CRL-Proficiency Test-FV-LC-1, 2007

Pesticide Residues in Pear Homogenate

Final Report

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QCG: Quality Control Group
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CRL-EUROPEAN COMMISSION PROFICIENCY TEST ON PESTICIDE RESIDUES IN FRUIT AND VEGETABLES AT LOW CONCENTRATIONS - 1 2007

The Council Directives 86/362/EEC[1] and 90/642/EEC[2] make provision for the organisation and financial support of regular proficiency testing (PT) of those laboratories that perform analyses for their official national monitoring programmes. These proficiency tests are carried out in order to ensure the quality, accuracy and comparability of the residue data sent by EU Member States to the European Commission (as well as other Member States) on an annual basis.

Regulation (EC) No 882/2004[3] lays down the general tasks, duties and requirements for Community Reference Laboratories (CRLs) for Food, Feed and Animal Health. Among these tasks is the organisation of comparative tests. Up to now, these tests have been performed using test materials containing residue levels above 0.1 mg/Kg. However, this year, in parallel with the normal Fruit and Vegetables European Proficiency Test 9, a second Proficiency Test in Fruit and Vegetables (but at low concentrations) was carried out for the first time. For this proficiency test the residue levels were all lower than 0.1 mg/Kg. This test was considered relevant because of the importance of being able to determe and quantify pesticide residues at low levels - especially in baby food and organically grown produce. Also from 2008, Regulation 396/05/EC will set LOD MRLs at 0.01 mg/Kg for all non-approved pesticides. This will mean that laboratories must be able to accurately determine residues around the 0.01 mg/kg level in order to enforce these regulations. The European Proficiency Test at Low Concentration - 1 has been organised under the umbrella of the CRL in Fruit and Vegetables at the University of Almería, Spain[4]. The Proficiency Test is an activity which will be carried out annually. Participation in this EUPT-FV-LC1 European Proficiency Test was open to all official national or regional analytical laboratories involved in the determination of pesticide residues in fruit and vegetables within Member States of the EU. It was especially important that National Reference Laboratories participated.

This report will be presented to the European Commission Standing Committee for Animal Health and the Food Chain.

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[1] Council Directive 86/362/EEC of 24 July 1986 on the fixing of maximum levels for pesticide residues in and on cereals. Published at OJ of the EU 221, 7.8.1986, p. 37. Directive as last amended by Commission Directive 2006/62/EC (OJ L 206, 27.7.2006, p. 27).

[2] Council Directive 90/642/EEC of 27 November 1990 on the fixing of maximum levels for pesticide residues in and on certain products of plant origin, including fruit and vegetables. Published at OJ L 350, 14.12.1990, p. 71. Directive as last amended by Commission Directive 2006/62/EC.

[3] Regulation (EC) N° 882 /2004 of the European Parliament and of the Council on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Published at OJ of the EU L191 of 28.05.2004

[4] Commission Regulation (EC) No 776/2006 of 23 May 2006 amending Annex VII to Regulation (EC) No 882/2004 of the European Parliament and of the Council as regards Community reference laboratories.

1. INTRODUCTION

Thirty laboratories agreed to participate in this 1st European Commission Proficiency Test at Low Concentrations.

This proficiency test was performed in 2007 using pear homogenate. The pears were grown in the north of Spain, in Navarra, and were treated post-harvest with a standard solution spiked onto homogenised pears and then diluted by the addition of non treated homogenised pears. Eleven pesticides were used for the treatment. Participating laboratories were provided with an untreated pear homogenate as well as the treated pear test material.

The test material, 300 g of pear homogenate containing residues of pesticides, together with 300 g of 'blank' pear homogenate, was shipped to participants on the 9th April 2007. The deadline for the submission of results to the Organiser was the 7th May 2007. The participants were provided with a list of forty-six pesticides (Annex 1), which could be present in the treated test material and were asked to determine the levels of all the pesticide residues that they detected. A Minimum Required Reporting Level (MRRL) of 0.005 mg/kg was assigned for all of the pesticides. This abbreviation is a replacement for MRPL or MPRL, as first used in previous EU PTs. Due to the fact that many other trace analysts in related fields, such as veterinarny drug residues, use a similar abbreviation and as a result, some confusion has arisen.The term MRRL will be maintained and used in future PTs.

Participants were also asked to analyse the blank test material and report residues of any pesticide they found which were included in the Pesticide List. This 'blank' material was intended to be used for recovery experiments for the pesticides detected in the test material, and if necessary, for the preparation of matrix-matched calibration standards.

The median values of the analytical data submitted were used to obtain the assigned (true) values for each of the eleven pesticide residues present. A fit-for-purpose relative target standard deviation (FFP RSD) of 25% was chosen to calculate the target standard deviations (σ) as well as the z-scores for each of the pesticides present.

For the assessment of the overall laboratory performance the Weighted Sum of z-Scores (WSZ), as used in the previous Proficiency Test, has been applied. Only laboratories that fulfilled the criteria of detecting at least nine of the eleven present pesticides (~90%), with no false positives reported, have been classified as having 'sufficient scope', and have therefore been placed in Category A. Within this category, the laboratories have been sub-divided as 'good', 'satisfactory' or 'unsatisfactory'. All the other laboratories have been placed in Category B, and classified as having 'insufficient scope'. For laboratories in Category B, individual z-scores were calculated, but their overall performance has not been assessed, although they have been placed in order of the number of pesticides sought and the number of acceptable z-scores achieved.

Classical procedures for summing z-scores (SSZ and RSZ) were employed using the individual z-scores of the participating laboratories.

2. TEST MATERIALS

2.1 Analytical methods

The two analytical methods, described briefly below, as well as other procedures used by the Organisers for the homogeneity and stability tests performed by the University of Almeria, were:

- GC method [1]: ethyl acetate extraction in the presence of sodium sulfate, filtration, addition of more sodium sulfate, evaporation, re-dissolution in cyclohexane and determination by GC-MS/MS.
- LC method [2]: ethyl acetate extraction in the presence of sodium sulfate and addition of sodium hydroxide, filtration, addition of more sodium sulfate, evaporation, re-dissolution in methanol, and determination by LC-MS/MS.

Acetamiprid, Carbaryl, Imazalil, Imidacloprid, Iprodione, Omethoate, Oxydemeton-methyl Pyrimethanil and Tetraconazole were determined using the LC-MS/MS method. The other pesticides (Diazinon and Dimethoate) were determined using the GC method. For confirmation purposes, MS/MS spectra were used.

2.2 Preparation of treated test material

Before preparing the test material, the pesticides and suitable residue levels for the study were selected following recommendations made by the Quality Control Group, which had been specifically appointed for Proficiency Test – FV – LC1. The pears were grown in the north of Spain, in Navarra. Ten kilogrammes of pears were treated post-harvest by spiking them with a standard solution. These ten kgs were mixed with a further fifty kgs to dilute the concentration and acheive low level residues. A portion was taken and analysed to check the residue levels in order to decide whether or not additional treatment was necessary. When the residue levels contained in the pears were close to those recommended by the Quality Control Group, the entire sample was frozen and chopped using liquid nitrogen and a mincer. The frozen chopped pears were mixed in a constantly spinning container, until a homogeneous material was obtained. 300g portions of the homogenate were weighed out into screw-capped polyethylene plastic bottles, sealed, and stored in a freezer at about - 20 °C prior to distribution to participants.

2.3 Preparation of 'blank' test material

The pears to be used for the production of the blank test material were organically grown in the same field as the test material. A homogenate was prepared in the same way as the treated test material described above. Low level traces of Thiabendazole at concentrations below 0.005 mg/Kg were found to be present together with 0.060mg/Kg of Dinocap. These two pesticides were removed from the Target Pesticide List.

2.4 Homogeneity test

Ten bottles of treated test material were randomly chosen from those stored in the freezer and analyses were performed on duplicate portions taken from each bottle. The sequence of analyses was determined using a table of randomly generated numbers. The injection sequence of the 20 extracts analysed by GC and LC was also randomly chosen. The quantification by GC and LC was performed using a 3-point calibration curve constructed from matrix-matched standards prepared from the 'blank' pear test material. A single standard mixture was used, for both GC and LC calibrations.

The statistical evaluation was performed according to the International Harmonized Protocol published by IUPAC, ISO and AOAC [3]. The individual residue data from the homogeneity tests are given in Appendix 1. The results of the statistical analyses are given in Table 2.1 The acceptance criteria for the test material to be sufficiently homogenous for the proficiency test were that $S_s/\sigma < 0.3$, S_s being the between sampling standard deviation and σ = RSD (25%) multiplied by the analytical sampling mean for all pesticides. It appeared that all pesticides were homogeneously distributed in the tes material.

Table 2.1. Statistical evaluation of the homogeneity test data (n = 20 analyses)

	Acetamiprid	Carbaryl	Diazinon	Dimethoate	Imidacloprid	Imazalil	Iprodione	Omethoate	Oxydemeton-methyl	Pyrimethanil	Tetraconazole
Mean Concentration (mg/Kg)	0.024	0.024	0.030	0.021	0.025	0.027	0.029	0.026	0.024	0.023	0.034
S_s/σ	0.15	0.21	0.080	0.25	0.19	0.15	0.17	0.092	0.18	0.18	0.078
Pass/Fail	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass

Ss: Between Sampling Standard Deviation

2.5 Stability tests

The two analytical methods described briefly above (in section 2.1) were also used for the stability tests.

The tests were performed on two occasions. On each occasion, a single bottle stored in the freezer at -20°C was chosen randomly and duplicate analyses were performed.

The two occasions were:

- Day 1: coinciding with the first sample shipment, which took place on 9th April 2007.
- Day 2: shortly after the deadline for reporting results, on 10th May 2007.

The individual results are given in Table 2.2. In general, these tests did not show any significant decrease in the levels of the pesticides. This demonstrates that, for the duration of the proficiency test and provided that the storage conditions prescribed were followed, the time elapsed until analysis was performed by the participants did not influence the results.

Table 2.2. Analytical datafrom stability test.

	Acetamiprid (mg/Kg)	Carbaryl (mg/Kg)	Diazinon (mg/Kg)	Dimethoate (mg/Kg)	Imidacloprid (mg/Kg)	Imazalil (mg/Kg)	Iprodione (mg/Kg)	Omethoate (mg/Kg)	Oxydemeton-methyl (mg/Kg)	Pyrimethanil (mg/Kg)	Tetraconazole (mg/Kg)
Day 1 (1st sample)	0.037	0.023	0.032	0.023	0.029	0.024	0.031	0.029	0.026	0.025	0.035
Day 1 (2nd sample)	0.033	0.024	0.028	0.024	0.028	0.025	0.027	0.023	0.023	0.024	0.033
Mean 1	0.035	0.024	0.030	0.024	0.029	0.025	0.029	0.026	0.025	0.025	0.034
Day 2 (1st sample)	0.036	0.024	0.033	0.022	0.027	0.023	0.031	0.028	0.024	0.025	0.034
Day 2 (2nd sample)	0.033	0.025	0.029	0.024	0.03	0.028	0.026	0.025	0.024	0.023	0.035
Mean 2	0.035	0.025	0.031	0.023	0.029	0.026	0.029	0.027	0.024	0.024	0.035
(M2-M1)/M1	0.014	-0.043	-0.033	0.021	0.000	-0.041	0.017	-0.019	0.020	0.020	-0.015
%	1.43	4.26	3.33	2.13	0.00	4.08	1.72	1.92	2.04	2.04	1.47

2.6 Distribution of test material and protocol to participants

One bottle of treated test material and one bottle of 'blank' material were shipped to each participant in boxes containing dry ice. The samples were sent on the 9th April, 2007.

Before shipment, the laboratories had received full instructions (Annex 1) for the receipt, storage and analysis of the test materials although they were encouraged to use their normal sample receipt procedure and method(s) of analysis. These instructions were uploaded onto the EUPT-FV-LC1 web page designed especially for this Proficiency Test. A password was required to enter a restricted zone where the Protocol and the Pesticide List with the Minimum Required Reporting Level (MRRL) set by the Organiser could be found. This information was sent by e-mail to all

participant laboratories. At the same time, they were informed that their Application Form for participation had been accepted. This ensured that confidentiality was maintained throughout the duration of Proficiency Test LC1.

3. STATISTICAL METHODS

3.1 False positives and negatives

3.2.1 False positives

In principle, results that show the presence of pesticides that were included in the pesticide list, and which were (i) not used in the sample treatment and (ii) not detected by the Organiser (even following a repeated analysis) were treated as false positives - if they were reported at concentrations at or above the Minimum Required Reporting Level (MRRL) as stipulated by the Organiser. Results reported which were lower than 0.005 mg/Kg have been disregarded by the Organiser and have not therefore been considered as false positives. No z-score values have been calculated for these results. A laboratory reporting a false positive, even if reporting the necessary number of pesticides to have sufficient scope, has been classified in Category B.

3.2.2 False negatives

Results for pesticides reported by the laboratories as not detected (ND), although they were used by the Organiser to treat the test material and were subsequently detected at, or above, the Minimum Required Reporting Level (MRRL) by the Organiser (and the majority of participating laboratories) have been considered to be false negatives. z-Scores have been calculated for all pesticides detected at levels exceeding the Minimum Required Reporting Level (MRRL) and for false negatives.

3.3 Estimation of the assigned values

To establish the assigned values, the median levels of all the reported results, excluding the outliers, were used. Individual results without any absolute values reported, such as detected (D), could not be used.

3.4 Fixed target standard deviations

Based on experience from previous EU proficiency tests and recommendations by the Advisory Group, a fixed relative standard deviation (FFP RSD) of 25 % was chosen. This is in line with the internationally accepted target-measurement uncertainty of 50% for multiresidue analysis of pesticides, which is derived from and linked to the EU-PTs. The same target RSD has been applied to all the pesticides, independent of the residue concentration. The target standard deviation (σ) for each individual pesticide was calculated by multiplying this FFP RSD by the assigned value.

3.5 z-Scores

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

$$z = (x-X) / \sigma \qquad \text{Eq.1}$$

Where:

- x is the result reported by the participant or the MRRL for those labs not having detected the pesticide present in the sample
- X is the assigned value
- σ is the target standard deviation (= FFP RSD of 25% multiplied by the assigned value)

z-Score classification is as follows:

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

- Any z-score values of $|z| > 5$ have been reported as '+5', or '-5'.

- No z-score calculation has been performed for any false positive results.

- For false negatives, the MRRL has been used to calculate the z-score. These z-scores are also included in the graphical representation.

3.6 Combined z-Scores

In order to evaluate each laboratory's overall performance, and taking into account all the pesticides analysed, three methods were used to combine z-scores; the 'Weighted sum of z-scores' that was first used in EUPT 6, the re-scaled sum of z-scores (RSZ) and the sum of squared z-scores (SSZ).

3.6.1 Weighted Sum of z-Scores

This function was only applied to labs with sufficient scope (Category A), i.e. those labs that have reported 90% or more of the total number of pesticides present in the sample and no false positives. The weighting factor ω is defined as follows:

$$\omega|Z_i| = \begin{cases} 1 & \text{if} \quad |Z| \le 2 \\ 3 & \text{if} \quad 2 < |Z| \le 3 \\ 5 & \text{if} \quad |Z| > 3 \end{cases}$$

Therefore, the 'Weighted Sum of z-Scores' |z| formula is:

$$\text{'Weighted sum of z-scores '} \ |z| \ = \frac{\sum_{i=1}^{n} |Z_i| \omega(Z_i)}{n}$$

So for each lab:

- The first term is the sum of absolute values of z-scores between zero and two, multiplied by one.
- The second term is the sum of absolute values of z-scores greater than two, but less than or equal to three, multiplied by three.
- The third term is the sum of absolute values of z-scores greater than three, multiplied by five.

The sum is then divided by the number of reported results (n) from each lab.

The 'Weighted sum of z-scores' has then been used to produce an overall classification of laboratories as 'good', 'satisfactory' or 'unsatisfactory' according to:

$\|z\| \le 2$	Good
$2 < \|z\| \le 3$	Satisfactory
$\|z\| > 3$	Unsatisfactory

In this way, a simple, single combined value, very similar to the single z-scores, is produced, that will encourage laboratories to not only improve the accuracy of their results but also to analyse a greater number of pesticides.

This evaluation has not been applied to those participants with insufficient scope i.e. in Category B - those laboratories reporting less than 90% of the pesticides present in the sample, or reporting any false positives.

3.6.2 RSZ

The RSZ was calculated for all z-score values for each laboratory according to:

$$RSZ = \Sigma \ |z| / (n)^{1/2}$$

where n is the number of z-scores.

The RSZ gives an averaged score for all pesticides analysed and indicates if a laboratory has a consistent bias in its results.

3.6.3 SSZ

The SSZ is the sum of all squared z-scores. It was calculated for all z-scores for each laboratory according to:

$$SSZ = (\text{z-score}_1)^2 + (\text{z-score}_2)^2 + ...(\text{z-score}_n)^2$$

where n is the number of z-scores.

4. RESULTS

4.1 Summary of reported results

Thirty laboratories agreed to participate in this proficiency test and twenty eight submitted results.

A summary of the results reported can be seen below in Table 4.1.

Table 4.1 Summary of Reported Results

Pesticides	No. of Reported Results	No. of Not Analysed Results	No. of False negatives	% of Laboratories that Reported Results *
Acetamiprid	26	1	1	93
Carbaryl	26	2	0	93
Diazinon	28	0	0	100
Dimethoate	27	0	1	96
Imazalil	22	3	3	79
Imidacloprid	24	2	2	86
Iprodione	21	1	6	75
Omethoate	26	1	1	93
Oxydemeton-methyl	18	7	3	64
Pyrimethanil	25	2	1	89
Tetraconazole	25	2	1	89

* The % of Laboratories with Reported Results is calculated relative to the total number of laboratories submitting results (28).

The laboratories that agreed to participate are listed in Annex 2. All analytical results reported by the participants are given in Appendix 3, whilst the recoveries and analytical methods used are shown in Appendix 8. For an explanation of the symbols used in these tables, see Annex 1.

4.1.1 False positives

Two laboratories reported additional pesticides to those applied to the test material. These pesticides and their residue levels reported are presented in Table 4.2, together with the MRRL. When the reported concentration of the erroneously detected pesticide was higher than the assigned MRRL value in the Pesticide List (Annex 1), the result was considered to be a false positive.

Even with only one false positive result, a laboratory cannot be classified in Category A.

Table 4.2. Laboratories that reported false positives in the treated test material

Pesticide	Laboratory Code	Concentration (mg/kg)	RL (mg/Kg)	MRRL (mg/Kg)
Dichlofluanid	EUPT-FV-LC1-018	0.042	0.005	0.005
Dicofol	EUPT-FV-LC1-018	0.039	0.005	0.005
Procymidone	EUPT-FV-LC1-018	0.045	0.005	0.005
Chlorpyrifos-methyl	EUPT-FV-LC1-026	0.036	0.005	0.005

4.1.2 False negatives

Pesticides actually present in the test material but reported as not detected (ND), were considered to be false negatives. Table 4.3 summarizes how many laboratories reported false negatives for each pesticide. This was quite a high number (ten out of the twenty eight laboratories reporting at least one false negative result).

Table 4.3 Laboratories that failed to report pesticides that were present in the treated test material

Laboratory Code	Acetamiprid	Carbaryl	Diazinon	Dimethoate	Imazalil	Imidacloprid	Iprodione	Omethoate	Oxydemeton-methyl	Pyrimethanil	Tetraconazole
EUPT-FV-LC1-002							ND				
EUPT-FV-LC1-003									ND		
EUPT-FV-LC1-005							ND				
EUPT-FV-LC1-012					ND						
EUPT-FV-LC1-016							ND		ND		
EUPT-FV-LC1-018							ND				
EUPT-FV-LC1-020	ND					ND	ND				
EUPT-FV-LC1-024					ND						
EUPT-FV-LC1-026				ND	ND		ND	ND		ND	ND
EUPT-FV-LC1-030						ND			ND		

4.1.3 Distribution of data

The distributions of the concentrations of the eleven pesticide residues reported by the laboratories have been plotted as histograms. See Appendix 2.

4.2 Assigned values and target standard deviations

To establish the assigned values, the medians of all the reported results were used, excluding those values that were distant from the median (considered to be outliers). The median did not change even when these outliers were included. A statistical programme was used to calculate the medians. All median values for all pesticides can be seen in Table 4.4.

The target standard deviation was obtained using a fixed FFP RSD value of 25%. For comparison, a robust standard deviation (Qn) was also calculated for informative purposes. These RSDs can be seen in Table 4.4.

Table 4.4 Median values and the %RSDs for all pesticides present in the test material

Pesticides	MRRL (mg/Kg)	Median (mg/Kg)	FFP RSD (%)	Qn RSD (%)
Acetamiprid	0.005	0.033	25	14
Carbaryl	0.005	0.026	25	26
Diazinon	0.005	0.024	25	28
Dimethoate	0.005	0.024	25	19
Imazalil	0.005	0.026	25	17
Imidacloprid	0.005	0.029	25	23
Iprodione	0.005	0.025	25	27
Omethoate	0.005	0.021	25	21
Oxydemeton-methyl	0.005	0.024	25	38
Pyrimethanil	0.005	0.023	25	19
Tetraconazole	0.005	0.029	25	15

4.3 Assessment of laboratory performance

4.3.1 z-Scores

z-Scores were calculated using the FFP RSD of 25% given for all the pesticides present. In Appendix 3, the individual z-scores are presented, together with the median for each laboratory and pesticide.

z-Scores for false negative results have been calculated using the MRRL value reported in the Pesticide List (Annex 1).

In Appendix 4, the graphical representations of the z-scores are presented. No z-scores have been calculated for false positives. False negative z-score results have been included on the chart for each pesticide. They are indicated by an asterisk.

The charts have been created using different colours according to the determination technique used for each particular pesticide.

4.3.2 Combined z-Scores

Appendix 5 shows a table with the values of individual z-scores for each pesticide and the combined 'Weighted Sum of z-Scores' for those laboratories in Category A. In this category are the laboratories that reported 9 or more results, and additionally, did not report any false positives. A graphical representation of the results for these laboratories in Category A can also be found in Appendix 6.

Twenty four out of the twenty eight laboratories that reported results, have been placed in Category A (80%) - out of which 71% were classified as 'good', 17% as 'satisfactory' and 13% as 'unsatisfactory'.

Two out of the twenty-eight laboratories that reported results for less than nine pesticides. Two more could have been classified into Category A based on their z-scores, but they also reported false positives.

Table 4.5 shows the laboratories in Category A, the number of pesticides reported, the WSZ value and the classification achieved.

Laboratories with false negatives in Category A are marked with an asterisk and laboratories with WSZ > 5 with a '↑' mark.

Table 4.6 shows the laboratories in Category B, the number of pesticides reported, the number of results, and the number of acceptable z-score results. Laboratories reporting a false negative are marked with an asterisk, and laboratories reporting a false positive are marked with a '+' mark.

The classical combined z-scores: RSZ and the SSZ values are listed in Appendix 7 for all laboratories.

Table 4.5 Performance and sub-classification of laboratories in Category A.

Lab Code	No. of Pesticides sought	WSZ	Classification
EUPT-FV-LC1-011	11	0.2	Good
EUPT-FV-LC1-017	11	0.2	Good
EUPT-FV-LC1-001	11	0.3	Good
EUPT-FV-LC1-022	11	0.4	Good
EUPT-FV-LC1-009	11	0.4	Good
EUPT-FV-LC1-023	11	0.5	Good
EUPT-FV-LC1-013	11	0.5	Good

Lab Code	No. of Pesticides sought	WSZ	Classification
EUPT-FV-LC1-008	11	0.6	Good
EUPT-FV-LC1-007	11	0.7	Good
EUPT-FV-LC1-010	11	0.7	Good
EUPT-FV-LC1-021	11	1.0	Good
EUPT-FV-LC1-019	11	1.0	Good
EUPT-FV-LC1-006	11	1.1	Good
EUPT-FV-LC1-015	11	1.2	Good
EUPT-FV-LC1-005*	11	2.1	Good
EUPT-FV-LC1-016*	11	3.2	Unsatisfactory
EUPT-FV-LC1-025	10	0.9	Good
EUPT-FV-LC1-004	10	0.9	Good
EUPT-FV-LC1-029	10	2.3	Satisfactory
EUPT-FV-LC1-003*	10	2.8	Satisfactory
EUPT-FV-LC1-012*	10	3.0	Satisfactory
EUPT-FV-LC1-002*	9	2.0	Good
EUPT-FV-LC1-020*↑	9	6.6	Unsatisfactory
EUPT-FV-LC1-030*↑	9	10.0	Unsatisfactory

↑ Laboratories with WSZ greater than 5.

* Laboratories reporting a false negative result.

Table 4.6 Performance of laboratories in Category B.

Lab Code	No. of Pesticides sought	Num of acceptable z-scores
EUPT-FV-LC1-018*+	11	10
EUPT-FV-LC1-026*+	9	1
EUPT-FV-LC1-024*	8	7
EUPT-FV-LC1-027	6	4

* Laboratories reporting a false negative.

+ Laboratories reporting a false positive.

5. CONCLUSIONS

30 laboratories applied to participate in this test and 28 laboratories submitted results. This is a very low number compred with the 128 laboratories that submitted results for EU FVPT-9.

The pesticide residue levels in the matrix concurred with the Quality Control Group´s proposed levels. Although these levels were low, laboratories still had to be able to demonstrate that they could accurately determine the concentrations present in the treated test material.

For each laboratory/pesticide combination, z-scores based on the FFP RSD were calculated. The different techniques used by the participating laboratories, either gas chromatography or liquid chromatography, are represented on the z-score graphs. Asterisks were used to mark each bar of the chart that represented a false negative result (ND) reported by a laboratory. A sub-classification was made using the simple descriptive terms 'acceptable, questionable and unacceptable'.

'The Weighted Sum of z-Scores', a criterion first introduced in the EUPT 6 proficiency test report, was used to demonstrate the overall performance of the laboratories. Those laboratories reporting nine or more results, and not having submitted any false positive results, have been classified as having sufficient scope and are therefore placed in Category A. Those laboratories that reported less than nine results are considered to have insufficient scope and were placed in Category B. Laboratories in Category A are also sub-classified as 'good', 'satisfactory' or 'unsatisfactory', depending on the values obtained after combining z-scores and obtaining a value for WSZ. Laboratories in Category A with WSZ > 5 are marked (↑) together with the laboratories reporting false negatives which are marked with an asterisk. The intention is to highlight those laboratories that, although reporting a sufficient number of the pesticides present in the sample, had unsatisfactory accuracy, or lacked sensitivity in their analysis.

For the remainder of the laboratories (Category B) no combined Weighted Sum of z-Scores was calculated. However, the number of satisfactory z-scores is presented.

The median value of each pesticide was used to obtain the assigned value or "true" concentration, which was also used to calculate the z-scores.

The presence of a very low level residue of Thiabendazole (<0.005 mg/Kg) in the blank pear homogenate supplied, prompted the Organiser to delete this pesticide from the Target Pesticide List.

The numbers of false positives were low.

In general, the z-scores obtained for each pesticide present in the sample were very good. In some case, the number of false negatives was high (e.g. Iprodione 6).

Since the MRRL was introduced in EUPT 6, the laboratories' 'reporting levels' have been decreasing and at the same time improved results have been achieved. The use of mass spectrometry, particularly LC-MS/MS, have improved the results over the years. However the accuracy of results at low levels (0.01-0.1 mg/Kg) could only be demonstrated by the small number of laboratories that participated in EUFVLC-1. Only twenty out of the twenty-seven National Reference Laboratories participated.

6. SUGGESTIONS FOR FUTURE WORK

The Organiser and the Scientific Committee of this 1st EU Proficiency Test in Low Concentrations consider that the results obtained by the majority of participants to be very good. However, because of the relatively small number of participants, further proficiency tests involving low levels of pesticide residues will need to be organised to encourage more laboratories to lower their reporting limits.

Future PTs will be carried out and statistically evaluated in the same way as previous EU FVPTs - with laboratories classified into Category A and Category B.

For next year, an attempt will be made to combine EUPT-FV-10 with the low concentrations proficiency test (EUPT-FV-LC2) into a single PT by using the same test material. A unique MRRL will be considered common to both PTs. This will force laboratories to decrease their reporting levels.

These new changes are aimed at ensuring that, year on year, laboratories increase the scope of their methods,improve their performance (in terms of ability to both detect residues and measure them accurately, even at low levels), and continue to assess and adopt new techniques to aid their improvement.

7. REFERENCES

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4. Muller C H and Uhlig S, Biometrijka, Estimation of Variance components with high breakdown point and high efficiency, 88 (2001), 353-336.

5. ILAC G-13:2000 Guidelines for the Requirements for the Competence of Providers of Profiency Testing Schemes.

6. UNE 66543 Proficiency testing by inter-laboratory comparisons – Part 1 and Part 2.

8. ACKNOWLEDGEMENTS

The Organiser is grateful to the European Commission for funding this 1st European Proficiency Test in Fruit and Vegetables at Low Concentrations.

The Organiser wishes to thank the members of the Advisory Group and the Scientific Committee for their invaluable and knowledgeable advice. Many thanks also to the Statistical Group for their cooperation.

The Organiser wishes to give a special thank-you to Almeria University for the use of their facilities.

APPENDIX 1. Homogeneity Data

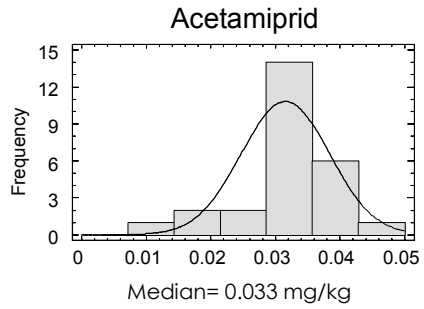
Acetamiprid (mg/Kg)		Carbaryl (mg/Kg)		Diazinon (mg/Kg)		Dimethoate (mg/Kg)	
Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
0.019	0.020	0.020	0.023	0.030	0.028	0.018	0.020
0.026	0.025	0.020	0.021	0.030	0.032	0.024	0.021
0.027	0.022	0.026	0.025	0.028	0.029	0.024	0.022
0.024	0.025	0.023	0.025	0.031	0.034	0.019	0.017
0.022	0.023	0.025	0.023	0.032	0.033	0.022	0.019
0.024	0.020	0.025	0.022	0.028	0.030	0.020	0.021
0.022	0.027	0.026	0.023	0.026	0.029	0.020	0.023
0.021	0.027	0.022	0.024	0.026	0.035	0.021	0.022
0.022	0.023	0.020	0.028	0.032	0.033	0.023	0.022
0.026	0.025	0.027	0.029	0.032	0.030	0.024	0.022

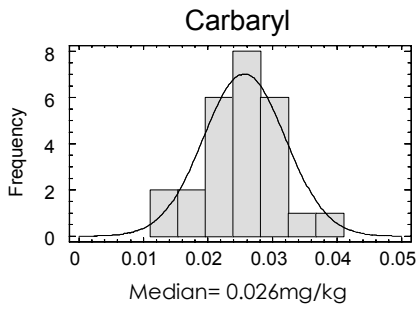
Imidacloprid (mg/Kg)		Imazalil (mg/Kg)		Iprodione (mg/Kg)		Omethoate (mg/Kg)	
Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
0.028	0.027	0.026	0.028	0.025	0.029	0.026	0.027
0.026	0.025	0.025	0.030	0.03	0.028	0.024	0.029
0.024	0.023	0.025	0.026	0.029	0.027	0.026	0.025
0.024	0.025	0.029	0.027	0.028	0.029	0.027	0.028
0.026	0.021	0.028	0.030	0.025	0.028	0.029	0.028
0.024	0.023	0.028	0.026	0.028	0.030	0.024	0.025
0.025	0.028	0.030	0.029	0.029	0.031	0.026	0.027
0.029	0.024	0.025	0.027	0.031	0.032	0.029	0.024
0.023	0.021	0.026	0.024	0.031	0.029	0.023	0.025
0.023	0.024	0.025	0.026	0.027	0.026	0.027	0.028

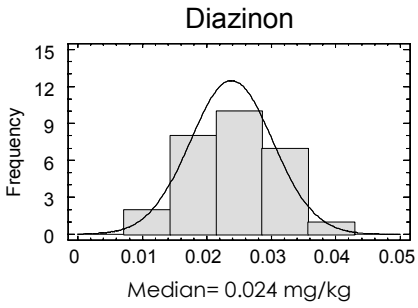
Oxydemeton-methyl (mg/Kg)		Pyrimethanil (mg/Kg)		Tetraconazole (mg/Kg)	
Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
0.022	0.021	0.022	0.023	0.033	0.035
0.028	0.023	0.021	0.022	0.036	0.034
0.025	0.026	0.023	0.024	0.035	0.037
0.025	0.022	0.026	0.025	0.035	0.034
0.023	0.022	0.020	0.026	0.033	0.035
0.020	0.021	0.018	0.020	0.034	0.036
0.026	0.025	0.025	0.022	0.033	0.035
0.023	0.024	0.024	0.020	0.031	0.033
0.022	0.028	0.022	0.023	0.035	0.032
0.024	0.022	0.023	0.024	0.032	0.033

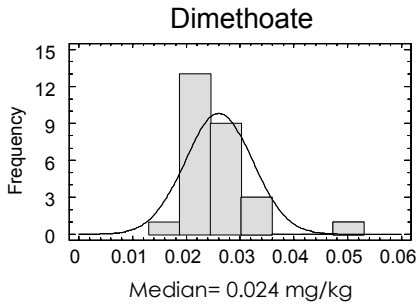
APPENDIX 2. Histograms of residue data for each pesticide for all the laboratories.

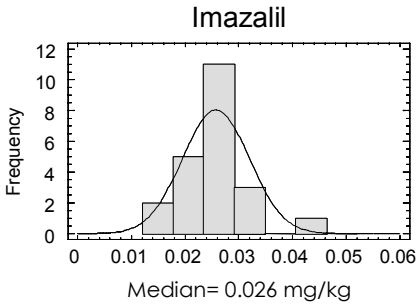
Results presented as histograms.

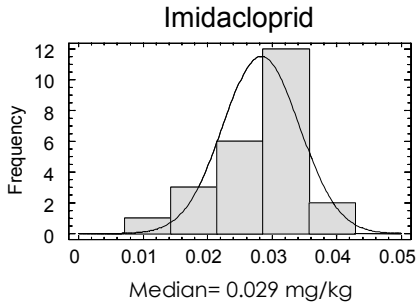


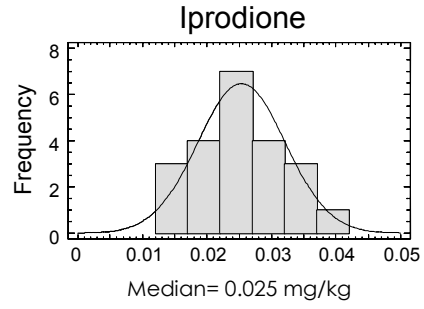


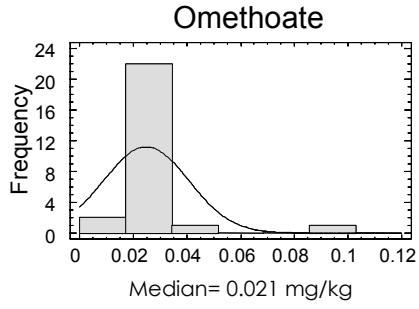






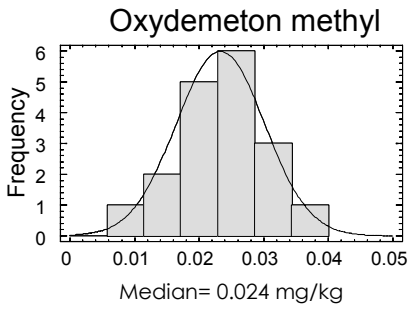


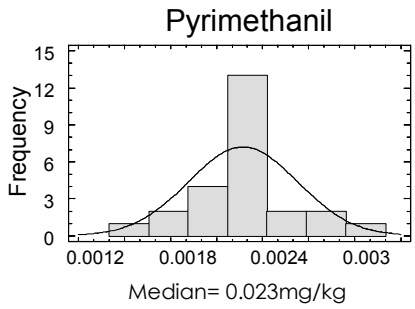


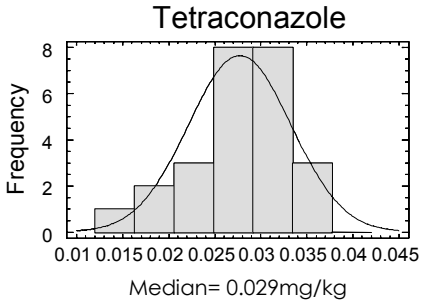


APPENDIX 2. Histograms of residue data for each pesticide for all the laboratories.

Results presented as histograms.







APPENDIX 3. Results (mg/kg) and z-scores for FFP RSD (25%).

Results given by the laboratories (mg/kg) and their calculated z-score value using FFP RSD 25%

Lab Code	Acetamiprid	z-Score (FFP RSD 25%)	Carbaryl	z-Score (FFP RSD 25%)	Diazinon	z-Score (FFP RSD 25%)	Dimethoate	z-Score (FFP RSD 25%)
MRRL	0.005		0.005		0.005		0.005	
Median (mg/kg)	0.033		0.026		0.024		0.024	
1	0.034	0.2	0.023	-0.4	0.027	0.5	0.029	0.8
2	0.033	0.1	0.022	-0.6	0.026	0.3	0.023	-0.2
3	0.036	0.4	0.022	-0.6	0.021	-0.5	0.023	-0.1
4	0.033	0.1	0.036	1.6	0.029	0.8	0.031	1.2
5	0.041	1.0	0.032	1.0	0.019	-0.8	0.029	0.8
6	0.024	-1.0	0.017	-1.3	0.018	-1.0	0.021	-0.5
7	0.037	0.6	0.032	1.0	0.026	0.3	0.028	0.7
8	0.031	-0.2	0.019	-1.0	0.016	-1.3	0.026	0.3
9	0.031	-0.2	0.028	0.4	0.024	0.0	0.026	0.3
10	0.032	-0.1	0.031	0.9	0.029	0.8	0.026	0.3
11	0.031	-0.2	0.021	-0.7	0.024	0.0	0.024	0.0
12	0.018	-1.8	0.032	1.0	0.023	-0.2	0.026	0.3
13	0.035	0.3	0.027	0.2	0.030	1.0	0.024	0.0
15	0.032	-0.1	0.030	0.6	0.029	0.8	0.022	-0.3
16	0.030	-0.3	0.021	-0.7	0.029	0.8	0.022	-0.3
17	0.035	0.3	0.024	-0.2	0.024	0.0	0.024	0.0
18	0.037	0.6	0.028	0.4	0.021	-0.5	0.027	0.5
19	0.043	0.2	0.039	2.1	0.026	0.3	0.028	0.7
20	ND	ND	0.014	-1.8	0.017	-1.2	0.021	-0.5
21	0.036	0.4	0.027	0.2	0.030	1.0	0.023	-0.2
22	0.034	0.2	0.023	-0.4	0.025	0.2	0.024	0.0
23	0.031	-0.1	0.024	-0.2	0.021	-0.6	0.023	-0.1
24	0.036	0.4	0.027	0.2	0.032	1.3	0.035	1.8
25	0.021	-1.4	0.013	-2.0	0.022	-0.3	0.032	1.3
26	NA		0.031	0.9	0.040	2.7	ND	-3.2
27	0.011	-2.6	NA		0.009	-2.5	0.015	-1.5
29	0.028	-0.6	0.024	-0.2	0.018	-1.0	0.021	-0.5
30	0.030	-0.3	NA		0.013	-1.8	0.050	4.3

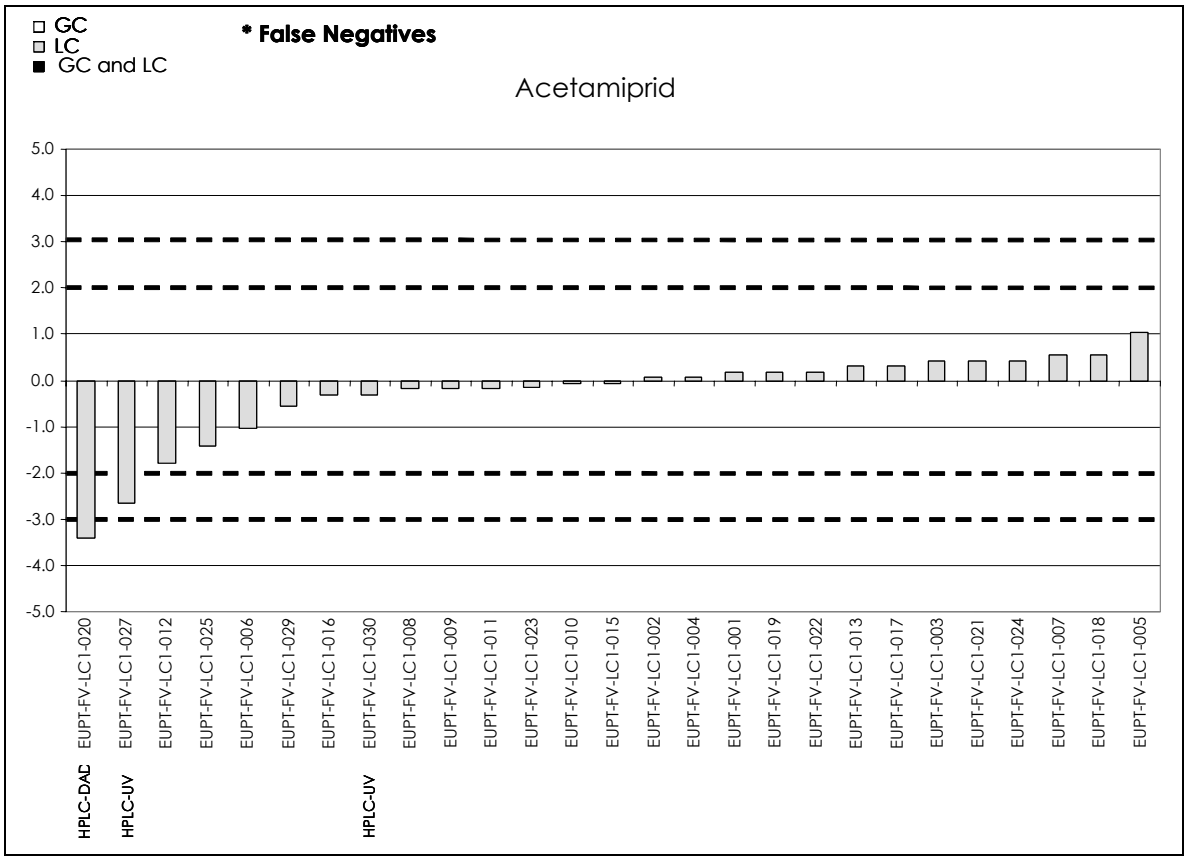
APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25%).

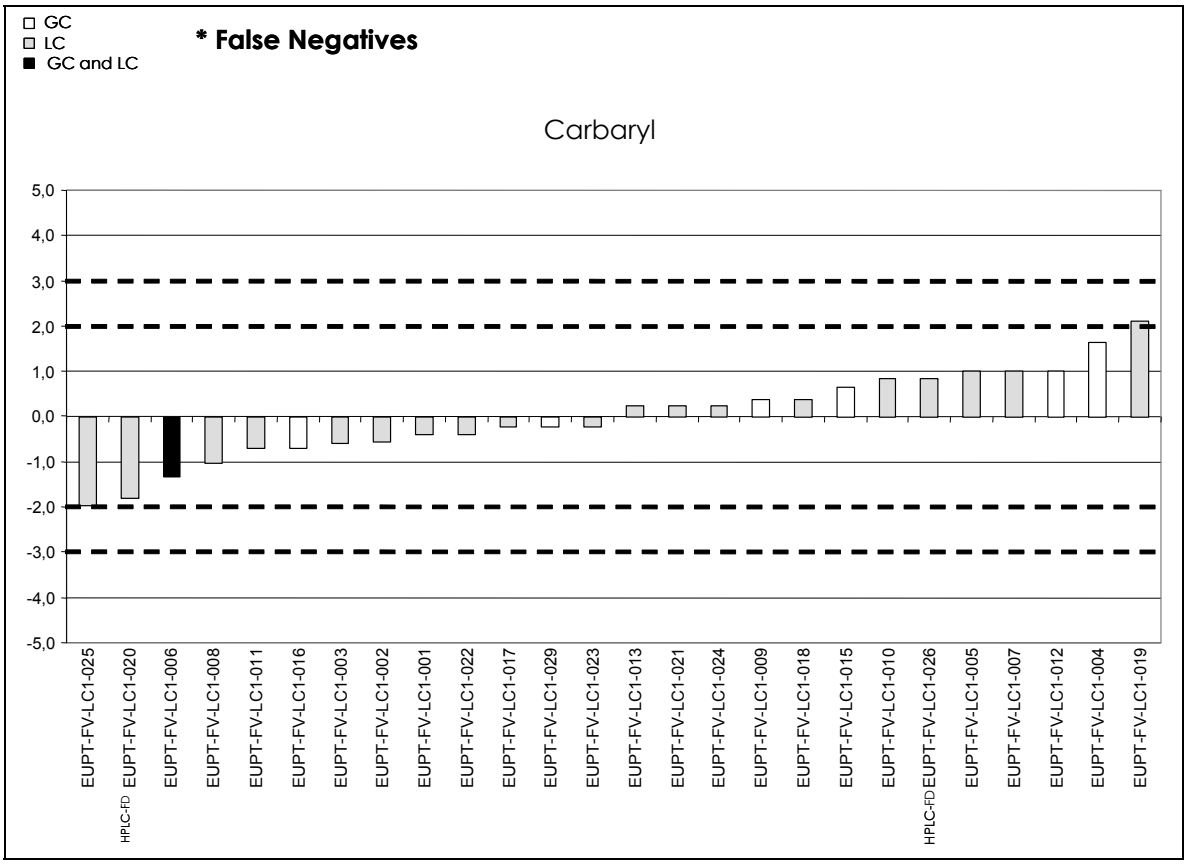
Lab Code	Imazalil	z-Score (FFP RSD 25%)	Imidacloprid	z-Score (FFP RSD 25%)	Iprodione	z-Score (FFP RSD 25%)	Omethoate	z-Score (FFP RSD 25%)
MRRL	0.005		0.005		0.005		0.005	
Median (mg/kg)	0.026		0.029		0.025		0.021	
1	0.027	0.2	0.030	0.1	0.023	-0.3	0.021	0.0
2	0.027	0.2	0.029	0.0	ND	-3.2	0.022	0.2
3	0.045	2.9	NA		0.028	0.4	0.020	-0.2
4	0.022	-0.6	0.033	0.6	0.017	-1.3	0.030	1.7
5	0.026	0.0	0.032	0.4	ND	-3.2	0.022	0.2
6	0.014	-1.8	0.021	-1.1	0.018	-1.1	0.020	-0.2
7	0.029	0.5	0.035	0.8	0.035	1.6	0.020	-0.2
8	0.021	-0.8	0.029	0.0	0.015	-1.6	0.023	0.4
9	0.031	0.8	0.027	-0.3	0.024	-0.2	0.029	1.5
10	0.028	0.3	0.033	0.6	0.022	-0.5	0.028	1.3
11	0.026	0.0	0.029	0.0	0.025	0.0	0.018	-0.6
12	ND	-3.2	0.011	-2.5	0.036	1.8	0.020	-0.2
13	0.033	1.1	0.031	0.3	0.029	0.6	0.020	-0.2
15	0.018	-1.2	0.028	-0.1	0.028	0.5	0.008	-2.5
16	0.025	-0.2	0.023	-0.8	ND	-3.2	0.024	0.6
17	0.030	0.6	0.029	0.0	0.028	0.5	0.020	-0.2
18	0.025	-0.2	0.039	1.4	<0.005	-3.2	0.025	0.8
19	0.027	0.2	0.036	1.0	0.026	0.2	0.021	0.0
20	NA		ND	-3.3	ND	-3.2	0.020	-0.2
21	0.026	0.0	0.033	0.6	0.027	0.3	0.012	-1.7
22	0.026	0.0	0.026	-0.4	0.025	0.0	0.018	-0.6
23	0.021	-0.7	0.029	-0.1	0.022	-0.6	0.021	0.0
24	ND	-3.2	0.026	-0.4	NA		0.029	1.5
25	0.022	-0.6	0.021	-1.1	0.024	-0.2	0.018	-0.6
26	ND	-3.2	NA		ND	-3.2	ND	-3.0
27	NA		0.021	-1.1	0.034	1.4	NA	
29	0.017	-1.4	0.029	0.0	0.019	-1.0	0.039	3.4
30	NA		ND	-3.3	0.040	2.4	0.097	5.0

APPENDIX 3. Results (mg/kg) and z-scores for FFP RSD (25%).

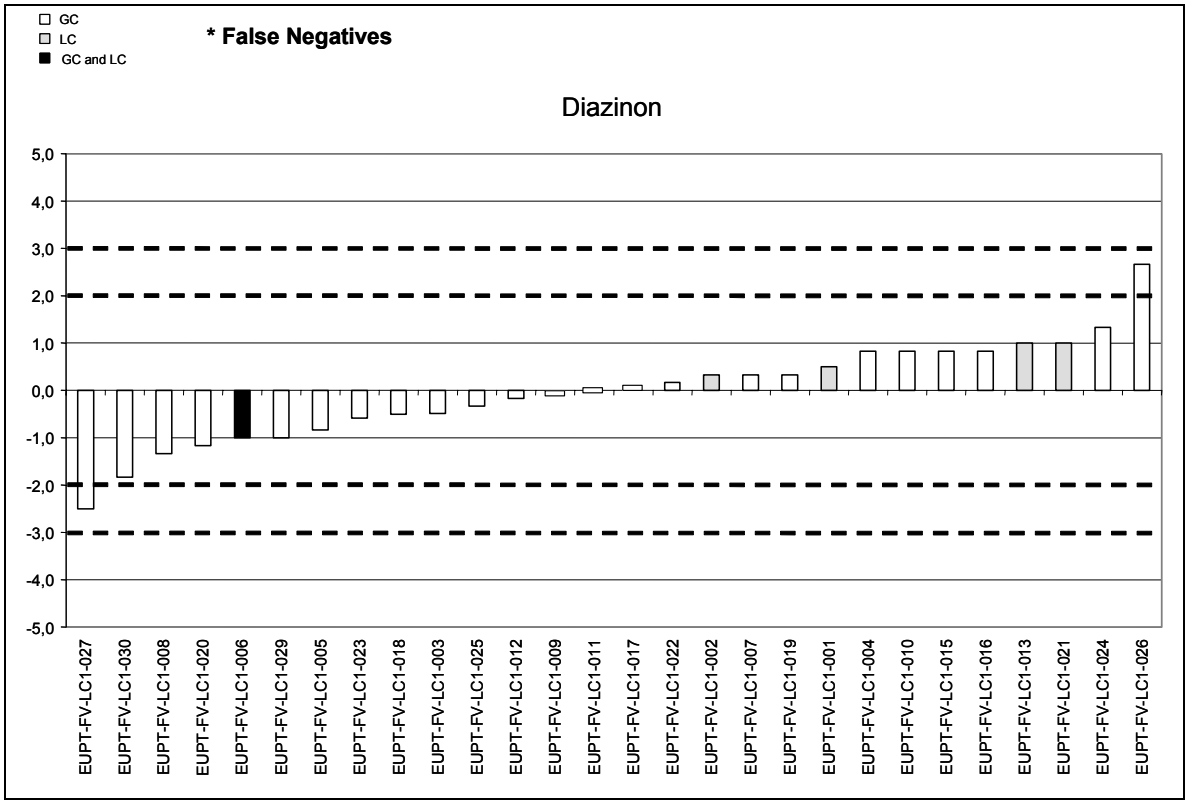
Lab Code	Oxydemeton-methyl	z-Score (FFP RSD 25%)	Pyrimethanil	z-Score (FFP RSD 25%)	Tetraconazole	z-Score (FFP RSD 25%)
MRRL	0.005		0.005		0.005	
Median (mg/kg)	0.024		0.023		0.029	
1	0.023	-0.1	0.020	-0.5	0.029	0.0
2	0.018	-0.9	NA		NA	
3	ND	-3.1	0.020	-0.5	0.036	0.9
4	NA		0.024	0.2	0.037	1.1
5	0.013	-1.8	0.017	-1.0	0.026	-0.4
6	0.019	-0.8	0.015	-1.4	0.017	-1.7
7	0.028	0.8	0.025	0.3	0.032	0.4
8	0.028	0.8	0.022	-0.2	0.028	-0.1
9	0.028	0.8	0.022	-0.2	0.030	0.1
10	0.031	1.3	0.017	-1.0	0.030	0.1
11	0.025	0.3	0.022	-0.2	0.029	0.0
12	NA		0.020	-0.5	0.027	-0.3
13	0.020	-0.6	0.027	0.7	0.034	0.7
15	0.029	0.9	0.028	0.9	0.028	-0.1
16	ND	-3.1	0.023	0.0	0.028	-0.1
17	0.024	0.1	0.023	0.0	0.032	0.4
18	0.020	-0.6	0.024	0.2	0.029	0.0
19	0.032	1.4	0.026	0.5	0.032	0.4
20	NA		0.024	0.2	0.014	-2.1
21	0.011	-2.1	0.024	0.2	0.030	0.1
22	0.017	-1.1	0.031	1.4	0.030	0.1
23	0.017	-1.0	0.020	-0.6	0.022	-1.0
24	NA		0.024	0.2	NA	
25	NA		0.024	0.2	0.021	-1.1
26	0.036	2.1	ND	-3.1	ND	-3.3
27	NA		NA		0.030	0.1
29	NA		0.022	-0.2	0.022	-1.0
30	ND	-3.1	0.024	0.2	0.020	-1.2

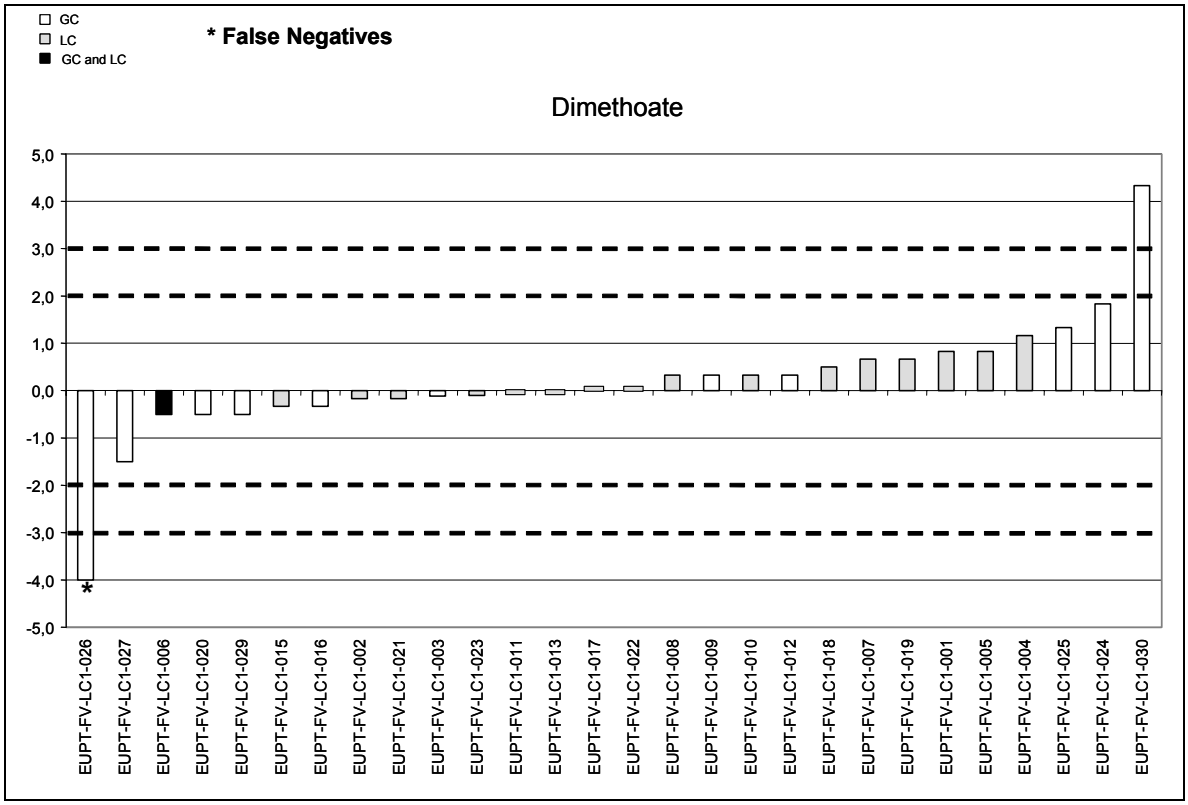
APPENDIX 4. Graphical Representation of z-scores for FFP RSD (25%).



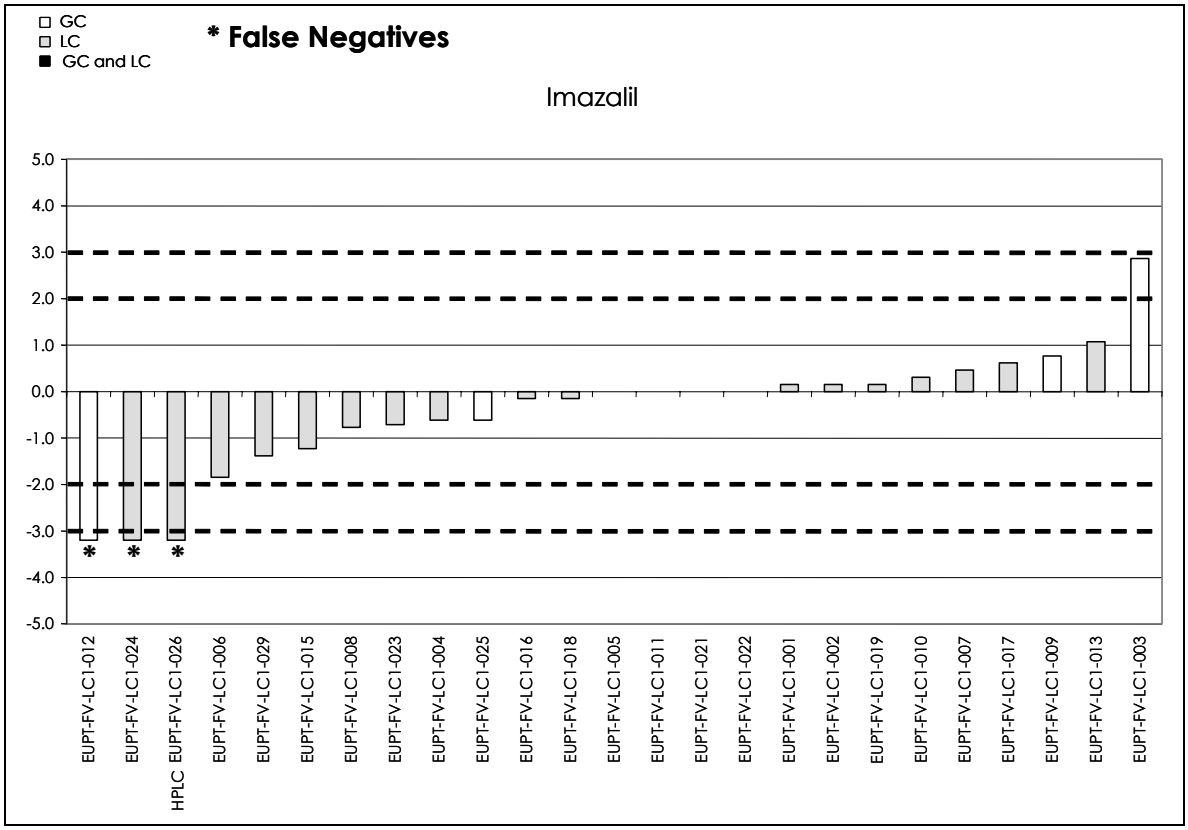


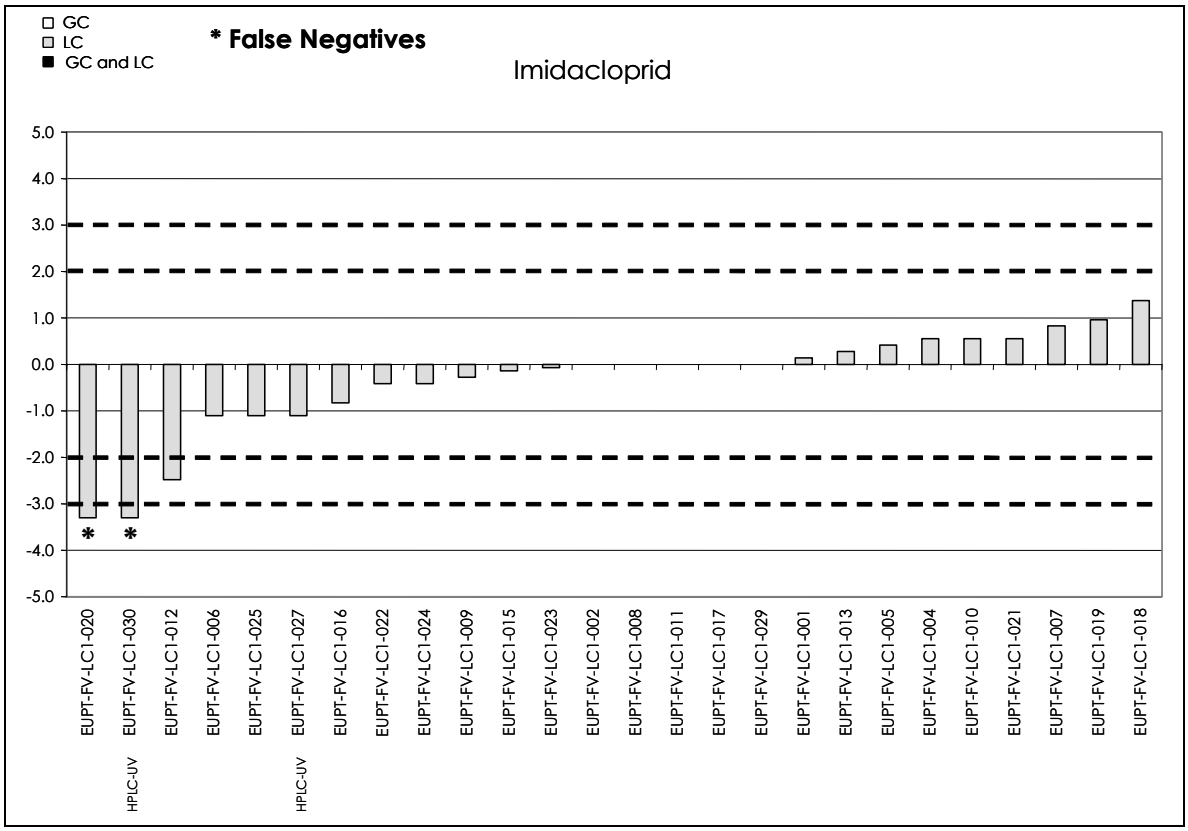
APPENDIX 4. Graphical Representation of z-scores for FFP RSD (25%).



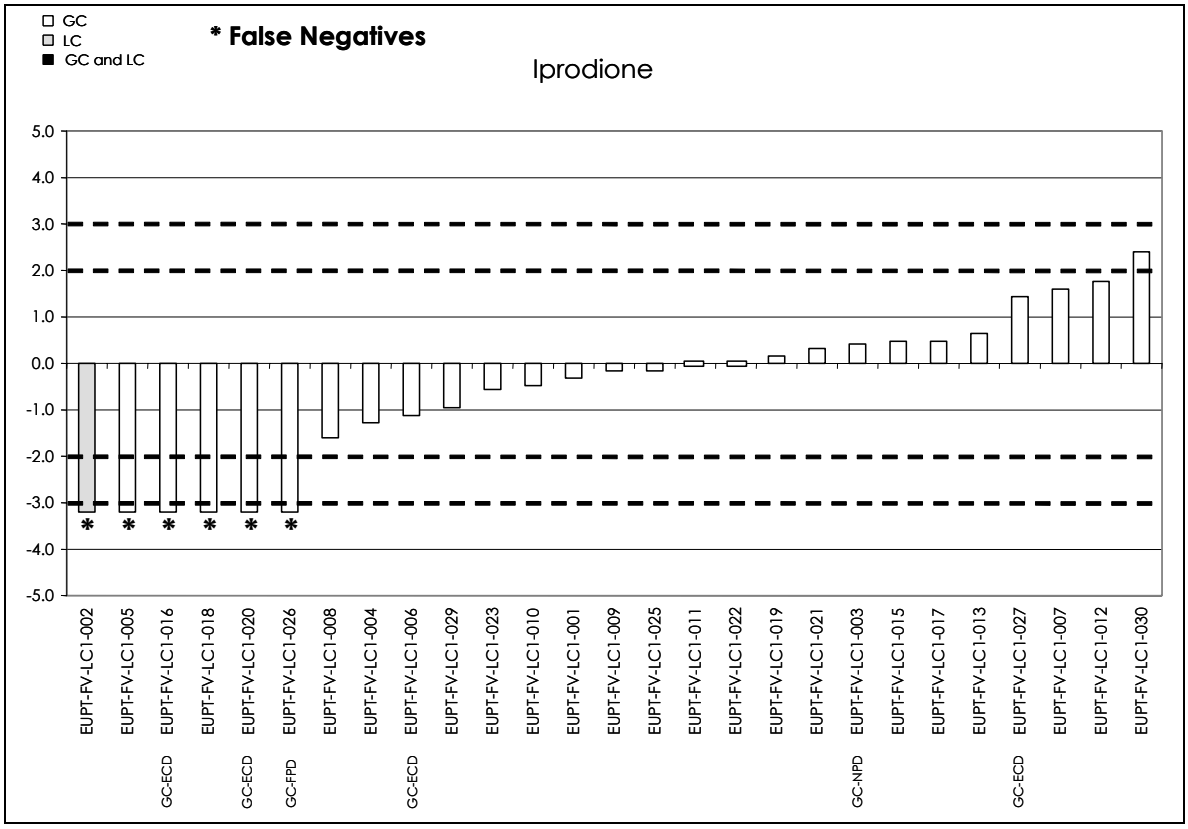


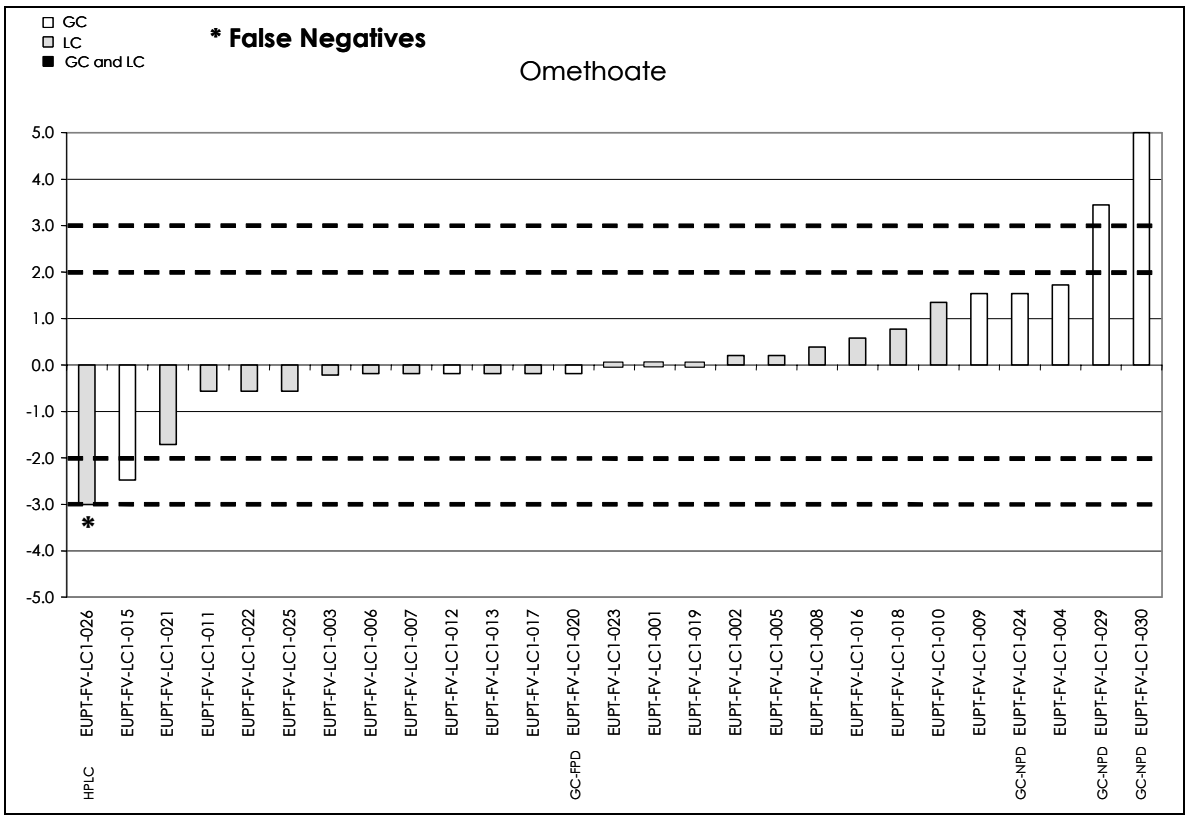
APPENDIX 4. Graphical Representation of z-scores for FFP RSD (25%).



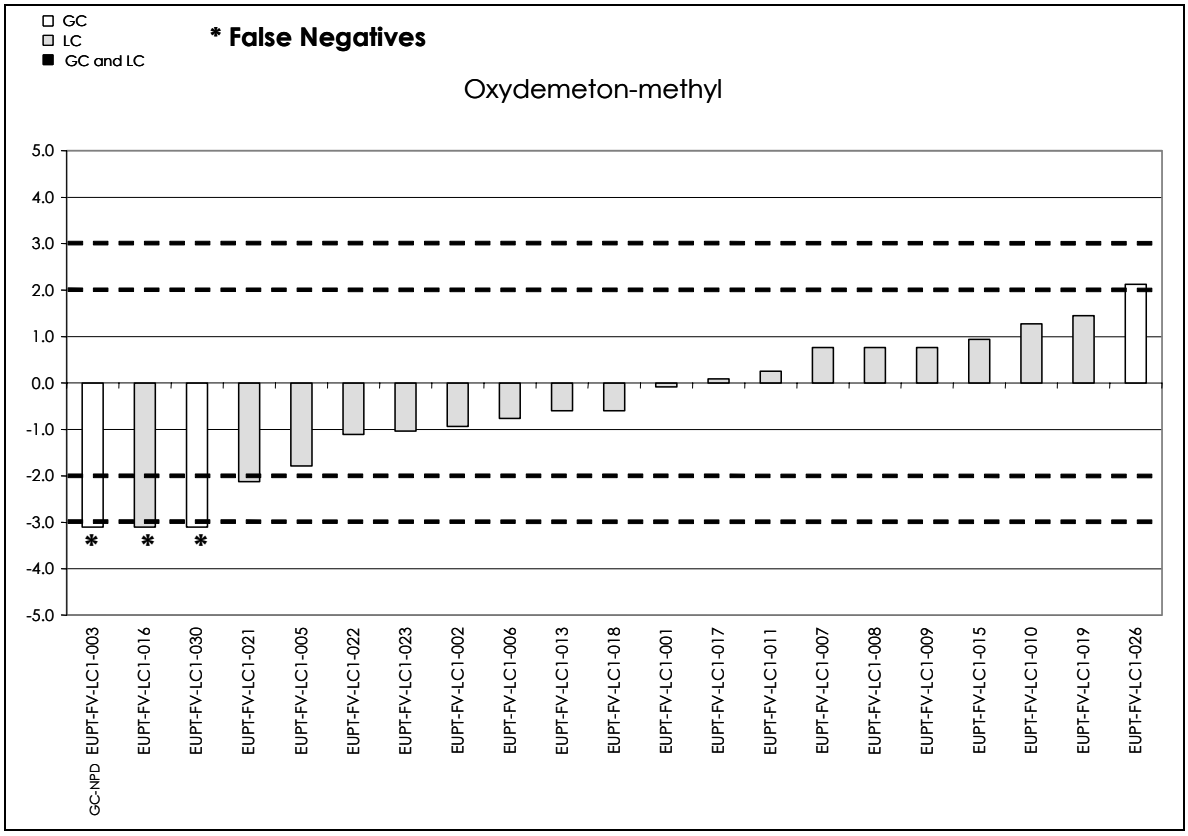


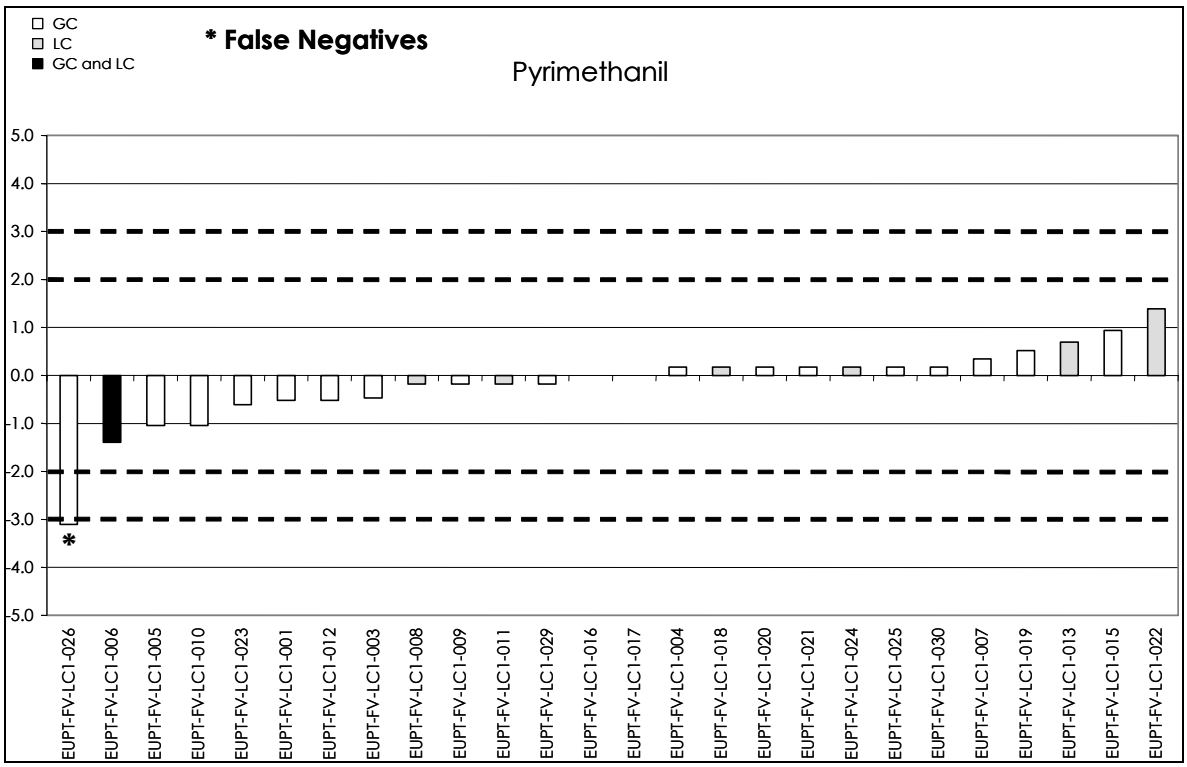
APPENDIX 4. Graphical Representation of z-scores for FFP RSD (25%).



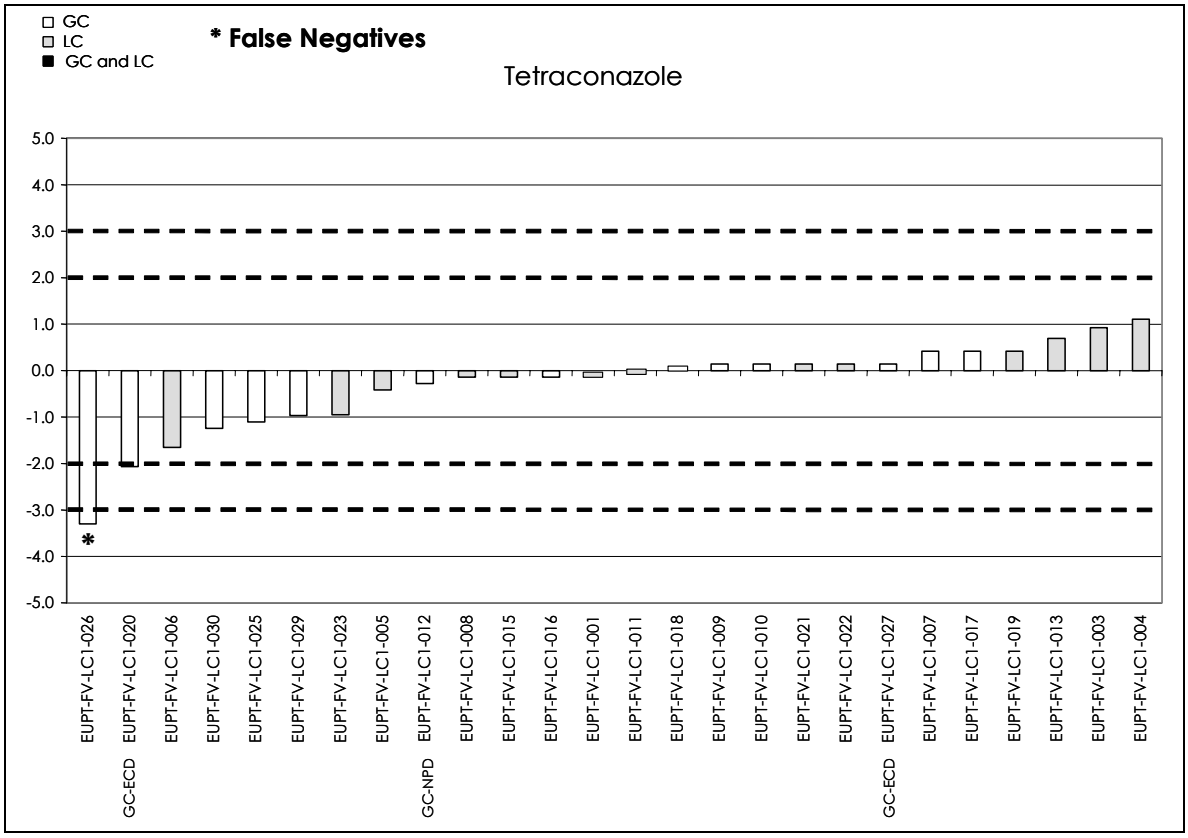


APPENDIX 4. Graphical Representation of z-scores for FFP RSD (25%).

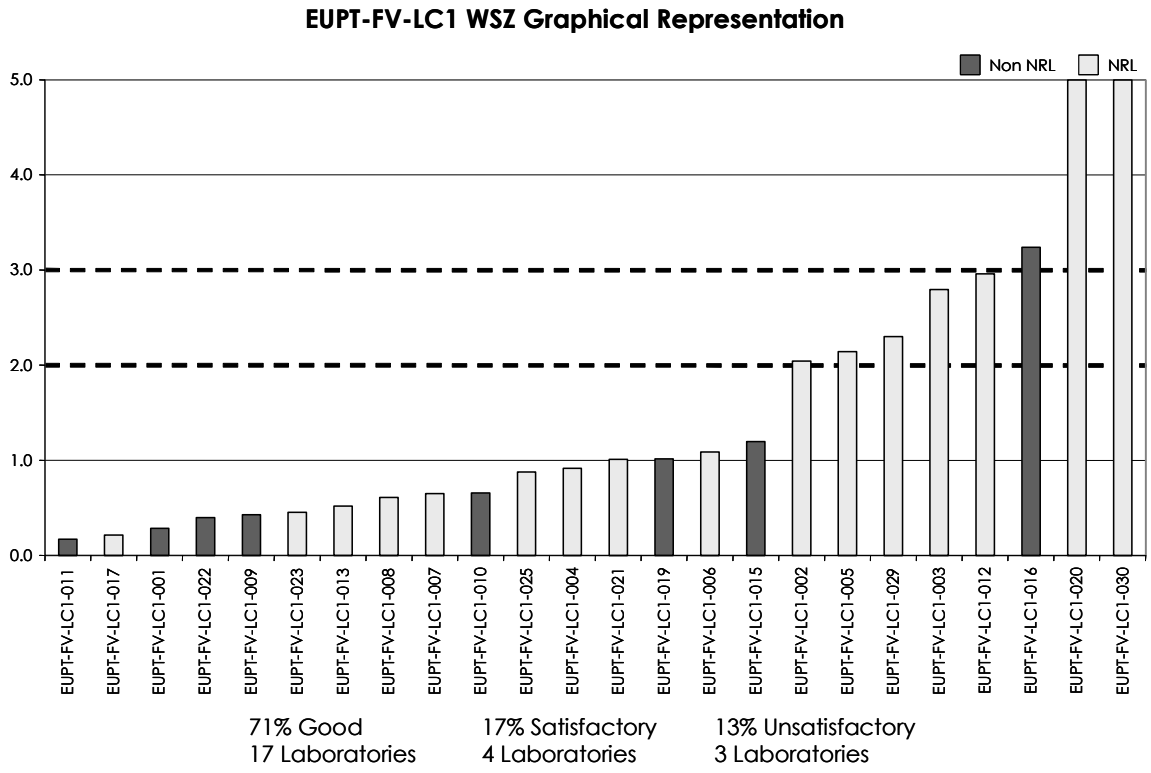




APPENDIX 4. Graphical Representation of z-scores for FFP RSD (25%).



APPENDIX 5. 'Weighted Sum of z-Score' (WSZ) for laboratories in Category A.



APPENDIX 6. EUPT-FV-LC1 WSZ graphical representations for laboratories in Category A.

Lab Code	z-Score Results											N of Pesticides	WSZ
	Acetamiprid	Carbaryl	Diazinon	Dimethoate	Imazalil	Imidacloprid	Iprodione	Omethoate	Oxydemeton-Methyl	Pyrimethanil	Tetraconazole		
1	0.2	-0.4	0.5	0.8	0.2	0.1	-0.3	0.0	-0.1	-0.5	0.0	11	0.3
2	0.1	-0.6	0.3	-0.2	0.2	0.0	-3.2	0.2	-0.9			9	2.0
3	0.4	-0.6	-0.5	-0.1	2.9		0.4	-0.2	-3.1	-0.5	0.9	10	2.8
4	0.1	1.6	0.8	1.2	-0.6	0.6	-1.3	1.7		0.2	1.1	10	0.9
5	1.0	1.0	-0.8	0.8	0.0	0.4	-3.2	0.2	-1.8	-1.0	-0.4	11	2.1
6	-1.0	-1.3	-1.0	-0.5	-1.8	-1.1	-1.1	-0.2	-0.8	-1.4	-1.7	11	1.1
7	0.6	1.0	0.3	0.7	0.5	0.8	1.6	-0.2	0.8	0.3	0.4	11	0.7
8	-0.2	-1.0	-1.3	0.3	-0.8	0.0	-1.6	0.4	0.8	-0.2	-0.1	11	0.6
9	-0.2	0.4	0.0	0.3	0.8	-0.3	-0.2	1.5	0.8	-0.2	0.1	11	0.4
10	-0.1	0.9	0.8	0.3	0.3	0.6	-0.5	1.3	1.3	-1.0	0.1	11	0.7
11	-0.2	-0.7	0.0	0.0	0.0	0.0	0.0	-0.6	0.3	-0.2	0.0	11	0.2
12	-1.8	1.0	-0.2	0.3	-3.2	-2.5	1.8	-0.2		-0.5	-0.3	10	3.0
13	0.3	0.2	1.0	0.0	1.1	0.3	0.6	-0.2	-0.6	0.7	0.7	11	0.5
15	-0.1	0.6	0.8	-0.3	-1.2	-0.1	0.5	-2.5	0.9	0.9	-0.1	11	1.2
16	-0.3	-0.7	0.8	-0.3	-0.2	-0.8	-3.2	0.6	-3.1	0.0	-0.1	11	3.2
17	0.3	-0.2	0.0	0.0	0.6	0.0	0.5	-0.2	0.1	0.0	0.4	11	0.2
19	0.2	2.1	0.3	0.7	0.2	1.0	0.2	0.0	1.4	0.5	0.4	11	1.0
20	-3.4	-1.8	-1.2	-0.5		-3.3	-3.2	-0.2		0.2	-2.1	9	6.6
21	0.4	0.2	1.0	-0.2	0.0	0.6	0.3	-1.7	-2.1	0.2	0.1	11	1.0
22	0.2	-0.4	0.2	0.0	0.0	-0.4	0.0	-0.6	-1.1	1.4	0.1	11	0.4
23	-0.1	-0.2	-0.6	-0.1	-0.7	-0.1	-0.6	0.0	-1.0	-0.6	-1.0	11	0.5
25	-1.4	-2.0	-0.3	1.3	-0.6	-1.1	-0.2	-0.6		0.2	-1.1	10	0.9
29	-0.6	-0.2	-1.0	-0.5	-1.4	0.0	-1.0	3.4		-0.2	-1.0	10	2.3
30	-0.3		-1.8	4.3		-3.3	2.4	5.0	-3.1	0.2	-1.2	9	10.0

APPENDIX 7. Combined z-scores RSZ and SSZ.

Lab Code	No. Of Pesticides Sought (n)	RSZ	SSZ
1	11	0.95	1.56
2	9	1.87	11.63
3	10	3.05	20.16
4	10	2.89	11.29
5	11	3.25	18.41
6	11	3.60	15.31
7	11	2.16	6.25
8	11	2.02	6.92
9	11	1.42	3.98
10	11	2.18	6.72
11	11	0.57	0.95
12	10	3.71	24.42
13	11	1.72	4.14
15	11	2.48	10.89
16	11	3.09	22.63
17	11	0.70	0.97
18	11	2.48	14.10
19	11	2.10	8.54
20	9	5.26	41.88
21	11	2.06	9.17
22	11	1.32	3.89
23	11	1.50	3.59
24	8	3.25	18.38
25	10	2.77	10.94
26	9	8.24	73.10
27	6	3.81	18.81
29	10	2.92	17.29
30	9	7.25	75.44

APPENDIX 8. Methods used by participants for determining pesticides.

NUMBER	REFERENCE
1	§ 64 LFGB Nr. L 00.00-34 (DFG-Method) S 19, former § 35 LMBG Nr. L 00.00-34
2	Analytical Methods for Pesticide Residues in Foodstuffs. Ministry of Welfare, health and cultural affairs, Netherlands, Multiresidue Method 1, 3.1.2, 6th Ed, 1996
3	Application note 2003/1 1-15 Sabdra, Tienpont, David Research Institute for Chromatography Belgium
4	Cano, De La Plaza, Muñoz. Pestic. Sci 1987
5	EN-12393
6	EN-14333 or EN-14185
7	Fillion et al. Journal of AOAC International 78-5-1995
8	FP017 or FP018 or FP086
9	Fresenius J Anal Chem. (1995) 353: 183 - 190
10	Gilvydis Dm Walters SM (1990) JAOA Chem. 73
11	Internal Method MI/C/10/100 Rev. 3 or Local SOP
12	Internal Method SAR (based on No. 7)
13	ISTIAN 97/23
14	Janson et al. Journal of Chromatography A 1023 (2004,9, 93-104
15	JB Leary
16	Klein, J., Alder, L. JAOAC 86, 1015 (2003)
17	KM 21 or KM 22
18	Leothay, S. Et al. JAOAC 88 (2005)
19	Luke, M.A., Froberg, J.E., Doose, G.M., Masumoto, H.T. (1981) J. Assoc. Off. Anal. Chem. 64(5): 1187-1195
20	M. Anastassiades et al JAOAC 86 (2003)
21	Methodenvorschlag EG Proficiency Test 1996/97
22	Multi Residues Method draft BfR
23	Official Method of Analysis (1990) 15th Ed., 985.22 AOAC Arlington VA
24	Proc. Int. Citriculture (1997) Vol. 3
25	Rev 3, 1, 1995 Method 531,1. National Exposure Research Laboratory Office of Research and Development, US Environmental Protection Agency, Cincinnati Ohio 45268
26	SC/PB-07; 28.10.2004 wyd.1
27	SLV M200
28	Validated Internal Method JAOAC 79-2 (1996)
29	VVMDC-T-012-023
30	Wyd. Met. PZH 2002
31	Internal Method (specify any reference)
32	QuEChERS, CEN/TC 275 WG 4N0236

APPENDIX 8. Methods used by participants for determining pesticides.

ACETAMIPRID													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	92	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	16
003	M	LC-MS/MS	0.03	93.1	1	15	4			1	Splitless	GC-NPD	2
004	M		0.01	83	1	15	4	GPC		2	Loop	LC-MS/MS	18
005	S		0.01	119	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.005	101	1	50	1			5		LC-MS/MS	31
007	M	LC-MS/MS	0.005	108	1	10	5	O (dispersive SPE)		5	Loop	LC-MS/MS	32
008	M	LC-MS/MS	0.001	94	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	LC-MS/MS	1
010	M	LC-MS/MS	0.001			15	5	dispersive SPE				HPLC-MS/MS	18
011	M	LC-MS/MS	0.005	95	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	S	LC-MS/MS	0.01	82	2	15	4			10		LC-MS/MS	2
013	M	none	0.005	97	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS/MS (ESI)	20
014	No Results Given												
015	S		0.005			10	6	Diatomaceous Earth		25		LC-MS/MS	31
016	M	LC-MS	0.005			10	5	O		20		LC-MS/MS	32
017	M	LC-MS/MS	0.01	89	1	10	6			5		LC-MS/MS	16
018	S	LC-MS/MS	0.005	105	1	10	5	O		1	As	LC-MS/MS	20
019			0.005	96	1	20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020*			0.01			50	1 (in the presence of NaOH)	GPC		10	Reodyne	HPLC-DAD	5
021	M	LC-MS/MS	0.005	98.9	1	75	1			5		LC-MS/MS	31
022	M	LC-MS/MS	0.005	120	1	10	5	DSPE		20		LC-MS/MS	20
023	M	LC-MS	0.005	116	1	10	5			3	Particial Loop	LC-MS/MS	20
024	M	LC-MS/MS	0.005	96	1	10	5	LL		10		LC-MS/MS	11
025	M	LC-MS		86	1	10	1			25		HPLC-MS	
026	NA												
027	S	HPLC-UV	0.01	70	1	20	6	LL, SPE		10	Autosampler	HPLC-UV	
028	No Results Given												
029	S	LC-MS/MS	0.005	90	1	5	5			5		LC-MS/MS	14
030	S	HPLC-UV	< 0.02	82	1	10	5	SPE (cleanup mixture: PSA and $MgSO_4$)	TCDPP (PF 38)	20	Solvent Injection	HPLC-UV	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

CARBARYL													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	95	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003	M	LC-MS/MS	0.02	99	1	15	4			1	Splitless	GC-NPD	2
004	M		0.02	107	1	15	4	GPC		2	Splitless	GC-MS	2
005	S	GC-ITD	0.01	116	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.005	92	1	50	1	None HP-GPC		5 1	None Splitless	LC-MS/MS GC-ITD	31
007	M	LC-MS/MS	0.005	109	1	10	5	O (dispersive SPE)		5	Loop	LC-MS/MS	32
008	M	GC-MS	0.005	99	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	GC-MS	1
010	M	LC-MS/MS	0.005			15	5	Dispersive SPE				HPLC-MS/MS	18
011	M	LC-MS/MS	0.005	100	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	S	GC-MS	0.01	75	2	50	1	SPE (only for ECD and ELCD detections)		1 to 3	Splitless, On Column, SPI	GC-NPD, GC-ITD	5
013	M	none	0.01	99	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	M		0.005			100	2	GPC	TPP	5	PTV	GC-MS	1
016	M	GC-MS	0.005			10	5	O		1.5	Split/Splitless	GC-ECD, GC-MS	32
017	M	LC-MS/MS	0.01	93	1	10	6			5		LC-MS/MS	16
018	S	LC-MS/MS	0.005	93	1	10	5	O		1	AS	LC-MS/MS	20
019		GC-MS	0.005	94	1	20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020	S		0.005	80	1	50	1	GPC	Trimetacarb	200	Reodyne	HPLC-FD	5
021	M	LC-MS/MS	0.005	104	1	75	1			5		LC-MS/MS	31
022	M	LC-MS/MS	0.005	92	1	10	5	DSPE		20		LC-MS/MS	20
023	M	LC-MS	0.005	105	1	10	5			3	Particial Loop	LC-MS/MS	20
024	M	LC-MS/MS	0.005	94	1	10	5	LL		10		LC-MS/MS	11
025	M	LC-MS		77	1	10	1			25		HPLC-MS	
026	S		0.01	92	1	50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	NA												
028	No Results Given												
029	M	GC-MS/MS	0.01	108	1	10	5	PSA	Triphenylphosphate	5	Large Volume	GC-MSMS (ion trap)	20
030	NA												

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

DIAZINON													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	91	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003	M	GC-ECD	0.02	85.8	1	15	4			1	Splitless	GC-NPD	2
004	M		0.02	103	1	15	4	GPC		2	Splitless	GC-MS	2
005	M	GC-ITD	0.01	105	1	5	7 Aceton Ethylacetate Hexane		TPP	1	Splitless	GC-MS/MS	31
006	M		0.01	99	1	50	1	None HP-GPC		5 1	None Splitless	LC-MS/MS GC-ITD	31
007	M	GC-MS	0.005	107	1	50	4		Ditalimphos	1	Splitless	GC-MS	23
008	M	LC-MS/MS	0.001	78	1	15	4		Yes	5	PTV	GC-ITD	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	GC-MS	1
010	M	GC-MS/MS	0.002			15	4	LL				GC-MS/MS	19
011	M	GC-MS/MS	0.005	101	2	10	5	SPE	Triphenylmethane	2	PTV	GC-MS/MS	20
012	S	GC-MS	0.01	91	2	50	1	SPE (only for ECD and ELCD detections)		1 to 3	Splitless, On Column, SPI	GC-PFPD, GC-ITD	5
013	M	GC-MS	0.01	100	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	M		0.005			100	2	GPC	TPP	5	PTV	GC-MS	1
016	M	GC-MS	0.005			10	5	O		1.5	Split/Splitless	GC-ECD, GC-MS	32
017	M	GC-MS	0.01	81	1	15	4			1	Splitless	GC-MS	19
018	M	GC-MS	0.005	102	1	10	5			1	AS	GC-MS(single-quad)	20
019		GC-PND	0.005	72	2	20	6	SPE	p,p-DDE	1	Splittless	GC-MS	16
020	M	GC-TOF-MS	0.005	84	1	50	1	GPC	TPP	1	Splittless	GC-NPD	5
021	M	LC-MS/MS	0.005	109	1	75	1			5		LC-MS/MS	31
022	M	GC-MS	0.005	97	1	10	5	DSPE	PCB 138	1	Solvent Vent PTV	GC-MS	20
023	M	GC-MS	0.005	96	1	30	1	GPC	Tetraphenylethlene	2	Splitless	GC-MS	31
024	M	GC/TOF	0.004	95	1	50	1	GPC		2	Splitless	GC-NPD	11
025	M	GC-MS		81	1	10	4			2	Splitless	GC-ECD/FPD/NPD/MS	19
026	S	GC-MS	0.005	74	2	50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	S	GC-NPD	0.002	90	1	20	4	LL, SPE		2	Autosampler	GC-ECD,GC-NPD	5
028	No Results Given												
029	M	GCMSMS	0.005	92	1	37.5	1	GPC		1	Splitless	GC-ECD,NPD,FPD	5
030	S	GC-MS	< 0.01	78	1	10	5			2	Splitless	GC-MS(ion trap)	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

DIMETHOATE													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	95	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003	M	GC-ECD	0.02	112	1	15	4			1	Splitless	GC-NPD	2
004	M		0.02	112	1	15	4	GPC		2	Splitless	GC-MS	2
005	S		0.01	95	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.005	101	1	50	1	None HP-GPC		5 2	None Splitless	LC-MS/MS GC-FPD	31
007	M	LC-MSMS	0.005	107	1	10	5	O (Dispersive SPE)		5	Loop	LC-MS/MS	32
008	M	GC-MS	0.001	85	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	GC-NPD	1
010	M	LC-MS/MS	0.002			15	5	Dispersive SPE				HPLC-MS/MS	18
011	M	LC-MS/MS	0.005	95	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	S	GC-MS	0.01	72	2	50	1	SPE (only for ECD and ELCD detections)		1 to 3	Splitless, on Column, SPI	GC-PFPD, GC-ITD	5
013	M	none	0.001	97	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	S	GC-MS	0.005			10	6	Diatomaceous Earth		25		LC-MS/MS	31
016	M	GC-MS	0.005			10	5	O		1.5	Split/Splitless	GC-ECD, GC-MS	32
017	M	LC-MS/MS	0.01	86	1	10	6			5		LC-MS/MS	16
018	S	LC-MS-MS	0.005			10	5	O		1	AS	LC-MS/MS	20
019		GC-MS	0.005	92	1	20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020	M	GC-TOF-MS	0.005	92	1	50	1	GPC	TPP	1	Splitless	GC-FPD	5
021	M	LC-MS/MS	0.005	95.5	1	75	1			5		LC-MS/MS	31
022	M	LC-MSMS	0.005	100	1	10	5	DSPE		20		LC-MS/MS	20
023	M	LC-MS	0.005	88	1	10	5			3	Particial Loop	LC-MS/MS	20
024	M	GC/TOF	0.006	92	1	50	1	GPC		2	Splitless	GC-NPD	11
025	M	GC-MS		83	1	10	4			2	Splitless	GC-ECD/FPD/NPD/MS	19
026*						50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	S	GC-NPD	0.002	110	1	20	4	LL, SPE		2	Autosampler	GC-ECD,GC-NPD	5
028	No Results Given												
029	M	GCNPD, FPD	0.01	74	1	37.5	1	GPC		1	Splitless	GC-ECD,NPD,FPD	5
030	S	GC-NPD	< 0.01	86.3	1	10	5			1		GC-NPD	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

IMAZALIL													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	77	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003	M	GC-ECD	0.02	92.5	1	15	4			1	Splitless	GC-NPD	2
004	M		0.01	62	1	15	4	GPC		2	Loop	LC-MS/MS	18
005	S		0.01	90	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.01	83	1	50	1			5		LC-MS/MS	31
007	M	LC-MSMS	0.005	105	1	10	5	O (Dispersive SPE)		5	Loop	LC-MS/MS	32
008	M	LC-MS/MS	0.001	83	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.001			15	5	Dispersive SPE				HPLC-MS/MS	18
010	M	LC-MS/MS	0.001			15	5	Dispersive SPE				HPLC-MS/MS	
011	M	LC-MS/MS	0.005	102	2	10	5	SPE	TPP	5		LC-MS/MS	20
012*			0.02			50	1	SPE (Only for ECD and ELCD Detections)		1 to 3	Splitless, on Column, SPI	GC-ITD	5
013	M	none	0.005	98	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	S	GC-MS	0.005			10	6	Diatomaceous Earth		25		LC-MS/MS	31
016	M	LC-MS	0.01			10	5	O		20		LC-MS/MS	32
017	M	LC-MS/MS	0.01	107	1	10	6			5		LC-MS/MS	16
018	S	LC-MS-MS	0.005	96	1	10	5	O		1	AS	LC-MS/MS	20
019			0.005	92	1	20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020	NA												
021	M	LC-MS/MS	0.005	89.9	1	75	1			5		LC-MS/MS	31
022	M	LC-MSMS	0.005	120	1	10	5	DSPE		20		LC-MS/MS	20
023	M	LC-MS	0.005	94	1	10	5			3	Particial Loop	LC-MS/MS	20
024*			0.005			10	5	LL		10		LC-MS/MS	11
025	M	GC-MS		54	1	10	4			2	Splitless	GC-ECD/FPD/NPD/MS	19
026*						50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	NA												
028	No Results Given												
029	S	LCMSMS	0.006	63	1	5	5			5		LC-MS/MS	14
030	NA												

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

IMIDACLOPRID													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	101	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003	NA												
004	M		0.01	90	1	15	4	GPC		2	Loop	LC-MS/MS	18
005	S		0.01	110	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.01	89	1	50	1			5		LC-MS/MS	31
007	M	LC-MSMS	0.005	107	1	10	5	O (Dispersive SPE)		5	Loop	LC-MS/MS	32
008	M	LC-MS/MS	0.005	94	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	LC-MS/MS	1
010	M	LC-MS/MS	0.001			15	5	Dispersive SPE				HPLC-MS/MS	18
011	M	LC-MS/MS	0.005	93	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	S	LC-MS/MS	0.01	75	2	15	4			10		LC-MS/MS	2
013	M	none	0.005	96	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	S		0.005			10	6	Diatomaceous Earth		25		LC-MS/MS	31
016	M	LC-MS	0.01			10	5	O		20		LC-MS/MS	32
017	M	LC-MS/MS	0.01	92	1	10	6			5		LC-MS/MS	16
018	S	LC-MS-MS	0.005	102	1	10	5	O		1	AS	LC-MS/MS	20
019			0.005			20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020*			0.01			50	1 (in the Presence of NaOH)	GPC		10	Reodyne	HPLC-DAD	5
021	M	LC-MS/MS	0.005	102	1	75	1			5		LC-MS/MS	31
022	M	LC-MSMS	0.005	105	1	10	5	DSPE		20		LC-MS/MS	20
023	M	LC-MS	0.005	98	1	10	5			3	Particial Loop	LC-MS/MS	20
024	M	LC-MS/MS	0.002	81	1	10	5	LL		10		LC-MS/MS	11
025	M	LC-MS		79	1	10	1			25		HPLC-MS	
026	NA												
027	S	HPLC-UV	0.01	85	1	25	1	SPE		10	Autosampler	HPLC-UV	
028	No Results Given												
029	S	LCMSMS	0.005	95	1	5	5			5		LC-MS/MS	14
030*	S	HPLC-UV	< 0.05			10	5	SPE (Cleanup Mixture: PSA and $MgSO_4$)	TCDPP (PF 38)	20	Solvent Injection	HPLC-UV	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

IPRODIONE													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	GC-MS/MS	0.005	88	1	75	1		Ditalimfos	4	Splitless	GC-MS/MS	27
002*	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003*	M	GC-ECD	0.02	97.2	1	15	4			1	Splitless	GC-NPD	2
004	M		0.02	132	1	15	4	GPC		2	Splitless	GC-MS	2
005	M	GC-ITD	0.02	70	1	5	7 Acetone Ethylacetate Hexane		TPP	1	Splitless	GC-MS/MS	31
006	M		0.01	108	1	50	1	HP-GPC		1 2	Splitless	GC-ITD GC-ECD	31
007	M	GC-MS	0.005	118	1	50	4		Ditalimphos	1	Splitless	GC-MS	23
008	M	GC-MS	0.005	82	1	15	4		Yes	5	PTV	GC-ITD	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	GC-MS	1
010	M	GC-MS/MS	0.004			15	4	LL				GC-MS/MS	19
011	M	GC-MS	0.005	101	2	10	5	SPE	Tris-(1,3-dichloroisoproyl)-phosphate	2	PTV	GC-MS	20
012	S	GC-MS	0.01	83	2	50	1	SPE (only for ECD and ELCD Detections)		1 to 3	Splitless, on Column, SPI	GC-NPD, GC-ITD	5
013	M	none	0.005	100	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3	PTV	GC-MS EI	20
014	No Results Given												
015	M		0.005			100	2	GPC	TPP	5	PTV	GC-MS	1
016*		GC-MS	0.07			10	5	O		1,5	Split/Splitless	GC-ECD, GC-MS	32
017	M	GC-MS	0.015	98	1	15	4			1	Splitless	GC-MS	19
018	M		0.005			10	5			1	AS	GC-MS(single-quad)	20
019			0.005	102	2	20	6	SPE	p,p-DDE	1	Splittless	GC-MS	16
020*			0.01									GC-ECD	
021	M	GC-MS/MS	0.005	96.9	1	75	1			2	Split/Splitless	LC-MS/MS	31
022	M	GC-MS	0.005	97	1	10	5	DSPE	PCB 138	1	Solvent Vent PTV	GC-MS	20
023	M	GC-MS	0.005	100	1	30	1	GPC	Tetraphenylethlene	2	Splitless	GC-MS	31
024	NA												
025	M	GC-MS		70	1	10	4			2	Splitless	GC-ECD/FPD/NPD/MS	19
026*						50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	S	GC-ECD	0.01	70	1	20	4	LL, SPE		2	Autosampler	GC-ECD,GC-NPD	5
028	No Results Given												
029	M	GCMSMS	0.01	112	1	10	5	PSA	Triphenylphosphate	5	Large Volume	GC-MSMS (ion trap)	20
030	S	GC-MS	< 0.01	117.7	1	10	5			2	Splitless	GC-MS(ion trap)	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

OMETHOATE													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	95	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003	M	LC-MS-MS	0.01	58.1	1	15	4			1	Splitless	GC-NPD	2
004	M		0.02	123	1	15	4	GPC		2	Splitless	GC-MS	2
005	S		0.01	103	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.005	103	1	50	1			5		LC-MS/MS	31
007	M	LC-MSMS	0.005	102	1	10	5	O (Dispersive SPE)		5	Loop	LC-MS/MS	32
008	M	LC-MS/MS	0.005	80	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	GC-MS	1
010	M	LC-MS/MS	0.001			15	5	Dispersive SPE				HPLC-MS/MS	18
011	M	LC-MS/MS	0.005	86	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	S	GC-MS	0.02	68	2	50	1	SPE (only for ECD and ELCD Detections)		1 to 3	Splitless, on Column, SPI	GC-PFPD, GC-ITD	5
013	M	none	0.001	87	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	M		0.005			100	2	GPC	TPP	5	PTV	GC-MS	1
016	M	LC-MS	0.005			10	5	O		20		LC-MS/MS	32
017	M	LC-MS/MS	0.01	74	1	10	6			5		LC-MS/MS	16
018	S	LC-MS-MS	0.005	93	1	10	5	O		1	AS	LC-MS/MS	20
019		GC-MS	0.005	92	1	20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020	M		0.005	72	1	50	1	GPC	TPP	1	Splitless	GC-FPD	5
021	M	LC-MS/MS	0.005	67.9	1	75	1			5		LC-MS/MS	31
022	M	LC-MSMS	0.005	80	1	10	5	DSPE		20		LC-MS/MS	20
023	M	LC-MS	0.005	98	1	10	5			3	Particial Loop	LC-MS/MS	20
024	M	GC/TOF	0.01	99	1	50	1	GPC		2	Splitless	GC-NPD	11
025	M	GC-MS		54	1	10	1			25		HPLC-MS	
026*						50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	NA												
028	No Results Given												
029	M	GCNPD,FPD	0.01	105	1	37.5	1	GPC		1	Splitless	GC-ECD,NPD,FPD	5
030	S	GC-NPD	< 0.01	87.6	1	10	5			1		GC-NPD	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

OXYDEMETON-METHYL													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	97	1	75	1			5		LC-MS/MS	27
002	M	LC-MS/MS	0.01			10	5	Dispersive Solid-Phase Extraction		50		LC-MS/MS	20
003*			0.02			15	4			1	Splitless	GC-NPD	2
004	NA												
005	S		0.01	128	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.005	94	1	50	1			5		LC-MS/MS	31
007	M	LC-MSMS	0.005	103	1	10	5	O (Dispersive SPE)		5	Loop	LC-MS/MS	32
008	M	LC-MS/MS	0.001	95	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	LC-MS/MS	1
010		LC-MS/MS	0.001			15	5	Dispersive SPE				HPLC-MS/MS	18
011	M	LC-MS/MS	0.005	88	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	NA												
013	M	none	0.002	90	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	S		0.005			10	6	Diatomaceous Earth		25		LC-MS/MS	31
016*		LC-MS	0.005			10	5	O		20		LC-MS/MS	32
017	M	LC-MS/MS	0.01	84	1	10	6			5		LC-MS/MS	16
018	S	LC-MS-MS	0.005	102	1	10	5	O		1	AS	LC-MS/MS	20
019			0.005	98	1	20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020	NA												
021	M	LC-MS/MS	0.005	75.7	1	75	1			5		LC-MS/MS	31
022	M	LC-MSMS	0.005	90	1	10	5	DSPE		20		LC-MS/MS	20
023	M		0.005	99	1	10	5			3	Particial Loop	LC-MS/MS	20
024	NA												
025	NA												
026	S	GC-MS	0.01	88	1	50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	NA												
028	No Results Given												
029	NA												
030*		GC-MS	< 0.01			10	5			2	Splitless	GC-MS(ion trap)	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

PYRIMETHANIL													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	GC-MS/MS	0.005	84	1	75	1		Ditalimfos	4	Splitless	GC-MS/MS	27
002	NA												
003	M	GC-MS	0.05	91	1	15	4			1	Splitless	GC-NPD	2
004	M		0.01	89	1	15	4	GPC		2	Loop	LC-MS/MS	18
005	M	GC-ITD	0.01	88	1	5	7 Acetona Ethylacetate Hexane		TPP	1	Splitless	GC-MS/MS	31
006	M		0.01	96	1	50	1	None HP-GPC		5 1	None Splitless	LC-MS/MS GC-ITD	31
007	M	GC-MS	0.005	106	1	50	4		Ditalimphos	1	Splitless	GC-MS	23
008	M	GC-MS	0.001	98	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	GC-MS	1
010	M	GC-MS/MS	0.002			15	4	LL				GC-MS/MS	19
011	M	LC-MS/MS	0.005	97	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	S	GC-MS	0.01	85	2	50	1	SPE (only for ECD and ELCD Detections)		1 to 3	Splitless, on Column, SPI	GC-NPD, GC-ITD	5
013	M	GC-MS	0.005	99	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	M		0.005			100	2	GPC	TPP	5	PTV	GC-MS	1
016	M	LC-MS	0.005			10	5	O		20		LC-MS/MS	32
017	M	GC-MS	0.01	86	1							GC-MS	
018	S	LC-MS-MS		102	1	10	5	O		1	AS	LC-MS/MS	20
019			0.005	88	2	20	6	SPE	p,p-DDE	1	Splittless	GC-MS	16
020	S	GC-TOF-MS	0.01	90	1	50	1 (in the Presence of NaOH)	GPC		10	Reodyne	HPLC-DAD	5
021	M	GC-MS/MS	0.005	99.3	1	75	1			5		LC-MS/MS	31
022	M	LC-MSMS	0.005	104	1	10	5	DSPE		20		LC-MS/MS	20
023	M	GC-MS	0.005	97	1	30	1	GPC	Tetraphenylethlene	2	Splitless	GC-MS	31
024	M	LC-MS/MS	0.003	90	1	10	5	LL		10		LC-MS/MS	11
025	M	GC-MS		109	1	10	4			2	Splitless	GC-ECD/FPD/NPD/MS	19
026*						50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	NA												
028	No Results Given												
029	M	GCMSMS	0.01	99	1	10	5	PSA	Triphenylphosphate	5	Large Volume	GC-MSMS (ion trap)	20
030		GC-NPD	< 0.01	83.5		10	5			1		GC-NPD	11

* NOT DETECTED

APPENDIX 8. Methods used by participants for determining pesticides.

TETRACONAZOLE													
Lab Code	Quantification Using Standards in Solvent or in Matrix	Confirmation Method	RL(mg/kg)	Recovery (%)	Recovery (1) or (2)	Sample Weight (g)	Extraction Solvent	Clean-Up Step	Internal standard	Injection Volume (µl)	Injection Type	Determination	Reference Method (see page 41)
001	M	LC-MS/MS	0.005	93	1	75	1			5		LC-MS/MS	27
002	NA												
003	M	LC-MS-MS	0.01	94	1	15	4			1	Splitless	GC-NPD	2
004	M		0.02	100	1	15	4	GPC		2	Splitless	GC-MS	2
005	S	GC-ITD	0.01	95	1	10	4			5	Partial Loop	LC-MS/MS	31
006	M		0.005	92	1	50	1			5		LC-MS/MS	31
007	M	GC-MS	0.005	98	1	50	4		Ditalimphos	1	Splitless	GC-MS	23
008	M	GC-MS	0.005	124	1	7.5	4 + Na_2SO_4 (7.5 g)			5	Loop	LC-MS/MS	
009	M	LC-MS/MS	0.005	94	1	50	3	GPC		1 20	Split	GC-MS	1
010	M	GC-MS/MS	0.001			15	4	LL				GC-MS/MS	19
011	M	LC-MS/MS	0.005	99	2	10	5	SPE	TPP	5		LC-MS/MS	20
012	S	GC-MS	0.01	78	2	50	1	SPE (only for ECD and ELCD Detections)		1 to 3	Splitless, on Column, SPI	GC-NPD, GC-ITD	5
013	M	none	0.01	95	1	10	5	DSPE	PCB 138, Triphenylphosphate (TPP)	3		LC-MS MS (ESI)	20
014	No Results Given												
015	S	GC-MS	0.005			10	6	Diatomaceous Earth		25		LC-MS/MS	31
016	M	GC-MS	0.005			10	5	O		1.5	Split/Splitless	GC-ECD, GC-MS	32
017	M	GC-MS	0.01	108	1	15	4			1	Splitless	GC-MS	19
018	M	GG-MS	0.005	101	1	10	5			1	AS	GC-MS(single-quad)	20
019		GC-MS	0.005	100	1	20	6	SPE	TPP	2	Partial Loop With Needle Overfill	LC-MS/MS	16
020	M	GC-TOF-MS	0.005	64	1	50	1	GPC	TPP	1	Splittless	GC-NPD	5
021	M	LC-MS/MS	0.005	92.6	1	75	1			5		LC-MS/MS	31
022	M	LC-MSMS	0.005	115	1	10	5	DSPE		20		LC-MS/MS	20
023	M	LC-MS	0.005	106	1	10	5			3	Particial Loop	LC-MS/MS	20
024	NA												
025	M	GC-MS		72	1	10	4			2	Splitless	GC-ECD/FPD/NPD/MS	19
026*						50	1			1	Split/Splittless	GC-FPD, HPLC/PICKERING	13
027	S	GC-ECD	0.005	70	1	20	4	LL, SPE		2	Autosampler	GC-ECD,GC-NPD	5
028	No Results Given												
029	M	GCMSMS	0.01	99	1	10	5	PSA	Triphenylphosphate	5	Large Volume	GC-MSMS (ion trap)	20
030	S	GC-MS	< 0.01	71.3	1	10	5			2	Splitless	GC-MS(ion trap)	11

* NOT DETECTED

Protocol

Instructions

Only laboratories that are involved in providing residue data on fruit and vegetables for their national monitoring programmes, and/or the EU co-ordinated monitoring programme are invited to participate in this CRL – 1st European Proficiency Test in Fruit and Vegetables for residues at low concentrations (EUPT-FV-LC1).

To participate, each laboratory will have to complete and return by e-mail the **Application Form** to the Organiser. They will then receive acceptance confirmation by e-mail of their participation with a **Laboratory Code;** subsequently, this code must always be used in all communicating with the Organiser. Any e-mail without this code will not be answered. This code will only be known by the participant, the Organiser, and the Commission. This will ensure confidentiality during the test. In the Final Report there will not be any correlation between the code and the laboratory name. However, some results may need to be presented on a country basis to the Standing Committee on the Food Chain and Animal Health, and a link between codes and laboratories is possible, especially if there are only a few laboratories in any one country. A **web security code** will be given to enable laboratories to access the **Protocol** and the **Forms**.

This **Protocol**, together with three **Forms (1-3)** will be uploaded onto the web page and access will be by using the security code. Each form will have a deadline; please ensure you adhere strictly to these deadlines. The completed forms must be returned to the Organiser. On receipt of each form, the Organiser will respond with a confirmation of receipt e-mail.

The **Pesticide List** will also be accessible at this website without using the security code. This list will include all the possible pesticides that could be present in the test material. This list will specify which compounds to look for. The list will be based on EUPT-FV9 which was available from 10th January 2007, so that all participants are aware in good time, well before receipt of the test materials, which pesticides might be present. This time MRRL values (minimum performance reporting levels) for each pesticide will be unique to 0.005mg/Kg. It will be important that laboratories report their RL (Reporting Level) in Form 2.

The official language used in this Proficiency Test will be English.

Communication between participating laboratories during the test is not allowed.

Invoices to cover the cost of transporting the test materials will be available from the start of the test so that, once the shipping begins; laboratories will be able to receive the test materials. Only laboratories that have paid the transport costs will receive the test materials. If laboratories need more time to pay, they must send a payment record by **fax** or **e-mail** to verify that the payment procedure has started. **Payments without a laboratory code to identify them will not be considered as paid.**

General Characteristics

Objectives

The objective of this proficiency test is to obtain information about the quality, accuracy and comparability of the low concentration pesticide residue data on fruit and vegetables. Participating laboratories will be provided with an assessment of their own analytical performance and the acceptability of their data compared to other laboratories.

Steps to Follow

The Proficiency Test is made up of the following 8 steps that are essential for the generation of satisfactory results:

1. Invitation to the participating laboratories. Also supplying details of the web site and web page, where they can download the Application Form and Possible Pesticide List.
2. Preparation of the test materials. Homogeneity and stability testing performed by the Organiser.
3. Receipt confirmation of the participant's Application Form and notification of the Laboratory Codes and Security Code to gain access to the Forms and to this Protocol.
4. Payment in advance for the shipment of the test materials indicating the Lab Code, and receipt of a fax demonstrating that the payment procedure has started.
5. Shipment of the test material, together with the blank.
6. The participant laboratories will be responsible for reporting their data to the Organiser using the Forms supplied, by the stipulated deadline.
7. The Organiser will evaluate the results at the end of the proficiency test, once the deadline for receipt of the results has passed.
8. The Organiser will send a hard copy of the Final Report to each participant laboratory. This report will include information regarding the design of the test, the homogeneity and stability test results, a record of the shipped samples, a statistical evaluation of the participant's results as well as graphical displays of the results and conclusions. Any other relevant information considered of value will also be included.

Evaluation of the Results

The statistics used for the treatment and assessment of the data will be described in detail in the Final Report. A short summary of how the results will be treated is given below. It should be pointed out that this is the first time a low concentration EUPT is being performed, so decisions on to how to handle the results will be made on a case-by-case basis and always with the Advisory Group's approval.

The results will be grouped into:

- ***False Positives***

These are the results that show the presence of pesticides which are listed in the pesticide list and which were (i) not used in the sample treatment, (ii) and not detected by the Organiser even in a repeat analysis. However, if a number of laboratories detect the same additional pesticide, or if the concentration is close to 0.005mg/kg, then a decision as to whether or not this should be considered to be a false positive result will be made on a case-by-case basis.

Nevertheless, any results reported that are lower than 0.005 mg/kg will be ignored by the Organiser and will not therefore be considered as false positives.

- ***False Negatives***

These are results for pesticides that were not reported by the laboratories although they were used by the Organiser to treat the test material and were detected by the majority of participants at, or above, the 0.005mg/kg.

- ***Establishing the true concentration (μ)***

The true concentration in all cases will be determined by the median of all the results. Therefore a **median value** for every pesticide present will be calculated.

- ***Establishing the assigned value for the standard deviation***

The standard deviation (δ_i) of each individual analyte ($_i$) will be assigned by the the Organiser using the following formula.

$$\delta = b_i * \mu_i$$

Where b_i **= %SD/100% and** μ_i **=** ***the assigned true concentration for a certain compound***

As a first default calculation approach the Fit-For-Purpose (FFP) Standard Deviation of 25% will be used. This model worked well for the previous EUPTs at higher concentration levels. However, the Organiser reserves the right to vary this value in certain cases, after consultation with the committee of experts.

- ***z-Scores***

This parameter is calculated using this formula:

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

Where x_i is the value reported by the laboratories, μ_i the assigned value and δ_i the standard deviation at that level, for each pesticide ($_i$). Two z-score set may be obtained for each laboratory and each pesticides as two standard deviation values can be used.

Any z-score values of /z/ > 5 will be reported as '+5', or '-5'.

z-Score values will be interpreted in the following way:

$|z| \leq 2$ Acceptable

$2 < |z| \leq 3$ Questionable

$|z| > 3$ Unacceptable

For the values considered to be false negative results, z-scores will be will be considered by the advisory group on a case-by-case basis. Probably it will be assigned a cero value for x_i

However, a z-score will not be assigned to any false positive results.

The Organiser will consider whether, or not, these values should appear in the histograms.

- ***Combined z-Score values***

Although classical combined z-scores formulae are generally less used in other PT schemes, both will be calculated: the re-scaled sum of z-scores (RSZ), and the sum of squared z-scores (SSZ).

The equations are:

$$RSZ = \Sigma z/(n)^{1/2}$$

$$SSZ = \Sigma z^2$$

n = number of reported results

These formulae will only have an informative purpose and will not be used for laboratory evaluations.

In order to evaluate each laboratory's performance, only those laboratories that have reported at least 90% of the pesticides present, and have reported no false positive results, will be classified according by the Weighted Sum of z-Scores.

The Weighted Sum of z-Scores formula uses the z-score values with a fixed maximum value of 5 as a default z-score using the following formula:

$$\text{'Weighted Sum of z-Scores' (Z)} = \frac{\sum_{i=0}^{i\leq 2} |z| \cdot 1 + \sum_{i>2}^{i\leq 3} |z| \cdot 3 + \sum_{i>3}^{\infty} |z| \cdot 5}{n}$$

n = number of reported results

So for each lab:

- The first factor is the sum of all their /z-scores/ between zero to two, multiplied by one.
- The second factor is the sum of all their /z-scores/ greater than two but less than or equal to, three, multiplied by three.
- The third factor is the sum of all their z-scores greater than three, multiplied by five.

This WSZ has the following classification similar to the z-score:

$|z| \leq 2$ Good

$2 < |z| \leq 3$ Satisfactory

Note: It has been considered in the Final Report, a third z-score classification for $|z| > 3$ being Unsatisfactory.

For a laboratory to be in Category A it must achieve: report a 90% of the pesticides present in the sample, not report a false positive, achieve a WSZ less than or equal to, three.
Laboratories reporting a WSZ above 3 will not be in Category A.

Organisation Address

The official postal address, phone number, fax number and e-mail address of the Organiser are as follows:

Universidad de Almería

Edificio Químicas CITE I

Ctra. Sacramento s/n

04120 Almería - Spain

Phone Numbers: +34 950015034 or +34 950015645

Fax Number: +34 950015645

E-mail: pmedina@ual.es or amadeo@ual.es

On-Line News

The latest information currently updated can be found at the web address:

http://www.ual.es/GruposInv/EUPT/lc

Introduction

This proficiency test is based on low pesticide residues analysis of pears. The pears were grown in Spain.

The pesticide applications will be carried out as a post harvest treatment using a commercial formulation in micro spray solutions. The test material will be frozen (using liquid nitrogen), chopped, homogenized and sub-sampled into polyethylene bottles that have previously been coded.

Ten of these bottles, containing the test material, will be chosen randomly and analysed by an independent laboratory to check for homogeneity.

The test material will be stored frozen (–20ºC) prior to shipment to participants.

Two bottles, again chosen randomly, will be analysed over a period of time to confirm the stability of the pesticides in the test material (firstly when the test materials are shipped, and then a few days after the deadline for receipt of results from the participants). These results will not be included in the statistical analysis of the proficiency test.

The aim is only to check the stability during the shipping process and the proficiency test.

Calendar

The following table shows the programme for this EUPT-FV-LC1

Activity	Date
- Deadline for receiving the Application Form from invited laboratories.	2nd March 2007
- Sample Treatment, Homogenisation, and Storage Stability Tests.	March 2007
- Deadline for the Payment of Shipping Costs and/or demonstration that payment procedure has been initiated	30th March 2007
- Sample distribution.	9th -12th April 2007
- Deadline for receiving Form 1.	13th April 2007
- Deadline for receiving results: Forms 2 and 3.	7th May 2007
- Preliminary Report: **only results, no statistical treatment.**	July 2007
- Final Report to the laboratories.	December 2007

Participant Laboratories

It is up to the contact points/authorities/organisations responsible for the official monitoring of pesticide residues in each country to select the laboratories that should participate, although it is a requirement that a laboratory must be active in contributing results to the national monitoring programme and/or the EU co-ordinated programme. It is up to the participants to complete and return the Application Form so the Organiser has all their details before the deadline. The Organiser will not be responsible if a laboratory does not receive information regarding of the web page address, which is necessary to take part in the test.

Amount of Sample

Approximately 300g of pears test material will be shipped together with 300g of 'blank' pears surrounded with dry ice and packed in boxes. The courier costs are charged to and must be paid for by the participants before shipment of the samples. There will only be a limited amount of test material and laboratories should not ask for more than they require to be able to perform the analysis.

Application Form

Using the web page site: http://www.ual.es/GruposInv/EUPT/lc the participating laboratories must complete the Application Form and return it by e-mail to the Organiser.

It is important that laboratories data is updated and that laboratories make sure their e-mail system is working throughout the duration of the test.

In the Application Form there is also information that must be provided in order to make an official invoice. If an invoice is required it must be clearly stated when the Form is returned. The Application Form must be sent to the Organiser by 16th March 2007, at the latest.

Shipping of Samples

The shipment of the test materials will be carried out during a one-week period to try to ensure that all the shipments arrive at once. A warning message will be sent out a week before shipment, and laboratories must make their own arrangements for the reception of the test materials. They must inform the Organiser of any possible public holidays in their country/city during the delivery period mentioned in the calendar and make every effort to receive the shipment even if the laboratory is closed.

Form 1

Once the laboratory has received the test materials they **must** complete Form 1, by filling in the date of receipt, the condition of the test material, and its acceptance. Form 1 has a deadline, so if it is not returned by e-mail, by the latest 13th April 2007, the Organiser will assume the laboratory has received and accepted the test material.

Please note that you must include the laboratory code assigned to you on this form.

Analyses and Results Forms (Form 2)

Significant Figures

The results must be expressed in mg/kg in the following way:

- Concentrations < 0.100 mg/kg, to be expressed to two significant figures (three decimals places, i.e. 0.058 mg/kg).
- Concentrations ≥ 0.100 mg/kg, to be expressed to three significant figures, i.e. 0.156, 1.64, 10.3 mg/kg.

In cases where a pesticide was not detected, it should be recorded as ND. If it was not sought, it should be recorded as NA.

The results/concentrations must be reported as numbers. Any other form of data will not be considered.

Correction of Results

The results must **not** be corrected using recovery factors. If the laboratory usually corrects the results using their recoveries, they should provide the correction factor used for each pesticide as informative data only. It must also be reported if recoveries originated from experiments performed together with the test materials or if they have originated from the validation data. This information must be sent together with the results in Form 2.

Test Material for Analysis

The test material contains a certain number of pesticides from the Pesticide List. Laboratories must be aware that this year, Form 2 will have space to report separately the individual contributions for parent compounds and transformation product(s), as well as the sum specified in the residue definition. The residue definitions have been given in the Pesticide List.

It should **not** be assumed that only pesticides registered for use on pears are present in the test material.

Each laboratory must report only **one** result for each of the pesticide residues present in the test material, using their normal routine analytical procedure(s). This does not mean that more than one method has to be used to cover all the compounds present.

The analytical units used must be reported using Form 2. The results, expressed as concentration levels in mg/kg, must also be reported, together with the laboratories reporting limit (RL) for each pesticide. This level will only be used for information purposes.

The confirmation technique must be reported on this Form.

Form 2 must be sent to the Organiser by 7th May 2007, at the latest. Results received after this date will not be included in the statistical treatment, or in the Final Report. The laboratories are responsible for reporting their results to the Organiser. The Organiser will acknowledge receipt of the results by e-mail and the order of receipt of this Form will be recorded. Please note that you must include the laboratory code assigned to you on this Form.

Analytical Procedures Used (Form 3)

A brief summary of the analytical procedure(s) used is required from each laboratory on Form 3.

If more than one method has been used, please label each of them with different letters or codes in Form 2, and use as many copies of Form 3 as are needed (one for each method). Form 2 requires the confirmation method and Form 3 the determination method, please differentiate between them.

The Organiser must receive Form 3 by mail by 7th May 2007, at the latest. For this year, the time taken to submit Form 2 will not penalise the laboratory's classification, although the order of receipt will be recorded.

Please note that you must include the laboratory code assigned to you on this Form.

Advice on Sample Handling

Once received, the test material must be stored frozen until it is to be analysed.

Be sure to mix the contents of the bottle thoroughly, to ensure homogeneity of the test material, before taking the analytical portion(s).

Form 1

Laboratory Code: *EUPT-FV-LC1-Lab-* ☐

Date of receipt: ☐ */ /2007*

Test material code: *(Check both the blank bottle and the test material)*

EUPT-FV-LC1-blank- ☐ EUPT-FV-LC1-sample- ☐

Losses: YES ☐ NO ☐

Frozen: YES ☐ NO ☐

☒ I accept the test material. I do not need more.

Please, fill in this form and send it back by e-mail (pmedina@ual.es) as soon as you have received the test material, latest 13th April 2007.
If no Form1 is received by the Organiser, it will be assumed that the test material has been accepted by the laboratory.

Name:

Laboratories should fill in this form and send it to the following e-mail address: pmedina@ual.es

Form 2 (Results)

Laboratory Code: Date:
Test material and blank code:

Pesticide	Scope of your Method (1)	Analytical Procedure (2)	Conc. (mg/kg) (3)	Quantification Using Standards in Solvents or Matrix (4)	Confirmation Method (5)	RL (mg/kg) (6)	Recovery % (7)	Recovery (1 or 2) (8)
Acephate								
Acetamiprid								
Acrinathrin								
Azoxystrobin								
Bifenthrin								
Bromopropylate								
Carbaryl								
Chlorothalonil								
Chlorpyrifos								
Chlorpyrifos-methyl								
Cypermethrin								
Cyprodinil								
Deltamethrin								
Diazinon								
Demeton-S-Methyl								
Demeton-S-Methyl sulfone								
Dichlofluanid								
Dichlorvos								
Dicofol								
Dimethoate								
Fenhexamid								
Fenitrothion								
Fludioxonil								
Imazalil								
Imidacloprid								
Iprodione								
Kresoxim-methyl								
Lambda-cyhalothrin								
Methamidophos								
Monocrotophos								
Myclobutanil								
Omethoate								
Oxamyl								
Oxydemeton-methyl								
Parathion								
Pirimicarb								
Pirimiphos-methyl								
Prochloraz								
Procymidone								
Propiconazole								
Pyrimethanil								
Tebuconazole								
Tetraconazole								
Thiophanate-methyl								

Pesticide	Scope of your Method (1)	Analytical Procedure (2)	Conc. (mg/kg) (3)	Quantification Using Standards in Solvents or Matrix (4)	Confirmation Method (5)	RL (mg/kg) (6)	Recovery % (7)	Recovery (1 or 2) (8)
Tolylfluanid								
Vinclozolin								

(1) If the pesticide is not included in your analysis, put **NA**. If the pesticide is included in your scope (analysed) put **D.**
(2) Write codes (e.g. A, B, C…) for each analytical method used, the same as you will use in Form 3.
(3) Concentration determined in the sample (report only one result). **Record the concentrations for all pesticides and give individual contributions for parent compounds and transformation products when required.**
(4) Standards: **S** = standard/calibration in pure solvent, **M** = standard/calibration in matrix extract
(5) Give the confirmation technique used if any e.g. GC-FPD, HPLC-UV, GC-MS, LC-MS, LC-MS/MS
(6) RL Reporting Limit must be given for all pesticides.
(7) The concentration/results reported in **(3)** must not be corrected using recovery factors even if the laboratory usually corrects them. Nevertheless, you may give the correction factor for each pesticide as informative data.
(8) Write "1" if recoveries reported originated from experiments performed at the same time as the test and write "2" if recoveries reported have been originated from validation data.

I agree to be responsible for completing and returning this form to the Organizer latest 7th May 2007. In case of no e-mail confirmation of reception of this document (in 3 or 4 days), I will contact the Organiser as soon as possible.

Name:

Laboratories should fill in this form and send it to the following e-mail address: pmedina@ual.es

Form 3 (Analytical Procedures Used)

Laboratory Code: Date:

Complete one of these forms for every different analytical procedure used

Analytical Procedure **(1)**:_____

Sample Weight (g):_____

Extraction solvent/s **(2)**:_____

Cleanup step **(3)**:_____

Derivatization step (in any) **(4)**:_____

Internal standard (if any):_____

Injection Volume: _____ Injection Type: _____

Determination Technique **(5)**: _____

Reference Method (Obligatory):_____

Signature (only if the form is send by Fax or ordinary mail):

☐ I agree to be responsible for delivering this form to the Organizer. In case of no e-mail confirmation of receipt of this form (in 3 or 4 days), I will contact the Organizer as soon as possible.

Please return this Form not later than the 25th of September 2006

(1) Write the same code as you use in Form 2 for the analytical method used, e.g. A, B, C…

(2) Denoted as **1** = ethyl acetate, **2** = acetone followed by cyclohexane and ethyl acetone, **3** = acetone followed by dichloromethane, **4** = acetone followed by dichloromethane and petroleum ether, **5** = acetonitrile, **6** = methanol, **7** = other (specify which).

(3) **Clean-up:** GPC **= gel permeation chromatography,** SPE **= solid phase extraction,** LL **= liquid-liquid partition,** NO **= no clean-up,** O **= other clean-up method**

(4) **Derivatization step: e.g. Pentafluorobenzylbromide/Na_2CO_3**

(5) **Determination Technique: e.g.** GC-ECD, GC-NPD, GC-FPD, GC-MS (single-quad), GC-ITD, HPLC-FL, HPLC-UV, HPLC-DAD, LC-MS, LC-MS/MS **(specify the one used for each pesticide determination)**

Laboratories should fill-in this form and send it to the following e-mail: pmedina@ual.es

EUPT-FV-LC1 PESTICIDE LIST

Pesticide	MRRL* (mg/Kg)	Pesticide	MRRL* (mg/Kg)
Acephate	0.005	Imidacloprid (only parent compound)	0.005
Acetamiprid	0.005	Iprodione	0.005
Acrinathrin	0.005	Kresoxim-methyl	0.005
Azoxystrobin	0.005	Lambda-cyhalothrin	0.005
Bifenthrin	0.005	Methamidophos	0.005
Bromopropylate	0.005	Monocrotophos	0.005
Carbaryl	0.005	Myclobutanil	0.005
Chlorothalonil	0.005	Omethoate (expressed as Omethoate)	0.005
Chlorpyrifos	0.005	Oxamyl (expressed as Oxamyl)	0.005
Chlorpyrifos-methyl	0.005	Oxydemeton-methyl (expressed as Oxydemeton-methyl)	0.005
Cypermethrin	0.005	Parathion	0.005
Cyprodinil	0.005	Pirimicarb	0.005
Deltamethrin	0.005	Pirimiphos-methyl	0.005
Diazinon	0.005	Prochloraz	0.005
Demeton-S-Methyl (expressed as Demeton-S-Methyl)	0.005	Procymidone	0.005
Demeton-S-methyl sulfone (expressed as Demeton-S-Methyl sulfone)	0.005	Propiconazole	0.005
Dichlofluanid	0.005	Pyrimethanil	0.005
Dichlorvos	0.005	Tebuconazole	0.005
Dicofol	0.005	Tetraconazole	0.005
Dimethoate (expressed as Dimethoate)	0.005	Thiophanate-methyl	0.005
Fenhexamid	0.005	Tolylfluanid	0.005
Fenitrothion	0.005	Vinclozolin (only parent compound)	0.005
Fludioxonil	0.005		0.005
Imazalil	0.005		

* In order to avoid further confusion, the term Minimum Required Reporting Level (MRRL) is used consistently in this report to replace the terms Minimum Required Performance Level (MRPL), which was used in the text of previous reports, and Minimum Performance Reporting Level (MPRL), which was used in the possible pesticides list.

ANNEX 2. List of laboratories invited to participate in PT-FV-LC1.

COUNTRY	CITY	LABORATORY NAME	REPORTED RESULTS
AUSTRIA	INNSBRUCK	AUSTRIAN AGENCY FOR FOOD AND HEALTH SAFETY (AGES) ANALYTICAL COMPETENCE FOR PLANT PROTECTION PRODUCTS	YES
BELGIUM	ZWIJNAARDE	FYTOLAB	YES
BULGARY	SOFIA	CENTRAL LABORATORY FOR CHEMICAL TESTING AND CONTROL	YES
CYPRUS	NICOSIA	STATE GENERAL LABORATORY	YES
CZECH REPUBLIC	PRAHA 5	CZECH AGRICULTURE AND FOOD INSPECTION AUTHORITY	YES
FINLAND	ESPOO	FINNISH CUSTOMS LABORATORY	YES
FRANCE	MONTPELLIER	LABORATOIRE DU SCL DE MONTPELLIER	YES
GERMANY	HALLE/S.	LANDESAMT FUR VERBRAUCHERSCHUTZ	YES
GERMANY	ERLANGEN	BAYERISCHES LANDESAMT FÜR GESUNDHEIT UND LEBENSMITTELSICHERHEIT	YES
GERMANY	FELLBACH	CHEMISCHES UND VETERINÄRUNTERSUCHUNGSAMT (CVUA) STUTTGART	YES
GERMANY	BERLIN	FEDERAL OFFICE OF CONSUMER PROTECTION AND FOOD SAFETY (BVL)	NO
GERMANY	SAARBRÜCKEN	LSGV (LANDESAMT FÜR SOZIALES, GESUNDHEIT UND VERBRAUCHERSCHUTZ)	YES
GERMANY	DÜSSELDORF	39/2 CHEMISCHEN UND LEBENSMITTELUNTERSUCHUNG	YES
GERMANY	BIELEFELD	CHEMISCHES UND VETERINÄRUNTERSUCHUNGSAMT-OSTWESTFALEN-LIPPE (CVUA-OWL)	YES
GERMANY	NEUMÜENSTER	LANDESLABOR SCHLESWIG-HOLSTEIN	YES
GERMANY	OLDENBURG	LAVES LEBENSMITTELINSTITUT OLDENBURG	YES
GREECE	KIPHISSIA, ATHENS	PESTICIDE RESIDUES LABORATORY, BENAKI PHYTOPATHOLOGICAL INSTITUTE	YES
HUNGARY	MISKOLC	PESTICIDE RESIDUE ANALYTICAL LABORATORY	YES
IRELAND	CELBRIDGE, COUNTY KILDARE	PESTICIDE CONTROL LABORATORY. DEPARTMENT OF AGRICULTURE AND FOOD	YES
ITALY	ROMA	I.S.S. DIP. AMBIENTE E CONNESSA PREVENZIONE PRIMARIA	YES
LATVIA	RIGA	NATIONAL DIAGNOSTIC CENTRE	YES
POLAND	WARSAW	NATIONAL INSTITUTE OF HYGIENE ENVIROMENTAL TOXICOLOGICAL LABORATORY	NO
PORTUGAL	OEIRAS	PESTICIDE RESIDUE LABORATORY. DIRECÇÃO-GERAL DE PROTECÇÃO DAS CULTURAS.	YES
SLOVAKIA	BRATISLAVA	STATE VETERINARY AND FOOD INSTITUTE	YES
SPAIN	BURJASSOT (VALENCIA)	LABORATORIO AGROALIMENTARIO DE VALENCIA	YES
SPAIN	MAJADAHONDA (MADRID)	CENTRO NACIONAL DE ALIMENTACION	YES
SWEDEN	LIDKÖPING	LANTMÄNNEN ANALYCEN AB	YES
SWEDEN	UPPSALA	NATIONAL FOOD ADMINISTRATION, CHEMISTRY DIVISION 1	YES
THE NETHERLANDS	AMSTERDAM	VWA-FOOD AND CONSUMER PRODUCT SAFETY AUTHORITY	YES
UNITED KINGDOM	YORK	CENTRAL SCIENCE LABORATORY	YES