National Food Institute
Technical University of Denmark

Proficiency Test on pesticide residues in rapeseed cake

EU Reference Laboratory on Cereals & Feeding stuff

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EUPT-CF15, 2021

Pesticide Residues in Rapeseed Cake

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PREFACE

Regulation (EU) No 2017/625 [1], defines the general tasks and duties of the European Union Reference Laboratories (EURLs) for Food, Feed and Animal Health including the organisation of comparative tests. These proficiency tests (PTs) are carried out on an annual basis, and aim to improve the quality, accuracy and comparability of the analytical results generated by EU Member States within the framework of the EU multi-annual co-ordinated control and national monitoring programmes. Participation in the proficiency test scheme "European Union Proficiency Tests (EUPTs) for pesticide residues" is mandatory according to Article 28 of Regulation (EC) No 396/2005 on maximum residue levels of pesticides in, or on, food and feed of plant and animal origin [2], as long as the analytical scope of the PT and the laboratory overlap.

The present EUPT was the fifteenth organized within the frame of the EURL activities with cereal or feed matrices as Test Items. The previous PTs were EUPT-C1/SRM2 on wheat, EUPT-C2 on wheat, EUPT-C3/SRM4 on hay, EUPT-C4 on rye, EUPT-C5/SRM6 on rice, EUPT-C6 on barley, EUPT-CF7 on animal feed, EUPT-CF8 on wheat, EUPT-CF9 on maize, EUPT-CF10 on rye flour, EUPT-CF11 on oat flour, EUPT-CF12 on hay flour, EUPT-CF13 on rye kernels andEUPT-CF14 on Rice Kernels . The PTs in 2007, 2009, 2011, 2015 and 2020 were jointly organised by the EURL-CF and EURL-SRM using same cereal and focusing on both MRM and SRM pesticides. The orther PTshave only focused on MRM-pesticides. The test rape plants used for EUPT-CF15 were treated both with formulations in the field and post-harvest in the laboratory.

Participation in EUPT-CF15 was compulsory for all National Reference Laboratories (NRLs) and Official Laboratories (OfLs) within the EU involved in the determination of pesticide residues in cereals for human or animal consumption using multi residue methods for their national programmes. Official laboratories from EFTA countries (Iceland, Norway and Switzerland), as well as official laboratories from EU-candidate states, were invited to take part in this EUPT. Selected laboratories from Third Countries were also allowed to take part in this exercise, but their results, together with the EU-candidate state laboratories, were not used when establishing the Assigned Values for each pesticide.

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

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EUROPEAN COMMISSION EURL PROFICIENCY TEST ON PESTICIDE RESIDUES IN CEREALS EUPT-CF15, 2020

1. INTRODUCTION

On 1 December 2020 the announcement of the 15th European Commission's Proficiency Test on Cereals and Feed (EUPT-CF15) was published on the EURL website, together with the Calendar and the Pesticide Target List including all compounds that could potentially be present in the Test Item. The Target Pesticides List included 172 individual compulsory compounds and 43 voluntary requiring the use of multi residue 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-CF15, were provided via the homepage. Laboratories were able to register online from December 2020 to 8 of February 2021. In total 129 laboratories from EU and EFTA countries agreed to participate in the test as well as 88 laboratories from EU-Candidate States and Third Countries (**Appendix 1**).

The rape plants were sprayed in the field with 16 pesticides. The cultivation was performed in 2020 in Denmark by the Danish Centre for Food and Agriculture at Aarhus University. After analyses of the pesticide residues content, it was decided to additionally spike in the laboratory with 15 pesticides, which were either not included in the field treatments or where residues were too low for the evaluation. After the spike treatment the seeds was sent to Rapsol I/S, a company specialised in pressing oil out of rapeseeds. Due to the small amount of rapeseeds, this was done using their laboratory equipment, which resulted in a rapeseed cake test item with up to 20% fat.
The pesticides employed for the field treatment were selected by the EURL-CF and the EUPT quality control group. The application rates and harvest intervals chosen were based on previous experience and data from supervised residue trials. The test material was 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 100 g portions of the rapeseed cake Test Item. The Test Items were shipped to participants on 1 March 2021 and the deadline for submission of results to the Organiser was the 19 April 2021. The deadline for submission of additional information for false negative results was the 28 April 2021 The participants were asked to analyse the 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 DTU Webtool.

1.1 Analytical methods

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

- QuEChERS -EMR: Cold water was added to a milled portion of the test item and shaken. Acetonitrile was added immediately and the tube was shaken again. A salt and buffer mixture was then added, together with ceramic homogenizers, and the sample was shaken vigorously for 1 min. After centrifugation, an aliquot of the supernatant was cleaned by freezing out. After additional centrifugation of the cold extract 1 ml from supernatant was filtered and transferred in glass vial for LC/MS/MS analyses and six ml was transferred to a tube containing PSA and $MgSO_4$. The tube was shaken and centrifuged ad five ml were transferred into a d-SPE EMR tube which was previously activated with 5 mL of water, shaken and centrifuged. Supernatant was transferred to a 15 mL EMR-Polish tube, shaken and centrifuged aging and after that it was ready for GC-MS/MS analysis

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, the working document, and pesticides according to their relevance and risk-potential, as well as pesticides relevant to the specific commodity (rapeseed). 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 in general set at 0.01 mg/kg. However, for 2020 pesticides the MRRL were set at or below 0.005 mg/kg.

1.3 Preparation of the Test Item

The field spraying was performed in 2020 in Denmark and organised by Danish Centre for Food and Agriculture at Aarhus University. Approximately, 110 kg of the harvested rapeseeds were used for this PT. It was decided to additionally spike in the laboratory with fifteen pesticides, which were either not included in the field treatments or where residues were too low for the evaluation (**Table 1**). Spiking in the laboratory was performed using formulations or pure standards. Seven portions of 1.4 kg of the field treated rapeseeds was spiked and subsequently mixed with 100 kg of field treated rapeseeds and homogenised thoroughly. The rapeseeds were shipped to Rapsol I/S and rapeseed cake was returned after the oil was pressed out of the seed as far as possible. As the seed was homogenised before the pressing, no further homogenisation of the rapeseed oil was done. One hundred gram portions of the rapeseed cake were then 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.

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

Pesticides	Application in field	Spike in laboratory	Formulation/standard
Acetamiprid		x	Analytical standard
Aldrin*		x	Analytical standard
Azoxystrobin	x	x	Amistar/Analytical standard
Boscalid	x		Cantus
Clomazone*	x		Centium
Cyantraniliprole		x	Analytical standard
Fluopyram	x	x	Propulse / analytical standard
Imidacloprid		x	Analytical standard
Indoxacarb	x	x	Steward / Analytical standard
Metconazole	x		Juventus
Pendimethalin	x		Stomp
Penthiopyrad*		x	Analytical standard
Pirimicarb	x	x	Pirimor/analytical standard
Prosulfocarb	x		Boxer
Prothioconazole	x		Proline/propulse
Pyraclostrobin	x		Comet pro
Pyridalyl		x	Analytical standard
Tebuconazole	x	x	Orius 200 / analytical standard
Tebufenozide		x	Analytical standard
Tefluthrin		x	Analytical standard
Tetraconazole		x	Analytical standard
Thiacloprid	x	x	Biscaya / analytical standard

*Voluntary pesticides.

The rapeseed were also sprayed with cypermethrin, lambda-cyhalothrin, and tau-fluvalinate. However, the concentration were very low and it was decided not to overspike these compounds.

1.4 Homogeneity test

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

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

The homogeneity test is to show that the between-bottle variance is not greater than the within-bottle variance. The acceptance criteria to show that the Test Items were sufficiently homogeneous for the proficiency test was that: $S_s^2 < c$ where S_s is the between-bottle sample standard deviation and $c = F_1 \times \sigma_{all}^2 + F_2 \times s_{an}^2$; F1 and F2 being constants with values of 1.83 and 0.93, respectively, from the 11 samples taken, $\sigma_{all}^2 = 0.3$ 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, when the Test Item was stored at -18 °C, the Test Item was considered to be sufficiently homogenous and suitable for the EUPT-CF15.

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

Pesticides	Mean, mg/kg	S_s^2	c	$S_s^2 < c$
Acetamiprid	0.088	0.00001	0.0002	Pass
Aldrin	0.028	0.00000	0.0000	Pass
Azoxystrobin	0.034	0.00003	0.0000	Pass
Boscalid	0.097	0.00008	0.0003	Pass
Clomazone	0.074	0.00002	0.0001	Pass
Cyantraniliprole	0.012	0.00000	0.0000	Pass
Fluopyram	0.033	0.00002	0.0000	Pass
Imidacloprid	0.291	0.00009	0.0023	Pass
Indoxacarb	0.022	0.00001	0.0000	Pass
Pendimethalin	0.028	0.00000	0.0000	Pass
Penthiopyrad	0.022	0.00000	0.0000	Pass
Pirimicarb	0.058	0.00002	0.0001	Pass
Prosulfocarb	0.452	0.00096	0.0045	Pass
Prothioconazole-desthio	0.044	0.00002	0.0001	Pass
Pyraclostrobin	0.031	0.00003	0.0001	Pass
Pyridalyl	0.005	0.00000	0.0000	Pass
Tebuconazole	0.069	0.00005	0.0003	Pass
Tebufenozide	0.012	0.00000	0.0000	Pass
Tefluthrin	0.008	0.00000	0.0000	Pass
Tetraconazole	0.020	0.00000	0.0000	Pass
Thiacloprid	0.052	0.00000	0.0001	Pass

1.5 Stability tests

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

The stability test was performed according to ISO 13528, Annex B [5]. Two different storage temperatures were used; room temperature and -18 °C. Six sub-samples (analytical portions) were analysed on each test day. A pesticide is considered to be adequately stable if $| x_1 - y_i | \leq 0.3 \times \sigma$, where x_1 is the mean value of the first stability test, y_i the mean value of the last stability test and σ the standard deviation used for proficiency assessment (25% of the assigned value):

The dates of testing were as follows:

Day 1: 1 March 2021
Day 2: 15 March 2021
Day 3: 29 April 2021

The results of the stability test for storage temperature -18 °C are given in **Table 3**. All pesticides passed the test at -18 °C. At room temperature indoxacarb and pirimicarb did not pass the test. All the laboratories were instructed to store the test item at -18 degree and the stability test was consequently accepted. See the individual stability figures for all pesticides in **Appendix 4**.

Table 3. Statistical evaluation of the stability test data at -18 °C.

Pesticides	Mean, mg/kg	| x1 - yi |	0.3×σ	| x1 - yi | ≤ 0.3×σ
Acetamiprid	0.113	0.001	0.009	Pass
Aldrin	0.007	0.001	0.001	Pass
Azoxystrobin	0.044	0.002	0.004	Pass
Boscalid	0.119	0.005	0.009	Pass
Clomazone	0.085	0.002	0.007	Pass
Cyantraniliprole	0.016	0.001	0.001	Pass
Fluopyram	0.034	0.002	0.003	Pass
Imidacloprid	0.407	0.008	0.031	Pass
Indoxacarb	0.022	0.000	0.002	Pass
Pendimethalin	0.028	0.001	0.003	Pass
Penthiopyrad	0.022	0.001	0.002	Pass
Pirimicarb	0.064	0.000	0.005	Pass
Prosulfocarb	0.752	0.038	0.0495	Pass
Prothioconazole desthio	0.070	0.002	0.005	Pass
Pyraclostrobin	0.047	0.004	0.004	Pass
Pyridalyl	0.004	0.001	0.001	Pass
Tebuconazole	0.074	0.006	0.006	Pass
Tebufenozide	0.019	0.001	0.002	Pass
Tefluthrin	0.009	0.000	0.001	Pass
Tetraconazole	0.020	0.000	0.002	Pass
Thiacloprid	0.065	0.003	0.005	Pass

1.6 Organisational details

1.6.1 Access to documents, registration and confidentiality

In the invitation letter, all NRLs and OfLs were requested to register using the online registration link from December 2020. 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 Candidate countries and third countries did also have access to another online registration link. On 16 February, the participants received a link to DTU web tool, along withlogin credentials and were asked to enter the web tool and to select the scope of pesticides they wanted to be evaluated on. This had to be done before the samples were shipped to the participants (1 March 2021).

1.6.2 Distribution of the Test Item

On 1 March 2021, the Test Item (100 g) was 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 web tool to report whether they accept/not accept the Test Item. No blank test material was send.

1.6.3 Submission of results

The participants had to submit their results via a web tool. All participants had access to the result-submission website from a few days after shipment until the result-submission deadline (19 April 2021). 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 Item.

2. EVALUATION OF THE RESULTS

The results were evaluated according to the general and specific protocols (**Annex 1 and 2**). However, the main points are listed below.

2.1 False positives and negatives

2.1.1 False positives

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

2.1.2 False negatives

These are results for pesticides reported by the laboratories as 'analysed' but without reporting numerical values although they were: a) used by the Organiser to treat the Test Item and b) detected by the Organiser as well as the majority of the participants that had targeted these specific pesticides at, or above the respective MRRLs. Results reported as '< RL' (RL= Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary. In cases of the assigned value being less than a factor of 3 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 (x_{pt})

In order to minimise the influence of out-lying results on the statistical evaluation, the assigned value xpt (= consensus concentration) will typically be estimated using robust estimate of the participants' mean (x*) as described in ISO 13528:2015, taking into account the results reported by only EU and EFTA countries laboratories. In special justifiable cases, the EUPT-Panel may decide to eliminate certain results traceably associated with gross errors, 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 u(xpt) is calculated according to ISO 13528:2015 as:

$$u(x\text{pt}) = 1.25\ \frac{s^*}{\sqrt{p}}$$

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

2.4 Standard deviation of the assigned value (target standard deviation)

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

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

The percentage FFP-RSD is set at 25% based on experience from results of 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.
For informative purposes the robust relative standard deviation (CV*) is calculated according to ISO 13528:2015; Chapter 7.7 (Consensus value from participant results) following Algorithm A in Annex C.

2.5 Z scores

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

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

where x_i is the value reported by the laboratory, x_{pt} is the assigned value, and FFP-σ_{pt} is the standard deviation using FFP approach. Z scores was 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 > 5 will be typically reported as '> 5' and a value of '5' will be used to calculate combined z scores.

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

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

For results considered as false negatives, z scores will be calculated using the MRRL or RL (the laboratory's Reporting Limit) if RL $<$ MRRL. Where, using this approach, the calculated z scores for false negatives are > -3 (still questionable), they will be fixed at -3.5 to underline that these are unacceptable results. These z-scores will typically appear in the z-score histograms and used in the calculation of combined z-scores.

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

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

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

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

where "n" is the number of each laboratory's z scores that were considered in this formula. For the calculation, any z-score > 5 was set at "5". Based on the AZ^2 achieved, the laboratories are classified as follows:

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

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

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

3. RESULTS

3.1 Summary of reported results

In total, 129 EU and EFTA laboratories, from 29 different countries (26 EU member states), agreed to participate in this proficiency test. Seven EU participants did not submit results. Additionally, eight participants from non-EU Countries registered for the PT. The participating laboratories are listed in **Appendix 1**.

An overview of results submitted by laboratories from the EU and EFTA can be seen in **Table 4**. All reported analytical results for the pesticide residues are shown in **Table 10a-c** and in **Appendix 5**. However, only results submitted by laboratories from EU and EFTA countries are included in **Table 4, 8-9** and **13** and the z scores histograms are shown in **Appendix 5.**

Table 4. Overview of number of results, number of not analysed (NA), number of not detected (ND = false negatives) and the percentage of laboratories that reported results for the pesticides in the Test Item. Only results submitted by laboratories from the EU and EFTA are included in this table.

Pesticides	No. of reported results	No. of NA	False negatives	% of labs reporting results[1]
Acetamiprid	100	22	2	82
Azoxystrobin	113	9	0	93
Boscalid	112	10	0	92
Clomazone	70	52	0	57
Fluopyram	104	18	2	85
Imidacloprid	99	23	2	81
Pendimethalin	114	8	3	93
Pirimicarb	104	18	1	85
Prosulfocarb	90	32	1	74
Prothioconazole-desthio	96	26	6	79
Pyraclostrobin	101	21	4	83
Tebuconazole	113	9	1	93
Thiacloprid	99	23	3	81
Aldrin	116	6	33	95
Cyantraniliprole	62	60	13	51
Indoxacarb	105	17	9	86
Metconazole	97	25	0	80
Penthiopyrad	65	57	3	53
Pyridalyl	69	53	0	57
Tebufenozide	96	26	13	79
Tefluthrin	103	19	35	84
Tetraconazole	110	12	5	90

[1] '% 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 = 122). False negatives are included in reported results.

Aldrin, azoxystrobin, boscalid, pendimethalin, tebuconazole, and tetraconazole were the most frequently analysed compounds with ≥90 % of the labs submitting results for these compounds. Acetamiprid, fluopyram, imidacloprid, indoxacarb, metconazole, pirimicarb, prosulfocarb, prothioconazole-desthio, pyraclostrobin, tebufenozide, tefluthrin, and thiacloprid were analysed and reported by 73-86% of the participants. Clomazone, cyantraniliprole, penthiopyrad, and pyridalyl were only analysed and reported by 50-57% of participants.

3.1.1 *False positives*

Seven participants (six from EU and EFTA) countries reported nine results for eight different additional pesticides above the MRRL that had not been used to treat the Test Item (**Table 5**). The pesticides were: HCH-beta, biphenyl, diazinon, isocarbophos, lindane, metolachlor, spirotetramat, BYI 03380-monohydroxy, and teflubenzuron. 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.

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	Pesticides	Concentration mg/kg	Determination technique	RL, mg/kg	MRRL, mg/kg
14	HCH-beta	0.0259	GC-MS/MS (QQQ)	0.01	0.01
16	Biphenyl	0.045	GC-MS/MS (QQQ)	0.01	0.01
20	Spirotetramat, BYI 03380-monohydroxy	0.0674	LC-MS/MS QQQ	0.01	0.01
36	Lindane	0.0186	GC- (μ) ECD	0.01	0.01
36	Metolachlor	0.195	LC-MS/MS QQQ	0.004	0.004
42	Diazinon	0.195	GC-MS	0.01	0.01
83	Biphenyl	0.032	GC-MS/MS (QQQ)	0.01	0.01
92	Isocarbophos	0.011	GC-MS	0.01	0.01
92	Teflubenzuron	0.031	LC - MS/MS	0.01	0.01

3.1.2 *Findings of compounds below the MRRL mg/kg*

Apart from the false positive results above and the results for the pesticides listed in **Table 10a-c**, two participants reported results for two other pesticides, see **Table 6**. These results were not evaluated as false positives because the concentrations are below the MRRL at 0.01 mg/kg.

Table 6. Reported results in mg/kg at or below the MRRL at 0.01 mg/kg

Lab code	Pesticides	Concentration mg/kg	Determination technique	RL, mg/kg	MRRL, mg/kg
36	Trifloxystrobin	0.0038	LC-MS/MS QQQ	0.004	0.01
92	Permethrin	0.005	GC-MS	0.005	0.01

3.1.3 *False negatives*

Not reported results for pesticides actually present in the Test Item were judged as false negatives. **Table 7** summarizes the number of reported false negatives for each pesticide. Twenty participants submitted 26 false negatives results for 13 different pesticides, which represents 1.5% of the total number of results. Around 16% of the participants (20 laboratories) reported false negative results. This at the level typically seen in the EUPT-CF and show that despite the difficult matrix, the laboratories performed well in terms of false negative results.

Table 7. False negative results (FN).

Lab code	Acetamiprid	Azoxystrobin	Boscalid	Clomazone	Fluopyram	Imidacloprid	Pendimethalin	Pirimicarb	Prosulfocarb	Prothioconazole-desthio	Pyraclostrobin	Tebuconazole	Thiacloprid
5										FN			
9											FN		
16					FN								
44											FN		
45										FN			FN
55							FN	FN		FN	FN		
59										FN			
60	FN												
63						FN							
81					FN								
82	FN												
84										FN			
89							FN						
92								FN					
101										FN			
106													FN
107											FN		
113							FN		FN			FN	
115													FN
132						FN							

3.2 Assigned values, target standard deviations and Alg A standard deviations

3.2.1 Assigned values

The Assigned Values were calculated as the Algorithm A mean (Alg A mean), including the reported results submitted by laboratories from EU and EFTA countries.

All assigned values for the pesticides can be seen in **Table 8**. For the evaluated pesticides the assigned values were in the range of 0.032-0.361 mg/kg. The calculated Algorithm A means for aldrin, cyantraniliprole, indoxacarb metconazole, penthiopyrad, pyridalyl, tebufenozide, tefluthrin, tetraconazol*e* was less than three times the MRRL. Consequently, the results for these compounds cannot be evaluated and the values for the compounds are given for informative purposes only

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

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

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

Table 8. Assigned values and their uncertainty in mg/kg, Fit-For-Purpose Relative Standard Deviation (FFP RSD) and Robust Relative Standard Deviation (Alg A RSD) for the pesticides present in the Test Item.

Pesticides	MRRL, mg/kg	Assigned value, mg/kg	Uncertainty, mg/kg	FFP RSD, %	Alg A RSD, %
Acetamiprid	0.01	0.100	0.005	25	38
Azoxystrobin	0.01	0.042	0.001	25	26
Boscalid	0.01	0.105	0.003	25	26
Clomazone	0.01	0.076	0.003	25	25
Fluopyram	0.01	0.032	0.001	25	28
Imidacloprid	0.01	0.361	0.015	25	34
Pendimethalin	0.01	0.040	0.001	25	25
Pirimicarb	0.01	0.059	0.002	25	28
Prosulfocarb	0.01	0.567	0.028	25	38
Prothioconazole-desthio	0.01	0.053	0.002	25	28
Pyraclostrobin	0.01	0.045	0.002	25	33
Tebuconazole	0.01	0.070	0.003	25	32
Thiacloprid	0.01	0.054	0.002	25	29
Aldrin[1]	*0.005*	*0.013*	*0.001*	*25*	*39*
Cyantraniliprole[1]	*0.01*	*0.014*	*0.000*	*25*	*21*
Indoxacarb[1]	*0.01*	*0.022*	*0.001*	*25*	*24*
Metconazole[1]	*0.01*	*0.012*	*0.000*	*25*	*17*
Penthiopyrad[1]	*0.01*	*0.023*	*0.001*	*25*	*20*
Pyridalyl[1]	*0.01*	*0.014*	*0.001*	*25*	*32*
Tebufenozide[1]	*0.01*	*0.019*	*0.000*	*25*	*18*
Tefluthrin[1]	*0.01*	*0.012*	*0.000*	*25*	*18*
Tetraconazole[1]	*0.01*	*0.020*	*0.000*	*25*	*20*

[1] The assigned values are less than 3 times the MRRL and consequently shown for informative purposes only.

3.2.2 Target standard deviations and Alg A standard deviations

The target standard deviation was obtained using a fixed FFP-RSD value of 25%. In parallel, the Algorithm A standard deviation (Alg A-RSD) was calculated for informative purposes only. The range of Alg A-RSD values was for the evaluated pesticide in the range of 25-38% but on average, the Alg A-RSD was 30%, and thus remarkably higher than 25% FFP-RSD used for the z score calculations. It is also much higher than seen in the previous eight EUPTs where the average Alg A-RSD were 20% or lower.

The high Alg A-RSD indicate that the methods used by the laboratories have higher bias and might not all be fit for purpose, probably due to the high fat content of 20%. The data has been tested for bimodality and this has not been detected, so probably multiple sources for variation is contributing to the high Alg A-RSD. In this report we have focussed on the contribution that arise from the different way that the laboratories have calibrated their instruments. To look into this issue, the data has been separated in four group depending of the calibration approach using 1) standards in solvent, 2) standards in matrix (different matrix), 3) procedural calibration (different matrix), or 4) standard addition. For each group (two by two) it was determined if the data sets was significantly different (p value ≤ 0.05) by using a two tailed, unequal sample sizes, unequal variances Student's t-test.

For acetamiprid, clomazone and thiacloprid a clear significant difference ($p<0.05$) was seen between using calibration standards in solvent and all the other three calibrations/quantitation approaches. For imidacloprid, the difference was only seen between standards in solvent versus standard addition and procedural calibration. For

other pesticides, the outcome of the t-tests were more unclear, e.g. significant difference was seen between standard in matrix and procedural calibration or between procedural calibration and standard addition (azoxystrobin, boscalid, fluopyram, pirimicarb, prosulfocarb and tebuconazole. Finally, no significant differences were seen for pendimethalin, prothioconazole-desthio, and pyraclostrobin. However, a statistical power analysis shows that for pesticides where no significant difference was determined between the calibration groups, it can be due to the number of results was too low. In the some of the groups it was as low as nine. As an example the difference in the Alg A mean for azoxystrobin between standard in solvent and procedural calibration was 20%. A statistical power analysis (β=0.1) shows that the minimum required number of data to evaluate if this difference is significant, when the standard division is 30%, requires at least 31 results. But the two groups consist of only 17 and 10 results. Consequently, it is not possible to determine if the data set are significantly different or not. The Alg A means and STD, number of results and the p values from the T-test are shown in **Appendix 6**. Figure 1 show the Alg A means normalised to the assigned values. As clearly seen, the Alg A mean for standards in solvent were the lowest for many of the compounds but especially for acetamiprid, clomazone, imidacloprid and thiacloprid (0.76-0.88).

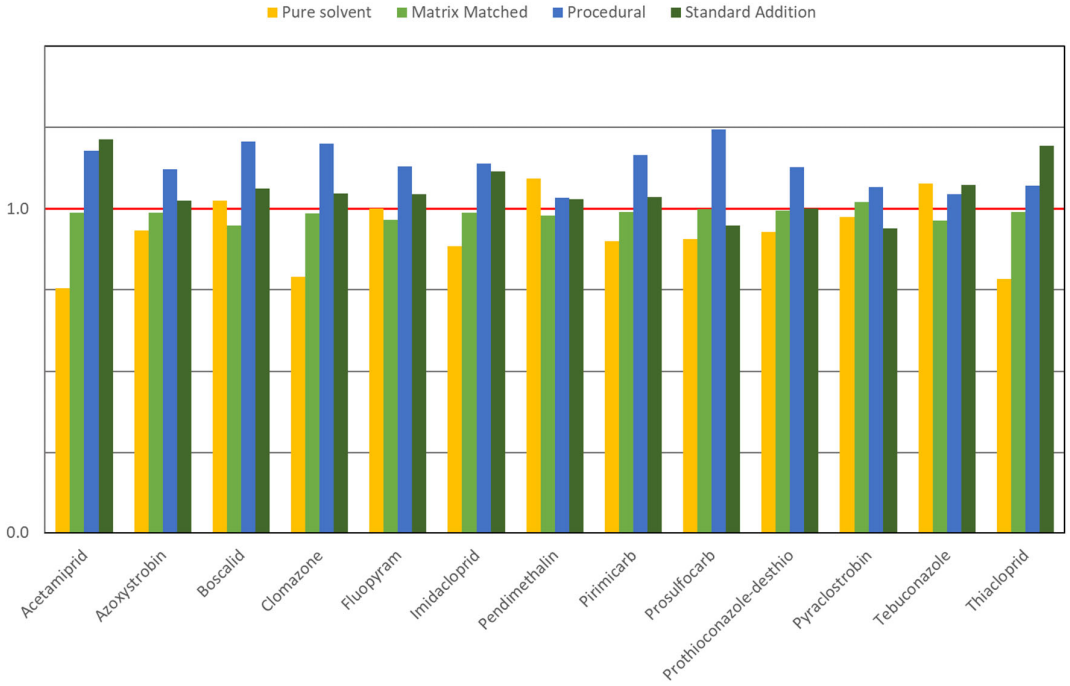


Figure 1. Alg A means for the four different calibration approaches normalised to the assigned values.

As described above, the statistical evaluation shows that at least for acetamiprid, clomazone, imidacloprid, and thiacloprid show high matrix effect when analysed in rapeseed cake. SANTE/12682/2019 requires a comparison between the response from solvent standards and matrix-matched standards during validation. If the difference is higher than 20% then this must be addressed in calibrations. For matrices that has not yet been included in the validation it is recommended to check the matrix effects. If high matrix effects are seen, SANTE/12682/2019 recommends to use either standard addition or procedural calibration. Further statistical evaluation might reveal other contributions to the uncertainty and bias.

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/e- 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 5**. Of the reported results for the evaluated pesticides, more than 90% were acceptable azoxystrobin, boscalid, clomazone, fluopyram, pendimethalin, and prosulfocarb. For acetamiprid, imidacloprid, pirimicarb, prothioconazole-desthio, praclostrobin, tebuconazole, and thiacloprid between 80-89% of the results were acceptable.

Table 9. Number of acceptable, questionable, unacceptable z scores, and false negatives.

Pesticides	No. of reported results	Assigned values	Acceptable %	Questionable %	Unacceptable[1] %	False negatives %
Acetamiprid	100	0.100	83	7	10	2
Azoxystrobin	113	0.042	102	10	1	0
Boscalid	112	0.105	103	9	0	0
Clomazone	70	0.076	63	3	4	0
Fluopyram	104	0.032	94	6	4	2
Imidacloprid	99	0.361	79	8	12	2
Pendimethalin	114	0.040	104	5	5	3
Pirimicarb	104	0.058	93	8	3	1
Prosulfocarb	90	0.567	82	2	6	1
Prothioconazole-desthio	96	0.053	80	8	8	6
Pyraclostrobin	101	0.045	84	10	7	4
Tebuconazole	113	0.070	101	9	3	1
Thiacloprid	99	0.054	83	8	8	3
Aldrin	*116*	*0.013*	*66*	*16*	*34*	*33*
Cyantraniliprole	*62*	*0.014*	*57*	*2*	*3*	*13*
Indoxacarb	*105*	*0.022*	*91*	*1*	*13*	*9*
Metconazole	*97*	*0.012*	*48*	*3*	*46*	*44*
Penthiopyrad	*65*	*0.023*	*61*	*0*	*4*	*3*
Pyridalyl	*69*	*0.014*	*66*	*3*	*0*	*35*
Tebufenozide	*96*	*0.019*	*80*	*1*	*15*	*13*
Tefluthrin	*103*	*0.012*	*64*	*1*	*38*	*35*
Tetraconazole	*110*	*0.020*	*103*	*7*	*0*	*5*

[1] Unacceptable z scores includes false negative results.

3.3.2 Analytical methods used

More than five different analytical methods have been used by the laboratories. For the majority of the results , 72%, QuEChERS, Citrate buffered (EN 151662) was used. However, variations in the clean-up procedures were reported by the labs, e.g. some used a freezing out step (38% of the participants), centrifugation (4%), some used d-SPE with PSA/MgSO4 (34%), some used d-SPE with ODS/ $MgSO_4$ (13%). Liquid-liquid partition was used by 9% of the participants and only 1% used SPE column. So it was not one specific method.

Other extraction methods have been used; the original QuEChERS version method (J. AOAC 86, 2003) and QuEChERS-Acetate buffered (AOAC Official method 2007.01) were both used by 7% of the participants. The Mini-Luke method and the SweEt method were each used by 2-3% of the participants. The remaining 9% of the participants used other methods. More than 92% of the reported results derived from a method where water was added before extraction.

For milling, 58% of the labs used a knife mill and 24% of the labs used centrifugal mill. Moreover, 6% used a disk mill, 3% used an horizontal mill, and 3% used a hammer mill. Furthermore, 7% of the labs did not specify the type of mill used.

GC instruments was used for 29% of the results, mainly GC-MS/MS (89%), but also GC-MS (6%) and GC- (μ) ECD (5%) was used. GC-NPD was used for 2 results, GC-iontrap and GC-TOF for only 1 result each. LC instruments was used for 71% of the reported results, mainly LC-MS/MS (94%) but 5% used high resolution instrument like LC-Orbitrap, LC-Q-Orbitrap or LC-Q-TOF. Finally, 1 % if the results were based on LC-Iontrap. No result were analysed using specific detectors such as LC-Fluorescence, LC-UV or LC-DAD.

Table 10a. Results for acetamiprid, azoxystrobin, boscalid, fluopyram, imidacloprid, pendimethalin, pirimicarb, and prosulfocarb in mg/kg, the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Acetamiprid	Z-scores (FFP RSD (25%)	Azoxystrobin	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Fluopyram	Z-scores (FFP RSD (25%)	Imidacloprid	Z-scores (FFP RSD (25%)	Pendimethalin	Z-scores (FFP RSD (25%)	Pirimicarb	Z-scores (FFP RSD (25%)	Prosulfocarb	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.100**		**0.043**		**0.105**		**0.032**		**0.361**		**0.040**		**0.059**		**0.567**	
2	0.137	1.5	0.05	0.7	0.127	0.9	0.045	1.6	0.465	1.2	0.041	0.1	0.063	0.3	0.658	0.6
3	0.024	-3.0	0.036	-0.6	0.163	2.2	0.052	2.5	0.033	-3.6	0.043	0.3	0.075	1.1	0.539	-0.2
4	0.1	0.0	0.048	0.6	0.141	1.4	0.039	0.9	0.44	0.9	0.03	-1.0	0.063	0.3	0.625	0.4
5	0.124	1.0	0.044	0.2	0.109	0.2	0.044	1.5	0.639	3.1	0.069	2.9	0.061	0.2	0.301	-1.9
6																
7	0.118	0.7	0.047	0.5	0.118	0.5	0.033	0.1	0.398	0.4	0.038	-0.2	0.053	-0.4	0.557	-0.1
8	0.096	-0.2	0.054	1.1	0.118	0.5	0.033	0.1	0.417	0.6	0.057	1.7	0.053	-0.4	0.508	-0.4
9	0.151	2.0	0.033	-0.9	0.085	-0.8	0.034	0.2	0.521	1.8	0.025	-1.5	0.07	0.8		
10	0.0658	-1.4	0.0386	-0.3	0.0991	-0.2	0.0315	-0.1	0.275	-1.0	0.0476	0.7	0.0606	0.1	0.696	0.9
11	0.076	-1.0	0.026	-1.5	0.106	0.1	0.021	-1.4	0.168	-2.1	0.042	0.2	0.022	-2.5	0.269	-2.1
12	0.05	-2.0	0.056	1.3	0.117	0.5	0.037	0.6	0.227	-1.5	0.034	-0.6	0.06	0.1	0.363	-1.4
13	0.067	-1.3	0.035	-0.7	0.099	-0.2	0.035	0.4	0.271	-1.0	0.035	-0.5	0.061	0.2	0.523	-0.3
14	0.11	0.4	0.0422	0.0	0.136	1.2	0.0307	-0.2	0.382	0.2	0.0607	2.0	0.051	-0.5	0.385	-1.3
15	0.094	-0.2	0.017	-2.4	0.051	-2.1			0.2	-1.8	0.031	-0.9	0.047	-0.8		
16	0.072	-1.1	0.033	-0.9	0.086	-0.7	FN	-2.8	0.376	0.2	0.046	0.6	0.053	-0.4	0.626	0.4
17	0.04	-2.4	0.033	-0.9	0.1	-0.2			0.37	0.1	0.028	-1.2	0.063	0.3		
18	0.0605	-1.6							0.312	-0.5	0.0462	0.6				
19											0.0484	0.8				
20	0.0545	-1.8	0.0312	-1.0	0.0607	-1.7	0.0234	-1.1	0.41	0.5	0.0431	0.3	0.0396	-1.3	0.428	-1.0
21	0.011	-3.6	0.014	-2.7	0.06	-1.7	0.007	-3.1	0.027	-3.7	0.037	-0.3	0.018	-2.8	0.156	-2.9
22											0.05	1.0				
23	0.136	1.4	0.0456	0.3	0.124	0.7	0.0331	0.1	0.412	0.6	0.0465	0.6	0.0651	0.4	0.664	0.7
25	0.1955	3.8	0.0497	0.7	0.1331	1.1	0.0337	0.2	0.4167	0.6	0.033	-0.7	0.071	0.9	0.421	-1.0
27																
28	0.117	0.7	0.055	1.2	0.134	1.1			0.41	0.5	0.041	0.1	0.072	0.9		
29	0.154	2.2	0.072	2.8	0.17	2.5	0.05	2.2	0.45	1.0	0.052	1.2	0.1	2.8	1.15	4.1
30	0.124	1.0	0.058	1.5	0.121	0.6	0.044	1.5	0.392	0.3	0.043	0.3	0.068	0.6	0.658	0.6
31	0.124	1.0	0.061	1.8	0.132	1.0	0.048	2.0	0.413	0.6	0.036	-0.4	0.074	1.1	0.835	1.9
32	0.088	-0.5	0.048	0.6			0.033	0.1	0.151	-2.3	0.031	-0.9	0.021	-2.6		
33	0.09	-0.4	0.058	1.5	0.16	2.1	0.052	2.5	0.325	-0.4	0.051	1.1	0.064	0.4	0.755	1.3
34	0.109	0.4	0.046	0.4	0.104	0.0	0.0318	0.0	0.328	-0.4	0.0582	1.8	0.0562	-0.2	0.91	2.4
35			0.056	1.3	0.119	0.5	0.0304	-0.2			0.0424	0.2				
36	0.138	1.5	0.0691	2.6	0.134	1.1			0.382	0.2	0.0617	2.1	0.0855	1.8		
37																
38	0.127	1.1	0.0437	0.2	0.12	0.6	0.0376	0.7	0.409	0.5	0.0384	-0.2	0.0647	0.4	0.729	1.1
39																
40	0.112	0.5	0.049	0.7	0.144	1.5	0.03	-0.3	0.343	-0.2	0.046	0.6	0.057	-0.1	0.724	1.1
41	0.073	-1.1	0.035	-0.7	0.072	-1.2	0.029	-0.4	0.211	-1.7	0.035	-0.5	0.041	-1.2	0.33	-1.7

Laboratory code	Acetamiprid	Z-scores (FFP RSD (25%)	Azoxystrobin	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Fluopyram	Z-scores (FFP RSD (25%)	Imidacloprid	Z-scores (FFP RSD (25%)	Pendimethalin	Z-scores (FFP RSD (25%)	Pirimicarb	Z-scores (FFP RSD (25%)	Prosulfocarb	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.100**		**0.043**		**0.105**		**0.032**		**0.361**		**0.040**		**0.059**		**0.567**	
42	0.091	-0.4	0.043	0.1	0.086	-0.7			0.32	-0.5	0.075	3.5	0.04	-1.3		
43	0.086	-0.6	0.049	0.7	0.095	-0.4	0.032	0.0	0.321	-0.4	0.028	-1.2	0.076	1.2	0.647	0.6
44	0.12	0.8	0.013	-2.8	0.045	-2.3	0.012	-2.5	0.39	0.3	0.033	-0.7	0.015	-3.0	0.19	-2.7
45	0.0074	-3.7	0.032	-1.0	0.099	-0.2	0.0047	-3.4	0.091	-3.0	0.046	0.6	0.036	-1.5	0.049	-3.7
46	0.113	0.5	0.053	1.0	0.12	0.6	0.046	1.7	0.396	0.4	0.035	-0.5	0.071	0.9	0.484	-0.6
47	0.0634	-1.5	0.047	0.5	0.115	0.4	0.0424	1.3	0.689	3.6	0.0392	-0.1	0.074	1.1	0.754	1.3
48	0.108	0.3	0.0448	0.3	0.176	2.7	0.0298	-0.3	0.438	0.9	0.0328	-0.7	0.0622	0.3	0.568	0.0
49			0.041	-0.1	0.102	-0.1	0.0285	-0.4			0.0406	0.0				
50	0.188	3.5	0.041	-0.1	0.139	1.3	0.053	2.6	0.544	2.0	0.045	0.5	0.122	4.3	0.758	1.4
51	0.197	3.9	0.052	0.9	0.163	2.2	0.031	-0.1	0.584	2.5	0.035	-0.5	0.083	1.7	0.728	1.1
52			0.0317	-1.0	0.0646	-1.5	0.0249	-0.9			0.0379	-0.2				
53	0.107	0.3	0.0486	0.6	0.0684	-1.4	0.0313	-0.1	0.422	0.7	0.0469	0.7	0.0894	2.1	0.876	2.2
54			0.0407	-0.1	0.0918	-0.5	0.0232	-1.1			0.0424	0.2				
55			0.021	-2.0	0.073	-1.2	0.029	-0.4			FN	-3.0	FN	-3.3	0.543	-0.2
56	0.095	-0.2	0.042	0.0	0.084	-0.8	0.033	0.1	0.37	0.1	0.014	-2.6	0.076	1.2		
57	0.128	1.1	0.037	-0.5	0.102	-0.1	0.029	-0.4	0.419	0.6	0.036	-0.4	0.046	-0.9	0.294	-1.9
58	0.094	-0.2	0.047	0.5	0.128	0.9	0.038	0.7	0.314	-0.5	0.044	0.4	0.056	-0.2	0.504	-0.4
59	0.0966	-0.1	0.0958	5.1	0.0504	-2.1	0.045	1.6	0.428	0.7	0.019	-2.1	0.0807	1.5	1.09	3.7
60	FN	-3.6	0.0296	-1.2	0.0708	-1.3	0.0215	-1.3	0.0236	-3.7	0.0257	-1.4	0.0249	-2.3	0.287	-2.0
61	0.149	2.0	0.061	1.8	0.116	0.4	0.0402	1.0	0.525	1.8	0.0524	1.2	0.076	1.2	0.753	1.3
62			0.042	0.0	0.094	-0.4	0.024	-1.0			0.042	0.2				
63	0.104	0.2	0.053	1.0	0.11	0.2	0.037	0.6	FN	-3.9	0.03	-1.0	0.067	0.6		
64	0.058	-1.7	0.031	-1.1	0.079	-1.0	0.02	-1.5	0.18	-2.0	0.027	-1.3	0.039	-1.3	0.31	-1.8
65			0.033	-0.9	0.065	-1.5	0.021	-1.4			0.028	-1.2	0.042	-1.1	0.431	-1.0
66																
67	0.055	-1.8	0.031	-1.1	0.129	0.9	0.025	-0.9	0.241	-1.3	0.055	1.5	0.03	-1.9	0.379	-1.3
68	0.141	1.6	0.055	1.2	0.134	1.1	0.025	-0.9	0.461	1.1	0.05	1.0	0.082	1.6	0.808	1.7
69																
70	0.103	0.1	0.048	0.6	0.138	1.3	0.042	1.2	0.459	1.1	0.041	0.1	0.072	0.9	0.694	0.9
71	0.026	-3.0	0.02	-2.1	0.076	-1.1	0.016	-2.0	0.063	-3.3	0.049	0.9	0.019	-2.7	0.542	-0.2
72	0.078	-0.9	0.047	0.5	0.124	0.7	0.034	0.2	0.437	0.8	0.039	-0.1	0.059	0.0	0.503	-0.4
73																
74	0.12	0.8	0.055	1.2	0.13	1.0	0.045	1.6	0.49	1.4	0.055	1.5	0.055	-0.2	1	3.1
75	0.133	1.3	0.049	0.7	0.146	1.6	0.042	1.2	0.416	0.6	0.052	1.2	0.064	0.4	0.746	1.3
76	0.132	1.3	0.0423	0.0	0.129	0.9	0.03	-0.3	0.435	0.8	0.0467	0.6	0.043	-1.1	0.605	0.3
77	0.0878	-0.5	0.049	0.7	0.0891	-0.6	0.0348	0.3	0.378	0.2	0.059	1.9	0.0751	1.1	0.612	0.3
78	0.128	1.1	0.043	0.1	0.091	-0.5			0.6	2.6	0.039	-0.1	0.054	-0.3	0.926	2.5
79			0.018	-2.3	0.057	-1.8					0.036	-0.4	0.01	-3.3		
80																
81	0.041	-2.4	0.017	-2.4	0.061	-1.7	FN	-2.8	0.098	-2.9	0.086	4.6	0.037	-1.5	0.334	-1.6

Laboratory code	Acetamiprid	Z-scores (FFP RSD (25%)	Azoxystrobin	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Fluopyram	Z-scores (FFP RSD (25%)	Imidacloprid	Z-scores (FFP RSD (25%)	Pendimethalin	Z-scores (FFP RSD (25%)	Pirimicarb	Z-scores (FFP RSD (25%)	Prosulfocarb	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.100**		**0.043**		**0.105**		**0.032**		**0.361**		**0.040**		**0.059**		**0.567**	
82	FN	-3.6	0.024	-1.7	0.092	-0.5	0.018	-1.8			0.039	-0.1	0.06	0.1		
83			0.014	-2.7	0.029	-2.9	0.015	-2.1			0.035	-0.5				
84	0.095	-0.2	0.045	0.3	0.123	0.7	0.035	0.4	0.258	-1.1	0.035	-0.5	0.065	0.4	0.452	-0.8
85	0.068	-1.3	0.036	-0.6	0.114	0.4	0.016	-2.0	0.227	-1.5	0.03	-1.0	0.052	-0.4	0.446	-0.9
86	0.133	1.3	0.028	-1.3	0.111	0.2	0.038	0.7	0.502	1.6	0.045	0.5	0.086	1.9	0.88	2.2
87	0.0555	-1.8	0.0426	0.0	0.0867	-0.7	0.0315	-0.1	0.307	-0.6	0.0328	-0.7	0.0521	-0.4	0.564	0.0
88	0.096	-0.2	0.042	0.0	0.102	-0.1	0.03	-0.3	0.329	-0.4	0.034	-0.6	0.055	-0.2	0.561	0.0
89	0.116	0.6	0.046	0.4	0.124	0.7	0.033	0.1	0.415	0.6	FN	-3.0	0.067	0.6	0.568	0.0
90																
91	0.121	0.8	0.044	0.2	0.11	0.2	0.051	2.4	0.402	0.5	0.039	-0.1	0.069	0.7	0.655	0.6
92	0.021	-3.2	0.039	-0.3	0.09	-0.6	0.041	1.1	0.078	-3.1	0.035	-0.5	FN	-3.3	1.22	4.6
93	0.114	0.6	0.0389	-0.3	0.118	0.5	0.039	0.9	0.255	-1.2	0.044	0.4	0.059	0.0	0.561	0.0
94	0.0384	-2.5	0.0105	-3.0			0.0105	-2.7	0.0606	-3.3	0.0112	-2.9				
95	0.093	-0.3	0.039	-0.3	0.093	-0.4	0.033	0.1	0.405	0.5	0.037	-0.3	0.053	-0.4	0.417	-1.1
96	0.096	-0.2	0.039	-0.3	0.081	-0.9	0.03	-0.3	0.302	-0.7	0.037	-0.3	0.055	-0.2	0.335	-1.6
97	0.089	-0.4	0.043	0.1	0.12	0.6	0.032	0.0	0.32	-0.5	0.034	-0.6	0.054	-0.3	0.42	-1.0
98	0.19	3.6	0.036	-0.6	0.11	0.2	0.035	0.4	0.98	>5	0.045	0.5	0.066	0.5	0.57	0.0
99															0.543	-0.2
100	0.082	-0.7	0.041	-0.1	0.068	-1.4	0.023	-1.1	0.39	0.3	0.043	0.3	0.058	0.0	0.46	-0.8
101	0.077	-0.9	0.055	1.2	0.113	0.3	0.032	0.0	0.427	0.7	0.041	0.1	0.057	-0.1	0.595	0.2
102	0.104	0.2	0.043	0.1	0.167	2.4	0.038	0.7	0.383	0.2	0.047	0.7	0.06	0.1	0.92	2.5
103	0.126	1.0	0.046	0.4	0.117	0.5	0.035	0.4	0.414	0.6	0.057	1.7	0.076	1.2	0.686	0.8
104	0.134	1.4	0.0482	0.6	0.134	1.1	0.0361	0.5	0.468	1.2	0.0384	-0.2	0.0613	0.2	0.694	0.9
105	0.141	1.6	0.078	3.4	0.19	3.3	0.046	1.7	0.496	1.5	0.065	2.5	0.078	1.3	1.1	3.8
106	0.114	0.6	0.068	2.5	0.091	-0.5	0.036	0.5	0.687	3.6	0.037	-0.3	0.063	0.3	0.496	-0.5
107	0.114	0.6	0.0396	-0.2	0.106	0.1	0.032	0.0	0.36	0.0	0.033	-0.7	0.058	0.0	0.396	-1.2
108	0.039	-2.4	0.026	-1.5	0.085	-0.8	0.016	-2.0	0.04	-3.6	0.035	-0.5	0.029	-2.0	0.145	-3.0
109	0.0221	-3.1	0.0652	2.2	0.1107	0.2	0.0365	0.6	0.1001	-2.9	0.0346	-0.6	0.0635	0.3	0.4961	-0.5
110																
111	0.105	0.2	0.06	1.7	0.138	1.3	0.047	1.9	0.265	-1.1	0.063	2.3	0.088	2.0	0.763	1.4
112	0.151	2.0	0.036	-0.6	0.0891	-0.6	0.0362	0.5	0.523	1.8	0.0413	0.1	0.064	0.4	0.832	1.9
113	0.056	-1.8	0.035	-0.7	0.104	0.0	0.026	-0.8	0.442	0.9	FN	-3.0	0.038	-1.4	FN	-3.9
114	0.0402	-2.4	0.0391	-0.3	0.0876	-0.7	0.0278	-0.5	0.21	-1.7	0.0303	-1.0	0.0538	-0.3	0.339	-1.6
115	0.027	-2.9	0.04	-0.2	0.103	-0.1	0.032	0.0	0.025	-3.7	0.037	-0.3	0.08	1.5	0.696	0.9
116	0.14	1.6	0.043	0.1	0.122	0.7	0.048	2.0	0.433	0.8	0.036	-0.4	0.079	1.4	0.78	1.5
117	0.113	0.5	0.036	-0.6	0.0859	-0.7	0.0281	-0.5	0.368	0.1	0.0322	-0.8	0.0494	-0.6	0.38	-1.3
118			0.0431	0.1	0.0981	-0.3	0.0283	-0.5			0.0423	0.2				
119	0.151	2.0	0.054	1.1	0.11	0.2	0.031	-0.1	0.372	0.1	0.032	-0.8	0.054	-0.3	0.511	-0.4
120			0.0395	-0.2	0.085	-0.8	0.0293	-0.3			0.0456	0.5				
121	0.13	1.2	0.024	-1.7	0.09	-0.6	0.035	0.4	0.4	0.4	0.026	-1.4	0.036	-1.5	0.47	-0.7

Laboratory code	Acetamiprid	Z-scores (FFP RSD (25%)	Azoxystrobin	Z-scores (FFP RSD (25%)	Boscalid	Z-scores (FFP RSD (25%)	Fluopyram	Z-scores (FFP RSD (25%)	Imidacloprid	Z-scores (FFP RSD (25%)	Pendimethalin	Z-scores (FFP RSD (25%)	Pirimicarb	Z-scores (FFP RSD (25%)	Prosulfocarb	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.100**		**0.043**		**0.105**		**0.032**		**0.361**		**0.040**		**0.059**		**0.567**	
122	0.12	0.8	0.0452	0.3	0.109	0.2	0.0358	0.5	0.391	0.3	0.0466	0.6	0.0647	0.4	0.591	0.2
123	0.067	-1.3	0.033	-0.9	0.052	-2.0	0.022	-1.3	0.32	-0.5	0.033	-0.7	0.064	0.4	0.045	-3.7
124																
125			0.048	0.6	0.11	0.2					0.041	0.1	0.058	0.0		
126																
127	0.105	0.2	0.037	-0.5	0.09	-0.6	0.027	-0.6	0.305	-0.6	0.041	0.1	0.045	-0.9		
128	0.127	1.1	0.051	0.8	0.124	0.7	0.035	0.4	0.454	1.0	0.057	1.7	0.087	1.9	0.849	2.0
129	0.14	1.6	0.048	0.6	0.123	0.7	0.037	0.6	0.455	1.0			0.068	0.6	0.85	2.0
130	0.028	-2.9	0.031	-1.1	0.075	-1.1	0.025	-0.9	0.077	-3.1	0.025	-1.5	0.038	-1.4	0.36	-1.5
131			0.0279	-1.4	0.0834	-0.8	0.0202	-1.5			0.0271	-1.3	0.0298	-2.0		
132	0.0506	-2.0	0.0517	0.9	0.101	-0.1	0.029	-0.4	FN	-3.9	0.035	-0.5	0.0565	-0.1	0.659	0.7
133	0.13	1.2	0.055	1.2	0.137	1.2	0.046	1.7	0.43	0.8	0.053	1.3	0.061	0.2	1.27	5.0
134	0.128	1.1	0.036	-0.6	0.094	-0.4	0.029	-0.4	0.372	0.1	0.042	0.2	0.059	0.0	0.599	0.2
135	0.094	-0.2	0.047	0.5	0.094	-0.4	0.037	0.6	0.3	-0.7	0.024	-1.6	0.058	0.0	0.49	-0.5
136	0.0526	-1.9	0.0242	-1.7	0.069	-1.4	0.016	-2.0	0.228	-1.5	0.0256	-1.5	0.0272	-2.1	0.2792	-2.0
137			0.044	0.2	0.1	-0.2	0.025	-0.9			0.045	0.5				
138																
139	0.131	1.2	0.046	0.4	0.116	0.4			0.474	1.3			0.063	0.3		
140																

Table 10b. Results for the mandatory pesticides prothioconazole-desthio, pyraclostrobin, tebuconazole, thiacloprid and the voluntary pesticides clomazone, aldrin and penthiopyrad. Additional assigned values, MRRL, preliminary z scores. The data for aldrin and penthiopyrad is only for informative purposes.

Laboratory code	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Tebuconazole	Z-scores (FFP RSD (25%)	Thiacloprid	Z-scores (FFP RSD (25%)			Clomazone	Z-scores (FFP RSD (25%)	Aldrin	Z-scores (FFP RSD (25%)	Penthiopyrad	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**				**0.01**		**0.01**		**0.01**	
Assigned value	**0.053**		**0.045**		**0.070**		**0.054**				**0.076**		***0.013***		***0.023***	
2	0.066	1.0	0.07	2.2	0.099	1.7	0.072	1.4			0.079	0.2	*0.008*	*-1.5*	*0.026*	*0.5*
3	0.062	0.7	0.075	2.6	0.105	2.0	0.019	-2.6			0.084	0.4				
4			0.072	2.4	0.104	2.0	0.054	0.0					*0.006*	*-2.1*		
5	FN	-3.2	0.048	0.2	0.075	0.3	0.061	0.5			0.123	2.5			*0.014*	*-1.6*
6													*0.015*	*0.7*		
7	0.066	1.0	0.062	1.5	0.085	0.9	0.055	0.1			0.074	-0.1	*0.014*	*0.3*	*0.022*	*-0.2*
8	0.056	0.2	0.05	0.4	0.083	0.8	0.061	0.5			0.072	-0.2	*0.011*	*-0.6*	*0.026*	*0.5*
9	0.046	-0.5	FN	-3.1	0.062	-0.5	0.071	1.3								
10	0.0538	0.1	0.0389	-0.6	0.0656	-0.2	0.0397	-1.0			0.0738	-0.1	*0.0214*	*2.6*	*0.022*	*-0.2*
11	0.02	-2.5	0.034	-1.0	0.047	-1.3	0.067	1.0			0.023	-2.8	*0.015*	*0.7*	*0.027*	*0.6*
12	0.055	0.2	0.048	0.2	0.069	-0.1	0.021	-2.4					*0.013*	*0.0*		
13	0.058	0.4	0.042	-0.3	0.068	-0.1	0.043	-0.8								
14	0.069	1.2	0.0706	2.2	0.0897	1.1	0.059	0.4			0.0734	-0.1	*0.011*	*-0.6*	*0.0261*	*0.5*
15			0.026	-1.7	0.059	-0.6	0.039	-1.1								
16	0.042	-0.8	0.032	-1.2	0.06	-0.6	0.046	-0.6			0.062	-0.7	*0.011*	*-0.6*	*0.024*	*0.1*
17			0.037	-0.7	0.121	2.9	0.025	-2.1					*0.009*	*-1.2*		
18							0.0509	-0.2					*0.0208*	*2.5*		
19													*0.0184*	*1.7*		
20	0.0322	-1.6	0.0325	-1.1	0.0584	-0.7	0.0358	-1.3			0.0486	-1.4	*0.0058*	*-2.2*	*0.0162*	*-1.2*
21	0.014	-2.9	0.022	-2.1	0.028	-2.4	0.006	-3.6			0.01	-3.5	*0.015*	*0.7*		
22			0.0551	0.9									*0.0197*	*2.1*		
23	0.0632	0.8	0.0602	1.3	0.0827	0.7	0.0666	1.0			0.0659	-0.5	*0.0121*	*-0.2*	*0.0267*	*0.6*
25	0.0655	1.0	0.0375	-0.7	0.0588	-0.6	0.0667	1.0					*0.0145*	*0.5*		
27																
28			0.068	2.0	0.103	1.9	0.075	1.6								
29	0.104	3.9	0.088	3.8	0.12	2.9	0.084	2.2			0.11	1.8	*0.013*	*0.0*		
30	0.076	1.7	0.074	2.5	0.101	1.8	0.074	1.5			0.083	0.4	*0.016*	*1.0*	*0.023*	*0.0*
31	0.096	3.3	0.05	0.42	0.107	2.1	0.082	2.1			0.105	1.5				
32					0.06	-0.6	0.05	-0.3								
33	0.61	>5	0.055	0.9	0.113	2.5	0.05	-0.3					*0.023*	*3.1*		
34	0.0532	0.0	0.0537	0.7	0.0804	0.6	0.0594	0.4			0.0609	-0.8	*0.0163*	*1.1*		
35	0.0578	0.4			0.0656	-0.2							*0.0093*	*-1.1*		
36			0.0736	2.5	0.113	2.5	0.0667	1.0			0.111	1.8	*0.0202*	*2.3*		
37													*0.0145*	*0.5*		
38	0.0533	0.0	0.0396	-0.5	0.0718	0.1	0.0659	0.9			0.0858	0.5	*0.0131*	*0.1*	*0.0234*	*0.0*
39																
40	0.062	0.7	0.053	0.7	0.093	1.3	0.062	0.6			0.077	0.0	*0.014*	*0.3*	*0.024*	*0.1*
41	0.042	-0.8	0.028	-1.5	0.051	-1.1	0.03	-1.8			0.069	-0.4	*0.0059*	*-2.2*		

Laboratory code	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Tebuconazole	Z-scores (FFP RSD (25%)	Thiacloprid	Z-scores (FFP RSD (25%)			Clomazone	Z-scores (FFP RSD (25%)	Aldrin	Z-scores (FFP RSD (25%)	Penthiopyrad	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**				**0.01**		**0.01**		**0.01**	
Assigned value	**0.053**		**0.045**		**0.070**		**0.054**				**0.076**		***0.013***		***0.023***	
42			0.03	-1.3	0.055	-0.9	0.051	-0.2								
43	0.053	0.0	0.043	-0.2	0.084	0.8	0.059	0.4			0.093	0.9			*0.028*	*0.8*
44	0.016	-2.8	FN	-3.1	0.03	-2.3	0.056	0.2			0.085	0.5	*0.01*	*-0.9*	*0.019*	*-0.7*
45	FN	-3.2	0.0051	-3.5	0.0054	-3.7	FN	-3.3					*0.025*	*3.8*		
46	0.06	0.5	0.059	1.22	0.09	1.2	0.075	1.6			0.066	-0.5			*0.03*	*1.2*
47	0.0529	0.0	0.0704	2.2	0.0702	0.0	0.046	-0.6			0.0877	0.6	*0.0106*	*-0.7*	*0.0306*	*1.3*
48	0.0611	0.6	0.044	-0.1	0.0769	0.4	0.06	0.5							*0.0198*	*-0.6*
49	0.0529	0.0			0.0643	-0.3							*0.0087*	*-1.3*		
50	0.087	2.6	0.067	1.9	0.092	1.3	0.136	>5			0.121	2.4	*0.018*	*1.6*	*0.028*	*0.8*
51	0.061	0.6	0.054	0.8	0.071	0.1	0.101	3.5			0.103	1.4	*0.016*	*1.0*	*0.027*	*0.6*
52	0.0418	-0.8			0.0465	-1.3							*0.0108*	*-0.6*		
53	0.0486	-0.3	0.0522	0.6	0.0761	0.4	0.0596	0.4					*0.014*	*0.3*		
54	0.0566	0.3			0.0635	-0.4							*0.011*	*-0.6*		
55	FN	-3.2	FN	-3.1	0.058	-0.7					0.042	-1.8				
56			0.03	-1.3	0.052	-1.0	0.051	-0.2								
57	0.041	-0.9	0.038	-0.6	0.059	-0.6	0.061	0.5								
58	0.047	-0.4	0.05	0.4	0.076	0.4	0.054	0.0			0.072	-0.2	*0.011*	*-0.6*	*0.019*	*-0.7*
59	FN	-3.2	0.0979	4.7	0.0251	-2.6	0.0657	0.9			0.16	4.4				
60	0.0344	-1.4	0.0259	-1.7	0.0437	-1.5	0.0225	-2.3								
61	0.0631	0.8	0.058	1.1	0.0933	1.3	0.062	0.6			0.1	1.3	*0.0136*	*0.2*	*0.0266*	*0.6*
62	0.056	0.2			0.064	-0.3							*0.011*	*-0.6*		
63	0.065	0.9	0.052	0.6	0.096	1.5	0.054	0.0								
64	0.032	-1.6	0.027	-1.6	0.046	-1.4	0.035	-1.4								
65					0.039	-1.8					0.057	-1.0	*0.004*	*-2.8*	*0.015*	*-1.4*
66																
67	0.046	-0.5	0.061	1.4	0.066	-0.2	0.062	0.6					*0.016*	*1.0*		
68	0.067	1.1	0.051	0.5	0.091	1.2	0.062	0.6			0.101	1.3	*0.015*	*0.7*	*0.029*	*1.0*
69													*0.015*	*0.7*		
70	0.066	1.0	0.053	0.7	0.065	-0.3	0.11	4.2			0.081	0.3	*0.011*	*-0.6*	*0.034*	*1.8*
71	0.016	-2.8	0.027	-1.6	0.027	-2.5	0.013	-3.0			0.014	-3.3	*0.017*	*1.3*	*0.02*	*-0.6*
72	0.052	-0.1	0.041	-0.4	0.092	1.3	0.045	-0.7			0.075	-0.1	*0.01*	*-0.9*	*0.025*	*0.3*
73													*0.015*	*0.7*		
74	0.076	1.7	0.06	1.3	0.08	0.6	0.051	-0.2			0.095	1.0	*0.021*	*2.5*	*0.028*	*0.8*
75	0.067	1.1	0.055	0.9	0.09	1.2	0.062	0.6			0.085	0.5	*0.013*	*0.0*	*0.026*	*0.5*
76	0.0466	-0.5	0.0318	-1.2	0.0599	-0.6	0.0624	0.6			0.0616	-0.8	*0.0117*	*-0.4*	*0.0189*	*-0.8*
77	0.0651	0.9	0.0358	-0.8	0.0851	0.9	0.0285	-1.9							*0.0194*	*-0.7*
78			0.049	0.3	0.068	-0.1	0.065	0.8								
79					FN	-3.4										
80																
81			0.025	-1.8	0.039	-1.8	0.02	-2.5								

Laboratory code	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Tebuconazole	Z-scores (FFP RSD (25%)	Thiacloprid	Z-scores (FFP RSD (25%)			Clomazone	Z-scores (FFP RSD (25%)	Aldrin	Z-scores (FFP RSD (25%)	Penthiopyrad	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**				**0.01**		**0.01**		**0.01**	
Assigned value	**0.053**		**0.045**		**0.070**		**0.054**				**0.076**		***0.013***		***0.023***	
82	0.014	-2.9			0.041	-1.7							*0.018*	*1.6*		
83	0.028	-1.9			0.041	-1.7							*0.026*	*4.1*		
84	FN	-3.2	0.047	0.2	0.091	1.2	0.065	0.8			0.086	0.5			*0.028*	*0.8*
85	0.032	-1.6	0.056	1.0	0.066	-0.2	0.05	-0.3								
86	0.061	0.6	0.051	0.5	0.082	0.7	0.054	0.0			0.103	1.4	*0.014*	*0.3*	*0.024*	*0.1*
87	0.0423	-0.8	0.0425	-0.2	0.0552	-0.8	0.0403	-1.0			0.0698	-0.3			*0.0197*	*-0.6*
88			0.04	-0.5	0.064	-0.3	0.038	-1.2								
89	0.059	0.5	0.044	-0.1	0.077	0.4	0.067	1.0			0.085	0.5			*0.024*	*0.1*
90																
91	0.058	0.4	0.046	0.1	0.101	1.8	0.064	0.8			0.088	0.6	*0.017*	*1.3*	*0.028*	*0.8*
92	0.046	-0.5	0.042	-0.3	0.081	0.6	0.033	-1.5			0.043	-1.7	*0.018*	*1.6*	*0.017*	*-1.1*
93	0.053	0.0	0.0538	0.8	0.067	-0.2	0.0574	0.3			0.068	-0.4	*0.009*	*-1.2*	*0.027*	*0.6*
94					0.0127	-3.3	0.0169	-2.7								
95	0.052	-0.1	0.034	-1.0	0.061	-0.5	0.044	-0.7			0.066	-0.5	*0.0056*	*-2.3*	*0.02*	*-0.6*
96			0.031	-1.3			0.035	-1.4			0.062	-0.7	*0.008*	*-1.5*	*0.018*	*-0.9*
97	0.048	-0.4	0.048	0.2	0.07	0.0	0.04	-1.0			0.072	-0.2	*0.017*	*1.3*		
98	0.054	0.1	0.034	-1.0	0.056	-0.8	0.048	-0.4			0.063	-0.7	*0.021*	*2.5*	*0.019*	*-0.7*
99	0.039	-1.1	0.045	0.0	0.063	-0.4										
100	0.048	-0.4	0.042	-0.3	0.061	-0.5	0.052	-0.1			0.061	-0.8	*0.008*	*-1.5*	*0.023*	*0.0*
101	FN	-3.2	0.069	2.1	0.091	1.2	0.05	-0.3					*0.0085*	*-1.4*	*0.022*	*-0.2*
102	0.071	1.4	0.056	1.0	0.104	2.0	0.05	-0.3			0.1	1.3	*0.0063*	*-2.0*	*0.021*	*-0.4*
103	0.055	0.2	0.04	-0.5	0.079	0.5	0.065	0.8			0.092	0.8	*0.012*	*-0.3*		
104	0.0558	0.2	0.0486	0.3	0.0711	0.1	0.0734	1.5			0.0849	0.5	*0.014*	*0.3*	*0.0257*	*0.4*
105	0.086	2.5	0.082	3.3	0.11	2.3	0.072	1.4			0.12	2.3	*0.016*	*1.0*		
106	0.06	0.5	0.051	0.5	0.081	0.6	FN	-3.3			0.053	-1.2	*0.0056*	*-2.3*	*0.029*	*1.0*
107	0.0415	-0.9	FN	-3.1	0.052	-1.0	0.0599	0.5			0.0657	-0.5			*0.018*	*-0.9*
108	0.018	-2.6	0.019	-2.3	0.046	-1.4	0.045	-0.7			0.017	-3.1			*0.022*	*-0.2*
109	0.0708	1.4	0.0424	-0.2	0.044	-1.5	0.0594	0.4			0.0804	0.2	*0.011*	*-0.6*	*0.0245*	*0.2*
110																
111	0.051	-0.1	0.034	-1.0	0.0077	-3.6	0.055	0.1			0.093	0.9	*0.018*	*1.6*		
112	0.0551	0.2	0.0295	-1.4	0.0735	0.2	0.0733	1.5			0.0848	0.5			*0.0237*	*0.1*
113	0.046	-0.5	0.038	-0.6	FN	-3.4	0.017	-2.7								
114	0.0383	-1.1	0.0359	-0.8	0.0449	-1.4	0.0221	-2.4			0.0564	-1.0	*0.0095*	*-1.0*	*0.0197*	*-0.6*
115	0.051	-0.1	0.041	-0.4	0.071	0.1	FN	-3.3			0.071	-0.3	*0.01*	*-0.9*	*0.021*	*-0.4*
116	0.072	1.4	0.061	1.4	0.105	2.0	0.047	-0.5			0.086	0.5			*0.024*	*0.1*
117	0.0404	-0.9	0.036	-0.8	0.0645	-0.3	0.057	0.2			0.0754	0.0			*0.0207*	*-0.4*
118	0.0566	0.3			0.0634	-0.4							*0.0108*	*-0.6*		
119	0.047	-0.4	0.045	0.0	0.077	0.4	0.066	0.9			0.06	-0.8	*0.007*	*-1.8*	*0.024*	*0.1*
120	0.0497	-0.2			0.0599	-0.6							*0.0118*	*-0.3*		
121	0.053	0.0	0.032	-1.2	0.068	-0.1	0.062	0.6			0.064	-0.6			*0.017*	*-1.1*

Laboratory code	Prothioconazole-desthio	Z-scores (FFP RSD (25%)	Pyraclostrobin	Z-scores (FFP RSD (25%)	Tebuconazole	Z-scores (FFP RSD (25%)	Thiacloprid	Z-scores (FFP RSD (25%)			Clomazone	Z-scores (FFP RSD (25%)	Aldrin	Z-scores (FFP RSD (25%)	Penthiopyrad	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**				**0.01**		**0.01**		**0.01**	
Assigned value	**0.053**		**0.045**		**0.070**		**0.054**				**0.076**		***0.013***		***0.023***	
122	0.0651	0.9	0.0537	0.7	0.0732	0.2	0.0535	0.0			0.0791	0.2	*0.0072*	*-1.8*	*0.0256*	*0.4*
123	0.044	-0.7	0.032	-1.2	0.057	-0.7	0.042	-0.9			0.069	-0.4	*0.01*	*-0.9*	*0.013*	*-1.8*
124																
125			0.06	1.3	0.079	0.5										
126																
127			0.028	-1.5	0.084	0.8	0.051	-0.2					*0.017*	*1.3*		
128	0.07	1.3	0.083	3.3	0.1	1.7	0.041	-1.0					*0.012*	*-0.3*	*0.041*	*3.0*
129	0.065	0.9	0.048	0.2	0.095	1.4	0.055	0.1			0.089	0.7	*0.007*	*-1.8*		
130	0.036	-1.3	0.028	-1.5	0.042	-1.6	0.015	-2.9			0.05	-1.4			*0.015*	*-1.4*
131			0.0289	-1.4	0.0441	-1.5							*0.0071*	*-1.8*		
132	0.0455	-0.6	0.0446	-0.1	0.0605	-0.5	0.0339	-1.5			0.06	-0.8	*0.0099*	*-0.9*	*0.0235*	*0.0*
133	0.073	1.5	0.059	1.2	0.086	0.9	0.074	1.5			0.082	0.3	*0.009*	*-1.2*	*0.024*	*0.1*
134	0.052	-0.1	0.034	-1.0	0.066	-0.2	0.058	0.3			0.087	0.6	*0.014*	*0.3*	*0.032*	*1.5*
135	0.036	-1.3	0.043	-0.2	0.042	-1.6	0.05	-0.3			0.076	0.0			*0.021*	*-0.4*
136	0.025	-2.1	0.0174	-2.5	0.0418	-1.6	0.0346	-1.4					*0.0155*	*0.8*		
137	0.06	0.5			0.068	-0.1										
138													*0.0177*	*1.5*		
139					0.088	1.0	0.066	0.9					*0.013*	*0.0*		
140													*0.02*	*2.2*		

Table 10c. Results for cyantraniliprole, indoxacarb, metconazole, pyridalyl, tebufenozide, tefluthrin, and tetraconazole. Additional, Alg A means, MRRLs and z scores. The data is only shown for informative purposes as the levels were too low for evaluation.

Laboratory code	Cyantraniliprole	Z-scores (FFP RSD (25%)	Indoxacarb	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Pyridalyl	Z-scores (FFP RSD (25%)	Tebufenozide	Z-scores (FFP RSD (25%)	Tefluthrin	Z-scores (FFP RSD (25%)	Tetraconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Alg A mean	***0.014***		***0.022***		***0.012***		***0.014***		***0.019***		***0.012***		***0.020***	
2	*0.011*	*-0.9*	*0.019*	*-0.5*	*0.012*	*0.1*			*0.019*	*0.0*			*0.019*	*-0.1*
3	*0.009*	*-1.5*	*0.027*	*1.0*	*0.017*	*1.8*			*0.021*	*0.4*			*0.024*	*0.9*
4			*0.02*	*-0.3*					*0.016*	*-0.6*			*0.016*	*-0.7*
5											*0.015*	*1.2*	*0.019*	*-0.1*
6														
7	*0.014*	*0.0*	*0.02*	*-0.3*	*0.012*	*0.1*	*0.011*	*-0.8*	*0.018*	*-0.2*	*0.01*	*-0.6*	*0.018*	*-0.3*
8	*0.016*	*0.5*	*0.024*	*0.4*	*0.012*	*0.1*	*0.02*	*1.8*	*0.02*	*0.2*	*0.013*	*0.5*	*0.022*	*0.5*
9			*0.017*	*-0.9*	*0.01*	*-0.6*							*0.016*	*-0.7*
10	*0.0138*	*-0.1*	*0.0174*	*-0.8*			*0.0196*	*1.7*	*0.0172*	*-0.4*	*0.0139*	*0.8*	*0.0192*	*-0.1*
11			*0.024*	*0.4*			*0.022*	*2.4*	*0.02*	*0.2*	*0.012*	*0.1*	*0.017*	*-0.5*
12	*0.014*	*0.0*	*0.028*	*1.2*	*0.012*	*0.1*	*0.017*	*0.9*	*0.022*	*0.6*	*0.014*	*0.8*	*0.025*	*1.1*
13	*0.013*	*-0.3*	*0.028*	*1.2*	*0.011*	*-0.2*					*0.01*	*-0.6*	*0.017*	*-0.5*
14			*0.0243*	*0.5*					*0.022*	*0.6*			*0.0258*	*1.2*
15			*0.017*	*-0.9*									*0.016*	*-0.7*
16	*0.011*	*-0.9*	*0.02*	*-0.3*			*0.01*	*-1.1*	*0.015*	*-0.8*	*0.013*	*0.5*	*0.018*	*-0.3*
17			*0.015*	*-1.2*	*0.012*	*0.1*			*0.017*	*-0.4*	*0.01*	*-0.6*	*0.027*	*1.5*
18			*0.0252*	*0.7*										
19			*0.0476*	*4.8*										
20			*0.0182*	*-0.6*	*0.01*	*-0.6*			*0.0131*	*-1.2*			*0.0123*	*-1.5*
21			*0.015*	*-1.2*	*0.002*	*-3.3*	*0.007*	*-2.0*	*0.012*	*-1.5*	*0.013*	*0.5*	*0.017*	*-0.5*
22											*0.0122*	*0.2*		
23	*0.0158*	*0.5*	*0.0233*	*0.3*	*0.01*	*-0.6*	*0.0098*	*-1.1*	*0.0211*	*0.4*	*0.0098*	*-0.6*	*0.0231*	*0.7*
25	*0.0175*	*0.9*	*0.0215*	*0.0*			*0.0125*	*-0.4*	*0.0201*	*0.2*	*0.011*	*-0.2*	*0.0232*	*0.7*
27														
28			*0.025*	*0.6*					*0.021*	*0.4*			*0.027*	*1.5*
29	*0.023*	*2.5*	*0.038*	*3.0*	*0.016*	*1.5*	*0.011*	*-0.8*	*0.028*	*1.9*	*0.015*	*1.2*	*0.023*	*0.7*
30	*0.012*	*-0.6*	*0.024*	*0.4*	*0.013*	*0.4*			*0.021*	*0.4*	*0.0088*	*-1.0*	*0.018*	*-0.3*
31			*0.024*	*0.4*	*0.016*	*1.5*	*0.024*	*3.0*	*0.017*	*-0.4*			*0.021*	*0.3*
32			*0.022*	*0.1*					*0.016*	*-0.6*				
33			*0.03*	*1.5*	*0.013*	*0.4*					*0.025*	*4.6*	*0.02*	*0.1*
34			*0.024*	*0.4*							*0.0158*	*1.4*	*0.0251*	*1.1*
35					*0.011*	*-0.2*					*0.0108*	*-0.3*	*0.0246*	*1.0*
36			*0.0265*	*0.9*	*0.019*	*2.4*							*0.0228*	*0.6*
37														
38			*0.0229*	*0.2*					*0.0194*	*0.1*	*0.0134*	*0.6*	*0.021*	*0.3*
39														
40	*0.017*	*0.8*	*0.031*	*1.7*	*0.012*	*0.1*	*0.014*	*0.1*	*0.02*	*0.2*	*0.012*	*0.1*	*0.019*	*-0.1*
41	*0.011*	*-0.9*	*0.011*	*-2.0*					*0.015*	*-0.8*			*0.015*	*-1.0*

Laboratory code	Cyantraniliprole	Z-scores (FFP RSD (25%)	Indoxacarb	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Pyridalyl	Z-scores (FFP RSD (25%)	Tebufenozide	Z-scores (FFP RSD (25%)	Tefluthrin	Z-scores (FFP RSD (25%)	Tetraconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Alg A mean	***0.014***		***0.022***		***0.012***		***0.014***		***0.019***		***0.012***		***0.020***	
42									*0.011*	*-1.7*				
43	*0.023*	*2.5*	*0.016*	*-1.0*	*0.013*	*0.4*			*0.021*	*0.4*			*0.022*	*0.5*
44	*0.012*	*-0.6*	*0.027*	*1.0*			*0.01*	*-1.1*	*0.018*	*-0.2*			*0.012*	*-1.6*
45			*0.044*	*4.1*							*0.01*	*-0.6*		
46	*0.016*	*0.5*	*0.027*	*1.0*	*0.015*	*1.1*	*0.012*	*-0.5*	*0.02*	*0.2*			*0.027*	*1.5*
47			*0.0255*	*0.7*	*0.012*	*-0.1*							*0.0149*	*-1.0*
48			*0.019*	*-0.5*					*0.0157*	*-0.7*			*0.0094*	*-2.1*
49					*0.01*	*-0.6*					*0.0102*	*-0.5*	*0.0201*	*0.1*
50			*0.028*	*1.2*	*0.016*	*1.5*			*0.031*	*2.5*	*0.012*	*0.1*	*0.024*	*0.9*
51	*0.018*	*1.1*	*0.023*	*0.2*	*0.011*	*-0.2*	*0.015*	*0.4*	*0.022*	*0.6*	*0.01*	*-0.6*	*0.021*	*0.3*
52											*0.0108*	*-0.3*	*0.0155*	*-0.9*
53	*0.0129*	*-0.4*	*0.022*	*0.1*	*0.01*	*-0.4*	*0.0134*	*-0.1*	*0.0179*	*-0.2*	*0.0111*	*-0.2*	*0.0124*	*-1.5*
54					*0.01*	*-0.6*					*0.0101*	*-0.5*	*0.0255*	*1.2*
55														
56			*0.025*	*0.6*							*0.013*	*0.5*	*0.018*	*-0.3*
57			*0.022*	*0.1*					*0.019*	*0.0*			*0.015*	*-1.0*
58			*0.029*	*1.4*					*0.022*	*0.6*	*0.01*	*-0.6*	*0.02*	*0.1*
59			*0.0211*	*-0.1*	*0.018*	*2.3*			*0.0618*	*>5*			*0.0111*	*-1.7*
60			*0.0113*	*-1.9*									*0.0155*	*-0.9*
61	*0.01*	*-1.2*	*0.0278*	*1.1*	*0.012*	*0.2*			*0.0179*	*-0.2*	*0.0105*	*-0.4*	*0.0229*	*0.7*
62					*0.01*	*-0.6*					*0.01*	*-0.6*	*0.023*	*0.7*
63			*0.021*	*-0.1*	*0.013*	*0.4*			*0.019*	*0.0*			*0.021*	*0.3*
64	*0.012*	*-0.6*											*0.013*	*-1.4*
65			*0.014*	*-1.4*							*0.01*	*-0.6*	*0.012*	*-1.6*
66														
67	*0.022*	*2.2*	*0.022*	*0.1*	*0.012*	*0.1*			*0.022*	*0.6*	*0.013*	*0.5*	*0.018*	*-0.3*
68	*0.017*	*0.8*	*0.024*	*0.4*	*0.014*	*0.8*	*0.023*	*2.7*	*0.023*	*0.8*	*0.011*	*-0.2*	*0.025*	*1.1*
69														
70	*0.011*	*-0.9*	*0.018*	*-0.7*	*0.011*	*-0.2*	*0.01*	*-1.1*	*0.019*	*0.0*	*0.011*	*-0.2*	*0.021*	*0.3*
71			*0.022*	*0.1*			*0.018*	*1.2*	*0.014*	*-1.1*	*0.013*	*0.5*	*0.021*	*0.3*
72	*0.014*	*0.0*	*0.024*	*0.4*			*0.013*	*-0.2*	*0.021*	*0.4*	*0.01*	*-0.6*	*0.022*	*0.5*
73														
74	*0.016*	*0.5*	*0.022*	*0.1*	*0.013*	*0.4*	*0.019*	*1.5*	*0.02*	*0.2*	*0.014*	*0.8*	*0.02*	*0.1*
75	*0.013*	*-0.3*	*0.026*	*0.8*	*0.012*	*0.1*	*0.01*	*-1.1*	*0.019*	*0.0*	*0.01*	*-0.6*	*0.021*	*0.3*
76	*0.0139*	*-0.1*	*0.021*	*-0.1*			*0.0132*	*-0.2*	*0.0161*	*-0.6*			*0.017*	*-0.5*
77													*0.0241*	*0.9*
78			*0.04*	*3.4*					*0.026*	*1.5*				
79														
80														
81											*0.027*	*>5*		

Laboratory code	Cyantraniliprole	Z-scores (FFP RSD (25%)	Indoxacarb	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Pyridalyl	Z-scores (FFP RSD (25%)	Tebufenozide	Z-scores (FFP RSD (25%)	Tefluthrin	Z-scores (FFP RSD (25%)	Tetraconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Alg A mean	***0.014***		***0.022***		***0.012***		***0.014***		***0.019***		***0.012***		***0.020***	
82											*0.016*	*1.5*	*0.021*	*0.3*
83			*0.017*	*-0.9*							*0.015*	*1.2*	*0.014*	*-1.2*
84			*0.032*	*1.9*	*0.011*	*-0.2*			*0.02*	*0.2*	*0.025*	*4.6*	*0.023*	*0.7*
85	*0.012*	*-0.6*	*0.037*	*2.8*	*0.01*	*-0.6*			*0.015*	*-0.8*			*0.02*	*0.1*
86	*0.014*	*0.0*	*0.021*	*-0.1*	*0.011*	*-0.2*			*0.023*	*0.8*	*0.011*	*-0.2*	*0.024*	*0.9*
87			*0.0124*	*-1.7*					*0.0145*	*-0.9*			*0.0152*	*-0.9*
88			*0.019*	*-0.5*					*0.023*	*0.8*			*0.021*	*0.3*
89	*0.029*	*4.2*	*0.022*	*0.1*	*0.01*	*-0.4*			*0.021*	*0.4*	*0.0109*	*-0.2*	*0.022*	*0.5*
90														
91	*0.014*	*0.0*	*0.021*	*-0.1*	*0.01*	*-0.6*			*0.019*	*0.0*	*0.015*	*1.2*	*0.019*	*-0.1*
92			*0.021*	*-0.1*	*0.01*	*-0.6*	*0.021*	*2.1*	*0.0081*	*-2.3*	*0.027*	*>5*	*0.014*	*-1.2*
93			*0.0264*	*0.9*	*0.026*	*4.9*	*0.019*	*1.5*	*0.0174*	*-0.3*	*0.009*	*-0.9*	*0.0181*	*-0.3*
94														
95	*0.015*	*0.2*	*0.015*	*-1.2*	*0.01*	*-0.7*			*0.019*	*0.0*	*0.009*	*-0.9*	*0.023*	*0.7*
96			*0.017*	*-0.9*					*0.015*	*-0.8*			*0.017*	*-0.5*
97			*0.018*	*-0.7*					*0.018*	*-0.2*				
98			*0.024*	*0.4*	*0.008*	*-1.4*	*0.0117*	*-0.6*	*0.026*	*1.5*	*0.012*	*0.1*	*0.017*	*-0.5*
99			*0.026*	*0.8*					*0.017*	*-0.4*	*0.018*	*2.2*	*0.016*	*-0.7*
100	*0.014*	*0.0*	*0.017*	*-0.9*			*0.014*	*0.1*	*0.02*	*0.2*	*0.011*	*-0.2*	*0.021*	*0.3*
101			*0.023*	*0.2*			*0.011*	*-0.8*	*0.016*	*-0.6*			*0.017*	*-0.5*
102	*0.014*	*0.0*	*0.021*	*-0.1*	*0.02*	*2.8*			*0.016*	*-0.6*			*0.017*	*-0.5*
103	*0.013*	*-0.3*	*0.024*	*0.4*	*0.011*	*-0.2*	*0.017*	*0.9*	*0.018*	*-0.2*	*0.01*	*-0.6*	*0.019*	*-0.1*
104	*0.0128*	*-0.4*	*0.023*	*0.2*					*0.0217*	*0.6*	*0.0112*	*-0.1*	*0.0272*	*1.5*
105	*0.022*	*2.2*	*0.043*	*3.9*	*0.022*	*3.5*			*0.03*	*2.3*	*0.016*	*1.5*	*0.028*	*1.7*
106	*0.032*	*5.0*	*0.014*	*-1.4*	*0.012*	*0.1*	*0.01*	*-1.1*			*0.01*	*-0.6*	*0.016*	*-0.7*
107	*0.0137*	*-0.1*							*0.017*	*-0.4*	*0.01*	*-0.6*	*0.02*	*0.1*
108	*0.01*	*-1.2*	*0.012*	*-1.8*			*0.016*	*0.7*	*0.016*	*-0.6*			*0.019*	*-0.1*
109	*0.012*	*-0.6*	*0.0182*	*-0.6*	*0.011*	*-0.2*			*0.0197*	*0.1*	*0.0111*	*-0.2*	*0.0221*	*0.5*
110														
111			*0.022*	*0.1*	*0.01*	*-0.6*	*0.013*	*-0.2*	*0.024*	*1.1*	*0.011*	*-0.2*	*0.022*	*0.5*
112			*0.0196*	*-0.4*	*0.011*	*-0.2*	*0.013*	*-0.2*	*0.0189*	*0.0*			*0.0259*	*1.3*
113			*0.023*	*0.2*										
114			*0.0152*	*-1.2*					*0.0163*	*-0.6*			*0.0185*	*-0.2*
115			*0.021*	*-0.1*					*0.016*	*-0.6*			*0.018*	*-0.3*
116	*0.036*	*>5*	*0.031*	*1.7*	*0.012*	*0.1*			*0.022*	*0.6*			*0.026*	*1.3*
117	*0.0157*	*0.4*	*0.0214*	*0.0*	*0.006*	*-1.8*	*0.0079*	*-1.7*	*0.0176*	*-0.3*	*0.0103*	*-0.4*	*0.0191*	*-0.1*
118					*0.01*	*-0.5*					*0.0105*	*-0.4*	*0.0211*	*0.3*
119	*0.013*	*-0.3*	*0.019*	*-0.5*	*0.012*	*0.1*			*0.024*	*1.1*	*0.011*	*-0.2*	*0.022*	*0.5*
120					*0.01*	*-0.5*					*0.0118*	*0.1*	*0.0198*	*0.0*
121	*0.017*	*0.8*	*0.021*	*-0.1*					*0.015*	*-0.8*			*0.018*	*-0.3*

Laboratory code	Cyantraniliprole	Z-scores (FFP RSD (25%)	Indoxacarb	Z-scores (FFP RSD (25%)	Metconazole	Z-scores (FFP RSD (25%)	Pyridalyl	Z-scores (FFP RSD (25%)	Tebufenozide	Z-scores (FFP RSD (25%)	Tefluthrin	Z-scores (FFP RSD (25%)	Tetraconazole	Z-scores (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Alg A mean	***0.014***		***0.022***		***0.012***		***0.014***		***0.019***		***0.012***		***0.020***	
122			*0.0171*	*-0.8*					*0.019*	*0.0*			*0.0196*	*0.0*
123	*0.02*	*1.7*	*0.013*	*-1.6*			*0.01*	*-1.1*	*0.015*	*-0.8*	*0.011*	*-0.2*	*0.023*	*0.7*
124														
125													*0.019*	*-0.1*
126														
127											*0.014*	*0.8*	*0.022*	*0.5*
128	*0.015*	*0.2*	*0.042*	*3.8*			*0.013*	*-0.2*	*0.033*	*2.9*	*0.012*	*0.1*	*0.019*	*-0.1*
129			*0.02*	*-0.3*					*0.019*	*0.0*	*0.008*	*-1.2*	*0.019*	*-0.1*
130	*0.011*	*-0.9*	*0.012*	*-1.8*					*0.016*	*-0.6*	*0.007*	*-1.6*	*0.012*	*-1.6*
131			*0.016*	*-1.0*									*0.0152*	*-0.9*
132									*0.0151*	*-0.8*			*0.0197*	*0.0*
133	*0.013*	*-0.3*	*0.022*	*0.1*	*0.014*	*0.8*			*0.02*	*0.2*	*0.015*	*1.2*	*0.017*	*-0.5*
134	*0.013*	*-0.3*	*0.021*	*-0.1*	*0.011*	*-0.2*	*0.013*	*-0.2*	*0.02*	*0.2*	*0.012*	*0.1*	*0.019*	*-0.1*
135	*0.012*	*-0.6*	*0.022*	*0.1*					*0.012*	*-1.5*	*0.013*	*0.5*	*0.018*	*-0.3*
136			*0.013*	*-1.6*					*0.0138*	*-1.1*	*0.0105*	*-0.4*	*0.016*	*-0.7*
137													*0.028*	*1.7*
138														
139			*0.025*	*0.6*					*0.027*	*1.7*			*0.022*	*0.5*
140														

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

To be classified into Category A, the laboratories had to submit quantitative results for at least 90% of the compulsory pesticides present in the Test Item (≥11 pesticide residues, exclusive of any false negatives results), analyse for more than 90% of the compulsory pesticides on the target list and also report no false positive results. For the 69 EU and EFTA laboratories in Category A (57%), the results were additionally evaluated by calculating the Average of the Squared -Score (AZ^2). Of the 69 participants only 46 participants (67%) obtained AZ2 score at or below 2 (good), 8 participants (12%) obtained AZ2 values between 2-3 (satisfactory) and 15 participants (22%) obtained AZ2 values ≥3 (unsatisfactory). An additional three laboratories from Third Countries were evaluated and classified into Category A. The AZ2 scores achieved by the labs can be seen in **Table 11**. The low number of laboratories obtaining AZ^2 score ≤2 shows that the matrix has been difficult to analyse for a number of laboratories.

Table 11. Sum of Weighted z scores (AZ^2) for laboratories in Category A, the number of pesticides detected and quantified by the laboratories, the number of false negatives reported and the classification as good, satisfactory and unsatisfactory. The table includes data for both EU and non-EU participants.

Lab code	No. of detected mandatory pesticides	No. of detected volutary pesticides	AZ^2	False negative	Classification	NRL
2	12	3	1.5	0	Good	NRL-CE
3	12	1	4.5	0	Unsatisfactory	
5	11	2	3.0	1	Unsatisfactory	
7	12	3	0.4	0	Good	
8	12	3	0.5	0	Good	
10	12	3	0.5	0	Good	
11	12	3	2.5	0	Satisfactory	
12	12	1	1.4	0	Good	
13	12	0	0.4	0	Good	NRL-CE
14	12	3	1.3	0	Good	
16	11	3	1.1	1	Good	
20	12	3	1.4	0	Good	NRL-CF
23	12	3	0.7	0	Good	
25	12	1	1.8	0	Good	NRL-CF
29	12	2	7.9	0	Unsatisfactory	
30	12	3	1.8	0	Good	NRL-FE
31	12	1	2.9	0	Satisfactory	NRL-CF
33	12	1	4.0	0	Unsatisfactory	NRL-CF
34	12	2	0.9	0	Good	
38	12	3	0.4	0	Good	NRL-CF
40	12	3	0.6	0	Good	
43	12	2	0.4	0	Good	
44	11	3	4.9	1	Unsatisfactory	
46	12	2	1.0	0	Good	
50	12	3	6.9	0	Unsatisfactory	NRL-CF
51	12	3	3.7	0	Unsatisfactory	
53	12	1	1.1	0	Good	

Lab code	No. of detected mandatory pesticides	No. of detected volutary pesticides	AZ[2]	False negative	Classification	NRL
58	12	3	0.2	0	Good	NRL-CE
59	11	1	7.7	1	Unsatisfactory	NRL-FE
61	12	3	1.7	0	Good	NRL-CF
64	12	0	2.2	0	Satisfactory	
67	12	1	1.5	0	Good	
70	12	3	2.1	0	Satisfactory	
71	12	3	5.2	0	Unsatisfactory	
72	12	3	0.4	0	Good	
74	12	3	2.0	0	Good	
75	12	3	1.1	0	Good	NRL-CF
76	12	3	0.6	0	Good	NRL-CF
77	12	1	1.0	0	Good	
84	11	2	1.3	1	Good	
85	12	0	1.1	0	Good	NRL-FE
86	12	3	1.4	0	Good	
87	12	2	0.6	0	Good	
89	11	2	1.0	1	Good	
91	12	3	1.0	0	Good	
92	11	3	4.8	1	Unsatisfactory	
93	12	3	0.3	0	Good	
95	12	3	0.3	0	Good	NRL-FE
98	12	3	3.4	0	Unsatisfactory	
100	12	3	0.4	0	Good	NRL-CE
101	11	2	1.6	1	Good	
102	12	3	1.6	0	Good	NRL-CF
103	12	2	0.7	0	Good	
104	12	3	0.7	0	Good	
105	12	2	6.4	0	Unsatisfactory	
106	11	3	2.7	1	Satisfactory	NRL-CF
107	11	2	1.2	1	Good	NRL-CF
109	12	3	2.4	0	Satisfactory	
112	12	2	1.3	0	Good	
114	12	3	1.9	0	Good	
115	11	3	3.0	1	Unsatisfactory	
116	12	2	1.7	0	Good	
117	12	2	0.5	0	Good	
119	12	3	0.6	0	Good	NRL-CF
121	12	2	1.0	0	Good	NRL-CF

Lab code	No. of detected mandatory pesticides	No. of detected volutary pesticides	AZ²	False negative	Classification	NRL
122	12	3	0.3	0	Good	NRL-CF
123	12	3	2.1	0	Satisfactory	
128	12	2	2.6	0	Satisfactory	NRL-CF
129	11	2	1.1	0	Good	
130	12	2	3.5	0	Unsatisfactory	
132	11	3	2.0	1	Good	
133	12	3	3.4	0	Unsatisfactory	
134	12	3	0.3	0	Good	
135	12	2	0.7	0	Good	NRL-CF
136	12	1	3.4	0	Unsatisfactory	

The 54 laboratories that did not fulfil the requirements described above, were classified in Category B. The number of reported quantitative results, analysed compounds from the Target List and acceptable z scores as well as information on false negative and positive results are shown in **Table 12**. No laboratories was moved from Category A to B due to false positive results. Twelve participants fulfilled the criteria of detecting 90% of the compulsory pesticides in the Test Item but did not fulfil the criteria of analysing for 90% of the compulsory pesticides on the Target List. One participant analysed more than 90% of the pesticides on the Target List but reported <11 pesticides in the Test Item.

Table 12. Number and percentage of compulsory pesticides detected and quantified, number of compulsory compounds analysed from the Target List, number of voluntary pesticides detected and quantified, number of acceptable z scores, false negative and positive results, and NRL status for the laboratories in Category B.

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected in test item, %	Analysed of compulsory pesticides on Target List, %	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
4	11	92	77	1	10	0	0	
6	0	0	3	1	0	0	0	
9	10	92	60	0	9	1	0	NRL-CE
15	9	75	59	0	7	0	0	
17	9	75	74	1	6	0	0	
18	4	33	27	1	4	0	0	NRL-CF
19	1	8	24	1	1	0	0	
21	12	100	85	2	2	0	0	NRL-CF
22	2	17	33	1	2	0	0	
27	0	0	33	0	0	0	0	
28	9	75	58	0	8	0	0	
32	8	67	37	0	6	0	0	
35	6	50	42	1	6	0	0	
36	9	75	42	2	5	0	3	
37	0	0	3	1	0	0	0	
39	0	0	95	0	0	0	0	
41	12	100	88	2	12	0	0	
42	9	75	55	0	8	0	1	

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected in test item, %	Analysed of compulsory pesticides on Target List, %	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
45	10	100	81	1	4	2	0	NRL-CF
47	12	100	87	3	10	0	0	
48	12	100	57	1	11	0	0	NRL-FE
49	6	50	43	1	6	0	0	
52	6	50	43	1	6	0	0	
54	6	50	41	1	6	0	0	
55	5	75	77	1	5	4	0	
56	10	83	61	0	9	0	0	
57	12	100	85	0	12	0	0	
60	11	100	77	0	8	1	0	NRL-CF
62	6	50	41	1	6	0	0	
63	10	92	84	0	10	1	0	
65	7	58	62	3	7	0	0	
66	0	0	56	0	0	0	0	
68	12	100	89	3	12	0	0	
69	0	0	3	1	0	0	0	
73	0	0	4	1	0	0	0	
78	10	83	57	0	8	0	0	
79	5	42	33	1	2	0	0	
80	0	0	100	0	0	0	0	
81	10	92	80	0	5	1	0	
82	7	67	51	1	6	1	0	
83	6	50	56	1	3	0	1	
88	11	92	83	0	11	0	0	
90	0	0	100	0	0	0	0	
94	7	58	66	0	0	0	0	
96	10	83	83	3	10	0	0	
97	12	100	74	2	12	0	0	NRL-FE
99	4	33	39	0	4	0	0	
108	12	100	81	2	5	0	0	
110	0	0	3	0	0	0	0	
111	12	100	80	2	9	0	0	
113	9	100	97	0	8	3	0	
118	6	50	42	1	6	0	0	
120	6	50	42	1	6	0	0	
124	0	0	83	0	0	0	0	
125	6	50	48	0	6	0	0	
126	0	0	68	0	0	0	0	
127	10	83	66	1	10	0	0	
131	7	58	59	1	7	0	0	
137	6	50	40	0	6	0	0	

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected in test item, %	Analysed of compulsory pesticides on Target List, %	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
138	0	0	5	1	0	0	0	
139	7	58	58	1	7	0	0	
140	0	0	5	1	0	0	0	

[1] Laboratories that reported false positive results and consequently were moved from Category A to Category B

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 but has settled at around 150. However, part of the network do not have feed in there scope, so consequently, there is a drop in the number of participants, when the matrix is feed. This was also seen in EUPT-CF15 where 129 participants registered. Nevertheless, the number of participant is the highest seen so far in EUPT-CF on exclusively feed matrices. The numbers from EUPT-CF9 and forward can be seen in **Table 13**.

Table 13. Overall trends in participation of laboratories, pesticides in the target list and test item, and performance of laboratories in the 7 latest EUPTs cereals (excluding EUPT-CF7 on feed and EUPT-CF12 on hay).

PT and types of test item	EUPT-CF9 Maize flour	EUPT-CF10 Rye flour	EUPT-CF11 Oat flour	EUPT-CF12 Hay flour	EUPT-CF13 Oat kernels	EUPT-CF14 Rice kernels	EUPT-CF15 Rapeseed cake
Participants submitting results (EU+EFTA)	143	160	149	111	149	156	129
MRM pesticides in the Target Pesticide List	117	134/7	153/9	155/23	160/32	164/38	172/41
MRM pesticides in the test material	18	16	18	8	18	19	22
No. of results for MRM pesticides	2012	2012	2172	808	2007	2298	1315
Average of 'reported results', %	78	79	83	74	75	80	83
Range of 'reported results', %	61-94	58-90	65-93	40-91	44-94	26-93	57-93
Acceptable z scores, %	89	95	89	93	93	91	87
Questionable z scores, %	2	2	3	3	3.1	3	7
Unacceptable z scores, %	3	2	8	3	3.4	6	6
False negatives, %	2	2	4	1	2.3	3.4	2.0
Number of false positives	9	0	19	7	3	14	9
Category A, % of participating laboratories	57	53	45	51	57	57	57
Good AZ[2], %	96	93	92	92	91	91	67
Satisfactory AZ[2], %	1	5	1.5	3.4	5.7	6.7	12
Unsatisfactory AZ[2], %	3	2	6.2	5.1	3.4	2.2	22
Alg A RSD%	19	17	17	20	18	19	30

The number of pesticides included in the Target Pesticide List has also increased during this 14-year period, from 43 to 172 compulsory compounds and 41 voluntary compounds. Thus, the demands put on the participating laboratories has increased every year. Many laboratories have a limited scope and are therefore not able to cover all pesticides in the PT. In this EUPT, 25% of the laboratories were not able to analyse and detect more than 70% of pesticides present in the Test Item. Last EUPT the number was 18% and the year before it was also 25%. So no improvement was seen on this issue.

The overall analytical performance (accuracy of measurement) if looking at the percentage of acceptable, questionable, unacceptable z scores has not changed significantly during the previous 6 EUPTs, but in EUPT-CF15 only 87% of the results were acceptable and more questionable z scores were seen. The analytical scope was in average 83%. The average percent of reported results in the last seven EUPT-CF has been between 74-83%. The false negative results have decreased to 2.0% and the number of false positive results reported has also decreased to levels seen earlier. This could indicate that rapeseed cake matrix was relatively easy to analyse. However, the high Alg A STD (25-38%) on the result show differently. Not all methods used have been fit for purpose probably due to the high fat content (20%).

The percentage of Category A laboratories has varied slightly over the years and 57% of the participants were evaluated as Category A in this EUPT. For Category A the percentage of participant with AZ^2 was <2 (good) has been >90% for many year. However, for the rapeseed cake EUPT this has dropped significantly to 67% indicating that the methods used by some of the participant was not fit for purpose, see **3.2.2.**

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

The EUPT-CF15 Test Item consisted of rapeseeds cake containing incurred and spiked pesticides. The rapeseeds have been sprayed in the field with commercially available pesticide formulations and additionally spiked post-harvest in the laboratory. The final Test Item contained the following pesticides: acetamiprid, aldrin*, azoxystrobin, boscalid, clomazone, cyantraniliprole*, fluopyram, imidacloprid, indoxacarb*, metconazole*, pendimethalin, penthiopyrad*, pirimicarb, prosulfocarb, prothioconazole-desthio, pyraclostrobin, pyridalyl*, tebuconazole, tebufenozide*, tefluthrin*, tetraconazole*, thiacloprid (*concentration too low to be evaluated)
One hundred tweenty-nine EU and EFTA laboratories, from 26 different countries agreed to participate in this proficiency test. Seven of them did not report any results due to different reasons An additional 8laboratories from EU candidate states and Third Countries registered for the PT and all submitted results. The Target Pesticide List distributed to the laboratories prior to the test contained 172 individual compulsory and 43 voluntary compounds.

The number of false positives and false negatives has varied between the EUPTs. Nine positive results were reported and the number of false negatives represented 2.0% of the total number of results. This is at levels typically seen in EUPT-CFs.

The average Alg A-RSD was at 30%, significantly higher than the FFP-RSD of 25%. The data has been tested for bimodality and this has not been detected, so probably multiple sources for variation is contributing to the high SD. For acetamiprid, clomazone, imidacloprid, and thiacloprid, the statistical evaluation shows high matrix effect when analysed in rapeseed cake. For other pesticides, the outcome of the t-tests were more unclear, e.g. significant difference was seen between standard in matrix and procedural calibration or between procedural calibration and standard addition (azoxystrobin, boscalid, fluopyram, pirimicarb, prosulfocarb and tebuconazole. Finally, no significant differences were seen for pendimethalin, prothioconazole-desthio, and pyraclostrobin. However, a statistical power analysis shows that for pesticides where no significant difference was determined between the calibration groups, it can be due to the number of results was too low (see 3.2.2). Further statistical evaluation might reveal other contributions to the uncertainty and bias. To overcome matrix effects SANTE/12682/2019 recommend to use either standard addition or procedural calibration.

Of the reported results for the evaluated pesticides, more than 90% were acceptable azoxystrobin, boscalid, clomazone, fluopyram, pendimethalin, and prosulfocarb. For acetamiprid, imidacloprid, pirimicarb, prothioconazole-desthio, pyraclostrobin, tebuconazole and thiacloprid between 80-89% of the results were acceptable.

The Test Item for EUPT-CF16 will be barley, and are planned to be shipped to the laboratories in March/April 2022. The selection of pesticides will continue to be focused on pesticides included in the scope of the EU multi-annual coordinated control programme, the working document as well as additional pesticides of relevance to feed and/or cereal production in Europe and in other parts of the world from where significant quantities of feed and cereals are imported.

4. ACKNOWLEDGEMENTS

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

5. REFERENCES

[1] Regulation (EU) No 2017/625 of the European Parliament and of the Council on official controls and other official activities performed to ensure the application of food and feed law, rules on animal health and welfare, plant health and plant protection products. Published at OJ of the EU L 95/1 of 07.04.2017

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

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

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

[5] ISO 13528:2015 – Statistical methods for use in proficiency testing by interlaboratory comparison

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

APPENDICES

Appendix 1 List of laboratories registered to participate in the EUPT-CF15

Participating labs from EU and EFTA member states

Country	Institution	City	NRL	Results reported
Austria	Department for Pesticide and Food Analytics (PLMA)	Innsbruck	NRL-CF	
Belgium	PRIMORIS (Phytolab) - Belgium, Gent	Gent - Zwijnaarde		
Belgium	FLVVT	Tervuren		
Belgium	Sciensano - Pesticide Lab	Brussels	NRL-CF	
Bulgaria	CLCTC - Sofia | Pesticide Lab	Sofia		
Croatia	Sample Control - Pesticide Lab	Lucko		
Croatia	Primorsko-goranska County, Rijeka - Pesticide Lab	Kotar County, Rijeka		
Croatia	Center for Food Control - PBF, Zagreb	Zagreb		
Croatia	Eurofins Croatiakontrola - Croatia, Zagreb	Zagreb		
Croatia	CROATIAN VETERINARY INSTITUTE	Zagreb	NRL-FE	
Croatia	Croatian National Institute of Public Health-HZJZ	Zagreb		
Croatia	Inspecto d.o.o. Laboratorij	Osijek		
Cyprus	Animal Feeds and Feed Additives - Pesticide Lab	Nicosia	NRL-FE	
Czech Republic	Czech Agriculture and Food Inspection Authority	Praha	NRL-CE	
Czech Republic	VSCHT Praha, Analyza potravin	Praha		
Czech Republic	Central Institute for Supervising and Testing in Agriculture	Brno	NRL-FE	
Denmark	Laboratoriet Ringsted - Pesticide Lab	Ringsted	NRL-FE	
Estonia	Agricultural Research Center - Estonia, Saku	Saku	NRL-CF	
Finland	Finnish Customs Laboratory	Espoo	NRL-CE	
Finland	Finnish Food Authority	Helsinki	NRL-FE	
France	CAMP Méditerrannée (Perpignan)	Perpignan		
France	CAPINOV (Landerneau)	Landerneau		
France	INOVALYS	Le Mans		
France	Phytocontrol (Nimes) - Pesticide Lab	Nimes		
France	SCL - Massy Cedex	Massy Cedex	NRL-CF	
Germany	Landesbetrieb Hessisches Landeslabor - Standort Wiesbaden	Wiesbaden		
Germany	LAVES - Pesticide Lab	Stade		
Germany	CVUA RRW - Pesticide Lab	Krefeld		
Germany	TLLLR	Jena		
Germany	LLG Halle/Saale	Halle/Saale		
Germany	BVL Unit 504 NRL for Pesticide Residues	Berlin	NRL-CF	
Germany	Landwirtschaftliches Technologiezentrum Augustenberg (LTZ)	Karlsruhe		
Germany	State Department of Environmental and Agricultural Operations in Saxony (BfUL)	Nossen		
Germany	LUFA Speyer	Speyer		
Germany	Landesamt für Landwirtschaft, Lebensmittelsicherheit und Fischerei	Rostock		
Germany	Eurofins Dr. Specht Laboratorien GmbH	Hamburg		
Germany	Landeslabor Berlin-Brandenburg, Potsdam	Potsdam		
Germany	SYNLAB A&S - Germany, Jena	Jena		
Germany	Niedersächsisches Landesamt für Verbraucherschutz und Lebensmittelsicherheit	Oldenburg		

Country	Institution	City	NRL	Results reported
Germany	AGROLAB LUFA GmbH	Kiel		
Germany	Bundeswehr - Pesticide Lab (Garching-Hochbrück)	Garching-Hochbrück		
Greece	GENERAL CHEMICAL STATE LABORATORY	Athens	NRL-CF	
Greece	Pesticide Residue Labolatory of Regional Centre of Plant Protection, Quality and Phytosanitary Control	Thessaloniki		
Greece	LABORATORY OF PESTICIDE RESIDUES/ BENAKI PHYTOPATHOLOGICAL INSTITUTE	Kifissia	NRL-CF	
Hungary	Food Chain Safety Centre Non-profit Ltd., Pesticide Residue Analytical Laboratory	Szolnok		
Hungary	Food Chain Safety Centre Non-profit Ltd. Pesticide Residue Analytical Laboratory	Hódmezovásárhely		
Hungary	National Food Chain Safety Laboratory Directorate Pesticide Analytical National Reference Laboratory	Velence	NRL-CF	
Hungary	FCSCN Ltd. Pesticide Residue Analytical Laboratory	Miskolc		
Iceland	Matís - Iceland, Reykjavík	Reykjavík	NRL-CF	
Ireland	Pesticide Residue Laboratory, Department of Agriculture, Food & Marine	Co. Kildare	NRL-CF	
Italy	DAP BARI Polo di Specializzazione Alimenti	Bari		
Italy	ARPA Veneto (Laboratorio di Verona)	Verona		
Italy	IZSUM - Italy, Perugia	Perugia		
Italy	APPA Bolzano	Bolzano		
Italy	ASF - Pesticide Lab	Firenze		
Italy	IZS LT - Italy, Rome	Roma		
Italy	Please fill-in!	Genova	NRL-CF	
Italy	ARPA VDA - Pesticide Lab	Saint Christophe		
Italy	Laboratorio di Prevenzione ATS Bergamo	Bergamo		
Italy	IZSLER - Pesticide Lab	Brescia		
Italy	ARPA Lazio (sez. Latina) - Pesticide Lab	Latina		
Italy	Istituto Superiore di Sanità - Roma	Roma		
Italy	IZS PB - Pesticide Lab	Foggia		
Italy	IZSLT Sede di FIRENZE	San Martino alla Palma Scandicci (FI)		
Italy	ATS Milano - Laboratorio di Prevenzione	Milano		
Italy	IZSAM - Pesticide Lab	Teramo		
Italy	IZSVe - Pesticide Lab	Legnaro (Padova)		No
Italy	ARPAL -Dipartimento Laboratorio - U.O. Laboratorio Chimico - Sett. Levante	La Spezia		No
Italy	ARPAM - Pesticide Lab	Macerata		
Italy	IZS Sicilia - Pesticide Lab	Palermo		No
Italy	IZS Sardegna - Pesticide Lab	Sassari		
Latvia	BIOR (Riga) - Pesticide Lab	Riga	NRL-CF	
Lithuania	NMVRVI - Pesticide Lab (Vilnius)	Vilnius	NRL-CF	
Luxembourg	LNS Food lab	Dudelange	NRL-CE	
Netherlands	Groen Agro Control	Delfgauw		
Netherlands	Wageningen Food Safety Research	Wageningen	NRL-CF	
Netherlands	Dr. A. Verwey B.V.	Rotterdam		
Netherlands	Eurofins Lab Zeeuws-Vlaanderen B.V. - Pesticiden	Graauw		
Norway	NIBIO Pesticides and Natural Products Chemistry	ÅS	NRL-CF	
Poland	WIW ZHW Poznan Pesticide Lab	Poznan		
Poland	IPP-NRI - Pesticide Lab (Sosnicowice)	Sosnicowice		

Country	Institution	City	NRL	Results reported
Poland	WIW ZHW (Szczecin) - Pesticide Lab	Szczecin		
Poland	WIW ZHW (Katowice) - Pesticide Lab	Katowice		
Poland	WIW ZHW (Wroclaw) - Pesticide Lab	Wroclaw		
Poland	WIW ZHW (Opole) - Pesticide Lab	Opole		
Poland	VSES Opole - Pesticide Lab	Opole		
Poland	IPP-NRI - Pesticide Lab (Poznan)	Poznan	NRL-FE	
Poland	Laboratory of Food & Feed Safety in Bialystok	Bialystok		
Poland	VSES Warszawa - Pesticide Lab	Warszaw	NRL-CE	
Poland	WIW ZHW (Gdansk) - Pesticide Lab	Gdansk		
Poland	Please fill-in!	Bialystok		
Poland	Food Safety Laboratory / The National Institute of Horticultural Research	Skierniewice		
Poland	Hamilton UO-Technologia	Grójec		
Poland	WIW ZHW (Warsaw) - Pesticide Lab	Warszaw		
Portugal	INIAV Pesticide Lab (vegetable & Animal Products).	Vairão - Vila do Conde	NRL-CE	
Portugal	Laboratório Regional de Veterinária e Segurança Alimentar	Funchal - Madeira Island		
Portugal	Labiagro – Laboratório Químico	Oeiras - Lisboa		
Romania	"Institute for Hygiene and Veterinary Public Health			
"	Bucharest	NRL-CF		
Romania	Pesticide Lab (Cluj Napoca)	Cluj Napoca		
Romania	National Phytosanitary Authority-Laboratory for Pesticides Residues Control in Plants and Vegetable Products	Bucharest	NRL-CF	
Romania	Pesticides Residues Laboratory - Dolj	Craiova		
Romania	Pesticides Residues Laboratory - Bistrita	Bistrita		
Slovakia	SLAPe/UKSUP	Bratislava		
Slovakia	State Veterinary and Food Institute	Bratislava	NRL-CF	
Spain	LABORATORIO AGRARIO REGIONAL de Castilla y León.	Burgos		
Spain	Agricultural and Phytopathological Lab. of Galicia	Abegondo. A Coruña		No
Spain	LABORTORIO DE SALUD PUBLICA DE GALICIA	Lugo		
Spain	Analytica Alimentaria GmbH - Almeria, Spain	Almeria		
Spain	Labs & Technological Services AGQ - Burguillos	Burguillos		
Spain	LAC - Generalitat de Catalunya	Cabrils		
Spain	SOIVRE - Almeria	Almería		No
Spain	Laboratorio Analítico Bioclínico - Spain, Almeria	Almeria		
Spain	Nasertic - Spain, Villava	Villava		
Spain	EUROFINS ECOSUR, S.A.	LORQUI - MURCIA		No
Spain	LABORATORIO DE SALUD PUBLICA DE CUENCA	Cuenca		
Spain	LARAGA - Pesticide Lab	Toledo		
Spain	Laboratorio Agroalimentario de Extremadura	Cáceres		
Spain	Laboratorio Agroambiental de Zaragoza (Gobierno de Aragón)	Zaragoza		
Spain	National Center for Technology and Food Safety (CNTA)	San Adrián (Navarra)		
Spain	Laboratorio Regional de la CCAA de LA Rioja	Logroño		
Spain	Laboratorio Agroalimentario - Spain, Valencia	Valencia		
Spain	Laboratorio Arbitral Agroalimentario, Madrid	Madrid	NRL-CF	
Spain	Laboratori Agència de Salut Pública de Barcelona	Barcelona		
Spain	National Centre for Food	Majadahonda	NRL-CF	

Country	Institution	City	NRL	Results reported
Spain	INSTITUTO TECNOLÓGICO DE CANARIAS, S. A. Laboratorio de Residuos. Departamento de Análisis Ambiental	Agüimes, Gran Canaria		
Sweden	Eurofins Food & Feed Testing Sweden AB	Lidköping		
Sweden	National Food Agency - Sweden	Uppsala	NRL-CF	
Switzerland	Kantonales Labor Zürich	Zürich		

Participating labs from EU candidate states and other non EU countries

Country	Institution	City	Report data
Belarus	BelGIM/ Food testing laboratory	Minsk	
Kenya	KEPHIS - Kenya, Nairobi	Nairobi	
Peru	Inspectorate Services Perú S.A.C.	LIMA - CALLAO	
Serbia	SP Laboratorija - Pesticide Lab	BECEJ	
Serbia	Inst. of Public Health of Belgrade - Pesticide Lab	Belgrade	
Thailand	Central Laboratory - Pesticide Lab	Bangkok	
United Kingdom	Fera Science Ltd	York	No
United Kingdom	Agri-Food and Biosciences Institute, Belfast	Belfast	

Appendix 2

Target Pesticide List

Pesticides	MRRL (mg/kg)
Compulsory Compounds (will be considered in Category A/B classification)	
2-phenylphenol	0.01
Acephate	0.01
Aclonifen	0.01
Acetamiprid	0.01
Acrinathrin	0.01
Aldrin	0.005
Ametoctradin	0.01
Azinphos-methyl	0.005
Azoxystrobin	0.01
Bifenthrin	0.01
Biphenyl	0.01
Bitertanol (sum of isomers)	0.01
Bixafen	0.01
Boscalid	0.01
Bromuconazole (sum of isomers)	0.01
Buprofezin	0.01
Cadusafos	0.005
Carbaryl	0.005
Carbendazim	0.01
Carbofuran	0.005
Carbofuran-3-hydroxy	0.005
Carboxin	0.01
Chlorantraniliprole	0.01
Chlorfenapyr	0.01
Chlorfenvinphos	0.01
Chlorpropham	0.01
Chlorpyrifos	0.005
Chlorpyrifos-methyl	0.01
Clothianidin	0.01
Cyantraniliprole	0.01
Cyazofamid	0.01
Cyfluthrin (sum of isomers)	0.01
Cymoxanil	0.01
Cypermethrin (sum of isomers)	0.01
Cyproconazole	0.01
Cyprodinil	0.01
Deltamethrin,cis-	0.01
Demeton-S-methylsulfone	0.005
Diazinon	0.005
Dichlorvos	0.005
Dieldrin	0.005

Pesticides	MRRL (mg/kg)
Difenoconazole	0.01
Diflubenzuron	0.01
Dimethoate	0.003
Dimethomorph (sum of isomers)	0.01
Diniconazole (sum of isomers)	0.01
Endosulfan-alpha	0.01
Endosulfan-beta	0.01
Endosulfan-sulfate	0.01
Epoxiconazole	0.01
Ethion	0.01
Ethirimol	0.01
Ethoprophos	0.005
Etoxazole	0.01
Famoxadone	0.01
Fenbuconazole	0.005
Fenhexamid	0.01
Fenitrothion	0.01
Fenpropathrin	0.01
Fenpropidin	0.01
Fenpropimorph (sum of isomers)	0.01
Fenpyrazamine	0.01
Fenpyroximate	0.01
Fenthion	0.01
Fenthion-oxon	0.01
Fenthion-oxon-sulfone	0.01
Fenthion-oxon-sulfoxide	0.01
Fenthion-sulfone	0.01
Fenthion-sulfoxide	0.01
Fenvalerate (sum of isomers)	0.01
Fipronil	0.004
Fipronil-sulfone	0.004
Flonicamid	0.01
Flubendiamide	0.01
Fludioxonil	0.01
Flufenoxuron	0.01
Fluopicolide	0.01
Fluopyram	0.01
Fluquinconazole	0.01
Flusilazole	0.01
Flutolanil	0.01
Flutriafol	0.01
Fluxapyroxad	0.01
Formetanate	0.01
Hexaconazole	0.01
Imazalil	0.005

Pesticides	MRRL (mg/kg)
Imidacloprid	0.01
Indoxacarb	0.01
Iprodione	0.01
Isocarbophos	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
Mandipropamid	0.01
Metaflumizone (sum of E- and Z- isomers)	0.01
Metalaxyl	0.01
Metconazole (sum of isomers)	0.01
Methacrifos	0.01
Methamidophos	0.01
Methomyl	0.01
Metolachlor	0.01
Metrafenone	0.01
Metribuzin	0.01
Omethoate	0.003
Oxydemeton-methyl	0.005
Paclobutrazol	0.01
Parathion	0.01
Penconazole	0.01
Pencycuron	0.01
Pendimethalin	0.01
Permethrin (sum of isomers)	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
Profenofos	0.01
Propamocarb (only parent compound)	0.01
Propiconazole (sum of isomers)	0.01
Proquinazid	0.01
Prosulfocarb	0.01
Prothioconazole-desthio	0.01
Prothiofos	0.01
Pymetrozine	0.01
Pyraclostrobin	0.01

Pesticides	MRRL (mg/kg)
Pyridaben	0.01
Quinoxyfen	0.01
Spinetoram	0.01
Spirodiclofen	0.01
Spiromesifen	0.01
Spirotetramat	0.01
Spirotetramat metabolite BYI08330 enol-glucoside	0.01
Spirotetramat metabolite BYI08330-enol	0.01
Spirotetramat metabolite BYI08330-ketohydroxy	0.01
Spirotetramat metabolite BYI08330-monohydroxy	0.01
Spiroxamine	0.01
Sulfoxaflor	0.01
Tau-Fluvalinate	0.01
Tebuconazole	0.01
Tebufenozide	0.01
Teflubenzuron	0.01
Tefluthrin	0.01
Terbuthylazine	0.01
Tetraconazole	0.01
Tetradifon	0.01
Tetramethrin	0.01
Thiabendazole	0.01
Thiacloprid	0.01
Thiamethoxam	0.01
Thiodicarb	0.01
Thiophanate-methyl	0.01
Tolclofos-methyl	0.01
Triadimefon	0.01
Triadimenol	0.01
Triflumizole	0.01
Triflumizole metabolite (FM-6-1)	0.01
Triazophos	0.005
Tricyclazole	0.01
Vinclozolin (parent compound only)	0.01
Zoxamide	0.01
Voluntary Compounds (will not be considered in Category A/B classification)	
Benalaxyl (sum)	0.01
Benzovindiflupyr	0.01
Chlordane-cis	0.01
Chlordane-trans	0.01
Chlordane-oxy	0.01
Chlorfluazuron	0.01
Clomazone	0.01
Cyflufenamid	0.01

Pesticides	MRRL (mg/kg)
Cyhalofop-butyl	0.01
DDD-pp	0.01
DDE-pp	0.01
DDT-op	0.01
DDT-pp	0.01
Dinotefuran	0.01
Endrin	0.01
Endrin, ketone-	0.01
Fenobucarb	0.01
Fenpicoxamid	0.01
Florpyrauxyfen benzyl	0.01
Fluensulfone	0.01
Flutianil	0.01
HCH-alpha	0.01
HCH-beta	0.01
Heptachlor	0.01
Heptachlorepoxid-cis	0.01
Heptachlorepoxid-trans	0.01
Isofetamid	0.01
Isopyrazam	0.01
Mefentrifluconazole	0.01
Novaluron	0.01
Oxadiargyl	0.01
Oxathiapiprolin	0.01
Oxyfluorfen	0.01
Penflufen	0.01
Pentachloro-aniline	0.01
Penthiopyrad	0.01
Pyrethrins	0.01
Pyridate	0.01
Pyriofenone	0.01
Quinalphos	0.01
Quintozene	0.01
Tolfenpyrad	0.01
Tri-allate	0.01

Appendix 3 Homogeneity data

	Acetamiprid mg/kg		Aldrin mg/kg		Azoxystrobin mg/kg		Boscalid mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
13	0.089	0.081	0.027	0.024	0.028	0.029	0.083	0.084
41	0.083	0.080	0.028	0.027	0.032	0.036	0.092	0.098
58	0.100	0.074	0.031	0.025	0.046	0.040	0.119	0.099
83	0.089	0.099	0.032	0.036	0.049	0.046	0.126	0.114
106	0.077	0.089	0.028	0.026	0.039	0.029	0.114	0.096
120	0.088	0.101	0.027	0.027	0.031	0.032	0.104	0.098
142	0.101	0.105	0.023	0.029	0.027	0.033	0.079	0.095
174	0.075	0.081	0.027	0.028	0.023	0.030	0.070	0.086
203	0.060	0.090	0.028	0.029	0.038	0.029	0.127	0.084
230	0.092	0.088	0.030	0.026	0.031	0.028	0.091	0.087
241	0.098	0.087	0.027	0.030	0.035	0.030	0.091	0.087

	Clomazone mg/kg		Cyantraniliprole mg/kg		Fluopyram mg/kg		Imidacloprid mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
13	0.074	0.073	0.013	0.012	0.031	0.030	0.298	0.273
41	0.075	0.078	0.009	0.011	0.030	0.033	0.280	0.277
58	0.082	0.079	0.011	0.009	0.041	0.035	0.333	0.250
83	0.084	0.085	0.013	0.015	0.052	0.043	0.285	0.328
106	0.080	0.071	0.011	0.012	0.037	0.029	0.261	0.290
120	0.077	0.073	0.010	0.013	0.032	0.032	0.284	0.337
142	0.067	0.071	0.014	0.014	0.028	0.031	0.339	0.355
174	0.057	0.072	0.010	0.009	0.024	0.031	0.250	0.272
203	0.073	0.070	0.011	0.013	0.033	0.030	0.195	0.304
230	0.072	0.073	0.012	0.011	0.031	0.031	0.302	0.288
241	0.075	0.071	0.014	0.013	0.034	0.030	0.319	0.287

	Indoxacarb mg/kg		Pendimethalin mg/kg		Penthiopyrad mg/kg		Pirimicarb mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
13	0.019	0.021	0.027	0.024	0.021	0.022	0.059	0.057
41	0.023	0.023	0.028	0.027	0.020	0.022	0.058	0.060
58	0.021	0.020	0.031	0.025	0.020	0.021	0.063	0.062
83	0.027	0.028	0.032	0.036	0.025	0.027	0.066	0.070
106	0.027	0.021	0.028	0.026	0.024	0.023	0.063	0.057
120	0.023	0.027	0.027	0.027	0.025	0.024	0.060	0.061
142	0.021	0.020	0.023	0.029	0.023	0.024	0.054	0.062
174	0.018	0.020	0.027	0.028	0.016	0.020	0.043	0.055
203	0.024	0.023	0.028	0.029	0.021	0.023	0.057	0.058
230	0.021	0.020	0.030	0.026	0.022	0.022	0.055	0.054
241	0.021	0.021	0.027	0.030	0.022	0.020	0.057	0.056

	Prosulfocarb mg/kg		Prothioconazole-dest. mg/kg		Pyraclostrobin mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
13	0.470	0.510	0.037	0.037	0.028	0.030
41	0.454	0.475	0.043	0.049	0.037	0.034
58	0.535	0.467	0.064	0.045	0.048	0.028
83	0.533	0.511	0.061	0.048	0.044	0.036
106	0.418	0.456	0.043	0.039	0.027	0.028
120	0.357	0.383	0.037	0.037	0.028	0.024
142	0.422	0.479	0.043	0.048	0.026	0.040
174	0.394	0.444	0.036	0.041	0.026	0.000
203	0.346	0.485	0.049	0.044	0.033	0.032
230	0.409	0.469	0.042	0.046	0.034	0.035
241	0.443	0.479	0.046	0.041	0.040	0.035

	Pyridalyl mg/kg		Tebuconazole mg/kg		Tebufenozide mg/kg	
Sample no.	Portion 1	Portion 1	Portion 1	Portion 2	Portion 1	Portion 2
13	0.006	0.006	0.058	0.053	0.015	0.003
41	0.005	0.005	0.069	0.071	0.012	0.014
58	0.005	0.005	0.111	0.068	0.002	0.011
83	0.006	0.006	0.110	0.075	0.010	0.003
106	0.005	0.005	0.075	0.059	0.014	0.015
120	0.005	0.005	0.060	0.062	0.016	0.014
142	0.006	0.006	0.055	0.068	0.016	0.015
174	0.004	0.004	0.050	0.061	0.011	0.012
203			0.093	0.062	0.009	0.016
230	0.004	0.004	0.067	0.063	0.014	0.013
241	0.006	0.006	0.070	0.062	0.018	0.013

	Tefluthrin mg/kg		Tetraconazole mg/kg		Thiacloprid mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
13	0.007	0.008	0.019	0.019	0.056	0.053
41	0.007	0.007	0.018	0.019	0.045	0.051
58	0.007	0.007	0.019	0.020	0.061	0.044
83	0.009	0.008	0.022	0.024	0.059	0.058
106	0.007	0.008	0.022	0.020	0.044	0.056
120	0.007	0.008	0.023	0.023	0.052	0.053
142	0.007	0.008	0.022	0.022	0.057	0.053
174	0.007	0.006	0.015	0.019	0.044	0.051
203	0.008	0.008	0.020	0.022	0.044	0.052
230	0.007	0.007	0.020	0.020	0.050	0.051
241	0.008	0.008	0.022	0.019	0.057	0.047

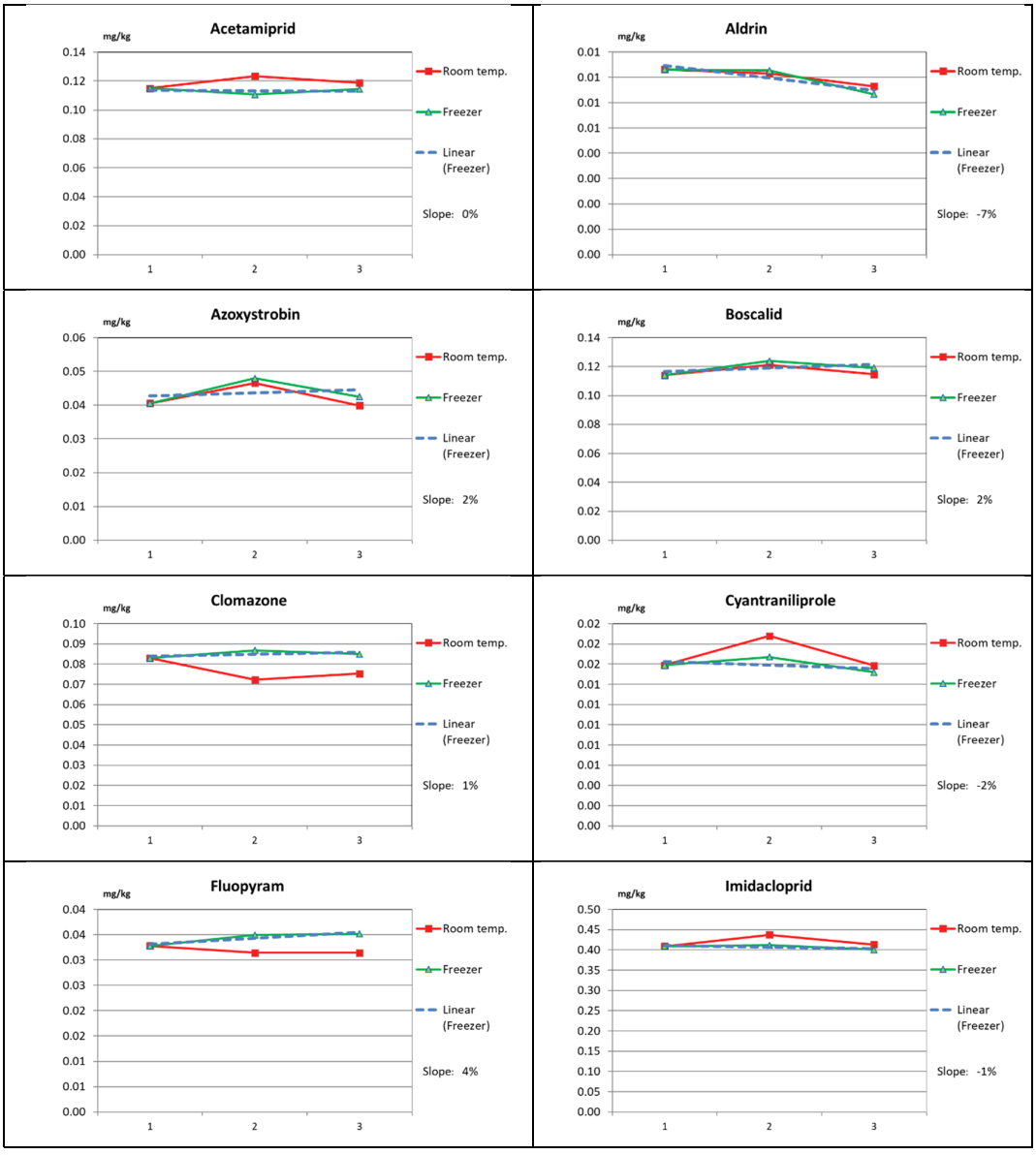
Appendix 4 Stability figures

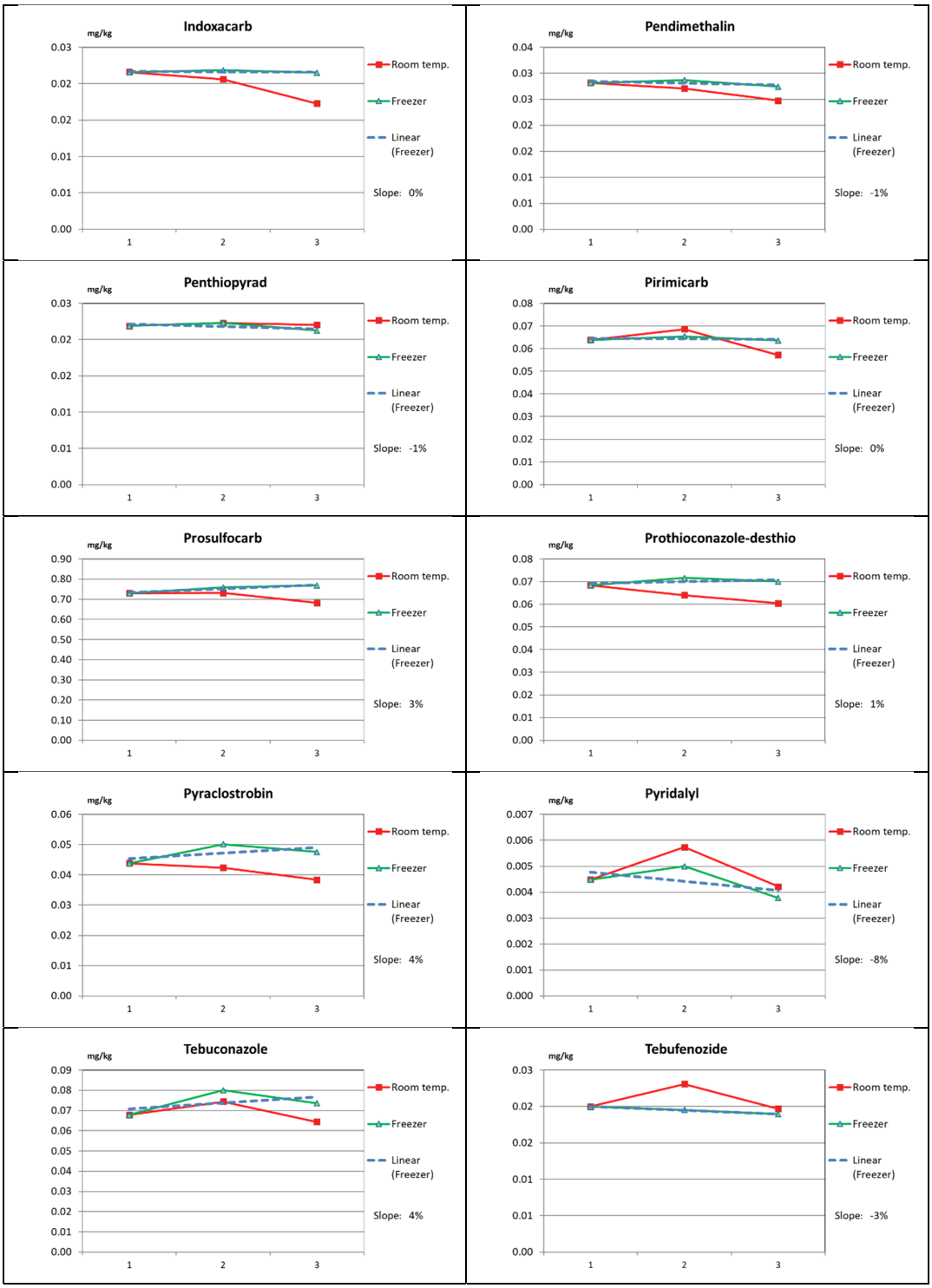
The stability test was performed according to ISO 13528 Annex B [5]. Two different storage temperatures were used; room temperature and -18 °C.

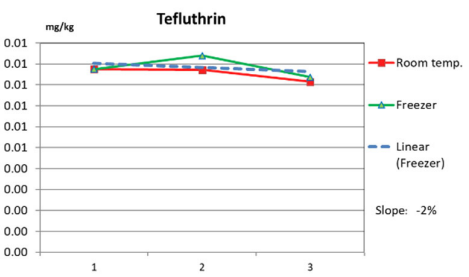
The dates of testing were as follows:

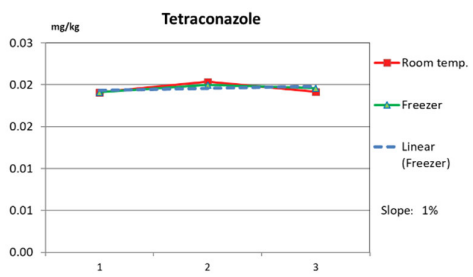
Day 1: 1 March 2021
Day 2: 15 March 2021
Day 3: 29 April 2021

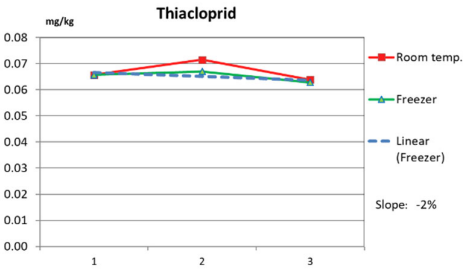
All pesticides passed the test at -18 °C see **1.6 Stability test**. At room temperature indoxacarb and pirimicarb did not pass the test when stored for 11 weeks.



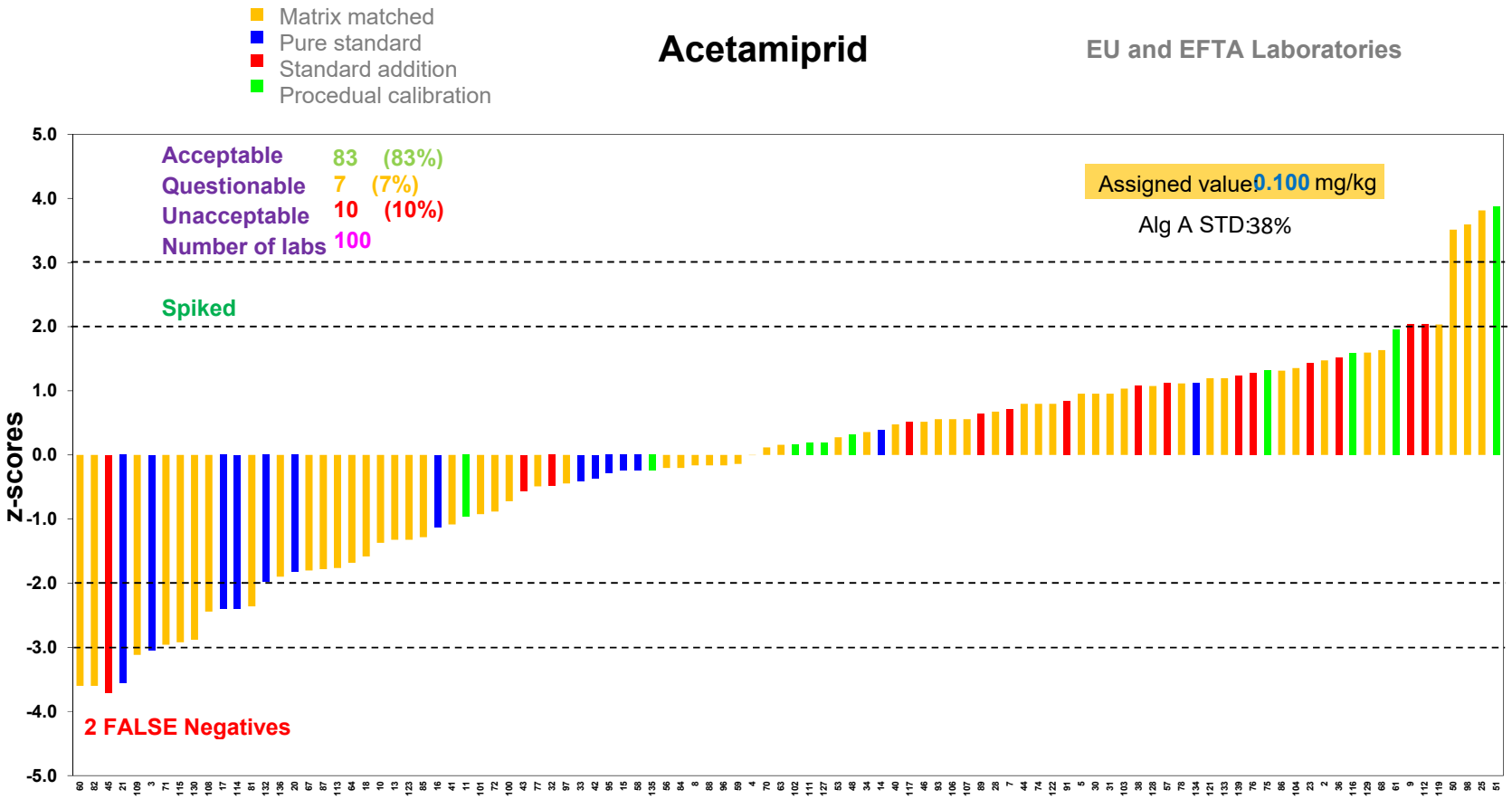

Indoxacarb
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: 0%
Pendimethalin
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: -1%
Penthiopyrad
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: -1%
Pirimicarb
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: 0%
Prosulfocarb
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: 3%
Prothioconazole-desthio
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: 1%
Pyraclostrobin
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: 4%
Pyridalyl
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: -8%
Tebuconazole
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: 4%
Tebufenozide
mg/kg
Room temp.
Freezer
Linear (Freezer)
Slope: -3%

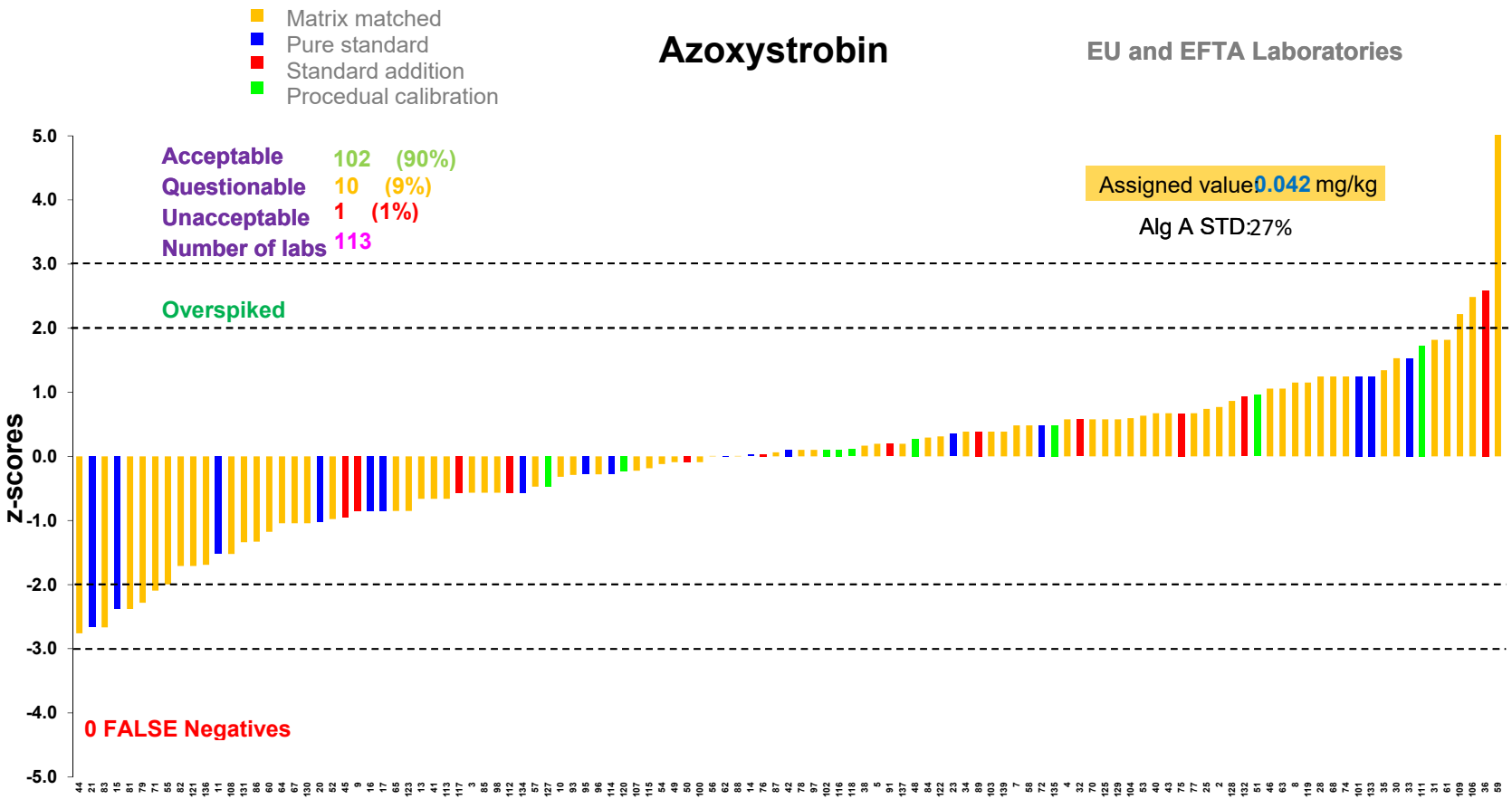

Tefluthrin
mg/kg
0.01
0.01
0.01
0.01
0.01
0.01
0.00
0.00
0.00
0.00
0.00
1
2
3
Room temp.
Freezer
Linear (Freezer)
Slope: -2%

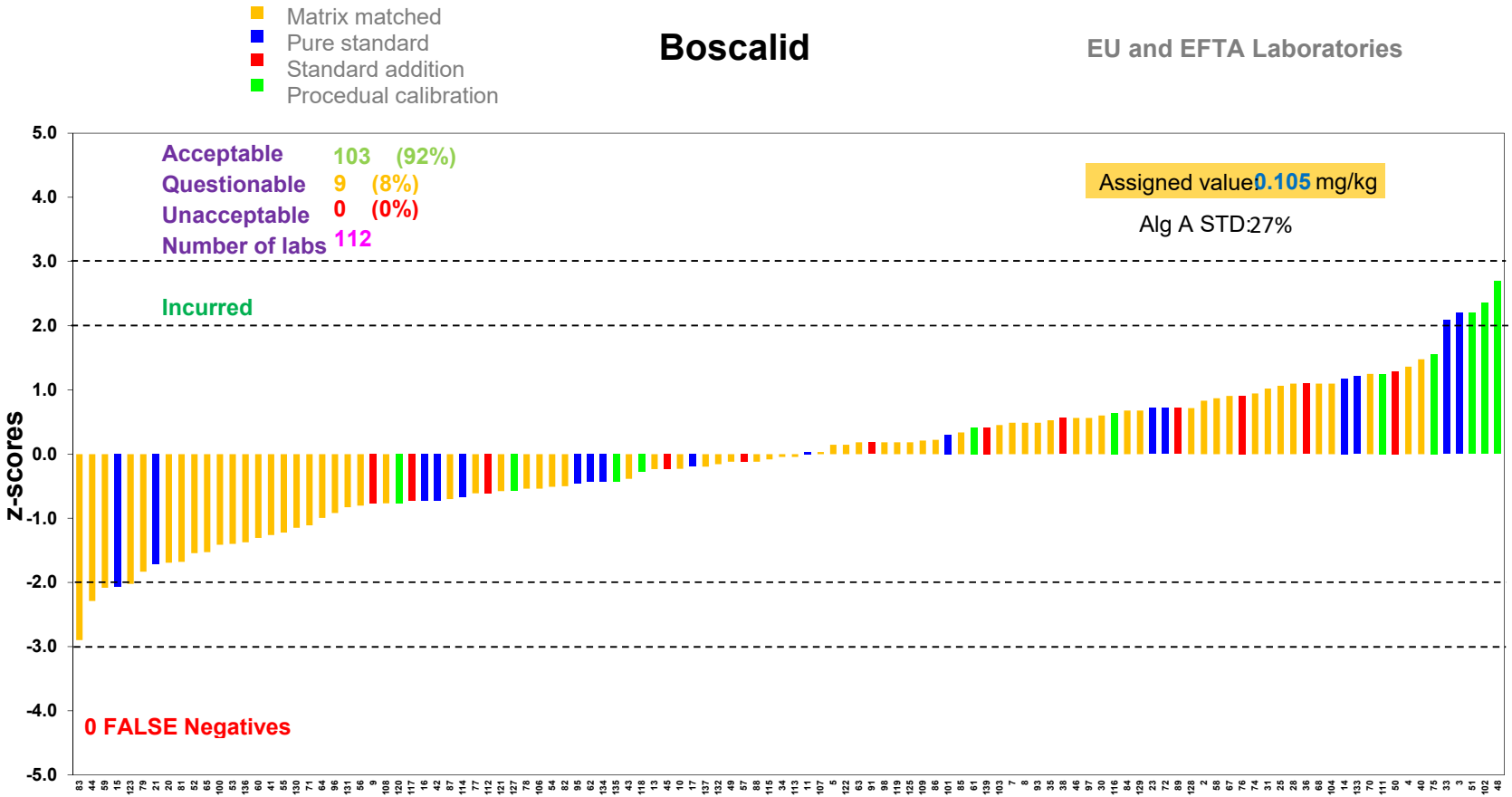

Tetraconazole
mg/kg
0.03
0.02
0.02
0.01
0.01
0.00
1
2
3
Room temp.
Freezer
Linear (Freezer)
Slope: 1%

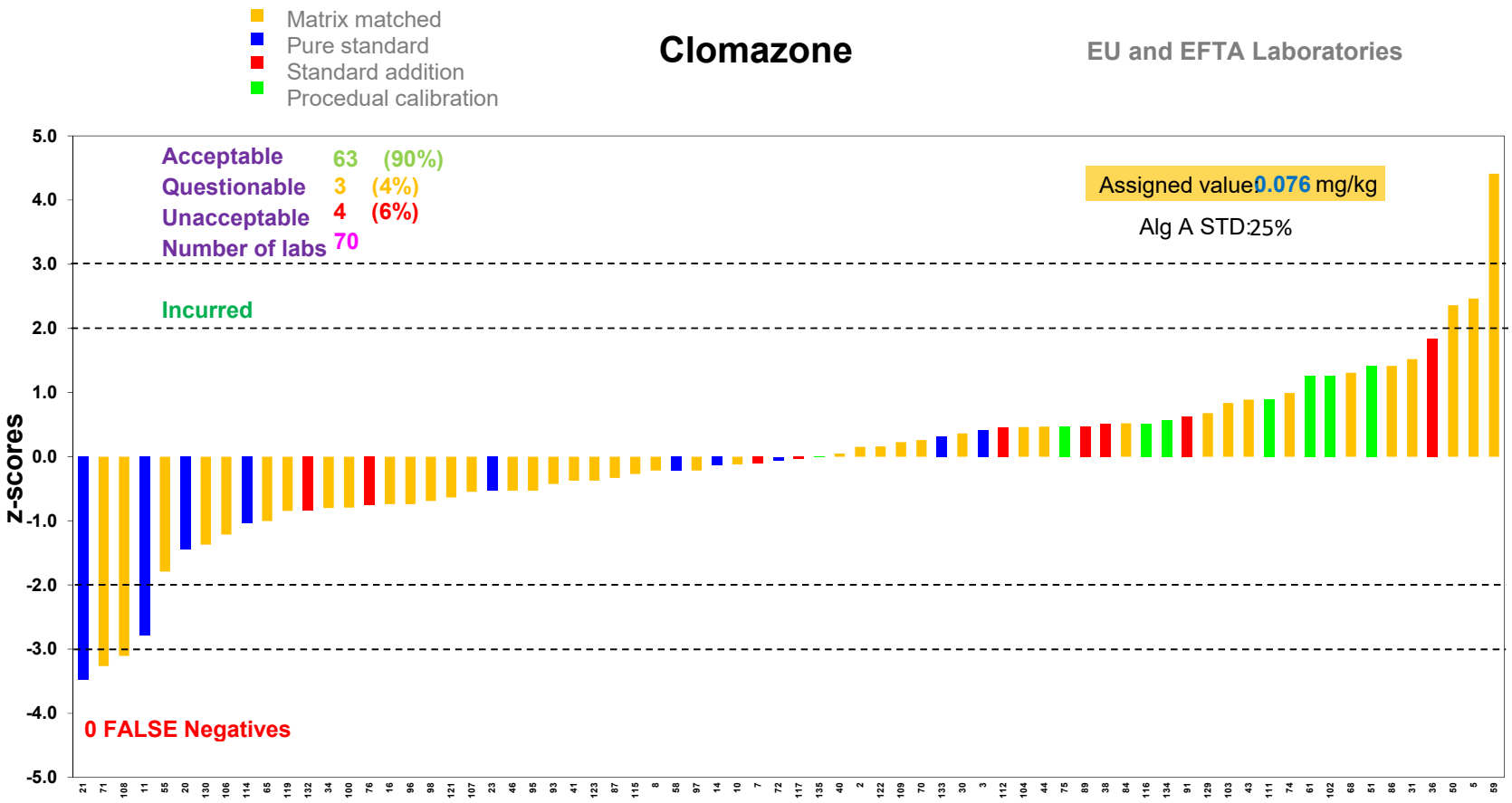

Thiacloprid
mg/kg
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
1
2
3
Room temp.
Freezer
Linear (Freezer)
Slope: -2%

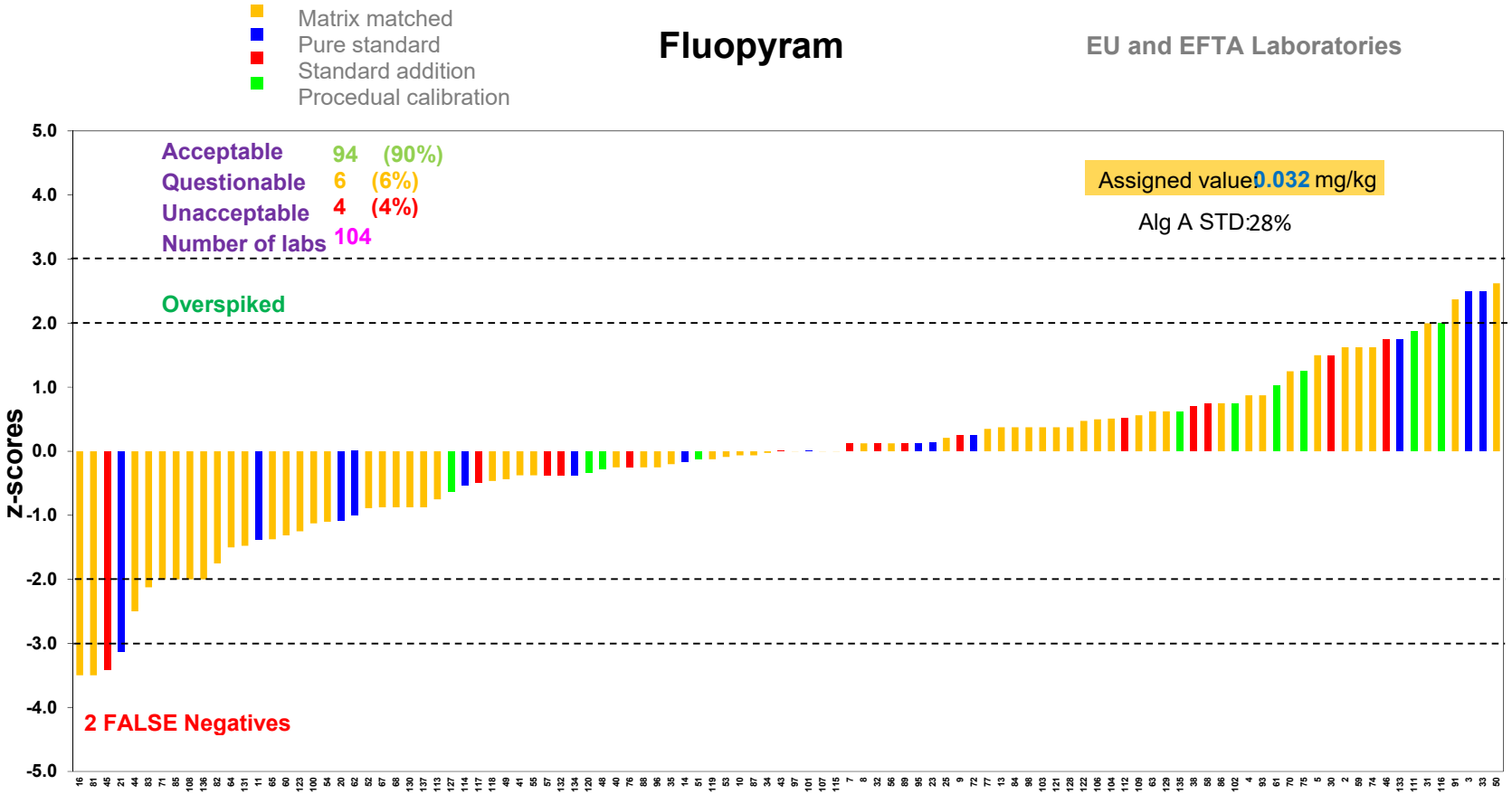
Appendix 5 Graphical presentation of z-scores

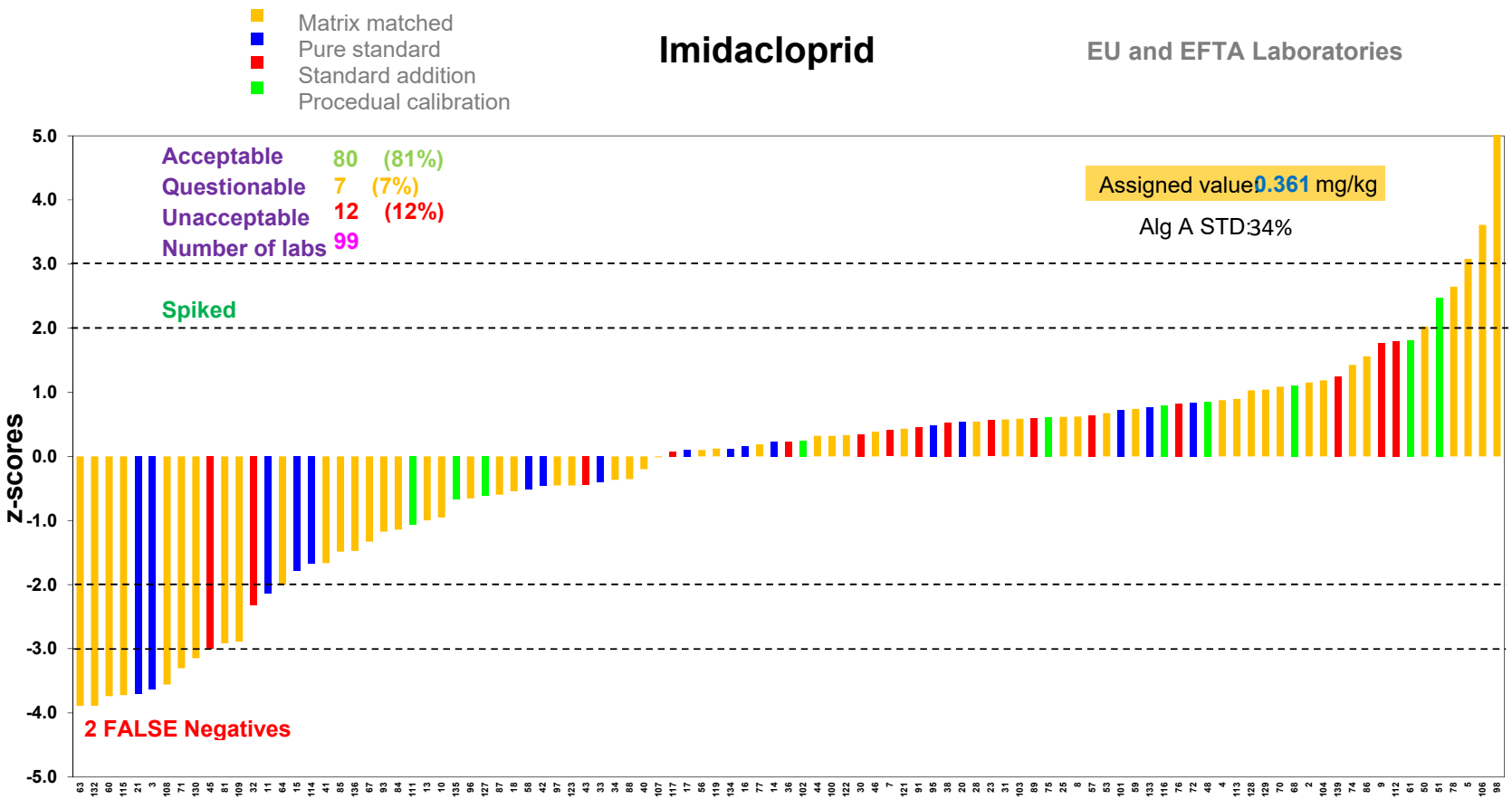


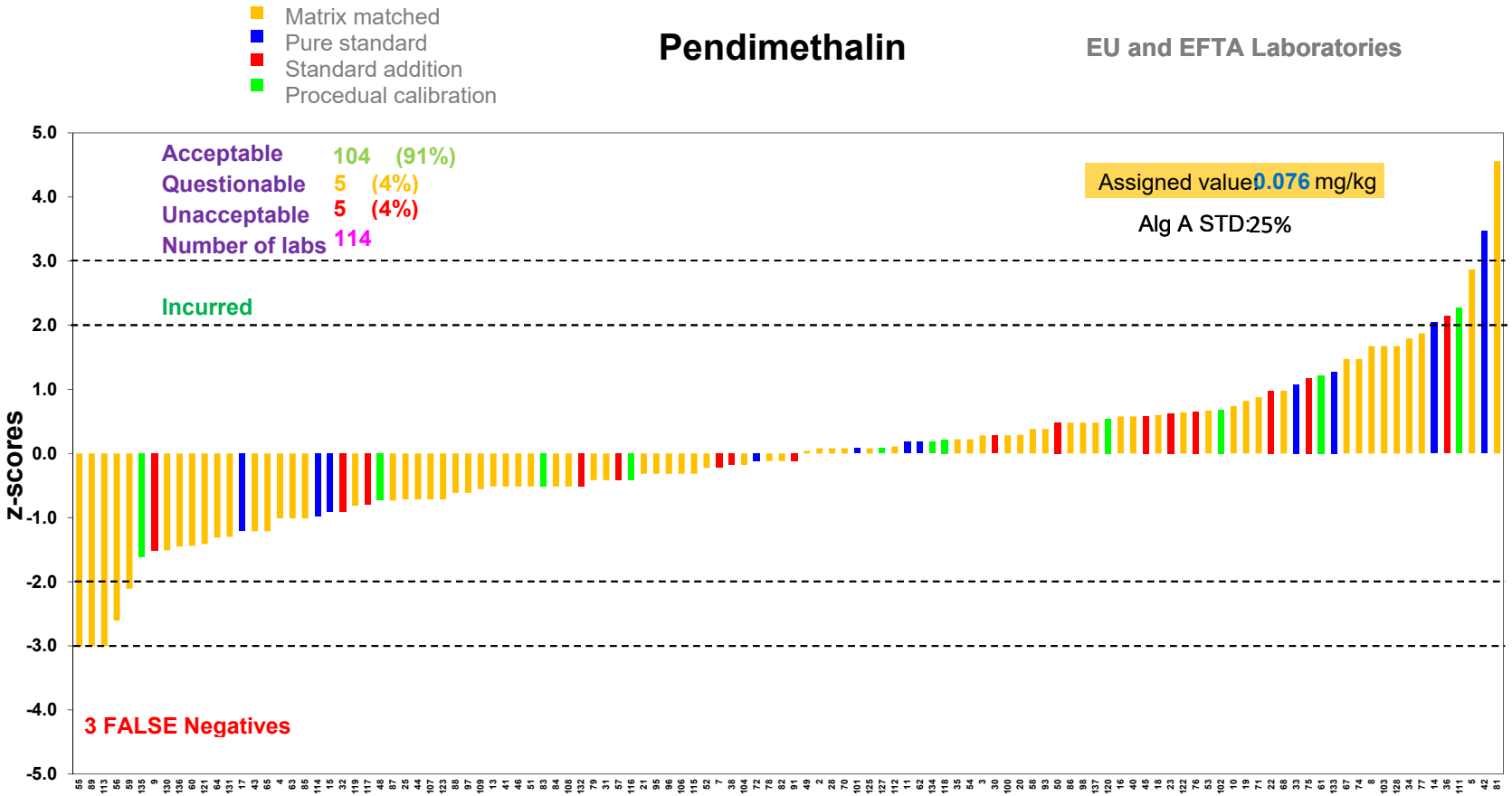

Matrix matched
Pure standard
Standard addition
Procedual calibration
Azoxystrobin
EU and EFTA Laboratories
Acceptable 102 (90%)
Questionable 10 (9%)
Unacceptable 1 (1%)
Number of labs 113
Assigned value 0.042 mg/kg
Alg A STD:27%
Overspiked
0 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0

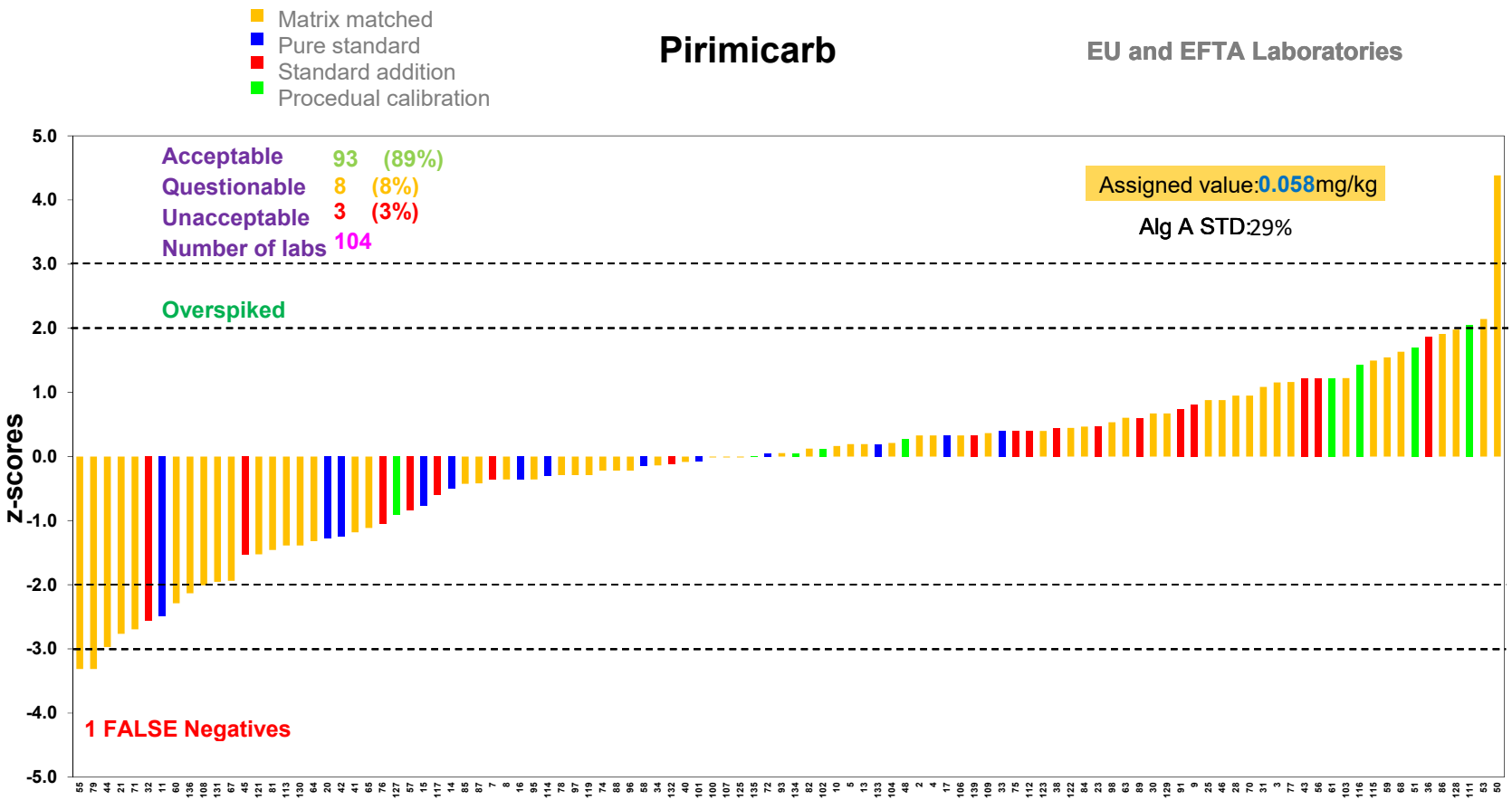

Matrix matched
Pure standard
Standard addition
Procedual calibration
Boscalid
EU and EFTA Laboratories
Acceptable 103 (92%)
Questionable 9 (8%)
Unacceptable 0 (0%)
Number of labs 112
Incurred
Assigned value 0.105 mg/kg
Alg A STD: 27%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0 FALSE Negatives

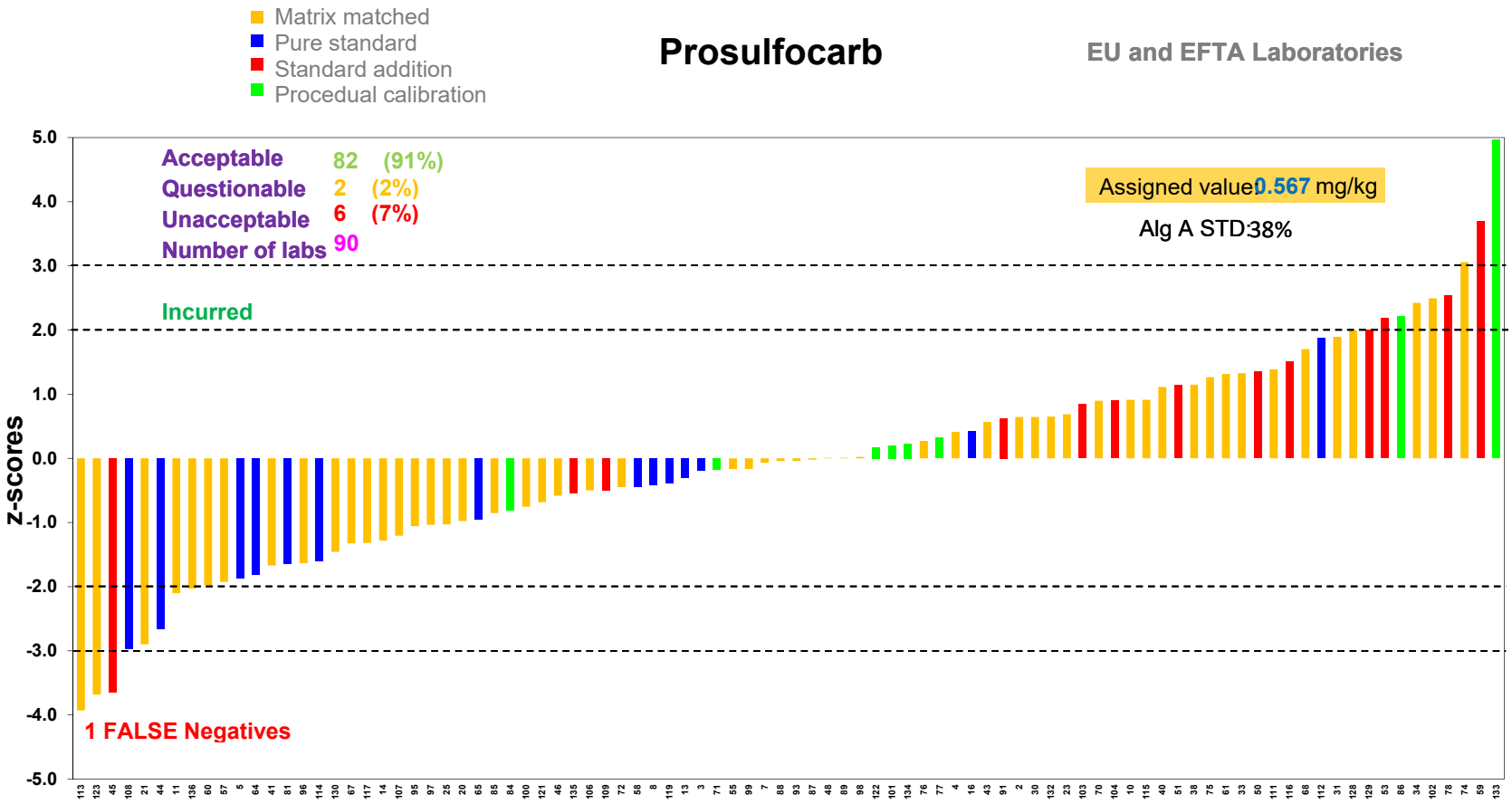

Matrix matched
Pure standard
Standard addition
Procedual calibration
Clomazone
EU and EFTA Laboratories
Acceptable 63 (90%)
Questionable 3 (4%)
Unacceptable 4 (6%)
Number of labs 70
Incurred
Assigned value 0.076 mg/kg
Alg A STD:25%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0 FALSE Negatives
21 71 108 11 55 20 130 106 114 65 119 132 34 100 76 16 96 98 121 107 23 46 95 93 41 123 87 115 8 58 97 14 10 7 72 117 135 40 2 122 109 70 133 30 3 112 104 44 75 89 38 84 116 134 91 129 103 43 111 74 61 102 68 51 86 31 36 50 5 59

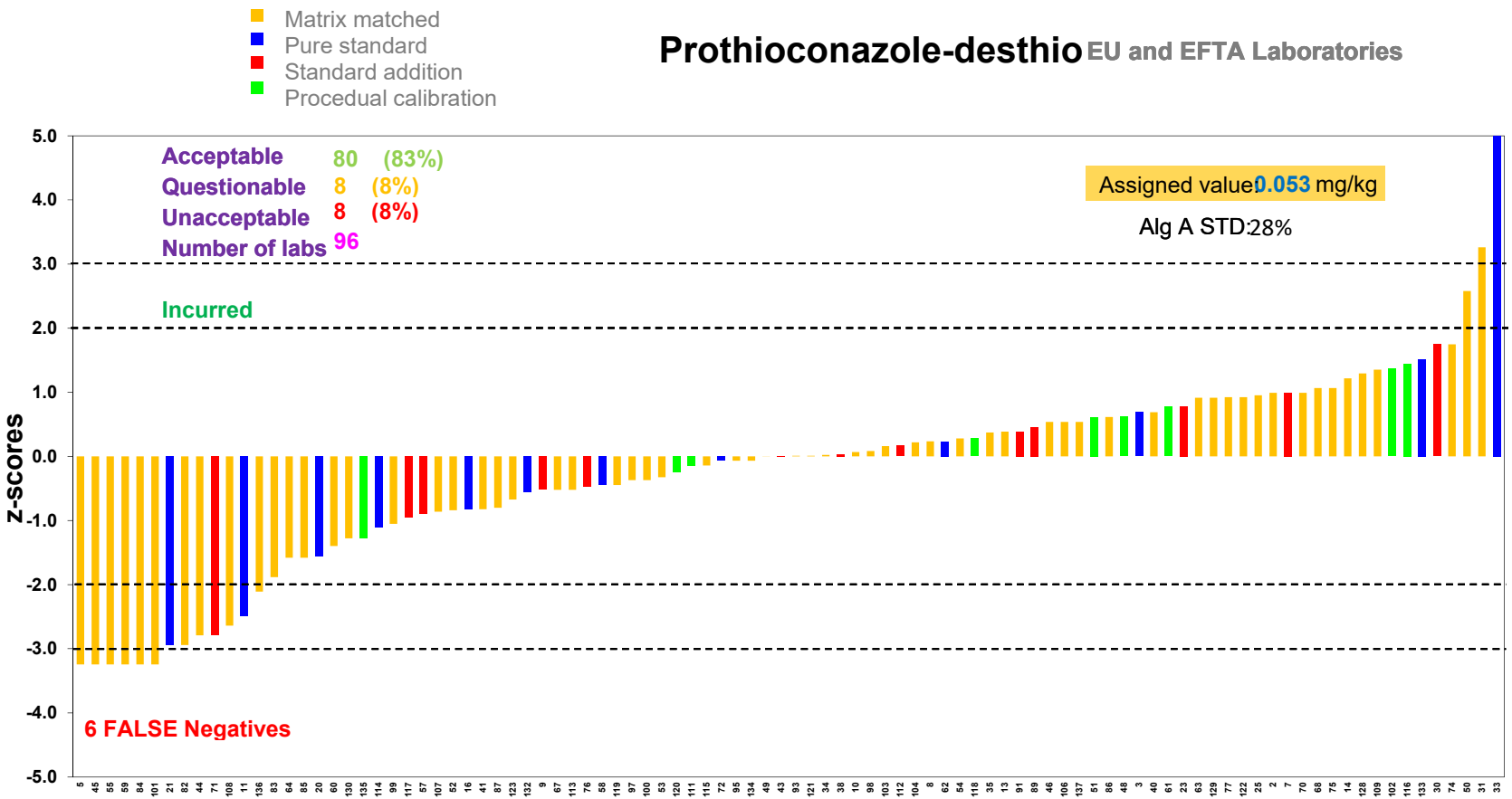

Matrix matched
Pure standard
Standard addition
Procedual calibration
Fluopyram
EU and EFTA Laboratories
Acceptable 94 (90%)
Questionable 6 (6%)
Unacceptable 4 (4%)
Number of labs 104
Assigned value 0.032 mg/kg
Alg A STD: 28%
Overspiked
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 FALSE Negatives

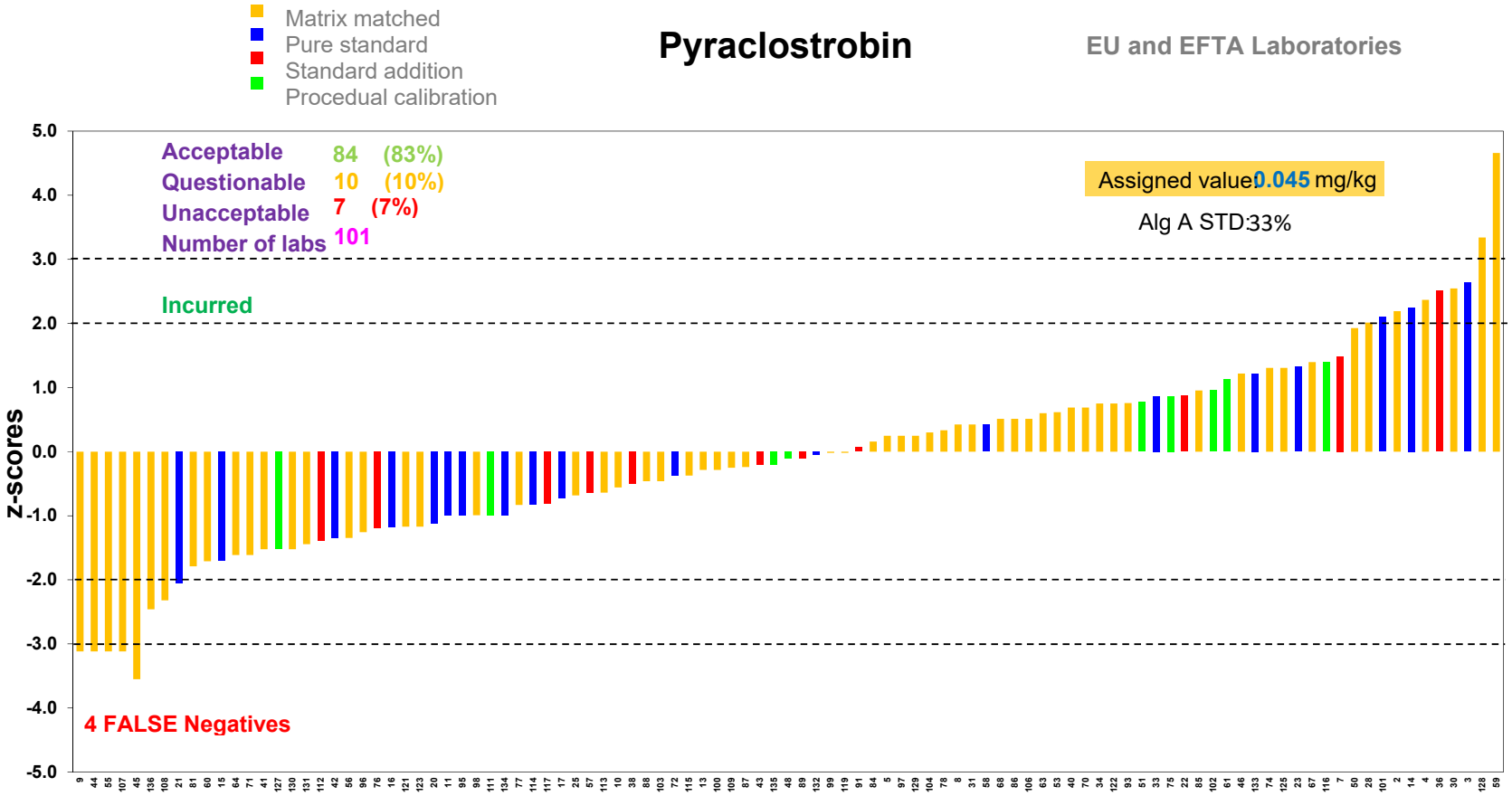

Matrix matched
Pure standard
Standard addition
Procedual calibration
Imidacloprid
EU and EFTA Laboratories
Acceptable 80 (81%)
Questionable 7 (7%)
Unacceptable 12 (12%)
Number of labs 99
Assigned value 0.361 mg/kg
Alg A STD 34%
Spiked
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 FALSE Negatives

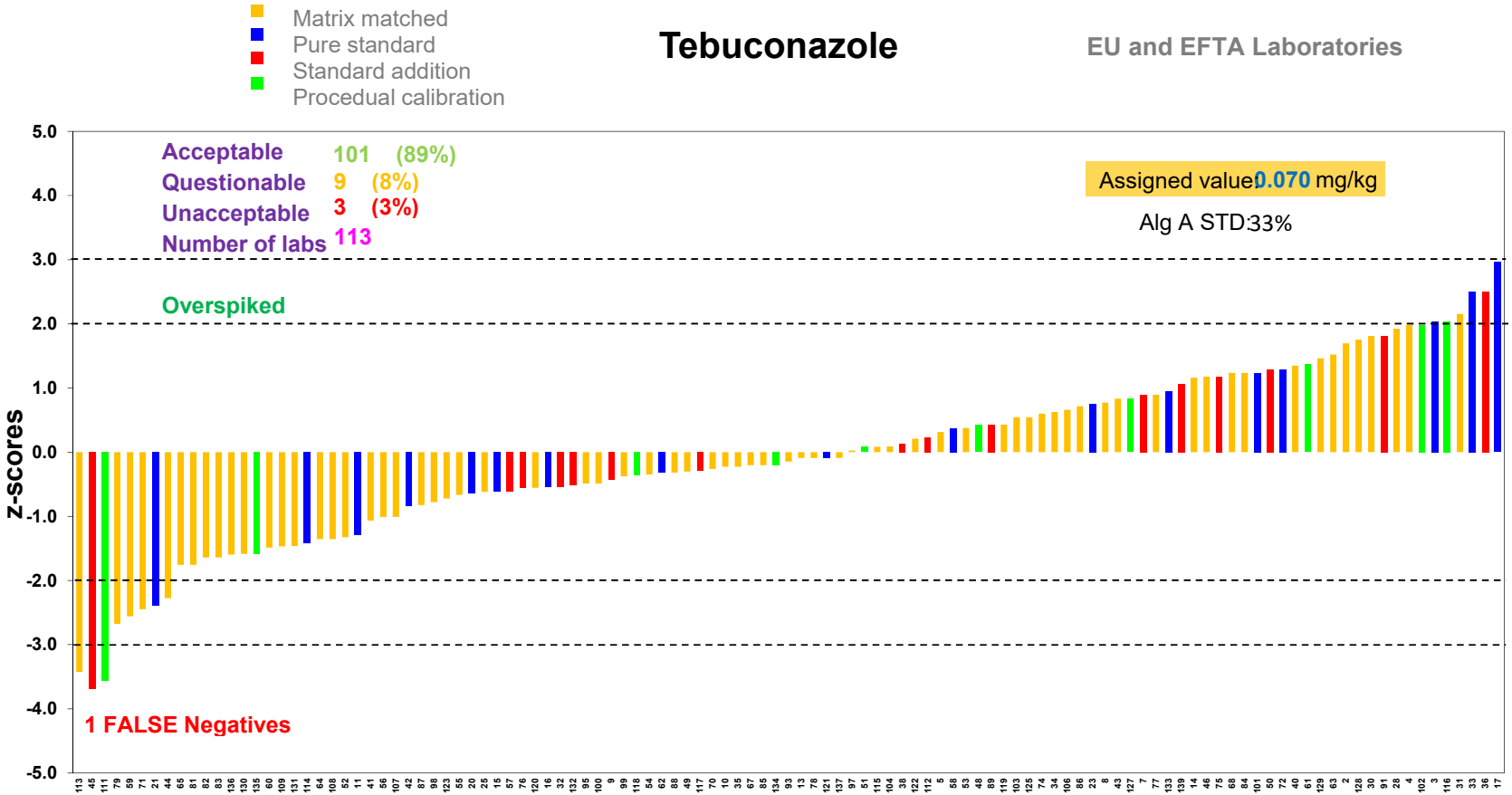

Matrix matched
Pure standard
Standard addition
Procedual calibration
Pendimethalin
EU and EFTA Laboratories
Acceptable 104 (91%)
Questionable 5 (4%)
Unacceptable 5 (4%)
Number of labs 114
Incurred
Assigned value 0.076 mg/kg
Alg A STD 25%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
3 FALSE Negatives

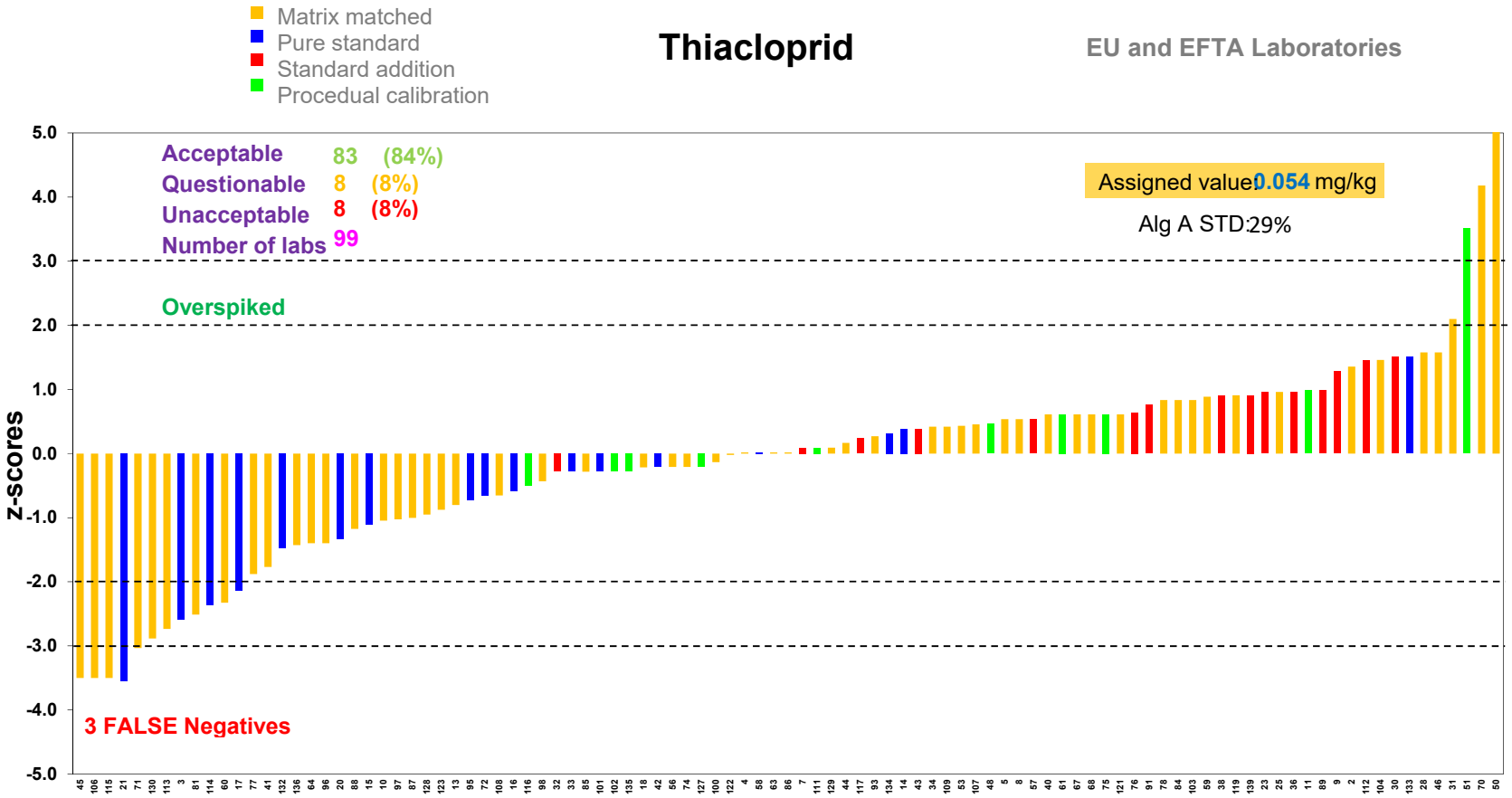

Matrix matched
Pure standard
Standard addition
Procedual calibration
Pirimicarb
EU and EFTA Laboratories
Acceptable 93 (89%)
Questionable 8 (8%)
Unacceptable 3 (3%)
Number of labs 104
Assigned value:0.058mg/kg
Alg A STD:29%
Overspiked
1 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0


Matrix matched
Pure standard
Standard addition
Procedual calibration
Prosulfocarb
EU and EFTA Laboratories
Acceptable 82 (91%)
Questionable 2 (2%)
Unacceptable 6 (7%)
Number of labs 90
Incurred
Assigned value 0.567 mg/kg
Alg A STD 38%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 FALSE Negatives


Matrix matched
Pure standard
Standard addition
Procedual calibration
Prothioconazole-desthio
EU and EFTA Laboratories
Acceptable 80 (83%)
Questionable 8 (8%)
Unacceptable 8 (8%)
Number of labs 96
Assigned value 0.053 mg/kg
Alg A STD:28%
Incurred
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
6 FALSE Negatives


Matrix matched
Pure standard
Standard addition
Procedual calibration
Pyraclostrobin
EU and EFTA Laboratories
Acceptable 84 (83%)
Questionable 10 (10%)
Unacceptable 7 (7%)
Number of labs 101
Incurred
Assigned value 0.045 mg/kg
Alg A STD 33%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
4 FALSE Negatives


Matrix matched
Pure standard
Standard addition
Procedual calibration
Tebuconazole
EU and EFTA Laboratories
Acceptable 101 (89%)
Questionable 9 (8%)
Unacceptable 3 (3%)
Number of labs 113
Assigned value 0.070 mg/kg
Alg A STD 33%
Overspiked
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 FALSE Negatives


Matrix matched
Pure standard
Standard addition
Procedual calibration
Thiacloprid
EU and EFTA Laboratories
Acceptable 83 (84%)
Questionable 8 (8%)
Unacceptable 8 (8%)
Number of labs 99
Overspiked
Assigned value 0.054 mg/kg
Alg A STD: 29%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
3 FALSE Negatives

Appendix 6 Student's t-test

All results from the validated pesticides has been separated in four group depending of the calibration approach using 1) standards in solvent, 2) standards in matrix (different), 3) procedural calibration (different matrix) or 4) standard addition. For each group (two by two) it was determined if the data sets was significantly different (p value ≤ 0.05) by using a two tailed, unequal sample sizes, unequal variances Student's t-test.

Below are listed the Alg A mean and STD, the number of results in the groups and p values.
p values ≤ 0.05 are coloured green

Acetamiprid	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.076	0.099	0.118	0.121
Alg A STD	50%	40%	26%	20%
Number of results	17	55	10	15
p values				
Pure solvent	0.5	0.010	0.002	0.001
Matrix Matched		0.5	0.051	0.066
Procedural			0.5	0.368
Standard Addition				0.5
Azoxystrobin	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.039	0.041	0.047	0.043
Alg A STD	33%	30%	20%	17%
Number of results	17	69	10	16
p values				
Pure solvent	0.5	0.190	0.021	0.084
Matrix Matched		0.5	0.048	0.216
Procedural			0.5	0.181
Standard Addition				0.5
Boscalid	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.108	0.100	0.127	0.112
Alg A STD	30%	28%	30%	18%
Number of results	18	69	11	13
p values				
Pure solvent	0.5	0.129	0.070	0.339
Matrix Matched		0.5	0.010	0.021
Procedural			0.5	0.097
Standard Addition				0.5

Clomazone	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.060	0.075	0.091	0.080
Alg A STD	43%	26%	12%	19%
Number of results	10	42	8	9
p values				
Pure solvent	0.5	0.041	0.001	0.018
Matrix Matched		0.5	0.002	0.225
Procedural			0.5	0.052
Standard Addition				0.5
Fluopyram	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.032	0.031	0.036	0.033
Alg A STD	38%	31%	24%	17%
Number of results	14	61	11	15
p values				
Pure solvent	0.5	0.416	0.142	0.430
Matrix Matched		0.5	0.032	0.295
Procedural			0.5	0.141
Standard Addition				0.5
Imidacloprid	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.319	0.356	0.411	0.402
Alg A STD	38%	39%	28%	18%
Number of results	17	53	10	16
p values				
Pure solvent	0.5	0.106	0.015	0.044
Matrix Matched		0.5	0.095	0.252
Procedural			0.5	0.254
Standard Addition				0.5
Pendimethalin	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.044	0.039	0.042	0.041
Alg A STD	32%	25%	24%	20%
Number of results	11	71	11	17
p values				
Pure solvent	0.5	0.154	0.296	0.254
Matrix Matched		0.5	0.295	0.274
Procedural			0.5	0.465
Standard Addition				0.5

Pirimicarb	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.052	0.058	0.068	0.060
Alg A STD	20%	33%	24%	25%
Number of results	13	62	9	18
p values				
Pure solvent	0.5	0.080	0.006	0.055
Matrix Matched		0.5	0.036	0.317
Procedural			0.5	0.090
Standard Addition				0.5
Prosulfocarb	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.514	0.566	0.705	0.537
Alg A STD	38%	40%	21%	41%
Number of results	15	54	9	10
p values				
Pure solvent	0.5	0.364	0.025	0.422
Matrix Matched		0.5	0.009	0.286
Procedural			0.5	0.022
Standard Addition				0.5
Prothioconazole-desthio	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.049	0.053	0.060	0.053
Alg A STD	43%	28%	18%	23%
Number of results	14	52	10	13
p values				
Pure solvent	0.5	0.206	0.253	0.204
Matrix Matched		0.5	0.065	0.463
Procedural			0.5	0.102
Standard Addition				0.5
Pyraclostrobin	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.044	0.046	0.048	0.042
Alg A STD	40%	32%	26%	35%
Number of results	19	56	9	12
p values				
Pure solvent	0.5	0.270	0.241	0.355
Matrix Matched		0.5	0.396	0.187
Procedural			0.5	0.170
Standard Addition				0.5

Tebuconazole	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.075	0.067	0.073	0.075
Alg A STD	37%	33%	36%	26%
Number of results	17	67	11	16
p values				
Pure solvent	0.5	0.119	0.335	0.401
Matrix Matched		0.5	0.347	0.188
Procedural			0.5	0.412
Standard Addition				0.5

Thiacloprid	Pure solvent	Matrix Matched	Procedural	Standard Addition
Alg A mean	0.042	0.053	0.058	0.064
Alg A STD	40%	31%	36%	11%
Number of results	17	53	10	15
p values				
Pure solvent	0.5	0.011	0.004	0.000
Matrix Matched		0.5	0.137	0.002
Procedural			0.5	0.264
Standard Addition				0.5

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

The following four EURLs for pesticide residues were appointed by DG-SANTE based on regulation 882/2004/EC that was repealed by regulation 625/2017/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-SANTE = European Commission, Health and Food Safety Directorate-General

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

[3] Regulation (EU) 2017/625 of the European Parliament and of the Council on official controls and other official activities performed to ensure the application of food and feed law, rules on animal health and welfare, plant health and plant protection products.. Published at OJ of the EU L95 of 07.04.2017

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

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 collaboration.

An **Organising Team** (in the following named Organisers) 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, the production of the PT-material (Test Item), the undertaking of homogeneity and stability tests, the packing and shipment of the PT-materials, the handling and evaluation of the results and method information submitted by the participants, the drafting of the preliminary and final reports as well as generation and distribution of EUPT-participation certificates.

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

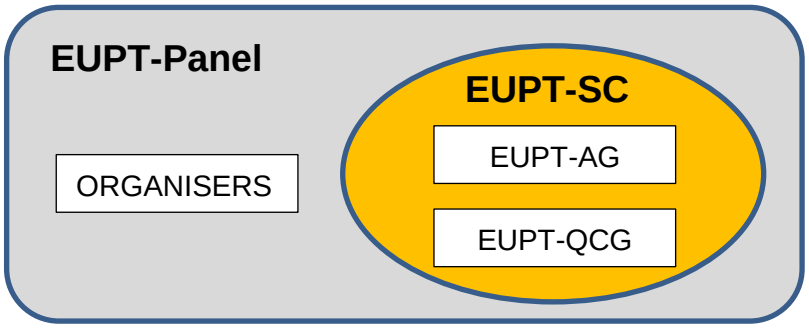
The EUPT-SC's role is to help the Organisers make decisions regarding the EUPT design: the selection of the commodity, the selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the statistical treatment and evaluation of the 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.

[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-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 approximate concentrations at which they should be present.

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 assist 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.

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 38 (b) of Reg. 625/2017/EC and 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. 101 (1)(a) of Reg. 625/2017/EC (for all NRLs)

[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. 625/2017/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.

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

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

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 This also applies to any participating laboratories that fail to report results.

OfLs not paying the EUPT sample delivery fee will be initially warned that their participation in subsequent EUPTs could be denied. In case of a repetitive non-payment, the EUPT organisers will inform the corresponding NRL to take action.

Confidentiality and Communication

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

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

As laid down in Regulation 625/2017/EC, 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 PT-relevant documents in their latest version are linked. In case of important modifications on any of these documents, the participating laboratories will be informed via e-mail. In any case, as soon as the PT-period starts the participants are encouraged to visit the particular EUPT-Website, to make sure that they are using the latest versions of all PT-relevant documents.

The official language used in all EUPTs is English.

Announcement / Invitation Letter

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

Target Pesticide List

This list contains all analytes (pesticides and metabolites) to be sought for, 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 usually 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 ISO 13528, Annex B or to the International Harmonized Protocols jointly published by ISO, AOAC and IUPAC. 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-Panel, considering all relevant aspects (e.g. the homogeneity results of other pesticides spiked at the same time, the overall distribution of the participants' results (CV*), 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. For certain analytes with comparable properties, an equivalent distribution within the sample can be expected if they were spiked/used at simultaneously. The homogeneity test, of one or more of these analytes, may thus be skipped or simplified. If, however, the distribution of participants' results for an analyte that was not or not fully tested for homogeneity, is found to be atypically broad, compared to the tested analytes, the EUPT-SC may decide that a homogeneity test should be performed a posteriori by the EURL.

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-Panel will finally decide whether

analytes for which the stability test was not undertaken will be included in the Final EUPT-Report, considering all relevant aspects such as the distribution of the participant's results (CV*).

A pesticide is considered to be adequately stable if $|y_i - y| \leq 0.3 \times \sigma_{pt}$, with y_i being the mean value of the results of the last phase of the stability test, y being the mean value of the results of the first phase of the stability test and σ_{pt} being 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 measurement variability, analytical difficulties faced during the test and 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.

Stability during shipment: Considering knowledge about the expected susceptibility of pesticides in the Test Item to possible losses, the Organisers will choose 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 keep track of the shipment duration and then decide whether it is reasonable to 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 by the EUPT-Panel considering all relevant aspects including the duration and conditions of the shipment to the laboratory as well as the feedback by the 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. Laboratories should not report results below their reporting limits.

Correction of results for recovery

Correction of results for recovery is recommended if the average recovery rate significantly deviates from 100 % (typically if outside the 80–120% range). Approaches for recovery correction explicitly stated in the DG-SANTE document are

a) the use of recovery correction factors,
b) the use of stable isotope labelled analogues of the target analytes as Internal Standards (ILISs),
c) the 'procedural calibration' approach as well as
d) the approach of 'standard addition' with additions of analyte(s) being made to analytical portions.

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 rate (in percentage) must also be reported. If one or more of the approaches b), c) and d) were employed, in which correction for recovery is inherent to the procedures, the apparent recovery figures obtained during validation experiments are not mandatory, and the approached followed are to be reported in the appropriate fields within the data submission tool.

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 EUPT-Report or in a separate report. Where necessary the methods are evaluated and discussed, especially in those cases where the result distribution is not unimodal or very broad (e.g. CV* > 35 %). If no sufficient information on the methodology used is provided, the Organisers reserve the right not to accept the analytical results reported by the participants concerned or even refuse participation in the following PT.

Results evaluation

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

- ***False Positive results***

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

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

- ***False Negative results***

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

In cases of the assigned value being less than a factor of 3 times the MRRL, false negatives will typically not be assigned. The EUPT-Panel may decide to take case-by-case decisions in this respect after considering all relevant factors such as the result distribution and the reporting limits of the affected labs.

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

In order to minimise the influence of out-lying results on the statistical evaluation, the assigned value x_{pt} (= consensus concentration) will typically be estimated using the robust estimate of the

participant's mean (x^*) as described in ISO 13528:2015[8], taking into account the results reported by EU and EFTA countries laboratories only. 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 or similar compounds 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), inappropriate storage or transport conditions (in case of susceptible compounds), and the use of inappropriate analytical steps or procedures that demonstrably lead to significantly biased results (e.g. employing inappropriate internal standards or analytical steps or conditions leading to considerable losses, due to degradations, adsorptions, incomplete extractions, partitioning etc.). Where the Organisers (e.g. after the publication of the preliminary report) receive information of such gross errors, having a significant impact on a generated result, the affected results will be examined on a case-by-case basis to decide whether, or not, they should be excluded from the population used for robust statistics. Results may also be omitted e.g. if an inappropriate method has been used even if they are not outliers. All decisions to omit/exclude results will be discussed with the EUPT-SC and the reasoning for the omission of each result clearly stated in the Final EUPT-Report. However, z scores will be calculated for all results irrespective of the fact that they were omitted from the calculation of the assigned value.

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

Results reported by laboratories from non EU member states are typically excluded from the population that is used to derive the assigned value (see also "Estimation of the assigned value").

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

- ***Uncertainty of the assigned value***

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

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

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

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

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

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

Based on experience from previous EUPTs9, a percentage FFP-RSD of 25 % is currently used for all analyte-matrix combination, with the target standard deviation being calculated as follows:

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

The EUPT-Panel reserves the right to also employ other FFP-RSDs or other approaches for setting the assigned value on a case-by-case basis, considering analytical difficulties and experience gained from previous proficiency tests.

For informative purposes the robust relative standard deviation (CV*) of the participants results is calculated according to ISO 13528:2015; Chapter 7.7 following Algorithm A in Annex C (so called "consensus approach").

[9] 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.

- ***z scores***

This parameter is calculated using the following formula:

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

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

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

Z scores will be interpreted in the following way, as is set in the ISO 17043:2010[10]:

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

For results considered as false negatives, z scores will be calculated using the MRRL or RL (the laboratory's Reporting Limit) if RL < MRRL. Where, using this approach, the calculated z scores for false negatives are > −3 (still questionable), they will be fixed at −3.5 to underline that these are unacceptable results. These z-scores will typically appear in the z-score histograms and used in the calculation of combined z-scores.

- **Collection of measurement uncertainty (MU) figures**

The participating labs will be asked to report the MU figure they would routinely report with each EUPT result. The EUPT-Panel will decide whether and how to evaluate these figures and whether indications will be made to the laboratories in this respect.

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

- ***Category classification***

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

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

No. of compulsory pesticides present in the Test Item / Target Pesticides List (N)	90 %	No. of pesticides needed to be correctly detected and quantified / targeted to have sufficient scope (n)	n
3	2.7	3	N
4	3.6	4	
5	4.5	4	N - 1
6	5.4	5	
7	6.3	6	
8	7.2	7	
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	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	

The EUPT-Panel reserves the right to develop and apply alternative classification rules.

- ***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)[11,12] (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 set as 5. Based on the AZ^2 achieved, the laboratories are classified as follows:

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

Combined z scores are considered to be of lesser importance than 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 set as 5. The z-scores appointed to false negatives will be also included in the calculation of the combined z-scores.

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

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

[12] 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.

Publication of results

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

The Final EUPT-Report will be published after the EUPT-Panel has discussed the results. Taking into account that the EUPT-Panel meets normally only once a year (typically in late summer or autumn) to discuss the results of all EUPTs organised by the EURLs earlier in the year, the Final EUPT-Report may be published up to 10 months after the deadline for results submission. Results submitted by non-EU/EFTA laboratories might not always be used in the tables or figures in the Final EUPT-Report.

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 Categories.

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 like. The online version of the Final EUPT report will be replaced by the new one and all affected labs will be contacted.

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

Follow-up activities

Laboratories are expected to undertake follow-up activities to trace back the sources of erroneous or strongly deviating results (typically those with $|z| > 2.0$) - including all false positives. In exceptional cases, follow-up activities may even be indicated for results within $|z| \leq 2.0$ (e.g. where two errors with opposed tendency cancel each other leading to acceptable results).

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

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

NRLs will be considered as **underperforming in relation to scope** if in at least two of the last four EUPTs falling within their responsibility area they: a) haven't participated, or b) targeted less than 90% of the compulsory pesticides in the target lists (80% for SRM-compounds), or c) detected less than 90% of the compulsory compounds present in the test items (80% for SRM-compounds). Additionally, NRLs that obtained AZ^2 higher than 3 (AAZ higher than 1.3 for SRM-compounds) in two consecutive EUPTs of the last four EUPTs, will be considered as **underperforming in accuracy**. A two-step protocol established by DG-SANTE will be applied as soon as underperformance of an NRL is detected[13]:

Phase 1:

- Identifying the origin of the bad results (failure in EUPTs).

[13] Article 101 of Regulation (EC) 625/2017

- Actions: On the spot visits and training if necessary and repetition of the comparative test if feasible and close the assessment of results by the EURL.

Phase 2:

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

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

Disclaimer

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

SPECIFIC PROTOCOL

for the EU Proficiency Test for Pesticide Residues in Cereals/Feeding stuff using Multi Residue Methods, EUPT-CF15 (2021)

(last updated: 23 March 2021)

Introduction

This protocol is complementary to the General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed (9th Edition). The current proficiency test covers pesticides that are determined by Multi Residue Methods. This EUPT is to be performed by all National Reference Laboratories for Cereals and/or Feeding stuffs (NRL-CFs) as well as by all official EU laboratories (OfLs) responsible for official pesticide residue controls on feeding stuff, as far as their scope overlaps with that of the EUPT-CF15.

Test Item (Test Material)

This proficiency test concerns the analysis of pesticide residues in rapeseed cake with up to 20% fat. The rapeseed was grown in Denmark and pesticides were applied in the field.

The Organiser, will check the Test Items for sufficient homogeneity and for stability at conditions reproducing sample shipment and storage during the duration of the test, according to ISO 13528, Annex B. All these tests will be conducted by the organiser, the EURL-CF which is (ISO 17025 accredited).

Analytical Parameters

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

Laboratories must report their results as stated in the Target Pesticides List.

Amount of Test Item

The participants will receive:

- approximately 100 g of rapeseed cake Test Item with incurred and spiked pesticides

Blank material will not be distributed to the participants.

Shipment of Test Items

The Test Items are planned to be shipped on 1 March 2021.

Test Items will be shipped frozen and packed in thermo-boxes together with a freezer block. The organiser 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 below) before analysis to avoid any possible deterioration/spoilage and to minimize pesticide losses. The test Item should be milled before analysis. After milling, mix the flour thoroughly, before taking the analytical portion(s).

All participants should use their own routine standard operating procedures for milling, extraction, clean-up and analytical measurement and their own reference standards for identification and quantification purposes.

The homogeneity test is conducted using 2 g of milled 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 to or larger than the ones stated above.

EUPT Webtool and Deadlines

To select pesticide scope and report results and method information, the participants should log in to the **EUPT Webtool** using the username and password send by email. Please, save the credentials, as it will be valid for the EUPTs next year.

Selection/deselection of scope: The analytical scope must be selected prior to the shipment of the samples. This is done via the **EUPT Webtool**. The scope selection subpage will be open from 16 March to 1 March 2021. As default all pesticides are preselected.

Results and method submission: The **EUPT Webtool** will be accessible from 05 April 2021 for sample receipt acknowledgement and submission results and method information.

The deadline for submission is 19 April 2021 at 23.00 CET.

IMPORTANT: After the final submission it will NOT be possible to edit the results. Participants will receive an email confirming the submission of their results. Attached to the email will be an excel file with their submitted data.

Test Item Receipt and Acceptance: Once the laboratory has received the Test Items it must report to the organiser, via the **EUPT Webtool**, the date of receipt, and its acceptance. If the laboratory does not respond by 5 March 2021 at 12.00 CET, the Organiser will assume that the Test Items have been received and accepted.

If participants have not received the Test Items by **the 5 March 2021 at noon**, they must inform the Organiser immediately by e-mail to eurl-cf@food.dtu.dk.

Reporting Quantitative Results:

Results should not be reported where a pesticide

a) was not detected,
b) was detected below the RL (Reporting Limit) of the laboratory, or

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.

Reporting Analytical method: The laboratory must to report details of the analytical methods they used. If not it will not be possible to submit results.

Reporting of supplementary information in case of false negative results

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 has also to be done by accessing EUPT Webtool. Deadline for this is 7 April 2021.

Follow-up actions

In accordance with Art. 32 1b of Regulation (EC) No 2017/625, underperformance of any NRL-CF in comparative testing will be followed by EURL-CF.

Documents

All documents related to EUPT-CF15 can be found on EUPT-CF15 website.

https://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?LabID=400&CntID=1163&Theme_ID=1&Pdf=False&Lang=EN

Calendar

Activity	Dates
Announcement Calendar Target Pesticide List	December 2020
EUPT-Registration Website open	December 2020
Deadline for registration	8 February 2021
Specific Protocol published	22 February 2021
Website for selecting pesticide scope open	16 February 2021
Website for selecting pesticide scope closed	1 March 2021
Distribution of Test items	1 March 2021
Deadline for receipt and acceptance of Test Materials	within 24 hr on receipt
Deadline for Result Submission	19 April 2021 at 23.00 CET
Deadline for submission of additional method information for false negative results	14 April 2021 at 24.00 CET
Preliminary Report (only compilation of results) published	11 June 2021
Final Report published	December 2021

Participation Fees

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

- 200 €

The participation fees for laboratories from third countries will be:

- 350 €

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

Delays in Payment

The participants will receive an invoice from DTU. 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.

If the participant ask DTU to issue a new invoice because additional/new information are needed on the invoice, or just want a copy of the original invoice, that may add additional cost due to the administrative workload.

Any questions concerning invoices must be directed to Tom Schmidt Christensen, tomsc@adm.dtu.dk at the financial department of DTU.

Contact information:

DTU Food
National Food Institute

DANAK
PT Reg.nr. 516

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