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

Proficiency Test Final Report AQA 22-19 Pesticides in River Water

March 2023

ACKNOWLEDGMENTS

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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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SUMMARY

AQA 22-19 Pesticides in River Water commenced in October 2022. Eleven laboratories registered to participate, and all 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 99 results, 56 numeric results (57%) were submitted. Fifteen results were a 'less than' value (< *x*) or Not Reported (NR), and 28 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 **2**, **3** and **6** reported numeric results for all analytes of interest in this study.

Three participants did not report numeric results for analytes which they tested for and were present in the test samples (total of 7 results). Four participants reported numeric results for analytes not spiked into the test samples (total of 8 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 15 *z*-scores, 12 (80%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Of 15 E_n-scores, 13 (87%) 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 river water.*

Participants reported a wide variety of methods. No significant trend was observed.

Five participants reported recoveries, however no participant reported correcting 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 56 numeric results, all were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 8.6% to 50%.

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

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

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO/IEC 17043:2010,[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:

Invitations sent	24/10/2022
Samples sent	22/11/2022
Results due	13/01/2023
Interim report	30/01/2023

An extended results reporting period was given due to sample delivery delays and to account for end-of-year shut down periods. The interim report was delayed to accommodate exceptional circumstances affecting a participant.

2.2 Participation and Laboratory Code

Eleven laboratories registered to participate in this study, and all participants were assigned a confidential laboratory code number for this study. All 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

Aldicarb	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 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 Values of Test Samples

Sample	Analyte	Spiked Value (µg/L)	Uncertainty[a] (µg/L)
S1[b]	p,p'-DDT	1.08	0.05
	Hexazinone	6.73	0.34
	Imidacloprid	11.0	0.6
S2	Total Chlordane[c]	1.05	0.05
	Molinate	2.17	0.11
	Parathion-methyl	3.04	0.15
	Simazine	2.88	0.14
S3	AMPA	27.3	1.4
	Glyphosate	16.2	0.8

[a] 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.

[b] Sample S1 was also spiked with omethoate, however this analyte was highly unstable in the river water matrix and was not detected by the majority of participants.

[c] Sample S2 was spiked with *trans*-chlordane only. Participants were requested to report for total chlordane.

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 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. Robust averages for all analytes except Sample S1 p,p'-DDT and Sample S2 total chlordane were within 75% to 96% of the spiked values, which is similar to what has been observed in previous NMI pesticides in river water studies. p,p'-DDT and *trans*-chlordane (the chlordane isomer spiked for this study) have been used in previous studies and similar, low recoveries were also observed in these studies;[6,7] these analytes were not scored in this study.

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 22 November 2022.

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 12 December 2022 by email to proficiency@measurement.gov.au.

The results due date was extended to 13 January 2023 due to customs clearance delays to some international participants, and to then account for end-of-year shut down periods. An additional extension was given to one participant due to exceptional circumstances.

2.8 Interim Report

An interim report was emailed to all participants on 30 January 2023.

The interim report release was delayed to allow the participant given the additional extension to report their results.

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.

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 - CRM Duplicate analysis Instrument calibration	Recoveries of SS	
2	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
3	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
4	Top Down - precision and estimates of the method and laboratory bias	Control samples	Recoveries of SS	ISO/GUM
5	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis	CRM	ISO/GUM
6	Top Down - reproducibility (standard deviation) from PT studies used directly	Control samples - SS Duplicate analysis Instrument calibration	Recoveries of SS	Eurachem/CITAC Guide
7	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)		Instrument calibration Laboratory bias from PT studies Recoveries of SS	Eurachem/CITAC Guide
8	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - SS Instrument calibration	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
9	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Standard purity	NMI Uncertainty Course
10	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM	CRM Recoveries of SS	Eurachem/CITAC Guide
11	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide

* 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
10	All	Date analysed between 16/12/2022 - 03/01/2023

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.

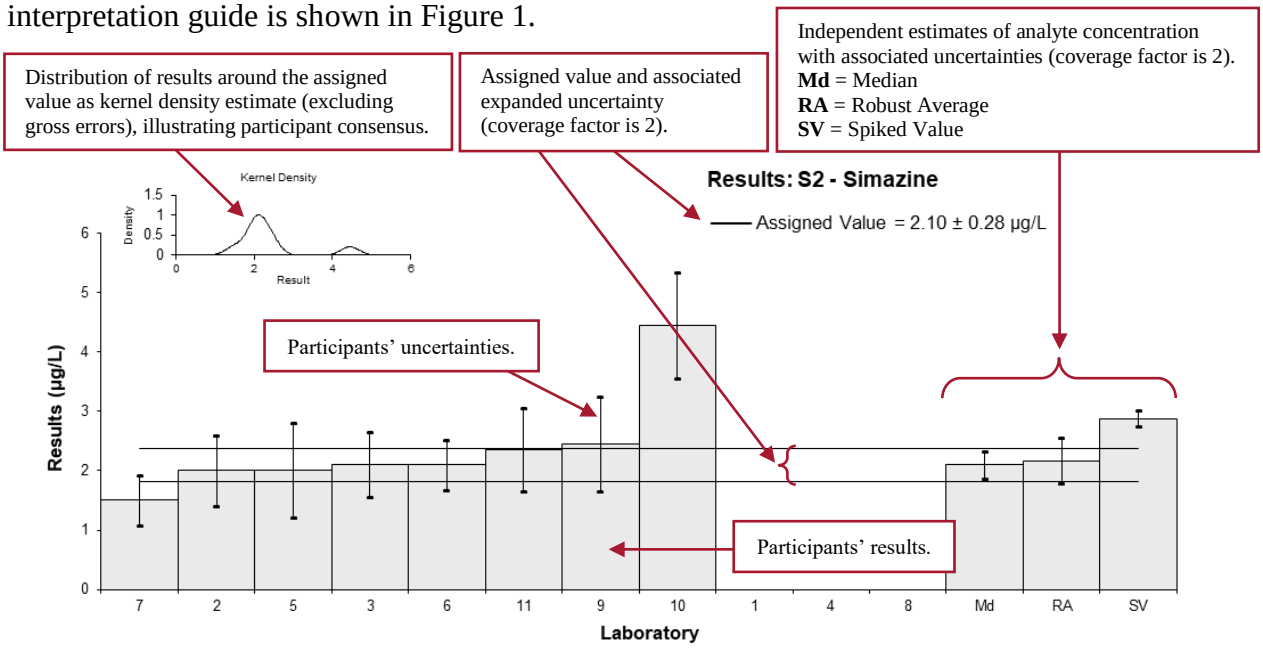


Figure 1 Guide to Presentation of Results

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 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 13528:2022.[8]

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.[9] 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 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.[10]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[11]

5 TABLES AND FIGURES

Table 5

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.27	0.08	NR
2	0.42	0.13	NR
3	1	0.33	NR
4	<1	0.45	NR
5	0.293	0.12	61
6	0.62	0.12	102
7	<2	0.8	NR
8	0.58	0.05	98
9	0.34	0.1	NR
10	<1	NR	NR
11	0.59	0.177	NR

Statistics

Assigned Value	Not Set	
Spike Value	1.08	0.05
Robust Average	0.49	0.19
Median	0.50	0.18
Mean	0.51	
N	8	
Max	1	
Min	0.27	
Robust SD	0.22	
Robust CV	44%	

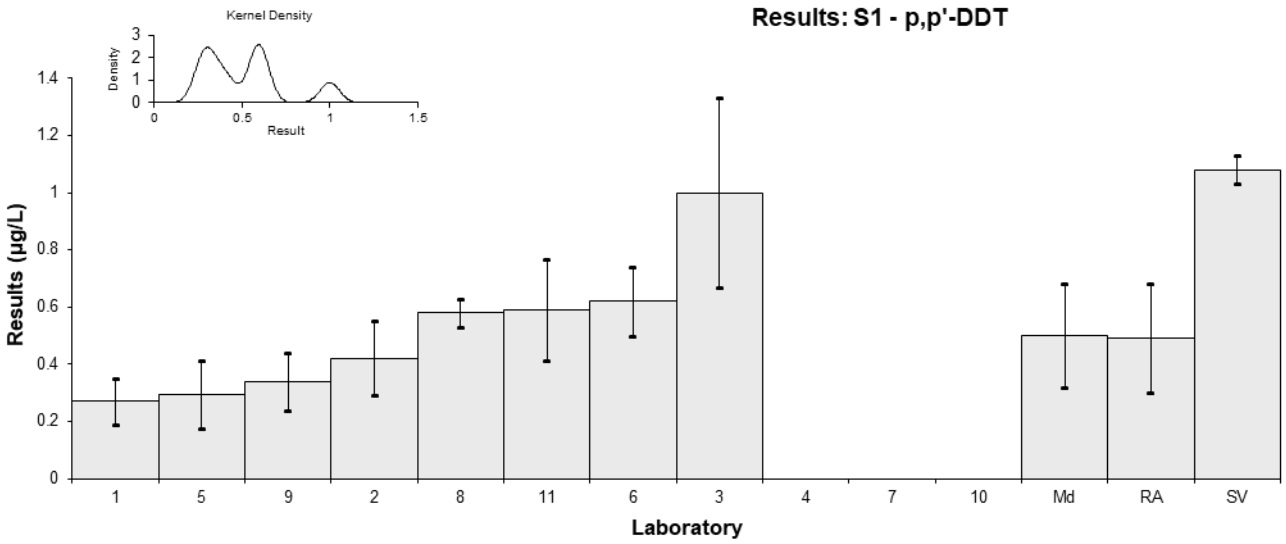

Results: S1 - p,p'-DDT
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1
5
9
2
8
11
6
3
4
7
10
Md
RA
SV

Figure 2

Table 6

Sample Details

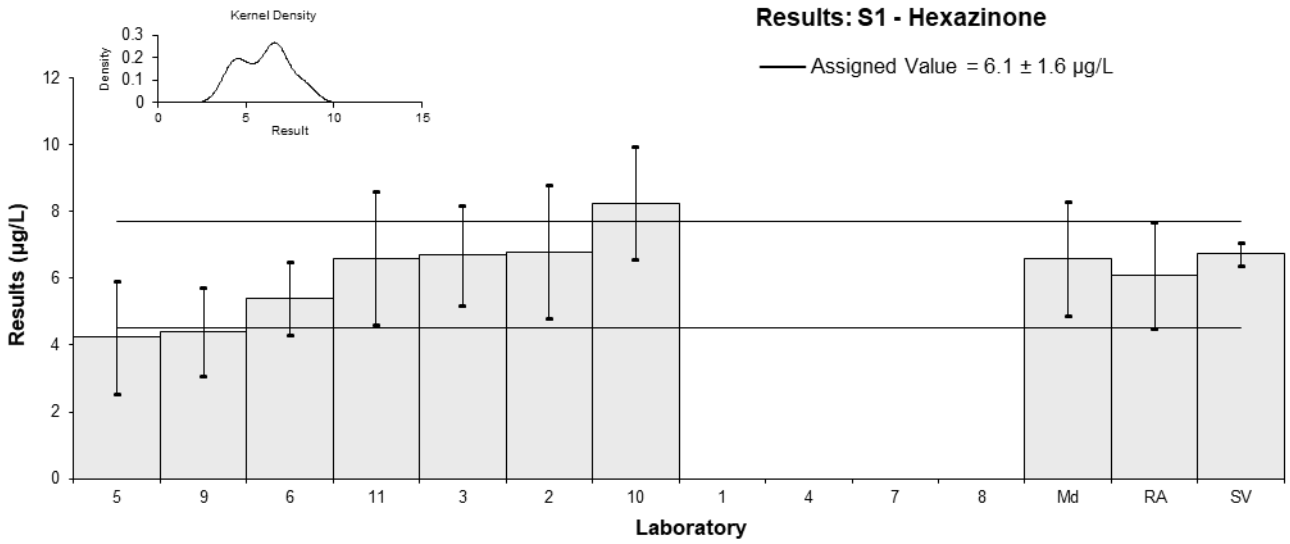
Sample No.	S1
Matrix	River Water
Analyte	Hexazinone
Unit	µg/L

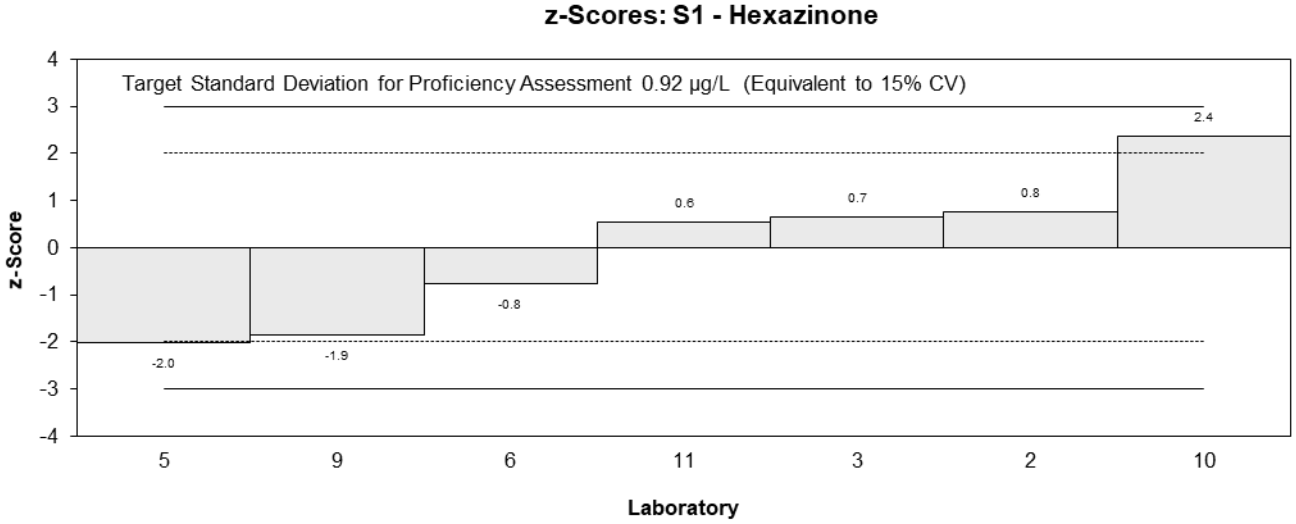
Participant Results

Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	6.8	2	NR	0.77	0.27
3	6.7	1.5	NR	0.66	0.27
4	NT	NT	NT		
5	4.24	1.7	62	-2.03	-0.80
6	5.4	1.1	106	-0.77	-0.36
7	NR	NR	NR		
8	NT	NT	NT		
9	4.4	1.32	NR	-1.86	-0.82
10	8.26	1.7	NR	2.36	0.93
11	6.6	2	100	0.55	0.20

Statistics

Assigned Value	6.1	1.6
Spike Value	6.73	0.34
Robust Average	6.1	1.6
Median	6.6	1.7
Mean	6.1	
N	7	
Max	8.26	
Min	4.24	
Robust SD	1.6	
Robust CV	27%	


Results: S1 - Hexazinone
Assigned Value = 6.1 ± 1.6 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
5
9
6
11
3
2
10
1
4
7
8
Md
RA
SV


z-Scores: S1 - Hexazinone
Target Standard Deviation for Proficiency Assessment 0.92 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.0
-1.9
-0.8
0.6
0.7
0.8
2.4

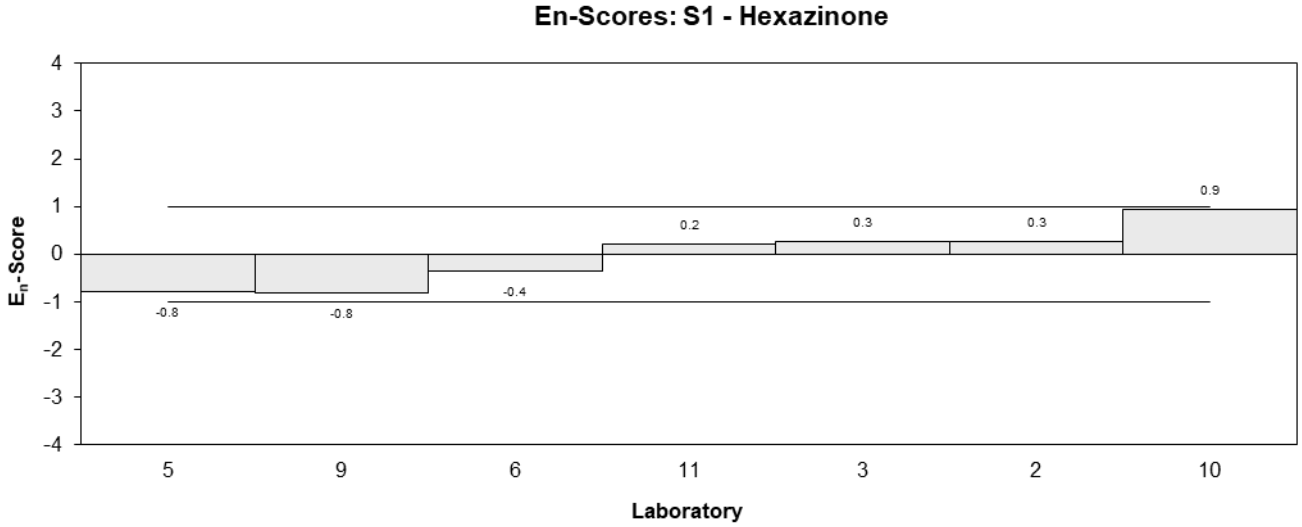

En-Scores: S1 - Hexazinone
En-Score
Laboratory
-0.8
-0.8
-0.4
0.2
0.3
0.3
0.9

Figure 3

Table 7

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	12.6	3.8	NR
3	8.5	2.1	NR
4	NT	NT	NT
5	NT	NT	NT
6	10	2.5	92
7	NR	NR	NR
8	NT	NT	NT
9	8.8	2.6	NR
10	<10	NR	NR
11	11	3.3	100

Statistics

Assigned Value	Not Set	
Spike Value	11.0	0.6
Median	10.0	2.0
Mean	10.2	
N	5	
Max	12.6	
Min	8.5	

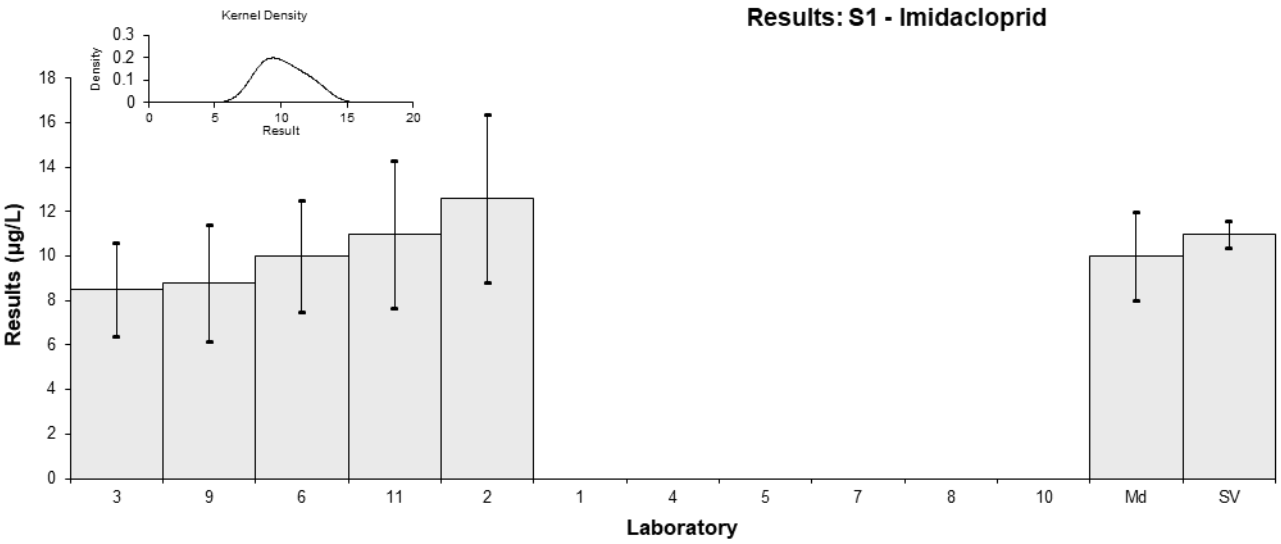

Results: S1 - Imidacloprid
Kernel Density
Density
0.3
0.2
0.1
0
0
5
10
15
20
Result
Results (µg/L)
18
16
14
12
10
8
6
4
2
0
3
9
6
11
2
1
4
5
7
8
10
Md
SV
Laboratory

Figure 4

Table 8

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	<0.6	0.18	NR
2	0.41	0.12	NR
3	0.33	0.11	NR
4	NT	NT	NT
5	0.29	0.12	64
6	0.29	0.06	98
7	<0.5	0.13	NR
8	NT	NT	NT
9	0.2	0.1	NR
10	<1	NR	NR
11	0.48	0.144	NR

Statistics

Assigned Value	Not Set	
Spike Value	1.05	0.05
Robust Average	0.33	0.11
Median	0.310	0.091
Mean	0.333	
N	6	
Max	0.48	
Min	0.2	
Robust SD	0.11	
Robust CV	34%	

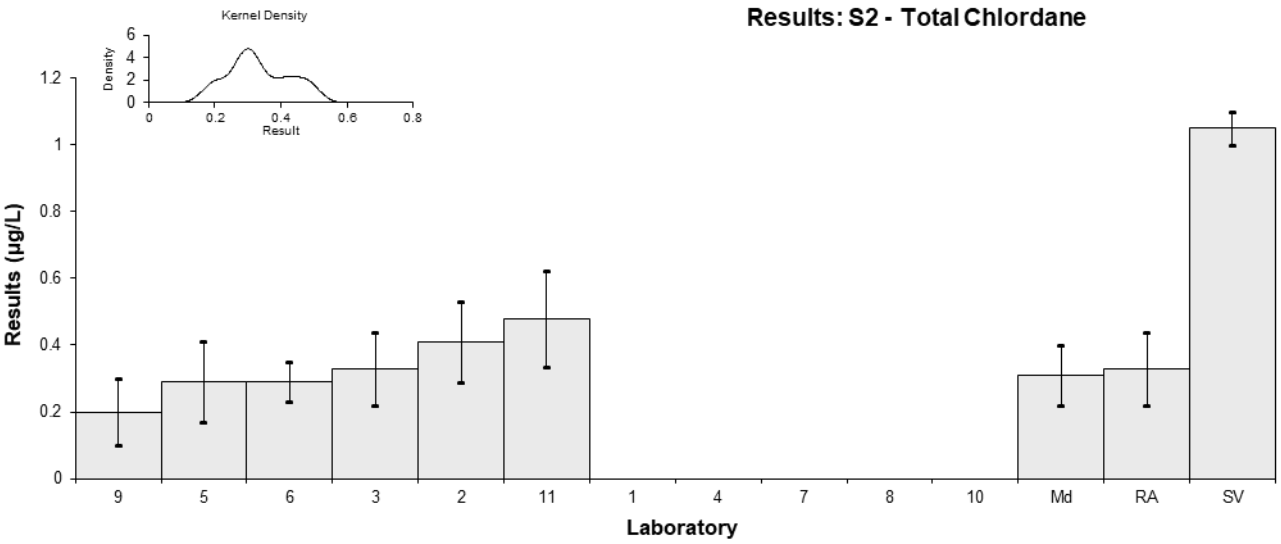

Results: S2 - Total Chlordane
Kernel Density
Density
Result
Results (µg/L)
Laboratory
9
5
6
3
2
11
1
4
7
8
10
Md
RA
SV

Figure 5

Table 9

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	NT	NT	NT
2	1.6	0.5	NR
3	1.94	0.54	NR
4	NT	NT	NT
5	NT	NT	NT
6	1.6	0.32	91
7	NR	NR	NR
8	NT	NT	NT
9	NT	NT	NT
10	2.29	0.51	NR
11	1.9	0.54	100

Statistics

Assigned Value	Not Set	
Spike Value	2.17	0.11
Median	1.90	0.50
Mean	1.87	
N	5	
Max	2.29	
Min	1.6	

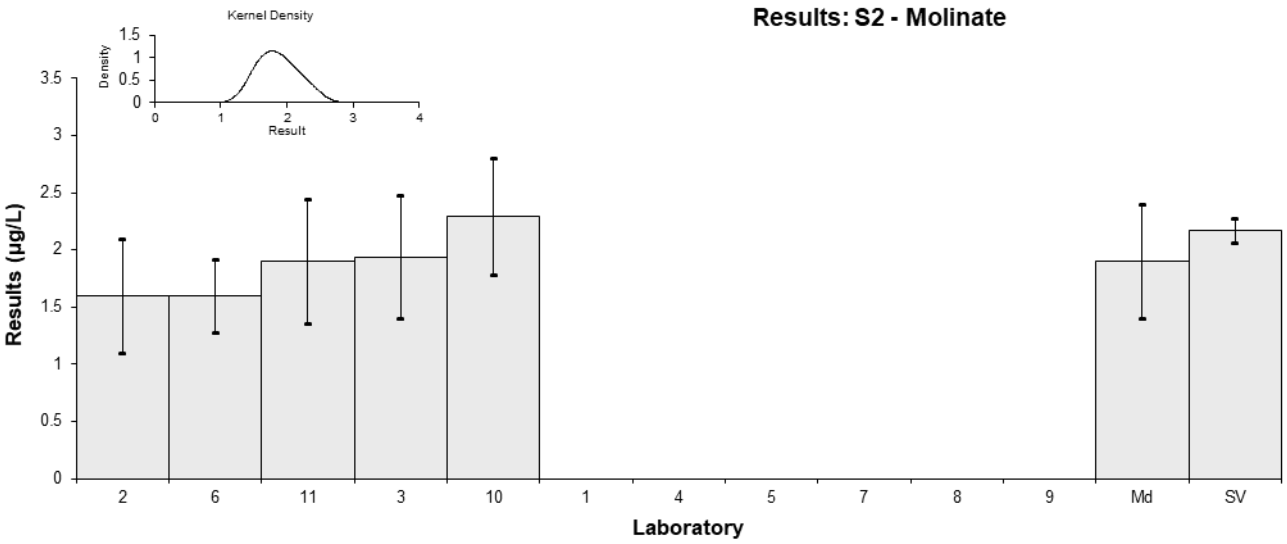

Results: S2 - Molinate
Kernel Density
Density
Result
Results (µg/L)
Laboratory
2
6
11
3
10
1
4
5
7
8
9
Md
SV

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Parathion-methyl
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	3.6	1.1	NR
2	3.3	1	NR
3	1.29	0.33	NR
4	2.39	0.98	NR
5	<0.5	0.5	NR
6	1.7	0.34	106
7	<2	0.74	NR
8	NR	NR	NR
9	1.6	0.5	NR
10	3.32	1.6	NR
11	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	3.04	0.15
Robust Average	2.5	1.0
Median	2.4	1.3
Mean	2.46	
N	7	
Max	3.6	
Min	1.29	
Robust SD	1.1	
Robust CV	44%	

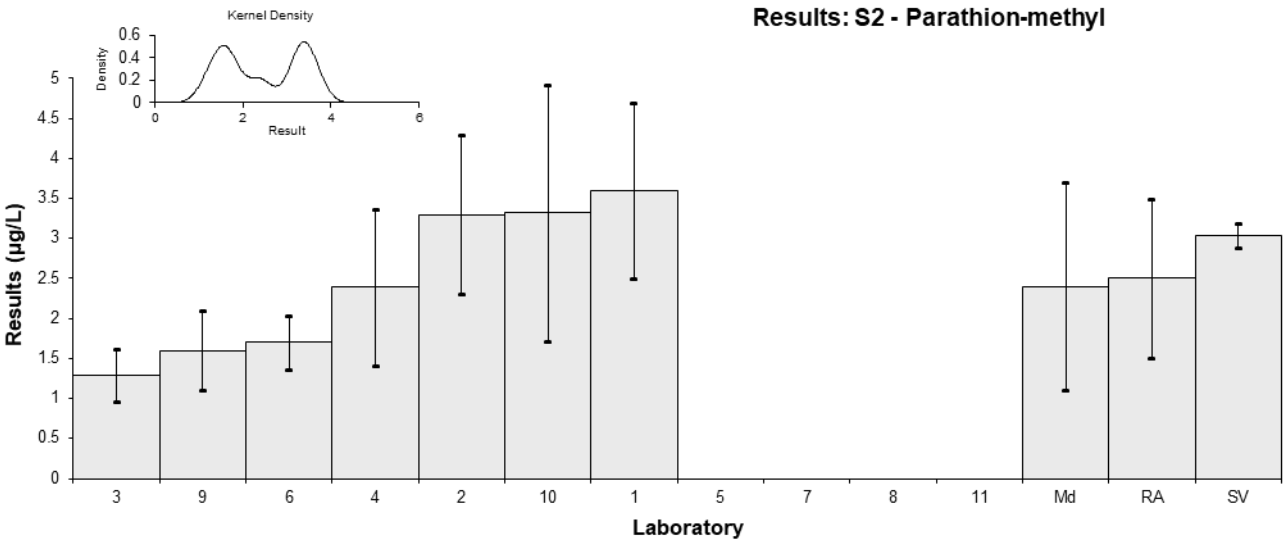

Results: S2 - Parathion-methyl
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3
9
6
4
2
10
1
5
7
8
11
Md
RA
SV

Figure 7

Table 11

Sample Details

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

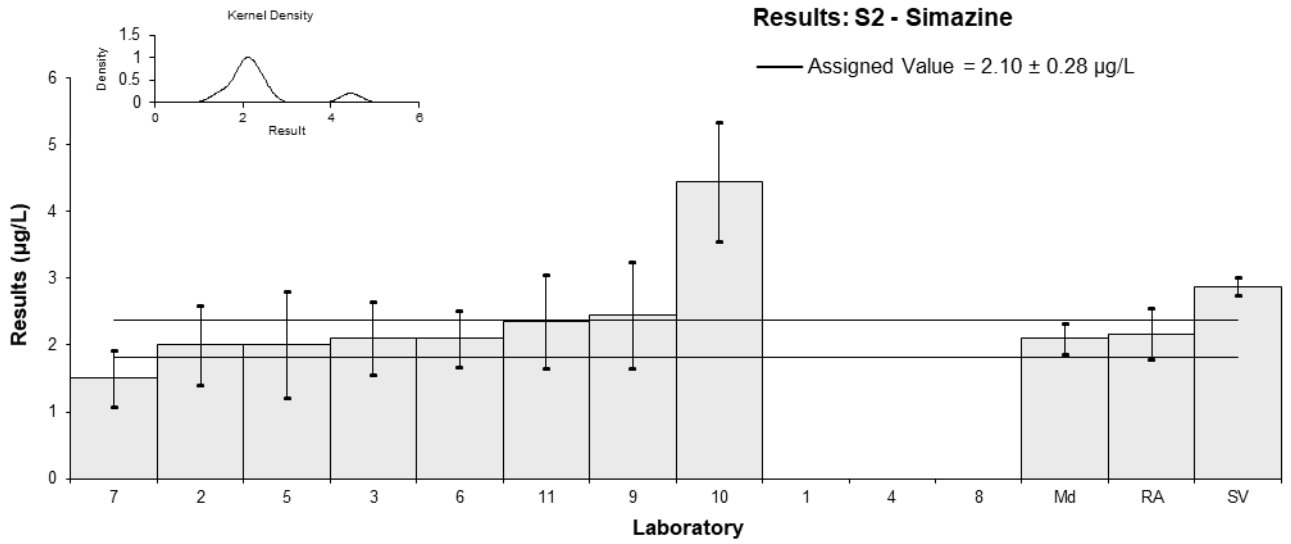
Participant Results

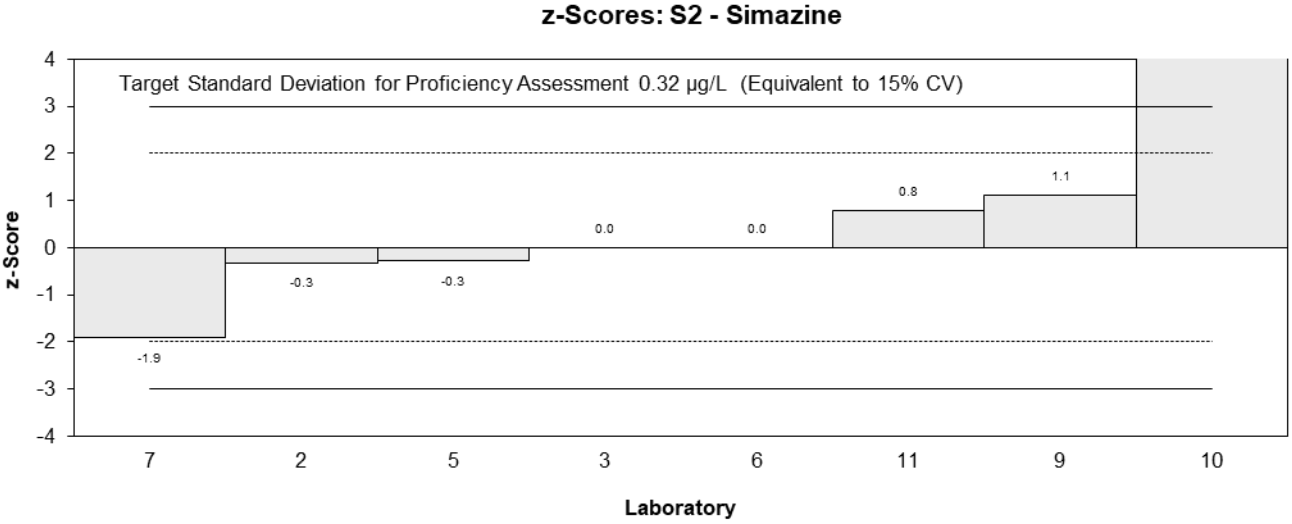
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	2	0.6	NR	-0.32	-0.15
3	2.1	0.55	NR	0.00	0.00
4	NT	NT	NT		
5	2.01	0.8	58	-0.29	-0.11
6	2.1	0.42	114	0.00	0.00
7	1.5	0.43	NR	-1.90	-1.17
8	NT	NT	NT		
9	2.45	0.8	NR	1.11	0.41
10*	4.454	0.89	NR	7.47	2.52
11	2.35	0.7	100	0.79	0.33

* Outlier, see Section 4.2

Statistics

Assigned Value	2.10	0.28
Spike Value	2.88	0.14
Robust Average	2.17	0.38
Median	2.10	0.23
Mean	2.37	
N	8	
Max	4.454	
Min	1.5	
Robust SD	0.43	
Robust CV	20%	


Kernel Density
Density
Result
Results: S2 - Simazine
Assigned Value = 2.10 ± 0.28 µg/L
Results (µg/L)
Laboratory
7
2
5
3
6
11
9
10
1
4
8
Md
RA
SV


z-Scores: S2 - Simazine
Target Standard Deviation for Proficiency Assessment 0.32 µg/L (Equivalent to 15% CV)
z-Score
-1.9
-0.3
-0.3
0.0
0.0
0.8
1.1
Laboratory

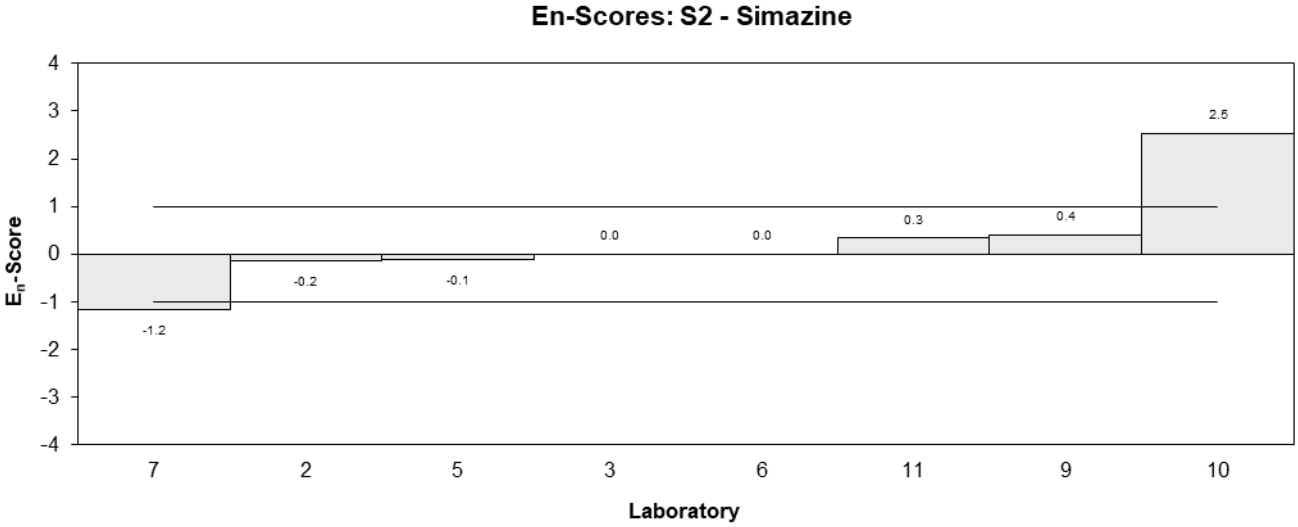

En-Scores: S2 - Simazine
En-Score
-1.2
-0.2
-0.1
0.0
0.0
0.3
0.4
2.5
Laboratory

Figure 8

Table 12

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	17.1	3.078	NR
2	31	9	NR
3	15.8	5.1	88
4	NT	NT	NT
5	NT	NT	NT
6	26	5.2	101
7	NR	NR	NR
8	23.90	2.25	92
9	NT	NT	NT
10	NT	NT	NT
11	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	27.3	1.4
Median	24	11
Mean	22.8	
N	5	
Max	31	
Min	15.8	

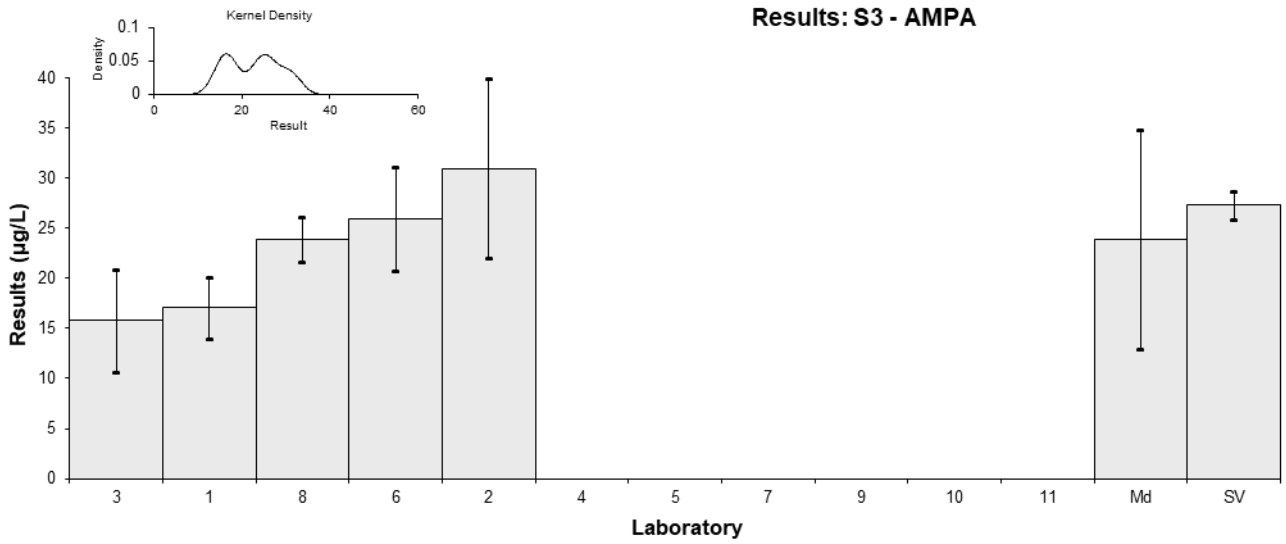

Results: S3 - AMPA
Kernel Density
Density
0.1
0.05
0
0
20
40
60
Result
Results (µg/L)
40
35
30
25
20
15
10
5
0
3
1
8
6
2
4
5
7
9
10
11
Md
SV
Laboratory

Figure 9

Table 13

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	16.3	2.6	NR
2	18	5	NR
3	13.7	4	88
4	NT	NT	NT
5	NT	NT	NT
6	16	3.4	102
7	NR	NR	NR
8	13.84	1.25	97
9	NT	NT	NT
10	NT	NT	NT
11	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	16.2	0.8
Median	16.0	3.3
Mean	15.6	
N	5	
Max	18	
Min	13.7	

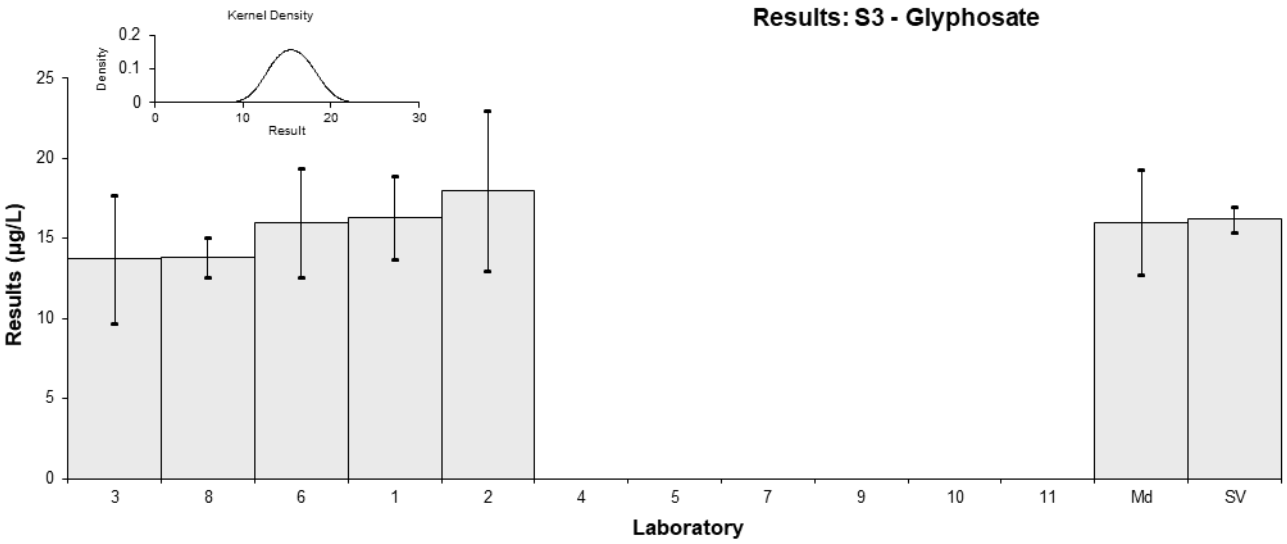

Results: S3 - Glyphosate
Kernel Density
Density
0.2
0.1
0
0
10
20
30
Result
Results (µg/L)
25
20
15
10
5
0
3
8
6
1
2
4
5
7
9
10
11
Md
SV
Laboratory

Figure 10

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages of participants' results were used as the assigned values for scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2022.[8] Results less than 50% and greater than 150% of the robust average were removed before the calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using hexazinone in Sample S1 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 14.

No assigned value was set for Sample S1 imidacloprid, S2 molinate and S3 glyphosate, as there were too few numeric results reported; however, participants' results were in very good agreement with each other as well as the spiked values. No assigned value was set for Sample S1 p,p'-DDT, Sample S2 total chlordane and parathion-methyl, and Sample S3 AMPA, as the numeric results reported by participants were too variable. For these analytes without assigned values, participants may still compare their results with the descriptive statistics and spiked values as presented in Section 5.

Recoveries of analytes were relatively high for the majority of the analytes. Except for Sample S1 p,p'-DDT and Sample S2 total chlordane, the assigned values (or robust averages) ranged from 73% to 96% of the spiked value, which is similar to ratios observed in previous NMI pesticides in river water PT studies.

p,p'-DDT and *trans*-chlordane (the chlordane isomer spiked in this study's samples) have been used previously in NMI pesticides in river water PT studies. Similar, low recoveries were also observed in these studies.[6,7]

Table 14 Comparison of Assigned Value and Spiked Value

Sample	Analyte	Assigned Value *(Robust Average)* (µg/L)	Spiked Value (µg/L)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	p,p'-DDT	*(0.49)*	1.08	*(45)*
	Hexazinone	6.1	6.73	91
	Imidacloprid	*(10.2)*	11.0	*(93)*
S2	Total Chlordane	*(0.33)*	1.05	*(31)*
	Molinate	*(1.87)*	2.17	*(86)*
	Parathion-methyl	*(2.5)*	3.04	*(82)*
	Simazine	2.10	2.88	73
S3	AMPA	*(22.8)*	27.3	*(84)*
	Glyphosate	*(15.6)*	16.2	*(96)*

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.[10]

Of 56 numeric results submitted for the analytes of interest in this study, all (100%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3).

The magnitude of reported uncertainties was within the range of 8.6% to 50% 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 56 MUs reported for this study, three were less than 15% relative.

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

Laboratories **1**, **4**, **5** and **7** 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.[11]

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 17.1 ± 3.078 µg/L, it is better to report this as 17.1 ± 3.1 µg/L.[11]

6.3 *z*-Score

Target SDs equivalent to 15% PCV were used to calculate *z*-scores. CVs predicted by the Thompson-Horwitz equation,[9] the between-laboratory CVs and target SDs (as PCV) for this study are presented for comparison in Table 15.

Table 15 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	p,p'-DDT	*(0.49)*	22	44	Not Set
	Hexazinone	6.1	22	27	15
	Imidacloprid	*(10.2)*	22	19	Not Set
S2	Total Chlordane	*(0.33)*	22	34	Not Set
	Molinate	*(1.87)*	22	17	Not Set
	Parathion-methyl	*(2.5)*	22	44	Not Set
	Simazine	2.10	22	14	15
S3	AMPA	*(22.8)*	22	32	Not Set
	Glyphosate	*(15.6)*	22	13	Not Set

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

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

Of 15 results for which *z*-scores were calculated, 12 (80%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **2**, **3** and **6** reported numeric results for all analytes of interest in this study.

Laboratories **2**, **3**, **6**, **9** and **11** returned satisfactory *z*-scores for all scored analytes.

Laboratory **10** did not return any satisfactory *z*-scores.

Laboratories **1**, **4** and **8** did not report results for the analytes that were scored.

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

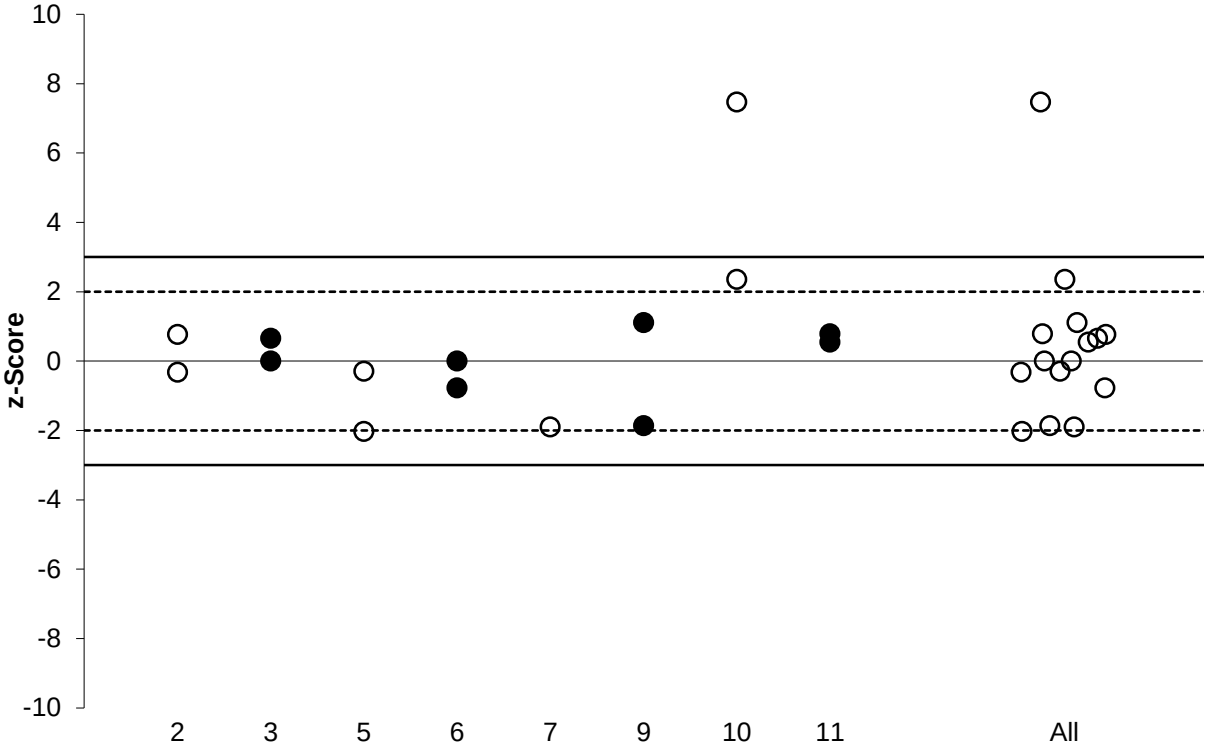


Figure 11 *z*-Score Dispersal by Laboratory

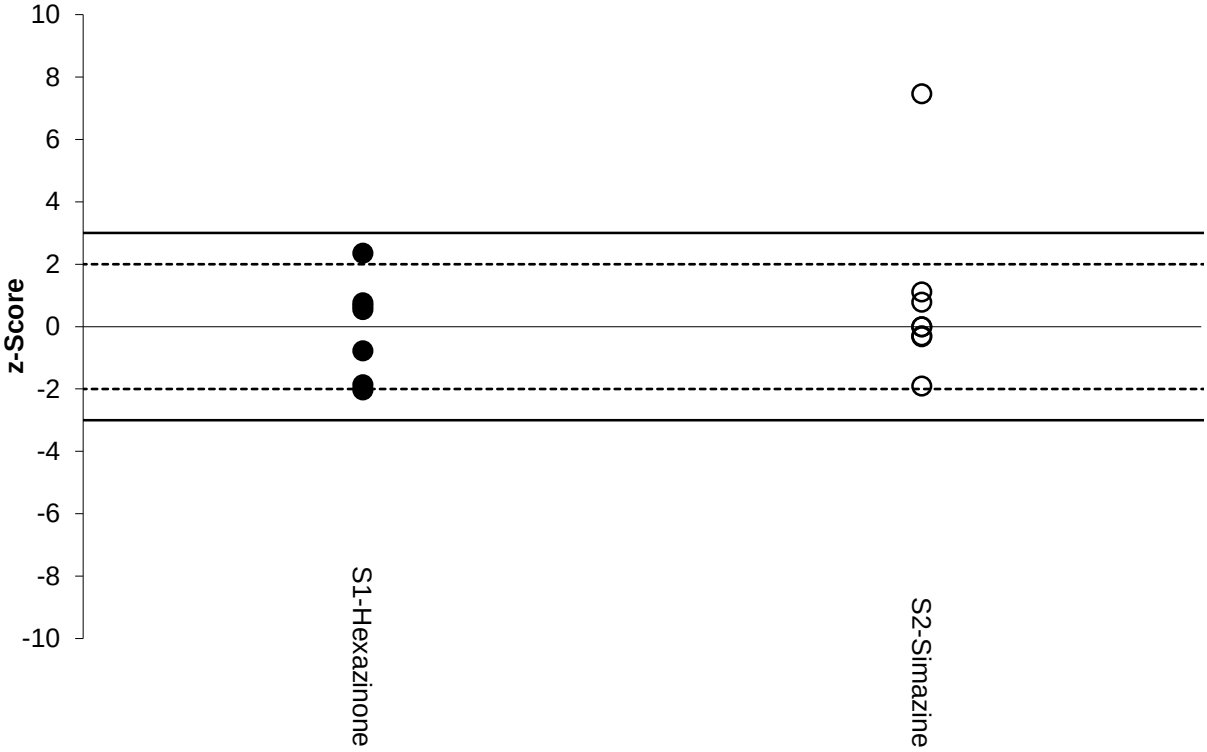


Figure 12 *z*-Score Dispersal by Analyte

6.4 E_n-Score

E_n-scores can be interpreted in conjunction with z-scores, as an unsatisfactory 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.

Of 15 results for which E_n-scores were calculated, 13 (87%) 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.

Laboratories **2**, **3**, **5**, **6**, **9** and **11** returned satisfactory E_n-scores for all scored analytes.

Laboratory **7** did not return any satisfactory E_n-scores.

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

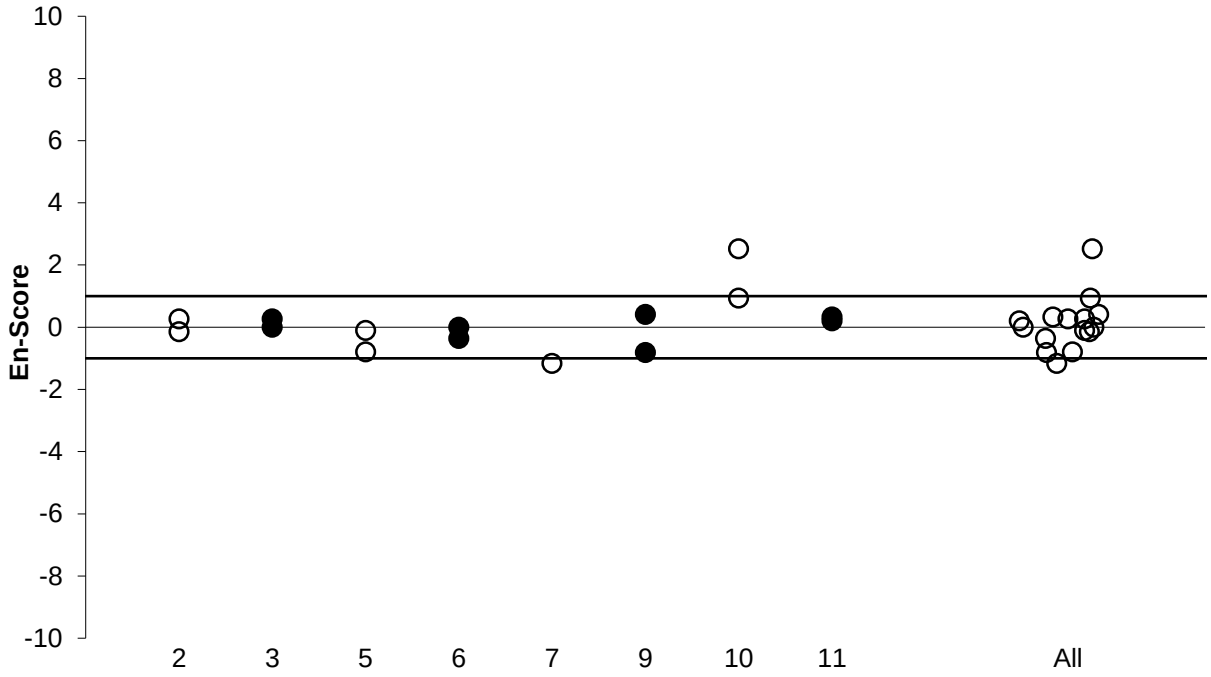


Figure 13 E_n-Score Dispersal by Laboratory

6.5 Non-Scored Analytes

As discussed in Section 6.1, assigned values were not able to be set for a number of analytes.

In this study, participants' results for Sample S1 imidacloprid, Sample S2 molinate and Sample S3 glyphosate were in very good agreement with each other, as well as the spiked value. However, it is NMI PT's policy to only set an assigned value by the consensus of participants' results if there are a minimum of six results,[3] and therefore these analytes were not able to be scored as there were too few numeric results reported. For Sample S1 imidacloprid, Laboratories **2**, **3**, **6**, **9** and **11** reported numeric results. For Sample S2 molinate, Laboratories **2**, **3**, **6**, **10** and **11** reported numeric results. For Sample S3 glyphosate, Laboratories **1**, **2**, **3**, **6** and **8** reported numeric results. All numeric results for these analytes were within two target standard deviations of both the median and spiked value, indicating that these participants' performances were likely to be satisfactory for these analytes.

For the other non-scored analytes, the results reported by participants were generally too variable to set an assigned value. However, no significant trends were observed with participant methodology (Section 6.9), and no fill order or transportation stability trends were identified either (Appendix 2).

6.6 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)
5	S2	Parathion-methyl	*(2.5)*	3.04	<0.5
7	S1	Hexazinone	6.1	6.73	NR
		Imidacloprid	*(10.2)*	11.0	NR
	S2	Molinate	*(1.87)*	2.17	NR
	S3	AMPA	*(22.8)*	27.3	NR
		Glyphosate	*(15.6)*	16.2	NR
8	S2	Parathion-methyl	*(2.5)*	3.04	NR

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

6.7 Reporting of Additional Analytes

Four participants reported analytes that were not spiked into the test samples (total of 8 results). These are listed in Table 17. Participants should take care to avoid any potential cross-contamination when analysing their samples.

The p,p'-DDD and p,p'-DDE reported by participants in Sample S1 may be the result of the breakdown of p,p'-DDT during analysis in, for example, hot GC injector liners.[12] This may also partially account for the lower ratio of the robust average of participants' results versus the spiked value of p,p'-DDT in Sample S1. Participants reporting p,p'-DDD and/or p,p'-DDE at significant levels should revise their method to minimise the breakdown.

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

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
3	S1	Heptachlor	0.06	0.04	NR
6	S1	p,p'-DDD	0.017	0.003	86
9*	S1	MCPA	0.01	0.003	NR
		Metolachlor	0.01	0.003	NR
	S2	MCPA	0.016	0.005	NR
		Metolachlor	0.012	0.004	NR
11	S1	p,p'-DDD	0.00955	0.002865	NR
		p,p'-DDE	0.01	0.003	NR

* Laboratory **9** also reported a numeric result for omethoate in Sample S1. Omethoate was spiked into this sample, and therefore has not been considered as an additional reported analyte. This analyte however was highly unstable in the river water matrix and therefore was not included in this report.

Sample S1 was spiked with p,p'-DDT, and this was the analyte of interest in this study. Six participants also reported a total DDT value. These results are presented in Table 18 for information only.

Table 18 Reported Results for Sample S1 Total DDT

Lab. Code	Result (µg/L)	Uncertainty (µg/L)	Recovery (%)
2	0.42	0.13	NR
3	1	0.33	NR
5	0.293	0.12	61
6	0.64	0.13	102
8	0.58	0.05	98
11	0.6	0.18	NR

6.8 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, nine 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 19.

Laboratories **2**, **3**, **6** and **7** 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, p,p'-DDT was tested for by the highest proportion of participants (100%). The proportion of participants testing for each analyte in this study ranged from 55% to 100%.

Table 19 Summary of Pesticides Analysed by Participants

Lab. Code / Analyte	1	2	3	4	5	6	7	8	9	10	11	Proportion of Participants (%)
AMPA	✓	✓	✓	NT	NT	✓	✓	✓	NT	NT	NT	55
Total Chlordane	✓	✓	✓	NT	✓	✓	✓	NT	✓	✓	✓	82
p,p'-DDT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
Glyphosate	✓	✓	✓	NT	NT	✓	✓	✓	NT	NT	NT	55
Hexazinone	NT	✓	✓	NT	✓	✓	✓	NT	✓	✓	✓	73
Imidacloprid	NT	✓	✓	NT	NT	✓	✓	NT	✓	✓	✓	64
Molinate	NT	✓	✓	NT	NT	✓	✓	NT	NT	✓	✓	55
Parathion-methyl	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	91
Simazine	NT	✓	✓	NT	✓	✓	✓	NT	✓	✓	✓	73
Proportion of Analytes (%)	56	100	100	22	56	100	100	44	67	78	67	

6.9 Participants' Analytical Methods

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

For Samples S1 and S2, participants reported using the test portions ranging from 1 mL to the whole bottle (500 mL), as shown in Figure 14. While there were few scored results, it was seen that the participant using 1 mL for their analyses reported results biased high. Caution should be exercised when a small sample size is taken for analysis and to also ensure that it is a suitable representation of the whole sample.

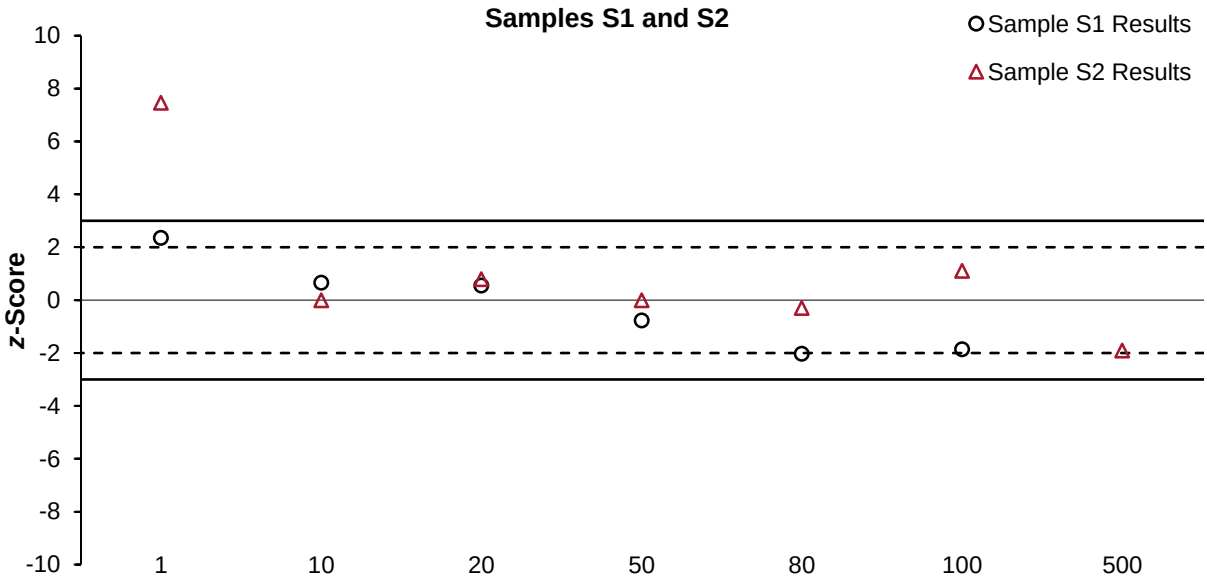


Figure 14 Samples S1 and S2 *z*-Score vs Sample Volume

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 (ACN), dichloromethane (DCM), ethyl acetate (EtOAc), hexane (HEX), pentane (PENT), or mixtures of these solvents. The majority of participants did not report a further clean-up step, with only two participants reporting filtration for certain analytes. Participants reported using gas chromatography (GC) coupled to electron capture detection (ECD), mass spectrometry (MS) or tandem mass spectrometry (MS/MS), or liquid chromatography (LC) coupled to MS/MS.

Plots of numeric results and methodology employed (extraction technique, extraction solvent and measurement instrument) for analytes in this study are presented in Figures 15 to 21 (results from participants not reporting any methodology have not been included). A wide variety of methodologies was employed by participants, and in general no trend was observed where more than one participant used a particular methodology for an analyte.

For Sample S1 p,p'-DDT, the majority of participants used LLE. One participant used SPE with DCM/EtOAc as the extraction solvent; this participant's reported result was closer to the spiked value than the other results reported.

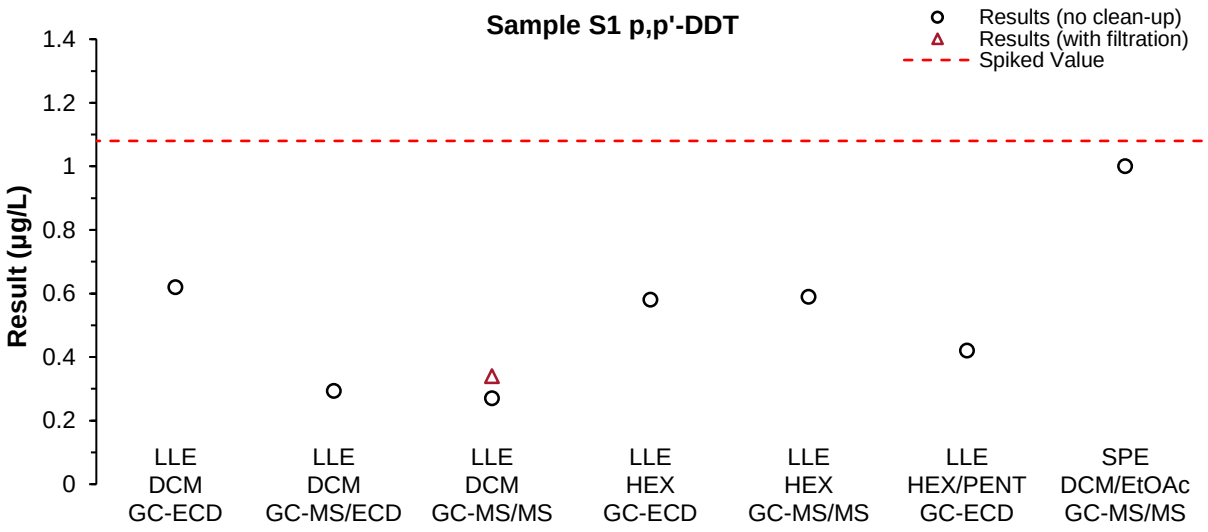


Figure 15 Sample S1 p,p'-DDT Result vs Methodology

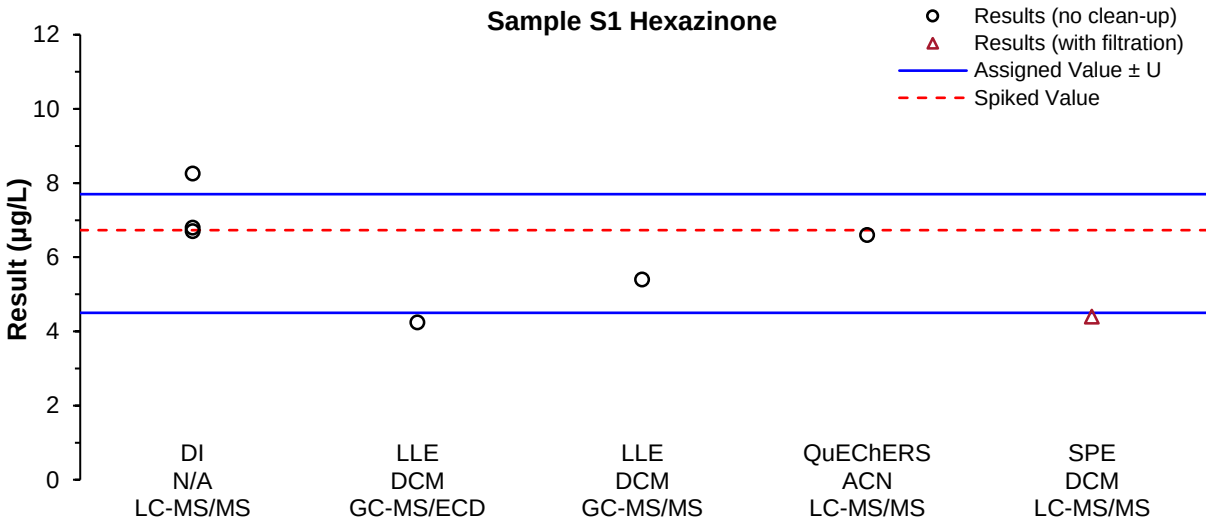


Figure 16 Sample S1 Hexazinone Result vs Methodology

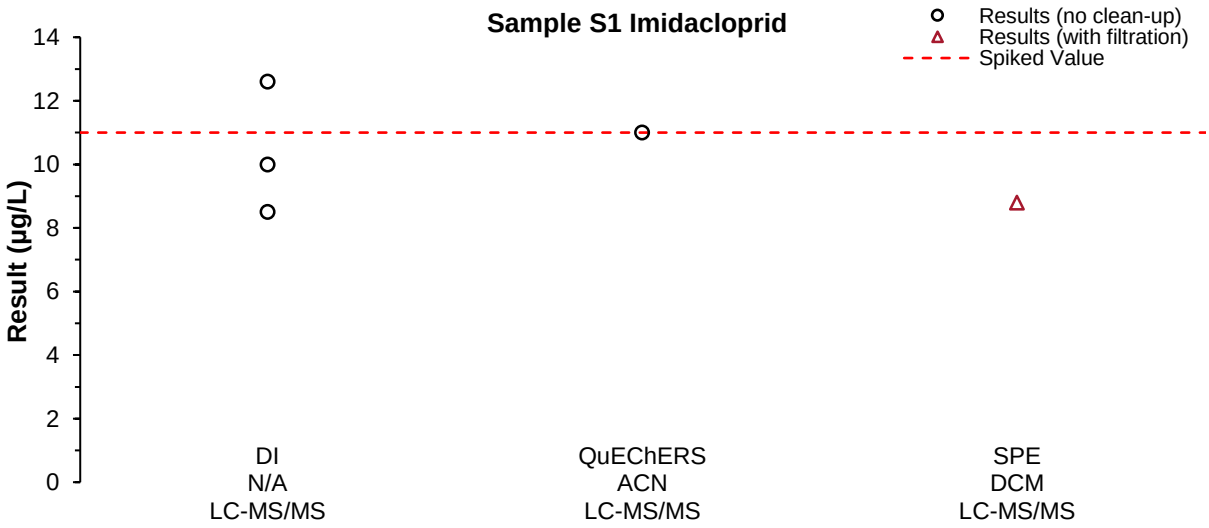


Figure 17 Sample S1 Imidacloprid Result vs Methodology

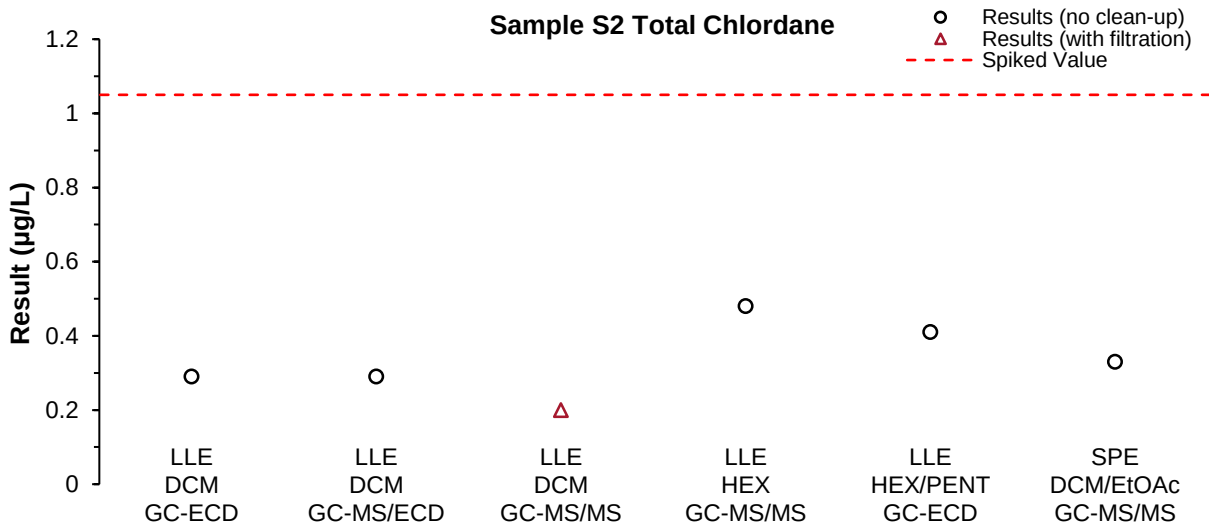


Figure 18 Sample S2 Total Chlordane Result vs Methodology

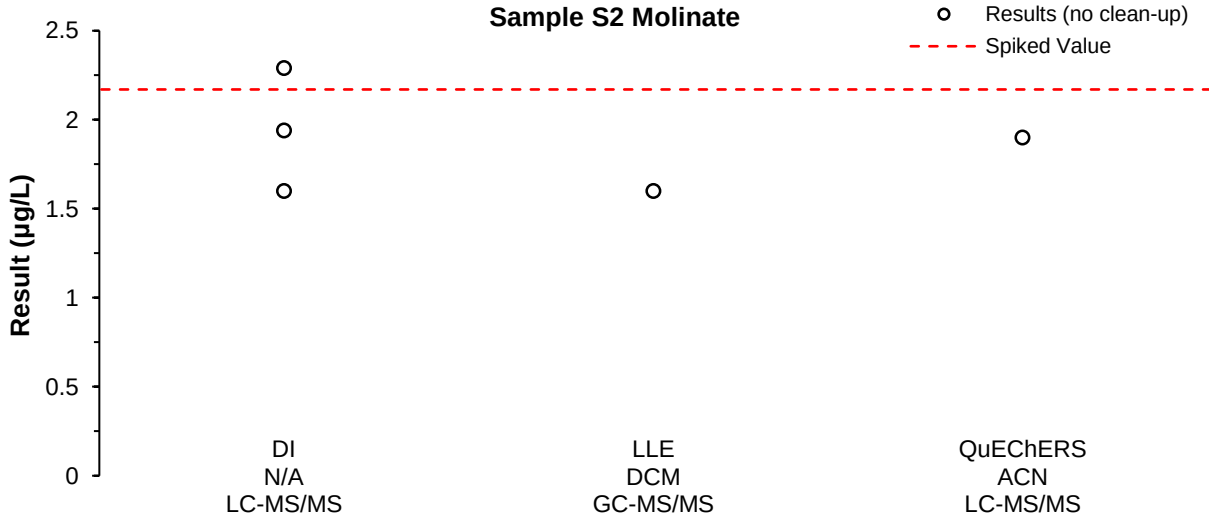


Figure 19 Sample S2 Molinate Result vs Methodology

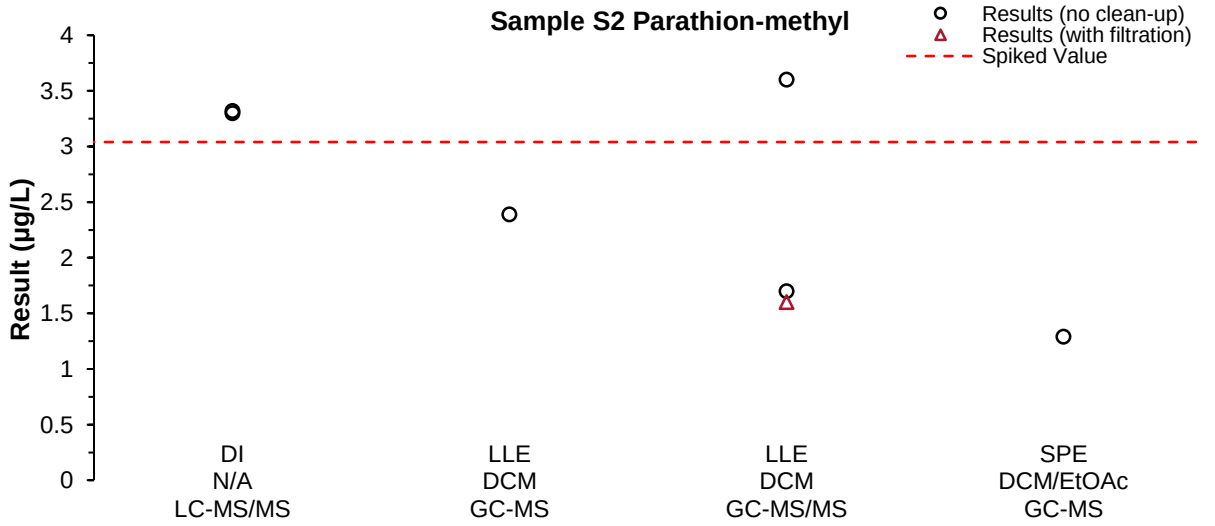


Figure 20 Sample S2 Parathion-methyl Result vs Methodology

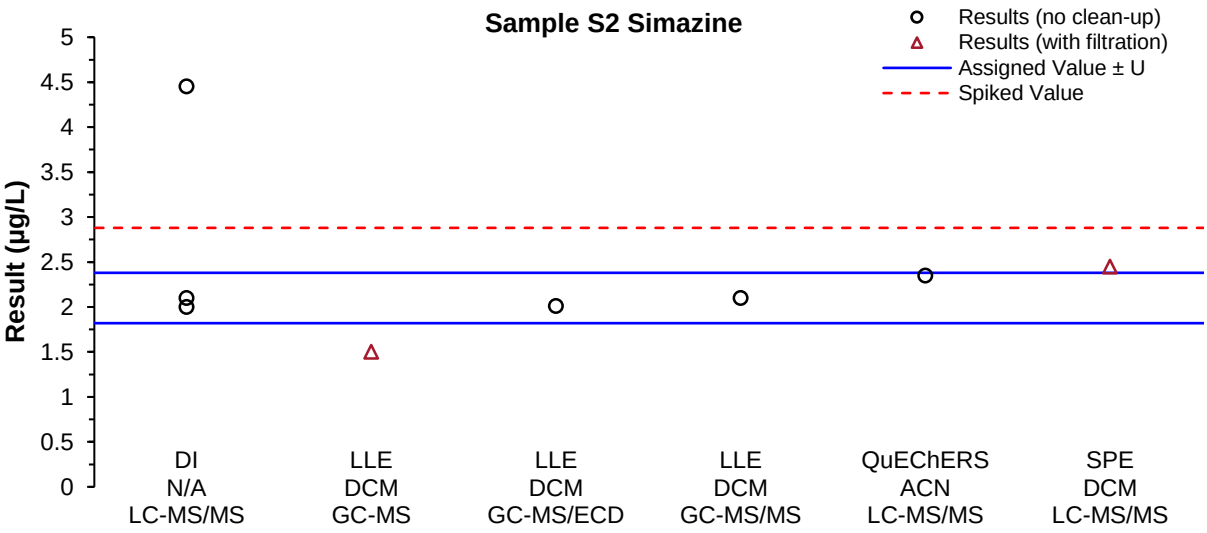


Figure 21 Sample S2 Simazine Result vs Methodology

For Sample S3, participants reported using DI, or extraction techniques such as LLE and evaporation. Two participants reported derivatisation pre-column using fluorenylmethyloxycarbonyl group (FMOC). One participant used high performance liquid chromatography (HPLC) coupled to fluorescence detection (FLD), while the other participants used LC-MS/MS for quantification.

Plots of numeric results and methodology employed (extraction technique, derivatisation and measurement instrument) for Sample S3 analytes are presented in Figures 22 and 23 (results from participants not reporting any methodology have not been included). Each participant that had a numeric result for these analytes reported using a unique methodology from the other participants.

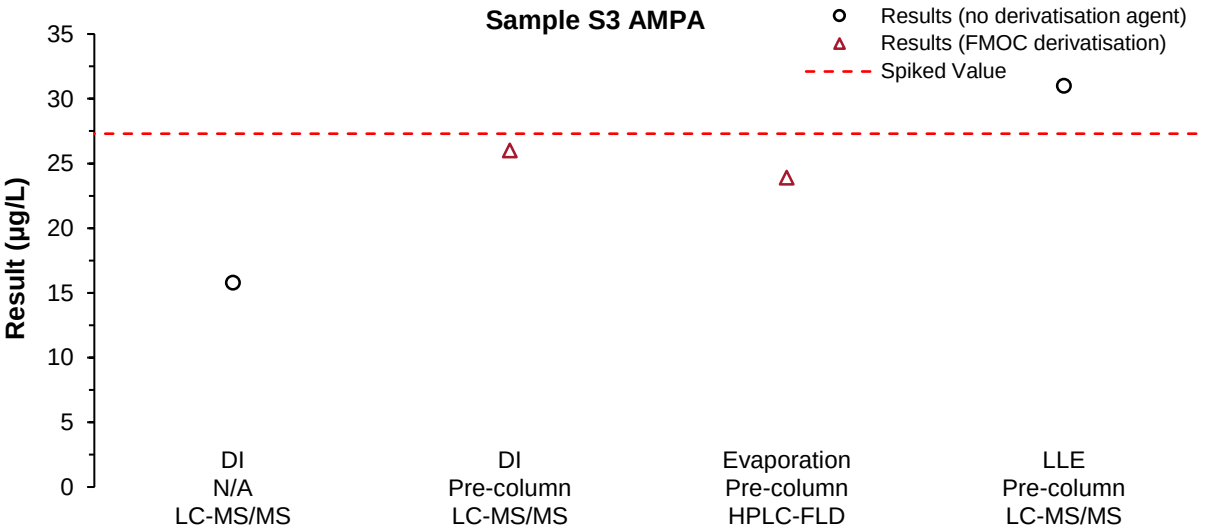


Figure 22 Sample S3 AMPA Result vs Methodology

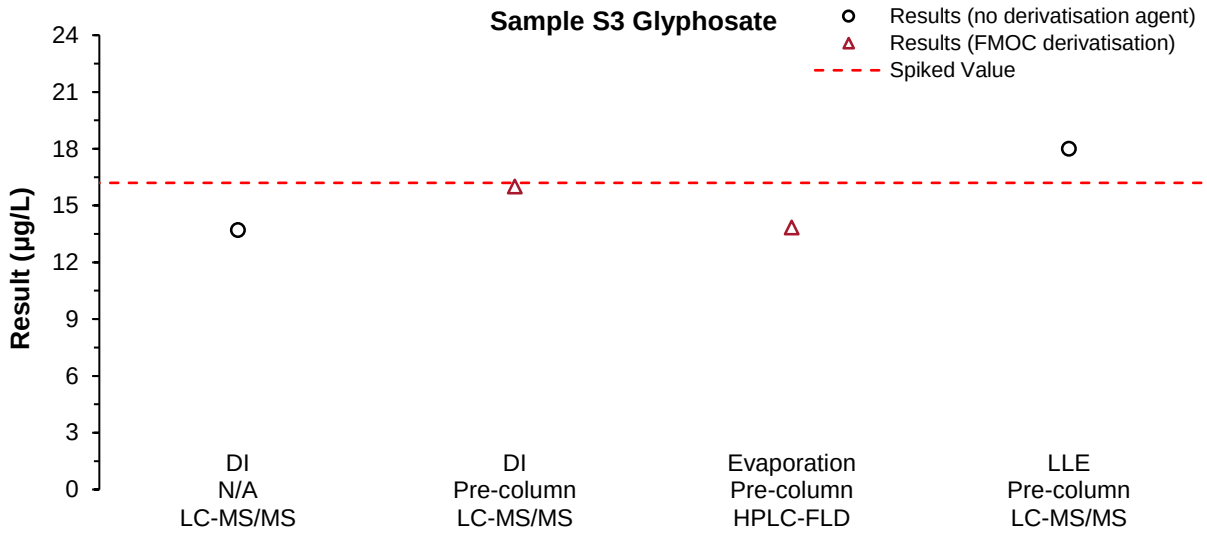


Figure 23 Sample S3 Glyphosate Result vs Methodology

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 **3**, **5**, **6**, **8** and **11** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 58% to 114%. No laboratory reported that they corrected their results for recoveries.

6.10 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.

Five participants reported using certified standards. The following were listed:

- ChemLab
- Dr Ehrenstorfer
- Restek
- 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*'[13]

6.11 Summary of Participants' Results and Performances

Summaries of participants' results and performances in this PT study are presented in Table 20.

Table 20 Summary of Participants' Results*

Lab. Code	Sample S1			Sample S2				Sample S3	
	p,p'-DDT	Hexazinone	Imidacloprid	Total Chlordane	Molinate	Parathion-methyl	Simazine	AMPA	Glyphosate
AV	Not Set	6.1	Not Set	Not Set	Not Set	Not Set	2.10	Not Set	Not Set
SV	1.08	6.73	11.0	1.05	2.17	3.04	2.88	27.3	16.2
1	0.27	NT	NT	<0.6	NT	3.6	NT	17.1	16.3
2	0.42	6.8	12.6	0.41	1.6	3.3	2	31	18
3	1	6.7	8.5	0.33	1.94	1.29	2.1	15.8	13.7
4	<1	NT	NT	NT	NT	2.39	NT	NT	NT
5	0.293	4.24	NT	0.29	NT	<0.5	2.01	NT	NT
6	0.62	5.4	10	0.29	1.6	1.7	2.1	26	16
7	<2	NR	NR	<0.5	NR	<2	1.5	NR	NR
8	0.58	NT	NT	NT	NT	NR	NT	23.90	13.84
9	0.34	4.4	8.8	0.2	NT	1.6	2.45	NT	NT
10	<1	8.26	<10	<1	2.29	3.32	4.454	NT	NT
11	0.59	6.6	11	0.48	1.9	NT	2.35	NT	NT

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

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 10 studies (2014–2022) is presented in Figure 24.

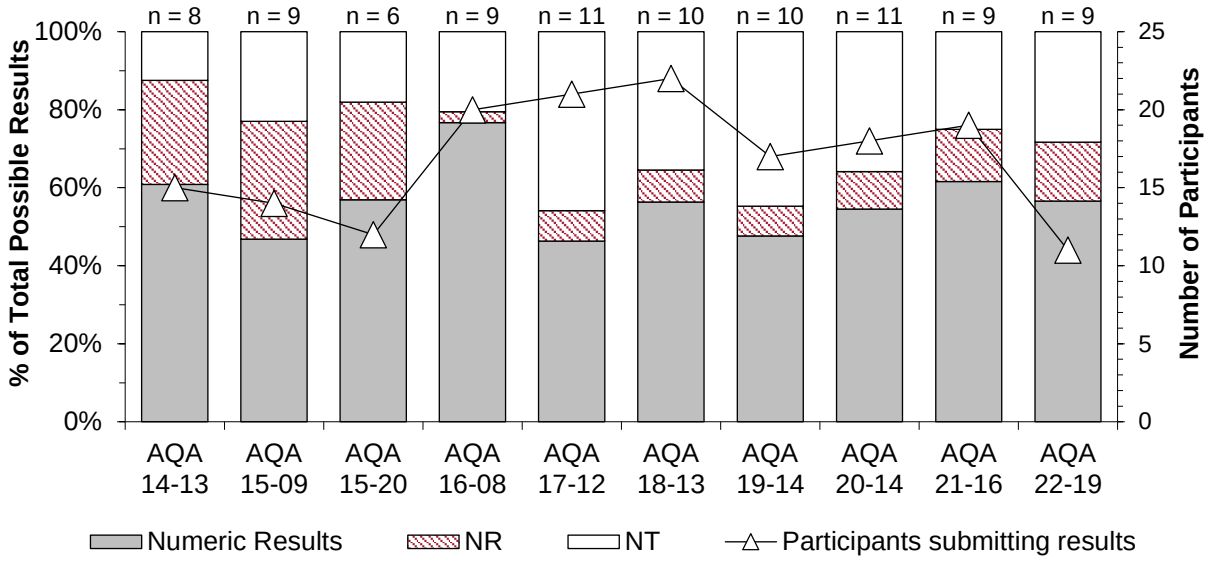


Figure 24 Summary of Participation and Reported Results in NMI Pesticides in River Water PT Studies (n = number of spiked analytes)

A summary of the satisfactory performance (presented as a percentage of the total number of scores for each study) in NMI pesticides in river water PT studies over the last 10 studies (2014–2022) 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 77% for E_n-scores.

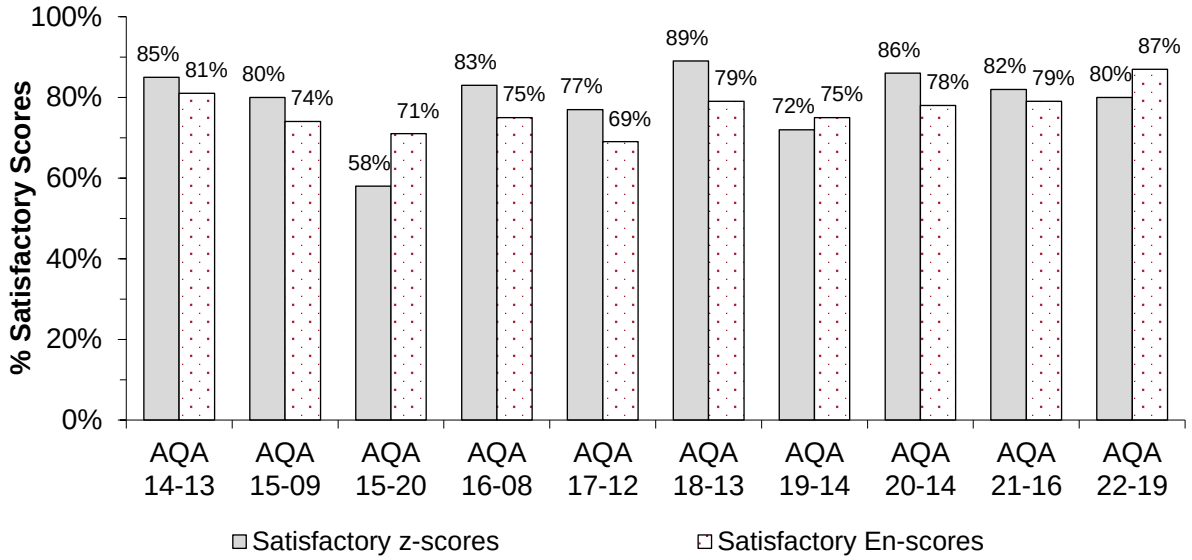


Figure 25 Satisfactory *z*-Scores and E_n-Scores in NMI Pesticides in River Water PT Studies

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. Figure 26 presents a summary of the relative uncertainties as reported by participants over the last 10 studies (2014–2022). Over this time period, the vast majority of numeric results were reported with uncertainties (96%), with 86% of participants reporting that they were accredited to ISO/IEC 17025. In this study, all results were reported with a MU, and there was a greater proportion of participants reporting relative uncertainties between 15% and 50% relative as compared to previous studies.

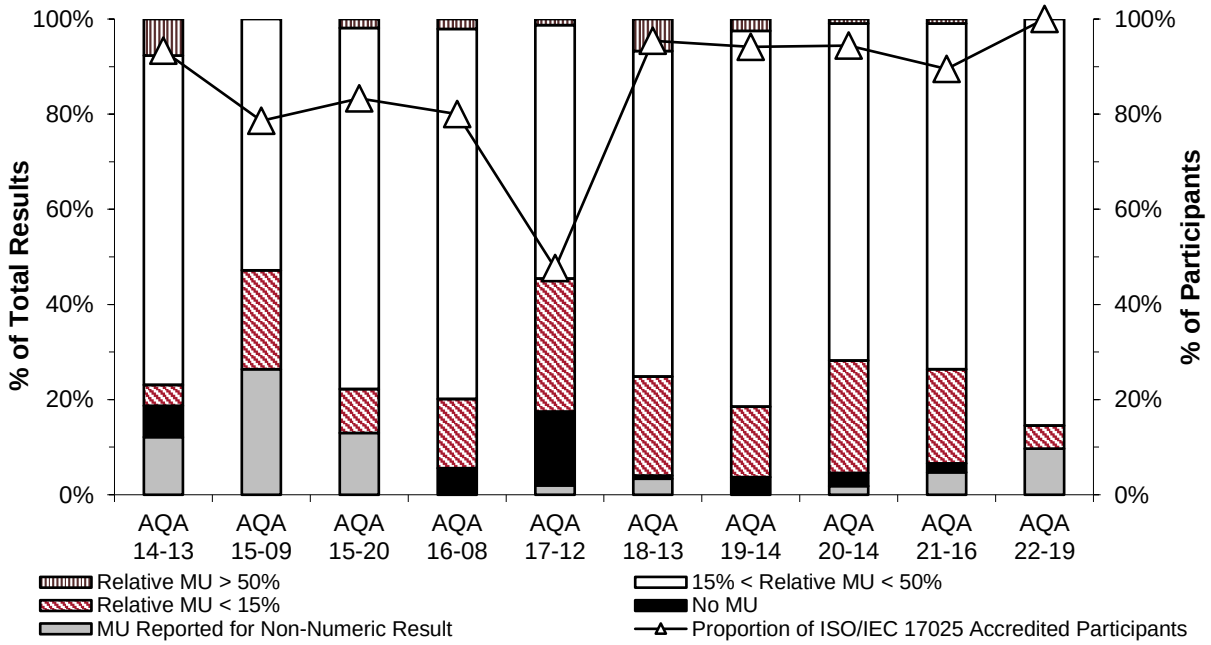


Figure 26 Summary of Participants' Relative Uncertainties for NMI Pesticides in River Water PT Studies

7 REFERENCES

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

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

[2] NMI, 2021, *Study Protocol for Proficiency Testing*, viewed February 2023, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>

[3] NMI, 2022, *Chemical Proficiency Testing Statistical Manual*, viewed February 2023, <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 February 2023, <https://www.legislation.gov.au/Details/F2013C00288/Html/Volume_2>

[6] NMI, 2021, *Proficiency Test Final Report AQA 20-14 Pesticides in Water.*

[7] NMI, 2013, *Proficiency Study AQA 12-12 Pesticides in Water*.

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

[9] 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.

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

[11] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd ed., viewed February 2023, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>

[12] US EPA, 2007, *SW-846 Test Method 8081B: Organochlorine Pesticides by Gas Chromatography*, viewed February 2023, <https://www.epa.gov/sites/default/files/2015-12/documents/8081b.pdf>

[13] 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 spiking solutions for Samples S1 and S2 were prepared by dissolving the pesticide standards in acetone, except for imidacloprid which was dissolved in dichloromethane. The glyphosate and AMPA standards were dissolved in water. A diluted spiking solution of p,p'-DDT was 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 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 results reported to container number analysed by participants are presented in Figures 27 to 35 (results have only been included when the participant was only sent one bottle); no fill order trend was observed.

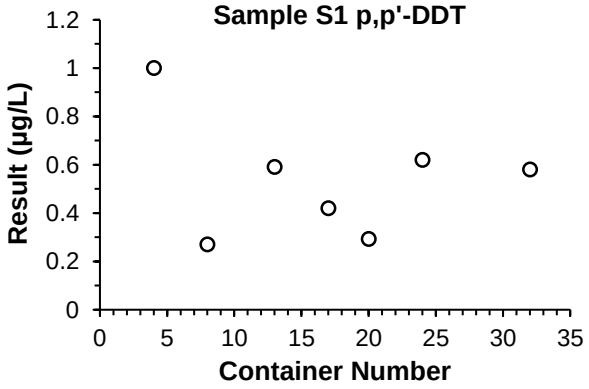


Figure 27 S1 p,p'-DDT Result vs Container

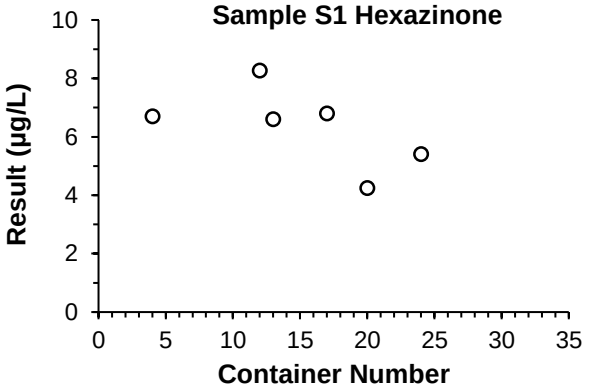


Figure 28 S1 Hexazinone Result vs Container

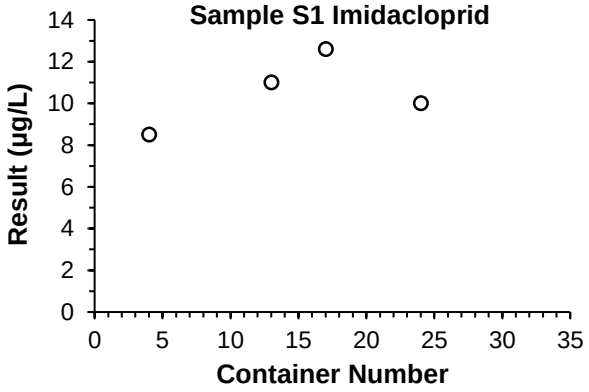


Figure 29 S1 Imidacloprid Result vs Container

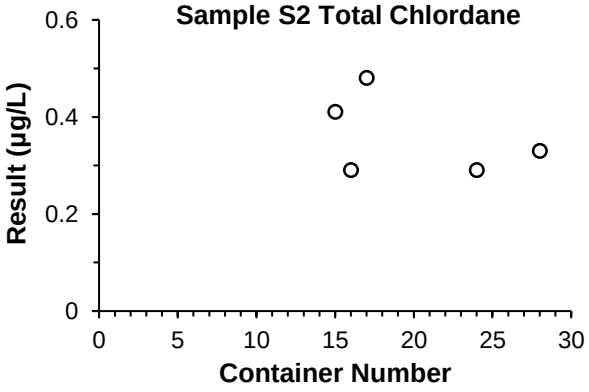


Figure 30 S2 Total Chlordane Result vs Container

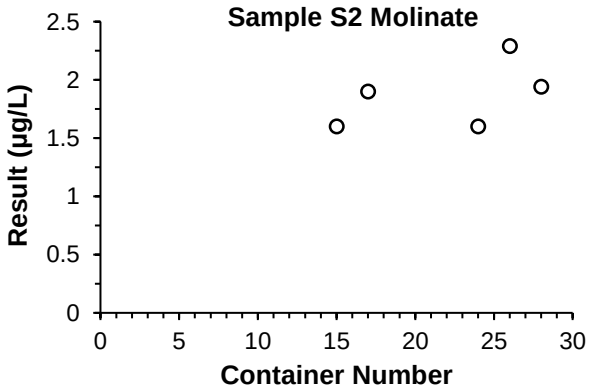


Figure 31 S2 Molinate Result vs Container

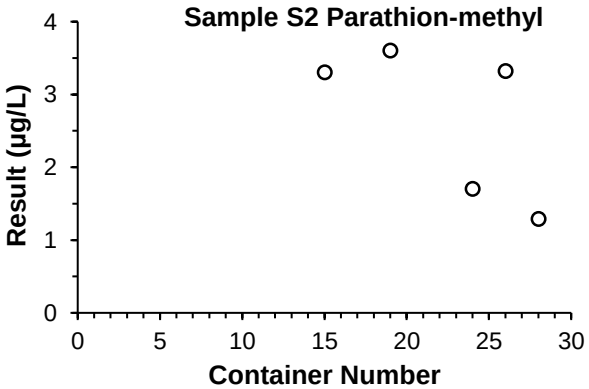


Figure 32 S2 Parathion-methyl Result vs Container

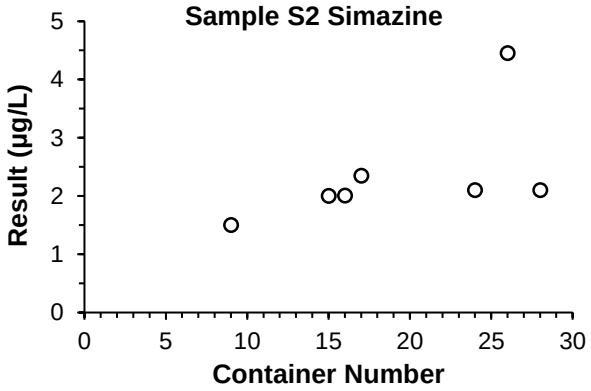


Figure 33 S2 Simazine Result vs Container

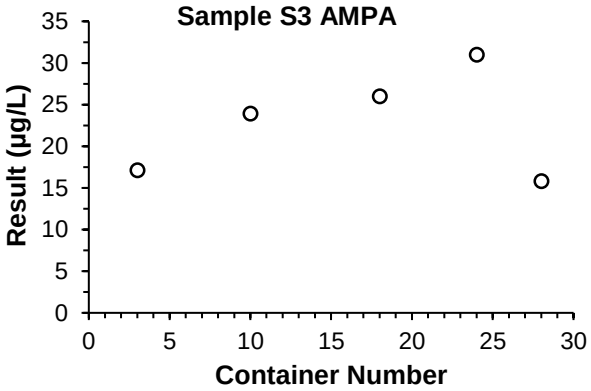


Figure 34 S3 AMPA Result vs Container

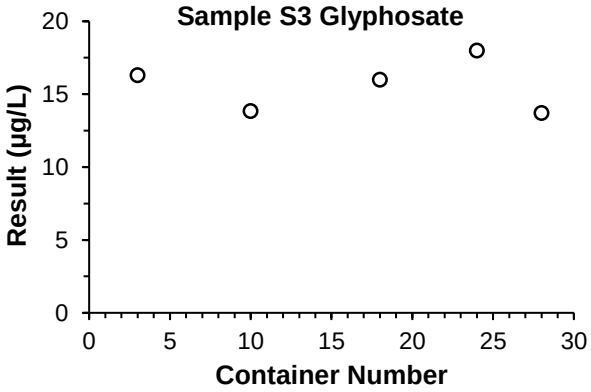


Figure 35 S3 Glyphosate Result vs Container

A2.2 Stability

No stability testing was conducted for this study, though previous use of these pesticides and similar analytes gave assurance that they were stable in transit. 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 are presented in Figures 36 to 44; no significant analyte degradation with respect to the amount of time spent in transit was observed.

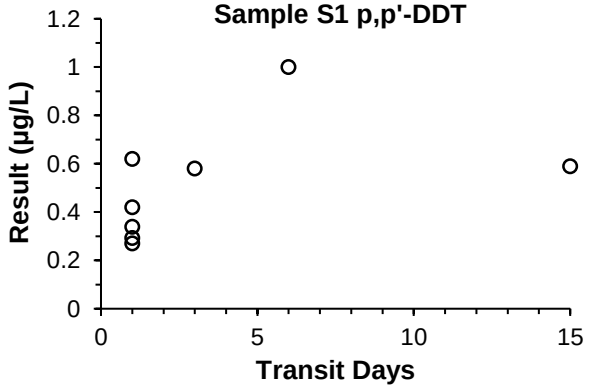


Figure 36 S1 p,p'-DDT Result vs Transit Days

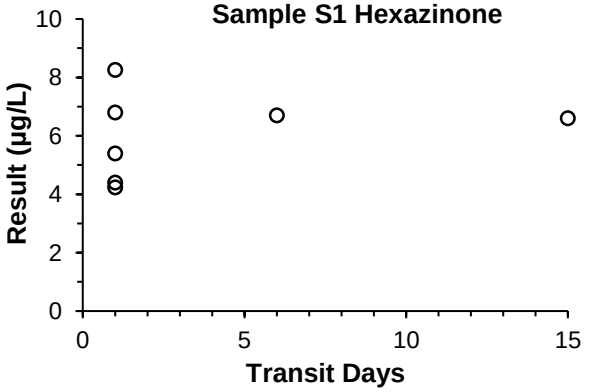


Figure 37 S1 Hexazinone Result vs Transit Days

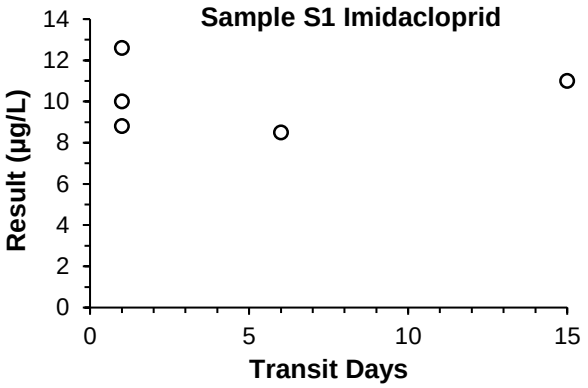


Figure 38 S1 Imidacloprid Result vs Transit Days

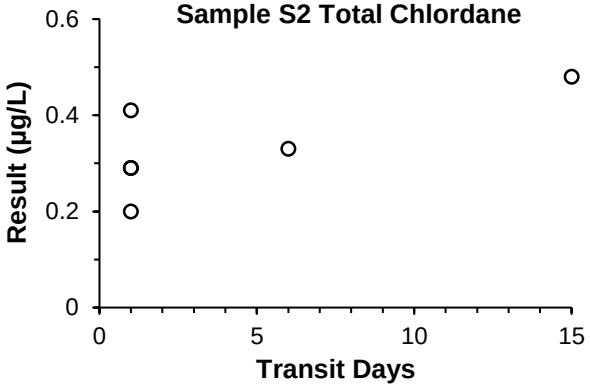


Figure 39 S2 Total Chlordane Result vs Transit Days

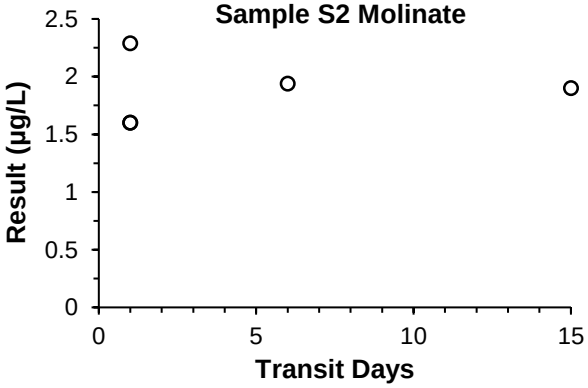


Figure 40 S2 Molinate Result vs Transit Days

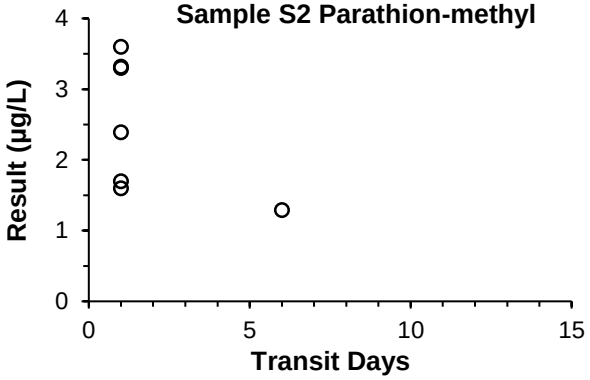


Figure 41 S2 Parathion-methyl Result vs Transit Days

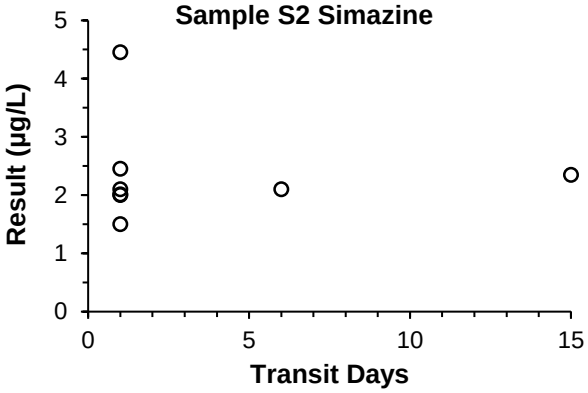


Figure 42 S2 Simazine Result vs Transit Days

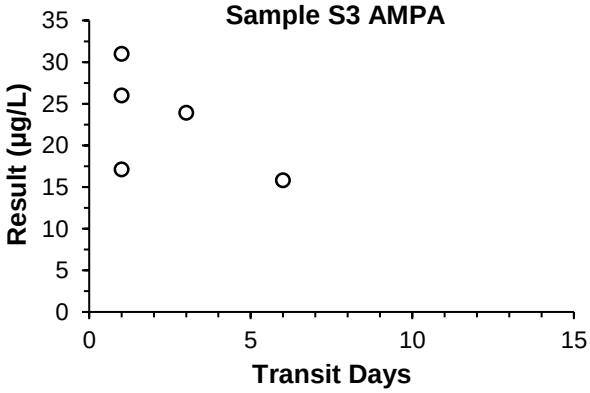


Figure 43 S3 AMPA Result vs Transit Days

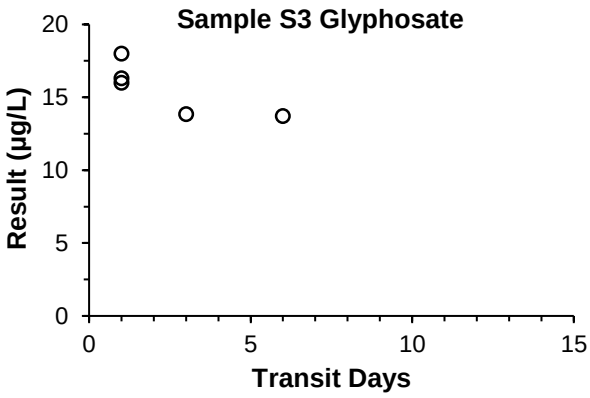


Figure 44 S3 Glyphosate Result vs Transit Days

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 13528:2022.[8] 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 21.

Table 21 Uncertainty of Robust Average for Hexazinone in Sample S1

Number of results (p)	7
Robust Average	6.1 µg/L
$S_{rob\ av}$	1.6 µg/L
$u_{rob\ av}$	0.8 µg/L
k	2
$U_{rob\ av}$	1.6 µg/L

Therefore, the robust average for hexazinone in Sample S1 is 6.1 ± 1.6 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 22, using the result reported by Laboratory 2 for Sample S1 hexazinone.

Table 22 *z*-Score and E_n-Score for Sample S1 Hexazinone Result Reported by Laboratory 2

Participant Result (µg/L)	Assigned Value (µg/L)	Target Standard Deviation	*z*-Score	E_n-Score
6.8 ± 2	6.1 ± 1.6	15% as PCV, or: $0.15 \times 6.1 = 0.915$ µg/L	$z = \frac{6.8 - 6.1}{0.915} = 0.77$	$E_n = \frac{6.8 - 6.1}{\sqrt{2^2 + 1.6^2}} = 0.27$

APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 23 to 31. Some responses may be modified so that the participant cannot be identified.

Table 23 Methodology – p,p'-DDT

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	35	Liquid-Liquid	DCM	none	GC-MS/MS
2	50	Liquid-Liquid	Hexane/Pentane		GC-ECD
3	500	SPE	DCM/EtOAc		GC-MS/MS
4	100	Liquid-Liquid	DCM		GC-MS
5	80	Liquid-Liquid	DCM		GC-MS/ECD
6	50	Liquid-Liquid	DCM	N/A	GC-ECD
7	500	Liquid-Liquid	DCM	Filtration	GC-MS
8	150	Liquid-Liquid	hexane	None	GC-ECD
9	500	Liquid-Liquid	DCM	Filtration	GC-MS/MS
10					
11	40	Liquid-Liquid	Hexane	None	GC-MS/MS

Table 24 Methodology – Hexazinone

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT				
2		Direct Injection			LC-MS/MS
3	10	Direct Injection			LC-MS/MS
4	NT				
5	80	Liquid-Liquid	DCM		GC-MS/ECD
6	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
7					
8	NT				
9	100	SPE	DCM	Filtration	LC-MS/MS
10	1	Direct Injection	N/A	N/A	LC-MS/MS
11	20	Quechers	Acetonitrile	None	LC-MS/MS

Table 25 Methodology – Imidacloprid

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT				
2		Direct Injection			LC-MS/MS
3	10	Direct Injection			LC-MS/MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
4	NT				
5	NT				
6	5	Direct Injection		N/A	LC-MS/MS
7					
8	NT				
9	100	SPE	DCM	Filtration	LC-MS/MS
10					
11	20	Quechers	Acetonitrile	None	LC-MS/MS

Table 26 Methodology – Total Chlordane

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	35	Liquid-Liquid	DCM	none	GC-MS/MS
2	50	Liquid-Liquid	Hexane/Pentane		GC-ECD
3	500	SPE	DCM/EtOAc		GC-MS/MS
4	NT				
5	80	Liquid-Liquid	DCM		GC-MS/ECD
6	50	Liquid-Liquid	DCM	N/A	GC-ECD
7	500	Liquid-Liquid	DCM	Filtration	GC-MS
8	NT				
9	500	Liquid-Liquid	DCM	Filtration	GC-MS/MS
10					
11	40	Liquid-Liquid	Hexane	None	GC-MS/MS

Table 27 Methodology – Molinate

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT				
2		Direct Injection			LC-MS/MS
3	10	Direct Injection			LC-MS/MS
4	NT				
5	NT				
6	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
7					
8	NT				
9	NT				
10	1	Direct Injection	N/A	N/A	LC-MS/MS
11	20	Quechers	Acetonitrile	None	LC-MS/MS

Table 28 Methodology – Parathion-methyl

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	35	Liquid-Liquid	DCM	none	GC-MS/MS
2		Direct Injection			LC-MS/MS
3	500	SPE	DCM/EtOAc		GC-MS
4	100	Liquid-Liquid	DCM		GC-MS
5	80	Liquid-Liquid	DCM		GC-MS/ECD
6	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
7	500	Liquid-Liquid	DCM	Filtration	GC-MS
8					
9	500	Liquid-Liquid	DCM	Filtration	GC-MS/MS
10	1	Direct Injection	N/A	N/A	LC-MS/MS
11	NT				

Table 29 Methodology – Simazine

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT				
2		Direct Injection			LC-MS/MS
3	10	Direct Injection			LC-MS/MS
4	NT				
5	80	Liquid-Liquid	DCM		GC-MS/ECD
6	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
7	500	Liquid-Liquid	DCM	Filtration	GC-MS
8	NT				
9	100	SPE	DCM	Filtration	LC-MS/MS
10	1	Direct Injection	N/A	N/A	LC-MS/MS
11	20	Quechers	Acetonitrile	None	LC-MS/MS

Table 30 Methodology – AMPA

Lab. Code	Sample Volume (mL)	Extraction	Derivatisation Procedure	Derivatisation Agent	Measurement Instrument
1					
2	1	Liquid-Liquid	Pre-column		LC-MS/MS
3	10	Direct Injection	Analysed no derivatisation		LC-MS/MS
4	NT				
5	NT				
6	4	Direct Injection	Pre-column	FMOC	LC-MS/MS
7					

Lab. Code	Sample Volume (mL)	Extraction	Derivatisation Procedure	Derivatisation Agent	Measurement Instrument
8	100	Evaporation	Pre-column	FMOC-Cl	HPLC-FLD
9	NT				
10	NT				
11	NT				

Table 31 Methodology – Glyphosate

Lab. Code	Sample Volume (mL)	Extraction	Derivatisation Procedure	Derivatisation Agent	Measurement Instrument
1					
2	1	Liquid-Liquid	Pre-column		LC-MS/MS
3	10	Direct Injection	Analysed no derivatisation		LC-MS/MS
4	NT				
5	NT				
6	4	Direct Injection	Pre-column	FMOC	LC-MS/MS
7					
8	100	Evaporation	Pre-column	FMOC-Cl	HPLC-FLD
9	NT				
10	NT				
11	NT				

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

ACN	Acetonitrile
AMPA	Aminomethylphosphonic acid
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
DI	Direct Injection
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
FLD	Fluorescence Detection
FMOC	Fluorenylmethyloxycarbonyl
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
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
NR	Not Reported
NT	Not Tested
p,p’-DDD	Dichlorodiphenyldichloroethane

p,p'-DDE	Dichlorodiphenyldichloroethylene
p,p'-DDT	Dichlorodiphenyltrichloroethane
PCV	Performance Coefficient of Variation
PENT	Pentane
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

END OF REPORT