Australian Government
Department of Industry, Innovation and Science
National Measurement Institute

Proficiency Test Report
AQA 18-13
Pesticides in Water

January 2019

ACKNOWLEDGMENTS

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

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

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

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Accredited for compliance with ISO/IEC 17043

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SUMMARY

AQA 18-13 commenced in September 2018. Twenty-three laboratories registered to participate and twenty-two submitted results.

The sample set consisted of three water samples. Samples were prepared in the NMI Sydney laboratory using tap water for Sample S1 and surface water from Browns Waterhole in the Turramurra area of Sydney for Samples S2 and S3. Samples were prepared as described in Annex 2 and spiked with selected pesticides (Table 2).

Of a possible 220 numeric results a total of 124 (56%) were submitted.
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:

(i) *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 81 results for which z-scores were calculated, 72 (89%) returned a satisfactory score of $|z| \leq 2$.

Of 81 results for which E_n-scores were calculated, 64 (79%) returned a satisfactory score of $E_n \leq 1$.

Laboratory **6**, **7** and **17** returned satisfactory z-scores and E_n-scores for all seven analytes for which scores were calculated.

Laboratories **12**, **15** and **16** did not report results for analytes for which they tested (Table 17) and that were present in the test samples (total of 6 results).

Five laboratories (Table 18) reported results for analytes not added to the test samples (total of 14 results).

(ii) *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.

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

All one hundred and twenty-four numerical results were reported with an expanded measurement uncertainty, indicating that laboratories have addressed this requirement of ISO 17025.

The magnitude of reported uncertainties was within the range of 0.2% to 108%.

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, 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 Chemical Proficiency Testing Study Protocol.[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 Proficiency Testing of (Chemical) Analytical 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 Table1. 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;
- National Environmental Protection Council Schedule B1 *Guidelines on the 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	Metsulfuron-methyl
Chlordane	beta-Endosulfan	Molinate
Chlorfenvinphos	Endosulfan sulfate	Parathion
Chlorpyrifos	Ethion	Parathion-methyl
Cypermethrin	Fenitrothion	Permethrin
Diazinon	Fenthion	Prothiofos
p,p'-DDD	Fenvalerate	Simazine
p,p'-DDE	Heptachlor	Trifluralin
p,p'-DDT	Heptachlor epoxide	
Total DDT	Hexachlorobenzene	

Table 2 Formulated Concentrations of Test Samples

Sample S1	Spike (µg/L)	U (µg/L)[1]
Bifenthrin	25.4	1.3
Chlorpyrifos	4.20	0.21
Diuron	4.27	0.21
Molinate	10.80	0.54
Sample S2		
Atrazine	7.29	0.36
p,p'-DDE	1.91	0.10
Diuron	5.06	0.25
Trifluralin	10.9	0.55
Sample S3		
AMPA	27.5	1.4
Glyphosate	20.3	1.0

[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	04 September 2018
Samples dispatched	03 October 2018
Results due	07 November 2018
Interim report issued	15 November 2018

2.3 Participation

Participation was as follows:

Invited	91
Participated:	23
Submitted results	22

The laboratories that participated are listed in Appendix 1.

2.4 Test Sample Preparation and Homogeneity Testing

The preparation of the study samples is described in Appendix 2.

The samples were spiked, mixed and packaged using a process that has been demonstrated to produce homogeneous samples for previous NMI proficiency test 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. Bifenthrin and chlorpyrifos in Sample S1 and p,p'-DDE and trifluralin in Sample S2 seem to have degraded. For p,p'-DDE there was a reasonable consensus between participants' results and an assigned value was set. For bifenthrin, chlorpyrifos and trifluralin the laboratories' performance was not assessed.

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^{o}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. correct 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 (eg 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 provide a brief summary of your test method.
- Return the completed results sheet by e-mail to proficiency@measurement.gov.au
- **Please return completed result sheet by 30 October 2018. Late results cannot be included in the study report.**

2.9 Interim Report

An interim report tabling results and reported uncertainties was emailed to all participants on 15 November 2018.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summaries

Participants were requested to provide information about their test methods. This is transcribed in Appendix 5.

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	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples	Certified Reference Materials Recoveries of Spiked Samples	ISO/GUM
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate analysis Instrument calibration	Certified Reference Materials Recoveries of Spiked Samples Instrument Calibration	Nata Technical Note 33
4	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Recoveries of Spiked Samples Instrument Calibration	
5	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis		Eurachem/CITAC Guide
6	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples	Certified Reference Materials	Eurachem/CITAC Guide
7	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis Instrument calibration	Certified Reference Materials Recoveries of Spiked Samples Instrument Calibration Standard Purity	Nata Technical Note 33
8	Professional judgment	Control Samples Duplicate analysis Instrument calibration	Recoveries of Spiked Samples Instrument Calibration Standard Purity	Nata Technical Note 33
9	Control Charts	Control Samples	Recoveries of Spiked Samples	In house based on NATA Technical Note 33
10		Control Samples	Recoveries of Spiked Samples Standard Purity	Eurachem/CITAC Guide
11	NMI, P 20002-3 Estimating measurement in an afternoon: a case study	Duplicate analysis Instrument calibration	Certified Reference Materials Instrument Calibration Standard Purity	In-house method validation
12	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate analysis	Certified Reference Materials Laboratory bias from PT studies Recoveries of Spiked Samples	Nata Technical Note 33
13	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate analysis Instrument calibration		Nata Technical Note 33
14	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis	Recoveries of Spiked Samples	ISO/GUM
15	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate analysis Instrument calibration	Certified Reference Materials Recoveries of Spiked Samples Instrument Calibration	Nata Technical Note 33
16	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate analysis	Recoveries of Spiked Samples Standard Purity	ISO/GUM

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision	Method Bias	
17	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate analysis Instrument calibration	Certified Reference Materials Recoveries of Spiked Samples Instrument Calibration	ISO/GUM
18	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of Spiked Samples	Nata Technical Note 33
19	Estimation of uncertainty generated through the use of control charts			Control charts
20	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis	Recoveries of Spiked Samples	Eurachem/CITAC Guide
21	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate analysis Instrument calibration	Certified Reference Materials Recoveries of Spiked Samples InstrumentCalibration Standard Purity	Nata Technical Note 33
22	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of Spiked Samples	Eurolab Technical Report No1/2007
23	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples	Recoveries of Spiked Samples Standard Purity	ISO/GUM

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
12	S1	S1 analysed on LCMSMS

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.

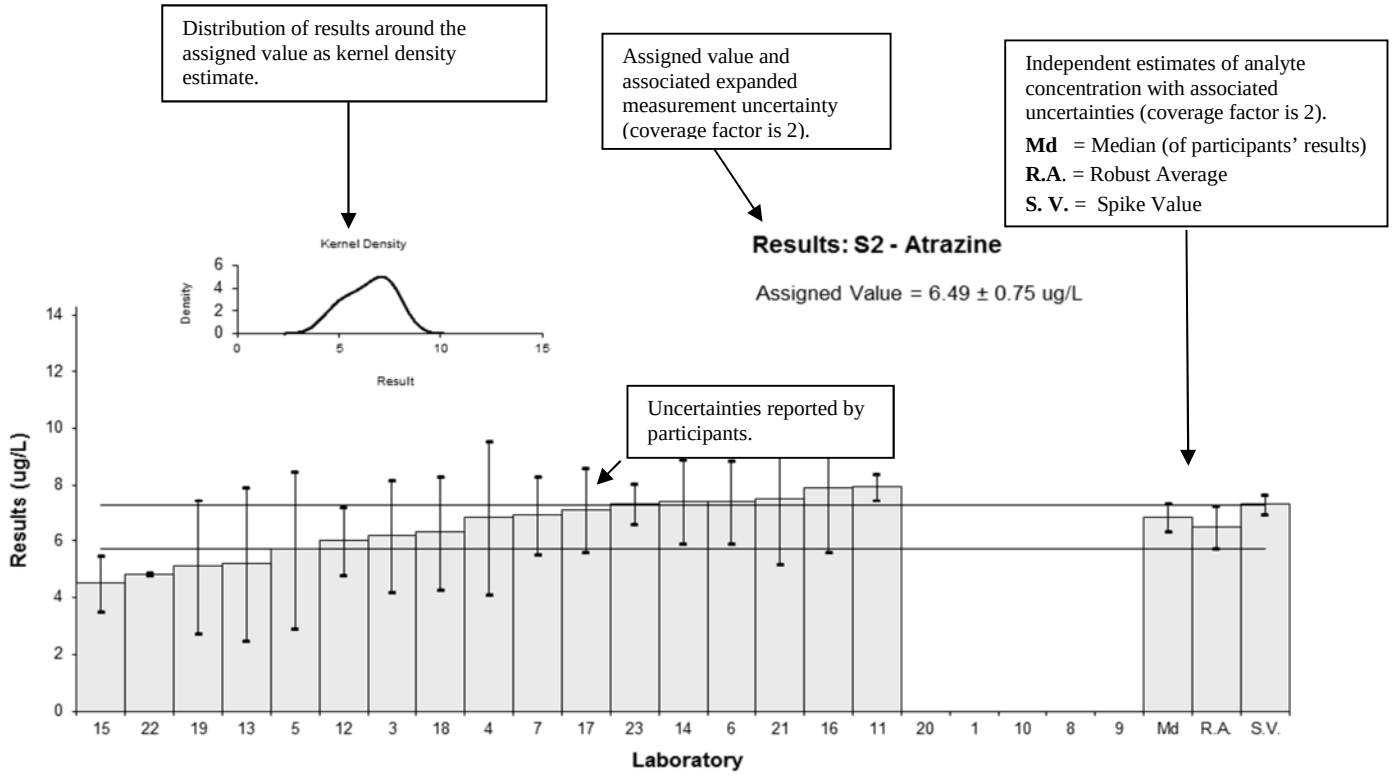


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

The assigned value is defined as: 'value attributed to a particular property of a proficiency test item.' [1] In this study, the property is the concentration of 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). This value is used in the calculation of z-scores.

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

4.5 z-Score

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

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

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:

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

where:

E_n is E_n-score
χ is a participant's result
X is the assigned value
U_χ is the expanded uncertainty of the participant's result
U_X is the expanded uncertainty of the assigned value

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

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

4.7 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017[6] 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.[7]

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 interlaboratory comparisons'.[8]

5 TABLES AND FIGURES

Table 5

Sample Details

Sample No.	S1
Matrix.	Water
Analyte.	Bifenthrin
Units	ug/L

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	NT	NT	NT
3	13	4	80-110
4	17.72	7.09	96
5	13.2	3.2	NR
6	NT	NT	NT
7	3.26	0.653	99
8	NT	NT	NT
9	9.4	3.5	NR
10	NT	NT	NT
11	NR	NR	NR
12	NT	NT	NT
13	8.89	2.67	NR
14	28	5.6	NR
15	13	4	80-110
16	20	3	NR
17	NT	NT	NT
18	NT	NT	NT
19	9.88	3.952	NR
20	4.60	0.30	NR
21	18	6	NR
22	15.34	0.03	105.47
23	17.50	1.20	95

Statistics

Assigned Value	Not set	
Spike	25.4	1.3
Robust Average	13.4	4.3
Median	13.1	3.7
Mean	13.7	
N	14	
Max.	28	
Min.	3.26	
Robust SD	6.4	
Robust CV	48%	

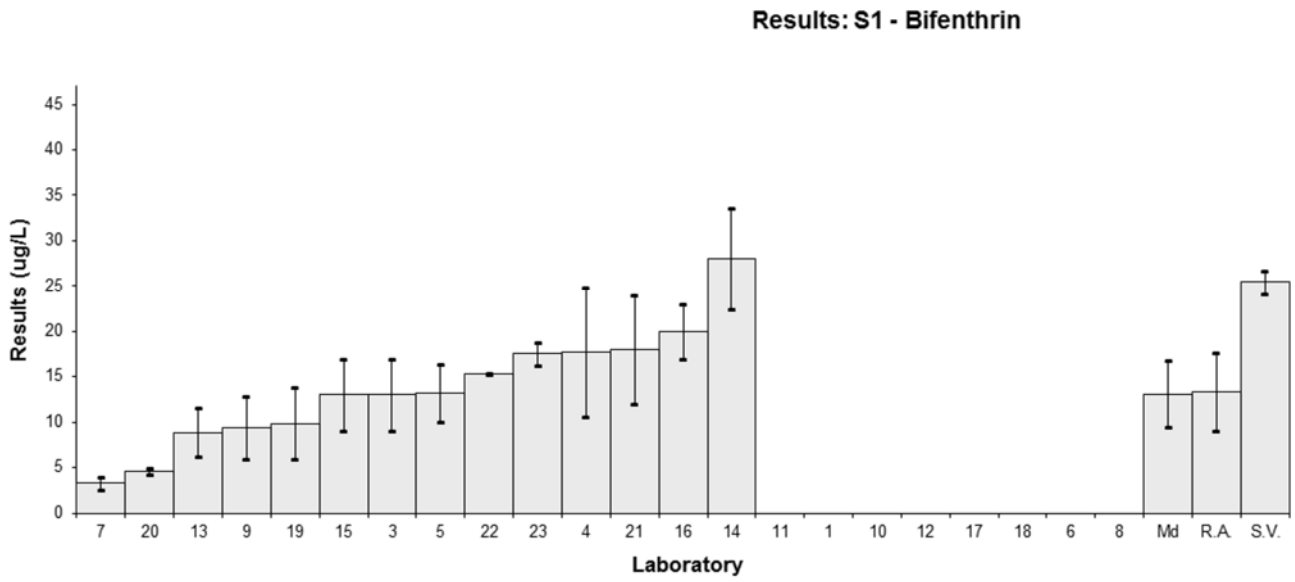

Results: S1 - Bifenthrin
Results (ug/L)
45
40
35
30
25
20
15
10
5
0
7
20
13
9
19
15
3
5
22
23
4
21
16
14
11
1
10
12
17
18
6
8
Md
R.A.
S.V.
Laboratory

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix.	Water
Analyte.	Chlorpyrifos
Units	ug/L

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	NT	NT	NT
3	1.6	0.5	80-110
4	0.8	0.32	84
5	1.65	0.53	NR
6	0.7	0.14	NR
7	1.68	0.336	88
8	<4	1.2	NR
9	< 2	0.4	NR
10	0.194	0.02	NR
11	1.71	0.08	NR
12	<0.1	0.02	86
13	1.17	0.59	NR
14	0.88	0.18	NR
15	1.5	0.5	80-110
16	1.9	0.6	NR
17	0.61	0.122	92
18	1.8	0.5	80-110
19	< 2	< 0.6	NR
20	0.30	0.02	NR
21	2.2	0.7	NR
22	1.82	0.03	137.13
23	0.88	0.09	95

Statistics

Assigned Value	Not Set	
Spike	4.20	0.21
Robust Average	1.26	0.41
Median	1.50	0.30
Mean	1.258	
N	17	
Max.	2.2	
Min.	0.194	
Robust SD	0.68	
Robust CV	54%	

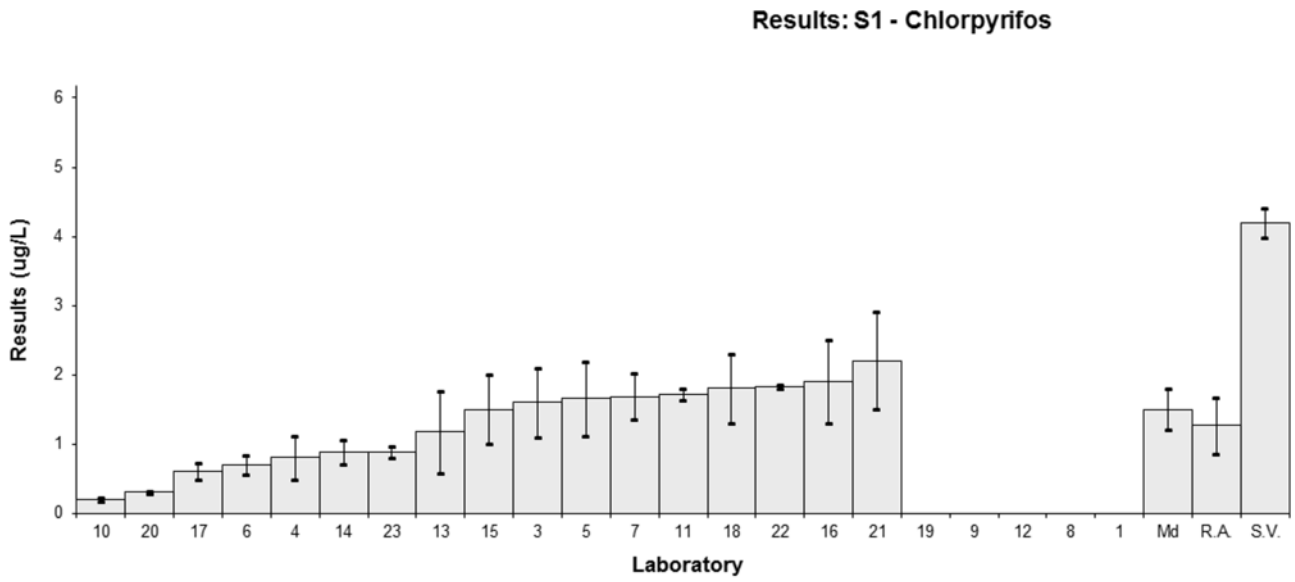

Results: S1 - Chlorpyrifos
Results (ug/L)
0
1
2
3
4
5
6
10
20
17
6
4
14
23
13
15
3
5
7
11
18
22
16
21
19
9
12
8
1
Md
R.A.
S.V.
Laboratory

Figure 3

Table 7

Sample Details

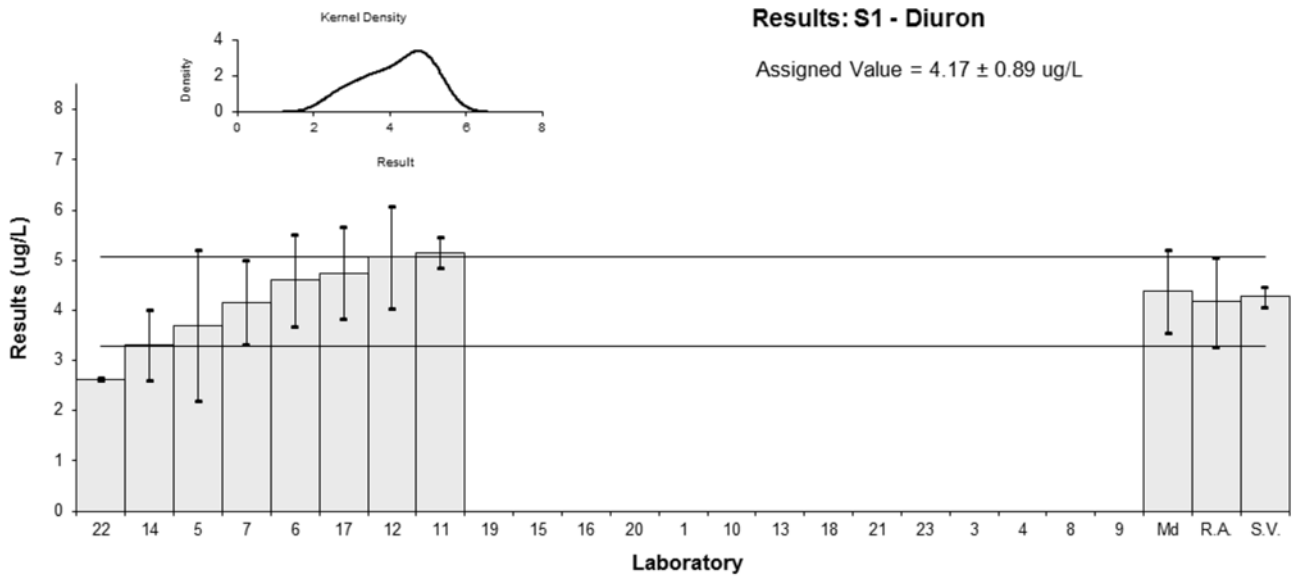
Sample No.	S1
Matrix.	Water
Analyte.	Diuron
Units	ug/L

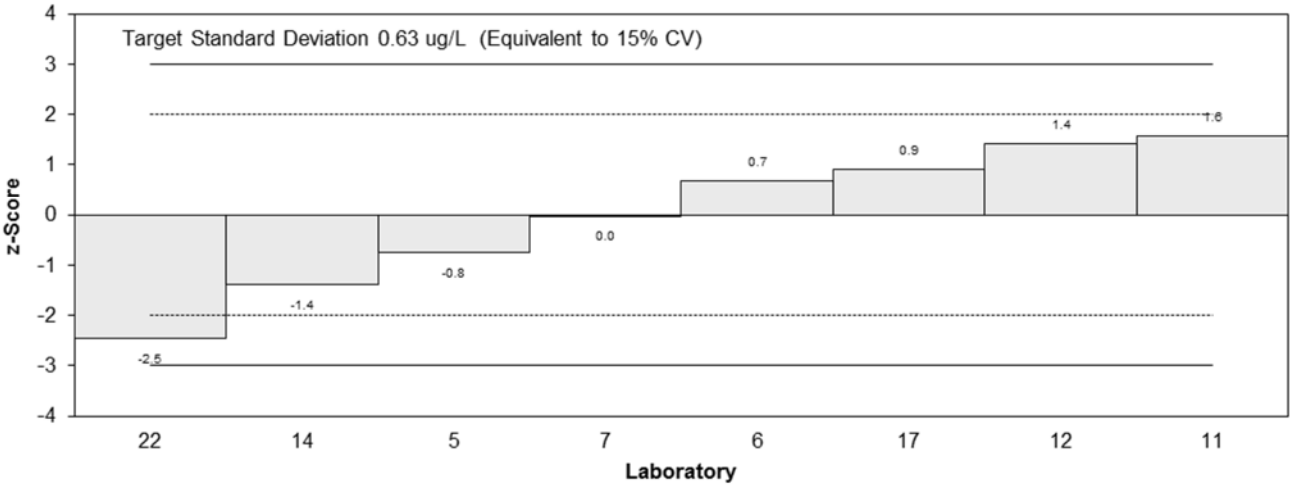
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	3.7	1.5	NR	-0.75	-0.27
6	4.6	0.92	NR	0.69	0.34
7	4.16	0.832	110	-0.02	-0.01
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	5.15	0.31	NR	1.57	1.04
12	5.06	1.02	88	1.42	0.66
13	NT	NT	NT		
14	3.3	0.7	NR	-1.39	-0.77
15	<2	NR	80-110		
16	<2	NR	NR		
17	4.74	0.92	NR	0.91	0.45
18	NT	NT	NT		
19	< 10	3	NR		
20	NR	NR	NR		
21	NT	NT	NT		
22	2.63	0.03	92.03	-2.46	-1.73
23	NT	NT	NT		

Statistics

Assigned Value	4.17	0.89
Spike	4.27	0.21
Robust Average	4.17	0.89
Median	4.38	0.84
Mean	4.17	
N	8	
Max.	5.15	
Min.	2.63	
Robust SD	1.0	
Robust CV	24%	


Kernel Density
Density
Result
Results: S1 - Diuron
Assigned Value = 4.17 ± 0.89 ug/L
Results (ug/L)
22 14 5 7 6 17 12 11 19 15 16 20 1 10 13 18 21 23 3 4 8 9 Md R.A. S.V.
Laboratory


z-Scores: S1 - Diuron
Target Standard Deviation 0.63 ug/L (Equivalent to 15% CV)
z-Score
-2.5
-1.4
-0.8
0.0
0.7
0.9
1.4
1.6
22 14 5 7 6 17 12 11
Laboratory

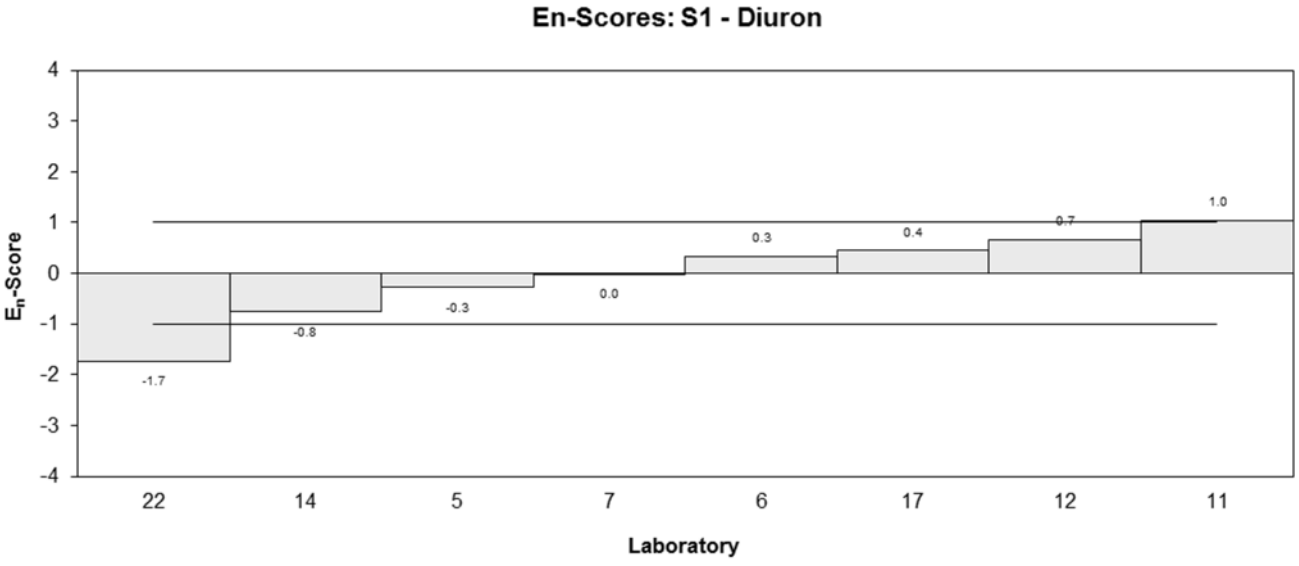

En-Scores: S1 - Diuron
En-Score
-1.7
-0.8
-0.3
0.0
0.3
0.4
0.7
1.0
22 14 5 7 6 17 12 11
Laboratory

Figure 4

Table 8

Sample Details

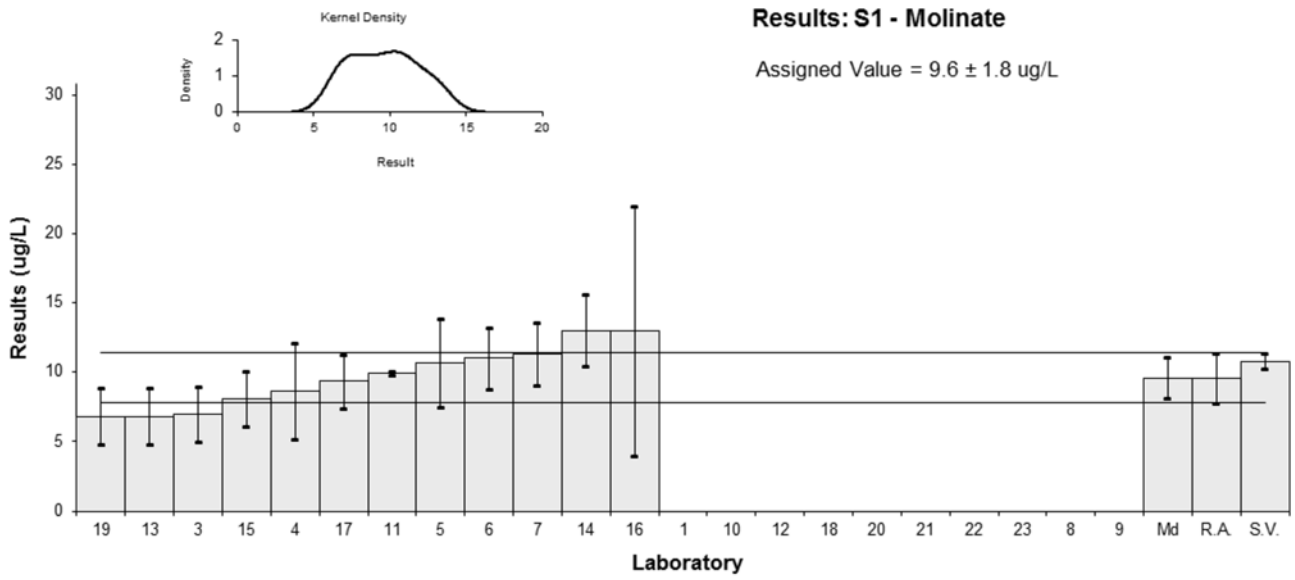
Sample No.	S1
Matrix.	Water
Analyte.	Molinate
Units	ug/L

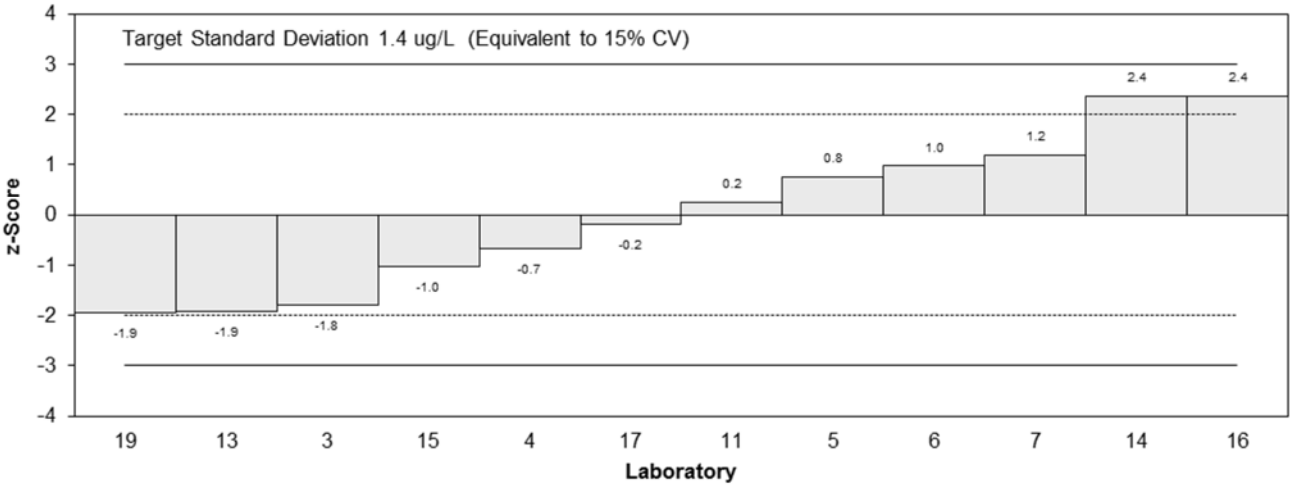
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
3	7.0	2	80-110	-1.81	-0.97
4	8.64	3.46	84	-0.67	-0.25
5	10.7	3.2	NR	0.76	0.30
6	11	2.20	NR	0.97	0.49
7	11.3	2.26	86	1.18	0.59
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	9.94	0.13	NR	0.24	0.19
12	NT	NT	NT		
13	6.82	2.05	NR	-1.93	-1.02
14	13	2.6	NR	2.36	1.08
15	8.1	2	80-110	-1.04	-0.56
16	13	9	NR	2.36	0.37
17	9.34	1.9614	104	-0.18	-0.10
18	NT	NT	NT		
19	6.81	2.04	NR	-1.94	-1.03
20	NT	NT	NT		
21	NT	NT	NT		
22	NT	NT	NT		
23	NT	NT	NT		

Statistics

Assigned Value	9.6	1.8
Spike	10.80	0.54
Robust Average	9.6	1.8
Median	9.6	1.5
Mean	9.64	
N	12	
Max.	13	
Min.	6.81	
Robust SD	2.5	
Robust CV	26%	


Kernel Density
Density
Result
Results: S1 - Molinate
Assigned Value = 9.6 ± 1.8 ug/L
Results (ug/L)
Laboratory
19 13 3 15 4 17 11 5 6 7 14 16 1 10 12 18 20 21 22 23 8 9 Md R.A. S.V.


z-Scores: S1 - Molinate
Target Standard Deviation 1.4 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
19 13 3 15 4 17 11 5 6 7 14 16
-1.9 -1.9 -1.8 -1.0 -0.7 -0.2 0.2 0.8 1.0 1.2 2.4 2.4

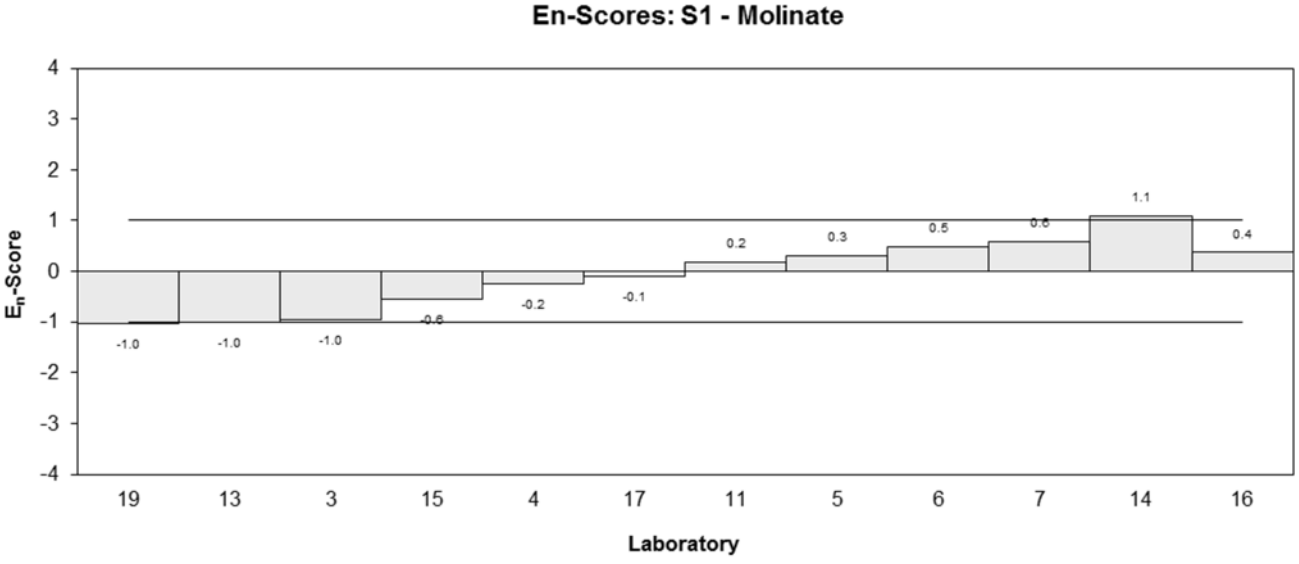

En-Scores: S1 - Molinate
En-Score
Laboratory
19 13 3 15 4 17 11 5 6 7 14 16
-1.0 -1.0 -1.0 -0.6 -0.2 -0.1 0.2 0.3 0.5 0.6 1.1 0.4

Figure 5

Table 9

Sample Details

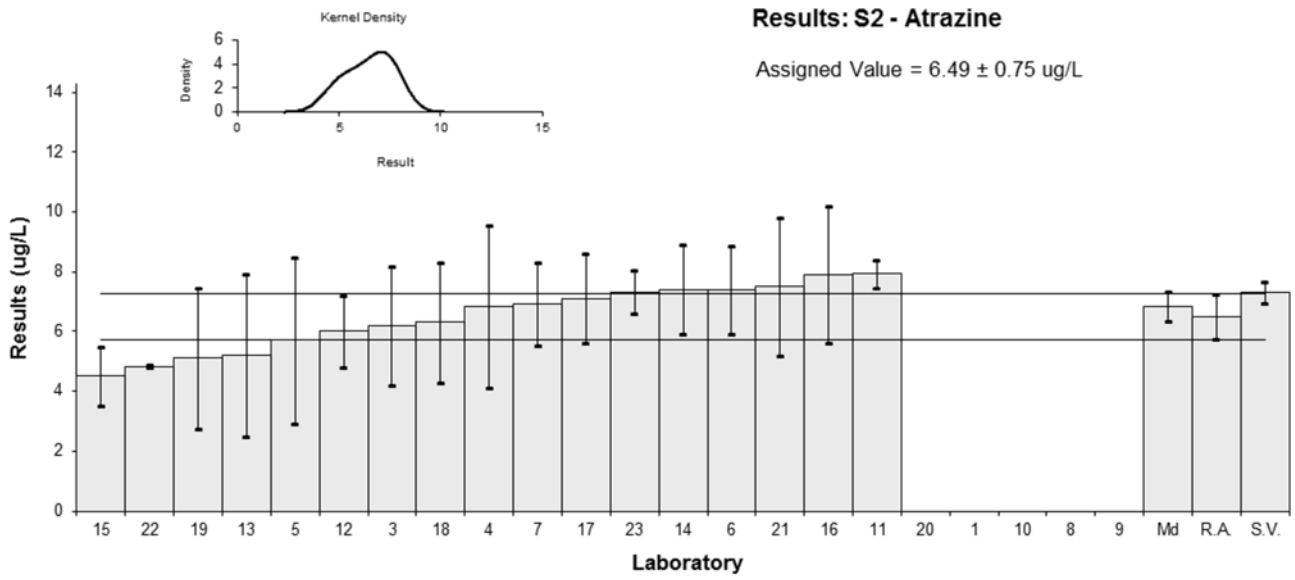
Sample No.	S2
Matrix.	Water
Analyte.	Atrazine
Units	ug/L

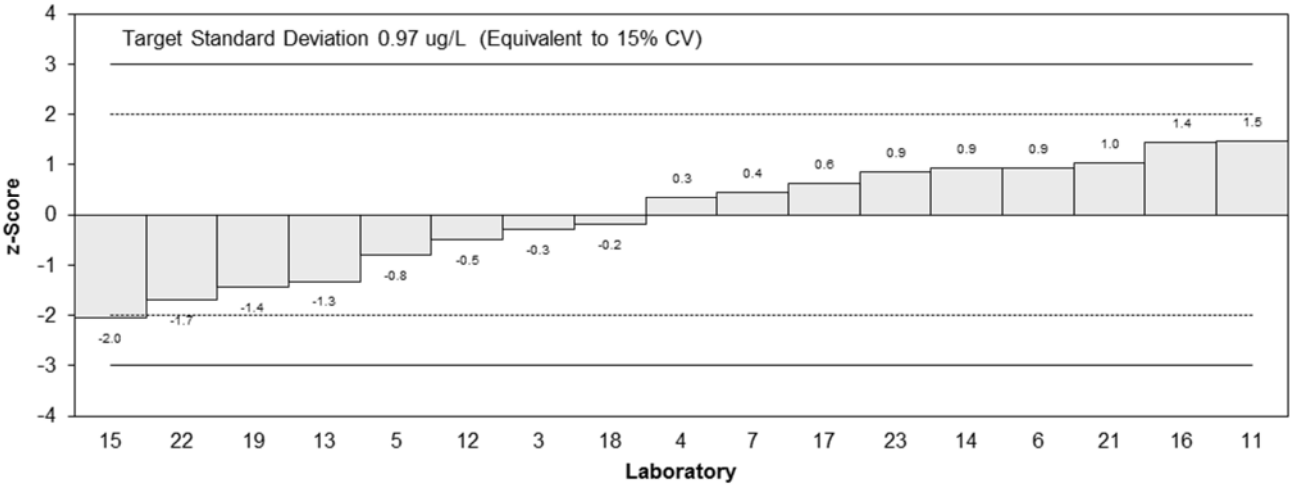
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
3	6.2	2	80-110	-0.30	-0.14
4	6.83	2.73	110	0.35	0.12
5	5.7	2.8	NR	-0.81	-0.27
6	7.4	1.48	NR	0.93	0.55
7	6.92	1.38	111	0.44	0.27
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	7.93	0.48	NR	1.48	1.62
12	6.00	1.2	107	-0.50	-0.35
13	5.2	2.72	NR	-1.33	-0.46
14	7.4	1.5	NR	0.93	0.54
15	4.5	1	80-110	-2.04	-1.59
16	7.9	2.3	NR	1.45	0.58
17	7.11	1.4931	110	0.64	0.37
18	6.3	2	80-110	-0.20	-0.09
19	5.100	2.346	NR	-1.43	-0.56
20	NR	NR	NR		
21	7.5	2.3	NR	1.04	0.42
22	4.84	0.03	111.59	-1.69	-2.20
23	7.32	0.73	84	0.85	0.79

Statistics

Assigned Value	6.49	0.75
Spike	7.29	0.36
Robust Average	6.49	0.75
Median	6.83	0.51
Mean	6.48	
N	17	
Max.	7.93	
Min.	4.5	
Robust SD	1.23	
Robust CV	19%	


Kernel Density
Density
Result
Results: S2 - Atrazine
Assigned Value = 6.49 ± 0.75 ug/L
Results (ug/L)
15 22 19 13 5 12 3 18 4 7 17 23 14 6 21 16 11 20 1 10 8 9 Md R.A. S.V.
Laboratory


z-Scores: S2 - Atrazine
Target Standard Deviation 0.97 ug/L (Equivalent to 15% CV)
z-Score
-2.0 -1.7 -1.4 -1.3 -0.8 -0.5 -0.3 -0.2 0.3 0.4 0.6 0.9 0.9 0.9 1.0 1.4 1.5
15 22 19 13 5 12 3 18 4 7 17 23 14 6 21 16 11
Laboratory

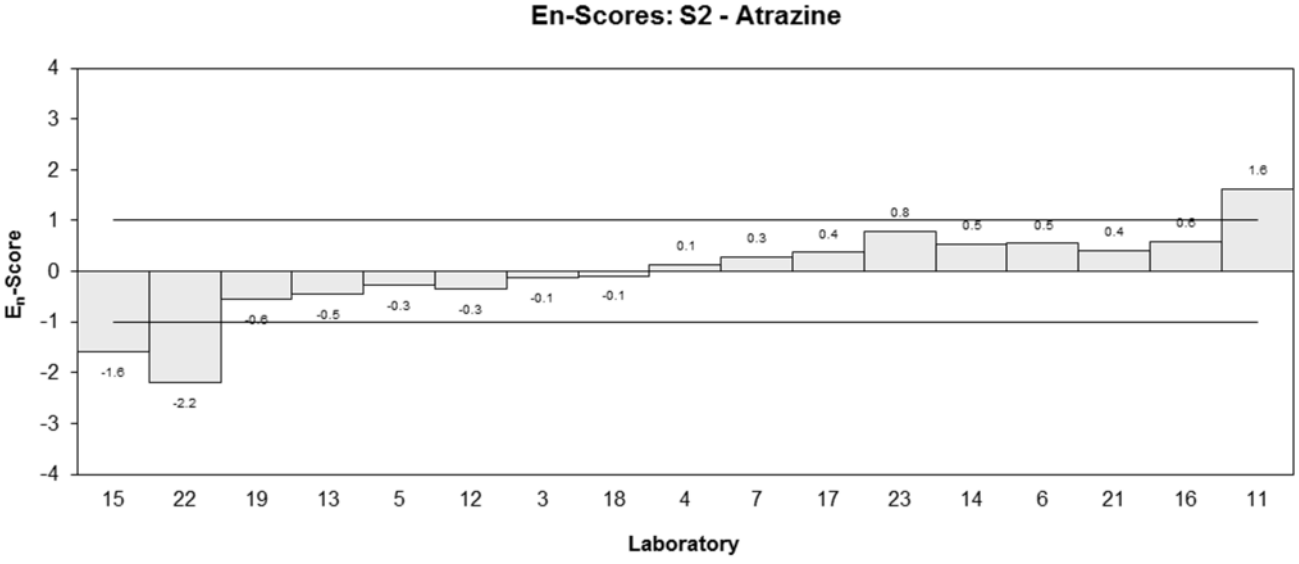

En-Scores: S2 - Atrazine
En-Score
-1.6 -2.2 -0.6 -0.5 -0.3 -0.3 -0.1 -0.1 0.1 0.3 0.4 0.8 0.5 0.5 0.4 0.6 1.6
15 22 19 13 5 12 3 18 4 7 17 23 14 6 21 16 11
Laboratory

Figure 6

Table 10

Sample Details

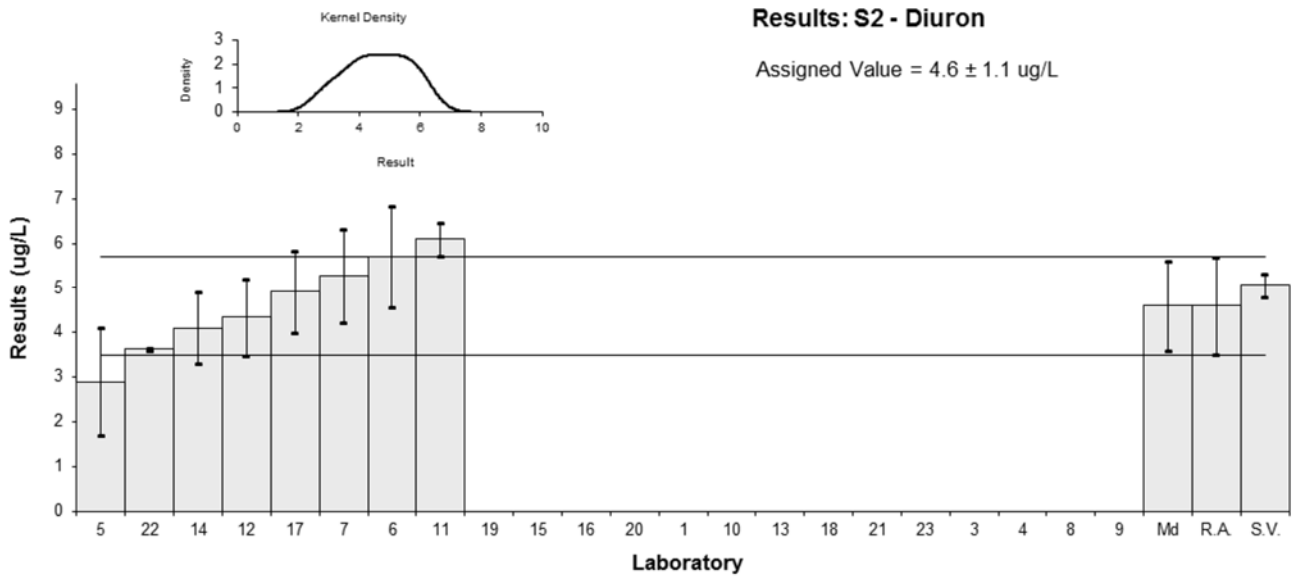
Sample No.	S2
Matrix.	Water
Analyte.	Diuron
Units	ug/L

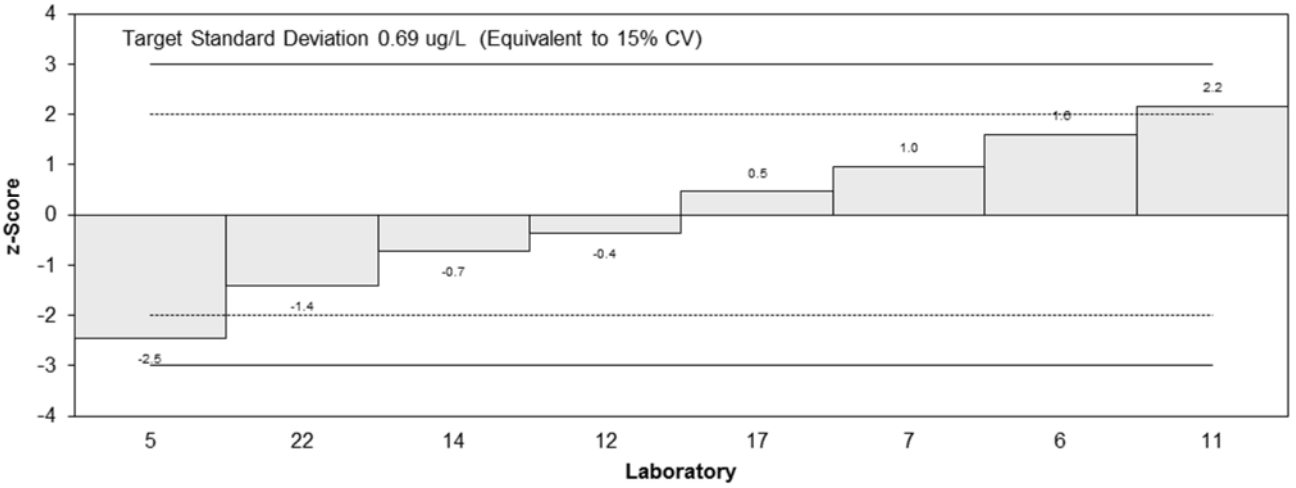
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	2.9	1.2	NR	-2.46	-1.04
6	5.7	1.14	NR	1.59	0.69
7	5.26	1.05	110	0.96	0.43
8	NT	NT	NT		
9	NT	NT	NT		
10	NT	NT	NT		
11	6.09	0.36	NR	2.16	1.29
12	4.34	0.868	119	-0.38	-0.19
13	NT	NT	NT		
14	4.1	0.8	NR	-0.72	-0.37
15	<2	NR	80-110		
16	<2	NR	NR		
17	4.92	0.92	NR	0.46	0.22
18	NT	NT	NT		
19	< 10	3	NR		
20	NR	NR	NR		
21	NT	NT	NT		
22	3.62	0.03	92.03	-1.42	-0.89
23	NT	NT	NT		

Statistics

Assigned Value	4.6	1.1
Spike	5.06	0.25
Robust Average	4.6	1.1
Median	4.6	1.0
Mean	4.6	
N	8	
Max.	6.09	
Min.	2.9	
Robust SD	1.2	
Robust CV	26%	


Kernel Density
Density
Result
Results: S2 - Diuron
Assigned Value = 4.6 ± 1.1 ug/L
Results (ug/L)
Laboratory
5 22 14 12 17 7 6 11 19 15 16 20 1 10 13 18 21 23 3 4 8 9 Md R.A. S.V.


z-Scores: S2 - Diuron
Target Standard Deviation 0.69 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
5 22 14 12 17 7 6 11
-2.5
-1.4
-0.7
-0.4
0.5
1.0
1.6
2.2

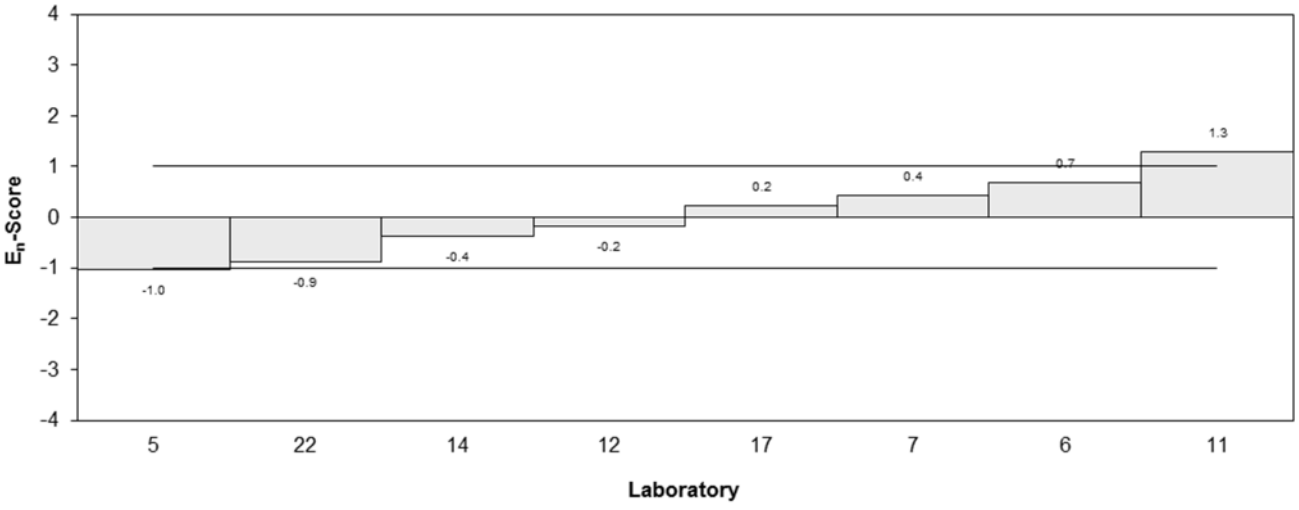

En-Scores: S2 - Diuron
En-Score
Laboratory
5 22 14 12 17 7 6 11
-1.0
-0.9
-0.4
-0.2
0.2
0.4
0.7
1.3

Figure 7

Table 11

Sample Details

Sample No.	S2
Matrix.	Water
Analyte.	p,p'-DDE
Units	ug/L

Participant Results

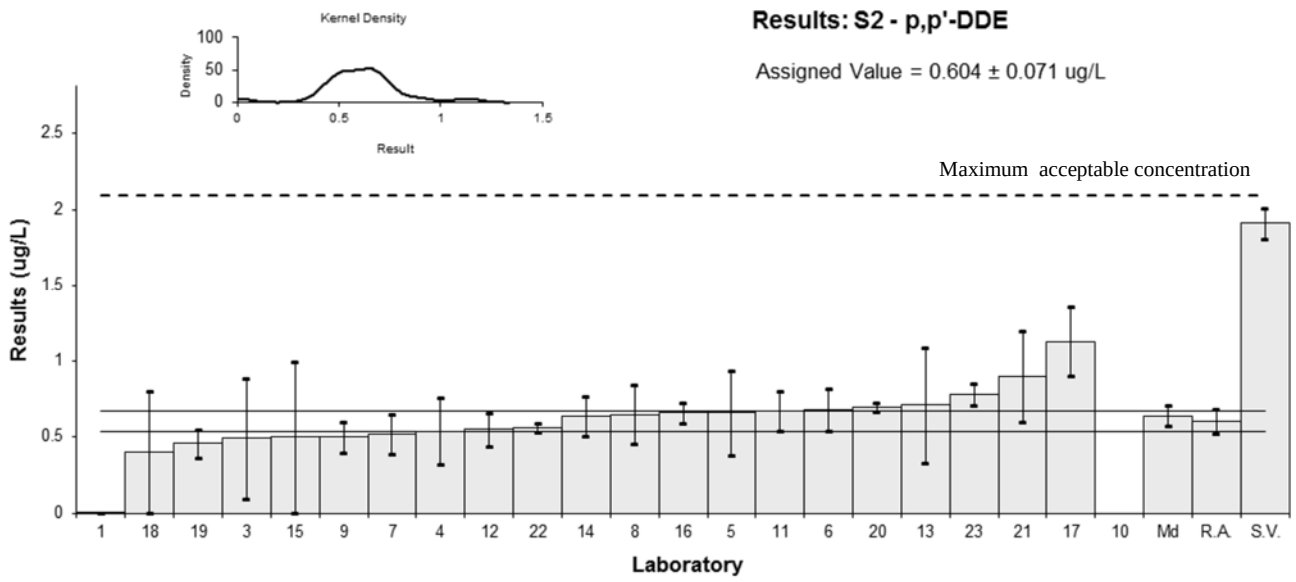
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.00065	0.0002	NR	-6.66	-8.50
3	0.49	0.4	80-110	-1.26	-0.28
4	0.54	0.22	66	-0.71	-0.28
5	0.66	0.28	NR	0.62	0.19
6	0.68	0.14	NR	0.84	0.48
7	0.520	0.130	70	-0.93	-0.57
8	0.65	0.195	NR	0.51	0.22
9	0.5	0.1	NR	-1.15	-0.85
10	NT	NT	NT		
11	0.67	0.13	NR	0.73	0.45
12	0.55	0.11	129	-0.60	-0.41
13	0.71	0.38	NR	1.17	0.27
14	0.64	0.13	NR	0.40	0.24
15	0.5	0.5	80-110	-1.15	-0.21
16	0.66	0.07	NR	0.62	0.56
17**	1.13	0.226	NR	2.00	1.00
18	0.4	0.4	80-110	-2.25	-0.50
19	0.457	0.096	NR	-1.62	-1.23
20	0.70	0.03	NR	1.06	1.25
21**	0.9	0.3	NR	2.00	0.96
22	0.56	0.03	113.36	-0.49	-0.57
23	0.78	0.07	98	1.94	1.77

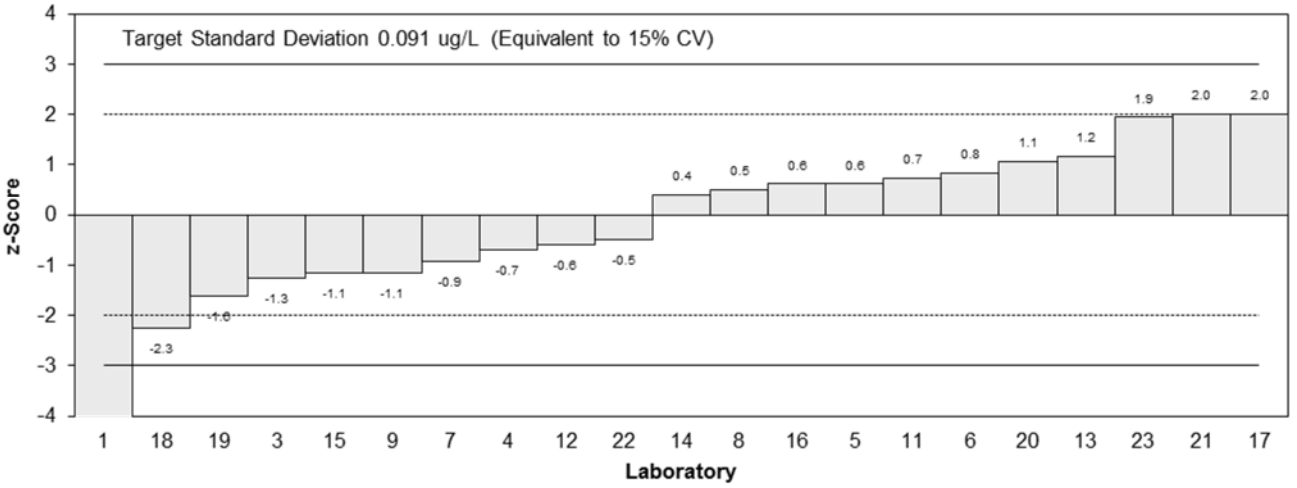
Statistics

Assigned Value*	0.604	0.071
Spike	1.91	0.10
Maximum acceptable conc.**	0.18	
Robust Average	0.605	0.079
Median	0.640	0.067
Mean	0.605	
N	21	
Max.	1.13	
Min.	0.00065	
Robust SD	0.15	
Robust CV	24%	

*Robust average excluding laboratories 1 and 17.

**z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S2 - p,p'-DDE
Assigned Value = 0.604 ± 0.071 ug/L
Maximum acceptable concentration
Results (ug/L)
Laboratory
1 18 19 3 15 9 7 4 12 22 14 8 16 5 11 6 20 13 23 21 17 10 Md R.A. S.V.


z-Scores: S2 - p,p'-DDE
Target Standard Deviation 0.091 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
1 18 19 3 15 9 7 4 12 22 14 8 16 5 11 6 20 13 23 21 17

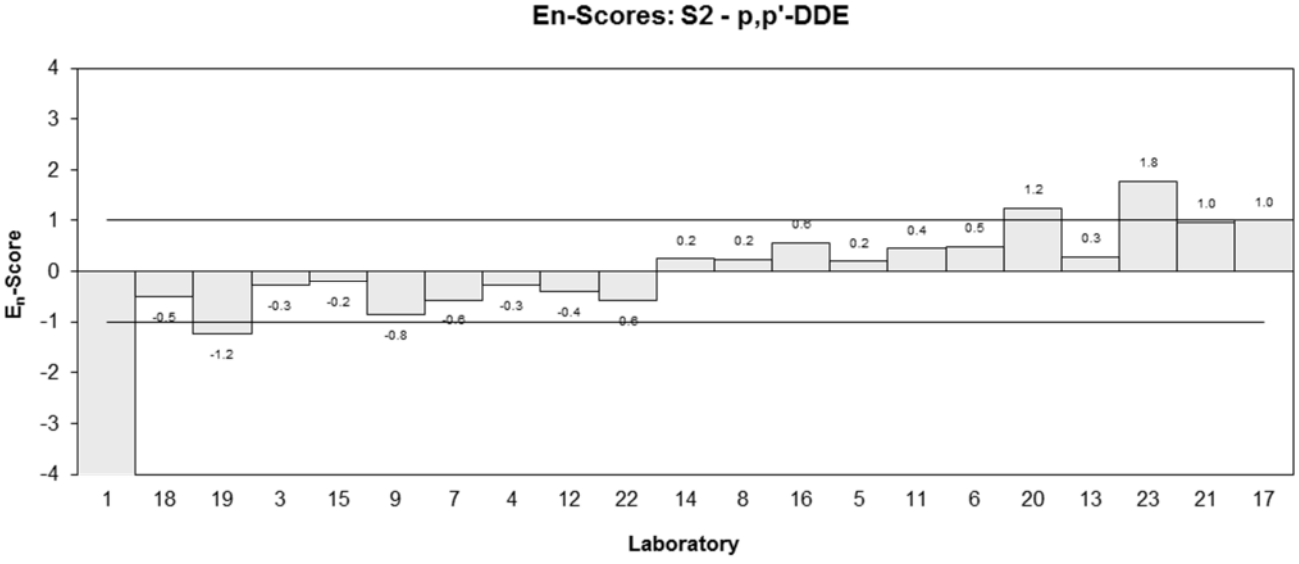

En-Scores: S2 - p,p'-DDE
En-Score
Laboratory
1 18 19 3 15 9 7 4 12 22 14 8 16 5 11 6 20 13 23 21 17

Figure 8

Table 12

Sample Details

Sample No.	S2
Matrix.	Water
Analyte.	Trifluralin
Units	ug/L

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	NT	NT	NT
3	NT	NT	NT
4	3.09	1.24	110
5	5.2	1.8	NR
6	2	0.40	NR
7	5.23	1.05	98
8	NT	NT	NT
9	NT	NT	NT
10	NT	NT	NT
11	3.60	0.17	NR
12	3.87	0.774	70
13	2.66	0.8	NR
14	1.6	0.3	NR
15	2.6	0.8	80-110
16	4.8	2.2	NR
17	3.74	0.7854	100.4
18	NT	NT	NT
19	NT	NT	NT
20	1.78	0.10	NR
21	NT	NT	NT
22	NT	NT	NT
23	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike	10.90	0.55
Robust Average	3.30	1.00
Median	3.34	0.98
Mean	3.35	
N	12	
Max.	5.23	
Min.	1.6	
Robust SD	1.5	
Robust CV	46%	

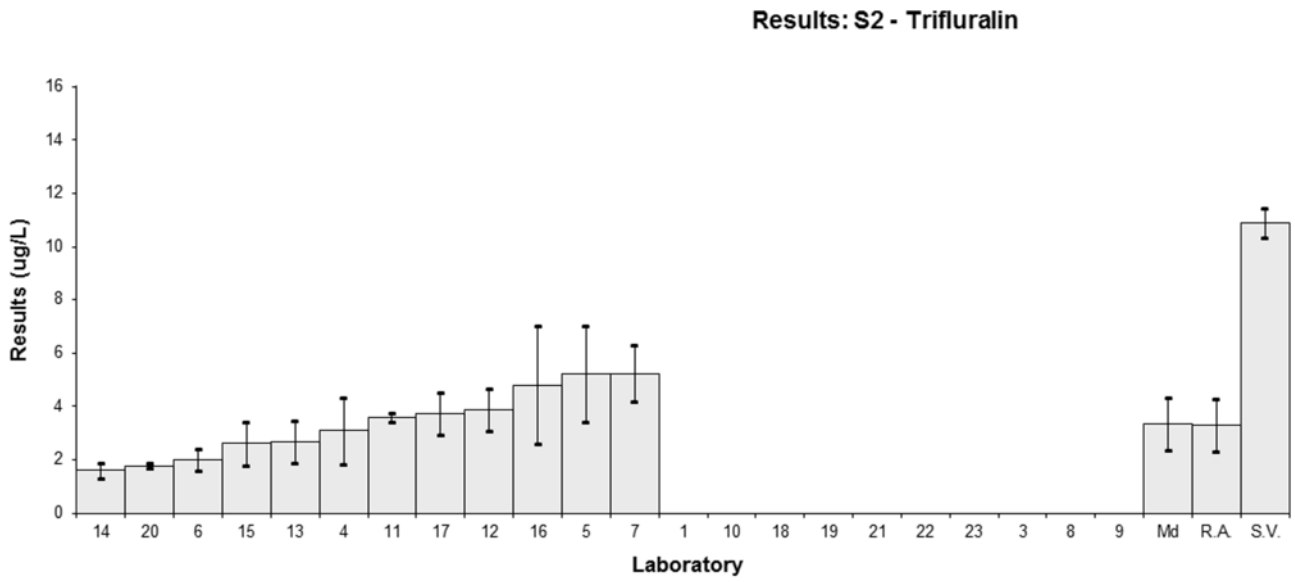

Results: S2 - Trifluralin
Results (ug/L)
16
14
12
10
8
6
4
2
0
14 20 6 15 13 4 11 17 12 16 5 7 1 10 18 19 21 22 23 3 8 9 Md R.A. S.V.
Laboratory

Figure 9

Table 13

Sample Details

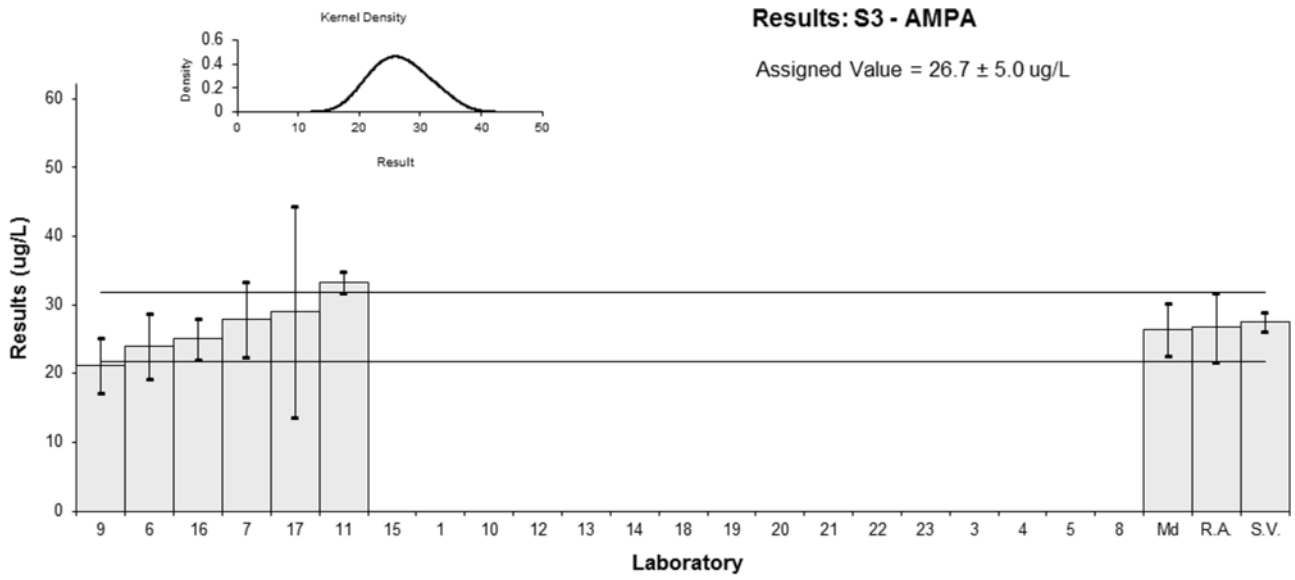
Sample No.	S3
Matrix.	Water
Analyte.	AMPA
Units	ug/L

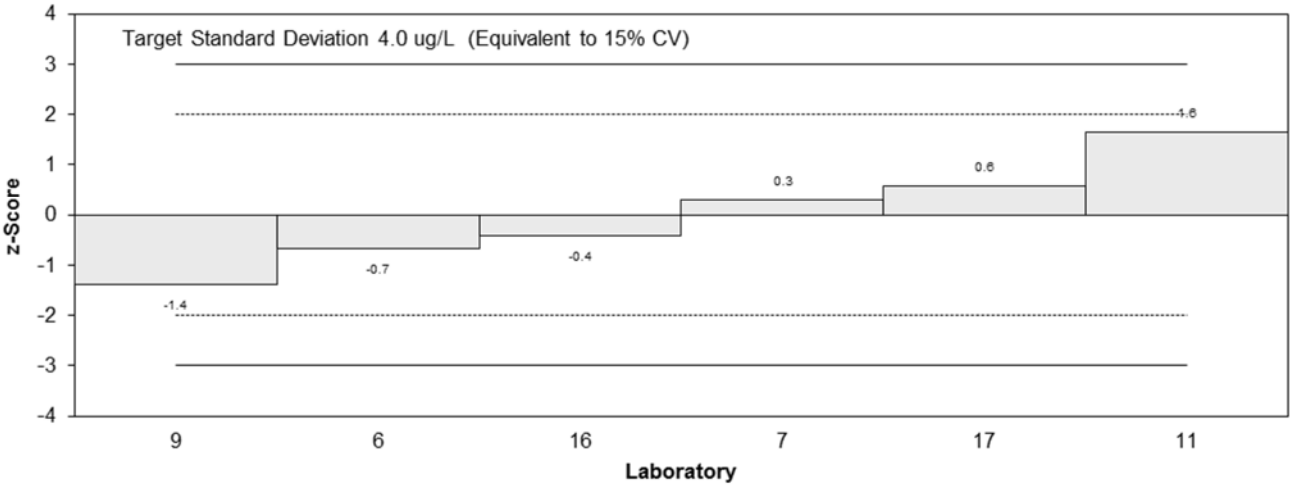
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NR	NR	NR		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6	24	4.80	NR	-0.67	-0.39
7	27.9	5.57	98	0.30	0.16
8	NT	NT	NT		
9	21.1	4	73	-1.40	-0.87
10	NT	NT	NT		
11	33.28	1.67	NR	1.64	1.25
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	<20	NR	80-120		
16	25	3	NR	-0.42	-0.29
17	29.02	15.38	114.40	0.58	0.14
18	NT	NT	NT		
19	NT	NT	NT		
20	NT	NT	NT		
21	NT	NT	NT		
22	NT	NT	NT		
23	NT	NT	NT		

Statistics

Assigned Value	26.7	5.0
Spike	27.5	1.4
Robust Average	26.7	5.0
Median	26.4	3.9
Mean	26.7	
N	6	
Max.	33.28	
Min.	21.1	
Robust SD	4.9	
Robust CV	18%	


Kernel Density
Density
Result
Results: S3 - AMPA
Assigned Value = 26.7 ± 5.0 ug/L
Results (ug/L)
Laboratory
9 6 16 7 17 11 15 1 10 12 13 14 18 19 20 21 22 23 3 4 5 8 Md R.A. S.V.


z-Scores: S3 - AMPA
Target Standard Deviation 4.0 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
9 6 16 7 17 11
-1.4
-0.7
-0.4
0.3
0.6
1.6

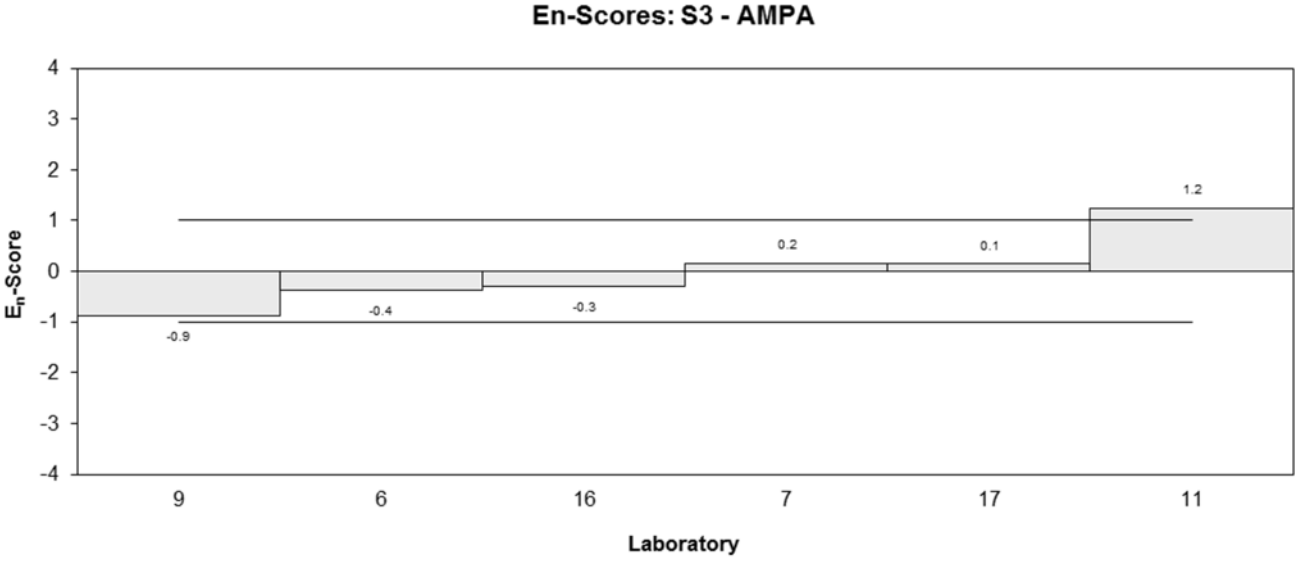

En-Scores: S3 - AMPA
En-Score
Laboratory
9 6 16 7 17 11
-0.9
-0.4
-0.3
0.2
0.1
1.2

Figure 10

Table 14

Sample Details

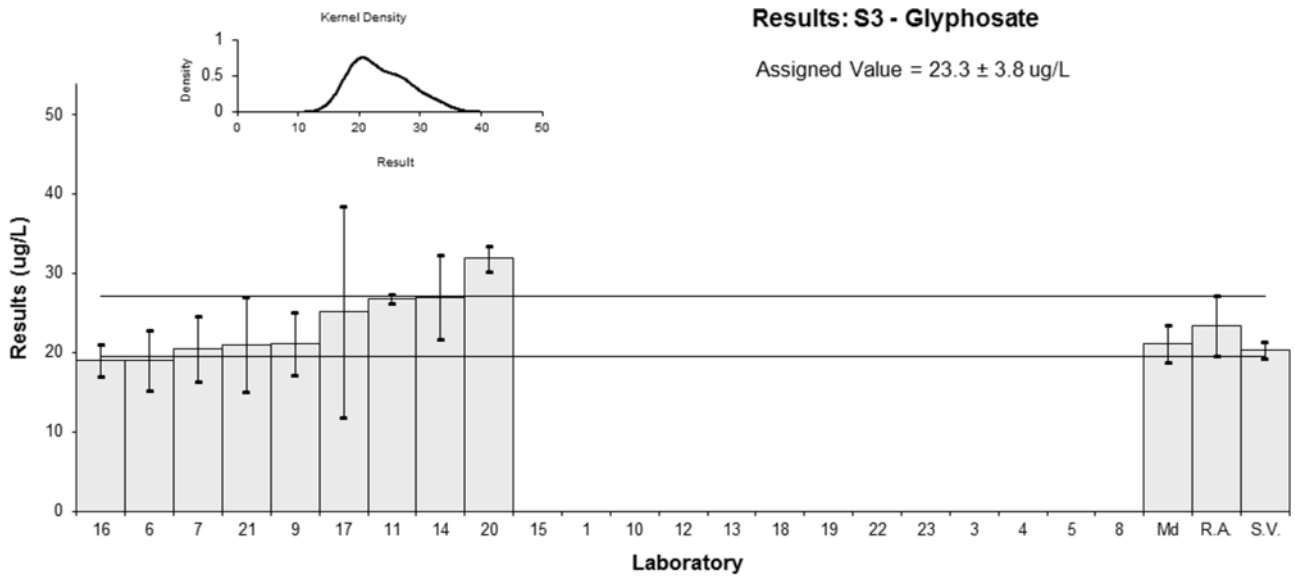
Sample No.	S3
Matrix.	Water
Analyte.	Glyphosate
Units	ug/L

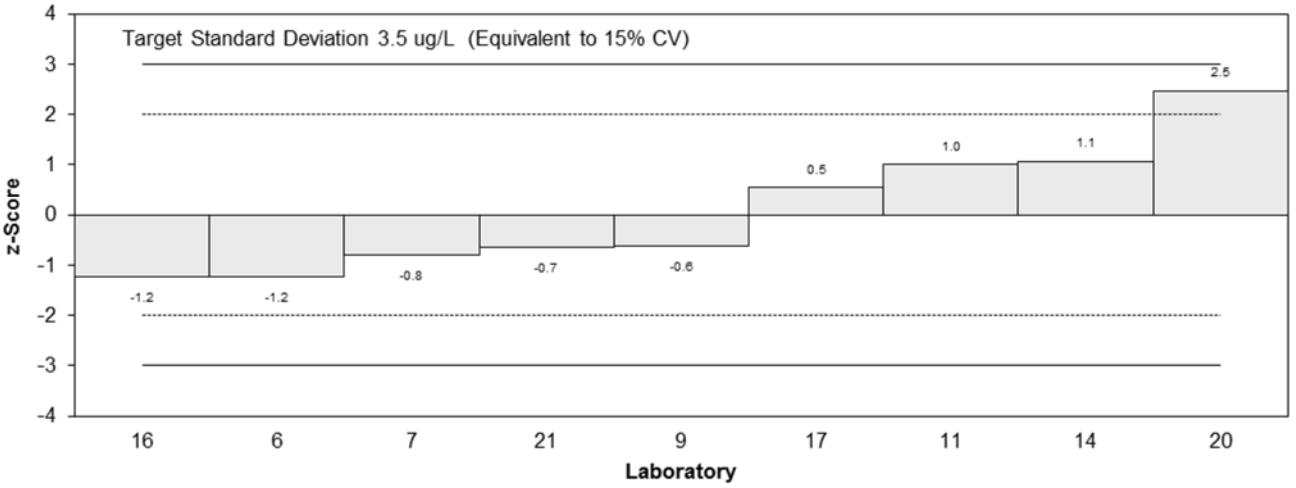
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NR	NR	NR		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6	19	3.80	NR	-1.23	-0.80
7	20.5	4.10	99	-0.80	-0.50
8	NT	NT	NT		
9	21.1	4	81	-0.63	-0.40
10	NT	NT	NT		
11	26.79	0.57	NR	1.00	0.91
12	NT	NT	NT		
13	NT	NT	NT		
14	27	5.4	NR	1.06	0.56
15	<20	NR	80-120		
16	19	2	NR	-1.23	-1.00
17	25.18	13.34	95.10	0.54	0.14
18	NT	NT	NT		
19	NT	NT	NT		
20	31.9	1.6	NR	2.46	2.09
21	21	6	NR	-0.66	-0.32
22	NT	NT	NT		
23	NT	NT	NT		

Statistics

Assigned Value	23.3	3.8
Spike	20.3	1.0
Robust Average	23.3	3.8
Median	21.1	2.4
Mean	23.5	
N	9	
Max.	31.9	
Min.	19	
Robust SD	4.6	
Robust CV	20%	


Kernel Density
Density
Result
Results: S3 - Glyphosate
Assigned Value = 23.3 ± 3.8 ug/L
Results (ug/L)
16 6 7 21 9 17 11 14 20 15 1 10 12 13 18 19 22 23 3 4 5 8 Md R.A. S.V.
Laboratory


z-Scores: S3 - Glyphosate
Target Standard Deviation 3.5 ug/L (Equivalent to 15% CV)
z-Score
-1.2 -1.2 -0.8 -0.7 -0.6 0.5 1.0 1.1 2.5
16 6 7 21 9 17 11 14 20
Laboratory

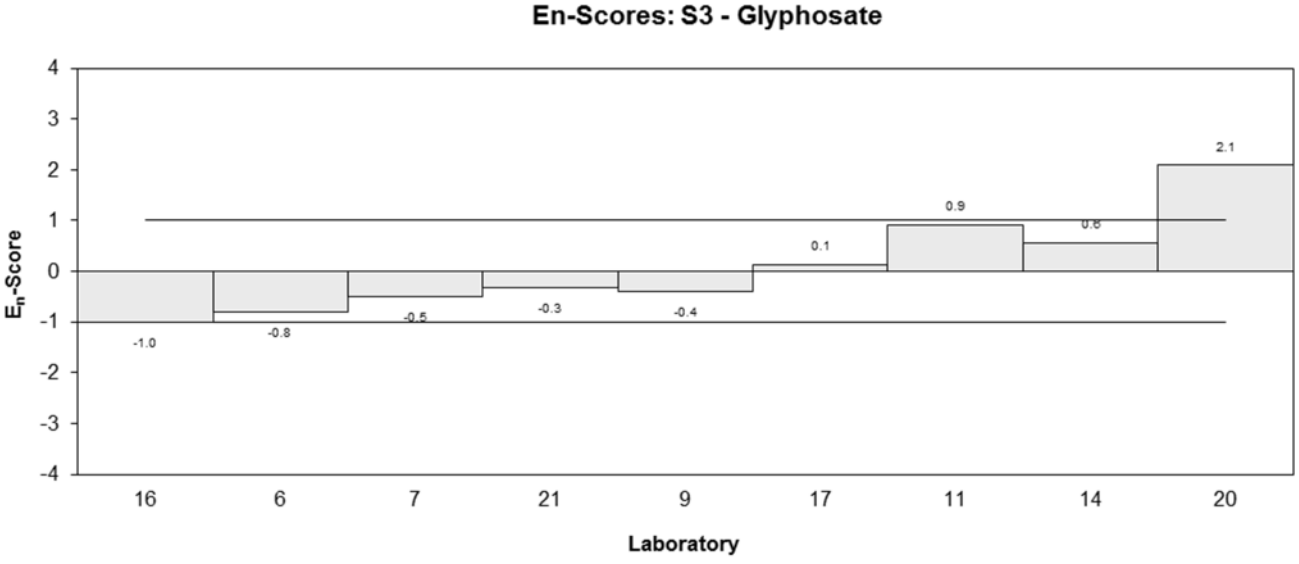

En-Scores: S3 - Glyphosate
En-Score
-1.0 -0.8 -0.5 -0.3 -0.4 0.1 0.9 0.6 2.1
16 6 7 21 9 17 11 14 20
Laboratory

Figure 11

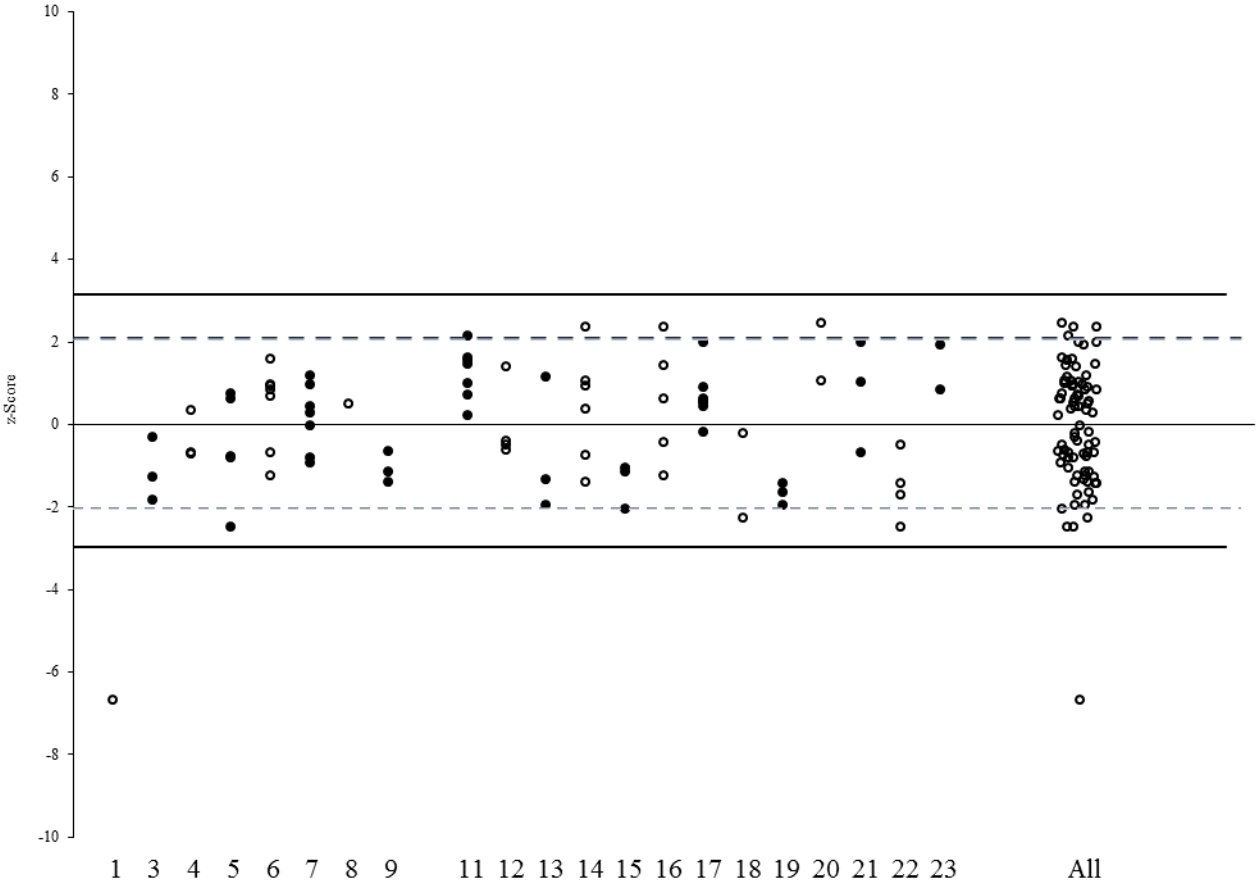


Figure 12 z-Score Dispersal by Laboratory

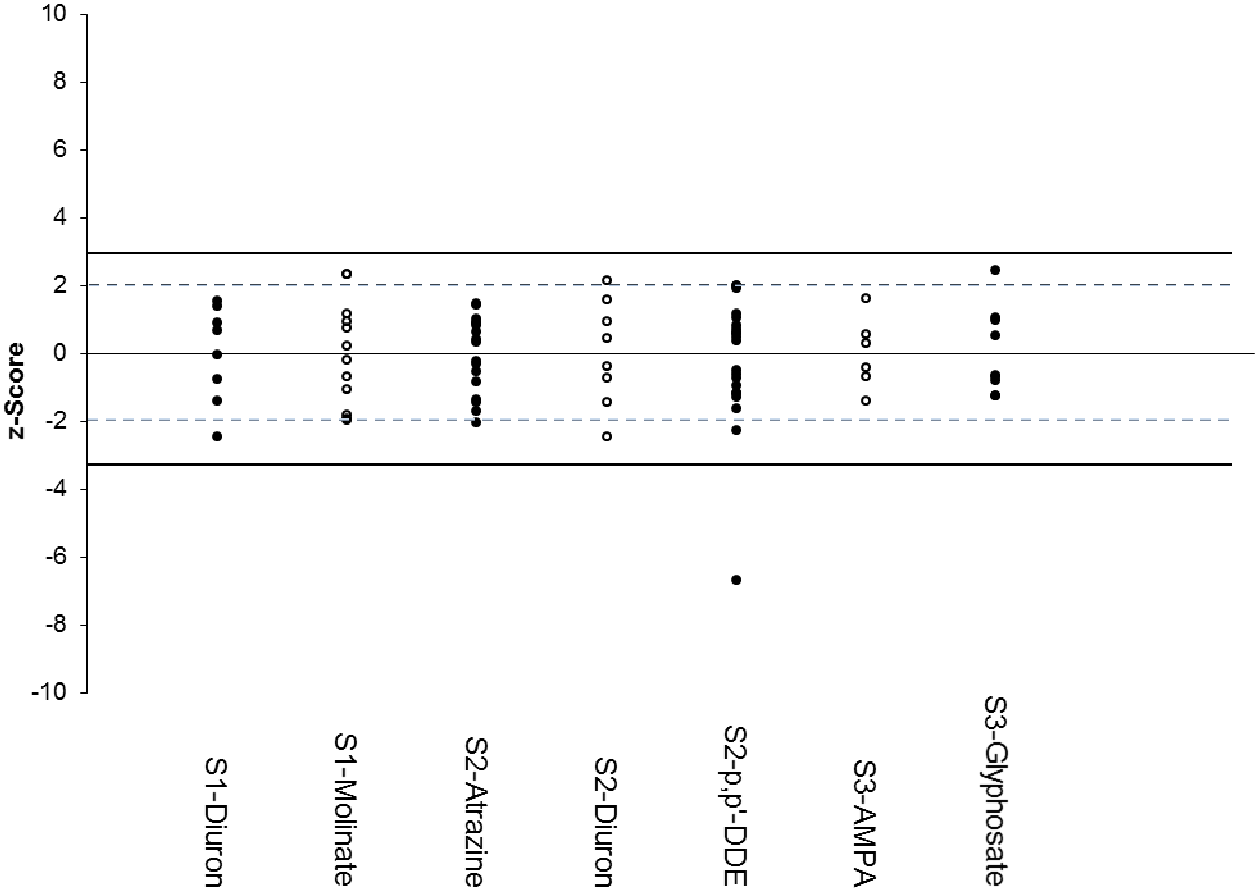


Figure 13 z-Score Dispersal by Pesticide

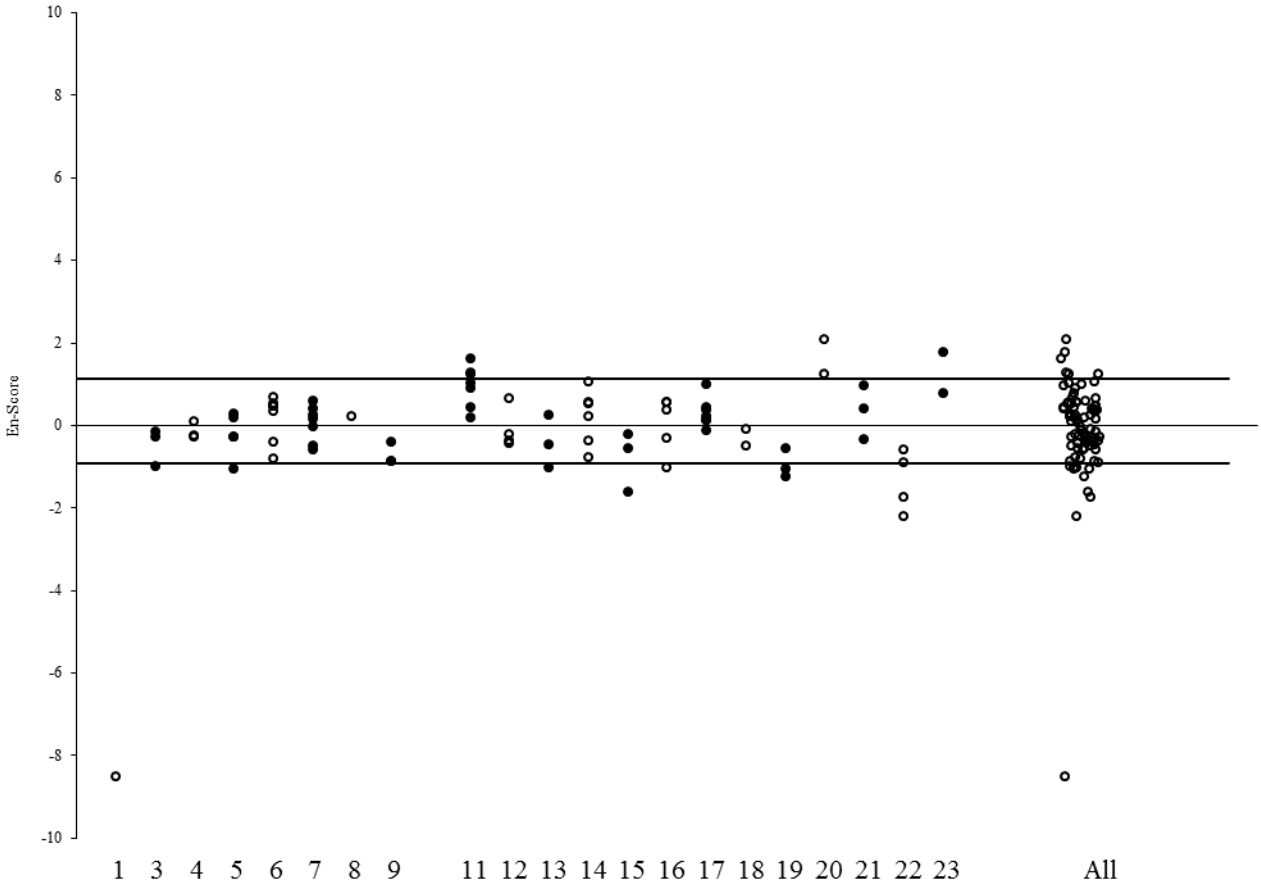


Figure 14 E_n-Score Dispersal by Laboratory

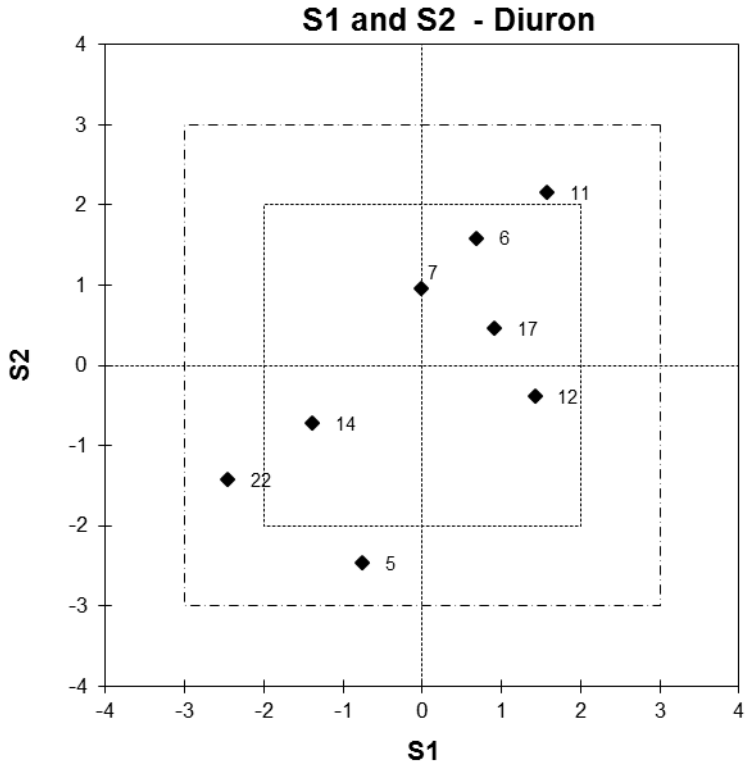


Figure 15 z-score Scatter Plot for Diuron in Samples S1 and S2

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 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'.[8] Appendix 3 sets out the calculation for the expanded uncertainty of the robust average of atrazine in Sample S2.

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

The robust average of participants' results was significantly lower than the spiked concentration for bifenthrin and chlorpyrifos in Sample S1, p,p'-DDE and trifluralin in Sample S2. No assigned value was set for bifenthrin, chlorpyrifos and trifluralin due to high variability of the results (CV between 46 to 54%). For p,p'-DDE there was a reasonable consensus (CV of 24%) and an assigned value was set.

For all other pesticides the assigned values were within the range of 89-115% 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 and Spiked Concentration

Analyte	Spiked Concentration (µg/L)	Assigned Value *(robust average)* (µg/L)	Assigned*(robust average)*/spike*)* (%)
Bifenthrin	25.4	*(13.4)*	*53*
Chlorpyrifos	4.20	*(1.26)*	*30*
Diuron (S1)	4.27	4.17	98
Molinate	10.8	9.60	89
Atrazine	7.29	6.49	89
Diuron (S2)	5.06	4.60	91
p,p'-DDE	1.91	0.604	32
Trifluralin	10.9	*(3.30)*	*30*
AMPA	27.5	26.7	97
Glyphosate	20.3	23.3	115

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.'

One hundred and twenty-four numerical results (100%) were reported with an expanded measurement uncertainty, indicating that laboratories have addressed this requirement of ISO 17025.

The magnitude of reported uncertainties was within the range of 0.2% to 108%. Twenty-seven 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.

Laboratories 8, 9, 12 and 19 attached estimates of the expanded measurement uncertainty to results reported as less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[7]

Laboratories 15 and 18 reported an estimate of expanded uncertainty for their p,p'-DDE measurement result larger or equal to the result itself.

Participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

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 7.11 ± 1.4931 ug/L better 7.1 ± 1.5 ug/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 and between laboratories coefficient of variation obtained in this study are presented in Table 16.

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

Sample	Analyte	Assigned value (ug/L)	Target SD (as PCV)	Thompson -Horwitz CV	Between Laboratories CV
S1	Diuron	4.17	15%	22%	24%
S1	Molinate	9.60	15%	22%	26%
S2	Atrazine	6.49	15%	22%	19%
S2	Diuron	4.60	15%	22%	26%
S2	*p,p'*-DDE	0.604	15%	22%	24%
S3	AMPA	26.7	15%	22%	18%
S3	Glyphosate	23.3	15%	22%	20%

To account for possible bias in the consensus value due to laboratories using inefficient extraction techniques, z-scores were adjusted for p,p'-DDE in Sample S2 so that any z-score greater than 2 was set at 2. This ensured that laboratories reporting results close to the spiked concentration were not penalised. A maximum acceptable concentration was set to two target standard deviations more than the spiked level. Scores of less than 2 were left unaltered.

The dispersal of participants' z-scores is graphically presented in Figures 12 and 13.

Of 81 results for which z-scores were calculated, 72 (89%) returned a satisfactory score of $|z| \leq 2$.

Only laboratories **6**, **7**, **11** and **17** reported results for all seven analytes for which z-scores were calculated. Laboratories **6**, **7** and **17** had satisfactory z-scores for all seven analytes

The z-score scatter plot for diuron in Samples S1 and S2 is presented in Figure 15. Most laboratories are plotted in the upper-right or lower-left quadrants. This is consistent with laboratory bias being the major contributor to the observed variations in results.

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.

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

Of 81 results, 64 (79%) returned a satisfactory score of $E_n \leq 1$.

Laboratories **6**, **7** and **17** had satisfactory E_n-scores for all seven analytes for which E_n-scores were calculated.

6.5 False negatives

Table 17 lists false negative results – a pesticide present for which a laboratory tested but did not report a result (eg. laboratories reporting as '<' result when the assigned value was significantly higher than the < figure).

Table 17 False Negatives

Lab Code	Sample	Pesticide
12	S1	Chlorpyrifos
15	S1, S2	Diuron
15	S3	AMPA
16	S1, S2	Diuron

6.6 Reporting of Pesticides Not Spiked Into the Test Samples

Five 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 (%)
1	S2	Dieldrin	0.00065	0.0002	NR
6	S1	Atrazine	0.2	0.04	NR
12	S1	Atrazine	0.01	0.002	112
20	S1	Endosulfan sulfate	0.32	0.02	NR
22	S1	Cypermethrin	1.84	0.03	106.83
22	S1	Simazine	0.11	0.03	218.63
22	S1	Permethrin	0.17	0.03	110.52
22	S1	Diazinon	0.11	0.03	129.94
22	S2	Diazinon	0.06	0.03	129.94
22	S2	Cypermethrin	0.13	0.03	106.83
22	S2	Chlorpyrifos	0.19	0.03	137.13
22	S2	Bifenthrin	0.05	0.03	105.47
22	S2	Simazine	1.46	0.03	218.63
22	S2	Permethrin	0.138	0.03	110.52

Sample S2 was spiked with p,p'-DDE only. Laboratories 5, 6, 7, 12, 16 and 17 reported also Total DDT in Sample S2. These results were not considered false positives as they were equal to the reported p,p'-DDE values consistent with the formulation.

6.7 Participants' Analytical Methods

A variety of analytical methods were used for each group of analytes (Appendix 5). For Samples S1 and S2 participants used direct injection or different extractions techniques such as liquid-liquid, solid phase extractions or headspace solid phase microextraction. One participant used Florisil for the clean-up step. Dichloromethane, hexane, methanol, ether and ethyl-acetate were used as extraction solvents. Participants reported using GC-ECD (FPD, FID), GC-MS(MS) and LC-MS(MS). Five laboratories reported using the entire sample (500 mL) for the extraction.

For Sample S3 two participants used direct injection and LC-MSMS for quantification, while the other laboratories used FMOC (fluorenylmethyloxycarbonyl chloride) or p-toluenesulfonyl chloride to derivatise and either LC with fluorescence detector or MS(MS) for quantification.

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

Recoveries were reported by participants in the range of 66-218%. Four 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.

Eleven laboratories reported using 'certified standards'.

- Restek
- Sigma Aldrich
- PM Separation
- Chemservice
- 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'* [9]

6.9 Summary of Participants' Performance in Pesticides in Water PTs since 2008

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 16.

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

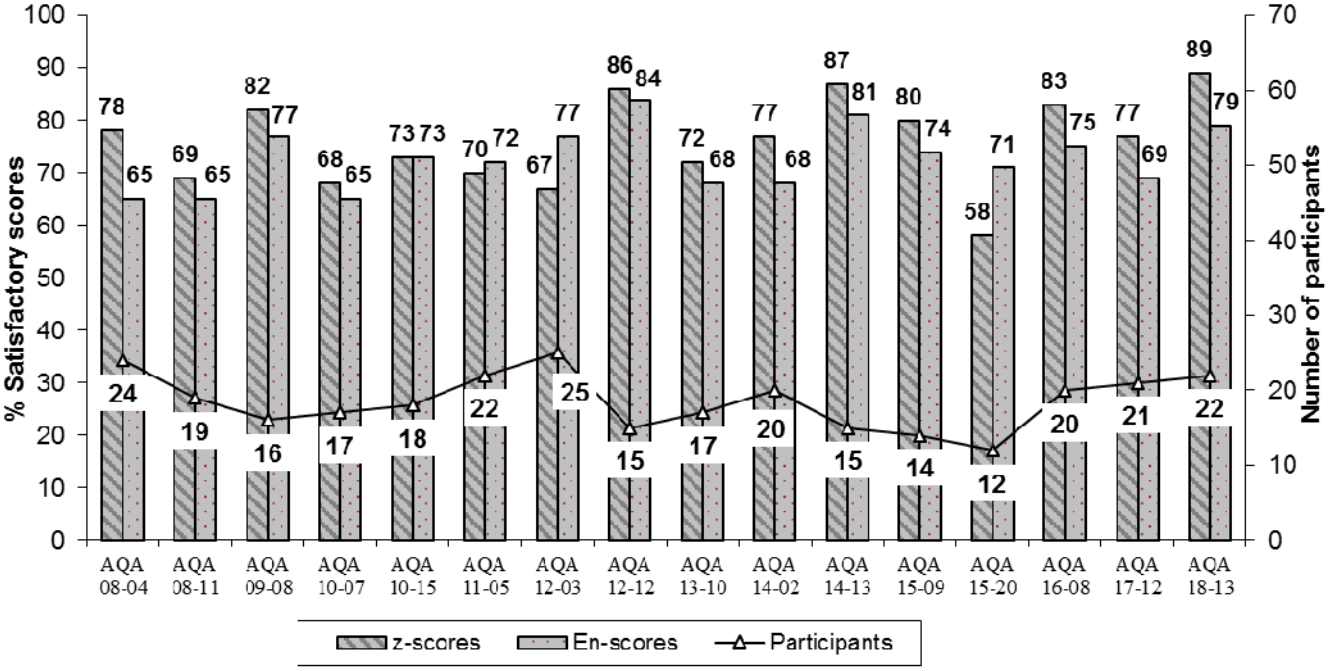


Figure 16 Satisfactory z and E_n-scores – comparison with previous PT studies

7 REFERENCES

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

APPENDIX 1 - PARTICIPANTS

Analytica Laboratories Ltd, NEW ZEALAND	Analytical Reference Laboratory (WA) Pty Ltd WA
Asure Quality Limited, NEW ZEALAND	Central Laboratory (Thailand) Co., Ltd Songkhla Branch, Song Khla Province, THAILAND
CHEMCENTRE WA	Envirolab Services NSW
Envirolab Services VIC	Eurofins mgt NSW
Eurofins mgt VIC	Forensic & Analytical Science Service (FASS) NSW
Hill Laboratories, NEW ZEALAND	Kenya Plant Health Inspectorate Service (KEPHIS), KENYA
MPL Laboratories, WA	Office of Environment and Heritage, Department of Premier and Cabinet, NSW
S.N.P.Scientific, THAILAND.	SGS Australia, VIC
SGS Environmental Services, NSW.	SGS Environmental Services, WA.
Sydney Environmental & Soil Laboratory NSW	Symbio Alliance QLD
Symbio Alliance NSW	TS Lab Sdn Bhd, MALAYSIA
Watercare Services Limited Laboratory Services, NEW ZEALAND	

APPENDIX 2 - SAMPLE PREPARATION AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was prepared using tap water that had been allowed to stand over the weekend to allow the chlorine to dissipate. Before spiking the pH of Sample S1 was adjusted to 6.2 with hydrochloric acid.

Samples S2 and S3 were prepared from surface water obtained from Browns Waterhole in the Turramurra area of Sydney. The water was filtered through a glass fibre filter, autoclaved and spiked with pesticides dissolved 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. Between preparation and dispatch the samples were stored in a coolroom at 4ºC.

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 related 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 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 interlaboratory 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 all fifteen numerical results was calculated (Table 19).

Table 19 Uncertainty of robust average for Atrazin in Sample S2

No. results (p)	17
Robust Average	6.488 µg/L
$S_{rob\ av}$	1.229 µg/L
$u_{rob\ av}$	0.373
k	2
$U_{rob\ av}$	0.745 µg/L

The robust average for Atrazine in Sample S2 is 6.49 ± 0.75 µg/L.

APPENDIX 4 - ACRONYMS AND ABBREVIATIONS

CITAC	Co-Operation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
ECD	Electron Capture Detector
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
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	Organophosphate Pesticides
PT	Proficiency Test
S	Spiked or formulated concentration of a PT sample
SD	Standard Deviation
SPE	Solid Phase Extraction
Target SD	Target Standard Deviation
σ	Target standard deviation

APPENDIX 5 – PARTICIPANTS' TEST METHODS

Table 20 Test methods Samples S1 Bifenthrin

Lab. Code	Sample Vol. (mL)	Extraction	Solvent	Measurement
1	40			
3	100	Liquid-Liquid	DCM	GCMS
4				
5				
6	500	SPE	DCM:EtOAc	GCMS
7	100	SPE		GCMS
8	250	NT		
9				
10	500			
11	10	Liquid-Liquid	DCM	GCMS
12		SPE	Methanol	GCMS
13	80	Liquid-Liquid	DCM	GCMS
14	500	Liquid-Liquid	DCM	GC-MS-MS
15	100	Liquid-Liquid	DCM	GCMS
16	150	Liquid-Liquid	15% Ether in Hexane	GC-ECD
17	Varies	nt		
18	100			
19	100	Liquid-Liquid	DCM	GC-ECD
20	500	Liquid-Liquid	Hexane/DCM	GC-FID
21	500	Liquid-Liquid	DCM	GCMS
22	250	Liquid-Liquid	DCM	GCMSMS/LCMSMS
23	150	Liquid-Liquid	Hexane	GC-ECD

Table 21 Test methods Samples S1 Chlorpyrifos

Lab. Code	Extraction	Solvent	Measurement
1			
3	Liquid-Liquid	DCM	GCMS
4			
5			
6	SPE	DCM:EtOAc	GCMS
7	SPE		LCMS
8	Liquid-Liquid	DCM	GCMS
9			
10	Liquid-Liquid	DCM	GC-FPD
11	Liquid-Liquid	DCM	GCMS
12	Liquid-Liquid	DCM	GCMS
13	Liquid-Liquid	DCM	GCMS
14	Liquid-Liquid	DCM	GC-MS
15	Liquid-Liquid	DCM	GCMS
16	Liquid-Liquid	DCM	GC-MS
17	Liquid-Liquid	DCM	gc ms ms
18	Liquid-Liquid	DCM	GCMS
19	Liquid-Liquid	DCM	GCMS
20	Liquid-Liquid	Hexane/DCM	GC-FID
21	Liquid-Liquid	DCM	GCMS
22	Liquid-Liquid	DCM	GCMSMS/LCMSMS
23	Liquid-Liquid	Ethyl acetate	GC-FPD

Table 22 Test methods Samples S1 Molinate

Lab. Code	Extraction	Solvent	Measurement
1			
3	Liquid-Liquid	DCM	GCMS
4			
5			
6	SPE	DCM:EtOAc	GCMS
7	SPE		LCMS
8			
9			
10			
11	Direct Injection		LCMSMS
12			
13	Liquid-Liquid	DCM	GCMS
14	Direct injection		LC-MS-MS
15	Liquid-Liquid	DCM	GCMS
16	Liquid-Liquid	DCM	GC-MS
17	Liquid-Liquid	DCM	gc ms ms
18			
19	Liquid-Liquid	DCM/ETHER	HPLC-DAD
20			
21			
22			
23			

Table 23 Test methods Samples S1 and S2 Diuron

Lab. Code	Extraction	Solvent	Measurement
1			
3		DCM	GCMS
4			
5			
6	Liquid-Liquid		LCMS
7	SPE		LCMS
8			
9			
10			
11	Direct Injection		LCMSMS
12	SPE	Methanol	LCMSMS
13			
14	Direct injection		LC-MS-MS
15	Liquid-Liquid	DCM	GCMS
16	Liquid-Liquid	DCM	GC-MS
17	Direct Injection		LCMS
18			
19	Liquid-Liquid	DCM/ETHER	HPLC-DAD
20	Liquid-Liquid	Hexane/DCM	GC-FID
21			
22	Liquid-Liquid	DCM	GCMSMS/LCMSMS
23			

Table 24 Test methods Sample S2 Atrazine

Lab. Code	Sample Vol. (mL)	Extraction	Solvent	Measurement
1	40			
3	100	Liquid-Liquid	DCM	GCMS
4				
5				
6	500	SPE	DCM:EtOAc	GCMS
7	100	SPE		LCMS
8	250			
9				
10	500			
11	10	Direct Injection		LCMSMS
12		SPE	Methanol	LCMSMS
13	80	Liquid-Liquid	DCM	GCMS
14	500	Direct injection		LC-MS-MS
15	100	Liquid-Liquid	DCM	GCMS
16	150	Liquid-Liquid	DCM	GC-MS
17	Varies	Liquid-Liquid	DCM	gc ms ms
18	100	Liquid-Liquid	DCM	GCMS
19	100	Liquid-Liquid	DCM	GCMS
20	500	Liquid-Liquid	Hexane/DCM	GC-FID
21	500	Liquid-Liquid	DCM	GCMS
22	250	Liquid-Liquid	DCM	GCMSMS/LCMSMS
23	150	Liquid-Liquid	Ethyl acetate	GC-NPD

Table 25 Test methods Sample S2 *p,p'*-DDE

Lab. Code	Extraction	Clean-up	Solvent	Measurement
1	Liquid-Liquid	Florisil	hexane	GCMSMS
3	Liquid-Liquid		DCM	GCMS
4				
5				
6	SPE		DCM:EtOAc	GCMS
7	Liquid-Liquid		DCM	GCMS
8	Liquid-Liquid		DCM	GC-ECD
9				
10				
11	Liquid-Liquid		DCM	GCMS
12	Liquid-Liquid		DCM	GCMS
13	Liquid-Liquid		DCM	GCMS
14	Liquid-Liquid		DCM	GC-MS
15	Liquid-Liquid		DCM	GCMS
16	Liquid-Liquid		15% Ether in Hexane	GC-ECD
17	Liquid-Liquid		DCM	GCMSMS
18	Liquid-Liquid		DCM	GCMS
19	Liquid-Liquid		DCM	GC-ECD
20	Liquid-Liquid		Hexane/DCM	GC-FID
21	Liquid-Liquid		DCM	GCMS
22	Liquid-Liquid		DCM	GCMSMS/LCMSMS
23	Liquid-Liquid		Hexane	GC-ECD

Table 26 Test methods Sample S2 Trifluralin

Lab. Code	Extraction	Solvent	Measurement
1			
3		DCM	GCMS
4			
5			
6	SPE	DCM:EtOAc	GCMS
7	Liquid-Liquid	DCM	GCMS
8	NT		
9			
10			
11	Liquid-Liquid	DCM	GCMS
12	Liquid-Liquid	DCM	GCMS
13	Liquid-Liquid	DCM	GCMS
14	Liquid-Liquid	DCM	GC-MS
15	Liquid-Liquid	DCM	GCMS
16	Liquid-Liquid	DCM	GC-MS
17	Liquid-Liquid	DCM	gc ms ms
18			
19			
20	Liquid-Liquid	Hexane/DCM	GC-FID
21			
22			
23			

Table 27 Test methods Sample S3 AMPA and Glyphosate

Lab. Code	Sample Vol. (mL)	Extraction	Clean-up	Solvent	Measurement
1					
3					
4					
5					
6	500	Liquid-Liquid	Pre-column	FMOC-CL	LCMS
7	1			Fmoc chloride	
8					
9	1	direct injection with internal standards			LC-MS/MS
10					
11	1		Pre-column	FMOC	LCMSMS
12					
13					
14	1				LC-MS-MS
15					
16	0.9		Pre-column	Fmoc-Cl	LC-MS (QQQ)
17	0.5		Pre-column	FMOC Chloride	LCMS
18					
19					
20	500	Evaporation	Pre-column	p-toluenesulfonyl chloride	HPLC
21	0.4		Pre-column	9-Fluorenylmethyl Chloroformate	UPLC-Fluorescence
22					
23					

NOTE: Laboratories 14, 20 & 21 did not analyse for AMPA.

END of REPORT