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Proficiency Test Final Report AQA 24-03 Pesticides in Soil

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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.

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Jenny Xu

Geoff Morschel

Jasmine Duong

Luminita Antin

Lesley Johnston

Raluca Iavetz

Manager, Chemical Reference Values

105 Delhi Road, North Ryde NSW 2113

Phone: +61 2 9449 0178

Email: raluca.iavetz@measurement.gov.au

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SUMMARY

AQA 24-03 Pesticides in Soil commenced in February 2024. Twenty-four laboratories enrolled to participate, and all participants submitted results.

Two soil samples were prepared by spiking soil with various pesticides.

Of a possible 240 results, a total of 140 numeric results (58%) were submitted. Twenty-two results were submitted as a 'less than' value (<*x*) or Not Reported (NR), and 78 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 **4**, **18**, **19**, **21** and **23** reported results for all scored analytes.

Laboratory **14** did not report a numeric result for a spiked analyte that they tested for.

Two participants reported analytes that were not spiked into the test samples (total of two results).

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

Of 123 *z*-scores, 115 (93%) returned $|z| \leq 2.0$, indicating an acceptable performance.

Of 118 E_n-scores, 101 (86%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratory **4** returned acceptable *z*-scores 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 140 numeric results, 116 (83%) were reported with an associated estimate of expanded uncertainty. The magnitude of these expanded uncertainties ranged from 4.2% to 88% 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 interlaboratory comparisons'.[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, vegetables and herbs, 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 17043:2023 as a provider of PT schemes.[1] This study is within the scope of NMI's accreditation.

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitations sent	19/02/2024
Samples sent	18/03/2024
Results due	1/05/2024
Interim Report	3/05/2024
Preliminary Report	9/05/2024

2.2 Participation and Laboratory Code

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

2.3 Selection of Pesticides

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 Environment Protection (Assessment of Site Contamination) Measure Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

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

Table 1 List of Possible Analytes

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

2.4 Test Material Preparation

Two soils were used as the starting materials in this study: topsoil purchased from a local supplier was used for both samples, and soil from a residential garden was also added to Sample S2.

The soil was spiked with various pesticides to obtain the mass fractions listed in Table 2.

Table 2 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty[a] (mg/kg)
S1	*cis*-Chlordane[b]	0.398	0.020
	trans-Chlordane[b]	0.202	0.010
	Dieldrin	0.0339	0.0017
	Propiconazole	0.195	0.010
S2	Atrazine	0.198	0.010
	Diazinon	0.905	0.045
	Imidacloprid	0.150	0.008
	Metsulfuron-methyl	1.20	0.06
	Tebuconazole	1.20	0.06

[a] 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.

[b] Total Chlordane has also been assessed in this PT study.

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, stored and dispatched using a process that has been demonstrated to produce sufficiently homogeneous and stable samples in previous NMI Pesticides in Soil PT studies.

Participants' results also gave no reason to question the homogeneity or transport stability 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 66% to 86% 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 18 March 2024.

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. This figure will be used in all statistical analysis in the study report.
- Report results as you would report to a client, i.e. corrected for recovery or not, according to your standard procedure, and applying the limit of reporting of the method used for analysis (no limit of reporting has been set for this study).
- For each analyte in each sample, report the associated expanded uncertainty in units of mg/kg (e.g. 0.50 ± 0.02 mg/kg).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Report any listed pesticide not tested with NT as the result.
- Report the basis of your uncertainty estimates as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- 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 15 April 2024. Late results may not be included in the study report.

The results due date was extended to 1 May 2024 as samples for an international participant were delayed by customs.

2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 3 May 2024.

A Preliminary Report was emailed to all participants on 9 May 2024. This report included a summary of the results reported by participants, assigned values, performance coefficient of variations (PCVs), *z*-scores and E_n-scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

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 4.

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	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Control samples	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS Duplicate analysis	CRM Recoveries of SS	Eurachem/ CITAC Guide
3	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Duplicate analysis	Instrument calibration	
4	k = 2	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/ CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples	CRM Instrument calibration Recoveries of SS	ISO/GUM
6	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	Eurachem/ CITAC Guide
7	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis	CRM Recoveries of SS	ISO/GUM
8	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Duplicate analysis	Recoveries of SS	Eurachem/ CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies 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 Coverage factor not reported	Control samples - RM Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies	Eurachem/ CITAC Guide
11	Coverage factor not reported			
12	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - CRM		ISO/GUM
13	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/ CITAC Guide
14	Coverage factor not reported			
15	Top Down - precision and estimates of the method and laboratory bias k = 2	Duplicate analysis	CRM Instrument calibration Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
16	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies Recoveries of SS Standard purity	Eurachem/ CITAC Guide
17	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported			ISO/GUM
18	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/ CITAC Guide
19	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	ISO/GUM
20	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples		ISO/GUM
21	Standard uncertainty based on historical data Coverage factor not reported	Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	Eurachem/ CITAC Guide
22	Coverage factor not reported			

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 k = 2	Control samples - SS	CRM Recoveries of SS	NMI Uncertainty Course
24	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples Duplicate analysis	Recoveries of 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
8	All	Paraquat in Soils	Thank you for your feedback, we will consider this analyte in future studies.
16	All	Data analysed should be by test, and sometimes get analysed several times by different operators	Thank you for your feedback, we will look into adding additional date analysed fields in future results sheets.
19	S2	Glyphosate breakdown AMPA seen in sample at 0.03mg/kg	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 14 with the 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), and other estimates of analyte mass fraction. Bar charts of results and performance scores are presented in Figures2 to 1, with an example chart with interpretation guide shown in Figure 1.

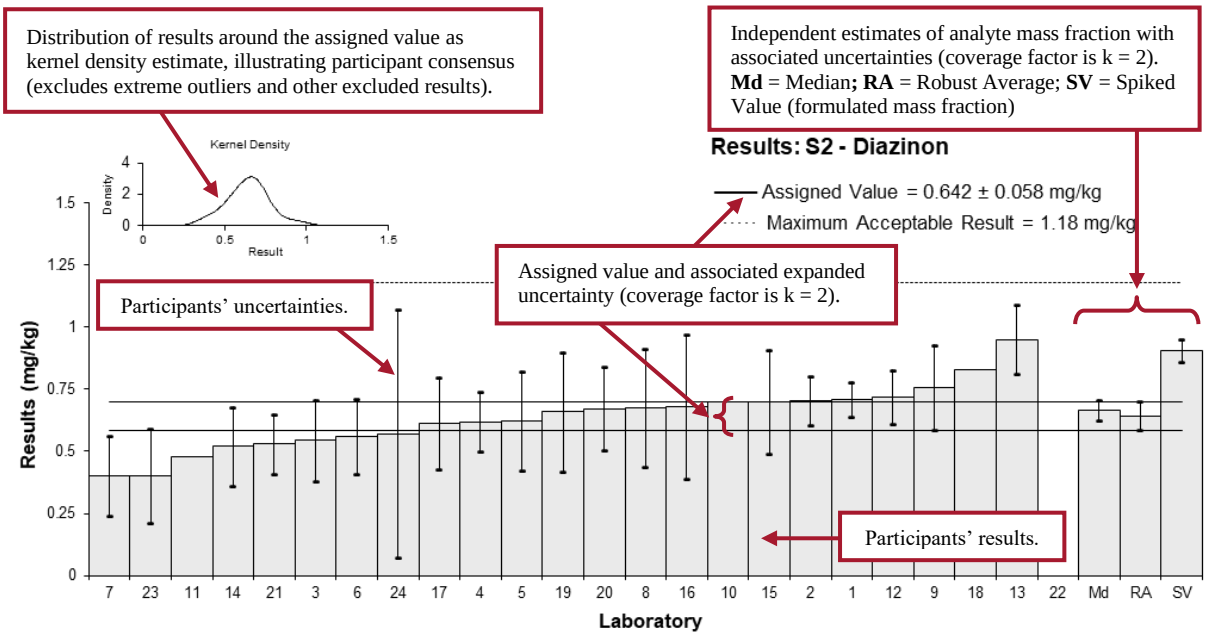


Figure 1 Guide to Presentation of Results

4.2 Outliers, Extreme Outliers and Other Excluded Results

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] Extreme outliers, 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]

After the release of the Interim Report, Laboratory **11** identified that they had reported incorrect results for Sample S1 propiconazole, and Sample S2 diazinon and tebuconazole (dilution adjustment error). These results have been removed from all statistical calculations.

4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property or characteristic 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 3).

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.[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 for Proficiency Assessment

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

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

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 for proficiency assessment 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 acceptable;
- $2.0 < |z| < 3.0$ is questionable; and
- $|z| \geq 3.0$ is unacceptable.

4.8 E_n-Score

The E_n-score is complementary to the *z*-score in assessment of laboratory performance. The E_n-score includes expanded 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:

- $|E_n| < 1.0$ is acceptable; and
- $|E_n| \geq 1.0$ is unacceptable.

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 No.	S1
Matrix	Soil
Analyte	*cis*-Chlordane
Unit	mg/kg

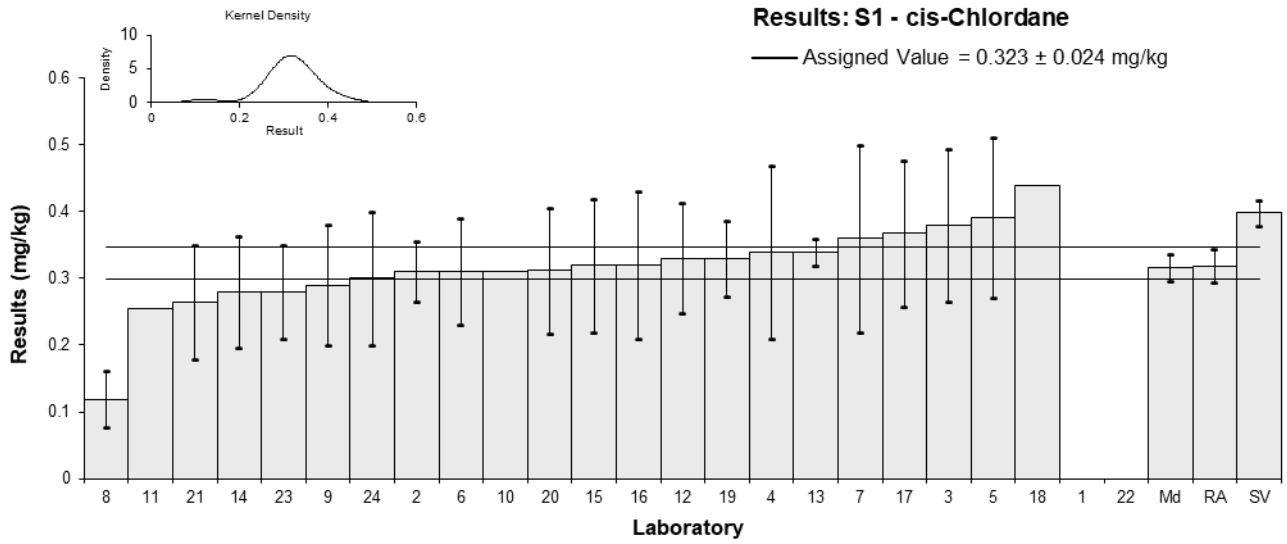
Participant Results

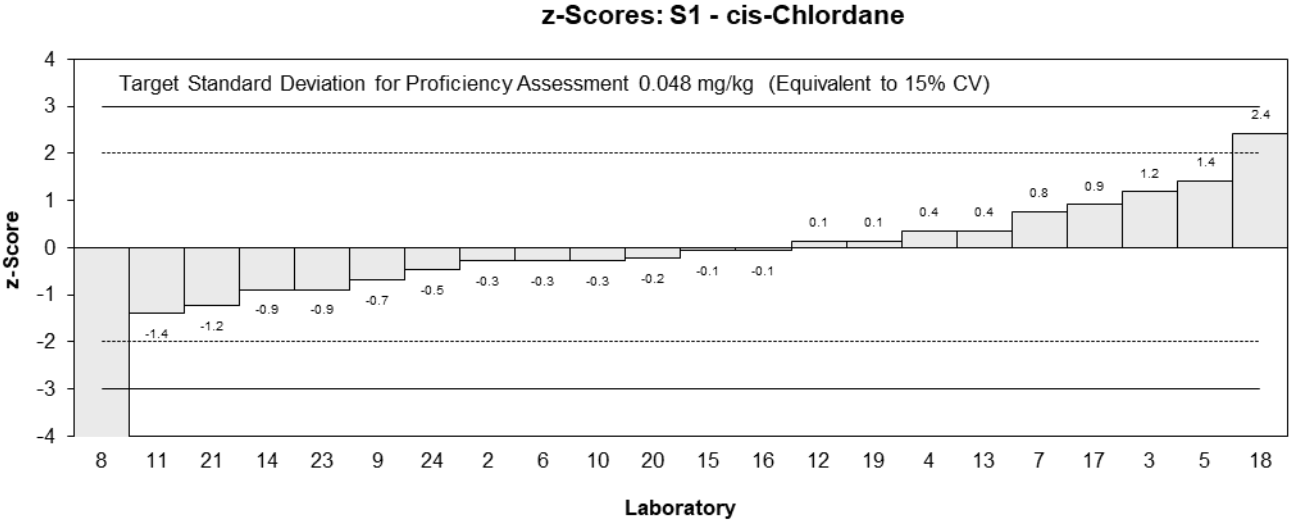
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.310	0.045	NR	-0.27	-0.25
3	0.38	0.114	NR	1.18	0.49
4	0.34	0.13	120	0.35	0.13
5	0.392	0.120	NR	1.42	0.56
6	0.31	0.08	96.6	-0.27	-0.16
7	0.36	0.14	NR	0.76	0.26
8*	0.119	0.042	85	-4.21	-4.22
9	0.29	0.09	NR	-0.68	-0.35
10	0.31	NR	NR	-0.27	-0.54
11	0.255	NR	115	-1.40	-2.83
12	0.33	0.0825	NR	0.14	0.08
13	0.34	0.02	NR	0.35	0.54
14	0.28	0.084	NR	-0.89	-0.49
15	0.32	0.10	NR	-0.06	-0.03
16	0.32	0.11	NR	-0.06	-0.03
17	0.3673	0.1102	NR	0.91	0.39
18	0.44	NR	NR	2.41	4.88
19	0.33	0.057	NR	0.14	0.11
20	0.312	0.094	NR	-0.23	-0.11
21	0.264	0.085	NR	-1.22	-0.67
22	NT	NT	NT		
23	0.28	0.07	NR	-0.89	-0.58
24	0.3	0.1	93	-0.47	-0.22

* Outlier, see Section 4.2

Statistics

Assigned Value	0.323	0.024
Spike Value	0.398	0.020
Robust Average	0.319	0.025
Median	0.316	0.020
Mean	0.316	
N	22	
Max	0.44	
Min	0.119	
Robust SD	0.046	
Robust CV	14%	


Kernel Density
Density
Result
Results: S1 - cis-Chlordane
Assigned Value = 0.323 ± 0.024 mg/kg
Results (mg/kg)
Laboratory
8 11 21 14 23 9 24 2 6 10 20 15 16 12 19 4 13 7 17 3 5 18 1 22 Md RA SV


z-Scores: S1 - cis-Chlordane
Target Standard Deviation for Proficiency Assessment 0.048 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
8 11 21 14 23 9 24 2 6 10 20 15 16 12 19 4 13 7 17 3 5 18
-1.4 -1.2 -0.9 -0.9 -0.7 -0.5 -0.3 -0.3 -0.3 -0.2 -0.1 -0.1 0.1 0.1 0.4 0.4 0.8 0.9 1.2 1.4 2.4

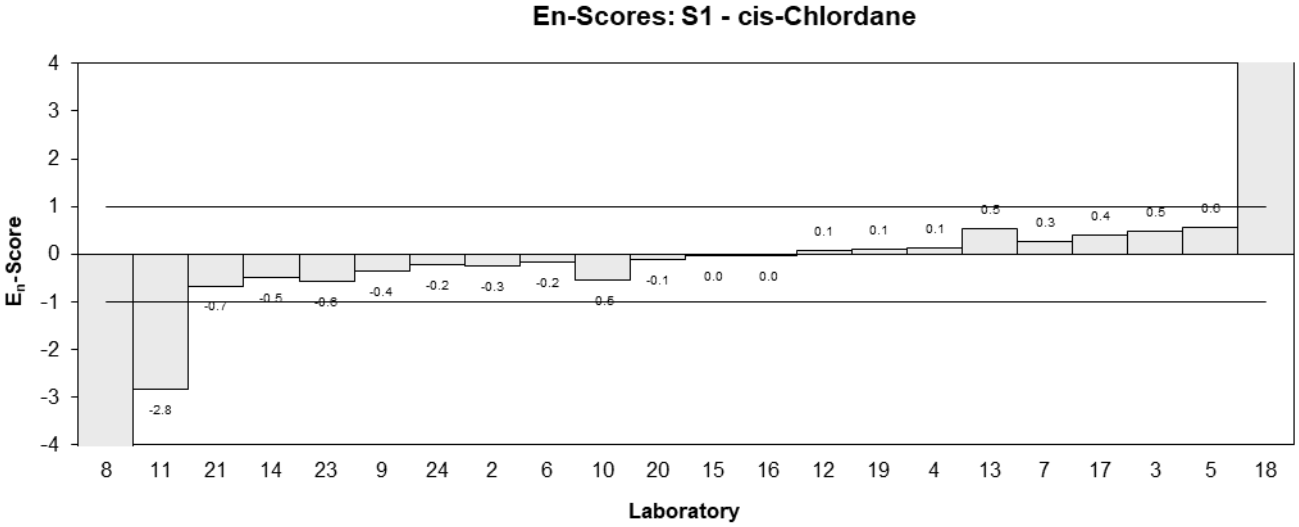

En-Scores: S1 - cis-Chlordane
En-Score
Laboratory
8 11 21 14 23 9 24 2 6 10 20 15 16 12 19 4 13 7 17 3 5 18
-2.8 -0.7 -0.5 -0.6 -0.4 -0.2 -0.3 -0.2 -0.5 -0.1 0.0 0.0 0.1 0.1 0.1 0.5 0.3 0.4 0.5 0.6

Figure 2

Table 6

Sample Details

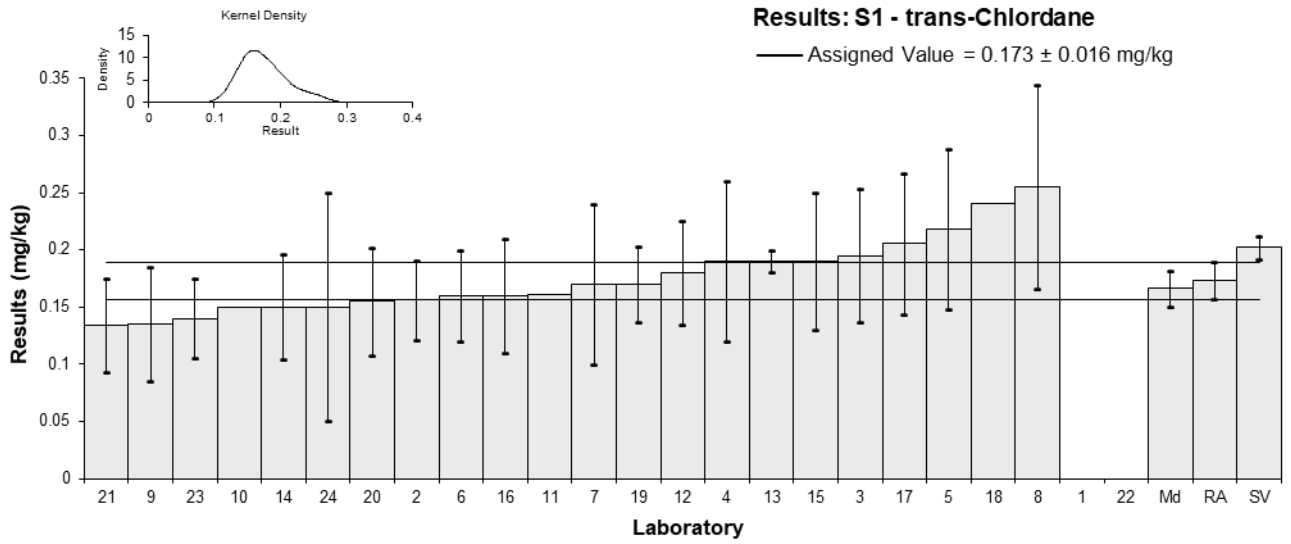
Sample No.	S1
Matrix	Soil
Analyte	*trans*-Chlordane
Unit	mg/kg

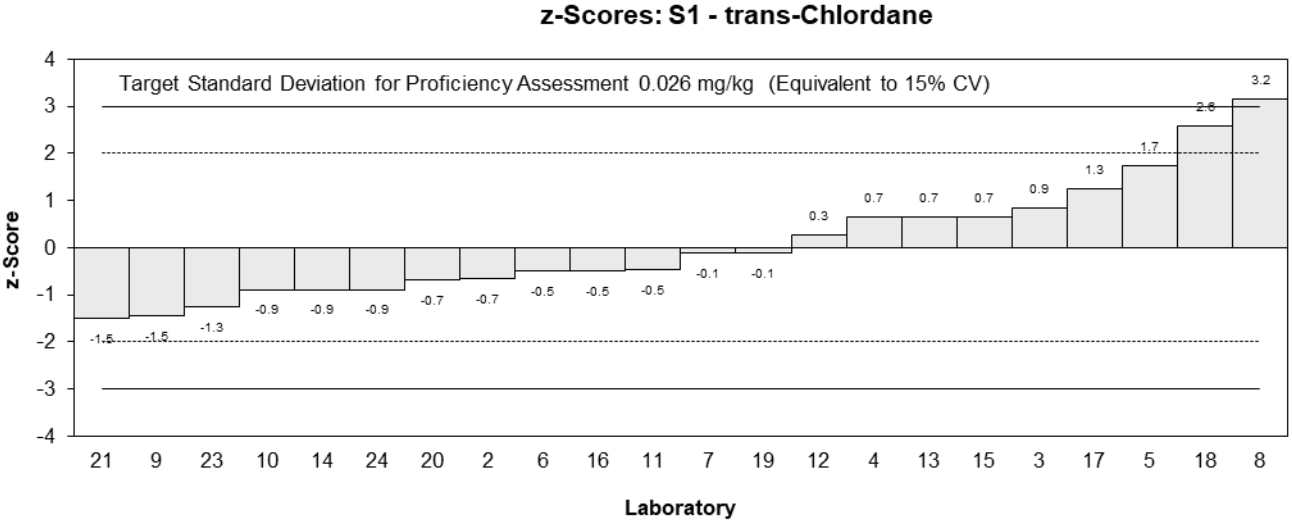
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.156	0.035	NR	-0.66	-0.44
3	0.195	0.0585	NR	0.85	0.36
4	0.19	0.07	120	0.66	0.24
5	0.218	0.070	NR	1.73	0.63
6	0.16	0.04	96.6	-0.50	-0.30
7	0.17	0.07	NR	-0.12	-0.04
8	0.255	0.089	80	3.16	0.91
9	0.135	0.05	NR	-1.46	-0.72
10	0.15	NR	NR	-0.89	-1.44
11	0.161	NR	118	-0.46	-0.75
12	0.18	0.045	NR	0.27	0.15
13	0.19	0.01	NR	0.66	0.90
14	0.15	0.046	NR	-0.89	-0.47
15	0.19	0.06	NR	0.66	0.27
16	0.16	0.05	NR	-0.50	-0.25
17	0.2054	0.0616	NR	1.25	0.51
18	0.24	NR	NR	2.58	4.19
19	0.17	0.033	NR	-0.12	-0.08
20	0.155	0.047	NR	-0.69	-0.36
21	0.134	0.041	NR	-1.50	-0.89
22	NT	NT	NT		
23	0.14	0.035	NR	-1.27	-0.86
24	0.15	0.1	93	-0.89	-0.23

Statistics

Assigned Value	0.173	0.016
Spike Value	0.202	0.010
Robust Average	0.173	0.016
Median	0.166	0.016
Mean	0.175	
N	22	
Max	0.255	
Min	0.134	
Robust SD	0.031	
Robust CV	18%	


Kernel Density
Density
Result
Results: S1 - trans-Chlordane
Assigned Value = 0.173 ± 0.016 mg/kg
Results (mg/kg)
Laboratory
21 9 23 10 14 24 20 2 6 16 11 7 19 12 4 13 15 3 17 5 18 8 1 22 Md RA SV


z-Scores: S1 - trans-Chlordane
Target Standard Deviation for Proficiency Assessment 0.026 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
21 9 23 10 14 24 20 2 6 16 11 7 19 12 4 13 15 3 17 5 18 8

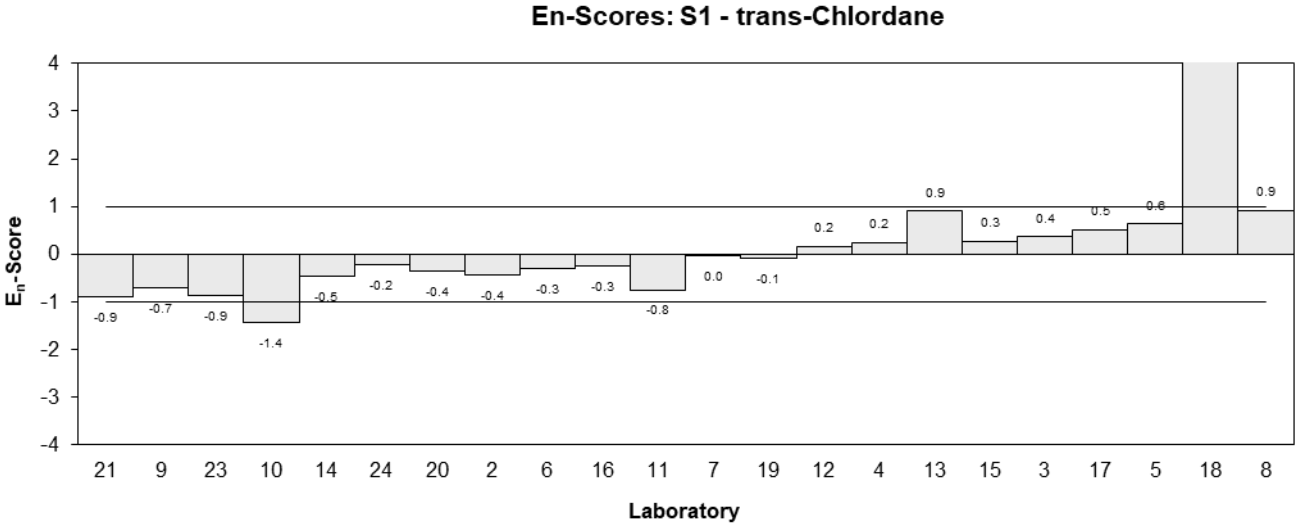

En-Scores: S1 - trans-Chlordane
En-Score
Laboratory
21 9 23 10 14 24 20 2 6 16 11 7 19 12 4 13 15 3 17 5 18 8

Figure 3

Table 7

Sample Details

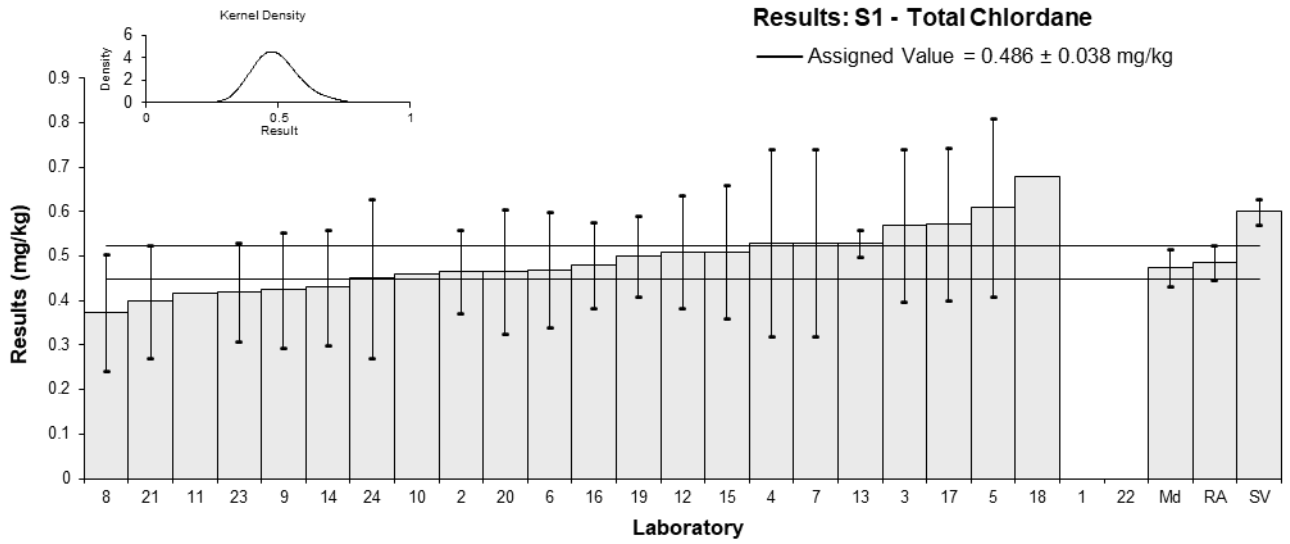
Sample No.	S1
Matrix	Soil
Analyte	Total Chlordane
Unit	mg/kg

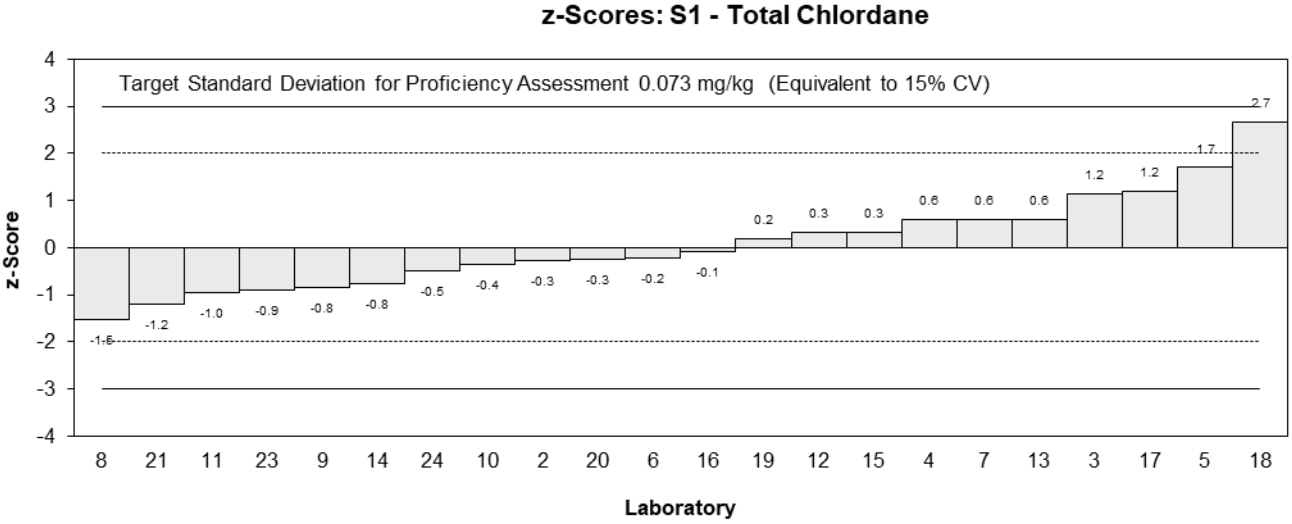
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	0.466	0.094	NR	-0.27	-0.20
3	0.57	0.171	NR	1.15	0.48
4	0.53	0.21	120	0.60	0.21
5	0.610	0.200	NR	1.70	0.61
6	0.47	0.13	96.6	-0.22	-0.12
7	0.53	0.21	NR	0.60	0.21
8	0.374	0.131	NR	-1.54	-0.82
9	0.425	0.13	NR	-0.84	-0.45
10	0.46	NR	NR	-0.36	-0.68
11	0.416	NR	NR	-0.96	-1.84
12	0.51	0.1275	NR	0.33	0.18
13	0.53	0.03	NR	0.60	0.91
14	0.43	0.13	NR	-0.77	-0.41
15	0.51	0.15	NR	0.33	0.16
16	0.48	0.096	NR	-0.08	-0.06
17	0.5732	0.172	NR	1.20	0.50
18	0.68	NR	NR	2.66	5.11
19	0.50	0.090	NR	0.19	0.14
20	0.467	0.140	NR	-0.26	-0.13
21	0.398	0.126	NR	-1.21	-0.67
22	NT	NT	NT		
23	0.42	0.11	NR	-0.91	-0.57
24	0.45	0.18	93	-0.49	-0.20

Statistics

Assigned Value	0.486	0.038
Spike Value	0.600	0.030
Robust Average	0.486	0.038
Median	0.475	0.041
Mean	0.491	
N	22	
Max	0.68	
Min	0.374	
Robust SD	0.071	
Robust CV	15%	


Kernel Density
Density
Result
Results: S1 - Total Chlordane
Assigned Value = 0.486 ± 0.038 mg/kg
Results (mg/kg)
Laboratory
8 21 11 23 9 14 24 10 2 20 6 16 19 12 15 4 7 13 3 17 5 18 1 22 Md RA SV


z-Scores: S1 - Total Chlordane
Target Standard Deviation for Proficiency Assessment 0.073 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
8 21 11 23 9 14 24 10 2 20 6 16 19 12 15 4 7 13 3 17 5 18

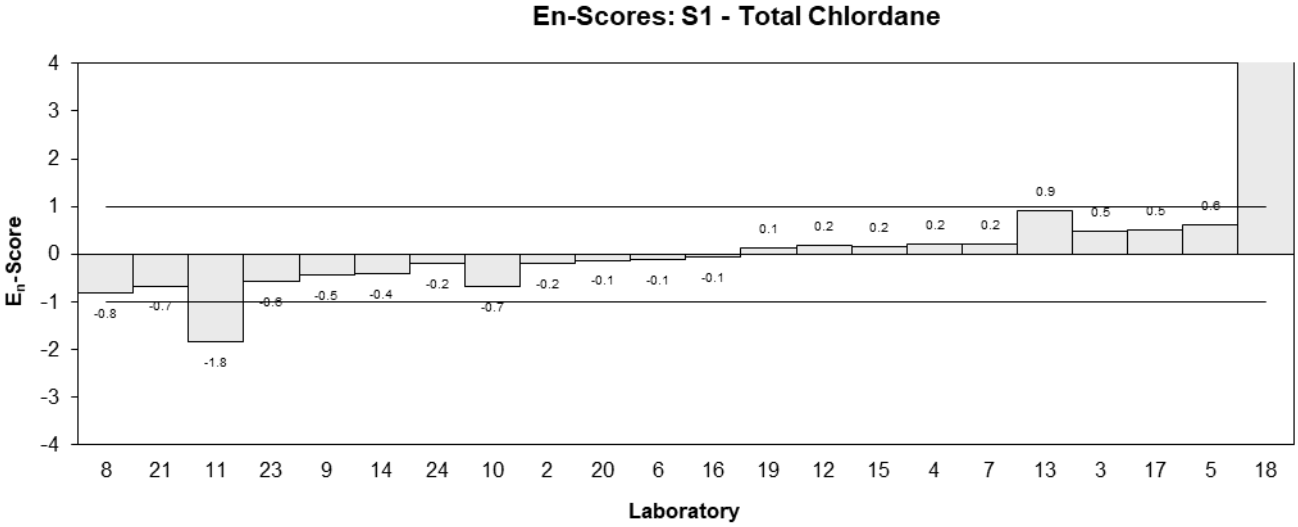

En-Scores: S1 - Total Chlordane
En-Score
Laboratory
8 21 11 23 9 14 24 10 2 20 6 16 19 12 15 4 7 13 3 17 5 18

Figure 4

Table 8

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Dieldrin
Unit	mg/kg

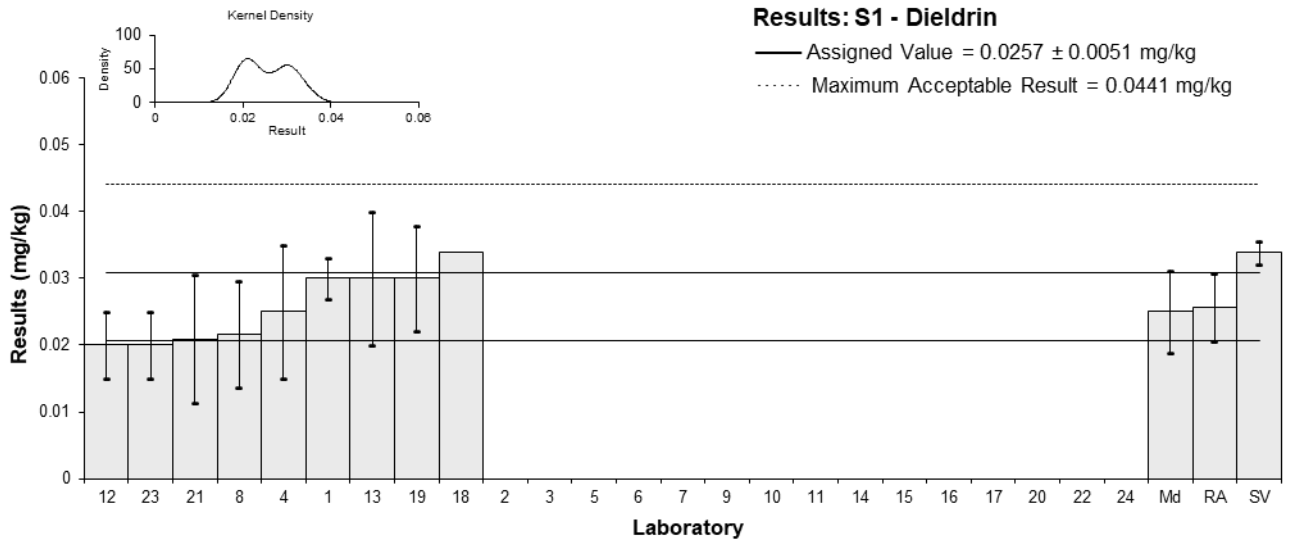
Participant Results

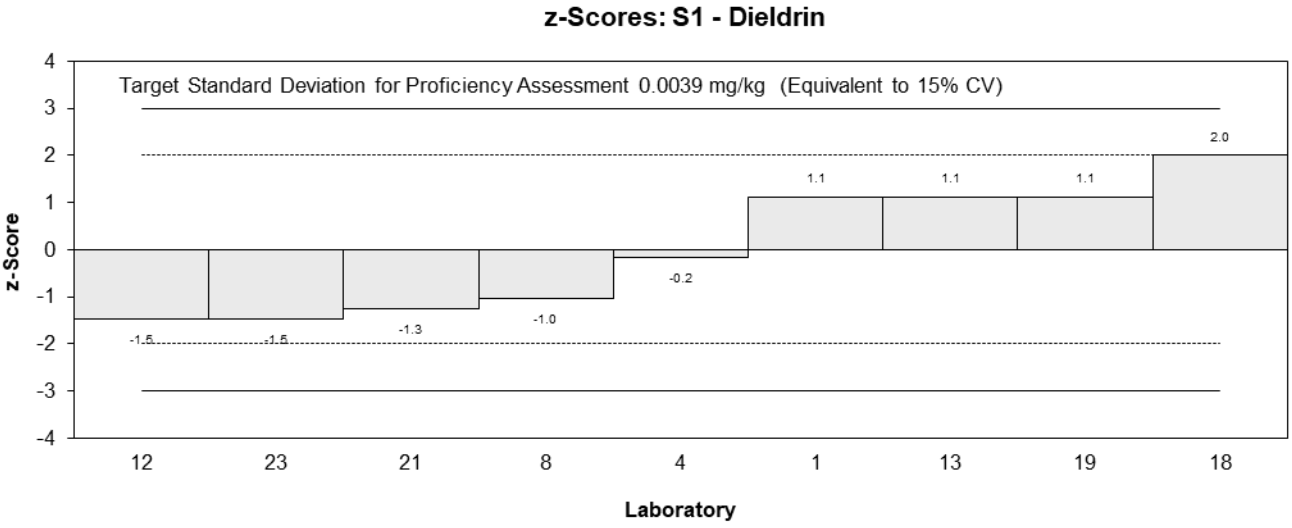
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.03	0.003	74	1.12	0.73
2	<0.05	NR	NR		
3	<0.05	NR	NR		
4	0.025	0.010	120	-0.18	-0.06
5	<0.05	NR	NR		
6	<0.05	NR	96.6		
7	<0.1	NR	113		
8	0.0217	0.008	102	-1.04	-0.42
9	<0.05	NR	NR		
10	<0.05	NR	NR		
11	<0.05	NR	NR		
12	0.02	0.005	NR	-1.48	-0.80
13	0.03	0.01	NR	1.12	0.38
14	NT	NT	NT		
15	< 0.05	NR	NR		
16	<0.05	0.02	NR		
17	<0.05	NR	NR		
18	0.034	NR	NR	2.00▼	
19	0.03	0.0079	NR	1.12	0.46
20	< 0.05	NR	NR		
21	0.0209	0.0096	NR	-1.25	-0.44
22	NT	NT	NT		
23	0.02	0.005	NR	-1.48	-0.80
24	<0.2	0.2	NR		

▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.0257	0.0051
Spike Value	0.0339	0.0017
Robust Average	0.0257	0.0051
Max Acceptable Result	0.0441	
Median	0.0250	0.0062
Mean	0.0257	
N	9	
Max	0.034	
Min	0.02	
Robust SD	0.0061	
Robust CV	24%	


Kernel Density
Density
Result
Results: S1 - Dieldrin
Assigned Value = 0.0257 ± 0.0051 mg/kg
Maximum Acceptable Result = 0.0441 mg/kg
Results (mg/kg)
Laboratory
12 23 21 8 4 1 13 19 18 2 3 5 6 7 9 10 11 14 15 16 17 20 22 24 Md RA SV


z-Scores: S1 - Dieldrin
Target Standard Deviation for Proficiency Assessment 0.0039 mg/kg (Equivalent to 15% CV)
z-Score
-1.5
-1.5
-1.3
-1.0
-0.2
1.1
1.1
1.1
2.0
Laboratory
12 23 21 8 4 1 13 19 18

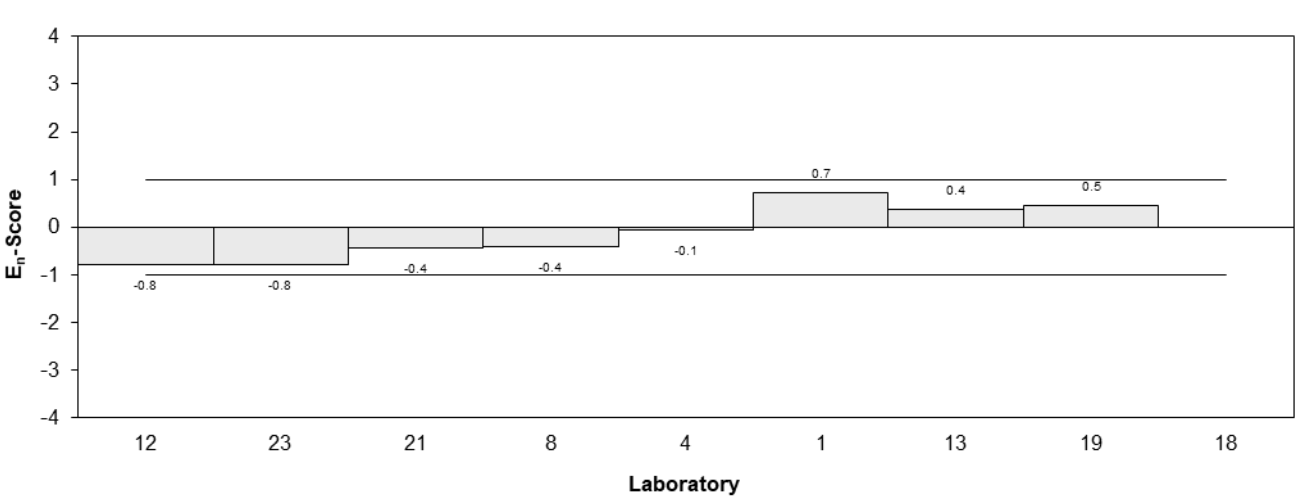

En-Scores: S1 - Dieldrin
En-Score
-0.8
-0.8
-0.4
-0.4
-0.1
0.7
0.4
0.5
Laboratory
12 23 21 8 4 1 13 19 18

Figure 5

Table 9

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Propiconazole
Unit	mg/kg

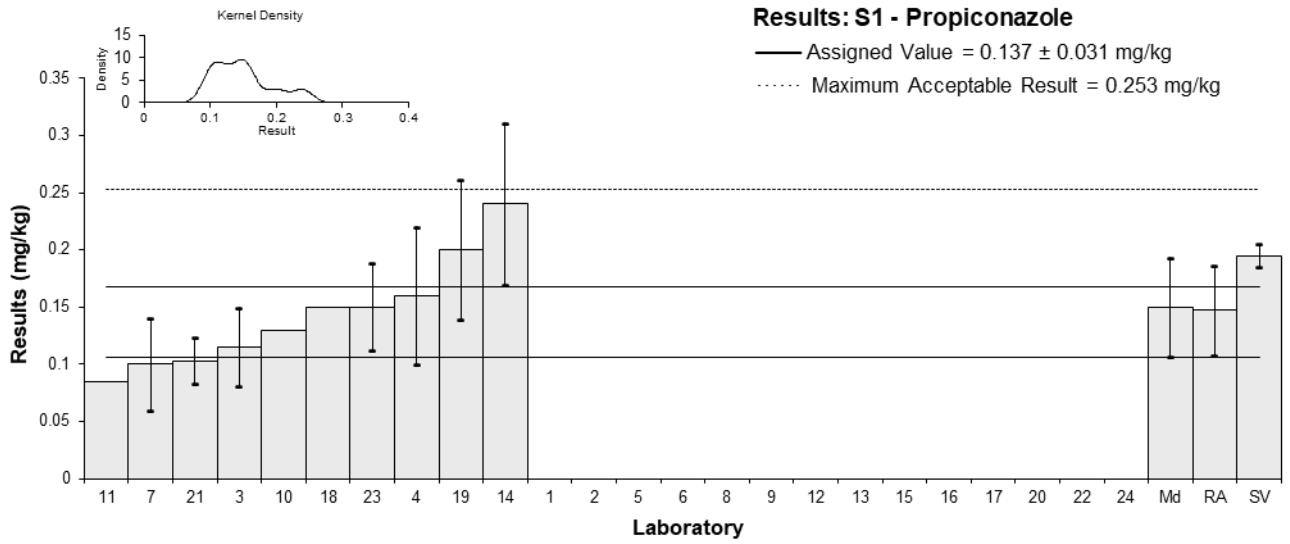
Participant Results

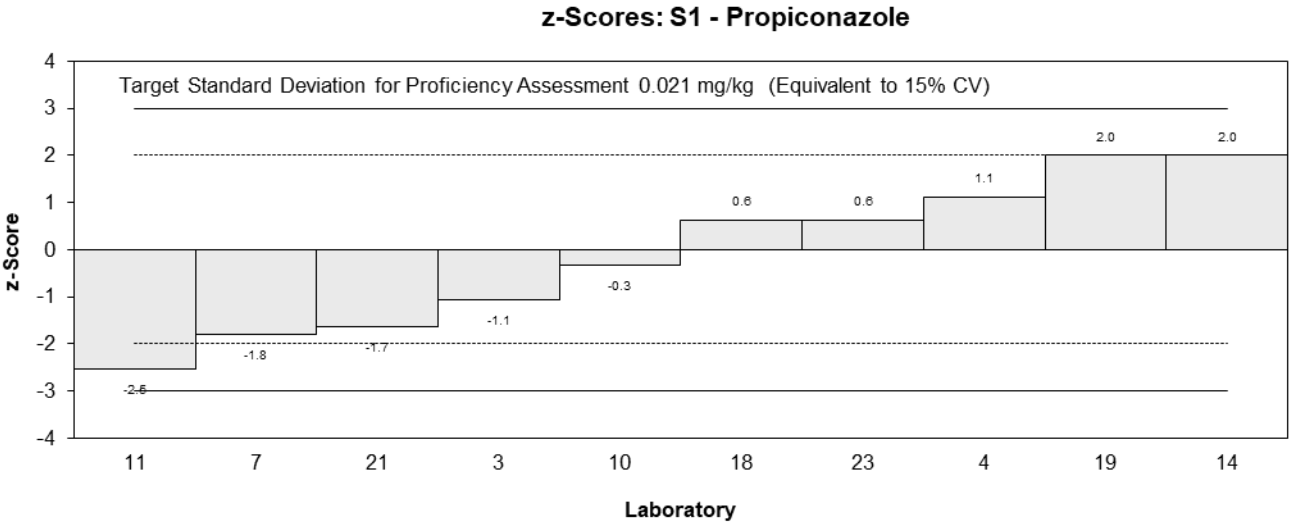
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	NT	NT	NT		
3	0.115	0.0345	NR	-1.07	-0.47
4	0.16	0.06	120	1.12	0.34
5	NT	NT	NT		
6	NT	NT	NT		
7	0.1	0.04	NR	-1.80	-0.73
8	NT	NT	NT		
9	NT	NT	NT		
10	0.13	NR	NR	-0.34	-0.23
11**	0.085	NR	95	-2.53	-1.68
12	NT	NT	NT		
13	NT	NT	NT		
14*	0.24	0.071	NR	2.00▼	
15	NT	NT	NT		
16	NT	NT	NT		
17	NT	NT	NT		
18	0.15	NR	NR	0.63	0.42
19	0.20	0.061	NR	2.00▼	
20	NT	NT	NT		
21	0.103	0.02	NR	-1.65	-0.92
22	NT	NT	NT		
23	0.15	0.038	NR	0.63	0.27
24	<0.5	0.5	NR		

* Outlier, ** Excluded Result, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.137	0.031
Spike Value	0.195	0.010
Robust Average	0.147	0.039
Max Acceptable Result	0.253	
Median	0.150	0.043
Mean	0.150	
N	9	
Max	0.24	
Min	0.1	
Robust SD	0.046	
Robust CV	31%	


Kernel Density
Density
Result
Results: S1 - Propiconazole
Assigned Value = 0.137 ± 0.031 mg/kg
Maximum Acceptable Result = 0.253 mg/kg
Results (mg/kg)
Laboratory
11 7 21 3 10 18 23 4 19 14 1 2 5 6 8 9 12 13 15 16 17 20 22 24 Md RA SV


z-Scores: S1 - Propiconazole
Target Standard Deviation for Proficiency Assessment 0.021 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
11 7 21 3 10 18 23 4 19 14
-2.6 -1.8 -1.7 -1.1 -0.3 0.6 0.6 1.1 2.0 2.0

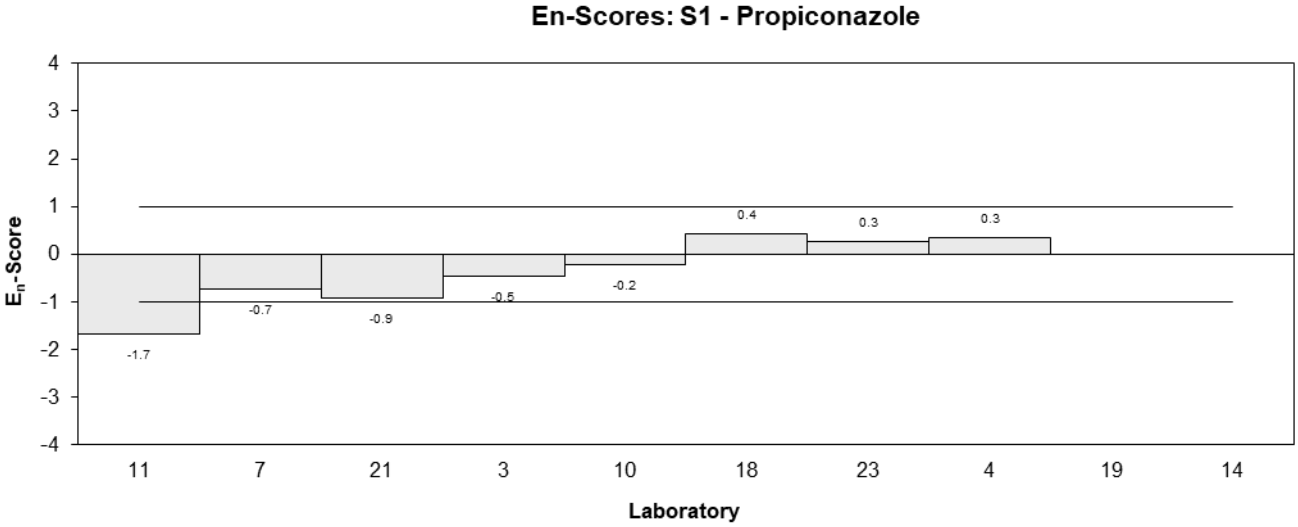

En-Scores: S1 - Propiconazole
En-Score
Laboratory
11 7 21 3 10 18 23 4 19 14
-1.7 -0.7 -0.9 -0.5 -0.2 0.4 0.3 0.3

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Atrazine
Unit	mg/kg

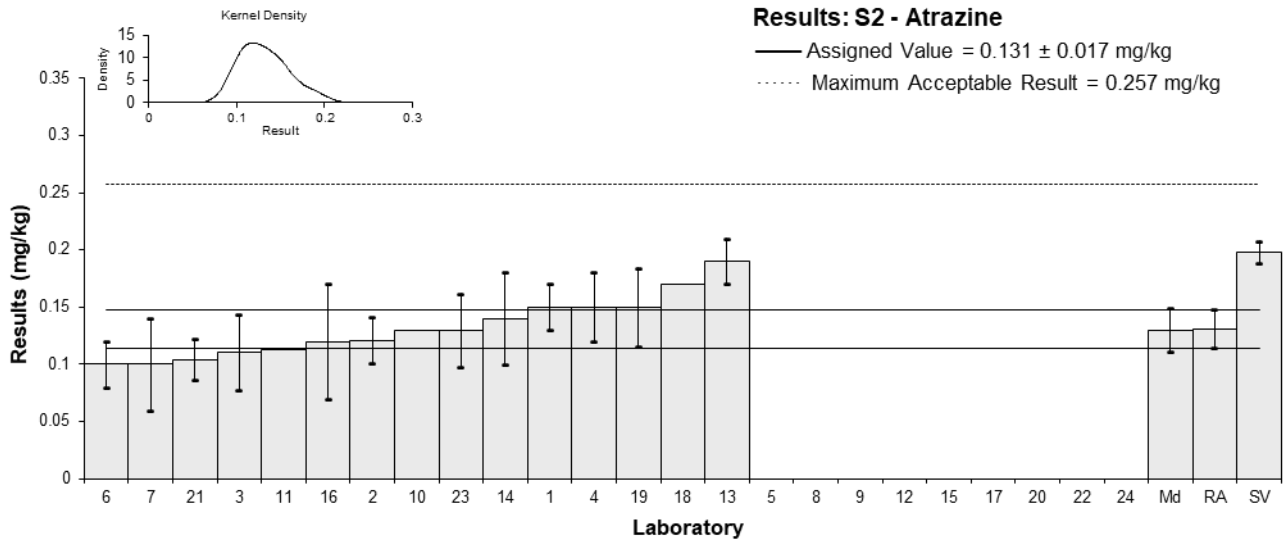
Participant Results

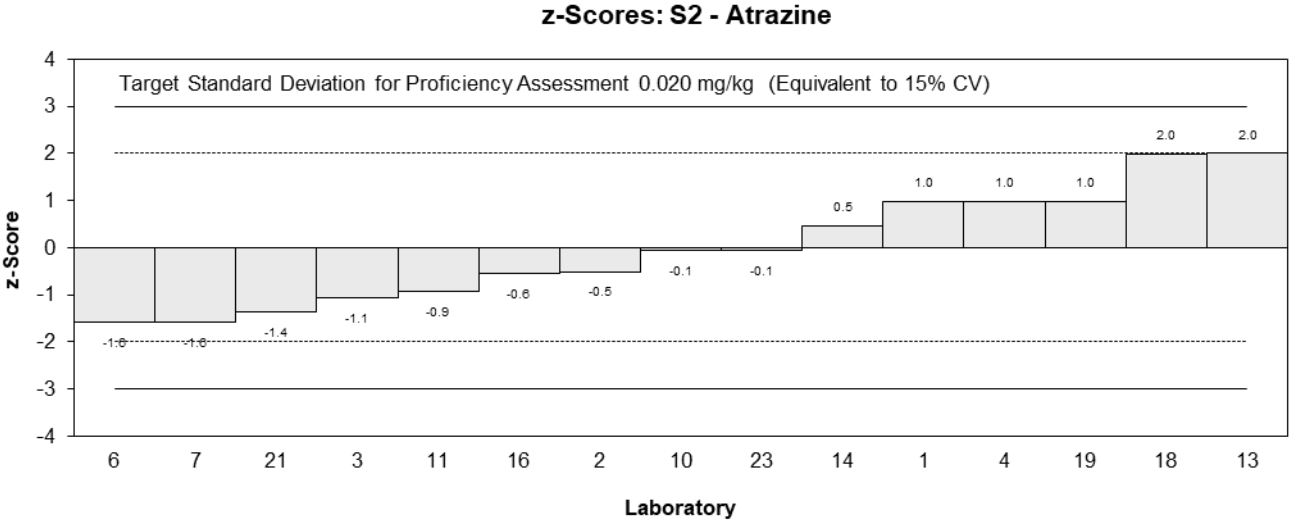
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.15	0.02	101	0.97	0.72
2	0.121	0.02	NR	-0.51	-0.38
3	0.11	0.033	NR	-1.07	-0.57
4	0.15	0.03	104	0.97	0.55
5	<0.3	NR	NR		
6	0.10	0.02	NR	-1.58	-1.18
7	0.1	0.04	NR	-1.58	-0.71
8	NT	NT	NT		
9	<0.5	NR	NR		
10	0.13	NR	NR	-0.05	-0.06
11	0.113	NR	88	-0.92	-1.06
12	NT	NT	NT		
13	0.19	0.02	NR	2.00▼	
14	0.14	0.04	NR	0.46	0.21
15	< 0.2	NR	NR		
16	0.12	0.05	NR	-0.56	-0.21
17	NT	NT	NT		
18	0.17	NR	NR	1.98	2.29
19	0.15	0.034	NR	0.97	0.50
20	NT	NT	NT		
21	0.104	0.018	NR	-1.37	-1.09
22	NT	NT	NT		
23	0.13	0.032	NR	-0.05	-0.03
24	<0.5	0.5	NR		

▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.131	0.017
Spike Value	0.198	0.010
Robust Average	0.131	0.017
Max Acceptable Result	0.257	
Median	0.130	0.019
Mean	0.132	
N	15	
Max	0.19	
Min	0.1	
Robust SD	0.027	
Robust CV	21%	


Kernel Density
Density
Result
Results: S2 - Atrazine
Assigned Value = 0.131 ± 0.017 mg/kg
Maximum Acceptable Result = 0.257 mg/kg
Results (mg/kg)
Laboratory
6 7 21 3 11 16 2 10 23 14 1 4 19 18 13 5 8 9 12 15 17 20 22 24 Md RA SV


z-Scores: S2 - Atrazine
Target Standard Deviation for Proficiency Assessment 0.020 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 7 21 3 11 16 2 10 23 14 1 4 19 18 13

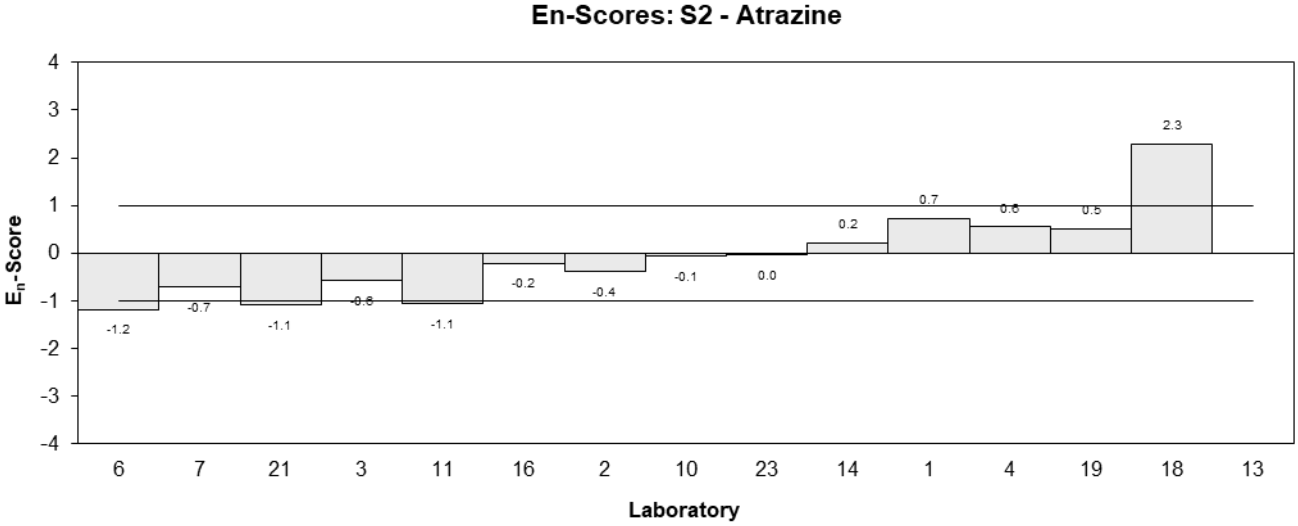

En-Scores: S2 - Atrazine
En-Score
Laboratory
6 7 21 3 11 16 2 10 23 14 1 4 19 18 13

Figure 7

Table 11

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Diazinon
Unit	mg/kg

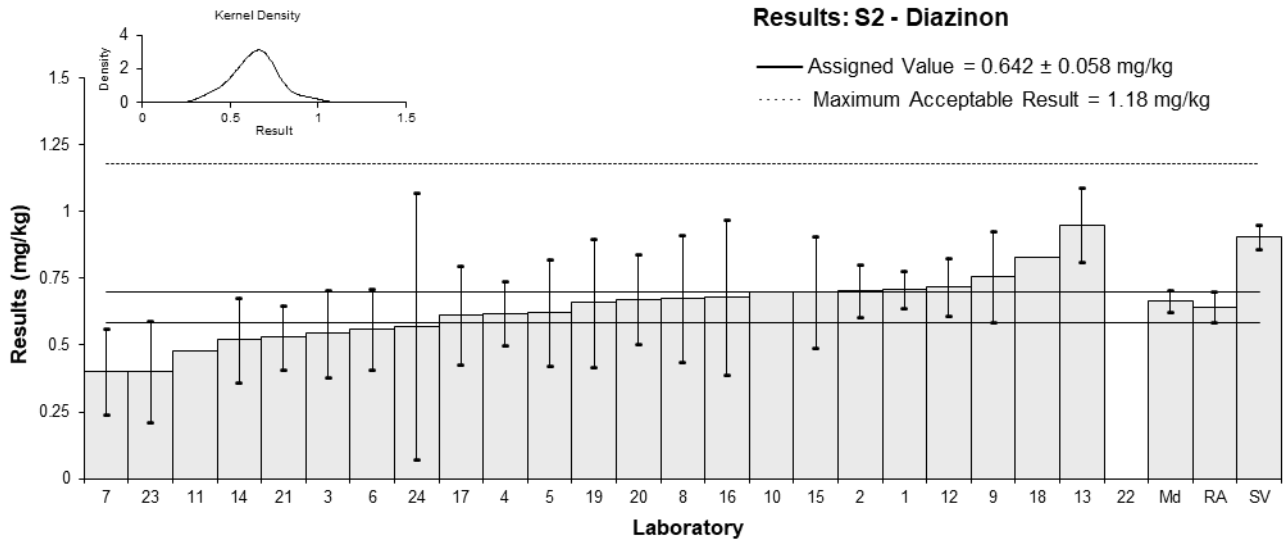
Participant Results

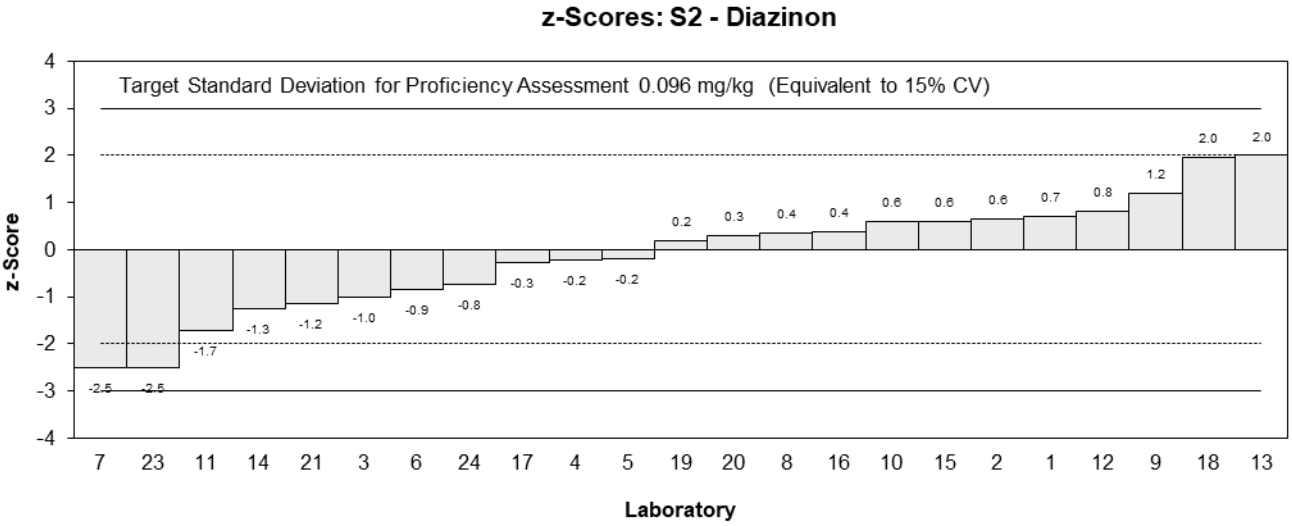
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.71	0.07	92	0.71	0.75
2	0.704	0.097	NR	0.64	0.55
3	0.545	0.1635	NR	-1.01	-0.56
4	0.62	0.12	104	-0.23	-0.17
5	0.624	0.200	NR	-0.19	-0.09
6	0.56	0.15	73.8	-0.85	-0.51
7	0.4	0.16	NR	-2.51	-1.42
8	0.676	0.237	82	0.35	0.14
9	0.758	0.17	NR	1.20	0.65
10	0.7	NR	NR	0.60	1.00
11**	0.476	NR	115	-1.72	-2.86
12	0.72	0.108	NR	0.81	0.64
13	0.95	0.14	NR	2.00▼	
14	0.52	0.16	NR	-1.27	-0.72
15	0.70	0.21	NR	0.60	0.27
16	0.68	0.29	NR	0.39	0.13
17	0.6139	0.1842	NR	-0.29	-0.15
18	0.83	NR	NR	1.95	3.24
19	0.66	0.24	NR	0.19	0.07
20	0.671	0.168	NR	0.30	0.16
21	0.53	0.12	NR	-1.16	-0.84
22	NT	NT	NT		
23	0.4	0.19	NR	-2.51	-1.22
24	0.57	0.5	94	-0.75	-0.14

** Excluded Result, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.642	0.058
Spike Value	0.905	0.045
Robust Average	0.642	0.058
Max Acceptable Result	1.18	
Median	0.666	0.042
Mean	0.643	
N	22	
Max	0.95	
Min	0.4	
Robust SD	0.11	
Robust CV	17%	


Kernel Density
Density
Result
Results: S2 - Diazinon
Assigned Value = 0.642 ± 0.058 mg/kg
Maximum Acceptable Result = 1.18 mg/kg
Results (mg/kg)
Laboratory
7 23 11 14 21 3 6 24 17 4 5 19 20 8 16 10 15 2 1 12 9 18 13 22 Md RA SV


z-Scores: S2 - Diazinon
Target Standard Deviation for Proficiency Assessment 0.096 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
7 23 11 14 21 3 6 24 17 4 5 19 20 8 16 10 15 2 1 12 9 18 13

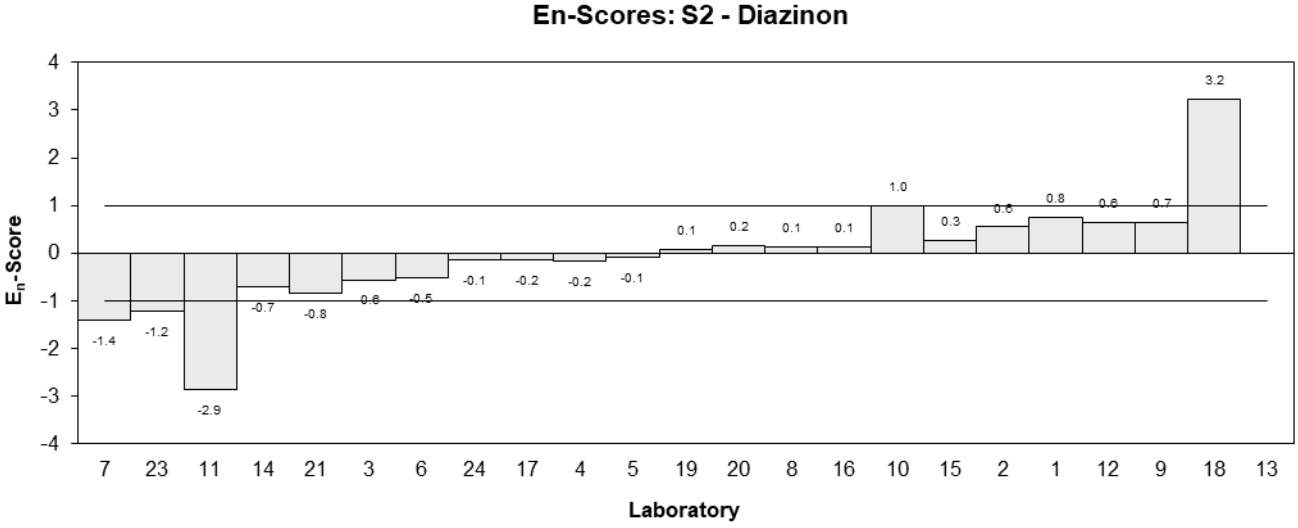

En-Scores: S2 - Diazinon
En-Score
Laboratory
7 23 11 14 21 3 6 24 17 4 5 19 20 8 16 10 15 2 1 12 9 18 13

Figure 8

Table 12

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Imidacloprid
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	0.11	0.033	NR
4	<0.5	NR	NR
5	NT	NT	NT
6	NT	NT	NT
7	0.08	0.02	NR
8	NT	NT	NT
9	<0.5	NR	NR
10	NT	NR	NT
11	0.027	NR	77
12	NT	NT	NT
13	NT	NT	NT
14	0.18	0.06	NR
15	NT	NT	NT
16	NT	NT	NT
17	NT	NT	NT
18	NT	NT	NT
19	0.11	0.049	NR
20	NT	NT	NT
21	NT	NT	NT
22	NT	NT	NT
23	NT	NT	NT
24	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.150	0.008
Robust Average	NA (N<6)	
Median	0.110	0.050
Mean	0.101	
N	5	
Max	0.18	
Min	0.027	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

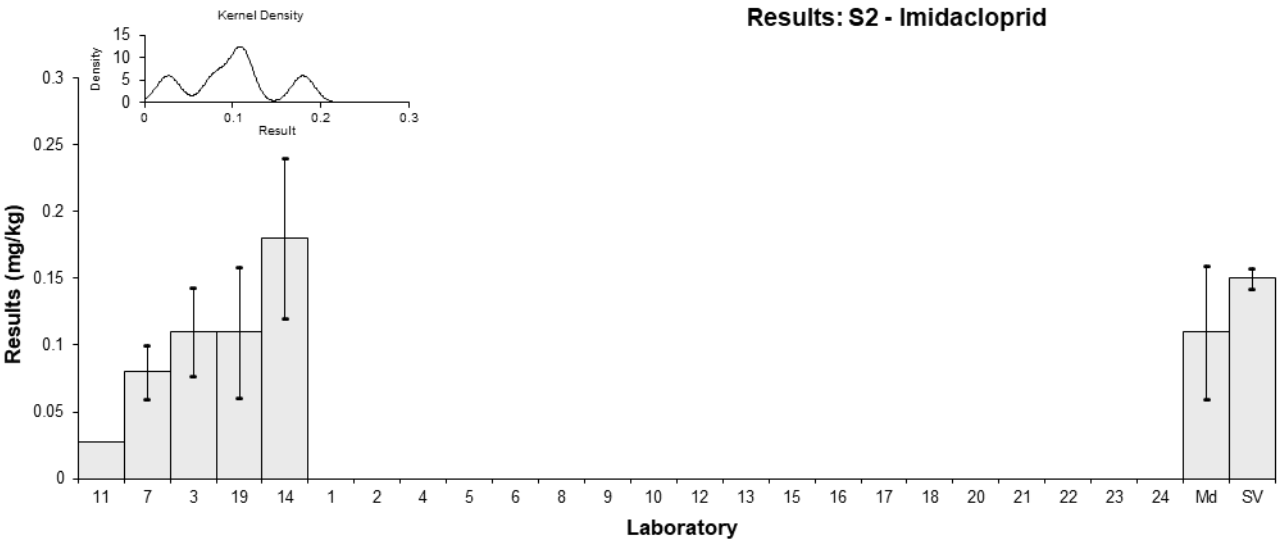

Results: S2 - Imidacloprid
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 7 3 19 14 1 2 4 5 6 8 9 10 12 13 15 16 17 18 20 21 22 23 24 Md SV

Figure 9

Table 13

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Metsulfuron-methyl
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	0.83	0.25	86
5	NT	NT	NT
6	NT	NT	NT
7	0.22	0.06	NR
8	NT	NT	NT
9	NT	NT	NT
10	NT	NR	NT
11	NT	NT	NT
12	NT	NT	NT
13	NT	NT	NT
14	<0.02	NR	NR
15	< 2	NR	NR
16	NT	NT	NT
17	NT	NT	NT
18	0.65	NR	NR
19	0.99	0.042	NR
20	NT	NT	NT
21	NT	NT	NT
22	NT	NT	NT
23	NT	NT	NT
24	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	1.20	0.06
Robust Average	NA (N<6)	
Median	0.74	0.32
Mean	0.67	
N	4	
Max	0.99	
Min	0.22	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

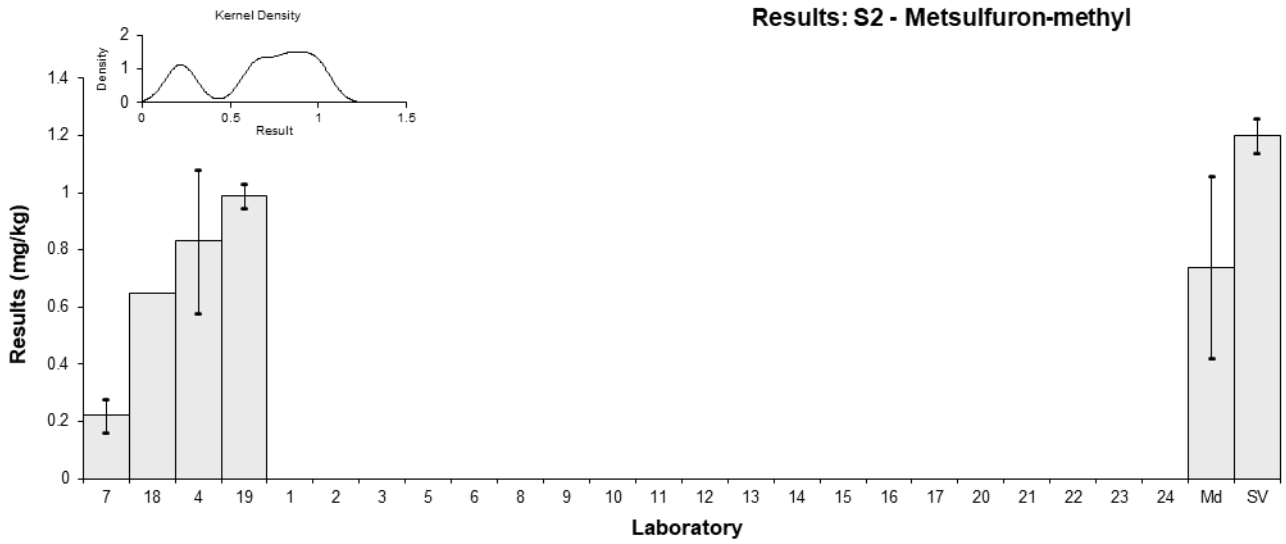

Results: S2 - Metsulfuron-methyl
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
7
18
4
19
1
2
3
5
6
8
9
10
11
12
13
14
15
16
17
20
21
22
23
24
Md
SV

Figure 10

Table 14

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Tebuconazole
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	0.675	0.2025	NR
4	NT	NT	NT
5	NT	NT	NT
6	NT	NT	NT
7	NT	NT	NT
8	NT	NT	NT
9	NT	NT	NT
10	0.887	NR	NR
11**	0.512	NR	89
12	NT	NT	NT
13	1.50	0.21	NR
14	0.43	0.13	NR
15	NT	NT	NT
16	NT	NT	NT
17	NT	NT	NT
18	1.28	NR	NR
19	1.1	0.42	NR
20	NT	NT	NT
21	0.55	0.15	NR
22	NT	NT	NT
23	NT	NT	NT
24	NT	NT	NT

** Excluded Result, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	1.20	0.06
Robust Average	0.92	0.42
Median	0.89	0.47
Mean	0.92	
N	7	
Max	1.5	
Min	0.43	
Robust SD	0.45	
Robust CV	49%	

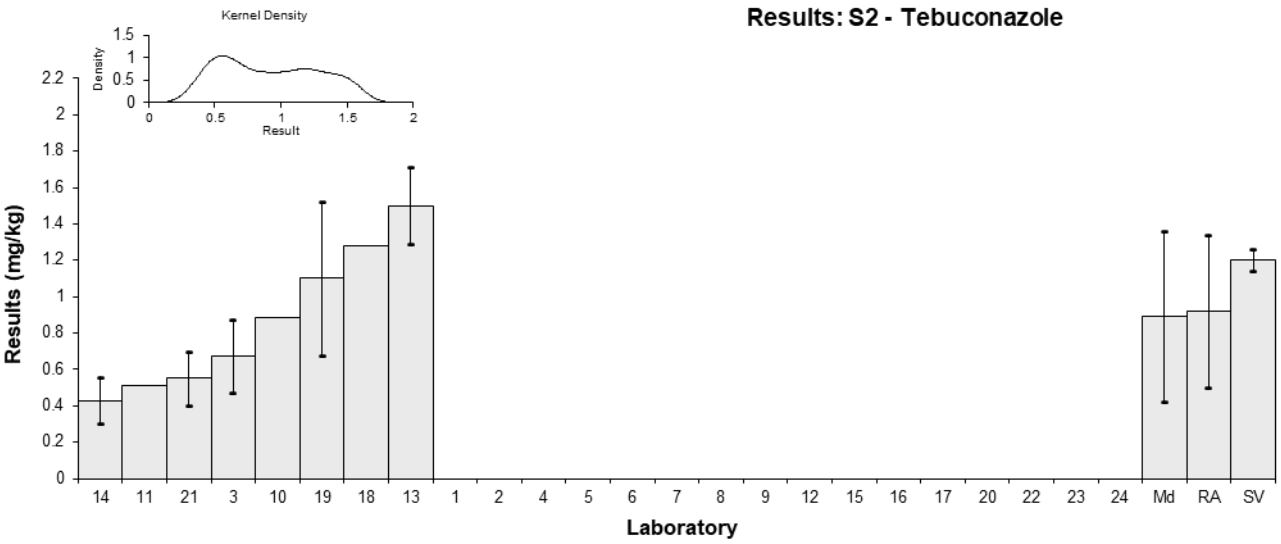

Results: S2 - Tebuconazole
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 11 21 3 10 19 18 13 1 2 4 5 6 7 8 9 12 15 16 17 20 22 23 24 Md RA SV

Figure 11

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The assigned values for all scored analytes were the robust averages of participants' results. If there were results less than 50% or greater than 150% of the robust average, these were excluded from the calculation of each assigned value.[3,4] The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[7] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S1 *trans*-Chlordane 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 values were set for Sample S2 imidacloprid and metsulfuron-methyl as there were too few numeric results reported for these analytes. No assigned value was set for Sample S2 tebuconazole as the numeric results reported for this analyte were too varied. For these analytes, participants may still compare their results with the descriptive statistics and spiked values as presented in Section 5.

A proportion of the spiked analyte may be strongly bound to the soil, and so may not be readily extracted and measured. What laboratories measure may best be described as 'extractable analyte', 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 analyte'.

A comparison of the assigned values (or robust average if no assigned value was set) and the spiked values is presented in Table 15. The assigned values were within the range of 66% to 86% of the spiked values. Similar ratios have been observed in previous NMI Pesticides in Soil PT studies,[6] and an assigned value was set if there was a reasonable consensus of results.

Table 15 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	*cis*-Chlordane	0.323	0.398	81
	trans-Chlordane	0.173	0.202	86
	Total Chlordane	0.486	0.600	81
	Dieldrin	0.0257	0.0339	76
	Propiconazole	0.137	0.195	70
S2	Atrazine	0.131	0.198	66
	Diazinon	0.642	0.905	71
	Imidacloprid	*(0.101)*	0.150	*(67)*
	Metsulfuron-methyl	*(0.67)*	1.20	*(56)*
	Tebuconazole	*(0.92)*	1.20	*(77)*

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 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 140 numeric results, 116 (83%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainties (Table 3). One participant reported using the NATA GAG Estimating and Reporting MU as their guide; NATA no longer publishes this document.[11]

Laboratories **10**, **11** and **18** did not report uncertainties for any of their reported results; these participants all reported being accredited to ISO/IEC 17025.

The magnitude of the reported expanded uncertainties was within the range 4.2% to 88% 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 and not fit-for-purpose. In this study, 12 expanded uncertainties were less than 15% relative, while two were greater than 50% relative.

Participants were also requested to report the coverage factor associated with their uncertainties (Table 3). Eleven participants reported a coverage factor of k = 2.

Uncertainties associated with results returning an acceptable *z*-score but an unacceptable E_n-score may have been underestimated.

Laboratories **16** and **24** attached estimates of expanded MU for results 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, 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 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 0.3673 ± 0.1102 mg/kg, it is better to report this as 0.37 ± 0.11 mg/kg.[10]

6.3 z-Score

Target SDs equivalent to 15% PCV were used to calculate *z*-scores. CVs predicted by the Thompson-Horwitz equation,[8] between-laboratory CVs and target SDs (as PCVs) for this study are presented for comparison in Table 16.

Table 16 Comparison of Thompson-Horwitz CVs, Between-Laboratory CVs and Target SDs

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Thompson-Horwitz CV[a] (%)	Between-Laboratory CV[b] (%)	Target SD (as PCV) (%)
S1	*cis*-Chlordane	0.323	19	13	15
	trans-Chlordane	0.173	21	18	15
	Total Chlordane	0.486	18	15	15
	Dieldrin	0.0257	22	24	15
	Propiconazole	0.137	22	26	15
S2	Atrazine	0.131	22	21	15
	Diazinon	0.642	17	17	15
	Imidacloprid	*(0.101)*	22	62	Not Set
	Metsulfuron-methyl	*(0.67)*	17	56	Not Set
	Tebuconazole	*(0.92)*	16	49	Not Set

[a] Calculated from the assigned value (robust average).

[b] Robust between-laboratory CV (outliers removed where applicable).

To account for possible low bias in consensus values due to participants using inefficient extraction or analytical techniques, a total of five *z*-scores were adjusted across the following analytes: Sample S1 dieldrin and propiconazole, and Sample S2 atrazine and diazinon. A maximum acceptable result was set as the spiked value plus two target SDs of the spiked value. 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 123 results for which *z*-scores were calculated, 115 (93%) returned a *z*-score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **4**, **18**, **19**, **21** and **23** reported results for all seven analytes for which *z*-scores were calculated. Of these participants, Laboratories **4**, **19** and **21** returned acceptable *z*-scores for all seven scored analytes.

Fifteen participants received acceptable *z*-scores for all analytes they reported results for: **3** (6), **10** (6), **13** (6), **14** (6), **2** (5), **6** (5), **12** (5), **16** (5), **5** (4), **9** (4), **15** (4), **17** (4), **20** (4), **24** (4) and **1** (3).

Laboratory **22** did not test for any of the spiked analytes in study.

The dispersal of participants' *z*-scores is presented graphically by laboratory in Figure 12 and by analyte in Figure 13.

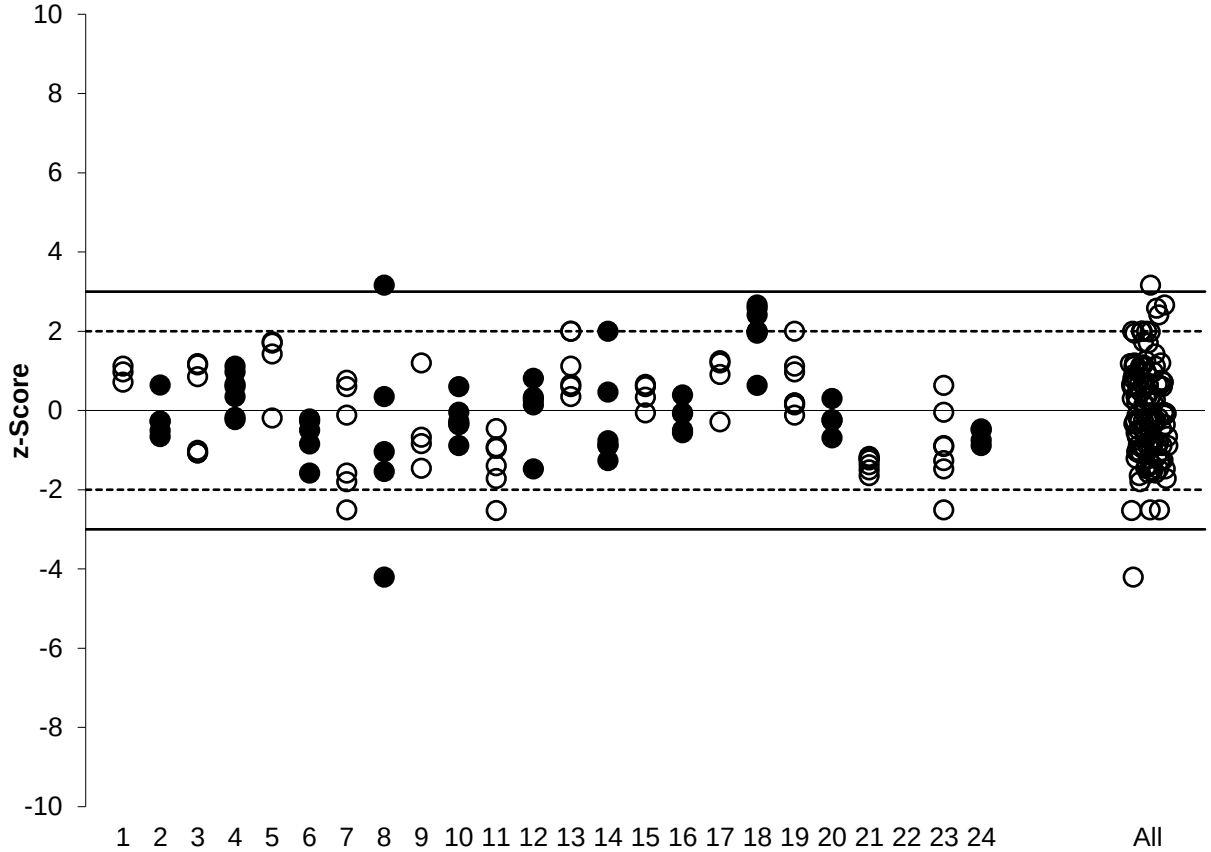


Figure 12 *z*-Score Dispersal by Laboratory

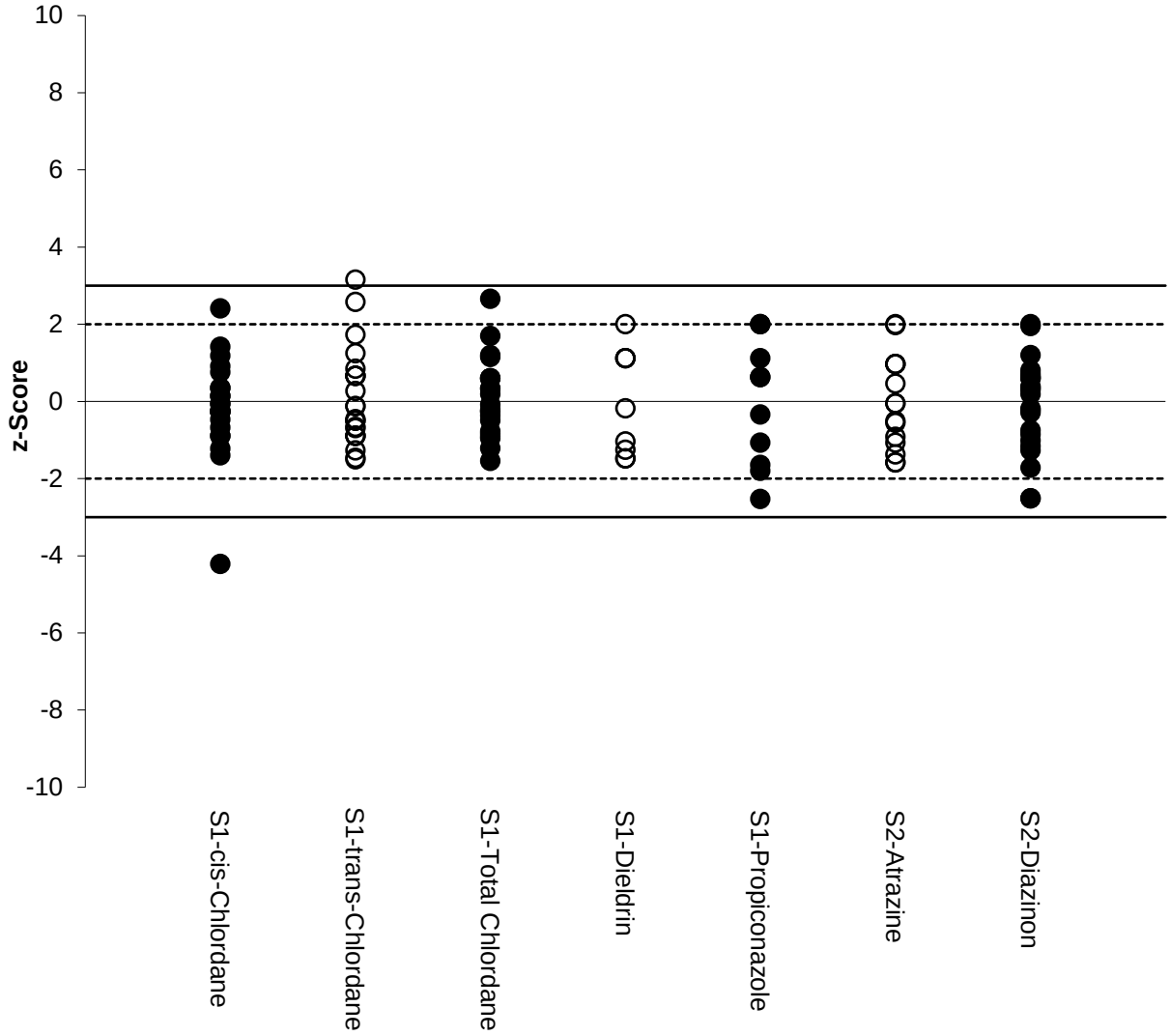


Figure 13 *z*-Score Dispersal by Analyte

6.4 E_n-Score

Where a laboratory did not report an uncertainty with a result, an expanded 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, no E_n-score has been reported.

Of 118 results for which E_n-scores were calculated, 101 (86%) were acceptable with $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratory **4** returned acceptable E_n-scores for all seven scored analytes.

Eleven participants received acceptable E_n-scores for all analytes they reported results for: **3** (6), **2** (5), **12** (5), **16** (5), **5** (4), **9** (4), **15** (4), **17** (4), **20** (4), **24** (4) and **1** (3).

Some participants had results where the *z*-score was adjusted as described above, and so E_n-scores were only calculated for some of their results. Of these participants, three participants received acceptable E_n-scores for all analytes that they reported results for and were scored: **19** (6), **14** (5) and **13** (4).

The dispersal of participants' E_n-scores is presented graphically by laboratory in Figure 14.

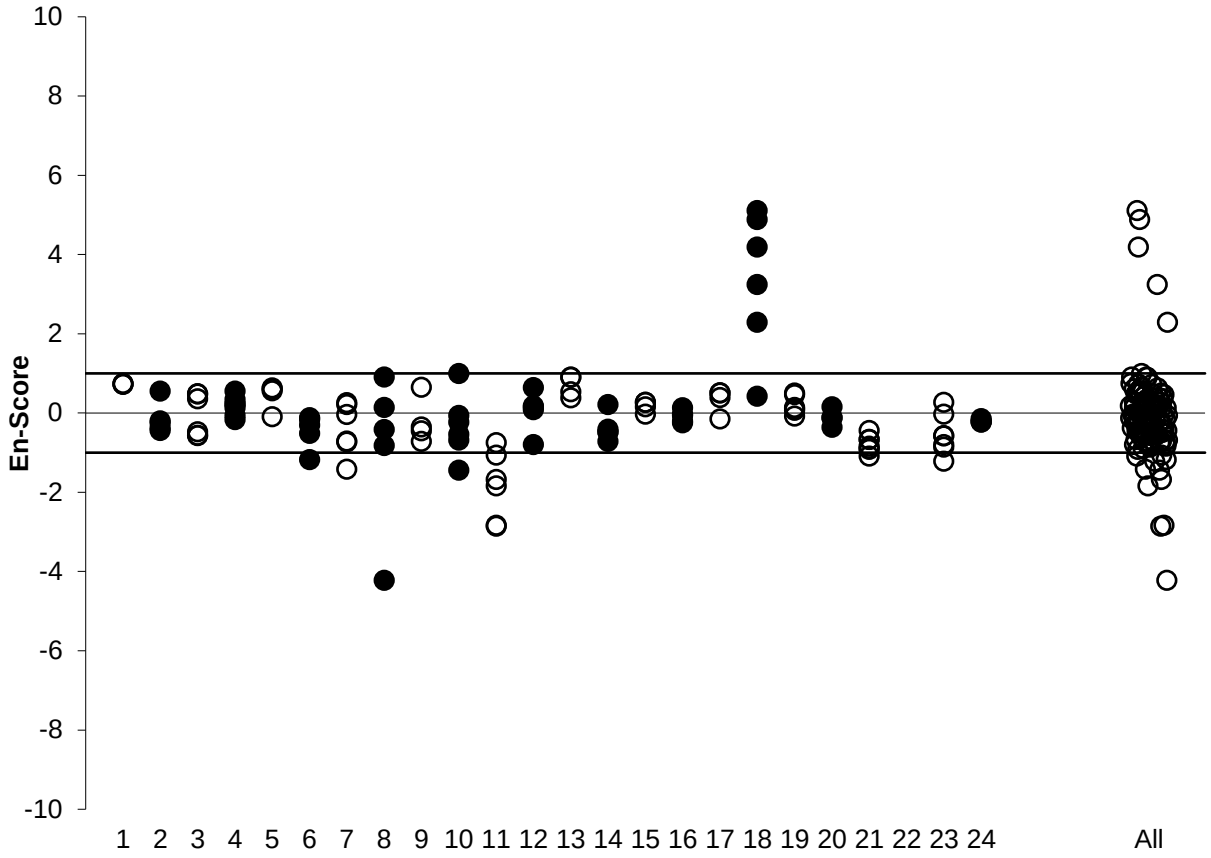


Figure 14 E_n-Score Dispersal by Laboratory

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, nine were spiked into the samples for this study (participants were also assessed on total chlordane 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 17.

Laboratory **19** reported testing for all spiked pesticides in this study, as well as reporting for total chlordane. Laboratory **22** did not test for any of the spiked pesticides in this study. Other than these two participants, the proportion of pesticides analysed by each participant ranged from 30% to 90%.

The proportion of participants analysing each pesticide in this study ranged from 25% (metsulfuron-methyl) to 96% (diazinon).

Table 17 Summary of Pesticides Analysed by Participants

Lab. Code	Atrazine	*cis*-Chlordane	*trans*-Chlordane	Total Chlordane	Diazinon	Dieldrin	Imidacloprid	Metsulfuron-methyl	Propiconazole	Tebuconazole	Proportion of Analytes (%)
1	✓	NT	NT	NT	✓	✓	NT	NT	NT	NT	30
2	✓	✓	✓	✓	✓	✓	NT	NT	NT	NT	60
3	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	90
4	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	90
5	✓	✓	✓	✓	✓	✓	NT	NT	NT	NT	60
6	✓	✓	✓	✓	✓	✓	NT	NT	NT	NT	60
7	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	90
8	NT	✓	✓	✓	✓	✓	NT	NT	NT	NT	50
9	✓	✓	✓	✓	✓	✓	✓	NT	NT	NT	70
10	✓	✓	✓	✓	✓	✓	NT	NT	✓	✓	80
11	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	90
12	NT	✓	✓	✓	✓	✓	NT	NT	NT	NT	50
13	✓	✓	✓	✓	✓	✓	NT	NT	NT	✓	70
14	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	90
15	✓	✓	✓	✓	✓	✓	NT	✓	NT	NT	70
16	✓	✓	✓	✓	✓	✓	NT	NT	NT	NT	60
17	NT	✓	✓	✓	✓	✓	NT	NT	NT	NT	50
18	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	90
19	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
20	NT	✓	✓	✓	✓	✓	NT	NT	NT	NT	50
21	✓	✓	✓	✓	✓	✓	NT	NT	✓	✓	80

Lab. Code	Atrazine	*cis*-Chlordane	*trans*-Chlordane	Total Chlordane	Diazinon	Dieldrin	Imidacloprid	Metsulfuron-methyl	Propiconazole	Tebuconazole	Proportion of Analytes (%)
22	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	0
23	✓	✓	✓	✓	✓	✓	NT	NT	✓	NT	70
24	✓	✓	✓	✓	✓	✓	NT	NT	✓	NT	70
Proportion of Participants (%)	79	92	92	92	96	92	29	25	46	33	

6.6 False Negatives

Table 18 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 limit of reporting (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 (i.e. the robust average minus the expanded uncertainty, and the spiked value minus the expanded uncertainty, were both greater than the LOR), or if no value was reported.

Table 18 False Negatives

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Result (mg/kg)
14	S2	Metsulfuron-methyl	*(0.67)*	1.2	<0.02

6.7 Reporting of Additional Analytes

Table 19 presents analytes reported by participants that were not spiked into the test samples by the study coordinator.

Table 19 Non-Spiked Analytes Reported by Participants

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
11	S1	alpha-Endosulfan	0.053	NR	83
14	S1	alpha-Endosulfan	0.025	0.007	NR

Several participants reported detecting p,p’-DDE and p,p’-DDT in Sample S2; these are likely incurred analytes present in the original soil matrix used to prepare this sample. Participants’ results for these analytes are presented in Table 20 for information only.

Table 20 Incurred DDE and DDT Reported by Participants in Sample S2

Lab. Code	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
1	p,p'-DDE	0.02	0.002	81
	p,p'-DDT	0.01	0.001	76
	Total DDT	0.01	0.001	76
3	p,p'-DDE	0.018	0.0054	NR
	p,p'-DDT	0.00755	0.002265	NR
	Total DDT	0.030	0.009	NR
4	p,p'-DDE	0.019	0.008	117
	Total DDT	0.019	0.008	117
8	p,p'-DDE	0.0148	0.005	98
	p,p'-DDT	0.00645	0.002	104
	Total DDT	0.0212	NR	NR
11	p,p'-DDE	0.013	NR	119
12	p,p'-DDE	0.02	0.005	NR
13	p,p'-DDE	0.27	0.01	NR
18	p,p'-DDE	0.02	NR	NR
	p,p'-DDT	0.01	NR	NR
19	p,p'-DDE	0.02	0.0046	NR
	p,p'-DDT	0.01	0.0057	NR
	Total DDT	0.04	0.011	NR
21	p,p'-DDE	0.0127	0.0068	NR
23	p,p'-DDE	0.01	NR	NR

6.8 Participants’ Analytical Methods

A variety of analytical methods were used for the different analytes (Appendix 4).

Results that were removed from all statistical calculations in Section 5 have also been removed from all discussion in this section.

For scored analytes, participants reported using a sample size between 2 g and 15 g per analysis. There was no significant trend between the results obtained and the sample mass used for analysis (Figure 15).

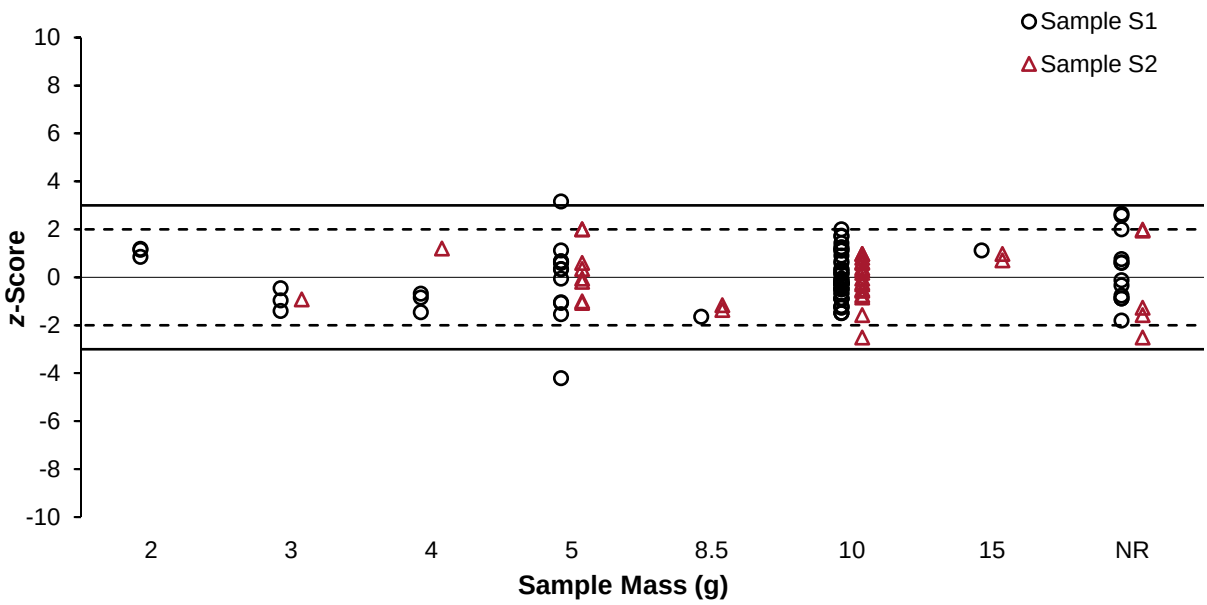


Figure 15 *z*-Score vs Sample Mass Used for Analysis

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 acetone (ACE), acetonitrile (ACN), dichloromethane (DCM), ethyl acetate (EtOAc), hexane (HEX), methanol (MeOH), water, acids and combinations of these solvents. Several participants reported using a clean-up step for their analyses.

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

Plots of results reported and methodology used are presented in Figures 16 to 25. Methodologies are listed in order of reported extraction technique, extraction solvent(s), clean-up (if applicable) and instrument. If a participant did not report any methodology, this has been recorded as 'NR' (for 'Not Reported'). Where charts refer to n = *x*, this corresponds to *x* number of participants using that methodology. For scored analytes, participants' results yielding unacceptable *z*-scores ($|z| \geq 3.0$) have been circled for reference.

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

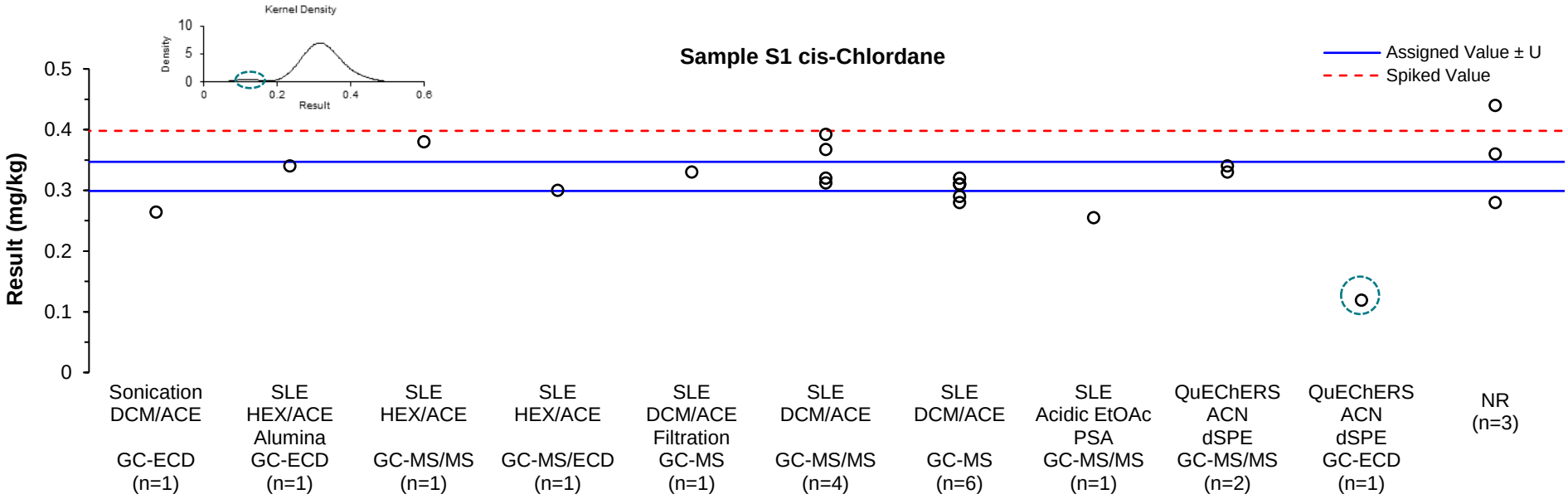


Figure 16 Sample S1 *cis*-Chlordane Results vs Methodology

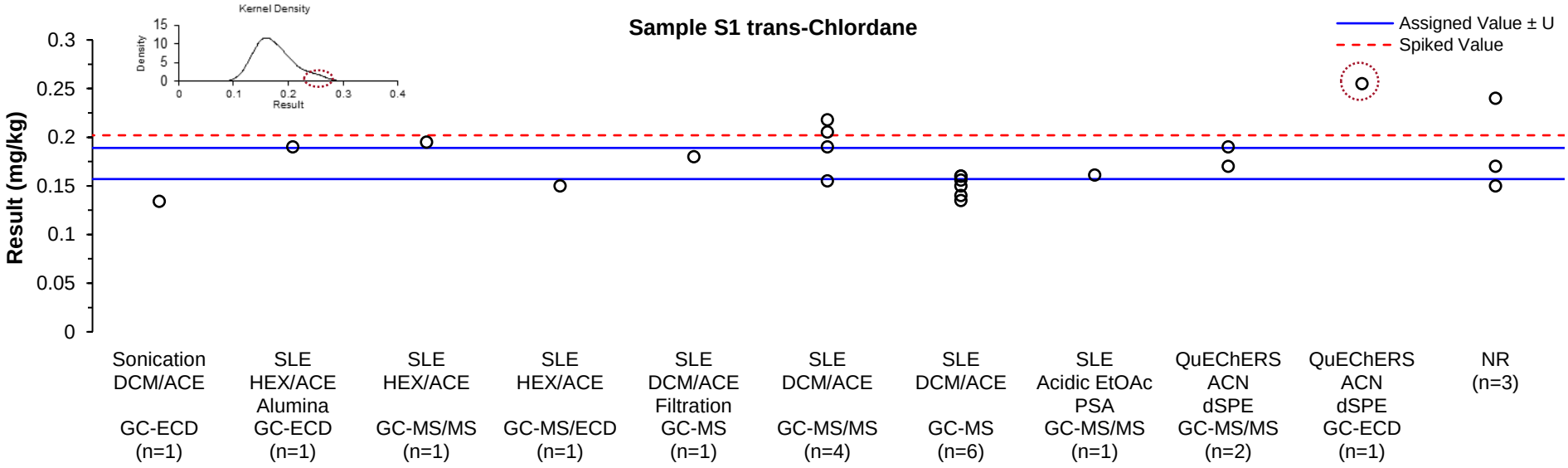


Figure 17 Sample S1 *trans*-Chlordane Results vs Methodology

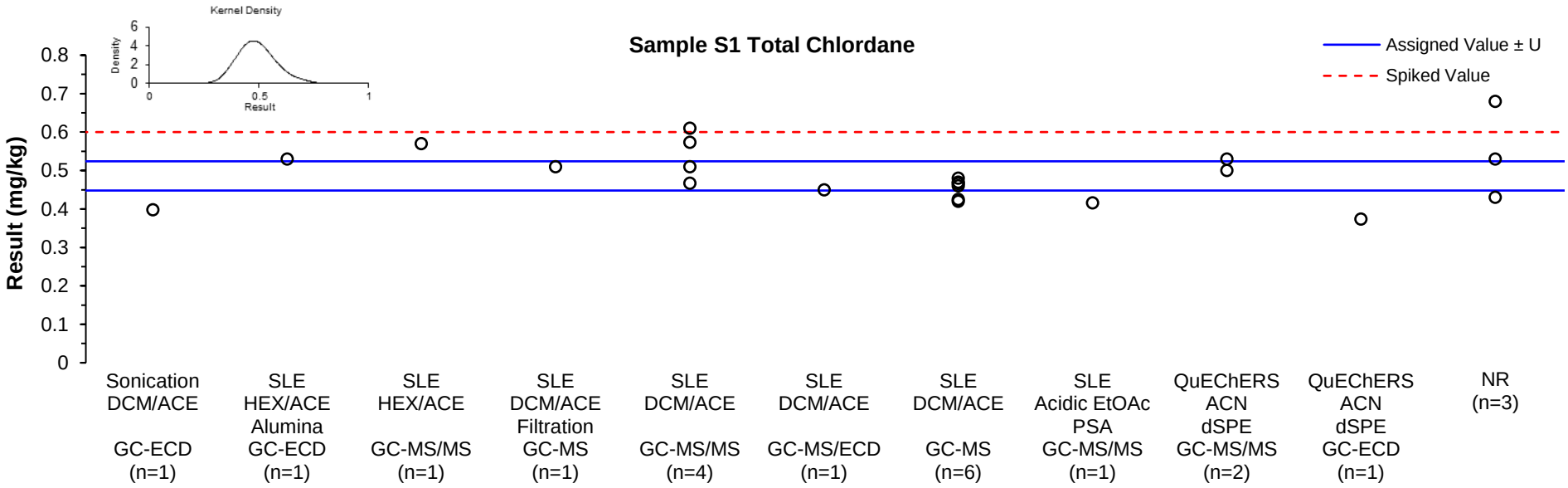


Figure 18 Sample S1 Total Chlordane Results vs Methodology

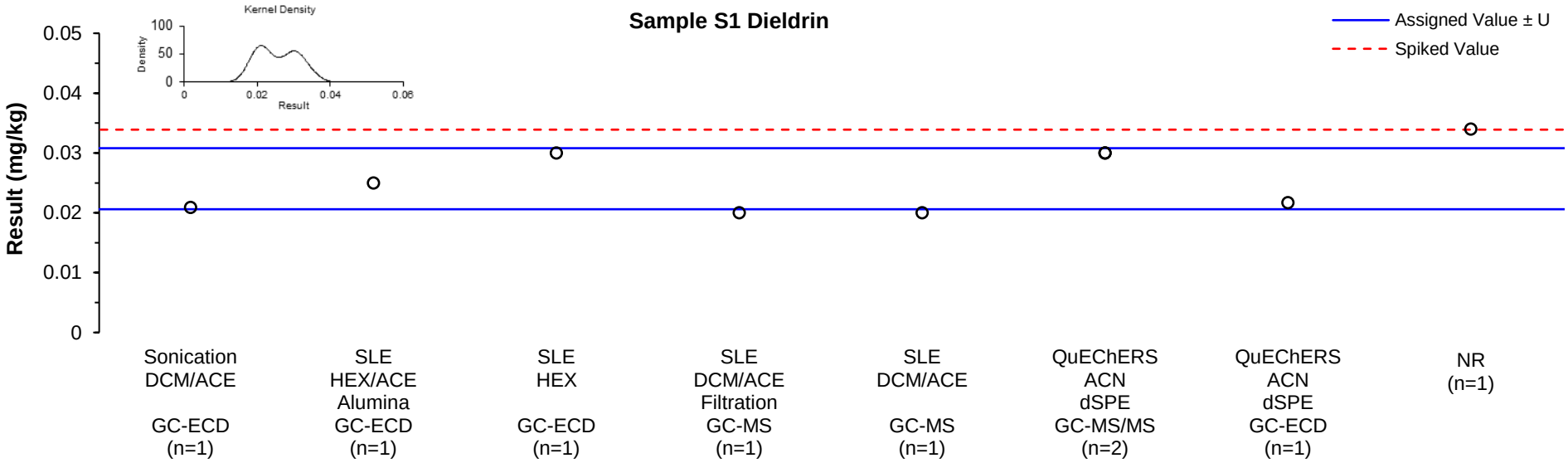


Figure 19 Sample S1 Dieldrin Results vs Methodology

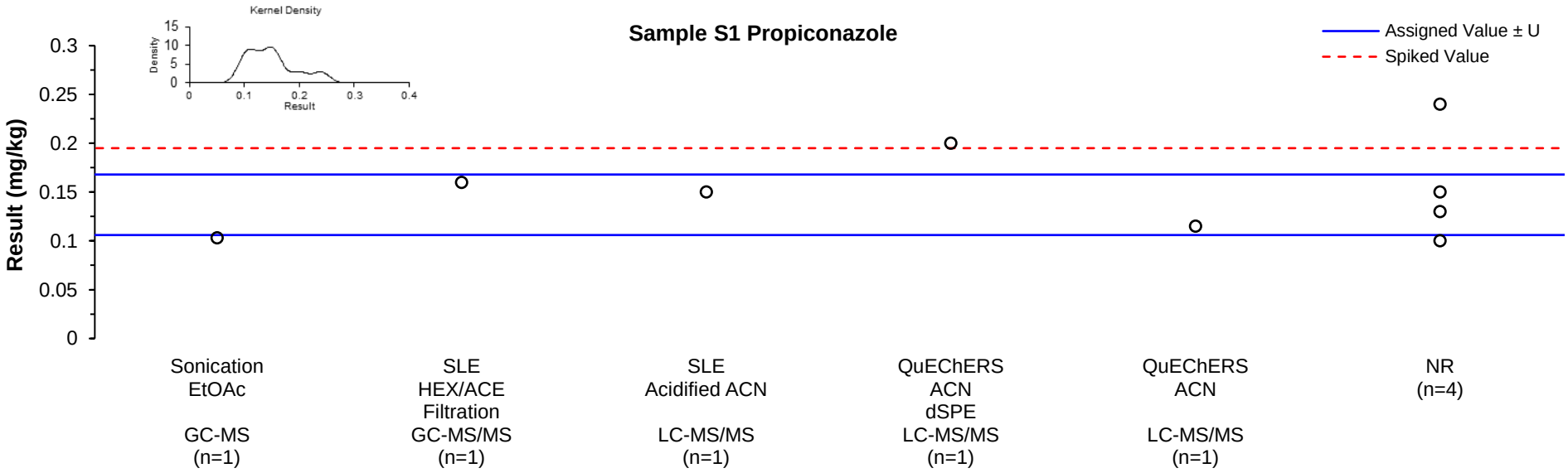


Figure 20 Sample S1 Propiconazole Results vs Methodology

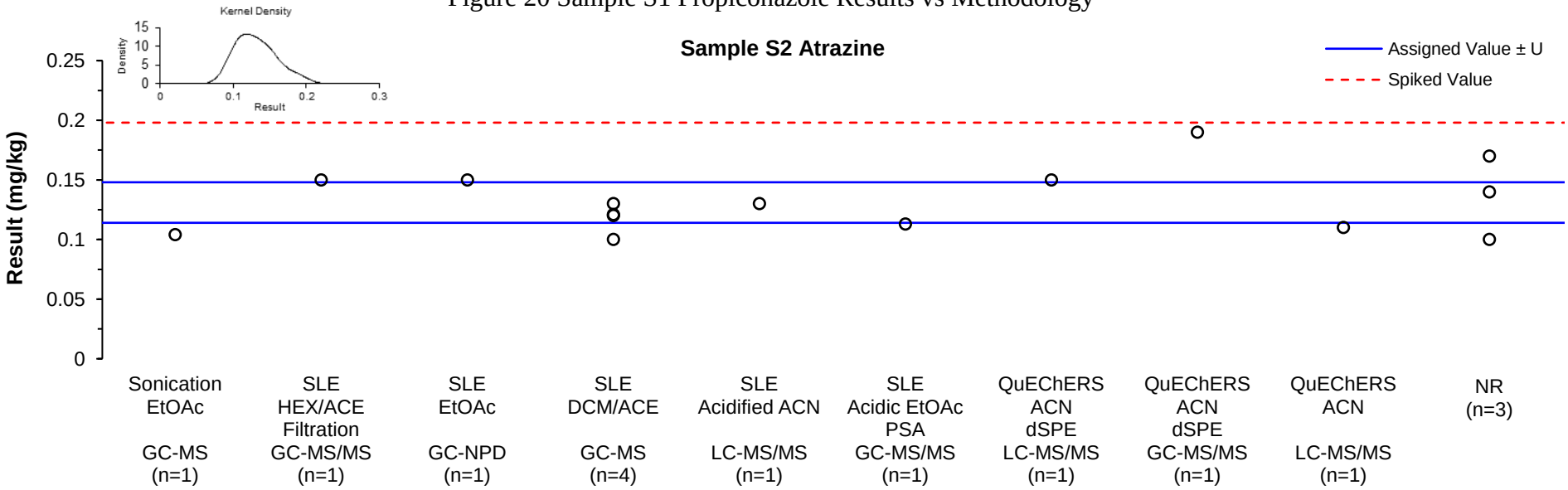


Figure 21 Sample S2 Atrazine Results vs Methodology

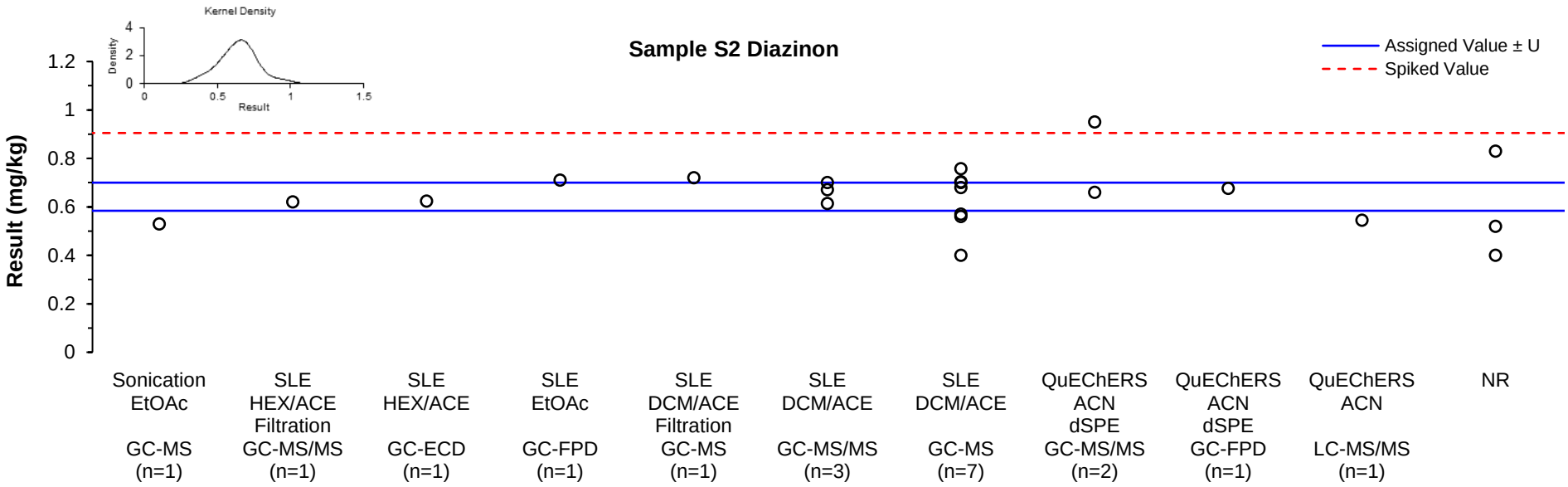


Figure 22 Sample S2 Diazinon Results vs Methodology

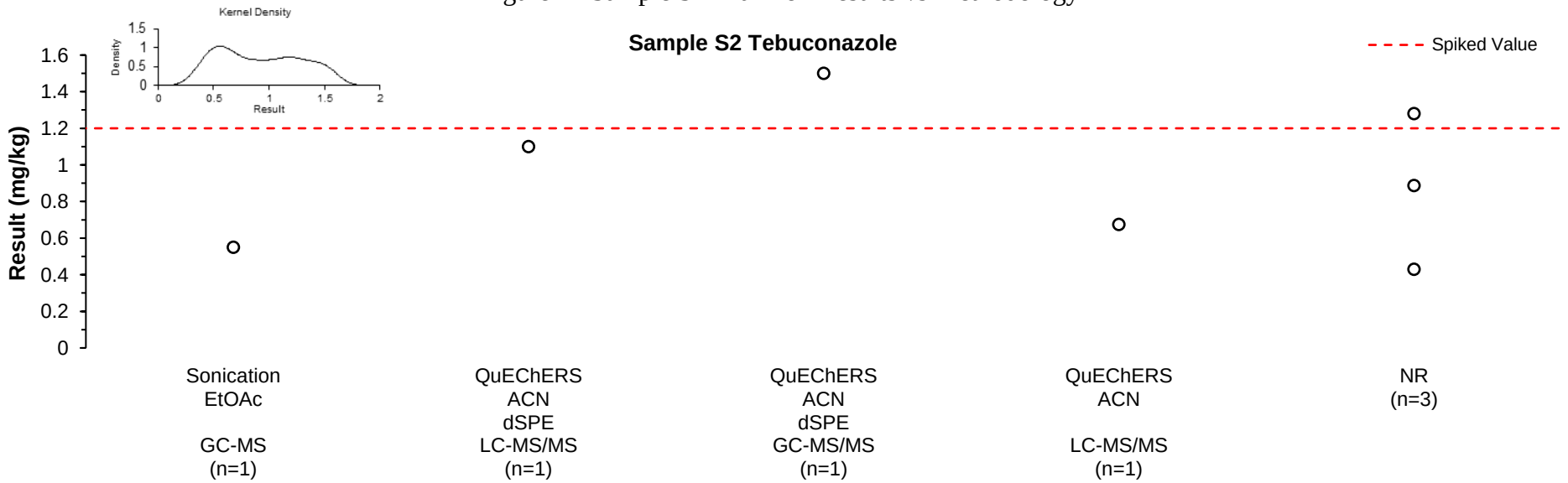


Figure 23 Sample S2 Tebuconazole Results vs Methodology

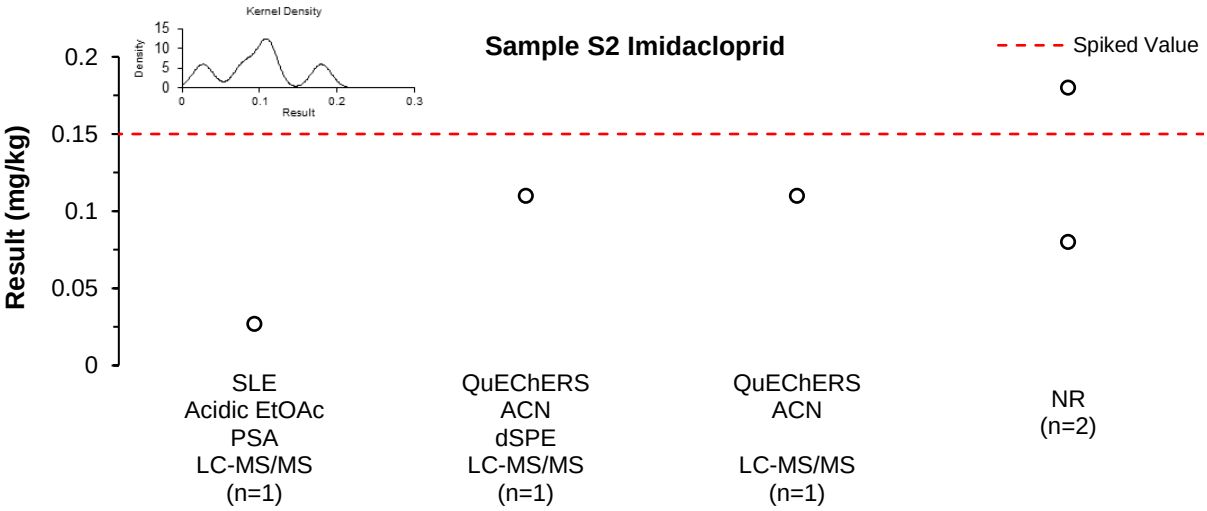


Figure 24 Sample S2 Imidacloprid Results vs Methodology

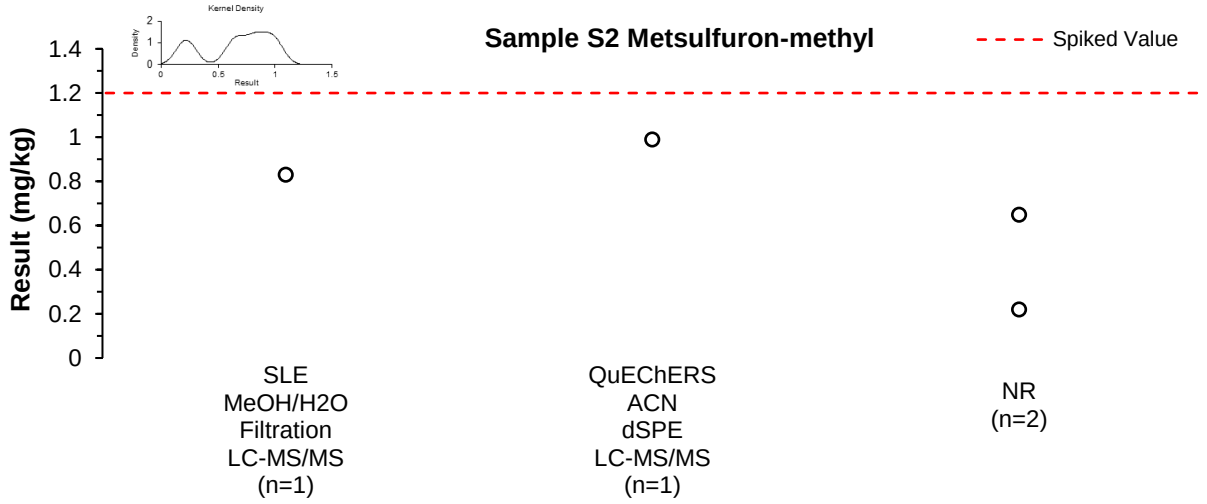


Figure 25 Sample S2 Metsulfuron-methyl Results vs Methodology

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 **1**, **4**, **6**, **7**, **8**, **11** and **24** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 73.8% to 120%. Laboratory **24** reported that they corrected results for recovery.

6.9 Certified Reference Materials

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 and two participants reported using matrix reference materials. The following were listed:

- AccuStandard
- Dr Ehrenstorfer
- o2si
- PM Separations
- Sigma Aldrich
- ISO 17034 standards
- Other pesticide reference 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 21 and Figure 26.

Table 21 Summary of Participants' Results*

Lab. Code	S1 *cis*-Chlordane	S1 *trans*-Chlordane	S1 Total Chlordane	S1 Dieldrin	S1 Propiconazole	S2 Atrazine	S2 Diazinon
AV	0.323	0.173	0.486	0.0257	0.137	0.131	0.642
SV	0.398	0.202	0.600	0.0339	0.195	0.198	0.905
1	NT	NT	NT	0.03	NT	0.15	0.71
2	0.310	0.156	0.466	<0.05	NT	0.121	0.704
3	0.38	0.195	0.57	<0.05	0.115	0.11	0.545
4	0.34	0.19	0.53	0.025	0.16	0.15	0.62
5	0.392	0.218	0.610	<0.05	NT	<0.3	0.624
6	0.31	0.16	0.47	<0.05	NT	0.10	0.56
7	0.36	0.17	0.53	<0.1	0.1	0.1	0.4
8	0.119	0.255	0.374	0.0217	NT	NT	0.676
9	0.29	0.135	0.425	<0.05	NT	<0.5	0.758
10	0.31	0.15	0.46	<0.05	0.13	0.13	0.7
11	0.255	0.161	0.416	<0.05	0.085	0.113	0.476
12	0.33	0.18	0.51	0.02	NT	NT	0.72
13	0.34	0.19	0.53	0.03	NT	0.19	0.95
14	0.28	0.15	0.43	NT	0.24	0.14	0.52
15	0.32	0.19	0.51	< 0.05	NT	< 0.2	0.70
16	0.32	0.16	0.48	<0.05	NT	0.12	0.68
17	0.3673	0.2054	0.5732	<0.05	NT	NT	0.6139
18	0.44	0.24	0.68	0.034	0.15	0.17	0.83
19	0.33	0.17	0.50	0.03	0.20	0.15	0.66

Lab. Code	S1 *cis*-Chlordane	S1 *trans*-Chlordane	S1 Total Chlordane	S1 Dieldrin	S1 Propiconazole	S2 Atrazine	S2 Diazinon
20	0.312	0.155	0.467	< 0.05	NT	NT	0.671
21	0.264	0.134	0.398	0.0209	0.103	0.104	0.53
22	NT	NT	NT	NT	NT	NT	NT
23	0.28	0.14	0.42	0.02	0.15	0.13	0.4
24	0.3	0.15	0.45	<0.2	<0.5	<0.5	0.57

* All results are given in mg/kg. Shaded cells are results which returned a questionable or unacceptable *z*-score. AV = Assigned Value; SV = Spiked Value.

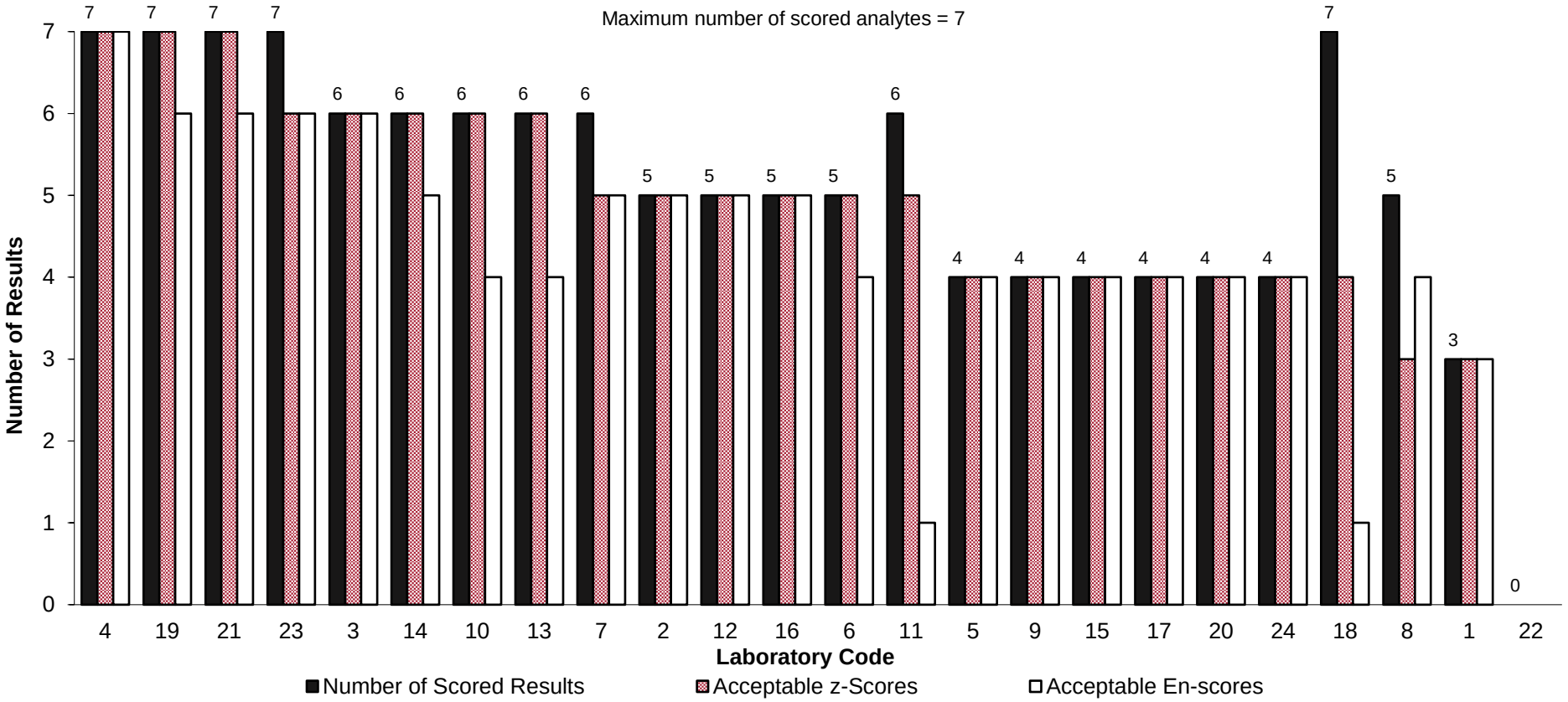


Figure 26 Summary of Participants' Performance

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 (2015 – 2024) is presented in Figure 27. The proportion of pesticides being tested for by participants has remained relatively steady over the last few years.

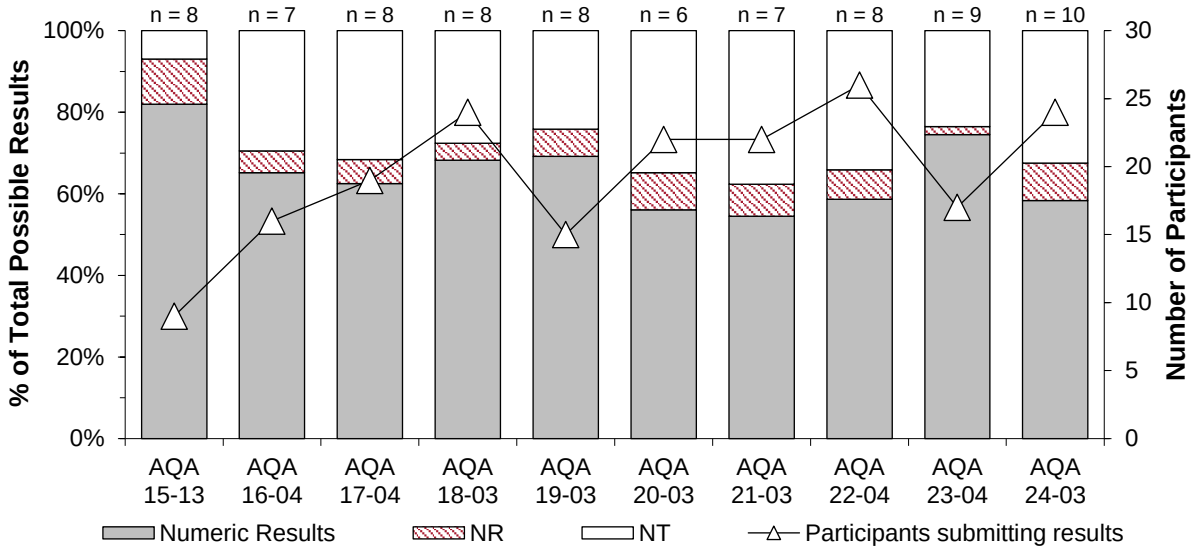


Figure 27 Summary of Participation and Reported Results in Pesticides in Soil PT Studies (n = number of spiked analytes)

A summary of the acceptable 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 (2015 – 2024) is presented in Figure 28. 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 acceptable *z*-scores and E_n-scores was 86% and 84% respectively.

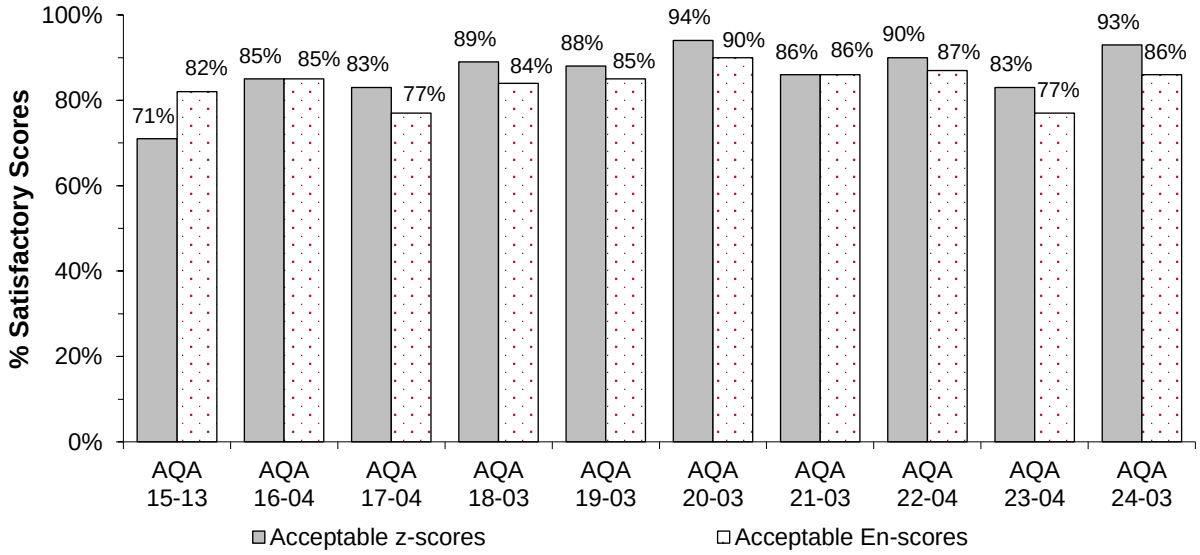


Figure 28 Acceptable *z*-Scores and E_n-scores in Pesticides in Soil PT Studies

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.

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties. Figure 29 presents a summary of the relative uncertainties as reported by participants over the last 10 studies (2015 – 2024). Over this time period, the vast majority of numeric results were reported with uncertainties (94%), with on average 87% of participants in each study reporting that they were accredited to ISO/IEC 17025. Most participants over this time period reported relative expanded uncertainties between 15% and 50%, however around 24% of relative uncertainties were outside this range, and may have been unrealistically small or too large and not fit-for-purpose.

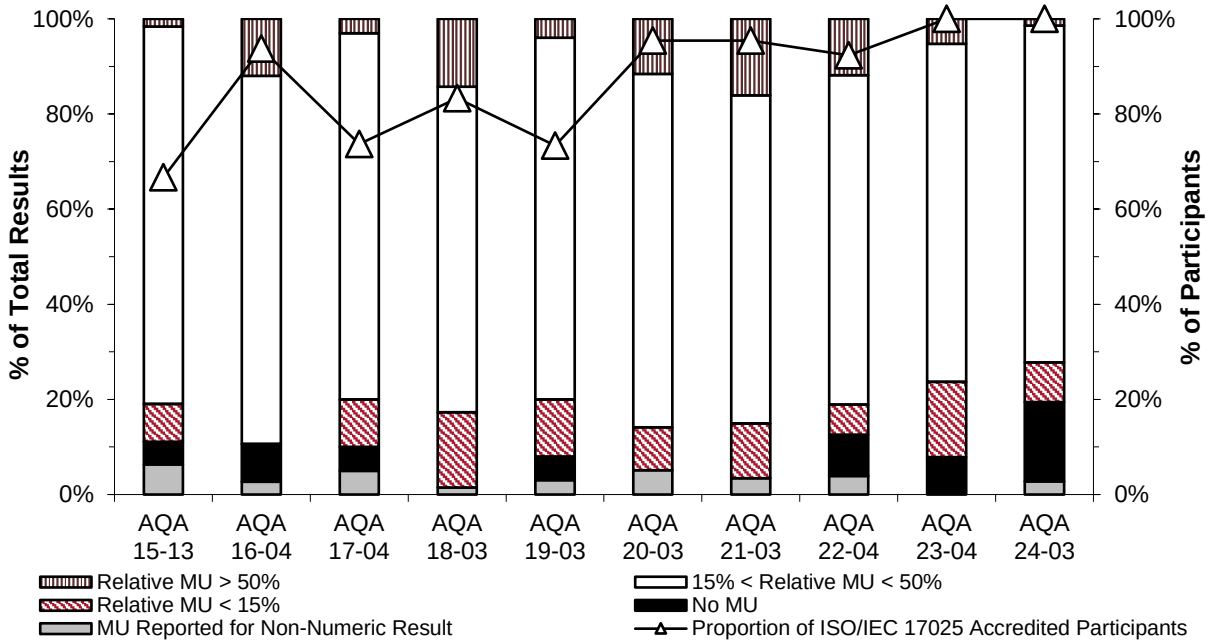


Figure 29 Summary of Participants' Relative Uncertainties for NMI Pesticides in Soil PT Studies

7 REFERENCES

Please note that for all undated references, the latest edition of the referenced document (including any amendments) applies.

[1] ISO/IEC 17043, *Conformity assessment – General requirements for the competence of proficiency testing providers*.

[2] NMI, 2024, *Study Protocol for Proficiency Testing*, viewed May 2024, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

[3] NMI, 2024, *Chemical Proficiency Testing Statistical Manual*, viewed May 2024, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

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

[5] National Environment Protection (Assessment of Site Contamination) Measure 1999 as amended 2013, viewed May 2024, <https://www.legislation.gov.au/F2008B00713/latest/text>.

[6] NMI, 2016, *Proficiency Test Report AQA 16-04 Pesticides in Soil*.

[7] ISO 13528, *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, *General requirements for the competence of testing and calibration laboratories.*

[10] Eurachem/CITAC Guide GC 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed May 2024, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[11] NATA, 2020, Update to Measurement Uncertainty resources, viewed May 2024, <https://nata.com.au/news/update-to-measurement-uncertainty-resources/>

[12] JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition.

APPENDIX 1 SAMPLE PREPARATION

Two soils were used as the starting materials in this study: uncontaminated topsoil purchased from a local suppler was used for both samples, and soil from a residential garden was also added to Sample S2.

The soil was dried at 160 °C for a minimum of 2 hours and then sieved, retaining the 355 – 850 µm fraction. The pesticide standards were prepared by dissolving them in acetone, dichloromethane or isopropyl alcohol.

For both samples, dried and sieved soil was added to a large stainless steel pot and saturated with acetone. Standards were spiked into the saturated soil before the mixture was mechanically stirred and solvent allowed to evaporate. The spiked soil was divided up equally into forty samples of 50 g each, packaged in 65 mL amber glass jars, labelled and then shrink wrapped.

All samples were stored at 4 °C prior to dispatch.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was conducted for this study as the samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples.

The results of this study also gave no reason to question the samples' homogeneity. Comparisons of results to bottle number for scored analytes are presented in Figures 30 to 36 (solid blue lines correspond to the assigned value ± U for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5, or if that participant was sent more than one container for that sample). No significant fill order trend was observed.

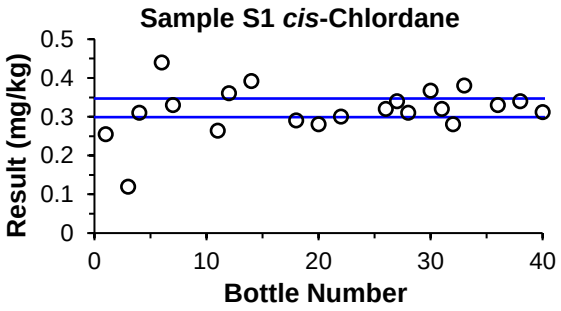


Figure 30 S1 *cis*-Chlordane Results vs Bottle Number

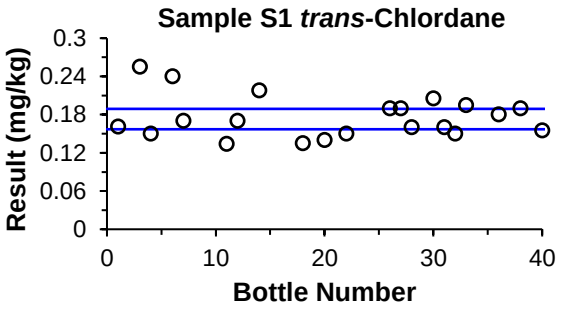


Figure 31 S1 *trans*-Chlordane Results vs Bottle Number

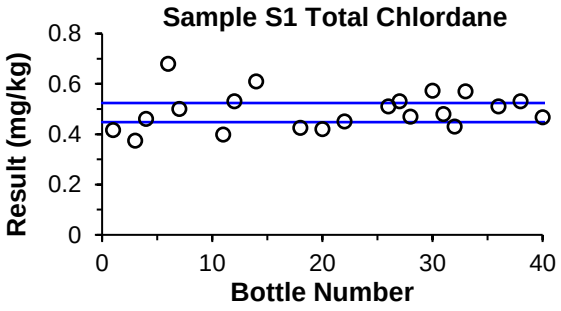


Figure 32 S1 Total Chlordane Results vs Bottle Number

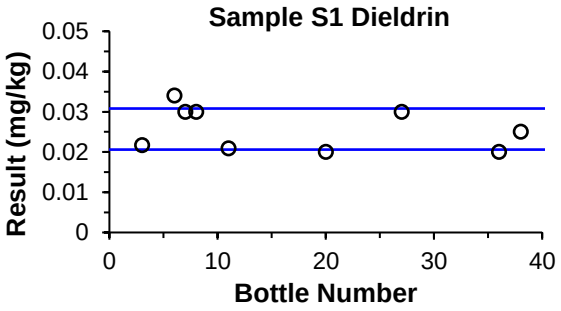


Figure 33 S1 Dieldrin Results vs Bottle Number

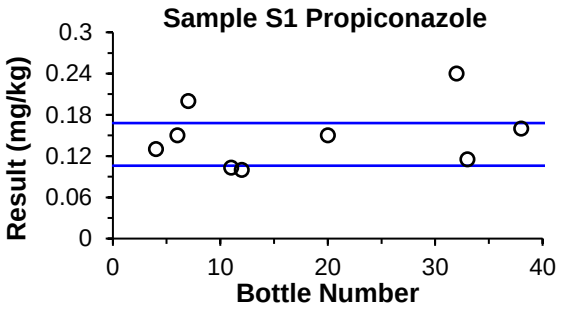


Figure 34 S1 Propiconazole Results vs Bottle Number

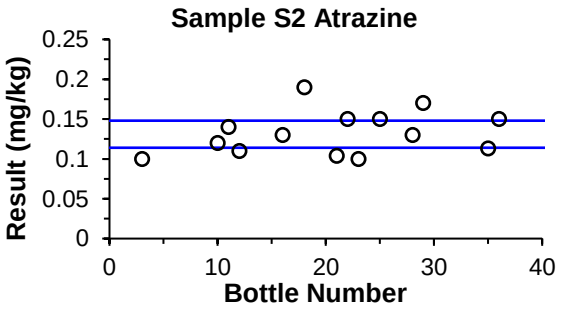


Figure 35 S2 Atrazine Results vs Bottle Number

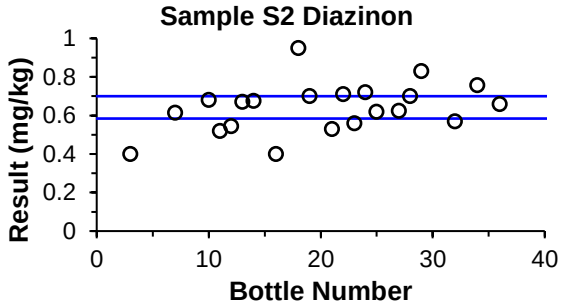


Figure 36 S2 Diazinon Results vs Bottle Number

A2.2 Stability

No stability testing was conducted for this study as the samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples for similar analytes and matrices over a similar time frame. After preparation and before dispatch, the samples were stored in a refrigerator at approximately 4 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks.

The results of this study also gave no reason to question the samples' transportation stability. Comparisons of results to days spent in transit for scored analytes are presented in Figures 37 to 43 (solid blue lines correspond to the assigned value ± U for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5). No significant trend was observed.

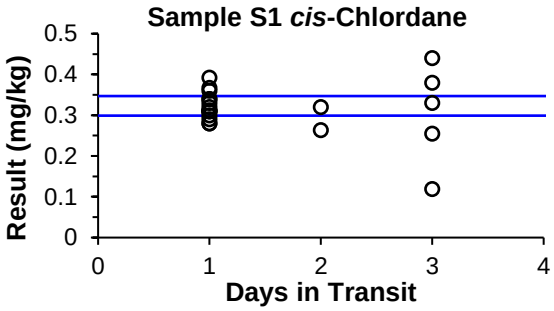


Figure 37 S1 *cis*-Chlordane Results vs Transit Days

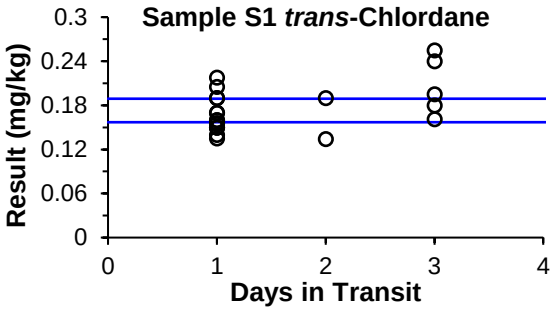


Figure 38 S1 *trans*-Chlordane Results vs Transit Days

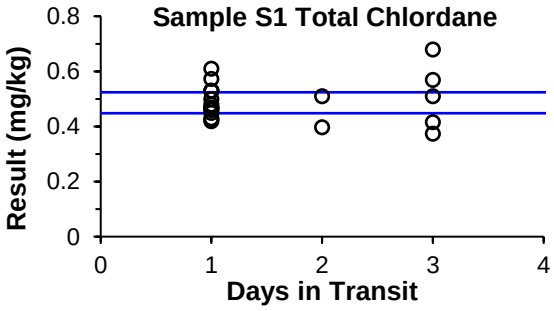


Figure 39 S1 Total Chlordane Results vs Transit Days

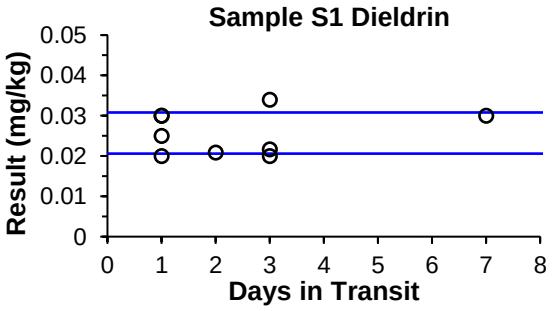


Figure 40 S1 Dieldrin Results vs Transit Days

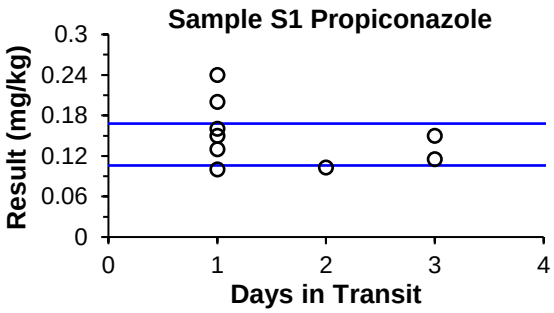


Figure 41 S1 Propiconazole Results vs Transit Days

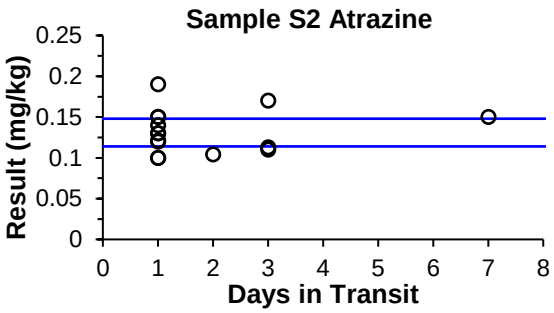


Figure 42 S2 Atrazine Results vs Transit Days

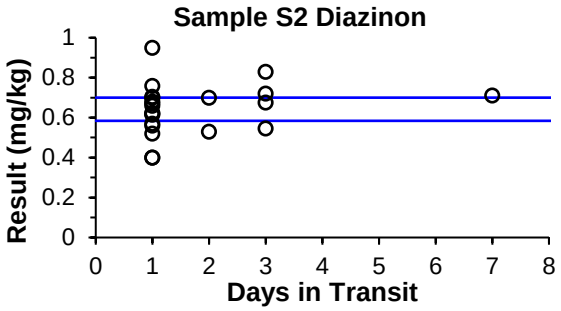


Figure 43 S2 Diazinon Results vs Transit Days

APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND E_n-SCORE CALCULATIONS

A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528.[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 is set out below in Table 22.

Table 22 Uncertainty of the Robust Average for Sample S1 *trans*-Chlordane

No. results (p)	22
Robust Average	0.173 mg/kg
$S_{rob\ av}$	0.031 mg/kg
$u_{rob\ av}$	0.008 mg/kg
k	2
$U_{rob\ av}$	0.016 mg/kg

Therefore, the robust average for Sample S1 *trans*-Chlordane is 0.173 ± 0.016 mg/kg.

A3.2 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 (Section 4).

A worked example is set out below in Table 23.

Table 23 *z*-Score and E_n-Score Calculation for Sample S1 *cis*-Chlordane Result Reported by Laboratory 2

Participant Result (mg/kg)	Assigned Value (mg/kg)	Target SD	*z*-Score	E_n-Score
0.310 ± 0.045	0.323 ± 0.024	15% as PCV, or: 0.15 × 0.323 = 0.04845 mg/kg	$z = \frac{0.310 - 0.323}{0.04845} = -0.27$	$E_n = \frac{0.310 - 0.323}{\sqrt{0.045^2 + 0.024^2}} = -0.25$

APPENDIX 4 TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 24 to 33. Some responses may be modified so that the participant cannot be identified.

Table 24 Methodology – *cis*-Chlordane

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	10	Solid-Liquid	DCM/Acetone	n/a	GC-MS
3	2	Solid-Liquid	Hex:Ace	NA	GC-MS/MS
4	10	Solid-Liquid	Acetone:Hexane	Alumina	GC-ECD
5	10	Solid-Liquid	DCM/Acetone		GC-MS/MS
6	10	Solid-Liquid	Acetone / DCM		GC-MS
7	NR				
8	5	QuEChERS	Acetonitrile	dSPE	GC-ECD
9	4	Solid-Liquid	DCM/ACETONE	NIL	GC-MS
10	10	Solid-Liquid	DCM-Acetone		GC-MS
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	GC-MS/MS
12	10	Solid-Liquid	DCM: ACETONE	Filtration	GC-MS
13	5	QuEChERS	ACN	dSPE	GC-MS/MS
14	NR				
15	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
16	10	Solid-Liquid	DCM:Acetone	NA	GC-MS
17	10	Solid-Liquid	DCM:ACE	N/A	GC-MS/MS
18	NR				
19	10	QuEChERS	ACN	dSPE	GC-MS/MS
20	10	Solid-Liquid	DCM/ Acetone (50:50)		GC-MS/MS
21	10	Sonication	DCM:Acetone	Nil	GC-ECD
22	NT				
23	10	Solid-Liquid	DCM/Acetone		GC-MS
24	10	Solid-Liquid	HEX/ACETONE	NA	GCMS/ ECD

Table 25 Methodology – *trans*-Chlordane

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	10	Solid-Liquid	DCM/Acetone	n/a	GC-MS
3	2	Solid-Liquid	Hex:Ace	NA	GC-MS/MS
4	10	Solid-Liquid	Acetone:Hexane	Alumina	GC-ECD
5	10	Solid-Liquid	DCM/Acetone		GC-MS/MS

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
6	10	Solid-Liquid	Acetone / DCM		GC-MS
7	NR				
8	5	QuEChERS	Acetonitrile	dSPE	GC-ECD
9	4	Solid-Liquid	DCM/ACETONE	NIL	GC-MS
10	10	Solid-Liquid	DCM-Acetone		GC-MS
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	GC-MS/MS
12	10	Solid-Liquid	DCM: ACETONE	Filtration	GC-MS
13	5	QuEChERS	ACN	dSPE	GC-MS/MS
14	NR				
15	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
16	10	Solid-Liquid	DCM:Acetone	NA	GC-MS
17	10	Solid-Liquid	DCM:ACE	N/A	GC-MS/MS
18	NR				
19	10	QuEChERS	ACN	dSPE	GC-MS/MS
20	10	Solid-Liquid	DCM/ Acetone (50:50)		GC-MS/MS
21	10	Sonication	DCM:Acetone	Nil	GC-ECD
22	NT				
23	10	Solid-Liquid	DCM/Acetone		GC-MS
24	10	Solid-Liquid	HEX/ACETONE	NA	GCMS/ ECD

Table 26 Methodology – Total Chlordane

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	10	Solid-Liquid	DCM/Acetone	n/a	GC-MS
3	2	Solid-Liquid	Hex:Ace	NA	GC-MS/MS
4	10	Solid-Liquid	Acetone:Hexane	Alumina	GC-ECD
5	10	Solid-Liquid	DCM/Acetone		GC-MS/MS
6	10	Solid-Liquid	Acetone / DCM		GC-MS
7	NR				
8	5	QuEChERS	Acetonitrile	dSPE	GC-ECD
9	4	Solid-Liquid	DCM/ACETONE	NIL	GC-MS
10	10	Solid-Liquid	DCM-Acetone		GC-MS
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	GC-MS/MS
12	10	Solid-Liquid	DCM: ACETONE	Filtration	GC-MS
13	5	QuEChERS	ACN	dSPE	GC-MS/MS
14	NR				

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
15	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
16	10	Solid-Liquid	DCM:Acetone	NA	GC-MS
17	10	Solid-Liquid	DCM:ACE	N/A	GC-MS/MS
18	NR				
19	10	QuEChERS	ACN	dSPE	GC-MS/MS
20	10	Solid-Liquid	DCM/ Acetone (50:50)		GC-MS/MS
21	10	Sonication	DCM:Acetone	Nil	GC-ECD
22	NT				
23	10	Solid-Liquid	DCM/Acetone		GC-MS
24	10	Solid-Liquid	DCM/ACETONE	NA	GCMS/ ECD

Table 27 Methodology – Dieldrin

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	15	Solid-Liquid	Hexane	None	GC-ECD
2	10	Solid-Liquid	DCM/Acetone	n/a	GC-MS
3	2	Solid-Liquid	Hex:Ace	NA	GC-MS/MS
4	10	Solid-Liquid	Acetone:Hexane	Alumina	GC-ECD
5	10	Solid-Liquid	DCM/Acetone		GC-MS/MS
6	10	Solid-Liquid	Acetone / DCM		GC-MS
7	NR				
8	5	QuEChERS	Acetonitrile	dSPE	GC-ECD
9	4	Solid-Liquid	DCM/ACETONE	NIL	GC-MS
10	10	Solid-Liquid	DCM-Acetone		GC-MS
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	GC-MS/MS
12	10	Solid-Liquid	DCM: ACETONE	Filtration	GC-MS
13	5	QuEChERS	ACN	dSPE	GC-MS/MS
14	NT				
15	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
16	10	Solid-Liquid	DCM:Acetone	NA	GC-MS
17	10	Solid-Liquid	DCM:ACE	N/A	GC-MS/MS
18	NR				
19	10	QuEChERS	ACN	dSPE	GC-MS/MS
20	10	Solid-Liquid	DCM/ Acetone (50:50)		GC-MS/MS
21	10	Sonication	DCM:Acetone	Nil	GC-ECD
22	NT				
23	10	Solid-Liquid	DCM/Acetone		GC-MS

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
24	10	Solid-Liquid	HEX/ACETONE	NA	GCMS/ ECD

Table 28 Methodology – Propiconazole

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	NT				
3	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
4	10	Solid-Liquid	Acetone:Hexane	Filtration	GC-MS/MS
5	NT				
6	NT				
7	NR				
8	NT				
9	NT				
10	NR				
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	LC-MS/MS
12	NT				
13	NT				
14	NR				
15	NT				
16	NT				
17	NT				
18	NR				
19	10	QuEChERS	ACN	dSPE	LC-MS/MS
20	NT				
21	8.5	Sonication	Ethyl acetate	Nil	GC-MS
22	NT				
23	5	Solid-Liquid	Acidified Acetonitrile		LC-MS/MS
24	10	Solid-Liquid	DCM/ACETONE	NA	GC-MS

Table 29 Methodology – Atrazine

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	15	Solid-Liquid	Ethyl acetate	None	GC-NPD
2	10	Solid-Liquid	DCM/Acetone	n/a	GC-MS
3	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
4	10	Solid-Liquid	Acetone:Hexane	Filtration	GC-MS/MS
5	5	Solid-Liquid	DCM		GC-MS

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
6	10	Solid-Liquid	Acetone / DCM		GC-MS
7	NR				
8	NT				
9	4	Solid-Liquid	DCM/ACETONE	NIL	GC-MS
10	10	Solid-Liquid	DCM-Acetone		GC-MS
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	GC-MS/MS
12	NT				
13	5	QuEChERS	ACN	dSPE	GC-MS/MS
14	NR				
15	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
16	10	Solid-Liquid	DCM:Acetone	NA	GC-MS
17	NT				
18	NR				
19	10	QuEChERS	ACN	dSPE	LC-MS/MS
20	NT				
21	8.5	Sonication	Ethyl acetate	Nil	GC-MS
22	NT				
23	5	Solid-Liquid	Acidified Acetonitrile		LC-MS/MS
24	10	Solid-Liquid	DCM/ACETONE	NA	GC-MS

Table 30 Methodology – Diazinon

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	15	Solid-Liquid	Ethyl acetate	None	GC-FPD
2	10	Solid-Liquid	DCM/Acetone	n/a	GC-MS
3	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
4	10	Solid-Liquid	Acetone:Hexane	Filtration	GC-MS/MS
5	5	Solid-Liquid	Hexane/Acetone		GC-ECD
6	10	Solid-Liquid	Acetone / DCM		GC-MS
7	NR				
8	5	QuEChERS	Acetonitrile	dSPE	GC-FPD
9	4	Solid-Liquid	DCM/ACETONE	NIL	GC-MS
10	10	Solid-Liquid	DCM-Acetone		GC-MS
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	GC-MS/MS
12	10	Solid-Liquid	DCM: ACETONE	Filtration	GC-MS
13	5	QuEChERS	ACN	dSPE	GC-MS/MS
14	NR				

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
15	5	Solid-Liquid	DCM/ACE	NA	GC-MS/MS
16	10	Solid-Liquid	DCM:Acetone	NA	GC-MS
17	10	Solid-Liquid	DCM:ACE	N/A	GC-MS/MS
18	NR				
19	10	QuEChERS	ACN	dSPE	GC-MS/MS
20	10	Solid-Liquid	DCM/ Acetone (50:50)		GC-MS/MS
21	8.5	Sonication	Ethyl acetate	Nil	GC-MS
22	NT				
23	10	Solid-Liquid	DCM/Acetone		GC-MS
24	10	Solid-Liquid	DCM/ACETONE	NA	GC-MS

Table 31 Methodology – Imidacloprid

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	NT				
3	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
4	1	Solid-Liquid	MeOH - H2O	Filtration	LC-MS/MS
5	NT				
6	NT				
7	NR				
8	NT				
9	5	Solid-Liquid	ACETONITRILE/WATER	Filtration	LC-DAD
10	NT				
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	LC-MS/MS
12	NT				
13	NT				
14	NR				
15	NT				
16	NT				
17	NT				
18	NT				
19	10	QuEChERS	ACN	dSPE	LC-MS/MS
20	NT				
21	NT				
22	NT				
23	NT				

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
24	NT				

Table 32 Methodology – Metsulfuron-methyl

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	NT				
3	NT				
4	1	Solid-Liquid	MeOH - H2O	Filtration	LC-MS/MS
5	NT				
6	NT				
7	NR				
8	NT				
9	NT				
10	NT				
11	NT				
12	NT				
13	NT				
14	NR				
15	5	Solid-Liquid	MEOH	YES	HPLC-DAD
16	NT				
17	NT				
18	NR				
19	10	QuEChERS	ACN	dSPE	LC-MS/MS
20	NT				
21	NT				
22	NT				
23	NT				
24	NT				

Table 33 Methodology – Tebuconazole

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
1	NT				
2	NT				
3	5	QuEChERS	Acetonitrile	NA	LC-MS/MS
4	NT				
5	NT				

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-up	Measurement Instrument
6	NT				
7	NT				
8	NT				
9	NT				
10	NR				
11	3	Solid-Liquid	Acidic ethyl acetate	PSA	LC-MS/MS
12	NT				
13	5	QuEChERS	ACN	dSPE	GC-MS/MS
14	NR				
15	NT				
16	NT				
17	NT				
18	NR				
19	10	QuEChERS	ACN	dSPE	LC-MS/MS
20	NT				
21	8.5	Sonication	Ethyl acetate	Nil	GC-MS
22	NT				
23	NT				
24	NT				

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
dSPE	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
HPLC	High Performance Liquid Chromatography
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
k	Coverage Factor
LC	Liquid Chromatography
LOR	Limit Of Reporting
Max	Maximum
MCPA	2-Methyl-4-chlorophenoxyacetic acid
Md	Median
MeOH	Methanol
Min	Minimum
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

NPD	Nitrogen-Phosphorus Detection
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
Rec	Recovery
RM	Reference Material
SD	Standard Deviation
SI	International System of Units
SLE	Solid-Liquid Extraction
SS	Spiked Samples
SV	Spiked Value
Total DDT	Sum of DDD, DDE and DDT analytes
U	Expanded Uncertainty

END OF REPORT