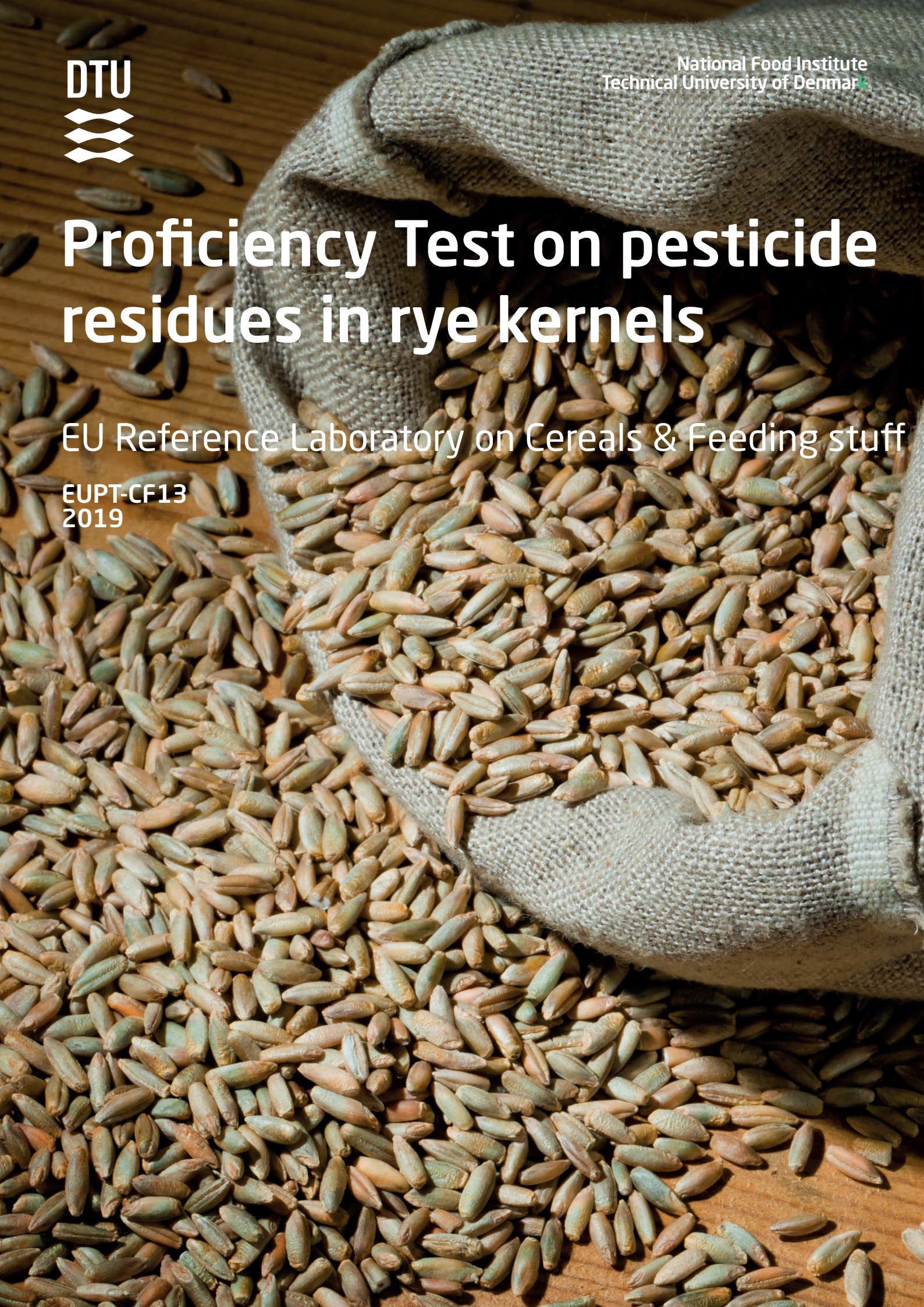
National Food Institute
Technical University of Denmark

Proficiency Test on pesticide residues in rye kernels

EU Reference Laboratory on Cereals & Feeding stuff

EUPT-CF13
2019



EU PROFICIENCY TESTS
EUPT-CF13, 2019

Pesticide Residues in Rye Kernels

Final Report

Version 1

Mette Erecius Poulsen
Susan Strange Herrmann
Elena Hakme

November 2019

Organiser:

DTU Food
National Food Institute

DTU

DANAK
PT Reg.nr. 516

Mette Erecius Poulsen
Director of EURL Cereals and Feedingstuff
National Food Institute
Research Group for Analytical Food Chemistry
Technical University of Denmark
Kemitorvet 1
DK-28 Lyngby
Phone: +45 3588 7463
Fax: +45 3588 7448
E-Mail: eurl-cf@food.dtu.dk
http://www.eurl-pesticides.eu

Organising Team at EURL for Pesticide Residues in Cereals and Feedingstuff:

Susan Strange Herrmann

Elena Hakme

Merete B. Ludwigsen

Lisbet Pilhkjær

Ban M. Kadhum

Quality Control Group:

Antonio Valverde	University of Almería, Spain
Paula Medina-Pastor	European Food Safety Authority (EFSA), Italy

Advisory Group

Amadeo R. Fernández-Alba	University of Almeria, Spain
André de Kok	WFSR - Wageningen Food Safety Research, Wageningen, The Netherlands
Finbarr O'Regan	Pesticide Control Laboratory, Co. Kildare, Ireland
Magnus Jezussek	Bavarian Authority of Health and Food Safety, Erlangen, Germany
Michelangelo Anastassiades	Chemisches und Veterinäruntersuchungsamt (CVUA) Stuttgart, Germany
Miguel Gamón	Pesticide Residue Laboratory of the Generalitat Valenciana, Valencia, Spain
Patrizia Pelosi	Istituto Superiore di Sanità, Roma, Italy
Ralf Lippold	Chemisches und Veterinäruntersuchungsamt (CVUA) Freiburg, Germany
Sonja Masselter	AGES, Institute for Food Safety, Innsbruck, Austria
Tuija Pihlström	National Food Agency, Uppsala, Sweden

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 thirteen 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 and EUPT-CF12 on hay flour. The PTs in 2007, 2009 and 2011 were jointly organised by the EURL-CF and EURL-SRM using and focusing on both MRM and SRM pesticides, whereas the present EUPT-CF13 on rye was only focused on MRM-pesticides. The rye Test Item used for EUPT-CF13 was treated with formulations in the field and post-harvest in the laboratory.

Participation in EUPT-CF13 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.

CONTENTS

EUROPEAN COMMISSION EURL PROFICIENCY TEST ON PESTICIDE RESIDUES IN CEREALS EUPT-CF13, 2019

1. INTRODUCTION

On 29 October 2018 the announcement of the 13th European Commission's Proficiency Test on cereals and feed (EUPT-CF13) 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 160 individual compulsory compounds and 32 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-CF13, were provided via the homepage. Laboratories were able to register on-line from 28 November to 10 January 2019. In total 152 laboratories from EU and EFTA countries agreed to participate in the test as well as 6 laboratories from EU-Candidate States and Third Countries (**Appendix 1**).

The present proficiency test was performed using rye kernels of Danish origin, which had been partly treated in the field, and partly spiked post-harvest at the facilities of the EURL-CF. The Test Item contained 18 compounds that could be evaluated. Danish Centre for Food and Agriculture at Aarhus University grew the rye and performed the field treatments in 2015. The pesticides employed for the field treatment were selected by the EURL-CF and the EURL quality control group and the application rates and harvest intervals chosen were based on previous experience and data from supervised residue trials. The harvested rye grains were spiked with 7 pesticides post-harvest, and then checked for homogeneity before shipping to participants. Furthermore, the stabilities of the pesticides in the Treated Test Item were checked several times during the period of time allowed for laboratories to complete the PT exercise.

The participating laboratories were provided with 100 g portions of the Treated rye Test Item and 100 g of untreated Blank rye Test Item. Both Test Items were shipped to participants on 20 April 2019 and the deadline for submission of results to the Organiser was the 19 May 2019. The participants were asked to analyse the Treated Test Item as well as the Blank Test Item and report the concentrations of any pesticide residues found that were included in the Target Pesticide List (**Appendix 2**). Submission of results was performed online via the website.

1.1 Analytical methods

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

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

1.2 Selection of Pesticides for the Target Pesticide List

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

1.3 Preparation of the treated Test Item

It was decided to use leftover kernels that previously has been used as a flour Test Item, but for this EUPT shipped as kernel. So the rye kernels used for this EUPT-CF13 has earlier been used for EUPT-CF10,. The field spraying was performed in 2015 by the Danish Centre for Food and Agriculture at Aarhus University. Approximately, 30 kg of the harvested rye grain was used for this PT. It was decided to additionally spike in the laboratory with seven pesticides, which were not included in the field treatments **(Table 1)**. Spiking in the laboratory was performed using formulations or pure standards. Five time one kilogram of the field treated rye was spiked and subsequently mixed with 28 kg of field treated rye and homogenised thoroughly. The resulting 33 kg of mixed rye grain. One hundred twenty-five gram portions were weighed out into screw-capped polyethylene plastic bottles, sealed, numbered, and stored in a freezer at about -20 °C prior to homogeneity testing and distribution to participants.

1.4 Preparation of the 'blank' Test Item

The rye used to prepare the blank Test Item was also produced in 2015 by the Danish Centre for Food and Agriculture at Aarhus University under similar growing conditions as the treated crop but without any pesticide treatment in the field or spiking in the laboratory. One hundred and twenty-five gram portions were weighed out into screw-capped polyethylene plastic bottles, sealed, and stored in a freezer at about -20 °C prior to distribution to participants.

1.5 Homogeneity test

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

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

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

As all pesticides passed the homogeneity test, the treated Test Item was considered to be sufficiently homogenous and suitable for the EUPT-CF13.

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

Pesticides [1]	Application in field	Spike in laboratory	Formulation/standard
Ametoctradin		x	Analytical Standard
Azoxystrobin	x		Amistar
Bixafen	x		Aviator
Boscalid	x		Viverda
Carbendazim	x		Benlate
Chlorantraniliprole		x	Analytical Standard
Cypermethrin	x		Cyperb
Epoxiconazole	x		Viverda
Etoxazole		x	Analytical Standard
Fenpropidin	x		Tern
Fluopyram	x		Propulse
HCH-alpha		x	Analytical Standard
Metrafenone	x		Flexity
Prosulfocarb		x	Analytical Standard
Prothioconazole-Desthio	x		Aviator and Propulse
Pyraclostrobin	x		Viverda
Quintozene		x	Analytical Standard
Spinetoram		x	Analytical Standard
Tebuconazole	x		Folicur

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

1.6 Stability tests

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

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

The dates of testing were as follows:

Day 1: 29 January 2019
Day 2: 12 February 2019
Day 3: 26 February 2019

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

Pesticide	Mean, mg/kg	S_s^2	c	$S_s^2 < c$
Ametoctradin	0.048	0.00000	0.0000	Pass
Azoxystrobin	0.073	0.00000	0.0001	Pass
Bixafen	0.066	0.00000	0.0001	Pass
Boscalid	0.335	0.00003	0.0016	Pass
Carbendazim	0.131	0.00000	0.0003	Pass
Chlorantraniliprole	0.071	0.00001	0.0001	Pass
Epoxiconazole	0.156	0.00001	0.0003	Pass
Etoxazole	0.033	0.00000	0.0000	Pass
Fenpropidin	0.285	0.00002	0.0010	Pass
Fluopyram	0.222	0.00004	0.0006	Pass
HCH-alpha	0.030	0	0.0000	Pass
Metrafenone	0.032	0.00000	0.0000	Pass
Prosulfocarb	0.042	0.00000	0.0000	Pass
Prothioconazole-desthio	0.133	0.00001	0.0002	Pass
Pyraclostrobin	0.082	0	0.0001	Pass
Quintozene	0.060	0.00002	0.0001	Pass
Spinetoram	0.089	0.00005	0.0003	Pass
Tebuconazole	0.080	0.00000	0.0001	Pass

Table 3. Statistical evaluation of the stability test data

Pesticide	Mean, mg/kg	| x1 - yi |	0.3×σ	| x1 - yi | ≤ 0.3×σ
Ametoctradin	0.045	0.000	0.005	Pass
Azoxystrobin	0.077	0.001	0.006	Pass
Bixafen	0.064	0.000	0.006	Pass
Boscalid	0.366	0.004	0.029	Pass
Carbendazim	0.106	0.001	0.007	Pass
Chlorantraniliprole	0.073	0.003	0.006	Pass
Epoxiconazole	0.165	0.004	0.012	Pass
Etoxazole	0.034	0.001	0.003	Pass
Fenpropidin	0.309	0.004	0.025	Pass
Fluopyram	0.231	0.005	0.018	Pass
HCH-alpha	0.041	0.001	0.003	Pass
Metrafenone	0.032	0.000	0.003	Pass
Prosulfocarb	0.041	0.001	0.004	Pass
Prothioconazole-desthio	0.132	0.008	0.010	Pass
Pyraclostrobin	0.083	0.003	0.007	Pass
Quintozene	0.088	0.004	0.005	Pass
Spinetoram	0.121	0.005	0.009	Pass
Tebuconazole	0.079	0.003	0.006	Pass

The results of the stability test for storage temperature -18 °C are given in **Table 3**. All pesticides passed the test at -18 °C. However, the spiked pesticides, ametoctradin, chlorantraniliprole, etoxazole, quintozene and spinetoram did not pass the test when stored for 4 weeks at room temperature. But, the stability test was performed as worst case scenario on flour and on not kernels and the laboratories were instructed to store the test item at -18 degree. The results showed were very good with robust RSDs at 17%, 19%, 14%, 20% and 16% respectively so the stability of the test material was consequently acceptable for all pesticides. See the individual stability figures for all pesticides in Appendix 4.

1.7 Organisational details

1.7.1 Access to documents, registration and confidentiality

In the invitation letter, all NRLs and OfLs were requested to register using the online registration link from 29 October 2018. 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 had access to another online registration link. On 21 January, the participants received a link to DTU web tool as well as login credentials and were ask 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 (28 January 2019).

1.7.2 Distribution of the Test Item

On 28 January 2019, one bottle of treated Test Item (100 g) and one bottle of blank Test Item (100 g) were shipped to all participants in insulated polystyrene boxes containing a freezer block. The laboratories were asked to check the state of the sample on receipt and to enter the web tool to report whether they accept/not accept the Test Items. Test Items for Third Countries were shipped one week earlier due the often very time-consuming customs procedures at the borders.

1.7.3 Submission of results

The participants 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 (25 February 2019). Participants were asked not only to report their analytical results, but also to give information regarding accreditation, reporting limits and details regarding the methods they used to analyse the Test Items.

2. EVALUATION OF THE RESULTS

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 participant's mean (x*) as described in ISO 13528:2015, 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 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 $u(x_{pt})$ is calculated according to ISO 13528:2015 as:

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

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 be rounded to one decimal place. For the calculation of combined z scores (see below) the original z scores will be used and rounded to one decimal place after calculation.

Any z scores > 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 the RL < MRRL. The EUPT-Panel will decide whether, or not, these values should appear in the z-score histograms.

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

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, 152 EU and EFTA laboratories, from 30 different countries (27 EU member states), agreed to participate in this proficiency test. Additionally, Malta was represented by UK NRL. Three EU participants did not submit results among these was one NRL. Additionally, 6 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 10-12** and in **Appendix 5**. However, only results submitted by laboratories from EU and EFTA countries are included in **Table 4**, **8-9** and **15** 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 treated Test Item. Only results submitted by laboratories from the EU and EFTA are included in this table.

Pesticide	No. of reported results	No. of NA	No. of false negatives	% of labs reporting results [1]
Ametoctradin	80	69	1	54
Azoxystrobin	140	9	1	94
Bixafen	100	49	5	67
Boscalid	138	11	2	93
Carbendazim	117	32	2	79
Chlorantraniliprole	108	41	5	72
Cypermethrin	139	10	17	93
Epoxiconazole	135	14	1	91
Etoxazole	102	47	1	68
Fenpropidin	112	37	4	75
Fluopyram	121	28	2	81
HCH-alpha	118	31	1	79
Metrafenone	99	50	5	66
Prosulfocarb	102	47	5	68
Prothioconazole-Desthio	107	42	4	72
Pyraclostrobin	121	28	2	81
Quintozene	101	48	4	68
Spinetoram	66	83	1	44

[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 = 149). False negatives are included in reported results.

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

3.1.1 False positives

Two participants from EU and EFTA countries reported 3 results for 3 different additional pesticides above the MRRL that had not been used to treat the Test Item (**Table 5**). The pesticides were: 2-phenylphenol, tau-fluvalinate and tetramethrin. 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. The participant reported that the compounds were also found in the blank test item

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
368	Tau-Fluvalinate	0.0624	GC-MS/MS (QQQ)	0.01	0.01
368	Tetramethrin	0.0149	GC-MS/MS (QQQ)	0.01	0.01
520	Orthophenylphenol	0.011	GC-MS/MS (QQQ)	0.01	0.01

3.1.2 Findings of compounds below 0.01 mg/kg

Apart from the false positive results above and the results for the pesticides listed in **Table 10-12**, three participants reported results for three other pesticides, see **Table 6**. As the rye field was treated with pirimcarb, this explains the findings of pirimicarb and pirimicarb-desmethyl. However, the finding of difenoconazole cannot be explained from treatment, but still this result is not evaluated as false positives because the concentrations are below the MRRL at 0.01.

However, all the results reported were below the laboratories own reporting limit, and should therefore not have been reported.

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
368	Difenoconazole	0.0059	GC-MS/MS (QQQ)	0.01	0.01
254	Pirimicarb	0.0017	LC-MS/MS QQQ	0.005	0.01
368	Pirimicarb	0.0027	GC-MS/MS (QQQ)	0.005	0.01
460	Pirimicarb	0.002	LC-MS/MS QQQ	0.05	0.01
254	Pirimicarb-desmethyl	0.0012	LC-MS/MS QQQ	0.005	0.01
368	Pirimicarb-desmethyl	0.0019	LC - MS/MS	0.01	0.01
460	Pirimicarb-desmethyl	0.001	LC-MS/MS QQQ	0.02	0.01

3.1.3 False negatives

Not reported results for pesticides actually present in the treated Test Item were judged as false negatives. **Table 7** summarizes the number of reported false negatives for each pesticide. Twenty-three laboratories submitted 47 false negatives results for 18 different pesticides, which represents 1.8% of the total number of results. Around 15% of the participants (23 laboratories) reported false negative results. This is lower than for previous EUPTs on cereals where 20-30% of the labs reported false negative results. False negatives results were reported for all evaluated compounds. Not reported results for cypermethrin, deltamethrin, cis- and lambda-cyhalothrin were not judged to be false negatives as the assigned values were less than 3 times the MRRL, see 3.2 and **Table 12**.

Table 7. False negative results (FN).

Lab code	Ametoctradin	Azoxystrobin	Bixafen	Boscalid	Carbendazim	Chlorantraniliprole	Epoxiconazole	Etoxazole	Fenpropidin	Fluopyram	Metrafenone	Prosulfocarb	Prothioconazole-Desthio	Pyraclostrobin	Tebuconazole	HCH-alpha	Quintozene	Spinetoram
208																	FN	
236																		FN
240			FN															
252						FN			FN		FN							
270												FN						
282					FN	FN						FN		FN				
302			FN															
304		FN		FN			FN		FN	FN	FN	FN	FN	FN	FN		FN	
310						FN												
324																	FN	
350						FN												
376												FN	FN					
384																FN		
396																	FN	
422													FN					
460								FN										
470											FN							
492			FN															
504									FN		FN							
508			FN															
512					FN	FN												
514				FN														
520	FN		FN						FN	FN	FN	FN	FN					

3.2 Assigned values and target standard deviations

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

All assigned values for the pesticides can be seen in **Table 8**. The assigned values for cypermethrin was less than 3 times the MRRL (equal to 0.03 mg/kg). Consequently, the assigned values for this compound is given for informative purposes only. Deltamethrin and lambda-cyhalothrin were present in very low levels around 0.01 and are not included in the tables below.

The target standard deviation was obtained using a fixed FFP-RSD value of 25 %. In parallel, the Algorithm A standard deviation (Alg A-RSD) was calculated for informative purposes only. The range of Alg A-RSD values was 14-25 % but on average the Alg A-RSD was 18 %, and thus below the 25 % FFP-RSD used for the calculations.

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

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

Where s* is the robust standard deviation estimate and n is the number of datapoints equal to the number of results used to calculate the assigned value (number of results in **Table 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, %
Ametoctradin	0.01	0.054	0.001	25	17
Azoxystrobin	0.01	0.072	0.001	25	17
Bixafen	0.01	0.063	0.001	25	16
Boscalid	0.01	0.334	0.006	25	16
Carbendazim	0.01	0.085	0.002	25	21
Chlorantraniliprole	0.01	0.069	0.002	25	19
Cypermethrin[1]	0.01	0.025	0.001	25	21
Epoxiconazole	0.01	0.143	0.002	25	16
Etoxazole	0.01	0.037	0.001	25	14
Fenpropidin	0.01	0.286	0.008	25	25
Fluopyram	0.01	0.204	0.004	25	19
HCH-alpha	0.01	0.034	0.001	25	18
Metrafenone	0.01	0.030	0.001	25	18
Prosulfocarb	0.01	0.042	0.001	25	17
Prothioconazole-Desthio	0.01	0.119	0.002	25	15
Pyraclostrobin	0.01	0.081	0.002	25	19
Quintozene	0.01	0.056	0.001	25	20
Spinetoram	0.01	0.108	0.003	25	16
Tebuconazole	0.01	0.071	0.001	25	16

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

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/b-13a/b** show the individual results and z scores for each laboratory and pesticide together with the assigned values. A graphical representation of the z scores (for EU and EFTA countries) can be seen in **Appendix 4**.

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

Pesticide	No. of reported results	Assigned values	Acceptable	Questionable	Unacceptable[2]	False negatives
Ametoctradin	80	0.054	75	2	3	1
Azoxystrobin	140	0.072	135	2	3	1
Bixafen	100	0.063	93	1	6	5
Boscalid	138	0.334	131	2	5	2
Carbendazim	117	0.085	111	2	4	2
Chlorantraniliprole	108	0.069	94	4	10	5
Cypermethrin[1]	139	0.025	115	17	7	17
Epoxiconazole	135	0.143	130	3	2	1
Etoxazole	102	0.037	93	7	2	1
Fenpropidin	112	0.286	101	6	5	4
Fluopyram	121	0.204	115	4	2	2
HCH-alpha	118	0.034	112	5	1	1
Metrafenone	99	0.030	89	8	2	5
Prosulfocarb	102	0.042	93	2	7	5
Prothioconazole-Desthio	107	0.119	100	0	7	4
Pyraclostrobin	121	0.081	114	5	2	2
Quintozene	101	0.056	93	4	4	4
Spinetoram	66	0.108	61	2	3	1
Tebuconazole	140	0.071	135	4	1	1

1 The assigned value is less than 3 times the MRRL and consequently for informative purposes only.
2 Unacceptable z scores include false negative results.

For azoxystrobin, boscalid, carbendazim, epoxiconazole, fluopyram, HCH-alpha and tebuconazole acceptable results were obtained by 95-99% of the laboratories. For ametoctradin, bixafen, etoxazole, fenpropidin, metrafenone, prosulfocarb, prothioconazole-desthio, pyraclostrobin, quintozene and spinetoram acceptable results were obtained by 90-94% of the laboratories. Only 87% of the laboratories obtained acceptable z scores for chlorantraniliprole.

In previous EUPTs on cereals some laboratories reported very high results for carbendazim. This is probably due to the low solubility of the compound in organic solvent, e.g. for ethyl acetate it is only 0.135 mg/ml. It is therefore crucial to check if the carbendazim in stock solution is completely dissolved. It is recommended to prepare stock solutions of carbendazim at a concentration no higher than 0.1 mg/ml. However, in this EUPT only one laboratory obtained z scores >5.

Several different analytical methods have been used by the laboratories. QuEChERS, Citrate buffered (EN 151662) was used for 71% of the reported results. However, variations in the clean-up procedures were reported by the labs, e.g. some used a freezing out step, centrifugation, some used PSA or C18, others PSA/C18 or PSA/ODS or

PSA/GCB, PSA/EnviCarb or Z-sep. So it is not one specific method. Two other QuEChERS methods were used, the Original Version (J. AOAC 86, (2003) 412) and the Acetate buffered (AOAC Official Method 2007.01). These were used for 7% and 6% of the results, respectively. The SweEt method (NMKL 195, 2013) was used for 4%, Mini Luke 4%. Finally 8% of the results were analysed by other methods and for 1% of the results no information on the reference method was given by the laboratories.

More than 96% of the reported results derived from a method where water was added before extraction and for 1% of the results no information was given.

For milling, 58% used a kind of knife mill, 31% centrifugal mill, while hammer mill and horizontal mill were used by 3% and 4%, respectively. Furthermore, one participant used a disc mill, and 2% of the participants did not report the type of mill, although some of them reported the particle size. Finally, one participant reported not milling the sample. This lab got a low z score for the spiked pesticide HCH-alpha and 11 false negatives result for the incurred pesticide.

GC instruments was used for 38% of the results, mainly GC-MS/MS and GC-MSD (30% and 5%), 1 % used GC-TOF or GC-Orbitrap instruments, and the rest used GC with specific detectors, ECD and NPD. LC instruments was used for 62% of the reported results, mainly LC-MS/MS (58%) but 3% used high resolution instrument like LC-Orbitrap or LC-Q-TOF. No result were analysed using specific detectors such as LC-Fluorescence, LC-UV or LC-DAD.

Table 10a. Results for ametoctradin, azoxystrobin, bixafen, boscalid, carbendazim, chlorantraniliprole, epoxiconazole and etoxazole in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Ametoctradin	Z score (FFP RSD (25%)	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Chlorantraniliprole	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Etoxazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.054**		**0.072**		**0.063**		**0.334**		**0.085**		**0.069**		**0.143**		**0.037**	
200	0.061	0.5	0.069	-0.2	0.07	0.4	0.28	-0.6	0.067	-0.8	0.07	0.0	0.14	-0.1	0.03	-0.7
202			0.067	-0.3	0.064	0.0	0.331	0.0	0.087	0.1	0.062	-0.4	0.142	0.0	0.034	-0.3
204			0.0749	0.2	0.0625	-0.1	0.314	-0.2	0.088	0.2	0.0646	-0.3	0.134	-0.2		
206																
208			0.0609	-0.6	0.0631	0.0	0.332	0.0	0.108	1.1	0.0617	-0.4	0.137	-0.2	0.0408	0.4
210	0.046	-0.6	0.074	0.1	0.06	-0.2	0.325	-0.1	0.067	-0.8	0.065	-0.3	0.155	0.3	0.032	-0.5
212																
214			0.0714	0.0	0.0606	-0.2	0.306	-0.3					0.16	0.5		
216	0.0442	-0.7	0.0811	0.5	0.0671	0.2	0.373	0.5	0.0921	0.4	0.0651	-0.2	0.174	0.9	0.0341	-0.3
218	0.0525	-0.1	0.0663	-0.3	0.0584	-0.3	0.307	-0.3	0.0867	0.1	0.0676	-0.1	0.143	0.0	0.0346	-0.2
220	0.047	-0.5	0.064	-0.4	0.048	-1.0	0.252	-1.0	0.065	-0.9	0.062	-0.4	0.118	-0.7	0.035	-0.2
224	0.055	0.1	0.082	0.6	0.089	1.6	0.389	0.7	0.075	-0.5	0.091	1.2	0.176	0.9	0.041	0.5
226	0.0485	-0.4	0.056	-0.9	0.0435	-1.3	0.245	-1.1	0.0915	0.3	0.0648	-0.3	0.1138	-0.8	0.0325	-0.5
228			0.0687	-0.2			0.372	0.5	0.0896	0.2			0.125	-0.5	0.0381	0.1
230	0.069	1.1	0.08	0.5			0.378	0.5	0.085	0.0	0.083	0.8	0.155	0.3	0.037	0.0
232	0.0691	1.1	0.0658	-0.3	0.0608	-0.2	0.34	0.1	0.0881	0.2			0.124	-0.5		
234			0.0499	-1.2			0.235	-1.2	0.0775	-0.3	0.068	-0.1	0.093	-1.4		
236			0.0485	-1.3			0.227	-1.3			0.079	0.6	0.104	-1.1	0.059	2.4
238			0.067	-0.3												
240			0.062	-0.5	FN	-3.4	0.337	0.0	0.066	-0.9	0.058	-0.7	0.115	-0.8	0.034	-0.3
242			0.061	-0.6			0.361	0.3					0.13	-0.4		
244	0.052	-0.1	0.086	0.8	0.088	1.6	0.403	0.8	0.069	-0.7	0.074	0.3	0.17	0.8	0.036	-0.1
246	0.051	-0.2	0.074	0.1	0.045	-1.2	0.36	0.3	0.072	-0.6	0.059	-0.6	0.135	-0.2	0.04	0.4
248	0.0605	0.5	0.0653	-0.4	0.0414	-1.4	0.331	0.0	0.114	1.4	0.0853	0.9	0.131	-0.3	0.0424	0.6
250																
252			0.053	-1.0			0.225	-1.3			FN	-3.4	0.082	-1.7		
254	0.0478	-0.5	0.0561	-0.9	0.0444	-1.2	0.274	-0.7	0.0789	-0.3	0.0606	-0.5	0.109	-0.9	0.0328	-0.4
256	0.044	-0.7	0.0725	0.0	0.063	0.0	0.313	-0.2	0.0753	-0.4	0.0627	-0.4	0.14	-0.1	0.035	-0.2
258			0.0755	0.2	0.0598	-0.2	0.334	0.0					0.152	0.3		
260			0.06	-0.7											0.075	4.2
262	0.0627	0.6	0.0608	-0.6	0.0749	0.7	0.276	-0.7	0.1035	0.9	0.0936	1.4	0.1373	-0.2	0.0469	1.1
264	0.055	0.1	0.082	0.6	0.08	1.0	0.342	0.1	0.095	0.5	0.083	0.8	0.16	0.5	0.035	-0.2
266	0.044	-0.7	0.06	-0.7	0.062	-0.1	0.313	-0.2	0.094	0.4	0.064	-0.3	0.136	-0.2	0.034	-0.3
268			0.062	-0.5			0.28	-0.6					0.11	-0.9		
270			0.0551	-0.9	0.0422	-1.3	0.248	-1.0	0.0622	-1.1	0.0511	-1.1	0.106	-1.0	0.0346	-0.2
272			0.078	0.3	0.0592	-0.3	0.316	-0.2					0.148	0.1		
274	0.029	-1.9	0.078	0.3	0.064	0.0	0.36	0.3	0.1	0.7	0.059	-0.6	0.17	0.8	0.033	-0.4
276			0.071	0.0	0.059	-0.3	0.299	-0.4	0.066	-0.9	0.066	-0.2	0.132	-0.3	0.034	-0.3
278			0.045	-1.5			0.311	-0.3	0.088	0.2			0.12	-0.6		
280			0.0762	0.2	0.0616	-0.1	0.307	-0.3					0.152	0.3		
282			0.057	-0.8			0.356	0.3	FN	-3.5	FN	-3.4	0.129	-0.4	0.037	0.0

Table 10b. Results for ametoctradin, azoxystrobin, bixafen, boscalid, carbendazim, chlorantraniliprole, epoxiconazole and etoxazole in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Ametoctradin	Z score (FFP RSD (25%)	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Chlorantraniliprole	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Etoxazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.054**		**0.072**		**0.063**		**0.334**		**0.085**		**0.069**		**0.143**		**0.037**	
284			0.069	-0.2			0.347	0.2								
288																
290			0.066	-0.3	0.072	0.5	0.468	1.6	0.097	0.6			0.18	1.0		
292	0.044	-0.7	0.067	-0.3	0.063	0.0	0.33	0.0	0.071	-0.6	0.068	-0.1	0.14	-0.1	0.027	-1.1
294	0.074	1.5	0.082	0.6	0.064	0.0	0.363	0.4	0.093	0.4	0.075	0.3	0.154	0.3	0.084	>5
296			0.0756	0.2	0.0639	0.0	0.328	-0.1					0.148	0.1		
298	0.116	4.6	0.079	0.4	0.067	0.2	0.378	0.5	0.092	0.3	0.072	0.1	0.173	0.8	0.035	-0.2
300	0.0465	-0.6	0.0773	0.3	0.0738	0.7	0.366	0.4	0.0734	-0.5			0.153	0.3	0.0343	-0.3
302	0.033	-1.6	0.08	0.5	FN	-3.4	0.5	2.0	0.053	-1.5	0.071	0.1	0.12	-0.6	0.03	-0.7
304			FN	-3.4			FN	-3.9					FN	-3.7		
306																
308	0.061	0.5	0.069	-0.2	0.068	0.3	0.317	-0.2	0.089	0.2	0.071	0.1	0.093	-1.4	0.041	0.5
310			0.0719	0.0			0.204	-1.6	0.0733	-0.5	FN	-3.4	0.0631	-2.2	0.0303	-0.7
312			0.074	0.1	0.059	-0.3	0.304	-0.4					0.143	0.0		
314			0.083	0.6	0.071	0.5	0.395	0.7	0.076	-0.4	0.063	-0.4	0.137	-0.2	0.04	0.4
316	0.0453	-0.6	0.0736	0.1	0.0585	-0.3	0.339	0.1	0.0713	-0.6	0.0634	-0.3	0.135	-0.2	0.0347	-0.2
318			0.0552	-0.9	0.051	-0.8	0.268	-0.8					0.145	0.1	0.0344	-0.3
320			0.056	-0.9			0.256	-0.9	0.063	-1.0	0.031	-2.2	0.112	-0.9		
322	0.0492	-0.4	0.0729	0.1	0.064	0.0	0.365	0.4	0.0845	0.0	0.0681	-0.1	0.181	1.1	0.0376	0.1
324			0.1	1.6	0.0677	0.3	0.353	0.2	0.046	-1.8	0.0598	-0.6	0.154	0.3		
326	0.075	1.6	0.071	0.0	0.065	0.1	0.341	0.1	0.104	0.9	0.07	0.0	0.149	0.2	0.041	0.5
328	0.054	0.0	0.076	0.2	0.054	-0.6	0.354	0.2	0.078	-0.3	0.071	0.1	0.159	0.5	0.036	-0.1
330	0.055	0.1	0.072	0.0	0.059	-0.3	0.36	0.3	0.116	1.5	0.059	-0.6	0.149	0.2	0.033	-0.4
332	0.0665	0.9	0.0751	0.2	0.0622	-0.1	0.36	0.3	0.0804	-0.2	0.0885	1.1	0.1507	0.2	0.0412	0.5
334			0.0788	0.4			0.356	0.3					0.148	0.1		
336	0.184	>5	0.089	1.0			0.41	0.9	0.09	0.3	0.049	-1.2	0.145	0.1	0.035	-0.2
338	0.061	0.5	0.082	0.6	0.07	0.4	0.39	0.7	0.092	0.3	0.07	0.0	0.17	0.8	0.042	0.6
340	0.0471	-0.5	0.12	2.7			0.417	1.0	0.133	2.3	0.0769	0.4	0.198	1.5	0.0376	0.1
342			0.065	-0.4			0.274	-0.7	0.078	-0.3			0.12	-0.6	0.01	-2.9
344	0.05	-0.3	0.073	0.1	0.066	0.2	0.34	0.1	0.07	-0.7	0.072	0.1	0.15	0.2	0.037	0.0
348	0.055	0.1	0.071	0.0	0.064	0.0	0.395	0.7	0.095	0.5	0.072	0.1	0.158	0.4	0.037	0.0
350			0.213	>5	0.167	>5	1.18	>5			FN	-3.4				
352	0.0496	-0.3	0.0706	-0.1	0.0577	-0.4	0.348	0.2	0.937	>5	0.0624	-0.4	0.155	0.3	0.0301	-0.7
354	0.056	0.2	0.078	0.3	0.068	0.3	0.372	0.5	0.093	0.4	0.071	0.1	0.167	0.7	0.039	0.2
356	0.0481	-0.4	0.0642	-0.4			0.291	-0.5	0.066	-0.9	0.0559	-0.8	0.13	-0.4	0.0332	-0.4
358	0.014	-3.0	0.021	-2.8	0.022	-2.6	0.101	-2.8	0.054	-1.4	0.018	-3.0	0.063	-2.2	0.013	-2.6
360	0.051	-0.2	0.0735	0.1	0.0656	0.1	0.334	0.0	0.092	0.3	0.068	-0.1	0.15	0.2	0.0352	-0.2
362	0.0508	-0.2	0.0683	-0.2	0.0589	-0.3	0.318	-0.2	0.0844	0.0	0.0619	-0.4	0.135	-0.2	0.0372	0.1
364	0.06	0.4	0.091	1.1	0.072	0.5	0.378	0.5	0.074	-0.5	0.11	2.3	0.161	0.5	0.033	-0.4
366	0.0575	0.3	0.0631	-0.5	0.0528	-0.7	0.25	-1.0	0.115	1.4	0.0659	-0.2	0.116	-0.8	0.0329	-0.4
368			0.0935	1.2			0.1085	-2.7	0.0938	0.4			0.154	0.3		

Table 10c. Results for ametoctradin, azoxystrobin, bixafen, boscalid, carbendazim, chlorantraniliprole, epoxiconazole and etoxazole in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Ametoctradin	Z score (FFP RSD (25%)	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Chlorantraniliprole	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Etoxazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.054**		**0.072**		**0.063**		**0.334**		**0.085**		**0.069**		**0.143**		**0.037**	
370	0.0455	-0.6	0.0755	0.2	0.0551	-0.5	0.34	0.1	0.0748	-0.5	0.0672	-0.1	0.139	-0.1	0.0326	-0.4
372	0.058	0.3	0.058	-0.8	0.054	-0.6	0.311	-0.3	0.09	0.3	0.111	2.4	0.13	-0.4	0.042	0.6
374			0.076	0.2	0.066	0.2	0.34	0.1	0.087	0.1	0.072	0.1	0.165	0.6		
376			0.091	1.1			0.42	1.0	0.071	-0.6			0.14	-0.1		
378	0.047	-0.5	0.0744	0.1	0.066	0.2	0.323	-0.1	0.0702	-0.7	0.073	0.2	0.152	0.3	0.037	0.0
380	0.06	0.4	0.083	0.6	0.07	0.4	0.404	0.8	0.103	0.9	0.08	0.6	0.176	0.9	0.043	0.7
382	0.055	0.1	0.086	0.8	0.079	1.0	0.418	1.0	0.101	0.8	0.085	0.9	0.18	1.0	0.045	0.9
384																
386	0.0491	-0.4	0.0564	-0.9	0.0698	0.4	0.272	-0.7	0.0841	0.0	0.0582	-0.6	0.138	-0.1	0.0405	0.4
388	0.058	0.3	0.051	-1.2	0.048	-1.0	0.263	-0.8	0.048	-1.7	0.067	-0.1	0.114	-0.8	0.029	-0.8
392	0.062	0.6	0.083	0.6	0.061	-0.2	0.314	-0.2	0.101	0.8	0.086	1.0	0.16	0.5	0.045	0.9
394	0.045	-0.7	0.081	0.5	0.059	-0.3	0.322	-0.1	0.086	0.1	0.049	-1.2	0.135	-0.2	0.041	0.5
396			0.052	-1.1	0.054	-0.6	0.233	-1.2	0.064	-1.0	0.056	-0.8	0.093	-1.4	0.019	-1.9
398	0.05	-0.3	0.07	-0.1	0.062	-0.1	0.315	-0.2	0.063	-1.0	0.045	-1.4	0.137	-0.2	0.036	-0.1
400					0.0742	0.7	0.397	0.8	0.0971	0.6			0.185	1.2		
402																
404	0.046	-0.6	0.065	-0.4	0.0664	0.2	0.296	-0.5	0.0804	-0.2	0.0583	-0.6	0.151	0.2	0.0378	0.1
406			0.078	0.3	0.0642	0.1	0.353	0.2	0.0804	-0.2	0.0743	0.3	0.149	0.2	0.045	0.9
408			0.088	0.9			0.444	1.3	0.066	-0.9			0.194	1.4		
410			0.074	0.1			0.37	0.4	0.12	1.7	0.077	0.4	0.156	0.4	0.034	-0.3
412	0.0631	0.7	0.0833	0.6	0.0627	0.0	0.439	1.3	0.1	0.7	0.0912	1.3	0.162	0.5	0.0364	0.0
414			0.064	-0.4					0.086	0.1	0.058	-0.7	0.141	-0.1	0.036	-0.1
416	0.06	0.4	0.073	0.1	0.076	0.8	0.35	0.2	0.095	0.5	0.085	0.9	0.165	0.6	0.045	0.9
418																
420	0.063	0.7	0.097	1.4			0.357	0.3	0.075	-0.5	0.072	0.1	0.118	-0.7	0.048	1.2
422			0.045	-1.5			0.166	-2.0	0.121	1.7	0.048	-1.2	0.119	-0.7		
424			0.042	-1.7			0.32	-0.2	0.095	0.5			0.095	-1.3		
426	0.0431	-0.8	0.0624	-0.5			0.338	0.1	0.0982	0.6	0.0552	-0.8	0.1625	0.6	0.0343	-0.3
428	0.0493	-0.3	0.07	-0.1	0.0623	-0.1	0.329	-0.1	0.117	1.5	0.0657	-0.2	0.16	0.5	0.0403	0.4
430			0.074	0.1	0.059	-0.3	0.308	-0.3					0.146	0.1		
432	0.0513	-0.2	0.064	-0.4	0.0525	-0.7	0.282	-0.6	0.079	-0.3	0.0672	-0.1	0.1211	-0.6	0.0373	0.1
434			0.089	1.0			0.43	1.2	0.095	0.5	0.081	0.7	0.14	-0.1	0.042	0.6
436																
438			0.077	0.3			0.326	-0.1	0.071	-0.6	0.067	-0.1	0.129	-0.4	0.037	0.0
440	0.0551	0.1	0.0703	-0.1	0.0535	-0.6	0.297	-0.4	0.0748	-0.5	0.0682	-0.1	0.126	-0.5	0.0399	0.3
442			0.091	1.1	0.094	1.9	0.311	-0.3	0.042	-2.0	0.085	0.9	0.164	0.6		
444	0.06	0.4	0.085	0.7	0.067	0.2	0.389	0.7	0.089	0.2	0.079	0.6	0.136	-0.2	0.041	0.5
446	0.063	0.7	0.081	0.5	0.075	0.7	0.34	0.1	0.13	2.1	0.083	0.8	0.168	0.7	0.038	0.1
448	0.046	-0.6	0.081	0.5	0.07	0.4	0.48	1.8	0.084	0.0	0.063	-0.4	0.165	0.6	0.033	-0.4
450			0.068	-0.2	0.081	1.1	0.358	0.3	0.08	-0.2	0.075	0.3	0.167	0.7	0.036	-0.1
452			0.064	-0.4			0.3262	-0.1					0.1437	0.0		

Table 10d. Results for ametoctradin, azoxystrobin, bixafen, boscalid, carbendazim, chlorantraniliprole, epoxiconazole and etoxazole in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Ametoctradin	Z score (FFP RSD (25%)	Azoxystrobin	Z score (FFP RSD (25%)	Bixafen	Z score (FFP RSD (25%)	Boscalid	Z score (FFP RSD (25%)	Carbendazim	Z score (FFP RSD (25%)	Chlorantraniliprole	Z score (FFP RSD (25%)	Epoxiconazole	Z score (FFP RSD (25%)	Etoxazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.054**		**0.072**		**0.063**		**0.334**		**0.085**		**0.069**		**0.143**		**0.037**	
454	0.053	-0.1	0.078	0.3	0.066	0.2	0.337	0.0	0.084	0.0	0.072	0.1	0.214	2.0	0.042	0.6
456	0.07	1.2	0.126	3.0	0.075	0.7	0.495	1.9	0.104	0.9	0.122	3.0	0.221	2.2	0.056	2.1
458	0.0563	0.2	0.0675	-0.2	0.0627	0.0	0.364	0.4	0.0872	0.1	0.0682	-0.1	0.14	-0.1	0.0377	0.1
460	0.056	0.2	0.067	-0.3	0.081	1.1	0.27	-0.8	0.089	0.2	0.056	-0.8	0.127	-0.4	FN	-2.9
462			0.049	-1.3			0.35	0.2	0.09	0.3			0.18	1.0		
464	FN	-3.3	0.071	0.0			0.33	0.0	0.081	-0.2	0.06	-0.5	0.133	-0.3	0.042	0.6
466	0.0547	0.1	0.0841	0.7	0.0714	0.5	0.323	-0.1	0.094	0.4	0.071	0.1	0.158	0.4	0.0395	0.3
468			0.086	0.8			0.318	-0.2			0.1	1.8	0.15	0.2		
470	0.074	1.5	0.067	-0.3			0.329	-0.1	0.051	-1.6	0.062	-0.4	0.112	-0.9	0.012	-2.7
472			0.061	-0.6			0.251	-1.0	0.037	-2.3	0.064	-0.3	0.108	-1.0	0.023	-1.5
474			0.12	2.7	0.087	1.5	0.775	>5	0.16	3.6	0.17	>5	0.29	4.1	0.061	2.6
476	0.071	-0.1			0.067	0.2	0.316	-0.2	0.0742	-0.5	0.0613	-0.5	0.147	0.1	0.0363	0.0
478	0.0511	-0.2	0.0649	-0.4	0.0622	-0.1	0.31	-0.3	0.0749	-0.5	0.0609	-0.5	0.134	-0.2	0.0354	-0.1
480			0.083	0.6			0.3	-0.4	0.088	0.2	0.07	0.0	0.149	0.2	0.036	-0.1
482	0.04	-1.0	0.07	-0.1			0.32	-0.2	0.08	-0.2	0.06	-0.5	0.16	0.5	0.04	0.4
484			0.055	-0.9			0.339	0.1					0.142	0.0		
486			0.076	0.2			0.43	1.2	0.601	>5	0.081	0.7	2.243	>5		
488																
490			0.078	0.3			0.34	0.1								
492	0.058	0.3	0.073	0.1	FN	-3.4	0.304	-0.4	0.079	-0.3	0.098	1.6	0.153	0.3	0.037	0.0
494			0.083	0.6			0.406	0.9	0.101	0.8			0.149	0.2		
496	0.06	0.4	0.082	0.6			0.6	3.2	0.114	1.4	0.097	1.6	0.154	0.3	0.037	0.0
498																
500	0.05	-0.3	0.061	-0.6	0.069	0.4	0.3	-0.4	0.08	-0.2	0.58	>5	0.135	-0.2	0.036	-0.1
502	0.09	2.7	0.08	0.5	0.08	1.0	0.38	0.6	0.12	1.7	0.14	4.1	0.18	1.0	0.04	0.4
504			0.0655	-0.4	0.0576	-0.4	0.324	-0.1					0.123	-0.6		
506			0.087	0.8			0.246	-1.1								
508			0.093	1.2	FN	-3.4	0.5	2.0	0.122	1.8	0.132	3.6	0.128	-0.4		
510	0.0449	-0.7	0.0589	-0.7	0.059	-0.3	0.311	-0.3	0.0991	0.7	0.0663	-0.2	0.131	-0.3	0.0336	-0.3
512			0.076	0.2			0.349	0.2	FN	-3.5	FN	-3.4	0.151	0.2	0.035	-0.2
514	0.047	-0.5	0.061	-0.6	0.046	-1.1	FN	-3.9	0.1	0.7	0.055	-0.8	0.13	-0.4	0.028	-1.0
516	0.038	-1.2	0.062	-0.5	0.051	-0.8	0.289	-0.5	0.069	-0.7	0.05	-1.1	0.138	-0.1	0.026	-1.2
518	0.047	-0.5	0.07	-0.1	0.045	-1.2	0.304	-0.4	0.076	-0.4	0.064	-0.3	0.131	-0.3	0.043	0.7
520	FN	-3.3	0.072	0.0	FN	-3.4	0.466	1.6	0.065	-0.9	0.055	-0.8	0.146	0.1	0.034	-0.3
894	0.054	0.0	0.06	-0.7	0.053	-0.7	0.354	0.2	0.055	-1.4	0.064	-0.3	0.114	-0.8	0.031	-0.6

Table 11a. Results for fenpropidin, fluopyram, metrafenone, prosulfocarb, prothioconazole-desthio, pyraclostrobin and tebuconazole in mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Prosulfocarb	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.286**		**0.204**		**0.03**		**0.042**		**0.119**		**0.081**		**0.071**	
200	0.21	-1.1	0.16	-0.9	0.022	-1.1	0.036	-0.5	0.103	-0.5	0.089	0.4	0.075	0.2
202	0.276	-0.1	0.2	-0.1	0.032	0.3	0.04	-0.2	0.123	0.2	0.084	0.2	0.077	0.3
204	0.326	0.6	0.186	-0.4	0.0267	-0.4			0.109	-0.3	0.0759	-0.2	0.066	-0.3
206														
208	0.357	1.0	0.216	0.2	0.0285	-0.2	0.0381	-0.3	0.107	-0.4	0.0797	0.0	0.0679	-0.2
210	0.325	0.5	0.275	1.4	0.037	0.9	0.037	-0.4	0.112	-0.2	0.092	0.6	0.079	0.5
212														
214			0.237	0.6					0.105	-0.5			0.0718	0.0
216	0.316	0.4	0.216	0.2	0.0352	0.7			0.129	0.4	0.118	1.9	0.0813	0.6
218	0.296	0.1	0.19	-0.3	0.0308	0.1	0.0487	0.7	0.122	0.1	0.0845	0.2	0.0718	0.0
220	0.155	-1.8	0.152	-1.0	0.022	-1.1	0.037	-0.4	0.066	-1.8	0.066	-0.7	0.064	-0.4
224	0.35	0.9	0.292	1.7	0.035	0.7	0.044	0.2	0.124	0.2	0.095	0.7	0.075	0.2
226	0.2112	-1.0	0.1575	-0.9	0.022	-1.1	0.0372	-0.4	0.1015	-0.6	0.059	-1.1	0.0575	-0.8
228	0.269	-0.2									0.0815	0.0	0.0712	0.0
230	0.295	0.1	0.228	0.5	0.03	0.0					0.086	0.3	0.08	0.5
232	0.194	-1.3	0.173	-0.6			0.0403	-0.1			0.0874	0.3	0.0521	-1.1
234	0.169	-1.6	0.121	-1.6			0.0265	-1.5			0.0595	-1.0	0.0405	-1.7
236			0.0795	-2.4							0.0515	-1.4	0.0205	-2.8
238													0.061	-0.6
240	0.085	-2.8					0.035	-0.6			0.06	-1.0	0.053	-1.0
242	0.331	0.6	0.211	0.1									0.058	-0.7
244	0.36	1.0	0.313	2.1	0.041	1.5	0.044	0.2	0.162	1.5	0.1	1.0	0.068	-0.2
246	0.274	-0.2	0.194	-0.2	0.031	0.1	0.043	0.1	0.11	-0.3	0.079	-0.1	0.075	0.2
248	0.236	-0.7	0.176	-0.5	0.0235	-0.9	0.0501	0.8	0.121	0.1	0.071	-0.5	0.0664	-0.3
250														
252	FN	-3.9	0.057	-2.9	FN	-3.0	0.033	-0.8					0.042	-1.6
254	0.257	-0.4	0.156	-0.9	0.0247	-0.7	0.0382	-0.3	0.1	-0.6	0.0615	-0.9	0.0588	-0.7
256	0.273	-0.2	0.201	-0.1	0.0313	0.2	0.046	0.4	0.116	-0.1	0.0842	0.2	0.0743	0.2
258			0.222	0.4					0.121	0.1			0.0693	-0.1
260													0.047	-1.4
262	0.278	-0.1	0.238	0.7	0.0253	-0.6	0.0406	-0.1	0.141	0.8	0.0903	0.5	0.0818	0.6
264	0.4	1.6	0.238	0.7	0.034	0.5	0.046	0.4	0.141	0.8	0.084	0.2	0.113	2.4
266	0.181	-1.5	0.163	-0.8	0.024	-0.8	0.043	0.1	0.133	0.5	0.084	0.2	0.07	-0.1
268									0.1	-0.6			0.064	-0.4
270	0.196	-1.3	0.147	-1.1	0.0224	-1.0	FN	-3.0	0.0901	-1.0	0.0594	-1.1	0.053	-1.0
272			0.195	-0.2					0.118	0.0			0.073	0.1
274	0.36	1.0	0.24	0.7	0.035	0.7	0.046	0.4	0.13	0.4	0.088	0.4	0.08	0.5
276			0.202	0.0	0.031	0.1	0.04	-0.2					0.068	-0.2
278	0.301	0.2									0.07	-0.5	0.057	-0.8
280			0.217	0.3					0.116	-0.1			0.071	0.0
282	0.27	-0.2	0.172	-0.6			FN	-3.0			FN	-3.5	0.04	-1.7

Table 11b. Results for fenpropidin, fluopyram, metrafenone, prosulfocarb, prothioconazole-desthio, pyraclostrobin and tebuconazolein mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Prosulfocarb	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.286**		**0.204**		**0.03**		**0.042**		**0.119**		**0.081**		**0.071**	
284													0.077	0.3
288														
290	0.401	1.6	0.254	1.0	0.058	3.8			0.126	0.3	0.09	0.5	0.1	1.6
292	0.28	-0.1	0.22	0.3	0.027	-0.4	0.039	-0.2	0.11	-0.3	0.085	0.2	0.074	0.2
294	0.321	0.5	0.212	0.2	0.032	0.3	0.045	0.3	0.129	0.4	0.082	0.1	0.081	0.6
296			0.22	0.3					0.111	-0.3			0.0734	0.1
298	0.381	1.3	0.251	0.9	0.034	0.5	0.042	0.0	0.131	0.4	0.084	0.2	0.079	0.5
300	0.33	0.6	0.239	0.7	0.0328	0.4	0.0395	-0.2	0.133	0.5	0.0845	0.2	0.0797	0.5
302	0.25	-0.5	0.24	0.7	0.027	-0.4	0.03	-1.1	0.11	-0.3	0.052	-1.4	0.061	-0.6
304	FN	-3.9	FN	-3.8	FN	-3.0	FN	-3.0	FN	-3.7	FN	-3.5	FN	-3.4
306														
308	0.311	0.4	0.185	-0.4	0.032	0.3	0.042	0.0	0.121	0.1	0.085	0.2	0.071	0.0
310											0.0486	-1.6	0.0585	-0.7
312			0.204	0.0					0.124	0.2			0.066	-0.3
314	0.468	2.6	0.267	1.2	0.034	0.5	0.044	0.2	0.148	1.0	0.091	0.5	0.089	1.0
316	0.282	-0.1	0.176	-0.5	0.0299	0.0	0.0391	-0.2	0.111	-0.3	0.0835	0.1	0.0687	-0.1
318	0.266	-0.3	0.146	-1.1	0.0226	-1.0			1	>5			0.067	-0.2
320	0.196	-1.3	0.214	0.2			0.033	-0.8	0.097	-0.7	0.053	-1.4	0.054	-1.0
322	0.291	0.1	0.233	0.6	0.0313	0.2	0.0437	0.2	0.137	0.6	0.082	0.1	0.0766	0.3
324	0.331	0.6	0.224	0.4							0.0683	-0.6	0.0806	0.5
326	0.287	0.0	0.203	0.0	0.028	-0.3	0.04	-0.2	0.118	0.0	0.078	-0.1	0.071	0.0
328	0.281	-0.1	0.176	-0.5	0.026	-0.5	0.042	0.0	0.12	0.0	0.081	0.0	0.08	0.5
330	0.264	-0.3	0.212	0.2	0.033	0.4	0.043	0.1	0.122	0.1	0.078	-0.1	0.073	0.1
332	0.3598	1.0	0.228	0.5	0.0326	0.4	0.0415	0.0	0.151	1.1	0.0801	0.0	0.0752	0.2
334													0.0763	0.3
336	0.13	-2.2	0.226	0.4	0.035	0.7	0.028	-1.3	0.105	-0.5	0.097	0.8	0.07	-0.1
338	0.36	1.0	0.25	0.9	0.034	0.5	0.051	0.9	0.135	0.6	0.09	0.5	0.085	0.8
340	0.228	-0.8	0.333	2.5	0.0348	0.7	FN	-3.0	0.155	1.2	0.0946	0.7	0.0706	0.0
342											0.131	2.5	0.047	-1.4
344	0.32	0.5	0.23	0.5	0.032	0.3	0.04	-0.2	0.12	0.0	0.091	0.5	0.075	0.2
348	0.248	-0.5	0.215	0.2	0.031	0.1	0.048	0.6	0.124	0.2	0.091	0.5	0.074	0.2
350														
352	0.347	0.9	0.221	0.3	0.0319	0.3	0.0337	-0.8	0.093	-0.9	0.072	-0.4	0.0717	0.0
354	0.332	0.6	0.23	0.5	0.033	0.4	0.047	0.5	0.136	0.6	0.094	0.7	0.081	0.6
356	0.25	-0.5	0.167	-0.7			0.0305	-1.1	0.101	-0.6	0.0751	-0.3	0.0691	-0.1
358	0.114	-2.4	0.097	-2.1	0.012	-2.4	0.014	-2.7	0.046	-2.4	0.027	-2.7	0.03	-2.3
360	0.258	-0.4	0.186	-0.4	0.0329	0.4	0.0433	0.2	0.123	0.2	0.103	1.1	0.0768	0.3
362	0.291	0.1	0.195	-0.2	0.0265	-0.5	0.0501	0.8	0.112	-0.2	0.0743	-0.3	0.0706	0.0
364	0.308	0.3	0.208	0.1	0.031	0.1	0.04	-0.2	0.131	0.4	0.082	0.1	0.076	0.3
366	0.192	-1.3	0.155	-1.0	0.022	-1.1	0.0379	-0.4	0.0837	-1.2	0.0703	-0.5	0.056	-0.8
368			0.186	-0.4							0.078	-0.1	0.0313	-2.2

Table 11c. Results for fenpropidin, fluopyram, metrafenone, prosulfocarb, prothioconazole-desthio, pyraclostrobin and tebuconazolein mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Prosulfocarb	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.286**		**0.204**		**0.03**		**0.042**		**0.119**		**0.081**		**0.071**	
370	0.293	0.1	0.204	0.0	0.0303	0.1	0.0426	0.1	0.117	-0.1	0.0859	0.3	0.0718	0.0
372	0.202	-1.2	0.159	-0.9	0.028	-0.3	0.041	-0.1	0.096	-0.8	0.064	-0.8	0.062	-0.5
374	0.38	1.3	0.209	0.1	0.033	0.4	0.042	0.0	0.132	0.5	0.088	0.4	0.074	0.2
376							FN	-3.0	FN	-3.7	0.12	2.0	0.071	0.0
378	0.275	-0.2	0.21	0.1	0.0268	-0.4	0.0422	0.1	0.115	-0.1	0.0711	-0.5	0.0739	0.2
380	0.38	1.3	0.244	0.8	0.038	1.1	0.051	0.9	0.134	0.5	0.094	0.7	0.084	0.7
382	0.41	1.7	0.258	1.1	0.039	1.2	0.051	0.9	0.142	0.8	0.093	0.6	0.096	1.4
384														
386	0.277	-0.1	0.17	-0.7	0.0295	-0.1	0.0314	-1.0	0.107	-0.4	0.0625	-0.9	0.0645	-0.4
388	0.162	-1.7	0.147	-1.1	0.026	-0.5	0.038	-0.3	0.094	-0.8	0.067	-0.7	0.061	-0.6
392	0.3	0.2	0.23	0.5	0.031	0.1	0.047	0.5	0.13	0.4	0.084	0.2	0.079	0.5
394	0.277	-0.1	0.147	-1.1	0.029	-0.1	0.049	0.7	0.124	0.2	0.067	-0.7	0.06	-0.6
396	0.216	-1.0	0.185	-0.4	0.011	-2.5	0.027	-1.4	0.094	-0.8	0.06	-1.0	0.068	-0.2
398	0.253	-0.5	0.185	-0.4	0.036	0.8	0.038	-0.3	0.12	0.0	0.084	0.2	0.07	-0.1
400	0.403	1.6	0.278	1.5					0.0947	-0.8			0.0942	1.3
402														
404	0.257	-0.4	0.221	0.3	0.0297	0.0	0.0427	0.1	0.119	0.0	0.079	-0.1	0.0637	-0.4
406	0.324	0.5	0.216	0.2	0.0311	0.2			0.123	0.2	0.0826	0.1	0.0765	0.3
408											0.1	1.0	0.088	1.0
410	0.342	0.8	0.221	0.3	0.03	0.0			0.116	-0.1	0.08	0.0	0.077	0.3
412	0.2	-1.2	0.166	-0.7	0.0262	-0.5	0.048	0.6	0.104	-0.5	0.0734	-0.4	0.0758	0.3
414											0.076	-0.2	0.037	-1.9
416	0.3	0.2	0.25	0.9	0.032	0.3	0.045	0.3	0.13	0.4	0.09	0.5	0.075	0.2
418														
420	0.21	-1.1	0.204	0.0	0.024	-0.8	0.052	1.0	0.115	-0.1	0.089	0.4	0.063	-0.5
422	0.188	-1.4	0.165	-0.8			0.048	0.6	FN	-3.7	0.064	-0.8	0.07	-0.1
424											0.056	-1.2	0.072	0.1
426	0.345	0.8	0.1107	-1.8	0.0254	-0.6	0.0395	-0.2	0.1273	0.3	0.0813	0.0	0.0459	-1.4
428	0.316	0.4	0.198	-0.1	0.031	0.1	0.0387	-0.3	0.137	0.6	0.083	0.1	0.076	0.3
430			0.196	-0.2					0.121	0.1			0.069	-0.1
432	0.266	-0.3	0.184	-0.4	0.0259	-0.5	0.0382	-0.3	0.114	-0.2	0.0666	-0.7	0.0665	-0.3
434	0.35	0.9	0.2	-0.1			0.049	0.7	0.14	0.7	0.096	0.8	0.086	0.8
436														
438	0.235	-0.7			0.028	-0.3			0.117	-0.1	0.082	0.1	0.069	-0.1
440	0.225	-0.9	0.18	-0.5	0.0235	-0.9	0.0461	0.4	0.0998	-0.6	0.0674	-0.7	0.0547	-0.9
442	0.232	-0.8	0.221	0.3					0.121	0.1	0.099	0.9	0.082	0.6
444	0.337	0.7	0.256	1.0	0.031	0.1	0.047	0.5	0.132	0.5	0.097	0.8	0.076	0.3
446	0.155	-1.8	0.24	0.7	0.036	0.8	0.048	0.6			0.1	1.0	0.085	0.8
448	0.413	1.8	0.289	1.7	0.034	0.5	0.042	0.0	0.136	0.6	0.081	0.0	0.077	0.3
450	0.335	0.7	0.214	0.2	0.028	-0.3	0.04	-0.2	0.14	0.7	0.125	2.2	0.083	0.7
452	0.3334	0.7	0.228	0.5			0.0414	0.0					0.0746	0.2

Table 11d. Results for fenpropidin, fluopyram, metrafenone, prosulfocarb, prothioconazole-desthio, pyraclostrobin and tebuconazolein mg/kg, and the corresponding z scores, MRRLs and the assigned values.

Laboratory code	Fenpropidin	Z score (FFP RSD (25%)	Fluopyram	Z score (FFP RSD (25%)	Metrafenone	Z score (FFP RSD (25%)	Prosulfocarb	Z score (FFP RSD (25%)	Prothioconazole-desthio	Z score (FFP RSD (25%)	Pyraclostrobin	Z score (FFP RSD (25%)	Tebuconazole	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.286**		**0.204**		**0.03**		**0.042**		**0.119**		**0.081**		**0.071**	
454			0.221	0.3	0.037	0.9	0.042	0.0	0.124	0.2	0.116	1.8	0.079	0.5
456	0.455	2.4	0.244	0.8	0.044	1.9	0.05	0.8	0.153	1.2	0.131	2.5	0.102	1.7
458	0.286	0.0	0.196	-0.2	0.0278	-0.3	0.0514	0.9	0.134	0.5	0.0614	-1.0	0.0696	-0.1
460	0.221	-0.9	0.17	-0.7	0.023	-0.9	0.033	-0.8	0.114	-0.2	0.079	-0.1	0.069	-0.1
462					0.032	0.3					0.073	-0.4	0.093	1.2
464	0.305	0.3	0.226	0.4	0.024	-0.8	0.044	0.2	0.116	-0.1	0.083	0.1	0.066	-0.3
466	0.243	-0.6	0.201	-0.1	0.0381	1.1	0.051	0.9	0.115	-0.1	0.101	1.0	0.0843	0.7
468											0.073	-0.4	0.072	0.1
470	0.223	-0.9	0.171	-0.6	FN	-3.0	0.0085	-3.2	0.117	-0.1	0.064	-0.8	0.047	-1.4
472	0.108	-2.5	0.124	-1.6	0.019	-1.5	0.027	-1.4	0.071	-1.6	0.062	-0.9	0.048	-1.3
474	0.51	3.1	0.2	-0.1	0.053	3.1	0.074	3.1	0.22	3.4	0.124	2.2	0.105	1.9
476	0.292	0.1	0.207	0.1	0.0325	0.3	0.0401	-0.1	0.135	0.6	0.0765	-0.2	0.0727	0.1
478	0.271	-0.2	0.214	0.2	0.0278	-0.3	0.0413	0.0	0.0918	-0.9	0.0751	-0.3	0.0729	0.1
480	0.38	1.3	0.26	1.1	0.036	0.8					0.09	0.5	0.07	-0.1
482	0.3	0.2	0.19	-0.3	0.03	0.0	0.04	-0.2	0.09	-1.0	0.09	0.5	0.07	-0.1
484	0.338	0.7	0.222	0.4			0.07	2.7			0.097	0.8	0.076	0.3
486											0.078	-0.1	0.849	>5
488														
490											0.085	0.2	0.075	0.2
492	0.301	0.2	0.23	0.5	0.027	-0.4	0.047	0.5	0.13	0.4	0.088	0.4	0.076	0.3
494							0.052	1.0			0.097	0.8	0.066	-0.3
496	0.375	1.2	0.22	0.3	0.033	0.4	0.039	-0.2			0.07	-0.5	0.08	0.5
498														
500	0.282	-0.1	0.196	-0.2	0.028	-0.3	0.041	-0.1	0.12	0.0	0.078	-0.1	0.075	0.2
502	0.35	0.9	0.28	1.5	0.05	2.7	0.05	0.8	0.15	1.1	0.09	0.5	0.09	1.1
504	FN	-3.9	0.164	-0.8	FN	-3.0			0.109	-0.3	0.0708	-0.5	0.0631	-0.4
506													0.0766	0.3
508			0.26	1.1							0.098	0.9	0.105	1.9
510	0.262	-0.3	0.212	0.2	0.0226	-1.0	0.0373	-0.4	0.115	-0.1	0.0687	-0.6	0.0609	-0.6
512	0.218	-0.9	0.206	0.0	0.03	0.0					0.112	1.6	0.074	0.2
514	0.3	0.2	0.2	-0.1	0.031	0.1	0.035	-0.6	0.12	0.0	0.067	-0.7	0.063	-0.5
516	0.294	0.1	0.214	0.2	0.029	-0.1	0.031	-1.0	0.106	-0.4	0.092	0.6	0.067	-0.2
518	0.289	0.0	0.182	-0.4	0.033	0.4	0.04	-0.2	0.111	-0.3	0.075	-0.3	0.079	0.5
520	FN	-3.9	FN	-3.8	FN	-3.0	FN	-3.0	FN	-3.7	0.065	-0.8	0.069	-0.1
894	0.267	-0.3	0.124	-1.6	0.019	-1.5	0.031	-1.0	0.086	-1.1	0.062	-0.9	0.057	-0.8

Table 12a. Results for the voluntary pesticides HCH-alpha, quintozene and spinetoram in mg/kg, and the corresponding z scores, MRRLs and the assigned values. Also results for cypermethrin, deltamethrin-cis and lambda-cyhalothrin are shown. The z scores for cypermethrin are only for informative purposes.

Laboratory code	HCH-alpha	Z score (FFP RSD (25%)	Quintozene	Z score (FFP RSD (25%)	Spinetoram	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Deltamethrin, cis-	Z score (FFP RSD (25%)	Lambda-cyhalothrin	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.034**		**0.056**		**0.108**		**0.025**		**0.009**		**0.01**	
200	0.031	-0.4	0.061	0.3			0.022	-0.5				
202	0.037	0.3	0.061	0.3			0.018	-1.2				
204	0.0346	0.0	0.0583	0.1			0.023	-0.4			0.01	
206	0.035	0.1										
208	0.0293	-0.6	FN	-3.3	0.109	0.0	0.023	-0.4	0.0059		0.0083	
210	0.035	0.1	0.079	1.6	0.105	-0.1	0.026	0.1				
212	0.035	0.1										
214	0.0372	0.3					0.027	0.3			0.0127	
216	0.0335	-0.1	FN	-3.3	0.113	0.2	0.03	0.7				
218	0.0353	0.1	0.0579	0.1	0.111	0.1	0.036	1.7				
220	0.032	-0.3	0.057	0.0			0.024	-0.2				
224	0.035	0.1	0.051	-0.4			0.035	1.5				
226	0.028	-0.7	0.051	-0.4	0.0993	-0.3	0.025	-0.1	0.0055		0.0055	
228												
230	0.042	0.9	0.057	0.0			0.027	0.3				
232					0.119	0.4	0.032	1.0			0.0142	
234												
236	0.0253	-1.0			FN	-3.6	0.022	-0.5				
238			0.052	-0.3								
240	0.013	-2.5	0.023	-2.4			0.01	-2.4			0.002	
242												
244	0.037	0.3	0.067	0.8	0.11	0.1	0.031	0.9			0.011	
246	0.032	-0.3	0.046	-0.7	0.094	-0.5	0.016	-1.5				
248	0.0377	0.4	0.0623	0.4	0.0943	-0.5	0.031	0.9			0.0117	
250	0.0336	-0.1	0.0687	0.9			0.021	-0.7	0.0065		0.0095	
252	0.032	-0.3										
254	0.0336	-0.1	0.0579	0.1	0.0971	-0.4	0.026	0.1	0.0065		0.0079	
256	0.0336	-0.1	0.054	-0.2	0.117	0.3	0.03	0.8			0.0109	
258											0.0112	
260			0.094	2.7			0.05	3.9				
262	0.0323	-0.2	0.053	-0.2	0.1163	0.3	0.024	-0.2				
264	0.034	0.0	0.065	0.6			0.027	0.3				
266	0.044	1.1	0.055	-0.1	0.183	2.8	0.017	-1.3	0.01		0.009	
268							0.013	-1.9			0.008	
270	0.0284	-0.7	0.0475	-0.6			0.022	-0.5				
272							0.021	-0.7			0.0154	
274	0.036	0.2	0.048	-0.6	0.11	0.1	0.027	0.3				
276	0.033	-0.1	0.05	-0.4			0.026	0.1	0.008		0.008	
278	0.029	-0.6	0.054	-0.2								
280											0.0126	
282	0.052	2.1					0.028	0.4				

Table 12b. Results for the voluntary pesticides HCH-alpha, quintozene and spinetoram in mg/kg, and the corresponding z scores, MRRLs and the assigned values. Also results for cypermethrin, deltamethrin-cis and lambda-cyhalothrin are shown. The z scores for cypermethrin are only for informative purposes.

Laboratory code	HCH-alpha	Z score (FFP RSD (25%)	Quintozene	Z score (FFP RSD (25%)	Spinetoram	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Deltamethrin, cis-	Z score (FFP RSD (25%)	Lambda-cyhalothrin	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.034**		**0.056**		**0.108**		**0.025**		**0.009**		**0.01**	
284									0.016			
288	0.037	0.3										
290							0.026	0.1				
292	0.033	-0.1	0.058	0.1	0.24	4.9	0.024	-0.2	0.005		0.007	
294	0.039	0.6	0.059	0.2	0.158	1.9	0.029	0.6	0.011		0.011	
296	0.0401	0.7									0.0115	
298	0.036	0.2	0.065	0.6	0.114	0.2	0.023	-0.4				
300	0.031	-0.4	0.0406	-1.1	0.115	0.3	0.02	-0.8				
302	0.033	-0.1	0.056	0.0	0.058	-1.8	0.024	-0.2	0.019		0.014	
304	0.0202	-1.6	FN	-3.3								
306	0.034	0.0	0.0685	0.9			0.022	-0.5	0.0062		0.0087	
308	0.042	0.9	0.073	1.2	0.121	0.5	0.023	-0.4	0.01		0.011	
310	0.0269	-0.9			0.0797	-1.0	0.018	-1.2				
312	0.041	0.8									0.011	
314	0.024	-1.2	0.044	-0.9			0.032	1.1	0.012		0.007	
316	0.0358	0.2	0.0613	0.4	0.108	0.0	0.028	0.4				
318							0.024	-0.2				
320	0.023	-1.3	0.044	-0.9			0.016	-1.5				
322	0.0389	0.5	0.056	0.0	0.0925	-0.6	0.026	0.0				
324	0.0332	-0.1	FN	-3.3								
326	0.04	0.7	0.066	0.7	0.113	0.2	0.029	0.6				
328	0.029	-0.6	0.045	-0.8	0.118	0.4	0.025	0.0				
330	0.045	1.3	0.078	1.5	0.096	-0.4	0.022	-0.5				
332	0.0364	0.3	0.0663	0.7	0.1493	1.5	0.03	0.7	0.0082		0.0105	
334	0.0348	0.1	0.0635	0.5			0.023	-0.4				
336	0.035	0.1	0.041	-1.1	0.061	-1.7	0.03	0.7	0.013		0.014	
338	0.046	1.4	0.063	0.5	0.122	0.5	0.043	2.8			0.012	
340	0.0311	-0.4	0.0842	2.0			0.018	-1.2				
342												
344	0.034	0.0	0.053	-0.2			0.024	-0.2				
348	0.038	0.4	0.064	0.5			0.026	0.1				
350	0.0357	0.2					0.034	1.4	0.0102		0.0206	
352	0.0259	-1.0	0.0534	-0.2	0.0874	-0.8	0.02	-0.8			0.0102	
354	0.037	0.3	0.065	0.6	0.125	0.6	0.027	0.3				
356							0.021	-0.7				
358	0.016	-2.1	0.025	-2.2	0.035	-2.7	0.01	-2.4			0.004	
360			0.0657	0.7	0.117	0.3	0.027	0.2			0.012	
362	0.0377	0.4	0.0513	-0.4	0.102	-0.2	0.029	0.6			0.0063	
364	0.029	-0.6	0.044	-0.9	0.095	-0.5	0.017	-1.3				
366	0.0303	-0.5	0.0421	-1.0	0.0872	-0.8	0.022	-0.5				
368	0.0039	-3.5										

Table 12c. Results for the voluntary pesticides HCH-alpha, quintozene and spinetoram in mg/kg, and the corresponding z scores, MRRLs and the assigned values. Also results for cypermethrin, deltamethrin-cis and lambda-cyhalothrin are shown. The z scores for cypermethrin are only for informative purposes.

Laboratory code	HCH-alpha	Z score (FFP RSD (25%)	Quintozene	Z score (FFP RSD (25%)	Spinetoram	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Deltamethrin, cis-	Z score (FFP RSD (25%)	Lambda-cyhalothrin	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.034**		**0.056**		**0.108**		**0.025**		**0.009**		**0.01**	
370	0.0334	-0.1	0.0566	0.0	0.109	0.0	0.047	3.5				
372							0.028	0.4				
374							0.025	0.0	0.008			
376							0.025	0.0			0.01	
378	0.0392	0.6	0.0726	1.2	0.102	-0.2	0.022	-0.6				
380	0.046	1.4	0.061	0.3	0.135	1.0	0.025	0.0				
382	0.029	-0.6					0.027	0.3				
384	FN	-2.8										
386	0.0363	0.2	0.0571	0.1			0.024	-0.2			0.01	
388	0.028	-0.7	0.058	0.1			0.024	-0.2				
392	0.039	0.6	0.053	-0.2			0.029	0.6	0.01		0.01	
394	0.035	0.1	0.052	-0.3	0.072	-1.3	0.026	0.1	0.005		0.006	
396	0.021	-1.5	FN	-3.3								
398	0.027	-0.8	0.052	-0.3			0.023	-0.4				
400	0.0192	-1.8	0.0383	-1.3			0.018	-1.1				
402												
404	0.0278	-0.8	0.0542	-0.1			0.04	2.3				
406	0.033	-0.1					0.023	-0.4	0.01			
408			0.033	-1.7			0.02	-0.8			0.01	
410	0.042	0.9	0.072	1.1			0.031	0.9	0.014			
412	0.0282	-0.7	0.0458	-0.7	0.125	0.6	0.023	-0.3				
414	0.036	0.2			0.105	-0.1	0.026	0.1	0.008		0.008	
416	0.04	0.7	0.06	0.3	0.11	0.1	0.024	-0.2	0.01		0.01	
418												
420	0.037	0.3	0.071	1.0	0.09	-0.7						
422												
424							0.065	>5			0.015	
426			0.0327	-1.7	0.1031	-0.2	0.011	-2.3				
428	0.041	0.8	0.0487	-0.5	0.101	-0.2	0.024	-0.2				
430	0.034	0.0									0.011	
432	0.0392	0.6	0.0444	-0.8			0.023	-0.3				
434					0.14	1.2	0.028	0.4	0.011		0.01	
436												
438	0.032	-0.3	0.05	-0.4			0.026	0.1	0.0084		0.0089	
440	0.0324	-0.2	0.0488	-0.5	0.107	0.0	0.033	1.2				
442												
444	0.031	-0.4					0.025	0.0			0.0075	
446	0.027	-0.8	0.036	-1.4	0.09	-0.7	0.03	0.7				
448	0.032	-0.3	0.052	-0.3	0.118	0.4	0.026	0.1	0.009		0.01	
450	0.03	-0.5	0.045	-0.8			0.03	0.7				
452			0.0531	-0.2			0.022	-0.5			0.0117	

Table 12d. Results for the voluntary pesticides HCH-alpha, quintozene and spinetoram in mg/kg, and the corresponding z scores, MRRLs and the assigned values. Also results for cypermethrin, deltamethrin-cis and lambda-cyhalothrin are shown. The z scores for cypermethrin are only for informative purposes.

Laboratory code	HCH-alpha	Z score (FFP RSD (25%)	Quintozene	Z score (FFP RSD (25%)	Spinetoram	Z score (FFP RSD (25%)	Cypermethrin	Z score (FFP RSD (25%)	Deltamethrin, cis-	Z score (FFP RSD (25%)	Lambda-cyhalothrin	Z score (FFP RSD (25%)
MRRL	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Assigned value	**0.034**		**0.056**		**0.108**		**0.025**		**0.009**		**0.01**	
454	0.032	-0.3	0.051	-0.4			0.03	0.7				
456	0.045	1.3	0.079	1.6			0.052	4.2	0.01		0.013	
458	0.0402	0.7	0.0608	0.3	0.12	0.5	0.029	0.6				
460	0.035	0.1	0.061	0.3			0.03	0.7	0.006		0.007	
462							0.021	-0.7				
464	0.033	-0.1	0.055	-0.1			0.027	0.3	0.01		0.014	
466	0.04	0.7	0.0687	0.9	0.088	-0.7	0.027	0.3	0.008		0.01	
468							0.021	-0.7				
470	0.029	-0.6					0.02	-0.8				
472	0.018	-1.9	0.037	-1.4	0.073	-1.3	0.012	-2.1				
474	0.049	1.7	0.092	2.5			0.037	1.9	0.011		0.012	
476	0.0302	-0.5	0.048	-0.6	0.12	0.5	0.023	-0.4				
478	0.0419	0.9	0.0669	0.8	0.11	0.1	0.023	-0.4				
480	0.035	0.1	0.06	0.3	0.112	0.2	0.028	0.4	0.008		0.012	
482	0.03	-0.5	0.04	-1.2	0.11	0.1					0.01	
484	0.029	-0.6					0.025	0.0				
486	0.034	0.0					0.024	-0.2				
488	0.055	2.4										
490							0.02	-0.8				
492	0.035	0.1	0.056	0.0	0.119	0.4	0.022	-0.5	0.0096		0.01	
494	0.037	0.3					0.022	-0.5				
496	0.036	0.2	0.048	-0.6	0.103	-0.2	0.029	0.6				
498	0.031	-0.4										
500	0.044	1.1	0.084	2.0	0.217	4.1	0.034	1.4			0.013	
502	0.035	0.1	0.051	-0.4	0.12	0.5	0.03	0.7				
504							0.026	0.1				
506	0.048	1.6	0.063	0.5			0.058	>5				
508	0.033	-0.1	0.063	0.5			0.031	0.9	0.016			
510	0.0327	-0.2	0.0542	-0.1	0.108	0.0	0.03	0.7	0.0088		0.0088	
512							0.027	0.3	0.01		0.012	
514	0.028	-0.7	0.055	-0.1	0.09	-0.7	0.023	-0.4				
516	0.039	0.6	0.066	0.7	0.071	-1.4	0.019	-1.0			0.006	
518	0.043	1.0	0.074	1.3	0.11	0.1	0.014	-1.8			0.011	
520	0.037	0.3	0.062	0.4	0.11	0.1	0.021	-0.7			0.012	
894	0.027	-0.8	0.058	0.1	0.121	0.5	0.026	0.1	0.006		0.011	

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

To be classified into Category A, the laboratories had to submit quantitative results for at least 90 % of the compulsory pesticides present in the Test Item (≥13 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 88 EU and EFTA laboratories in Category A (58%), the results were additionally evaluated by calculating the Average of the Squared -Score (AZ^2). Of the 88 participants, 80 participants (91%) obtained AZ^2 values at or below 2 (good) and 5 participants (5.7%) obtained AZ^2 values between 2-3 (satisfactory) and 3 participants (3.4%) obtained AZ^2 values ≥3 (unsatisfactory). An additional one laboratory from Third Countries were evaluated and classified into Category A. The AZ^2 scores achieved by the labs can be seen in **Table 13.**

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

Lab code	No. of detected compulsory pesticides	No. of detected voluntary pesticides	AZ^2	No. Of False negative	Classification	NRL
200	15	2	0.4	0	Good	
202	14	2	0.0	0	Good	NRL-FE
208	14	3	0.2	1	Good	
210	15	3	0.4	0	Good	NRL-CF
216	14	3	0.5	1	Good	
218	15	3	0.1	0	Good	NRL-CF
220	15	2	0.9	0	Good	NRL-CF
224	15	2	0.7	0	Good	
226	15	3	0.7	0	Good	NRL-CF
244	15	3	1.1	0	Good	NRL-CE
246	15	3	0.2	0	Good	
248	15	3	0.5	0	Good	
254	15	3	0.5	0	Good	
256	15	3	0.1	0	Good	
262	15	3	0.5	0	Good	
264	15	2	0.8	0	Good	
266	15	3	0.3	0	Good	
270	13	2	1.7	1	Good	NRL-CF
274	15	3	0.5	0	Good	
292	15	3	0.2	0	Good	
294	15	3	1.9	0	Good	
298	15	3	1.7	0	Good	NRL-CF
300	14	3	0.2	0	Good	
302	14	3	1.7	1	Good	
308	15	3	0.2	0	Good	
314	14	2	0.9	0	Good	
316	15	3	0.1	0	Good	

Lab code	No. of detected compulsory pesticides	No. of detected voluntary pesticides	AZ[2]	No. Of False negative	Classification	NRL
322	15	3	0.2	0	Good	
326	15	3	0.2	0	Good	
328	15	3	0.1	0	Good	
330	15	3	0.2	0	Good	
332	15	3	0.3	0	Good	
336	14	3	2.6	0	Satisfactory	
338	15	3	0.4	0	Good	NRL-CF
340	13	2	2.5	1	Satisfactory	
344	15	2	0.1	0	Good	
348	15	2	0.1	0	Good	
352	15	3	1.9	0	Good	NRL-CE
354	15	3	0.2	0	Good	NRL-CF
358	15	3	>5	0	Unsatisfactory	
360	15	2	0.1	0	Good	
362	15	3	0.1	0	Good	NRL-CF
364	15	3	0.6	0	Good	NRL-CF
366	15	3	0.7	0	Good	NRL-CF
370	15	3	0.1	0	Good	
372	15	0	0.7	0	Good	
374	13	0	0.2	0	Good	NRL-CE
378	15	3	0.1	0	Good	
380	15	3	0.6	0	Good	
382	15	1	1.0	0	Good	
386	15	2	0.3	0	Good	NRL-FE
388	15	2	0.9	0	Good	NRL-CF
392	15	2	0.3	0	Good	NRL-CE
394	15	3	0.3	0	Good	
396	14	2	1.5	1	Good	NRL-FE
398	15	2	0.3	0	Good	NRL-CF
404	15	2	0.1	0	Good	
406	13	1	0.1	0	Good	
412	15	3	0.5	0	Good	
416	15	3	0.3	0	Good	
420	14	3	0.6	0	Good	
426	14	2	0.6	0	Good	
428	15	3	0.2	0	Good	
432	15	2	0.2	0	Good	NRL-CE
440	15	3	0.3	0	Good	NRL-CF

Lab code	No. of detected compulsory pesticides	No. of detected voluntary pesticides	AZ^2	No. Of False negative	Classification	NRL
444	15	1	0.3	0	Good	NRL-FE
446	14	3	1.0	0	Good	NRL-CF
448	15	3	0.8	0	Good	
454	14	2	0.6	0	Good	NRL-CF
456	15	2	3.7	0	Unsatisfactory	
458	15	3	0.2	0	Good	
460	14	2	0.9	1	Good	NRL-CF
464	13	2	0.9	1	Good	
466	15	3	0.3	0	Good	NRL-CE
470	13	1	2.4	1	Satisfactory	
472	13	3	2.1	0	Satisfactory	
474	14	2	>5	0	Unsatisfactory	
476	15	3	0.3	0	Good	
478	15	3	0.1	0	Good	
482	14	3	0.2	0	Good	
492	14	3	1.0	1	Good	
496	13	3	1.4	0	Good	
500	15	3	1.7	0	Good	
502	15	3	2.8	0	Satisfactory	
510	15	3	0.3	0	Good	
514	14	3	1.4	1	Good	
516	15	3	0.5	0	Good	
518	15	3.0	0.2	0	Good	
894	15	3.0	0.8	0	Good	

The laboratories that did not fulfil the requirements described above, were classified in Category B. The number of reported quantitative results, analysed compounds from the Target List and acceptable z scores as well as information on false negative and positive results are shown in **Table 14.** Two participants fulfilled the criteria of detecting 90 % of the compulsory pesticides in the Test Item but did not fulfil the criteria of analysing for 90 % of the compulsory pesticides on the Target List. The reverse was the case for four participants. Forty-four participants (28%) analysed and detected less than 70% of the pesticides present in the Test Item.

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

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected, %	Analysed of compulsory pesticides on Target List, %	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
204	12	80	95	2	12	0	0	
206	0	0	4	1	0	0	0	
212	0	0	4	1	0	0	0	
214	7	47	41	1	7	0	0	
228	8	53	61	0	8	0	0	
230	12	80	78	2	12	0	0	
232	11	73	83	1	11	0	0	
234	10	67	67	0	10	0	0	
236	8	53	66	2	5	1	0	
238	2	13	35	1	2	0	0	
240	10	73	72	2	9	1	0	
242	6	40	41	0	6	0	0	
250	0	0	32	2	0	0	0	NRL-CF
252	6	60	72	1	5	3	0	
258	7	47	44	0	7	0	0	
260	3	20	37	1	2	0	0	
268	5	33	44	0	5	0	0	
272	7	47	44	0	7	0	0	
276	11	73	65	2	11	0	0	
278	7	47	64	2	7	0	0	
280	7	47	46	0	7	0	0	
282	7	73	75	1	7	4	0	
284	3	20	24	0	3	0	0	
288	0	0	4	1	0	0	0	
290	11	73	91	0	10	0	0	NRL-CF
296	7	47	44	1	7	0	0	
304	0	67	74	2	0	11	0	
306	0	0	18	2	0	0	0	
310	7	53	77	2	6	1	0	

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected, %	Analysed of compulsory pesticides on Target List, %	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
312	7	47	46	1	7	0	0	
318	10	67	66	0	9	0	0	
320	11	73	91	2	10	0	0	
324	10	67	70	2	10	1	0	NRL-FE
334	4	27	42	2	4	0	0	NRL-CF
342	7	47	43	0	5	0	0	
350	3	27	41	1	0	1	0	NRL-CF
356	13	87	76	0	13	0	0	
368	7	47	78	1	5	0	2	
376	6	53	74	0	6	2	0	
384	0	0	18	1	0	1	0	
400	8	53	44	2	8	0	0	NRL-FE
402	0	0	49	0	0	0	0	
408	6	40	59	1	6	0	0	
410	12	80	88	2	12	0	0	
414	7	47	73	2	7	0	0	
418	0	0	63	0	0	0	0	
422	10	73	84	0	9	1	0	
424	6	40	67	0	6	0	0	
430	7	47	44	1	7	0	0	
434	12	80	86	1	12	0	0	NRL-CE
436	0	0	36	0	0	0	0	NRL-CE
438	11	73	84	2	11	0	0	
442	11	73	65	0	10	0	0	
450	14	93	89	2	13	0	0	
452	7	47	58	1	7	0	0	
462	7	47	63	0	7	0	0	
468	6	40	59	0	6	0	0	
480	11	73	89	3	11	0	0	
484	8	53	78	1	7	0	0	
486	7	47	59	1	4	0	0	
488	0	0	4	1	0	0	0	
490	4	27	53	0	4	0	0	
494	7	47	61	1	7	0	0	
498	0	0	4	1	0	0	0	
504	8	67	76	0	8	2	0	NRL-CF
506	3	20	36	2	3	0	0	
508	8	60	80	2	7	1	0	

Lab code	No. of compulsory pesticides detected	Compulsory pesticides detected, %	Analysed of compulsory pesticides on Target List, %	No. Of voluntary pesticides detected	No. of acceptable z score	No. of false negative	No. of false positive	NRL
512	9	73	73	0	9	2	0	
520	8	100	100	3	8	7	1	

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. In EUPT-C3 in 2009 102 labs participated and in the latest EUPT-CF13 149 labs participated. The numbers from EUPT-C5 and forward can be seen in **Table 15**. The number of pesticides included in the Target Pesticide List has also increased during this 12-years period, from 43 to 160 compulsory compounds and 32 voluntary compounds. The number of spiked or incurred pesticides contained in the Test Items has in the same period increased from 13 to 18 (two of them not evaluated in this EUPT-CF13). Thus, the demands put on the participating laboratories has increased every year. Many laboratories have a limited scope and are therefore not able to cover all pesticides in the PT. Of the laboratories submitting results, 25 % submitted results for less than 70% of pesticides present in the Test Item.

Table 15. Overall trends in participation of laboratories, pesticides in the target list and test item, and performance of laboratories in the 7 latest EUPTs cereals (excluding EUPT-CF7 on feed and EUPT-CF12 on hay).

PT and type of test item	EUPT-C5 Rice flour	EUPT-C6 Barley flour	EUPT-CF8 Wheat flour	EUPT-CF9 Maize flour	EUPT-CF10 Rye flour	EUPT-CF11 Oat flour	EUPT-CF13 Rye kernels
Participants submitting results (EU + EFTA)	133	127	142	143	160	149	149
MRM pesticides in the Target Pesticide List	103	107	111	117	134/7	153/9	160/32
MRM pesticides in the test material	16	18	17	18	16	18	18
No. of results for MRM pesticides	1521	1741	1893	2012	2012	2172	2007
Average of 'reported results', %	71	76	78	78	79	83	75
Range of 'reported results', %	41-95	50-95	49-93	61-94	58-90	65-93	44-94
Acceptable z scores, %	87	90	90	89	95	89	93
Questionable z scores, %	4	5	6	2	2	3	3.1
Unacceptable z scores, %	9	4	4	3	2	8	3.4
False negatives, %	3	1	3	2	2	4	2.3
Number of false positives	16	2	4	9	0	19	3
Category A, % of participating laboratories	44	55	50	57	53	45	57
Good SWZ/AZ^2, %	80	79	85	96	93	92	91
Satisfactory SWZ/AZ^2, %	15	14	10	1	5	1.5	5.7
Unsatisfactory SWZ/AZ^2, %	5	7	4	3	2	6.2	3.4

As for previous years an improvement was seen in the overall analytical performance (accuracy of measurement) if looking at the percentage of acceptable, questionable, unacceptable z scores, while this was not the case for the analytical scope. The average % of reported results has in the last four cereal EUPT-CF been between 75-83%. This was because a lot of participants analysed for less than 50% of the pesticide residues present in the test Item. The false negative results has been relatively low, for the last PT it was only 2.3% of the results and 3 positive results were reported.

The percentage of Category A laboratories has varied slightly and this year an improvement was seen as 57% of the participants were evaluated as Category A. For Category A an improvement in AZ^2 was seen in EUPT-CF9 where 96% of the results were Good, and in EUPT-CF13 still 91% of the laboratories were evaluated as Good. However, it is difficult to assess any improvement/deterioration in laboratory performance between the Proficiency Tests, because the number of pesticides in the Test item and the number of laboratories participating in the PTs have both significantly increased.

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

The EUPT-CF13 Test Item consisted of rye flour containing incurred and spiked pesticides. The rye crop had been sprayed in the field with commercially available pesticide formulations. The final Test Item contained the following pesticides: ametoctradin, azoxystrobin, bixafen, boscalid, carbendazim, chlorantraniliprole, epoxiconazole, etoxazole, fenpropidin, fluopyram, HCH-alpha, metrafenone, prosulfocarb, prothioconazole-desthio, pyraclostrobin, quintozene, spinetoram and tebuconazole. One hundred forty-nine laboratories, representing 31 EU and EFTA countries submitted results. Three more laboratories registered, but did not submit any results. All NRLs, except one from Slovakia, participated in the PT. Malta was represented in the PT by the NRL for the UK. An additional 6 laboratories 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 160 individual compulsory and 32 voluntary compounds..

The number of false positives and false negatives has varied between the EUPTs. Three false positive results were reported and the number of false negatives represented 2.3% of the total number of results. This is very similar to the percentage of false negatives reported in the previous EUPTs. The average Alg A-RSD was at 18%, well below the FFP-RSD of 25% with a range from 14-25% for the individual compounds.

For azoxystrobin, boscalid, carbendazim, epoxiconazole, fluopyram, HCH-alpha and tebuconazole acceptable results were obtained by 95-99% of the laboratories. For ametoctradin, bixafen, etoxazole, fenpropidin, metrafenone, prosulfocarb, prothioconazole-desthio, pyraclostrobin, quintozene and spinetoram acceptable results were obtained by 90-94% of the laboratories. Only 87% of the laboratories obtain acceptable z scores for chlorantraniliprole.

The EUPT-CF14 will be with rice as test item, which will be shipped to the laboratories in April/May 2020. The selection of pesticides will continue to be focused on pesticides included in the scope of the EU multi-annual coordinated control programme, as well as additional pesticides of relevance to feed and/or cereal production in Europe and in other parts of the world from where significant quantities of feed and cereals are imported.

4. ACKNOWLEDGEMENTS

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

5. REFERENCES

[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-

[7] Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. SANTE/11813/2017.
https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrkdoc_2017-11813.pdf

APPENDICES

Appendix 1 List of laboratories registered to participate in the EUPT-CF13

Participating labs from EU and EFTA member states

Country	Institution	City	NRL-CF	Report data
Austria	AGES Innsbruck - Institute for Food Safety/PLMA	Innsbruck	NRL-CF	Yes
Belgium	PRIMORIS (Phytolab) - Belgium	Gent - Zwijnaarde		Yes
Belgium	Sciensano	Brussels	NRL-CF	Yes
Bulgaria	CLCTC - Sofia | Pesticide Lab	Sofia		Yes
Bulgaria	Primoris Bulgaria AD - Pesticide Lab	Plovdiv		Yes
Croatia	Croatiakontrola - Pesticide Lab	Zagreb		Yes
Croatia	Croatian National Institute of Public Health-HZJZ	Zagreb	NRL-CE	Yes
Croatia	Dr. Andrija Štampar - Pesticide Lab	Zagreb		Yes
Croatia	Food Control Center, Faculty of Food Technology and Biotechnology	Zagreb		Yes
Croatia	Inspecto d.o.o. Laboratorij	Osijek		Yes
Croatia	Laboratorij za odredivanje rezidua/Hrvatski Veterinarski Institut	Zagreb	NRL-FE	Yes
Croatia	Nastavni Zavod za javno zdravstvo Primorsko-goranske županije	Rijeka		Yes
Cyprus	Animal Feeds and Feed Additives - Pesticide Lab	Nicosia	NRL-FE	Yes
Cyprus	Pesticide Residues Lab of S.G.L	Nicosia	NRL-CE	Yes
Czech Republic	Central Institute for Supervising and Testing in Agriculture	Brno	NRL-FE	Yes
Czech Republic	Czech Agriculture and Food Inspection Authority	Praha	NRL-CE	Yes
Czech Republic	VSCHT Praha	Praha		Yes
Denmark	Laboratoriet Ringsted - Pesticide Lab	Ringsted	NRL-FE	Yes
Estonia	Pesticide Lab (Saku)	Saku	NRL-CF	Yes
Finland	Finnish Customs Laboratory	Espoo	NRL-CE	Yes
Finland	Finnish Food Safety Authority (Evira)	Helsinki	NRL-FE	Yes
France	CAPINOV (Landerneau)	Landerneau		Yes
France	Centre d'Analyses Méditerranée Pyrénées	Perpignan		Yes
France	CERECO	Garons		Yes
France	GIRPA-FREDON Pays de la Loire - Pesticide Lab	Beaucouzé		Yes
France	INOVALYS - Le Mans	Le Mans		Yes
France	Phytocontrol (Nimes) - Pesticide Lab	Nimes		Yes
France	SCL - Massy Cedex	Massy Cedex	NRL-CF	Yes
France	SCL Laboratoire de Montpellier	Montpellier		Yes
Germany	Amt für Verbraucherschutz - PSM (Düsseldorf)	Düsseldorf		Yes
Germany	Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit	Erlangen		Yes
Germany	Bundeswehr - Pesticide Lab (Garching-Hochbrück)	Garching-Hochbrück		Yes
Germany	Chemisches und Veterinäruntersuchungsamt Rhein Ruhr Wupper	Krefeld		Yes
Germany	Chemisches und Veterinäruntersuchungsamt Stuttgart	Fellbach		Yes
Germany	Eurofins Dr. Specht Laboratorien GmbH	Hamburg		Yes
Germany	Federal Office of Consumer Protection and Food Safety, NRL for Pesticide Residues	Berlin	NRL-CF	Yes
Germany	Institut für Lebensmittelchemie Speyer	Speyer		Yes
Germany	LALLF - Pesticide Lab	Rostock		Yes
Germany	Landesamt für Verbraucherschutz Sachsen-Anhalt, FB Lebensmittel-sicherheit	Halle/Saale		Yes

Country	Institution	City	NRL-CF	Report data
Germany	Landeslabor Berlin-Brandenburg (LLBB)	Potsdam		Yes
Germany	Landeslabor Schleswig-Holstein	Neumünster		Yes
Germany	Landesuntersuchungsanstalt Sachesen Fachgebiet 2.5 - Pestizide	Dresden		Yes
Germany	LAVES - Pesticide Lab (Stade)	Stade		Yes
Germany	LLG Landesanstalt für Landwirtschaft und Gartenbau	Halle/Saale		Yes
Germany	LTZ Augustenberg	Karlsruhe		Yes
Germany	LUA Saarland - Pesticide Lab	Saarbrücken		Yes
Germany	LUFA Kiel - Pesticide Lab	Kiel		Yes
Germany	LUFA Speyer	Speyer		Yes
Germany	Niedersächsisches Landesamt für Verbraucherschutz und Lebens-mittelsicherheit, LVI Oldenburg	Oldenburg		Yes
Germany	Pesticide Lab (Jena)	Jena		Yes
Germany	Pesticide Lab (Kassel)	Kassel		Yes
Germany	Pesticide Lab (Nossen)	Nossen		Yes
Greece	BPI - Pesticide Lab (Kifissia)	Kifissia	NRL-CF	Yes
Greece	Pesticide Residues Laboratory/ General Chemical State Laboratory	Athens	NRL-CF	Yes
Greece	Regional Centre of Plant Protection, Quality & Phytosanitery Control	Thessaloniki		Yes
Hungary	Food Chain Safety Centre Non-profit Ltd. Pesticide Residue Analyti-cal Laboratory, Hódmezovásárhely	Hódmezovásárhely		Yes
Hungary	Food Chain Safety Centre Non-profit Ltd., Pesticide Residue Analyti-cal Laboratory, Szolnok	Szolnok		Yes
Hungary	NFCSO FCSLD Pesticide Analytical NRL	Velence	NRL-CF	Yes
Hungary	NFCSO Pesticide Lab	Miskolc		Yes
Iceland	Matís ohf. / Icelandic Food and Biotech R&D	Reykjavík	NRL-CF	Yes
Ireland	The Pesticide Control Laboratory	Co. Kildare	NRL-CF	Yes
Italy	APPA Bolzano	Bolzano		Yes
Italy	APPA-Puglia | Polo Alimenti Bari - Pesticide Lab	Bari		Yes
Italy	APPA-SL Trento - Pesticide Lab	Trento		Yes
Italy	ARPA FVG - Pesticide Lab	Udine		Yes
Italy	ARPA Lazio Latina	Latina		Yes
Italy	ARPA Marche	Macerata		Yes
Italy	ARPA VDA - Pesticide Lab	Saint Christophe		Yes
Italy	ARPA Veneto	Verona		Yes
Italy	ARPAE Ferrara	Ferrara		Yes
Italy	ARPAL Sez. di La Spezia	La Spezia		Yes
Italy	ATS Milano-Laboratorio di Prevenzione	Milano		Yes
Italy	ISS - Pesticide Lab	Roma		Yes
Italy	IZS LT - Pesticide Lab	Roma		Yes
Italy	IZS PB - Pesticide Lab	Foggia		Yes
Italy	IZS Sardegna - Pesticide Lab	Sassari		No
Italy	IZS Sicilia	Palermo		Yes
Italy	IZSAM - Pesticide Lab	Teramo		Yes
Italy	IZSLER - Pesticide Lab	Brescia		Yes
Italy	IZSLT Sezione di Firenze	Scandicci		Yes
Italy	IZSUM - Italy, Perugia	Perugia		Yes
Italy	IZSVe - Pesticide Lab	Legnaro (Padova)		Yes
Italy	Laboratorio Chimico Liguria	Genova	NRL-CF	Yes

Country	Institution	City	NRL-CF	Report data
Italy	Laboratorio di Prevenzione	Bergamo		Yes
Italy	Laboratorio di Sanità Pubblica USL Toscana Centro	Firenze		Yes
Latvia	BIOR - Pesticide Lab	Riga	NRL-CF	Yes
Lithuania	NMVRVI - Pesticide Lab	Vilnius	NRL-CF	Yes
Luxembourg	LNS Food lab	Dudelange	NRL-CE	Yes
Netherlands	Eurofins Lab Zeeuws-Vlaanderen B.V. - Pesticiden	Graauw		Yes
Netherlands	Handelslaboratorium Dr. Verwey - Pesticide Lab	Rotterdam		Yes
Netherlands	NofaLab - Pesticide Lab	Schiedam		Yes
Netherlands	NVWA - NRL for Pesticide Residues in Food and Feed	Wageningen	NRL-CF	Yes
Netherlands	RIKILT - Pesticide Lab	Wageningen		Yes
Norway	NIBIO, Department of Pesticides and Natural Products Chemistry	Ås	NRL-CF	Yes
Poland	InHort - Pesticide Lab	Skierniewice		Yes
Poland	IPP-NRI - Pesticide Lab (Poznan)	Poznan	NRL-FE	Yes
Poland	IPP-NRI - Pesticide Lab (Sosnicowice)	Sosnicowice		Yes
Poland	Laboratory of Food & Feed Safety in Bialystok	Bialystok		Yes
Poland	VSES Opole - Pesticide Lab	Opole		Yes
Poland	VSES Warszawa - Pesticide Lab	Warszaw	NRL-CE	Yes
Poland	WIW ZHW Gdansk -Pesticide Lab	Gdansk		Yes
Poland	WIW ZHW (Bialystok) - Pesticide Lab	Bialystok		Yes
Poland	WIW ZHW (Katowice) - Pesticide Lab	Katowice		Yes
Poland	WIW ZHW (Opole) - Pesticide Lab	Opole		Yes
Poland	WIW ZHW (Poznan) - Pesticide Lab	Poznan		Yes
Poland	WIW ZHW (Szczecin) - Pesticide Lab	Szczecin		Yes
Poland	WIW ZHW (Wroclaw) - Pesticide Lab	Wroclaw		Yes
Portugal	INIAV - Laboratório de Resíduos de Pesticidas(Oeiras)	Oeiras	NRL-CE	No
Portugal	Laboratório de Química	Oeiras - Lisboa		Yes
Portugal	Laboratório Regional de Veterinária e Segurança Alimentar	Funchal		Yes
Portugal	Vairão - Pesticide Lab (Plant Origin Products)	Vairão		Yes
Romania	DSVSA DOLJ, LSVSA DOLJ	Craiova		Yes
Romania	IISPV (Bucharest) - Pesticide Lab	Bucharest	NRL-CF	Yes
Romania	Laboratorul Reziduuri Pesticide / Directia Sanitara Veterinara si pentru Siguranta Alimentelor	Bucharest		Yes
Romania	LCCRPPP (Bucharest) - Pesticide Lab	Bucharest	NRL-CF	Yes
Romania	LRCRPPPV Mures	Tirgu Mures		Yes
Romania	Pesticides Residues Laboratory - Bistrita	Bistrita		Yes
Romania	Sanitary Veterinary and Food Safety Directorate Cluj, Gas-Chromatography Laboratory	Cluj Napoca		Yes
Slovakia	Pesticide Lab of PHA SR - Bratislava	Bratislava		Yes
Slovenia	NLZOH-MB	Ljubljana		Yes
Slovenia	Pesticide Lab – Maribor	Maribor	NRL-CE	Yes
Spain	Agricultural and Phytopathological Lab. of Galicia	Abegondo. A Coruña		Yes
Spain	Ainia	Valencia		Yes
Spain	Analytica Alimentaria GmbH - Almeria, Spain	Almeria		Yes
Spain	CNTA	San Adrián		Yes
Spain	Eurofins Ecosur - Pesticide Lab	Lorquí		Yes
Spain	Instituto Tecnológico de Canaria, S.A. laboratorio de Residuos.	Agüimes, Gran		Yes

Country	Institution	City	NRL-CF	Report data
	Departament de Análisis Ambiental	Canaria		
Spain	Laboratori Agència de Salut Pública de Barcelona	Barcelona		Yes
Spain	Laboratori Agroalimentari	Cabrils		Yes
Spain	Laboratorio Agroalimentario	Valencia		Yes
Spain	Laboratorio Agroalimentario de Extremadura	Cáceres		Yes
Spain	Laboratorio Agroambiental de Zaragoza	Zaragoza		Yes
Spain	Laboratorio Analítico Bioclínico	Almeria		Yes
Spain	Laboratorio Arbitral Agroalimentario	Madrid	NRL-CF	Yes
Spain	Laboratorio de la Direccion Provincial de Sanidad de Cuenca	Cuenca		Yes
Spain	Laboratorio de Salud Pública de Galicia	Lugo		No
Spain	Laboratorio del SOIVRE	Almería		Yes
Spain	Laboratorio Kudam, S.L.	Alicante		Yes
Spain	Laboratorio Regional Agroaalimentario y Ambiental de Castilla la Mancha (Laraga)	Toledo		Yes
Spain	Laboratorio Regional de la CCAA de La Rioja	Logroño		Yes
Spain	Laboratorio Salud Pública de Badajoz	Badajoz		Yes
Spain	Labs & Technological Services AGQ	Burguillos		Yes
Spain	Nasertic	Villava		Yes
Spain	Pesticide Lab (Majadahonda)	Majadahonda	NRL-CF	Yes
Spain	Salud Publica (LSP - Madrid Salud)	Madrid		Yes
Spain	SOIVRE Tenerife	Santa Cruz de Tenerife		Yes
Sweden	Eurofins Food & Feed Sweden AB	Lidköping		Yes
Sweden	Swedish National Food Agency	Uppsala	NRL-CF	Yes
Switzerland	Kantonales Labor Zürich	Zürich		Yes
United Kingdom	AFBI - Pesticide Lab	Belfast		Yes
United Kingdom	Fera Science Ltd	York	NRL-CF	Yes

Participating labs from EU candidate states and other non EU countries

Country	Institution	City	Report data
Serbia	Center for Food Analysis (Belgrade)	Belgrade	Yes
Serbia	Institute of Public Health of Belgrade	Belgrade	Yes
Serbia	SP Laboratorija - Pesticide Lab	Bejec	Yes
Singapore	Agri-food Authority of Singapore - Pesticide Lab	Singapore	Yes
Thailand	Central Laboratory - Pesticide Lab (Bangkok)	Bangkok	Yes
Uruguay	GACT, Pharmacognody& DQL UdelaR	Montevideo	Yes

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
Acetamiprid	0.01
Acrinathrin	0.01
Aldrin	0.01
Ametoctradin	0.01
Azinphos-methyl	0.01
Azoxystrobin	0.01
Bifenthrin	0.01
Biphenyl	0.01
Bixafen	0.01
Boscalid	0.01
Bromuconazole	0.01
Buprofezin	0.01
Cadusafos	0.01
Carbaryl	0.01
Carbendazim	0.01
Carbofuran	0.01
Carbofuran, 3-hydroxy-	0.01
Carboxin	0.01
Chlorantraniliprole	0.01
Chlorfenapyr	0.01
Chlorfenvinphos	0.01
Chlorpropham	0.01
Chlorpyrifos	0.01
Chlorpyrifos-methyl	0.01
Clothianidin	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	0.01
Diazinon	0.01
Dichlorvos	0.01
Dieldrin	0.01
Difenoconazole	0.01
Diflubenzuron	0.01
Dimethoate	0.01
Dimethomorph	0.01
Diniconazole	0.01
Endosulfan, alpha-	0.01
Endosulfan, beta-	0.01
Endosulfan-sulfate	0.01

Pesticides	MRRL (mg/kg)
Epoxiconazole	0.01
Ethion	0.01
Ethirimol	0.01
Ethoprophos	0.01
Etoxazole	0.01
Famoxadone	0.01
Fenbuconazole	0.01
Fenhexamid	0.01
Fenitrothion	0.01
Fenpropathrin	0.01
Fenpropidin	0.01
Fenpropimorph	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 and Esfenvalerate (Sum of RR/SS and RS/SR isomers)	0.01
Fipronil	0.01
Fipronil sulfone	0.01
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	0.01
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
Metalaxyl	0.01
Metconazole	0.01

Pesticides	MRRL (mg/kg)
Methacrifos	0.01
Methamidophos	0.01
Methomyl	0.01
Metolachlor	0.01
Metrafenone	0.01
Metribuzin	0.01
Omethoate	0.01
Oxydemeton-methyl	0.01
Paclobutrazol	0.01
Parathion	0.01
Penconazole	0.01
Pencycuron	0.01
Pendimethalin	0.01
Permethrin (sum of isomers)	0.01
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	0.01
Propiconazole	0.01
Prosulfocarb	0.01
Prothioconazole-desthio	0.01
Prothiofos	0.01
Pyraclostrobin	0.01
Pyridaben	0.01
Pyrimethanil	0.01
Pyriproxyfen	0.01
Quinoxyfen	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
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

Pesticides	MRRL (mg/kg)
Thiodicarb	0.01
Thiophanate-methyl	0.01
Tolclofos-methyl	0.01
Triadimefon	0.01
Triadimenol	0.01
Triazophos	0.01
Tricyclazole	0.01
Trifloxystrobin	0.01
Trifluralin	0.01
Triticonazole	0.01
Vinclozolin (parent compound only)	0.01
Zoxamide	0.01
Voluntary Compounds	
(will not be considered in Category A/B classification)	
Benalaxyl (sum of isomers)	0.01
Benzovindiflupyr	0.01
Chlordane, cis-	0.01
Chlordane, oxy-	0.01
Chlordane, trans-	0.01
Chlorfluazuron	0.01
Clomazone	0.01
Cyflufenamid	0.01
DDD, p,p'-	0.01
DDE, p,p'-	0.01
DDT, o,p'-	0.01
DDT, p,p'-	0.01
Endrin	0.01
Endrin, ketone-	0.01
Fenpyrazamine	0.01
HCH, alpha-	0.01
HCH, beta-	0.01
Heptachlor	0.01
Heptachlorepoxid, cis-	0.01
Heptachlorepoxid, trans-	0.01
Isopyrazam	0.01
Novaluron	0.01
Penflufen	0.01
Pentachloro-aniline	0.01
Penthiopyrad	0.01
Proquinazid	0.01
Pyrethrins	0.01
Pyridalil	0.01
Pyriofenone	0.01
Quintozene	0.01
Spinetoram	0.01
Sulfoxaflor	0.01

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

Appendix 3 Homogeneity data

	Ametoctradin, mg/kg		Azoxystrobin, mg/kg		Bixafen, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
007	0.049	0.052	0.074	0.077	0.063	0.072
030	0.047	0.047	0.072	0.071	0.061	0.062
051	0.048	0.049	0.073	0.076	0.067	0.069
086	0.048	0.045	0.071	0.078	0.068	0.074
140	0.050	0.052	0.068	0.069	0.062	0.065
165	0.050	0.047	0.079	0.073	0.070	0.063
199	0.046	0.048	0.071	0.074	0.067	0.066
210	0.049	0.047	0.071	0.072	0.067	0.065
223	0.044	0.046	0.073	0.073	0.069	0.062
252	0.049	0.048	0.075	0.074	0.075	0.066
289	0.046	0.042	0.072	0.064	0.065	0.064

	Boscalid, mg/kg		Carbendazim, mg/kg		Chlorantraniliprole, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
007	0.345	0.376	0.139	0.128	0.069	0.078
030	0.318	0.353	0.124	0.135	0.072	0.071
051	0.326	0.338	0.116	0.136	0.074	0.071
086	0.327	0.354	0.131	0.142	0.073	0.072
140	0.323	0.318	0.119	0.142	0.075	0.075
165	0.372	0.332	0.134	0.127	0.072	0.069
199	0.339	0.351	0.117	0.135	0.066	0.070
210	0.312	0.305	0.128	0.139	0.073	0.072
223	0.345	0.291	0.126	0.133	0.068	0.066
252	0.346	0.347	0.138	0.132	0.075	0.069
289	0.352	0.310	0.143	0.129	0.069	0.059

	Epoxiconazole, mg/kg		Etoxazole, mg/kg		Fenpropidin, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
007	0.161	0.178	0.033	0.036	0.269	0.314
030	0.153	0.152	0.032	0.033	0.276	0.258
051	0.156	0.163	0.033	0.032	0.282	0.304
086	0.150	0.151	0.032	0.032	0.269	0.273
140	0.157	0.141	0.035	0.035	0.284	0.294
165	0.160	0.154	0.036	0.033	0.288	0.317
199	0.151	0.157	0.033	0.034	0.293	0.295
210	0.155	0.144	0.034	0.033	0.275	0.276
223	0.159	0.151	0.031	0.031	0.273	0.289
252	0.162	0.162	0.033	0.033	0.293	0.293
289	0.159	0.150	0.033	0.028	0.291	0.273

	Fluopyram, mg/kg		HCH-alpha, mg/kg		Metrafenone, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
007	0.221	0.237	0.021	0.032	0.033	0.035
030	0.224	0.224	0.031	0.037	0.032	0.030
051	0.233	0.243	0.025	0.037	0.031	0.032
086	0.209	0.234	0.036	0.037	0.032	0.034
140	0.213	0.221	0.027	0.024	0.031	0.031
165	0.236	0.225	0.024	0.035	0.032	0.032
199	0.219	0.227	0.036	0.033	0.033	0.033
210	0.207	0.211	0.033	0.018	0.032	0.032
223	0.213	0.211	0.033	0.027	0.032	0.031
252	0.226	0.220	0.023	0.025	0.033	0.032
289	0.225	0.216	0.023	0.037	0.032	0.031

	Prosulfocarb, mg/kg		Prothioconazole-desthio, mg/kg		Pyraclostrobin, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
007	0.041	0.047	0.130	0.152	0.081	0.087
030	0.042	0.043	0.127	0.130	0.078	0.081
051	0.042	0.043	0.136	0.137	0.082	0.083
086	0.040	0.040	0.127	0.137	0.081	0.084
140	0.047	0.043	0.131	0.120	0.080	0.077
165	0.043	0.042	0.140	0.140	0.086	0.084
199	0.040	0.040	0.128	0.132	0.083	0.080
210	0.042	0.041	0.129	0.120	0.079	0.078
223	0.039	0.039	0.133	0.130	0.086	0.078
252	0.042	0.043	0.144	0.135	0.085	0.084
289	0.040	0.037	0.134	0.133	0.081	0.083

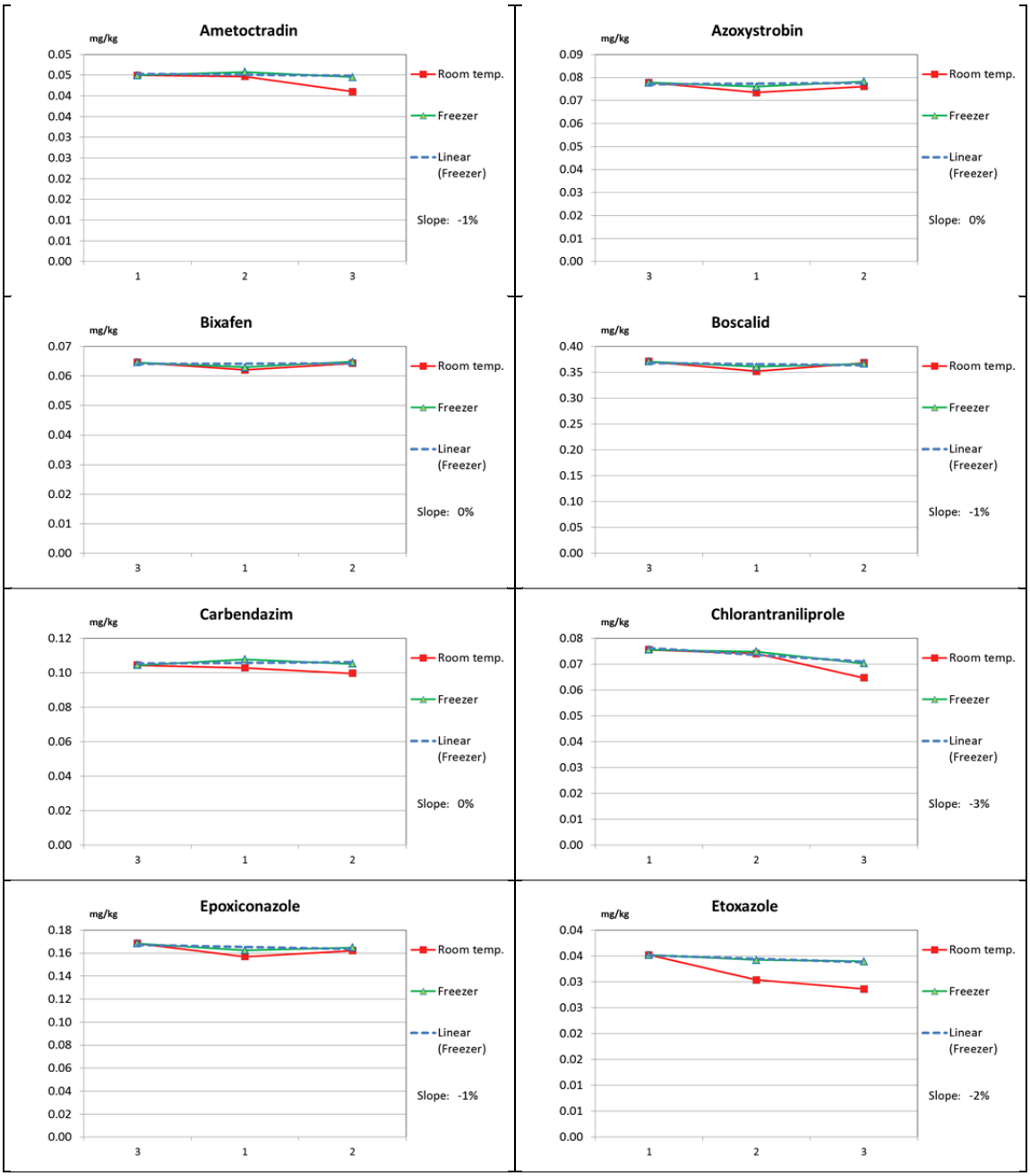
	Quintozene, mg/kg		Spinetoram, mg/kg		Tebuconazole, mg/kg	
Sample no.	Portion 1	Portion 2	Portion 1	Portion 2	Portion 1	Portion 2
007	0.063	0.070	0.085	0.086	0.081	0.087
030	0.030	0.056	0.074	0.071	0.078	0.076
051	0.051	0.053	0.099	0.093	0.079	0.081
086	0.033	0.069	0.105	0.100	0.076	0.080
140	0.060	0.066	0.084	0.072	0.081	0.078
165	0.068	0.068	0.085	0.085	0.079	0.080
199	0.065	0.068	0.076	0.073	0.083	0.078
210	0.057	0.050	0.108	0.111	0.076	0.080
223	0.055	0.073	0.096	0.095	0.084	0.076
252	0.073	0.070	0.100	0.096	0.083	0.081
289	0.065	0.053	0.066	0.069	0.076	0.077

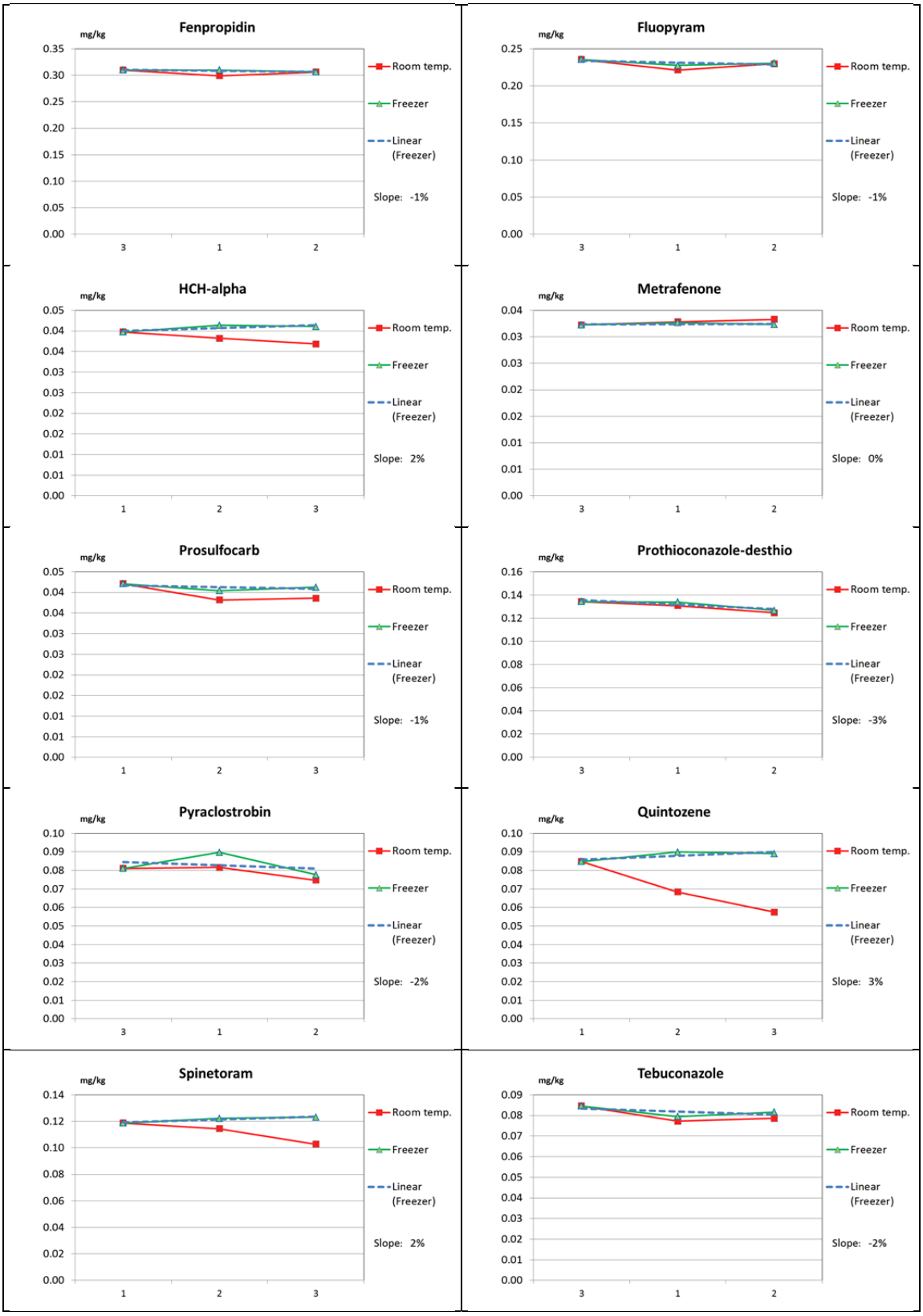
Appendix 4 Stability figures

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

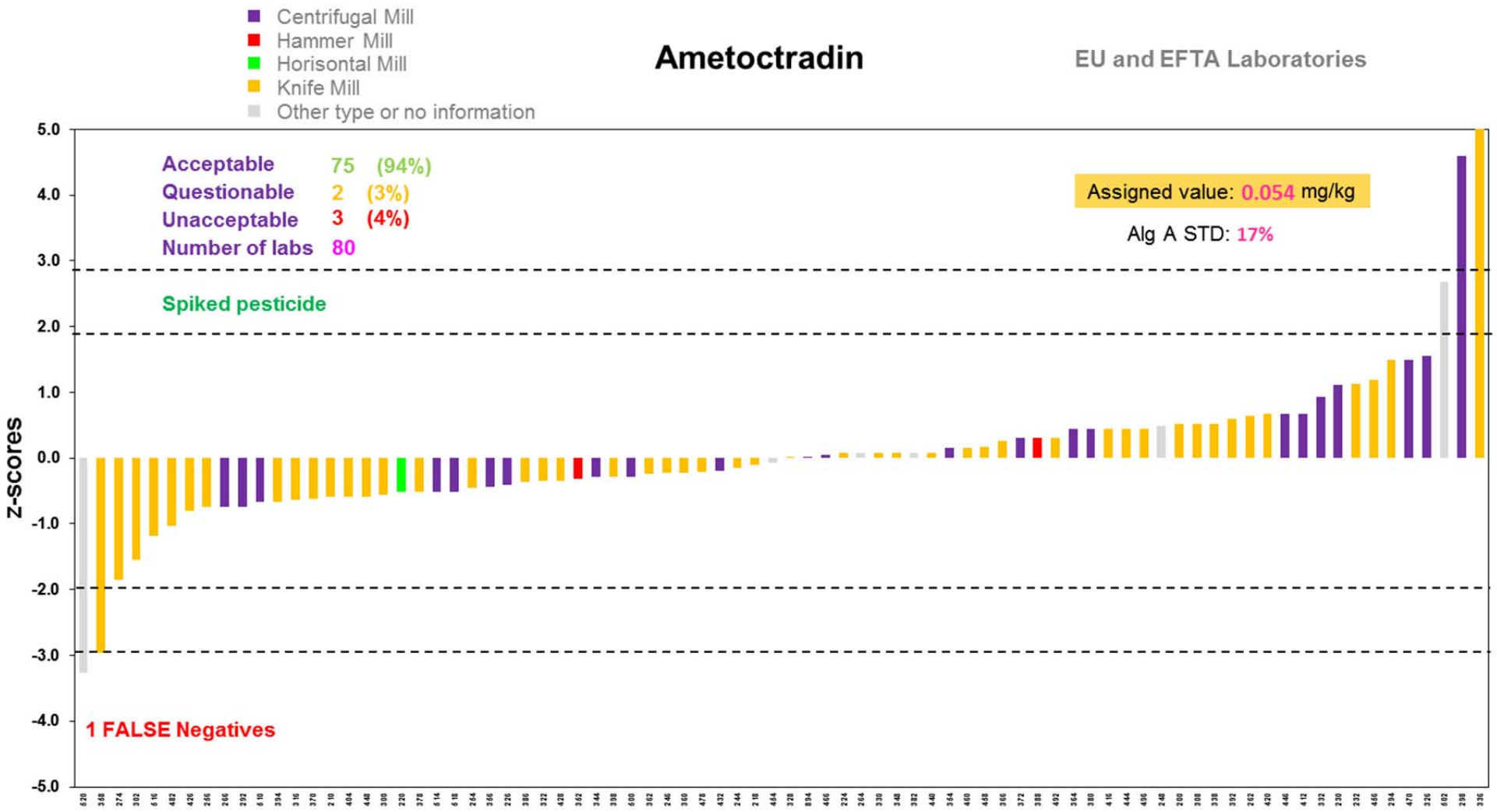
The dates of testing were as follows:
Day 1: 29 January 2019
Day 2: 12 February 2019
Day 3: 26 February 2019

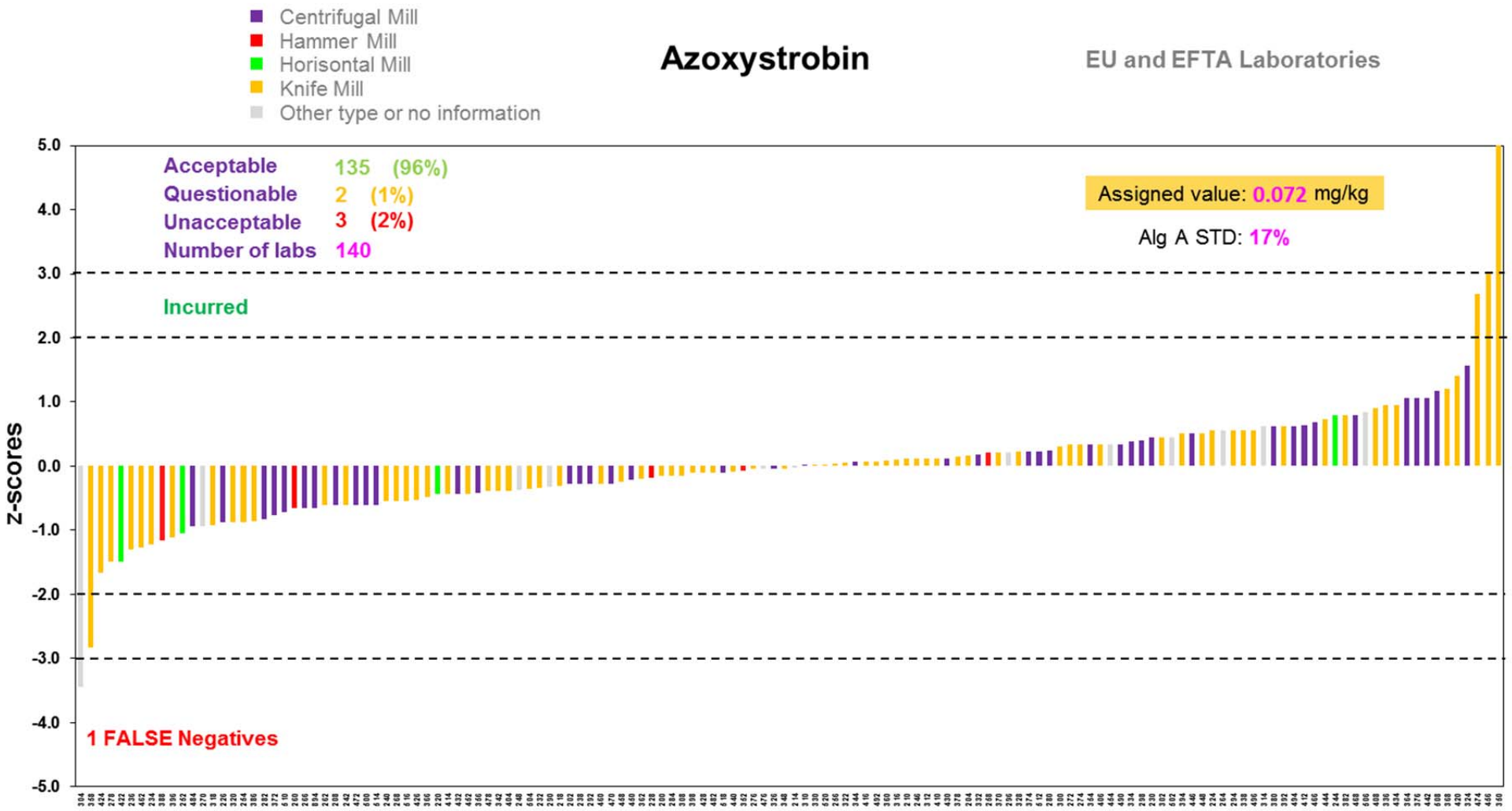
All pesticides passed the test at -18 °C, see **1.6 Stability test**.

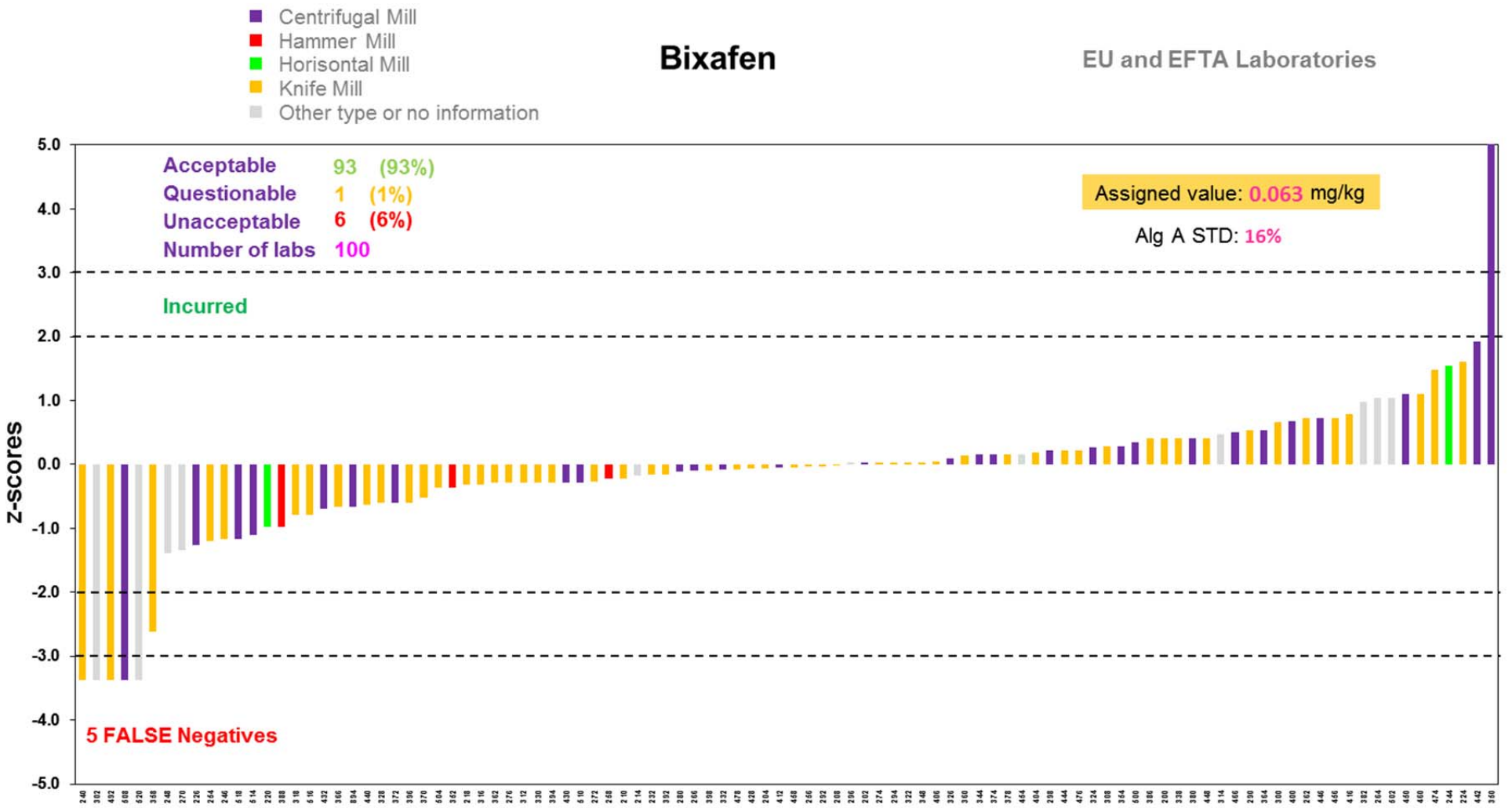


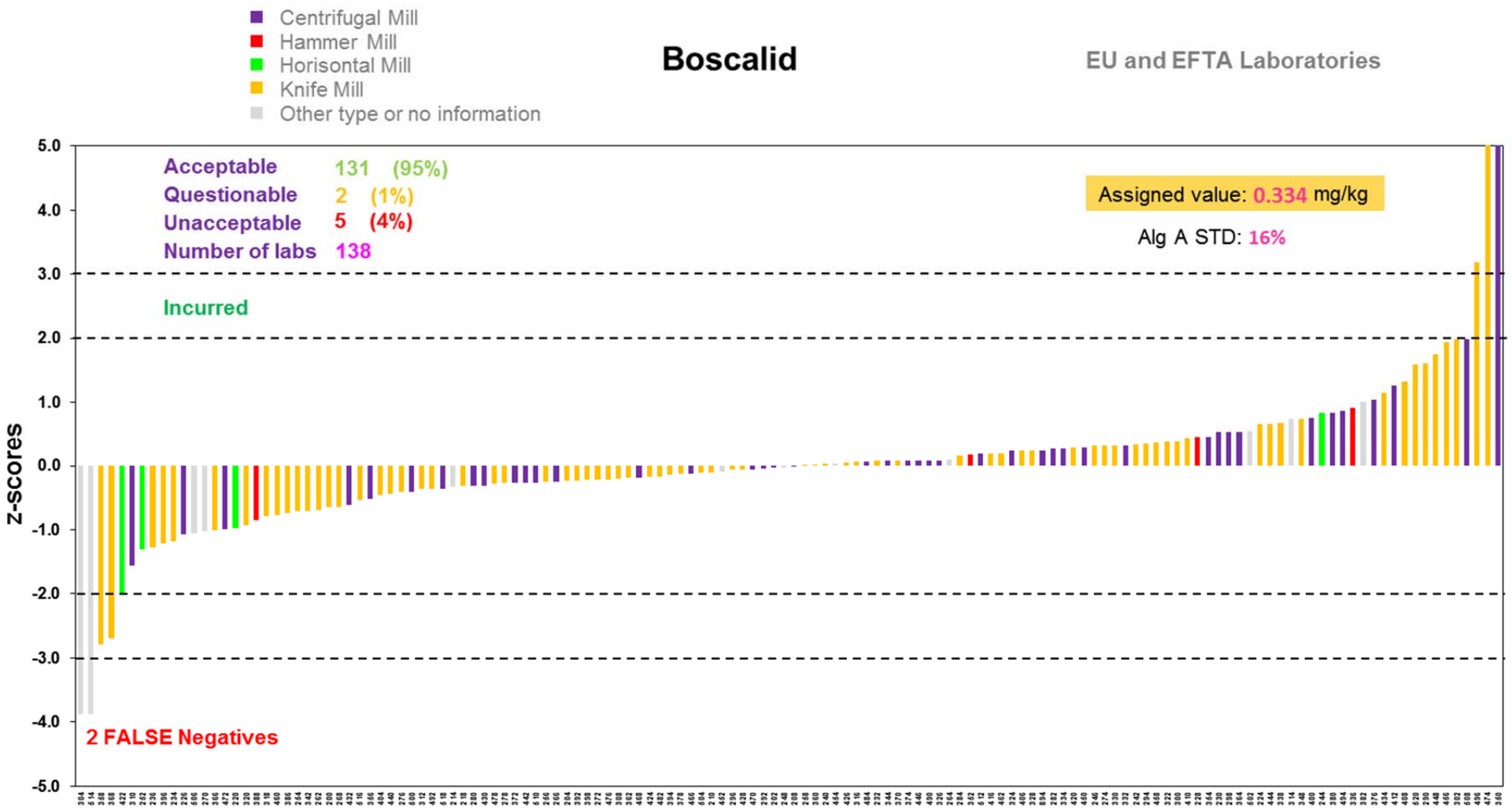

Fenpropidin
mg/kg
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3
1
2
Room temp.
Freezer
Linear (Freezer)
Slope: -1%
Fluopyram
mg/kg
0.25
0.20
0.15
0.10
0.05
0.00
3
1
2
Room temp.
Freezer
Linear (Freezer)
Slope: -1%
HCH-alpha
mg/kg
0.05
0.04
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
1
2
3
Room temp.
Freezer
Linear (Freezer)
Slope: 2%
Metrafenone
mg/kg
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
3
1
2
Room temp.
Freezer
Linear (Freezer)
Slope: 0%
Prosulfocarb
mg/kg
0.05
0.04
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
1
2
3
Room temp.
Freezer
Linear (Freezer)
Slope: -1%
Prothioconazole-desthio
mg/kg
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3
1
2
Room temp.
Freezer
Linear (Freezer)
Slope: -3%
Pyraclostrobin
mg/kg
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
3
1
2
Room temp.
Freezer
Linear (Freezer)
Slope: -2%
Quintozene
mg/kg
0.10
0.09
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: 3%
Spinetoram
mg/kg
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
1
2
3
Room temp.
Freezer
Linear (Freezer)
Slope: 2%
Tebuconazole
mg/kg
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
3
1
2
Room temp.
Freezer
Linear (Freezer)
Slope: -2%

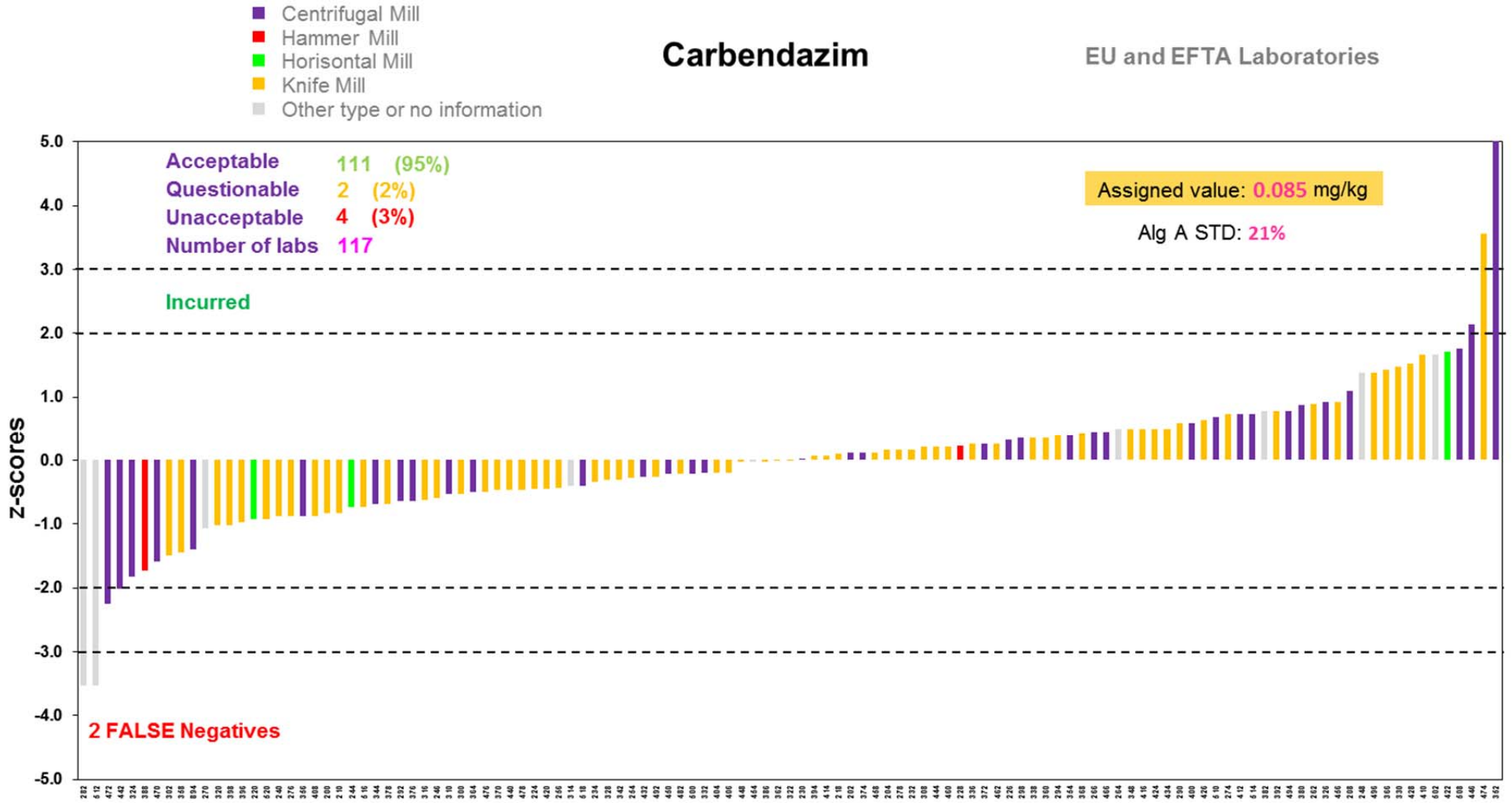
Appendix 5 Graphical presentation of z-scores




Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Azoxystrobin
EU and EFTA Laboratories
Acceptable 135 (96%)
Questionable 2 (1%)
Unacceptable 3 (2%)
Number of labs 140
Assigned value: 0.072 mg/kg
Alg A STD: 17%
Incurred
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

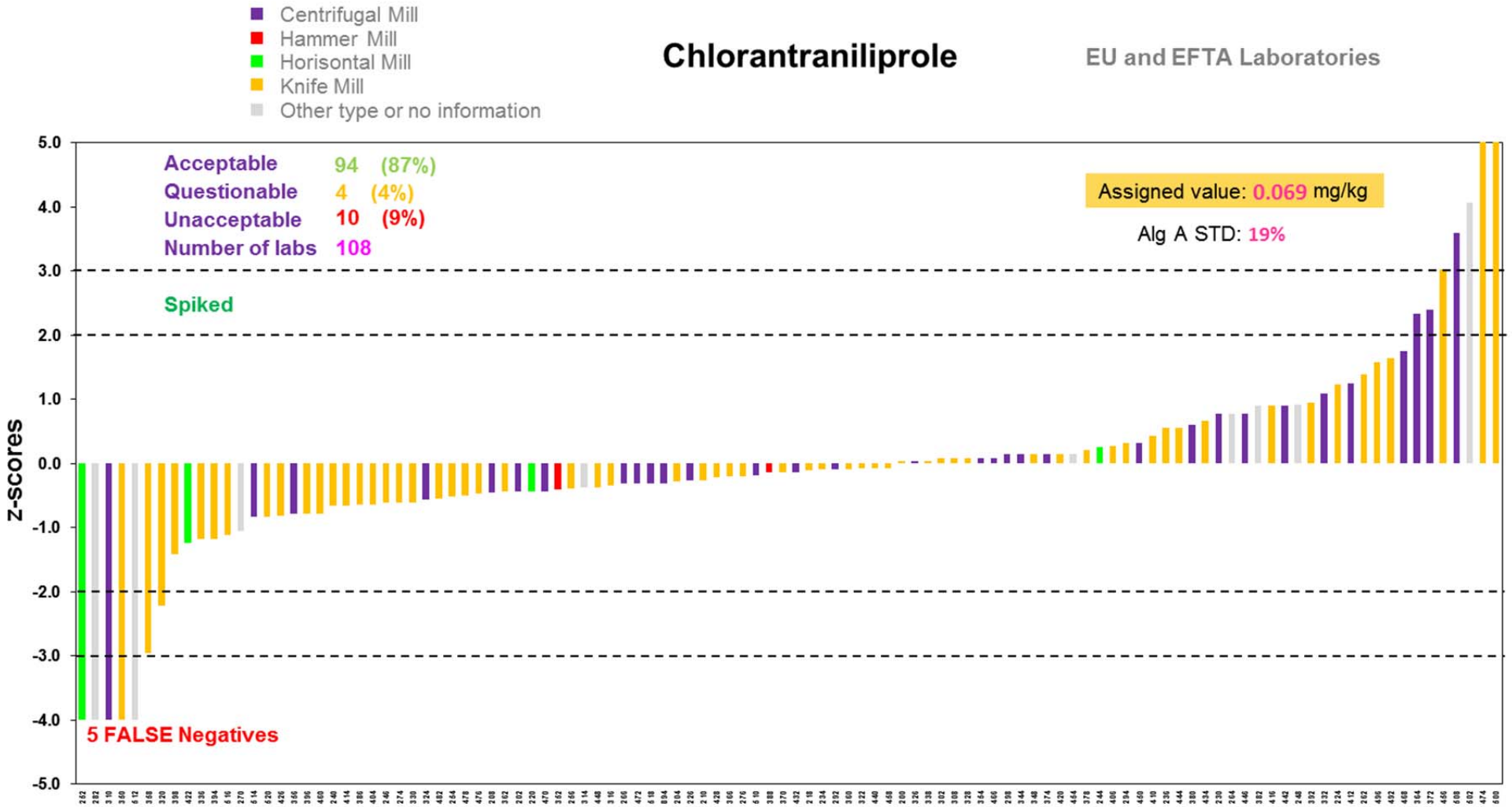

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Bixafen
EU and EFTA Laboratories
Acceptable 93 (93%)
Questionable 1 (1%)
Unacceptable 6 (6%)
Number of labs 100
Assigned value: 0.063 mg/kg
Alg A STD: 16%
Incurred
5 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0

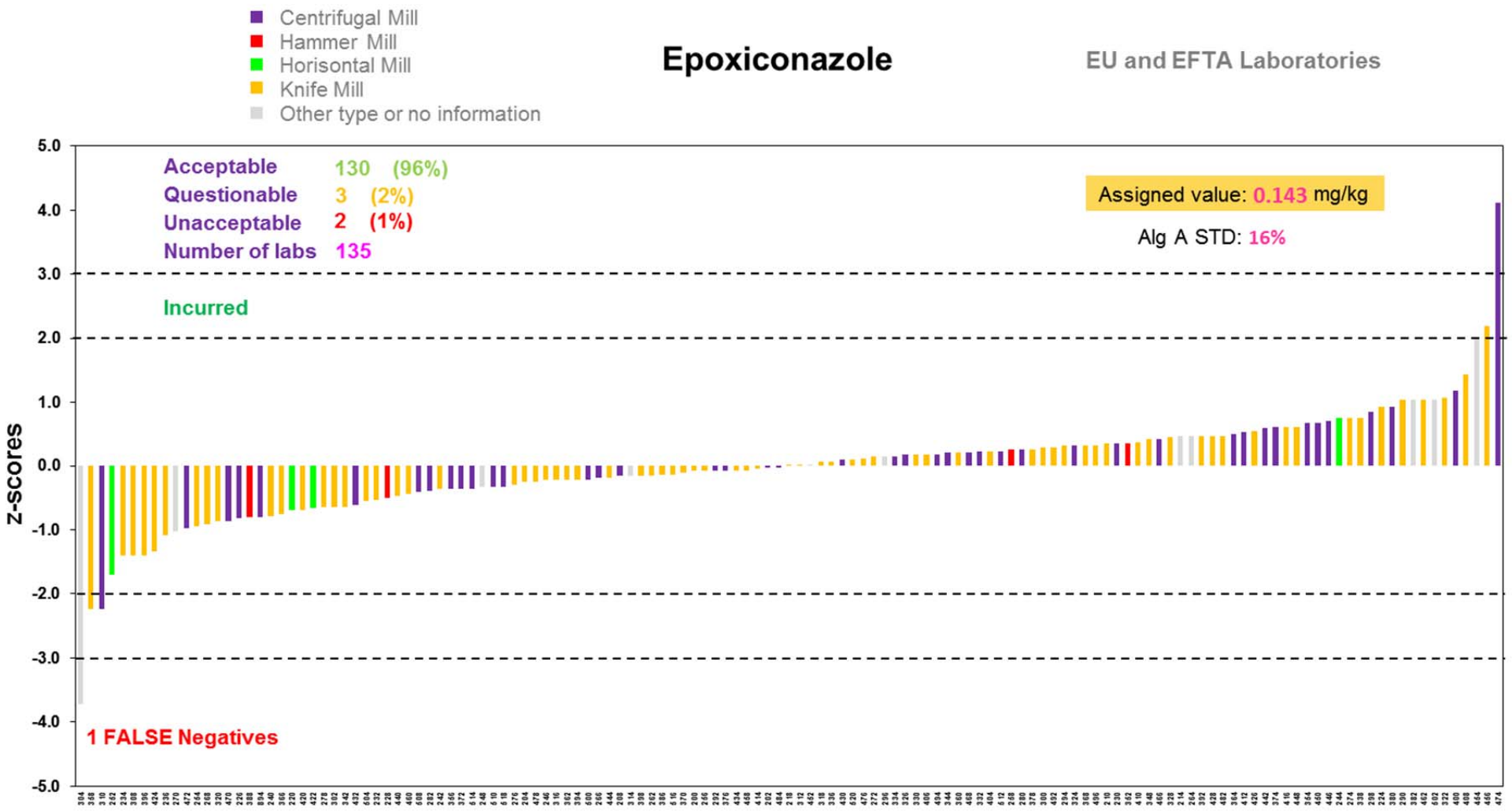

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Boscalid
EU and EFTA Laboratories
Acceptable 131 (95%)
Questionable 2 (1%)
Unacceptable 5 (4%)
Number of labs 138
Assigned value: 0.334 mg/kg
Alg A STD: 16%
Incurred
2 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0

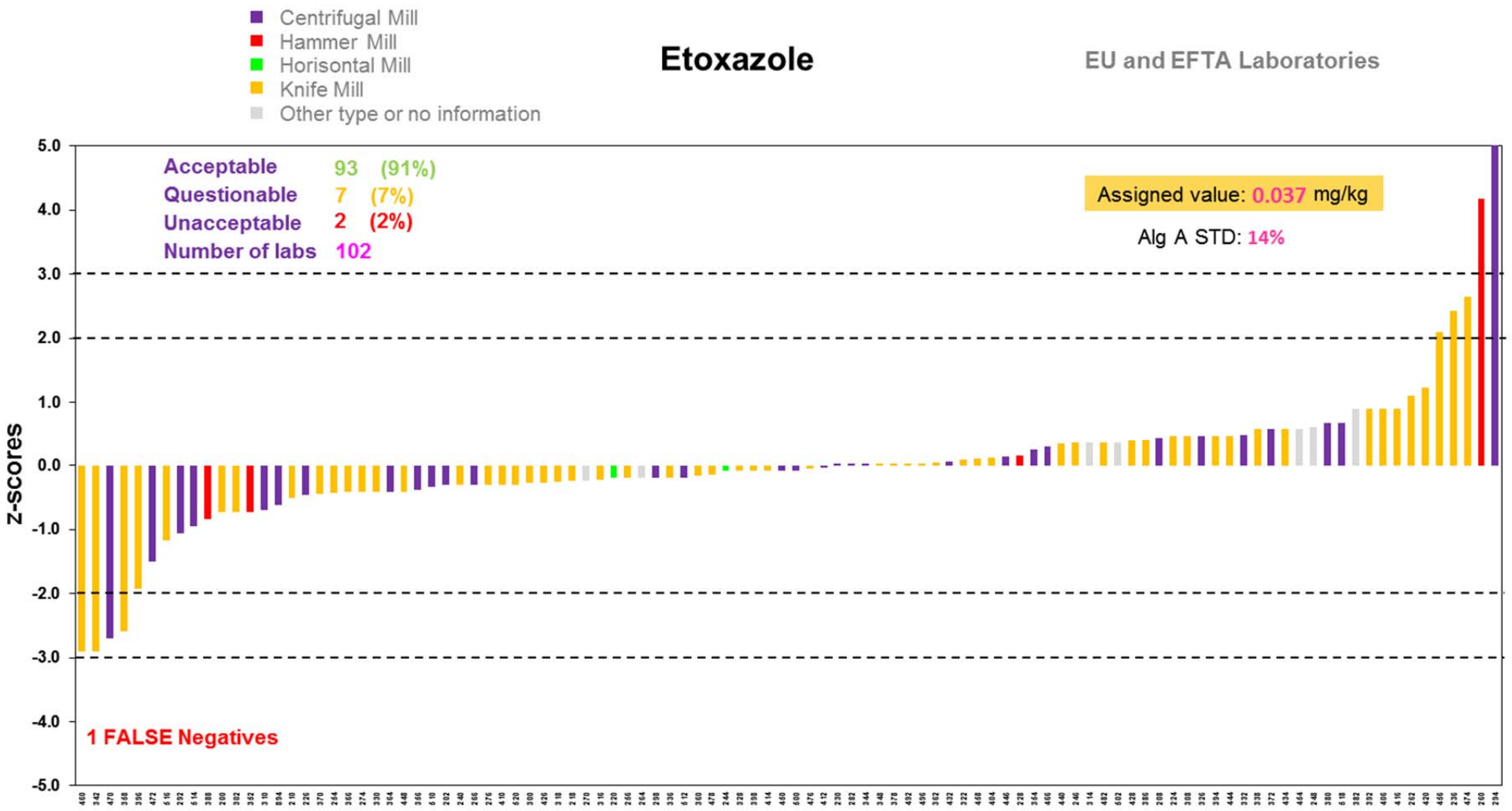

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Carbendazim
EU and EFTA Laboratories
Acceptable 111 (95%)
Questionable 2 (2%)
Unacceptable 4 (3%)
Number of labs 117
Assigned value: 0.085 mg/kg
Alg A STD: 21%
Incurred
2 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0

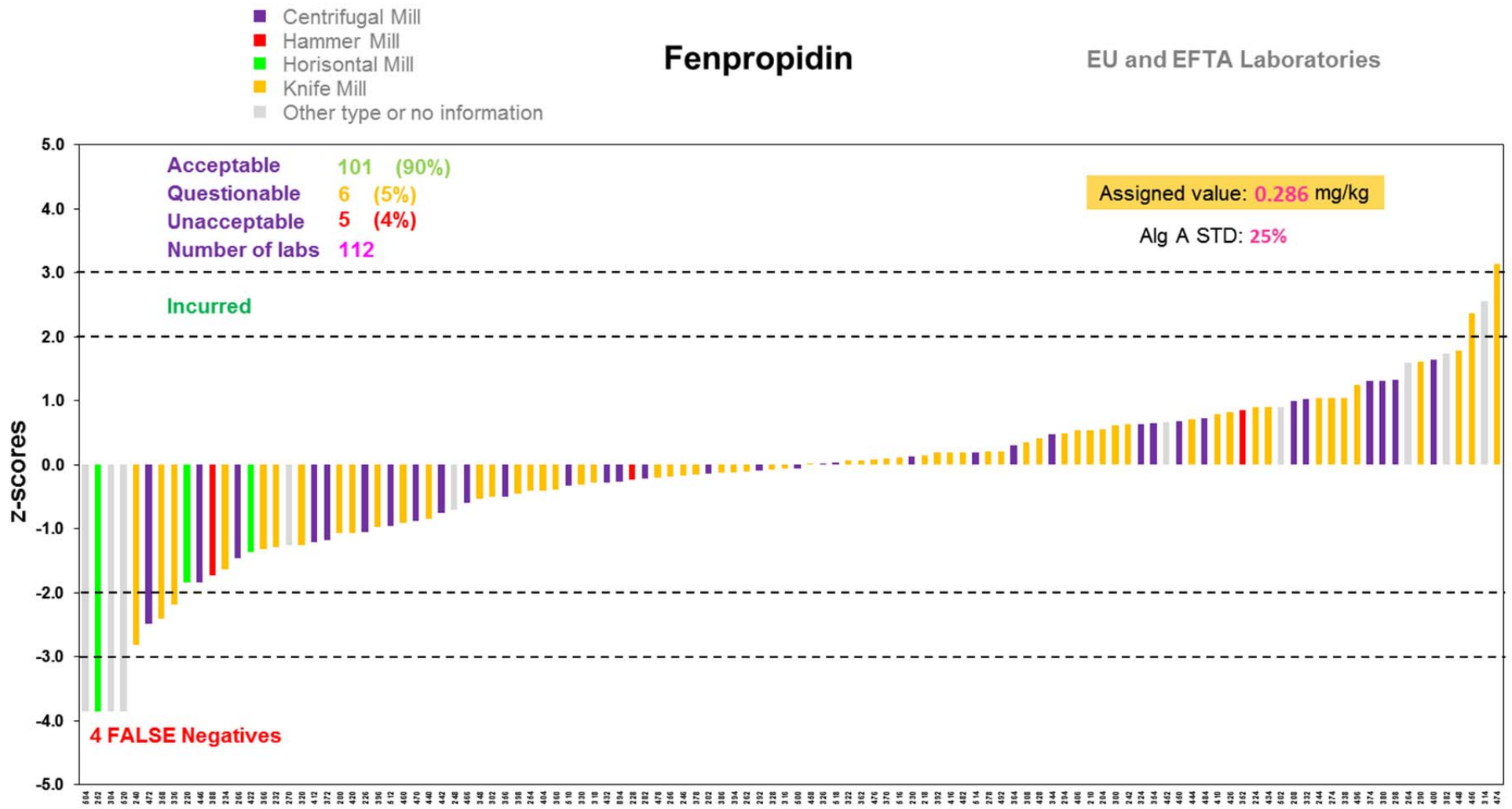
2

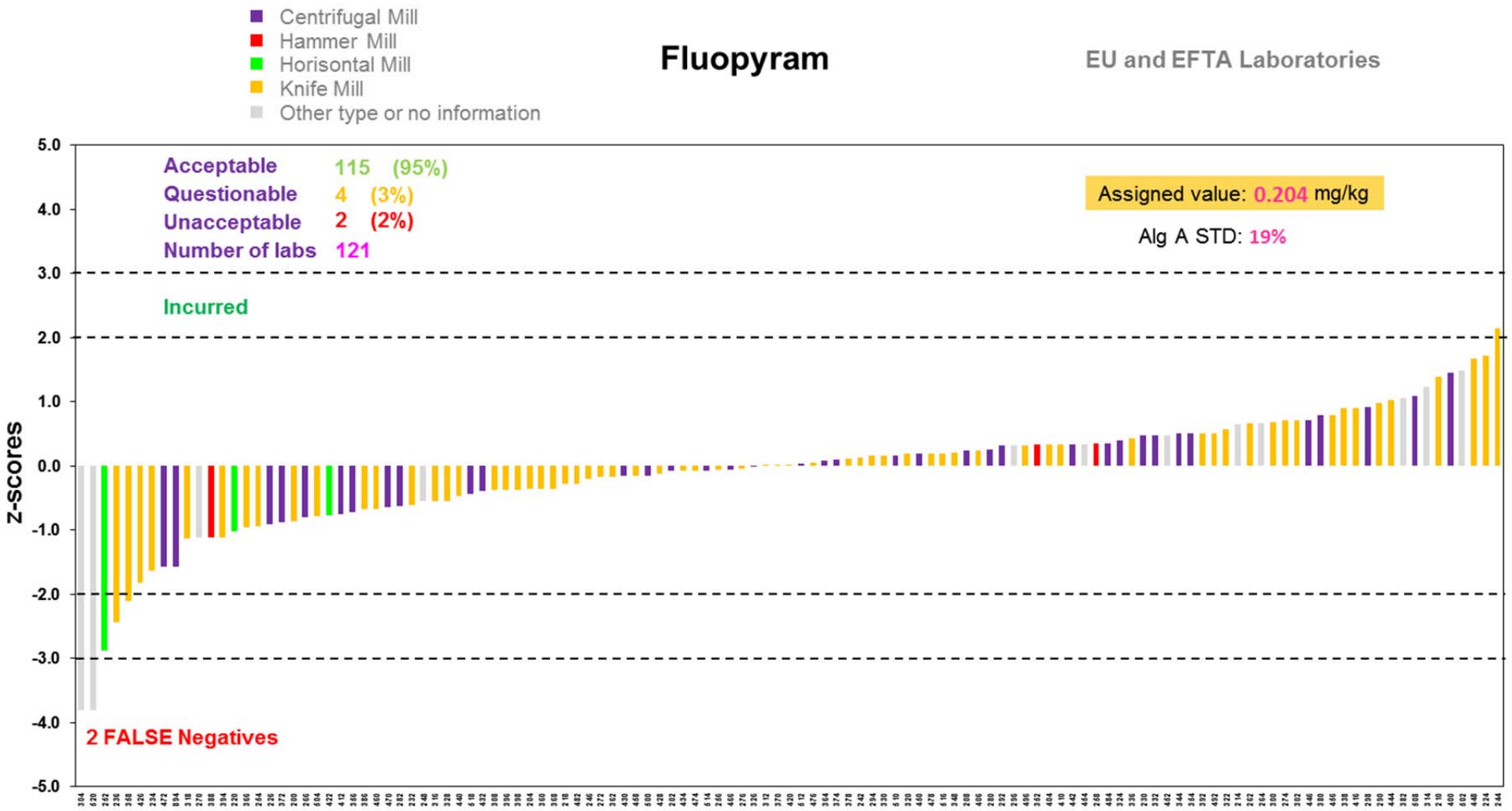
2

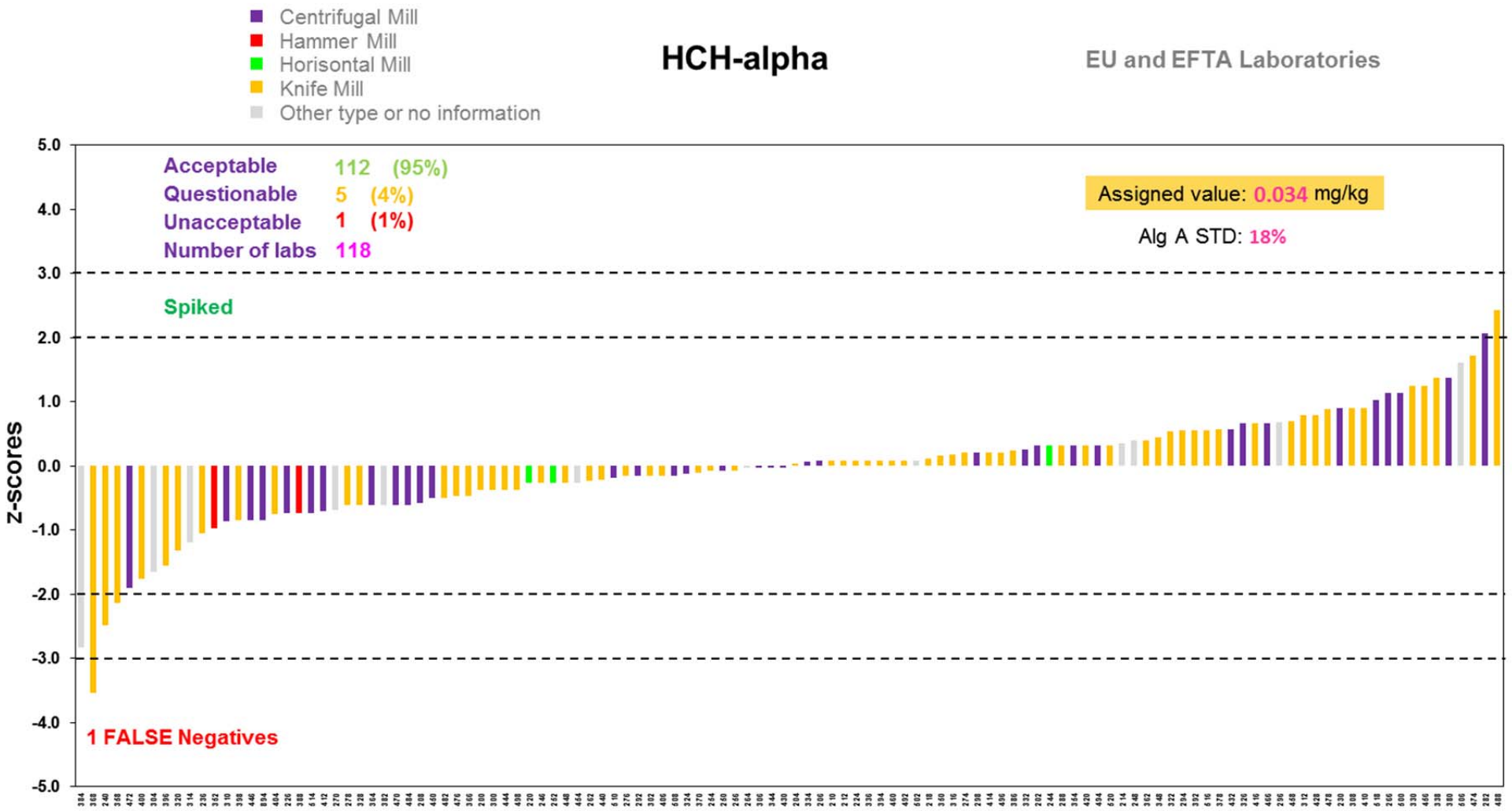

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Chlorantraniliprole
EU and EFTA Laboratories
Acceptable 94 (87%)
Questionable 4 (4%)
Unacceptable 10 (9%)
Number of labs 108
Assigned value: 0.069 mg/kg
Alg A STD: 19%
Spiked
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
5 FALSE Negatives

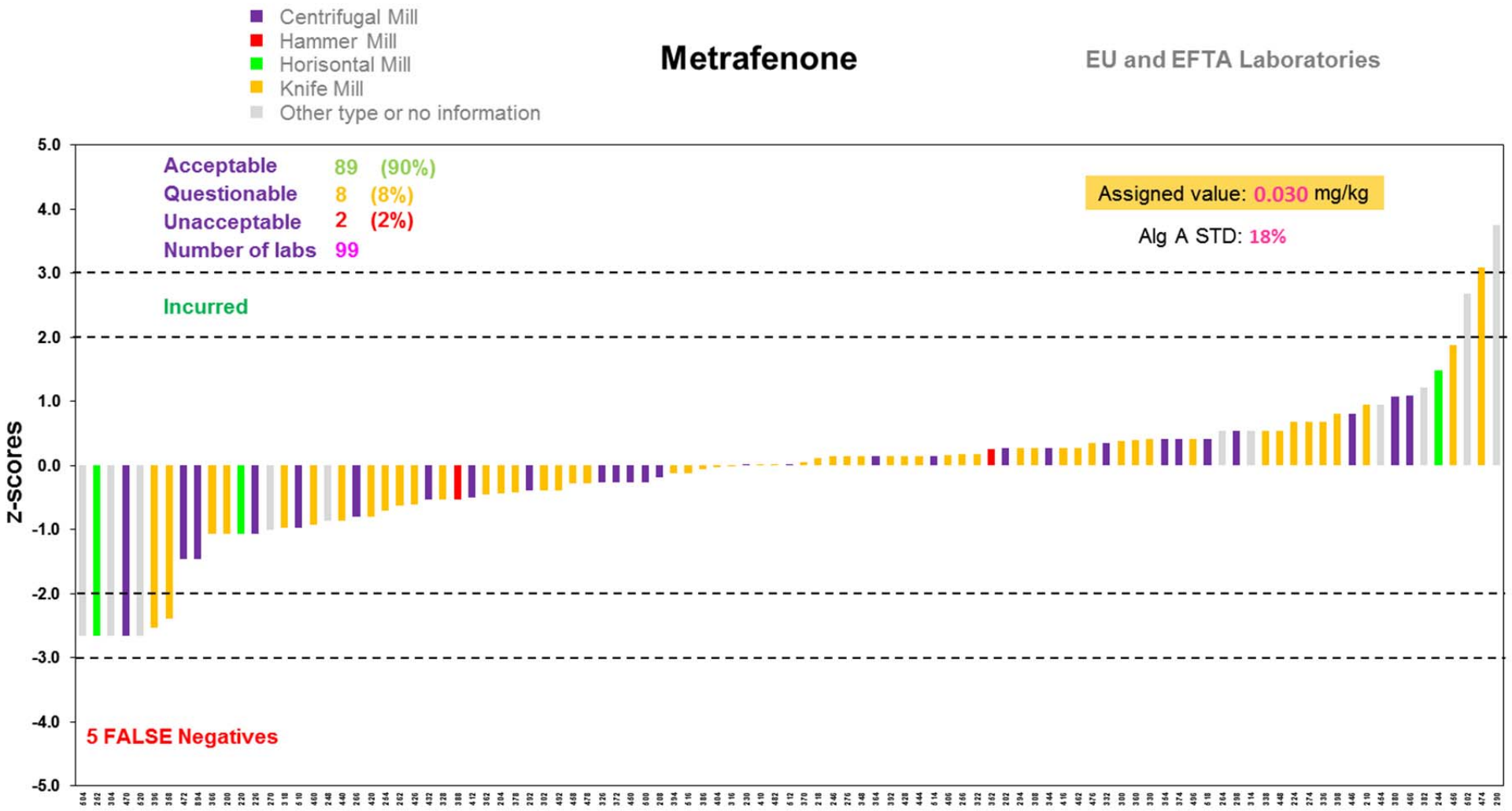

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Epoxiconazole
EU and EFTA Laboratories
Acceptable 130 (96%)
Questionable 3 (2%)
Unacceptable 2 (1%)
Number of labs 135
Assigned value: 0.143 mg/kg
Alg A STD: 16%
Incurred
1 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0

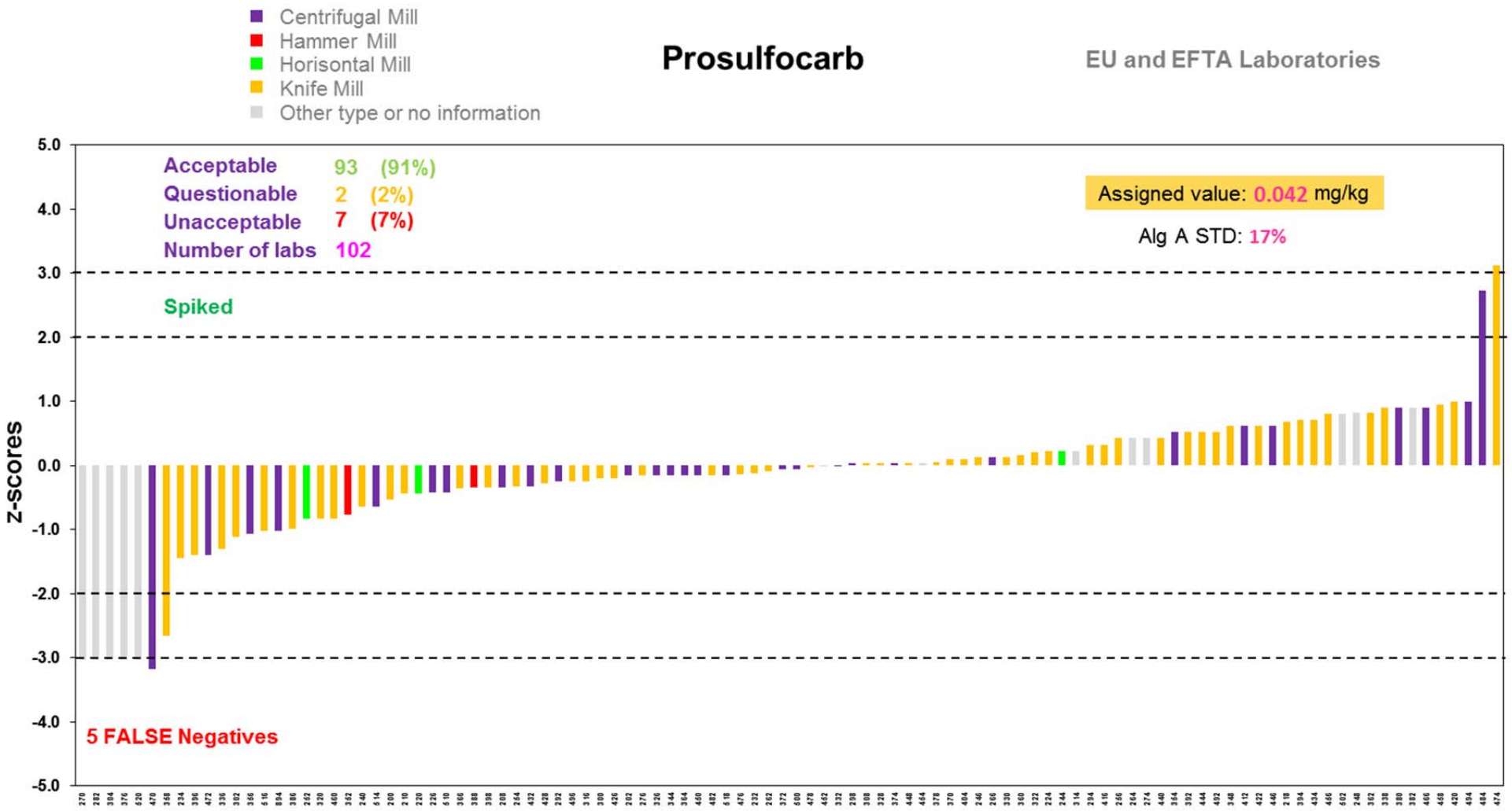

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Etoxazole
EU and EFTA Laboratories
Acceptable 93 (91%)
Questionable 7 (7%)
Unacceptable 2 (2%)
Number of labs 102
Assigned value: 0.037 mg/kg
Alg A STD: 14%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 FALSE Negatives

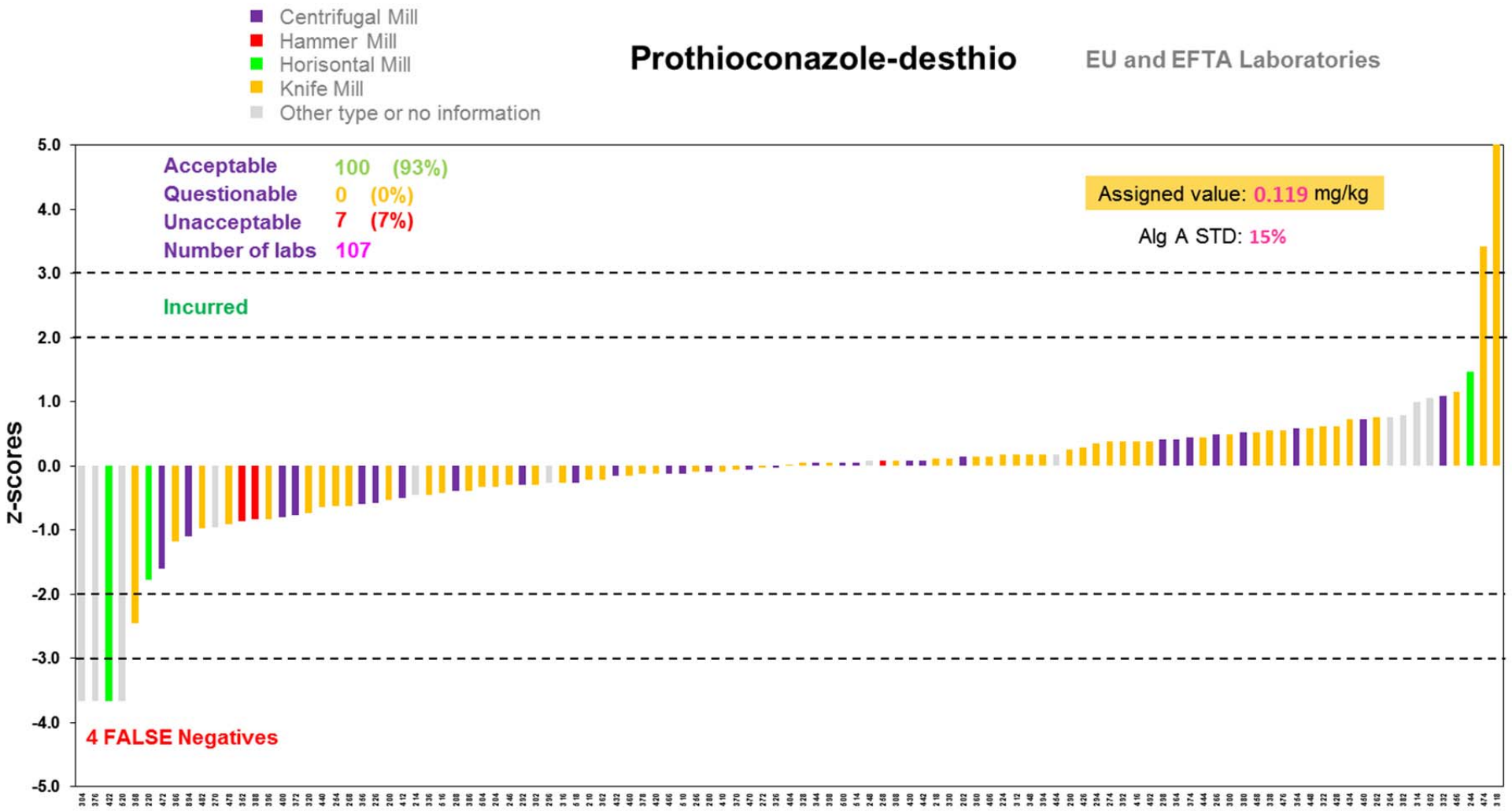

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Fenpropidin
EU and EFTA Laboratories
Acceptable 101 (90%)
Questionable 6 (5%)
Unacceptable 5 (4%)
Number of labs 112
Assigned value: 0.286 mg/kg
Alg A STD: 25%
Incurred
4 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0

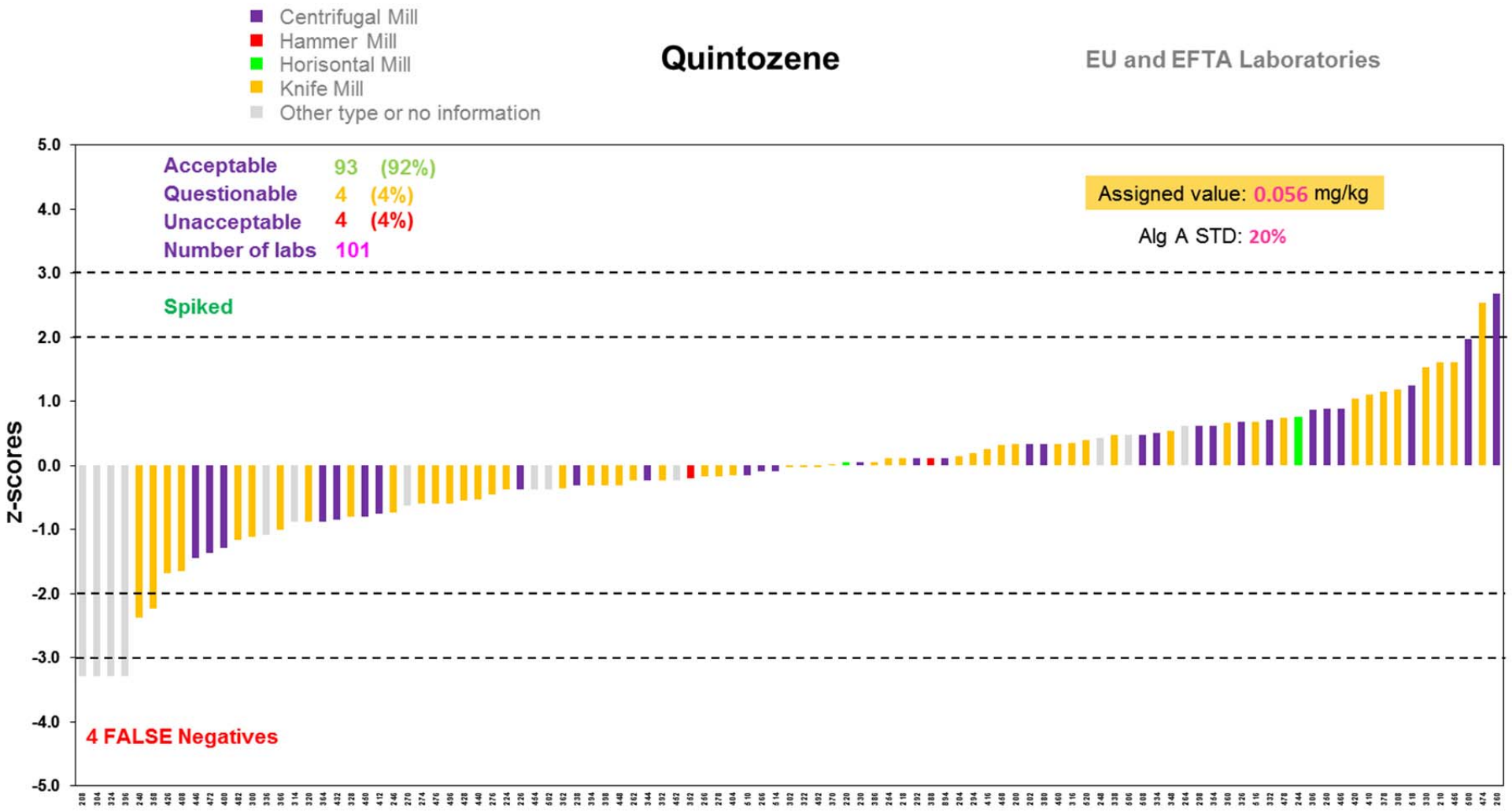

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Fluopyram
EU and EFTA Laboratories
Acceptable 115 (95%)
Questionable 4 (3%)
Unacceptable 2 (2%)
Number of labs 121
Assigned value: 0.204 mg/kg
Alg A STD: 19%
Incurred
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
2 FALSE Negatives

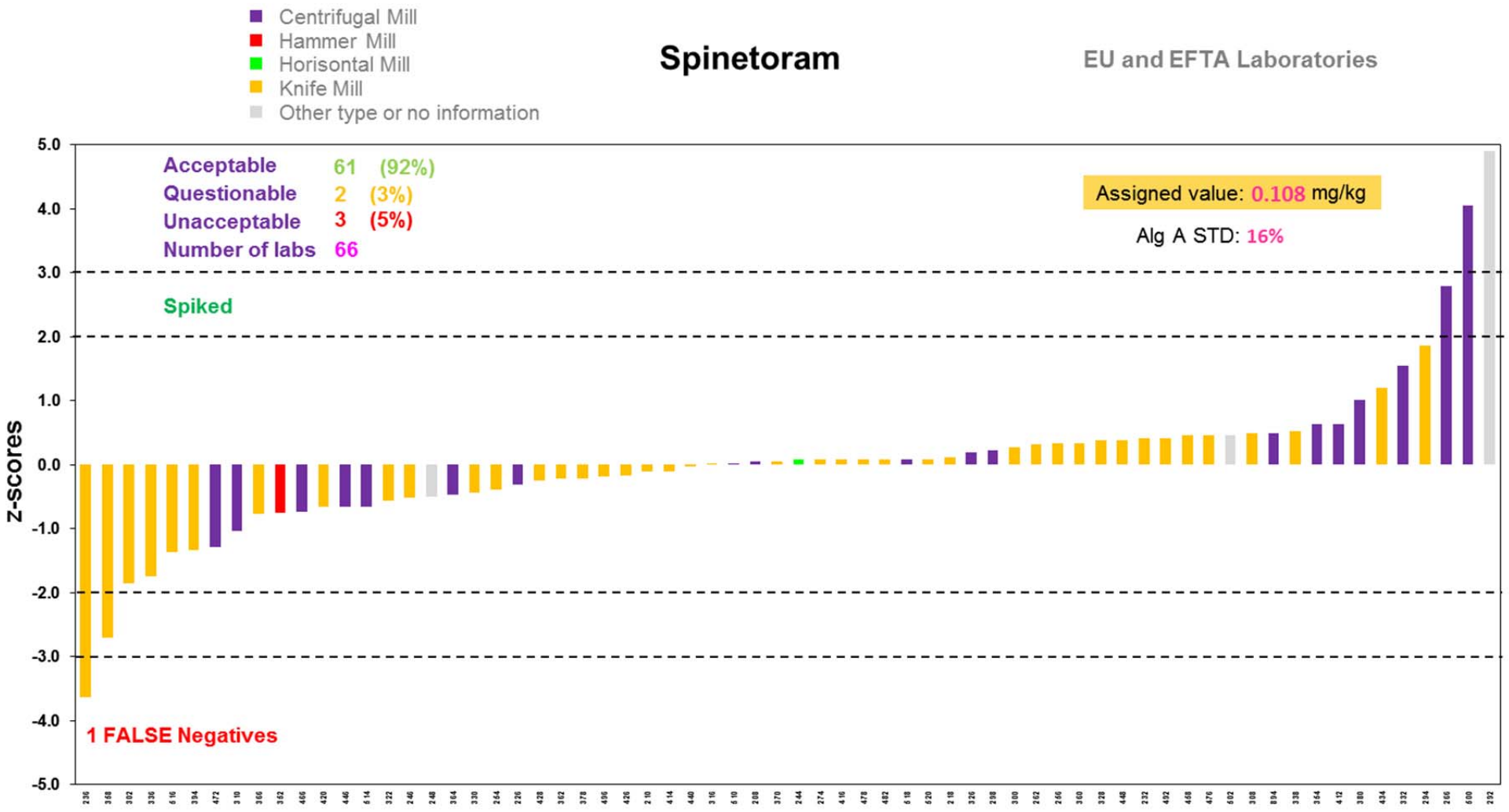

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
HCH-alpha
EU and EFTA Laboratories
Acceptable 112 (95%)
Questionable 5 (4%)
Unacceptable 1 (1%)
Number of labs 118
Assigned value: 0.034 mg/kg
Alg A STD: 18%
Spiked
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1 FALSE Negatives

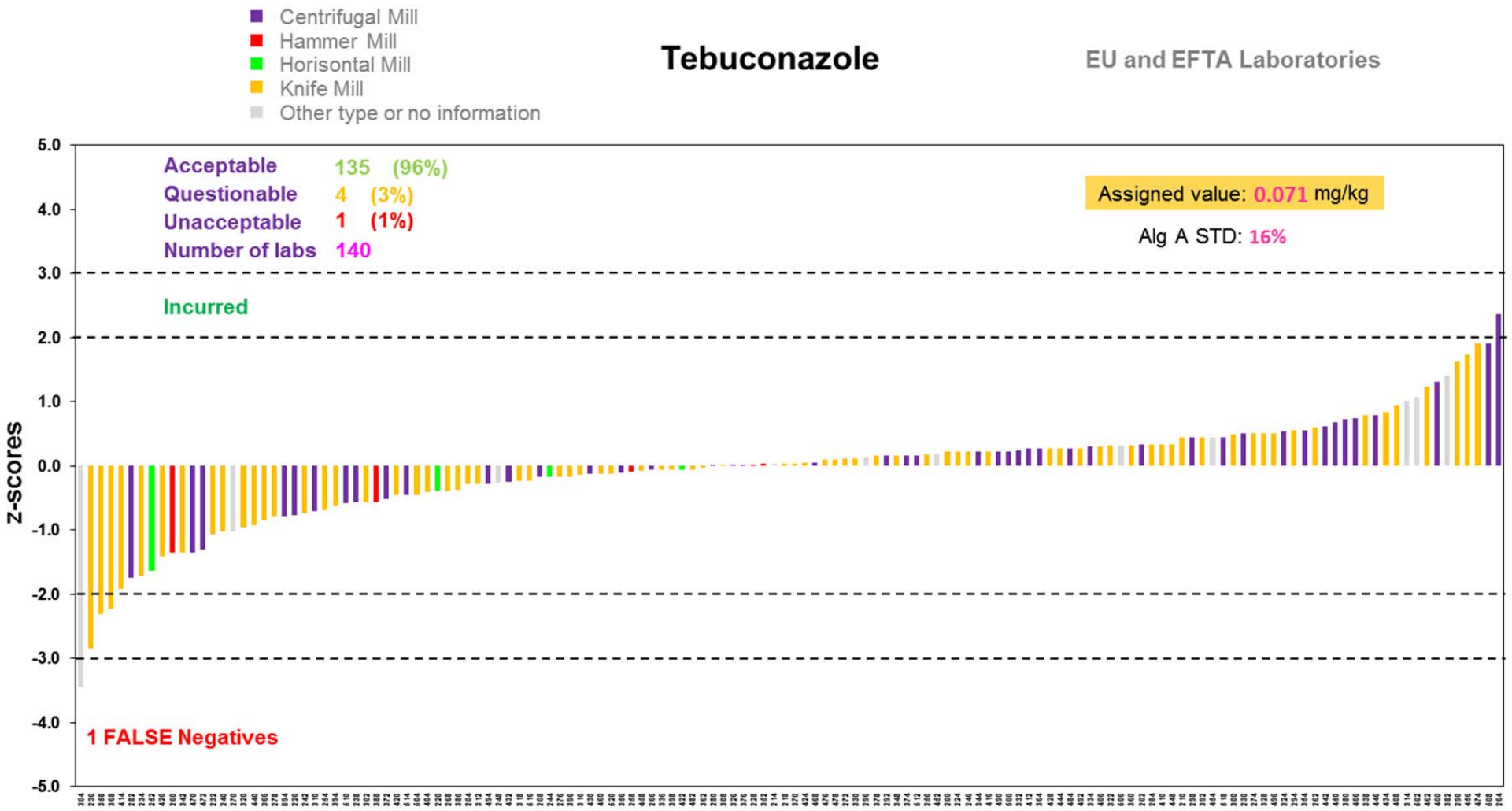

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Metrafenone
EU and EFTA Laboratories
Acceptable 89 (90%)
Questionable 8 (8%)
Unacceptable 2 (2%)
Number of labs 99
Assigned value: 0.030 mg/kg
Alg A STD: 18%
Incurred
5 FALSE Negatives
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0

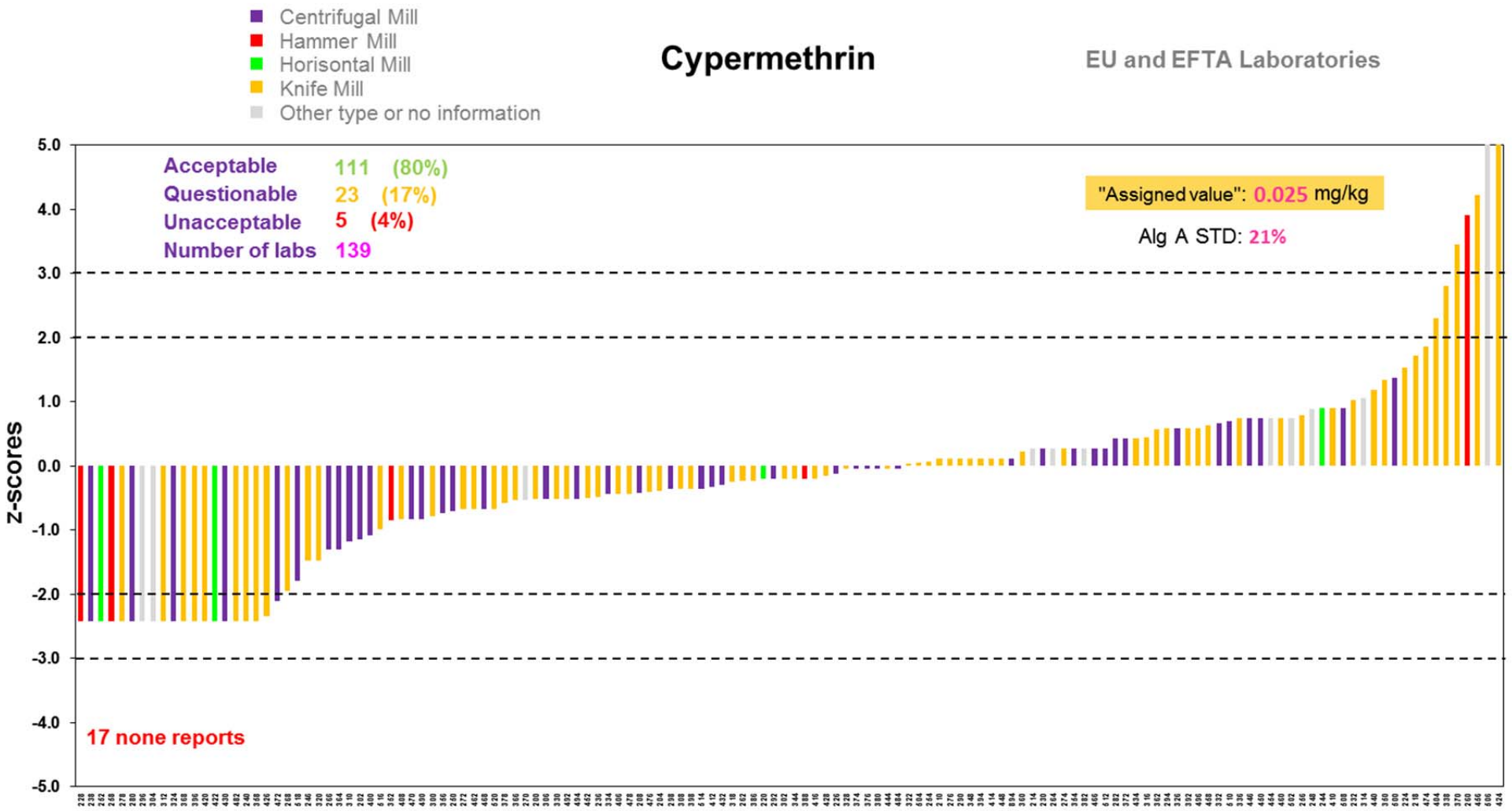

Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Prosulfocarb
EU and EFTA Laboratories
Acceptable 93 (91%)
Questionable 2 (2%)
Unacceptable 7 (7%)
Number of labs 102
Assigned value: 0.042 mg/kg
Alg A STD: 17%
Spiked
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
5 FALSE Negatives


Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Prothioconazole-desthio
EU and EFTA Laboratories
Acceptable 100 (93%)
Questionable 0 (0%)
Unacceptable 7 (7%)
Number of labs 107
Assigned value: 0.119 mg/kg
Alg A STD: 15%
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
4 FALSE Negatives


Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Quintozene
EU and EFTA Laboratories
Acceptable 93 (92%)
Questionable 4 (4%)
Unacceptable 4 (4%)
Number of labs 101
Assigned value: 0.056 mg/kg
Alg A STD: 20%
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
4 FALSE Negatives


Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Spinetoram
EU and EFTA Laboratories
Acceptable 61 (92%)
Questionable 2 (3%)
Unacceptable 3 (5%)
Number of labs 66
Assigned value: 0.108 mg/kg
Alg A STD: 16%
Spiked
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


Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Tebuconazole
EU and EFTA Laboratories
Acceptable 135 (96%)
Questionable 4 (3%)
Unacceptable 1 (1%)
Number of labs 140
Assigned value: 0.071 mg/kg
Alg A STD: 16%
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
1 FALSE Negatives


Centrifugal Mill
Hammer Mill
Horisontal Mill
Knife Mill
Other type or no information
Cypermethrin
EU and EFTA Laboratories
Acceptable 111 (80%)
Questionable 23 (17%)
Unacceptable 5 (4%)
Number of labs 139
"Assigned value": 0.025 mg/kg
Alg A STD: 21%
z-scores
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
17 none reports

8th Edition: Revised 23th January, 2018

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 (EC) 625/2017[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.

EURL EU REFERENCE LABORATORIES FOR RESIDUES OF PESTICIDES

8th Edition: Revised 23th January, 2018

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

EUPT-Organisers and Scientific Committee

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

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

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

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

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

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

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

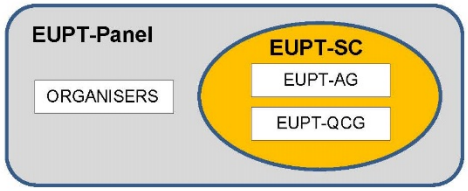
The EUPT-QCG has the additional function of supervising the quality of EUPTs and of assisting the EURLs in confidential aspects such as the choice of the pesticides to be present in the Test Item and the concentrations at which they should be present.

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

www.eurl-pesticides.eu

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

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



The decisions of the EUPT-Panel will be documented.

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

EUPT Participants

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

- Art. 28 of Reg. 396/2005/EC[6] (for all OfLs analysing for pesticide residues within the framework of official controls[7] of food or feed)
- Art. 101 (1)(a) of Reg. (EC) 625/2017 (for all NRLs)

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

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

[7] Official controls in the sense of Reg. (EC) 625/2017. 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.

EURL EU REFERENCE LABORATORIES FOR RESIDUES OF PESTICIDES

8th Edition: Revised 23th January, 2018

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

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

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

Based on Reg. (EC) 625/2017, 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 competent authority 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, NRLs are responsible for supporting and improving their own OfL-Network. On request from the NRLs, the EURLs will provide them with the PT-codes of the participating OfLs belonging to their OfL-Network. This will allow NRLs to follow the participation and performance of the laboratories within their network.

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

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

The official language used in all EUPTs is English.

Announcement / Invitation Letter

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

Target Pesticide List

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

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

Specific Protocol

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

Homogeneity of the Test Item

The Test Item will be tested for homogeneity typically before distribution to participants. The homogeneity tests 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-SC considering all relevant aspects (e.g. the homogeneity results of other pesticides spiked at the same time, the overall distribution of the participants'

EURL EU REFERENCE LABORATORIES FOR RESIDUES OF PESTICIDES

8th Edition: Revised 23th January, 2018

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

Stability of the analytes contained in the Test Item

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

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

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

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 conduct additional stability tests at conditions simulating shipment. Should critical losses be detected for certain pesticides the EUPT-SC will be informed (or the EUPT-QCG before or during the test). Case-by-case decisions may be taken considering all relevant aspects including the shipment time of the samples to each laboratory.

Methodologies to be used by the participants

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

General procedures for reporting results

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

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

Correction of results for recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed[8], it is common practice that pesticide analysis results are not corrected for recovery if the recovery rates range between 70 and 120 %. Correction of results for recovery is recommended if the average recovery is significantly different from 100 % (typically if outside the 70 – 120 % range). Approaches for recovery correction explicitly stated in the DG-SANTE document are the use of recovery correction factors, the use of stable isotope labelled analogues

[8] Document N° SANTE/11813/2017; Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed

EURL EU REFERENCE LABORATORIES FOR RESIDUES OF PESTICIDES

8th Edition: Revised 23th January, 2018

of the target analytes as Internal Standards (ILISs), the 'procedural calibration' approach as well as 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. No recovery data are required where correction for recovery is automatic by adding amounts of analytes to the test portion for using the 'standard addition' approach, or isotopically-labelled internal standards (in both cases with spiking into the Test Item at the beginning of the extraction procedures) or procedural calibration. In these cases, the laboratories should report the actual approach that was followed.

Methodology information

All laboratories are requested to provide information on the analytical method(s) they have used. A compilation of the methodology information submitted by all participants is presented in an Annex of the final report or in a separate report. Where necessary the methods are evaluated and discussed, especially in those cases where the result distribution is not unimodal or very broad (e.g. CV* > 35 %). If no sufficient information on the methodology used is provided, the Organiser reserves the right not to accept the analytical results reported by the participants concerned 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 robust estimate of the participant's mean (x^*) as described in ISO 13528:2015[9], 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 compound in the past.

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

Before estimating the assigned value results associated with obvious mistakes have to be examined to decide whether they should be removed from the population. Such gross errors may include incorrect recording (e.g. due to transcription errors by the participant, decimal point faults or transposed digits, incorrect unit), calculation errors (e.g. missing factors), analysis of a wrong sample/extract (e.g. a spiked blank), use of wrong concentrations of standard solutions, incorrect

[9] 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).

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

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

Uncertainty of the assigned value

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

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

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

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

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

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

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

The percentage FFP-RSD is set at 25% based on experience from results of previous EUPTs[10]. The EUPT-Panel reserves the right to also employ other approaches on a case-by-case basis considering analytical difficulties and experience gained from previous proficiency tests.

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

– ***z scores***

This parameter is calculated using the following formula:

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

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

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[11]:

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

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

[10] 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.

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

EURL EU REFERENCE LABORATORIES FOR RESIDUES OF PESTICIDES

8th Edition: Revised 23th January, 2018

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

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

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

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

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

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

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

Where n is the number of z scores to be considered in the calculation. In the calculation of the AZ^2, z scores higher than 5 will be 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 the individual z scores. The EUPT-Panel retains the right not to calculate AZ^2 if it is considered as not being useful or if the number of results reported by any participant is considered to be too low.

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

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

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

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

EURL EU REFERENCE LABORATORIES FOR RESIDUES OF PESTICIDES

8th Edition: Revised 23th January, 2018

Publication of results

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

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

Feedback

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

Correction of errors

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

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

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

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

Follow-up activities

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

Upon request, the laboratory's corresponding NRL and EURL are to be informed of the outcome of any investigative activities for false positives, false negatives and for results with $|z| \geq 3.0$. Concerning z scores between 2.0 and 3.0 the communication of the outcome of 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 if they: a) haven't participated, or b) targeted less than 90% of the compulsory pesticides in the target lists (80% for SRM-compounds), or c) detected less than 90% of the compulsory compounds present in the test items (80% for SRM-compounds). Additionally, NRLs that obtained AZ^2 higher than 3 in two consecutive EUPTs of the last four EUPTs, will be considered as **underperforming in accuracy**. A two-step protocol established by DG-SANTE will be applied as soon as underperformance of an NRL is detected[14]:

Phase 1:

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

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

EURL EU REFERENCE LABORATORIES FOR RESIDUES OF PESTICIDES

8th Edition: Revised 23th January, 2018

- 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.

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

SPECIFIC PROTOCOL

for the EU Proficiency Test for Pesticide Residues in Cereals/Feeding stuff using Multi Residue Methods, EUPT-CF12 (2018)

(last updated: 22 January 2018)

Introduction

This protocol is complementary to the General Protocol for EU Proficiency Tests for Pesticide Residues in Food and Feed. The current proficiency test covers pesticides that are determined by Multi Residue Methods. This EUPT is to be performed by all National Reference Laboratories for Cereals and/or Feeding stuffs (NRL-CFs) as well as by all official EU laboratories (OfLs) responsible for official pesticide residue controls on cereals and/or feeding stuff, as far as their scope overlaps with that of the EUPT-CF12.

Test Item (Test Material)

This proficiency test concerns the analysis of pesticide residues in hay flour. The hay has been grown in Denmark and pesticides were applied in the field.

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

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

Analytical Parameters

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

Laboratories should carefully read the Target Pesticides List, where important information about reporting of results, as well as the Minimum Required Reporting Levels (MRRLs), is given. The Target Pesticides List contains only individual compounds, and results should only be reported for individual compounds, no matter how the residue definitions have been set.

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

Amount of Test Item

The participants will receive:

- approximately 100 g of rye kernel Test Item with incurred and spiked pesticides and
- approximately 100 g of blank rye kernel Test Item.

Shipment of Test Items

The Test Items are planned to be shipped on 28 January 2019.

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. Contrary to previous EUPT-CF this Test Item is not flour and the participant must mill before analyses. 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 5 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.

DTU EUPT Webtool and Deadlines

To select pesticide scope and report results and method information, the participants should log in to the DTU EUPT Webtool using the username and password send by email. For this current EUPT it will not be possible to change the password or ask for a new one. So it is important to save the information.

The analytical scope must be selected prior to the shipment of the samples. This can be done via the DTU EUPT Webtool. The scope selection subpage will be open from 21-28 January 2019.

The DTU EUPT Webtool will be accessible from 29 January 2019 for sample receipt acknowledgement and submission results and method information.

The deadline for submission is 25 February 2019 at 24.00 CET.

Test Item Receipt and Acceptance

Once the laboratory has received the Test Items it must report to the organiser, via the DTU EUPT Webtool, the date of receipt, and its acceptance. If the laboratory does not respond by 8 February 2019, the Organiser will assume that the Test Items have been received and accepted.

If participants have not received the Test Items by the 1 February 2019 at noon, they must inform the Organiser immediately by e-mail to eurl-cf@food.dtu.dk.

Reporting Quantitative Results and method information

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

a) was not detected,

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

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

Significant Figures:

Residue levels <0.010 mg/kg;

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

Residue levels ≥ 0.010 mg/kg;

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

Method information on the analytical method(s) used must also be reported

Deadline: All results and method information must be reported and submitted via DTU EUPT Webtool by **25 February 2019 at 24.00 CET**. The website will NOT be accessible for result submission after this date and time. The results and method information must be submitted before deadline by using the submit button

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 can also be done by accessing DTU EUPT Webtool. Deadline for this is 6 March 2019.

Follow-up actions

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

Documents

All documents related to EUPT-CF13 can be found on EUPT–CF13 Website.

Calendar

Activity	Dates
Announcement Calendar Target Pesticide List	Oktober 2018
EUPT-Registration Website open	November 2018
Deadline for registration	10 January 2019
Specific Protocol published	21 January 2019
Website for selecting pesticide scope open	21 January 2019
Website for selecting pesticide scope closed	28 January 2019
Distribution of Test items	28 January 2019
Deadline for receipt and acceptance of Test Materials	within 24 hr on receipt
Deadline for Result Submission	25 February 2019 at 24.00 CET
Deadline for submission of additional method information for false negative results	6 March 2019 at 24.00 CET
Preliminary Report (only compilation of results) published	26 April 2019
Final Report published	December 2019

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.

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

Mette Erecius Poulsen

Head of EURL Cereals and Feeding stuff

National Food Institute
Technical University of Denmark
Kemitorvet, Building 202
DK-2800 Lyngby
Phone: +45-3588-7463
E-Mail: eurl-cf@food.dtu.dk
http://www.eurl-pesticides.eu

Organising Team:

Susan Strange Herrmann, Chemist	EURL for Cereals and Feeding stuff
Elena Hakme, Chemist	EURL for Cereals and Feeding stuff
Merete B. Ludwigsen, Technician	EURL for Cereals and Feeding stuff
Lisbet Pilhkjær, Technician	EURL for Cereals and Feeding stuff
Ban M. Kadhum, Technician	EURL for Cereals and Feeding stuff

Quality Control Group:

Dr. Antonio Valverde	University of Almeria, Spain
Dr. Paula Medina	European Food Safety Agency, Italy

Advisory Group

Prof. Amadeo R. Fernández-Alba	University of Almeria, Spain
Dr. Miguel Gamón	Pesticide Residue Laboratory of the Generalitat Valenciana, Valencia, Spain
Dr. André de Kok	Food and Consumer Product Safety Authority (NVWA), Wageningen, The Netherlands
Mr. Ralf Lippold	Chemisches und Veterinäruntersuchungsamt (CVUA) Freiburg, Germany
Dr. Michelangelo Anastassiades	Chemisches und Veterinäruntersuchungsamt (CVUA) Stuttgart, Germany
Dr. Sonja Masselter	AGES Competence Center for Residues of Plant Protection Products, Innsbruck, Austria
Dr. Tuija Pihlström	National Food Administration, Uppsala, Sweden
Dr. Magnus Jezussek	Bavarian Authority of Health an Food Safety, Erlangen, Germany
Mr. Finbarr o'Regan	Pesticide Control Laboratory, Celbridge, Ireland
Dr. Patrizia Pelosi	Istituto Superiore di Sanità, Roma, Italy

National Food Institute
Technical University of Denmark
Building 202
Kemitorvet
2800 Lyngby
Denmark

Tel: +45 35 88 70 00

ISBN: 978-87-93565-61-6

www.food.dtu.dk