Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

Proficiency Test Report
AQA 18-03
Pesticides in Soil

May 2018

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.

Raluca Iavetz

Geoff Morschel

Alexander Sadler

Paul Armishaw

Manager, Chemical Reference Values

105 Delhi Road, North Ryde NSW 2113

GPO Box 2013 Canberra ACT 2601

Phone: 61-2-9449 0149 Fax: 61-2-9449 0123

paul.armishaw@measurement.gov.au

Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

This page is intentionally blank.

SUMMARY

AQA 18-03 was conducted in March 2018. Twenty-five laboratories registered to participate and twenty four submitted results.

Two soil test samples were prepared. Sample S1 was prepared by spiking Menangle topsoil obtained from a Sydney supplier with bifenthrin, dieldrin, tebuconazole and trifluralin. Sample S2 was prepared by spiking clay soil obtained from regional NSW with atrazine, chlorpyrifos, endosulfan sulfate and ethion.

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 192 numeric results a total of 131 results (68%) were submitted. Fifty-three results (28%) were reported as Not Tested (NT).

The robust average of participants' results was used as the assigned value for all eight analytes.

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 131 z-scores, 117 (89%) were satisfactory with $|z| \leq 2$.
  Of 131 E_n-scores, 110 (84%) were satisfactory with $|E_n| \leq 1$.

  Laboratory **5** returned satisfactory z and E_n-scores for all analytes for which scores were calculated.

- *assess the ability of participant laboratories to correctly identify pesticides in soil;*
  Five laboratories **8**, **15**, **20**, **21** and **24** did not report results for pesticides for which they tested and that were present in the test samples (total of 5 false negatives)
  Laboratory **13** reported pesticides that were not spiked into the test samples (total of 2 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. Chlorpyrifos in S2 was the most 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 0.4% to 200% of the reported value.

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: '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;
- metals in soil, water, food and pharmaceuticals;
- controlled drug assay;
- 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:

- 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.

1.3 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.

2 STUDY INFORMATION

2.1 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 S1	Spike (mg/kg)	U (mg/kg)[1]
Bifenthrin	1.300	0.064
Dieldrin	0.551	0.028
Tebuconazole	0.947	0.047
Trifluralin	0.799	0.040
Sample S2		
Atrazine	1.097	0.055
Chlorpyrifos	1.097	0.045
Endosulfan sulfate	0.602	0.030
Ethion	0.223	0.011

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

2.2 Study Timetable

The timetable of the study was:

Invitation issued	12 February 2018
Samples dispatched	28 February 2018
Results due	9 April 2018
Interim report issued	17 April 2018

2.3 Participation

Eighty-five Australian and international laboratories were invited to participate. Twenty-five laboratories participated (see Appendix 1) and twenty-four submitted results by the due date.

2.4 Test Sample Preparation and Homogeneity Testing

Two soil samples, Menangle topsoil purchased from a Sydney supplier and clay soil from country NSW, were prepared by spiking. Solutions of pesticides were added to obtain the concentrations in Table 2. The preparation of the study samples is described in Appendix 2.

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

2.5 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 47-86% of the spiked concentration. Similar ratios have been observed in previous NMI PT of pesticides in soil (as presented in AQA 16-04[6]). A summary of atrazine, endosulfan sulfate and chlorpyrifos recoveries in different soils across previous studies is given in Appendix 4.

2.6 Laboratory Code

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

2.7 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 28 February 2018.

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.

2.8 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 9 April 2018. Late results cannot be included in the study report.

2.9 Interim Report

An interim report was emailed to participants on 17 April 2018.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

Table 3. Test Methods

Lab. Code	Sample Mass. (g)	Extraction	Clean-up	Measurement
1	15	Extracted soil with ethyl acetate in shaker for 4 hours. 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.
2	10	DCM/ACETONE 1:1		GC-MS
3	10	DCM:Acetone		GC-MS
4	10	OP Pesticides: 1:1 DCM:Acetone. OC Pesticides: 1:1 Hexane:Acetone		OP Pesticides: GC-MS/MS. OC Pesticides: GC-ECD (dual column).
5	10	DCM/ACETONE 1:1		GC-MS
7	10	DCM:acetone 1:1		GCMS SIM mode(majority), LCMS (2,4-D,dicamba,diuron,metsulfuron,MCPA,triclopyr)
8	10	OCP: 20ml ACETONE/HEXANE (50:50)		GC-MS (OPP) , GC-ECD (OCP), HPLC-DAD (Herbicides and Pyrethroids)
9	10	Organic Solvent		GC-ECD, GC-MS
10	10	DCM/Acetone		GC-MS
11	5	GCMS: DCM/Acetone (1:1) LCMS: Acetonitrile with 1% Formic Acid		GC-MS/MS and LC-MS/MS
12	10	1:1 Hexane:Acetone		GC-ECD & GC-MS
13	8.5	Ethyl acetate		GC-MS
14	10	acetone	Liquid - Liquid Partition and Solid Phase Extraction	GC-ECD, GC-NPD
15	10	Acetone, Dichloromethane, Hexane	Multi-residue method (SPE (Florisil, Envicarb)	ECD and FPD GC

Lab. Code	Sample Mass. (g)	Extraction	Clean-up	Measurement
16	2	Hexane/Acetone 1:1	Florisil	GC-MS/MS
17	5.06, 5.01	Acetonitrile; Or methyl tert-butyl ether	dSPE (50 mg PSA, 50 mg C18, 150 mg MgSO4); Or SPE (florisil)	GC-MS, GC-MS/MS, LC-MS/MS
18	10	DCM and Hexane		GC-ECD and GC-MS
19	15	Ethyl Acetate	DSPE	GC with ECD/NPD/FPD
20	10	Acetone/DCM For PAH and SVOC		GCMS for PAH & SVOC, GC ECD for OC
21	5	1:1 Acetone: Hexanes		GC-ECD, GC-MS
22	~10	DCM / Acetone (1:1)	Passed through sodium sulphate	GC QQQ
23	10	acetone; liquid-liquid partition dichloromethane:distilled water	graphitized carbon SPE; Florisil SPE	GC-ECD; GC-MS; GC-MS/MS
24	10	Acetone : Dichloromethane (Liquid:Liquid extraction)	SPE: Graphitized Carbon and Florisil	Gas Chromatography with Nitrogen Phosphorous Detector and Micro Electron Capture Detector
25	10	1:1 DCM:Acetone		GC-MS

3.2 Basis of Participants' Measurement Uncertainty Estimates

Table 4. Basis of Uncertainty Estimate

Lab. Code	Basis of Uncertainty Estimate
1	U sample = 2 U_c, when U_c = C sample * (RSD2purity + RSD2 sample weight + RSD2balance + RSD2method precision + RSD2final volume + RSD2Calibration curve + RSD2dilution)1/2
2	30% at >10*PQL
3	30% at >10*PQL
4	Control charts.
5	30% at >10*PQL
7	Long-term reproducibility
8	Standard deviation based on control charts.
9	Top down approach. NATA technical note 33.
10	Precision and estimates of the method and Laboratory bias
11	Included reproducibility, inhomogeneity, and purity
12	Professional judgement.
13	Standard uncertainty based on historical data.
14	Top Down Approach
15	2SD
16	Repeatability Precision
17	Uncertainty budget
18	"bottom-up" approach
19	Spiking Recovery
20	40%
21	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%.
22	in house validation
23	Repeatability precision (2*SD).
24	Repeatability of trials and injection
25	Tech Note 33

Table 5. Additional Participants' Comments

Lab Code	Sample	Comment or Discussion	Study co-ordinator Response
5	S1	Don't include compounds requiring derivatisation unless spiked into the samples. Sufficient sample preparation time was used for non-detects (2,4-D, Diuron, Metsulforun-methyl etc.)	The list is designed to include a variety of pesticides from different groups in order to assess the ability of participant laboratories to correctly identify only the pesticides present in the soil sample.
11	S1 & S2	LOR = 0.1 mg/kg for all analytes	
16	S1 & S2	Recovery from LCS (Laboratory Control Spike)	
23	S1	ND means no detection at LOQ = 0.05 mg/kg.	
	S2	The sample is screened using GC-MS, quantified using GC-ECD, and used GC-MS/MS as confirmatory; Recovery results is not corrected; ND means no detection at LOQ = 0.05 mg/kg.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 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 9.

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

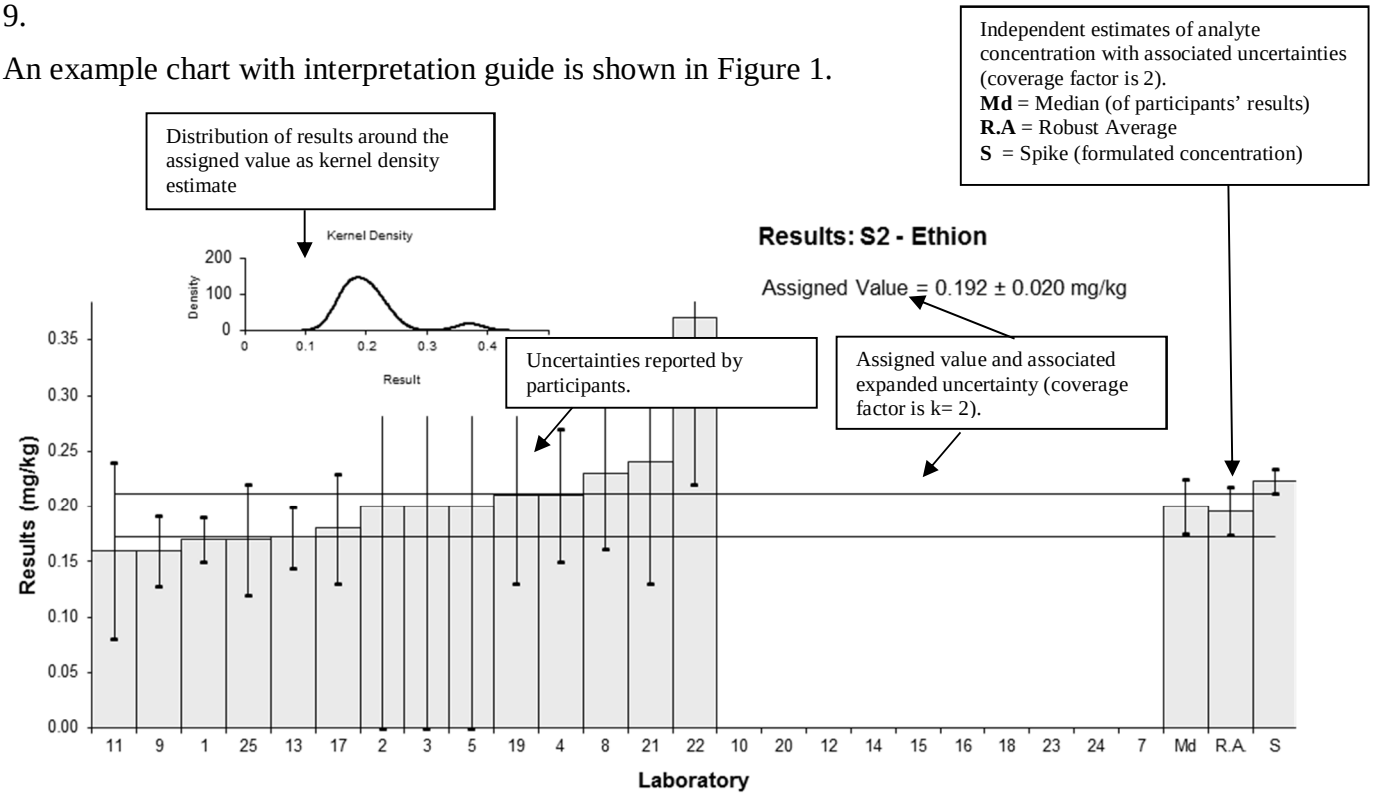


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

The assigned value is defined[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.

4.3 Between-Laboratory Coefficient of Variation

The between laboratory coefficient of variation is a measure of the between laboratory variation that in the judgement of the study coordinator would be expected from participants given the analyte concentration. It is important to note this is a performance measure set by the study coordinator; it is not the coefficient of variation of participant results.

4.4 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (*X)* and the between-laboratory coefficient of variation (CV). This value is used for calculation of participant z-score.

$$\sigma = X * CV \qquad \text{Equation 1}$$

4.5 z-Score

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

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

where:

z is z-score
χ is participant 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.

4.6 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 below:

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

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

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

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

4.7 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017[8] 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.[9]

4.8 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by inte-rlaboratory comparisons'.[10]

5 TABLES AND FIGURES

Table 6

Sample Details

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

Participant Results

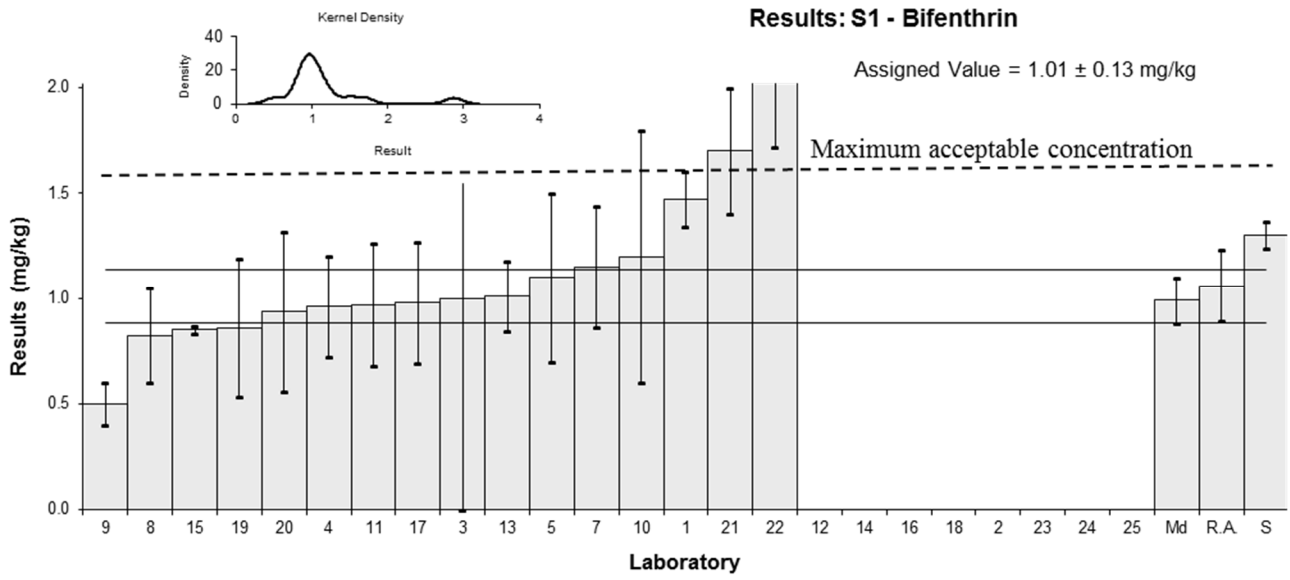
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1**	1.47	0.13	93	2.00	1.00
2	NT	NT	NT		
3	1	1	80-120	-0.07	-0.01
4	0.96	0.24	NR	-0.33	-0.18
5	1.1	0.4	80-120	0.59	0.21
7	1.15	0.29	NR	0.92	0.44
8	0.824	0.223	NR	-1.23	-0.72
9	0.50	0.10	NR	-3.37	-3.11
10	1.2	0.6	NR	1.25	0.31
11	0.97	0.29	45	-0.26	-0.13
12	NT	NT	NT		
13	1.01	0.17	NR	0.00	0.00
14	NT	NT	NT		
15	0.85	0.02	NR	-1.06	-1.22
16	NT	NT	NT		
17	0.98	0.29	NR	-0.20	-0.09
18	NT	NT	NT		
19	0.86	0.33	NR	-0.99	-0.42
20	0.94	0.38	92	-0.46	-0.17
21	1.7	0.3	NR	4.55	2.11
22	2.87	1.15	NR	12.28	1.61
23	NT	NT	NT		
24	NT	NT	NT		
25	NT	NT	NT		

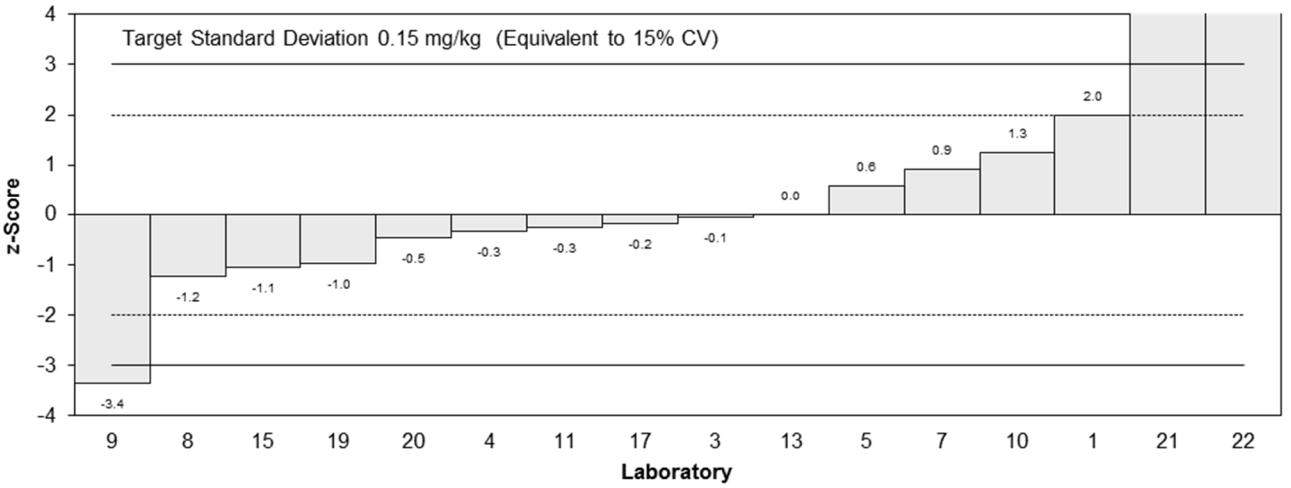
Statistics

Assigned Value*	1.01	0.13
Spike	1.300	0.064
Maximum acceptable conc.**	1.60	
Robust Average	1.06	0.17
Median	0.99	0.11
Mean	1.15	
N	16	
Max.	2.87	
Min.	0.5	
Robust SD	0.28	
Robust CV	26%	

*Robust average excluding laboratory 22.

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


Kernel Density
Density
Result
Results: S1 - Bifenthrin
Assigned Value = 1.01 ± 0.13 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
9 8 15 19 20 4 11 17 3 13 5 7 10 1 21 22 12 14 16 18 2 23 24 25 Md R.A. S


z-Scores: S1 - Bifenthrin
Target Standard Deviation 0.15 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
9 8 15 19 20 4 11 17 3 13 5 7 10 1 21 22
-3.4 -1.2 -1.1 -1.0 -0.5 -0.3 -0.3 -0.2 -0.1 0.0 0.6 0.9 1.3 2.0

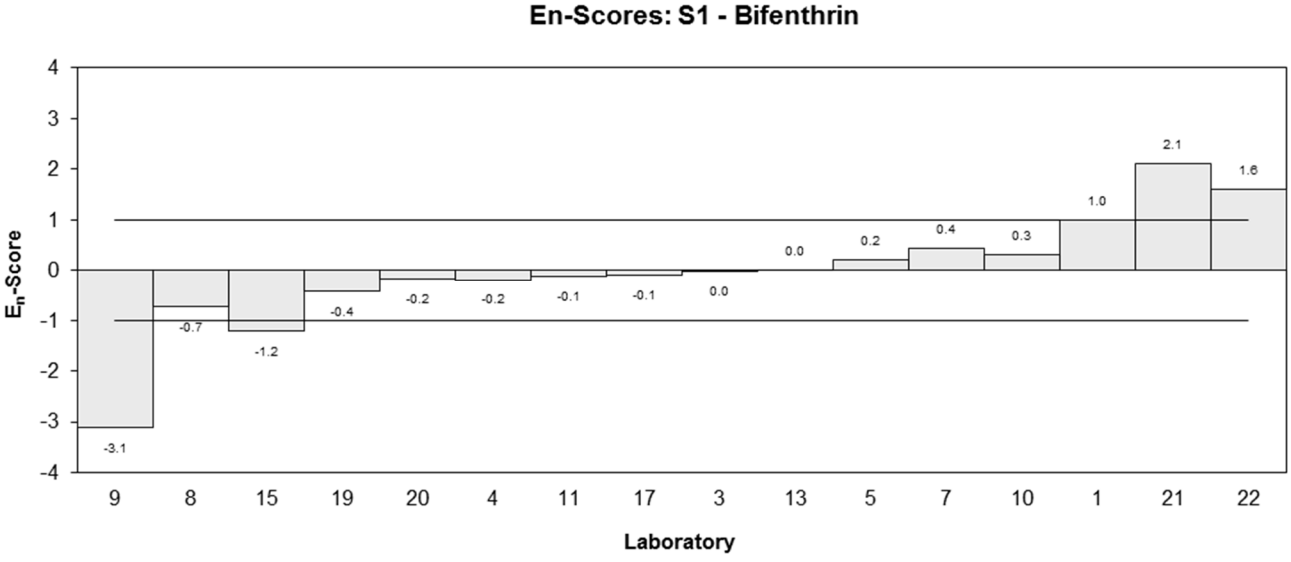

En-Scores: S1 - Bifenthrin
En-Score
Laboratory
9 8 15 19 20 4 11 17 3 13 5 7 10 1 21 22
-3.1 -0.7 -1.2 -0.4 -0.2 -0.2 -0.1 -0.1 0.0 0.0 0.2 0.4 0.3 1.0 2.1 1.6

Figure 2

Table 7

Sample Details

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

Participant Results

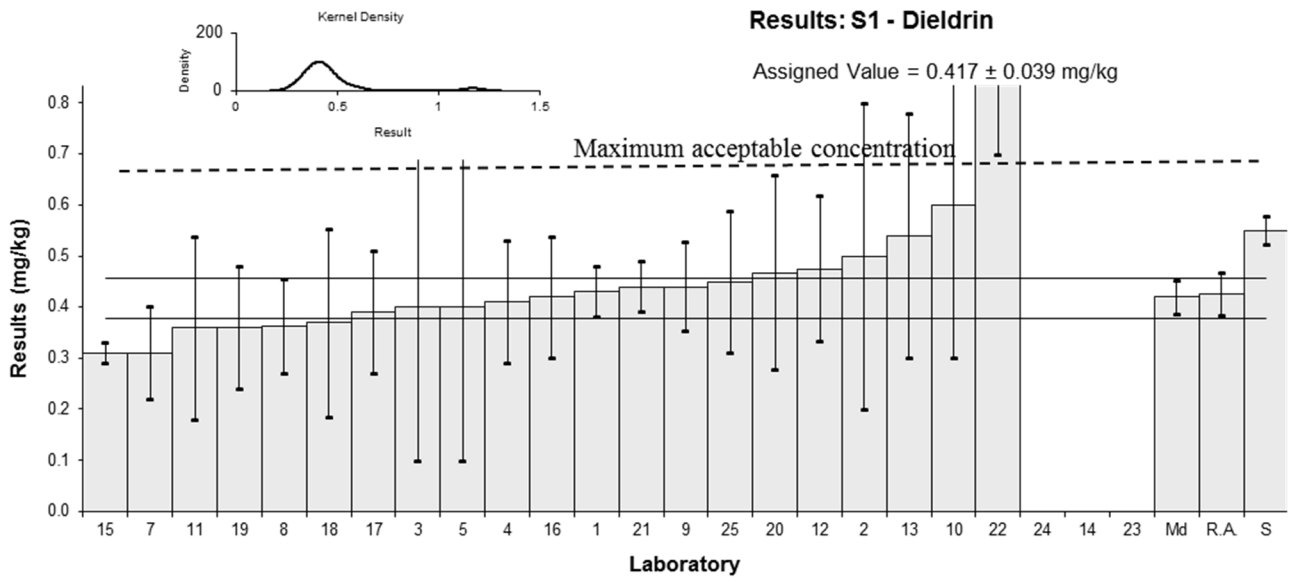
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.43	0.05	89	0.21	0.21
2	0.5	0.3	80-120	1.33	0.27
3	0.4	0.3	80-120	-0.27	-0.06
4	0.41	0.12	NR	-0.11	-0.06
5	0.4	0.3	80-120	-0.27	-0.06
7	0.31	0.09	NR	-1.71	-1.09
8	0.363	0.093	NR	-0.86	-0.54
9	0.44	0.088	NR	0.37	0.24
10**	0.6	0.3	NR	2.00	0.60
11	0.36	0.18	58	-0.91	-0.31
12	0.475	0.143	NR	0.93	0.39
13	0.54	0.24	NR	1.97	0.51
14	NT	NT	NT		
15	0.31	0.02	NR	-1.71	-2.44
16	0.42	0.12	111.6	0.05	0.02
17	0.39	0.12	NR	-0.43	-0.21
18	0.370	0.185	98	-0.75	-0.25
19	0.36	0.12	NR	-0.91	-0.45
20	0.468	0.19	90	0.82	0.26
21	0.44	0.05	NR	0.37	0.36
22	1.17	0.47	NR	12.04	1.60
23	NT	NT	NT		
24	NR	NR	90		
25	0.45	0.14	100	0.53	0.23

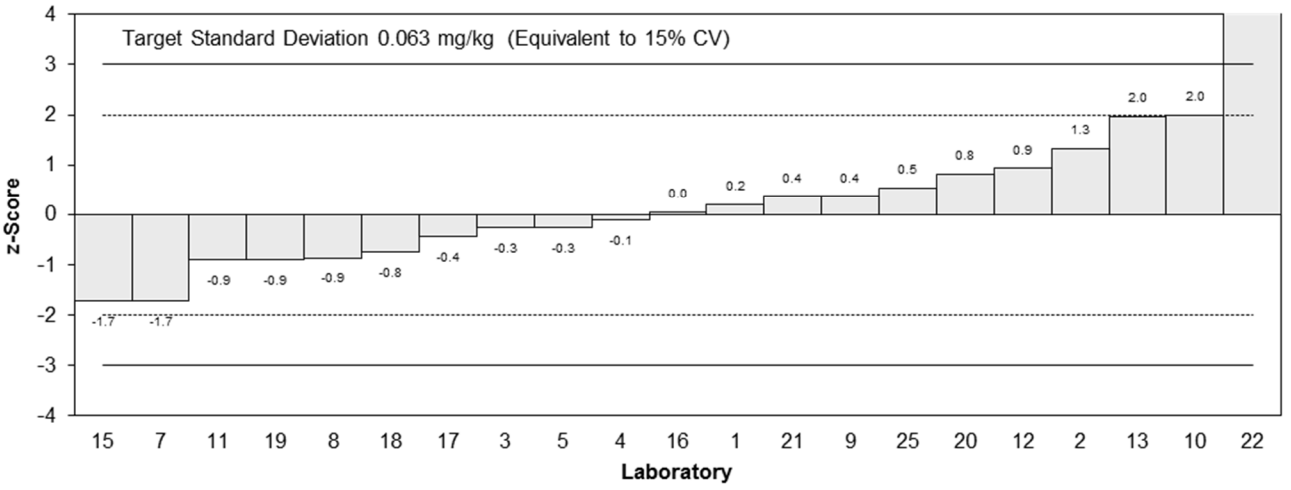
Statistics

Assigned Value*	0.417	0.039
Spike	0.551	0.028
Maximum acceptable conc**	0.677	
Robust Average	0.425	0.043
Median	0.420	0.034
Mean	0.457	
N	21	
Max.	1.17	
Min.	0.31	
Robust SD	0.079	
Robust CV	19%	

*Robust average excluding laboratory 22.

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


Kernel Density
Density
Result
Results: S1 - Dieldrin
Assigned Value = 0.417 ± 0.039 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
15 7 11 19 8 18 17 3 5 4 16 1 21 9 25 20 12 2 13 10 22 24 14 23 Md R.A. S


z-Scores: S1 - Dieldrin
Target Standard Deviation 0.063 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
15 7 11 19 8 18 17 3 5 4 16 1 21 9 25 20 12 2 13 10 22

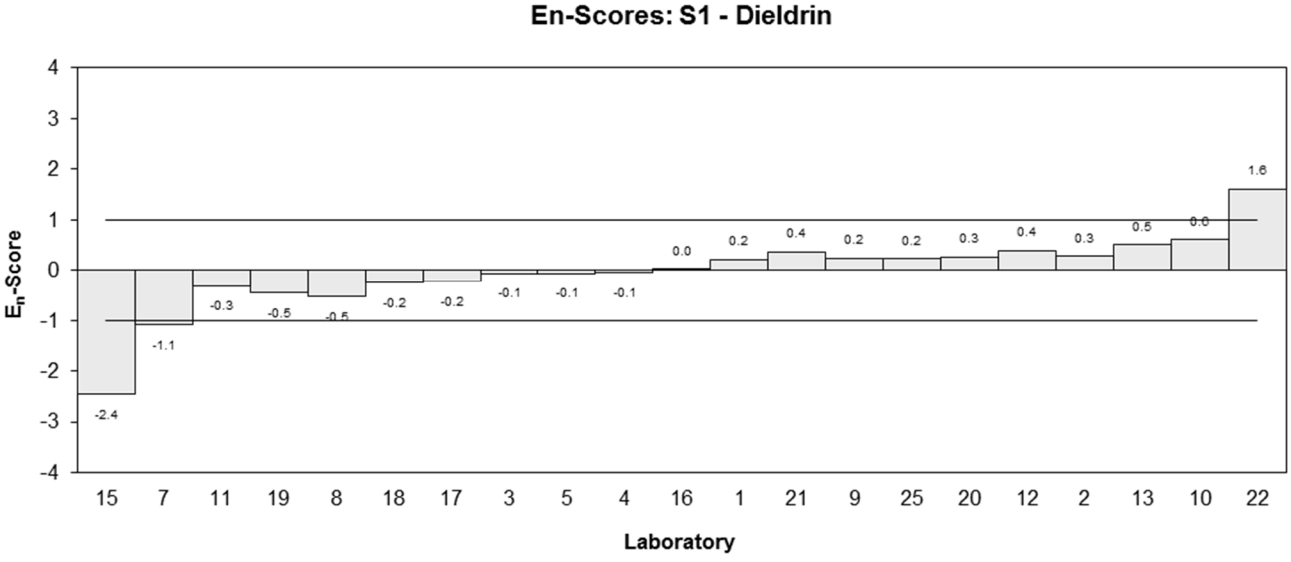

En-Scores: S1 - Dieldrin
En-Score
Laboratory
15 7 11 19 8 18 17 3 5 4 16 1 21 9 25 20 12 2 13 10 22

Figure 3

Table 8

Sample Details

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

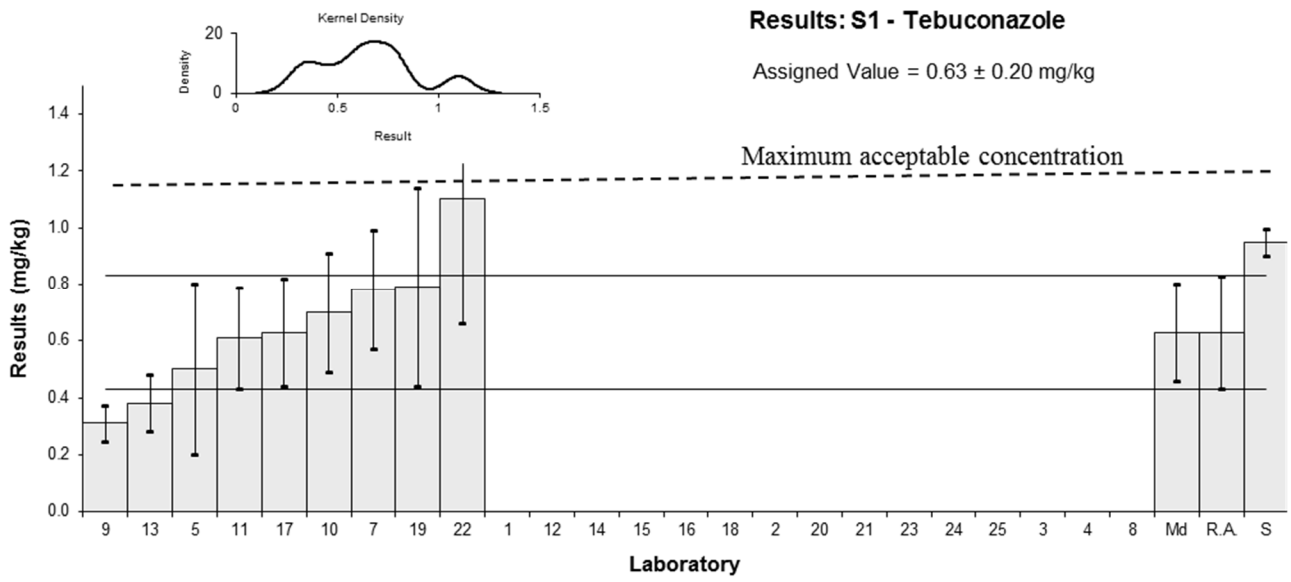
Participant Results

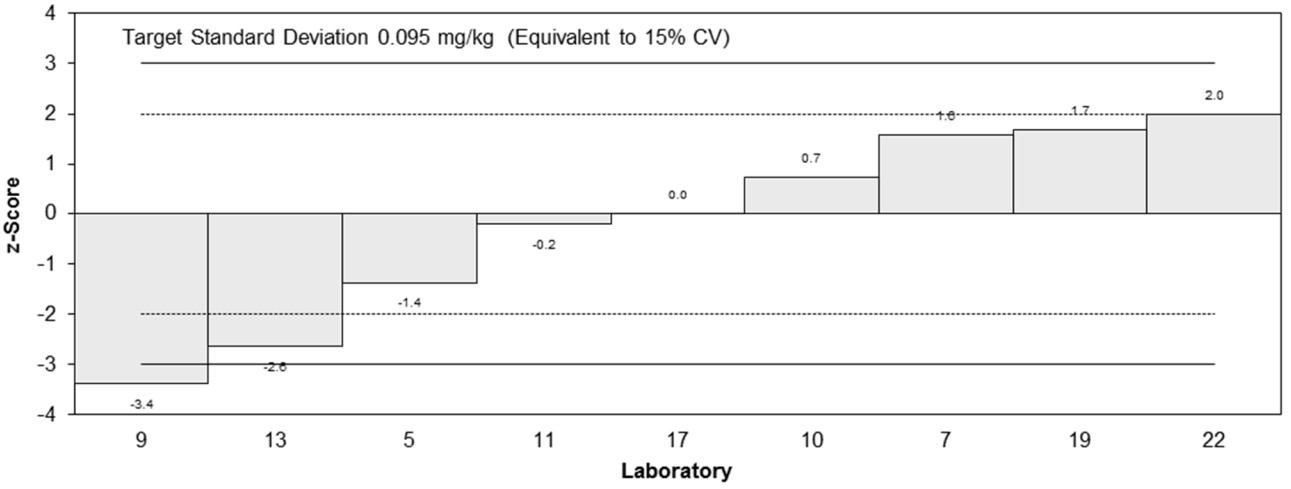
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	0.5	0.3	80-120	-1.38	-0.36
7	0.78	0.21	NR	1.59	0.52
8	NT	NT	NT		
9	0.31	0.062	NR	-3.39	-1.53
10	0.7	0.21	NR	0.74	0.24
11	0.61	0.18	80	-0.21	-0.07
12	NT	NT	NT		
13	0.381	0.099	NR	-2.63	-1.12
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.63	0.19	NR	0.00	0.00
18	NT	NT	NT		
19	0.79	0.35	NR	1.69	0.40
20	NT	NT	NT		
21	NT	NT	NT		
22**	1.10	0.44	NR	2.00	0.97
23	NT	NT	NT		
24	NT	NT	NT		
25	NT	NT	NT		

Statistics

Assigned Value	0.63	0.20
Spike	0.947	0.047
Maximum acceptable conc**	1.14	
Robust Average	0.63	0.20
Median	0.63	0.17
Mean	0.65	
N	9	
Max.	1.1	
Min.	0.31	
Robust SD	0.24	
Robust CV	38%	

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


Kernel Density
Density
Result
Results: S1 - Tebuconazole
Assigned Value = 0.63 ± 0.20 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
9 13 5 11 17 10 7 19 22 1 12 14 15 16 18 2 20 21 23 24 25 3 4 8 Md R.A. S


z-Scores: S1 - Tebuconazole
Target Standard Deviation 0.095 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-3.4 -2.6 -1.4 -0.2 0.0 0.7 1.6 1.7 2.0
9 13 5 11 17 10 7 19 22

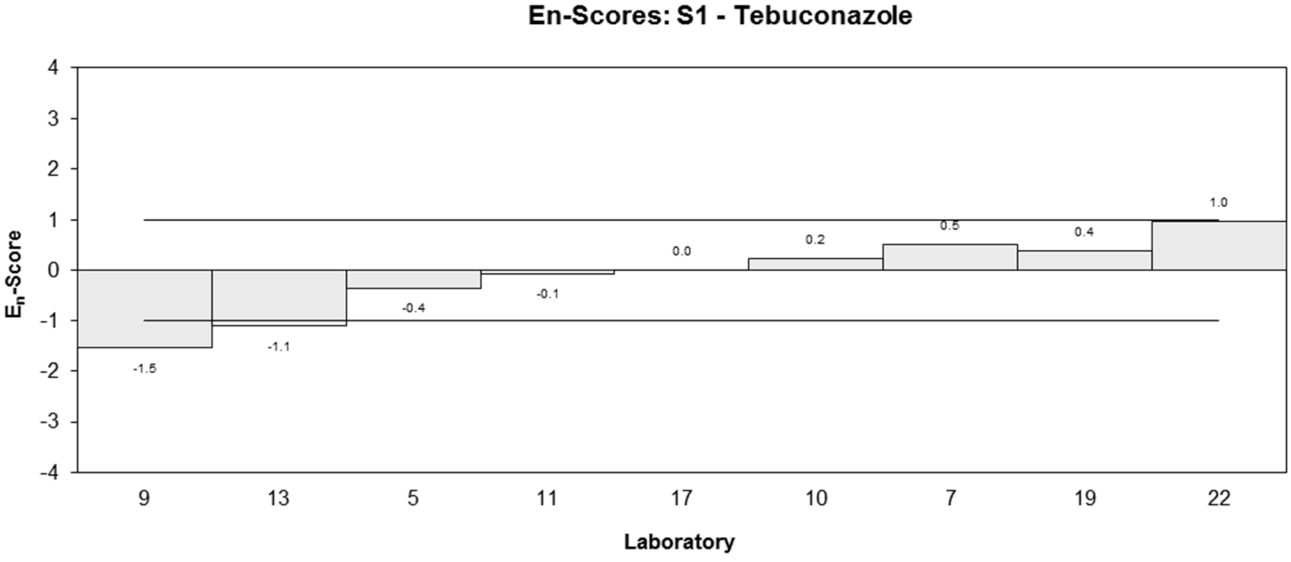

En-Scores: S1 - Tebuconazole
En-Score
Laboratory
-1.5 -1.1 -0.4 -0.1 0.0 0.2 0.5 0.4 1.0
9 13 5 11 17 10 7 19 22

Figure 4

Table 9

Sample Details

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

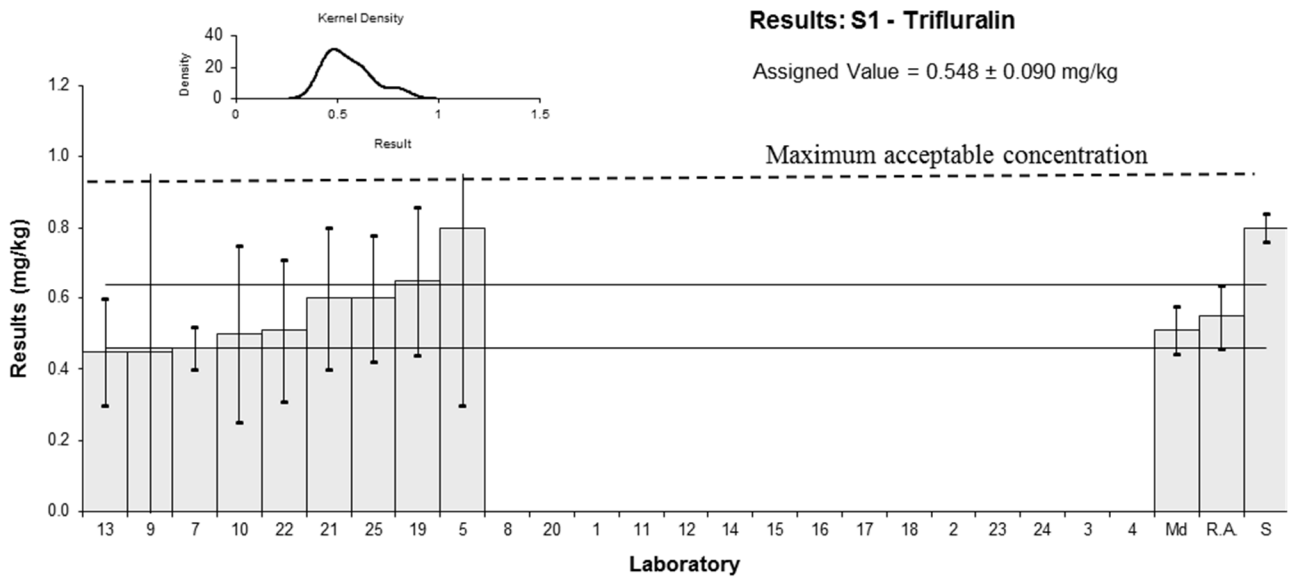
Participant Results

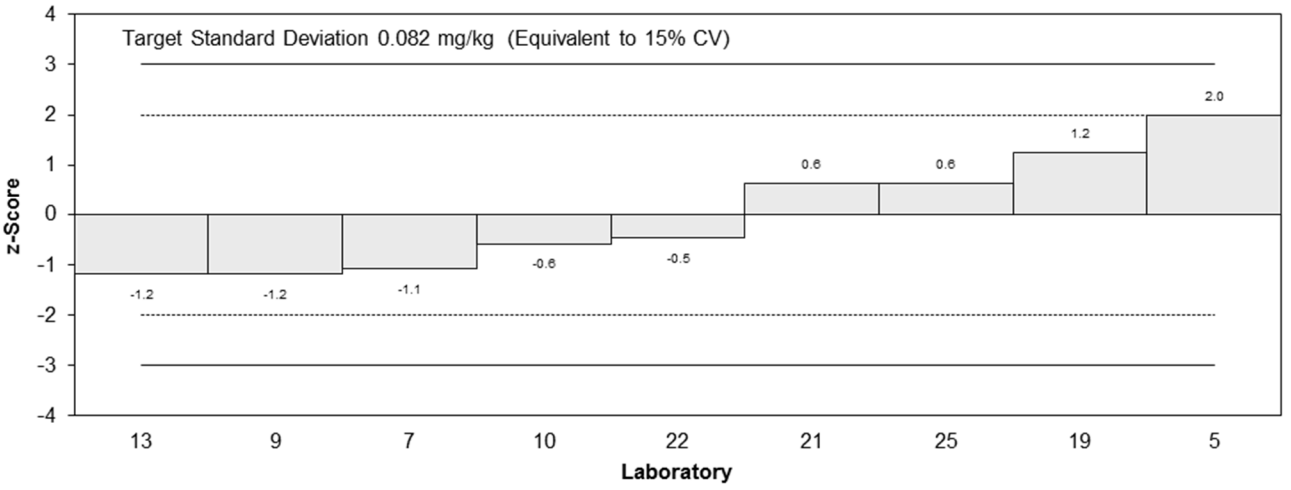
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5**	0.8	0.5	80-120	2.00	0.50
7	0.46	0.06	NR	-1.07	-0.81
8	< 0.5	0.15	NR		
9	0.45	0.90	NR	-1.19	-0.11
10	0.5	0.25	NR	-0.58	-0.18
11	NT	NT	NT		
12	NT	NT	NT		
13	0.45	0.15	NR	-1.19	-0.56
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	0.65	0.21	NR	1.24	0.45
20	<0.5	NR	NR		
21	0.6	0.2	NR	0.63	0.24
22	0.51	0.20	NR	-0.46	-0.17
23	NT	NT	NT		
24	NT	NT	NT		
25	0.60	0.18	94	0.63	0.26

Statistics

Assigned Value	0.548	0.090
Spike	0.799	0.040
Maximum acceptable conc**	0.963	
Robust Average	0.548	0.090
Median	0.510	0.068
Mean	0.558	
N	9	
Max.	0.8	
Min.	0.45	
Robust SD	0.108	
Robust CV	20%	

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


Kernel Density
Density
Result
Results: S1 - Trifluralin
Assigned Value = 0.548 ± 0.090 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
13 9 7 10 22 21 25 19 5 8 20 1 11 12 14 15 16 17 18 2 23 24 3 4 Md R.A. S


z-Scores: S1 - Trifluralin
Target Standard Deviation 0.082 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
13 9 7 10 22 21 25 19 5
-1.2 -1.2 -1.1 -0.6 -0.5 0.6 0.6 1.2 2.0

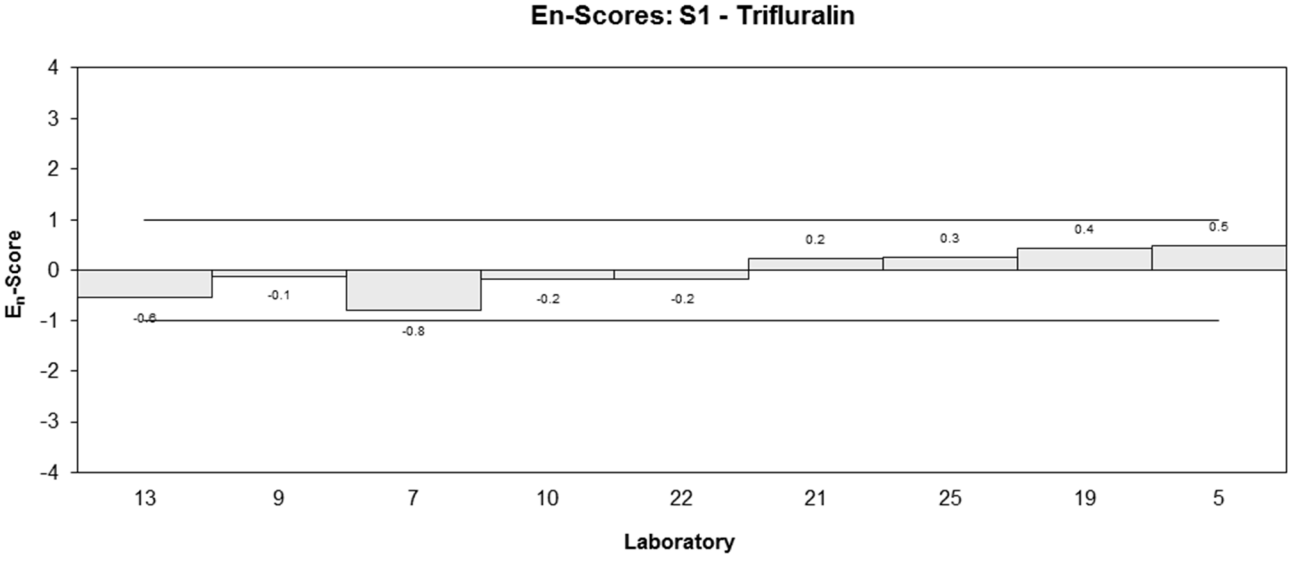

En-Scores: S1 - Trifluralin
En-Score
Laboratory
13 9 7 10 22 21 25 19 5
-0.6 -0.1 -0.8 -0.2 -0.2 0.2 0.3 0.4 0.5

Figure 5

Table 10

Sample Details

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

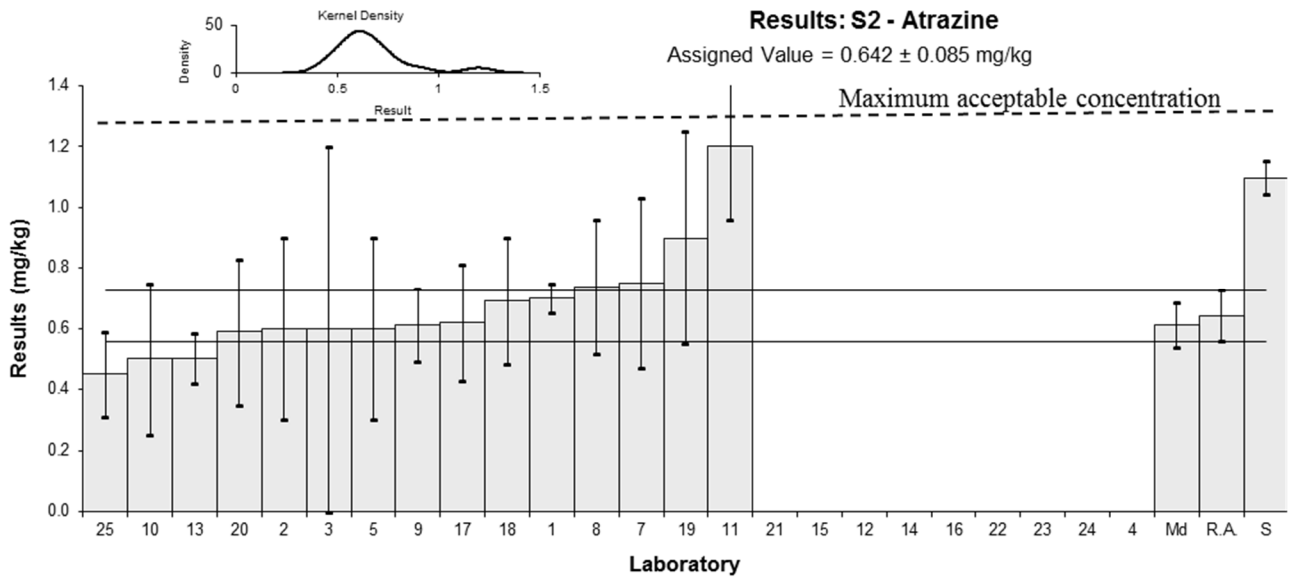
Participant Results

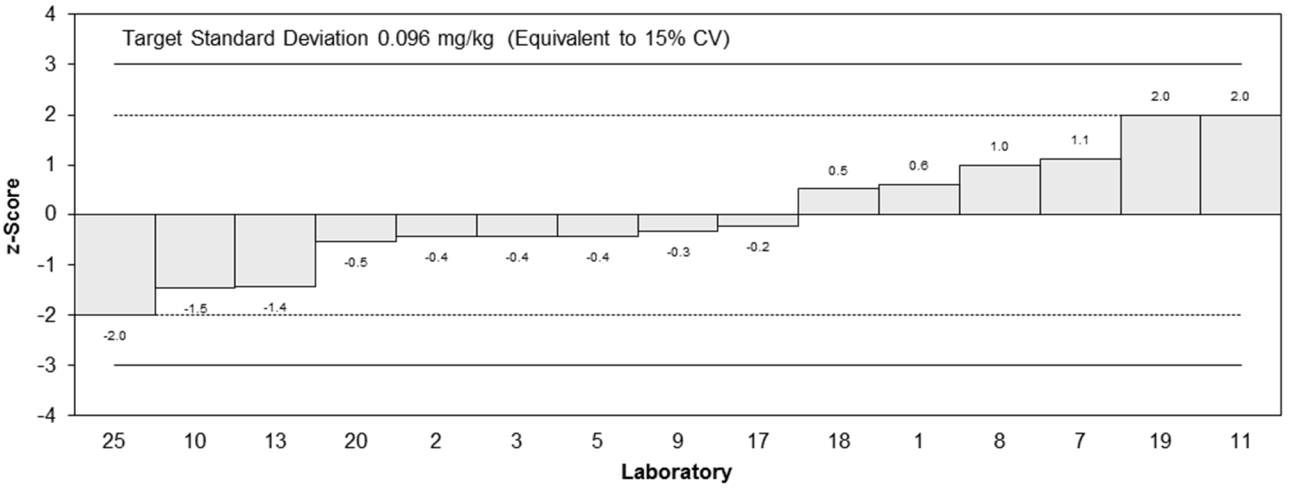
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.70	0.05	86	0.60	0.59
2	0.6	0.3	80-120	-0.44	-0.13
3	0.6	0.6	80-120	-0.44	-0.07
4	NT	NT	NT		
5	0.6	0.3	80-120	-0.44	-0.13
7	0.75	0.28	NR	1.12	0.37
8	0.737	0.222	NR	0.99	0.40
9	0.61	0.12	NR	-0.33	-0.22
10	0.5	0.25	NR	-1.47	-0.54
11**	1.2	0.24	65	2.00	1.00
12	NT	NT	NT		
13	0.504	0.082	NR	-1.43	-1.17
14	NT	NT	NT		
15	NR	NR	NR		
16	NT	NT	NT		
17	0.62	0.19	NR	-0.23	-0.11
18	0.692	0.208	83	0.52	0.22
19**	0.90	0.35	NR	2.00	0.72
20	0.59	0.24	94	-0.54	-0.20
21	<0.1	NR	NR		
22	NT	NT	NT		
23	NT	NT	NT		
24	NT	NT	NT		
25	0.45	0.14	NR	-1.99	-1.17

Statistics

Assigned Value	0.642	0.085
Spike	1.097	0.055
Maximum acceptable conc**	1.29	
Robust Average	0.642	0.085
Median	0.610	0.074
Mean	0.670	
N	15	
Max.	1.2	
Min.	0.45	
Robust SD	0.132	
Robust CV	21%	

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


Kernel Density
Density
Result
Results: S2 - Atrazine
Assigned Value = 0.642 ± 0.085 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
25 10 13 20 2 3 5 9 17 18 1 8 7 19 11 21 15 12 14 16 22 23 24 4 Md R.A. S


z-Scores: S2 - Atrazine
Target Standard Deviation 0.096 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
25 10 13 20 2 3 5 9 17 18 1 8 7 19 11
-2.0 -1.5 -1.4 -0.5 -0.4 -0.4 -0.4 -0.3 -0.2 0.5 0.6 1.0 1.1 2.0 2.0

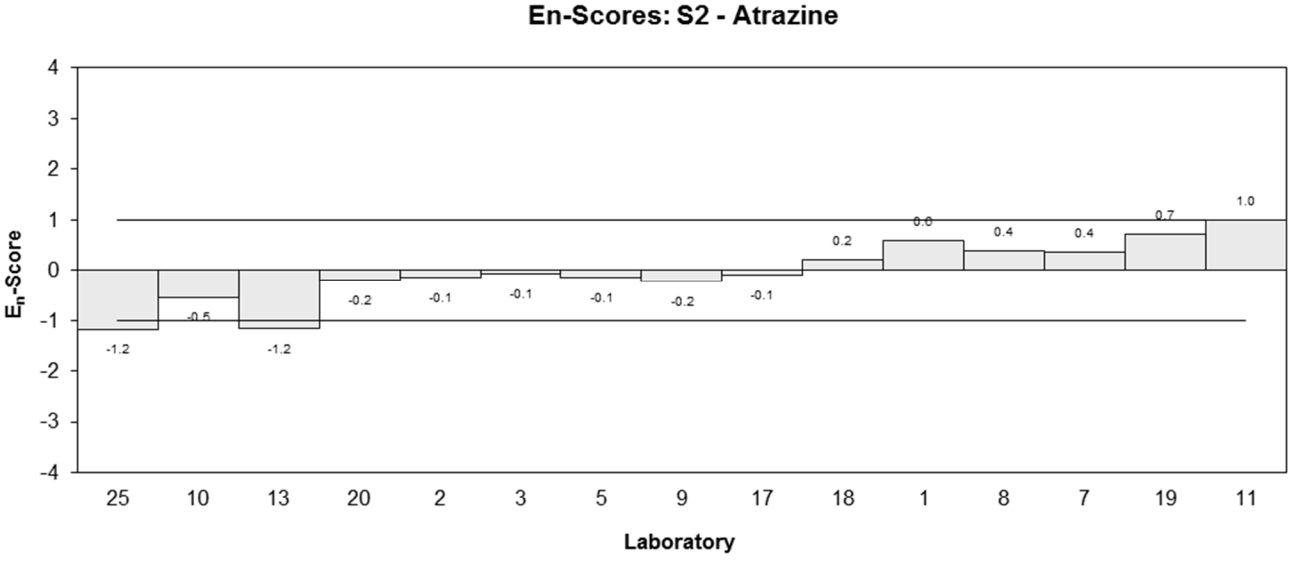

En-Scores: S2 - Atrazine
En-Score
Laboratory
25 10 13 20 2 3 5 9 17 18 1 8 7 19 11
-1.2 -0.5 -1.2 -0.2 -0.1 -0.1 -0.1 -0.2 -0.1 0.2 0.6 0.4 0.4 0.7 1.0

Figure 6

Table 11

Sample Details

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

Participant Results

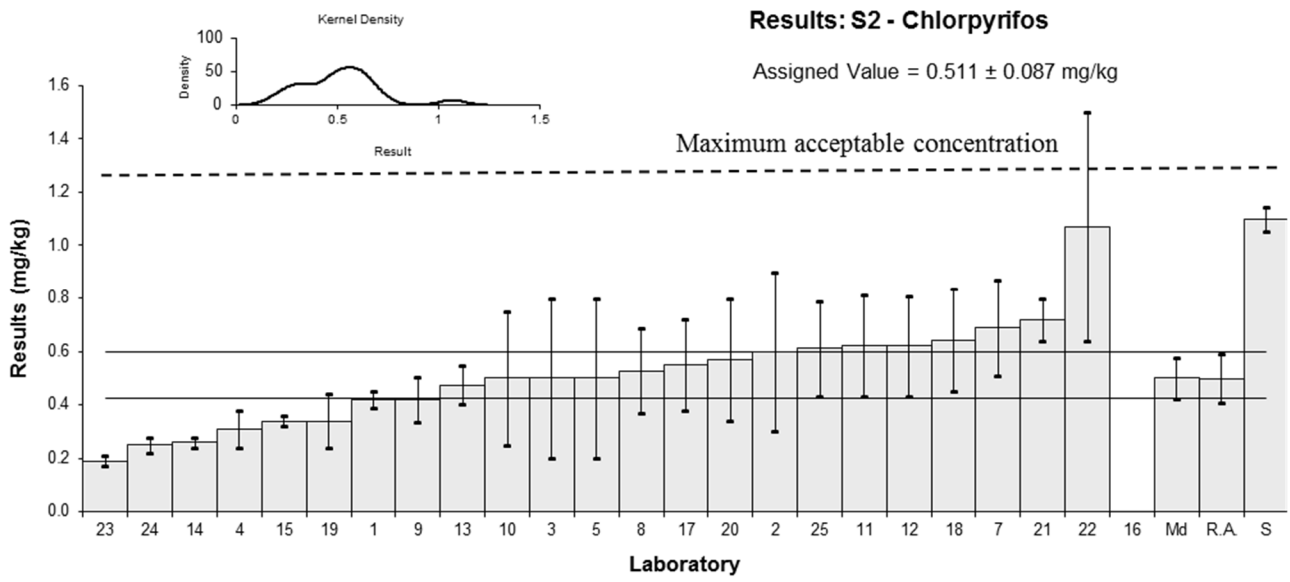
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.42	0.03	94	-1.19	-0.99
2	0.6	0.3	80-120	1.16	0.28
3	0.5	0.3	80-120	-0.14	-0.04
4	0.31	0.07	NR	-2.62	-1.80
5	0.5	0.3	80-120	-0.14	-0.04
7**	0.69	0.18	NR	2.00	0.90
8	0.528	0.158	NR	0.22	0.09
9	0.42	0.084	NR	-1.19	-0.75
10	0.5	0.25	NR	-0.14	-0.04
11	0.62	0.19	61	1.42	0.52
12	0.620	0.186	NR	1.42	0.53
13	0.474	0.071	NR	-0.48	-0.33
14	0.26	0.02	93	-3.27	-2.81
15	0.34	0.02	NR	-2.23	-1.92
16	NT	NT	NT		
17	0.55	0.17	NR	0.51	0.20
18	0.642	0.193	83	1.71	0.62
19	0.34	0.10	NR	-2.23	-1.29
20	0.57	0.23	100	0.77	0.24
21**	0.72	0.08	NR	2.00	1.00
22**	1.07	0.43	NR	2.00	1.00
23	0.19	0.019	157	-4.19	-3.60
24	0.25	0.03	93	-3.41	-2.84
25	0.61	0.18	NR	1.29	0.50

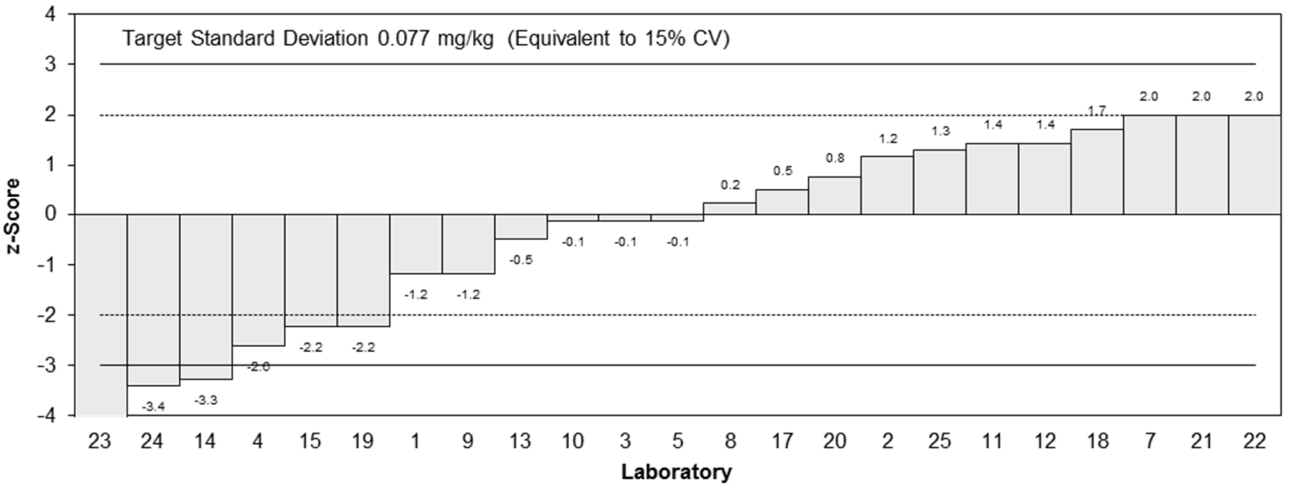
Statistics

Assigned Value*	0.511	0.087
Spike	1.097	0.045
Maximum acceptable conc**	1.251	
Robust Average	0.498	0.091
Median	0.500	0.077
Mean	0.510	
N	23	
Max.	1.07	
Min.	0.19	
Robust SD	0.175	
Robust CV	35%	

*Robust average excluding laboratory 23.

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


Kernel Density
Density
Result
Results: S2 - Chlorpyrifos
Assigned Value = 0.511 ± 0.087 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
23 24 14 4 15 19 1 9 13 10 3 5 8 17 20 2 25 11 12 18 7 21 22 16 Md R.A. S


z-Scores: S2 - Chlorpyrifos
Target Standard Deviation 0.077 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
23 24 14 4 15 19 1 9 13 10 3 5 8 17 20 2 25 11 12 18 7 21 22

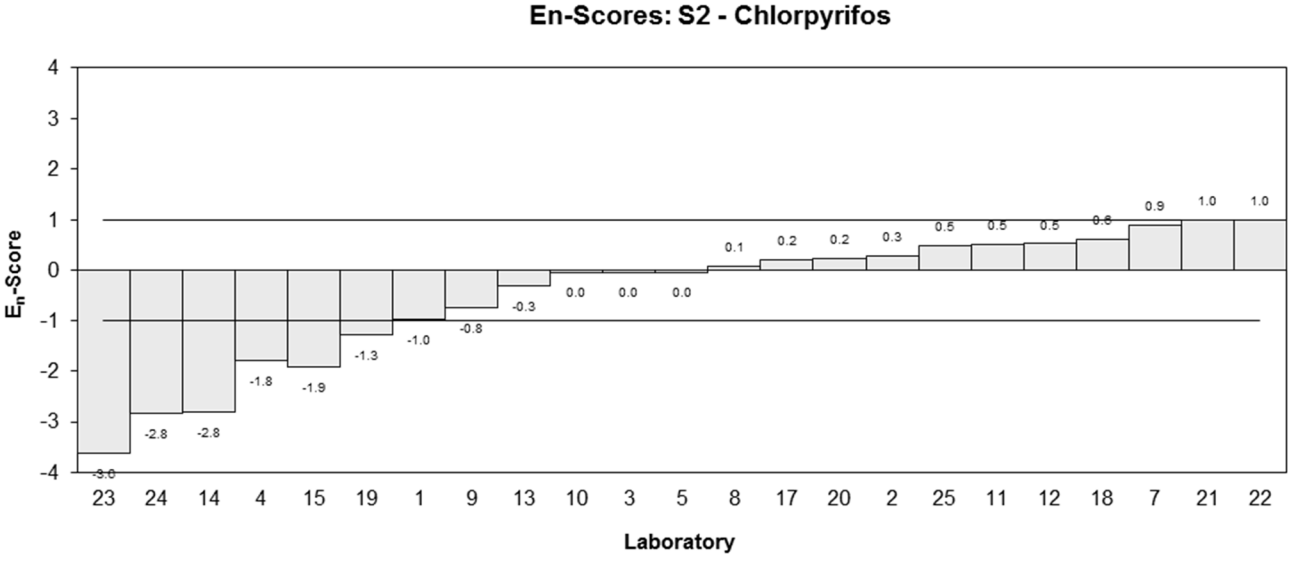

En-Scores: S2 - Chlorpyrifos
En-Score
Laboratory
23 24 14 4 15 19 1 9 13 10 3 5 8 17 20 2 25 11 12 18 7 21 22

Figure 7

Table 12

Sample Details

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

Participant Results

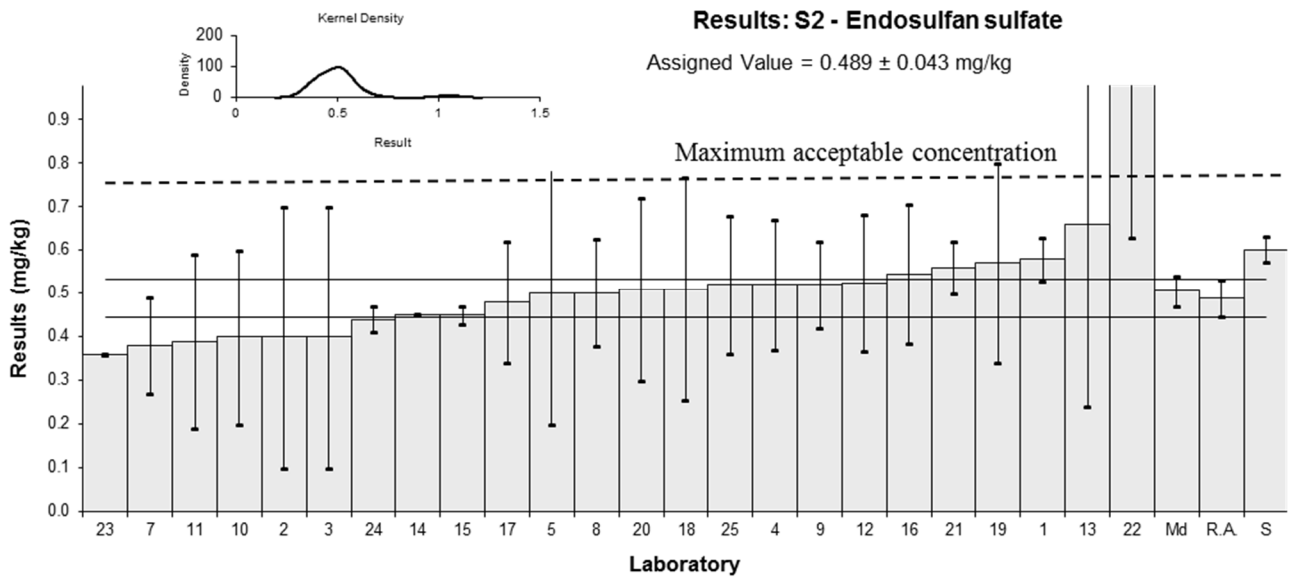
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.58	0.05	92	1.24	1.38
2	0.4	0.3	80-120	-1.21	-0.29
3	0.4	0.3	80-120	-1.21	-0.29
4	0.52	0.15	NR	0.42	0.20
5	0.5	0.3	80-120	0.15	0.04
7	0.38	0.11	NR	-1.49	-0.92
8	0.502	0.123	NR	0.18	0.10
9	0.52	0.10	NR	0.42	0.28
10	0.4	0.2	NR	-1.21	-0.44
11	0.39	0.20	64	-1.35	-0.48
12	0.525	0.158	NR	0.49	0.22
13**	0.66	0.42	NR	2.00	0.41
14	0.45	0.002	82	-0.53	-0.91
15	0.45	0.02	NR	-0.53	-0.82
16	0.544	0.16	90.1	0.75	0.33
17	0.48	0.14	NR	-0.12	-0.06
18	0.511	0.256	98	0.30	0.08
19	0.57	0.23	NR	1.10	0.35
20	0.51	0.21	96	0.29	0.10
21	0.56	0.06	NR	0.97	0.96
22	1.05	0.42	NR	7.65	1.33
23	0.36	0.0014	81	-1.76	-3.00
24	0.44	0.03	97	-0.67	-0.93
25	0.52	0.16	NR	0.42	0.19

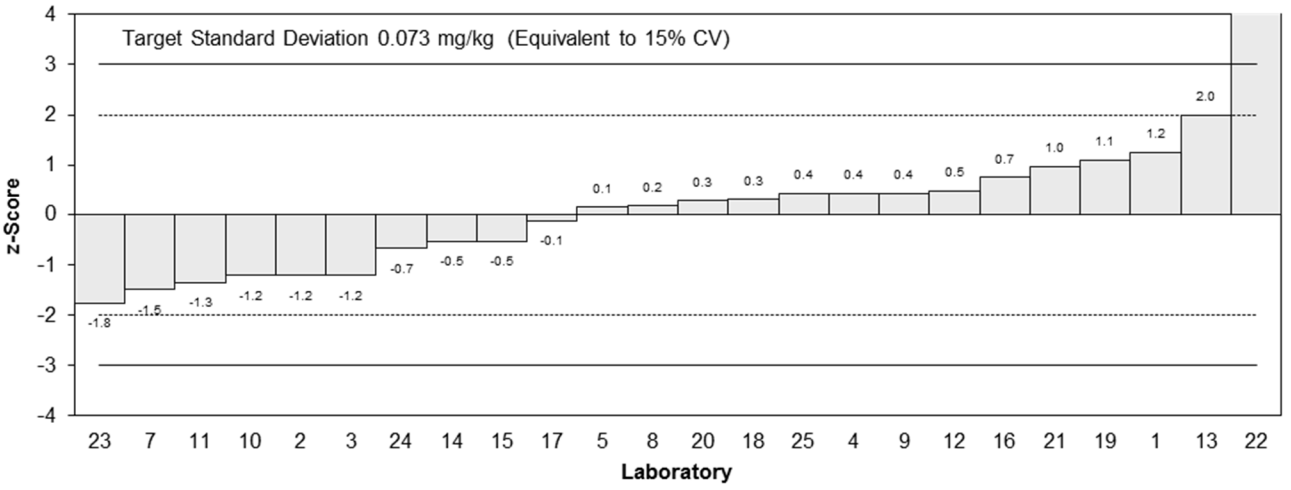
Statistics

Assigned Value*	0.483	0.043
Spike	0.602	0.030
Maximum acceptable conc**	0.748	
Robust Average	0.489	0.043
Median	0.506	0.035
Mean	0.509	
N	24	
Max.	1.05	
Min.	0.36	
Robust SD	0.084	
Robust CV	17%	

*Robust average excluding laboratory 22.

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


Kernel Density
Density
Result
Results: S2 - Endosulfan sulfate
Assigned Value = 0.489 ± 0.043 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
23 7 11 10 2 3 24 14 15 17 5 8 20 18 25 4 9 12 16 21 19 1 13 22 Md R.A. S


z-Scores: S2 - Endosulfan sulfate
Target Standard Deviation 0.073 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
23 7 11 10 2 3 24 14 15 17 5 8 20 18 25 4 9 12 16 21 19 1 13 22
-1.8 -1.5 -1.3 -1.2 -1.2 -1.2 -0.7 -0.5 -0.5 -0.1 0.1 0.2 0.3 0.3 0.4 0.4 0.4 0.5 0.7 1.0 1.1 1.2 2.0

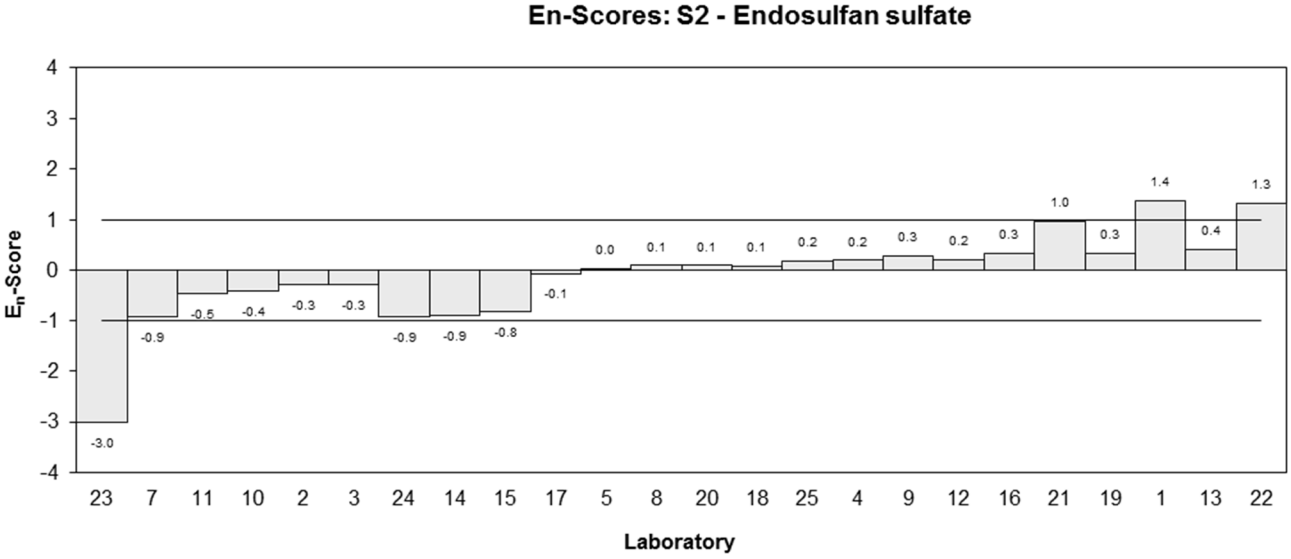

En-Scores: S2 - Endosulfan sulfate
En-Score
Laboratory
23 7 11 10 2 3 24 14 15 17 5 8 20 18 25 4 9 12 16 21 19 1 13 22
-3.0 -0.9 -0.5 -0.4 -0.3 -0.3 -0.9 -0.9 -0.8 -0.1 0.0 0.1 0.1 0.1 0.2 0.2 0.3 0.2 0.3 1.0 0.3 1.4 0.4 1.3

Figure 8

Table 13

Sample Details

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

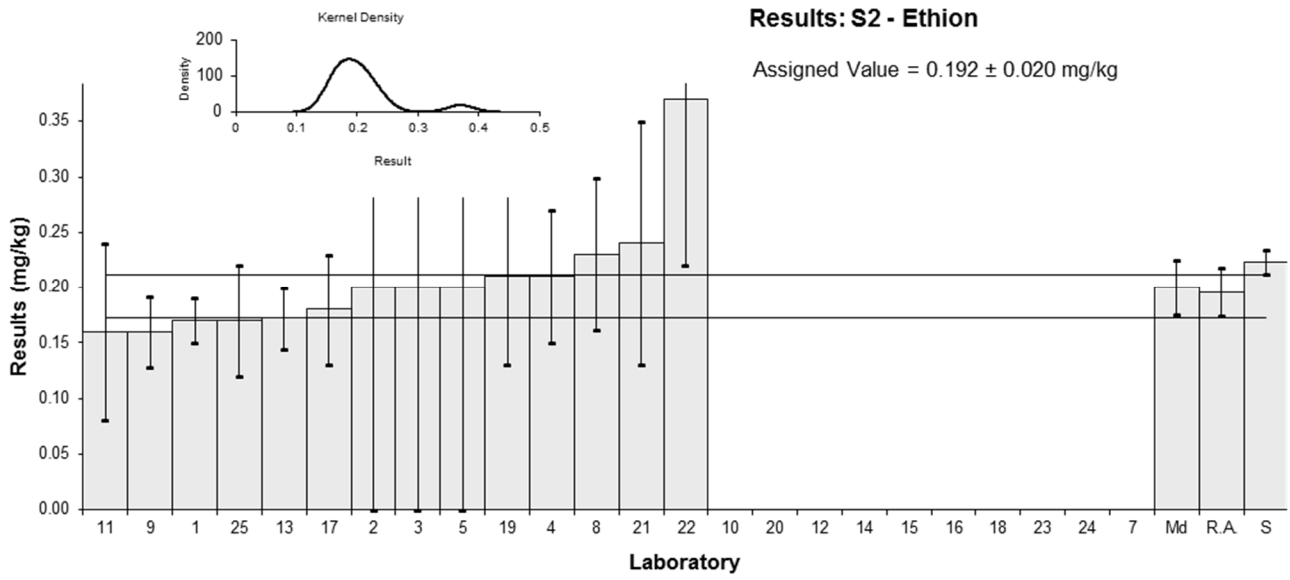
Participant Results

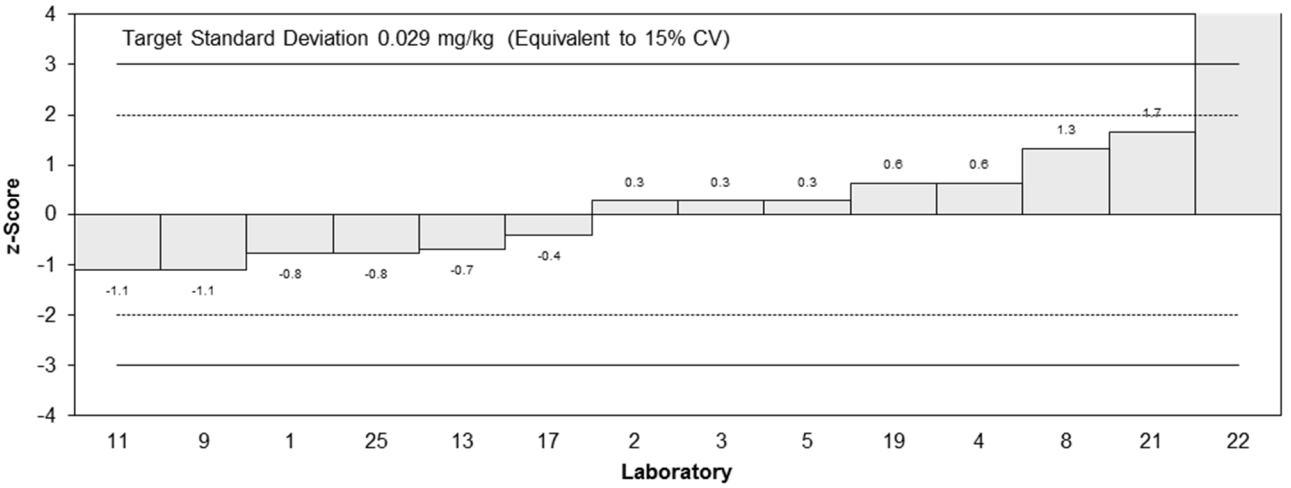
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.17	0.02	95	-0.76	-0.78
2	0.2	0.2	80-120	0.28	0.04
3	0.2	0.2	80-120	0.28	0.04
4	0.21	0.06	NR	0.62	0.28
5	0.2	0.2	80-120	0.28	0.04
7	NT	NT	NT		
8	0.230	0.069	NR	1.32	0.53
9	0.16	0.032	NR	-1.11	-0.85
10	<0.2	NR	NR		
11	0.16	0.08	37	-1.11	-0.39
12	<0.4	0.12	NR		
13	0.172	0.028	NR	-0.69	-0.58
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	0.18	0.05	NR	-0.42	-0.22
18	NT	NT	NT		
19	0.21	0.080	NR	0.62	0.22
20	<0.2	NR	NR		
21	0.24	0.11	NR	1.67	0.43
22	0.37	0.15	NR	6.18	1.18
23	NT	NT	NT		
24	NT	NT	NT		
25	0.17	0.05	NR	-0.76	-0.41

Statistics

Assigned Value	0.192	0.020
Spike	0.223	0.011
Robust Average	0.196	0.022
Median	0.200	0.025
Mean	0.205	
N	14	
Max.	0.37	
Min.	0.16	
Robust SD	0.033	
Robust CV	17%	

*Robust average excluding laboratory 22.


Kernel Density
Density
Result
Results: S2 - Ethion
Assigned Value = 0.192 ± 0.020 mg/kg
Results (mg/kg)
Laboratory
11 9 1 25 13 17 2 3 5 19 4 8 21 22 10 20 12 14 15 16 18 23 24 7 Md R.A. S


z-Scores: S2 - Ethion
Target Standard Deviation 0.029 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
11 9 1 25 13 17 2 3 5 19 4 8 21 22
-1.1 -1.1 -0.8 -0.8 -0.7 -0.4 0.3 0.3 0.3 0.6 0.6 1.3 1.7

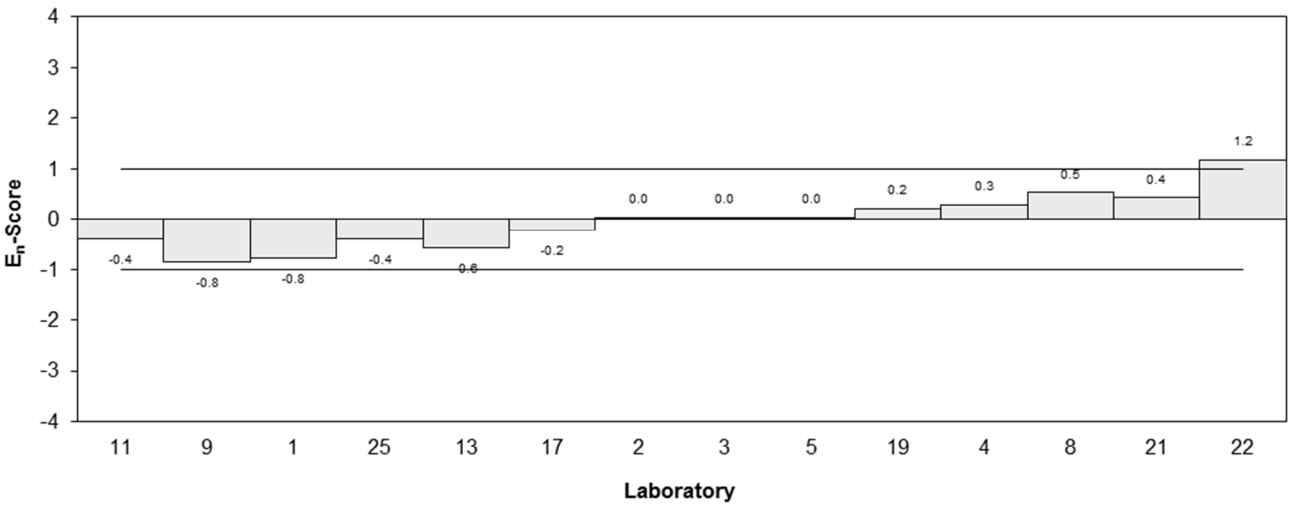

En-Scores: S2 - Ethion
En-Score
Laboratory
11 9 1 25 13 17 2 3 5 19 4 8 21 22
-0.4 -0.8 -0.8 -0.4 -0.6 -0.2 0.0 0.0 0.0 0.2 0.3 0.5 0.4 1.2

Figure 9

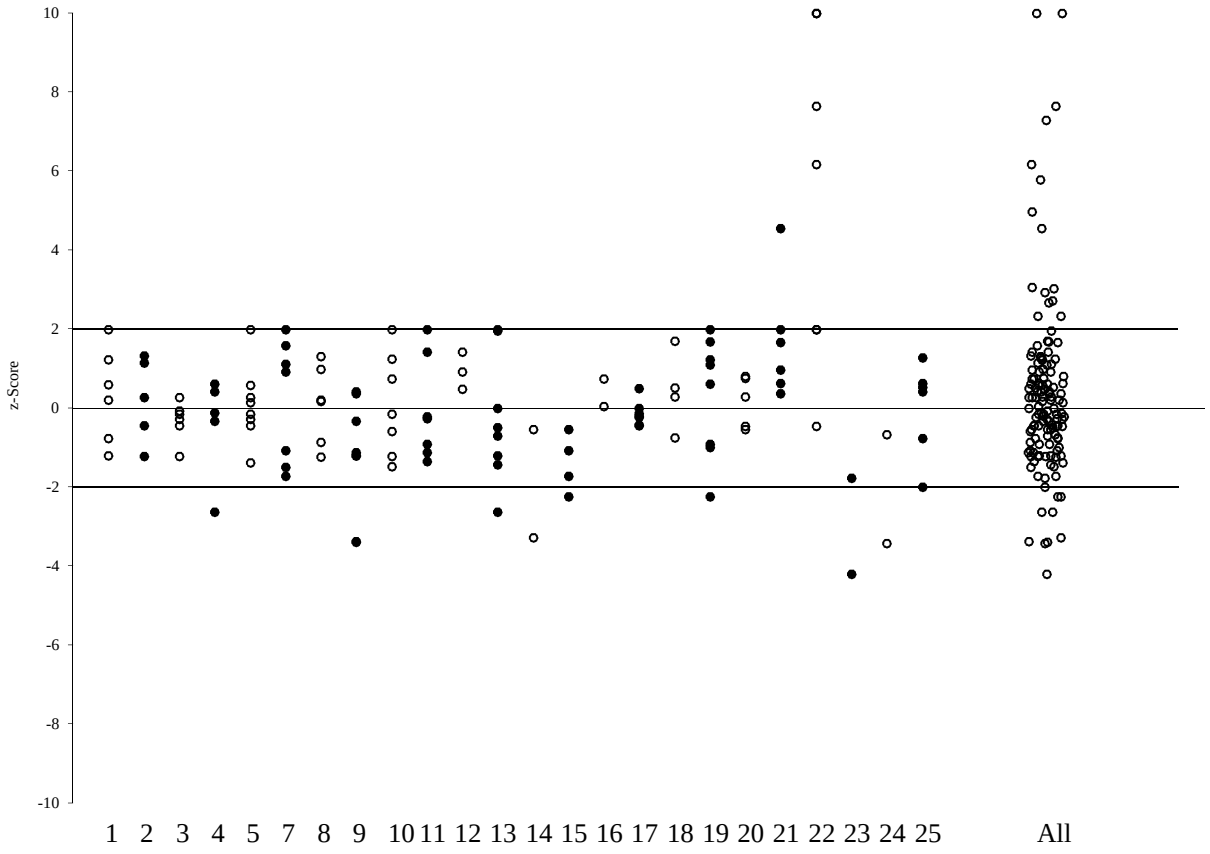


Figure 10 z-Score Dispersal by Laboratory

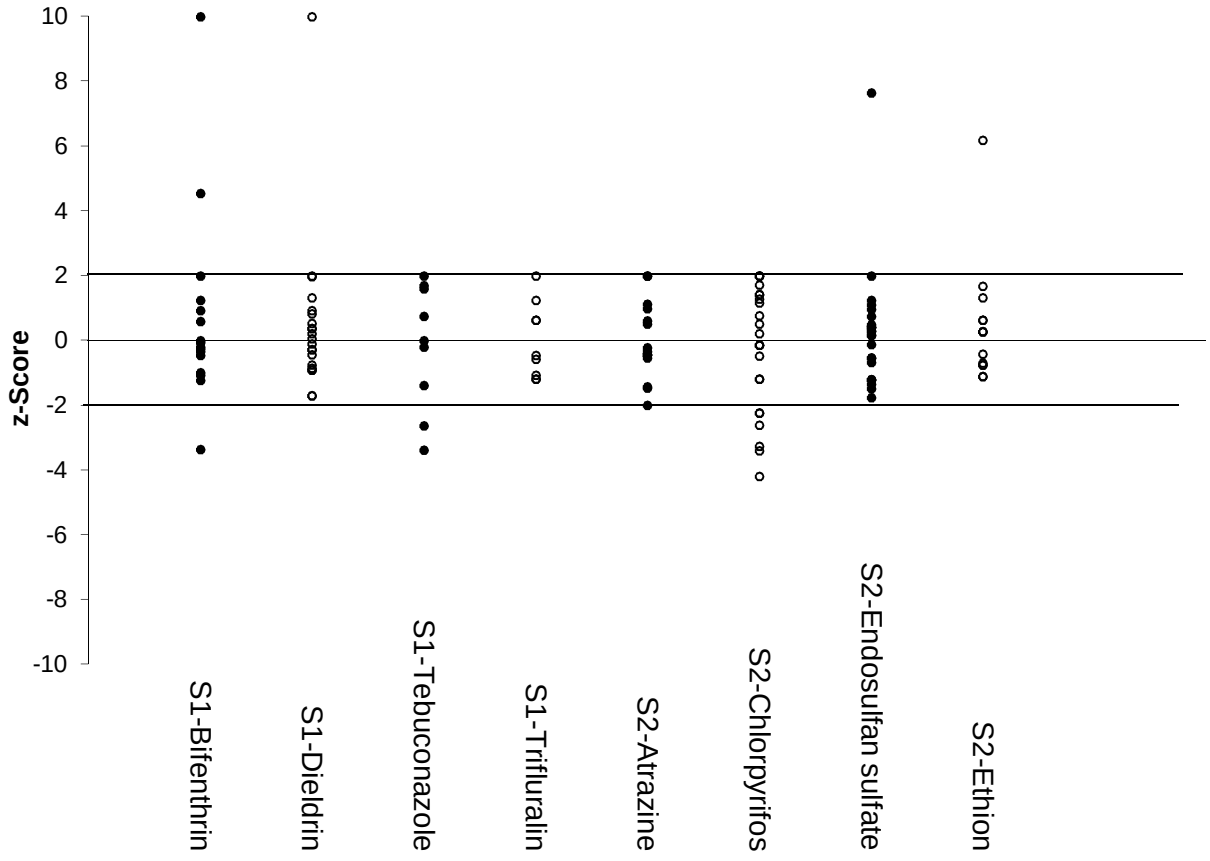


Figure 11 z-Score Dispersal by Analyte

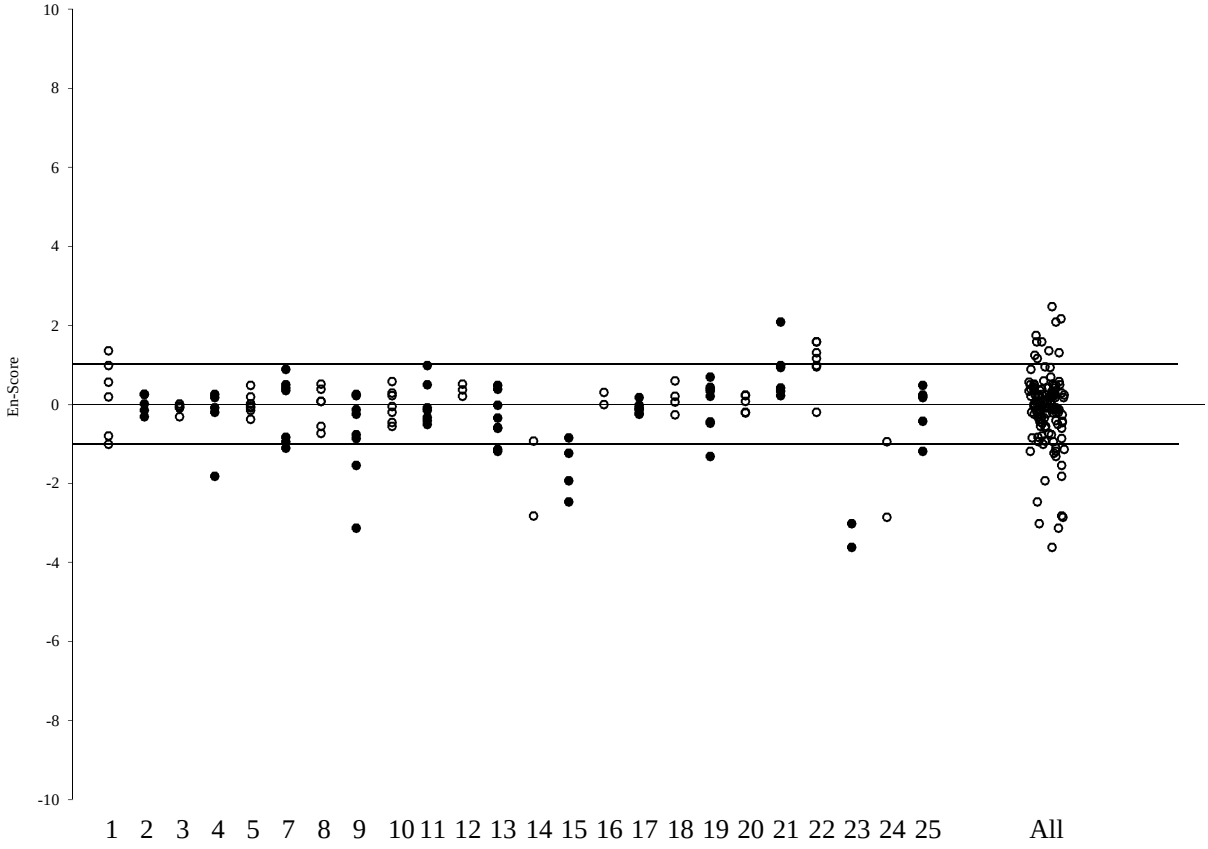


Figure 12 E_n-Score Dispersal by Laboratory

6 DISCUSSION OF RESULTS

6.1 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'.[10] The calculation of the expanded uncertainty for the robust average of atrazine in Sample S2 is presented in Appendix 3.

All assigned values were within the range 47-86% 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]

Assigned value for Chlorpyrifos in Sample S2 was significantly lower than the spiked concentration. However there was good consensus amongst the participants' results and an assigned value was set.

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.

Analyte	Sample	Spiked Concentration (mg/kg)	Assigned Value (mg/kg)	Assigned/ spike
Bifenthrin	S1	1.300	1.010	78%
Dieldrin	S1	0.551	0.417	76%
Tebuconazole	S1	0.947	0.630	67%
Trifluralin	S1	0.799	0.548	69%
Atrazine	S2	1.097	0.642	59%
Chlorpyrifos	S2	1.097	0.511	47%
Endosulfan Sulfate	S2	0.602	0.483	80%
Ethion	S2	0.223	0.192	86%

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 (Table 4).

It is a requirement of the ISO Standard 17025[7] 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.'

All numeric results were reported with an associated estimate of expanded measurement uncertainty.

The magnitude of the reported expanded uncertainties was within the range 0.4% to 200% of the reported value. Twenty were less than 15% relative, which the study coordinator believes is unrealistically small for a routine pesticide residue measurement.

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

Some participants attached an estimate of the expanded measurement uncertainty to a result reported as less than their limit of reporting. 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 0.692 ± 0.208 mg/kg better report 0.69 ± 0.21 mg/kg)[8].

6.3 z-Score

A target standard deviation equivalent to 15% coefficient of variation (CV) was used to calculate z-scores. The between laboratory coefficient of variation predicted by the modified Horwitz equation[10] 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 CV, %)
S1	Bifenthrin	1.010	16	15
S1	Dieldrin	0.417	18	15
S1	Tebuconazole	0.630	17	15
S1	Trifluralin	0.548	18	15
S2	Atrazine	0.642	17	15
S2	Chlorpyrifos	0.511	18	15
S2	Endosulfan Sulfate	0.483	18	15
S2	Ethion	0.192	21	15

To account for possible bias in the consensus values due to laboratories using inefficient extraction techniques, z-scores were adjusted for all analytes in sample S1, as well as atrazine, chlorpyrifos and endosulfan sulfate in S2 so that 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 10 and by analyte in Figure 11.

Of the 131 results for which z-scores were calculated, 117 (89%) returned a satisfactory z-score of $|z| \leq 2$.

Laboratory **5** returned satisfactory z-scores for all analytes for which z-scores were calculated.

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.

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 131 calculated E_n-scores, 110 (84%) were satisfactory with $|E_n| \leq 1$.

Laboratory **5** returned satisfactory E_n-scores for all analytes for which E_n-scores were calculated.

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

6.5 False Negatives and NT Results

Five 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)
24	S1	Dieldrin	NR
8	S1	Trifluralin	< 0.5
20	S1	Trifluralin	< 0.5
15	S2	Atrazine	NR
21	S2	Atrazine	< 0.1

Of 192 possible results submitted, 53 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 **12** reported < 0.4 mg/kg for ethion in Sample S2. This has not been counted as a false negative.

6.6 Reporting of Pesticides Not Spiked Into the Soil

One laboratory 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 (%)
13	S2	Bifenthrin	0.0032	0.0021	NR
13	S2	Beta-Endosulfan	0.0026	0.0012	NR

6.7 Participants' Methods

A variety of analytical methods were used for each group of analytes (Table 3). Dichloromethane, acetone, hexane, acetonitrile, ethyl acetate, were used as extraction solvents. Florisil and SPE clean-ups were used.

Instrumental techniques included gas chromatography (GC) coupled with MS(MS) or selective detector ECD and liquid chromatography (LC) with MS(MS). No correlation between results and method used by participants' was evident.

6.8 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 twelve participants in the range of 37-157%. Two laboratories **9** and **11** corrected results for recovery.

6.9 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.

Sixteen laboratories reported using certified standards. The following were listed: Sigma Aldrich, Accustandard, Dr Ehrenstorfer, Certiprep, Supelco, OCP-CRM847-50G and OPP-CRM47908.

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]

6.10 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 2018 is presented in Figure 13.

To enable direct comparison, the target standard deviation used to calculate z-scores has been kept constant at 15% CV. The proportion of satisfactory z-scores over 9 years on average is 72%. 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 73%. The increase in percentage satisfactory E_n-scores suggests that laboratories are reporting more realistic estimates of measurement uncertainty.

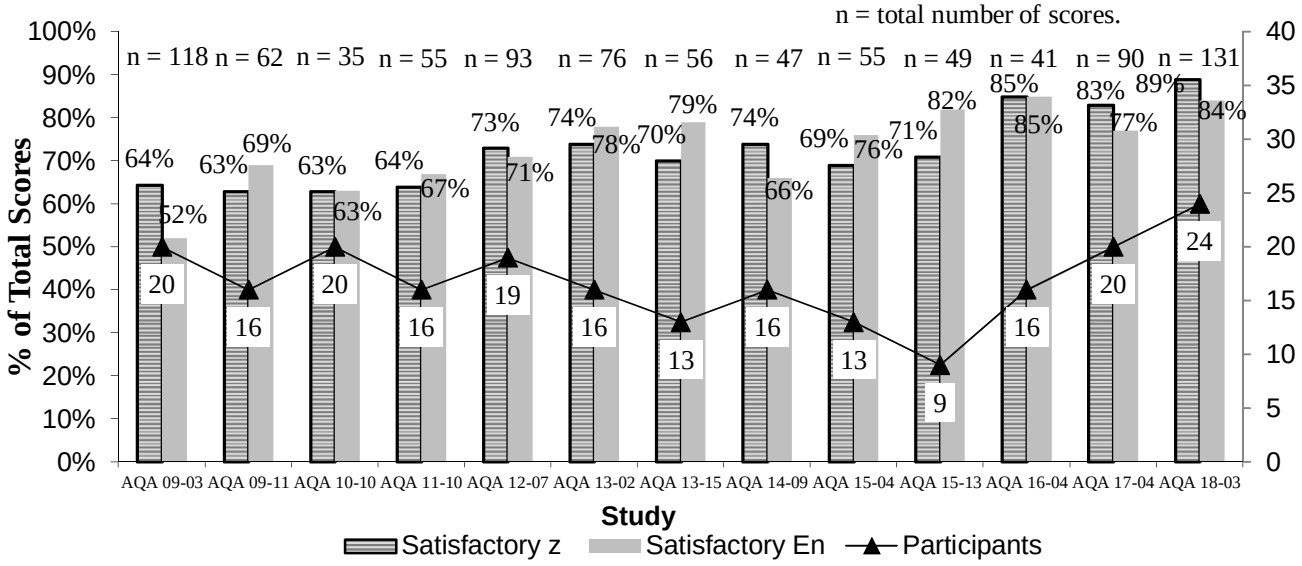


Figure 13 Summary of participation in Pesticides in Soil studies since 2009

7 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 6 April 2017, <http://www.comlaw.gov.au/details/F2013C00288/html/volume_2>

[6] NMI 2016, *AQA 16-04 Pesticides in Soil*, viewed 19 June 2017, <http://www.measurement.gov.au/Publications/ProficiencyStudyReports/Pages/default.aspx>

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

[8] Eurachem 2012, *Quantifying Uncertainty in Analytical Measurement,* 3rd edition, viewed 10 May 2017, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[9] ISO/IEC 98-3 2008, *Uncertainty of measurement – Part 3 Guide to the expression of uncertainty in measurement.*

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

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

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

[13] Racke, K. D.; Steele, K. P.; Yoder, R. N.; Dick, W. A.; Avidov, E. 1996. 'Factors Affecting the Hydrolytic Degradation of Chlorpyrifos in Soil', *J. Agric. Food. Chem.*, vol 44, pp 1582-1592

[14] Chai, L. K.; Wong, M. H.; Hansen, H. C. B. 2013. 'Degradation of chlorpyrifos in humid tropical soils', *Journal of Environmental Management*, vol 125, pp 28-32

[15] Gebremariam, S. Y.; Beutel, M. W.; Yonge, D. R.; Flury, M.; Harsh, J. B. 2012. 'Adsorption and Desorption of Chlorpyrifis to Soils and Sediments', *Reviews of Environmental Contamination and Toxicology*, vol 215, pp 123-175

[16] Baskaran, S.; Kookana, R. S.; Naidu, R. 2003. 'Contrasting behaviour of chlorpyrifos and its primary metabolite, TCP (3,5,6-trichloro-2-pyridinol), with depth in soil profiles', *Australian Journal of Soil Research*, vol 41, pp 749-760

[17] Francioso, O.; Bak, E.; Rossi, N.; Sequi, P. 1992. ‘Sorption of atrazine and trifluralin in relation to the physio-chemical characteristics of selected soils’, *The Science of the Total Environment*, vol 123/124, pp 503-512

[18] Spark, K. M.; Swift, R. S. 2002. ‘Effect of soil composition and dissolved organic matter on pesticide sorption’, *The Science of the Total Environment*, vol 298, pp 147-161

[19] Getzin, L. W. 1985. ‘Factors Influencing the Persistence and Effectiveness of Chlorpyrifos in Soil’, *Journal of Economical Entomology*, vol 78, pp 412-418

[20] Huang, Y.; Liu, Z.; He, Y.; Li, Y. 2015. ‘Impact of soil primary size fractions on sorption and desorption of atrazine on organo-mineral fractions’, *Environmental Science and Pollution Research International*, vol 22, pp 4396-4405

APPENDIX 1 – PARTICIPATING LABORATORIES

AMAL Analytical VIC	Analytica Laboratories Ltd NEW ZEALAND
Analytical Reference Laboratory Pty Ltd WA	Analytical Services TAS
Baguio Pesticide Analytical Laboratory PHILIPPINES	Cagayan de Oro Pesticide Analytical Laboratory PHILIPPINES
Cebu Pesticides Analytical Laboratories PHILIPPINES	CHEMCENTRE WA
Davao Pesticide Analytical Laboratory PHLIPPINES	Envirolab Services NSW
Envirolab Services VIC	Eurofins | mgt NSW
Eurofins | mgt VIC	Hill Laboratories NEW ZEALAND
MPL Laboratories WA	National Measurement Institute NSW
Office of Environment and Heritage, Department of Premier and Cabinet Environmental Protection Science NSW	Pesticide Residue Laboratory, Pesticide Research Group Agricultural Production Science Research and Development Office (APSRDO) THAILAND
Pesticides Analytical Laboratory Section Bureau of Plant Industry – Quezon PHILIPPINES	SGS Environmental Services NSW
SGS Environmental Services Newburn WA	Sydney Environmental & Soil Laboratory NSW
Sydney Water Corporation NSW	Symbio Alliance QLD
Watercare Services Limited NEW ZEALAND	

APPENDIX 2 - SAMPLE PREPARATION AND HOMOGENEITY TESTING

Sample Preparation

Two sets of soil samples were prepared. One using dried, ground and sieved Menangle topsoil purchased from a Sydney supplier and the second sample using dried, ground and sieved clay soil with a lower TOC obtained from a pile of clay in country 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 suspension along with 20mL of Milli-Q water to minimise the amount of resultant dust. The solvent was allowed to evaporate in a fume cupboard. The Menangle topsoil dried well and was able to be divided using Retsch sample divider and dispensed into 65mL glass jars. The clay failed to dry overnight so it was placed in a Pyrex tray in the fume cupboard and turned regularly. The dry material was forced through an 850 µm sieve to break the large particles, divided and dispensed into 65mL glass jars.

The samples were prepared in February 2018 and had been stored in a refrigerator at 4^{o}C.

Forty bottles of each of Sample S1 and Sample S2 were prepared.

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.

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 3 - 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:

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

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 atrazine in Sample S2 was calculated (Table 18).

Table 18 Uncertainty estimate for atrazine in Sample S2

No. results (p)	15
Robust Average	0.6422 mg/kg
$S_{rob\ av}$	0.1323 mg/kg
$u_{rob\ av}$	0.0427 mg/kg
k	2
$U_{rob\ av}$	0.0854 mg/kg

The robust average for atrazine in Sample S2 is 0.642 ± 0.085 mg/kg.

APPENDIX 4 – SUMMARY OF ATRAZINE, ENDOSULFAN SULFATE AND CHLORPYRIFOS RECOVERIES IN PREVIOUS STUDIES

A4.1 Atrazine and Chlopyrifos

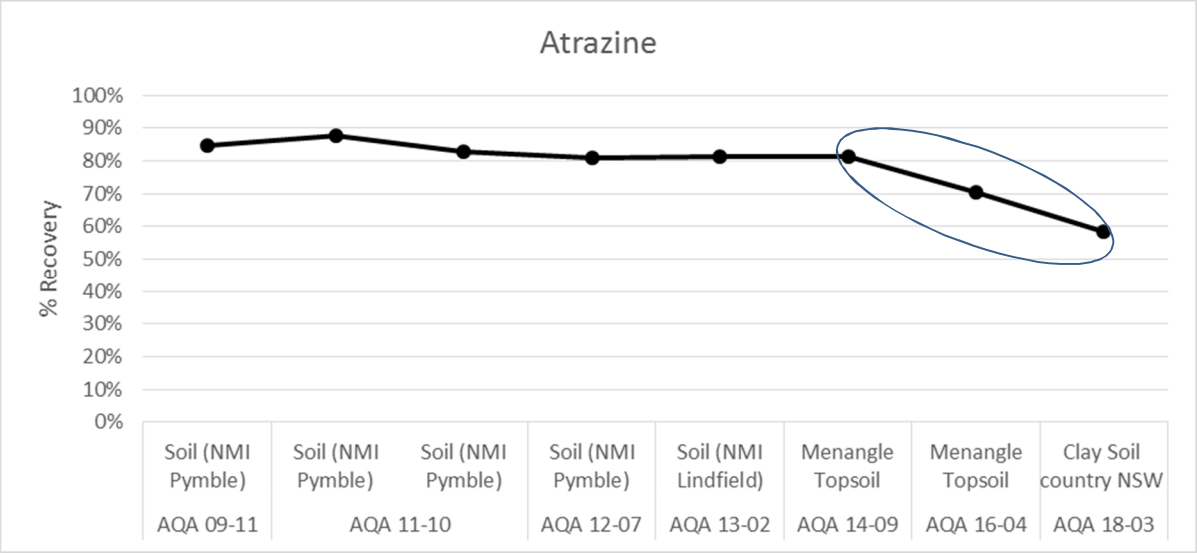


Figure 14 Atrazine recoveries in different soils in previous studies.

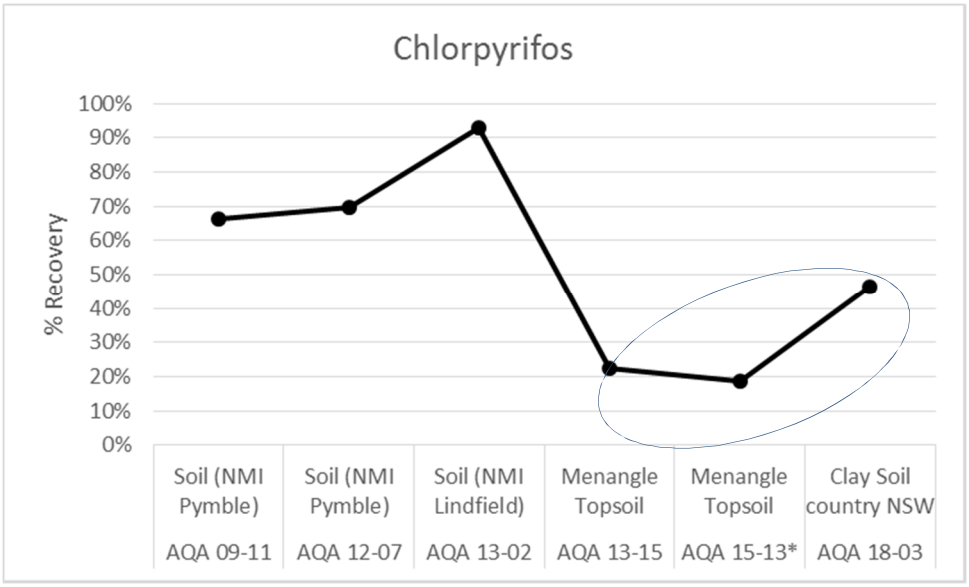


Figure 15 Chlorpyrifos recoveries in different soils in previous studies

As Figures 14 and 15 shows, the use of Menangle Topsoil and a clay soil emphasises how the nature of the soil matrix can affect the recovery of certain pesticides. Possible reasons for the decline in recovery in more recent studies (blue) include the high organic matter/carbon content in the Menangle Topsoil and the much smaller particle size of the clay soil, both of which can contribute to greater adsorption of pesticides such as atrazine onto the soil.[17, 18, 20]

In this study, chlorpyrifos was spiked in clay soil and an improved average recovery compared to Menangle Topsoil was observed, which might be attributable to the lower organic matter/carbon content.

A4.2 Endosulfan Sulfate

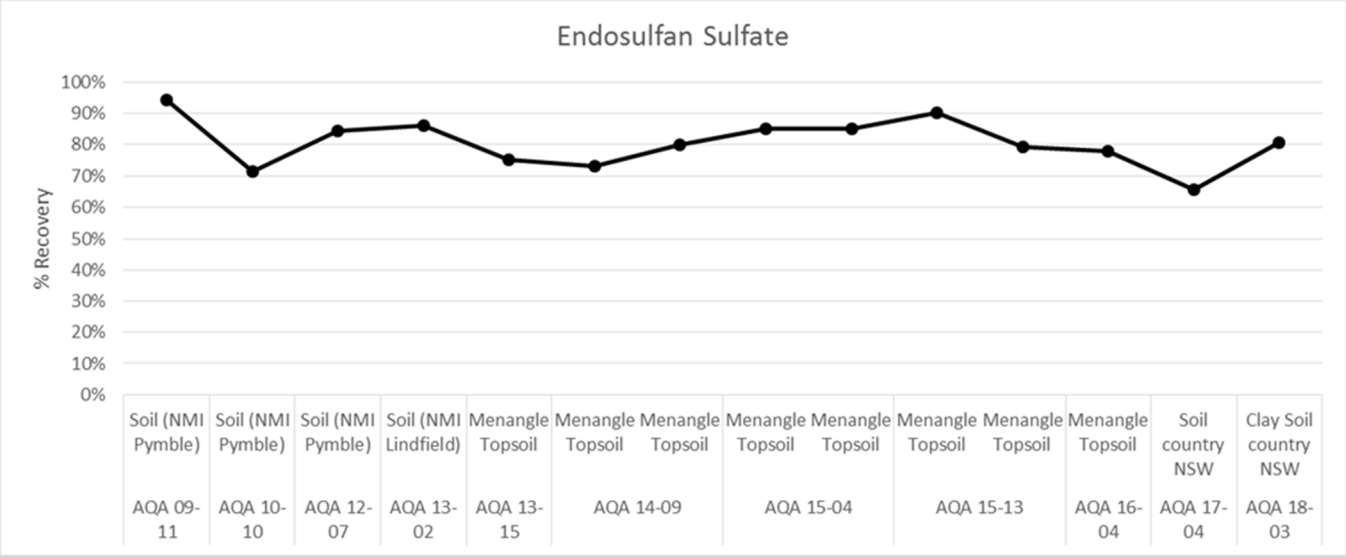


Figure 16 Endosulfan sulfate recoveries in different soils in previous studies

Figure 16 indicates that endosulfan sulfate recovery has been largely consistent across studies and soil types.

APPENDIX 5 - 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