Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Report
AQA 20-03
Pesticides in Soil

June 2020

ACKNOWLEDGMENTS

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

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

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

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Accredited for compliance with ISO/IEC 17043

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SUMMARY

AQA 20-03 Pesticides in Soil commenced in March 2020. Twenty-three laboratories participated and twenty-two participants submitted results.

Two soil samples were prepared using soil bought from a Sydney supplier. Sample S1 was prepared by spiking the soil with bifenthrin, dicamba, and p,p'-DDE. Sample S2 was prepared by spiking the soil with 2,4-D, *cis*- and *trans*-chlordane, and metsulfuron-methyl.

Each participant received a set of two 50 g test samples and was instructed to identify and measure the pesticides using their normal test methods.

Of a possible 132 numeric results, a total of 74 numeric results (56%) were submitted. Twelve results were submitted as a 'less than' value (<*x*) or Not Reported (NR), and forty-six 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 pesticides in soil.*

Laboratories **6**, **8** and **11** reported numeric results for all analytes scored in this study.

Three laboratories did not report results for analytes that they tested for and were present in the test samples (Table 13, total of 5 results).

Two laboratories reported analytes that were not spiked into the test samples (Table 14, total of 2 results).

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

Laboratory performance was assessed using both z-scores and E_n-scores.

Of 71 z-scores, 67 (94%) were satisfactory with $|z| \leq 2.0$.

Of 71 E_n-scores, 64 (90%) were satisfactory with $|E_n| \leq 1.0$.

Laboratory **11** returned satisfactory z and E_n-scores for all five analytes which were scored.

Laboratory **6** returned satisfactory E_n-scores for all five analytes which were scored.

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

Participants used a wide variety of methods. No correlation between results and method was evident.

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

All numeric results were reported with an associated estimate of expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 8% to 250% of the reported value.

Metrological traceability of the assigned values has not been established as they were the consensus of participants' results.

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, food and pharmaceuticals;
- controlled drug assay and clandestine laboratory;
- PFAS in water, soil and biota;
- folic acid in flour; and
- allergens in food.

1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify pesticides in 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; and
- develop the practical application of traceability and measurement uncertainty.

1.3 Study Conduct

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

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

2 STUDY INFORMATION

2.1 Selection of Pesticides

A list of possible analytes for Samples S1 and S2 is presented in Table 1. The spiked concentrations are presented in Table 2. The pesticides and spiked concentrations used in this study were selected with consideration to:

- A variety of pesticides, including some amenable to both gas chromatography and liquid chromatography; and
- National Environmental Protection (Assessment of Site Contamination) Measure Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

Table 1 List of Possible Analytes

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

Table 2 Spiked Values of Test Samples

Sample	Analyte	Spike (mg/kg)	Uncertainty (mg/kg)*
S1	Bifenthrin	0.0823	0.0041
	Dicamba	0.678	0.034
	p,p'-DDE	1.097	0.055
S2	2,4-D	1.003	0.050
	cis-Chlordane**	0.803	0.040
	trans-Chlordane**	0.745	0.037
	Metsulfuron-methyl	0.648	0.032

* 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 concentration of pesticide at the time of spiking.

** While both *cis*- and *trans*-chlordane were spiked into Sample S2, participants were requested to report the total chlordane present in the sample and therefore Total Chlordane was scored in this PT study.

2.2 Study Timetable

The timetable of the study was:

Invitation issued	9 March 2020
Samples dispatched	1 April 2020
Results due	11 May 2020
Interim report issued	14 May 2020

2.3 Participation

Twenty-three laboratories participated, and twenty-two participants submitted results.

2.4 Laboratory Code

All participants were assigned a confidential laboratory code number.

2.5 Sample Preparation

Two soil samples were prepared by spiking soil purchased from a Sydney supplier with various pesticides to obtain the concentrations listed in Table 2. The preparation of the samples is described in Appendix 1.

2.6 Homogeneity of Samples

The samples were prepared and packaged using a process that has been demonstrated to produce homogeneous samples from previous NMI Pesticides in Soil PT studies. No homogeneity testing was conducted and the participants' results gave no reason to question the homogeneity of the samples.

2.7 Stability of Analytes

No assessment of the stability of the pesticides was made before the samples were sent. To assess possible instability, the results returned by participants were compared to the spiked values. Assigned values (or robust averages) of participants' results were within 72 – 91% of the spiked values. This provides good support for the stability of these analytes in the test samples and similar ratios have been observed in previous NMI Pesticides in Soil PT studies (as presented in PT Report AQA 16-04 Pesticides in Soil).[6]

2.8 Sample Storage, Dispatch and Receipt

The test samples were refrigerated at 4°C prior to dispatch.

Participants were sent one 50 g jar of spiked soil for each of Samples S1 and S2. The samples were packed in a foam box with a cooler brick and sent by courier on 1 April 2020.

The following items were packaged with the samples:

- a covering 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 e-mailed to participants.

2.9 Instructions to Participants

Participants were instructed as follows:

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

- For each analyte in each sample report a single result in mg/kg expressed as if reporting to a client (i.e. corrected for recovery or not, according to your standard procedure). This is the figure that will be used in all statistical analysis in the study report.
- For each analyte report the associated uncertainty (e.g. 0.50 ± 0.02 mg/kg).
- Report any listed pesticide not tested as NT.
- 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 (i.e. uncertainty budget, repeatability precision, long term result variability).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by e-mail (proficiency@measurement.gov.au).
- Return the completed results sheet by 27 April 2020. Late results cannot be included in the study report.

The results due date was extended to 11 May 2020 due to the exceptional national and international circumstances occurring during this time.

2.10 Interim Report

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

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses are presented in Appendix 2.

3.2 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of 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	Nata Technical Note 33
2	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - RM Duplicate analysis	Recoveries of SS	
4	Top Down - precision and estimates of the method and laboratory bias		CRM Instrument calibration Recoveries of SS	Nata Technical Note 33
5	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - SS Duplicate analysis	Recoveries of SS	
6	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA GAG Estimating and reporting measurement uncertainty of chemical test results January 2018 & NATA GAG Validation and verification of quantitative and qualitative test method January 2018
7	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS	Recoveries of SS	Nata Technical Note 33
8	Standard uncertainty based on historical data	Duplicate analysis Instrument calibration	Instrument calibration	
9	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	CRM 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	
11	Top Down - precision and estimates of the method and laboratory bias		CRM Instrument calibration Recoveries of SS	Nata Technical Note 33
12	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
13	Professional judgment	Control samples - SS Duplicate analysis	Recoveries of SS	Nata Technical Note 33
14	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
15	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
16	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
17	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
18	Control charts			Control Charts
19	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
20	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
21	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
22	Top Down - precision and estimates of the method and laboratory bias	Instrument calibration	Recoveries of SS	Nata Technical Note 33
23	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Recoveries of SS	Nordtest Report TR537

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

3.3 Participants' Comments

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

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
5	S2	Soil spike recovery: Lindane:103 %, Heptachlor: 79%, Aldin: 106%, Dieldrin: 128%, Endrin: 121%, DDT: 80%.	
8	All	It is noted that Total Chlordane is calculated using the following formula: Total Chlordane [(cis+trans)*100/42] The formula takes into account the isomer ratio's.	
9	S1	Recovery results for S1 are from a spike onto the sample S1. DDE recovery was outside calibration range due to incurred concentration	
	S2	Recovery results for S2 are from a spike onto blank matrix.	
13	All	Pesticides result from GC - ECD	
23	All	Our laboratory is performing sub-ppm level analysis for pesticides; as such the higher levels present in samples introduces dillutions and greater uncertainties.	Samples were prepared to contain analytes at various levels to cater for the needs of different laboratories. In this study scored analytes were spiked at around 0.08 – 1.5 mg/kg.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 10 with the summary statistics: robust average, mean, median, 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 7.

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

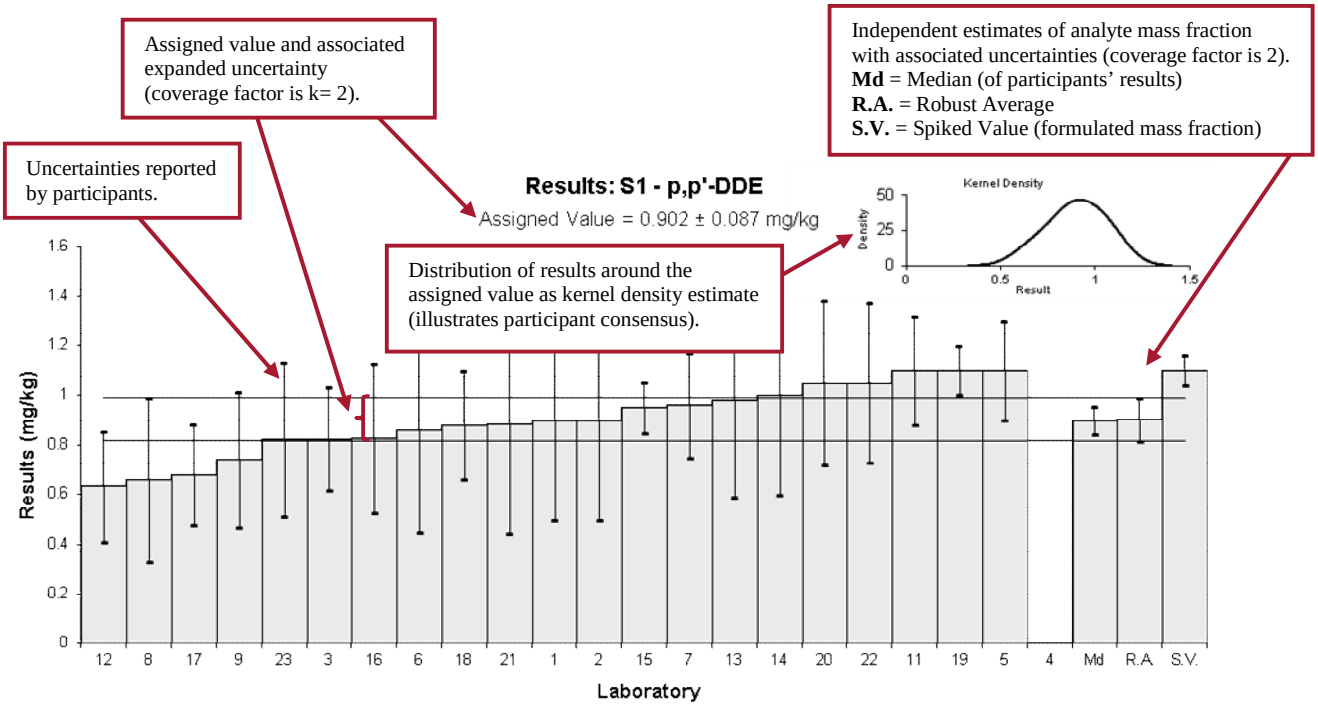


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

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

4.3 Robust Average and Robust Between Laboratory Coefficient of Variation

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

4.4 Performance Coefficient of Variation

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

4.5 Target Standard Deviation

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

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

4.6 z-Score

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

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

where:

z is z-score

χ is a participant's result

X is the assigned value

σ is the target standard deviation from Equation 1

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

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

4.7 E_n-Score

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

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

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

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

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

4.8 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	Bifenthrin
Units	mg/kg

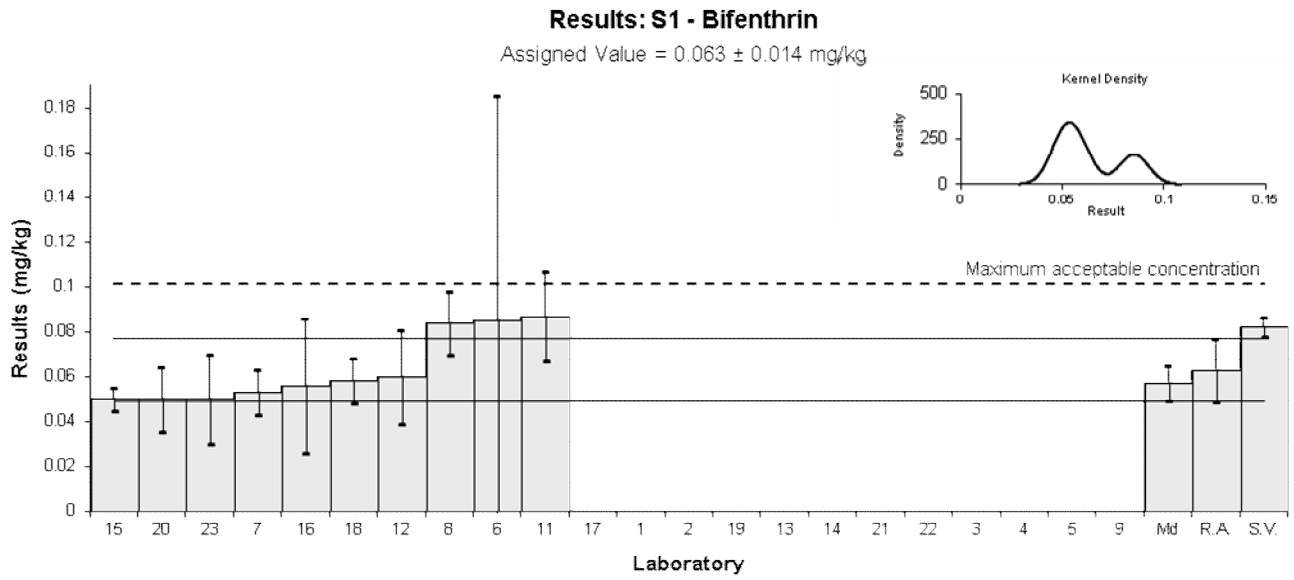
Participant Results

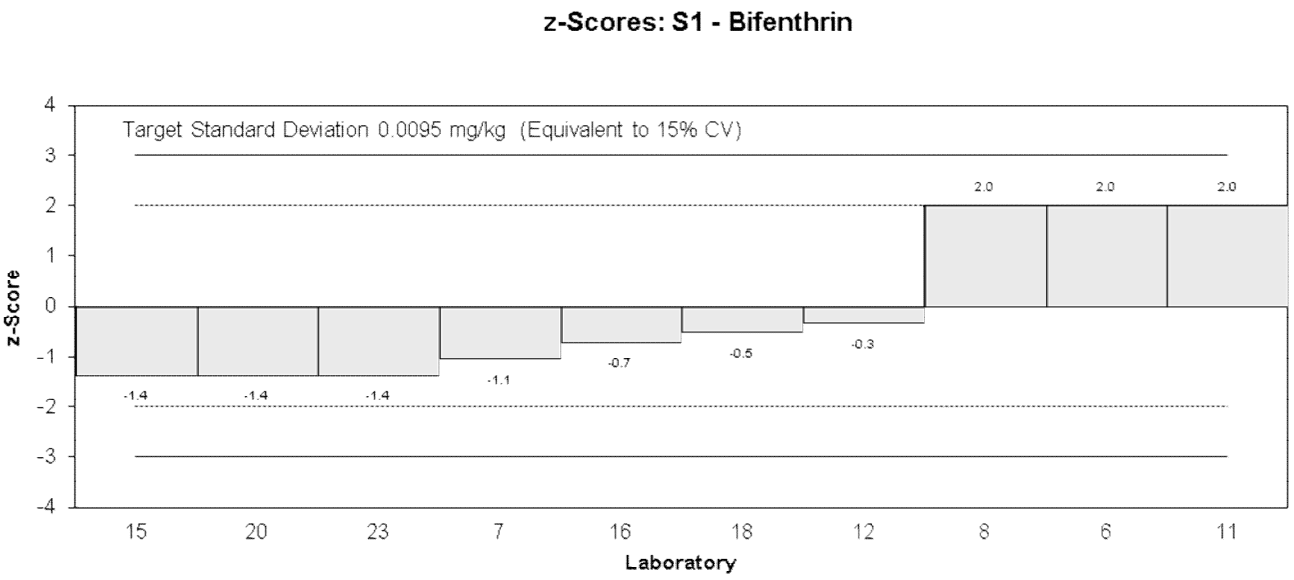
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	<0.1	NR	80-120		
2	<0.1	NR	80-120		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6*	0.085	0.1	49	2.00	0.22
7	0.053	0.01	NR	-1.06	-0.58
8*	0.084	0.014	NR	2.00	1.00
9	NT	NT	NT		
11*	0.087	0.02	88	2.00	0.98
12	0.0598	0.0209	88	-0.34	-0.13
13	<0.5	0.5	NR		
14	<0.5	NR	80-120		
15	0.05	0.005	103	-1.38	-0.87
16	0.0561	0.03	NR	-0.73	-0.21
17	<0.01	NR	NR		
18	0.058	0.01	NR	-0.53	-0.29
19	<0.2	NR	NR		
20	0.05	0.014	NR	-1.38	-0.66
21	NT	NT	NT		
22	NT	NT	NT		
23	0.05	0.02	95	-1.38	-0.53

Statistics

Assigned Value	0.063	0.014
Spike	0.0823	0.0041
Max. Acceptable Conc.*	0.101	
Robust Average	0.063	0.014
Median	0.0571	0.0075
Mean	0.0633	
N	10	
Max.	0.087	
Min.	0.05	
Robust SD	0.018	
Robust CV	28%	

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


Results: S1 - Bifenthrin
Assigned Value = 0.063 ± 0.014 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
Laboratory
15 20 23 7 16 18 12 8 6 11 17 1 2 19 13 14 21 22 3 4 5 9 Md R.A. S.V.


z-Scores: S1 - Bifenthrin
Target Standard Deviation 0.0095 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
15 20 23 7 16 18 12 8 6 11

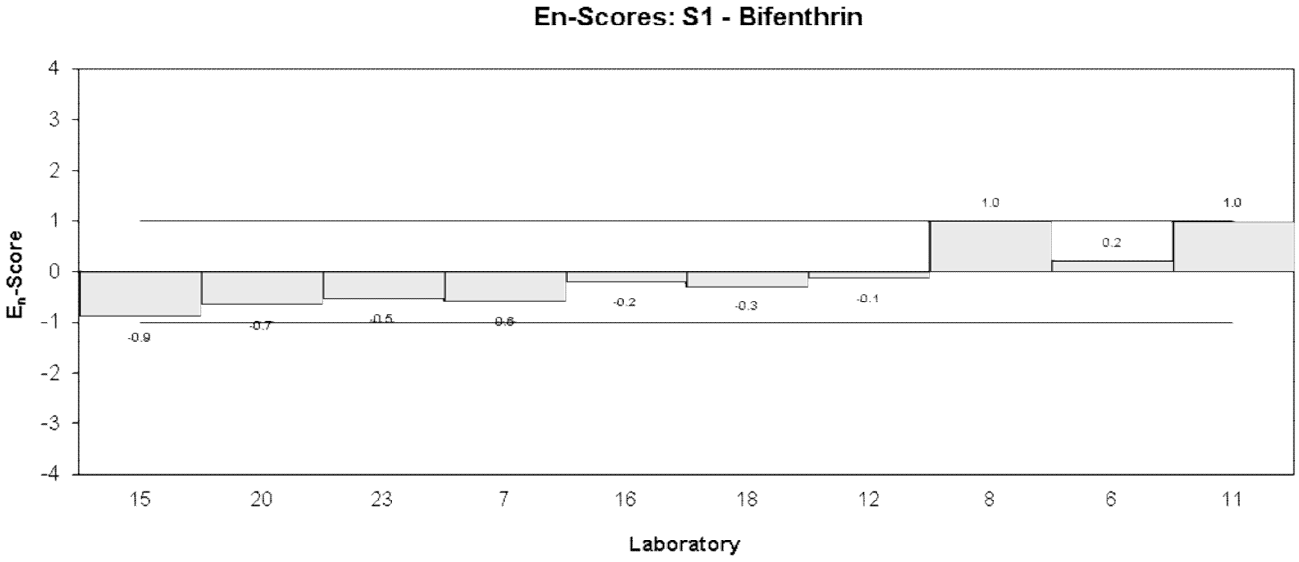

En-Scores: S1 - Bifenthrin
En-Score
Laboratory
15 20 23 7 16 18 12 8 6 11

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Dicamba
Units	mg/kg

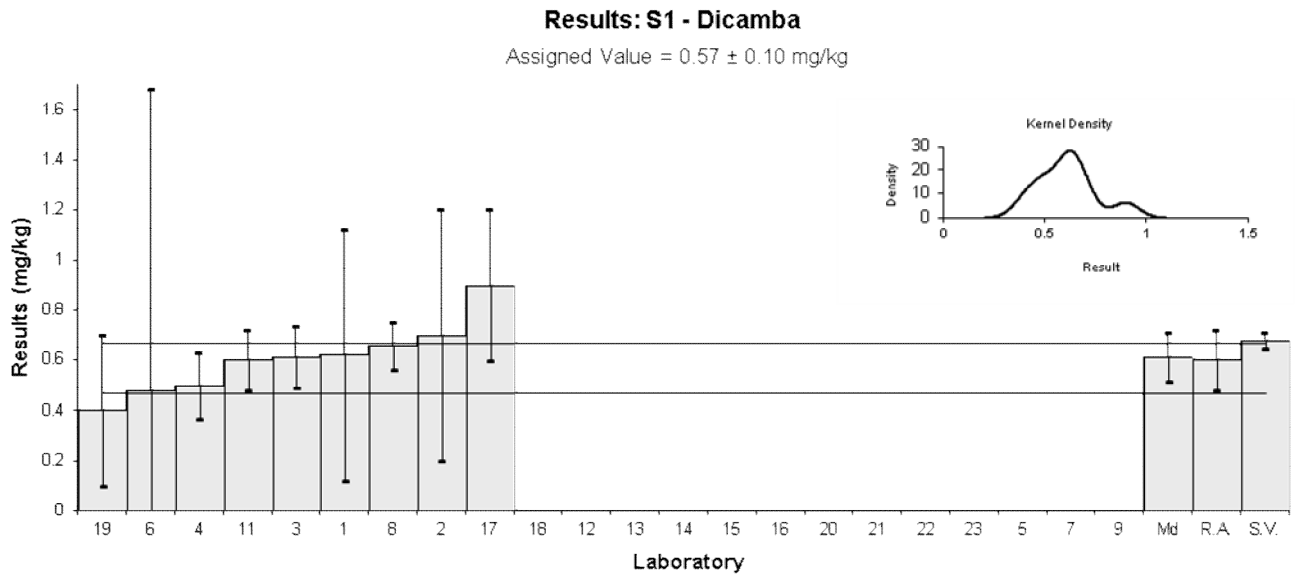
Participant Results

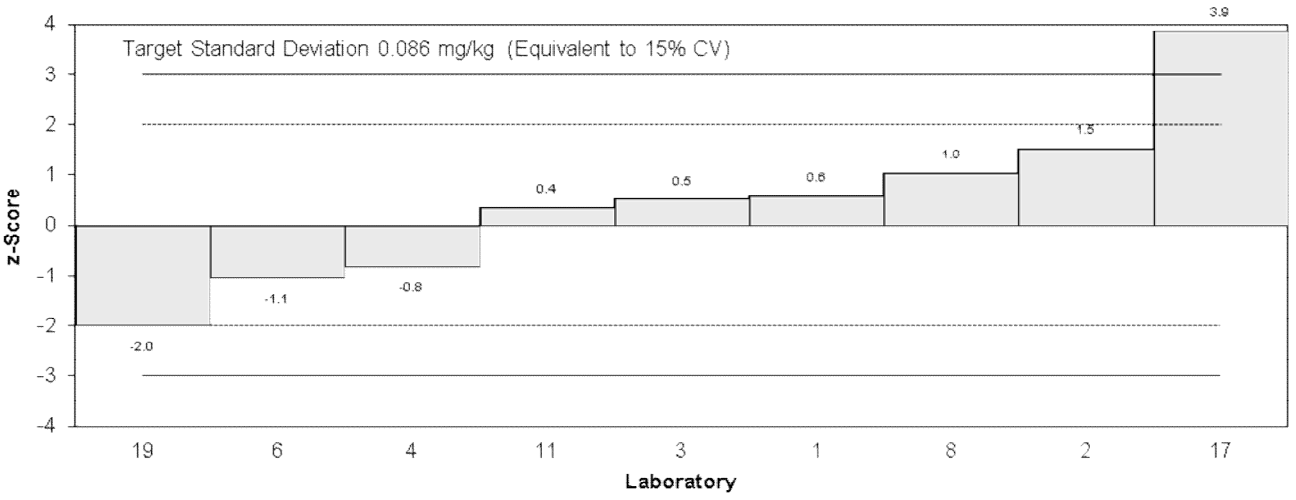
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.62	0.5	80-120	0.58	0.10
2	0.7	0.5	80-120	1.52	0.25
3	0.614	0.123	85	0.51	0.28
4	0.5	0.13	99	-0.82	-0.43
5	NT	NT	NT		
6	0.48	1.2	38	-1.05	-0.07
7	NT	NT	NT		
8	0.658	0.093	NR	1.03	0.64
9	NT	NT	NT		
11	0.6	0.12	89	0.35	0.19
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.9	0.3	NR	3.86	1.04
18	< 0.5	0.12	NR		
19	0.4	0.3	NR	-1.99	-0.54
20	NT	NT	NT		
21	NT	NT	NT		
22	NT	NT	NT		
23	NT	NT	NT		

Statistics

Assigned Value*	0.57	0.10
Spike	0.678	0.034
Robust Average	0.60	0.12
Median	0.614	0.098
Mean	0.608	
N	9	
Max.	0.9	
Min.	0.4	
Robust SD	0.11	
Robust CV	20%	

* Robust average excluding laboratory 17.


Results: S1 - Dicamba
Assigned Value = 0.57 ± 0.10 mg/kg
Results (mg/kg)
Laboratory
19 6 4 11 3 1 8 2 17 18 12 13 14 15 16 20 21 22 23 5 7 9 Md R.A. S.V.
Kernel Density
Density
Result


z-Scores: S1 - Dicamba
Target Standard Deviation 0.086 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
19 6 4 11 3 1 8 2 17
-2.0
-1.1
-0.8
0.4
0.5
0.6
1.0
1.5
3.9

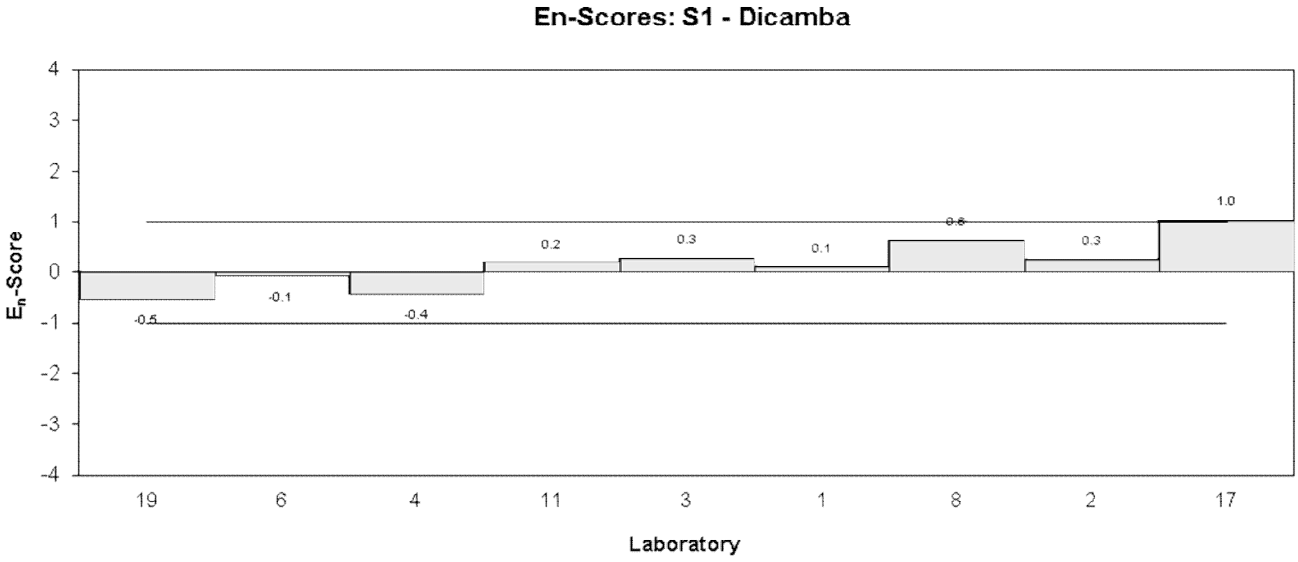

En-Scores: S1 - Dicamba
En-Score
Laboratory
19 6 4 11 3 1 8 2 17
-0.5
-0.1
-0.4
0.2
0.3
0.1
0.6
0.3
1.0

Figure 3

Table 7

Sample Details

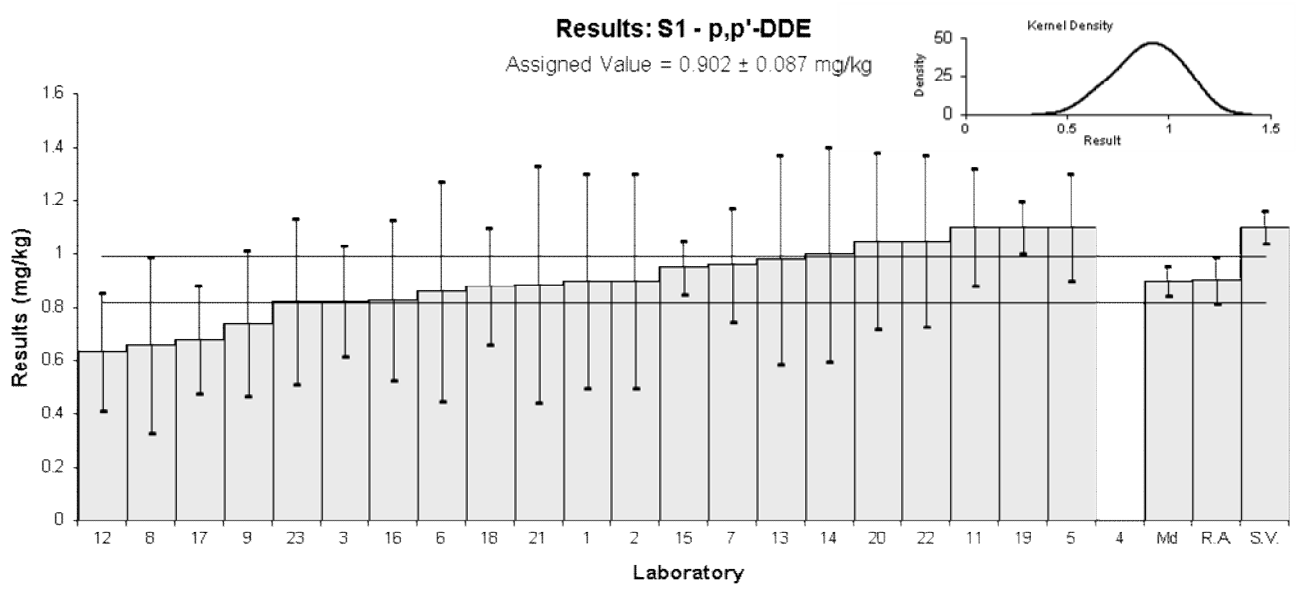
Sample No.	S1
Matrix	Soil
Analyte	p,p'-DDE
Units	mg/kg

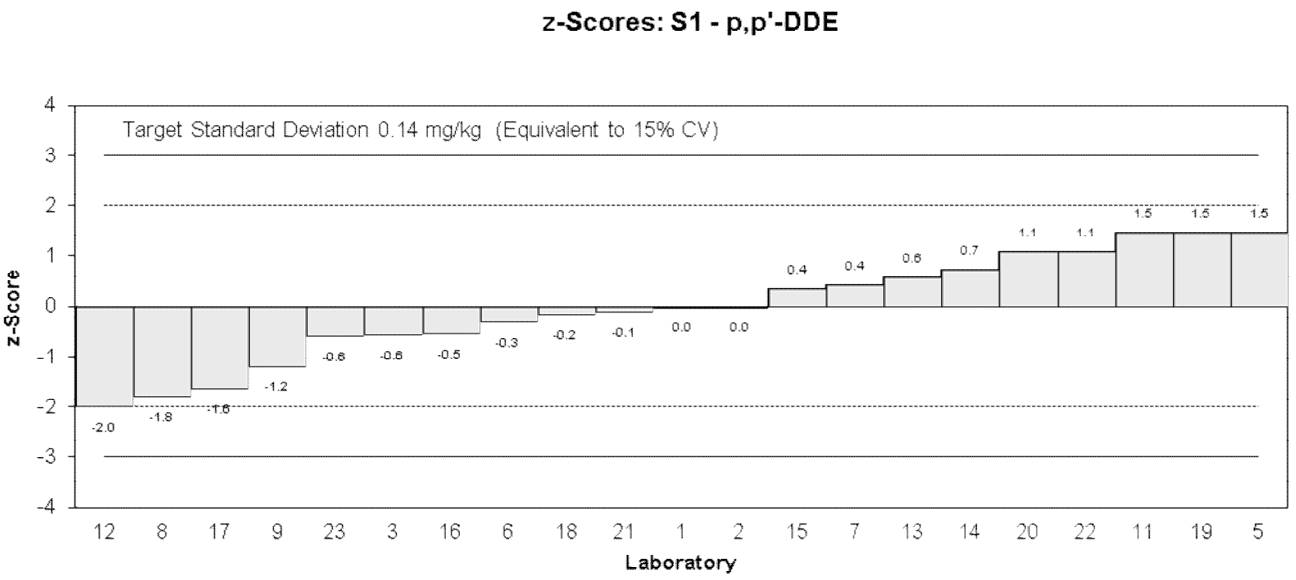
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.9	0.4	80-120	-0.01	0.00
2	0.9	0.4	80-120	-0.01	0.00
3	0.824	0.206	NR	-0.58	-0.35
4	NR	NR	NR		
5	1.1	0.2	NR	1.46	0.91
6	0.86	0.41	72	-0.31	-0.10
7	0.96	0.21	NR	0.43	0.26
8	0.66	0.33	NR	-1.79	-0.71
9	0.74	0.27	NR	-1.20	-0.57
11	1.1	0.22	95	1.46	0.84
12	0.633	0.222	74	-1.99	-1.13
13	0.981	0.39	121	0.58	0.20
14	1	0.4	80-120	0.72	0.24
15	0.95	0.1	79	0.35	0.36
16	0.828	0.3	NR	-0.55	-0.24
17	0.68	0.2	NR	-1.64	-1.02
18	0.88	0.22	NR	-0.16	-0.09
19	1.1	0.1	NR	1.46	1.49
20	1.05	0.33	NR	1.09	0.43
21	0.886	0.443	NR	-0.12	-0.04
22	1.05	0.32	NR	1.09	0.45
23	0.82	0.31	97	-0.61	-0.25

Statistics

Assigned Value	0.902	0.087
Spike	1.097	0.055
Robust Average	0.902	0.087
Median	0.900	0.055
Mean	0.900	
N	21	
Max.	1.1	
Min.	0.633	
Robust SD	0.16	
Robust CV	18%	


Results: S1 - p,p'-DDE
Assigned Value = 0.902 ± 0.087 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
12 8 17 9 23 3 16 6 18 21 1 2 15 7 13 14 20 22 11 19 5 4 Md R.A S.V.


z-Scores: S1 - p,p'-DDE
Target Standard Deviation 0.14 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 8 17 9 23 3 16 6 18 21 1 2 15 7 13 14 20 22 11 19 5

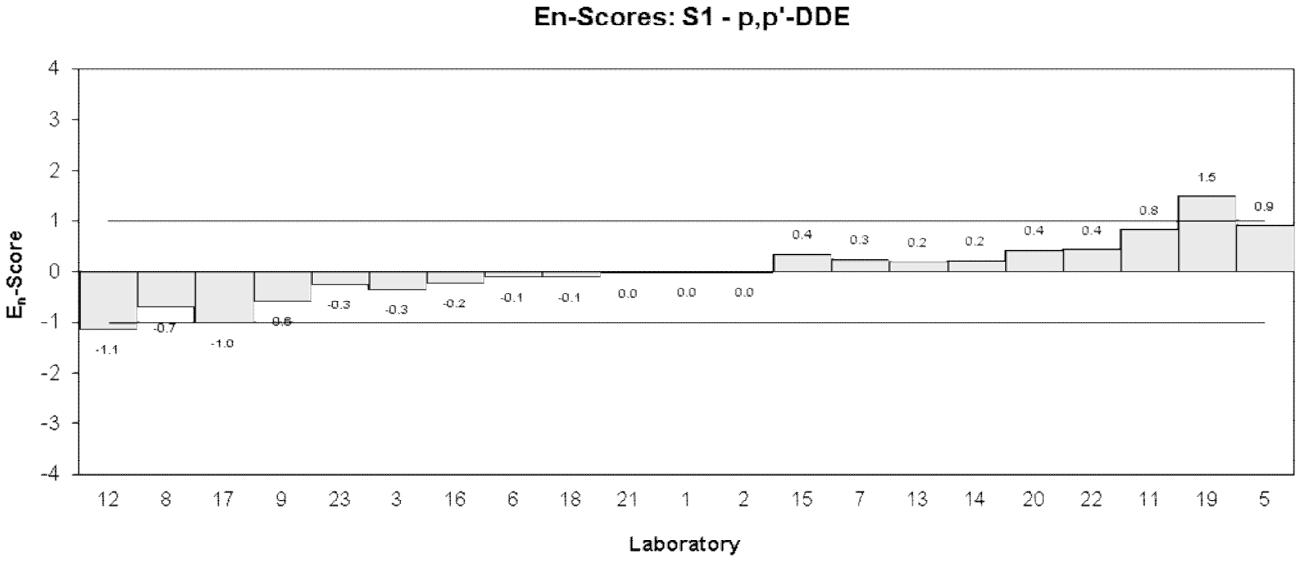

En-Scores: S1 - p,p'-DDE
En-Score
Laboratory
12 8 17 9 23 3 16 6 18 21 1 2 15 7 13 14 20 22 11 19 5

Figure 4

Table 8

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	2,4-D
Units	mg/kg

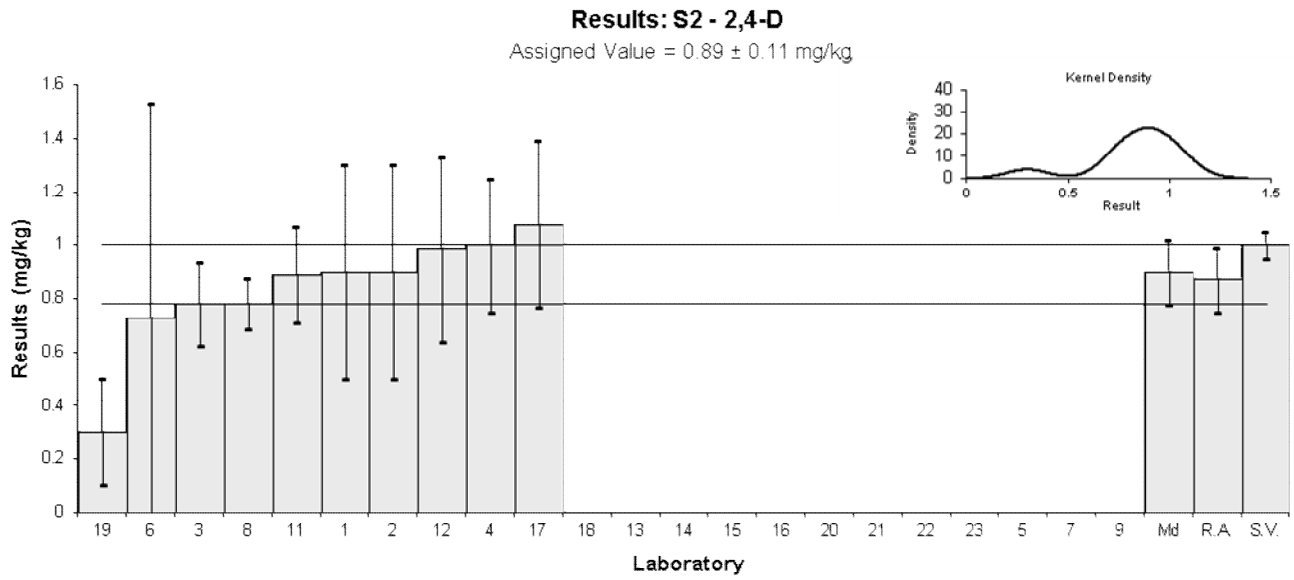
Participant Results

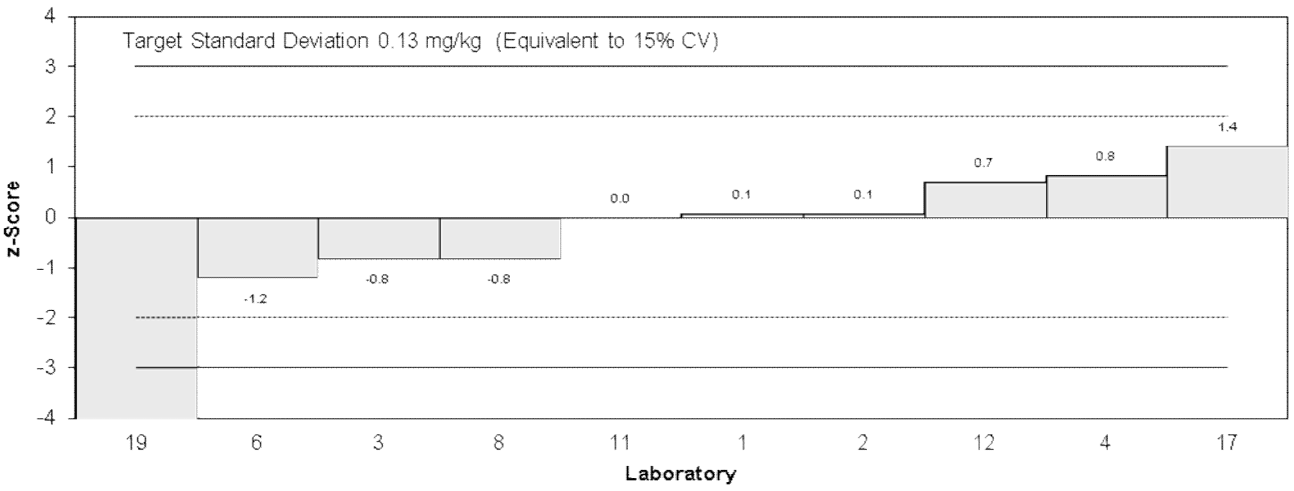
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.9	0.4	80-120	0.07	0.02
2	0.9	0.4	80-120	0.07	0.02
3	0.779	0.156	85	-0.83	-0.58
4	1	0.25	90	0.82	0.40
5	NT	NT	NT		
6	0.73	0.8	54	-1.20	-0.20
7	NT	NT	NT		
8	0.779	0.094	NR	-0.83	-0.77
9	NT	NT	NT		
11	0.89	0.18	88	0.00	0.00
12	0.985	0.345	101	0.71	0.26
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	1.08	0.31	NR	1.42	0.58
18	< 0.5	0.01	NR		
19	0.3	0.2	NR	-4.42	-2.58
20	NT	NT	NT		
21	NT	NT	NT		
22	NT	NT	NT		
23	NT	NT	NT		

Statistics

Assigned Value*	0.89	0.11
Spike	1.003	0.050
Robust Average	0.87	0.12
Median	0.90	0.12
Mean	0.83	
N	10	
Max.	1.08	
Min.	0.3	
Robust SD	0.13	
Robust CV	15%	

* Robust average excluding laboratory 19.


Results: S2 - 2,4-D
Assigned Value = 0.89 ± 0.11 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
19 6 3 8 11 1 2 12 4 17 18 13 14 15 16 20 21 22 23 5 7 9 Md R.A S.V.


z-Scores: S2 - 2,4-D
Target Standard Deviation 0.13 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
19 6 3 8 11 1 2 12 4 17

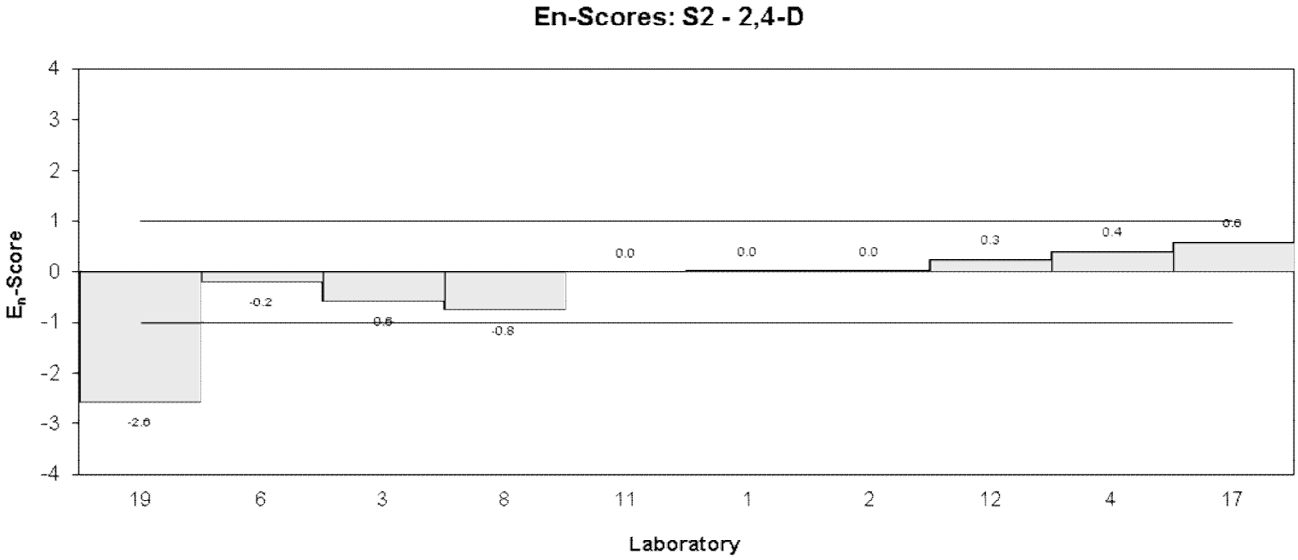

En-Scores: S2 - 2,4-D
En-Score
Laboratory
19 6 3 8 11 1 2 12 4 17

Figure 5

Table 9

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Recovery
1	<2	NR	80-120
2	NT	NT	NT
3	NT	NT	NT
4	0.716	0.18	95
5	NT	NT	NT
6	0.46	0.12	82
7	NT	NT	NT
8	NT	NT	NT
9	NT	NT	NT
11	0.58	0.12	90
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	<0.01	NR	NR
18	< 0.5	0.12	NR
19	NT	NT	NT
20	NT	NT	NT
21	NT	NT	NT
22	NT	NT	NT
23	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike	0.648	0.032
Robust Average	0.59	0.21
Median	0.58	0.44
Mean	0.59	
N	3	
Max.	0.716	
Min.	0.46	
Robust SD	0.15	
Robust CV	25%	

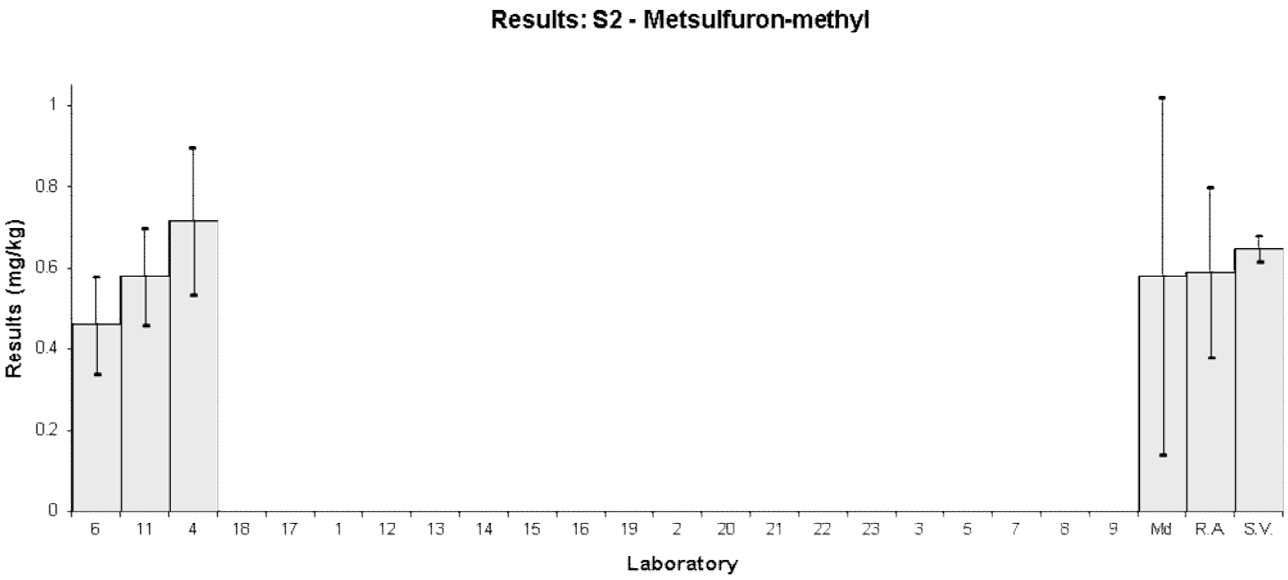

Results: S2 - Metsulfuron-methyl
Results (mg/kg)
1
0.8
0.6
0.4
0.2
0
6
11
4
18
17
1
12
13
14
15
16
19
2
20
21
22
23
3
5
7
8
9
Md
R.A.
S.V.
Laboratory

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Total Chlordane
Units	mg/kg

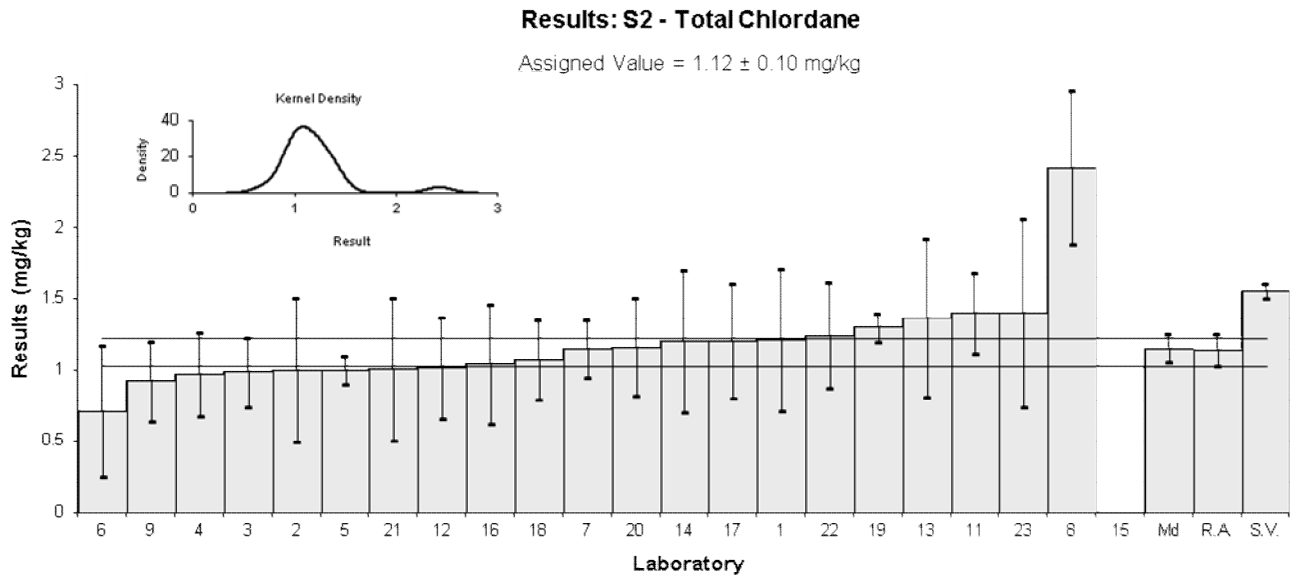
Participant Results

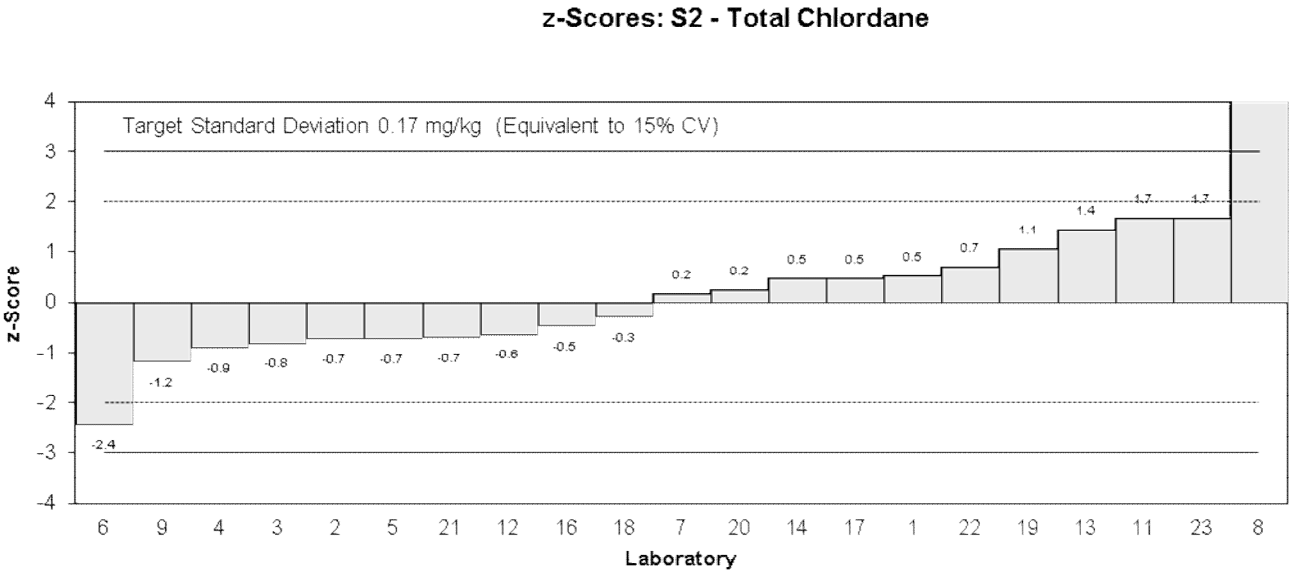
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.21	0.5	80-120	0.54	0.18
2	1	0.5	80-120	-0.71	-0.24
3	0.983	0.246	NR	-0.82	-0.52
4	0.97	0.29	87	-0.89	-0.49
5	1	0.1	NR	-0.71	-0.85
6	0.71	0.46	67	-2.44	-0.87
7	1.15	0.2	NR	0.18	0.13
8	2.42	0.54	NR	7.74	2.37
9	0.92	0.28	72	-1.19	-0.67
11	1.4	0.28	96	1.67	0.94
12	1.013	0.355	87	-0.64	-0.29
13	1.363	0.55	117	1.45	0.43
14	1.2	0.5	80-120	0.48	0.16
15	NT	NT	NT		
16	1.04	0.42	NR	-0.48	-0.19
17	1.2	0.4	NR	0.48	0.19
18	1.07	0.28	NR	-0.30	-0.17
19	1.3	0.1	NR	1.07	1.27
20	1.16	0.34	NR	0.24	0.11
21	1.004	0.502	NR	-0.69	-0.23
22	1.24	0.37	NR	0.71	0.31
23	1.4	0.66	97	1.67	0.42

Statistics

Assigned Value*	1.12	0.10
Spike	1.548	0.054
Robust Average	1.14	0.11
Median	1.15	0.10
Mean	1.18	
N	21	
Max.	2.42	
Min.	0.71	
Robust SD	0.18	
Robust CV	16%	

* Robust average excluding laboratory 8.


Results: S2 - Total Chlordane
Assigned Value = 1.12 ± 0.10 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 9 4 3 2 5 21 12 16 18 7 20 14 17 1 22 19 13 11 23 8 15 Md R.A S.V.


z-Scores: S2 - Total Chlordane
Target Standard Deviation 0.17 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 9 4 3 2 5 21 12 16 18 7 20 14 17 1 22 19 13 11 23 8
-2.4 -1.2 -0.9 -0.8 -0.7 -0.7 -0.7 -0.6 -0.5 -0.3 0.2 0.2 0.5 0.5 0.5 0.7 1.1 1.4 1.7 1.7

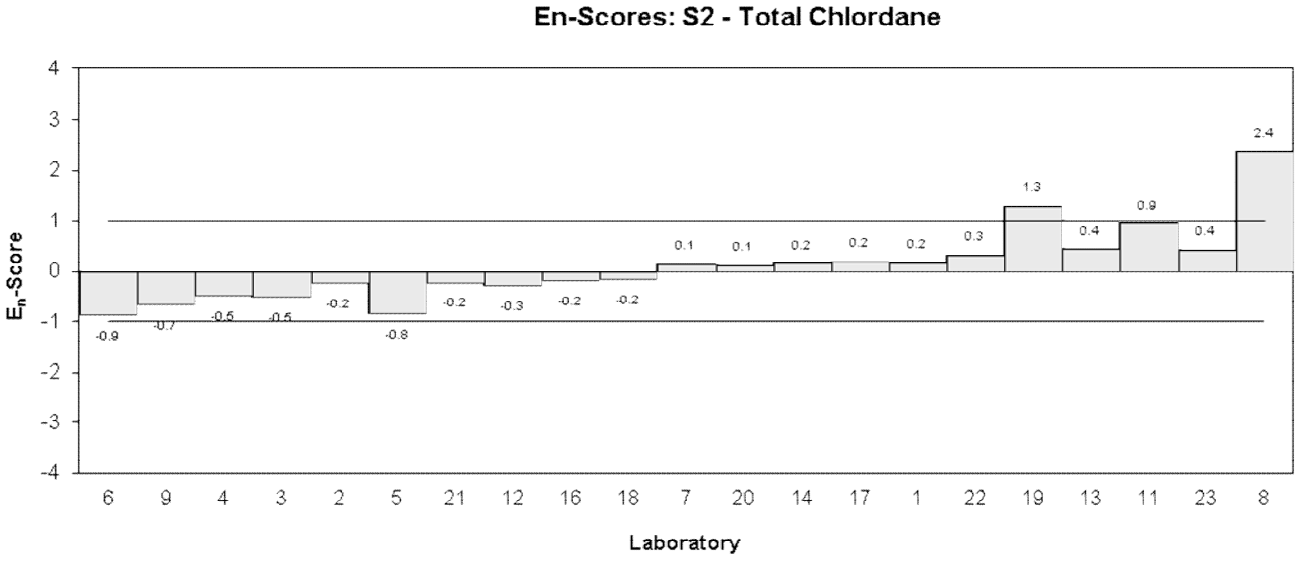

En-Scores: S2 - Total Chlordane
En-Score
Laboratory
6 9 4 3 2 5 21 12 16 18 7 20 14 17 1 22 19 13 11 23 8
-0.9 -0.7 -0.5 -0.5 -0.2 -0.8 -0.2 -0.3 -0.2 -0.2 0.1 0.1 0.2 0.2 0.2 0.3 1.3 0.4 0.9 0.4 2.4

Figure 7

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust average of participants' results was used as the assigned value for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2015.[7] Results less than 50% and greater than 150% of the robust average were removed before calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented Appendix 3, using p,p'-DDE in Sample S1 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 metsulfuron-methyl in Sample S2 as there were too few reported numeric results.

A comparison of the assigned value (or robust average if no assigned value was set) and the spiked value is presented in Table 11. The assigned values (robust averages) were within the range of 72% to 91% of the spiked values; similar ratios have been observed in previous Pesticides in Soil PT studies. The best estimate of the 'true' mass fraction of the pesticides in the 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. Whilst this may be an underestimate of the total amount of pesticide, it is likely that strongly bound pesticide is of little environmental significance. For this study, the assigned value is therefore the best estimate of the amount of 'extractable pesticide'.

Table 11 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	Bifenthrin	0.063	0.0823	77
	Dicamba	0.57	0.678	84
	p,p'-DDE	0.902	1.097	82
S2	2,4-D	0.89	1.003	89
	Metsulfuron-methyl	*(0.59)*	0.648	*(91)*
	Total Chlordane	1.12	1.548	72

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]

All 74 numerical results submitted were reported with an associated expanded measurement uncertainty. Participants used a wide variety of procedures to estimate the expanded measurement uncertainty (Table 3).

The magnitude of the reported expanded uncertainties was within the range 8% to 250% of the reported value. In general, when the uncertainty estimate is smaller than 15% or larger than 50% of the reported value then this should be reviewed as suspect. In this study, seven expanded uncertainties were less than 15% relative while nine 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 **13** and **18** attached estimates of the expanded measurement uncertainty for results reported as less than their limit of detection. 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. 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 0.633 ± 0.222 mg/kg, it is better to report this as 0.63 ± 0.22 mg/kg.[10]

6.3 z-Score

Target SDs equivalent to 15% PCV was used to calculate z-scores. Target SDs (as PCV), CVs predicted by the Thomspon-Horwitz equation[8] and between laboratories CVs obtained in this study for scored analytes are presented for comparison in Table 12.

Table 12 Comparison of Target SDs, Thompson-Horwitz CVs and Between Laboratories CVs

Sample	Analyte	Assigned value (mg/kg)	Target SD (as PCV) (%)	Thompson-Horwitz CV (%)	Between Laboratories CV (%)
S1	Bifenthrin	0.063	15	22	28
	Dicamba	0.57	15	17	20
	p,p'-DDE	0.902	15	16	18
S2	2,4-D	0.89	15	16	15
	Total Chlordane	1.12	15	16	16

To account for possible low bias in the consensus values due to participants using inefficient analytical or extraction techniques, three z-scores were adjusted for bifenthrin in Sample S1. A maximum acceptable concentration was set to two target SDs more than the spiked value, and results lower than the maximum acceptable concentration but with a z-score greater than 2 had their z-score adjusted to 2. This ensured that participants reporting results close to the spiked value were not penalised. z-Scores for results higher than the maximum acceptable concentration were not adjusted, and z-scores less than 2 were left unaltered.

Of 71 results for which z-scores were calculated, 67 (94%) returned a satisfactory z-score of $|z| \leq 2.0$.

Laboratories **6**, **8** and **11** reported results for all five analytes for which z-scores were calculated. Laboratory **11** returned satisfactory z-scores for all five analytes.

Laboratories **1**, **2**, **3** and **12** returned satisfactory z-scores for all four reported scored analytes. Laboratories **4**, **7**, **16**, **18**, **20** and **23** returned satisfactory z-scores for all three reported scored analytes. Laboratories **5**, **9**, **13**, **14**, **15**, **21** and **22** returned satisfactory z-scores for all two reported scored analytes.

The dispersal of participants' z-scores is presented graphically by laboratory in Figure 8 and by analyte in Figure 9.

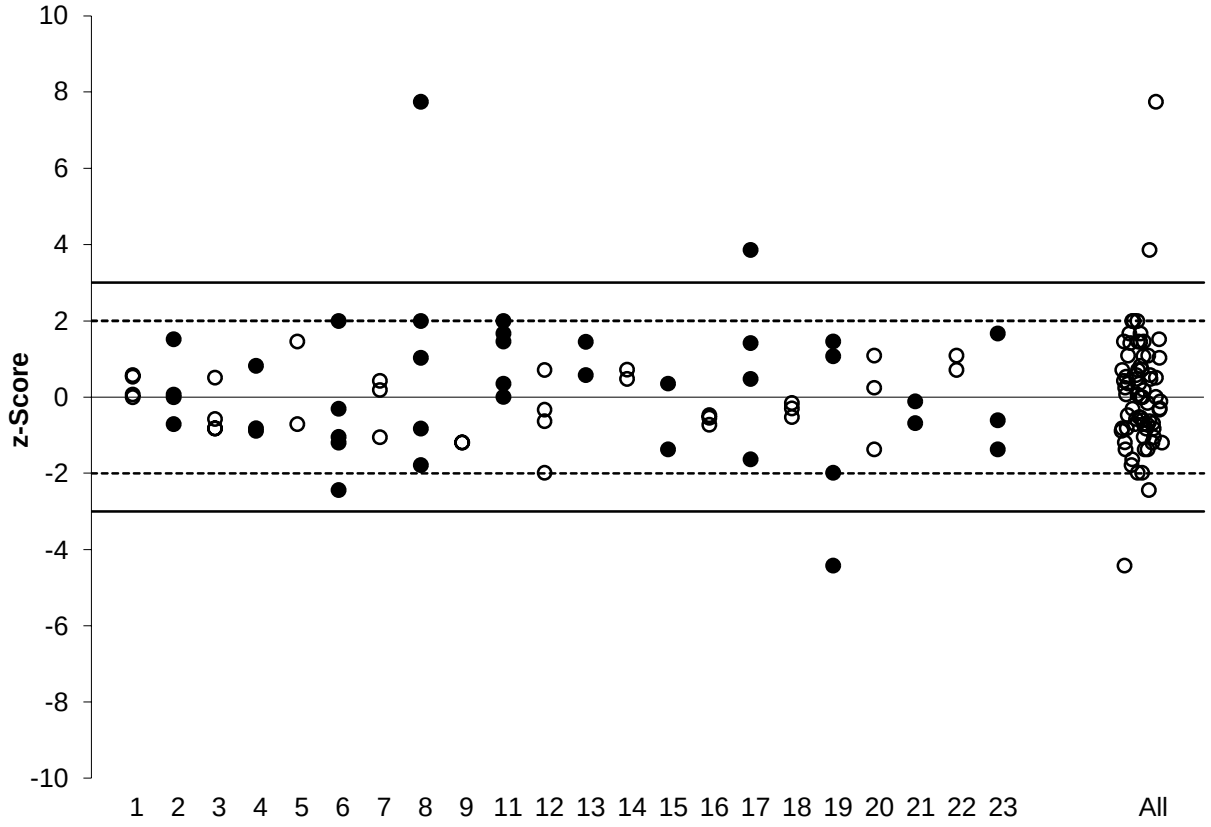


Figure 8 z-Score Dispersal by Laboratory

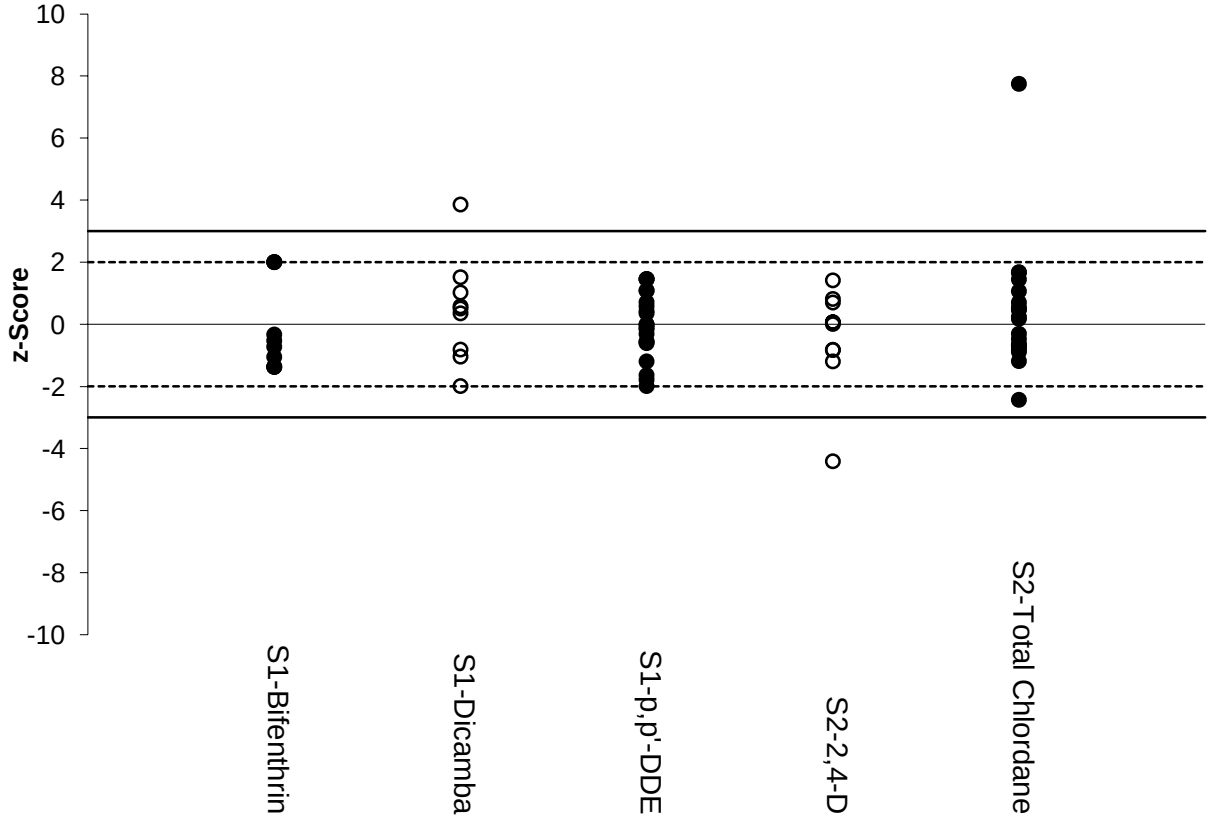


Figure 9 z-Score Dispersal by Analyte

6.4 E_n-Score

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

Of 71 results for which E_n-scores were calculated, 64 (90%) were satisfactory with $|E_n| \leq 1.0$.

Laboratories **6** and **11** returned satisfactory E_n-scores for all five analytes which were scored.

Laboratories **1**, **2** and **3** returned satisfactory E_n-scores for all four reported scored analytes. Laboratories **4**, **7**, **16**, **18**, **20** and **23** returned satisfactory E_n-scores for all three reported scored analytes. Laboratories **5**, **9**, **13**, **14**, **15**, **21** and **22** returned satisfactory E_n-scores for all two reported scored analytes.

The dispersal of participants' E_n-scores by laboratory is presented in Figure 10.

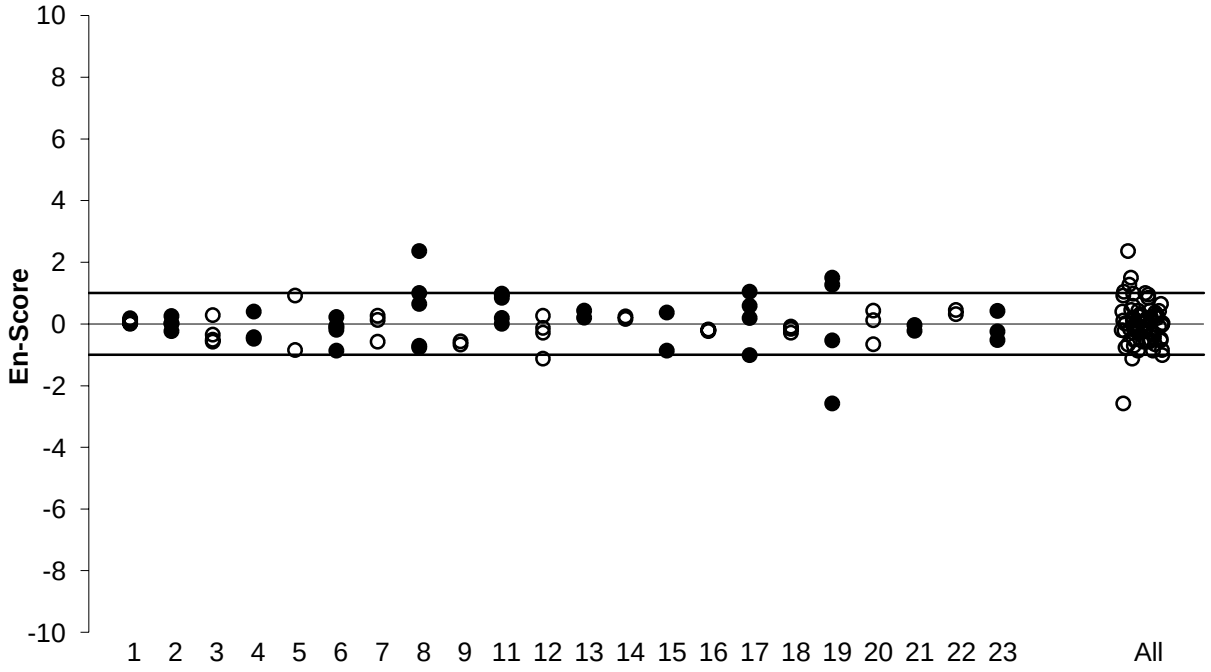


Figure 10 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 13 presents false negative results – an analyte present which a laboratory tested for but did not report a result, e.g. laboratories reporting a '<' or NR result when the assigned and spiked value was higher than the participants' reporting limit; or laboratories that didn't report any value. For Sample S2 metsulfuron-methyl where no assigned value was set, results have only been considered to be false negatives for laboratories reporting '<' results where the robust average and spiked value were significantly higher than the '<' figure.

Table 13 False Negatives

Lab. Code	Sample	Analyte
4	S1	p,p'-DDE
17	S1	Bifenthrin
	S2	Metsulfuron-methyl
18	S1	Dicamba
	S2	2,4-D

6.6 Reporting of Additional Analytes

Two participants reported analytes that were not spiked into the test samples. These are presented in Table 14.

Table 14 Analytes reported by participants but not spiked into the samples

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
6	S2	alpha-Endosulfan	0.057	0.018	80
9	S2	alpha-Endosulfan	0.23	0.07	59

Some participants reported results for analytes that were spiked into the sample but were not scored in this study.

Sample S1 was spiked with p,p'-DDE and this was the analyte scored. Ten participants also reported a Total DDT value. These results are presented in Table 15 for information only.

Table 15 Analytes reported by participants present in the sample but not scored

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
6	S1	Total DDT	0.86	0.41	72
8	S1	Total DDT	0.66	0.33	NR
11	S1	Total DDT	1.1	0.22	NR
12	S1	Total DDT	0.633	0.222	74
16	S1	Total DDT	0.828	0.3	NR
19	S1	Total DDT	1.1	0.1	NR
20	S1	Total DDT	1.05	0.33	NR
21	S1	Total DDT	0.886	0.443	NR
22	S1	Total DDT	1.05	0.32	NR
23	S1	Total DDT	0.82	0.31	NR

Sample S2 was spiked with *cis*- and *trans*-chlordane and the total chlordane was scored. Two participants also reported the values of the individual chlordane isomers. These results are presented in Table 16 for information only.

Table 16 Analytes reported by participants present in the sample but not scored

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
8	S2	cis-Chlordane	0.53	0.17	NR
		trans-Chlordane	0.49	0.15	NR
22	S2	g-Chlordane	0.59	0.18	NR
		a-Chlordane	0.65	0.2	NR

6.7 Participants' Analytical Methods

A variety of analytical methods were used for the different analytes (Appendix 2).

Participants used a sample size between 1 g and 30 g per analysis. There was no evident correlation overall between the results obtained and the sample mass used for analysis (Figure 11).

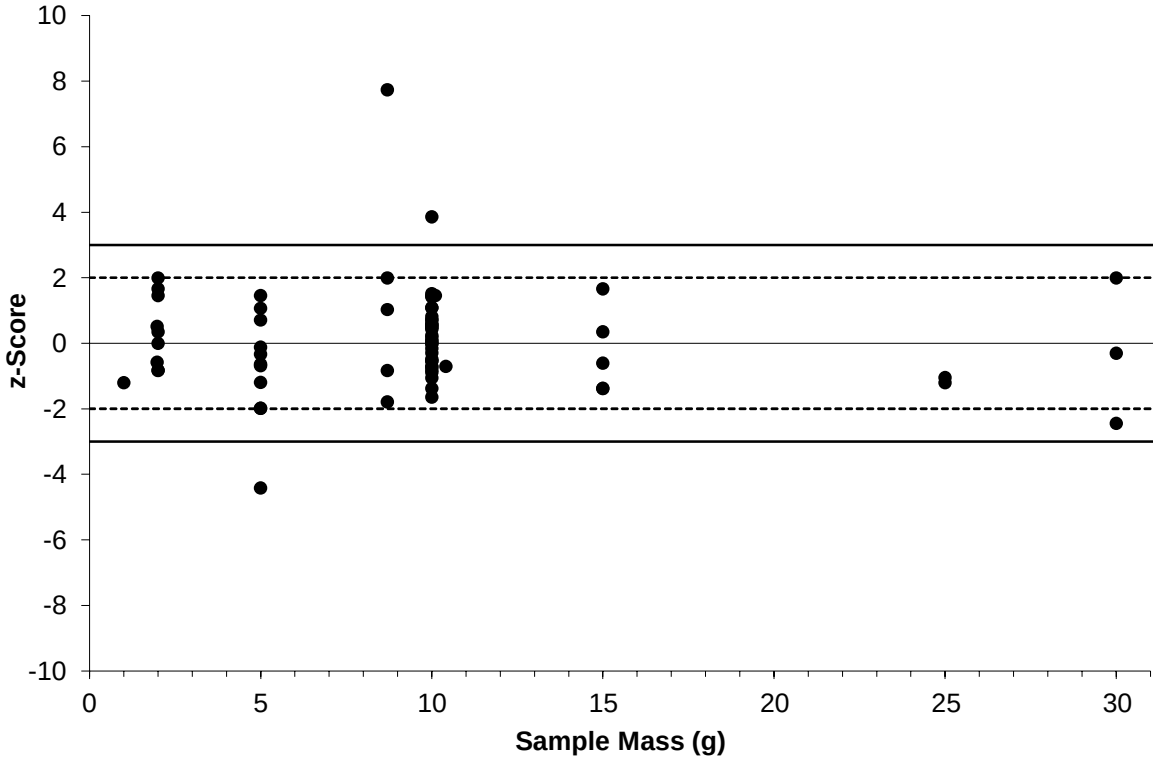


Figure 11 z-Score vs Sample Mass Used for Analysis

Participants used a variety of extraction techniques including sonication, solid-liquid, liquid-liquid and solid phase extraction, using dichloromethane, acetone, hexane, ethyl acetate, acetonitrile, methanol, formic acid and combinations of these as the extraction solvent. Five participants reported using a clean-up step; these included using Florisil, SPE, PSA/C18 and QuECheRS. Instruments employed by participants included GC-MS(MS), GC-ECD/FPD/NPD, LC-Orbitrap, LC-MS(MS) and HPLC-DAD.

Plots of results reported and method used are presented in Figures 12 to 16 for scored analytes. Test methods are listed in order of extraction technique, extraction solvent, clean-up, and instrument. Solvent abbreviations used in figures: DCM = Dichloromethane; ACE = Acetone; ACN = Acetonitrile; HEX = Hexane; MeOH = Methanol; FA = Formic Acid; EA = Ethyl Acetate. Extraction method abbreviations used in figures: SLE = Solid-Liquid Extraction; LLE = Liquid-Liquid Extraction; SPE = Solid-Phase Extraction.

The most common methodology used in this study was solid-liquid extraction with dichloromethane/acetone as the extraction solvent, with no clean-up and using GC-MSMS for analysis.

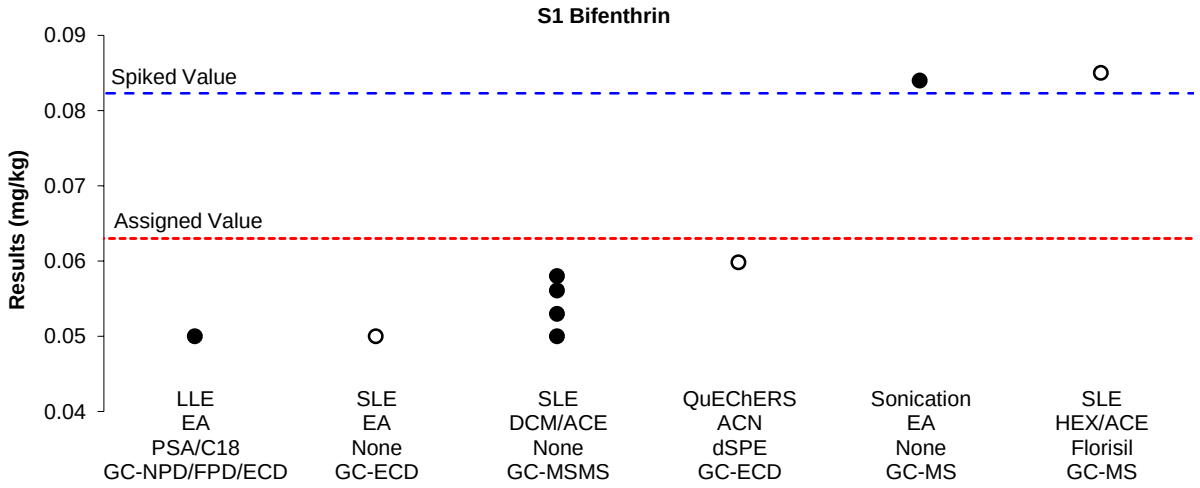


Figure 12 S1 Bifenthrin Results vs Test Method

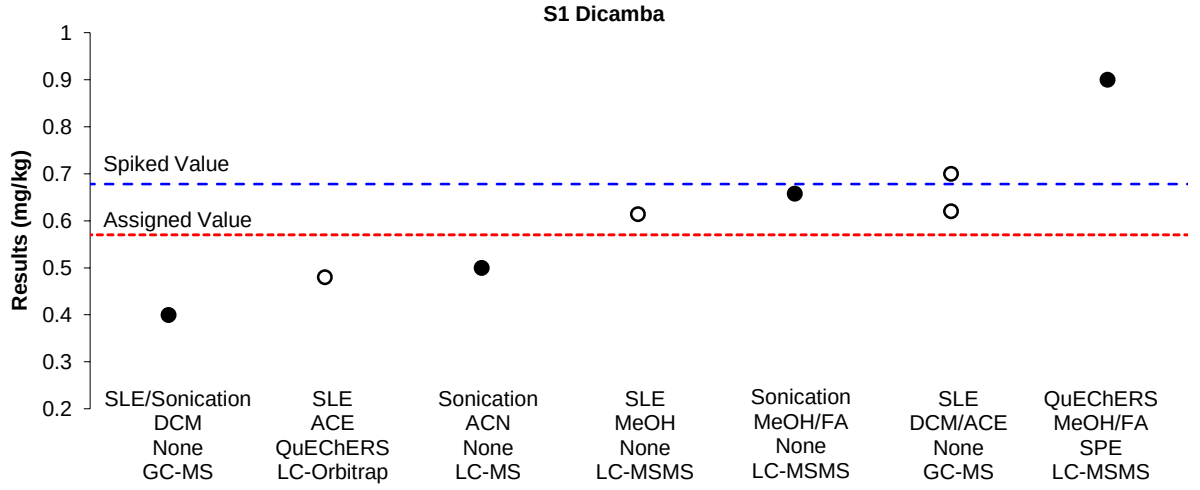


Figure 13 S1 Dicamba Results vs Test Method

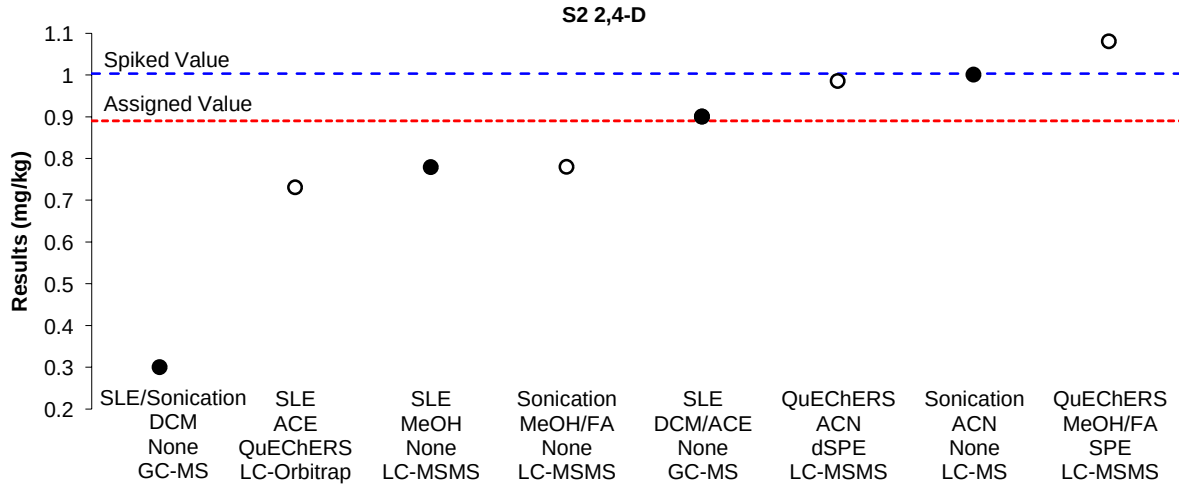


Figure 14 S2 2,4-D Results vs Test Method

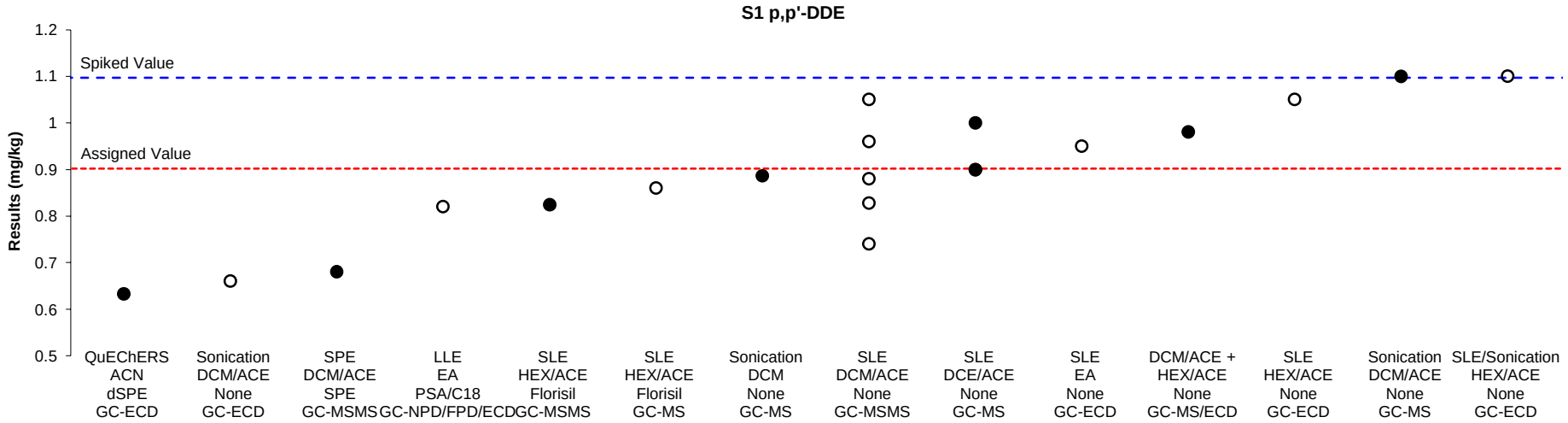


Figure 15 S1 p,p'-DDE Results vs Test Method

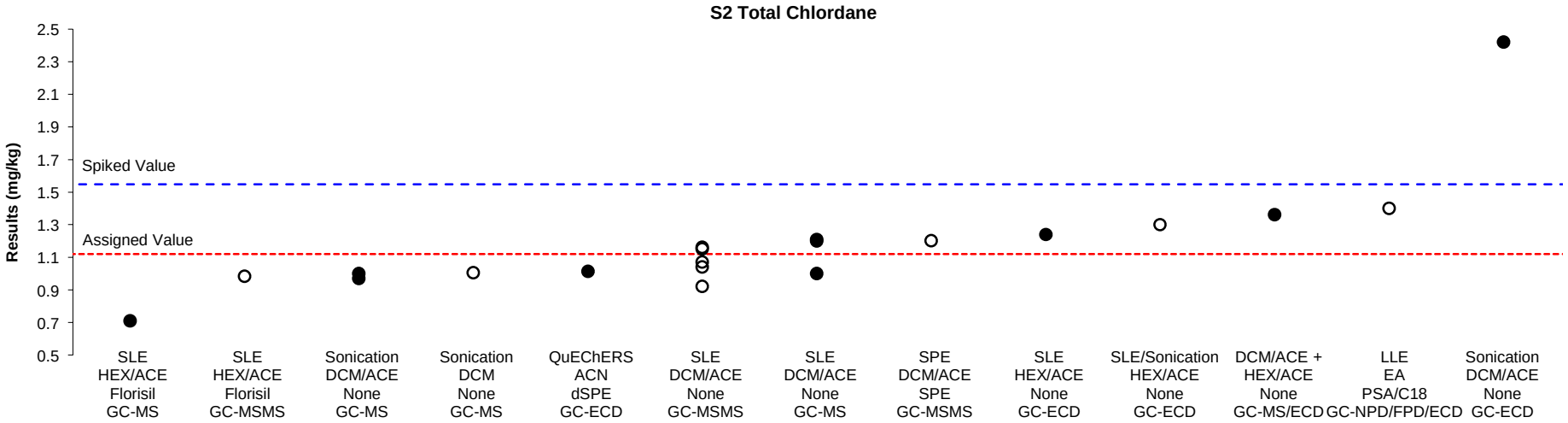


Figure 16 S2 Total Chlordane Results vs Test Method

Participants were requested to analyse the samples using their normal test method and to report a single result as they would to a client, that is, corrected for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **1**, **2**, **3**, **4**, **6**, **9**, **11**, **12**, **13**, **14**, **15** and **23** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 38% to 121%. Laboratories **4** and **11** reported that they corrected results for recovery.

6.8 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 the analysis.

Eighteen laboratories reported using certified standards. The following were listed:

- ISO Guide 34 / ISO 17034 traceable standards
- Accustandard
- PM Separations
- Sigma Aldrich (e.g. SQC009, CRM47426, 48391)
- Phenomenex
- Dr Ehrenstorfer
- Restek
- Agilent (e.g. US-127)
- Custom pesticide 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'*[11]

6.9 Summary of Participants' Results and Performances

Summaries of participants' results and performances in this PT study are presented in Table 17 and Figure 17.

Table 17 Summary of Participants' Results*

Lab. Code	S1 Bifenthrin (mg/kg)	S1 Dicamba (mg/kg)	S1 p,p'-DDE (mg/kg)	S2 2,4-D (mg/kg)	S2 Total Chlordane (mg/kg)
Assigned Value	0.063	0.57	0.902	0.89	1.12
Spiked Value	0.0823	0.678	1.097	1.003	1.548
1	<0.1	0.62	0.9	0.9	1.21
2	<0.1	0.7	0.9	0.9	1
3	NT	0.614	0.824	0.779	0.983
4	NT	0.5	NR	1	0.97
5	NT	NT	1.1	NT	1
6	0.085	0.48	0.86	0.73	0.71
7	0.053	NT	0.96	NT	1.15
8	0.084	0.658	0.66	0.779	2.42
9	NT	NT	0.74	NT	0.92
11	0.087	0.6	1.1	0.89	1.4
12	0.0598	NT	0.633	0.985	1.013
13	<0.5	NT	0.981	NT	1.363
14	<0.5	NT	1	NT	1.2
15	0.05	NT	0.95	NT	NT
16	0.0561	NT	0.828	NT	1.04
17	<0.01	0.9	0.68	1.08	1.2
18	0.058	< 0.5	0.88	< 0.5	1.07
19	<0.2	0.4	1.1	0.3	1.3
20	0.05	NT	1.05	NT	1.16
21	NT	NT	0.886	NT	1.004
22	NT	NT	1.05	NT	1.24
23	0.05	NT	0.82	NT	1.4

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

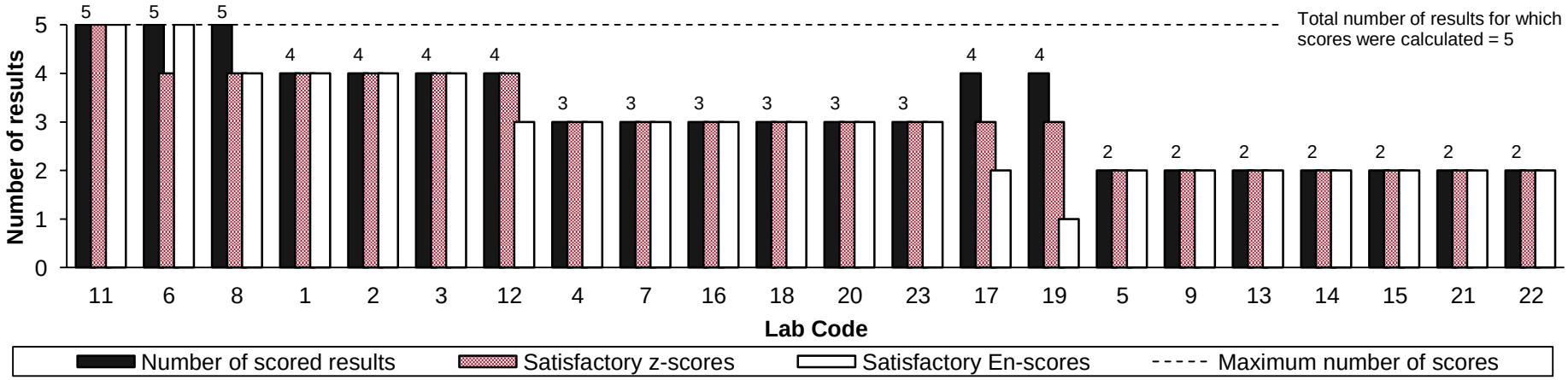


Figure 17 Summary of Participants' Performance

6.10 Comparison with Previous Pesticides in Soil PT Studies

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) obtained by the participants in Pesticides in Soil PT studies over the last 10 studies (2013 to 2020) is presented in Figure 18.

To enable direct comparison, the target standard deviation used to calculate z-scores has been kept constant at 15% PCV. Over this period, the average proportion of satisfactory z-scores was 80%, and the average proportion of satisfactory E_n-scores was also 80%.

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.

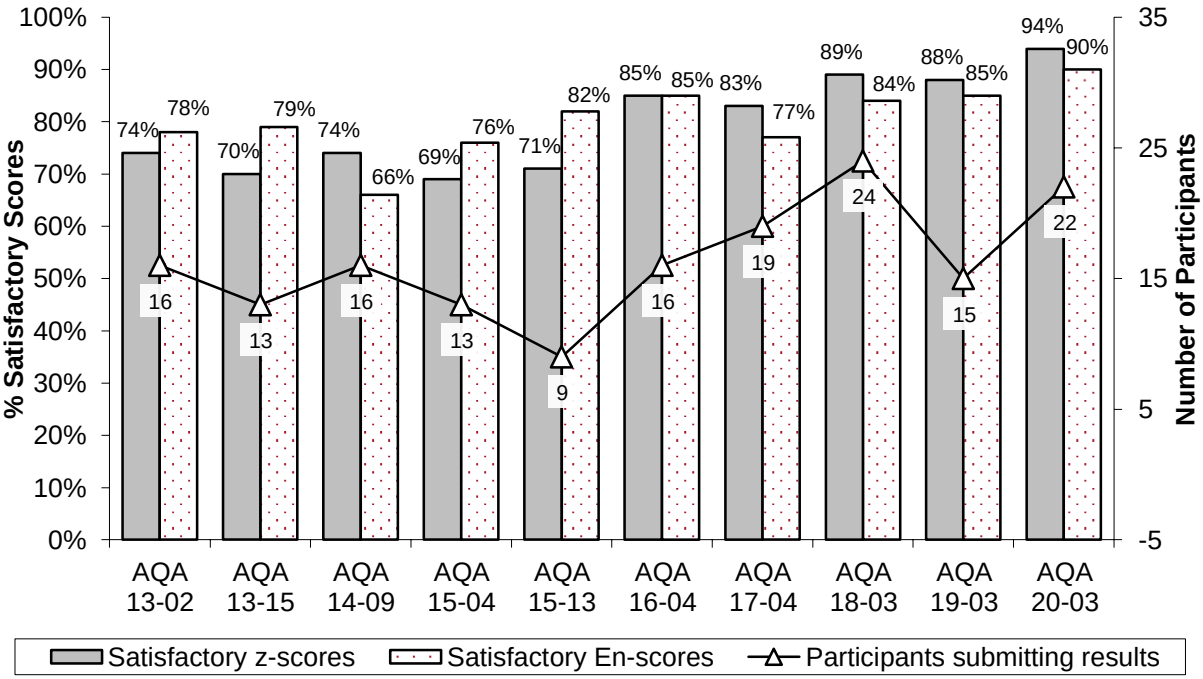


Figure 18 Summary of participants' performance for Pesticides in Soil PT studies

Individual performance history reports are emailed to each participant at the end of the study; the consideration of z-scores over time provides much more useful information than a single z-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.

7 REFERENCES

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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 1102.0 g of topsoil into a 3 L round bottom flask. The soil was covered with acetone and spiked with the standard solutions. Ten millilitres of Milli-Q water was added to minimise dust creation. The round bottom flask was shaken and placed on the Büchi Rotary Evaporator. The solvent was evaporated with the water temperature at 50°C and minimal vacuum. After evaporating the solvent off, the soil was placed in a V-mixer along with 1101.1 g of un-spiked topsoil and mixed for two hours. The resultant soil was then divided using a Retsch sample divider, placed in 65 mL jars and labelled.

Sample S2 was prepared by weighing 2206.2 g of soil into a 35.5 L stainless steel drum and adding acetone to cover the soil and allow it to be stirred. The stirred soil suspension was spiked with the standard solutions. The solvent was allowed to evaporate in the fume cupboard. After drying the soil was divided using a Retsch sample divider and dispensed into 65 mL glass jars.

APPENDIX 2 – TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 18 to 24.

Table 18 Sample Mass Used for Analysis

Lab. Code	S1 Sample Mass (g)	S2 Sample Mass (g)
1	10	10
2	10	10
3	1.98	2
4	10	10
5	10.1053	10.41585
6	55 (25 g used for LC-Orbitrap analysis, 30 g used for GC-MS analysis)	55 (25 g used for LC-Orbitrap analysis, 30 g used for GC-MS analysis)
7	10	10
8	8.7	8.7
9	1	5
11	2	2
12	5	5
13	10	10
14	10	10
15	15	15
16	10	10
17	10	10
18	10	10
19	5	5
20	10	10
21	5	5
22	10	10
23	15	15

Table 19 Test Methods S1 Bifenthrin

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Comments
1	Solid-liquid	DCM:Acetone	none	GC-MS	
2	Solid-Liquid	DCM:Acetone		GC-MS	
3	NT				
4	NT				
5	NT				
6	Liquid-Solid	Hexane/Acetone	Florisil	GC-MS	25g used for LC-Orbitrap analysis, 30g used for GC-MS analysis.
7	Solid-liquid	DCM/Acetone	None	GC-MSMS	
8	Sonication	Ethyl Acetate	None	GC-MS	
9	NT				
11					
12	QuEChERS	Acetonitrile	d-SPE	GC/ECD	
13	USEPA 8270	DCM/ACE	None	GC-MS	
14	Solid-Liquid	DCM:Acetone	None	GC-MS	
15	Solid-Liquid	Ethyl acetate	None	GC-ECD	
16	Soil-Liquid	DCM/Acetone	None	GC-MSMS	
17	NT	NT	NT		
18	solid-liquid	50:50 DCM/ACETONE	None	GC-MS/MS	
19	Solid-Liquid Ultrasonic	1:1 Acetone:Hexane	none	GC-ECD	
20	Solid-Liquid	DCM:Acetone	None	GC-MS/MS	
21	NT				
22	NT				
23	Liquid-Liquid	Ethyl Acetate	PSA / C18	GC-NPD/FPD/ECD	

Table 20 Test Methods S1 Dicamba

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Comments
1	Solid-liquid	DCM:Acetone	none	GC-MS	
2	Solid-Liquid	DCM:Acetone		GC-MS	
3	Solid-Liquid	methanol	NA	LC-MSMS	
4	Sonication	Acetonitrile		LCMS	
5	NT				
6	Liquid-Solid	Acetone	QuEChERS	LC-Orbitrap	25g used for LC-Orbitrap analysis, 30g used for GC-MS analysis.
7	NT				
8	Sonication	MeOH:Formic acid 98:2	None	LC-MS/MS	
9	NT				
11					
12	NT				
13	NT				
14	NT				
15	NT				
16	NT				
17	SPE	1%formic in MeOH	SPE	LCMSMS	Quechers type extraction
18	solid-liquid	METHANOL	None	HPLC-DAD	
19	Solid-Liquid Ultrasonic	DCM	none	GC-MS	
20	Solid-Liquid	DCM:Acetone	None	GC-MS/MS	
21	NT				
22	NT				
23	NT				

Table 21 Test Methods S1 p,p'-DDE

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Comments
1	Solid-liquid	DCM:Acetone	none	GC-MS	
2	Solid-Liquid	DCM:Acetone		GC-MS	
3	Solid-Liquid	acetone-hexane	florisil	GC-MSMS	
4					
5	Sonication	DCM:ACE	None	GC-MS	
6	Liquid-Solid	Hexane/Acetone	Florisil	GC-MS	25g used for LC-Orbitrap analysis, 30g used for GC-MS analysis.
7	Solid-liquid	DCM/Acetone	None	GC-MSMS	
8	Sonication	DCM:Acetone 1:1	None	GC-ECD	
9	Liquid-solid	1:1 DCM:Acetone	None	GC-MS/MS	
11					
12	QuEChERS	Acetonitrile	d-SPE	GC/ECD	
13	USEPA 8080	DCM/ACE & Hex/Ace	None	GC-MS & GC ECD	
14	Solid-Liquid	DCM:Acetone	None	GC-MS	
15	Solid-Liquid	Ethyl acetate	None	GC-ECD	
16	Soil-Liquid	DCM/Acetone	None	GC-MSMS	
17	SPE	DCM:acetone 1:1	SPE	GC-MS/MS	
18	solid-liquid	50:50 DCM/ACETONE	None	GC-MS/MS	
19	Solid-Liquid Ultrasonic	1:1 Acetone:Hexane	none	GC-ECD	
20	Solid-Liquid	DCM:Acetone	None	GC-MS/MS	
21	Sonication	DCM Extraction	None	GC-MS	
22	Solid-Liquid	Hexane:Acetone	None	GC-ECD	
23	Liquid-Liquid	Ethyl Acetate	PSA / C18	GC-NPD/FPD/ECD	

Table 22 Test Methods S2 2,4-D

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Comments
1	Solid-liquid	DCM:Acetone	none	GC-MS	
2	Solid-Liquid	DCM:Acetone		GC-MS	
3	Solid-Liquid	methanol	NA	LC-MSMS	
4	Sonication	Acetonitrile		LCMS	
5	NT				
6	Liquid-Solid	Acetone	QuEChERS	LC-Orbitrap	25g used for LC-Orbitrap analysis, 30g used for GC-MS analysis.
7	NT				
8	Sonication	MeOH:Formic acid 98:2	None	LC-MS/MS	
9	NT				
11					
12	QuEChERS	Acetonitrile	d-SPE	LC-MS/MS	
13	NT				
14	NT				
15	NT				
16	NT				
17	SPE	1%formic in MeOH	SPE	LCMSMS	Quechers type extraction
18	solid-liquid	METHANOL	None	HPLC-DAD	
19	Solid-Liquid Ultrasonic	DCM	none	GC-MS	
20	Solid-Liquid	DCM:Acetone	None	GC-MS/MS	
21	NT				
22	NT				
23	NT				

Table 23 Test Methods S2 Metsulfuron-methyl

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Comments
1	Solid-liquid	DCM:Acetone	none	GC-MS	
2	NT				
3	NT				
4	Sonication	Acetonitrile		LCMS	
5	NT				
6	Liquid-Solid	Acetone	QuEChERS	LC-Orbitrap	25g used for LC-Orbitrap analysis, 30g used for GC-MS analysis.
7	NT				
8	NT				
9	NT				
11					
12	NT				
13	NT				
14	NT				
15	NT				
16	NT				
17	SPE	DCM:acetone 1:1	SPE	LCMSMS	
18	solid-liquid	METHANOL	None	HPLC-DAD	
19	NT				
20	Solid-Liquid	DCM:Acetone	None	GC-MS/MS	
21	NT				
22	NT				
23	NT				

Table 24 Test Methods S2 Total Chlordane

Lab. Code	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Comments
1	Solid-liquid	DCM:Acetone	none	GC-MS	
2	Solid-Liquid	DCM:Acetone		GC-MS	
3	Solid-Liquid	acetone-hexane	florisil	GC-MSMS	
4	Sonication	DCM/Acetone (1:1)		GCMS	
5	Sonication	DCM:ACE	None	GC-MS	
6	Liquid-Solid	Hexane/Acetone	Florisil	GC-MS	25g used for LC-Orbitrap analysis, 30g used for GC-MS analysis.
7	Solid-liquid	DCM/Acetone	None	GC-MSMS	
8	Sonication	DCM:Acetone 1:1	None	GC-ECD	
9	Liquid-solid	1:1 DCM:Acetone	None	GC-MS/MS	
11					
12	QuEChERS	Acetonitrile	d-SPE	GC/ECD	
13	USEPA 8080	DCM/ACE & Hex/Ace	None	GC-MS & GC ECD	
14	Solid-Liquid	DCM:Acetone	None	GC-MS	
15	NT				
16	Soil-Liquid	DCM/Acetone	None	GC-MSMS	
17	SPE	DCM:acetone 1:1	SPE	GC-MS/MS	
18	solid-liquid	50:50 DCM/ACETONE	None	GC-MS/MS	
19	Solid-Liquid Ultrasonic	1:1 Acetone:Hexane	none	GC-ECD	
20	Solid-Liquid	DCM:Acetone	None	GC-MS/MS	
21	Sonication	DCM Extraction	None	GC-MS	
22	Solid-Liquid	Hexane:Acetone	None	GC-ECD	
23	Liquid-Liquid	Ethyl Acetate	PSA / C18	GC-NPD/FPD/ECD	

APPENDIX 3 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY

When the assigned value is the robust average as calculated using the procedure described in ISO 13528:2015 (Annex C),[7] the uncertainty is estimated as:

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

where:

$u_{rob\ av}$	is the standard uncertainty of the robust average
$S_{rob\ av}$	is the standard deviation of the robust average
p	is the number of results

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

A worked example for p,p'-DDE in Sample S1 is set out below in Table 25.

Table 25 Uncertainty of the Robust Average for p,p'-DDE in Sample S1

No. results (p)	21
Robust Average	0.902 mg/kg
$S_{rob\ av}$	0.16 mg/kg
$u_{rob\ av}$	0.0436 mg/kg
k	2
$U_{rob\ av}$	0.0872 mg/kg

Therefore, the robust average for p,p'-DDE in Sample S1 is 0.902 ± 0.087 mg/kg.

APPENDIX 4 – ACRONYMS AND ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
ACE	Acetone
ACN	Acetonitrile
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DAD	Diode Array Detector
DCM	Dichloromethane
EA	Ethyl Acetate
ECD	Electron Capture Detector
FA	Formic Acid
FPD	Flame Photometric Detector
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 Standards Organisation
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
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
MSMS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
NATA	National Association of Testing Authorities
NMI	National Measurement Institute (of Australia)
NPD	Nitrogen Phosphorus Detector
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 Test
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe preparation method
R.A.	Robust Average
RM	Reference Material
S.V.	Spiked Value
SD	Standard Deviation
SLE	Solid-Liquid Extraction
SPE	Solid Phase Extraction
SS	Spiked Samples
Total DDT	Sum of DDD, DDE and DDT compounds
σ	Target Standard Deviation

END OF REPORT