Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

Proficiency Test Report
AQA 19-03
Pesticides in Soil

June 2019

ACKNOWLEDGMENTS

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

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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1 SUMMARY

AQA 19-03 was conducted in March 2019. Fifteen laboratories registered to participate and all submitted results.

Two soil test samples were prepared from garden soil collected from Randwick. Sample S1 was prepared by spiking the soil with diazinon, p,p'-DDE, p,p'-DDT and simazine. Sample S2 was prepared by spiking the soil with diuron, endosulfan sulfate, fenvalerate and permethrin. Measurement of total DDT in S1 was also included in the program.

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 135 numeric results, a total of 85 results (63%) were submitted. Twenty-nine results (20%) were reported as Not Tested (NT).

The assigned values were the robust average of participants' results. The associated uncertainties were estimated from the robust standard deviation 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:

- *compare the performances of participant laboratories and assess their accuracy;*

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

  Of 97 z-scores, 85 (88%) were satisfactory with $|z| \leq 2$.

  Of 97 En-scores, 82 (85%) were satisfactory with $|E_n| \leq 1$.

  Laboratory **1** returned satisfactory z and E_n-scores for all analytes for which scores were calculated except for one.

  Laboratories **2**, **6**, **7**, **8, 10, 13** and **15** returned satisfactory z and E_n-scores for all reported results.

  Laboratories **5**, **12** and **14** reported numeric results for all pesticides in the two study samples.

- *assess the ability of participant laboratories to correctly identify pesticides in soil;*

  Three laboratories **(4, 9** and **11)** did not report results for pesticides that they tested and that were present in the test samples (total of 3 false negatives).

  Laboratories **1**, **3**, **4, 5, 8** and **14** reported >0.01 mg/kg levels of p,p'-DDT analogue (p,p'-DDD). Samples were spiked only with p,p'-DDT and p,p'-DDE, so this analogue is most likely the result of breakdown of p,p'-DDT during analysis in hot GC injector liners.

  Laboratories **3, 4, 5, 7** and **12** reported pesticides that were not spiked into the test samples (total of 6 false positives).

- *evaluate the laboratories' methods for the measurement of trace pesticides in soil;*

  Participants used a wide variety of methods. No correlation between results and method was evident. Endosulfan sulfate in S1 was the least challenging analyte for participants to extract.

- *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 6% to 54% of the reported value.

2 INTRODUCTION

2.1 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: '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;
- PFAS in water, soil and biota;
- folic acid in flour; and
- allergens in food.

2.2 Study Aims

The aims of the study were to:

- compare the performances of participant laboratories and assess their accuracy;
- assess the ability of participant laboratories to correctly identify pesticides in soil;
- evaluate the laboratories' methods for the measurement of trace pesticides in soil; and
- develop the practical application of traceability and measurement uncertainty.

2.3 Study Conduct

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

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

3 STUDY INFORMATION

3.1 Selection of Pesticides and Matrices

A list of possible analytes for the NMI pesticides in soil PT is presented in Table 1. The spiked concentrations are presented in Table 2.

The pesticides and spiked concentrations were selected with consideration to:

- A variety of pesticides, including some amenable to both gas chromatography and liquid chromatography; and
- National Environmental Protection Council Schedule B(1) *Guidelines on the Investigation Levels for Soil and Groundwater.* [5]

Table 1 List of Possible Analytes.

Aldrin	Total DDT	Hexachlorobenzene
Atrazine	Dieldrin	Lindane
Bifenthrin	Diuron	Malathion
Chlordane	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 Concentrations of Test Samples

Sample	Analyte	Spike (mg/kg)	U (mg/kg)[1]
S1	Diazinon	0.863	0.043
S1	p,p'-DDE	1.3	0.07
S1	p,p'-DDT	1.3	0.07
S1	Simazine	0.807	0.043
S2	Diuron	1.11	0.06
S2	Endosulfan sulfate	0.455	0.023
S2	Fenvalerate	1.79	0.09
S2	Permethrin	0.202	0.01

[1] The uncertainty is an expanded uncertainty at approximately 95% confidence using a coverage factor of 2.

3.2 Study Timetable

The timetable of the study was:

Invitation issued	26 February 2019
Samples dispatched	20 March 2019
Results due	18 April 2019
Interim report issued	24 April 2019

3.3 Participation

Ninety-three Australian and international laboratories were invited to participate. Fifteen laboratories participated and all submitted results.

3.4 Test Sample Preparation and Homogeneity Testing

Two soil samples of topsoil collected from Randwick were prepared by spiking. Pesticide solutions were added to obtain the concentrations in Table 2. The preparation of the study samples is described in Appendix 1.

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

3.5 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 concentration. Robust averages of participants' results were within 55-81% of the spiked concentration. Similar ratios have been observed in previous NMI PT of pesticides in soil (as presented in AQA 16-04).[6]

3.6 Laboratory Code

All laboratories that agreed to participate were assigned a confidential code number.

3.7 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 Sample S1 and Sample S2. The samples were packed in a foam box with a cooler brick and sent by courier on 20 March 2019.

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 faxback form for participants to confirm the receipt and condition of the samples.

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

3.8 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. correct 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 18 April 2019. Late results cannot be included in the study report.

3.9 Interim Report

An interim report was emailed to participants on 24 April 2019.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Test Methods Reported by Participants

Table 3. Test Methods

Lab. Code	Sample Mass. (g)	Extraction	Clean-up	Measurement
1	15	Ethyl Acetate	PSA / C18 / Magnesium Sulphate	GC-ECD, GC-FPD, GC-NPD
2	10	1:1 Acetone/DCM and 1:1 Acetone/Hexane		GC-MS/MS & GC-ECD
3	10	"GCMS: DCM/Acetone (1:1) LCMS: Acetonitrile "		GC-MS and LC-MS
4	10	DCM:acetone 1:1, quechers extraction when using LCMSMS		Gc-MS SIM for organochlorines and most pesticides. LCMSMS for acid herbicides and diuron
5	10	Ethyl acetate		GC-MS
6	5	10ml of DCM:ACETONE 50:50 v/v		GC-MS/MS
7	10	50% Dichloromethane 50% Acetone	Na_2SO_4	GCMS
8	10	extracted soil with ethyl acetate in shaker for 4 hour.Filtered, evaporated, adjusted with ethyl acetate (PR) and divided to two parts, one for GC-ECD and another for GC-FPD.		GC: FPD column , DB-5, 30.0 m x 0.25 mm x 0.25 um film thickness and ECD column , DB 1701 P, 30.0 m x 0.32 mm x 0.25 um film thickness.
9	5	"GCMS: DCM/Acetone (1:1) LCMS: Acetonitrile with 1% Formic Acid"		GC-MS/MS and LC-MS/MS
10	10	Hexane:Acetone		GC-ECD; GC-MS
11	5	"1:1 Hexane:Acetone DCM"		"GC-ECD GC-MS"
12	5	Organonitrate and organophosphate pesticides analysis by LC-MS/MS: acetonitrile	Organonitrate and organophosphate pesticides analysis by LC-MS/MS: QuEChERs	Organonitrate and organophosphate pesticides analysis by LC-MS/MS: LC-MS/MS

Table 3 Test Methods (continues)

Lab. Code	Sample Mass. (g)	Extraction	Clean-up	Measurement
13	10	Dichloromethane and Acetone		GCMS and GC-ECD
14	5	Acetone	50 mg PSA + 150 mg $MgSO_4$	GC/FPD, GC/uECD and UPLC-MS/MS
15	10	20 mL of DCM/Acetone, 1/1, v/v		GC-MS/MS

4.2 Basis of Participants' Measurement Uncertainty Estimates

Table 4. Basis of Uncertainty Estimate

Lab. Code	Basis of Uncertainty Estimate
2	Control charts.
3	Included reproducibility, inhomogeneity, and purity
4	Longterm reproducibility
5	Standard uncertainty based on historical data.
6	Control Charts
7	20%
8	U sample = 2 Uc, when Uc = C sample * (RSD2purity+RSD2 sample weigh + RSD2balance+ RSD2method precision+ RSD2final volume + RSD2Calibration curve+ RSD2dilution)1/2
9	Included reproducibility, inhomogeneity, and purity
10	Professional judgement
11	The estimate is compliant with the "ISO Guide to the Uncertainty in Measurement" and is based on in-house validation and quality control data. A coverage factor of 2 is used to give a confidence level of approximately 95%.
12	Organonitrate and organophosphate pesticides analysis by LC-MS/MS: repeatability precision
13	Top Down measurement of Uncertainty
14	Eurachem/CITAC Guide
15	Reproducibility studies

4.3 Additional Comments Made by Participants

Participants were invited to make any comments on the samples, the study or their experience with NMI Proficiency testing. No laboratories made any comments

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 5 to 13 with the summary statistics robust average, mean, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 10.

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

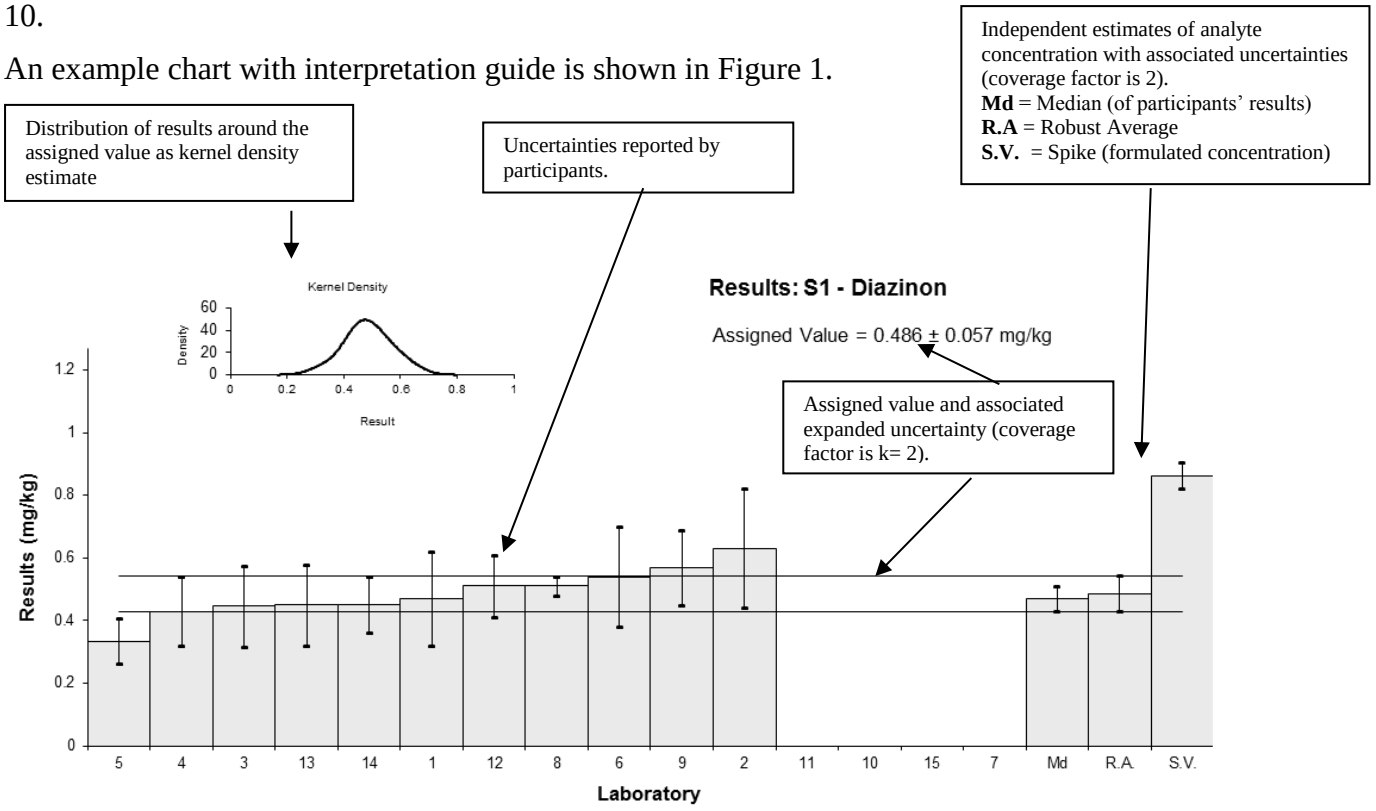


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

The assigned value is defined[1] as: 'value attributed to a particular property of a proficiency test item.' In this study property is the mass fraction of analyte. Assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations.

5.3 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015(E)'.[7]

5.4 Robust Between-Laboratory Coefficient of Variation

The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO 13528:2015(E).[7]

5.5 Target Standard Deviation

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

$$\sigma = (X) * PCV \qquad \text{Equation 1.}$$

This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value. It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation.[8] By setting a fixed and realistic value for PCV, the participant's performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

5.6 z-Score

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

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

where:

z is z-score
χ is participants' result
X is the study assigned value
σ is the target standard deviation from Equation 1

A z-score with absolute value (|z|):

- $|z| \leq 2$ is satisfactory;
- $2 < |z| < 3$ is questionable;
- $|z| \geq 3$ is unsatisfactory.

5.7 E_n-Score

An example of E_n-score calculation using data from the present study is given in Appendix 2. 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 below:

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

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

An E_n-score with absolute value ($|E_n|$):

- $|E_n| \leq 1$ is satisfactory;
- $|E_n| > 1$ is unsatisfactory.

5.8 Traceability and Measurement Uncertainty

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

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

6 TABLES AND FIGURES

Table 5

Sample Details

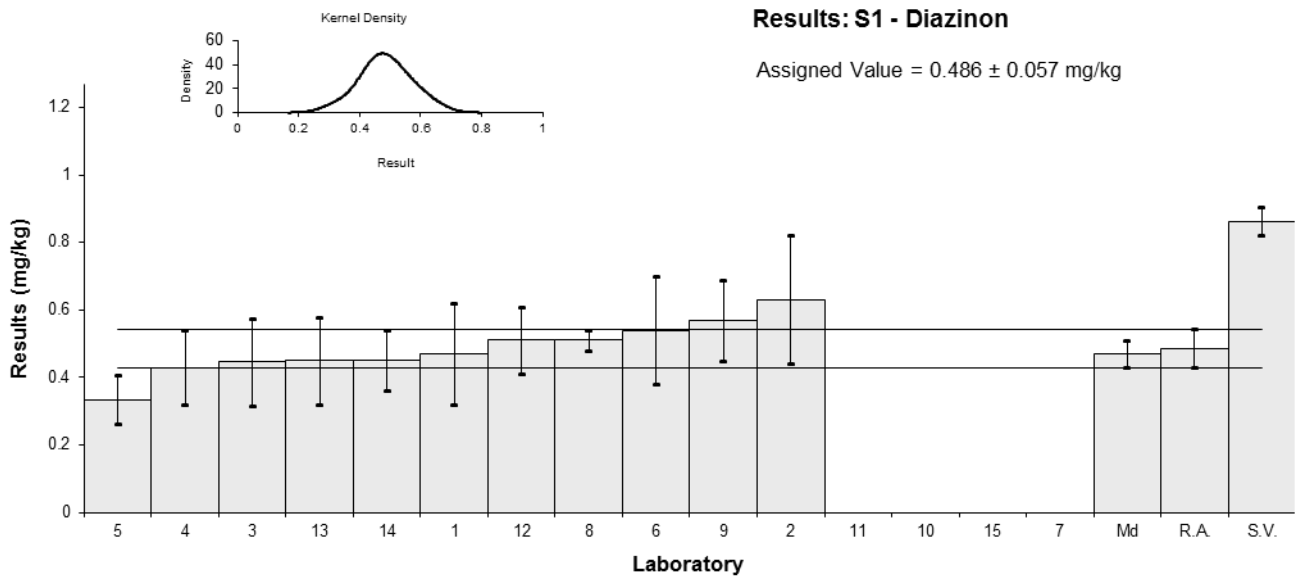
Sample No.	S1
Matrix.	Soil
Analyte.	Diazinon
Units	mg/kg

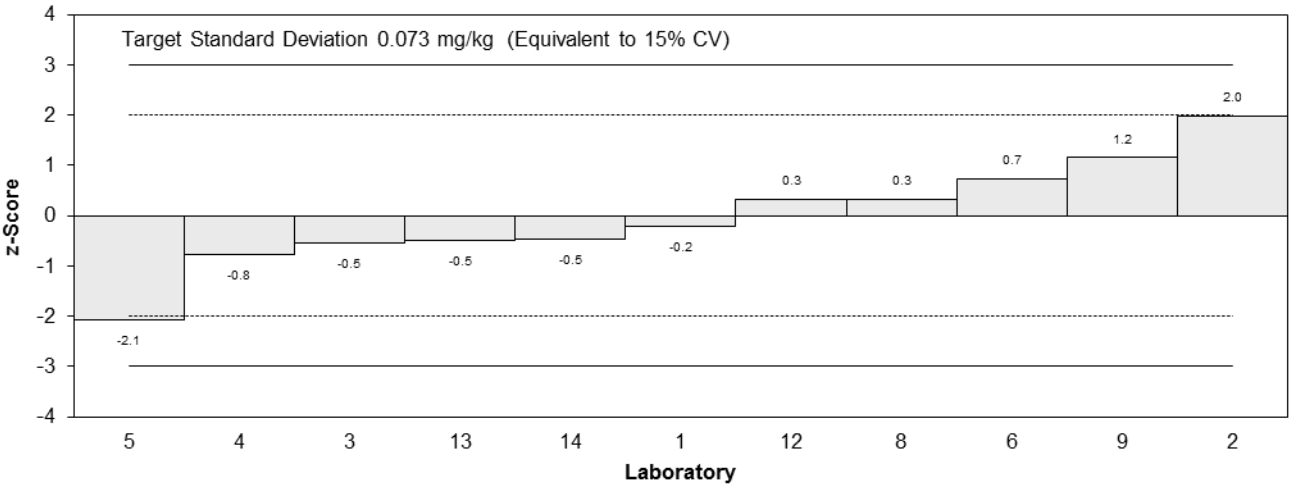
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.47	0.15	NR	-0.22	-0.10
2	0.63	0.19	NR	1.98	0.73
3	0.446	0.13	119	-0.55	-0.28
4	0.43	0.11	NR	-0.77	-0.45
5	0.334	0.072	NR	-2.09	-1.66
6	0.54	0.16	NR	0.74	0.32
7	NT	NT	NT		
8	0.51	0.03	97.3	0.33	0.37
9	0.57	0.12	97	1.15	0.63
10	NT	NT	NT		
11	<1	NR	NR		
12	0.51	0.10	86	0.33	0.21
13	0.45	0.13	83	-0.49	-0.25
14	0.451	0.090	102	-0.48	-0.33
15	NT	NT	NT		

Statistics

Assigned Value	0.486	0.057
Spike	0.863	0.043
Robust Average	0.486	0.057
Median	0.470	0.040
Mean	0.486	
N	11	
Max.	0.63	
Min.	0.334	
Robust SD	0.075	
Robust CV	15%	


Kernel Density
Density
Result
Results: S1 - Diazinon
Assigned Value = 0.486 ± 0.057 mg/kg
Results (mg/kg)
Laboratory
5 4 3 13 14 1 12 8 6 9 2 11 10 15 7 Md R.A. S.V.


z-Scores: S1 - Diazinon
Target Standard Deviation 0.073 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
5 4 3 13 14 1 12 8 6 9 2
-2.1 -0.8 -0.5 -0.5 -0.5 -0.2 0.3 0.3 0.7 1.2 2.0

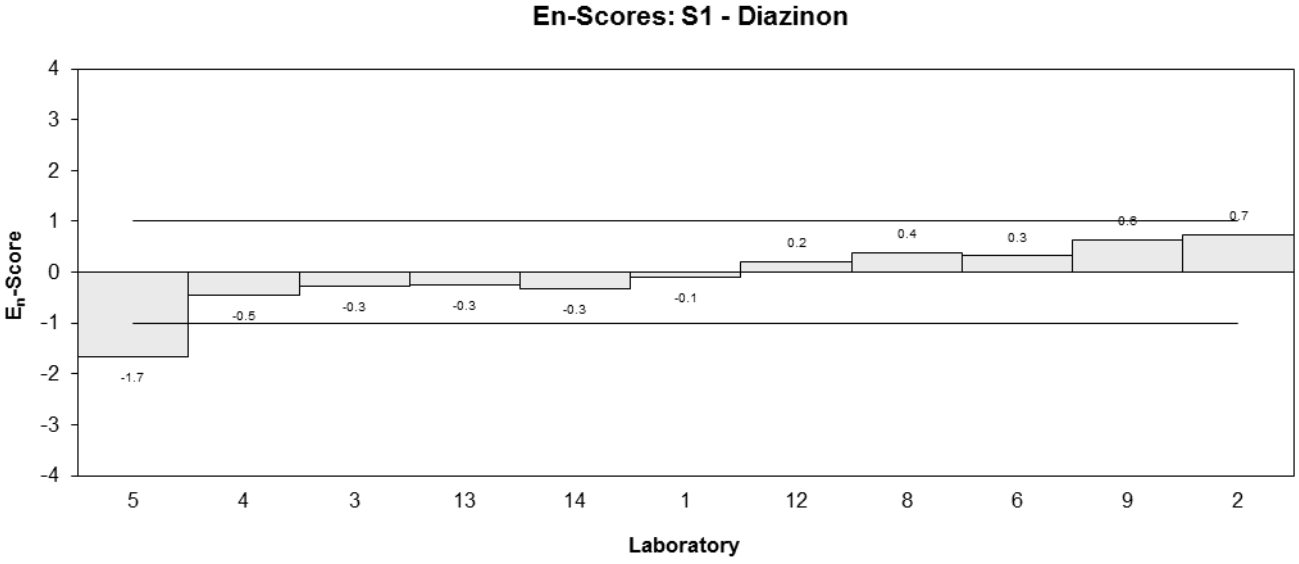

En-Scores: S1 - Diazinon
En-Score
Laboratory
5 4 3 13 14 1 12 8 6 9 2
-1.7 -0.5 -0.3 -0.3 -0.3 -0.1 0.2 0.4 0.3 0.6 0.7

Figure 2

Table 6

Sample Details

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

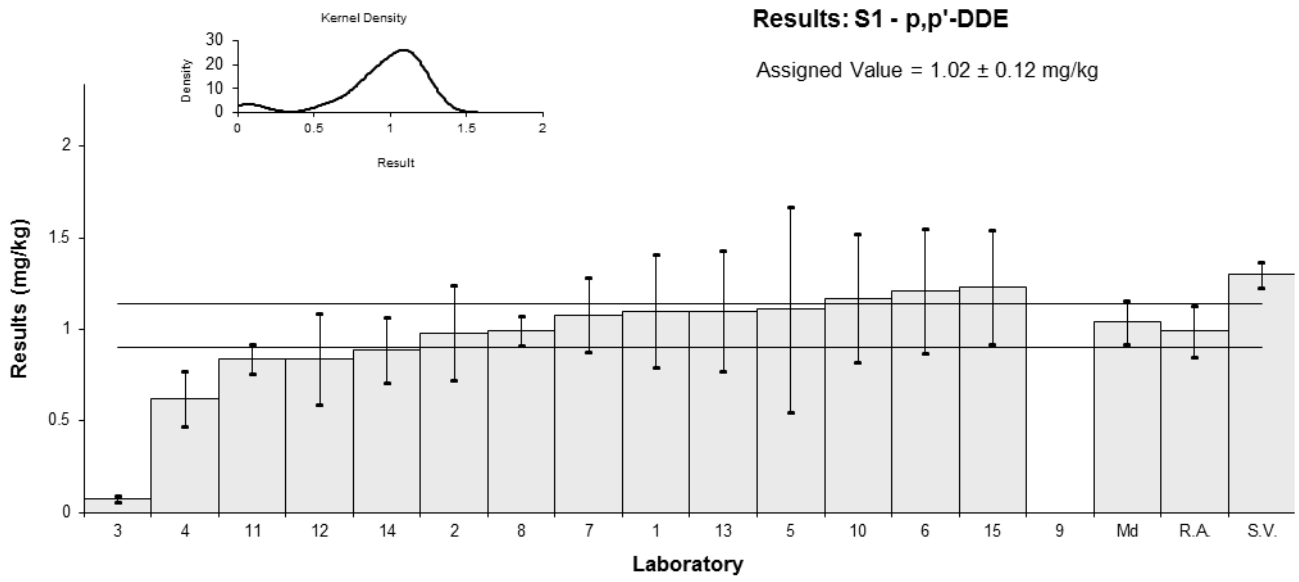
Participant Results

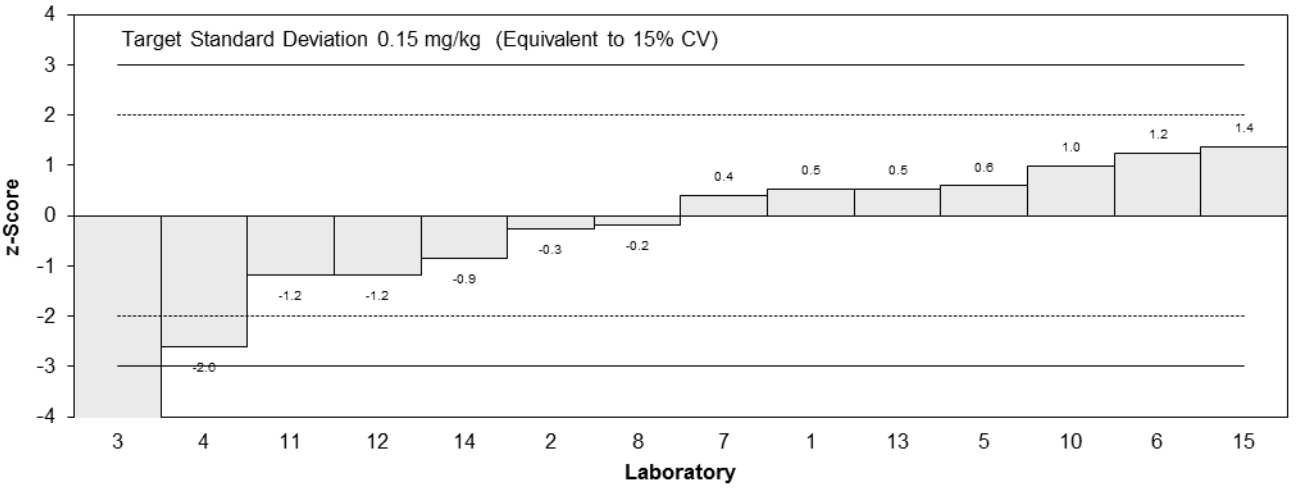
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.1	0.31	NR	0.52	0.24
2	0.98	0.26	NR	-0.26	-0.14
3	0.073	0.02	104	-6.19	-7.78
4	0.62	0.15	76	-2.61	-2.08
5	1.11	0.56	NR	0.59	0.16
6	1.21	0.34	NR	1.24	0.53
7	1.08	0.2	NR	0.39	0.26
8	0.99	0.08	85.0	-0.20	-0.21
9	NR	NR	NR		
10	1.17	0.35	NR	0.98	0.41
11	0.84	0.08	NR	-1.18	-1.25
12	0.84	0.25	NR	-1.18	-0.65
13	1.10	0.33	87	0.52	0.23
14	0.889	0.178	95	-0.86	-0.61
15	1.23	0.31	NR	1.37	0.63

Statistics

Assigned Value*	1.02	0.12
Spike	1.30	0.07
Robust Average	0.99	0.14
Median	1.04	0.12
Mean	0.945	
N	14	
Max.	1.23	
Min.	0.073	
Robust SD	0.20	
Robust CV	21%	

*Robust average excluding laboratory 3.


Kernel Density
Density
Result
Results: S1 - p,p'-DDE
Assigned Value = 1.02 ± 0.12 mg/kg
Results (mg/kg)
Laboratory
3 4 11 12 14 2 8 7 1 13 5 10 6 15 9 Md R.A. S.V.


z-Scores: S1 - p,p'-DDE
Target Standard Deviation 0.15 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
3 4 11 12 14 2 8 7 1 13 5 10 6 15
-2.0 -1.2 -1.2 -0.9 -0.3 -0.2 0.4 0.5 0.5 0.6 1.0 1.2 1.4

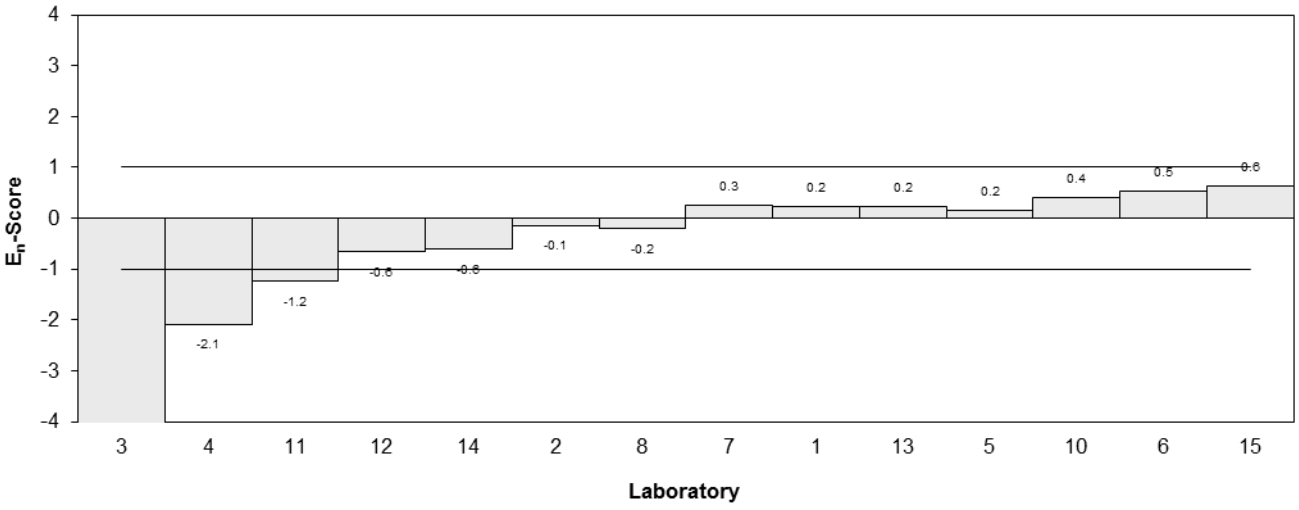

En-Scores: S1 - p,p'-DDE
En-Score
Laboratory
3 4 11 12 14 2 8 7 1 13 5 10 6 15
-2.1 -1.2 -0.6 -0.6 -0.1 -0.2 0.3 0.2 0.2 0.2 0.4 0.5 0.6

Figure 3

Table 7

Sample Details

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

Participant Results

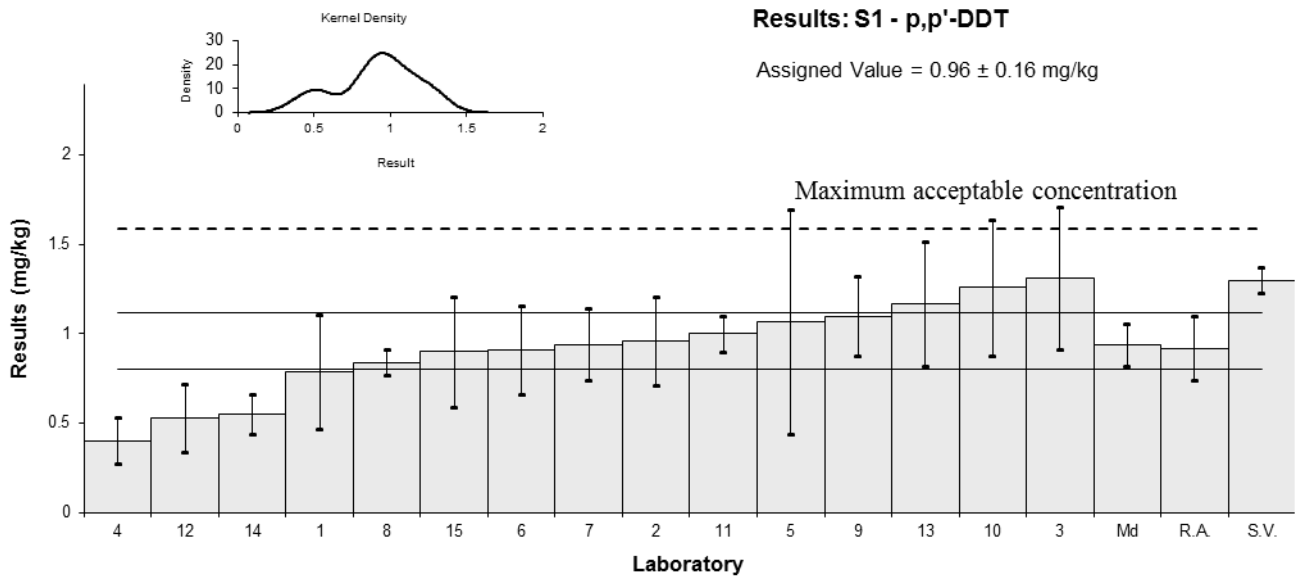
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.79	0.32	NR	-1.18	-0.48
2	0.96	0.25	NR	0.00	0.00
3**	1.312	0.40	91	2.00	0.82
4	0.40	0.13	97	-3.89	-2.72
5	1.07	0.63	NR	0.76	0.17
6	0.91	0.25	NR	-0.35	-0.17
7	0.94	0.2	61	-0.14	-0.08
8	0.84	0.07	89.4	-0.83	-0.69
9	1.1	0.22	96	0.97	0.51
10**	1.26	0.38	NR	2.00	0.73
11	1.0	0.1	NR	0.28	0.21
12	0.53	0.19	NR	-2.99	-1.73
13	1.17	0.35	87	1.46	0.55
14	0.552	0.110	65	-2.83	-2.10
15	0.90	0.31	NR	-0.42	-0.17

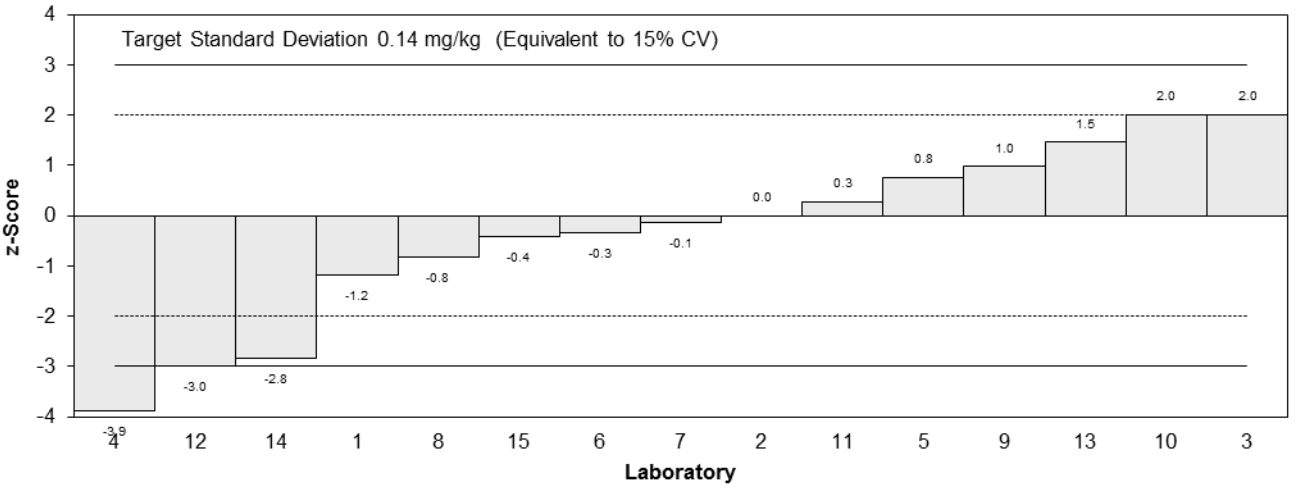
Statistics

Assigned Value*	0.96	0.16
Spike	1.30	0.07
Robust Average	0.92	0.18
Maximum acceptable conc**	1.58	
Median	0.94	0.12
Mean	0.92	
N	15	
Max.	1.312	
Min.	0.4	
Robust SD	0.29	
Robust CV	32%	

*Robust average excluding laboratory 4.

**z-Score adjusted to 2 (see Section 6.3).


Kernel Density
Density
Result
Results: S1 - p,p'-DDT
Assigned Value = 0.96 ± 0.16 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
4 12 14 1 8 15 6 7 2 11 5 9 13 10 3 Md R.A. S.V.


z-Scores: S1 - p,p'-DDT
Target Standard Deviation 0.14 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 12 14 1 8 15 6 7 2 11 5 9 13 10 3
-3.9 -3.0 -2.8 -1.2 -0.8 -0.4 -0.3 -0.1 0.0 0.3 0.8 1.0 1.5 2.0 2.0

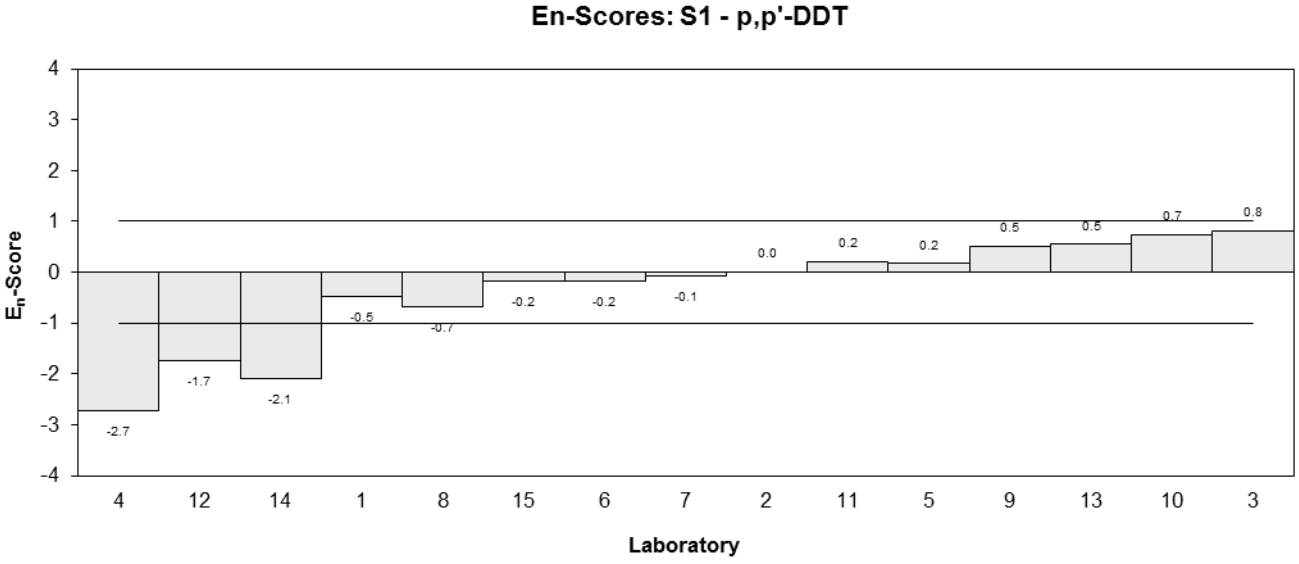

En-Scores: S1 - p,p'-DDT
En-Score
Laboratory
4 12 14 1 8 15 6 7 2 11 5 9 13 10 3
-2.7 -1.7 -2.1 -0.5 -0.7 -0.2 -0.2 -0.1 0.0 0.2 0.2 0.5 0.5 0.7 0.8

Figure 4

Table 8

Sample Details

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

Participant Results

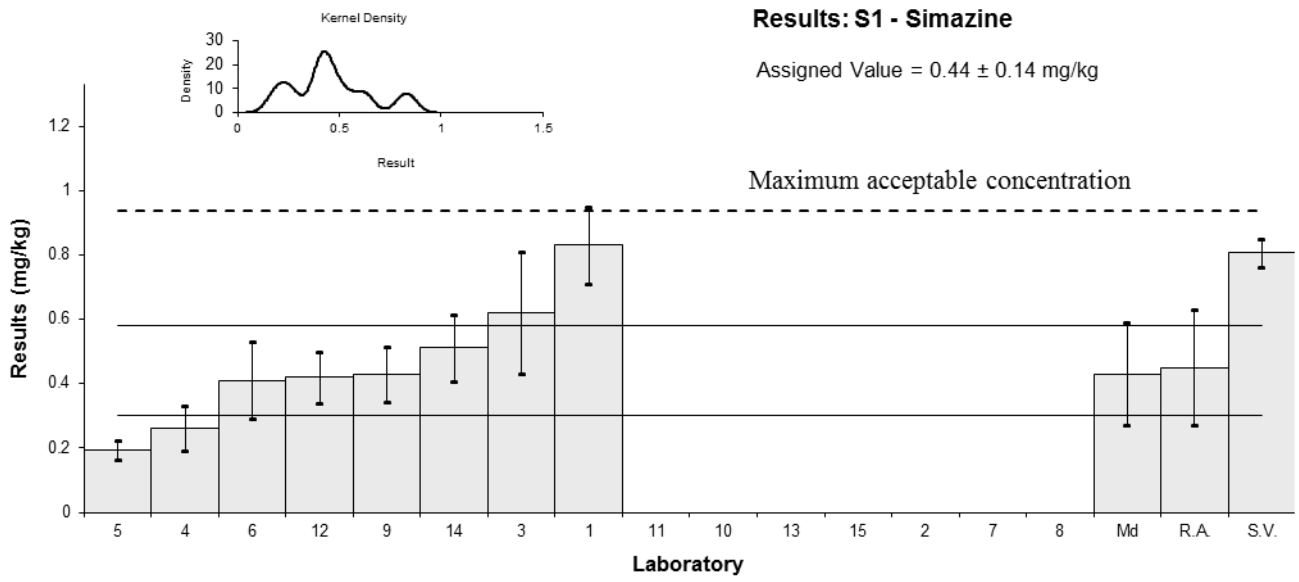
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1**	0.83	0.12	NR	2.00	1.00
2	NT	NT	NT		
3**	0.62	0.19	120	2.00	0.76
4	0.26	0.07	72	-2.73	-1.15
5	0.192	0.030	NR	-3.76	-1.73
6	0.41	0.12	NR	-0.45	-0.16
7	NT	NT	NT		
8	NT	NT	NT		
9	0.43	0.086	95	-0.15	-0.06
10	NT	NT	NT		
11	<0.3	NR	NR		
12	0.42	0.08	85	-0.30	-0.12
13	NT	NT	NT		
14	0.511	0.102	109	1.08	0.41
15	NT	NT	NT		

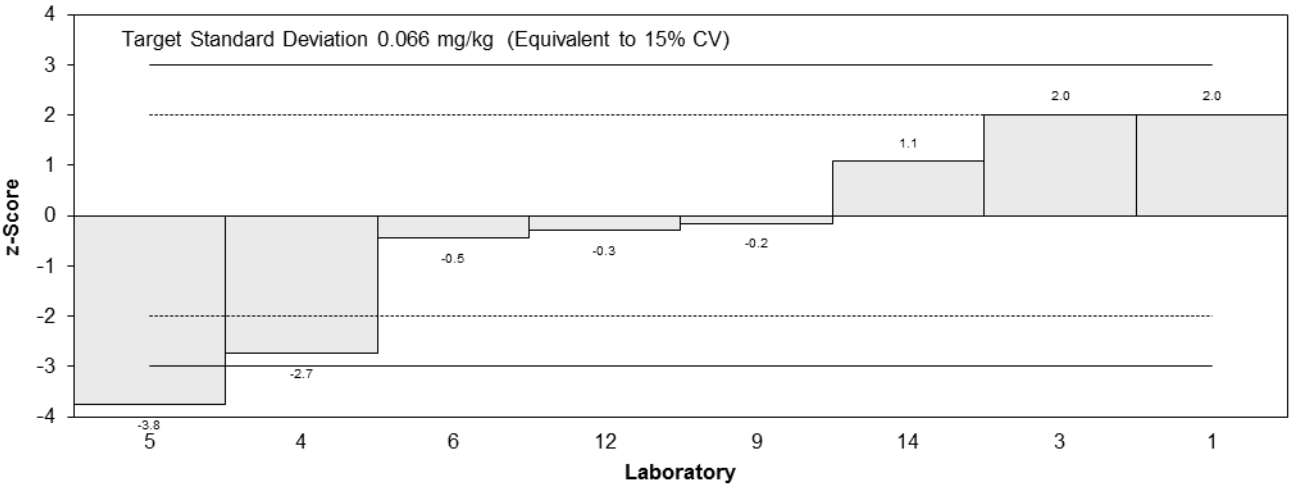
Statistics

Assigned Value*	0.44	0.14
Spike	0.807	0.043
Robust Average	0.45	0.18
Maximum acceptable conc**	0.939	
Median	0.43	0.16
Mean	0.46	
N	8	
Max.	0.83	
Min.	0.192	
Robust SD	0.21	
Robust CV	47%	

*Robust average excluding laboratories 1 and 5

**z-Score adjusted to 2 (see Section 6.3).


Kernel Density
Density
Result
Results: S1 - Simazine
Assigned Value = 0.44 ± 0.14 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
5 4 6 12 9 14 3 1 11 10 13 15 2 7 8 Md R.A. S.V.


z-Scores: S1 - Simazine
Target Standard Deviation 0.066 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
5 4 6 12 9 14 3 1
-3.8
-2.7
-0.5
-0.3
-0.2
1.1
2.0
2.0

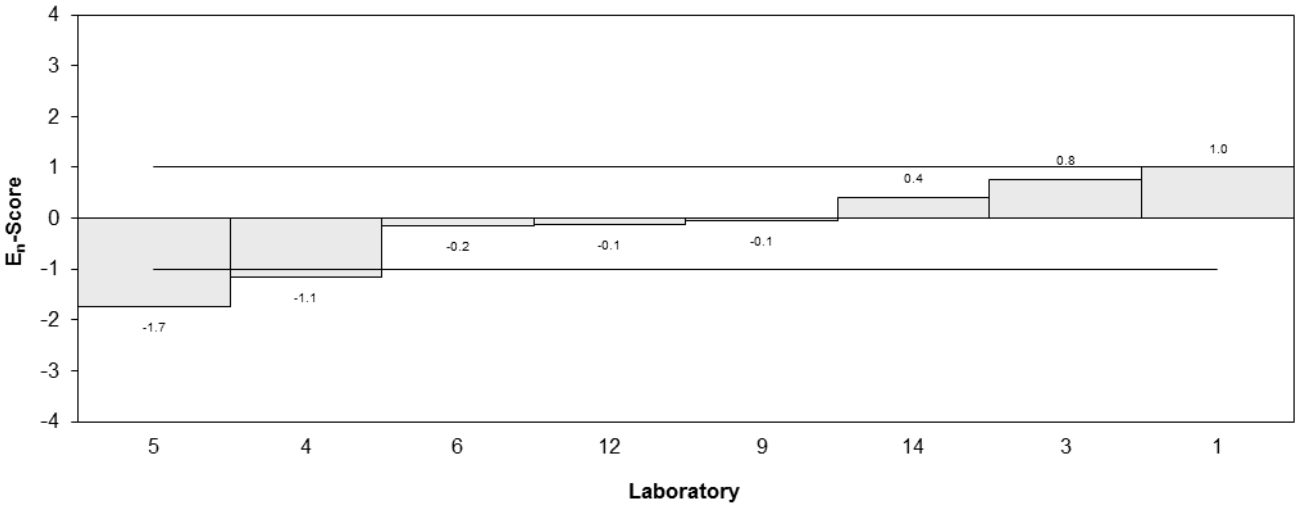

En-Scores: S1 - Simazine
En-Score
Laboratory
5 4 6 12 9 14 3 1
-1.7
-1.1
-0.2
-0.1
-0.1
0.4
0.8
1.0

Figure 5

Table 9

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Total DDT
Units	mg/kg

Participant Results

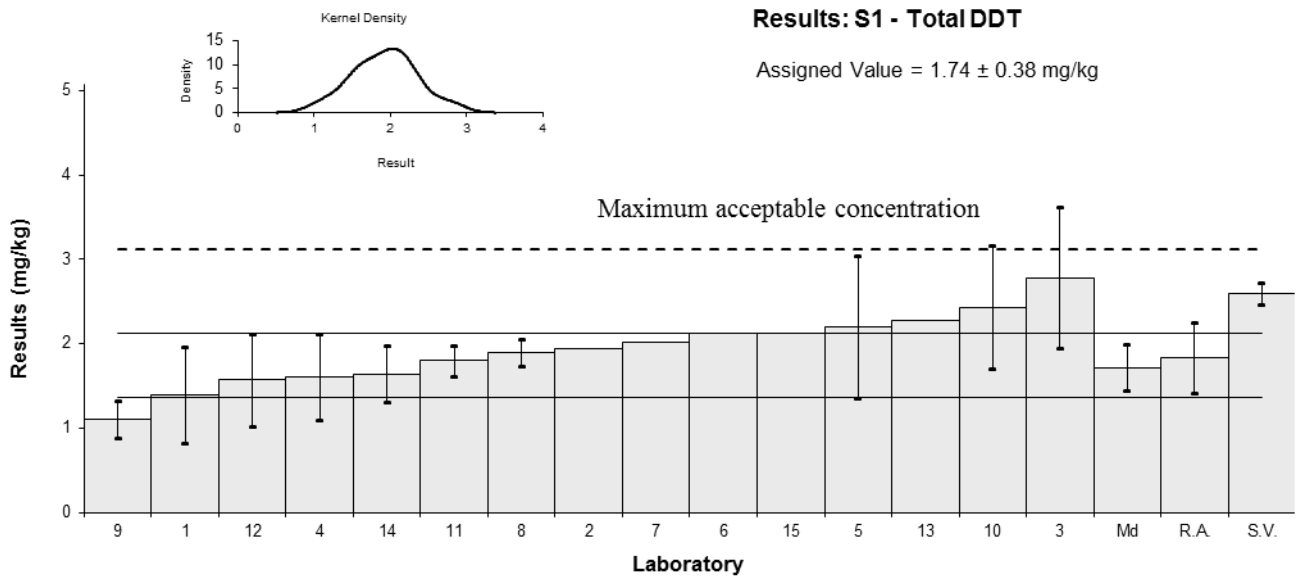
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.4	0.57	NR	-1.30	-0.50
2	1.94	NR	NR	0.77	0.53
3**	2.785	0.84	NR	2.00	1.00
4	1.60	0.51	NR	-0.54	-0.22
5	2.20	0.84	NR	1.76	0.50
6	2.12	NR	NR	1.46	1.00
7	2.02	NR	NR	1.07	0.74
8	1.90	0.16	NT	0.61	0.39
9	1.1	0.22	NR	-2.45	-1.46
10**	2.43	0.73	NR	2.00	0.84
11	1.8	0.18	NR	0.23	0.14
12	1.57	0.55	NR	-0.65	-0.25
13**	2.27	NR	NR	2.00	1.00
14	1.643	0.329	NR	-0.37	-0.19
15	2.13	NR	NR	1.49	1.03

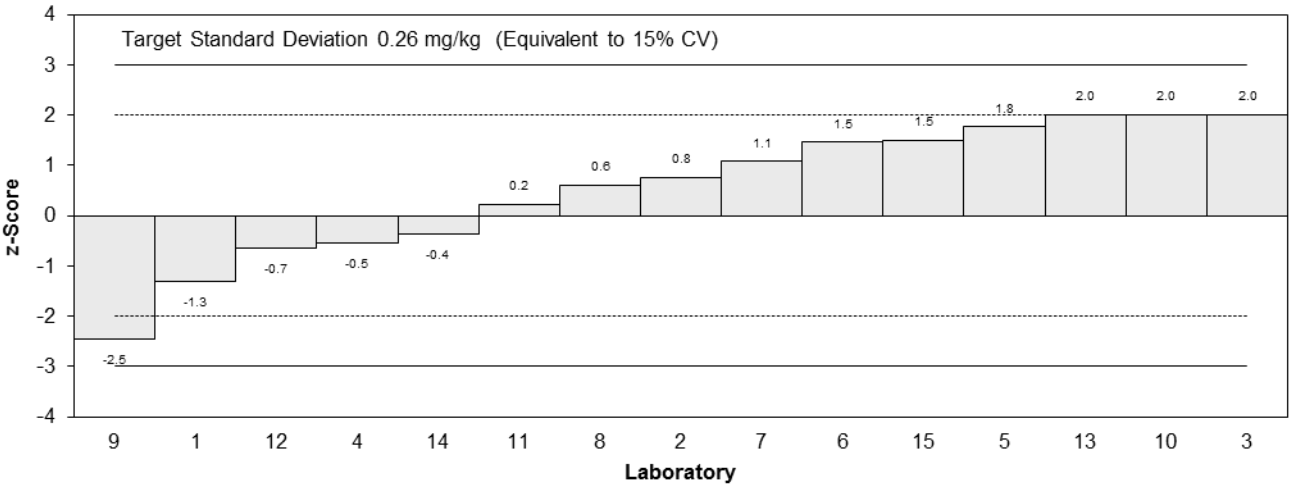
Statistics

Assigned Value*	1.74	0.38
Spike	2.60	0.13
Robust Average	1.83	0.42
Maximum acceptable conc**	3.12	
Median	1.72	0.27
Mean	1.93	
N	15	
Max.	2.785	
Min.	1.1	
Robust SD	0.54	
Robust CV	30%	

*Robust average excluding laboratory 3.

**z-Score adjusted to 2 (see Section 6.3).


Kernel Density
Density
Result
Results: S1 - Total DDT
Assigned Value = 1.74 ± 0.38 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
9 1 12 4 14 11 8 2 7 6 15 5 13 10 3 Md R.A. S.V.


z-Scores: S1 - Total DDT
Target Standard Deviation 0.26 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
9 1 12 4 14 11 8 2 7 6 15 5 13 10 3
-2.5 -1.3 -0.7 -0.5 -0.4 0.2 0.6 0.8 1.1 1.5 1.5 1.8 2.0 2.0 2.0

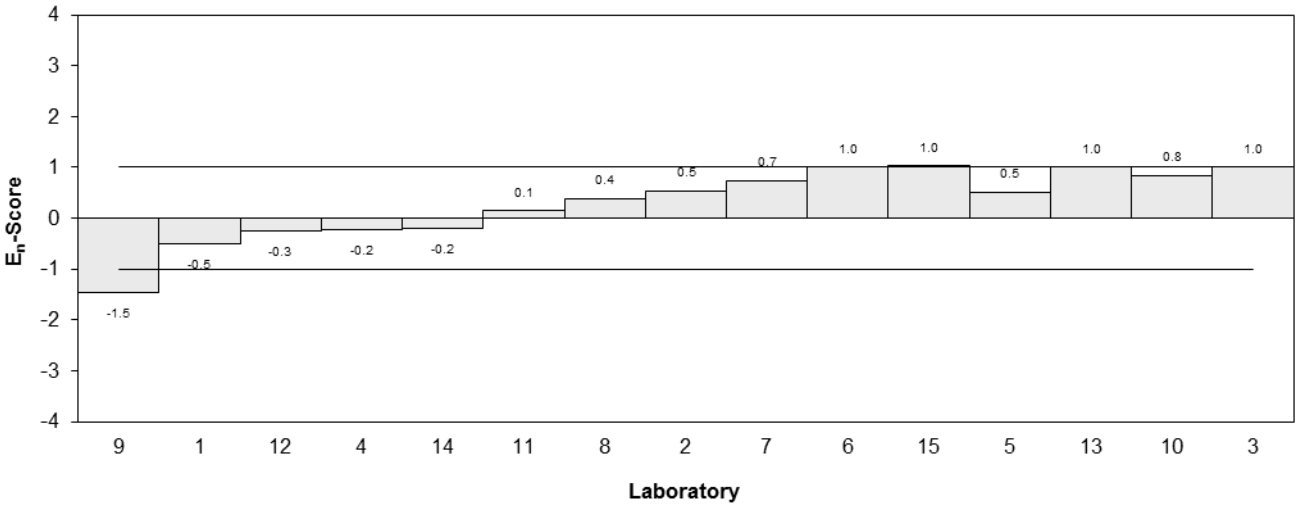

En-Scores: S1 - Total DDT
En-Score
Laboratory
9 1 12 4 14 11 8 2 7 6 15 5 13 10 3
-1.5 -0.5 -0.3 -0.2 -0.2 0.1 0.4 0.5 0.7 1.0 1.0 0.5 1.0 0.8 1.0

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Diuron
Units	mg/kg

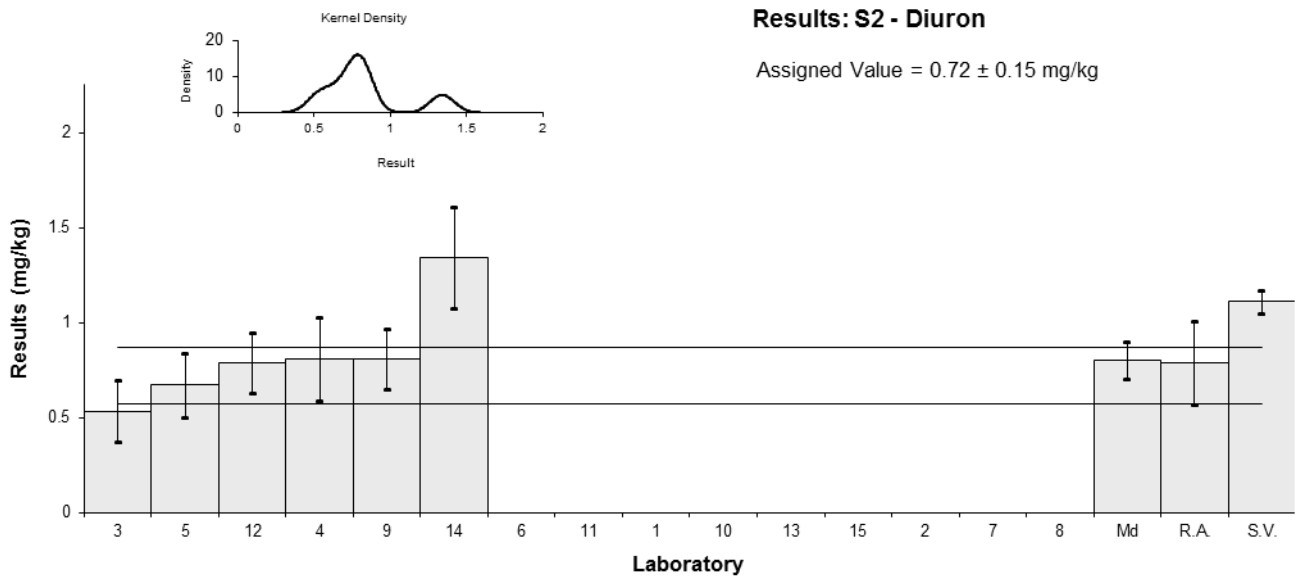
Participant Results

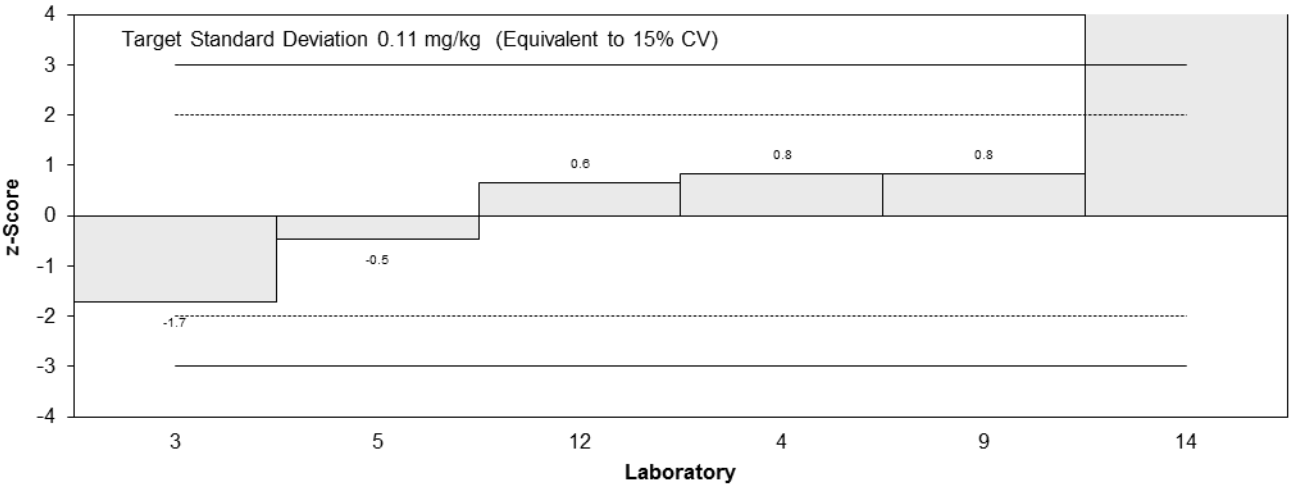
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	0.534	0.16	145	-1.72	-0.85
4	0.81	0.22	73	0.83	0.34
5	0.67	0.17	NR	-0.46	-0.22
6	< 2	0.6	NR		
7	NT	NT	NT		
8	NT	NT	NT		
9	0.81	0.16	93	0.83	0.41
10	NT	NT	NT		
11	<2	NR	NR		
12	0.79	0.16	85	0.65	0.32
13	NT	NT	NT		
14	1.342	0.268	122	5.76	2.03
15	NT	NT	NT		

Statistics

Assigned Value*	0.72	0.15
Spike	1.11	0.06
Robust Average	0.79	0.22
Median	0.80	0.10
Mean	0.83	
N	6	
Max.	1.342	
Min.	0.534	
Robust SD	0.22	
Robust CV	28%	

*Robust average excluding laboratory 14.


Kernel Density
Density
Result
Results: S2 - Diuron
Assigned Value = 0.72 ± 0.15 mg/kg
Results (mg/kg)
Laboratory
3 5 12 4 9 14 6 11 1 10 13 15 2 7 8 Md R.A. S.V.


z-Scores: S2 - Diuron
Target Standard Deviation 0.11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
3 5 12 4 9 14
-1.7
-0.5
0.6
0.8
0.8

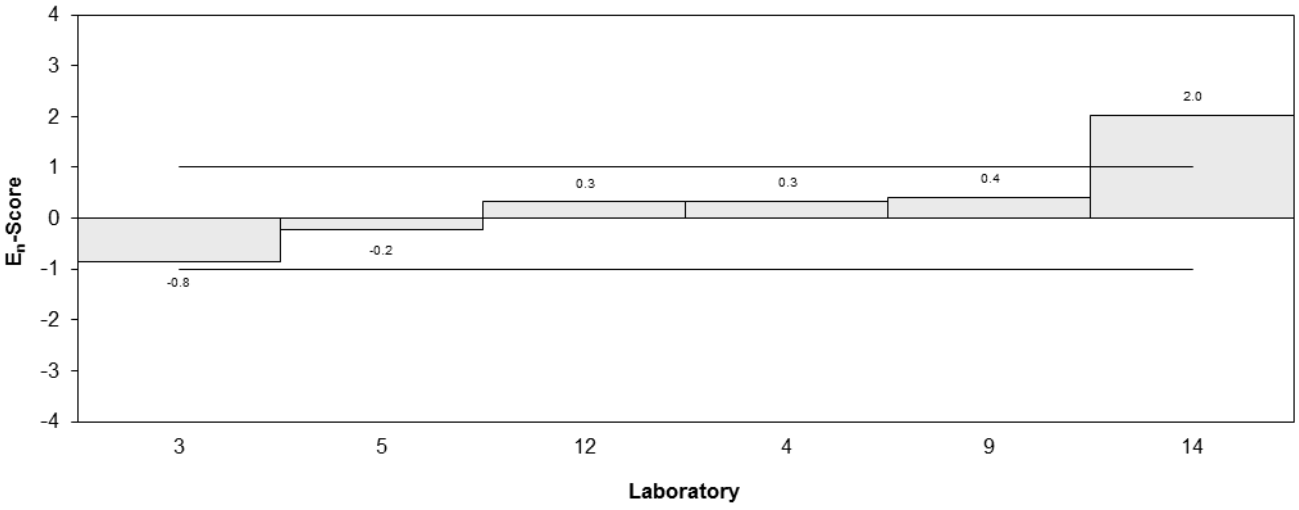

En-Scores: S2 - Diuron
En-Score
Laboratory
3 5 12 4 9 14
-0.8
-0.2
0.3
0.3
0.4
2.0

Figure 7

Table 11

Sample Details

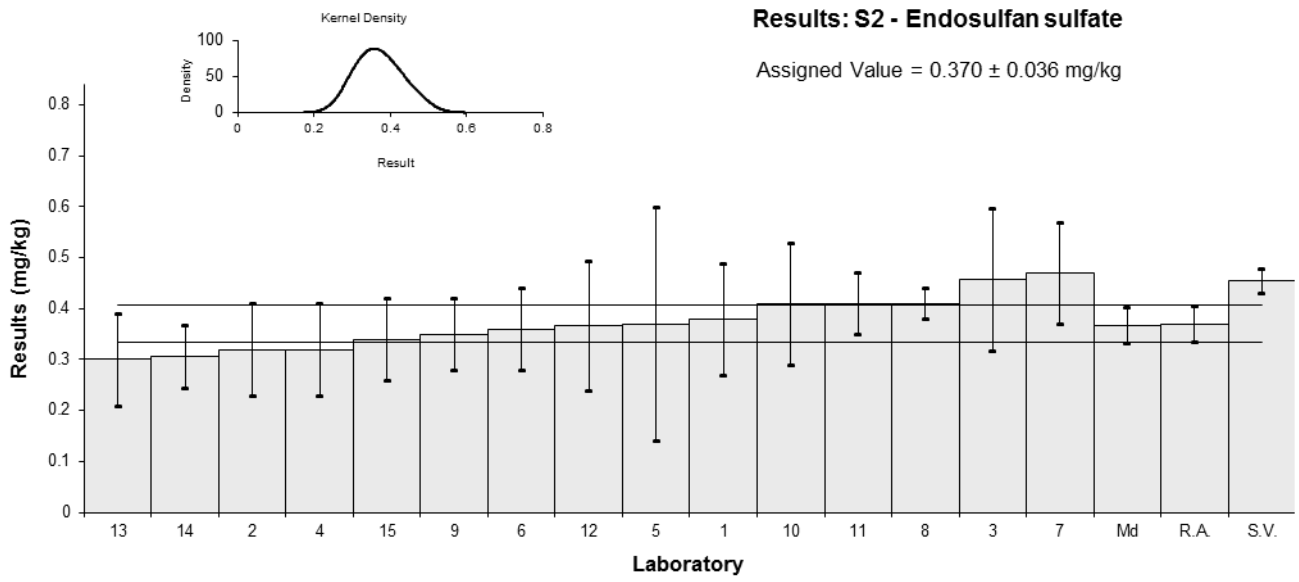
Sample No.	S2
Matrix.	Soil
Analyte.	Endosulfan sulfate
Units	mg/kg

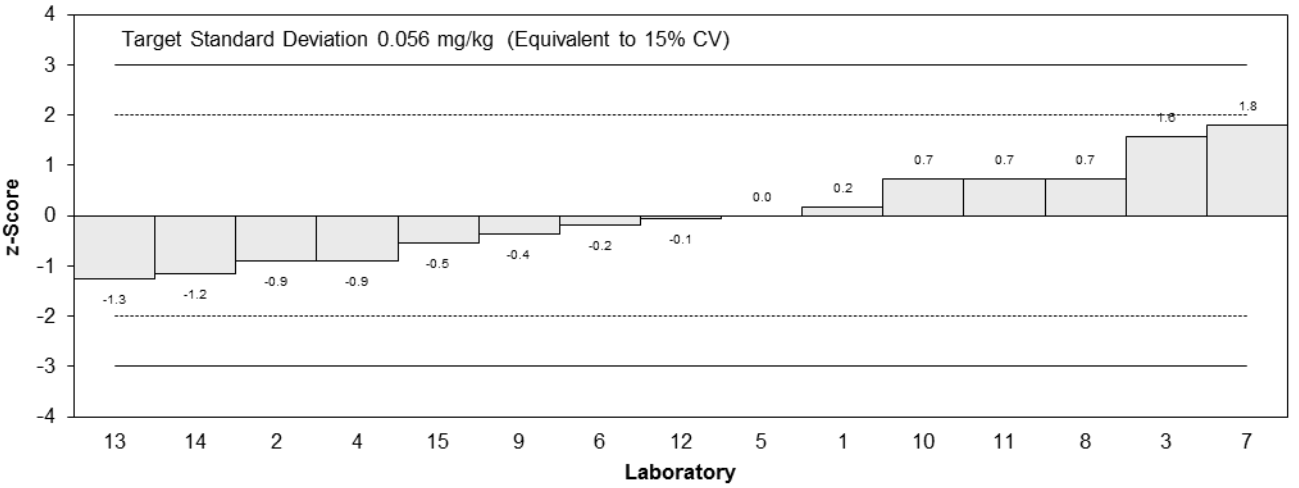
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.38	0.11	NR	0.18	0.09
2	0.32	0.09	NR	-0.90	-0.52
3	0.457	0.14	99	1.57	0.60
4	0.32	0.09	95	-0.90	-0.52
5	0.37	0.23	NR	0.00	0.00
6	0.36	0.08	NR	-0.18	-0.11
7	0.47	0.1	NR	1.80	0.94
8	0.41	0.03	91.3	0.72	0.85
9	0.35	0.070	95	-0.36	-0.25
10	0.41	0.12	NR	0.72	0.32
11	0.41	0.06	NR	0.72	0.57
12	0.367	0.128	NR	-0.05	-0.02
13	0.30	0.09	104	-1.26	-0.72
14	0.306	0.061	108	-1.15	-0.90
15	0.34	0.08	NR	-0.54	-0.34

Statistics

Assigned Value	0.370	0.036
Spike	0.455	0.023
Robust Average	0.370	0.036
Median	0.367	0.035
Mean	0.371	
N	15	
Max.	0.47	
Min.	0.3	
Robust SD	0.057	
Robust CV	15%	


Kernel Density
Density
Result
Results: S2 - Endosulfan sulfate
Assigned Value = 0.370 ± 0.036 mg/kg
Results (mg/kg)
Laboratory
13 14 2 4 15 9 6 12 5 1 10 11 8 3 7 Md R.A. S.V.


z-Scores: S2 - Endosulfan sulfate
Target Standard Deviation 0.056 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
13 14 2 4 15 9 6 12 5 1 10 11 8 3 7
-1.3 -1.2 -0.9 -0.9 -0.5 -0.4 -0.2 -0.1 0.0 0.2 0.7 0.7 0.7 1.6 1.8

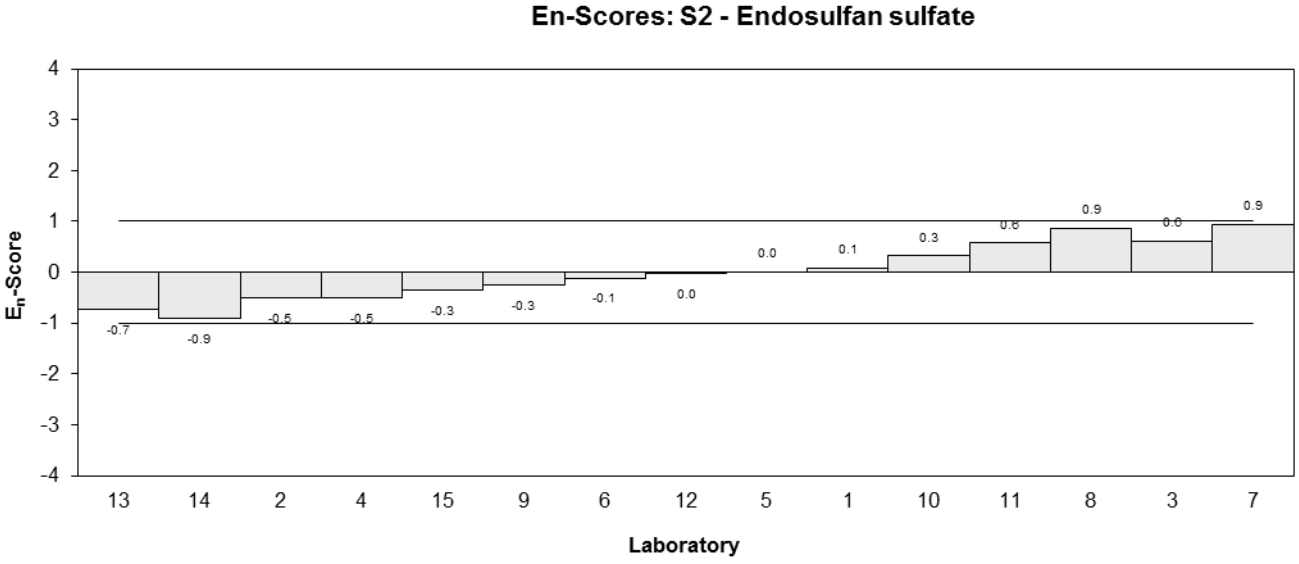

En-Scores: S2 - Endosulfan sulfate
En-Score
Laboratory
13 14 2 4 15 9 6 12 5 1 10 11 8 3 7
-0.7 -0.9 -0.5 -0.5 -0.3 -0.3 -0.1 0.0 0.0 0.1 0.3 0.6 0.9 0.6 0.9

Figure 8

Table 12

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Fenvalerate
Units	mg/kg

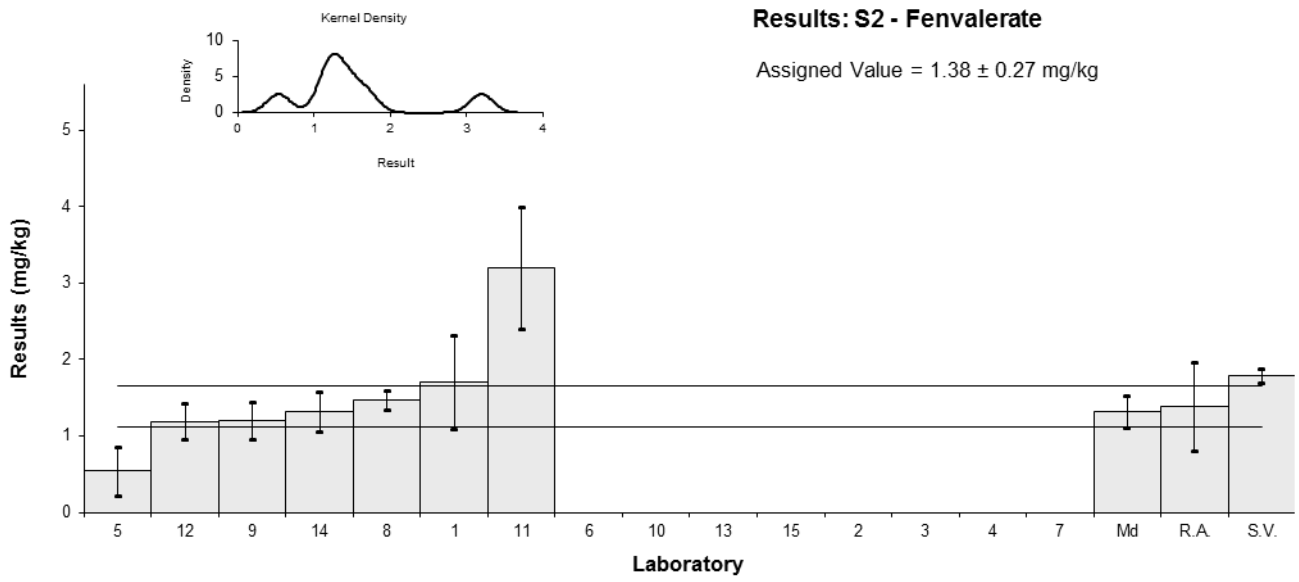
Participant Results

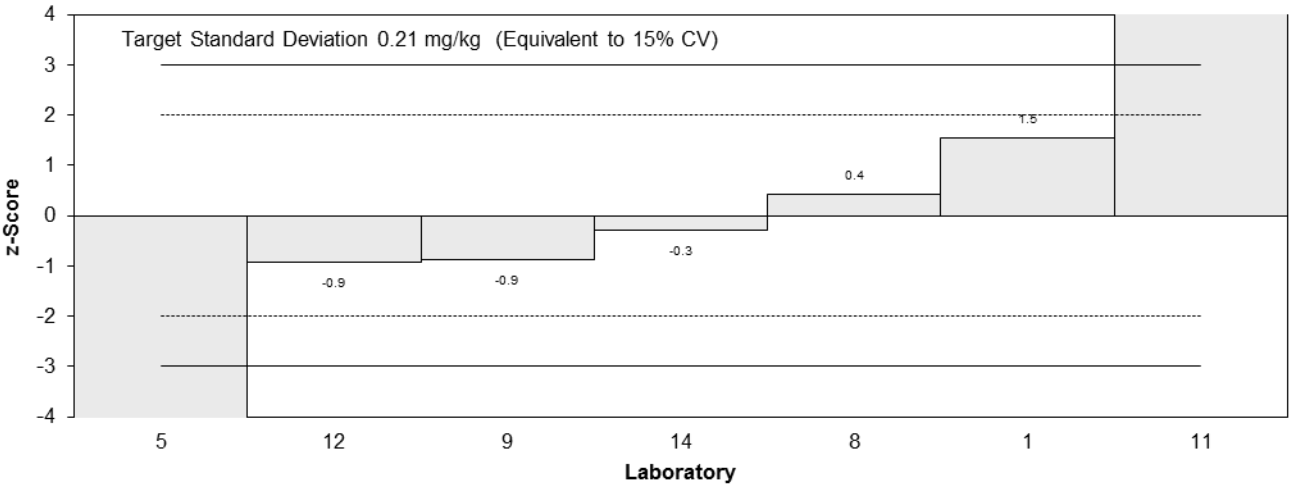
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.7	0.61	NR	1.55	0.48
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	0.54	0.32	NR	-4.06	-2.01
6	< 5	1	NR		
7	NT	NT	NT		
8	1.47	0.13	97.1	0.43	0.30
9	1.2	0.24	100	-0.87	-0.50
10	NT	NT	NT		
11	3.2	0.8	NR	8.79	2.16
12	1.19	0.24	83	-0.92	-0.53
13	NT	NT	NT		
14	1.318	0.264	115	-0.30	-0.16
15	NT	NT	NT		

Statistics

Assigned Value	1.38	0.27
Spike	1.79	0.09
Robust Average	1.39	0.58
Median	1.32	0.21
Mean	1.52	
N	7	
Max.	3.2	
Min.	0.54	
Robust SD	0.61	
Robust CV	44%	

*Robust average excluding laboratories 5 and 11.


Kernel Density
Density
Result
Results: S2 - Fenvalerate
Assigned Value = 1.38 ± 0.27 mg/kg
Results (mg/kg)
Laboratory
5 12 9 14 8 1 11 6 10 13 15 2 3 4 7 Md R.A. S.V.


z-Scores: S2 - Fenvalerate
Target Standard Deviation 0.21 mg/kg (Equivalent to 15% CV)
z-Score
-0.9
-0.9
-0.3
0.4
1.5
Laboratory
5 12 9 14 8 1 11

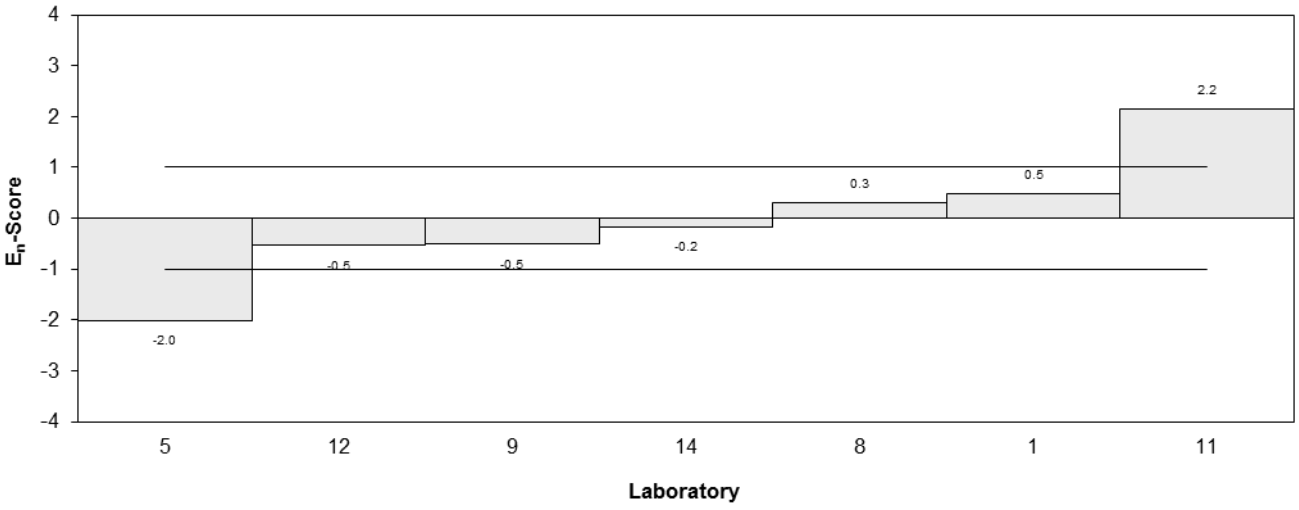

En-Scores: S2 - Fenvalerate
En-Score
-2.0
-0.5
-0.5
-0.2
0.3
0.5
2.2
Laboratory
5 12 9 14 8 1 11

Figure 9

Table 13

Sample Details

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

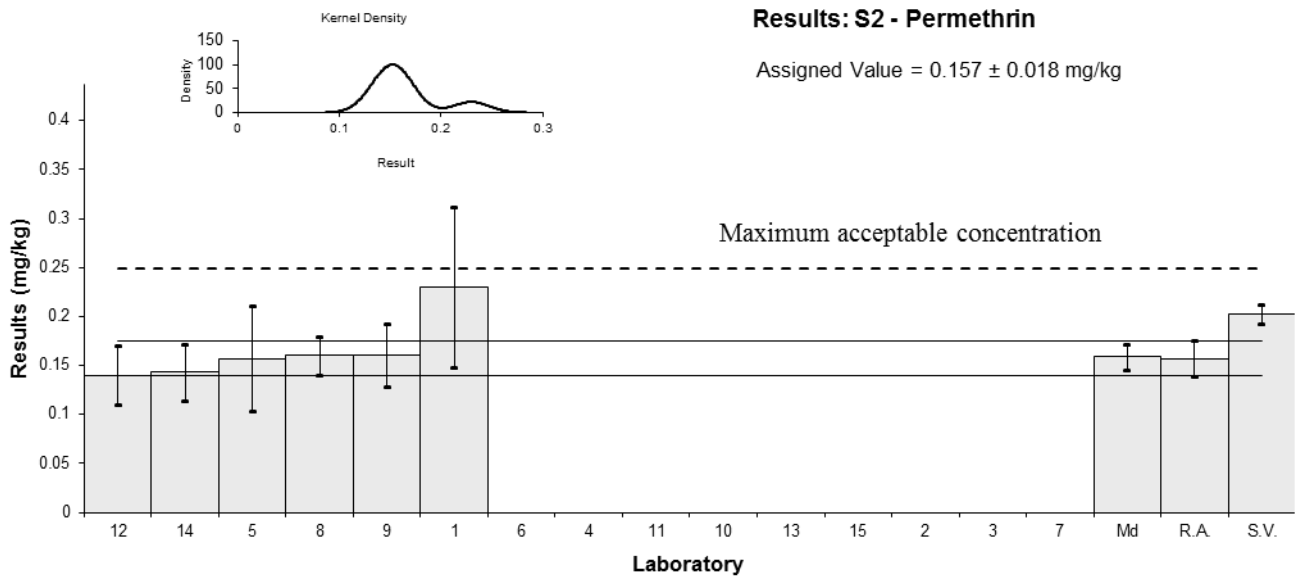
Participant Results

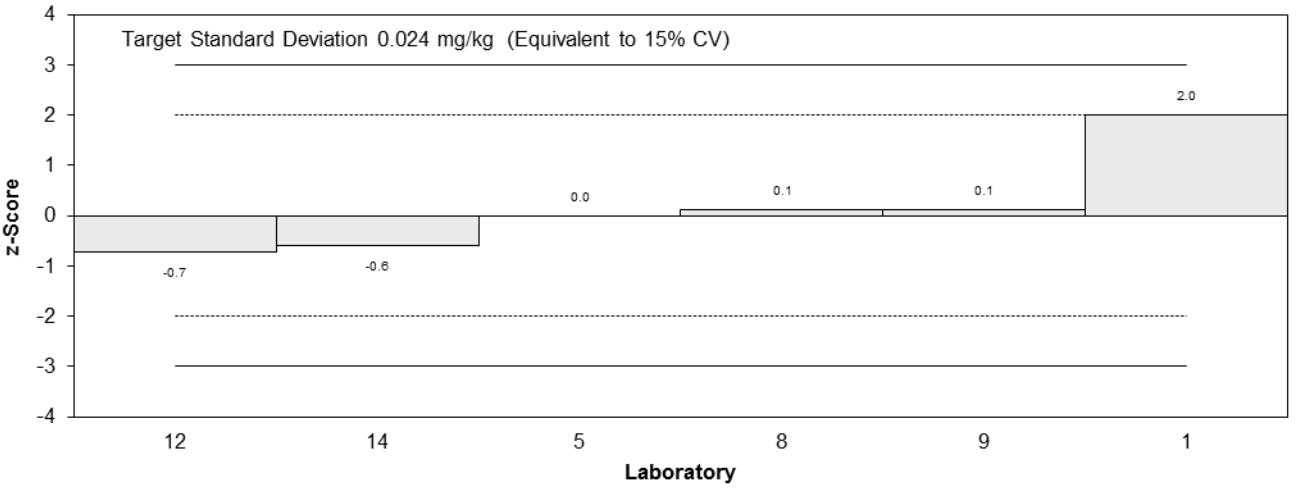
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1*	0.23	0.082	NR	2.00	0.87
2	NT	NT	NT		
3	NT	NT	NT		
4	<0.01	NR	NR		
5	0.157	0.054	NR	0.00	0.00
6	< 2	0.6	NR		
7	NT	NT	NT		
8	0.16	0.02	93.8	0.13	0.11
9	0.16	0.032	88	0.13	0.08
10	NT	NT	NT		
11	<0.4	NR	NR		
12	0.14	0.03	82	-0.72	-0.49
13	NT	NT	NT		
14	0.143	0.029	104	-0.59	-0.41
15	NT	NT	NT		

Statistics

Assigned Value	0.157	0.018
Spike	0.202	0.010
Robust Average	0.157	0.018
Maximum acceptable conc*	0.250	
Median	0.159	0.013
Mean	0.165	
N	6	
Max.	0.23	
Min.	0.14	
Robust SD	0.018	
Robust CV	11%	

*z-Score adjusted to 2 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - Permethrin
Assigned Value = 0.157 ± 0.018 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
12 14 5 8 9 1 6 4 11 10 13 15 2 3 7 Md R.A. S.V.


z-Scores: S2 - Permethrin
Target Standard Deviation 0.024 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 14 5 8 9 1
-0.7
-0.6
0.0
0.1
0.1
2.0

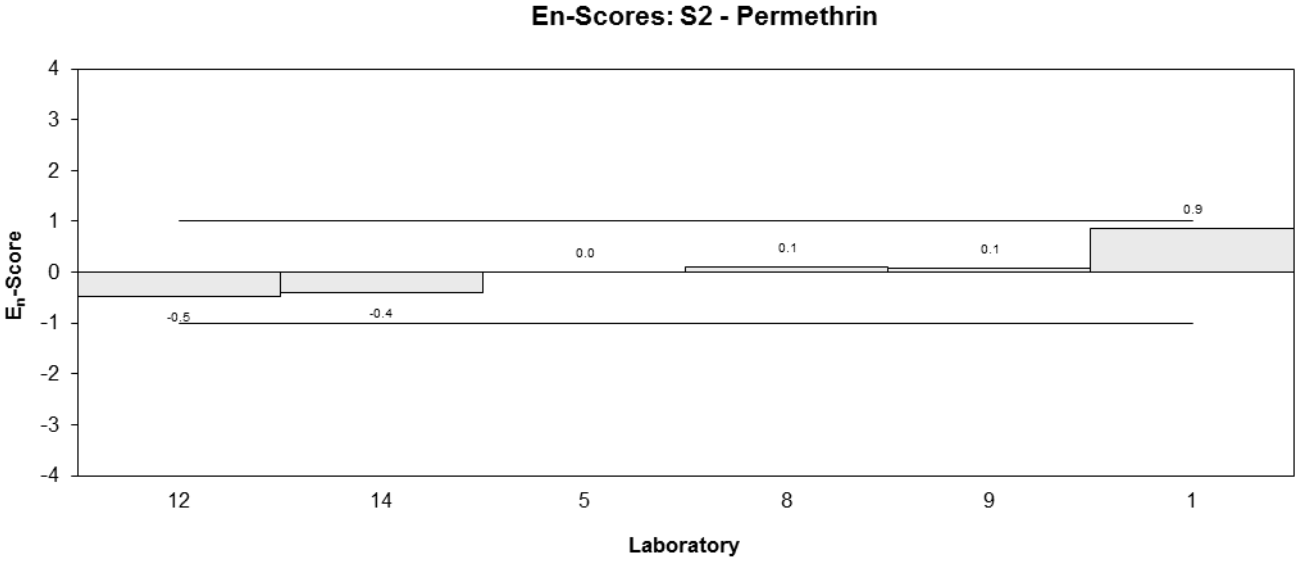

En-Scores: S2 - Permethrin
En-Score
Laboratory
12 14 5 8 9 1
-0.5
-0.4
0.0
0.1
0.1
0.9

Figure 10

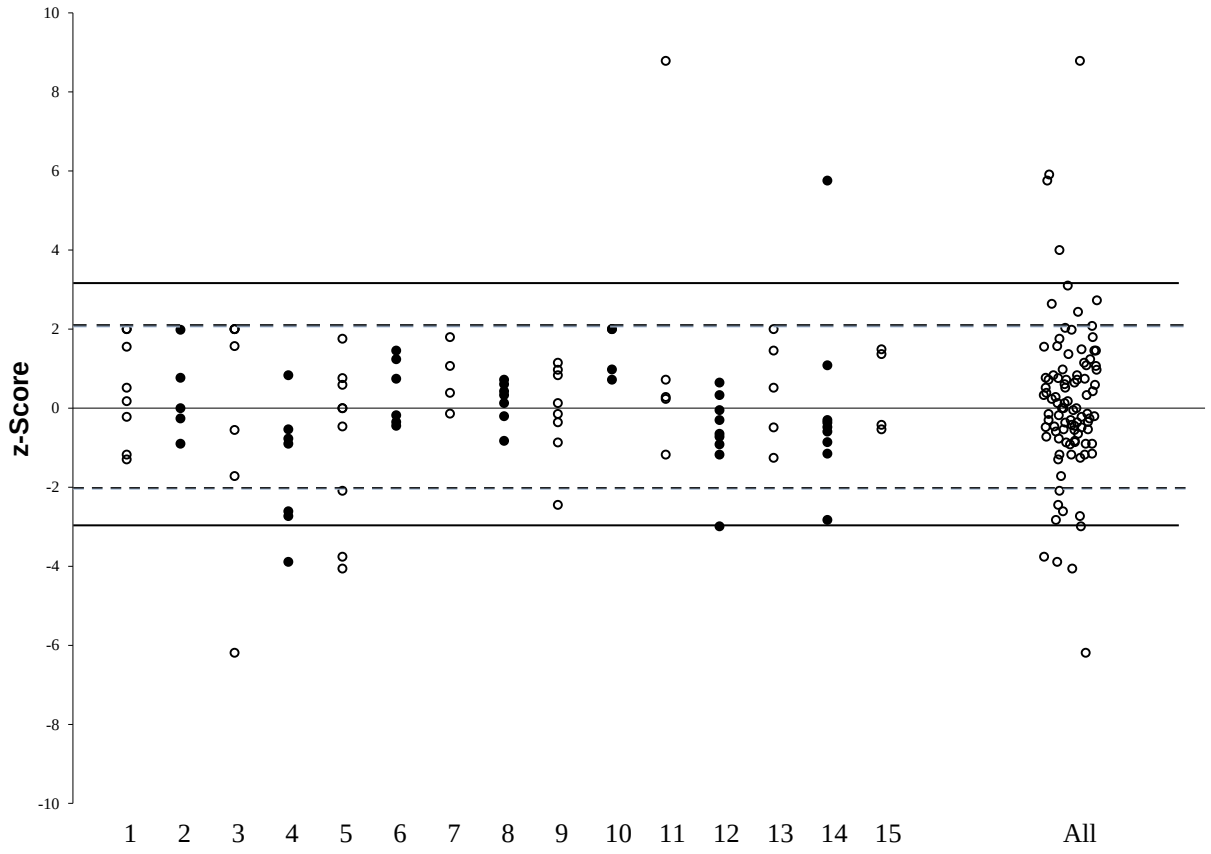


Figure 11 z-Score Dispersal by Laboratory

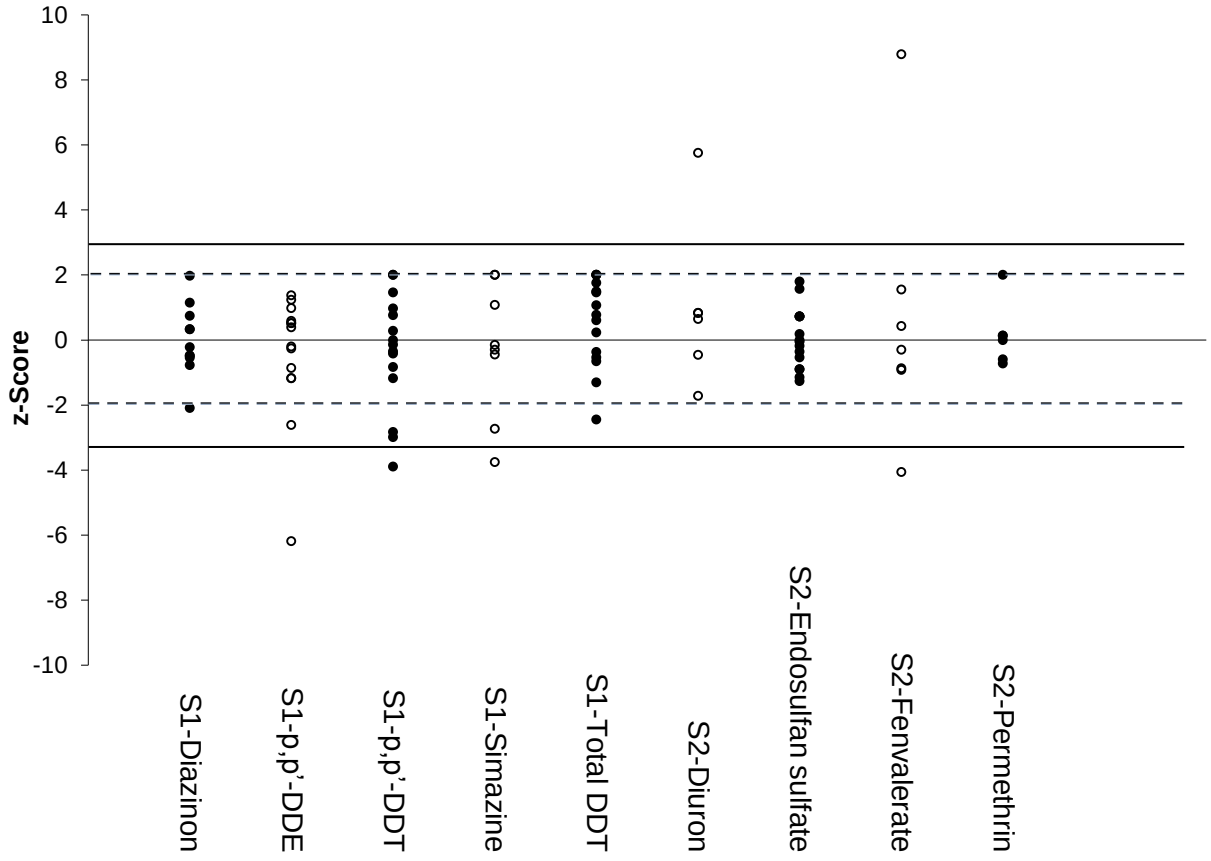


Figure 12 z-Score Dispersal by Analyte

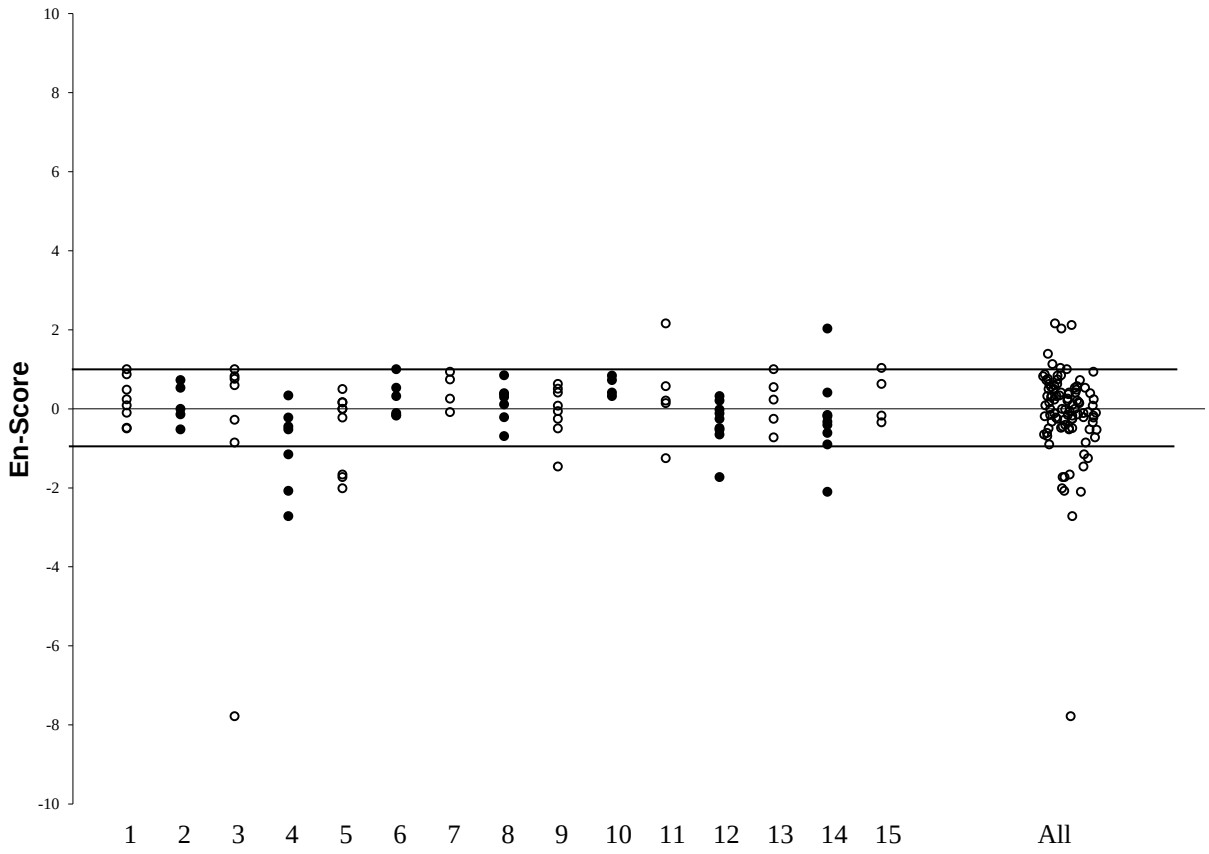


Figure 13 E_n-Score Dispersal by Laboratory

7 DISCUSSION OF RESULTS

7.1 Assigned Value

The robust average of participants' results was used as the assigned value for all samples. The robust averages and associated expanded uncertainties, were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons'.[7] The calculation of the expanded uncertainty for the robust average of diazinon in Sample S1 is presented in Appendix 2.

All assigned values were within the range 55-81% of the spiked concentrations (Table 14). The best estimate of the 'true' concentration of total pesticides in the soil is most likely the formulated (spiked) concentration. 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'. Results less than 50% and greater than 150% of the robust average were removed before calculation of the assigned value.[3,4]

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.

Table 14 Comparison of Assigned Value and Spiked Concentration.

AnalyteName	Sample No.	Assigned Value	Spiked value	Assigned Value / Spike Value
Diazinon	S1	0.486	0.863	56%
p,p'-DDE	S1	1.02	1.3	78%
p,p'-DDT	S1	0.96	1.3	74%
Simazine	S1	0.44	0.807	55%
Total DDT	S1	1.74	2.6	67%
Diuron	S2	0.72	1.11	65%
Endosulfan sulfate	S2	0.37	0.455	81%
Fenvalerate	S2	1.38	1.79	77%
Permethrin	S2	0.157	0.202	78%

7.2 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 the ISO Standard 17025[9] 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.

Of 97 numerical results, 92 were reported with an expanded measurement uncertainty. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 4.

Proficiency tests allow a check of participants' uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figures 2 to 10). In this study the magnitude of the reported expanded uncertainties was within the range 6% to 54% of the reported value.

The reported expanded measurement uncertainty has been under-estimated in some cases (e.g. Lab 8 for diazinon, in sample S1) or over-estimated (e.g. Lab 5 for p,p'-DDE in S1). As a simple rule of thumb, when the uncertainty estimate is smaller than 15% of the reported value or larger thsn 50% of the reported value then this should be reviewed as suspect.

Results returning a satisfactory z-score but an unsatisfactory E_n-score may have underestimated the uncertainty.

Laboratories 4 and 5 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 0.889 ± 0.178 mg/kg, it is better to report 0.89 ± 0.18 mg/kg or instead of 0.446 ± 0.13 mg/kg it is better to report 0.45 ± 0.13 mg/kg). [10]

7.3 z-Score

A target standard deviation equivalent to 15% performance coefficient of variation (PCV) was used to calculate z-scores. The between laboratory coefficient of variation predicted by the modified Horwitz equation[8] is presented for comparison in Table 15.

Table 15 Target standard deviations and modified Horwitz values

Sample	Pesticide	Assigned value (mg/kg)	Modified Horwitz CV (%)	Target SD (as PCV, %)
S1	Diazinon	0.486	18	15
S1	p,p'-DDE	1.02	16	15
S1	p,p'-DDT	0.96	16	15
S1	Simazine	0.44	18	15
S1	Total DDT	1.74	15	15
S2	Diuron	0.72	17	15
S2	Endosulfan sulfate	0.37	19	15
S2	Fenvalate	1.38	15	15
S2	Permethrin	0.157	21	15

To account for possible biases in the consensus values caused by laboratories using inefficient extraction techniques, z-scores were adjusted for p,p'-DDT, simazine and total DDT in S1 and for permethrin in S2. z-Scores greater than 2 were set at 2. A maximum acceptable concentration was set to two target standard deviations more than the spiked level. For results higher than the maximum acceptable concentration z-scores were not adjusted. This ensured that laboratories reporting results close to the spiked concentration were not penalised. Scores of less than 2 were left unaltered.

The dispersal of participants' z-scores is graphically presented by laboratory in Figure 11 and by analyte in Figure 12.

Of the 97 results for which z-scores were calculated, 85 (88%) returned a satisfactory z-score of $|z| \leq 2$.

7.4 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.

E_n-scores greater than 1 were set to 1 for participants for which z-scores were adjusted as discussed in Chapter 6.3 z-Scores.

Of 97 calculated E_n-scores, 82 (85%) were satisfactory with $|E_n| \leq 1$.

The dispersal of participants' E_n-scores by laboratory is presented in Figure 13.

7.5 False Negatives and NT Results

Three laboratories reported at least one false negative, a pesticide present for which they tested but did not report a result, as listed in Table 16.

Table 16 False Negatives

Lab Code	Sample	Pesticide	Result (mg/kg)
11	S1	Simazine	<0.3
9	S1	p,p'-DDE	NR
4	S2	Permethrin	<0.01

Of 147 possible results submitted, 29 results were reported as Not Tested (NT).

Where a laboratory reported a 'less-than' value (e.g < 0.5 mg/kg), this has been included as a false negative only if the assigned value was in fact greater. For example laboratory **6** reported < 5 mg/kg for fenvalerate in Sample S2. This has not been counted as a false negative.

7.6 Reporting of Pesticides Not Spiked Into the Soil

Eight laboratories reported trace levels of pesticides that had not been spiked into one of the samples (Table 17).

Table 17 Pesticides reported by participants but not spiked into the samples

Lab Code	Sample	Pesticide	Concentration (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
1	S1	p,p'-DDD	0.033	0.01	NR
3	S2	Dicamba	0.031	0.01	78
3	S1	p,p'-DDD	1.4	0.42	93
3	S1	Dicamba	0.022	0.007	78
4	S1	Permethrin	0.24	0.07	90
4	S1	p,p'-DDD	0.58	0.16	89
5	S2	p,p'-DDE	0.0109	0.0059	NR
5	S1	p,p'-DDD	0.022	0.011	NR
7	S2	p,p'-DDT	0.04	0.02	61
8	S1	p,p'-DDD	0.06	0.01	83.8
12	S2	p,p'-DDE	0.008	0.002	NR
14	S1	p,p'-DDD	0.201	0.04	130

Table 18 Summary of Participants' Results and Performance

Lab Code	S1-Diazinon (mg/kg)	S1-p,p'-DDE (mg/kg)	S1-p,p'-DDT (mg/kg)	S1-Simazine (mg/kg)	S1-Total DDT (mg/kg)	S2-Diuron (mg/kg)	S2-Endosulfan -sulfate (mg/kg)	S2-Fenvalerate (mg/kg)	S2-Permethrin (mg/kg)
A.V.	0.486	1.02	0.96	0.44	1.74	0.72	0.370	1.38	0.157
1	0.47	1.1	0.79	0.83	1.4	NT	0.38	1.7	0.23
2	0.63	0.98	0.96	NT	1.94	NT	0.32	NT	NT
3	0.446	0.073	1.312	0.62	2.785	0.534	0.457	NT	NT
4	0.43	0.62	0.40	0.26	1.60	0.81	0.32	NT	<0.01
5	0.334	1.11	1.07	0.192	2.20	0.67	0.37	0.54	0.157
6	0.54	1.21	0.91	0.41	2.12	< 2	0.36	< 5	< 2
7	NT	1.08	0.94	NT	2.02	NT	0.47	NT	NT
8	0.51	0.99	0.84	NT	1.90	NT	0.41	1.47	0.16
9	0.57	NR	1.1	0.43	1.1	0.81	0.35	1.2	0.16
10	NT	1.17	1.26	NT	2.43	NT	0.41	NT	NT
11	<1	0.84	1.0	<0.3	1.8	<2	0.41	3.2	<0.4
12	0.51	0.84	0.53	0.42	1.57	0.79	0.367	1.19	0.14
13	0.45	1.10	1.17	NT	2.27	NT	0.30	NT	NT
14	0.451	0.889	0.552	0.511	1.643	1.342	0.306	1.318	0.143
15	NT	1.23	0.90	NT	2.13	NT	0.34	NT	NT

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value

Sample S1 was spiked with p,p'-DDT and p,p'-DDE only. Samples were stored at 4°C and so there was unlikely to have been significant breakdown of the p,p'-DDT to p,p'-DDD.

Any p,p'-DDD reported in these samples is the result of breakdown of p,p'-DDT during analysis, most likely in hot GC injector liners.[11]

Laboratories **3, 4, 5, 7** and **12** reported trace levels pesticides that were not spiked into the test samples.

7.7 Participants' Results and Methods

A summary of participants' results and performance is presented in Table 18 and in Figures 11 and 12.

All participants reported results for endosufan-sulfate in S2 and all performed satisfactorily.

Permethrin in S2 was the test that had the lowest number of reported results. p,p'-DDT in S1 followed by p,p'-DDE and simazine were the tests that had the most unsatisfactory z-scores.

A variety of analytical methods were used for each group of analytes (Table 3). Participants used a sample size of between 5 g to 15 g and dichloromethane, acetone, hexane, acetonitrile or ethyl acetate as extraction solvents. Two laboratories reported using PSA and magnesium sulphate clean-ups, and one used sodium sulphate.

Instrumental techniques employed by participants included gas chromatography (GC) coupled with MS (MS), or selective detectors (ECD or FPD) and liquid chromatography (LC) with MS(MS).

There was no evident correlation between results and participant method.

7.8 Use of Recoveries in Reporting Test Results

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. Recoveries were reported by 8 participants in the range of 61-120%. Laboratories **3**, **9** and **13** corrected results for recovery.

7.9 Certified Reference Materials (CRM)

Participants were requested to indicate whether a matrix reference material or certified standards had been used as part of the quality assurance for the analysis.

Nine laboratories reported using certified standards. The following were listed: Sigma Aldrich, ISO Guide 34 compliant standards, Accustandard, Dr Ehrenstorfer, Custom Mix from Restek 17034, and CRM47426.

These materials may not meet the internationally recognised definition of a Certified Reference Material:

> *'**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]

7.10 Summary of Participation and Performance in Pesticides in Soil Studies

Overall percentages of satisfactory performance (presented as a percentage of the total number of scores for each study) obtained by the participant laboratories analysing pesticides in soil from 2009 to 2019 is presented in Figure 14.

To enable direct comparison, the target standard deviation used to calculate z-scores has been kept constant at 15% PCV. The proportion of satisfactory z-scores over 10 years is on average is 74%. 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.

The proportion of satisfactory E_n-scores on average for the same period is 74%. The increase in percentage satisfactory E_n-scores suggests that laboratories are reporting more realistic estimates of measurement uncertainty.

Individual performance history reports are emailed to each participant at the end of the study; the consideration of z-scores for an analyte 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 $|z| \leq 2$. Scores in the range $2 < |z| < 3$ 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.

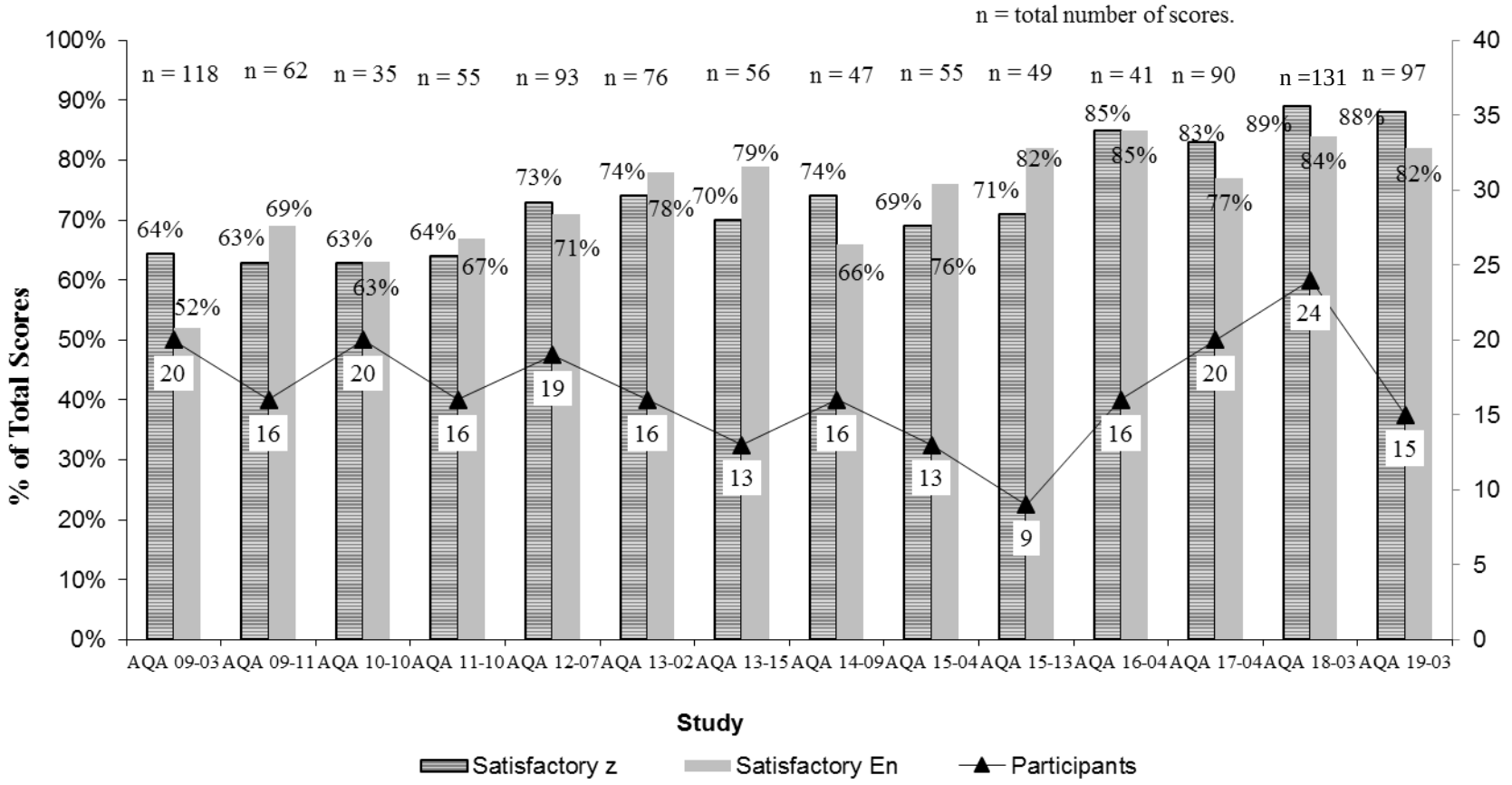


Figure 14 Summary of participation in Pesticides in Soil studies since 2009

8 REFERENCES

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

[2] NMI 2016, *Chemical Proficiency Testing Study Protocol,* viewed 3 May 2017, <http://www.measurement.gov.au>.

[3] NMI 2016, *Chemical Proficiency Testing Statistical Manual*, viewed 3 May 2017, <http://www.measurement.gov.au >.

[4] Thompson, M., Ellison, SLR. & Wood, R. 2005. 'The international harmonized protocol for proficiency testing of (chemical) analytical laboratories', *Pure Appl. Chem,* vol 78, pp 145-196.

[5] National Environmental Protection (Assessment of Site Contamination) Measure Vol 2: Schedule B1, 1999, *Guidelines on the Investigation Levels for Soil and Groundwater,* viewed June 2019, <http://www.comlaw.gov.au/details/F2013C00288/html/volume_2>

[6] NMI 2016, *AQA 16-04 Pesticides in Soil*, viewed June 2018, http://www.measurement.gov.au/Publications/ProficiencyStudyReports/Pages/default.aspx

[7] ISO/IEC 13528 2015, *Statistical methods for use in proficiency testing by interlaboratory comparisons*.

[8] Thompson, M. and Lowthian, P.J. 1995. 'A Horwitz-like function describes precision in a proficiency test', *Analyst*, vol 120, pp 271-272

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

[10] Eurachem 2012, *Quantifying Uncertainty in Analytical Measurement,* 3rd edition, viewed June 2019, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[11] US EPA method 8270D, *Semivolatile Organic Compounds by Gas Chromatography Mass Spectrometry,* viewed June 2019, <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8270d.pdf >

[12] JCGM 200:2008, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM),* 3rd edition.

APPENDIX 1 - SAMPLE PREPARATION AND HOMOGENEITY TESTING

Sample Preparation

Forty bottles of each of Sample S1 and Sample S2 were prepared using dried, ground and sieved topsoil collected from Randwick, NSW. The 350 μm to 850 μm fraction was used to prepare the samples.

To prepare the spiked samples, the sieved soil was suspended in solvent and the standard solutions were added into the stirred. The solvent was allowed to evaporate in a fume cupboard. After drying the soil was divided using Retsch sample divider and dispensed into 65 mL glass jars.

Expanded uncertainties were estimated for the spiked concentration. Contributions to these uncertainties included the gravimetric and volumetric operation involved in spiking the samples and the purity of the pesticide reference standards.

The expanded uncertainty of the spiked concentration at approximately 95% confidence was estimated to be 5% relative for all pesticides.

The samples were prepared in February 2019 and had been stored in a refrigerator at 4^{o}C.

Homogeneity Testing

The process used to prepare the samples was the same as the one used in the previous NMI proficiency test of pesticides in soil. This process has been demonstrated to produce homogeneous samples and no homogeneity testing was conducted.

APPENDIX 2 - ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY

The robust average was calculated using the procedure described in 'ISO13258:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'[8] the uncertainty was estimated as:

$$u_{rob\ av} = 1.25 * S_{rob\ av} / \sqrt{p} \qquad \text{Equation 1}$$

where:

$u_{rob\ av}$ robust average standard uncertainty

$S_{rob\ av}$ robust average standard deviation

p 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.

The robust average of results for diazinon in Sample S1 was calculated (Table 19).

Table 19 Uncertainty estimate for diazinon in Sample S1

No. results (p)	11
Robust Average	0.4863mg/kg
$S_{rob\ av}$	0.0754 mg/kg
$u_{rob\ av}$	0.0284 mg/kg
k	2
$U_{rob\ av}$	0.0568 mg/kg

The robust average for diazinon in Sample S1 is 0.486 ± 0.057 mg/kg.

z-Score and E_n-score

For each participant's result z-score and E_n-score are calculated according to Equation 2 and Equation 3 respectively (see page 11).

A worked example is set out below in Table 20.

Table 20 z-Score and E_n-score for diazinon result reported by Laboratory 1 in S1

Diazinon Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E_n-Score
0.47±0.15	0.486±0.057	15% as PCV or 0.15x0.486 = =0.0729 mg/kg	$z = \frac{(0.47 - 0.486)}{0.0729}$ z = -0.219	$En = \frac{(0.47 - 0.486)}{\sqrt{0.15^2 + 0.057^2}}$ E_n=-0.10

APPENDIX 4 - ACRONYMS AND ABBREVIATIONS

ASE	Accelerated Solvent Extraction
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
ECD	Electron Capture Detector
GC	Gas Chromatography
ISO	International Standards Organisation
LC	Liquid Chromatography
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
MS	Mass Spectrometry
NEPC	National Environmental Protection Council
NATA	National Association of Testing Authorities
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
OCP	Organochlorine Pesticides
OPP	Organophospate Pesticides
PT	Proficiency Test
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe (Method of pesticide analysis)
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
Target SD	Target Standard Deviation
σ	Target standard deviation

END OF REPORT