Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Final Report
AQA 20-14
Pesticides in Water

March 2021

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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 20-14 Pesticides in Water commenced in November 2020. Eighteen laboratories registered to participate and all submitted results.

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

Of a possible 198 results, 108 numeric results (55%) were submitted. Nineteen results were a 'less than' value (<*x*) or Not Reported (NR), and seventy-one results were Not Tested (NT).

The assigned values for all scored analytes were the robust averages of participants' results. The associated uncertainties were estimated from the robust standard deviations of the participants' results.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

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

- *Assess the ability of participants to correctly identify environmentally significant pesticides in water.*

Laboratories **9**, **11** and **12** reported numeric results for all 9 analytes scored in this study.

Four participants did not report analytes for which they tested and that were present in the test samples (total of 8 results).

Ten participants reported results for analytes not spiked into the samples (total of 15 results).

- *Compare the performance of participants and assess their accuracy in the measurement of pesticides in water.*

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

Of 94 results for which z-scores were calculated, 81 (86%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Of 94 results for which E_n-scores were calculated, 73 (78%) returned a score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

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

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

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

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

Of 108 numerical results, 105 (97%) were reported with an expanded measurement uncertainty.

The magnitude of reported uncertainties was within the range of 2.1% to 56%.

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;
- inorganic analytes in soil, water, food and pharmaceuticals;
- PFAS in biota, soil and water;
- controlled drug assay and clandestine laboratory; and
- allergens in food.

1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify environmentally significant pesticides in water;
- compare the performance of participants and assess their accuracy in the measurement of pesticides in water;
- evaluate the participants' methods for the measurement of 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/IEC 17043[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[4]

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

2 STUDY INFORMATION

2.1 Selection of Pesticides

When selecting matrices and spiking values for this study, consideration was given to:

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

A list of possible analytes for Samples S1 and S2 is presented in Table 1. Sample S3 was spiked with aminomethylphosphonic acid (AMPA) and glyphosate.

Table 1 List of Possible Analytes for Samples S1 and S2

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

The actual spiked concentrations are presented in Table 2.

Table 2 Formulated Concentrations of Test Samples

Sample	Analyte	Spiked Value (µg/L)	Uncertainty (µg/L)*
S1	Endosulfan sulfate	2.22	0.11
	Imidacloprid	119	6
	Omethoate	6.97	0.35
	p,p'-DDT	3.67	0.18
	Parathion-methyl	2.11	0.11
S2	Atrazine	12.7	0.6
	Heptachlor	1.72	0.09
	Imidacloprid	5.97	0.30
	Metsulfuron-methyl	18.2	0.9
S3	AMPA	25.9	1.3
	Glyphosate	59.8	3.0

* The uncertainty is an expanded uncertainty at approximately 95% confidence using a coverage factor of 2. It has been estimated with consideration to contributions from the gravimetric and volumetric operations involved in spiking, and the purity of the pesticide reference standards. Stability was not considered in the uncertainty budget and so the expanded uncertainty related to the concentration of pesticide at the time of spiking.

2.2 Study Timetable

The timetable of the study was:

Invitation issued	2 November 2020
Samples dispatched	26 November 2020
Results due	8 January 2021
Interim report issued	12 January 2021

2.3 Participation

Eighteen laboratories registered to participate, and all participants submitted results.

2.4 Laboratory Code

All participants were assigned a confidential laboratory code number for this study.

2.5 Sample Preparation

Three water samples were prepared by spiking water from Browns Waterhole, Turramurra with various pesticides to obtain the concentrations listed in Table 2. Additional information on the preparation of the samples is given in Appendix 1.

2.6 Homogeneity of Samples

The samples were spiked, mixed and packaged using a process that has been demonstrated to produce homogeneous samples in previous NMI Pesticides in Water PT studies. No homogeneity testing was conducted for this study, and participants' results gave no reason to question the homogeneity of the samples.

2.7 Stability of Analytes

No assessment of the stability of the pesticides was made before the samples were sent. To assess possible instability, the results returned by participants were compared to the spiked concentration.

Robust averages of participants' results for the scored analytes (excluding Sample S1 p,p'-DDT) were within 82 – 107% of the spiked concentration, which provides good support for the stability of these analytes in the samples. For p,p'-DDT, the robust average was 56% of the spiked value, but there was a reasonable consensus between participants' results and so an assigned value was set.

For Sample S1 omethoate and Sample S2 heptachlor there was degradation (the ratio of robust average to spiked concentration was 46% and 13% respectively) and also high variability between participants' results. Therefore, no assigned value was set and these analytes were not assessed.

2.8 Sample Storage, Dispatch and Receipt

The test samples were refrigerated at 4°C prior to dispatch. Samples were packaged into insulated foam boxes with cooler bricks and dispatched by courier on 26 November 2020.

The following items were packaged with the samples:

- a covering letter which included a description of the test samples and instructions for participants; and
- a form for participants to confirm the receipt and condition of the test samples.

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

2.9 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine 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 16 December 2020. Late results may not be included in the study report.

The results due date was extended to 8 January 2021 due to sample delivery delays and to account for participants' end-of-year shutdown periods.

2.10 Interim Report

An interim report was emailed to all participants on 12 January 2021.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Participants' Test Methods

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

3.2 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of Measurement 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	ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	CRM Instrument calibration Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
3		Control samples - CRM Duplicate analysis		
4	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NMI Uncertainty Course
5	Professional judgment		CRM	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
6	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	CRM Recoveries of SS	Eurachem/CITAC Guide
7	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
8	Top Down - precision and estimates of the method and laboratory bias	Instrument calibration	CRM Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
9	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
10	Standard deviation of replicate analyses multiplied by 2 or 3			
11	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from	NATA GAG Estimating and Reporting

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
			PT studies Recoveries of SS Standard purity	Measurement Uncertainty of Chemical Test Results
12	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
13	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
14	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
15	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
16	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
17	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	
18	Replicate data during validation	Duplicate analysis Instrument calibration	CRM Instrument calibration	

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

3.3 Participants' Comments

Participants were invited to make any comments or suggestions on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments for this study are presented in Table 4. Entries may be modified so that the participant cannot be identified.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments
16	S1/2	Omethoate and Methomyl are not NATA accredited methods.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 15 with summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max.), minimum (Min.), robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV).

Bar charts of results and performance scores are presented in Figures 2 to 12.

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

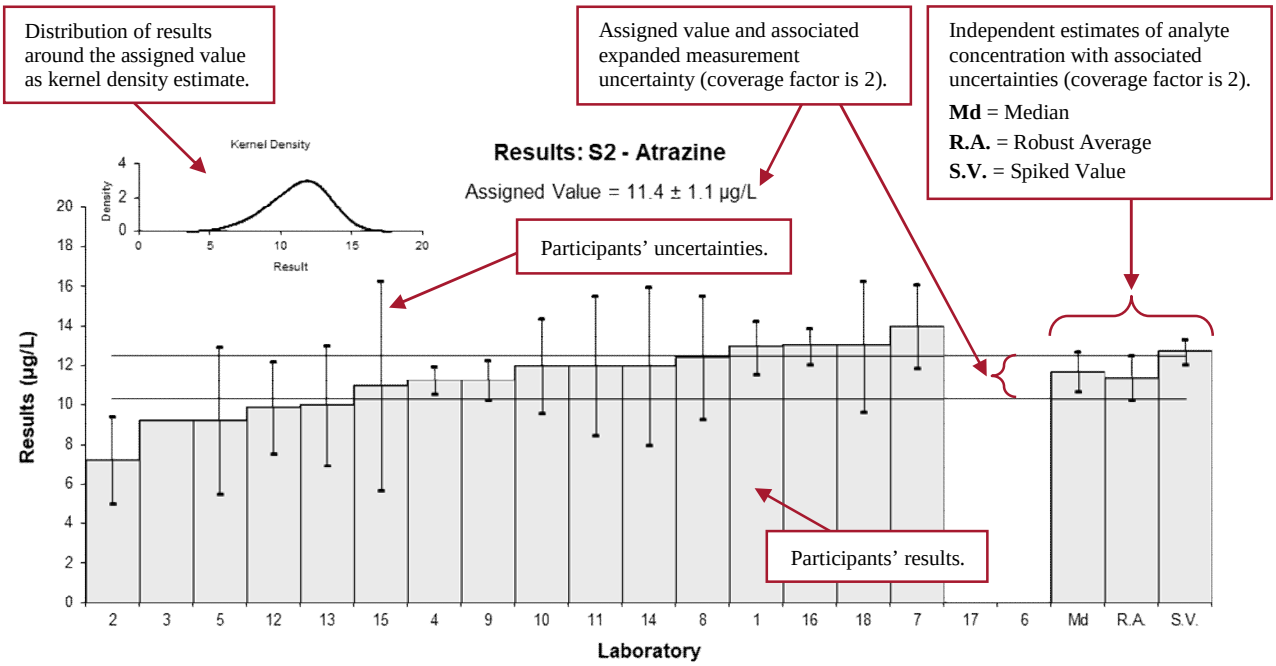


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

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

4.3 Robust Average and Robust Between Laboratory Coefficient of Variation

The robust averages and associated expanded MUs, and robust CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528:2015.[6]

4.4 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a fixed measure of the between laboratory variation that in the judgement of the study organiser would be expected from participants given the analyte concentrations. It is important to note that the PCV is set by the study coordinator; it is not calculated from the CV of participants' results. The PCV is based on the concentration of the analytes and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[7] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performances and can be compared from study to study.

4.5 Target Standard Deviation

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

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

4.6 z-Score

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

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

where:

z is z-score

χ is a participant's result

X is the assigned value

σ is the target standard deviation from Equation 1

For the absolute value of a z-score (|z|):

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

4.7 E_n-Score

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

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

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

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

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

4.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025 must establish and demonstrate the traceability and measurement uncertainty associated with their test results.[8]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[9]

5 TABLES AND FIGURES

Table 5

Sample Details

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

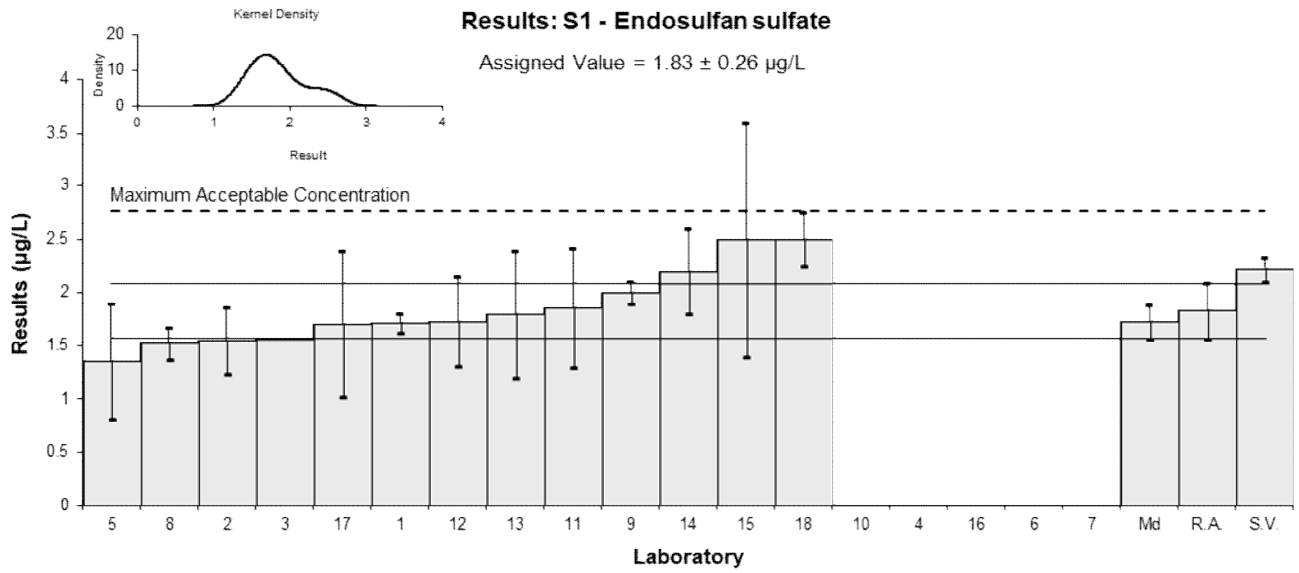
Participant Results

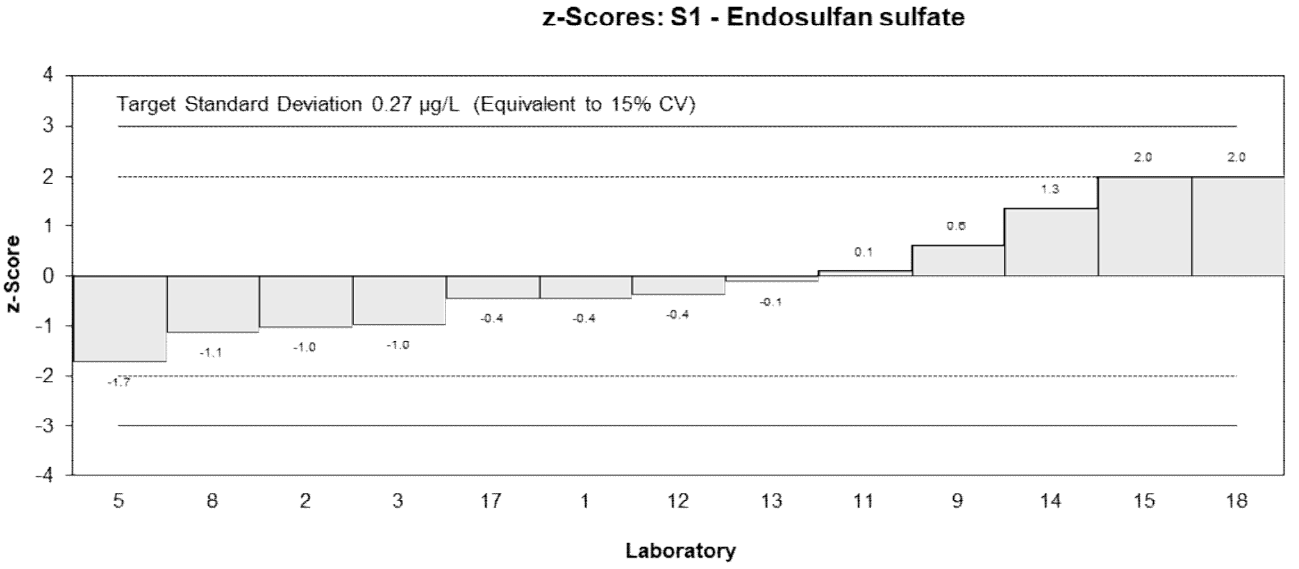
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.71	0.09	104	-0.44	-0.44
2	1.55	0.31	104	-1.02	-0.69
3	1.5632	NR	91	-0.97	-1.03
4	NR	NR	NR		
5	1.36	0.54	90	-1.71	-0.78
6	NT	NT	NT		
7	NT	NT	NT		
8	1.52	0.15	NR	-1.13	-1.03
9	2.0	0.1	NR	0.62	0.61
10	<0.01	NR	NR		
11	1.86	0.56	82	0.11	0.05
12	1.73	0.42	NR	-0.36	-0.20
13	1.8	0.6	NR	-0.11	-0.05
14	2.2	0.4	NR	1.35	0.78
15*	2.5	1.1	NR	2.00	0.59
16	NT	NT	NT		
17	1.708	0.6832	NR	-0.44	-0.17
18*	2.50	0.25	110.1	2.00	1.00

Statistics

Assigned Value	1.83	0.26
Spike	2.22	0.11
Max. Acceptable Concentration*	2.77	
Robust Average	1.83	0.26
Median	1.73	0.16
Mean	1.85	
N	13	
Max.	2.5	
Min.	1.36	
Robust SD	0.37	
Robust CV	20%	

* z-Score adjusted to 2.00 (see Section 6.3)


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 1.83 ± 0.26 µg/L
Maximum Acceptable Concentration
Results (µg/L)
Laboratory
5 8 2 3 17 1 12 13 11 9 14 15 18 10 4 16 6 7 Md R.A. S.V.


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation 0.27 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
5 8 2 3 17 1 12 13 11 9 14 15 18
-1.7 -1.1 -1.0 -1.0 -0.4 -0.4 -0.4 -0.1 0.1 0.6 1.3 2.0 2.0

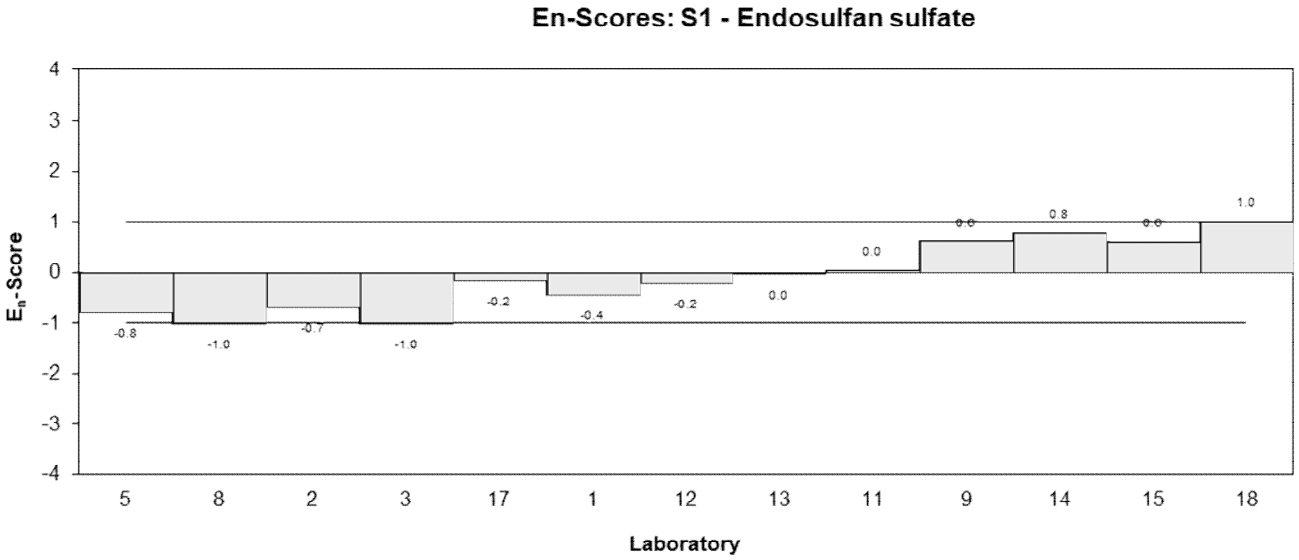

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
5 8 2 3 17 1 12 13 11 9 14 15 18
-0.8 -1.0 -0.7 -1.0 -0.2 -0.4 -0.2 0.0 0.0 0.8 0.6 1.0

Figure 2

Table 6

Sample Details

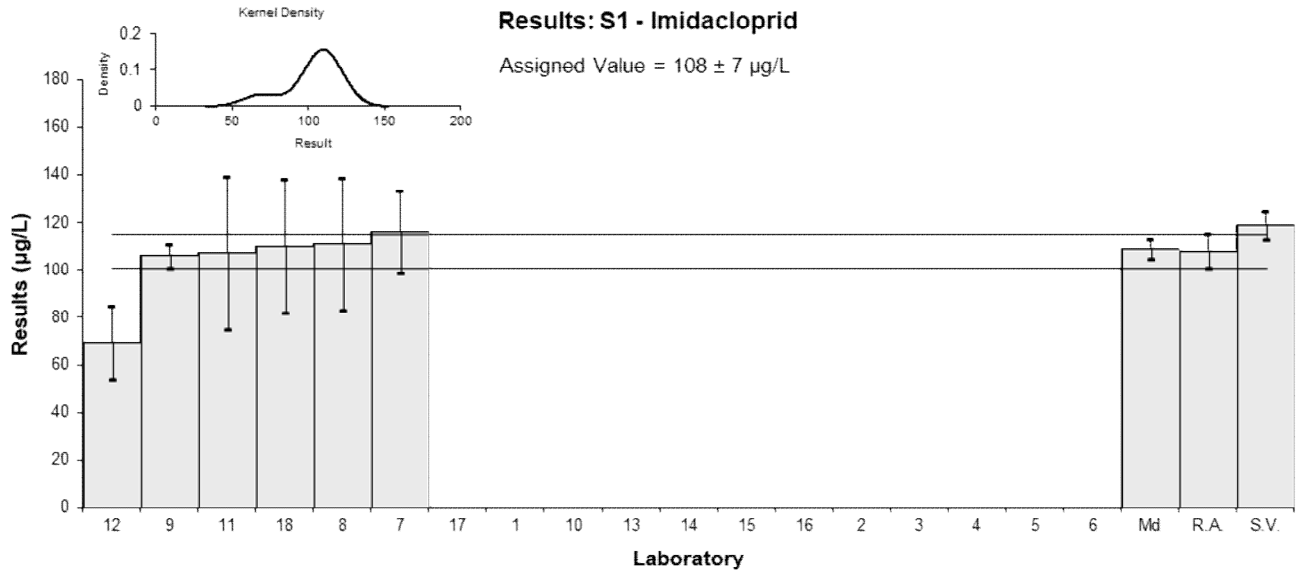
Sample No.	S1
Matrix	Water
Analyte	Imidacloprid
Units	µg/L

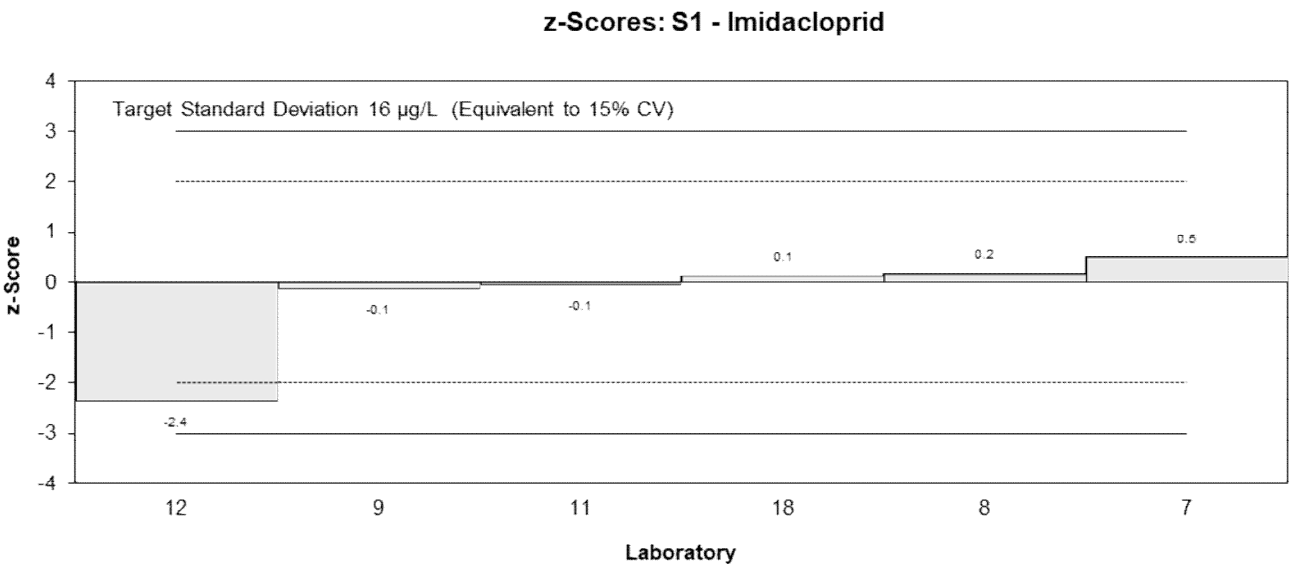
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6	NT	NT	NT		
7	116	17.4	NR	0.49	0.43
8	111	28	NR	0.19	0.10
9	106	5	NR	-0.12	-0.23
10	NT	NT	NT		
11	107	32.1	NR	-0.06	-0.03
12	69.4	15.3	NR	-2.38	-2.29
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	NR	NR	NR		
18	110	28	95	0.12	0.07

Statistics

Assigned Value	108	7
Spike	119	6
Robust Average	108	7
Median	109	4
Mean	103	
N	6	
Max.	116	
Min.	69.4	
Robust SD	7.2	
Robust CV	6.7%	


Kernel Density
Density
Result
Results: S1 - Imidacloprid
Assigned Value = 108 ± 7 µg/L
Results (µg/L)
Laboratory
12 9 11 18 8 7 17 1 10 13 14 15 16 2 3 4 5 6 Md R.A. S.V.


z-Scores: S1 - Imidacloprid
Target Standard Deviation 16 µg/L (Equivalent to 15% CV)
z-Score
-2.4
-0.1
-0.1
0.1
0.2
0.5
Laboratory
12 9 11 18 8 7

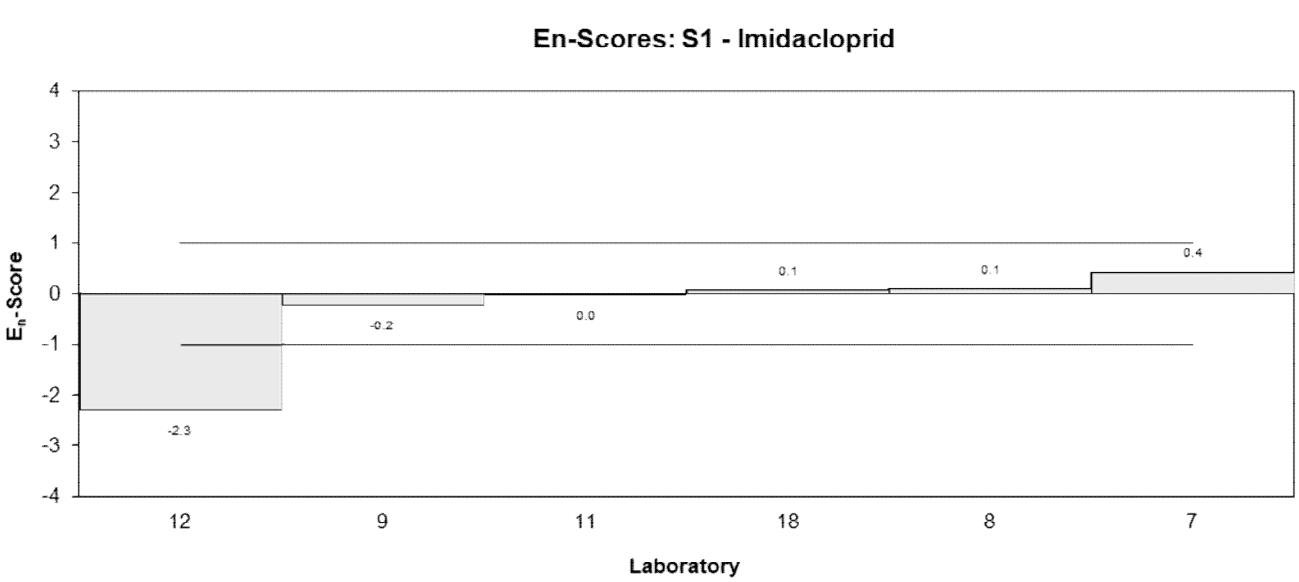

En-Scores: S1 - Imidacloprid
En-Score
-2.3
-0.2
0.0
0.1
0.1
0.4
Laboratory
12 9 11 18 8 7

Figure 3

Table 7

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Recovery
1	NT	NT	NT
2	NR	NR	NR
3	NR	NR	NR
4	NT	NT	NT
5	NT	NT	NT
6	NT	NT	NT
7	NT	NT	NT
8	4.43	1.1	NR
9	<0.1	0.1	NR
10	NT	NT	NT
11	4.3	1.3	78
12	<0.1	NR	NR
13	NT	NT	NT
14	0.9	0.5	NR
15	NT	NT	NT
16	4.78	1.43	NR
17	NR	NR	NR
18	1.5	0.38	90

Statistics

Assigned Value	Not Set	
Spike	6.97	0.35
Robust Average	3.2	2.3
Median	4.30	0.88
Mean	3.18	
N	5	
Max.	4.78	
Min.	0.9	
Robust SD	2.1	
Robust CV	65%	

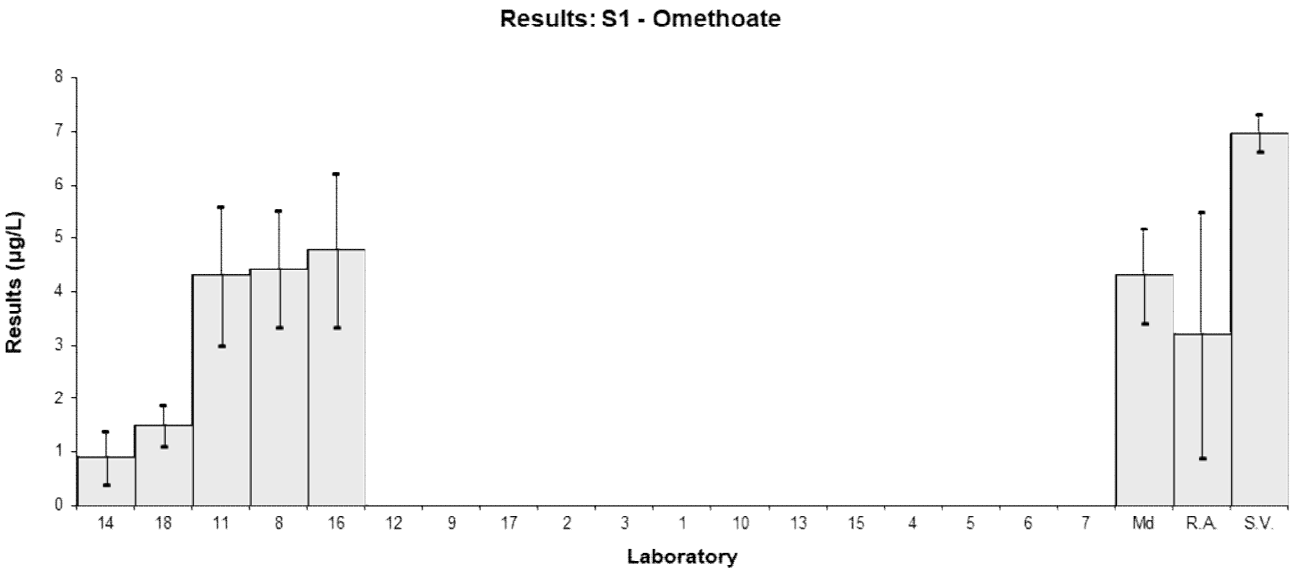

Results: S1 - Omethoate
Results (µg/L)
0
1
2
3
4
5
6
7
8
14
18
11
8
16
12
9
17
2
3
1
10
13
15
4
5
6
7
Md
R.A.
S.V.
Laboratory

Figure 4

Table 8

Sample Details

Sample No.	S1
Matrix	Water
Analyte	p,p'-DDT
Units	µg/L

Participant Results

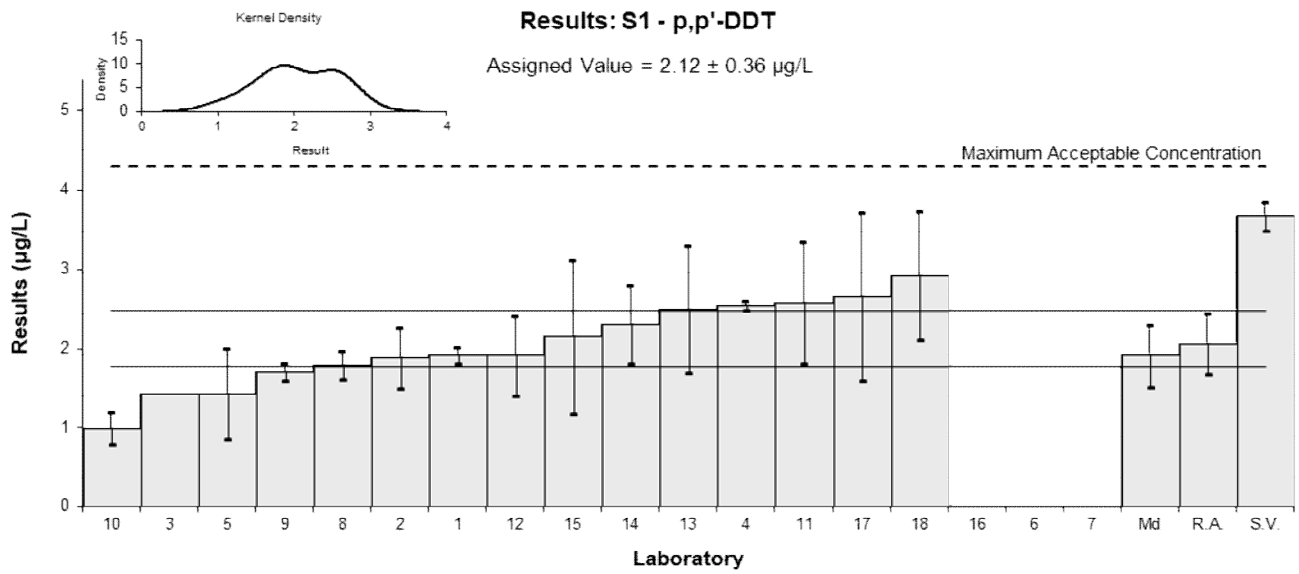
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.91	0.10	114	-0.66	-0.56
2	1.88	0.38	105	-0.75	-0.46
3	1.4192	NR	105.5	-2.20	-1.95
4	2.54	0.06	NR	1.32	1.15
5	1.43	0.57	90	-2.17	-1.02
6	NT	NT	NT		
7	NT	NT	NT		
8	1.79	0.18	NR	-1.04	-0.82
9	1.7	0.1	NR	-1.32	-1.12
10	0.99	0.2	NR	-3.55	-2.74
11	2.58	0.77	93	1.45	0.54
12	1.91	0.5	NR	-0.66	-0.34
13	2.5	0.8	NR	1.19	0.43
14	2.3	0.5	NR	0.57	0.29
15	2.15	0.97	NR	0.09	0.03
16	NT	NT	NT		
17	2.658	1.0632	NR	1.69	0.48
18**	2.92	0.81	122.9	2.00	0.90

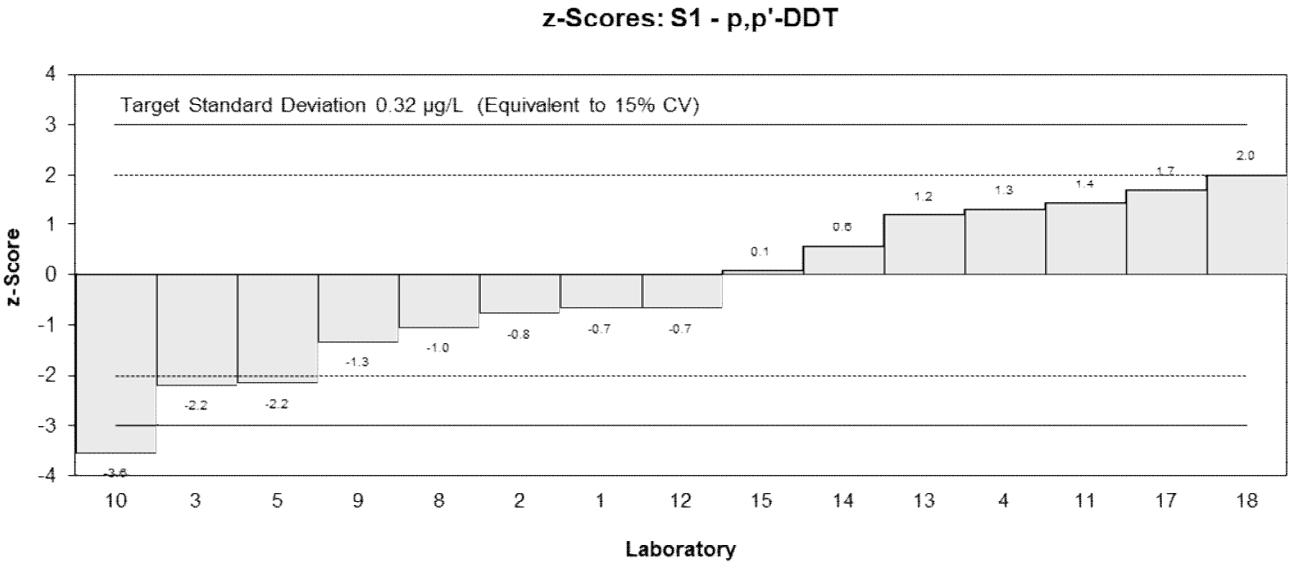
Statistics

Assigned Value*	2.12	0.36
Spike	3.67	0.18
Max. Acceptable Concentration**	4.31	
Robust Average	2.06	0.38
Median	1.91	0.39
Mean	2.05	
N	15	
Max.	2.92	
Min.	0.99	
Robust SD	0.58	
Robust CV	28%	

* Robust average excluding Laboratory 10.

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


Kernel Density
Density
Result
Results: S1 - p,p'-DDT
Assigned Value = 2.12 ± 0.36 µg/L
Maximum Acceptable Concentration
Results (µg/L)
10 3 5 9 8 2 1 12 15 14 13 4 11 17 18 16 6 7 Md R.A. S.V.
Laboratory


z-Scores: S1 - p,p'-DDT
Target Standard Deviation 0.32 µg/L (Equivalent to 15% CV)
z-Score
-3.6 -2.2 -2.2 -1.3 -1.0 -0.8 -0.7 -0.7 0.1 0.6 1.2 1.3 1.4 1.7 2.0
10 3 5 9 8 2 1 12 15 14 13 4 11 17 18
Laboratory

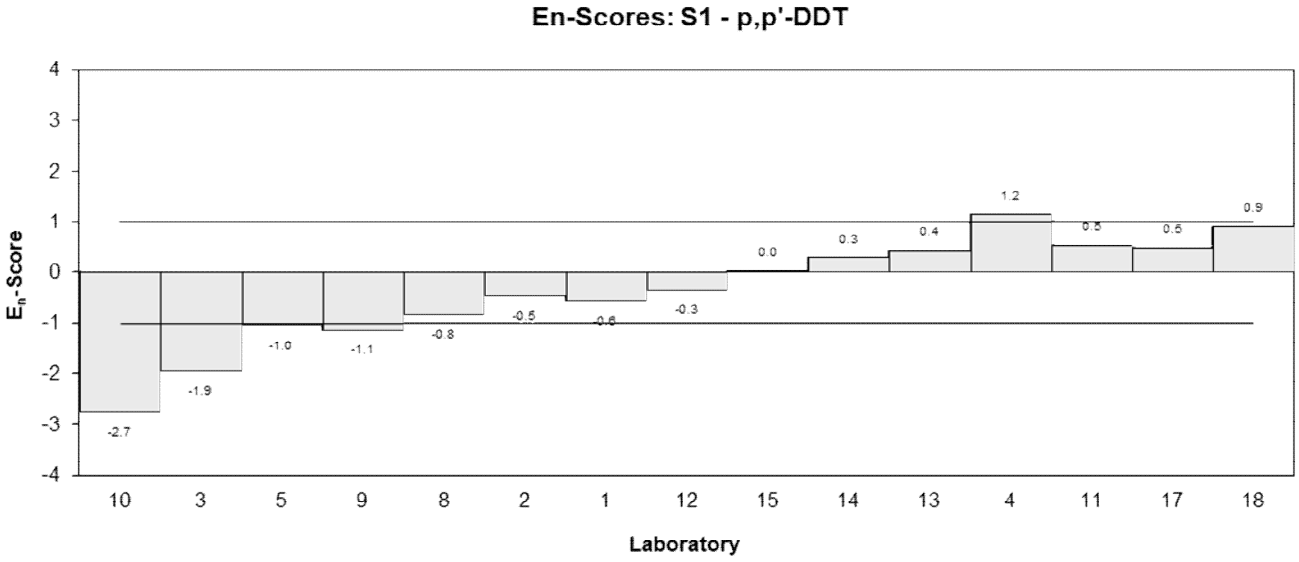

En-Scores: S1 - p,p'-DDT
En-Score
-2.7 -1.9 -1.0 -1.1 -0.8 -0.5 -0.6 -0.3 0.0 0.3 0.4 1.2 0.5 0.5 0.9
10 3 5 9 8 2 1 12 15 14 13 4 11 17 18
Laboratory

Figure 5

Table 9

Sample Details

Sample No.	S1
Matrix	Water
Analyte	Parathion-methyl
Units	µg/L

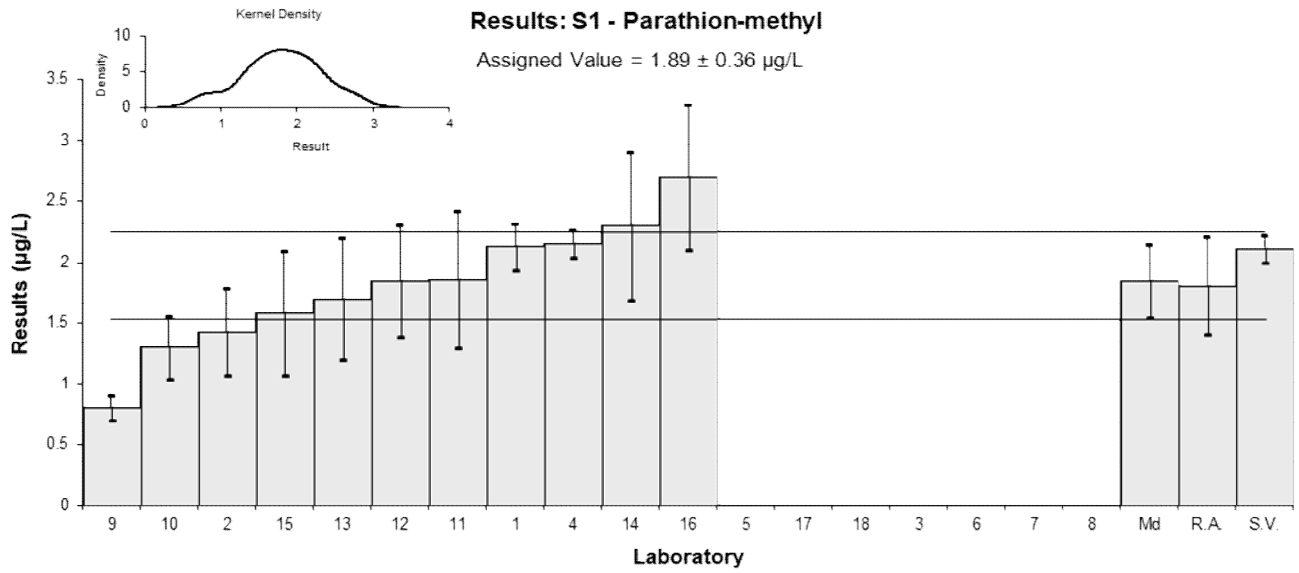
Participant Results

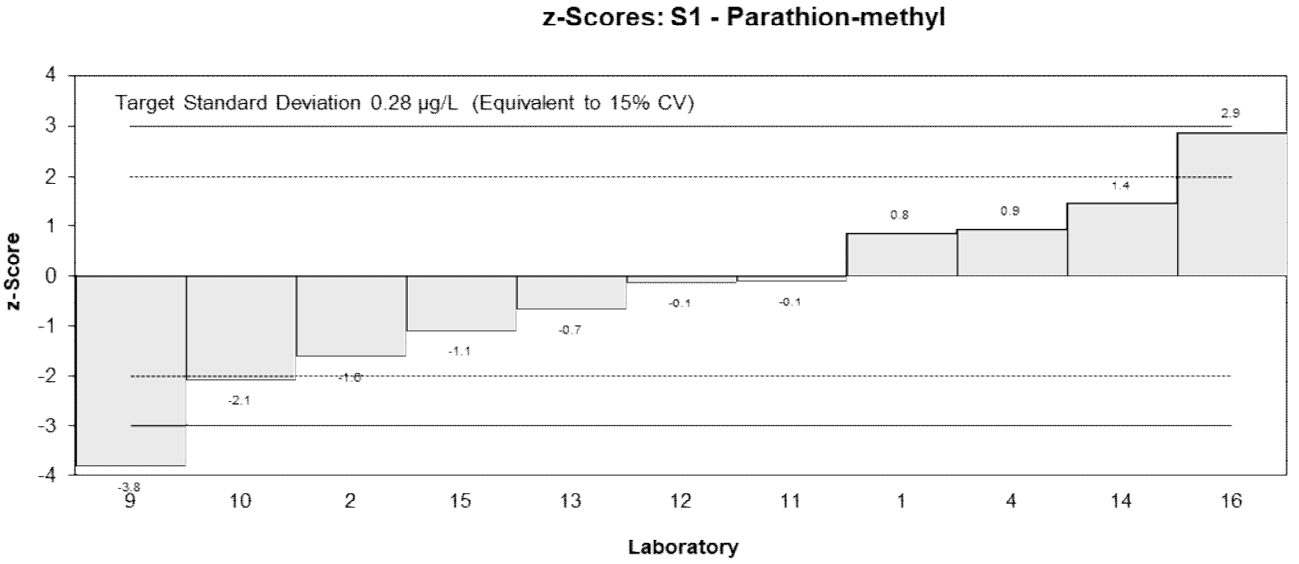
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	2.13	0.19	94	0.85	0.59
2	1.43	0.36	81	-1.62	-0.90
3	NT	NT	NT		
4	2.15	0.11	NR	0.92	0.69
5	<0.5	0.5	NR		
6	NT	NT	NT		
7	NT	NT	NT		
8	NT	NT	NT		
9	0.81	0.1	NR	-3.81	-2.89
10	1.3	0.26	NR	-2.08	-1.33
11	1.86	0.56	80	-0.11	-0.05
12	1.85	0.46	NR	-0.14	-0.07
13	1.7	0.5	NR	-0.67	-0.31
14	2.3	0.6	NR	1.45	0.59
15	1.58	0.51	NR	-1.09	-0.50
16	2.7	0.59	NR	2.86	1.17
17	NR	NR	NR		
18	NT	NT	NT		

Statistics

Assigned Value*	1.89	0.36
Spike	2.11	0.11
Robust Average	1.81	0.40
Median	1.85	0.30
Mean	1.80	
N	11	
Max.	2.7	
Min.	0.81	
Robust SD	0.53	
Robust CV	29%	

* Robust average excluding Laboratory 9.


Kernel Density
Density
Result
Results: S1 - Parathion-methyl
Assigned Value = 1.89 ± 0.36 µg/L
Results (µg/L)
Laboratory
9 10 2 15 13 12 11 1 4 14 16 5 17 18 3 6 7 8 Md R.A. S.V.


z-Scores: S1 - Parathion-methyl
Target Standard Deviation 0.28 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
9 10 2 15 13 12 11 1 4 14 16
-3.8 -2.1 -1.6 -1.1 -0.7 -0.1 -0.1 0.8 0.9 1.4 2.9

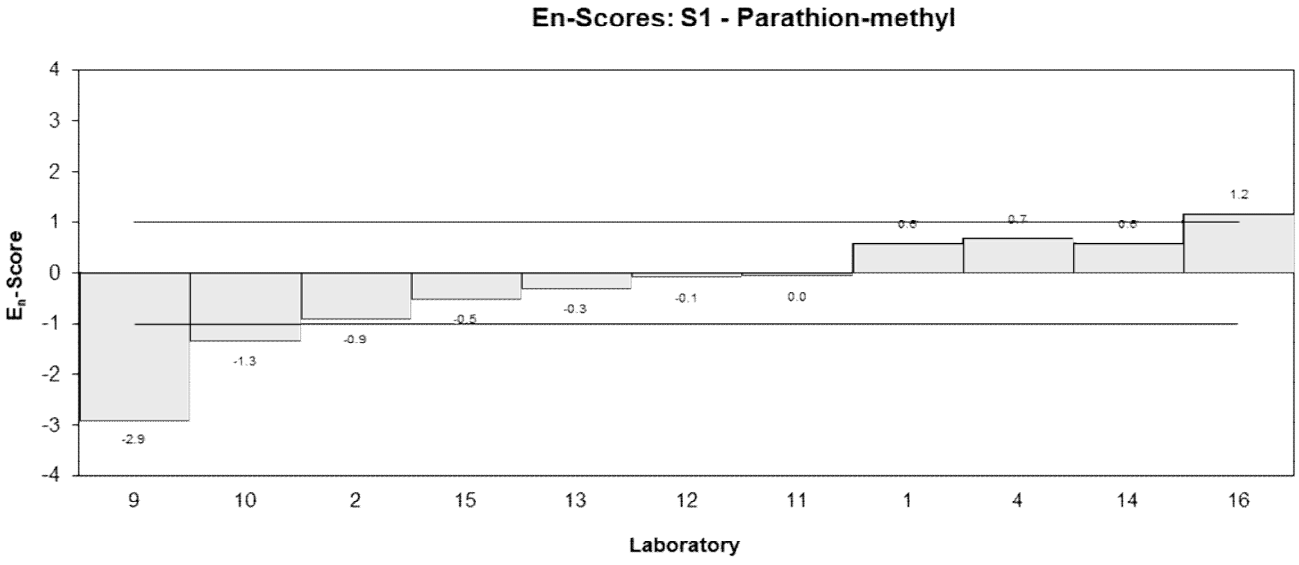

En-Scores: S1 - Parathion-methyl
En-Score
Laboratory
9 10 2 15 13 12 11 1 4 14 16
-2.9 -1.3 -0.9 -0.5 -0.3 -0.1 0.0 0.6 0.7 0.6 1.2

Figure 6

Table 10

Sample Details

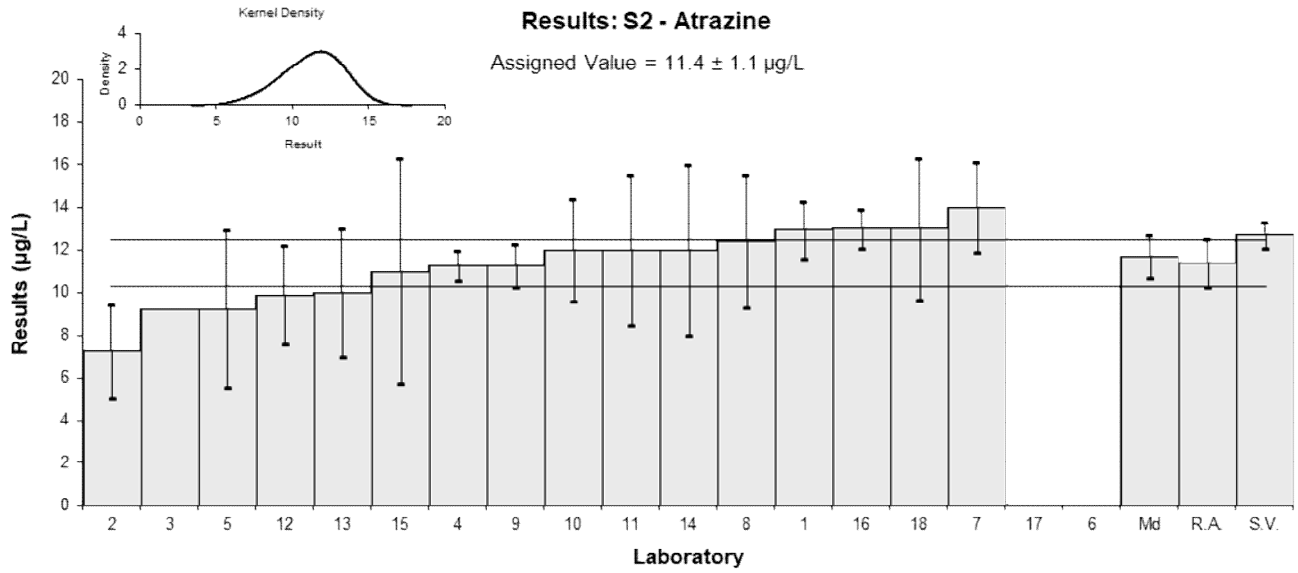
Sample No.	S2
Matrix	Water
Analyte	Atrazine
Units	µg/L

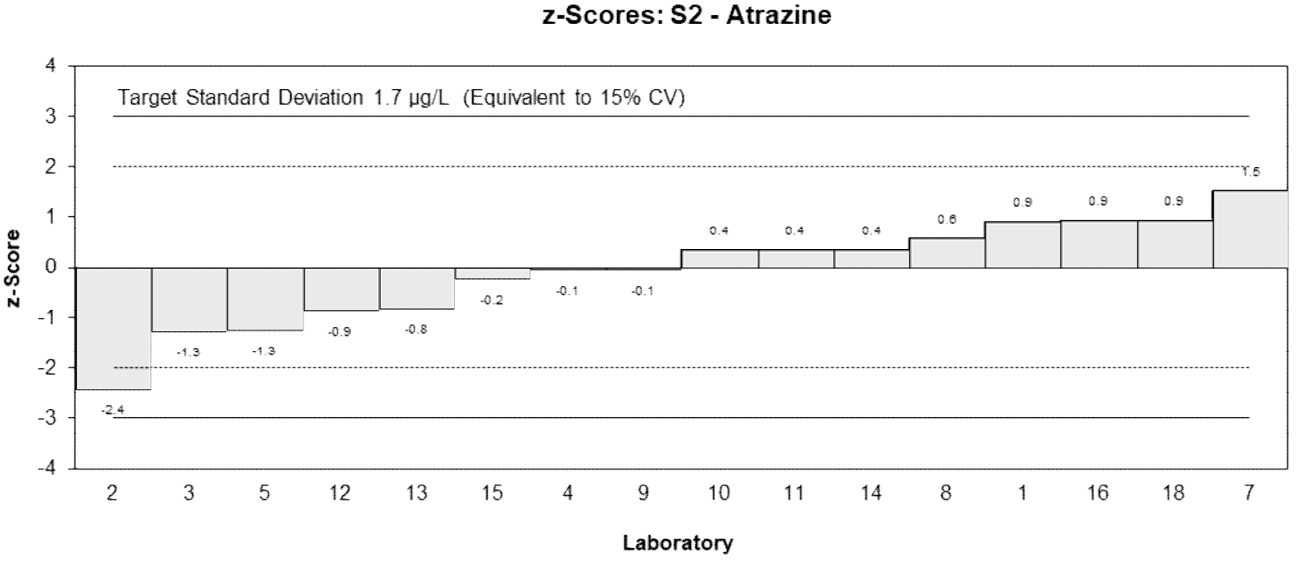
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	12.94	1.30	111	0.90	0.90
2	7.25	2.19	81	-2.43	-1.69
3	9.2201	NR	92.6	-1.27	-1.98
4	11.29	0.69	NR	-0.06	-0.08
5	9.24	3.7	72	-1.26	-0.56
6	NT	NT	NT		
7	14	2.1	NR	1.52	1.10
8	12.4	3.1	NR	0.58	0.30
9	11.3	1	NR	-0.06	-0.07
10	12	2.4	NR	0.35	0.23
11	12	3.5	101	0.35	0.16
12	9.9	2.3	NR	-0.88	-0.59
13	10	3	NR	-0.82	-0.44
14	12	4	NR	0.35	0.14
15	11	5.3	NR	-0.23	-0.07
16	13	0.9	NR	0.94	1.13
17	NR	NR	NR		
18	13	3.3	95	0.94	0.46

Statistics

Assigned Value	11.4	1.1
Spike	12.7	0.6
Robust Average	11.4	1.1
Median	11.7	1.0
Mean	11.3	
N	16	
Max.	14	
Min.	7.25	
Robust SD	1.8	
Robust CV	16%	


Kernel Density
Density
Result
Results: S2 - Atrazine
Assigned Value = 11.4 ± 1.1 µg/L
Results (µg/L)
Laboratory
2 3 5 12 13 15 4 9 10 11 14 8 1 16 18 7 17 6 Md R.A. S.V.


z-Scores: S2 - Atrazine
Target Standard Deviation 1.7 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
2 3 5 12 13 15 4 9 10 11 14 8 1 16 18 7
-2.4 -1.3 -1.3 -0.9 -0.8 -0.2 -0.1 -0.1 0.4 0.4 0.4 0.6 0.9 0.9 0.9 1.6

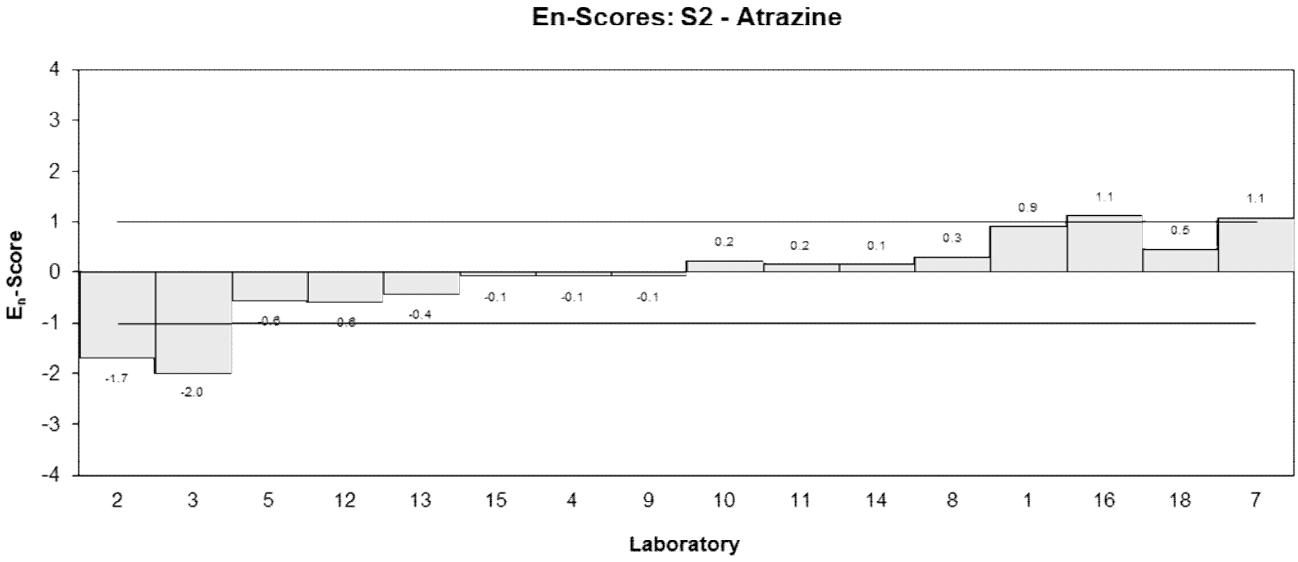

En-Scores: S2 - Atrazine
En-Score
Laboratory
2 3 5 12 13 15 4 9 10 11 14 8 1 16 18 7
-1.7 -2.0 -0.6 -0.6 -0.4 -0.1 -0.1 -0.1 0.2 0.2 0.1 0.3 0.9 1.1 0.5 1.1

Figure 7

Table 11

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Recovery
1	0.15	0.01	106
2	0.23	0.05	93
3	NR	NR	NR
4	NR	NR	NR
5	0.162	0.065	95
6	NT	NT	NT
7	NT	NT	NT
8	<0.1	NR	NR
9	0.32	0.1	NR
10	0.63	0.13	NR
11	0.22	0.07	82
12	<0.1	NR	NR
13	<0.4	NR	NR
14	0.36	0.06	NR
15	0.097	0.042	NR
16	NT	NT	NT
17	0.033	0.0132	NR
18	<0.01	NR	NR

Statistics

Assigned Value	Not Set	
Spike	1.72	0.09
Robust Average	0.22	0.12
Median	0.22	0.11
Mean	0.24	
N	9	
Max.	0.63	
Min.	0.033	
Robust SD	0.15	
Robust CV	66%	

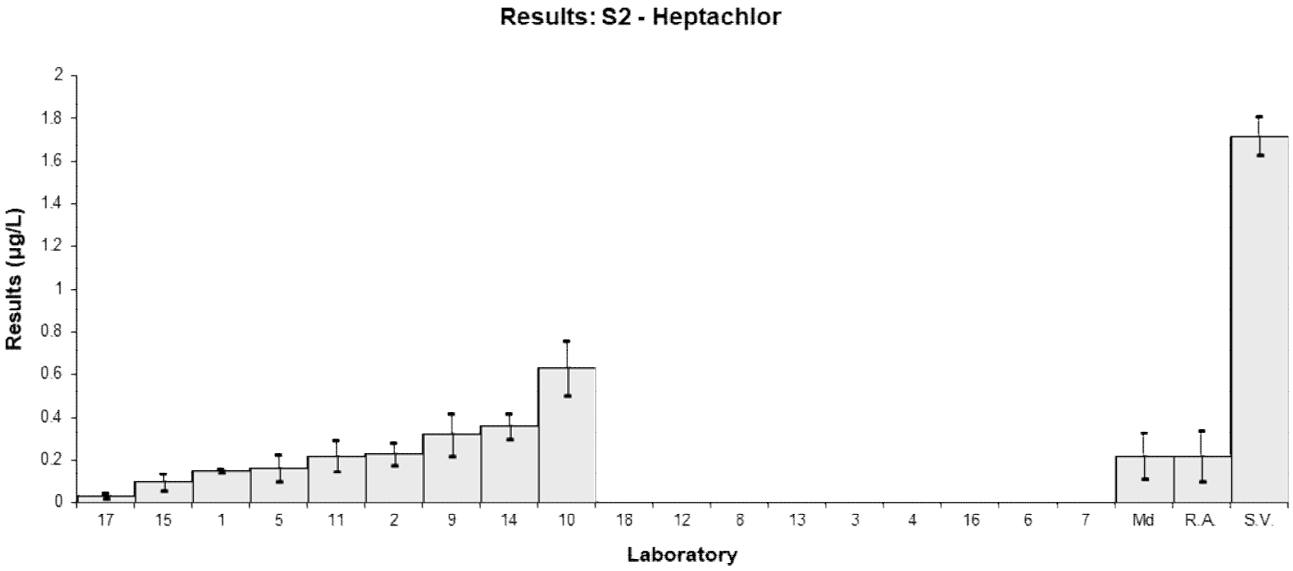

Results: S2 - Heptachlor
Results (µg/L)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
17
15
1
5
11
2
9
14
10
18
12
8
13
3
4
16
6
7
Md
R.A.
S.V.
Laboratory

Figure 8

Table 12

Sample Details

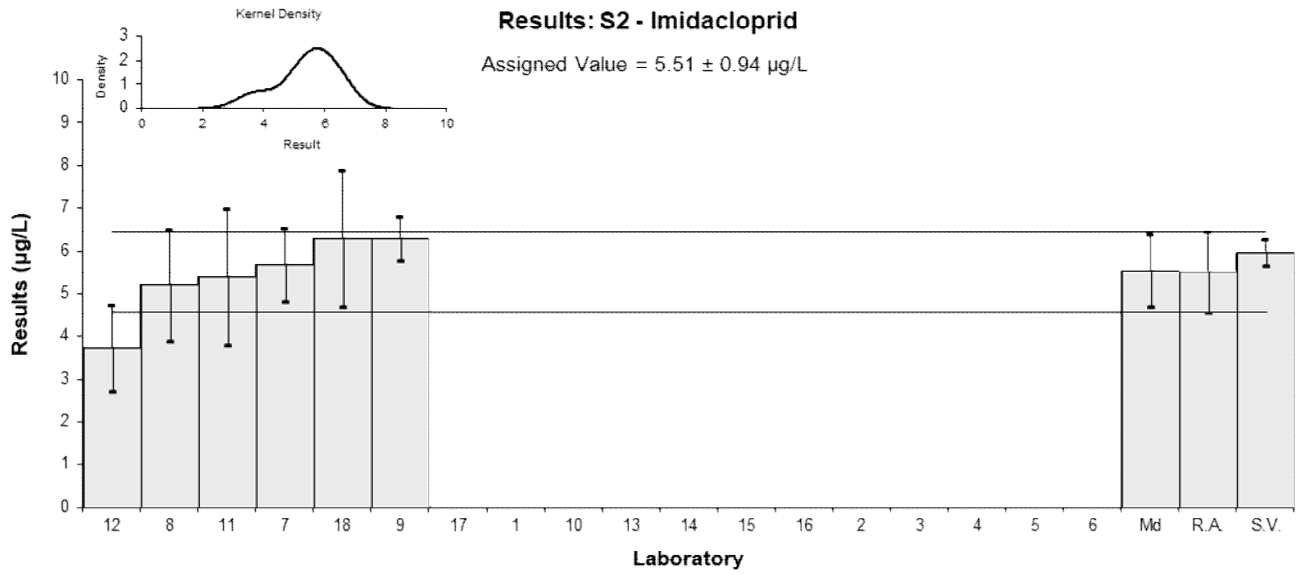
Sample No.	S2
Matrix	Water
Analyte	Imidacloprid
Units	µg/L

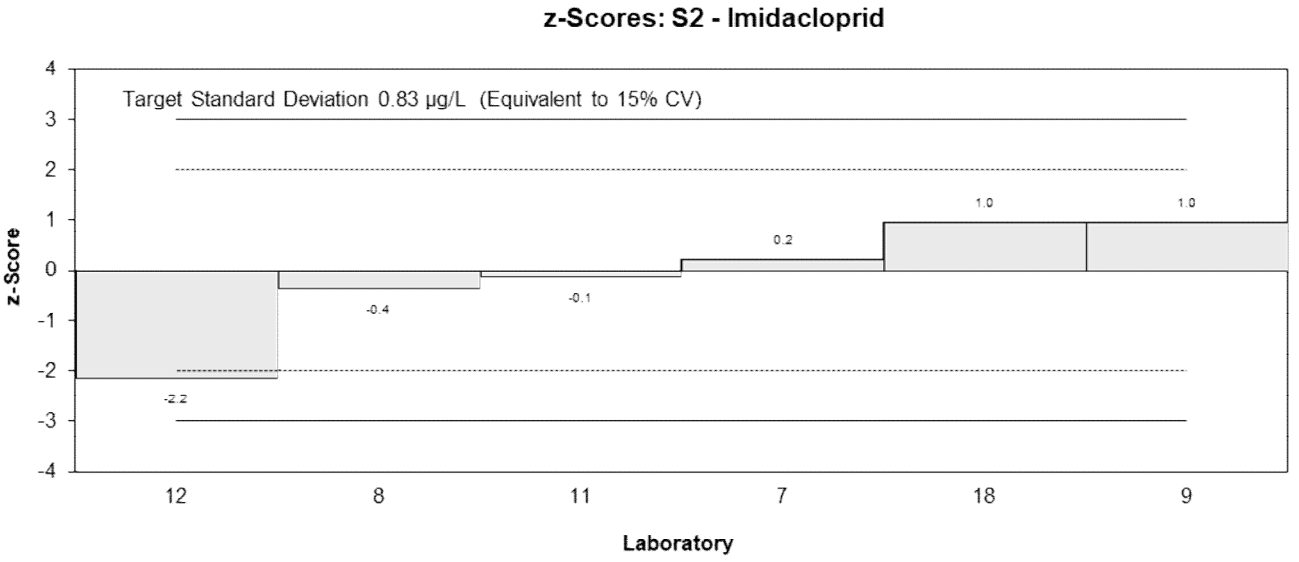
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6	NT	NT	NT		
7	5.7	0.855	NR	0.23	0.15
8	5.21	1.3	NR	-0.36	-0.19
9	6.3	0.5	NR	0.96	0.74
10	NT	NT	NT		
11	5.4	1.6	83	-0.13	-0.06
12	3.73	1.01	NR	-2.15	-1.29
13	NT	NT	NT		
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	NR	NR	NR		
18	6.3	1.6	95	0.96	0.43

Statistics

Assigned Value	5.51	0.94
Spike	5.97	0.30
Robust Average	5.51	0.94
Median	5.55	0.85
Mean	5.44	
N	6	
Max.	6.3	
Min.	3.73	
Robust SD	0.92	
Robust CV	17%	


Kernel Density
Density
Result
Results: S2 - Imidacloprid
Assigned Value = 5.51 ± 0.94 µg/L
Results (µg/L)
12 8 11 7 18 9 17 1 10 13 14 15 16 2 3 4 5 6 Md R.A. S.V.
Laboratory


z-Scores: S2 - Imidacloprid
Target Standard Deviation 0.83 µg/L (Equivalent to 15% CV)
z-Score
-2.2
-0.4
-0.1
0.2
1.0
1.0
12 8 11 7 18 9
Laboratory

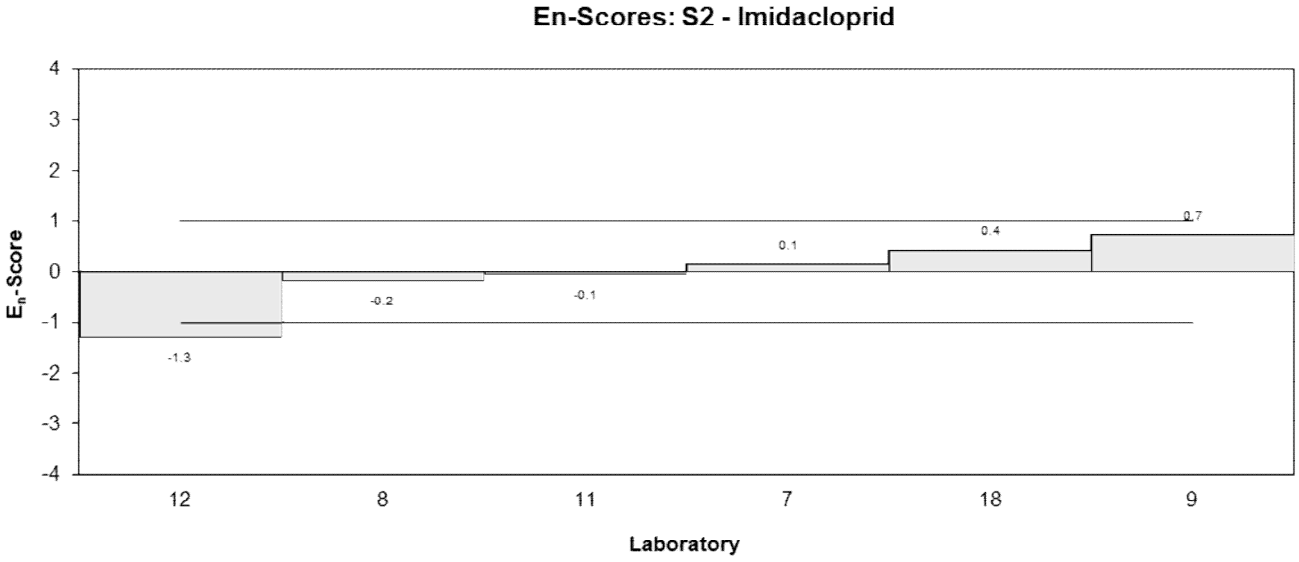

En-Scores: S2 - Imidacloprid
En-Score
-1.3
-0.2
-0.1
0.1
0.4
0.7
12 8 11 7 18 9
Laboratory

Figure 9

Table 13

Sample Details

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

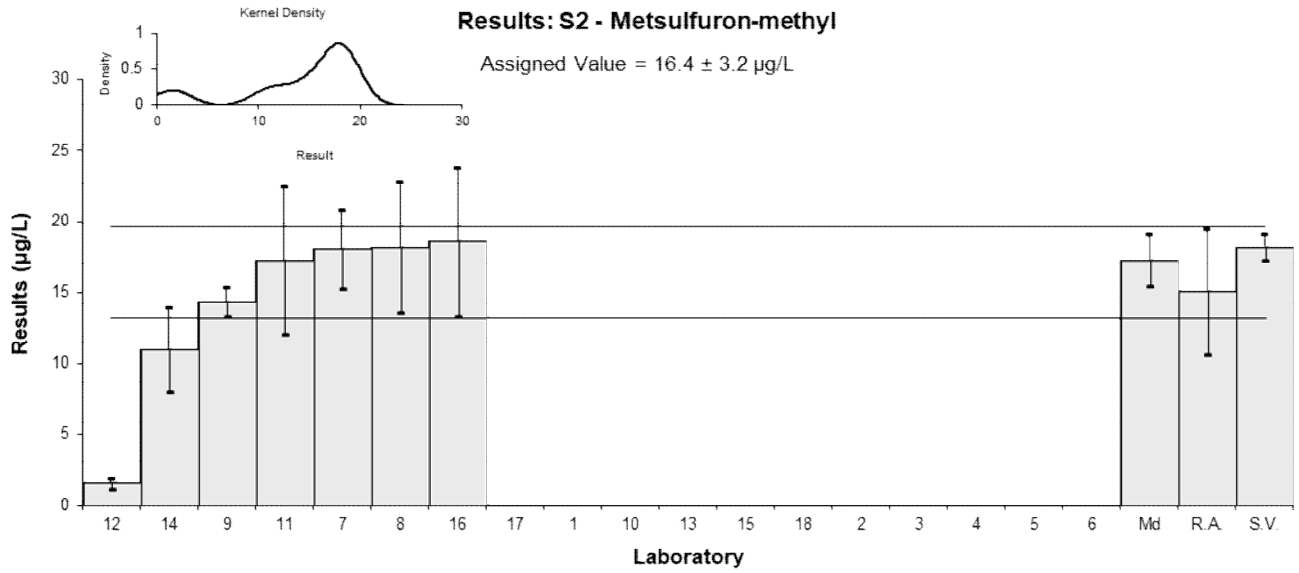
Participant Results

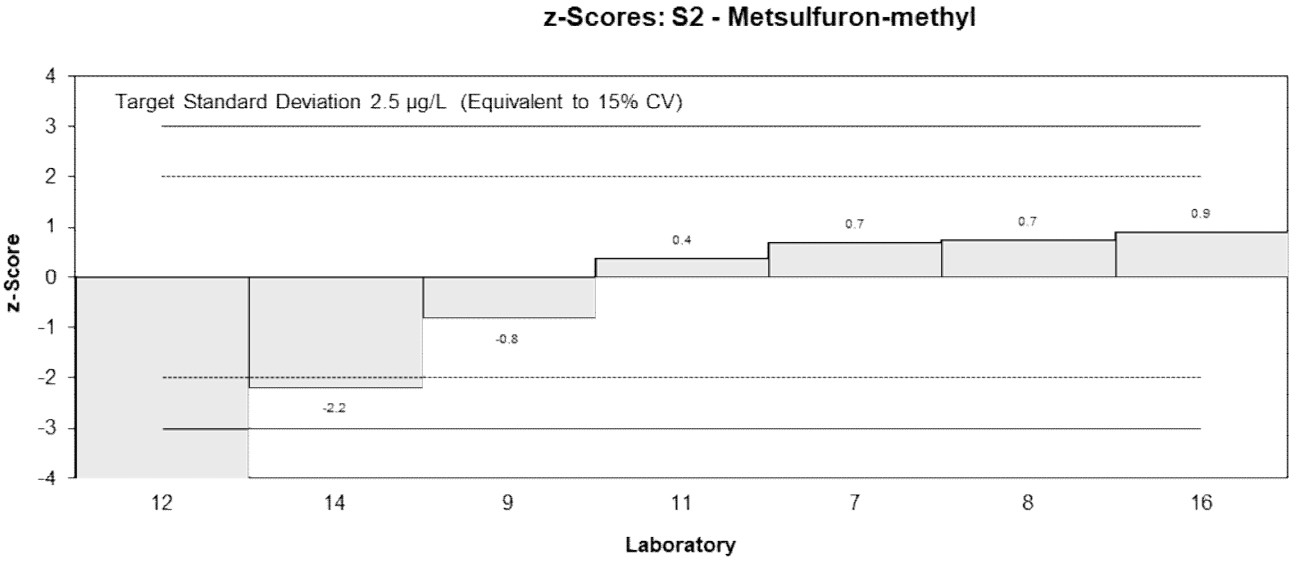
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	NT	NT	NT		
6	NT	NT	NT		
7	18.1	2.72	NR	0.69	0.40
8	18.2	4.6	NR	0.73	0.32
9	14.4	1	NR	-0.81	-0.60
10	NT	NT	NT		
11	17.3	5.2	99	0.37	0.15
12	1.56	0.39	NR	-6.03	-4.60
13	NT	NT	NT		
14	11	3	NR	-2.20	-1.23
15	NT	NT	NT		
16	18.6	5.2	NR	0.89	0.36
17	NR	NR	NR		
18	NT	NT	NT		

Statistics

Assigned Value*	16.4	3.2
Spike	18.2	0.9
Robust Average	15.1	4.4
Median	17.3	1.8
Mean	14.2	
N	7	
Max.	18.6	
Min.	1.56	
Robust SD	4.7	
Robust CV	31%	

* Robust average excluding Laboratory 12.


Kernel Density
Density
Results: S2 - Metsulfuron-methyl
Assigned Value = 16.4 ± 3.2 µg/L
Result
Results (µg/L)
Laboratory
12 14 9 11 7 8 16 17 1 10 13 15 18 2 3 4 5 6 Md R.A. S.V.


z-Scores: S2 - Metsulfuron-methyl
Target Standard Deviation 2.5 µg/L (Equivalent to 15% CV)
z-Score
0.4
0.7
0.7
0.9
-0.8
-2.2
Laboratory
12 14 9 11 7 8 16

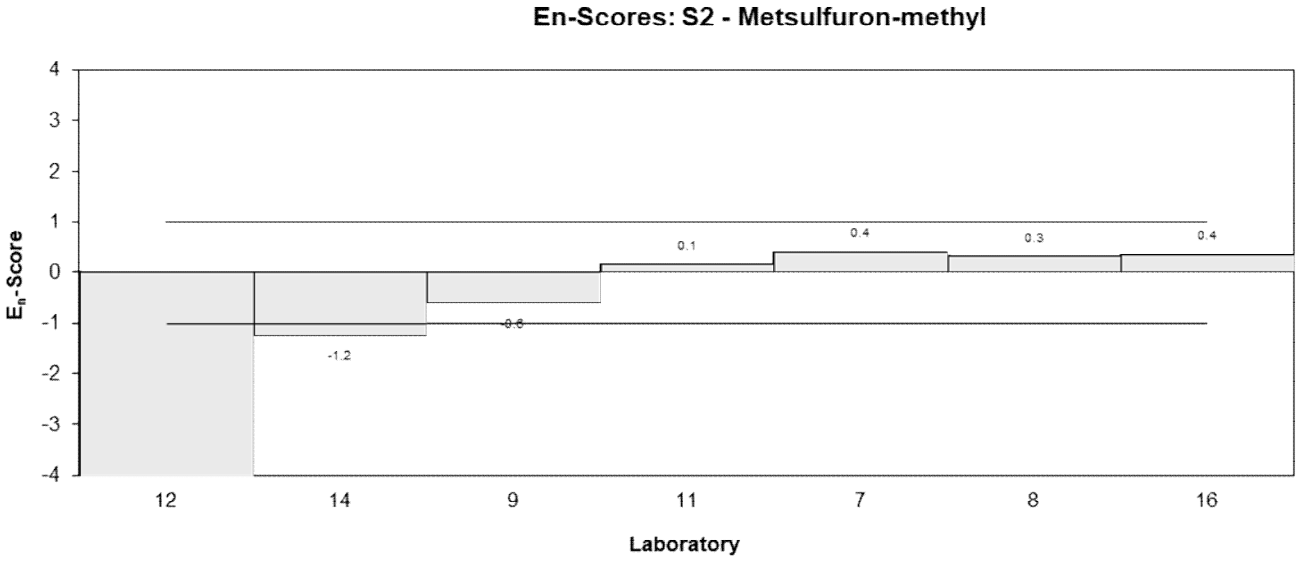

En-Scores: S2 - Metsulfuron-methyl
En-Score
0.1
0.4
0.3
0.4
-0.6
-1.2
Laboratory
12 14 9 11 7 8 16

Figure 10

Table 14

Sample Details

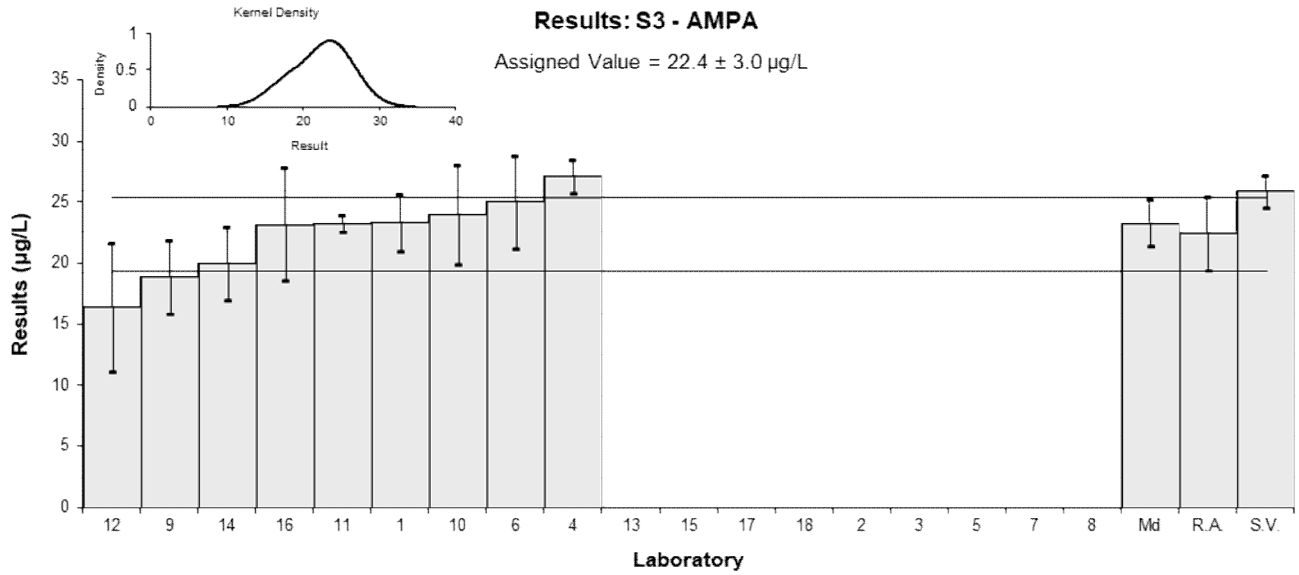
Sample No.	S3
Matrix	Water
Analyte	AMPA
Units	µg/L

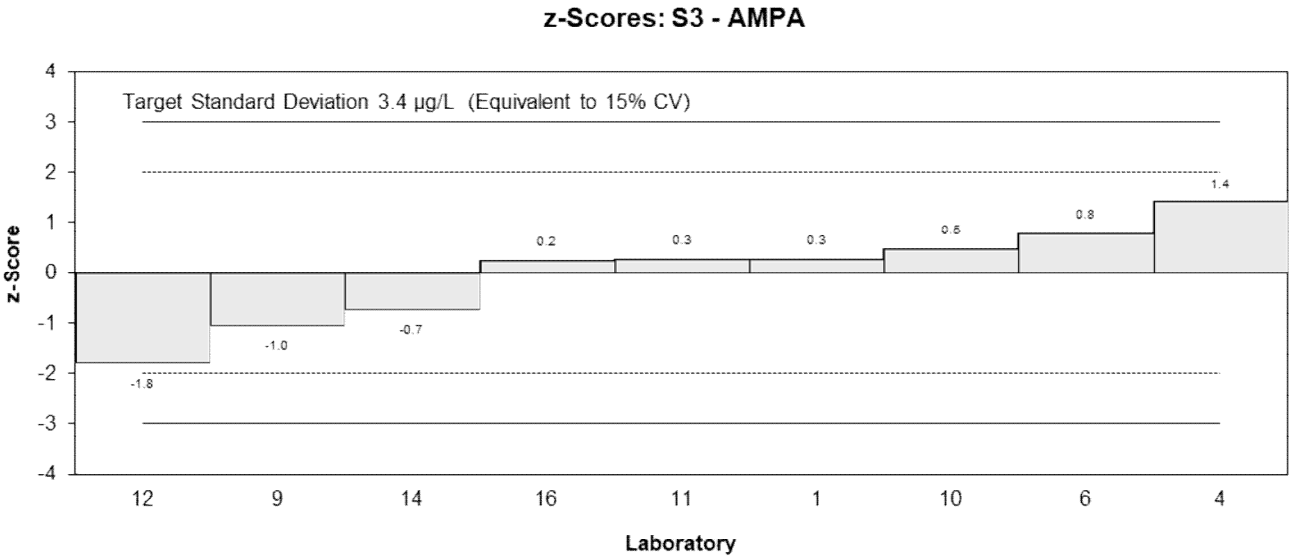
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	23.32	2.33	80	0.27	0.24
2	NT	NT	NT		
3	NT	NT	NT		
4	27.13	1.36	NR	1.41	1.44
5	NT	NT	NT		
6	25	3.8	104	0.77	0.54
7	NT	NT	NT		
8	NT	NT	NT		
9	18.9	3	NR	-1.04	-0.82
10	24	4	91	0.48	0.32
11	23.3	0.70	98	0.27	0.29
12	16.4	5.2	94	-1.79	-1.00
13	NT	NT	NT		
14	20	3	NR	-0.71	-0.57
15	NT	NT	NT		
16	23.2	4.6	NR	0.24	0.15
17	NT	NT	NT		
18	NT	NT	NT		

Statistics

Assigned Value	22.4	3.0
Spike	25.9	1.3
Robust Average	22.4	3.0
Median	23.3	1.9
Mean	22.4	
N	9	
Max.	27.13	
Min.	16.4	
Robust SD	3.6	
Robust CV	16%	


Kernel Density
Density
Result
Results: S3 - AMPA
Assigned Value = 22.4 ± 3.0 µg/L
Results (µg/L)
Laboratory
12 9 14 16 11 1 10 6 4 13 15 17 18 2 3 5 7 8 Md R.A. S.V.


z-Scores: S3 - AMPA
Target Standard Deviation 3.4 µg/L (Equivalent to 15% CV)
z-Score
-1.8
-1.0
-0.7
0.2
0.3
0.3
0.5
0.8
1.4
Laboratory
12 9 14 16 11 1 10 6 4

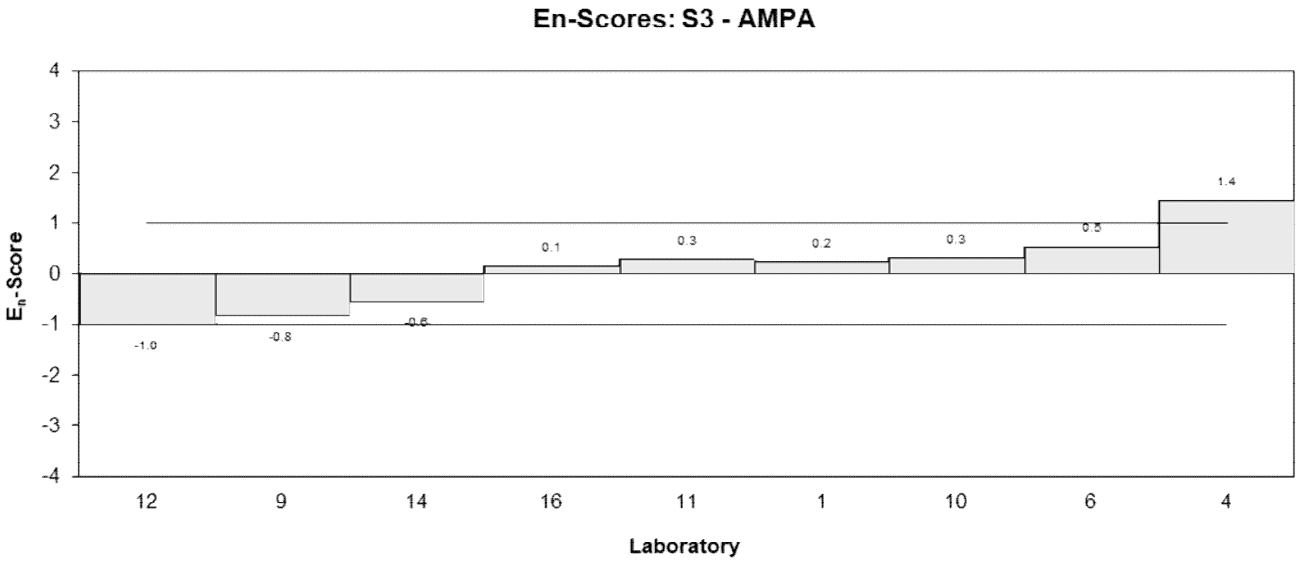

En-Scores: S3 - AMPA
En-Score
-1.0
-0.8
-0.6
0.1
0.3
0.2
0.3
0.5
1.4
Laboratory
12 9 14 16 11 1 10 6 4

Figure 11

Table 15

Sample Details

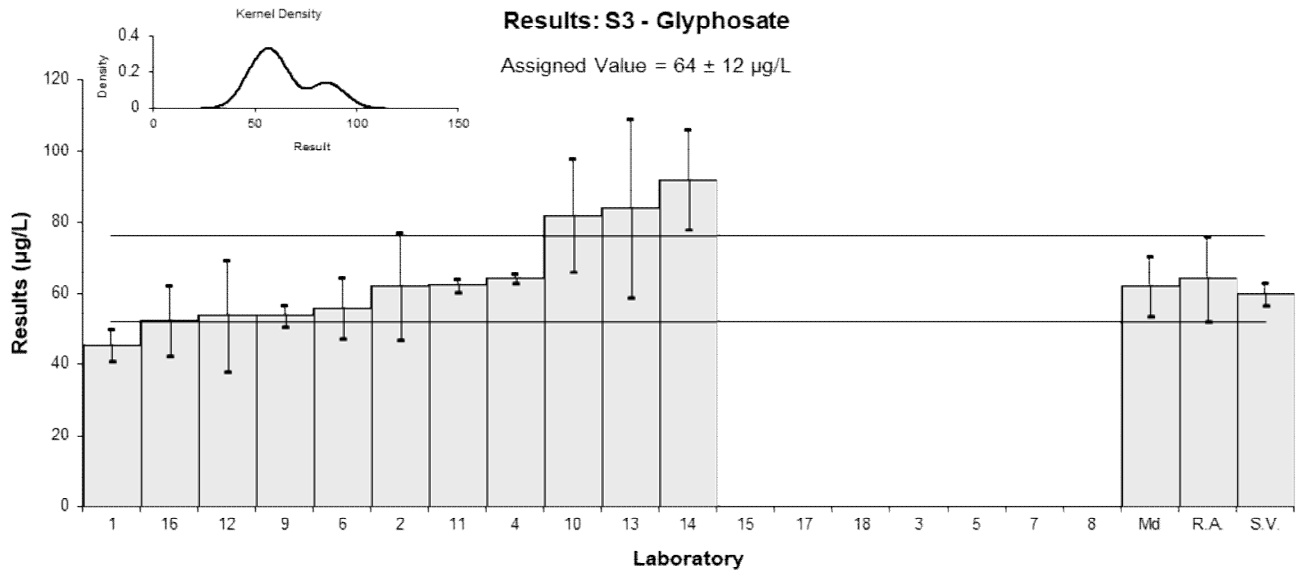
Sample No.	S3
Matrix	Water
Analyte	Glyphosate
Units	µg/L

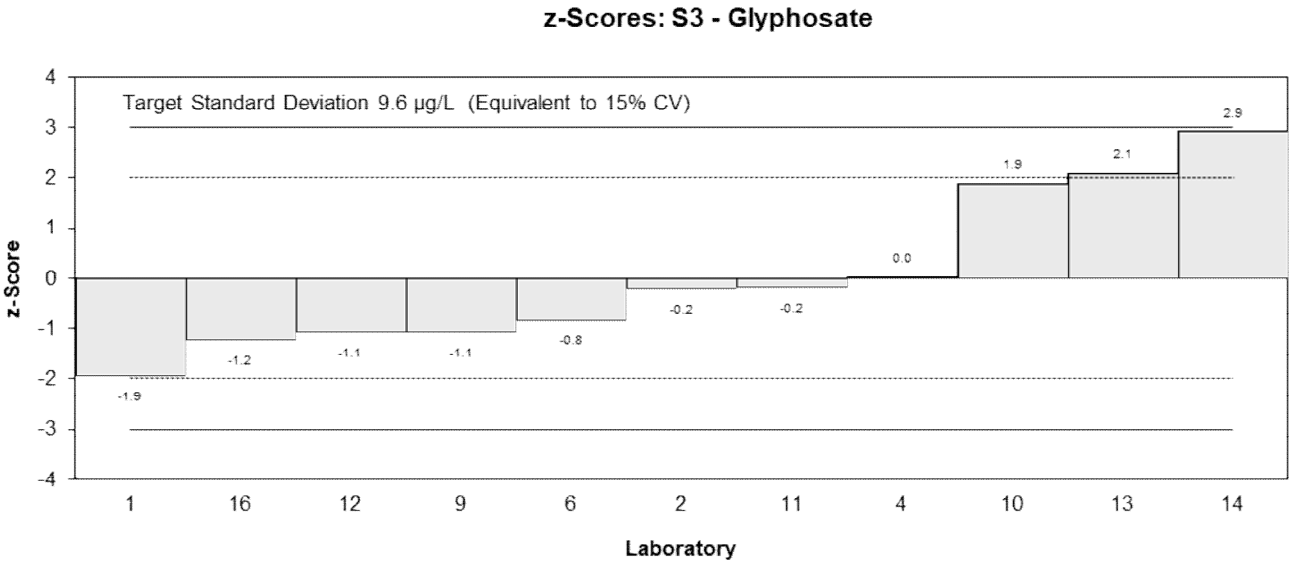
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	45.32	4.53	92	-1.95	-1.46
2	62	15	122	-0.21	-0.10
3	NT	NT	NT		
4	64.2	1.36	NR	0.02	0.02
5	NT	NT	NT		
6	56	8.4	69	-0.83	-0.55
7	NT	NT	NT		
8	NT	NT	NT		
9	53.7	3	NR	-1.07	-0.83
10	82	16	92	1.88	0.90
11	62.3	1.87	95	-0.18	-0.14
12	53.7	15.6	76	-1.07	-0.52
13	84	25	NR	2.08	0.72
14	92	14	NR	2.92	1.52
15	NT	NT	NT		
16	52.2	9.9	NR	-1.23	-0.76
17	NT	NT	NT		
18	NT	NT	NT		

Statistics

Assigned Value	64	12
Spike	59.8	3.0
Robust Average	64	12
Median	62.0	8.3
Mean	64.3	
N	11	
Max.	92	
Min.	45.32	
Robust SD	16	
Robust CV	26%	


Kernel Density
Density
Result
Results: S3 - Glyphosate
Assigned Value = 64 ± 12 µg/L
Results (µg/L)
Laboratory
1 16 12 9 6 2 11 4 10 13 14 15 17 18 3 5 7 8 Md R.A. S.V.


z-Scores: S3 - Glyphosate
Target Standard Deviation 9.6 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
1 16 12 9 6 2 11 4 10 13 14
-1.9 -1.2 -1.1 -1.1 -0.8 -0.2 -0.2 0.0 1.9 2.1 2.9

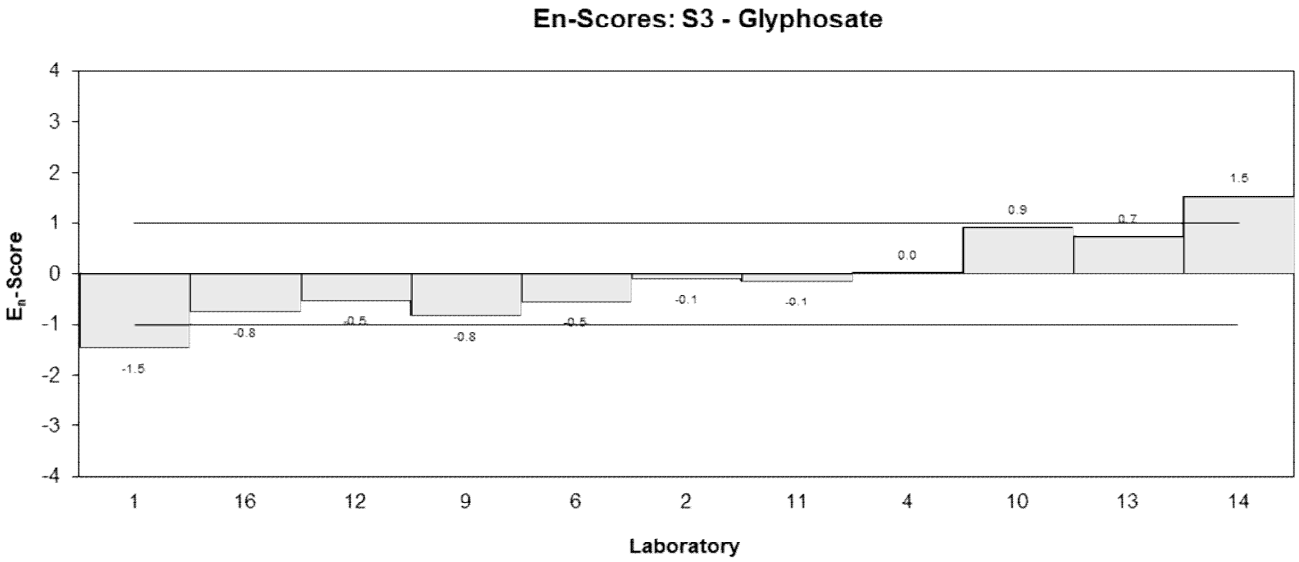

En-Scores: S3 - Glyphosate
En-Score
Laboratory
1 16 12 9 6 2 11 4 10 13 14
-1.5 -0.8 -0.5 -0.8 -0.5 -0.1 -0.1 0.0 0.9 0.7 1.5

Figure 12

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust average of participants' results was used as the assigned value for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2015.[6] Results less than 50% and greater than 150% of the robust average were removed before the calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using atrazine in Sample S2 as an example.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

A comparison of the assigned values (or robust average if no assigned value was set) and spiked values is presented in Table 16.

No assigned values were set for Sample S1 omethoate and Sample S2 heptachlor as there was significant degradation of these analytes, and the few reported numeric results for these analytes were highly variable. For Sample S1 p,p'-DDT, the robust average was 56% of the spiked value, but there was a reasonable consensus between participants' results and so an assigned value was set.

For all other analytes, the assigned values were within the range of 82% to 107% of the spiked values. Similar ratios have been observed in previous Pesticides in Water PT studies, and provides good support for the assigned values.

Table 16 Comparison of Assigned Value (or Robust Average) and Spiked Value

Sample	Analyte	Assigned Value *(Robust Average)* (µg/L)	Spiked Value (µg/L)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	Endosulfan sulfate	1.83	2.22	82%
	Imidacloprid	108	119	91%
	Omethoate	*(3.2)*	6.97	*(46%)*
	p,p'-DDT	2.12	3.67	58%
	Parathion-methyl	1.89	2.11	90%
S2	Atrazine	11.4	12.7	90%
	Heptachlor	*(0.22)*	1.72	*(13%)*
	Imidacloprid	5.51	5.97	92%
	Metsulfuron-methyl	16.4	18.2	90%
S3	AMPA	22.4	25.9	86%
	Glyphosate	64	59.8	107%

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate. It is a requirement of ISO/IEC 17025 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.[8]

Of 108 numerical results submitted for the analytes of interest in this study, 105 (97%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their MU (Table 3).

Laboratory **3** did not provide uncertainties for any result despite reporting that they were accredited to ISO/IEC 17025.

The magnitude of reported uncertainties was within the range of 2.1% to 56% relative. In general, an expanded uncertainty of less than 15% relative is likely to be unrealistically small for the routine measurement of a pesticide residue. Of the 105 MUs reported for this study, 26 were less than 15% relative. Participants reporting these uncertainties may wish to reconsider if their MUs are realistic or fit-for-purpose.

Results returning a satisfactory z-score but an unsatisfactory E_n-score may have underestimated the expanded MU associated with their result.

Some participants attached an estimate of the expanded MU to a non-value result reported. An estimate of uncertainty expressed as a value should not be attached to a non-value result.[9]

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write the 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 1.708 ± 0.6832 µg/L, it is better to report this as 1.71 ± 0.68 µg/L.[9]

6.3 z-Score

Target SDs equivalent to 15% PCV were used to calculate z-scores. CVs predicted by the Thompson-Horwitz equation,[7] target SDs (as PCV), and the between laboratories CVs obtained in this study for scored analytes are presented for comparison in Table 17.

Table 17 Comparison of Target SDs, Thompson-Horwitz CVs and Between Laboratories CVs

Sample	Analyte	Assigned Value (µg/L)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between Laboratories CV* (%)
S1	Endosulfan sulfate	1.83	22	15	20
	Imidacloprid	108	22	15	6.7
	p,p'-DDT	2.12	22	15	25
	Parathion-methyl	1.89	22	15	24
S2	Atrazine	11.4	22	15	16
	Imidacloprid	5.51	22	15	17
	Metsulfuron-methyl	16.4	22	15	19
S3	AMPA	22.4	22	15	16
	Glyphosate	64	22	15	26

* Robust between laboratories CVs with outliers removed, if applicable.

To account for possible low bias in the consensus value due to laboratories using inefficient analytical or extraction techniques, a total of 3 z-scores were adjusted in the following analytes: Sample S1 endosulfan sulfate and p,p'-DDT. A maximum acceptable concentration was set to two target SDs more than the spiked value, and results lower than the maximum acceptable concentration with a z-score greater than 2 had their z-score adjusted to 2. This ensured that laboratories reporting results close to the spiked value were not penalised.

z-Scores for results higher than the maximum acceptable concentration were not adjusted, and z-scores less than 2 were also not adjusted.

Of 94 results for which z-scores were calculated, 81 (86%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **9**, **11** and **12** reported results for all 9 analytes for which z-scores were calculated. Laboratory **11** returned satisfactory z-score for all 9 analytes.

Satisfactory z-scores were achieved for all scored analytes reported by Laboratories **1** (6), **8** (6), **4** (5), **18** (5), **7** (4), **15** (4), **6** (2) and **17** (2).

The dispersal of participants' z-scores is presented by laboratory in Figure 13, and by analyte in Figure 14.

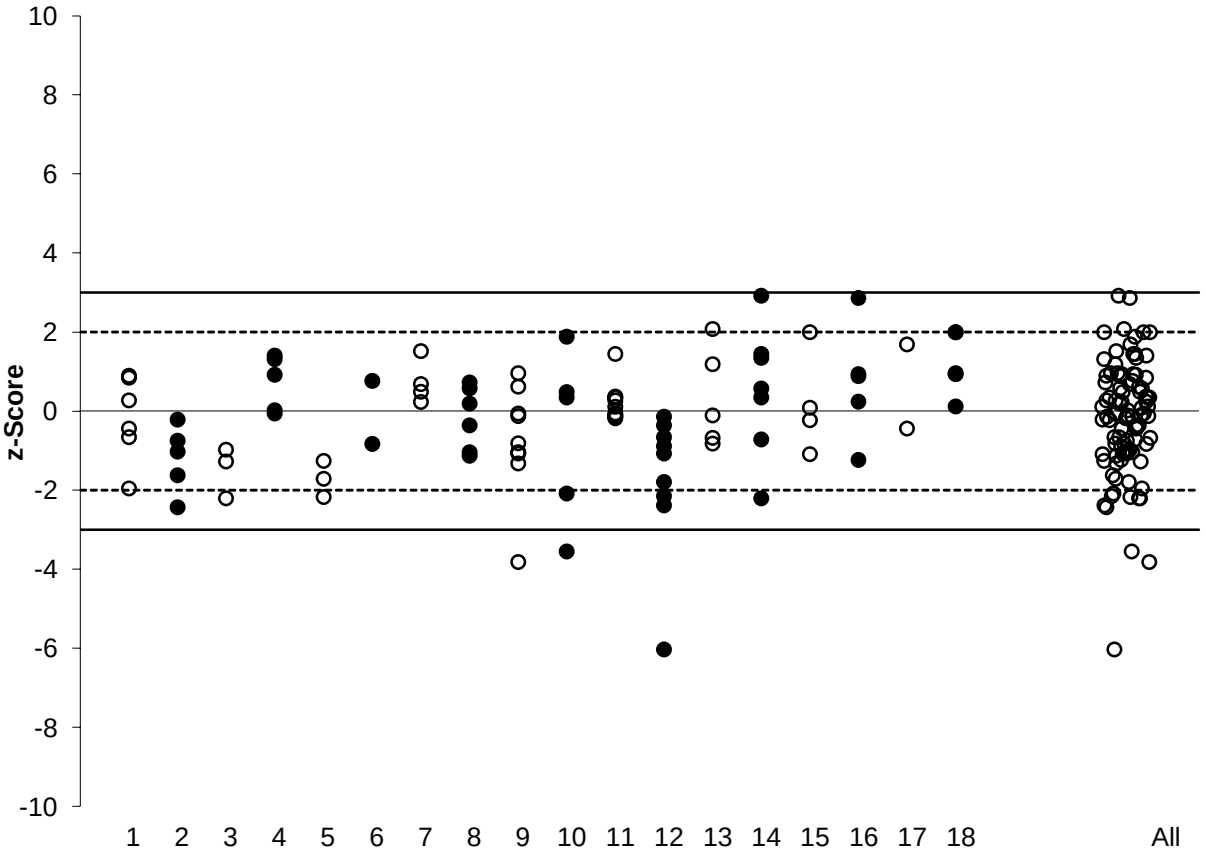


Figure 13 z-Score Dispersal by Laboratory

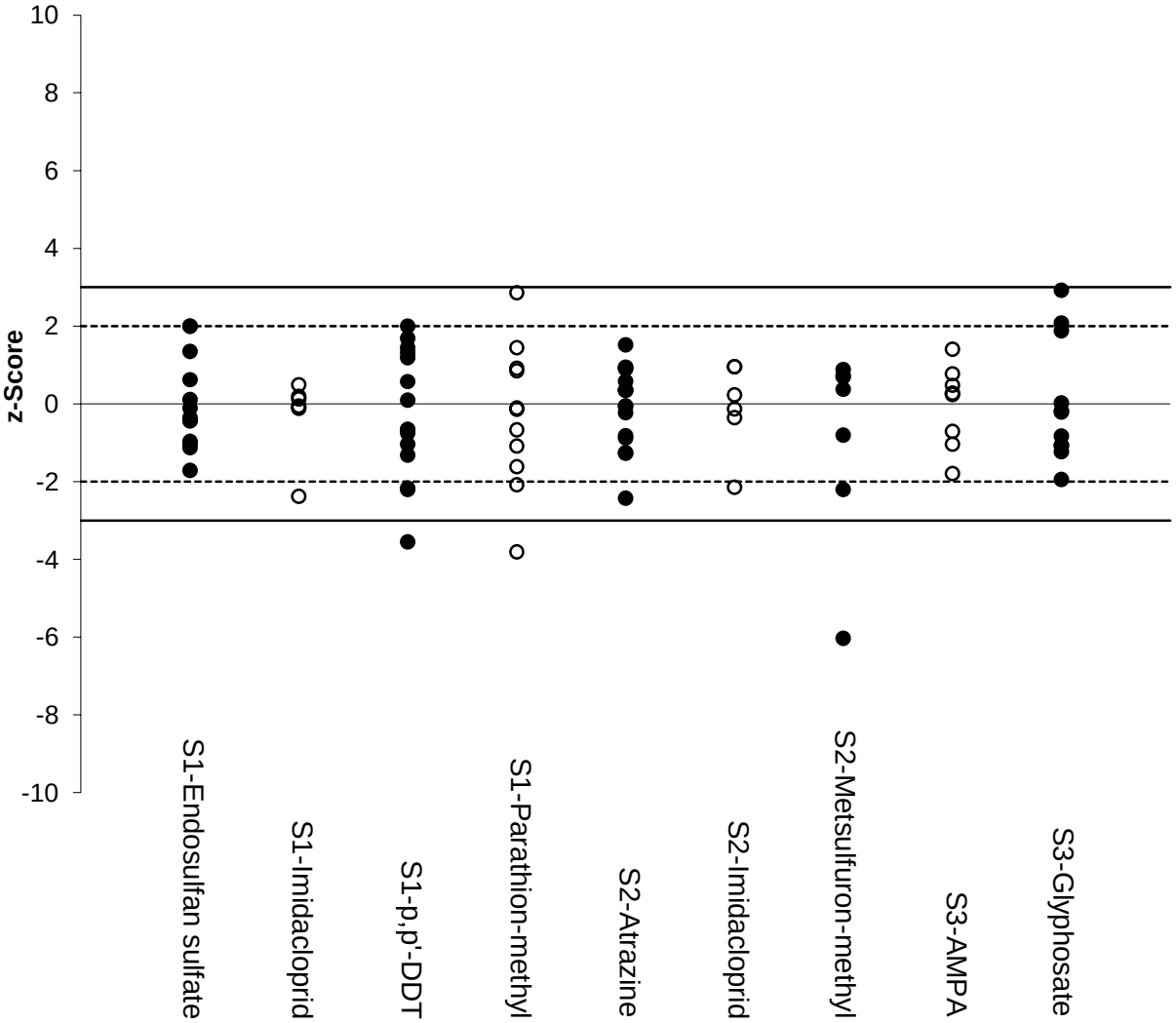


Figure 14 z-Score Dispersal by Pesticide

6.4 E_n-Score

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

Of 94 results for which E_n-scores were calculated, 73 (78%) returned a score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **11** returned satisfactory E_n-scores for all 9 scored analytes.

Satisfactory E_n-scores were achieved for all scored analytes reported by Laboratory **13** (5), **18** (5), **15** (4), **6** (2) and **17** (2).

No results reported by Laboratory **3** returned a satisfactory E_n-score.

The dispersal of participants' E_n-scores by laboratory is presented graphically in Figure 15.

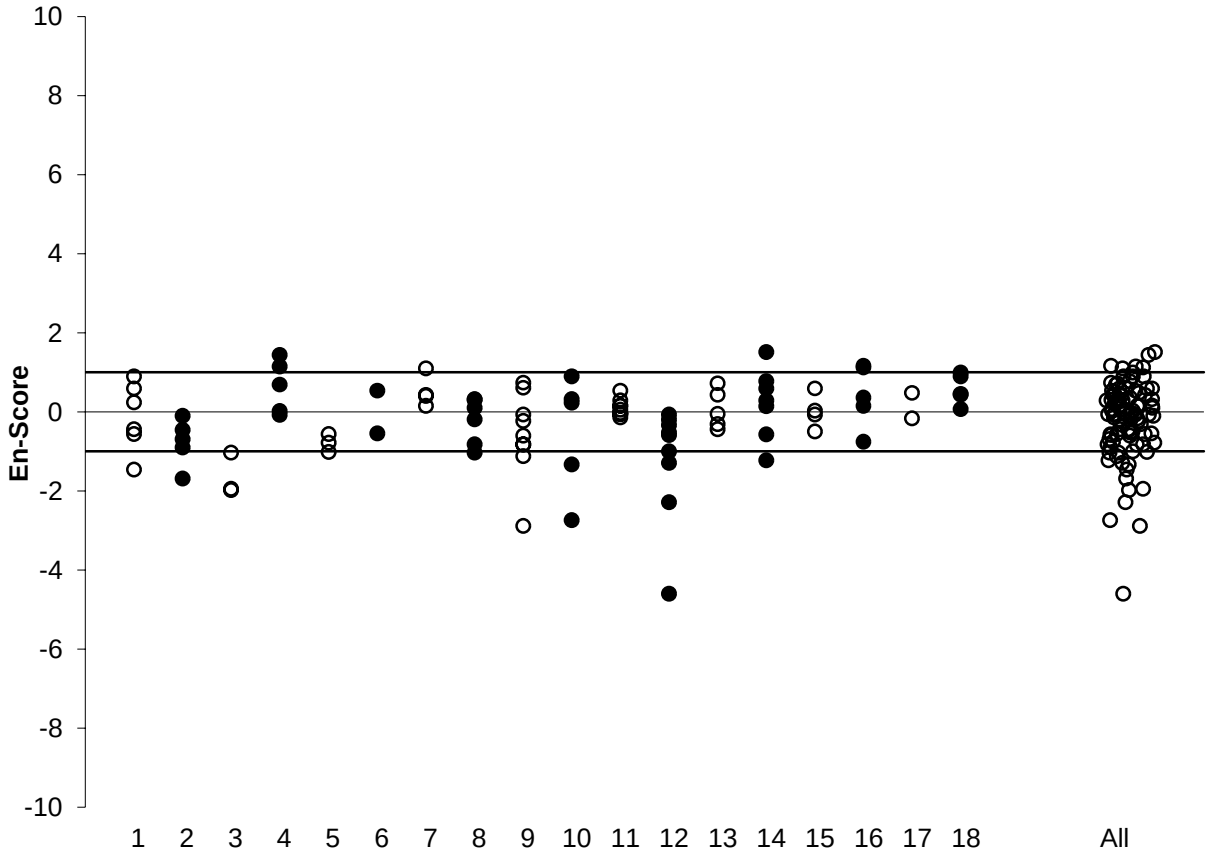


Figure 15 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 18 presents false negative results – analytes present in the samples for which a participant tested for but did not report a result (e.g. laboratories reporting a '<' or NR result when the assigned and spiked value was higher than the participants' reporting limit, or laboratories that did not report any value).

No false negatives have been assigned for Sample S1 omethoate and Sample S2 heptachlor as these had significant degradation and no assigned values were set for these analytes.

Table 18 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (µg/L)	Spiked Value (µg/L)	Reported Result (µg/L)
4	S1	Endosulfan sulfate	1.83	2.22	NR
5	S1	Parathion-methyl	1.89	2.11	<0.5
10	S1	Endosulfan sulfate	1.83	2.22	<0.01
17	S1	Imidacloprid	108	119	NR
		Parathion-methyl	1.89	2.11	NR
	S2	Atrazine	11.4	12.7	NR
		Imidacloprid	5.51	5.97	NR
		Metsulfuron-methyl	16.4	18.2	NR

6.6 Reporting of Additional Analytes

Sample S1 was spiked with p,p'-DDT and this was the analyte scored for this study. Ten participants also reported a Total DDT value for this sample. These results are presented in Table 19 for information only and are not scored.

Table 19 Total DDT in Sample S1 Reported by Participants

Lab. Code	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
1	1.96	0.10	NR
3	1.6094	NR	NR
5	1.43	0.57	90
8	1.79	0.18	NR
9	1.7	0.1	NR
11	2.58	0.77	NR
14	2.3	0.5	NR
15	2.2	NR	NR
17	2.806	1.1224	NR
18	3.025	0.75	NR

Ten laboratories reported analytes that were not spiked into the test samples (total of 15 results). These are listed in Table 20.

Table 20 Analytes Reported by Participants Not Spiked in the Test Samples

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
1	S1	p,p'-DDE	0.05	0.01	110
2	S2	Simazine	0.05	0.02	74
3	S1	p,p'-DDD	0.1902	NR	89.5
7	S1	Simazine	0.01	0.01	NR
	S2	Simazine	0.06	0.03	NR
9	S1	p,p'-DDD	0.05	0.05	NR
10	S1	p,p'-DDD	0.04	0.01	NR
		p,p'-DDE	0.02	0.005	NR
15	S1	p,p'-DDD	0.061	0.03	NR
16	S1	Simazine	0.034	0.008	NR
	S2	Simazine	0.034	0.008	NR
17	S1	p,p'-DDD	0.101	0.0404	NR
		p,p'-DDE	0.047	0.0188	NR
18	S1	p,p'-DDD	0.093	0.023	116.6
		p,p'-DDE	0.012	0.0012	114.4

The p,p'-DDD and p,p'-DDE reported by participants in Sample S1 may be the result of the break-down of p,p'-DDT during analysis in, for example, hot GC injector liners.[10] This may also partially account for the lower ratio of participants' results' robust average to spiked

value of p,p'-DDT in Sample S1. Participants reporting p,p'-DDD and p,p'-DDE at significant levels should revise their method to minimise the breakdown.

6.7 Participants' Analytical Methods

A variety of analytical methods were used for each group of analytes (Appendix 2).

For Samples S1 and S2, participants reported using the sample test portions ranging from 0.15 mL to the whole bottle (500 mL) for analysis. Participants may be reporting sample volumes used during different methodology steps.

For the analytes present in Samples S1 and S2 participants used direct injection (DI), or different extractions techniques such as liquid-liquid extraction (LLE), QuEChERS and other solid phase extractions (SPE). The majority of participants did not report a further clean-up step, with only one participant reporting using filtration. For extraction solvents, participants used hexane (HEX), dichloromethane (DCM), ethyl acetate (EtOAc), ether, acetonitrile (ACN), or mixtures of these solvents. Participants reported using GC-(ECD, FPD, NPD), GC-MS(/MS), LC-MS(/MS) and HPLC-FLD for analysis. Plots of results reported and methodology employed (extraction technique, extraction solvent and measurement instrument) for scored analytes are presented in Figures 16 to 21. No trends were apparent with the wide range of methodologies employed.

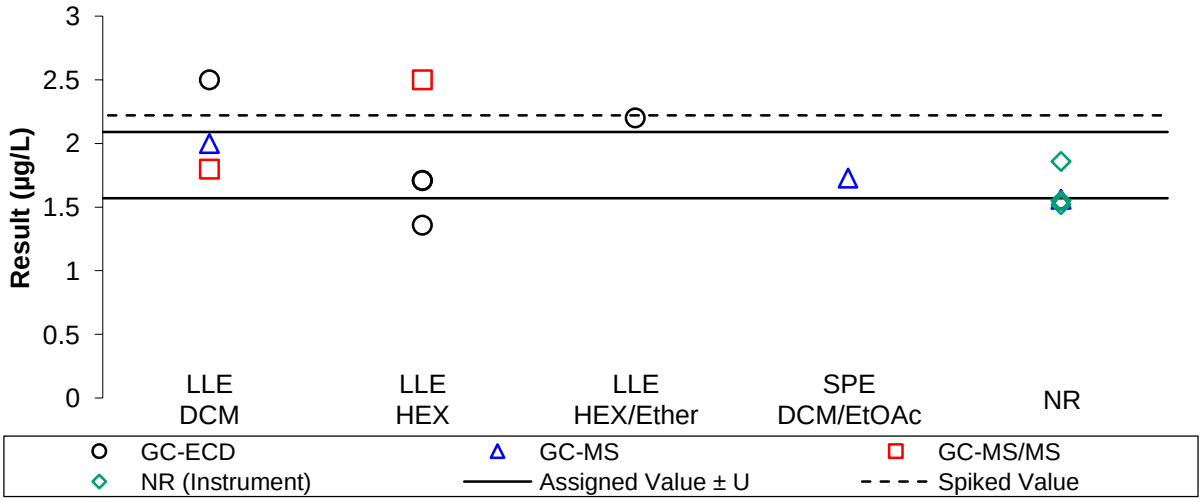


Figure 16 Sample S1 Endosulfan Sulfate Result vs Methodology

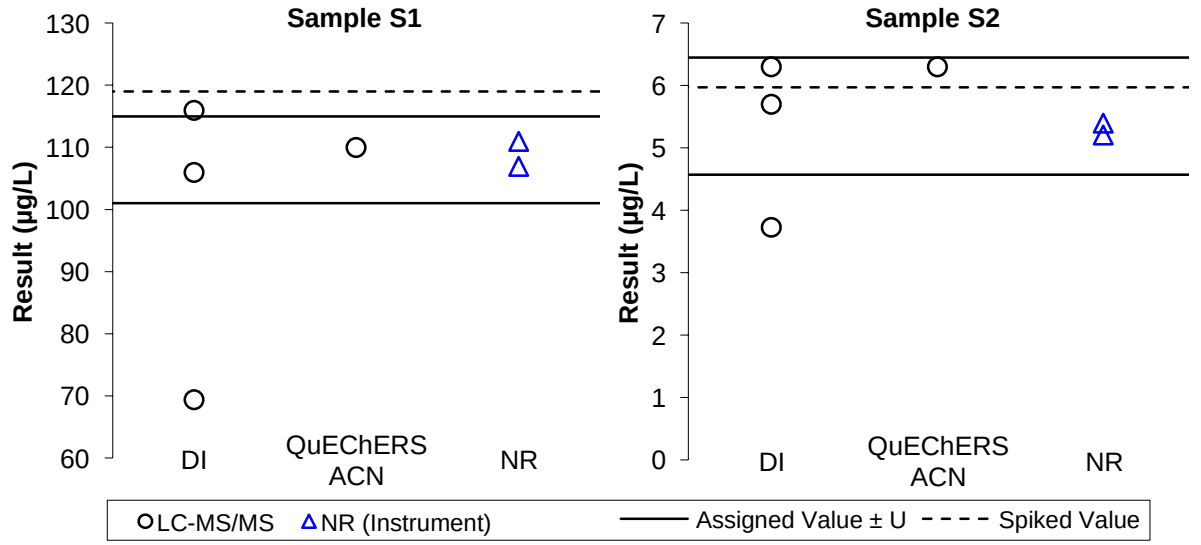


Figure 17 Sample S1 and Sample S2 Imidacloprid Result vs Methodology

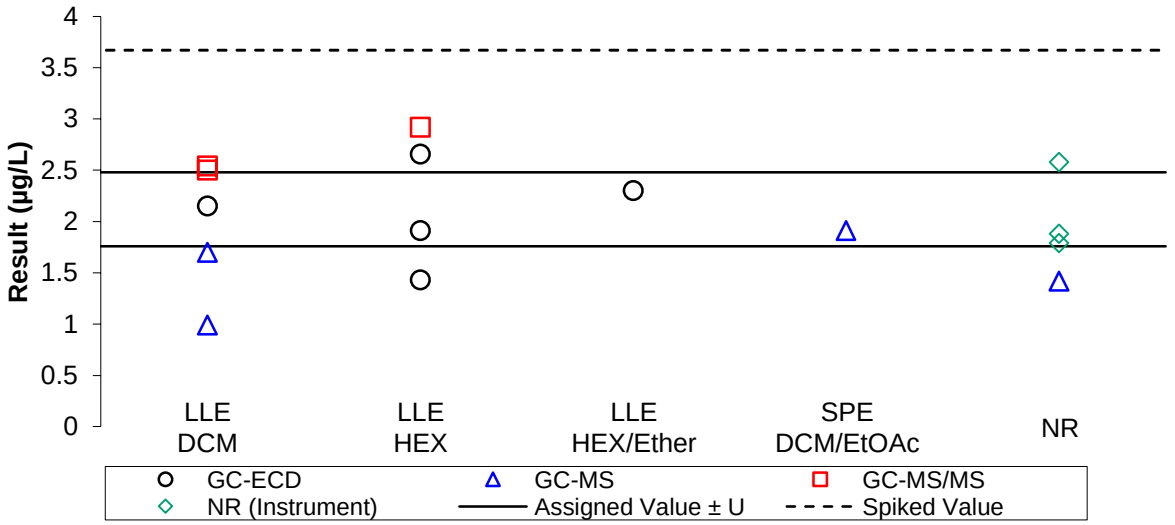


Figure 18 Sample S1 p,p'-DDT Result vs Methodology

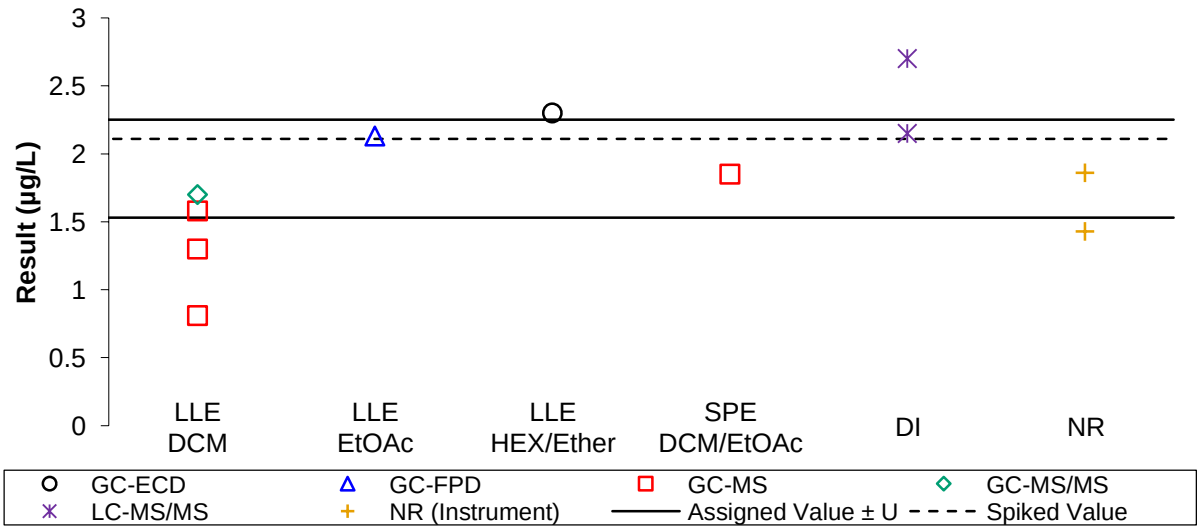


Figure 19 Sample S1 Parathion-methyl Result vs Methodology

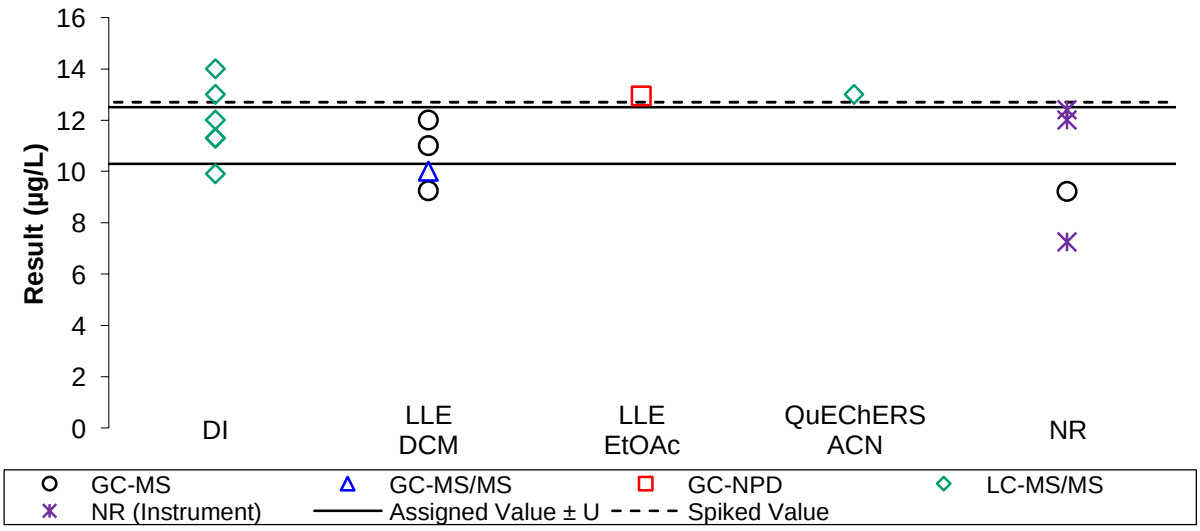


Figure 20 Sample S2 Atrazine Result vs Methodology

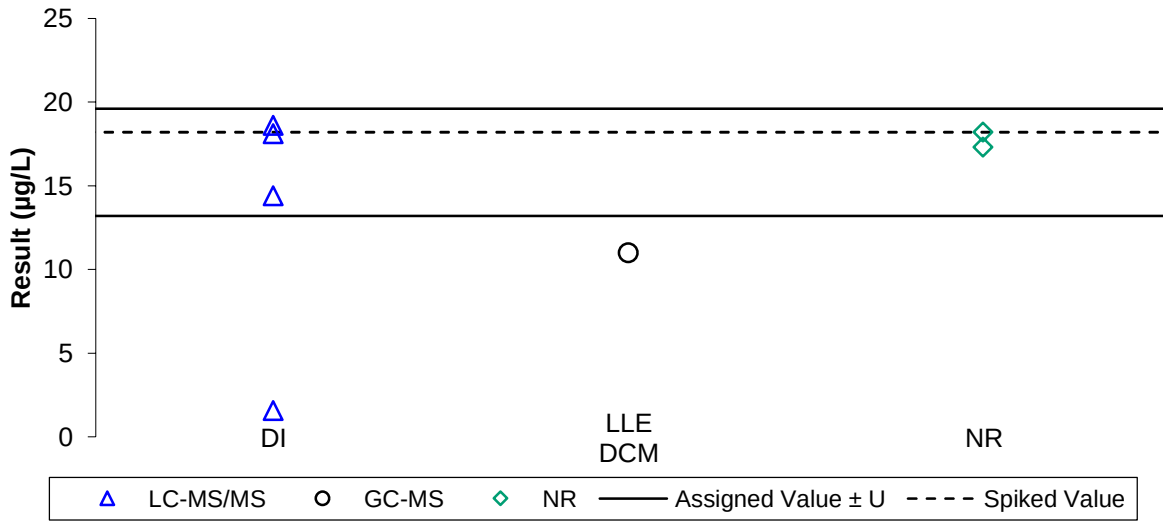


Figure 21 Sample S2 Metsulfuron-methyl Result vs Methodology

For Sample S3, participants reported using sample test portions ranging from 0.01 mL to 100 mL for analysis. Participants may be reporting sample volumes used during different methodology steps.

Participants reported using direct injection, or extraction techniques including liquid-liquid extraction and evaporation. All reported methodologies except two participants included derivatisation using fluorenylmethyloxycarbonyl group (FMOC) pre-column. One participant used HPLC-FLD, while all other participants used LC-MS/MS for quantification.

Participants were requested to analyse the samples using their normal test method and to report a single result as they would to a client, that is, reported for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **1**, **2**, **3**, **5**, **6**, **10**, **11**, **12** and **18** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 69 to 122.9%. Laboratories **8** and **11** reported that they corrected their results for recoveries.

6.8 Certified Reference Materials (CRM)

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

Fourteen laboratories reported using ‘certified standards’. The following were listed:

- Dr Ehrenstorfer
- PM Separations
- Merck / Sigma Aldrich
- Accustandard
- Chemservice
- Restek
- ISO 17034 standards

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*’[11]

6.9 Summary of Participants' Results and Performances

Summaries of participants' results and performance in this PT study are presented in Table 21 and Figure 22.

Table 21 Summary of Participants' Results for Scored Analytes (all values are in µg/L)*

Lab. Code	S1 Endosulfan sulfate	S1 Imidacloprid	S1 p,p'-DDT	S1 Parathion-methyl	S2 Atrazine	S2 Imidacloprid	S2 Metsulfuron-methyl	S3 AMPA	S3 Glyphosate
Assigned Value	1.83	108	2.12	1.89	11.4	5.51	16.4	22.4	64
1	1.71	NT	1.91	2.13	12.94	NT	NT	23.32	45.32
2	1.55	NT	1.88	1.43	7.25	NT	NT	NT	62
3	1.5632	NT	1.4192	NT	9.2201	NT	NT	NT	NT
4	NR	NT	2.54	2.15	11.29	NT	NT	27.13	64.2
5	1.36	NT	1.43	<0.5	9.24	NT	NT	NT	NT
6	NT	NT	NT	NT	NT	NT	NT	25	56
7	NT	116	NT	NT	14	5.7	18.1	NT	NT
8	1.52	111	1.79	NT	12.4	5.21	18.2	NT	NT
9	2.0	106	1.7	0.81	11.3	6.3	14.4	18.9	53.7
10	<0.01	NT	0.99	1.3	12	NT	NT	24	82
11	1.86	107	2.58	1.86	12	5.4	17.3	23.3	62.3
12	1.73	69.4	1.91	1.85	9.9	3.73	1.56	16.4	53.7
13	1.8	NT	2.5	1.7	10	NT	NT	NT	84
14	2.2	NT	2.3	2.3	12	NT	11	20	92
15	2.5	NT	2.15	1.58	11	NT	NT	NT	NT
16	NT	NT	NT	2.7	13	NT	18.6	23.2	52.2
17	1.708	NR	2.658	NR	NR	NR	NR	NT	NT
18	2.50	110	2.92	NT	13	6.3	NT	NT	NT

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

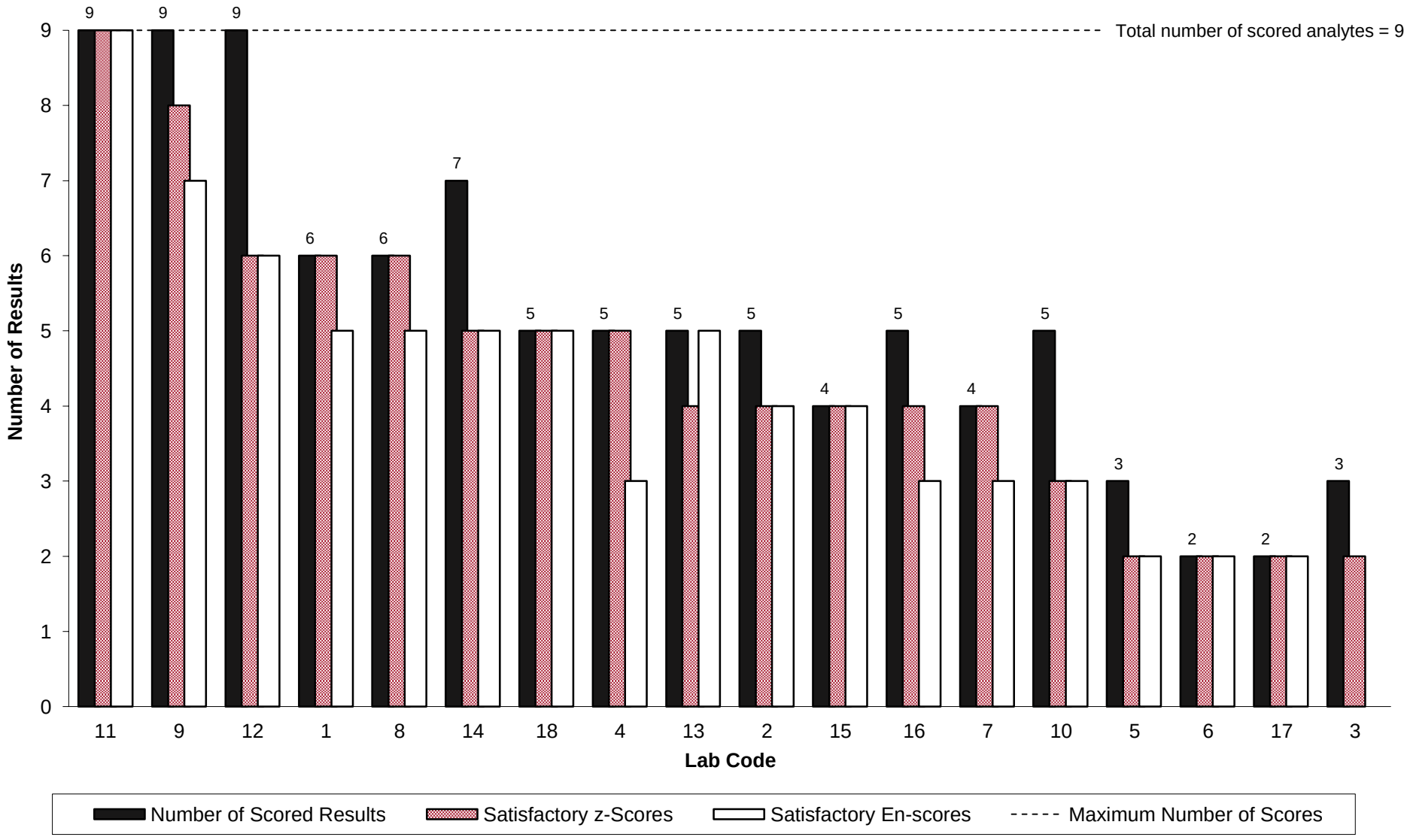


Figure 22 Summary of Participants' Performance

6.10 Comparison with Previous Studies

A summary of participation and reported results rates in Pesticides in Water PT studies over the last 10 studies (2013 – 2020) is presented in Figure 23.

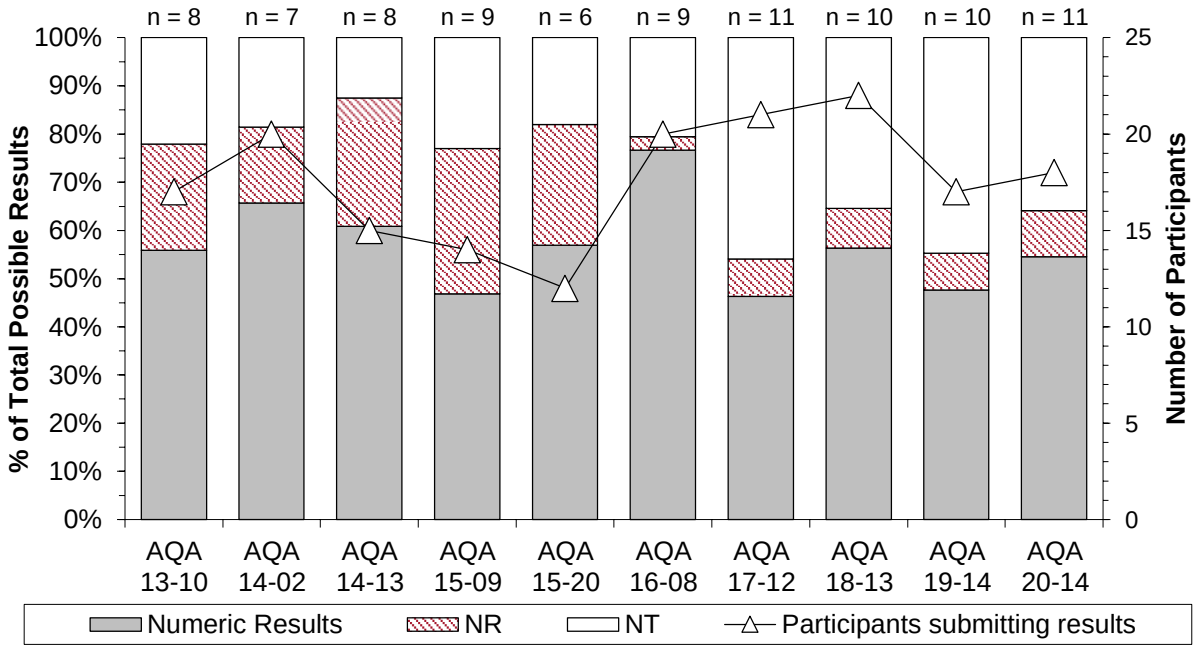


Figure 23 Summary of Participation and Reported Results in Pesticides in Water PT Studies (n = number of spiked analytes)

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) in Pesticides in Water PT studies over the last 10 studies (2013 – 2020) is presented in Figure 24. To enable direct comparison, the target SD used to calculate z-scores has been kept constant at 15% PCV. Over this period, the average proportion of satisfactory scores was 78% for z-scores and 74% for E_n-scores. While each PT study has a different sample set and a different group of participants, taken as a group, the performance over this period has improved.

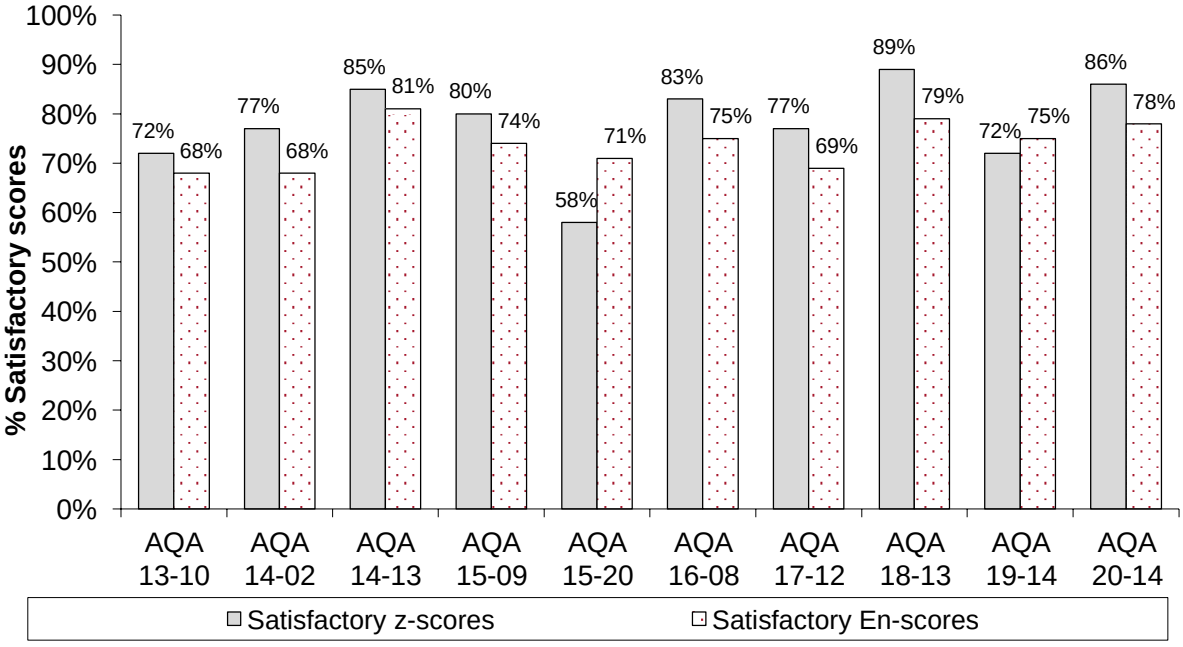


Figure 24 Satisfactory z- and E_n-Scores in Pesticides in Water PT studies

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APPENDIX 1 – SAMPLE PREPARATION

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 Sample S1 was adjusted to pH 6.9 using hydrochloric acid, while the pH of Sample S2 was not adjusted. The spiking solutions for Samples S1 and S2 were prepared by dissolving the standards in acetone, except for imidacloprid which was dissolved in isopropyl alcohol. After spiking, the water was stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL amber glass bottles.

The pH of the water used for Sample S3 was not adjusted. The glyphosate and (aminomethyl) phosphonic acid standards were dissolved in water. After spiking, the water was stirred using a top-drive impeller stirrer for at least two hours. Sample S3 was then dispensed into 500 mL PET bottles.

Between preparation and dispatch the samples were stored at 4ºC.

APPENDIX 2 – TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 22 to 32.

Table 22 Sample Volume Used for Analysis

Lab. Code	Sample S1 and S2 Volume (mL)	Sample S3 Volume (mL)
1	150	100
2	510	0.01
3	500	NT
4	10	1
5		NT
6	NT	
7	0.2	NT
8		NT
9		
10	490	0.04
11		
12	500	25
13	100	0.4
14	150	1
15	250	NT
16		1
17	0.15	NT
18		NT

Table 23 Methodology – Endosulfan Sulfate

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
1	Liquid-Liquid	None	hexane	GC-ECD	
2					
3				GC-MS	
4	Liquid-Liquid		DCM	GC-MS/MS	
5	Liquid-Liquid		Hexane	GC ECD	
6	NT				
7	NT				
8					
9	Liquid-Liquid	Filtration	DCM	GC-MS	Labelled Internal stds
10	Liquid-Liquid		DCM	GC-MS	
11					
12	SPE		DCM/EtOAc 1:1	GC-MS	

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
13	Liquid-Liquid	N/A	DCM	GC-MS/MS	
14	Liquid-Liquid		15% ether in hexane	GC-ECD	
15	Liquid-Liquid		DCM	GC-ECD	
16	NT				
17	Liquid-Liquid	NO	Hexane	GC-ECD	
18	Liquid-Liquid	N	Hexane	GC-MS/MS	

Table 24 Methodology – Imidacloprid

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument
1	NT			
2	NT			
3	NT			
4	NT			
5	NT			
6	NT			
7	Direct Injection			LC-MS/MS
8				
9	Direct Injection	Filtration	n/a	LC-MS/MS
10	NT			
11				
12	Direct Injection			LC-MS/MS
13	NT			
14	NT			
15	NT			
16	NT			
17				
18	QuEChERS	N	Acetonitrile	LC-MS/MS

Table 25 Methodology – Omethoate

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
1	NT				
2					
3				GC-MS	
4	NT				
5	NT				
6	NT				
7	NT				

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
8					
9	Liquid-Liquid	Filtration	DCM	GC-MS	Labelled Internal stds
10	NT				
11					
12					
13	NT				
14	Direct Injection		NA	LC-QQQ	
15	NT				
16	Direct Injection			LC-MS/MS	Not NATA Accredited
17					
18	QuEChERS	N	Acetonitrile	LC-MS/MS	

Table 26 Methodology – p,p'-DDT

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
1	Liquid-Liquid	None	hexane	GC-ECD	
2					
3				GC-MS	
4	Liquid-Liquid		DCM	GC-MS/MS	
5	Liquid-Liquid		Hexane	GC ECD	
6	NT				
7	NT				
8					
9	Liquid-Liquid	Filtration	DCM	GC-MS	Labelled Internal stds
10	Liquid-Liquid		DCM	GC-MS	
11					
12	SPE		DCM/EtOAc 1:1	GC-MS	
13	Liquid-Liquid	N/A	DCM	GC-MS/MS	
14	Liquid-Liquid		15% ether in hexane	GC-ECD	
15	Liquid-Liquid		DCM	GC-ECD	
16	NT				
17	Liquid-Liquid	NO	Hexane	GC-ECD	
18	Liquid-Liquid	N	Hexane	GC-MS/MS	

Table 27 Methodology – Parathion-methyl

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
1	Liquid-Liquid	None	ethyl acetate	GC-FPD	
2					

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
3	NT				
4	Direct Injection			LC-MS/MS	
5	Liquid-Liquid		DCM	GC MS	
6	NT				
7	NT				
8	NT				
9	Liquid-Liquid	Filtration	DCM	GC-MS	Labelled Internal stds
10	Liquid-Liquid		DCM	GC-MS	
11					
12	SPE		DCM/EtOAc 1:1	GC-MS	
13	Liquid-Liquid	N/A	DCM	GC-MS/MS	
14	Liquid-Liquid		15% ether in hexane	GC-ECD	
15	Liquid-Liquid		DCM	GC-MS	
16	Direct Injection			LC-MS/MS	
17					
18	NT				

Table 28 Methodology – Atrazine

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument
1	Liquid-Liquid	None	ethyl acetate	GC-NPD
2				
3				GC-MS
4	Direct Injection			LC-MS/MS
5	Liquid-Liquid		DCM	GC MS
6	NT			
7	Direct Injection			LC-MS/MS
8				
9	Direct Injection	Filtration	n/a	LC-MS/MS
10	Direct Injection			LC-MS/MS
11				
12	Direct Injection			LC-MS/MS
13	Liquid-Liquid	N/A	DCM	GC-MS/MS
14	Liquid-Liquid		DCM	GC-MS
15	Liquid-Liquid		DCM	GC-MS
16	Direct Injection			LC-MS/MS
17				
18	QuEChERS	N	Acetonitrile	LC-MS/MS

Table 29 Methodology – Heptachlor

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument	Comments
1	Liquid-Liquid	None	hexane	GC-ECD	
2					
3				GC-MS	
4	Liquid-Liquid		DCM	GC-MS/MS	
5	Liquid-Liquid		Hexane	GC ECD	
6	NT				
7	NT				
8					
9	Liquid-Liquid	Filtration	DCM	GC-MS	Labelled Internal stds
10	Liquid-Liquid		DCM	GC-MS	
11					
12	SPE		DCM/EtOAc 1:1	GC-MS	
13	Liquid-Liquid	N/A	DCM	GC-MS/MS	
14	Liquid-Liquid		15% ether in hexane	GC-ECD	
15	Liquid-Liquid		DCM	GC-ECD	
16	NT				
17	Liquid-Liquid	NO	Hexane	GC-ECD	
18	Liquid-Liquid	N	Hexane	GC-MS/MS	

Table 30 Methodology – Metsulfuron-methyl

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument
1	NT			
2	NT			
3	NT			
4	NT			
5	NT			
6	NT			
7	Direct Injection			LC-MS/MS
8				
9	Direct Injection	Filtration	n/a	LC-MS/MS
10	NT			
11				
12	Direct Injection			LC-MS/MS
13	NT			
14	Liquid-Liquid		DCM	GC-MS
15	NT			

Lab. Code	Extraction	Clean-up	Extraction Solvent	Instrument
16	Direct Injection			LC-MS/MS
17				
18	NT			

Table 31 Methodology – AMPA

Lab. Code	Extraction	Derivatisation Procedure	Derivatisation Agent	Instrument
1	Evaporation	Pre-column	FMOC-Cl	HPLC-FLD
2	NT			
3	NT			
4		Pre-column	FMOC	LC-MS/MS
5	NT			
6	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
7	NT			
8	NT			
9	Direct Injection	n/a	n/a	LC-MS/MS
10	Direct Injection			LC-MS/MS
11				
12	Direct Injection	Pre-column	FMOC-CL	LC-MS/MS
13	NT			
14	Direct Injection	Pre-column	FMOC-Cl	LC-MS/MS
15	NT			
16	Direct Injection	Pre-column	FMOC	LC-MS/MS
17	NT			
18	NT			

Table 32 Methodology – Glyphosate

Lab. Code	Extraction	Derivatisation Procedure	Derivatisation Agent	Instrument
1	Evaporation	Pre-column	FMOC-Cl	HPLC-FLD
2	Direct Injection			LC-MS/MS
3	NT			
4		Pre-column	FMOC	LC-MS/MS
5	NT			
6	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
7	NT			
8	NT			
9	Direct Injection	n/a	n/a	LC-MS/MS
10	Direct Injection			LC-MS/MS

Lab. Code	Extraction	Derivatisation Procedure	Derivatisation Agent	Instrument
11				
12	Direct Injection	Pre-column	FMOC-CL	LC-MS/MS
13	Liquid-Liquid	Pre-column	9-Fluorenylmethyl chloroformate(FMOCCl)	LC-MS
14	Direct Injection	Pre-column	FMOC-Cl	LC-MS/MS
15	NT			
16	Direct Injection	Pre-column	FMOC	LC-MS/MS
17	NT			
18	NT			

APPENDIX 3 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, Z-SCORE AND E_N-SCORE CALCULATIONS

A3.1 Robust Average and Associated Uncertainty

The robust average was calculated using the procedure described in ISO 13258:2015 – Annex C.[6] The uncertainty for the robust average was estimated as:

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

where:

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

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

A worked example is set out below in Table 33.

Table 33 Uncertainty of Robust Average for Atrazine in Sample S2

No. results (p)	16
Robust Average	11.37 µg/L
$S_{rob\ av}$	1.79 µg/L
$u_{rob\ av}$	0.56 µg/L
k	2
$U_{rob\ av}$	1.12 µg/L

Therefore, the robust average for atrazine in Sample S2 is 11.4 ± 1.1 µg/L.

A3.2 z-Score and E_n-Score Calculation

For each participant's result, a z-score and E_n-score are calculated according to Equations 2 and 3 respectively.

A worked example for is set out below in Table 34.

Table 34 z-Score and E_n-Score for Sample S1 Endosulfan Sulfate Result Reported by Laboratory 1

Participant Result (µg/L)	Assigned Value (µg/L)	Target Standard Deviation	z-Score	E_n-Score
1.71 ± 0.09	1.83 ± 0.26	15% as PCV, or: 0.15 × 1.83 = 0.2745 µg/L	z-Score = $\frac{1.71-1.83}{0.2745}$ = -0.44	E_n-Score = $\frac{1.71-1.83}{\sqrt{0.09^2+0.26^2}}$ = -0.44

APPENDIX 4 – 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
DI	Direct Injection
ECD	Electron Capture Detector
EtOAc	Ethyl Acetate
FLD	Fluorescence Detector
FMOC	Fluorenylmethyloxycarbonyl
FPD	Flame Photometric Detector
GAG	General Accreditation Guidance (NATA)
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
HEX	Hexane
HPLC	High Performance Liquid Chromatography
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
Max.	Maximum
Md	Median
Min.	Minimum
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
NATA	National Association of Testing Authorities (Australia)
NMI	National Measurement Institute (Australia)
NPD	Nitrogen-Phosphorus Detector
NR	Not Reported
NT	Not Tested
p,p’-DDD	Dichlorodiphenyldichloroethane
p,p’-DDE	Dichlorodiphenyldichloroethylene

p,p'-DDT	Dichlorodiphenyltrichloroethane
PCV	Performance Coefficient of Variation
PT	Proficiency Test
QQQ	Triple Quadrupole Mass Spectrometry
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe extraction method
R.A.	Robust Average
RM	Reference Material
S.V.	Spiked Value (or formulated concentration of a PT sample)
SD	Standard Deviation
SI	International System of Units
SPE	Solid Phase Extraction
SS	Spiked Samples

END OF REPORT