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National Measurement Institute

Proficiency Test Report
AQA 19-14
Pesticides in Water

February 2020

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

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

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Accredited for compliance with ISO/IEC 17043

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SUMMARY

AQA 19-14 commenced in October 2019. Seventeen laboratories registered to participate and all submitted results.

The sample set consisted of three water samples. Samples were prepared in the NMI North Ryde laboratory using surface water from Browns Waterhole in the Turramurra area of Sydney.

Of a possible 170 numeric results a total of 81 (48%) were submitted.

Traceability: Assigned values were the consensus of participants' results, so although expressed in SI units, metrological traceability of the assigned values has not been established.

The outcomes of the study were assessed against the aims as follows:

- *To assess participant laboratories' identification and measurement of environmentally significant pesticides in water.*

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

Of 65 results for which z-scores were calculated, 47 (72%) returned a satisfactory score of $|z| \leq 2$.

Of 65 results for which E_n-scores were calculated, 49 (75%) returned a satisfactory score of $|E_n| \leq 1$.

Laboratory **15** returned satisfactory z-scores and E_n-scores for all seven analytes for which scores were calculated.

No results reported by Laboratory **14** returned a satisfactory z-score or E_n-score.

Five laboratories did not report analytes for which they tested and that were present in the test samples (Table 17, total of 10 results).

Thirteen laboratories reported results for analytes not added to the test samples (Table 18, total of 29 results).

- *To evaluate the laboratories' methods for the measurement of trace pesticides in water.*

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

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

Of 81 numeric results reported, 78 (96%) were reported with an expanded measurement uncertainty.

The magnitude of reported uncertainties was within the range of 2.4% to 64%.

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 interlaboratory 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, anions, and inorganic analytes in soil, water, food and pharmaceuticals;
- PFAS in biota, soil and water;
- controlled drug assay;
- allergens in food; and
- folic acid in flour.

1.2 Study Aims

The aims of the study were to:

- assess participant laboratories' identification and measurement of environmentally significant pesticides in water;
- evaluate the laboratories' methods for the measurement of trace pesticides in water; and
- develop the practical application of traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates.

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

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO 17043[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[4] This study falls within the scope of NMI's accreditation as a proficiency testing provider.

2 STUDY INFORMATION

2.1 Selection of Pesticides and Matrices

A list of possible analytes for Samples S1 and S2 are presented in Table 1. Sample S3 was spiked with AMPA and glyphosate. The spiked concentrations are presented in Table 2.

The pesticides, and spiked concentrations used in this study were selected with consideration to:

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

Table 1 List of Possible Analytes for Samples S1 and S2

Aldrin	Dieldrin	Lindane
Atrazine	Diuron	Malathion
Bifenthrin	alpha-Endosulfan	Methomyl
Chlordane	beta-Endosulfan	Metsulfuron-methyl
Chlorfenvinphos	Endosulfan sulfate	Molinate
Chlorpyrifos	Ethion	Parathion
Cypermethrin	Fenitrothion	Parathion-methyl
Diazinon	Fenthion	Permethrin
p,p'-DDD	Fenvalerate	Prothiofos
p,p'-DDE	Heptachlor	Simazine
p,p'-DDT	Heptachlor epoxide	Trifluralin
Total DDT	Hexachlorobenzene	

Table 2 Formulated Concentrations of Test Samples

Sample S1	Spike (µg/L)	Uncertainty (µg/L)*
cis-Chlordane	24.8	1.2
Diuron	2.95	0.15
Endosulfan sulfate	4.02	0.20
Molinate	8.93	0.45
Sample S2		
Ethion	5.01	0.25
Methomyl	10.6	0.5
Metsulfuron-methyl	3.59	0.18
Simazine	10.0	0.5
Sample S3		
AMPA	32.0	1.6
Glyphosate	18.0	0.9

*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	18 October 2019
Samples dispatched	12 November 2019
Results due	09 December 2019
Interim report issued	06 January 2020

2.3 Participation

Participation was as follows:

Invited	106
Participated:	17
Submitted results	17

2.4 Test Sample Preparation and Homogeneity Testing

The preparation of the study samples is described in Appendix 1.

The samples were spiked, mixed and packaged using a process that has been demonstrated to produce homogeneous samples for previous NMI proficiency tests of pesticides in water. No homogeneity testing was conducted, and results of the study 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. Assigned values (or robust averages) of participants' results were within 72 to 129% of the spiked concentration, which provides good support for the stability of these analytes in the test samples.

2.6 Laboratory Code

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

2.7 Sample Storage, Dispatch and Receipt

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

The following items were packaged with the samples:

- a covering letter which included a description of the test samples and instructions for participants; and
- a form for participants to confirm the receipt and condition of the test 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 expressed as if reporting to a client (i.e. corrected for recovery or not, according to your standard procedure). This figure will be used in all statistical analysis in the study report.

- Report results in units of **µg/L**.
- For each analyte in each sample report the associated expanded uncertainty (e.g. 0.50 ± 0.02 µg/L).
- 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 (e.g. uncertainty budget, repeatability precision, long term result variability).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Please **complete the method details** as required by the Methodology sheet.
- Return the completed results sheet by e-mail (proficiency@measurement.gov.au).
- **Please return the completed results sheet by 9 December 2019. Late results may not be included in the study report.**

2.9 Interim Report

An interim report tabling results and reported uncertainties was emailed to all participants on 6 January 2020.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Participants' Test Method Summaries

Participants were requested to provide information about their test methods. This is transcribed in Appendix 4.

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 3).

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
1	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control Samples – SS	Recoveries of SS Standard Purity	ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples – RM Duplicate Analysis	CRM Instrument Calibration	Nata Technical Note 33
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – SS	Recoveries of SS	Nata Technical Note 33
4	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	CRM Standard Purity	Nata Technical Note 33
5	Control Charts	Control Samples – SS	Recoveries of SS	Nata Technical Note 33
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis	Recoveries of SS	Eurachem/CITAC Guide
7	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis Instrument Calibration	Instrument Calibration Standard Purity	Eurachem/CITAC Guide
8	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)			ISO/GUM
9	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control Samples – SS	Recoveries of Spiked Samples Instrument Calibration Standard Purity	ISO/GUM
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples – SS Instrument Calibration	CRM Recoveries of SS Instrument Calibration Standard Purity	Eurachem/CITAC Guide
11	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	Recoveries of SS	Nata Technical Note 33
12	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	
13	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	CRM Recoveries of SS	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
14	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – SS Duplicate Analysis Instrument Calibration	Recoveries of SS Instrument Calibration	Nata Technical Note 33
15	Top Down - precision and estimates of the method and laboratory bias	Instrument Calibration	CRM Recoveries of SS	Nata Technical Note 33
16	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM Laboratory Bias from PT Studies Recoveries of SS Instrument Calibration Standard Purity	Nata Technical Note 33
17	Top Down - precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis Instrument Calibration	Instrument Calibration	Nata Technical Note 33

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

3.3 Participants' Comments

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Such feedback may be useful in improving future studies. Participants' comments are reproduced in Table 4.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments or Discussion*
3	S1	Not set up for OP and triazines
	S2	No reportable OC for this laboratory, assuming this sample is reserved for analytes we don't have the ability to analyse (OP)
	All	Many analytes including the OP suite and a few OC are not set up to analyse in this laboratory yet. Resulting in the analytes we can report to be few
4	S1	Molinate was detected.

*Some entries have been modified so that the participant cannot be identified.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 14 with resultant summary statistics: robust average, 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 11.

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

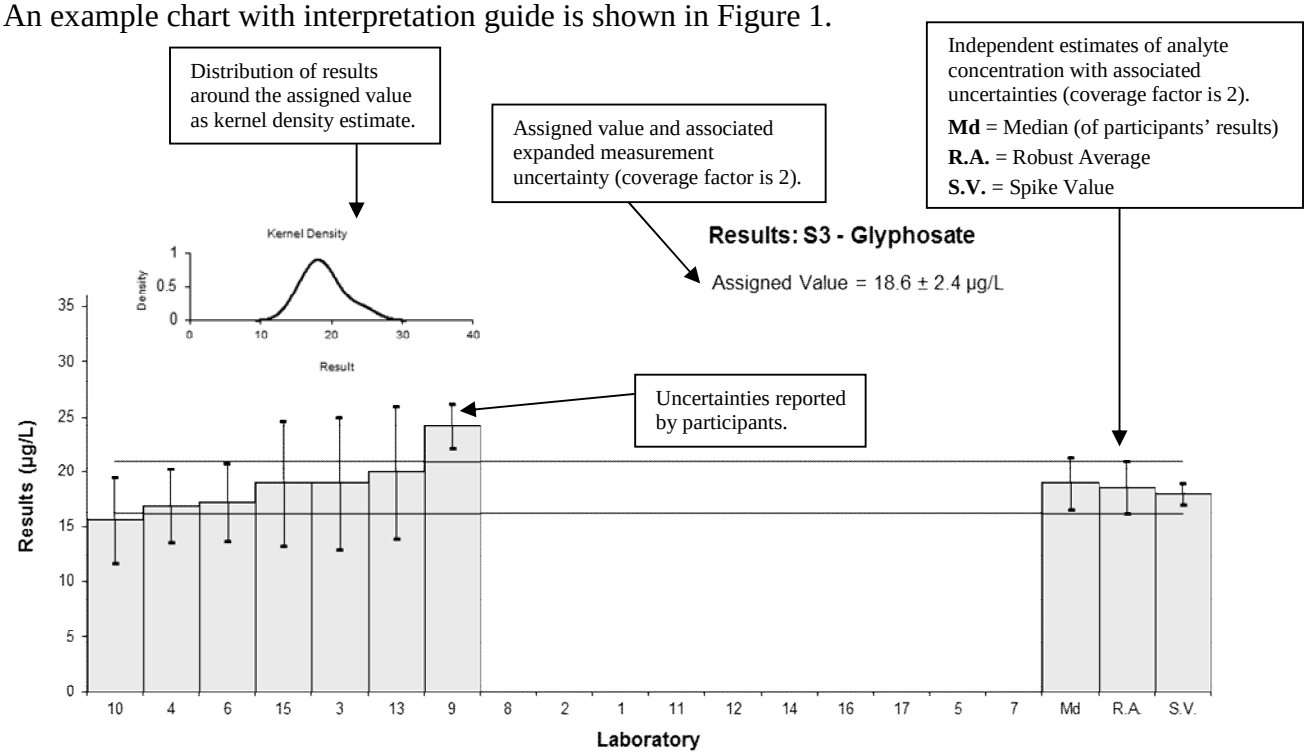


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

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

4.3 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratory variation that in the judgement of the study organiser would be expected from participants given the sample concentration. It is important to note that 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 performance coefficient of variation (PCV), as presented in Equation 1. This value is used in the calculation of z-scores.

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

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 a participant's result
X is the 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 must establish and demonstrate the traceability and measurement uncertainty associated with their test results.[6]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[7]

4.8 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'ISO 13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparison'.[8]

5 TABLES AND FIGURES

Table 5

Sample Details

Sample No.	S1
Matrix.	Water
Analyte.	cis-Chlordane
Units	µg/L

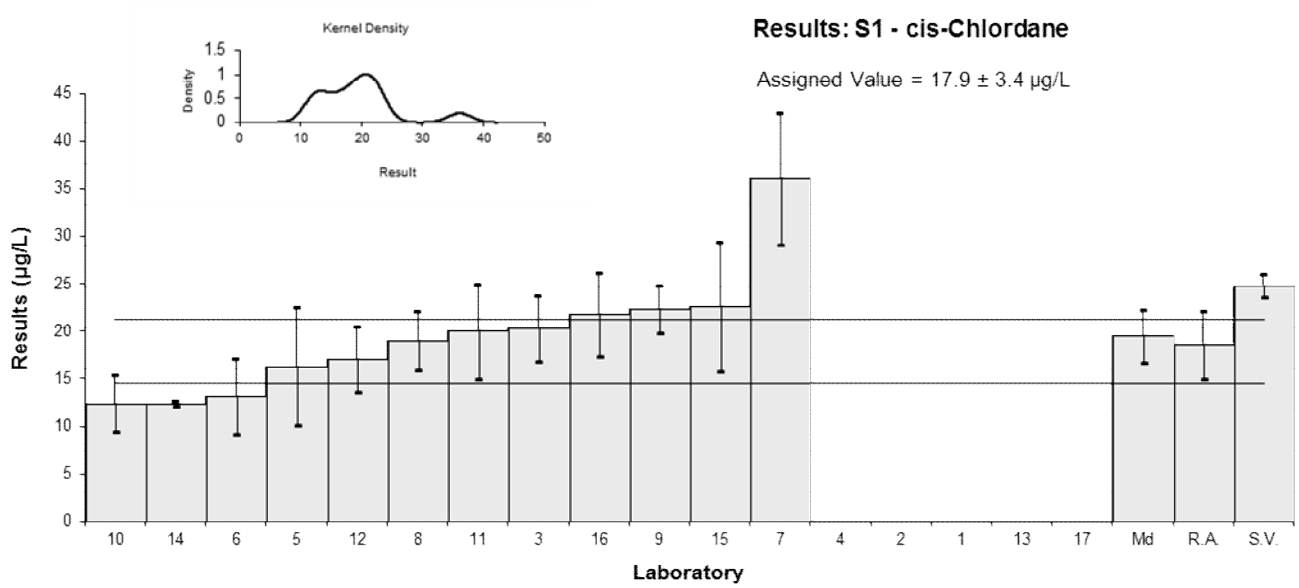
Participant Results

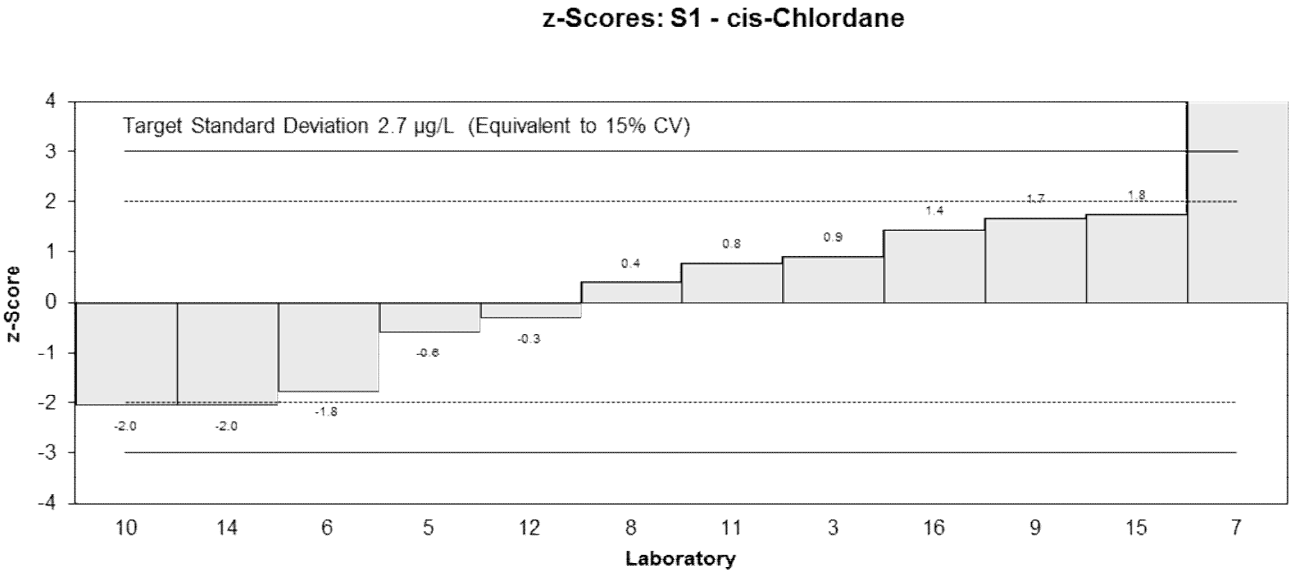
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NR	NR	NR		
3	20.32	3.39	NR	0.90	0.50
4	<0.1	NR	NR		
5	16.3	6.2	NR	-0.60	-0.23
6	13.16	3.95	65	-1.77	-0.91
7	36.1	6.9	NR	6.78	2.37
8	19	3.1	NR	0.41	0.24
9	22.4	2.5	NR	1.68	1.07
10	12.4	3.0	75	-2.05	-1.21
11	20	5.0	94	0.78	0.35
12	17.07	3.41	85	-0.31	-0.17
13	NT	NT	NT		
14	12.4	0.3	NR	-2.05	-1.61
15	22.6	6.78	68	1.75	0.62
16	21.787	4.357	118	1.45	0.70
17	NT	NT	NT		

Statistics

Assigned Value*	17.9	3.4
Spike	24.8	1.2
Robust Average	18.6	3.6
Median	19.5	2.8
Mean	19.5	
N	12	
Max.	36.1	
Min.	12.4	
Robust SD	4.5	
Robust CV	25%	

*Robust average excluding laboratory 7.


Kernel Density
Density
Result
Results: S1 - cis-Chlordane
Assigned Value = 17.9 ± 3.4 µg/L
Results (µg/L)
Laboratory
10 14 6 5 12 8 11 3 16 9 15 7 4 2 1 13 17 Md R.A. S.V.


z-Scores: S1 - cis-Chlordane
Target Standard Deviation 2.7 µg/L (Equivalent to 15% CV)
z-Score
-2.0 -2.0 -1.8 -0.6 -0.3 0.4 0.8 0.9 1.4 1.7 1.8
Laboratory
10 14 6 5 12 8 11 3 16 9 15 7

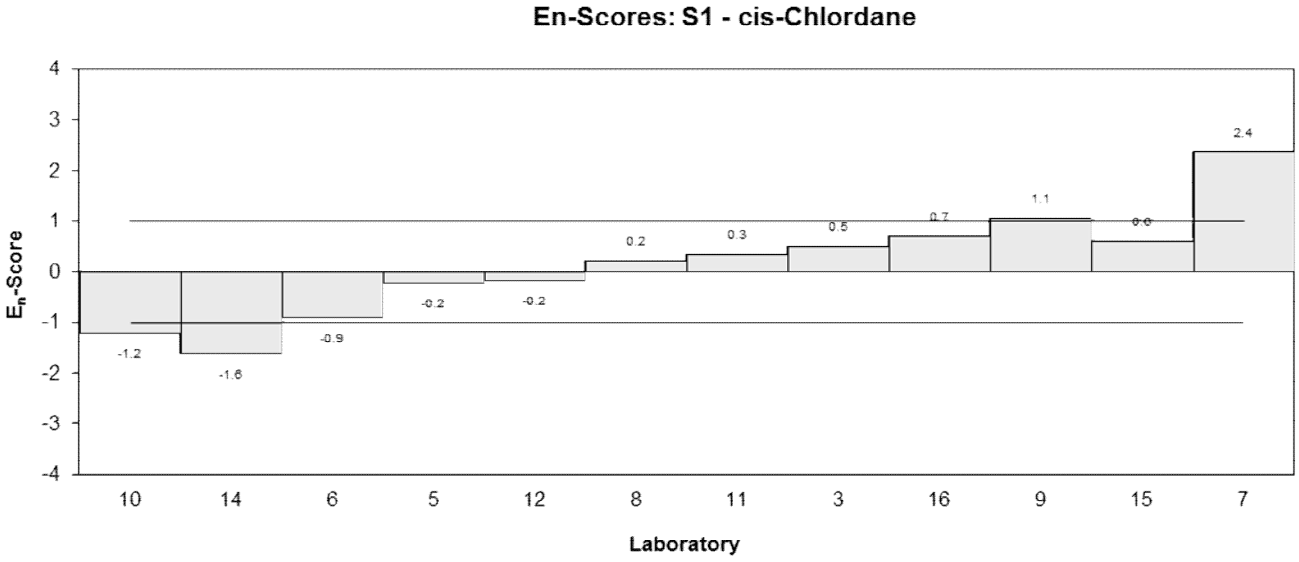

En-Scores: S1 - cis-Chlordane
En-Score
-1.2 -1.6 -0.9 -0.2 -0.2 0.2 0.3 0.5 0.7 1.1 0.6 2.4
Laboratory
10 14 6 5 12 8 11 3 16 9 15 7

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix.	Water
Analyte.	Diuron
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	NT	NT	NT
2	5.321	0.6651	NR
3	NT	NT	NT
4	4.96	1	NR
5	NT	NT	NT
6	2.82	0.7	83
7	2.35	0.94	NR
8	NT	NT	NT
9	NT	NT	NT
10	<0.1	NR	NR
11	NT	NT	NT
12	NR	NR	NR
13	NT	NT	NT
14	NT	NT	NT
15	3.4	1.02	97
16	3.83	0.9	90
17	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike	2.95	0.15
Robust Average	3.8	1.4
Median	3.6	1.6
Mean	3.8	
N	6	
Max.	5.321	
Min.	2.35	
Robust SD	1.3	
Robust CV	35%	

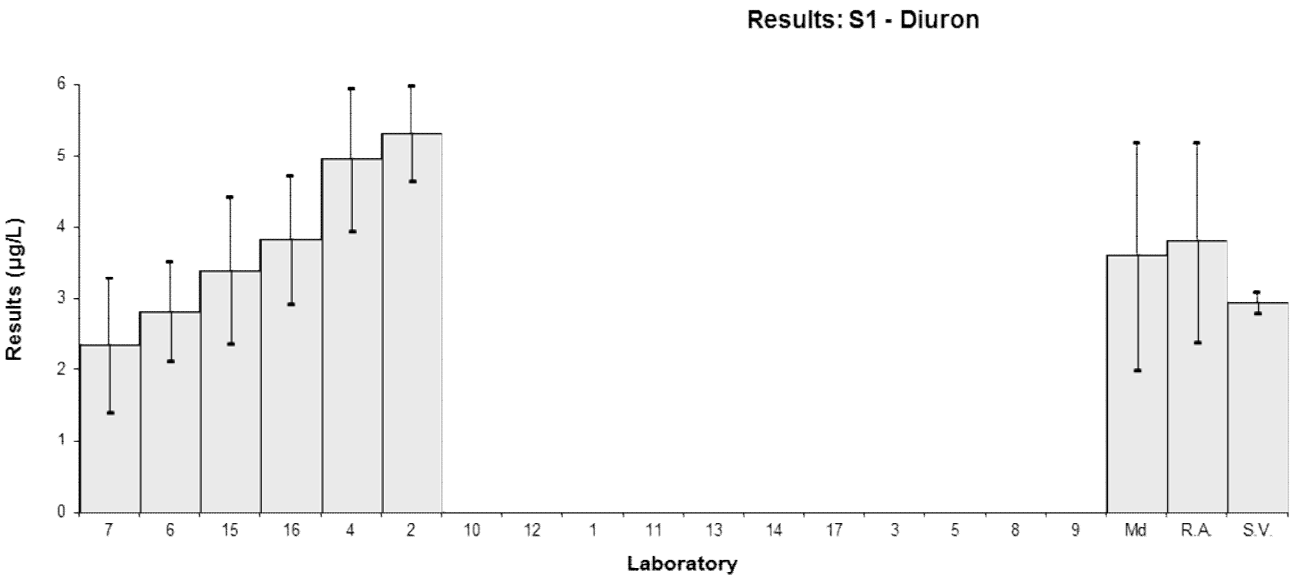

Results: S1 - Diuron
Results (µg/L)
0
1
2
3
4
5
6
7
6
15
16
4
2
10
12
1
11
13
14
17
3
5
8
9
Md
R.A.
S.V.
Laboratory

Figure 3

Table 7

Sample Details

Sample No.	S1
Matrix.	Water
Analyte.	Endosulfan sulfate
Units	µg/L

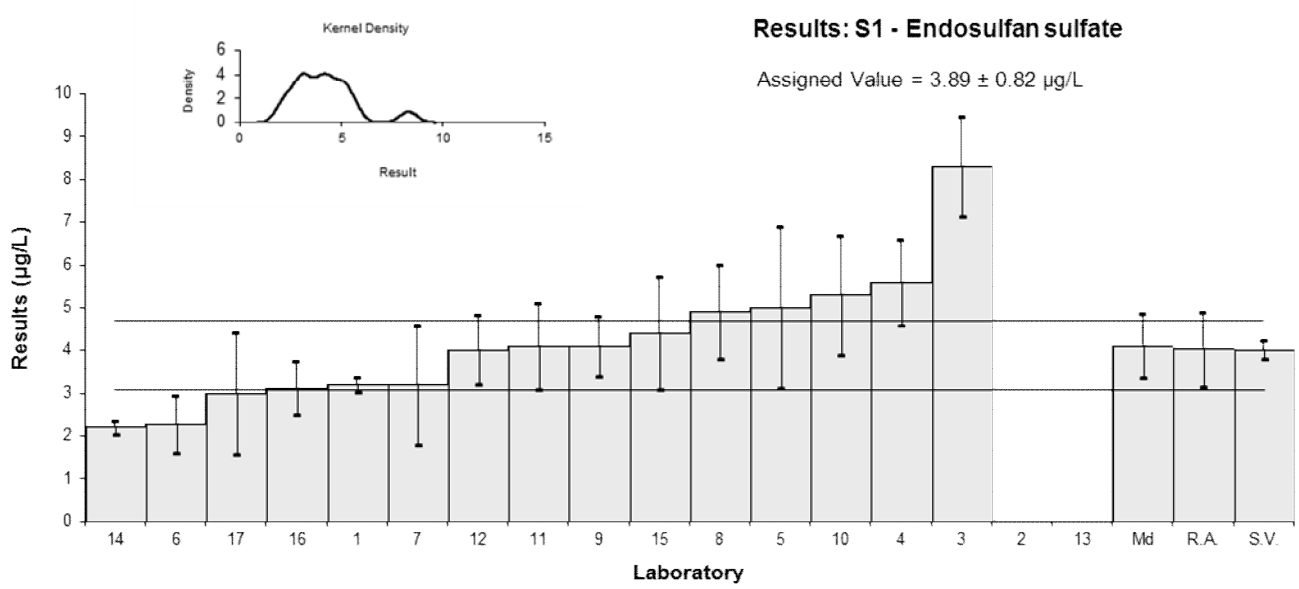
Participant Results

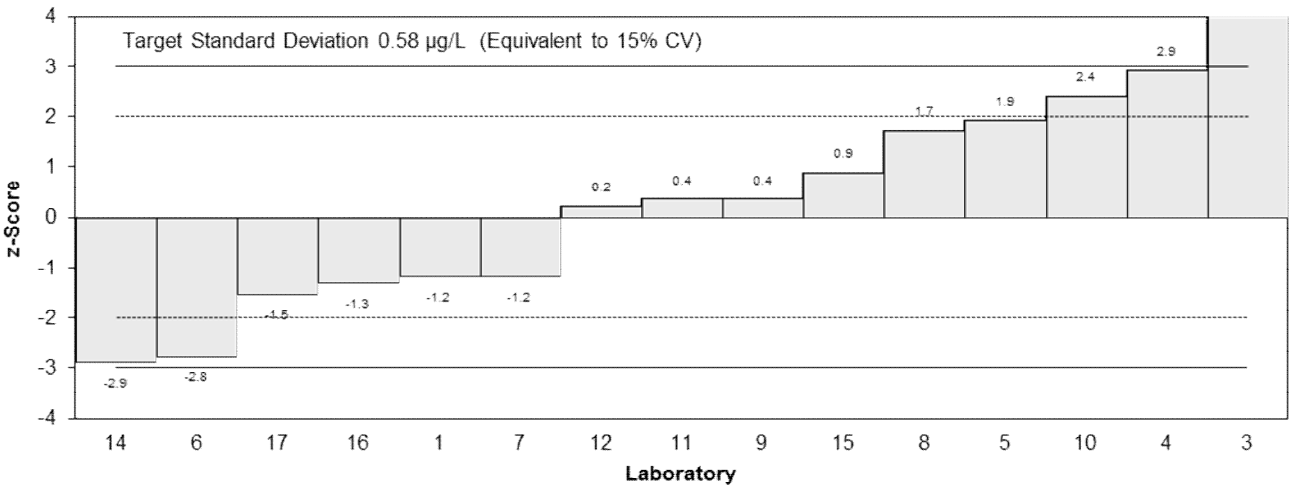
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	3.20	0.16	110	-1.18	-0.83
2	NR	NR	NR		
3	8.31	1.17	NR	7.57	3.09
4	5.6	1	NR	2.93	1.32
5	5.01	1.9	NR	1.92	0.54
6	2.27	0.68	65	-2.78	-1.52
7	3.2	1.4	NR	-1.18	-0.43
8	4.9	1.1	NR	1.73	0.74
9	4.1	0.7	NR	0.36	0.19
10	5.3	1.4	98	2.42	0.87
11	4.1	1.0	91	0.36	0.16
12	4.02	0.80	111	0.22	0.11
13	NT	NT	NT		
14	2.2	0.15	NR	-2.90	-2.03
15	4.4	1.32	66	0.87	0.33
16	3.122	0.624	103	-1.32	-0.75
17	2.99	1.41	NR	-1.54	-0.55

Statistics

Assigned Value*	3.89	0.82
Spike	4.02	0.20
Robust Average	4.03	0.87
Median	4.10	0.75
Mean	4.18	
N	15	
Max.	8.31	
Min.	2.2	
Robust SD	1.2	
Robust CV	32%	

*Robust average excluding laboratory 3.


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 3.89 ± 0.82 µg/L
Results (µg/L)
Laboratory
14 6 17 16 1 7 12 11 9 15 8 5 10 4 3 2 13 Md R.A. S.V.


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation 0.58 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 6 17 16 1 7 12 11 9 15 8 5 10 4 3
-2.9 -2.8 -1.5 -1.3 -1.2 -1.2 0.2 0.4 0.4 0.9 1.7 1.9 2.4 2.9

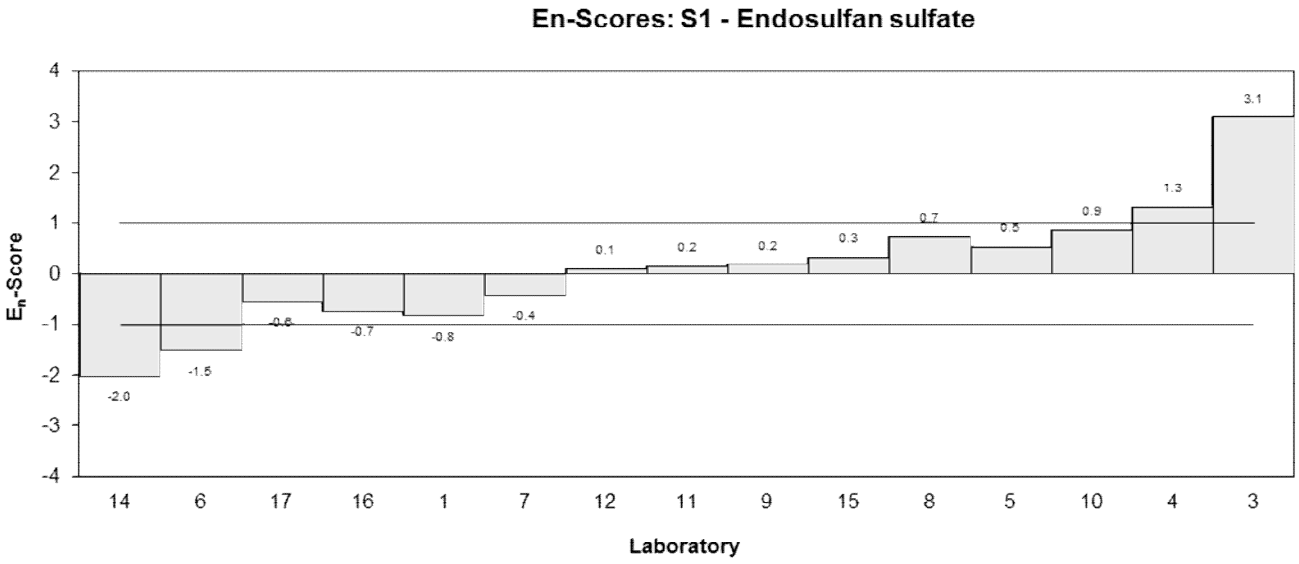

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
14 6 17 16 1 7 12 11 9 15 8 5 10 4 3
-2.0 -1.5 -0.6 -0.7 -0.8 -0.4 0.1 0.2 0.2 0.3 0.7 0.5 0.9 1.3 3.1

Figure 4

Table 8

Sample Details

Sample No.	S1
Matrix.	Water
Analyte.	Molinate
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	NT	NT	NT
2	NR	NR	NR
3	NT	NT	NT
4*	NR	NR	NR
5	NT	NT	NT
6	8.64	1.6	83
7	7.8	2.4	NR
8	NT	NT	NT
9	6.4	4.1	NR
10	10.5	2.7	102
11	NT	NT	NT
12	0.57	NR	NR
13	NT	NT	NT
14	NT	NT	NT
15	9.6	2.88	99
16	NT	NT	NT
17	NT	NT	NT

*Lab 4 detected molinate but did not report a value.

Statistics

Assigned Value	Not Set	
Spike	8.93	0.45
Robust Average	7.7	3.0
Median	8.2	2.5
Mean	7.3	
N	6	
Max.	10.5	
Min.	0.57	
Robust SD	2.9	
Robust CV	38%	

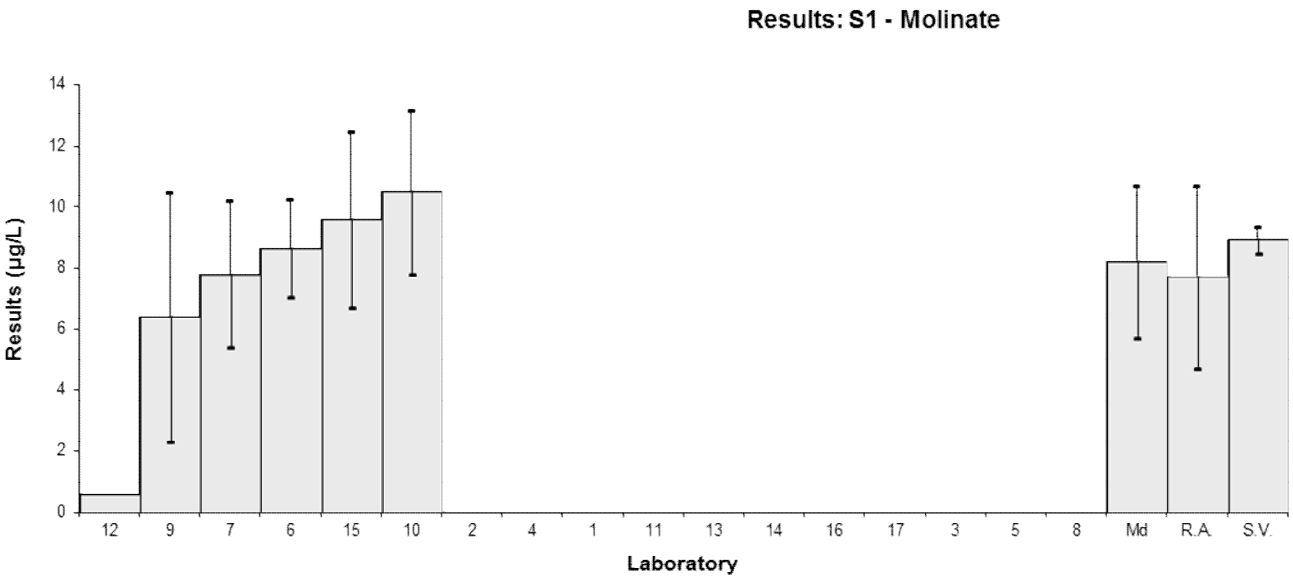

Results: S1 - Molinate
Results (µg/L)
14
12
10
8
6
4
2
0
12
9
7
6
15
10
2
4
1
11
13
14
16
17
3
5
8
Md
R.A.
S.V.
Laboratory

Figure 5

Table 9

Sample Details

Sample No.	S2
Matrix.	Water
Analyte.	Ethion
Units	µg/L

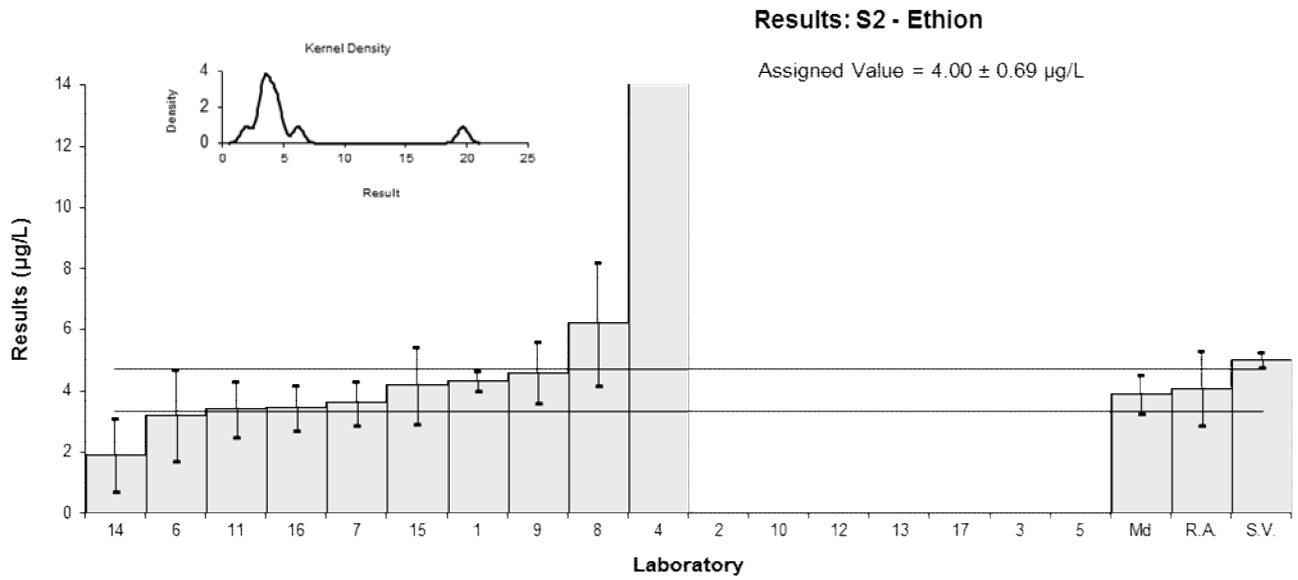
Participant Results

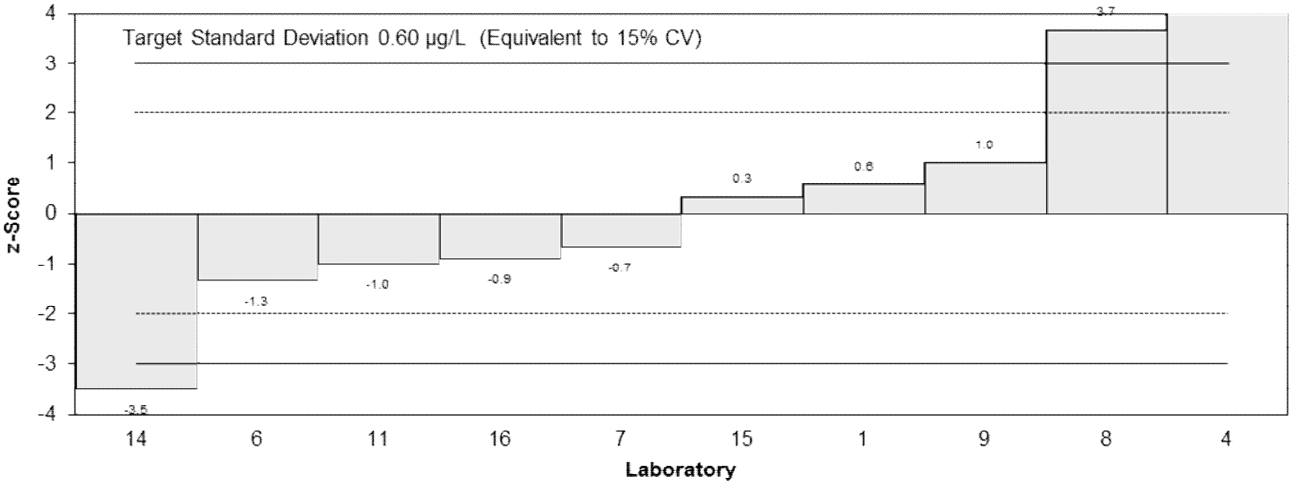
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	4.34	0.32	89	0.57	0.45
2	NR	NR	NR		
3	NT	NT	NT		
4	19.7	4	NR	26.17	3.87
5	NT	NT	NT		
6	3.2	1.5	90	-1.33	-0.48
7	3.6	0.73	NR	-0.67	-0.40
8	6.2	2.0	NR	3.67	1.04
9	4.6	1.0	NR	1.00	0.49
10	NT	NT	NT		
11	3.4	0.9	90	-1.00	-0.53
12	NT	NT	NT		
13	NT	NT	NT		
14	1.9	1.2	NR	-3.50	-1.52
15	4.2	1.26	96	0.33	0.14
16	3.46	0.732	85	-0.90	-0.54
17	NT	NT	NT		

Statistics

Assigned Value*	4.00	0.69
Spike	5.01	0.25
Robust Average	4.1	1.2
Median	3.90	0.64
Mean	5.46	
N	10	
Max.	19.7	
Min.	1.9	
Robust SD	0.78	
Robust CV	20%	

*Robust average excluding laboratories 4 and 14.


Results: S2 - Ethion
Assigned Value = 4.00 ± 0.69 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
14 6 11 16 7 15 1 9 8 4 2 10 12 13 17 3 5 Md R.A. S.V.


z-Scores: S2 - Ethion
Target Standard Deviation 0.60 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 6 11 16 7 15 1 9 8 4
-3.5 -1.3 -1.0 -0.9 -0.7 0.3 0.6 1.0 3.7

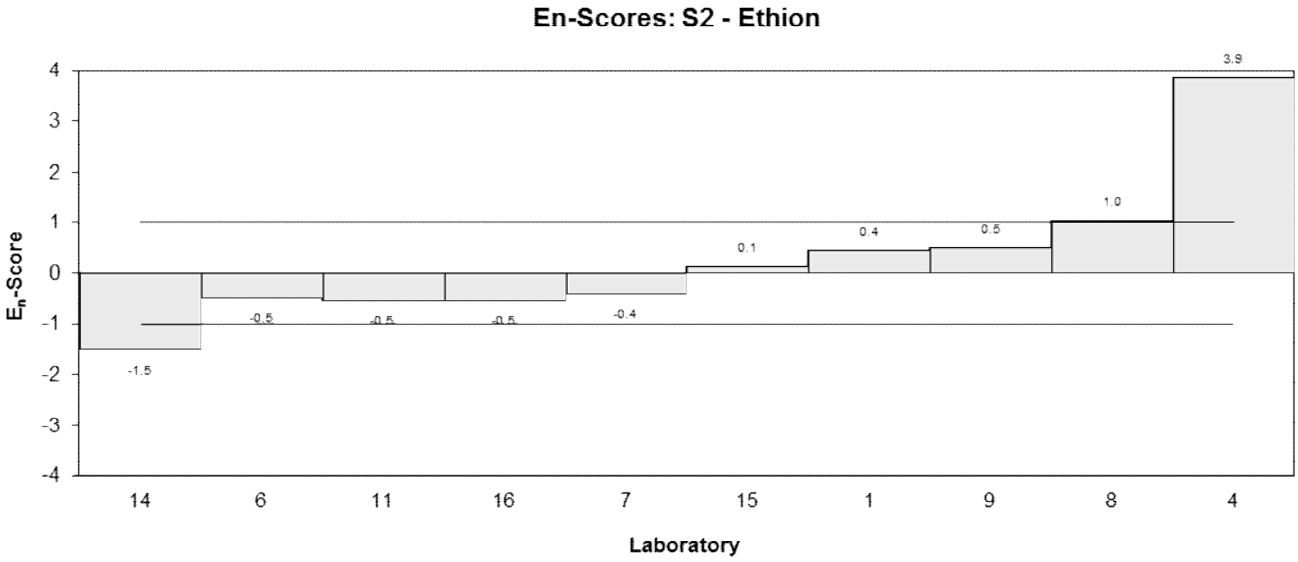

En-Scores: S2 - Ethion
En-Score
Laboratory
14 6 11 16 7 15 1 9 8 4
-1.5 -0.5 -0.5 -0.5 -0.4 0.1 0.4 0.5 1.0 3.9

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix.	Water
Analyte.	Methomyl
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	NT	NT	NT
2	NR	NR	NR
3	NT	NT	NT
4	17.6	3.5	NR
5	NT	NT	NT
6	NT	NT	NT
7	NT	NT	NT
8	NT	NT	NT
9	NT	NT	NT
10	NT	NT	NT
11	NT	NT	NT
12	0.85	NR	NR
13	NT	NT	NT
14	NT	NT	NT
15	11	3.3	101
16	10.975	2.70	70
17	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike	10.6	0.5
Robust Average	10.1	9.8
Median	11.0	7.8
Mean	10.1	
N	4	
Max.	17.6	
Min.	0.85	
Robust SD	7.8	
Robust CV	78%	

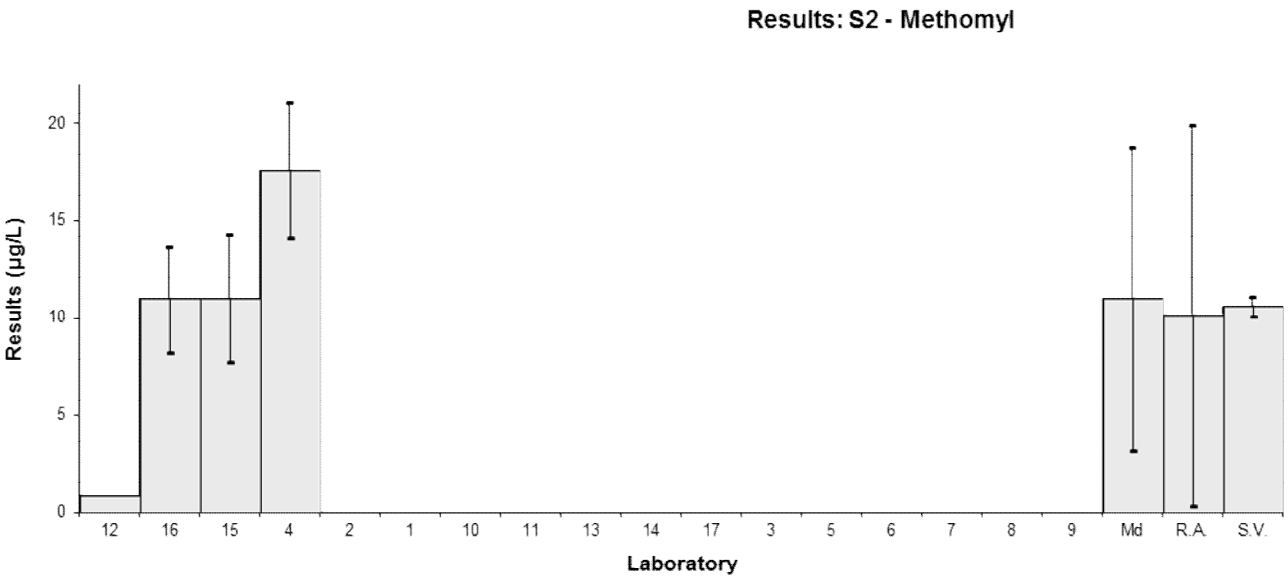

Results: S2 - Methomyl
Results (µg/L)
20
15
10
5
0
12
16
15
4
2
1
10
11
13
14
17
3
5
6
7
8
9
Md
R.A.
S.V.
Laboratory

Figure 7

Table 11

Sample Details

Sample No.	S2
Matrix.	Water
Analyte.	Metsulfuron-methyl
Units	µg/L

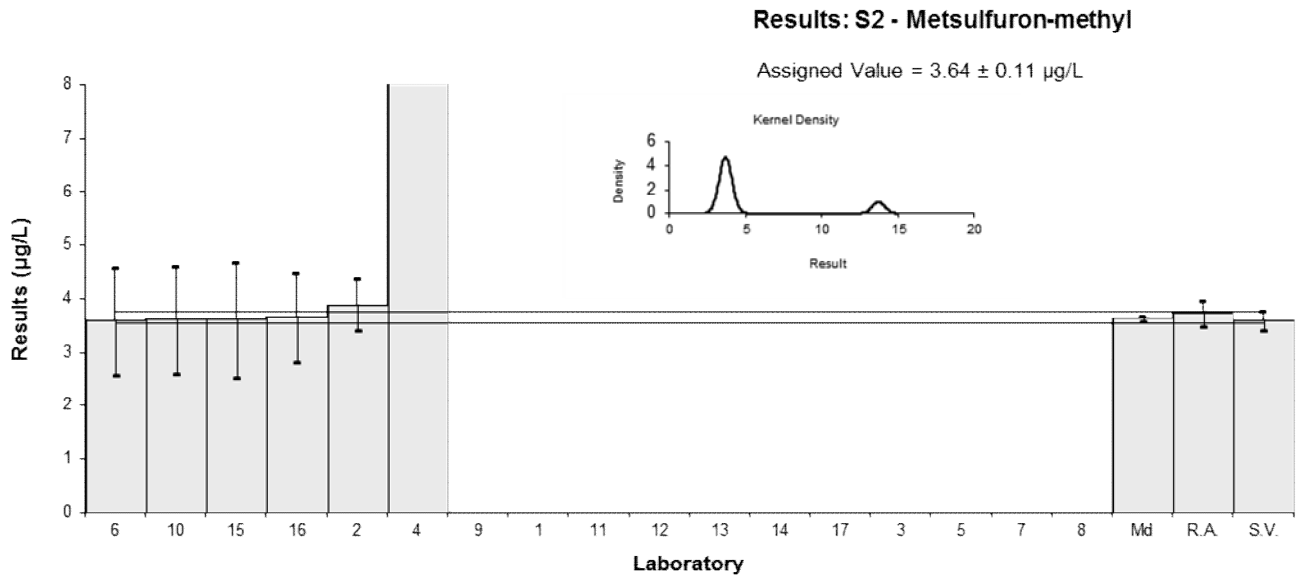
Participant Results

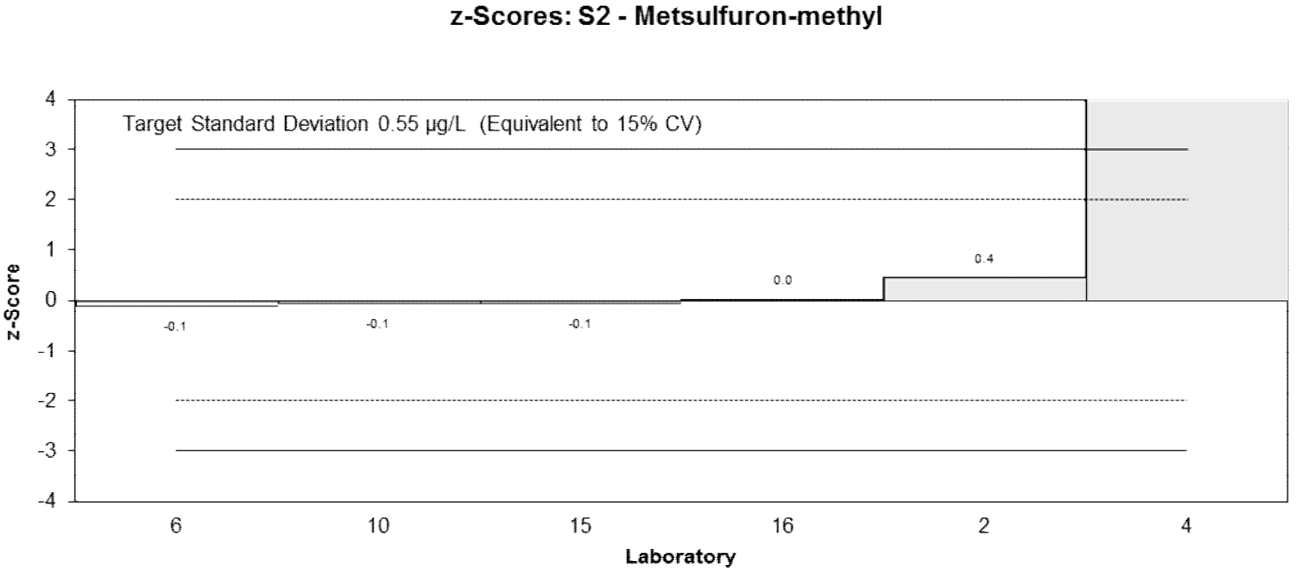
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	3.884	0.486	NR	0.45	0.49
3	NT	NT	NT		
4	13.7	2.7	NR	18.42	3.72
5	NT	NT	NT		
6	3.58	1	90	-0.11	-0.06
7	NT	NT	NT		
8	NT	NT	NT		
9	<2.5	NR	NR		
10	3.6	1.0	100	-0.07	-0.04
11	NT	NT	NT		
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	3.6	1.08	95	-0.07	-0.04
16	3.65	0.83	80	0.02	0.01
17	NT	NT	NT		

Statistics

Assigned Value*	3.64	0.11
Spike	3.59	0.18
Robust Average	3.73	0.24
Median	3.63	0.05
Mean	5.34	
N	6	
Max.	13.7	
Min.	3.58	
Robust SD	0.094	
Robust CV	2.6%	

*Robust average excluding laboratory 4.


Results: S2 - Metsulfuron-methyl
Assigned Value = 3.64 ± 0.11 µg/L
Kernel Density
Density
Result
Results (µg/L)
6 10 15 16 2 4 9 1 11 12 13 14 17 3 5 7 8 Md R.A. S.V.
Laboratory


z-Scores: S2 - Metsulfuron-methyl
Target Standard Deviation 0.55 µg/L (Equivalent to 15% CV)
z-Score
-0.1 -0.1 -0.1 0.0 0.4
6 10 15 16 2 4
Laboratory

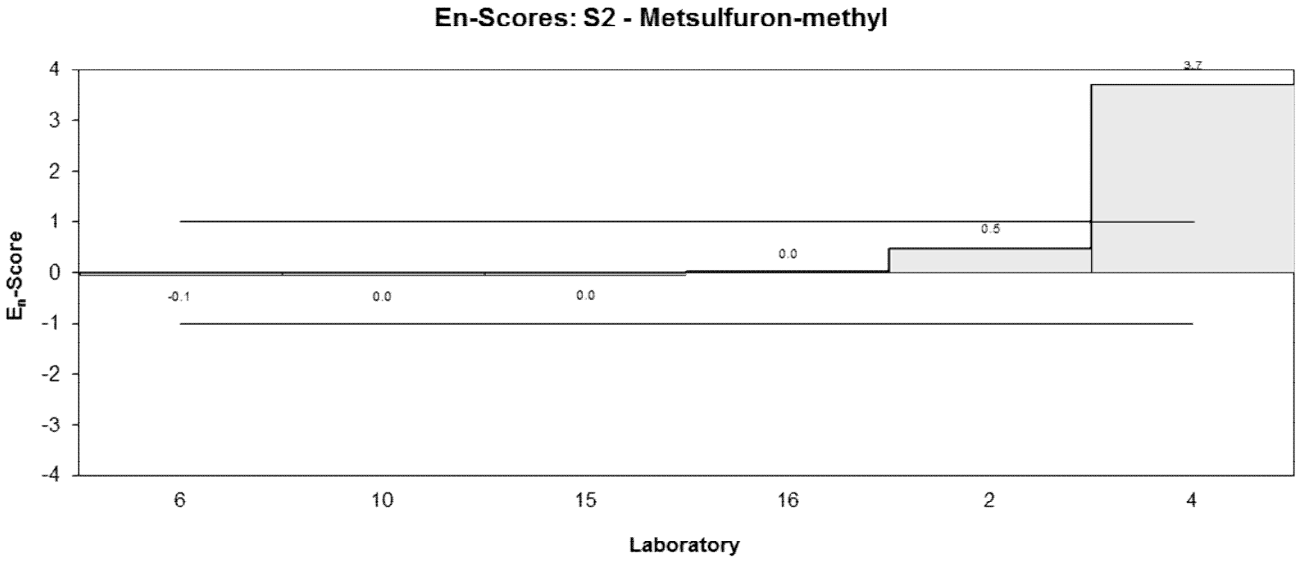

En-Scores: S2 - Metsulfuron-methyl
En-Score
-0.1 0.0 0.0 0.0 0.5 3.7
6 10 15 16 2 4
Laboratory

Figure 8

Table 12

Sample Details

Sample No.	S2
Matrix.	Water
Analyte.	Simazine
Units	µg/L

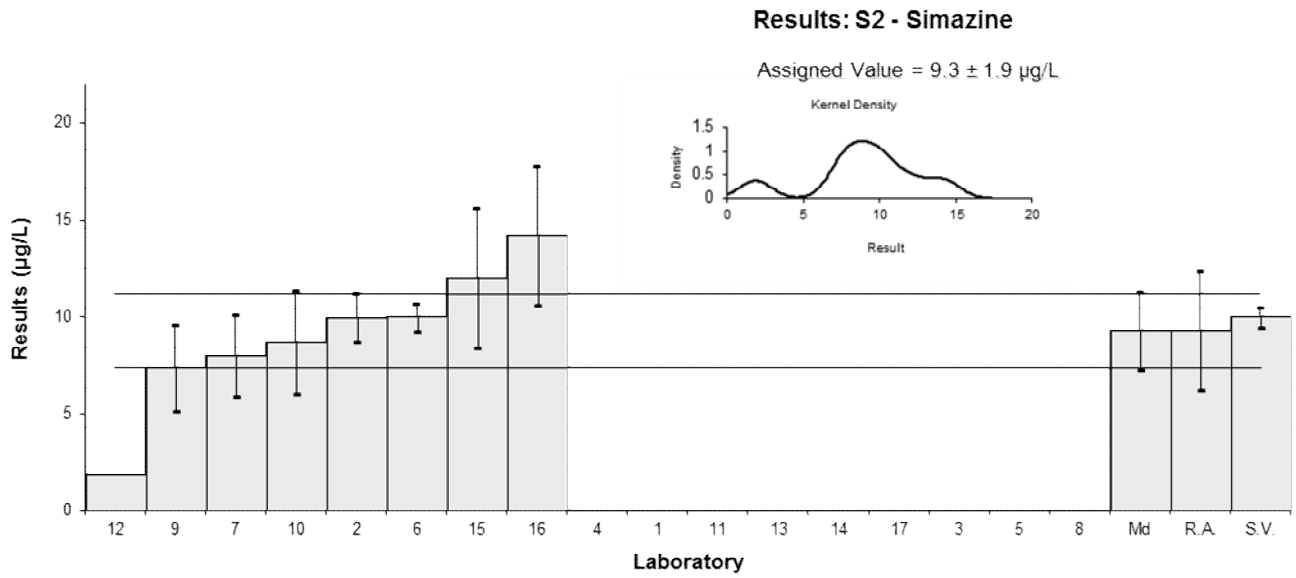
Participant Results

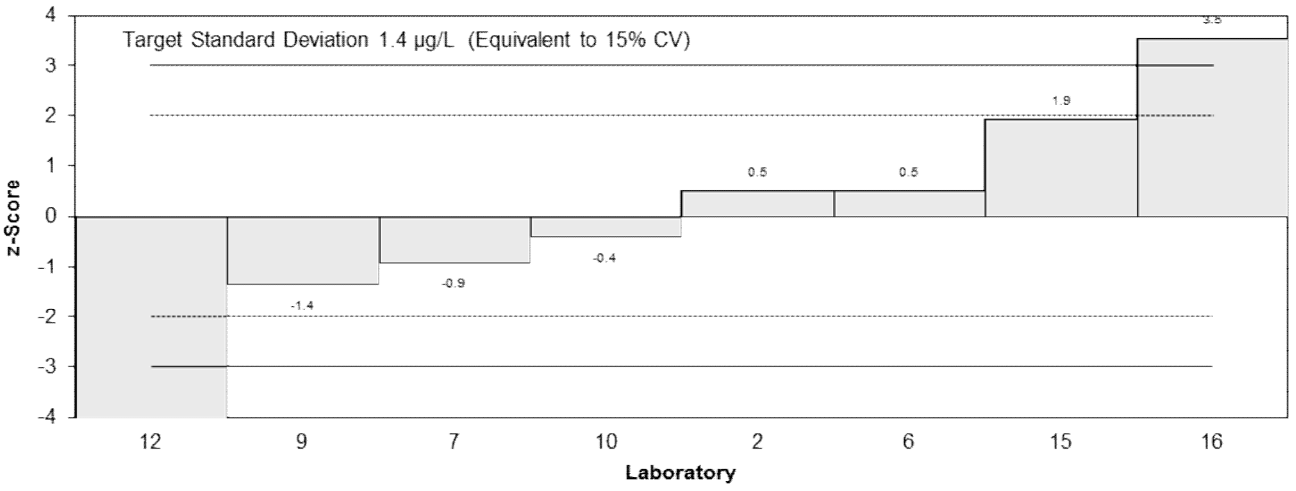
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	9.993	1.249	NR	0.50	0.30
3	NT	NT	NT		
4	NR	NR	NR		
5	NT	NT	NT		
6	10.0	0.7	90	0.50	0.35
7	8.0	2.1	NR	-0.93	-0.46
8	NT	NT	NT		
9	7.4	2.2	NR	-1.36	-0.65
10	8.7	2.7	60	-0.43	-0.18
11	NT	NT	NT		
12	1.84	NR	NR	-5.35	-3.93
13	NT	NT	NT		
14	NT	NT	NT		
15	12	3.6	98	1.94	0.66
16	14.224	3.556	70	3.53	1.22
17	NT	NT	NT		

Statistics

Assigned Value*	9.3	1.9
Spike	10.0	0.5
Robust Average	9.3	3.1
Median	9.3	2.0
Mean	9.0	
N	8	
Max.	14.224	
Min.	1.84	
Robust SD	1.9	
Robust CV	20%	

*Robust average excluding laboratories 12 and 16.


Results: S2 - Simazine
Assigned Value = 9.3 ± 1.9 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12 9 7 10 2 6 15 16 4 1 11 13 14 17 3 5 8 Md R.A. S.V.


z-Scores: S2 - Simazine
Target Standard Deviation 1.4 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
12 9 7 10 2 6 15 16

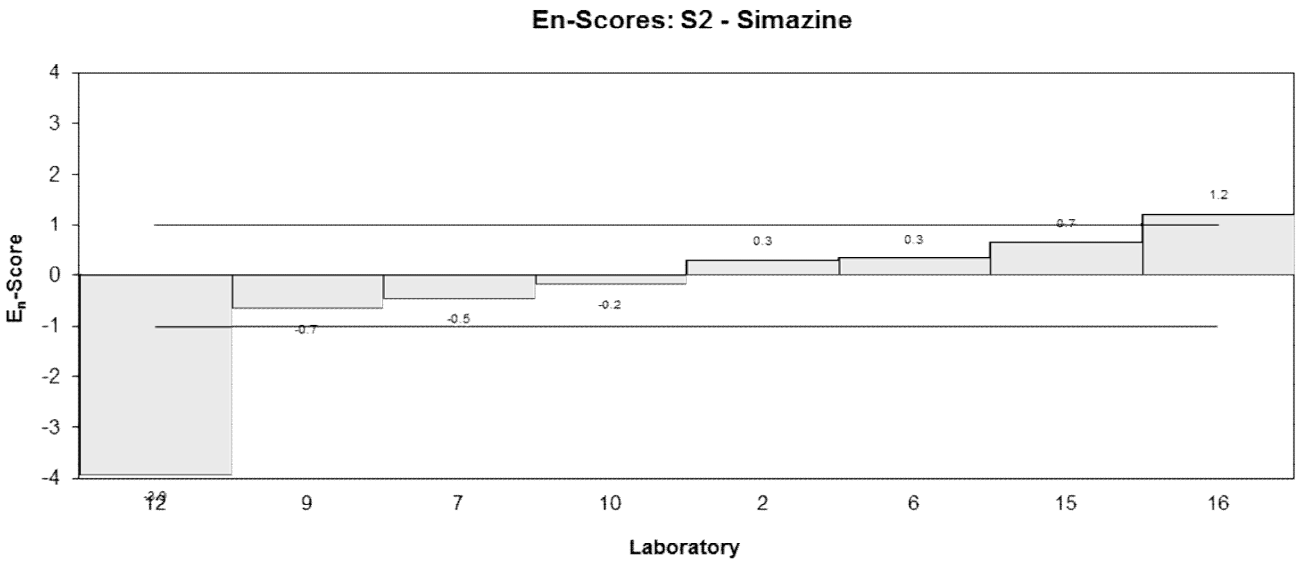

En-Scores: S2 - Simazine
En-Score
Laboratory
12 9 7 10 2 6 15 16

Figure 9

Table 13

Sample Details

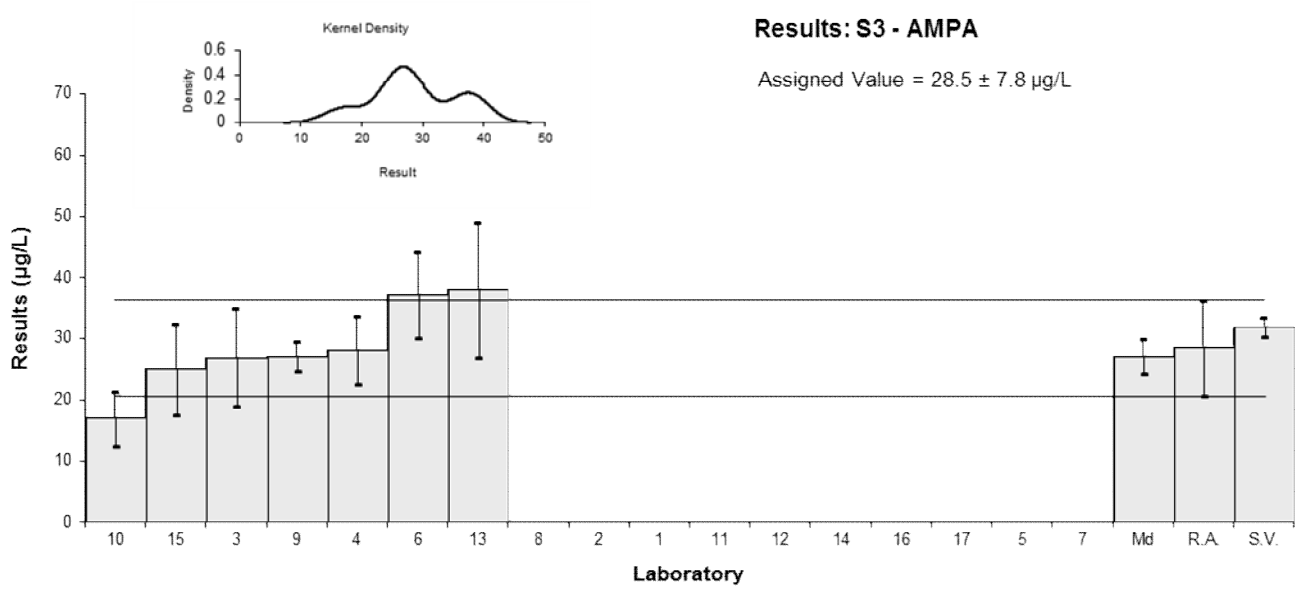
Sample No.	S3
Matrix.	Water
Analyte.	AMPA
Units	µg/L

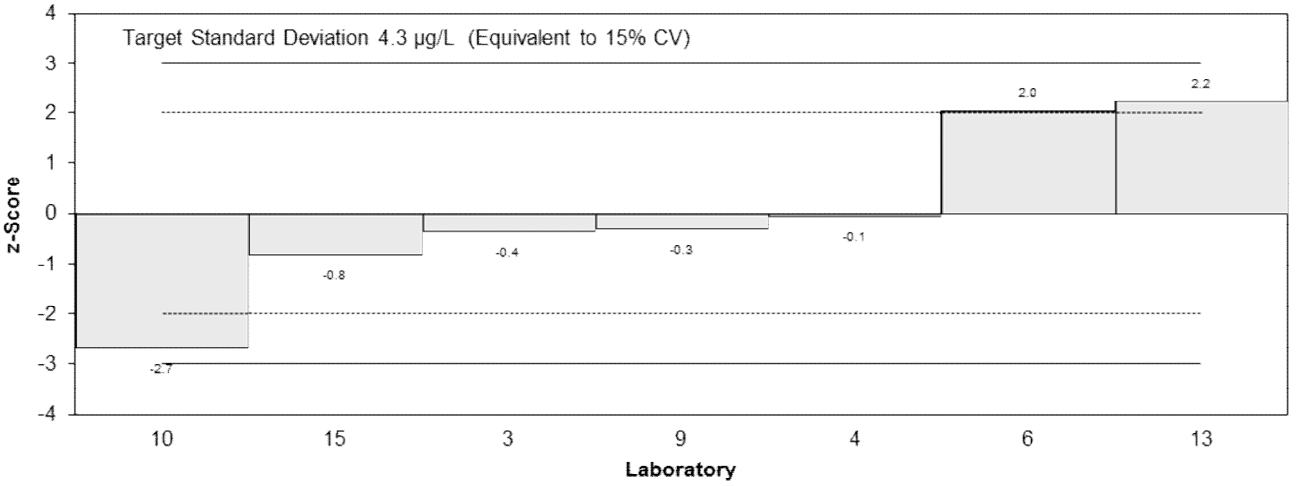
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	26.94	8	NR	-0.36	-0.14
4	28.2	5.5	85	-0.07	-0.03
5	NT	NT	NT		
6	37.2	7	NR	2.04	0.83
7	NT	NT	NT		
8	<100	NR	NR		
9	27.1	2.4	NR	-0.33	-0.17
10	17.0	4.4	79	-2.69	-1.28
11	NT	NT	NT		
12	NT	NT	NT		
13	38	11	92	2.22	0.70
14	NT	NT	NT		
15	25	7.5	96	-0.82	-0.32
16	NT	NT	NT		
17	NT	NT	NT		

Statistics

Assigned Value	28.5	7.8
Spike	32.0	1.6
Robust Average	28.5	7.8
Median	27.1	2.9
Mean	28.5	
N	7	
Max.	38	
Min.	17	
Robust SD	8.2	
Robust CV	29%	


Kernel Density
Density
Result
Results: S3 - AMPA
Assigned Value = 28.5 ± 7.8 µg/L
Results (µg/L)
Laboratory
10 15 3 9 4 6 13 8 2 1 11 12 14 16 17 5 7 Md R.A. S.V.


z-Scores: S3 - AMPA
Target Standard Deviation 4.3 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
10 15 3 9 4 6 13
-2.7
-0.8
-0.4
-0.3
-0.1
2.0
2.2

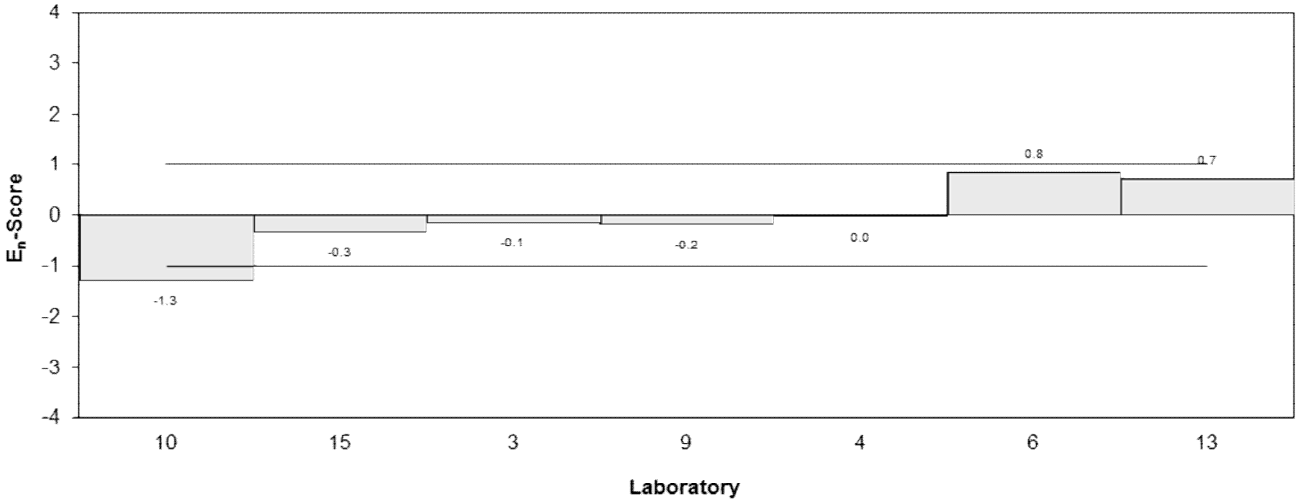

En-Scores: S3 - AMPA
En-Score
Laboratory
10 15 3 9 4 6 13
-1.3
-0.3
-0.1
-0.2
0.0
0.8
0.7

Figure 10

Table 14

Sample Details

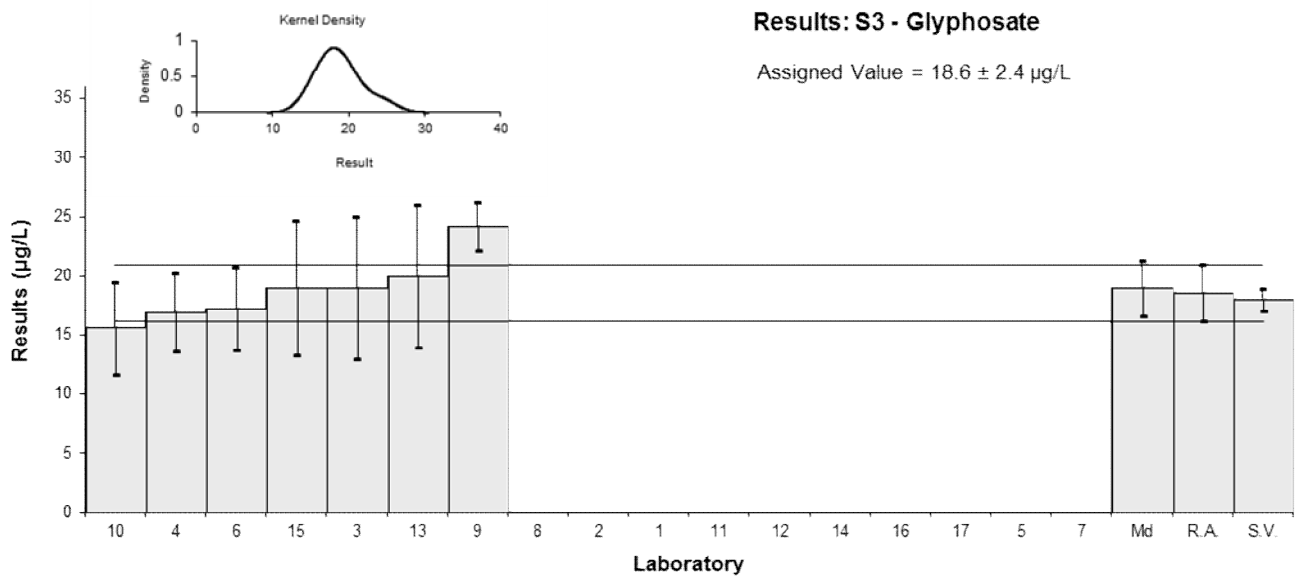
Sample No.	S3
Matrix.	Water
Analyte.	Glyphosate
Units	µg/L

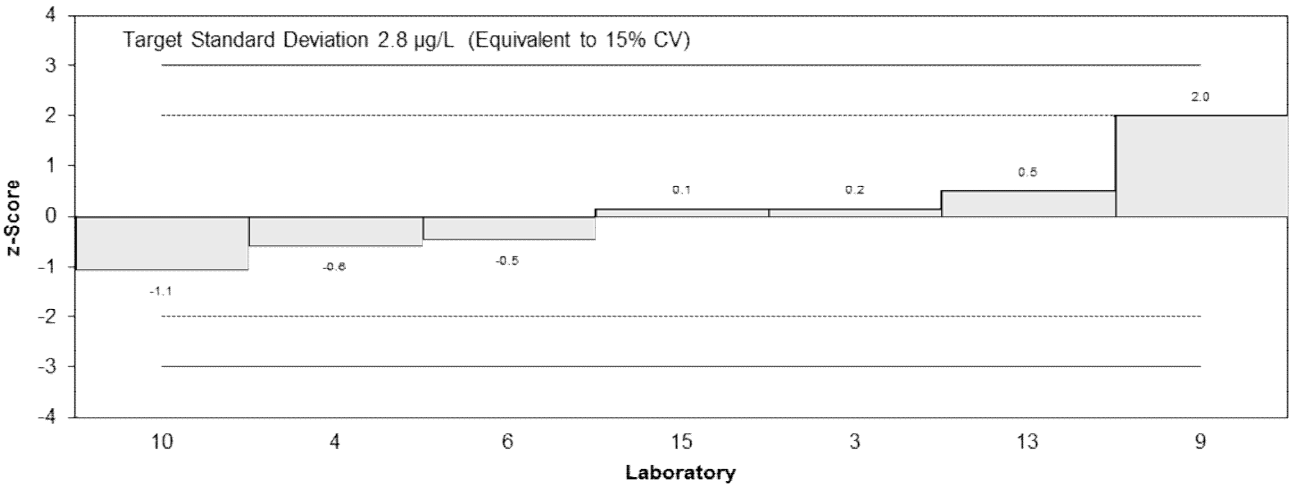
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	19.03	6	NR	0.15	0.07
4	16.9	3.3	120	-0.61	-0.42
5	NT	NT	NT		
6	17.3	3.5	NR	-0.47	-0.31
7	NT	NT	NT		
8	<100	NR	NR		
9	24.2	2.0	NR	2.01	1.79
10	15.6	3.9	79	-1.08	-0.66
11	NT	NT	NT		
12	NT	NT	NT		
13	20	6.0	95	0.50	0.22
14	NT	NT	NT		
15	19	5.7	104	0.14	0.06
16	NT	NT	NT		
17	NT	NT	NT		

Statistics

Assigned Value	18.6	2.4
Spike	18.0	0.9
Robust Average	18.6	2.4
Median	19.0	2.3
Mean	18.9	
N	7	
Max.	24.2	
Min.	15.6	
Robust SD	2.6	
Robust CV	14%	


Kernel Density
Density
Result
Results: S3 - Glyphosate
Assigned Value = 18.6 ± 2.4 µg/L
Results (µg/L)
Laboratory
10 4 6 15 3 13 9 8 2 1 11 12 14 16 17 5 7 Md R.A. S.V.


z-Scores: S3 - Glyphosate
Target Standard Deviation 2.8 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
10 4 6 15 3 13 9
-1.1
-0.6
-0.5
0.1
0.2
0.5
2.0

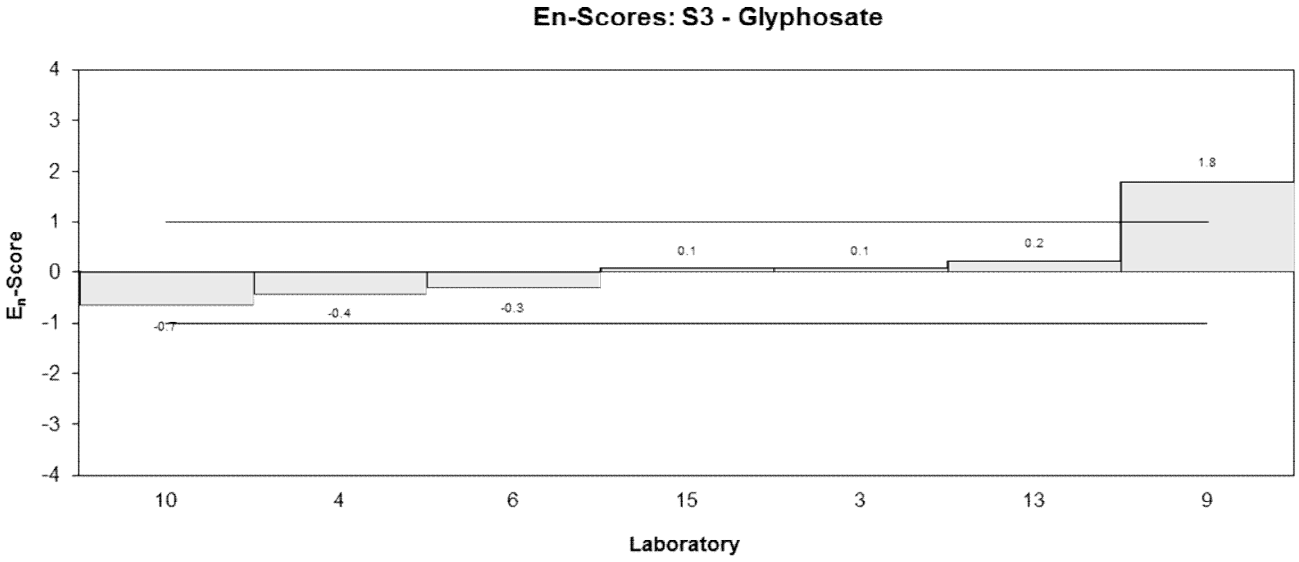
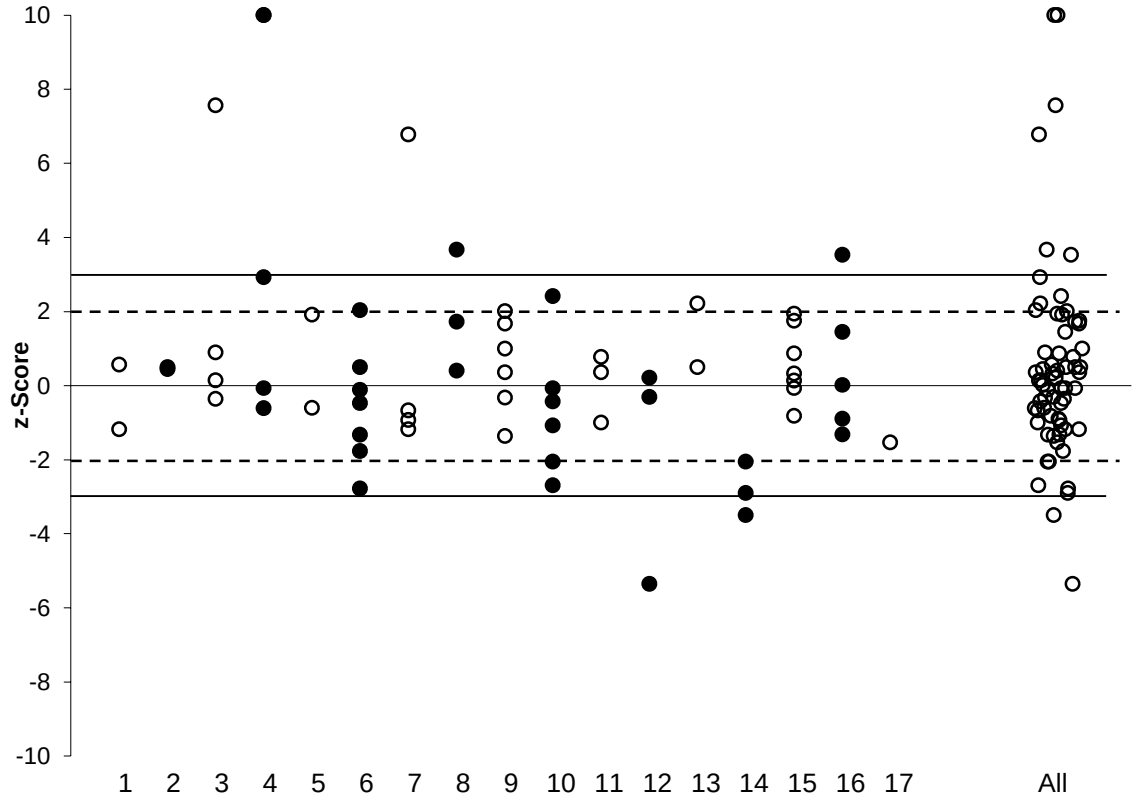
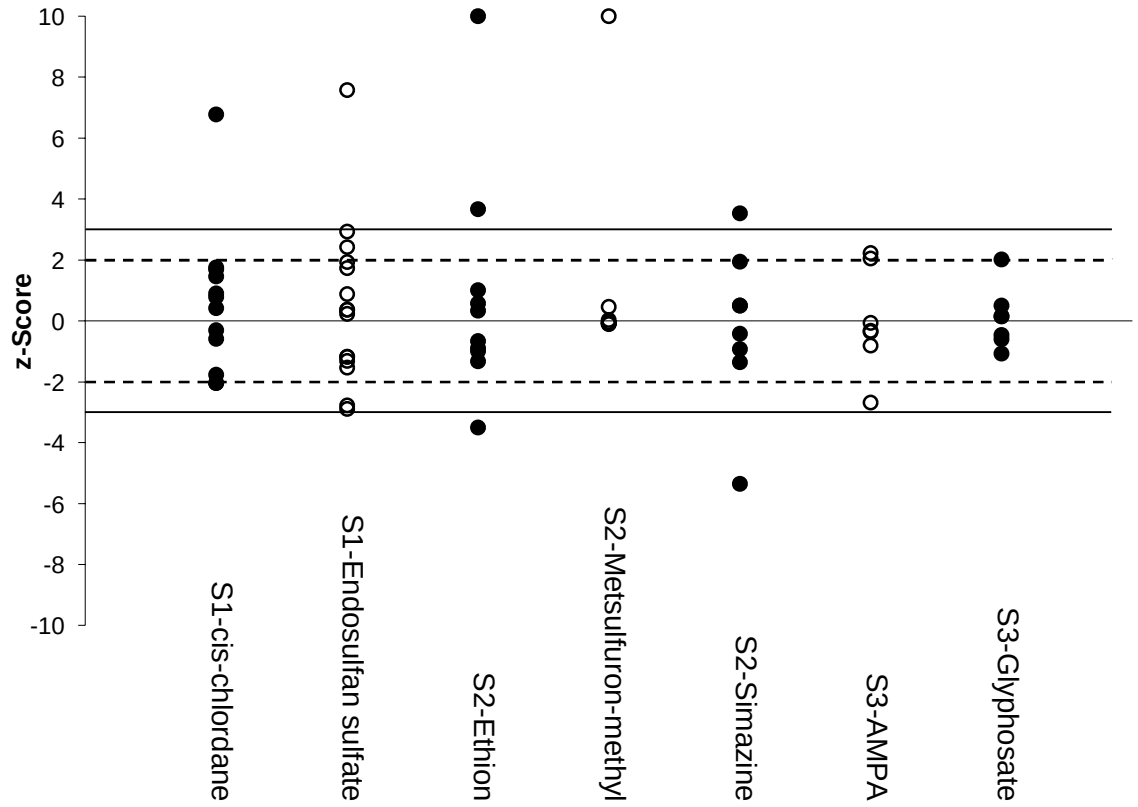

En-Scores: S3 - Glyphosate
En-Score
Laboratory
10 4 6 15 3 13 9
-0.7
-0.4
-0.3
0.1
0.1
0.2
1.8

Figure 11



Scores greater than 10 have been plotted as 10.

Figure 12 z-Score Dispersal by Laboratory



Scores greater than 10 have been plotted as 10.

Figure 13 z-Score Dispersal by Pesticide

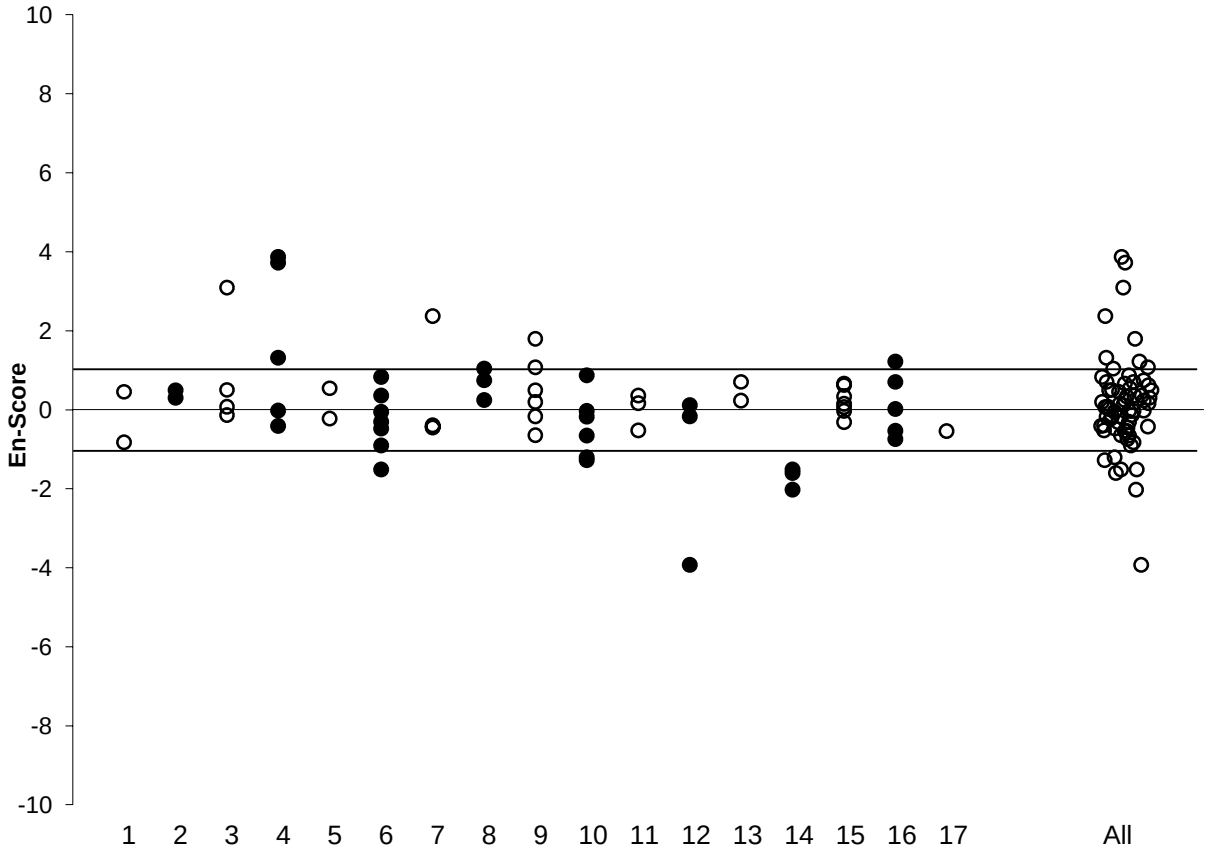


Figure 14 E_n-Score Dispersal by Laboratory

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Assigned values were the robust average of participants' results. The robust averages and associated expanded uncertainties were calculated using the procedure described in 'ISO 13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparison'.[8] Appendix 2 sets out the calculation for the expanded uncertainty of the robust average of AMPA in Sample S3.

A comparison of the spiked concentration and the assigned value (or robust average) is presented in Table 15.

No assigned value was set for diuron and molinate in Sample S1, and methomyl in Sample S2, as few laboratories reported numeric results and these were too variable.

For all other pesticides, the assigned values were within the range of 72 to 103% of the spiked concentration. This provides good support for the assigned value and is evidence for the stability of these analytes in the test samples.

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 15 Comparison of Assigned Value (or Robust Average) and Spiked Concentration

Analyte	Spiked Concentration (µg/L)	Assigned Value *(Robust Average)* (µg/L)	Assigned Value *(Robust Average)* / Spike Value (%)
cis-Chlordane	24.8	17.9	72
Diuron	2.95	*(3.8)*	*(129)*
Endosulfan sulfate	4.02	3.89	97
Molinate	8.93	*(7.7)*	*(86)*
Ethion	5.01	4.00	80
Methomyl	10.6	*(10.1)*	*(95)*
Metsulfuron-methyl	3.59	3.64	101
Simazine	10.0	9.3	93
AMPA	32.0	28.5	89
Glyphosate	18.0	18.6	103

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate.

It is a requirement of the ISO Standard 17025 that laboratories have procedures to estimate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including when the client's instruction so requires.[6]

Seventy-eight of eighty-one results (96%) were reported with an expanded measurement uncertainty. Participants used a wide variety of procedures to estimate the expanded measurement uncertainty (Table 3). Laboratory **12** did not report uncertainties for organonitrogen and organophosphorus pesticides for which they are unaccredited.

The magnitude of reported uncertainties was within the range of 2.4% to 64%. Twelve were less than 15% relative, which the study coordinator believes is unrealistically small for a pesticide residue measurement.

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

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 21.787 ± 4.357 µg/L, it is better to report this as 21.8 ± 4.4 µg/L).[7]

6.3 z-Score

Target standard deviations (SDs) equivalent to 15% performance coefficient of variation (PCV) were used to calculate z-scores. Target SDs, coefficient of variation predicted by Thompson-Horwitz equation[9] and between laboratories coefficient of variation obtained in this study are presented in Table 16.

Table 16 Target SDs, CV from predictive model and CV between laboratories

Sample	Analyte	Assigned value (µg/L)	Target SD (as PCV) (%)	Thompson-Horwitz CV (%)	Between Laboratories CV (%)
S1	cis-Chlordane	17.9	15	22	25
S1	Endosulfan sulfate	3.89	15	22	32
S2	Ethion	4.00	15	22	20
S2	Metsulfuron-methyl	3.64	15	22	2.6
S2	Simazine	9.3	15	22	20
S3	AMPA	28.5	15	22	29
S3	Glyphosate	18.6	15	22	14

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

Of 65 results for which z-scores were calculated, 47 (72%) returned a satisfactory score of $|z| \leq 2$.

Laboratories **6** and **15** reported results for all seven analytes for which z-scores were calculated. Laboratory **15** had satisfactory z-scores for all seven analytes.

No results reported by Laboratory **14** returned a satisfactory z-score.

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

Of 65 results, 49 (75%) returned a satisfactory score of $E_n \leq 1$.

Laboratory **15** had satisfactory E_n-scores for all seven analytes for which E_n-scores were calculated.

No results reported by Laboratory **14** returned a satisfactory E_n-score.

6.5 False negatives

Table 17 lists false negative results – a pesticide present for which a laboratory tested but did not report a result (e.g. laboratories reporting a '<' or NR result when the assigned value or spike value was higher than the participants' reporting limit, or laboratories that left the cell blank instead of entering NT as per instructions).

Table 17 False Negatives

Lab. Code	Sample	Pesticide
2	S1	Chlordane, Endosulfan sulfate, Molinate
	S2	Ethion, Methomyl
4	S1	Chlordane
	S2	Simazine
9	S2	Metsulfuron-methyl
10	S1	Diuron
12	S1	Diuron

6.6 Reporting of Pesticides Not Spiked Into the Test Samples

Thirteen laboratories reported pesticides that were not spiked into the test samples. These are listed in Table 18.

Table 18 Reported pesticides not spiked in the test samples

Lab. Code	Sample	Pesticide	Concentration (µg/L)	Uncertainty (µg/L)	Recovery (%)
2	S1	Atrazine	0.005	0.000625	NR
		Simazine	0.026	0.00325	NR
	S2	Atrazine	0.003	0.000375	NR
		Diuron	0.156	0.0195	NR
3	S1	alpha-Endosulfan	6.89	0.97	NR
4	S1	Bifenthrin	0.125	0.025	NR
		Chlorpyrifos	0.4	0.08	NR
		Permethrin	0.85	0.17	NR
		Simazine	0.25	0.05	NR
	S2	Bifenthrin	0.25	0.05	NR
		Chlorpyrifos	0.676	0.13	NR
		Diuron	0.14	0.02	NR
		Permethrin	1.56	0.3	NR
5	S1	alpha-Endosulfan	1.10	0.41	NR
6	S2	p,p'-DDD	0.94	0.28	68
		Total DDT	0.94	0.28	68
7	S1	beta-Endosulfan	0.0129	0.0078	NR
	S2	Diuron	0.060	0.029	NR
8	S1	alpha-Endosulfan	6.0	1.1	NR
		p,p'-DDT	0.4	0.1	NR
9	S1	beta-Endosulfan	0.014	0.003	NR
	S2	Chlordane	0.204	0.022	NR
12	S1	Simazine	0.01	NR	NR
14	S1	Prothiofos	26	1.2	NR
15	S1	Ethion	0.059	0.0295	95
	S2	Diuron	0.078	0.039	98

Lab. Code	Sample	Pesticide	Concentration (µg/L)	Uncertainty (µg/L)	Recovery (%)
16	S1	Ethion	0.053	0.016	75
	S2	Diuron	0.118	0.021	75
17	S1	alpha-Endosulfan	4.01	1.56	NR

6.7 Participants' Analytical Methods

A variety of analytical methods were used for each group of analytes (Appendix 4).

For Samples S1 and S2 participants used direct injection, or different extractions techniques such as liquid-liquid and solid phase extractions. For the clean-up step, two participants used filtration and two participants used QuEChERS. Dichloromethane, hexane, ether, ethyl acetate, acetonitrile and mixtures of these were used as extraction solvents. Participants reported using GC-MS(MS), GC-(ECD, FPD, NPD), and LC-MS(MS). Three participants reported using the entire sample (500 mL) for the extraction, while other participants reported sample test portions ranging from 1 – 400 mL. No trends were identified with consideration to whether the whole sample was used, or what sample volume was used (Figure 15).

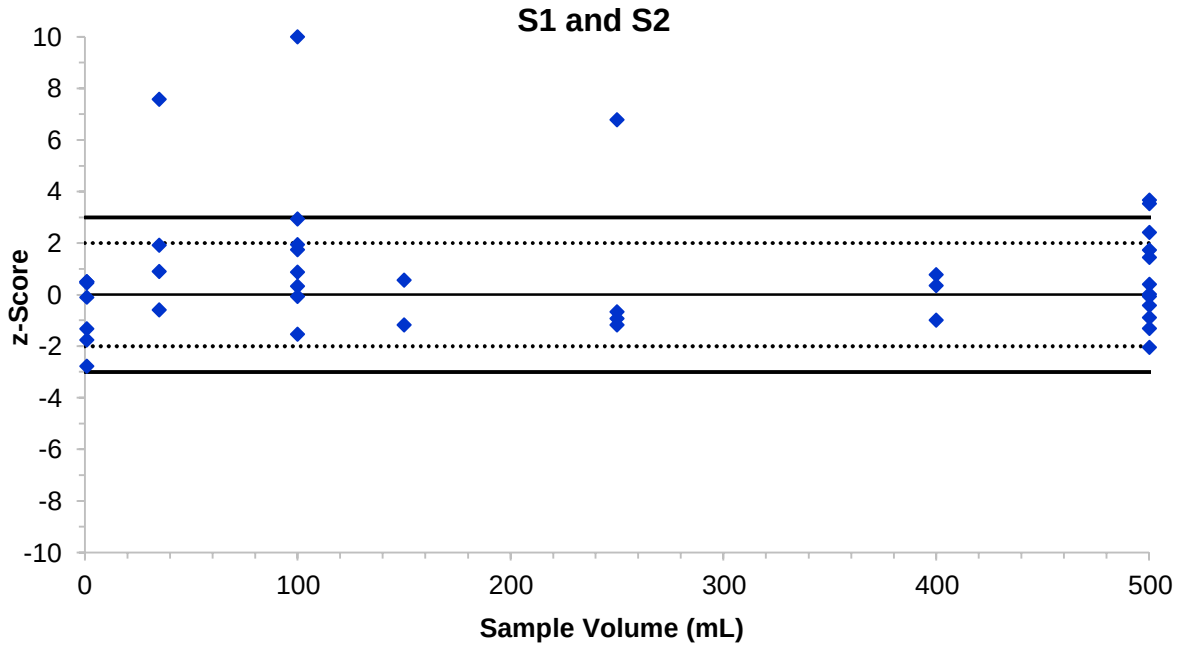


Figure 15 z-Score vs sample volume for pesticides in Samples S1 and S2

For Sample S3 (AMPA and glyphosate) two participants used direct injection and LC-MS(MS) for quantification, while the other participants used FMOC (fluorenylmethyloxycarbonyl chloride) to derivatise and LC-MS/MS for quantification. Participants reported sample test portions ranging from 0.5 – 100 mL. No trends were identified with consideration to what sample volume was used (Figure 16).

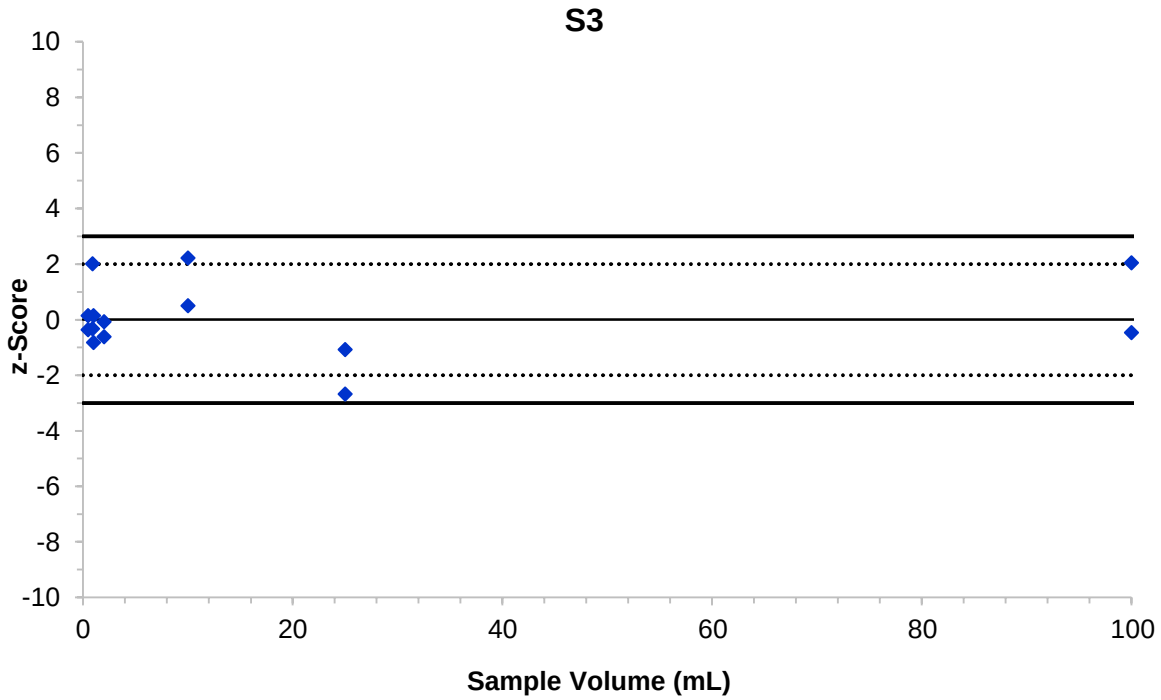


Figure 16 z-Score vs sample volume for AMPA and glyphosate in Samples S3

No trends were apparent with either the various extraction solvents used or the technique for quantification for all samples.

Recoveries were reported by participants in the range of 60 to 120%. Three laboratories reported correcting for recoveries.

6.8 Certified Reference Materials (CRM)

Participants were requested to indicate whether a matrix specific certified reference material (CRM) had been used as part of the quality assurance for the analysis.

Twelve laboratories reported using 'certified standards', including:

- Sigma Aldrich
- Accustandard
- Dr Ehrenstorfer

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*'[10]

6.9 Comparison with Previous Studies

Overall percentages of satisfactory performance (presented as a percentage of the total number of scores for each study) obtained by the participant laboratories in Pesticides in Water proficiency tests since 2008 is presented in Figure 17.

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 12 years on average is 76%, while for E_n-scores on average for the same period is 73%.

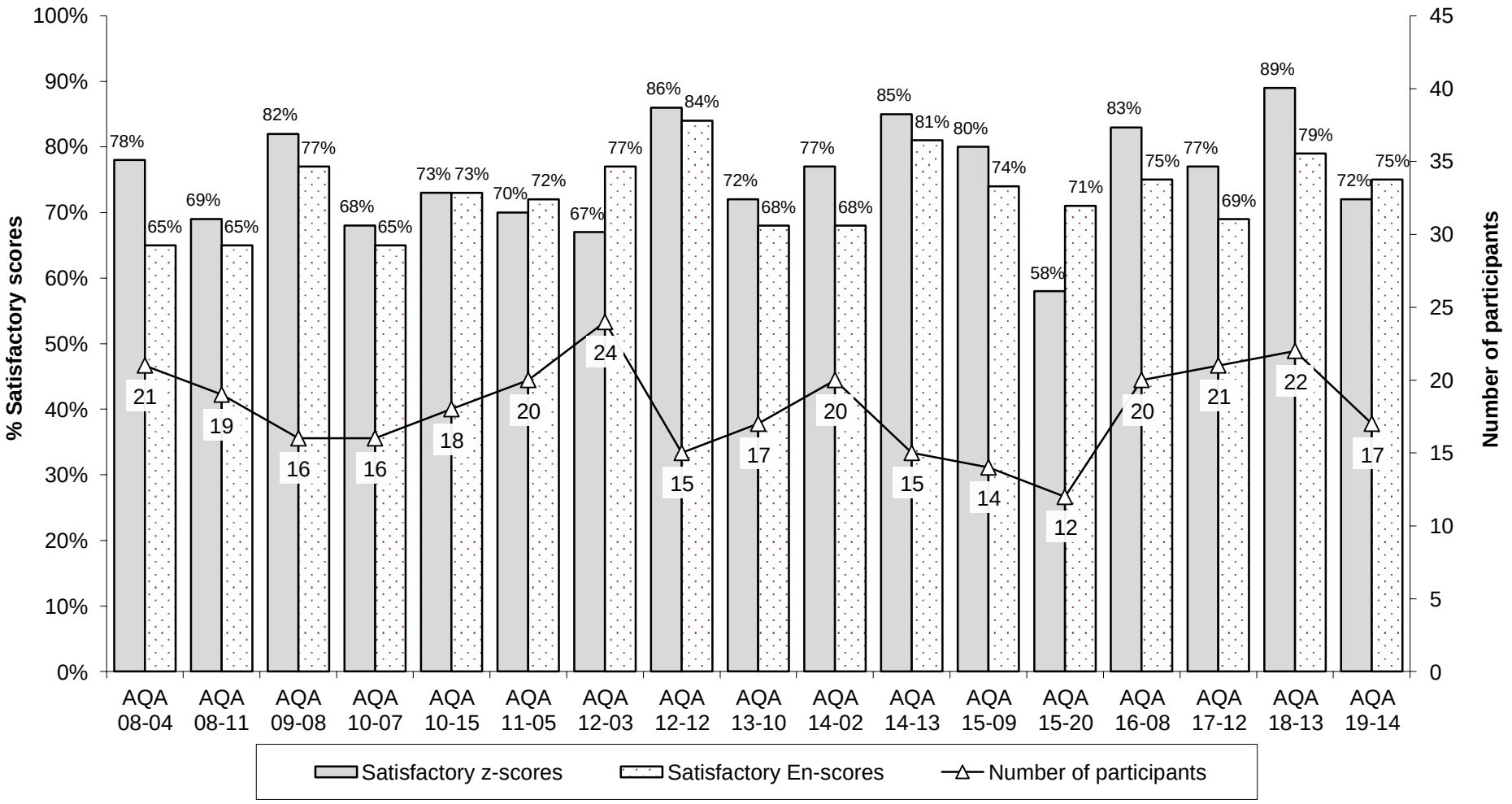


Figure 17 Satisfactory z and E_n-scores – comparison with previous PT studies

7 REFERENCES

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APPENDIX 1 – SAMPLE PREPARATION AND HOMOGENEITY TESTING

Sample Preparation

The three samples were prepared from surface water obtained from Browns Waterhole in the Turramurra area of Sydney. The water was filtered through a glass fibre filter and autoclaved.

The water used for Samples S1 and S2 was adjusted to pH 7.0 using hydrochloric acid. The spiking solutions were prepared by dissolving the standards in acetone. The test samples were stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL amber glass bottles.

Sample S3 was prepared using filtered and autoclaved but not pH adjusted water. The glyphosate and AMPA were dissolved in water. The test samples were stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL PET bottles.

Thirty-five bottles of each of Samples S1, S2 and S3 were prepared.

Between preparation and dispatch the samples were stored in a cool room at 4°C.

Expanded Uncertainties

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. Stability was not considered in the uncertainty budget and so the expanded uncertainty relates to the concentration of pesticide at the time of spiking.

Homogeneity Testing

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

APPENDIX 2 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY

When the robust average was calculated using the procedure described in 'ISO 13258:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons – Annex C',[8] the uncertainty was estimated as:

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

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.

A worked example is set out below in Table 19.

Table 19 Uncertainty of robust average for AMPA in Sample S3

No. results (p)	7
Robust Average	28.49 µg/L
$S_{rob\ av}$	8.22 µg/L
$u_{rob\ av}$	3.88 µg/L
k	2
$U_{rob\ av}$	7.76 µg/L

The robust average for AMPA in Sample S3 is 28.5 ± 7.8 µg/L.

APPENDIX 3 – ACRONYMS AND ABBREVIATIONS

ACN	Acetonitrile
AMPA	Aminomethylphosphonic acid
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
ECD	Electron Capture Detector
$\|E_n\|$	Absolute value of an E_n-score
FMOC	Fluorenylmethyloxycarbonyl chloride
FPD	Flame Photometric Detector
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
HPLC	High Performance Liquid Chromatography
IEC	International Electrotechnical Commission
ISO	International Standards Organisation
LC	Liquid Chromatography
LOR	Limit of Reporting
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
MS	Mass Spectrometry
MSMS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
NATA	National Association of Testing Authorities
NEPC	National Environmental Protection Council
NMI	National Measurement Institute (of Australia)
NPD	Nitrogen-Phosphorus Detector
NR	Not Reported
NT	Not Tested
OCP	Organochlorine Pesticides
ONP	Organonitrogen Pesticides
OPP	Organophosphorus Pesticides
p,p'-DDD	Dichlorodiphenyldichloroethane
p,p'-DDE	Dichlorodiphenyldichloroethylene

p,p'-DDT	Dichlorodiphenyltrichloroethane
PCV	Performance Coefficient of Variation
PT	Proficiency Test
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe extraction method
R.A.	Robust Average
S.V.	Spiked or formulated concentration of a PT sample
SD	Standard Deviation
SIM	Selective ion monitoring
SPE	Solid Phase Extraction
Target SD	Target Standard Deviation
|z|	Absolute value of a z-score
σ	Target standard deviation

APPENDIX 4 – PARTICIPANTS' TEST METHODS

Table 20 Test methods Sample S1 Chlordane

Lab. Code	Sample Vol. (mL)	Extraction	Clean-up	Solvent	Measurement
1	150				
2	1				
3	35	Liquid-Liquid	None	DCM	GCMS
4	100	Liquid-Liquid	None	Hex.DCM	GCMS
5	35	Liquid-Liquid	None	DCM	GC-MSMS
6	1	Liquid-Liquid	None	DCM	GCMS
7	250	Liquid-Liquid	None	DCM	GC-ECD
8	500	Liquid-Liquid	None	DCM	GCMS
9	150-200	Liquid-Liquid	None	15% Ether in Hexane	GC-ECD
10	500	SPE	None	DCM:ethyl acetate 1:1	gcms
11	400	Liquid-Liquid	Quechers	Ethyl Acetate	GC-ECD
12		Liquid-Liquid	None	Hexane	GC-MS
13					
14		Liquid-Liquid	None	DCM	GC-ECD
15	100				GCMS
16	500	Liquid-Liquid	None	DCM	GCMS
17	100				

Table 21 Test methods Sample S1 Diuron

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1				
2	Inline SPE	filtered on 0.22 um		LCMS
3				
4	Direct Injection	0.22u Filter		LCMSMS
5				
6	Direct Injection	None		LCMSMS
7	Liquid-Liquid	None	DCM	GCMS-SIM
8				
9				
10	Direct Injection	None		lcms lcms neat
11				
12	Liquid-Liquid	QuEChERS	Acetonitrile	LC_MS/MS
13				
14				
15				LCMS
16	SPE	None	ACN&DCM	LCMS
17				

Table 22 Test methods Sample S1 Endosulfan sulfate

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1	Liquid-Liquid	None	Hexane	GC-ECD
2				
3	Liquid-Liquid	None	DCM	GCMS
4	Liquid-Liquid	None	Hex.DCM	GCMS
5	Liquid-Liquid	None	DCM	GC-MSMS
6	Liquid-Liquid	None	DCM	GCMS
7	Liquid-Liquid	None	DCM	GC-ECD
8	Liquid-Liquid	None	DCM	GCMS
9	Liquid-Liquid	None	15% Ether in Hexane	GC-ECD
10	SPE	None	DCM:ethyl acetate 1:1	gcms
11	Liquid-Liquid	Quechers	Ethyl Acetate	GC-ECD
12	Liquid-Liquid	None	Hexane	GC-MS
13				
14	Liquid-Liquid	None	DCM	GC-ECD
15				GCMS
16	Liquid-Liquid	None	DCM	GCMS
17	Liquid-Liquid	None	DCM	GCMS

Table 23 Test methods Sample S1 Molinate

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1				
2				
3				
4	Liquid-Liquid	None	Hex.DCM	GCMS
5				
6	Direct Injection	None		LCMSMS
7	Liquid-Liquid	None	DCM	GCMS-SIM
8				
9	Liquid-Liquid	None	DCM	GC-MS
10	SPE	None	DCM:ethyl acetate 1:1	gcms/lcms LCMS neat
11				
12	Liquid-Liquid	QuEChERS	Acetonitrile	LC_MS/MS
13				
14				
15				LCMS
16				
17				

Table 24 Test methods Sample S2 Ethion

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1	Liquid-Liquid	None	Ethyl acetate	GC-FPD
2				
3				
4	Liquid-Liquid	None	Hex.DCM	GCMS
5				
6	Direct Injection	None		LCMSMS
7	Liquid-Liquid	None	DCM	GCMS-SIM
8	Liquid-Liquid	None	DCM	GCMS
9	Liquid-Liquid	None	15% Ether in Hexane	GC-ECD
10				
11	Liquid-Liquid	Quechers	Ethyl Acetate	GC-NPD
12				
13				
14	Liquid-Liquid	None	DCM	GCMS
15				GCMS
16	Liquid-Liquid	None	DCM	GCMS
17				

Table 25 Test methods Sample S2 Methomyl

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1				
2				
3				
4	Direct Injection	0.22u Filter		LCMSMS
5				
6				
7				
8			DCM	GCMS
9				
10				
11				
12	Liquid-Liquid	QuEChERS	Acetonitrile	LC_MS/MS
13				
14				
15				LCMS
16	SPE	None	ACN&DCM	LCMS
17				

Table 26 Test methods Sample S2 Metsulfuron-methyl

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1				
2	Inline SPE	filtered on 0.22 um		LCMS
3				
4	Direct Injection	0.22u Filter		LCMSMS
5				
6	Direct Injection	None		LCMSMS
7				
8			DCM	GCMS
9	Liquid-Liquid	None	DCM	GC-MS
10	Direct Injection	None		lcms LCMS neat
11				
12				
13				
14				
15				LCMS
16	SPE	None	ACN&DCM	LCMS
17				

Table 27 Test methods Sample S2 Simazine

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1				
2	Inline SPE	filtered on 0.22 um		LCMS
3				
4	Direct Injection	0.22u Filter		LCMSMS
5				
6	Direct Injection	None		LCMSMS
7	Liquid-Liquid	None	DCM	GCMS-SIM
8				
9	Liquid-Liquid	None	DCM	GC-MS
10	SPE	None	DCM:ethyl acetate 1:1	gcms/lcms LCMS neat
11				
12	Liquid-Liquid	QuEChERS	Acetonitrile	LC_MS/MS
13				
14				
15				LCMS
16	SPE	None	ACN&DCM	LCMS
17				

Table 28 Test methods Sample S3 AMPA and Glyphosate

Lab. Code	Sample Vol. (mL)	Extraction	Derivatisation Procedure	Derivatisation Agent	Measurement
1					
2					
3	0.5	n/a		n/a	LCMS-MS Direct injection method
4	2		Pre-column	FMOC	LCMSMS
5					
6	100		Pre-column	FMOC	LCMSMS
7					
8		Direct Injection			LCMS
9	0.9	nil	Pre-column	FMOC	LCMS-QQQ
10	25	None	Pre-column	FMOC-CL	LCMS QQQ
11					
12					
13	10	NA	Pre-column	FMOC	LC/MS/MS
14					
15	1			FMOC	LCMSMS
16					
17					

END OF REPORT