European Commission

EURL-SRM

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

EU Proficiency Test on the Analysis of Honey for incurred and spiked Pesticides Residues Requiring Single Residue Methods

EUPT–SRM19

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Final Report

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EU PROFICIENCY TEST
EUPT-SRM19, 2024

Residues of Pesticides Requiring Single Residue Methods

Test Item: Grape Homogenate

Final Report

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FOREWORD

The Official Controls Regulation (Reg. (EU) 625/2017) [1] defines the general tasks and duties of the EU Reference Laboratories (EURLs) for Food, Feed and Animal Health[1] including the organisation of comparative tests (= proficiency tests: PTs). These PTs are carried out on an annual basis with the aim of improving the quality, accuracy and comparability of the analytical results generated by EU Member States within the framework of the EU coordinated control programs as well as national monitoring programs. By participating in PTs laboratories can assess and at the same time demonstrate their analytical performance. The attention to detail that laboratories pay to PT analysis, together with the need to identify errors and take corrective action in cases of underperformance, leads to continuous improvement in the quality of analytical results.

According to Article 28 of Reg. (EU) 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin [2], all laboratories analysing for pesticide residues within the frame-work of official controls shall participate in the European Union Proficiency Tests (EUPTs) for pesticide residues. The participation of official laboratories (OfLs) in the comparative tests organized by the EURLs was layed down in Article 38 (2) of Reg. (EU) 625/2017. Furthermore, Article 101 (1)(a) of the same regulation requires the participation of National Reference Laboratories (NRLs) in these comparative tests.

Since 2006, the EURL for pesticide residues requiring the use of Single Residue Methods (EURL-SRM) has been annually organising one scheduled EUPT. In total, 19 EUPT-SRMs were organised during this timeframe. Twelve of these EUPTs were organised in cooperation with other EURLs and seven by the EURL-SRM unilaterally:

- Six PTs were organised in cooperation with the EURL for pesticide residues in Fruits and Vegetables (EURL-FV): EUPT-SRM17 (2022) on Tomatoes, EUPT-SRM11 (2016) on Spinach, EUPT-SRM8 (2013) on Potatoes, EUPT-SRM5 (2010) on Apple Puree, EUPT-SRM3 (2008) on Carrots, and EUPT-SRM1 (2006) on Apple Juice.
- Five PTs were organised in cooperation with EURL for pesticide residues in Cereals and Feeding Stuff (EURL-CV): EUPT-SRM15 (2020) on Rice, EUPT-SRM10 (2015) on Corn Flour, EUPT-C5/SRM6 (2011) on Rice, EUPT-C3/SRM4 (2009) on Oats and EUPT-C1/SRM2 (2007) on Wheat.
- A single PT was organised in cooperation with the EURL for pesticide residues in Food of Animal Origin (EURL-AO): EUPT-SRM14 (2019) on Bovine Liver.
- Among the seven PTs organized by the EURL-SRM unilaterally five were based on commodities of plant origin, thereof two on commodities of high water content: EUPT-SRM19 (2024) on Grapes and EUPT-SRM12 (2017) on Strawberries; two on dry commodities with high oil content: EUPT-SRM16 (2021) on Sesame and EUPT-SRM13 (2018) on Soybeans and one PT on a dry commodity of low lipid content: EUPT-SRM7 (2012) on Lentils. The remaining two PTs organised unilaterally concerned food of animal origin: EUPT-SRM9 (2014) on Milk and EUPT-SRM18 (2023) on Honey.

Participation in the respective EUPTs is mandatory for all NRLs for pesticides requiring Single Residue Methods (NRL-SRMs) and for all OfLs analysing pesticide residues within the framework of national or EU control programs in commodities represented by the respective EUPT test item. Laboratories in EU Member States analysing pesticide residues within the frame of import controls according to Reg. (EC) 1793/2019 are also considered to be performing official controls in the sense of Reg. (EU) 625/2017 and are thus also obliged to take part in EUPTs. OfLs from EFTA countries (Iceland, Norway and Switzerland) that are or used to be contributing data to the EU multiannual coordinated community control program (MACP), EU laboratories analysing official organic samples within the frame of Reg. (EU) 889/2008, as well as OfLs from EU-candidate countries (i.e. Albania, Bosnia and Herzegovina, Montenegro, North Macedonia, Serbia and Turkey) are also

[1] Formerly known as Community Reference Laboratories (CRLs)

invited to take part in EUPTs. A limited number of laboratories from third countries, in particular if they are involved in the control of food or feeding stuff exported to EU member states are allowed to take part in this exercise, too, as long as sufficient test material is available, as long as sufficient test material is available. However, only results submitted by labs from EU and EFTA countries are included in the calculation of the assigned values.

Based on information about the commodity scope and the labs' NRL-function, a tentative list of EU-labs considered being obliged to participate in the EUPTs organized within a PT-season, is uploaded onto the PT registration page. The pesticide scope is not taken into account in these lists. NRLs and OfLs can see their participation status during the registration. Laboratories listed as being obliged to participate in an EUPT exercise in a given year but deciding not to take part in, are asked to state the reason(s) for their non-participation. The same applies to laboratories originally registering to participate in a certain EUPT but finally not submitting results.

DG-SANTE has full access to all data of EUPTs including the lab-code/lab-name key. The same applies to all NRLs as far as laboratories belonging to their own country networks are concerned. Results for this EUPT or a series of EUPTs, evaluated on a country-by-country basis, may be further presented to the European Commission Standing Committee on Plants, Animals, Food and Feed (PAFF)-Section Pesticides Residues, or during the EURL-Workshops.

CONTENT

EUROPEAN COMMISSION –
EU-PROFICIENCY TEST ON RESIDUES OF PESTICIDES
REQUIRING SINGLE RESIDUE METHODS
TEST ITEM: GRAPE HOMOGENATE
EUPT-SRM19, 2024

INTRODUCTION

On 10 November 2023 the Announcement/Invitation Letter (Appendix ??) for the EUPT-SRM19, accompanied by SRM19 Calendar and Preliminary Target Pesticides List (Appendix ?? and ??), was published on the EUPT-SRM19-Website. All relevant National Reference Laboratories (NRLs) of the 27 EU-Member States (MS), as well as all relevant EU-Official Laboratories (OfLs) whose contact details were available to the organisers were invited to participate.

The preliminary Target Pesticides List (TPL), released on 10 November 2023 following consultation with the EUPT-Scientiffic Committee, entailed 19 compulsory, 7 optional analytes and 2 extra analytes. The two extra analytes (gamma-Cyhalothrin and Difluoroacetic acid) were included with the aim to highlight their importance and to explore how many laboratories are covering these compounds and with which analytical methods. These two compounds are not included in the evaluation of labs' proficiency. The list of optional analytes originally included meptyldinocap, its degradant 2,4-DNOP as well as meptyldinocap (sum following hydrolysis and expressed as meptyldinocap). On 20 November 2023 the TPL was updated by including meptyldinocap (sum, calculated). This sum was supposed to be calculated by summing up the results of the individual components (meptyldinocap and 2,4-DNOP expressed as meptyldinocap). So the number of optional parameters increased from 7 to 8. This change was communicated to all participants.

For each of the analytes on the Target Pesticides List (TPL) a residue definition valid for the PT and the minimum required reporting level (MRRL) were stipulated. The selection of the compounds considered the entries within the SANTE working document on pesticides to be considered in national control programmes[1], the relevance of compounds for grape, the possibility of application during cultivation, the availability of analytical standards, and the capability of laboratories.

On 15 December 2023, all EU-NRL-SRMs and all EU-OfLs analysing pesticide residues in fruits and vegetables within the framework of official controls, including import controls under Reg. (EU) 1793/2019 and organic food controls under Reg. (EU) 889/2008, were invited to register for the EUPT-SRM19. NRLs and OfLs from EFTA and EU-candidate countries were also invited if their contact data were available. All required laboratory information (i.e. contact data, function (NRL, OfL etc.) and scope (commodities covered)) was extracted from the EURL-DataPool. Several weeks prior to launching the registration, the OfLs and NRLs were asked to update/confirm the DataPool entries. Some official and commercial laboratories from 3rd countries having participated in previous EUPTs were also invited. Such labs are typically allowed to participate especially if they are verifiably involved in export controls of food or feed destined for the EU. However, only the results from EU and EFTA OfLs are taken into account for the establishment of the assigned values of the analytes..

[1] SANCO/12745/2013 rev. 10(3); 26 – 27 November 2018

Based on their commodity scope and NRL-function (NRL-SRMs), all official laboratories were allocated a tentative status as regards their obligation to participate in the EUPT-SRM19. This status was stored in the DataPool, so that every participant could see it during the registration. To ensure that all concerned official laboratories were informed about this EUPT, the NRLs were asked to forward the invitation to all relevant OfLs within their countries. It was made clear that the status of the laboratories was only tentative, and that the real obligation to participate was based on the respective regulations. From 15 December 2023 till 7 January 2024 laboratories that were obliged or interested to participate in this PT could register using the registration form on the EURL-Datapool. Obliged laboratories not intending to participate in the PT had to register for non-participation and state their reason. The SRM19 Specific Protocol (**Appendix 9**) was provided to the participants on 19 January 2024 via hyperlinks in e-mails. The SRM19 Webtool Guidance (**Appendix 12**) was made accessible via a web-link which was communicated in the Specific Protocol of the PT and the Webtool. This link was was also communicated to the participants via two emails, one sent manually by the organisers on 25 January, and one sent automatically by the Webtool together with the login credentials.

In total, 123 OfLs (incl. NRLs) from 29 countries (26 EU-Member States, 3 EFTA-countries), four laboratories from one EU candidate country and 8 laboratories from 6 countries outside Europe have registered for participation in the EUPT-SRM19 and completed the results submission for this PT.

The seedless red grapes used to produce the EUPT-SRM19 test material were purchased from a wholesale provider in Italy and arrived ripped off from the stems and deeply frozen in 15 kg bags. Our preliminary analysis showed that, except trace amounts of copper, phthalimide and trimethylsulfonium, which were much lower than the corresponding MRRLs, none of the other analytes on the Target Pesticides List were detected at relevant levels in the purchased material. More details are given in Chapter 1 **"TEST ITEM"**.

1. TEST ITEM

1.1 Selection of PT-Commodity and the Raw Material

During the meeting of the EUPT Scientific Committee in June 2023, it was decided to use grape as the matrix for the EUPT-SRM19. In order to avoid potential problems caused by seeds and facilitate the production of the homogenate, deeply frozen and destemmed seedless grapes were used. These were purchased from a wholesaler based in Italy. In a preliminary test, none of the compounds on the Target Pesticides List **(Appendix 10)** was found in the material at relevant levels with the exception of copper. Subsequently, in December 2023, 8 packages of 13.5 kg of frozen grapes, all from the same batch, were purchased and used to produce the SRM19 test material.

1.2 Selection of Compounds for the Target Pesticides List (TPL)

The compounds to be included in the Target Pesticides List (TPL, **Appendix 10)** were selected by the organiser and the EUPT-Scientific Committee (Advisory Group and Quality Control Group) taking the following points into account:

1) the scope of analytes recommended for the analysis in grape samples within the framework of the Multi-Annual National Monitoring Programs (MANCP) as listed in the Working Document (SANCO/12745/2013 rev. 15(3);
2) the scope of the EU-coordinated Multi-Annual Control Program (EU-MACP) as regulated, and the Implementing Reg. (EU) 2023/731;
3) the relevance of certain analytes to the matrix "grape" / matrix group (high acid content) based on the information collected from various sources;
4) the capabilities and interrests of the potential participants as revealed through a survey on SRM19 Target Pesticides run among the OfLs in November 2023
5) suggestions/voting by EUPT-Scientific Committee;
6) the intention to keep the number of different methods required to cover the full scope of analytes reasonably low.

The minimum required reporting levels (MRRLs) were set at the following levels (the compounds that were present in the test material are highlighted in bold and italic):

- at 0.01 mg/kg for *2,4-D (free acid),* ***avermectin B1a****, captan, chlormequat-Cl,* ***clopyralid, dithianon, DTC (expr. as CS_2),*** *emamectin B1a,* ***ethephon, folpet****, glufosinate, mepiquat-Cl,* ***MPP (aka MPPA), N-acetyl glufosinate, phthalimide,*** *THPI,* ***2,4 DNOP (meptyldinocap metab.),*** *amitrole, MCPA (free acid),* ***meptyldinocap, meptyldinocap (sum, following hydrolysis)****, triclopyr (free acid), trimethylsulfonium cation,* ***gamma-cyhalothrin***
- at 0.02 mg/kg for ***meptyldinocap (sum, calculated), difluoroacetic acid (DFA)***
- at 0.03 mg/kg for *captan (sum),* ***folpet (sum)***
- at 0.2 mg/kg for ***copper***

1.3 Preliminary Investigation: Analyte Stability in Grape

In order to verify the stability of the TPL-compounds during thawing of the test material, different analytical portions of blank grape homogenate were spiked in frozen condition and were extracted either immediately or after a pre-defined delay time (2 h, 4 h or 15 h) during which the samples were left at room temperature. After approx. 90 min the samples were fully defrosted. Most compounds were stable during the entire storage time with some exceptions. ***Captan*** was degraded by 40 – 50 % within 15 h, but only

by 15 % within 4 h. ***Folpet*** was degraded by 30 % within 15 h and by only 10 – 15 % within 4 h. ***Dithianon*** showed 80 % losses within 4 h and was no more detectable after 15 h. All other analytes showed satisfactory stability over the entire period.

1.4 Preparation of the Test Item and Preliminary Homogeneity Test

On the day before spiking, the slightly defrosted grapes were comminute using knife mills (in 300 – 400 g portions). The entire material was transferred into a large plastic container and stored over night in the freezer for cooling. On the next day, 98 kg of the grape homogenate, which was at –2.5 °C but already liquid, was stirred using a high shear batch mixer and spiked with the selected pesticides. Except metiram and copper, the pesticides as well as the concentrations and the amount of stock solutions listed in **Table 1-1** were mixed together to a final volume about 190 mL. The mixture consisted of 75 % water and 25 % acetonitril. 10 g of ascorbic acid were added to enhance the antioxidative properties of the grape. Copper was added separately, and the material was thoroughly stirred for 45 min. Metiram was spiked in form of an aqueous suspension of a commercial plant protection product. After metiram was spiked, the homogenate was stirred for a further 30 min. During homogenisation, the temperature of the homogenate was raised from –2,5 °C to 5 °C. After mixing, portions of approximately 600 – 800 g of the spiked homogenate were placed in zip-lock plastic bags, sealed and placed flat in a freezer to obtain thin plates that were easy to handle during the final mixing step. The frozen grape homogenate was further cryo-mixed six days later in 500 – 600 g portions using a knife mill and dry ice. This procedure resulted a material with a free-flowing snow-like consistency. The material was quickly filled into numbered bottles and sealed with a lid. The bottles were then quickly placed in a freezer to ensure that the snow-like consistency was maintained. However, due to the high sugar content of the homogenate the material partly collapsed in the freezer (–20 °C).

Table 1-1: Analytes present or spiked in the SRM19 test material and their application history

	Analytes spiked to the test item	Residues incurred	Spiked in lab	Form of compound spiked	Stock Solution		Expected conc. in the test material [mg/kg]
					Conc. [mg/ml]	Volume used for spiking [ml]	
Mandatory	**Abamectin B1a**	No	Yes	Abamectin (B1a + B1b)	1.0 [3)]	7.0	0.072
	Clopyralid	No	Yes	Clopyralid	1.0 [2)]	20.0	0.21
	Copper	Traces	Yes	$CuSO_4 \cdot 5\ H_2O$	200 [1)]	58.9	30.8
	Dithianon	No	Yes	Dithianon	1.0 [4)]	40.0	0.41
	Dithiocarbamates as CS2	No	Yes	Metiram (CELAFLOR)	0.7 [1)]	38.3	0.15
	Ethephon	No	Yes	Ethephon	1.0 [2)]	6.0	0.062
	Folpet	No	Yes	Folpet	1.0 [4)]	28.0	0.29
	MPP (aka MPPA)	No	Yes	MPP (aka MPPA)	1.0 [3)]	7.0	0.072
	N-Acetyl Glufosinate	No	Yes	N-Acetyl Glufosinate	1.0 [2)]	7.0	0.072
	Phthalimide	Traces	Yes	Phthalimide	1.0 [2)]	7.0	0.072
Optional	**2,4 DNOP (meptyldinocap metab.)**	No	Yes	2,4 DNOP (meptyldinocap metab.)	1.0 [3)]	5.0	0.051
	Meptyldinocap	No	Yes	Meptyldinocap	1.0 [3)]	10.0	0.10
Extra	**Difluoroacetic acid (DFA)**	Yes	Yes	Difluoroacetic acid (DFA)	1.0 [2)]	13.0	0.13
	gamma-Cyhalothrin	No	yes	gamma-Cyhalothrin	1.0 [3)]	3.4	0.061
				lambda-Cyhalothrin	1.0 [3)]	5.1	0.087 (sum)

[1)] in water; [2)] in water + 10 % acetonitrile ; [3)] in acetonitrile; [4)] acetone

During transport with dry ice (–78 °C) in the shipping packages, the material became quite hard. However, after leaving it for a short time at room temperature, it softened again and could be easily portioned. This material behavior was also communicated to the partricipants to avoid irritations.

Prior to bottling the material for shipment a preliminary test was conducted in order to check if all spiked compounds (and especially those prone to degradation) were present at appropriate levels (>3 MRRL) and if the material was sufficiently homogeneous. For this purpose, eight material portions á approx. 50 g were taken from different spots of the initial homogenate (98 kg). The samples were analysed for selected analytes via QuEChERS and QuPPe as well as for ***dithiocarbamates***. The relative standard deviations of all investigated analytes were between 1 % and 8 %, all determined levels of the spiked analytes were much higher than 3× of the concerned MRRLs. The material was thus deemed suitable for packaging and distribution.

1.5 Packaging and Delivery of PT Materials to Participants

On 5 February 2024, the day of dispatch, one test item (bottled PT-material) was packed into one thermo-insulated polystyrene box, filled-up with dry ice pellets (2 – 3 kg in each box) and transported by DHL-Express to each of the participating laboratories. Two boxes, each containing one test item, were sent to laboratories having ordered double amount. Once the parcel was picked up by the shipping company (DHL Germany), the main PT corresponding person of each participating laboratory received an e-mail from DHL entailing the individual online tracking number.

Among the 126 shipments to laboratories in EU and EFTA countries, 114 (92 %) reached the participating labs within 1 day on Tuesday, 6 February and 11 (9 %) within 2 days on Wednesday, 7 February. In all of those cases the material arrived the participants in frozen condition, mostly with dry ice still present in the package. Only one package to an EU lab (LabCode 117) arrived the participant on Friday, 9 February, and the material was thawed. The organiser arranged a new shipment for this laboratory on Monday, 12 February. However, this second package didn't reach the participant by 19 February, the organiser decided to ask DHL to destroy it. It turned out, that an error in the DHL logistics system was responsible for the delay of both shipments. Since the error couldn't be solved by DHL in a reasonable time and the same outcome was expected in a third shipment, it was decided to ask the affected lab to either withdraw its EUPT-SRM19 participation or to use the material of the first shipment. The lab agreed with the latter option, and it was decided to add remarks to the report in case of compounds being affected by prolonged exposition of the homogenate at room temeprature, i.e. ***folpet*** and its degradant ***phthalimide*** as well as ***dithianon***.

Among the 12 shipments to the participants in third countries (incl. one EU Candidate country), the parcels arrived the participating laboartories within 1 day in two cases (2× UK), within 3 days in three cases (CR, PE and RS), within 4 days in three cases (AU, IN, RS), within 7 days in two cases (PE, VN) and within 9 days in one case (RS). The delays were mainly caused by prolonged customs clearance. But even within the same country, the necessary time for clearance varied. In some cases DHL or the customs placed the package into the freezer or a refrigerator upon request by the recipients. Only two of the participants reported that the material was defrosted on arrival. Again, the organiser will take care of these cases during the evaluation and, wherever applicable, make a remark.

Given that 92 % of all packages arrived the participants within 2 days in frozen state and given that many of the other shipments were kept frozen till custom clearance was completed, the organisers assumed that, at least for these laboratories, differences in shipment duration would have most likely no significant influence on the analyte concentrations and the analytical results of the laboratories. As the impact of sample defrosting on certain analytes had been investigated in advance of the study, it was decided not to run an extra stability test under shipment simulation conditions (see also **Section 1.9: Transport Stability Test, p. 8**).

Since the delayed shipments concerned only laboratories outside the EU or EFTA zones, and since results from these labs are not taken into account when establishing the assigned values, it was concluded that any analyte concentration shifts in the material provided to those laboratories wouldn't influence the assigned values. However, those special cases where laboratories received their samples late are taken into account in the evaluation of the laboratories' performance. Details on shipment duration are shown in **Appendix 2.**

The organisers would like to appeal to the participants to track their own parcels via the online tracking tool of the shipping company in order to recognize delays and take measures which may include providing the customs with necessary documents, asking for an acceleration of the clearance procedure or asking the customs or the shipping company to place the parcel in the freezer until clearance is granted. The participants are furthermore encouraged to contact the local office of the shipping company to ensure optimal delivery timing.

1.6 Analytical Methods

The analytical methods used by the organisers to check the homogeneity and storage stability of the analytes contained in the test item and to verify the absence of the remaining TPL-analytes are summarized in **Table 1-2 (p. 5)**. For more details on the methods used, please refer to the EURL-SRM website: http://www.eurl-pesticides.eu (→EURL-SRM Methods or Analytical Observations).

1.7 Homogeneity Test

After filling the test item into bottles, 10 bottles were randomly chosen for the homogeneity test and two analytical portions per bottle were taken for each analytical method. Both the order of sample preparation and the order of extract injection into the analytical instruments were random. With the exception of ***copper***, matrix-matched calibration using blank extracts or procedural calibration using blank material were employed for quantification. In many cases, isotope labelled standards (ILISs) were used to minimize errors. For all compounds, analytical portions of 10 g were used, except ***copper*** (2 g).

The statistical evaluation of the homogeneity test data was performed according to the ISO 13528:2015 "Statistical methods for use in proficiency testing by interlaboratory comparison" [6]. An overview of the statistical evaluations of the homogeneity test is shown in **Table 1-3 (p. 6)**. The individual data of the homogeneity test is given in **Appendix 3**.

The acceptance criterion for the test item to be sufficiently homogeneous for the Proficiency Test is that the estimate of the between-sample standard deviation s_s is smaller than $0.3 \times \sigma_{pt,}$ where $\sigma_{pt} = 0.3 \times$ FFP-RSD (25 %) × the analytical sampling mean of the analyte. In addition and for informative purpose only, the actual sampling error and repeatability were also calculated and compared. If the between-sample standard deviation s_s is smaller than the check value $\sqrt{c}$, then the batch of the PT test items can be regarded as sufficiently homogeneous. The check value c is calculated as $F_1 \times {\sigma_{allow}}^2 + F_2 \times {s_w}^2$, with F_1 and F_2 being constants with values of 1.88 and 1.01, respectively, when duplicate samples are taken from 10 bottles. ${\sigma_{allow}}^2 = 0.3 \times$ FFP-RSD (25 %) × the analytical sampling mean of the analyte, and s_w is the within sample standard deviation.

As all target compounds passed the homogeneity test, the test item was considered sufficiently homogenous and suitable for the EUPT-SRM19.

Table 1-2: Analytical methods used by the organisers to check for the homogeneity and storage-stability of the pesticides present in the test item and to demonstrate the absence of other pesticides listed in the TPL.

QuEChERS Method [3]:
involving: weighing of 10 g grape homogenate into a sealable vessel, addition of IS/ILIS, addition of acetonitrile, shaking, addition and buffer/partitioning of salt mixture, centrifugation and direct determination by GC-MS/MS and LC-MS/MS.

Compound	IS	Determinative analysis		Notes
Abamectin B1a	**Propyzamid D_3**	**LC-MS/MS**	**ESI (pos)**	
Clopyralid	**BNPU**	**LC-MS/MS**	**ESI (neg)**	
Dithianon	**Dithianon D_4**	**LC-MS/MS**	**ESI (neg)**	
Folpet	**Folpet D_4**	**GC-MS/MS**	**EI (pos)**	
Phthalimide	**Propyzamid D_3**	**LC-MS/MS**	**ESI (pos)**	
2,4 DNOP	**BNPU**	**LC-MS/MS**	**ESI (neg)**	Special LC-gradient for separation
Meptyldinocap	**BNPU**	**LC-MS/MS**	**ESI (neg)**	
2,4-D (free acid)	*2,4-D $^{13}C_6$*	*LC-MS/MS*	*ESI (neg)*	
Captan	*Captan D_6*	*GC-MS/MS*	*EI (pos)*	
Emamectin B1a	*Propyzamid D_3*	*LC-MS/MS*	*ESI (pos)*	
THPI	*Propyzamid D_3*	*LC-MS/MS*	*ESI (pos)*	
MCPA (free acid)	*BNPU*	*LC-MS/MS*	*ESI (neg)*	
Triclopyr (free acid)	*BNPU*	*LC-MS/MS*	*ESI (neg)*	

QuPPe-PO Method [5]:
involving: weighing of 10 g grape homogenate into a sealable vessel, addition of ILISs, addition of methanol containing 1 % formic acid, shaking, centrifugation, filtration and direct determination by LC-MS/MS in the ESI (neg.) or ESI (pos.) mode

Compound	IS	Determinative analysis		Notes
Ethephon	**Ethephon D_4**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
MPP (aka MPPA)	**MPP D_3**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
N-Acetyl Glufosinate	**N-Acetyl Glufosinate D_3**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
Difluoroacetic acid (DFA)	**DFA ^{13}C**	**LC-MS/MS**	**ESI (neg)**	**QuPPe M1.3**
Chlormequat-chloride	*Chlormequat D_4*	*LC-MS/MS*	*ESI (pos)*	*QuPPe M4.2*
Glufosinate	*Glufosinate D_3*	*LC-MS/MS*	*ESI (neg)*	*QuPPe M1.3*
Mepiquat-chloride	*Mepiquat D_3*	*LC-MS/MS*	*ESI (pos)*	*QuPPe M4.2*
Amitrole	*Amitrole $^{13}C_2$*	*LC-MS/MS*	*ESI (pos)*	*QuPPe M4.2*
Trimethylsulfonium cation	*Trimethylsulfonium D_9*	*LC-MS/MS*	*ESI (pos)*	*QuPPe M4.2*

QuEChERS followed by alkaline hydrolysis [8]
involving: transfer of an aliquot of the QuEChERS extract into a vial, addition of 25 % ammonia solution and incubation for approx. 16 hours at room temperature overnight. The hydrolysate was "neutralized" with concentrated acetic acid, followed by LC-MS/MS analysis.

Compound	IS	Determinative analysis		Notes
Meptyldinocap (sum following hydrolysis)	–	**LC-MS/MS**	**ESI (neg)**	

Dithiocarbamate method [9]
involving: weighing of 10 g grape homogenate into a sealable vessel, addition of chloroform (as IS) and 10 ml isooctane and 75 ml $SnCl_2$ /HCl, followed by cleavage to CS_2 in a shaking waterbath for 3 hours at 85°C, followed by GC-MS/MS analysis

Compound	IS	Determinative analysis		Notes
Dithiocarbamates determined and expressed as carbon disulfide (CS_2)	**Chloroform**	**GC-MS/MS**	**EI (pos)**	

Copper method
involving: weighing of 2 g grape homogenate into a Teflon vessel, addition of nitric acid and hydrogen peroxide, microwave assisted thermal combustion measured by ICP-MS.

Compound	IS	Determinative analysis		Notes
Copper	–	**ICP-MS**	**(pos)**	

* : To check for absence of any relevant levels in the blank

Table 1-3: Statistical evaluation of homogeneity test data (n = 10), details please see **Appendix 3**.

	COMPULSORY COMPOUNDS							
	Avermectin B1a	Clopyralid	Copper	Dithianon	DTC (expr. as CS2)	Ethephon	Folpet	Folpet (sum)
Analytical portion size [g]	10	10	10	10	10	10	10	10
Mean [mg/kg]	0.0703	0.188	30.1	0.206	0.0924	0.0694	0.248	0.399
between-samples STD	$1.16\times^{-3}$	$1.21\times^{-2}$	0.23	$4.61\times^{-3}$	0.0	0.0	$1.58\times^{-3}$	0.0
Check Value	$5.27\times^{-3}$	$1.41\times^{-2}$	0.9	$1.55\times^{-2}$	$6.93\times^{-3}$	$5.20\times^{-3}$	$1.86\times^{-2}$	$2.99\times^{-2}$
Passed/Failed	passed	passed	passed	passed	passed	passed	passed	passed

	COMPULSORY COMPOUNDS			OPTIONAL COMPOUNDS			EXTRA COMP.
	MPP (= aka MPPA)	N-Acetyl glufosinate	Phthalimide	2,4-DNOP (free phenol)	Meptyldinocap	Meptyldinocap (sum, calculated)	Difluoroacetic acid (DFA)
Analytical portion size [g]	10	10	10	10	10	10	10
Mean [mg/kg]	0.0735	0.0732	0.0746	0.0499	0.0955	0.157	0.128
between-samples STD	$2.40\times^{-4}$	0.0	0.0	0.0	$1.81\times^{-3}$	$2.04\times^{-3}$	0.0
Check Value	$5.52\times^{-3}$	$5.49\times^{-3}$	$5.59\times^{-3}$	$3.75\times^{-3}$	$7.16\times^{-3}$	$1.18\times^{-2}$	$9.60\times^{-3}$
Passed/Failed	passed	passed	passed	passed	passed	passed	passed

1.8 Storage Stability Test

Within the Specific Protocol, laboratories were recommended storing the samples or analytical portions in the freezer until performing extraction. The bottles for the stability test were thus also stored in the freezer at –20 °C in the period between day 1 and day 3 of the stability test. Shortly after the sample dispatch to the participants, three of the 10 test items spared for the homogeneity test were chosen randomly for the conduction of the stability test and extracted immediately. The analytical results of these three bottles (6 results) were thus used for both the homogeneity test and the stability test (here extraction day 1). The three bottles with the remaining material for the extraction days 2 and 3 of the stability test were placed in the freezer at –20 °C until performing the tests. The methods described in **Section Table 1-3 (p. 6)** were also applied to the analysis of the stability test samples. The extracts of all stability test extractions were stored in the freezer at –20 °C and measured under repeatability conditions within the same measurement sequence on a day suitable for the laboratory (isochronous approach). The dates on which extractions by each method were carried out are shown below:

Extraction day 1: 07 February 2024 (QuEChERS-method)
09 February 2024 (QuPPe-method)
14 February 2024 (Dithiocarbamates-method)
15 March 2024 (Copper-method)

Table 1-4: Results of storage stability test (storage at –18 °C). For the details of each analytes please see the text and **Appendix 4**.

	COMPULSORY COMPOUNDS								
	Abamectin B1a	Clopyralid	Copper	Dithianon	Dithiocarbamates as CS2	Ethephon	Folpet	Folpet (sum)	MPP (= aka MPPA)
Storage at –18 °C (mean values in mg/kg)									
Extraction day 1	0.0651	0.209	29.9	0.227	0.0931	0.0688	0.245	0.386	0.0743
Extraction day 2	0.0658	0.196	–	0.196	–	0.0642	0.254	0.394	0.0691
Extraction day 3	0.0696	0.195	30.3	0.181	0.0994	0.0648	0.246	0.396	0.0732
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.00446 (6.9 %)	-0.0133 (-6.4 %)	0.362 (1.2 %)	-0.03593 (-16.6 %)	0.00639 (6.9 %)	-0.00394 (-5.7 %)	0.00146 (0.6 %)	0.00924 (2.4 %)	-0.00113 (-1.5 %)
$0.3 \times \sigma_{pt}$ [mg/kg]	0.00533	0.0144	0.897*	0.0177	0.00750	0.00437	0.0169	0.0316	0.00614
Passed/Failed	passed	passed	passed	failed	passed	passed	passed	passed	passed

* in case of copper: Instead of 25 % 10 % was used to calculate the check value.

	COMPULSORY COMPOUNDS		OPTIONAL COMPOUNDS			EXTRA COMPOUNDS
	N-Acetyl glufosinate	Phthalimide	2,4-DNOP (free phenol)	Meptyldinocap	Meptyldinocap (sum, calculated)	Difluoroacetic acid (DFA)
Storage at –18 °C (mean values in mg/kg)						
Extraction day 1	0.0739	0.0702	0.0513	0.0953	0.158	0.137
Extraction day 2	0.0698	0.0695	0.0497	0.0948	0.156	0.129
Extraction day 3	0.0752	0.0741	0.0514	0.0961	0.159	0.131
Deviation [mg/kg] ([%]) Analysis 3 vs. Analysis 1	0.00134 (1.8 %)	0.00386 (5.5 %)	0.00004 (0.1 %)	0.00081 (0.9 %)	0.00087 (0.5 %)	-0.00661 (-4.8 %)
$0.3 \times \sigma_{pt}$ [mg/kg]	0.0058	0.00615	0.00485	0.00645	0.0113	0.011
Passed/Failed	passed	passed	passed	passed	passed	passed

Extraction day 2: 29 February 2024 (QuEChERS-method)
05 March 2024 (QuPPe-method)
28 February 2024 (Dithiocarbamates-method)

Extraction day 3: 26 March 2024 (QuEChERS-method)
22 March 2024 (QuPPe-method)
27 March 2024 (Dithiocarbamates-method)
10 April 2024 (Copper-method)

A target compound is considered to be sufficiently stable if $|y_i - y| \leq 0.3 \times \sigma_{pt}$, where y_i is the mean value of the last period of the stability test, y is the mean value obtained from stability test 1 and σ_{pt} the standard deviation used for proficiency assessment, typically 25 % of the assigned value. In the period between the first and the third stability test, which was long enough to exceed the duration of the PT and during which the samples were stored under recommended condition at –18 °C, except ***dithianon*** all other analytes contained in the test item were shown to be sufficiently stable (**Table 1-4**). For those compounds passing the test, it was assumed that the time elapsed between sample receipt by a lab and its analysis had a negligible influence on the results, provided that the recommended storage conditions were followed.

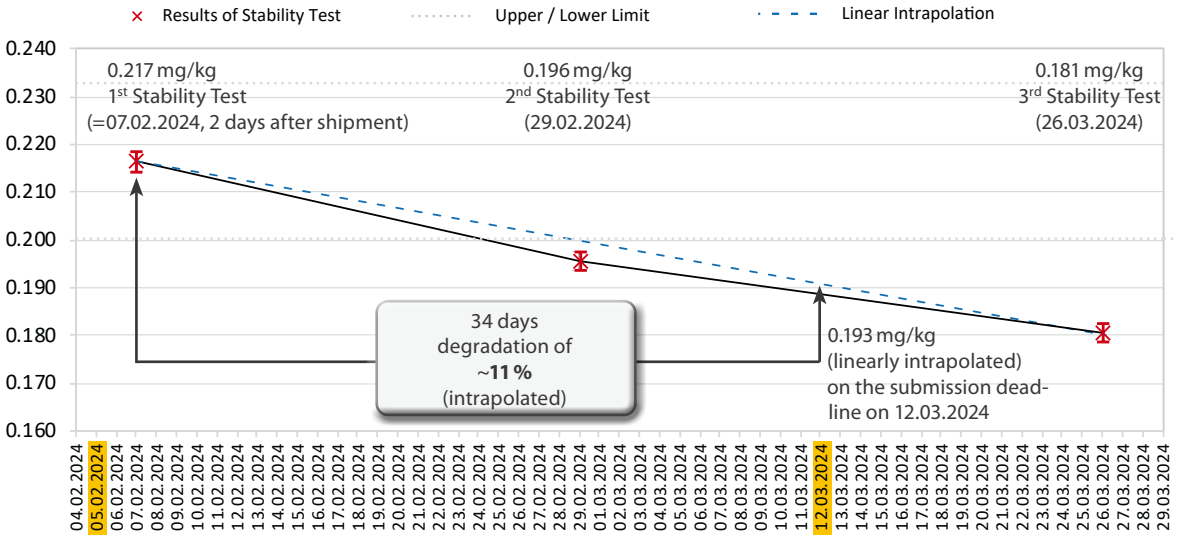

Figure 1-1: Decline of dithianon content in the test sample during storage in the freezer. February 5 was the day of shipment and March 12 the submission deadline. The approximate theoretical dithianon level on the submission deadline was calculated via linear intrapolation.

Dithianon is sensitive to higher temperatures, to higher pH-values as well as to oxidative environments. Although the test material was acidified with a moderate amount of ascorbic acid in order to increase the stability of ***dithianon***, a relevant degradation of this analyte during storage in the freezer over the duration of the stability test (**Figure 1-1, p. 8**). The stability test period lasted 14 days longer than the PT period. As the losses of ***dithianon*** during the stability test period followed a nearly linear trend, a simple linear interpolation was used to estimate the concentration of ***dithianon*** on the day of submission deadline. Based on this calculation, ***dithianon*** experienced losses of ~14 % during storage in the freezer, which exceeds the accepted limit of 7.5 % nearly two-fold. Considering the sensitive nature of ***dithianon*** and the overall broad distribution of the received data (mainly due to the participants defrosting their samples), the organiser refrained from conducting a second more refined stability test for this compound. In consultation with the Scientific Committee, it was decided to evaluate ***dithianon*** for information purposes only, and based on a robust mean value of a sub-population of laboratories having kept the sample frozen until analysis. It was also decided to highlight the need for laboratories to take measures to minimise ***dithianon*** losses during sample handling and analysis (please also refer to **Section 4.2.2, p. 30**). The unacceptable degradation rate of ***dithianon*** during sample storage in the freezer, has surely also influenced the overal distribution of results with labs having conducted the analysis of ***dithianon*** shortly after the sample arrival tentatively achieveing higherconcentrations than those extracting the samples for ***dithianon*** analysis at a late stage of the PT-period. The organisers would like to further highlight, that the homogeneity and stability values of ***dithianon*** presented in the final report deviate from those in the preliminary report and the EUPT-SRM19 presentation given at the NRL-workshop. The deviation is due to the use of a different calibration (previously matrix-matched, now procedural).

The detailed results of all analyses conducted within the framework of the stability test are shown in **Table 1-4** and **Appendix 4**.

1.9 Transport Stability Test

Except one laboratory in Poland that received the sample very late due to an error in the logistics system of the shipping company and the 10 laboratories outside the EU and EFTA, all other participants received the

sample packages within two days in deeply frozen condition and in most cases still with dry ice. As the assigned values of all analytes are calculated on the basis of results submitted by EU and EFTA laboratories, it was concluded that these delays had no influence on the assigned value. The organisers therefore decided to skip the transport stability test in this PT. Still, the individual laboratories having received the sample late may have been affected by significant concentration shifts of certain analytes. In a preliminary test of sample storage at room temperature the following analytes were found to be affected: ***dithianon***, ***folpet*** and ***phthalimide*** (resulting from ***folpet*** degradation). For these compounds the laboratories' results that were obviously affected by delayed delivery are marked and accompanied by a note.

1.10 Organisational Aspects

1.10.1 Laboratory Status: Mandatory and Optional Participation

Based on available information on NRL-status and commodity scope stored in the EURL-DataPool, the EU and EFTA OfLs, including the NRLs, were preliminarily divided into those with obligation to participate in this specific PT and those whose participation was on a voluntary basis. The OfLs were asked to update their status and analytical scope a few months prior to the PT. The NRLs were furthermore reminded of their responsibility of ensuring that the information concerning their network is up-to-date and that all obliged OfLs within their network were informed of this EUPT. All NRLs and OfLs were informed that the division into "obliged" and "voluntary" was tentative and that the real obligation to participate is derived from the respective regulations and their real scope.

Following DG-SANTE instructions, obliged labs that were not intending to participate in the EUPT-SRM19 were instructed to provide explanations for their non-participation.

1.10.2 Announcement / Invitation and EUPT-SRM19 Website

The EUPT-SRM19 was scheduled to run from 5 February till 12 March, 2024. Within the EURL-Web-Portal an EUPT-SRM19-Website was set up on 3 November, 2023. All documents relevant to this EUPT, i.e., Announcement/Invitation Letter (**Appendix 11**), Calendar and Target Pesticides List (TPL) (**Appendix 10**), Specific Protocol (**Appendix 9**) and General EUPT Protocol (**Appendix 8**), were linked to this website. These documents were uploaded both to the EURL-Web-Portal and to the CIRCA BC.

On 10 November, 2023 the Announcement/Invitation Letter for the EUPT-SRM19 was published on the EUPT-SRM19-Website and sent to all NRL-SRMs and all OfLs within the EU member states analysing pesticide residues. Therein the obligation of OfLs to participate in the EUPT-SRM19 was defined as following: all NRL-SRMs and OfLs performing pesticide residue analyses of fruits and vegetables within the frame of National and EU official controls. NRLs and OfLs from EFTA and EU-candidate countries not entailing the above commodities within the routine scope were also invited to participate on a voluntary basis. Laboratories involved in the import controls of products listed under Reg. (EU) 1793/2019 and could be tracked in the EURL-DataPool, as well as EU laboratories officially analysing organic samples within the frame of Reg. 889/2008/EC were also informed about this PT. The latter laboratories were considered eligible but not obliged to participate. All these labs were tracked on a list that was prepared by the EURL-SRM at the request of DG-SANTE following another survey. This list was made available on-line for the convenience of authorities involved in EU-import controls.

1.10.3 Registration

As in the previous EUPTs since 2017, the participants were able to register for this EUPT via a website connected to the EURL-DataPool. All laboratories being obliged to participate in the current EUPT- SRM19, re-

gardless of whether they were intending to participate in this exercise or not, were requested to either register or to state their reasons for non-participation using the same website from 15 December 2023 to 7 January 2024. During the registration, each participating laboratory had to name its main contact person well as at least one and up to three alternative contact persons for the concerned PT. During the registration period, the electronic confirmation for participation or non-participation in the EUPT-SRM19 could not take place due to technical issues. These confirmations were therefore sent manually by the organiser itself. The laboratories received the electronic confirmation within one week upon their registration or upon a change of their registration status.

1.10.4 Further instruction on Test Material and PT

On 19 January 2024, detailed instructions on how to treat the EUPT-SRM19 Test Item upon receipt were provided to the participating laboratories in the Specific Protocol (**Appendix 9**). On 25 January, a detailed guidance for results submission using the Webtool (**Appendix 12**) was also provided to the participants.

On 6 February, one day after dispatch, a few laboratories informed the organiser that the material received was not snow-like as announced but rather hard and thus difficult to take analytical portions. Following internal trials the organiser informed all participants still on the same day via e-mail that the reason for this consistency was the very low temperature of the samples upon arrival due to the use of dry ice (–78 °C.) Leaving the material to reach freezer temperature (approx. –20 °C), e.g. by leaving it over-night in the freezer, resulted in a softer, sorbet-like consistency allowing convenient portioning. In a further email, we also informed participants of a possible phase separation during the first extraction step of QuEChERS, also due to the high sugar content of the material, which did not affect the performance of QuEChERS on the particular sample.

1.10.5 Webtool for Results Submission and Confidentiality

The "Webtool", an online data submission tool, allows the PT main or alternative responsible persons to acknowledge sample receipt and to submit PT-results and method information via a web browser. It has been used since 2019 for all EUPTs on pesticides residues. Login to the Webtool requires the use of personalized login credentials, which are unique to the registered email address of the PT responsible person. These login credentials are created after a person registrers to the Webtool for the first time and are sent to his email address before the Webtool becomes accessible for acknowledgement of sample receipt (typically on the date of sample shipment). Using his personal login credentials, the PT-responsible person can access the results submission pages of all EUPTs to which he has registered using the same e-mail address.

Each laboratory participating in a certain EUPT receives a unique lab code, as soon as one of its PT-responsible persons logs into the particular EUPT-site within the Webtool. The personal login credentials and the unique lab code for a certain PT warrantee the confidentiality. For further information on confidentiality please refer to the General EUPT Protocol (**Appendix 8**).

The EUPT-SRM19 participants received their login credentials from the programmer at the DTU on the day of shipment (5 February). The Webtool was accessible from 12 February, the next Monday following the dispatch, till 12 March.

1.10.6 Actions following Results Submission

After the submission deadline on 12 March, participants were informed on 13 March by the organiser via e-mail about the analytes present in the test material. They were also prompted to check within the Webtool, if they had obtained any tentatively false positive or false negative results. In the latter case, they were requested to report method details for compounds of false negative results via the Webtool in the period

from 13 till 21 June.

Unfortunately, due to a mistake in set up of the PT in Webtool, ***folpet (sum)*** that was actually present in the material was defined in webtool as "not present", therefore, the judgement of false negative results for this analyte in Webtool was wrong causing confusion among the participating labs having analysed for ***folpet (sum)***. After realising this error, the organiser informed all participants about the correct judgement and asked Webtool programmer to solve the problem. The Programmer could localize the error and change the codes, so that such errors will not happen again in the future.

Prior to the PT, a survey was carried out and its results revealed that very few laboratories intended to analyse ***gamma-cyhalothrin***, which requires enantioselective separation on a chiral column. After the PT, the organisers realized that several labs had reported results, but it was suspected that these concerned the unresolved mixture, i.e. ***cyhalothrin (sum)***. In order to correctly evaluate the submitted results, a survey on the use of chiral separation in the analysis of this analyte was subsequently carried out. Except one lab all other participants having analysed for this compound did not use a chiral column and actually determined ***cyhalothirn (sum)***. For this reason, the organiser decided to evaluate ***cyhalothirn (sum)*** for informative purposes. In consultation with the EUPT Scientific Committee it was decided not to penalize the laboratories for submitting results for ***gamma-cyhalothrin*** despite analyzing ***cyhalothrin (sum)***.

1.10.7 Preliminary Report and follow up actions

On 19 April 2023, the preliminary report on the EUPT-SRM19 was released and sent to the participants. This report entailed the preliminary z scores of the compounds present in the PT material, which were calculated based on the preliminary assigned values (prAV). In addition, the organiser highlighted several issues of concern that add uncertainty to the calculated prAVs. These concerned the following analytes: ***dithianon*** (degradation improperly stored homogenates), ***dithiocarbamates*** (underestimations where cleavage conditions were too weak), ***phthalimide*** (biased GC-quantifications when not properly calibrating as well as due to ***folpet*** degradation in improperly stored homogenates), ***meptyldinocap***, ***mepthyldinocap (sum)*** and ***2,4-DNOP*** (uncertainty of prAV as the results population was relatively small and broadly distributed). The reason for evaluating ***cyhalothrin (sum)*** for informative purposes instead of ***gamma-cyhalothrin*** was also given. In some cases other prAVs deviating from the robust means of the entire population had to be used to calculate the preliminary z scores, e.g. because of the need to exclude sub-populations of results generated by laboratories using methods or practices that introduce bias. Laboratories that had submitted false positive results, as well as laboratories that had received preliminary | z scores | > 2, were asked to investigate the reasons for this poor performance and to provide feedback using a special Excel sheet provided by the organisers.

During the period when laboratories submitted reasons for poor performance, one participant claimed that the purity of abamectin standard stated in the analytical certificate of the purchased standard was incorrect. The organisers have purchased the standard in question and were able to confirm the laboratory's claim with their own experiments. In order to investigate whether this issue has affected the assigned value, a separate survey was sent to participating laboratories asking for details of the avermectin/abamectin standards used. Fortunately, only one lab used this batch. The concerned provider was informed on 05.07.2024 about this fact. Shortly afterwards, on 09.07.2024 this chemical supplier confirmed our observation and indicated that QM measures would be taken. At a later stage the supplier indicated that the reason for the bias could not be identified.

2. EVALUATION RULES

2.1 False Positives and Negatives

2.1.1 False Positives (FPs)

Any reported result with a concentration at or above the Minimum Required Reporting Level (MRRL) of an analyte in the Target Pesticides List which was (a) not detected by the organiser, even following repetitive analysis, and/or (b) not detected by the overwhelming majority (e.g. > 95 %) of the participants that analysed for this compound, is treated as a false positive result. Results of an analyte absent in the test item but with a value lower than the MRRL are normally disregarded by the organiser and not considered as false positives. No z scores are calculated for false positive results. Any results reported for analytes not present in the test material and below the MRRL are normally not considered false positives, even though these results should not have been reported. If these results are additionally lower than the lab's reporting limit, they will be attributed with FR ('False Reporting'), see below.

2.1.2 False Repoerting Results (FRs)

Numerical results below the laboratory's reporting limit, are assigned as FRs ('False Reportings'). Such results should not be reported. If the analytes concerned are present in the test material, z scores are calculated for FRs as for any other numerical results. Furthermore, these results are included in the population of results for the determination of the assigned value, unless they are excluded for other reasons (e.g. reported by laboratories outside EU or EFTA countries, generated using biased methods, etc.).

2.1.3 False Negatives (FNs)

These are results of target analytes reported as "analysed" and "not detected", although these analytes were used by the organiser to prepare the test item and were detected, at or above the MRRL, by the organiser and the overwhelming majority of the participating laboratories. In accordance with the General Protocol 11th ed., z scores for false negatives are set at "−4.0". In cases of the assigned value (see **Section 2.2)** being less than a factor of 3 times the MRRL, false negatives will typically not be assigned.

2.2 Assigned Values (x_{pt}) and Calculation of the Respective Uncertainties ($u(x_{pt})$)

In accordance with EUPT-General Protocol 11th ed. (**Appendix 8),** the assigned value x_{pt} of each pesticide in the PT is established using the mean value of robust statistics (x^*) using Algorithm A in ISO 13528:2015 [6] of all results reported by OfLs from EU and EFTA countries. Since the assigned values of the analytes are normally derived from the respective robust mean values of the participants' results and since these results are generated by a variety of analytical methods and standards, the assigned values are metrologically not traceable. Results associated with obvious mistakes and gross errors may be excluded from the population for the establishment of the assigned values. The add-in "RobStat" provided by Royal Society of Chemistry is used to calculate the assigned values with the convergence criterion = 10^{-6}.

The uncertainty of the assigned values of each analyte is calculated according to ISO 13528:2015 [6] using the following equation:

$$u(x_{pt}) = 1.25 \times [(s^*)/\sqrt{p}]$$

Where $u(x_{pt})$ is the uncertainty of the assigned value in mg/kg, s^* is the robust standard deviation estimate in mg/kg and p is the number of data points considered (=the number of results used to calculate the

assigned value). The factor 1.25 is based on the standard deviation of the median, or the efficiency of the median as an estimate of the mean, in a large set of results drawn from a normal distribution.

The tolerance for the uncertainty of the assigned value of each pesticide is calculated as $0.3 \times FFP\text{-}\sigma_{pt,}$ where $FFP\text{-}\sigma_{pt}$ is the target standard deviation of the assigned value derived using a fixed standard deviation of 25 % (see **Section 2.3**). If $u(x_{pt}) < 0.3 \times FFP\text{-}\sigma_{pt,}$ is met, then the uncertainty of the assigned value is considered to be negligible and not needed to be considered in the interpretation of the proficiency test results.

Using the assigned value derived from the robust mean, the z scores of the participants' results are calculated using the formula in **Section 2.4.** All results with z scores > 5 are preliminarily regarded as outliers. If they are confirmed by Grubbs' test as outliers, they are excluded from the results population for the establishment of the assigned value, and the corresponding analyte is calculated again without those results.

2.3 Fixed Target Standard Deviation using FFP-Approach ($FFP\text{-}\sigma_{pt}$)

Based on experience from previous EU Proficiency Tests on fruit and vegetables and cereals, the EUPT-Scientific Committee agreed to apply a fixed fit-for-purpose relative standard deviation (FFP-RSD) of 25 % for calculating the z scores. The fixed target standard deviation using the fit-for-purpose approach ($FFP\text{-}\sigma_{pt}$), for each individual target analyte is calculated by multiplying the assigned value by the FFP-RSD of 25 %. In addition, the robust relative standard deviation of the assigned value (CV^*) is calculated for informative purposes.

2.4 z Scores

For each combination of laboratory and target analyte a z score is calculated according to the following equation:

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

Where

- x_i is the numerical result for the target analyte (i) reported by the participant;
- x_{pt} is the assigned value for the target analyte (i);
- $FFP\text{-}\sigma_{pt}$ is the standard deviation for proficiency assessment using the fit-for-purpose approach (see above).

The z scores are set to −4 for results that are considered false negatives (see **2.1.3)**. Any z scores > 5 are set at 5 in calculations of combined z scores (see **2.5.2**).

The z scores are classified as follows:

$\lvert z \rvert \leq 2$	acceptable
$2 < \lvert z \rvert < 3$	questionable
$\lvert z \rvert \geq 3$	unacceptable

2.5 Laboratory Classification

Based on the scope of target analytes covered by the laboratories in this exercise, laboratories are subdivided into Categories (A and B) in accordance with the rules in the General Protocol (**Appendix 8**). In order to be classified into Category A, a laboratory should have

a) analysed at least 90 % of the compulsory pesticides on the Target Pesticides List,
b) correctly reported concentration values for at least 90 % of the compulsory pesticides present in the test item, and
c) not reported any false positive results.

2.5.1 Combined z Scores

For informative purposes and to allow comparison of the overall performance of the laboratories the Average of the Absolute z Scores (AAZ) is calculated for laboratories with 5 or more z scores. However, combined scores are considered to be of lesser importance than individual z scores..

The **Absolute z Scores (AAZ)** is calculated using the following formula:

$$AAZ = \frac{\sum_{i=1}^{n} |z_i|}{n}$$

where "n" is the number of each laboratory's z scores that are considered in this formula, including z scores assigned for false negative results.
For the calculation, any z score > 5 is set at 5.

3. PARTICIPATION

123 official laboratories (including NRLs) from 29 countries (26 EU-Member States, 3 EFTA-countries), 4 laboratories from 1 EU candidate country and 8 laboratories from 6 countries outside Europa registered for participation in the EUPT-SRM19 and completed the results submission. An overview of the participating laboratories and countries is given in **Table 3-1**. An overview of the participating laboratories and countries is given in **Appendix 11**.

With regard to the NRL-SRMs in EU member states, there was no participation from Estonia and Malta. Due to a major reorganisation of the OfL/NRLs network in Estonia the newly established NRL-SRM in Tartu had not yet managed to cover the full NRL-SRM functions and scope. Since Brexit and despite numerous requests from the PT organiser, Malta has not yet reported any newly subcontracted NRL-SRM to the EURLs..

In total,162 EU-OfLs, including NRL-SRMs, regardless of their commodity scope, as well as all EU-OfLs analysing for pesticide residues in fruits and vegetables, were considered tentatively obliged to participate in the present EUPT. The OfLs also included labs involved import controls according to Reg. (EU) 1793/2018, as far as these were registered in the EUPT-DataPool and approved by the respective NRLs. All these laboratories were aksed to access the online registration page within the EURL-DataPool and either register for participation in the current PT or provide an explanation for their non-participation. All other EU-OfLs, were also invited to participate in the current PT but on the voluntary basis..

One of the obliged OfLs initially registered for participation, but later stated in the Webtool that it was not able to submit any results as none of the pesticides on the TPL was within its lab's scope. Another obliged OfL also initially registered to participate, but ultimately failed to report any results. Despite numerous requests from the PT organiser, this laboratory has not yet responded to this concern.

The reason most frequently given by obliged labs for their decision not to participate in the present PT was that the EUPT-SRM19 target pesticides were out of their routine scope. Including the two above-mentioned labs, that gave sufficient explanations a posteriori, a total of 22 preliminarily obliged labs provided sufficient explanations for non-participation. The total number of EU-labs considered obliged to participate in the EUPT-SRM19 therefore decreased to 140. Thereof 109 labs (78 %) participated in the PT and completed the results submission. Among the 31 labs not giving any explanations for non-participation (22 % among the obliged labs) 9 from Spain, 7 from Italy, 2 each from Hungary and Poland, and one each from eight further countries (BG, CZ, EE, DE, GR, MT, RO and SI).

Two NRL-SRM from EFTA countries (Iceland and Norway) also participated in the PT. As these labs regularly participate in the EU-coordinated monitoring they are also obliged to participate in the EUPTs. Another 12 EU- or EFTA-OfLs participated on voluntary basis.

Table 3-1: Number of laboratories listed as being obliged to participate in the EUPT-SRM19, labs that registered to participate in the PT and completed results submission (grouped by contracting country)

Contracting Country	Labs originally considered to be obliged (*based on scope and NRL)	Labs providing expl. for non-participation	Obliged labs non particip. w/o giving expl.	Finally considered to be obliged	Registered for Participation and submitted results obliged + [on voluntary basis]		Notes
					All	NRL-SRM	
EU: NRLs and OfLs							
AT	1	0	0	1	1	1	
BE	6	0	0	6	6	1	
BE; FR; LU	1	0	0	1	1	0	
BE; NL	1	0	0	1	1	0	
BG	3	0	1	3	2	1	
CY	1	0	0	1	1	1	
CZ	4	0	1	4	2 + [1]	1	
DE	23	4	1	19	15 + [3]	1	
DK	1	0	0	1	1	1	
EE	2	0	1	2	1	0	
ES	37	6	9	31	21 + [1]	2	
FI	3	0	0	3	3	2	
FR	13	1	3	12	9	1	
GR	3	0	1	3	2	2	
HR	8	1	0	7	7	2	
HU	4	0	2	4	2	2	
IE	1	0	0	1	1	1	
IT	25	6	7	19	12	1	
LT	2	0	0	2	1 + [1]	1	
LU	1	0	0	1	1	1	
LV	1	0	0	1	1	1	
MT	2	0	1	2	1	0	No proxy NRL-SRM appointed, one lab in Spain was appointed as OfL for monitoring activities
NL	1	0	0	1	1	1	
PL	14	1	2	13	7 + [4]	1	
PT	3	1	0	2	2	1	
RO	7	3	1	4	3	1	
SE	2	0	0	2	2	1	
SI	2	0	1	2	1	1	
SK	1	0	0	1	1	1	
EU Total	173	23	31	150	**109 + [10]**	**30**	
EFTA: NRLs and OfLs							
CH	2	0	0	2	0 + [2]	0	
IS	1	0	0	1	1	1	
NO	1	0	0	1	1	1	NRL-SRM regarded as obliged lab due to data submission to EFSA
EU/EFTA Total	177	23	31	154	**111 + [12]**	**32**	

Table 3-1 (cont.): Number of laboratories listed as being obliged to participate in the EUPT-SRM19, labs that registered to participate in the PT and completed results submission (grouped by contracting country)

Contracting Country	Labs originally considered to be obliged (*based on scope and NRL)	Labs providing expl. for non-participation	Obliged labs non particip. w/o giving expl.	Finally considered to be obliged	Registered for Participation and submitted results obliged + [on voluntary basis]		Notes
					All	NRL-SRM	
Countries outside Europa							
AU					1		
CR					1		
IN					1		
PE					2		
SR					4		
UK					2		
VN					1		
Countries outside Europa Total					**12**		

4. RESULTS

4.1 Overview of Results

In addition to the compulsory and optional analytes, serving the assessment of labs' performance in terms of accuracy (both) and analyte scope (compulsory), the exercize also entailed two extra analytes. The extra analytes were difluoroacetic acid (DFA) and gamma-cyhalothrin. The aim of this extra group was to promote the analysis of these analytes, to check the current OfL-coverage of these analytes, and to get an idea about the analytical methodologies currently applied in the EU. As the laboratories reporting results for "gamma-cyhalothrin" have, with one exception, employed conventional chromatography for analysis, they have essentially quantified the sum of the constituent isomers of lambda-cyhalothrin (i.e. gamma-cyhalothrin and its enantiomer), which were spiked to the sample in a non-racemic composition. Spiking was done with a mixture of gamma-cyhalothrin and lambda-cyhalothrin.

An overview of the percentage of laboratories having targeted each of the analytes present in the Target Pesticides List is shown in **Table 4-1**. **Table 4-2 (p. 21)** gives an overview of all results submitted by each of the participating laboratories. The individual numerical results reported by the laboratories are shown in **Table 4-8 (p. 21)**.

Table 4-1: Percentage of EU and EFTA Official Laboratories (OfLs) that have analysed for the compounds in the Target Pesticides List

Compounds		Present in Test Item	EU and EFTA OfLs analyzed for the compunds				
			Obliged OfLs only			Incl. OfLs on Voluntary Basis	
			No. [1]	Based on n = 111 [2]	Based on n = 140 [3]	No. [1]	Based on n =123 [2]
Compulsory Compounds	2,4-D (free acid)	No	91	82 %	65 %	100	90 %
	Avermectin B1a	Yes	89	80 %	64 %	99	89 %
	Captan	No	78	70 %	56 %	88	79 %
	Captan (sum)	No	74	67 %	53 %	84	76 %
	Chlormequat-Cl	No	89	80 %	64 %	99	89 %
	Clopyralid	Yes	70	63 %	50 %	77	69 %
	Copper	Yes	70	63 %	50 %	75	68 %
	Dithianon	Yes	73	66 %	52 %	81	73 %
	DTC (expr. as CS2)	Yes	83	75 %	59 %	92	83 %
	Emamectin B1a	No	90	81 %	64 %	100	90 %
	Ethephon	Yes	85	77 %	61 %	96	86 %
	Folpet	Yes	78	70 %	56 %	88	79 %
	Folpet (sum)	Yes	74	67 %	53 %	83	75 %
	Glufosinate	No	82	74 %	59 %	91	82 %
	Mepiquat-Cl	No	89	80 %	64 %	99	89 %
	MPP (=aka MPPA)	Yes	67	60 %	48 %	75	68 %
	N-Acetyl glufosinate	Yes	71	64 %	51 %	79	71 %
	Phthalimide	Yes	78	70 %	56 %	87	78 %
	THPI	No	77	69 %	55 %	87	78 %
Optional Compounds	2,4-DNOP (free phenol)	Yes	13	12 %	9 %	14	13 %
	Amitrole	No	15	14 %	11 %	16	14 %
	MCPA (free acid)	No	80	72 %	57 %	90	81 %
	Meptyldinocap	Yes	18	16 %	13 %	19	17 %
	Meptyldinocap (sum, calculated)	Yes	13	12 %	9 %	14	13 %
	Meptyldinocap (sum, follow. hydr.)	Yes	17	15 %	12 %	19	17 %
	Triclopyr (free acid)	No	55	50 %	39 %	63	57 %
	Trimethylsulfonium cation	No	29	26 %	21 %	33	30 %
Extra	Difluoroacetic acid (DFA)	Yes	10	9 %	7 %	10	9 %
	Lambda-Cyhalothrin	Yes	13	12 %	9 %	16	14 %

1) Laboratories representing more than one country were counted only once.
2) 123 OfLs from EU and EFTA countries (incl. NRLs) have completed results submission, among them 111 laboratories were obliged to participate in this PT and 12 participated on voluntary basis.
3) Taking any explanations for non-participation into account, 140 OfLs (including NRLs) from EU and EFTA countries were finally considered obliged to participate in the EUPT-SRM19.

Table 4-2: Scope and categorization of participating laboratories (including third country laboratories)

			Compulsory Compounds															
Compounds listed on the Target List			2,4-D (free acid)	Avermectin B1a	Captan	Captan (sum)	Chlormequat-Cl	Clopyralid	Copper	Dithianon	DTC (expr. as CS_2)	Emamectin B1a	Ethephon	Folpet	Folpet (sum)	Glufosinate	Mepiquat-Cl	MPP (=aka MPPA)
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.
present in Test Item			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
evaluated in this PT			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
Lab-Code SRM19-	NRL-SRM	Cat.																
1		A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	V
2	x	A	ND	V	ND	ND	ND	V	V	V	**FN***	ND	V	V	V	ND	ND	V
3		B		V	ND	ND	ND					ND		V	V		ND	
4	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
5		B					ND		V		V						ND	
6		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
7		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
8		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
9		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
11		B	ND	V	ND	ND	ND	V	V		V	ND	V	V	V	ND	ND	
12		B	ND	V			ND	V		V		ND					ND	
13		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	**FN**	V	ND	ND	V
14		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
15	x	B	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	**FN**	ND	ND	V
16		A	ND	V	ND	ND	ND		V	V	V	ND	V	V	V	ND	ND	V
17	x	B	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	
18	x	B	ND		ND	ND								V	V	ND		
20		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
21		A	ND	V	ND	ND	ND		V	V	V	ND	V	V	V	ND	ND	V
22		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
23		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
24		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	
25		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
26		B	ND	V					V			ND	V			ND		V
27		B	ND	V	ND	ND	ND	V	V	V	**FN***	ND	V	V	V		ND	
28		A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	V
29	x	A	ND	V	ND	ND	ND		V	V	V	ND	V	V	V	ND	ND	V
30	x	A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	V
31	x	B	ND	V			ND	V	V	V	V	ND	V				ND	
32		B					ND		V									
33		B		V	ND	ND	ND		V	V	V	ND		V	V		ND	
34		B	ND	V	ND	ND	ND			V	V	ND	V		V		ND	
35		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
36	x	B	ND				ND	V	V	V		ND	V			ND	ND	

MACP-Reg.: Multiannual Control Program Regulation. Link: REGULATION (EU) 2023/731 of 03 April 2023; https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32023R0731
WD: Working document on pesticides to be considered in national control programs to ensure compliance with MRLs of pesticides residues in food; SANCO/12745/2013; 21-22 November 2022 rev. 14(5); https://www.eurl-pesticides.eu/userfiles/file/WD/SANCO_12745_2013_rev_14_5.pdf (Note: The link to the latest update will be publihsed as soon as it becomes available

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Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories)

			Compulsory Compds.				Optional Compounds									Total	Extra	
Compounds listed on the Target List			Glufosinate	Glufosinate	Glufosinate	analysed / correctly found (Compulsory Compounds), max: 19/11	2,4-DNOP (free phenol)	Amitrole	MCPA (free acid)	Meptyldinocap	Meptyldinocap (sum, calculated)	Meptyldinocap (sum, follow. hydr.)	Triclopyr (free acid)	Trimethylsulfonium cation	analysed / correctly found (Optional Compounds, max: 8/4	analysed / correctly found (Total: Compulsory + Optional Compounds), max: 27/15	Difluoroacetic acid (DFA)	Gamma-Cyhalothrin
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.		WD	WD	WD	WD	WD	WD	WD	WD			WD 2024	MACP/WD
present in Test Item			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			Yes	Yes
evaluated in this PT			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			No	No
Lab-Code SRM19-	NRL-SRM	Cat.																
1		A	V	V	ND	18 / 10	V	ND	ND				ND	ND	5 / 1	23 / 11		V
2	x	A	V	V	ND	19 / 10			ND				ND	ND	3 / 0	22 / 10		
3		B		V	ND	10 / 4									0 / 0	10 / 4		
4	x	A	V	V	ND	19 / 11		ND	ND				ND	ND	4 / 0	23 / 11	V	
5		B				4 / 2									0 / 0	4 / 2		
6		A	V	V	ND	19 / 11			ND	V					2 / 1	21 / 12		V
7		A	V	V	ND	19 / 11	V		ND	V	V	V	ND		6 / 4	25 / 15		
8		A	V	V	ND	19 / 11			ND			V	ND		3 / 1	22 / 12		V
9		A	V	V	ND	19 / 11	V		ND	V	V	V	ND	ND	7 / 4	26 / 15		
11		B		V	ND	16 / 8			ND				ND	ND	3 / 0	19 / 8		
12		B				7 / 3			ND						1 / 0	8 / 3		
13		A	V	V	ND	19 / 10			ND			V	ND		3 / 1	22 / 11		
14		A	V	V	ND	19 / 11		ND	ND			V	ND	ND	5 / 1	24 / 12	V	
15	x	B	V	**FN**	ND	19 / 9			ND				ND	ND	3 / 0	22 / 9		
16		A	V	V	ND	18 / 10			ND				ND		2 / 0	20 / 10		
17	x	B		V	ND	17 / 9			ND						1 / 0	18 / 9		
18	x	B	V	V	ND	9 / 4			ND						1 / 0	10 / 4		
20		A	V	V	ND	19 / 11	V	ND	ND	V	V	V	ND	ND	8 / 4	27 / 15		
21		A	V	V	ND	18 / 10			ND				ND	ND	3 / 0	21 / 10		
22		A	V	V	ND	19 / 11			ND				ND		2 / 0	21 / 11		
23		A	V	V	ND	19 / 11	V	ND	ND	V	V	V	ND	ND	8 / 4	27 / 15	V	
24		A	V	V	ND	18 / 10			ND				ND	ND	3 / 0	21 / 10		
25		A	V	V	ND	19 / 11	V		ND	V	V	V	ND		6 / 4	25 / 15		V
26		B	V			8 / 5			ND						1 / 0	9 / 5		
27		B		V	ND	16 / 8			ND				ND		2 / 0	18 / 8		
28		A	V	V	ND	18 / 10			ND	V			ND	ND	4 / 1	22 / 11		
29	x	A	V	V	ND	18 / 10			ND						1 / 0	19 / 10		
30	x	A	V	V	ND	18 / 10			ND				ND	ND	3 / 0	21 / 10		
31	x	B		V		11 / 7			ND						1 / 0	12 / 7		
32		B				2 / 1									0 / 0	2 / 1		
33		B		V	ND	13 / 7									0 / 0	13 / 7		
34		B		V	ND	13 / 6			ND				ND		2 / 0	15 / 6		
35		A	V	V	ND	19 / 11	V	ND	ND	V	V	V	ND	ND	8 / 4	27 / 15		
36	x	B				9 / 4			ND						1 / 0	10 / 4		

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Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories)

			Compulsory Compounds															
Compounds listed on the Target List			2,4-D (free acid)	Avermectin B1a	Captan	Captan (sum)	Chlormequat-Cl	Clopyralid	Copper	Dithianon	DTC (expr. as CS_2)	Emamectin B1a	Ethephon	Folpet	Folpet (sum)	Glufosinate	Mepiquat-Cl	MPP (=aka MPPA)
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.
present in Test Item			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
evaluated in this PT			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
Lab-Code SRM19-	NRL-SRM	Cat.																
37	x	B	ND	V			ND	V	V		V	ND	V			ND	ND	V
38	x	B		V								ND						
39	x	B	ND	V	**FP**	**FR**	ND		V	V	V		V	V	V	ND	ND	V
40		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
41	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
42		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
43	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
44		B	ND	V	ND	ND	ND			V	V	ND	V	V	V	ND	ND	
45		B	ND	V			ND	V	V	V	V	ND	V			ND	ND	V
46		B	ND	V	ND	ND	ND			**FN**	V	ND	V	V	V	ND	ND	
47	x	B	ND	V	ND			V			V	ND		V				
48	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
49		A	ND	V	ND	ND	ND	V			V	ND	V	V	V	ND	ND	V
50		B			ND	ND			V		V			V	V			
51		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
52	x	B	ND				ND									ND	ND	
53		A	ND	V	ND	ND	ND	V	V	V	**FN**	ND	V	V	V	ND	ND	V
54		A	ND	V	ND	ND	ND	V	V	**FN**	V	ND	V	V	V	ND	ND	V
55	x	A	ND	V	ND	ND	ND	V		V		ND	V	V	V	ND	ND	V
56		B	ND	V				V				ND	V			ND		
57		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
58		B	ND	V	ND	ND	ND	V		V	V	ND	V	**FN**	**FN**		ND	
59		A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	V
60		B	ND	V	ND	ND	ND	V		V		ND	V	V	V	ND	ND	**FN**
61		B	ND	V			ND		V	V		ND					ND	
62		B	ND	V			ND					ND		V		ND	ND	
63		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
64		B	ND		ND	ND			V		V		V	V	V			
65	x	B	ND	V	ND		ND	V			V	ND	V	V		ND	ND	V
66		B	ND	V	ND	ND	ND		V		V	ND	V	V	V	ND	ND	V
67		B			ND	ND			V				**FN**	V	V	ND		V
69		B	ND	V	ND	ND	ND	V	V	V	V	ND	V		V	ND	ND	
70		B	ND	V	ND	ND	ND	V		V		ND	V	V	V		ND	

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Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories)

			Compulsory Compds.				Optional Compounds								Total	Extra	
Compounds listed on the Target List			Glufosinate	Glufosinate	Glufosinate	analysed / correctly found (Compulsory Compounds), max: 19/11	2,4-DNOP (free phenol)	Amitrole	MCPA (free acid)	Meptyldinocap	Meptyldinocap (sum, calculated)	Meptyldinocap (sum, follow. hydr.)	Triclopyr (free acid)	Trimethylsulfonium cation	analysed / correctly found (Optional Compounds, max: 8/4	analysed / correctly found (Total: Compulsory + Optional Compounds), max: 27/15	Difluoroacetic acid (DFA)	Gamma-Cyhalothrin
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.		WD	WD	WD	WD	WD	WD	WD	WD			WD 2024	MACP/WD
present in Test Item			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			Yes	Yes
evaluated in this PT			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			No	No
Lab-Code SRM19-	NRL-SRM	Cat.																
37	x	B	V			12 / 7			ND						1 / 0	13 / 7		
38	x	B				2 / 1									0 / 0	2 / 1		
39	x	B	V	V	ND	17 / 10									0 / 0	17 / 10		
40		A	V	V	ND	19 / 11			ND				ND	ND	3 / 0	22 / 11		
41	x	A	V	V	ND	19 / 11			ND				ND		2 / 0	21 / 11		
42		A	V	V	ND	19 / 11	V	ND	ND	V	V		ND	ND	7 / 3	26 / 14		
43	x	A	V	V	ND	19 / 11			ND			V	ND		3 / 1	22 / 12		
44		B	V			14 / 7			ND				ND		2 / 0	16 / 7		
45		B	V	V	ND	15 / 9			ND						1 / 0	16 / 9		
46		B		V	ND	15 / 6				V	V		ND		3 / 2	18 / 8		
47	x	B		V	ND	9 / 5			ND						1 / 0	10 / 5		
48	x	A	V	V	ND	19 / 11		ND	ND				ND	ND	4 / 0	23 / 11	V	
49		A	V	V	ND	17 / 9			ND						1 / 0	18 / 9		
50		B		V	ND	8 / 5									0 / 0	8 / 5		
51		A	V	V	ND	19 / 11			ND				ND		2 / 0	21 / 11		
52	x	B	**FN**			5 / 0			ND						1 / 0	6 / 0		
53		A	V	V	ND	19 / 10			ND	V			ND		3 / 1	22 / 11		
54		A	V	V	ND	19 / 10									0 / 0	19 / 10		
55	x	A	V	V	ND	17 / 9									0 / 0	17 / 9		
56		B				6 / 3									0 / 0	6 / 3		
57		A	V	V	ND	19 / 11		ND	ND		V	V	ND	ND	6 / 2	25 / 13		V
58		B		V	ND	15 / 6			ND						1 / 0	16 / 6		
59		A	V	V	ND	18 / 10	**FN**		ND	V	**FN**	**FN**	ND		6 / 1	24 / 11		V
60		B		V	ND	16 / 7									0 / 0	16 / 7		
61		B				7 / 3			ND						1 / 0	8 / 3		
62		B				7 / 2			ND			V			2 / 1	9 / 3		
63		A	V	V	ND	19 / 11		ND	ND			V	ND	ND	5 / 1	24 / 12		
64		B		V	ND	10 / 6			ND				ND		2 / 0	12 / 6		
65	x	B	V			13 / 7			ND				ND	ND	3 / 0	16 / 7		
66		B	V	V	ND	17 / 9			ND					ND	2 / 0	19 / 9		V
67		B	V	V	ND	11 / 6									0 / 0	11 / 6		
69		B			ND	15 / 7			ND				ND		2 / 0	17 / 7		
70		B		V	ND	14 / 7			ND				ND		2 / 0	16 / 7		

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WD: Working document on pesticides to be considered in national control programs to ensure compliance with MRLs of pesticides residues in food; SANCO/12745/2013; 21-22 November 2022 rev. 14(5); https://www.eurl-pesticides.eu/userfiles/file/WD/SANCO_12745_2013_rev_14_5.pdf (Note: The link to the latest update will be publihsed as soon as it becomes available

Empty cells: not analysed; **V** = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **FN** = analysed for but falsely not detected (False Negative result); **FN*** = FN because of labs' RLs > assigned values; **FP** = false positive result; **FR** (False Rporting) = results reported lower than lab's reporting limit

Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories)

			Compulsory Compounds															
Compounds listed on the Target List			2,4-D (free acid)	Avermectin B1a	Captan	Captan (sum)	Chlormequat-Cl	Clopyralid	Copper	Dithianon	DTC (expr. as CS_2)	Emamectin B1a	Ethephon	Folpet	Folpet (sum)	Glufosinate	Mepiquat-Cl	MPP (=aka MPPA)
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.
present in Test Item			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
evaluated in this PT			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
Lab-Code SRM19-	NRL-SRM	Cat.																
71	x	B					ND	**FN**									ND	
72		B	ND	V	ND	ND	ND	V	V	V	V	ND	V	**FN**	V	**FP**	ND	V
73	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
75		B	ND	**FN**								ND						
76		B	**FR**															
77		B	ND	V					V	V	V	ND	V			ND		V
78		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
79	x	A	ND	V	ND	ND	ND	V	V		V	ND	V	V	V	ND	ND	V
80		B	ND	V	ND	ND	ND	V	V	V	V	ND	V	**FN**	V	ND	ND	
81		B					ND				V		V			ND	ND	V
82		B			ND	ND			V		V	ND						
83		B									V							
84		B	ND	V	ND		ND						**FN**$^{+}$				ND	
85		B		V							V							
87		B	ND				ND			**FN**			V			ND	ND	V
88		B	ND	V		ND	ND	V		V	V	ND	V			ND	ND	V
89		B			**FP**	**FP**	ND	V	V			ND	V	V	V		ND	
90		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
91		A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	V
92	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
93		A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	V
94		B		**FN**								ND	V	V	V	ND		V
95		A	ND	V	ND	ND	ND		V	V	V	ND	V	V	V	ND	ND	V
96		B	ND				ND		V		V	ND	V	V	V	ND	ND	
97	x	A	ND	V	ND	ND	ND	V		V		ND	V	V	V	ND	ND	V
98	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
99	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
100	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
101	x	B							V							ND		V
102		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
103		A	ND	V	ND	ND	ND	V	V		V	ND	V	V	V	ND	ND	V
104		A	ND	V	ND	ND	ND	V	V	V	**FN***	ND	V	V	V	ND	ND	V
105	x	B	ND	V					V	V						ND	ND	
106		B									V							

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Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories)

			Compulsory Compds.				Optional Compounds									Total	Extra	
Compounds listed on the Target List			Glufosinate	Glufosinate	Glufosinate	analysed / correctly found (Compulsory Compounds), max: 19/11	2,4-DNOP (free phenol)	Amitrole	MCPA (free acid)	Meptyldinocap	Meptyldinocap (sum, calculated)	Meptyldinocap (sum, follow. hydr.)	Triclopyr (free acid)	Trimethylsulfonium cation	analysed / correctly found (Optional Compounds, max: 8/4	analysed / correctly found (Total: Compulsory + Optional Compounds), max: 27/15	Difluoroacetic acid (DFA)	Gamma-Cyhalothrin
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.		WD	WD	WD	WD	WD	WD	WD	WD			WD 2024	MACP/WD
present in Test Item			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			Yes	Yes
evaluated in this PT			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			No	No
Lab-Code SRM19-	NRL-SRM	Cat.																
71	x	B				3 / 0									0 / 0	3 / 0		
72		B	V	**FN**	ND	19 / 9			ND				ND		2 / 0	21 / 9	V	
73	x	A	V	V	ND	19 / 11			ND					ND	2 / 0	21 / 11		
75		B				3 / 0			ND						1 / 0	4 / 0		
76		B				1 / 0									0 / 0	1 / 0		
77		B	V			10 / 7									0 / 0	10 / 7		
78		A	**FN**	V	ND	19 / 10			ND			V	ND		3 / 1	22 / 11	V	
79	x	A	V	V	ND	18 / 10			ND						1 / 0	19 / 10		
80		B		V	ND	17 / 8			ND	V	V		ND		4 / 2	21 / 10		
81		B	V			7 / 4								ND	1 / 0	8 / 4		
82		B			ND	6 / 2									0 / 0	6 / 2		
83		B				1 / 1									0 / 0	1 / 1		
84		B				6 / 1			ND				ND		2 / 0	8 / 1		
85		B				2 / 2									0 / 0	2 / 2		
87		B	V			8 / 3			ND						1 / 0	9 / 3		
88		B	V			13 / 7			ND				ND		2 / 0	15 / 7		
89		B		V	ND	12 / 6									0 / 0	12 / 6		**FN**
90		A	V	V	ND	19 / 11			ND				ND	ND	3 / 0	22 / 11		
91		A	V	V	ND	18 / 10	V	ND	ND	V	V	V	ND	ND	8 / 4	26 / 14	V	
92	x	A	V	V	ND	19 / 11			ND				ND		2 / 0	21 / 11		
93		A	V	V	ND	18 / 10			ND				ND	ND	3 / 0	21 / 10	V	V
94		B	V	V		9 / 6			ND						1 / 0	10 / 6		V
95		A	V	V	ND	18 / 10			ND				ND		2 / 0	20 / 10		
96		B		V	ND	12 / 6	**FN**	ND	ND						3 / 0	15 / 6		
97	x	A	V	V	ND	17 / 9	V	ND	ND	V	V	V	ND	ND	8 / 4	25 / 13		
98	x	A	V	V	ND	19 / 11			ND				ND	ND	3 / 0	22 / 11		V
99	x	A	V	V	ND	19 / 11			ND				ND	ND	3 / 0	22 / 11		
100	x	A	V	V		18 / 11			ND						1 / 0	19 / 11		
101	x	B	V			4 / 3									0 / 0	4 / 3		
102		A	V	V	ND	19 / 11		ND	ND			V	ND	ND	5 / 1	24 / 12	V	V
103		A	V	V	ND	18 / 10	V		ND	V	V		ND		5 / 3	23 / 13		
104		A	V	V	ND	19 / 10			ND				ND		2 / 0	21 / 10		
105	x	B				6 / 3									0 / 0	6 / 3		
106		B				1 / 1									0 / 0	1 / 1		

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Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories)

			Compulsory Compounds															
Compounds listed on the Target List			2,4-D (free acid)	Avermectin B1a	Captan	Captan (sum)	Chlormequat-Cl	Clopyralid	Copper	Dithianon	DTC (expr. as CS_2)	Emamectin B1a	Ethephon	Folpet	Folpet (sum)	Glufosinate	Mepiquat-Cl	MPP (=aka MPPA)
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.	MACP-Reg.
present in Test Item			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
evaluated in this PT			No	Yes	No	No	No	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes
Lab-Code SRM19-	NRL-SRM	Cat.																
107		B	ND	V	ND						V	ND	V	V		ND		
108		A	ND	V	ND	ND	ND	V		V	**FN**	ND	V	V	V	ND	ND	V
109		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
111	x	A	ND	V	ND	ND	ND	V		V	V	ND	V	**FN**	V	ND	ND	V
113		B	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	
114	x	B	ND	V	ND		**FP**	V		V	V	ND	**FN**	**FN**			**FP**	
115		B	ND	V	ND	ND	ND	V		V		ND	V	V	V		ND	
117		B		V	ND	ND	ND			V		ND	V	V		ND	ND	V
118		B									V							
119		B	ND	V								ND						
121		B											V			ND		V
122		B							V			ND		V				
124		B					ND				V						ND	
125		B	ND	V	ND	ND	ND	V		**FN**	V	ND	V	**FN**	V	ND	ND	V
126		B							V									
127		A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	**FN**
128	x	A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
129		B					ND		V		V						ND	
130		B	ND	V			ND		V		V	ND	V			ND	ND	V
132		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
134		A	ND	V	ND	ND	ND	**FN***	V	V	V	ND	V	V	V	ND	ND	V
137		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	**FN**	V	ND	ND	V
3rd-10		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
3rd-19		A	ND	V	ND	ND	ND	V		V	V	ND	V	V	V	ND	ND	V
3rd-68		A	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	V	ND	ND	V
3rd-86		B	ND	V	ND	ND	ND	V	V	V		ND	V		V	ND	ND	V
3rd-110		B							V		V							
3rd-112		B	ND	V	ND	ND	ND	V	V	V	V	ND	V	V	**FN**	ND	ND	**FN**
3rd-116		B	ND	V		ND		V	V		V	ND	V		V			
3rd-120		B	ND	V	ND	ND	ND		V	V	V	ND	V	V	V	ND	ND	
3rd-123		B	ND	V					V	V	V	ND	**FN**	**FN**		ND	ND	V
3rd-131		B	ND		ND	ND					V		**FN**	V	V	ND		
3rd-135		B	ND	V		ND	ND		V	V	V	ND	V		V	ND	ND	V
3rd-139		B	ND	V	ND	ND	ND	V	V			ND	V	**FN**	V	ND	ND	**FN**

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Table 4-2 (cont.): Scope and categorization of participating laboratories (including third country laboratories))

			Compulsory Compds.				Optional Compounds									Total	Extra	
Compounds listed on the Target List			Glufosinate	Glufosinate	Glufosinate	analysed / correctly found (Compulsory Compounds), max: 19/11	2,4-DNOP (free phenol)	Amitrole	MCPA (free acid)	Meptyldinocap	Meptyldinocap (sum, calculated)	Meptyldinocap (sum, follow. hydr.)	Triclopyr (free acid)	Trimethylsulfonium cation	analysed / correctly found (Optional Compounds, max: 8/4	analysed / correctly found (Total: Compulsory + Optional Compounds), max: 27/15	Difluoroacetic acid (DFA)	Gamma-Cyhalothrin
within ...			MACP-Reg.	MACP-Reg.	MACP-Reg.		WD	WD	WD	WD	WD	WD	WD	WD			WD 2024	MACP/WD
present in Test Item			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			Yes	Yes
evaluated in this PT			No	No	No		Yes	No	No	Yes	Yes	Yes	No	No			No	No
Lab-Code SRM19-	NRL-SRM	Cat.																
107		B				8 / 4			ND						1 / 0	9 / 4		
108		A	V	V	ND	18 / 9			ND				ND		2 / 0	20 / 9		
109		A	V	V	ND	19 / 11									0 / 0	19 / 11		
111	x	A	V	V	ND	18 / 9			ND						1 / 0	19 / 9		
113		B		V	ND	16 / 8			ND				ND		2 / 0	18 / 8		
114	x	B		V	ND	13 / 5									0 / 0	13 / 5		
115		B		V	ND	14 / 7			ND	V			ND		3 / 1	17 / 8		
117		B	V		ND	13 / 6			ND				ND		2 / 0	15 / 6		
118		B				1 / 1									0 / 0	1 / 1		
119		B				3 / 1			ND						1 / 0	4 / 1		V
121		B	V			4 / 3									0 / 0	4 / 3		
122		B		V		4 / 3									0 / 0	4 / 3		V
124		B	**FN**		ND	5 / 1									0 / 0	5 / 1		
125		B	V	V	ND	18 / 8		**FP**	ND	**FN**				ND	4 / 0	22 / 8		V
126		B				1 / 1									0 / 0	1 / 1		
127		A	V	V	ND	18 / 9			ND				ND	ND	3 / 0	21 / 9		V
128	x	A	V	V	ND	19 / 11			ND				ND		2 / 0	21 / 11		
129		B				4 / 2									0 / 0	4 / 2		
130		B	V	V	ND	13 / 7									0 / 0	13 / 7		
132		A	**FN***	V	ND	19 / 10	V		ND			V	ND		4 / 2	23 / 12		
134		A	V	V	ND	19 / 10			ND				ND	ND	3 / 0	22 / 10		
137		A	V	V	ND	19 / 10		ND	ND	V			ND		4 / 1	23 / 11	**FN**	
3rd-10		A	V	V	ND	19 / 11		ND	ND			V	ND		4 / 1	23 / 12		V
3rd-19		A	V	V	ND	18 / 10			ND				ND		2 / 0	20 / 10		
3rd-68		A	V	V	ND	19 / 11			ND				ND		2 / 0	21 / 11		
3rd-86		B	V		ND	16 / 8		ND	ND				ND		3 / 0	19 / 8		V
3rd-110		B				2 / 2									0 / 0	2 / 2		
3rd-112		B	**FN**	**FN**	ND	19 / 7		ND	ND				ND		3 / 0	22 / 7		V
3rd-116		B				9 / 6				V					1 / 1	10 / 7		V
3rd-120		B		V	ND	16 / 8							ND		1 / 0	17 / 8		
3rd-123		B	V		ND	13 / 6		ND	ND	V					3 / 1	16 / 7		
3rd-131		B		V	ND	10 / 4			ND						1 / 0	11 / 4		
3rd-135		B	V			14 / 8			ND				ND		2 / 0	16 / 8	V	V
3rd-139		B	V	V	ND	17 / 7	V		ND	**FN**	**FN**	V	ND		6 / 2	23 / 9		V

MACP-Reg.: Multiannual Control Program Regulation. Link: REGULATION (EU) 2023/731 of 03 April 2023; https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32023R0731
WD: Working document on pesticides to be considered in national control programs to ensure compliance with MRLs of pesticides residues in food; SANCO/12745/2013; 21-22 November 2022 rev. 14(5); https://www.eurl-pesticides.eu/userfiles/file/WD/SANCO_12745_2013_rev_14_5.pdf (Note: The link to the latest update will be publihsed as soon as it becomes available

Empty cells: not analysed; **V** = analysed for and submitted concentration Value > "MRRL" for a pesticide present in the test item; **ND** = analysed for and correctly reported as "Not Detected"; **FN** = analysed for but falsely not detected (False Negative result); **FN*** = FN because of labs' RLs > assigned values; **FP** = false positive result; **FR** (False Rporting) = results reported lower than lab's reporting limit

4.2 Assigned Values and Target Standard Deviations

In the majority of the cases (exceptions see below), the assigned value (x_{pt}; also referred to as AV) of each analyte present in the test item was established as the mean of robust statistics (x^*) of all numerical results submitted by OfLs from EU and EFTA countries, and using Algorithm A for calculation (**[6]**, **Appendix 8**). Results from laboratories outside EU and EFTA countries (i.e., 3rd countries and EU Candidate Countries) were not taken into account.

Before applying Algorithm A, the population was checked for outliers. Although the elimination of outliers prior to applying robust statistics does not have a relevant impact on the AVs and is therefore considered unnecessary, the coefficients of variation (CV^*) become, in most cases, noticeably smaller and reflect better the distribution of the vast bulk of laboratories. Therefore, before setting AVs, the results population of each analyte was checked for outliers. These were identified based on interim z scores, which were calculated using the robust mean of the entire population and additionally checked whether they are confirmed by the Grubbs' test (alpha = 0.05). Results having obtained z scores > 5 (calculated based on the initial robust mean and the FFP-RSD of 25 %) and confirmed as outliers by the Grubbs' test were excluded from the population for establishing the AVs. Following exclusion of outliers, the robust mean of each analyte was re-calculated using the remaining results and established as the AV. The outlier elimination step was repeated if necessary.

For all statistically established AVs the uncertainty of the AV (UAV, $u(x_{pt})$); also referred to as UAVs) was calculated, as described in Section **Section 2.2, p. 12**, and compared with the acceptable limits. The AVs, UAVs, UAV tolerances and CV^* based on robust statistics calculated for each analyte using entire population excluding outliers are shown in **Table 4-3**. Eight of the 11 compulsory compounds passed the UAV test, with CV^* values ranging between from 7.7 % for ***copper*** to 26.8 % for ***folpet*** (average CV^* 20.0 %). However three compounds failed the UAV-test (***dithianon***, ***phthalimide*** and ***DTCs***).

Where the robust mean values derived from the entire result population were deemed either too uncertain or too biased for assessing the participants' performance different procedures were followed:

For ***dithianon, phthalimide*** and ***cyhalothrin*** the Scientific Committee decided to calculate z scores based on robust mean values derived from sub-populations of results (i.e. results submitted by laboratories having employed adequate analytical procedures, according to the opinion of the Scientific Committee.

In seven cases, ***dithianon, phthalimide, 2,4-DNOP (free phenol), meptyldinocap, meptyldinocap (sum, calc.), meptyldinocap (sum, follow. hydrol.)*** and ***difluoroacetic acid***, the UAV exceeded the tolerance and the AVs were considered too uncertain for properly evaluating the laboratory performance. The Scientific Committee therefore decided, that only informative (non-official) evaluations should be done for these analytes in the final report.

In the case of ***DTCs*** (as CS_2), the UAV also exceeded the tolerance and it was furthermore considered. Given the wide range of methodologies used and the multitude of factors potentially contributing to bias in both directions, the Scientific Committee decided that the collected method information is not sufficient for defining a sub-population based on which the assigned value could be established via robust statistics. As it was considered important to make laboratories aware of error-sources and the need to take counter measures, the Scientific Committee decided that tentative z scores should be calculated based on a fixed value and only serve for informative purposes. The fixed value upon which the z scores were calculated was set taking into account extensive experimental data by the organisers, as well as method-dependent evaluations of participants' results confirming the experimental trends.

Table 4-3: Overview of the results and statistical figures of all analytes present in the test item. The data only refer to the OfLs from the EU and EFTA countries. Data in pale italic letters are for informative purposes only. For details please refer to the footnotes and the explanations in text

Data based on Results from EU and EFTA Laboratories									
	Compound	Population for AV	No. of FNs | Outlier	No. of numerical results (EU+EFTA)	Assigned Value [mg/kg]	$u(x_{pt})$ [1] [mg/kg]	$u(x_{pt})$ Tolerance [mg/kg]	UAV-Test	CV^* [2] [%]
Compulsory	Avermectin B1a	entire (EU+ EFTA)	2 | 1	97	0.0711	± 0.0022	0.0053	passed	24.6
	Clopyralid	entire (EU+ EFTA)	2 | 1	75	0.192	± 0.0065	0.0144	passed	23.4
	Copper	entire (EU+ EFTA)	0 | 1	75	29.9	± 0.3334	2.2425	passed	7.7
	Dithianon	only results generated under strong protection [3]	2 | 0	40	*0.236*	*± 0.0178*	*0.0177*	*failed*	*54.6*
	DTCs	0.1 mg/kg [4] was set as reference value	5 | 5	87	*0.1*	—	*0.0075*	—	*46.7*
	Ethephon	entire (EU+ EFTA)	3 | 2	93	0.0582	± 0.0011	0.0044	passed	14.7
	Folpet	entire (EU+ EFTA)	8 | 3	80	0.225	± 0.0086	0.0169	passed	26.8
	Folpet (sum)	entire (EU+ EFTA)	2 | 3	81	0.421	± 0.011	0.0316	passed	18.4
	MPP (=aka MPPA)	entire (EU+ EFTA)	2 | 2	73	0.0819	± 0.0028	0.0061	passed	22.8
	N-Acetyl glufosinate	entire (EU+ EFTA)	4 | 1	75	0.0773	± 0.0025	0.0058	passed	21.9
	Phthalimide	LC-based results only [4]	1 | 2	16	*0.082*	*± 0.0089*	*0.0062*	*failed*	*32.4*
	Average CV^* of compulsory compounds [5]								**20.0 [4]**
Optional	2,4-DNOP (free phenol)	entire (EU+ EFTA)	2 | 1	12	*0.0647*	*± 0.0114*	*0.0049*	*failed*	*46.9*
	Meptyldinocap	entire (EU+ EFTA)	1 | 5	18	*0.086*	*± 0.0088*	*0.0065*	*failed*	*29.6*
	Meptyldinocap (sum, calculated)	0.157 mg/kg [6] was set as reference value	1 | 3	13	*0.150*	*± 0.0139*	*0.0113*	*failed*	*23.4*
	Meptyldinocap (sum, follow. hydr.)	0.157 mg/kg [6] was set as reference value	1 | 3	18	*0.188*	*± 0.0188*	*0.0141*	*failed*	*30.9*
Extra	Difluoroacetic acid (DFA)	entire (EU+ EFTA)	1 | 0	9	*0.146*	*± 0.0131*	*0.0110*	*failed*	*21.7*
	Lambda-Cyhalothrin [7]	excl. one generated using chiral column [7]	1 | 1	14	*0.0773*	*± 0.0053*	*0.0058*	*passed*	*20.5*

1: $u(x_{pt})$**:** Uncertainty of assigned value (UAV) calculated as shown under **Section 2.2 (p. 38)**
2: CV^***:** Coefficient of variation (= relative standard deviation) based on robust statistics of entire result population after exclusion of outliers (a.k.a "robust RSD"). CV^* values were also given in the case of dithianon, dithiovarbamates, mepthyldinocap, 2,4-DNOP and mepthyldinocap (sum) as well as phthalimide where the assigned values were not established using robust mean of the entire population.
3: Sub-population of results submitted by laboratories having reportedly employed protective conditions, especially as regards sample-handling. Please refer to **Section 4.2.2, p. 30** for details
4: Please refer to **Section 4.2.3, p. 31** for details of AV of DTCs and **Section 4.2.4, p. 31**for details of AV of phthalimid.
5: excl. dithianon, DTCs, phthalimide. The average CV^* is given for information purposes only. CV^*s of individual compounds or average CV^*s of individual compounds or related compounds over many PTs are more relevant and conclusive.
6: Please refer to **Section 4.2.5, p. 33** for details of the reference value for mepthyldinocap (sum)
7: Lambda-Cyhalothrin was evaluated instead of gamma-cyhalothrin on the Target Pesticides List, since only one result was generated using chiral column

For ***2,4-DNOP (free phenol) and meptyldinocap*** both the z´score (a.k.a. z-prime score) as well as a z score range were calculated for each of submitted results by considering the uncertainty of the AV, but both of them were for information only. For ***meptyldinocap (sum, calculated)*** and ***meptyldinocap (sum, following hydrolysis)*** a fixed value of 0.157 mg/kg was set as the reference value to calculated informative z scores.

Although ***gamma-cyhalothrin*** was the analyte requested to be determined in this PT, a survey run by the organisers after the PT revealed that only one laboratory submitted a result generated using a chiral column. The submitted results, therefore, corresponded to the sum of the two constituent isomers of ***lambda-cyhalothrin***. Despite ***lambda-cyhalothrin*** not being the analyte requested, an AV was derived by applying

robust statistics to the entire population excluding the result submitted by the lab (lab code 25) that correctly reported a result for ***gamma-cyhalothrin***.

For details of each of these cases please see the following sections and especially **Section 4.2.2, p. 30**.

4.2.1 Evaluation of Results of Copper

The data reported by EU- and EFTA-laboratories for copper showed a more narrow distribution, compared to other analytes (CV^* = 7.7 %). Historical PT data on copper levels in various types of food matrices, which were kindly provided (anonymised) to the EURL-SRM by 9 different international PT-providers also showed an average CV^* in the range of 7-8 %. With this in mind, the Scientiffic Committee concluded that the FFP-RSD of 25 % would not be adequate for calculating the target standard deviation (σ_{pt}) for assessing the performance of labororatories. Following a proposal by the EURL-SRM, it was finally decided to calculate the z scores for copper using a FFP-RSD of 10 % (i.e. σ_{pt} = AV* 0.1). Consequently, results deviating between 20 and 30 % of the assigned value would be questionable and those deviating by 30 % or more would be unacceptable. The intention is to use the FFP-RSD copper for establishing a harmonized expanded measurement uncertainty for copper at 20 % (applying a coverage factor of 2), which should be introduced in the SANTE document 11312/20.

Table 4-4: Evaluation of dithianon based different population for

Analyte	Dithianon	
Population for Robust Mean (RM)	entire population	only results generated under strong protection
No. of numerical results	77	40
therein Outliers	0	0
No. of results for (RM)	77	40
No. of FNs	4	2
Robust Mean [mg/kg]	0.181	0.236
CV^*	54.6 %	38.1 %

4.2.2 Evaluation of Results of Dithianon

Dithianon is sensitive to oxidation and further reactions via radicals, and its levels drop rapidly when samples with low antioxidative potential are defrosted. Keeping temperatures low, the use of antioxidants (such as ascorbic acid) and acidification slow down degradation. During the preparation of the test material some ascorbic acid was added to reduce degradation, but the levels were kept moderate to keep the antioxidative potential within a realistic range, with degradation still taking place when the sample was exposed to high temperatures. Acidification during extraction (see document SRM-13) helps to reduce dithianon degradation, but in the particular PT-matrix, the losses during extraction by citrate-buffered QuEChERS (non-acidified) were shown to be rather negligible. The added ascorbic acid and the natural acidity of grapes surely contributed to this protection.

Despite the clear advice to keep the sample frozen till analysis, many labs have left their samples to defrost before taking analytical portions or after portioning them. A correlation between this practice of defrosting and the lower ***dithianon*** levels reported in this PT could be noticed. The distribution of the entire result population of dithianon was quite broad (CV^*= 54.6 %). Stability experiments by the EURL-SRM have confirmed the decomposition of ***dithianon*** in the grape test item during the defrosting procedure and even during storage in a freezer (Please refer to **Section 1.8, p. 6**)). Decomposition rates increase with the time that the analyte is exposed to the defrosted matrix and the temperature of the homogenate. And even under protection, the decomposition of ***dithianon*** cannot be ceased completely.

Considering the degradation behaviour of ***dithianon*** and after consultation with the EUPT advisory group, no assigned value was established for ***dithianon*** in the SRM19.

Based on the information on the methods provided by the participants, 40 of 77 results on dithianon were regarded as having been generated under sufficiently protective conditions. Using the robust mean of the results submitted by this subpopulation as a reference value, the corresponding z scores were calculated for informative purposes and for avoiding that the wrong labs are triggered to investigate the reasons for deviating results.

4.2.3 Evaluation of Results of Dithiocarbamates (DTCs, expressed as CS2)

Although the distribution of ***DTCs*** results of the EUPT-SRM19 exercise was quite broad (CV^*=46.7 %), the large number of results made the calculated uncertainty of the robust mean (UAV) to still fall within the limits required for qualifying the robust mean as an assigned value ("consensus approach"). Nevertheless, it was noticed that the data reported were quite heterogeneous and that the median values of different types of methods employed by participants varied significantly from each other. A general trend towards higher levels being reported by laboratories using stronger reaction conditions was recognizable. Experiments run by the EURL-SRM under differently strong reaction conditions confirmed this trend. Furthermore, it was noted that using the recently published EURL-SRM approach for the analysis of ***DTCs*** as CS2 (SRM-14(V3)) leads to significantly higher results than the previous method (V1 and V2).

Based on a large number of experiments conducted by the EURL-SRM, and taking into account results submitted by participants employing strong reaction conditions, the EURL-SRM estimates that the actual concentration of ***DTCs*** in the test item (expressed as CS2) is around 0.100 mg/kg. This value is considerably higher than the robust mean value of the entire population of results (0.0677 mg/kg).

Following the preliminary report, a survey on the methods and the reaction conditions for the conversion of the spiked ***DTCs*** to CS2 was conducted to collect a multitude of method details. However despite the large amount of data collected, only general trends could be recognised and no clear differentiation between various subpopulations could be made. This is due to the multitude of factors playing a role, which are partly opposing and partly difficult to reconstruct, such as the shaking intensity, leaks in reaction vessels, evaporation losses in standard solutions, and the age/stability of the Sn(II) reducing reagent etc. The experiments run by the organizers, studying certain aspects in a unifactorial way, were more conclusive and led to the conclusion that the robust mean of the total population is much lower than the real value. With this in mind, the EUPT Scientific Committee concluded that establishing the AV for ***DTCs*** based on robust statistics applied to the full results population would be inadequate. For the above explained reasons, a subpopulation of results upon which an assigned value could be establied via robust statistics could also not be identified. It was therefore decided to calculate the z scores based on a best estimate reference value derived from the results of the experiments conducted by the organisers. Doing so allowed to better identify and inform laboratories employing procedures generating biased results, triggering them to check their procedures. The reference value was set at 0.100 mg/kg and was mainly based on experiments run by the organizers during and after the PT, in which the impact of various factors was studied. The reference value chosen was a bit higher than the mean value of the homogeneity test (0.0924 mg/kg). The calculated z scores for the submitted results for ***DTCs*** as CS2 are for informative purposes only.

4.2.4 Evaluation of Results of Folpet and Phthalimide

As underlined in the EUPT-SRM17 and EUPT-SRM12, as well as in various EURL-SRM documents (e.g. SRM-07 (using GC-MS/MS), SRM-42 (APCI or ESI LC-MS/MS to cover parents+degradants), and SRM-49 (LC-MS/MS in the ESI-pos. mode to analyse THPI and PI), ***folpet*** undergoes decomposition to ***phthalimide*** in the GC-injector, which may result in an overestimation of the ***phthalimide*** results if this aspect is not taken into account. This issue has been repeatedly communicated in workshops and trainings, as well as in the final reports of the abovementioned PTs. Folpet itself can be analysed accurately by GC-based methods if matrix effects are properly addressed, but phthalimide is better analysed by LC-MS/MS. The advantage of LC- over GC-measurements is that no thermal decomposition of ***folpet*** to ***phthalimide*** takes place, which leads to overestimated ***phthalimide*** GC-results, unless the instrument-generated phthalimide is deducted. A separate, purely GC-based approach, involving deduction of the ***phthalimide*** amount formed in the GC-injector was published by the EURL-SRM (SRM-07-ExtCal and SRM-07-StdAdd). The same applies to captan where tetrahydrophtalimide is formed.

Table 4-5: Evaluation of folpet and phthalimide based different population

Analyte	Folpet			Phthalimide		
Population for Robust Mean (RM)	entire population	GC based	LC based	entire population	GC based	LC based
No. of numerical results	80	66	14	85	69	16
therein Outliers	3	3	0	3	1	2
No. of results for (RM)	77	63	14	82	68	14
No. of FNs	8	8	0	2	1	1
RM as Assigned Value [mg/kg]	0.225	0.218	0.247	0.106	0.112	0.082
CV^*	26.8 %	30.6 %	14.5 %	38.3 %	38.1 %	32.4 %
AV Uncertainty	0.0086	0.0105	0.012	0.0056	0.00649	0.0089
AV Tolerance	0.0169	0.0164	0.0185	0.008	0.0084	0.0062
UAV Test	passed	passed	passed	passed	passed	failed

Folpet: Among the 80 numerical results reported by the participants for ***folpet***, 66 were generated by GC methods. Although the distribution of all 80 numerical results for ***folpet*** was not particularly high (26.8 %), the histogram and kernel density revealed a slight hint of bimodality, with the 14 results generated by LC-based methods forming a narrowly distributed subpopulation ($CV^* = 14.5$ %). The robust mean of this subpopulation at 0.247 mg/kg (N = 14) is roughly 10 % higher that the overall robust mean at 0.225 mg/kg (N = 80) and roughly 13 % higher than the robust mean of the GC-based results of 0.218 mg/kg (N = 63). This shift may be partly due to the inadequate consideration of matrix effects or losses prior or during sample preparation by a certain share of the labs using GC. As the distance between the LC and the GC population was small, and as GC is not per se inadequate for analysing folpet accurately, the robust mean of the entire population was used as the assigned value and the z scores in this report are based on this value.

Phthalimide: Despite the numerous appeals by the EURL-SRM to consider the risk of overestimating the levels when using GC-based methods, 69 of the 85 numerical results (81 %) were generated by laboratories employing GC-based methods and only 16 numerical results were generated by LC-based methods. The overall distribution of the 85 received numerical results was quite broad ($CV^* = 38.3$ %) and again a certain bimodality was noticed, due to the LC-results forming a shifted population with a robust mean value of 0.082 mg/kg (N = 14 after elimination of two outliers). This value is roughly 23 % lower than the robust mean of the total population at 0.106 mg/kg (N = 82 after elimination of 3 outliers) and roughly 27 % lower than the robust mean of the GC-based results of 0.112 mg/kg (N = 69). This trend was expected for the reasons explained above. Unexpectedly, the LC based population was also broadly distributed ($CV^* = 32.4$ %) thus failing to meet the UAV criterion. The robust mean does thus not qualify for being established as the assigned value according to the so-called consensus approach. The EUPT Scientific Committee thus decided not to establish a proper assigned value for phthalimide in the SRM19 but to rather calculate informative z scores based on a reasonable reference value. Taking into account the spiking level as well as the results of numerous EURL-SRM experiments, it was decided that the robust mean of the LC-based results for ***phthalimide*** at 0.082 mg/kg would be an adequate reference value, even though it was based on a very small subpopulation. This value is close to the mean value of the EURL-SRM homogeneity test (0.0785 mg/kg), which was also derived using LC-MS/MS measurement. The z scores calculated based on this robust mean are for informative purpose only and should help the participatants with biased results to recognize the need for adjusting their methodology.

4.2.5 Notes to 2,4-DNOP, Meptyldinocap, Meptyldinocap (sum, calc.) and Meptyldinocap (sum, following hydr.)

Meptyldinocap is included in the SANTE working document, which provides guidance to EU member states on the design of multiannual national monitoring programs (MANCPs). Grapes are specifically mentioned there as a relevant commodity for checking ***meptyldinocap*** residues. In the present PT, only a very small number of laboratories have reported results for meptyldinocap (N = 18), its metabolite 2,4-DNOP (N = 12), the calculated sum of meptyldinocap (N = 13) as well as the meptyldinocap sum following hydrolysis (N = 18). The small population of results compromises the reliability of evaluations based on robust statistics, with the UAV-test failing in all cases to meet the criteria. Based on these facts, the EUPT Scientific Committee decided to set a reasonable reference value for meptyldinocap sum, which should apply to both the sum after hydrolysis and the calculated sum. Finally, considering the analytical results obtained by the organizer using the hydrolysis method as well as the individual results for meptyldinocap and 2,4-DNOP, also taking the spiking levels into account a reference value of 0.157 mg/kg was set for meptyldinocap (sum). Based on the established reference value, informative z scores would be calculated to serve as a guidance for the labs in order to recognize strong analytical bias and initiate counter measurer.

4.2.6 Notes to the Extra Compounds Difluoroacetic acid (DFA) and Gamma-Cyhalothrin

Difluoroacetic acid (DFA): Only 9 participating laboratories reported numerical results for ***DFA***, which is not sufficient for a reliable assigned value using robust statistics. After consultation with the EUPT advisory group, the robust mean of this small population of results was still used as a reference value for calculating both z' scores as well a z score range derived from the lower and upper limit of the robust mean uncertainty range.

Gamma-Cyhalothrin: ***Gamma-cyhalothrin*** (***γ-cyhalothrin***) is one of two enantiomers of which lambda-***cyhalothrin*** (***λ-cyhalothrin***) is composed in a racemic ratio. As ***gamma-cyhalothrin*** is much more toxic than its enantiomer, its quantification is of high interrest to risk assessors. When using conventional chromatographic techniques (GC- or LC-based) the two enantiomers are not separated. In order to quantify ***gamma-cyhalothrin***, chiral chromatography needs to be applied. In a survey run prior to the PT, many labs indicated their intention to analyze ***gamma-cyhalothrin***. A method for its analysis was previously published by the EURL-SRM (Doc. SRM-39). However, according to a survey run by the organisers after the PT, only one (Lab Code 25) of the 22 laboratories having submitted results for this analyte (15 EU-/EFTA OfLs and 7 based in 3rd countries) finally employed chiral chromatography. This means that the results reported essentially refer to the unresolved ***lambda-cyhalothrin*** mixture. Although ***lambda-cyhalothrin*** was not a target analyte, the Scientific Committee was decided to calculate the robust mean using the reported results (excluding the result of lab25, which had used chiral chromatography) and calculate informative z scores based on this value.

4.3 Assessment of Laboratory Performance

4.3.1 False Positives

Among the results received from EU-and EFTA-OfLs for the compulsory compounds, 6 results submitted by 4 laboratories were judged as FPs. These FPs concerned in two cases *captan*, and in one case each *captan (sum), chlormequat chloride, glufosinate and mepiqaut chloride*. Among the optional analytes only one result for *amitrole* was judged as a FP. Two laboratories reported in two cases (one each for *captan (sum)* and *2,4-D (free acid)*) numerical results lower than their reporting limit. Such results were judged as false reporting (FP). All these results are listed in **Table 4-6, p. 34.**

There were neither FP nor FR judgements among the results submitted by 3rd country laboratories.

Table 4-6: False positive results reported in EUPT-SRM19

	Compound	No. of FPs/FRs [1)]	Lab-Code	Analysed?	Conc. [mg/kg]	MRRL [mg/kg]	RL [mg/kg]	Judgement
Compulsory	2,4-D (free acid)	1	76	Yes	0.007	0.01	0.025	FR (result < RL)
	Captan	2	39	Yes	0.0276	0.01	0.01	FP
			89	Yes	0.033	0.01	0.01	FP
	Captan (sum)	2	39	Yes	0.0276	0.03	0.03	FR (result < RL)
			89	Yes	0.033	0.03	0.03	FP
	Chlormequat-Cl	1	114	Yes	0.054	0.01	0.01	FP
	Glufosinate	1	72	Yes	0.014	0.01	0.01	FP
	Mepiquat-Cl	1	114	Yes	0.119	0.01	0.01	FP
opt.	Amitrole	1	125	Yes	0.10	0.01	0.005	FP

1: FR = False Reporting, reported concentration was lower than the lab's reporting limit

4.3.2 False Negatives

32 EU/EFTA-OfLs reported in 41 cases results that had to be judged as false negatives (FNs). These mainly concerned compounds that were present in the test item at relevant levels and that were analysed by the labs without reporting any numeric results. Following the EUPT-General Protocol (11th Ed.), labs having reporting limits (RLs) higher than the assigned value (AV) of certain analytes present in the sample, and thus correctly reporting these analytes as not detected, also received a false negative judgement, but in the tables these results are shown as "FN*". In both cases, FN and FN*, the z scores were set at −4 as stipulated in the General Protocol.

In detail, FN judgements were made in 35 cases concerning 26 labs and 16 analytes. These analytes were ***folpet***(8× FN), ***dithianon*** (4× FN), ***N-acetyl glufosinate*** (3× FN), and furthermore ***2,4-DNOP (free phenol), avermectine B1a, DTCs, ethphone, folpet (sum), phthalimide,*** and ***MPP*** (2× FN each) as well as chlorpyralid, ***meptyldinocap***, ***meptyldinocap (sum, calc.)***, ***meptyldinocap (sum, follow. hydr.)***, ***gamma-/lambda-cyhalothrin*** and ***DFA*** (1× FN each). In all these cases the RLs of the labs were lower than the AVs.

In another 5 cases concerning three analytes, a FN* judgement was given. These concerned ***DTCs*** (3×FN*), ***dithianon*** (1xFN) and ***N-acetyl glufosinate*** (1xFN). In these cases the RLs were higher than the AV, so the concerned labs are encouraged to improve their analytical sensitivity. A special situation arose with the ***ethephon*** result of Lab 84, with the AV (0.0582 mg/kg) being slightly higher than the lab's RL (0.05 mg/kg) and with the laboratory communicating a result of 0.0411 mg/kg. Its "not detected" reporting was thus formally correct. Hence, this false negative result was also marked with an asterisk.

Four laboratories from 3rd countries reported in 11 cases false negative results. These FNs concerned ***ethephon***, ***folpet*** and ***MPP*** with two FN results each, as well as ***folpet (sum)***, ***phthalimide***, ***meptyldinocap*** and ***meptyldinocap (sum, calc.)*** with one FN result each.

All false negative results in the EUPT-SRM19 are listed in **Table 4-7, p. 35.** The reasons reported by the laboratories for the false negative are compiled in **Appendix 7**.

4.3.3 Laboratory Classification Based on Scope

All participating laboratories having reported at least one result were classified into Category A or B according to the rules cited in Section 2.5 (p. 35). Originally, there were 19 compulsory compounds, and 11 of them were present in the SRM19 test items. ***Copper*** was only recently included in the EU coordinated monitoring program on pesticides (MACP) and within this context MSs were urged by DG-SANTE to make

Table 4-7: Overview of false negative results reported by participating laboratories (incl. results from 3rd country laboratories)

	Compounds	No. of FNs/FN* EU/EFTA+3rd	Assigned Value [mg/kg]	PT-Code (SRM19-)	Analysed	Detected	RL [mg/kg]	Judgement
Compulsory	Avermectin B1a	2	0.0711	75	Yes	No	0.01	FN
				94	Yes	No	0.001	FN
	Clopyralid	2	0.192	71	Yes	No	0.01	FN
				134	Yes	No	0.5	FN* (AV < RL)
	Dithianon	4	0.236	46	Yes	No	0.01	FN
				54	Yes	No	0.01	FN
				87	Yes	No	0.01	FN
				125	Yes	No	0.01	FN
	DTC (expr. as CS_2)	5	0.1	2	Yes	No	0.2	FN* (AV < RL)
				27	Yes	No	0.1	FN* (AV < RL)
				53	Yes	No	0.01	FN
				104	Yes	No	0.3	FN* (AV < RL)
				108	Yes	No	0.05	FN
	Ethephon	3 + 2	0.0582	67	Yes	No	0.05	FN
				84	Yes	No	0.05	FN*(see text)
				114	Yes	No	0.01	FN
				3rd-123	Yes	No	0.01	FN
				3rd-131	Yes	No	0.05	FN
	Folpet	8 + 2	0.225	13	Yes	No	0.01	FN
				58	Yes	No	0.01	FN
				72	Yes	No	0.01	FN
				80	Yes	No	0.01	FN
				111	Yes	No	0.05	FN
				114	Yes	No	0.01	FN
				125	Yes	No	0.005	FN
				137	Yes	No	0.01	FN
				3rd-123	Yes	No	0.02	FN
				3rd-139	Yes	No	0.01	FN
	Folpet (sum)	2 + 1	0.421	15	Yes	No	0.03	FN
				58	Yes	No	0.03	FN
				3rd-112	Yes	No	0.03	FN
	MPP (=aka MPPA)	2 + 2	0.0819	60	Yes	No	0.01	FN
				127	Yes	No	0.01	FN
				3rd-112	Yes	No	0.01	FN
				3rd-139	Yes	No	0.01	FN
	N-Acetyl glufosinate	4 + 1	0.0773	52	Yes	No	0.01	FN
				78	Yes	No	0.01	FN
				124	Yes	No	0.01	FN
				132	Yes	No	0.10	FN* (AV < RL)
				3rd-112	Yes	No	0.01	FN
	Phthalimide	2 + 1	0.082	15	Yes	No	0.01	FN
				72	Yes	No	0.01	FN
				3rd-112	Yes	No	0.01	FN
Optional	2,4-DNOP (free phenol)	2	0.0647	59	Yes	No	0.01	FN
				96	Yes	No	0.01	FN
	Meptyldinocap	1 + 1	0.086	125	Yes	No	0.005	FN
				3rd-139	Yes	No	0.01	FN
	Meptyldinocap (sum, calc.)	1 + 1	0.157	59	Yes	No	0.02	FN
				3rd-139	Yes	No	0.02	FN
	Meptyldinocap (sum, follow. hydr.)	1	0.157	59	Yes	No	0.01	FN
Extra	Difluoroacetic acid (DFA)	1	0.146	137	Yes	No	0.01	FN
	Lambda-Cyhalothrin	1	0.0773	89	Yes	No	0.01	FN

sure that ***copper*** analyses are embedded within pesticide residues framework. Despite being classidffied as as pesticides, ***copper*** has, for practical and synergy reasons, traditionally been mostly analyzed in belonging to the framework of heavy metal contaminants, which in many cases involves different sampling and sample handling practices than those stipulated for pesticide controls. For this reason, many pesticide residue labs were not used to dealing with ***copper*** analyses till recently. At the time of the PT, many labs were still in the process of establishing the necessary protocols and logistics for routinely analyzing ***copper*** within the framework of pesticide residue controls, which involves forwarding aliquots of the homogenates prepared in pesticide residue labs to the metal-analyzing units within the same institution or even to external labs. With this in mind, the scientific Copmmittee decided that in the present PT, ***copper*** should be disregarded when classifying the labs based on their analytical scope within the EUPT-SRM19. Following the rules defined in the General Protocol (11th Edition, see **Appendix 8**), a laboratory had to fulfill the following conditions in order to be classified into Category A in the present PT: a) analysis of at least 16 out of the remaining 18 compulsory compounds on the Target Pesticides List; b) correct detection of at least nine out of the ten remaining compulsory compounds present in the test item, and c) no false positive results.

A total of 56 EU and EFTA laboratories (46 %) were classified into Category A and 67 (54 %) into Category B. Amount the 12 laboratories from EU candidate or 3rd countries only three (25 %) were classified into Category A.

Disregarding ***copper***, ***phthalimide***, ***dithianon*** and ***DTCs*** which were excluded from AAZ-calculation, and focusing only on the seven remaining compulsory compounds present in the test items only, 387 results were received from EU- and EFTA laboratories classified in Category A and 210 results from laboratories classified in Category B. The overall AAZ of the results submitted by Category A laboratories was 0.8, which translates in an average absolute bias of 20 %. For laboratories classified into Category B the overall AAZ calculates at 1.2, which translates in an average absolute bias of 30 %, which is considered too high, in view of the exanded measurement uncertainty of 50 %. The three laboratories from EU candidate and/or third countries classified into Category A achieved an overall AAZ of 0.7 with 21 results, whereas the other nine classified into Category B achieved an overall AAZ of 1.7 with only 41 results.

Table 4-8 (p. 37) and **Table 4-9 (p. 38)** show the details of laboratories classified into Category A and B, respectively. For informative purposes, the overall AAZs were calculated for laboratories with 5 or more individual z scores among the compulsory compounds. For the AAZ calculation any z scores > 5 were set at 5.

Table 4-8: Category A laboratories in EUPT-SRM19, ordered by lab codes. Copper was not considered in the Cat. A and B classification based on the analytical scope. The z scores for copper were calculated using 10 % of the AV as FFP-σpt, For dithianon, phthalimide and DTCs the z scores are shown for informative purposes only. For the former two z scores were calculated based on the robust means of selected subpopulations of results and for DTCs based on a reference value established taking into account experimental results generated by the organiser. The informative z scores (shown in italics) as well as the z scores for Copper were excluded from the AAZ calculation.

COMPULSORY Compounds			Avermectin B1a	Clopyralid	Ethephon	Folpet	Folpet (sum)	MPP (=aka MPPA)	N-Acetyl glufosinate		Copper [1]	Dithianon [2]	DTCs [2] (expr. as CS_2)	Phthalimide [2]
Assigned Value [mg/kg]			0.0711	0.192	0.0582	0.225	0.421	0.0819	0.077		29.9	*0.236* [2]	*0.100* [2]	*0.082* [2]
*CV**			24.6 %	23.4 %	14.7 %	26.8 %	18.4 %	22.8 %	21.9 %		7.7 %	38.1 %	43.6 %	32.4 %
MRRL [mg/kg]			0.01	0.01	0.01	0.01	0.03	0.01	0.01		0.2	0.01	0.01	0.01
Lab code SRM19-	NRL	Analysed / corr. found, max. 18[1]/ 10[1]	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	AAZ[3]	z Score (FFP-RSD = 10 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)
1		18 / 10	1.0	1.2	0.7	-1.4	-0.7	-1.5	-1.6	1.2		*-3.3*	*-1.1*	*0.9*
2	x	18 / 9	-0.5	-0.1	-0.5	0.0	-0.1	-0.1	-0.6	0.3	0.2	*2.2*	*-4.0*	*0.4*
4	x	18 / 10	-0.2	0.1	-0.4	1.2	0.1	-0.5	-0.2	0.4	0.2	*0.7*	*4.5*	*-0.7*
6		18 / 10	-2.4	-1.0	0.9	-2.4	6.3	-1.3	-1.1	2.0	-1.6	*-3.2*	*-3.0*	*19.7*
7		18 / 10	-0.7	0.8	-0.1	0.5	-0.5	-0.6	-0.4	0.5	-0.6	*3.3*	*0.1*	*-1.2*
8		18 / 10	0.3	-0.3	0.1	-0.4	0.0	1.5	1.3	0.6	-1.1	*-1.5*	*-1.8*	*1.4*
9		18 / 10	0.2	0.5	0.5	0.8	0.8	0.2	0.2	0.5	0.1	*-0.2*	*-3.5*	*1.6*
13		18 / 9	-0.3	-0.3	-0.2	-4.0	-0.6	-0.1	0.0	0.8	0.2	*-1.4*	*-2.8*	*4.8*
14		18 / 10	0.8	0.9	0.0	0.1	0.1	1.4	0.9	0.6	-1.0	*-0.1*	*-2.0*	*1.0*
16		17 / 9	-0.9		0.1	0.6	0.4	-0.2	-0.6	0.5	0.0	*-2.0*	*0.0*	*0.9*
20		18 / 10	0.1	0.0	0.3	0.1	0.9	0.4	0.1	0.3	0.7	*0.3*	*-0.3*	*2.9*
21		17 / 9	-0.2		-0.6	0.5	0.3	-0.6	-0.2	0.4	-0.6	*-1.0*	*-2.8*	*0.8*
22		18 / 10	0.2	0.3	-0.3	-1.1	-0.8	1.7	2.9	1.0	0.2	*-1.5*	*-3.0*	*0.3*
23		18 / 10	-0.5	-0.3	1.5	0.1	-0.8	2.4	1.5	1.0	0.4	*-1.1*	*-1.8*	*-1.3*
24		17 / 9	-1.1	-0.5	0.0	1.1	0.3		0.5	0.6	0.3	*2.4*	*0.6*	*0.0*
25		18 / 10	0.4	-0.4	-0.2	0.6	0.2	-0.7	-0.4	0.4	-0.5	*0.0*	*-1.3*	*0.3*
28		18 / 10	-0.6	0.3	0.1	-1.1	0.6	-0.9	-0.6	0.6		*0.0*	*-3.2*	*3.7*
29	x	17 / 9	14.6		-0.3	1.2	0.0	-0.5	-0.5	1.3	-0.3	*-0.1*	*-0.9*	*-0.9*
30	x	18 / 10	1.2	-0.1	0.1	-0.7	0.9	-0.7	-0.7	0.6		*1.7*	*-1.8*	*4.0*
35		18 / 10	0.1	1.5	-0.2	-1.4	-0.5	0.5	-0.2	0.6	0.6	*1.1*	*-1.1*	*1.4*
40		18 / 10	-1.1	0.5	0.0	0.4	0.0	0.2	-0.4	0.4	0.4	*-0.6*	*0.0*	*0.1*
41	x	18 / 10	-0.5	-0.5	0.2	0.9	0.5	-0.2	-0.4	0.5	-0.6	*-2.1*	*-0.4*	*0.8*
42		18 / 10	-1.9	-1.4	-0.6	0.3	0.4	-0.6	-0.2	0.8	-0.6	*-1.2*	*-0.9*	*1.4*
43	x	18 / 10	0.4	-3.5	0.4	0.3	-0.5	0.0	0.0	0.7	0.1	*2.5*	*-1.3*	*-1.1*
48	x	18 / 10	-1.7	0.5	0.0	1.3	0.6	-0.6	-0.2	0.7	0.1	*2.1*	*-0.2*	*0.5*
49		17 / 9	0.7	-1.1	0.0	0.5	0.5	-0.6	-0.3	0.5			*0.9*	*1.2*
51		18 / 10	1.6	-0.8	-0.1	-0.2	-0.2	0.7	0.1	0.5	1.4	*-3.2*	*-1.1*	*0.4*
53		18 / 9	-0.2	-0.8	-0.2	0.9	0.9	0.8	-0.7	0.6	0.7	*-0.3*	*-4.0*	*1.7*
54		18 / 9	-2.1	0.7	-0.7	-1.7	-1.0	-1.5	-0.4	1.2	-9.1	*-4.0*	*-2.7*	*0.6*
55	x	17 / 9	-0.2	0.7	0.4	0.1	-0.6	0.1	-1.0	0.4		*1.0*		*-1.0*
57		18 / 10	-0.3	0.0	0.3	-0.1	1.4	-0.2	-0.3	0.4	-1.3	*-1.5*	*-1.4*	*18.8*
59		18 / 10	-0.6	-0.2	-0.2	-0.4	-0.9	0.4	0.7	0.5		*-1.6*	*-2.0*	*2.3*
63		18 / 10	-0.3	-0.4	0.4	1.0	0.3	-0.3	-0.3	0.4	-1.6	*-0.3*	*-2.7*	*0.1*
73	x	18 / 10	0.5	1.7	-0.7	0.5	-0.6	2.3	-0.3	0.9	1.3	*-1.4*	*-1.9*	*-1.4*
78		18 / 9	0.7	0.8	-0.6	0.8	-0.5	-1.2	-4.0	1.2	0.7	*-0.4*	*0.4*	*-1.6*
79	x	17 / 9	0.5	-0.8	-0.7	-0.3	0.7	-0.2	-1.8	0.7	1.0		*-2.3*	*2.9*
90		18 / 10	5.0	-1.0	-0.2	-0.2	-0.4	-0.6	0.0	1.1	-1.3	*-2.5*	*0.5*	*0.1*
91		18 / 10	-0.6	0.8	0.2	1.5	0.4	0.7	-0.1	0.6		*-0.3*	*-0.5*	*-0.2*
92	x	18 / 10	0.3	-0.8	0.9	-1.1	0.5	5.8	2.0	1.5	1.4	*-1.1*	*-2.2*	*3.5*
93		18 / 10	2.2	0.7	0.5	-0.3	-0.6	0.0	-0.6	0.7		*-1.6*	*-0.6*	*-0.3*
95		17 / 9	-0.1		-0.1	-0.4	0.4	-0.8	0.1	0.3	0.4	*0.0*	*0.7*	*2.4*
97	x	17 / 9	-0.1	1.1	1.3	-1.5	-0.5	35.2	2.0	1.6		*1.2*		*1.7*

1) Copper was neither considered in the laboratory classification based on the analytical scopes nor in the AAZ calculation.
2) Dithianon, DTCs and phthalimide were considered in laboratory classification based on the analytical scope but to in the AAZ calculation. The given reference values and the corresponding informative z scores are for informative purposes only.

Table 4-8 (cont.): Category A laboratories in EUPT-SRM19, ordered by lab codes. Copper was not considered in the Cat. A and B classification based on the analytical scope. The z scores for copper were calculated using 10 % of the AV as FFP-σpt, For dithianon, phthalimide and DTCs the z scores are shown for informative purposes only. For the former two z scores were calculated based on the robust means of selected subpopulations of results and for DTCs based on a reference value established taking into account experimental results generated by the organiser. The informative z scores (shown in italics) as well as the z scores for Copper were excluded from the AAZ calculation.

COMPULSORY Compounds			Avermectin B1a	Clopyralid	Ethephon	Folpet	Folpet (sum)	MPP (=aka MPPA)	N-Acetyl glufosinate		Copper [1]	Dithianon [2]	DTCs [2] (expr. as CS_2)	Phthalimide [2]
Assigned Value [mg/kg]			0.0711	0.192	0.0582	0.225	0.421	0.0819	0.077		29.9	*0.236* [2]	*0.100* [2]	*0.082* [2]
*CV**			24.6 %	23.4 %	14.7 %	26.8 %	18.4 %	22.8 %	21.9 %		7.7 %	38.1 %	43.6 %	32.4 %
MRRL [mg/kg]			0.01	0.01	0.01	0.01	0.03	0.01	0.01		0.2	0.01	0.01	0.01
Lab code SRM19-	NRL	Analysed / corr. found, max. 18[1]/ 10[1]	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	AAZ[3]	z Score (FFP-RSD = 10 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)
98	x	18 / 10	2.2	0.5	0.4	0.6	0.2	-1.0	-0.7	0.8	-0.5	*-1.1*	*-0.7*	*0.4*
99	x	18 / 10	-0.3	-0.6	0.3	-0.3	-1.0	0.2	1.1	0.5	-0.3	*-0.4*	*-1.9*	*3.0*
100	x	17 / 10	0.6	1.3	-1.3	0.6	-0.2	6.7	3.9	1.8	0.4	*0.9*	*-0.2*	*-0.7*
102		18 / 10	-0.8	0.1	-0.5	0.5	1.0	0.2	-0.7	0.5	0.2	*-1.8*	*-0.3*	*2.7*
103		17 / 9	0.5	-0.7	-0.2	0.1	0.4	-0.6	-0.5	0.4	-0.8		*-0.9*	*1.6*
104		18 / 9	0.4	-1.6	0.2	-0.2	-0.2	0.5	0.1	0.5	-1.0	*-2.1*	*-4.0*	*0.3*
108		18 / 9	1.6	-0.7	-0.6	0.3	0.4	-0.8	-0.2	0.7		*-2.8*	*-4.0*	*1.4*
109		18 / 10	-0.1	1.0	0.0	-0.1	0.2	-0.3	-0.3	0.3	-0.3	*1.1*	*-0.8*	*1.5*
111	x	18 / 9	0.6	0.0	-1.1	-4.0	-0.7	-0.1	0.5	1.0		*-3.4*	*-1.1*	*4.4*
127		18 / 9	-2.3	-0.7	-0.8	-1.3	-0.4	-4.0	1.1	1.5		*0.2*	*-1.5*	*1.6*
128	x	18 / 10	-0.2	-0.1	0.1	0.5	0.2	0.0	-0.5	0.2	-0.1	*-2.5*	*-0.6*	*0.7*
132		18 / 9	2.2	-3.8	0.1	-1.9	-1.7	-0.1	-4.0	2.0	0.7	*-2.8*	*-1.2*	*-1.1*
134		18 / 9	0.6	-4.0	-0.6	0.6	1.7	0.3	1.3	1.3	0.6	*-1.7*	*-1.7*	*4.2*
137		18 / 9	0.7	4.3	0.1	-4.0	-0.8	-2.5	2.2	2.1	0.0	*1.1*	*-1.6*	*4.3*
3rd-10		18 / 10	0.2	0.6	-0.4	-0.8	0.4	-0.4	-0.4	0.5	0.2	*-1.7*	*-2.4*	*2.8*
3rd-19		18 / 10	0.1	-0.5	-1.1	-1.5	-1.2	-0.8	-0.1	0.8		*-0.2*	*-0.1*	*-0.3*
3rd-68		18 / 10	-1.4	0.8	-0.4	-0.7	1.5	-1.1	-0.7	0.9	-0.5	*-2.8*	*0.2*	*5.5*

1) Copper was neither considered in the laboratory classification based on the analytical scopes nor in the AAZ calculation.
2) Dithianon, DTCs and phthalimide were considered in laboratory classification based on the analytical scope but to in the AAZ calculation. The given reference values and the corresponding informative z scores are for informative purposes only.

Table 4-9: Category B laboratories in EUPT-SRM19, ordered by lab codes. Copper was not considered in the Cat. A and B classification based on the analytical scope. The z scores for copper were calculated using 10 % of the AV as FFP-σpt, For dithianon, phthalimide and DTCs the z scores are shown for informative purposes only. For the former two z scores were calculated based on the robust means of selected subpopulations of results and for DTCs based on a reference value established taking into account experimental results generated by the organiser. The informative z scores (shown in italics) as well as the z scores for Copper were excluded from the AAZ calculation.

COMPULSORY Compounds			Avermectin B1a	Clopyralid	Ethephon	Folpet	Folpet (sum)	MPP (=aka MPPA)	N-Acetyl glufosinate		Copper [1]	Dithianon [2]	DTCs [2] (expr. as CS_2)	Phthalimide [2]
Assigned Value [mg/kg]			0.0711	0.192	0.0582	0.225	0.421	0.0819	0.077		29.9	*0.236* [2]	*0.100* [2]	*0.082* [2]
*CV**			24.6 %	23.4 %	14.7 %	26.8 %	18.4 %	22.8 %	21.9 %		7.7 %	38.1 %	43.6 %	32.4 %
MRRL [mg/kg]			0.01	0.01	0.01	0.01	0.03	0.01	0.01		0.2	0.01	0.01	0.01
Lab code SRM19-	NRL	Analysed / corr. found, max. 18[1]/ 10[1]	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	AAZ[3]	z Score (FFP-RSD = 10 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)
3		10 / 4	0.6			1.4	2.9			–				*6.2*
5		3 / 1								–	0.7		*-0.8*	
11		15 / 7	0.5	0.7	1.0	0.9	0.2			0.7	-0.4		*-1.9*	*-0.1*
12		7 / 3	-0.8	0.5						–		*-0.7*		
15	x	18 / 8	-0.6	-0.6	-0.4	13.5	-4.0	-0.3	0.1	1.6	0.1	*-0.6*	*-1.7*	*-4.0*
17	x	16 / 8	0.6	-0.9	0.1	-0.7	-0.5			0.6	0.0	*-1.8*	*-1.0*	*0.6*

1) Copper was neither considered in the laboratory classification based on the analytical scopes nor in the AAZ calculation.
2) Dithianon, DTCs and phthalimide were considered in laboratory classification based on the analytical scope but to in the AAZ calculation. The given reference values and the corresponding informative z scores are for informative purposes only..
3) The transport took more than one week, and the test item was defrosted on arrivial. Supposedly, dithianon was mainly decomposed.

Table 4-9 (cont.): Category B laboratories in EUPT-SRM19, ordered by lab codes. Copper was not considered in the Cat. A and B classification based on the analytical scope. The z scores for copper were calculated using 10 % of the AV as FFP-σpt, For dithianon, phthalimide and DTCs the z scores are shown for informative purposes only. For the former two z scores were calculated based on the robust means of selected subpopulations of results and for DTCs based on a reference value established taking into account experimental results generated by the organiser. The informative z scores (shown in italics) as well as the z scores for Copper were excluded from the AAZ calculation.

COMPULSORY Compounds			Avermectin B1a	Clopyralid	Ethephon	Folpet	Folpet (sum)	MPP (=aka MPPA)	N-Acetyl glufosinate		Copper [1]	Dithianon [2]	DTCs [2] (expr. as CS_2)	Phthalimide [2]
Assigned Value [mg/kg]			0.0711	0.192	0.0582	0.225	0.421	0.0819	0.077		29.9	*0.236* [2]	*0.100* [2]	*0.082* [2]
*CV**			24.6 %	23.4 %	14.7 %	26.8 %	18.4 %	22.8 %	21.9 %		7.7 %	38.1 %	43.6 %	32.4 %
MRRL [mg/kg]			0.01	0.01	0.01	0.01	0.03	0.01	0.01		0.2	0.01	0.01	0.01
Lab code SRM19-	NRL	Analysed / corr. found, max. 18[1] / 10[1]	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	AAZ[3]	z Score (FFP-RSD = 10 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)
18	x	9 / 4				-0.4	-0.5		-0.7	–				*-0.1*
26		7 / 4	0.8		0.7			0.0	-0.4	–	0.3			
27		15 / 7	0.7	0.4	0.2	0.6	0.7			0.5	1.4	*-2.1*	*-4.0*	*1.6*
31	x	10 / 6	-1.2	-0.2	6.0					–	0.0	*-0.4*	*3.4*	*2.9*
32		1 / 0								–	-0.3			
33		12 / 6	-1.5			2.4	0.7			–	0.0	*-1.3*	*0.0*	*-1.0*
34		13 / 6	0.3		0.7		-0.6			–		*-3.5*	*-1.4*	*4.8*
36	x	8 / 3		0.8	0.5					–	-1.1	*-2.0*		
37	x	11 / 6	0.8	2.3	0.7			0.3	0.5	0.9	-0.3		*0.0*	
38	x	2 / 1	-0.3							–				
39	x	16 / 9	-0.3		0.1	3.5	2.7	1.4	5.3	2.2	-1.8	*-2.0*	*4.0*	*2.8*
44		14 / 7	-0.7		0.3	0.0	-0.6		0.1	0.3		*-3.2*	*14.4*	
45		14 / 8	1.4	-0.9	0.1			0.2	0.3	0.6	0.8	*-1.5*	*0.6*	*2.6*
46		15 / 6	1.6		0.5	-1.0	0.1			–		*-4.0*	*-3.6*	*2.3*
47	x	9 / 5	0.3	-0.5		-0.1				–			*-2.0*	*2.1*
50		7 / 4				1.1	1.4			–	0.5		*-3.5*	*2.8*
52	x	5 / 0							-4.0	–				
56		6 / 3	1.1	-2.3	0.4					–				
58		15 / 6	0.2	1.4	-0.2	-4.0	-4.0			2.0		*-2.2*	*-2.8*	*7.0*
60		16 / 7	1.6	0.2	0.4	-0.4	-0.8	-4.0		1.2		*1.6*		*-0.7*
61		6 / 2	0.1							–	0.7	*0.1*		
62		7 / 2	-0.8			0.1				–				
64		9 / 5			-0.4	0.3	-0.6			–	1.1		*-1.8*	*-1.0*
65	x	13 / 7	0.3	-0.1	-1.0	6.1		4.0	1.4	2.0			*-1.7*	
66		16 / 8	-0.7		-0.2	0.7	0.1	-0.5	-0.3	0.4	-1.1		*-3.4*	*0.0*
67		10 / 5			-4.0	1.0	0.4	-0.5	0.2	1.2	-0.1			*0.3*
69		14 / 6	-0.4	1.8	0.1		-0.3			–	0.0	*-2.1*	*-1.6*	
70		14 / 7	-0.2	0.1	-0.2	-1.2	-1.5			0.6		*-2.5*		*1.4*
71	x	3 / 0		-4.0						–				
72		18 / 8	-0.7	-1.3	-0.6	-4.0	1.0	0.8	-2.0	1.5	1.8	*-1.8*	*-1.8*	*-4.0*
75		3 / 0	-4.0							–				
77		9 / 6	-0.7		-0.1			0.1	0.3	–	0.1	*-0.3*	*-1.0*	
80		16 / 7	-0.1	1.4	0.5	-4.0	1.6			1.5	-0.8	*-2.5*	*-3.1*	*10.2*
81		7 / 4			1.4			-0.1	-0.2	–			*-0.6*	
82		5 / 1								–	-0.4		*-1.9*	
83		1 / 1								–			*-3.2*	
84		6 / 1	2.4		-4.0					–				
85		2 / 2	0.6							–			*1.4*	
87		8 / 3			0.6			0.3	1.5	–		*-4.0*		
88		13 / 7	-1.5	0.0	-0.2			1.0	0.1	0.6		*-3.3*	*0.0*	
89		11 / 5		-0.5	-2.4	2.6	0.0			–	-1.0			*-1.5*
94		9 / 6	-4.0		-2.0	-3.3	-3.2	-1.7	-1.9	2.7				*-3.0*

1) Copper was neither considered in the laboratory classification based on the analytical scopes nor in the AAZ calculation.
2) Dithianon, DTCs and phthalimide were considered in laboratory classification based on the analytical scope but to in the AAZ calculation. The given reference values and the corresponding informative z scores are for informative purposes only..
3) The transport took more than one week, and the test item was defrosted on arrivial. Supposedly, dithianon was mainly decomposed.

Table 4-9 (cont.): Category B laboratories in EUPT-SRM19, ordered by lab codes. Copper was not considered in the Cat. A and B classification based on the analytical scope. The z scores for copper were calculated using 10 % of the AV as FFP-σpt, For dithianon, phthalimide and DTCs the z scores are shown for informative purposes only. For the former two z scores were calculated based on the robust means of selected subpopulations of results and for DTCs based on a reference value established taking into account experimental results generated by the organiser. The informative z scores (shown in italics) as well as the z scores for Copper were excluded from the AAZ calculation.

COMPULSORY Compounds			Avermectin B1a	Clopyralid	Ethephon	Folpet	Folpet (sum)	MPP (=aka MPPA)	N-Acetyl glufosinate		Copper [1]	Dithianon [2]	DTCs [2] (expr. as CS_2)	Phthalimide [2]
Assigned Value [mg/kg]			0.0711	0.192	0.0582	0.225	0.421	0.0819	0.077		29.9	*0.236* [2]	*0.100* [2]	*0.082* [2]
*CV**			24.6 %	23.4 %	14.7 %	26.8 %	18.4 %	22.8 %	21.9 %		7.7 %	38.1 %	43.6 %	32.4 %
MRRL [mg/kg]			0.01	0.01	0.01	0.01	0.03	0.01	0.01		0.2	0.01	0.01	0.01
Lab code SRM19-	NRL	Analysed / corr. found, max. 18[1] / 10[1]	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	AAZ[3]	z Score (FFP-RSD = 10 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)	z Score (FFP-RSD = 25 %)
96		11 / 5			-0.7	-3.3	-2.1			–	-0.3		*-0.6*	*-0.2*
101	x	3 / 2						-0.9	-0.4	–	0.0			
105	x	5 / 2	-0.4							–	0.4	*-2.2*		
106		1 / 1								–			*1.2*	
107		8 / 4	0.1		2.4	-2.7				–			*-1.2*	
113		16 / 8	-2.6	-0.8	-1.1	-2.0	-0.5			1.4		*-0.4*	*-1.6*	*2.3*
114	x	13 / 5	-3.2	8.8	-4.0	-4.0				–		*0.8*	*-2.4*	*5.8*
115		14 / 7	-1.2	-0.4	1.2	7.0	5.8			2.6		*0.2*		*6.0*
117		13 / 6	-0.3		44.1	-2.1		32.2	59.5	3.5		*-3.5* [3]		
118		1 / 1								–			*-2.0*	
119		3 / 1	-1.5							–				
121		4 / 3			-0.9			-0.7	-1.5	–				
122		3 / 2				-1.0				–	-0.8			*0.8*
124		5 / 1							-4.0	–			*-1.6*	
125		18 / 8	2.8	-0.7	0.7	-4.0	-3.0	2.8	-0.7	2.1		*-4.0*	*6.8*	*-1.3*
126		0 / 0								–	0.3			
129		3 / 1								–	0.2		*-1.1*	
130		12 / 6	0.7		-0.3			2.0	1.7	–	0.6		*0.4*	*5.5*
3rd-86		15 / 7	-0.3	-1.5	0.3		0.3	-0.9	1.7	0.8	-0.9	*-3.0*		
3rd-110		1 / 1								–	-0.2		*-1.0*	
3rd-112		18 / 6	0.2	1.2	1.6	0.1	-4.0	-4.0	-4.0	2.2	-0.1	*-1.5*	*-2.0*	*-4.0*
3rd-116		8 / 5	-2.3	-2.8	0.4		9.3			–	0.2		*-3.3*	
3rd-120		15 / 7	-0.9		1.1	-0.1	0.0			–	-1.8	*-1.0*	*-2.8*	*0.9*
3rd-123		12 / 5	-0.3		-4.0	-4.0		-0.2	1.2	1.9	0.1	*-3.8*	*0.1*	
3rd-131		10 / 4			-4.0	-0.1	-0.9			–			*-0.6*	*-1.5*
3rd-135		13 / 7	-0.7		0.4		-1.5	-1.2	-0.3	0.8	1.0	*-3.0* [3]	*-0.6*	
3rd-139		16 / 6	-1.0	-1.7	-0.3	-4.0	0.9	-4.0	-0.9	1.8	0.7			*8.7*

1) Copper was neither considered in the laboratory classification based on the analytical scopes nor in the AAZ calculation.
2) Dithianon, DTCs and phthalimide were considered in laboratory classification based on the analytical scope but to in the AAZ calculation. The given reference values and the corresponding informative z scores are for informative purposes only..
3) The transport took more than one week, and the test item was defrosted on arrivial. Supposedly, dithianon was mainly decomposed.

Table 4-10: Overall performance of labs based on z score classifications and AAZ. Following a decision of the Scientific Committee, the z scores calculated for dithianon, phthalimide and DTCs are for information only as they are based on reference values derived from subpopulations (for dithianon, phthalimide) or a set value (for DTCs). For details please refer to **Section 4.2.2 – 4.2.4** and **Table 4-11**. For all optional compounds z scores, z' scores and z score ranges were calculated for information (see **Table 4-8**). The z scores calculated for lambda-cyhalothrin are also for informative purpose only

EU and EFTA Official Laboratories								
	Compound	No. of results [1]	Acceptable No. (%)	Questionable No. (%)	Unacceptable [1] No. (%)	FNs	AAZ [2]	AAZ [3]
Compulsory Compounds	Avermectin B1a	99	85 (86 %)	9 (9 %)	5 (5 %)	1	1.0	0.9
	Clopyralid	77	69 (90 %)	2 (3 %)	6 (8 %)	1	1.0	0.9
	Copper	75	74 (99 %)	0 (0 %)	1 (1 %)	1	0.7	0.6
	Dithianon	81	–	–	–	*0*	*1.3*	*1.2*
	DTCs	92	–	–	–	*5*	*1.8*	*1.6*
	Ethephon	96	88 (92 %)	3 (3 %)	5 (5 %)	2	0.7	0.6
	Folpet	88	68 (77 %)	6 (7 %)	14 (16 %)	3	1.3	1.1
	Folpet (sum)	83	74 (89 %)	4 (5 %)	5 (6 %)	3	0.9	0.8
	MPP (=aka MPPA)	75	63 (84 %)	5 (7 %)	7 (9 %)	2	1.1	1.0
	N-Acetyl glufosinate	79	69 (87 %)	3 (4 %)	7 (9 %)	1	1.0	0.9
	Phthalimide	87	–	–	–	*2*	*1.6*	*1.6*
	Subtotal (Excl. dithianon, DTCs and phthalimide)	**672**	**590 (88 %)**	**32 (5 %)**	**50 (7 %)**	14	**0.9**	**0.8**
Optional Compounds	*2,4-DNOP (free phenol)*	14	*8 (57 %)*	*1 (7 %)*	*5 (36 %)*	*1*	*2.0*	*1.6*
	Meptyldinocap	19	*11 (58 %)*	*0 (0 %)*	*8 (42 %)*	*5*	*2.2*	*2.1*
	Meptyldinocap (sum, calculated)	14	*9 (64 %)*	*1 (7 %)*	*4 (29 %)*	*3*	*1.9*	*1.8*
	Meptyldinocap (sum, following hydrolysis)	19	*14 (74 %)*	*0 (0 %)*	*5 (26 %)*	*3*	*2.0*	*1.9*
Extra	*Difluoroacetic acid (DFA)*	10	*9 (90 %)*	*0 (0 %)*	*1 (10 %)*	*0*	*1.0*	*0.6*
	Lambda-cyhalothrin	15	*13 (87 %)*	*0 (0 %)*	*2 (13 %)*	*1*	*1.0*	*0.8*
3rd Country / EU Candidate Country Laboratories								
	Compound	No. of results [1]	Acceptable No. (%)	Questionable No. (%)	Unacceptable [1] No. (%)	FNs	AAZ [2]	AAZ [3]
Compulsory Compounds	Avermectin B1a	10	9 (90 %)	1 (10 %)	0 (0 %)	0	0.7	0.7
	Clopyralid	7	6 (60 %)	1 (10 %)	0 (0 %)	0	1.3	1.3
	Copper	10	10 (100 %)	0 (0 %)	0 (0 %)	0	0.2	0.2
	Dithianon	8	–	–	–	*0*	*2.1*	*2.1*
	DTCs	10	–	–	–	*0*	*1.3*	*1.3*
	Ethephon	11	9 (90 %)	0 (0 %)	2 (20 %)	2	1.3	0.7
	Folpet	8	6 (60 %)	0 (0 %)	2 (20 %)	2	1.4	0.6
	Folpet (sum)	10	8 (80 %)	0 (0 %)	2 (20 %)	1	1.6	1.3
	MPP (=aka MPPA)	8	6 (60 %)	0 (0 %)	2 (20 %)	2	1.6	0.8
	N-Acetyl glufosinate	8	7 (70 %)	0 (0 %)	1 (10 %)	1	1.2	0.8
	Phthalimide	7	–	–	–	*1*	*2.8*	*2.6*
	Subtotal (Excl. dithianon, DTCs and phthalimide)	**72**	**61 (85 %)**	**2 (3 %)**	**9 (13 %)**	8		
Optional Compounds	*2,4-DNOP (free phenol)*	1	*1 (100 %)*	*0 (0 %)*	*0 (0 %)*	*0*		
	Meptyldinocap	3	*1 (33 %)*	*0 (0 %)*	*2 (67 %)*	*1*		
	Meptyldinocap (sum, calculated)	1	*0 (0 %)*	*0 (0 %)*	*1 (100 %)*	*1*		
	Meptyldinocap (sum, following hydrolysis)	2	*1 (50 %)*	*1 (50 %)*	*0 (0 %)*	*0*		
Extra	*Difluoroacetic acid (DFA)*	1	*1 (100 %)*	*0 (0 %)*	*0 (0 %)*	*0*		
	Lambda-cyhalothrin	6	*5 (83 %)*	*1 (17 %)*	*0 (0 %)*	*0*	*0.7*	*0.7*

1) including false negatives (FNs)
2) AAZ calculated for results with a population ≤ 5 and including FNs, (with a z score set at −4.0)
3) AAZ calculated for results with a population ≥ 5 but excluding FNs

Table 4-11: Results reported and z scores achieved by all participating laboratories for the compulsory compounds present in the SRM19 test material. Th

COMPULSORY Compounds				Avermectin B1a		Clopyralid		Copper		Ethephon		Folpet		Folpet (sum)	
Assigned Value [mg/kg]				0.0711		0.192		29.9		0.0582		0.225		0.421	
*CV**				24.6 %		23.4 %		7.7 %		14.7 %		26.8 %		18.4 %	
MRRL [mg/kg]				0.01		0.01		0.2		0.01		0.01		0.03	
Lab code SRM19-	NRL	Cat*	Analysed / corr. found, max. 15 / 10	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 10 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
1		A	18 / 10	0.088	1.0	0.25	1.2			0.069	0.7	0.149	-1.4	0.349	-0.7
2	x	A	19 / 10	0.0627	-0.5	0.188	-0.1	30.6	0.2	0.0510	-0.5	0.226	0.0	0.408	-0.1
3		B	10 / 4	0.082	0.6							0.305	1.4	0.728	2.9
4	x	A	19 / 11	0.0675	-0.2	0.197	0.1	30.45	0.2	0.0522	-0.4	0.294	1.2	0.432	0.1
5		B	4 / 2					32	0.7						
6		A	19 / 11	0.029	-2.4	0.144	-1.0	25.03	-1.6	0.072	0.9	0.088	-2.4	1.08	6.3
7		A	19 / 11	0.059	-0.7	0.231	0.8	28.0	-0.6	0.057	-0.1	0.255	0.5	0.37	-0.5
8		A	19 / 11	0.077	0.3	0.177	-0.3	26.6	-1.1	0.059	0.1	0.200	-0.4	0.420	0.0
9		A	19 / 11	0.0752	0.2	0.214	0.5	30.3	0.1	0.0657	0.5	0.268	0.8	0.50	0.8
11		B	16 / 8	0.080	0.5	0.224	0.7	28.8	-0.4	0.0722	1.0	0.278	0.9	0.437	0.2
12		B	7 / 3	0.0568	-0.8	0.218	0.5								
13		A	19 / 10	0.065	-0.3	0.180	-0.3	30.41	0.2	0.055	-0.2	FN	-4.0	0.36	-0.6
14		A	19 / 11	0.085	0.8	0.236	0.9	26.98	-1.0	0.058	0.0	0.230	0.1	0.436	0.1
15	x	B	19 / 9	0.060	-0.6	0.164	-0.6	30.2	0.1	0.052	-0.4	0.985	13.5	FN	-4.0
16		A	18 / 10	0.055	-0.9			30.0	0.0	0.060	0.1	0.260	0.6	0.462	0.4
17	x	B	17 / 9	0.0821	0.6	0.151	-0.9	30	0.0	0.0595	0.1	0.183	-0.7	0.371	-0.5
18	x	B	9 / 4									0.203	-0.4	0.366	-0.5
20		A	19 / 11	0.0731	0.1	0.192	0.0	32.1	0.7	0.0623	0.3	0.231	0.1	0.515	0.9
21		A	18 / 10	0.0675	-0.2			28.2	-0.6	0.0501	-0.6	0.255	0.5	0.455	0.3
22		A	19 / 11	0.0743	0.2	0.207	0.3	30.5	0.2	0.0542	-0.3	0.164	-1.1	0.342	-0.8
23		A	19 / 11	0.062	-0.5	0.178	-0.3	31	0.4	0.080	1.5	0.23	0.1	0.34	-0.8
24		A	18 / 10	0.0521	-1.1	0.166	-0.5	30.9	0.3	0.0586	0.0	0.287	1.1	0.452	0.3
25		A	19 / 11	0.0781	0.4	0.172	-0.4	28.46	-0.5	0.0546	-0.2	0.261	0.6	0.438	0.2
26		B	8 / 5	0.085	0.8			30.9	0.3	0.069	0.7				
27		B	16 / 8	0.084	0.7	0.212	0.4	34	1.4	0.061	0.2	0.261	0.6	0.493	0.7
28		A	18 / 10	0.061	-0.6	0.208	0.3			0.060	0.1	0.163	-1.1	0.480	0.6
29	x	A	18 / 10	0.33	14.6			29	-0.3	0.054	-0.3	0.29	1.2	0.424	0.0
30	x	A	18 / 10	0.093	1.2	0.188	-0.1			0.059	0.1	0.183	-0.7	0.516	0.9
31	x	B	11 / 7	0.0500	-1.2	0.182	-0.2	29.8	0.0	0.145	6.0				
32		B	2 / 1					29.1	-0.3						
33		B	13 / 7	0.044	-1.5			30	0.0			0.36	2.4	0.49	0.7
34		B	13 / 6	0.076	0.3					0.068	0.7			0.36	-0.6
35		A	19 / 11	0.072	0.1	0.265	1.5	31.8	0.6	0.055	-0.2	0.146	-1.4	0.368	-0.5
36	x	B	9 / 4			0.228	0.8	26.54	-1.1	0.065	0.5				
37	x	B	12 / 7	0.085	0.8	0.30	2.3	29	-0.3	0.069	0.7				
38	x	B	2 / 1	0.065	-0.3										
39	x	B	17 / 10	0.065	-0.3			24.4	-1.8	0.059	0.1	0.42	3.5	0.70	2.7
40		A	19 / 11	0.052	-1.1	0.218	0.5	31	0.4	0.058	0.0	0.250	0.4	0.419	0.0
41	x	A	19 / 11	0.0631	-0.5	0.168	-0.5	28.0	-0.6	0.0610	0.2	0.278	0.9	0.475	0.5
42		A	19 / 11	0.037	-1.9	0.127	-1.4	28.155	-0.6	0.049	-0.6	0.240	0.3	0.462	0.4
43	x	A	19 / 11	0.0790	0.4	0.0220	-3.5	30.2	0.1	0.0639	0.4	0.244	0.3	0.364	-0.5
44		B	14 / 7	0.0589	-0.7					0.062	0.3	0.223	0.0	0.362	-0.6
45		B	15 / 9	0.096	1.4	0.15	-0.9	32.4	0.8	0.059	0.1				
46		B	15 / 6	0.10	1.6					0.066	0.5	0.17	-1.0	0.43	0.1
47	x	B	9 / 5	0.0758	0.3	0.167	-0.5					0.222	-0.1		

Cat*: For the laboratory classification based on scope copper was not taken into account.

he reference values for dithianon, DTCs and phthalimide and the corresponding z scores are for informative purposes only.

	COMPULSORY Compounds			MPP (=aka MPPA)		N-Acetyl glufosinate		Dithianon		DTCs (expr. as CS2)		Phthalimide	
	Assigned / Reference Value [mg/kg]			0.0819		0.077		*0.236 1)*		*0.100 2)*		*0.082 3)*	
	*CV**			22.8 %		21.9 %		38.1 %		46.7 %		32.4 %	
	MRRL [mg/kg]			0.01		0.01		0.01		0.01		0.01	
	Lab code SRM19-	NRL	Cat*	Analysed / corr. found, max. 15 / 10	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
	1		B	18 / 10	0.052	-1.5	0.047	-1.6	0.041	*-3.3*	0.072	*-1.1*	0.1	*0.9*
	2	x	B	19 / 10	0.0790	-0.1	0.0659	-0.6	0.364	*2.2*	FN*	*-4.0*	0.0902	*0.4*
	3		B	10 / 4									0.210	*6.2*
	4	x	B	19 / 11	0.0725	-0.5	0.0730	-0.2	0.280	*0.7*	0.213	*4.5*	0.0684	*-0.7*
	5		B	4 / 2							0.081	*-0.8*		
	6		B	19 / 11	0.056	-1.3	0.057	-1.1	0.049	*-3.2*	0.024	*-3.0*	0.485	*19.7*
	7		B	19 / 11	0.069	-0.6	0.070	-0.4	0.430	*3.3*	0.103	*0.1*	0.057	*-1.2*
	8		A	19 / 11	0.113	1.5	0.103	1.3	0.150	*-1.5*	0.054	*-1.8*	0.110	*1.4*
	9		A	19 / 11	0.0852	0.2	0.0806	0.2	0.224	*-0.2*	0.013	*-3.5*	0.114	*1.6*
	11		B	16 / 8							0.0530	*-1.9*	0.0791	*-0.1*
	12		A	7 / 3					0.197	*-0.7*				
	13		A	19 / 10	0.080	-0.1	0.078	0.0	0.155	*-1.4*	0.030	*-2.8*	0.180	*4.8*
	14		B	19 / 11	0.111	1.4	0.094	0.9	0.231	*-0.1*	0.050	*-2.0*	0.102	*1.0*
	15	x	B	19 / 9	0.076	-0.3	0.079	0.1	0.203	*-0.6*	0.057	*-1.7*	FN	*-4.0*
	16		B	18 / 10	0.078	-0.2	0.066	-0.6	0.120	*-2.0*	0.099	*0.0*	0.100	*0.9*
	17	x	B	17 / 9					0.132	*-1.8*	0.075	*-1.0*	0.0933	*0.6*
	18	x	A	9 / 4			0.0631	-0.7					0.0808	*-0.1*
	20		B	19 / 11	0.0897	0.4	0.0783	0.1	0.253	*0.3*	0.0932	*-0.3*	0.141	*2.9*
	21		B	18 / 10	0.0691	-0.6	0.0732	-0.2	0.177	*-1.0*	0.0309	*-2.8*	0.0988	*0.8*
	22		A	19 / 11	0.117	1.7	0.133	2.9	0.148	*-1.5*	0.0259	*-3.0*	0.0879	*0.3*
	23		B	19 / 11	0.131	2.4	0.107	1.5	0.17	*-1.1*	0.056	*-1.8*	0.055	*-1.3*
	24		B	18 / 10			0.0879	0.5	0.375	*2.4*	0.115	*0.6*	0.0821	*0.0*
	25		A	19 / 11	0.0680	-0.7	0.0697	-0.4	0.234	*0.0*	0.0680	*-1.3*	0.0879	*0.3*
	26		A	8 / 5	0.082	0.0	0.070	-0.4						
	27		B	16 / 8					0.115	*-2.1*	FN*	*-4.0*	0.115	*1.6*
	28		B	18 / 10	0.063	-0.9	0.066	-0.6	0.236	*0.0*	0.020	*-3.2*	0.157	*3.7*
	29	x	B	18 / 10	0.071	-0.5	0.068	-0.5	0.23	*-0.1*	0.078	*-0.9*	0.064	*-0.9*
	30	x	B	18 / 10	0.067	-0.7	0.063	-0.7	0.337	*1.7*	0.054	*-1.8*	0.165	*4.0*
	31	x	A	11 / 7					0.210	*-0.4*	0.185	*3.4*	0.141	*2.9*
	32		A	2 / 1										
	33		A	13 / 7					0.16	*-1.3*	0.10	*0.0*	0.062	*-1.0*
	34		B	13 / 6					0.028	*-3.5*	0.064	*-1.4*	0.18	*4.8*
	35		A	19 / 11	0.092	0.5	0.073	-0.2	0.300	*1.1*	0.072	*-1.1*	0.11	*1.4*
	36	x	A	9 / 4					0.120	*-2.0*				
	37	x	B	12 / 7	0.088	0.3	0.087	0.5			0.10	*0.0*		
	38	x	B	2 / 1										
	39	x	B	17 / 10	0.11	1.4	0.18	5.3	0.12	*-2.0*	0.20	*4.0*	0.140	*2.8*
	40		A	19 / 11	0.085	0.2	0.069	-0.4	0.200	*-0.6*	0.101	*0.0*	0.084	*0.1*
	41	x	B	19 / 11	0.0777	-0.2	0.0691	-0.4	0.113	*-2.1*	0.0901	*-0.4*	0.0980	*0.8*
	42		A	19 / 11	0.069	-0.6	0.074	-0.2	0.166	*-1.2*	0.078	*-0.9*	0.110	*1.4*
	43	x	B	19 / 11	0.0825	0.0	0.0768	0.0	0.386	*2.5*	0.0667	*-1.3*	0.0594	*-1.1*
	44		B	14 / 7			0.080	0.1	0.045	*-3.2*	0.460	*14.4*		
	45		B	15 / 9	0.085	0.2	0.084	0.3	0.15	*-1.5*	0.115	*0.6*	0.135	*2.6*
	46		A	15 / 6					FN	*-4.0*	0.011	*-3.6*	0.13	*2.3*
	47	x	B	9 / 5							0.0501	*-2.0*	0.125	*2.1*

1) Reference value of dithianon based on the robust mean of results generated under strong protection (for information only, please refer to Section 4.2.2). In case of Lab 117 and 135 the transport took more than one week and the sample was completely defrosted on arrival. An extensive degradation of dithianon during transport is thus likely.
2) Reference value was set at 0.1 mg/kg (for information only, please refer to Section 4.2.3)
3) Reference value based on the robust mean of LC-based results (for information only, please refer to 4.2.4)

Table 4-11 (cont.): Results reported and z scores achieved by all participating laboratories for the compulsory compounds present in the SRM19 test ma

COMPULSORY Compounds				Avermectin B1a		Clopyralid		Copper		Ethephon		Folpet		Folpet (sum)	
Assigned Value [mg/kg]				0.0711		0.192		29.9		0.0582		0.225		0.421	
*CV**				24.6 %		23.4 %		7.7 %		14.7 %		26.8 %		18.4 %	
MRRL [mg/kg]				0.01		0.01		0.2		0.01		0.01		0.03	
Lab code SRM19-	NRL	Cat*	Analysed / corr. found, max. 15 / 10	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 10 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
48	x	A	19 / 11	0.041	-1.7	0.215	0.5	30.2	0.1	0.058	0.0	0.297	1.3	0.483	0.6
49		A	17 / 9	0.083	0.7	0.138	-1.1			0.058	0.0	0.251	0.5	0.47	0.5
50		B	8 / 5					31.4	0.5			0.286	1.1	0.569	1.4
51		A	19 / 11	0.0997	1.6	0.155	-0.8	33.95	1.4	0.0572	-0.1	0.215	-0.2	0.396	-0.2
52	x	B	5 / 0												
53		A	19 / 10	0.068	-0.2	0.153	-0.8	32.05	0.7	0.055	-0.2	0.278	0.9	0.512	0.9
54		A	19 / 10	0.033	-2.1	0.225	0.7	2.71	-9.1	0.048	-0.7	0.132	-1.7	0.321	-1.0
55	x	A	17 / 9	0.0677	-0.2	0.227	0.7			0.0637	0.4	0.231	0.1	0.354	-0.6
56		B	6 / 3	0.091	1.1	0.084	-2.3			0.064	0.4				
57		A	19 / 11	0.066	-0.3	0.192	0.0	26	-1.3	0.062	0.3	0.218	-0.1	0.567	1.4
58		B	15 / 6	0.075	0.2	0.257	1.4			0.056	-0.2	FN	-4.0	FN	-4.0
59		A	18 / 10	0.060	-0.6	0.182	-0.2			0.055	-0.2	0.200	-0.4	0.330	-0.9
60		B	16 / 7	0.100	1.6	0.200	0.2			0.064	0.4	0.200	-0.4	0.337	-0.8
61		B	7 / 3	0.072	0.1			32.14	0.7						
62		B	7 / 2	0.056	-0.8							0.232	0.1		
63		A	19 / 11	0.066	-0.3	0.174	-0.4	25	-1.6	0.064	0.4	0.280	1.0	0.449	0.3
64		B	10 / 6					33.27	1.1	0.053	-0.4	0.240	0.3	0.363	-0.6
65	x	B	13 / 7	0.076	0.3	0.187	-0.1			0.044	-1.0	0.570	6.1		
66		B	17 / 9	0.0587	-0.7			26.7	-1.1	0.0546	-0.2	0.267	0.7	0.431	0.1
67		B	11 / 6					29.7	-0.1	FN	-4.0	0.283	1.0	0.459	0.4
69		B	15 / 7	0.064	-0.4	0.28	1.8	30	0.0	0.059	0.1			0.39	-0.3
70		B	14 / 7	0.0678	-0.2	0.196	0.1			0.0556	-0.2	0.156	-1.2	0.266	-1.5
71	x	B	3 / 0			FN	-4.0								
72		B	19 / 9	0.058	-0.7	0.13	-1.3	35.2	1.8	0.049	-0.6	FN	-4.0	0.53	1.0
73	x	A	19 / 11	0.0793	0.5	0.274	1.7	33.7	1.3	0.0473	-0.7	0.253	0.5	0.360	-0.6
75		B	3 / 0	FN	-4.0										
76		B	1 / 0												
77		B	10 / 7	0.058	-0.7			30.1	0.1	0.057	-0.1				
78		A	19 / 10	0.083	0.7	0.232	0.8	32	0.7	0.049	-0.6	0.271	0.8	0.372	-0.5
79	x	A	18 / 10	0.0803	0.5	0.152	-0.8	33.0	1.0	0.0474	-0.7	0.210	-0.3	0.496	0.7
80		B	17 / 8	0.07	-0.1	0.2590	1.4	27.40	-0.8	0.0654	0.5	FN	-4.0	0.588	1.6
81		B	7 / 4							0.079	1.4				
82		B	6 / 2					28.8	-0.4						
83		B	1 / 1												
84		B	6 / 1	0.114	2.4					FN	-4.0				
85		B	2 / 2	0.0825	0.6										
87		B	8 / 3							0.067	0.6				
88		B	13 / 7	0.045	-1.5	0.19	0.0			0.055	-0.2				
89		B	12 / 6			0.169	-0.5	26.8	-1.0	0.024	-2.4	0.369	2.6	0.421	0.0
90		A	19 / 11	0.160	5.0	0.144	-1.0	25.9	-1.3	0.0560	-0.2	0.212	-0.2	0.383	-0.4
91		A	18 / 10	0.0605	-0.6	0.228	0.8			0.0607	0.2	0.309	1.5	0.465	0.4
92	x	A	19 / 11	0.076	0.3	0.153	-0.8	34	1.4	0.072	0.9	0.164	-1.1	0.476	0.5
93		A	18 / 10	0.11	2.2	0.225	0.7			0.066	0.5	0.21	-0.3	0.36	-0.6
94		B	9 / 6	FN	-4.0					0.029	-2.0	0.038	-3.3	0.080	-3.2
95		A	18 / 10	0.070	-0.1			31	0.4	0.0561	-0.1	0.200	-0.4	0.465	0.4
96		B	12 / 6					29.1	-0.3	0.0482	-0.7	0.0371	-3.3	0.196	-2.1

Cat*: For the laboratory classification based on scope copper was not taken into account.

terial. The reference values for dithianon, DTCs and phthalimide and the corresponding z scores are for informative purposes only.

	COMPULSORY Compounds			MPP (=aka MPPA)		N-Acetyl glufosinate		Dithianon		DTCs (expr. as CS_2)		Phthalimide	
	Assigned / Reference Value [mg/kg]			0.0819		0.077		*0.236 1)*		*0.100 2)*		*0.082 3)*	
	*CV**			22.8 %		21.9 %		38.1 %		46.7 %		32.4 %	
	MRRL [mg/kg]			0.01		0.01		0.01		0.01		0.01	
Lab code SRM19-	NRL	Cat*	Analysed / corr. found, max. 15 / 10	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
48	x	B	19 / 11	0.070	-0.6	0.074	-0.2	0.360	*2.1*	0.095	*-0.2*	0.092	*0.5*
49		B	17 / 9	0.069	-0.6	0.072	-0.3			0.122	*0.9*	0.107	*1.2*
50		B	8 / 5							0.012	*-3.5*	0.140	*2.8*
51		A	19 / 11	0.0968	0.7	0.0788	0.1	0.0473	*-3.2*	0.0720	*-1.1*	0.0897	*0.4*
52	x	A	5 / 0			FN	-4.0						
53		A	19 / 10	0.098	0.8	0.064	-0.7	0.216	*-0.3*	FN	*-4.0*	0.116	*1.7*
54		B	19 / 10	0.052	-1.5	0.069	-0.4	FN	*-4.0*	0.032	*-2.7*	0.094	*0.6*
55	x	B	17 / 9	0.0837	0.1	0.0574	-1.0	0.293	*1.0*			0.0608	*-1.0*
56		B	6 / 3										
57		B	19 / 11	0.078	-0.2	0.072	-0.3	0.149	*-1.5*	0.066	*-1.4*	0.467	*18.8*
58		A	15 / 6					0.106	*-2.2*	0.03	*-2.8*	0.225	*7.0*
59		B	18 / 10	0.090	0.4	0.090	0.7	0.144	*-1.6*	0.050	*-2.0*	0.130	*2.3*
60		A	16 / 7	FN	-4.0			0.330	*1.6*			0.068	*-0.7*
61		B	7 / 3					0.243	*0.1*				
62		B	7 / 2										
63		A	19 / 11	0.075	-0.3	0.072	-0.3	0.216	*-0.3*	0.032	*-2.7*	0.084	*0.1*
64		B	10 / 6							0.054	*-1.8*	0.061	*-1.0*
65	x	B	13 / 7	0.163	4.0	0.104	1.4			0.058	*-1.7*		
66		A	17 / 9	0.0719	-0.5	0.0708	-0.3			0.014	*-3.4*	0.082	*0.0*
67		A	11 / 6	0.0721	-0.5	0.0809	0.2					0.0884	*0.3*
69		B	15 / 7					0.11	*-2.1*	0.06	*-1.6*		
70		B	14 / 7					0.0873	*-2.5*			0.110	*1.4*
71	x	A	3 / 0										
72		A	19 / 9	0.099	0.8	0.038	-2.0	0.13	*-1.8*	0.055	*-1.8*	FN	*-4.0*
73	x	A	19 / 11	0.129	2.3	0.0721	-0.3	0.152	*-1.4*	0.0531	*-1.9*	0.0530	*-1.4*
75		A	3 / 0										
76		A	1 / 0										
77		B	10 / 7	0.084	0.1	0.084	0.3	0.219	*-0.3*	0.075	*-1.0*		
78		A	19 / 10	0.057	-1.2	FN	-4.0	0.212	*-0.4*	0.111	*0.4*	0.05	*-1.6*
79	x	B	18 / 10	0.0783	-0.2	0.0422	-1.8			0.0427	*-2.3*	0.142	*2.9*
80		B	17 / 8					0.0866	*-2.5*	0.0226	*-3.1*	0.292	*10.2*
81			7 / 4	0.080	-0.1	0.074	-0.2			0.086	*-0.6*		
82			6 / 2							0.0513	*-1.9*		
83			1 / 1							0.0210	*-3.2*		
84			6 / 1										
85			2 / 2							0.134	*1.4*		
87			8 / 3	0.088	0.3	0.106	1.5	FN	*-4.0*				
88			13 / 7	0.103	1.0	0.08	0.1	0.039	*-3.3*	0.099	*0.0*		
89			12 / 6									0.052	*-1.5*
90			19 / 11	0.0693	-0.6	0.0781	0.0	0.0913	*-2.5*	0.112	*0.5*	0.0846	*0.1*
91			18 / 10	0.0962	0.7	0.0762	-0.1	0.221	*-0.3*	0.087	*-0.5*	0.0770	*-0.2*
92	x		19 / 11	0.2	5.8	0.115	2.0	0.171	*-1.1*	0.045	*-2.2*	0.154	*3.5*
93			18 / 10	0.082	0.0	0.066	-0.6	0.14	*-1.6*	0.085	*-0.6*	0.076	*-0.3*
94			9 / 6	0.048	-1.7	0.040	-1.9					0.021	*-3.0*
95			18 / 10	0.0647	-0.8	0.080	0.1	0.238	*0.0*	0.118	*0.7*	0.131	*2.4*
96			12 / 6							0.0861	*-0.6*	0.0788	*-0.2*

1) Reference value of dithianon based on the robust mean of results generated under strong protection (for information only, please refer to Section 4.2.2). In case of Lab 117 and 135 the transport took more than one week and the sample was completely defrosted on arrival. An extensive degradation of dithianon during transport is thus likely.
2) Reference value was set at 0.1 mg/kg (for information only, please refer to Section 4.2.3)
3) Reference value based on the robust mean of LC-based results (for information only, please refer to 4.2.4)

Table 4-11 (cont.): Results reported and z scores achieved by all participating laboratories for the compulsory compounds present in the SRM19 test ma

COMPULSORY Compounds				Avermectin B1a		Clopyralid		Copper		Ethephon		Folpet		Folpet (sum)	
Assigned Value [mg/kg]				0.0711		0.192		29.9		0.0582		0.225		0.421	
*CV**				24.6 %		23.4 %		7.7 %		14.7 %		26.8 %		18.4 %	
MRRL [mg/kg]				0.01		0.01		0.2		0.01		0.01		0.03	
Lab code SRM19-	NRL	Cat*	Analysed / corr. found, max. 15 / 10	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 10 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
97	x	A	17 / 9	0.0699	-0.1	0.246	1.1			0.0766	1.3	0.140	-1.5	0.373	-0.5
98	x	A	19 / 11	0.111	2.2	0.216	0.5	28.3	-0.5	0.0646	0.4	0.259	0.6	0.44	0.2
99	x	A	19 / 11	0.066	-0.3	0.165	-0.6	29.0	-0.3	0.063	0.3	0.209	-0.3	0.312	-1.0
100	x	A	18 / 11	0.081	0.6	0.254	1.3	31.1	0.4	0.039	-1.3	0.261	0.6	0.395	-0.2
101	x	B	4 / 3					29.8	0.0						
102		A	19 / 11	0.057	-0.8	0.197	0.1	30.53	0.2	0.051	-0.5	0.254	0.5	0.530	1.0
103		A	18 / 10	0.080	0.5	0.160	-0.7	27.5	-0.8	0.056	-0.2	0.233	0.1	0.463	0.4
104		A	19 / 10	0.078	0.4	0.113	-1.6	27.0	-1.0	0.061	0.2	0.215	-0.2	0.395	-0.2
105	x	B	6 / 3	0.064	-0.4			31.1	0.4						
106		B	1 / 1												
107		B	8 / 4	0.0729	0.1					0.0925	2.4	0.0738	-2.7		
108		A	18 / 9	0.10	1.6	0.16	-0.7			0.050	-0.6	0.24	0.3	0.46	0.4
109		A	19 / 11	0.070	-0.1	0.241	1.0	29.1	-0.3	0.058	0.0	0.221	-0.1	0.447	0.2
111	x	A	18 / 9	0.081	0.6	0.191	0.0			0.042	-1.1	FN	-4.0	0.348	-0.7
113		B	16 / 8	0.025	-2.6	0.154	-0.8			0.042	-1.1	0.11	-2.0	0.37	-0.5
114	x	B	13 / 5	0.015	-3.2	0.613	8.8			FN	-4.0	FN	-4.0		
115		B	14 / 7	0.050	-1.2	0.173	-0.4			0.075	1.2	0.620	7.0	1.031	5.8
117		B	13 / 6	0.065	-0.3					0.700	44.1	0.105	-2.1		
118		B	1 / 1												
119		B	3 / 1	0.045	-1.5										
121		B	4 / 3							0.0449	-0.9				
122		B	4 / 3					27.6	-0.8			0.167	-1.0		
124		B	5 / 1												
125		B	18 / 8	0.12	2.8	0.16	-0.7			0.068	0.7	FN	-4.0	0.11	-3.0
126		B	1 / 1					30.8	0.3						
127		A	18 / 9	0.03	-2.3	0.16	-0.7			0.046	-0.8	0.153	-1.3	0.384	-0.4
128	x	A	19 / 11	0.068	-0.2	0.189	-0.1	29.7	-0.1	0.060	0.1	0.251	0.5	0.444	0.2
129		B	4 / 2					30.6	0.2						
130		B	13 / 7	0.084	0.7			31.8	0.6	0.054	-0.3				
132		A	19 / 10	0.11	2.2	0.01	-3.8	32	0.7	0.06	0.1	0.12	-1.9	0.24	-1.7
134		A	19 / 10	0.082	0.6	FN*	-4.0	31.7	0.6	0.049	-0.6	0.258	0.6	0.597	1.7
137		A	19 / 10	0.084	0.7	0.4	4.3	30	0.0	0.06	0.1	FN	-4.0	0.34	-0.8
3rd-10		A	19 / 11	0.075	0.2	0.22	0.6	30.61	0.2	0.052	-0.4	0.18	-0.8	0.46	0.4
3rd-19		A	18 / 10	0.0725	0.1	0.169	-0.5			0.0419	-1.1	0.140	-1.5	0.293	-1.2
3rd-68		A	19 / 11	0.0454	-1.4	0.228	0.8	28.4	-0.5	0.0530	-0.4	0.183	-0.7	0.577	1.5
3rd-86		B	16 / 8	0.0656	-0.3	0.120	-1.5	27.3	-0.9	0.0627	0.3			0.449	0.3
3rd-110		B	2 / 2					29.4	-0.2						
3rd-112		B	19 / 7	0.075	0.2	0.25	1.2	29.6	-0.1	0.082	1.6	0.23	0.1	FN	-4.0
3rd-116		B	9 / 6	0.030	-2.3	0.060	-2.8	30.35	0.2	0.064	0.4			1.40	9.3
3rd-120		B	16 / 8	0.055	-0.9			24.4	-1.8	0.074	1.1	0.222	-0.1	0.424	0.0
3rd-123		B	13 / 6	0.065	-0.3			30.096	0.1	FN	-4.0	FN	-4.0		
3rd-131		B	10 / 4							FN	-4.0	0.221	-0.1	0.324	-0.9
3rd-135		B	14 / 8	0.059	-0.7			33	1.0	0.064	0.4			0.26	-1.5
3rd-139		B	17 / 7	0.053	-1.0	0.11	-1.7	31.90	0.7	0.054	-0.3	FN	-4.0	0.52	0.9

Cat*: For the laboratory classification based on scope copper was not taken into account.

terial. The reference values for dithianon, DTCs and phthalimide and the corresponding z scores are for informative purposes only.

	COMPULSORY Compounds			MPP (=aka MPPA)		N-Acetyl glufosinate		Dithianon		DTCs (expr. as CS_2)		Phthalimide	
	Assigned / Reference Value [mg/kg]			0.0819		0.077		*0.236 1)*		*0.100 2)*		*0.082 3)*	
	*CV**			22.8 %		21.9 %		38.1 %		46.7 %		32.4 %	
	MRRL [mg/kg]			0.01		0.01		0.01		0.01		0.01	
Lab code SRM19-	NRL	Cat*	Analysed / corr. found, max. 15 / 10	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
97	x		17 / 9	0.802	35.2	0.115	2.0	0.307	*1.2*			0.116	*1.7*
98	x		19 / 11	0.0617	-1.0	0.0631	-0.7	0.169	*-1.1*	0.0820	*-0.7*	0.090	*0.4*
99	x		19 / 11	0.086	0.2	0.099	1.1	0.214	*-0.4*	0.053	*-1.9*	0.144	*3.0*
100	x		18 / 11	0.220	6.7	0.152	3.9	0.291	*0.9*	0.096	*-0.2*	0.067	*-0.7*
101	x		4 / 3	0.063	-0.9	0.070	-0.4						
102			19 / 11	0.085	0.2	0.063	-0.7	0.132	*-1.8*	0.092	*-0.3*	0.137	*2.7*
103			18 / 10	0.070	-0.6	0.067	-0.5			0.077	*-0.9*	0.114	*1.6*
104			19 / 10	0.093	0.5	0.080	0.1	0.111	*-2.1*	FN*	*-4.0*	0.089	*0.3*
105	x		6 / 3					0.107	*-2.2*				
106			1 / 1							0.131	*1.2*		
107			8 / 4							0.071	*-1.2*		
108			18 / 9	0.065	-0.8	0.073	-0.2	0.072	*-2.8*	FN	*-4.0*	0.11	*1.4*
109			19 / 11	0.075	-0.3	0.072	-0.3	0.303	*1.1*	0.081	*-0.8*	0.113	*1.5*
111	x		18 / 9	0.08	-0.1	0.087	0.5	0.037	*-3.4*	0.072	*-1.1*	0.173	*4.4*
113			16 / 8					0.21	*-0.4*	0.06	*-1.6*	0.13	*2.3*
114	x		13 / 5					0.281	*0.8*	0.039	*-2.4*	0.201	*5.8*
115			14 / 7					0.250	*0.2*			0.204	*6.0*
117			13 / 6	0.741	32.2	1.228	59.5	0.031‡	*-3.5*				
118			1 / 1							0.049	*-2.0*		
119			3 / 1										
121			4 / 3	0.0683	-0.7	0.0475	-1.5						
122			4 / 3									0.098	*0.8*
124			5 / 1			FN	-4.0			0.06	*-1.6*		
125			18 / 8	0.14	2.8	0.063	-0.7	FN	*-4.0*	0.27	*6.8*	0.055	*-1.3*
126			1 / 1										
127			18 / 9	FN	-4.0	0.099	1.1	0.247	*0.2*	0.063	*-1.5*	0.115	*1.6*
128	x		19 / 11	0.082	0.0	0.067	-0.5	0.090	*-2.5*	0.085	*-0.6*	0.096	*0.7*
129			4 / 2							0.072	*-1.1*		
130			13 / 7	0.123	2.0	0.111	1.7			0.111	*0.4*	0.195	*5.5*
132			19 / 10	0.08	-0.1	FN*	-4.0	0.07	*-2.8*	0.07	*-1.2*	0.06	*-1.1*
134			19 / 10	0.088	0.3	0.102	1.3	0.135	*-1.7*	0.058	*-1.7*	0.168	*4.2*
137			19 / 10	0.03	-2.5	0.12	2.2	0.3	*1.1*	0.06	*-1.6*	0.17	*4.3*
3rd-10			19 / 11	0.074	-0.4	0.07	-0.4	0.136	*-1.7*	0.04	*-2.4*	0.14	*2.8*
3rd-19			18 / 10	0.0665	-0.8	0.0749	-0.1	0.224	*-0.2*	0.0977	*-0.1*	0.0757	*-0.3*
3rd-68			19 / 11	0.0604	-1.1	0.0641	-0.7	0.0706	*-2.8*	0.106	*0.2*	0.195	*5.5*
3rd-86			16 / 8	0.0639	-0.9	0.111	1.7	0.0591	*-3.0*				
3rd-110			2 / 2							0.075	*-1.0*		
3rd-112			19 / 7	FN	-4.0	FN	-4.0	0.15	*-1.5*	0.049	*-2.0*	FN	*-4.0*
3rd-116			9 / 6							0.018	*-3.3*		
3rd-120			16 / 8					0.177	*-1.0*	0.03	*-2.8*	0.100	*0.9*
3rd-123			13 / 6	0.078	-0.2	0.100	1.2	0.012	*-3.8*	0.102	*0.1*		
3rd-131			10 / 4							0.0850	*-0.6*	0.0507	*-1.5*
3rd-135			14 / 8	0.058	-1.2	0.072	-0.3	0.060‡	*-3.0*	0.086	*-0.6*		
3rd-139			17 / 7	FN	-4.0	0.059	-0.9					0.26	*8.7*

1) Reference value of dithianon based on the robust mean of results generated under strong protection (for information only, please refer to Section 4.2.2). In case of Lab 117 and 135 the transport took more than one week and the sample was completely defrosted on arrival. An extensive degradation of dithianon during transport is thus likely.
2) Reference value was set at 0.1 mg/kg (for information only, please refer to Section 4.2.3)
3) Reference value based on the robust mean of LC-based results (for information only, please refer to 4.2.4)

Table 4-12: Results reported and informative z scores achieved by the 33 participating laboratories having analysed at least one of the four optional co
scores, z' scores and score ranges were calculated for informative purposes only for 2,4-DNOP (free phenol) and meptyldinocap based on the robust sta
For deitals please also refer to **Section 4.2.5, p. 33**.

Optional Compounds				*2,4-DNOP (free phenol)*					*Meptyldinocap*				
Assigned Value [mg/kg] (No. of Results)				*0.0647 (12)*			*Possible range of reference value considering uncertainty of robust mean*		*0.0860 (18)*			*Possible range of reference value considering uncertainty of robust mean*	
*CV**				*46.9 %*			*Lower value:*	*Upper value:*	*29.6 %*			*Lower value:*	*Upper value:*
MRRL [mg/kg]				0.01			*0.0533*	*0.0761*	0.01			*0.0772*	*0.0948*
Lab code SRM19-	NRL	Cat	Analysed / corr. found, max. 8 / 4	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	z' score (FFP-RSD = 25 %)	z Score range considering uncertainty of robust mean		Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	z' score (FFP-RSD = 25 %)	z Score range considering uncertainty of robust mean	
1		A	5 / 1	0.05	-0.9	-0.7	-1.6	-0.2					
6		A	2 / 1						1.960	87.2	80.6	86.8	87.6
7		A	6 / 4	0.062	-0.2	-0.1	-0.9	0.5	0.072	-0.7	-0.6	-1.1	-0.2
8		A	3 / 1										
9		A	7 / 4	0.0408	-1.5	-1.2	-2.2	-0.8	0.07779	-0.4	-0.4	-0.8	0.0
13		A	3 / 1										
14		A	5 / 1										
20		A	8 / 4	0.0473	-1.1	-0.9	-1.8	-0.4	0.0869	0.0	0.0	-0.4	0.5
23		A	8 / 4	0.119	3.4	2.7	2.7	4.1	0.013	-3.4	-3.1	-3.8	-3.0
25		A	6 / 4	0.0543	-0.6	-0.5	-1.3	0.1	0.0931	0.3	0.3	-0.1	0.7
28		A	4 / 1						0.082	-0.2	-0.2	-0.6	0.2
35		A	8 / 4	0.073	0.5	0.4	-0.2	1.2	0.078	-0.4	-0.3	-0.8	0.0
42		A	7 / 3	0.024	-2.5	-2.1	-3.2	-1.8	0.021	-3.0	-2.8	-3.4	-2.6
43	x	A	3 / 1										
46		B	3 / 2						1.1	47.2	43.6	46.8	47.6
53		A	3 / 1						0.091	0.2	0.2	-0.2	0.6
57		A	6 / 2										
59		A	6 / 1	FN	-4.0	-4.0	-4.0	-4.0	1.300	56.5	52.2	56.1	56.9
62		B	2 / 1										
63		A	5 / 1										
78		A	3 / 1										
80		B	4 / 2						2.94	132.7	122.8	132.3	133.2
91		A	8 / 4	0.0746	0.6	0.5	-0.1	1.3	0.118	1.5	1.4	1.1	1.9
97	x	A	8 / 4	0.244	11.1	9.1	10.4	11.8	0.0999	0.6	0.6	0.2	1.1
102		A	5 / 1										
103		A	5 / 3	0.065	0.0	0.0	-0.7	0.7	0.103	0.8	0.7	0.4	1.2
115		B	3 / 1						0.121	1.6	1.5	1.2	2.0
132		A	4 / 2	0.12	3.4	2.8	2.7	4.1					
137		A	4 / 1						2.5	112.3	103.8	111.9	112.7
3rd-10		A	4 / 1										
3rd-116		B	1 / 1						0.80	33.2	30.7	32.8	33.6
3rd-123		B	3 / 1						0.058	-1.3	-1.2	-1.7	-0.9
3rd-139		B	6 / 2	0.090	1.6	1.3	0.9	2.3	FN	-4.0	-4.0	-4.0	-4.0

ompounds present in the SRM19 test material. Since the results populations were small and the UAV-tests failed in all four cases, the assigned values, z atistics of the entire population. For meptyldinocap (sum) following hydrolysis as well as calculated, 0.157 mg/kg was set as a reasonable reference value.

	Optional Compounds				*Meptyldinocap, sum calculated*		*Meptyldinocap, sum follow. hydrolysis*	
	Reference Value [mg/kg] set by the organiser				*0.157*		*0.157*	
	*CV**				*23.4 %*		*30.9 %*	
	MRRL [mg/kg]				0.02		0.01	
	Lab code SRM19-	NRL	Cat	Analysed / corr. found, max. 8 / 4	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
	1		A	5 / 1				
	6		A	2 / 1				
	7		A	6 / 4	0.128	-0.7	0.128	-0.7
	8		A	3 / 1			1.018	21.9
	9		A	7 / 4	0.128	-0.7	0.137	-0.5
	13		A	3 / 1			0.33	4.4
	14		A	5 / 1			0.236	2.0
	20		A	8 / 4	0.145	-0.3	0.142	-0.4
	23		A	8 / 4	0.159	0.1	0.493	8.6
	25		A	6 / 4	0.160	0.1	0.162	0.1
	28		A	4 / 1				
	35		A	8 / 4	0.167	0.3	0.215	1.5
	42		A	7 / 3	0.051	-2.7		
	43	x	A	3 / 1			0.197	1.0
	46		B	3 / 2	1.1	24.0		
	53		A	3 / 1				
	57		A	6 / 2	0.127	-0.8	0.272	2.9
	59		A	6 / 1	FN	-4.0	FN	-4.0
	62		B	2 / 1			0.197	1.0
	63		A	5 / 1			0.192	0.9
	78		A	3 / 1			0.181	0.6
	80		B	4 / 2	1.79	41.6		
	91		A	8 / 4	0.210	1.4	0.228	1.8
	97	x	A	8 / 4	0.400	6.2	0.842	17.5
	102		A	5 / 1			0.105	-1.3
	103		A	5 / 3	0.183	0.7		
	115		B	3 / 1				
	132		A	4 / 2			0.15	-0.2
	137		A	4 / 1				
	3rd-10		A	4 / 1			0.21	1.4
	3rd-116		B	1 / 1				
	3rd-123		B	3 / 1				
	3rd-139		B	6 / 2	FN	-4.0	0.090	-1.7

4.3.4 Laboratory Performance Based on z Scores

As mentioned in **Section 4.2.1 (p. 30)**, in the case of ***copper***, the target standard deviation σ_{pt}, which is used to calculate the z scores, was set at 10 % of the AV (x_{pt}). The use of 10 % as the fit-for-purpose relative standard deviation (FFP-RSD) deviates from the 25 % defined in the General Protocol. Therefore, ***copper*** was excluded from the AAZ calculation.

Following a decission of the Scientific Committee only informative z scores should be calculated for ***dithianon***, ***phthalimide*** and ***DTCs***. For ***dithianon*** and ***phthalimide*** the informative z scores were calculated based on selected subpopulations, and in the case of ***DTCs*** they were based on a reference value which was set at 0.1 mg/kg on the basis of results of experiments by the organiser and considering the method-dependent trends of the participants results. For details please refer to **Section 4.2.2 – 4.2.4.**

For ***2,4-Dinocap (free phenol)***, ***meptyldinocap*** as well as ***DFA*** where the number of the numerical results was low and the uncertainty of the robust mean did not pass the limit for being accepted as an assigned value, z scores, z' scores, and z score ranges that consider the uncertainty of the robust mean were calculated for informative purposes. For ***meptyldinocap (sum, calc.)*** and ***meptyldinocap (sum, follow. hydr.)*** and considering the analytical results obtained by the organiser and the spiking levels 0.157 mg/kg was set as a reasonable reference value. For details please refer to **Section 4.2.5, p. 33.** The informative z scores based on this reference value serve as a guidance for the labs in order to recognize strong analytical bias and initiate counter measurer.

In the case of ***gamma-cyhalothrin***, only one of 16 laboratories having submitted a result for this analyte used a chiral column and was thus able to distinguish between the two enantiomers. All other laboratories essentially quantified ***lambda-cyhalothrin*** (the unresolved racemic mixture). Despite the failure of the labs to properly report ***gamma-cyhalothrin*** as required by the TPL, the Scientiffic Committee agreed to still make use of the data on ***lambda-cyhalothrin*** and to calculate an assigned value and the corresponding z scores but for informative purposes only. As a basis for the robust statistices, all data reported by EU and non-EU labs was used (N = 15 and 6, respectively) only exclusing the result generated by lab 25, which has correctly quantified ***gamma-cyhalothrin*** through enantioselective analysis.

Disregarding the above mentioned exceptions where proper evaluations of the laboratory performance was not possible the performance of the laboratories was overall satisfactory. As far as the eight remaining-compulsory compounds is concerned, 88 % of the results reported by EU/EFTA-OfLs fell within the "acceptable" z score range (**Table 4-10**). Looking at individual compounds, the frequency of acceptable z scores exceeded 90 % in the cases of ***copper*** (99 %), ***ethephon*** (92) and ***clopyralid*** (90 %). Frequencies of acceptable z scores between 80 and 90 % were observed for ***avermectin B1a*** (86 %), ***folpet (sum)*** (89 %), ***MPP*** (84 %), and ***N-acetyl glufosinate*** (84 %). In the case of ***folpet***, however, the frequency of acceptable z scores was only 77 %, thus remained below 80 %.

A lab-by-lab compilation of all individual results and z scores, including those for informative purposes only, is shown in **Table 4-11 (p. 42)** for compulsory compounds, in **Table 4-12 (p. 49)** for optional compounds and in **Table 4-13 (p. 51)** for the two extra compounds present in the test material. The corresponding kernel density histograms showing the distribution of the reported results for the compulsory and optional compounds are shown in **Appendix 5**. A graphic representation of the z score distribution of each target analyte present in the test item can be seen in **Appendix 6**.

Table 4-13: Results reported and z scores achieved by the 30 participating laboratories having analysed at least one of the two extra compounds present in the SRM19 test material. Since the results population for DFA was small and the UAV-test failed, the assigned values, z scores, z' scores and z score ranges were calculated for informative purposes only. And instead of γ cyhalothrin, the assigned valule of λ cyhalothrin was calculated, since only one lab (Lab Code 25) applied a chiral column in the analysis which would allow determining the γ isomor. For details please refer to Section 4.2.6.

Optional Compounds				*Difluoroacetic acid (DFA)*					Lambda-Cyhalothrin	
Assigned Value [mg/kg] (No. of Results)				*0.146 (9)*			*Possible range of reference value considering uncertainty of robust mean*		*0.077 (14)*	
*CV**				*21.7 %*			*Lower value:*	*Upper value:*	*20.5 %*	
MRRL [mg/kg]				0.02			*0.133*	*0.0.159*	0.01	
Lab code SRM19-	NRL	Cat	Analysed / corr. found, max. 2 / 2	Conc. [mg/kg]	z Score (FFP-RSD = 25 %)	z' score (FFP-RSD = 25 %)	z Score range considering uncertainty of robust mean		Conc. [mg/kg]	z Score (FFP-RSD = 25 %)
1		A	2 / 1						0.104	1.4
4		A	2 / 1	0.128	-0.5	-0.5	-0.9	-0.1		
6		A	2 / 1						0.071	-0.3
8		A	2 / 1						0.065	-0.6
14		A	2 / 1	0.132	-0.4	-0.4	-0.7	0.0		
23		A	2 / 1	0.141	-0.1	-0.1	-0.5	0.2		
25		A	2 / 1						0.0618 (isomer only!)	-0.8
48		A	2 / 1	0.125	-0.6	-0.5	-0.9	-0.2		
57		A	2 / 1						0.097	1.0
59		A	2 / 1						0.070	-0.4
66		B	2 / 1						0.061	-0.8
72		B	2 / 1	0.13	-0.4	-0.4	-0.8	-0.1		
78		A	2 / 1	0.16	0.4	0.4	0.0	0.7		
89	x	B	2 / 1						FN	-4.0
91		A	2 / 1	0.196	1.4	1.3	1.0	1.7		
93		A	2 / 2	0.115	-0.8	-0.8	-1.2	-0.5	0.068	-0.5
94		B	2 / 1						0.013	-3.3
98		A	2 / 1						0.0713	-0.3
102		A	2 / 2	0.186	1.1	1.0	0.7	1.5	0.07	-0.4
119		B	2 / 1						0.092	0.8
122		B	2 / 1						0.083	0.3
125		B	2 / 1						0.093	0.8
127		B	2 / 1						0.063	-0.7
137		A	2 / 1	FN	-4.0	-4.0	-4.0	-4.0		
3rd-10		A	2 / 1						0.097	1.0
3rd-86		B	2 / 1						0.0765	0.0
3rd-112		B	2 / 1						0.068	-0.5
3rd-116		B	2 / 1						0.070	-0.4
3rd-135		B	2 / 2	0.101	-1.2	0.0	-1.6	-0.9	0.078	0.0
3rd-139		B	2 / 1						0.034	-2.2

4.3.5 Feedback from Laboratories in Case of Poor performance

Like in the previous EUPT-SRMs, with the publication of the preliminary report, all participating laboratories having reported false positive results or having obtained questionable ($2 < |z\ score| < 3$) or unacceptable ($|z\ score| \geq 3$) results were asked to investigate the reasons for their poor performance and to report them to the organisers. The aim of this follow-up measure is to sensitize the laboratories to timely investigate the sources of errors in order to avoid making the same errors in the future.

In the present PT, there were 7 false positive results reported by 5 EU/EFTA-OfLs (**Table 4-14** and **Section 4.3.1**). Concerning compulsory compounds only and excluding ***dithianon***, ***DTCs*** and ***phthalimide***, for which only an informative reference value was established and which were not to be used for assessing the labs' proficiency in the final report (**Section 4.2.2 – 4.2.4**), 47 EU/EFTA-OfLs submitted 78 results insicating poor performance, among them 20× FNs and 3× FN* (**4.3.2, p. 34**).

Although it was decided not to officially evaluate the participants' results for ***dithianon, DTCs*** and ***phthalimide***, informative z scores based on reference values were still calculated in order to enable the labs to recognise whether their procedure generates biased results, so that corrective actions can be taken. For ***dithianon*** and ***phthalimide*** the reference values were based on the robust means of selected subpopulations and in the case of ***DTCs*** based on analytical results obtained by the organizer and taking into consideration method-dependent trends observed within the participants' results (**Section 4.2.2 – 4.2.4**). These reference values together with tentative z scores, were alraedy communicated to the participants with the preliminary report so corrective actions could be taken quickly and reasonably. If the robust mean values of the entire population were communicated at this stage corrective actions would have been taken by the wrong laboratories. The aim was to address the special analytical difficulties of these three analytes and to help the participants improve or replace their methodologies. Based on these informative reference values, 88 results reported by 64 EU/EFTA-OfLs received informative z scores >2.0 or <-2.0, among them 8× FN and 3× FN*.

Table 4-14: Number of false positive results and poor performance z scores obtained by the laboratories for each of analytes present in the SRM19 test material. Evaluation for compounds based on reference values for informative purposes is shown in gray italic letters.

Compounds NOT present in Test Item		No. of FP / FR	
		EU/EFTA-OfLs	3rd Countriy Labs
Compulsory	2,4-D (free acid)	0 / 1	0 / 0
	Captan	2 / 0	0 / 0
	Captan (sum)	1 / 1	0 / 0
	Chlormequat-Cl	1 / 0	0 / 0
	Glufosinate	1 / 0	0 / 0
	Mepiquat-Cl	1 / 0	0 / 0
	Subtotal	**6 / 2**	**0 / 0**
Opt.	Amitrole	1 / 0	0 / 0

Compounds present in Test Item		No. of Poor Performance Cases / therein FNs + FN*	
		EU/EFTA-OfLs	3rd Country Labs
Compulsory	Abamectin B1a	14 / 2	1 / 0
	Clopyralid	8 / 2	1 / 0
	Copper	1 / 0	0 / 0
	Ethephon	7 / 3	2 / 2
	Folpet	19 / 8	2 / 2
	Folpet (sum)	9 / 2	2 / 1
	MPP (=aka MPPA)	11 / 2	2 / 2
	N-Acetyl glufosinate	9 / 4	1 / 1
	Subtotal	**78 / 23**	**11 / 8**
	Dithianon	*29 / 4*	*4 / 0*
	DTCs (expr. as CS2)	*27 / 5*	*3 / 0*
	Phthalimide	*32 / 2*	*4 / 1*
	Subtotal	*88 / 11*	*11 / 1*
Optional	*2,4-DNOP (free phenol)*	*6 / 2*	*0 / 0*
	Meptyldinocap	*8 / 1*	*2 / 1*
	Meptyldinocap (sum, calc.)	*5 / 1*	*1 / 1*
	Meptyldinocap (sum, foll. hydr.)	*5 / 1*	*1 / 0*
	Subtotal	*24 / 5*	*4 / 2*
Extra	*Difluoroacetic acid (DFA)*	*1 / 1*	*0 / 0*
	Lambda-cyhalothrin	*2 / 1*	*1 / 0*
	Subtotal	*3 / 2*	*1 / 0*

For these four analytes, 24 results reported by 13 EU/EFTA-OfLs obtained informative z scores indicating poor performance, among them 5× FNs.

For both of the extra compounds ***DFA*** and ***lambda-cyhalothrin*** the assigned values were calculated for informative purposes only (**Section 4.2.6**). In the case of DFA, there was only one FN. All numerical results obtained acceptable informative z scores. In the case of ***lambda-cyhalothrin***, two results reported by EU/EFTA-OfLs were classified as poor, among them one FN. **Table 4-14** gives a summary of the poor performance z scores obtained by the participants for each of the analytes present in the test material.

Even though the assigned and reference values as well as the related lab performance assessments for several compounds were for information only, there is still the need to identify and communicate cases of poor or tentatively poor performance as these compounds are of high interrest and there is a need for the affected labs to take measures for improving their analysis. Some of these compounds are entailed in the EU coordinated monitoring program (MACP). These are ***dithianon***, ***DTCs***, ***phthalimide*** and the extra compound ***lambda-cyhalothrin*** (which unlike ***gamma-cyhalothrin*** is actually an MRM compound). Other compounds are listed in the SANTE working document for national monitoring programs. These are ***meptyldinocap*** together with its degradant ***2,4-DNOP*** as well as ***DFA***. After publishing the Preliminary Report the affected laboratories were therefore contacted and urged to give feedback on the reasons for their poor performance based on the preliminary z scores. Most of the preliminary z scores did not shift, but there were some exceptions: The AVs of meptyldinocal ***(sum, calc.)*** and of ***meptyldinocap*** (sum after hydrol) were different in the preliminary report but was set at 0.157 mg/kg in the final report. This value was based on analytical results obtained by the organizer using the hydrolysis method as well as the individual results for meptyldinocap and 2,4-DNOP and the spiking levels.

Among the 12 participating laboratories from seven non-EU or EFTA countries, there were no false positive results reported. One of these seven countries is an EU candidate country (RS) and the other six are 3rd countries (see **Table 3-1, p. 16**) For the 8 compsulsory compounds for which labs' proficiency was assessed, five of those laboratories reported poor results in 11 cases (thereof 8 FNs). For ***dithianon***, ***DTCs*** and ***phthalimide*** 11 results reported by 9 labs outside the EU-/EFTA countries were alocated with poor informative z scores (thereof 1× FN). For three of four optional compounds present in the SRM19 test item, four results were considerd poor, among them 2× FNs. For the extra compound ***lambda-cyhalothrin*** the result submitted by one non-EU or EFTA lab was classified as poor.

In total, 57 laboratories (52× EU/EFTA-OfLs and 5 laboratories outside EU-EFTA countries) having obtained poor performance scores, including informative scores, reported in 119 cases (= 54 %) the reasons for poor performance. A compilation of the feedback received by the laboratories is given in **Appendix 7**. With this compilation it is intended to make all participating labs aware of common and potential error sources so that they can be avoided or eliminated in the future. **This compilation also includes suggestions and hints from the organiser** that can help the affected labs as well as other interrested to deal with analytical difficulties concerning these compounds and eliminate sources of errors. NRLs could also use this information about "typical errors" for better educating and assisting the OfLs within their network with the goal of improving the overall analytical performance of their country.

Among the (possible) reasons stated by the participants to explain the poor performance, “Analyte losses during the procedures” (40×) was the most frequent reason. What is special in this respect is the increase in ***phthalimide*** resulting from decomposition of ***folpet*** in the hot GC-Injection (13×). Like in previous EUPT-SRMs, "Lacking of experience with the analyte or matrix or the combination of both” is another frequent reason stated to explain poor performance. Some of the labs utilized the EUPT-SRM as a possibility to check or verify the the performance of newly established methods. The organisers do hope that the participation in the PT and the hints provided in case of poor performance have contributed in improving the both old and newly established methods. A good perfomance will hopefully also facilitate the accreditation process of the concerned methods.

Further reported reasons for poor performance z scores were:

9× Measurement problems
9× Calculation error
8× Inappropriate / erroneous calibration approach
7× Erroneous analytical standard
5× Misinterpretation / Misevaluation of measurement data
4× Analytical procedure was appropriate but it was not properly performed
1× Result not or not properly corrected for recovery
1× Deficient QC-measures
23× Other reasons, that cannot be clearly assigned to the categories.

4.4 Special Topics

Compared to the EUPT-SRM18 the EUPT-SRM19 was much more challenging to the participants. Below are some issues that the organisers would like to highlight, so that laboratories can take them into account in routine controls and future PTs

Use of ILIS

Using isotope labelled internal standards (ILISs) typically helps to improve accuracy, especially when it comes to correcting for low absolute recoveries and/or for correcting for strong matrix effects that are not or not fully covered by the calibration approach used. As in previous EUPTs, this aspect was also checked by comparing the statistical evaluations of data submitted by labs using ILIS with data of labs not using ILIS. **Table 4-15** shows the comparison figures for the highly polar compounds ***MPP***, N-acetyl-glufosinate and ***ethephon***. Among these compounds, ILIS was most frequently employed in the case of ***ethephon*** (59 % of labs submitting quantitative results), followed by ***N-acetyl glufosinate*** (43 %) and ***MPP*** (38 %). In the vast majority of these cases, the ILIS was employed at the beginning of the procedure. The use of ILIS caused a negligible shift (<2 %) of the robust mean value in the cases of ***ethephon*** and ***N-acetyl glufosinate***, while in the case of ***MPP*** the shift was moderate (11.4 %). However in all cases the improvements in data dispersion were considerable. The robsut rel. standard deviation (CV^*) of the results generated not using ILIS ranged between 24.9 % and 32.3 % (avg. was 29.3 %), whereas for results using ILIS it ranged between 9.4 and 17.8 % (avg. 13.6 %). Given these clear trends, the organisers would like to urge laboratories once again to employ ILISs where this is beneficial (e.g., when poor recovery rates and/or strong matrix effects are not adequately addressed otherwise).

Table 4-15: Statistical data evaluation of MPP, N-acetyl glufosinate, and ethephon submitted by labs using ILIS compared to that of labs not using ILIS

	MPP		N-Acetyl Glufosinate		Ethephon	
	ILIS-Yes	ILIS-NO	ILIS-Yes	ILIS-NO	ILIS-Yes	ILIS-NO
Results (n =)	28	45	32	43	55	38
Freq. of ILIS Use	38 %		43 %		59 %	
Robust Mean (RM)	0.0105	0.0117	0.0771	0.0785	0.0589	0.0578
Diff. in RM		11.4 %		1.8 %		-1.9 %
CV^*	17.8 %	32.3 %	13.5 %	30.8 %	9,4 %	24.9 %
Avg CV^*	ILIS-Yes: 13.6 % ILIS-No:29.3 %					

Prevention of analyte losses

Due to increased reaction kinetics, degradation reactions of analytes are more pronounced at high temperatures. This also concerns enzymatically catalyzed reactions, such as hydrolyses and oxidations. Among the analytes present in the test item of the present PT, ***dithianon*** was the most affected by this effect. ***Dithianon*** tents to react via radical intermediates if not protected. These reactions slow down considerably under acidic conditions and/or in presence of antioxidants. Low temperatures are also helpful, although a notable degradation of ***dithianon*** was noticed even during long storage of the test item in the freezer. This is typical for reactions through radicals. During the preparation of the test material a moderate amount of ascorbic acid was added to protect ***dithianon*** from degradation. Still, considerable losses where observed when the homogenate was left to thaw and especially when the material was left standing in a thawed state over a long period. This trend could be also clearly seen in the laboratory results. Laboratories that according to the reported method information have left the test material to defrost over an extended period, either before or after withdrawing the analytical portions, reported tentatively too low results. **The laboratories are urged to keep the samples in a frozen state and to avoid defrosting them** (e.g. over-night). It is highlighted that defrosting of analytical portions is equally critical.

According to experiments by the organisers, ***dithianon*** was the analyte most affected by losses through exposure to high temperatures. The losses of the potentially critical compounds ***folpet*** and ***meptyldinocap*** was rather moderate if the exposure was not extended too long, while the losses of ***DTCs*** (as CS_2) and ***N-acetyl glufosinate*** were negligible. The resistance of the analyte ***DTCs*** (as CS_2) to losses during exposure to the thawed sample was surely related to the very poor solubility of the polymeric metal complex metiram. In the case of ***folpet*** and ***meptyldinocap***, which are known to degrade at high pH, the acidity of the gape homogenate has surely kept the losses (and the generation of their degradants (***phthalimide*** and ***2,4-DNOP***) moderate. This protection also extended during the extraction step, where acidification is typically needed when dealing with less protective matrices (e.g. matrices with high pH and low antioxidative potential). Even using non-acidified QuEChERS, recoveries were good.

Folpet and Phthalimide

As underlined in the EUPT-SRM17 and EUPT-SRM12, as well as in various EURL-SRM documents (e.g. SRM-07 (using GC-MS/MS), SRM-42 (APCI or ESI LC-MS/MS to cover parents+degradants); and SRM-49 (LC-MS/MS in the ESI-pos. mode to analyse THPI and PI), ***folpet*** undergoes decomposition to ***phthalimide*** in the GC-injector, which may result in an overestimation of the ***phthalimide*** results if this aspect is not taken into account. This aspect has been communicated several times in various workshops and trainings. ***Folpet*** itself can be analysed accurately by GC-based methods if matrix effects are properly addressed (e.g. via ILIS, or standard additions or APs), but ***phthalimide*** is better analysed by LC-MS/MS where the result is not overestimated due to extra ***phthalimide*** being generated when ***Folpet*** decomposes in the hot injector. The same applies to *captan* and *tetrahydrophtahlimide* (which were not spiked to the PT-itrem).

A separate, purely GC-based approach, involving deduction of the ***phthalimide*** amount formed in the GC-injector was also published by the EURL-SRM (SRM-07-ExtCal and SRM-07-StdAdd).

Polymeric DTCs require stronger reaction conditions

In the present PT metiram, a polymeric DTC was spiked to the sample. Such ***DTCs*** exhibit a very poor solubility and need to be spiked as suspensions. In contrast to thiram, which is typically used by labs to check the method recoveries, such polymeric ***DTCs*** require strong reactions conditions. Parameters such as reagent-to-sample-ratio, temperature, reaction time and shaking intensity play an important role. In this context please see the workshop presentation on the SRM19 (News on SRM and EUPT-SRM19 Part I & II) as well as the document SRM-14 (V3). Another aspect that needs attention is the stability of the $SnCl_2$ reagent as it tends to be consumed by air. Other typical error-sources include evaporation losses of CS_2 during the

preparation or storage of CS_2 stock and working standards. Losses of CS_2 in the sample during the reaction (in case of leaking vessels) or during the exposure of extracts.

Issues with the analysis of Meptyldinocap and 2,4-DNOP

Meptyldinocap is sensitive to hydrolysis at high pH and high temperatures with ***2,4-DNOP*** being formed. GC-analysis is therefore very tricky. LC-MS/MS analysis is more streightforward at first sight but the in-source fragmentation of ***meptyldinocap*** to ***2,4-DNOP*** in the ion-source makes analysis very tricky. As both compounds, ***meptyldinocap*** to ***2,4-DNOP***, are analyzed as ***2,4-DNOP*** (due to the in-source-fragmentation) a chromatographic separation between them is paramount.

A common error is the misallocation of the ***2,4-DNOP*** peak as ***meptyldinocap***. The reason behimnd this is that ***2,4-DNOP*** is much more sensitive in detection than ***meptyldinocap***. As ***meptyldinocap*** standards contain a certain percentage of free ***2,4-DNOP*** the latter always shows a peak when injecting ***meptyldinocap***. Already at a small percentage of free ***2,4-DNOP*** in the ***meptyldinocap*** standard (which is common, even in fresh standards), its signal may be larger than that of the much higher concentrated parent. So labs may erroneously allocate the ***2,4-DNOP*** peak as belonging to ***meptyldinocap*** diregarding the ***meptyldinocap*** peak. Where the two compounds coelute the alleged ***meptyldinocap*** peak (in reality a ***meptyldinocap***/***2,4-DNOP*** peak cluster) may appear as if having a shoulder. Depending on whether mixed or individual standards are used, whether the two compounds co-elute, and whether the ***meptyldinocap*** standard has degraded (which often happens if it is not stabilised by acidification), various scenarios of misinterpretation and peak misallocation may occur.

5. RESULTS

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6. REFERENCES

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7. APPENDICES

Appendix 1 List of Laboratories Registered to Participate in the EUPT-SRM19

(a): Participating labs of EU and EFTA Member States

Country (Location)	Analysed on behalf of	Institution	City	NRL-SRM
Austria	AT	AGES - Innsbruck	Innsbruck	x
Belgium	BE	LOVAP NV - Belgium, Geel	Geel	–
Belgium	BE	Sciensano - Belgium, Brussels	Brussels	x
Belgium	BE; FR; LU	Primoris Belgium, Gent	Gent - Zwijnaarde	–
Bulgaria	BG	CLCTC | Pesticide Lab	Sofia	x
Bulgaria	BG	Primoris - Bulgaria, Plovdiv	Plovdiv	–
Croatia	HR	Bioinstitut d.o.o., Cakovec	Cakovec	–
Croatia	HR	Croatian National Institute of Public Health-HZJZ	Zagreb	–
Croatia	HR	Croatian Veterinary Institute - Krizevci	Krizevci	x
Croatia	HR	Dr. Andrija Štampar - Pesticide Lab	Zagreb	x
Croatia	HR	Eurofins Croatiakontrola	Zagreb	–
Croatia	HR	INSPECTO d.o.o. Laboratorij (Osijek)	Osijek	–
Croatia	HR	Sample Control - Pesticide Lab	Lučko	–
Cyprus	CY	SGL - Pesticide Lab (Nicosia)	Nicosia	x
Czech Republic	CZ	CAFIA - Pesticide Lab (Praha)	Praha	x
Czech Republic	CZ	UKZUZ - Czech Republic, Brno	Brno	–
Czech Republic	CZ	VSCHT / UCT Prague - Food Analysis (323)	Praha	–
Denmark	DK	Laboratoriet Ringsted - Pesticide Lab	Ringsted	x
Estonia	EE	LABRIS - Laboratory of Chemistry (Tallinn)	Tallinn	–
Finland	FI	Finnish Customs Laboratory	Espoo	x
Finland	FI	Finnish Food Authority	Helsinki	x
Finland	FI	MetropoliLab - Pesticide Lab	Helsinki	–
France	FR	ANSES - LSAI (Unité PBM)	MAISONS-ALFORT Cedex	x
France	FR	CAMP Méditerrannée (Perpignan)	PERPIGNAN	–
France	FR	CAPINOV (Landerneau)	Landerneau	–
France	FR	CERECO (GARONS)	GARONS	–
France	FR	GIRPA	Beaucouzé	–
France	FR	INOVALYS Le Mans - Pesticide Lab	Le Mans	–
France	FR	SCL (Illkirch Graffenstaden)	Illkirch Graffenstaden	–
France	FR	SCL (Montpellier)	Montpellier	–
France	FR	SCL (PARIS)	Massy Cedex	–
France	BE	Phytocontrol (Nimes) - Pesticide Lab	Nimes	–
Germany	BE	AGROLAB LUFA Kiel - Pesticide Lab	Kiel	–
Germany	DE	BVL Unit 504 NRL for Pesticide Residues	Berlin	x
Germany	DE	CVUA RRW - Pesticide Lab (Krefeld)	Krefeld	–
Germany	DE	CVUA-MEL - Pesticide Lab (Münster)	Münster	–
Germany	DE	Eurofins Dr. Specht Express T&I - Hamburg	Hamburg	–
Germany	DE	GBA Fruit Analytic - Germany, Hamburg	Hamburg	–
Germany	DE	Hessisches Landeslabor Kassel	Kassel	–
Germany	DE	Labor Friedle - Germany, Tegernheim	Tegernheim	–
Germany	DE	Labor Mang - Pesticide Lab	Frankfurt	–
Germany	DE	LALLF - Pesticide Lab (Rostock)	Rostock	–
Germany	DE	Landesamt für Verbraucherschutz, Halle/Saale	Halle/Saale	–
Germany	DE	Landeslabor Berlin-Brandenburg, Frankfurt (Oder)	Frankfurt (Oder)	–
Germany	DE	Landeslabor Schleswig-Holstein, Neumünster	Neumünster	–

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

Country (Location)	Analysed on behalf of	Institution	City	NRL-SRM
Germany	DE	LAVES - Pesticide Lab (Oldenburg)	Oldenburg	–
Germany	DE	LGL Erlangen - Pesticide Lab	Erlangen	–
Germany	DE	LTZ Augustenberg - Organic Analysis	Karlsruhe	–
Germany	DE	LUA Rheinland-Pfalz, Institut für LM-Chemie Speyer	Speyer	–
Germany	DE	LUA Sachsen - Pesticide Lab, Dresden	Dresden	–
Germany	DE	LUFA Speyer	Speyer	–
Germany	LT	GALAB Laboratories GmbH - Hamburg	Hamburg	–
Germany	MT	Eurofins - Germany, Hamburg	Hamburg	–
Greece	GR	Benaki Phytopathological Institute, Kifissia	Kifissia	x
Greece	GR	GCSL - Pesticide Lab (Athens)	Athens	x
Hungary	HU	NFCSO - Pesticide Lab (Velence, site in Szolnok)	Szolnok	x
Hungary	HU	NFCSO FCSLD PPSCNRL (Velence)	Velence	x
Iceland	IS	Matís - Iceland, Reykjavík	Reykjavík	x
Ireland	IE	The Food Chemistry Laboratories - DAFM	Celbridge	x
Italy	IT	Agenzia di Tutela della Salute di Bergamo (ATS)	Bergamo	–
Italy	IT	APPA Bolzano - Pesticide Lab	Bolzano	–
Italy	IT	APPA-Puglia | Polo Alimenti Bari - Pesticide Lab	Bari	–
Italy	IT	ARPA ER (Ferrara, Via Bologna)	Ferrara	–
Italy	IT	ARPA FVG	Udine	–
Italy	IT	ATS Milano - Laboratorio di Prevenzione	Milano	–
Italy	IT	Azienda Sanitaria Locale di Firenze	Firenze	–
Italy	IT	Istituto Superiore di Sanità - Roma	Roma	x
Italy	IT	IZS LT - Italy, Rome	Roma	–
Italy	IT	IZSAM - Pesticide Lab	Teramo	–
Italy	IT	IZSLER - Pesticide Lab	Brescia	–
Italy	IT	IZSUM - Italy, Perugia	Perugia	–
Latvia	LV	BIOR (Riga) - Pesticide Lab	Riga	x
Lithuania	LT	NMVRVI - Pesticide Lab (Vilnius)	Vilnius	x
Luxembourg	LU	LNS Food lab	Dudelange	x
Norway	NO	NIBIO - Department of Pesticide Chemistry	ÅS	x
Poland	PL	Hamilton UO-Technologia, Grójec	Grójec	–
Poland	PL	InHort (Skierniewice) - Pesticide Lab	Skierniewice	–
Poland	PL	Intertek Poland Sp. z o.o.	Gostynin	–
Poland	PL	IPP-NRI - Pesticide Lab (Poznan)	Poznan	–
Poland	PL	Laboratory of Food & Feed Safety in Bialystok	Bialystok	–
Poland	PL	PIORIN - Central Laboratory (Torun)	Torun	–
Poland	PL	VSES Lodz - Pesticide Lab	Lodz	–
Poland	PL	VSES Opole - Pesticide Lab	Opole	–
Poland	PL	VSES Warszawa - Pesticide Lab	Warszaw	x
Poland	PL	VSES Wroclaw - Pesticide Lab	Wroclaw	–
Poland	PL	WSSE - Poland, Bydgoszcz	Bydgoszcz	–
Portugal	PT	Labiagro – Portugal, Oeiras	Oeiras - Lisboa	–
Portugal	PT	Pesticide Lab (Funchal - Madeira Island)	Funchal - Madeira Island	x
Romania	RO	IISPV (Bucharest) - Pesticide Lab	Bucharest	x
Romania	RO	LRCRPPPV (Tirgu Mures) - Pesticide Lab	Tirgu Mures	–
Romania	RO	NATIONAL PHITOSANITARY AUTHORITY	Bucharest	–
Slovakia	SK	State Veterinary and Food Institute (Bratislava)	Bratislava	x
Slovenia	SI	Pesticide Lab - Maribor	Maribor	x
Spain	ES	Ainia (Valencia)	Valencia	–
Spain	ES	Analytica Alimentaria GmbH - Almeria, Spain	Almeria	–

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

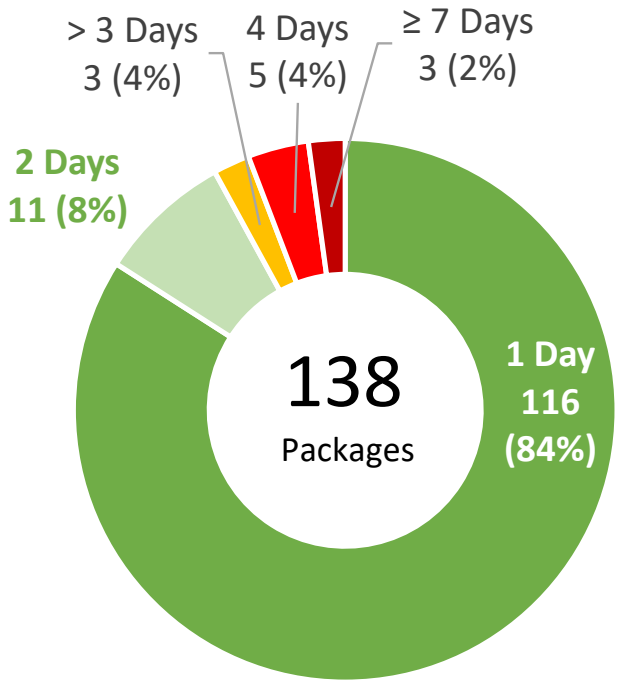
Country (Location)	Analysed on behalf of	Institution	City	NRL-SRM
Spain	ES	Dolmar Innova Tentamus, s.l.	Gimileo	–
Spain	ES	EURL-FV - Pesticide Residue Research Group	Almeria	–
Spain	ES	EUROFINS ECOSUR - Pesticide Lab	LORQUI - MURCIA	–
Spain	ES	Eurofins SiCA AgriQ - Almeria, Vícar	Almeria	–
Spain	ES	Fitosoil Laboratorios - Pesticide Lab	San Ginés (Murcia)	–
Spain	ES	Lab. de Produccion y Sanidad Vegetal de Almería	La Mojonera (Almeria)	–
Spain	ES	Labcolor-Coexphal - Spain, Almeria	La Mojonera, Almeria	–
Spain	ES	Laboratori Agència Salut Pública Barcelona	Barcelona	–
Spain	ES	Laboratorio Agroalimentario - Spain, Valencia	Burjassot, Valencia	–
Spain	ES	Laboratorio Agroalimentario de Extremadura	Cáceres	–
Spain	ES	Laboratorio Agroambiental de Zaragoza	Zaragoza	–
Spain	ES	Laboratorio Analítico Bioclínico - Spain, Almeria	Almeria	–
Spain	ES	Laboratorio Arbitral Agroalimentario, Madrid	Madrid	x
Spain	ES	LABORATORIO KUDAM, S.L.	Pilar de la Horadada (Alicante)	–
Spain	ES	Laboratorio Químico Microbiológico (San Gines)	San Ginés (Murcia)	–
Spain	ES	Laboratorios Tecnológicos de Levante	Paterna	–
Spain	ES	Labs & Technological Services AGQ - Burguillos	Burguillos	–
Spain	ES	National Center for Technology and Food Safety	San Adrián (Navarra)	–
Spain	ES	National Centre for Food (Majadahonda)	Majadahonda	x
Spain	ES	SALUD PUBLICA (LSP - MADRID SALUD)	Madrid	–
Sweden	SE	Eurofins Food & Feed - Pesticide Lab (Lidköping)	Lidköping	–
Sweden	SE	Swedish Food Agency - Sweden, Uppsala	Uppsala	x
Switzerland	CH	Kantonales Laboratorium Bern	Bern	–
Switzerland	CH	Kantonales Laboratorium Zürich	Zürich	–
The Netherlands	BE	Groen Agro Control - Netherlands	Delfgauw	–
The Netherlands	BE	NofaLab - Pesticide Lab	Schiedam	–
The Netherlands	BE; NL	Eurofins Lab Zeeuws-Vlaanderen B.V. - Pesticiden	Graauw	–
The Netherlands	NL	Wageningen Food Safety Research (WFSR)	Wageningen	x

Appendix 1-b: Participating labs from EU candidate countries and third countries

Country	Institution	City
Australia	Symbio Laboratories - Australia, Eight Mile Plains	Eight Mile Plains, QLD
Costa Rica	Ministry of Agriculture - Costa Rica, San José	San José
India	LT Foods LTD - India, Sonipat	Sonipat
Peru	Bureau Veritas - Peru, Lima	LIMA - CALLAO
Peru	SENASA - Peru, Lima	Lima
Serbia	Inst. of Public Health of Belgrade - Pesticide Lab	Belgrade
Serbia	SP Laboratorija - Serbia, Becej	BECEJ
Serbia	A BIO TECH LAB - Serbia, Sremska Kamenica	Sremska Kamenica
Serbia	MAFWM-Directorate for NRLs, Republic of Serbia	Belgrade
United Kingdom	FERA - Pesticide Lab	York
United Kingdom	SASA - Pesticide Lab	Edinburgh
Viet Nam	SGS - Vietnam, Ho Chi Minh	Ho Chi Minh

Appendix 2 Shipment Evaluation

Compilation of shipment duration



Dispatched on Monday, 5 Feb. 2024 (with dry ice in all cases)

- Arrival on Tue. (1 day): 84 %
- Arrival on Wed. (2 days): 8 %

EU and EFTA-labs:

All packages arrived within 2 days, except one package to PL which arrived due to IT problems in the DHL-System after 4 days (Friday) at ambient temp.

Other Countries:

- Arrival after 3 days (Thursday): 3 labs (CR, PE, RS)
- Arrival after 4 days (Fridays) : 43 Labs (AU, IN and 2x RS)
- Arrivel after 7 or more days: (7 d: PE and VN; 9 d: 1x RS)

Appendix 3 Data of Homogeneity Test

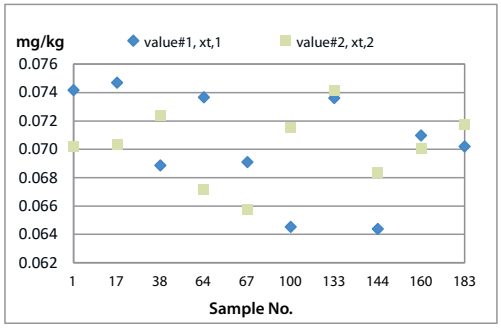
Compulsory Compounds

	Avermectin B1a		Clopyralid		Dithianon		DTCs (expr. as CS_2)		Ethephon		Folpet	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
001	0.0742	0.0702	0.196	0.167	0.201	0.195	0.0911	0.0962	0.0685	0.0679	0.248	0.0617
017	0.0747	0.0703	0.161	0.188	0.210	0.207	0.0940	0.0913	0.0671	0.0726	0.246	0.0635
038	0.0689	0.0724	0.180	0.154	0.204	0.206	0.0916	0.0905	0.0667	0.0689	0.241	0.0630
064	0.0737	0.0672	0.183	0.175	0.199	0.200	0.0944	0.0918	0.0656	0.0679	0.247	0.0637
067	0.0691	0.0658	0.174	0.191	0.198	0.211	0.0981	0.0895	0.0683	0.0701	0.251	0.0620
100	0.0645	0.0716	0.190	0.203	0.210	0.214	0.0971	0.0933	0.0713	0.0686	0.246	0.0614
133	0.0736	0.0741	0.207	0.202	0.204	0.207	0.0872	0.0899	0.0704	0.0694	0.253	0.0610
144	0.0644	0.0684	0.220	0.216	0.205	0.210	0.0928	0.0893	0.0703	0.0731	0.245	0.0606
160	0.0710	0.0700	0.204	0.185	0.217	0.216	0.0947	0.0921	0.0672	0.0720	0.255	0.0620
183	0.0702	0.0718	0.180	0.192	0.206	0.208	0.0901	0.0935	0.0691	0.0720	0.248	0.0648
mean / AV*	0.0703 / 0.0711		0.188 / 0.192		0.206 / *0.236*		0.0924 / *0.100*		0.0694 / 0.0582		0.248 / 0.225	

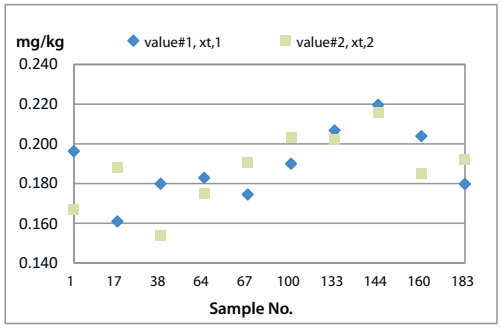
* mean / AV = Average value of the homogeneity test data [mg/kg] / Assigned value of PT [mg/kg] derived from the population of EU-/EFTA-Laboratories
Reference values for dithianon based on subpupolation and a fix value for DTCs for informative purpose were written in gray and italic.

Graphical presentation of the results:

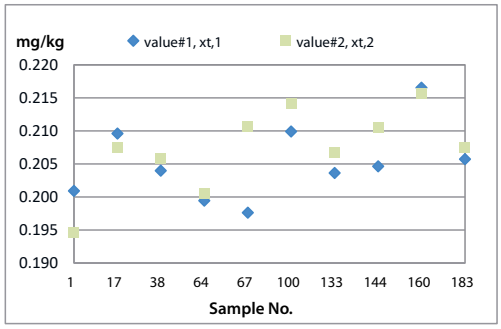
Avermectin B1a



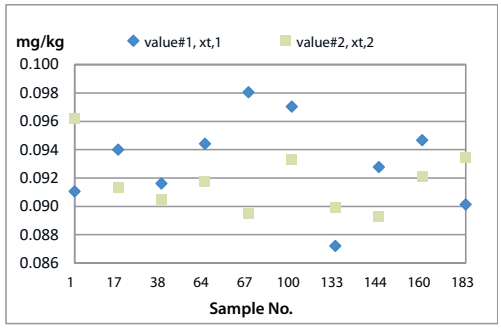
Clopyralid



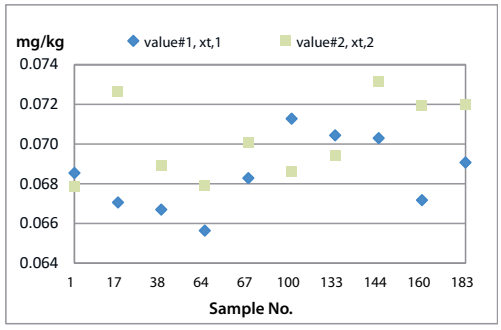
Dithianon



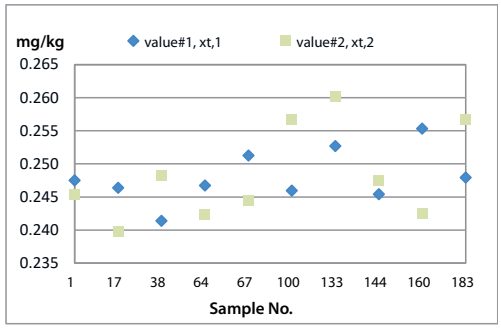
Dithiocarbamates (DTCs)



Ethephon



Folpet



Appendix 3 (cont.): Data of Homogeneity Test

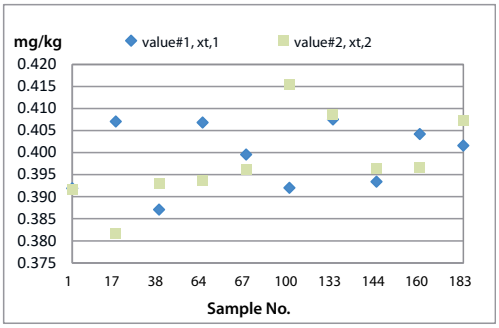
Compulsory Compounds

	Folpet (sum calc.)		MPP		N-Acetyl glufosinate		Phthalimide			Copper	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]
001	0.392	0.392	0.0742	0.0719	0.0722	0.0739	0.0716	0.0726	002	29.5	30.4
017	0.407	0.382	0.0719	0.0729	0.0721	0.0716	0.0797	0.0703	018	30.5	30.0
038	0.387	0.393	0.0714	0.0730	0.0733	0.0741	0.0723	0.0718	039	29.5	29.8
064	0.407	0.394	0.0732	0.0707	0.0716	0.0714	0.0794	0.0750	065	29.6	30.6
067	0.400	0.396	0.0737	0.0733	0.0753	0.0727	0.0736	0.0753	068	29.8	30.4
100	0.392	0.415	0.0760	0.0719	0.0749	0.0712	0.0724	0.0787	101	29.8	29.5
133	0.408	0.409	0.0754	0.0745	0.0751	0.0746	0.0768	0.0736	134	30.4	29.8
144	0.393	0.396	0.0734	0.0747	0.0724	0.0735	0.0734	0.0739	145	30.7	29.7
160	0.404	0.397	0.0734	0.0771	0.0711	0.0764	0.0739	0.0765	161	30.8	31.4
183	0.402	0.407	0.0745	0.0736	0.0722	0.0748	0.0762	0.0747	184	30.5	30.4
mean / AV*	0.399 / 0.421		0.0740 / 0.0819		0.0732 / 0.0773		0.0746 / *0.082*		mean / AV*	30.1 / 29.9	

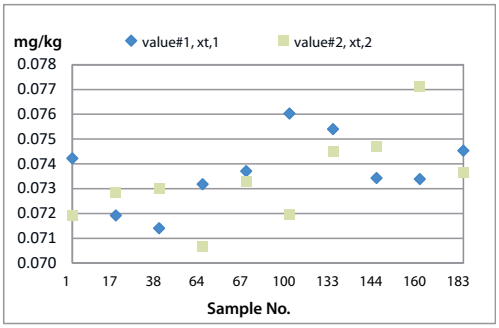
* mean / AV = Average value of the homogeneity test data [mg/kg] / Assigned value of PT [mg/kg] derived from the population of EU-/EFTA-Laboratories
Reference value for phthalimide based on subpupolation for informative purpose was written in gray and italic.

Graphical presentation of the results:

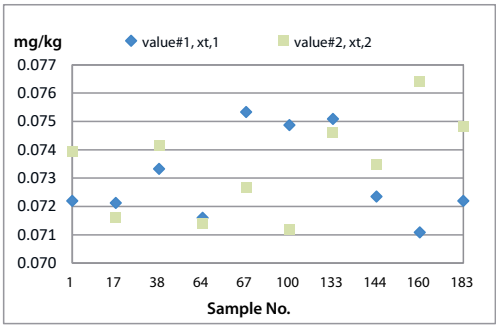
Folpet (sum, calculated)



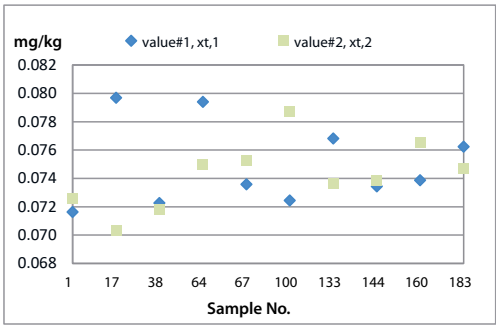
MPP



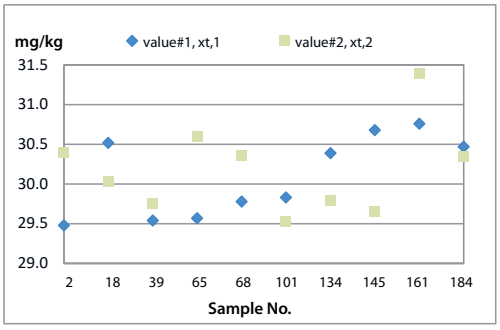
N-Acetyl glufosinate



Phthalimide



Copper



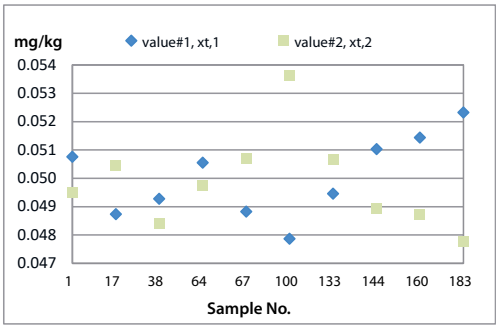
Appendix 3 (cont.): Data of Homogeneity Test

	Optional Compounds						Extra Compound	
	2,4-DNOP (free phenol)		Meptyldinocap		Meptyldinocap (sum, calculated)		Difluoroacetic acid (DFA)	
Sample No.	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]	Portion 1 [mg/kg]	Portion 2 [mg/kg]
001	0.0508	0.0508	0.0924	0.0924	0.155	0.155	0.124	0.124
017	0.0487	0.0487	0.0972	0.0972	0.157	0.157	0.123	0.123
038	0.0493	0.0493	0.0930	0.0930	0.154	0.154	0.123	0.123
064	0.0505	0.0505	0.0908	0.0908	0.153	0.153	0.124	0.124
067	0.0488	0.0488	0.0940	0.0940	0.154	0.154	0.128	0.128
100	0.0479	0.0479	0.0951	0.0951	0.154	0.154	0.134	0.134
133	0.0495	0.0495	0.1000	0.1000	0.161	0.161	0.133	0.133
144	0.0510	0.0510	0.0935	0.0935	0.156	0.156	0.129	0.129
160	0.0514	0.0514	0.0957	0.0957	0.159	0.159	0.124	0.124
183	0.0523	0.0523	0.0961	0.0961	0.160	0.160	0.129	0.129
mean / *AV**	0.0499 / *0.0647*		0.0955 / *0.0860*		0.157 / *0.150*		0.128 / *0.146*	

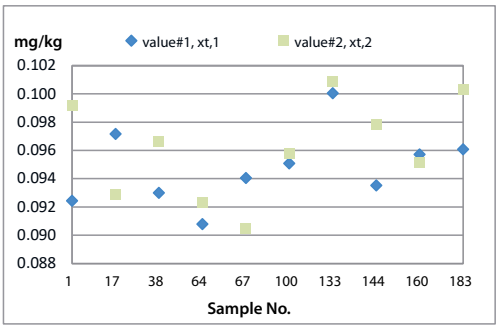
* mean / *AV* = Average value of the homogeneity test data [mg/kg] / *Assigned value* of PT [mg/kg] derived from the population of EU-/EFTA-Laboratories was calculated for informative puopose only and written in gray and italic.

Graphical presentation of the results:

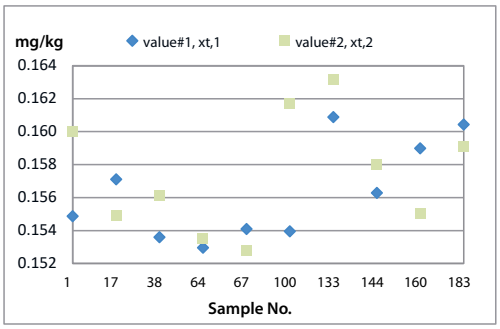
2,4-DNOP (free phenol)



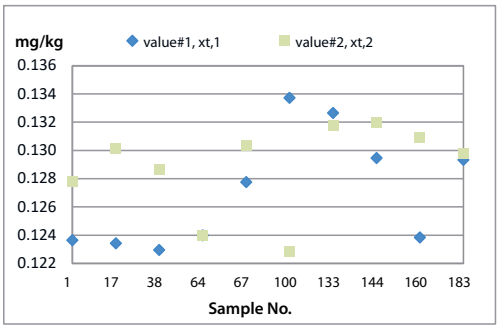
Meptyldinocap



Meptyldinocap (sum, calculated)



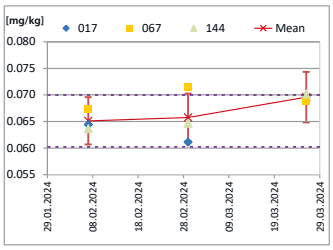
Difluoroacetic acid (DFA)



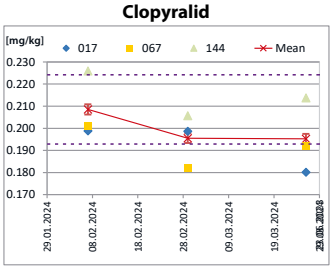
Appendix 4 Data of Stability Test

	Compulsory Compounds																	
	Avermectin B1a						Clopyralid						Dithianon					
AV [mg/kg]	0.0711						0.192						*0.236 (informative)*					
Date	07.02.2024		29.02.2024		26.03.2024		07.02.2024		29.02.2024		26.03.2024		07.02.2024		29.02.2024		26.03.2024	
Sample	[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]	
No. 017	0.0615	0.0673	0.0583	0.0639	0.0686	0.0707	0.193	0.205	0.212	0.185	0.192	0.168	0.219	0.217	0.194	0.198	0.182	0.185
No. 067	0.0698	0.0648	0.0748	0.0682	0.0741	0.0638	0.192	0.209	0.177	0.187	0.174	0.210	0.206	0.219	0.192	0.193	0.179	0.173
No. 144	0.0644	0.0629	0.0680	0.0614	0.0724	0.0680	0.227	0.225	0.203	0.208	0.228	0.199	0.221	0.217	0.198	0.199	0.183	0.182
Mean [mg/kg]	**0.0651**		**0.0658**		**0.0696**		**0.209**		**0.196**		**0.195**		**0.217**		**0.196**		**0.181**	
RSD* [%]	**3.0 %**		**8.0 %**		**0.9 %**		**7.2 %**		**6.2 %**		**8.7 %**		**1.6%**		**1.5%**		**2.3%**	
Deviation [%] (ref. 1st Anaylsis)	—		**1.0 %**		**6.9 %**		—		**-6.2 %**		**-6.4 %**		—		**-9.7 %**		**-16.6 %**	

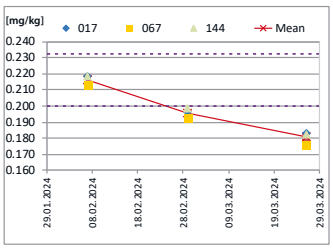
Avermectin B1a



Clopyralid



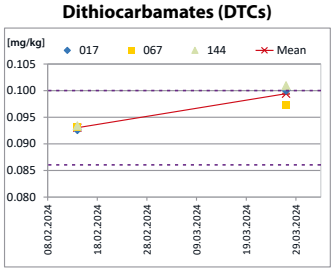
Dithianon



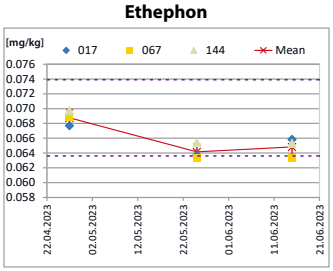
– – –: upper and lower tolerance of the stability test
calculated as mean value of the first stability test ± 0.3× standard deviation based on FPP-RSD of 25 %

	Compulsory Compounds																	
	DTC (expr. as CS_2)						Ethephon						Folpet					
AV [mg/kg]	*0.100 (informative)*						0.0582						0.225					
Date	14.02.2024		—		27.03.2024		09.02.2024		05.03.2024		22.03.2024		07.02.2024		29.02.2024		26.03.2024	
Sample‡	[mg/kg]		—		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]	
No. 017	0.0940	0.0913	—	—	0.1001	0.1000	0.0634	0.0720	0.0590	0.0685	0.0595	0.0722	0.249	0.238	0.252	0.250	0.249	0.255
No. 067‡	0.0944	0.0918	—	—	0.0984	0.0963	0.0662	0.0714	0.0606	0.0661	0.0597	0.0669	0.247	0.245	0.249	0.259	0.245	0.235
No. 144‡	0.0947	0.0921	—	—	0.1028	0.0991	0.0731	0.0664	0.0683	0.0626	0.0684	0.0622	0.249	0.241	0.257	0.257	0.246	0.248
Mean [mg/kg]	**0.0931**		—		**0.0994**		**0.0688**		**0.0642**		**0.0648**		**0.245**		**0.254**		**0.246**	
RSD* [%]	**0.4 %**		—		**1.9 %**		**1.5 %**		**1.7 %**		**2.1 %**		**0.6 %**		**1.1 %**		**2.6 %**	
Deviation [%] (ref. 1st Anaylsis)	—		—		**6.9 %**		—		**-6.7 %**		**-5.7 %**		—		**3.7 %**		**0.6 %**	
	‡ other portions (17, 64, 160) used																	

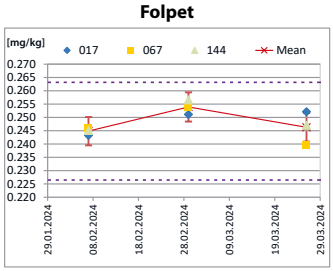
Dithiocarbamates (DTCs)



Ethephon



Folpet



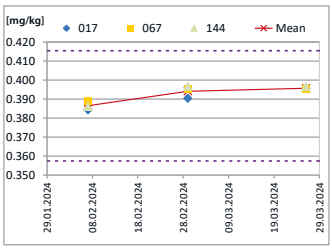
– – –: upper and lower tolerance of the stability test
calculated as mean value of the first stability test ± 0.3× standard deviation based on FPP-RSD of 25 %

* RSD = relative standard deviation

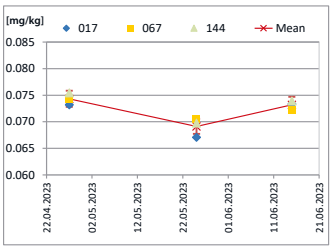
Appendix 4 (cont.): Data of Stability Test

	Compulsory Compounds																	
	Folpet (sum calc.)						MPP						N-Acetyl glufosinate					
AV [mg/kg]	0.421						0.0819						0.0773					
Date	07.02.2024		29.02.2024		26.03.2024		27.04.2023		25.05.2023		15.06.2023		09.02.2024		05.03.2024		22.03.2024	
Sample	[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]	
No. 017	0.386	0.383	0.386	0.395	0.400	0.391	0.0745	0.0719	0.0676	0.0666	0.0750	0.0716	0.0715	0.0738	0.0667	0.0682	0.0746	0.0746
No. 067	0.387	0.391	0.397	0.393	0.391	0.400	0.0751	0.0736	0.0738	0.0674	0.0728	0.0718	0.0739	0.0768	0.0703	0.0719	0.0741	0.0764
No. 144	0.392	0.380	0.397	0.397	0.399	0.394	0.0747	0.0761	0.0687	0.0708	0.0724	0.0754	0.0735	0.0739	0.0708	0.0709	0.0777	0.0740
Mean [mg/kg]	**0.386**		**0.394**		**0.396**		**0.0743**		**0.0691**		**0.0732**		**0.0739**		**0.0698**		**0.0752**	
RSD* [%]	**0.6 %**		**0.8 %**		**0.2 %**		**1.5 %**		**2.6 %**		**1.1 %**		**1.9 %**		**2.9 %**		**0.8 %**	
Deviation [%] (ref. 1st Anaylsis)	**—**		**2.0 %**		**2.4 %**		**—**		**-7.0 %**		**-1.5 %**		**—**		**-5.5 %**		**1.8 %**	

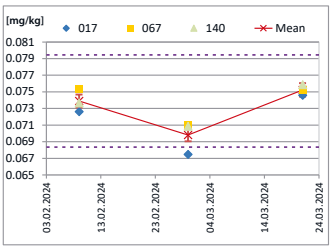
Folpet (sum, calc.)



MPP



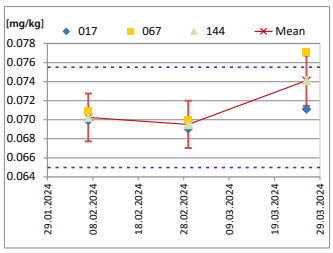
N-Acetyl gufosinate



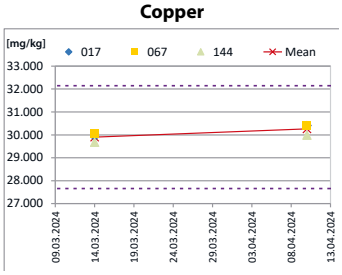
– – –: upper and lower tolerence of the stability test
calculated as mean value of the first stability test ± 0.3× standard deviation based on FPP-RSD of 25 %

	Compulsory Compounds																	
	Phthalimide							Copper										
AV [mg/kg]	*0.0820 (informative)*						AV [mg/kg]	29.9										
Date	07.02.2024		29.02.2024		26.03.2024		Date	14.03.2024		—				10.04.2024			
Sample	[mg/kg]		[mg/kg]		[mg/kg]		Sample	[mg/kg]		—				[mg/kg]			
No. 017	0.0677	0.0721	0.0663	0.0718	0.0750	0.0673	**No. 002**	29.5	30.4	—	—			30.6	30.2		
No. 067	0.0691	0.0728	0.0734	0.0666	0.0724	0.0818	**No. 065**	29.6	30.6	—	—			30.8	30.0		
No. 144	0.0708	0.0690	0.0693	0.0696	0.0758	0.0724	**No. 101**	29.8	29.5	—	—			30.7	29.3		
Mean [mg/kg]	**0.0702**		**0.0695**		**0.0741**		**Mean [mg/kg]**	**29.9**		—				**30.3**			
RSD* [%]	**0.8 %**		**0.7 %**		**4.0 %**		**RSD* [%]**	**0.7 %**		—				**0.8 %**			
Deviation [%] (ref. 1st Anaylsis)	**—**		**-1.1 %**		**5.5 %**			**—**		—				**1.2 %**			

Phthalimide



Copper



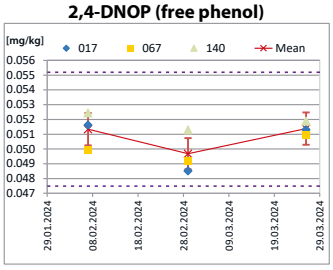
– – –: upper and lower tolerence of the stability test
calculated as mean value of the first stability test ± 0.3× standard deviation based on FPP-RSD of 25 %

* RSD = relative standard deviation

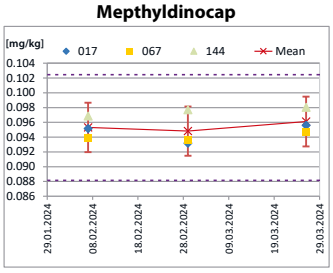
Appendix 4 (cont.): Data of Stability Test

	Optional Compounds																	
	2,4-DNOP (free phenol)						Meptyldinocap						Meptyldinocap (sum, calculated)					
AV [mg/kg]	*0.0647 (informative)*						*0.0860 (informative)*						*0.150 (informative)*					
Date	07.02.2024		29.02.2024		26.03.2024		07.02.2024		29.02.2024		26.03.2024		07.02.2024		29.02.2024		26.03.2024	
Sample	[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]		[mg/kg]	
No. 017	0.0502	0.0530	0.0486	0.0485	0.0489	0.0538	0.0940	0.0963	0.0933	0.0931	0.0906	0.1006	0.1558	0.1615	0.1530	0.1527	0.1507	0.1667
No. 067	0.0488	0.0511	0.0494	0.0491	0.0519	0.0500	0.0924	0.0954	0.0950	0.0921	0.0974	0.0920	0.1524	0.1582	0.1557	0.1525	0.1612	0.1535
No. 144	0.0522	0.0527	0.0509	0.0517	0.0523	0.0515	0.0956	0.0981	0.0970	0.0984	0.0996	0.0965	0.1597	0.1630	0.1597	0.1620	0.1639	0.1598
Mean [mg/kg]	**0.0513**		**0.0497**		**0.0514**		**0.0953**		**0.0948**		**0.0961**		**0.1584**		**0.1559**		**0.1593**	
RSD* [%]	**2.5 %**		**2.9 %**		**0.9 %**		**1.6 %**		**2.7 %**		**1.8 %**		**1.9 %**		**2.7 %**		**1.4 %**	
Deviation [%] (ref. 1st Anaylsis)	**—**		**-3.2 %**		**0.1 %**		**—**		**-0.5 %**		**0.9 %**		**—**		**-1.6 %**		**0.5 %**	

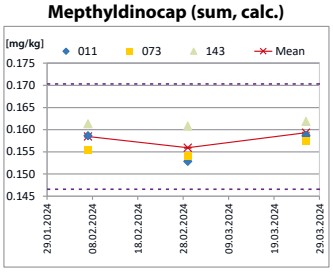
2,4-DNOP (free phenol)



Mepthyldinocap



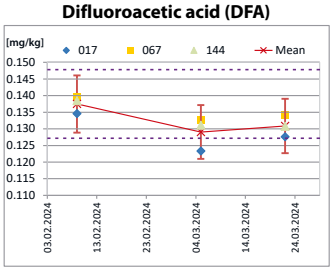
Mepthyldinocap (sum, calc.)



– – –: upper and lower tolerance of the stability test
calculated as mean value of the first stability test ± 0.3× standard deviation based on FPP-RSD of 25 %

	Extra Compound					
	DFA					
AV [mg/kg]	*0.146 (informative)*					
Date	07.02.2024		29.02.2024		26.03.2024	
Sample	[mg/kg]		[mg/kg]		[mg/kg]	
No. 017	0.139	0.131	0.130	0.117	0.128	0.128
No. 067	0.138	0.141	0.136	0.130	0.139	0.129
No. 144	0.134	0.143	0.126	0.136	0.125	0.137
Mean [mg/kg]	**0.137**		**0.129**		**0.131**	
RSD* [%]	**1.9 %**		**3.9 %**		**2.5 %**	
Deviation [%] (ref. 1st Anaylsis)	**—**		**-6.1 %**		**-4.8 %**	

Difluoroacetic acid (DFA)

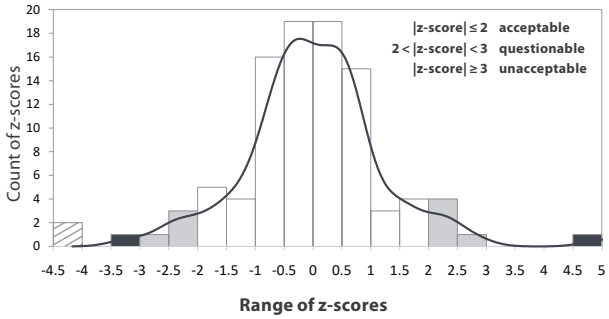


* RSD = relative standard deviation

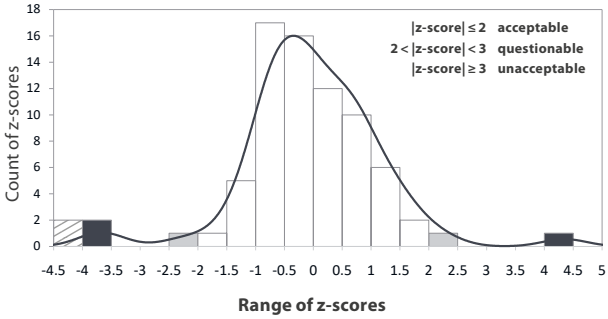
Appendix 5 Histograms and Kernel Density Estimates of z-score* Distributions
(Results from EU and EFTA Laboratories only)

Compulsory Compounds

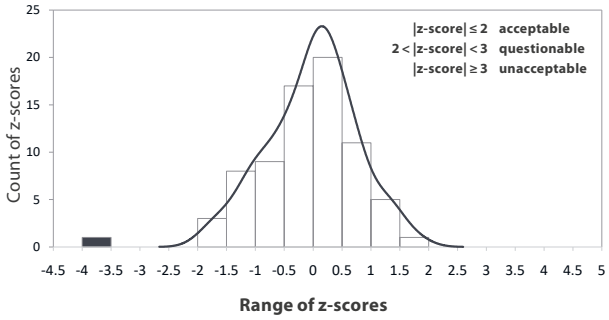
Avermectin B1a
(AV derived from entire population excl. one outlier)



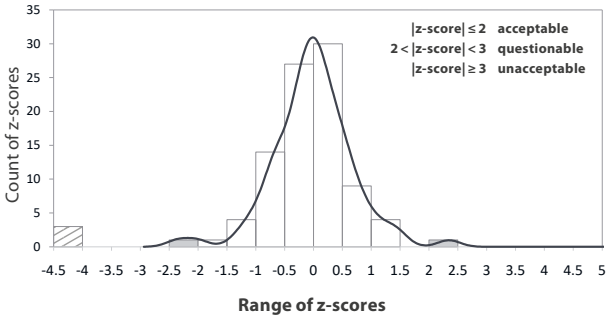
Clopyralid
(AV derived from entire population excl. one outlier)



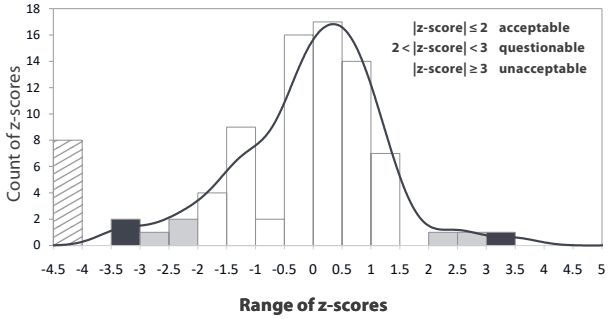
Copper
(AV derived from entire population excl. one outlier, FFP-RSD = 10 %)



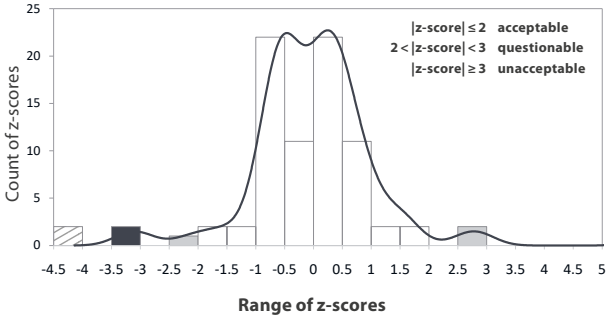
Ethephon
(AV derived from entire population excl. two outliers)



Folpet
(AV derived from entire population excl. three outliers)



Folpet (sum)
(AV derived from entire population excl. three outliers)



***** Cut-off at z-score = 5; ▨: false negative results

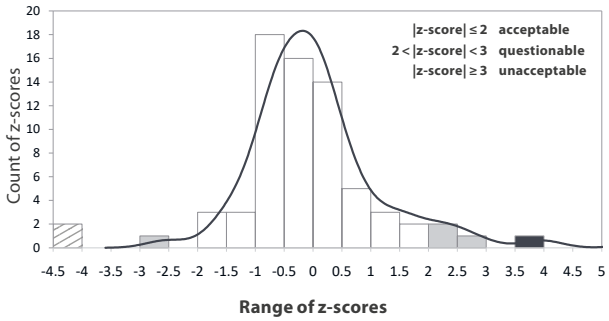
Appendix 5 (cont.) Histograms and Kernel Density Estimates of z-score* Distributions

(Results from EU and EFTA Laboratories only)

Compulsory Compounds (cont.)

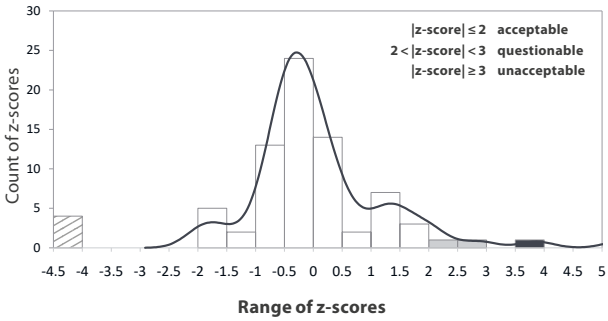
MPP

(AV derived from entire population excl. two outliers)



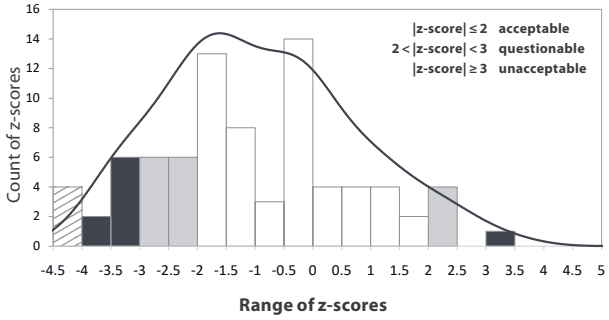
N-Acetyl glufosinate

(AV derived from entire population excl. one outlier)



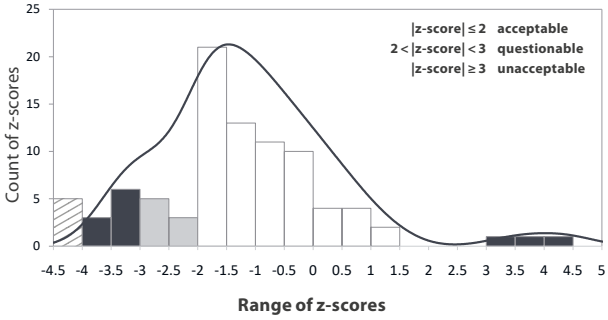
Dithianon

(AV based on subpopulation, informational only)



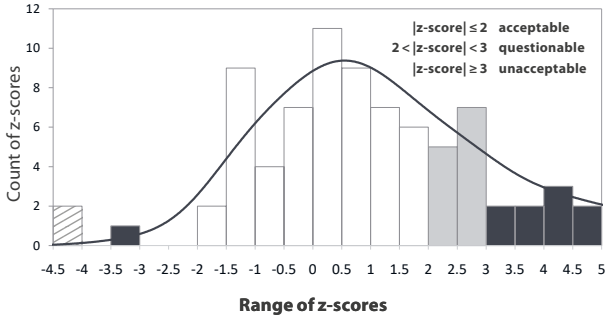
Dithiocarbamates

(Fix reference value, informational only)



Phthalimid

(AV based on subpopulation excl. three outliers, informational only)



***** Cut-off at z-score = 5; ▨: false negative results

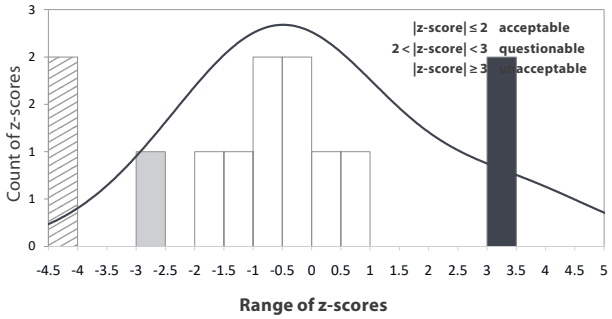
Appendix 5 (cont.) Histograms and Kernel Density Estimates of z-score* Distributions

(Results from EU and EFTA Laboratories only)

Optional Compounds

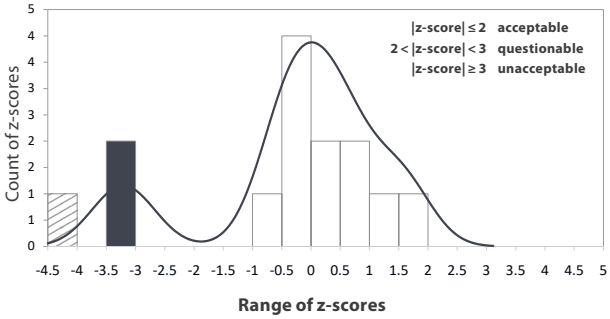
2,4-DNOP (free phenol)

(AV derived from entire population excl. one outlier, informational only)



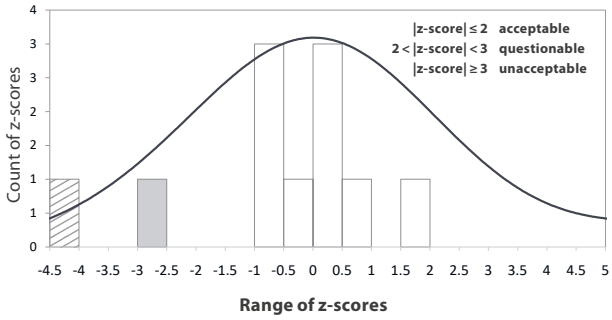
Meptyldinocap

(AV derived from entire population excl.five outliers, informational only)



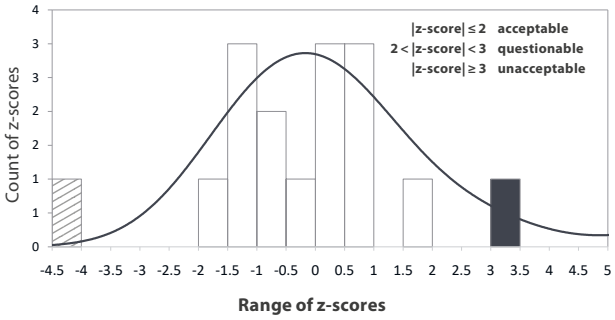
Meptyldinocap (sum, calc.)

(AV derived from entire population excl. three outliers, informational only)



Meptyldinocap (sum, follow. hydr.)

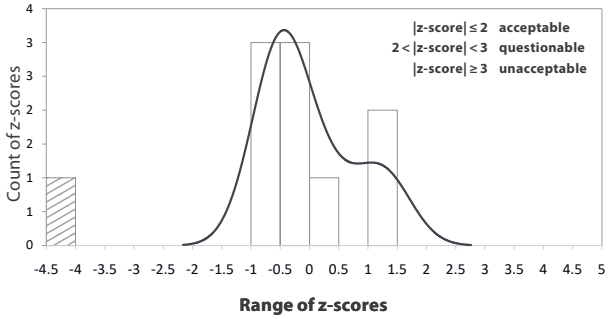
(AV derived from entire population excl. three outliers, informational only)



Extra Compounds

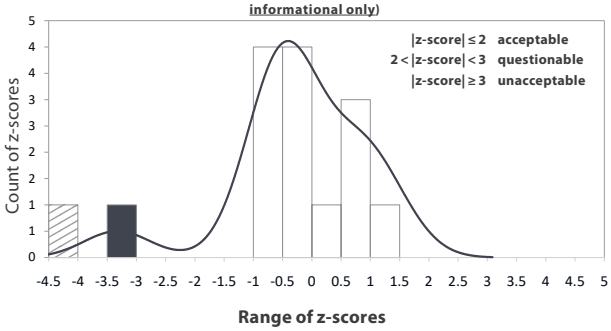
Difluoroacetic acid (DFA)

(AV derived from entire population, informational only)



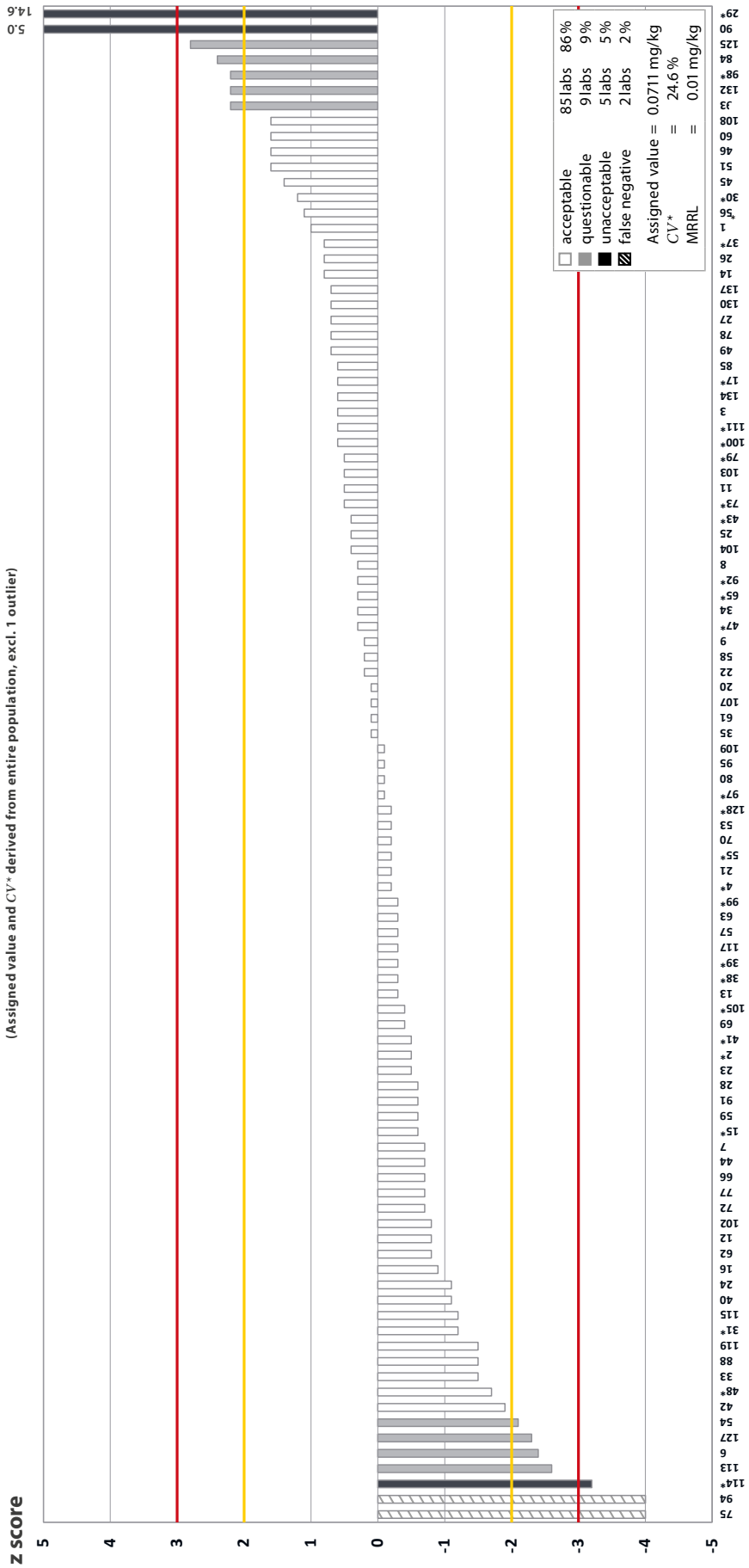
Cyhalothrin (sum)

(AV based results generated not using chiral columen and excl. one outlier, informational only)

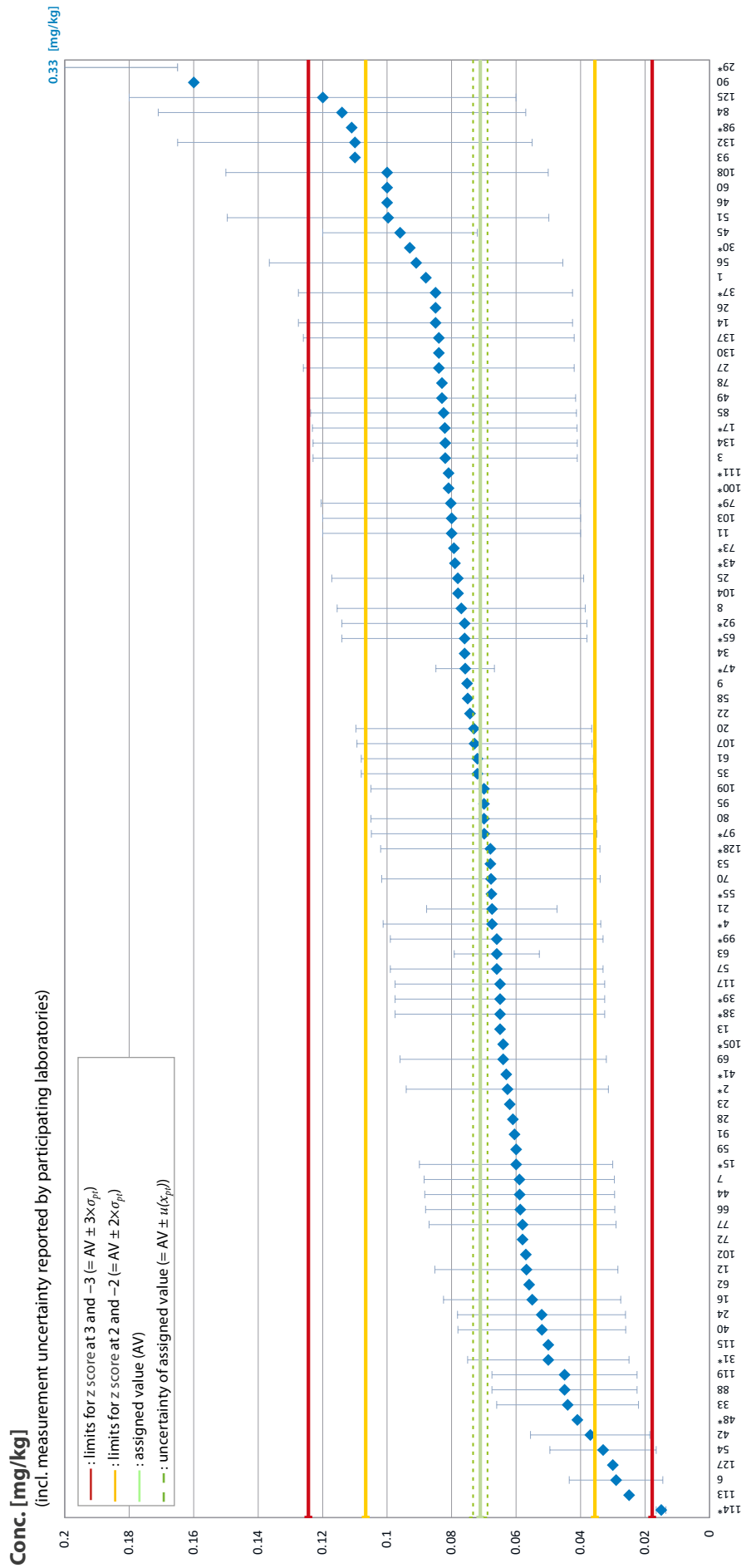


***** Cut-off at z-score = 5; ▨: false negative results

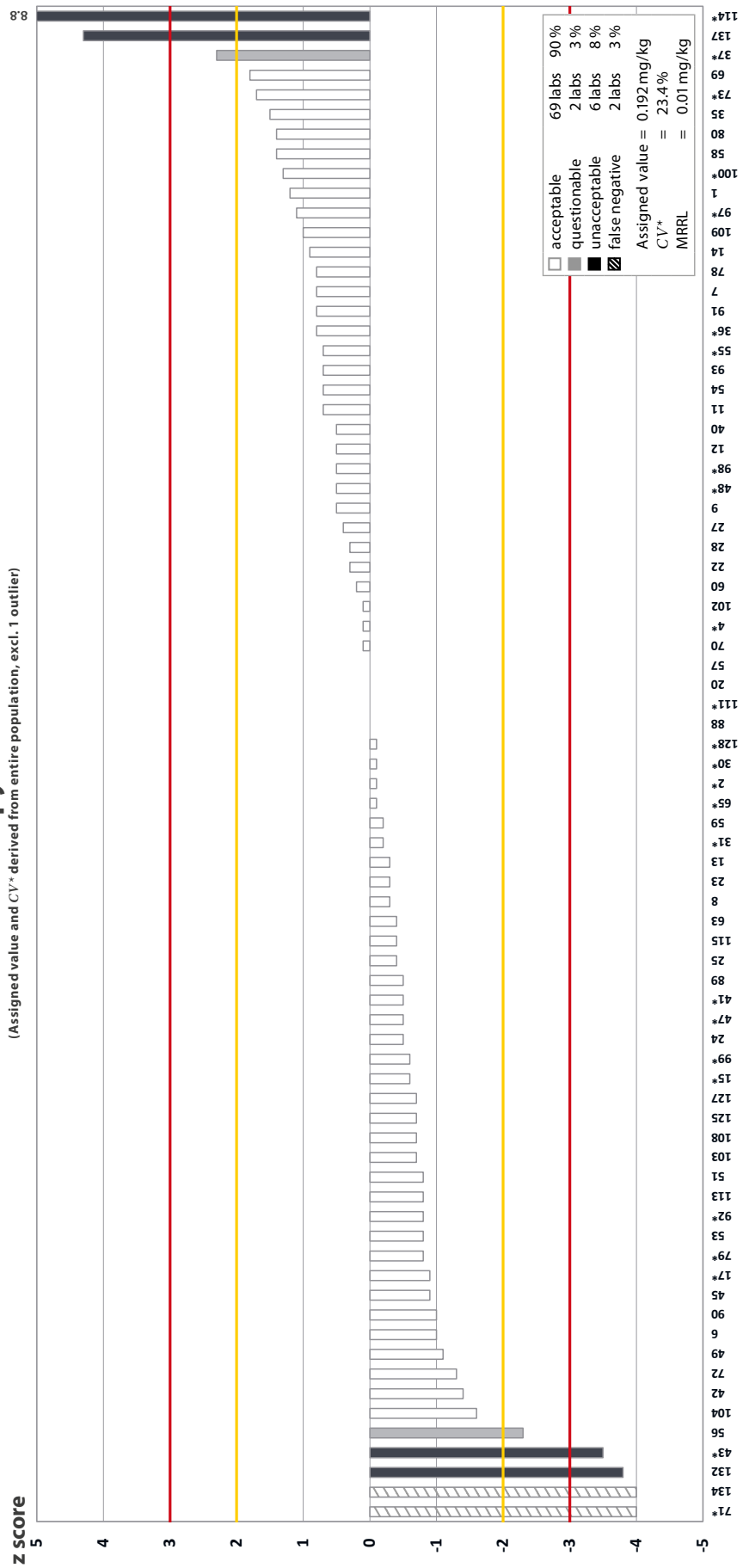
Appendix 6 Graphic Presentation of z scores : Compulsory Compounds(Results from EU and EFTA Laboratories only, * = NRL)



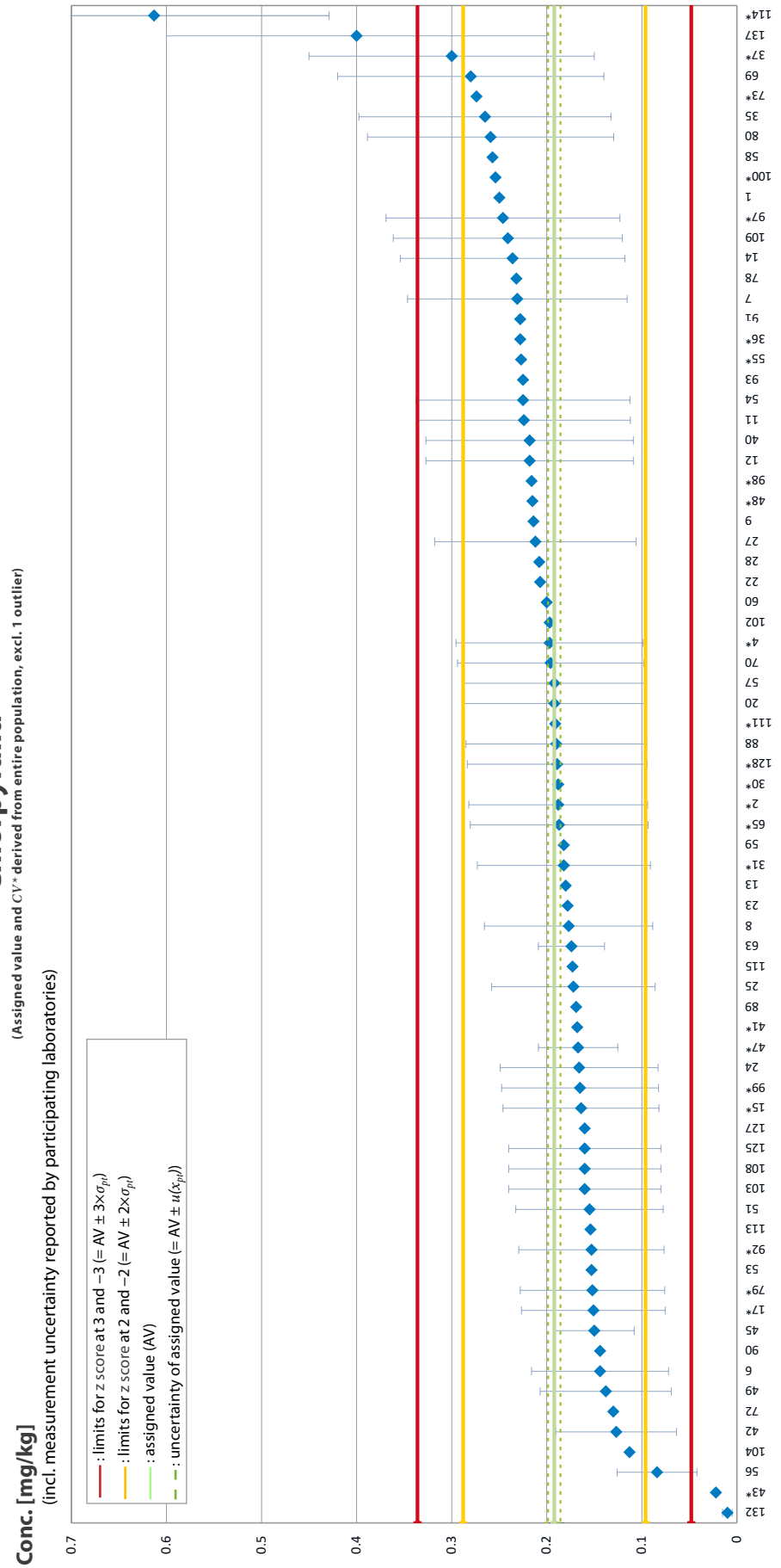
Appendix 6 Graphic Presentation of z scores : Compulsory Compounds(Results from EU and EFTA Laboratories only, * = NRL)



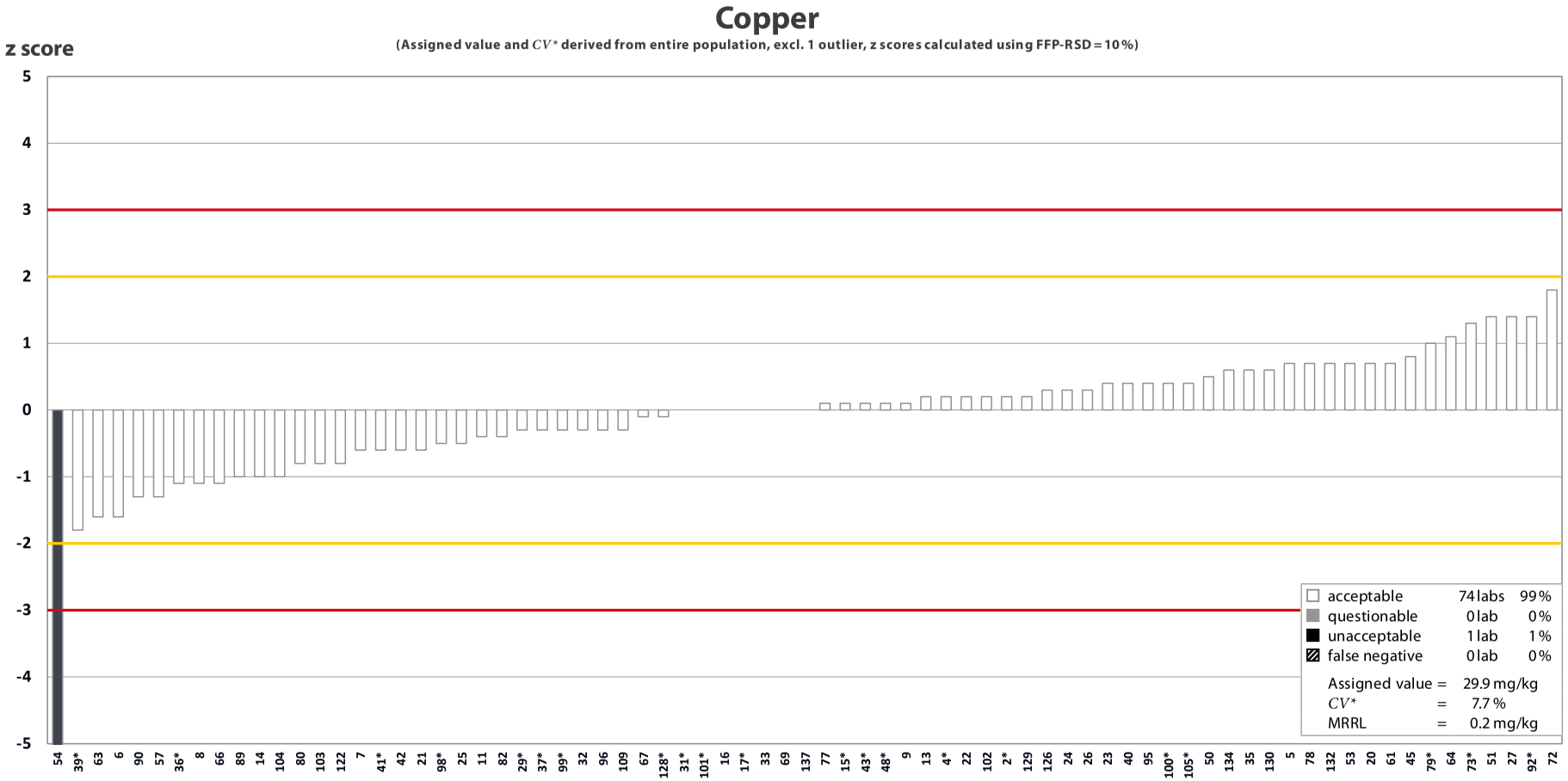
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



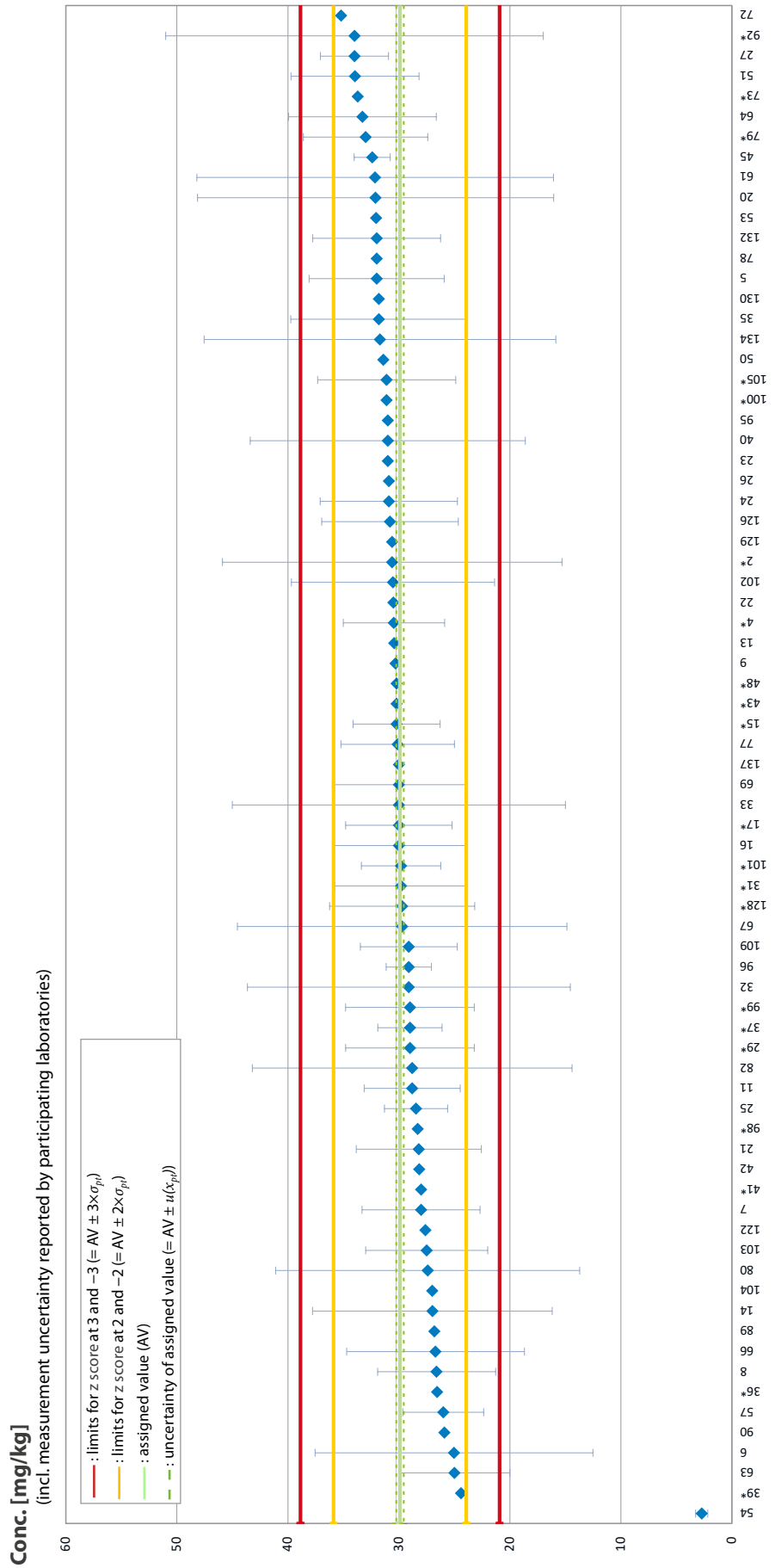
Appendix 6 (cont.) Graphic Presentation of z scores: Compulsory Compounds (Results from EU and EFTA Laboratories only, * = NRL)



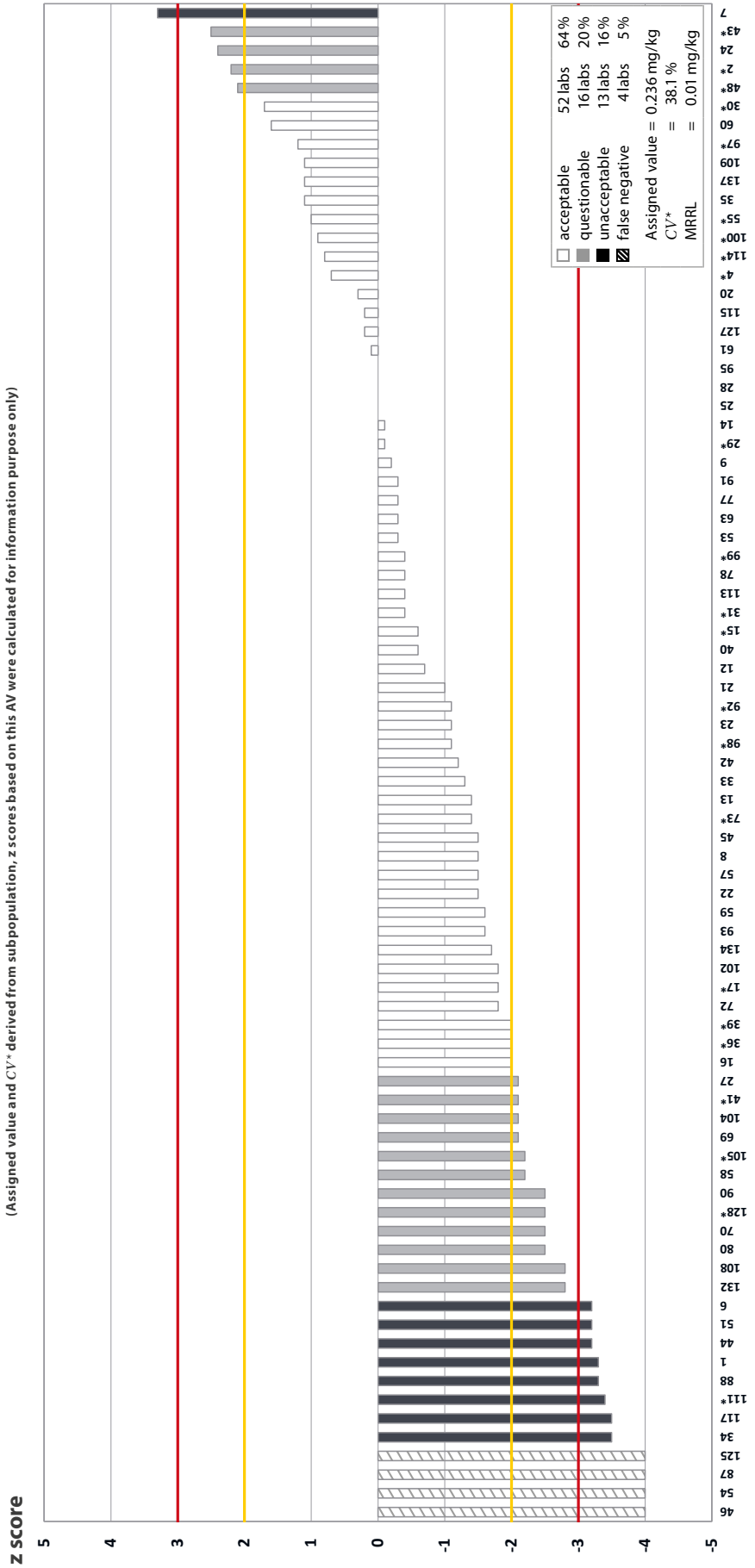
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



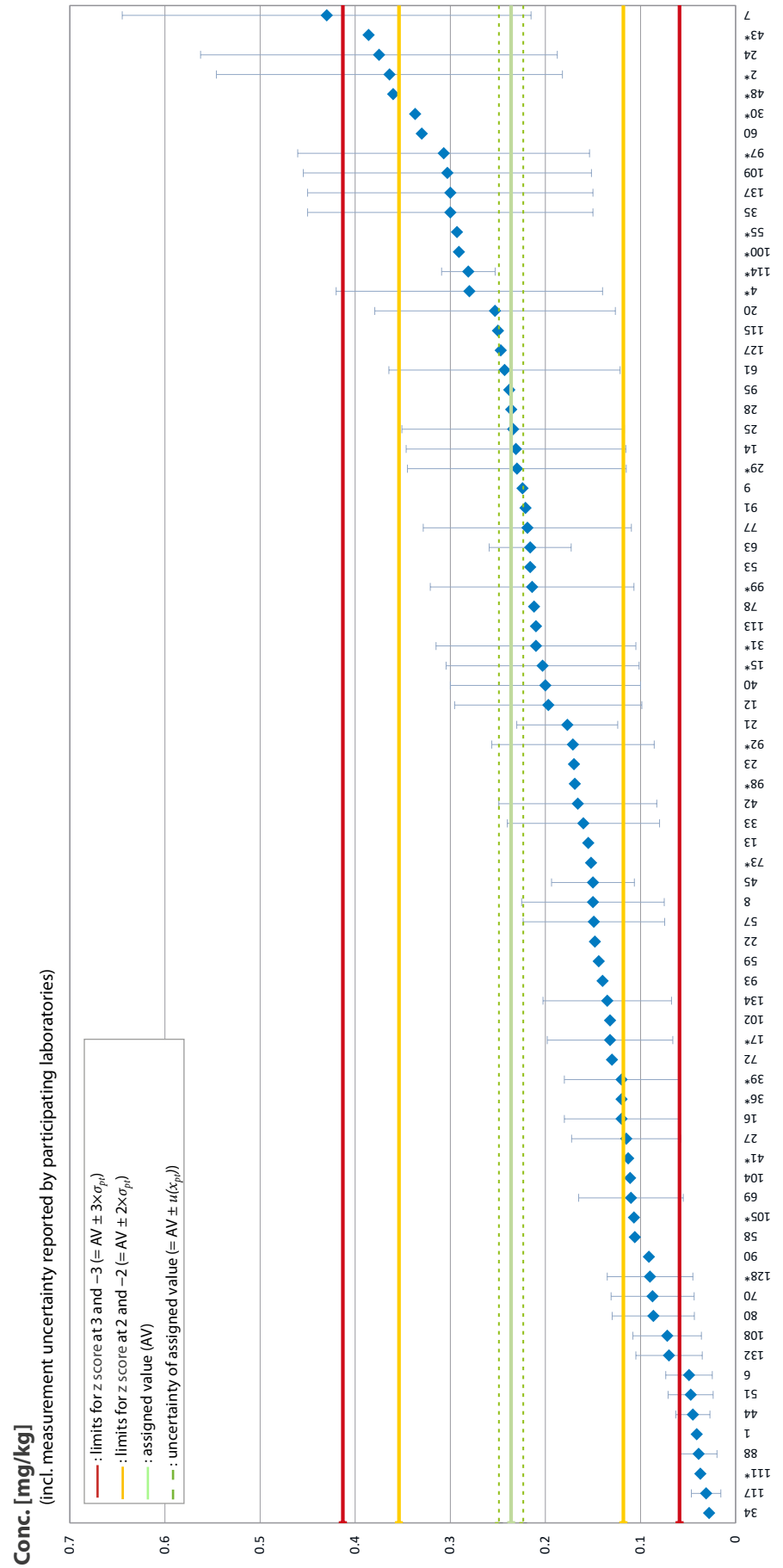
Appendix 6 (cont.) Graphic Presentation of z scores: Compulsory Compounds (Results from EU and EFTA Laboratories only, * = NRL)



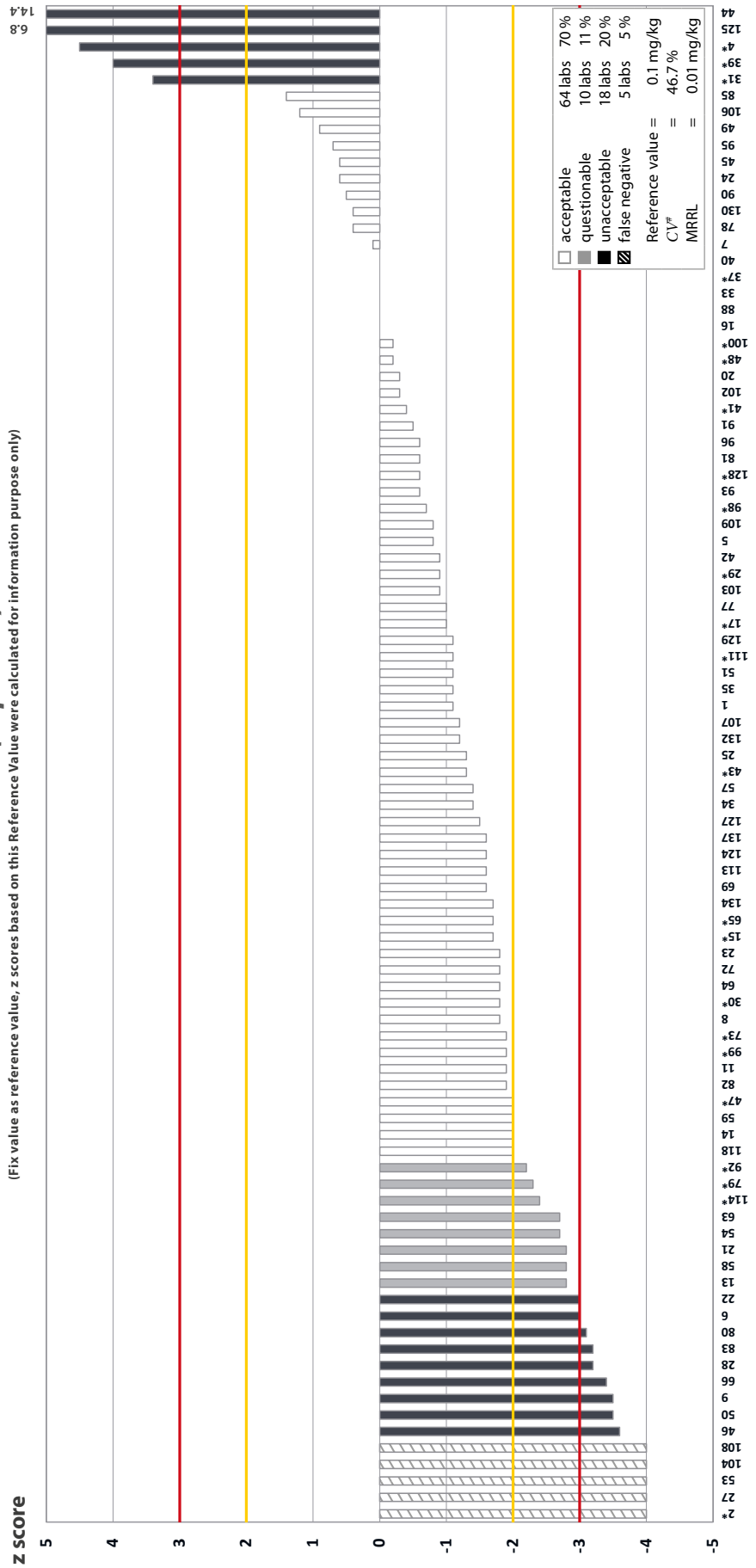
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



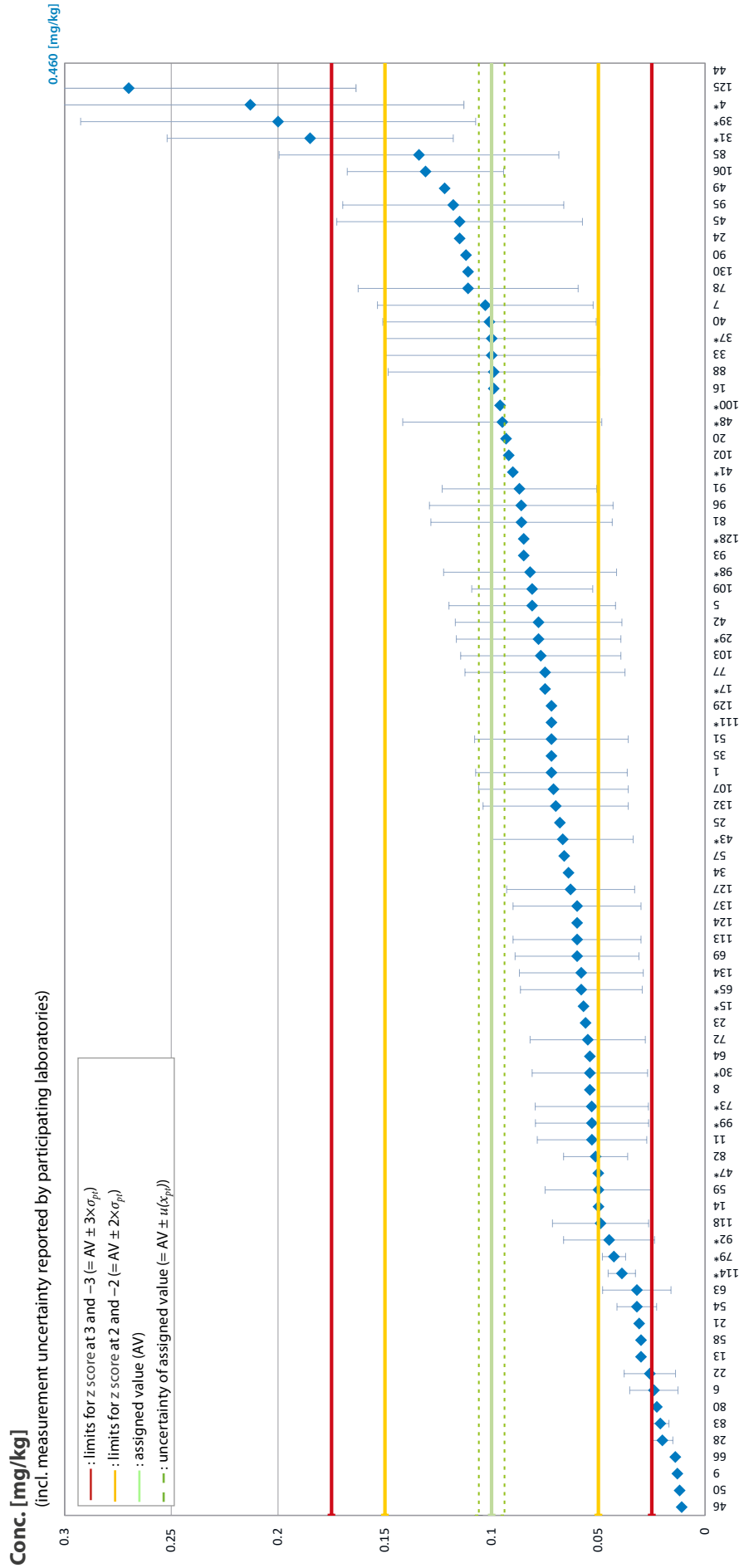
Appendix 6 (cont.) Graphic Presentation of z scores: Compulsory Compounds (Results from EU and EFTA Laboratories only, * = NRL)



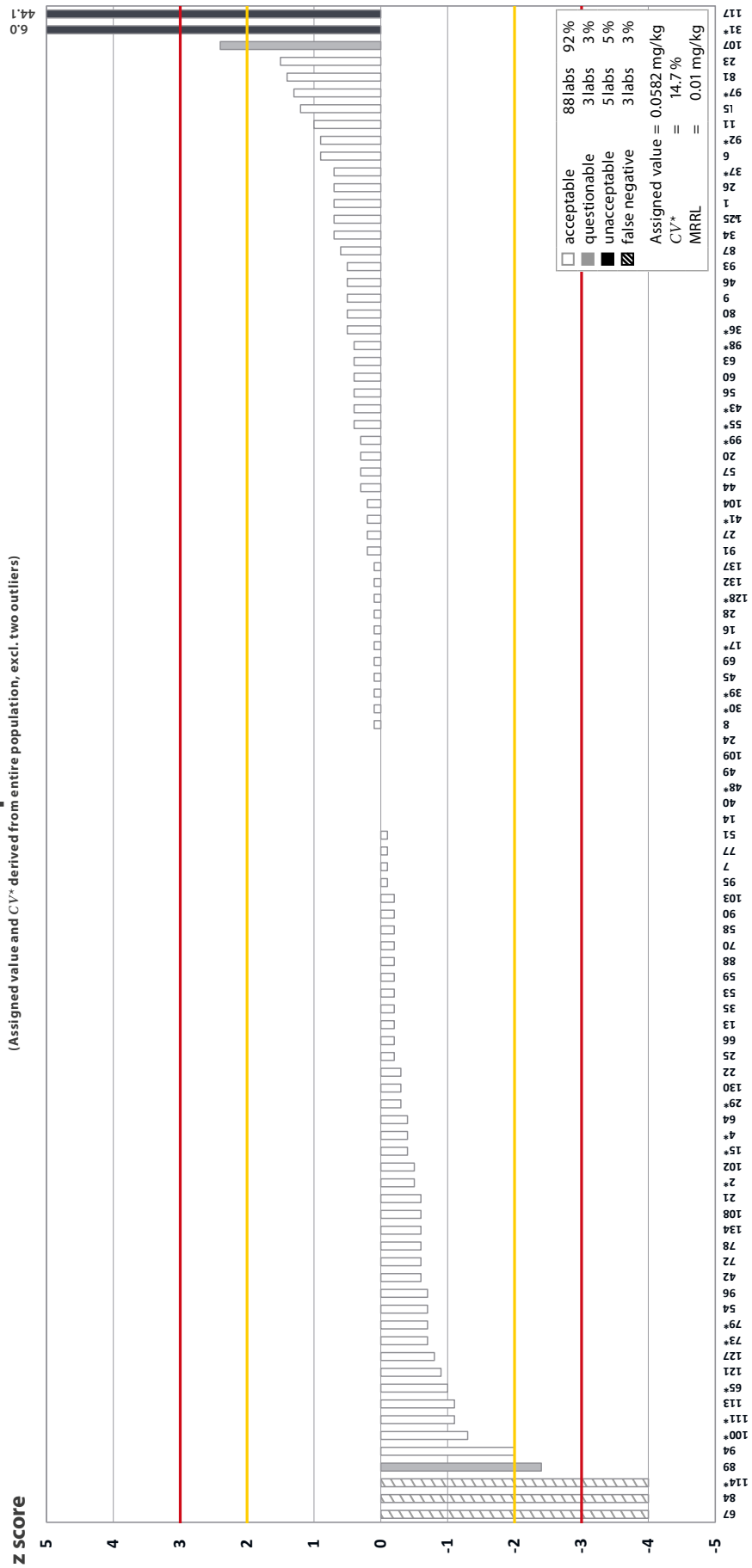
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



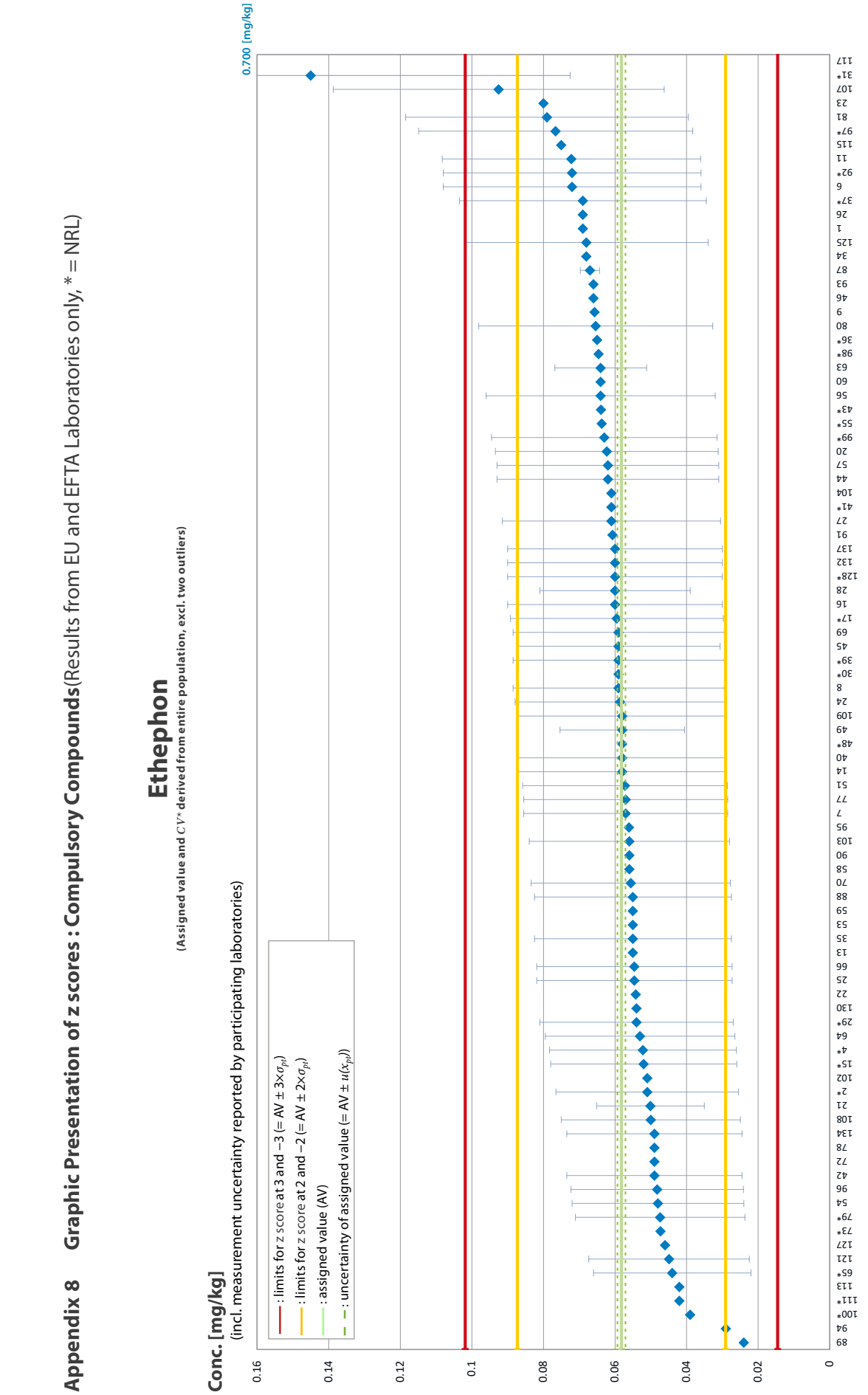
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



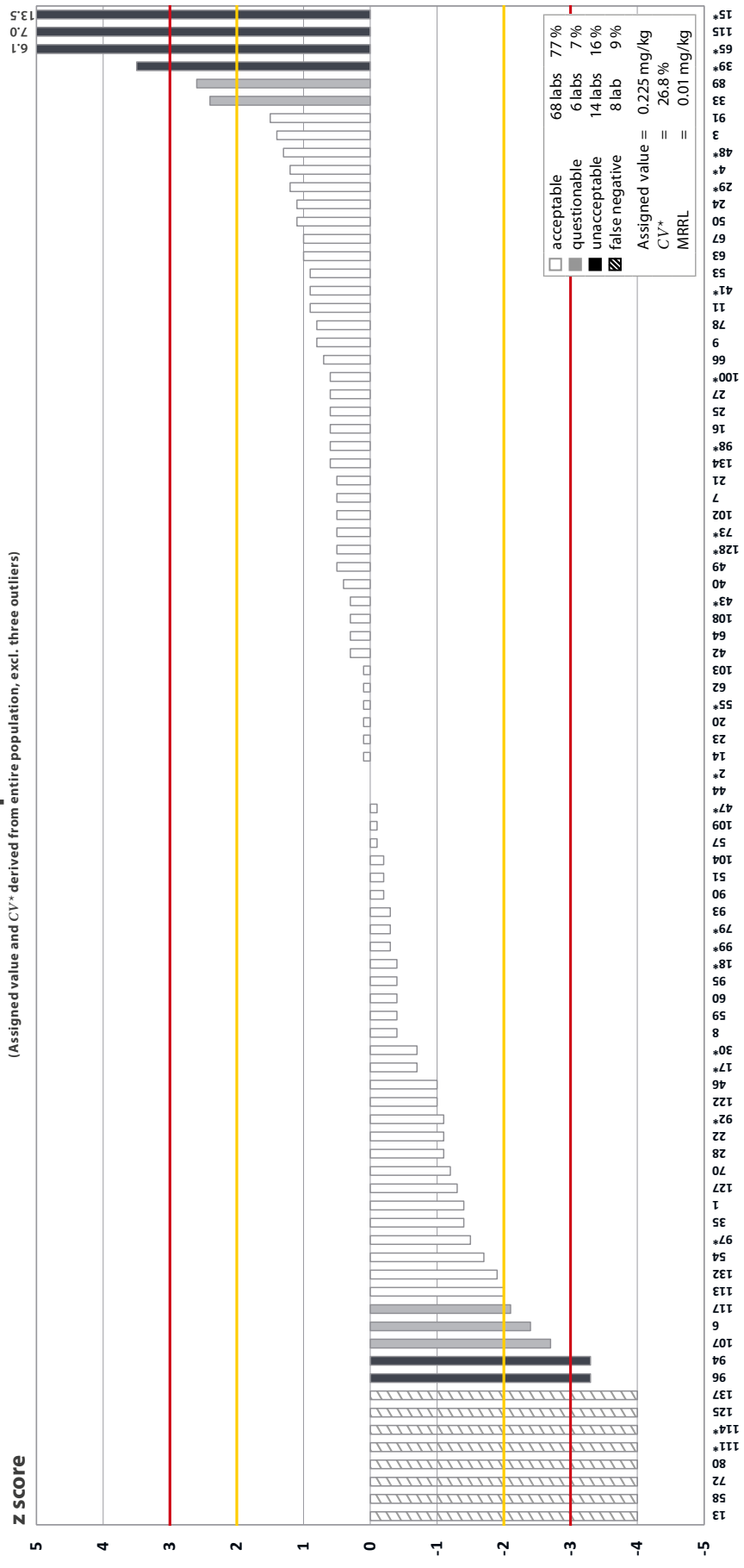
Appendix 7 Graphic Presentation of z scores : Compulsory Compounds(Results from EU and EFTA Laboratories only, * = NRL)



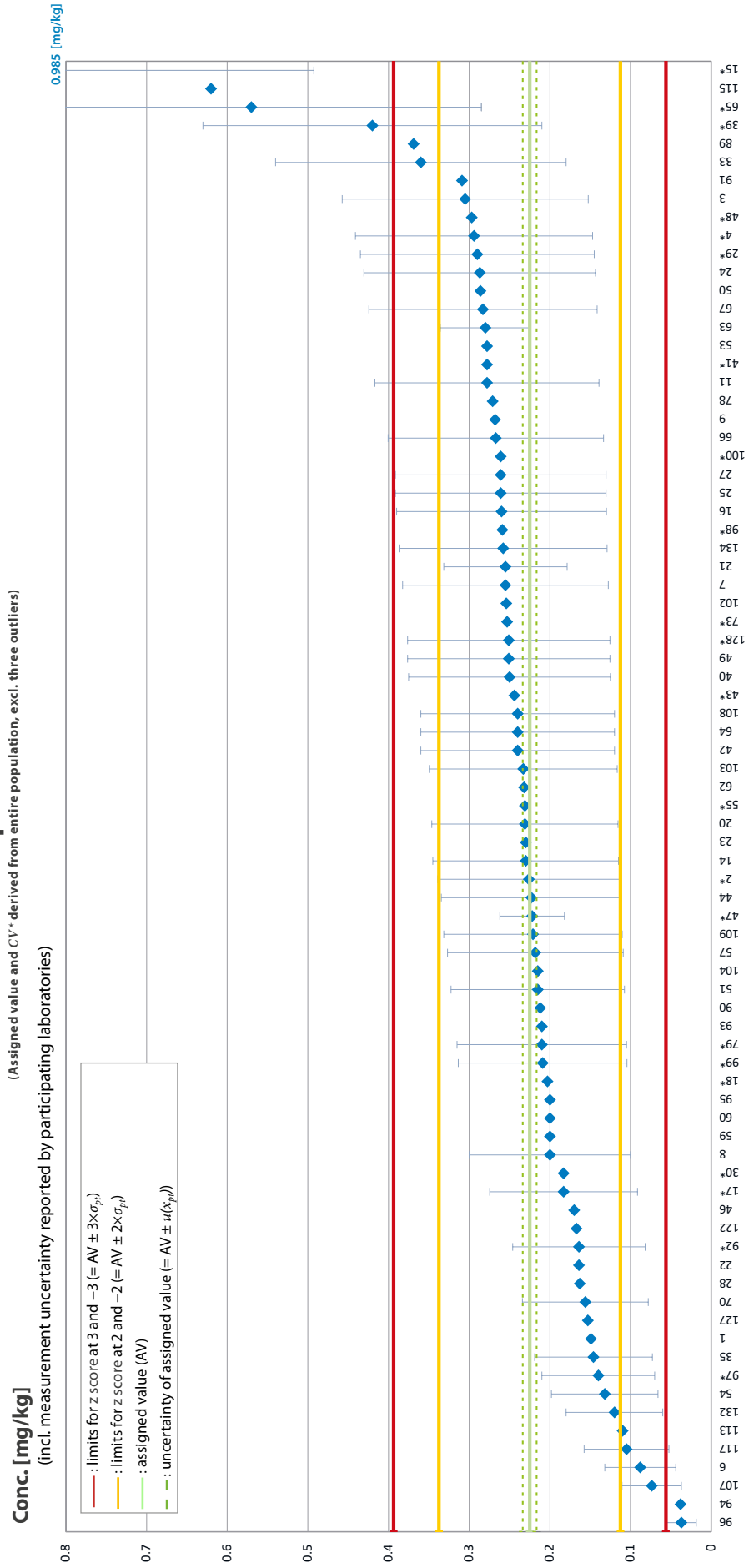
Appendix 8 Graphic Presentation of z scores : Compulsory Compounds(Results from EU and EFTA Laboratories only, * = NRL)

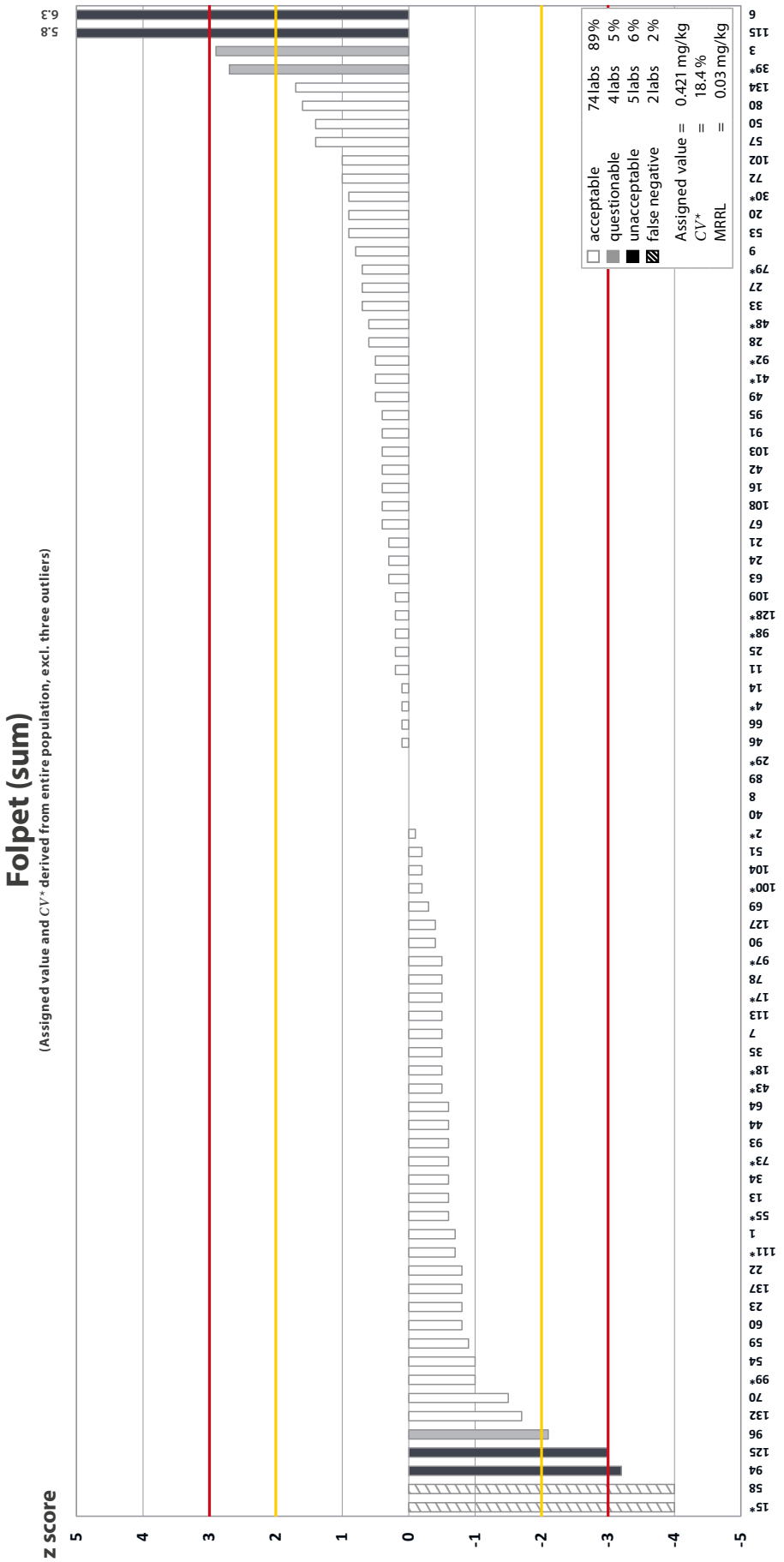


Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)

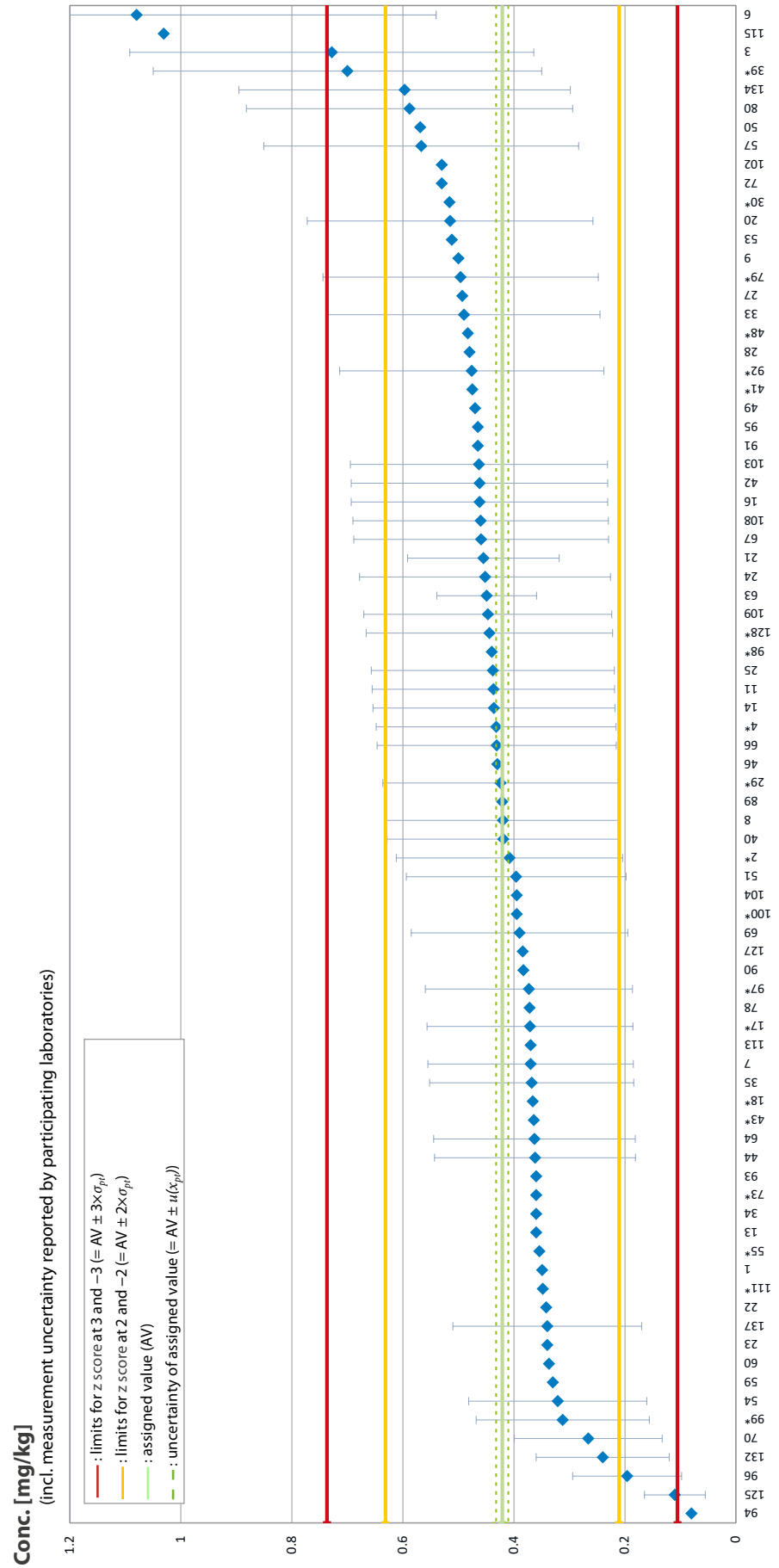


Appendix 6 (cont.) Graphic Presentation of z scores: Compulsory Compounds (Results from EU and EFTA Laboratories only, * = NRL)

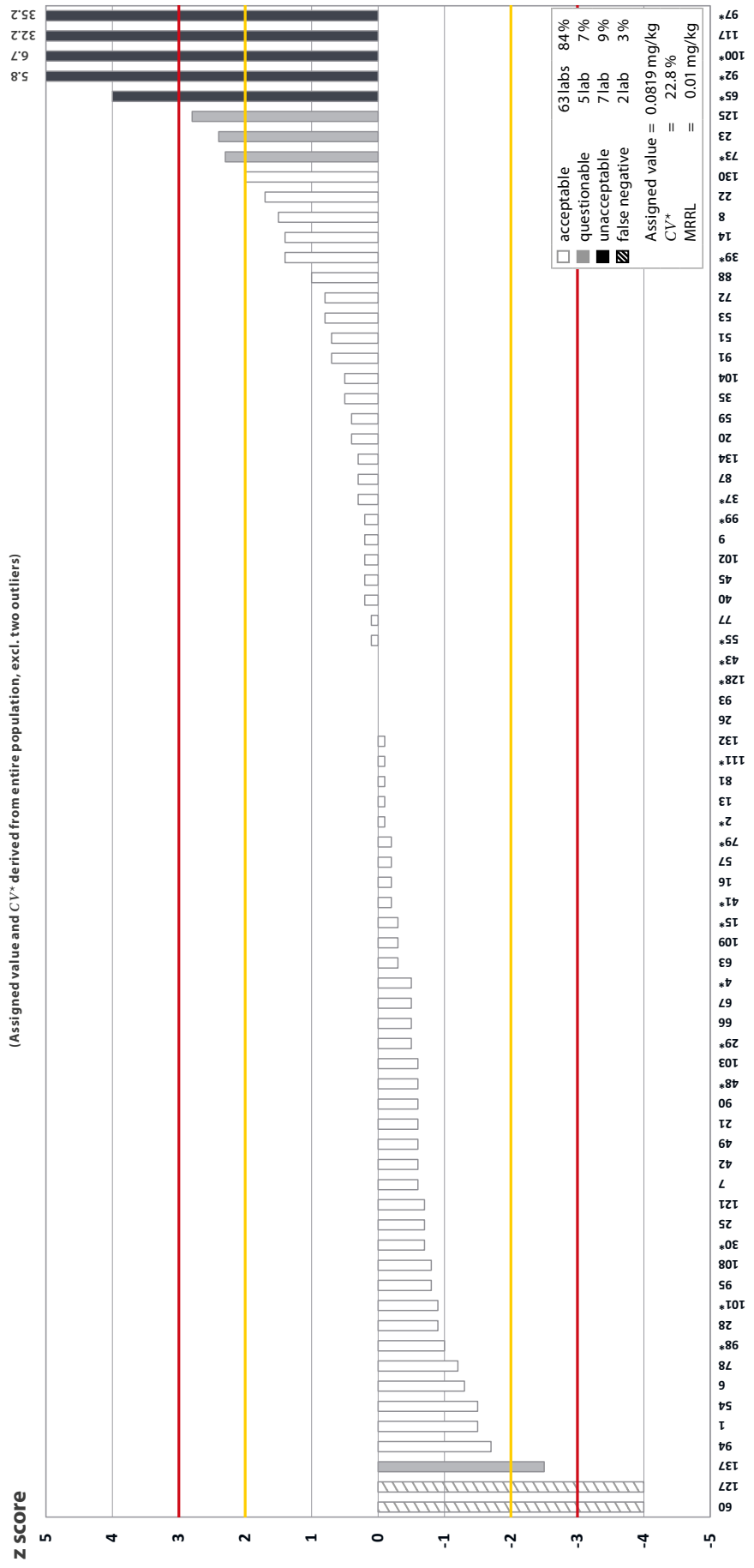



Folpet (sum)
(Assigned value and CV* derived from entire population, excl. three outliers)
z score
5
4
3
2
1
0
-1
-2
-3
-4
-5
acceptable 74 labs 89 %
questionable 4 labs 5 %
unacceptable 5 labs 6 %
false negative 2 labs 2 %
Assigned value = 0.421 mg/kg
CV* = 18.4 %
MRRL = 0.03 mg/kg

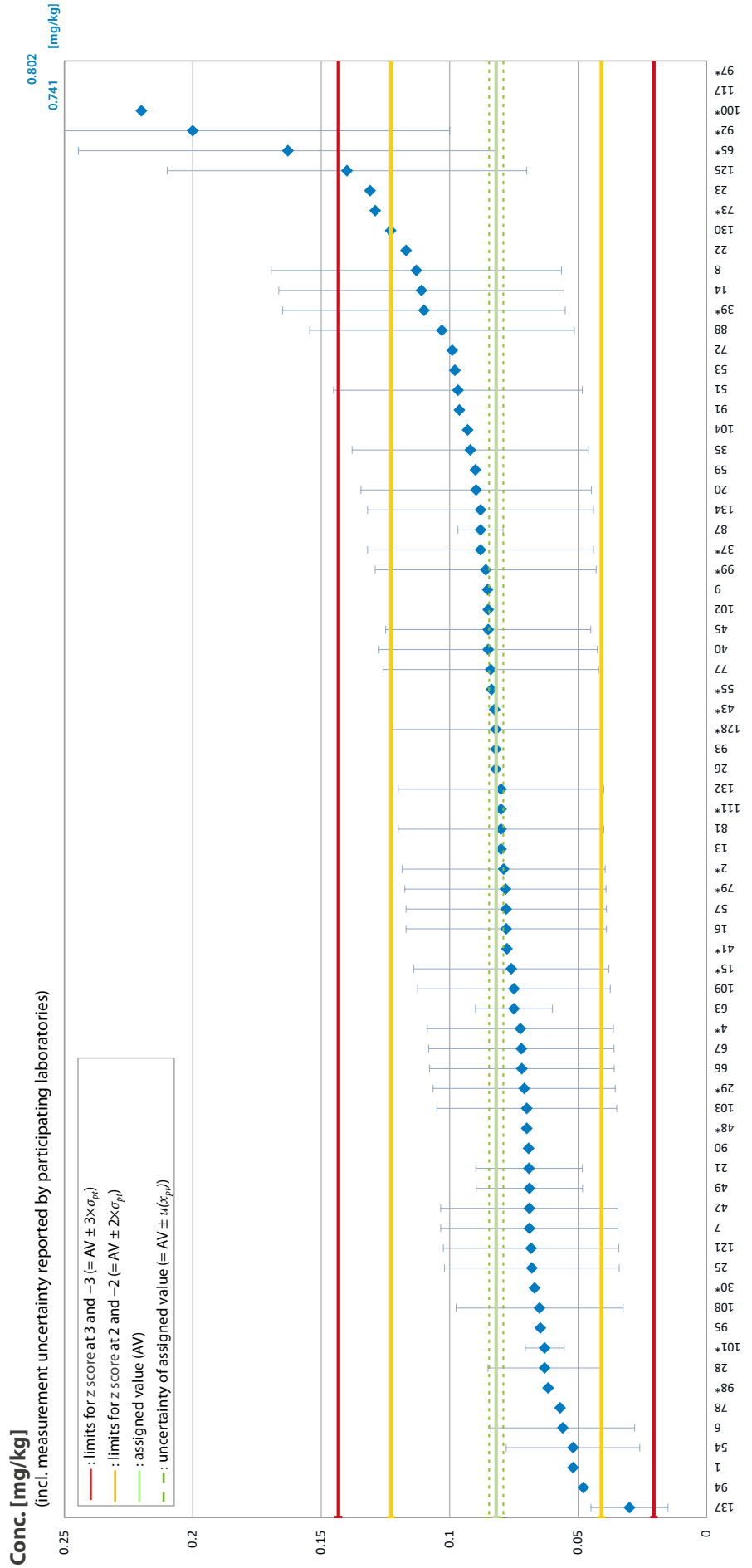
Appendix 6 (cont.) Graphic Presentation of z scores: Compulsory Compounds (Results from EU and EFTA Laboratories only, * = NRL)



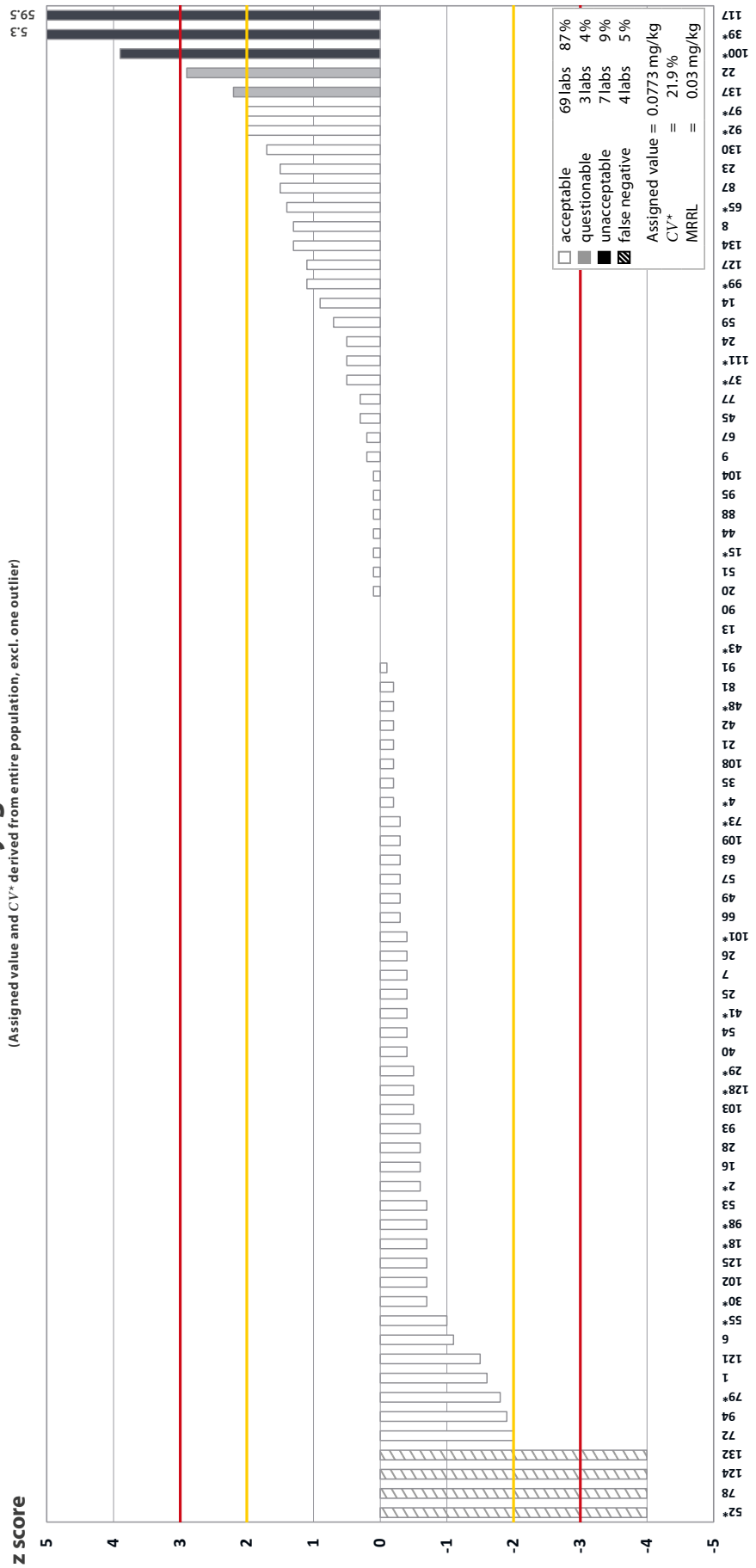
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



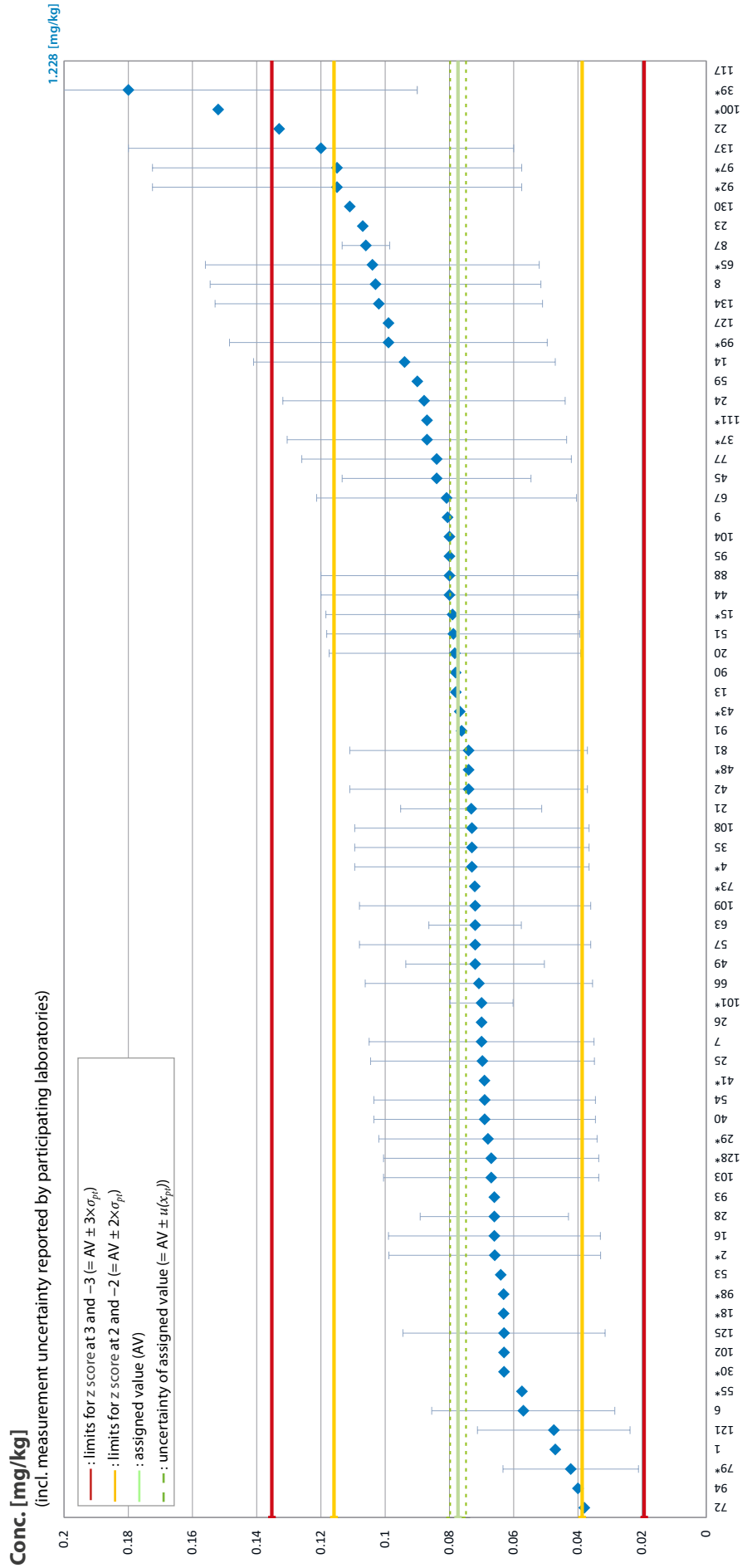
Appendix 6 (cont.) Graphic Presentation of z scores: Compulsory Compounds (Results from EU and EFTA Laboratories only, * = NRL)



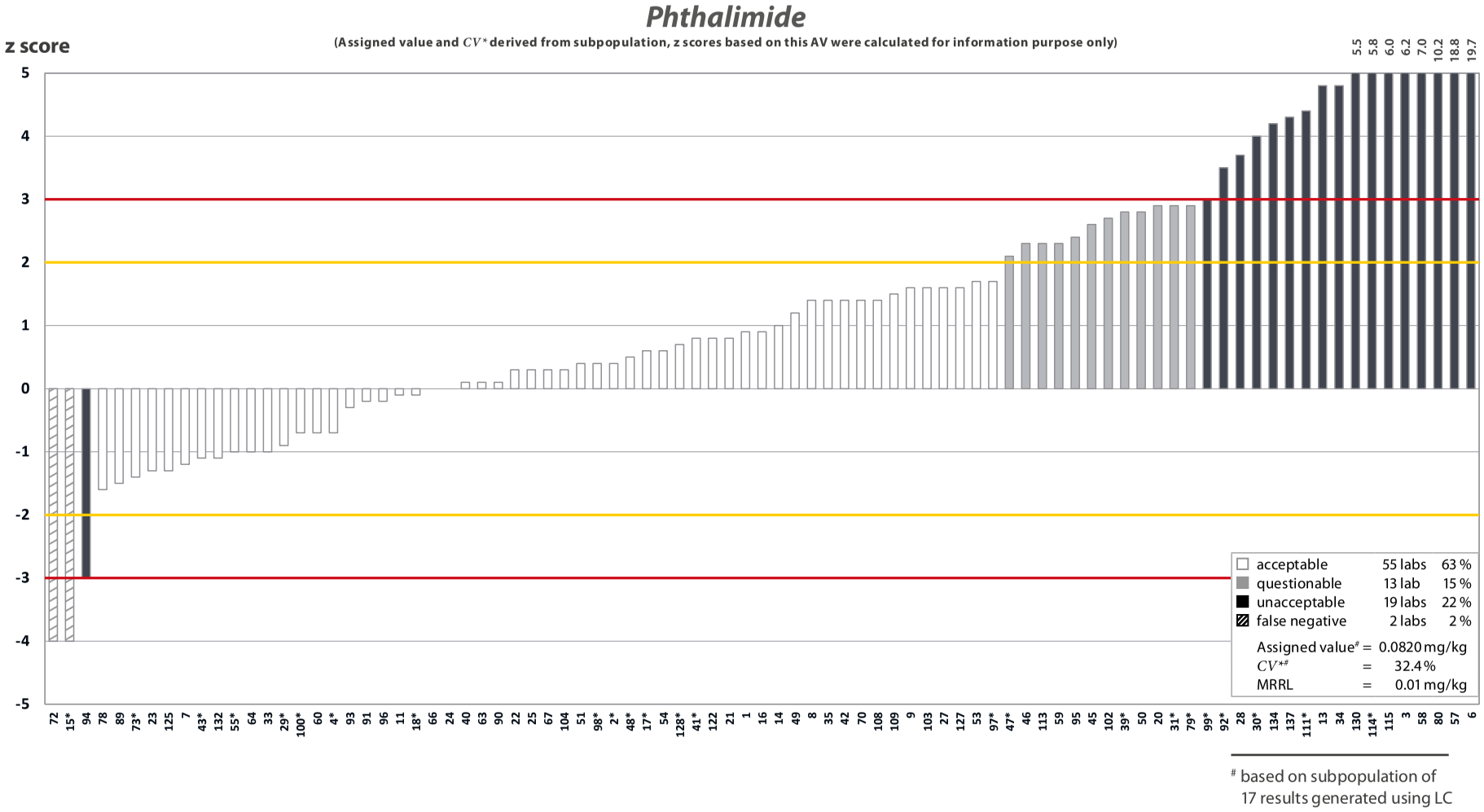
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



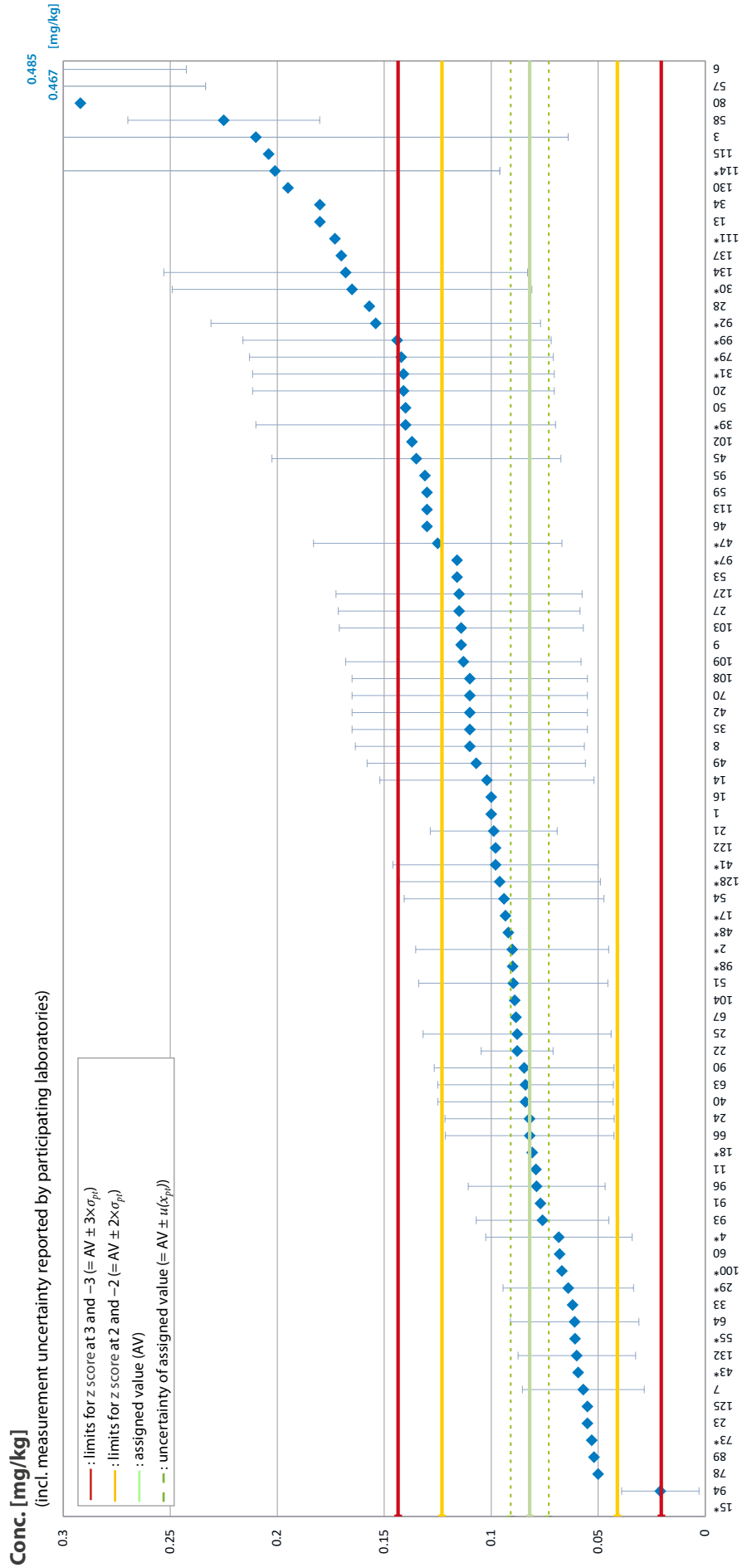
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



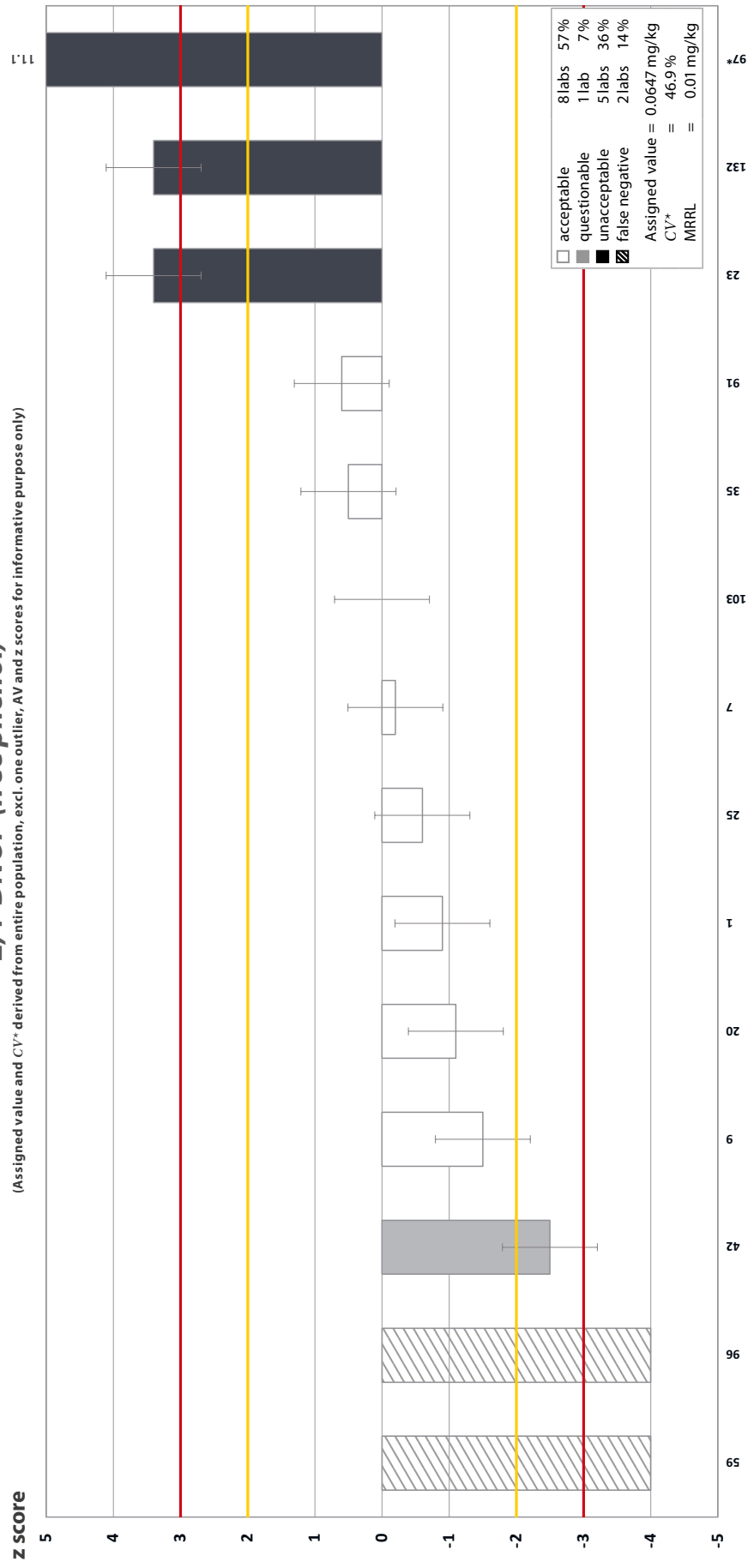
Appendix 6 (cont.) **Graphic Presentation of z scores: Compulsory Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



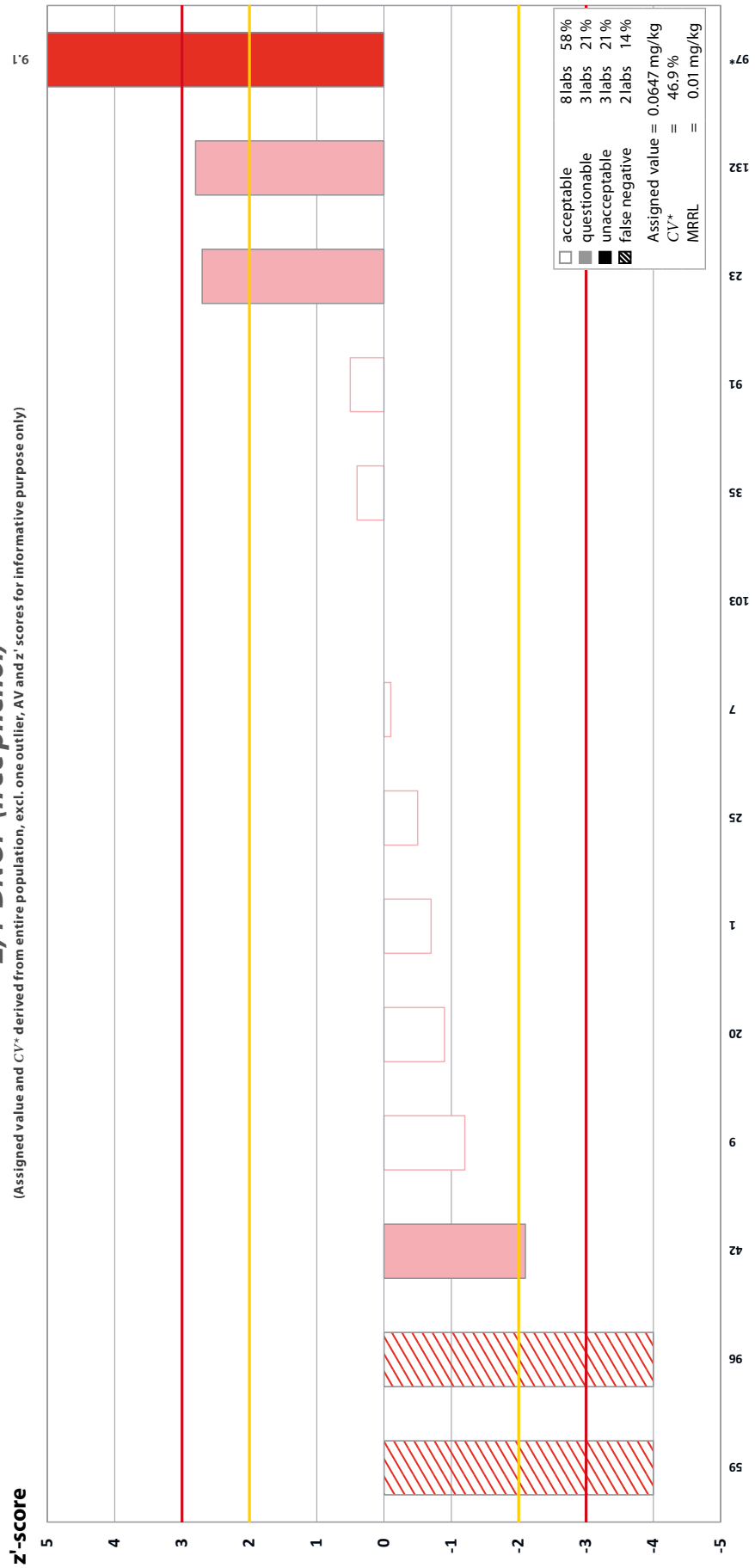
Appendix 6 (cont.) Graphic Presentation of z scores: Compulsory Compounds (results from EU and EFTA Laboratories only, * = NRL)



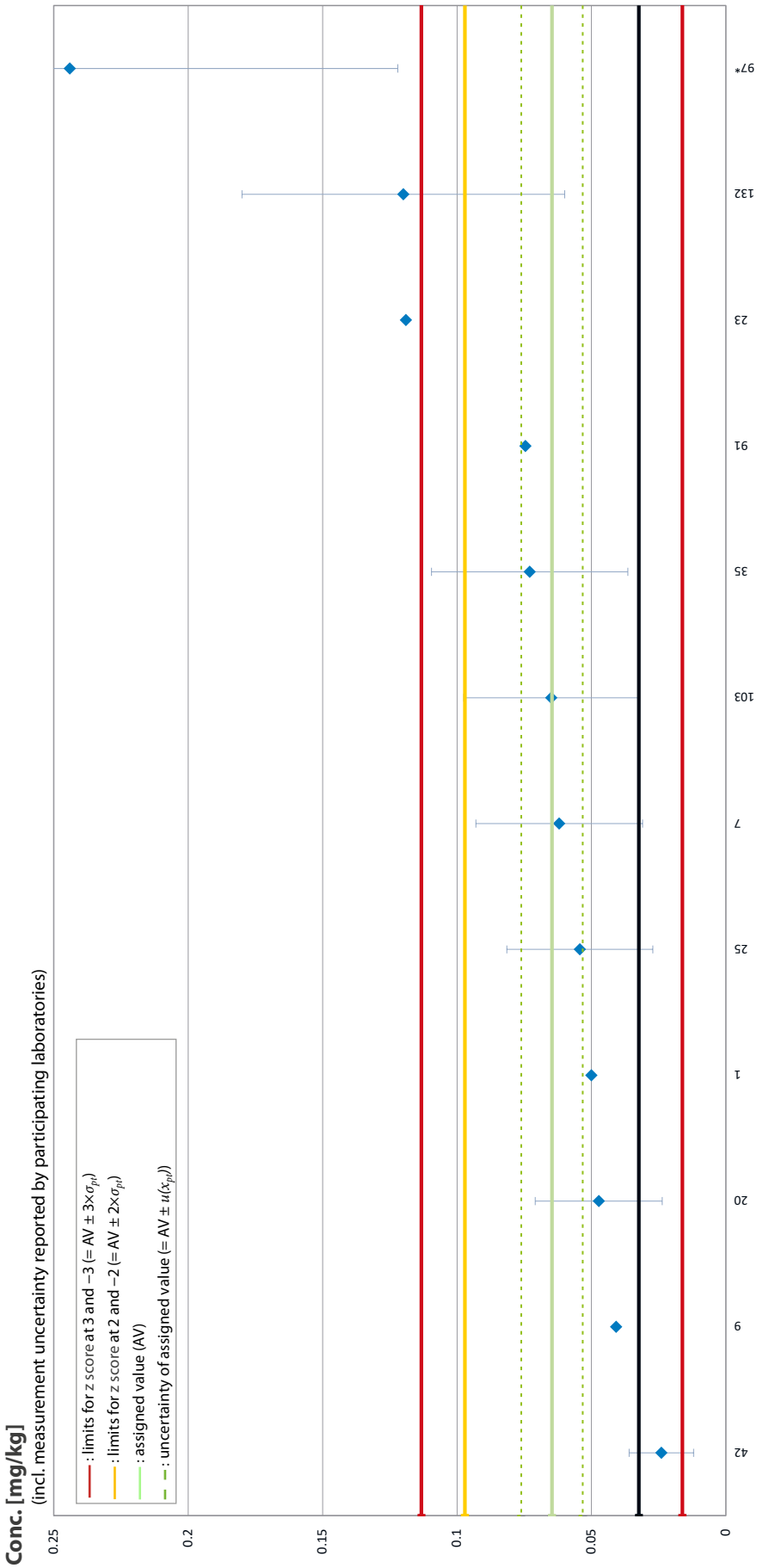
Appendix 6 (cont.) **Graphic Presentation of z scores: Optional Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



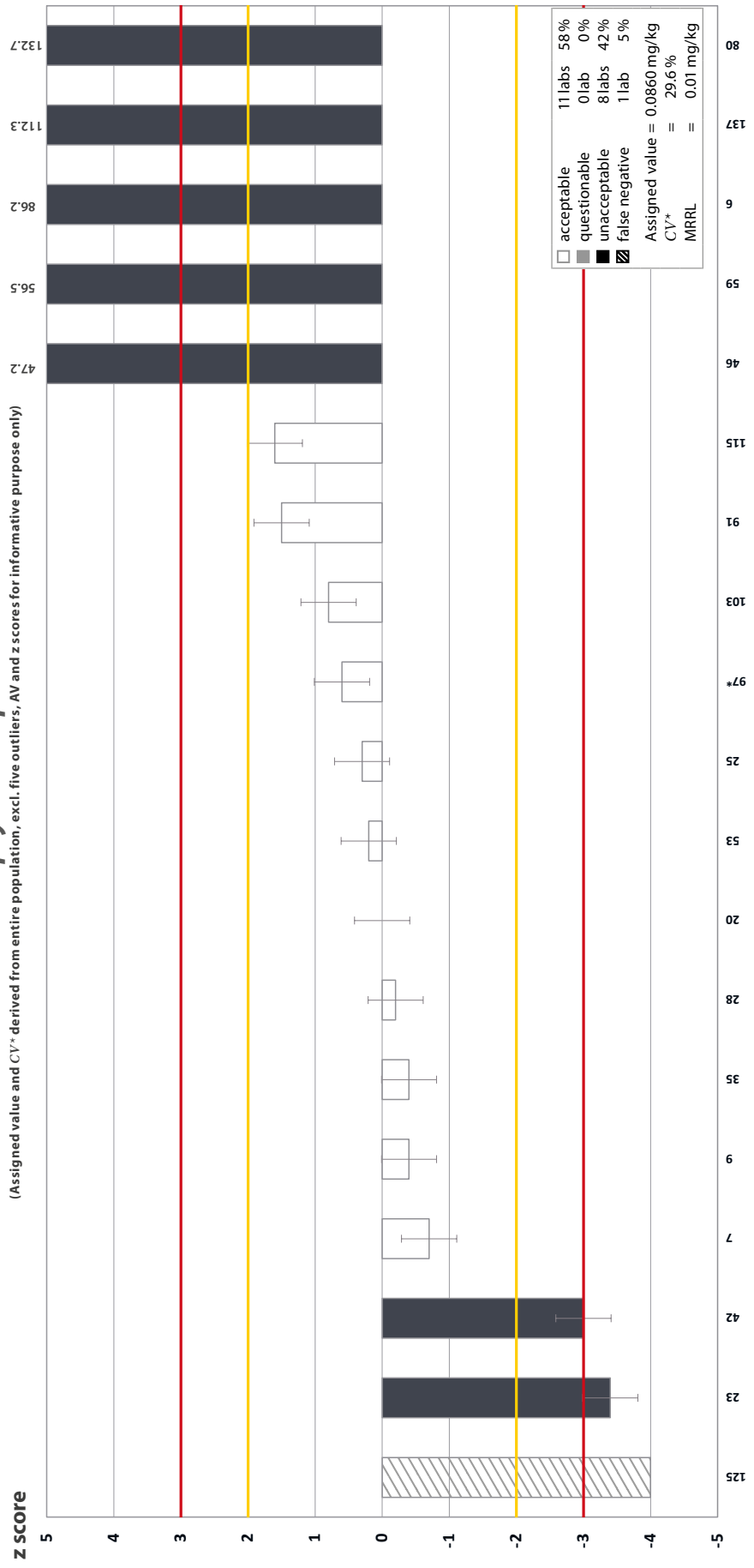
Appendix 6 (cont.) Graphic Presentation of z' scores: Optional Compounds (Results from EU and EFTA Laboratories only, * = NRL)



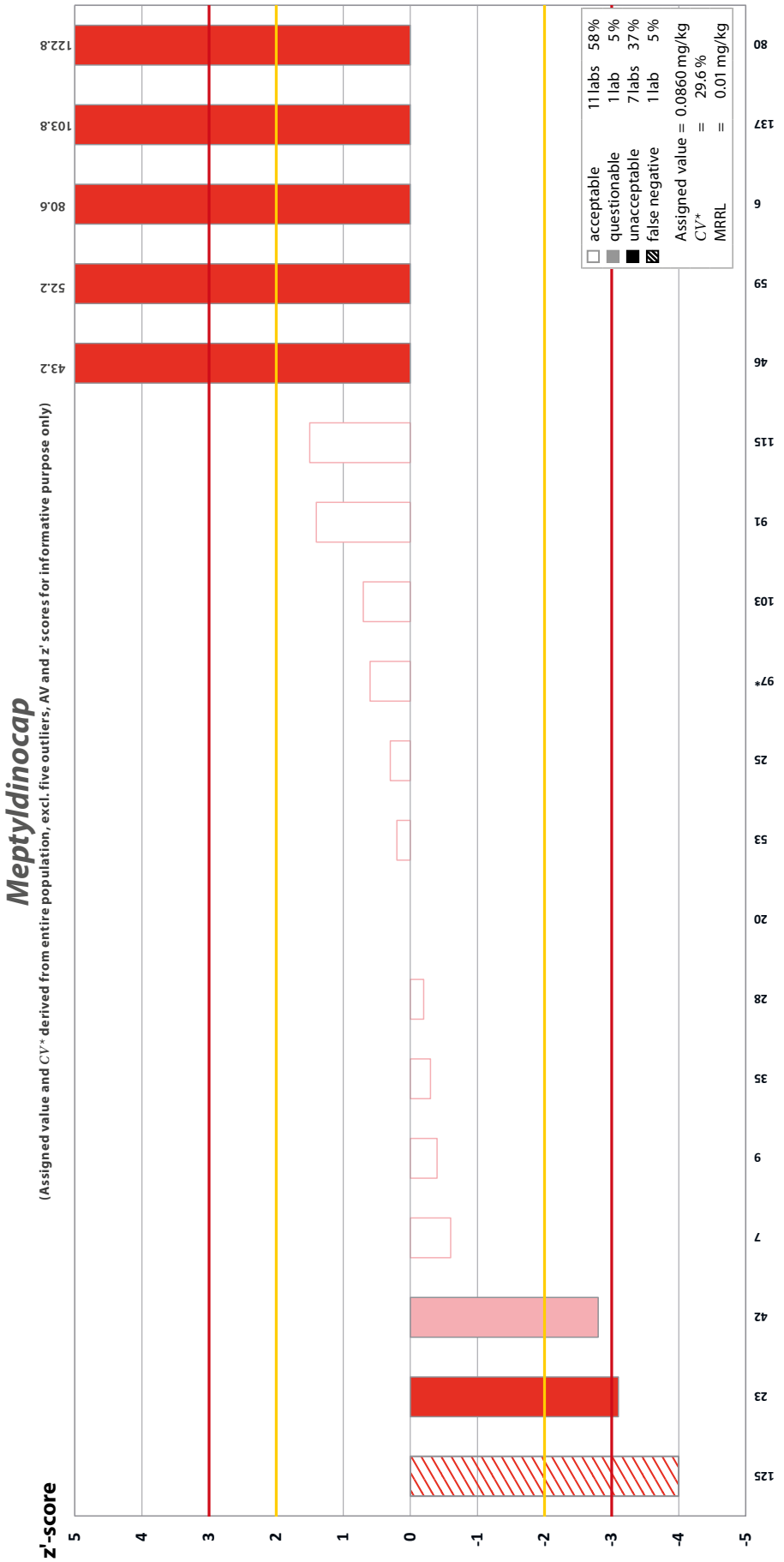
Appendix 6 (cont.) Graphic Presentation of z scores: Optional Compounds (Results from EU and EFTA Laboratories only, * = NRL)



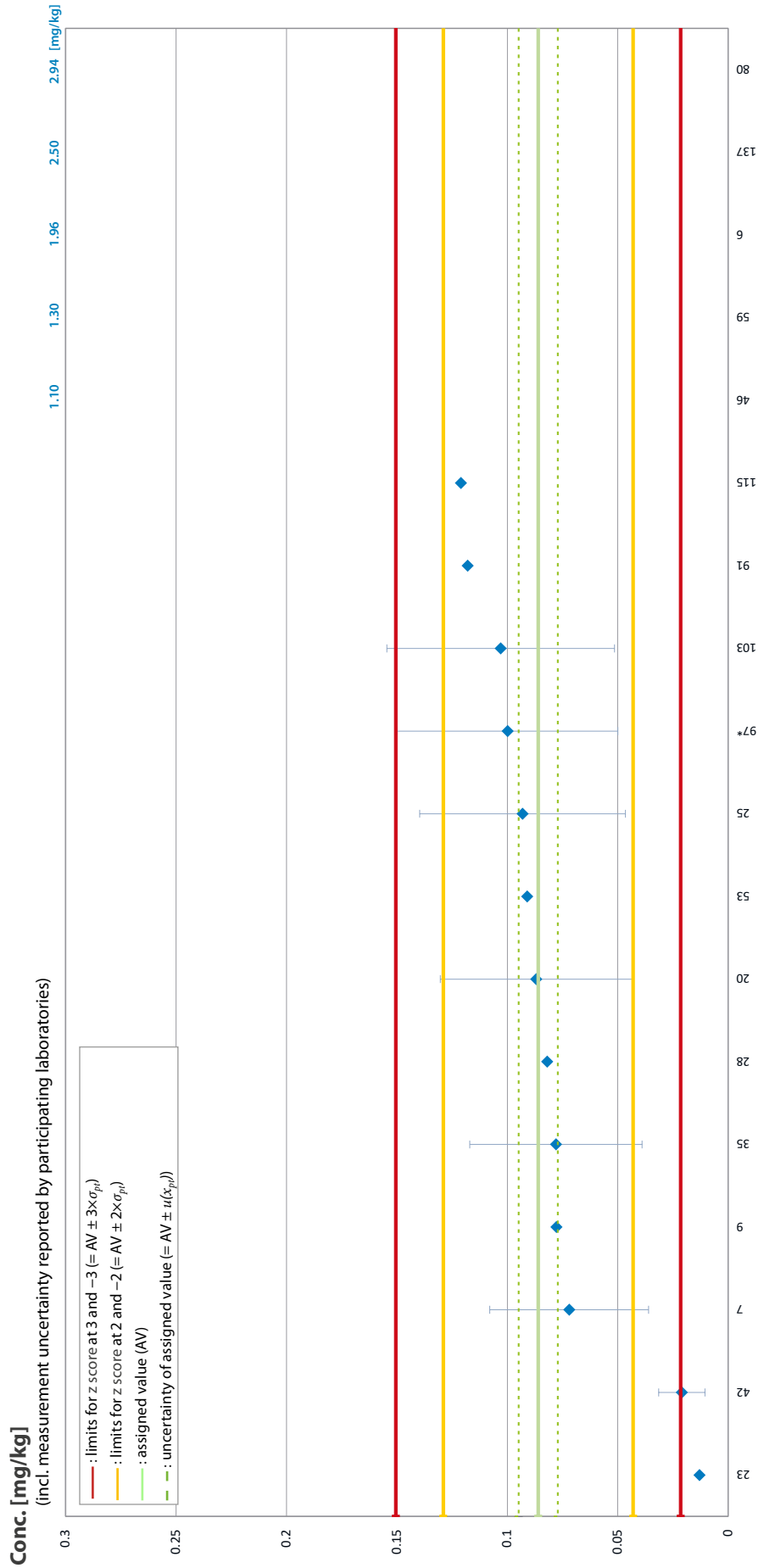
Appendix 6 (cont.) **Graphic Presentation of z scores: Optional Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



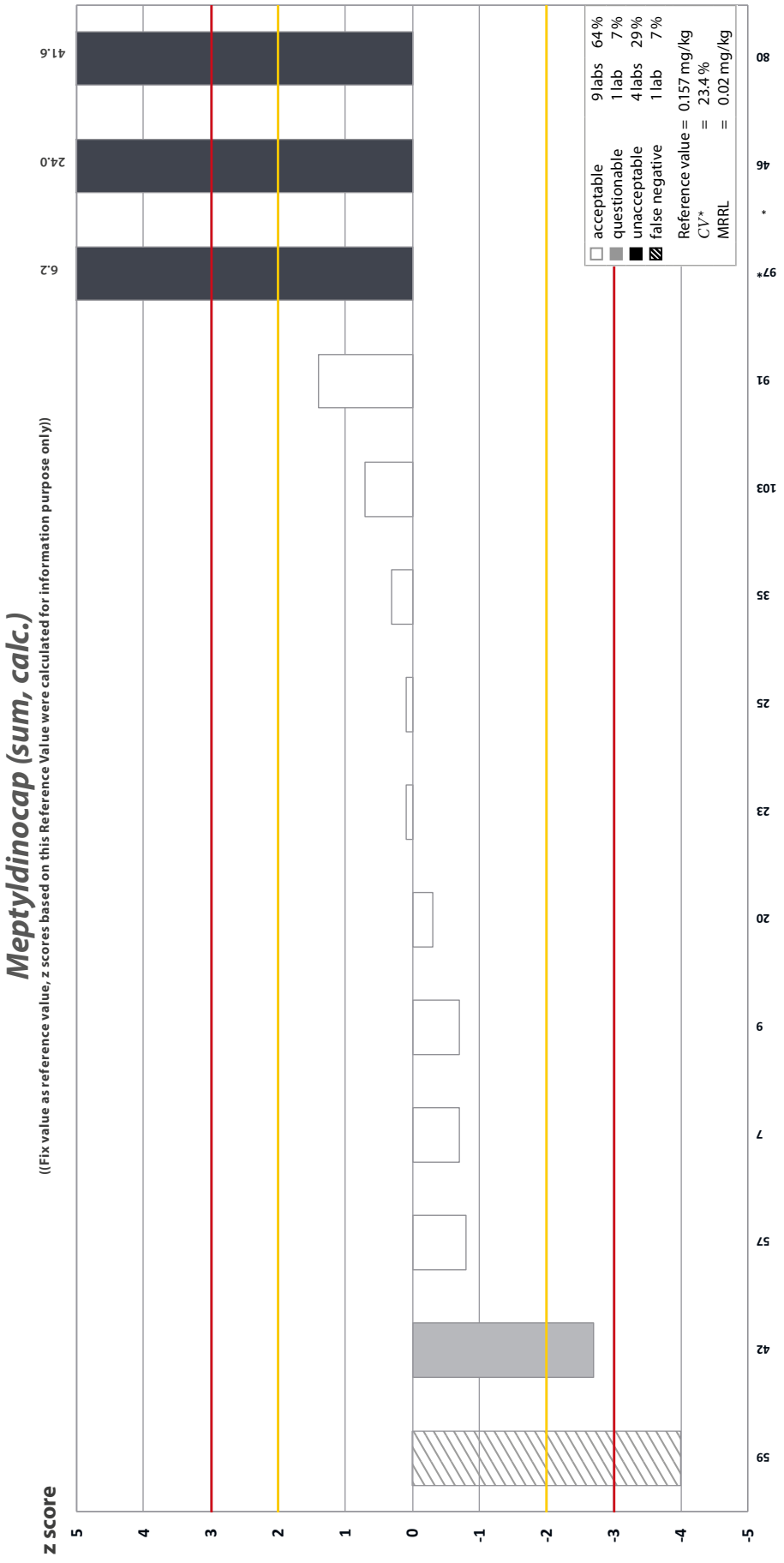
Appendix 6 (cont.) **Graphic Presentation of z' scores: Optional Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



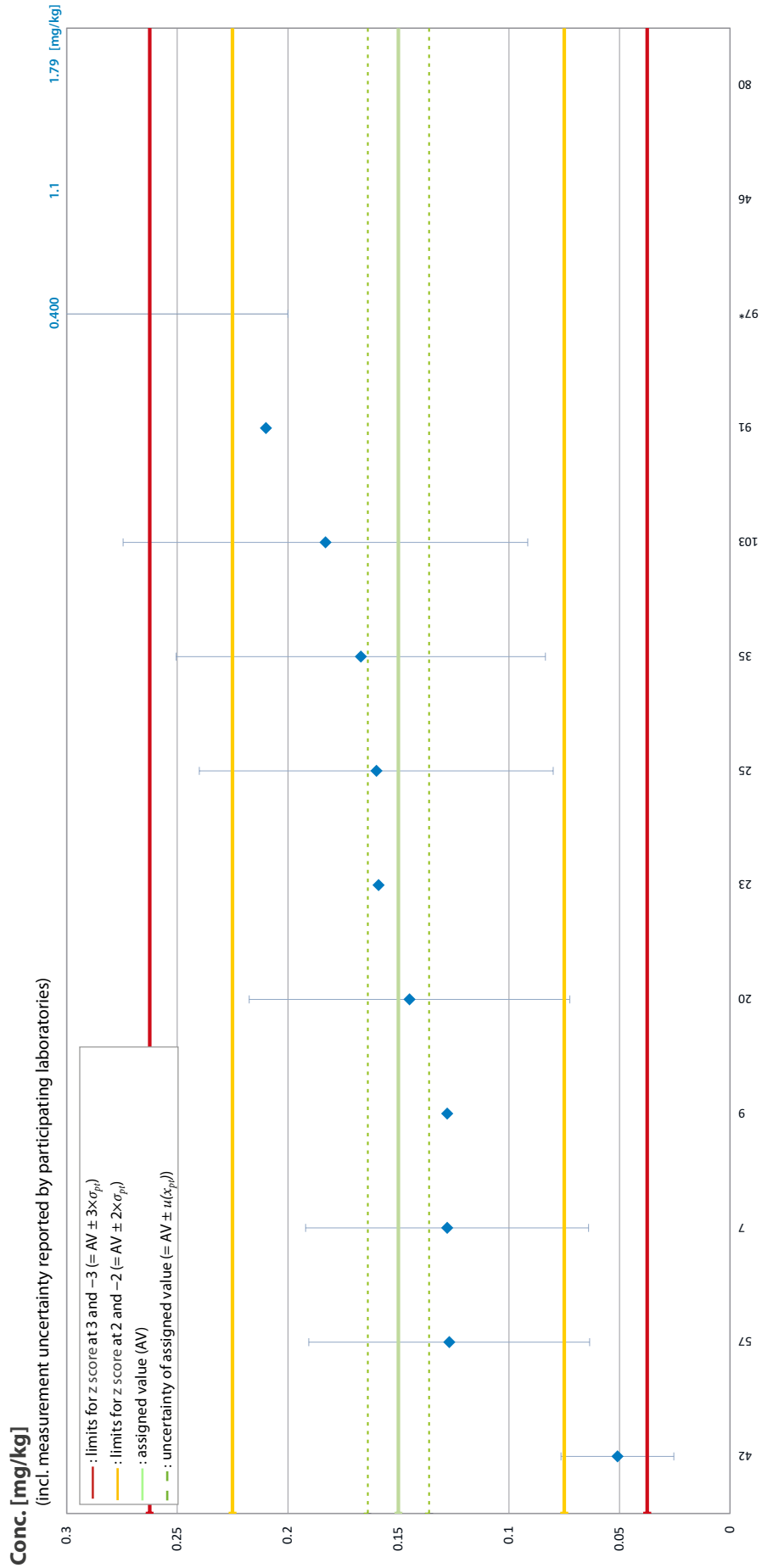
Appendix 6 (cont.) Graphic Presentation of z scores: Optional Compounds (Results from EU and EFTA Laboratories only, * = NRL)



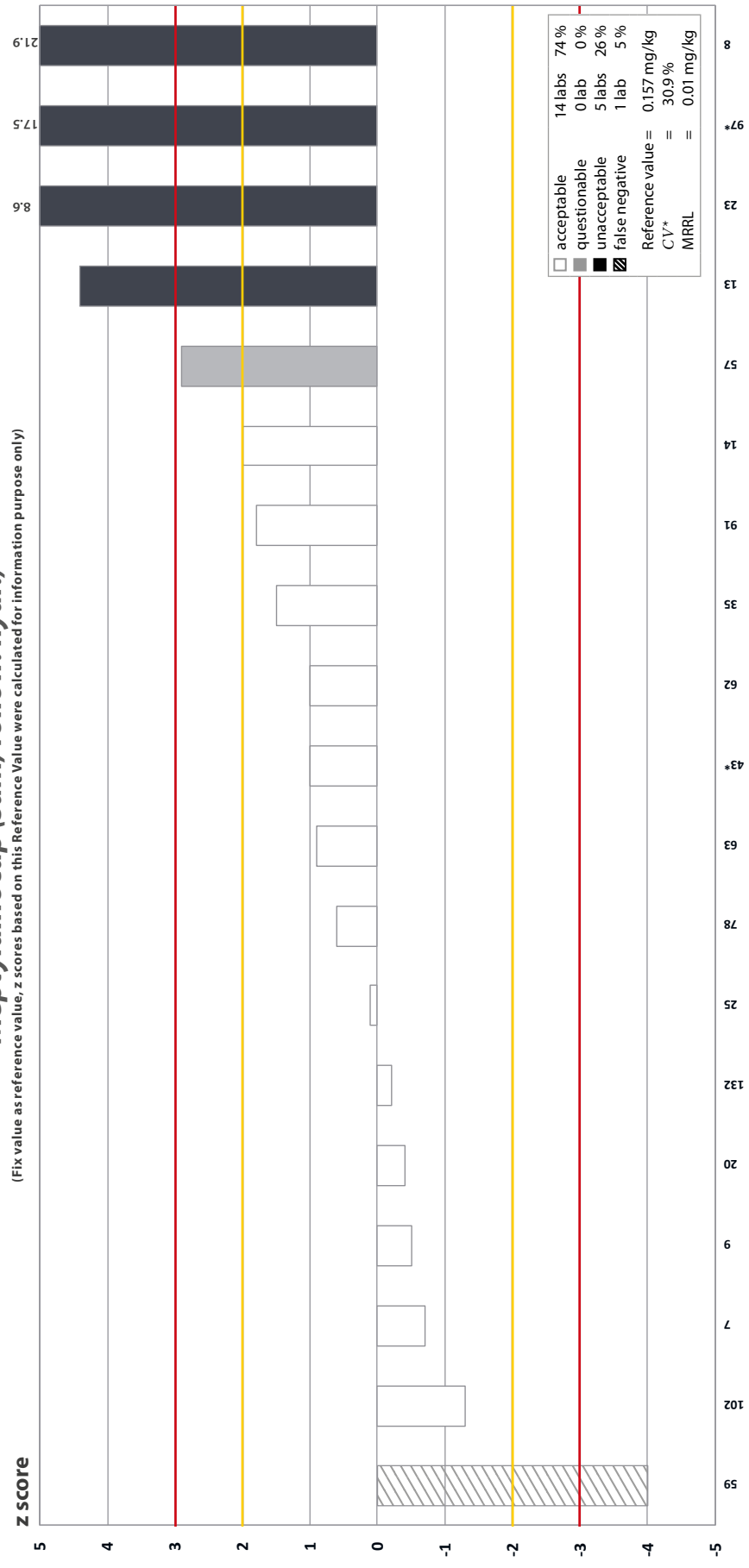
Appendix 6 (cont.) **Graphic Presentation of z scores: Optional Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



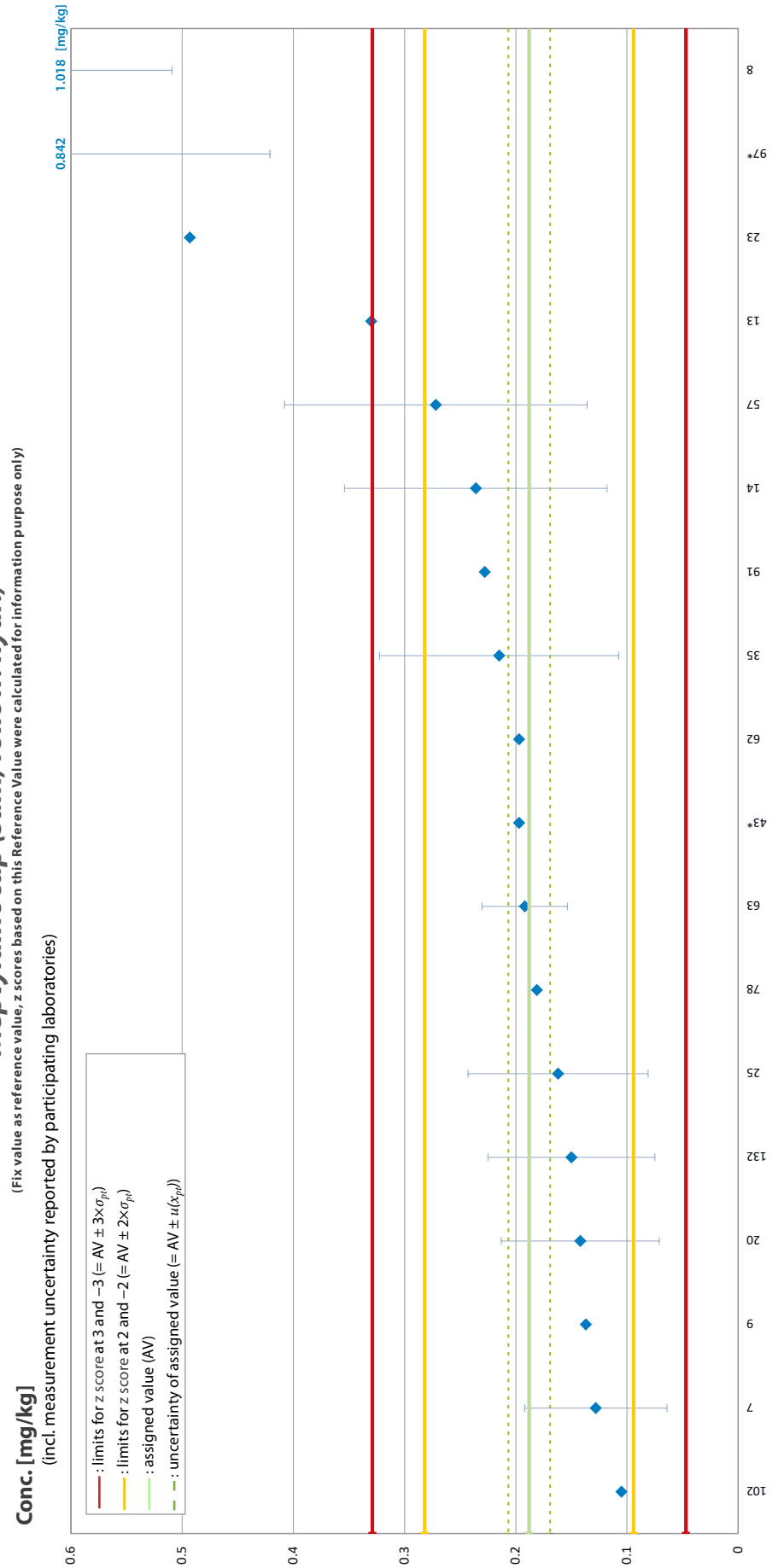
Appendix 6 (cont.) Graphic Presentation of z scores: Optional Compounds (Results from EU and EFTA Laboratories only, * = NRL)



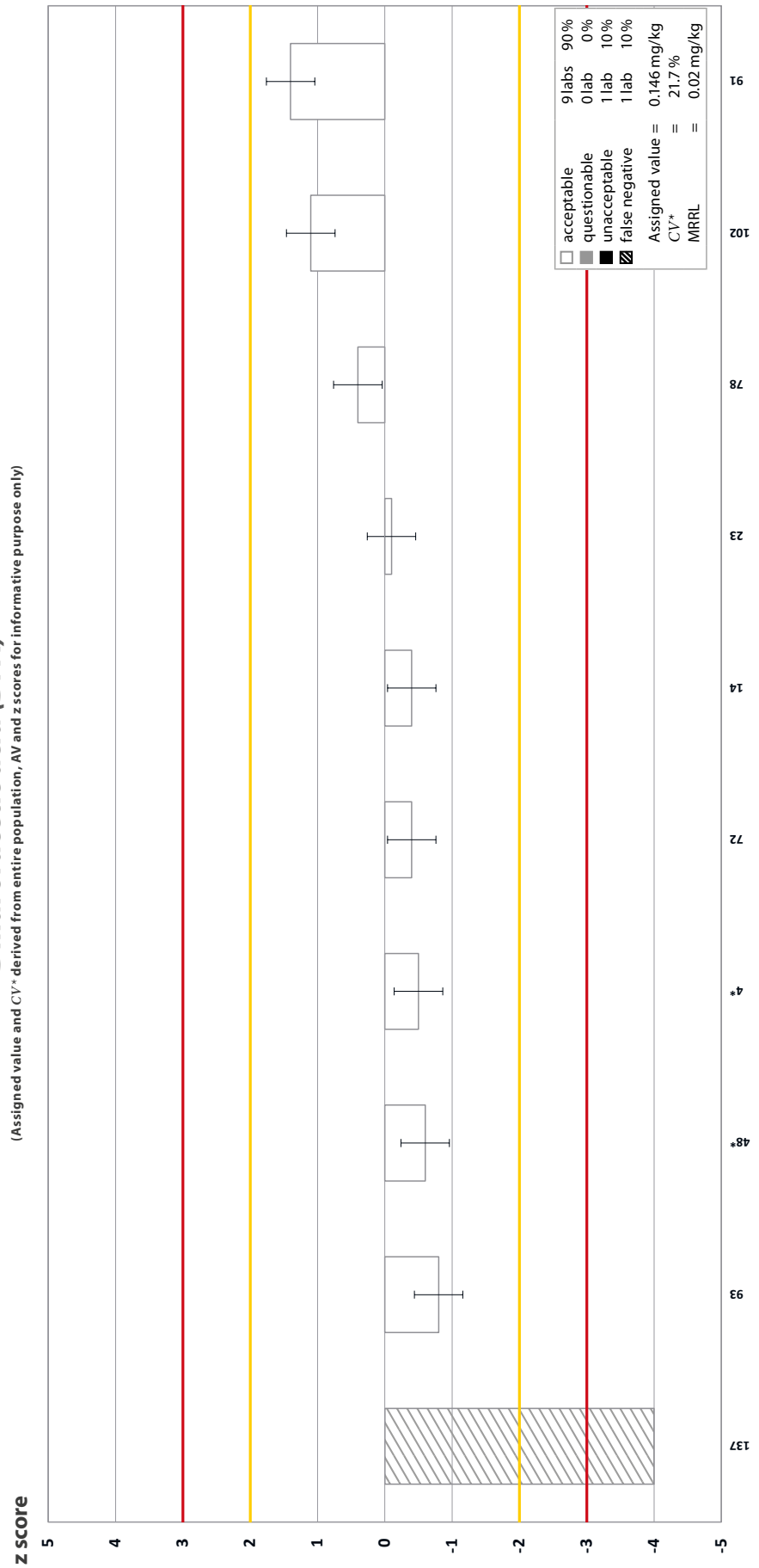
Appendix 6 (cont.) **Graphic Presentation of z scores: Optional Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



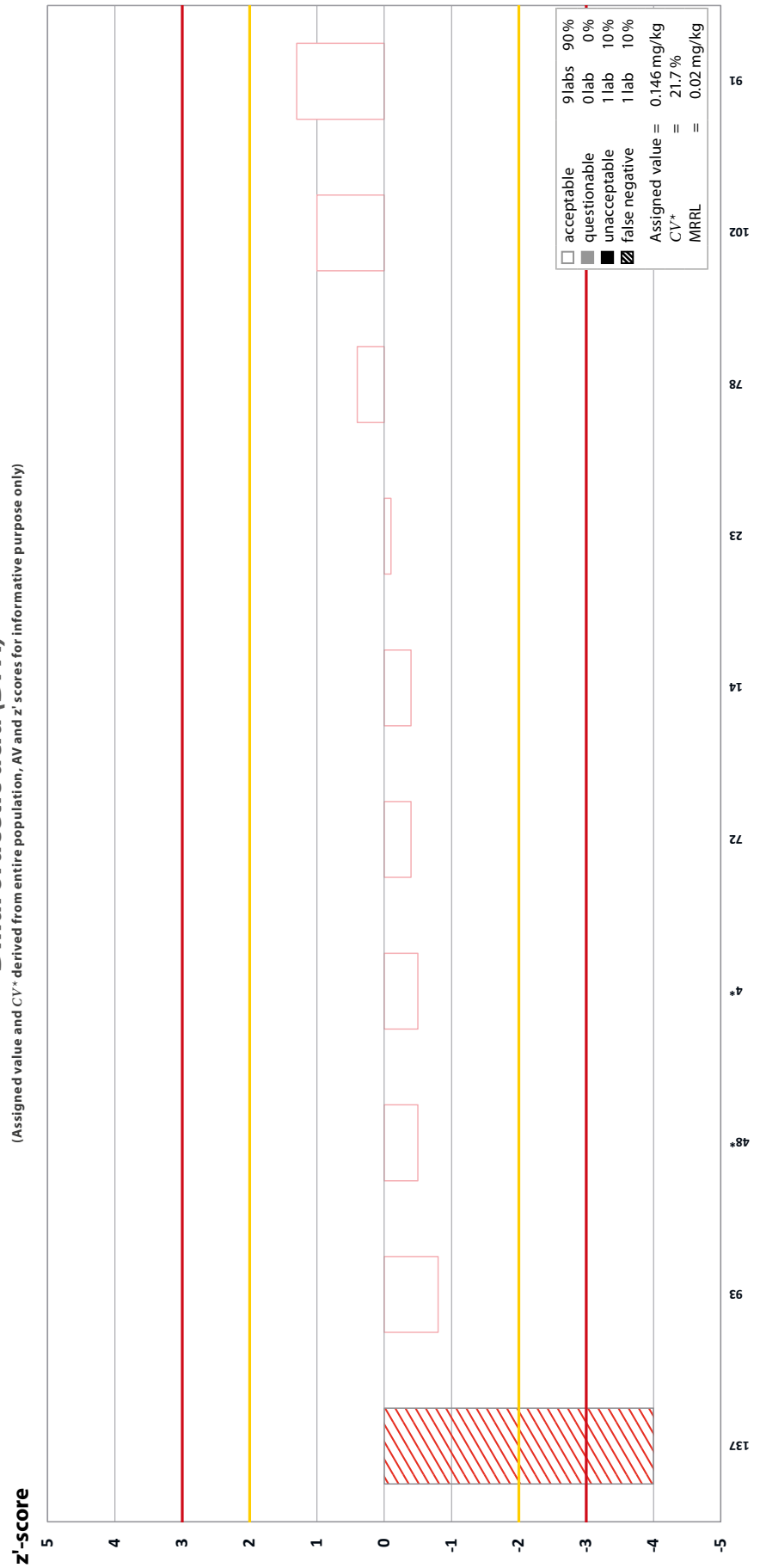
Appendix 6 (cont.) Graphic Presentation of z scores: Optional Compounds (Results from EU and EFTA Laboratories only, * = NRL)



Appendix 6 (cont.) **Graphic Presentation of z scores: Extra Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



Appendix 6 (cont.) **Graphic Presentation of z scores: Extra Compounds** (Results from EU and EFTA Laboratories only, * = NRL)



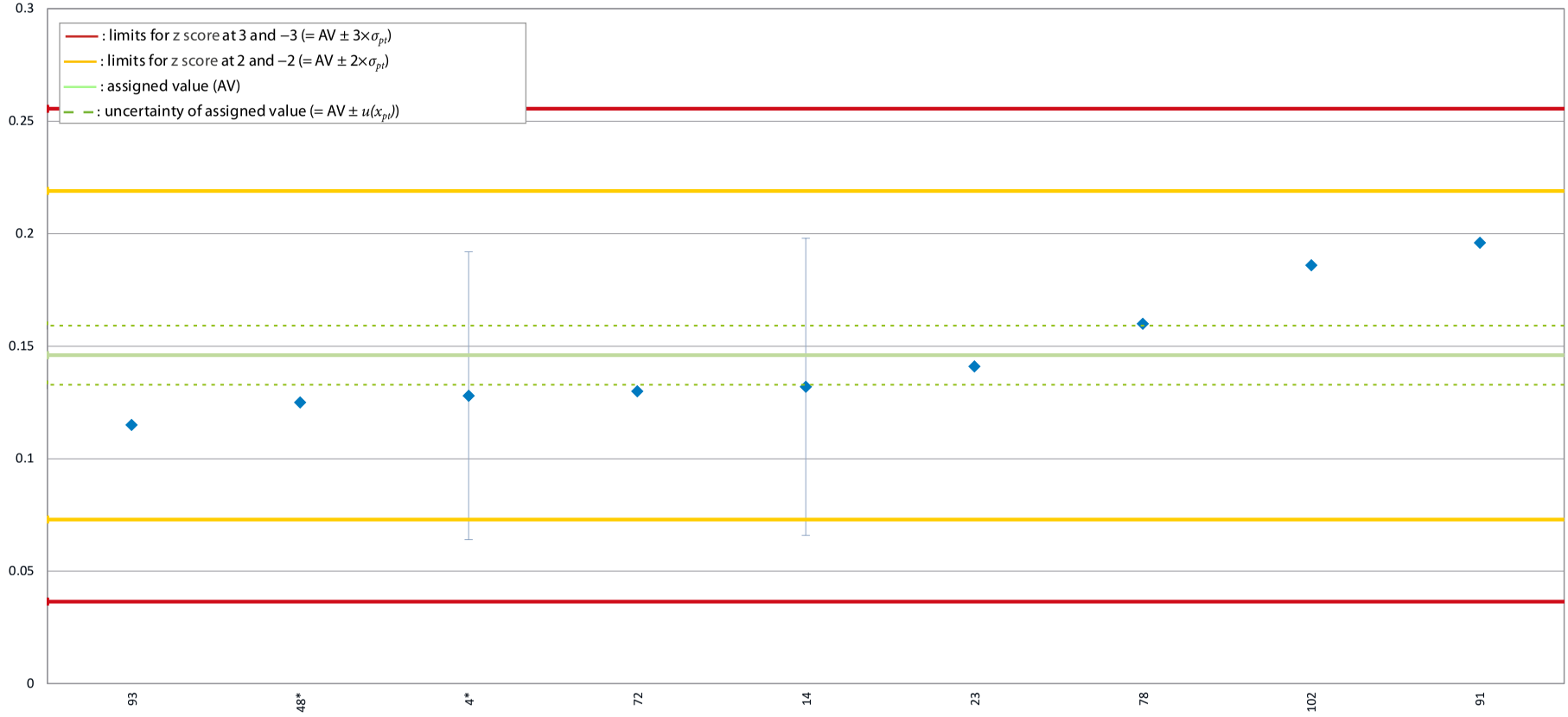
Appendix 6 (cont.) **Graphic Presentation of z scores: Extra Compounds** (Results from EU and EFTA Laboratories only, * = NRL)

Difluroracetic acid (DFA)

(Assigned value and CV^* derived from entire population, AV and z scores for informative purpose only)

Conc. [mg/kg]

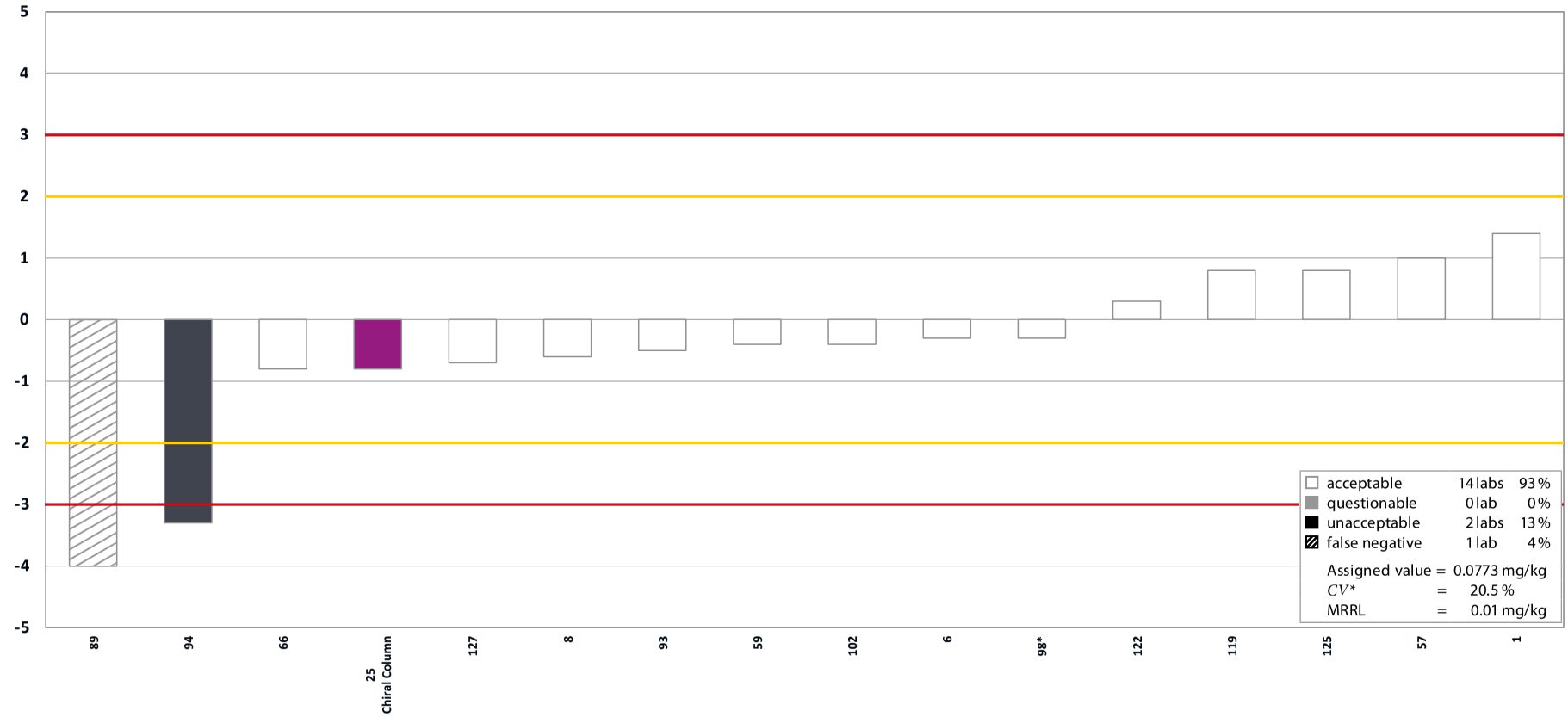
(incl. measurement uncertainty reported by participating laboratories)



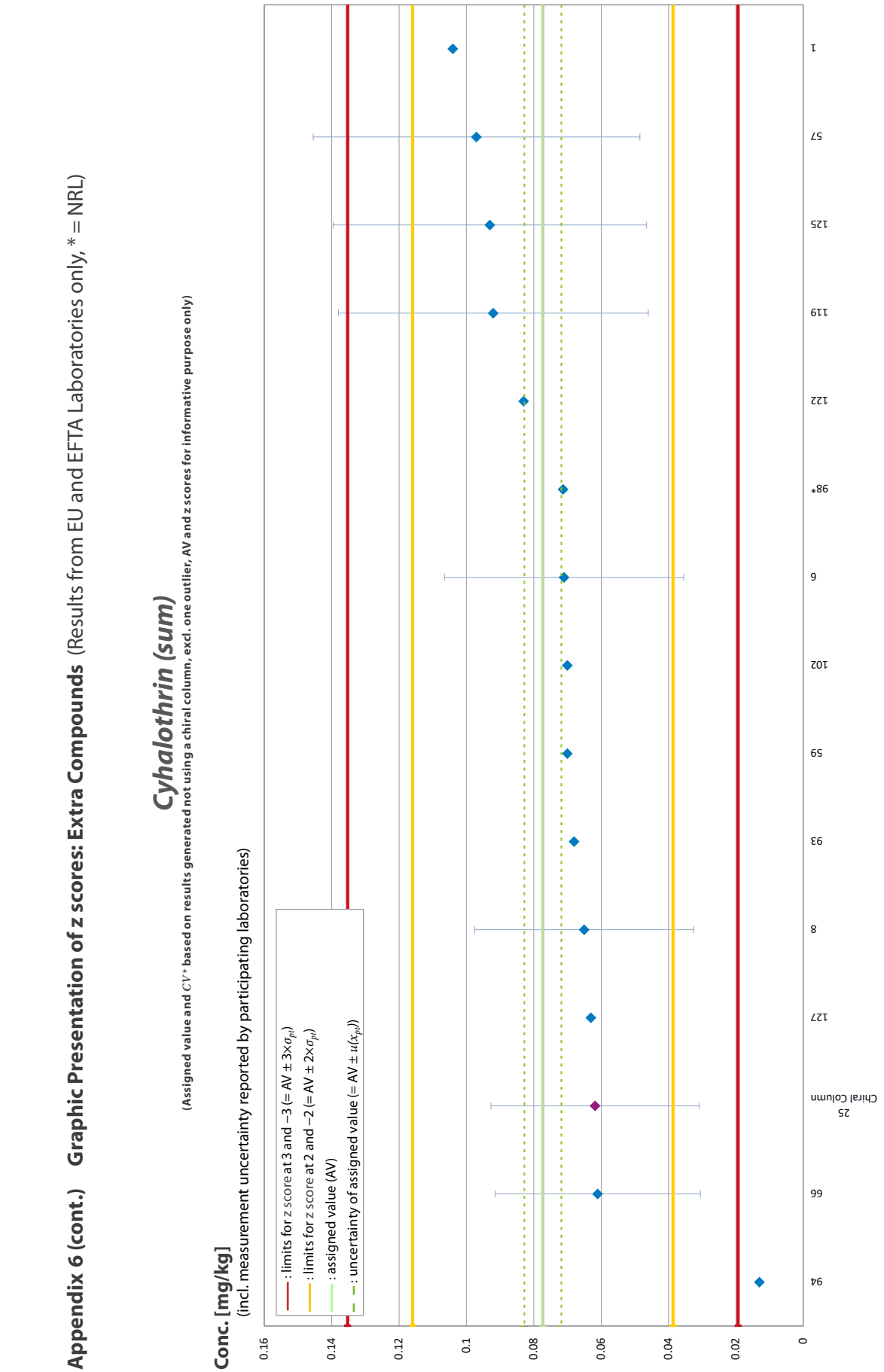
Appendix 6 (cont.) **Graphic Presentation of z scores: Extra Compounds** (Results from EU and EFTA Laboratories only, * = NRL)

Cyhalothrin (sum)

(Assigned value and CV^* based on results generated not using a chiral column, excl. one outlier, AV and z scores for informative purpose only)



Appendix 6 (cont.) Graphic Presentation of z scores: Extra Compounds (Results from EU and EFTA Laboratories only, * = NRL)



Appendix 7 Possible Reasons Reported for Poor Performance (ordered by z scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

2,4-D (free acid) not present in the test material

LabCode	Judgement	Reason	Remarks/Details
76	FR	L, M	When i reported the results, i checked by mistake that i analyzed 2.4-d; i saved the option and automatically the system asked us for the concentration found...the value of 0.000 mg/kg was not accepted, so we put a value much below loq in the idea that the system will warn us or not take this value into calculation. In conclusion, i analyzed 2.4-d but without finding this substance in the sample. (Not familiar with the Webtool procedure)

2,4-DNOP (free phenol) Assigned value: 0.0647 mg/kg, CV*: 46.9 %

LabCode	z Score	Reason	Remarks/Details
59	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. Consider checking if there was a peak mismatch between 2,4-DNOP and meptyldinocap. There are various scenarios of misinterpretations depending on whether mixed or individual standards of 2,4-DNOP and meptyldinocap are used, on whether the two compounds coelute or not, and on whether the meptyldinocap standard solution has strongly degraded. In any case, the mass-trace of 2,4-DNOP should show at least one signal independent on whether the sample extract or any of the analytes were injected. If only one signal was noticed and if this signal was mistakenly allocated to meptyldinocap, the question should have came up about the whereabouts of 2,4-DNOP or about whether the two compounds are analytically distinguishable or not.
96	-4.0 (FN)		**Feedback and advices by the organisers**: see comments for 2,4-DNOP and meptyldinocap for LabCode 59.
42	-2.5	A	No reason highlighted: sample analysed 3 times and always the same results. All control criteria are good (recoveries, linearity…). Problem of multiresiue analysis versus extraction with hydrolysis? **Feedback and advices by the organisers**: Looking at your method information there are no clear indications that would explain this underestimation of both 2,4-DNOP and meptyldinocap. Please check the comments on metyldinocap and 2,4-DNOP made for LabCode 59
23	3.4	M	strong amount seems provide from meptyldinocap degradation in DNOP at an unknown analytical step (amount dnop+meptyldinocap is good) **Feedback and advices by the organisers**: At first sight it looks as if a degradation of meptyldinocap to 2,4-DNOP took place in your sample or extract. Looking at your method information the only indication in this direction would be the cleanup by PSA. In case of a delayed reacidification this step may lead to a relevant degradation of meptyldinocap to 2,4-DNOP. Please also check the comments on metyldinocap and 2,4-DNOP made for LabCode 59
132	3.4		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.
97	11.1		**Feedback and advices by the organisers**: see comments for 2,4-DNOP and meptyldinocap for LabCode 59.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Avermectin B1a Assigned value: 0.0711 mg/kg, CV*: 24.6 %

LabCode	z Score	Reason	Remarks/Details
75	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also helps to localize the risk of false negatives.
94	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also helps to localize the risk of false negatives.
114	-3.2	M	The instrument has been failed. It's a 13 year old instrument, the original pump had been broken. It wasn't work with the alternative pump. During the relevant samples were tested, the instrument LC-MS/MS was maintained by the service. Now this problem no longer exists. **Feedback and advices by the organisers**: see comments on clopyralid
113	-2.6	D	
6	-2.4	L	Error in communicating the result. The correct value is 0.043 **Feedback and advices by the organisers**: Your revised result for abamectin would result in a z score of -1.6, which is within the acceptable range. The use of ACN with 1 % formic acid in combination with citrate buffered salts as well as in combination with dSPE with PSA does not make any sense.
127	-2.3	I	recalculated results = 0,056 mg/kg **Feedback and advices by the organisers**: Your new result would have resulted in a z score of -0.8 which is well within the acceptable range.
3rd-116	-2.3		
54	-2.1	A	
93	2.2		
98	2.2		
132	2.2		
84	2.4	G	The result was obtained using blank matrix of same type as the sample for calibration. Two days earlier the sample was analysed using a different matrix matched calibration (cucumber), result being 0.0755 mg/kg. **Feedback and advices by the organisers**: Your new result would have resulted in a z score of 0.2 which is well within the acceptable range.
125	2.8		
90	5.0	J	The analytical standard purity used for the EUPT-SMR19 by HPC (Lot 816066) was wrong. Testing HPC standard (Lot 816066) vs Dr Ehrenstorfer (Lot 1232505) , the difference was -65 %. The corrected result (0.160*(0.160*0.65))=0.056 mg/kg **Feedback and advices by the organisers**: We can confirm your claim as we have thoroughly checked the purity of the suspected standard (a separate standard of the same batch) obtaining very similar results. The producing company was informed but their internal checks did not reveal the reason for the deviating purity. The standard was replaced . Your new result would have resulted in a z score of -0.8 which is well within the acceptable range.
29	14.6		

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Amitrol not present in the test material			
LabCode	Judgement	Reason	Remarks/Details
125	FP		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Quality control measures should help to avoid FP results. Such measures could include the analysis of blanks, the comparison of (relative) retention time, mass transition signal ratios and peak shape with those of an analytical standard. Checking cross-contaminantions and carry-over effects also help detect false positive potentials. Overspikes with the analyte and comparison with the corresponsing ILIS in terms of retention time and peak shape also provide usefull hints. If ILIS is used, checking for cross-contaminantion is helpful.

Captan not present in the test material			
LabCode	Judgement	Reason	Remarks/Details
39	FP		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Quality control measures should help to avoid FP results. Such measures could include the analysis of blanks, the comparison of (relative) retention time, mass transition signal ratios and peak shape with those of an analytical standard. Checking cross-contaminantions and carry-over effects also help detect false positive potentials. Overspikes with the analyte and comparison with the corresponsing ILIS in terms of retention time and peak shape also provide usefull hints. If ILIS is used, checking for cross-contaminantion is helpful.
89	FP		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Quality control measures should help to avoid FP results. Such measures could include the analysis of blanks, the comparison of (relative) retention time, mass transition signal ratios and peak shape with those of an analytical standard. Checking cross-contaminantions and carry-over effects also help detect false positive potentials. Overspikes with the analyte and comparison with the corresponsing ILIS in terms of retention time and peak shape also provide usefull hints. If ILIS is used, checking for cross-contaminantion is helpful.

Captan (sum) not present in the test material			
LabCode	Judgement	Reason	Remarks/Details
39	FR		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Quality control measures should help to avoid FP results. Such measures could include the analysis of blanks, the comparison of (relative) retention time, mass transition signal ratios and peak shape with those of an analytical standard. Checking cross-contaminantions and carry-over effects also help detect false positive potentials. Overspikes with the analyte and comparison with the corresponsing ILIS in terms of retention time and peak shape also provide usefull hints. If ILIS is used, checking for cross-contaminantion is helpful.
89	FP		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Quality control measures should help to avoid FP results. Such measures could include the analysis of blanks, the comparison of (relative) retention time, mass transition signal ratios and peak shape with those of an analytical standard. Checking cross-contaminantions and carry-over effects also help detect false positive potentials. Overspikes with the analyte and comparison with the corresponsing ILIS in terms of retention time and peak shape also provide usefull hints. If ILIS is used, checking for cross-contaminantion is helpful.

Chlormequat chloride not present in the test material			
LabCode	Judgement	Reason	Remarks/Details
114	FP	M	The instrument has been failed. It's a 13 year old instrument, the original pump had been broken. It wasn't work with the alternative pump. During the relevant samples were tested, the instrument LC-MS/MS was maintained by the service. Now this problem no longer exists. **Feedback and advices by the organisers**: Quality control measures should help to avoid FP results caused by malfunctioning or poor performing instruments. Such measures could include the analysis of blanks, the comparison of (relative) retention time, mass transition signal ratios and peak shape with those of an analytical standard. Checking cross-contaminantions and carry-over effects also help detect false positive potentials. Overspikes with the analyte and comparison with the corresponsing ILIS in terms of retention time and peak shape also provide usefull hints. If ILIS is used, checking for cross-contaminantion is helpful.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Clopyralid Assigned value: 0.192 mg/kg, CV*: 23.4 %			
LabCode	z Score	Reason	Remarks/Details
71	-4.0 (FN)	A	The compound is not in the scope of the method. This compound was tested only during the PT **Feedback and advices by the organisers**: The organizers encourage labs taking advantage of the PTs for checking the performance of newly introduced methodologies for analytes outside of the routine scope. Consider introducing quality control measures that would help identify potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. In your case you havn't reported any recovery data, also it seems that you have employed dSPE cleanup with PSA as sorbent. As an acidic compound, clopyralid shows an affinity for PSA. The drop in concentration after this clean-up may have resulted in a false negative.
134	-4.0 (FN)	M	Due to the clopyralid amount detected being below our lab's reporting limit we were forced to exclude it in our reporting. However we included the detected amount in the comment section of the webtool as followed: Clopyralid was detected at 0.249 mg/kg which is below our LOQ (<0.5 mg/kg) **Feedback and advices by the organisers**: 1) If you did want to exclude the analyte from your report, you should have selected in the webtool "not analyted" instead of '"analysed" and "not detected"'. 2) From a quality control point of view, your result wouldn't be judged as a false negative. In fact your semi-quantitative result would have even obntained an acceptable z-score. However, in accordance with the rules of the EUPT General Protocol your result is to be penalized as your reporting limit is too high and not fit-for-purpose. Consider changing or adjusting your methodology for being able to monitor lower concentrations of this analyte. The MRRL gives an orientation of the sensitivity expected for a particular analyte.
132	-3.8		**Feedback and advices by the organisers**: Based on your method data, you have employed acetate buffered QuEChERS and dSPE cleanup with PSA as sorbent. As the partitioning of clopyralid to the organic phase is limited at the pH of the acetate buffered QuEChERS, low recoveries are expected. Unfortunately you have not provided any recovery data. Consider checking FA-QuEChERS for this analyte. As an acidic compound, clopyralid shows an affinity towards PSA. This step may have also caused losses on clopyralid.
43	-3.5	F, A	Clopyralid has same transitions and retention time as TFNA. I have no any experience with clopyralid, it was validated just at the begining of this year, but no any sample has been reported for this analyte yet. I checked again what was the problem for so different result and I found out that quantifier ion (also precursor) was same as for TFNA, retention time same too. When I chose different transition for quantification the results were fine, repeated analysis 6.5.2024 for clopyralid 0,176 mg/kg. EUPT SRM is quite demanding test in context of methods, for example SRM19 involves 5 LC methods to cover all analytes plus GC methods (some of them 50g sample weight). The more method the more test material we should have. We were thinking to buy additional test material but financial situation is not always good. Recently our institute hired new people so I hope next time we will have enough time for EUPT analysis. Selection of analytes in target list is crucial because sometimes it involves just two methods and sometimes six, so then we are limited in time and material too. **Feedback and advices by the organisers**: Thank you for this feedback. Your new value would have obtained a z score of -0.3 which is well within the acceptable range.
3rd-116	-2.8		**Feedback and advices by the organisers**: Consider checking FA-QuEChERS which provides good recoveries for this analyte.
56	-2.3		**Feedback and advices by the organisers**: Employing PSA in dSPE cleanup has surely caused some losses. Also solvent based calibration may have introduced some bias if matrix effects played a role.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Clopyralid Assigned value: 0.192 mg/kg, CV*: 23.4 %

LabCode	z Score	Reason	Remarks/Details
37	2.3		Result 0,12 mg/kg corrected with recovery 39 % in spiked (0,1 mg/kg) PT sample. In our control chart we see lower recovery for spiked oranges, grapefruits, grapes and broccoli compared to cucumber - therefore we assumed the correction was appropiate. Our standard curve is made matrix-matched in cucumber. Sample reanalysed afterwards with standard addition for Clopyralid and we get 0,206 mg/kg **Feedback and advices by the organisers**: Thank you for this feedback. Your new value would have obtained a z score of 0.3 which is well within the acceptable range. The recovery rate of 39 % is rather low considering that you conduct matrix-matched calibration and that you do not conduct clean-up with PSA which would have cause losses. Consider checking FA-QuEChERS which provides good recoveries for this analyte.
137	4.3		**Feedback and advices by the organisers**: Check whether matrix effect may have contributed to this biased result. The methodology used (e.g. use of dSPE with PSA) should rather lead to underestimated results.
114	8.8	M	The instrument has been failed. It's a 13 year old instrument, the original pump had been broken. It wasn't work with the alternative pump. During the relevant samples were tested, the instrument LC-MS/MS was maintained by the service. Now this problem no longer exists. **Feedback and advices by the organisers**: Quality control procedures in a laboratory should recognise when an instrument is not fit for purpose, or ensure that the accuracy of quantification meets the criteria, regardless of whether sensitivity is poor. Consider introducing control procedures to ensure analytical quality. For example, check whether residues at the RL are measurable and whether the calibration curve meets the AQC criteria. Where indicated, check whether the measurement is repeatable.

Copper Assigned value: 29.9 mg/kg, CV*: 7.7 %

LabCode	z Score	Reason	Remarks/Details
54	-3.6	L	Typing error, actual value is 27,1 mg/kg, hence acceptable z-score

Difluoroacetic acid (DFA) Assigned value (informative only): 0.146 mg/kg, CV*: 21.7 %

LabCode	z Score	Reason	Remarks/Details
137	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also helps to localize the risk of false negatives.

Dithianon Assigned value (informative only): 0.236 mg/kg, CV*: 38.1 %

LabCode	z Score	Reason	Remarks/Details
46	-4.0 (FN)	B	Sample was re-extracted and dithianon was detected. For quanitification, we must make measured additions. Unfortunately, we don't have enough matrix to give you a quantified result. **Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost, degradation surely took place. Based on your method information, it seems that you have not chosen to extract the sample under acidic conditions for reducing degradation, although it should be noted that in this particular matrix losses during extraction are not the main issue. The fact that you have detected dithianon in your re-analysis indicates that your left-over homogenate still contains dithianon. We suspect that the analytical portion(s) extracted during the PT may have been exposed to elevated temperatures for some time prior to analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
54	-4.0 (FN)	A	Result of 0.174 mg/kg achieved with µSPE 2DLC-HRMS not reported, because QuEChERS LC-TQMS showed negative result (didn´t confirm HRMS results) **Feedback and advices by the organisers**: With the knowledge that dithianon shows considerable degradation in defrosted homogenates, your positive result should have triggered reanalysis under more protective conditions. Your method information doesn't indicate any defrosting of the sample prior to extraction. Also it seems that you have employed the extraction solvent ACN with 1 % FA that keeps dithianon stable although other information provided, e.g. citrate buffer and dSPE cleanup raise doubts about this information. Please check whether the analytical portion(s) extracted during the PT may have been exposed to elevated temperatures for some time prior to analysis.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Dithianon Assigned value (informative only): 0.236 mg/kg, CV*: 38.1 %			
LabCode	z Score	Reason	Remarks/Details
87	-4.0 (FN)	L	As already mentioned, there was an error in selecyion of the scope. We do not analyze this data **Feedback and advices by the organisers**: Please be more careful with reporting. Your methodology information indicates that this analyte is part of your routine scope.
125	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, we have not received any method information or feedback regarding the false negative result from your laboratory. Please note that, according to the EUPT General Protocol, failure to submit method information may lead to exclusion from future PTs or exclusion from the final report. In any case, we encourage you to check whether any of the comments given to the other laboratories on dithianon would apply in your case.
3rd-123	-3.8		**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost, degradation most likely occurred. Your methodology information is inconclusive as you indicated the use of citrate-based QuEChERS, but additional information suggesting the use of FA-QuEChERS. In any case in this particular sample the impact of the extraction step on losses was rather moderate. Leaving the analytical portions in the freezer may reduce additional losses but not compensate for the losses that have occurred before. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
34	-3.5	D	**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was put to defrost over an extensive time period, dithianon degradation was most likely very extensive. Based on your method information, it seems that you have taken measures to reduce degradation during sample preparation and have even placed the analytical portion in the freezer prior to analysis. Unfortunately, all these protective measures could not compensate for the losses that occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
117	-3.5	D	Unfortunately, the sample arrived after the acceptable deadline. We reported this to the Organizer and the next shipment of the sample unfortunately did not reach us. Due to the problem with the International Courier DHL, the sample was sent for disposal. We decided to test the first sample that reached us. As you can see from the results, it was not a good decision. Our results, despite satisfactory recoveries, did not provide reliable results. All control samples used to assess the reliability of the obtained results met the established criteria, which allowed us to decide to report the PT results. By analyzing the fortified material with analytes detected in PT, the results were within the criteria - which confirms our competence in this area. Customer samples analyzed recently were analyzed, among the compounds detected there were none that were in PT. Appropriate actions were taken to establish a clear cause, although due to the inability to repeat the analyzed material in PT, it will be difficult to determine what had such a significant impact on the results obtained. Increased control has been introduced during the analysis of these compounds. 31.05.2024 dithianon, after a thorough analysis of the course of analysis and records, unfortunately this relationship had to break down and in this case all calculations are correct. **Feedback and advices by the organisers**: It was highly unfortunate that despite our repeated efforts to ensure that you obtain the sample in good condition, this wasn't accomplished. The problem was an error within the database of the shipment company, which strangely only affect your shimpent. The organizers were in permanent contact with both the shipment company and you, to ensure smooth shipment and arrival, without success. The interruption of the cool chain during shipment has surely led to a degradation of dithianon. Based on the information submitted we assume that you have defrosted the sample material prior to portioning and have also left the sample portions to reach room temperature prior to analysis. This has surely also contributed to the analyte loss. But overall no judgement on your routine performance can be done based on the z score obtained. In any case, we encourage you to check whether any of the comments given to the other laboratories on dithianon would apply in your case.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Dithianon Assigned value (informative only): 0.236 mg/kg, CV*: 38.1 %			
LabCode	z Score	Reason	Remarks/Details
111	-3.4	B, E	**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost in the fridge over an extensive time period, considerable degradation most likely occurred. The use of citrate-based QuEChERS rather than an acidified variant has surely also contributed to some extent to your underestimated concentration although in this particular sample the impact of the extraction step on losses was rather moderate. In any case, also consider introducing an extraction procedure entail acidification to protect dithianon. This is particularly important to samples with low acidity and poor antioxidative potential. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
1	-3.3		**Feedback and advices by the organisers**: Dithianon shows considerable degradation when the sample is defrosted. As you have fully defrosted your sample, dithianon degradation was most likely very extensive. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
88	-3.3		**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost in the fridge over an extensive time period, considerable degradation most likely occurred. Your method information is not clear as you have chose QuPPe as a reference method, but your further details suggest the use of citrate-based QuEChERS. Please make sure filling-up methodology information more diligently as this facilitates tracing back possible sources of error. Your method information suggests that you have added an ILIS at the beginning of the procedure to compensate for any errors during extraction, cleanup and measurement. Unfortunately, this compensatory measure could not compensate for the losses that had occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope. In any case, also consider introducing an extraction procedure entail acidification to protect dithianon. This is particularly important for samples with low acidity and poor antioxidative potential.
6	-3.2	K	Parameter outside the scope of accreditation. It is necessary to continue testing to improve the method **Feedback and advices by the organisers**: see comments for Lab 01
44	-3.2	D	**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost over an extensive time period, dithianon degradation was most likely very extensive. Based on your method information, you have employed an extraction procedure (FA-QuEChERS) that keeps dithianon stable and have also added an ILIS at the beginning of the procedure to compensate for any errors during extraction, cleanup and measurement. You have even placed the analytical portion into the freezer prior to analysis. Unfortunately, all these protective and compensatory measures could not compensate for the losses that occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
51	-3.2	D	**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost on the bench over an extensive time period, dithianon degradation was most likely very extensive. Based on your method information, you have employed an extraction procedure (FA-QuEChERS) that keeps dithianon stable and have also added an ILIS at the beginning of the procedure to compensate for any errors during extraction, cleanup and measurement. Unfortunately, all these protective and compensatory measures could not compensate for the losses that occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
3rd-135	-3.0	D	Sample arrived at 10 °C **Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates and it is thus very likely that considerable losses occurred during transport. However, based on your submitted information it seems as if you have frozen the sample after arrival and defrosted it again prior to analysis. If this was the case, additional degradation occurred. You indicate the use of an extraction procedure SA-QuEChERS that keeps dithianon stable. Unfortunately, this protective measure could not compensate for the losses that occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Dithianon Assigned value (informative only): 0.236 mg/kg, CV*: 38.1 %			
LabCode	z Score	Reason	Remarks/Details
3rd-86	-3.0		**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost degradation most likely occurred. Your method information (FA-QuEChERS) suggests that you have employed a methodology protective for dithianon, and by using procedural calibration any losses during extraction and cleanup should have been compensated. Unfortunately, these protective and compensatory measures could not compensate for the losses that had occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
108	-2.8	D	As reason of poor performance we have selected the D option, that means losses of the analyte during the procedure, included degradation during defrosting or at sample arrival. This is the sequence of actions followed in the lab after reception of the sample: - 07-02-2024 sample arrived at the lab correctly frozen. It was maintained frozen until analysis. - 07-03-2024 sample was kept in fridge in order to let defrosting during night. - 08-03-2024 extraction and analysis was performed for more sensitive analytes: o Dithianon, o DTC, o Folpet Due to the well-known issues of degradation of this type of analytes, extraction were performed just after defrosting the samples for the first time and maintaining low temperature during weighting. - 08-03-2023 Sample was frozen after extraction. - 11-03-2024 Sample was defrosted at room temperature. Extraction and analysis was performed for the rest of methods: o Abamectin, o Clopyralid, o Polar pesticides - 11-03-2023 Sample was frozen after extraction. An additional extraction and analysis was carried out after communication of poor performance (13-03-2024). Similar results were obtained. Specifically, in the case of DTC, there was no chromatographic detection in both analysis. After investigation through A to L options from the excel file, the possible reason that explain the poor results for DTC and dithianon is any issue related with the defrosting process. **Feedback and advices by the organisers**: First of all congratulations for the very meticulous and exemplary efforts for tracing back the error sources. Indeed dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost in the fridge over an extensive time period, considerable degradation most likely occurred. Based on your method information, you have frozen the sample portions prior to analysis, employed an extraction procedure (FA-QuEChERS) that keeps dithianon stable and have also added an ILIS at the beginning of the procedure to compensate for any errors during extraction, cleanup and measurement. Unfortunately, all this protective and compensatory measures could not compensate for the losses that occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
132	-2.8		**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost in the fridge over an extensive time period, considerable degradation most likely occurred. Your method information suggests that you have employed a methodology protective for dithianon (FA-QuEChERS) and that you have added an ILIS at the beginning of the procedure to compensate for any errors during extraction, cleanup and measurement. Unfortunately, these protective and compensatory measures could not compensate for the losses that had occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Dithianon Assigned value (informative only): 0.236 mg/kg, CV*: 38.1 %			
LabCode	z Score	Reason	Remarks/Details
3rd-68	-2.8	D	The sample was not frozen as we partially defrosted the sample to take a sub-sample. We were not aware of the clear advice that the sample should be extracted frozen. The assigned vale was based on a sub population of 40 where the sample was kept frozen. **Feedback and advices by the organisers**: Indeed defrosting the sample considerable degradation most likely occurred. Your method information is a bit ambiguous as you reported using the acetate buffered QuEChERS but other method details – ACN with 1 % formic acid as solvent and NaCl/ MgSO4 as partitioning salts –point towards the use of FA-QuEChERS. In any case, you have obtained good recoveries with this procedure. Unfortunately, any losses occurred prior to the actual analysis cannot be compensated afterwards. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
70	-2.5	J	**Feedback and advices by the organisers**: As the test sample was left to defrost on the bench over an extensive time period, dithianon degradation was most likely very extensive. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope. Furthermore, consider introducing an extraction procedure entail acidification to protect dithianon. This is particularly important for samples with low acidity and poor antioxidative potential.
80	-2.5		**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. Based on your method information "SA-QuEChERS", you have employed an extraction procedure that keeps dithianon stable. Unfortunately, these protective measures could not compensate for the losses that occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
90	-2.5	D	**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost in the fridge over an extensive time period, considerable degradation most likely occurred. Based on your method information "FA-QuEChERS", you have employed an extraction procedure that keeps dithianon stable. Unfortunately, all these protective measure could not compensate for the losses that had occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
128	-2.5	D	**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost degradation most likely occurred. The method you have used seems to deliver good recoveries. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
58	-2.2	D	For this analyte, only results of labs that kept the PT frozen until analysis were used to determine the assigned value. In our lab, the PT was defrosted over night in a refridgerator. This has possibly caused losses of the analyte. In the routine analysis, samples arrive at room temperature and are homogenized and tested usually on the day of arrival. **Feedback and advices by the organisers**: It seems that you have handled the test sample in a way similar to your routine practice, and that was "defroste". This is well understandable, as PTs should give an indication about the routine lab performance. The positive thing is that this PT has made you aware of how you currently handle samples in your routine, e.g. ambient milling and not freezing homogenates, which may affect certain susceptible analytes, such as dithianon. Of course, matrix type and duration of exposure also play a central role in this effect. Consider either adjusting your sample handling conditions by introducing cryogenic milling and frozen storage of homogenates. Alternatively, consider conducting experiments with different types of matrices to check how the analytes within your routine scope behave when spiked to non-frozen homogenates and left standing for a certain period of time reflecting your routine practice (quasi worst-case conditions). Analytes suffering considerable losses may need to be removed from your routine scope. Also consider introducing an extraction procedure entail acidification to protect dithianon. This is particularly important for samples with low acidity and poor antioxidative potential.
105	-2.2		**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost considerable degradation most likely occurred. Based on your method information, you have employed an extraction procedure (FA-QuEChERS) that keeps dithianon stable. Unfortunately, all this protective measure could not compensate for the losses that had occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Dithianon Assigned value (informative only): 0.236 mg/kg, CV*: 38.1 %			
LabCode	z Score	Reason	Remarks/Details
27	-2.1	G	a concentration of 0.180 mg/kg was found in a repeated measurement. **Feedback and advices by the organisers**: Your new result would have obtained a z score of -0.95. Leaving your sample to defrost, even for just one hour, has probably caused the degradation of dithianon, which is probably why your new result is still on the low site Leaving your analytical portion to be analyzed during the PT to reach room temperature prior to analysis has surely caused severe additional degradation, which led to the original result being questionable. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
41	-2.1	D	**Feedback and advices by the organisers**: see comments for lab 34
69	-2.1	D	The sample was extracted once thawed, this may be the main reason for the low recovery. **Feedback and advices by the organisers**: Indeed dithianon shows considerable degradation in defrosted homogenates. Based on your method information "SA-QuEChERS", you have employed an extraction procedure that keeps dithianon stable and have also added an ILIS at the beginning of the procedure to compensate for any errors during extraction, cleanup and measurement. Unfortunately, all these protective and compensatory measures could not compensate for the losses that occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
104	-2.1		**Feedback and advices by the organisers**: Dithianon shows considerable degradation in defrosted homogenates. As the test sample was left to defrost in the fridge over an extensive time period, considerable degradation most likely occurred. Based on your method information "FA-QuEChERS", you have employed an extraction procedure that keeps dithianon stable and have also added an ILIS at the beginning of the procedure to compensate for any errors during extraction, cleanup and measurement. Unfortunately, all this protective and compensatory measures could not compensate for the losses that had occurred prior to the actual analysis. If handling with non-frozen homogenates reflects your routine practice, consider either introducing cryogenic milling and cold storage of homogenates prior to extraction, or conducting experiments to check the influence of this practice on the stability of your target analytes. Analytes unacceptably affected may need to be removed from the routine scope.
48	2.1		**Feedback and advices by the organisers**: Thank you for this feedback. Please also refer to the comments made for LabCode 2 as regards the uncertainty of the assigned value.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Dithianon Assigned value (informative only): 0.236 mg/kg, CV*: 38.1 %			
LabCode	z Score	Reason	Remarks/Details
2	2.2	M	Knowing that Dithianon degradates quickly and losses may occur prior analysis, the laboratory kept the sample frozen and the analysis for Dithianon was carried out immediately after sample was received. In addition the use of the ILIS (Dithianon D4) corrected any method losses. Both factors contributed in submitting a higher result. We didn't identify any calculation/method errors, or errors that may occur by a bad dithianon standard, or even standard stability issue. Losses were identified from the recovery experiments as well as by the use of the ILIS internally in all sample portions. We are interested to know whether the same conlcusions have been made by other labs that used ILIS, therefore we would appreciate it if you could provide us with this information and their reported values. **Feedback and advices by the organisers**: Knowing that a large fraction of the labs have reported strongly underestimated results due to improper sample handling, and in order to avoid unnecessarily prompting corrective action in labs conducting proper analysis or falsely not informing labs that need to take action, it was decided not to use the robust mean of the entire result population as the AV. Instead, tentative z scores based on the robust mean of a sub-population of results submitted by labs reportedly employing sufficiently protective conditions for dithianon, especially prior to analysis. It is, however, conceivable that the tentative AV is still underestimated, e.g. because some labs may have not protected the homogenate to the extend indicated in the method information, or because of the moderate but signifficant degradation of dithianon during frozen storage of the test item (see stability test) leading to tentatively lower results when the analysis is done late within the PT-period. In this context, it should be also mentioned, that the average concentration of the homogeneity test was 0.206 mg/kg and thus also higher than the tentative AV used to calculate the z scores. Under different circumstances your result may have fallen within the acceptable z score range. In any case, it your statements suggest that you are well aware of the measures than need to be taken to protected dithianon from degrading. Still, it would be also reasonable to double -check the stability of the analytical standard as a possible error source, if not already done.
24	2.4	J	used too old calibration solutions (unfortunately used 3-month-old solutions, shelf life questionable, degradation in old solutions?). double re-measurement of the EUPT material with freshly prepared calibration solutions results in a dithianon content of 0.244 mg/kg and is thus almost exactly the value of the robust mean. **Feedback and advices by the organisers**: The stability of the standard probably depends on the type of solvent used as well as the exposure to light. In absence of reaction partners and light dithianon is quite stable. Standard degradation is a likely the source for overestimated results. It seems that you have taken measures to keep degradation during sample preparation low (use of SA-QuEChERS). Please also refer to the comments made for LabCode 2 as regards the uncertainty of the assigned value.
43	2.5	J, M	For dithianon I had first screening result and two parallel results from one measurement and results were within repeatability. I used rose grape for procedural matrixed matched calibration with internal standard dithianon-D4. I did not have any sample for quality control so I guessed that problem of poor performance should be with standard. Storage solution was prepared in february 2024, old one was compared against new one and difference was 1 %. I reanalysed sample but used white grape as matrix (no blank red grape) and my result was ok, 14.5.2024 – 0,196 mg/kg. I assume that problem was probably working standard solution, probably it is not stable 6 months. I will do experiment with stability and apply new procedure. **Feedback and advices by the organisers**: Thank you for this feedback. Please also refer to the comments made for LabCode 24 and LabCode 2 as regards the uncertainty of the assigned value.
7	3.3	J	Our solution is preserved in an acetone/acetonitrile mixture with acetic acid. We will study the conservation of this solution, buy an active ingredient from another supplier, remake our stock solution and compare it with the one used for the EUPT SRM19 analysis. **Feedback and advices by the organisers**: Indeed standard degradation is a likely source for overestimated results. It seems that you have taken measures to keep degradation during sample preparation low by acidifying during extraction with HCl.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Dithiocarbamates Reference value (informative only): 0.100 mg/kg			
LabCode	z Score	Reason	Remarks/Details
2	-4.0 (FN)	E	The LOQ of the applied method is 0.2 mg/kg, therefore it was not possible to detect concentrations less than 0.2 mg/kg. **Feedback and advices by the organisers**: Your reporting reflects the situation as is and from a quality control point of view your result wouldn't be judged as a false negative. However, in accordance with the rules of the EUPT General Protocol your result is to be penalized as your reporting limit is too high and not fit-for-purpose. As many MRLs for dithiocarbamates are set at low levels, there is a need to employ methods that are able to detect concentrations at 0.05 mg/kg. In the case of infant formulae and organic food even down to levels of 0.01 mg/kg. Consider changing or adjusting your methodology for being able to monitor lower concentrations of this analyte. The MRRL gives an orientation of the sensitivity expected for a particular analyte.
27	-4.0 (FN)	M	the concentration found was below our reporting limit (0.1 mg/kg) **Feedback and advices by the organisers**: From a quality control point of view your result wouldn't be judged as a false negative. However, in accordance with the rules of the EUPT General Protocol your result is to be penalized as your reporting limit is too high and not fit-for-purpose. As many MRLs for dithiocarbamates are set at low levels, there is a need to employ methods that are able to detect concentrations at 0.05 mg/kg. In the case of infant formulae and organic food even down to levels of 0.01 mg/kg. Consider changing or adjusting your methodology to be able to monitor lower concentrations of this analyte. The MRRL gives an orientation of the sensitivity expected for a particular analyte.
53	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also helps to localize the risk of false negatives. Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose.
104	-4.0 (FN)		**Feedback and advices by the organisers**: Your reporting reflects the situation as is and from a quality control point of view your result wouldn't be judged as a false negative. However, in accordance with the rules of the EUPT General Protocol your result is to be penalized as your reporting limit is too high and not fit-for-purpose. As many MRLs for dithiocarbamates are set at low levels, there is a need to employ methods that are able to detect concentrations at 0.05 mg/kg. In the case of infant formulae and organic food even down to levels of 0.01 mg/kg. Consider changing or adjusting your methodology for being able to monitor lower concentrations of this analyte. The MRRL gives an orientation of the sensitivity expected for a particular analyte.
108	-4.0 (FN)	D	see comments on Dithianon **Feedback and advices by the organisers**: Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also helps to localize the risk of false negatives. Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
46	-3.6	M	We performed another EIL at the same time on this molecule (BIPEA 19 H Pear) and the result was correct (z-score = -1.71). **Feedback and advices by the organisers**: Please note that there are various types of dithiocarbamates. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions. Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Dithiocarbamates Reference value (informative only): 0.100 mg/kg			
LabCode	z Score	Reason	Remarks/Details
9	-3.5	B	**Feedback and advices by the organisers**: From the information you have provided we cannot localize any obvious error-source. Nevertheless, please consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
50	-3.5		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
66	-3.4	D	We are undertaking follow-up actions and hope to be able to give more details until Monday 3 June in the survey about DTCs. **Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
3rd-116	-3.3		**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
28	-3.2	D	Rapid decomposition of DTC was observed in fine homogenized test samples during sample handling. Homogeneity of test sample was insufficient for 2 g test portions. **Feedback and advices by the organisers**: Experiments by the organizers did not showed only a moderate decomposition in the test item, which was spiked with metiram.
83	-3.2		**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
80	-3.1		**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
6	-3.0	D	Internal error in the sample thawing procedure, which resulted in losses of the compound before analysis. **Feedback and advices by the organisers**: As metiram was spiked, sample thawing didn't actually lead to a significant drop in the results of DTCs determined as CS2 according to our tests. Check for other sources of errors, such as the reaction conditions, the stability of the SnCl2 reagent and the calibration details. You are furthermore strongly encouraged to more diligently fill the method information as wrong information complicates the interpretation of the results. The use of dSPE with PSA in combination with headspace GC doesn't make any sense.
22	-3.0	C	In the reaction solution (Sn(II)chloride in HCl), a too small amount of HCl was added. **Feedback and advices by the organisers**: Indeed your reaction conditions seem to have been too weak. Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose.
13	-2.8	D	Degradation during defrosting. **Feedback and advices by the organisers**: From the experience of the organizers degradation during defrosting didn't play a decisive role, as the polymeric DTC-compound metiram was spiked and quite stable. Your reaction time or temperature might have been insufficient for this type of DTC.
21	-2.8	B	Reason as yet unclear. Problems with the conversion of the DTC to CS2 are suspected. It is possible that the samples in the agitator on the autosampler are not shaken sufficiently during the reaction. Further investigations will follow. Update: In the meantime, our method has been adapted on the basis of the EURL-SRM method (Analysis of residues of dithiocarbamate fungicides in low-oil content food of plant origin involving cleavage into carbon disulfide, partitioning into isooctane and measurement by GC-MS/MS or GC-ECD Version 3.1 (last update: June 2024). The concentration of tin(II)chloride was increased from 10 g/l to 15 g/l, the concentration of HCl was increased from 7 % to 12 % and the ratio of reagent to sample was increased from 6 ml/g to 10 ml/g. In addition, the reaction temperature was increased from 80 °C to 85 °C and the shaking-speed of the agitator was increased. The sample was analysed again and a DTC content of 0.0941 mg/kg was determined (n = 3, standard addition). It follows that the metiram contained in the sample was not completely converted to CS2 during the first measurement. **Feedback and advices by the organisers**: Thank you for the thorough and diligent investigation. This is a nice example of PTs helping to localize problems and triggering a solution-finding process, which in your case was also very successfull.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Dithiocarbamates Reference value (informative only): 0.100 mg/kg			
LabCode	z Score	Reason	Remarks/Details
58	-2.8	B	CS2 was measured by hydrolysis and partitioning into isooctane. Thiram was used for the standards, and the time for hydrolysis was 45 minutes. Newer versions of this method suggest 3 hours for the hydrolysis step (and other changes). Possibly this has resulted in insufficient hydrolysis of the Dithiocarbamate in the PT. Currently testing the effects of changes in our method and the hydrolysis step are ongoing. **Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher concersion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
3rd-120	-2.8		**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
54	-2.7	B, A	**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
63	-2.7		**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
114	-2.4	A	**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
3rd-10	-2.4	C	**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
79	-2.3		**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
92	-2.2		**Feedback and advices by the organisers**: Consider checking whether your reaction conditions would need an adjustment to ensure higher conversion yields to CS2. Better use polymeric dithiocarbamates for this purpose. Polymeric DTCs, such as the spiked metiram, are more difficult to break up and require stronger hydrolysis conditions.
31	3.4	M	The reason was not found yet. The method was checked (e.g. standard calculations, calibrations, processing of data), new standards were prepared and checked, and the sample was also reanalysed. The sample was kept frozen till analysis. Our measured concentration of reanalysed sample was still too high comparing to PreAV. **Feedback and advices by the organisers**: Check the way you prepare, store and handle the CS2 stock and working standards and check if the CS2 concentration is declining.
39	4.0		**Feedback and advices by the organisers**: Check the way you prepare, store and handle the CS2 stock and working standards and check if the CS2 concentration is declining.
4	4.5	I	**Feedback and advices by the organisers**: Check the way you prepare, store and handle the CS2 stock and working standards and check if the CS2 concentration is declining.
125	6.8		**Feedback and advices by the organisers**: Check the way you prepare, store and handle the CS2 stock and working standards and check if the CS2 concentration is declining.
44	14.4	L	**Feedback and advices by the organisers**: Check the way you prepare, store and handle the CS2 stock and working standards and check if the CS2 concentration is declining.

Ethephon Assigned value: 0.0582 mg/kg, CV*: 14.7 %			
LabCode	z Score	Reason	Remarks/Details
67	-4.0 (FN)	L, M	We determined the analyte ethephon at 0.0419 mg/kg. We didn't entere the concentration value found because it is lower than the LOQ of our method. **Feedback and advices by the organisers**: From a quality control point of view your result wouldn't be judged as a false negative. In fact your semi-quantitative result would have even obtained an acceptable z score. However, in accordance with the rules of the EUPT General Protocol your result is to be penalized as your reporting limit is too high and not fit-for-purpose. Consider changing or adjusting your methodology for being able to monitor lower concentrations of this analyte. The MRRL gives an orientation of the sensitivity expected for a particular analyte.
84	-4.0 (FN)	E, B G	The obtained result (below our RL 0.05 mg/kg) was 0.0434 mg/kg **Feedback and advices by the organisers**: Your reporting reflects the real situation and from a quality control point of view, your result wouldn't be judged as a false negative. In fact your semi-quantitative result would have even obtained an acceptable z score. However, in accordance with the rules of the EUPT General Protocol your result is to be penalized due to an insufficient performance as your reporting limit is too high and not fit-for-purpose. Consider changing or adjusting your methodology for being able to monitor lower concentrations of this analyte. The MRRL gives an orientation of the sensitivity expected for a particular analyte.
114	-4.0 (FN)	M	The instrument has been failed. It's a 13 year old instrument, the original pump had been broken. It wasn't work with the alternative pump. During the relevant samples were tested, the instrument LC-MS/MS was maintained by the service. Now this problem no longer exists. **Feedback and advices by the organisers**: see comments on clopyralid
3rd-123	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.
3rd-131	-4.0 (FN)	E, C J	**Feedback and advices by the organisers**: Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.
89	-2.4		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of ILIS is highly recommended. It becomes even more important if you chose to calibrate using a solvent-based calibration as in your case
107	2.4	A	**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of generic internal standards, including non matching ILISs, is always risky. If affected by matrix effects, these ISs can introduce bias to the results of all analytes.
31	6.0	F, I	Data processing method was corrected and the concentration of Ethephon was recalculated, giving good result (0.0653 mg/kg) **Feedback and advices by the organisers**: Your new result would have resulted in a z score of 0.5 and thus well within the acceptable range.
117	44.1	I	31.05.2024 Ethephon, after a thorough analysis of the analysis process, records and checking the conversion sheet, we found that the wrong conversion factor was used, the correct result is 0.070±0.035 As part of the activities, all spreadsheets for single methods PT were improved. **Feedback and advices by the organisers**: Your new result would have resulted in a z score of 0.7 and thus well within the acceptable range.

Folpet Assigned value: 0.225 mg/kg, CV*: 26.8 %			
LabCode	z Score	Reason	Remarks/Details
13	-4.0 (FN)	D, B	We do not analyze Folpet with chemical ionization, so it is degraded in the hot injection to Phthalimide. **Feedback and advices by the organisers**: Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector. Also consider introducing phthalimide in your acquisition method as this compound is valuable indicator for a folpet-treatment history (albeit not specific for folpet).

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Folpet Assigned value: 0.225 mg/kg, CV*: 26.8 %			
LabCode	z Score	Reason	Remarks/Details
58	-4.0 (FN)	D	Our result for Phthalimid was 0.225 mg/kg. Conversion to Folpet results in 0.454 mg/kg Folpet (sum). This result is relatively close to the target value 0.421 mg/kg (the z-score would be close to 0.4). This suggests a full degradation of Folpet to Phthalimide under the conditions of our GC-MS-MS. The Residue definition for Folpet uses the sum, the individual components do not have individual MRLs. The current method (that converts Folpet to Phthalimid) can be used to detect and measure Folpet (Sum). **Feedback and advices by the organisers**: Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector. Your result for phthalimide was very high indicating a quasi quantitative conversion of folpet within the GC injector. Phthalimide is actually a valuable indicator for a folpet-treatment history (albeit not specific for folpet) and its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.
72	-4.0 (FN)	M	We report folpet according to the pesticide residue definition and not individually due to quantification problems of folpet and pthalimide in the GC-MS/MS determination. The Z-Score of folpet sum is correct. **Feedback and advices by the organisers**: You are of course free to chose which analytes you would like to cover in a PT. Still reporting should accurately reflect the analyses conducted and the results obtained. If you have analyzed for PI without detecting it, the negative result and the FN judgement is appropriate. If you haven't analyzed for PI but had wrongly reported it as analyzed, then this would be an error in reporting. In risk asessment both would lead to wrong calculations and conclusions. The same applies to folpet. If you analyze for a compound but do not want to report a result, then better mark it as “not analyz” to avoid the FN penalty.
80	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector. Your result for phthalimide was very high indicating a quasi quantitative conversion of folpet within the GC injector. Phthalimide is actually a valuable indicator for a folpet-treatment history (albeit not specific for folpet) and its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.
111	-4.0 (FN)	D, E	**Feedback and advices by the organisers**: Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector. Your result for phthalimide was very high indicating a quasi quantitative conversion of folpet within the GC injector. Phthalimide is actually a valuable indicator for a folpet-treatment history (albeit not specific for folpet) and its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Folpet Assigned value: 0.225 mg/kg, CV*: 26.8 %

LabCode	z Score	Reason	Remarks/Details
114	-4.0 (FN)	A	**Feedback and advices by the organisers**: Unfortunately you didn't provide any details on your follow-up actions. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector.Your result for phthalimide was very high indicating a quasi quantitative conversion of folpet within the GC injector. Phthalimide is actually a valuable indicator for a folpet-treatment history (albeit not specific for folpet) and its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.
125	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. According to your method information you have employed ILIS, which was added at the beginning of the procedure. This ILIS should have also experienced losses to give you a hint for the extensive loss of folpet at any stages following its addition. As you have left your sample to defrost in the fridge over a long period of time, losses of folpet at this stage most likely occurred, with their extent depending on the exposure time. The use of a very long extraction time (120 min) has surely also contributed to folpet losses if any of it was left. Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector. Your result for phthalimide was strangely also very low. In any case, phthalimide is actually a valuable indicator for a folpet-treatment history (albeit not specific for folpet) and its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.
137	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector. Your result for phthalimide was very high indicating a quasi quantitative conversion of folpet within the GC injector. Phthalimide is actually a valuable indicator for a folpet-treatment history (albeit not specific for folpet) and its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.
3rd-123	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector. Also consider introducing phthalimide in your acquisition method as this compound is valuable indicator for a folpet-treatment history (albeit not specific for folpet).
3rd-139	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector.Also consider introducing phthalimide in your acquisition method as this compound is valuable indicator for a folpet-treatment history (albeit not specific for folpet).
94	-3.3		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. The fact that you have also underestimated the degradant pthalimide makes it difficult to interpret your results. On the other hand the methods you indicated using for phthalimide (FA-QuEChERS) and folpet (possibly QuEChERS with dSPE entailing PSA and solvent exchange) do not match together, which also means that losses of folpet haven't necessarily resulted in an increase of phthalimide. Check for a systematic error affecting more compounds as well as on whether matrix effects may have played a role. You have kept your sample frozen but left the analytical portions to reach room temperature. Some folpet losses may have occurred at this stage if this exposure was extensive. Consider also checking whether the use of PSA in dSPE has contributed to the folpet losses.
96	-3.3		**Feedback and advices by the organisers**: Unfortunately you didn't provide any details on your follow-up actions. Looking at your methodology data you have employed conditions that were not protective to folpet, such as leaving the test sample to defrost over an extended period in the fridge, the extensive extraction time of 60 min and use of dSPE with PSA. Your result for phthalimide was not increased, but you indicate the use of a different exctraction time (5 min) for this analyte, which means that folpet losses at a certain stage during extraction or cleanup of the sample portion used for folpet analysis didn't necessarily affect the result for phthalimide.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Folpet Assigned value: 0.225 mg/kg, CV*: 26.8 %			
LabCode	z Score	Reason	Remarks/Details
107	-2.7	D, B	Fopet was analyzed by gas chromatography, and the degradation product (phthalimide) was not quantified. **Feedback and advices by the organisers**: Please note that the degradation of folpet in the hot injector can be compensated by a suitable calibration approach such as matrix-matching, standard additions to extract aliquots and the use of ILIS. Looking at your methodology data you have employed conditions that were not protective to folpet, such as leaving the test sample to defrost over an extended period in the fridge, and the use of dSPE with PSA. As you haven't analyzed for phthalimide, no correlation between the two can be made.
6	-2.4	D, B	By mistake, these parameters will not be analyzed by the specific method (HPLC). The parameters were analyzed by GC, so it is not possible to quantify them separately correctly. **Feedback and advices by the organisers**: In principle both LC and GC methods may create accurate results for folpet as long as certain aspects are taken into account. Folpet parent is more sensitively analyzed by GC, but matrix effects need to be taken into account. LC-MS/MS analysis is less sensitive for folpet. Employing dSPE with PSA may have contributed to some losses for folpet although it is not clear whether you have employed citrate buffered QuEChERS or some variation, as you indicated ACN with 1 % FA as solvent,
117	-2.1	I	31.05.2024 Folpet, after a thorough analysis of the analysis process, records and checking the conversion sheet, we found that the wrong conversion factor was used, the correct result is 0.205±0.103 As part of the activities, all spreadsheets for single methods PT were improved. **Feedback and advices by the organisers**: Your new result would have resulted in a z score of -0.4 and thus well within the acceptable range. The conduction of dSPE cleanup with PSA may have contributed to folpet losses, especially if re-acidificiation was delayed.
33	2.4	D, B	**Feedback and advices by the organisers**: Consider checking the stability of your analytical standard as well as whether the matrix effects were properly compensated during measurement . Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector.
89	2.6		**Feedback and advices by the organisers**: Unfortunately you didn't provide any details on your follow-up actions. Consider checking the stability of your analytical standard as well as whether the matrix effects were properly compensated during measurement . Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector.
39	3.5		**Feedback and advices by the organisers**: Unfortunately you didn't provide any details on your follow-up actions. Consider checking the stability of your analytical standard as well as whether the matrix effects were properly compensated during measurement . Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector.
65	6.1	A, D B	Instrument anomoly, when sample was reextracted 0.29 mg/kg was obtained. APGC is a new technolgy used by the laboratory. **Feedback and advices by the organisers**: In case of overestimated results for folpet the stability of the folpet standard, which is often problematic, is something to look at. Nevertheless, as you have employed the same analytical standard for the new analysis, it is unlikely that this aspect had an impact.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Folpet Assigned value: 0.225 mg/kg, CV*: 26.8 %			
LabCode	z Score	Reason	Remarks/Details
115	7.0		**Feedback and advices by the organisers**: Unfortunately you didn't provide any details on your follow-up actions. Consider checking the stability of your analytical standard as well as whether the matrix effectswere properly compensated during measurement . Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider using analyte protectants to moderate degradation within the injector.
15	13.5		**Feedback and advices by the organisers**: You may need to check the stability of your analytical standard. ACN often needs acidification to ensure folpet stability.

Folpet (sum) Assigned value: 0.421 mg/kg, CV*: 18.4 %			
LabCode	z Score	Reason	Remarks/Details
15	-4.0 (FN)		**Feedback and advices by the organisers**: As you have detected both folpet and phthalimide, reporting a FN result for the sum seems to be paradox. Your result for Folpet was too high, whereas your PI result was a FN. Consider checking if you have misinterpreted the folpet peak as being PI. Folpet is very sensitive to degradation in the hot GC-injector (especially if the liner is dirty), and in the case of quasi quantitative conversion phthalimide is the predominant or only peak seen. Consider using analyte protectants to moderate degradation within the injector.
58	-4.0 (FN)	M	Our result for Phthalimid was 0.225 mg/kg. Conversion to Folpet results in 0.454 mg/kg Folpet (sum). This result is relatively close to the target value 0.421 mg/kg (the z-score would be close to 0.4). This suggests a full degradation of Folpet to Phthalimide under the conditions of our GC-MS-MS. The Residue definition for Folpet uses the sum, the individual components do not have individual MRLs. The current method (that converts Folpet to Phthalimid) can be used to detect and measure Folpet (Sum). **Feedback and advices by the organisers**: As you have detected phthalimide and have targeted folpet, reporting a FN result for the sum seems to be paradox. Your result for PI was too high, whereas that for folpet was a FN. Folpet is very sensitive to degradation in the hot GC-injector (especially if the liner is dirty), and in the case of quasi quantitative conversion phthalimide is the predominant or only peak seen. Consider introducing using analyte protectants to moderate degradation within the injector. Phthalimide is actually a valuable indicator for a folpet-treatment history (albeit not specific for folpet) and its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.
3rd-112	-4.0 (FN)	F	**Feedback and advices by the organisers**: Unfortunately you didn't provide any details on your follow-up actions. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. Folpet is very sensitive to degradation in the hot GC-injector, especially if the liner is dirty. Consider introducing the use of analyte protectants to moderate degradation within the injector. Your result on phthalimide was strangely also false negative. One would expect phthalimide to be overestimated if degradation in the GC injector was so strong to lead to a FN result. In any case, consider that phthalimide is a good indicator for a folpet-treatment history (albeit not specific for folpet) and that its detection should trigger a reanalysis under conditions more protective for folpet if this analyte is part of the analytical scope.
94	-3.2		**Feedback and advices by the organisers**: Please also consider the comments on folpet
125	-3.0		**Feedback and advices by the organisers**: Please also consider the comments on folpet
96	-2.1		**Feedback and advices by the organisers**: Please also consider the comments on folpet
39	2.7		**Feedback and advices by the organisers**: Please also consider the comments on folpet
3	2.9		The participants comments can be found under phthalimide **Feedback and advices by the organisers**: The high result of folpet (sum) is mainly due to the highly overestimated result for folpet (sum).
115	5.8		**Feedback and advices by the organisers**: Please also consider the comments on folpet
6	6.3	D, B	By mistake, these parameters will not be analyzed by the specific method (HPLC). The parameters were analyzed by GC, so it is not possible to quantify them separately correctly. **Feedback and advices by the organisers**: see comments on folper and phthalimide
3rd-116	9.3		**Feedback and advices by the organisers**: Although you have not submitted any results for folpet or phthalimide you have reported a result for the sum. You indicate that you have calibrated with phthalimide so we assume that you have observed a quasi complete loss of folpet in the GC. In such cases, the results should be normally underestimated as the conversion of folpet to phthalimide in GC is not quantitative. Check again your measurement conditions.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Lambda-Cyhalothrin Assigned value (informative only): 0.0773 mg/kg, CV*: 20.5 %

LabCode	z Score	Reason	Remarks/Details
89	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.
94	-3.3		
3rd-139	-2.2		
All but ID 25	–		**Feedback and advices by the organisers**: Using conventional (non-enantioselective) chromatography you have essentially determined the sum of the constituent isomers of lambda-cyhalothrin. For being able to distinguish between gamma-cyhalothrin and its enantiomer, and for being able to quantify the latter, chiral chromatography needs to be employed. Consider reading the residue definition within the TPL more carefully.

Glufosinate not present in the test material

LabCode	Judgement	Reason	Remarks/Details
72	FP	C	Our usual glufosinate determination method has LC 0.05 mg/kg, we are testing a different method with LC 0.01 mg/kg and carry-over of glufosinate has occurred and a false positive was obtained. **Feedback and advices by the organisers**: Consider introducing quality control measures that would help recognise potential false positive results, such as the analysis of blanks, the comparison of (relative) retention time, mass transition signal ratios and peak shape with those of an analytical standard, Checking cross-contaminantions and carry-over effects also help to detect false positive potentials. Overspikes with the analyte and comparison with the corresponsing ILIS (in terms of retention time and peak shape) also provide usefull hints. If ILIS is used checking for cross-contaminantion is helpfull. N-acetyl glufosinate ILIS marked on the acetyl group can potentially deacetylate to native glufosinate leading to a false positive result. Based on your information on N-acetyl glufosinate you do not seem to have used this particular ILIS.

Mepiquat chloride not present in the test material

LabCode	Judgement	Reason	Remarks/Details
114	FP	M	The instrument has been failed. It's a 13 year old instrument, the original pump had been broken. It wasn't work with the alternative pump. During the relevant samples were tested, the instrument LC-MS/MS was maintained by the service. Now this problem no longer exists. **Feedback and advices by the organisers**: see comments on chlormequat chloride

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Meptyldinocap Assigned value (informative only): 0.086 mg/kg, CV*: 29.6 %			
LabCode	z Score	Reason	Remarks/Details
125	-4.0 (FN)		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59. The defrosting of the sample over the weekend together with the very long extraction time of 120 min may have contributed to a degradation of meptyldinocap.
3rd-139	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. Meptyldinocap is very sensitive to degradation and the analytical standard solutions may need to be protected by acidification. Strangely you have reported using the hydrolysis method for meptyldinocap and FA-QuEChERS for meptyldinocap (sum). If this was the case intact meptyldinocap would not be found after hydrolysis and this would explain the false negative.
23	-3.4	D	strong amount seems provide from meptyldinocap degradation in DNOP at an unknown analytical step (amount dnop+meptyldinocap is good) **Feedback and advices by the organisers**: At first sight it looks as if a degradation of meptyldinocap to 2,4-DNOP took place in your sample or extract. Looking at your method information the only indication in this direction would be the cleanup by PSA. In case of a delayed reacidification this step may lead to a relevant degradation of meptyldinocap to 2,4-DNOP. Please also check the comments on metyldinocap and 2,4-DNOP made for LabCode 59.
42	-3.0	A	No reason highlighted : sample analysed 3 times and always the same results. All control criteria are good (recoveries, linearity…). Problem of multiresiue analysis versus extraction with hydrolysis? **Feedback and advices by the organisers**: Looking at your method information there are no clear indications that would explain this underestimation of both 2,4-DNOP and meptyldinocap. Please check the comments on metyldinocap and 2,4-DNOP made for LabCode 59.
3rd-116	33.2		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.
46	47.2	G	The quantification was done with an expired active substance. We were waiting for the delivery of the new active substance which arrived in the lab after the end of EUPT. The result of the new quantification is 0,191 mg/kg. It is acceptable **Feedback and advices by the organisers**: Indeed standard degradation is a common problem with meptyldinocap. Acidification helps to improve standard stability in ACN. Please check the comments on metyldinocap and 2,4-DNOP made for LabCode 59.
59	56.5		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Meptyldinocap is very sensitive to degradation and the analytical standard solutions may need to be protected by acidification. This may lead to overestimated results. Please also check whether you have misallocated the 2,4-DNOP peak to meptyldinocap. The two compounds share the same mass transitions due to in-source fragmentation of meptyldinocap in the LC-MS ion source. Meptyldinocap standards always contain some percentage of 2,4-DNOP impurities. If not protected, standard solutions of meptyldinocap may degrade further to 2,4-DNOP. The peaks elute close of each other and in some case (when separation is not fast) they even partly coelute. As 2,4-DNOP is much more sensitive than meptyldinocap its peak becomes larger than that of meptyldinocap even at a small share (e.g. 3-5 %) within the meptyldinocap standard. With the small-share impurity of 2,4-DNOP being regarded as meptyldinocap the 2,4-DNOP peak in the sample, which is mistakenly assumed to be meptyldinocap is strongly overestimated. This situation for example occurs when meptyldinocap is injected as an individual standard.
6	87.2	M	By mistake, these parameters will not be analyzed by the specific method (HPLC). The parameters were analyzed by GC, so it is not possible to quantify them separately correctly. **Feedback and advices by the organisers**: Indeed GC-MS is not the method of choice for meptyldinocap due to its tendency to degrade. Nevertheless, overestimations of meptyldinocap concentration may also originate from a degrated analytical standard. Please check also this aspect, keeping in mind that acidification is typically needed to reduce degradation. You are furthermore strongly encouraged to more diligently fill the method information as wrong information complicates the interpretation of the results. Under method information for example you indicated that you have employed LC-MS/MS in contrast to the information given here. You also indicated employing citrate buffered QuEChERS for analysis although other submitted information points towards the use of FA-QuEChERS (1 % formic acid). Should you have used LC-MS/MS in parallel peak mismatching between the parent and the much more sensitive daughter compound may have been a source of error to look to (see other comments on meptyldinocap).
137	112.3		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.
80	132.7		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Meptyldinocap (sum, calculated) Assigned value (informative only): 0.150 mg/kg, CV*: 23.4 %

LabCode	z Score	Reason	Remarks/Details
59	-4.0 (FN)		**Feedback and advices by the organisers**: As you have detected meptyldinocap, reporting FN for the calculated sum as well as for the sum following hydrolysis seems strange. You could have reported not analyzed for the "sum following hydrolysis" if you haven't conducted the hydrolysis. For the calculated sum you could have also reported not analyzed if you were not sure how to deal with the negative result for 2,4-DNOP. See also our comments on 2,4-DNOP and meptyldinocap.
3rd-139	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives. Meptyldinocap is very sensitive to degradation and the analytical standard solutions may need to be protected by acidification. Strangely, you have reported using the hydrolysis method for meptyldinocap and FA-QuEChERS for meptyldinocap (sum). As you have already reported a result for the free DNOP it is paradox that you have reported a false negative for the sum.
42	-2.6	A	No reason highlighted : sample analysed 3 times and always the same results. All control criteria are good (recoveries, linearity…). Problem of multiresiue analysis versus extraction with hydrolysis? **Feedback and advices by the organisers**: Please check the comments on metyldinocap and 2,4-DNOP
97	6.7		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.
46	25.3	L	The analysis was carried out in duplicate. The values obtained were 0.13 and 0.095 which correspond to z-scores of 1.81 and 0.49 with a CV of 32.4 %. So it's acceptable to us. **Feedback and advices by the organisers**: Please check the comments on metyldinocap and 2,4-DNOP
80	43.7		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.

Meptyldinocap (sum, following hydrolysis
Assigned value (informative only): 0.188 mg/kg, CV*: 30.9 %

LabCode	z Score	Reason	Remarks/Details
59	-4.0 (FN)		**Feedback and advices by the organisers**: See comments under "Meptyldinocap (sum, calculated)"
3rd-139	-2.1		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.as well the comments on your result for "Meptyldinocap (sum, calculated)"
13	3.0	M	We really quantify 2,4-DNOP, employing NH4OH, as indicated in the EURL-SRM. The addition of NH4OH was done in vialization step and the result with NH4OH was higher (but outside correct zscore) than without NH4OH. **Feedback and advices by the organisers**: We cannot localize any particular source of error. Make sure that peak allocation is correct as meptyldinocap and DNOP share the same mass transitions in LC-MS/MS. This regarding please also refer to the organiser comments on meptyldinocap for LabCode59
23	6.5	A	**Feedback and advices by the organisers**: The overestimation of 2,4-DNOP and of meptyldicocap (sum after hydrolysis) points towards a possible systematic error with the 2,4-DNOP standard. Please also check the comments on metyldinocap and 2,4-DNOP that were made for LabCode 59
97	13.9		**Feedback and advices by the organisers**: see comments for meptyldinocap for LabCode 59.
8	17.7	E, F	we have noticed that there was insufficient seperation between the phenol and meptyldinocp itself leading to errors in the calculation of the concentration. We have adapted our gradient and relauncehd the ring test : results are 37 ppb for the Phenol , 63 ppb for the meptyldinocpa and 108 ppb for the calculated sum, Z-scores are acceptable with this new results. **Feedback and advices by the organisers**: Congratulations for tracing back the error source and successfully adapting your methodology acoordingly. Indeed, in LC-MS/MS chromatographic separation between meptyldinocap and the DNOP is essential, as both have the same mass transitions due to the in-scource fragmentation of meptyldinocap to DNOP.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

MPP (=aka MPPA) Assigned value: 0.0819 mg/kg, CV*: 22.8 %			
LabCode	z Score	Reason	Remarks/Details
60	-4.0 (FN)	E, M	The reported RL (0.010 mg/kg) is incorrect. The true RL is 0.080 mg/kg due to a lack of sensitivity. **Feedback and advices by the organisers**: A RL of 0.08 better explains your FN result. However as you were not able to detect the analyte with an AV of 0.0819 suggests that your now reported RL might still be uncertain. It is always better setting the RLs conservatively to cover such situations also given the fact that analytical performance fluctuates. Following the rules of the EUPT General Protocol your result is still to be penalized as your reporting limit is too high and not fit-for-purpose. Consider changing or adjusting your methodology for being able to monitor lower concentrations of this analyte.
127	-4.0 (FN)	L	**Feedback and advices by the organisers**: Unfortunately, you didn't provide any details on the nature of the transcription error. Was this analyte erroneously marked as analyzed or did you fail to report that it was detected and the concentration determined?
3rd-112	-4.0 (FN)	A, L	This is not a routine analyte screened in our lab and we do not have the reference material for the time being. The reporting staff has failed to choose that this analyte is not being screened while submitting the results. Reference material has now been ordered and this analyte might be added as a routine screening anayte in the future. **Feedback and advices by the organisers**: We would like to highlight the possibility of creating an excel-file with the data to be reported to facilitate checking the data prior to submitting the results.
3rd-139	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.
137	-2.5		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of generic internal standards (including non matching ILISs) is always risky. If affected by matrix effects these ISs can introduce bias to the results of all analytes.
73	2.3		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of ILIS is highly recommended. Standard addition to sample portions is to be preferred over procedural calibration especially as in the QuPPe methods different matrices of the same type may exhibit different matrix effects.
23	2.4	G, A	No ILIS available in the lab (Glyphosate 13C was used) **Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of generic internal standards (including non matching ILISs) is always risky. If affected by matrix effects these ISs can introduce bias to the results of all analytes.
125	2.8		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of generic internal standards (including non matching ILISs) is always risky. If affected by matrix effects these ISs can introduce bias to the results of all analytes.
65	4.0	F	Incorrect peak was used in measurement. 0.060 mg/kg was the estimated result when correct peak was selected. **Feedback and advices by the organisers**:Your new result would have resulted in a z score of -1.1 and thus within the acceptable range.
92	5.8		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of ILIS is highly recommended.
100	6.7		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of ILIS is highly recommended. Standard addition to sample portions is to be preferred over procedural calibration especially as in the QuPPe methods different matrices of the same type may exhibit different matrix effects.
117	32.2	I	31.05.2024 MPP, after a thorough analysis of the analysis process, records and checking the conversion sheet, we found that the wrong conversion factor was used, the correct result is 0.074±0.037 As part of the activities, all spreadsheets for single methods PT were improved. **Feedback and advices by the organisers**: Your new result would have resulted in a z score of -0.4 and thus well within the acceptable range.
97	35.2		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of ILIS is highly recommended.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

N-Acetyl glufosinate Assigned value: 0.0773 mg/kg, CV*: 21.9 %			
LabCode	z Score	Reason	Remarks/Details
52	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.
78	-4.0 (FN)	G	**Feedback and advices by the organisers**: Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.
124	-4.0 (FN)		**Feedback and advices by the organisers**: Unfortunately, you didn't provide any feedback on this issue. Consider introducing quality control measures that would help recognise potential false negative results, including recoveries and injection of analyte standards at the RL. Overspikes with the analyte and using the corresponding ILIS also help to localize the risk of false negatives.
132	-4.0 (FN)		**Feedback and advices by the organisers**: From a quality control point of view your result wouldn't be judged as a false negative as the assigned value was lower. However, according to the rules of the EUPT General Protocol your result is to be penalized as your reporting limit is too high and not fit-for-purpose. Consider changing or adjusting your methodology for being able to monitor lower concentrations of this analyte. The MRRL gives an orientation of the sensitivity expected for a particular analyte.
3rd-112	-4.0 (FN)	A, L	This is not a routine analyte screened in our lab and we do not have the reference material for the time being. The reporting staff has failed to choose that this analyte is not being screened while submitting the results. Reference material has now been ordered and this analyte might be added as a routine screening anayte in the future. **Feedback and advices by the organisers**: See our comments on MPP
137	2.2		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of generic internal standards (including non matching ILISs) is always risky. If affected by matrix effects these ISs can introduce bias to the results of all analytes.
22	2.9	A, M	As internal standard, a standard of labelled glufosinate in stead of labelled N-acetyl glufosinate was used. **Feedback and advices by the organisers**: If methods strongly affected by matrix effects, the use of generic internal standards (including non matching ILISs) is always risky. If affected by matrix effects, these ISs can introduce bias to the results of all analytes.
100	3.9		**Feedback and advices by the organisers**: If methods strongly affected by matrix effects, the use of ILIS is highly recommended. Standard addition to sample portions is preferred to procedural calibration, particularly given that different matrices of the same type may exhibit different matrix effects in QuPPe methods.
39	5.3		**Feedback and advices by the organisers**: In methods strongly affected by matrix effects the use of ILIS is highly recommended. Based on your method information it is not clear if you have used one as you mention a D4 marking, which does not exist for glufosinate
117	59.5	I	31.05.2024 N-Acetyl glufosinate, after a thorough analysis of the analysis process, records and checking the conversion sheet, we found that the wrong conversion factor was used, the correct result is 0.123±0.061 As part of the activities, all spreadsheets for single methods PT were improved. **Feedback and advices by the organisers**: Your new result would have resulted in a z score of 2.4 which is still outside the acceptable range.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Phthalimide Assigned value (informative only): 0.0820 mg/kg, CV*: 32.4 %			
LabCode	z Score	Reason	Remarks/Details
15	-4.0 (FN)		**Feedback and advices by the organisers**: Degradation of folpet during injection is common. Quality control measures should be such to reveal any potential FN results. Consider introducing such measures, e.g. injection of folpet standard solution or use of a folpet ILIS. The presence of the marker compound PI, combined with the knowledge about the extensive degradation of folpet, should have given you a hint for additional tests to exclude a FN result.
72	-4.0 (FN)	M	We report folpet according to the pesticide residue definition and not individually due to quantification problems of folpet and pthalimide in the GC-MS/MS determination. The Z-Score of folpet sum is correct. **Feedback and advices by the organisers**: see comment on folpet.
3rd-112	-4.0 (FN)	A, L	This is not a routine analyte screened in our lab and we do not have the reference material for the time being. The reporting staff has failed to choose that this analyte is not being screened while submitting the results. Reference material has now been ordered and this analyte might be added as a routine screening anayte in the future. **Feedback and advices by the organisers**: See our comments on MPP
94	-3.0		**Feedback and advices by the organisers**: Please also consider the comments on folpet
47	2.1		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
46	2.3	G, D	The quantification was done with an expired active substance. We were waiting for the delivery of the new active substance which arrived in the lab after the end of EUPT. **Feedback and advices by the organisers**: Phthalimide is quite stable and we do not expect that overestimated result is related to the degradation of the standard. Please also consider the comments on phthalimide to LabCode 13.
59	2.3		**Feedback and advices by the organisers**: Your overestimated result despite the use of LC-MS/MS is unusual. Unfortunately you haven't provided any feedback on the sources of this error. A degradation of folpet during sample preparation might have taken place, which resulted in your rather low result for folpet. Please also check whether matrix effects may have contributed to the biased result.
113	2.3	I	**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
95	2.4		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
45	2.6	M, D	The validation procedure was only finished in 08.04.2024 **Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
102	2.7	M	After checking our results we find no inconsistencies since our results were all the time in this range. Our experiments were carried out under propper circumstances with fresh liner so we could avoid the transformation of Folpet in Phtahlimid. The result of Folpet Summe was correct so we cannot find a reason to explain this deviation. **Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
39	2.8		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
50	2.8		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
3rd-10	2.8	J	**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
20	2.9	D, B	GC measurement of Phtalimide and calculation with SRM-07-ExtCal **Feedback and advices by the organisers**: We cannot localize any particular source of error based on the information provided. Degradation in the sample prior to extraction should not have played a role based on pre-experiments by the organiser. Also your result for folpet was not overestimated (as ILIS was added to an aliquot there was no correction for recovery only for measurement variability). You may check if phthalimide was expressed as folpet rather than as such. Also consider introducing measurement via LC-MS/MS.
31	2.9	E, D	Slight interference in blank matrix background and maybe also slightly dirty GC-liner. The PT-sample was reanalysed using clean liner, giving better result for Phtalimide (0.102 mg/kg). **Feedback and advices by the organisers**: The thermal decomposition of folpet within the GC injector during injection is responsible for overestimated PI results. The extent of this effect depends on the condition of the liner (and the protecting effect of the matrix). Reducing decomposition by employing a less active liner will reduces the analytical bias. Your explanation seems therefore plausible. Please also consider the comments on phthalimide to LabCode 13.
79	2.9		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

A: Lack of experience; **B:** Analytical procedure was inappropriate (e. g. hydrolysis conditions too weak; recovery too low; sensitivity too poor, RL < AV); **C:** Analytical procedure was appropriate, but not properly performed (e. g. important component, e. g. water, not used, extraction time too short/long); **D:** Analyte losses during the procedure (e. g. due to degradation, unfavorable partitioning, adsorption); **E:** Measurement problems (e. g. poor chromatographic separation, poor sensitivity, signal interfered by matrix); **F:** Misinterpretation / Misevaluation of measurement data / Misunderstanding of the target pesticide; **G:** Inappropriate / erroneous calibration approach (e. g. matrix effects not properly compensated); **H:** Result not properly corrected for recovery; **I:** Calculation error (e. g. use of wrong factor to express residue as required in PT or to address dilutions etc.); **J:** Erroneous analytical standard (e. g. due to degradation, wrong purity, wrong dilution); **K:** Deficient QC-measures that would have helped to recognize that method generates FNs, FPs or strongly biased results (e. g. no recovery test); **L:** Transcription- / documentation-/ communication-/ error; **M:** other reason.

Phthalimide Assigned value (informative only): 0.0820 mg/kg, CV*: 32.4 %			
LabCode	z Score	Reason	Remarks/Details
99	3.0		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
92	3.5		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
28	3.7	I	Wrong conversion factor to express residues was used (multiplying the value instead of dividing). **Feedback and advices by the organisers**: Phthalimide was supposed to be expressed as such. No factor involved. In this case your result would be 0.078, which is very close to the preAV.
30	4.0	G, D	Result 0,165 mg/kg was calculated using matrix-matched calibration prepared from blank white grapes (i.e. different matrix when compared to EUPT sample). When preliminary report was distributed, repeated analysis of phtalimide by standard addition to EUPT sample extract was performed in our laboratory. Using this approach we achieved result for phtalimide 0,081 mg/kg. **Feedback and advices by the organisers**: Folpet degradation in the injector is matrix dependent, and it cannot be excluded that differences in matrix effects have caused analytical bias. Standard addition (we assume with PI) is not the way to go as the bias caused by the PI generated from folpet during injection will not be eliminated. Please also consider the comments on phthalimide to LabCode 13.
134	4.2	H	The result from GC-QQQ (original phthalimide + breakdown from folpet) was corrected with the recovery factor for phthalimide determined from spiking only phthalimide. This lead to an overcorrection, as the breakdown from folpet to phthalimid in the GC inlet should have been excluded from the correction for recovery. After exluding this breakdown, the corrected value was assigned at 0.113. **Feedback and advices by the organisers**: Thank you for this valuable and reinforcing feedback. Please also consider the comments on phthalimide to LabCode 13.
137	4.3		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
111	4.4	A, D B	In our method (Quechers + GC-MS/MS measurement), Folpet is not detected (fully transformed to its metabolite phthalimide), that could explain our overestimation for phthalimide but a good value for folpet sum
13	4.8	D, B (Leer)	As Folpet is degraded in the hot injection to Phthalimide, we have measured Phthalimide (itself spiked) puls Phthalimide (from Folpet degradation in the injector). **Feedback and advices by the organisers**: We agree with your judgement. Consider introducing measurement or calibration procedures in which the quantification of PI is not affected by the presence of folpet. Unlike in GC, in LC folpet does not convert to PI during injection and allows for accurate quantification of PI in the presence of excess amounts of the parent. Where GC is used, the PI share generated during injection (due to thermal degradation) should be deducted to avoid that the PI originally present in the sample/extract is overestimated. Such an approach is described in SRM-07 with a "Supporting Excel Sheets on SRM-07" available for convenient calculations.
34	4.8	D, E	According to the results of the various laboratories, the quantification of phthalimide reported by the GC MS/MS technique is always higher than the expected result. Additionally, the test was also carried out using the LC MS/MS technique, obtaining the expected result. However, phthalimide is not accredited by LC MS/Ms, so the result obtained by GC MS/MS was reported. **Feedback and advices by the organisers**: Thank you for the valuable and reinforcing feedback. We hope that you can use your LC-MS/MS to support the accreditation of this approach. A flexible accreditation would indicated.

Appendix 7 (cont.) Possible Reasons for Poor Performance (ordered by z-scores)

Phthalimide Assigned value (informative only): 0.0820 mg/kg, CV*: 32.4 %			
LabCode	z Score	Reason	Remarks/Details
130	5.5	B, D	In the presece of Folpet, phthalimide can not be quantified by this method. The unacceptable result is due to the fact that Folpet has decomposed into phthalimide in the GC Injector. **Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
3rd-68	5.5	D, B	The analysis was carried out by GC. As we don't have an LCMS method in place for this compound. The report used 16 results generated by labs using LC-MS to calculate robust mean. **Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13. We would like to emphasise that your result would still have been unacceptable even if we had chosen to use the robust mean value of the entire population as the AV. Please also consider the comments on phthalimide to LabCode 13.
114	5.8	A, D B	**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
115	6.0		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
3	6.2	D, B	During a second analytical session, the regression line was redone only for Phthalimide and the already extracted grape sample was analyzed, without repeating the extraction, obtaining on the same extract, previously analyzed, a result equal to 0.210 mg/Kg. The accuracy of the second source control, in the second analytical session, fell better within the expected tolerance range of ± 20 % on the concentration assigned to the control 0.05 mg/l (± 0.010 mg/l) even if the profile of the chromatographic peaks was not good, probably due to the system that had gotten dirty (guard chip and liner had to be replaced). It also emerged the need to dilute the sample obtained in the second analytical session at least twice to bring the concentration back within the linearity field of the working line (up to 0.10 mg/l with a tolerance not exceeding +20 %) and to repeat the analyses with the method of additions to better evaluate the results obtained on the same extract with the two different working lines in the two analytical sessions. But the now tight delivery times of the results did not allow to deepen this analytical aspect." B) It is worth highlighting that the circuit organizers have carried out the performance evaluation of the laboratories on Phthalimide using as expected value the consensus value obtained with the LCMSMS technique. If the values obtained for the specific technique equal to 0.112 mg/Kg had been used and the actual CV of 38.1 % considered, the result sent for Phthalimide 0.210 mg/Kg would have been less penalizing for our Laboratories. In fact, the z-Score for Phthalimide with a CV equal to 38.1 %, would have been +2.3. C) Furthermore, it was evaluated that both the result of Phthalimide equal to 0.106 mg/Kg (average of all the PT results) and the value 0.112 mg/Kg (average of the results obtained in GC_MS) fall within the range of values included in the measurement uncertainty adopted by the laboratory (+/- 50 % or 0.105-0.315 mg/kg) **Feedback and advices by the organisers**: Thanks for this feedback. Your result for phthalimide is strongly overestimated. Based on the information provided, it is difficult to localize any particular error sources. Your method information is a bit ambiguous as you have indicated using a citrate-based QuEChERS method (SRM-07) but also the use of ethylacetate as extraction solvent. In GC it is important to consider that the detected PI originates from both, the PI originally contained in the extract (originating from the sample) and the PI formed during injection when folpet thermally degrades. If the latter PI share is not deducted (e.g. as described in the "Supporting Excel Sheets for SRM-07"), results will be overestimated. From the information you have provided it cannot be concluded whether this aspect was adequately addressed.
58	7.0	D	**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
3rd-139	8.7		**Feedback and advices by the organisers**: Unfortunately, you haven't provided any feedback on the sources of this error. Your overestimated result despite the use of LC-MS/MS is unusual. The very long extraction time >3 h and the dSPE with PSA have led to a degradation of folpet for which you have reported a false negative result. Your result for folpet (sum) ended up being within the acceptable range.
80	10.2		**Feedback and advices by the organisers**: Please also consider the comments on phthalimide to LabCode 13.
57	18.8		**Feedback and advices by the organisers**: Your overestimated result despite the use of LC-MS/MS is unusual. Unfortunately you haven't provided any feedback on the sources of this error. A degradation of folpet during sample preparation (e.g. during dSPE with PSA sorbent) might have taken place, but due to the use of a calibration through standard addition to analyticsl portions any losses were compensated . Your result for the sum is overestimated but still within the acceptable range.
6	19.7	L	Error in communicating the result. The correct value is 0.13 **Feedback and advices by the organisers**: Note that the concentration of 0.13 corresponds to a z-score of 2.3, which is questionable. You are furthermore strongly encouraged to more diligently fill the method information as wrong information complicates the interpretation of the results. Under method information you indicated the use of the QuPPe method, but using ACN with 1 % formic acid for extraction and the conduction of dSPE cleanup with PSA. This combination is unusual

11th Edition: Released on 30 December 2023

GENERAL PROTOCOL

for EU Proficiency Testings on Pesticide Residues in Food and Feed

Introduction

This protocol contains general procedures valid for all European Union Proficiency Testings (EUPTs) organised on behalf of the European Commission, DG-SANTE[1] by the four European Union Reference Laboratories (EURLs) responsible for the area of pesticide residues analysis in food and feed. These EUPTs are organised for 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 the official controls Regulation (EU) No. 2017/625[3]:

- EURL for Fruits and Vegetables (EURL-FV),
- EURL for Cereals and Feedingstuff (EURL-CF),
- EURL for food of Animal Origin and commodities with high fat content (EURL-AO) and
- EURL for 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 they can use to demonstrate their (ongoing) analytical proficiency and compare themselves with other participating laboratories. By pointing out areas of analytical deficiencies, EUPTs contribute to the continuous improvement of the analytical quality of OfLs, thus helping to increase the confidence on the results generated by them.

[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

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Table of Content

EUPT- Organisers and Scientific Committee

EUPTs are organised either by single EURLs, or collaboratively by more than one EURL.

An **organising team** (in the following named **organisers**[5]) is appointed by the EURL(s) in charge of a given PT. The organisers are in charge of all administrative and technical PT activities of a proficiency testing (PT) round. These tasks include the PT-announcement, the production of the proficiency testing item (PT-item), the undertaking of homogeneity and stability assessments, the portioning, packing and shipment of the PT-Items, the handling and evaluation of the results and method information submitted by the participants, the drafting of the preliminary and final reports as well as the generation and distribution of EUPT-participation certificates.

To complement the internal expertise of the EURLs, a group of external consultants forming the **EUPT-Scientific Committee** (EUPT-SC)[6] 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 latest composition of the EUPT-SC and the affiliation of each of its members is shown on the EURL-Website. The members of the EUPT-SC are also listed in the Specific Protocol and the Final Report of each EUPT.

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

a) An independent **Quality Control Group** (EUPT-QCG) and
b) An **Advisory Group** (EUPT-AG).

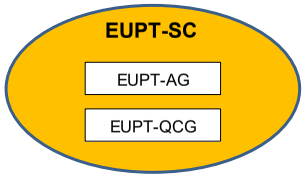

Figure 1: *Composition of EUPT-Scientific Committee*

The EUPT-SC's role is to assist the organisers during the planning and the data evaluation phase of a PT-round. Input from the EUPT-SC is requested, when it comes to e.g. selecting the commodities for the EUPTs of the following season, selecting the analytes to be included in the Target Pesticides List (p. 8), establishing the Minimum Required Reporting Levels (MRRLs) for each of the analytes,

[5] The term organisers is to be considered equivalent to the term PT-provider in ISO 17043:2023

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

and statistically evaluating the participants' results (in anonymous form). The EUPT-SC is furthermore consulted when it comes to drafting and updating 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 analytes to be present in the PT item and the approximate concentrations at which they should be present.

The EUPT-SC typically meets once a year, after all EUPTs of the season have been conducted and preliminarily evaluated by the four pesticide EURLs. The aim of these meetings is to discuss the preliminary evaluation of the EUPT-results, especially where case-by-case decisions are needed. PT plans for the next EUPT season and, if needed, possible changes in the EUPT-General Protocol are also discussed during these meetings. The main topics and decisions on these meetings are documented.

The present EUPT General Protocol (EUPT-GP) was drafted by the EURLs and reviewed by the EUPT-SC. Follow the link to access a website giving an overview of EUPT-GP versions. The latest version of the EUPT-GP is highlighted.

EUPT Participants – Eligibility and Obligation for Participation

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

- Art 38 (2) of Regulation (EU) No. 2017/625[3]
- Art. 28 (3) of Reg. (EC) No. 2005/396 (for all OfLs analysing for pesticide residues within the framework of official controls of food or feed[7])
- Art. 101 (1)(a) of Regulation (EU) No. 2017/625[3] (for all NRLs).

Every year, shortly before launching the registration period of the first of the four EUPTs in a given EUPT-Season, all OfLs and NRLs are asked to update their routine scope of commodities as well their contact information within the EURL-DataPool. Based on this information the OfLs are classified into those that are obliged and those that are eligible to participate in each of the EUPTs to be conducted within a given year.

[7] Official controls in the sense of Regulation (EU) 2017/625. This includes labs involved in controls within the framework of national and/or EU programs, as well as labs involved in import controls according to Regulation (EU) 2019/1793 (which repealed Regulation (EC) No. 2009/669).

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

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

Labs that are obliged to participate in a given EUPT, but are not able to participate, must provide the reasons for their non-participation. This also applies to any participating laboratories failing to report results.

EUPTs are furthermore open to the following laboratories as long as sufficient material is available:

a) any other OfLs from EU countries that are not covered by the above obligations to participate;

b) NRLs and OfLs from EU-candidate countries and EFTA countries;

c) other laboratories from EU or EFTA countries analysing official organic samples within the frame of Reg. 889/2008/EC;

d) governmental laboratories from Third Countries (countries outside EU)

e) other laboratories from Third Countries as long as they are involved in controls of products destined for export to the EU.

Note on a): Laboratories having been designated as OfLs, according to Art. 37(2)(b) of Regulation (EU) No. 2017/625[3] by a Competent Authority of an EU Member State (MS1) will normally also need to be commissioned with OfL activities in a different EU Member State (MS2) for being eligible for participation. Scan-copies of documents giving information about the period and scope of these OfL activities for MS2 may be requested by the EUPT organizers. The responsible NRL and/or Competent Authority of MS2 may be contacted before deciding whether the laboratory in question is eligible or even obliged to participate in a certain PT. A laboratory whose OfL-appointment in the area of pesticide residue analysis has ceased, will normally loose its eligibility (and obligation) to participate in EUPTs, but participation may be allowed if the responsible NRL and/or Competent Authority of MS1 or MS2 considers its participation essential for judging the proficiency in view of a planned or potential OfL activity in the future.

Laboratories of groups c) and e) will be requested to provide a proof of their function (e.g. scan copy of a document stating official appointment).

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Obligation of OfLs and NRLs to double-check Status of EUPT-Participation:

Based on the latest information within the DataPool and considering the selected commodities of the upcoming EUPTs, the OfLs (including the NRLs) are grouped into those for which participation in a given EUPT is **obligatory** and those for which participation is **voluntary** ("OV-grouping").

Upon accessing the EUPT Registration Form within the EURL-DataPool, laboratories can choose the EUPTs they would like to participate and view their OV-grouping status for each of the selected PTs. If a laboratory does not agree with its OV-Grouping, it should promptly contact the corresponding NRL and the EUPT-organisers and give the reasons why it believes it should be grouped differently. The reasons provided by the laboratories will be noted by the organisers and if indicated, the DataPool will be updated accordingly. In any case, the OV-grouping prepared by the EURLs is indicative only, as the real obligation to participate in a given EUPT arises from the above-mentioned EU-regulations, not the DataPool entries or any lab's claims. Additional requirements may arise from accreditation bodies or local rules and regulations.

Within the DataPool, NRLs have the possibility to view data relevant to OfLs within their network (OV- grouping, registration progress) and are responsible for checking whether the OV- grouping of all relevant OfLs within their network is correct.

OfLs that are obliged but not able to participate in a given EUPT must provide the reasons for their non-participation. This also applies to any participating laboratories that fail to submit PT-results.

Participation fee and Invoicing

By completing the registration for participation in a given EUPT, a laboratory agrees to proceed with a timely payment of the participation fee after being accepted for participation and after the invoice issued by the organiser is received. The invoice fee covers the costs of production, handling and delivery of the PT-materials. The organisers will issue digital invoices in PDF format only, and without any electronic signature. By registering to an EUPT the laboratories also accept that the pdf invoice, issued by the organisers and sent via e-mail to the participant, is sufficient for triggering the payment of the participation fee. The EURLs retain the right to decline any request for supplementary forms or additional paperwork in connection to the payment. The laboratories should note that additional costs may incur if such extra services are requested, depending on the incurring extra workload. Extra costs may also incur if new modified invoice is requested, e.g. because of missing or erroneous information caused by errors or omissions by the registered laboratory during registration. OfLs not paying the EUPT participation fee will be initially reminded, and then warned that information concerning their laboratory may be blacked out in the final report of the concerned EUPT and the certificate of participation may not be issued to them, and that their participation in subsequent

EUPTs could be denied. In case of a repetitive non-payment, the EUPT organisers may inform the corresponding NRL and/or the competent authority responsible for the OfL.

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 laboratory or country performance as requested by DG-SANTE.

As laid down in Regulation (EU) No. 2017/625[3], NRLs are responsible for evaluating and improving their own OfL-Network. On request from the NRLs, the EURLs will provide them with the PT-codes of the participating OfLs belonging to their OfL-Network. This will allow NRLs to follow the participation and performance of the laboratories within their network.

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

For each EUPT the organising EURL prepares a specific EUPT-Website where all PT-relevant documents in their latest version are linked. In case of important modifications on any of these documents, the participating laboratories will be informed via e-mail. In any case, as soon as the PT-period starts the participants are encouraged to visit the particular EUPT-Website, to make sure that they are using the latest versions of all PT-relevant documents.

The official language used in all EUPTs is English.

Announcement / Invitation Letter

Approximately 3 months before the distribution of the PT items to the participants 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 for preparing the PT item, as well as links to the tentative EUPT-Target Pesticides List and the tentative EUPT-Calendar.

Target Pesticides List and PT-Residue Definitions

The Target Pesticides List contains all analytes (pesticides and metabolites) to be sought for, along with the Minimum Required Reporting Levels (MRRLs) valid for the specific EUPT. The MRRLs are typically based upon the lowest MRLs found either in Regulation (EC) No. 2005/396 or in Regulation (EU) No. 2016/128 (Baby Food Directive).

The residue definition in an EUPT may differ from the legal one if this is deemed necessary by the organisers for ensuring a better evaluation of the results. Participants must express their results as defined in the Target Pesticides List of the respective EUPT. Separately quantifiable analytes are typically listed separately unless stated otherwise.

Specific Protocol

For each EUPT, the organising EURL will publish a Specific Protocol at least 2 weeks before the PT 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 PT item upon receipt and on how to submit results, as well as other relevant information.

Assessing the Homogeneity of the PT Item

A suitable homogeneity of the EUPT item is of high importance as it ensures that portion-to-portion variability has only a negligible impact on the evaluation of the participant's performance. The PT item is tested for homogeneity, typically after bottling and before distribution to participants, but in justifiable cases the tests for homogeneity assessment may also be conducted after the distribution of the material to the participants[8]. The homogeneity assessment usually involves analysis of two replicate analytical portions, taken from at least ten randomly chosen units (bottled portions) of treated PT item. Measurements should be conducted in random order with the aim of minimizing the risk of misinterpreting signal drifts within a measurement sequence as concentration shifts linked to the bottle numbering, i.e. the order of the bottle filling.

The homogeneity test data are statistically evaluated according to ISO 13528:2022, Annex B[9] or to the International Harmonized Protocols jointly published by ISO, AOAC and IUPAC[10]. The results of all homogeneity assessment are presented to the EUPT-SC. In special cases, where the above

[8] To minimize the risk of PT item not being acceptably homogeneous, the organisers may opt to conduct a small-scale preliminary homogeneity test prior to bottling the PT item for shipment. The pre-tests may focus on a selected fraction of the analytes, and may also serve for verifying the presence and the approximate levels of the analytes spiked.

[9] ISO 13528:2022: 'Statistical methods for use in proficiency testing by interlaboratory comparisons", International Organization for Standardization.

[10] Thompson M., Ellison S.L.R., Wood R., "The International Harmonized Protocol for the proficiency testing of analytical chemistry laboratories" (IUPAC Technical Report). Pure Appl. Chem. 2006, 78, 145 – 196

criteria are not met, the EUPT-SC, considering all relevant aspects (e.g. the homogeneity results of other analytes spiked at the same time, the overall distribution of the participants' results (CV^*), the analytical difficulties faced during the tests, and knowledge of the analytical behaviour of the compound in question), may decide to overrule the test. The reasons of this overruling have to be transparently explained in the Final EUPT-Report. For certain analytes with comparable properties, an equivalent distribution within the sample can be expected if they were spiked/used simultaneously. The homogeneity test of one or more of these analytes may thus be skipped or simplified. The organisers should keep an eye on the participants' results of such analytes not tested for homogeneity in order to detect at an early stage any signs that could raise doubts about the homogeneity of the material (e.g. an atypically broad distribution of the results compared to other analytes). In such a case, the EUPT-SC may decide that a proper homogeneity assessment should still be performed to clarify the situation.

Assessing the Stability of the Analytes Contained in the PT Item

The PT item will also be tested for stability - according to ISO 13528:2022, Annex B[9]. The time delay between the first and the last stability test (stability assessment period) must exceed the period of the EUPT-exercise. Typically, the first analysis is carried out shortly before the shipment of the PT items and the last one shortly after the deadline for submission of results. If justifiable, the stability assessment period may precede the PT period, partly overlap with it or postdate it. Close proximity to the PT-period is to be favoured, however, to minimize the risk that matrix properties alter in a way that will affect analyte stability. To better recognise trends and gain additional certainty, one or more additional tests may be conducted by the organisers in the interim. 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 analytes contained in the PT 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 EUPT-Report, considering all relevant aspects, such as the distribution of the participant's results (CV^*).

An analyte is considered to be adequately stable if $|y_1 - y| \leq 0.3 \times \sigma_{pt}$, with y_1 being the mean value of the results of the last stability test, y being the mean value of the results of the first stability test and σ_{pt} being the standard deviation used for proficiency assessment (typically 25 % of the assigned value by default).

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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 compound in 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 storage conditions other than those recommended to the participants e.g. at ambient temperature.

If insight about insufficient analyte stability is gained before the end of the PT-period, the EUPT-QCG will be contacted in order to decide whether the EUPT-SC should be involved in the discussion (as confidential information is involved), whether the PT-participants should be informed about this insight and whether the affected analytes should be removed from the target list.

Stability during shipment: Considering knowledge about the expected susceptibility of analytes in the PT item to possible losses, the organisers will choose suitable shipping conditions to minimize such losses, e.g. shipment of frozen samples, addition of dry ice. As shipment duration can vary from labs/countries to labs/countries, it is recommended that the organisers keep track of the shipment duration and then decide whether it is reasonable to conduct additional stability tests at conditions simulating shipment. Should critical losses be detected for certain analytes, the EUPT-SC will be informed (or the EUPT-QCG before or during the test). Case-by-case decisions may be made by the EUPT-SC, considering all relevant aspects including the duration and conditions of the shipment to the laboratory as well as the feedback by the laboratory. Follow-up measures in case of instability during shipment may include the exclusion of the affected results from the population used for establishing the assigned value (x_{pt}) and the non-calculation of z scores for the affected analytes in order to avoid unfair penalization of the laboratories involved.

If the PT entails analytes that are expected to have a high risk of degradation within the PT item, the organisers should conduct model tests prior to the final preparation of the test item in order to gain insight about the stability behavior of the analytes intended to be spiked during homogenization, transport and storage of the samples. Based on the results of these experiments measures should be taken to minimize the risk of certain analytes failing to meet the stability criteria, which may include adjusting the conditions of homogenization and/or storage and/or shipment or even deciding not to spike the material with certain analytes.

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. This can be done via the EURL data submission tool (in the following named Webtool) by answering the question whether the concerned analyte is included within the routine scope of the laboratory and the question about the analytical experience with the compound.

General Procedures for Reporting Results

Participating laboratories are responsible for reporting their own quantitative results to the organiser within the stipulated deadline. Any analyte targeted by a participating laboratory should be reported as "analysed" in the Webtool. In EUPTs by EURLs responsible for MRM compounds (FV, CF, AO) this is done before shipment of the PT test Item. In EUPT-SRMs this is done in the period during which the platform is open for result submission. Each laboratory will be able to report only one result for each analyte detected in the PT item. The concentrations of the analytes detected should be expressed in 'mg/kg' unless indicated otherwise in the specific protocol of the respective EUPT.

For reporting, concentration values ≤ 0.01 mg/kg are recommended being rounded to two significant figures (e.g. 0.0078; 0.010) and values > 0.01 mg/kg to three significant figures (e.g. 0.123; 1.23; 12.3 mg/kg). No penalties will apply where a laboratory reports deviating numbers of significant figures, but in case of less significant figures, zeros will be assumed after the last significant figure (e.g. 0.1 = 0.100 and 0.11 = 0.110). For the calculation of z scores the values will be used as reported. In the preliminary and final report the results will be shown with up to three significant figures.

Laboratories should not report results below their own reporting limits (RLs). Any reported numerical result that is lower than the RL will be marked as a 'False Reporting' (FR) but it will be allocated a z score as any other numerical result. Such results will be, furthermore, included in the results population for establishing the assigned value (x_{pt}), unless they are eliminated for other reasons (e.g. laboratory status, use of biased methodology).

Correction of Results for Bias

According to the DG-SANTE Guidelines, the result of an analyte needs to be adjusted for method bias if the bias exceeds 20%. Unless the method used inherently accounts for method bias (see cases a – c below), laboratories are required to report the recovery (in percent), and whether their results was corrected mathematically using a recovery factor reflecting the reported recovery.

The EUPT-Panel will examine whether results, for which no correction for bias was undertaken, should be omitted from the population used for calculating the assigned value.

When the laboratory uses any of the following approaches inherently accounting for method bias, this needs to be indicated in the appropriate fields within the Webtool. In such cases, reporting of the recovery rate is not mandatory.

a) use of stable isotope labelled analogues of the target analytes as Internal Standard (ILISs), added to the analytical portion at an early stage of the procedure

b) 'procedural calibration' approach

c) 'standard addition' approach with additions of analyte(s) to the analytical portions before extraction.

Methodology Information

All laboratories are requested to provide information on the analytical method(s) they have used. The Webtool, which serves for submitting analytical results, is typically also used for collecting method information.

The collection of method information is considered very important by the EUPT-SC as it facilitates the interpretation of results and the identification of analytical patterns associated with systematically biased results. A compilation of the methodology information submitted by all participants may be presented in an Annex of the Final EUPT-Report or in a separate report. Where the initial method information provided by the participating laboratories is not sufficient for evaluating methodology-related errors or where additional information critical for results evaluation is needed, the EURLs and/or the EUPT-Panel may decide to conduct specific follow-up surveys among the concerned laboratories. If no sufficient information on the methodology used is provided, the organisers reserve the right not to accept the analytical results reported by the participants concerned or even refuse participation in the following PT.

Where necessary, the methods are evaluated and discussed within the EUPT-SC, especially in those cases where the result distribution is not unimodal or very broad (e.g. CV^* > 35 %).

Where certain methodologies or analytical steps are suspected to lead to biased or otherwise erroneous results, the PT-organisers will substantiate this suspicion by own experiments and discuss the issue with the EUPT-SC. Laboratories affected will be informed, e.g. via direct contact and/or via EURL-workshops or trainings and/or through the inclusion of recommendations within the Final EUPT Report.

Cases where reporting limits (RL) of laboratories exceed the MRRL indicate insufficient sensitivity and may be highlighted in the final report as with "PS" for poor sensitivity.

Results Evaluation

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

- ***False Positive (FP) Results***

These are results of analytes on the Target Pesticides List that are reported at or above their respective MRRL although they were: (i) "not detected"[11] 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 analytes. In certain instances, case-by-case decisions by the EUPT-SC 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. If these results are additionally lower than the lab's reporting limit, they will be attributed with FR ('False Reporting').

- ***False Negative (FN) Results***

These are results of analytes reported by the laboratories as 'analysed' but without reporting numerical values although they were: a) used by the organiser to treat the PT item and b) detected by the organiser as well as the majority of the participants that had targeted these specific analytes at or above the respective MRRLs. Numerical results < RL (RL= Reporting Limit of the laboratory) may be judged as false negatives and may be also regarded as "not correctly found" when it comes to categorization in A and B based on scope. Such results wouldn't be reported in a routine laboratory environment. Case-by-case decisions by the EUPT-Panel will be taken by the EUPT-SC in such cases.

Where the RL of a laboratory for a certain analyte present in the PT item exceeds the assigned value, with the laboratory not reporting a numerical value, the result may still be judged as a false negative, despite this reporting being unobjectionable in a routine working environment. The FN judgement should in this case penalize the laboratory for not being able to achieve sufficient sensitivity for the analyte in question.

[11] The term "not detected" is also used in the Webtool. In this context this term entails also all cases where no numerical result were reported (e.g. because the level determined was < MRRL and/or < RL)

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In cases of the robust mean of the participant results being less than 3 times higher than the MRRL, false negatives will typically not be assigned. The EUPT-SC may decide to make case-by-case decisions in this respect after considering all relevant factors such as the result distribution and the RLs of the affected labs. In case where the not fixing a valid assigned value is due to other reasons, e.g. because the uncertainty of the assigned value (UAV) criteria were not met and/or because of a bimodal distribution of the participant results, the EUPT-SC will decide on case-by-case basis whether FNs should be assigned for the respective analyte or not.

- ***Estimation of the Assigned Value (x_{pt})***

To minimise the influence of out-lying results on the statistical evaluation, the assigned value x_{pt} (= consensus concentration) will typically be estimated using the robust mean estimate of the participant results (x^*) as described in ISO 13528:2022[12], taking into account the results reported by EU and EFTA countries laboratories only. In special justifiable cases, the EUPT-Panel may decide to include results submitted by laboratories not belonging to the EU-/EFTA-OfLs network or even to use only the results of a subgroup of ('expert') laboratories that have previously repeatedly demonstrated good performance for the specific or similar compounds.

Furthermore, the EUPT-Panel may decide to eliminate certain results traceably associated with bias or gross errors for establishing the assigned value (see 'Omission or Exclusion of results' below).

In special justifiable cases, the EUPT-Panel may furthermore decide to use the spiked concentration of an analyte as the best estimate of the assigned value. In such cases, a detailed explanation of the reasons behind this decision will be given and a comparison with calculations involving robust statistics will be undertaken.

In reports, assigned values will be rounded to 3 significant figures if ≥ 0.01 mg/kg and to 2 significant figures if < 0.01 mg/kg (i.e. 0.0078; 0,123; 1.23; 12.3 mg/kg). For the calculation of z scores, the organisers may opt to use assigned values rounded to more significant figures than those stated above.

Since the assigned values of the EUPT analytes are typically generated using robust mean concentrations of participant results, which are generated by a variety of analytical standards and methods, the assigned values of EUPTs are typically metrologically not traceable.

[12] ISO 13528:2022 '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).

– ***Omission or Exclusion of Results***

Results reported by laboratories from non-EU and non-EFTA Member States are typically excluded from the population used to derive the assigned value (for exceptions see 'Estimation of the assigned value').

Before estimating the assigned value, results associated with obvious mistakes have to be examined to decide whether they should be removed from the population. Such gross errors may include incorrect recording (e.g. due to transcription errors by the participant, decimal point faults or transposed digits, incorrect unit), calculation errors (e.g. missing factors), analysis of a wrong sample/extract (e.g. a spiked blank), use of wrong concentrations of standard solutions, incorrect data processing (e.g. integration of wrong peak), inappropriate storage or transport conditions (in case of susceptible compounds), and the use of inappropriate analytical steps or procedures that demonstrably lead to significantly biased results (e.g. employing inappropriate internal standards or analytical steps or conditions leading to considerable losses, due to degradations, adsorptions, incomplete extractions, partitioning etc.). Where the organisers (e.g. after the publication of the preliminary report) receive information that certain participant's results are associated with gross errors, 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.

In case of traceable calculation errors by the participants (e.g. use of wrong factors to express the result as required by the PT's residue definition[13]), and in case of non-reporting results that can be calculated from reported values (e.g. summed result not calculated and not reported), the EUPT-Panel may decide to correct or complement results within the population by applying (the correct) factors. The new population of results may then be used for establishing the assigned values. The z score of the concerned results will, however, be calculated using the originally reported values.

Although robust statistics are applied for estimating assigned values and robust standard deviations, certain results showing a strong bias compared to the rest of the population may be, in certain cases, eliminated before applying robust statistics[14]. To identify such strongly biased results, a preliminary consensus calculation of the robust mean (prelim-x^*) may be conducted and any results being ≥ 3-fold the prelim-x^*[15] may be potentially eliminated. This approach may need to be iterated if the population still entails obvious outliers.

[13] irrespective of who is accounted responsible for the confusion

[14] Please see ISO 13528:2022 Chapter 6.6." Outlier techniques for individual results', therein 6.6.3, Note 3.

[15] Corresponds to preliminary z scores ≥ 8 using the FFP-approach

The result population remaining after the elimination of certain results as described above may be then used to establish the actual assigned value (x_{pt}) and the robust standard deviation (s^*) according to the consensus approach described above. The z scores of all results, including those corrected or removed, are to be recalculated using the new assigned value.

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 ($u(x_{pt})$)***

The uncertainty of the robust mean values (x_{pt}) is calculated according to ISO 13528:2022 as:

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

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

A broad results distribution (high s^*) and/or a limited number of results (p) will increase the uncertainty of the robust mean $u(x_{pt})$ values exceeding $0.3 \times \sigma_{pt}$ (see ISO 13528:2022) will typically mean that the robust mean is too uncertain for the purpose and cannot be straightforwardly taken up as the assigned value. In each of these cases, investigations for elucidating the reasons behind the high uncertainty should be undertaken. Taking into account all relevant aspects[16] the EUPT-SC may decide that the analyte results should be re-evaluated based on a refined or extended result population or an alternative approach. If, despite these considerations and irrespective of the outcome of the UAV test the EUPT-SC concludes that, the assigned value of a specific analyte is too uncertain for a valid evaluation, it may decide that the results for the analyte in question should not be evaluated or only evaluated for informative purposes.

– ***Considering the UAV when Calculating z Scores***

Where the vast majority of the results is close to the robust mean and narrowly distributed but the UAV-test is still marginally failing[17] (e.g. where $u(x_{pt})$ is up to $0.4 \times \sigma_{pt}$ = 10% in absolute terms), the

[16] e.g. information about methodologies used by the participants (especially if these are likely to produce biased results), multimodality, number of submitted results, homogeneity data, stability data

[17] e.g. due to a combination of few results, and sporadic biased results.

EUPT-Panel may consider to calculate z' scores using the following formula, which considers the uncertainty of the assigned value:

$$z' = \frac{x_i - x_{pt}}{\sqrt{{\sigma_{pt}}^2 + u^2\,(x_{pt})}}$$

where $u(x_{pt})$ being the uncertainty of the assigned value and σ_{pt} being the standard deviation of the assigned value that may be set equal to $FFP\text{-}\sigma_{pt}$ (see below). z' scores will be shown for Informative purposes only.

In special cases[18], the EUPT-SC may consider useful to proceed with the calculation of z scores for both extremes of the assigned value as derived by applying the UAV (i.e. $x_{pt} \pm (x_{pt})$). This upper and lower bound calculation of the z scores will also be for informative purposes only. The aim of this calculation is to help laboratories having performed well in a PT demonstrate their good performance even in cases where the UAV-test has not passed the criteria. Example: x_{pt} = 1.0 mg/kg, (x_{pt}) = 0.1. Taking into account the calculated uncertainty, the AV should range between 0.9 and 1.1 mg/kg. If the result of a laboratory is 0.7 mg/kg, the z score calculates to -1.2 using x_{pt} = 1.0 mg/kg, For the upper limit of x_{pt} = 1.1 the z score calculates to -1.76 and for the lower limit of x_{pt} =0.9 the z score calculates to -0.72. This means that, even at worst-case scenario, the laboratory's result remains within the acceptable range.

– ***Standard Deviation for Proficiency Assessment (Target Standard Deviation)***

The standard deviation for proficiency assessment (σ_{pt}) will be calculated using a Fit-For-Purpose approach with a fixed Relative Standard Deviation (FFP-RSD). Based on experience from previous EUPTs[19], a percentage of 25 % is currently used as FFP-RSD for all analyte-matrix combination, and the Fit-For-Purpose target standard deviation ($FFP\text{-}\sigma_{pt}$) is calculated as follows:

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

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

For informative purposes the robust relative standard deviation (CV^*) of the participants results is calculated according to ISO 13528:2022; Chapter 7.7 following Algorithm A in Annex C (so called "consensus approach from participant results").

[18] E.g. where the population of results is narrow, but the UAV tests fails due to a few deviating results in combination with a relatively small number of results, e.g. <20

[19] 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. DOI:10.1021/jf104060h

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– ***z Scores***

This parameter is calculated using the following formula:

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

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

For practical reasons, any z scores > 5 will be typically reported as '> 5' and a value of '5' will be used to calculate combined z scores (p. 19). Following ISO 17043:2023[20], z scores will be classified as follows:

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

All false negatives will be assigned a z score of -4. These z scores will typically appear in the z score histograms and will be used in the calculation of combined z scores.

– ***Collection of Measurement Uncertainty (MU) Figures***

For each EUPT the participating labs are asked to voluntarily report the MU figure they would report in routine analyses. The EUPT-SC will decide how to evaluate these figures and whether indications will be made to the laboratories in this regard.

– ***Categorization of Laboratories***

The EUPT-SC will decide if and how to classify the laboratories into categories based on their scope and/or performance. Currently, a scope-based classification into Category A and Category B is employed. Laboratories that have:

a) analysed at least 90% of the compulsory analytes in the target pesticides list,
b) reported numerical results for at least 90 % of the compulsory analytes present in the PT item
c) reported no false positives

[20] ISO/IEC 17043:2023. Conformity assessment – General requirements for the competence of proficiency testing providers

are considered to have demonstrated 'sufficient scope' and will be therefore classified into Category A. For the 90% criterion, the number of analytes needed to be correctly analysed to have sufficient scope will be calculated by multiplying the number of compulsory analytes 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: *Number of analytes from the Target Pesticides List needed to be targeted or analytes present in the PT item that need to be correctly detected and quantified to have sufficient scope.*

No. of compulsory analytes present in the PT item / target pesticides list (N)	90 %	No. of compulsory analytes 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 the average of the squared z scores (AZ^2)[21] and/or the average of the absolute z scores (AAZ) can be calculated for informative purposes. To minimize the influence of outlying results, the calculation of AZ^2 and AAZ will not be conducted in the case of < 10 and < 5 results, respectively, and z scores higher than 5 will be set as 5. Combined z scores are typically only calculated for laboratories within Category A and considering results of

[21] 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. DOI:10.1007/s00216-010-3877-3

compulsory analytes, but the organisers may deviate from this if considered reasonable, provided that a minimum number of results (z scores) have been reported. Combined z scores may be also calculated using results of across PTs.

Considering the cut-off of high z scores at 5, 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.

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

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

Combined z scores are considered to be of lesser importance than individual z scores. The EUPT-SC 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 being too low.

In the case of EUPT-SRMs, where only a few results per laboratory may be available, the average of the absolute z scores (AAZ) may be calculated for informative purposes, but only for labs that have reported enough results to obtain 5 or more z scores. For the calculation of the AAZ, z scores higher than 5 will also be set as 5. The z scores appointed to false negatives will be also included in the calculation of the combined z scores. In general, laboratories should aim to achieve AAZ scores < 0.9, which corresponds to an average bias of 22.5 %[22].

Laboratories within Category B will be typically ranked according to the total number of analytes they correctly reported to be present in the PT item. The number of acceptable z scores achieved may be presented, too.

Publication of Results

The EURLs will publish a preliminary report, containing tentative assigned values and z score values for all analytes present in the PT item, within 2 months of the deadline for result submission. An early

[22] At 22,5% average bias (i.e. AAZ=0.9) and assuming a precision of 10%, the uncertainty calculates to 24.6% (error propagation formula), which is just acceptable. At a precision of 15%, the maximally tolerable average bias calculates to 20%, which translates to an AAZ of 0.8. The uncertainty of the bias was not considered in these calculations.

distribution of the preliminary report, entailing preliminary assigned values (prAV), will allow an early investigation of possible errors by the participants.

The Final EUPT-Report will be published after the EUPT-SC has discussed the results. Taking into account that the EUPT-SC meets normally only once a year (typically in late summer or autumn) to discuss the results of all EUPTs organised by the EURLs earlier in the year, the Final EUPT-Report may be published up to 12 months after the deadline for results submission. Results submitted by non-EU/EFTA laboratories might not always be included in all tables or figures in the Final EUPT-Report.

Certificates of Participation

Together with the Final EUPT-Report, the EUPT organiser will deliver a Certificate of Participation to each participating laboratory showing the z scores achieved for each individual analyte, the classification into Categories, and if deemed necessary also combined z scores. The certificates of participation will be uploaded onto the EURL-DataPool and can be accessed by the concerned laboratories only.

Feedback and Complaints

Participants have the right to complain about any aspect concerning the PT (e.g. about the on-line tools used for registration and data submission, the organisation and communication with the participants, the timing of the PT, transcription errors and the result evaluation if it is not compliant with the provisions of the general protocol). Complaints about a non-arrival of a PT item or about the bad condition of the PT item upon arrival should be done through the Webtool shortly as indicated in the specific protocols. The EURLs will track the complaints and will try to accommodate all substantiated complaints in due time. After the publication of the final EUPT report, the organizers reserve the right not to consider any complaints arriving more than two months after its publication.

Appeals and complaints concerning the principles of organisation and statistical analysis of the results according to the General Protocol should be made prior to the start of a PT. By signing up to an EUPT, the participant agrees with the provisions of the General Protocol valid for the PT-season in question.

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

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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 and carefully study the latest version of these documents.**

If substantial errors are discovered in the Preliminary EUPT-Report the organisers will distribute a new corrected version, therein it will be stated that the previous version is no longer valid. The online version on the PT website will be replaced.

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

If a new version of any EUPT document is released, each page of the new version must be marked in a way distinguishing it from previous versions, e.g. with the version number.

Where errors are discovered in EUPT-Certificates, the revised certificates will be issued and uploaded to the DataPool. The concerned laboratories will be informed and asked to download the corrected ones.

Follow-up Activities

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

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.

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

NRLs will be considered as **underperforming in relation to scope** if in at least two of the last four EUPTs falling within their responsibility area they: a) haven't participated, or b) targeted less than 90% of the compulsory analytes in the target lists (80% for SRM-compounds), or c) detected less than 90% of the compulsory compounds present in the PT items (80% for SRM-compounds). Additionally, NRLs that obtained AZ^2 higher than 3 (AAZ higher than 1.3 for SRM-compounds) in two consecutive EUPTs of the last four EUPTs, will be considered as underperforming in accuracy. As soon as underperformance of an NRL is detected, a two-step protocol established by DG-SANTE will be applied[23]:

Phase 1:

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

Phase 2:

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

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

Disclaimer

The EUPT-SC 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.

[23] Article 101 of Regulation (EU) 2017/625

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

SPECIFIC PROTOCOL

for the 19th EU Proficiency Test
on Pesticides requiring Single Residue Methods
EUPT – SRM19 (2024)
(released on 19 January 2024)

Introduction

This protocol is complementary to the valid version of the **"General Protocol for EU Proficiency Testings for Pesticide Residues in Food and Feed, 11th Ed."** for all EUPTs in 2024.
The EUPT-SRM19 is organized by the EU Reference Laboratory for pesticides requiring Single Residue Methods (EURL-SRM), named "**organizers**" in the following. The EURL-SRM is an accredited provider of proficiency tests according to ISO 17043 (see **EURL-SRM accreditation**).

The EUPT-SRM19 deals with the analysis of SRM-pesticides in grape homogenate. Participation is obligatory for all National Reference Laboratories for Single Residue Methods (NRL-SRMs), as well as for all official EU laboratories (OfLs) involved in the official analyses of pesticide residues in fruits and vegetables. The tentative classification of labs into "obliged" and "not obliged" to participate in this PT was based on information on the scope of commodities covered by each laboratory, as stated within the EURL DataPool. Prior to the classification, the laboratories were asked to update this information within the DataPool and the responsible NRLs were asked to verify this information.

The registration of the labs to the PT was run within the DataPool website. Laboratories classified as obliged were notified that they should enter the online registration platform, irrespective if they intend to participate or not. In the latter case, the labs had to state their reasons for non-participation. The reasons for non-participation received from obliged laboratories during registration, especially details considering the scope, will be considered in the final list of obliged laboratories.

Communication

On matters concerning the EUPT-SRM19, the organizers will communicate with the participating laboratories via emails to the respective "Main Contact Persons" and "Alternative Contact Person(s)" stated in the EUPT-SRM19 registration form. These persons are in the following referred to as "**participants**" or "**PT-participants**".
Additional emails will be automatically issues by the Webtool.

The most important documents related to this PT can be accessed via the **EUPT-SRM19-Website**.

PT Item

The PT Item of this EUPT is "**Grape Homogenate**".
Participants will receive one bottle of PT Item containing **approximately 400 g deeply frozen grape homogenate with incurred and spiked analytes** from the **Target Pesticides List**. Deeply frozen grape was cryogenically milled, spiked with selected compounds and homogenized at low temperature. Additional cryogenic milling using dry ice was carried out. The final material was filled into the bottles in a snow-like state, and will be sent with the addition of dry ice into the parcels, so that the analytical portions can be easily withdrawn. NO Blank material will be sent to the participants for this PT.

Using randomly chosen bottles, the Organisers will check the PT Item for sufficient homogeneity and for the stability of the analytes contained over the period of the exercise.

Target Analytes and MRRLs

The PT Item will contain several analytes from the mandatory, optional and extra section of the **EUPT-SRM19 Target Pesticides List** (TPL). Laboratories should read the TPL carefully as it shows how the residues should be reported as well as the **Minimum Required Reporting Levels (MRRLs)**. The MRRL values will be used to help identify false positive and false negative results. **Make sure to download and carefully study the latest version of the EUPT-SRM19 Target Pesticides List before starting with analysis and reporting results**.

Shipment of PT Item

Dispatch of the PT Item is planned on 5 February 2024.
PT Item will be packed into thermo-boxes together with dry ice and will be shipped from Germany via DHL Express to the participants. Prior to shipment, a reminder will be sent to the participating laboratories by e-mail.
The participating laboratories must make their own arrangements for the receipt of the package. They should inform the Organisers 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.

IMPORTANT:
The PT participants are responsible for facilitating quick customs clearance.
In case of delays at the customs or any other unusual delays within the recipient's country, the participants will be informed by the DHL and are strongly encouraged to contact the local DHL Express office and/or the customs in order to accelerate the clearance and delivery procedures and/or to ensure that the parcel is stored in a freezer during the delay period.

The PT participants are responsible for facilitating quick customs clearance. Where complications during customs clearance or shipment are expected, the participants should provide the Organisers in advance (by 25 January) with all **necessary documents to be stuck/attached on the package or to be uploaded, in order to ensure a smooth customs procedure**. Such documents may include a **permission** for importing organic material for scientific purposes (analysis) or an **instruction in local language** indicating the need to keep the package in a freezer in case of delay during shipment or custom's clearance. The participants should also inform the organizers if a **phytosanitary certificate** of the PT-material is required by their countries. Where the organizers will not be able to obtain the required phytosanitary certificate, the shipment (and the PT-participation) may need to be cancelled.

After the shipment is tracked within the DHL delivery system and the waybill is printed out, the main contact person for the PT will be informed by DHL on the tracking number of his package. The participants can track their own packages online and must make any necessary arrangements to receive the parcel upon delivery.

Instructions on Handling the PT Item

Once arrived, **the PT Item should be kept deeply frozen (at -18°C or lower) until analysis** in order to avoid any possible deterioration/spoilage of the sample material and to minimize analyte losses.

Participating laboratories are recommended using their routine standard operating procedures for extraction, clean-up and analytical measurement as well as their own reference standards for identification and quantification purposes. Laboratories may also employ methods not yet implemented routinely, for example, if they are in the test-phase of implementing them. In this case, the limited experience and the non-inclusion of the analytes in the routine scope should be indicated in the **EUPT-SRM19 result submission Webtool**.

The homogeneity tests will be conducted using 10 g portions in the case of pesticides and a 1 g portion in the case of copper. As sub-sampling variability increases with decreasing analytical portion size, sufficient homogeneity can be guaranteed only for sample portions roughly equal to or bigger than the portion size used in the homogeneity test.

Results Submission Webtool

Sample receipt acknowledgement, analytical results and method information are to be submitted via the **EUPT-SRM19 Result Submission Webtool**:

- **Sample receipt acknowledgement: From 6 February, 2024 onwards.**
- **Reporting of analytical results and method information: 12 February – 12 March 11:30 pm (23 h) CET.**
- **Deadline for result submission is 12 March, 11 pm (23 h) (CET), 2024.**
- **Reporting of additional information on methods used for tentatively false negative results: 13 – 21 March, 2024.**

A guideline for the new **EUPT-SRM19 result submission Webtool** will be provided to the participants in due time and a link to it can also be found in the info-box on the Webtool. The **participants are urged to read it carefully before submitting their results**.

– Login Credentials and Lab code

To access the EUPT-SRM19 Result Submission Webtool, participants must use their PERSONAL LOGIN CREDENTIALS (username and password).
Only persons listed as Main or Alternative Contact Persons for the EUPT-SRM19 will have access to the EUPT-SRM19 section within the Webtool. Prior to opening the EUPT-SRM19 section within the Webtool, the DTU will send a personalized username to each participant via email.
The participants can retrieve their personalized passwords via the following link using either their received usenames or the email address stated during registration: https://guest.dtu.dk/Sites/GuestLogin/RetrievePassword.aspx
PT participants can change their password using the following link: **https://guest.dtu.dk/Sites/GuestLogin/Default.aspx**
For security reasons you are encouraged to update your password once a year.

The lab's unique lab code for the EUPT-SRM19 will be provided to the participants following the first access to EUPT-SRM19 Result Submission Webtool upon submitting the sample acknowledgement at the first time**.** Since the lab code is absolutely necessary for the whole PT organisation, **please access the EUPT-SRM19 Webtool and submit sample acknowledgement as soon as possible,** once this page becomes accessible and the package with the PT Item arrives your laboratory.

– Acknowledgement of Package Receipt and Acceptance of PT Item

Once the laboratory has received the package with the PT Item, it must report to the organiser via the **EUPT-SRM19 Result Submission Webtool** the date of receipt, the condition of the package, the condition of the PT Item at arrival and any other comments concerning the test material. **In case of problems with the sample receipt, sample condition or complaints, the sample receipt form should be completed as soon as possible and not later than 9 February 11:00 am CET** to ensure that corrective actions can be taken as early as possible. If a laboratory does not respond by this deadline, the Organisers will assume that the PT Item has been received and accepted.

Participants are encouraged to follow the whereabouts of their parcels using the tracking number of the shipping company, which they will receive via e-mail, and to intervene at the shipping company, the customs or the organisers if they notice any delays. **Any participants not having received the PT Item by the afternoon of Thu. 8 February must inform the Organiser via e-mail (EURL-SRM@cvuas.bwl.de) as soon as possible and not later than 9 February 11:00 am CET. The Organiser will consult the shipping company to localize the package and decide on further actions, e.g. arrange a new shipment if necessary.**

Please note that **saving and closing the sample receipt form is a pre-requisite for accessing the results submission areas and generating participants' lab codes for this PT.** However, you can still access sample receipt form and edit it later.

– Reporting of Results

To report their results, participants must access the **EUPT-SRM19 Result Submission Webtool**.
All results must be reported on this website by 12 March, 11:00 pm (CET), 2024. The pages for the "scope, detected and results" will not be accessible after this deadline, and no results submitted afterwards will be accepted.

Before entering the results, please study the **EUPT-SRM19 Target Pesticides List** carefully. Please note that the compound names within the Webtool may appear in a shorter form than in the TPL. Please refer to the **EUPT-SRM19 Target Pesticides List** for the actual residue definitions applying to the present PT.

IMPORTANT NOTE CONCERNING OUTSOURCING OF ANALYSES
If routine procedures foresee the analysis of certain analytes (e.g. **copper**) by another laboratory*, this practice should be reflected in the PT.
When reporting PT-results participants are obliged to inform the organisers of any outsourced analyses and to provide the details of the laboratories having conducted these analyses.
The above information serves the transparency and allows identifying cases, where multiple results originate from a single source, which may need to be considered when establishing the assigned value.
Please note, that the information concerning the outsourcing of analyses may be highlighted in the PT-certificates.

* This also applies to cases where the analysing laboratory belongs to the same institution/company but runs its own quality control system.

Among others, the following fields will be available for reporting the quantitative results:

- "**Concentration in mg/kg":** the numerical pesticide concentrations that would be reported in routine work.
  If a pesticide was not detected or **if it was detected but the quantitative result is below the RL (Reporting Limit) of the laboratory, no result should be reported.**

  The residue levels of the pesticides should be reported in mg/kg preferably using **three significant figures,**:
  e.g. 0.0585; 0.156, 1.64, 20.3 mg/kg.

  Where a target analyte on the target pesticide list is defined as the sum of two or more components, a result for this "summed target analyte" should only be reported if
  a) the method used covers the entire residue definition of this "summed target analyte", e.g. if the method involves a chemical conversion to one component, or
  b) if all individual components entailed in this residue definition were targeted.

  In the latter case, the concentrations of the individual components of the "summed target analyte" should be added-up and expressed as stated in the residue definition on the target pesticide list. If at least one of the components within the "summed target analyte" was not analysed, this "summed target analyte" should be marked as "not analysed". In case one of the components within the complex residue definition was targeted but not encountered at a quantifiable level (<RL), its concentration should be considered equal to zero when calculating the summed result.

  Bias-corrected results should be reported only if this practice reflects the lab's actual or envisaged routine procedure. Where a **result was corrected for bias,** the approach(es) applied to achieve this correction (e.g. standard additions to sample portions, procedural calibration, recovery factor, use of ILIS) must be reported in the respective fields.

- **Reporting Limit (RL) in mg/kg:** the lab's reporting limit for an analyte.
  Where two or more components **of a complex residue definition** are analyzed individually, the **RL of the sum** is also formally required. It should be calculated by summing up the individual RLs of the constituent components expressed as prescribed by the residue definition (applying conversion factors based on the molecular weight of the components). The individual RLs of each component (without conversion) can be reported in the respective fields of the individual components or, if these are not available, in the "Comments" field of the analyte with the complex residue definition. Where the analytical method for the analysis of a complex residue definition involves a chemical transformation, thus generating a single analytical result, the RL of the method is to be reported, but again expressed as prescribed by the residue definition.

- **"Experience with this compound":** Use the dropdown-menu to indicate how many years you have been analysing for the concerned compound using the method applied in this EUPT.

– Reporting of Information on the Analytical Methodologies Applied

On the page of "**Edit methods"** of **EUPT-SRM19 Result Submission Webtool** the participating laboratories have to provide information on the analytical method(s) applied for the analysis of the target analytes detected in the PT Item.

The participating laboratories are urged to thoroughly fill-in all requested information as this information may serve in localizing methodology-related systematic bias.
If entries in required fields within the Result Submission Webtool are missing, you will not be able to proceed with the final submission. Therefore, please fill-in your method information in due time to be on the safe side.

For detailed information on how to fill-in the columns on the "Edit methods" page, please refer to the Guideline for Results Submission that will be distributed to all participants in due time. A link to this guideline can also be found in the info-box on the Webtool.
For quick information please read the **mouse-over messages** popping-up when your mouse cursor meets a field name in the table header for a few seconds.

– Submission of Results

Once you have entered all your results and checked their correctness, you have to submit them by clicking "Final Submission" button before the submission deadline. The "Final submission" button can be found at the bottom of each page. To avoid accidents, a confirmation is requested after clicking the "Final Submission" button.

IMPORTANT:
Following "Final Submission", you will NOT be able to change your data anymore.
Without "Final Submission" your results and method information will not be included in the evaluation!

– Additional Information

After the results submission deadline, **if a laboratory has obtained a tentatively false negative result**, it will be asked to enter the method information for this analyte within 7 working days.

Establishment of Assigned Values

In addition to OfLs from EU Member States or EFTA countries, a limited number of laboratories from EU candidate countries and third countries are allowed to take part in this exercise. For the establishment of the assigned values, typically only results submitted by OfLs from EU and EFTA countries are taken into account.

Subcontracting/External Services

The following tasks are conducted by the EURL-CF, Lyngby, Denmark:
a) Generation of login credentials
b) Generation of Lab Codes in the present PT
c) Programming and administration of EUPT-SRM19 result submission website

Follow-up Actions

After the distribution of the EUPT-SRM19 Preliminary Report, laboratories having submitted poor results (absolute z-scores > 2, false negatives or false positives) will be asked to investigate the reason behind the poor performance, and to report their insights and possible corrective actions to the organiser. This information will be forwarded to the corresponding NRL-SRMs upon request. All EUPT-SRM19 participants are welcome to ask the EURL-SRM for technical assistance.

In the course of results evaluation, the organiser may ask laboratories to provide additional methodology information relevant to the evaluation and interpretation of the PT results.
NRLs should take into account the "**Protocol for management of underperformance in comparative testing and/or lack of collaboration of NRLS"** by DG-SANTE.

Documents

All documents related to the EUPT–SRM19 can be downloaded from the **EUPT-SRM19 Website** or the **EURL-Document Repository (CIRCA-BC)**.
For any questions, please contact the organisers **EURL-SRM@cvuas.bwl.de**

IMPORTANT:
Please check the **EUPT-SRM19 Website** before starting with the analysis in order to **make sure, that you have the latest version of all documents available**. In case of major changes, the participants will be informed via e-mail.

Participation Fees and Payment Details

To cover the costs of production, handling and shipment of the PT-materials the following fees will be charged for one unit of the PT-Material to the participating laboratories:

- OfLs (including NRLs) from EU countries, EU-candidate countries and EFTA countries: 250 €
- Labs based in third countries: 400 €

After the shipment, the EURL-SRM will issue an invoice in pdf format directed to the "invoice address" stated in the registration form. The invoice will be sent to the invoice contact person as well as to the PT-contact persons stated in the registration form. Should the payment being taken care of by another department/institution, the recipient of the invoice is requested to timely forward the invoice accordingly. **Details on payment will be given in the invoices**. The participants should get informed about the basic requirements of their payment system and are responsible for the correctness of the invoice data stated during registration.

As stated in the **General EUPT Protocol**:

1) every lab that has registered for participation in the EUPT-SRM19 and received the test material in good condition has to pay the total fee, irrespective of whether results are submitted or not. This also includes cases where a lab realizes with-in the course of the PT that none of the compounds it has targeted is present at a quantifiable level in the PT-material, or if it realizes that for whatever reasons it cannot conduct any analyses or it cannot submit any results.
2) the EURLs will issue digital invoices in PDF format only and without any electronic signature. If, due to locally applying legal requirements, a participating laboratory needs an electronic invoice, e.g. certificated or signed e-invoice in XML or using a special billing platform to generate and submit an e-invoice, it has to provide the PT-Organizers a suitable and free tool to generate the necessary e-invoice and provide full assistance in case this tool requires the use of a language other than English. Otherwise, the PT-Organiser will not issue an e-invoice. Depending on the incurring extra workload, the participating laboratory may be charged for this extra service.
3) Additional cost may occur if extra services are requested in relation to the payment, such as the completion of additional paperwork and the generation of a new modified invoice in order to include information that was missing or incorrectly provided during registration.
4) The EURLs will not complete any special forms required by the participating laboratories for their financial department or payment office. If completion of such forms is prerequisite for payment in the institution of the participating laboratory, this laboratory or its payment office is requested to fill-in the forms based on the data in the **financial identification note** (**https://www.eurl-pesticides.eu/library/docs/srm/SRM-Bank_m_Financial_Identification.pdf**) and to send the pre-filled form to the EUPT Organisers. The EURLs are willing to provide any information required in the form as long as it is readily available, but they do not agree to provide any personalized (private) data for this purpose. After verification, and if necessary correction, of the information, the EUPT Organisers will return the form with signature and stamp.

Payment is expected to be made within 30 days upon the invoice issue date, unless special information was provided by the participant during registration and/or otherwise agreed between the participant and the Organisers.
If, for any reason, payment cannot be carried out before this date, please contact the Organisers to give explanations.
If no payment or no proof of payment is received and no explanation is given to the Organisers, the Organisers reserve the right not to issue the participation certificate for the concerned laboratory, to exclude its results and its name from the Final EUPT-Report, and to refuse its participation in future EUPT-SRMs.

Bank Details:

Bank account holder:	**Landesoberkasse Baden Wuerttemberg**
Bank Name :	**Baden Wuerttembergische Bank**
IBAN:	**DE 02 6005 0101 7495 5301 02**
BIC/SWIFT:	**SOLADESTXXX**
Payee identification text:	***See invoice (This number MUST be indicated in the payment!)***
VAT of CVUA Stuttgart	**DE 811 600 510**

Please note:

- **Do not make any remittance before you receive the invoice with the Payee Identification Text.**
- **EURL-AO (@ CVUA Freiburg) and EURL-SRM (@ CVUA Stuttgart) belong to the same Ministry and have thus the same bank account.**
  If your laboratory is participating in both PTs (EUPT-SRM19 and EUPT-AO19), please ask your financial department to transfer the fee for each of the PTs separately using the respective payee identification text (= invoice number) given in each invoice. Without this text, your payment will not be able to reach the correct EURL.

Calendar of EUPT-SRM19

(please see https://www.eurl-pesticides.eu/userfiles/file/EurlSRM/EUPT-SRM19_Calendar.pdf)

Target Pesticides List of EUPT-SRM19

(please see https://www.eurl-pesticides.eu/userfiles/file/EurlSRM/EUPT-SRM19_TargetPesticideList.xlsx)

Contact Information

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Organizing Group at the EURL-SRM (Stuttgart)

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Radim Štěpán	Czech Agriculture and Food Inspection Authority, Prague, Czech Republic
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Appendix 10 Calendar and Target Pesticides List of EUPT-SRM19

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

CALENDAR for the EUPT – SRM19

Matrix: Grape Homogenate

(update on 20/11/2023)

Activity	Dates
Announcement of the EUPT-SRM19 opening of the EUPT-SRM19 Website with links to all relevant documents	10 Nov. 2023
Registration Period for EUPT-SRM19 via "**EURL-DataPool**" **Labs classified as "OBLIGED" to participate in the EUPT-SRM19 MUST enter the EUPT-Registration Form within the EURL-DataPool and either register OR give explanations for non-participation**	15 Dec. 2023 – 7 Jan. 2024*
Dispatch of EUPT-SRM19-Specific Protocol	by 18 Jan. 2024
Shipment of EUPT-SRM19 Test Item	5 Feb. 2024
Confirming Sample Receipt and Acceptance via "EUPT-SRM19 Result Submission Webtool"	From 6 Feb. 2024 onwards
Submission of Results (Pesticide scope, Results, Method Info) via "EUPT-SRM19 Result Submission Webtool"	12 Feb. –12 March 23 h (11 p.m.) CET
Submission of Additional/Missing Information e.g. Method info on tentatively false negative results via "EUPT-SRM19 Result Submission Webtool"	13 – 21 March 2024
Dispatch of Preliminary Report containing results as well as preliminary assigned values and z-scores only	Within 3 weeks after the submission deadline
Collection of reasons for underperformance and missing information on methods	April & May 2024
Dispatch of Final Report	Dec. 2024

*Please make sure to register for the EUPT from 15 December 2023 to the deadline 7 January 2024 via EURL-DataPool. Any wish for registration after this deadline or not using the registration website cannot be considered.

REMARK:
Please note that the dates given above may be subject to minor changes. In case of changes significantly affecting the participants or their results, the participants will be informed via e-mail. However, please still check periodically our website for possible updates in case the email does not get through to you.
Contact: eurl-srm@cvuas.bwl.de

The EUPT-SRM Team

EURL-SRM

EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

Target Pesticides List

for the EUPT–SRM19 (2024), Grape Homogenate
(updated on 05.02.2024)

Analytes are grouped into Mandatory, Optional and Extra
For alphabetical sorting in the same order as in the Webtool: See "Ordered from A to Z"

Only mandatory (=compulsory) analytes will be considered in the scope-based classification, optional (=voluntary) and extra analytes not.
Please also refer to the EUPT General Protocol.

M: Mandatory O: Optional E: Extra	Analytes	Notes	Listed in	MRRL [mg/kg]	Update
M	**2,4-D (free acid)**	No hydrolysis required	MACP-Reg. (grapes explicitly named)	0.01	
M	**Abamectin B1a**	Only B1a component	MACP-Reg.	0.01	
M	**Captan**		MACP-Reg.	0.01	
M	**Captan (sum)**	Sum of captan and THPI expessed as captan	MACP-Reg.	0.03	MRRL changed (20.11.2023)
M	Captan metabolite **THPI**	**Expressed as such!**	MACP-Reg.	0.01	
M	**Chlormequat-chloride**	Expressed as chloride salt!	MACP-Reg. (grapes explicitly named)	0.01	
M	**Clopyralid**	No hydrolysis required	MACP-Reg. (grapes explicitly named)	0.01	
M	**Copper**		MACP-Reg.	0.2	
M	**Dithianon**		MACP-Reg. (grapes explicitly named)	0.01	
M	**Dithiocarbamates as CS_2**	Expressed as CS_2	MACP-Reg.	0.01	
M	**Emamectin B1a**	Only B1a component	MACP-Reg.	0.01	
M	**Ethephon**		MACP-Reg. (grapes explicitly named)	0.01	
M	**Folpet**		MACP-Reg.	0.01	
M	**Folpet (sum)**	Sum of folpet and phthalimide expessed as folpet	MACP-Reg.	0.03	MRRL changed (20.11.2023)
M	Folpet metabolite **Phthalimide**	**Expressed as such!**	MACP-Reg.	0.01	
M	**Glufosinate**		MACP-Reg.	0.01	
M	Glufosinate metabolite **MPP (aka MPPA)**		MACP-Reg.	0.01	
M	Glufosinate metabolite **N-Acetyl Glufosinate**		MACP-Reg.	0.01	
M	**Mepiquat chloride**	Expressed as chloride salt!	MACP-Reg.	0.01	
O	**Amitrole**		WD (need data on cummul. risk asessmer	0.01	
O	**MCPA** (free acid)	No hydrolysis required	WD (grapes explicitly named)	0.01	
O	**Meptyldinocap**	Note: You may skip the analysis of meptyldinocap as such if you cover the sum only following chemical conversion of meptyldinocap to 2,4-DNOP.	WD (grapes explicitly named)	0.01	MRRL changed (20.11.2023)
O	**Meptyldinocap (sum following hydrolysis)**	Sum of meptyldinocap and 2,4 DNOP expressed as meptyldinocap,**following hydrolysis and determined as 2,4-DNOP.** Note: If you cover meptyldinocap (sum) only following chemical conversion to 2,4-DNOP, you may skip the analysis of the two individual components.	WD (grapes explicitly named)	0.01	Based on how the sum result was obtained, Meptyldinocap (sum) was splitted in two lines with different MRRLs. (20.11.2023)
O	**Meptyldinocap (sum calculated)**	**Sum of meptyldinocap and 2,4 DNOP expressed as meptyldinocap (calculated sum)**	**WD (grapes explicitly named)**	0.02	
O	Meptyldinocap metabolite **2,4 DNOP**	Free phenol (**expressed as such!**) Note: You may skip the analysis of free 2,4-DNOP if you only quantify this compound following chemical conversion of meptyldinocap to 2,4-DNOP.	WD (grapes explicitly named)	0.01	MRRL changed (20.11.2023)
O	**Triclopyr (free acid)**	No hydrolysis required	WD (grapes explicitly named)	0.01	
O	**Trimethylsulfonium cation**		WD (grapes explicitly named)	0.01	
E	**Difluoroacetic acid (DFA)**		WD 2024	0.02	
E	**Gamma Cyhalothrin**	Only SR enantiomer	MACP/WD	0.01	

MACP-Reg.: Multiannual Control Program Regulation.
Link: REGULATION (EU) 2023/731 of 03 April 2023; https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32023R0731.
WD: Working document on pesticides to be considered in national control programs to ensure compliance with MRLs of pesticides residues in food; SANCO/12745/2013; 21-22 November 2022 rev. 14(5); https://www.eurl-pesticides.eu/userfiles/file/WD/SANCO_12745_2013_rev_14_5.pdf (Note: The link to the latest update will be publihsed as soon as it becomes available

EURL-SRM — EU Reference Laboratories for Residues of Pesticides — Single Residue Methods

Target Pesticides List

for the EUPT–SRM19 (2024), Grape Homogenate
(updated on 05.02.2024)

alytes are sorted alphabetically in the same order as in the Webtool.
grouping into Mandatory and Optional (incl. Extra): See sheet "Grouped into Mandatory-Optional"

y mandatory (=compulsory) analytes will be considered in the scope-based classification, optional (=voluntary) and extra analytes not.
ase also refer to the EUPT General Protocol.

Mandatory Optional xtra	Analytes	Notes	Listed in	MRRL [mg/kg]	Update
M	**2,4-D (free acid)**	No hydrolysis required	MACP-Reg. (grapes explicitly named)	0.01	
O	**2,4 DNOP** (Meptyldinocap metabolite)	Free phenol (**expressed as such!**) (Note: You may skip the analysis of free 2,4-DNOP if you only quantify this compound following chemical conversion of meptyldinocap to 2,4-DNOP)	WD (grapes explicitly named)	0.01	MRRL changed (20.11.2023)
M	**Abamectin B1a**	Only B1a component	MACP-Reg.	0.01	
O	**Amitrole**		WD (need data on cummul. risk asessmer	0.01	
M	**Captan**		MACP-Reg.	0.01	
M	**Captan (sum)**	Sum of captan and THPI expessed as captan	MACP-Reg.	0.03	MRRL changed (20.11.2023)
M	**Chlormequat-chloride**	Expressed as chloride salt!	MACP-Reg. (grapes explicitly named)	0.01	
M	**Clopyralid**	No hydrolysis required	MACP-Reg. (grapes explicitly named)	0.01	
M	**Copper**		MACP-Reg.	0.2	
M	**DTC (expr. as CS_2)**	Expressed as CS_2	MACP-Reg.	0.01	the same order as in the webtool! (05.02.2024)
E	**Difluoroacetic acid (DFA, extra analyte)**		WD 2024	0.02	
M	**Dithianon**		MACP-Reg. (grapes explicitly named)	0.01	
M	**Emamectin B1a**	Only B1a component	MACP-Reg.	0.01	
M	**Ethephon**		MACP-Reg. (grapes explicitly named)	0.01	
M	**Folpet**		MACP-Reg.	0.01	
M	**Folpet (sum)**	Sum of folpet and phthalimide expessed as folpet	MACP-Reg.	0.03	MRRL changed (20.11.2023)
E	**Gamma Cyhalothrin (extra analyte)**	Only SR enantiomer	MACP/WD	0.01	
M	**Glufosinate**		MACP-Reg.	0.01	
O	**MCPA** (free acid)	No hydrolysis required	WD (grapes explicitly named)	0.01	
M	**MPP (aka MPPA)** (Glufosinate metabolite)		MACP-Reg.	0.01	the same order as in the webtool! (05.02.2024)
M	**Mepiquat chloride**	Expressed as chloride salt!	MACP-Reg.	0.01	
O	**Meptyldinocap**	Note: You may skip the analysis of meptyldinocap as such if you cover the sum only following chemical conversion of meptyldinocap to 2,4-DNOP)	WD (grapes explicitly named)	0.01	MRRL changed (20.11.2023)
O	**Meptyldinocap (sum, calculated)**	**Sum of meptyldinocap and 2,4 DNOP expressed as meptyldinocap (calculated sum)**	**WD (grapes explicitly named)**	0.02	Based on how the sum result was obtained, Meptyldinocap (sum) was splitted in two lines with different MRRLs. (20.11.2023)
O	**Meptyldinocap (sum following hydrolysis)**	Sum of meptyldinocap and 2,4 DNOP expressed as meptyldinocap,**following hydrolysis and determined as 2,4-DNOP.** Note: If you cover meptyldinocap (sum) only following chemical conversion to 2,4-DNOP, you may skip the analysis of the two individual components.	WD (grapes explicitly named)	0.01	
M	**N-Acetyl glufosinate** (Glufosinate metabolite)		MACP-Reg.	0.01	
M	**Phthalimide** (Folpet metabolite)	**Expressed as such!**	MACP-Reg.	0.01	
M	**THPI** (Captan metabolite)	**Expressed as such!**	MACP-Reg.	0.01	
O	**Triclopyr (free acid)**	No hydrolysis required	WD (grapes explicitly named)	0.01	
O	**Trimethylsulfonium cation**		WD (grapes explicitly named)	0.01	

:P-Reg.: Multiannual Control Program Regulation.
REGULATION (EU) 2023/731 of 03 April 2023; https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32023R0731.
Working document on pesticides to be considered in national control programs to ensure compliance with MRLs of pesticides residues in food; SANCO/12745/2013; 21-22 November 2022 rev. 14(5); https://www.eurl-icides.eu/userfiles/file/WD/SANCO_12745_2013_rev_14_5.pdf (Note: The link to the latest update will be publihsed as soon as it becomes available)

Schreiter, Pat (CVUA-S)

Von: Schreiter, Pat (CVUA-S) <Pat.Schreiter@cvuas.bwl.de> im Auftrag von EURL-SRM Pesticides (CVUA-S) <EURL-SRM@cvuas.bwl.de>
Gesendet: Freitag, 15. Dezember 2023 07:24
An: EURL-SRM Pesticides (CVUA-S)
Cc: EURL pesticides (CVUA-FR); Carmen Ferrer; 'eurl-cf@food.dtu.dk'
Betreff: Call for Registration (EUPT-SRM19, Grape) (EU/EFTA_OfLs)

Dear Colleagues from EU- and EFTA-OfLs,

The EUPT-SRM19 using grape as matrix is now open for registration, and your laboratory is welcome to register for the EUPT-SRM19 **by 07 January, 2024, 11.30 p.m.**

NEW!

- **From now on you can register for any of the 4 EUPTs on analysis of pesticides residues (EUPT-SRM19, -CF18, -FV26 and -AO19) as well as two Interlaboratory Studys organized by the EURL-AO** (Interlaboratory Study on Fish (ILS-01) and on Pyrethroids) **to be conducted in 2024 in parallel.**
  Please refer to the website of each of the PTs for detailed information (matrix, calendar, TPL ...). The websites of the EUPT-AO19 and information on the two additional Interlaboratory Studys will be published later.
- **To register for these EUPTs, please log in to the EURL-DataPool using your EURL-DataPool login credentials and click the register "EUPT", then "Register".**
  Based on the data stored in the OfL-Network Database concerning commodity scope and lab status (e.g. OfL, NRL) and verified by the NRLs, all OfLs labs were tentatively classified as "obliged" or "non-obliged/voluntary" to participate in a certain EUPT on pesticides residues. The classification of your lab for each PT is displayed on the EUPT-Registration page after logging in.
  Below are the links to the instructions on registration:
  - Instruction on registration as an obliged participating laboratory
  - Instruction on registration as a participating laboratory on voluntary basis

Please read this email carefully, before you register for the EUPT-SRM19.

- **NRLs-SRM and OfLs analyzing fruits and vegetables were classified as obliged to participate in the EUPT-SRM19.**
- **All obliged laboratories have to enter the registration form**.
- **Obliged labs not intending to participate** in the EUPT-SRM19 still have to access the registration page and choose "No" under "I want to REGISTER my lab for this EUPT" and **provide an explanation for non-participation** (requirement by DG-SANTE).
- If your lab is classified as **non-obliged** and you are not going to participate in this PT, you don't have to do anything.
- If you think that the EUPT-SRM19 classification of your laboratory is erroneous, please contact your NRL and the eurl-srm@cvuas.bwl.de.
- **Please check first, if your laboratory is able to analyse at least one of the compounds on the Target Pesticides List,** before you register for participation in the EUPT-SRM19.
  Every lab that had registered for participation in the EUPT-SRM19 and received the test material has to pay the total fee, even though it recognized later that it is not able to analyse any one of the compounds in this PT and has to withdraw its participation.

During your registration:

1. One portion of the test material will contain approx. **400 g** grape homogenate. For ordering double amount, please give your reason in the registration form and the fee will double.

2. The **lab name for shipment** is limited to **40** letters.
   A short acronym is preferred and please write it in your local language phonetics using LATIN letters.
3. Please do not use language-specific letters, e.g. Š, Ă, í , ł... Greek or Cyrillic, in any entries of your shipping address, as those are not accepted to prepare the waybills.
4. **The "City" in the sample delivery address MUST be written in English (e.g. "Rome", "Prague" instead of "Roma" or "Praha")**!
5. Please enter your **phone or mobile number in international format including country and city code**, e.g. for EURL-SRM (Germany, Stuttgart): +49 711 34261234
6. Please **check carefully the sample delivery address in the registration confirmation** sent to you upon your registration. For any error please correct it on the registration form by the registration deadline. During the registration period you or any member of your laboratory can edit any of your laboratory's entries on the registration page as often as you like. Following any change of your registration data, you will receive a new email confirming registration for participation / non-participation with the changed data.

For further information (e.g. Target Pesticides List, Calendar, Participation Fee...) on the EUPT-SRM19 please visit the EUPT-SRM19 Website.
The Specific Protocol for the EUPT-SRM19 will be dispatched two weeks prior to the shipment.
If you have any questions, please contact us EURL-SRM@cvuas.bwl.de

Best regards,
The EURL-SRM Team

Guide to EUPT-SRM19 Results Submission Webtool

Version: 2024-02, Date: 05-02-2024, Authors: P: Schreiter, M. Anasatassiades

In order to get familiar with the Webtool, please read this guideline carefully before you start entering your data.

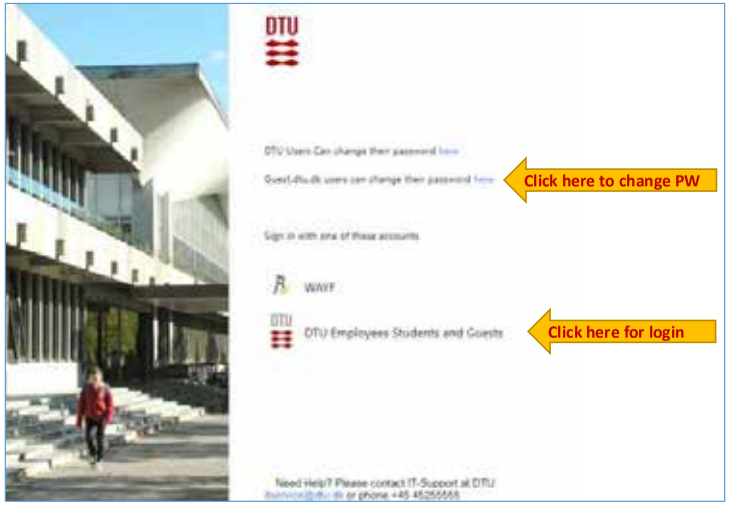
General Information:

- **Please only use GOOGLE CHROME, EDGE or FIREFOX Web-browsers under INCOGNITO mode.**
  The latest software version of these browsers is recommended.
- **Your data are automatically saved as soon as you move the cursor from one edited field to another.** Therefore, almost all pages and tables do not have any save button.
- You can access the Webtool as often as you need during the results submission period. However, **before deadline you must submit your results and method information by clicking "*FINAL SUBMISSION*". Otherwise, your result will not be included in the evaluation!**
- **After FINAL SUBMISSION, you will NOT be able to change your results anymore!**

Getting started

Link to Webtool: www.eurl.dtu.dk

Choose "**DTU Employees Students and Guests**"



PT-contact persons can **login** to the Webtool using their personal login credentials, which are valid for all EUPTs-CF, -FV, -AO, -SRM, -MN and -PC and linked to their email address.

As a reminder, PT-contact persons will receive an e-mail sent by DTU with their **personal username** shortly prior to the opening of the EUPT-SRM19 Webtool.

Using your username or your e-mail address, your can **ask for your password**, also in case you have **forgotten your passwor,** using this link:
https://guest.dtu.dk/Sites/GuestLogin/RetrievePassword.aspx.

In order to increase security we recommend changing your password once a year.

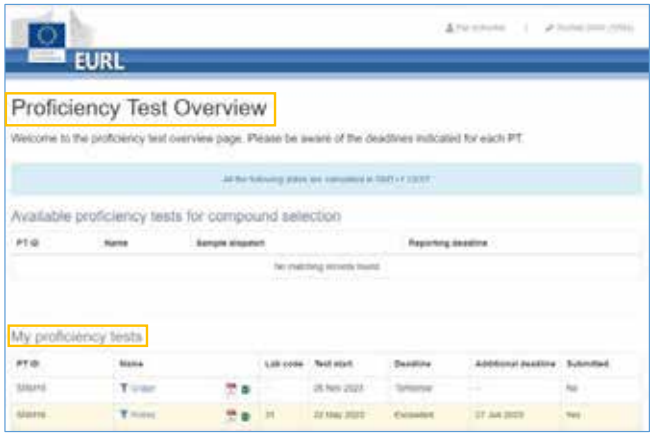
To **change your password** you use this link: https://guest.dtu.dk/Sites/GuestLogin/Default.aspx

After signing-in, you will be guided to the *Proficiency Test Overview* page.

Proficiency Test Overview

On the **page *"Proficiency Test Overview"***, you will see on the top the section "*Available proficiency tests for compound selection*" with the PTs that are available for compound selection and below the section "*My proficiency tests*" showing information on the currently active EUPT(s), as well as on EUPTs in which your lab has participated in the past and in which you have been declared as contact person (main or alternative) along with the e-mail address you have just used to login.

A new PT-specific lab code will be automatically generated when the Webtool-section of the concerned PT is opened for the first time.



Sample receipt and acceptance

By clicking on "**SRM19 | Grape**" under "*My proficiency tests*", you will see the pop-up window "**Edit sample Receipt"**. In addition, your lab code for this PT is generated (in our case: 7 in the background window)

Please fill-in the information requested within this pop-up-window:

- **Sample Number**: Please enter the bottle number of the Test Item you received.
- **Material Accepted**: Based on condition upon receipt please indicate "Yes" or "No".
  If you do not accept the PT-materials, please contact the PT-Organizers via E-mail, too.
- **Sample received:** Please enter the date when the parcel arrived at your institution.

"Material Accepted" (Yes, unchangable) changed to yes/no dropdown

- **Remarks e.g. on dry ice condition:** Please enter here any remarks concerning the **condition of the parcels, the bottles and the test item**, e.g. if there was any detected **leakage** on the bottle, if there was a **delay** between package arrival and its opening (indicate storage temperature during this period), **whether dry ice was still present** in the parcel when it was opened, indicate the **temperature or the state of the test item** at the time the bottle was opened (e.g. frozen, partly frozen, fully defrosted but cold, defrosted >15°C).

Completing the "*Edit Sample Receipt*" window is a **precondition for being able to access the submission page.** This should be done **ideally shortly after parcel receipt** in order to **receive your lab code** that is absolutely necessary for the PT organisation.

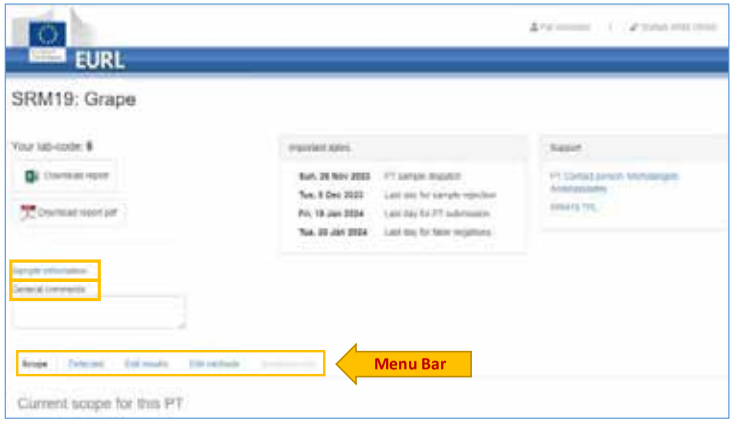
At any time throughout the PT-period you can come back and edit your entries on "*Edit sample receipt*" under "*Sample information*" (please see next screenshot, left navigation bar).

Upon clicking on "*Save and close*" you will be guided to the following page on which you can see your **Lab-code,** a **button for downloading the report (=your results and all data),** a **button for downloading your results only,** and a **text field "General Comments" for any remarks** you may want to pass to the organizer in relation to this PT.

Tip: Using the button, you can export the concentrations you entered for the analytes you sought for and detected every time, e.g. for check the values just before you click final submission. New!

Under "**General comments"**, you may track or highlight information that you would like to communicate to the organizers, e.g. problems with data tracking in the webtool, accidents or inappropriate handling of the material that may have had an influence on your results. If some information communicated here is also requested under "edit result" or "edit methods", please still fill-in the requested information despite being redundant.

On the right side of the page, you can find **important dates** and **Supporting Information** with useful links. If you scroll further down, you will find a **Menu Bar** with the following tables: "***Scope"***, "***Detected"***, "***Edit results"***, "***Edit methods"*** and "***Additional info"***.



On the bottom of each table you will see the button for ***Final submission.***

Use this button only after you have already entered all your data for this PT and want to submit them for the PT evaluation.

After the Final Submission
you will NOT be able to change your results any more !!

Scope

On this table you can see the **current scope for this EUPT** in alphabetic order.

FOR EUPT-SRMs THERE IS NO NEED TO INDICATE YOUR ANALYTE SCOPE IN ADVANCE!

In contrast to other EUPTs organized by EURL-CF, -FV and -AO**, in the case of EUPT-SRMs you don't need to select the analyte scope before sample shipment.**

The Table "Scope" remains accessible and editable during the whole results submission period, from opening of the Webtool till the deadline for result submission. Thus, you are able to change your scope selection at any time.

Only analytes marked as "Analysed" on this page will show up in the table "Detected".

In this table, please first select the compounds you have targeted within the EUPT-SRM19 and then enter your Reporting Limit (RL) of each analyte within your PT Scope.

The MRRLs were set as default reporting limits for each pesticide within your PT Scope. Please make sure to **change the Reporting Limit (RL) to that of your laboratory**!

Please also state for each analyte whether it is "*within your routine scope*" or not. This information is mandatory for all compounds on the Target Pesticides List regardless of whether they were targeted in this PT or not. In case that a compound is within your routine scope but skipped in the present PT, please state the "*Reason for not analyzing compound within your scope*".

Even if your laboratory doesn't analyze for certain compounds routinely, you are encouraged to analyze them in this PT and to use this opportunity as a starting point for assessing your newly introduced methods or for expanding your scope.

Detected

This table will only list analytes that were selected as "analysed" under the table "Scope". Please mark the analytes that you have detected in the Test Item so that you can report their concentrations.

The following exemplary selections are used as filters for the subsequent "*Edit results*" table.

Edit results

Click on the *"Edit results"* tab to enter your quantitative results of the detected analytes in this PT. You can see only those analytes that have been marked on the "*Detected*" table.

NOTE: The system will automatically save your inputs when moving from one field to another.

- Use the scroll bar to reach other parts of the table.
- Use copy function to copy the information from one pesticide to others.

The **copy function** works only if all mandatory fields for the template compound were filled-in. Otherwise, the icon of copy function becomes red .
Be aware that the concentration in the template analyte is also copied in the target analyte(s). Please don't forget to check and change the concentration(s) in the target analyte(s).

New!

Further information about the "*Edit test results*" table is summarized below.

Field(s)	Explanation
Concentration [mg/kg] **(=Concentration in Test Item)**	Concentration in Test Item **in mg/kg preferably with 3 significant figures**, (syntax: e.g., 0.0413; 0.345; 3,49; 13,8) **Only numerical values are accepted; pls. use a dot as a decimal separator.**
Concentration blank [mg/kg]	Deactivated, since no blank material was sent to the participants.
Expanded measurement uncertainty [%]	Please indicate the expanded measurement uncertainty value in % (e.g., "50") that you would report for the specific compound-matrix combination (e.g. in case of an MRL-Violation)
Rec. Corr. by factor?	Please indicate **"yes" only if the result reported was corrected using a RECOVERY FACTOR**. Other means of recovery-based correction (correction for bias) are covered by other questions.
Recovery rate % [%]	(Mean) recovery rate or bias in % (syntax: e.g., "125") used for deriving the recovery corrected result that was submitted.
Recovery Obtained	Please choose among the dropdown-options to indicate how the recovery rate used for correcting for bias was obtained.
Recovery individuals	Number of replicate experiments conducted to obtain the recovery rate/recovery factor that was used for the correction of results
Recovery details	Please give brief details of, e.g., how the reported recovery rate was obtained, the matrix used if not matching, the spiked compound, the measured compound, the spiking level/range etc.
Comments (incl. Outsourcing of Analysis)	Please give information on whether this analysis was **OUTSOURCED/SUBCONTRACTED** to another lab* (please name the analyzing lab and indicate if the outsourcing reflects the routine procedures). You may also add any remarks concerning other aspects covered by this subpage." * This also applies to cases where the analysing laboratory belongs to the same institution/company but runs its own quality control system.

Edit methods

Click on the "*Edit methods*" tab to start reporting method information.

NOTE: the system will automatically save your inputs when moving from one row to another.

- Use the scroll bar to reach other parts of the table.
- You can get short description about the columns via mouse-over messages. In some systems or browsers these mouse-over messages do not show up. In this case, please refer to the table below for the explanation and further information about the fields on this page.
- Use the edit function to get an overview of all method-information fields of a selected pesticide in a different format (edit view, see screenshot below). However, please note that there is no mouse-over information on this edit view.
- Please note: On the edit view, if you change any fields of a selected compound, you can save them and **return to the table view only if all mandatory fields of this compound are filled-in**.

Otherwise, you have to return to the initial table view by clicking on the button "cancel" without saving the changes.

- Use copy function (on the table view) to copy the information from one pesticide to another.

The copy function works only if all mandatory fields for the template compound were filled in. Otherwise, the icon of copy function becomes red .

Further information about the "*Edit methods*" table is summarized below.

Field(s)	Explanation
Ref. method	Choose from the dropdown list. If you have used a modified form of the mth, pls. give details under "Mth Details"
Ref. method modified	Specify if you have introduced any noteworthy modifications to the selected reference method. If yes, pls. give brief details of the modification under "Mth. details".
Mth. details	Describe your method shortly if it is not on the dropdown menu or indicate shortly the modifications introduced to the selected reference method.
Experience with this compound	Experience of your lab with the analysis of this pesticide (with any type of commodity).
Water addition	Please choose "Yes" if water or a water-containing solvent mixture was added to the sample to assist extraction.
Water addition details	Details on water addition (e.g. amount in mL, step of addition)
Initial Sample Temp	Initial Temperature of sample when you have started with the extraction procedure (choose closest value)
Sample thawed prior to analysis	Please indicate if and for how long approximately your sample was left in a THAWED state after reception until analysis of the compound
Details on sample thawing	Please provide any details relevant to the thawing to the sample (e.g. "thawed overnight in refrigerator"; left for 4 h on the bench to partly thaw followed by milling)
Sample Weight (g)	Enter the weight (in gram) for the analytical portion.
Extraction/partitioning solvent 1	Choose the solvent from the dropdown menu
Extraction/partitioning solvent 2	Choose the solvent from the dropdown menu, if you use more than one solvent.
Extraction/partitioning solvent 3	Choose the solvent from the dropdown menu, if you use more than two solvents.
Extraction solvent details	Enter details on solvents used in extraction or partitioning steps or if the solvent is not in the drop down menu
Extraction Time	Duration of main extraction step including any waiting time after addition of solvent (Please choose the closest value). If extraction is combined with a chemical transformation, then chose "Combined w. chem. transformation" and indicate the time under "Chemical transformation Time"
Extraction approach	Choose extraction approach from dropdown list
Partitioning salts used	Choose partitioning salt used from dropdown list
pH modified	Indicate if you have modified the pH at any stage of the procedure (e.g. by buffering, acid/base addition)
pH modified details	Please give details on pH modification step(s)
Clean up 1	Choose the clean-up approach employed from the dropdown list
Clean up 2	Choose the clean-up approach employed from the dropdown list, if you use more than one clean up step

Field(s)	Explanation
Clean up 3	Choose the clean-up approach employed from the dropdown list, if you use more than two clean up steps
Clean up details	Please give details on clean-up step or describe your clean up procedure if it is not listed in the dropdown menu
Chemical transformation	Mark if your procedure included a chemical transformation e.g. hydrolysis, derivatization, reductive cleavage to CS_2, etc.
Chemical transformation Time	Please chose closest time from dropdown list. **If extraction and chem. transf. were combined, indicate closest combined time here.**
Chemical transformation Temp.	Please choose the closest temperature from the dropdown list
Chem. Transf. Details	Please give details on chemical transformation step(s) conducted
Calibration approach	Choose the calibration approach used. **NOTE:** "Procedural calibration" and "Standard additions to sample portions" involve inherent correction for recovery/bias.
Determination Technique	Choose the instrumental technique used to generate your quantitative result
Headspace or SPME	Here you can choose your headspace or SPME method
Determ./Headspace/SPME Details	Here you can add any relevant details on Determination technique used e.g. columen, mobile phase, Headspace or SPME sampling (incubation time/temperature; injected volume; SPME fiber type)
Other Approaches to Corr. PT-Result for Recov.	Shortly describe any OTHER APPROACHES employed for correction of results for recovery/bias. **NOTE:** Corrections for recovery via ILIS or via RECOVERY FACTOR are covered by other specific questions. "PROCEDURAL calibration" and "STANDARD ADDITIONS TO SAMPLE PORTIONS" are covered under "calibration"
Matrix used for calibration	Blank commodity used for matrix-based, matrix-matched or procedural calibration
Matrix calibration details	Please name the blank commodity used to prepare the calibration solutions and any other details of importance, such as differences between sample extract and calibration solution (e.g. in cleanup, dilution etc.)
Compound(s) used for Calibration	Here you can choose your compounds used for calibration
Compound(s) used for Calibration Detail	Here you can specify your compounds used for calibration, in particular, if it is not within the dropdown options.
IS used	**Please choose "No" if no "IS" was used or if the IS was used only for quality control purposes and not for the calculation of the target analyte result**. Please choose one of the two "Yes" options if the IS was used for calculating the target analyte concentration.
IS Name	Please give details on the IS used
When was IS added?	Mark at what stage of the procedure the IS was added
Comments **(= Comments on methods)**	Please enter here any comments concerning the analytical method of the selected compound

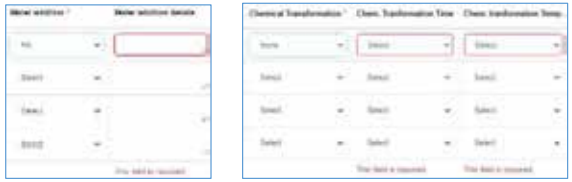
Final Submission

VERY IMPORTANT REMARK!

Make sure to enter values in all mandatory fields. Validate by ensuring ***no red frames*** are found in the table. Otherwise, you are not able to submit your data.

Please note:

- **Red frames** or information showing that a field is mandatory are not always immediately updated after entering or saving data. You may have to **actively click the cells to see the updated status**.
- In some cases, you may probably see the following situation:



In both screenshots, the entries are correct, since no water was added or chemical transformation was conducted and water added details or chem. transformation time/temp are actually not required.
To "remove" the red rings or the sentence "This field is required": **just click on "select" or on the field with the red frame.**

When all fields are filled-in and you have checked their correctness, you are ready to submit your results. Accept and submit your final results by clicking the check box and then click on "*Final submission*".

Additional Information

Pesticides present in the Test Item and reported as "analysed", but not reported as "detected" are regarded as **tentative false negatives**. For those compounds **method information is required**.

After the PT deadline, if you have submitted tentative false negative or false positive result(s) in this PT, the PT-row will be highlighted in pale yellow on the *Proficiency Test Overview* page.

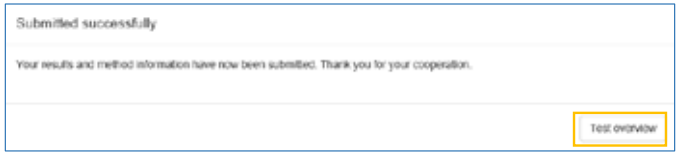
If there are **mandatory cells with missing data**, you will obtain an **error message upon clicking "Final submission"**, and those cells are marked with the **red frames**. Please fill in all the missing data and click again "Final submission".

IMPORTANT:

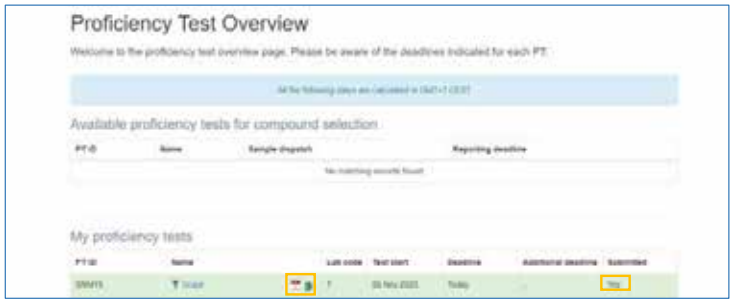
You will **NOT** be able to edit your results after the final submission!
We thus recommend you checking the concentrations you entered for the analyted detected using the exported pdf-file by click the button on the PT Overview.
Your data have to be submitted before the deadline on **Tue. 12 March, 2024, 23 h (11 p.m.), CET.**

New

Once "Final submission" is successful, the following pop-up window confirming successful submission of the data will appear on the screen. In parallel, you will receive an email with an attached Excel and pdf files, in which your submitted data is compiled. You can also download it form the "*Test Overview*" (please see below).



By clicking on the "*Test Overview*" button on the pop-up message you return to the *Proficiency test overview* page. The status of the PT is now: *Submitted= "Yes"*.

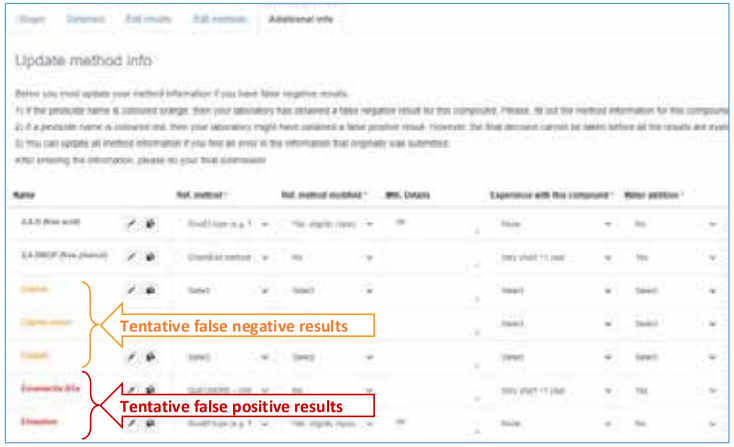


By clicking on the excel-icon you can download your submitted data "results + all information", even for PT with exceeded deadline. By clicking on the pdf-icon , you will see your submitted results only at a glance.

IMPORTANT:

After final submission, you will not be able to edit your results any more!
If you find any errors in your results in the exported pdf-file before the submission deadline and want to correct them, please contact the SRM19 organizers via email.

Click on the yellow-marked EUPT:



Tentative false positives are written in red colour.

Tentative false negatives are written in orange colour.

Please fill-in **the missing method information for the compounds identified as tentatively false negatives. Submit this information by 21 March.**

Please note:
During this period, you can edit the method information not only of the analytes preliminarily judged as FNs, but also of all other analytes listed in the table.
Therefore, please use this opportunity to check your data for your methods again and, if necessary, correct them.

Appendix 12 (cont.) „Guide to EUPT-SRM19 Results Submission Webtool"