Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Report AQA 20-06 Pesticides in Fruit & Vegetables

October 2020

ACKNOWLEDGMENTS

This study was conducted by the National Measurement Institute (NMI). Support funding was provided by the Australian Government Department of Industry, Science, Energy and Resources.

I would like to thank the management and staff of the participating laboratories for supporting the study. It is only through widespread participation that we can provide an effective service to laboratories.

The assistance of the following NMI staff members in the planning, conduct and reporting of the study is acknowledged.

Jenny Xu

Geoff Morschel

Daniel Khaziran

Luke Baker

Raluca Iavetz

Manager, Chemical Reference Values

105 Delhi Rd, North Ryde, NSW 2113, Australia

Phone: +61 2 9449 0178

Email: raluca.iavetz@measurement.gov.au

Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

SUMMARY

AQA 20-06 Pesticides in Fruit & Vegetables commenced in May 2020. Twenty-two laboratories registered to participate, and all participants submitted results.

Four sets of test samples were prepared at the NMI laboratory in North Ryde, NSW. Samples were prepared by adding pesticide standard solutions to pureed tomatoes (Sample S1), celery (Sample S2), capsicums (Sample S3) and grapes (Sample S4).

Of a possible 352 results, 225 numeric results (64%) were submitted. Six results were a 'less than' value (<*x*) or Not Reported (NR), and 121 results were Not Tested (NT).

The assigned values for all scored analytes were the robust averages of participants' results. The associated uncertainties were estimated from the robust standard deviations of the participants' results.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

The outcomes of the study was assessed against the aims as follows:

- *Assess the ability of participants to correctly identify pesticides in fruit and vegetables*

Four laboratories did not report results for analytes that they tested for and were present in the test samples (total of 6 results).

Three laboratories reported analytes that were not spiked into the samples (total of 5 results).

Laboratories **3**, **6**, **7**, **11**, **14**, **15**, **18** and **21** reported results for all 15 scored analytes.

- *Compare the performances of participants and assess their accuracy in the measurement of pesticides in fruit and vegetables*

Of 213 results for which z-scores were calculated, 171 (80%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

Of 213 results for which E_n-scores were calculated, 158 (74%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **18** returned satisfactory z- and E_n-scores for all 15 scored analytes. Laboratory **15** returned satisfactory z-scores for all 15 analytes.

- *Evaluate the ability of participants to assess compliance of pesticides in fruit and vegetables against regulatory standards*

Six laboratories incorrectly identified or had a questionable identification of the compliance or non-compliance of pesticides with Australian maximum residue limits (total of 7 results).

- *Evaluate the participants' methods for the measurement of pesticides in fruit and vegetables*

Participants used a variety of methods, and no significant trends with any particular sample preparation method or instrumental technique was evident.

- *Develop the practical application of traceability and measurement uncertainty*

Of 225 numerical results, 204 (91%) were reported with an associated expanded measurement uncertainty. Laboratories **5**, **9**, **10**, **13**, **20** and **21** did not provide uncertainties for at least one reported result (including for analytes not spiked into the samples). The magnitude of the reported uncertainties for scored analytes was within the range 1% to 82% relative.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

The National Measurement Institute (NMI) is responsible for Australia's national measurement infrastructure, providing a range of services including a chemical proficiency testing program.

Proficiency testing (PT) is the: 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparison'.[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMI offers PT studies in:

- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- inorganic analytes in soil, water, food and pharmaceuticals;
- PFAS in soil, water and biota;
- controlled drug assay and clandestine laboratory; and
- allergens in food.

1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify pesticides in fruit and vegetables;
- compare the performances of participants and assess their accuracy in the measurement of pesticides in fruit and vegetables,
- evaluate the ability of participants to assess compliance of pesticides in fruit and vegetables against regulatory standards;
- evaluate the participants' methods for the measurement of pesticides in fruit and vegetables; and
- develop the practical application of traceability and measurement uncertainty.

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO/IEC 17043[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[4]

NMI is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes. This study is within the scope of NMI's accreditation.

2 STUDY INFORMATION

2.1 Selection of Pesticides and Matrices

A list of possible analytes for the samples in this study is presented in Table 1.

Table 1 List of Possible Analytes

2,4-D	Chlorfenvinphos	Dithiocarbamates	Linuron	Permethrin
Abamectin	Chlorothalonil	Endosulfan sulfate	Maldison	Pirimicarb
Acetamiprid	Chlorpyrifos	Fenamiphos	Metalaxyl	p,p'-DDT
alpha-Endosulfan	Clothianidin	Fenitrothion	Methamidophos	Procymidone
Azinphos-methyl	Cyfluthrin	Fenthion	Methidathion	Profenofos
Azoxystrobin	Cyhalothrin	Fenthion sulfone	Methomyl	Propargite
beta-Endosulfan	Cypermethrin	Fenthion sulfoxide	Methomyl oxime	Pyraclostrobin
Bifenazate	Cyprodinil	Fenvalerate	Mevinphos	Spinosad
Bifenthrin	Deltamethrin	Fludioxonil	Monocrotophos	Thiabendazole
Buprofezin	Diazinon	Imazalil	Omethoate	Triadimefon
Captan	Dicofol	Imidacloprid	Parathion	
Carbaryl	Dieldrin	Indoxacarb	Parathion methyl	
Carbendazim	Dimethoate	Iprodione	Penconazole	

The actual spiked values and Australian maximum residue limits (MRLs) are presented in Table 2. When selecting matrices and pesticides for this study, consideration was given to:

- a variety of pesticides amenable to both gas chromatography and liquid chromatography;
- a variety of matrices;
- the availability of matrix material with incurred analytes;
- feedback from participants;
- current Australian agricultural practice; and
- Australian MRLs promulgated in the Food Standards Code for Australia & New Zealand.[5]

Table 2 Spiked Values of Test Samples[5]

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty (mg/kg)[a]	MRL (mg/kg)[b]
S1 (Tomato)	Azoxystrobin	1.29	0.07	T1
	Endosulfan sulfate	0.791	0.040	-
	Methamidophos	0.946	0.047	2
	Permethrin	0.805	0.040	0.4[c]
S2 (Celery)	Chlorpyrifos	1.41	0.07	T5
	Imidacloprid	0.300	0.015	0.3[d]
	Linuron	0.111	0.006	*0.05[e]
	Permethrin	1.20	0.06	5[c]

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty (mg/kg)[a]	MRL (mg/kg)[b]
S3 (Capsicum)	Chlorpyrifos	0.200	0.010	T1
	Clothianidin	0.220	0.011	T0.7
	Methomyl	1.40	0.07	T2
	Pyraclostrobin	0.804	0.040	0.5
S4 (Grapes)	Acetamiprid	0.503	0.025	0.35
	Imidacloprid	0.101	0.005	1[d]
	Iprodione	1.81	0.09	20
	Pyraclostrobin	1.15	0.06	2

[a] Expanded uncertainty at 95% confidence interval using a coverage factor of 2.

[b] '*' indicates that the maximum residue limit is set at the limit of determination; 'T' indicates that the maximum residue limit is a temporary maximum residue limit.

[c] Sum of isomers.

[d] Sum of imidacloprid and metabolites containing the 6-chloropyridinylmethylene moiety.

[e] Sum of linuron plus 3,4-dichloroaniline.

2.2 Study Timetable

The timetable of the study was:

Invitation issued 27 May 2020

Samples dispatched 24 June 2020

Results due 11 August 2020

Interim report issued 14 August 2020

2.3 Participation

Twenty-two laboratories registered to participate, and all participants submitted results.

2.4 Laboratory Code

All participants were assigned a confidential laboratory code number.

2.5 Sample Preparation

Four test samples were prepared at NMI by adding pesticide standard solutions to pureed tomatoes (Sample S1), celery (Sample S2), capsicums (Sample S3) and grapes (Sample S4). Additional sample preparation details are provided in Appendix 1.

2.6 Homogeneity of Samples

These samples were prepared and packaged using a process that has been demonstrated to produce homogeneous samples for previous NMI Pesticides in Fruit & Vegetables PTs. No homogeneity testing was conducted for this study. The results of the study gave no reason to question the homogeneity of these samples.

2.7 Stability of Analytes

No stability testing was conducted for this study. Reports in the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) database,[6] together with previous use of these analytes in NMI PT studies, gave some assurance that the pesticides selected were stable in frozen fresh produce. To assess possible instability, the results returned by participants were compared to the spiked concentration. Robust averages for scored analytes were 80% to 104% of the spiked values, which gave no reason to question the stability of these pesticides.

2.8 Samples Storage and Dispatch

The test samples were stored in a freezer at approximately -20°C prior to dispatch. Participants were sent 100 g portions of both spiked and unspiked Samples S1, S2, S3 and S4. The samples were packaged into insulated polystyrene foam boxes with a cooler brick and dispatched by courier on 24 June 2020.

The following items were also sent to participants:

- a covering letter which included a description of the test samples and instructions for participants; and
- a form for participants to return to confirm receipt and condition of the test samples.

An Excel spreadsheet for the electronic reporting of results was e-mailed to participants.

2.9 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- The unspiked material need not be analysed, it is provided for participants to use if they wish.
- Participants need not test for all analytes listed.
- Please thaw and thoroughly mix the PT samples before analysis.
- For each analyte in each sample report a single result in mg/kg expressed as if reporting to a client (i.e. corrected for recovery or not, according to your standard procedure). This figure will be used in all statistical analysis in the study report.
- For each analyte in each sample report the associated expanded measurement uncertainty (e.g. 0.50 ± 0.02 mg/kg).
- Report any listed pesticide not tested as NT.
- Do not correct results for any pesticide found in the unspiked sample.
- No limit of reporting has been set for this study. Report results as you would to a client, applying the limit of reporting of the method used for analysis.
- Report the basis of your uncertainty estimates (e.g. uncertainty budget, repeatability precision, long term result variability).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by e-mail (proficiency@measurement.gov.au).
- Please return completed result sheet by 21 July 2020. Late results may not be included in the study report.

The results due date was later extended to 11 August 2020 due to delays with sample delivery.

2.10 Interim Report

An interim report was e-mailed to all participants on 14 August 2020.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses are presented in Appendix 2. The study coordinator thanks participants for completing the methodology questionnaire.

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about their basis of measurement uncertainty (MU). Responses are presented in Table 3.

Table 3 Basis of MU Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Standard purity	NATA Technical Note 33
2	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	EU SANTE/12682/2019: Analytical Quality Control and method Validation Procedures for Pesticide Residues Analysis in Food and Feed
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS Duplicate analysis	Recoveries of SS	SANTE/11813/2017
4	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Recoveries of SS Standard purity	Eurolab Technical Report No1/2007
5	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
6	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide
7	Top Down - reproducibility (standard deviation) from PT studies used directly	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
8	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS Standard purity	EU No. SANTE 12862-2019: ANALYTICAL QUALITY CONTROL AND METHOD VALIDATION PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED
9		Standard deviation from PT studies only		

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
10	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
11	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
12	Top Down - precision and estimates of the method and laboratory bias			ISO/GUM
13	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	CRM Recoveries of SS Standard purity	NATA Technical Note 33
14	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Recoveries of SS	NMI Uncertainty Course
15	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS Duplicate analysis	Recoveries of SS	NATA Technical Note 33
16	Horwitz formula	Control samples - SS Duplicate analysis	CRM Recoveries of SS Standard purity	NMI Uncertainty Course
17	Top Down - precision and estimates of the method and laboratory bias	Instrument calibration	Laboratory bias from PT studies Recoveries of SS Standard purity	
18	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		NATA Technical Note 33
19	Standard deviation of replicate analyses multiplied by 2 or 3	Standard deviation from PT studies only		
		Duplicate analysis	Recoveries of SS Standard purity	
20	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
21	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
22	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Recoveries of SS Standard purity	SANTE 12682/2019

* CRM = Certified Reference Material; RM = Reference Material; SS = Spiked Samples

3.3 Participants' Comments

Participants were invited to make any comments on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments, and the study coordinator's response (if applicable) are presented in Table 4.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
5	S1	Bifenthrin is not under laboratory scope	
	S4	No detection for all active ingredients tested by laboratory.	
	All	Keep it up	Thank you.
6	S4	Clothianidin detected in the Blank sample 0.09mg/kg and Azoxystrobin also detected trace level in blank.	
7	S2	Celery had too much water content, it's difficult to sample the sample for analysis.	A range of matrices are chosen to cater for the needs and requests of different laboratories. The samples are processed so that they are homogeneous.
	S3	Capsicum had too much water content, it's difficult to sample the sample for analysis.	
	S4	Clothianidin had incurred in sample blank.	
8	All	The concentration of residue reported is an average of two determinations made on the same sample. The unspiked sample was also analysed and found to have no residues at or above the Limit of Quantitation (LOQ) at 0.01 mg/kg. The reported uncertainty of result is an expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%. This PT is important for the reliability and assessment of our laboratory's results, and also for compliance in accreditation. We would like to suggest PT studies for pesticide residues in other sample matrices such as rice, banana, pineapple, mango and water. Uncertainty: The reported uncertainty of result is an expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%.	NMI currently runs a Pesticides in Water PT study annually. The other matrix suggestions will be taken into consideration when planning future pesticide PT studies.
9	All	ND=Tested but Not Detected, NT=Not tested	
13	S4	The unspiked S4 sample contained 0.01 azoxystrobin and 0.11 clothianidin	
14	S4	Clothiandin (incurred) S4 Unspiked: 0.13 mg/kg and S4 Spiked: 0.12 mg/kg Chlorantrilipole (Incurred) S4 Unspiked:0.011 mg/kg and S4 Spiked: 0.011 mg/kg. Dithiocarbamates (incurred) S4 Unspiked:0.12 mg/kg and S4 Spiked: 0.13 mg/kg.	
16	S1	Note methamidophos is corrected for recovery as known to lose analyte in water phase of method.	
	S4	Note Clothianidin present in blank grape at same level as S4, note trace level chlorpyrifos in blank & Spiked sample at around 0.005 mg/kg, below laboratory LOR	
18	S4	Nearly same level of concentraion of Clothianidin found in both unspiked and spiked sample.	
21	All	Samples found to have high residue were further diluted to 50X, and 100X.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 20 with summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max.), minimum (Min.), robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV).

Bar charts of results and performance scores are presented in Figures 2 to 17.

An example chart with interpretation guide is shown in Figure 1.

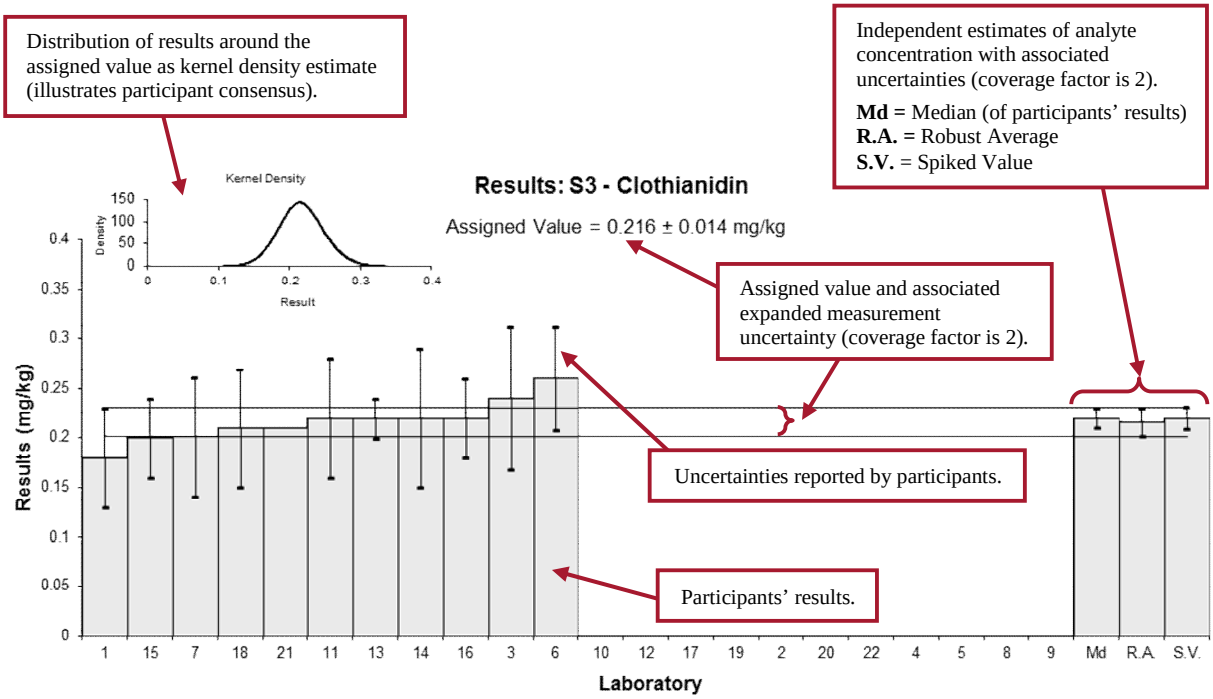


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

The assigned value is defined as the: 'value attributed to a particular property of a proficiency test item'.[1] In this PT study, the property is the mass fraction of the analytes in the samples. Assigned values in this study were the robust averages of participants' results and the expanded uncertainties were estimated from the associated robust SDs (Appendix 3).

4.3 Robust Average and Robust Between Laboratory Coefficient of Variation

The robust averages and associated expanded MUs, and robust CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528:2015.[7]

4.4 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between laboratories variation that in the judgement of the study coordinator would be expected from participants given levels of analytes present. It is important to note that this is a performance measure set by the study coordinator; it is not the robust CV of participants' results. The PCV is based on the mass fraction of the analytes and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[8] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on the other participants' performance and can be compared from study to study.

4.5 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (X) and the PCV, as presented in Equation 1.

$$\sigma = X \times PCV \qquad \textit{Equation 1}$$

This value is used for calculation of participant z-score.

4.6 z-Score

For each participant result, a z-score is calculated according to Equation 2.

$$z = \frac{(\chi - X)}{\sigma} \qquad \textit{Equation 2}$$

where:

z is z-score

χ is a participant's result

X is the assigned value

σ is the target standard deviation from Equation 1

For a z-score with absolute value (|z|):

- $|z| \leq 2.0$ is satisfactory;
- $2.0 < |z| < 3.0$ is questionable; and
- $|z| \geq 3.0$ is unsatisfactory.

4.7 E_n-Score

The E_n-score is complementary to the z-score in assessment of laboratory performance. E_n-score includes measurement uncertainty and is calculated according to Equation 3.

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}} \qquad \textit{Equation 3}$$

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded measurement uncertainty of the participant's result

U_X is the expanded measurement uncertainty of the assigned value

For an E_n-score with absolute value ($|E_n|$):

- $|E_n| \leq 1.0$ is satisfactory; and
- $|E_n| > 1.0$ is unsatisfactory.

4.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025:2017 must establish and demonstrate the traceability and measurement uncertainty associated with their test results.[9]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[10]

5 TABLES AND FIGURES

Table 5

Sample Details

Sample No.	S1
Matrix	Tomato
Analyte	Azoxystrobin
Units	mg/kg

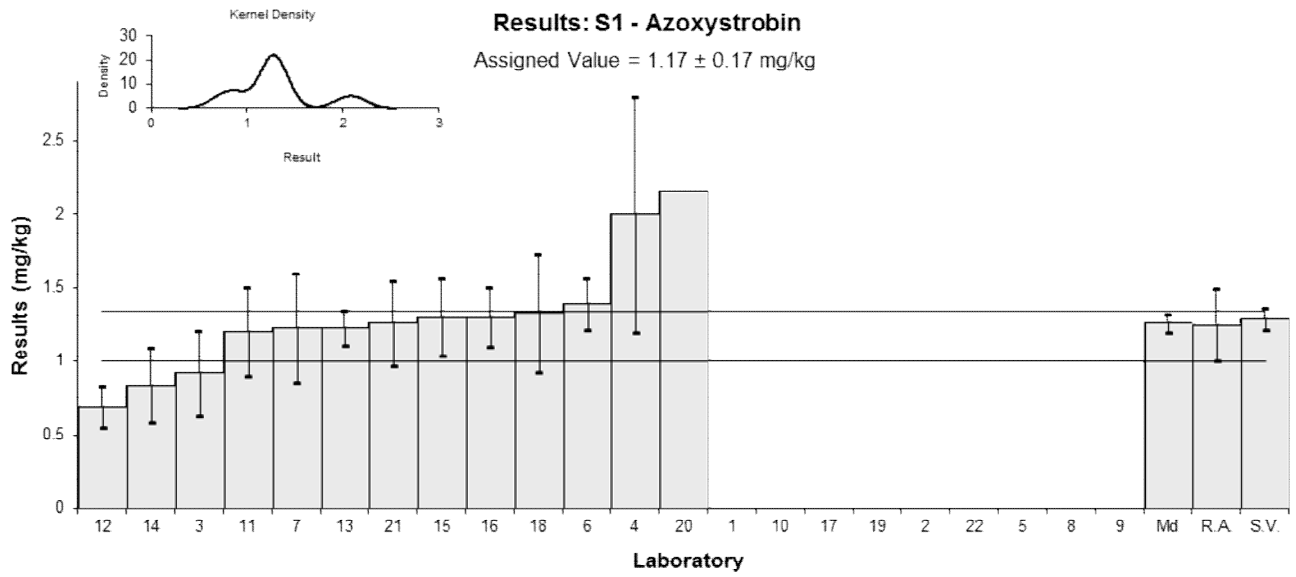
Participant Results

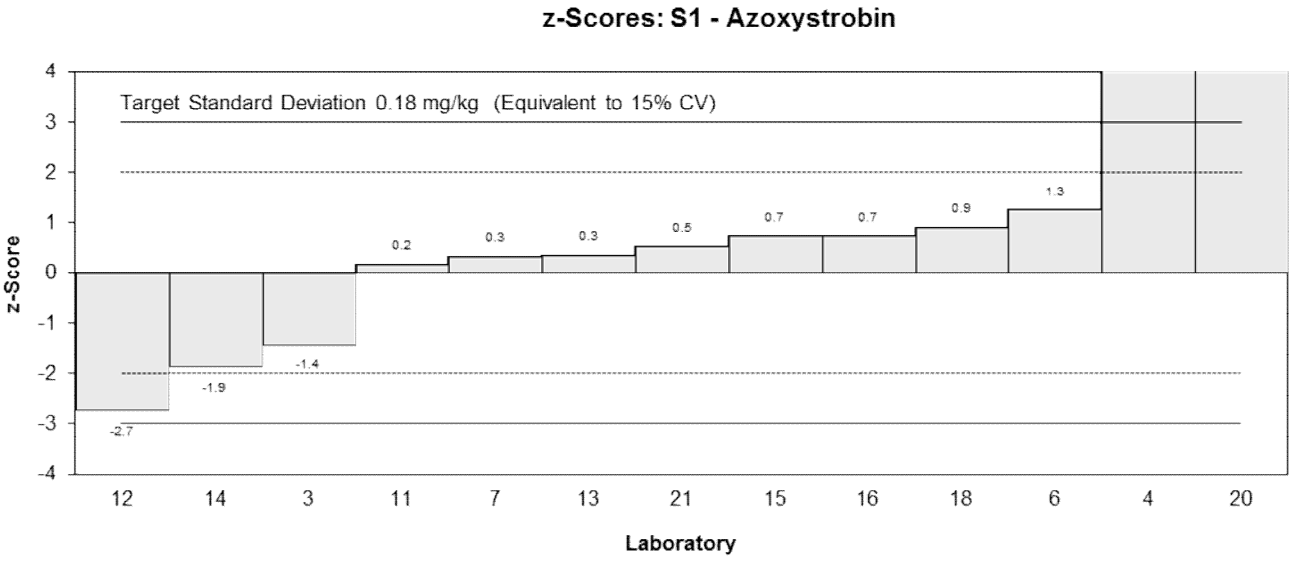
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	0.92	0.29	97	-1.42	-0.74
4	2.0	0.8	NR	4.73	1.01
5	NT	NT	NT		
6	1.39	0.17	113	1.25	0.92
7	1.227	0.368	98	0.32	0.14
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	1.20	0.30	NR	0.17	0.09
12	0.69	0.14	NR	-2.74	-2.18
13	1.23	0.12	111	0.34	0.29
14	0.84	0.252	110	-1.88	-1.09
15	1.3	0.26	NR	0.74	0.42
16	1.3	0.2	96	0.74	0.50
17	NT	NT	NT		
18	1.33	0.40	99.6	0.91	0.37
19	NT	NT	NT		
20	2.16	NR	109	5.64	5.82
21	1.261	0.286	76	0.52	0.27
22	NT	NT	NT		

Statistics

Assigned Value*	1.17	0.17
Spike	1.29	0.07
Robust Average	1.25	0.24
Median	1.26	0.06
Mean	1.30	
N	13	
Max.	2.16	
Min.	0.69	
Robust SD	0.35	
Robust CV	28%	

* Robust average excluding Laboratories 4 and 20.


Kernel Density
Density
Result
Results: S1 - Azoxystrobin
Assigned Value = 1.17 ± 0.17 mg/kg
Results (mg/kg)
Laboratory
12 14 3 11 7 13 21 15 16 18 6 4 20 1 10 17 19 2 22 5 8 9 Md R.A. S.V.


z-Scores: S1 - Azoxystrobin
Target Standard Deviation 0.18 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 14 3 11 7 13 21 15 16 18 6 4 20
-2.7
-1.9
-1.4
0.2
0.3
0.3
0.5
0.7
0.7
0.9
1.3

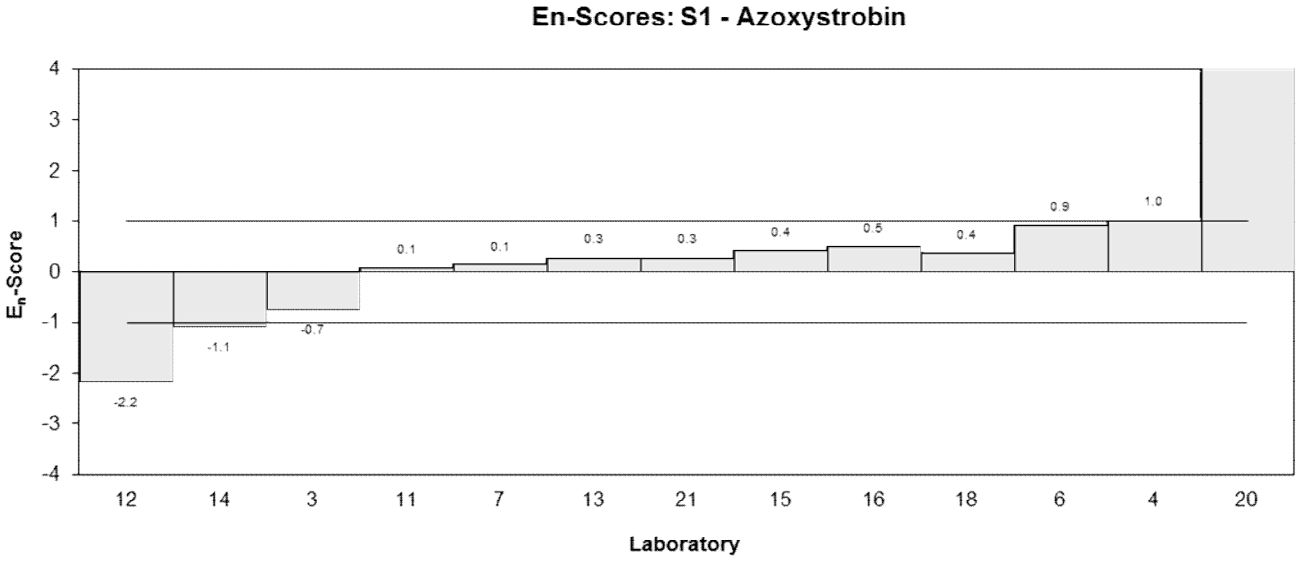

En-Scores: S1 - Azoxystrobin
En-Score
Laboratory
12 14 3 11 7 13 21 15 16 18 6 4 20
-2.2
-1.1
-0.7
0.1
0.1
0.3
0.3
0.4
0.5
0.4
0.9
1.0

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix	Tomato
Analyte	Endosulfan sulfate
Units	mg/kg

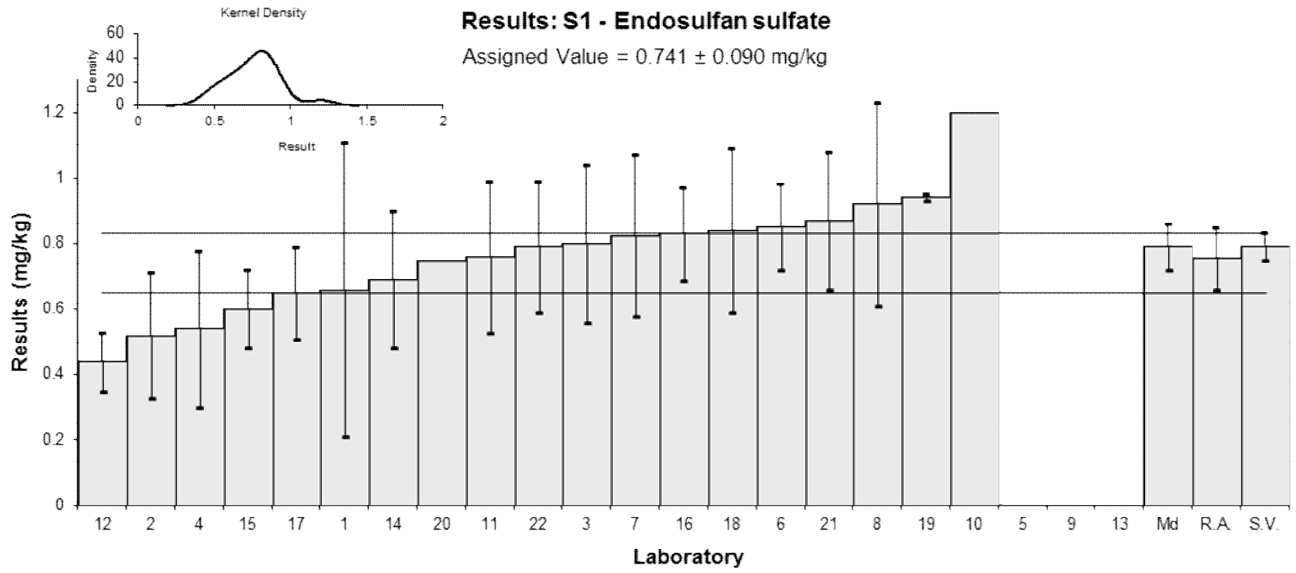
Participant Results

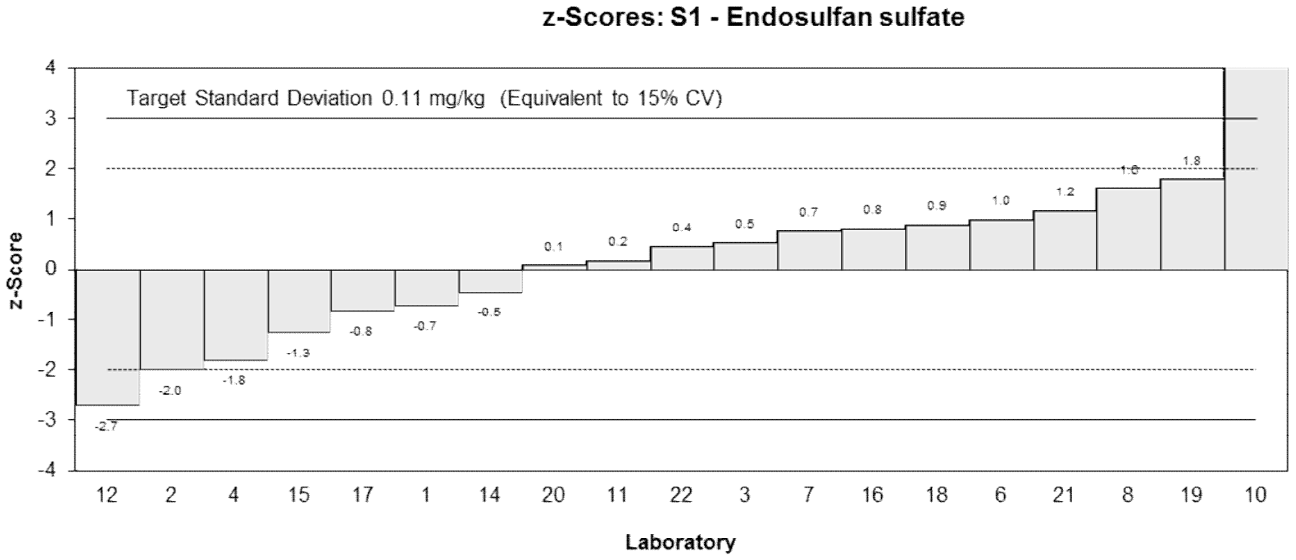
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.66	0.45	103	-0.73	-0.18
2	0.52	0.19	90	-1.99	-1.05
3	0.80	0.24	101	0.53	0.23
4	0.54	0.24	NR	-1.81	-0.78
5	NR	NR	NR		
6	0.85	0.13	80	0.98	0.69
7	0.824	0.247	88	0.75	0.32
8	0.92	0.31	93.49	1.61	0.55
9	NR	NR	NR		
10	1.2	NR	90	4.13	5.10
11	0.76	0.23	NR	0.17	0.08
12	0.44	0.09	NR	-2.71	-2.36
13	NT	NT	NT		
14	0.69	0.21	95	-0.46	-0.22
15	0.6	0.12	NR	-1.27	-0.94
16	0.83	0.14	89	0.80	0.53
17	0.65	0.14	97	-0.82	-0.55
18	0.84	0.25	94	0.89	0.37
19	0.94	0.01	NR	1.79	2.20
20	0.75	NR	96	0.08	0.10
21	0.87	0.209	88	1.16	0.57
22	0.79	0.2	68	0.44	0.22

Statistics

Assigned Value*	0.741	0.090
Spike	0.791	0.040
Robust Average	0.755	0.094
Median	0.790	0.071
Mean	0.762	
N	19	
Max.	1.2	
Min.	0.44	
Robust SD	0.16	
Robust CV	22%	

* Robust average excluding Laboratory 10.


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 0.741 ± 0.090 mg/kg
Results (mg/kg)
Laboratory
12 2 4 15 17 1 14 20 11 22 3 7 16 18 6 21 8 19 10 5 9 13 Md R.A. S.V.


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation 0.11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 2 4 15 17 1 14 20 11 22 3 7 16 18 6 21 8 19 10

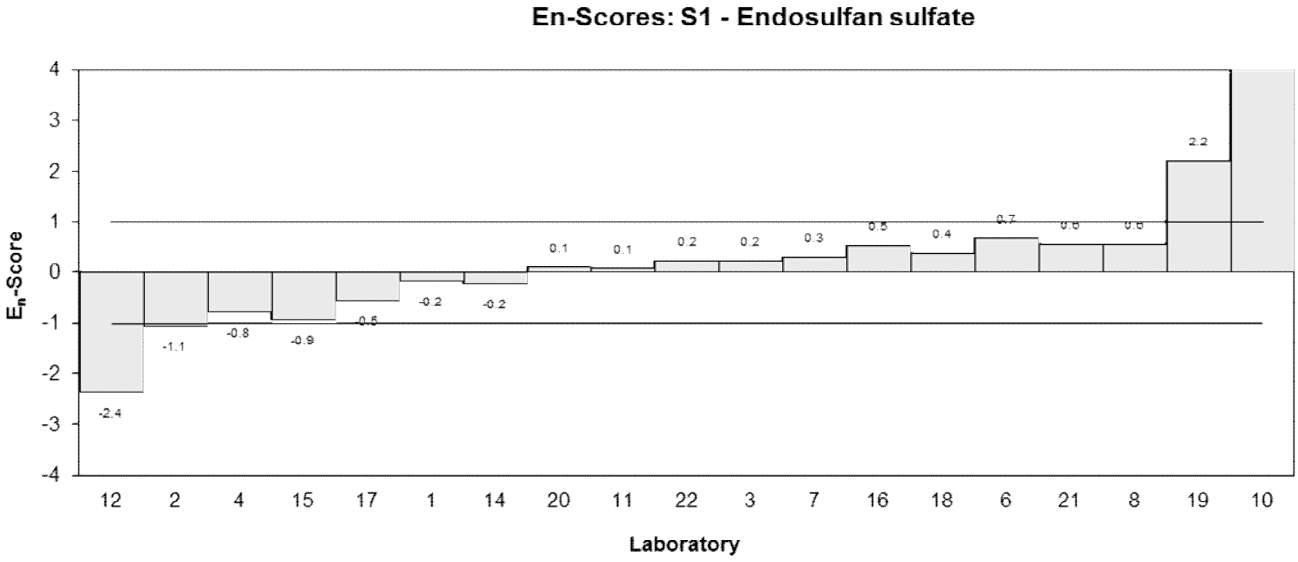

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
12 2 4 15 17 1 14 20 11 22 3 7 16 18 6 21 8 19 10

Figure 3

Table 7

Sample Details

Sample No.	S1
Matrix	Tomato
Analyte	Methamidophos
Units	mg/kg

Participant Results

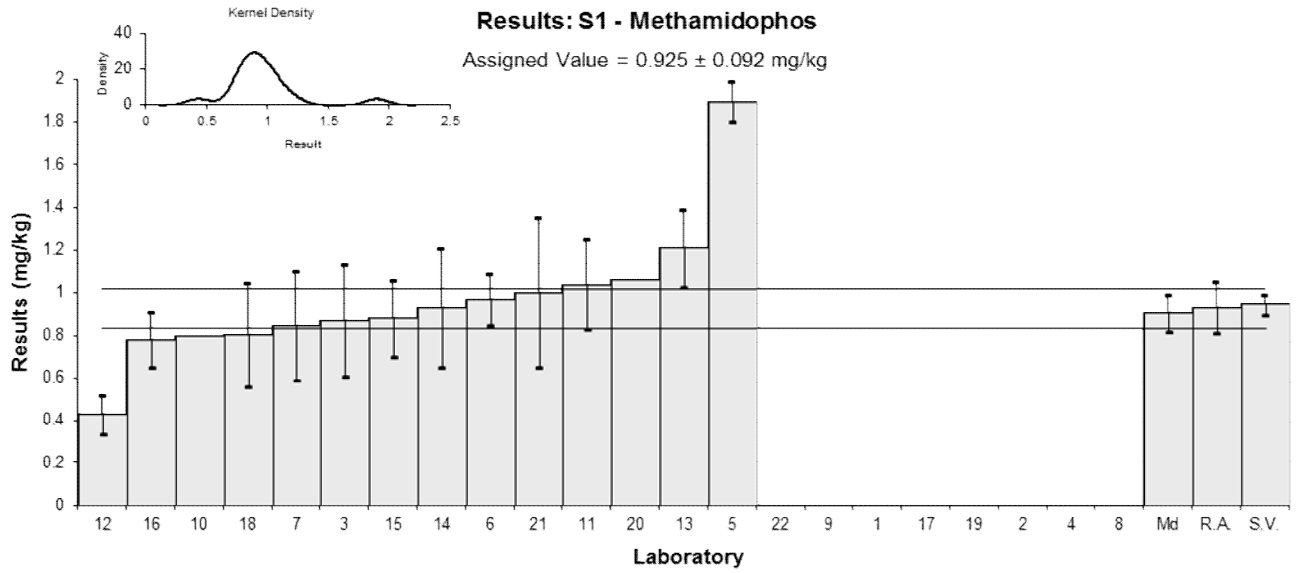
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	0.87	0.26	96	-0.40	-0.20
4	NT	NT	NT		
5	1.897	0.091	101.45	7.01	7.51
6	0.97	0.12	90	0.32	0.30
7	0.845	0.254	80	-0.58	-0.30
8	NT	NT	NT		
9	NR	NR	NR		
10	0.8	NR	70	-0.90	-1.36
11	1.04	0.21	NR	0.83	0.50
12	0.43	0.09	NR	-3.57	-3.85
13	1.21	0.18	116	2.05	1.41
14	0.93	0.28	90	0.04	0.02
15	0.88	0.18	NR	-0.32	-0.22
16	0.78	0.13	61	-1.05	-0.91
17	NT	NT	NT		
18	0.804	0.241	75	-0.87	-0.47
19	NT	NT	NT		
20	1.06	NR	101	0.97	1.47
21	1.001	0.35	59	0.55	0.21
22	<LOQ	NR	NR		

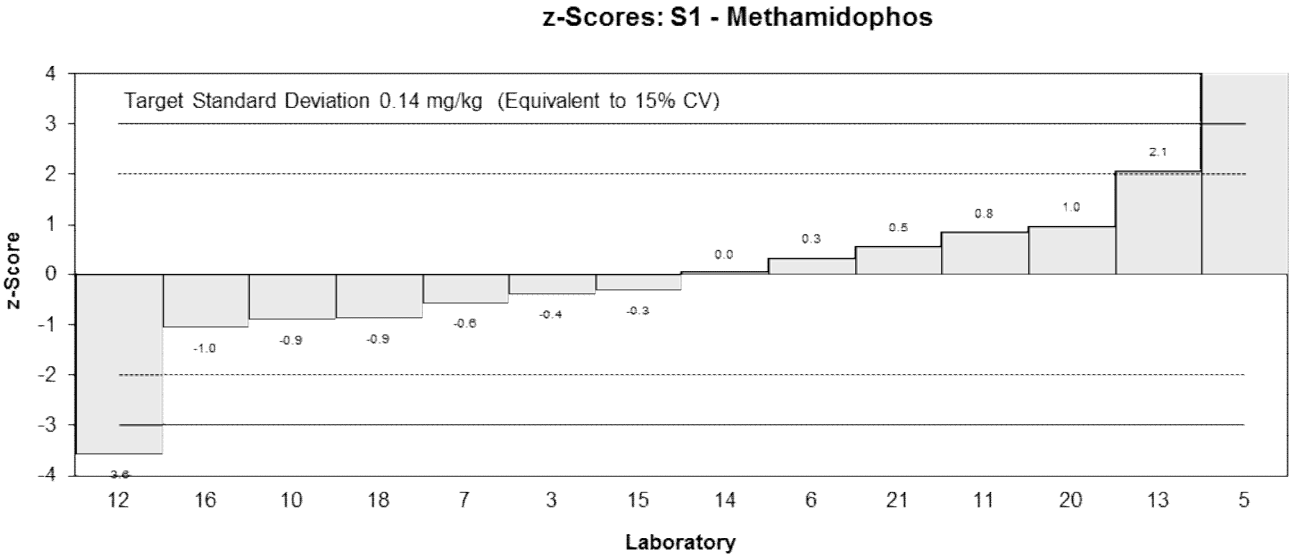
Statistics

Assigned Value*	0.925	0.092
Spike	0.946	0.047
Robust Average	0.93	0.12
Median	0.905	0.088
Mean	0.966	
N	14	
Max.	1.897	
Min.	0.43	
Robust SD	0.18	
Robust CV	19%	

* Robust average excluding Laboratories 5 and 12.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S1 - Methamidophos
Assigned Value = 0.925 ± 0.092 mg/kg
Results (mg/kg)
Laboratory
12 16 10 18 7 3 15 14 6 21 11 20 13 5 22 9 1 17 19 2 4 8 Md R.A. S.V.


z-Scores: S1 - Methamidophos
Target Standard Deviation 0.14 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 16 10 18 7 3 15 14 6 21 11 20 13 5
-3.6 -1.0 -0.9 -0.9 -0.6 -0.4 -0.3 0.0 0.3 0.5 0.8 1.0 2.1

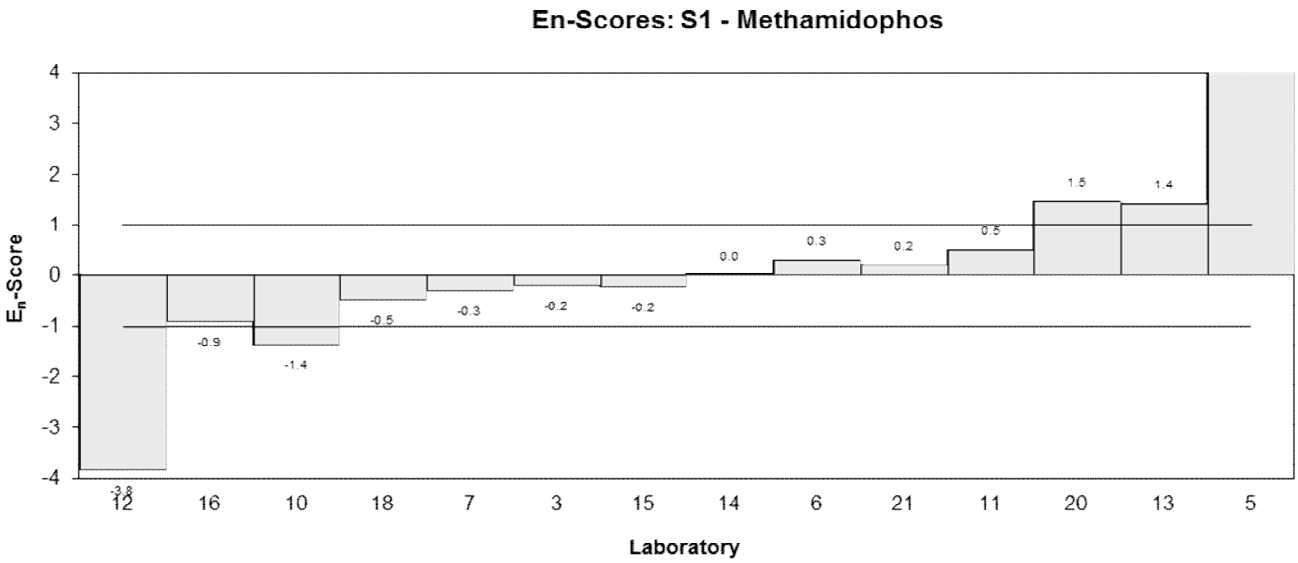

En-Scores: S1 - Methamidophos
En-Score
Laboratory
12 16 10 18 7 3 15 14 6 21 11 20 13 5
-3.8 -0.9 -1.4 -0.5 -0.3 -0.2 -0.2 0.0 0.3 0.2 0.5 1.5 1.4

Figure 4

Table 8

Sample Details

Sample No.	S1
Matrix	Tomato
Analyte	Permethrin
Units	mg/kg

Participant Results

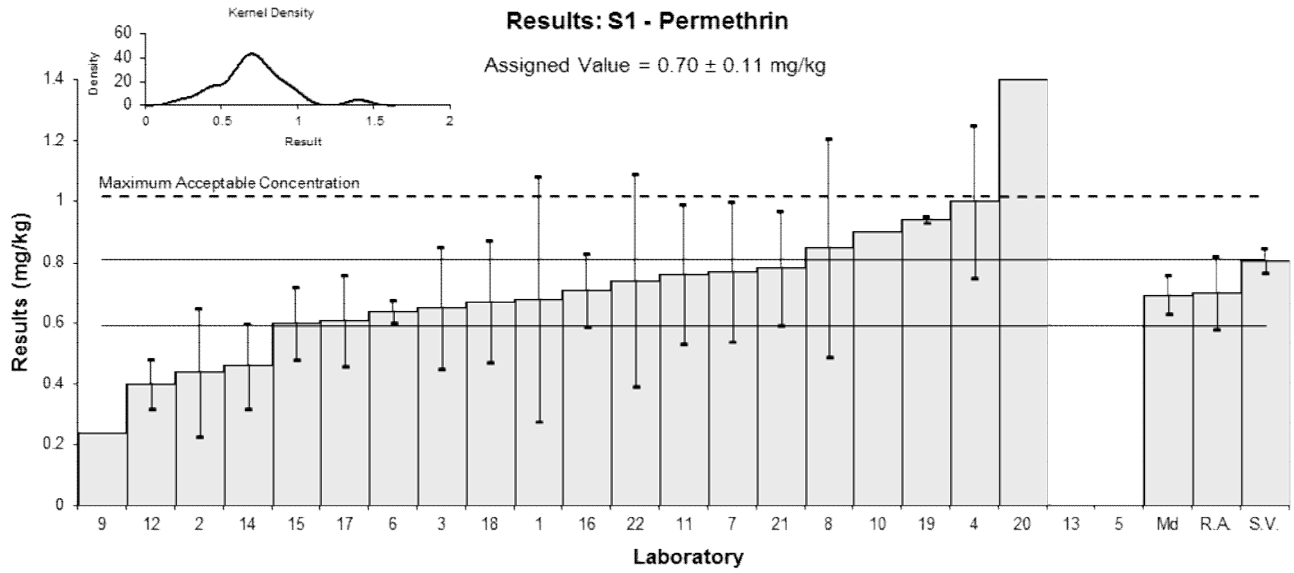
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.68	0.4	117	-0.19	-0.05
2	0.44	0.21	76	-2.48	-1.10
3	0.65	0.20	100	-0.48	-0.22
4**	1.0	0.25	NR	2.00	1.00
5	NT	NT	NT		
6	0.64	0.037	93	-0.57	-0.52
7	0.768	0.230	104	0.65	0.27
8	0.85	0.36	101.73	1.43	0.40
9	0.24	NR	NR	-4.38	-4.18
10	0.9	NR	101	1.90	1.82
11	0.76	0.23	NR	0.57	0.24
12	0.40	0.08	NR	-2.86	-2.21
13	NT	NT	NT		
14	0.46	0.14	95	-2.29	-1.35
15	0.6	0.12	NR	-0.95	-0.61
16	0.71	0.12	102	0.10	0.06
17	0.61	0.15	93	-0.86	-0.48
18	0.67	0.20	125	-0.29	-0.13
19**	0.94	0.01	NR	2.00	1.00
20	1.4	NR	66	6.67	6.36
21	0.78	0.187	97	0.76	0.37
22	0.74	0.35	72	0.38	0.11

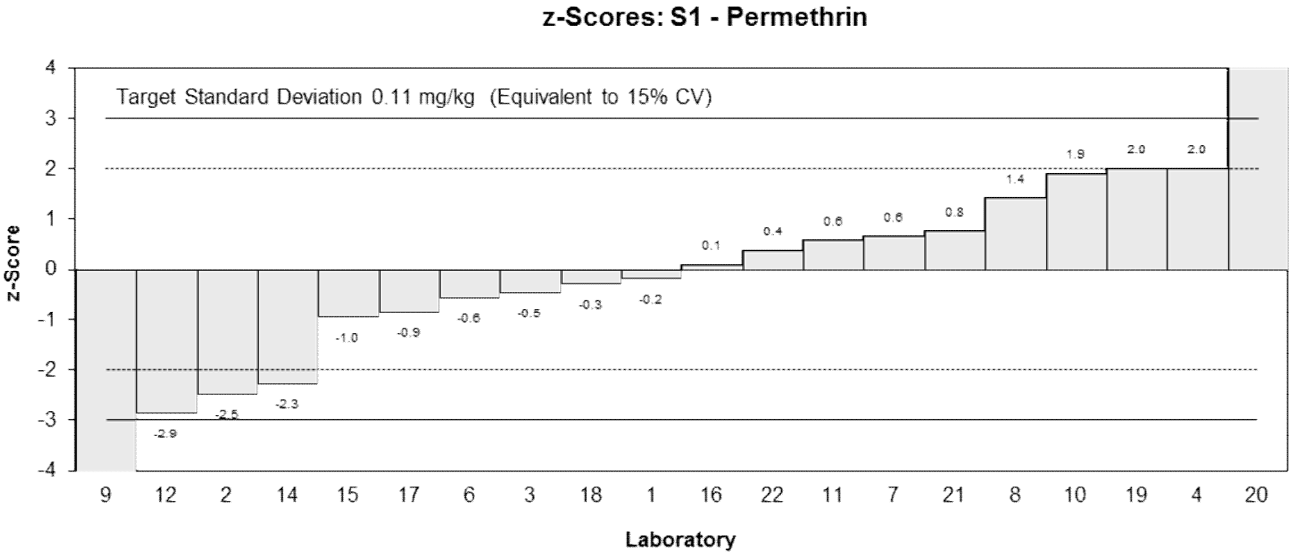
Statistics

Assigned Value*	0.70	0.11
Spike	0.805	0.040
Max. Acceptable Conc.**	1.02	
Robust Average	0.70	0.12
Median	0.695	0.062
Mean	0.712	
N	20	
Max.	1.4	
Min.	0.24	
Robust SD	0.21	
Robust CV	30%	

* Robust average excluding Laboratories 9 and 20.

** z-Score adjusted to 2.00 (see Section 6.3).


Results: S1 - Permethrin
Assigned Value = 0.70 ± 0.11 mg/kg
Kernel Density
Density
Result
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
9 12 2 14 15 17 6 3 18 1 16 22 11 7 21 8 10 19 4 20 13 5 Md R.A. S.V.


z-Scores: S1 - Permethrin
Target Standard Deviation 0.11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
9 12 2 14 15 17 6 3 18 1 16 22 11 7 21 8 10 19 4 20
-2.9 -2.5 -2.3 -1.0 -0.9 -0.6 -0.5 -0.3 -0.2 0.1 0.4 0.6 0.6 0.8 1.4 1.9 2.0 2.0

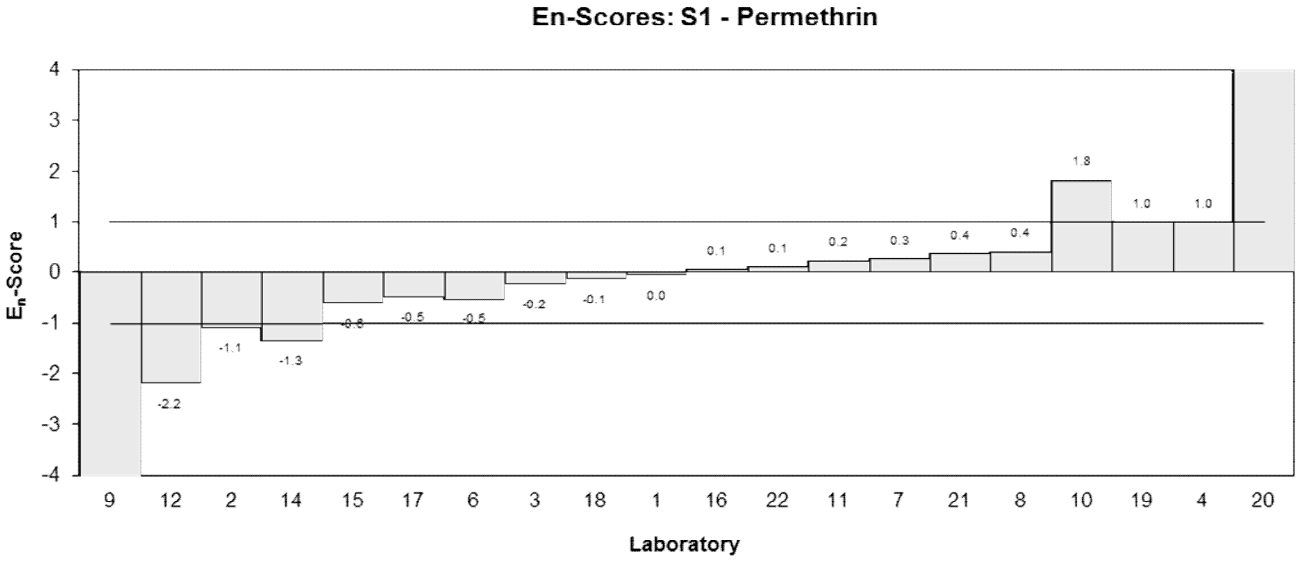

En-Scores: S1 - Permethrin
En-Score
Laboratory
9 12 2 14 15 17 6 3 18 1 16 22 11 7 21 8 10 19 4 20
-2.2 -1.1 -1.3 -0.6 -0.5 -0.5 -0.2 -0.1 0.0 0.1 0.1 0.2 0.3 0.4 0.4 1.8 1.0 1.0

Figure 5

Table 9

Sample Details

Sample No.	S2
Matrix	Celery
Analyte	Chlorpyrifos
Units	mg/kg

Participant Results

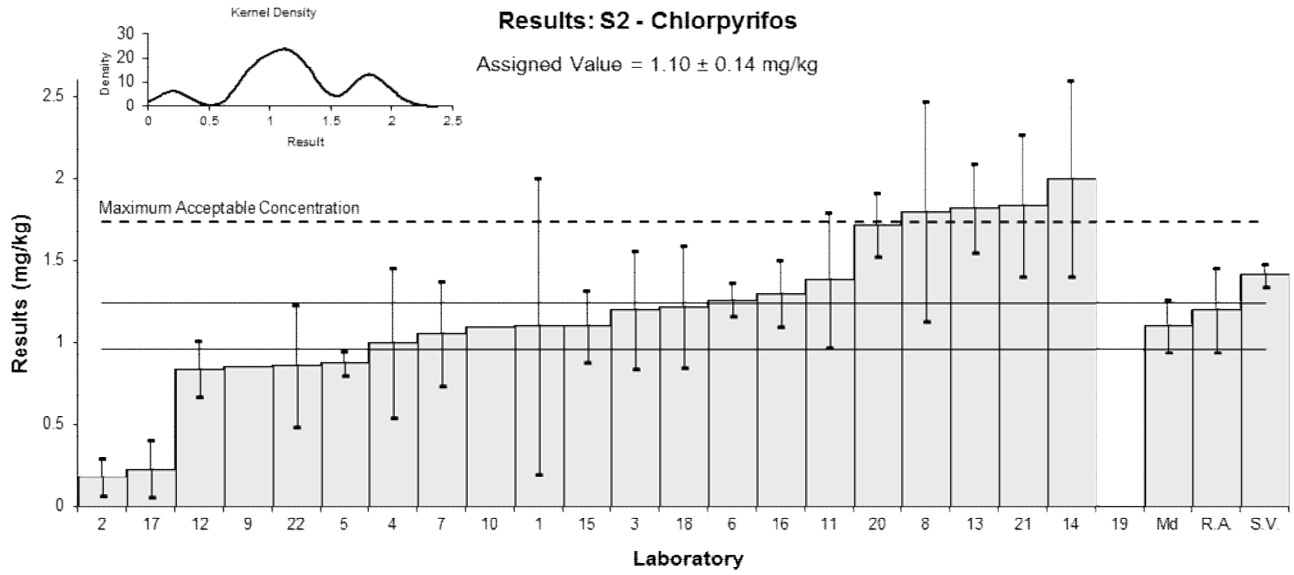
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.1	0.9	95	0.00	0.00
2	0.18	0.11	70	-5.58	-5.17
3	1.2	0.36	103	0.61	0.26
4	1.0	0.46	NR	-0.61	-0.21
5	0.873	0.073	82.51	-1.38	-1.44
6	1.26	0.10	96	0.97	0.93
7	1.057	0.317	100	-0.26	-0.12
8	1.8	0.67	67.41	4.24	1.02
9	0.85	NR	NR	-1.52	-1.79
10	1.09	NR	74	-0.06	-0.07
11	1.38	0.41	NR	1.70	0.65
12	0.84	0.17	NR	-1.58	-1.18
13	1.82	0.27	99	4.36	2.37
14	2.0	0.60	90	5.45	1.46
15	1.1	0.22	NR	0.00	0.00
16	1.3	0.2	96	1.21	0.82
17	0.23	0.17	60	-5.27	-3.95
18	1.22	0.37	103	0.73	0.30
19	NT	NT	NT		
20**	1.72	0.19	102	2.00	1.00
21	1.835	0.434	87	4.45	1.61
22	0.86	0.37	81	-1.45	-0.61

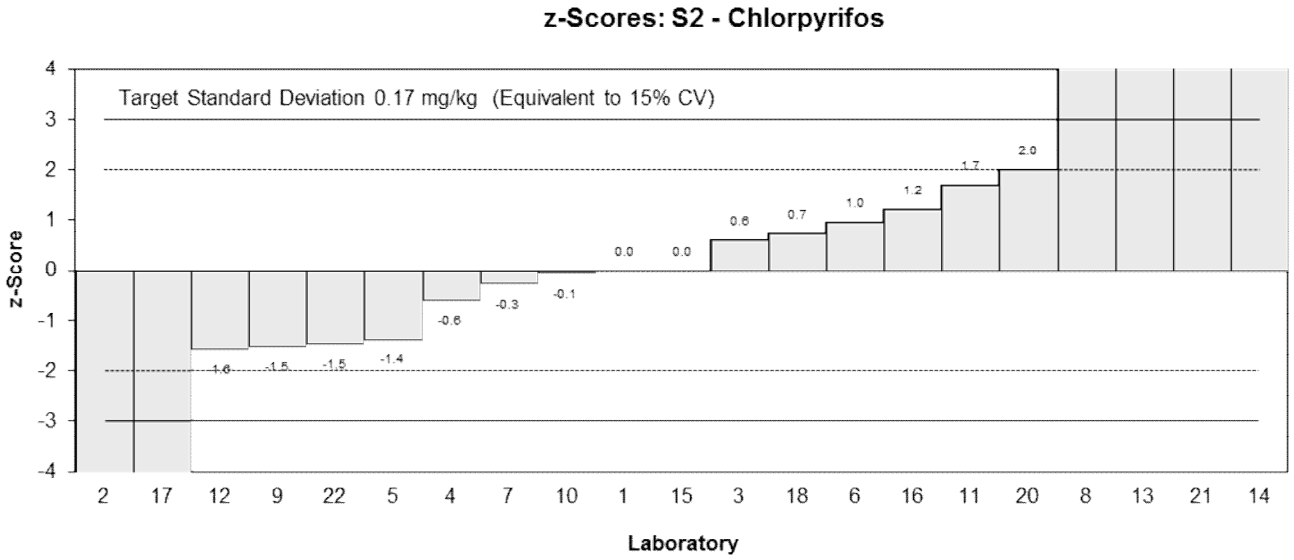
Statistics

Assigned Value*	1.10	0.14
Spike	1.41	0.07
Max. Acceptable Conc.**	1.74	
Robust Average	1.20	0.26
Median	1.10	0.16
Mean	1.18	
N	21	
Max.	2.0	
Min.	0.18	
Robust SD	0.48	
Robust CV	40%	

* Robust average excluding laboratories 2, 8, 13, 14, 17 and 21.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - Chlorpyrifos
Assigned Value = 1.10 ± 0.14 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
2 17 12 9 22 5 4 7 10 1 15 3 18 6 16 11 20 8 13 21 14 19 Md R.A. S.V.


z-Scores: S2 - Chlorpyrifos
Target Standard Deviation 0.17 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
2 17 12 9 22 5 4 7 10 1 15 3 18 6 16 11 20 8 13 21 14

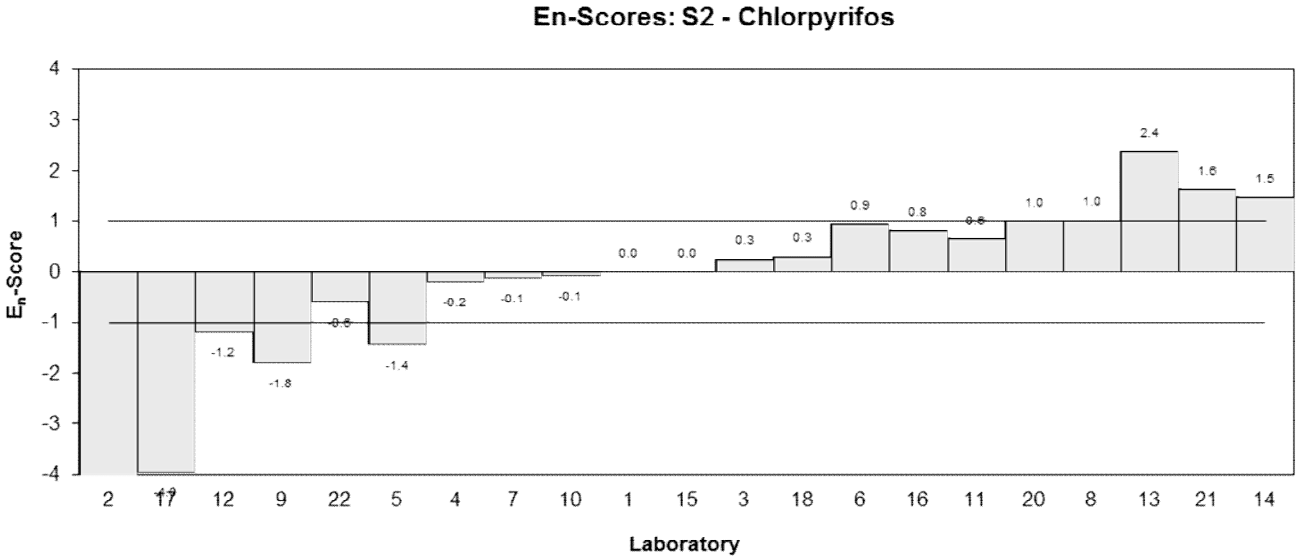

En-Scores: S2 - Chlorpyrifos
En-Score
Laboratory
2 17 12 9 22 5 4 7 10 1 15 3 18 6 16 11 20 8 13 21 14

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix	Celery
Analyte	Imidacloprid
Units	mg/kg

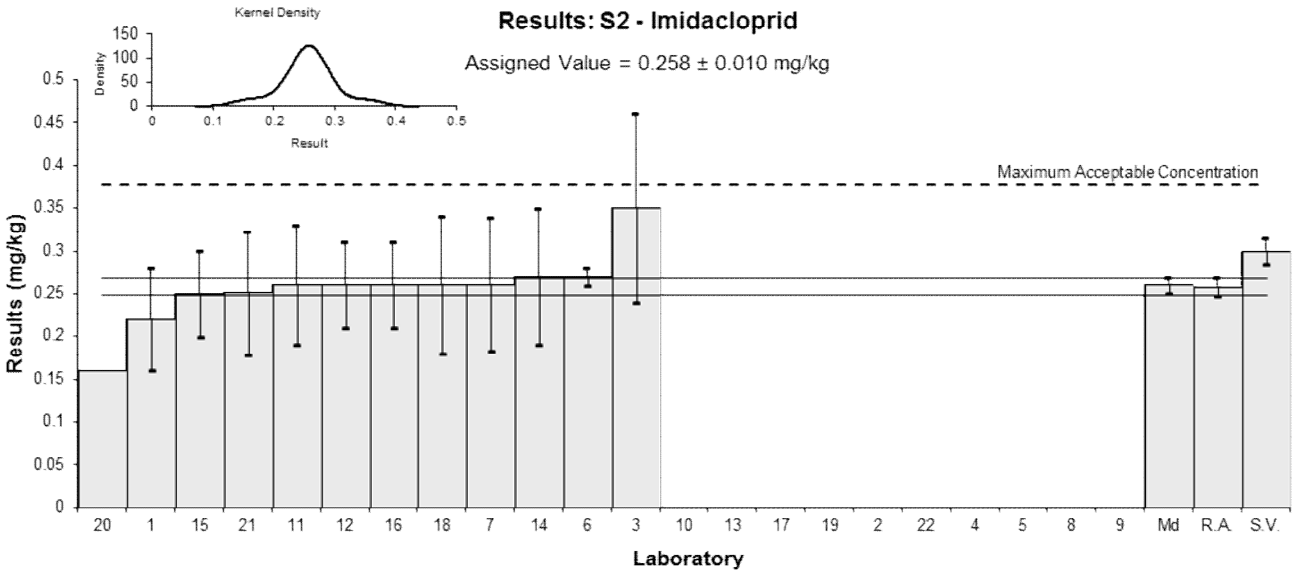
Participant Results

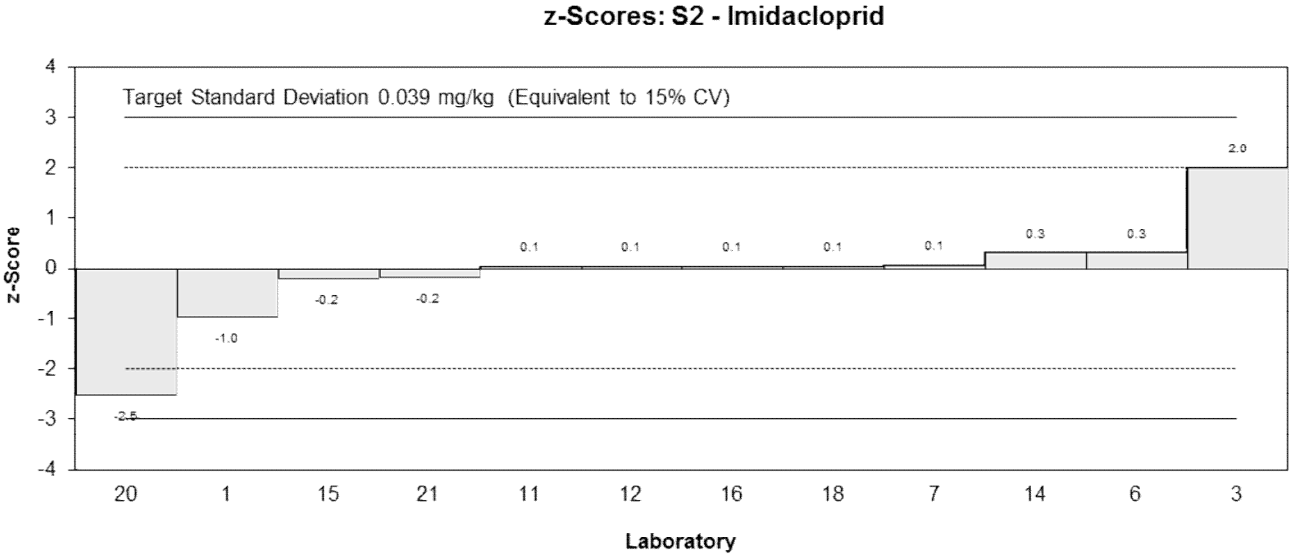
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.22	0.06	88	-0.98	-0.62
2	NT	NT	NT		
3*	0.35	0.11	113	2.00	0.83
4	NT	NT	NT		
5	NT	NT	NT		
6	0.27	0.01	95	0.31	0.85
7	0.261	0.078	97	0.08	0.04
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	0.26	0.07	NR	0.05	0.03
12	0.26	0.05	NR	0.05	0.04
13	NT	NT	NT		
14	0.27	0.08	111	0.31	0.15
15	0.25	0.05	NR	-0.21	-0.16
16	0.26	0.05	96	0.05	0.04
17	NT	NT	NT		
18	0.26	0.08	92	0.05	0.02
19	NT	NT	NT		
20	0.16	NR	112	-2.53	-9.80
21	0.251	0.072	84	-0.18	-0.10
22	NT	NT	NT		

Statistics

Assigned Value	0.258	0.010
Spike	0.300	0.015
Max. Acceptable Conc.*	0.38	
Robust Average	0.258	0.010
Median	0.260	0.009
Mean	0.256	
N	12	
Max.	0.35	
Min.	0.16	
Robust SD	0.014	
Robust CV	5.4%	

* z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - Imidacloprid
Assigned Value = 0.258 ± 0.010 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
20 1 15 21 11 12 16 18 7 14 6 3 10 13 17 19 2 22 4 5 8 9 Md R.A. S.V.


z-Scores: S2 - Imidacloprid
Target Standard Deviation 0.039 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
20 1 15 21 11 12 16 18 7 14 6 3

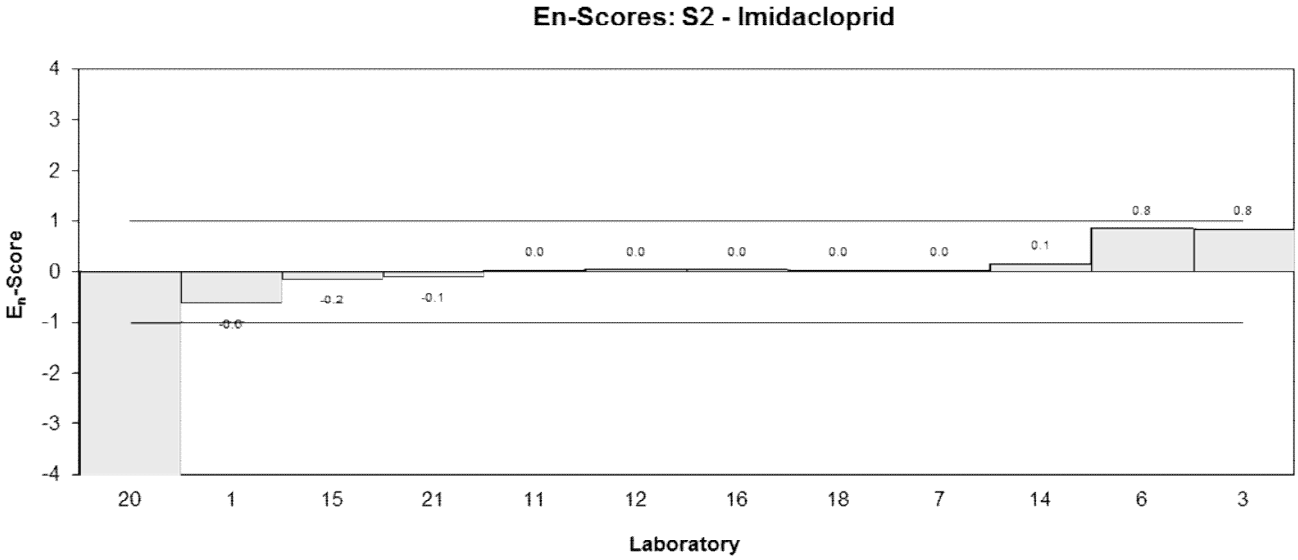

En-Scores: S2 - Imidacloprid
En-Score
Laboratory
20 1 15 21 11 12 16 18 7 14 6 3

Figure 7

Table 11

Sample Details

Sample No.	S2
Matrix	Celery
Analyte	Linuron
Units	mg/kg

Participant Results

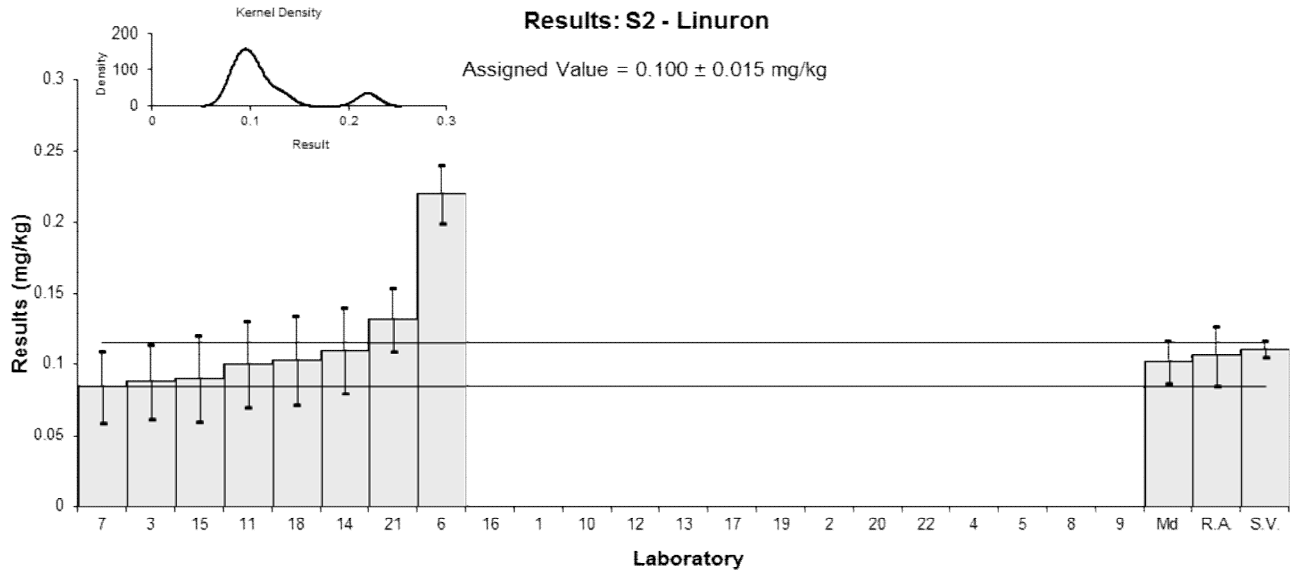
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	0.088	0.026	86	-0.80	-0.40
4	NT	NT	NT		
5	NT	NT	NT		
6	0.22	0.02	90	8.00	4.80
7	0.0844	0.025	83	-1.04	-0.54
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	0.10	0.03	NR	0.00	0.00
12	NT	NT	NT		
13	NT	NT	NT		
14	0.11	0.03	113	0.67	0.30
15	0.09	0.03	NR	-0.67	-0.30
16	NR	NR	NR		
17	NT	NT	NT		
18	0.103	0.031	73	0.20	0.09
19	NT	NT	NT		
20	NT	NT	NT		
21	0.132	0.022	65	2.13	1.20
22	NT	NT	NT		

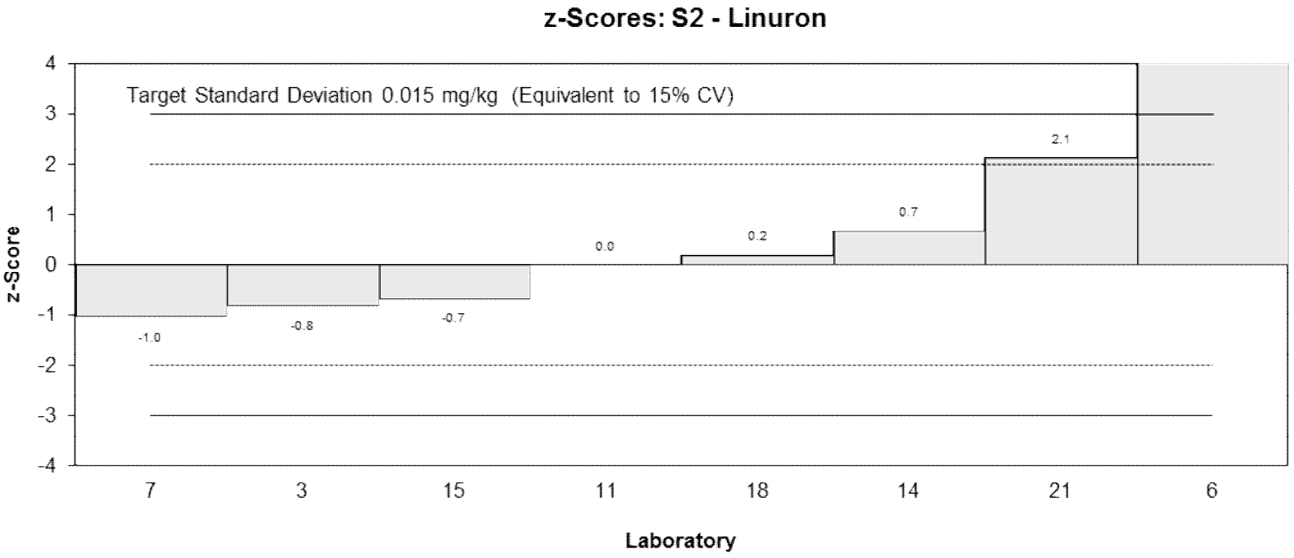
Statistics

Assigned Value*	0.100	0.015
Spike	0.111	0.006
Robust Average	0.106	0.021
Median	0.102	0.015
Mean	0.116	
N	8	
Max.	0.22	
Min.	0.0844	
Robust SD	0.024	
Robust CV	22%	

* Robust average excluding Laboratory 6.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - Linuron
Assigned Value = 0.100 ± 0.015 mg/kg
Results (mg/kg)
Laboratory
7 3 15 11 18 14 21 6 16 1 10 12 13 17 19 2 20 22 4 5 8 9 Md R.A. S.V.


z-Scores: S2 - Linuron
Target Standard Deviation 0.015 mg/kg (Equivalent to 15% CV)
z-Score
-1.0
-0.8
-0.7
0.0
0.2
0.7
2.1
Laboratory
7 3 15 11 18 14 21 6

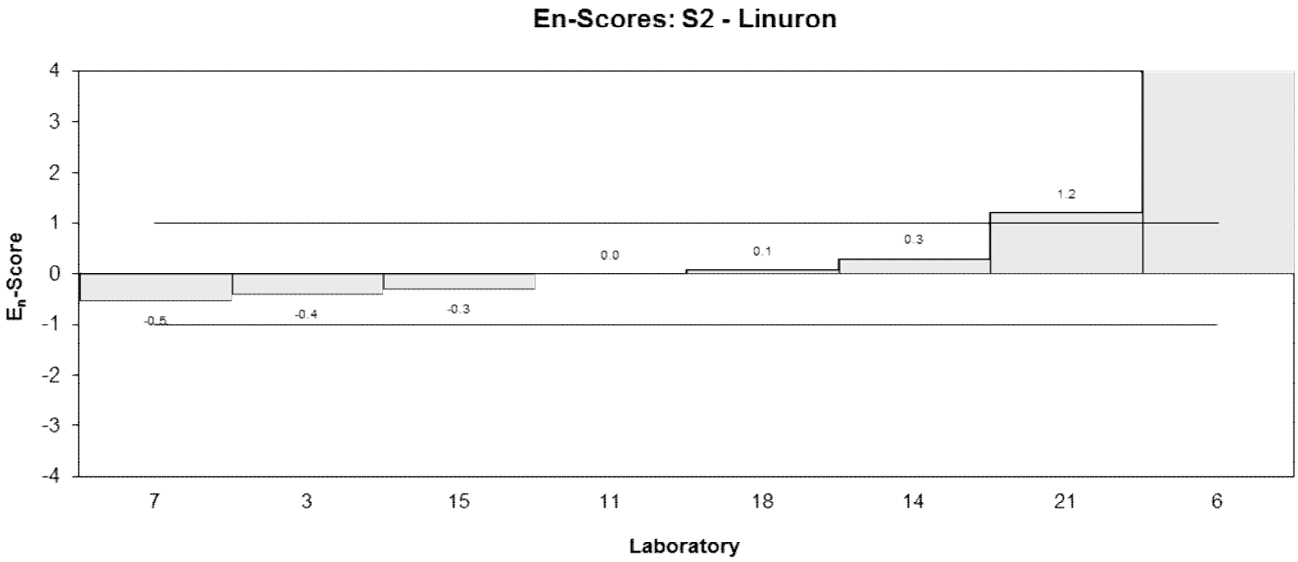

En-Scores: S2 - Linuron
En-Score
-0.5
-0.4
-0.3
0.0
0.1
0.3
1.2
Laboratory
7 3 15 11 18 14 21 6

Figure 8

Table 12

Sample Details

Sample No.	S2
Matrix	Celery
Analyte	Permethrin
Units	mg/kg

Participant Results

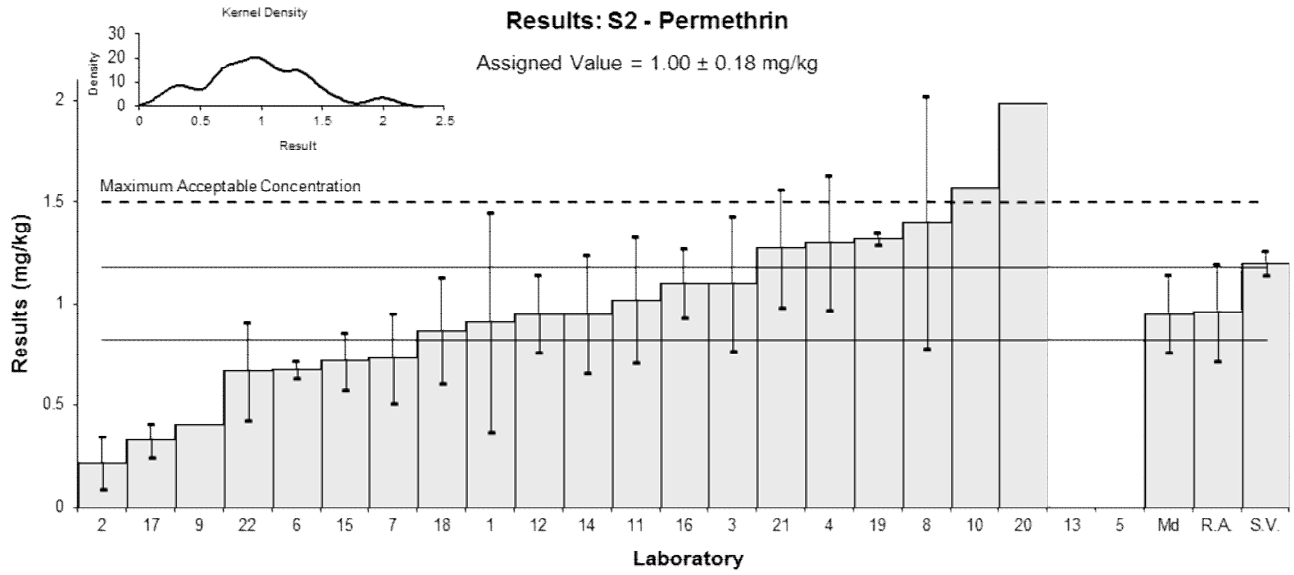
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.91	0.54	122	-0.60	-0.16
2	0.22	0.13	63	-5.20	-3.51
3	1.1	0.33	103	0.67	0.27
4	1.3	0.33	NR	2.00	0.80
5	NT	NT	NT		
6	0.68	0.04	96	-2.13	-1.74
7	0.732	0.220	116	-1.79	-0.94
8**	1.4	0.62	101.73	2.00	0.62
9	0.41	NR	NR	-3.93	-3.28
10	1.57	NR	101	3.80	3.17
11	1.02	0.31	NR	0.13	0.06
12	0.95	0.19	NR	-0.33	-0.19
13	NT	NT	NT		
14	0.95	0.29	93	-0.33	-0.15
15	0.72	0.14	NR	-1.87	-1.23
16	1.1	0.17	96	0.67	0.40
17	0.33	0.08	81	-4.47	-3.40
18	0.87	0.26	115	-0.87	-0.41
19**	1.32	0.03	NR	2.00	1.00
20	1.99	NR	66	6.60	5.50
21	1.273	0.288	83	1.82	0.80
22	0.67	0.24	90	-2.20	-1.10

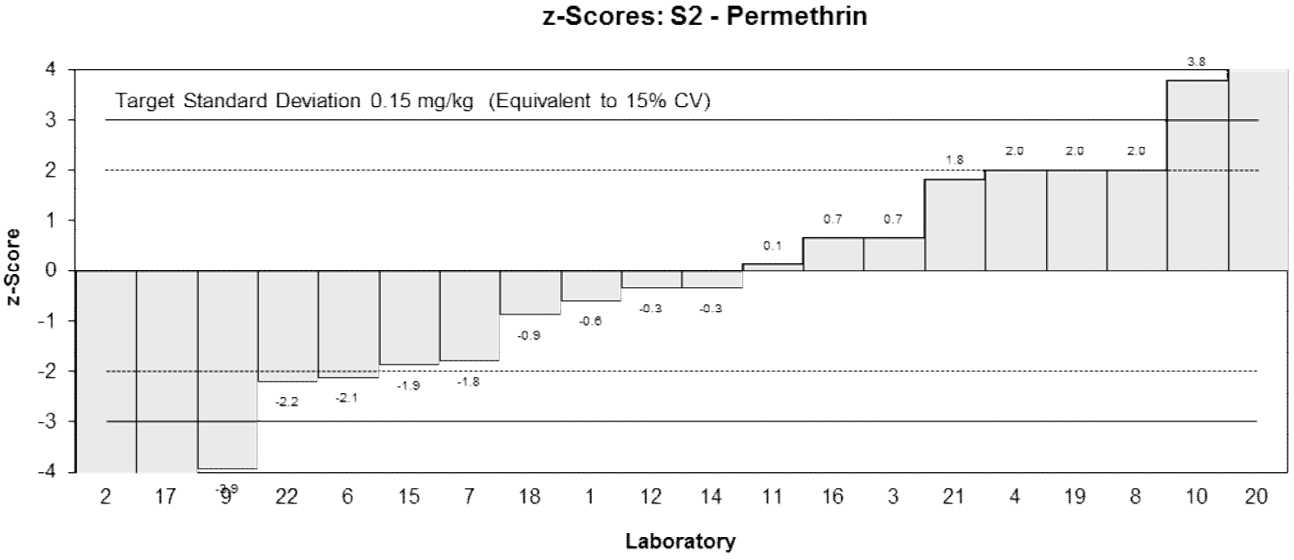
Statistics

Assigned Value*	1.00	0.18
Spike	1.20	0.06
Max. Acceptable Conc.**	1.5	
Robust Average	0.96	0.24
Median	0.95	0.19
Mean	0.98	
N	20	
Max.	1.99	
Min.	0.22	
Robust SD	0.43	
Robust CV	45%	

* Robust average excluding Laboratories 2, 9, 10, 17 and 20.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - Permethrin
Assigned Value = 1.00 ± 0.18 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
2 17 9 22 6 15 7 18 1 12 14 11 16 3 21 4 19 8 10 20 13 5 Md R.A. S.V.


z-Scores: S2 - Permethrin
Target Standard Deviation 0.15 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
2 17 9 22 6 15 7 18 1 12 14 11 16 3 21 4 19 8 10 20

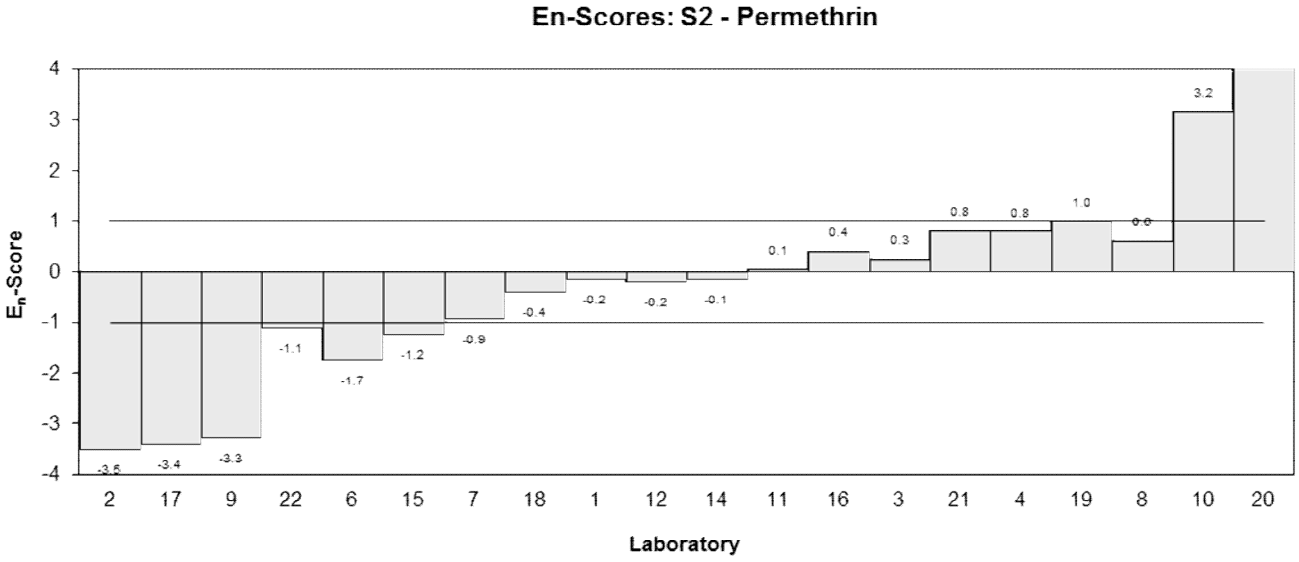

En-Scores: S2 - Permethrin
En-Score
Laboratory
2 17 9 22 6 15 7 18 1 12 14 11 16 3 21 4 19 8 10 20

Figure 9

Table 13

Sample Details

Sample No.	S3
Matrix	Capsicum
Analyte	Chlorpyrifos
Units	mg/kg

Participant Results

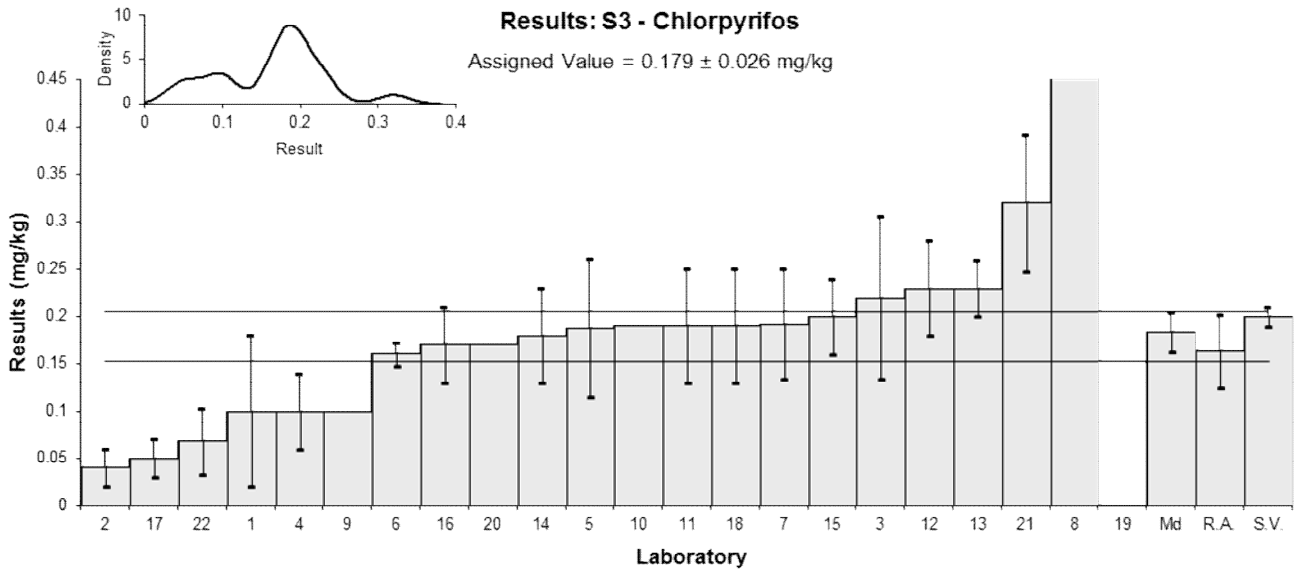
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.10	0.08	90	-2.94	-0.94
2	0.04	0.02	92	-5.18	-4.24
3	0.22	0.086	76	1.53	0.46
4	0.10	0.04	NR	-2.94	-1.66
5	0.188	0.073	82.51	0.34	0.12
6	0.16	0.012	94	-0.71	-0.66
7	0.192	0.058	113	0.48	0.20
8	3.1	1.1	67.41	108.79	2.65
9	0.1	NR	NR	-2.94	-3.04
10	0.19	NR	74	0.41	0.42
11	0.19	0.06	NR	0.41	0.17
12	0.23	0.05	NR	1.90	0.90
13	0.23	0.03	99	1.90	1.28
14	0.18	0.05	91	0.04	0.02
15	0.2	0.04	NR	0.78	0.44
16	0.17	0.04	98	-0.34	-0.19
17	0.05	0.02	81	-4.80	-3.93
18	0.19	0.06	87	0.41	0.17
19	NT	NT	NT		
20	0.17	NR	102	-0.34	-0.35
21	0.32	0.072	109	5.25	1.84
22	0.068	0.035	80	-4.13	-2.55

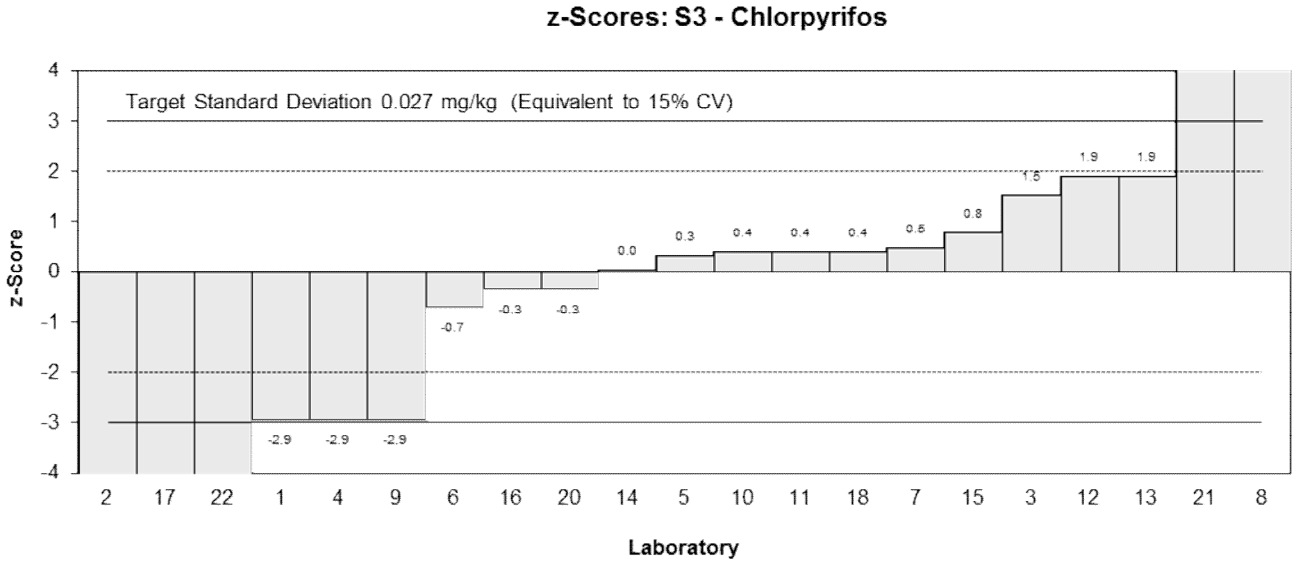
Statistics*

Assigned Value**	0.179	0.026
Spike	0.200	0.010
Robust Average	0.163	0.039
Median	0.184	0.021
Mean	0.164	
N	20	
Max.	0.32	
Min.	0.04	
Robust SD	0.069	
Robust CV	42%	

* Result from Laboratory 8 was omitted from all statistical calculations.

** Robust average excluding Laboratories 2, 17, 21 and 22.


Results: S3 - Chlorpyrifos
Assigned Value = 0.179 ± 0.026 mg/kg
Density
Result
Results (mg/kg)
Laboratory
2 17 22 1 4 9 6 16 20 14 5 10 11 18 7 15 3 12 13 21 8 19 Md R.A. S.V.


z-Scores: S3 - Chlorpyrifos
Target Standard Deviation 0.027 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
2 17 22 1 4 9 6 16 20 14 5 10 11 18 7 15 3 12 13 21 8

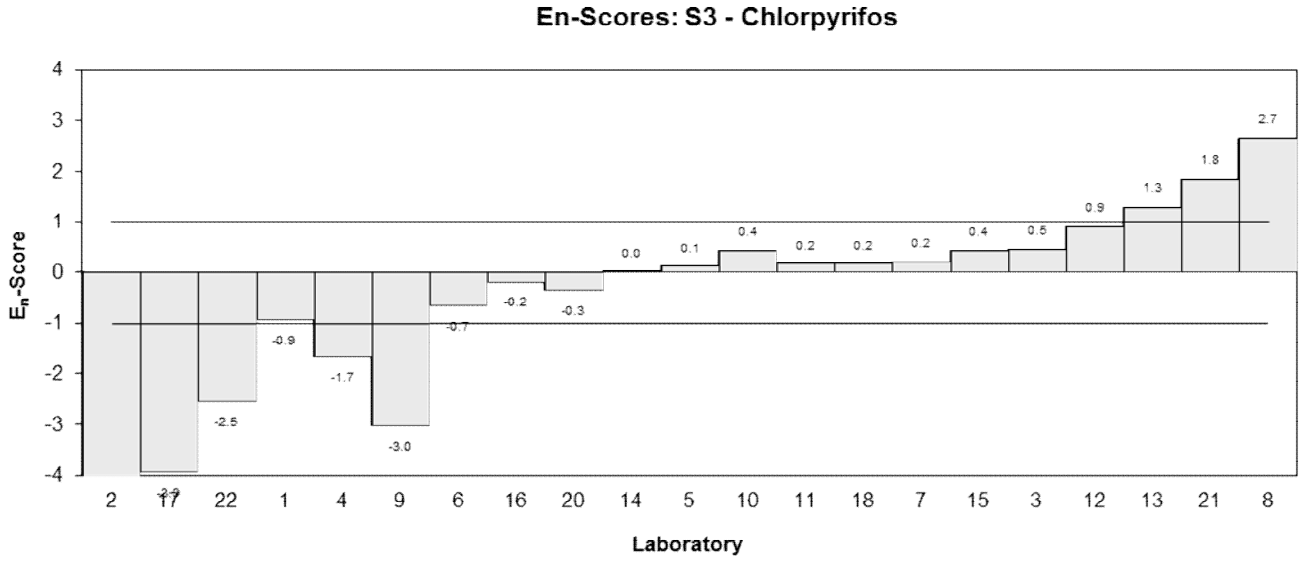

En-Scores: S3 - Chlorpyrifos
En-Score
Laboratory
2 17 22 1 4 9 6 16 20 14 5 10 11 18 7 15 3 12 13 21 8

Figure 10

Table 14

Sample Details

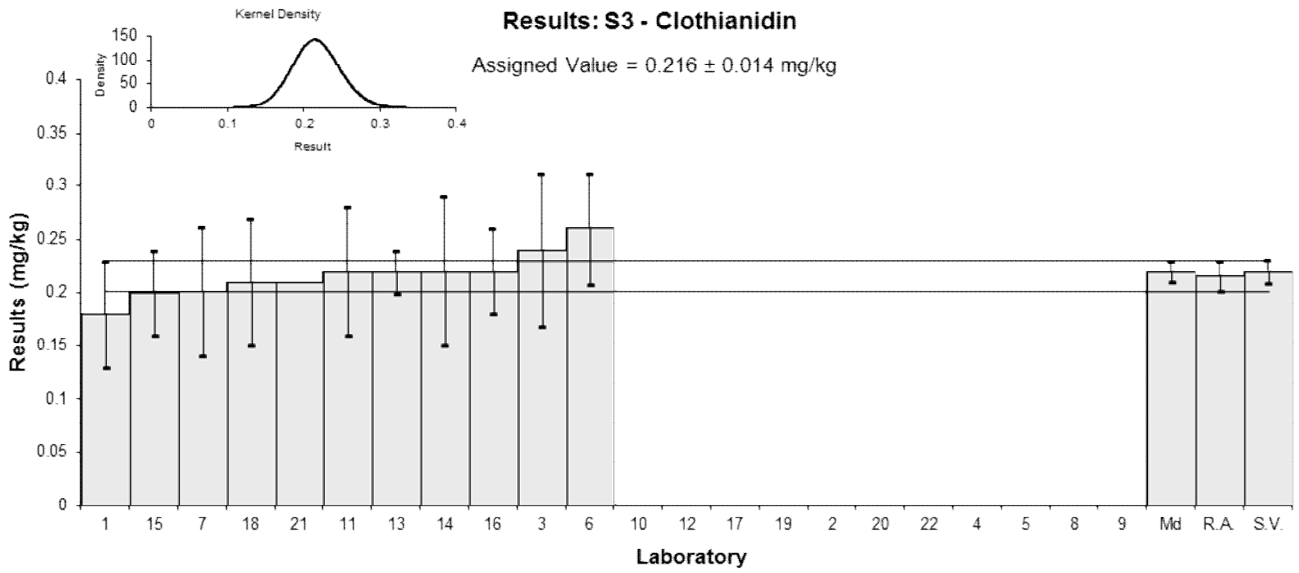
Sample No.	S3
Matrix	Capsicum
Analyte	Clothianidin
Units	mg/kg

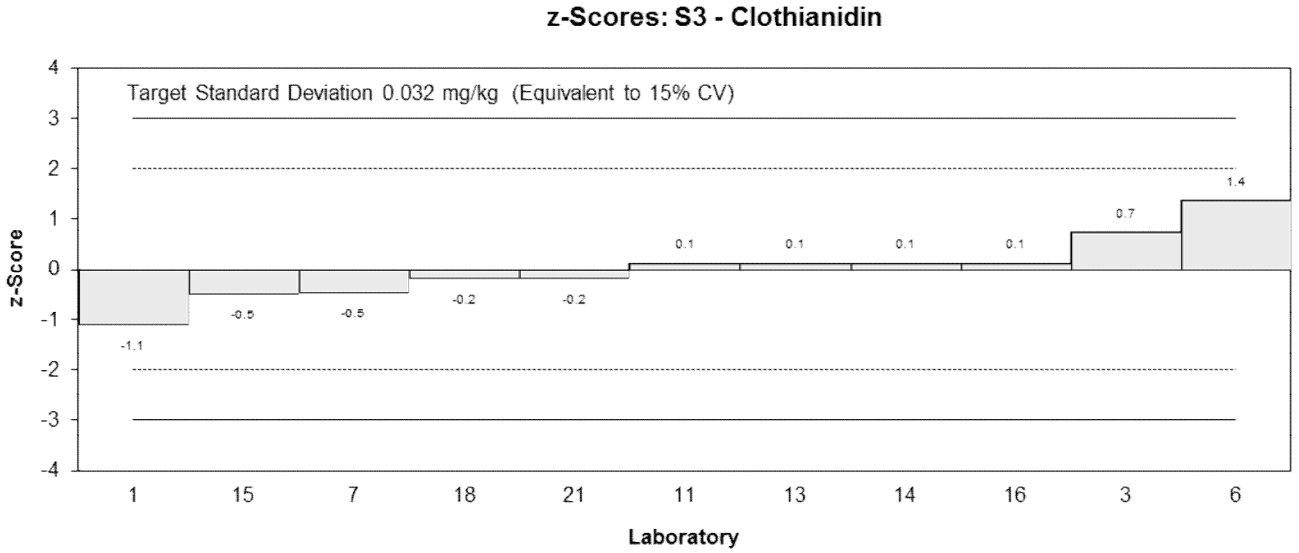
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.18	0.05	75	-1.11	-0.69
2	NT	NT	NT		
3	0.24	0.072	83	0.74	0.33
4	NT	NT	NT		
5	NT	NT	NT		
6	0.26	0.052	88	1.36	0.82
7	0.201	0.060	97	-0.46	-0.24
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	0.22	0.06	NR	0.12	0.06
12	NT	NT	NT		
13	0.22	0.02	110	0.12	0.16
14	0.22	0.07	108	0.12	0.06
15	0.2	0.04	NR	-0.49	-0.38
16	0.22	0.04	93	0.12	0.09
17	NT	NT	NT		
18	0.21	0.06	81	-0.19	-0.10
19	NT	NT	NT		
20	NT	NT	NT		
21	0.21	NR	65	-0.19	-0.43
22	NT	NT	NT		

Statistics

Assigned Value	0.216	0.014
Spike	0.220	0.011
Robust Average	0.216	0.014
Median	0.220	0.010
Mean	0.216	
N	11	
Max.	0.26	
Min.	0.18	
Robust SD	0.019	
Robust CV	8.8%	


Kernel Density
Density
Result
Results: S3 - Clothianidin
Assigned Value = 0.216 ± 0.014 mg/kg
Results (mg/kg)
Laboratory
1 15 7 18 21 11 13 14 16 3 6 10 12 17 19 2 20 22 4 5 8 9 Md R.A. S.V.


z-Scores: S3 - Clothianidin
Target Standard Deviation 0.032 mg/kg (Equivalent to 15% CV)
z-Score
-1.1 -0.5 -0.5 -0.2 -0.2 0.1 0.1 0.1 0.1 0.7 1.4
Laboratory
1 15 7 18 21 11 13 14 16 3 6

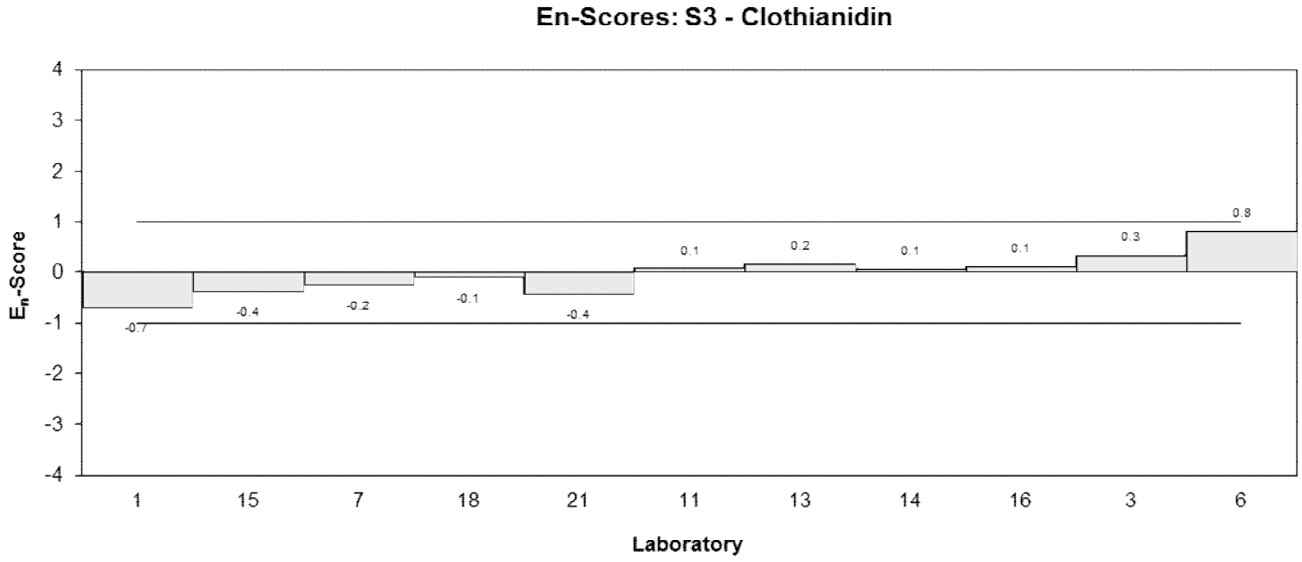

En-Scores: S3 - Clothianidin
En-Score
-0.7 -0.4 -0.2 -0.1 -0.4 0.1 0.2 0.1 0.1 0.3 0.8
Laboratory
1 15 7 18 21 11 13 14 16 3 6

Figure 11

Table 15

Sample Details

Sample No.	S3
Matrix	Capsicum
Analyte	Methomyl
Units	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Recovery
1	NT	NT	NT
2	NT	NT	NT
3	0.84	0.25	128
4	NT	NT	NT
5	NT	NT	NT
6	0.14	0.013	95
7	0.0125	0.0036	99
8	NT	NT	NT
9	NT	NT	NT
10	NT	NT	NT
11	0.37	0.09	NR
12	0.3	0.06	NR
13	0.32	0.03	96
14	0.20	0.06	100
15	0.35	0.07	NR
16	0.35	0.07	95
17	NT	NT	NT
18	0.53	0.16	81
19	NT	NT	NT
20	0.17	NR	94
21	0.559	0.14	63
22	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike	1.40	0.07
Robust Average	0.33	0.15
Median	0.34	0.14
Mean	0.35	
N	12	
Max.	0.84	
Min.	0.0125	
Robust SD	0.21	
Robust CV	63%	

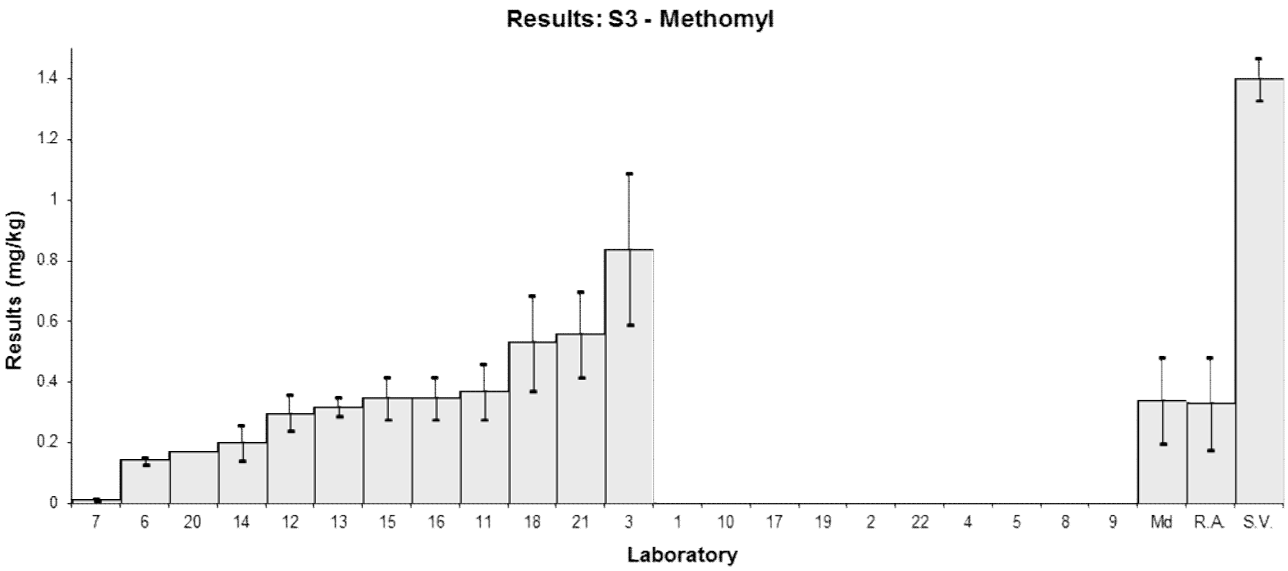

Results: S3 - Methomyl
Results (mg/kg)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
7
6
20
14
12
13
15
16
11
18
21
3
1
10
17
19
2
22
4
5
8
9
Md
R.A.
S.V.
Laboratory

Figure 12

Table 16

Sample Details

Sample No.	S3
Matrix	Capsicum
Analyte	Pyraclostrobin
Units	mg/kg

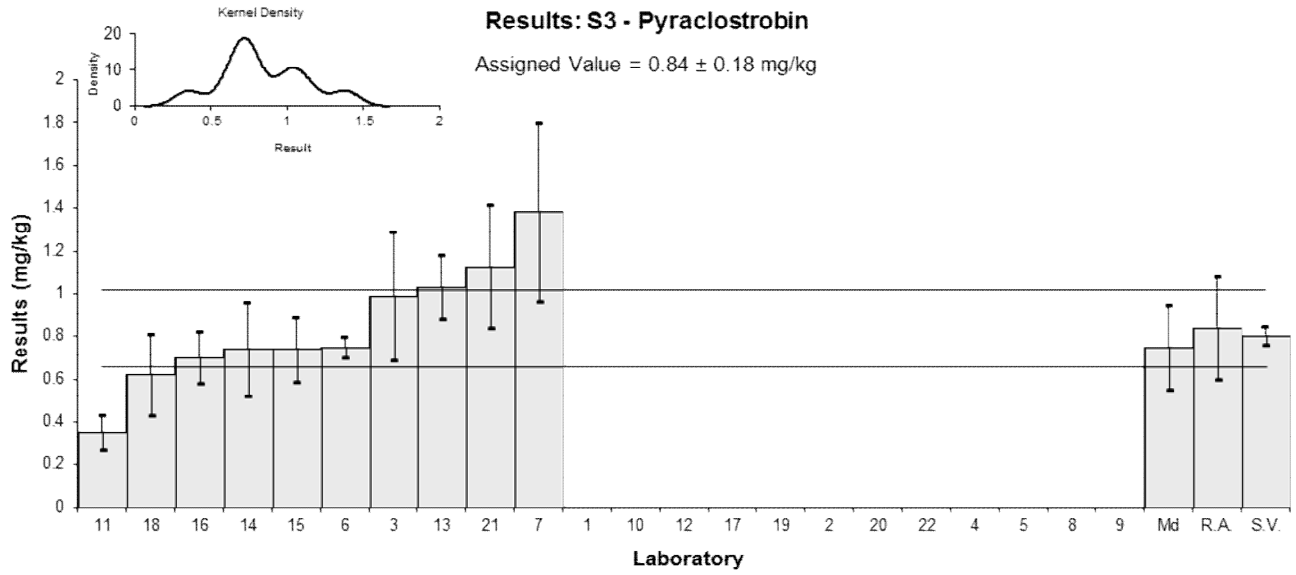
Participant Results

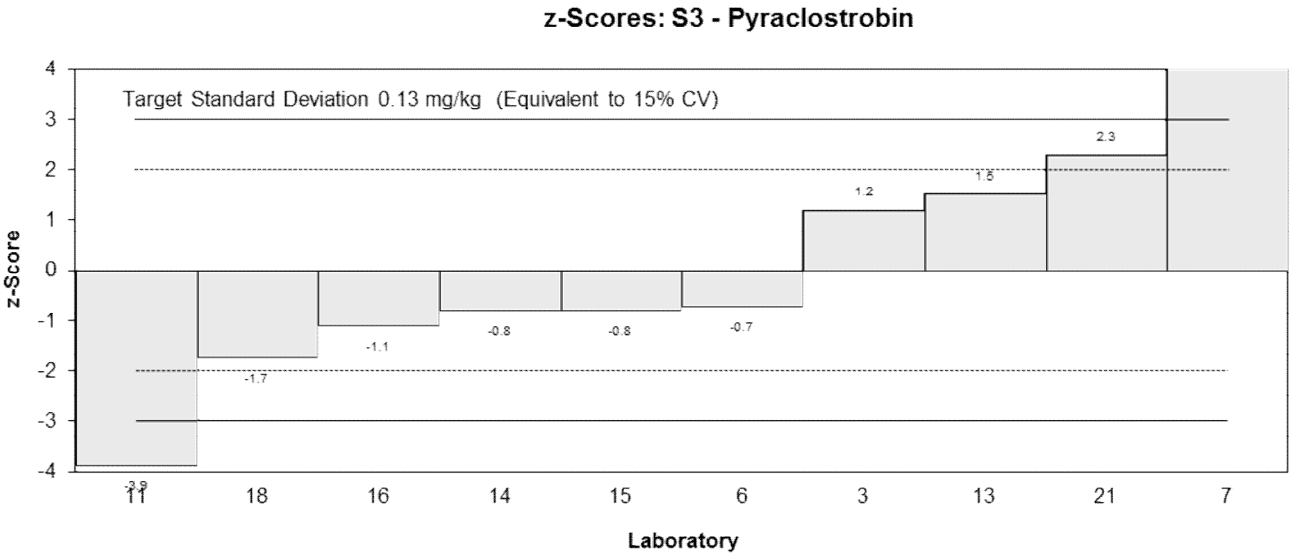
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	0.99	0.3	106	1.19	0.43
4	NT	NT	NT		
5	NT	NT	NT		
6	0.75	0.05	98	-0.71	-0.48
7	1.383	0.415	97	4.31	1.20
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	0.35	0.08	NR	-3.89	-2.49
12	NT	NT	NT		
13	1.03	0.15	117	1.51	0.81
14	0.74	0.22	100	-0.79	-0.35
15	0.74	0.15	NR	-0.79	-0.43
16	0.70	0.12	95	-1.11	-0.65
17	NT	NT	NT		
18	0.62	0.19	62	-1.75	-0.84
19	NT	NT	NT		
20	NT	NT	NT		
21	1.128	0.286	41	2.29	0.85
22	NT	NT	NT		

Statistics

Assigned Value*	0.84	0.18
Spike	0.804	0.040
Robust Average	0.84	0.24
Median	0.75	0.20
Mean	0.84	
N	10	
Max.	1.383	
Min.	0.35	
Robust SD	0.31	
Robust CV	37%	

* Robust average excluding Laboratories 7 and 11.


Kernel Density
Density
Result
Results: S3 - Pyraclostrobin
Assigned Value = 0.84 ± 0.18 mg/kg
Results (mg/kg)
Laboratory
11 18 16 14 15 6 3 13 21 7 1 10 12 17 19 2 20 22 4 5 8 9 Md R.A. S.V.


z-Scores: S3 - Pyraclostrobin
Target Standard Deviation 0.13 mg/kg (Equivalent to 15% CV)
z-Score
-2.9
-1.7
-1.1
-0.8
-0.8
-0.7
1.2
1.5
2.3
Laboratory
11 18 16 14 15 6 3 13 21 7

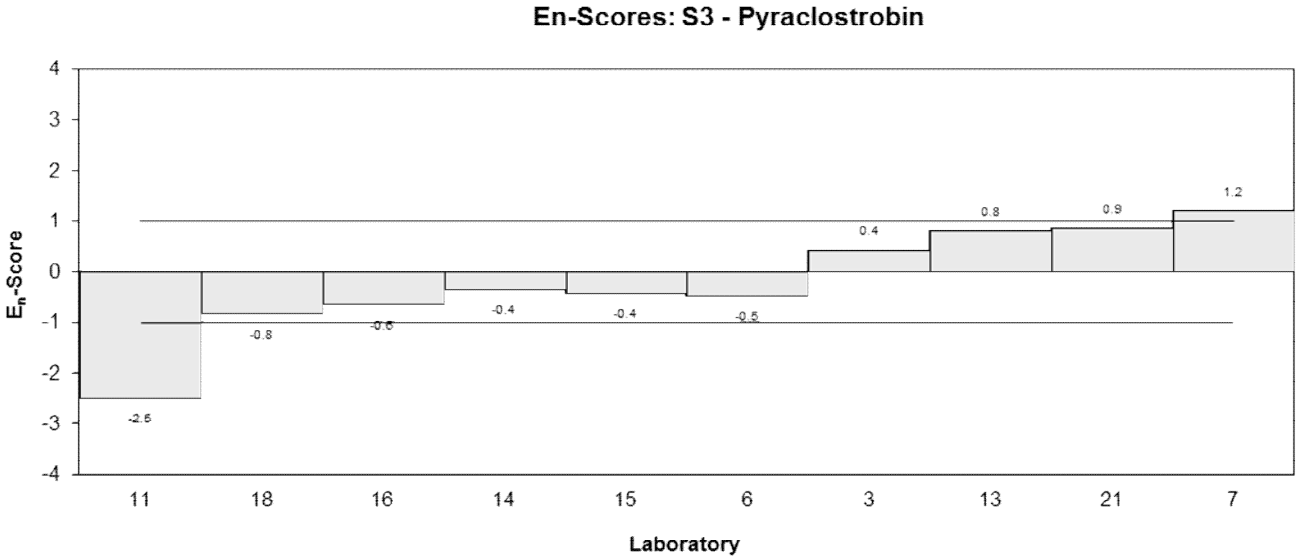

En-Scores: S3 - Pyraclostrobin
En-Score
-2.6
-0.8
-0.6
-0.4
-0.4
-0.5
0.4
0.8
0.9
1.2
Laboratory
11 18 16 14 15 6 3 13 21 7

Figure 13

Table 17

Sample Details

Sample No.	S4
Matrix	Grape
Analyte	Acetamiprid
Units	mg/kg

Participant Results

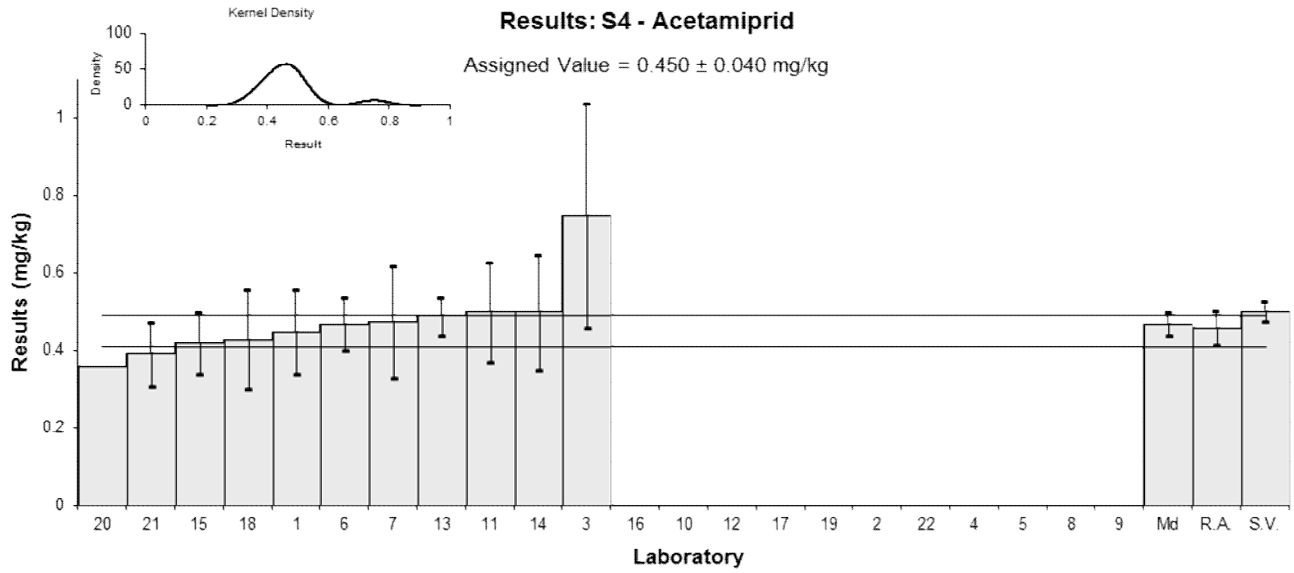
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.45	0.11	85	0.00	0.00
2	NT	NT	NT		
3	0.75	0.29	117	4.44	1.02
4	NT	NT	NT		
5	NT	NT	NT		
6	0.47	0.07	97	0.30	0.25
7	0.475	0.143	99	0.37	0.17
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	0.50	0.13	NR	0.74	0.37
12	NT	NT	NT		
13	0.49	0.05	111	0.59	0.62
14	0.50	0.15	118	0.74	0.32
15	0.42	0.08	NR	-0.44	-0.34
16**	NR	NR	NR		
17	NT	NT	NT		
18	0.43	0.13	81	-0.30	-0.15
19	NT	NT	NT		
20	0.36	NR	118	-1.33	-2.25
21	0.391	0.084	75	-0.87	-0.63
22	NT	NT	NT		

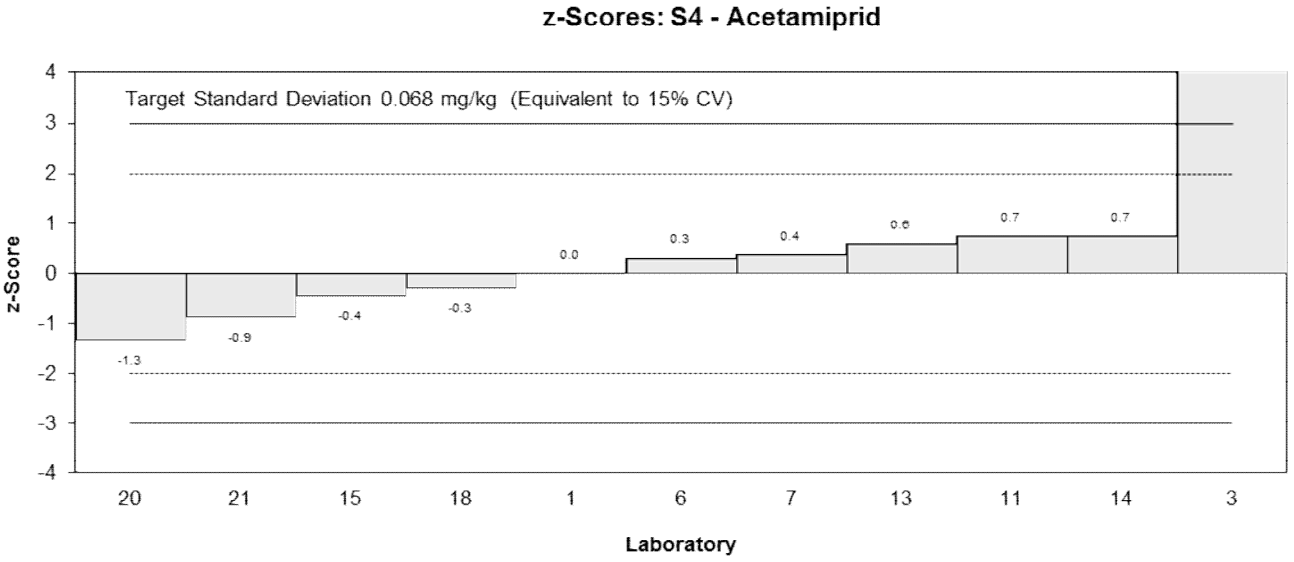
Statistics

Assigned Value*	0.450	0.040
Spike	0.503	0.025
Robust Average	0.458	0.045
Median	0.470	0.030
Mean	0.476	
N	11	
Max.	0.75	
Min.	0.36	
Robust SD	0.060	
Robust CV	13%	

* Robust average excluding Laboratory 3.

** After the interim report was released, Laboratory 16 reported that they did not test for this analyte.


Kernel Density
Density
Result
Results: S4 - Acetamiprid
Assigned Value = 0.450 ± 0.040 mg/kg
Results (mg/kg)
Laboratory
20 21 15 18 1 6 7 13 11 14 3 16 10 12 17 19 2 22 4 5 8 9 Md R.A. S.V.


z-Scores: S4 - Acetamiprid
Target Standard Deviation 0.068 mg/kg (Equivalent to 15% CV)
z-Score
-1.3 -0.9 -0.4 -0.3 0.0 0.3 0.4 0.6 0.7 0.7
Laboratory
20 21 15 18 1 6 7 13 11 14 3

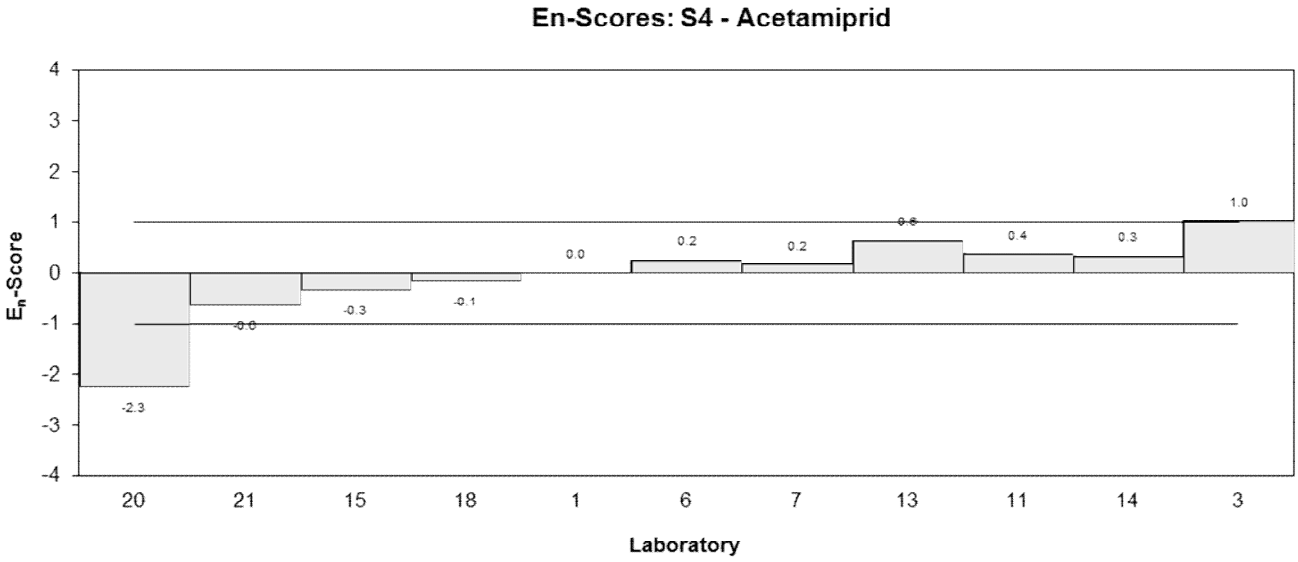

En-Scores: S4 - Acetamiprid
En-Score
-2.3 -0.6 -0.3 -0.1 0.0 0.2 0.2 0.6 0.4 0.3 1.0
Laboratory
20 21 15 18 1 6 7 13 11 14 3

Figure 14

Table 18

Sample Details

Sample No.	S4
Matrix	Grape
Analyte	Imidacloprid
Units	mg/kg

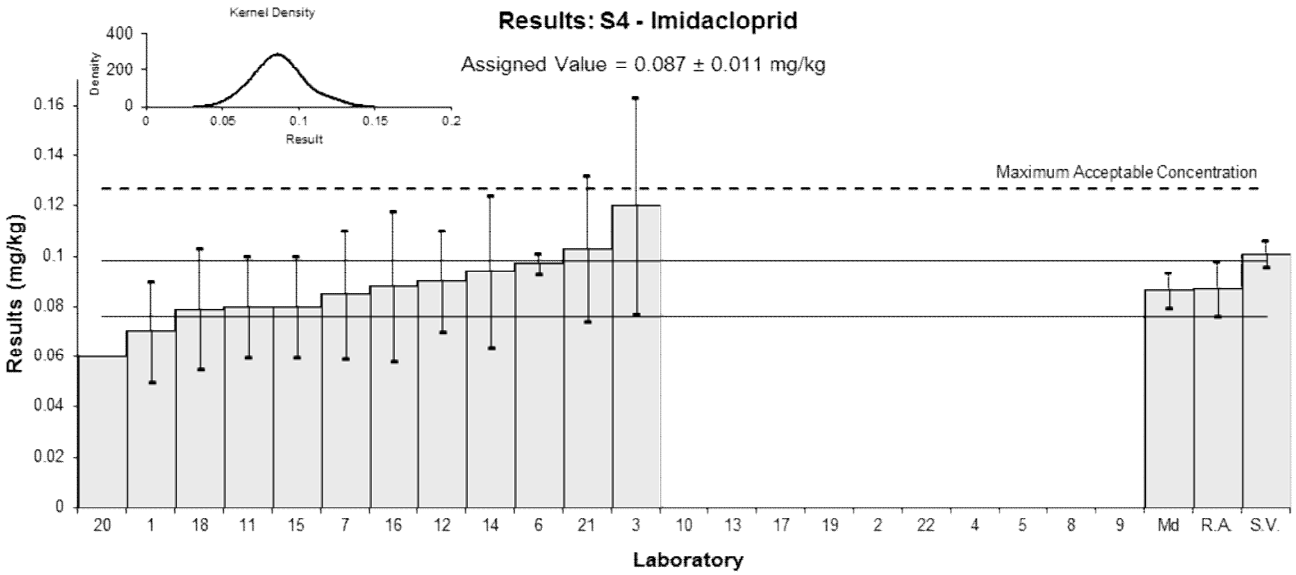
Participant Results

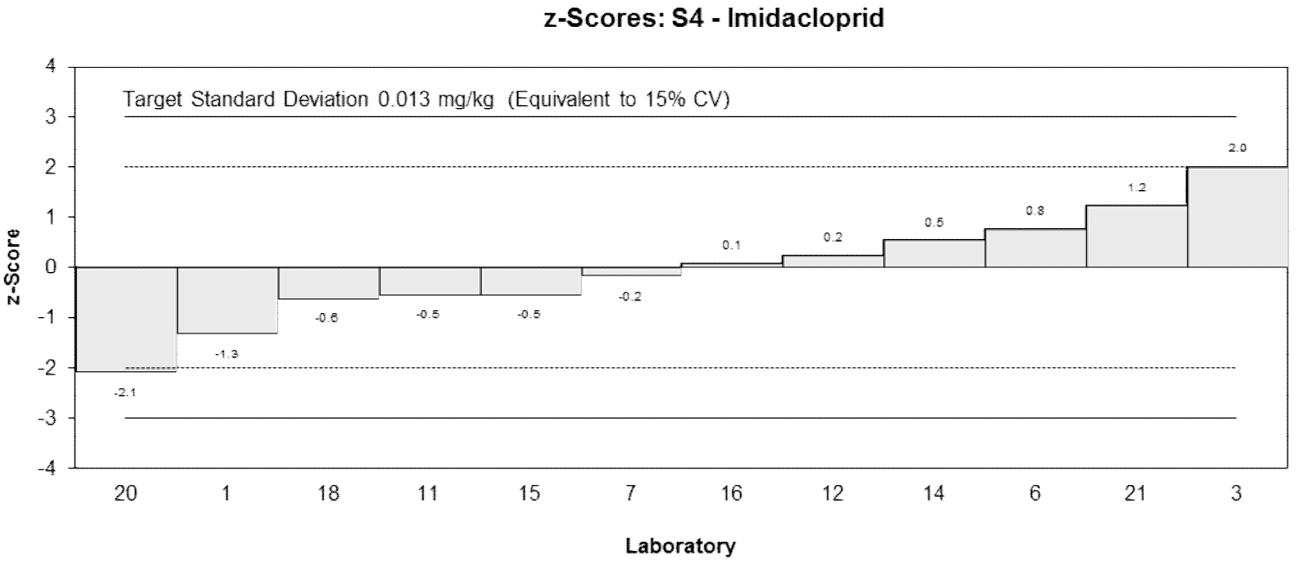
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.07	0.02	88	-1.30	-0.74
2	NT	NT	NT		
3*	0.12	0.043	95	2.00	0.74
4	NT	NT	NT		
5	NT	NT	NT		
6	0.097	0.004	107	0.77	0.85
7	0.0849	0.0255	97	-0.16	-0.08
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	0.08	0.02	NR	-0.54	-0.31
12	0.09	0.02	NR	0.23	0.13
13	NT	NT	NT		
14	0.094	0.03	139	0.54	0.22
15	0.08	0.02	NR	-0.54	-0.31
16	0.088	0.03	95	0.08	0.03
17	NT	NT	NT		
18	0.079	0.024	84	-0.61	-0.30
19	NT	NT	NT		
20	0.06	NR	112	-2.07	-2.45
21	0.103	0.029	65	1.23	0.52
22	NT	NT	NT		

Statistics

Assigned Value	0.087	0.011
Spike	0.101	0.005
Max. Acceptable Conc.*	0.127	
Robust Average	0.087	0.011
Median	0.0865	0.0071
Mean	0.0872	
N	12	
Max.	0.12	
Min.	0.06	
Robust SD	0.015	
Robust CV	17%	

* z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S4 - Imidacloprid
Assigned Value = 0.087 ± 0.011 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
20 1 18 11 15 7 16 12 14 6 21 3 10 13 17 19 2 22 4 5 8 9 Md R.A. S.V.


z-Scores: S4 - Imidacloprid
Target Standard Deviation 0.013 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
20 1 18 11 15 7 16 12 14 6 21 3
-2.1 -1.3 -0.6 -0.5 -0.5 -0.2 0.1 0.2 0.5 0.8 1.2 2.0

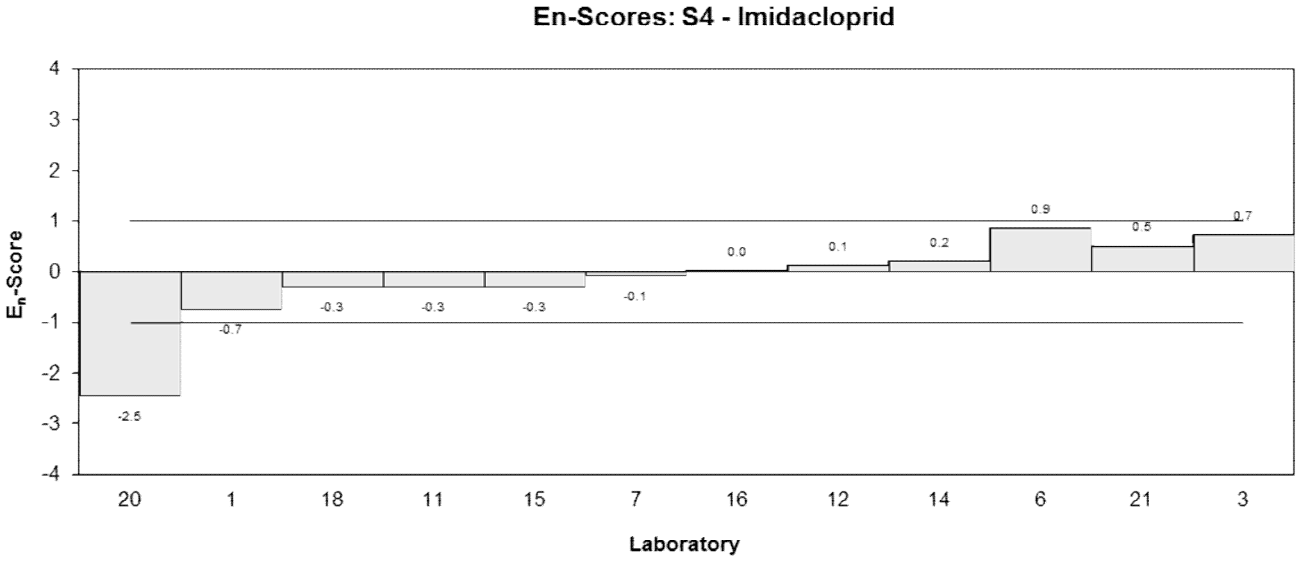

En-Scores: S4 - Imidacloprid
En-Score
Laboratory
20 1 18 11 15 7 16 12 14 6 21 3
-2.5 -0.7 -0.3 -0.3 -0.3 -0.1 0.0 0.1 0.2 0.9 0.5 0.7

Figure 15

Table 19

Sample Details

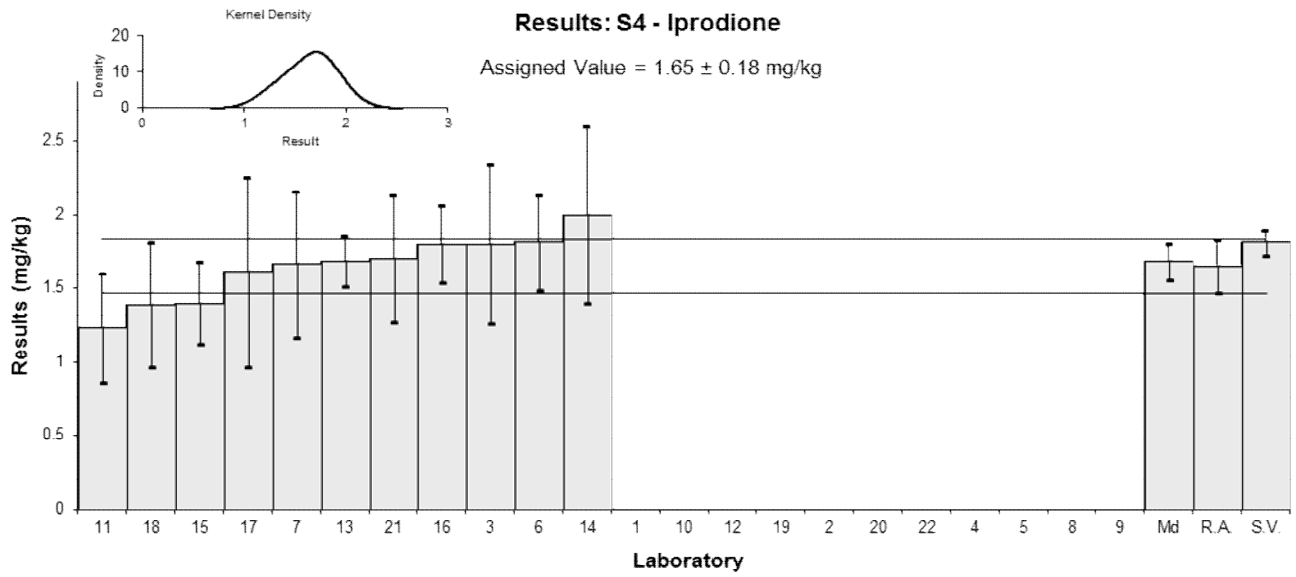
Sample No.	S4
Matrix	Grape
Analyte	Iprodione
Units	mg/kg

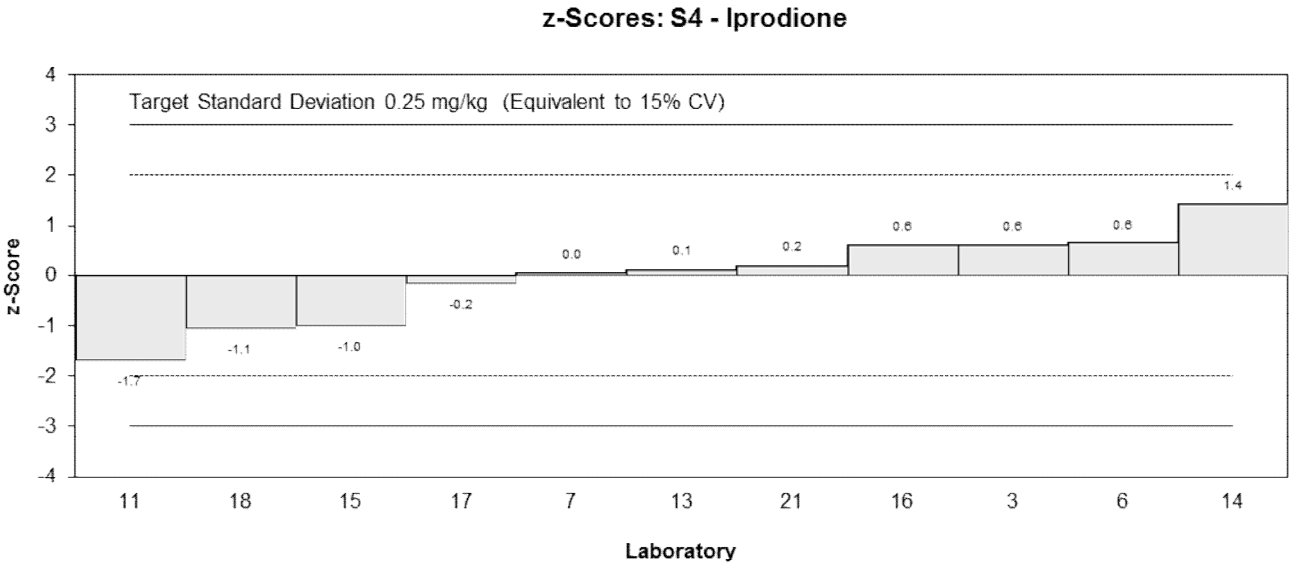
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	1.8	0.54	94	0.61	0.26
4	NT	NT	NT		
5	NT	NT	NT		
6	1.81	0.32	114	0.65	0.44
7	1.662	0.499	93	0.05	0.02
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	1.23	0.37	NR	-1.70	-1.02
12	NT	NT	NT		
13	1.68	0.17	106	0.12	0.12
14	2.0	0.6	83	1.41	0.56
15	1.4	0.28	NR	-1.01	-0.75
16	1.8	0.26	99	0.61	0.47
17	1.61	0.64	120	-0.16	-0.06
18	1.39	0.42	120	-1.05	-0.57
19	NT	NT	NT		
20	NT	NT	NT		
21	1.7	0.432	101	0.20	0.11
22	NT	NT	NT		

Statistics

Assigned Value	1.65	0.18
Spike	1.81	0.09
Robust Average	1.65	0.18
Median	1.68	0.12
Mean	1.64	
N	11	
Max.	2.0	
Min.	1.23	
Robust SD	0.24	
Robust CV	15%	


Kernel Density
Density
Result
Results: S4 - Iprodione
Assigned Value = 1.65 ± 0.18 mg/kg
Results (mg/kg)
Laboratory
11 18 15 17 7 13 21 16 3 6 14 1 10 12 19 2 20 22 4 5 8 9 Md R.A. S.V.


z-Scores: S4 - Iprodione
Target Standard Deviation 0.25 mg/kg (Equivalent to 15% CV)
z-Score
-1.7 -1.1 -1.0 -0.2 0.0 0.1 0.2 0.6 0.6 0.6 1.4
Laboratory
11 18 15 17 7 13 21 16 3 6 14

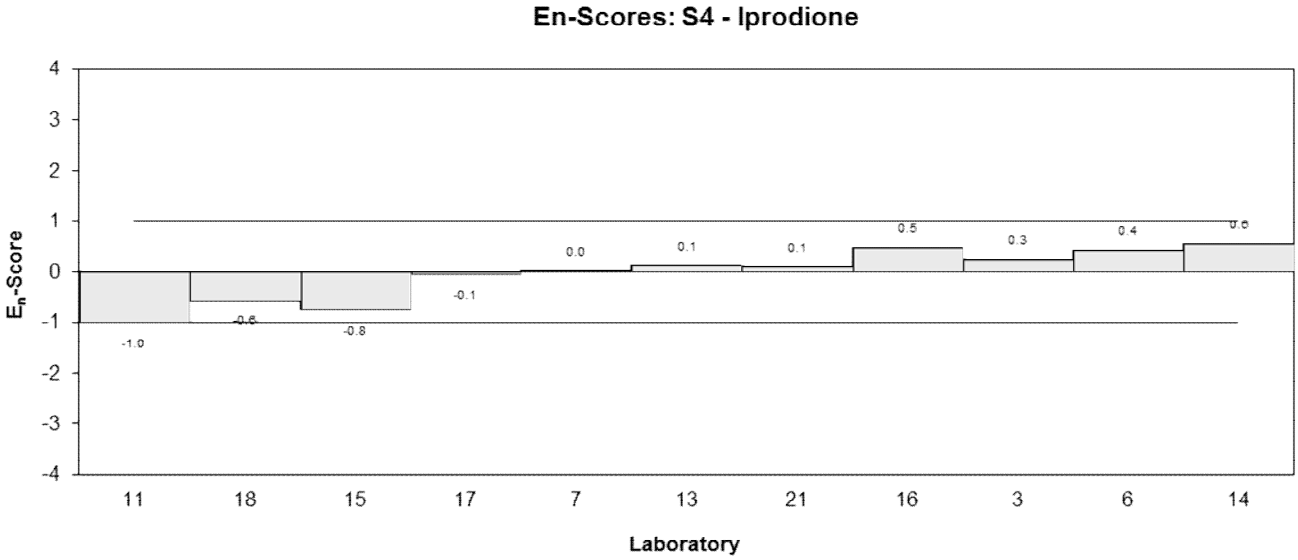

En-Scores: S4 - Iprodione
En-Score
-1.0 -0.6 -0.8 -0.1 0.0 0.1 0.1 0.5 0.3 0.4 0.6
Laboratory
11 18 15 17 7 13 21 16 3 6 14

Figure 16

Table 20

Sample Details

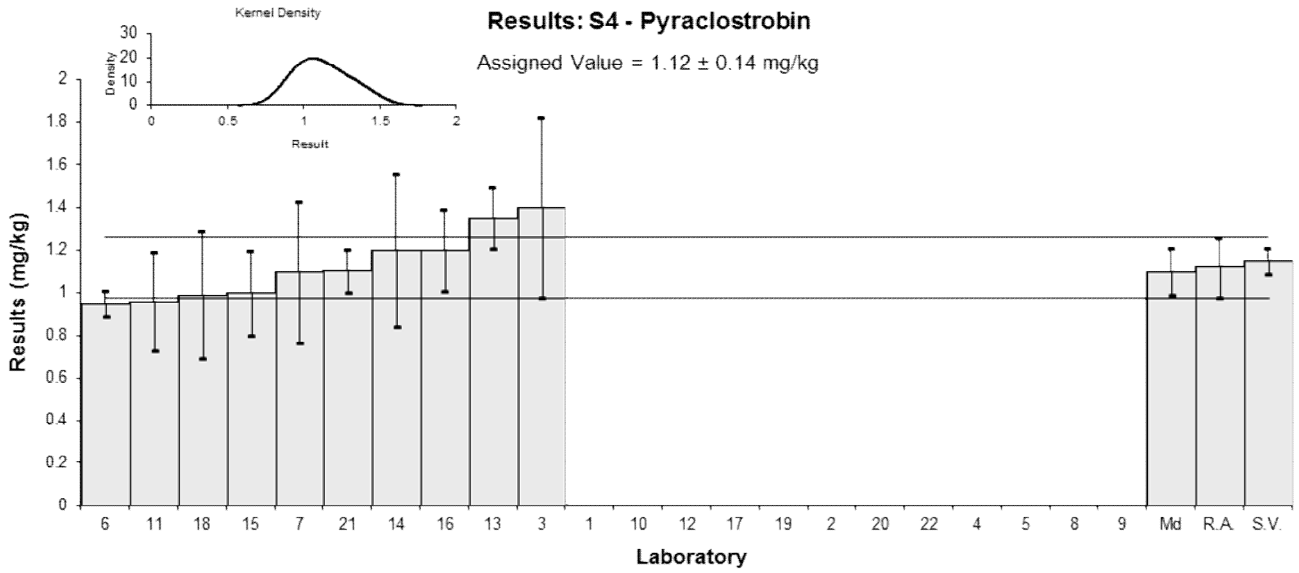
Sample No.	S4
Matrix	Grape
Analyte	Pyraclostrobin
Units	mg/kg

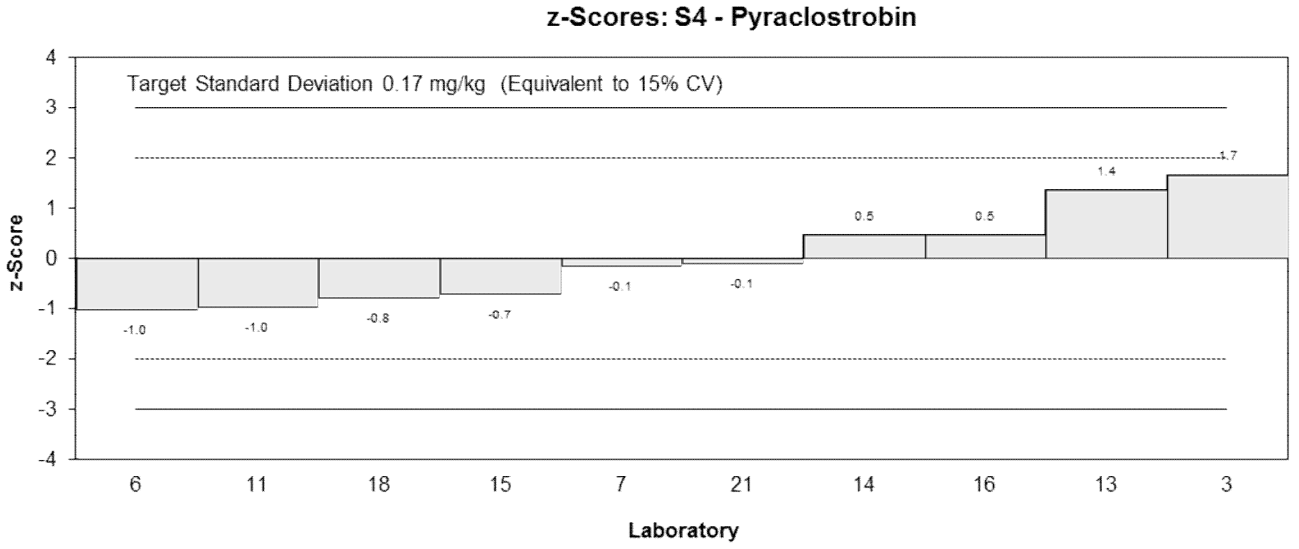
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	1.4	0.42	121	1.67	0.63
4	NT	NT	NT		
5	NT	NT	NT		
6	0.95	0.06	110	-1.01	-1.12
7	1.096	0.329	94	-0.14	-0.07
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	0.96	0.23	NR	-0.95	-0.59
12	NT	NT	NT		
13	1.35	0.14	117	1.37	1.16
14	1.2	0.36	77	0.48	0.21
15	1.0	0.2	NR	-0.71	-0.49
16	1.2	0.19	95	0.48	0.34
17	NT	NT	NT		
18	0.99	0.30	84	-0.77	-0.39
19	NT	NT	NT		
20	NT	NT	NT		
21	1.102	0.1	88	-0.11	-0.10
22	NT	NT	NT		

Statistics

Assigned Value	1.12	0.14
Spike	1.15	0.06
Robust Average	1.12	0.14
Median	1.10	0.11
Mean	1.12	
N	10	
Max.	1.4	
Min.	0.95	
Robust SD	0.18	
Robust CV	16%	


Kernel Density
Density
Result
Results: S4 - Pyraclostrobin
Assigned Value = 1.12 ± 0.14 mg/kg
Results (mg/kg)
Laboratory
6 11 18 15 7 21 14 16 13 3 1 10 12 17 19 2 20 22 4 5 8 9 Md R.A. S.V.


z-Scores: S4 - Pyraclostrobin
Target Standard Deviation 0.17 mg/kg (Equivalent to 15% CV)
z-Score
-1.0 -1.0 -0.8 -0.7 -0.1 -0.1 0.5 0.5 1.4 1.7
Laboratory
6 11 18 15 7 21 14 16 13 3

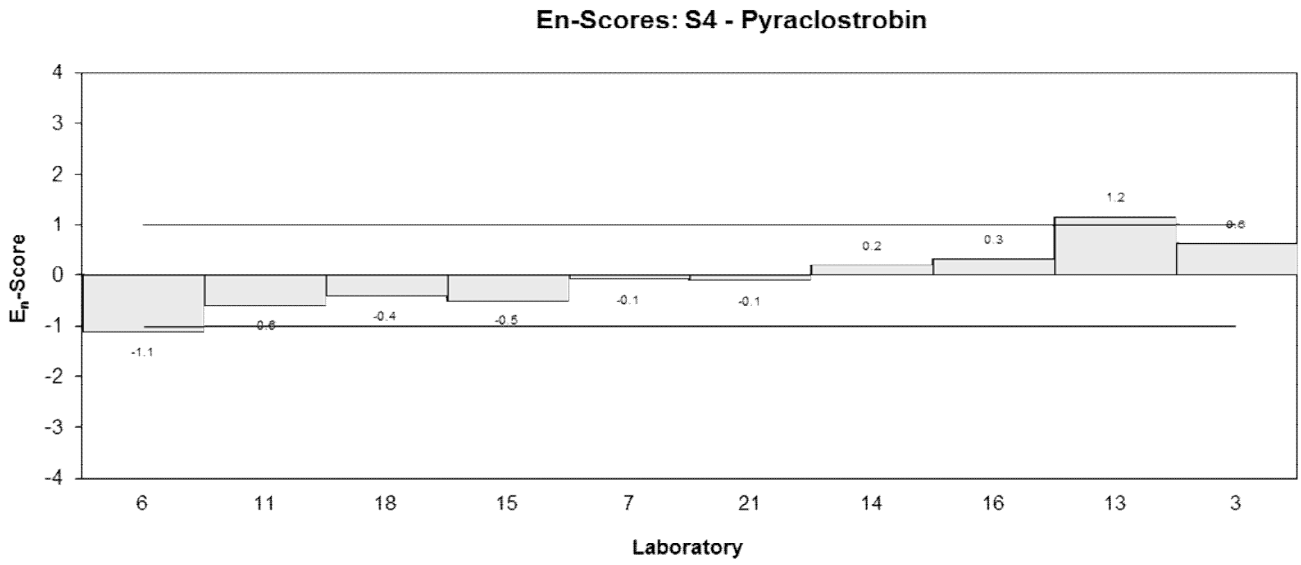

En-Scores: S4 - Pyraclostrobin
En-Score
-1.1 -0.6 -0.4 -0.5 -0.1 -0.1 0.2 0.3 1.2 0.6
Laboratory
6 11 18 15 7 21 14 16 13 3

Figure 17

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust average of participants' results was used as the assigned value for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2015.[7] Results less than 50% and greater than 150% of the robust average were removed before the calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for the robust average is presented in Appendix 3, using clothianidin in Sample S3 as an example.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

A comparison of the assigned value (or robust average if no assigned value was set) and the spiked value is presented in Table 21.

No assigned value was set for methomyl in Sample S3 as reported numeric results were too variable and the robust average was significantly lower than the spiked value (24%).

For all other pesticides, the assigned value was within the range 78% to 104% of the spiked value, providing good support for the assigned values and is evidence for the stability of these analytes in the test samples.

Table 21 Comparison of Assigned Values (or Robust Averages) and Spiked Values

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	Azoxystrobin	1.17	1.29	91
	Endosulfan sulfate	0.741	0.791	94
	Methamidophos	0.925	0.946	98
	Permethrin	0.70	0.805	87
S2	Chlorpyrifos	1.10	1.41	78
	Imidacloprid	0.258	0.300	86
	Linuron	0.100	0.111	90
	Permethrin	1.00	1.20	83
S3	Chlorpyrifos	0.179	0.200	90
	Clothianidin	0.216	0.220	98
	Methomyl	*(0.33)*	1.40	*(24)*
	Pyraclostrobin	0.84	0.804	104
S4	Acetamiprid	0.450	0.503	89
	Imidacloprid	0.087	0.101	86
	Iprodione	1.65	1.81	91
	Pyraclostrobin	1.12	1.15	97

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded MU associated with their results and the basis of this estimate. It is a requirement of ISO/IEC 17025:2017 that laboratories have procedures to estimate the uncertainty of chemical measurements and to report this in specific circumstances, including when the client's instruction so requires.[9]

Of 225 numerical results for the analytes of interest in this study, 204 (91%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate the expanded measurement uncertainty (Table 3).

Laboratory **18** reported their uncertainties as a percentage rather than in mg/kg. These values were modified accordingly by the study coordinator for this report.

Laboratories **5**, **9**, **10**, **13**, **20** and **21** did not provide MUs for at least one reported result (including for analytes not spiked into the samples). All of these laboratories have stated that they are accredited to ISO/IEC 17025 for these analyses. Laboratory **5** did not report an uncertainty for one analyte (bifenthrin; not spiked into the samples), commenting that this analyte was not under their laboratory's scope; they have reported uncertainties for all their other results. Laboratories **9** and **10** did not report an uncertainty for any result.

The magnitude of the reported uncertainties for analytes in this study was within the range 1% to 82% relative. In general, an expanded uncertainty of less than 15% relative is likely to be unrealistically small for the routine measurement of a pesticide residue, while over 50% is likely too large. Of the 204 expanded uncertainties, 31 were less than 15% relative and 9 were greater than 50% relative.

Laboratories having a satisfactory z-score but an unsatisfactory E_n-score may have underestimated the expanded MU associated with their result.

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write the uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 0.0849 ± 0.0255 mg/kg, the recommended format is 0.085 ± 0.026 mg/kg.[10]

6.3 z-Scores

Target SDs equivalent to 15% PCV were used to calculate z-scores. CVs predicted by the Thompson-Horwitz equation,[8] target SDs (as PCV), and the between laboratories CVs obtained in this study for scored analytes are presented for comparison in Table 22.

Table 22 Comparison of Thompson-Horwitz CVs, Target SDs, and Between Laboratories CV

Sample	Analyte	Assigned value (mg/kg)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between Laboratories CV* (%)
S1	Azoxystrobin	1.17	16	15	20
	Endosulfan sulfate	0.741	17	15	21
	Methamidophos	0.925	16	15	14
	Permethrin	0.70	17	15	26
S2	Chlorpyrifos	1.10	16	15	20
	Imidacloprid	0.258	20	15	5.4
	Linuron	0.100	22	15	16
	Permethrin	1.00	16	15	28
S3	Chlorpyrifos	0.179	21	15	23
	Clothianidin	0.216	20	15	8.8
	Pyraclostrobin	0.84	16	15	25

Sample	Analyte	Assigned value (mg/kg)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between Laboratories CV* (%)
S4	Acetamiprid	0.450	18	15	11
	Imidacloprid	0.087	22	15	17
	Iprodione	1.65	15	15	15
	Pyraclostrobin	1.12	16	15	16

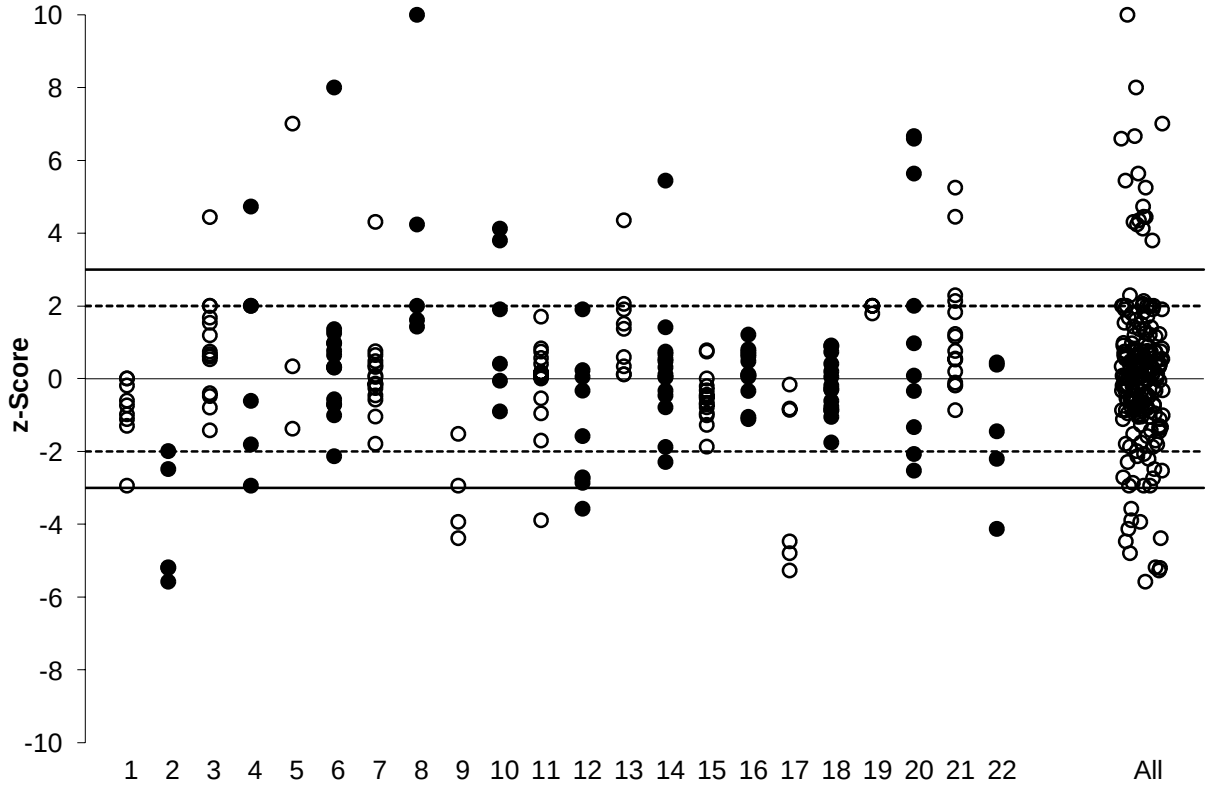
* Robust between laboratories CVs with outliers removed, if applicable.

To account for possible low bias in the consensus value due to laboratories using inefficient analytical or extraction techniques, a total of 7 z-scores were adjusted for the following analytes: permethrin in Sample S1, chlorpyrifos, imidacloprid and permethrin in Sample S2, and imidacloprid in Sample S4. A maximum acceptable concentration was set to two target SDs more than the spiked value, and results lower than the maximum acceptable concentration but with a z-score greater than 2 had their z-score adjusted to 2. This ensured that laboratories reporting results close to the spiked value were not penalised. z-Scores for results higher than the maximum acceptable concentration were not adjusted, and z-scores less than 2 were also not adjusted.

Of 213 results for which z-scores were calculated, 171 (80%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

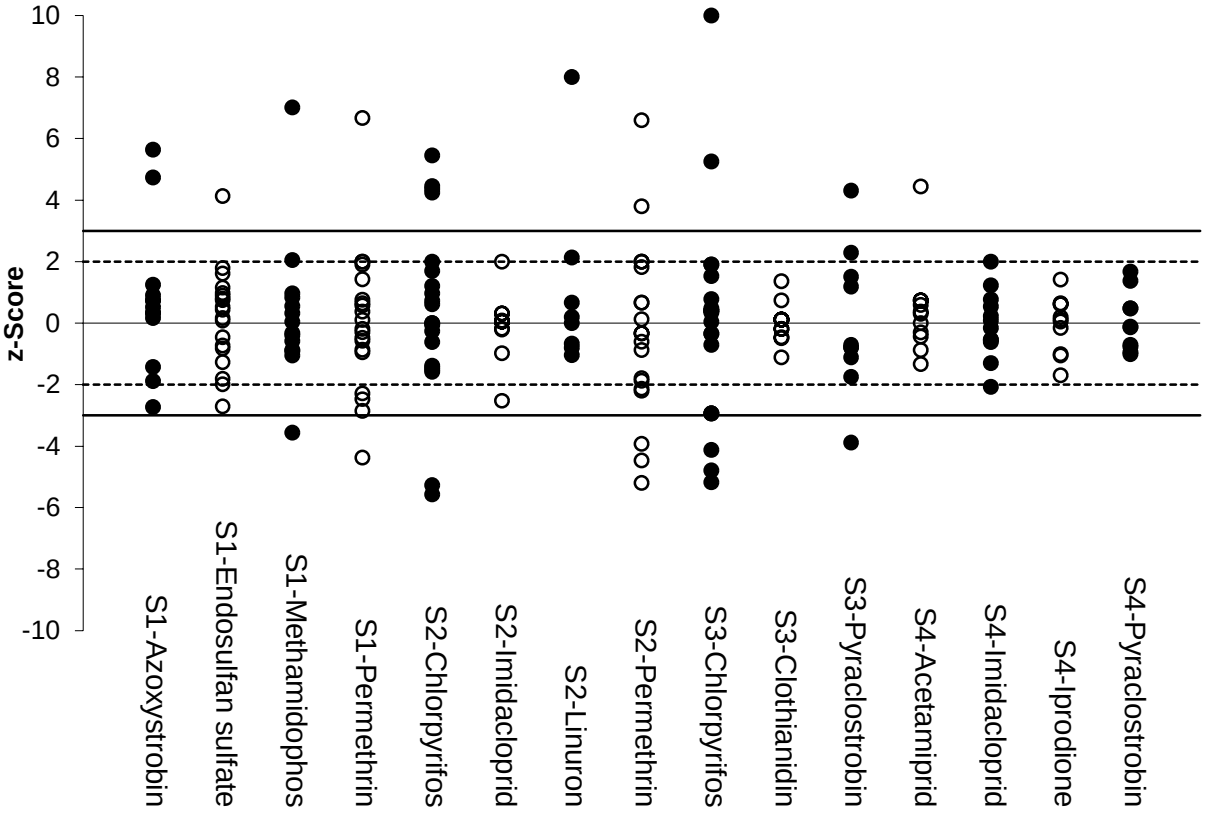
Laboratories **3**, **6**, **7**, **11**, **14**, **15**, **18** and **21** reported results for all 15 scored analytes. Laboratories **15** and **18** returned satisfactory z-scores for all 15 analytes. Satisfactory z-scores were achieved for all scored analytes reported by laboratories **16** (13) and **19** (3).

The dispersal of participants' z-scores is presented graphically by laboratory in Figure 18 and by analyte in Figure 19.



z-Scores greater than 10 have been plotted at 10.

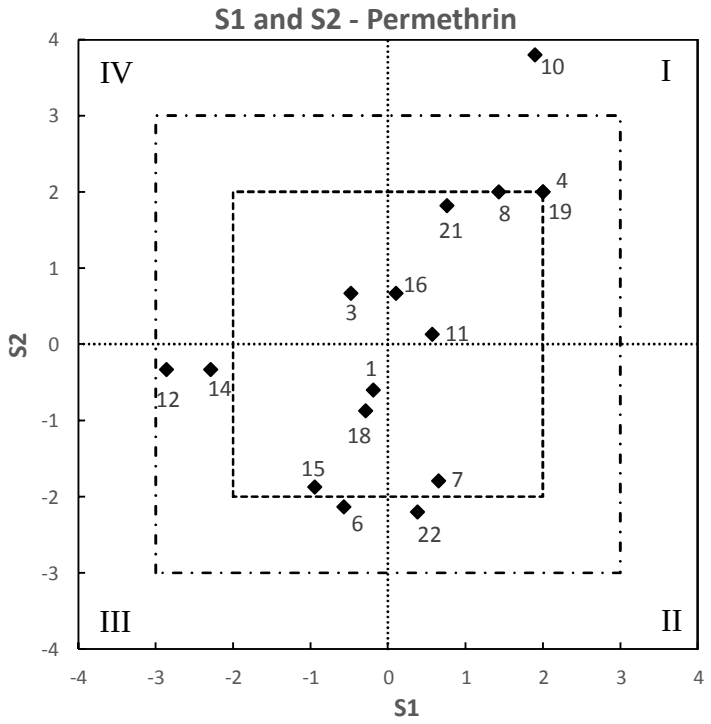
Figure 18 z-Score Dispersal by Laboratory



z-Scores greater than 10 have been plotted at 10.

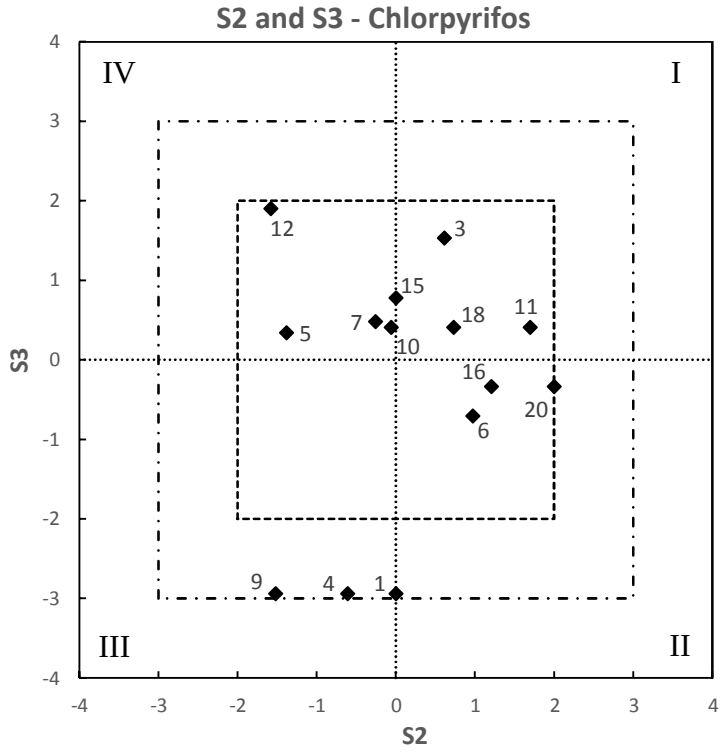
Figure 19 z-Score Dispersal by Analyte

Scatter plots of z-scores for permethrin, chlorpyrifos, imidacloprid, and pyraclostrobin in different samples are presented in Figures 20 to 23. Scores are predominantly in quadrants I and III, indicating that laboratory bias is the major contributor to the variability of results.



Laboratories 2, 9, 17 and 20 are off-scale.

Figure 20 z-Score Scatter Plot – Permethrin in Samples S1 and S2.



Laboratories 2, 8, 13, 14, 17, 21 and 22 are off-scale.

Figure 21 z-Score Scatter Plot – Chlorpyrifos in Samples S2 and S3.

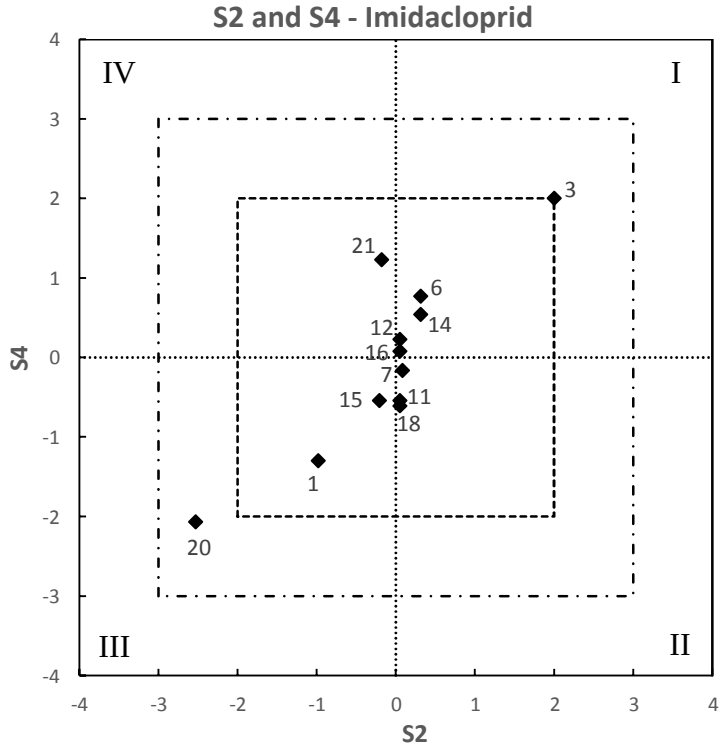
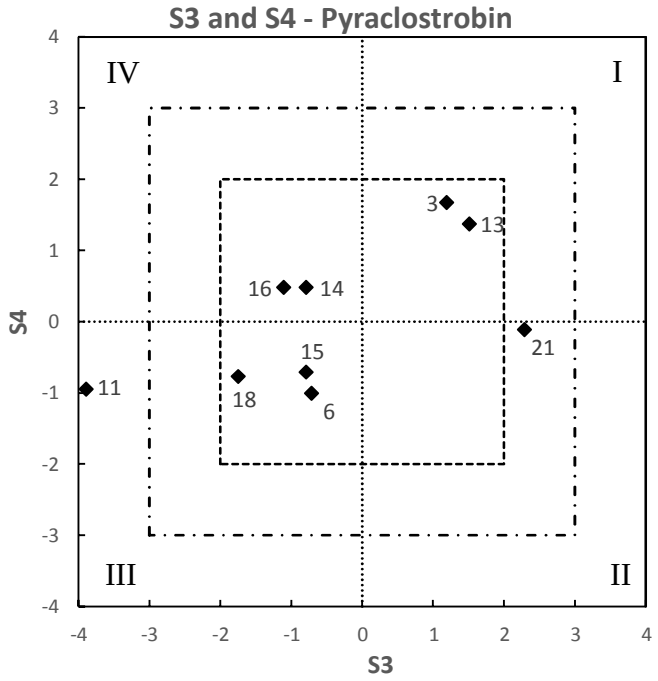


Figure 22 z-Score Scatter Plot – Imidacloprid in Samples S2 and S4.



Laboratory 7 is off-scale.

Figure 23 z-Score Scatter Plot – Pyraclostrobin in Samples S3 and S4.

6.4 E_n-Scores

Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score. E_n-scores greater than 1 were set to 1 for results for z-scores that were adjusted as discussed in Section 6.3 z-Scores.

Of 213 results for which E_n-scores were calculated, 158 (74%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **18** returned satisfactory E_n-scores for all 15 scored analytes. Satisfactory E_n-scores were achieved for all scored analytes reported by laboratories **16** (13) and **1** (9).

The dispersal of participants' E_n-scores is presented graphically by laboratory in Figure 24.

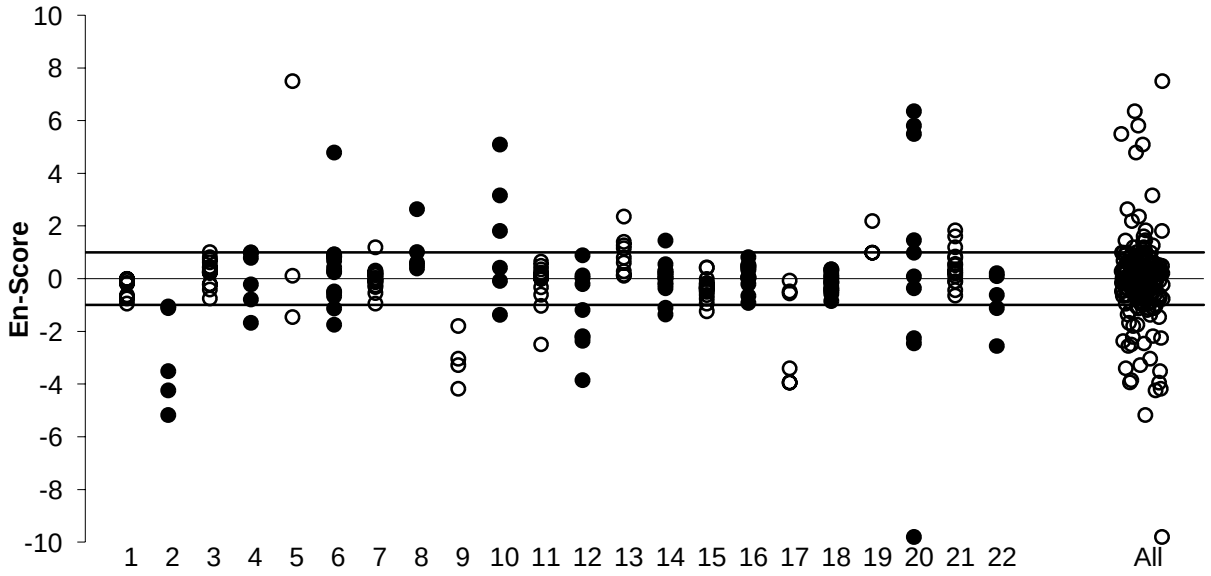


Figure 24 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 23 presents false negative results – an analyte present for which a laboratory tested but did not report a result (e.g. laboratories reporting a '<' or NR result when the assigned and spiked value was higher than the participants' reporting limit, or laboratories that didn't report any value).

Table 23 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Reported Result (mg/kg)
5	S1	Endosulfan sulfate	0.741	0.791	NR
9	S1	Endosulfan sulfate	0.741	0.791	NR
		Methamidophos	0.925	0.946	NR
16	S2	Linuron	0.100	0.111	NR
	S4	Acetamiprid	0.450	0.503	NR*
22	S1	Methamidophos	0.925	0.946	<LOQ**

* After the interim report was released, Laboratory 16 reported that they did not test for acetamiprid.
** Laboratory 22 did not report their LOQ for methamidophos. Depending on the actual LOQ, this result may or may not be a false negative.

6.6 Reporting of Additional Analytes

Three laboratories reported at least one pesticide which was not spiked into the test samples by the study coordinator. These are presented in Table 24.

Table 24 Non-Spiked Analytes Reported by Participants

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
5	S1	Bifenthrin	0.070	NR	99
9	S1	beta-Endosulfan	0.38	NR	NR
	S4	beta-Endosulfan	0.14	NR	NR
13	S2	Methamidophos	1.21	NR	NR
	S4	Chlorpyrifos	1.82	NR	NR

6.7 Incurred Pesticides in Sample S4

The grapes used to prepare Sample S4 were not organically grown. Several participants reported detecting pesticides in both the unspiked portion and spiked Sample S4. These are summarised in Table 25 for information only.

Table 25 Analytes Reported by Participants in Unspiked S4

Lab. Code	Analyte	Result Unspiked S4 (mg/kg)	Result Sample S4 (mg/kg)	Uncertainty Sample S4 (mg/kg)
1	Clothianidin	NR	0.08	0.02
3	Azoxystrobin	NR	0.015	0.0045
	Clothianidin	NR	0.16	0.053
6	Azoxystrobin	Trace	Trace	NR
	Clothianidin	0.09	0.084	0.017
7	Clothianidin	Detected	0.128	0.038

Lab. Code	Analyte	Result Unspiked S4 (mg/kg)	Result Sample S4 (mg/kg)	Uncertainty Sample S4 (mg/kg)
9	Dithiocarbamates	NR	0.02	NR
11	Azoxystrobin	NR	0.01	0.003
	Clothianidin	NR	0.10	0.03
13	Azoxystrobin	0.01	0.01	0.01
	Clothianidin	0.11	0.11	0.01
14	Chlorantrilipole	0.011	0.011	NR
	Clothiandin	0.13	0.12	0.04
	Dithiocarbamates	0.12	0.13	0.04
15	Dithiocarbamates	NR	0.2	0.04
	Clothianidin	NR	0.11	0.02
16	Chlorpyrifos	Trace	Trace	NR
	Clothianidin	0.12	0.12	0.03
21	Clothianidin	NR	0.091	NR

6.8 Fitness for Purpose of Pesticide Results

The Australia New Zealand Food Standards Code specifies the MRLs for various pesticides in different food products.[5] Laboratories should be able to identify if a sample is compliant or not with the relevant MRL. In particular, a laboratory should not classify a sample as compliant if the pesticide level is greater than the MRL, and vice versa. Table 26 summaries instances of incorrect and questionable compliance and non-compliance identifications.

Table 26 Summary of Incorrect and Questionable MRL Compliance Identification

Lab. Code	Incorrect Compliance Identification*	Incorrect Non-Compliance Identification**	Questionable Compliance Identification***	Questionable Non-Compliance Identification****
3	-	-	S1 Azoxystrobin	S2 Imidacloprid
8	-	S3 Chlorpyrifos	-	-
9	S1 Permethrin	-	-	-
11	S3 Pyraclostrobin	-	-	-
12	S1 Azoxystrobin	-	-	-
14	-	-	S1 Azoxystrobin	-

* Participant's result, including expanded uncertainty, is lower than the relevant MRL when the assigned value is greater.

** Participant's result, including expanded uncertainty, is greater than the relevant MRL when the assigned value is lower.

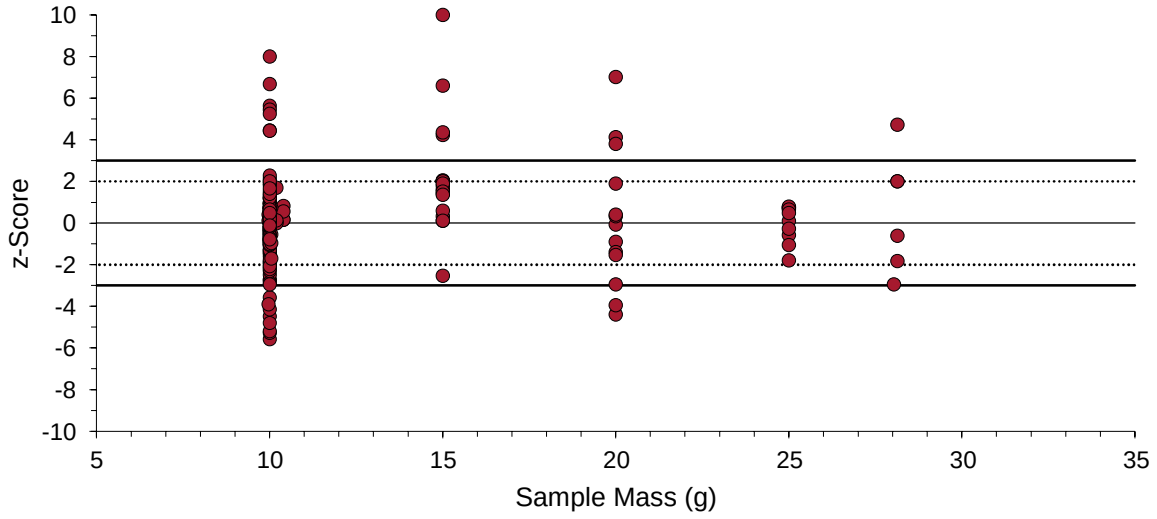
*** Participant's result is lower than the relevant MRL when the assigned value is greater, but the result's expanded uncertainty spans the MRL.

**** Participant's result is greater than the relevant MRL when the assigned value is lower, but the result's expanded uncertainty spans the MRL.

6.9 Participants' Analytical Methods

A variety of analytical methods were used by participants in this study (Appendix 2).

Participants used a sample size between 10 g and 28 g per analysis, with the majority of participants using around 10 g. There was no evident correlation between the results obtained and sample mass used for analysis (Figure 25).



z-Scores greater than 10 have been plotted at 10.

Figure 25 z-Score vs Sample Mass Used for Analysis

Participants reported using a variety of extraction techniques including QuEChERS, liquid-liquid, solid-liquid and solid phase extraction, using acetonitrile, acetone, hexane, ethyl acetate, dichloromethane, methanol, water, acetic acid, and combinations of these as the extraction solvent. Most participants reported using a clean-up step for analysis, such as Florisil and various forms of SPE and dSPE. Participants reported using a number of different instruments, including GC-MS(MS), LC-MS(MS) and GC-NPD/ECD/FPD. The most common methodology used in this study was QuEChERS extraction and clean-up procedure,[11] with acetonitrile as the extraction solvent and using LC-MS/MS for analysis.

Methodology and results obtained are summarised in Figures 26 to 41. Solvent abbreviations used: DCM = Dichloromethane; ACE = Acetone; ACN = Acetonitrile; HEX = Hexane; MeOH = Methanol; EA = Ethyl Acetate, AA = Acetic Acid. Extraction method abbreviations used: SLE = Solid-Liquid Extraction; LLE = Liquid-Liquid Extraction; SPE = Solid-Phase Extraction.

Participants were also requested to analyse the samples using their normal test method and to report a single result as they would to a client, that is, corrected for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **1**, **2**, **3**, **5**, **6**, **7**, **8**, **10**, **13**, **14**, **16**, **17**, **18**, **20**, **21** and **22** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 41% to 139%. Laboratories **3**, **8**, **11**, **14**, **15** and **22** reported that they corrected results for recovery.

No trend with the methodology employed by participants was observed.

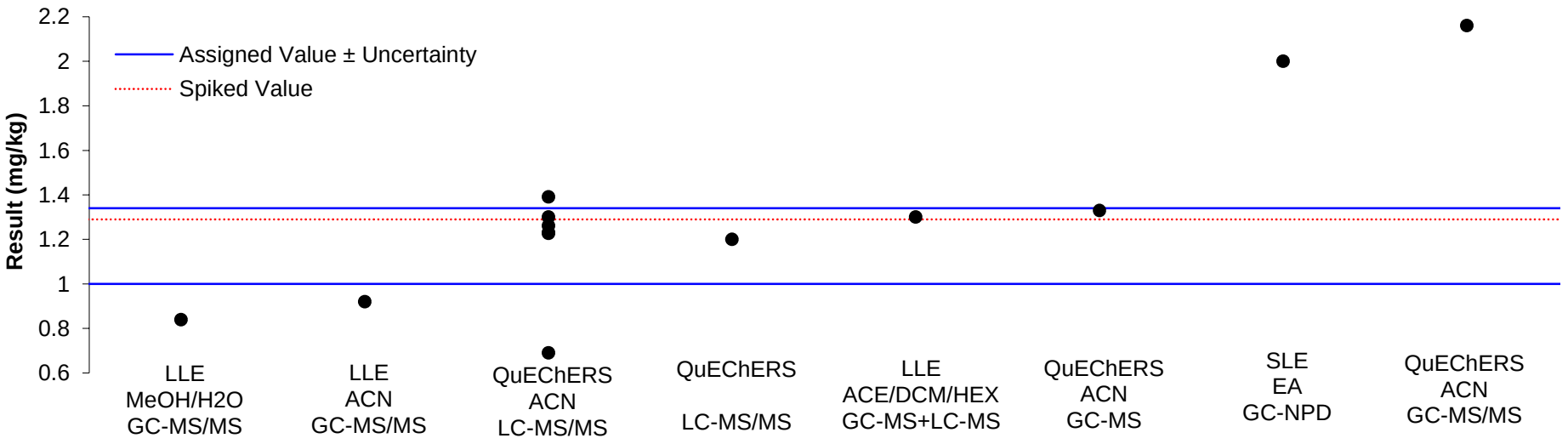


Figure 26 S1 Tomato Azoxystrobin Results vs Methodology

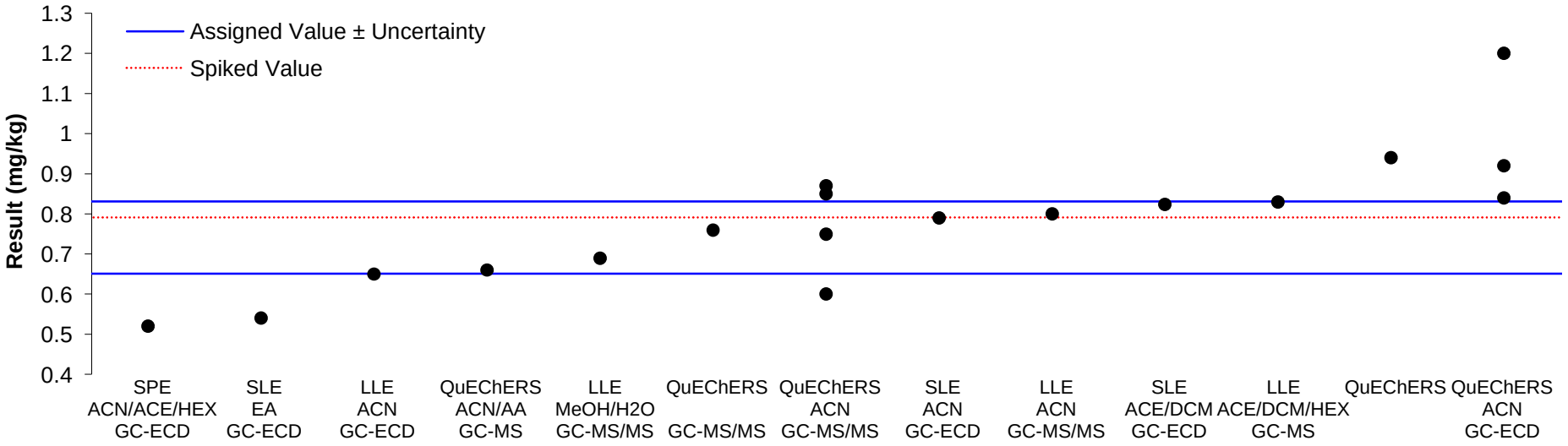


Figure 27 S1 Tomato Endosulfan Sulfate Results vs Methodology

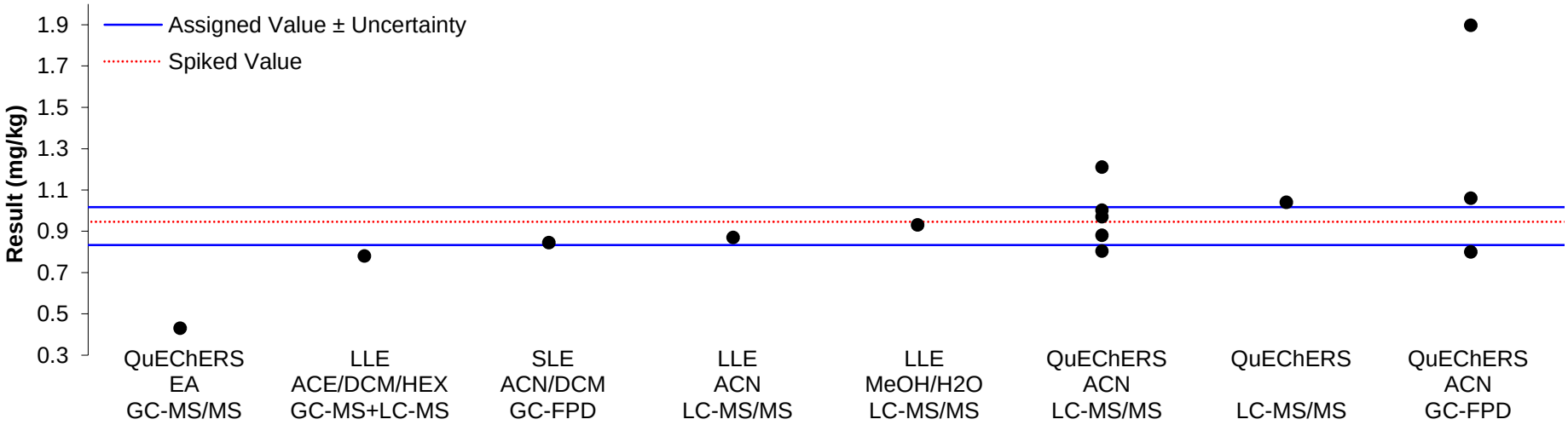


Figure 28 S1 Tomato Methamidophos Results vs Methodology

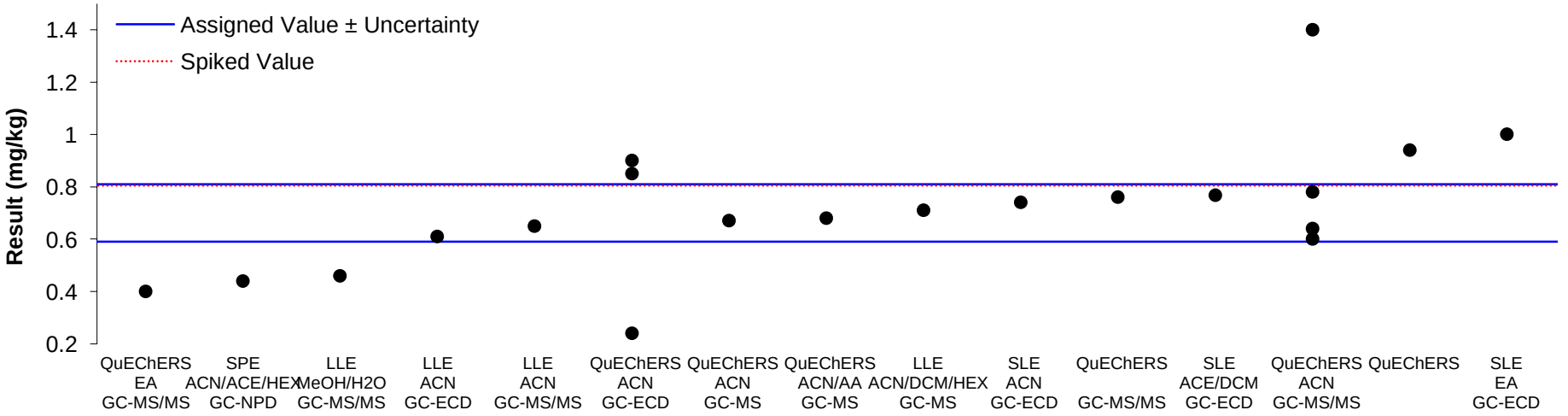


Figure 29 S1 Tomato Permethrin Results vs Methodology

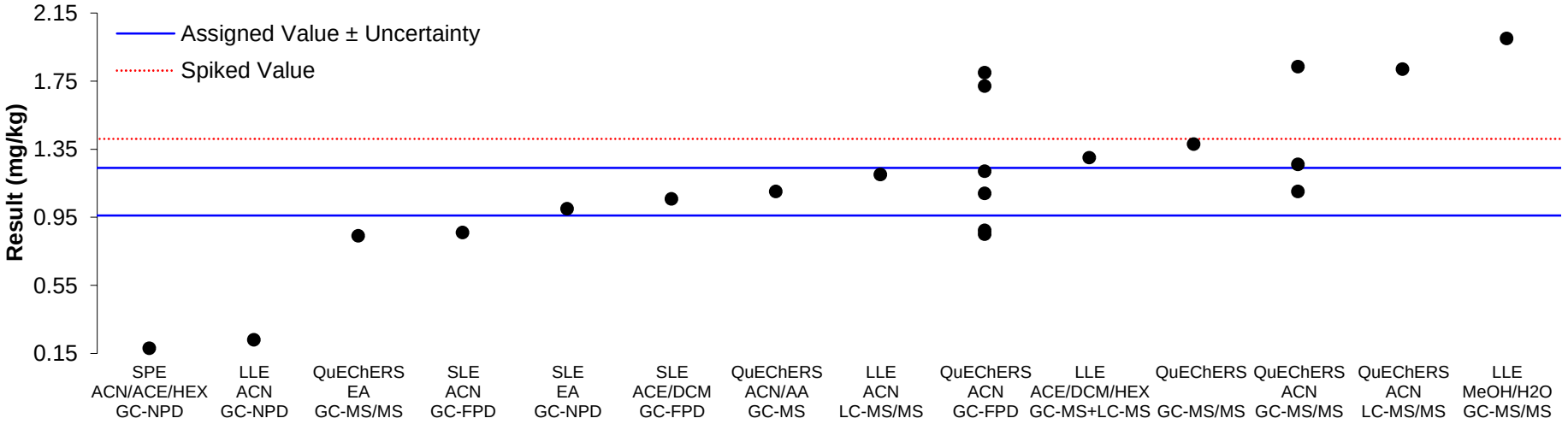


Figure 30 S2 Celery Chlorpyrifos Results vs Methodology

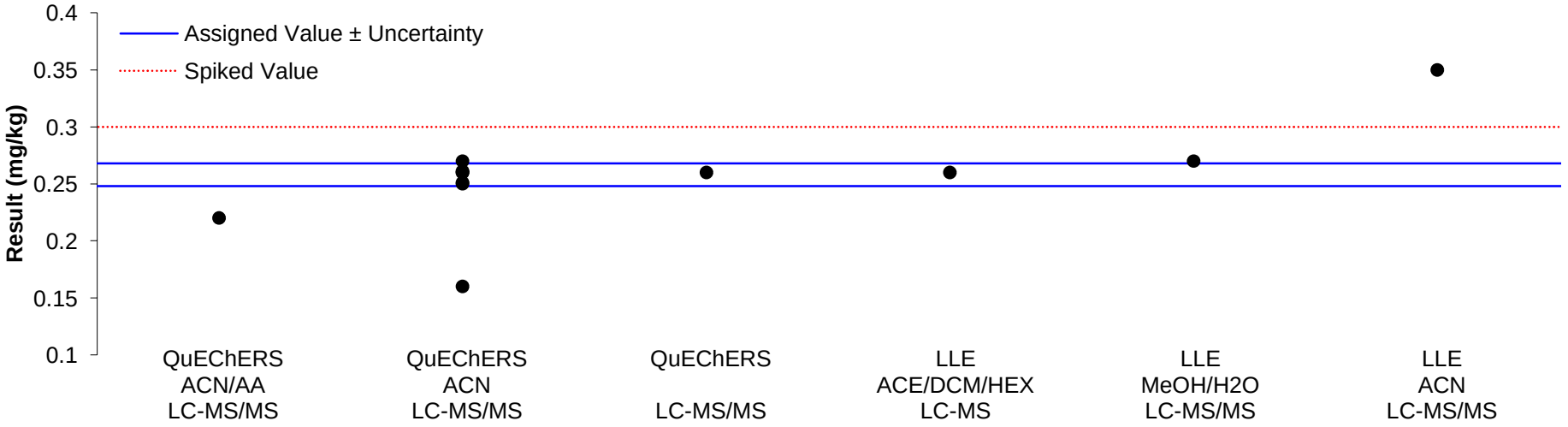


Figure 31 S2 Celery Imidacloprid Results vs Methodology

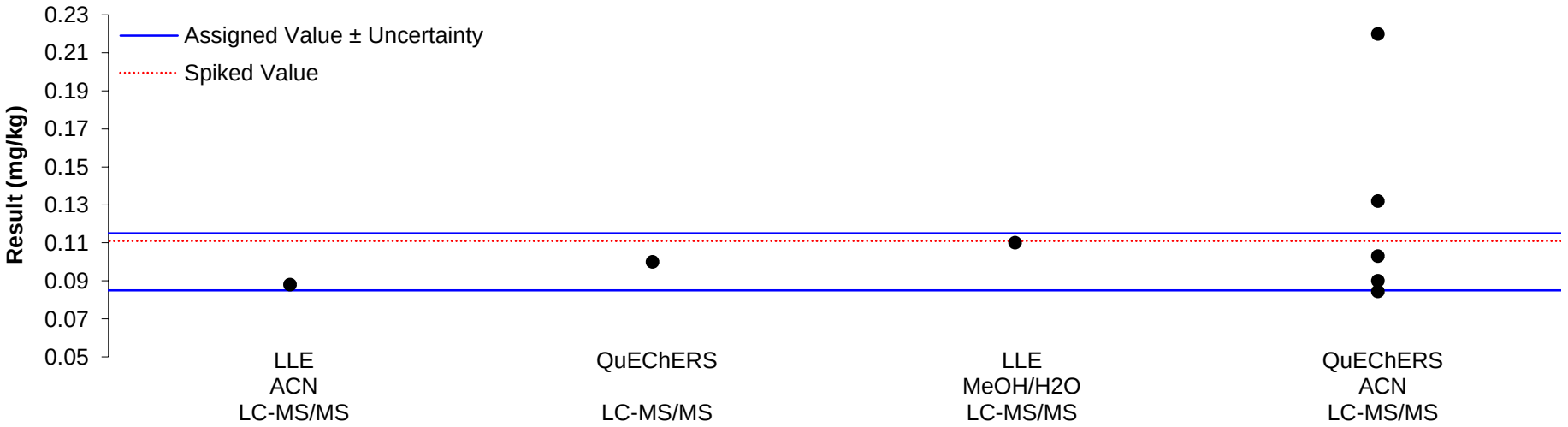


Figure 32 S2 Celery Linuron Results vs Methodology

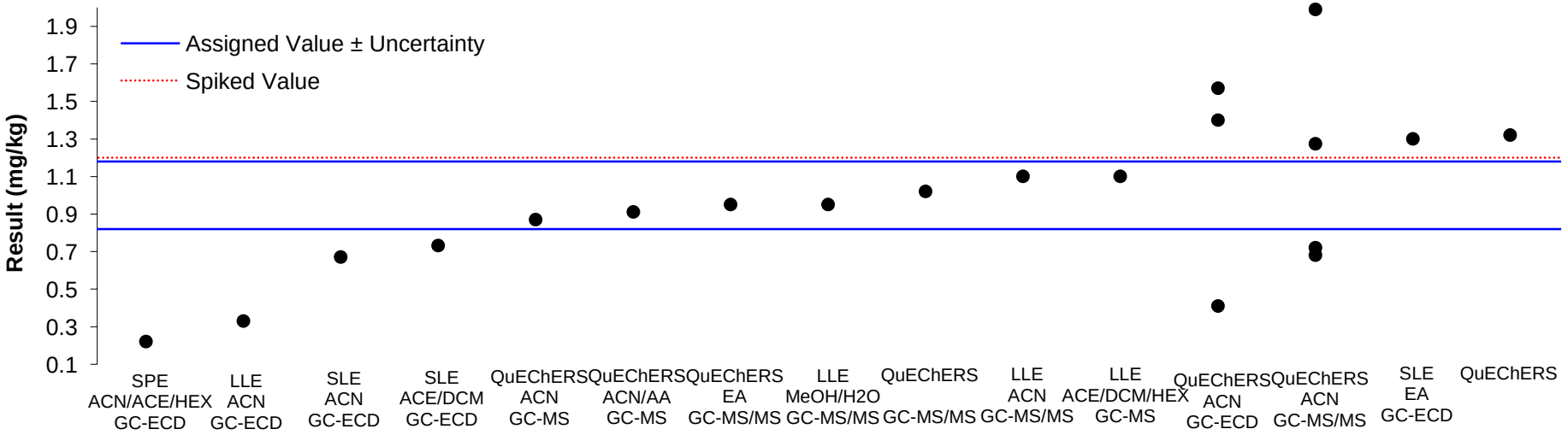
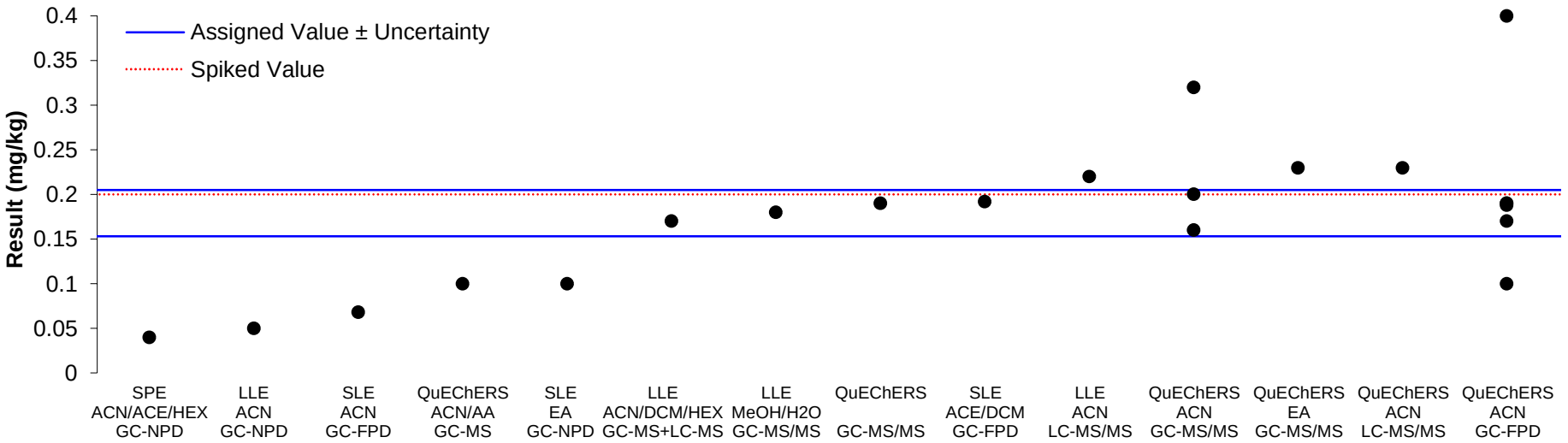


Figure 33 S2 Celery Permethrin Results vs Methodology



Results greater than 0.4 have been plotted at 0.4.

Figure 34 S3 Capsicum Chlopyrifos Results vs Methodology

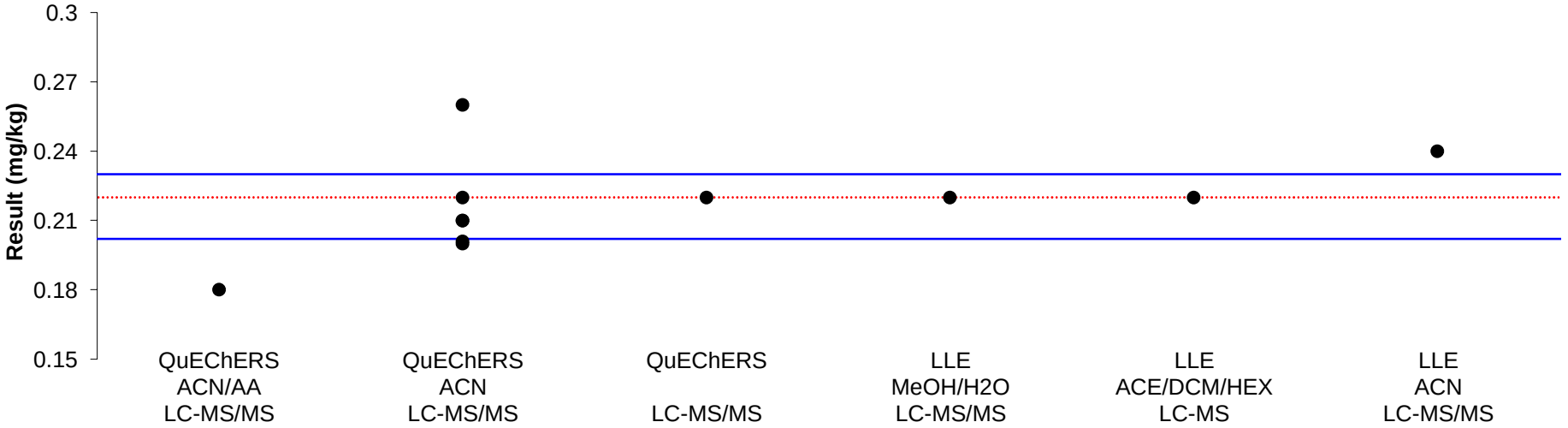


Figure 35 S3 Capsicum Clothianidin Results vs Methodology

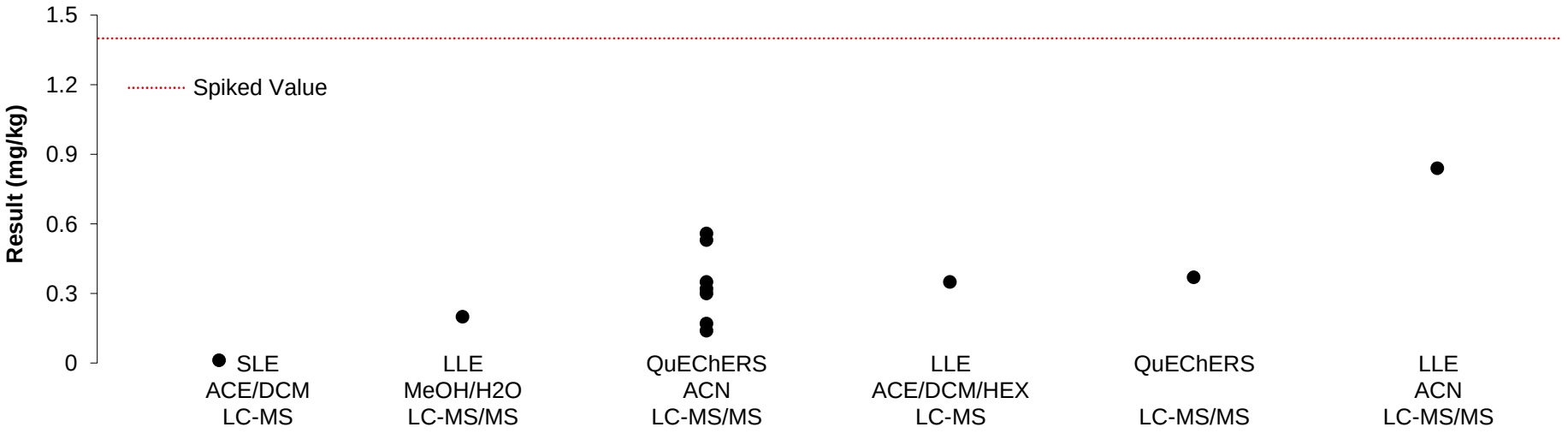


Figure 36 S3 Capsicum Methomyl Results vs Methodology

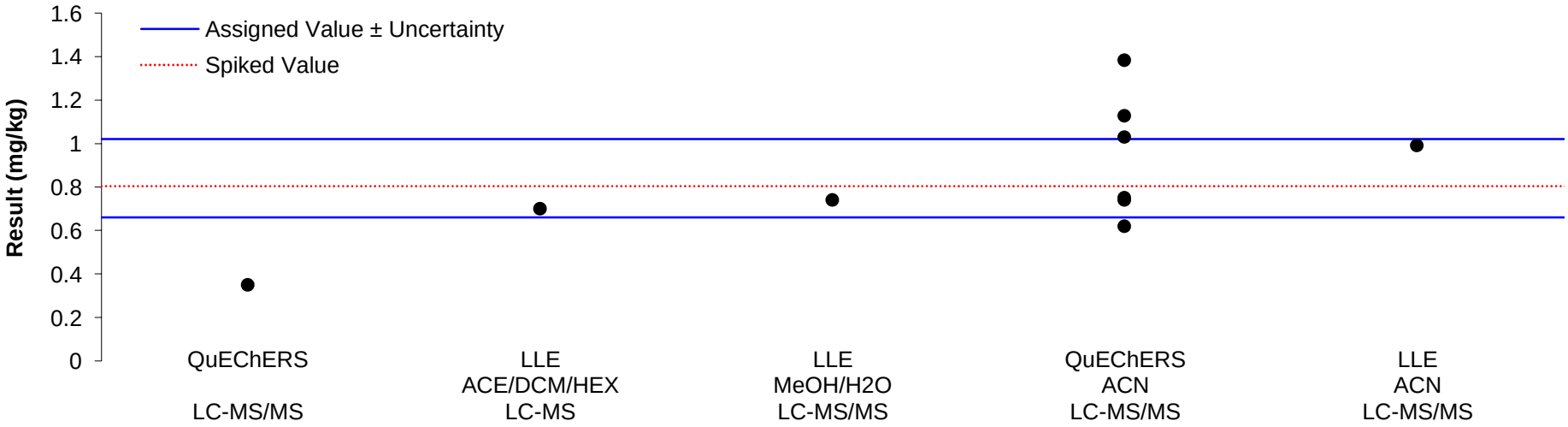


Figure 37 S3 Capsicum Pyraclostrobin Results vs Methodology

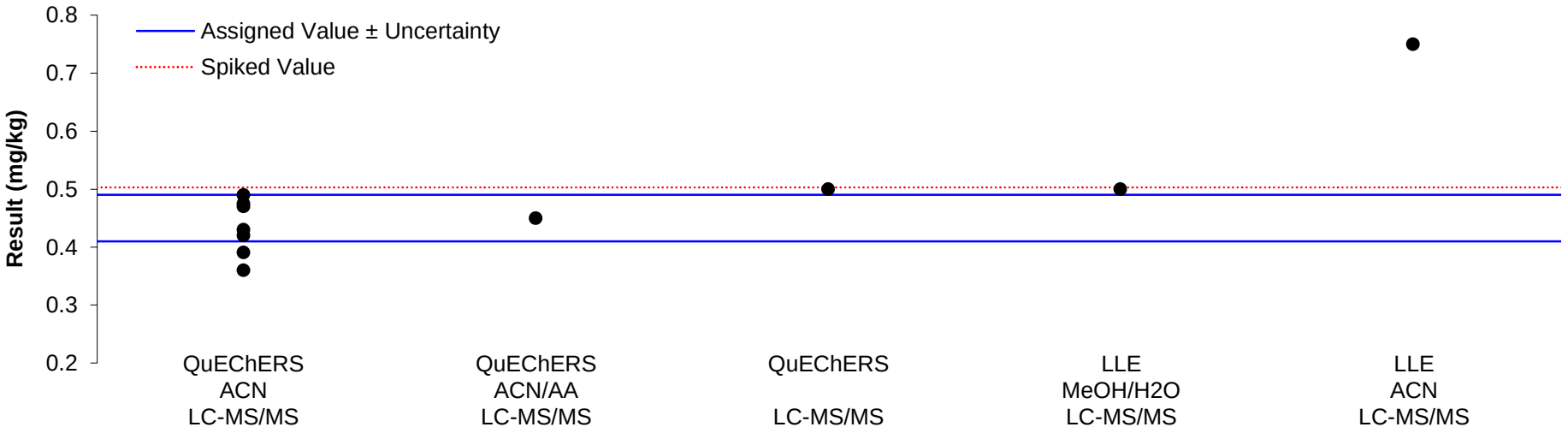


Figure 38 S4 Grapes Acetamiprid Results vs Methodology

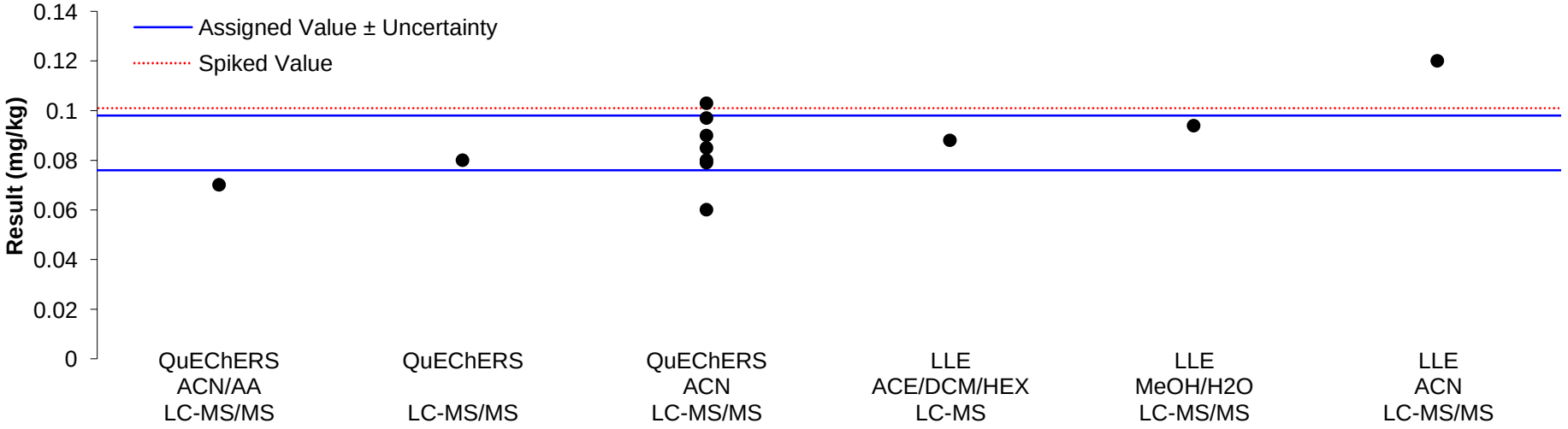


Figure 39 S4 Grapes Imidacloprid Results vs Methodology

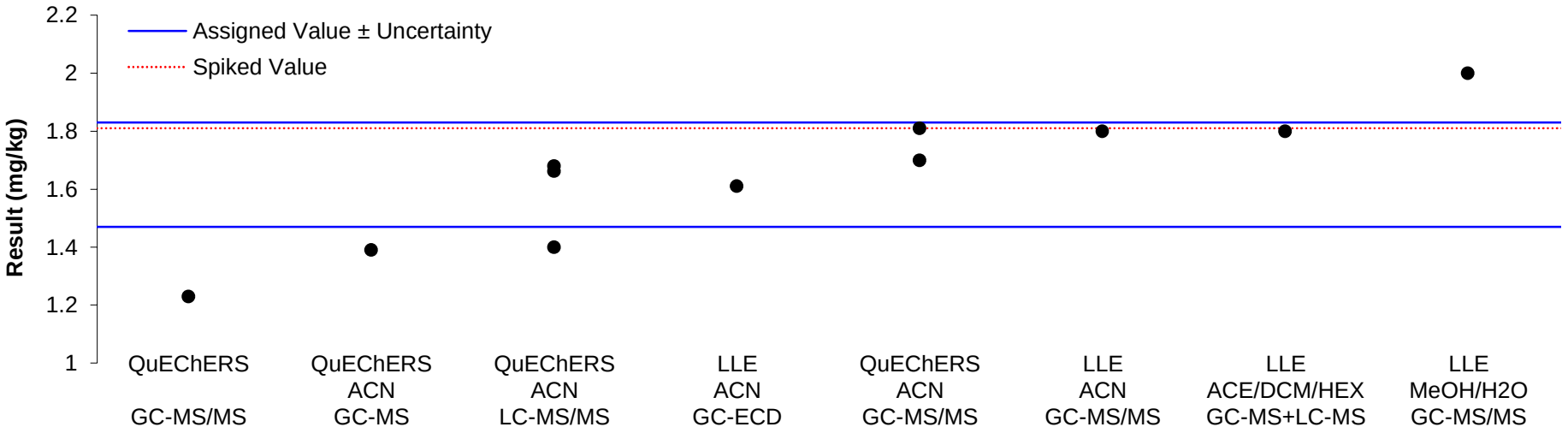


Figure 40 S4 Grapes Iprodione Results vs Methodology

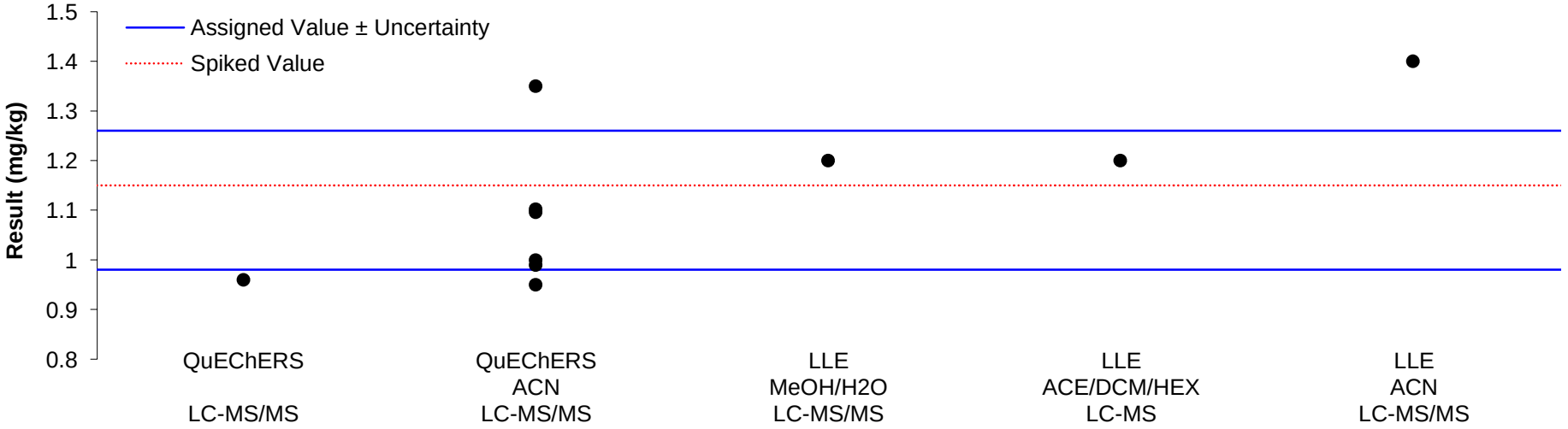


Figure 41 S4 Grapes Pyraclostrobin Results vs Methodology

6.10 Certified Reference Materials (CRM)

Participants were requested to indicate whether certified standards or matrix reference materials had been used as part of the quality assurance for their analysis. Fifteen participants reported using certified standards and one participant reported using matrix reference materials. The following were listed:

- Dr Ehrenstorfer
- AccuStandards
- Sigma Aldrich
- Certified or reference compounds and standards from other suppliers
- Neat materials and other laboratory control samples

These materials may or may not meet the internationally recognised definition of a CRM:

> *'**reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'*[12]

6.11 Effect of Sample Matrix

The samples in this study were purees of tomatoes (S1), celery (S2), capsicums (S3) and grapes (S4). A summary of the results reported and z-scores obtained is presented in Table 27.

The proportion of results reported relative to expected number of results ranged from 50% to 75%, and the proportion of satisfactory z-scores ranged from 74% to 95%. Sample S4 Grapes had the lowest proportion of results reported, but also had the highest rate of satisfactory z-scores.

Table 27 z-Score Comparison by Matrix

Sample	Matrix	Expected Number of Results	Results Reported	z-Scores	Satisfactory z-Scores
S1	Tomato	88	66 (75%)	66	53 (80%)
S2	Celery	88	61 (69%)	61	45 (74%)
S3	Capsicum	88	54 (61%)	42	31 (74%)
S4	Grapes	88	44 (50%)	44	42 (95%)

6.12 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 28 and 29, and Figure 42.

Table 28 Summary of Participants' S1 and S2 Results

Lab. Code	S1 Azoxystrobin (mg/kg)	S1 Endosulfan Sulfate (mg/kg)	S1 Methamidophos (mg/kg)	S1 Permethrin (mg/kg)	S2 Chlorpyrifos (mg/kg)	S2 Imidacloprid (mg/kg)	S2 Linuron (mg/kg)	S2 Permethrin (mg/kg)
Assigned Value	1.17	0.741	0.925	0.7	1.1	0.258	0.1	1
Spiked Value	1.29	0.791	0.946	0.805	1.41	0.3	0.111	1.2
1	NT	0.66	NT	0.68	1.1	0.22	NT	0.91
2	NT	0.52	NT	0.44	0.18	NT	NT	0.22
3	0.92	0.80	0.87	0.65	1.2	0.35	0.088	1.1
4	2.0	0.54	NT	1.0	1.0	NT	NT	1.3
5	NT	NR	1.897	NT	0.873	NT	NT	NT
6	1.39	0.85	0.97	0.64	1.26	0.27	0.22	0.68
7	1.227	0.824	0.845	0.768	1.057	0.261	0.0844	0.732
8	NT	0.92	NT	0.85	1.8	NT	NT	1.4
9	NT	NR	NR	0.24	0.85	NT	NT	0.41
10	NT	1.2	0.8	0.9	1.09	NT	NT	1.57
11	1.20	0.76	1.04	0.76	1.38	0.26	0.10	1.02
12	0.69	0.44	0.43	0.40	0.84	0.26	NT	0.95
13	1.23	NT	1.21	NT	1.82	NT	NT	NT
14	0.84	0.69	0.93	0.46	2.0	0.27	0.11	0.95
15	1.3	0.6	0.88	0.6	1.1	0.25	0.09	0.72
16	1.3	0.83	0.78	0.71	1.3	0.26	NR	1.1
17	NT	0.65	NT	0.61	0.23	NT	NT	0.33
18	1.33	0.84	0.804	0.67	1.22	0.26	0.103	0.87
19	NT	0.94	NT	0.94	NT	NT	NT	1.32
20	2.16	0.75	1.06	1.4	1.72	0.16	NT	1.99
21	1.261	0.87	1.001	0.78	1.835	0.251	0.132	1.273
22	NT	0.79	<LOQ	0.74	0.86	NT	NT	0.67

Shaded cells are results which returned a questionable or unsatisfactory z-score.

Table 29 Summary of Participants' S3 and S4 Results

Lab. Code	S3 Chlorpyrifos (mg/kg)	S3 Clothianidin (mg/kg)	S3 Pyraclostrobin (mg/kg)	S4 Acetamiprid (mg/kg)	S4 Imidacloprid (mg/kg)	S4 Iprodione (mg/kg)	S4 Pyraclostrobin (mg/kg)
Assigned Value	0.179	0.216	0.84	0.45	0.087	1.65	1.12
Spiked Value	0.2	0.22	0.804	0.503	0.101	1.81	1.15
1	0.10	0.18	NT	0.45	0.07	NT	NT
2	0.04	NT	NT	NT	NT	NT	NT
3	0.22	0.24	0.99	0.75	0.12	1.8	1.4
4	0.10	NT	NT	NT	NT	NT	NT
5	0.188	NT	NT	NT	NT	NT	NT
6	0.16	0.26	0.75	0.47	0.097	1.81	0.95
7	0.192	0.201	1.383	0.475	0.0849	1.662	1.096
8	3.1	NT	NT	NT	NT	NT	NT
9	0.1	NT	NT	NT	NT	NT	NT
10	0.19	NT	NT	NT	NT	NT	NT
11	0.19	0.22	0.35	0.50	0.08	1.23	0.96
12	0.23	NT	NT	NT	0.09	NT	NT
13	0.23	0.22	1.03	0.49	NT	1.68	1.35
14	0.18	0.22	0.74	0.50	0.094	2.0	1.2
15	0.2	0.2	0.74	0.42	0.08	1.4	1.0
16	0.17	0.22	0.70	NR	0.088	1.8	1.2
17	0.05	NT	NT	NT	NT	1.61	NT
18	0.19	0.21	0.62	0.43	0.079	1.39	0.99
19	NT	NT	NT	NT	NT	NT	NT
20	0.17	NT	NT	0.36	0.06	NT	NT
21	0.32	0.21	1.128	0.391	0.103	1.7	1.102
22	0.068	NT	NT	NT	NT	NT	NT

Shaded cells are results which returned a questionable or unsatisfactory z-score.

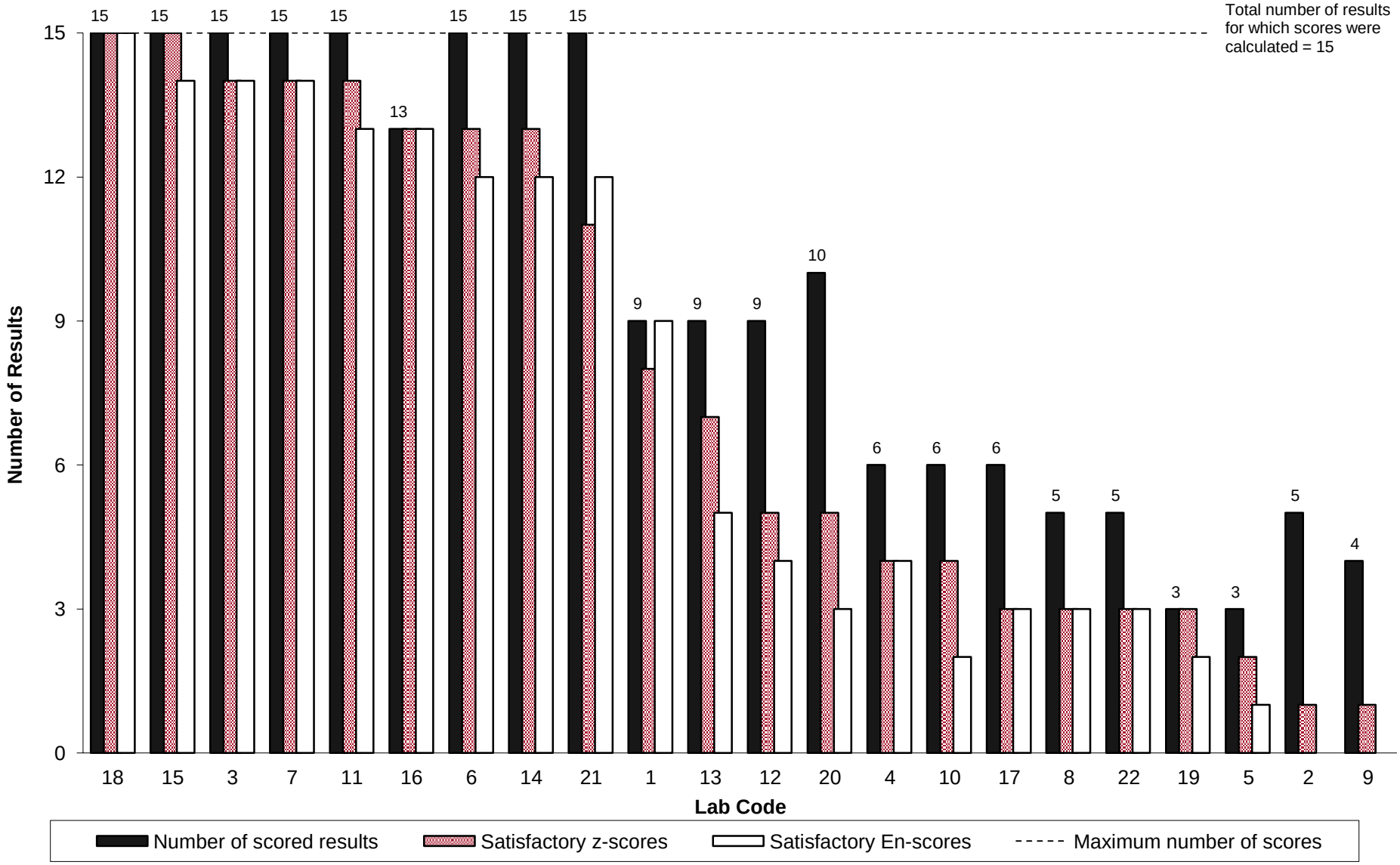


Figure 42 Summary of Participants' Performance

6.13 Comparison with Previous Pesticides in Fruit & Vegetables PT Studies

A summary of participation and reported results rates in Pesticides in Fruit & Vegetables PT studies over the last 10 studies (2014 to 2020) is presented in Figure 43.

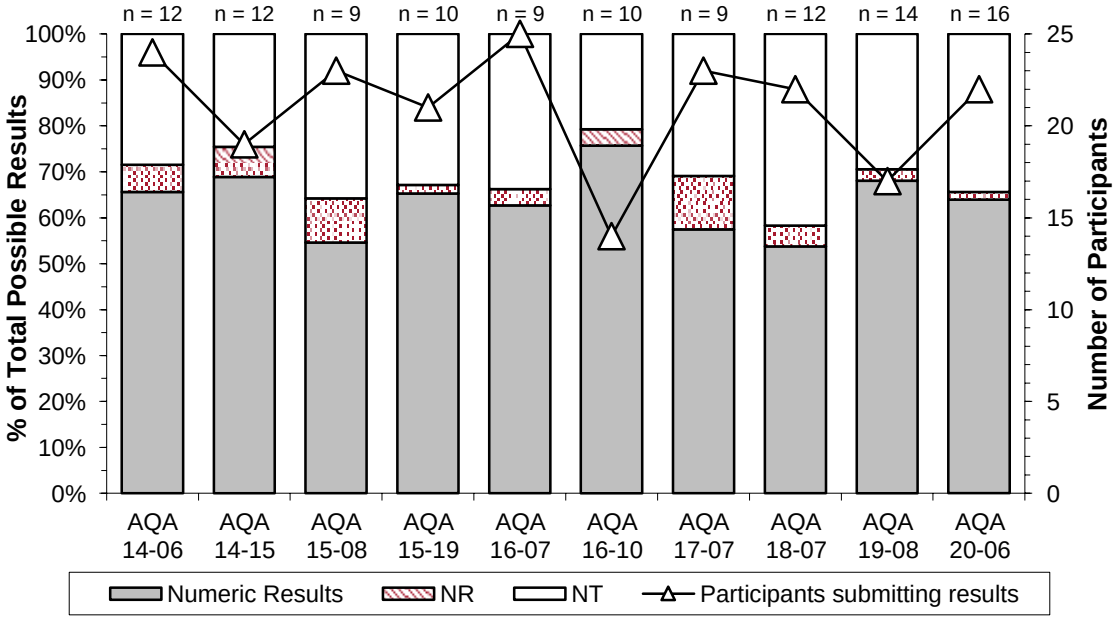


Figure 43 Summary of Participation and Reported Results in Pesticides in Fruit & Vegetables PT Studies (n = number of spiked analytes)

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) in Pesticides in Fruit & Vegetables PT studies over the last 10 studies (2014 to 2020) is presented in Figure 44. To enable direct comparison, the target SD used to calculate z-scores has been kept constant at 15% PCV. Over this period, the average proportion of satisfactory scores was 75% for z-scores and 67% for E_n-scores. While each PT study has a different sample set and a different group of participants, taken as a group, the performance over this period has improved.

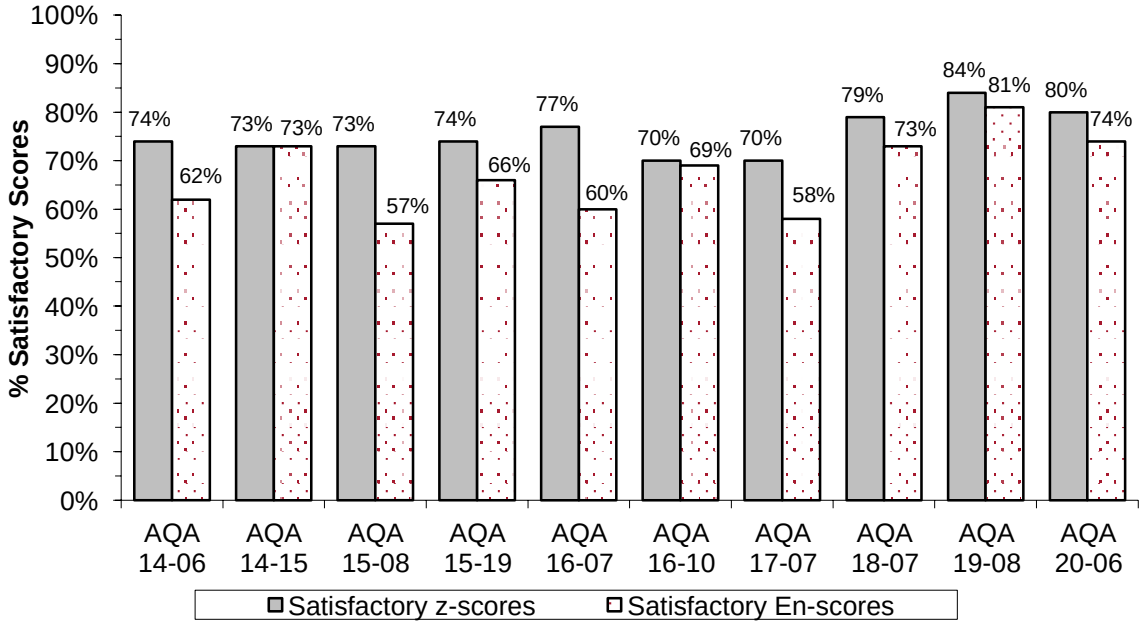


Figure 44 Summary of Participants' Performance for Pesticides in Fruit & Vegetables PT Studies

Individual performance history reports are emailed to participants at the end of each PT study; the consideration of z-scores over time provides much more useful information that a single z-score. Over time, laboratories should expect at least 95% of their z-scores to lie within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ can occasionally occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line is an indication of method or laboratory bias.

7 REFERENCES

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

[2] NMI, 2019, *Study Protocol for Proficiency Testing*, viewed May 2020, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_study_protocol.pdf>.

[3] NMI, 2019, *Chemical Proficiency Testing Statistical Manual*, viewed May 2020, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

[4] Thompson, M., Ellison, S.L.R. and Wood, R., 2006, 'The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem.*, vol 78, pp 145-196.

[5] Federal Register of Legislation, 2020, *Australia New Zealand Food Standards Code – Schedule 20 – Maximum residue limits*, viewed May 2020, <https://www.legislation.gov.au/Details/F2020C00390>.

[6] Food and Agriculture Organization of the United Nations, *NSP – JMPR Reports and evaluations*, viewed May 2020, <http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmpr/jmpr-rep/en/>.

[7] ISO 13528:2015, *Statistical methods for use in proficiency testing by interlaboratory comparison.*

[8] Thompson, M., 2000, 'Recent Trends in Inter-laboratory Precision at ppb and Sub-ppb Concentrations in Relation to Fitness for Purpose Criteria in Proficiency Testing', *Analyst*, vol 125, pp 385-386.

[9] ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories.*

[10] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed May 2020, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[11] Anastassiades, M., Lehotay, S.J., Štajnbaher, D. and Schenck, F.J., 2003, 'Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce', *J. AOAC Int.*, vol 86, pp 412-431.

[12] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition, viewed May 2020, <https://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf>.

APPENDIX 1 – SAMPLE PREPARATION

Test Sample Preparation

Tomatoes, celery and capsicums were bought from a Sydney organic fruit and vegetable wholesaler. As there were no organic grapes available from the normal supplier, red seedless grapes were purchased from a local grocery. In this study, pesticides were spiked at between 5% and 250% of the relevant MRL.

Preparation of Samples S1 (Tomato)

The tomatoes were rinsed using tap water and allowed to air dry. The whole tomato, including the peel, was chopped, pureed and passed through an 850 µm sieve. The sieved puree was continuously stirred while fifty aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution, stirred for at least two hours and bottled. Each bottle was then labelled and shrink-wrapped in plastic film and placed in a freezer.

Preparation of Sample S2 (Celery)

The celery were rinsed using tap water and allowed to air dry. The celery were then chopped, placed in a stainless steel drum, pureed with a stick mixer and passed through an 850 µm sieve. To the resultant 10751 g of sieved puree, 493.8 g of Milli-Q water was added. The puree was continuously stirred while fifty aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution, stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

Preparation of Sample S3 (Capsicum)

The capsicums were rinsed with tap water and allowed to dry. They were placed into a stainless steel drum and blended using a stick mixer to form a puree which was passed through an 850 µm sieve. The puree was continuously stirred while fifty aliquots of at least 100 g were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution, stirred for at least two hours and bottled. Each bottle was then labelled, shrink-wrapped and placed in a freezer.

Preparation of Sample S4 (Grapes)

The grapes were washed and allowed to dry overnight. The stalks were then removed and the grapes were placed in a stainless steel drum and blended using a stick mixer to create a puree which was sieved through an 850 µm sieve. The sieved grapes were stirred and unspiked samples were dispensed into 200 mL amber bottles. The remaining grape puree was adjusted to 6560 g by removing excess puree with an Optifix pump. The puree was then spiked with each pesticide standard solution, stirred for one and a half hours and dispensed into bottles which were then labelled, shrink-wrapped and placed in a freezer.

APPENDIX 2 – PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 30 to 46.

Table 30 Sample Mass Used for Analysis

Lab. Code	S1 Sample Mass (g)	S2 Sample Mass (g)	S3 Sample Mass (g)	S4 Sample Mass (g)
1	10	10	10	10
2	10	10		
3	10	10	10	10
4	28.13	28.13	28.03	20.09
5	20	20	20	20
6	10	10	10	10
7	10 (25 for Endosulfan sulfate, Methamidophos and Permethrin)	25 for Chlorpyrifos and Permethrin	25 for Chlorpyrifos and Methomyl	
8	15	15	15	15
9	20	20	20	20
10	20	20	20	20
11	10.4	10.2	9.97	10.05
12	10	10	10	10
13	15	15	15	15
14	10	10	10	10
15	10	10	10	10
16	25			
17	10	10	10	10
18	10	10	10	10
19	15			
20	10	20 and 10	10	10
21	10	10	10	10
22	10	10	10	10

Table 31 Sample S1 Tomato Azoxystrobin Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	NT				
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	GC-MS/MS	
4	Solid-Liquid	Quechers	Ethyl Acetate	GC-NPD	
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	QuEChERS	SPE (PSA)	Acetonitrile	LC-MS/MS	
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS, LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-MS	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	GC-MS/MS	
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 32 Sample S1 Tomato Endosulfan Sulfate Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS	Florisil	1%Acetic acid/Acetonitrile	GC-MS	
2	SPE	C18/Envicarb/Florisil	Acetonitrile/Acetone/Hexane	GC-ECD	
3	Liquid-Liquid	dSPE	Acetonitrile	GC-MS/MS	
4	Solid-Liquid	Quechers	Ethyl Acetate	GC-ECD	
5	QuEChERS	deactivate silica gel	Hexane	GC-ECD	
6	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
7	Solid-Liquid	Florisil	Acetone : DCM	GC-ECD	Sample weight 25 g
8	QuEChERS	SPE(C18, GCB/PSA)	Acetonitrile	GC-ECD	
9	QuEChERS	Florisil	Acetonitrile	GC-ECD	
10	QuEChERS	Dispersive Solid Phase Extraction Clean-up	Acetonitrile	GC-ECD	
11	QuEChERS			GC-MS/MS	
12					
13	NT				
14	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ	
15	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS	averaged
17	Liquid-Liquid	C18,GCB & florisil	Acetonitrile	GC-ECD	
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-ECD	
19	QuEChERS				MODIFIED
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	GC-MS/MS	
21	QuEChERS	PSA	Acetonitrile	GCMSMS	
22	Solid-Liquid	Carbon-C18-Florisil	Acetonitrile	GC-ECD	

Table 33 Sample S1 Tomato Methamidophos Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	NT				
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	QuEChERS		Acetonitrile	GC-FPD	
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	Solid-Liquid	-	Acetone : DCM	GC-FPD	Sample weight 25 g
8	NT				
9					
10	QuEChERS	Dispersive Solid Phase Extraction Clean-up	Acetonitrile	GC-FPD	
11	QuEChERS			LC-MS/MS	
12	QuEChERS	SPE (PSA)	Ethyl Acetate	GC-MS/MS	
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS, LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	GC-FPD	
21	QuEChERS		Acetonitrile	LCMSMS	
22	Solid-Liquid	Carbon-C18-Florisil	Acetonitrile	GC-FPD	

Table 34 Sample S1 Tomato Permethrin Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS	Florisil	1%Acetic acid/Acetonitrile	GC-MS	
2	SPE	C18/Envicarb/Florisil	Acetonitrile/Acetone/Hexane	GC-NPD	
3	Liquid-Liquid	dSPE	Acetonitrile	GC-MS/MS	
4	Solid-Liquid	Quechers	Ethyl Acetate	GC-ECD	
5	NT				
6	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
7	Solid-Liquid	Florisil	Acetone : DCM	GC-ECD	Sample weight 25 g
8	QuEChERS	SPE(C18, GCB/PSA)	Acetonitrile	GC-ECD	
9	QuEChERS	Florisil	Acetonitrile	GC-ECD	
10	QuEChERS	Dispersive Solid Phase Extraction Clean-up	Acetonitrile	GC-ECD	
11	QuEChERS			GC-MS/MS	
12	QuEChERS	SPE (PSA)	Ethyl Acetate	GC-MS/MS	
13	NT				
14	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ	
15	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS	averaged
17	Liquid-Liquid	C18,GCB & florisil	Acetonitrile	GC-ECD	
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-MS	
19	QuEChERS				MODIFIED
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	GC-MS/MS	
21	QuEChERS	PSA	Acetonitrile	GCMSMS	
22	Solid-Liquid	Carbon-C18-Florisil	Acetonitrile	GC-ECD	

Table 35 Sample S2 Celery Chlorpyrifos Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS	Florisil	1%Acetic acid/Acetonitrile	GC-MS	
2	SPE	C18/Envicarb/Florisil	Acetonitrile/Acetone/Hexane	GC-NPD	
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	Solid-Liquid	Quechers	Ethyl Acetate	GC-NPD	
5	QuEChERS		Acetonitrile	GC-FPD	
6	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
7	Solid-Liquid	-	Acetone : DCM	GC-FPD	Sample weight 25 g
8	QuEChERS	SPE(C18, GCB/PSA)	Acetonitrile	GC-FPD	
9	QuEChERS	Florisil	Acetonitrile	GC-FPD	
10	QuEChERS	Dispersive Solid Phase Extraction Clean-up	Acetonitrile	GC-FPD	
11	QuEChERS			GC-MS/MS	
12	QuEChERS	SPE (PSA)	Ethyl Acetate	GC-MS/MS	
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ	
15	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS, LCMS	averaged
17	Liquid-Liquid	C18,GCB & florisil	Acetonitrile	GC-NPD	
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-FPD	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	GC-FPD	
21	QuEChERS	PSA	Acetonitrile	GCMSMS	
22	Solid-Liquid	Carbon-C18-Florisil	Acetonitrile	GC-FPD	

Table 36 Sample S2 Celery Imidacloprid Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS		1%Acetic acid/Acetonitrile	LC-MS/MS	
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	QuEChERS	SPE (PSA)	Acetonitrile	LC-MS/MS	
13	NT				
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	LC-MS/MS	
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 37 Sample S2 Celery Linuron Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	NT				
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	NT				
13	NT				
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16					
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	NT				
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 38 Sample S2 Celery Permethrin Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS	Florisil	1%Acetic acid/Acetonitrile	GC-MS	
2	SPE	C18/Envicarb/Florisil	Acetonitrile/Acetone/Hexane	GC-ECD	
3	Liquid-Liquid	dSPE	Acetonitrile	GC-MS/MS	
4	Solid-Liquid	Quechers	Ethyl Acetate	GC-ECD	
5	NT				
6	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
7	Solid-Liquid	Florisil	Acetone : DCM	GC-ECD	Sample weight 25 g
8	QuEChERS	SPE(C18, GCB/PSA)	Acetonitrile	GC-ECD	
9	QuEChERS	Florisil	Acetonitrile	GC-ECD	
10	QuEChERS	Dispersive Solid Phase Extraction Clean-up	Acetonitrile	GC-ECD	
11	QuEChERS			GC-MS/MS	
12	QuEChERS	SPE (PSA)	Ethyl Acetate	GC-MS/MS	
13	NT				
14	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ	
15	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS	averaged
17	Liquid-Liquid	C18,GCB & florisil	Acetonitrile	GC-ECD	
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-MS	
19	QuEChERS				MODIFIED
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	GC-MS/MS	
21	QuEChERS	PSA	Acetonitrile	GCMSMS	
22	Solid-Liquid	Carbon-C18-Florisil	Acetonitrile	GC-ECD	

Table 39 Sample S3 Capsicum Chlorpyrifos Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS	Florisil	1%Acetic acid/Acetonitrile	GC-MS	
2	SPE	C18/Envicarb/Florisil	Acetonitrile/Acetone/Hexane	GC-NPD	
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	Solid-Liquid	Quechers	Ethyl Acetate	GC-NPD	
5	QuEChERS		Acetonitrile	GC-FPD	
6	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
7	Solid-Liquid	-	Acetone : DCM	GC-FPD	Sample weight 25 g
8	QuEChERS	SPE(C18, GCB/PSA)	Acetonitrile	GC-FPD	
9	QuEChERS	Florisil	Acetonitrile	GC-FPD	
10	QuEChERS	Dispersive Solid Phase Extraction Clean-up	Acetonitrile	GC-FPD	
11	QuEChERS			GC-MS/MS	
12	QuEChERS	SPE (PSA)	Ethyl Acetate	GC-MS/MS	
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ	
15	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS, LCMS	averaged
17	Liquid-Liquid	C18,GCB & florisil	Acetonitrile	GC-NPD	
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-FPD	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	GC-FPD	
21	QuEChERS	PSA	Acetonitrile	GCMSMS	
22	Solid-Liquid	Carbon-C18-Florisil	Acetonitrile	GC-FPD	

Table 40 Sample S3 Capsicum Clothianidin Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS		1%Acetic acid/Acetonitrile	LC-MS/MS	
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	NT				
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	NT				
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 41 Sample S3 Capsicum Methomyl Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	NT				
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	Solid-Liquid	NH2	Acetone : DCM	LC-MS	Sample weight 25 g
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	QuEChERS	SPE (PSA)	Acetonitrile	LC-MS/MS	
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	LC-MS/MS	
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 42 Sample S3 Capsicum Pyraclostrobin Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	NT				
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	NT				
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	NT				
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 43 Sample S4 Grape Acetamiprid Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS		1%Acetic acid/Acetonitrile	LC-MS/MS	
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	NT				
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16					
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	LC-MS/MS	
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 44 Sample S4 Grape Imidacloprid Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	QuEChERS		1%Acetic acid/Acetonitrile	LC-MS/MS	
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	QuEChERS	SPE (PSA)	Acetonitrile	LC-MS/MS	
13	NT				
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	QuEChERS	dispersive solid phase extraction cleanup	acetonitrile	LC-MS/MS	
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

Table 45 Sample S4 Grape Iprodione Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	NT				
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	GC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	GC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			GC-MS/MS	
12	QuEChERS	SPE (PSA)	Ethyl Acetate	GC-MS/MS	
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	GCMS, LCMS	averaged
17	Liquid-Liquid	C18,GCB & florisil	Acetonitrile	GC-ECD	
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-MS	
19	NT				
20	NT				
21	QuEChERS	PSA	Acetonitrile	GCMSMS	
22	NT				

Table 46 Sample S4 Grape Pyraclostrobin Methodology

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Measurement Instrument	Comments
1	NT				
2	NT				
3	Liquid-Liquid	dSPE	Acetonitrile	LC-MS/MS	
4	NT				
5	NT				
6	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
7	QuEChERS	Dispersive SPE	Acetonitrile	LC-MS/MS	
8	NT				
9	NT				
10	NT				
11	QuEChERS			LC-MS/MS	
12	NT				
13	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
14	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ	
15	QuEChERS	PSA	Acetonitrile	LC-MS/MS	
16	Liquid-Liquid		Acetone,DCM, Hexane	LCMS	averaged
17	NT				
18	QuEChERS	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS	
19	NT				
20	NT				
21	QuEChERS		Acetonitrile	LCMSMS	
22	NT				

APPENDIX 3 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, Z-SCORE AND E_N-SCORE CALCULATIONS

Robust Average and Associated Uncertainty

The robust average was calculated using the procedure described in ISO 13258:2015 'Statistical methods for use in proficiency testing by interlaboratory comparisons–Annex C'.[7] The uncertainty was estimated as:

$$u_{rob\ av} = 1.25 \times S_{rob\ av} / \sqrt{p} \qquad \textit{Equation 4}$$

where:

$u_{rob\ av}$ is the standard uncertainty of the robust average

$S_{rob\ av}$ is the standard deviation of the robust average

p is the number of results

The expanded uncertainty ($U_{rob\ av}$) is the standard uncertainty multiplied by a coverage factor of 2 at approximately 95% confidence level.

A worked example is set out below in Table 47.

Table 47 Uncertainty of Robust Average for Clothianidin in Sample S3

No. results (p)	11
Robust Average	0.216 mg/kg
$S_{rob\ av}$	0.019 mg/kg
$u_{rob\ av}$	0.007 mg/kg
k	2
$U_{rob\ av}$	0.014 mg/kg

The robust average for clothianidin in Sample S3 is 0.216 ± 0.014 mg/kg.

z-Score and E_n-Score Calculation

For each participant's result, a z-score and E_n-score are calculated according to Equations 2 and 3 respectively.

A worked example for is set out below in Table 48.

Table 48 z-Score and E_n-Score for Sample S1 Azoxystrobin Result Reported by Laboratory 3

Participant Result (mg/kg)	Assigned Value (mg/kg)	Target Standard Deviation	z-Score	E_n-Score
0.92 ± 0.29	1.17 ± 0.17	15% as CV, or: $0.15 \times 1.17 = 0.1755$ mg/kg	z-Score = $\frac{0.92-1.17}{0.1755}$ = -1.42	E_n-Score = $\frac{0.92-1.17}{\sqrt{0.29^2+0.17^2}}$ = -0.74

APPENDIX 4 – ACRONYMS AND ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
AA	Acetic Acid
ACE	Acetone
ACN	Acetonitrile
CITAC	Co-Operation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
dSPE	Dispersive Solid Phase Extraction
EA	Ethyl Acetate
ECD	Electron Capture Detector
FAO	Food and Agriculture Organization of the United Nations
FPD	Flame Photometric Detector
GC	Gas Chromatography
GUM	Guides to the expression of Uncertainty in Measurement
HEX	Hexane
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOR	Limit of Reporting
Max.	Maximum value in a set of results
Md	Median value in a set of results
Min.	Minimum value in a set of results
MRL	Maximum Residue Limit
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
NATA	National Association of Testing Authorities, Australia
NMI	National Measurement Institute, Australia
NPD	Nitrogen Phosphorus Detector
NR	Not Reported
NT	Not Tested

p,p'-DDT	Dichlorodiphenyltrichloroethane
PCV	Performance Coefficient of Variation
PSA	Primary/Secondary Amines
PT	Proficiency Test
QuEChERS	Quick Easy Cheap Effective Rapid Safe (an extraction technique)
R.A.	Robust Average
RM	Reference Material
S.V.	Spiked or formulated Value of a PT sample
SANTE	Directorate-General for Health and Food Safety
SD	Standard Deviation
SI	International System of Units
SLE	Solid-Liquid Extraction
SPE	Solid Phase Extraction
SS	Spiked Samples
WHO	World Health Organisation

END OF REPORT