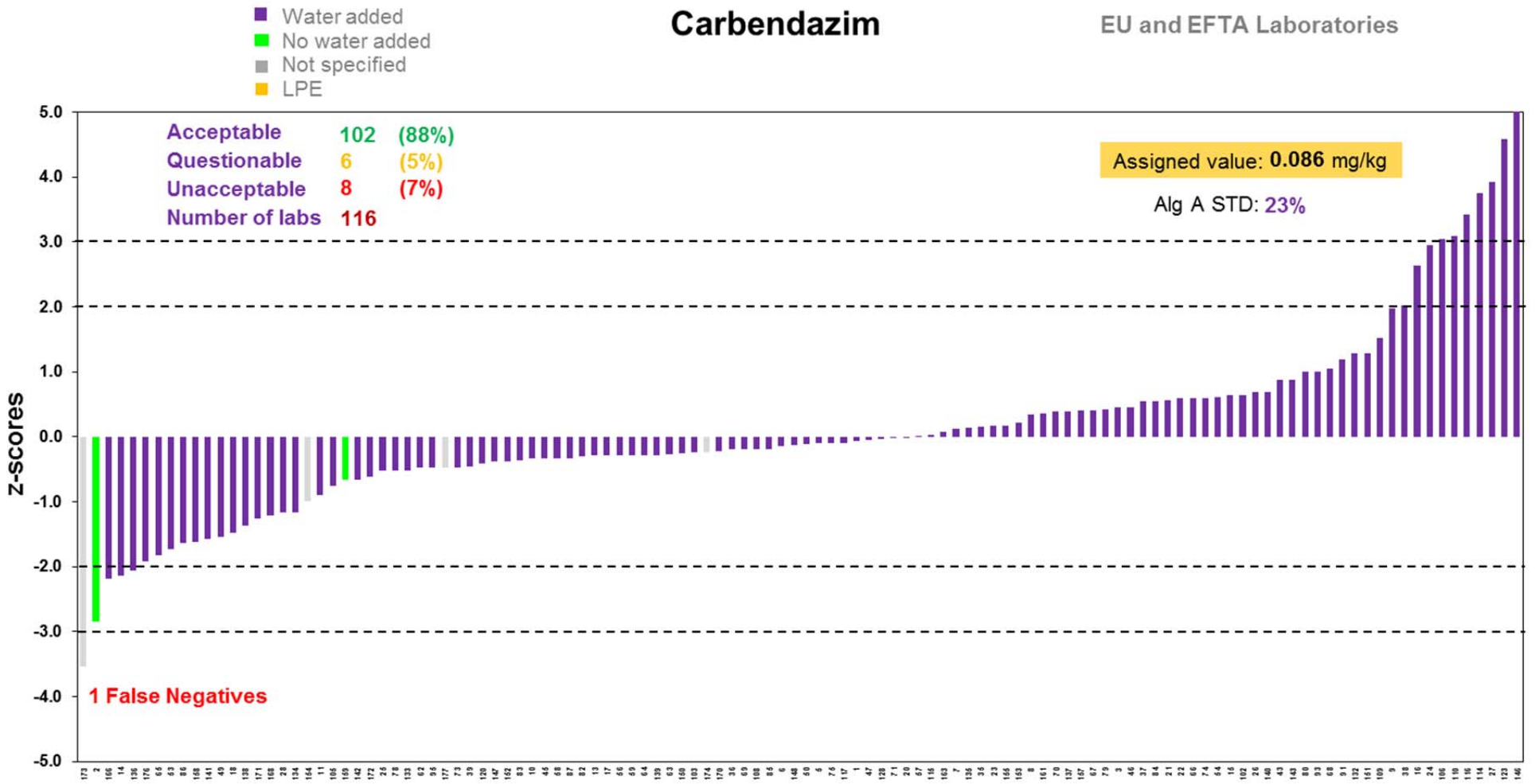
Appendix 5 Graphical presentation of z-scores

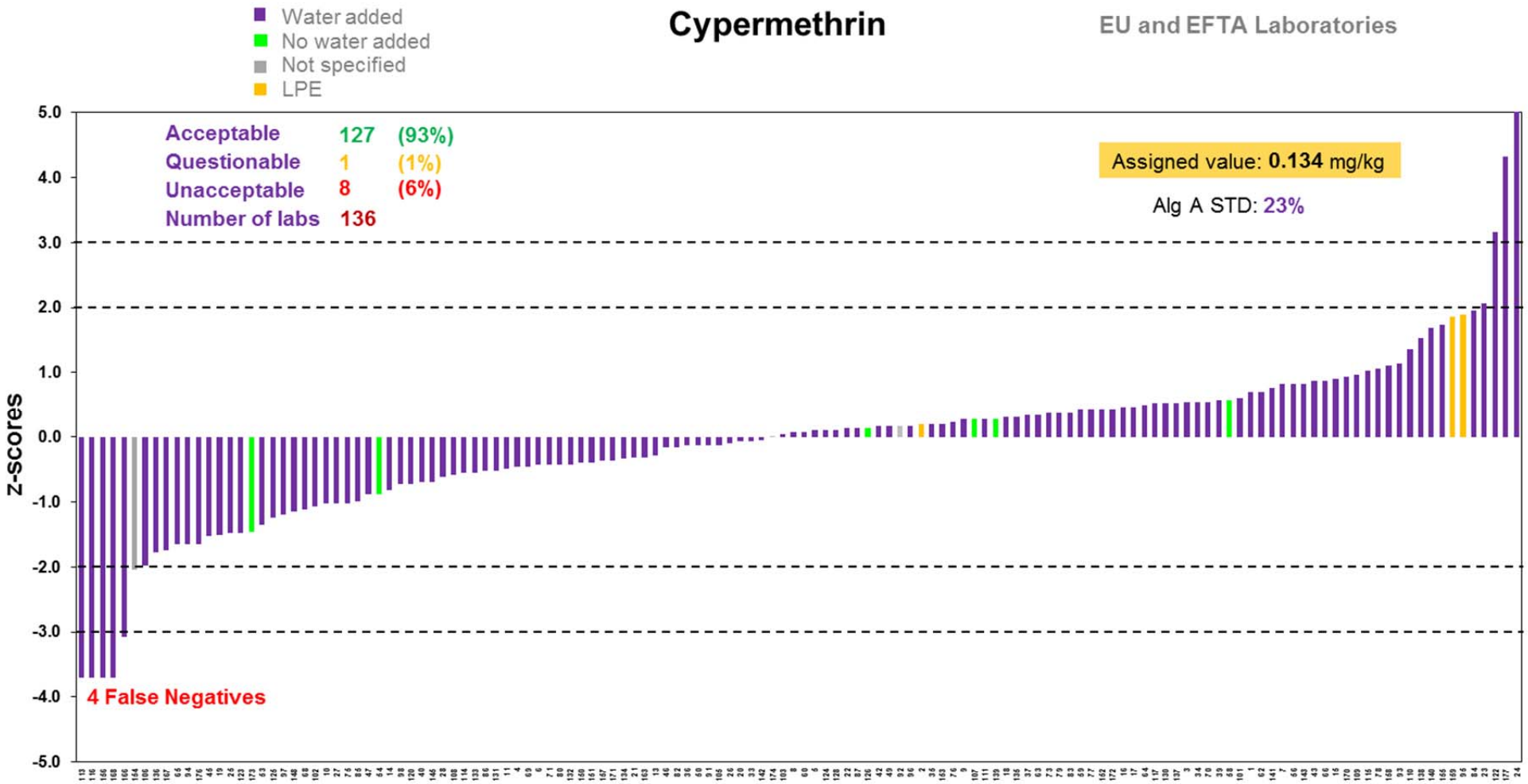


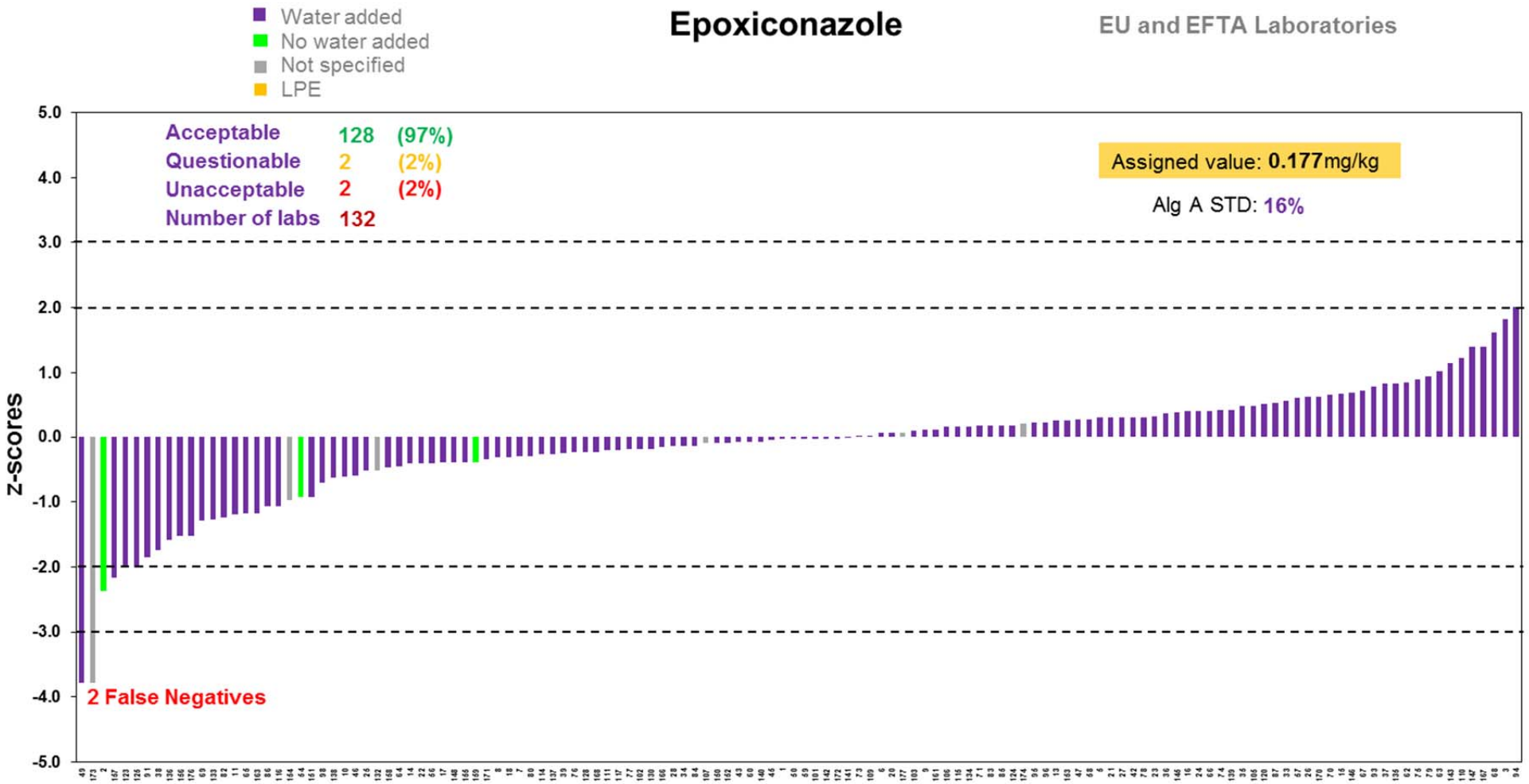

Water added
No water added
Not specified
LPE
Bixafen
EU and EFTA Laboratories
Acceptable 84 (94%)
Questionable 2 (2%)
Unacceptable 3 (3%)
Number of labs 89
Assigned value: 0.074 mg/kg
Alg A STD: 15%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
3 False Negatives
5 110 153 2 125 91 123 143 22 133 69 65 132 140 163 7 6 14 18 10 25 152 8 9 137 43 82 64 23 35 172 134 45 148 177 27 56 95 142 154 60 1 159 117 49 50 66 83 39 73 13 46 105 16 150 54 80 42 20 138 87 174 85 47 139 21 103 120 57 36 58 84 63 115 70 59 155 26 37 147 79 170 68 78 135 62 71 109 106

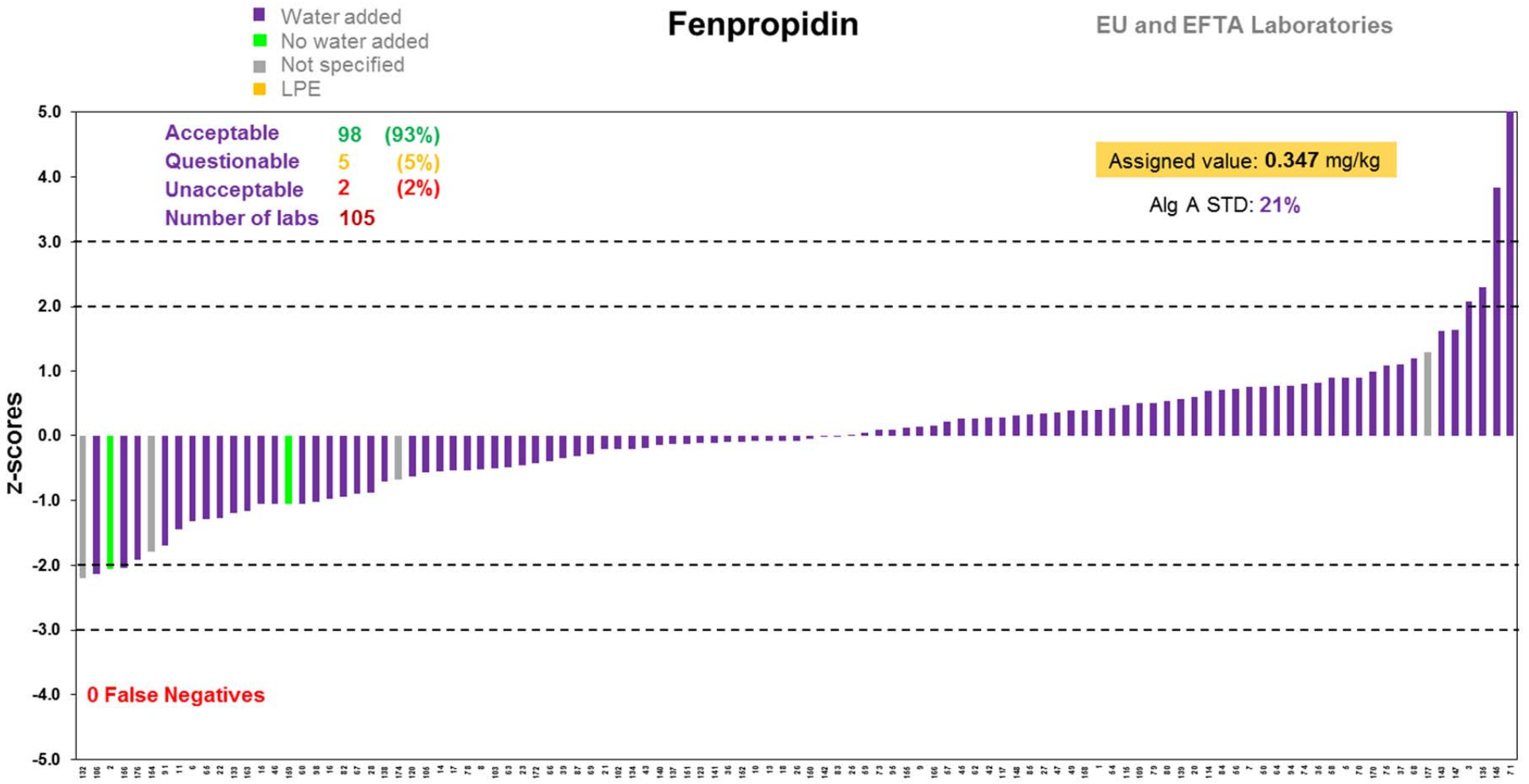

Water added
No water added
Not specified
LPE
Boscalid
EU and EFTA Laboratories
Acceptable 134 (98%)
Questionable 2 (1%)
Unacceptable 1 (1%)
Number of labs 137
Assigned value: 0.414 mg/kg
Alg A STD: 14%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0 False Negatives

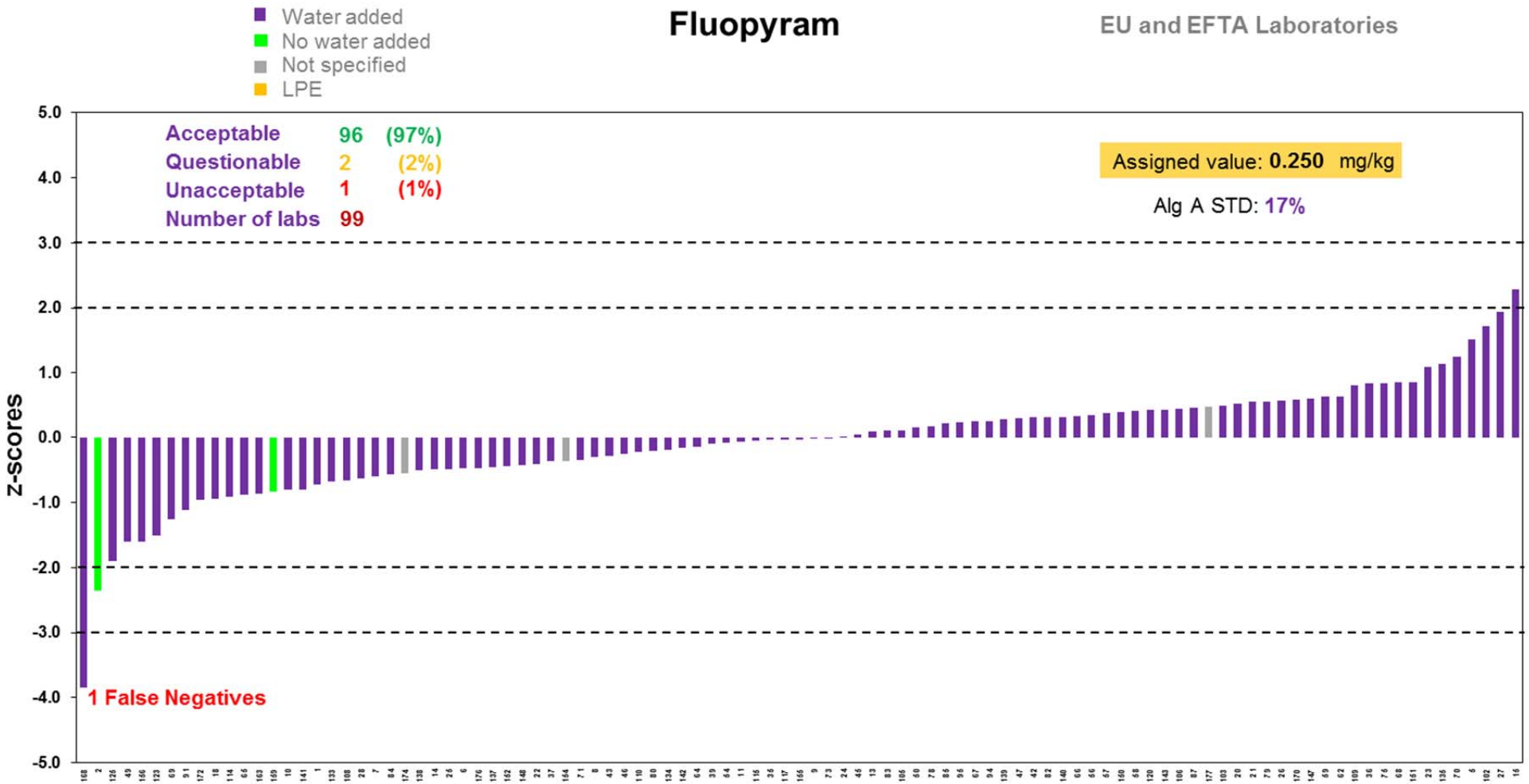

Water added
No water added
Not specified
LPE
Buprofezin
EU and EFTA Laboratories
Acceptable 133 (96%)
Questionable 2 (1%)
Unacceptable 3 (2%)
Number of labs 138
Assigned value: 0.048 mg/kg
Alg A STD: 16%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 False Negatives

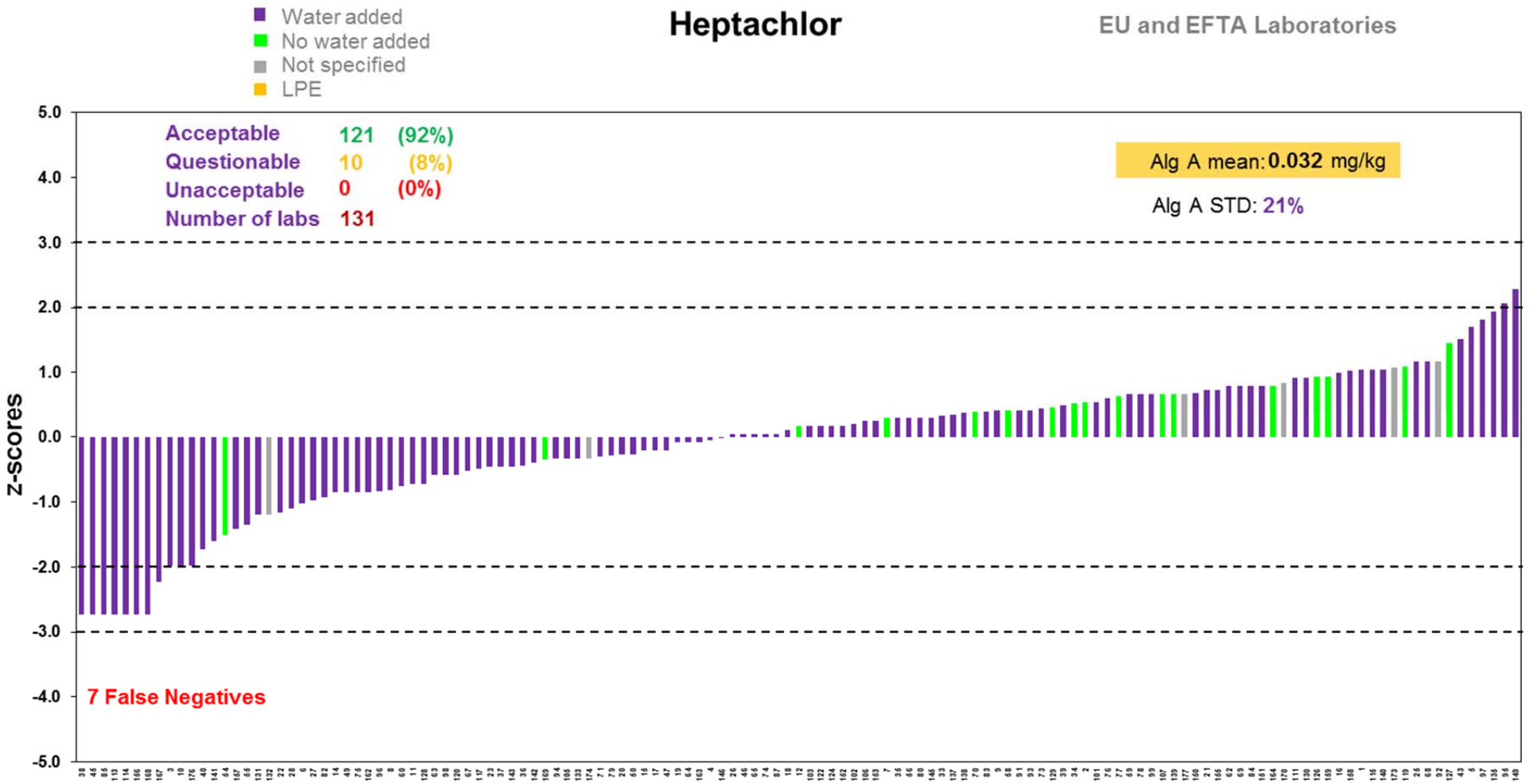

Water added
No water added
Not specified
LPE
Carbendazim
EU and EFTA Laboratories
Acceptable 102 (88%)
Questionable 6 (5%)
Unacceptable 8 (7%)
Number of labs 116
Assigned value: 0.086 mg/kg
Alg A STD: 23%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 False Negatives

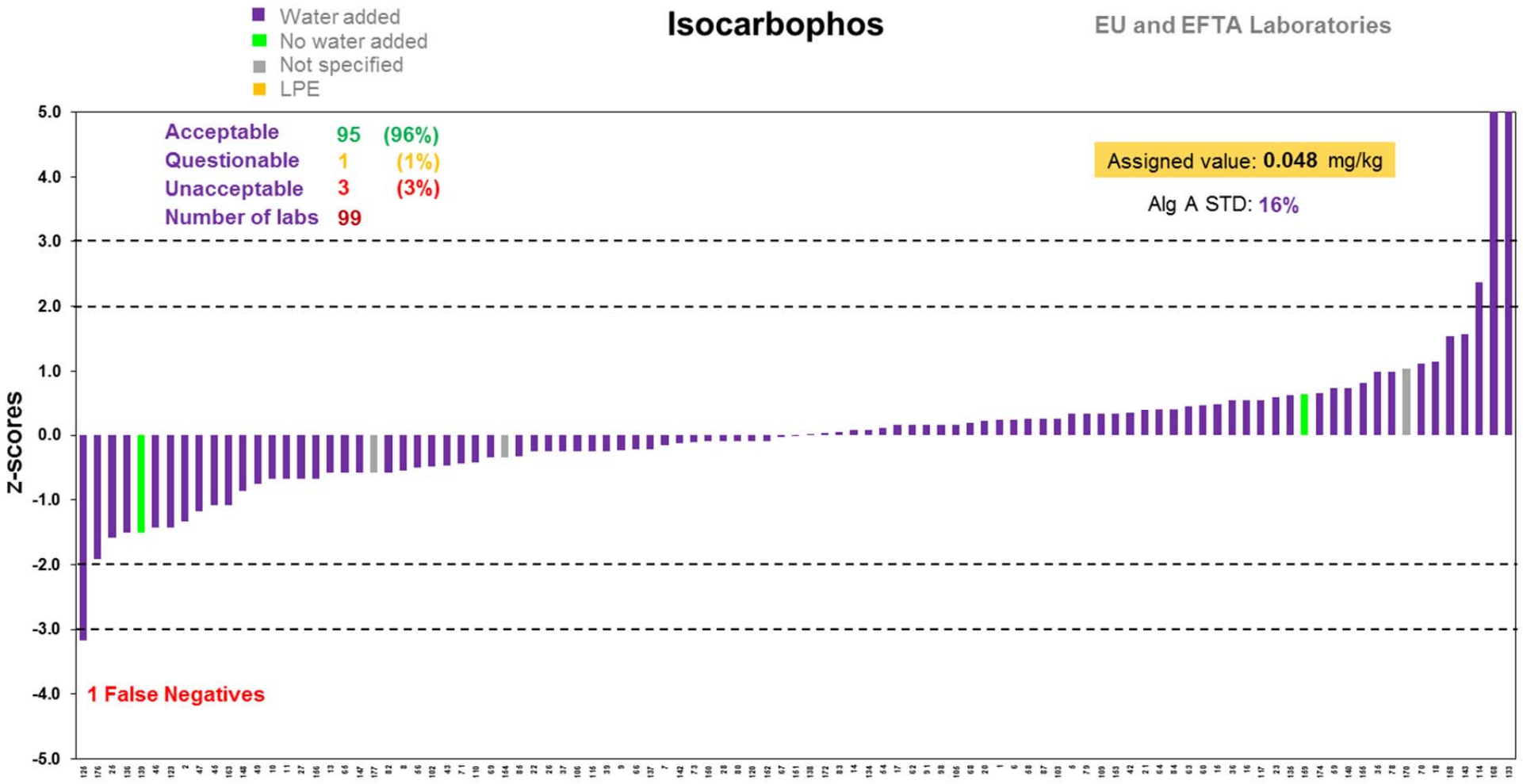

Water added
No water added
Not specified
LPE
Cypermethrin
EU and EFTA Laboratories
Acceptable 127 (93%)
Questionable 1 (1%)
Unacceptable 8 (6%)
Number of labs 136
Assigned value: 0.134 mg/kg
Alg A STD: 23%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
4 False Negatives

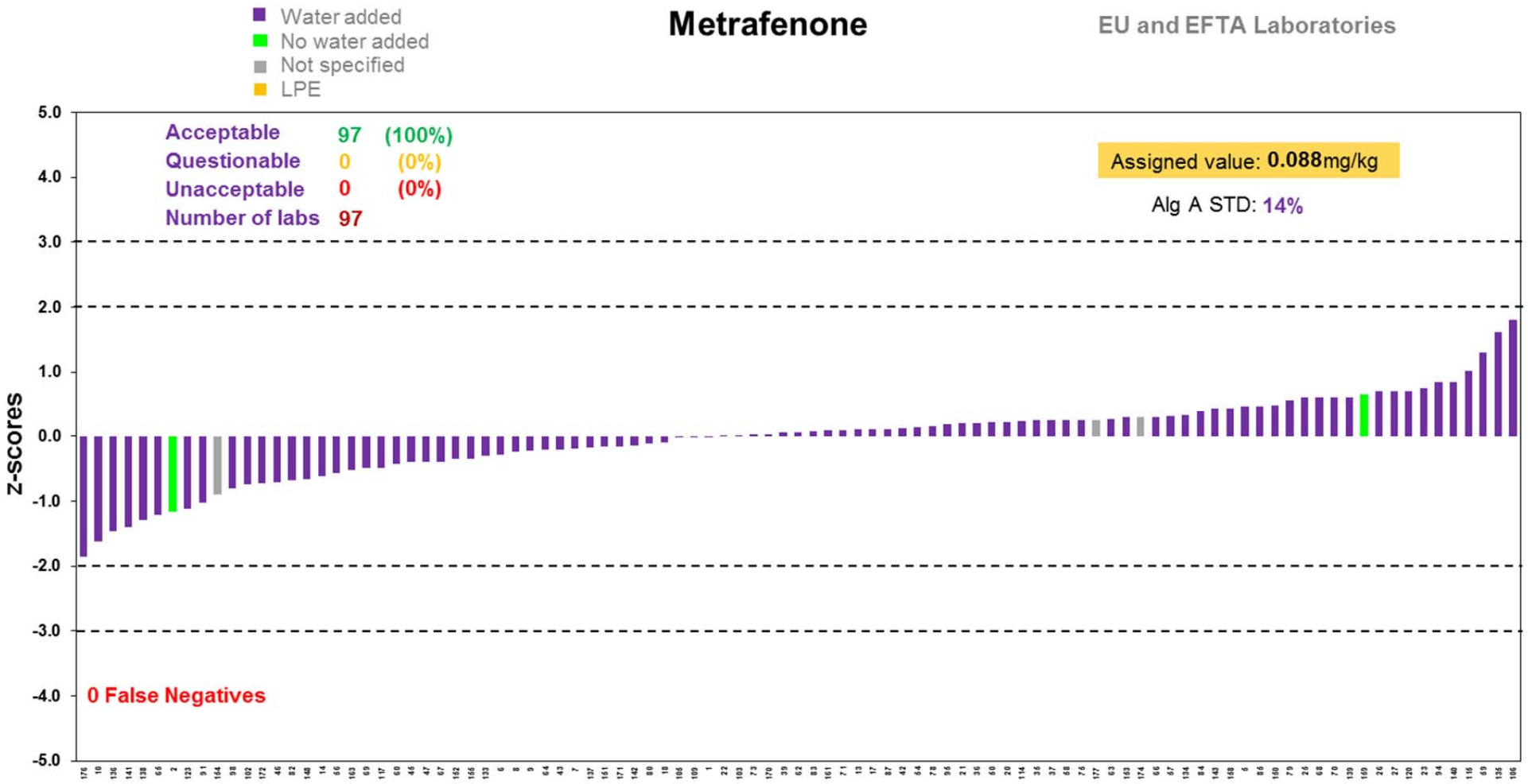

Water added
No water added
Not specified
LPE
Epoxiconazole
EU and EFTA Laboratories
Acceptable 128 (97%)
Questionable 2 (2%)
Unacceptable 2 (2%)
Number of labs 132
Assigned value: 0.177mg/kg
Alg A STD: 16%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 False Negatives

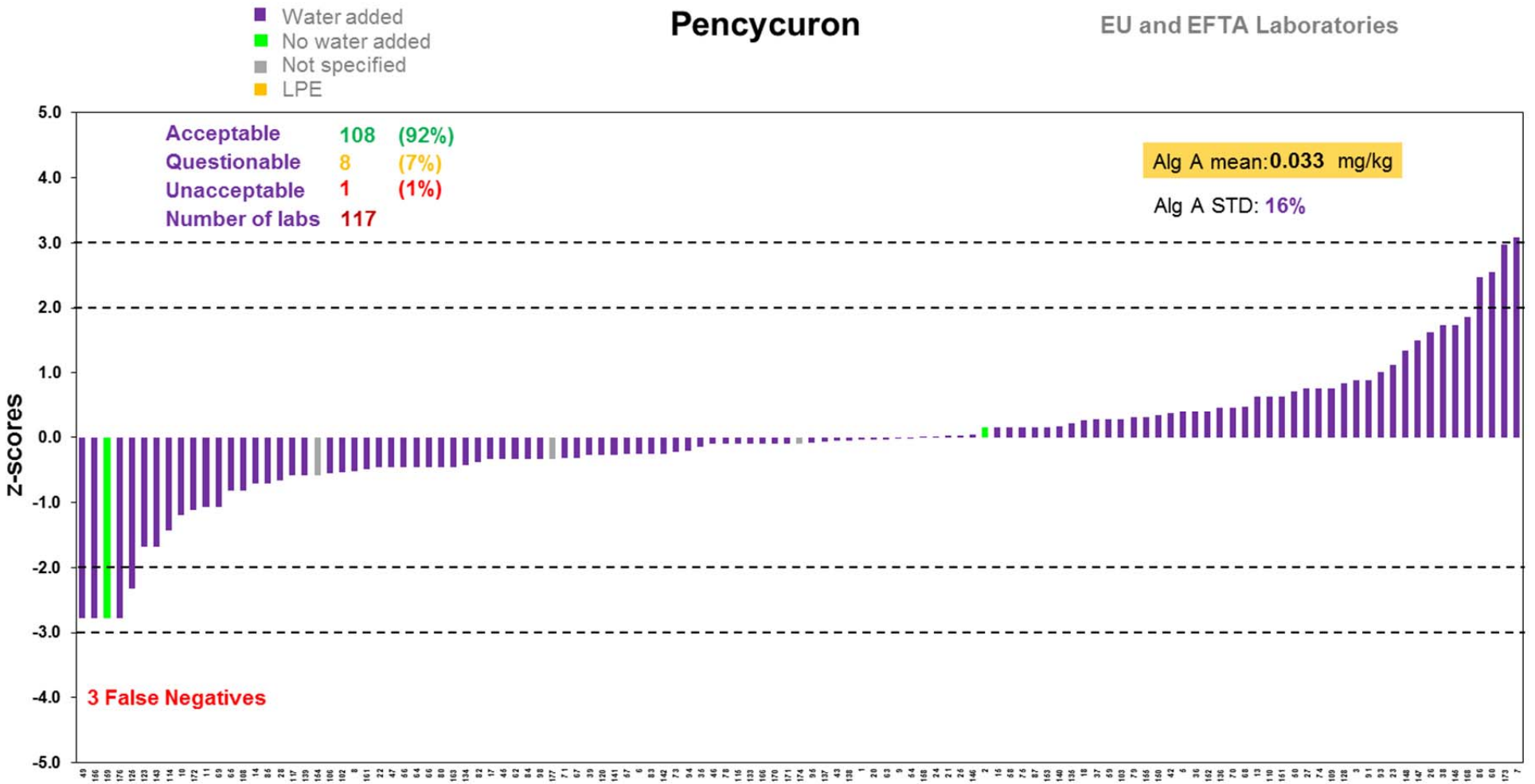

Water added
No water added
Not specified
LPE
Fenpropidin
EU and EFTA Laboratories
Acceptable 98 (93%)
Questionable 5 (5%)
Unacceptable 2 (2%)
Number of labs 105
Assigned value: 0.347 mg/kg
Alg A STD: 21%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0 False Negatives

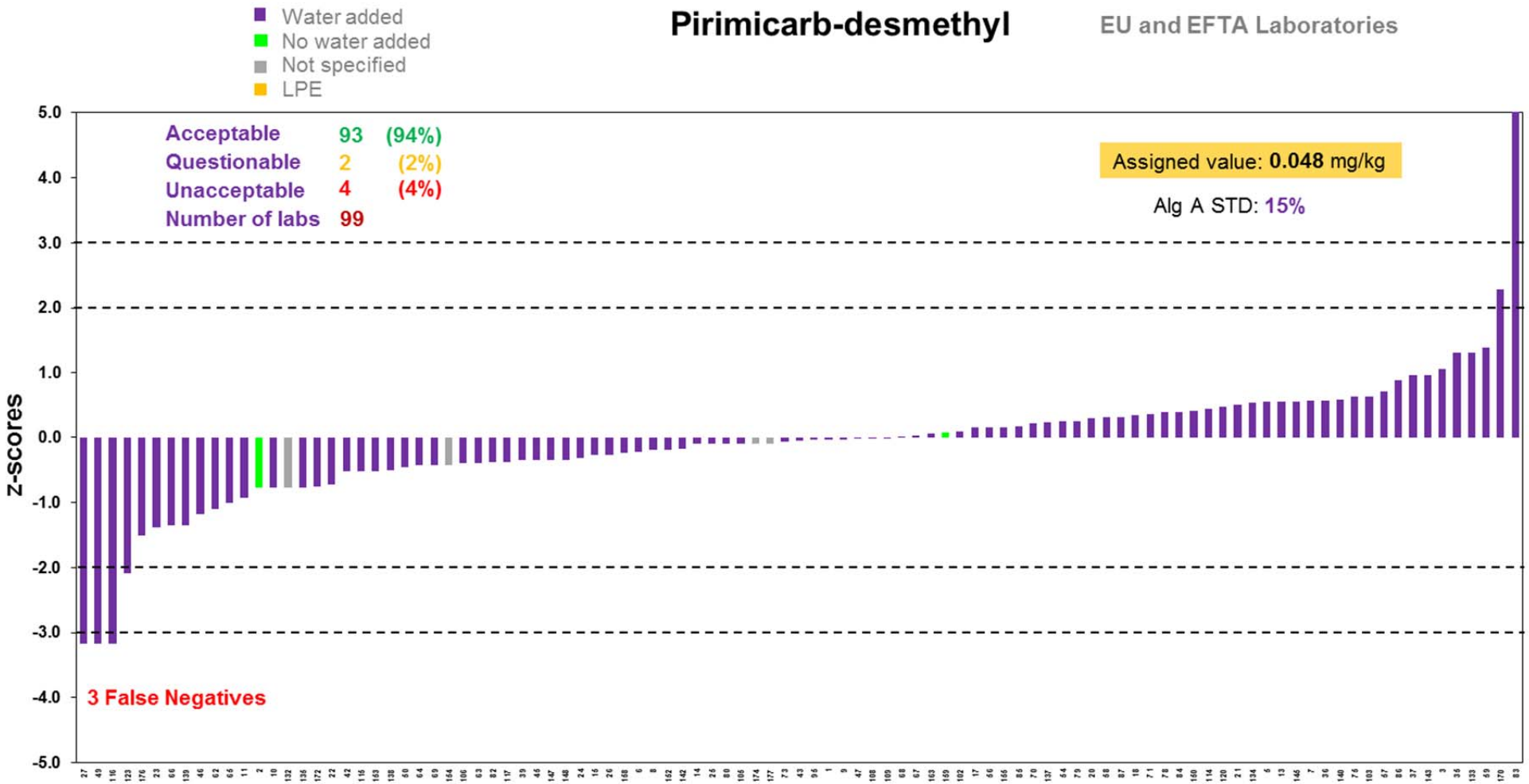

Water added
No water added
Not specified
LPE
Fluopyram
EU and EFTA Laboratories
Acceptable 96 (97%)
Questionable 2 (2%)
Unacceptable 1 (1%)
Number of labs 99
Assigned value: 0.250 mg/kg
Alg A STD: 17%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 False Negatives

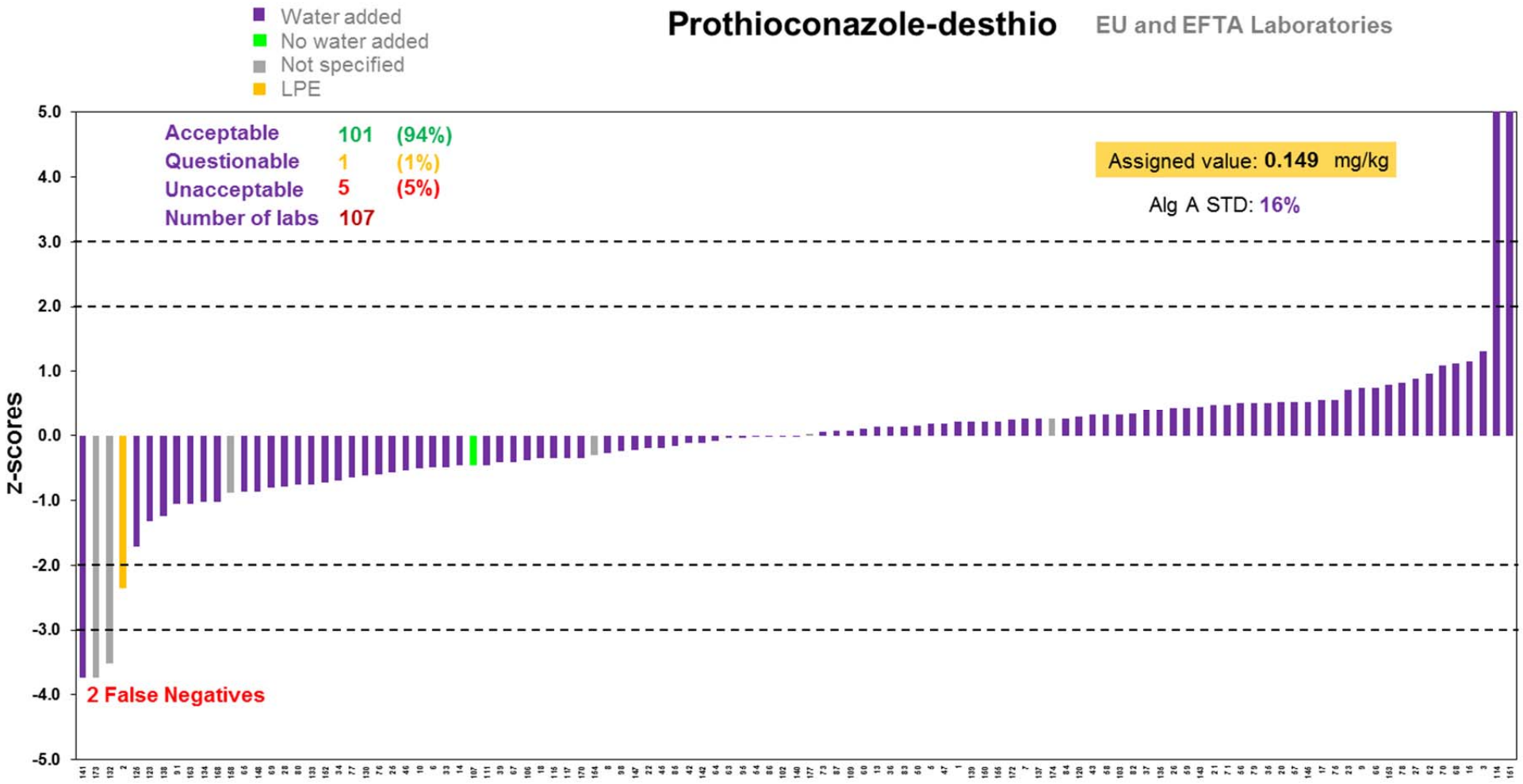

Water added
No water added
Not specified
LPE
Heptachlor
EU and EFTA Laboratories
Acceptable 121 (92%)
Questionable 10 (8%)
Unacceptable 0 (0%)
Number of labs 131
Alg A mean: 0.032 mg/kg
Alg A STD: 21%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
7 False Negatives

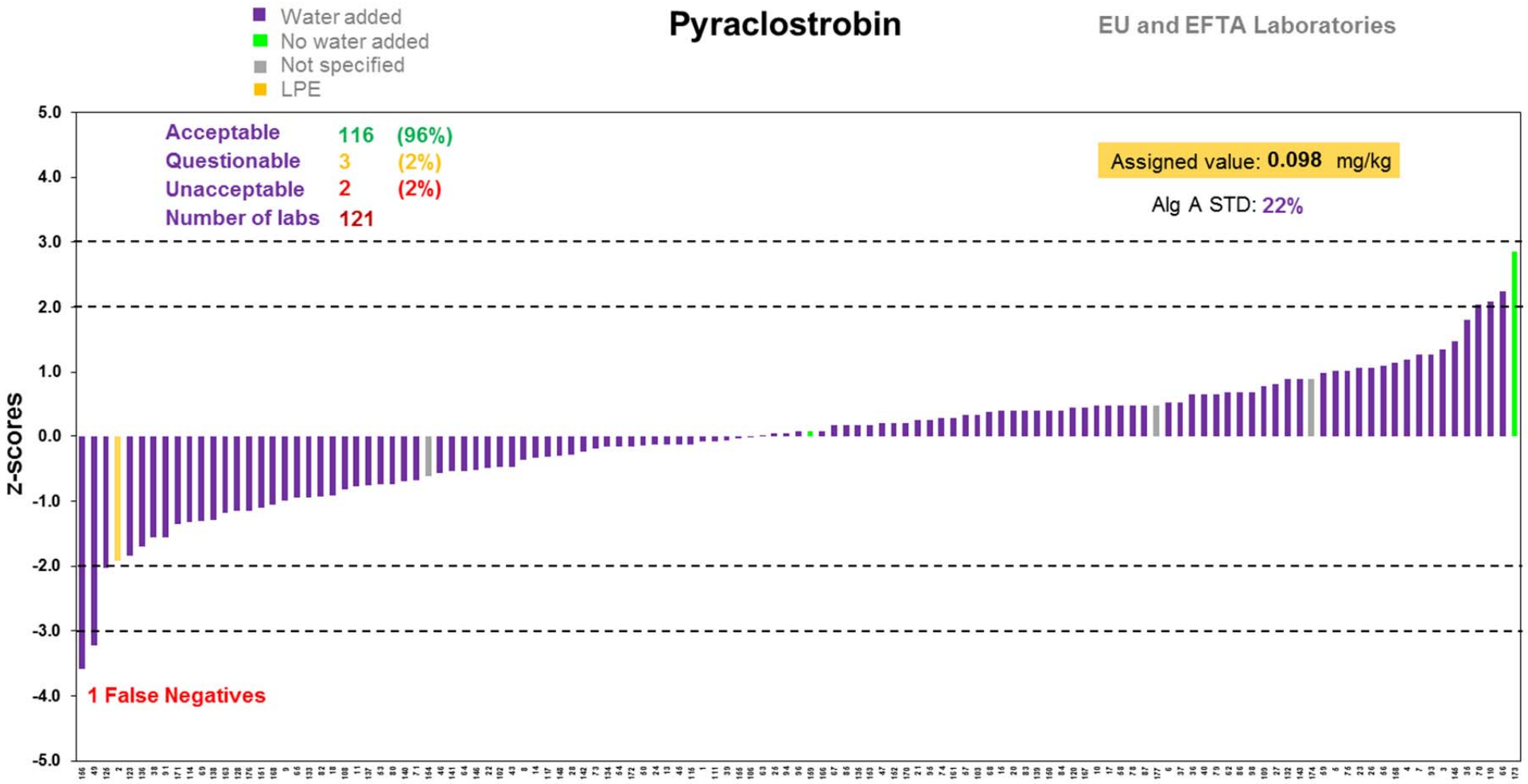

Water added
No water added
Not specified
LPE
Isocarbophos
EU and EFTA Laboratories
Acceptable 95 (96%)
Questionable 1 (1%)
Unacceptable 3 (3%)
Number of labs 99
Assigned value: 0.048 mg/kg
Alg A STD: 16%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 False Negatives

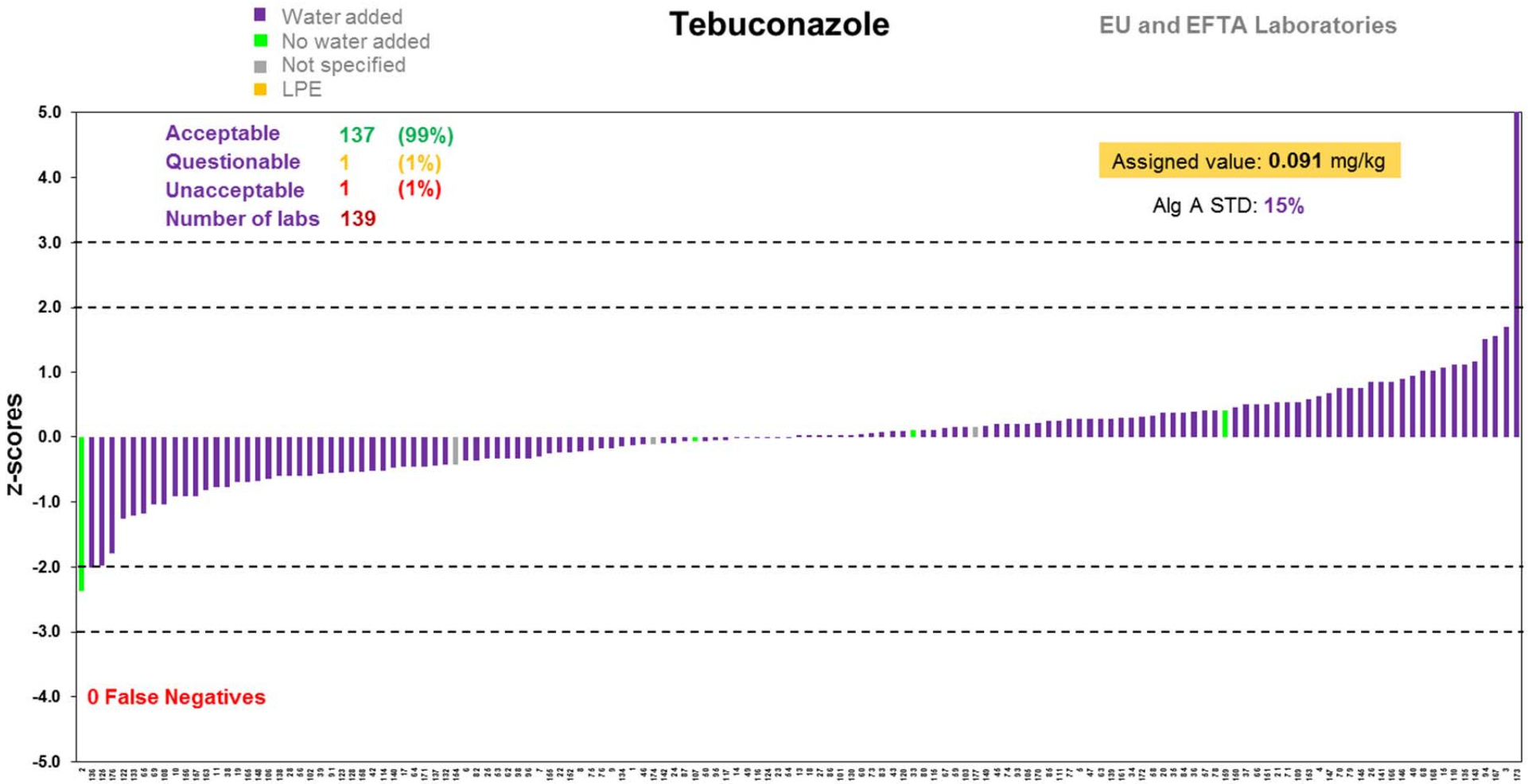

Water added
No water added
Not specified
LPE
Metrafenone
EU and EFTA Laboratories
Acceptable 97 (100%)
Questionable 0 (0%)
Unacceptable 0 (0%)
Number of labs 97
Assigned value: 0.088mg/kg
Alg A STD: 14%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0 False Negatives

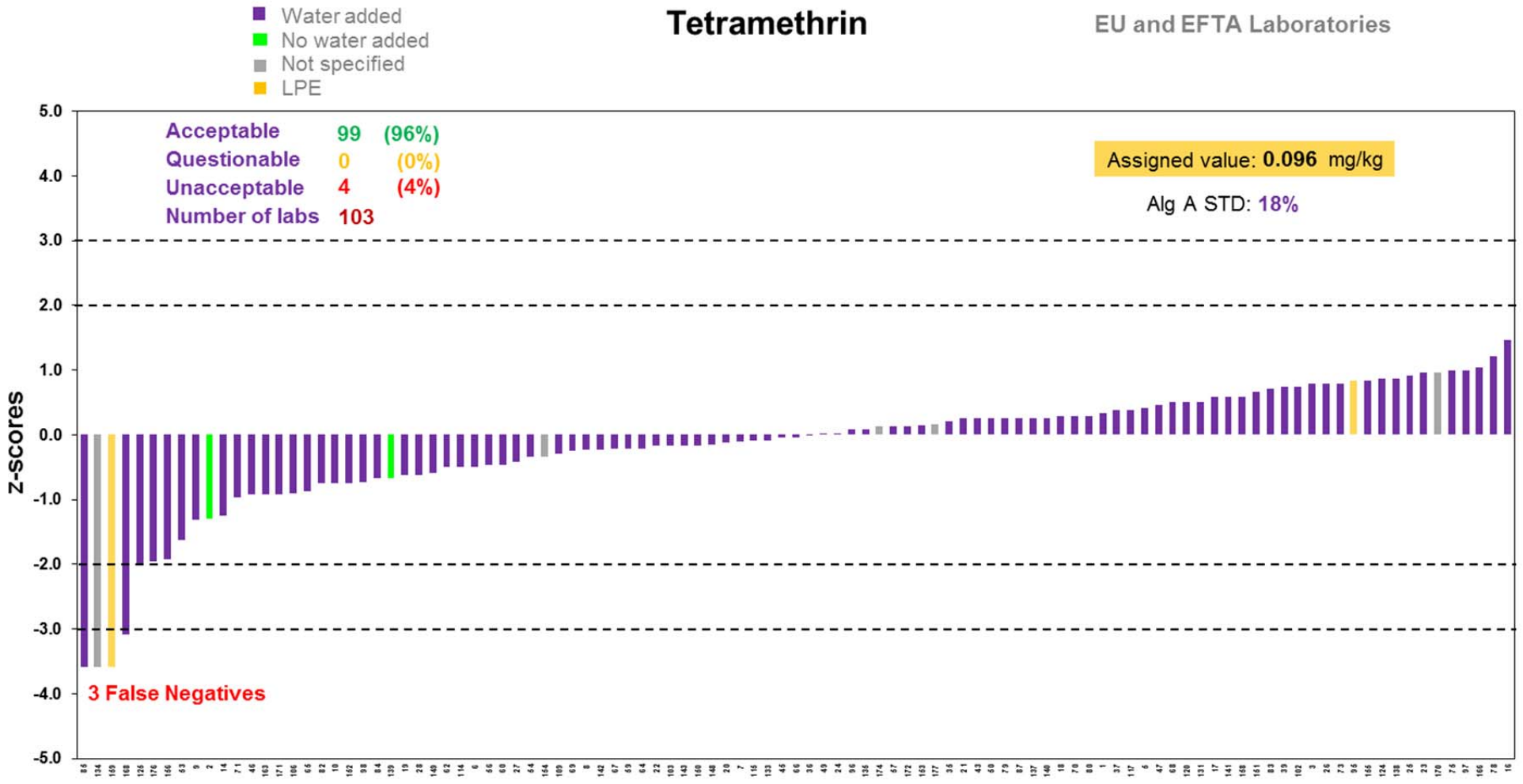

Water added
No water added
Not specified
LPE
Pencycuron
EU and EFTA Laboratories
Acceptable 108 (92%)
Questionable 8 (7%)
Unacceptable 1 (1%)
Number of labs 117
Alg A mean: 0.033 mg/kg
Alg A STD: 16%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
3 False Negatives


Water added
No water added
Not specified
LPE
Pirimicarb-desmethyl
EU and EFTA Laboratories
Acceptable 93 (94%)
Questionable 2 (2%)
Unacceptable 4 (4%)
Number of labs 99
Assigned value: 0.048 mg/kg
Alg A STD: 15%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
3 False Negatives


Water added
No water added
Not specified
LPE
Prothioconazole-desthio
EU and EFTA Laboratories
Acceptable 101 (94%)
Questionable 1 (1%)
Unacceptable 5 (5%)
Number of labs 107
Assigned value: 0.149 mg/kg
Alg A STD: 16%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 False Negatives


Water added
No water added
Not specified
LPE
Pyraclostrobin
EU and EFTA Laboratories
Acceptable 116 (96%)
Questionable 3 (2%)
Unacceptable 2 (2%)
Number of labs 121
Assigned value: 0.098 mg/kg
Alg A STD: 22%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 False Negatives


Water added
No water added
Not specified
LPE
Tebuconazole
EU and EFTA Laboratories
Acceptable 137 (99%)
Questionable 1 (1%)
Unacceptable 1 (1%)
Number of labs 139
Assigned value: 0.091 mg/kg
Alg A STD: 15%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0 False Negatives


Water added
No water added
Not specified
LPE
Tetramethrin
EU and EFTA Laboratories
Acceptable 99 (96%)
Questionable 0 (0%)
Unacceptable 4 (4%)
Number of labs 103
Assigned value: 0.096 mg/kg
Alg A STD: 18%
Z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
3 False Negatives

6th Edition: Revised 8th February, 2016

GENERAL PROTOCOL

for EU Proficiency Tests on Pesticide Residues in Food and Feed

Introduction

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

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

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

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

[1] DG-SANTÉ = European Commission, Health and Food Safety Directorate-General

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

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

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

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

EUPT-Organisers and Scientific Committee

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

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

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

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

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

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

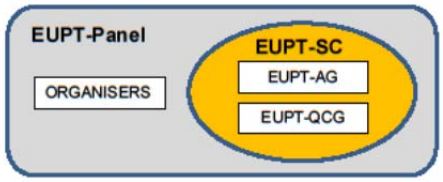
The EUPT-SC's role is to help the Organisers make decisions regarding the EUPT design: the selection of the commodity, the selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the statistical treatment and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

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

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

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

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



The decisions of the EUPT-Panel will be documented.

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

EUPT Participants

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

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

The four EURLs will annually issue and distribute, via the EURL-website, a joint list of all OfLs that must participate in each of the EUPTs to be conducted within a given year. The list of obliged labs will be updated every year to take account of any changes in the lab profiles. Interim updates will be issued to eliminate any possible errors.

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

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

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

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

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

Confidentiality and Communication

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

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

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

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

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

The official language used in all EUPTs is English.

Announcement / Invitation Letter

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

Target Pesticide List

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

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

Specific Protocol

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

Homogeneity of the Test Item

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

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

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with values of 1.88 and 1.01, respectively, if 10 samples are used. $\sigma_{all}^2 = 0.3 \times$ FFP-RSD[8] (FFP-RSD=0.25 × the mean of the homogeneity test), and s_{an} is the estimate of the analytical standard deviation.

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

Stability of the analytes contained in the Test Item

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

A pesticide is considered to be adequately stable if $| y_l - y | \leq 0.3 \times \sigma_{pt}$, where y_l the mean value of the last period of the stability test, y is the mean value of the first period of the stability test and σ_{pt} the standard deviation used for proficiency assessment (typically 25% of the assigned value).

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

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

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

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

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

Methodologies to be used by the participants

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

General procedures for reporting results

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

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

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Correction of results for recovery

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

Methodology information

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

[9] Document N° SANTE/11945/2015; Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed

Results evaluation

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

– ***False Positive results***

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

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

– ***False Negative results***

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

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

– ***Estimation of the assigned value (x_{pt})***

In order to minimise the influence of out-lying results on the statistical evaluation, the assigned value x_{pt} (= consensus concentration) will typically be estimated using robust estimate of the participant's mean (x^*) as described in ISO 13528:2015[10]. In special justifiable cases, the EUPT-

[10] DIN ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization. Therein a specific robust method for determination of the consensus mean and standard deviation without the need for removal of deviating results is described (Algorithm A in Annex C).

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

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

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

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

Uncertainty of the assigned value

The uncertainty of the assigned values $u(x_{pt})$ is calculated according to ISO 13528:2015 as:

$$u\left(x_{pt}\right) = 1{,}25 \times \frac{s^*}{\sqrt{p}}$$

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

In certain cases and considering all relevant factors (e.g. the result distribution, multimodality), the number of submitted results, information regarding analyte homogeneity/stability, information regarding the use of methodologies that might produce a bias that were used by the participants), the EUPT-Panel may consider the assigned value of a specific analyte to be too uncertain and decide that the results should not be evaluated, or only evaluated for informative purposes. The provisions of ISO 13528:2015 concerning the uncertainty of the assigned value will be taken into account.

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

The target standard deviation of the assigned value (FFP-σ_{pt}) will be calculated using a Fit-For-Purpose approach with a fixed Relative Standard Deviation (FFP-RSD) of 25% as follows:

$$\text{FFP-}\sigma_{pt} = 0.25 \times x_{pt}$$

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

For informative purposes the robust relative standard deviation (CV*) is calculated according to ISO 13528:2015; Chapter 7.7 (Consensus value from participant results) following Algorithm A in Annex C.

– ***z scores***

This parameter is calculated using the following formula:

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

where x_i is the value reported by the laboratory, x_{pt} is the assigned value, and FFP-σ_{pt} is the standard deviation using FFP approach. Z scores will be rounded to one decimal place. For the calculation of combined z scores (see below) the original z scores will be used and rounded to one decimal place after calculation.

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

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

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

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

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

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

The EUPT-Panel will decide if and how to classify the laboratories into two categories - A or B. Currently, laboratories that are able to analyse at least 90% of the compulsory pesticides in the target pesticides list, have correctly detected and quantified a sufficiently high percentage of the pesticides present in the Test Item (at least 90 %) and reported no false positives will have demonstrated 'sufficient scope' and can therefore be classified into Category A. For the 90% criterion the number of pesticides needed to be correctly analysed to have sufficient scope will be calculated by multiplying the number of compulsory pesticides from the Target Pesticides List by 0.9 and rounding to the nearest full number with 0.5 decimals being rounded downwards (see some examples in Table 1).

Table 1. No. of pesticides from the Target Pesticides List needed to be targeted or pesticides present in the Test Item that need to be correctly detected and quantified to have sufficient scope.

No. of compulsory pesticides present in the Test Item / Target Pesticides List (N)	90 %	No. of pesticides needed to be correctly detected and quantified / targeted 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	

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

No. of compulsory pesticides present in the Test Item / Target Pesticides List (N)	90 %	No. of pesticides needed to be correctly detected and quantified / targeted to have sufficient scope (n)	n
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	
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	N - 2
20	18	18	
21	18.9	19	
22	19.8	20	
23	20.7	21	
24	21.6	22	
25	22.5	22	N - 3
26	23.4	23	

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

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

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

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

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

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

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

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

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

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

Publication of results

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

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

Certificates of participation

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

Feedback

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

Correction of errors

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

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

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

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

Follow-up activities

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

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

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

NRLs will be considered as **underperforming in relation to scope** if in two EUPTs of the last four EUPTs falling within their responsibility area if they: a) haven't participated, or b) targeted less than 90% of the compulsory pesticides in the target lists (80% for SRM-compounds), or c) detected less than 90% of the compulsory compounds present in the test items (80% for SRM-compounds).

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Additionally, NRLs that obtained AZ^2 higher than 3 in two consecutive EUPTs of the last four EUPTs, will be considered as **underperforming in accuracy**. A two-step protocol established by DG-SANTE will be applied as soon as underperformance of an NRL is detected[15]:

Phase 1:

- Identifying the origin of the bad results (failure in EUPTs).
- Actions: On the spot visits and training if necessary and repetition of the comparative test if feasible and close the assessment of results by the EURL.

Phase 2:

- If the results still reveal underperformance the Commission shall be informed officially by the EURL including a report of the main findings and corrective actions.
- The Commission shall inform the Competent Authority and require that appropriate actions are taken.

Underperformance rules for the OfLs will be established at a later stage.

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.

[15] Article 32 of the Regulation 882/2004

SPECIFIC PROTOCOL

for the EU Proficiency Test for Pesticide Residues in Cereals/Feeding stuff using Multi-Residue Methods, EUPT-CF10 (2016)

(last updated: 1 March 2016)

Introduction

This protocol is complementary to the General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed. The current proficiency test covers pesticides that are determined by Multi-Residue Methods. This EUPT is to be performed by all National Reference Laboratories for Cereals and/or Feeding stuffs (NRL-CFs) as well as by all official EU laboratories (OfLs) responsible for official pesticide residue controls on cereals and/or feeding stuff, as far as their scope overlaps with that of the EUPT-CF10.

Test Item (Test Material)

This proficiency test concerns the analysis of pesticide residues in rye flour. The rye was grown in Denmark in 2015 and pesticides were applied in the field. Following harvest, the rye kernels were spiked with additional pesticides.

The blank Test Item provided, can be used for recovery experiments as well as for the preparation of matrix-matched calibration standards. However, the blank Test Item must also be analysed and possible detected pesticides reported.

The Organizers will check the 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 also be checked to prove that the target analytes are not contained at any relevant levels. All these tests will be conducted by the EURL-CF, which is ISO 17025 accredited.

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 only individual compounds, and results should only be reported for individual compounds, no matter how the residue definitions have been set.

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

Amount of Test Item

The participants will receive:

- approximately 125 g of rye flour Test Item with incurred and spiked pesticides and
- approximately 125 g of blank rye flour Test Item.

Shipment of Test Items

The Test Items are planned to be shipped on 7 March, 2016.

Test Items will be shipped frozen and packed in thermo-boxes together with a freezer block. 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 Items should be stored deep-frozen (at -18°C or less) before analysis to avoid any possible deterioration/spoilage and to minimize pesticide losses. The Test Items 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 Items, laboratories employing methods requiring large analytical portions are advised to scale them down.

The homogeneity tests will be conducted using 5 g of Test Item in all cases. 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 Deadlines

Sample receipt acknowledgement, analytical results and method information are to be submitted via the EUPT-CF10 Result Submission Website.

Links to this and other document can be found on the EURL-CF webpage: EUPT–CF10 Website.

The website will be accessible from 9 March 2016. The webpage 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). **Username and password will be email to the participants on 4 March 2016.**

To access the data submission forms participants must use their unique login data (username and password), which will be sent by e-mail on 4 March 2016.

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

The deadline for result submission is 11 April 2016 at 13.00 CEST.

Test Item Receipt and Acceptance - Subpage 0

Once the laboratory has received the Test Items it must report to the organiser, via the EUPT-CF10 Result Submission Website, the date of receipt, the condition of the Test Item, and its acceptance. The deadline for acceptance is the 11 March 2016. If the laboratory does not respond by this deadline, the Organisers will assume that the Test Items have been received and accepted.

If participants have not received the Test Items by the 11 March 2016 at noon, they must inform the Organiser immediately by e-mail (eurl-cf@food.dtu.dk).

Reporting Qualitative and Quantitative Results - Subpages 1 and 2

To report their results, laboratories must access the EUPT-CF10 Result Submission Website.

Deadline: All results must be reported on the online result submission website by 11 April 2016 at 13.00 CEST. The website will NOT be accessible for result submission after this date and time, and any results reported after the deadline will not be included in the statistical treatment, or in the final report.

Results should **not** be reported where a pesticide

a) was not detected,

b) was detected below the RL (Reporting Limit) of the laboratory, or

c) below the MRRL.

Results reported as <RL will be considered as „Not Detected".

Significant Figures:

Residue levels <0.010 mg/kg;

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

Residue levels ≥ 0.010 mg/kg;

- to be expressed by 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 you should fill in the results 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 what 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 the result, 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-CF10 Result Submission Website. The laboratories are asked to thoroughly fill in this important information in order to minimize the administrative burden of collecting this information at a later stage.

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-CF10 Result Submission Website. This subpage will be accessible from 13-15 April 2016.

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 Art. 32 1b of Regulation (EC) No 882/2004, underperformance of any NRL-CF in comparative testing will be followed by EURL-CF.

Documents

All documents relating to EUPT-CF10 can be found on EUPT–CF10 Website.

Calendar

Activity	Dates
Announcement Calendar Target Pesticide List	December 2015
EUPT-Registration Website	11 January 2016
Deadline for registration	1 February 2016
Release of Specific Protocol	29 February 2016
Distribution of Test items	7 March 2016
Deadline for Receipt and Acceptance of Test Materials	within 24 hr on receipt
Deadline for Result Submission	11 April 2016 at 13.00 CET
Deadline for submission of additional method information for false negative results	15 April 2016
Preliminary Report (only compilation of results)	30 May 2016
Final Report	December 2016

Participation Fees

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

- 175 €

The participation fees for laboratories from third countries:

- 350 €

For further information, visit this website www.eurl-pesticides.eu

Delays in Payment

The participants will receive an invoice from DTU. 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 questions concerning invoices must be directed to Joachim Nilsson joani@adm.dtu.dk or Tina Holst Beck <tihb@adm.dtu.dk> at the financial department.

Contact information:

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