Australian Government
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National Measurement Institute

Proficiency Test Final Report
AQA 21-16
Pesticides in Water

February 2022

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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 21-16 Pesticides in Water commenced in October 2021. Twenty laboratories registered to participate and nineteen participants 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 Sydney.

Of 164 results, 101 numeric results (62%) were submitted. Twenty-two results were a 'less than' value (<*x*) or Not Reported (NR), and forty-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 **13** and **17** reported numeric results for all 7 analytes scored in this study.

Eight participants did not report numeric results for analytes which they tested for and were present in the test samples (total of 14 results). Three participants reported numeric results for analytes not spiked into the samples (total of 11 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 78 z-scores, 64 (82%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Of 78 E_n-scores, 62 (79%) 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.

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

Participants used a wide variety of methods, with the most common being liquid-liquid extraction with dichloromethane, followed by analysis using GC-MS(/MS).

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

Of 101 numeric results, 99 (98%) were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 2.1% to 53%. Participants used a wide variety of procedures to estimate their uncertainty.

- *Produce materials that can be used in method validation and as control samples.*

The test samples of this proficiency study are homogeneous and are well characterised. Surplus samples are available for purchase from NMI and can be used for quality control and method validation purposes.

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 the '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, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, water, biota and food;
- controlled drug assay, drugs in wipes 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;
- develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates; and
- produce materials that can be used in method validation and as control samples.

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 17043:2010,[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 as a provider of proficiency testing schemes.[1] This study falls within the scope of NMI's accreditation.

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitation issued 5 October 2021

Samples dispatched 9 November 2021

Results due 15 December 2021

Interim report issued 5 January 2022

2.2 Participation and Laboratory Code

Twenty laboratories registered to participate in this study, and all participants were assigned a confidential laboratory code number for this study. Nineteen participants submitted results.

2.3 Selection of Pesticides

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

- a variety of pesticides (amenable to gas and/or 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 potential analytes spiked into 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	Metolachlor
Atrazine	p,p'-DDT	Fenvalerate	Metsulfuron-methyl
Azinphos-methyl	Total DDT	Heptachlor	Molinate
Bifenthrin	Dieldrin	Heptachlor epoxide	Omethoate
Chlordane	Diuron	Hexachlorobenzene	Parathion
Chlorfenvinphos	alpha-Endosulfan	Imidacloprid	Parathion-methyl
Chlorpyrifos	beta-Endosulfan	Lindane	Permethrin
Cypermethrin	Endosulfan sulfate	Malathion	Prothiofos
Diazinon	Ethion	MCPA	Simazine
p,p'-DDD	Fenitrothion	Methomyl	Trifluralin

2.4 Test Material Preparation

Water samples were prepared by spiking water from a local river with various pesticides to obtain the concentrations listed in Table 2.

Additional information on the preparation of the samples is given in Appendix 1.

Table 2 Spiked Concentrations of Test Samples

Sample	Analyte	Spiked Value (µg/L)	Uncertainty* (µg/L)
S1	Diuron	15.0	0.7
	Endosulfan sulfate	3.29	0.16
	Imidacloprid	7.99	0.40

Sample	Analyte	Spiked Value (µg/L)	Uncertainty* (µg/L)
S2	Atrazine	8.04	0.40
	Lindane	11.1	0.6
	MCPA	0.510	0.026
	Metolachlor	0.645	0.032
S3	AMPA	12.0	0.6
	Glyphosate	33.1	1.7

* Expanded uncertainty at approximately 95% confidence using a coverage factor of 2. This 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 is related to the concentration of the pesticides at the time of spiking.

2.5 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted before the samples were sent. The samples were prepared, packaged and stored using a process that has been demonstrated to produce homogeneous and stable samples in previous NMI Pesticides in Water PT studies.

Participants' results gave no reason to question the homogeneity or transportation stability of the samples (Appendix 2).

To further assess possible instability, the results returned by participants were compared to the spiked concentrations. Assigned values for scored analytes were within 82% to 110% of the spiked values, which provides good support for the stability of these analytes in the samples.

2.6 Test Material Storage and Dispatch

After preparation, the samples were stored in a refrigerator at 4 °C. Samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 9 November 2021.

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 emailed to participants.

2.7 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 in units of µg/L 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.
- For each analyte in each sample, report the associated expanded uncertainty in units of µg/L (e.g. 0.50 ± 0.02 µg/L), if determined.
- 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.
- Give details of your methodology and basis of uncertainty estimate as requested by the results sheet emailed to you.
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by 6 December 2021 by email to proficiency@measurement.gov.au.

The results due date was extended to 15 December 2021 due to sample delivery delays to some participants.

2.8 Interim Report

An interim report was emailed to all participants on 5 January 2022.

The interim report was delayed because of an extension granted to a participant due to exceptional circumstances, as well as the NMI end-of-year shut down period.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Participants' Test Methods

Participants were requested to provide information about their test methods. Responses are presented in Appendix 3.

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 Instrument calibration	Recoveries of SS	ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias	Instrument calibration	CRM	
3	Top Down - precision and estimates of the method and laboratory bias	Standard deviation from PT studies only		NMI Uncertainty Course
		Control samples - SS Duplicate analysis Instrument calibration	Laboratory bias from PT studies Recoveries of SS Standard purity	
4	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis	CRM Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
5	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
6	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	Recoveries of SS	
7	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
8	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		ISO/GUM
10	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis	Recoveries of SS	ISO/GUM
11	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS	Recoveries of SS	NMI Uncertainty Course
12		Control samples - CRM Duplicate analysis		

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
13	Top Down - precision and estimates of the method and laboratory bias	Control samples Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
14	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	ISO/GUM
15	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	Instrument calibration Laboratory bias from PT studies Recoveries of SS Standard purity	
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 Recoveries of SS Standard purity	Eurachem/CITAC Guide
18	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
19	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
20	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM	CRM	

* 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 received for this study are presented in Table 4.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments
8	All	MU took from control chart 1st Aug 201 to 26 Nov 2021
18	S3	No % recoveries for AMPA and Glyphosate
19	S3	AMPA and Glyphosate results were corrected for surrogate recovery.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 13 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 10. An example chart with interpretation guide is shown in Figure 1.

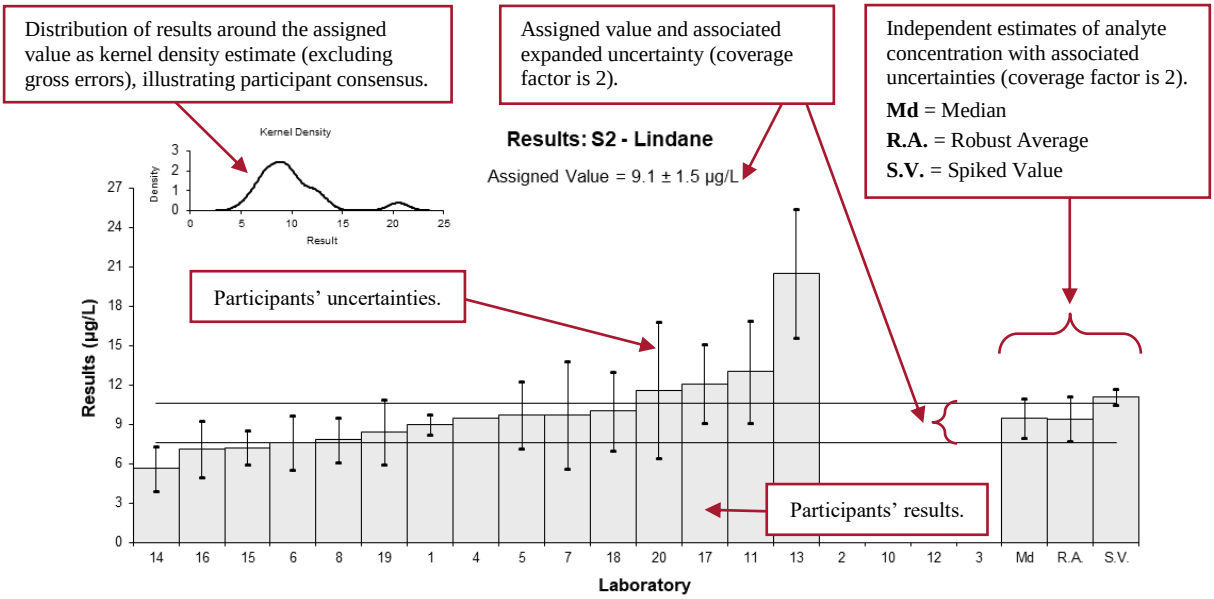


Figure 1 Guide to Presentation of Results

4.2 Outliers and Gross Errors

Outliers were results less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value.[3,4] Gross errors were obvious blunders, e.g. results reported with incorrect units or basis, and such results were removed for the calculation of all summary statistics.[3,4]

4.3 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, this 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 4).

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

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

4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between-laboratory variation that in the judgement of the study coordinator would be expected from participants given the analyte concentrations. The PCV is not the CV of participants' results; it is set by the study coordinator and is based on the analyte concentrations 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.

4.6 Target Standard Deviation

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

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

4.7 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:

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

4.8 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:

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

4.9 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025 must establish and demonstrate the traceability and MU 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

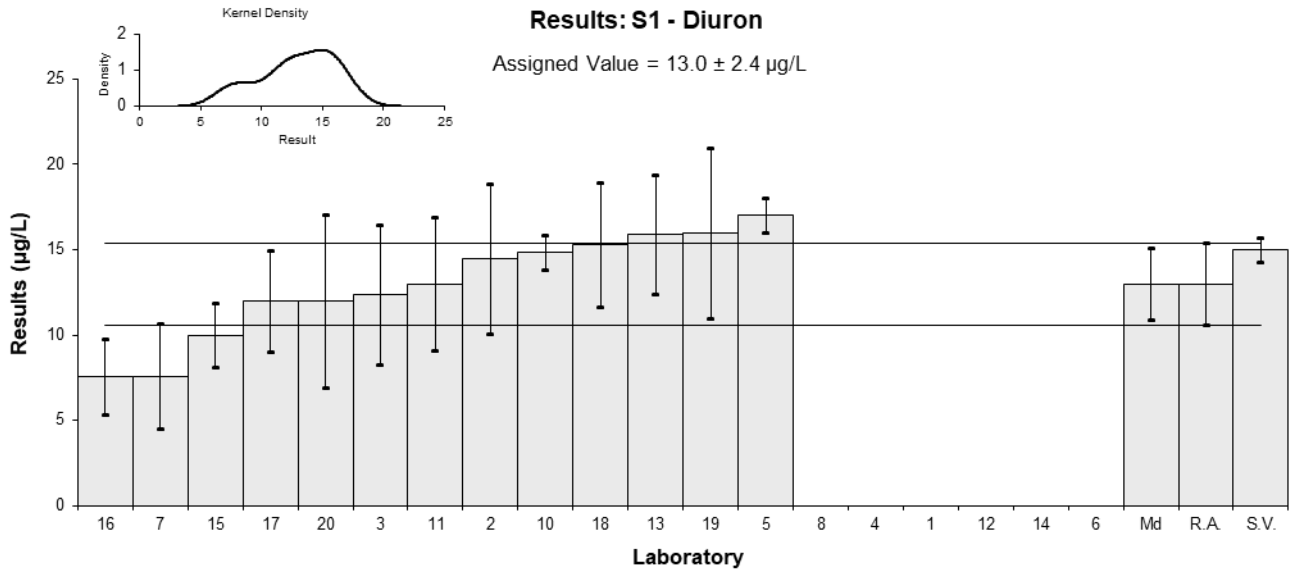
Sample No.	S1
Matrix	Water
Analyte	Diuron
Units	µg/L

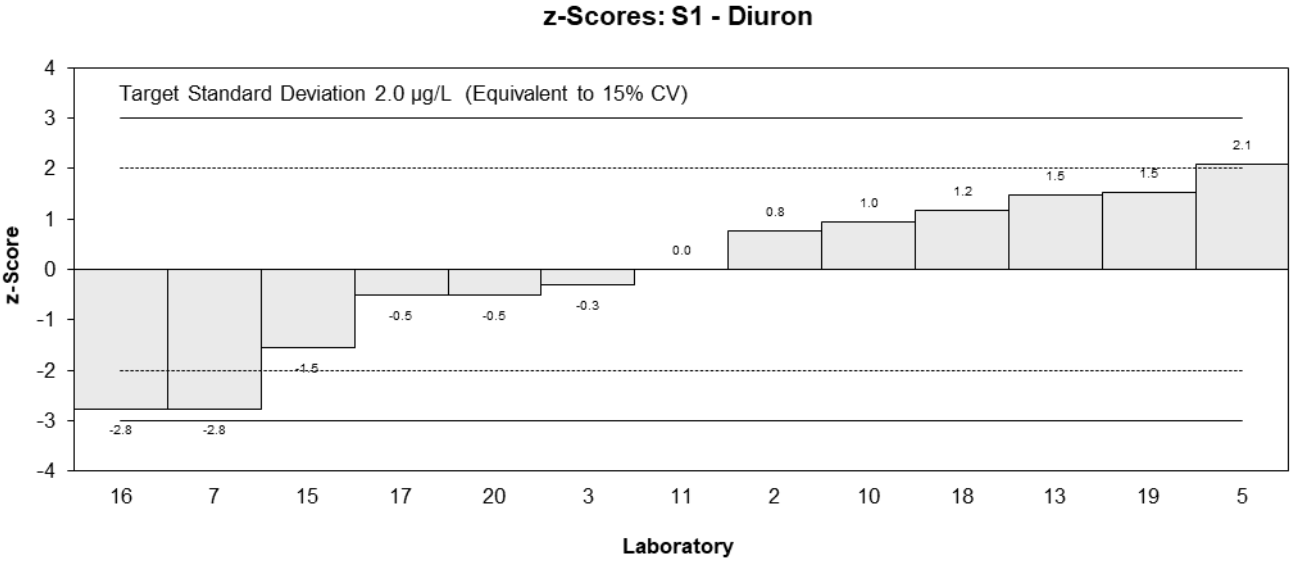
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	14.5	4.4	NR	0.77	0.30
3	12.4	4.1	NR	-0.31	-0.13
4	<0.1	NR	NR		
5	17.06	1.02	NR	2.08	1.56
6	NT	NT	NT		
7	7.6	3.1	NR	-2.77	-1.38
8	< 0.2	0.06	NR		
10	14.86	1	NR	0.95	0.72
11	13	3.9	NR	0.00	0.00
12	NT	NT	NT		
13	15.9	3.5	NR	1.49	0.68
14	NT	NT	NT		
15	10	1.9	NR	-1.54	-0.98
16	7.58	2.22	NR	-2.78	-1.66
17	12	3.0	94	-0.51	-0.26
18	15.3	3.67	99	1.18	0.52
19	16	5	NR	1.54	0.54
20	12	5.1	NR	-0.51	-0.18

Statistics

Assigned Value	13.0	2.4
Spike	15.0	0.7
Robust Average	13.0	2.4
Median	13.0	2.1
Mean	12.9	
N	13	
Max.	17.06	
Min.	7.58	
Robust SD	3.4	
Robust CV	26%	


Kernel Density
Density
Result
Results: S1 - Diuron
Assigned Value = 13.0 ± 2.4 µg/L
Results (µg/L)
Laboratory
16 7 15 17 20 3 11 2 10 18 13 19 5 8 4 1 12 14 6 Md R.A. S.V.


z-Scores: S1 - Diuron
Target Standard Deviation 2.0 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
16 7 15 17 20 3 11 2 10 18 13 19 5
-2.8 -2.8 -1.5 -0.5 -0.5 -0.3 0.0 0.8 1.0 1.2 1.5 1.5 2.1

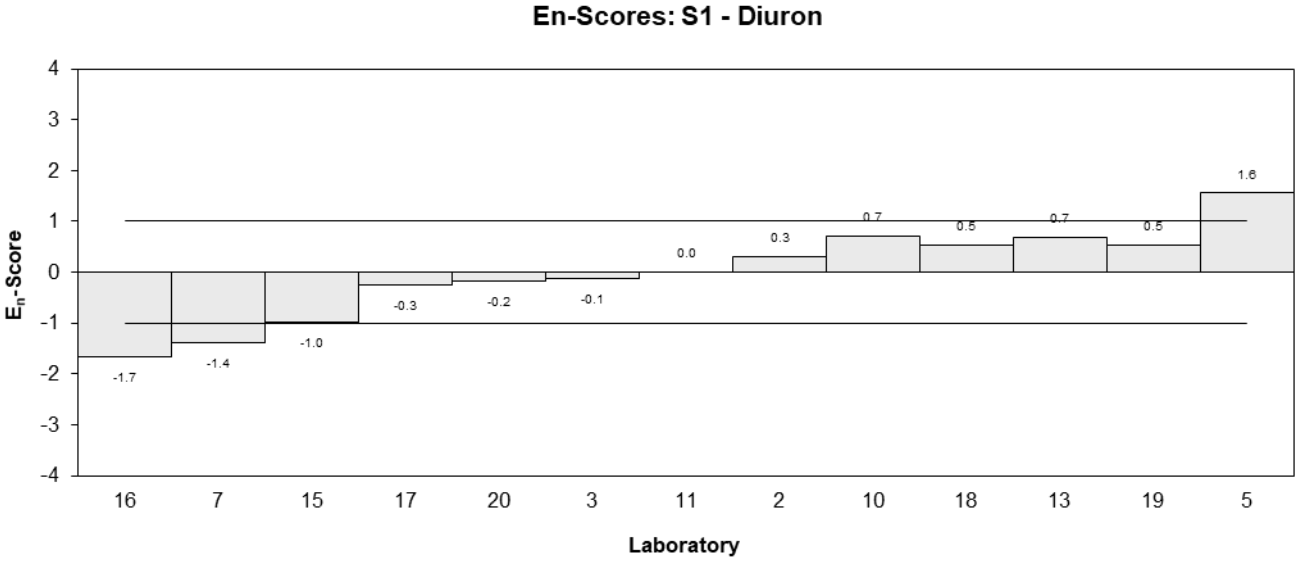

En-Scores: S1 - Diuron
En-Score
Laboratory
16 7 15 17 20 3 11 2 10 18 13 19 5
-1.7 -1.4 -1.0 -0.3 -0.2 -0.1 0.0 0.3 0.7 0.5 0.7 0.5 1.6

Figure 2

Table 6

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Recovery
1	4.25	0.40	87
2	3.4	1	NR
3	2.66	0.79	NR
4	3.6	NR	NR
5	4.00	1.51	NR
6	2.02	0.58	NR
7	2.6	1.2	NR
8	2.077	0.573	NR
10	4.70	0.5	NR
11	4.6	1.4	NR
12	NT	NT	NT
13	5.8	1.5	NR
14	1.21	0.363	NR
15	2.1	0.34	NR
16	1.9	0.47	NR
17	1.86	0.47	81
18	2.9	0.87	89
19	2.5	0.8	NR
20	3.53	1.2	NR

Statistics

Assigned Value	Not Set	
Spike	3.29	0.16
Robust Average	3.05	0.75
Median	2.78	0.58
Mean	3.09	
N	18	
Max.	5.8	
Min.	1.21	
Robust SD	1.3	
Robust CV	42%	

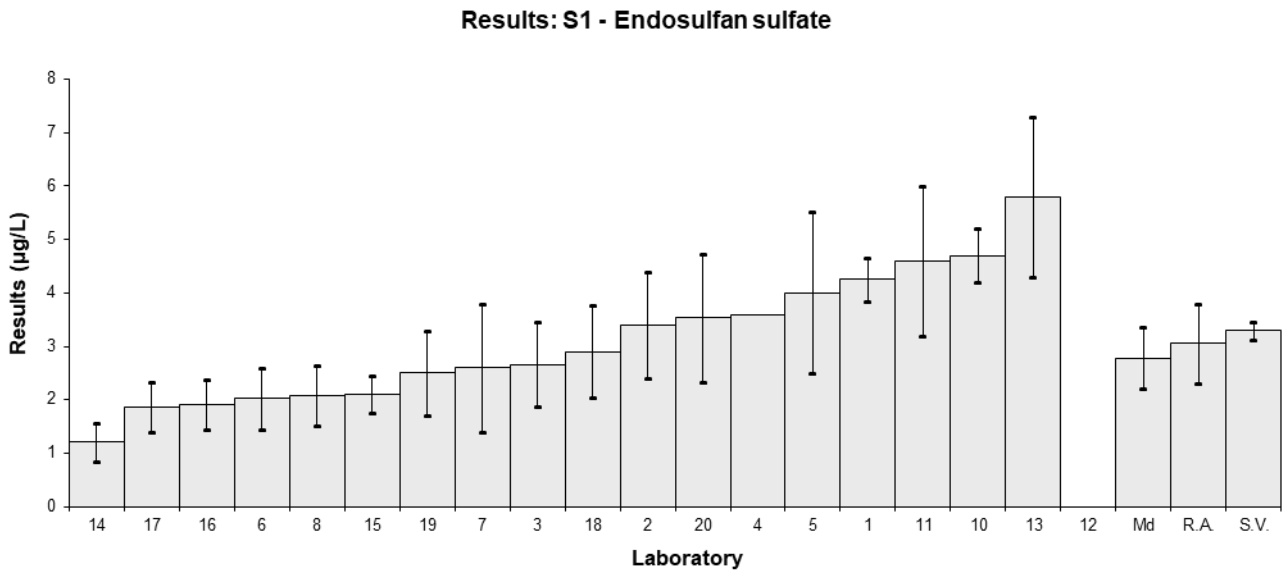

Results: S1 - Endosulfan sulfate
Results (µg/L)
0
1
2
3
4
5
6
7
8
14
17
16
6
8
15
19
7
3
18
2
20
4
5
1
11
10
13
12
Md
R.A.
S.V.
Laboratory

Figure 3

Table 7

Sample Details

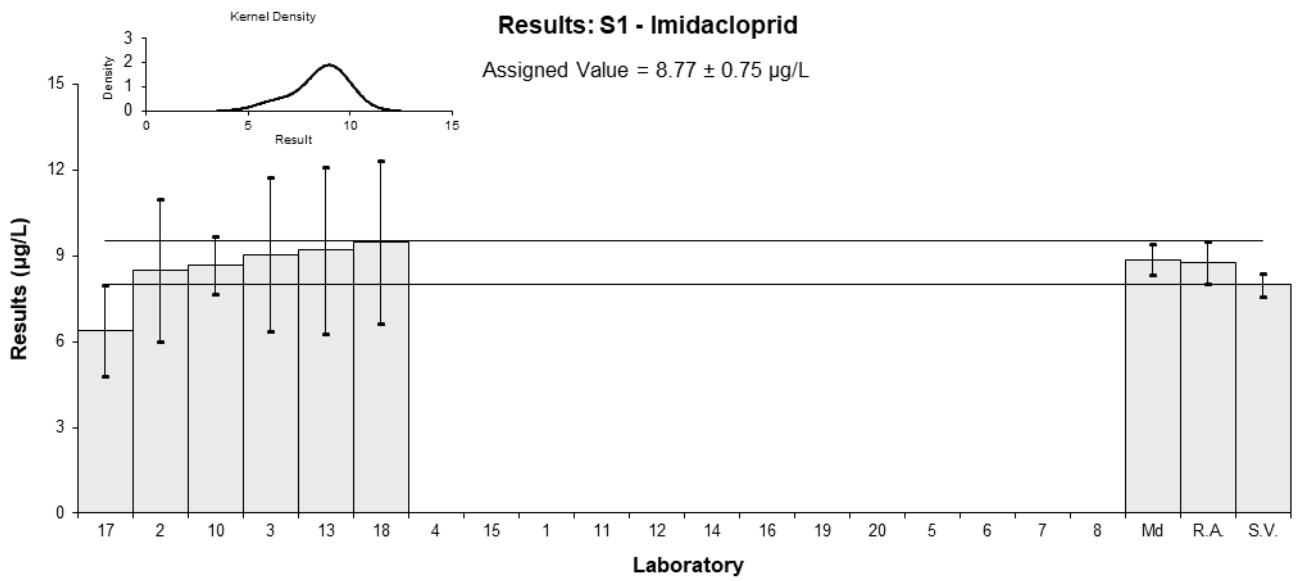
Sample No.	S1
Matrix	Water
Analyte	Imidacloprid
Units	µg/L

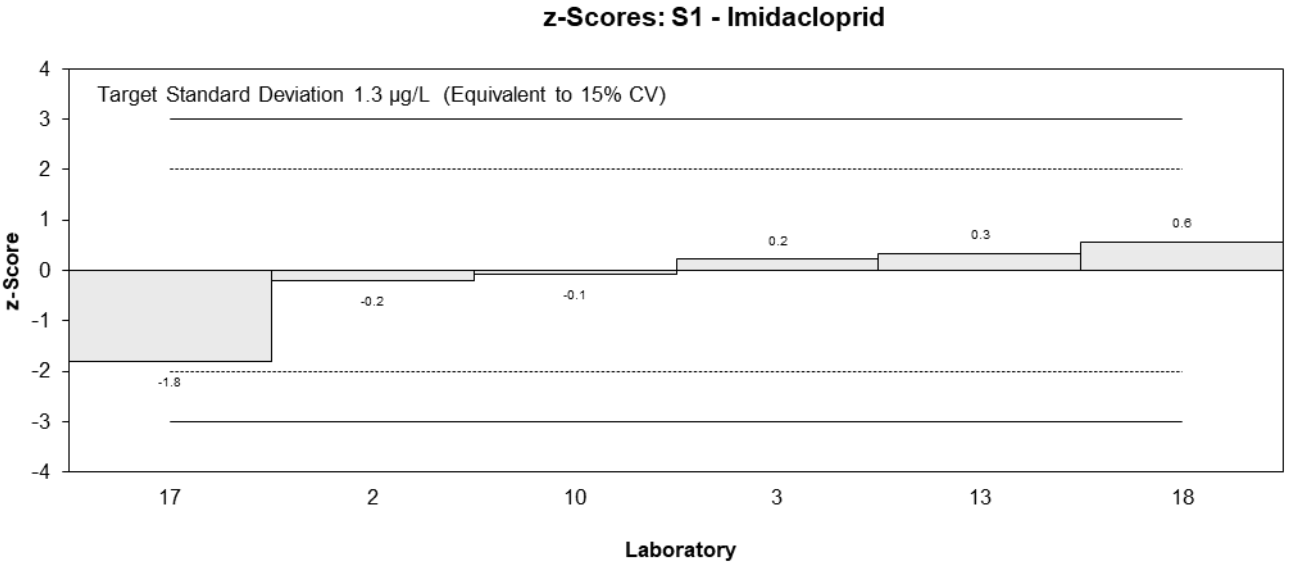
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	8.5	2.5	NR	-0.21	-0.10
3	9.06	2.7	NR	0.22	0.10
4	<0.1	NR	NR		
5	NT	NT	NT		
6	NT	NT	NT		
7	NT	NT	NT		
8	NT	NT	NT		
10	8.68	1	NR	-0.07	-0.07
11	NT	NT	NT		
12	NT	NT	NT		
13	9.2	2.9	NR	0.33	0.14
14	NT	NT	NT		
15	<100	NR	NR		
16	NT	NT	NT		
17	6.4	1.6	93	-1.80	-1.34
18	9.5	2.85	99	0.55	0.25
19	NT	NT	NT		
20	NT	NT	NT		

Statistics

Assigned Value	8.77	0.75
Spike	7.99	0.40
Robust Average	8.77	0.75
Median	8.87	0.54
Mean	8.56	
N	6	
Max.	9.5	
Min.	6.4	
Robust SD	0.74	
Robust CV	8.4%	


Kernel Density
Density
Result
Results: S1 - Imidacloprid
Assigned Value = 8.77 ± 0.75 µg/L
Results (µg/L)
Laboratory
17 2 10 3 13 18 4 15 1 11 12 14 16 19 20 5 6 7 8 Md R.A. S.V.


z-Scores: S1 - Imidacloprid
Target Standard Deviation 1.3 µg/L (Equivalent to 15% CV)
z-Score
-1.8
-0.2
-0.1
0.2
0.3
0.6
Laboratory
17 2 10 3 13 18

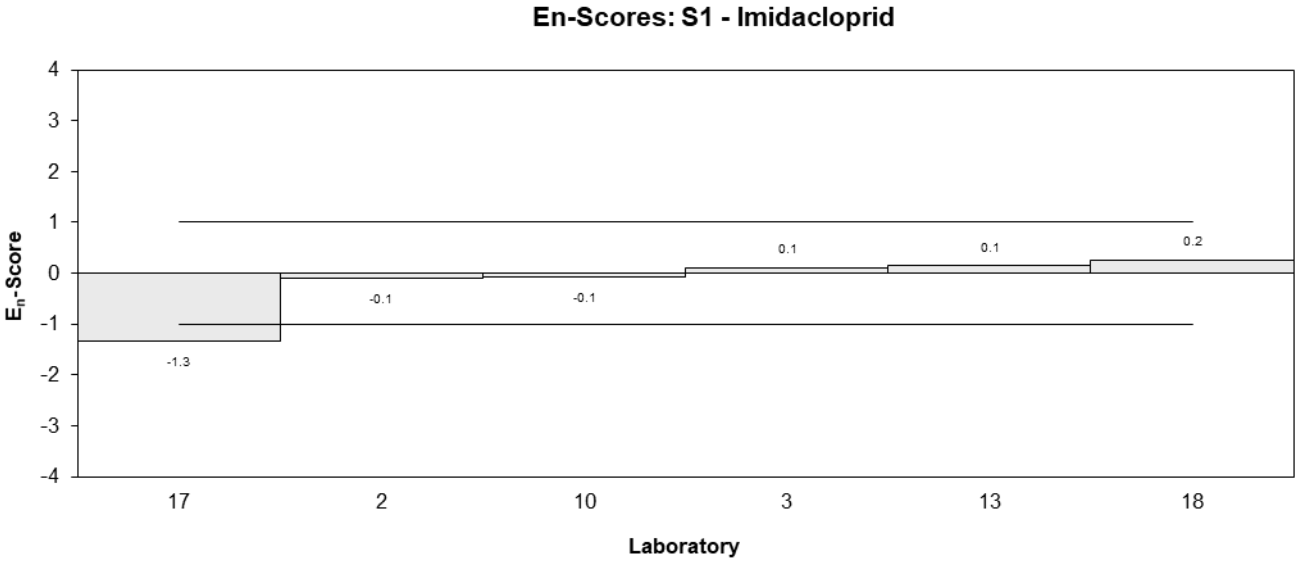

En-Scores: S1 - Imidacloprid
En-Score
-1.3
-0.1
-0.1
0.1
0.1
0.2
Laboratory
17 2 10 3 13 18

Figure 4

Table 8

Sample Details

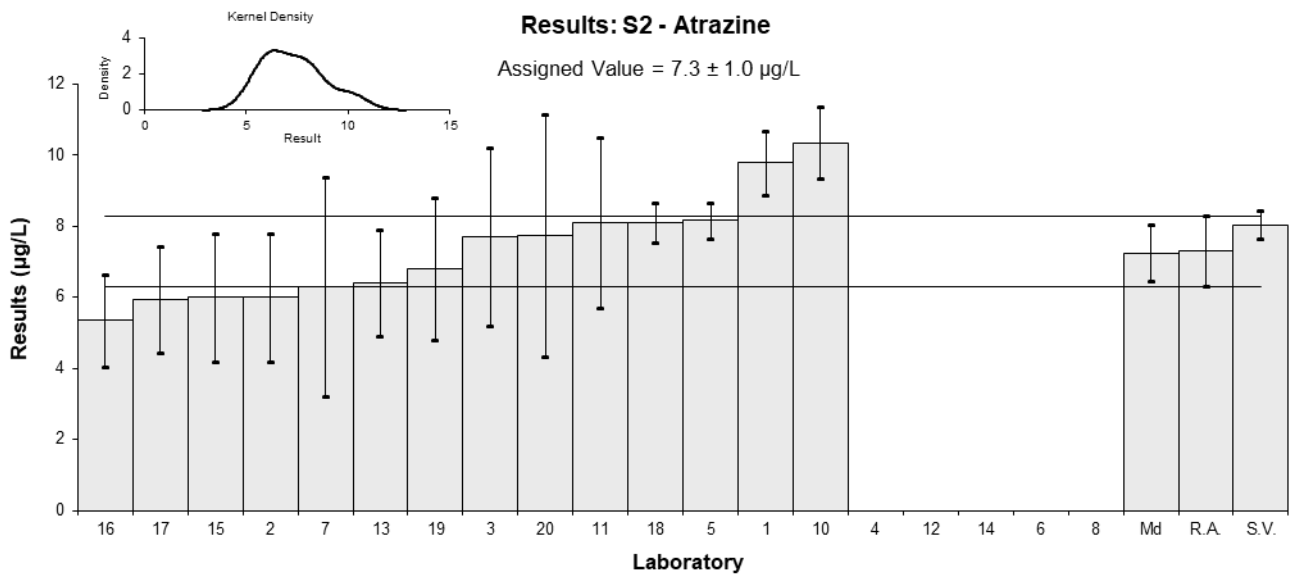
Sample No.	S2
Matrix	Water
Analyte	Atrazine
Units	µg/L

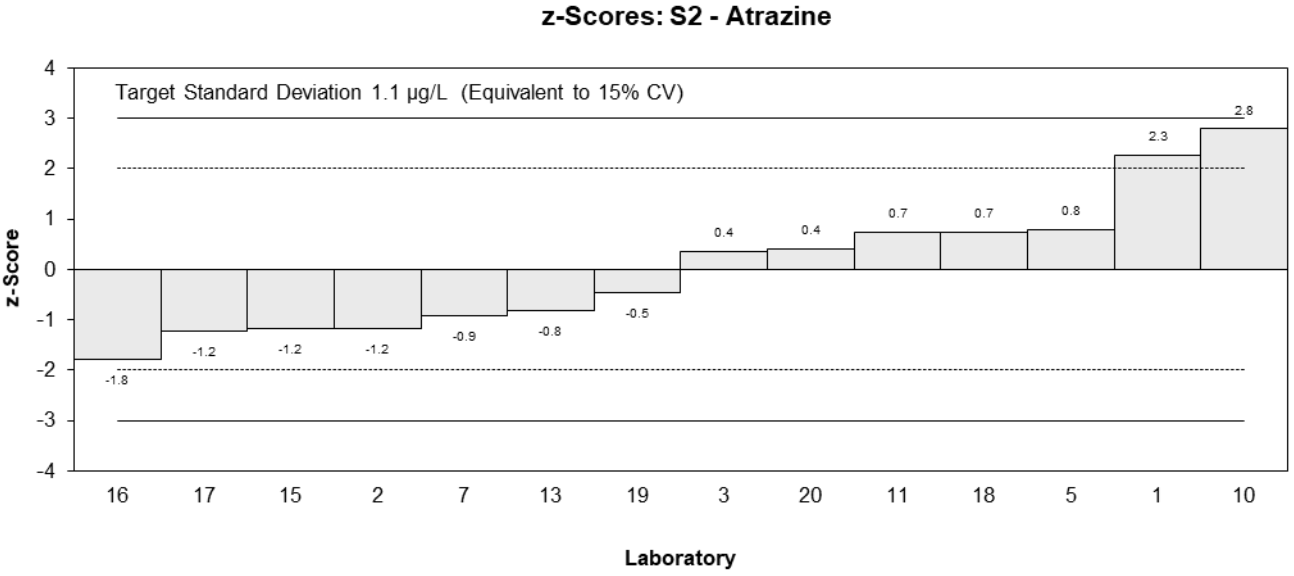
Participant Results

Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	9.79	0.90	88	2.27	1.85
2	6	1.8	NR	-1.19	-0.63
3	7.7	2.5	NR	0.37	0.15
4	<0.1	NR	NR		
5	8.16	0.50	NR	0.79	0.77
6	NT	NT	NT		
7	6.3	3.1	NR	-0.91	-0.31
8	NT	NT	NT		
10	10.35	1	NR	2.79	2.16
11	8.1	2.4	NR	0.73	0.31
12	NT	NT	NT		
13	6.4	1.5	NR	-0.82	-0.50
14	NT	NT	NT		
15	6.0	1.8	NR	-1.19	-0.63
16	5.35	1.3	NR	-1.78	-1.19
17	5.95	1.5	91	-1.23	-0.75
18	8.1	0.57	99	0.73	0.70
19	6.8	2.0	NR	-0.46	-0.22
20	7.75	3.4	NR	0.41	0.13

Statistics

Assigned Value	7.3	1.0
Spike	8.04	0.40
Robust Average	7.3	1.0
Median	7.25	0.80
Mean	7.34	
N	14	
Max.	10.35	
Min.	5.35	
Robust SD	1.5	
Robust CV	21%	


Kernel Density
Density
Result
Results: S2 - Atrazine
Assigned Value = 7.3 ± 1.0 µg/L
Results (µg/L)
16 17 15 2 7 13 19 3 20 11 18 5 1 10 4 12 14 6 8 Md R.A. S.V.
Laboratory


z-Scores: S2 - Atrazine
Target Standard Deviation 1.1 µg/L (Equivalent to 15% CV)
z-Score
-1.8 -1.2 -1.2 -1.2 -0.9 -0.8 -0.5 0.4 0.4 0.7 0.7 0.8 2.3 2.8
16 17 15 2 7 13 19 3 20 11 18 5 1 10
Laboratory

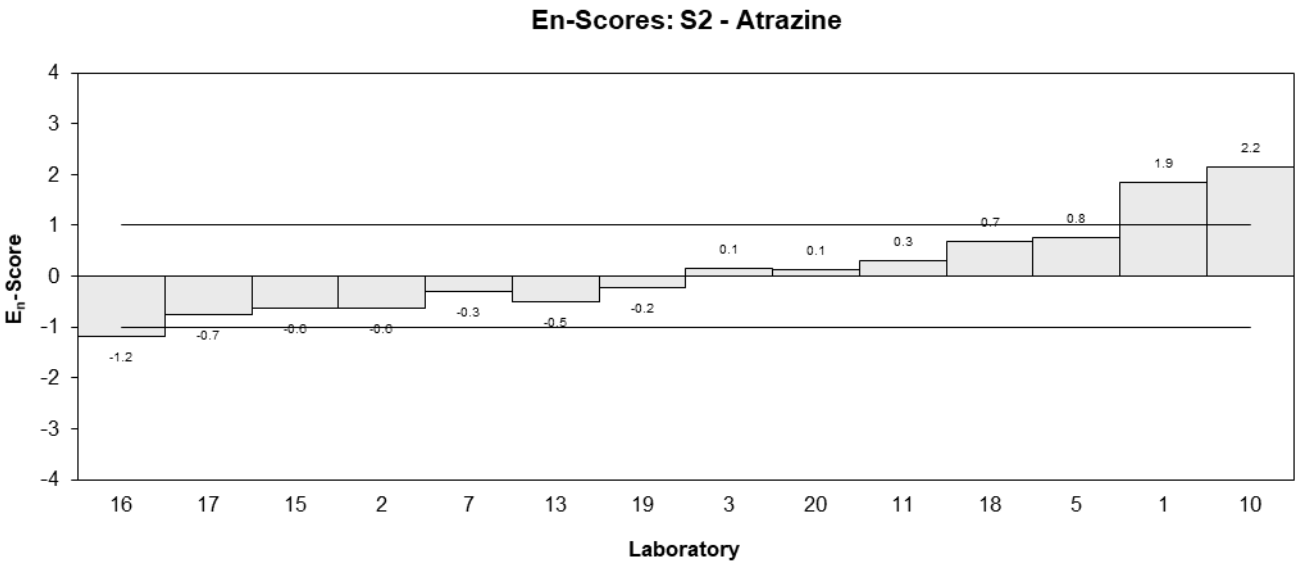

En-Scores: S2 - Atrazine
En-Score
-1.2 -0.7 -0.0 -0.0 -0.3 -0.5 -0.2 0.1 0.1 0.3 0.7 0.8 1.9 2.2
16 17 15 2 7 13 19 3 20 11 18 5 1 10
Laboratory

Figure 5

Table 9

Sample Details

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

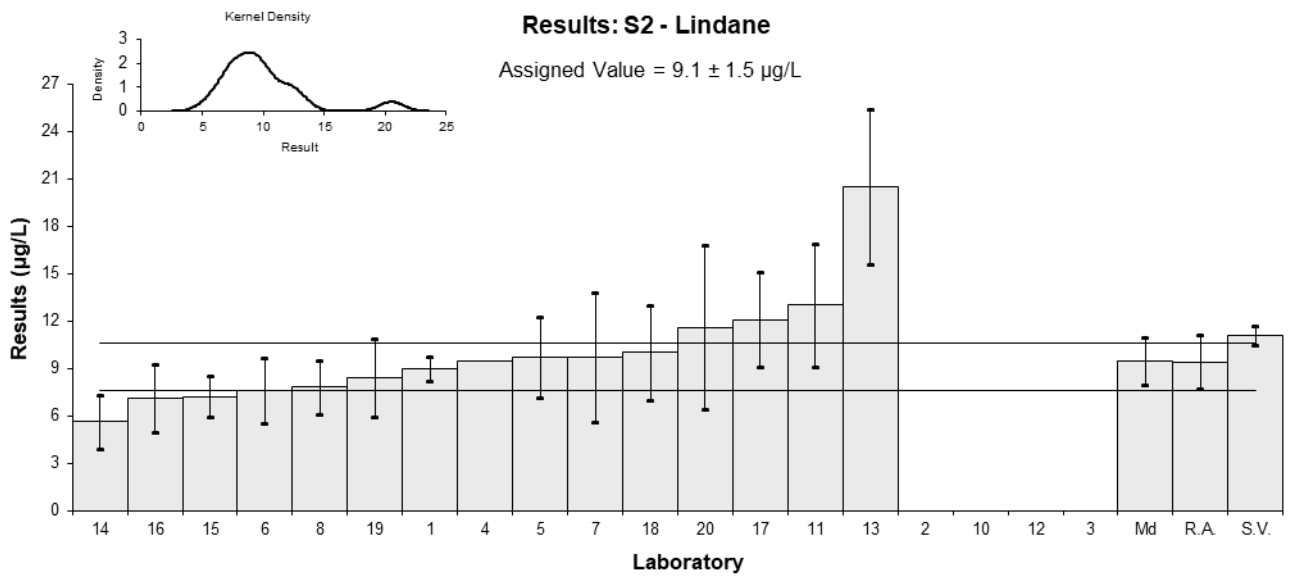
Participant Results

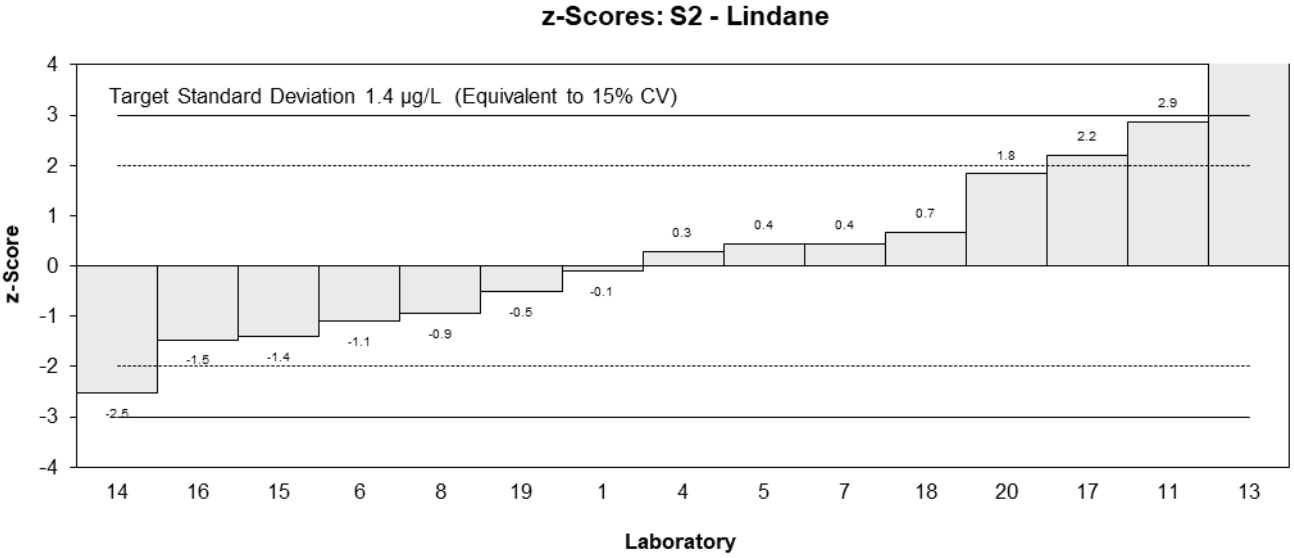
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	8.97	0.80	85	-0.10	-0.08
2	<0.01	NR	NR		
3	NT	NT	NT		
4	9.5	NR	NR	0.29	0.27
5	9.70	2.55	NR	0.44	0.20
6	7.62	2.06	NR	-1.08	-0.58
7	9.7	4.1	NR	0.44	0.14
8	7.811	1.676	NR	-0.94	-0.57
10	<0.1	0.1	NR		
11	13	3.9	NR	2.86	0.93
12	NT	NT	NT		
13	20.5	4.9	NR	8.35	2.22
14	5.65	1.7	NR	-2.53	-1.52
15	7.2	1.3	NR	-1.39	-0.96
16	7.1	2.13	NR	-1.47	-0.77
17	12.1	3.0	131	2.20	0.89
18	10.01	3	98	0.67	0.27
19	8.4	2.5	NR	-0.51	-0.24
20	11.6	5.2	NR	1.83	0.46

Statistics

Assigned Value*	9.1	1.5
Spike	11.1	0.6
Robust Average	9.4	1.7
Median	9.5	1.5
Mean	9.9	
N	15	
Max.	20.5	
Min.	5.65	
Robust SD	2.6	
Robust CV	27%	

* Robust average excluding Laboratory 13.


Kernel Density
Density
Result
Results: S2 - Lindane
Assigned Value = 9.1 ± 1.5 µg/L
Results (µg/L)
Laboratory
14 16 15 6 8 19 1 4 5 7 18 20 17 11 13 2 10 12 3 Md R.A. S.V.


z-Scores: S2 - Lindane
Target Standard Deviation 1.4 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 16 15 6 8 19 1 4 5 7 18 20 17 11 13
-2.5 -1.5 -1.4 -1.1 -0.9 -0.5 -0.1 0.3 0.4 0.4 0.7 1.8 2.2 2.9

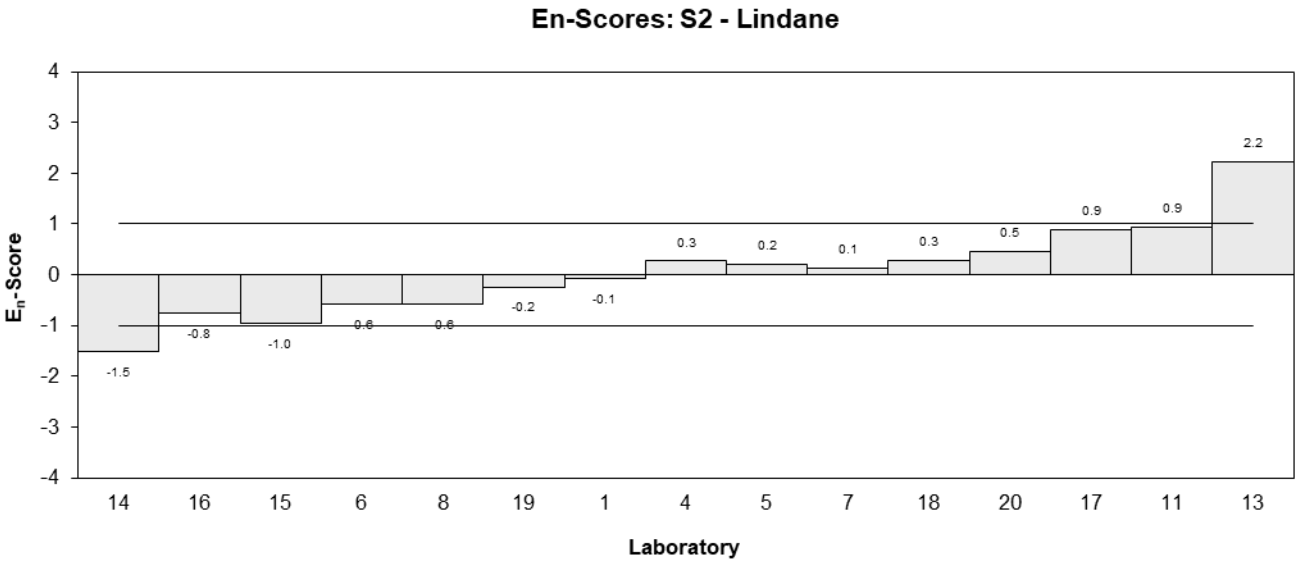

En-Scores: S2 - Lindane
En-Score
Laboratory
14 16 15 6 8 19 1 4 5 7 18 20 17 11 13
-1.5 -0.8 -1.0 -0.6 -0.6 -0.2 -0.1 0.3 0.2 0.1 0.3 0.5 0.9 0.9 2.2

Figure 6

Table 10

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Recovery
1	NT	NT	NT
2	0.6	0.18	NR
3	0.684	0.21	NR
4	0.088	0.018	100
5	NR	NR	NR
6	NT	NT	NT
7	NT	NT	NT
8	NT	NT	NT
10	NT	NT	NT
11	<1	NR	NR
12	NT	NT	NT
13	0.64	0.17	NR
14	NT	NT	NT
15	<0.3	NR	NR
16	< 5	1.5	NR
17	<1	NR	NR
18	0.52	0.03	93
19	<20	NR	NR
20	<0.05	NR	NR

Statistics

Assigned Value	Not Set	
Spike	0.510	0.026
Robust Average	0.53	0.24
Median	0.60	0.15
Mean	0.51	
N	5	
Max.	0.684	
Min.	0.088	
Robust SD	0.22	
Robust CV	41%	

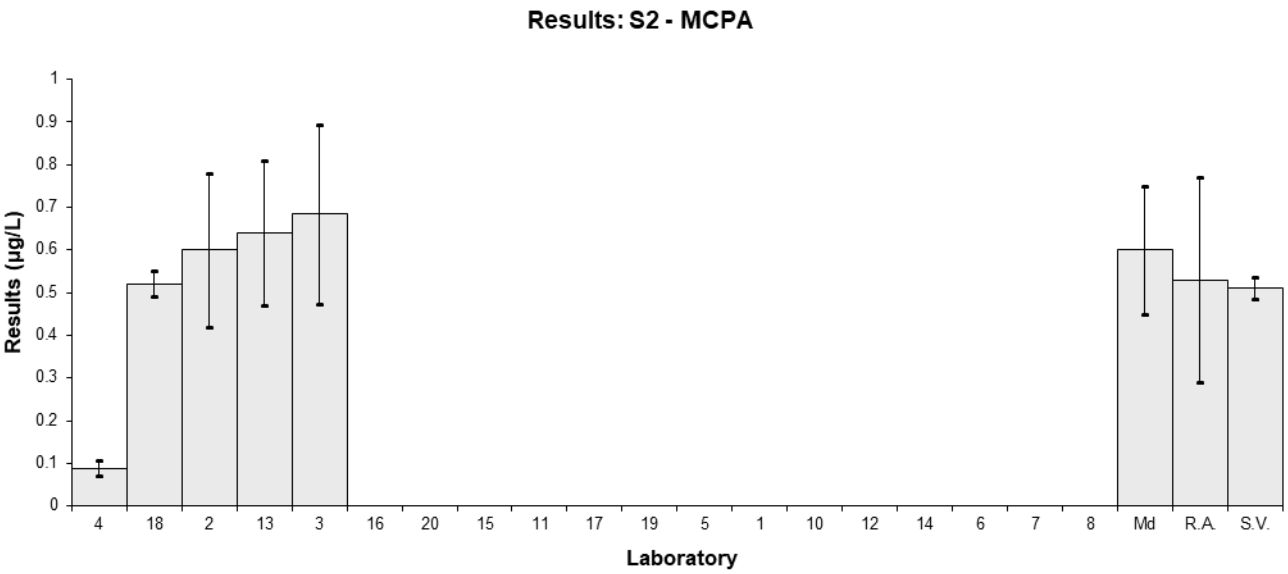

Results: S2 - MCPA
Results (µg/L)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4
18
2
13
3
16
20
15
11
17
19
5
1
10
12
14
6
7
8
Md
R.A.
S.V.
Laboratory

Figure 7

Table 11

Sample Details

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

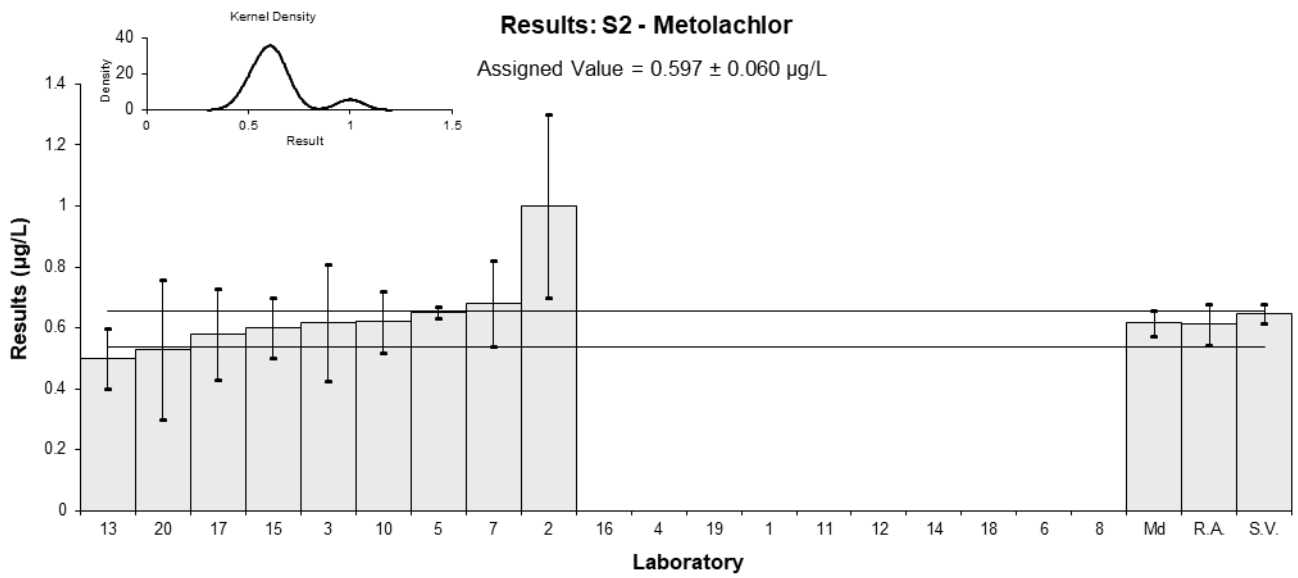
Participant Results

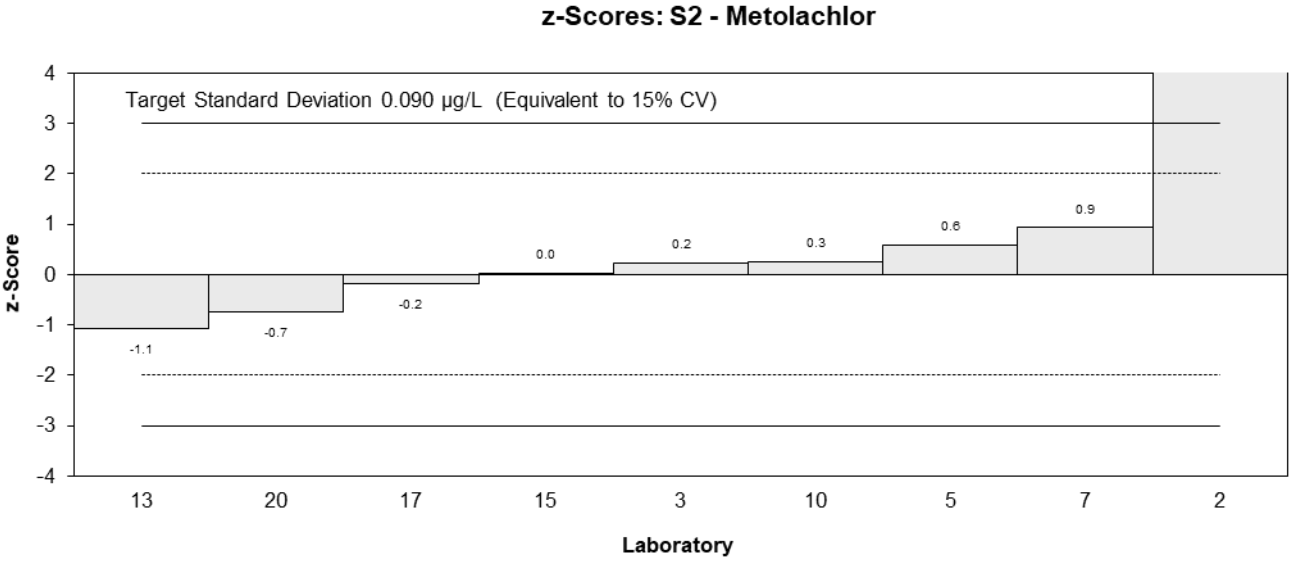
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	1	0.3	NR	4.50	1.32
3	0.617	0.19	NR	0.22	0.10
4	<0.1	NR	NR		
5	0.65	0.02	NR	0.59	0.84
6	NT	NT	NT		
7	0.68	0.14	NR	0.93	0.54
8	NT	NT	NT		
10	0.62	0.1	NR	0.26	0.20
11	NT	NT	NT		
12	NT	NT	NT		
13	0.5	0.1	NR	-1.08	-0.83
14	NT	NT	NT		
15	0.6	0.1	NR	0.03	0.03
16	< 1	0.3	NR		
17	0.58	0.15	91	-0.19	-0.11
18	NT	NT	NT		
19	<2	NR	NR		
20	0.53	0.23	NR	-0.75	-0.28

Statistics

Assigned Value*	0.597	0.060
Spike	0.645	0.032
Robust Average	0.612	0.068
Median	0.617	0.042
Mean	0.642	
N	9	
Max.	1	
Min.	0.5	
Robust SD	0.082	
Robust CV	13%	

* Robust average excluding Laboratory 2.


Kernel Density
Density
Result
Results: S2 - Metolachlor
Assigned Value = 0.597 ± 0.060 µg/L
Results (µg/L)
Laboratory
13 20 17 15 3 10 5 7 2 16 4 19 1 11 12 14 18 6 8 Md R.A. S.V.


z-Scores: S2 - Metolachlor
Target Standard Deviation 0.090 µg/L (Equivalent to 15% CV)
z-Score
-1.1 -0.7 -0.2 0.0 0.2 0.3 0.6 0.9
Laboratory
13 20 17 15 3 10 5 7 2

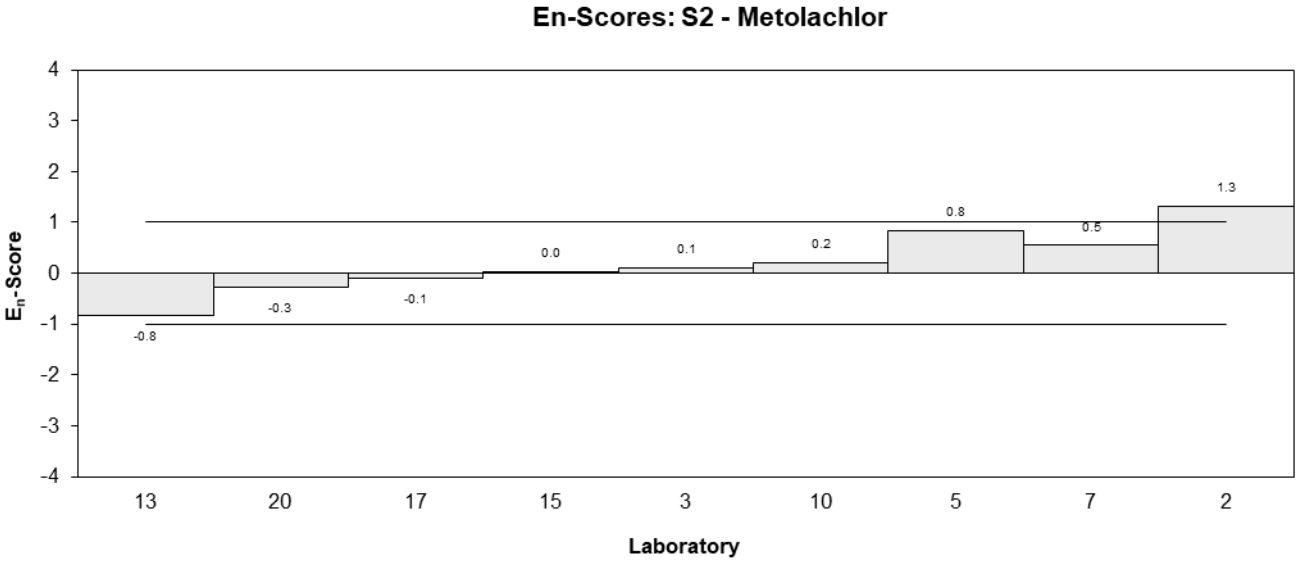

En-Scores: S2 - Metolachlor
En-Score
-0.8 -0.3 -0.1 0.0 0.1 0.2 0.8 0.5 1.3
Laboratory
13 20 17 15 3 10 5 7 2

Figure 8

Table 12

Sample Details

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

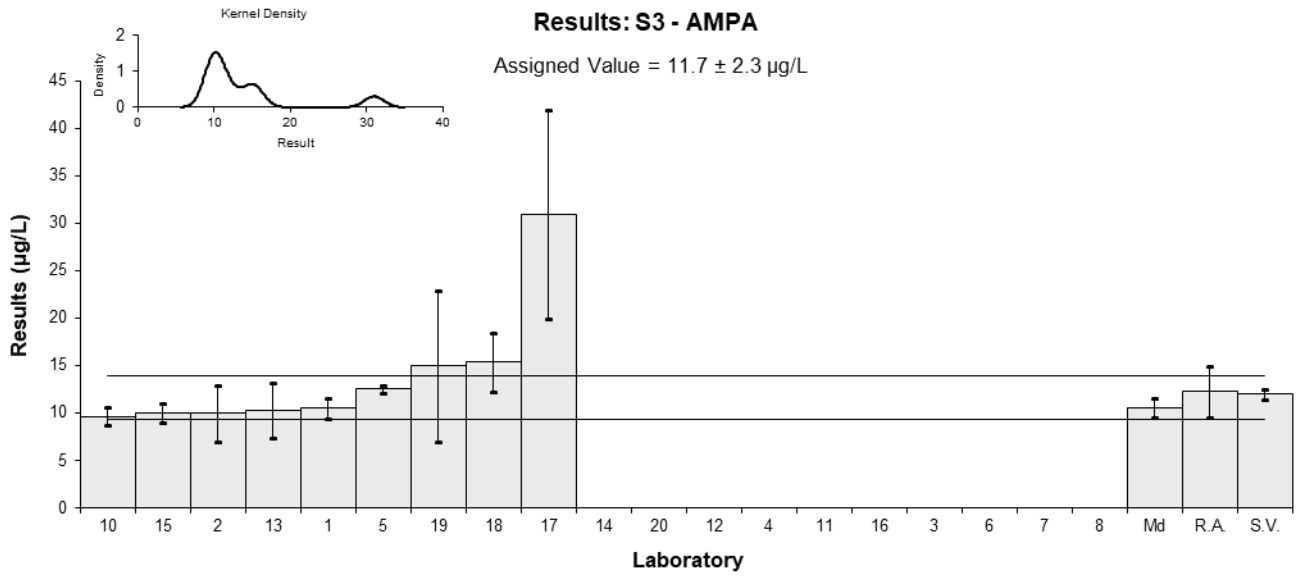
Participant Results

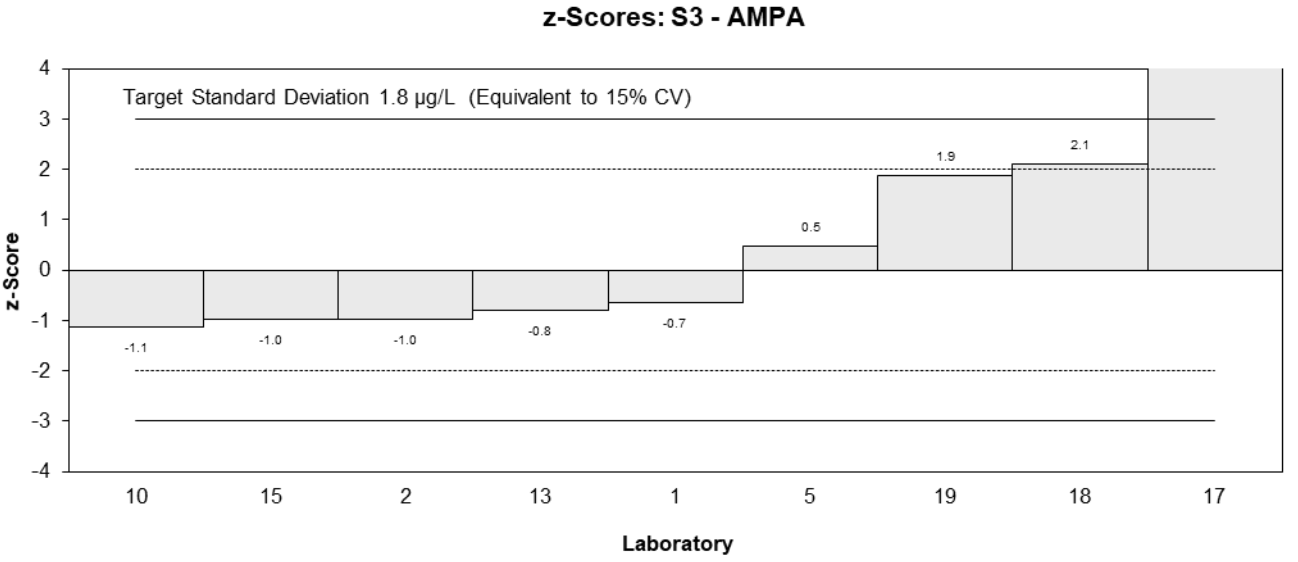
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	10.55	1.10	72	-0.66	-0.45
2	10	3	NR	-0.97	-0.45
3	NT	NT	NT		
4	NR	NR	NR		
5	12.55	0.42	NR	0.48	0.36
6	NT	NT	NT		
7	NT	NT	NT		
8	NT	NT	NT		
10	9.7	1	NR	-1.14	-0.80
11	NT	NT	NT		
12	<10	NR	NR		
13	10.3	2.9	NR	-0.80	-0.38
14	<0.01	0.002	83		
15	10	1	NR	-0.97	-0.68
16	NT	NT	NT		
17	31	11	102	11.00	1.72
18	15.41	3.08	NT	2.11	0.97
19	15	8	84	1.88	0.40
20	<0.01	NR	NR		

Statistics

Assigned Value*	11.7	2.3
Spike	12.0	0.6
Robust Average	12.3	2.7
Median	10.6	1.0
Mean	13.8	
N	9	
Max.	31	
Min.	9.7	
Robust SD	3.2	
Robust CV	26%	

* Robust average exclduing Laboratory 17.


Kernel Density
Density
Result
Results: S3 - AMPA
Assigned Value = 11.7 ± 2.3 µg/L
Results (µg/L)
10 15 2 13 1 5 19 18 17 14 20 12 4 11 16 3 6 7 8 Md R.A. S.V.
Laboratory


z-Scores: S3 - AMPA
Target Standard Deviation 1.8 µg/L (Equivalent to 15% CV)
z-Score
-1.1 -1.0 -1.0 -0.8 -0.7 0.5 1.9 2.1
10 15 2 13 1 5 19 18 17
Laboratory

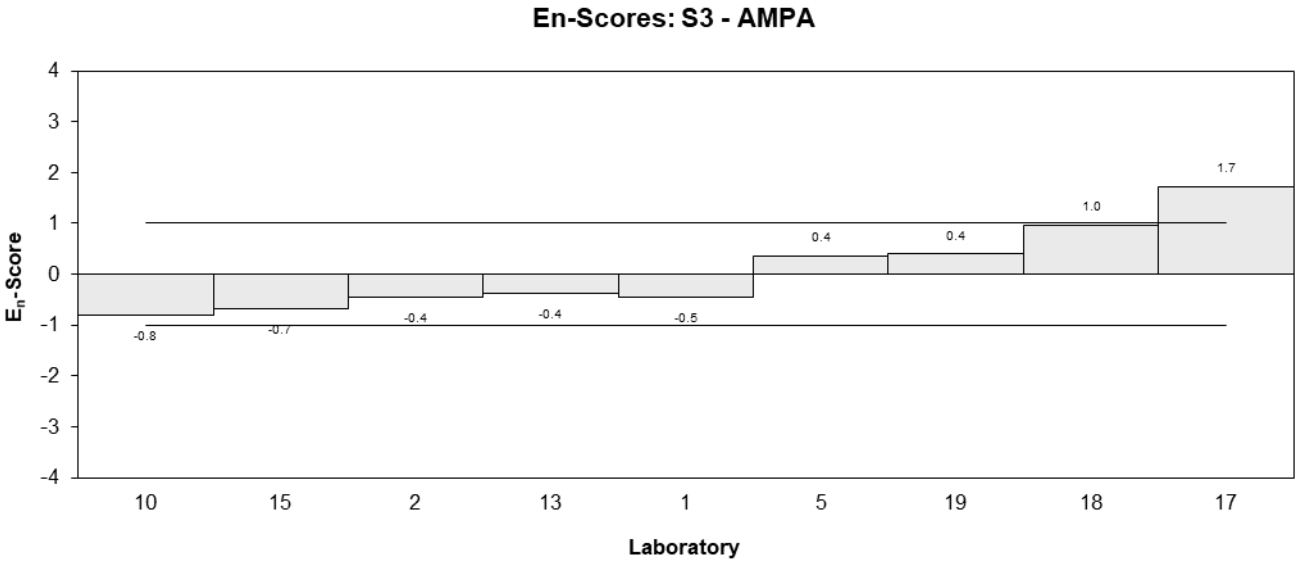

En-Scores: S3 - AMPA
En-Score
-0.8 -0.7 -0.4 -0.4 -0.5 0.4 0.4 1.0 1.7
10 15 2 13 1 5 19 18 17
Laboratory

Figure 9

Table 13

Sample Details

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

Participant Results

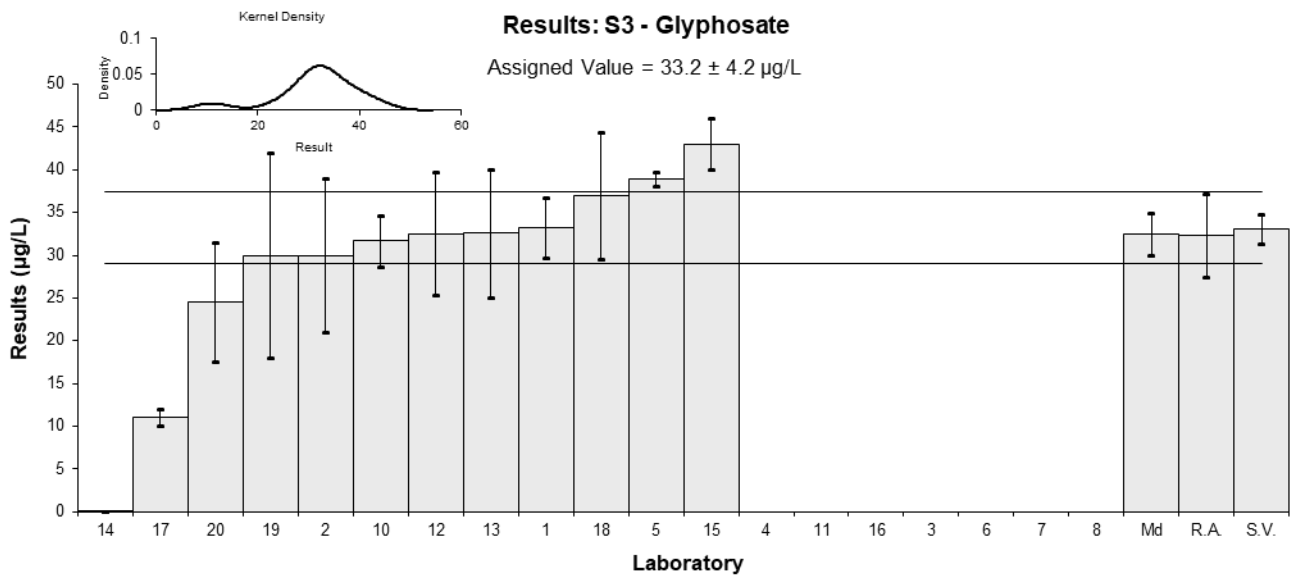
Lab. Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	33.2	3.50	88	0.00	0.00
2	30	9	NR	-0.64	-0.32
3	NT	NT	NT		
4	NR	NR	NR		
5	38.93	0.83	NR	1.15	1.34
6	NT	NT	NT		
7	NT	NT	NT		
8	NT	NT	NT		
10	31.7	3	NR	-0.30	-0.29
11	NT	NT	NT		
12	32.54	7.16	102	-0.13	-0.08
13	32.6	7.5	NR	-0.12	-0.07
14	0.0232	0.0036	115	-6.66	-7.90
15	43	3	NR	1.97	1.90
16	NT	NT	NT		
17	11	1.0	104	-4.46	-5.14
18	37	7.4	NT	0.76	0.45
19	30	12	79	-0.64	-0.25
20	24.5	7	NR	-1.75	-1.07

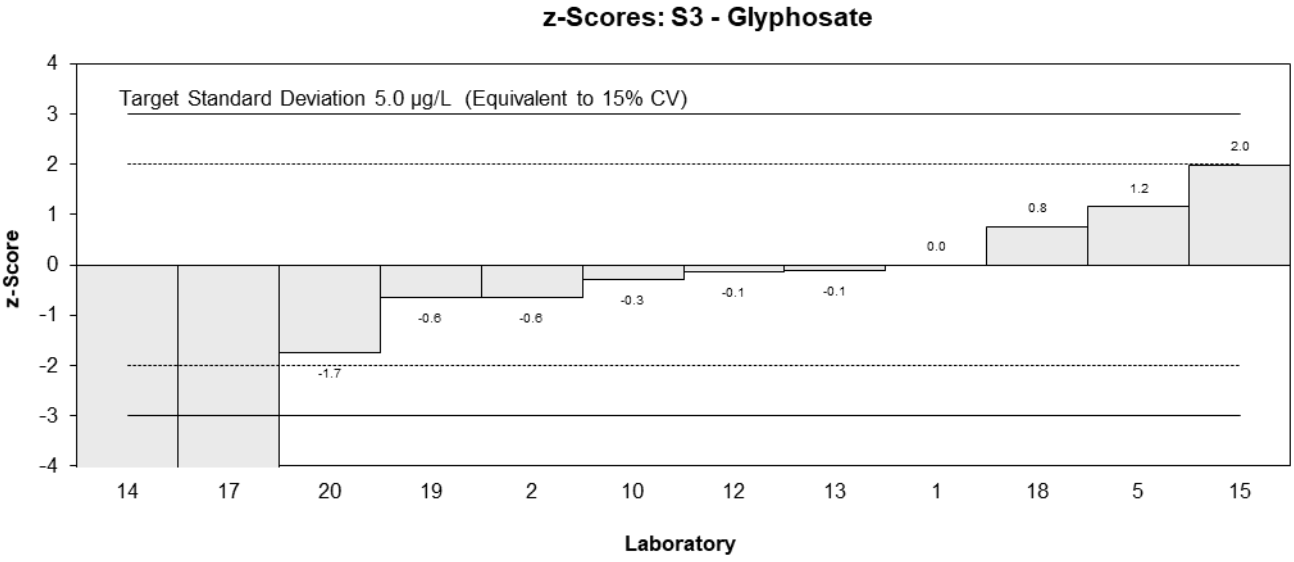
Statistics*

Assigned Value**	33.2	4.2
Spike	33.1	1.7
Robust Average	32.3	4.9
Median	32.5	2.5
Mean	31.3	
N	11	
Max.	43	
Min.	11	
Robust SD	6.5	
Robust CV	20%	

* Laboratory 14 excluded from all statistical calculations (gross error).

** Robust average excluding Laboratory 17.


Results: S3 - Glyphosate
Assigned Value = 33.2 ± 4.2 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
14 17 20 19 2 10 12 13 1 18 5 15 4 11 16 3 6 7 8 Md R.A. S.V.


z-Scores: S3 - Glyphosate
Target Standard Deviation 5.0 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 17 20 19 2 10 12 13 1 18 5 15
-1.7 -0.6 -0.6 -0.3 -0.1 -0.1 0.0 0.8 1.2 2.0

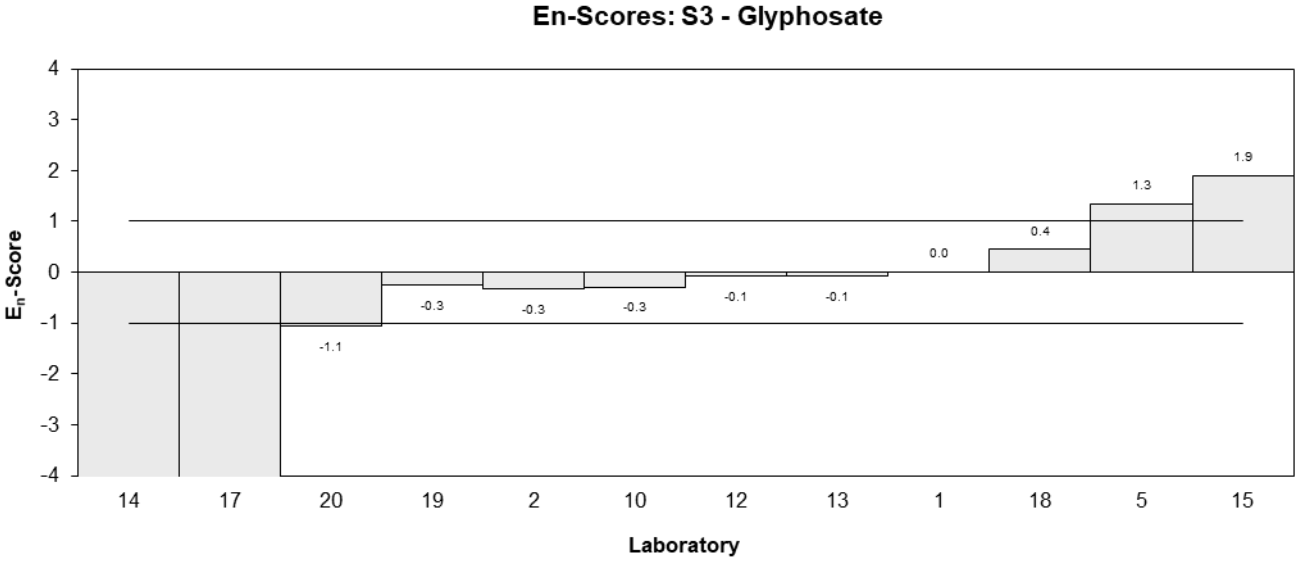

En-Scores: S3 - Glyphosate
En-Score
Laboratory
14 17 20 19 2 10 12 13 1 18 5 15
-1.1 -0.3 -0.3 -0.3 -0.1 -0.1 0.0 0.4 1.3 1.9

Figure 10

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust average of participants' results was used as the assigned value for each scored analyte. 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 4, 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 14.

No assigned value was set for Sample S1 endosulfan sulfate as participants' results were too variable. No assigned value was set for Sample S2 MCPA as there were too few reported numeric results.

For the scored analytes, assigned values were within the range of 82% to 110% of the spiked values. Similar ratios have been observed in previous NMI Pesticides in Water PT studies, and provides good support for the assigned values.

Table 14 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	Diuron	13.0	15.0	87
	Endosulfan sulfate	*(3.05)*	3.29	*(93)*
	Imidacloprid	8.77	7.99	110
S2	Atrazine	7.3	8.04	91
	Lindane	9.1	11.1	82
	MCPA	*(0.53)*	0.510	*(104)*
	Metolachlor	0.597	0.645	93
S3	AMPA	11.7	12.0	98
	Glyphosate	33.2	33.1	100

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 17025:2017 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 101 numeric results submitted for the analytes of interest in this study, 99 (98%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3). A number of participants reported using the NATA GAG Estimating and Reporting MU as their guide; NATA no longer publishes this document.[10]

Laboratory **14** reported Sample S3 uncertainties as relative uncertainties rather than absolute uncertainties in units of µg/L as requested for this study (i.e. uncertainty values were reported as '*x*%'). These values were modified accordingly by the study coordinator.

Laboratory **4** did not report uncertainties for two of the three analytes they submitted numeric results for, despite reporting that they were accredited to ISO/IEC 17025.

The magnitude of reported uncertainties was within the range of 2.1% to 53% relative to the result. In general, an expanded uncertainty of less than 15% relative is likely to be unrealistically small for the routine measurement of a pesticide residue, while an uncertainty of greater than 50% relative is likely to be too large. Of 99 MUs reported for this study, 21 were less than 15% relative and one was greater than 50% relative; participants reporting these uncertainties may wish to reconsider if their MUs are realistic or fit-for-purpose.

Uncertainties associated with results returning a satisfactory z-score but an unsatisfactory E_n-score may have been underestimated.

Laboratories **8**, **10**, **14** and **16** attached an estimate of 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. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write the uncertainty to no more than two significant figures, and then write the result with the corresponding number of decimal places. For example, instead of 2.077 ± 0.573 µg/L, it is better to report this as 2.08 ± 0.57 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-laboratory CVs obtained in this study for scored analytes are presented for comparison in Table 15.

Table 15 Comparison of Thompson-Horwitz CV, Target SD and Between-Laboratory CV

Sample	Analyte	Assigned Value (µg/L)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between-Laboratory CV* (%)
S1	Diuron	13.0	22	15	26
	Imidacloprid	8.77	22	15	8.4
S2	Atrazine	7.3	22	15	21
	Lindane	9.1	22	15	25
	Metolachlor	0.597	22	15	11
S3	AMPA	11.7	22	15	23
	Glyphosate	33.2	22	15	16

* Robust between-laboratory CV with outliers removed, if applicable.

Of 78 results for which z-scores were calculated, 64 (82%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

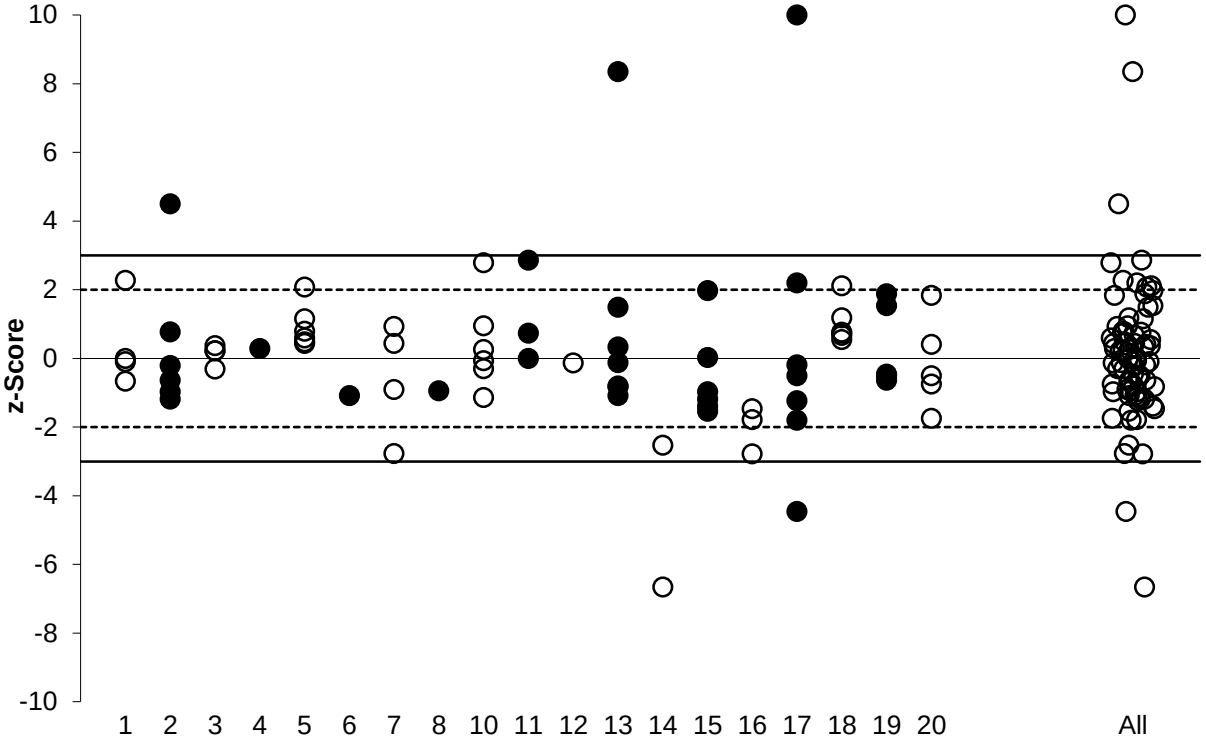
Laboratories **13** and **17** reported results for all 7 scored analytes.

Satisfactory z-scores were achieved for all scored analytes reported by Laboratories **15** (6), **19** (5), **20** (5), **3** (4), **4** (1), **6** (1), **8** (1) and **12** (1).

Laboratory **17** returned unsatisfactory z-scores for both analytes in Sample S3. This participant may have switched their results for glyphosate and AMPA.

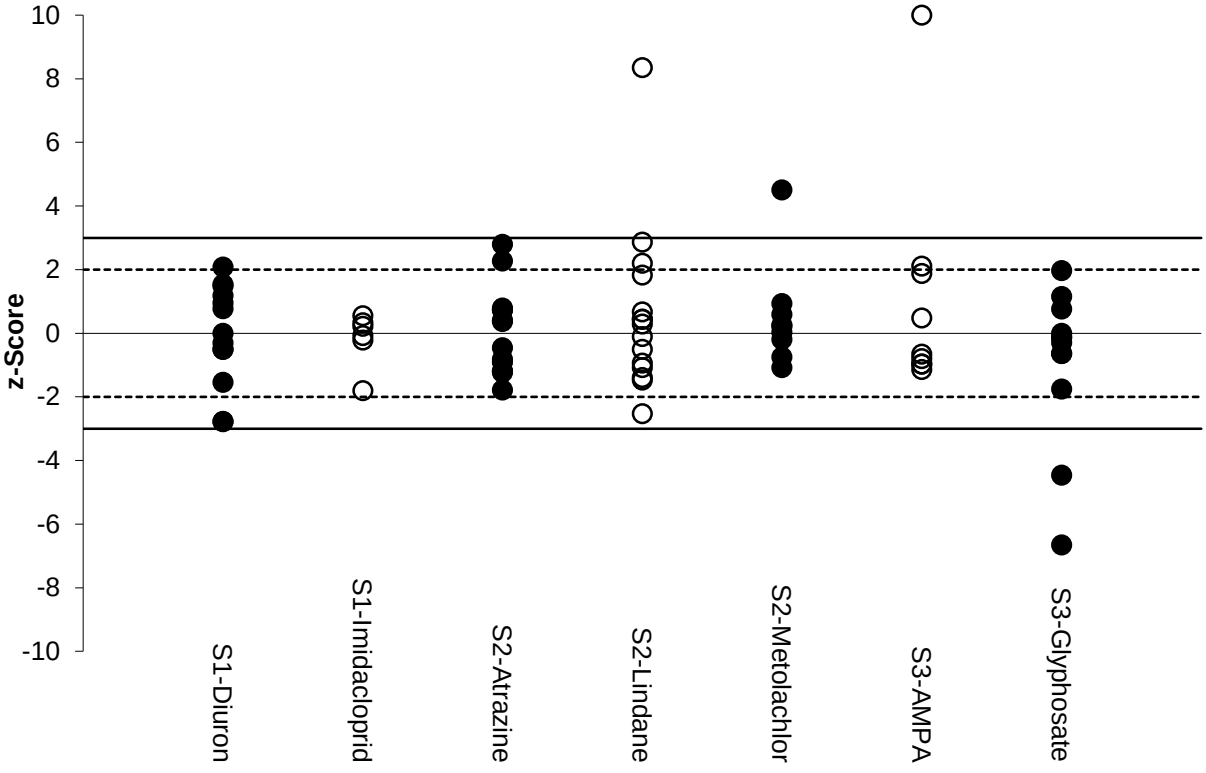
No results reported by Laboratory **14** returned a satisfactory z-score.

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



z-Scores greater than 10 have been plotted as 10.

Figure 11 z-Score Dispersal by Laboratory



z-Scores greater than 10 have been plotted as 10.

Figure 12 z-Score Dispersal by Analyte

6.4 E_n-Score

E_n-scores should be interpreted in conjunction with z-scores; an unsatisfactory E_n-score can either be caused by an inappropriate measurement or uncertainty, or both. If a participant did not report an expanded MU with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of 78 results for which E_n-scores were calculated, 62 (79%) 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.

Satisfactory E_n-scores were achieved for all scored analytes reported by Laboratory **18** (6), **19** (5), **3** (4), **11** (3), **4** (1), **6** (1), **8** (1) and **12** (1).

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

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

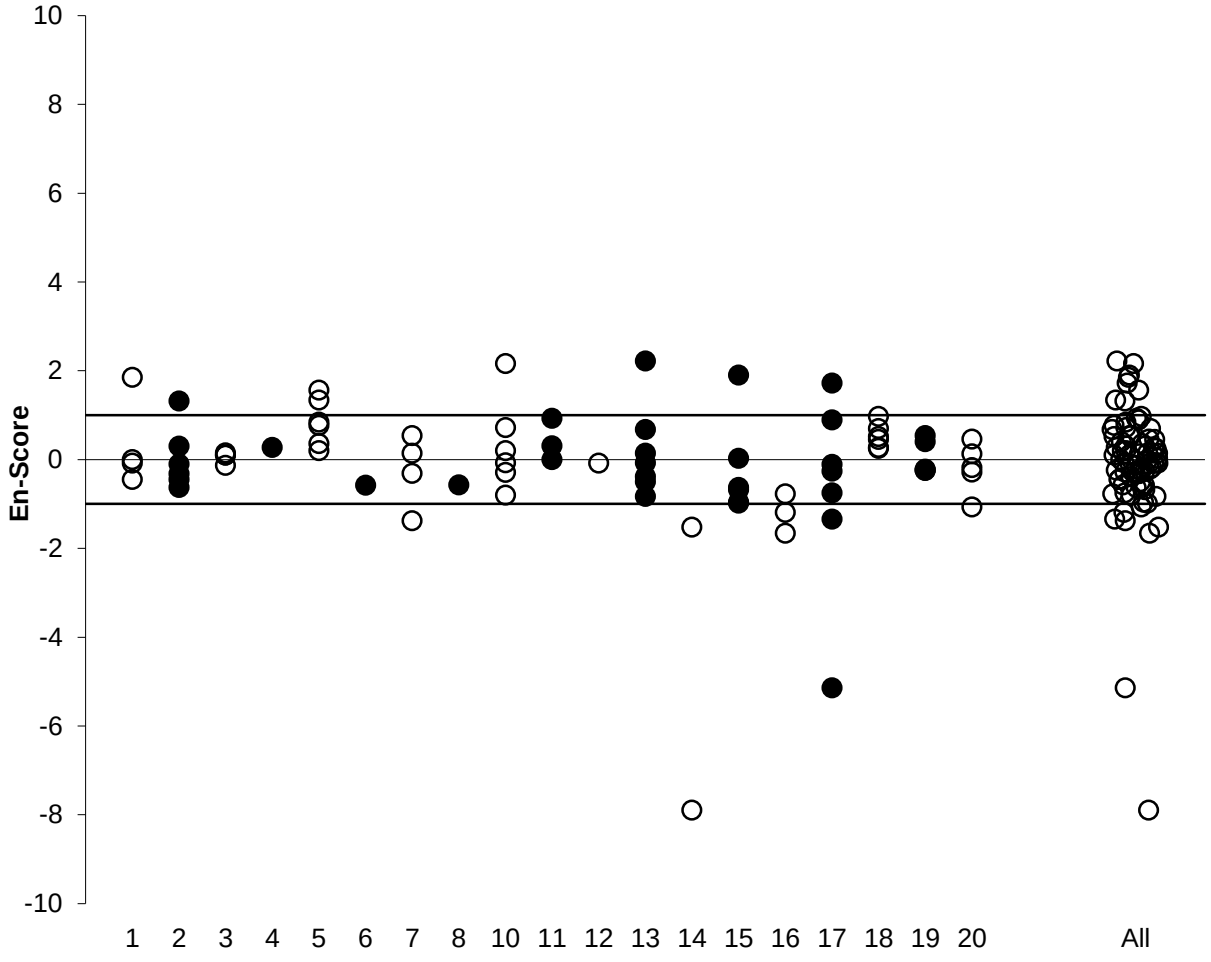


Figure 13 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 16 presents false negative results. These are analytes present in the samples which a participant tested for, but did not report a numeric result (for example, participants reporting a 'less than' result (< *x*) when the assigned value was higher than their limit of reporting (LOR), or participants that did not report anything). For analytes where no assigned value was set, results have only been considered to be false negatives where the robust average and spiked value were significantly higher than the participants' LOR, or if no value was reported.

Table 16 False Negatives

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (µg/L)	Spiked Value (µg/L)	Result* (µg/L)
2	S2	Lindane	9.1	11.1	<0.01
4	S1	Diuron	13.0	15.0	<0.1
		Imidacloprid	8.77	7.99	<0.1
	S2	Atrazine	7.3	8.04	<0.1
		Metolachlor	0.597	0.645	<0.1
	S3	AMPA	11.7	12.0	NR
		Glyphosate	33.2	33.1	NR
5	S2	MCPA	*(0.53)*	0.510	NR
8	S1	Diuron	13.0	15.0	< 0.2
10	S2	Lindane	9.1	11.1	<0.1
12	S3	AMPA	11.7	12.0	<10
14	S3	AMPA	11.7	12.0	<0.01
20	S2	MCPA	*(0.53)*	0.510	<0.05
	S3	AMPA	11.7	12.0	<0.01

* Results reported as NR may or may not be false negatives, depending on the participants' actual LOR.

6.6 Reporting of Additional Analytes

Three participants reported analytes that were not spiked into the test samples (total of 11 results). These are listed in Table 17. Participants should take care to avoid any potential cross-contamination when analysing their samples.

Table 17 Analytes Reported by Participants Not Spiked in the Test Samples

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
2	S1	p,p'-DDT	0.03	0.01	NR
		Total DDT	0.03	0.01	NR
		Lindane	13	3.9	NR
		Simazine	0.16	0.05	NR
	S2	Simazine	0.15	0.05	NR
4	S1	MCPA	0.085	0.017	100
13	S1	MCPA	0.11	0.05	NR
	S1	Picloram	0.59	NR	NR
	S1	Triclopyr	0.24	NR	NR
	S2	Picloram	0.63	0.19	NR
	S2	Triclopyr	0.09	0.03	NR

6.7 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential pesticides that could have been spiked into Samples S1 and S2 (Table 1), in addition to AMPA and glyphosate in Sample S3. Of these, 9 different pesticides were used for spiking in this study. Participants were not required to test for all potential pesticides, and were requested to report 'NT' (for 'Not Tested') for any that they did not analyse the samples for.

A summary of participants' testing of the spiked pesticides is presented in Table 18. Shaded cells indicate that the participant did not receive (and therefore did not analyse) the samples containing that pesticide.

Laboratories **2**, **4**, **13**, **15** and **17** reported that they tested for all spiked analytes. All participants tested for at least one analyte spiked into the samples, with the proportion of analytes being tested for by each participant ranging from 22% to 100%.

Of the spiked analytes in this study, endosulfan sulfate was tested for by the highest proportion of participants (100%). The proportion of participants testing for each analyte in this study ranged from 44% to 100%.

Table 18 Summary of Pesticides Analysed by Participants

Lab. Code / Analyte	1	2	3	4	5	6	7	8	10	11	12	13	14	15	16	17	18	19	20	Proportion of Participants (%)
AMPA	✓	✓	NT	✓	✓	NT	NT	NT	✓	NT	✓	✓	✓	✓	NT	✓	✓	✓	✓	68
Atrazine	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓		✓	NT	✓	✓	✓	✓	✓	✓	83
Diuron	NT	✓	✓	✓	✓	NT	✓	✓	✓	✓		✓	NT	✓	✓	✓	✓	✓	✓	83
Endosulfan sulfate	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	100
Glyphosate	✓	✓	NT	✓	✓	NT	NT	NT	✓	NT	✓	✓	✓	✓	NT	✓	✓	✓	✓	68
Imidacloprid	NT	✓	✓	✓	NT	NT	NT	NT	✓	NT		✓	NT	✓	NT	✓	✓	NT	NT	44
Lindane	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	94
MCPA	NT	✓	✓	✓	✓	NT	NT	NT	NT	✓		✓	NT	✓	✓	✓	✓	✓	✓	67
Metolachlor	NT	✓	✓	✓	✓	NT	✓	NT	✓	NT		✓	NT	✓	✓	✓	NT	✓	✓	67
Proportion of Analytes (%)	56	100	67	100	89	22	56	33	89	56	100 (S3 only)	100	44	100	67	100	89	89	89	

6.8 Participants' Analytical Methods

Participants used a variety of analytical methods for the test samples (Appendix 3).

For Samples S1 and S2, participants reported using the test portions ranging from 1 mL to the whole bottle (500 mL), with one participant reporting a range. There was no evident correlation overall between the results obtained and the reported sample volume used (Figure 14).

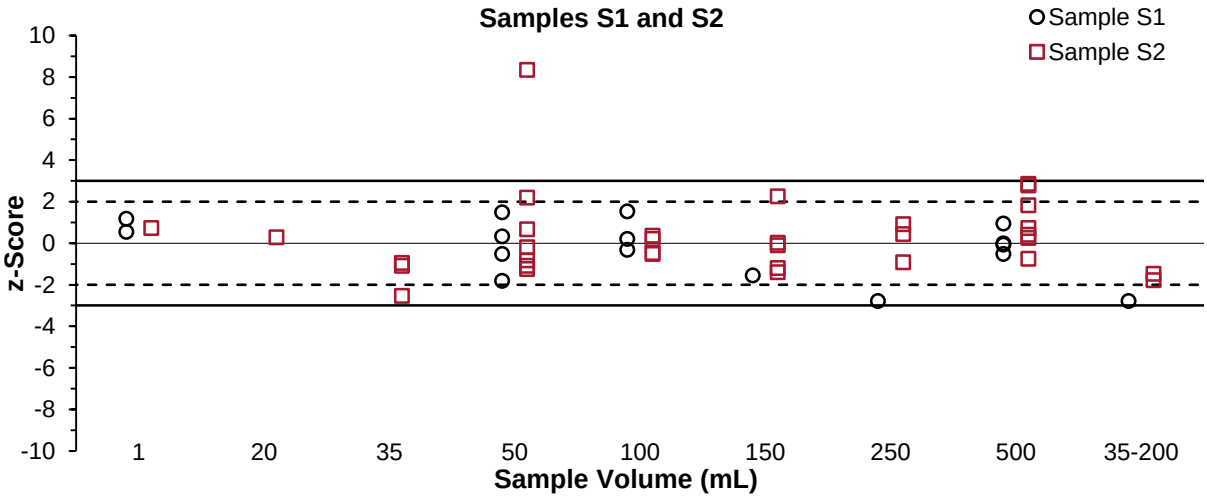


Figure 14 Samples S1 and S2 z-Score vs Sample Volume

For the analytes 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). For extraction solvents, participants used acetonitrile, dichloromethane (DCM), ether, ethyl acetate (EtOAc), hexane (HEX), methanol (MeOH), pentane (PENT), toluene, or mixtures of these solvents. The majority of participants did not report a further clean-up step, with only one participant reporting filtration for certain analytes. Participants reported using GC-(ECD, NPD), LC-DAD, HPLC-UV, GC-MS(/MS), and LC-MS(/MS) for analysis. The most common methodology used for this study was liquid-liquid extraction with dichloromethane, followed by analysis using GC-MS(/MS).

Plots of numeric results and methodology employed (extraction technique, extraction solvent and measurement instrument) for scored analytes are presented in Figures 15 to 19 (results from participants not reporting any methodology have not been included; 'NR' has been used where participants did not report only part of their methodology).

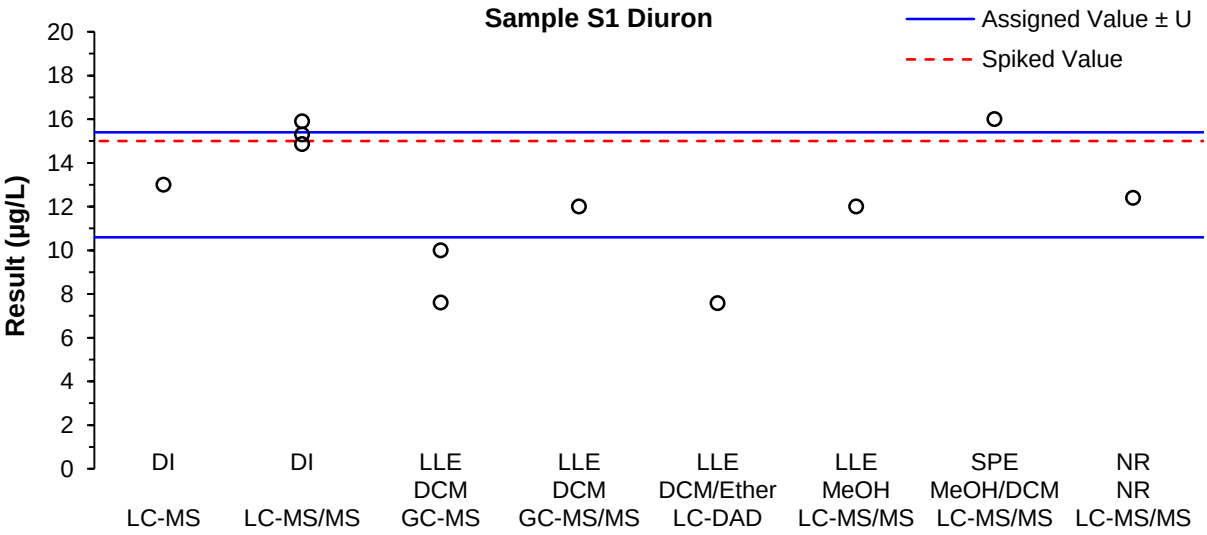


Figure 15 Sample S1 Diuron Result vs Methodology

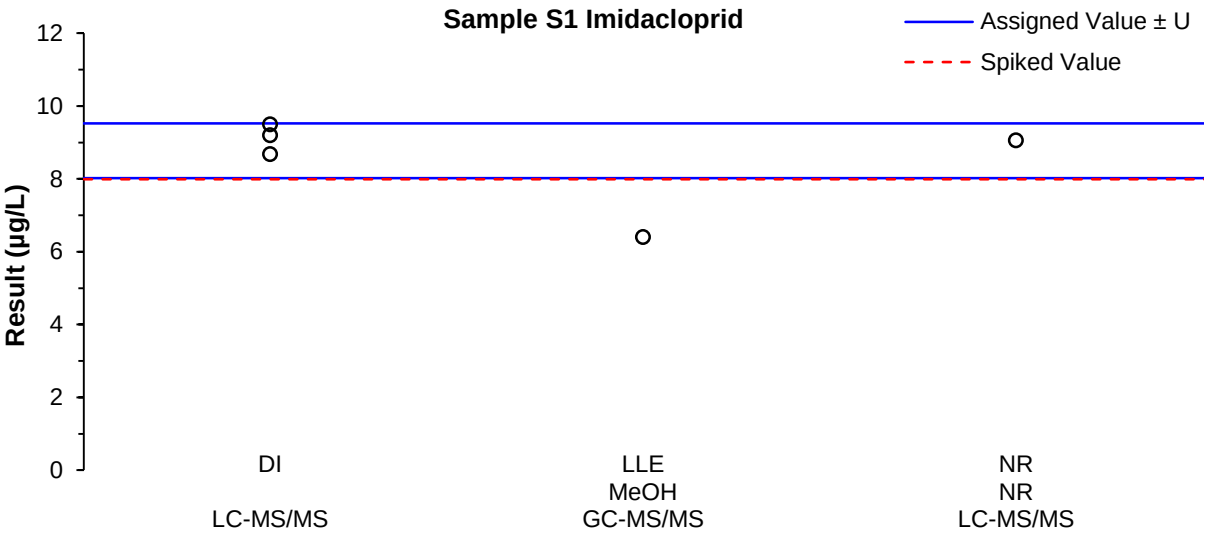


Figure 16 Sample S1 Imidacloprid Result vs Methodology

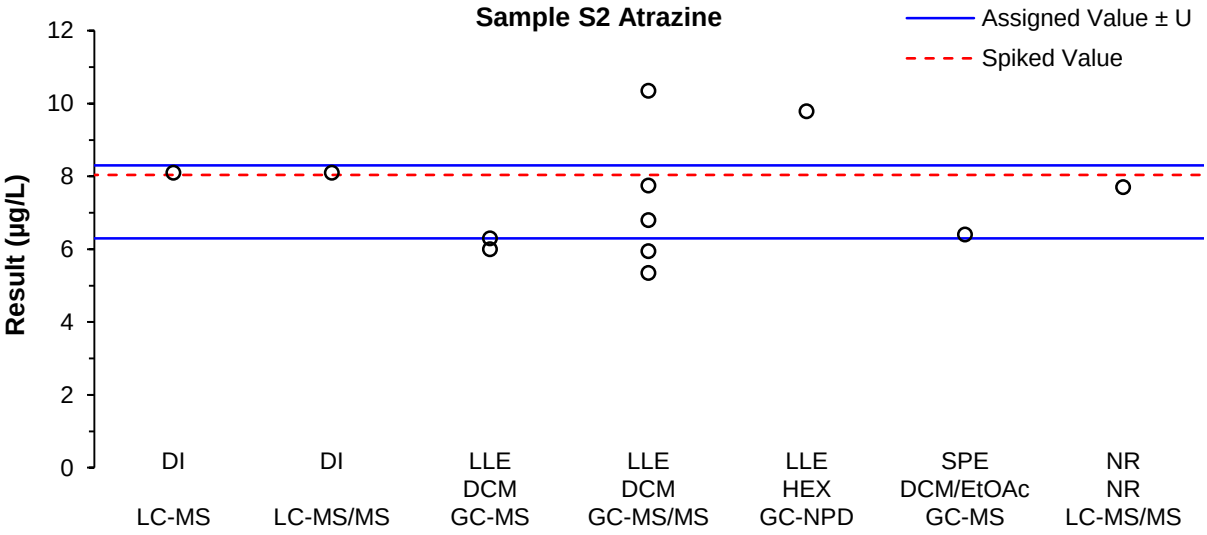


Figure 17 Sample S2 Atrazine Result vs Methodology

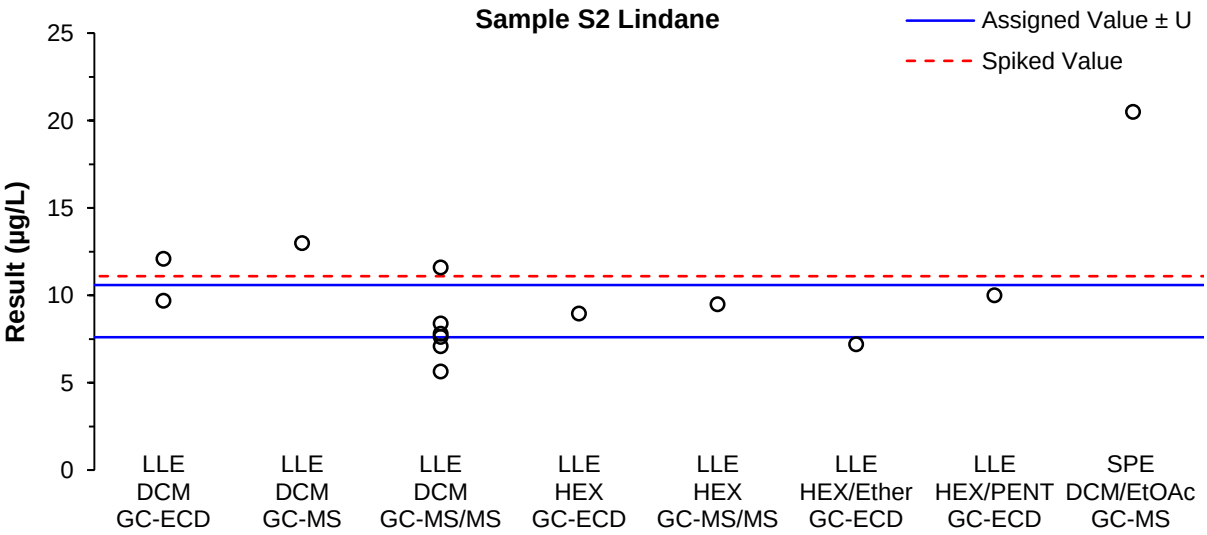


Figure 18 Sample S2 Lindane Result vs Methodology

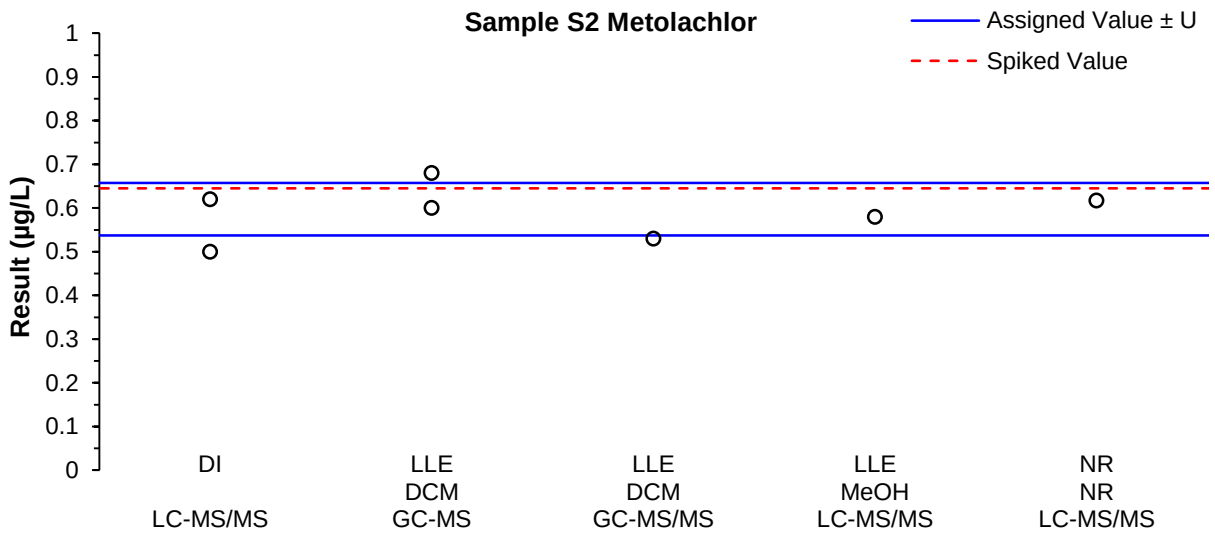


Figure 19 Sample S2 Metolachlor Result vs Methodology

For Sample S3, participants reported using test portions ranging from 0.5 mL to the whole bottle (500 mL) for analysis. There was no evident correlation overall between the results obtained and the reported sample volume used for analysis (Figure 20, gross errors have been removed).

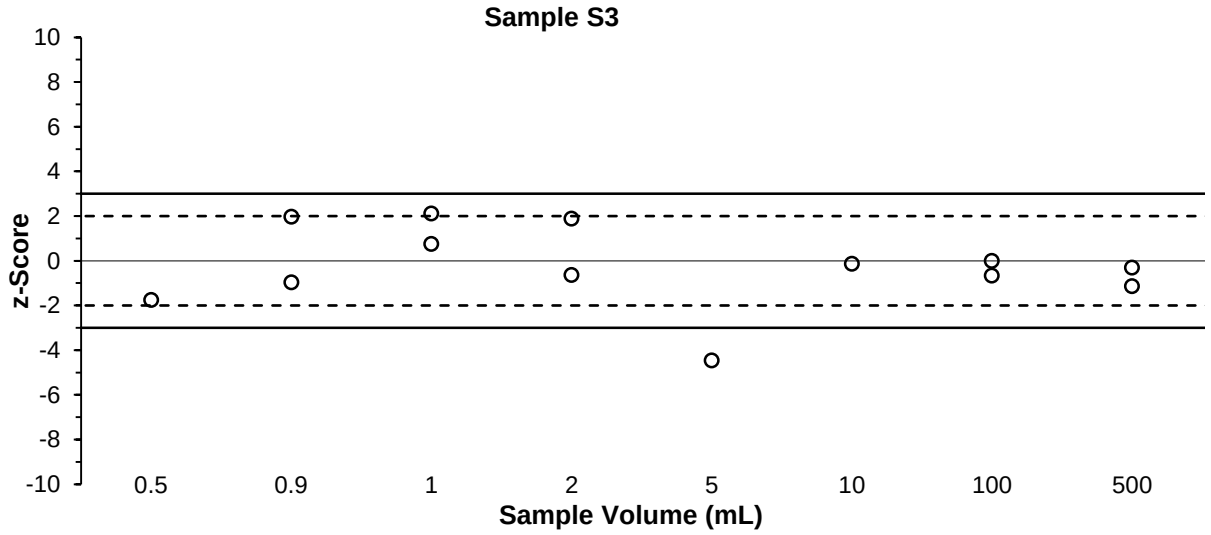


Figure 20 Sample S3 z-Score vs Sample Volume

Participants reported using direct injection, or extraction techniques such as liquid-liquid extraction and evaporation. Five participants reported derivatisation pre-column using fluorenylmethyloxycarbonyl group (FMOC). One participant used HPLC-FLD, while all other participants used LC-MS/MS for quantification. The most common methodology was direct injection and LC-MS/MS, with no derivatisation.

Plots of numeric results and methodology employed (extraction technique, derivatisation and measurement instrument) for Sample S3 analytes are presented in Figures 21 and 22 (results from participants not reporting any methodology have not been included, and gross errors have been removed).

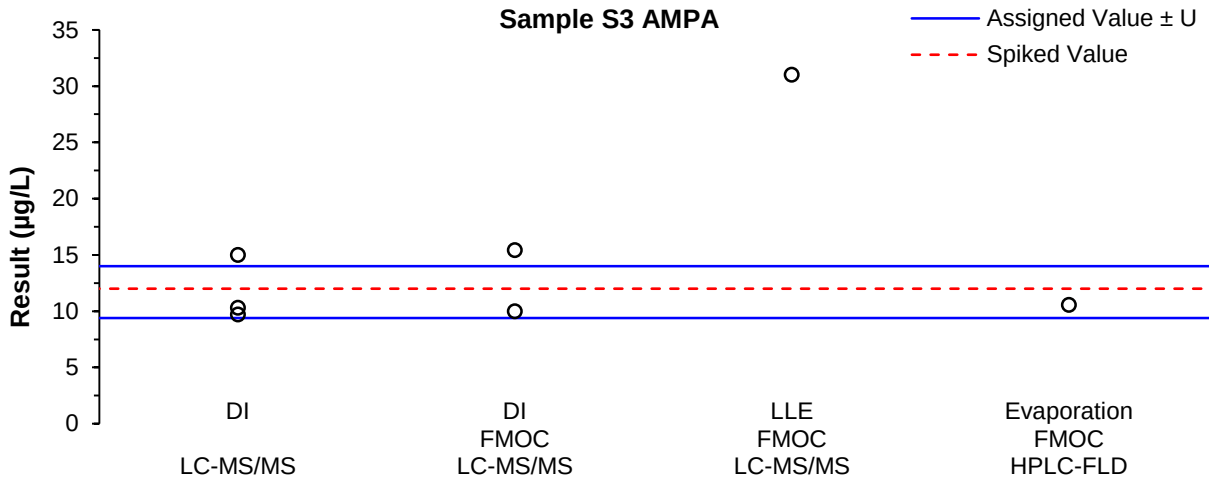


Figure 21 Sample S3 AMPA Result vs Methodology

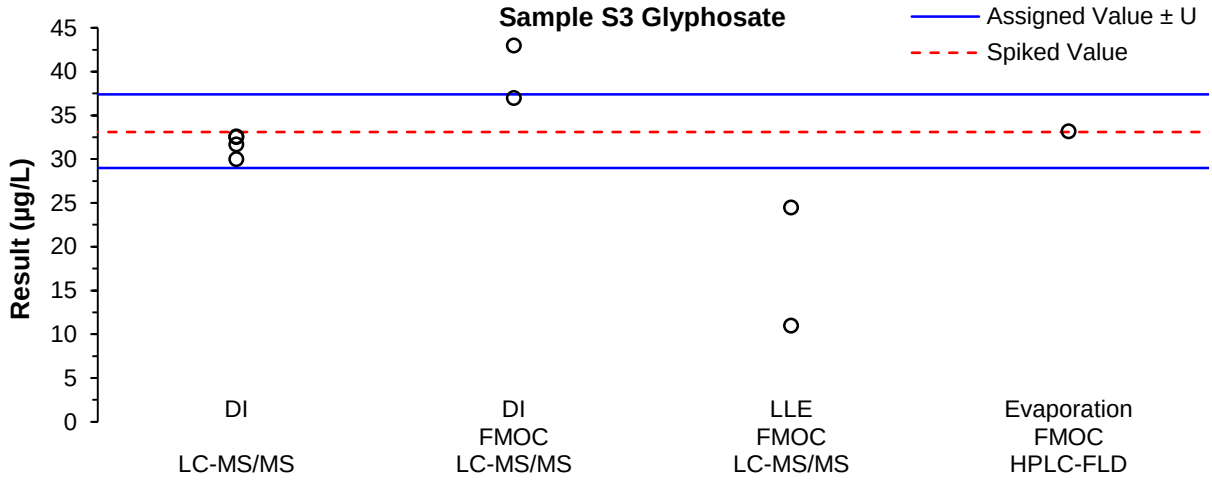


Figure 22 Sample S3 Glyphosate Result vs Methodology

Participants were requested to analyse the samples using their routine 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**, **4**, **12**, **14**, **17**, **18** and **19** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 72 to 131%. Laboratories **2** and **19** reported that they corrected their results for recoveries.

6.9 Certified Reference Materials

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

Fifteen participants reported using certified standards and one participant reported using certified standards and matrix reference materials. The following were listed:

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

These materials may or 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]

6.10 Summary of Participants' Results and Performances

Summaries of participants' results and performances in this PT study are presented in Table 19 and Figure 23.

Table 19 Summary of Participants' Results for Scored Analytes (all values are in µg/L)*

Lab. Code	S1 Diuron	S1 Imidacloprid	S2 Atrazine	S2 Lindane	S2 Metolachlor	S3 AMPA	S3 Glyphosate
Assigned Value	13.0	8.77	7.3	9.1	0.597	11.7	33.2
1	NT	NT	9.79	8.97	NT	10.55	33.2
2	14.5	8.5	6	<0.01	1	10	30
3	12.4	9.06	7.7	NT	0.617	NT	NT
4	<0.1	<0.1	<0.1	9.5	<0.1	NR	NR
5	17.06	NT	8.16	9.7	0.65	12.55	38.93
6	NT	NT	NT	7.62	NT	NT	NT
7	7.6	NT	6.3	9.7	0.68	NT	NT
8	< 0.2	NT	NT	7.811	NT	NT	NT
10	14.86	8.68	10.35	<0.1	0.62	9.7	31.7
11	13	NT	8.1	13	NT	NT	NT
12	NT	NT	NT	NT	NT	<10	32.54
13	15.9	9.2	6.4	20.5	0.5	10.3	32.6
14	NT	NT	NT	5.65	NT	<0.01	0.0232
15	10	<100	6.0	7.2	0.6	10	43
16	7.58	NT	5.35	7.1	< 1	NT	NT
17	12	6.4	5.95	12.1	0.58	31	11
18	15.3	9.5	8.1	10.01	NT	15.41	37
19	16	NT	6.8	8.4	<2	15	30
20	12	NT	7.75	11.6	0.53	<0.01	24.5

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

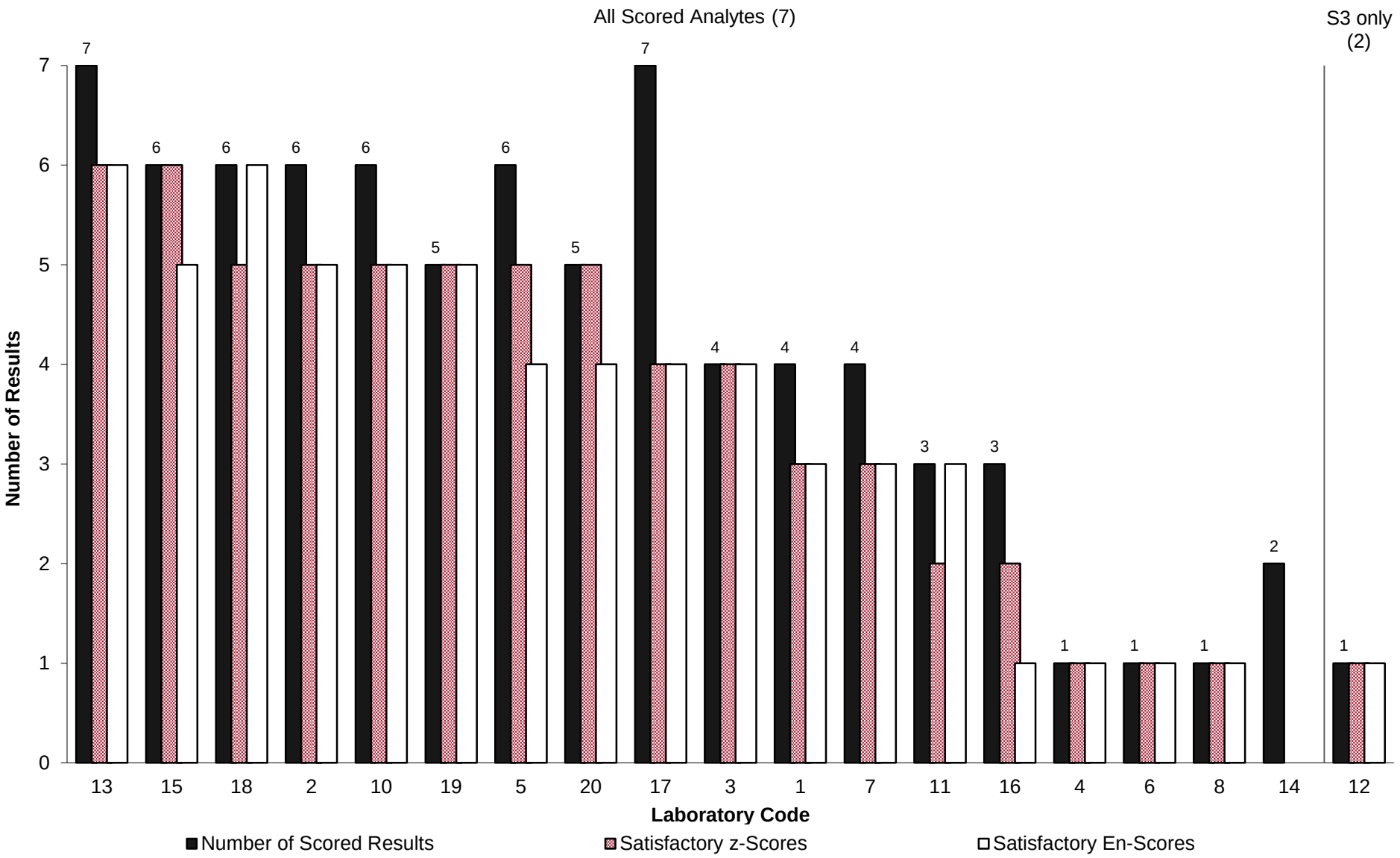


Figure 23 Summary of Participants' Performance

6.11 Comparison with Previous Studies

A summary of participation and rates of reported results in NMI Pesticides in Water PT studies over the last 10 studies (2014–2021) is presented in Figure 24.

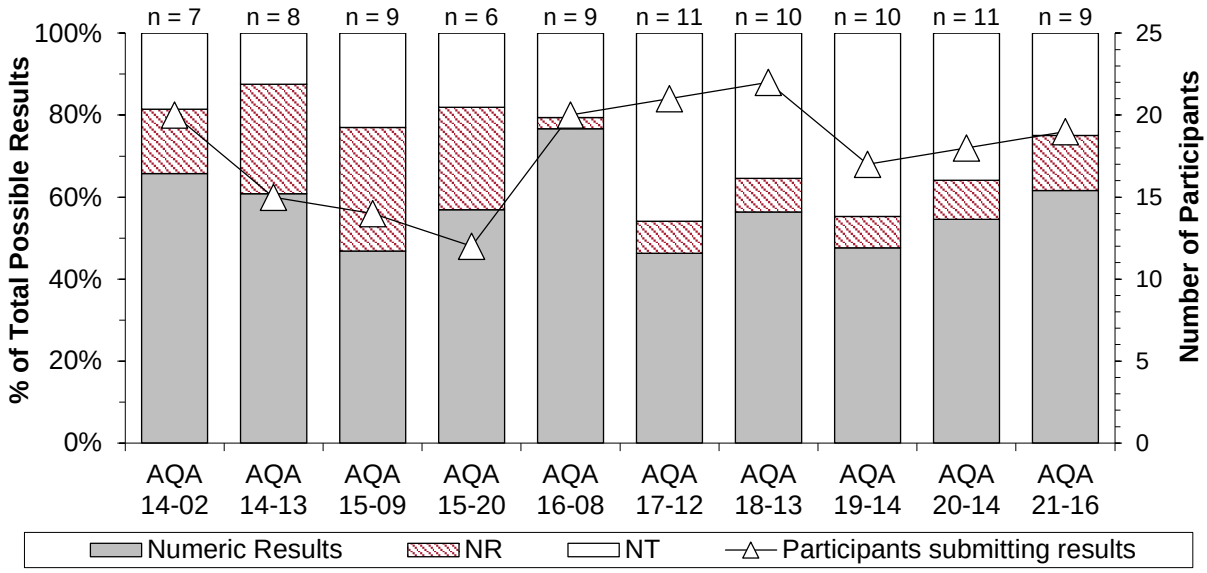


Figure 24 Summary of Participation and Reported Results in Pesticides in Water PT Studies (n = number of spiked analytes)

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 (2014–2021) is presented in Figure 25. 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 79% for z-scores and 75% for E_n-scores.

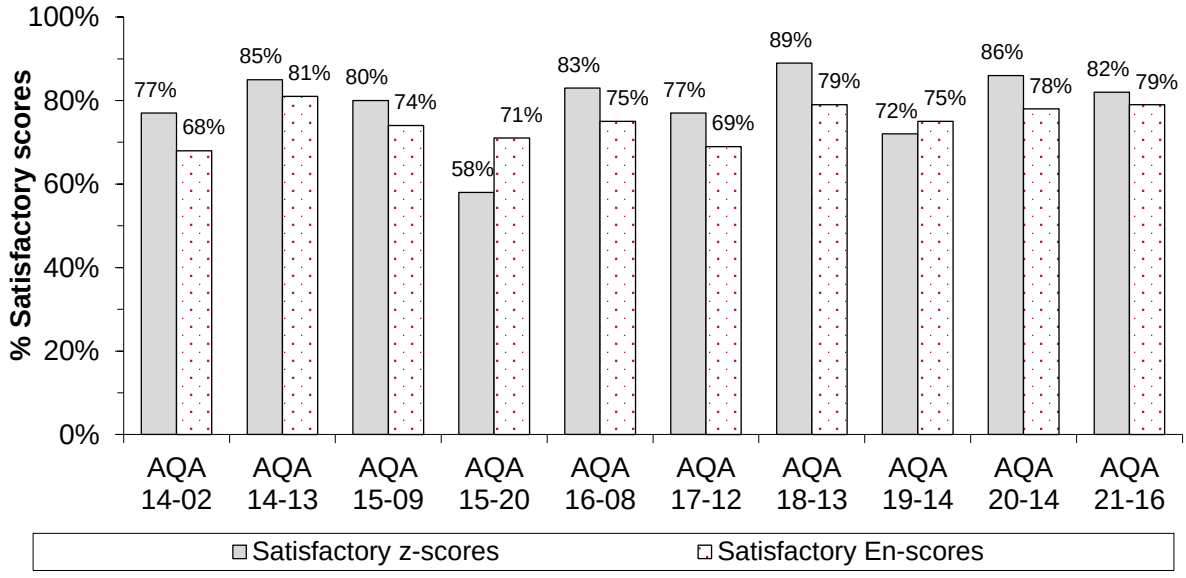


Figure 25 Satisfactory z-Scores and E_n-Scores in Pesticides in Water PT studies

Individual performance history reports are emailed to participants at the end of each PT study; the consideration of z-scores over time provides much more useful information than a single z-score. Over time, laboratories should expect at least 95% of their z-scores to lie within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ can occasionally occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line is an indication of laboratory bias.

7 REFERENCES

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[10] NATA, 2020, Update to Measurement Uncertainty resources, viewed January 2022, <https://nata.com.au/news/update-to-measurement-uncertainty-resources/>

[11] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd ed.

APPENDIX 1 – SAMPLE PREPARATION

The three samples were prepared from surface water obtained from Browns Waterhole in 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. The pH of the water used for Samples S2 and S3 was not adjusted.

The spiking solutions for Samples S1 and S2 were prepared by dissolving the pesticide standards in acetone, except for imidacloprid which was dissolved in isopropyl alcohol. The glyphosate and AMPA standards were dissolved in water. Diluted spiked solutions of MCPA and metolachlor were prepared.

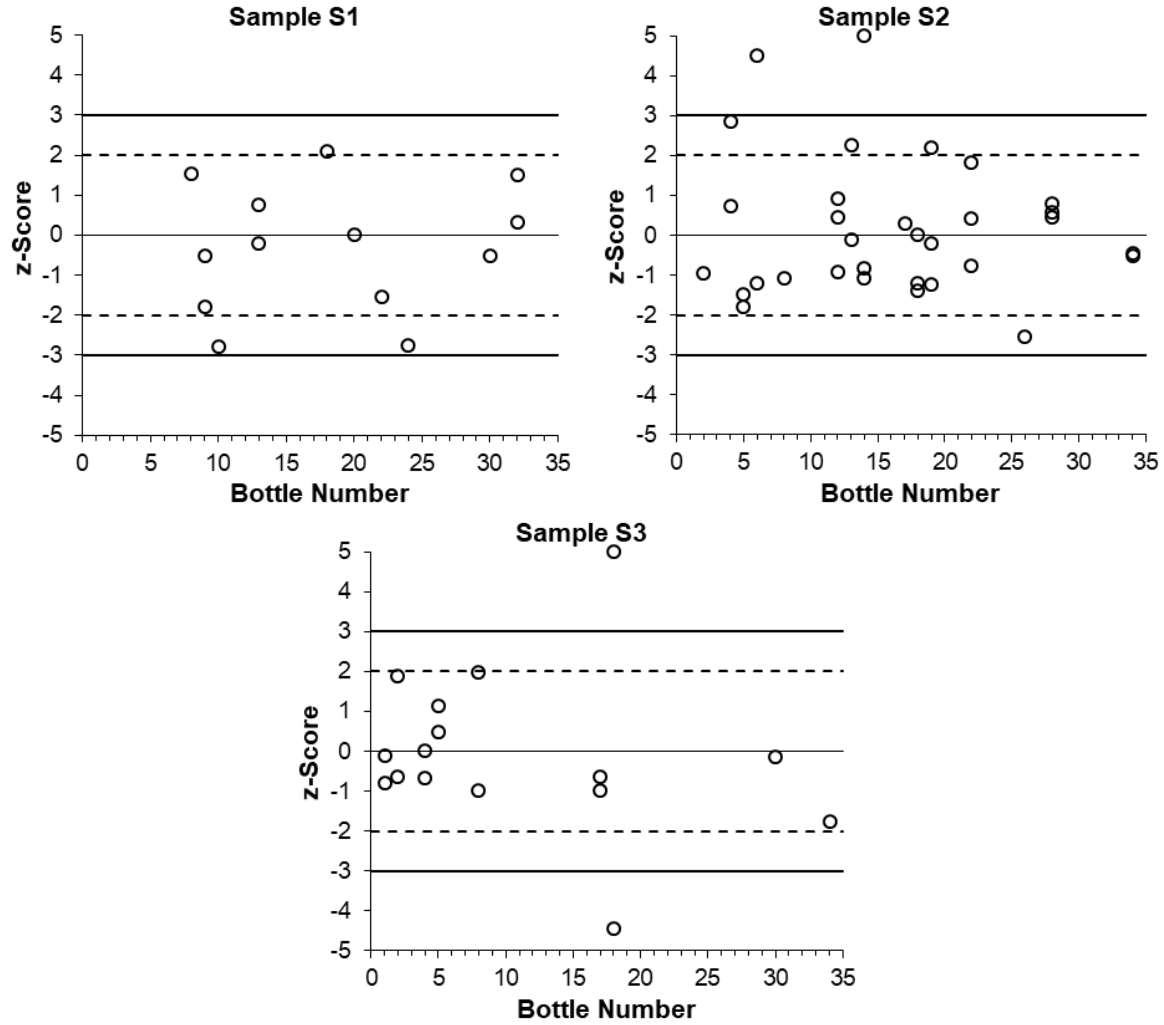
The water of each sample was stirred using a top-driven impeller stirrer for at least two hours after spiking. Samples S1 and S2 were then dispensed into 500 mL amber glass bottles. Sample S3 was dispensed into 500 mL PET bottles.

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

APPENDIX 2 – ASSESSMENT OF HOMOGENEITY AND TRANSPORTATION STABILITY

A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce homogeneous samples. The results of this study also have no reason to question the samples' homogeneity. Comparisons of z-scores obtained for all scored analytes to bottle number analysed by participants are presented in Figure 26 (gross errors have been removed, and only known bottle numbers, i.e. the participant received one bottle only or reported which bottle number they used for their result, have been included). No significant trend was observed.



z-Scores greater than 5 have been plotted at 5.

Figure 26 z-Score vs Bottle Number for Samples S1, S2 and S3

A2.2 Stability

No stability testing was conducted for this study, though previous use of these pesticides and similar analytes, as well as comparison between participant results and spiked values, gave assurance that they were stable. The samples were stored in a coolroom at 4 ºC after preparation and prior to dispatch. For dispatch, the samples were packaged into insulated polystyrene foam boxes with cooler bricks. Comparisons of results to days spend in transit for scored analytes for presented in Figures 27 to 29 (gross errors have been removed). No evidence of analyte degradation with respect to the amount of time spent in transit was observed.

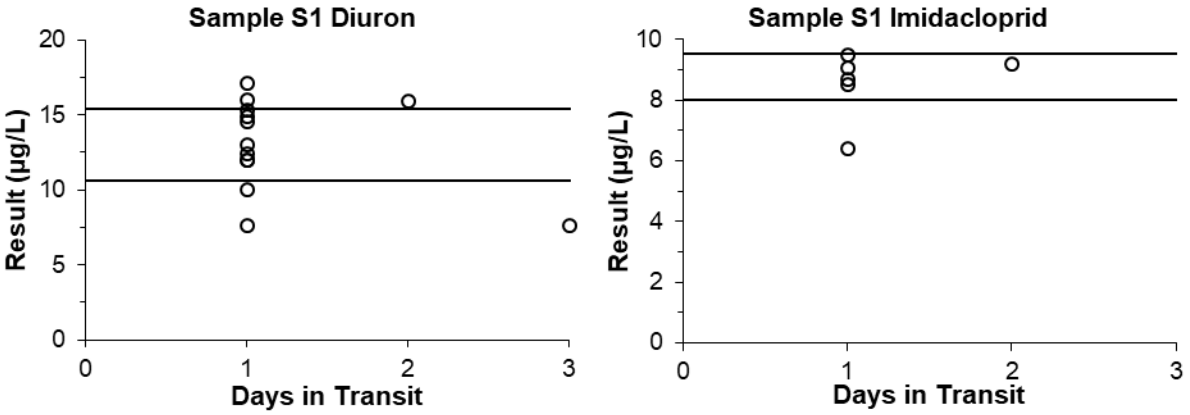


Figure 27 Result vs Days in Transit for Sample S1 Scored Analytes*

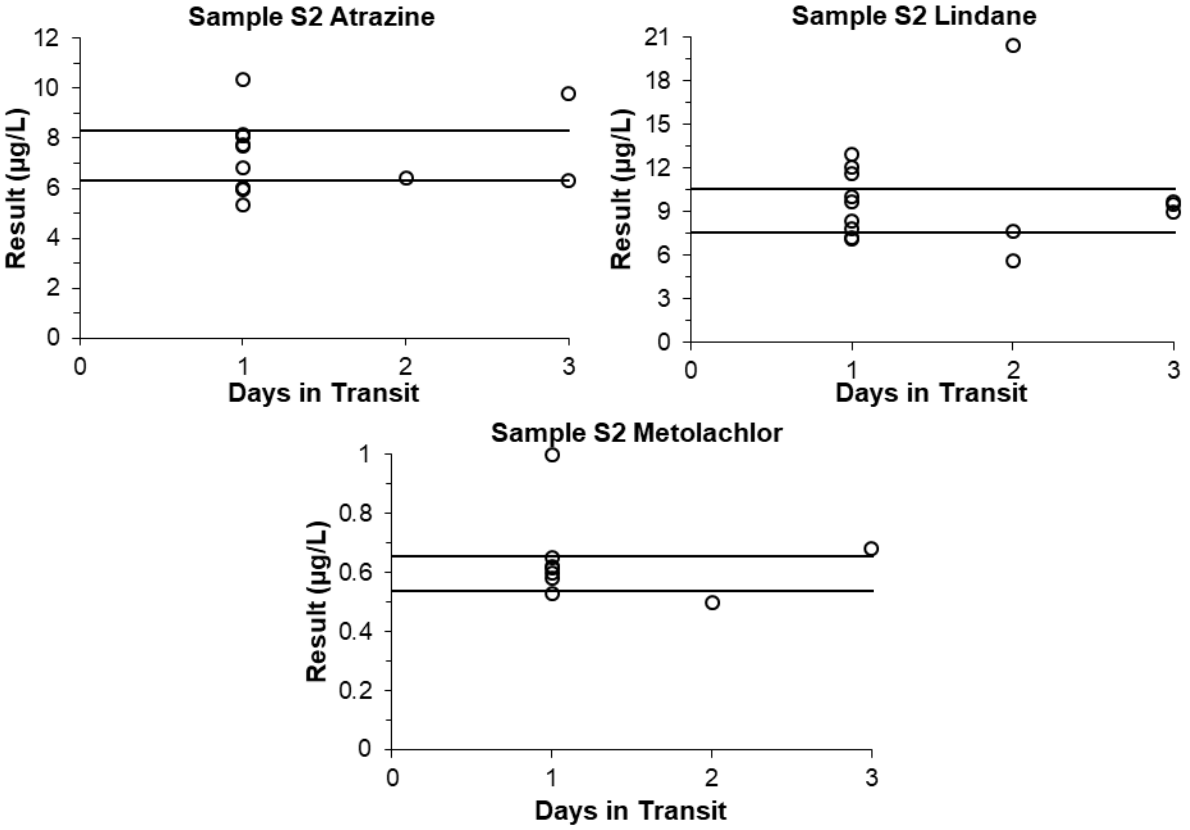


Figure 28 Result vs Days in Transit for Sample S2 Scored Analytes*

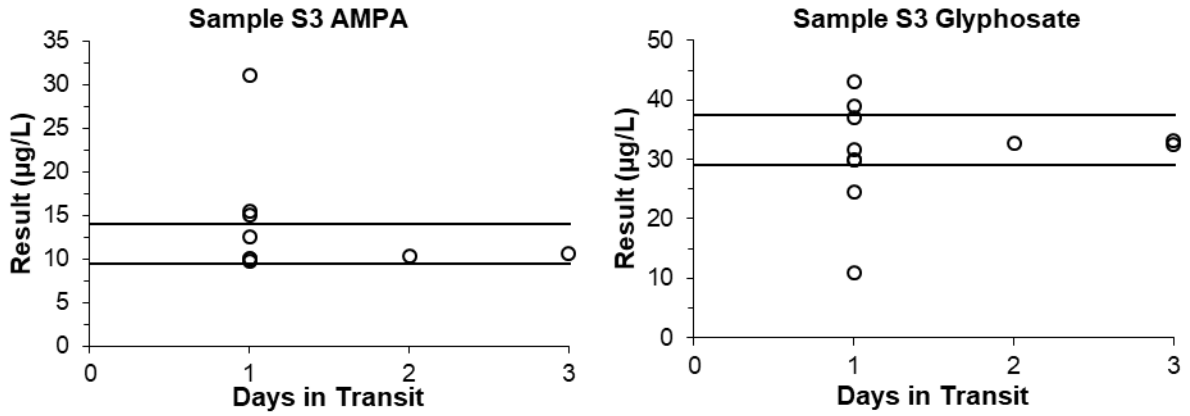


Figure 29 Result vs Days in Transit for Sample S3 Scored Analytes*

* Solid lines correspond to the assigned value ± U for each analyte

APPENDIX 3 – PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 20 to 29.

Table 20 Sample Volume Used for Analysis

Lab. Code	Samples S1 and S2 Volume (mL)	Sample S3 Volume (mL)
1	150	100
2		
3	100	NT
4	20	
5		
6	35	NT
7	250	NT
8	35	NT
10	500	500
11	500	NT
12	NT	10
13	50	
14	35	0.5
15	150	0.9
16	35-200	NT
17	50	5
18	Atrazine, Diuron, Imidacloprid, MCPA: 1 Endosulfan sulfate, Lindane: 50	1
19	100	2
20	500	0.5

Table 21 Methodology – Atrazine

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Instrument
1	Liquid-Liquid	None	hexane	GC-NPD
2				
3				LC-MS/MS
4	QuEChERS	N	Acetonitrile	LC-MS/MS
5				
6	NT			
7	Liquid-Liquid	Nil	DCM	GC-MS
8	NT			
10	Liquid-Liquid		DCM	GC-MS/MS
11	Direct Injection			LC-MS
12	NT			
13	SPE	None	DCM:EtOAC	GC-MS
14	NT			
15	Liquid-Liquid		DCM	GCMS
16	Liquid-Liquid	N/A	DCM	GC-MS/MS
17	Liquid-Liquid		DCM	GC-MS/MS
18	Direct Injection			LC-MS/MS
19	Liquid-Liquid	Nil	DCM	GC-MS/MS
20	Liquid-Liquid	None	DCM	GC-MS/MS

Table 22 Methodology – Diuron

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Instrument
1	NT			
2				
3				LC-MS/MS
4	QuEChERS	N	Acetonitrile	LC-MS/MS
5				
6	NT			
7	Liquid-Liquid	Nil	DCM	GC-MS
8				
10	Direct Injection	Filtration		LC-MS/MS
11	Direct Injection			LC-MS
12	NT			
13	Direct Injection	None	None	LC-MS/MS
14	NT			
15	Liquid-Liquid		DCM	GCMS
16	Liquid-Liquid	N/A	DCM/Ether	LC-DAD
17	Liquid-Liquid		Methanol	LC-MS/MS
18	Direct Injection			LC-MS/MS
19	SPE	Nil	Methanol/DCM	LC-MS/MS
20	Liquid-Liquid	None	DCM	GC-MS/MS

Table 23 Methodology – Endosulfan sulfate

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Instrument
1	Liquid-Liquid	None	hexane	GC-ECD
2				
3				GC-MS/MS
4	Liquid-Liquid	N	Hexane	GC-MS/MS
5				
6	Liquid-Liquid	N/A	DCM	GC-MS/MS
7	Liquid-Liquid	Nil	DCM	GC-ECD
8	Liquid-Liquid		DCM	GC-MS/MS
10	Liquid-Liquid		DCM	GC-MS/MS
11	Liquid-Liquid		DCM	GC-MS
12	NT			
13	SPE	None	DCM:EtOAC	GC-MS
14	Liquid-Liquid		DCM	GC-MS/MS
15	Liquid-Liquid		15%ether in hexane	GC-ECD
16	Liquid-Liquid	N/A	DCM	GC-MS/MS
17	Liquid-Liquid		DCM	GC-ECD
18	Liquid-Liquid		Hexane:Pentane	GC-ECD
19	Liquid-Liquid	Nil	DCM	GC-MS/MS
20	Liquid-Liquid	None	DCM	GC-MS/MS

Table 24 Methodology – Imidacloprid

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Instrument
1	NT			
2				
3				LC-MS/MS
4	QuEChERS	N	Acetonitrile	LC-MS/MS
5	NT			
6	NT			
7	NT			
8	NT			
10	Direct Injection	Filtration		LC-MS/MS
11	NT			
12	NT			
13	Direct Injection			LC-MS/MS
14	NT			
15	Direct Injection			HPLC-UV
16	NT			
17	Liquid-Liquid		Methanol	GC-MS/MS
18	Direct Injection			LC-MS/MS
19	NT			
20	NT			

Table 25 Methodology – Lindane

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Instrument
1	Liquid-Liquid	None	hexane	GC-ECD
2				
3	NT			
4	Liquid-Liquid	N	Hexane	GC-MS/MS
5				
6	Liquid-Liquid	N/A	DCM	GC-MS/MS
7	Liquid-Liquid	Nil	DCM	GC-ECD
8	Liquid-Liquid		DCM	GC-MS/MS
10	Liquid-Liquid		DCM	GC-MS/MS
11	Liquid-Liquid		DCM	GC-MS
12	NT			
13	SPE	None	DCM:EtOAC	GC-MS
14	Liquid-Liquid		DCM	GC-MS/MS
15	Liquid-Liquid		15%ether in hexane	GC-ECD
16	Liquid-Liquid	N/A	DCM	GC-MS/MS
17	Liquid-Liquid		DCM	GC-ECD
18	Liquid-Liquid		Hexane:Pentane	GC-ECD
19	Liquid-Liquid	Nil	DCM	GC-MS/MS
20	Liquid-Liquid	None	DCM	GC-MS/MS

Table 26 Methodology – MCPA

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Instrument
1	NT			
2				
3				LC-MS/MS
4	Direct Injection	N		LC-MS/MS
5				
6	NT			
7	NT			
8	NT			
10	NT			
11	Direct Injection			LC-MS
12	NT			
13	Direct Injection			LC-MS/MS
14	NT			
15	Liquid-Liquid		DCM	GCMS
16	Liquid-Liquid	N/A	DCM/Ether	LC-DAD
17	Liquid-Liquid		Toluene	GC-MS/MS
18	Direct Injection			LC-MS/MS
19	SPE	Nil	Methanol/DCM	LC-MS/MS
20	Liquid-Liquid	None	DCM	GC-MS/MS

Table 27 Methodology – Metolachlor

Lab. Code	Extraction	Clean-Up	Extraction Solvent	Instrument
1	NT			
2				
3				LC-MS/MS
4	QuEChERS	N	Acetonitrile	LC-MS/MS
5				
6	NT			
7	Liquid-Liquid	Nil	DCM	GC-MS
8	NT			
10	Direct Injection	Filtration		LC-MS/MS
11	NT			
12	NT			
13	Direct Injection			LC-MS/MS
14	NT			
15	Liquid-Liquid		DCM	GCMS
16	Liquid-Liquid	N/A	DCM/Ether	LC-DAD
17	Liquid-Liquid		Methanol	LC-MS/MS
18	NT			
19	SPE	Nil	Methanol/DCM	LC-MS/MS
20	Liquid-Liquid	None	DCM	GC-MS/MS

Table 28 Methodology – AMPA

Lab. Code	Extraction	Derivatisation Procedure	Derivatisation Agent	Instrument
1	Evaporation	Pre-column	FMOC-Cl	HPLC-FLD
2				
3	NT			
4				
5				
6	NT			
7	NT			
8	NT			
10	Direct Injection			LC-MS/MS
11	NT			
12	Direct Injection			LC-MS/MS
13	Direct Injection	None		LC-MS/MS
14	Direct Injection			LC-MS/MS
15	Direct Injection	Pre-column	FMOC-Cl	LCMSMS
16	NT			
17	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
18	Direct Injection	Pre-column	FMOC	LC-MS/MS
19	Direct Injection	Nil	Nil	LC-MS/MS
20	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS

Table 29 Methodology – Glyphosate

Lab. Code	Extraction	Derivatisation Procedure	Derivatisation Agent	Instrument
1	Evaporation	Pre-column	FMOC-Cl	HPLC-FLD
2				
3	NT			
4				
5				
6	NT			
7	NT			
8	NT			
10	Direct Injection			LC-MS/MS
11	NT			
12	Direct Injection			LC-MS/MS
13	Direct Injection	None		LC-MS/MS
14	Direct Injection			LC-MS/MS
15	Direct Injection	Pre-column	FMOC-Cl	LCMSMS
16	NT			
17	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
18	Direct Injection	Pre-column	FMOC	LC-MS/MS
19	Direct Injection	Nil	Nil	LC-MS/MS
20	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS

APPENDIX 4 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND E_N-SCORE CALCULATIONS

A4.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528:2015.[6] The associated uncertainties were estimated as according to Equation 4.

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

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 30.

Table 30 Uncertainty of Robust Average for Atrazine in Sample S2

Number of results (p)	14
Robust Average	7.3 µg/L
$S_{rob\ av}$	1.5 µg/L
$u_{rob\ av}$	0.5 µg/L
k	2
$U_{rob\ av}$	1.0 µg/L

Therefore, the robust average for atrazine in Sample S2 is 7.3 ± 1.0 µg/L.

A4.2 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 (Section 4).

A worked example is set out below in Table 31, using the result reported by Laboratory 2 for Sample S1 diuron.

Table 31 z-Score and E_n-Score for Sample S1 Diuron Result Reported by Laboratory 2

Participant Result (µg/L)	Assigned Value (µg/L)	Target Standard Deviation	z-Score	E_n-Score
14.5 ± 4.4	13.0 ± 2.4	15% as PCV, or: 0.15 × 13.0 = 1.95 µg/L	z-Score = $\frac{14.5-13.0}{1.95}$ = 0.77	E_n-Score = $\frac{14.5-13.0}{\sqrt{4.4^2+2.4^2}}$ = 0.30

APPENDIX 5 – ACRONYMS AND ABBREVIATIONS

AMPA	Aminomethylphosphonic acid
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DAD	Diode Array Detector
DCM	Dichloromethane
DI	Direct Injection
ECD	Electron Capture Detector
EtOAc	Ethyl Acetate
FLD	Fluorescence Detector
FMOC	Fluorenylmethyloxycarbonyl
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
LOR	Limit of Reporting
Max.	Maximum
MCPA	2-methyl-4-chlorophenoxyacetic acid
Md	Median
MeOH	Methanol
Min.	Minimum
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
N	Number of numeric results
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
Total DDT	Total amount of DDD, DDE and DDT
PCV	Performance Coefficient of Variation
PENT	Pentane
PT	Proficiency Test
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
UV	Ultraviolet (detector)

END OF REPORT