Proficiency Test on incurred and spiked pesticides in wheat

EU Reference Laboratory on Cereals & Feeding stuff

EUPT-CF8 2014

DTU Food
National Food Institute

EU PROFICIENCY TESTS
EUPT-CF8, 2014

Incurred and Spiked Pesticide Residues in Wheat

Final Report

Version 1

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PREFACE

Regulation 882/2004/EC [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 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 396/2005/EC 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 eighth organized within the frame of the EURL activities with cereal or feed matrix as Test Items. The previous PTs were EUPT-C1/SRM2 on wheat (2007), EUPT-C2 on wheat (2008), EUPT-C3/SRM4 on oats (2009), EUPT-C4 on rye (2010), EUPT-C5/SRM6 on rice (2011), EUPT-C6 on barley and EUPT-CF7 on animal feed. 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-CF8 on wheat (2014) was only focused on MRM-pesticides. The wheat Test Item used for EUPT-CF8 was treated with 19 compounds partly in the field and partly post-harvest in the laboratory.

Participation in EUPT-CF8 was compulsory for all National Reference Laboratories (NRLs) and Official Laboratories (OfLs) within the EU involved in the determination of pesticide residues in cereal 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. All NRLs and OfLs that were supposed to participate in this exercise, but decided not to take part, were asked to state the reasons for their non-participation.

DG-SANCO 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 3 February 2014 the announcement of the 8th European Commission's Proficiency Test on cereals and feeds(EUPT-CF8) was published on the EURL homepage, 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 116 individual compounds 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-CF8 was provided via the homepage. Laboratories were able to register on-line from the 18 February to 30 April 2014. 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 wheat 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 19 compounds in total. Danish Centre for Food and Agriculture at Aarhus University grew the wheat and performed the field treatments in 2013. The pesticides employed for field treatment were selected by the EURL-CF and the quality group and the application rates and harvest intervals chosen were based on previous experience and data from supervised residue trials. The harvested grain was spiked with ten pesticides post-harvest, and then checked for homogeneity before shipping to participants. Furthermore, the stabilities of the pesticides in the 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 wheat Test Item and 125 g of untreated Blank Test Item. Both Test Items were shipped to participants on 19 May 2014 and the deadline for submission of results to the Organiser was the 16 June 2014. 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] and the SweEt method [4], were 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 treated test item, shakena and acetonitrile was added immediately. Salt and buffer mixture was added and the sample shaken again. After centrifugation an aliquot of the supernatant was by freezing out. After an additional centrifugation of the cold extract the supernatant was transferred to a tube with PSA and $MgSO_4$. After shaking and centrifugation the extract was ready for analysis by GC-MS/MS and LC-MS/MS.
- SweEt: The grinded sample is extracted after water addition with acidified (1 % acetic acid) ethyl acetate and Na2SO4. The sample extract is centrifuged and filtered prior to injection to 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 (wheat). 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 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, 45 kg of the harvested wheat 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 eight pesticides, which were not included in the field treatments (**Table 1)**. Spiking in the laboratory was performed using formulations or pure standards. One kilogram of the field treated wheat was spiked with all 10 pesticide standards or formulations and was subsequently mixed with 45 kg field treated wheat and homogenised thoroughly. The 45 kg of mixed wheat grain was milled separately as four kilograms portions. To ensure that a well-homogenised bulk, with respect to both incurred and spiked residues, was obtained, the 4 kg portions were initially mixed individually, then doubled and mixed again and finally all mixed together. 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 wheat 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

Eleven bottles of pesticide treated Test Items were randomly chosen and analyses were performed on duplicate portions taken from each bottle with the analytical methods described in section 1.1. The sequence of analyses and injection sequence were also both 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 [5]. 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 theTest Item were sufficiently homogenous for the proficiency test was that: $S_s^2 < c$ where Ss is the between-bottle sampling 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. σ_{all}^2 = 0.3 x 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 Test Item was considered to be sufficiently homogenous and suitable for the EUPT-CF8.

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

Pesticide	Application in field	Spike in laboratory	Formulation
Azoxystrobin	x		
Bixafen	x		
Boscalid	x		
Carbendazim		x	Analytical Standard
Chlorothalonil	x	x	Bravo 500 SC
Cypermethrin	x	x	Cyperb
Deltamethrin-cis	x	x	Decis EW 50
Endosulfan-sulfate		x	Analytical Standard
Epoxiconazole	x		
Flonicamid	x		
Fluxapyroxad	x		
Lindane		x	Analytical Standard
Linuron		x	Analytical Standard
Metconazole	x		
Metrafenone	x	x	Flexity
Prothioconazole	x		
Pyraclostrobin	x		
Spiroxamine	x	x	Spiroxamin EC 500
Trifluralin		x	Analytical Standard

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. Two different storage temperatures were used; room temperature and -18 °C. Six sub-samples (analytical portions) was 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: 25 May 2014

Day 2: 4 June 2014

Day 3: 18 June 2014

The results of the stability test for storage temperature -18 are given in **Table 3**. All pesticides passed the test at -18 °C. However, bixafen and fluxapyroxade did not pass when stored 4 week at room temperature. But the results did not show any degradation (less residue after 4 week) so the 'instability' was probably associated with analytical variances. The laboratories was instructed to store the test item at -18 degree and the results for both compounds were very good with 20% and 13% robust RSD respectively, and only 2 questionable results for bixafen and 2 unacceptable results for fluxapyroxade – all false negatives. The test material was consequently accepted for all pesticides.

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	0.211	0.00000	0.0033	Pass
Bixafen	0.082	0.00005	0.0001	Pass
Boscalid	0.324	0	0.0063	Pass
Carbendazim	0.055	0.00001	0.0001	Pass
Chlorthalonil	0.029	0.00001	0.0001	Pass
Cypermethrin	0.891	0	0.0482	Pass
Deltamethrin	0.053	0	0.0002	Pass
Endosulfan-sulfate	0.057	0	0.0002	Pass
Epoxiconazole	0.122	0	0.0008	Pass
Flonicamid	0.102	0	0.0003	Pass
Fluxapyroxade	0.179	0.00017	0.0004	Pass
Lindane	0.035	0	0.0000	Pass
Linuron	0.069	0.00002	0.0003	Pass
Metconazole	0.110	0.00014	0.0001	Pass
Metrafenone	0.381	0	0.0081	Pass
Prothioconazole desthio	0.179	0.00040	0.0004	Pass
Pyraclostrobin	0.070	0.00004	0.0001	Pass
Spiroxamin	0.064	0.00006	0.0001	Pass
Trifluralin	0.058	0	0.0001	Pass

Table 3. Statistical evaluation of the stability test data

Pesticide	Mean, mg/kg	| x1 - yi |	0.3×σ	| x1 - yi | ≤ 0.3×σ
Azoxystrobin	0.243	0.017	0.017	Pass
Bixafen	0.071	0.001	0.006	Pass
Boscalid	0.305	0.015	0.025	Pass
Carbendazim	0.058	0.000	0.000	Pass
Chlorothalonil	0.027	0.003	0.003	Pass
Cypermethrin	0.908	0.053	0.057	Pass
Deltamethrin	0.042	0.003	0.003	Pass
Endosulfan-sulfate	0.034	0.000	0.003	Pass
Epoxiconazole	0.118	0.005	0.009	Pass
Flonicamid	0.088	0.004	0.008	Pass
Fluxapyroxade	0.150	0.012	0.012	Pass
Lindane	0.038	0.003	0.003	Pass
Linuron	0.065	0.004	0.006	Pass
Metconazole	0.098	0.005	0.008	Pass
Metrafenone	0.362	0.015	0.028	Pass
Prothioconazole-desthio	0.159	0.005	0.015	Pass
Pyraclostrobin	0.061	0.004	0.006	Pass
Spiroxamin	0.057	0.003	0.005	Pass
Trifluralin	0.034	0.002	0.003	Pass

1.7 Organisational details

1.7.1 Access to documents, registration and confidentiality

In the invitation letter of 3 February 2014, all NRLs and OfLs were requested to register using the online registration link from 18 February to 30 April 2014. 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 a username, password, laboratory code and the 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 19 May 2014, 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 communicate 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 (16 June 2014). 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 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.

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 (= consensus concentration) will typically be estimated using robust statistics as described in ISO 13528:2009-01. In special justifiable cases, the EUPT-Panel may decide to eliminate certain results traceably associated with gross errors (see "Omission or Exclusion of results" below) or to use only the results of a subgroup consisting of laboratories that have repeatedly demonstrated good performance for the specific compound in the past

2.3 Uncertainty of the assigned value

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

$$\mu_i = 1.25 \frac{s*}{\sqrt{n}}$$

Where:

- μ_i is the uncertainty in mg/kg.
- s* is the robust standard deviation estimate
- n is the total number of laboratories giving a result for each pesticide, excluding outliers.

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:

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

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

2.5 Z-scores

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

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

Where:

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

Z-scores will be rounded to one decimal place. For the calculation of combined z-scores (see below) the original z-scores will be used and rounded to one decimal place after calculation. Any z-scores of > 5 will be reported as >5 and where combined z-scores are calculated a value of "5" will be used.

Z-scores will be interpreted in the following way:

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

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.

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

Laboratories that have detected at least 90% of the pesticides present in the Test Item and reported no false positives are classified into Category A. For evaluation of the overall performance of laboratories within Category A, the Average of the squared z-score (AZ^2), are calculated.

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

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

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

The $AZ^2$is considered being of lesser importance than the individual z-scores. Therefore the organiser, in agreement with the EUPT-Panel, retains the right not to use them if they are considered to be unhelpful.

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, 141 EU and EFTA laboratories, from 29 different countries (27 EU member states), agreed to participate in this proficiency test. Malta was represented by UK NRL. Three NRLs did not register and six EU/EFTA participants did not submit data. Among these was one NRL. Additionally, 22 Third Countries registered for the PT. Two samples did not reach the laboratories due to difficulties with customs clearance and five 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 17 evaluated pesticides and are shown in **Table 10a-j** and in **Appendix 5** for chlorothalonil and lindane that were not evaluated. 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 4-9** and in the z-scores histograms in **Appendix 4.**

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]	False negatives	% results [2]
Azoxystrobin	116	19	2	85
Bixafen	67	68	0	49
Boscalid	117	18	1	86
Carbendazim	97	38	1	71
Chlorothalonil [3]	*90*	*45*	*22*	*66*
Cypermethrin	125	10	1	92
Deltamethrin-cis	123	12	10	90
Endosulfan-sulfate	126	9	7	93
Epoxiconazole	110	25	1	81
Flonicamid	79	56	0	58
Fluxapyroxad	60	75	3	44
Lindane [4]	*126*	*10*	*5*	*93*
Linuron	95	40	2	70
Metconazole	87	48	2	64
Metrafenone	83	52	1	61
Prothioconazole-desthio	86	49	3	63
Pyraclostrobin	97	38	2	71
Spiroxamine	97	38	4	71
Trifluralin	106	29	2	78

[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 = 103). False negatives are included in reported results.

[3] Result for chlorothalonil is not evaluated due to too high robust standard deviation of the results and the high number of false negatives

[4] Result for lindane is not evaluated because the assigned value was less than 4 times the MRRL.

Cypermethrin, deltamethrin-cis, endosulfan-sulfate and Lindane were the most frequently analysed compounds with 90 % or more of the labs submitting results for these compounds. Azoxystrobin, boscalid, carbendazim, epoxiconazole, linuron, pyraclostrobin, spiroxamine and trifluralin were analysed by 70-86% of the participants and bixafen, chlorothalonil, flonicamid, fluxapyroxad, metconazole, metrafenone and prothioconazole-desthio were only reported by 49-63% of participants.

3.1.1 False positives

Four participants from EU and EFTA countries reported 4 results above the MRRL for additional pesticides that had not been used to treat the Test Item (**Table 5**). The pesticides were: captan, fenvalerate/esfenvalerate, HCH-beta and quinoxyfen. In all cases the compounds were not detected either by the Organizer, or by the other participating laboratories. The reported results were therefore considered to be false positives.

One laboratory reported two results below the MRRL for additional pesticides but about their own Reporting Level (**Table 6**).

Table 5. False positive results at or above 0.01 mg/kg, the concentration detected in mg/kg, the determination technique used, the reporting level and the MRRL in mg/kg.

Lab code	Pesticide	Concentration mg/kg	Determination technique	RL, mg/kg	MRRL, mg/kg
1	Fenvalerate and Esfenvalerate	0.01	GC-Ion Trap	0.01	0.01
104	Captan	0.209	LC-MS/MS QQQ	0.06	0.01
111	Quinoxyfen	0.01	[1]	[1]	0.01
147	HCH-beta	0.0294	GC-MS/MS (QQQ)	0.01	0.01

[1] No information received.

Table 6. False positive results below 0.01 mg/kg, the concentration detected in mg/kg, the determination technique used, the reporting level and the MRRL in mg/kg.

Lab code	Pesticide	Concentration mg/kg	Determination technique	RL, mg/kg
100	Acephate	0.0031	LC-MS/MS QQQ	0.01
100	Permethrin [1]	0.0035	LC-MS/MS QQQ	0.005

[1] This laboratory also reported that they found same amount of permethrin in the Blank Test Item.

3.1.2 False negatives

Missing results for pesticides actually present in the treated Test Item were judged as false negatives. **Table 7** summarizes the number of reported false negatives for each pesticide. Forty-two results were judged as false negatives, which represents 3 % of the total number of results. Around 20 % of the participants (28 laboratories) reported false negative results. This is equivalent to previous EUPT on cereals where 20-30% of the labs reported false negative results. No false negatives results were reported for bixafen and flonicamid.

Table 7. False negative results (FN).

Lab code	Azoxystrobin	Boscalid	Carbendazim	Cypermethrin	Deltamethrin-cis	Endosulfan-sulfate	Epoxiconazole	Fluxapyroxad	Linuron	Metconazole	Metrafenone	Prothioconazole-desthio	Pyraclostrobin	Spiroxamine	Trifluralin
21										FN					
23													FN	FN	
30															FN
33								FN							
38												FN			
56 [1]	FN	FN	FN		FN	FN	FN		FN	FN			FN	FN	FN
71						FN									
78						FN									
79					FN										
85				FN	FN	FN									
86						FN									
92												FN			
95	FN													FN	
96								FN							
99					FN										
104					FN										
111								FN							
119														FN	
120									FN						
122					FN										
127						FN									
133					FN	FN									
140												FN			
142											FN				
147															
150					FN										
156					FN										
163					FN										

[1] The laboratory reported after deadline that the sample extract had not been injected correctly.

3.2 Assigned values and target standard deviations

The Assigned Values was calculated as the Algorithm A mean, including the reported results submitted by laboratories from EU and EFTA countries. However, due to 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 8**.

The assigned value for lindane was below 0.04 mg/kg and the assigned value and therefore the z-scores have been calculated for informative purposes only. The assigned value for chlorothalonil is also only for informative purposes. This is because of the very high robust standard deviation and high number of false

negative results reported. Contrary to lindane, acceptable z-scores calculated with the assigned value for chlorothalonil, should not necessarily be taken as good performance. See further details on page 24.

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 were in the range of 13-31 % but on average the Qn-RSD was 20 %, and thus close to the 25 % FFP-RSD used for the calculations.

The uncertainty of the assigned values is calculated according ISO 13528 [6] as:

$$u = 1.25 \frac{s*}{\sqrt{n}}$$

Where s* is the robust standard deviation estimate and n is the number of datapoint equal to the number of results used to calculate the assigned value (number of results in **Table 9**)

Table 8. Assigned values, the 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	0.228	0.004	25	15
Bixafen	0.01	0.079	0.002	25	19
Boscalid	0.01	0.328	0.005	25	14
Carbendazim	0.01	0.073	0.003	25	31
Chlorothalonil 1	0.01	0.042	0.003	25	49
Cypermethrin	0.01	0.766	0.003	25	31
Deltamethrin-cis	0.01	0.040	0.001	25	29
Endosulfan-sulfate	0.01	0.040	0.001	25	24
Epoxiconazole	0.01	0.117	0.003	25	20
Flonicamid	0.01	0.104	0.002	25	16
Fluxapyroxad	0.01	0.165	0.004	25	13
Lindane 2	0.01	0.038	0.001	25	16
Linuron	0.01	0.074	0.002	25	16
Metconazole	0.01	0.101	0.003	25	20
Metrafenone	0.01	0.376	0.003	25	15
Prothioconazole-desthio	0.01	0.201	0.008	25	15
Pyraclostrobin	0.01	0.074	0.002	25	23
Spiroxamine	0.01	0.060	0.002	25	21
Trifluralin	0.01	0.040	0.001	25	19

[1] Result for chlorothalonil is not evaluated due to too high robust standard deviation of the results and the high number of false negatives

[2] Result for lindane is not evaluated because the assigned value was less than 4 times the MRRL.

3.3 Assessment of laboratory performance

3.3.1 Z-scores

Z-scores have been calculated for all the quantified pesticides using the FFP RSD of 25 %. **Table 9** shows an overview of the acceptable, questionable and unacceptable z-scores and **Tables 10a-j** 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**. Results for the two not evaluated pesticides, chlorothalonil and lindane residues can be seen in **Appendix 5.**

Table 9. Number of acceptable, questionable, unacceptable z-scores and false negatives. The unacceptable z-scores include the false negatives.

	No. of reported results	Acceptable	Questionable[1]	Unacceptable[1]	False negatives[1]
Azoxystrobin	117	114	1	2	2
Bixafen	67	65	2	0	0
Boscalid	117	112	3	2	1
Carbendazim	98	81	5	12	1
Chlorothalonil [2]	*91*	*51*	*31*	*9*	*23*
Cypermethrin	126	106	12	8	1
Deltamethrin-cis	124	102	14	8	11
Endosulfan-sulfate	127	110	16	1	8
Epoxiconazole	110	104	3	3	1
Flonicamid	79	75	1	3	0
Fluxapyroxad	60	57	0	3	3
Lindane [3]	*126*	*112*	*10*	*4*	*6*
Linuron	95	91	2	2	2
Metconazole	87	82	2	3	2
Metrafenone	83	79	1	3	1
Prothioconazole-desthio	86	78	4	4	3
Pyraclostrobin	97	89	4	4	2
Spiroxamine	97	89	2	6	4
Trifluralin	106	102	1	3	2

[1] Questionable and unacceptable z-scores include the false negative results.
[2] Result for chlorothalonil is not evaluated due to too high robust standard deviation of the results and the high number of false negatives
[3] Result for lindane is not evaluated because the assigned value was less than 4 times the MRRL.

For azoxystrobin, bixafen, boscalid, epoxiconazole, flonicamid, fluxapyroxad, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin acceptable results were obtained by 91-97% of the laboratories. For carbendazim, cypermethrin, deltamethrin-cis and endosulfan-sulfate acceptable results were obtained by 84-87% of the laboratories.

The Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed, SANCO/12571/2013 [7] recommends the addition of water to the samples prior to extraction to improve the extraction efficiency of low moisture containing commodities like cereals (paragraf C7). The result from this PT and former EUPT on cereals show that for many pesticides this is essential. Below is a conclusion on the results per pesticides and for the pesticides where water addition is

essential, this includes also procedures where water and solvent simultaneously or to use ASE extraction as this give good extraction efficiencies in line with adding water prior to extraction. For some of the organochlorine pesticides adding water prior to extraction do not affect the extraction, not positively nor negatively. However, for malathion, phenthoate, methacrifos Yoshii et all (2000, 2006 and 2007) [8, 9, 10] have shown the carboxylesterase converts the pesticides to di-carboxylic acids. To aviod this it is important to not leave the samples after the water is added, but quickly add the solvent and extract.

Conclusion and recommendations is given below.

The azoxystrobin residue was incurred in the wheat and the performance of the participants were good. However, the results showed that it is important to add water to the samples before the extraction with solvent. All seven laboratory that reported not to have added water all negative values for their z-scores. Consequently, it is recommended to add water to the sample before extraction to optimize the extraction efficiency (for adding water see above).

The bixafen residue was incurred and the performance of the participants were good with only 2 questionable results. All participants added water to the sample before extraction. However, a relatively low number of participants reported results for this pesticide.

The boscalid residue was incurred and the performance of the participants were good. However, the results showed that it is important to add water to the samples before the extraction with solvent. All nine laboratory that reported not to have added water obtained z-scores below 0. Consequently, it is recommended to add water to the sample before extraction to optimize the extraction efficiency (for adding water see above).

Carbendazim residue was spiked. As seen in previous EUPTs on cereals some laboratories reported very high results. 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 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 chlorothalonil residue was both incurred and over spiked. The performance for this pesticide was very poor with 23 false negative results and a robust standard deviation of 49%. Due to this high deviation the compound has not been evaluated. The assigned value and z-scores are for information only. Furthermore, the calculated assigned value seen in Table 8 and the z-scores given in **Appendix 5** should be viewed with great caution. It has been evaluated whether, the method (QuEChERS, SweEt, Mini-luke etc.), pH, soaking time, extraction time or recovery gave any indication on the performance. From the results and the method information reported by the laboratories it is not possible to give any recommendation on how to obtain good results.

The cypermethrin residue was both incurred and over spiked. For analysis of cypermethrin it is not necessary to add water before extraction. As for carbendazim a number of high results are often seen for pyrethroid in the EUPT for cereals. However, here the it is probably due to calculation of the results as the standard contains the sum of all isomers. The isomer pattern in the standard can be differentto that in the samples and caution should be taken when calculating the result as different calculation methods can significantly affect the result.

The deltamethrin-cis residue was both incurred and over spiked. As for cypermethrin it is not necessary to add water before extraction. Also for deltamethrin-cis a number of high results was seen for pyrethroid in the EUPT for cereals and it might be due to differences in isomer pattern between standard and the samples.

Endosulfan-sulfate residue was spiked. For analysis of endosulfan-sulfate it is not necessary to add water before extraction. The results showed 8 false negatives which probably is caused by the extensive fragmentation of the compound in the ion source when analysing with GC-MS. This will result in higher LOQ.

The epoxiconazole residue was incurred and the performance of the participants were good. However, the results showed that it is important to add water to the samples before the extraction with solvent (for adding water see above). All four out of five laboratory that reported not to add water obtained z-scores below 0.

The flonicamid residue was incurred and the performance of the participants were good. Two very high results were due to the inclusion of degradation products in the reported results. Also for this compound it seems to enhance the extraction efficiency if water is added before to the samples before extraction (for adding water see above). A relative low number of participant reported results for this pesticide probably because it was a new addition to the target list.

The fluxapyroxad residue was incurred and the performance of the participants was good apart from three false negative results. All participant added water to the sample before extraction. A relative low number of participant reported results for this pesticide probably because it was a new addition to the target list.

The lindane residue was spiked and the performance of the participants was good was good apart from six false negative results. Because the calculated assigned value (0.038 mg/kg) was below four time the MRRL of 0.01 mg/kg, this compound has not been evaluated. The assigned value in Table 8 and z-scores given in **Appendix 5** are for information only. However, contrary to chlorothalonil the assigned value and the z-scores are to be considered reasonably valid. For analysis of lindane it is not necessary to add water before extraction.

The linuron residue was incurred and the performance of the participants was good apart from two false negative results. It is not possible to evaluate if adding water before extraction does enhance the extraction efficiency.

The metconazole residue was incurred and the performance of the participants was good apart from two false negative results and one high results. It is not possible to evaluate if adding water before extraction does enhance the extraction efficiency.

The metrafenone residue was both incurred and over spike and the performance of the participants was good apart from one false negative result. It is not possible to evaluate if adding water before extraction does enhance the extraction efficiency.

The prothioconazole-desthio residue was incurred resulting from the treatment of the wheat in the field with prothioconazole. The performance of the participants was good apart from three false negative results. The false negative results can arise from laboratory analysing for prothioconazole and not including the degradation product desthio. It is not possible to evaluate if adding water before extraction can enhance the extraction efficiency.

The pyraclostrobin residue was incurred and the performance of the participants was good. Also for this compound it seems to enhance the extraction efficiency if water is added before to the samples before the extraction (for adding water see above).

The spiroxamine residue was spiked and the performance of the participants resulted in four false negative results and one z-score above 5. It is not possible to evaluate if adding water before extraction can enhance the extraction efficiency.

The trifluralin residue was spiked and the performance of the participants resulted in four false negative results and one z-score above 5. For analysis of trifluralin it is not necessary to add water before extraction.

Table 10a. Results for azoxystrobin, bixafen, boscalid, carbendazim, cypermethrin, deltamethrin-cis, endosulfan-sulfate, epoxiconazole in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z-scores (FFP RSD (25%)	Bixafen	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Carbendazim	Z-scores (FFP RSD (25%)	Cypermethrin	Z-scores (FFP RSD (25%)	Deltamethrin-cis	Z-scores (FFP RSD (25%)	Endosulfan-sulfate	Z-scores (FFP RSD (25%)	Epoxiconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.228**		**0.079**		**0.328**		**0.073**		**0.766**		**0.040**		**0.040**		**0.117**	
1	0.232	0.1	0.065	-0.7	0.314	-0.2			0.613	-0.8	0.034	-0.6	0.041	0.1	0.096	-0.7
2	0.258	0.5	0.087	0.4	0.359	0.4	0.08	0.4	0.879	0.6	0.048	0.8	0.045	0.5	0.133	0.5
3	0.203	-0.4	0.079	0.0	0.276	-0.6	0.068	-0.3	0.93	0.9	0.036	-0.4	0.039	-0.1	0.106	-0.4
4	0.188	-0.7	0.077	-0.1	0.323	-0.1	0.06	-0.7	0.722	-0.2	0.042	0.2	0.036	-0.4	0.11	-0.3
5	0.217	-0.2	0.081	0.1	0.317	-0.1	0.071	-0.1	0.721	-0.2	0.049	0.9	0.039	-0.1	0.126	0.3
6													0.048	0.8		
7	0.268	0.7			0.341	0.2	0.053	-1.1	0.608	-0.8	0.058	1.8	0.03	-0.9	0.123	0.2
8	0.195	-0.6			0.469	1.7	0.117	2.4	2.81	>5	0.027	-1.3	0.034	-0.6	0.181	2.2
9													0.045	0.5		
10	0.262	0.6			0.261	-0.8			0.69	-0.4	0.045	0.5	0.041	0.1	0.135	0.6
11	0.256	0.5	0.076	-0.1	0.385	0.7	0.067	-0.3	0.773	0.0	0.03	-1.0	0.03	-1.0	0.101	-0.6
12	0.155	-1.3			0.294	-0.4	0.06	-0.7	0.917	0.8	0.051	1.1	0.069	3.0	0.123	0.2
13	0.216	-0.2	0.068	-0.5	0.311	-0.2	0.067	-0.3	0.778	0.1	0.038	-0.3	0.038	-0.2	0.102	-0.5
14	0.255	0.5	0.083	0.2	0.366	0.5	0.073	0.0	0.755	-0.1	0.046	0.6	0.04	0.0	0.122	0.2
15	0.269	0.7			0.491	2.0			3.52	>5	0.026	-1.4			0.12	0.1
16	0.252	0.4	0.127	2.5	0.34	0.1	0.067	-0.3	0.691	-0.4	0.045	0.5	0.038	-0.2	0.133	0.5
17	0.179	-0.9	0.077	-0.1	0.272	-0.7	0.057	-0.8	0.791	0.1	0.056	1.6	0.033	-0.6	0.096	-0.7
18	0.28	0.9	0.102	1.2	0.391	0.8	0.079	0.3	0.561	-1.1	0.034	-0.6	0.033	-0.7	0.156	1.3
19	0.248	0.4	0.095	0.8	0.316	-0.1	0.066	-0.3	0.646	-0.6	0.039	-0.2	0.043	0.3	0.128	0.4
20	0.233	0.1	0.078	0.0	0.327	0.0	0.087	0.8	0.872	0.6	0.052	1.2	0.04	0.0	0.135	0.6
21	0.206	-0.4	0.084	0.3	0.267	-0.7	0.085	0.7	0.779	0.1	0.032	-0.8	0.034	-0.6	0.092	-0.9
22							0.134	3.4	1.55	4.1	0.088	4.7	0.041	0.1	0.226	3.7
23	0.157	-1.2			0.299	-0.4			0.807	0.2	0.033	-0.7			0.09	-0.9
24	0.176	-0.9			0.291	-0.4			0.725	-0.2	0.036	-0.4	0.04	0.0	0.12	0.1
25	0.184	-0.8			0.289	-0.5			0.786	0.1	0.039	-0.1	0.041	0.1	0.109	-0.3
26	0.235	0.1			0.35	0.3	0.065	-0.4	0.81	0.2	0.055	1.5	0.042	0.2	0.13	0.4
27	0.2	-0.5			0.279	-0.6	0.075	0.1	3	>5	0.243	>5	0.079	3.9	0.093	-0.8
28							0.052	-1.2								
29	0.23	0.0			0.318	-0.1	0.065	-0.5	0.638	-0.7	0.02	-2.0	0.034	-0.6	0.081	-1.3
30	0.238	0.2	0.083	0.2	0.323	-0.1	0.06	-0.7	1.02	1.3	0.047	0.6	0.017	-2.3	0.123	0.2
31	0.212	-0.3			0.326	0.0	0.102	1.6							0.119	0.1
32	0.273	0.8			0.414	1.1	0.06	-0.7	0.718	-0.3	0.041	0.1	0.035	-0.5	0.118	0.0
33	0.27	0.7			0.44	1.4	0.036	-2.0	0.57	-1.0	0.058	1.8	0.013	-2.7	0.15	1.1
34	0.224	-0.1	0.058	-1.0	0.293	-0.4	0.095	1.2	0.741	-0.1	0.035	-0.5	0.035	-0.4	0.113	-0.1
35	0.152	-1.3	0.05	-1.5	0.235	-1.1	0.05	-1.3	0.673	-0.5	0.035	-0.5	0.032	-0.8	0.074	-1.5
36	0.2	-0.5			0.28	-0.6	0.162	4.9	0.98	1.1	0.028	-1.2	0.042	0.2	0.077	-1.4
37	0.2	-0.5			0.289	-0.5			0.776	0.1	0.038	-0.2	0.047	0.8	0.122	0.2

Table 10b. Results for flonicamid, fluxapyroxad, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Flonicamid	Z-scores (FFP RSD (25%)	Fluxapyroxad	Z-scores (FFP RSD (25%)	Linuron	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Metrafenone	Z-scores (FFP RSD (25%)	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Spiroxamine	Z-scores (FFP RSD (25%)	Trifluralin	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.104**		**0.165**		**0.074**		**0.101**		**0.376**		**0.201**		**0.074**		**0.060**		**0.040**	
1	0.109	0.2	0.156	-0.2					0.375	0.0	0.176	-0.5					0.039	-0.2
2	0.116	0.5	0.18	0.4	0.084	0.5	0.117	0.6	0.436	0.6	0.23	0.6	0.076	0.1	0.062	0.1	0.04	-0.1
3	0.089	-0.6			0.076	0.1	0.092	-0.4	0.412	0.4	0.21	0.2	0.064	-0.5	0.06	0.0	0.048	0.8
4	0.111	0.3	0.172	0.2	0.062	-0.7	0.073	-1.1	0.4	0.3	0.185	-0.3	0.078	0.2	0.062	0.1	0.039	-0.1
5	0.092	-0.5	0.156	-0.2	0.074	0.0	0.1	-0.1	0.372	0.0	0.198	-0.1	0.075	0.1	0.057	-0.2	0.038	-0.2
6																		
7					0.06	-0.8	0.105	0.1					0.061	-0.7	0.065	0.3	0.049	0.9
8					0.063	-0.6							0.062	-0.6	0.048	-0.8	0.031	-0.9
9																		
10					0.087	0.7	0.117	0.6	0.328	-0.5	0.193	-0.2	0.076	0.1	0.061	0.1	0.029	-1.1
11	0.119	0.6	0.167	0.0	0.082	0.4	0.11	0.3	0.401	0.3	0.177	-0.5	0.074	0.0	0.056	-0.3	0.029	-1.1
12	FN	-3.6			0.048	-1.4	0.084	-0.7	0.34	-0.4	0.055	-2.9	0.028	-2.5	0.065	0.3	0.017	-2.3
13	0.1	-0.2	0.151	-0.3	0.07	-0.2	0.083	-0.7	0.352	-0.3	0.173	-0.6	0.059	-0.8	0.06	0.0	0.035	-0.5
14	0.101	-0.1	0.195	0.7	0.079	0.3	0.101	0.0	0.374	0.0	0.228	0.5	0.077	0.2	0.062	0.1	0.043	0.3
15					0.055	-1.0									0.036	-1.6		
16	0.12	0.6	0.17	0.1	0.089	0.8	0.12	0.7	0.404	0.3	0.205	0.1	0.088	0.8	0.063	0.2	0.044	0.4
17	0.103	0.0	0.117	-1.2	0.067	-0.4	0.077	-0.9	0.366	-0.1	0.153	-1.0	0.085	0.6	0.051	-0.6	0.048	0.8
18	0.076	-1.1	0.223	1.4	0.092	1.0	0.13	1.1	0.451	0.8	0.258	1.1	0.104	1.6	0.075	1.0	0.027	-1.3
19	0.107	0.1	0.173	0.2	0.06	-0.8	0.075	-1.0	0.32	-0.6	0.222	0.4	0.079	0.3	0.056	-0.3	0.038	-0.3
20	0.119	0.6			0.09	0.9	0.122	0.8	0.404	0.3	0.208	0.1	0.087	0.7	0.048	-0.8	0.034	-0.6
21	0.113	0.3	0.167	0.0	0.077	0.2	FN	-3.6	0.331	-0.5	0.183	-0.4	0.076	0.1	0.047	-0.9	0.033	-0.7
22																		
23											0.155	-0.9	FN	-3.5	FN	-3.3	0.053	1.3
24											0.24	0.8					0.045	0.5
25																		
26	0.12	0.6			0.072	-0.1	0.098	-0.1	0.38	0.0	0.22	0.4	0.082	0.4	0.065	0.3	0.045	0.5
27					0.059	-0.8	0.086	-0.6			0.173	-0.6	0.056	-1.0	0.044	-1.1	0.151	>5
28																		
29					0.079	0.3							0.055	-1.0			0.038	-0.2
30	0.095	-0.4	0.154	-0.3	0.072	-0.1	0.093	-0.3	0.404	0.3	0.187	-0.3	0.079	0.3	0.069	0.6	FN	-3.0
31							0.263	>5	0.783	4.3			0.059	-0.8	0.078	1.2		
32	0.104	0.0			0.072	-0.1	0.103	0.1	0.348	-0.3	0.222	0.4	0.089	0.8	0.057	-0.2	0.035	-0.5
33	0.12	0.6	FN	-3.8	0.1	1.4	0.14	1.5	0.68	3.2	0.23	0.6	0.11	2.0	0.11	3.3	0.056	1.5
34	0.112	0.3	0.131	-0.8	0.092	0.9	0.093	-0.3	0.415	0.4	0.323	2.4	0.101	1.5	0.085	1.7	0.045	0.4
35	0.081	-0.9	0.089	-1.8	0.047	-1.5	0.066	-1.4	0.286	-1.0	0.129	-1.4	0.049	-1.3	0.056	-0.3	0.031	-0.9
36															0.074	0.9	0.038	-0.3
37																		

Table 10c. Results for azoxystrobin, bixafen, boscalid, carbendazim, cypermethrin, deltamethrin-cis, endosulfan-sulfate, epoxiconazole in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z-scores (FFP RSD (25%)	Bixafen	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Carbendazim	Z-scores (FFP RSD (25%)	Cypermethrin	Z-scores (FFP RSD (25%)	Deltamethrin-cis	Z-scores (FFP RSD (25%)	Endosulfan-sulfate	Z-scores (FFP RSD (25%)	Epoxiconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.228**		**0.079**		**0.328**		**0.073**		**0.766**		**0.040**		**0.040**		**0.117**	
38	0.23	0.0	0.074	-0.2	0.33	0.0	0.041	-1.7	0.805	0.2	0.027	-1.3	0.04	0.0	0.102	-0.5
39	0.297	1.2			0.426	1.2	0.162	4.9	1.23	2.4	0.074	3.4	0.051	1.2	0.161	1.5
40	0.216	-0.2			0.324	0.0	0.048	-1.4	0.817	0.3	0.025	-1.5	0.05	1.1	0.105	-0.4
41									0.574	-1.0	0.038	-0.2	0.024	-1.6		
42	0.291	1.1			0.479	1.8	0.071	-0.1	0.892	0.7	0.088	4.8	0.051	1.2	0.193	2.6
43	0.23	0.0	0.071	-0.4	0.32	-0.1	0.068	-0.3	0.76	0.0	0.024	-1.6	0.042	0.2	0.11	-0.3
44	0.212	-0.3	0.074	-0.2	0.346	0.2	0.056	-0.9	0.703	-0.3	0.062	2.1	0.047	0.8	0.121	0.1
45	0.237	0.2			0.432	1.3	0.082	0.5	0.839	0.4	0.041	0.1	0.04	0.0	0.163	1.6
46	0.266	0.7	0.089	0.5	0.344	0.2	0.219	>5	0.488	-1.5	0.022	-1.8	0.055	1.5	0.078	-1.4
47	0.203	-0.4	0.071	-0.4	0.294	-0.4	0.073	0.0	0.764	0.0	0.049	0.9	0.035	-0.5	0.105	-0.4
48	0.304	1.3	0.098	1.0	0.481	1.9	0.079	0.3	0.782	0.1	0.049	0.9	0.055	1.5	0.148	1.0
49	0.241	0.2	0.089	0.5	0.349	0.3	0.072	-0.1	0.792	0.1	0.049	0.9	0.047	0.8	0.136	0.6
50	0.235	0.1			0.513	2.3			1.383	3.2	0.022	-1.8	0.023	-1.7		
51	0.18	-0.8			0.279	-0.6			0.75	-0.1	0.037	-0.3	0.042	0.2	0.111	-0.2
52	0.188	-0.7			0.302	-0.3			0.802	0.2	0.043	0.3	0.04	0.0	0.127	0.3
53	0.241	0.2	0.078	0.0	0.345	0.2	0.064	-0.5	0.766	0.0	0.032	-0.8	0.044	0.4	0.139	0.7
54	0.197	-0.5			0.278	-0.6			0.72	-0.2	0.04	0.0	0.01	-3.0		
55	0.146	-1.4	0.028	-2.6	0.137	-2.3	0.014	-3.3	0.551	-1.1	0.044	0.4	0.031	-0.8	0.021	-3.3
56	FN	-3.8			FN	-3.9	FN	-3.5	0.75	-0.1	FN	-3.0	FN	-3.0	FN	-3.7
57	0.244	0.3			0.356	0.3			0.744	-0.1	0.054	1.4	0.044	0.4	0.135	0.6
58	0.22	-0.1			0.26	-0.8			0.8	0.2	0.05	1.0	0.05	1.1	0.08	-1.3
59	0.264	0.6	0.088	0.5	0.321	-0.1	0.07	-0.2	0.568	-1.0	0.035	-0.6	0.05	1.0	0.118	0.0
60	1.303	>5	0.085	0.3	0.338	0.1	0.188	>5	0.819	0.3	0.051	1.1	0.027	-1.3	0.119	0.1
61	0.242	0.3	0.092	0.7	0.331	0.0	0.088	0.9	0.906	0.7	0.043	0.3	0.043	0.3	0.114	-0.1
62	0.22	-0.1							0.83	0.3			0.045	0.5		
63	0.212	-0.3	0.074	-0.2	0.314	-0.2	0.085	0.7	0.698	-0.4	0.036	-0.4	0.035	-0.4	0.095	-0.8
64	0.199	-0.5	0.096	0.9	0.296	-0.4	0.075	0.1	0.634	-0.7	0.042	0.2	0.033	-0.7	0.125	0.3
65	0.263	0.6	0.099	1.0	0.36	0.4	0.07	-0.2	0.63	-0.7	0.042	0.2	0.039	-0.1	0.148	1.0
66	0.259	0.5	0.082	0.2	0.297	-0.4	0.102	1.6	0.707	-0.3	0.038	-0.2	0.042	0.2	0.118	0.0
67	0.224	-0.1	0.065	-0.7	0.357	0.4	0.081	0.5	0.961	1.0	0.046	0.5	0.044	0.5	0.119	0.1
68													0.05	1.1		
69	0.166	-1.1			FN	-3.9	0.02	-2.9							FN	-3.7
70	0.228	0.0	0.073	-0.3	0.335	0.1	0.072	0.0	0.836	0.4	0.034	-0.6	0.041	0.2	0.106	-0.4
71	0.222	-0.1	0.081	0.1	0.318	-0.1	0.828	>5	0.923	0.8	0.041	0.1	FN	-3.0	0.137	0.7
72	0.231	0.1			0.331	0.0			0.732	-0.2	0.023	-1.7	0.039	-0.1	0.11	-0.3
73	0.24	0.2	0.063	-0.8	0.29	-0.5	0.164	5.0	0.788	0.1	0.042	0.2	0.06	2.1	0.079	-1.3

Table 10d. Results for flonicamid, fluxapyroxad, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Flonicamid	Z-scores (FFP RSD (25%)	Fluxapyroxad	Z-scores (FFP RSD (25%)	Linuron	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Metrafenone	Z-scores (FFP RSD (25%)	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Spiroxamine	Z-scores (FFP RSD (25%)	Trifluralin	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.104**		**0.165**		**0.074**		**0.101**		**0.376**		**0.201**		**0.074**		**0.060**		**0.040**	
38	0.093	-0.4	0.18	0.4	0.067	-0.4	0.089	-0.5	0.35	-0.3	FN	-3.8	0.081	0.4	0.046	-0.9	0.038	-0.2
39					0.094	1.1	0.132	1.2			0.262	1.2	0.099	1.4	0.063	0.2	0.052	1.2
40	0.088	-0.6			0.068	-0.3	0.093	-0.3					0.079	0.3	0.045	-1.0	0.032	-0.8
41																		
42	0.124	0.8			0.068	-0.3	0.111	0.4	0.124	-2.7	0.212	0.2	0.121	2.6	0.059	-0.1	0.045	0.5
43	0.1	-0.2	0.16	-0.1	0.077	0.2	0.1	-0.1	0.36	-0.2	0.17	-0.6	0.084	0.6	0.051	-0.6	0.045	0.5
44	0.093	-0.4	0.156	-0.2	0.071	-0.2	0.105	0.1	0.428	0.5	0.196	-0.1	0.064	-0.5	0.055	-0.3	0.044	0.4
45	0.138	1.3			0.106	1.7			0.447	0.8			0.085	0.6	0.067	0.5	0.041	0.1
46					0.08	0.3	0.106	0.2			0.254	1.0	0.064	-0.5	0.068	0.6	0.021	-1.9
47	2.786	>5	0.175	0.2	0.079	0.3	0.091	-0.4	0.389	0.1	0.185	-0.3	0.066	-0.4	0.053	-0.5	0.042	0.2
48	0.127	0.9	0.237	1.7	0.1	1.4	0.168	2.6	0.522	1.5	0.245	0.9	0.08	0.3	0.08	1.3	0.04	-0.1
49	0.115	0.4	0.178	0.3	0.077	0.2	0.118	0.7	0.39	0.1	0.256	1.1	0.079	0.3	0.058	-0.2	0.042	0.2
50																		
51											0.23	0.6					0.052	1.2
52											0.228	0.5					0.058	1.8
53	0.099	-0.2	0.189	0.6	0.072	-0.1	0.144	1.7	0.402	0.3	0.223	0.4	0.077	0.2	0.048	-0.8	0.047	0.7
54																		
55					0.044	-1.6			0.345	-0.3	0.039	-3.2	0.031	-2.3			0.036	-0.5
56					FN	-3.5	FN	-3.6					FN	-3.5	FN	-3.3	FN	-3.0
57	0.104	0.0			0.084	0.5	0.127	1.0	0.375	0.0	0.22	0.4			0.074	0.9	0.04	0.0
58	0.09	-0.5			0.08	0.3	0.1	-0.1	0.33	-0.5	0.18	-0.4	0.07	-0.2			0.04	0.0
59	0.117	0.5	0.204	0.9	0.075	0.1	0.116	0.6	0.453	0.8	0.209	0.2	0.077	0.2	0.06	0.0	0.026	-1.4
60	0.097	-0.3	FN	-3.8	0.067	-0.4	0.085	-0.6	0.73	3.8	0.021	-3.6	0.075	0.1	0.035	-1.7	0.034	-0.6
61	0.124	0.8	0.174	0.2	0.076	0.1	0.144	1.7	0.415	0.4	0.262	1.2	0.097	1.3	0.061	0.1	0.04	-0.1
62	0.086	-0.7			0.066	-0.4							0.075	0.1			0.04	0.0
63	0.102	-0.1	0.144	-0.5	0.074	0.0	0.092	-0.4	0.385	0.1	0.15	-1.0	0.065	-0.5	0.085	1.7	0.038	-0.2
64	0.137	1.3	0.133	-0.8	0.063	-0.6	0.089	-0.5	0.422	0.5	0.213	0.2	0.068	-0.3	0.066	0.4	0.031	-0.9
65	0.109	0.2	0.193	0.7	0.079	0.3	0.11	0.3	0.408	0.3	0.218	0.3	0.085	0.6	0.068	0.5	0.038	-0.2
66	0.106	0.1	0.155	-0.2	0.089	0.8	0.118	0.7	0.406	0.3	0.315	2.3	0.117	2.3	0.082	1.5	0.037	-0.3
67	0.102	-0.1	0.145	-0.5	0.081	0.4	0.092	-0.4	0.398	0.2	0.201	0.0	0.056	-1.0	0.07	0.7	0.045	0.4
68																		
69					0.065	-0.5												
70	0.098	-0.2	0.165	0.0	0.072	-0.1	0.103	0.1	0.382	0.1	0.202	0.0	0.07	-0.2	0.058	-0.2	0.034	-0.7
71	0.099	-0.2	0.168	0.1	0.075	0.1	0.106	0.2	0.402	0.3	0.21	0.2	0.07	-0.2	0.054	-0.4	0.044	0.4
72													0.06	-0.7	0.05	-0.7	0.037	-0.3
73	0.132	1.1	0.173	0.2	0.071	-0.2	0.088	-0.5	0.346	-0.3	0.14	-1.2	0.036	-2.0	0.049	-0.7	0.049	0.9

Table 10e. Results for azoxystrobin, bixafen, boscalid, carbendazim, cypermethrin, deltamethrin-cis, endosulfan-sulfate, epoxiconazole in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z-scores (FFP RSD (25%)	Bixafen	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Carbendazim	Z-scores (FFP RSD (25%)	Cypermethrin	Z-scores (FFP RSD (25%)	Deltamethrin-cis	Z-scores (FFP RSD (25%)	Endosulfan-sulfate	Z-scores (FFP RSD (25%)	Epoxiconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.228**		**0.079**		**0.328**		**0.073**		**0.766**		**0.040**		**0.040**		**0.117**	
74	0.16	-1.2	0.055	-1.2	0.261	-0.8	0.044	-1.6	0.687	-0.4	0.033	-0.7	0.029	-1.1	0.119	0.1
75									0.131	-3.3	0.011	-2.9				
76	0.191	-0.6	0.065	-0.7	0.274	-0.7	0.082	0.5	0.599	-0.9	0.035	-0.5	0.035	-0.5	0.108	-0.3
77	0.198	-0.5			0.294	-0.4			0.778	0.1	0.041	0.1	0.038	-0.2	0.115	-0.1
78	0.246	0.3	0.094	0.8	0.333	0.1	0.124	2.8	1.31	2.8	0.091	>5	FN	-3.0	0.122	0.2
79	0.267	0.7							1.11	1.8	FN	-3.0	0.055	1.6	0.135	0.6
80	0.208	-0.3	0.102	1.2	0.27	-0.7	0.074	0.1	0.895	0.7	0.046	0.5	0.035	-0.4	0.093	-0.8
81	0.269	0.7			0.416	1.1	0.038	-1.9							0.152	1.2
82	0.247	0.3	0.086	0.4	0.333	0.1	0.067	-0.3	0.841	0.4	0.038	-0.2	0.039	-0.1	0.124	0.2
83	0.243	0.3	0.087	0.4	0.389	0.7	0.052	-1.1	0.697	-0.4	0.053	1.3	0.05	1.1	0.136	0.6
84	0.215	-0.2	0.07	-0.4	0.29	-0.5	0.07	-0.2	0.75	-0.1	0.035	-0.5	0.035	-0.5	0.08	-1.3
85									FN	-3.9	FN	-3.0	FN	-3.0		
86													FN	-3.0		
87	0.247	0.3	0.068	-0.5	0.34	0.1	0.062	-0.6	0.812	0.2	0.046	0.6	0.049	0.9	0.149	1.1
88	0.266	0.7			0.364	0.4	0.073	0.0	0.886	0.6	0.043	0.3			0.146	1.0
89	0.226	0.0	0.09	0.6	0.312	-0.2	0.092	1.0	0.472	-1.5	0.034	-0.6	0.031	-0.9	0.11	-0.3
90																
91	0.207	-0.4	0.069	-0.5	0.313	-0.2	0.066	-0.4	0.656	-0.6	0.028	-1.2	0.039	-0.1	0.096	-0.7
92	0.182	-0.8			0.273	-0.7	0.083	0.6	0.717	-0.3	0.027	-1.3	0.027	-1.3	0.091	-0.9
93	0.311	1.5					0.161	4.9	0.19	-3.0	FN	-3.0	FN	-3.0		
94																
95	FN	-3.8			0.242	-1.0	0.023	-2.8	0.962	1.0	0.079	3.9	0.06	2.0	0.033	-2.9
96	0.248	0.4	0.054	-1.3	0.316	-0.1	0.336	>5	0.827	0.3	0.031	-0.9	0.02	-1.9	0.105	-0.4
97	0.132	-1.7	0.048	-1.5	0.203	-1.5	0.031	-2.3	0.408	-1.9	0.02	-2.0	0.042	0.2	0.078	-1.3
98	0.233	0.1	0.085	0.3	0.337	0.1	0.084	0.6	0.944	0.9	0.044	0.4	0.042	0.2	0.123	0.2
99	0.222	-0.1	0.068	-0.5	0.326	0.0	0.02	-2.9	0.554	-1.1	FN	-3.0	0.03	-1.0	0.14	0.8
100	0.226	0.0			0.374	0.6			0.757	0.0	0.062	2.2				
101																
102	0.256	0.5			0.292	-0.4	0.059	-0.8	0.072	-3.6	0.093	>5	0.033	-0.7	0.081	-1.2
103	0.404	3.1			FN	-3.9			1.71	4.9	FN	-3.0	0.033	-0.7		
104	0.218	-0.2			0.301	-0.3	0.04	-1.8	0.799	0.2	FN	-3.0				
105	0.245	0.3			0.325	0.0	0.058	-0.8	0.783	0.1			0.062	2.3	0.141	0.8
106	0.266	0.7	0.085	0.3	0.389	0.7	0.148	4.1	0.797	0.2	0.048	0.8	0.037	-0.3	0.145	0.9
107	0.199	-0.5	0.062	-0.9	0.309	-0.2	0.059	-0.8	0.677	-0.5	0.04	0.0	0.039	-0.1	0.088	-1.0
108					0.263	-0.8			0.593	-0.9	0.037	-0.3	0.038	-0.2		
109	0.236	0.1	0.107	1.4	0.317	-0.1	0.068	-0.3	0.751	-0.1	0.053	1.3	0.036	-0.4	0.128	0.4

Table 10f. Results for flonicamid, fluxapyroxad, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Flonicamid	Z-scores (FFP RSD (25%)	Fluxapyroxad	Z-scores (FFP RSD (25%)	Linuron	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Metrafenone	Z-scores (FFP RSD (25%)	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Spiroxamine	Z-scores (FFP RSD (25%)	Trifluralin	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.104**		**0.165**		**0.074**		**0.101**		**0.376**		**0.201**		**0.074**		**0.060**		**0.040**	
74	0.079	-1.0			0.06	-0.7	0.073	-1.1	0.402	0.3	0.125	-1.5	0.109	1.9	0.072	0.8	0.033	-0.7
75																		
76	0.104	0.0	0.171	0.1	0.071	-0.2	0.092	-0.4	0.279	-1.0	0.183	-0.4	0.055	-1.0	0.061	0.1	0.036	-0.4
77											0.26	1.2					0.051	1.1
78					0.09	0.9	0.11	0.3							0.075	1.0	0.038	-0.2
79																	0.042	0.2
80	0.113	0.3	0.172	0.2	0.067	-0.4	0.094	-0.3	0.266	-1.2	0.167	-0.7	0.054	-1.1	0.053	-0.5	0.038	-0.3
81					0.079	0.3							0.079	0.3	0.047	-0.9		
82	0.113	0.3			0.054	-1.1	0.129	1.1	0.398	0.2	0.222	0.4	0.082	0.4	0.07	0.7	0.033	-0.7
83	0.089	-0.6	0.188	0.6	0.07	-0.2	0.128	1.1	0.413	0.4	0.216	0.3	0.088	0.8	0.063	0.2	0.041	0.1
84	0.14	1.4	0.15	-0.4	0.07	-0.2	0.081	-0.8	0.34	-0.4	0.175	-0.5	0.064	-0.5	0.065	0.3	0.026	-1.4
85																		
86																	0.052	1.1
87	0.11	0.2	0.153	-0.3	0.075	0.1	0.096	-0.2	0.377	0.0	0.201	0.0	0.098	1.3	0.059	-0.1	0.04	0.0
88	0.107	0.1			0.07	-0.2	0.091	-0.4	0.432	0.6			0.077	0.2	0.059	-0.1		
89	0.11	0.2	0.165	0.0	0.079	0.3	0.098	-0.1	0.425	0.5	0.2	0.0	0.085	0.6	0.053	-0.5	0.041	0.0
90																		
91	0.081	-0.9	0.163	-0.1	0.065	-0.5	0.099	-0.1	0.329	-0.5	0.184	-0.3	0.061	-0.7	0.05	-0.7	0.036	-0.4
92	0.09	-0.5			0.032	-2.3	0.068	-1.3	0.274	-1.1	FN	-3.8	0.059	-0.8	0.035	-1.7	0.031	-0.9
93																		
94																		
95	0.028	-2.9			0.046	-1.5			0.386	0.1			0.036	-2.1	FN	-3.3	0.042	0.2
96	0.1	-0.2	FN	-3.8	0.073	0.0	0.082	-0.8	0.269	-1.1			0.077	0.2	0.073	0.9	0.035	-0.5
97	0.398	>5	0.112	-1.3	0.043	-1.7	0.068	-1.3	0.195	-1.9	0.128	-1.5	0.032	-2.2	0.021	-2.6	0.094	>5
98	0.124	0.8	0.179	0.3	0.078	0.2	0.103	0.1	0.408	0.3	0.208	0.1	0.07	-0.2	0.065	0.3	0.044	0.4
99	0.058	-1.8			0.064	-0.5	0.094	-0.3	0.254	-1.3	0.172	-0.6	0.064	-0.5	0.044	-1.1	0.032	-0.8
100													0.079	0.3				
101																		
102	0.084	-0.8					0.13	1.1	0.269	-1.1			0.078	0.2	0.062	0.1	0.034	-0.6
103	FN	-3.6			0.045	-1.6									FN	-3.3	0.01	-3.0
104					0.031	-2.3			0.302	-0.8			0.063	-0.6			0.054	1.4
105													0.056	-1.0			0.043	0.3
106	0.113	0.3	0.178	0.3	0.08	0.3	0.113	0.5	0.391	0.2	0.237	0.7	0.079	0.3	0.051	-0.6	0.038	-0.2
107	0.09	-0.5	0.145	-0.5	0.059	-0.8	0.07	-1.2	0.289	-0.9	0.128	-1.5	0.054	-1.1	0.053	-0.5	0.039	-0.1
108																		
109	0.106	0.1	0.189	0.6	0.073	-0.1	0.12	0.7	0.375	0.0	0.225	0.5	0.082	0.4	0.063	0.2	0.039	-0.1

Table 10g. Results for azoxystrobin, bixafen, boscalid, carbendazim, cypermethrin, deltamethrin-cis, endosulfan-sulfate, epoxiconazole in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z-scores (FFP RSD (25%)	Bixafen	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Carbendazim	Z-scores (FFP RSD (25%)	Cypermethrin	Z-scores (FFP RSD (25%)	Deltamethrin-cis	Z-scores (FFP RSD (25%)	Endosulfan-sulfate	Z-scores (FFP RSD (25%)	Epoxiconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.228**		**0.079**		**0.328**		**0.073**		**0.766**		**0.040**		**0.040**		**0.117**	
110	0.227	0.0	0.083	0.2	0.399	0.9	0.05	-1.3	0.752	-0.1	0.046	0.6	0.052	1.3	0.129	0.4
111	0.171	-1.0	0.06	-0.9	0.292	-0.4	0.072	0.0	0.874	0.6	0.033	-0.7	0.011	-2.9	0.088	-1.0
112	0.226	0.0	0.09	0.6	0.517	2.3	0.09	0.9	0.656	-0.6	0.026	-1.4	0.044	0.5	0.099	-0.6
113																
114									0.803	0.2	0.042	0.2	0.052	1.3		
115																
116	0.266	0.7			0.434	1.3	0.09	0.9	0.574	-1.0	0.062	2.2			0.14	0.8
117													0.051	1.1		
118									0.947	0.9	0.02	-2.1	0.045	0.6		
119					0.276	-0.6			0.475	-1.5	0.025	-1.5	0.027	-1.3		
120	0.195	-0.6	0.06	-0.9	0.33	0.0	0.075	0.1	1.33	2.9	0.056	1.6	0.051	1.2	0.115	-0.1
121	0.23	0.0	0.089	0.5	0.338	0.1	0.073	0.0	0.814	0.2	0.042	0.2	0.057	1.8	0.121	0.1
122	0.196	-0.6	0.099	1.0	0.282	-0.6	0.066	-0.4	0.704	-0.3	FN	-3.0	0.045	0.5	0.143	0.9
123	0.227	0.0			0.328	0.0	0.051	-1.2	0.738	-0.1	0.037	-0.3	0.042	0.2	0.119	0.1
124	0.226	0.0	0.066	-0.6	0.358	0.4	0.077	0.3	1.018	1.3	0.059	1.9	0.054	1.5	0.097	-0.7
125	0.21	-0.3			0.33	0.0	0.08	0.4	0.75	-0.1	0.04	0.0	0.04	0.0	0.11	-0.3
126	0.228	0.0	0.087	0.4	0.317	-0.1	0.067	-0.3	0.872	0.6	0.051	1.1	0.04	0.0	0.109	-0.3
127	0.373	2.6			0.688	4.4			1.584	4.3			FN	-3.0		
128													0.052	1.3		
129																
130																
131																
132	0.211	-0.3			0.283	-0.5			0.798	0.2	0.043	0.3	0.05	1.1	0.109	-0.3
133	0.267	0.7			0.334	0.1			0.866	0.5	FN	-3.0	FN	-3.0	0.115	-0.1
134	0.188	-0.7	0.068	-0.5	0.293	-0.4	0.103	1.7	0.51	-1.3	0.035	-0.5	0.042	0.2	0.087	-1.0
135									0.522	-1.3	0.047	0.7	0.033	-0.7		
136	0.19	-0.7			0.27	-0.7	0.04	-1.8	0.65	-0.6	0.037	-0.3	0.035	-0.5		
137																
138									0.781	0.1	0.038	-0.2	0.049	0.9		
139																
140	0.191	-0.6			0.315	-0.2	0.016	-3.1	1.01	1.3	0.041	0.1	0.027	-1.3	0.093	-0.8
141	0.208	-0.3			0.291	-0.4	0.061	-0.7	0.872	0.6	0.034	-0.6	0.04	0.1	0.105	-0.4
142	0.195	-0.6			0.348	0.2	0.109	2.0	0.354	-2.2	0.033	-0.7	0.026	-1.4	0.117	0.0
143	0.19	-0.7			0.306	-0.3	0.058	-0.8	0.657	-0.6	0.03	-1.0			0.134	0.6
144									1.422	3.4	0.044	0.4	0.044	0.4		
145	0.224	-0.1	0.084	0.2	0.307	-0.3	0.05	-1.3	0.882	0.6	0.073	3.3	0.053	1.4	0.121	0.1

Table 10h. Results for flonicamid, fluxapyroxad, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Flonicamid	Z-scores (FFP RSD (25%)	Fluxapyroxad	Z-scores (FFP RSD (25%)	Linuron	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Metrafenone	Z-scores (FFP RSD (25%)	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Spiroxamine	Z-scores (FFP RSD (25%)	Trifluralin	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.104**		**0.165**		**0.074**		**0.101**		**0.376**		**0.201**		**0.074**		**0.060**		**0.040**	
110	0.097	-0.3	0.218	1.3	0.082	0.4	0.1	-0.1	0.388	0.1	0.203	0.0	0.096	1.2	0.08	1.3	0.035	-0.5
111	0.113	0.3	FN	-3.8	0.07	-0.2	0.082	-0.8	0.314	-0.7	0.163	-0.8	0.052	-1.2	0.05	-0.7	0.034	-0.6
112	0.11	0.2	0.151	-0.3	0.101	1.5	0.13	1.1	0.405	0.3	0.333	2.6	0.07	-0.2	0.093	2.2	0.037	-0.4
113																		
114																		
115																		
116					0.081	0.4	0.115	0.5					0.071	-0.2			0.036	-0.4
117																		
118																		
119	0.102	-0.1											0.044	-1.6	FN	-3.3		
120	0.02	-3.2	0.135	-0.7	FN	-3.5	0.1	-0.1	0.504	1.4	0.15	-1.0	0.05	-1.3	0.047	-0.9	0.048	0.8
121	0.095	-0.3	0.166	0.0	0.088	0.8	0.081	-0.8	0.412	0.4	0.193	-0.2	0.064	-0.5	0.043	-1.1	0.042	0.2
122	0.081	-0.9	0.173	0.2	0.066	-0.4	0.159	2.3	0.347	-0.3	0.189	-0.2	0.15	4.1	0.067	0.5	0.036	-0.4
123					0.089	0.8	0.104	0.1	0.388	0.1					0.087	1.8	0.042	0.2
124	0.11	0.2	0.141	-0.6	0.079	0.3	0.095	-0.3	0.395	0.2	0.178	-0.5	0.063	-0.6	0.052	-0.5	0.05	0.9
125					0.08	0.3	0.09	-0.4					0.06	-0.7	0.06	0.0	0.04	0.0
126	0.086	-0.7	0.161	-0.1	0.095	1.2	0.072	-1.2	0.502	1.3	0.204	0.1	0.078	0.2	0.057	-0.2	0.05	0.9
127													0.157	4.5				
128																		
129																		
130																		
131																		
132											0.26	1.2					0.05	1.0
133							0.104	0.1			0.317	2.3			0.163	>5	0.058	1.7
134	0.101	-0.1	0.136	-0.7	0.066	-0.4	0.087	-0.6	0.337	-0.4	0.146	-1.1	0.057	-0.9	0.045	-1.0	0.039	-0.2
135																		
136					0.08	0.3							0.08	0.3			0.16	>5
137																		
138																		
139																		
140					0.071	-0.2					FN	-3.8	0.051	-1.2	0.05	-0.7	0.031	-0.9
141	0.093	-0.4	0.157	-0.2	0.064	-0.6	0.094	-0.3	0.342	-0.4	0.168	-0.7	0.058	-0.9	0.047	-0.8	0.04	0.0
142					0.07	-0.2	0.11	0.3	FN	-3.9	0.202	0.0	0.075	0.1	0.06	0.0	0.044	0.4
143	0.1	-0.2			0.062	-0.6	0.104	0.1	0.294	-0.9			0.072	-0.1	0.055	-0.3	0.033	-0.7
144																	0.044	0.4
145	0.081	-0.9	0.173	0.2	0.069	-0.3	0.113	0.5	0.317	-0.6	0.236	0.7	0.062	-0.7	0.061	0.1	0.044	0.4

Table 10i. Results for azoxystrobin, bixafen, boscalid, carbendazim, cypermethrin, deltamethrin-cis, endosulfan-sulfate, epoxiconazole in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Azoxystrobin	Z-scores (FFP RSD (25%)	Bixafen	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Carbendazim	Z-scores (FFP RSD (25%)	Cypermethrin	Z-scores (FFP RSD (25%)	Deltamethrin-cis	Z-scores (FFP RSD (25%)	Endosulfan-sulfate	Z-scores (FFP RSD (25%)	Epoxiconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.228**		**0.079**		**0.328**		**0.073**		**0.766**		**0.040**		**0.040**		**0.117**	
146									0.61	-0.8	0.037	-0.3	0.011	-2.9		
147	0.16	-1.2			0.326	0.0	0.065	-0.4	0.357	-2.1	0.019	-2.1	0.026	-1.3	0.091	-0.9
148													0.057	1.7		
149																
150	0.231	0.1	0.075	-0.2	0.328	0.0	0.102	1.6	0.845	0.4	FN	-3.0	0.035	-0.5	0.113	-0.1
151																
152																
153	0.178	-0.9			0.288	-0.5	0.159	4.7	0.38	-2.0	FN	-3.0	0.028	-1.2	0.094	-0.8
154	0.215	-0.2			0.38	0.6	0.067	-0.3	0.659	-0.6	0.04	0.0	0.036	-0.4	0.088	-1.0
155	0.24	0.2			0.322	-0.1	0.064	-0.5	0.717	-0.3			0.038	-0.1		
156	0.33	1.8			0.34	0.1	0.065	-0.4	0.69	-0.4	FN	-3.0	0.025	-1.5	0.095	-0.8
157	0.223	-0.1			0.366	0.5	0.068	-0.3	0.801	0.2	0.035	-0.5	0.061	2.2	0.135	0.6
158																
159	0.212	-0.3	0.091	0.6	0.294	-0.4	0.095	1.2	0.817	0.3	0.038	-0.2	0.034	-0.5	0.109	-0.3
160	0.237	0.2	0.079	0.0	0.364	0.4	0.066	-0.3	0.698	-0.4	0.037	-0.4	0.035	-0.5	0.135	0.6
161	0.245	0.3	0.068	-0.5	0.318	-0.1	0.063	-0.5	0.734	-0.2	0.025	-1.5	0.035	-0.5	0.11	-0.3
162	0.313	1.5			0.357	0.4			0.52	-1.3			FN	-3.0	0.08	-1.3
163	0.188	-0.7			0.32	-0.1			0.323	-2.3	FN	-3.0	0.046	0.6		

Table 10j. Results for flonicamid, fluxapyroxad, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin in mg/kg, the corresponding z-scores, MRRLs and the assigned values.

Laboratory code	Flonicamid	Z-scores (FFP RSD (25%)	Fluxapyroxad	Z-scores (FFP RSD (25%)	Linuron	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Metrafenone	Z-scores (FFP RSD (25%)	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Spiroxamine	Z-scores (FFP RSD (25%)	Trifluralin	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assign. value	**0.104**		**0.165**		**0.074**		**0.101**		**0.376**		**0.201**		**0.074**		**0.060**		**0.040**	
146																		
147	0.105	0.0			0.068	-0.3			0.316	-0.6			0.06	-0.7	0.037	-1.6	0.03	-1.1
148																		
149																		
150	0.117	0.5	0.155	-0.2	0.087	0.7	0.105	0.1	0.385	0.1	0.169	-0.6	0.068	-0.3	0.065	0.3	0.041	0.1
151																		
152																		
153	0.087	-0.7			0.062	-0.6	0.088	-0.5	0.23	-1.6	FN	-3.8	0.071	-0.2	0.071	0.7	0.026	-1.4
154			FN	-3.8	0.064	-0.5	0.077	-1.0	0.435	0.6			0.059	-0.8	0.056	-0.3	0.036	-0.4
155													0.07	-0.2				
156							0.08	-0.8							0.04	-1.3	0.05	1.0
157					0.071	-0.2	0.053	-1.9			0.174	-0.5	0.096	1.2	0.08	1.3	0.04	0.0
158																		
159	0.09	-0.5	0.176	0.3	0.061	-0.7	0.083	-0.7	0.345	-0.3	0.225	0.5	0.09	0.9	0.088	1.8	0.041	0.1
160	0.083	-0.8	0.184	0.5	0.076	0.1	0.118	0.7	0.409	0.3	0.224	0.5	0.088	0.8	0.06	0.0	0.028	-1.2
161	0.089	-0.6			0.073	-0.1	0.092	-0.4	0.322	-0.6	0.164	-0.7	0.068	-0.3	0.05	-0.7	0.037	-0.3
162									0.21	-1.8	0.296	1.9			0.11	3.3		
163																		

3.3.2 Sum of Weighted Z-Scores (AZ^2) – Category A

To be classified into Category A, the labs had to submit quantitative results for at least 90 % of the pesticides present in the Test Item (≥15 pesticide residues, inclusive of false negatives) and report no false positive results. For the 67 EU and EFTA laboratories in Category A, the results were additionally evaluated by calculating the Average of the Squared -Score (AZ^2). Of the 67 participants, 57 participants (85 %) obtained AZ^2 values at or below 2 (good) and 7 participants (10 %) obtained AZ^2 values above 2 but at, or below, 3 (satisfactory) and 3 participants (4 %) obtained AZ^2 values above 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 11.**

Table 11 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.

Lab code	No. of detected pesticides	AZ^2	False negative	Classification	NRL
2	17	0.2	0	Good	
3	16	0.2	0	Good	
4	17	0.2	0	Good	NRL
5	17	0.1	0	Good	
11	17	0.3	0	Good	
12	15	3.2	1	Unsatisfactory	
13	17	0.2	0	Good	NRL
14	17	0.1	0	Good	
16	17	0.6	0	Good	
17	17	0.6	0	Good	NRL
18	17	1.1	0	Good	
19	17	0.2	0	Good	
20	16	0.4	0	Good	NRL
21	17	1.0	1	Good	
26	15	0.3	0	Good	NRL
30	17	1.1	1	Good	
32	15	0.3	0	Good	
33	16	4.1	1	Unsatisfactory	
34	17	1.0	0	Good	
35	17	1.4	0	Good	NRL
38	17	1.3	1	Good	
42	15	3.4	0	Unsatisfactory	
43	17	0.3	0	Good	
44	17	0.5	0	Good	
47	17	1.6	0	Good	
48	17	2.4	0	Satisfactory	NRL
49	17	0.2	0	Good	
53	17	0.4	0	Good	
59	17	0.4	0	Good	
60	17	5.8	1	Unsatisfactory	
61	17	0.5	0	Good	

Lab code	No. of detected pesticides	AZ^2	False negative	Classification	NRL
63	17	0.4	0	Good	
64	17	0.4	0	Good	
65	17	0.3	0	Good	
66	17	1.0	0	Good	NRL
67	17	0.3	0	Good	
70	17	0.1	0	Good	
71	17	2.1	1	Satisfactory	
73	17	2.4	0	Satisfactory	
74	16	1.1	0	Good	
76	17	0.3	0	Good	
80	17	0.4	0	Good	NRL
82	16	0.3	0	Good	NRL
83	17	0.5	0	Good	NRL
84	17	0.5	0	Good	
87	17	0.3	0	Good	NRL
89	17	0.4	0	Good	
91	17	0.3	0	Good	NRL
92	15	2.2	1	Satisfactory	
96	16	3.0	1	Satisfactory	
97	17	5.7	0	Unsatisfactory	NRL
98	17	0.2	0	Good	
99	16	1.9	1	Good	
106	17	1.3	0	Good	
107	17	0.6	0	Good	NRL
109	17	0.3	0	Good	
110	17	0.6	0	Good	
112	17	1.5	0	Good	
120	17	2.5	1	Satisfactory	NRL
121	17	0.4	0	Good	
122	17	2.1	1	Satisfactory	NRL
124	17	0.6	0	Good	NRL
126	17	0.5	0	Good	NRL
134	17	0.7	0	Good	NRL
141	16	0.3	0	Good	NRL
145	17	1.0	0	Good	NRL
150	17	0.8	1	Good	
153	15	3.9	2	Unsatisfactory	
159	17	0.5	0	Good	NRL
160	17	0.3	0	Good	NRL
161	16	0.3	0		

Table 12 shows the 68 EU and EFTA laboratories in Category B and the 10 laboratories from Third Countries. The table includes information on the number of reported results, the number of acceptable z-scores as well as information on false negative and false positive results.

Table 12 Number of pesticides analysed, number of acceptable z-scores, false negative and positive for the laboratories in Category B.

Lab code	No. of detected pesticides	No. of acceptable z-scores	False negative	False positive	NRL
111 [1]	17	16	1	1	
46	14	13	0	0	
142	14	13	1	0	NRL
154	14	13	1	0	
10	13	13	0	0	
27	13	9	0	0	
39	13	11	0	0	
40	13	13	0	0	
45	13	13	0	0	
55	13	10	0	0	
57	13	13	0	0	
58	13	13	0	0	
95	13	10	2	0	NRL
102	13	11	0	0	
143	13	13	0	0	
147	13	13	0	1	
157	13	13	0	0	
1	12	12	0	1	
7	12	12	0	0	NRL
56	12	4	11	0	
78	12	11	1	0	
88	12	12	0	0	
123	12	12	0	0	
125	12	12	0	0	
140	12	10	1	0	
8	11	10	0	0	
29	10	10	0	0	
116	10	10	0	0	
133	10	9	2	0	
156	10	10	1	0	NRL
23	9	7	2	0	
36	9	8	0	0	NRL
72	9	9	0	0	
103	9	4	4	0	
104	9	9	1	1	NRL
136	9	8	0	0	
24	8	8	0	0	

Lab code	No. of detected pesticides	No. of acceptable z-scores	False negative	False positive	NRL
31	8	6	0	0	
51	8	8	0	0	
52	8	8	0	0	
77	8	8	0	0	
105	8	8	0	0	
132	8	8	0	0	
162	8	7	1	0	
15	7	6	0	0	
62	7	7	0	0	
81	7	7	0	0	
119	7	6	1	0	
25	6	6	0	0	
37	6	6	0	0	
79	6	6	1	0	
155	6	6	0	0	
22	5	1	0	0	NRL
50	5	4	0	0	
54	5	5	0	0	
69	5	3	2	1	
93	5	4	2	0	
100	5	5	0	0	
127	5	2	1	0	
163	5	5	1	0	NRL
108	4	4	0	0	
144	4	3	0	0	
41	3	3	0	0	
85	3	2	3	0	
114	3	3	0	0	
118	3	3	0	0	
135	3	3	0	0	
138	3	3	0	0	NRL
146	3	3	0	0	
75	2	1	0	1	
86	2	2	1	0	
6	1	1	0	0	
9	1	1	0	0	
28	1	1	0	0	
68	1	1	0	0	
117	1	1	0	0	
128	1	1	0	0	
148	1	1	0	0	

[1] Laboratory moved from Category A to Category B due to a false positive result.

3.4 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-C1 in 2007 63 labs participated and in the latest EUPT-C8 141 labs participated. (**Table 13**). The number of pesticides included in the Target Pesticide List has also increased during the 8-year period, from 34 to 111 individual compounds. The number of spiked or incurred pesticides contained in the Test Items has in the same period increased from 7 to 19 (two of them not evaluated in this PT). Thus the demands put on the participating laboratories increase every year. Many laboratories have a limited scope and are therefore is not able to cover all pesticides in the PT. Of the laboratories submitting results 30 % submitted results for less than 10 out of the 17 pesticides present in the Test Item.

Table 13. Overall trends in participation, pesticides and performance of laboratories in the 7 EUPTs cereals focusing on MRM pesticides.

	EUPT-C1	EUPT-C2	EUPT-C3	EUPT-C4	EUPT-C5	EUPT-C6	EUPT-CF8
Type of test material	Wheat flour	Wheat flour	Oat flour	Rye flour	Rice flour	Barley flour	Wheat flour
Participants submitting results (EU and EFTA)	63	72	102	115	133	127	141
MRM pesticides in the Target Pesticide List	34	43	51	64	103	107	111
MRM pesticides in the test material	7	13	14	16	16	18	19
No. of results for MRM pesticides	323	830	981	1624	1521	1741	1893
Range of 'reported results', %	63 – 95	60 - 96	48 - 95	55 - 95	41-95	50-95	49-93
Acceptable z-scores, %	87	85	87	87	87	90	90
Questionable z-scores, %	7	12	8	6	4	5	6
Unacceptable z-scores, %	6	3	5	7	9	4	4
False negatives, %	2	3	3	4	3	1	3
Number of false positives	1	2	3	17	16	2	4
Catagory A, % of participating laboratories		60	46	46	44	55	50
Good SWZ/AZ^2, %		70	72	77	80	79	85
Satisfactory SWZ/AZ^2, %		9	15	8	15	14	10
Unsatisfactory SWZ/AZ^2, %		21	13	15	5	7	4

Improvement in the overall analytical performance (compound identification and accuracy of measurement) is, however, observed if looking at the percentage of acceptable, questionable, unacceptable z-scores, false negative and false positive results. Especially, the number of false positives has dropped significantly from 17 in EUPT-C4 to 2 in EUPT-C6 and now 4 in EUPT-CF8. Also the number of false negatives has decreased from 60 in EUPT-C4 to 40 and 42 in EUPT-F6 and EUPT-CF8, respectively. The percentage of Category A laboratories has varied but a general increase is indicated, with 44% in EUPT-C5 to 55% and 50% in EUPT-C6 to EUPT-CF8, respectively. However, it is difficult to assess any improvement/deterioration in laboratory performance between the six Proficiency Tests, because the pesticides in the Test item and the laboratories participating in the PTs have both significantly increased.

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

EUPT-CF8 consisted of wheat containing both incurred and spiked pesticides. The wheat had been sprayed in the field with commercially available pesticide formulations. The final Test Item contained the following pesticides: azoxystrobin, bixafen, boscalid, carbendazim, chlorothalonil, cypermethrin, deltamethrin-cis, endosulfan-sulfate, epoxiconazole, flonicamid, fluxapyroxad, lindane, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin. One

hundred and thirty-five laboratories, representing 28 EU and EFTA countries submitted results. Six further laboratories registered, but did not submit any results. All NRLs, except Finland (one out of two), and Latvia, participated in the PT. Malta was represented in the PT by the NRL for the UK. An additional 22 laboratories from EU candidate states and Third Countries registered for the PT and 15 submitted results. The Target Pesticide List distributed to the laboratories prior to the test contained 111 individual compounds.

The number of false positives and false negatives has varied between the EUPTs. The 4 false positive results in EUPT-CF8 were: captan, fenvalerate/esfenvalerate, HCH-beta and quinoxyfen. This small number is in good agreement with the majority of the previous EUPTs. The number of false negatives represented only 3% of the total number of results. This is also in good agreement with the percentage of false negatives reported in the previous EUPTs. The average Qn-RSD (robust RSD) was at 20 %, close to the FFP-RSD of 25 % with a range from 13 to 31 % for the individual compounds.

For azoxystrobin, bixafen, boscalid, epoxiconazole, flonicamid, fluxapyroxad, linuron, metconazole, metrafenone, prothioconazole-desthio, pyraclostrobin, spiroxamine and trifluralin acceptable results were obtained by 91-97% of the laboratories. For carbendazim, cypermethrin, deltamethrin-cis and endosulfan-sulfate acceptable results were obtained by 84-87% of the laboratories.

The EUPT-CF9 will be on maize and will be sent out during April 2015. The selection of pesticides will continue to focus 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. The MRRL will in general be lowered from 0.01 mg/kg to 0.005 mg/kg.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

[1] Regulation (EC) N° 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

[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] NMKL No. 195:2013. Pesticide residues. Analysis in foods with ethyl acetate extraction using gas and liquid chromatography with tandem mass spectrometric determination, Nordic Committee on Food Analysis

[5] 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.

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

[7] Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. SANCO/12571/2013. http://www.eurl-pesticides.eu/library/docs/allcrl/AqcGuidance_Sanco_2013_12571.pdf

[8] Yoshii et all, J. Agric. Food Chem. (2000): Degradation of malathion and phenthoate by glutathione reductase in wheat germ

[9] Yoshii et all, J. Health Science (2006): Malathion residue in wheat kernels is degraded by thion OPP-specific carboxylesterase

[10] Yoshii et all, J. Health Science (2007): Kinetic analysis for hydrolysis of malathion by carboxylesterase in wheat kernels.

APPENDICES

Appendix 1 List of laboratories registered to participate in the EUPT-CF8

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 - LUA	Vienna		Yes
Belgium	Scientific Institute of Public Health	Brussels	NRL	Yes
Belgium	Fytolab - Belgium	Gent - Zwijnaarde		Yes
Belgium	Federal Laboratory for Safety of Food Chain	Tervuren		Yes
Bulgaria	Central Laboratory for Chemical Testing and Control	Sofia	NRL	Yes
Bulgaria	SGS - Bulgaria Ltd.	Varna		Yes
Bulgaria	Fytolab	Plovdiv		Yes
Croatia	Croatian National Institute of Public Health	Zagreb	NRL	Yes
Croatia	Institute of Public Health, Split	Dalmatia County, Split		Yes
Croatia	Faculty of Food Technology and Biotechnology, Food Control Center	Zagreb		Yes
Croatia	Croatian Veterinary Institute	Zagreb		No
Croatia	Euroinspekt - Croatiakontrola d.o.o.	Zagreb		Yes
Cyprus	Laboratory of Pesticide Residues Analysis, State General Laboratory	Nicosia	NRL	Yes
Cyprus	Animal Feeds and Feed Additives Laboratory of the Analytical Laboratories of the Department of Agriculture	Nicosia		Yes
Czech Republic	Central Institute for Supervising and Testing in Agriculture	Brno	NRL	Yes
Czech Republic	Czech Agriculture and Food Inspection Authority	Praha	NRL	Yes
Czech Republic	Institute of Chemical Technology, Dept. of Food Chemistry and Analysis	Praha		Yes
Denmark	Danish Veterinary and Food Administration, Department of Residues	Ringsted	NRL	Yes
Estonia	Agricultural Research Centre, Saku, Lab for Residues and Contaminants	Saku	NRL	Yes
Finland	Finnish Customs Laboratory	Espoo	NRL	Yes
France	Service Commun des Laboratoires / Laboratoire Ile de France	Massy Cedex	NRL	Yes
France	Service Commun des Laboratoires / Laboratoire de Montpellier	Montpellier		Yes
France	Laboratoire Départemental d`Analyses des LANDES	Mont de Marsan		Yes
France	Analysis Center Mediterranean Pyrenees	perpignan		Yes
France	Laboratoire Départemental d`Analyses de la Sarthe, Département de Chimie	Le Mans		Yes
France	CERECO SUD	Garons		Yes
Germany	Federal Office of Consumer Protection and Food Safety, NRL for Pesticide Residues	Berlin	NRL	Yes
Germany	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei Mecklenburg-Vorpommern	Rostock		Yes

Country	Institution	City	NRL-CF	Report data
Germany	Food and Veterinary Institute	Oldenburg		Yes
Germany	CVUA-MEL Chemisches und Veterinäruntersuchungsamt Münsterland-Emscher-Lippe	Münster		Yes
Germany	State Laboratory Schleswig-Holstein	Neumünster		Yes
Germany	Landesamt für Verbraucherschutz - Sachsen-Anhalt	Halle/Saale		Yes
Germany	Landesuntersuchungsamt Institut für Lebensmittelchemie	Speyer		Yes
Germany	Chemisches und Veterinäruntersuchungsamt Rheinland, Standort	Bonn		Yes
Germany	Bavarian Health and Food Safety Authority Office	Erlangen		Yes
Germany	Chemisches und Veterinäruntersuchungsamt Ostwestfalen-Lippe	Detmold		Yes
Germany	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld		Yes
Germany	State Institute for Chemical and Veterinary Analysis of Food, Stuttgart (Residues)	Fellbach		Yes
Germany	Landesbetrieb Hessisches Landeslabor	Wiesbaden		Yes
Germany	Berlin-Brandenburg State Laboratory	Potsdam		Yes
Germany	Landwirtschaftliches Technologiezentrum Augustenberg	Karlsruhe		Yes
Germany	Niedersächsisches Landesamt für Verbraucherschutz und Lebensmittelsicherheit	Stade		Yes
Germany	Landwirtschaftliche Untersuchungs- und Forschungsanstalt	Speyer		Yes
Germany	State Department of Environmental and Agricultural Operations in Saxony	Nossen		Yes
Germany	Landesanstalt für Landwirtschaft, Forsten und Gartenbau	Halle/Saale		Yes
Germany	Thuringian Institute of Agriculture	Jena		Yes
Germany	LUFA-ITL GmbH	Kiel		Yes
Germany	Eurofins - Dr. Specht Laboratorien GmbH	Hamburg		Yes
Germany	Labor Friedle GmbH	Tegernheim		Yes
Greece	Benaki Phytopathological Institute, Pesticide Residues Laboratory	Kifissia	NRL	Yes
Greece	Regional Center of Plant Protection and Quality Control of Ioannina, Pesticide Residues Laboratory	Ioannina		Yes
Greece	General Chemical State Laboratory, D Division, Pesticide Residues Laboratory	Athens	NRL	Yes
Hungary	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-environment - Pesticide Analytical Laboratory	Velence	NRL	Yes
Hungary	National Food Chain Safety Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory	Miskolc		Yes
Hungary	Agricultural Office, Directorate of Plant Protection, Soil Conservation and Agri-Environment, Pesticide Residue Analytical Laboratory	Hódmezovásárhely		Yes
Hungary	National Food Chain Safety Office Directorate of Plant Protection, Soil Conservation and Agri-environment, Pesticide Residue Analytical Laboratory	Szolnok		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	Centro di referenza nazionale per la sorveglianza ed il controllo degli alimenti per animali	Genova	NRL	Yes
Italy	Istituto Superiore di Sanità, Pesticide Section	Roma		No
Italy	APPA Bolzano - Labor für Chromatographie	Bolzano		Yes
Italy	ARPA Emilia Romagna, Area Fitofarmaci	Ferrara		Yes
Italy	Environmental Regional Protection Agency - Laboratory of Pordenone	Pordenone		Yes
Italy	Laboratorio di Sanità Pubblica ASL	Bergamo		Yes
Italy	ARPA Puglia - Dipartimento di Bari	Bari		Yes
Italy	ARPA VENETO DIP.REG.LAB. S.L.	Verona		Yes
Italy	ARPA Piemonte POLO ALIMENTI	La Loggia (Torino)		Yes
Italy	ARPAM Dipartimento di Macerata	Macerata		Yes
Italy	Istituto Zooprofilattico Sperimentale Lazio e Toscana	Roma		Yes
Italy	Istituto Zooprofilattico Sperimentale Lombardia ed Emilia Romagna	Brescia		Yes
Italy	Istituto Zooprofilattico Sperimentale Sicilia	Palermo		Yes
Italy	Istituto Zooprofilattico Sperimentale Umbria e Marche	Perugia		Yes
Italy	Istituto Zooprofilattico Sperimentale Abruzzo e Molise	Teramo		Yes
Italy	ARPAL Sez. di La Spezia	La Spezia		No
Italy	ARPALAZIO RIETI	Rieti		Yes
Italy	Public Health Laboratory	FLORENCE		Yes
Italy	ARPAB - DIPARTIMENTO PROVINCIALE DI POTENZA - LABORATORIO STRUMENTALE	Potenza		No
Italy	Laboratorio di Prevenzione - ASL Provincia di Milano	Milano		Yes
Lithuania	National Food and Veterinary Risk Assessment Institute	Vilnius	NRL	Yes
Luxembourg	National Health Laboratory Luxembourg (Food Laboratory)	Dudelange		Yes
Netherlands	NVWA - Netherlands Food and Consumer Product Safety Authority	Wageningen	NRL	Yes
Netherlands	RIKILT Institute of Food Safety (Natural Toxins & Pesticides)	Wageningen		Yes
Netherlands	Handelslaboratorium Dr. Verwey	Rotterdam		Yes
Netherlands	Laboratorium Zeeuws-Vlaanderen B.V.	Graauw		Yes
Netherlands	NofaLab	Schiedam		Yes
Netherlands	Groen Agro Control	Delfgauw		Yes
Norway	Norwegian Institute for Agricultural and Environmental Research, Plant Health and Plant Protection Division, Pesticide Chemistry Section	Aas	NRL	Yes
Poland	Institute of Plant Protection, Department of Pesticide Residue Research	Poznan	NRL	Yes
Poland	Institute of Plant Protection - National Research Institute, Branch Sosnicowice	Sosnicowice		Yes
Poland	Voievodship Sanitary - Epidemiological Station in Warszaw	Warszaw		Yes
Poland	Institute of Plant Protection - National Research Institute, Regio-	Rzeszow		Yes

Country	Institution	City	NRL-CF	Report data
	nal Experimental Station in Rzeszow			
Poland	Voievodship Sanitary - Epidemiological Station in Opole	Opole		Yes
Poland	Institute of Horticulture, Food Safety Laboratory	Skierniewice		Yes
Poland	Regional Veterinary Laboratory Wroclaw	Wroclaw		Yes
Poland	Institute of Plant Protection Pesticide Residue Laboratory	Bialystok		Yes
Poland	Regional Veterinary Laboratory in Bialystok	Bialystok		Yes
Poland	Regional Veterinary Laboratory in Gdansk (Kartuska)	Gdansk		Yes
Poland	Regional Veterinary Laboratory in Katowice	Katowice		Yes
Poland	Regional Veterinary Laboratory in Opole	Opole		Yes
Poland	Provincial Veterinary Inspectorate Establishment of Veterinary Hygiene	Poznan		Yes
Poland	Regional Veterinary Laboratory in Szczecin	Szczecin		Yes
Poland	Regional Veterinary Laboratory in Warsaw	Warszawa		Yes
Portugal	INIAV- Pesticide Residues Laboratory	Oeiras	NRL	Yes
Portugal	Regional Laboratory of Veterinary and Food Safety	Funchal - Madeira Island		Yes
Republic of Belarus	Scientific practical centre of hygiene	Minsk		Yes
Romania	Institute for Hygiene and Veterinary Public Health - Bucharest	Bucharest		Yes
Romania	Central Laboratory for Pesticides Residues Control in Plants and Vegetable Products	Bucharest	NRL	Yes
Romania	Sanitary Veterinary and Food Safety Directorate, Bucharest	Bucharest		Yes
Romania	Sanitary Veterinary and Food Safety Directorate Cluj, Sanitary Veterinary and Food Safety Laboratory	Cluj- Napoca		Yes
Romania	Sanitary Veterinary and Food Safety Laboratory	Iasi		Yes
Romania	Zonal Laboratory for pesticides Residues in feed	Braila		Yes
Romania	Zonal Laboratory for pesticides infeed	Bistrita		Yes
Romania	LABORATORY SANITARY VETERINARY for FOOD SAFETY DOLJ	CRAIOVA		Yes
Slovakia	State Veterinary and Food Institute Bratislava	Bratislava	NRL	Yes
Slovakia	Public Health Authority of the Slovak Republic	Bratislava		Yes
Slovenia	Agricultural Institute of Slovenia, Central Laboratories	Ljubljana		Yes
Slovenia	National Laboratory of Health, Environment and Foodstuffs - Maribor	Maribor	NRL	Yes
Slovenia	National Laboratory of Health, Environment and Foodstuffs	Ljubljana		Yes
Spain	National Centre for Food	Majadahonda		Yes
Spain	Laboratorio Arbitral Agroalimentario	Madrid	NRL	Yes
Spain	Laboratorio Regional CCAA La Rioja	Logroño		Yes
Spain	Agrofood Laboratory of the Comunidad Valenciana	Burjassot-Valencia		Yes
Spain	Laboratorio de Producción y Sanidad Vegetal de Huelva	Cartaya (Huelva)		Yes
Spain	Laboratorio Agrario Regional - Junta de Castilla y Leon	Burgos		Yes

Country	Institution	City	NRL-CF	Report data
Spain	Laboratori Agroalimentari de la Generalitat de Catalunya	Cabrils		Yes
Spain	Navarra de Servicios y Tecnologias, S.A.	Villava		No
Spain	Agricultural and Phytopathological Laboratory of Galicia	Abegondo. A Coruña		No
Spain	Laboratorio Agroalimentario de Zaragoza	Zaragoza		Yes
Spain	Laboratorio de Salud Pública de Badajoz	Badajoz		Yes
Spain	Laboratory of Barcelona Public Health Agency	Barcelona		Yes
Spain	Laboratorio de Salud Pública , Drogodependencia y Consumo. SS PP de Sanidad y Asuntos Sociales de Cuenca	Cuenca		Yes
Spain	Servicio de Laboratorio y Control de Santander	Santander		Yes
Spain	Analytica Alimentaria GmbH Sucursal España	Almeria		Yes
Spain	Labs & Technological Services AGQ, S.L.	Burguillos (Sevilla)		Yes
Spain	Laboratorios Ecosur, S.A.L.	Lorquí (Murcia)		Yes
Spain	National Centre for Technology and Food Safety - Laborytory of Ebro	San Adrián (Navarra)		Yes
Sweden	National Food Agency, Science Department, Chemistry Division 1	Uppsala	NRL	Yes
Sweden	Eurofins - Food&Agro Sweden, Lidköping	Lidköping		Yes
United Kingdom	The Food and Environment Research Agency - York	York	NRL	Yes
United Kingdom	Laboratory of the Government Chemist - Teddington	Teddington		Yes
United Kingdom	Agri-Food and Biosciences Institute	Belfast		Yes

Participating labs from EU candidate state and the 3rd countries

Country	Institution	City	Report data
Argentina	INTI-LACTEOS	SAN MARTIN - BUENOS AIRES	No
Argentina	CEPROCOR	STA.MARIA DE PUNILLA CORDOBA	No
Argentina	PRINARC FIQ UNL -Program of Research and Analysis of Chemical Residues and Contaminants- National University of Litoral - Argentina	Santa Fe	Yes
Brazil	Laboratório Nacional Agropecuário - LANAGRO/MG	Pedro Leopoldo	No
Brazil	Center of Research and Analysis of Residues and Contaminants (CEPARC)/Federal University of Santa Maria (UFSM) - Brazil	Campus, Camobi,Santa Maria, RS	No
Brazil	Bioagri Analises de Alimentos Ltda	São Paulo	Yes
Brazil	National Agricultural Laboratory in Goiás	Goiânia	Yes
Brazil	Eurofins do Brasil Análises de Alimentos Ltda	Indaiatuba	No
Burkino Faso	LABORATOIRE NATIONAL DE SANTE PUBLIQUE	OUAGADOUGOU	No
Egypt	Central Lab of Residue Analysis of Pesticides and Heavy Metals in Foods	Giz	Yes
India	Project Coordinating Cell, All India Network Project on Pesticide Residues	New Delhi	Yes
India	Natioional Institute of Occupational Health	Ahmedabad	Yes
Indonesia	PT. ANGLER BIOCHEMLAB	SURABAYA	Yes
Kenya	KEPHIS Analytical Chemistry Laboratory	Nairobi	Yes
Kenya	Kenya Bureau of Standards Testing Laboratory	NAIROBI	No
New Zealand	AsureQuality Ltd - Wellington	Wellington	Yes
Serbia	Center for Food Analysis, Belgrade	Belgrade	Yes
Serbia	SP LABORATORY	BECEJ	Yes
Singapore	Veterinary Public Health Laboratory	Singapore	Yes
Tanzania	TROPICAL PESTICIDES RESEARCH INSTITUTE LABORATORY	ARUSHA	Yes
Thailand	Central Laboratory (Thailand) Co., Ltd. Bangkok branch	Jatujak, Bangkok	No

Appendix 2 Target Pesticide List

Pesticides	MRRL (mg/kg)
Acephate	0.01
Azinphos-methyl	0.01
Azoxystrobin	0.01
Bifenthrin	0.01
Bixafen	0.01
Boscalid	0.01
Captan	0.01
Carbaryl	0.01
Carbendazim	0.01
Carbofuran	0.01
Carbofuran, 3-hydroxy	0.01
Carboxin	0.01
Chlorfenvinphos	0.01
Chlorothalonil	0.02
Chlorpropham (parent compound only)	0.02
Chlorpyrifos	0.02
Chlorpyrifos-methyl	0.01
Clothianidin	0.01
Cyfluthrin (sum of isomers)	0.01
Cypermethrin (sum of isomers)	0.01
Cyproconazole	0.01
Cyprodinil	0.01
Deltamethrin-cis	0.01
Demeton-S-methylsulfone	0.01
Diazinon	0.01
Dichlorvos	0.01
Difenoconazole	0.01
Diflubenzuron	0.01
Dimethoate	0.01
Endosulfan-alpha	0.01
Endosulfan-beta	0.01
Endosulfan-sulfate	0.01
Epoxiconazole	0.01
Ethion	0.01
Fenbuconazole	0.01
Fenhexamid	0.01
Fenitrothion	0.01
Fenpropidin	0.01
Fenpropimorph	0.01
Fenthion	0.01
Fenthion-oxon	0.01

Pesticides	MRRL (mg/kg)
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
Fluquinconazole	0.01
Flusilazole	0.01
Flutriafol	0.01
Fluxapyroxad	0.01
HCH-alpha	0.01
HCH-beta	0.01
Hexaconazole	0.01
Imazalil	0.01
Imidacloprid	0.01
Iprodione	0.01
Isoprothiolane	0.01
Isoproturon	0.01
Kresoxim-methyl	0.01
Lambda-cyhalothrin	0.01
Lindane	0.01
Linuron	0.01
Malaoxon	0.01
Malathion	0.01
Metconazole	0.01
Methacrifos	0.01
Methomyl	0.01
Metrafenone	0.01
Metribuzin	0.01
Omethoate	0.01
Oxydemeton-methyl	0.01
o,p'-DDT	0.01
p,p'-DDE	0.01
p,p'-DDT	0.01
p,p'-TDE	0.01
Paclobutrazol	0.01
Parathion	0.01
Penconazole	0.01
Pendimethalin	0.01
Permethrin (sum of isomers)	0.01

Pesticides	MRRL (mg/kg)
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
Propiconazole	0.01
Prothioconazole-desthio	0.01
Pyraclostrobin	0.01
Pyrimethanil	0.01
Quinoxyfen	0.01
Spiroxamine	0.01
Tebuconazole	0.01
Tebufenozide	0.01
Thiabendazole	0.01
Thiacloprid	0.01
Thiamethoxam	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

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
005	0.175	0.255	0.074	0.076	0.274	0.386
027	0.168	0.271	0.084	0.076	0.262	0.414
083	0.142	0.307	0.072	0.069	0.229	0.422
120	0.258	0.154	0.088	0.083	0.400	0.255
125	0.190	0.197	0.083	0.087	0.260	0.324
165	0.198	0.207	0.090	0.090	0.314	0.332
197	0.278	0.187	0.098	0.098	0.432	0.306
263	0.209	0.222	0.080	0.078	0.338	0.367
279	0.228	0.175	0.079	0.080	0.354	0.269
312	0.215	0.217	0.088	0.079	0.333	0.296
324	0.202	0.185	0.078	0.077	0.287	0.266

	Carbendazim, mg/kg		Cypermethrin, mg/kg		Deltamethrin, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
005	0.062	0.047	0.817	1.063	0.042	0.064
027	0.044	0.052	0.676	1.174	0.036	0.072
083	0.046	0.052	0.610	1.185	0.036	0.072
120	0.050	0.054	1.101	0.738	0.058	0.041
125	0.052	0.058	0.688	0.882	0.061	0.048
165	0.054	0.056	0.819	0.859	0.048	0.047
197	0.057	0.062	1.084	0.884	0.066	0.045
263	0.052	0.053	0.952	1.068	0.053	0.053
279	0.056	0.054	0.989	0.735	0.065	0.049
312	0.067	0.060	0.964	0.834	0.056	0.058
324	0.057	0.071	0.762	0.728	0.050	0.049

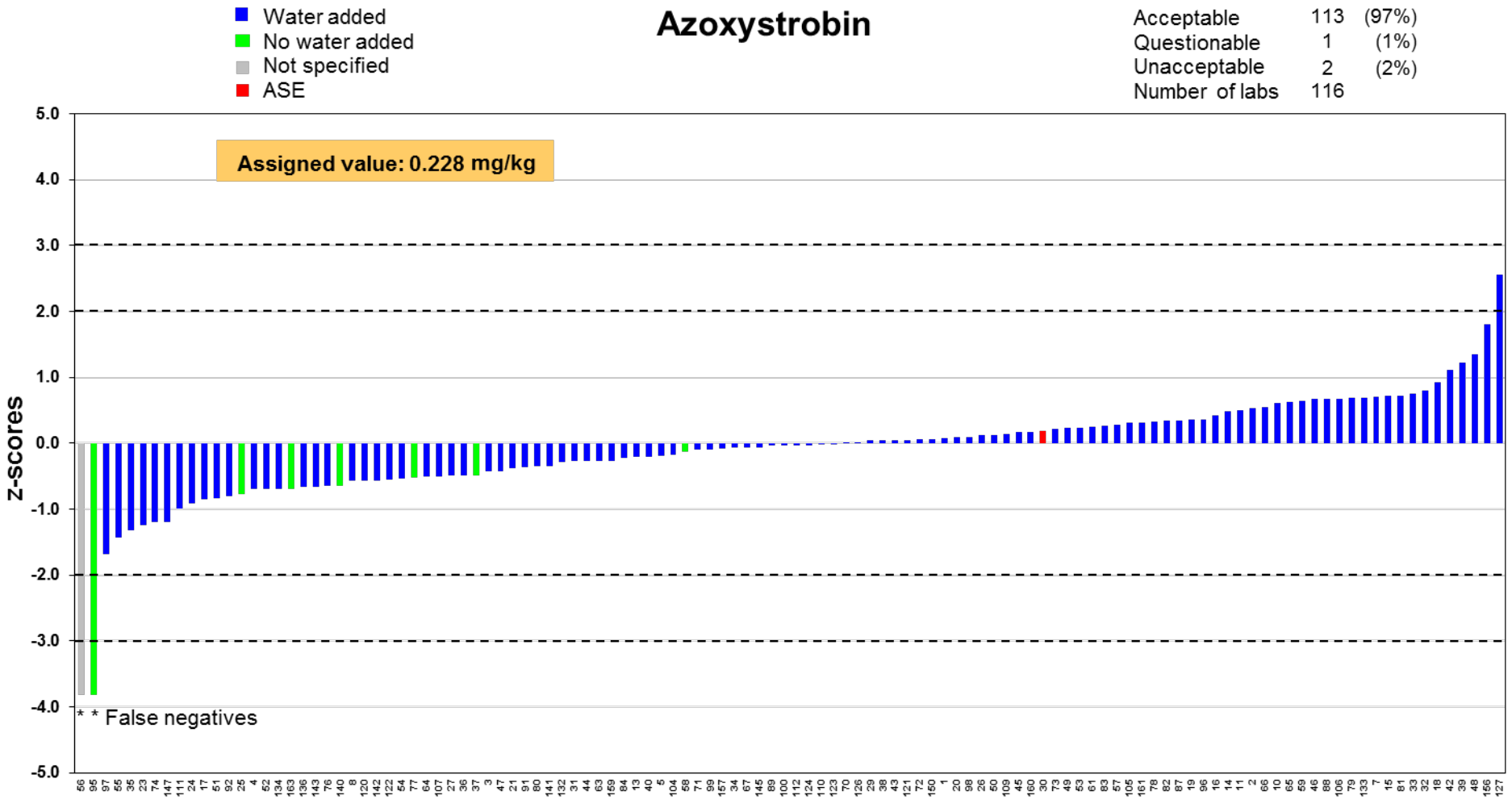
	Endosulfan-sulfate, mg/kg		Epoxiconazole, mg/kg		Flonicamid, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
005	0.053	0.073	0.098	0.154	0.091	0.120
027	0.049	0.076	0.107	0.156	0.097	0.126
083	0.041	0.072	0.090	0.151	0.083	0.110
120	0.071	0.049	0.147	0.103	0.110	0.089
125	0.045	0.056	0.093	0.116	0.087	0.103
165	0.059	0.056	0.112	0.115	0.100	0.101
197	0.070	0.062	0.177	0.115	0.119	0.105
263	0.058	0.068	0.128	0.148	0.111	0.126
279	0.061	0.043	0.124	0.104	0.097	0.091
312	0.060	0.046	0.114	0.111	0.096	0.094
324	0.040	0.041	0.107	0.107	0.093	0.100

	Fluxapyroxade, mg/kg		Linuron, mg/kg		Metconazole, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
005	0.154	0.163	0.067	0.062	0.087	0.089
027	0.180	0.166	0.067	0.065	0.105	0.104
083	0.160	0.146	0.076	0.068	0.096	0.090
120	0.176	0.174	0.078	0.066	0.106	0.104
125	0.172	0.190	0.057	0.058	0.103	0.121
165	0.171	0.204	0.064	0.060	0.113	0.117
197	0.212	0.208	0.073	0.122	0.133	0.130
263	0.183	0.180	0.060	0.078	0.119	0.113
279	0.182	0.176	0.057	0.055	0.113	0.110
312	0.191	0.176	0.101	0.055	0.123	0.117
324	0.188	0.178	0.058	0.062	0.119	0.112

	Metrafenone, mg/kg		Prothioconazole desthio, mg/kg		Pyraclostrobin, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
005	0.348	0.486	0.139	0.152	0.067	0.063
027	0.306	0.525	0.167	0.163	0.068	0.066
083	0.276	0.480	0.149	0.151	0.060	0.057
120	0.485	0.331	0.170	0.169	0.070	0.071
125	0.293	0.342	0.163	0.195	0.074	0.082
165	0.334	0.353	0.180	0.204	0.071	0.073
197	0.477	0.363	0.222	0.219	0.084	0.082
263	0.444	0.440	0.187	0.181	0.069	0.067
279	0.404	0.318	0.181	0.183	0.066	0.065
312	0.374	0.346	0.203	0.188	0.074	0.075
324	0.323	0.328	0.189	0.187	0.073	0.067

	Spiroxamin, mg/kg		Trifluralin, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2
5	0,051	0,052	0,058	0,069
30	0,054	0,060	0,051	0,065
76	0,056	0,052	0,049	0,060
126	0,060	0,060	0,062	0,058
162	0,059	0,064	0,061	0,056
188	0,062	0,067	0,054	0,054
208	0,074	0,078	0,064	0,064
226	0,070	0,066	0,054	0,055
240	0,072	0,067	0,066	0,052
310	0,075	0,069	0,056	0,052

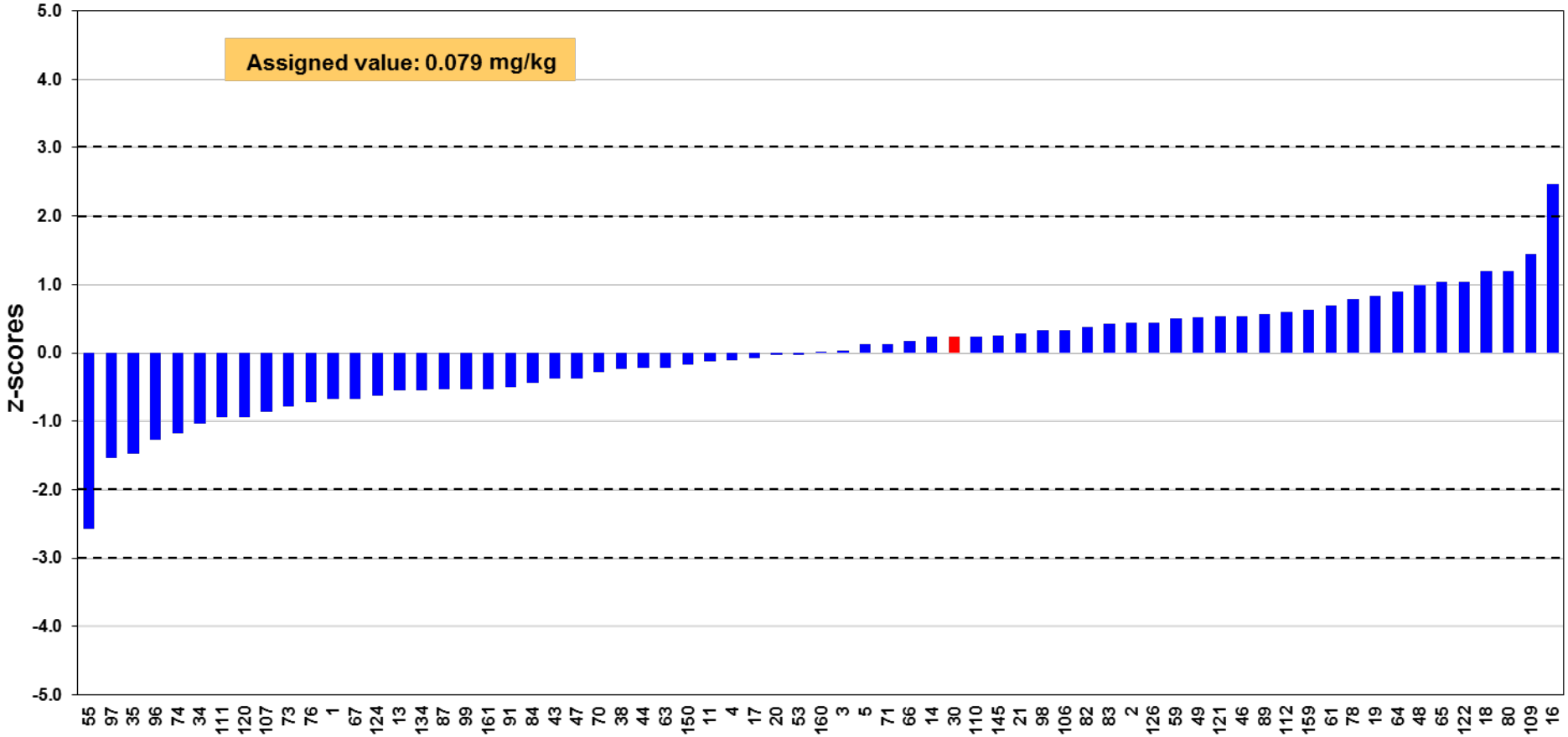
Appendix 4 Graphical presentation of z-scores

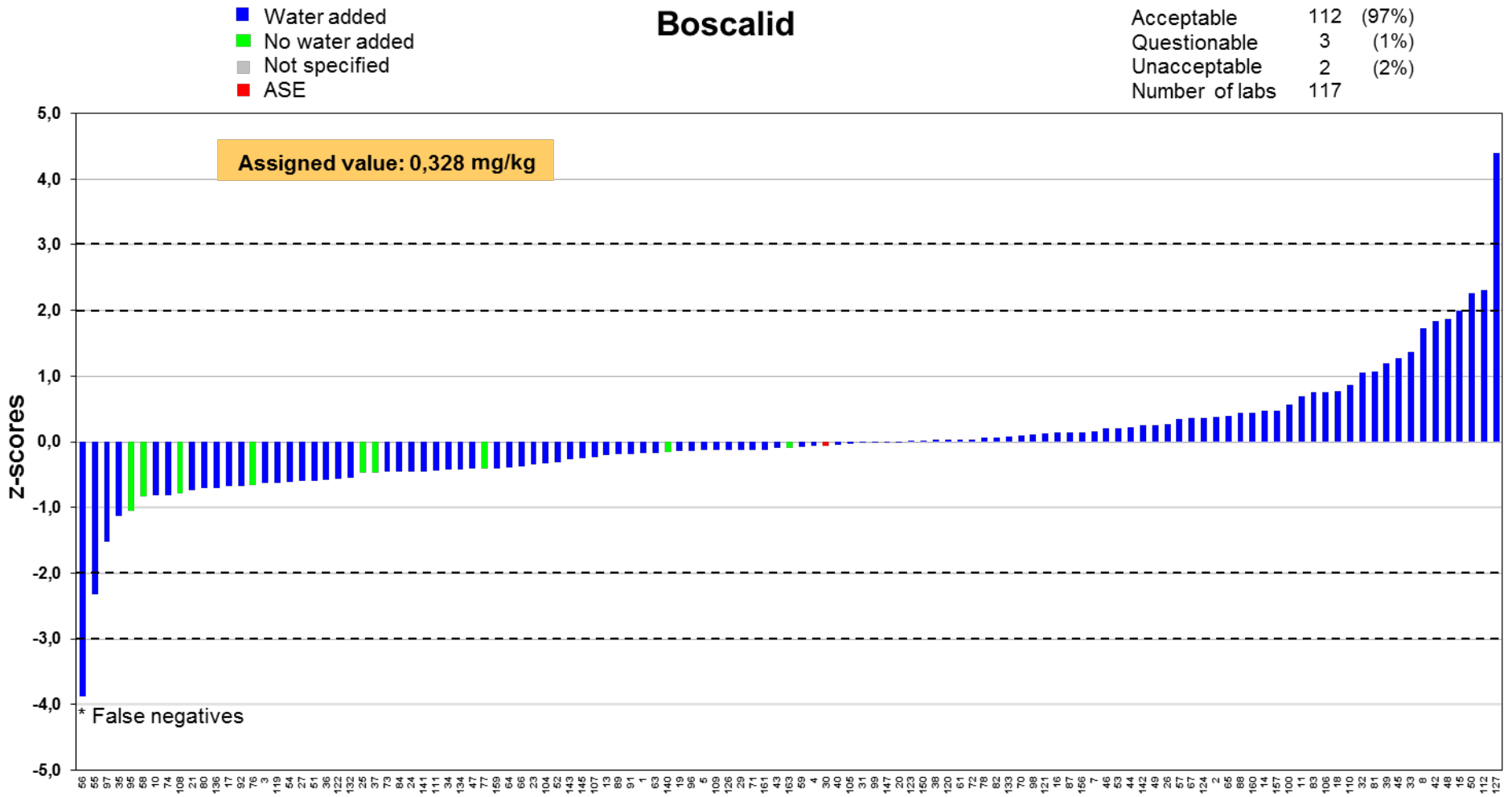


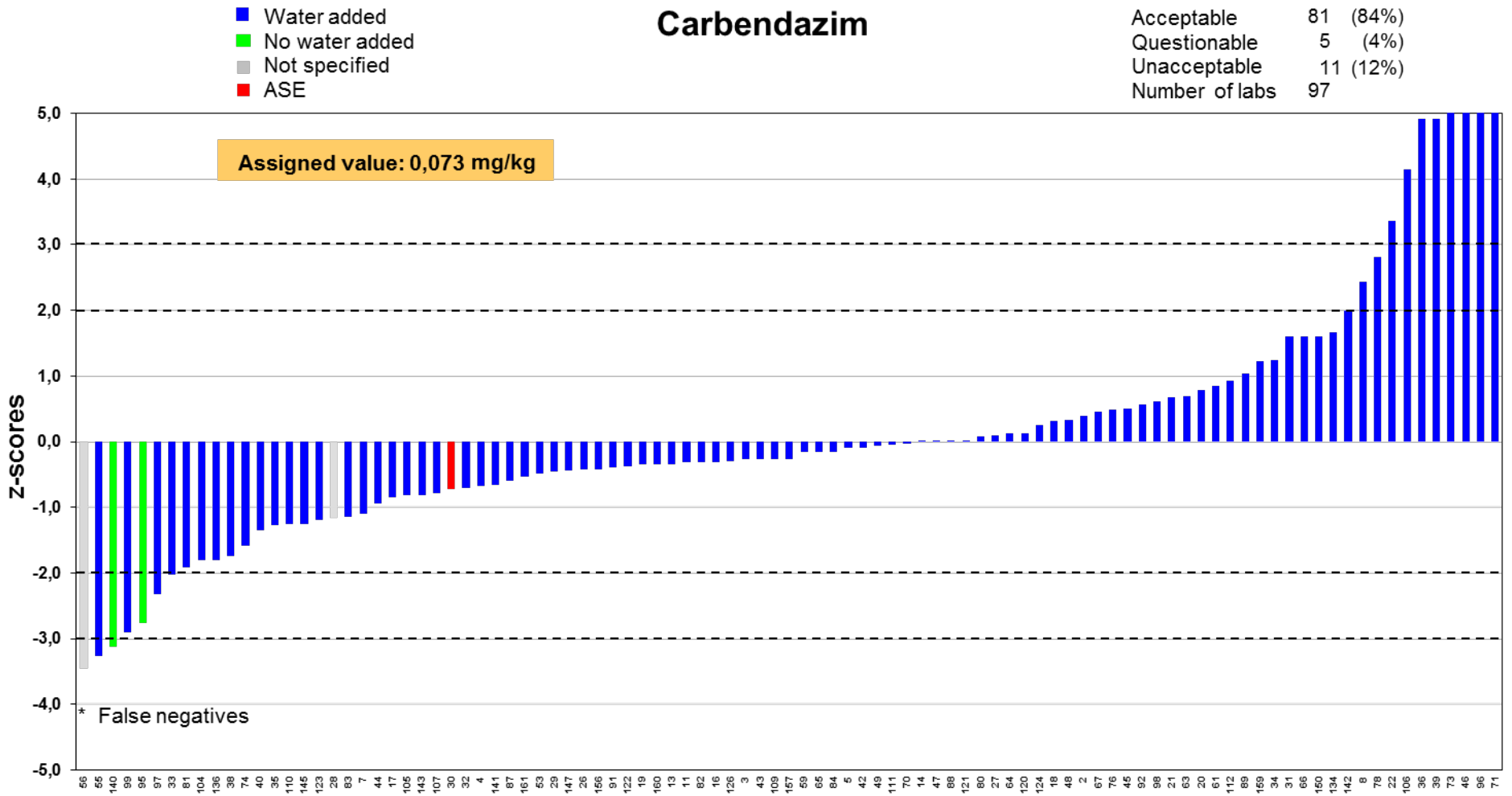
Bixafen

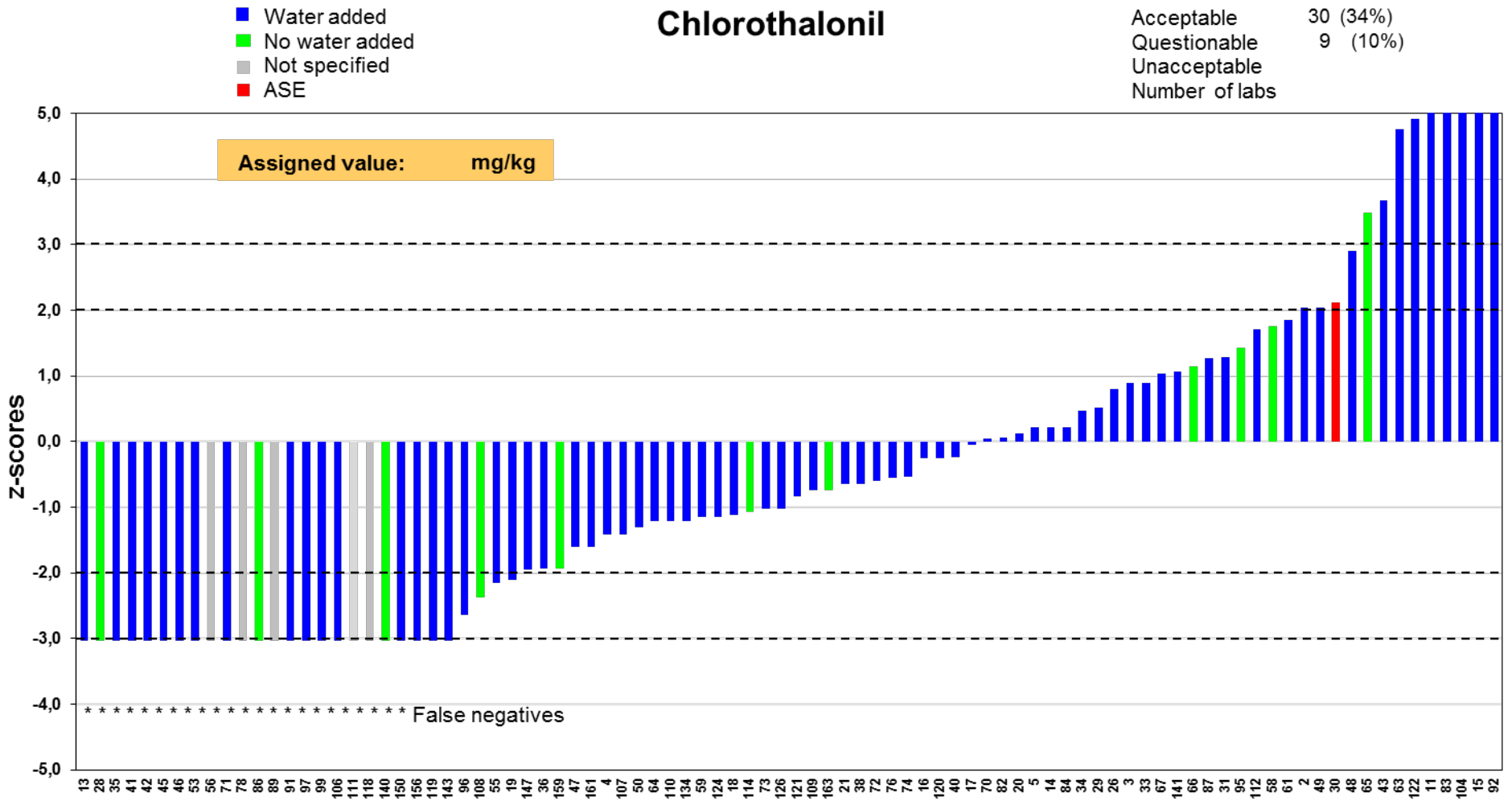
Water added
No water added
Not specified
ASE

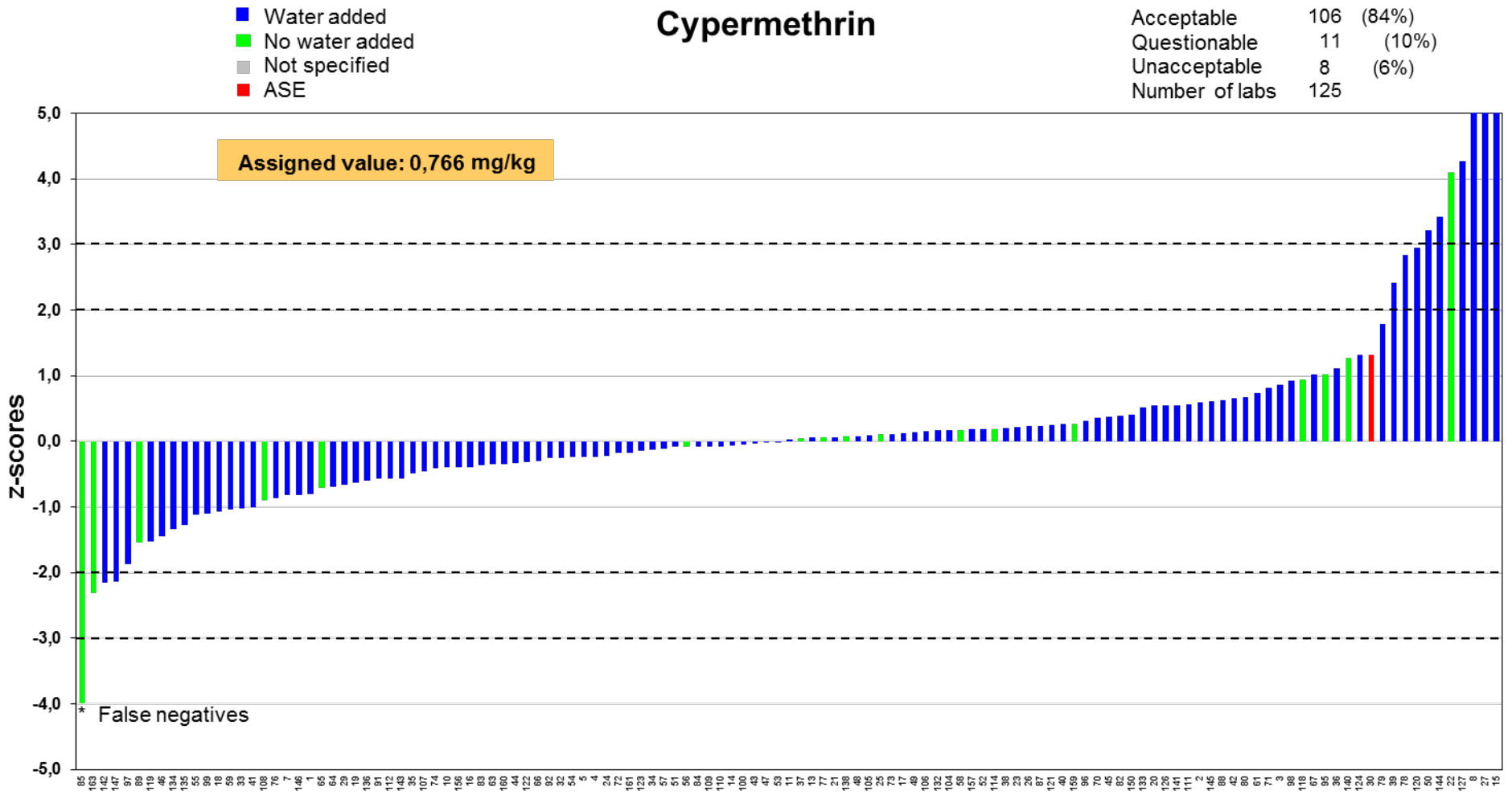
Acceptable	65	(97%)
Questionable	2	(3%)
Unacceptable	0	(0%)
Number of labs	67	

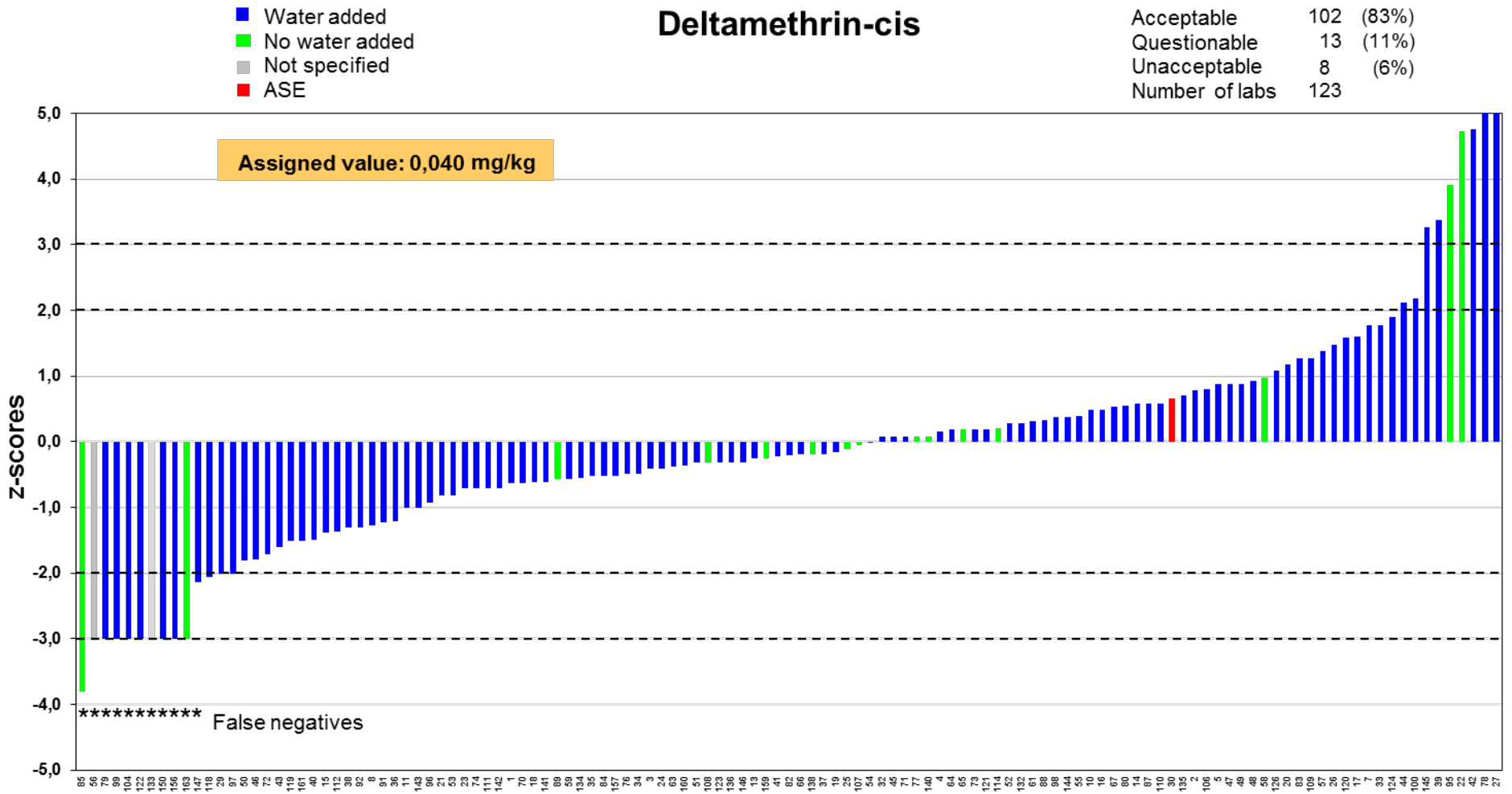


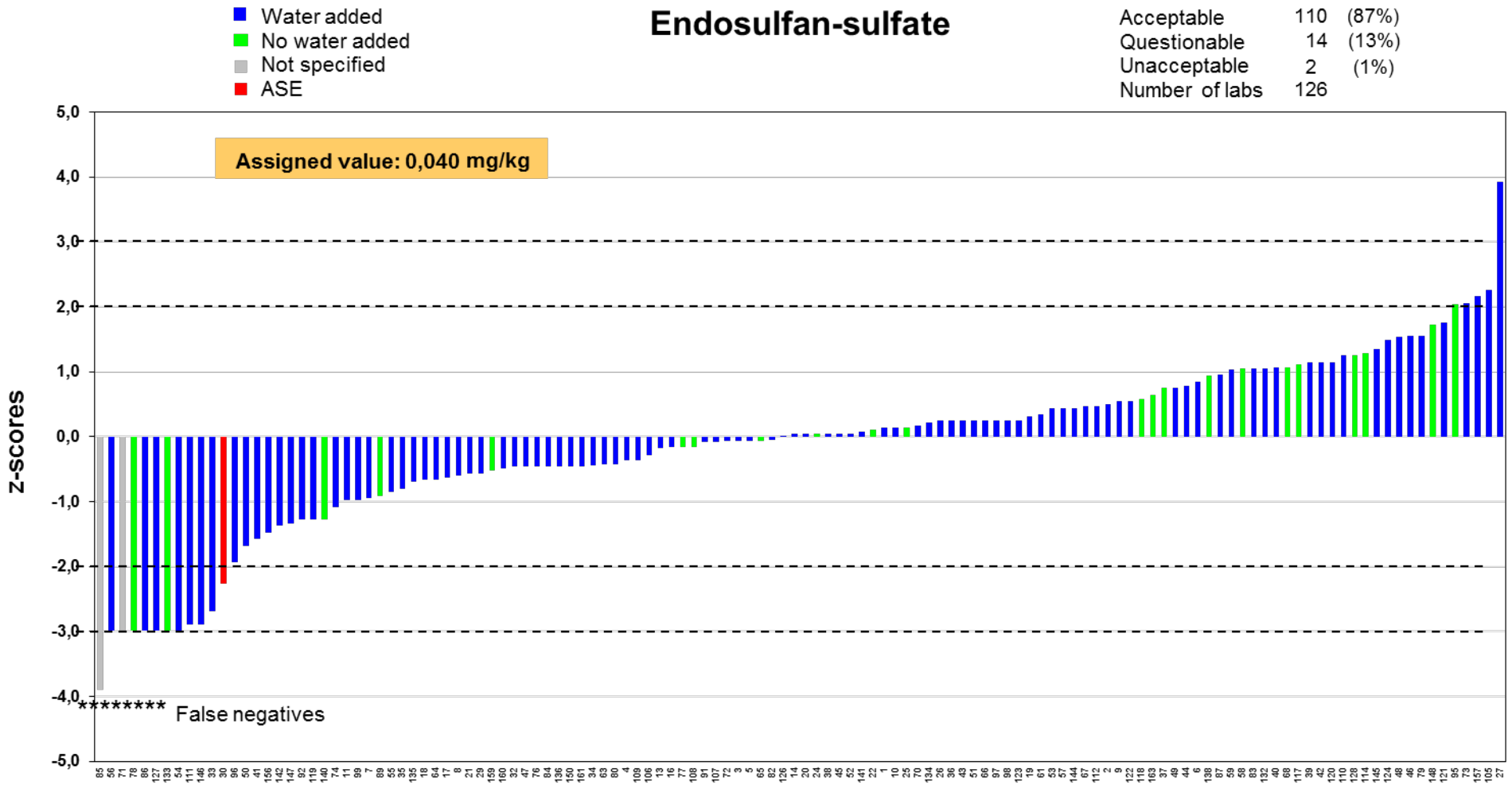

Water added
No water added
Not specified
ASE
Boscalid
Acceptable 112 (97%)
Questionable 3 (1%)
Unacceptable 2 (2%)
Number of labs 117
Assigned value: 0,328 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* False negatives
56 55 97 35 95 58 10 74 108 21 80 136 17 92 76 3 119 54 27 51 36 122 132 25 37 73 84 24 141 111 34 134 47 77 159 64 66 23 104 52 143 145 107 13 89 91 1 63 140 19 96 5 109 126 29 71 161 43 163 59 4 30 40 105 31 99 147 20 123 150 38 120 61 72 78 82 133 70 98 121 16 87 156 7 46 53 44 142 49 26 57 67 124 2 65 88 160 14 157 100 11 83 106 18 110 32 81 39 45 33 8 42 48 15 50 112 127

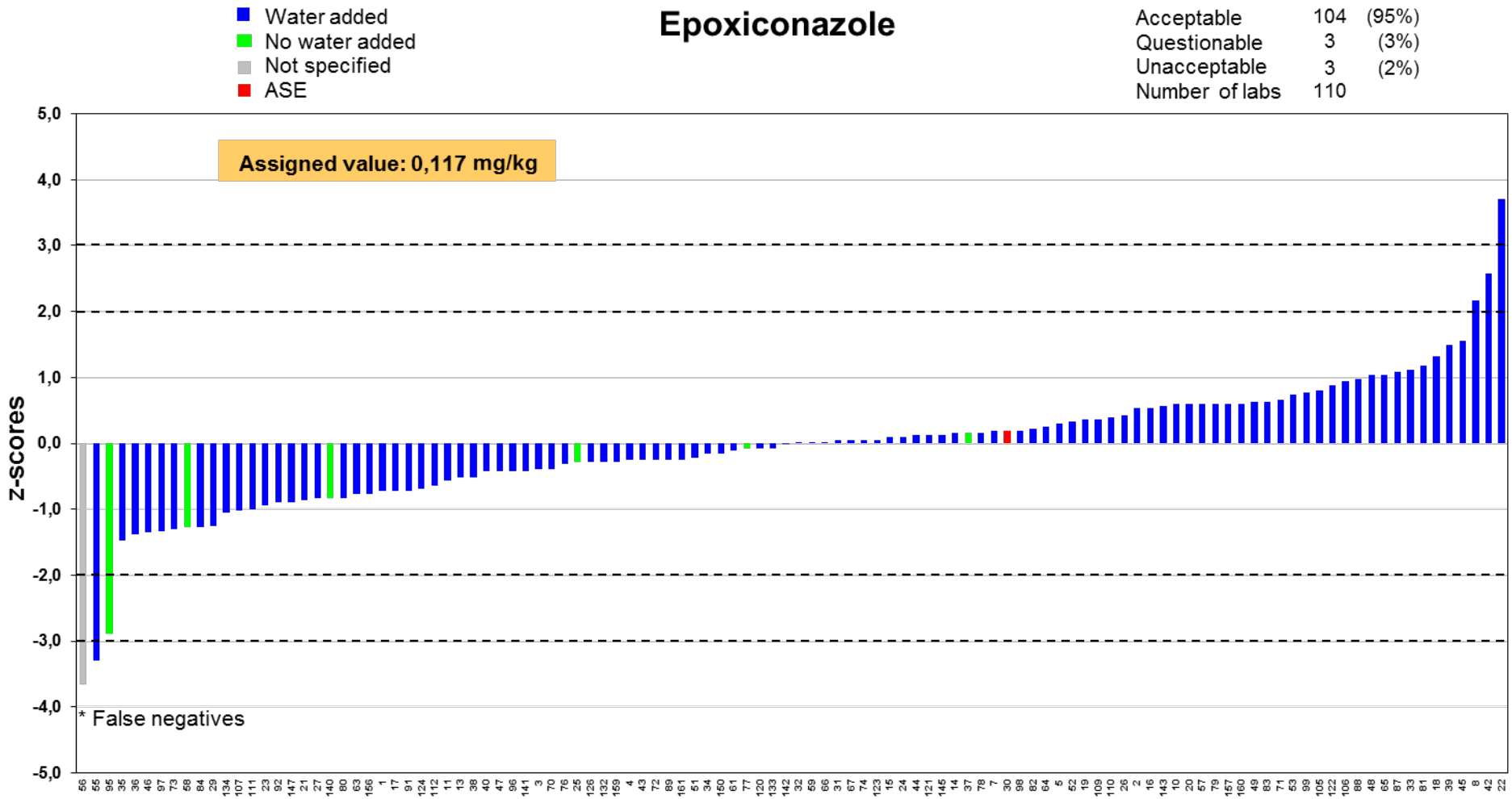

Water added
No water added
Not specified
ASE
Carbendazim
Acceptable 81 (84%)
Questionable 5 (4%)
Unacceptable 11 (12%)
Number of labs 97
Assigned value: 0,073 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* False negatives
56 55 140 99 95 97 33 81 104 136 38 74 40 35 110 145 123 28 83 7 44 17 105 143 107 30 32 4 141 87 161 53 29 147 26 156 91 122 19 160 13 11 82 16 126 3 43 109 157 59 65 84 5 42 49 111 70 14 47 88 121 80 27 64 120 124 18 48 2 67 76 45 92 98 21 63 20 61 112 89 159 34 31 66 150 134 142 8 78 22 106 36 39 73 46 96 71

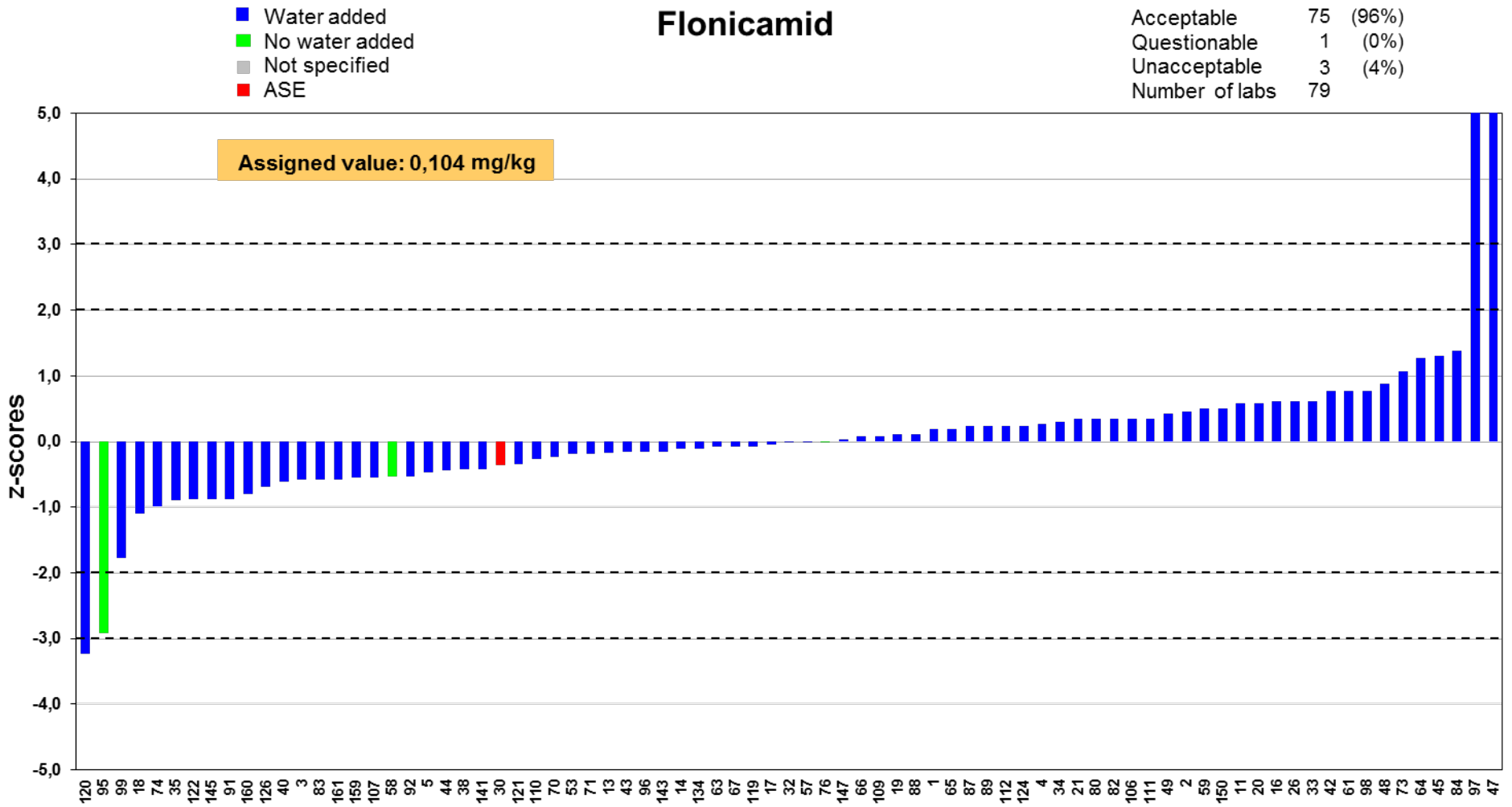

Water added
No water added
Not specified
ASE
Chlorothalonil
Acceptable 30 (34%)
Questionable 9 (10%)
Unacceptable
Number of labs
Assigned value: mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* False negatives
13 28 35 41 42 45 46 53 56 71 78 86 89 91 97 99 106 111 118 140 150 156 119 143 96 108 55 19 147 36 159 47 161 4 107 50 64 110 134 59 124 18 114 73 126 121 109 163 21 38 72 76 74 16 120 40 17 70 82 20 5 14 84 34 29 26 3 33 67 141 66 87 31 95 112 58 61 2 49 30 48 65 43 63 122 11 83 104 15 92

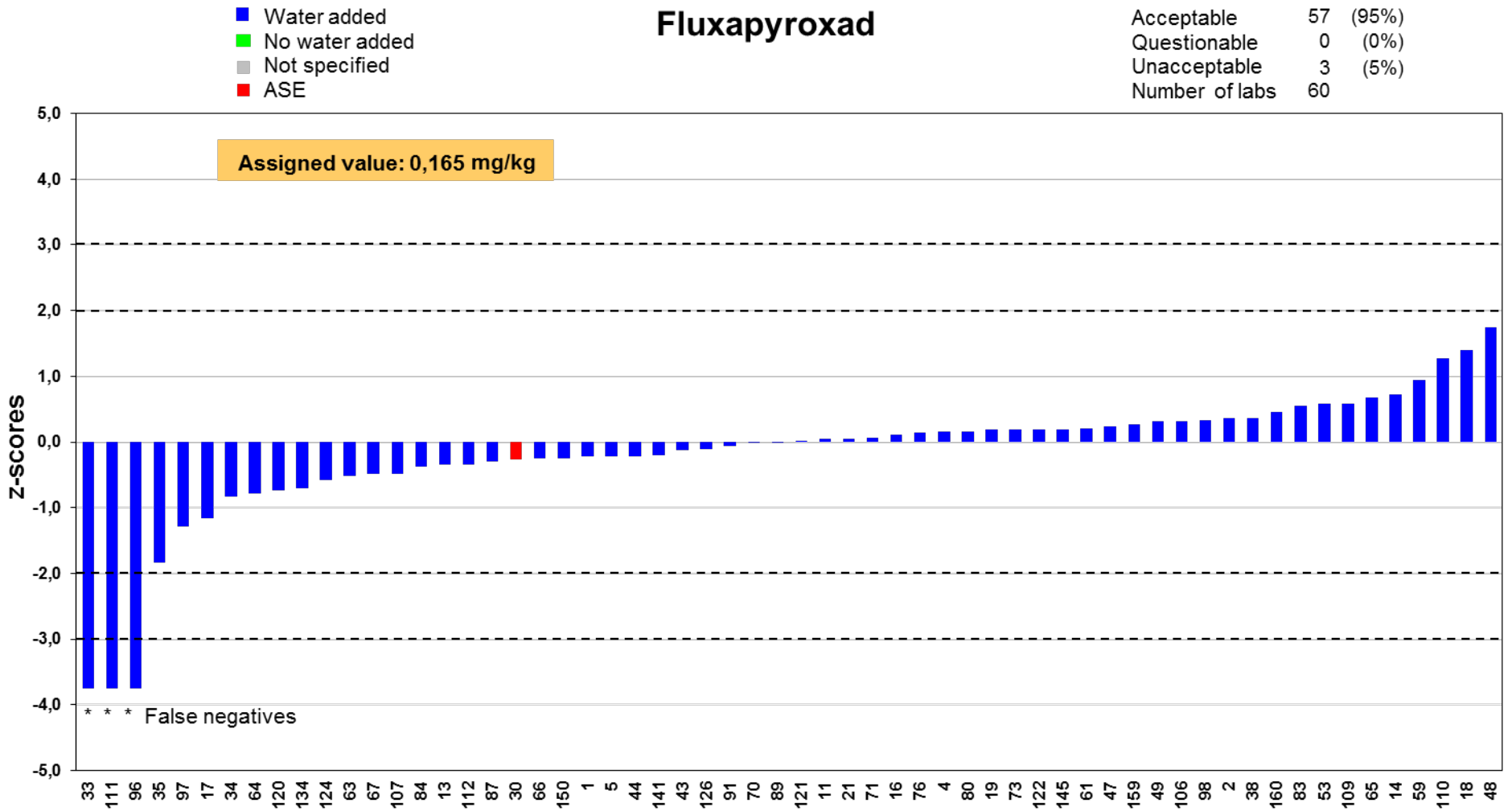

Water added
No water added
Not specified
ASE
Cypermethrin
Acceptable 106 (84%)
Questionable 11 (10%)
Unacceptable 8 (6%)
Number of labs 125
Assigned value: 0,766 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* False negatives

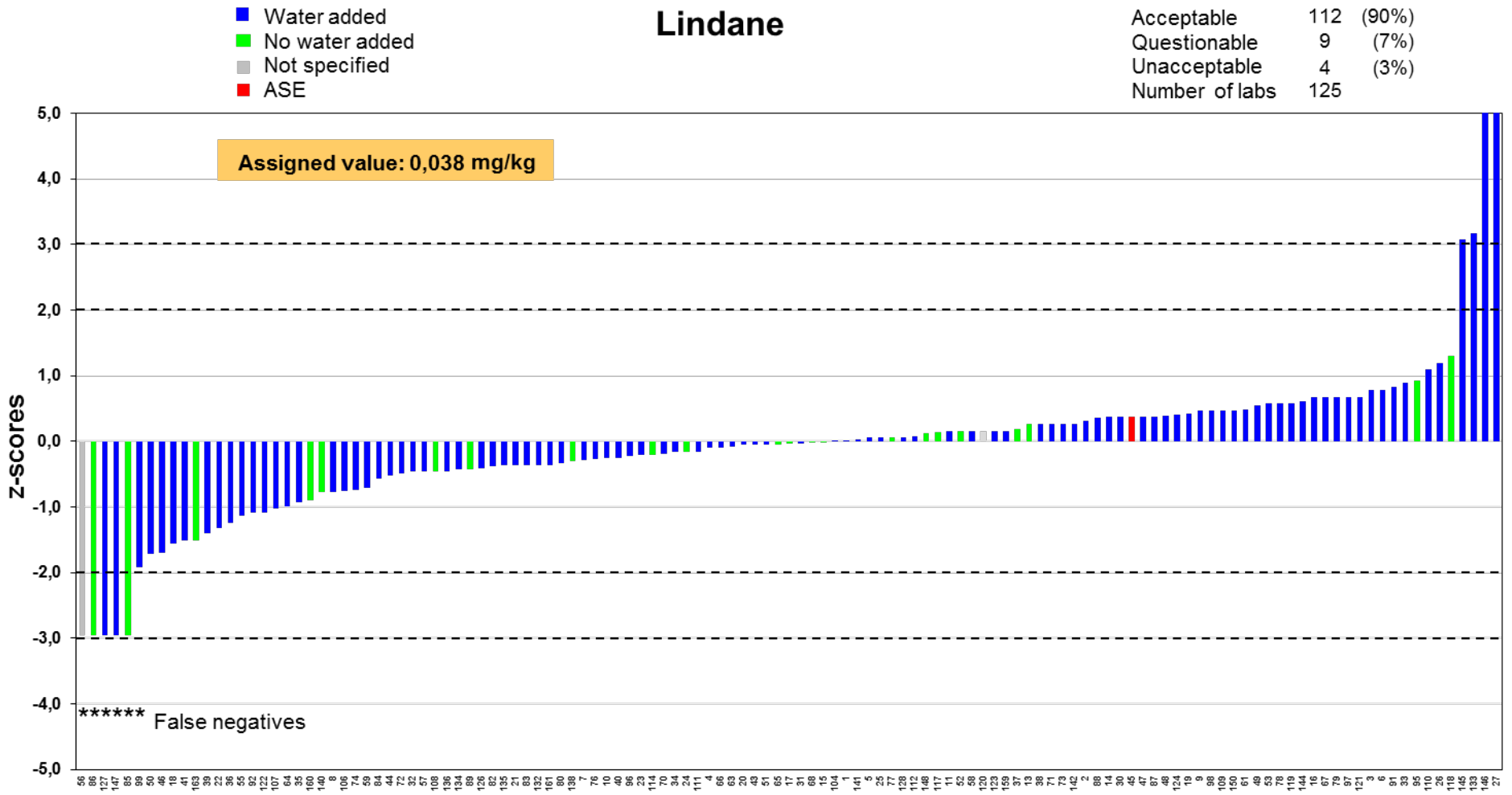

Water added
No water added
Not specified
ASE
Deltamethrin-cis
Acceptable 102 (83%)
Questionable 13 (11%)
Unacceptable 8 (6%)
Number of labs 123
Assigned value: 0,040 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
********** False negatives

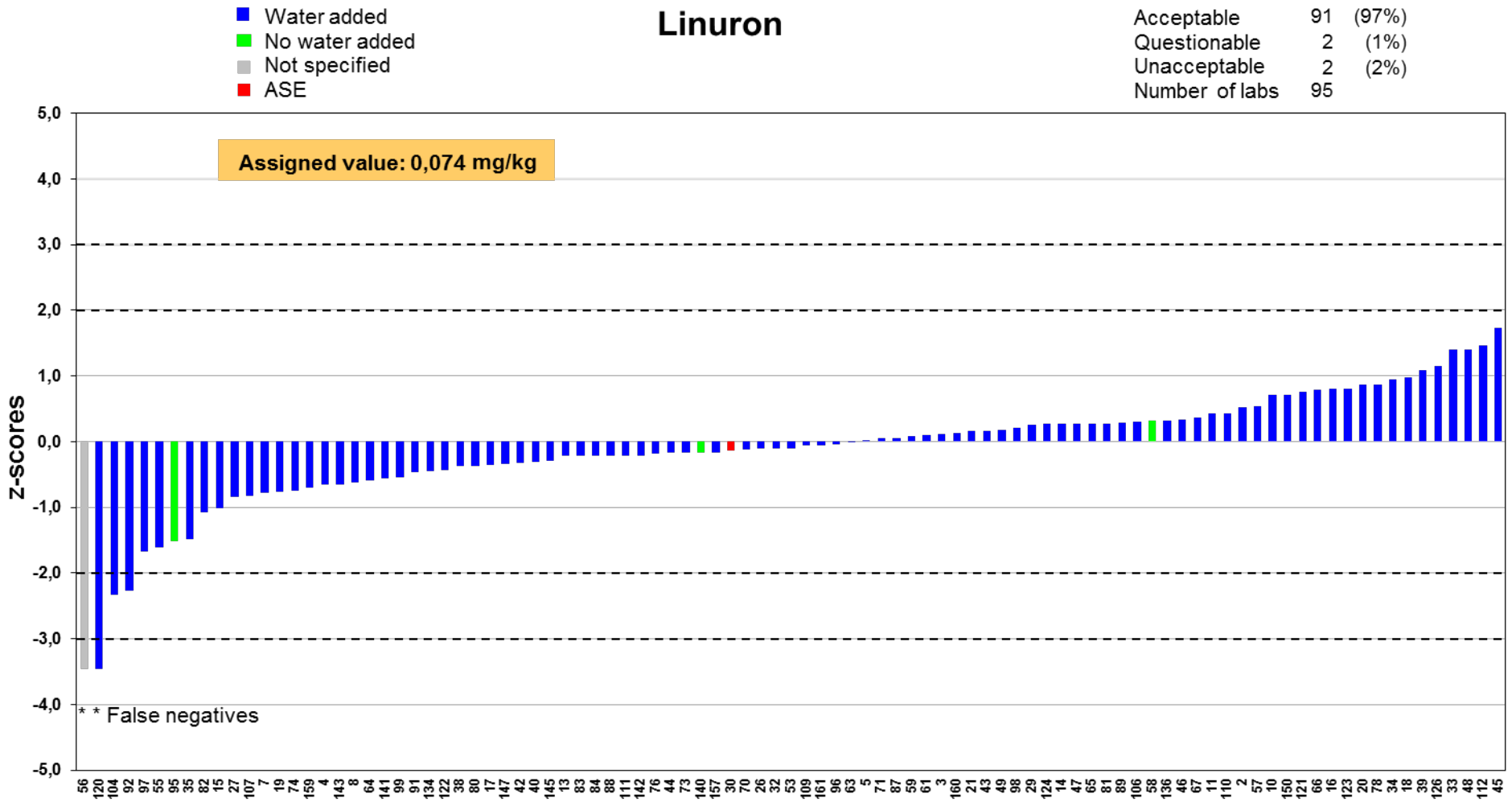

Water added
No water added
Not specified
ASE
Endosulfan-sulfate
Acceptable 110 (87%)
Questionable 14 (13%)
Unacceptable 2 (1%)
Number of labs 126
Assigned value: 0,040 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
******** False negatives

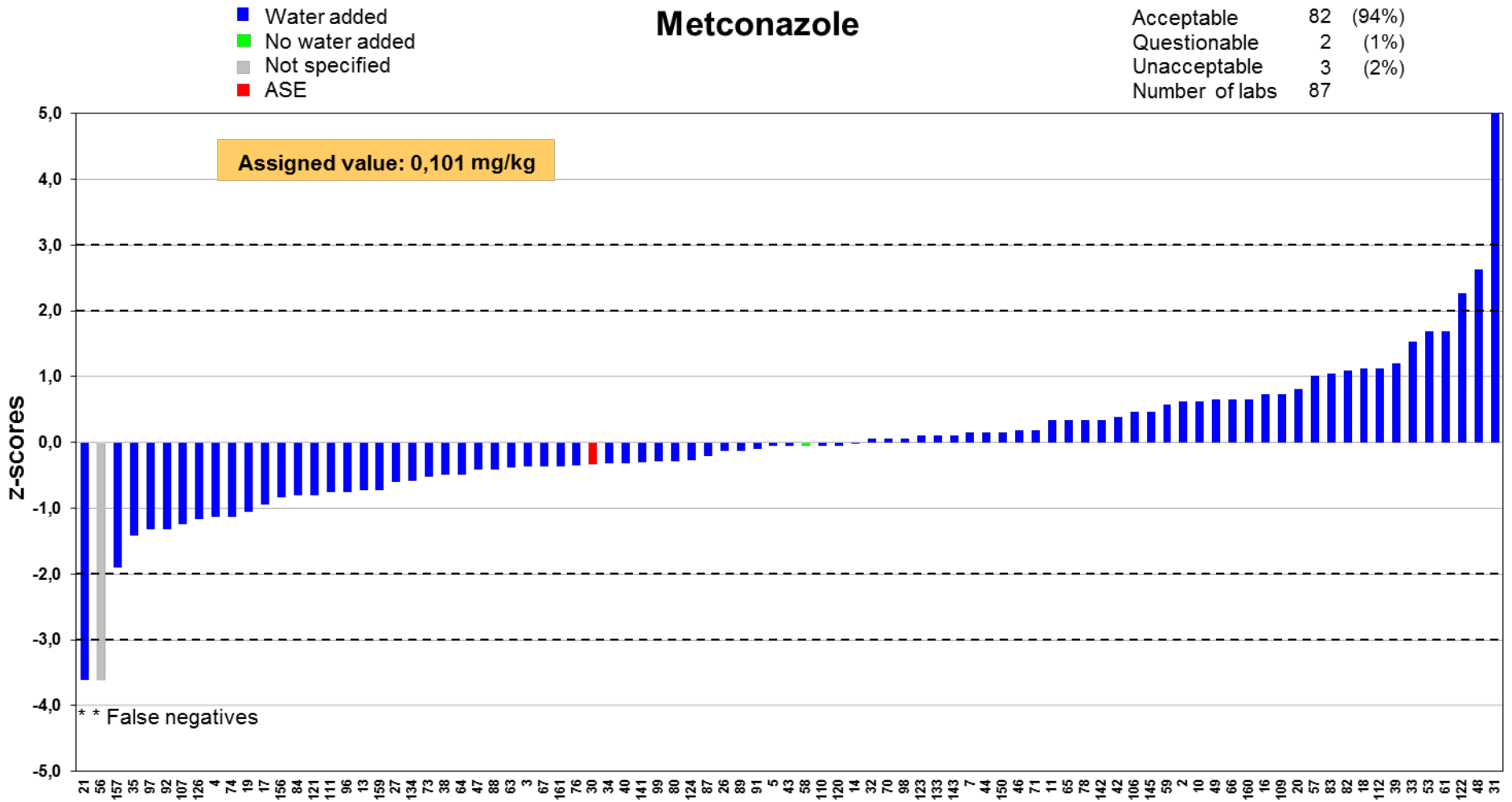

Water added
No water added
Not specified
ASE
Epoxiconazole
Acceptable 104 (95%)
Questionable 3 (3%)
Unacceptable 3 (2%)
Number of labs 110
Assigned value: 0,117 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* False negatives

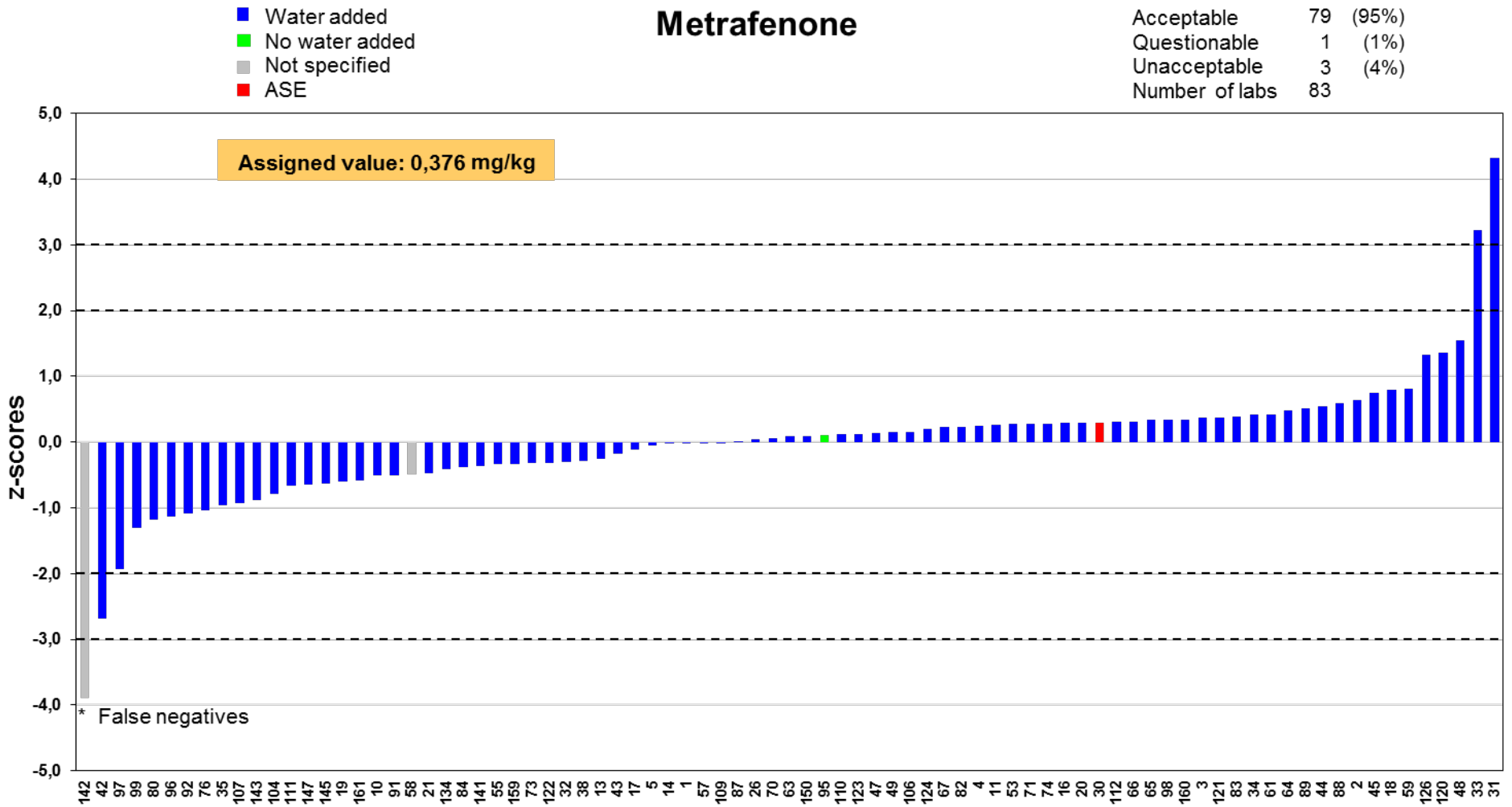

Water added
No water added
Not specified
ASE
Flonicamid
Acceptable 75 (96%)
Questionable 1 (0%)
Unacceptable 3 (4%)
Number of labs 79
Assigned value: 0,104 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
120 95 99 18 74 35 122 145 91 160 126 40 3 83 161 159 107 58 92 5 44 38 141 30 121 110 70 53 71 13 43 96 143 14 134 63 67 119 17 32 57 76 147 66 109 19 88 1 65 87 89 112 124 4 34 21 80 82 106 111 49 2 59 150 11 20 16 26 33 42 61 98 48 73 64 45 84 97 47

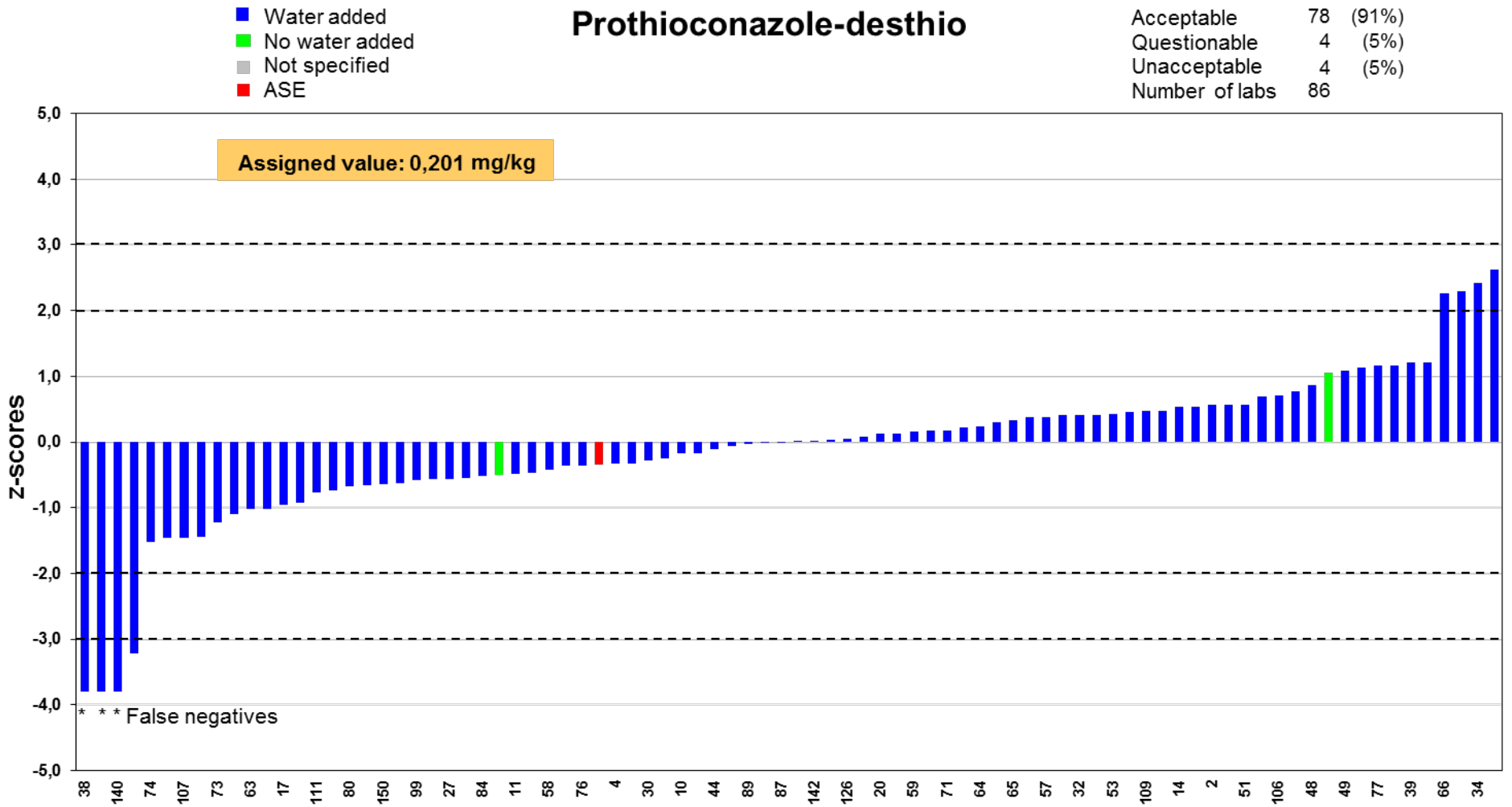

Water added
No water added
Not specified
ASE
Fluxapyroxad
Acceptable 57 (95%)
Questionable 0 (0%)
Unacceptable 3 (5%)
Number of labs 60
Assigned value: 0,165 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* * * False negatives
33 111 96 35 97 17 34 64 120 134 124 63 67 107 84 13 112 87 30 66 150 1 5 44 141 43 126 91 70 89 121 11 21 71 16 76 4 80 19 73 122 145 61 47 159 49 106 98 2 38 160 83 53 109 65 14 59 110 18 48

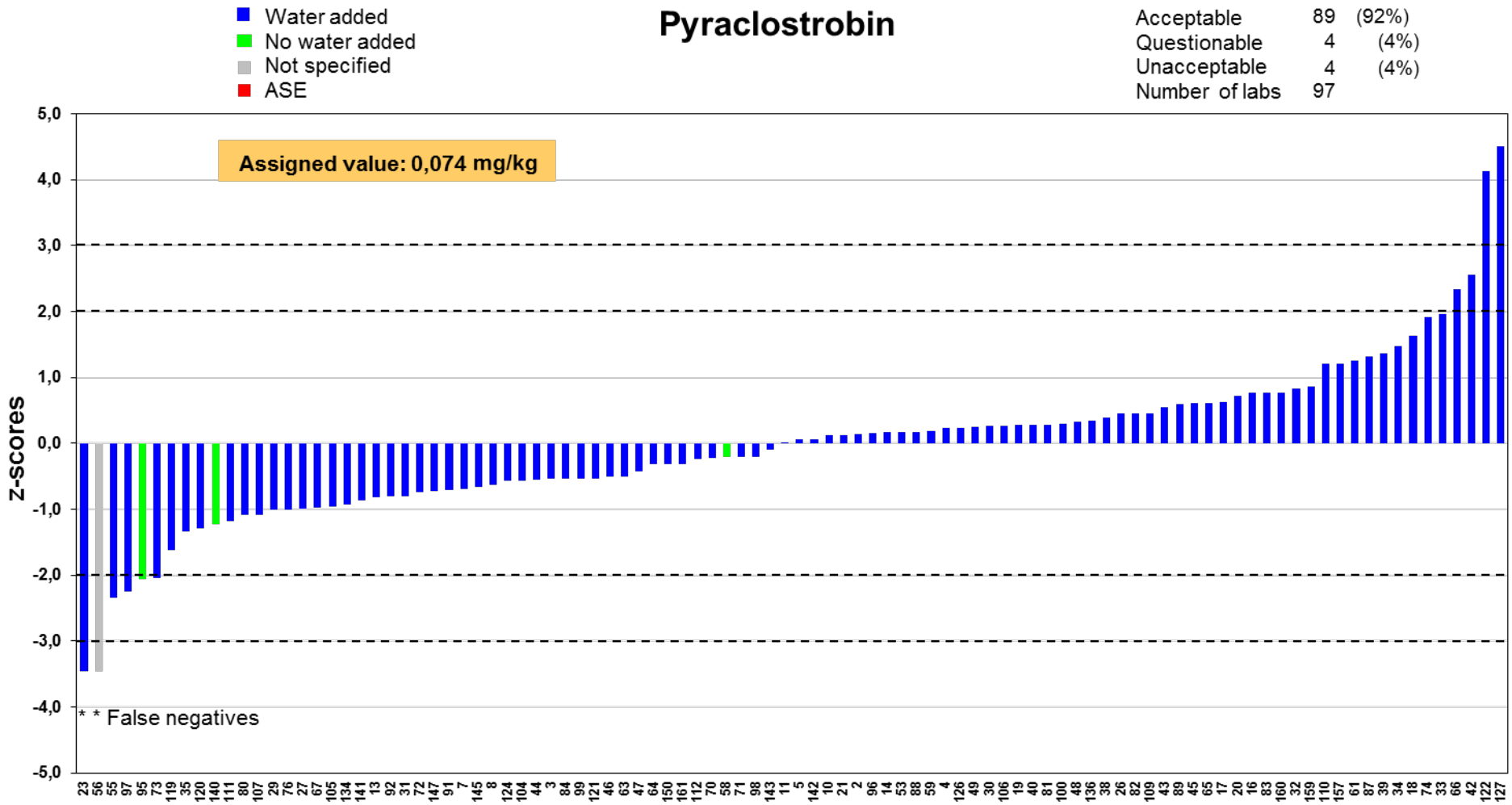

Water added
No water added
Not specified
ASE
Lindane
Acceptable 112 (90%)
Questionable 9 (7%)
Unacceptable 4 (3%)
Number of labs 125
Assigned value: 0,038 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
****** False negatives

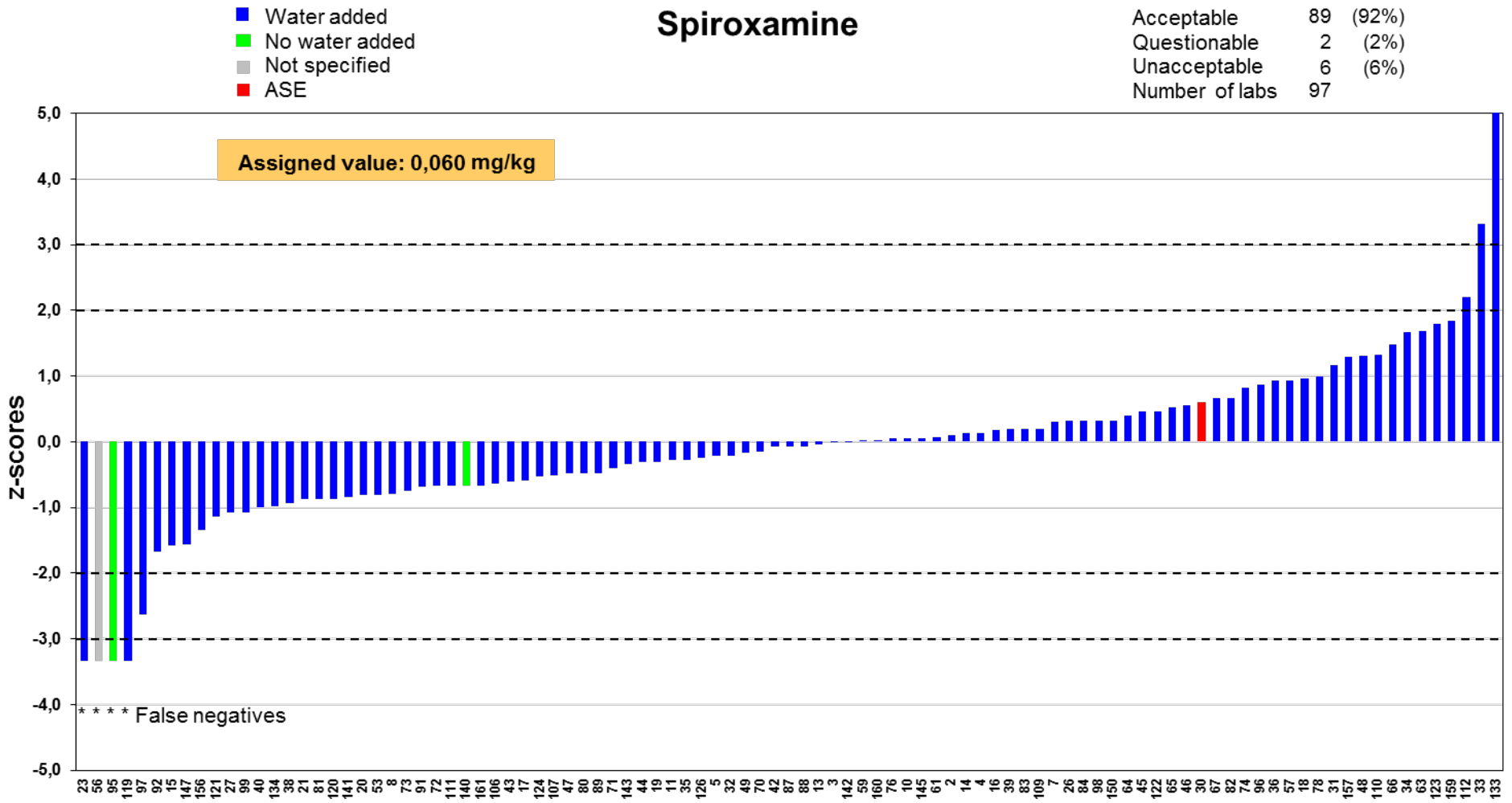

Water added
No water added
Not specified
ASE
Linuron
Acceptable 91 (97%)
Questionable 2 (1%)
Unacceptable 2 (2%)
Number of labs 95
Assigned value: 0,074 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* * False negatives
56 120 104 92 97 55 95 35 82 15 27 107 7 19 74 159 4 143 8 64 141 99 91 134 122 38 80 17 147 42 40 145 13 83 84 88 111 142 76 44 73 140 157 30 70 26 32 53 109 161 96 63 5 71 87 59 61 3 160 21 43 49 98 29 124 14 47 65 81 89 106 58 136 46 67 11 110 2 57 10 150 121 66 16 123 20 78 34 18 39 126 33 48 112 45

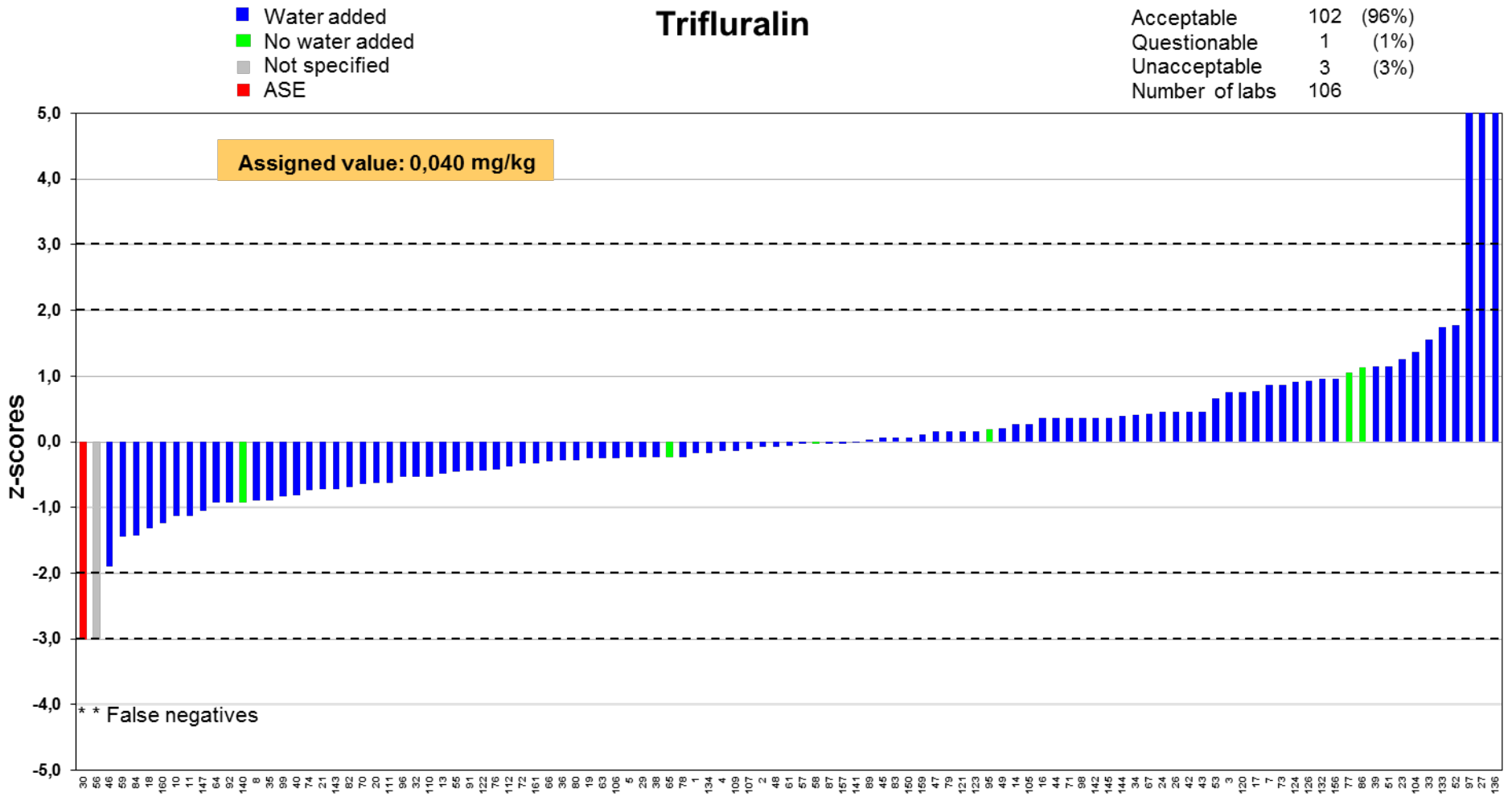

Water added
No water added
Not specified
ASE
Metconazole
Acceptable 82 (94%)
Questionable 2 (1%)
Unacceptable 3 (2%)
Number of labs 87
Assigned value: 0,101 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* * False negatives
21 56 157 35 97 92 107 126 4 74 19 17 156 84 121 111 96 13 159 27 134 73 38 64 47 88 63 3 67 161 76 30 34 40 141 99 80 124 87 26 89 91 5 43 58 110 120 14 32 70 98 123 133 143 7 44 150 46 71 11 65 78 142 42 106 145 59 2 10 49 66 160 16 109 20 57 83 82 18 112 39 33 53 61 122 48 31


Water added
No water added
Not specified
ASE
Metrafenone
Acceptable 79 (95%)
Questionable 1 (1%)
Unacceptable 3 (4%)
Number of labs 83
Assigned value: 0,376 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* False negatives
142 42 97 99 80 96 92 76 35 107 143 104 111 147 145 19 161 10 91 58 21 134 84 141 55 159 73 122 32 38 13 43 17 5 14 1 57 109 87 26 70 63 150 95 110 123 47 49 106 124 67 82 4 11 53 71 74 16 20 30 112 66 65 98 160 3 121 83 34 61 64 89 44 88 2 45 18 59 126 120 48 33 31


Water added
No water added
Not specified
ASE
Prothioconazole-desthio
Acceptable 78 (91%)
Questionable 4 (5%)
Unacceptable 4 (5%)
Number of labs 86
Assigned value: 0,201 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* * * False negatives
38 140 74 107 73 63 17 111 80 150 99 27 84 11 58 76 4 30 10 44 89 87 142 126 20 59 71 64 65 57 32 53 109 14 2 51 106 48 49 77 39 66 34


Water added
No water added
Not specified
ASE
Pyraclostrobin
Acceptable 89 (92%)
Questionable 4 (4%)
Unacceptable 4 (4%)
Number of labs 97
Assigned value: 0,074 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* * False negatives
23 56 55 97 95 73 119 35 120 140 111 80 107 29 76 27 67 105 134 141 13 92 31 72 147 91 7 145 8 124 104 44 3 84 99 121 46 63 47 64 150 161 112 70 58 71 98 143 11 5 142 10 21 2 96 14 53 88 59 4 126 49 30 106 19 40 81 100 48 136 38 26 82 109 43 89 45 65 17 20 16 83 160 32 159 110 157 61 87 39 34 18 74 33 66 42 122 127


Water added
No water added
Not specified
ASE
Spiroxamine
Acceptable 89 (92%)
Questionable 2 (2%)
Unacceptable 6 (6%)
Number of labs 97
Assigned value: 0,060 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* * * * False negatives
23 56 95 119 97 92 15 147 156 121 27 99 40 134 38 21 81 120 141 20 53 8 73 91 72 111 140 161 106 43 17 124 107 47 80 89 71 143 44 19 11 35 126 5 32 49 70 42 87 88 13 3 142 59 160 76 10 145 61 2 14 4 16 39 83 109 7 26 84 98 150 64 45 122 65 46 30 67 82 74 96 36 57 18 78 31 157 48 110 66 34 63 123 159 112 33 133


Water added
No water added
Not specified
ASE
Trifluralin
Acceptable 102 (96%)
Questionable 1 (1%)
Unacceptable 3 (3%)
Number of labs 106
Assigned value: 0,040 mg/kg
z-scores
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
* * False negatives
30 56 46 59 84 18 160 10 11 147 64 92 140 8 35 99 40 74 21 143 82 70 20 111 96 32 110 13 55 91 122 76 112 72 161 66 36 80 19 63 106 5 29 38 65 78 1 134 4 109 107 2 48 61 57 58 87 157 141 89 45 83 150 159 47 79 121 123 95 49 14 105 16 44 71 98 142 145 144 34 67 24 26 42 43 53 3 120 17 7 73 124 126 132 156 77 86 39 51 23 104 33 133 52 97 27 136

Appendix 5

Results for chlorothalonil and lindane in mg/kg, the pseudo z-scores, the pseudo assigned values and MRRLs.

Laboratory code	Chlorothalonil	Z-scores (FFP RSD (25%)	Lindane	Z-scores (FFP RSD (25%)
MRRL	0.01		0.01	
Assign. value	0.042		0.038	
1			0.039	0.0
2	0.063	2.0	0.041	0.3
3	0.051	0.9	0.046	0.8
4	0.027	-1.4	0.038	-0.1
5	0.044	0.2	0.039	0.1
6			0.046	0.8
7			0.036	-0.3
8			0.031	-0.8
9			0.043	0.5
10			0.036	-0.3
11	0.095	>5	0.04	0.2
12	0.022	-1.9	0.027	-1.2
13	FN	-3.0	0.041	0.3
14	0.044	0.2	0.042	0.4
15	0.247	>5	0.038	0.0
16	0.039	-0.3	0.045	0.7
17	0.041	0.0	0.038	0.0
18	0.03	-1.1	0.024	-1.6
19	0.02	-2.1	0.043	0.4
20	0.043	0.1	0.038	0.0
21	0.035	-0.6	0.035	-0.4
22			0.026	-1.3
23			0.037	-0.2
24			0.037	-0.2
25			0.039	0.1
26	0.05	0.8	0.05	1.2
27			0.144	>5
28	FN	-3.0		
29	0.047	0.5		
30	0.064	2.1	0.042	0.4
31	0.055	1.3	0.038	0.0
32			0.034	-0.5
33	0.051	0.9	0.047	0.9
34	0.047	0.5	0.0369	-0.2
35	FN	-3.0	0.0295	-0.9
36	0.022	-1.9	0.0265	-1.2
37			0.0403	0.2
38	0.035	-0.6	0.041	0.3
39			0.025	-1.4
40	0.039	-0.2	0.0361	-0.2
41	FN	-3.0	0.024	-1.5
42	FN	-3.0		
43	0.08	3.7	0.038	0.0
44			0.0335	-0.5
45	FN	-3.0	0.042	0.4
46	FN	-3.0	0.0221	-1.7
47	0.025	-1.6	0.042	0.4
48	0.072	2.9	0.0422	0.4
49	0.063	2.0	0.0438	0.6
50	0.028	-1.3	0.022	-1.7
51			0.038	0.0
52			0.04	0.2
53	FN	-3.0	0.044	0.6
54				
55	0.019	-2.1	0.0275	-1.1
56	FN	-3.0	FN	-3.0
57			0.034	-0.5
58	0.06	1.8	0.04	0.2
59	0.03	-1.2	0.0317	-0.7
60	FN	-3.0	0.02	-1.9
61	0.061	1.9	0.0431	0.5
62			0.0301	-0.9
63	0.091	4.8	0.0377	-0.1
64	0.029	-1.2	0.029	-1.0
65	0.078	3.5	0.038	0.0
66	0.054	1.2	0.0375	-0.1
67	0.052	1.0	0.045	0.7
68			0.038	0.0
69				
70	0.042	0.0	0.037	-0.2
71	FN	-3.0	0.041	0.3
72	0.036	-0.6	0.034	-0.5
73	0.031	-1.0	0.041	0.3
74	0.036	-0.5	0.031	-0.7
75	0.004	-3.6	FN	-3.0
76	0.036	-0.6	0.036	-0.3
77			0.039	0.1
78	FN	-3.0	0.044	0.6
79			0.045	0.7
80			0.035	-0.3
81				
82	0.042	0.1	0.035	-0.4
83	0.114	>5	0.035	-0.4
84	0.044	0.2	0.033	-0.6
85			FN	-3.0
86	FN	-3.0	FN	-3.0
87	0.055	1.3	0.042	0.4
88			0.042	0.4
89	FN	-3.0	0.034	-0.4
90				
91	FN	-3.0	0.047	0.8
92	0.323	>5	0.028	-1.1
93	FN	-3.0	FN	-3.0
94				
95	0.057	1.4	0.047	0.9
96	0.014	-2.6	0.036	-0.2
97	FN	-3.0	0.045	0.7
98			0.043	0.5
99	FN	-3.0	0.02	-1.9

Appendix 5 continued

Results for chlorothalonil and lindane in mg/kg, the pseudo z-scores, the pseudo assigned values and MRRLs.

Laboratory code	Chlorothalonil	Z-scores (FFP RSD (25%)	Lindane	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**	
Assign. value	**0.042**		**0.038**	
100				
101				
102	FN	-3.0	0.039	0.1
103			0.035	-0.4
104	0.151	>5	0.039	0.0
105				
106	FN	-3.0	0.031	-0.8
107	0.027	-1.4	0.029	-1.0
108	0.017	-2.4	0.034	-0.5
109	0.034	-0.7	0.043	0.5
110	0.029	-1.2	0.049	1.1
111	FN	-3.0	0.037	-0.2
112	0.06	1.7	0.039	0.1
113				
114	0.031	-1.1	0.037	-0.2
115				
116			0.038	-0.1
117			0.04	0.1
118	FN	-3.0	0.051	1.3
119	0.01	-3.0	0.044	0.6
120	0.039	-0.3	0.04	0.2
121	0.033	-0.8	0.045	0.7
122	0.093	4.9	0.028	-1.1
123			0.04	0.2
124	0.03	-1.1	0.042	0.4
125	0.07	2.7	0.04	0.2
126	0.031	-1.0	0.035	-0.4
127			FN	-3.0
128			0.039	0.1
129				
130				
131			0.03	-0.8

Laboratory code	Chlorothalonil	Z-scores (FFP RSD (25%)	Lindane	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**	
Assign. value	**0.042**		**0.038**	
132			0.035	-0.4
133			0.069	3.2
134	0.029	-1.2	0.034	-0.4
135			0.035	-0.4
136			0.034	-0.5
137				
138			0.036	-0.3
139				
140	FN	-3.0	0.031	-0.8
141	0.053	1.1	0.039	0.0
142			0.041	0.3
143	0.01	-3.0		
144			0.044	0.6
145			0.068	3.1
146			0.088	>5
147	0.021	-2.0	FN	-3.0
148			0.04	0.1
149				
150	FN	-3.0	0.043	0.5
151				
152				
153	FN	-3.0	0.03	-0.9
154	0.024	-1.7	0.038	0.0
155			0.037	-0.2
156	FN	-3.0		
157				
158				
159	0.022	-1.9	0.04	0.2
160			0.03	-0.9
161	0.025	-1.6	0.035	-0.4
162	FN	-3.0	FN	-3.0
163	0.034	-0.7	0.024	-1.5

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GENERAL PROTOCOL

for EU Proficiency Tests on Pesticide Residues in Food and Feed

Introduction

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

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

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

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

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

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

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

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

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

EUPT-Organisers and Scientific Committee

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

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

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

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

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

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

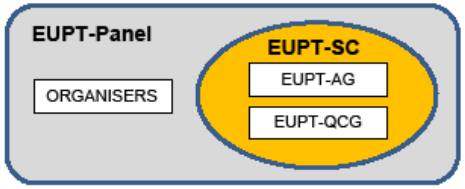
The EUPT-SC's role is to help the Organisers make decisions regarding the EUPT design: the selection of the commodity, the selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the statistical treatment and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

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

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

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

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



The decisions of the EUPT-Panel will be documented.

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

EUPT Participants

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

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

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

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

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

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

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

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

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

Confidentiality and Communication

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

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

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

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

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

The official language used in all EUPTs is English.

Announcement / Invitation Letter

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

Target Pesticide List

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

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

Specific Protocol

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

Homogeneity of the Test Item

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

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

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

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

Stability of the analytes contained in the Test Item

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

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

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

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

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

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

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

Methodologies to be used by the participants

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

General procedures for reporting results

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

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

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Correction of results for recovery

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

Methodology information

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

Results evaluation

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

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

- ***False Positive results***

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

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

- ***False Negative results***

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

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

Estimation of the assigned value (μ)

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

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

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

- ***Omission or Exclusion of results***

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

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

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

Uncertainty of the assigned value

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

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

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

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

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

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

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

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

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

- ***z-scores***

This parameter is calculated using the following formula:

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

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

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

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

Z-scores will be interpreted in the following way:

$\|z\| \leq 2.0$	Acceptable
$2.0 < \|z\| \leq 3.0$	Questionable
$\|z\| > 3.0$	Unacceptable

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

Category A and B classification

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

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

No. of Pesticides Present in the Test Item (N)	90 %	No. of Pesticides needed to be reported to have sufficient scope (n)	n
3	2.7	3	N
4	3.6	4	
5	4.5	4	N - 1
6	5.4	5	
7	6.3	6	
8	7.2	7	
9	8.1	8	
10	9.0	9	
11	9.9	10	
12	10.8	11	
13	11.7	12	
14	12.6	13	
15	13.5	13	N - 2
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	
20	18.0	18	

21	18.9	19	
22	19.8	20	
23	20.7	21	
24	21.6	22	
25	22.5	22	N - 3
26	23.4	23	

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

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

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

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

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

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

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

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

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

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

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

Publication of results

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

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

Certificates of participation

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

Feedback

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

Correction of errors

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

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

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

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

Follow-up activities

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

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

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

Disclaimer

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

EURL EUROPEAN UNION REFERENCE LABORATORY PESTICIDE RESIDUES IN CEREALS & FEEDING STUFF

DTU

SPECIFIC PROTOCOL

for the EU Proficiency Test for Pesticide Residues in Cereals/Feeding stuff using Multi-Residue Methods, EUPT-CF8 (2014)

(last updated: 5 May 2014)

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 Feeding stuffs (NRL-CFs) as well as by all official EU laboratories (OfLs) responsible for official pesticide residue controls on feeding stuff, as far as their scope overlaps with that of the EUPT-CF8.

Test Item (Test Material)

This proficiency test concerns the analysis of pesticide residues in wheat. The wheat was grown in Denmark in 2013 and pesticides were applied in the field. Following harvest, the wheat 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 feed Test Item with incurred and spiked pesticides and
- approximately 125 g of blank feed Test Item.

Shipment of Test Items

The Test Items are planned to be shipped on 19 May, 2014.

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-CF8 Result Submission Website. Links to this can be found on the EURL-CF webpage: http://www.crl-pesticides.eu/docs/public/tmplt_article.asp?LabID=400&CntID=926&Theme_ID=1&Pdf=False&Lang=EN

The website will be accessible from 20 May 2014. 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) given in the confirmation e-mails sent to the laboratories upon registration.

To access the data submission forms participants must use their unique login data (username and password), which will be sent by e-mail on 15 May.

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 13 June 2014 at 13.00 CET.

Test Item Receipt and Acceptance - Subpage 0

Once the laboratory has received the Test Items it must report to the organiser, via the **EUPT-CF8 Result Submission Website**, the date of receipt, the condition of the Test Item, and its acceptance. The deadline for acceptance is the 23 May 2014. 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 26 May 2014 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-CF8 Result Submission Website**.

Deadline: All results must be reported on the online result submission website by 13 June 2014. 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-CF8 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-CF8 Result Submission Website**. This subpage will be accessible from 16-18 June 2014.

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 AO in comparative testing will be followed by EURL-CF..

Documents

All documents relating to EUPT-CF8 can be found in the EURL-Document Repository (CIRCA/FIS-VL). Links to the documents can be found in the EUPT–CF8 Website.

Calendar

Activity	Dates
Announcement Calendar Target Pesticide List	January 2014
EUPT-Registration Website	18 February 2014
Deadline for registration	30 April 2014
Release of Specific Protocol	5 May 2014
Distribution of Test items	19 May 2014
Deadline for Receipt and Acceptance of Test Materials	within 24 hr on reciept
Deadline for Result Submission	13 June 2014 at 13.00 CET
Deadline for submission of additional method information for false negative results	18 June 2014
Preliminary Report (only compilation of results)	31 August 2014
EUPT Evaluation Meeting	September 2014
Final Report	December 2014

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 Peter Dahm-Jappe at the financial department pdahm@adm.dtu.dk.

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