Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 22-04A Pesticides in Soil

July 2022

This report replaces AQA 22-04.

REVISION HISTORY

Date	Report Number	Reason for review
July 2022	AQA 22-04	Final Report – Original issue.
July 2022	AQA 22-04A	Summary, Section 2.2 – Correction to Sample S2 spiked analyte name (p,p'-DDD was spiked).

ACKNOWLEDGMENTS

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

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Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

SUMMARY

AQA 22-04 Pesticides in Soil commenced in March 2022. Twenty-six laboratories enrolled to participate, and all participants submitted results.

Two soil samples were prepared using topsoil bought from a Sydney supplier. The soil was spiked with known amounts of various pesticides (atrazine, ethion, imidacloprid and metsulfuron-methyl for Sample S1, and fipronil, lindane, MCPA and p,p'-DDD for Sample S2).

Of a possible 208 results, a total of 122 numeric results (59%) were submitted. Fifteen results were submitted as a 'less than' value (<*x*) or Not Reported (NR), and 71 results were submitted as 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 were assessed against the aims as follows:

- *Assess the ability of participants to correctly identify environmentally significant pesticides in soil.*

Laboratories **3**, **9** and **15** reported results for all scored analytes.

Four laboratories did not report results for spiked analytes that they tested for (total of seven results). One laboratory reported an analyte that was not spiked into the test sample.

- *Compare the performances of participants and assess their accuracy in the measurement of pesticides in soil.*

Of 115 z scores, 104 (90%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

Of 115 E_n scores, 100 (87%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratory **9** returned satisfactory z and E_n scores for all scored analytes.

- *Evaluate participants' methods for the measurement of pesticides in soil.*

Participants used a wide variety of methods, and no correlation with results was evident.

- *Develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates.*

Of 122 numeric results, 111 (92%) were reported with an associated estimate of uncertainty. The magnitude of these expanded uncertainties ranged from 5.0% to 100% of the reported value.

- *Produce materials that can be used in method validation and as control samples.*

The test samples produced for this study are homogeneous and are well characterised. Surplus of these samples is available for purchase and can be used for quality control and for method validation purposes.

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 inter-laboratory 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 studies in:

- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- controlled drug assay, drugs in wipes and clandestine laboratory;
- per- and polyfluoroalkyl substances in water, soil, biota and food; and
- allergens in food.

1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify environmentally significant pesticides in soil;
- compare the performances of participants and assess their accuracy in the measurement of pesticides in soil;
- evaluate participants' methods for the measurement of pesticides in soil;
- develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates; and
- produce materials that can be used in method validation and as control samples.

The choice of the test method was left to the participating laboratories.

1.3 Study Conduct

The conduct of NMI PT studies 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 and The International Harmonized Protocol for The Proficiency Testing of Analytical Chemistry Laboratories.[1,4]

NMI is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of PT schemes.[1] This study is within the scope of NMI's accreditation.

2 STUDY INFORMATION

2.1 Selection of Pesticides

A list of possible analytes spiked into Samples S1 and S2 is presented in Table 1. This list was also provided to all participants.

Table 1 List of Possible Analytes

2,4-D	alpha-Endosulfan	Malathion
Aldrin	beta-Endosulfan	MCPA
Atrazine	Endosulfan sulfate	Metsulfuron-methyl
Bifenthrin	Ethion	p,p'-DDD
cis-Chlordane	Fenitrothion	p,p'-DDE
trans-Chlordane	Fenthion	p,p'-DDT
Total Chlordane	Fenvalerate	Total DDT
Chlorpyrifos	Fipronil	Parathion
Cyfluthrin	Glyphosate	Parathion-methyl
Cypermethrin	Heptachlor	Permethrin
Diazinon	Heptachlor epoxide	Simazine
Dicamba	Hexachlorobenzene	Tebuconazole
Dieldrin	Imidacloprid	Triclopyr
Diuron	Lindane	Trifluralin

The actual spiked pesticides for Samples S1 and S2 are presented in Table 2. The pesticides and spiked values used in this study were selected with consideration to:

- a variety of pesticides amenable to gas and/or liquid chromatography; and
- the National Environmental Protection (Assessment of Site Contamination) Measure Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

Table 2 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty (mg/kg)*
S1	Atrazine	0.353	0.018
	Ethion	0.199	0.010
	Imidacloprid	0.151	0.008
	Metsulfuron-methyl	0.851	0.043
S2	Fipronil	1.50	0.07
	Lindane	0.350	0.017
	MCPA	0.756	0.038
	p,p'-DDD	0.600	0.030

* The uncertainty is an expanded uncertainty at approximately 95% confidence using a coverage factor of 2. It has been estimated with consideration to contributions from the gravimetric and volumetric operations involved in spiking the samples, and the purity of the pesticide reference standards. Stability was not considered in the uncertainty budget and so the expanded uncertainty relates to the mass fraction of analyte at the time of spiking.

2.2 Study Timetable

The timetable of the study was:

Invitation sent	18/03/2022
Samples dispatched	19/04/2022
Results due	3/06/2022
Interim report sent	8/06/2022

2.3 Participation and Laboratory Code

Twenty-six laboratories enrolled to participate in this study, and all participants were assigned a confidential laboratory code number. All participants submitted results.

2.4 Sample Preparation

Two soil samples were prepared by spiking soil purchased from a Sydney supplier with various pesticides to obtain the mass fractions listed in Table 2. Further information on the preparation of the samples is given in Appendix 1.

2.5 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this PT study's samples. The samples were prepared, packaged and stored using a process that has been demonstrated to produce homogeneous and stable samples in previous NMI Pesticides in Soil PT studies.

Participants' results gave no reason to question the transport stability or homogeneity of the samples (Appendix 2).

To further assess possible instability, the results returned by participants were compared to the spiked values. Assigned values for scored analytes were within 52% to 84% of the spiked value, which is similar to ratios observed in previous NMI Pesticides in Soil PT studies (for example, as presented in PT Report AQA 16-04 Pesticides in Soil).[6] An assigned value was set if there was a reasonable consensus of participants' results.

2.6 Sample Storage, Dispatch and Receipt

The test samples were refrigerated at 4 °C prior to dispatch. Participants were sent 50 g spiked soil for each of Samples S1 and S2. The samples were packed in a polystyrene foam box with cooler bricks and sent by courier on 19 April 2022.

The following items were packaged with the samples:

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

An Excel spreadsheet for the electronic reporting of results was emailed to participants.

2.7 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- Participants need not test for all listed analytes.

- For each analyte in each sample report a single result on as received basis in units of mg/kg.
- Report results as you would report 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 uncertainty (e.g. 0.50 ± 0.02 mg/kg).
- Report any listed pesticide not tested with NT as the result.
- 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 as requested in the results sheet (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.
- Please complete the method details as requested in the Methodology sheet.
- Please return the completed results sheet by email (proficiency@measurement.gov.au).
- Return the completed results sheet by 16 May 2022. Late results may not be included in the study report.

The results due date was extended to 3 June 2022 due to courier delivery delays to some international participants.

2.8 Interim Report

An interim report was emailed to all participants on 8 June 2022.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses received are presented in Appendix 3.

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about their basis of measurement uncertainty (MU). Responses received are presented in Table 3. Some responses may be modified so that the participant cannot be identified.

Table 3 Basis of Uncertainty 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	Recoveries of SS	ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	CRM Instrument calibration Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
3	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	CRM Laboratory bias from PT studies Recoveries of SS Standard purity	
4	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Recoveries of SS	ISO/GUM
5	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	CRM Recoveries of SS	
6	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies	Eurachem/CITAC Guide
7		Instrument calibration	Recoveries of SS	
8	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	Eurachem/CITAC Guide
9	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
10	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	
11	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
12	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA Technical Note 33
13	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	Eurachem/CITAC Guide
14	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	ISO/GUM
15	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
16	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples Duplicate analysis	CRM Laboratory bias from PT studies Recoveries of SS	Nordtest Report TR537
17	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis		ISO/GUM
18		Control samples Duplicate analysis Instrument calibration	Recoveries of SS	
19	Top down approach using reference material results.	Control samples - RM Duplicate analysis	Recoveries of SS	ISO/GUM
20	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	Eurachem/CITAC Guide
21	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM	CRM	ISO/GUM
22	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA Technical Note 33

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
23	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	CRM Recoveries of SS	Eurachem/CITAC Guide
24	Standard uncertainty based on historical data	Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	Eurachem/CITAC Guide
25	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
26	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		ISO/GUM

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

3.3 Participants' Comments

Participants were invited to make comments on the samples, study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments are presented in Table 4. Some comments may be modified so that the participant cannot be identified.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
5	S2	Fipronil result is express as the sum of Fipronil + Fipronil sulfone	For this report we have calculated the value for fipronil only by subtracting the reported value of fipronil sulfone from the original reported result.
6	All	Uncertainty: Laboratory Macro MU Calculation Pack based on QC Data	
16	All	Methodology sheet not useful for pre-treatments + methods We have examined the offered parameters of the AQA 22-04 with different analysis methods (LC, GC). However, the sheet is designed for only one method, e.g. only one sample weight could be noted in the header (either that of the LC method or that of the GC method). It would make sense to enter the following data for each method used: Weighed-in quantity; Extraction agent; Extraction volume; Concentration; Clean-up	Thank you for your feedback. We will take these suggestions into consideration for future PT studies.
23	All	NMI should consider spiking more target analytes rather than a select few.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 12 with the summary statistics: robust average, median, mean, 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 9, with an example chart with interpretation guide shown in Figure 1.

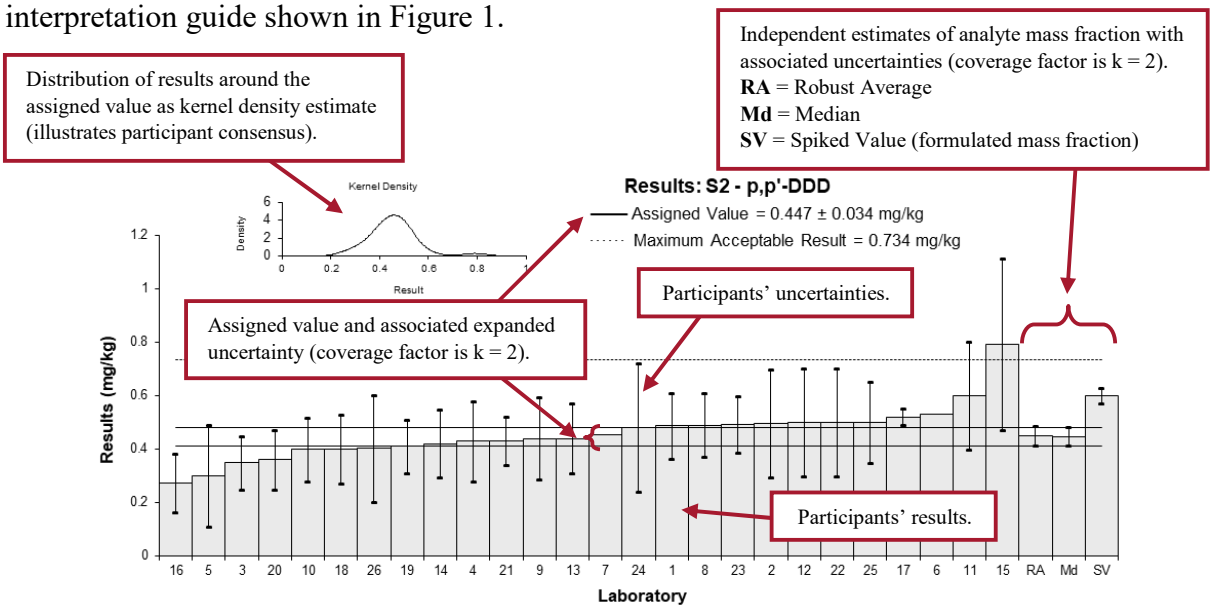


Figure 1 Guide to Presentation of Results

4.2 Outliers and Gross Errors

Outliers were results less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value.[3,4] Gross errors, if applicable, were obvious blunders, e.g. results with incorrect units, or for a different analyte or sample, and such results were removed before the calculation of all summary statistics.[3]

4.3 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 were the robust averages of participants' results and the expanded uncertainties were estimated from the associated robust SDs (Appendix 4).

4.4 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 as described in ISO 13528:2015.[7]

4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between-laboratory variation that in the judgement of the study coordinator would be expected from participants, given the levels of analytes present. The PCV is not the CV of participants' results. It is set by the study coordinator and 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 other participants' performance and can be compared from study to study.

4.6 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (X) and the PCV, as presented in Equation 1. This value is used for calculation of z scores.

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

4.7 z Score

For each participant's 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

To account for potential low bias in consensus value due to inefficient methodologies, scores may be adjusted for a 'maximum acceptable result' (see Section 6.3 for more information).

For the absolute value of a z score:

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

4.8 E_n Score

The E_n score is complementary to the z score in assessment of laboratory performance. E_n score includes 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 uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

For the absolute value of an E_n score:

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

4.9 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025 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	S1
Analyte	Atrazine
Matrix	Soil
Unit	mg/kg

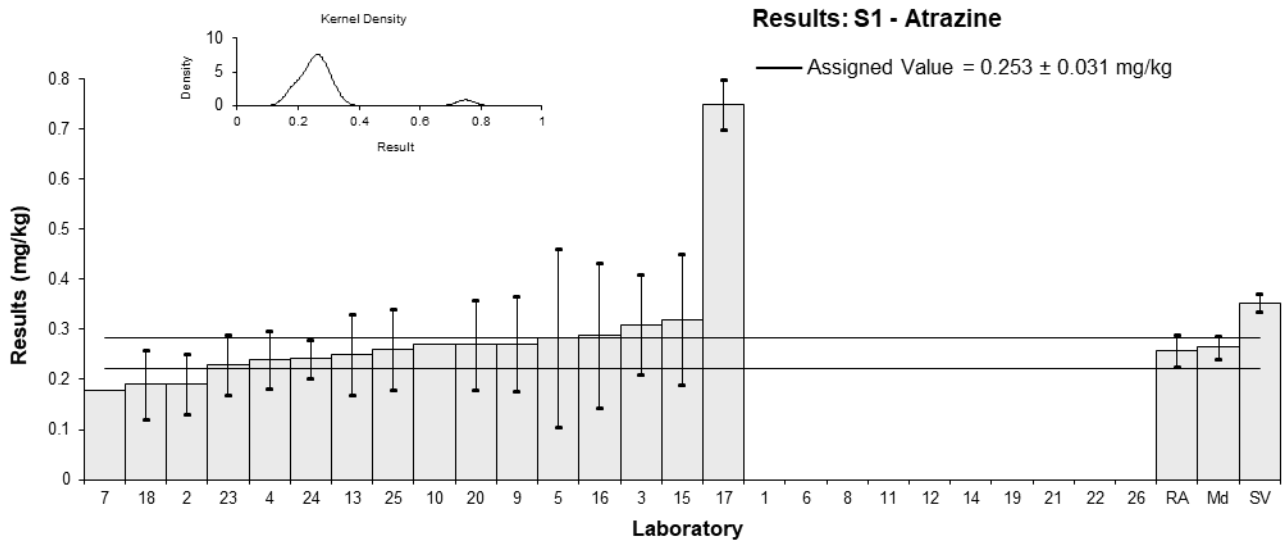
Participant Results

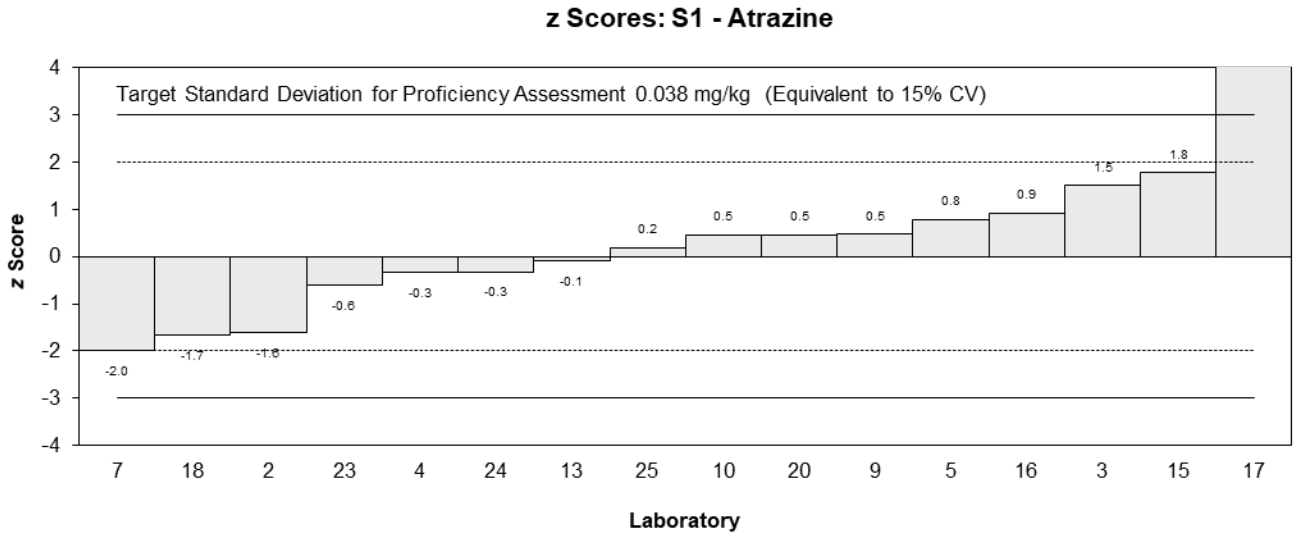
Lab. Code	Result	U	Rec	z	E_n
1	<0.5	NR	NR		
2	0.192	0.06	NR	-1.61	-0.90
3	0.31	0.1	112	1.50	0.54
4	0.24	0.058	88	-0.34	-0.20
5	0.283	0.178	108	0.79	0.17
6	NT	NT	NT		
7	0.178	NR	75	-1.98	-2.42
8	NT	NT	NT		
9	0.271	0.0948	91	0.47	0.18
10	0.27	NR	NR	0.45	0.55
11	<0.5	NR	80-120		
12	<0.5	NR	NR		
13	0.25	0.08	NR	-0.08	-0.03
14	NT	NT	NT		
15	0.32	0.13	88	1.77	0.50
16	0.288	0.144	NR	0.92	0.24
17*	0.75	0.05	NR	13.10	8.45
18	0.19	0.07	NR	-1.66	-0.82
19	<0.5	0.5	NR		
20	0.27	0.09	108	0.45	0.18
21	NT	NT	NT		
22	<0.5	NR	80-120		
23	0.23	0.06	65.2	-0.61	-0.34
24	0.241	0.039	NR	-0.32	-0.24
25	0.26	0.08	84	0.18	0.08
26	NT	NT	NT		

* Outlier

Statistics

Assigned Value	0.253	0.031
Spiked Value	0.353	0.018
Robust Average	0.258	0.032
Median	0.265	0.023
Mean	0.284	0.065
N	16	
Max	0.75	
Min	0.178	
Robust SD	0.051	
Robust CV (%)	20	


Results: S1 - Atrazine
Kernel Density
Density
Result
Assigned Value = 0.253 ± 0.031 mg/kg
Results (mg/kg)
Laboratory
7 18 2 23 4 24 13 25 10 20 9 5 16 3 15 17 1 6 8 11 12 14 19 21 22 26 RA Md SV


z Scores: S1 - Atrazine
Target Standard Deviation for Proficiency Assessment 0.038 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
-2.0 -1.7 -1.6 -0.6 -0.3 -0.3 -0.1 0.2 0.5 0.5 0.5 0.8 0.9 1.5 1.8
7 18 2 23 4 24 13 25 10 20 9 5 16 3 15 17

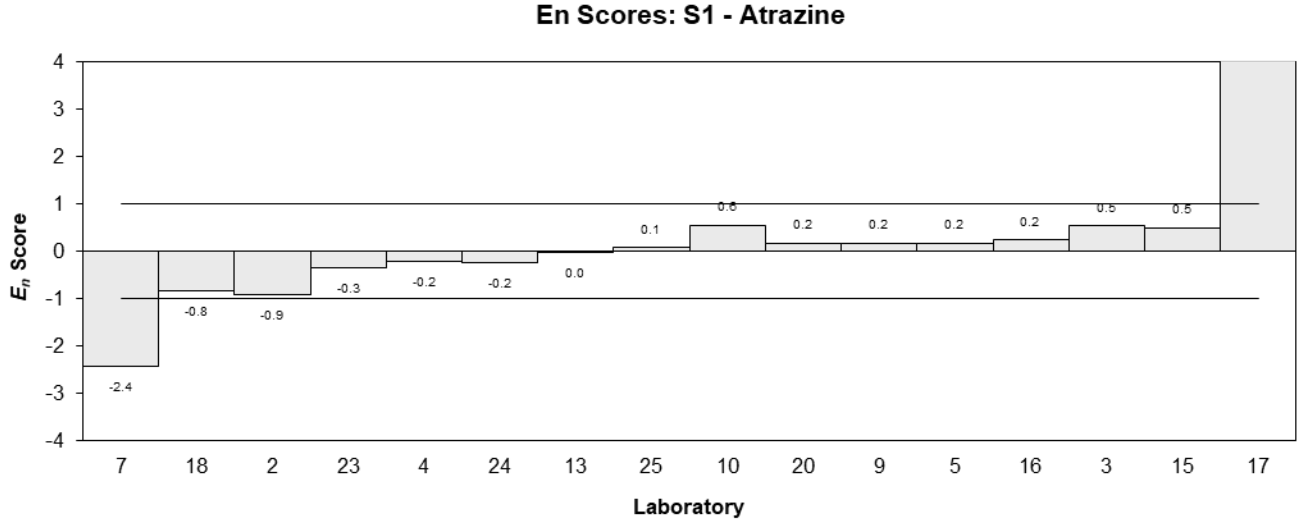

En Scores: S1 - Atrazine
En Score
Laboratory
-2.4 -0.8 -0.9 -0.3 -0.2 -0.2 0.0 0.1 0.6 0.2 0.2 0.2 0.2 0.5 0.5
7 18 2 23 4 24 13 25 10 20 9 5 16 3 15 17

Figure 2

Table 6

Sample Details

Sample	S1
Analyte	Ethion
Matrix	Soil
Unit	mg/kg

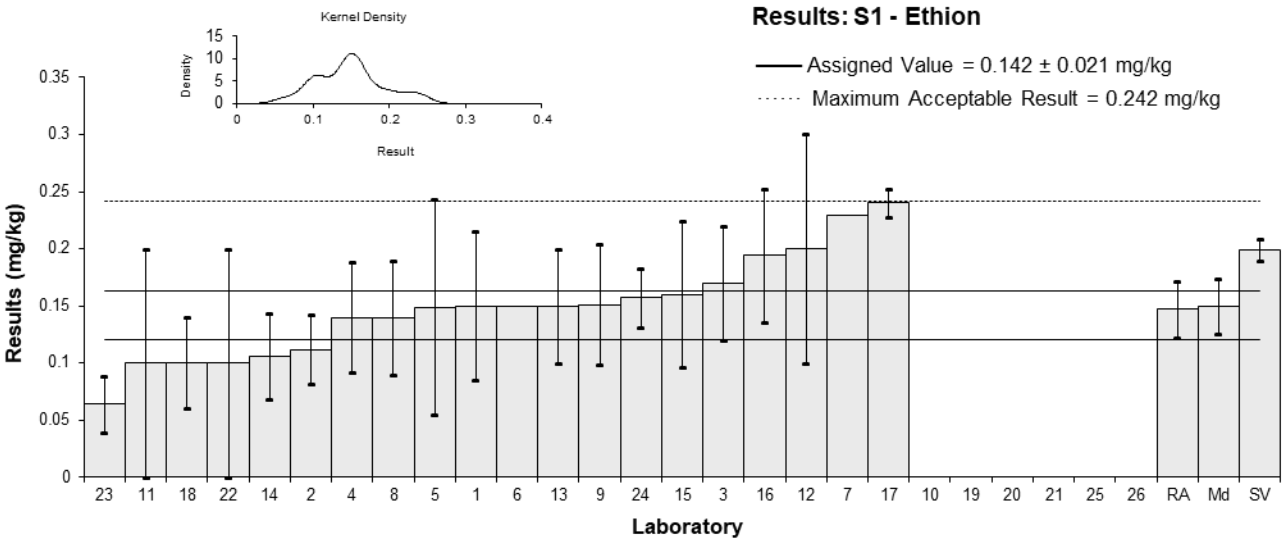
Participant Results

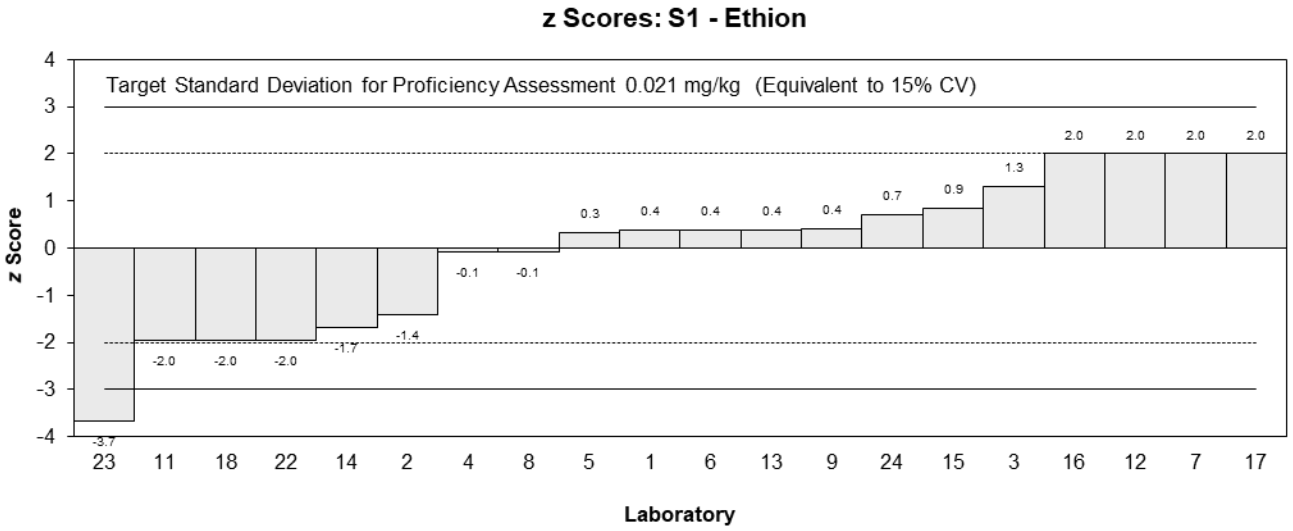
Lab. Code	Result	U	Rec	z	E_n
1	0.150	0.065	NR	0.38	0.12
2	0.112	0.03	NR	-1.41	-0.82
3	0.17	0.05	112	1.31	0.52
4	0.14	0.048	81	-0.09	-0.04
5	0.149	0.094	97	0.33	0.07
6	0.15	NR	NR	0.38	0.38
7*	0.229	NR	114	2.00▼	1.00▼
8	0.14	0.05	NR	-0.09	-0.04
9	0.151	0.0528	90	0.42	0.16
10	NR	NR	NR		
11	0.1	0.1	80-120	-1.97	-0.41
12	0.2	0.1	NR	2.00▼	0.57
13	0.15	0.05	NR	0.38	0.15
14	0.106	0.038	NR	-1.69	-0.83
15	0.16	0.064	110	0.85	0.27
16	0.194	0.0582	NR	2.00▼	0.84
17*	0.24	0.012	NR	2.00▼	1.00▼
18	0.1	0.04	NR	-1.97	-0.93
19	<0.2	0.2	NR		
20	NT	NT	NT		
21	NT	NT	NT		
22	0.1	0.1	80-120	-1.97	-0.41
23*	0.064	0.025	105	-3.66	-2.39
24	0.157	0.026	NR	0.70	0.45
25	NT	NT	NT		
26	< 0.2	0.06	NR		

* Outlier, ▼ Adjusted score

Statistics

Assigned Value	0.142	0.021
Spiked Value	0.199	0.010
Robust Average	0.147	0.025
Max Acceptable Result	0.242	
Median	0.150	0.024
Mean	0.148	0.020
N	20	
Max	0.24	
Min	0.064	
Robust SD	0.044	
Robust CV (%)	30	


Results: S1 - Ethion
Kernel Density
Density
Result
Assigned Value = 0.142 ± 0.021 mg/kg
Maximum Acceptable Result = 0.242 mg/kg
Results (mg/kg)
Laboratory
23 11 18 22 14 2 4 8 5 1 6 13 9 24 15 3 16 12 7 17 10 19 20 21 25 26 RA Md SV


z Scores: S1 - Ethion
Target Standard Deviation for Proficiency Assessment 0.021 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
23 11 18 22 14 2 4 8 5 1 6 13 9 24 15 3 16 12 7 17

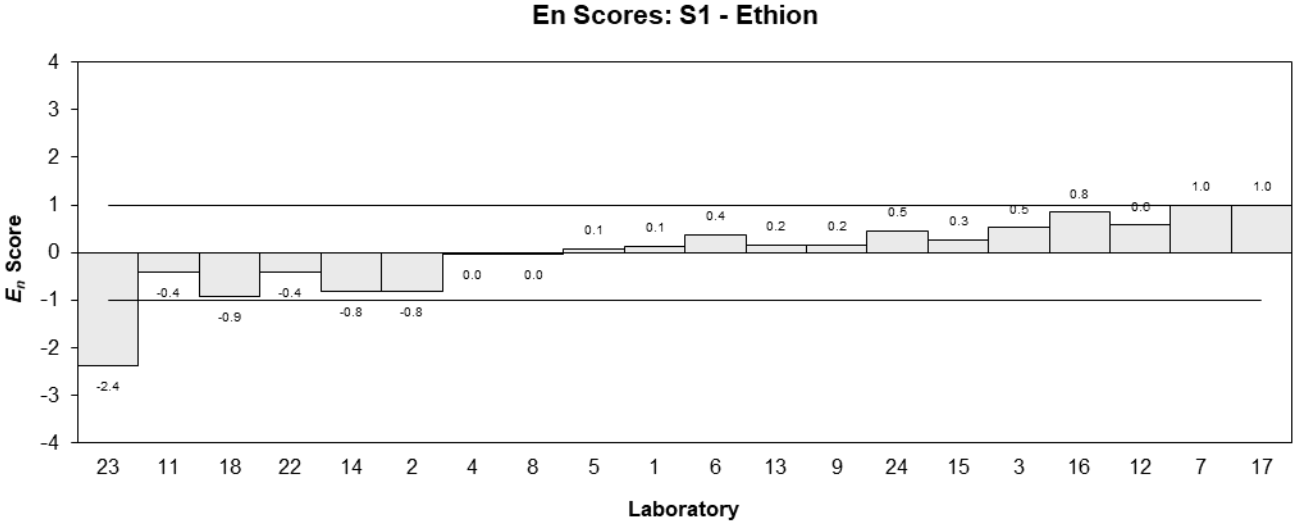

En Scores: S1 - Ethion
En Score
Laboratory
23 11 18 22 14 2 4 8 5 1 6 13 9 24 15 3 16 12 7 17

Figure 3

Table 7

Sample Details

Sample	S1
Analyte	Imidacloprid
Matrix	Soil
Unit	mg/kg

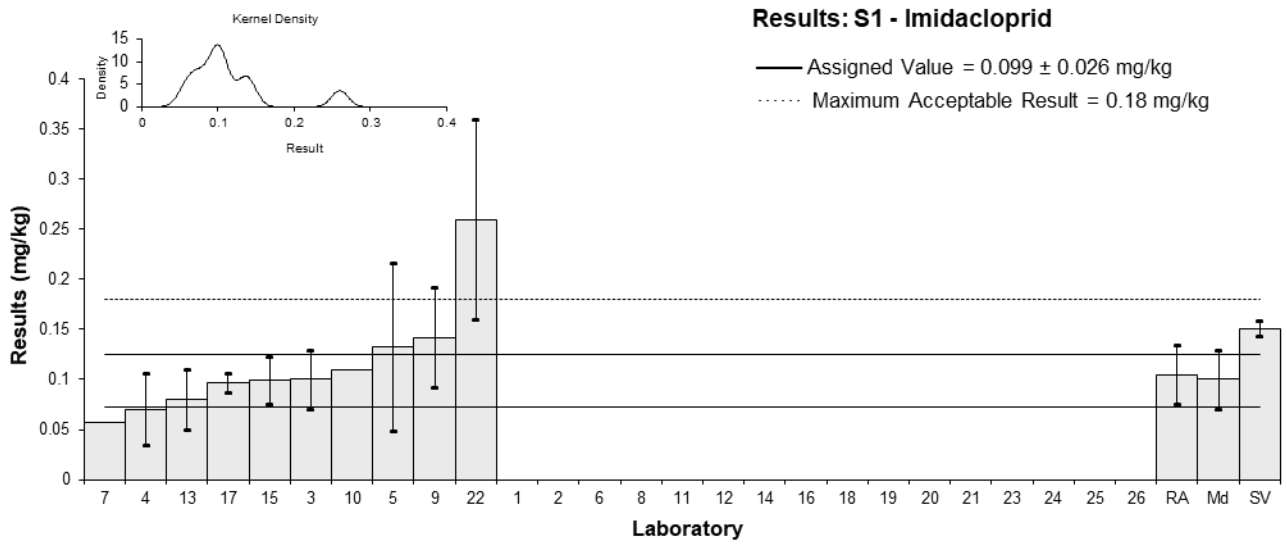
Participant Results

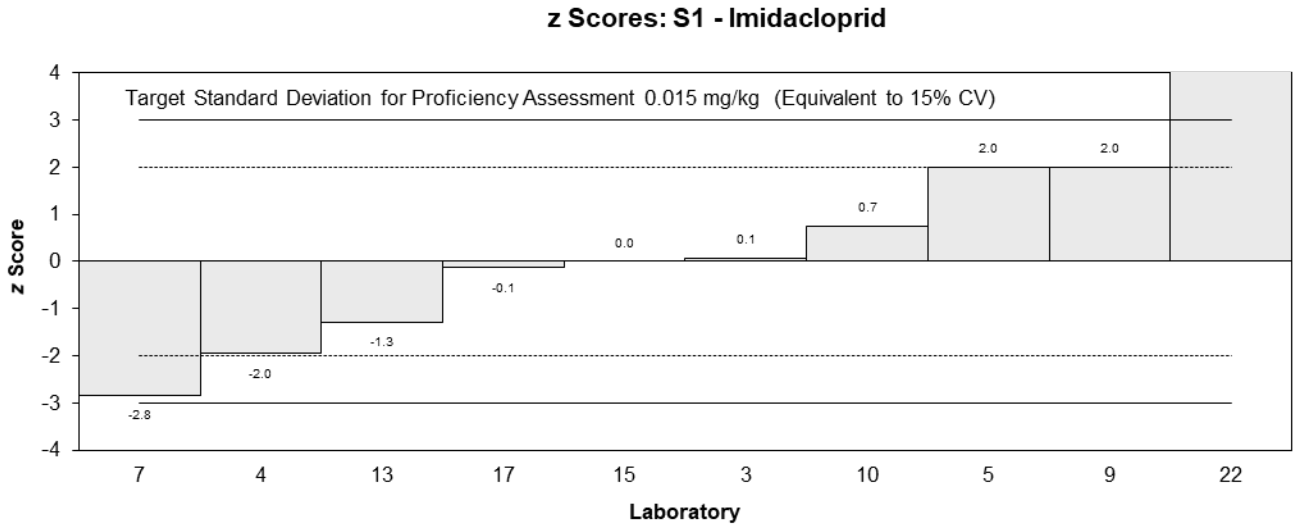
Lab. Code	Result	U	Rec	z	E_n
1	NT	NT	NT		
2	NT	NT	NT		
3	0.1	0.03	104	0.07	0.03
4	0.07	0.036	76	-1.95	-0.65
5	0.133	0.084	126	2.00▼	0.39
6	NT	NT	NT		
7	0.057	NR	90	-2.83	-1.62
8	NT	NT	NT		
9	0.142	0.0497	96	2.00▼	0.77
10	0.11	NR	NR	0.74	0.42
11	NT	NT	NT		
12	NT	NT	NT		
13	0.080	0.03	NR	-1.28	-0.48
14	NT	NT	NT		
15	0.099	0.024	84	0.00	0.00
16	NT	NT	NT		
17	0.097	0.01	NR	-0.13	-0.07
18	NT	NT	NT		
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		
22*	0.26	0.1	80-120	10.84	1.56
23	NT	NT	NT		
24	NT	NT	NT		
25	NT	NT	NT		
26	NT	NT	NT		

* Outlier, ▼ Adjusted score

Statistics

Assigned Value	0.099	0.026
Spiked Value	0.151	0.008
Robust Average	0.105	0.029
Max Acceptable Result	0.18	
Median	0.100	0.029
Mean	0.115	0.036
N	10	
Max	0.26	
Min	0.057	
Robust SD	0.037	
Robust CV (%)	35	


Results: S1 - Imidacloprid
Assigned Value = 0.099 ± 0.026 mg/kg
Maximum Acceptable Result = 0.18 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
7 4 13 17 15 3 10 5 9 22 1 2 6 8 11 12 14 16 18 19 20 21 23 24 25 26 RA Md SV


z Scores: S1 - Imidacloprid
Target Standard Deviation for Proficiency Assessment 0.015 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
7 4 13 17 15 3 10 5 9 22
-2.8 -2.0 -1.3 -0.1 0.0 0.1 0.7 2.0 2.0

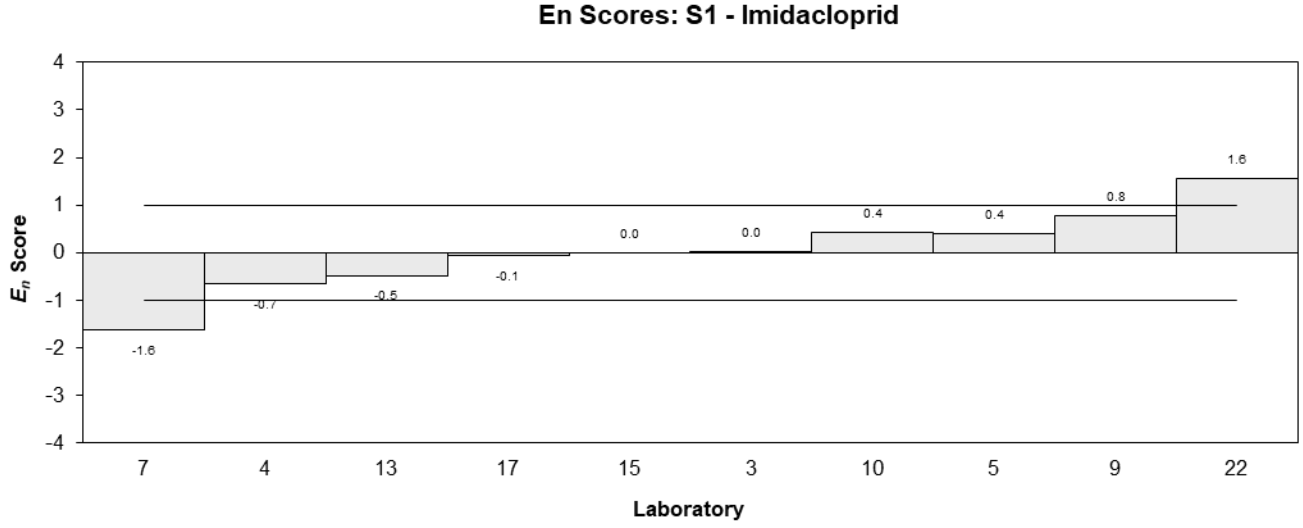

En Scores: S1 - Imidacloprid
En Score
Laboratory
7 4 13 17 15 3 10 5 9 22
-1.6 -0.7 -0.5 -0.1 0.0 0.0 0.4 0.4 0.8 1.6

Figure 4

Table 8

Sample Details

Sample	S1
Analyte	Metsulfuron-methyl
Matrix	Soil
Unit	mg/kg

Participant Results

Lab. Code	Result	U	Rec
1	NT	NT	NT
2	< 2	0.6	NR
3	0.48	0.15	113
4	0.32	0.24	56
5	NT	NT	NT
6	NT	NT	NT
7	NT	NT	NT
8	NT	NT	NT
9	NT	NT	NT
10	NR	NR	NR
11	NT	NT	NT
12	NT	NT	NT
13	0.23	0.07	NR
14	NT	NT	NT
15	0.59	0.15	91
16	NT	NT	NT
17	0.56	0.03	NR
18	NT	NT	NT
19	NT	NT	NT
20	0.08	0.03	76
21	NT	NT	NT
22	0.44	0.2	80-120
23	NT	NT	NT
24	NT	NT	NT
25	NT	NT	NT
26	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spiked Value	0.851	0.043
Robust Average	0.39	0.20
Median	0.44	0.17
Mean	0.39	0.14
N	7	
Max	0.59	
Min	0.08	
Robust SD	0.21	
Robust CV (%)	54	

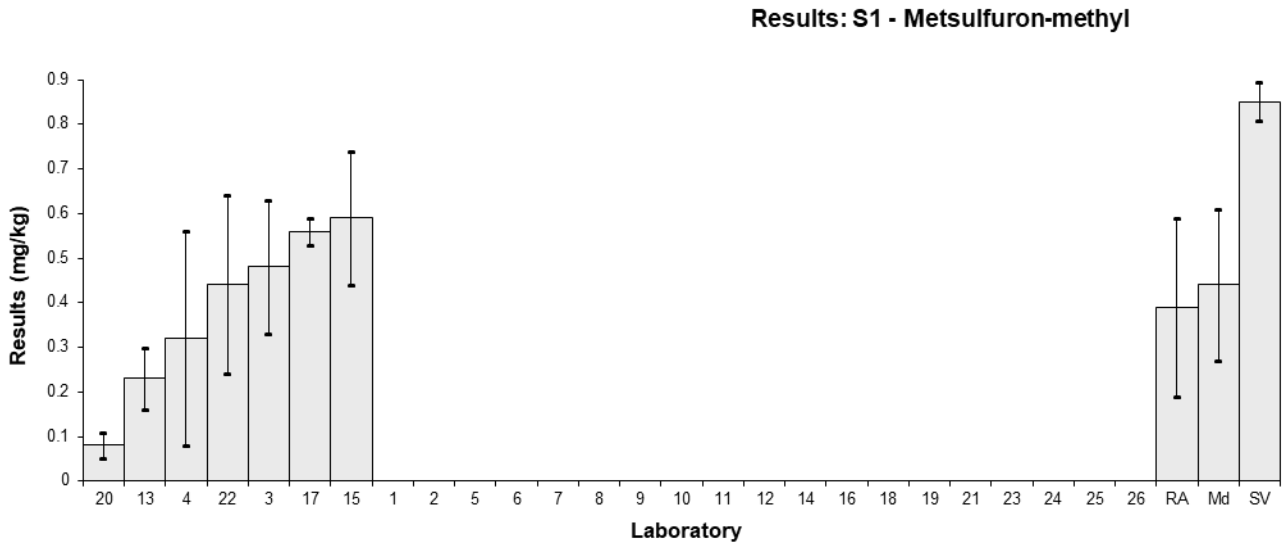

Results: S1 - Metsulfuron-methyl
Results (mg/kg)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20 13 4 22 3 17 15 1 2 5 6 7 8 9 10 11 12 14 16 18 19 21 23 24 25 26 RA Md SV
Laboratory

Figure 5

Table 9

Sample Details

Sample	S2
Analyte	Fipronil
Matrix	Soil
Unit	mg/kg

Participant Results

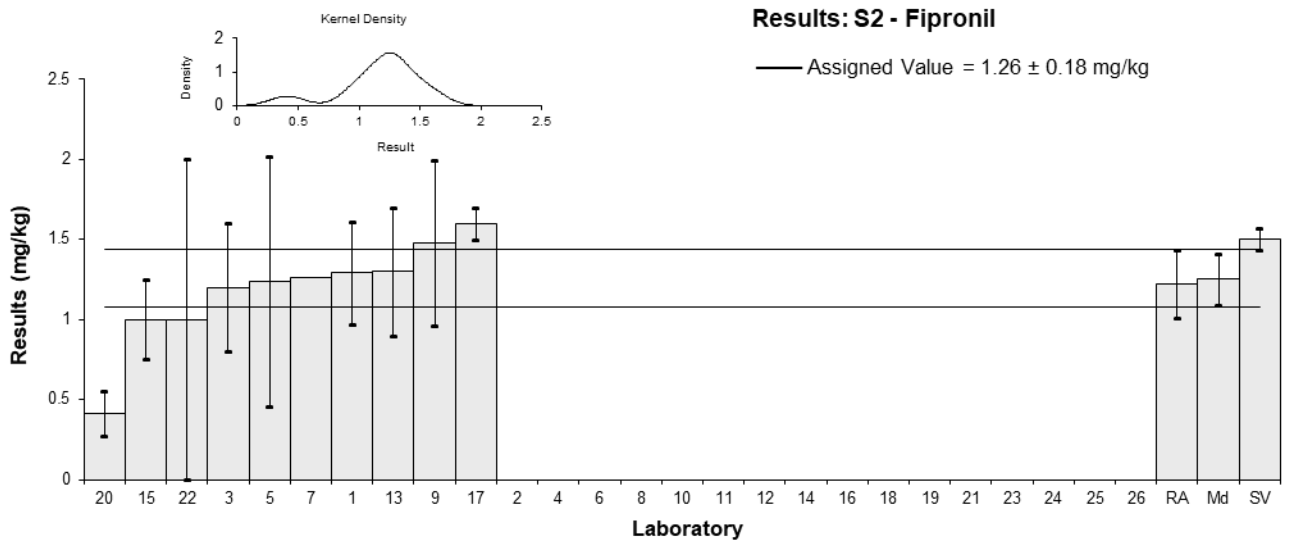
Lab. Code	Result	U	Rec	z	E_n
1	1.29	0.32	NR	0.16	0.08
2	NT	NT	NT		
3	1.2	0.4	119	-0.32	-0.14
4	NT	NT	NT		
5#	1.240	0.780	NR	-0.11	-0.02
6	NT	NT	NT		
7	1.259	NR	NR	-0.01	-0.01
8	NT	NT	NT		
9	1.479	0.518	112	1.16	0.40
10	NR	NR	NR		
11	NT	NT	NT		
12	NT	NT	NT		
13	1.3	0.4	NR	0.21	0.09
14	NT	NT	NT		
15	1.0	0.25	90	-1.38	-0.84
16	NT	NT	NT		
17	1.6	0.1	NR	1.80	1.65
18	NT	NT	NT		
19	NT	NT	NT		
20*	0.41	0.14	81	-4.50	-3.73
21	NT	NT	NT		
22	1	1	80-120	-1.38	-0.26
23	<0.05	NR	NR		
24	NT	NT	NT		
25	NT	NT	NT		
26	NT	NT	NT		

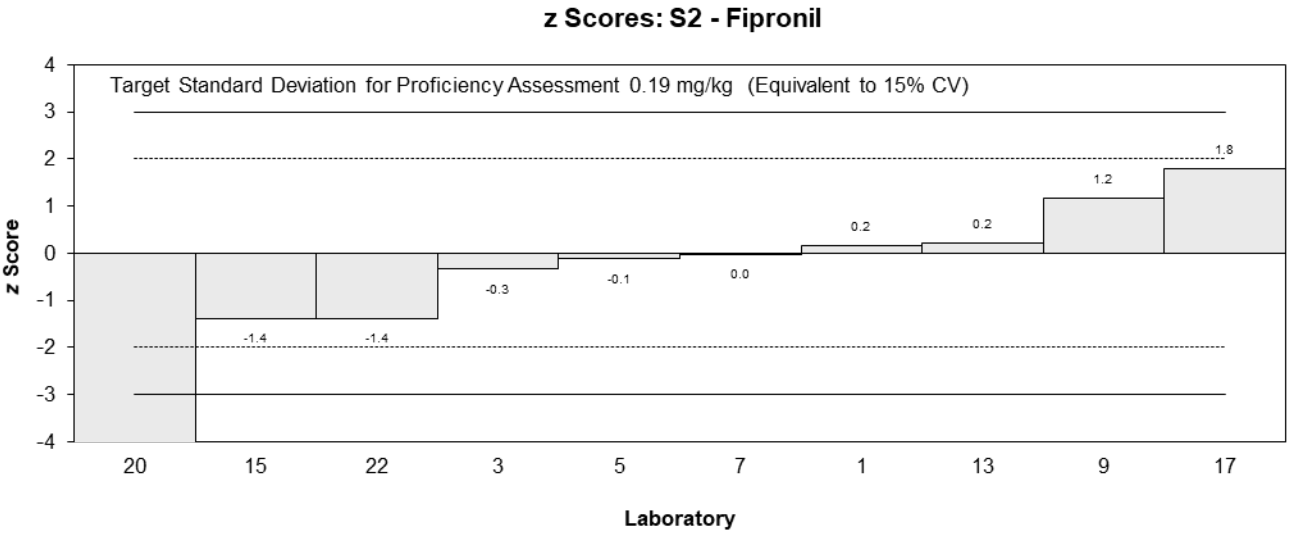
* Outlier

Statistics

Assigned Value	1.26	0.18
Spiked Value	1.50	0.07
Robust Average	1.22	0.21
Median	1.25	0.16
Mean	1.18	0.21
N	10	
Max	1.6	
Min	0.41	
Robust SD	0.26	
Robust CV (%)	21	

Laboratory 5 reported the sum of fipronil and fipronil sulfone. The study coordinator has calculated the value of fipronil only by subtracting the reported value of fipronil sulfone from the original reported result.


Results: S2 - Fipronil
Assigned Value = 1.26 ± 0.18 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
20 15 22 3 5 7 1 13 9 17 2 4 6 8 10 11 12 14 16 18 19 21 23 24 25 26 RA Md SV


z Scores: S2 - Fipronil
Target Standard Deviation for Proficiency Assessment 0.19 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
20 15 22 3 5 7 1 13 9 17
-1.4 -1.4 -0.3 -0.1 0.0 0.2 0.2 1.2 1.8

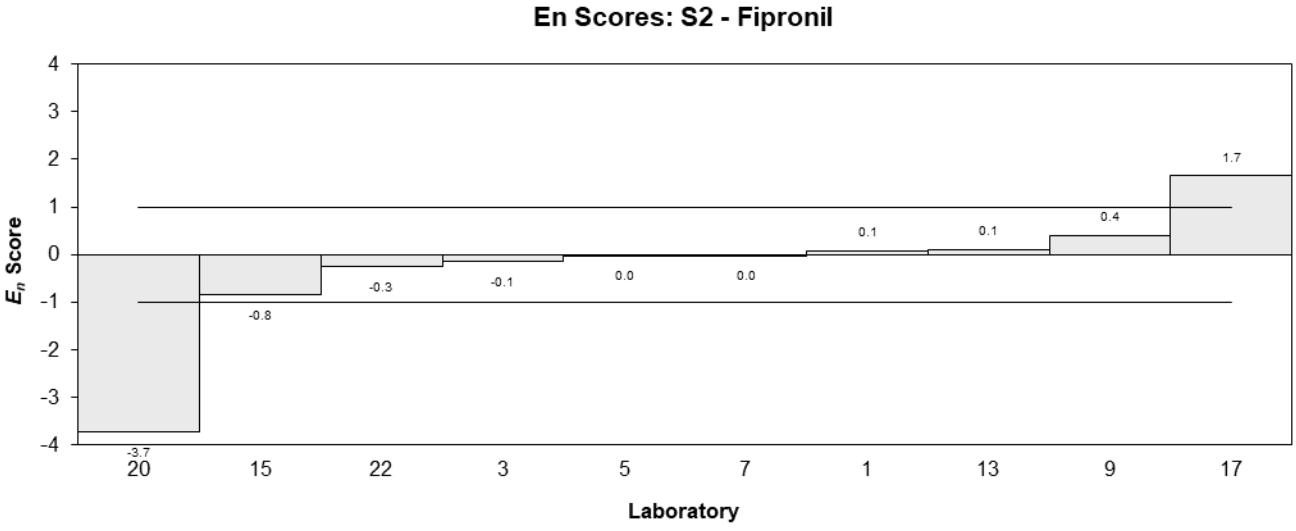

En Scores: S2 - Fipronil
En Score
Laboratory
20 15 22 3 5 7 1 13 9 17
-3.7 -0.8 -0.3 -0.1 0.0 0.0 0.1 0.1 0.4 1.7

Figure 6

Table 10

Sample Details

Sample	S2
Analyte	Lindane
Matrix	Soil
Unit	mg/kg

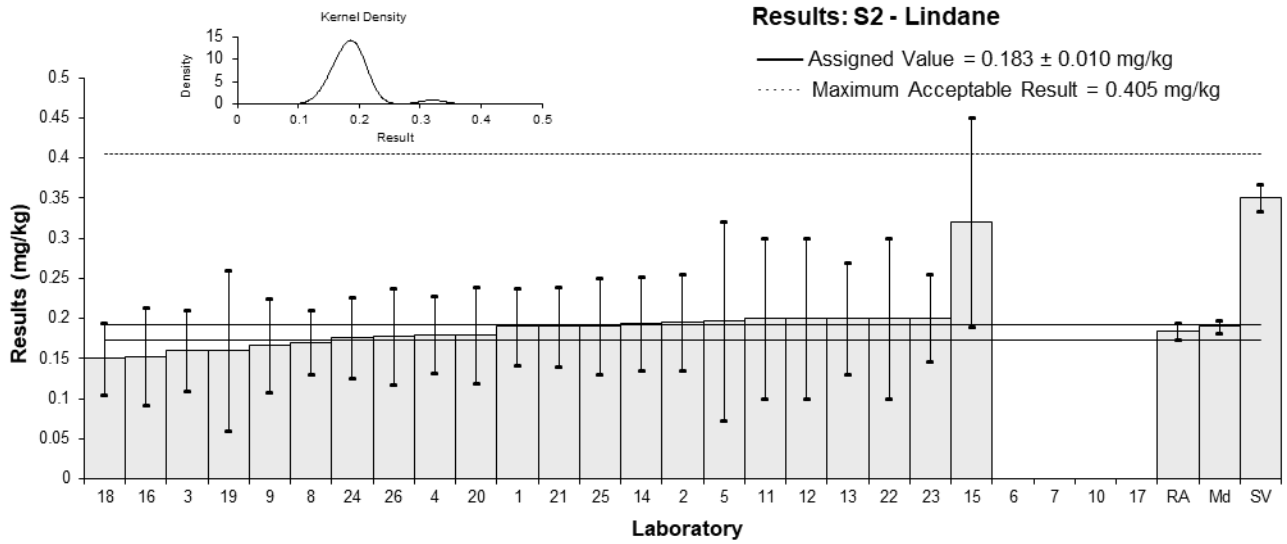
Participant Results

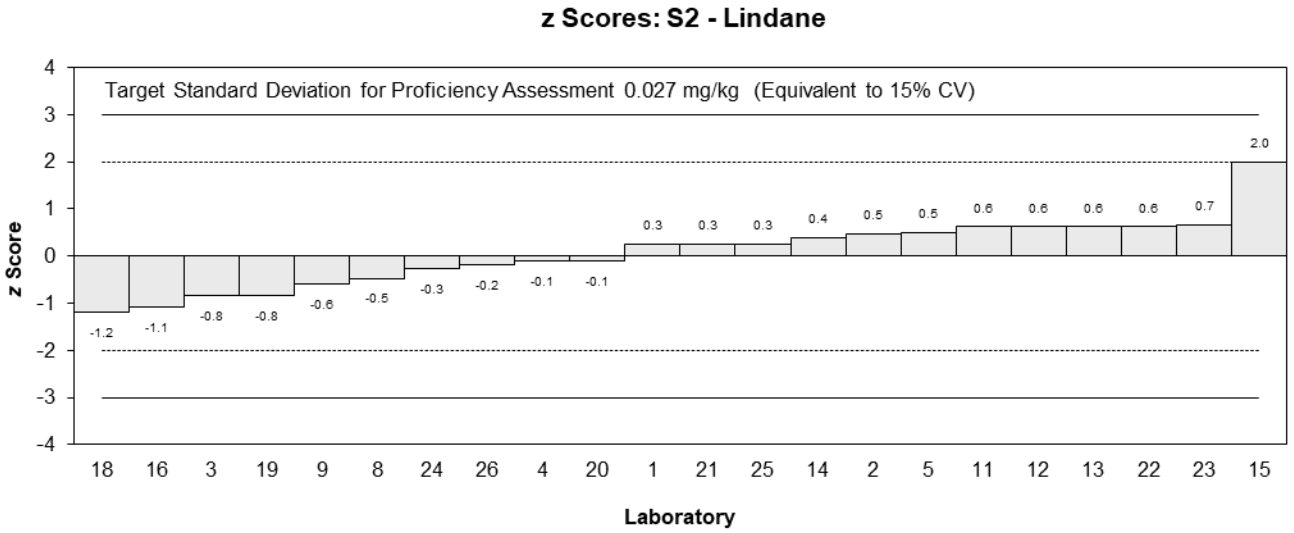
Lab. Code	Result	U	Rec	z	E_n
1	0.190	0.048	NR	0.26	0.14
2	0.196	0.06	NR	0.47	0.21
3	0.16	0.05	91	-0.84	-0.45
4	0.18	0.048	92	-0.11	-0.06
5	0.197	0.124	84	0.51	0.11
6	NT	NT	NT		
7	NT	NT	NT		
8	0.17	0.04	NR	-0.47	-0.32
9	0.167	0.0584	94	-0.58	-0.27
10	NR	NR	NR		
11	0.2	0.1	80-120	0.62	0.17
12	0.2	0.1	NR	0.62	0.17
13	0.20	0.07	NR	0.62	0.24
14	0.194	0.058	NR	0.40	0.19
15*	0.32	0.13	97	2.00▼	1.00▼
16	0.153	0.0612	NR	-1.09	-0.48
17	NT	NT	NT		
18	0.15	0.045	NR	-1.20	-0.72
19	0.16	0.1	81	-0.84	-0.23
20	0.18	0.06	71	-0.11	-0.05
21	0.19	0.05	NR	0.26	0.14
22	0.2	0.1	80-120	0.62	0.17
23	0.201	0.054	65.2	0.66	0.33
24	0.176	0.05	NR	-0.26	-0.14
25	0.19	0.06	84	0.26	0.12
26	0.178	0.06	NR	-0.18	-0.08

* Outlier, ▼ Adjusted score

Statistics

Assigned Value	0.183	0.010
Spiked Value	0.350	0.017
Robust Average	0.184	0.010
Max Acceptable Result	0.405	
Median	0.190	0.008
Mean	0.189	0.014
N	22	
Max	0.32	
Min	0.15	
Robust SD	0.019	
Robust CV (%)	10	


Kernel Density
Density
Result
Results: S2 - Lindane
Assigned Value = 0.183 ± 0.010 mg/kg
Maximum Acceptable Result = 0.405 mg/kg
Results (mg/kg)
Laboratory
18 16 3 19 9 8 24 26 4 20 1 21 25 14 2 5 11 12 13 22 23 15 6 7 10 17 RA Md SV


z Scores: S2 - Lindane
Target Standard Deviation for Proficiency Assessment 0.027 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
18 16 3 19 9 8 24 26 4 20 1 21 25 14 2 5 11 12 13 22 23 15
-1.2 -1.1 -0.8 -0.8 -0.6 -0.5 -0.3 -0.2 -0.1 -0.1 0.3 0.3 0.3 0.4 0.5 0.5 0.6 0.6 0.6 0.6 0.7 2.0

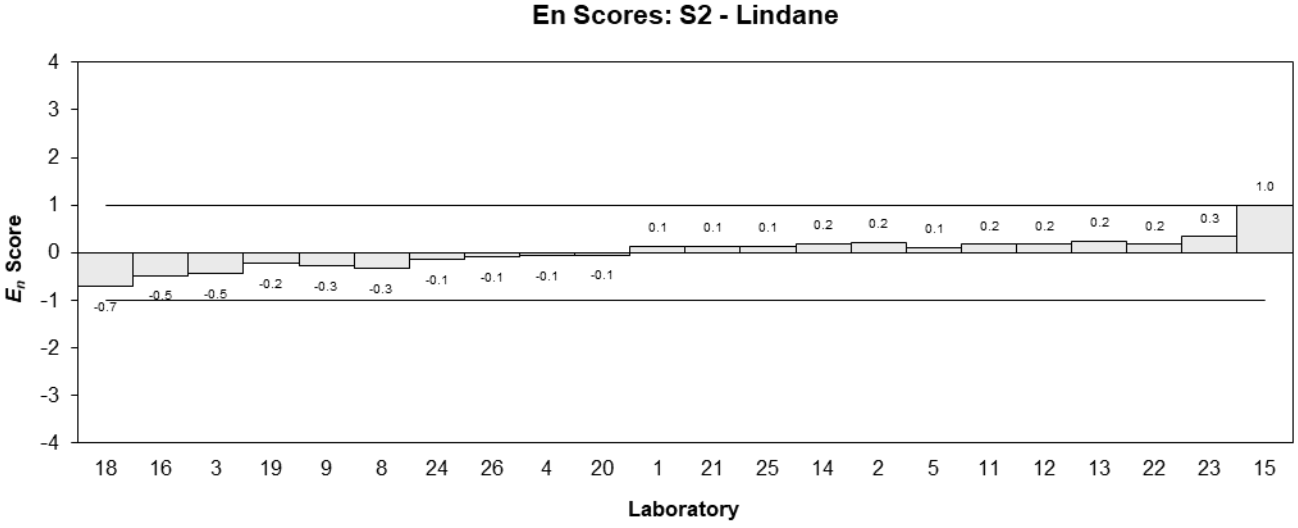

En Scores: S2 - Lindane
En Score
Laboratory
18 16 3 19 9 8 24 26 4 20 1 21 25 14 2 5 11 12 13 22 23 15
-0.7 -0.5 -0.5 -0.2 -0.3 -0.3 -0.1 -0.1 -0.1 -0.1 0.1 0.1 0.1 0.2 0.2 0.1 0.2 0.2 0.2 0.2 0.3 1.0

Figure 7

Table 11

Sample Details

Sample	S2
Analyte	MCPA
Matrix	Soil
Unit	mg/kg

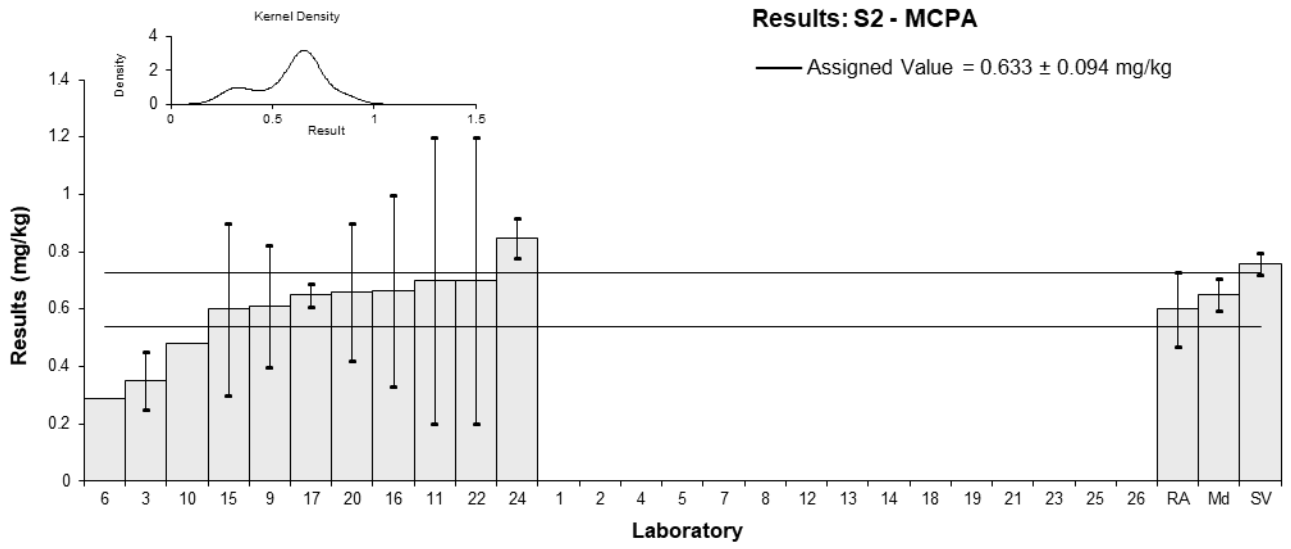
Participant Results

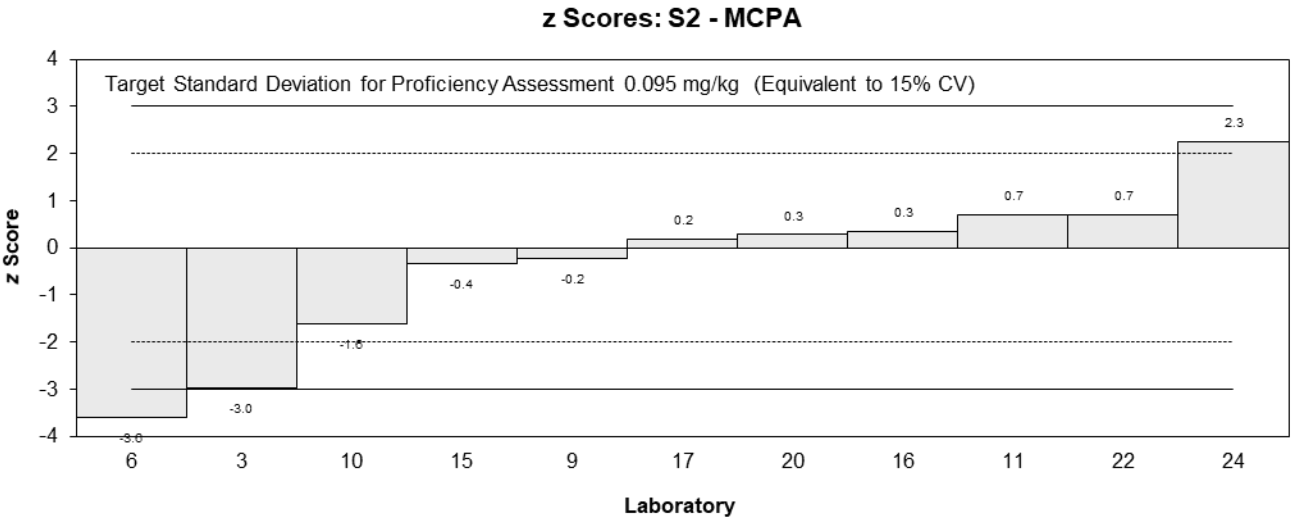
Lab. Code	Result	U	Rec	z	E_n
1	<0.5	NR	NR		
2	<0.5	0.15	NR		
3	0.35	0.1	117	-2.98	-2.06
4	NT	NT	NT		
5	NT	NT	NT		
6*	0.29	NR	NR	-3.61	-3.65
7	NT	NT	NT		
8	NT	NT	NT		
9	0.610	0.214	93	-0.24	-0.10
10	0.48	NR	NR	-1.61	-1.63
11	0.7	0.5	80-120	0.71	0.13
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	0.60	0.3	NR	-0.35	-0.10
16	0.665	0.333	NR	0.34	0.09
17	0.65	0.04	NR	0.18	0.17
18	NT	NT	NT		
19	NT	NT	NT		
20	0.66	0.24	82	0.28	0.10
21	NT	NT	NT		
22	0.7	0.5	80-120	0.71	0.13
23	NT	NT	NT		
24	0.848	0.069	NR	2.26	1.84
25	NT	NT	NT		
26	NT	NT	NT		

* Outlier

Statistics

Assigned Value	0.633	0.094
Spiked Value	0.756	0.038
Robust Average	0.60	0.13
Median	0.650	0.056
Mean	0.596	0.098
N	11	
Max	0.848	
Min	0.29	
Robust SD	0.17	
Robust CV (%)	29	


Results: S2 - MCPA
Assigned Value = 0.633 ± 0.094 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 3 10 15 9 17 20 16 11 22 24 1 2 4 5 7 8 12 13 14 18 19 21 23 25 26 RA Md SV


z Scores: S2 - MCPA
Target Standard Deviation for Proficiency Assessment 0.095 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
6 3 10 15 9 17 20 16 11 22 24
-3.6
-3.0
-1.6
-0.4
-0.2
0.2
0.3
0.3
0.7
0.7
2.3

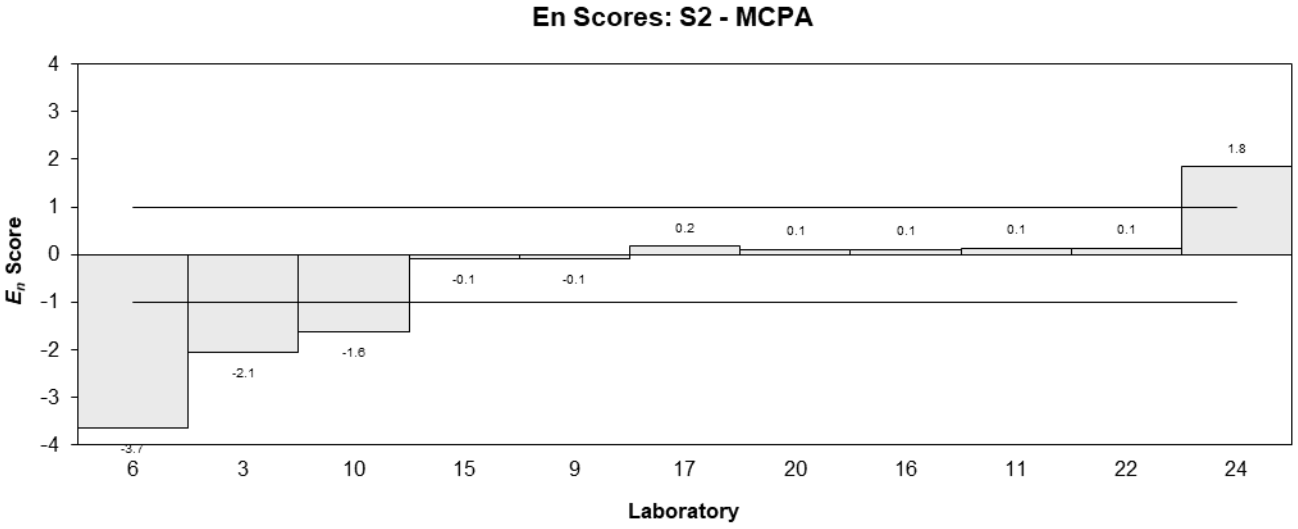

En Scores: S2 - MCPA
En Score
Laboratory
6 3 10 15 9 17 20 16 11 22 24
-3.7
-2.1
-1.6
-0.1
-0.1
0.2
0.1
0.1
0.1
0.1
1.8

Figure 8

Table 12

Sample Details

Sample	S2
Analyte	p,p'-DDD
Matrix	Soil
Unit	mg/kg

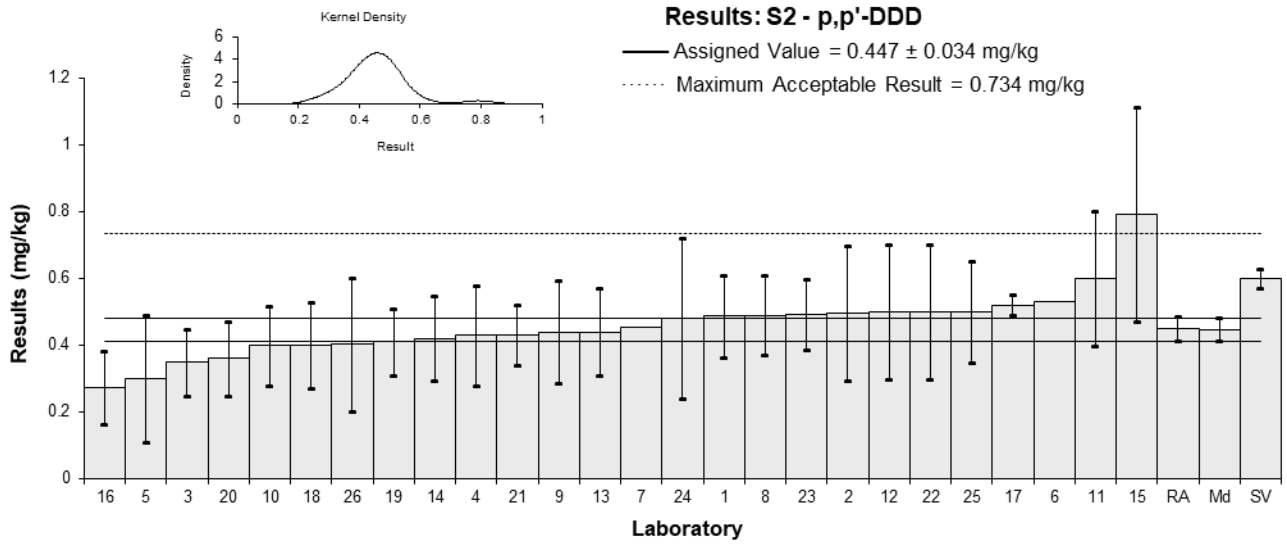
Participant Results

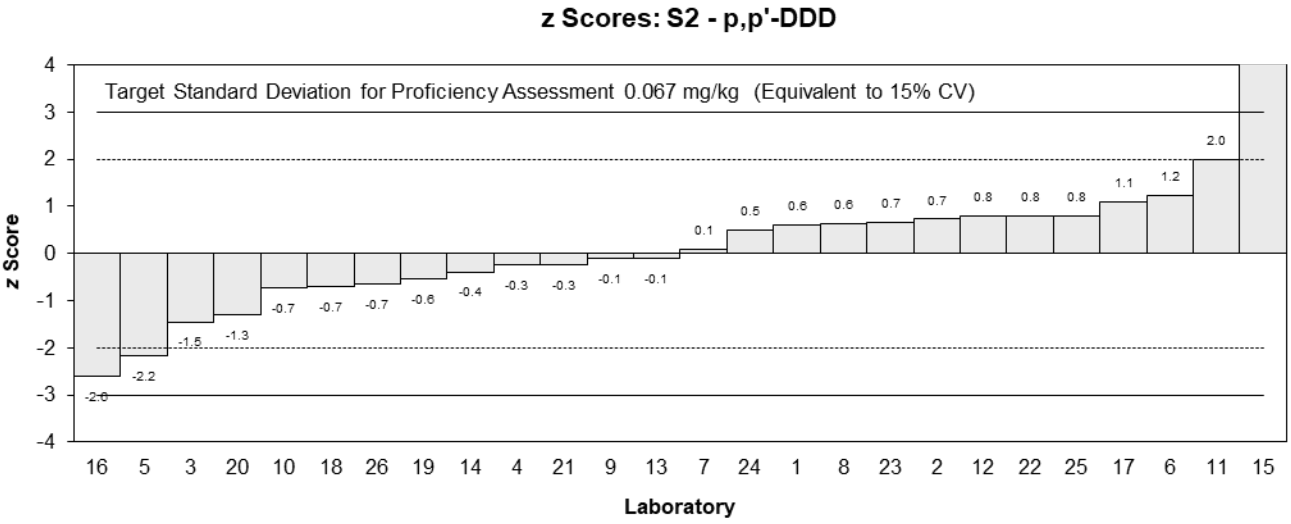
Lab. Code	Result	U	Rec	z	E_n
1	0.487	0.123	NR	0.60	0.31
2	0.496	0.2	NR	0.73	0.24
3	0.35	0.1	103	-1.45	-0.92
4	0.43	0.15	91	-0.25	-0.11
5	0.302	0.19	85	-2.16	-0.75
6	0.53	NR	NR	1.24	2.44
7	0.453	NR	NR	0.09	0.18
8	0.49	0.12	NR	0.64	0.34
9	0.440	0.154	82	-0.10	-0.04
10	0.399	0.1197	NR	-0.72	-0.39
11	0.6	0.2	80-120	2.00▼	0.75
12	0.5	0.2	NR	0.79	0.26
13	0.44	0.13	NR	-0.10	-0.05
14	0.421	0.126	NR	-0.39	-0.20
15*	0.79	0.32	NR	5.12	1.07
16	0.273	0.109	NR	-2.60	-1.52
17	0.52	0.03	NR	1.09	1.61
18	0.4	0.13	NR	-0.70	-0.35
19	0.41	0.1	81	-0.55	-0.35
20	0.36	0.11	73	-1.30	-0.76
21	0.43	0.09	NR	-0.25	-0.18
22	0.5	0.2	80-120	0.79	0.26
23	0.492	0.105	105	0.67	0.41
24	0.48	0.24	NR	0.49	0.14
25	0.50	0.15	85	0.79	0.34
26	0.403	0.2	NR	-0.66	-0.22

* Outlier, ▼ Adjusted score

Statistics

Assigned Value	0.447	0.034
Spiked Value	0.600	0.030
Robust Average	0.451	0.036
Max Acceptable Result	0.734	
Median	0.447	0.034
Mean	0.458	0.039
N	26	
Max	0.79	
Min	0.273	
Robust SD	0.073	
Robust CV (%)	16	


Kernel Density
Density
Result
Results: S2 - p,p'-DDD
Assigned Value = 0.447 ± 0.034 mg/kg
Maximum Acceptable Result = 0.734 mg/kg
Results (mg/kg)
16 5 3 20 10 18 26 19 14 4 21 9 13 7 24 1 8 23 2 12 22 25 17 6 11 15 RA Md SV
Laboratory


z Scores: S2 - p,p'-DDD
Target Standard Deviation for Proficiency Assessment 0.067 mg/kg (Equivalent to 15% CV)
z Score
16 5 3 20 10 18 26 19 14 4 21 9 13 7 24 1 8 23 2 12 22 25 17 6 11 15
Laboratory

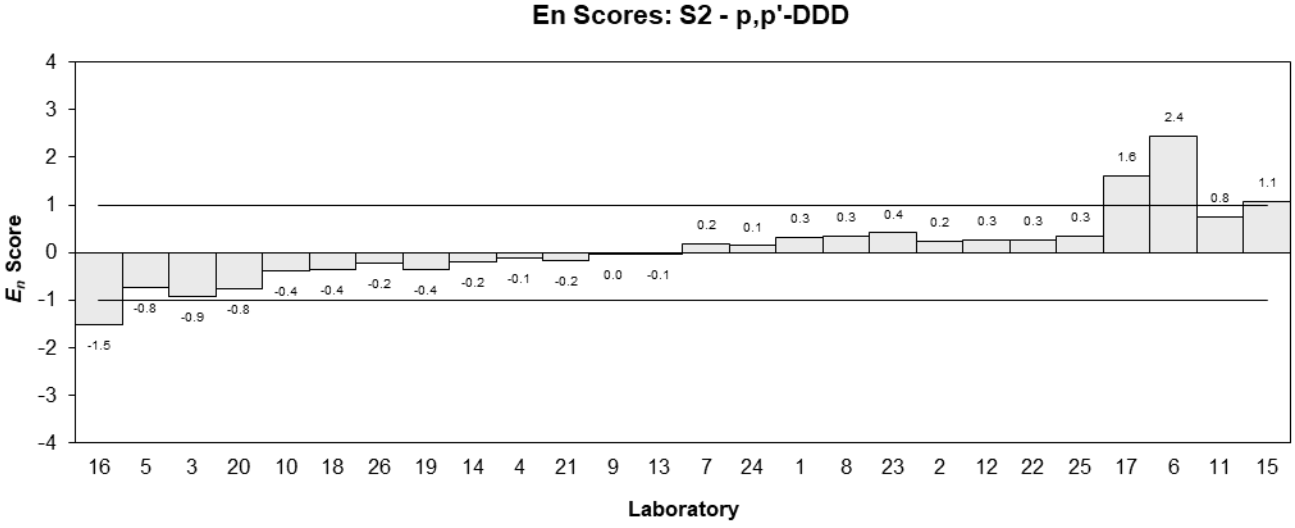

En Scores: S2 - p,p'-DDD
En Score
16 5 3 20 10 18 26 19 14 4 21 9 13 7 24 1 8 23 2 12 22 25 17 6 11 15
Laboratory

Figure 9

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages of participants' results were used as the assigned values 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 calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 4, using Sample S2 p,p'-DDD 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.

No assigned value was set for Sample S1 metsulfuron-methyl as few numeric results were reported for this analyte, and the results that were reported were highly variable.

A comparison of the assigned values (or robust average if no assigned value was set) and the spiked values is presented in Table 13. The assigned values were within the range of 52% to 84% of the spiked values. Similar ratios have been observed in previous Pesticides in Soil PT studies,[6] and an assigned value was set if there was a reasonable consensus of results.

Table 13 Comparison of Assigned Value (Robust Average) and Spiked Value

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	Atrazine	0.253	0.353	72
	Ethion	0.142	0.199	71
	Imidacloprid	0.099	0.151	66
	Metsulfuron-methyl	*(0.39)*	0.851	*(46)*
S2	Fipronil	1.26	1.50	84
	Lindane	0.183	0.350	52
	MCPA	0.633	0.756	84
	p,p'-DDD	0.447	0.600	75

The best estimate of the 'true' mass fraction of the pesticides in soil is most likely the spiked value. However, a proportion of the spiked pesticide is strongly bound to the soil and so is not readily extracted and measured. What laboratories actually measure may best be described as 'extractable pesticide', and the result may be influenced by the efficiency of the extraction process used. Therefore, for this study, the assigned value is the best estimate of the amount of 'extractable pesticide'.

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty 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 uncertainty in specific circumstances, including when the client's instruction so requires.[9]

Of 122 numeric results, 111 (91%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainties (Table 3). A number of participants reported using the NATA GAG Estimating and Reporting MU or Technical Note 33 as their guide; NATA no longer publishes these documents.[11]

Laboratories **6**, **7** and **10** did not report uncertainties for at least one of their reported numeric results; all of these participants reported being accredited to ISO/IEC 17025.

The magnitude of the reported expanded uncertainties was within the range 5.0% to 100% of the reported value. In general, an expanded uncertainty of less than 15% is likely to be unrealistically small for the routine measurement of a pesticide residue, while over 50% is likely to be too large. In this study, eight expanded uncertainties were less than 15% relative, while 15 were greater than 50% relative.

Uncertainties associated with results returning a satisfactory *z* score but an unsatisfactory E_n score may have been underestimated.

Laboratories **2**, **19** and **26** attached MU estimates to at least one result reported as less than their limit of reporting (LOR). An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[10]

In some cases the results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write 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 0.399 ± 0.1197 mg/kg, it is better to report this as 0.40 ± 0.12 mg/kg.[10]

6.3 *z* Score

Target SDs equivalent to 15% PCV were used to calculate *z* scores. CVs predicted by the Thomspon-Horwitz equation,[8] target SDs (as PCV), and between-laboratory CVs obtained in this study for scored analytes are presented for comparison in Table 14.

Table 14 Comparison of Thompson-Horwitz CVs, Target SDs and Between-Laboratory CVs

Sample	Analyte	Assigned value (mg/kg)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between-Laboratory CV* (%)
S1	Atrazine	0.253	20	15	19
	Ethion	0.142	21	15	24
	Imidacloprid	0.099	22	15	32
S2	Fipronil	1.26	15	15	17
	Lindane	0.183	21	15	10
	MCPA	0.633	17	15	19
	p,p'-DDD	0.447	18	15	15

* Robust between-laboratory CV with outliers removed, if applicable.

To account for possible low bias in consensus values due to participants using inefficient extraction or analytical techniques, a total of eight *z* scores were adjusted across the following analytes: Sample S1 ethion and imidacloprid, and Sample S2 lindane and p,p'-DDD. A maximum acceptable result was set to two target SDs more than the spiked value, and results

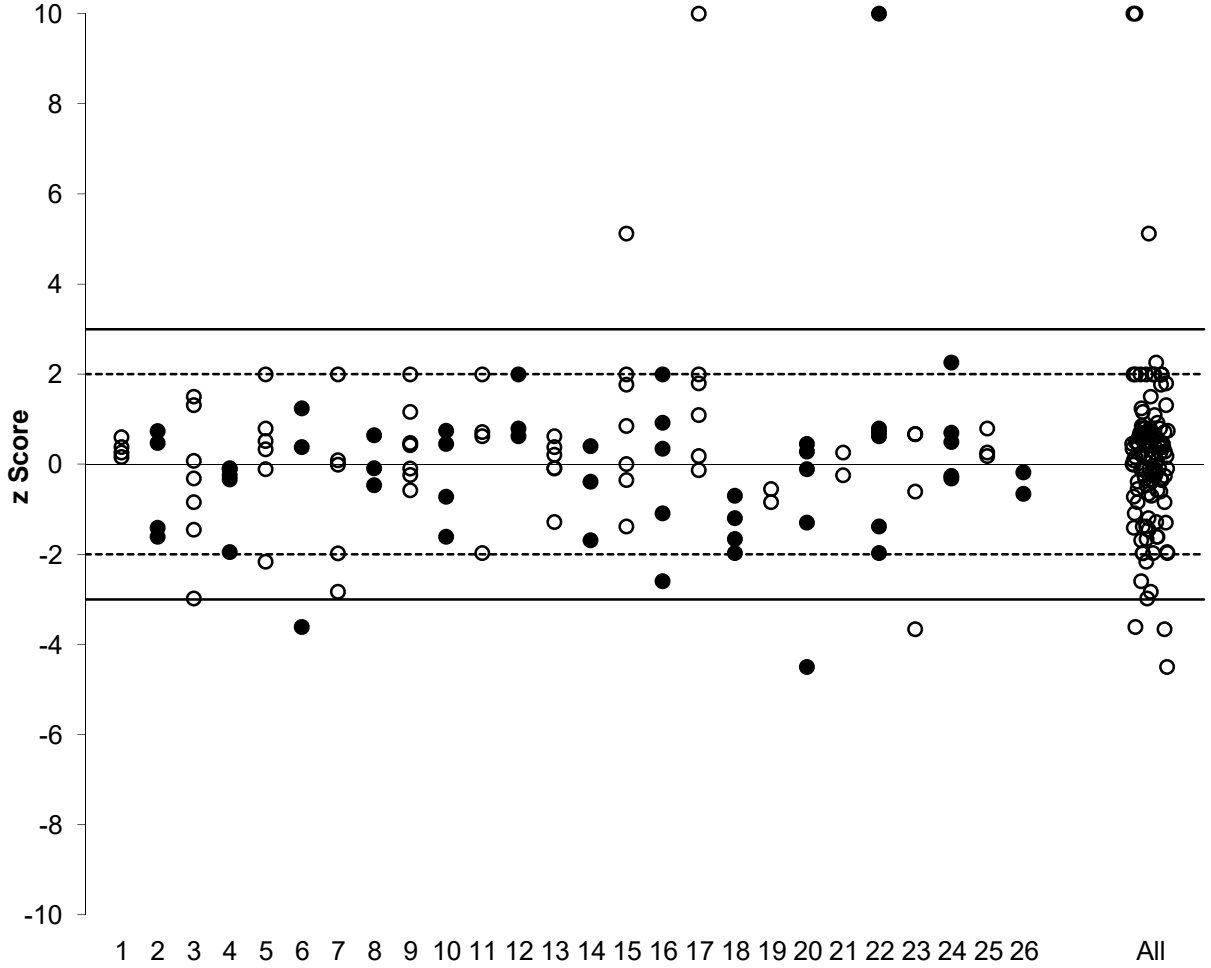
lower than the maximum acceptable result but with a *z* score greater than 2.0 had their *z* score adjusted to 2.0. This ensured that participants reporting results close to the spiked value were not penalised. *z* Scores for results higher than the maximum acceptable result and *z* scores less than 2.0 were left unaltered.

Of 115 results for which *z* scores were calculated, 104 (90%) returned a satisfactory *z* score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **3**, **9** and **15** reported results for all seven analytes for which *z* scores were calculated. Laboratory **9** returned satisfactory *z* scores for all seven scored analytes.

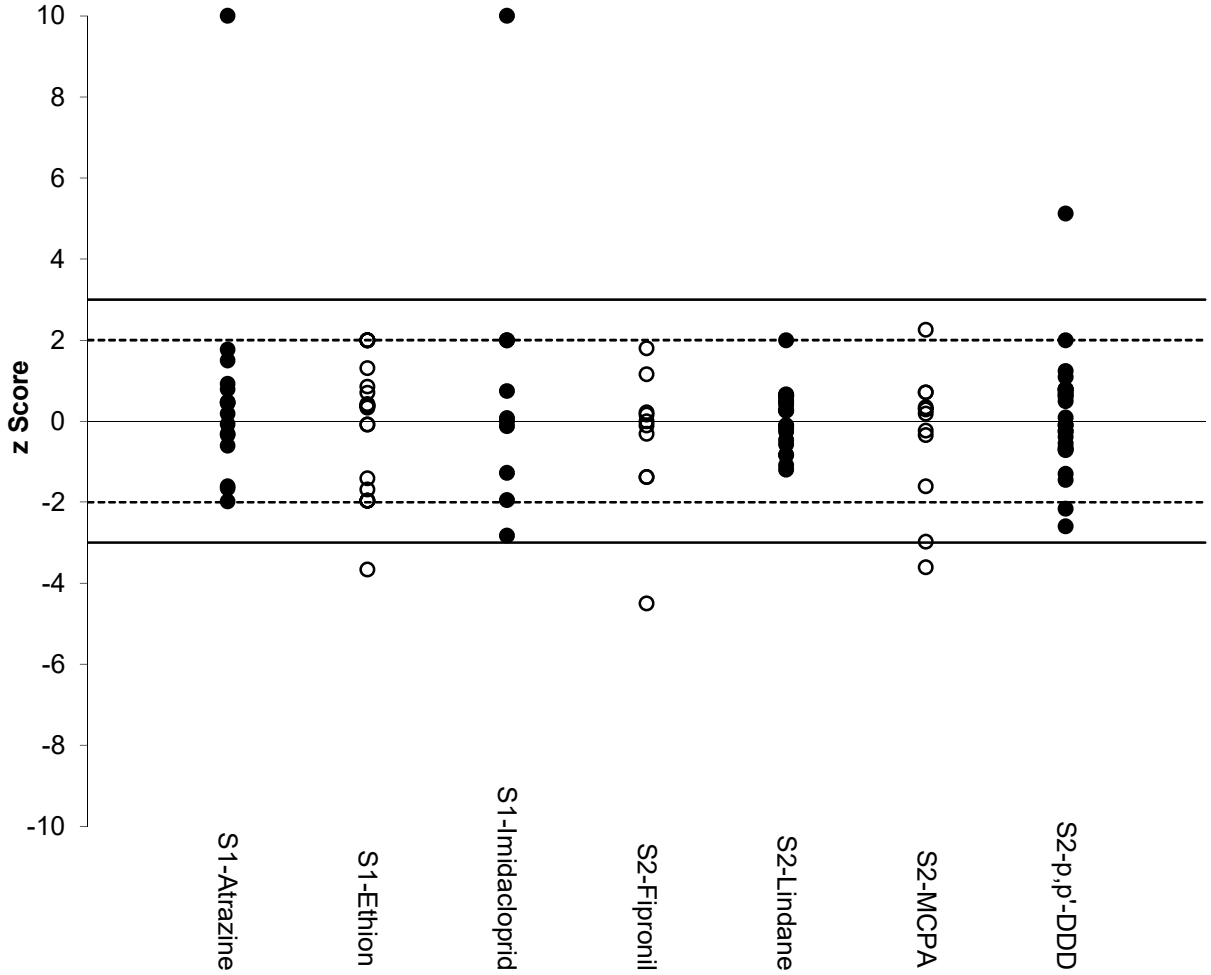
Satisfactory *z* scores were achieved for all scored results reported by Laboratories **13** (6), **4** (5), **1** (4), **2** (4), **10** (4), **11** (4), **18** (4), **8** (3), **12** (3), **14** (3), **25** (3), **19** (2), **21** (2) and **26** (2).

The dispersal of participants' *z* scores is presented graphically by laboratory in Figure 10 and by analyte in Figure 11.



z Scores greater than 10.0 have been plotted at 10.0.

Figure 10 *z* Score Dispersal by Laboratory



z Scores greater than 10.0 have been plotted at 10.0.

Figure 11 *z* Score Dispersal by Analyte

6.4 E_n Score

Where a laboratory did not report an expanded uncertainty with a result, an uncertainty of zero (0) was used to calculate the E_n score. For results whose *z* scores were adjusted as discussed in Section 6.3 *z* Score, any E_n scores greater than 1.0 were set to 1.0.

Of 115 results for which E_n scores were calculated, 100 (87%) were satisfactory with $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratory **9** achieved satisfactory E_n scores for all seven scored analytes.

Satisfactory E_n scores were achieved for all scored results reported by Laboratories **13** (6), **5** (6), **4** (5), **1** (4), **2** (4), **11** (4), **18** (4), **8** (3), **12** (3), **14** (3), **25** (3), **19** (2), **21** (2) and **26** (2).

The dispersal of participants' E_n scores is presented graphically by laboratory in Figure 12.

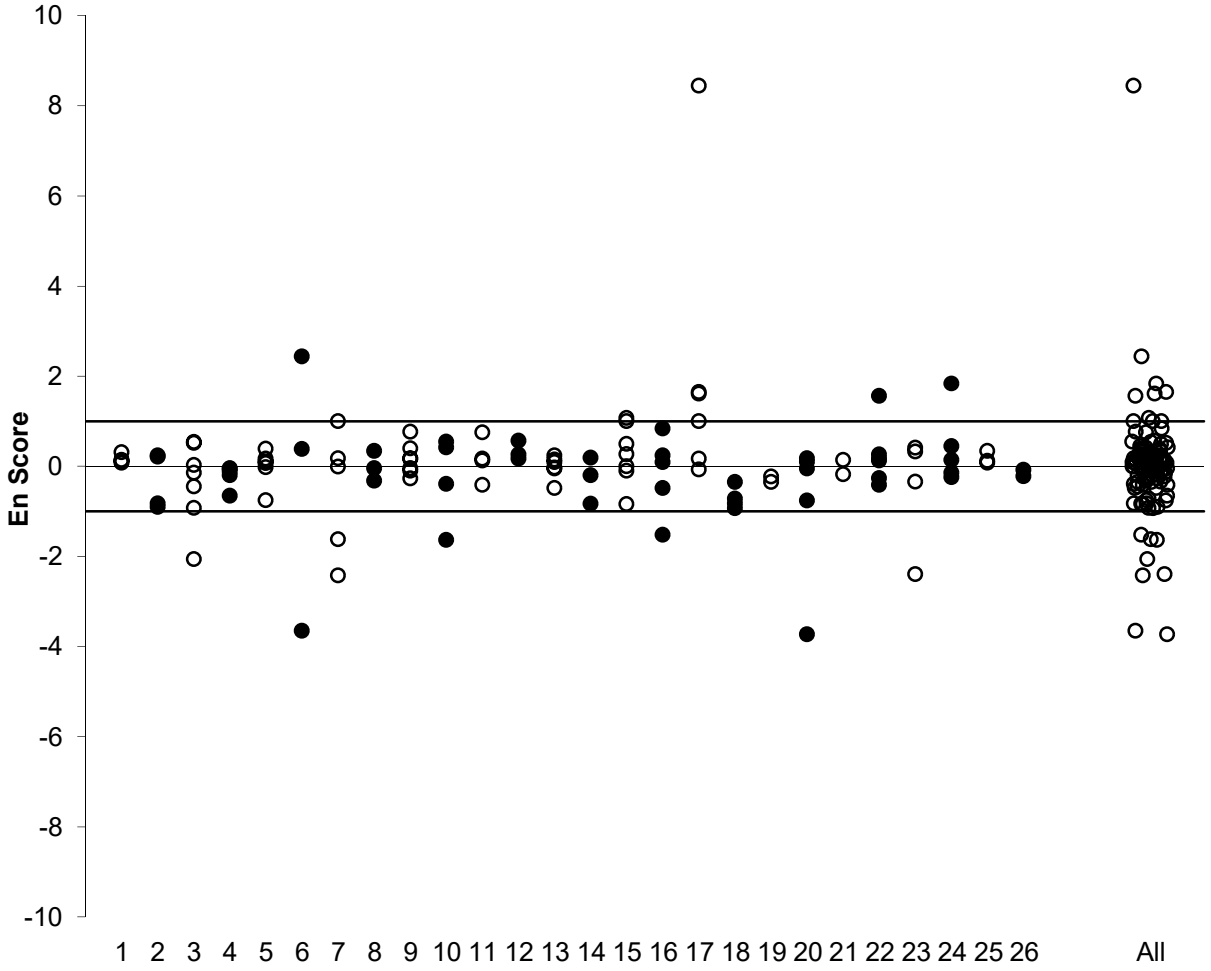


Figure 12 E_n Score Dispersal by Laboratory

6.5 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential analytes that could have been spiked into the test samples (Table 1). Of these analytes, eight were spiked into the samples for this study. Participants were not required to test for all potential analytes, and were requested to report 'NT' (for 'Not Tested') for pesticides they did not analyse the samples for.

A summary of the participants' testing of the spiked pesticides is presented in Table 15.

Laboratories **3**, **10**, **15** and **22** reported testing for all eight spiked pesticides. All participants tested for at least one of the spiked pesticides, with the proportion of pesticides analysed by each participant ranging from 25% to 100%.

The proportion of participants analysing each pesticide in this study ranged from 35% (metsulfuron-methyl) to 100% (p,p'-DDD).

Table 15 Summary of Pesticides Analysed by Participants

Lab. Code	Atrazine	Ethion	Fipronil	Imidacloprid	Lindane	MCPA	Metsulfuron-methyl	p,p'-DDD	Proportion of Analytes (%)
1	✓	✓	✓	NT	✓	✓	NT	✓	75
2	✓	✓	NT	NT	✓	✓	✓	✓	75
3	✓	✓	✓	✓	✓	✓	✓	✓	100
4	✓	✓	NT	✓	✓	NT	✓	✓	75
5	✓	✓	✓	✓	✓	NT	NT	✓	75
6	NT	✓	NT	NT	NT	✓	NT	✓	38
7	✓	✓	✓	✓	NT	NT	NT	✓	63
8	NT	✓	NT	NT	✓	NT	NT	✓	38
9	✓	✓	✓	✓	✓	✓	NT	✓	88
10	✓	✓	✓	✓	✓	✓	✓	✓	100
11	✓	✓	NT	NT	✓	✓	NT	✓	63
12	✓	✓	NT	NT	✓	NT	NT	✓	50
13	✓	✓	✓	✓	✓	NT	✓	✓	88
14	NT	✓	NT	NT	✓	NT	NT	✓	38
15	✓	✓	✓	✓	✓	✓	✓	✓	100
16	✓	✓	NT	NT	✓	✓	NT	✓	63
17	✓	✓	✓	✓	NT	✓	✓	✓	88
18	✓	✓	NT	NT	✓	NT	NT	✓	50
19	✓	✓	NT	NT	✓	NT	NT	✓	50
20	✓	NT	✓	NT	✓	✓	✓	✓	75

Lab. Code	Atrazine	Ethion	Fipronil	Imidacloprid	Lindane	MCPA	Metsulfuron-methyl	p,p'-DDD	Proportion of Analytes (%)
21	NT	NT	NT	NT	✓	NT	NT	✓	25
22	✓	✓	✓	✓	✓	✓	✓	✓	100
23	✓	✓	✓	NT	✓	NT	NT	✓	63
24	✓	✓	NT	NT	✓	✓	NT	✓	63
25	✓	NT	NT	NT	✓	NT	NT	✓	38
26	NT	✓	NT	NT	✓	NT	NT	✓	38
Proportion of Participants (%)	81	88	46	38	88	50	35	100	66

6.6 False Negatives

Table 16 presents false negative results. These are analytes present in the samples which a participant tested for, but did not report a numeric result (for example, participants reporting a 'less than' result (< *x*) when the assigned value was higher than their LOR, or participants that did not report anything). For analytes where no assigned value was set, results have only been considered to be false negatives where the robust average and spiked value were significantly higher than the participants' LOR, or if no value was reported.

Table 16 False Negatives

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Result (mg/kg)
1	S2	MCPA	0.633	0.756	<0.5
2	S2	MCPA	0.633	0.756	< 0.5
10	S1	Ethion	0.142	0.199	NR*
		Metsulfuron-methyl	*(0.39)*	0.851	NR*
	S2	Fipronil	1.26	1.50	NR*
		Lindane	0.183	0.350	NR*
23	S2	Fipronil	1.26	1.50	<0.05

* Result may or may not be a false negative, depending on the participant's actual LOR.

6.7 Reporting of Additional Analytes

Additional analytes as reported by participants are presented in Table 17.

Laboratory **5** reported fipronil sulfone in Sample S2; this is a known impurity (approximately 3% mass fraction) in the fipronil standard used to spike this sample. Laboratory **20** reported propazine in Sample S1; this may be a trace impurity in the atrazine standard used to spike this sample.

Laboratory **10** reported a value for BHC-beta in Sample S2 at around the same mass fraction as the assigned value for lindane, while not reporting a result for lindane. These analytes are isomers, and participants should take care to analyse and report for the correct analyte.

Table 17 Reported Results for Additional Analytes

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
5	S2	Fipronil sulfone	0.043	0.027	96
		Fipronil + Fipronil sulfone	1.283	0.808	95
10	S2	BHC-beta	0.2	0.06	NR
20	S1	Propazine	0.002	NR	NR

Sample S2 was spiked with p,p'-DDD, and this was a scored analyte. Eighteen participants also reported a total DDT value, which was not scored for this study. These results are presented in Table 18 for information only.

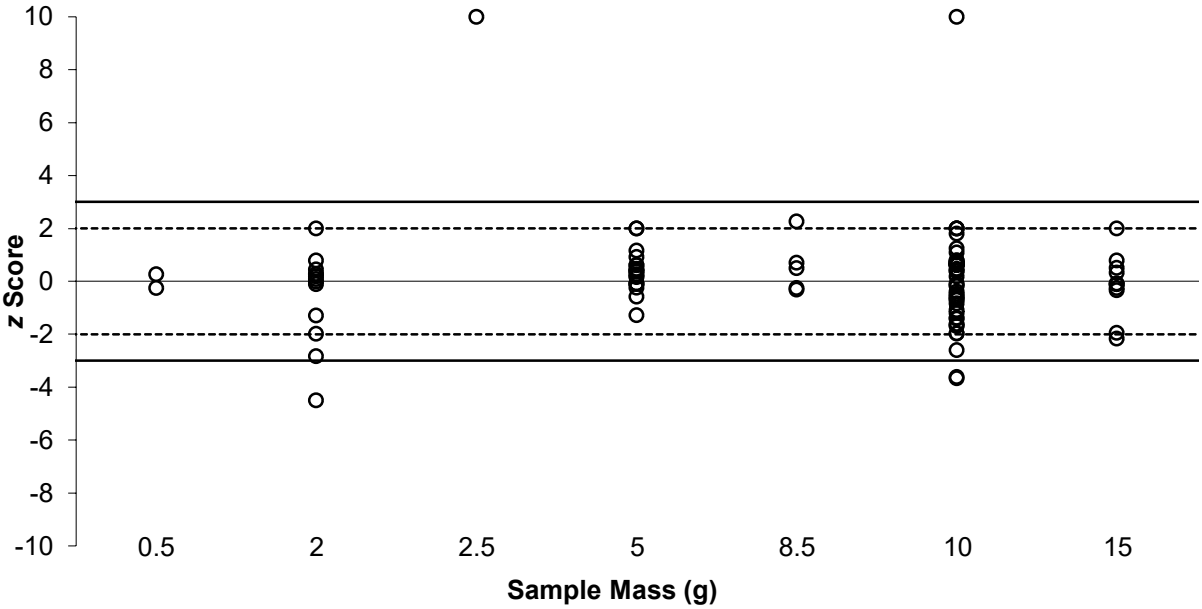
Table 18 Reported Results for Sample S2 Total DDT

Lab. Code	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
1	0.487	0.123	NR
2	0.496	0.2	NR
3	0.35	0.1	NR
4	0.43	0.079	98
5	0.302	0.19	NR
6	0.53	NR	NR
9	0.440	0.154	82
10	0.4	0.12	NR
11	0.6	0.2	80-120
12	0.5	0.2	NR
13	0.44	0.13	NR
14	0.421	0.126	NR
15	0.79	0.32	NR
17	0.52	0.005	NR
20	0.36	0.12	73
22	0.5	0.2	80-120
24	0.48	0.24	NR
26	0.403	0.2	NR

6.8 Participants' Analytical Methods

A variety of analytical methods were used for the different analytes (Appendix 3).

Participants used a sample size between 0.5 g and 15 g per analysis. There was no significant trend between the results obtained and the sample mass used for analysis (Figure 13).



z Scores greater than 10.0 have been plotted at 10.0.

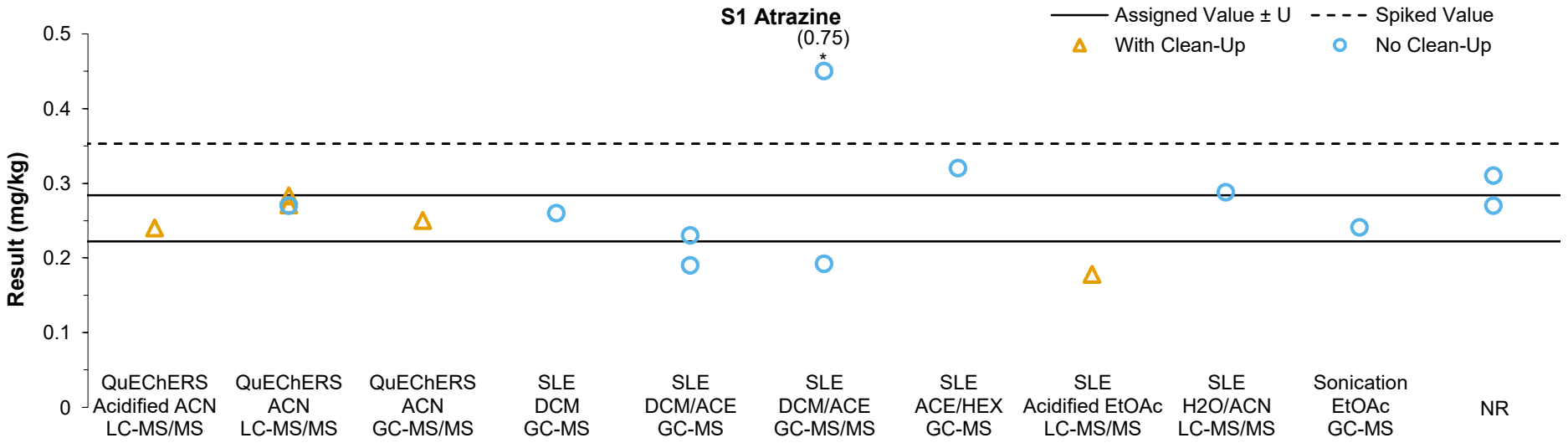
Figure 13 *z* Score vs Sample Mass Used for Analysis

Participants used a variety of extraction techniques including solid-liquid extraction (SLE), QuEChERS and sonication. Participants also used a range of extraction solvents, such as dichloromethane (DCM), acetone (ACE), ethyl acetate (EtOAc), hexane (HEX), acetonitrile (ACN), methanol (MeOH), toluene (TOL), water, and combinations of these solvents. Six participants reported using a clean-up step for their analyses; these included using Florisil, d-SPE / QuEChERS, and PSA/C18.

Instrumental techniques employed by participants for the analysis of pesticides of interest in this study included liquid chromatography coupled with mass spectrometry or tandem mass spectrometry (LC-MS(/MS)), or diode array detection (LC-DAD), and gas chromatography coupled to mass spectrometry or tandem mass spectrometry (GC-MS(/MS)), electron capture detection (GC-ECD) or flame photometric detection (GC-FPD).

Plots of results reported and methodology used are presented in Figures 14 to 20 for scored analytes. If a participant did not report any methodology, this has been recorded as NR.

There was a very wide variety of methodologies employed across the analytes in this study, and no significant trend was observed.



* Result has been modified to fit on chart; original result in parentheses.

Figure 14 Sample S1 Atrazine Results vs Methodology

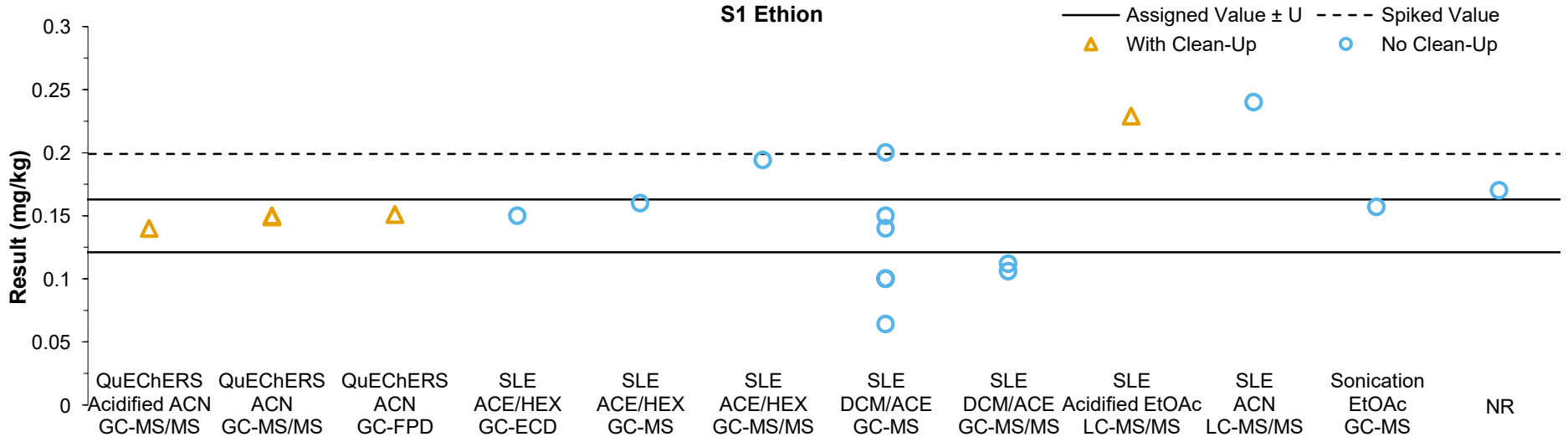


Figure 15 Sample S1 Ethion Results vs Methodology

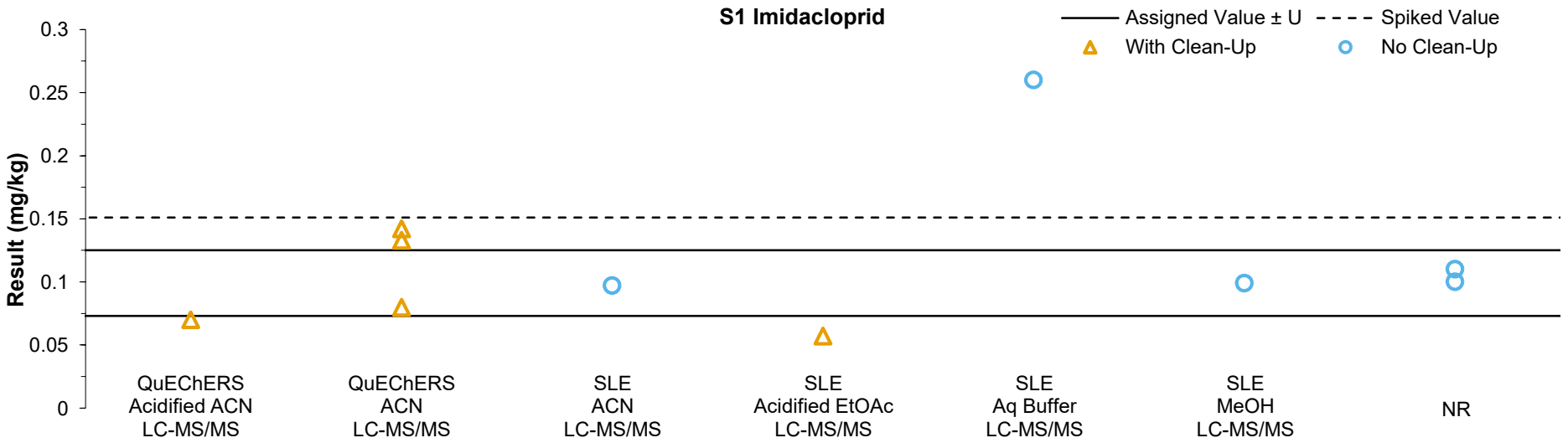


Figure 16 Sample S1 Imidacloprid Results vs Methodology

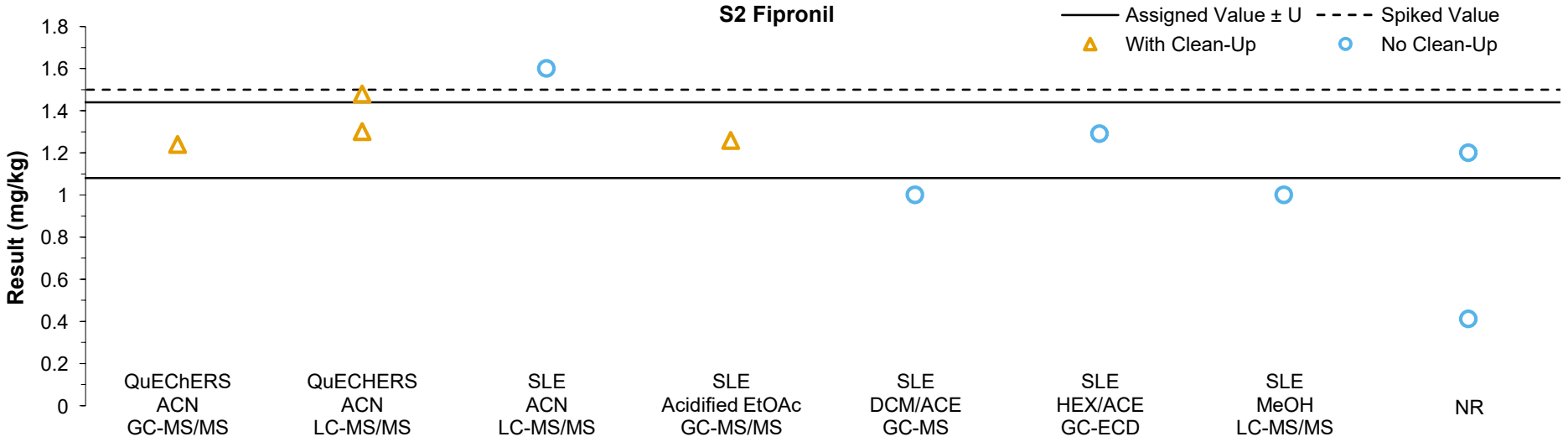


Figure 17 Sample S2 Fipronil Results vs Methodology

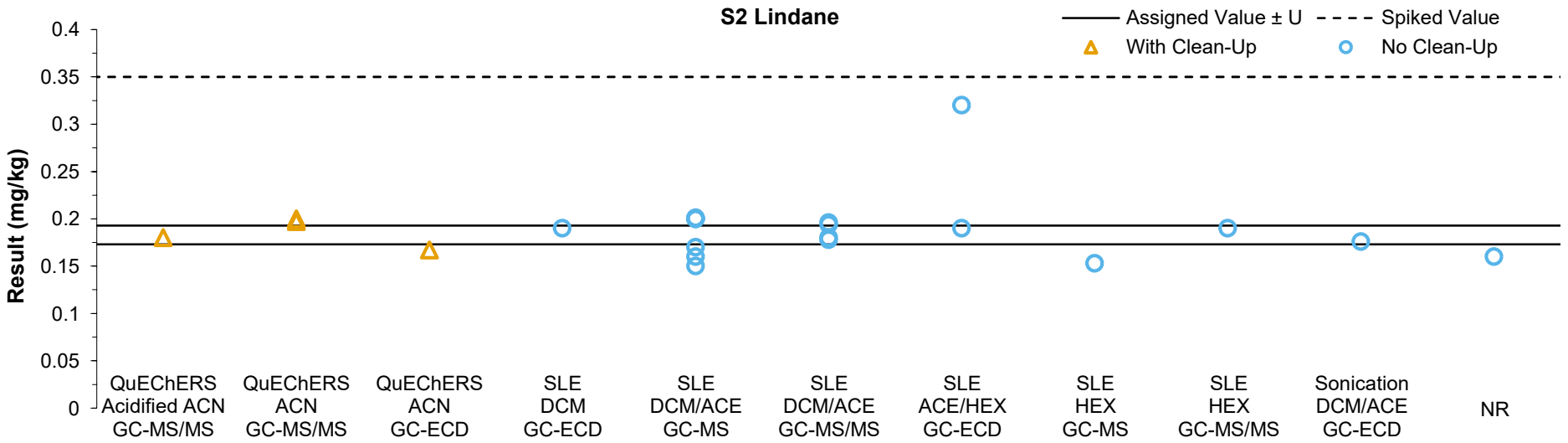


Figure 18 Sample S2 Lindane Results vs Methodology

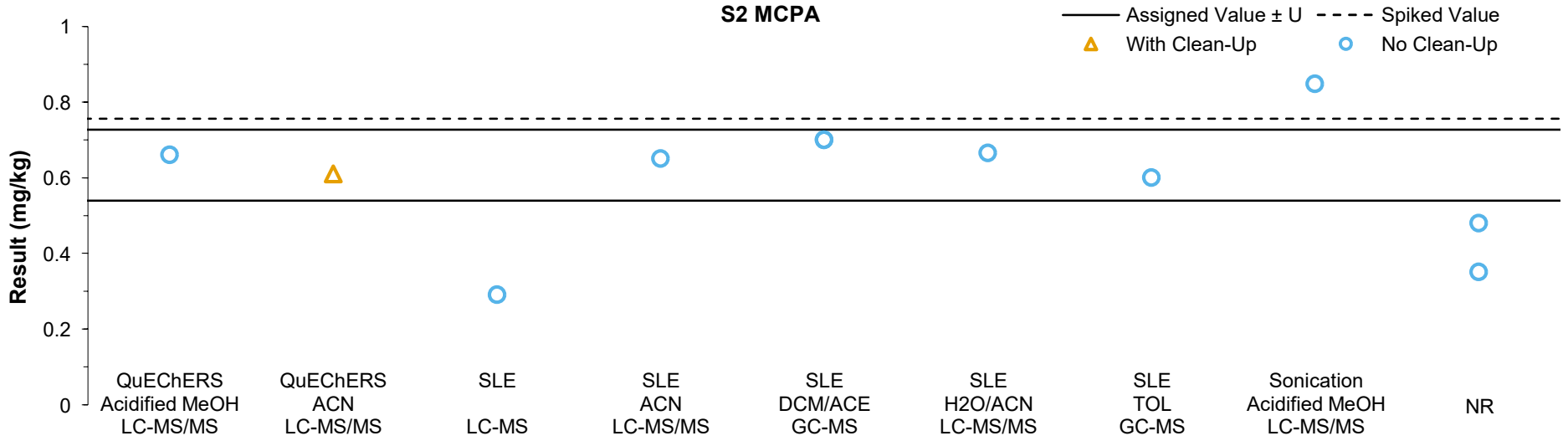


Figure 19 Sample S2 MCPA Results vs Methodology

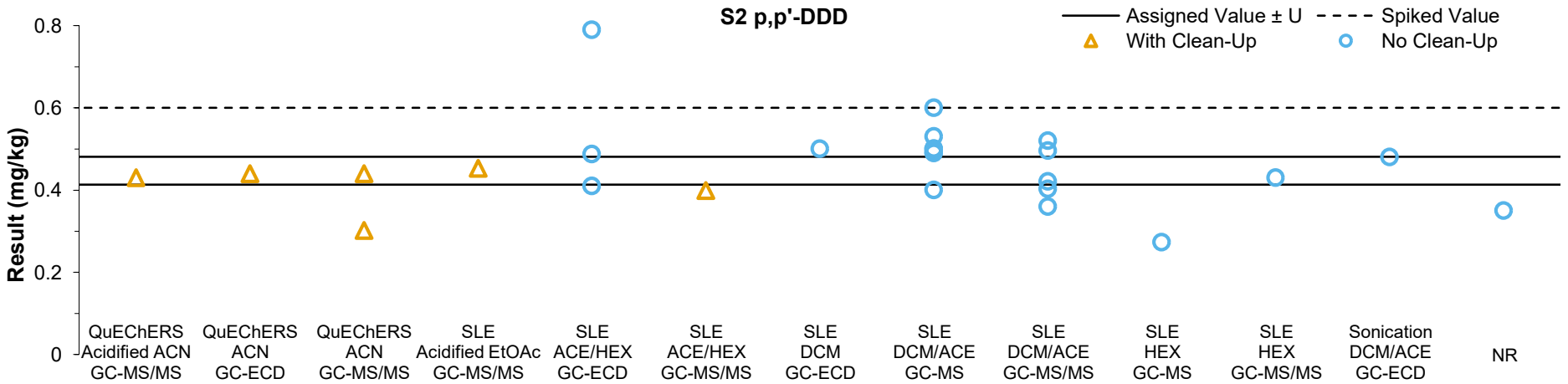


Figure 20 Sample S2 p,p'-DDD Results vs Methodology

Participants were requested to analyse the samples using their routine 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 **3**, **4**, **5**, **7**, **9**, **11**, **15**, **19**, **20**, **22**, **23** and **25** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 56% to 126%. Laboratory **3** reported that they corrected results for recovery.

6.9 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. Sixteen participants reported using certified standards, two participants reported using matrix reference materials, and two participants reported using both. The following were listed:

- Accustandard
- Dr Ehrenstorfer
- ERA (e.g. CRM 727)
- LGC
- Neochema
- Restek (e.g. 32291, 32415, 32231)
- Sigma Aldrich (e.g. 40008, CRM821, CRM107, SQC009)
- PM Separations
- ISO 17034 traceable standards
- ISO 17025 compliant standards

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]

6.10 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Table 19 and Figure 21.

Table 19 Summary of Participants' Results* (all results in mg/kg)

Lab. Code	S1 Atrazine	S1 Ethion	S1 Imidacloprid	S2 p,p'-DDD	S2 Fipronil	S2 Lindane	S2 MCPA
AV	0.253	0.142	0.099	0.447	1.26	0.183	0.633
SV	0.353	0.199	0.151	0.600	1.50	0.350	0.756
1	<0.5	0.150	NT	0.487	1.29	0.190	<0.5
2	0.192	0.112	NT	0.496	NT	0.196	< 0.5
3	0.31	0.17	0.1	0.35	1.2	0.16	0.35
4	0.24	0.14	0.07	0.43	NT	0.18	NT
5	0.283	0.149	0.133	0.302	1.240	0.197	NT
6	NT	0.15	NT	0.53	NT	NT	0.29
7	0.178	0.229	0.057	0.453	1.259	NT	NT
8	NT	0.14	NT	0.49	NT	0.17	NT
9	0.271	0.151	0.142	0.440	1.479	0.167	0.610
10	0.27	NR	0.11	0.399	NR	NR	0.48
11	<0.5	0.1	NT	0.6	NT	0.2	0.7
12	<0.5	0.2	NT	0.5	NT	0.2	NT
13	0.25	0.15	0.080	0.44	1.3	0.20	NT
14	NT	0.106	NT	0.421	NT	0.194	NT
15	0.32	0.16	0.099	0.79	1.0	0.32	0.60
16	0.288	0.194	NT	0.273	NT	0.153	0.665
17	0.75	0.24	0.097	0.52	1.6	NT	0.65
18	0.19	0.1	NT	0.4	NT	0.15	NT
19	<0.5	<0.2	NT	0.41	NT	0.16	NT

Lab. Code	S1 Atrazine	S1 Ethion	S1 Imidacloprid	S2 p,p'-DDD	S2 Fipronil	S2 Lindane	S2 MCPA
20	0.27	NT	NT	0.36	0.41	0.18	0.66
21	NT	NT	NT	0.43	NT	0.19	NT
22	<0.5	0.1	0.26	0.5	1	0.2	0.7
23	0.23	0.064	NT	0.492	<0.05	0.201	NT
24	0.241	0.157	NT	0.48	NT	0.176	0.848
25	0.26	NT	NT	0.50	NT	0.19	NT
26	NT	< 0.2	NT	0.403	NT	0.178	NT

* Shaded cells are results which returned a questionable or unsatisfactory *z* score. AV = Assigned Value; SV = Spiked Value.

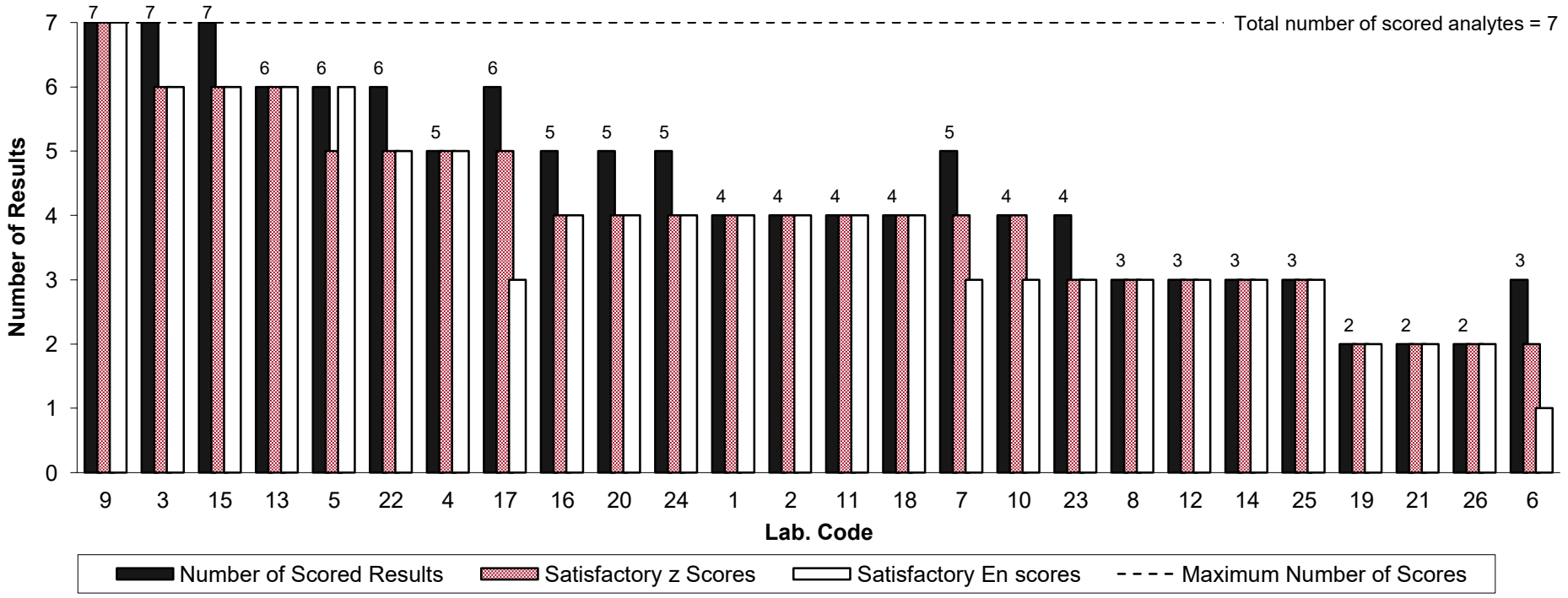


Figure 21 Summary of Participants' Performance

6.11 Comparison with Previous Pesticides in Soil PT Studies

A summary of participation and reported results rates in NMI Pesticides in Soil PT studies over the last 10 studies (2014 – 2022) is presented in Figure 22. The proportion of pesticides being tested for by participants has remained relatively steady over the last few years.

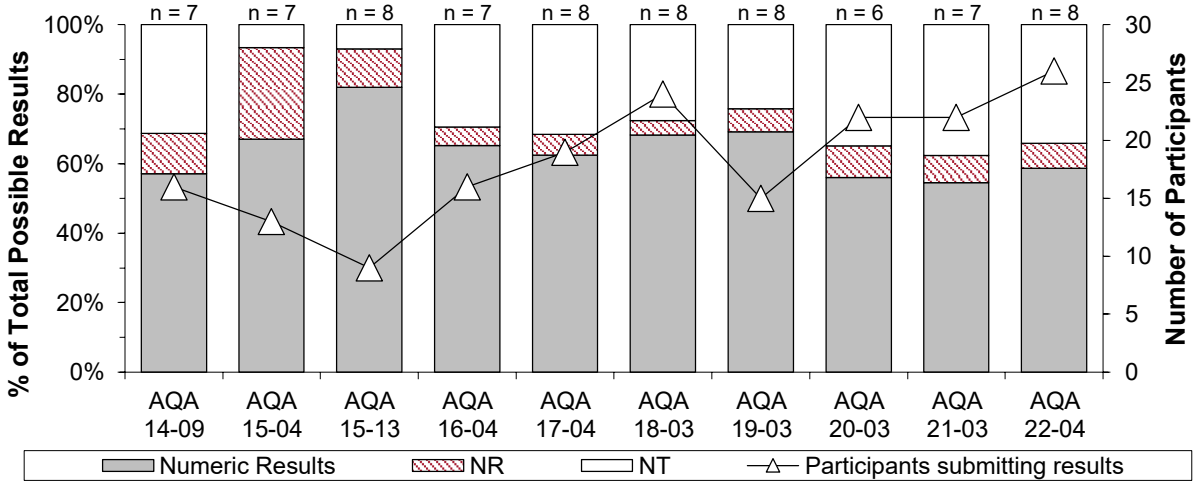


Figure 22 Summary of Participation and Reported Results in Pesticides in Soil PT Studies (n = number of spiked analytes)

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) obtained by participants in NMI Pesticides in Soil PT studies over the last 10 studies (2014 – 2022) is presented in Figure 23. 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 *z* scores and E_n scores was 83% and 82% respectively. While each proficiency testing study has a different sample set and a different group of participant laboratories, taken as a group, the performance over this period has improved.

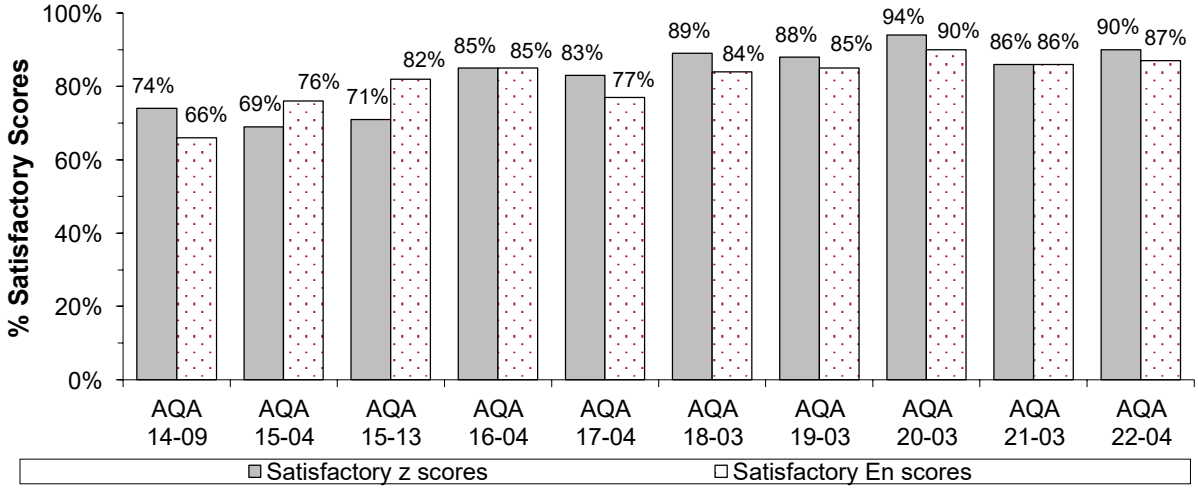


Figure 23 Satisfactory *z* Scores and E_n Scores in Pesticides in Soil PT Studies

Individual performance history reports are emailed to participants at the end of each study; the consideration of *z* scores over time provides much more useful information than a single score. Over time, laboratories should expect at least 95% of their 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.

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APPENDIX 1 SAMPLE PREPARATION

Forty bottles of each of Sample S1 and Sample S2 were prepared using dried, ground and sieved Australian Native Landscapes Menangle topsoil. The 350 µm to 850 µm fraction was used to prepare the samples.

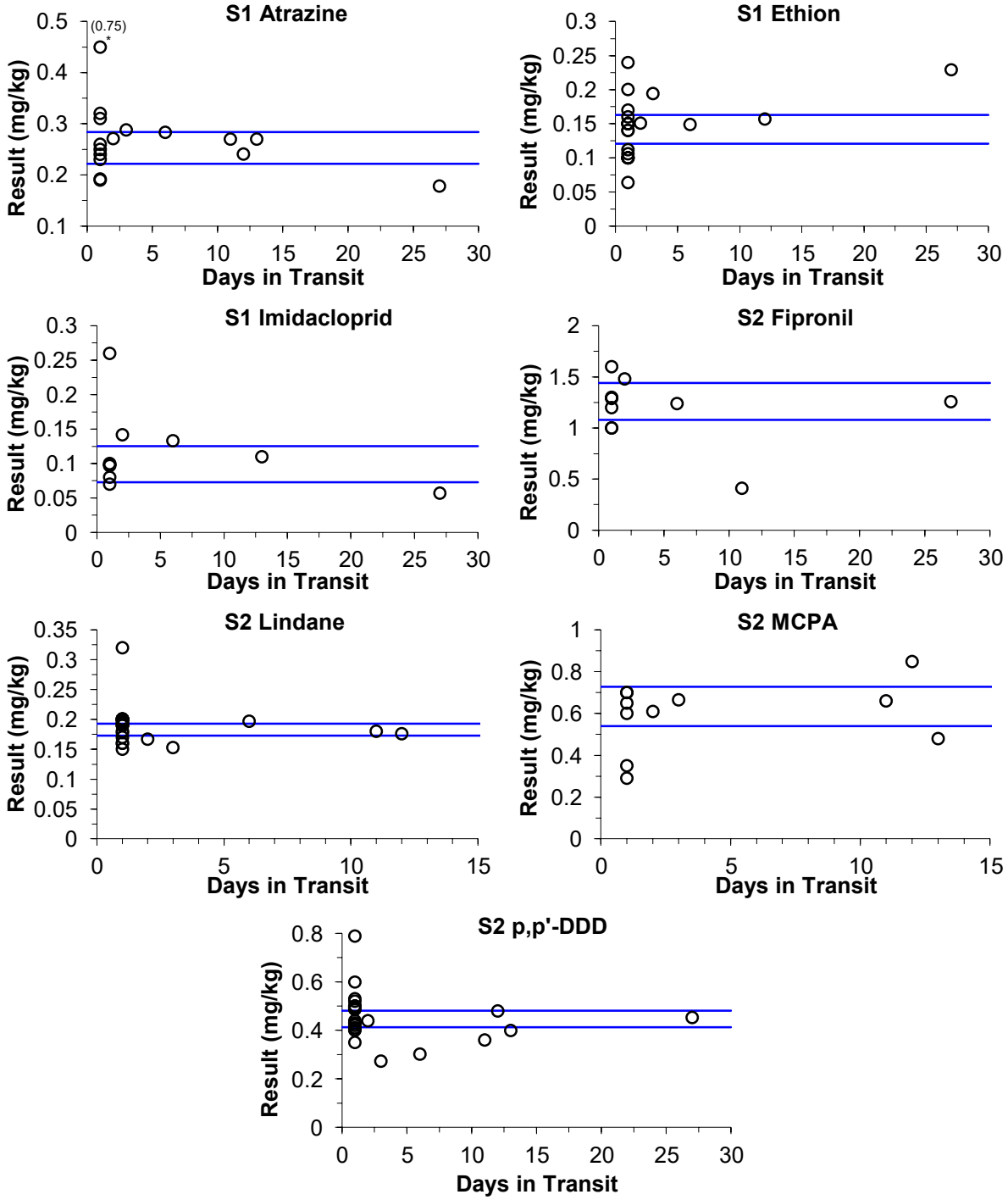
Sample S1 was prepared by weighing 2114 g of soil into a 25 litre stainless steel drum and adding acetone to cover the soil and allow it to be stirred. The stirred soil suspension was spiked with pesticide standard solutions. The solvent was allowed to evaporate in the fume cupboard. After drying, the soil was divided using a Retsch PT100 sample divider and dispensed into 65 mL glass jars.

Sample S2 was prepared by weighing 2100 g of soil into a 42 litre stainless steel drum and adding acetone to cover the soil and allow it to be stirred. The stirred soil suspension was spiked with pesticide standard solutions. The solvent was allowed to evaporate in the fume cupboard. After drying, the soil was divided using a Retsch PT100 sample divider and dispensed into 65 mL glass jars.

APPENDIX 2 ASSESSMENT OF STABILITY AND HOMOGENEITY

A2.1 Transportation Stability

No stability testing was conducted for this study, though previous use of these pesticides and similar analytes gave some assurance they were stable. Samples were refrigerated at 4 °C after preparation and prior to dispatch. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks. Comparisons of results obtained to days spent in transit for scored analytes are presented in Figure 24. No statistically significant evidence of analyte degradation with respect to the amount of time spent in transit was observed.

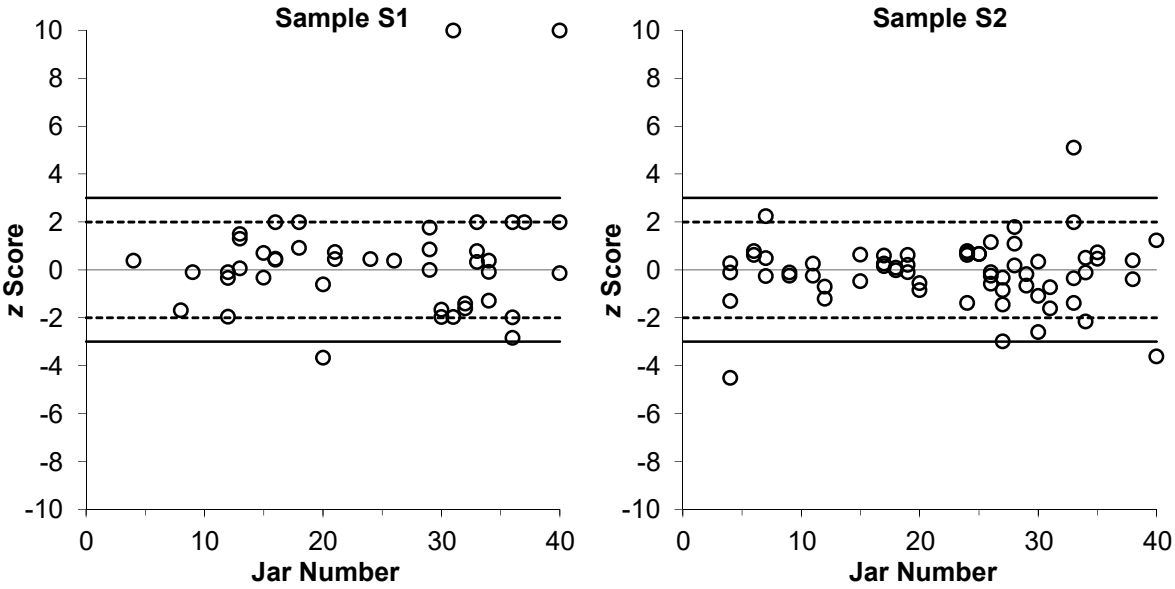


Solid lines correspond to the assigned value ± U for each analyte.

Figure 24 Participant Results vs Days in Transit

A2.2 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce homogeneous samples. The results of this study also gave no reason to question the samples' homogeneity. Comparisons of the *z* scores obtained for all scored analytes to bottle number analysed by participants are presented in Figure 25 (only known jar numbers, i.e. the participant received one jar only, have been included). No significant trend was observed.



z Scores greater than 10.0 have been plotted at 10.0

Figure 25 *z* Scores vs Jar Number

APPENDIX 3 TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 20 to 28. Some responses may be modified so that the participant cannot be identified.

Table 20 Sample Mass Used for Analysis

Lab. Code	S1 Sample Mass (g)	S2 Sample Mass (g)
1	5	5
2	10	10
3		
4	15	15
5	15	15
6	10	10
7	2	2
8	10	10
9	5	5
10		
11	10	10
12	10	10
13	5	5
14	10	10
15	Various	Various
16	Atrazine, Ethion: 5	MCPA: 5 Lindane, p,p'-DDD: 10
17	10	10
18	10	10
19	10g	10g
20	2	2
21	0.5	0.5
22	10 Imidacloprid, Metsulfuron-methyl: 2.5 g extraction weight	10
23	10	10
24	8.5	8.5
25	2	2
26	10	10

Table 21 Methodology – Atrazine

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	Solid-Liquid	DCM		GC-MS
2	Solid-Liquid	DCM/ACE (1:1)	N/A	GC-MS/MS
3				
4	QuEChERS	Acetonitrile (0.1% acetic acid)	PSA/C18	LC-MS/MS
5	QuEChERS	ACN	PSA	LC-MS/MS
6	NT			
7	Solid-Liquid	acidic ethyl acetate	PSA	LC-MS/MS
8	NT			
9	QuEChERS	Acetonitrile	d-SPE	LC-MS/MS
10				
11	Solid-Liquid	DCM:Acetone		GC-MS
12	Solid-Liquid	DCM:Acetone		GC-MS
13	QuEChERS	Acetonitrile	dSPE	GC-MS/MS
14	NT			
15	Solid-Liquid	Acetone/hexane		GC-MS
16	Solid-Liquid	water/ACN	-	LC-MS/MS
17	Solid-Liquid	DCM/Acetone		GC-MS/MS
18	Solid-Liquid	DCM:Acetone		GC-MS
19	Solid-Liquid	DCM:Acetone	N/A	GC-MS
20	QuEChERS	Acetonitrile	None	LC-MS/MS
21	NT			
22	Solid-Liquid	DCM:Acetone		GC-MS
23	Solid-Liquid	DCM:Acetone		GC-MS
24	Sonication	Ethyl acetate	NIL	GC-MS
25	Solid-Liquid	DCM		GC-MS
26	NT			

Table 22 Methodology – Ethion

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	Solid-Liquid	Hexane/Acetone		GC-ECD
2	Solid-Liquid	DCM/ACE (1:1)	N/A	GC-MS/MS
3				
4	QuEChERS	Acetonitrile (0.1% acetic acid)	PSA/C18	GC-MS/MS
5	QuEChERS	ACN	PSA	GC-MS/MS
6	Solid-Liquid	1: 1 DCM: ACETONE		GC-MS

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
7	Solid-Liquid	acidic ethyl acetate	PSA	LC-MS/MS
8	Solid-Liquid	Acetone / DCM		GC-MS
9	QuEChERS	Acetonitrile	d-SPE	GC-FPD
10				
11	Solid-Liquid	DCM:Acetone		GC-MS
12	Solid-Liquid	DCM:Acetone		GC-MS
13	QuEChERS	Acetonitrile	dSPE	GC-MS/MS
14	Solid-Liquid	DCM:ACE	None	GC-MS/MS
15	Solid-Liquid	Acetone/hexane		GC-MS
16	Solid-Liquid	Acetone/n-Hexane	-	GC-MS/MS
17	Solid-Liquid	Acetonitrile		LC-MS/MS
18	Solid-Liquid	DCM:Acetone		GC-MS
19	Solid-Liquid	DCM:Acetone	N/A	GC-MS
20	NT			
21	NT			
22	Solid-Liquid	DCM:Acetone		GC-MS
23	Solid-Liquid	DCM:Acetone		GC-MS
24	Sonication	Ethyl acetate	NIL	GC-MS
25	NT			
26	Solid-Liquid	DCM:Acetone		GC-MS/MS

Table 23 Methodology – Fipronil

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	Solid-Liquid	Hexane/Acetone		GC-ECD
2	NT			
3				
4	NT			
5	QuEChERS	ACN	PSA	GC-MS/MS
6	NT			
7	Solid-Liquid	acidic ethyl acetate	PSA	GC-MS/MS
8	NT			
9	QuEChERS	Acetonitrile	d-SPE	LC-MS/MS
10				
11	NT			
12	NT			
13	QuEChERS	Acetonitrile	dSPE	LC-MS/MS

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
14	NT			
15	Solid-Liquid	MeOH solution		LC-MS/MS
16	NT			
17	Solid-Liquid	Acetonitrile		LC-MS/MS
18	NT			
19	NT			
20				
21	NT			
22	Solid-Liquid	DCM:Acetone		GC-MS
23	Solid-Liquid	DCM:Acetone		GC-MS
24	NT			
25	NT			
26	NT			

Table 24 Methodology – Imidacloprid

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT			
2	NT			
3				
4	QuEChERS	Acetonitrile (0.1% acetic acid)	PSA/C18	LC-MS/MS
5	QuEChERS	ACN	PSA	LC-MS/MS
6	NT			
7	Solid-Liquid	acidic ethyl acetate	PSA	LC-MS/MS
8	NT			
9	QuEChERS	Acetonitrile	d-SPE	LC-MS/MS
10				
11	NT			
12	NT			
13	QuEChERS	Acetonitrile	dSPE	LC-MS/MS
14	NT			
15	Solid-Liquid	MeOH solution		LC-MS/MS
16	NT			
17	Solid-Liquid	Acetonitrile		LC-MS/MS
18	NT			
19	NT			
20	NT			

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
21	NT			
22	Solid-Liquid	Aqueous buffer		LC-MS/MS
23	NT			
24	NT			
25	NT			
26	NT			

Table 25 Methodology – Lindane

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	Solid-Liquid	Hexane/Acetone		GC-ECD
2	Solid-Liquid	DCM/ACE (1:1)	N/A	GC-MS/MS
3				
4	QuEChERS	Acetonitrile (0.1% acetic acid)	PSA/C18	GC-MS/MS
5	QuEChERS	ACN	PSA	GC-MS/MS
6	NT			
7	NT			
8	Solid-Liquid	Acetone / DCM		GC-MS
9	QuEChERS	Acetonitrile	d-SPE	GC-ECD
10	Solid-Liquid	Hexane/Acetone	Florisil	GC-MS/MS
11	Solid-Liquid	DCM:Acetone		GC-MS
12	Solid-Liquid	DCM:Acetone		GC-MS
13	QuEChERS	Acetonitrile	dSPE	GC-MS/MS
14	Solid-Liquid	DCM:ACE	None	GC-MS/MS
15	Solid-Liquid	Acetone/hexane		GC-ECD
16	Solid-Liquid	n-Hexane	-	GC-MS
17	NT			
18	Solid-Liquid	DCM:Acetone		GC-MS
19	Solid-Liquid	DCM:Acetone	N/A	GC-MS
20	Solid-Liquid	DCM/acetone	None	GC-MS/MS
21	Solid-Liquid	Hexane (0.5 g extracted into 10 mL hexane)		GC-MS/MS
22	Solid-Liquid	DCM:Acetone		GC-MS
23	Solid-Liquid	DCM:Acetone		GC-MS
24	Sonication	DCM:Acetone 1:1	NIL	GC-ECD
25	Solid-Liquid	DCM		GC-ECD
26	Solid-Liquid	DCM:Acetone		GC-MS/MS

Table 26 Methodology – MCPA

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	Solid-Liquid	DCM		GC-MS
2	Solid-Liquid	MeOH	N/A	LC-DAD
3				
4	NT			
5	NT			
6	Solid-Liquid			LC-MS
7	NT			
8	NT			
9	QuEChERS	Acetonitrile	d-SPE	LC-MS/MS
10				
11	Solid-Liquid	DCM:Acetone		GC-MS
12	NT			
13	NT			
14	NT			
15	Solid-Liquid	Toluene		GC-MS
16	Solid-Liquid	water/ACN	-	LC-MS/MS
17	Solid-Liquid	Acetonitrile		LC-MS/MS
18	NT			
19	NT			
20	QuEChERS	Methanol (contains 1% formic acid)	None	LC-MS/MS
21	NT			
22	Solid-Liquid	DCM:Acetone		GC-MS
23	NT			
24	Sonication	MeOH:Formic acid 98:2	NIL	LC-MS/MS
25	NT			
26	NT			

Table 27 Methodology – Metsulfuron-methyl

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT			
2	Solid-Liquid	MeOH	N/A	LC-DAD
3				
4	QuEChERS	Acetonitrile (0.1% acetic acid)	PSA/C18	LC-MS/MS
5	NT			
6	NT			
7	NT			

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
8	NT			
9	NT			
10				
11	NT			
12	NT			
13	QuEChERS	Acetonitrile	dSPE	LC-MS/MS
14	NT			
15	Solid-Liquid	MeOH solution		LC-MS/MS
16	NT			
17	Solid-Liquid	DCM/Acetone		GC-MS/MS
18	NT			
19	NT			
20	QuEChERS	Acetonitrile	None	LC-MS/MS
21	NT			
22	Solid-Liquid	Aqueous buffer		LC-MS/MS
23	NT			
24	NT			
25	NT			
26	NT			

Table 28 Methodology – p,p'-DDD

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	Solid-Liquid	Hexane/Acetone		GC-ECD
2	Solid-Liquid	DCM/ACE (1:1)	N/A	GC-MS/MS
3				
4	QuEChERS	Acetonitrile (0.1% acetic acid)	PSA/C18	GC-MS/MS
5	QuEChERS	ACN	PSA	GC-MS/MS
6	Solid-Liquid	1: 1 DCM: ACETONE		GC-MS
7	Solid-Liquid	acidic ethyl acetate	PSA	GC-MS/MS
8	Solid-Liquid	Acetone / DCM		GC-MS
9	QuEChERS	Acetonitrile	d-SPE	GC-ECD
10	Solid-Liquid	Hexane/Acetone	Florisil	GC-MS/MS
11	Solid-Liquid	DCM:Acetone		GC-MS
12	Solid-Liquid	DCM:Acetone		GC-MS
13	QuEChERS	Acetonitrile	dSPE	GC-MS/MS
14	Solid-Liquid	DCM:ACE	None	GC-MS/MS
15	Solid-Liquid	Acetone/hexane		GC-ECD

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
16	Solid-Liquid	n-Hexane	-	GC-MS
17	Solid-Liquid	DCM/Acetone		GC-MS/MS
18	Solid-Liquid	DCM:Acetone		GC-MS
19	Solid-Liquid	Hexane:Acetone	N/A	GC-ECD
20	Solid-Liquid	DCM/acetone	None	GC-MS/MS
21	Solid-Liquid	Hexane (0.5 g extracted into 10 mL hexane)		GC-MS/MS
22	Solid-Liquid	DCM:Acetone		GC-MS
23	Solid-Liquid	DCM:Acetone		GC-MS
24	Sonication	DCM:Acetone 1:1	NIL	GC-ECD
25	Solid-Liquid	DCM		GC-ECD
26	Solid-Liquid	DCM:Acetone		GC-MS/MS

APPENDIX 4 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, *z* SCORE AND E_N SCORE CALCULATIONS

A4.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528:2015.[7] The associated uncertainties were estimated as according to Equation 4.

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

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 for Sample S2 p,p'-DDD is set out below in Table 29.

Table 29 Uncertainty of the Robust Average for Sample S2 p,p'-DDD

No. results (p)	26
Robust Average	0.451 mg/kg
$S_{rob\ av}$	0.073 mg/kg
$u_{rob\ av}$	0.018 mg/kg
k	2
$U_{rob\ av}$	0.036 mg/kg

Therefore, the robust average for p,p'-DDD in Sample S2 is 0.451 ± 0.036 mg/kg.

A4.2 *z* Score and E_n Score Calculations

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

A worked example is set out below in Table 30.

Table 30 *z* Score and E_n Score Calculation for Sample S1 Atrazine Result Reported by Laboratory 2

Participant Result (mg/kg)	Assigned Value (mg/kg)	Target SD	*z* Score	E_n Score
0.192 ± 0.06	0.253 ± 0.031	15% as PCV, or: 0.15 × 0.253 = 0.038 mg/kg	z Score $= \frac{0.192-0.253}{0.038}$ = -1.61	E_n Score $= \frac{0.192-0.253}{\sqrt{0.06^2+0.031^2}}$ = -0.90

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
ACE	Acetone
ACN	Acetonitrile
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DAD	Diode Array Detection
DCM	Dichloromethane
d-SPE	Dispersive Solid Phase Extraction
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
FPD	Flame Photometric Detection
GAG	General Accreditation Guidance (NATA)
GC	Gas Chromatography
GUM	Guide to the expression of Uncertainty in Measurement
HEX	Hexane
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LC	Liquid Chromatography
LOR	Limit Of Reporting
Max	Maximum value in a set of results
MCPA	2-methyl-4-chlorophenoxyacetic acid
Md	Median
MeOH	Methanol
Min	Minimum value in a set of results
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
N	Number of numeric results
NATA	National Association of Testing Authorities, Australia
NMI	National Measurement Institute (Australia)
NR	Not Reported
NT	Not Tested
p,p'-DDD	Dichlorodiphenyldichloroethane
p,p'-DDE	Dichlorodiphenyldichloroethylene

p,p'-DDT	Dichlorodiphenyltrichloroethane
PCV	Performance Coefficient of Variation
PSA	Primary-Secondary Amine
PT	Proficiency Testing
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe preparation method
RA	Robust Average
RM	Reference Material
SD	Standard Deviation
SI	International System of Units
SLE	Solid-Liquid Extraction
SS	Spiked Samples
SV	Spiked Value
TOL	Toluene
Total DDT	Sum of DDD, DDE and DDT analytes
U	Expanded Uncertainty

END OF REPORT