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National Measurement Institute

Proficiency Test Final Report AQA 23-20 Pesticides in River Water

February 2024

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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.

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SUMMARY

AQA 23-20 Pesticides in River Water commenced in October 2023. Twenty-four laboratories registered to participate, and twenty-three participants submitted results.

The sample set consisted of three river water samples. Samples were prepared in the Sydney NMI laboratory using water from the Wingecarribee River in New South Wales, Australia.

Of 251 results, 176 numeric results (70%) were submitted. Nine results were a 'less than' value (< *x*) or Not Reported (NR), and 66 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 river water.*

Laboratories **3**, **8**, **13** and **21** reported numeric results for all scored analytes in this study.

Five participants did not report numeric results for analytes which they tested for and were present in the test samples (total of seven results). Three participants reported numeric results for analytes that were not spiked into the test samples by the study coordinator (total of 16 results).

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

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

Of 172 *z*-scores, 152 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Of 166 E_n-scores, 125 (75%) 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 **21** returned acceptable *z*-scores and E_n-scores across all ten scored analytes.

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

Participants reported a wide variety of methods to analyse the range of pesticides considered in this study.

Eight participants reported correcting their results for recoveries.

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

Of 176 numeric results, 158 (90%) were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 1.4% to 59%.

- *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 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, vegetables and herbs, 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 river water;
- compare the performance of participants and assess their accuracy in the measurement of pesticides in river water;
- evaluate the participants' methods for the measurement of pesticides in river 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,[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:

Invitations sent	17/10/2023
Samples sent	13/11/2023
Results due	12/12/2023
Interim Report	13/12/2023
Preliminary Report	14/12/2023

2.2 Participation and Laboratory Code

Twenty-four laboratories registered to participate in this study, and all participants were assigned a confidential laboratory code number for this study. Twenty-three 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]

Participants were provided with a list of analytes that were potentially spiked into Samples S1 and S2; this list 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

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

2.4 Test Material Preparation

Water samples were prepared by spiking river water 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 Values of Test Samples

Sample	Analyte	Spiked Value (µg/L)	Uncertainty* (µg/L)
S1	Acetamiprid	7.50	0.38
	Atrazine	11.4	0.6
	Fenthion	10.1	0.5
	Lindane	9.98	0.50
S2	Chlorpyrifos	20.3	1.0
	Dieldrin	5.01	0.25
	Ethion	8.77	0.44
	Imidacloprid	16.6	0.8
	Simazine	5.00	0.25
S3	AMPA	19.0	1.0
	Glyphosate	27.2	1.4

* 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, stored and dispatched using a process that has been demonstrated to produce sufficiently homogeneous and stable samples in previous NMI pesticides in river 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 values. Assigned values for all scored analytes were within 63% to 103% of the spiked values, which is similar to what has been observed in previous NMI pesticides in river water studies.

2.6 Test Material Storage, Dispatch and Receipt

After preparation, the samples were stored at 4 °C. Samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 13 November 2023.

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.
- If analyses cannot be commenced on the day of receipt, please store the samples chilled.
- 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 1 December 2023 by email to proficiency@measurement.gov.au.

The results due date was extended to 12 December 2023 in response to several participants' requests, due to their end-of-year staffing constraints.

2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 13 December 2023.

A Preliminary Report was emailed to all participants on 14 December 2023. This report included a summary of the results reported by participants, assigned values, performance coefficients of variation (PCVs), *z*-scores and E_n-scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Participants' Test Methods

Participants were requested to provide information about their test methods. Responses are presented in Appendix 4.

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. Some responses may be modified so that the participant cannot be identified.

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	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	NATA General Accreditation Guidance Estimating and Reporting Measurement Uncertainty of Chemical Test Results
2	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	Eurachem/CITAC Guide
3	Top Down - reproducibility (standard deviation) from PT studies used directly	Control samples - SS Duplicate analysis Instrument calibration		
4	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
6				
7	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis	CRM	Eurachem/CITAC Guide
8	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis Instrument calibration		Eurachem/CITAC Guide
9	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Instrument calibration	Standard purity	ISO/GUM

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
10	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	CRM Instrument calibration Recoveries of SS Standard purity	NMI Uncertainty Course
12	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis		
13	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis	CRM	ISO/GUM
14	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	NMI Uncertainty Course
15	Standard deviation of replicate analyses multiplied by 2 or 3	Standard deviation from PT studies only		ISO/GUM
16	Standard deviation of replicate analyses multiplied by 2 or 3			
17		Duplicate analysis	Standard purity	ISO/GUM
18				
19	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis Instrument calibration	Instrument calibration Laboratory bias from PT studies Recoveries of SS Standard purity	Eurachem/CITAC Guide
20	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies Recoveries of SS	Eurachem/CITAC Guide
21	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	CRM Recoveries of SS	ISO/GUM
22	Repeatability precision - based upon internal historical data	Control samples - CRM	CRM Laboratory bias from PT studies	
23	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
24	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	CRM Recoveries of SS	Eurachem/CITAC Guide

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

Participants were also requested to report their coverage factor. Reported coverage factors are presented in Table 4.

Table 4 Coverage Factor

Lab. Code	Coverage Factor
1	2
2	2
13	2
14	2
21	2.3
22	2

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 5; some responses may be modified so that the participant cannot be identified.

Table 5 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
1	S3	Glyphosate and AMPA results were corrected for surrogate recovery.	
7	S3	Unfortunately these two analytes are not analysed onsite.	
	All	It was great to have the 100mL option for sample volume.	Thank you for your feedback. We are looking into providing this option for more samples in future.
10	All	1/ NT = Laboratory does not test for this analyte 2/ ND = Not detected, below method reporting limit 3/ NR = Uncertainty not reported.	
14	S3	S3 was analysed 23/11/23	
20	S3	High uncertainty is expected to the AMPA result reported due to the LOR for our in-house method is 30 ug/L.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 16 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), as well as other estimates of analyte concentration. 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.

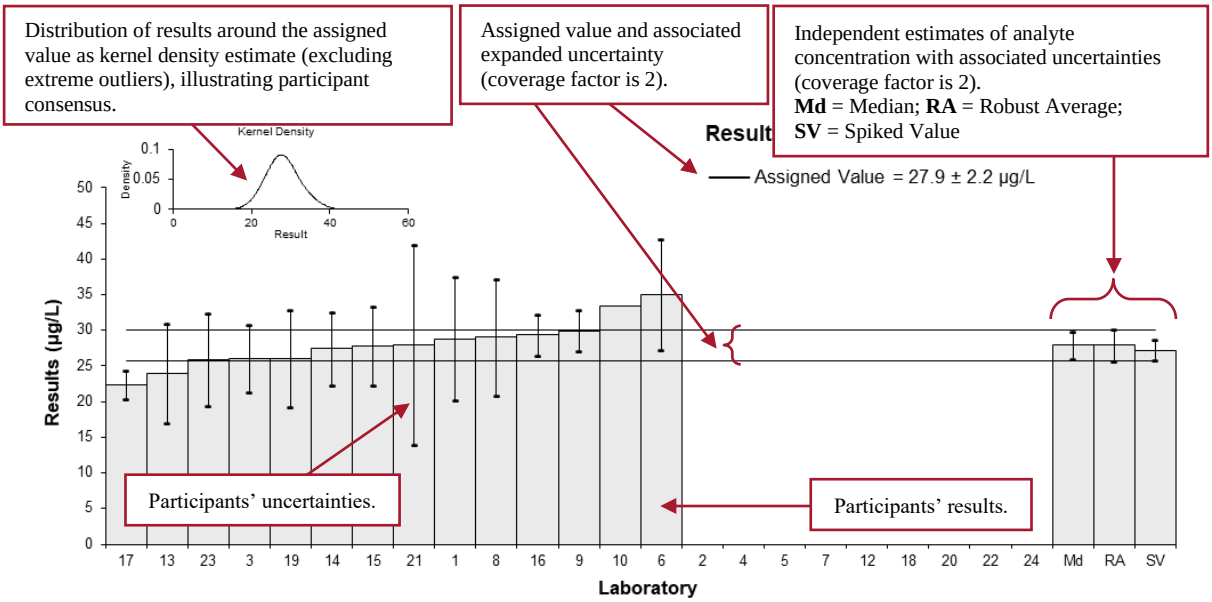


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

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, if applicable.[3,4] Extreme outliers were obvious blunders, e.g. results reported with incorrect units, 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 3).

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.[6]

4.5 Performance Coefficient of Variation

The 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 for Proficiency Assessment

The target standard deviation for proficiency assessment (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 for proficiency assessment from Equation 1

For the absolute value of a *z*-score:

- $|z| \leq 2.0$ is acceptable;
- $2.0 < |z| < 3.0$ is questionable; and
- $|z| \geq 3.0$ is unacceptable.

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 acceptable; and
- $|E_n| > 1.0$ is unacceptable.

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 6

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	Acetamiprid
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	NT	NT	NT
6	9.5	NR	NR
7	NT	NT	NT
8	NT	NT	NT
9	NT	NT	NT
10	NT	NT	NT
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	7.74	0.8	NR
18	6.2	1.9	NR
19	NT	NT	NT
20	NT	NT	NT
21	8.1	4.1	108
22	NT	NT	NT
23	NT	NT	NT
24	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	7.50	0.38
Robust Average	NA (N<6)	
Median	7.9	1.6
Mean	7.9	
N	4	
Max	9.5	
Min	6.2	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

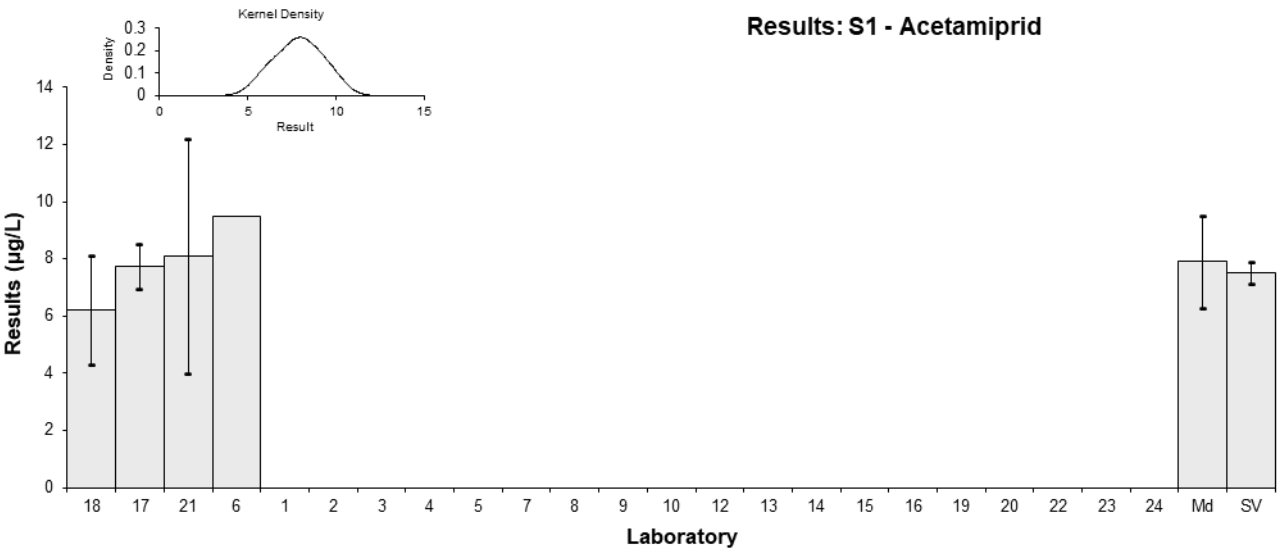

Kernel Density
Density
0.3
0.2
0.1
0
0
5
10
15
Result
Results: S1 - Acetamiprid
Results (µg/L)
14
12
10
8
6
4
2
0
18
17
21
6
1
2
3
4
5
7
8
9
10
12
13
14
15
16
19
20
22
23
24
Md
SV
Laboratory

Figure 2

Table 7

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	Atrazine
Unit	µg/L

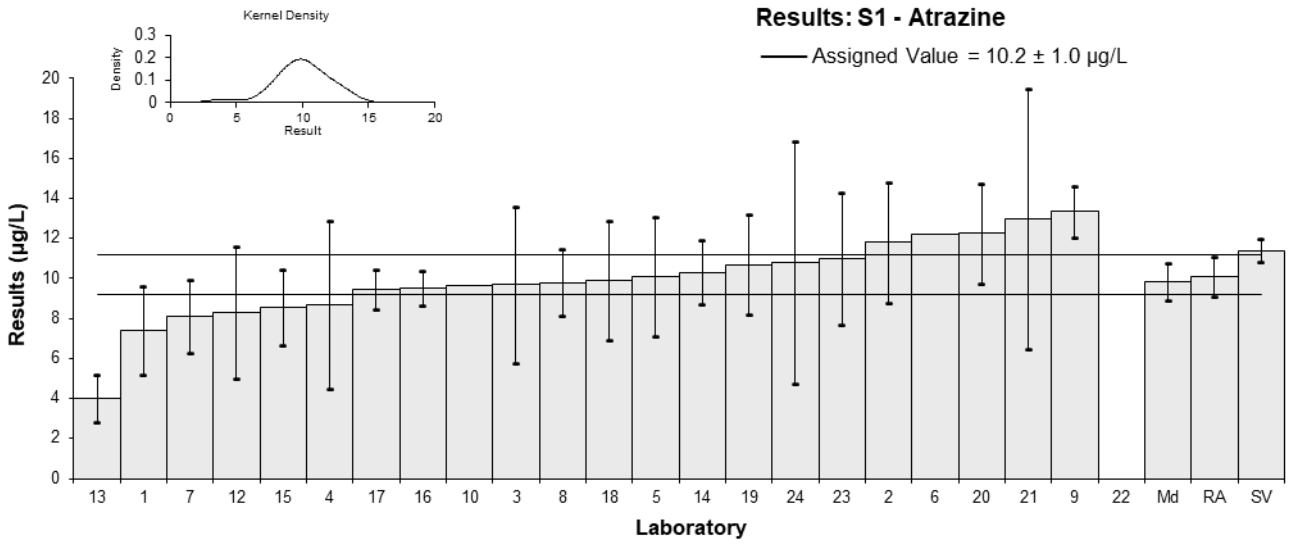
Participant Results

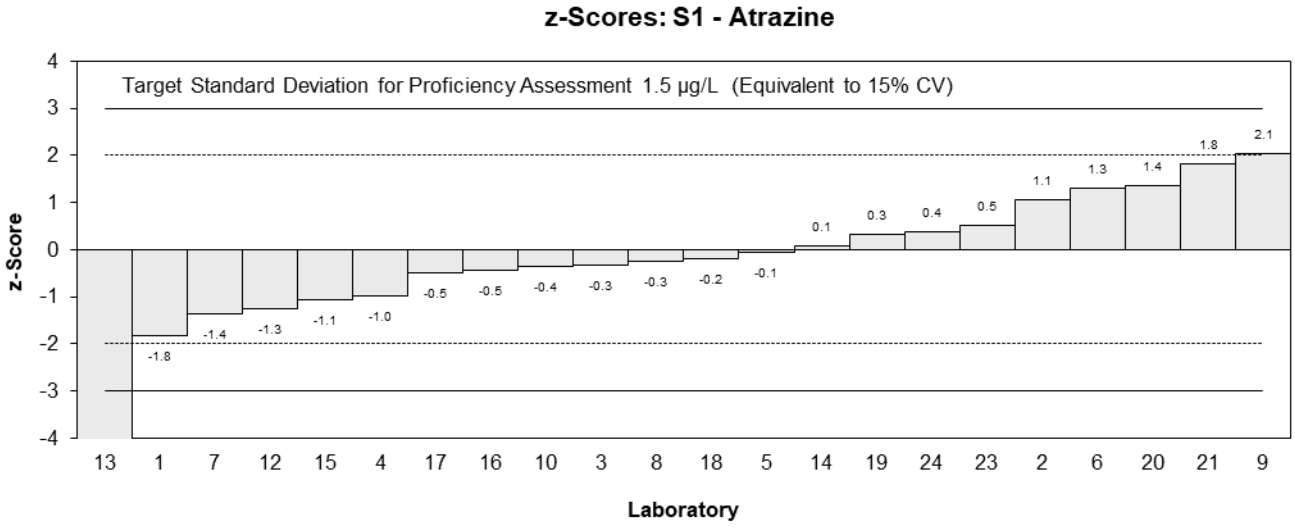
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	7.41	2.22	NR	-1.82	-1.15
2	11.8	3	88.6	1.05	0.51
3	9.7	3.9	NR	-0.33	-0.12
4	8.7	4.2	NR	-0.98	-0.35
5	10.1	3	110	-0.07	-0.03
6	12.2	NR	NR	1.31	2.00
7	8.1	1.81	NR	-1.37	-1.02
8	9.8	1.67	NR	-0.26	-0.21
9	13.33	1.3	81	2.05	1.91
10	9.66	NR	NR	-0.35	-0.54
12	8.27	3.3	56	-1.26	-0.56
13*	4	1.2	NR	-4.05	-3.97
14	10.3	1.6	NR	0.07	0.05
15	8.558	1.89	99	-1.07	-0.77
16	9.51	0.89	101	-0.45	-0.52
17	9.44	1.0	NR	-0.50	-0.54
18	9.9	3	NR	-0.20	-0.09
19	10.7	2.5	NR	0.33	0.19
20	12.26	2.5	NR	1.35	0.77
21	13	6.5	101	1.83	0.43
22	NT	NT	NT		
23	11	3.3	NR	0.52	0.23
24	10.8	6.04	NR	0.39	0.10

* Outlier, see Section 4.2

Statistics

Assigned Value	10.2	1.0
Spike Value	11.4	0.6
Robust Average	10.1	1.0
Median	9.85	0.91
Mean	9.93	
N	22	
Max	13.33	
Min	4	
Robust SD	1.9	
Robust CV	19%	


Kernel Density
Density
Result
Results: S1 - Atrazine
Assigned Value = 10.2 ± 1.0 µg/L
Results (µg/L)
13 1 7 12 15 4 17 16 10 3 8 18 5 14 19 24 23 2 6 20 21 9 22 Md RA SV
Laboratory


z-Scores: S1 - Atrazine
Target Standard Deviation for Proficiency Assessment 1.5 µg/L (Equivalent to 15% CV)
z-Score
13 1 7 12 15 4 17 16 10 3 8 18 5 14 19 24 23 2 6 20 21 9
Laboratory

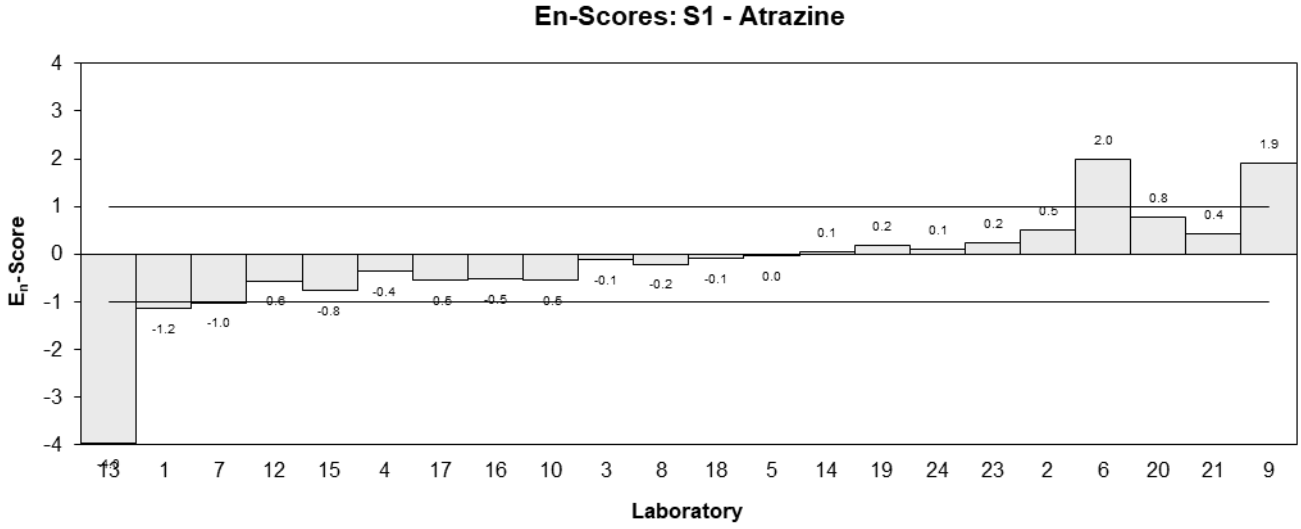

En-Scores: S1 - Atrazine
En-Score
13 1 7 12 15 4 17 16 10 3 8 18 5 14 19 24 23 2 6 20 21 9
Laboratory

Figure 3

Table 8

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	Fenthion
Unit	µg/L

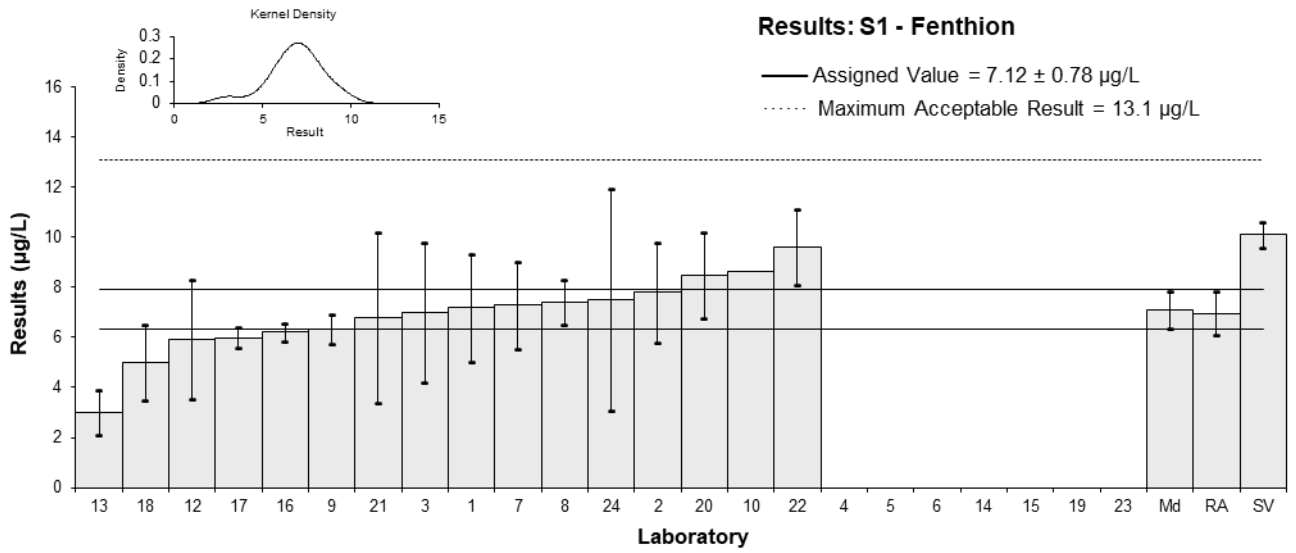
Participant Results

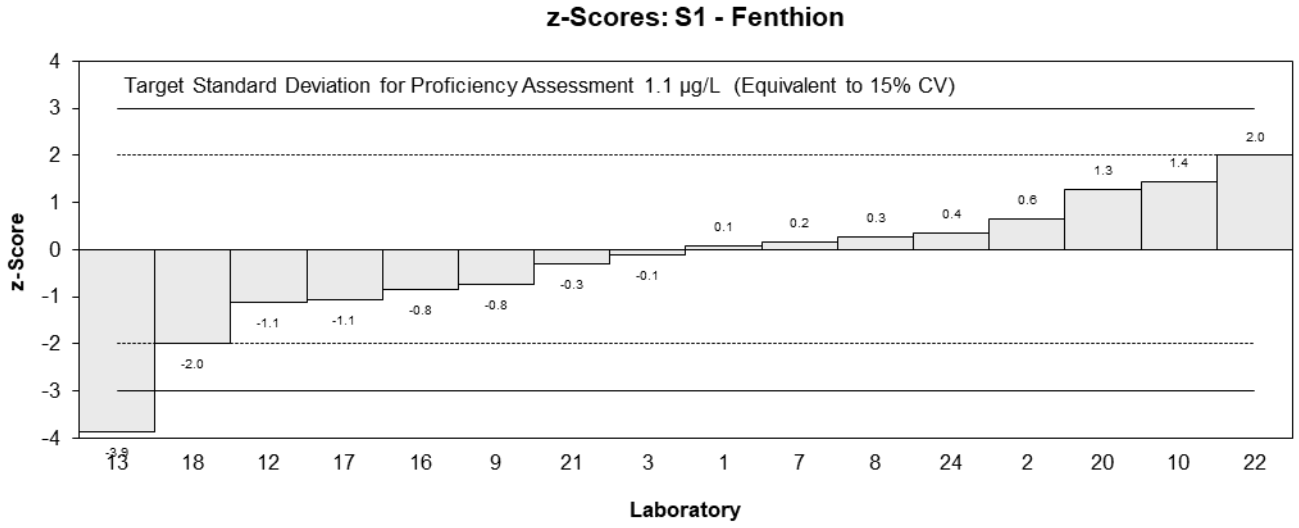
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	7.19	2.16	NR	0.07	0.03
2	7.8	2	95.1	0.64	0.32
3	7.0	2.8	NR	-0.11	-0.04
4	NT	NT	NT		
5	NT	NT	NT		
6	NT	NT	NT		
7	7.3	1.74	NR	0.17	0.09
8	7.4	0.91	NR	0.26	0.23
9	6.32	0.6	106	-0.75	-0.81
10	8.65	NR	NR	1.43	1.96
12	5.92	2.4	76	-1.12	-0.48
13*	3	0.9	NR	-3.86	-3.46
14	NT	NT	NT		
15	NT	NT	NT		
16	6.22	0.35	42	-0.84	-1.05
17	5.99	0.4	NR	-1.06	-1.29
18	5.0	1.5	NR	-1.99	-1.25
19	NT	NT	NT		
20	8.49	1.7	NR	1.28	0.73
21	6.8	3.4	118	-0.30	-0.09
22	9.6	1.5	96	2.00▼	
23	NT	NT	NT		
24	7.5	4.43	NR	0.36	0.08

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	7.12	0.78
Spike Value	10.1	0.5
Robust Average	6.97	0.85
Max Acceptable Result	13.1	
Median	7.10	0.76
Mean	6.89	
N	16	
Max	9.6	
Min	3	
Robust SD	1.4	
Robust CV	20%	


Kernel Density
Density
Result
Results: S1 - Fenthion
Assigned Value = 7.12 ± 0.78 µg/L
Maximum Acceptable Result = 13.1 µg/L
Results (µg/L)
Laboratory
13 18 12 17 16 9 21 3 1 7 8 24 2 20 10 22 4 5 6 14 15 19 23 Md RA SV


z-Scores: S1 - Fenthion
Target Standard Deviation for Proficiency Assessment 1.1 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
13 18 12 17 16 9 21 3 1 7 8 24 2 20 10 22
-3.9 -2.0 -1.1 -1.1 -0.8 -0.8 -0.3 -0.1 0.1 0.2 0.3 0.4 0.6 1.3 1.4 2.0

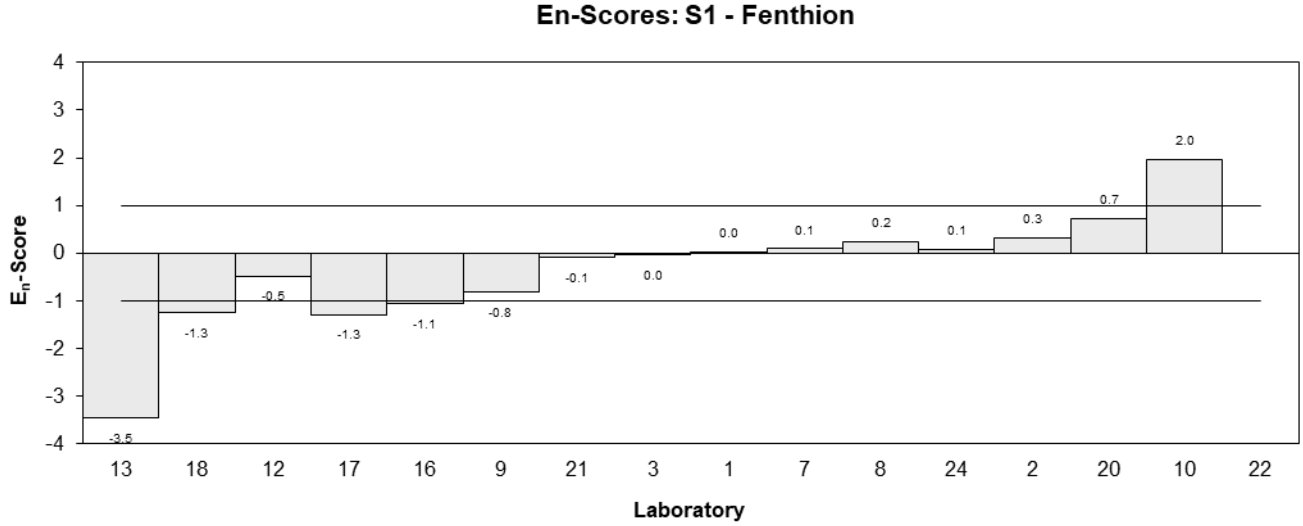

En-Scores: S1 - Fenthion
En-Score
Laboratory
13 18 12 17 16 9 21 3 1 7 8 24 2 20 10 22
-3.5 -1.3 -0.5 -1.3 -1.1 -0.8 -0.1 0.0 0.0 0.1 0.2 0.1 0.3 0.7 2.0

Figure 4

Table 9

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	Lindane
Unit	µg/L

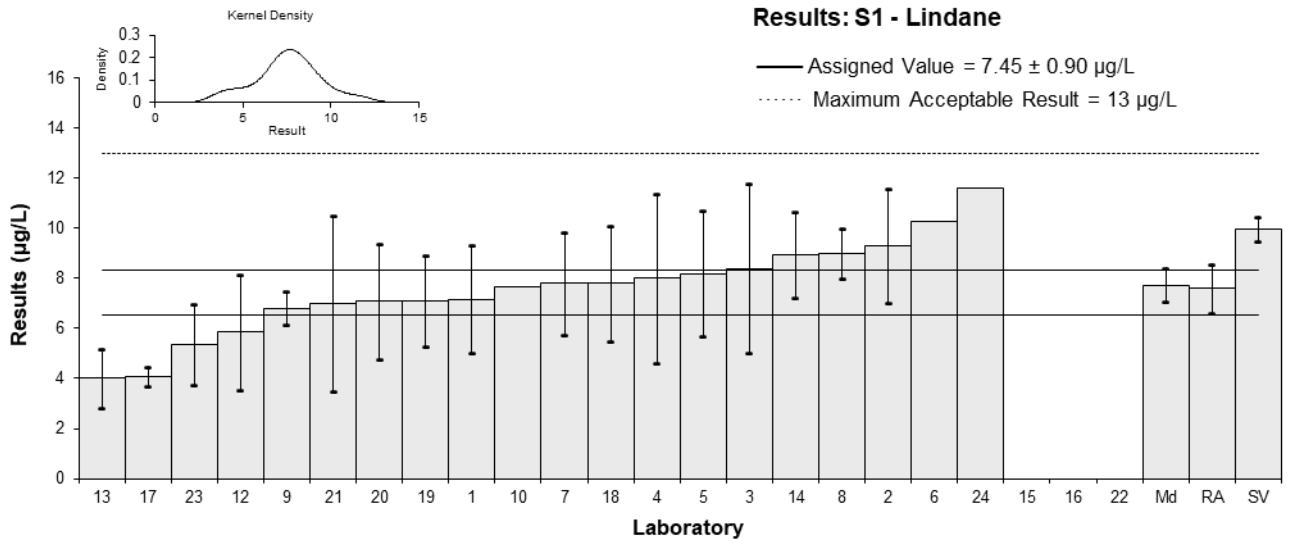
Participant Results

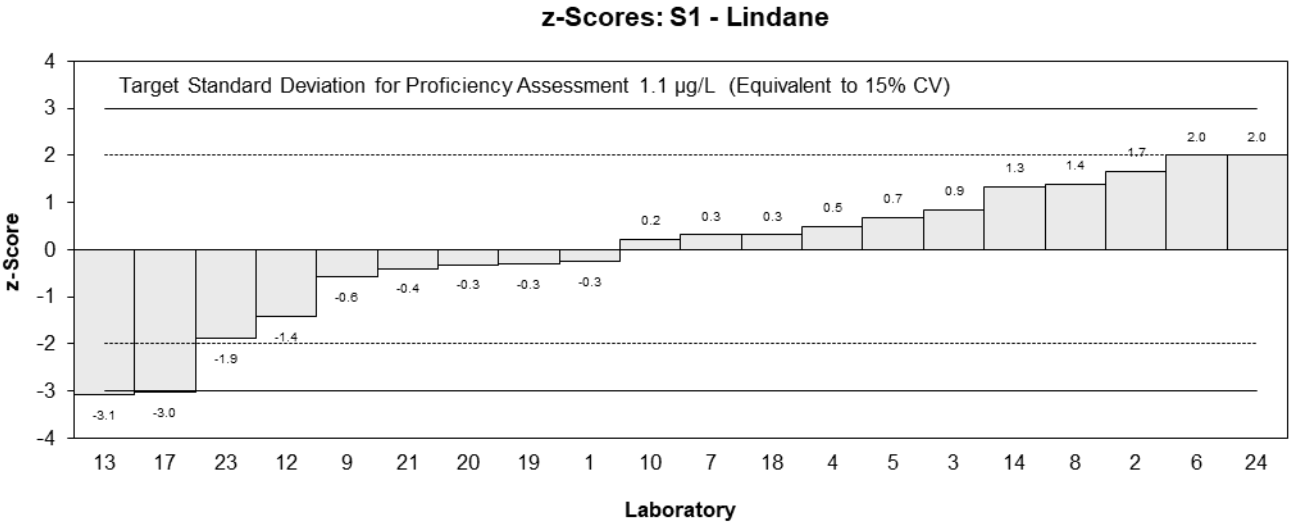
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	7.16	2.15	NR	-0.26	-0.12
2	9.3	2.3	85.6	1.66	0.75
3	8.4	3.4	NR	0.85	0.27
4	8	3.4	NR	0.49	0.16
5	8.2	2.5	98	0.67	0.28
6	10.3	NR	NR	2.00▼	
7	7.8	2.05	NR	0.31	0.16
8	9	1	NR	1.39	1.15
9	6.81	0.65	103	-0.57	-0.58
10	7.68	NR	NR	0.21	0.26
12	5.85	2.3	57	-1.43	-0.65
13	4	1.2	NR	-3.09	-2.30
14	8.95	1.70	NR	1.34	0.78
15	NT	NT	NT		
16	NT	NT	NT		
17	4.07	0.4	NR	-3.02	-3.43
18	7.8	2.3	NR	0.31	0.14
19	7.1	1.8	NR	-0.31	-0.17
20	7.09	2.3	NR	-0.32	-0.15
21	7	3.5	91	-0.40	-0.12
22	<1	NR	NR		
23	5.35	1.605	NR	-1.88	-1.14
24*	11.6	NR	NR	2.00▼	

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	7.45	0.90
Spike Value	9.98	0.50
Robust Average	7.59	0.98
Max Acceptable Result	13.0	
Median	7.74	0.69
Mean	7.57	
N	20	
Max	11.6	
Min	4	
Robust SD	1.7	
Robust CV	23%	


Kernel Density
Density
Result
Results: S1 - Lindane
Assigned Value = 7.45 ± 0.90 µg/L
Maximum Acceptable Result = 13 µg/L
Results (µg/L)
13 17 23 12 9 21 20 19 1 10 7 18 4 5 3 14 8 2 6 24 15 16 22 Md RA SV
Laboratory


z-Scores: S1 - Lindane
Target Standard Deviation for Proficiency Assessment 1.1 µg/L (Equivalent to 15% CV)
z-Score
-3.1 -3.0 -1.9 -1.4 -0.6 -0.4 -0.3 -0.3 -0.3 0.2 0.3 0.3 0.5 0.7 0.9 1.3 1.4 1.7 2.0 2.0
13 17 23 12 9 21 20 19 1 10 7 18 4 5 3 14 8 2 6 24
Laboratory

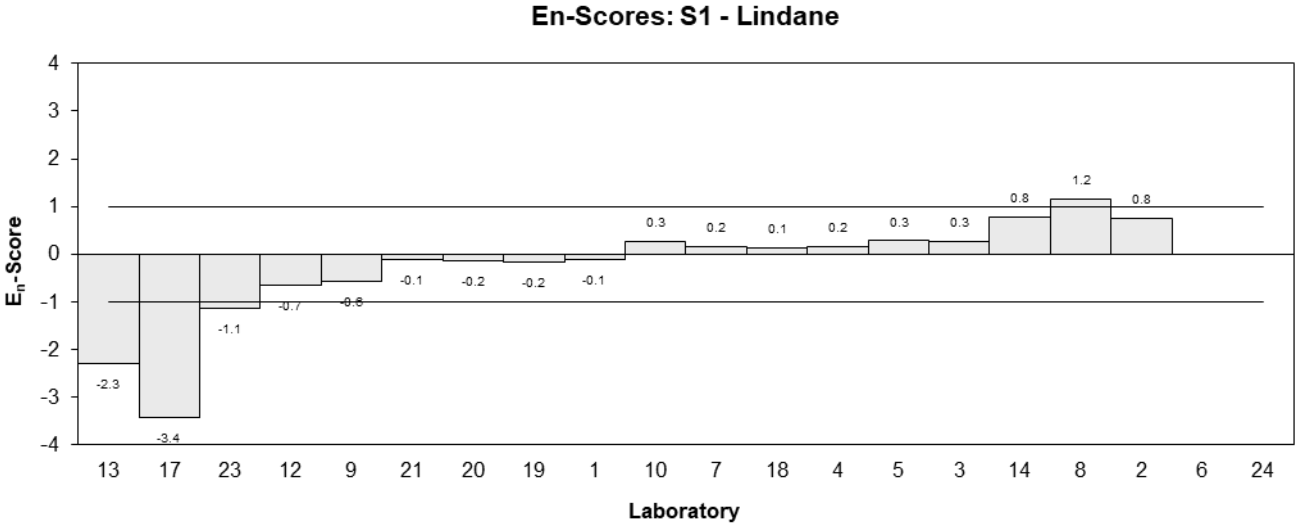

En-Scores: S1 - Lindane
En-Score
-2.3 -3.4 -1.1 -0.7 -0.6 -0.1 -0.2 -0.2 -0.1 0.3 0.2 0.1 0.2 0.3 0.3 0.8 1.2 0.8
13 17 23 12 9 21 20 19 1 10 7 18 4 5 3 14 8 2 6 24
Laboratory

Figure 5

Table 10

Sample Details

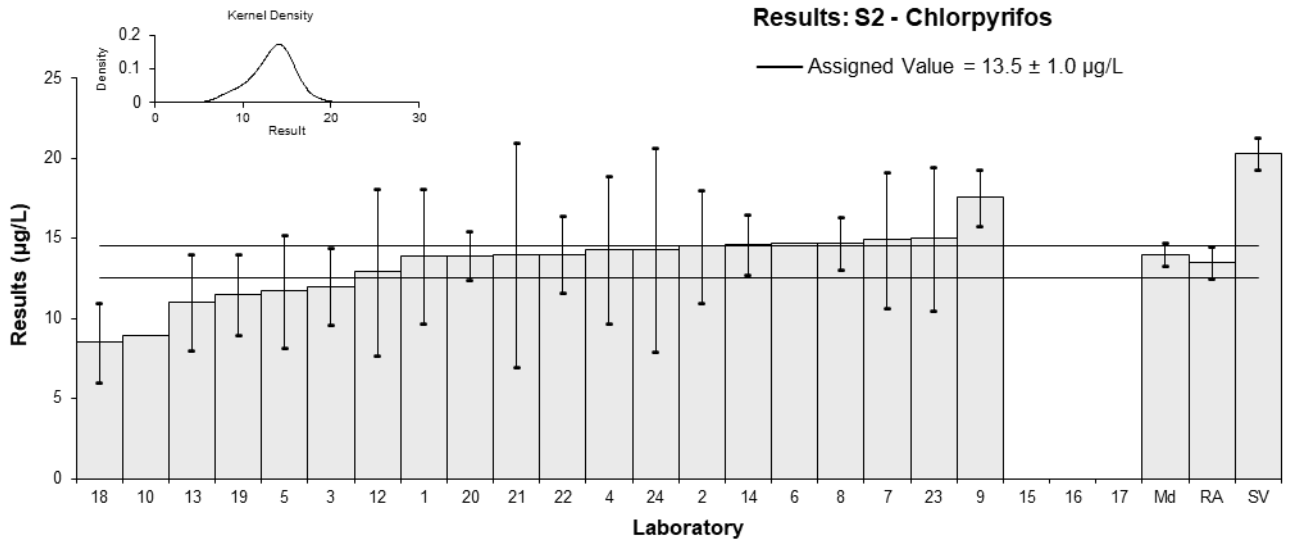
Sample No.	S2
Matrix	River Water
Analyte	Chlorpyrifos
Unit	µg/L

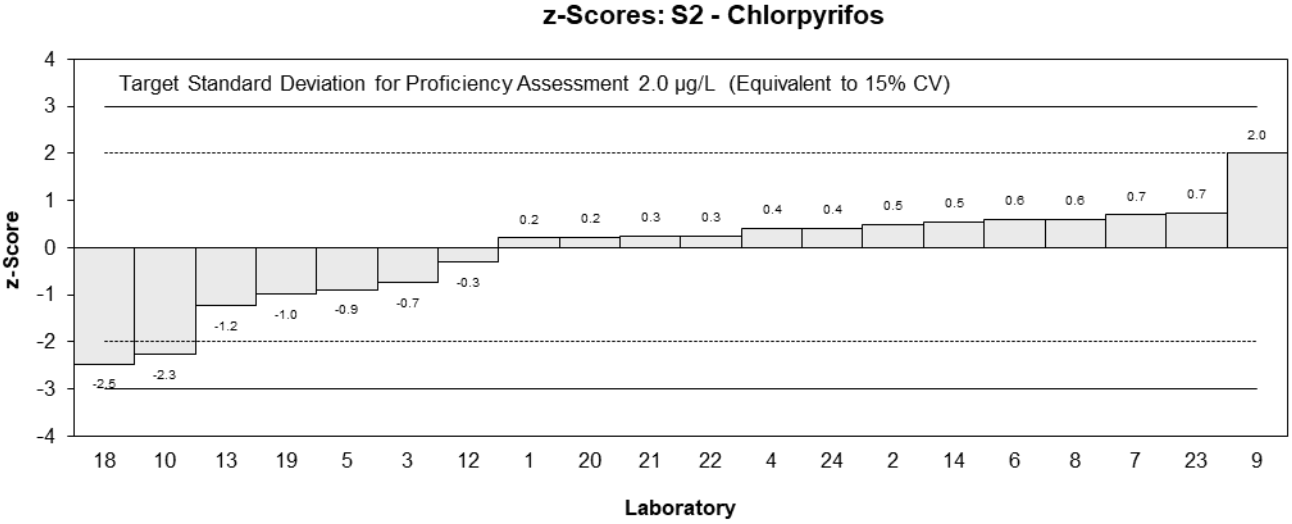
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	13.9	4.17	NR	0.20	0.09
2	14.5	3.5	100	0.49	0.27
3	12	2.4	NR	-0.74	-0.58
4	14.3	4.6	NR	0.40	0.17
5	11.7	3.5	98	-0.89	-0.49
6	14.7	NR	NR	0.59	1.20
7	14.9	4.21	NR	0.69	0.32
8	14.7	1.65	NR	0.59	0.62
9	17.55	1.75	104	2.00	2.01
10	8.92	NR	NR	-2.26	-4.58
12	12.9	5.2	100	-0.30	-0.11
13	11	3	NR	-1.23	-0.79
14	14.6	1.9	NR	0.54	0.51
15	NT	NT	NT		
16	NT	NT	NT		
17	NT	NT	NT		
18	8.5	2.5	NR	-2.47	-1.86
19	11.5	2.5	NR	-0.99	-0.74
20	13.93	1.5	NR	0.21	0.24
21	14	7	101	0.25	0.07
22	14	2.4	94	0.25	0.19
23	15	4.5	NR	0.74	0.33
24	14.3	6.33	NR	0.40	0.12

Statistics

Assigned Value	13.5	1.0
Spike Value	20.3	1.0
Robust Average	13.5	1.0
Median	14.0	0.7
Mean	13.3	
N	20	
Max	17.55	
Min	8.5	
Robust SD	1.9	
Robust CV	14%	


Kernel Density
Density
Result
Results: S2 - Chlorpyrifos
Assigned Value = 13.5 ± 1.0 µg/L
Results (µg/L)
Laboratory
18 10 13 19 5 3 12 1 20 21 22 4 24 2 14 6 8 7 23 9 15 16 17 Md RA SV


z-Scores: S2 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 2.0 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
18 10 13 19 5 3 12 1 20 21 22 4 24 2 14 6 8 7 23 9
-2.5 -2.3 -1.2 -1.0 -0.9 -0.7 -0.3 0.2 0.2 0.3 0.3 0.4 0.4 0.5 0.5 0.6 0.6 0.7 0.7 2.0

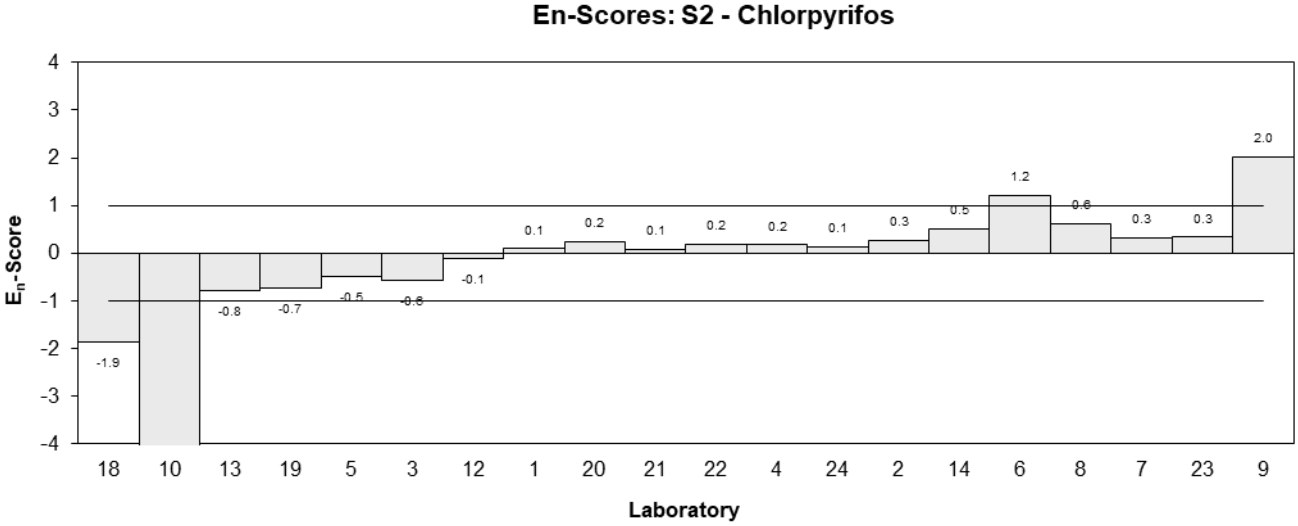

En-Scores: S2 - Chlorpyrifos
En-Score
Laboratory
18 10 13 19 5 3 12 1 20 21 22 4 24 2 14 6 8 7 23 9
-1.9 -0.8 -0.7 -0.5 -0.6 -0.1 0.1 0.2 0.1 0.2 0.2 0.1 0.3 0.5 1.2 0.6 0.3 0.3 2.0

Figure 6

Table 11

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Dieldrin
Unit	µg/L

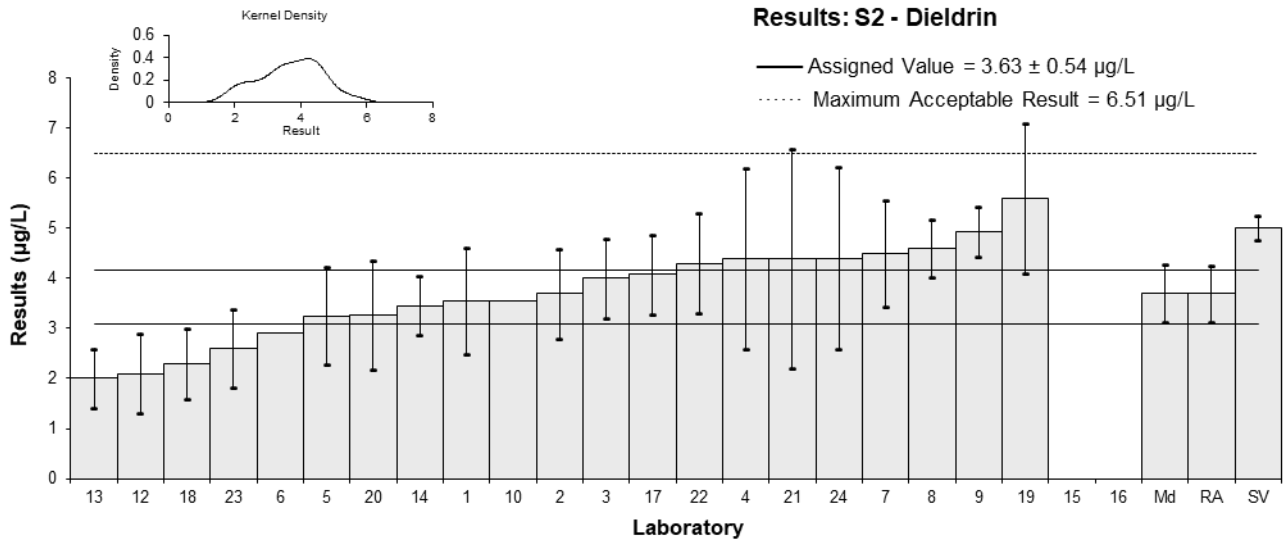
Participant Results

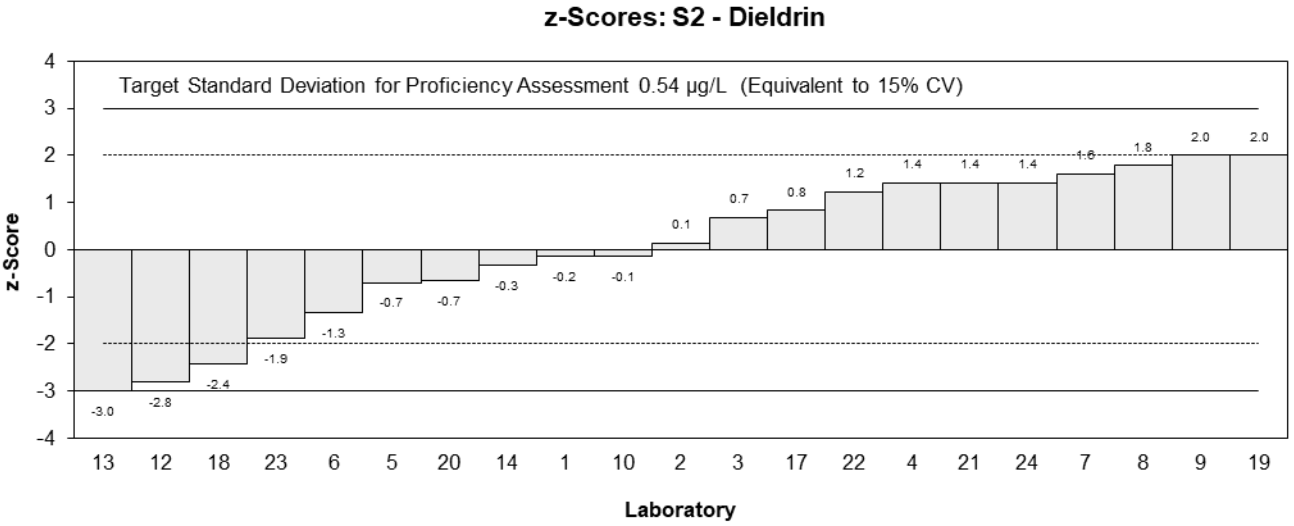
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	3.55	1.07	NR	-0.15	-0.07
2	3.7	0.9	90.5	0.13	0.07
3	4.0	0.8	NR	0.68	0.38
4	4.4	1.8	NR	1.41	0.41
5	3.25	0.98	95	-0.70	-0.34
6	2.9	NR	NR	-1.34	-1.35
7	4.5	1.06	NR	1.60	0.73
8	4.6	0.58	NR	1.78	1.22
9	4.94	0.5	103	2.00▼	
10	3.56	NR	NR	-0.13	-0.13
12	2.1	0.8	65	-2.81	-1.59
13	2	0.6	NR	-2.99	-2.02
14	3.45	0.59	NR	-0.33	-0.23
15	NT	NT	NT		
16	NT	NT	NT		
17	4.08	0.8	NR	0.83	0.47
18	2.3	0.7	NR	-2.44	-1.50
19*	5.6	1.5	NR	2.00▼	
20	3.27	1.1	NR	-0.66	-0.29
21	4.4	2.2	104	1.41	0.34
22	4.3	1	92	1.23	0.59
23	2.6	0.78	NR	-1.89	-1.09
24	4.4	1.82	NR	1.41	0.41

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	3.63	0.54
Spike Value	5.01	0.25
Robust Average	3.70	0.56
Max Acceptable Result	6.51	
Median	3.70	0.57
Mean	3.71	
N	21	
Max	5.6	
Min	2	
Robust SD	1.0	
Robust CV	28%	


Kernel Density
Density
Result
Results: S2 - Dieldrin
Assigned Value = 3.63 ± 0.54 µg/L
Maximum Acceptable Result = 6.51 µg/L
Results (µg/L)
13 12 18 23 6 5 20 14 1 10 2 3 17 22 4 21 24 7 8 9 19 15 16 Md RA SV
Laboratory


z-Scores: S2 - Dieldrin
Target Standard Deviation for Proficiency Assessment 0.54 µg/L (Equivalent to 15% CV)
z-Score
-3.0 -2.8 -2.4 -1.9 -1.3 -0.7 -0.7 -0.3 -0.2 -0.1 0.1 0.7 0.8 1.2 1.4 1.4 1.4 1.6 1.8 2.0 2.0
13 12 18 23 6 5 20 14 1 10 2 3 17 22 4 21 24 7 8 9 19
Laboratory

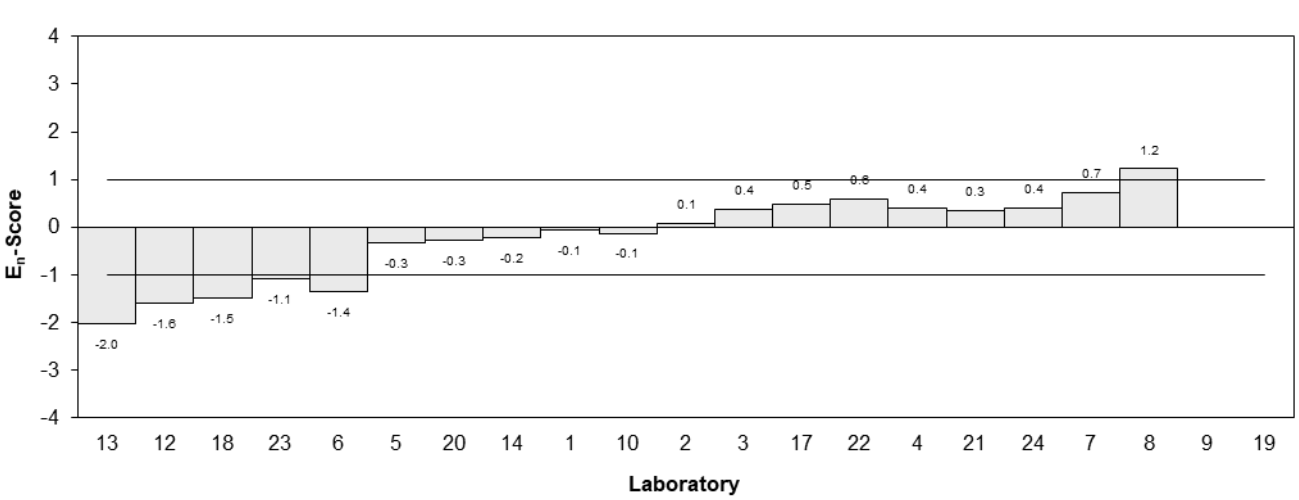

En-Scores: S2 - Dieldrin
En-Score
-2.0 -1.6 -1.5 -1.1 -1.4 -0.3 -0.3 -0.2 -0.1 -0.1 0.1 0.4 0.5 0.6 0.4 0.3 0.4 0.7 1.2
13 12 18 23 6 5 20 14 1 10 2 3 17 22 4 21 24 7 8 9 19
Laboratory

Figure 7

Table 12

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Ethion
Unit	µg/L

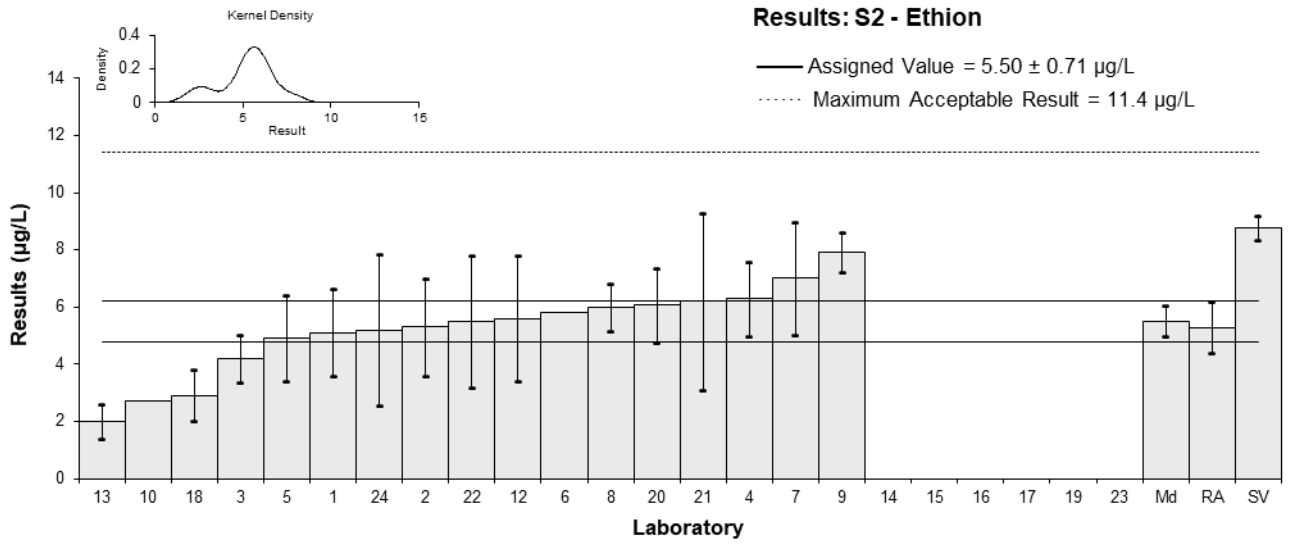
Participant Results

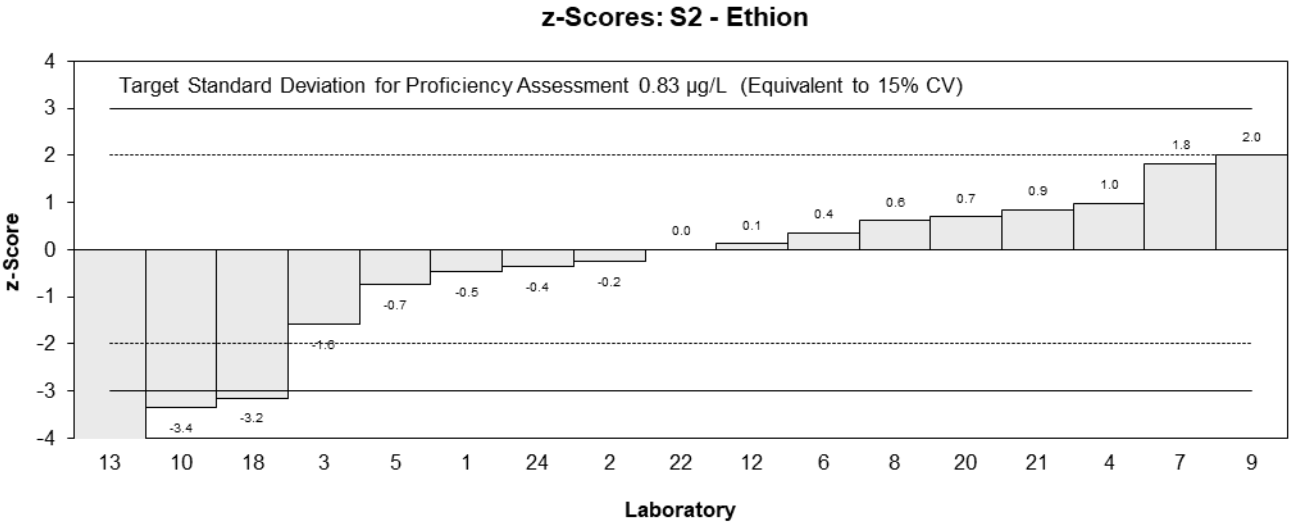
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	5.11	1.53	NR	-0.47	-0.23
2	5.3	1.7	71.1	-0.24	-0.11
3	4.2	0.84	NR	-1.58	-1.18
4	6.3	1.3	NR	0.97	0.54
5	4.9	1.5	101	-0.73	-0.36
6	5.8	NR	NR	0.36	0.42
7	7.0	1.99	NR	1.82	0.71
8	6	0.83	NR	0.61	0.46
9	7.93	0.7	105	2.00▼	
10	2.73	NR	NR	-3.36	-3.90
12	5.6	2.2	100	0.12	0.04
13*	2	0.6	NR	-4.24	-3.77
14	NT	NT	NT		
15	NT	NT	NT		
16	NT	NT	NT		
17	NT	NT	NT		
18	2.9	0.9	NR	-3.15	-2.27
19	NT	NT	NT		
20	6.07	1.3	NR	0.69	0.38
21	6.2	3.1	139	0.85	0.22
22	5.5	2.3	94	0.00	0.00
23	NT	NT	NT		
24	5.2	2.65	NR	-0.36	-0.11

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	5.50	0.71
Spike Value	8.77	0.44
Robust Average	5.29	0.90
Max Acceptable Result	11.4	
Median	5.50	0.54
Mean	5.22	
N	17	
Max	7.93	
Min	2	
Robust SD	1.5	
Robust CV	28%	


Kernel Density
Density
Result
Results: S2 - Ethion
Assigned Value = 5.50 ± 0.71 µg/L
Maximum Acceptable Result = 11.4 µg/L
Results (µg/L)
Laboratory
13 10 18 3 5 1 24 2 22 12 6 8 20 21 4 7 9 14 15 16 17 19 23 Md RA SV


z-Scores: S2 - Ethion
Target Standard Deviation for Proficiency Assessment 0.83 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
13 10 18 3 5 1 24 2 22 12 6 8 20 21 4 7 9
-3.4 -3.2 -1.6 -0.7 -0.5 -0.4 -0.2 0.0 0.1 0.4 0.6 0.7 0.9 1.0 1.8 2.0

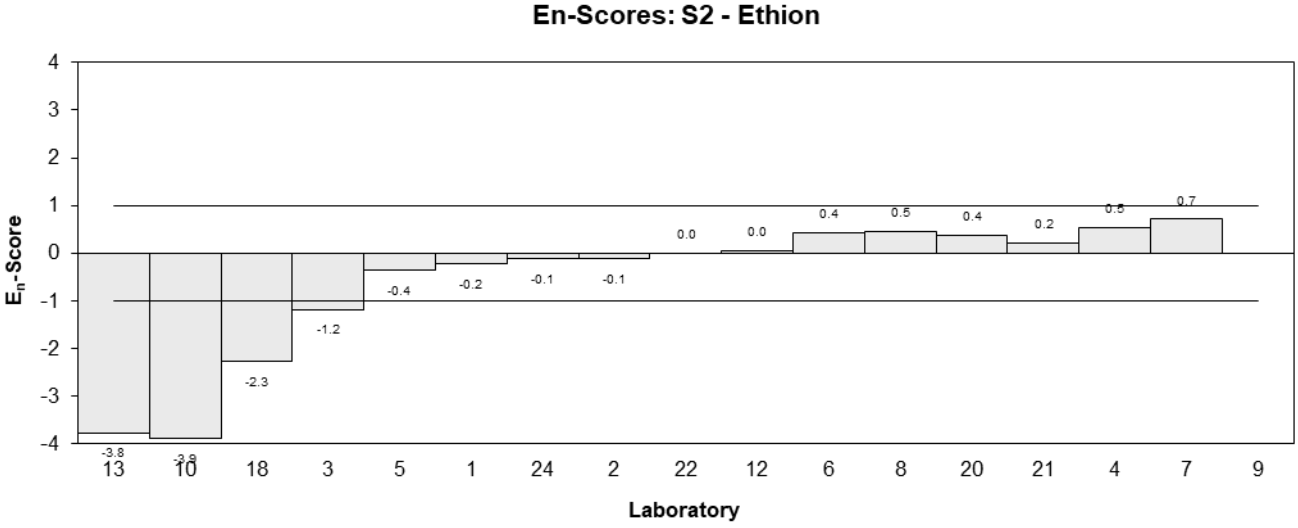

En-Scores: S2 - Ethion
En-Score
Laboratory
13 10 18 3 5 1 24 2 22 12 6 8 20 21 4 7 9
-3.8 -3.9 -2.3 -1.2 -0.4 -0.2 -0.1 -0.1 0.0 0.0 0.4 0.5 0.4 0.2 0.5 0.7

Figure 8

Table 13

Sample Details

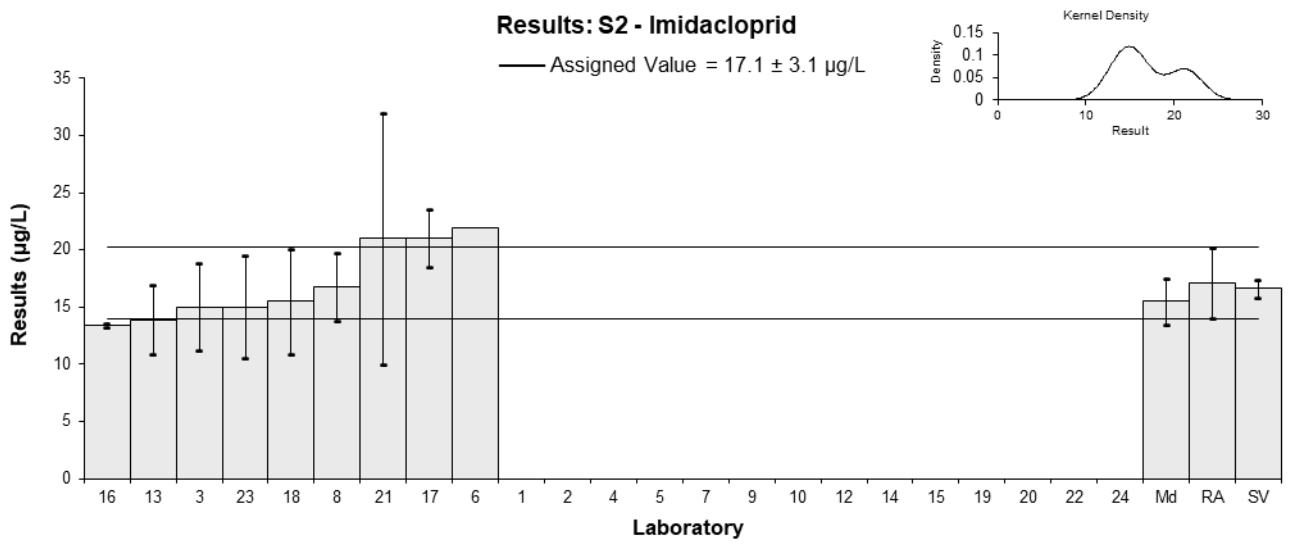
Sample No.	S2
Matrix	River Water
Analyte	Imidacloprid
Unit	µg/L

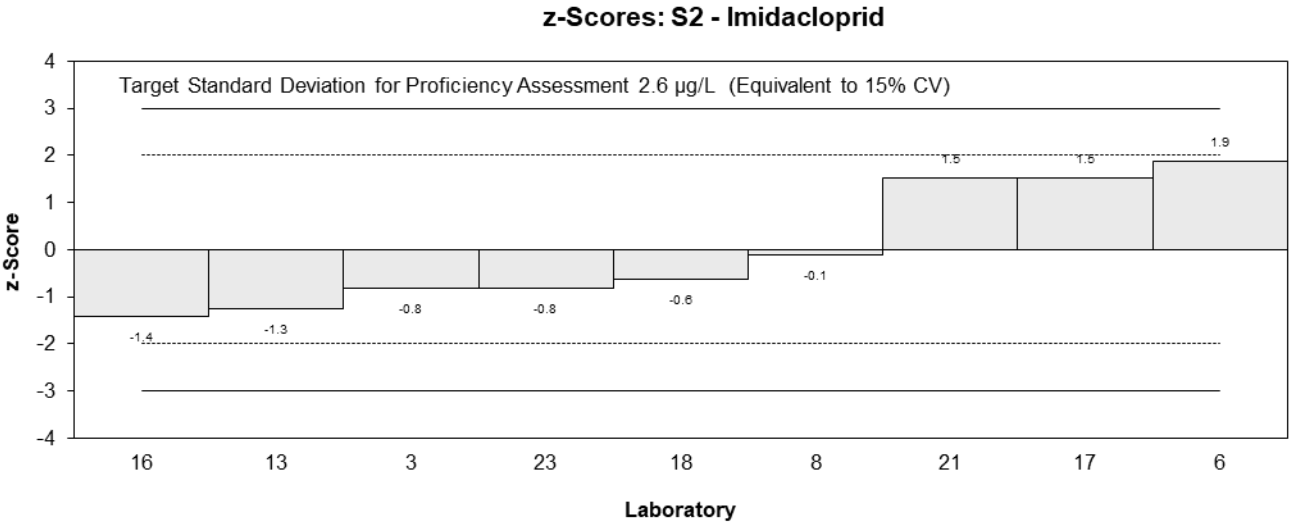
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	NT	NT	NT		
3	15	3.8	NR	-0.82	-0.43
4	NT	NT	NT		
5	NT	NT	NT		
6	21.9	NR	NR	1.87	1.55
7	NT	NT	NT		
8	16.8	2.96	NR	-0.12	-0.07
9	NT	NT	NT		
10	NT	NT	NT		
12	NT	NT	NT		
13	13.9	3	NR	-1.25	-0.74
14	NT	NT	NT		
15	NT	NT	NT		
16	13.43	0.19	106	-1.43	-1.18
17	21.03	2.5	NR	1.53	0.99
18	15.5	4.6	NR	-0.62	-0.29
19	<0.1	NR	NR		
20	<50	NR	NR		
21	21	11	110	1.52	0.34
22	NT	NT	NT		
23	15	4.5	NR	-0.82	-0.38
24	NT	NT	NT		

Statistics

Assigned Value	17.1	3.1
Spike Value	16.6	0.8
Robust Average	17.1	3.1
Median	15.5	2.0
Mean	17.1	
N	9	
Max	21.9	
Min	13.43	
Robust SD	3.8	
Robust CV	22%	


Results: S2 - Imidacloprid
Assigned Value = 17.1 ± 3.1 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
16 13 3 23 18 8 21 17 6 1 2 4 5 7 9 10 12 14 15 19 20 22 24 Md RA SV


z-Scores: S2 - Imidacloprid
Target Standard Deviation for Proficiency Assessment 2.6 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
16 13 3 23 18 8 21 17 6
-1.4
-1.3
-0.8
-0.8
-0.6
-0.1
1.5
1.5
1.9

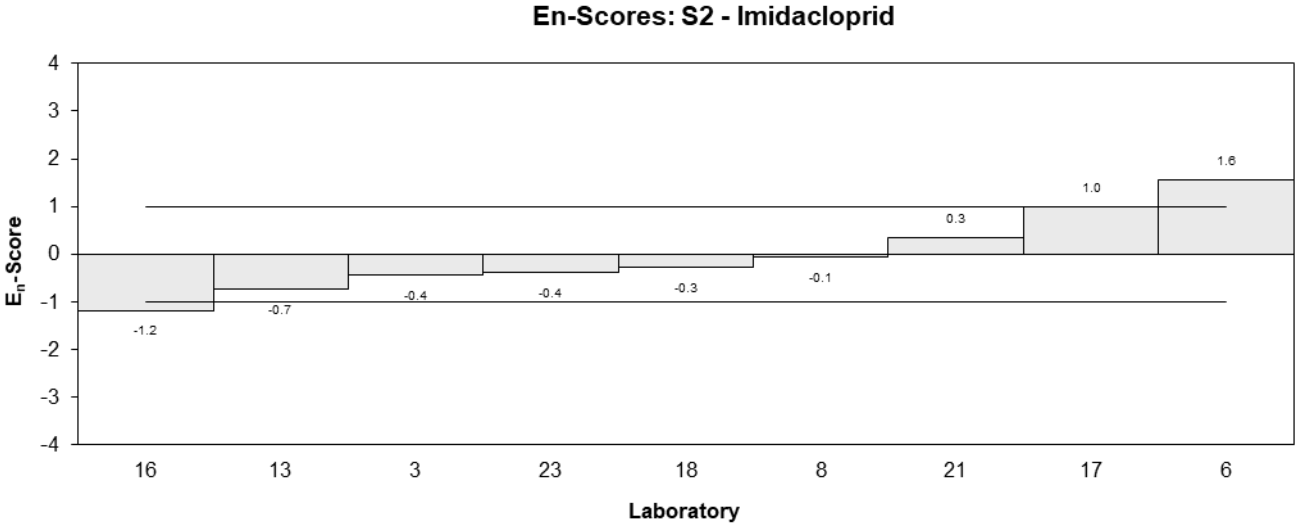

En-Scores: S2 - Imidacloprid
En-Score
Laboratory
16 13 3 23 18 8 21 17 6
-1.2
-0.7
-0.4
-0.4
-0.3
-0.1
0.3
1.0
1.6

Figure 9

Table 14

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Simazine
Unit	µg/L

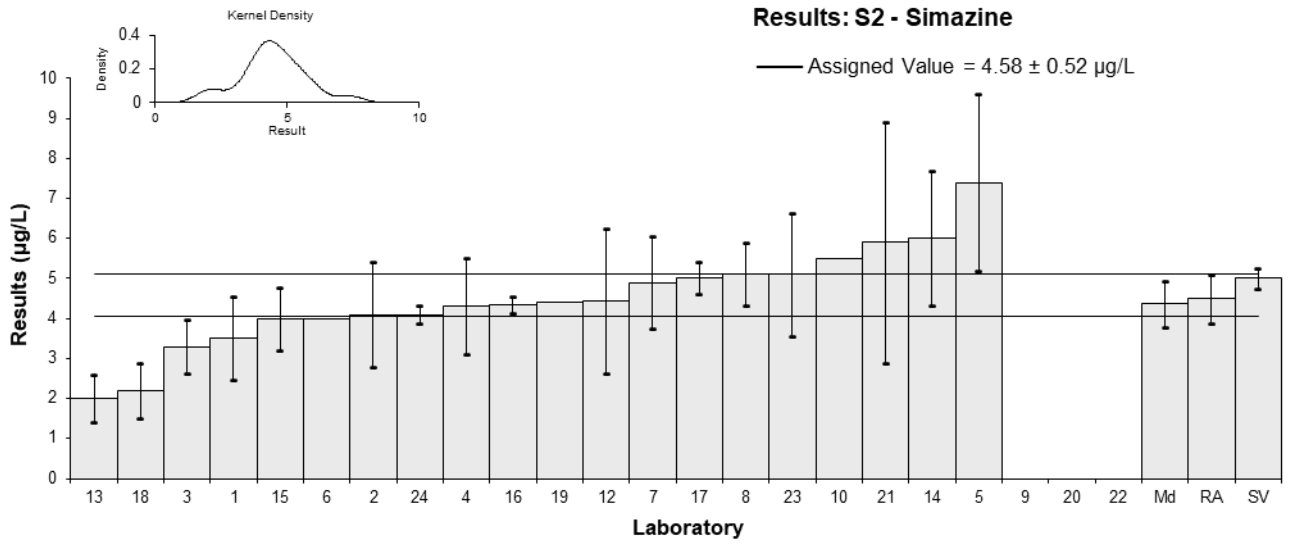
Participant Results

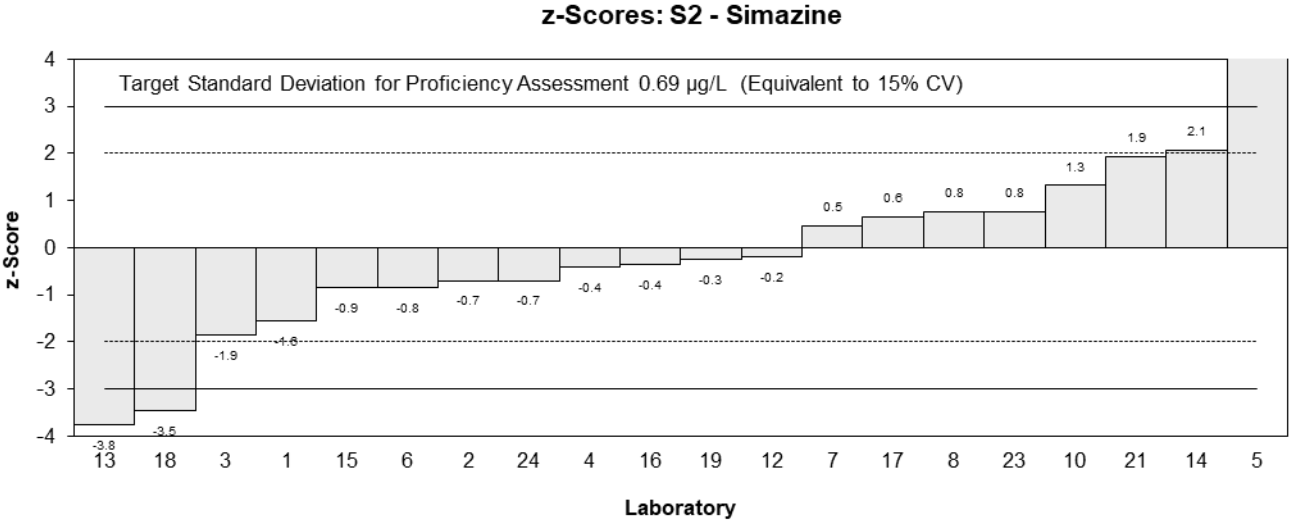
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	3.51	1.05	NR	-1.56	-0.91
2	4.1	1.3	107	-0.70	-0.34
3	3.3	0.66	NR	-1.86	-1.52
4	4.3	1.2	NR	-0.41	-0.21
5*	7.4	2.2	106	4.10	1.25
6	4.0	NR	NR	-0.84	-1.12
7	4.9	1.15	NR	0.47	0.25
8	5.1	0.78	NR	0.76	0.55
9	NT	NT	NT		
10	5.49	NR	NR	1.32	1.75
12	4.44	1.8	48	-0.20	-0.07
13*	2	0.6	NR	-3.76	-3.25
14	6.00	1.68	NR	2.07	0.81
15	3.989	0.7978	103	-0.86	-0.62
16	4.33	0.21	107	-0.36	-0.45
17	5.02	0.4	NR	0.64	0.67
18*	2.2	0.7	NR	-3.46	-2.73
19	4.4	NR	NR	-0.26	-0.35
20	NT	NT	NT		
21	5.9	3	104	1.92	0.43
22	NT	NT	NT		
23	5.1	1.53	NR	0.76	0.32
24	4.1	0.21	NR	-0.70	-0.86

* Outlier, see Section 4.2

Statistics

Assigned Value	4.58	0.52
Spike Value	5.00	0.25
Robust Average	4.49	0.61
Median	4.37	0.58
Mean	4.48	
N	20	
Max	7.4	
Min	2	
Robust SD	1.1	
Robust CV	24%	


Kernel Density
Density
Result
Results: S2 - Simazine
Assigned Value = 4.58 ± 0.52 µg/L
Results (µg/L)
13 18 3 1 15 6 2 24 4 16 19 12 7 17 8 23 10 21 14 5 9 20 22 Md RA SV
Laboratory


z-Scores: S2 - Simazine
Target Standard Deviation for Proficiency Assessment 0.69 µg/L (Equivalent to 15% CV)
z-Score
-3.8 -3.5 -1.9 -1.6 -0.9 -0.8 -0.7 -0.7 -0.4 -0.4 -0.3 -0.2 0.5 0.6 0.8 0.8 1.3 1.9 2.1
13 18 3 1 15 6 2 24 4 16 19 12 7 17 8 23 10 21 14 5
Laboratory

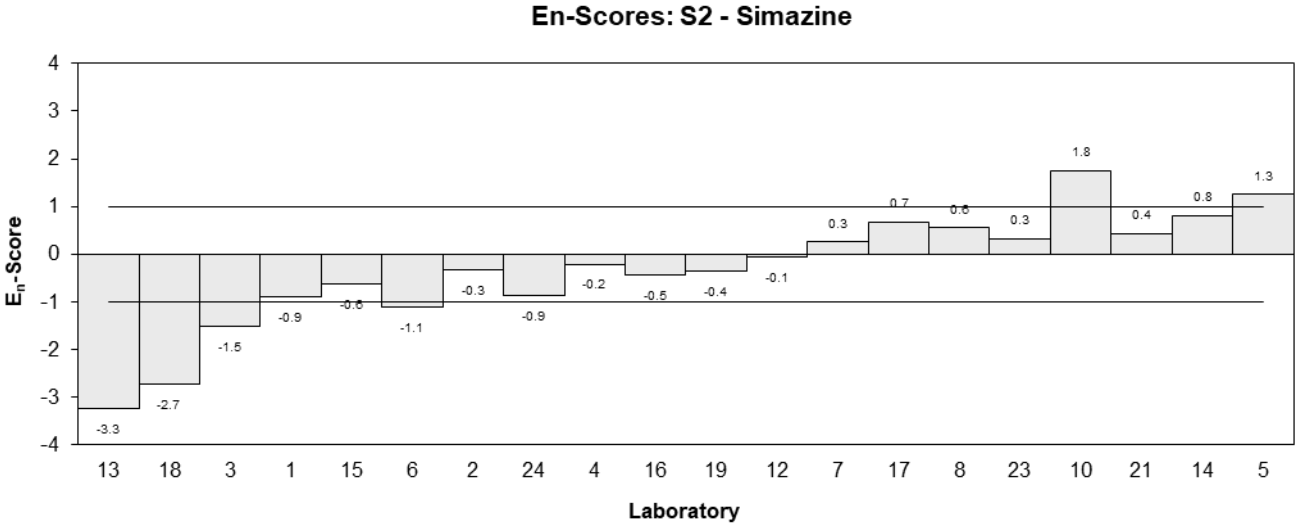

En-Scores: S2 - Simazine
En-Score
-3.3 -2.7 -1.5 -0.9 -0.6 -1.1 -0.3 -0.9 -0.2 -0.5 -0.4 -0.1 0.3 0.7 0.6 0.3 1.8 0.4 0.8 1.3
13 18 3 1 15 6 2 24 4 16 19 12 7 17 8 23 10 21 14 5
Laboratory

Figure 10

Table 15

Sample Details

Sample No.	S3
Matrix	River Water
Analyte	AMPA
Unit	µg/L

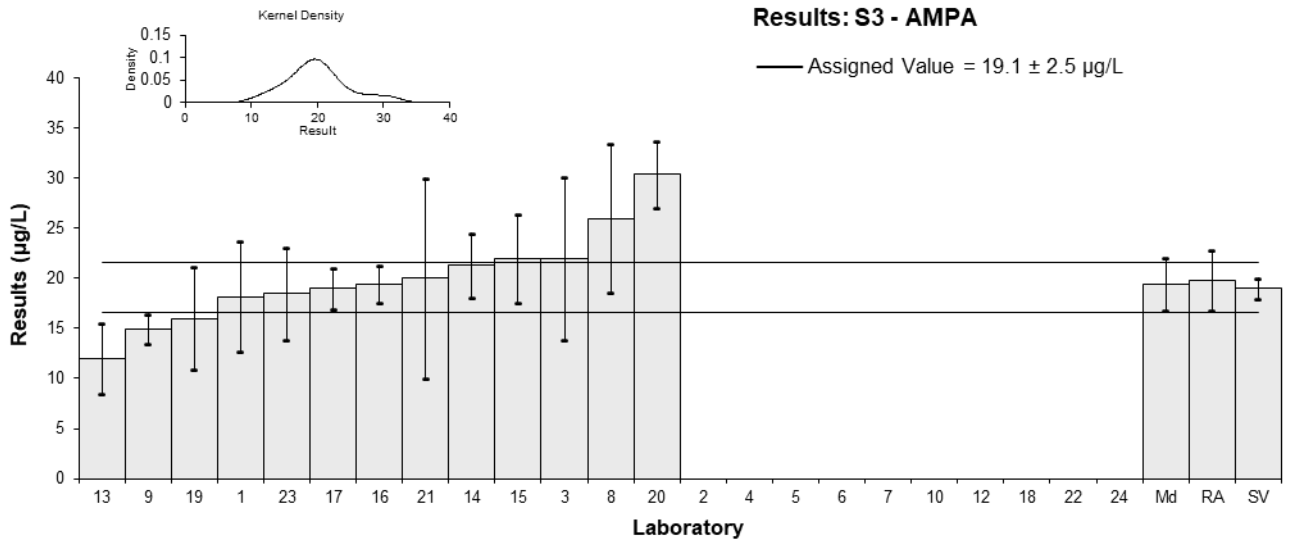
Participant Results

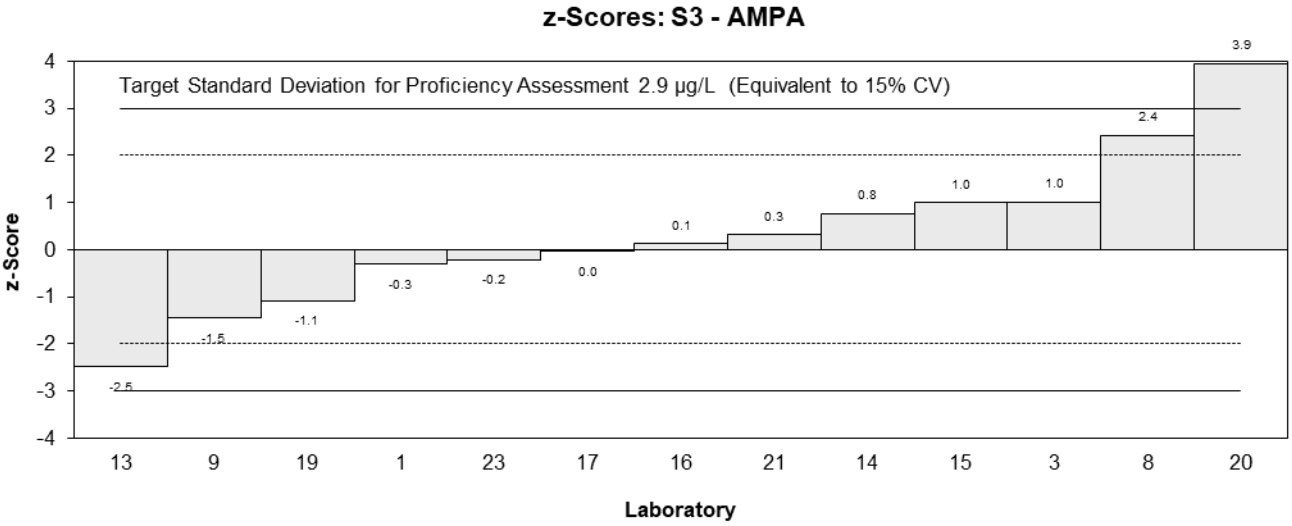
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	18.2	5.46	98	-0.31	-0.15
2	NT	NT	NT		
3	22	8.1	NR	1.01	0.34
4	NT	NT	NT		
5	NR	NR	NR		
6	<10	NR	NR		
7	NT	NT	NT		
8	26	7.4	NR	2.41	0.88
9	14.94	1.5	80	-1.45	-1.43
10	NT	NT	NT		
12	NT	NT	NT		
13	12	3.5	NR	-2.48	-1.65
14	21.3	3.2	NR	0.77	0.54
15	21.95	4.39	111	0.99	0.56
16	19.43	1.91	102	0.12	0.10
17	18.98	2.0	NR	-0.04	-0.04
18	NR	NR	NR		
19	16	5.1	35	-1.08	-0.55
20*	30.4	3.3	NR	3.94	2.73
21	20	10	100	0.31	0.09
22	NS	NS	NS		
23	18.5	4.6	100	-0.21	-0.11
24	NT	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	19.1	2.5
Spike Value	19.0	1.0
Robust Average	19.8	3.0
Median	19.4	2.6
Mean	20.0	
N	13	
Max	30.4	
Min	12	
Robust SD	4.4	
Robust CV	22%	


Results: S3 - AMPA
Assigned Value = 19.1 ± 2.5 µg/L
Kernel Density
Density
Result
Results (µg/L)
13 9 19 1 23 17 16 21 14 15 3 8 20 2 4 5 6 7 10 12 18 22 24 Md RA SV
Laboratory


z-Scores: S3 - AMPA
Target Standard Deviation for Proficiency Assessment 2.9 µg/L (Equivalent to 15% CV)
z-Score
13 9 19 1 23 17 16 21 14 15 3 8 20
Laboratory

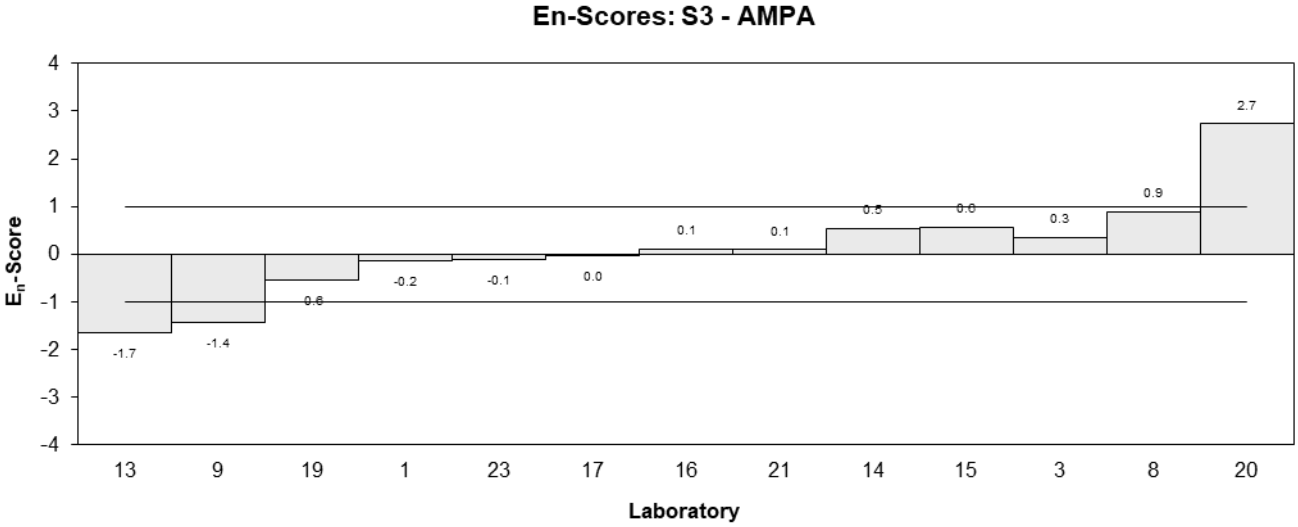

En-Scores: S3 - AMPA
En-Score
13 9 19 1 23 17 16 21 14 15 3 8 20
Laboratory

Figure 11

Table 16

Sample Details

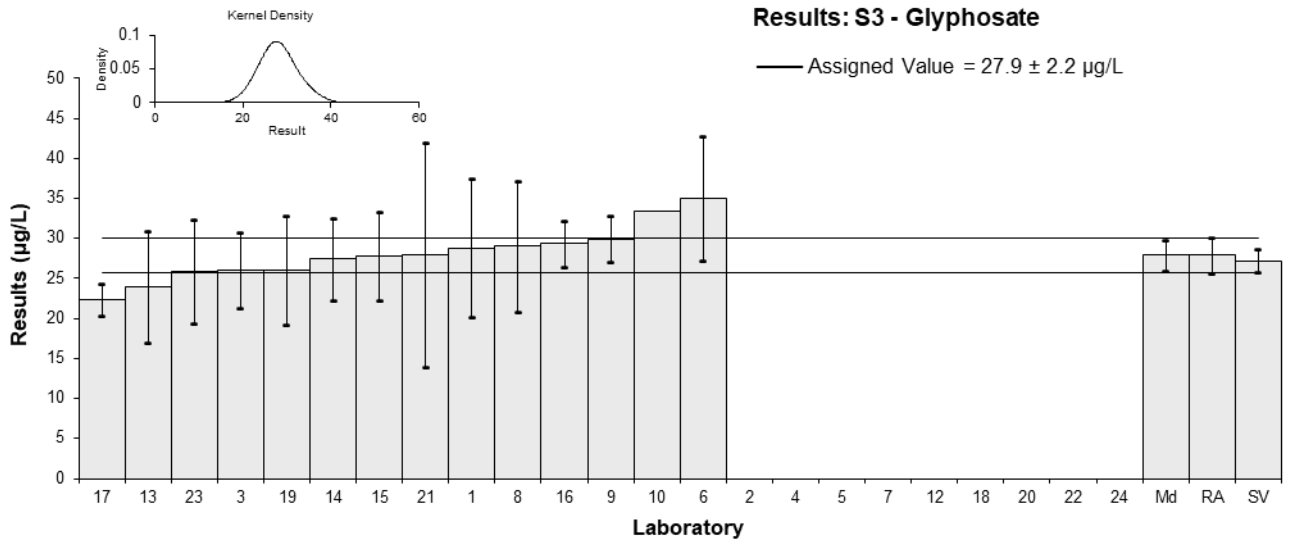
Sample No.	S3
Matrix	River Water
Analyte	Glyphosate
Unit	µg/L

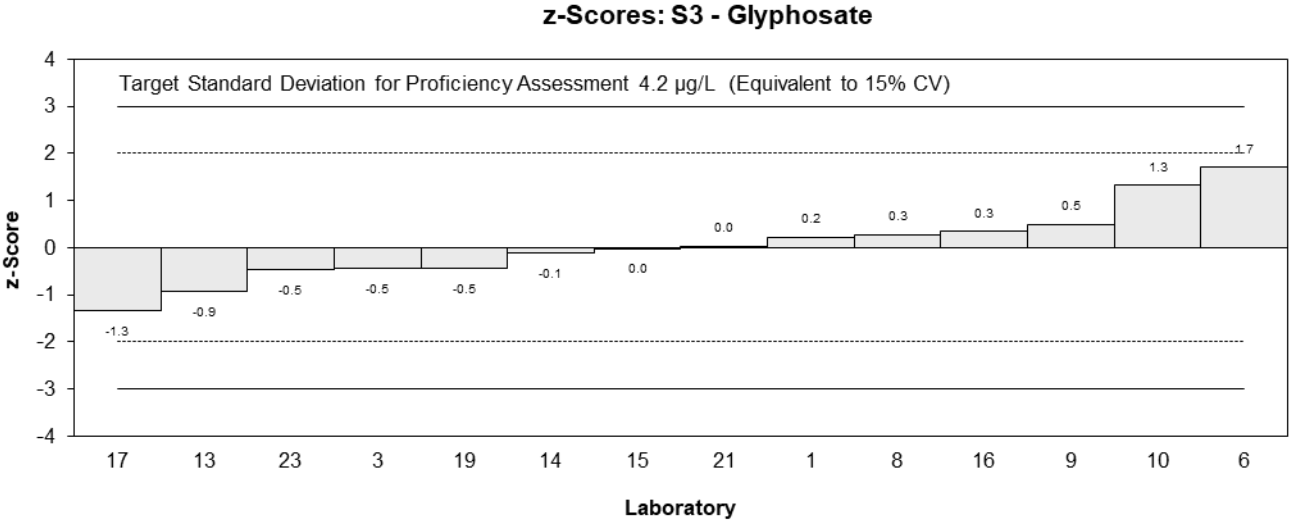
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	28.8	8.64	71	0.22	0.10
2	NT	NT	NT		
3	26	4.7	NR	-0.45	-0.37
4	NT	NT	NT		
5	NR	NR	NR		
6	35	7.7	NR	1.70	0.89
7	NT	NT	NT		
8	29	8.2	NR	0.26	0.13
9	29.94	2.9	110	0.49	0.56
10	33.41	NR	NR	1.32	2.50
12	NT	NT	NT		
13	24	7	NR	-0.93	-0.53
14	27.4	5.2	NR	-0.12	-0.09
15	27.81	5.56	115.5	-0.02	-0.02
16	29.33	2.93	105	0.34	0.39
17	22.31	2.0	NR	-1.34	-1.88
18	NR	NR	NR		
19	26	6.8	80	-0.45	-0.27
20	<30	NR	NR		
21	28	14	98	0.02	0.01
22	NS	NS	NS		
23	25.9	6.5	100	-0.48	-0.29
24	NT	NT	NT		

Statistics

Assigned Value	27.9	2.2
Spike Value	27.2	1.4
Robust Average	27.9	2.2
Median	27.9	1.9
Mean	28.1	
N	14	
Max	35	
Min	22.31	
Robust SD	3.2	
Robust CV	12%	


Kernel Density
Density
Result
Results: S3 - Glyphosate
Assigned Value = 27.9 ± 2.2 µg/L
Results (µg/L)
Laboratory
17 13 23 3 19 14 15 21 1 8 16 9 10 6 2 4 5 7 12 18 20 22 24 Md RA SV


z-Scores: S3 - Glyphosate
Target Standard Deviation for Proficiency Assessment 4.2 µg/L (Equivalent to 15% CV)
z-Score
-1.3 -0.9 -0.5 -0.5 -0.5 -0.1 0.0 0.0 0.2 0.3 0.3 0.5 1.3 1.7
Laboratory
17 13 23 3 19 14 15 21 1 8 16 9 10 6

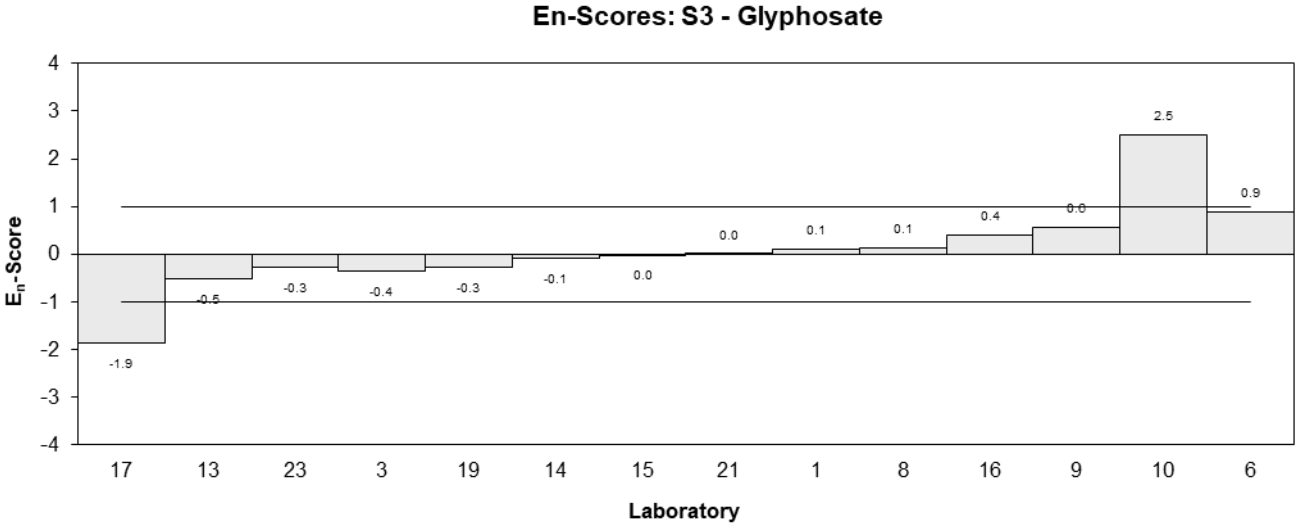

En-Scores: S3 - Glyphosate
En-Score
-1.9 -0.5 -0.3 -0.4 -0.3 -0.1 0.0 0.0 0.1 0.1 0.4 0.6 2.5 0.9
Laboratory
17 13 23 3 19 14 15 21 1 8 16 9 10 6

Figure 12

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[6] The assigned values for all scored analytes were the robust averages of participants' results, after results less than 50% and greater than 150% of the robust average had been removed.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S2 chlorpyrifos 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 averages if no assigned value was set) and spiked values is presented in Table 17.

No assigned value was set for Sample S1 acetamiprid as there were too few numeric results reported; however, participants' results were in good agreement with each other as well as the spiked value. Participants may still compare their results with the descriptive statistics and spiked value as presented in Section 5.

For the scored analytes, assigned values were within the range of 63% to 103% of the spiked values. Similar ratios have been observed in previous NMI pesticides in river water PT studies.

Table 17 Comparison of Assigned Value *(Robust Average)* and Spiked Value

Sample	Analyte	Assigned Value *(Robust Average)* (µg/L)	Spiked Value (µg/L)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	Acetamiprid	*(7.9)*	7.50	*(105)*
	Atrazine	10.2	11.4	89
	Fenthion	7.12	10.1	70
	Lindane	7.45	9.98	75
S2	Chlorpyrifos	13.5	20.3	67
	Dieldrin	3.63	5.01	72
	Ethion	5.50	8.77	63
	Imidacloprid	17.1	16.6	103
	Simazine	4.58	5.00	92
S3	AMPA	19.1	19.0	101
	Glyphosate	27.9	27.2	103

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate. It is a requirement of 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 176 numeric results submitted for the analytes of interest in this study, 158 (90%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3). A participant reported using the NATA GAG Estimating and Reporting MU as their guide; NATA no longer publishes this document.[10]

Laboratory **6** did not report uncertainties for all except one numeric result, and Laboratory **10** did not report any uncertainties for their numeric results; these participants both reported being accredited to ISO/IEC 17025. Laboratories **19** and **24** each did not report an uncertainty for one of their numeric results; these participants both reported being accredited to ISO/IEC 17025.

The magnitude of reported uncertainties was within the range of 1.4% to 59% relative to the result. In general, an expanded uncertainty of less than 15% relative may be unrealistically small for the routine measurement of a pesticide residue, while an uncertainty of greater than 50% relative may be too large and not fit-for-purpose. Of the 158 MUs reported for this study, 31 were less than 15% relative and six were greater than 50% relative.

Participants were requested to report the coverage factor associated with their uncertainty (Table 4). Five participants reported a coverage factor of 2, and one participant reported a coverage factor of 2.3.

Uncertainties associated with results returning an acceptable *z*-score but an unacceptable E_n-score may have been underestimated.

In some cases the results and/or uncertainties 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 8.558 ± 1.89 µg/L, it is better to report this as 8.6 ± 1.9 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] between-laboratory CVs and target SDs (as PCV) for this study are presented for comparison in Table 18.

Table 18 Comparison of Thompson-Horwitz CV, Between-Laboratory CV and Target SD

Sample	Analyte	Assigned Value *(Robust Average)* (µg/L)	Thompson-Horwitz CV[a] (%)	Between-Laboratory CV[b] (%)	Target SD (as PCV) (%)
S1	Acetamiprid	*(7.9)*	22	19	Not Set
	Atrazine	10.2	22	17	15
	Fenthion	7.12	22	17	15
	Lindane	7.45	22	21	15
S2	Chlorpyrifos	13.5	22	14	15
	Dieldrin	3.63	22	27	15
	Ethion	5.50	22	21	15
	Imidacloprid	17.1	22	22	15
	Simazine	4.58	22	19	15
S3	AMPA	19.1	22	18	15
	Glyphosate	27.9	22	12	15

[a] Calculated from the assigned value (robust average).

[b] Robust between-laboratory CV (outliers removed where applicable).

To account for possible low bias in the consensus value due to laboratories using inefficient analytical or extraction techniques, six *z*-scores were adjusted across Sample S1 fenthion and lindane, and Sample S2 dieldrin and ethion. A maximum acceptable result was set as the spiked value plus two target SDs of the spiked value. Results lower than the maximum acceptable result but with a *z*-score greater than 2.0 had their *z*-score adjusted to 2.0. This ensured that any participants reporting results close to the spiked value were not penalised. *z*-Scores for results greater than the maximum acceptable result, and *z*-scores less than 2.0, were left unaltered.

Of 172 results for which *z*-scores were calculated, 152 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **3**, **8**, **13** and **21** reported numeric results for all scored analytes in this study. Of these participants, Laboratories **3** and **21** returned acceptable *z*-scores for all analytes.

Eleven other participants received acceptable *z*-scores for all reported results that were scored: **1** (9), **6** (8), **23** (8), **2** (7), **7** (7), **19** (7), **24** (7), **4** (6), **16** (6), **15** (4) and **22** (4).

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

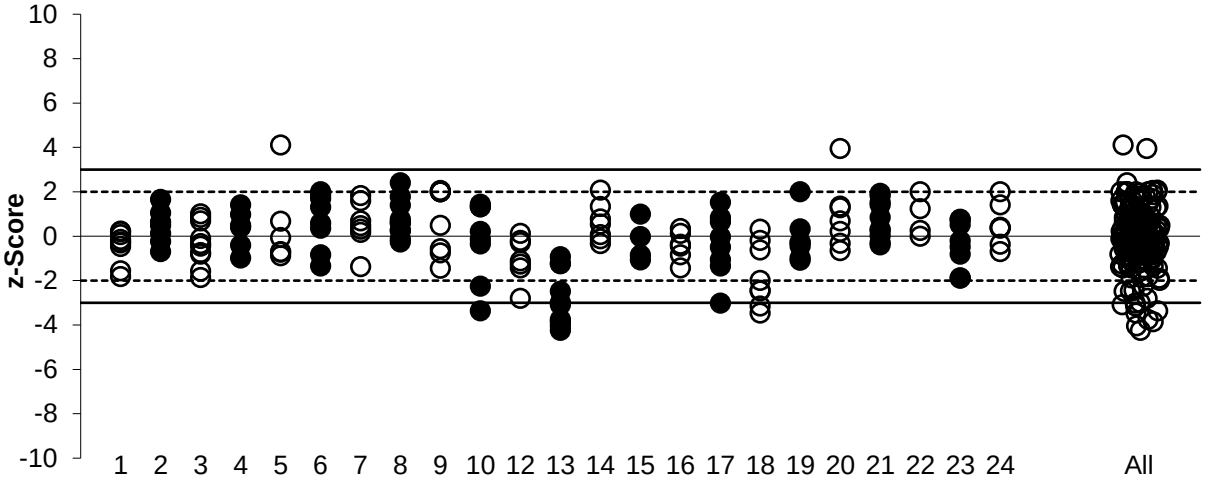


Figure 13 *z*-Score Dispersal by Laboratory

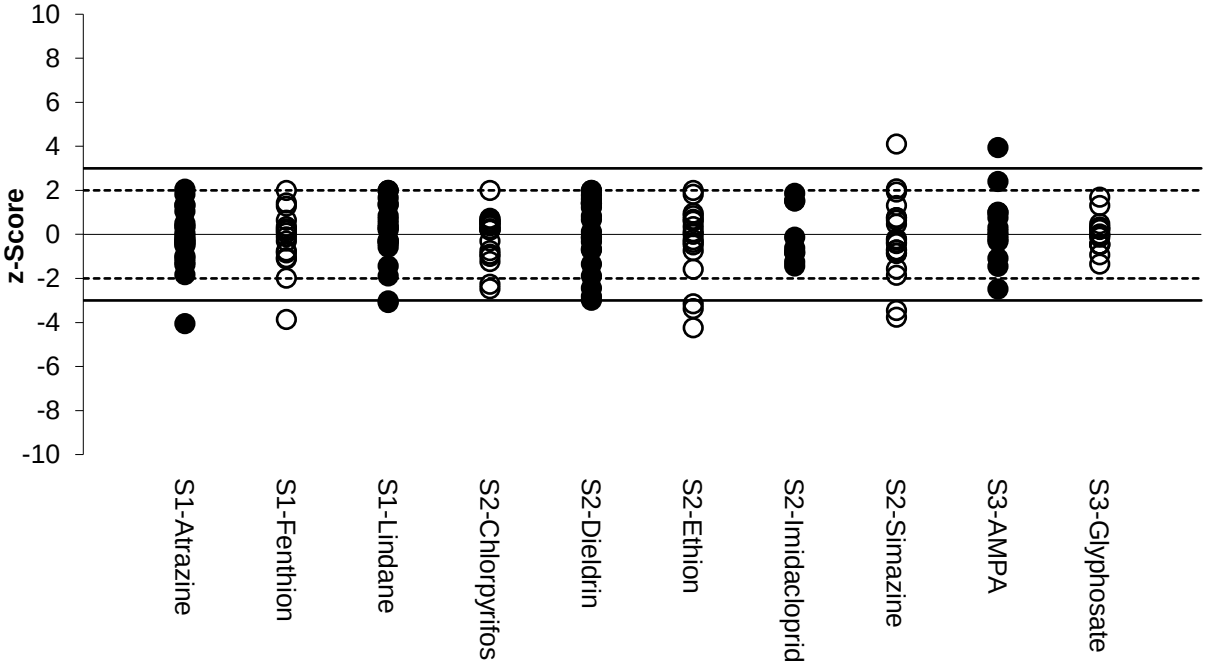


Figure 14 *z*-Score Dispersal by Analyte

6.4 E_n-Score

E_n-scores can be interpreted in conjunction with *z*-scores, as an unacceptable E_n-score can either be caused by issues with 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. For results whose *z*-scores were adjusted as discussed in Section 6.3 *z*-Score, no E_n-score has been calculated.

Of 166 results for which E_n-scores were calculated, 125 (75%) 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 **21** returned acceptable E_n-scores for all ten scored analytes.

Four other participants received acceptable *z*-scores for all reported results that were scored: **2** (7), **14** (7), **4** (6) and **15** (4).

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

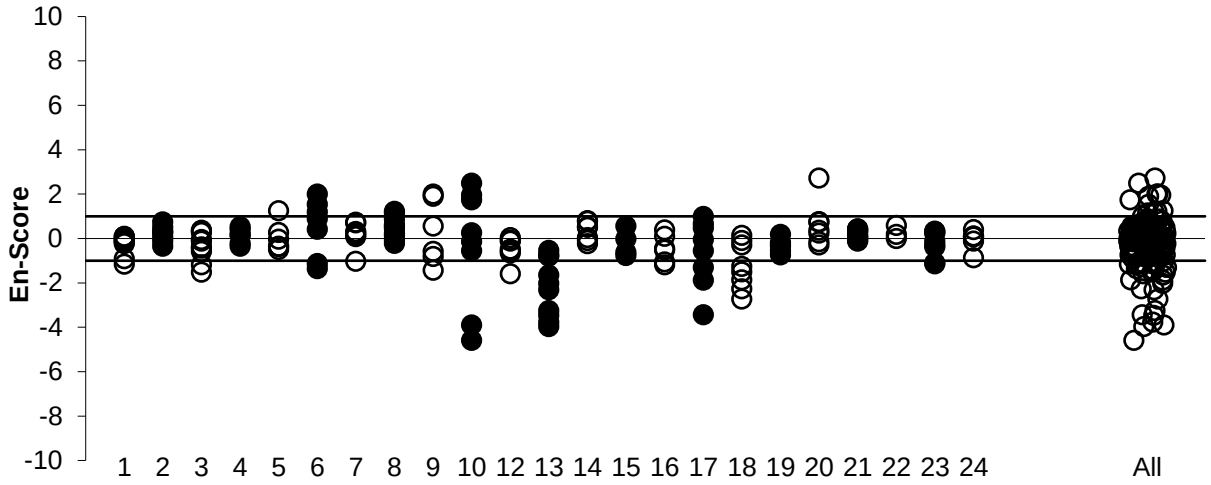


Figure 15 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 19 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.

Table 19 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (µg/L)	Spiked Value (µg/L)	Result* (µg/L)
5	S3	AMPA	19.1	19	NR
		Glyphosate	27.9	27.2	NR
6	S3	AMPA	19.1	19	<10
18	S3	AMPA	19.1	19	NR
		Glyphosate	27.9	27.2	NR
19	S2	Imidacloprid	17.1	16.6	<0.1
22	S1	Lindane	7.45	9.98	<1

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

6.6 Reporting of Additional Analytes

Table 20 presents analytes reported by participants that were not spiked into the test samples by the study coordinator.

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

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
15	S1	MCPA	0.062	0.0124	98.4
		Simazine	0.023	0.0046	103
	S2	Atrazine	0.008	0.00177	99
		MCPA	0.051	0.0102	98.4
19	S1	MCPA	0.053	NR	NR
		Simazine	0.02	NR	NR
		Propazine	0.05	NR	NR
	S2	MCPA	0.053	NR	NR
21	S1	MCPA	0.05	0.03	103
		Simazine	0.04	0.02	104
		DEET	0.06	0.03	104
		Tris(Chloropropyl)Phosphate	0.7	0.35	91
		Propazine	0.07	0.035	116
	S2	MCPA	0.06	0.03	103
		DEET	0.06	0.03	104
		Tris(Chloropropyl)Phosphate	1	0.5	91

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. In total, eleven 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 21.

Laboratories **18** and **21** 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 36% to 100%.

Of the spiked analytes in this study, atrazine was tested for by the highest proportion of participants (96%), while acetamiprid was tested for by the lowest proportion of participants (17%).

Table 21 Summary of Pesticides Analysed by Participants

Analyte \ Lab. Code	1	2	3	4	5	6	7	8	9	10	12	13	14	15	16	17	18	19	20	21	22*	23	24	Proportion of Participants (%)
Acetamiprid	NT	NT	NT	NT	NT	✓	NT	NT	NT	NT	NT	NT	NT	NT	NT	✓	✓	NT	NT	✓	NT	NT	NT	17
AMPA	✓	NT	✓	NT	✓	✓	NT	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	NT	74
Atrazine	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	96
Chlorpyrifos	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	NT	✓	✓	✓	✓	✓	✓	✓	87
Dieldrin	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	✓	✓	91
Ethion	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	NT	NT	✓	NT	✓	✓	✓	NT	✓	74
Fenthion	✓	✓	✓	NT	NT	NT	✓	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	NT	✓	✓	✓	NT	✓	70
Glyphosate	✓	NT	✓	NT	✓	✓	NT	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	NT	78
Imidacloprid	NT	NT	✓	NT	NT	✓	NT	✓	NT	NT	NT	✓	NT	NT	✓	✓	✓	✓	✓	✓	NT	✓	NT	48
Lindane	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	✓	✓	91
Simazine	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	87
Proportion of Analytes (%)	82	64	91	55	73	91	64	91	73	73	64	91	64	36	55	82	100	73	82	100	56	73	64	

* Laboratory **22** was not supplied Sample S3; analytes spiked into this sample only have been shaded.

6.8 Participants' Analytical Methods

Participants used a variety of analytical methods for the test samples (Appendix 4).

For Samples S1 and S2, participants were given the option of samples as 1 x 500 mL (13 participants) or as 3 x 100 mL (10 participants), depending on what suited their laboratory's method. Participants reported test portions ranging from 0.5 mL to 500 mL. A comparison of *z*-scores and sample volume used for scored analytes is presented in Figure 16; there was no correlation observed in this study.

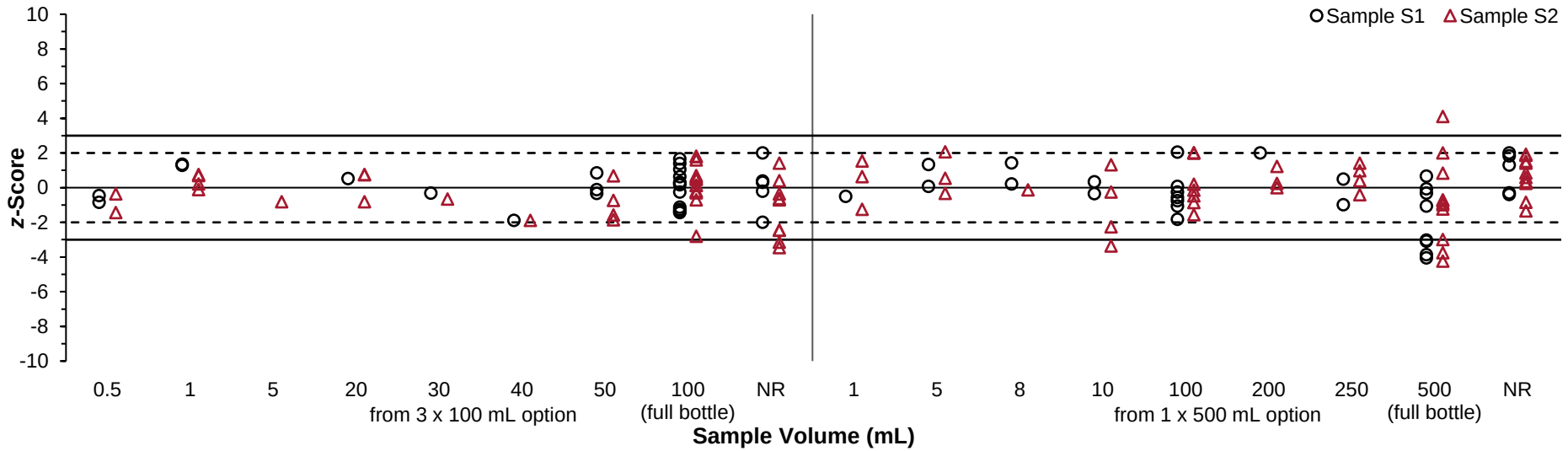


Figure 16 Samples S1 and S2 *z*-Score vs Sample Volume

For the analytes in Samples S1 and S2, participants used direct injection (DI), or different extractions techniques such as liquid-liquid extraction (LLE), dispersive liquid-liquid microextraction (DLLME), solid-phase extraction (SPE) and 'Quick, Easy, Cheap, Effective, Rugged and Safe' extraction (QuEChERS). For extraction solvents, participants used acetonitrile (ACN), dichloromethane (DCM), ethyl acetate (EtOAc), hexane (HEX), methanol (MeOH), or mixtures of these solvents. The majority of participants did not report a further clean-up step, with only a few participants reporting centrifugation (Centr.) or filtration (Filtr.) for certain analytes. Participants reported using gas chromatography (GC) coupled to electron capture detection (ECD), flame photometric detection (FPD), nitrogen phosphorus detection (NPD), mass spectrometry (MS) or tandem mass spectrometry (MS/MS), liquid chromatography (LC) coupled to MS/MS, or high performance liquid chromatography (HPLC) coupled to diode array detection (DAD).

Plots of numeric results and methodology employed (extraction technique, extraction solvent, clean-up and measurement instrument) for scored analytes in this study are presented in Figures 17 to 24. Participants results yielding unacceptable z scores ($|z| \geq 3.0$) have been circled for reference. As a wide variety of methodologies was employed by participants, no significant trend was observed.

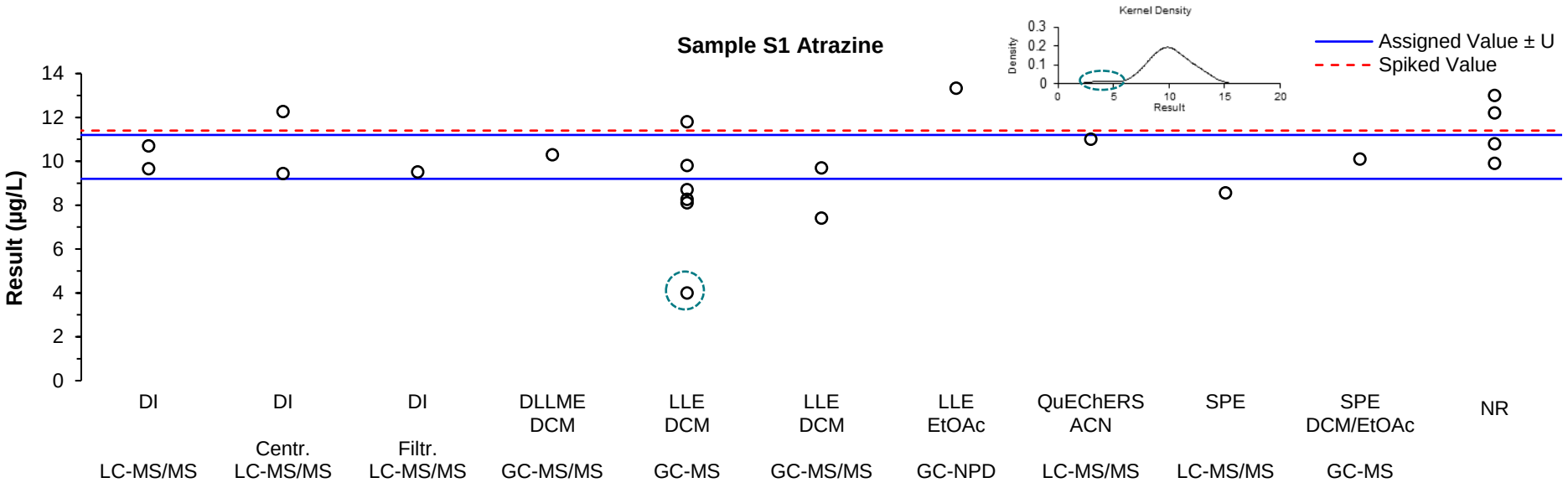


Figure 17 Sample S1 Atrazine Result vs Methodology

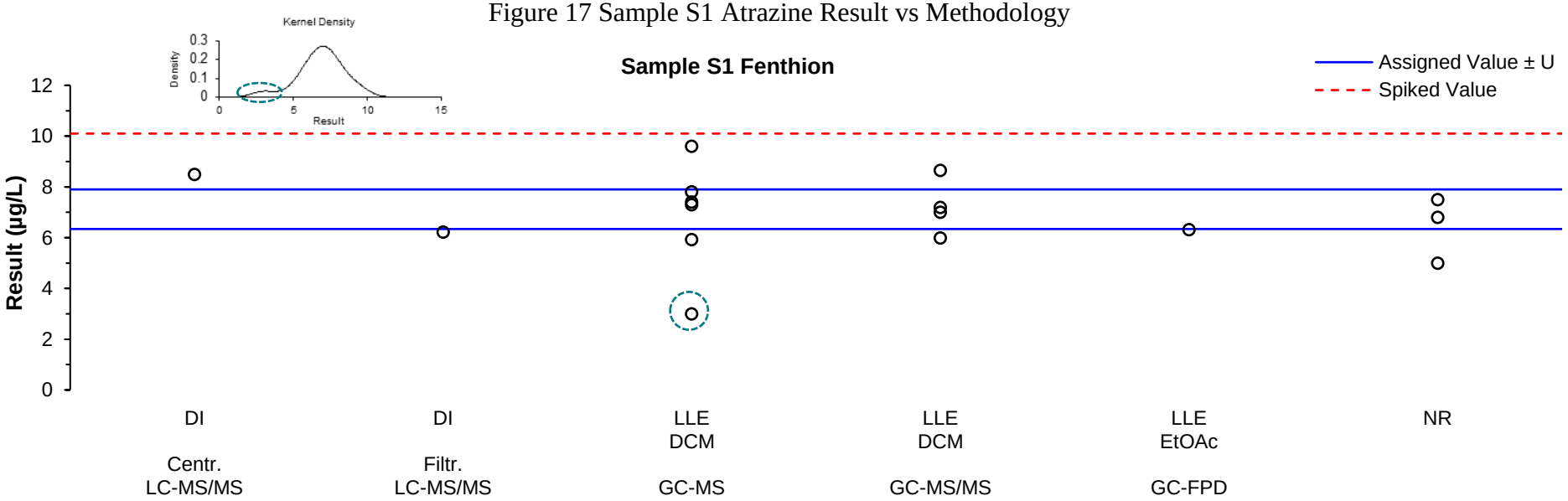


Figure 18 Sample S1 Fenthion Result vs Methodology

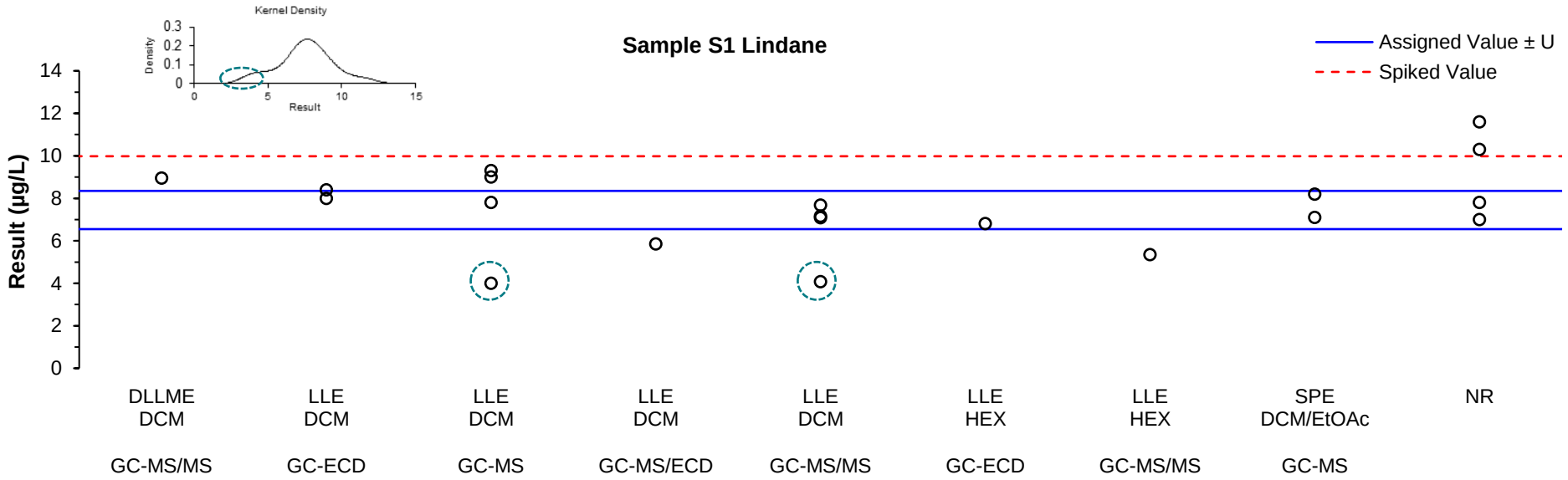


Figure 19 Sample S1 Lindane Result vs Methodology

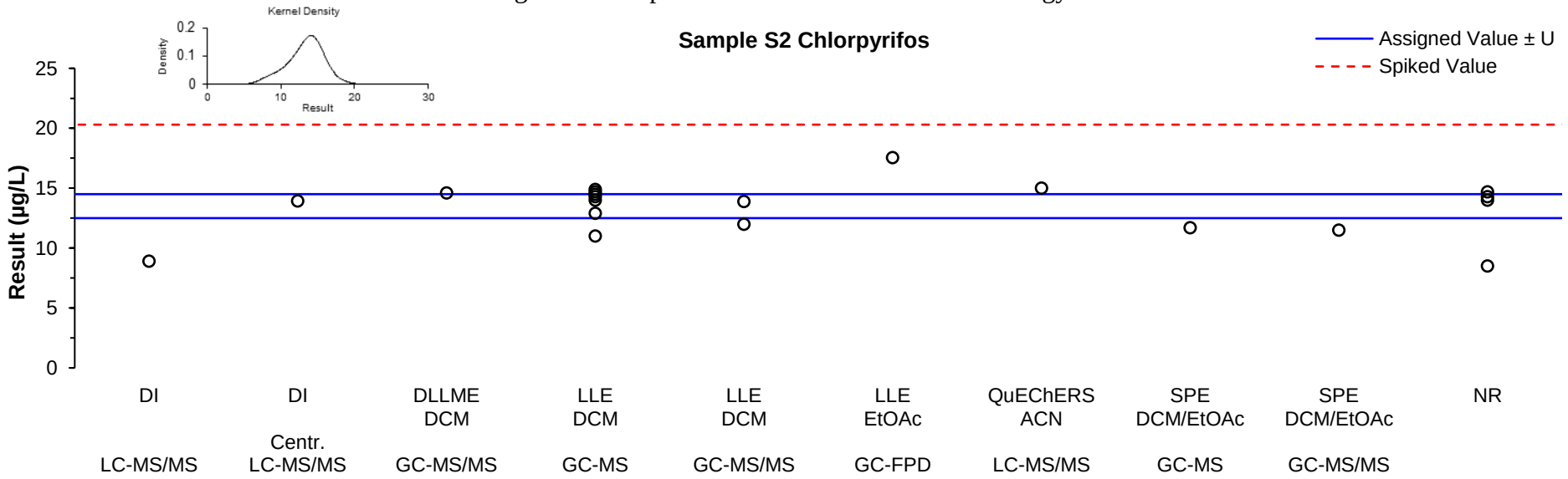


Figure 20 Sample S2 Chlorpyrifos Result vs Methodology

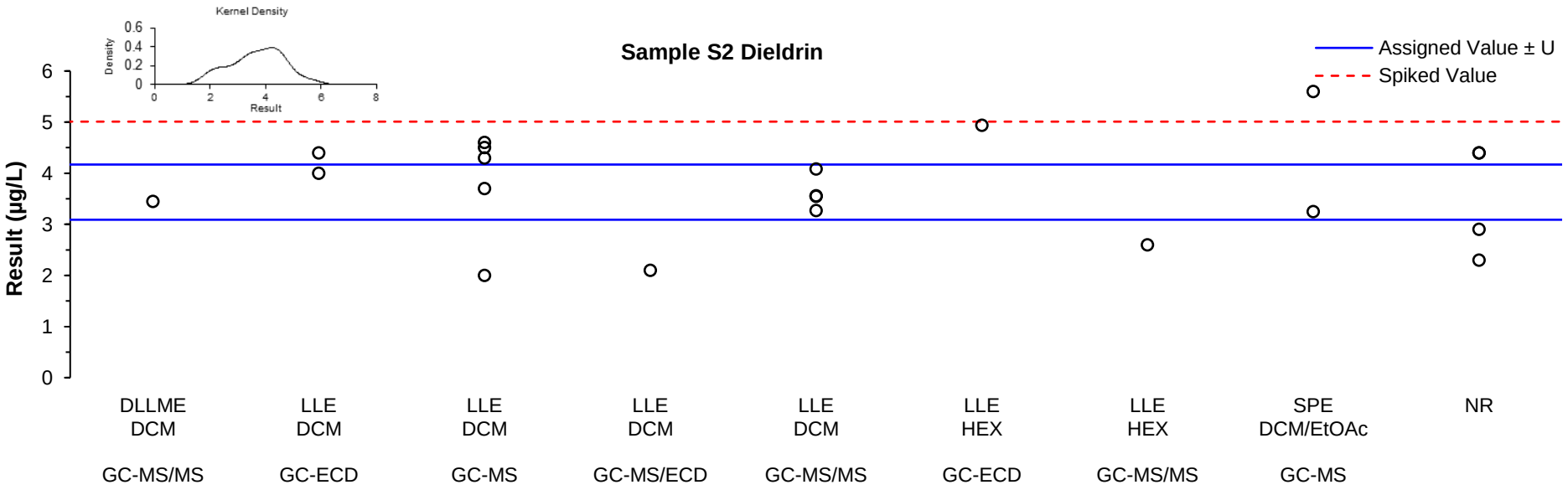


Figure 21 Sample S2 Dieldrin Result vs Methodology

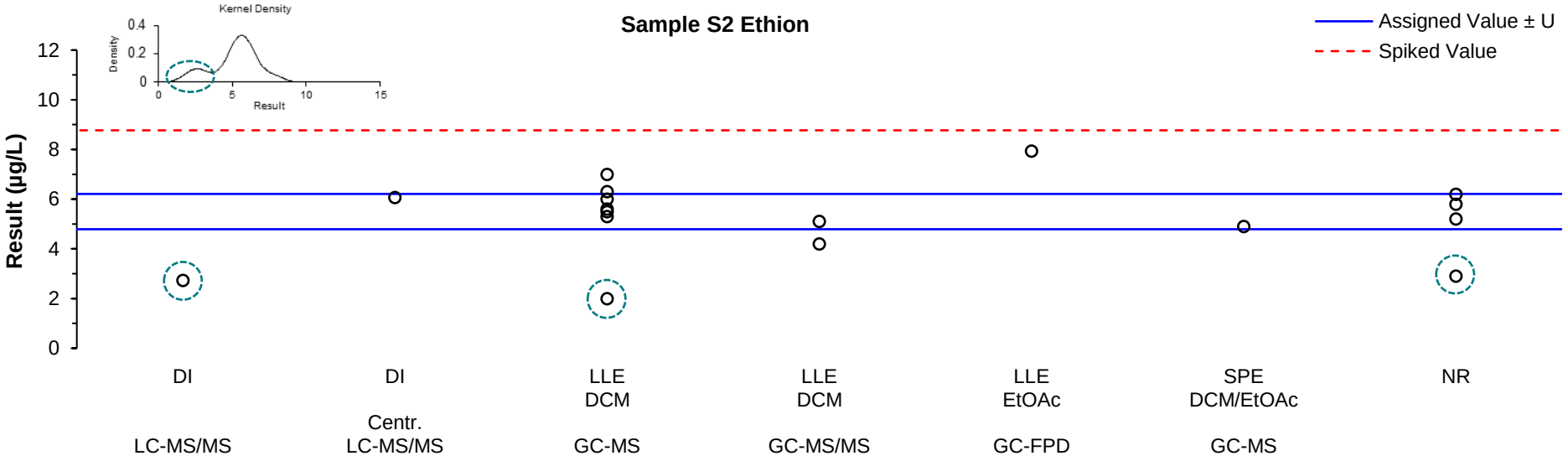


Figure 22 Sample S2 Ethion Result vs Methodology

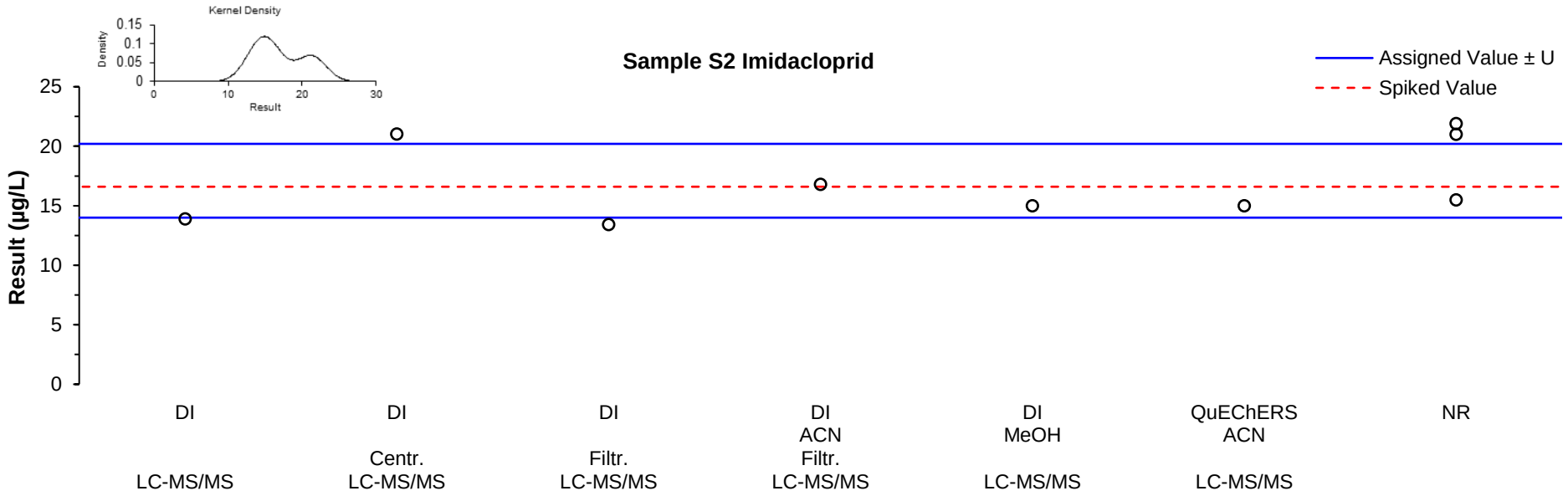


Figure 23 Sample S2 Imidacloprid Result vs Methodology

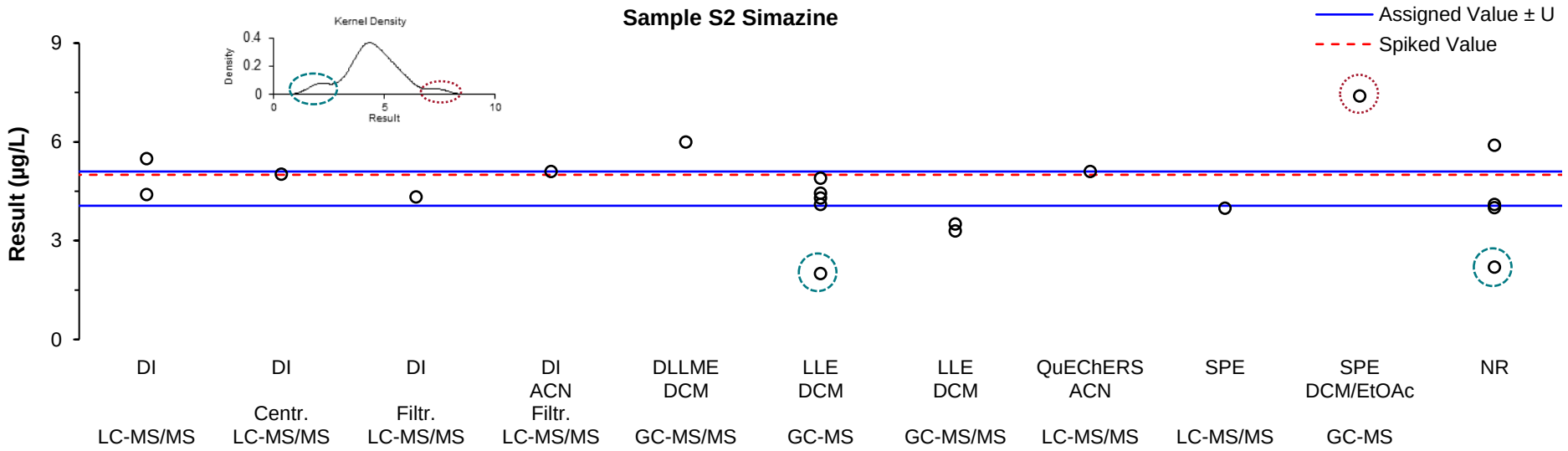


Figure 24 Sample S2 Simazine Result vs Methodology

For Sample S3, participants were supplied a 500 mL bottle. Participants reported test portions ranging from 0.125 mL to 100 mL. A comparison of *z*-scores and sample volume used for scored analytes is presented in Figure 25; there was no evident correlation in this study.

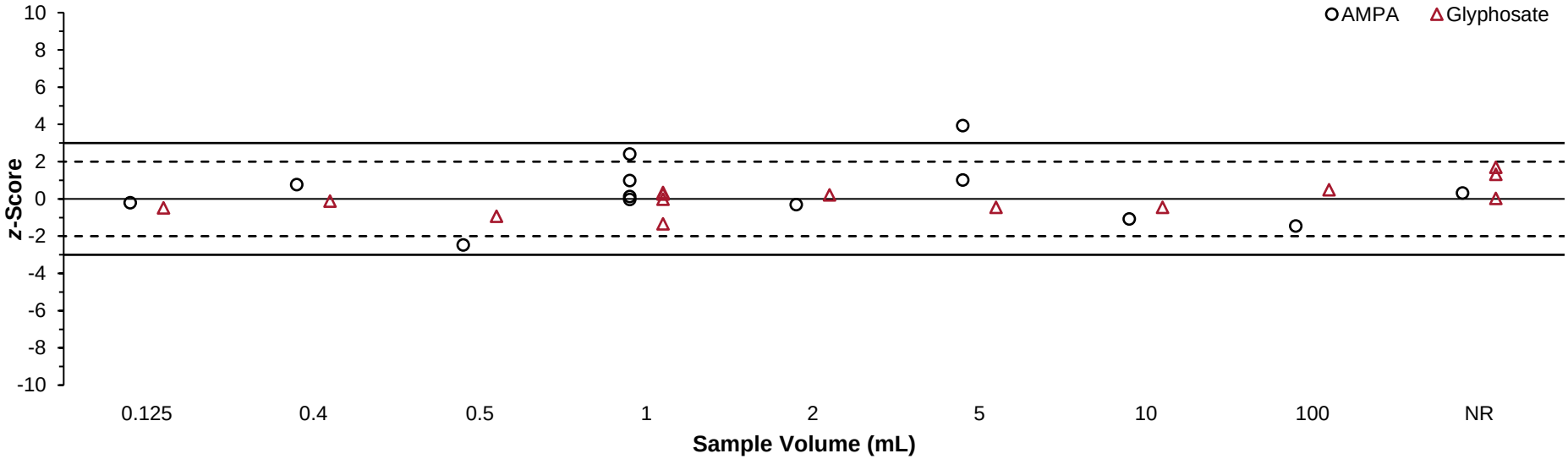


Figure 25 Sample S3 *z*-Score vs Sample Volume

For Sample S3, participants reported using DI or LLE. Most participants reported derivatisation pre-column using fluorenylmethyloxycarbonyl group (FMOC). Participants used LC techniques (e.g. HPLC, ultra high performance liquid chromatography (UHPLC)) coupled with MS, MS/MS or fluorescence detection (FLD).

Plots of numeric results and methodology employed (extraction technique, derivatisation and measurement instrument) for Sample S3 analytes are presented in Figures 26 and 27. Participants results yielding unacceptable z scores ($|z| \geq 3.0$) have been circled for reference.

In this study, those participants not derivatising with FMOC reported AMPA results that were generally closer to the spiked and assigned values; this was not observed for the glyphosate results.

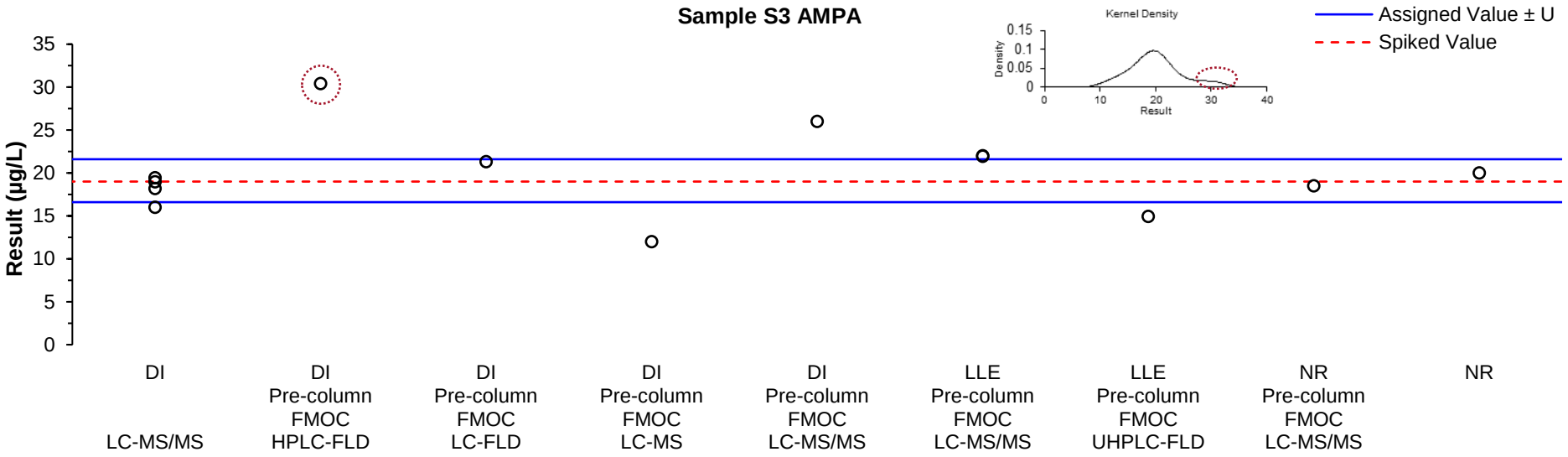


Figure 26 Sample S3 AMPA Result vs Methodology

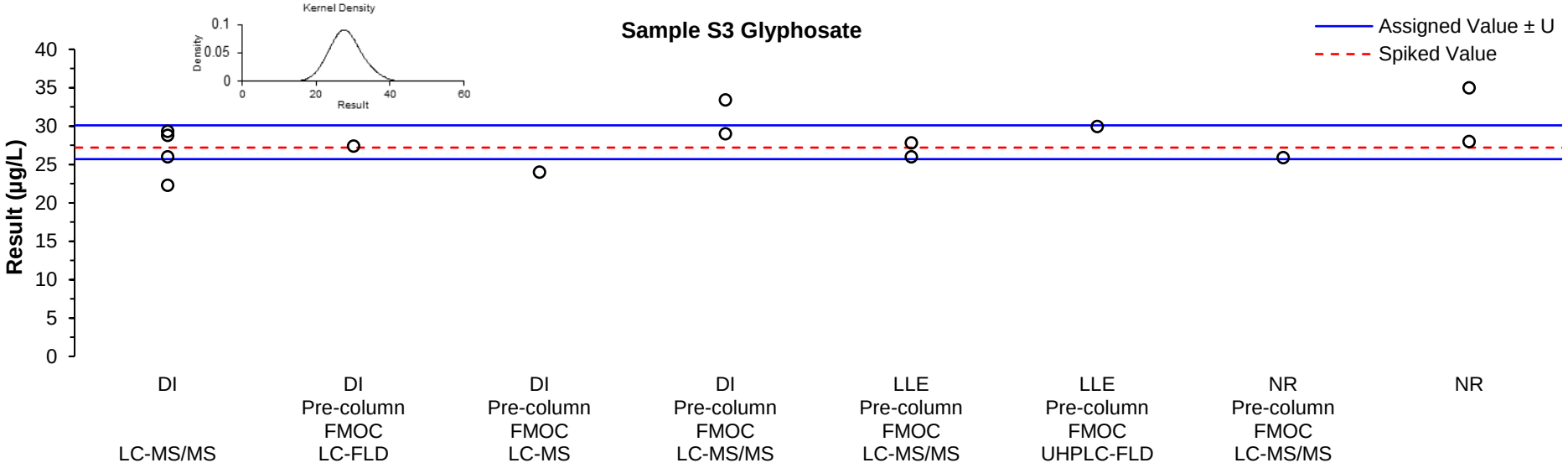


Figure 27 Sample S3 Glyphosate Result vs Methodology

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**, **2**, **5**, **9**, **12**, **15**, **16**, **19**, **21**, **22** and **23** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 35% to 139%. Laboratories **3**, **6**, **8**, **10**, **12**, **15**, **16** and **22** 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.

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

- Accustandard
- Dr Ehrenstorfer
- o2Si
- PM Separations
- 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 for scored analytes are presented in Table 22 and Figure 28.

Table 22 Summary of Participants' Results*

Lab. Code	Sample S1			Sample S2					Sample S3	
	Atrazine	Fenthion	Lindane	Chlorpyrifos	Dieldrin	Ethion	Imidacloprid	Simazine	AMPA	Glyphosate
AV	10.2	7.12	7.45	13.5	3.63	5.50	17.1	4.58	19.1	27.9
SV	11.4	10.1	9.98	20.3	5.01	8.77	16.6	5.00	19.0	27.2
1	7.41	7.19	7.16	13.9	3.55	5.11	NT	3.51	18.2	28.8
2	11.8	7.8	9.3	14.5	3.7	5.3	NT	4.1	NT	NT
3	9.7	7.0	8.4	12	4.0	4.2	15	3.3	22	26
4	8.7	NT	8	14.3	4.4	6.3	NT	4.3	NT	NT

Lab. Code	Sample S1			Sample S2					Sample S3	
	Atrazine	Fenthion	Lindane	Chlorpyrifos	Dieldrin	Ethion	Imidacloprid	Simazine	AMPA	Glyphosate
5	10.1	NT	8.2	11.7	3.25	4.9	NT	7.4	NR	NR
6	12.2	NT	10.3	14.7	2.9	5.8	21.9	4.0	<10	35
7	8.1	7.3	7.8	14.9	4.5	7.0	NT	4.9	NT	NT
8	9.8	7.4	9	14.7	4.6	6	16.8	5.1	26	29
9	13.33	6.32	6.81	17.55	4.94	7.93	NT	NT	14.94	29.94
10	9.66	8.65	7.68	8.92	3.56	2.73	NT	5.49	NT	33.41
12	8.27	5.92	5.85	12.9	2.1	5.6	NT	4.44	NT	NT
13	4	3	4	11	2	2	13.9	2	12	24
14	10.3	NT	8.95	14.6	3.45	NT	NT	6.00	21.3	27.4
15	8.558	NT	NT	NT	NT	NT	NT	3.989	21.95	27.81
16	9.51	6.22	NT	NT	NT	NT	13.43	4.33	19.43	29.33
17	9.44	5.99	4.07	NT	4.08	NT	21.03	5.02	18.98	22.31
18	9.9	5.0	7.8	8.5	2.3	2.9	15.5	2.2	NR	NR
19	10.7	NT	7.1	11.5	5.6	NT	<0.1	4.4	16	26
20	12.26	8.49	7.09	13.93	3.27	6.07	<50	NT	30.4	<30
21	13	6.8	7	14	4.4	6.2	21	5.9	20	28
22	NT	9.6	<1	14	4.3	5.5	NT	NT	NS	NS
23	11	NT	5.35	15	2.6	NT	15	5.1	18.5	25.9
24	10.8	7.5	11.6	14.3	4.4	5.2	NT	4.1	NT	NT

* All values are in µg/L. Shaded cells are results which returned a questionable or unacceptable *z*-score for scored analytes. AV = Assigned Value, SV = Spiked Value.

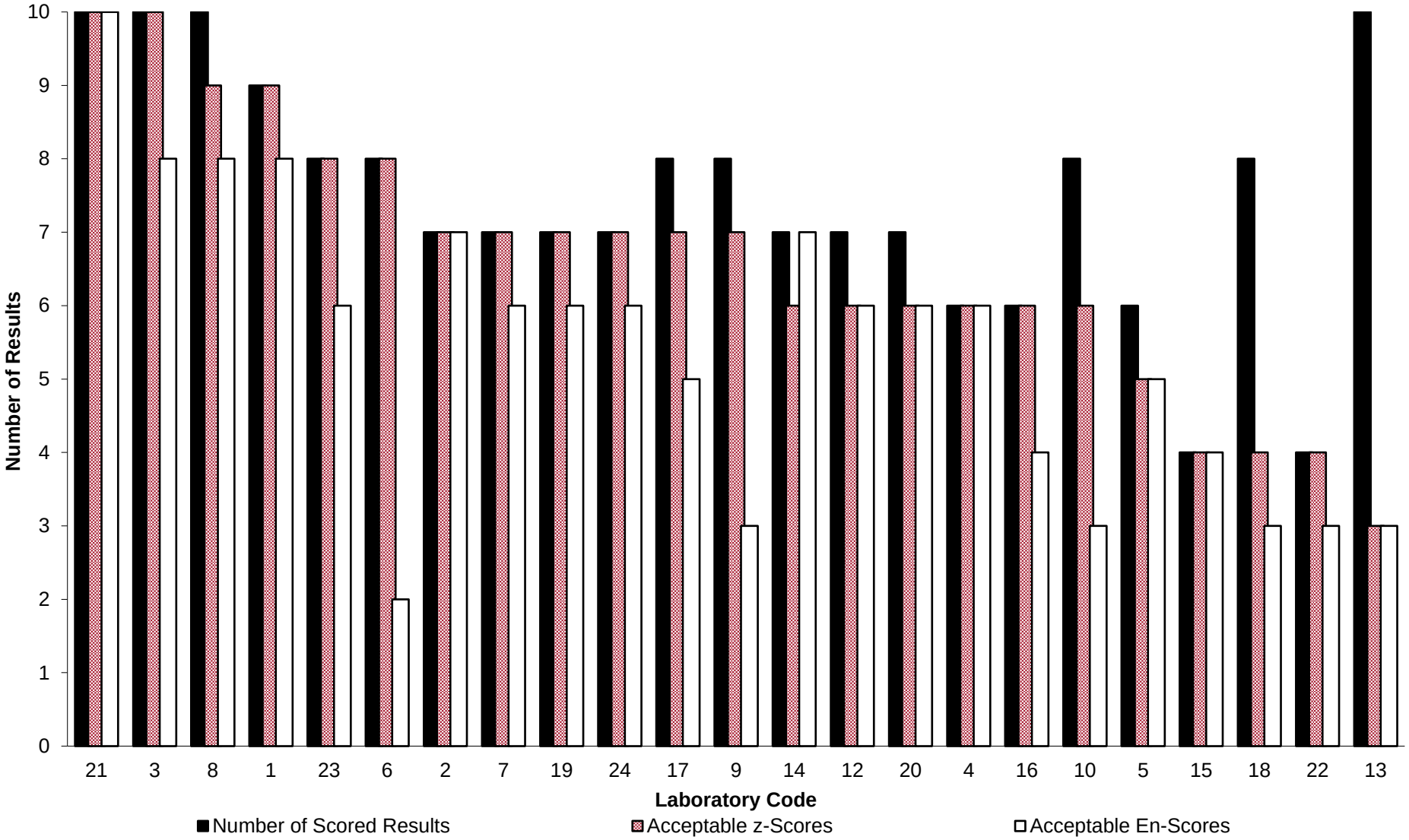


Figure 28 Summary of Participants' Performance

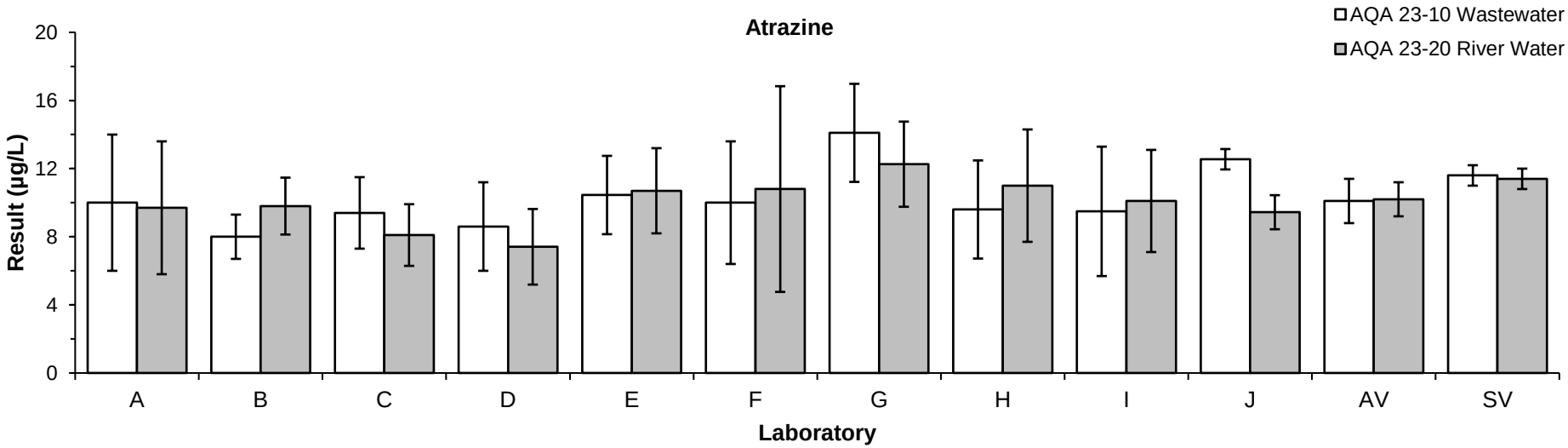
6.11 Comparison with Pesticides in Wastewater

For this study, a number of pesticides (atrazine, chlorpyrifos, dieldrin, lindane and simazine) were spiked at similar concentrations as they were spiked in NMI's recent PT study, AQA 23-10 Organic Compounds and Pesticides in Wastewater.[12]

Comparisons of the assigned values and spiked values in both studies, as well as results from participants who reported numeric results in both studies, are given in Figures 29 to 33 (laboratory identifiers are not consistent across the charts of the different analytes).

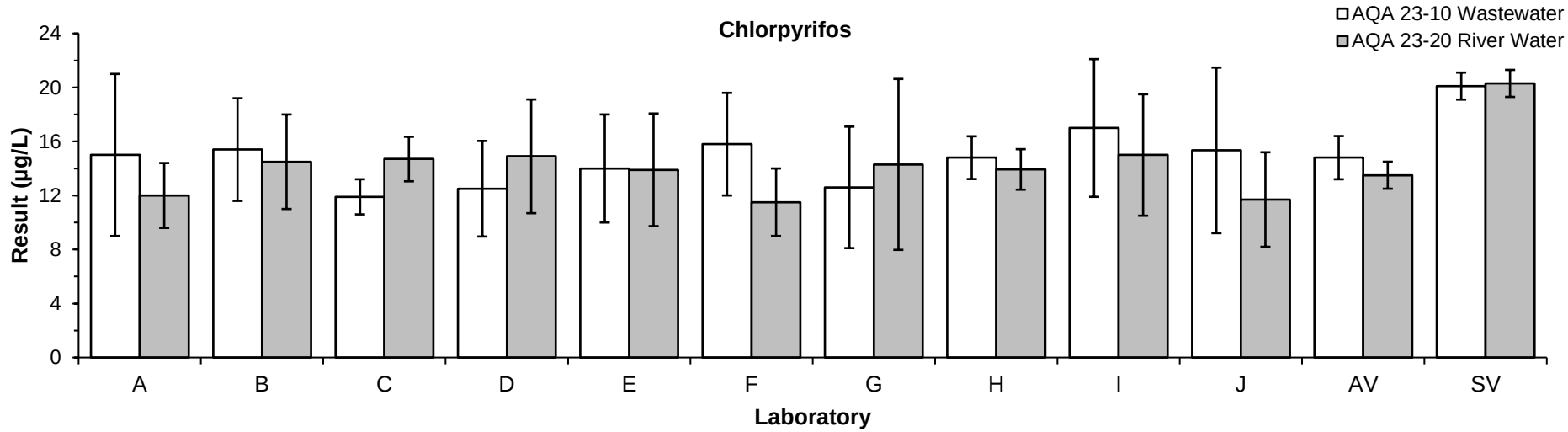
For all analytes, the assigned values in both AQA 23-10 and AQA 23-20 were in agreement with each other within their respective uncertainties, with the proportion of the assigned value in AQA 23-10 to the assigned value in AQA 23-20 ranging from 91% to 111%. The assigned values were greater (and therefore closer to the spiked value) for atrazine and simazine in the river water samples, and for chlorpyrifos, dieldrin and lindane in the wastewater samples.

In most circumstances, laboratories participating in both AQA 23-10 and AQA 23-20 reported results that were in agreement with each other within their respective uncertainties. There were six sets of results where this was not the case (Laboratory J for atrazine, Laboratories C, G and K for lindane, and Laboratories B and H for simazine). This was due to either the participant reporting significantly different results across the different studies, or reporting too small (or in some circumstances, no) uncertainty for their results.



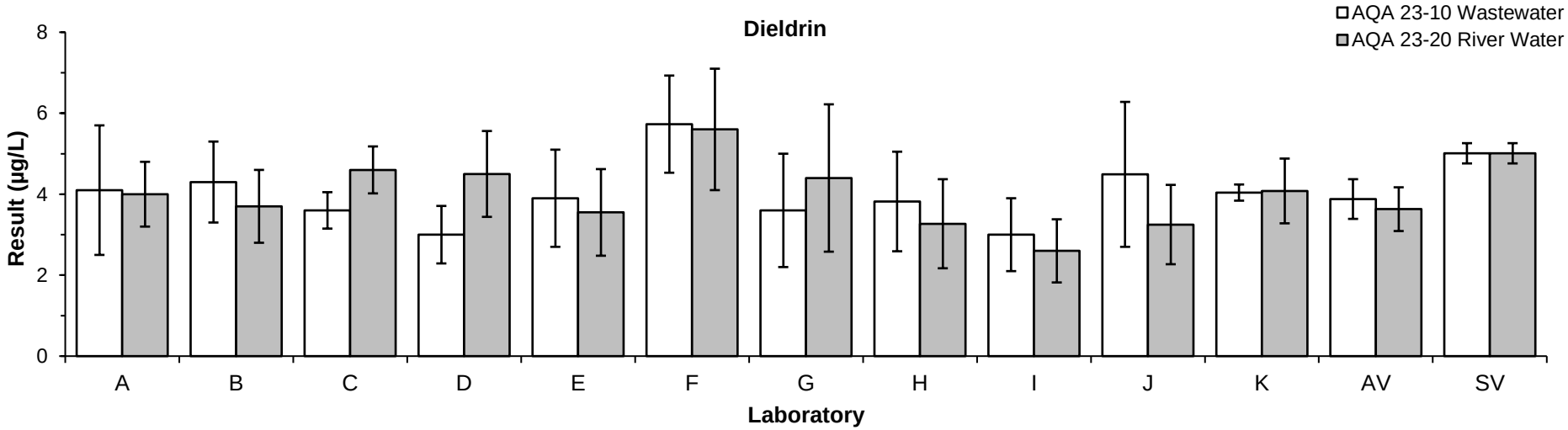
AV = Assigned Value; SV = Spiked Value

Figure 29 Atrazine Results in AQA 23-10 (Wastewater) and AQA 23-20 (River Water)



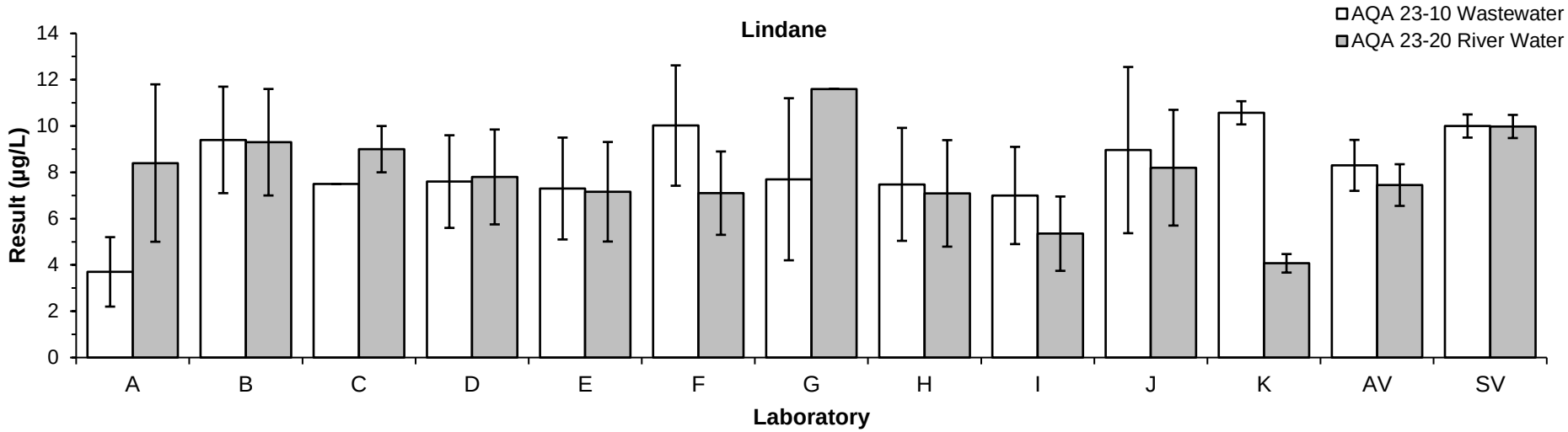
AV = Assigned Value; SV = Spiked Value

Figure 30 Chlorpyrifos Results in AQA 23-10 (Wastewater) and AQA 23-20 (River Water)



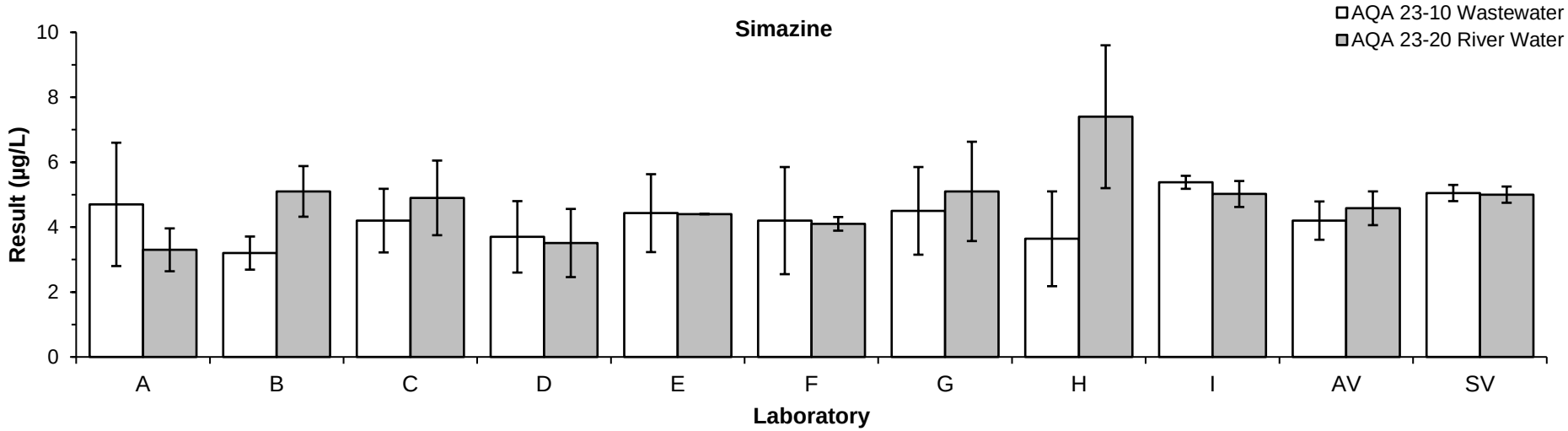
AV = Assigned Value; SV = Spiked Value

Figure 31 Dieldrin Results in AQA 23-10 (Wastewater) and AQA 23-20 (River Water)



AV = Assigned Value; SV = Spiked Value

Figure 32 Lindane Results in AQA 23-10 (Wastewater) and AQA 23-20 (River Water)



AV = Assigned Value; SV = Spiked Value

Figure 33 Simazine Results in AQA 23-10 (Wastewater) and AQA 23-20 (River Water)

6.12 Comparison with Previous Studies

A summary of participation and rates of reported results in NMI pesticides in river water PT studies over the last ten studies (2015–2023) is presented in Figure 34.

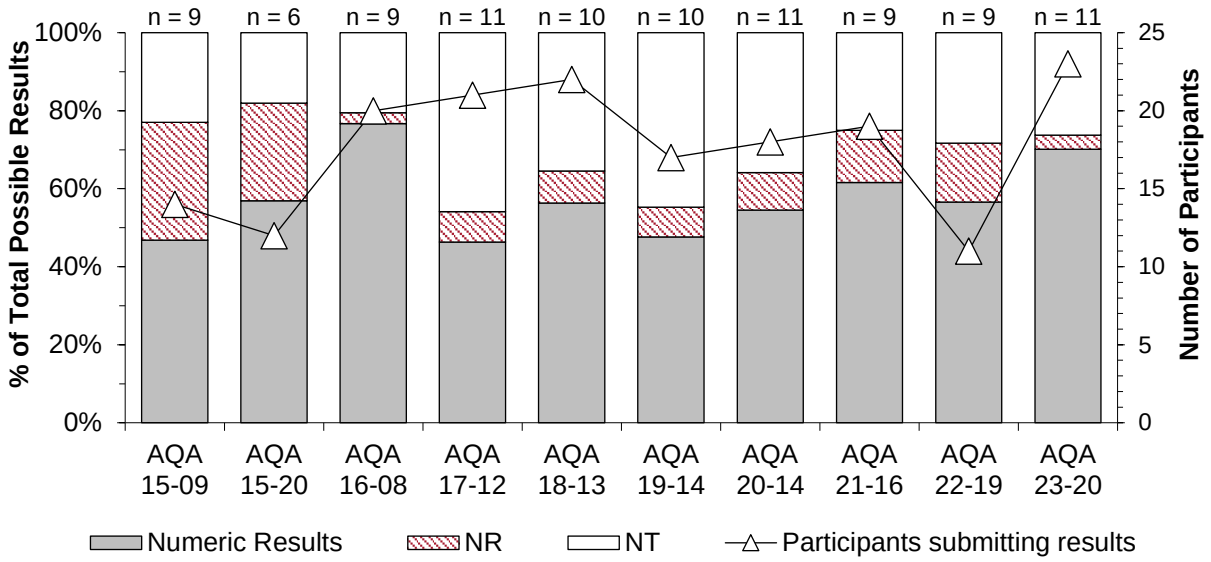


Figure 34 Summary of Participation and Reported Results in NMI Pesticides in River Water PT Studies (n = number of spiked analytes)

A summary of the acceptable performance (presented as a percentage of the total number of scores for each study) in NMI pesticides in river water PT studies over the last ten studies (2015–2023) is presented in Figure 35. 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 acceptable scores was 80% for *z*-scores and 76% for E_n-scores.

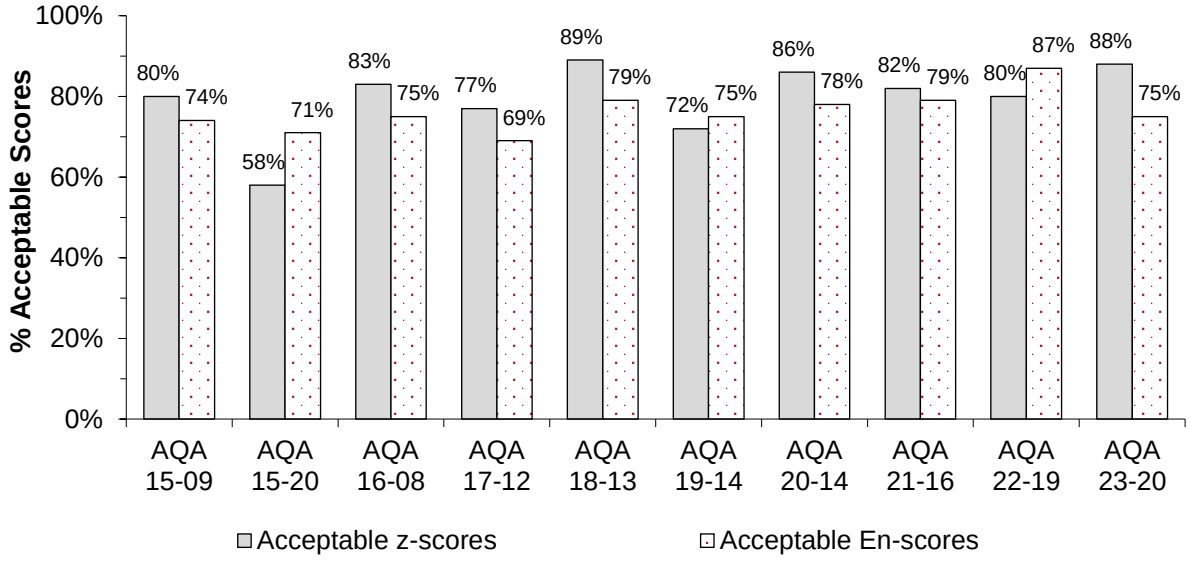


Figure 35 Acceptable *z*-Scores and E_n-Scores in NMI Pesticides in River Water PT Studies

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.

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties.[8] Figure 36 presents a summary of the relative uncertainties as reported by participants over the last ten studies (2015–2023). Over this time period, the vast majority of numeric results were reported with uncertainties (96%), with 84% of participants reporting that they were accredited to ISO/IEC 17025.

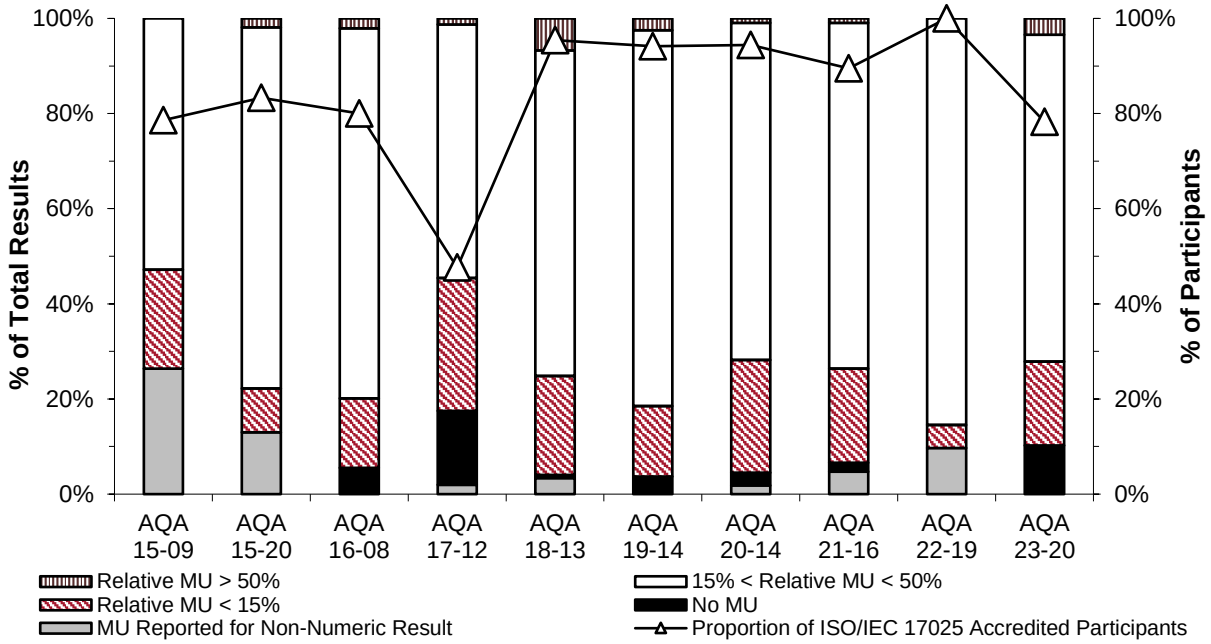


Figure 36 Summary of Participants' Relative Uncertainties for NMI Pesticides in River Water PT Studies

7 REFERENCES

Please note that for all undated references, the latest edition of the referenced document (including any amendments) applies.

[1] ISO/IEC 17043:2010, *Conformity assessment – General requirements for proficiency testing.*

[2] NMI, 2023, *Study Protocol for Proficiency Testing*, viewed January 2024, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>

[3] NMI, 2023, *Chemical Proficiency Testing Statistical Manual*, viewed January 2024, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>

[4] Thompson, M., Ellison, S.L.R. and Wood, R., 2006, 'The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem.*, vol 78, pp 145–196.

[5] National Environment Protection (Assessment of Site Contamination) Measure 1999 as amended 2013, Volume 2: Schedule B1, *Guideline on Investigation Levels for Soil and Groundwater*, viewed January 2024, <https://www.legislation.gov.au/F2008B00713/latest/text/12>

[6] ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*.

[7] Thompson, M., 2000, 'Recent Trends in Inter-laboratory Precision at ppb and sub-ppb Concentrations in Relation to Fitness for Purpose Criteria in Proficiency Testing', *Analyst*, vol 125, pp 385–386.

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

[9] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd ed., viewed January 2024, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>

[10] NATA, 2020, *Update to Measurement Uncertainty resources*, viewed January 2024, <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.

[12] Department of Industry, Science and Resources (NMI), 2023, *Proficiency Test Final Report AQA 23-10 Organic Compounds and Pesticides in Wastewater*.

APPENDIX 1 SAMPLE PREPARATION

The three samples were prepared using river water obtained from the Wingecarribee River. The water was filtered through a glass fibre filter and autoclaved. The water used for Sample S1 was adjusted to pH 6.55 using hydrochloric acid. The pH of the water used for Samples S2 and S3 was not adjusted.

The spiking solutions for S1 and S2 were prepared by dissolving the standards in acetone except for imidacloprid which was dissolved in isopropyl alcohol. The glyphosate and AMPA for Sample S3 were dissolved in water.

The filtered autoclaved water was dispensed into a stainless steel pot through a Sartorius filter using a peristaltic pump. The pot had been pre-rinsed with 70% ethanol:30% reagent grade water. Each analyte was spiked in the stainless steel pot, and then stirred using a top-driven impeller stirrer for at least two hours.

Samples S1 and S2 were dispensed into 100 mL and 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 4ºC.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was performed for this study as the samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples. Participants' results in this study also gave no reason to question the samples' homogeneity.

A2.2 Stability

No stability testing was conducted for this study, though previous use of these pesticides and similar analytes gave assurance that these samples were sufficiently 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 in this study are presented in Figures 37 to 46 (solid blue lines are the assigned value ± U). No significant analyte degradation with respect to the amount of time spent in transit was observed.

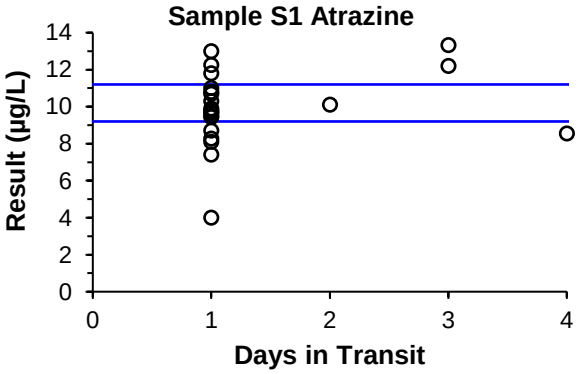


Figure 37 S1 Atrazine Result vs Transit Days

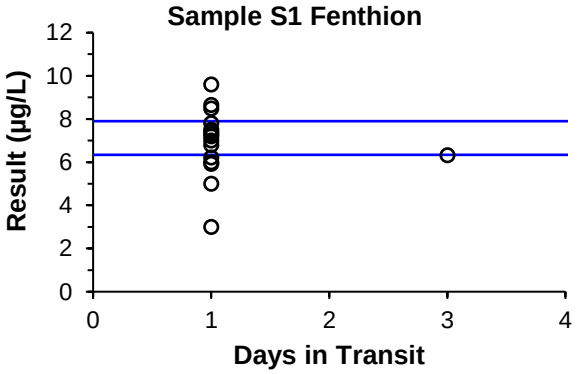


Figure 38 S1 Fenthion Result vs Transit Days

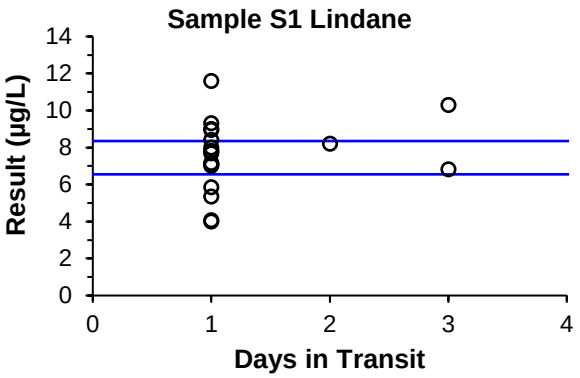


Figure 39 S1 Lindane Result vs Transit Days

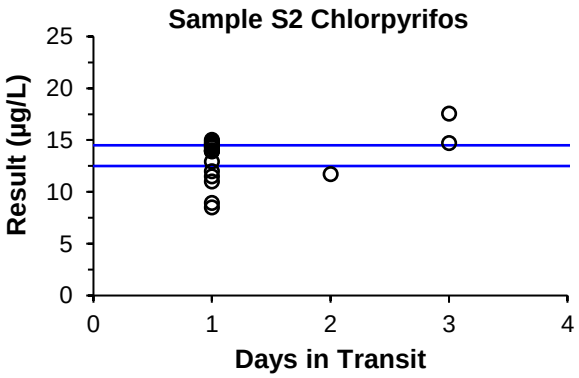


Figure 40 S2 Chlorpyrifos Result vs Transit Days

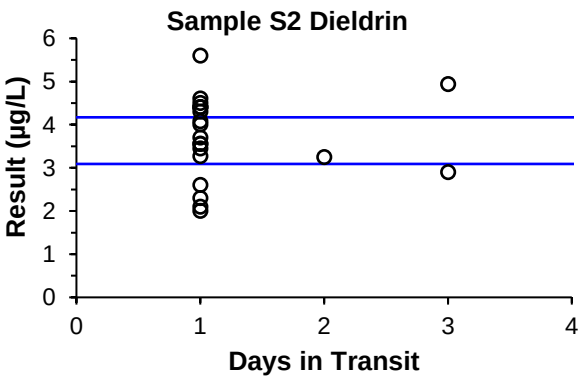


Figure 41 S2 Dieldrin Result vs Transit Days

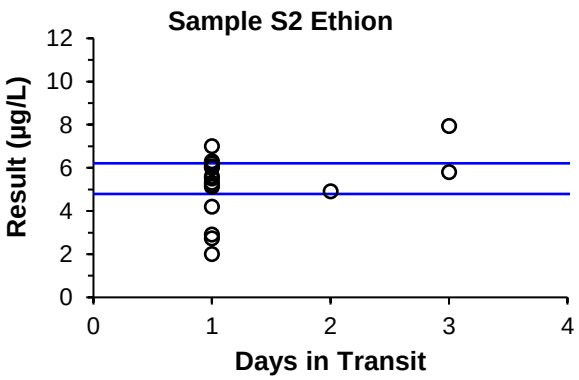


Figure 42 S2 Ethion Result vs Transit Days

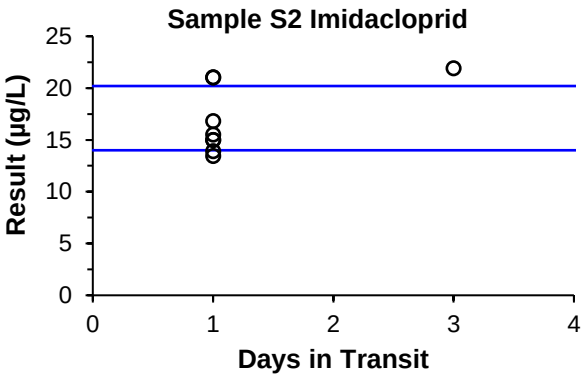


Figure 43 S2 Imidacloprid Result vs Transit Days

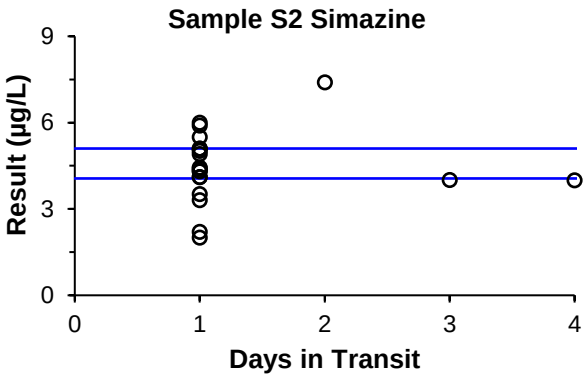


Figure 44 S2 Simazine Result vs Transit Days

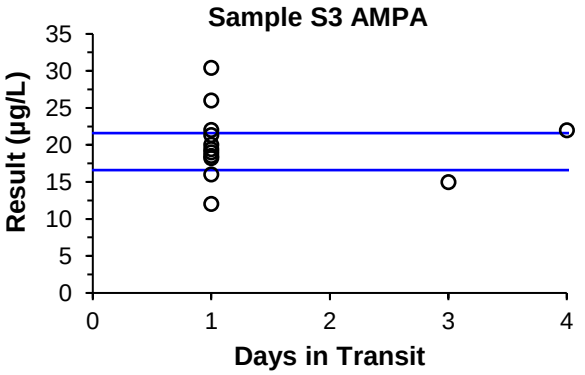


Figure 45 S3 AMPA Result vs Transit Days

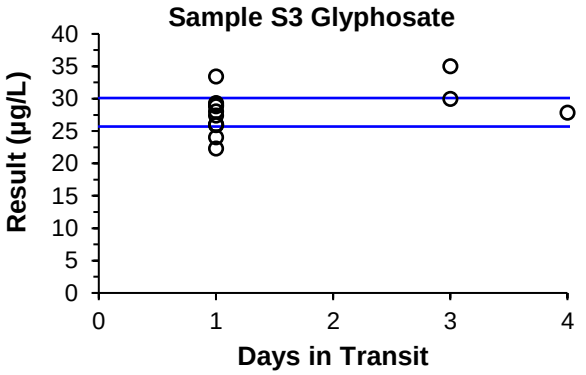


Figure 46 S3 Glyphosate Result vs Transit Days

APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, *z*-SCORE AND E_n-SCORE CALCULATIONS

A3.1 Robust Average and Associated Uncertainty

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

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

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 23.

Table 23 Uncertainty of Robust Average for Chlorpyrifos in Sample S2

Number of results (p)	20
Robust Average	13.5 µg/L
$S_{rob\ av}$	1.9 µg/L
$u_{rob\ av}$	0.5 µg/L
k	2
$U_{rob\ av}$	1.0 µg/L

Therefore, the robust average for chlorpyrifos in Sample S2 is 13.5 ± 1.0 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 (Section 4).

A worked example is set out below in Table 24.

Table 24 *z*-Score and E_n-Score for Sample S1 Atrazine Result Reported by Laboratory 1

Participant Result (µg/L)	Assigned Value (µg/L)	Target Standard Deviation	*z*-Score	E_n-Score
7.41 ± 2.22	10.2 ± 1.0	15% as PCV, or: 0.15 × 10.2 = 1.53 µg/L	$z = \frac{7.41 - 10.2}{1.53} = -1.82$	$E_n = \frac{7.41 - 10.2}{\sqrt{2.22^2 + 1.0^2}} = -1.15$

APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 25 to 35. Some responses may be modified so that the participant cannot be identified.

Table 25 Methodology – Acetamiprid

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
12					
13					
14					
15					
16					
17	1	Direct Injection		centrifuge	LC-MS/MS
18					
19					
20					
21					
22					
23					
24					

Table 26 Methodology – Atrazine

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	100	Liquid-Liquid	DCM	None	GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS
3	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
4	250	Liquid-Liquid	DCM	Nil	GC-MS
5	500	SPE	DCM/EtOAc	None	GC-MS
6					

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
7	100	Liquid-Liquid	DCM	None	GC-MS
8	100	Liquid-Liquid	DCM	NONE	GC-MS
9	100	Liquid-Liquid	Ethyl acetate	None	GC-NPD
10	10	Direct injection			LC-MS/MS
12	100	Liquid-Liquid	DCM	NA	GCMS
13	500	Liquid-Liquid	DCM	N/A	GC-MS
14	5	DLLME	DCM	None	GC-MS/MS
15	100	SPE			LC-MS/MS
16	0.5	Direct Injection		Filtration	LC-MS/MS
17	1	Direct Injection		centrifuge	LC-MS/MS
18					
19	10	Direct Injection			LC-MS/MS
20	1	Direct Injection	N/A	Centrifugation	LC-MS/MS
21					
22					
23	20	Quechers	acetonitrile	None	LC-MS/MS
24					

Table 27 Methodology – Chlorpyrifos

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	100	Liquid-Liquid	DCM	None	GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS
3	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
4	250	Liquid-Liquid	DCM	Nil	GC-MS
5	500	SPE	DCM/EtOAc	None	GC-MS
6					
7	100	Liquid-Liquid	DCM	None	GC-MS
8	100	Liquid-Liquid	DCM	NONE	GC-MS
9	100	Liquid-Liquid	Ethyl acetate	None	GC-FPD
10	10	Direct injection			LC-MS/MS
12	100	Liquid-Liquid	DCM	NA	GCMS
13	500	Liquid-Liquid	DCM	N/A	GC-MS
14	5	DLLME	DCM	None	GC-MS/MS
15					
16					
17					
18					

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
19	500	SPE	dcm/EtOAc		GC-MS/MS
20	1	Direct Injection	N/A	Centrifugation	LC-MS/MS
21					
22	200	Liquid-Liquid	DCM	NONE	GC-MS
23	20	Quechers	acetonitrile	None	LC-MS/MS
24					

Table 28 Methodology – Dieldrin

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	100	Liquid-Liquid	DCM	None	GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS
3	50	Liquid-Liquid	DCM	N/A	GC-ECD
4	250	Liquid-Liquid	DCM	Nil	GC-ECD
5	500	SPE	DCM/EtOAc	None	GC-MS
6					
7	100	Liquid-Liquid	DCM	None	GC-MS
8	100	Liquid-Liquid	DCM	NONE	GC-MS
9	100	Liquid-Liquid	Hexane	None	GC-ECD
10	8	Liquid-Liquid	DCM		GC-MS/MS
12	100	Liquid-Liquid	DCM	NA	GCMS/ECD
13	500	Liquid-Liquid	DCM	N/A	GC-MS
14	5	DLLME	DCM	None	GC-MS/MS
15					
16					
17	500	Liquid-Liquid	DCM		GC-MS/MS
18					
19	500	SPE	dcm/EtOac		GC-MS
20	30	Liquid-Liquid	DCM	NA	GC-MS/MS
21					
22	200	Liquid-Liquid	DCM	NONE	GC-MS
23	40	Liquid-Liquid	Hexane	None	GC-MS/MS
24					

Table 29 Methodology – Ethion

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	100	Liquid-Liquid	DCM	None	GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
3	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
4	250	Liquid-Liquid	DCM	Nil	GC-MS
5	500	SPE	DCM/EtOAc	None	GC-MS
6					
7	100	Liquid-Liquid	DCM	None	GC-MS
8	100	Liquid-Liquid	DCM	NONE	GC-MS
9	100	Liquid-Liquid	Ethyl acetate	None	GC-FPD
10	10	Direct injection			LC-MS/MS
12	100	Liquid-Liquid	DCM	NA	GCMS
13	500	Liquid-Liquid	DCM	N/A	GC-MS
14					
15					
16					
17					
18					
19					
20	1	Direct Injection	N/A	Centrifugation	LC-MS/MS
21					
22	200	Liquid-Liquid	DCM	NONE	GC-MS
23					
24					

Table 30 Methodology – Fenthion

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	100	Liquid-Liquid	DCM	None	GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS
3	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
4					
5					
6					
7	100	Liquid-Liquid	DCM	None	GC-MS
8	100	Liquid-Liquid	DCM	NONE	GC-MS
9	100	Liquid-Liquid	Ethyl acetate	None	GC-FPD
10	8	Liquid-Liquid	DCM		GC-MS/MS
12	100	Liquid-Liquid	DCM	NA	GCMS
13	500	Liquid-Liquid	DCM	N/A	GC-MS
14					

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
15					
16	0.5	Direct Injection		Filtration	LC-MS/MS
17	500	Liquid-Liquid	DCM		GC-MS/MS
18					
19					
20	1	Direct Injection	N/A	Centrifugation	LC-MS/MS
21					
22	200	Liquid-Liquid	DCM	NONE	GC-MS
23					
24					

Table 31 Methodology – Imidacloprid

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1					
2					
3	5	Direct Injection	Methanol	N/A	LC-MS/MS
4					
5					
6					
7					
8	1	Direct Injection	Acetonitrile	Filtration	LC-MS/MS
9					
10					
12					
13	1	Direct Injection	N/A	N/A	LC-MS/MS
14					
15					
16	0.5	Direct Injection		Filtration	LC-MS/MS
17	1	Direct Injection		centrifuge	LC-MS/MS
18					
19	10	Direct Injection			LC-MS/MS
20	1.6	Direct Injection	Acetonitrile	Filtration	HPLC-DAD
21					
22					
23	20	Quechers	acetonitrile	None	LC-MS/MS
24					

Table 32 Methodology – Lindane

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	100	Liquid-Liquid	DCM	None	GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS
3	50	Liquid-Liquid	DCM	N/A	GC-ECD
4	250	Liquid-Liquid	DCM	Nil	GC-ECD
5	500	SPE	DCM/EtOAc	None	GC-MS
6					
7	100	Liquid-Liquid	DCM	None	GC-MS
8	100	Liquid-Liquid	DCM	NONE	GC-MS
9	100	Liquid-Liquid	Hexane	None	GC-ECD
10	8	Liquid-Liquid	DCM		GC-MS/MS
12	100	Liquid-Liquid	DCM	NA	GCMS/ECD
13	500	Liquid-Liquid	DCM	N/A	GC-MS
14	5	DLLME	DCM	None	GC-MS/MS
15					
16					
17	500	Liquid-Liquid	DCM		GC-MS/MS
18					
19	500	SPE	dcm/EtOac		GC-MS
20	30	Liquid-Liquid	DCM	NA	GC-MS/MS
21					
22	200	Liquid-Liquid	DCM	NONE	GC-MS
23	40	Liquid-Liquid	Hexane	None	GC-MS/MS
24					

Table 33 Methodology – Simazine

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	100	Liquid-Liquid	DCM	None	GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS
3	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
4	250	Liquid-Liquid	DCM	Nil	GC-MS
5	500	SPE	DCM/EtOAc	None	GC-MS
6					
7	100	Liquid-Liquid	DCM	None	GC-MS
8	1	Direct Injection	Acetonitrile	Filtration	LC-MS/MS
9					
10	10	Direct injection			LC-MS/MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
12	100	Liquid-Liquid	DCM	NA	GCMS
13	500	Liquid-Liquid	DCM	N/A	GC-MS
14	5	DLLME	DCM	None	GC-MS/MS
15	100	SPE			LC-MS/MS
16	0.5	Direct Injection		Filtration	LC-MS/MS
17	1	Direct Injection		centrifuge	LC-MS/MS
18					
19	10	Direct Injection			LC-MS/MS
20					
21					
22					
23	20	Quechers	acetonitrile	None	LC-MS/MS
24					

Table 34 Methodology – AMPA

Lab. Code	Sample Volume (mL)	Extraction	Derivatisation Procedure	Derivatisation Agent	Measurement Instrument
1	2	Direct Injection	None	None	LC-MS/MS
2					
3	5	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
4					
5					
6					
7					
8	1	Direct Injection	Pre-column	FMOC	LC-MS/MS
9	100	Liquid-Liquid	Pre-column	FMOC	UHPLC/FLD
10					
12					
13	0.5	Direct Injection	Pre-column	9-Fluorenylmethoxy-carbonyl chloride	LC-MS
14	0.4	Direct Injection	Pre-column	FMOC	LC-FLD
15	1	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
16	1	Direct Injection			LC-MS/MS
17	1	Direct Injection			LC-MS/MS
18					
19	10	Direct Injection			LC-MS/MS
20	5	Direct Injection	Pre-column	9-fluorenyl-methylchloroformate	HPLC-FLD

Lab. Code	Sample Volume (mL)	Extraction	Derivatisation Procedure	Derivatisation Agent	Measurement Instrument
21					
22	NS	NS	NS	NS	NS
23	0.125	Derivatisation	Pre-column	FMOC-Cl	LC-MS/MS
24					

Table 35 Methodology – Glyphosate

Lab. Code	Sample Volume (mL)	Extraction	Derivatisation Procedure	Derivatisation Agent	Measurement Instrument
1	2	Direct Injection	None	None	LC-MS/MS
2					
3	5	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
4					
5					
6					
7					
8	1	Direct Injection	Pre-column	FMOC	LC-MS/MS
9	100	Liquid-Liquid	Pre-column	FMOC	UHPLC/FLD
10		Direct Injection	Pre-column	FMOC	LC-MS/MS
12					
13	0.5	Direct Injection	Pre-column	9-Fluorenylmethoxy-carbonyl chloride	LC-MS
14	0.4	Direct Injection	Pre-column	FMOC	LC-FLD
15	1	Liquid-Liquid	Pre-column	FMOC	LC-MS/MS
16	1	Direct Injection			LC-MS/MS
17	1	Direct Injection			LC-MS/MS
18					
19	10	Direct Injection			LC-MS/MS
20	5	Direct Injection	Pre-column	9-fluorenyl-methylchloroformate	HPLC-FLD
21					
22	NS	NS	NS	NS	NS
23	0.125	Derivatisation	Pre-column	FMOC-Cl	LC-MS/MS
24					

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

ACN	Acetonitrile
AMPA	Aminomethylphosphonic acid
AV	Assigned Value
Centr.	Centrifugation
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DAD	Diode Array Detection
DCM	Dichloromethane
DEET	*N*,*N*-Diethyl-3-methylbenzamide
DI	Direct Injection
DLLME	Dispersive Liquid-Liquid Microextraction
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
Filtr.	Filtration
FLD	Fluorescence Detection
FMOC	Fluorenylmethyloxycarbonyl
FPD	Flame Photometric Detection
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
NA	Not Applicable
NATA	National Association of Testing Authorities, Australia
NMI	National Measurement Institute, Australia
NPD	Nitrogen Phosphorus Detection
NR	Not Reported
NS	Not Supplied
NT	Not Tested
p,p'-DDD	Dichlorodiphenyldichloroethane
p,p'-DDE	Dichlorodiphenyldichloroethylene
p,p'-DDT	Dichlorodiphenyltrichloroethane
PCV	Performance Coefficient of Variation
PT	Proficiency Testing
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe extraction method
RA	Robust Average
Rec	Recovery
RM	Reference Material
SD	Standard Deviation
SI	International System of Units
SPE	Solid Phase Extraction
SS	Spiked Samples
SV	Spiked Value (or formulated concentration of a PT sample)
Total DDT	Total amount of DDD, DDE and DDT
UHPLC	Ultra High Performance Liquid Chromatography

END OF REPORT