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National Measurement Institute

Proficiency Test Final Report AQA 24-09 Pesticides in Potable Water

September 2024

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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TABLE OF CONTENTS

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SUMMARY

AQA 24-09 Pesticides in Potable Water commenced in May 2024. Twenty-four laboratories registered to participate, and 23 participants submitted results.

The sample set consisted of two potable water samples. Samples were prepared in the NMI Sydney laboratory by spiking potable water with various pesticides.

Of a possible 253 results, 165 numeric results (65%) were submitted. Sixteen results were a 'less than' value (< *x*) or Not Reported (NR), and 72 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 pesticides in potable water.*

Laboratories **4**, **8**, **10**, **11**, **15**, **17** and **20** reported numeric results for all six scored analytes.

Laboratories **4**, **10**, **17** and **19** did not report numeric results for analytes that they tested for and were present in the test samples (total of four results).

Five participants reported analytes that were not spiked into the test samples (total of eight results).

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

Of 108 *z*-scores, 95 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Of 103 E_n-scores, 81 (79%) returned a score of $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories **8** and **10** achieved acceptable *z*-scores and E_n-scores across all six scored analytes.

Laboratory **3** did not achieve any acceptable *z*-scores or E_n-scores in this study; this participant may have reported their results in the incorrect units.

- *Assess the consequence of participants' results for pesticides in potable water against regulatory guidelines.*

Of the 108 results assessed against the Australian Drinking Water Guidelines, 104 (96%) correctly reflected whether the sample exceeded the guideline or not.

Laboratories **4**, **8**, **10**, **11**, **15**, **17** and **20** returned the correct consequence for all six analytes assessed.

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

Participants used a wide variety of methods, with the most common methodology used in this study was liquid-liquid extraction (LLE) with dichloromethane (DCM), followed by analysis using GC-MS.

For most analytes no correlation with results was evident. For Sample S2 MCPA, it was seen that participants using direct injection into LC-MS/MS returned results much closer to the spiked value as compared to participants who used other methodologies and instruments.

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

Of 165 numeric results, 147 (89%) were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 6.4% to 62%. Participants used a wide variety of procedures to estimate their uncertainty.

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

The test samples produced for this study are homogeneous and 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 comparisons'.[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 soil and water, fruit, vegetables and herbs;
- hydrocarbons, phenols and volatile organic compounds in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, biosolid, 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 pesticides in potable water;
- compare the performance of participants and assess their accuracy in the measurement of pesticides in potable water;
- assess the consequence of participants' results for pesticides in potable water against regulatory guidelines;
- evaluate the participants' methods for the measurement of pesticides in potable 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 PT studies 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 17043:2023 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 6/05/2024

Samples sent 3/06/2024

Results due 15/07/2024

Interim Report 18/07/2024

Preliminary Report 24/07/2024

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 Analytes

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

- the Australian Drinking Water Guidelines (ADWG);[5]
- a variety of analytes amenable to gas and/or liquid chromatography; and
- feedback from participants and other stakeholders.

The potential analytes spiked into the test samples are presented in Table 1.

Table 1 List of Possible Analytes for Samples S1 and S2

Aldicarb	DDT	Heptachlor	Permethrin
Aldrin	Deltamethrin	Hexazinone	Picloram
Atrazine	Diazinon	Imazapyr	Piperonyl butoxide
Azinphos-methyl	Dichlorvos	Lindane	Pirimicarb
Chlorpyrifos	Dieldrin	Malathion	Pirimiphos-ethyl
Chlordane	Dimethoate	MCPA	Pirimiphos-methyl
Chlorfenvinphos	Diuron	Metolachlor	Propiconazole
Clopyralid	Endosulfan	Metsulfuron-methyl	Simazine
Cyfluthrin	Ethion	Omethoate	Tetrachlorvinphos
Cypermethrin	Fenthion	Parathion	
2,4-D	Glyphosate	Pendimethalin	

2.4 Test Material Preparation

Two test samples were prepared by adding pesticide standard solutions to potable water. The spiked values for the samples and corresponding ADWG values,[5] are presented in Table 2.

Table 2 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/L)	Uncertainty[a] (mg/L)	ADWG Health Guideline Value (mg/L)
S1[b]	Atrazine	0.0100	0.0005	0.02
	Chlorpyrifos	0.00782	0.00039	0.01
	Dieldrin	0.00995	0.00050	0.0003[c]
	Lindane	0.00605	0.00030	0.01
	Pirimicarb	0.000181	0.000009	0.007
S2	2,4-D	0.0703	0.0035	0.03
	Ethion	0.00203	0.00010	0.004
	Hexazinone	0.00200	0.00010	0.4
	MCPA	0.0301	0.0015	0.04
	Metsulfuron-methyl	0.0603	0.0030	0.04
	Simazine	0.0101	0.0005	0.02

[a] Estimated expanded uncertainty at time of spiking at approximately 95% confidence using a coverage factor of 2.

[b] Aldicarb was also spiked into Sample S1 at 0.0238 ± 0.0012 mg/L, however this analyte was not detected by any participant. See also Section 6.1.

[c] The ADWG value is for aldrin and dieldrin combined. Participants were requested in this study to report for aldrin and dieldrin separately. Sample S1 was spiked with dieldrin only.

Additional sample preparation details are provided in Appendix 1.

2.5 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this study. 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 PT studies with similar analytes and matrices.

To further assess possible instability, the results returned by participants were compared to the spiked concentrations. For scored analytes, assigned values were within the range of 61% to 100% of the spiked values, which is similar to ratios observed in previous NMI PT studies for pesticides in water. Analytes have only been scored when there was a reasonable consensus between participants' results.

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

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 3 June 2024.

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 mg/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 mg/L (e.g. 0.05 ± 0.02 mg/L), if determined.
- No limit of reporting has been set for this study. Report results as you would to a client, applying the limit of reporting of the method used for analysis.
- Report any listed pesticide not tested as NT.
- 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 July 2024 by email to proficiency@measurement.gov.au.

The results due date was later extended to 15 July 2024 for all participants.

2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 18 July 2024.

A Preliminary Report was emailed to all participants on 24 July 2024. This report included a summary of the results reported by participants, assigned values, performance coefficients of variation, *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 k = 2	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
2	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NMI Uncertainty Course
3	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples Duplicate analysis Instrument calibration	Instrument calibration	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	Recoveries of SS Standard purity	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - CRM	CRM Recoveries of SS	ISO/GUM
6	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	Eurachem/CITAC Guide
8	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - CRM Duplicate analysis	CRM Recoveries of SS	Eurachem/CITAC Guide

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 Coverage factor not reported	Control samples - RM Duplicate analysis Instrument calibration		Eurachem/CITAC Guide
11	Coverage factor not reported			
12	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - CRM	Recoveries of SS	ISO/GUM
13	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS		ISO/GUM
14	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Control samples	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
15	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
16	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - CRM Duplicate analysis Instrument calibration		
17	Coverage factor not reported	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	
18	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - RM Duplicate analysis	CRM Instrument calibration Recoveries of SS	NMI Uncertainty Course
19	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Control samples - RM Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies Recoveries of SS	Eurachem/CITAC Guide
20	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	CRM Instrument calibration Recoveries of SS	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
21	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
22	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS		Eurachem/CITAC Guide
23	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
24	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	NATA

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

3.3 Participants' Comments

Participants were invited to make 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, along with the study coordinator's response where applicable. Some responses may be modified so that the participant cannot be identified.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
17	S1	Is the propazine due to a breakdown or impurity of the atrazine? I think that we may have seen it before at low levels in the presence of atrazine.	Please see Section 6.7.
	All	Uncertainty: Measurement uncertainty is currently being re-evaluated so no uncertainties have been included.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

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

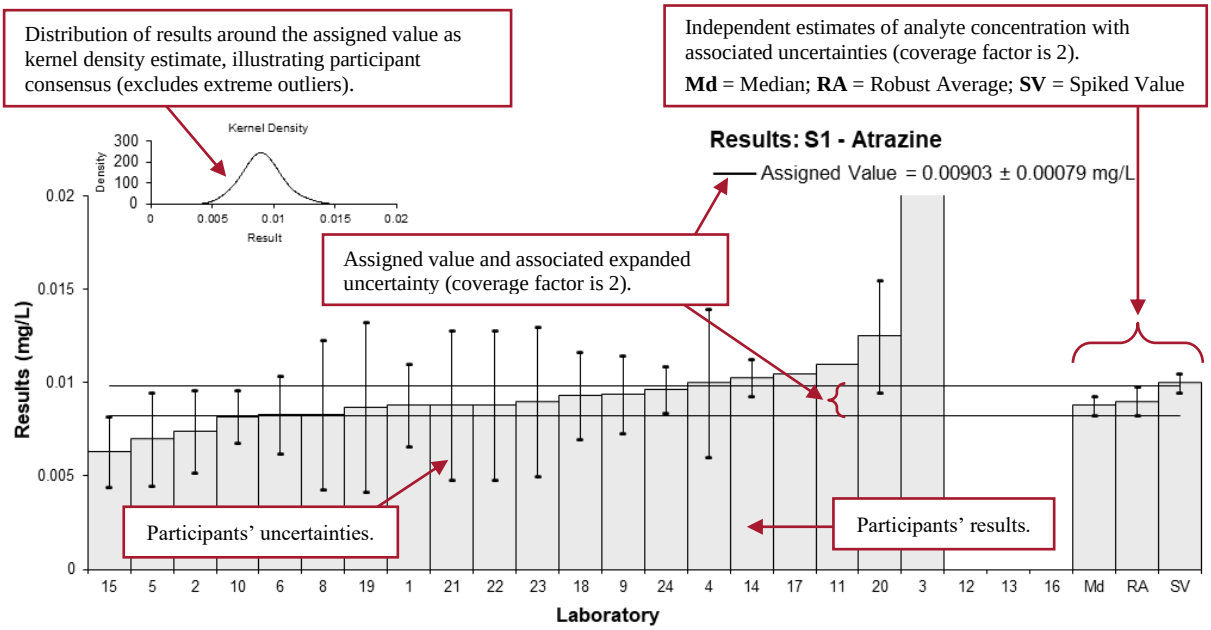


Figure 1 Guide to Presentation of Results

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.[3,4] Extreme outliers, if applicable, were obvious blunders, e.g. results reported with incorrect units or for a different analyte or sample, 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 or characteristic 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 MUs, and robust CVs (a measure of the variability of participants' results) were calculated as described in ISO 13528.[6]

4.5 Performance Coefficient of Variation

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

4.6 Target Standard Deviation 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.

To account for potential low bias in the consensus value due to inefficient methodologies, z-scores may be adjusted for a 'maximum acceptable result' (see Section 6.3).

4.8 E_n-Score

The E_n-score is complementary to the z-score in the assessment of laboratory performance. The E_n-score includes expanded 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:

- $|E_n| < 1.0$ is acceptable; and
- $|E_n| \geq 1.0$ 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 5

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Atrazine
Unit	mg/L

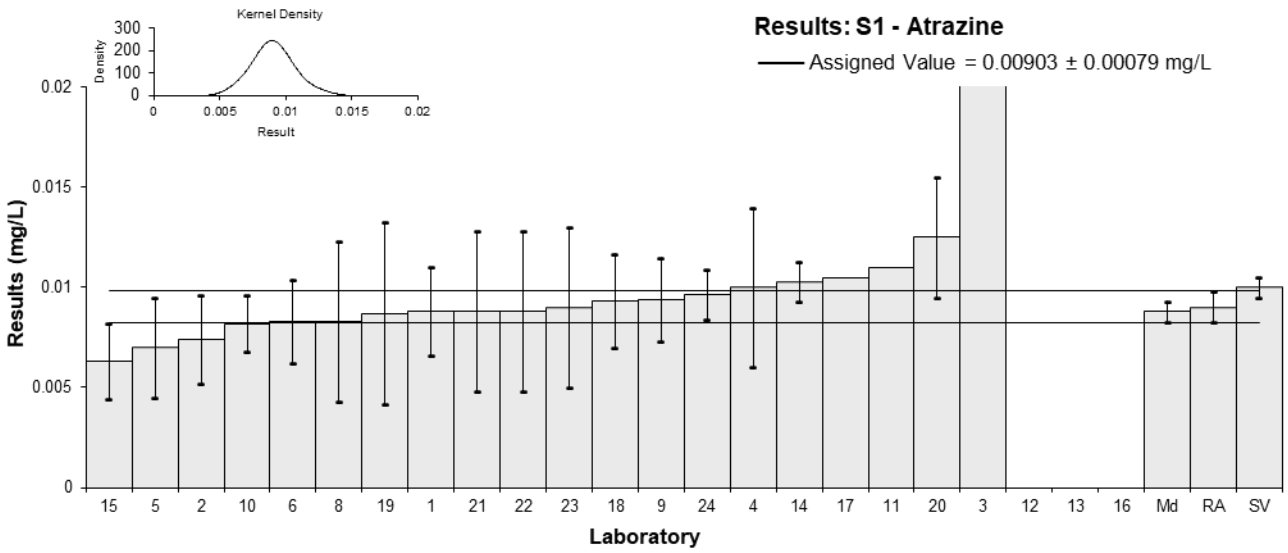
Participant Results

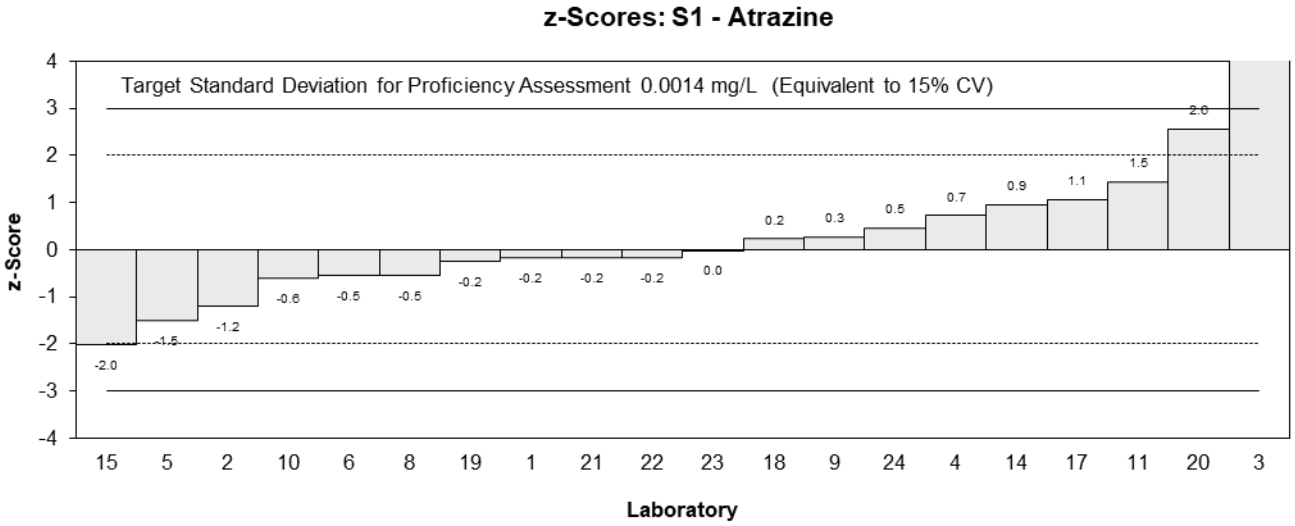
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0088	0.0022	96	-0.17	-0.10
2	0.0074	0.0022	NR	-1.20	-0.70
3**	9.3	2.79	NR	6,859.34	3.33
4	0.010	0.004	99	0.72	0.24
5	0.0070	0.0025	NR	-1.50	-0.77
6	0.0083	0.0021	81.4	-0.54	-0.33
8	0.0083	0.004	NR	-0.54	-0.18
9	0.0094	0.00209	NR	0.27	0.17
10	0.0082	0.0014	NR	-0.61	-0.52
11	0.011	NR	104	1.45	2.49
12	NT	NT	NT		
13	NT	NT	NT		
14	0.0103	0.001	103	0.94	1.00
15	0.0063	0.0019	80	-2.02	-1.33
16	NT	NT	NT		
17	0.01047	NR	NR	1.06	1.82
18	0.00934	0.00234	109	0.23	0.13
19	0.0087	0.00456	NR	-0.24	-0.07
20	0.0125	0.003	NR	2.56	1.12
21	0.0088	0.004	NR	-0.17	-0.06
22	0.0088	0.004	NR	-0.17	-0.06
23	0.009	0.004	80-120	-0.02	-0.01
24	0.00964	0.00125	NR	0.45	0.41

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00903	0.00079
Spike Value	0.0100	0.0005
Robust Average	0.00903	0.00079
Median	0.00880	0.00051
Mean	0.00907	
N	19	
Max	0.0125	
Min	0.0063	
Robust SD	0.0014	
Robust CV	15%	


Kernel Density
Density
Result
Results: S1 - Atrazine
Assigned Value = 0.00903 ± 0.00079 mg/L
Results (mg/L)
Laboratory
15 5 2 10 6 8 19 1 21 22 23 18 9 24 4 14 17 11 20 3 12 13 16 Md RA SV


z-Scores: S1 - Atrazine
Target Standard Deviation for Proficiency Assessment 0.0014 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
15 5 2 10 6 8 19 1 21 22 23 18 9 24 4 14 17 11 20 3

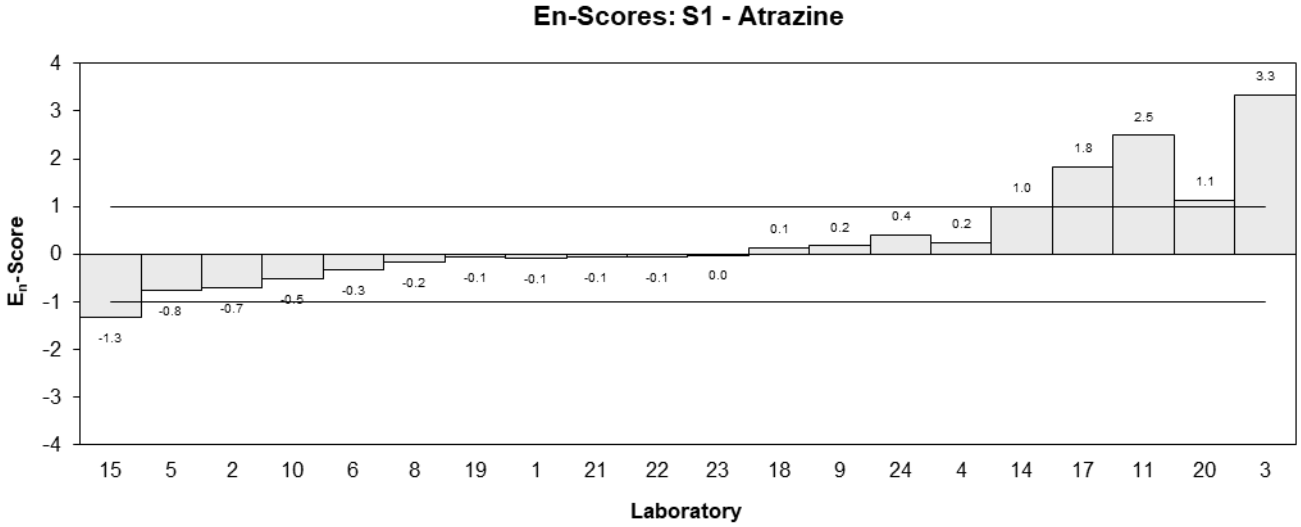

En-Scores: S1 - Atrazine
En-Score
Laboratory
15 5 2 10 6 8 19 1 21 22 23 18 9 24 4 14 17 11 20 3

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Chlorpyrifos
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.0023	0.0007	90
2	0.0021	0.0006	NR
3**	1.95	0.585	NR
4	0.0021	0.00084	99
5	0.0011	0.0004	NR
6	0.0019	0.0005	72.4
8	0.00203	0.00066	NR
9	0.0023	0.00066	NR
10	0.0019	0.00021	NR
11	<0.002	NR	NR
12	<0.02	NR	NR
13	0.0012	0.0004	NR
14	0.0027	0.0004	99
15	0.0018	0.0005	91
16	<0.002	NR	NR
17	0.0011	NR	NR
18	0.00153	0.00038	106
19	0.0015	0.00093	NR
20	0.00188	0.0002	NR
21	0.0016	0.0005	NR
22	0.001	0.0005	NR
23	0.0018	0.0005	80-120
24	NT	NT	NT

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	0.00782	0.00039
Robust Average	0.00176	0.00030
Median	0.00184	0.00025
Mean	0.00177	
N	18	
Max	0.0027	
Min	0.001	
Robust SD	0.00051	
Robust CV	29%	

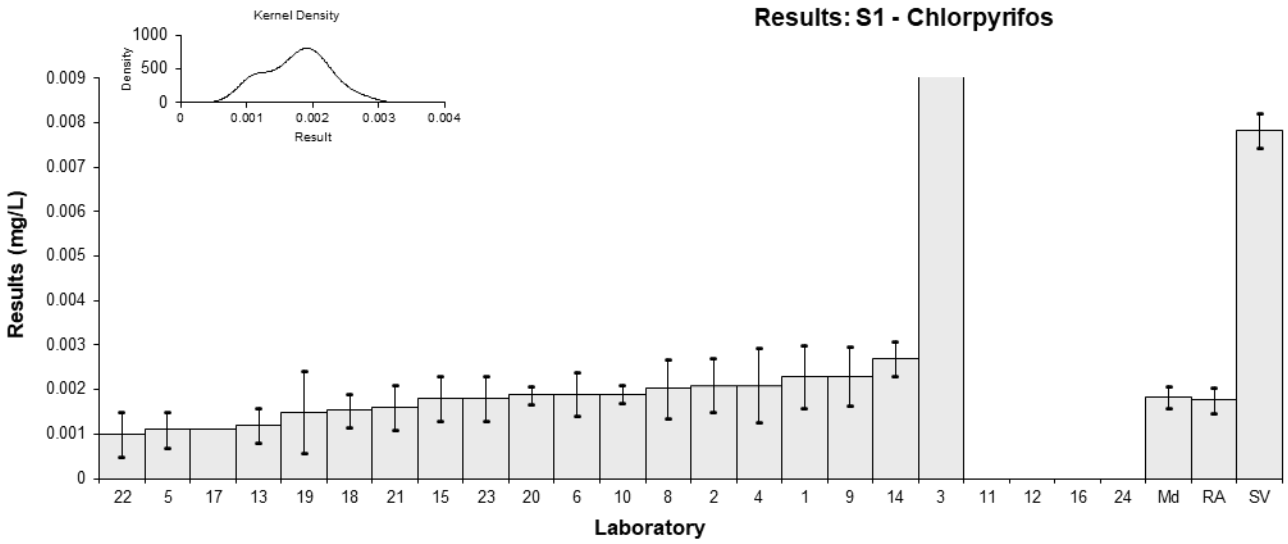

Results: S1 - Chlorpyrifos
Kernel Density
Density
Result
Results (mg/L)
Laboratory
22 5 17 13 19 18 21 15 23 20 6 10 8 2 4 1 9 14 3 11 12 16 24 Md RA SV

Figure 3

Table 7

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Dieldrin
Unit	mg/L

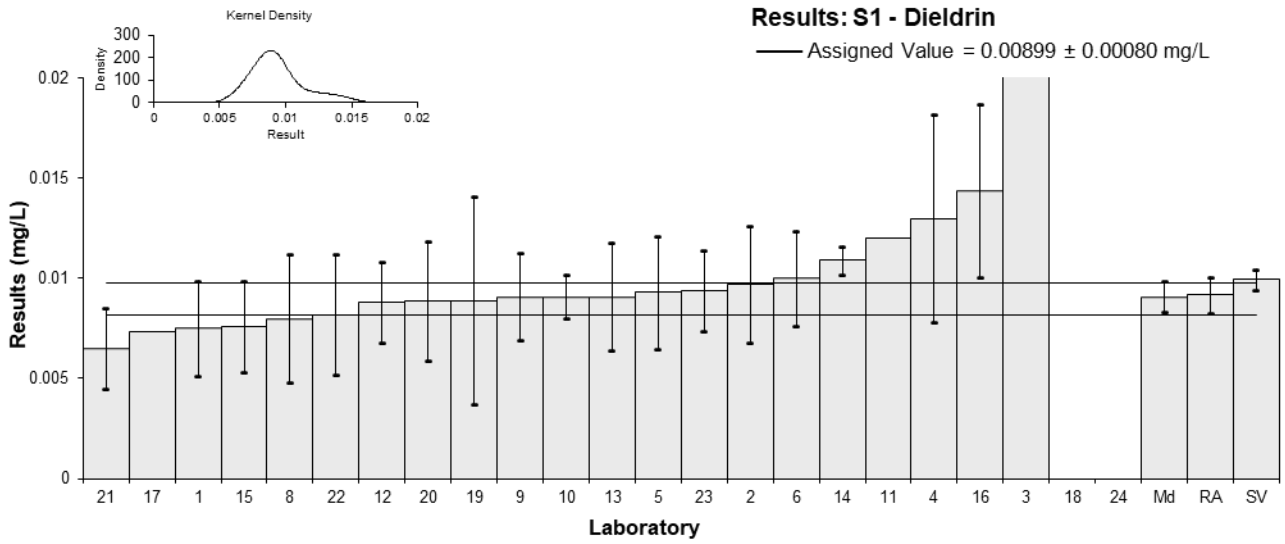
Participant Results

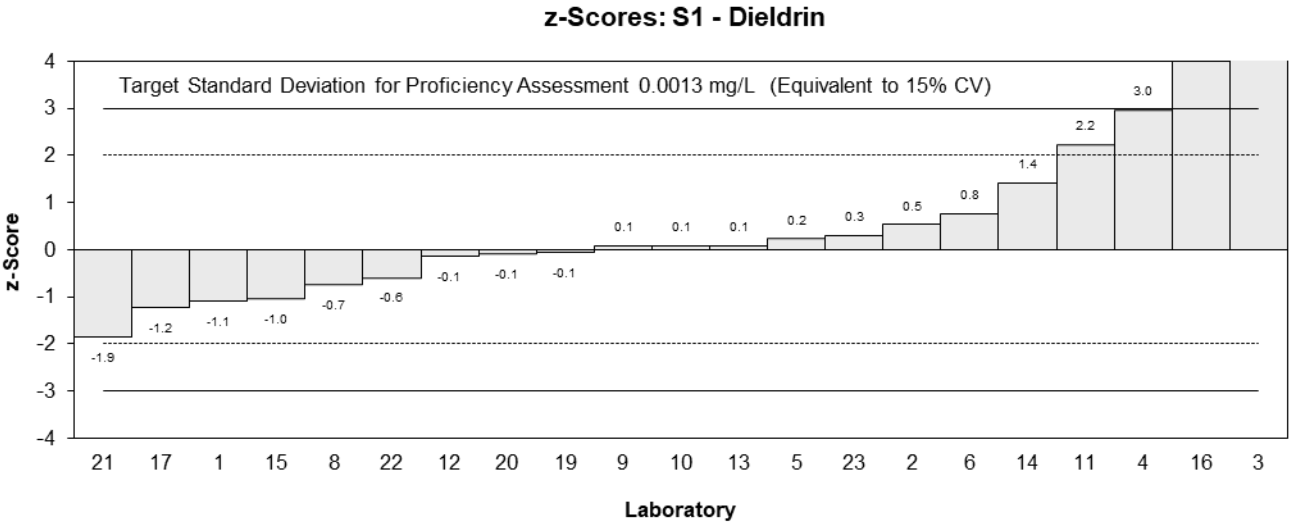
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0075	0.0024	87	-1.10	-0.59
2	0.0097	0.0029	NR	0.53	0.24
3**	10.5	3.15	NR	7,779.76	3.33
4	0.013	0.0052	117	2.97	0.76
5	0.0093	0.0028	NR	0.23	0.11
6	0.0100	0.0024	72.3	0.75	0.40
8	0.008	0.0032	NR	-0.73	-0.30
9	0.0091	0.00215	NR	0.08	0.05
10	0.0091	0.0011	NR	0.08	0.08
11	0.012	NR	100	2.23	3.76
12	0.0088	0.002	NR	-0.14	-0.09
13	0.0091	0.0027	NR	0.08	0.04
14	0.0109	0.0007	99	1.42	1.80
15	0.0076	0.0023	96	-1.03	-0.57
16*	0.0144	0.00432	NR	4.01	1.23
17	0.00733	NR	NR	-1.23	-2.07
18	NT	NT	NT		
19	0.0089	0.0052	NR	-0.07	-0.02
20	0.00887	0.003	NR	-0.09	-0.04
21	0.0065	0.002	NR	-1.85	-1.16
22	0.0082	0.003	NR	-0.59	-0.25
23	0.0094	0.002	80-120	0.30	0.19
24	NT	NT	NT		

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00899	0.00080
Spike Value	0.00995	0.00050
Robust Average	0.00917	0.00090
Median	0.00910	0.00075
Mean	0.00939	
N	20	
Max	0.0144	
Min	0.0065	
Robust SD	0.0016	
Robust CV	18%	


Kernel Density
Density
Result
Results: S1 - Dieldrin
Assigned Value = 0.00899 ± 0.00080 mg/L
Results (mg/L)
Laboratory
21 17 1 15 8 22 12 20 19 9 10 13 5 23 2 6 14 11 4 16 3 18 24 Md RA SV


z-Scores: S1 - Dieldrin
Target Standard Deviation for Proficiency Assessment 0.0013 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
21 17 1 15 8 22 12 20 19 9 10 13 5 23 2 6 14 11 4 16 3

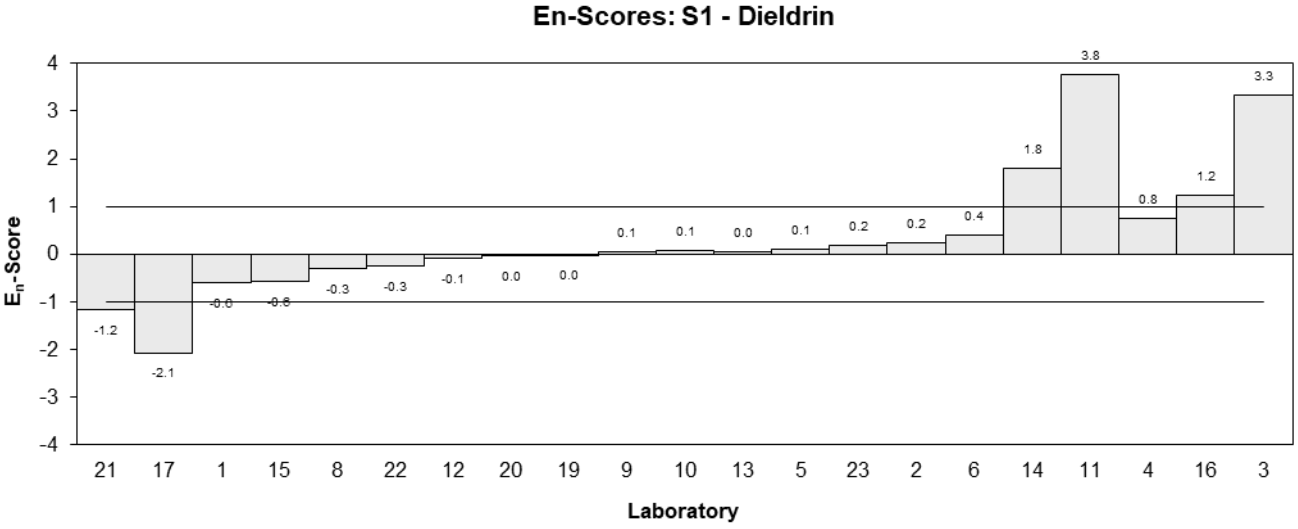

En-Scores: S1 - Dieldrin
En-Score
Laboratory
21 17 1 15 8 22 12 20 19 9 10 13 5 23 2 6 14 11 4 16 3

Figure 4

Table 8

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Lindane
Unit	mg/L

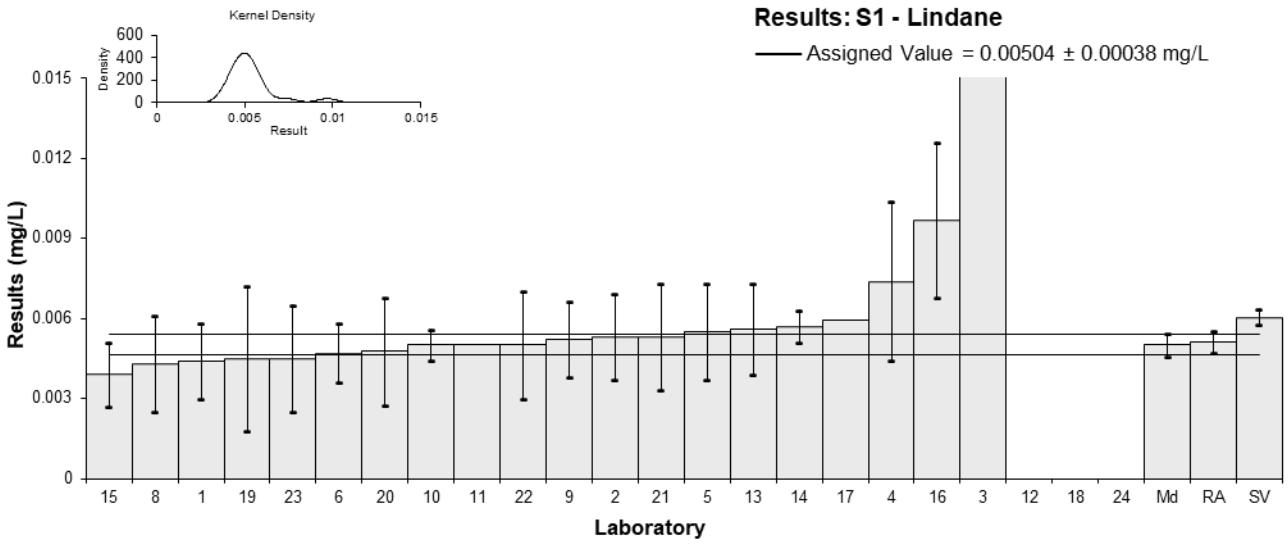
Participant Results

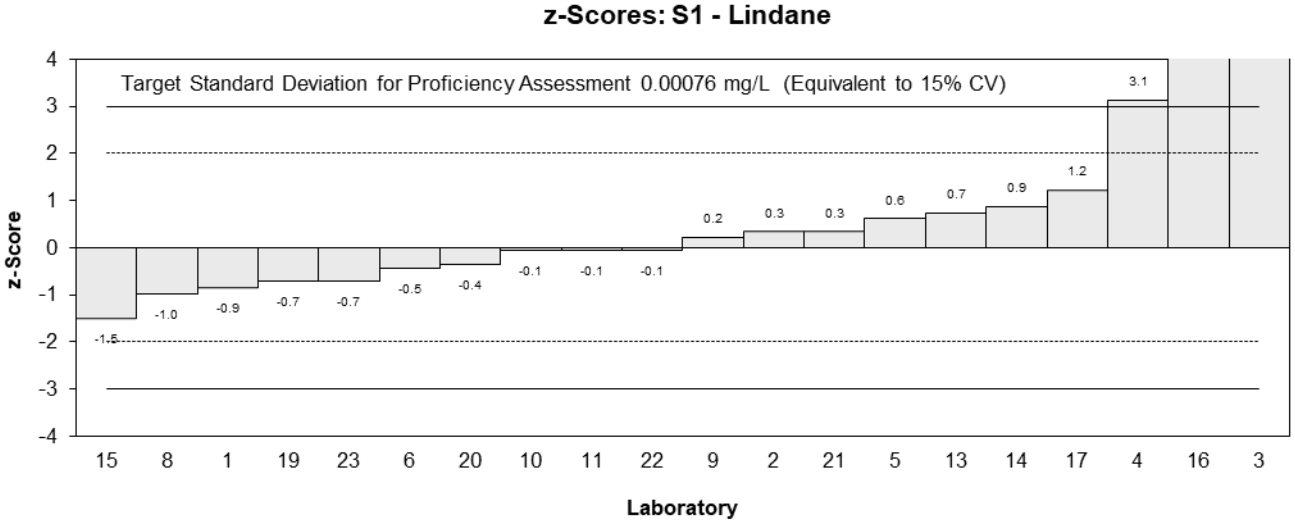
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0044	0.0014	97	-0.85	-0.44
2	0.0053	0.0016	NR	0.34	0.16
3**	6.1	1.83	NR	8,062.12	3.33
4	0.0074	0.0030	117	3.12	0.78
5	0.0055	0.0018	NR	0.61	0.25
6	0.0047	0.0011	80.5	-0.45	-0.29
8	0.0043	0.0018	NR	-0.98	-0.40
9	0.0052	0.00142	NR	0.21	0.11
10	0.005	0.00059	NR	-0.05	-0.06
11	0.005	NR	120	-0.05	-0.11
12	NT	NT	NT		
13	0.0056	0.0017	NR	0.74	0.32
14	0.0057	0.0006	87	0.87	0.93
15	0.0039	0.0012	77	-1.51	-0.91
16*	0.0097	0.00291	NR	6.16	1.59
17	0.00596	NR	NR	1.22	2.42
18	NT	NT	NT		
19	0.0045	0.002702	NR	-0.71	-0.20
20	0.00476	0.002	NR	-0.37	-0.14
21	0.0053	0.002	NR	0.34	0.13
22	0.005	0.002	NR	-0.05	-0.02
23	0.0045	0.002	80-120	-0.71	-0.27
24	NT	NT	NT		

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00504	0.00038
Spike Value	0.00605	0.00030
Robust Average	0.00511	0.00041
Median	0.00500	0.00043
Mean	0.00535	
N	19	
Max	0.0097	
Min	0.0039	
Robust SD	0.00072	
Robust CV	14%	


Kernel Density
Density
Result
Results: S1 - Lindane
Assigned Value = 0.00504 ± 0.00038 mg/L
Results (mg/L)
Laboratory
15 8 1 19 23 6 20 10 11 22 9 2 21 5 13 14 17 4 16 3 12 18 24 Md RA SV


z-Scores: S1 - Lindane
Target Standard Deviation for Proficiency Assessment 0.00076 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
15 8 1 19 23 6 20 10 11 22 9 2 21 5 13 14 17 4 16 3

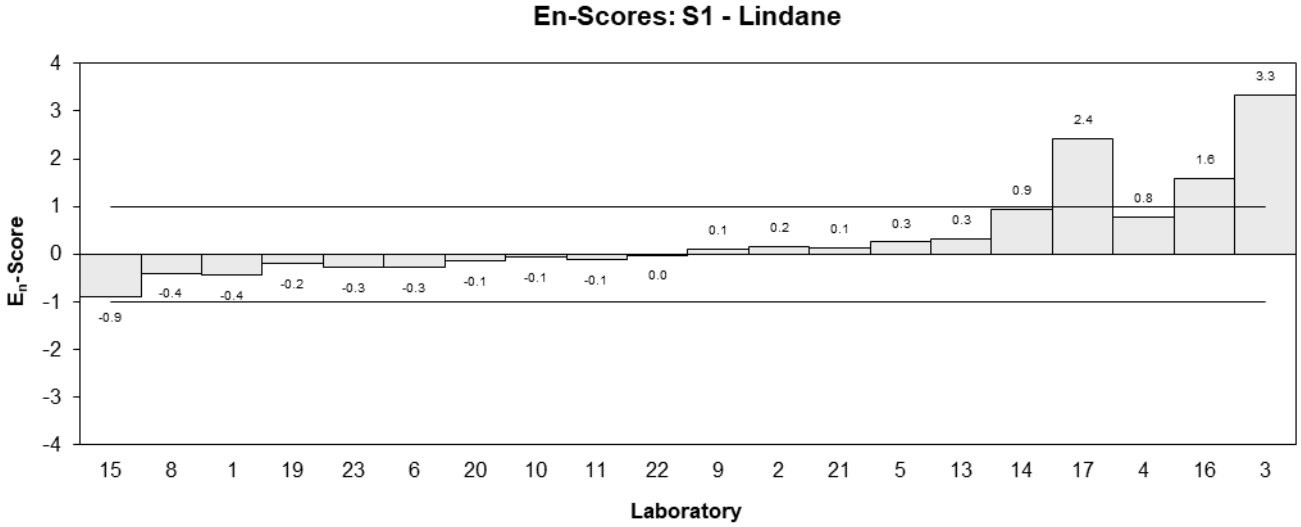

En-Scores: S1 - Lindane
En-Score
Laboratory
15 8 1 19 23 6 20 10 11 22 9 2 21 5 13 14 17 4 16 3

Figure 5

Table 9

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Pirimicarb
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.0002	0.0001	NR
2	NT	NT	NT
3**	0.17	0.051	NR
4	0.00024	0.000096	99
5	0.00024	0.0001	NR
6	NT	NT	NT
8	0.000135	0.000047	NR
9	NT	NT	NT
10	0.0001	0.00003	NR
11	<0.001	NR	NR
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	0.00018	NR	NR
18	NT	NT	NT
19	NT	NT	NT
20	NT	NT	NT
21	NT	NT	NT
22	<0.0005	NR	NR
23	NT	NT	NT
24	NT	NT	NT

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	0.000181	0.000009
Robust Average	0.000183	0.000065
Median	0.000190	0.000076
Mean	0.000183	
N	6	
Max	0.00024	
Min	0.0001	
Robust SD	0.000064	
Robust CV	35%	

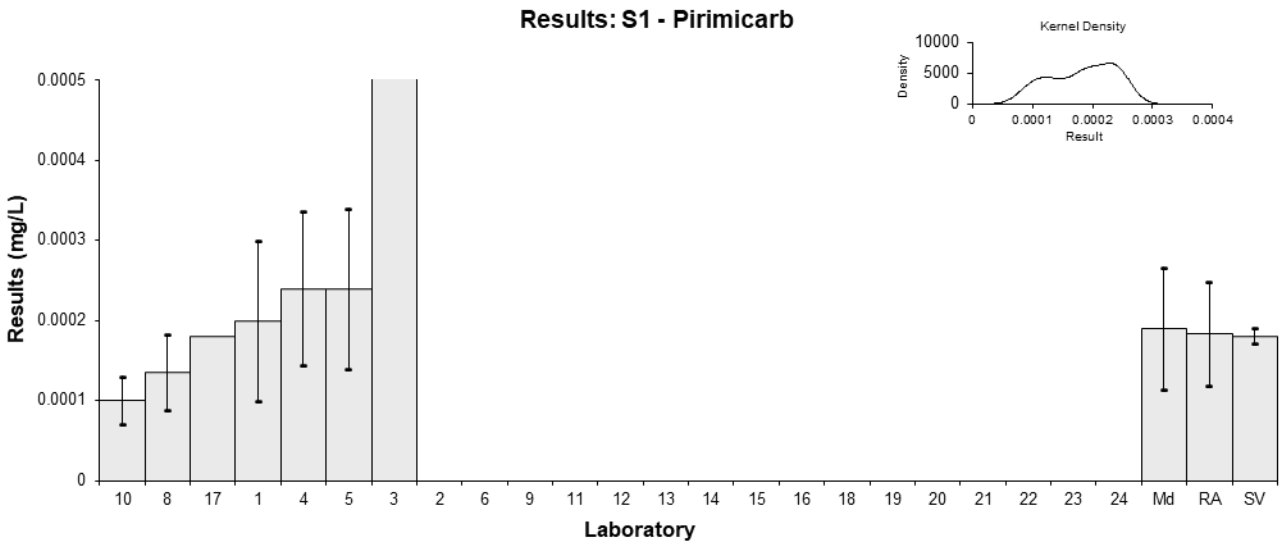

Results: S1 - Pirimicarb
Kernel Density
Density
10000
5000
0
0
0.0001
0.0002
0.0003
0.0004
Result
Results (mg/L)
0.0005
0.0004
0.0003
0.0002
0.0001
0
10
8
17
1
4
5
3
2
6
9
11
12
13
14
15
16
18
19
20
21
22
23
24
Md
RA
SV
Laboratory

Figure 6

Table 10

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	2,4-D
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.026	0.007	70
2	0.0161	0.0048	NR
3**	32.5	9.75	NR
4	0.030	0.010	101
5	0.021	0.007	NR
6	NT	NT	NT
8	0.0391	0.0063	NR
9	NT	NT	NT
10	0.032	0.0056	NR
11	0.034	NR	108
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	0.0371	NR	NR
18	0.03520	0.00880	101
19	NT	NT	NT
20	0.0314	0.006	NR
21	NT	NT	NT
22	0.022	0.007	NR
23	0.024	0.007	80-120
24	NT	NT	NT

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	0.0703	0.0035
Robust Average	0.0291	0.0057
Median	0.0307	0.0059
Mean	0.0290	
N	12	
Max	0.0391	
Min	0.0161	
Robust SD	0.0079	
Robust CV	27%	

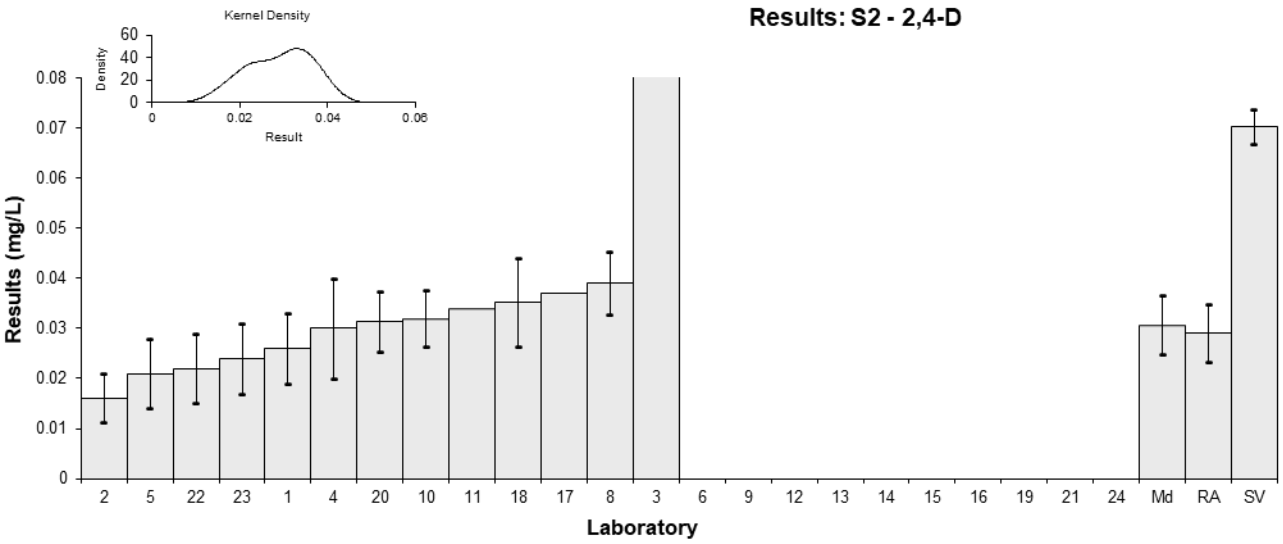

Results: S2 - 2,4-D
Kernel Density
Density
Result
Results (mg/L)
Laboratory
2 5 22 23 1 4 20 10 11 18 17 8 3 6 9 12 13 14 15 16 19 21 24 Md RA SV

Figure 7

Table 11

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Ethion
Unit	mg/L

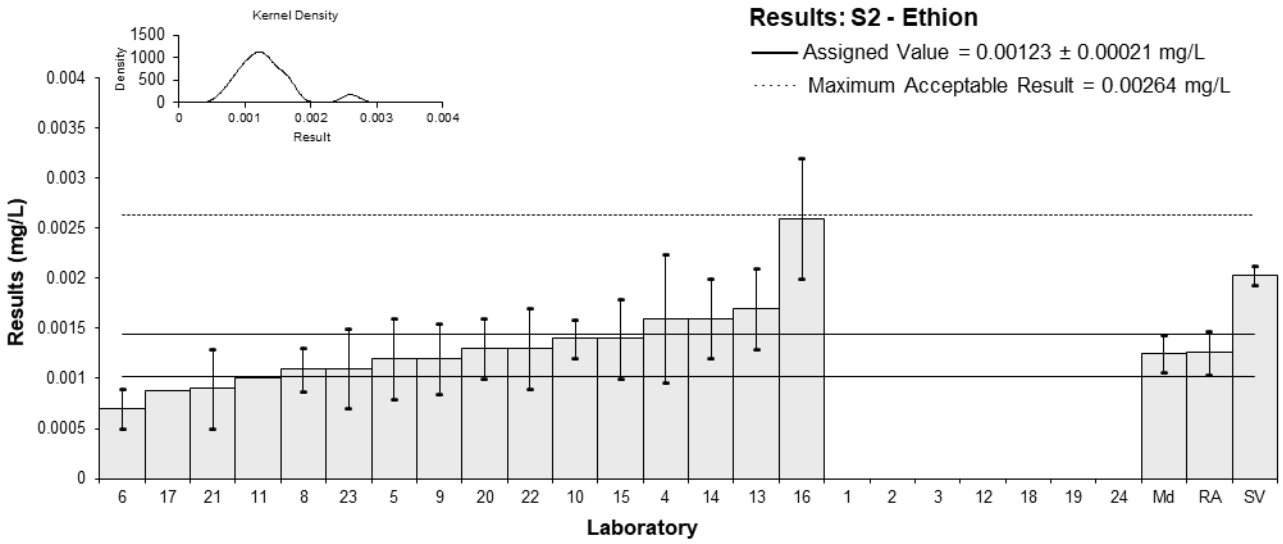
Participant Results

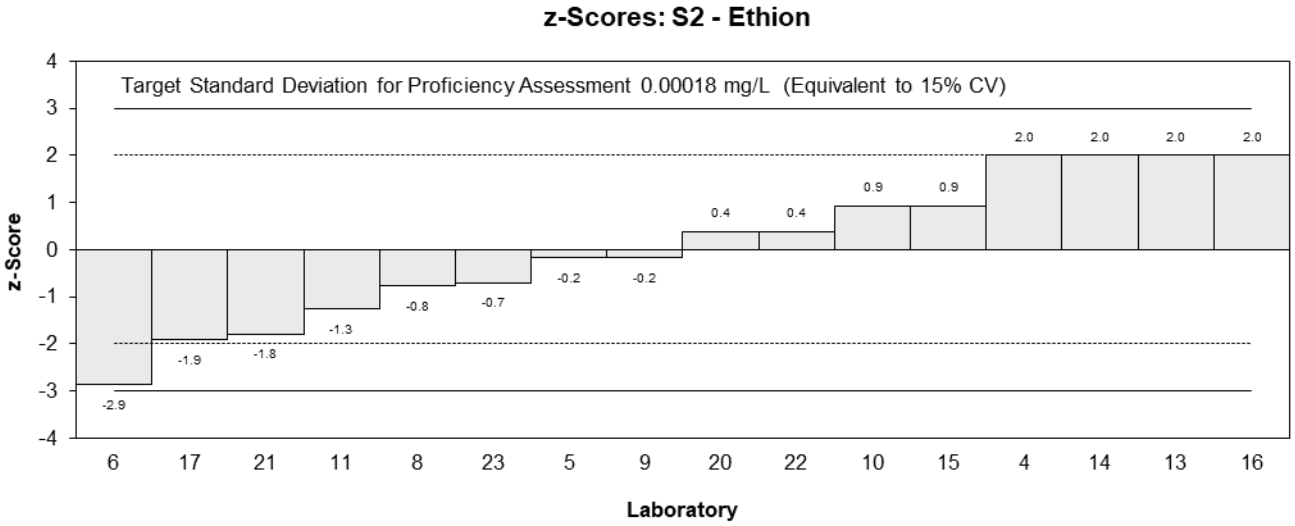
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	NT	NT	NT		
2	< 0.002	NR	NR		
3	NT	NT	NT		
4	0.0016	0.00064	94	2.00▼	
5	0.0012	0.0004	NR	-0.16	-0.07
6	0.0007	0.0002	54.3	-2.87	-1.83
8	0.00109	0.00022	NR	-0.76	-0.46
9	0.0012	0.00035	NR	-0.16	-0.07
10	0.0014	0.00019	NR	0.92	0.60
11	0.001	NR	119	-1.25	-1.10
12	<0.01	NR	NR		
13	0.0017	0.0004	NR	2.00▼	
14	0.0016	0.0004	99	2.00▼	
15	0.0014	0.0004	116	0.92	0.38
16*	0.0026	0.0006	NR	2.00▼	
17	0.00088	NR	NR	-1.90	-1.67
18	NT	NT	NT		
19	<0.0005	0.00035	NR		
20	0.0013	0.0003	NR	0.38	0.19
21	0.0009	0.0004	NR	-1.79	-0.73
22	0.0013	0.0004	NR	0.38	0.15
23	0.0011	0.0004	80-120	-0.70	-0.29
24	NT	NT	NT		

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

Statistics

Assigned Value	0.00123	0.00021
Spike Value	0.00203	0.00010
Robust Average	0.00126	0.00022
Max Acceptable Result	0.00264	
Median	0.00125	0.00019
Mean	0.00131	
N	16	
Max	0.0026	
Min	0.0007	
Robust SD	0.00035	
Robust CV	27%	


Kernel Density
Density
Result
Results: S2 - Ethion
Assigned Value = 0.00123 ± 0.00021 mg/L
Maximum Acceptable Result = 0.00264 mg/L
Results (mg/L)
Laboratory
6 17 21 11 8 23 5 9 20 22 10 15 4 14 13 16 1 2 3 12 18 19 24 Md RA SV


z-Scores: S2 - Ethion
Target Standard Deviation for Proficiency Assessment 0.00018 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
6 17 21 11 8 23 5 9 20 22 10 15 4 14 13 16
-2.9 -1.9 -1.8 -1.3 -0.8 -0.7 -0.2 -0.2 0.4 0.4 0.9 0.9 2.0 2.0 2.0 2.0

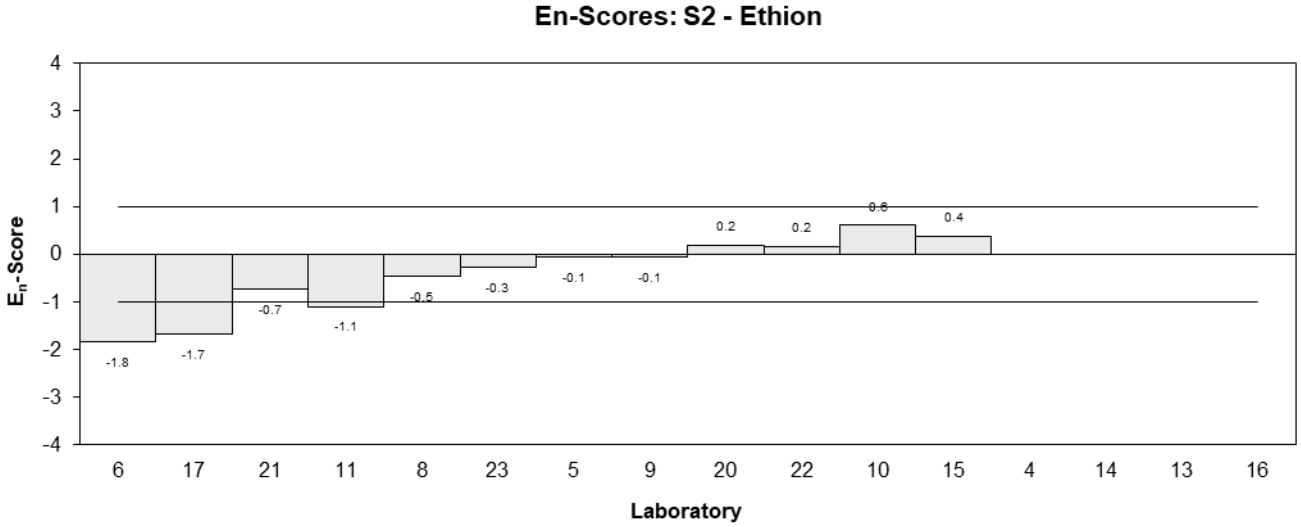

En-Scores: S2 - Ethion
En-Score
Laboratory
6 17 21 11 8 23 5 9 20 22 10 15 4 14 13 16
-1.8 -1.7 -0.7 -1.1 -0.5 -0.3 -0.1 -0.1 0.2 0.2 0.6 0.4

Figure 8

Table 12

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Hexazinone
Unit	mg/L

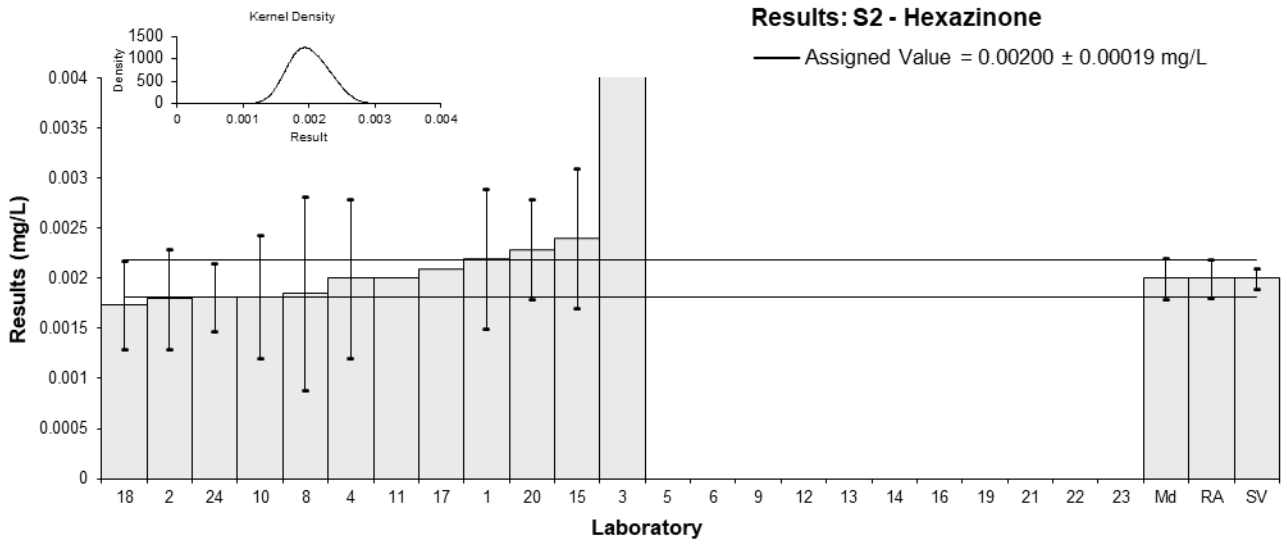
Participant Results

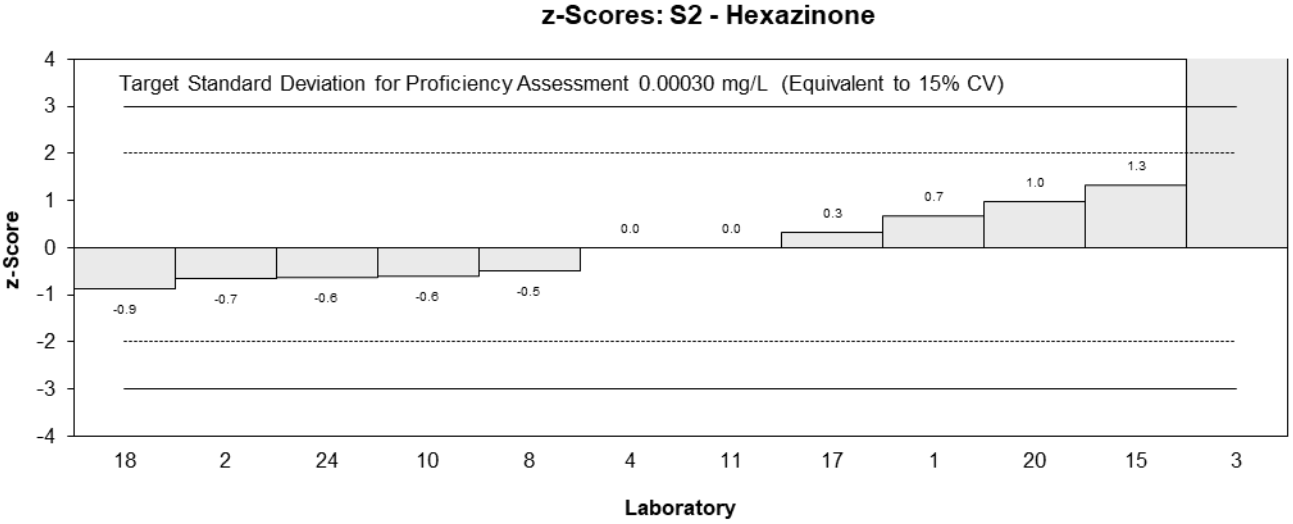
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.0022	0.0007	111	0.67	0.28
2	0.0018	0.0005	NR	-0.67	-0.37
3**	1.8	0.54	NR	5,993.33	3.33
4	0.0020	0.0008	94	0.00	0.00
5	<0.002	NR	NR		
6	NT	NT	NT		
8	0.00185	0.00097	NR	-0.50	-0.15
9	NT	NT	NT		
10	0.00182	0.00061	NR	-0.60	-0.28
11	0.002	NR	129	0.00	0.00
12	<0.002	NR	NR		
13	NT	NT	NT		
14	NT	NT	NT		
15	0.0024	0.0007	106	1.33	0.55
16	NT	NT	NT		
17	0.0021	NR	NR	0.33	0.53
18	0.00174	0.00044	103	-0.87	-0.54
19	NT	NT	NT		
20	0.00229	0.0005	NR	0.97	0.54
21	<0.002	NR	NR		
22	<0.002	NR	NR		
23	<0.002	NR	80-120		
24	0.00181	0.00034	NR	-0.63	-0.49

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00200	0.00019
Spike Value	0.00200	0.00010
Robust Average	0.00200	0.00019
Median	0.00200	0.00021
Mean	0.00200	
N	11	
Max	0.0024	
Min	0.00174	
Robust SD	0.00025	
Robust CV	12%	


Results: S2 - Hexazinone
Assigned Value = 0.00200 ± 0.00019 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
18 2 24 10 8 4 11 17 1 20 15 3 5 6 9 12 13 14 16 19 21 22 23 Md RA SV


z-Scores: S2 - Hexazinone
Target Standard Deviation for Proficiency Assessment 0.00030 mg/L (Equivalent to 15% CV)
z-Score
-0.9 -0.7 -0.6 -0.6 -0.5 0.0 0.0 0.3 0.7 1.0 1.3
Laboratory
18 2 24 10 8 4 11 17 1 20 15 3


En-Scores: S2 - Hexazinone
En-Score
-0.6 -0.4 -0.5 -0.3 -0.2 0.0 0.0 0.5 0.3 0.5 0.6 3.3
Laboratory
18 2 24 10 8 4 11 17 1 20 15 3

Figure 9

Table 13

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	MCPA
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.028	0.007	70
2	0.0165	0.0050	NR
3**	34	10.2	NR
4	<0.001	NR	NR
5	0.018	0.006	NR
6	NT	NT	NT
8	0.0386	0.007	NR
9	NT	NT	NT
10	0.033	0.0062	NR
11	0.035	NR	114
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	0.0376	NR	NR
18	0.03531	0.00883	99
19	NT	NT	NT
20	0.0307	0.006	NR
21	NT	NT	NT
22	0.003	0.0009	NR
23	0.003	0.0009	80-120
24	NT	NT	NT

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	0.0301	0.0015
Robust Average	0.025	0.011
Median	0.0307	0.0077
Mean	0.0253	
N	11	
Max	0.0386	
Min	0.003	
Robust SD	0.015	
Robust CV	59%	

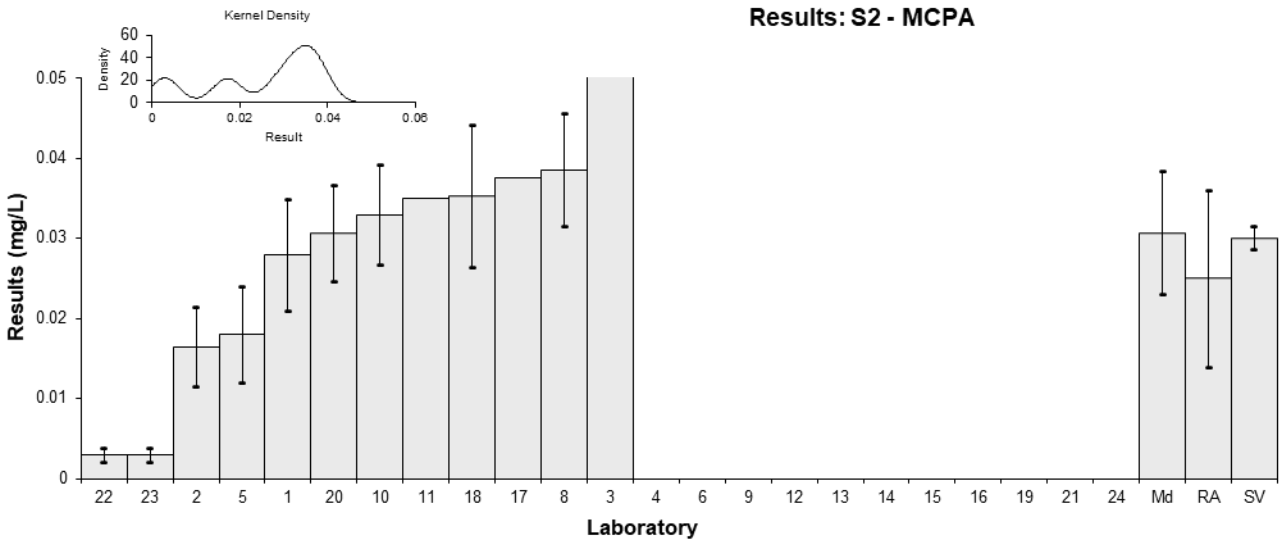

Results: S2 - MCPA
Kernel Density
Density
Result
Results (mg/L)
Laboratory
22 23 2 5 1 20 10 11 18 17 8 3 4 6 9 12 13 14 15 16 19 21 24 Md RA SV

Figure 10

Table 14

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Metsulfuron-methyl
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	Rec
1	0.041	0.011	NR
2	0.0524	0.0157	NR
3	NT	NT	NT
4	0.073	0.036	93
5	0.032	0.01	NR
6	NT	NT	NT
8	NT	NT	NT
9	NT	NT	NT
10	<0.005	NR	NR
11	NT	NT	NT
12	NT	NT	NT
13	NT	NT	NT
14	NT	NT	NT
15	NT	NT	NT
16	NT	NT	NT
17	NR	NR	NR
18	0.06946	0.01737	100
19	NT	NT	NT
20	NT	NT	NT
21	NT	NT	NT
22	0.068	0.02	NR
23	NT	NT	NT
24	NT	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	0.0603	0.0030
Robust Average	0.056	0.020
Median	0.060	0.017
Mean	0.056	
N	6	
Max	0.073	
Min	0.032	
Robust SD	0.019	
Robust CV	34%	

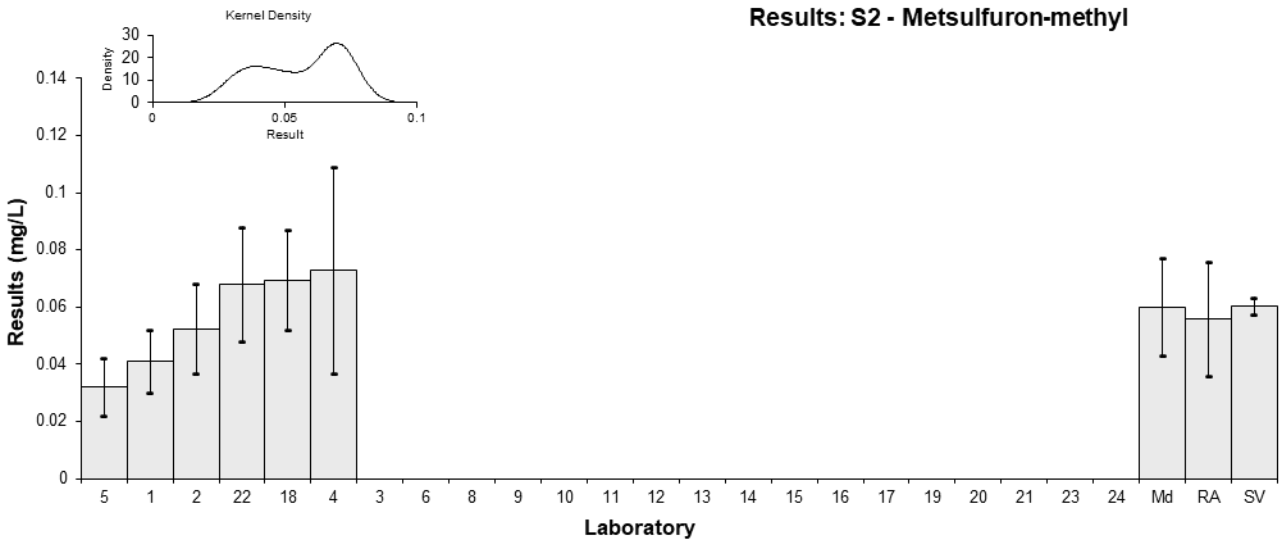

Results: S2 - Metsulfuron-methyl
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5
1
2
22
18
4
3
6
8
9
10
11
12
13
14
15
16
17
19
20
21
23
24
Md
RA
SV

Figure 11

Table 15

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Simazine
Unit	mg/L

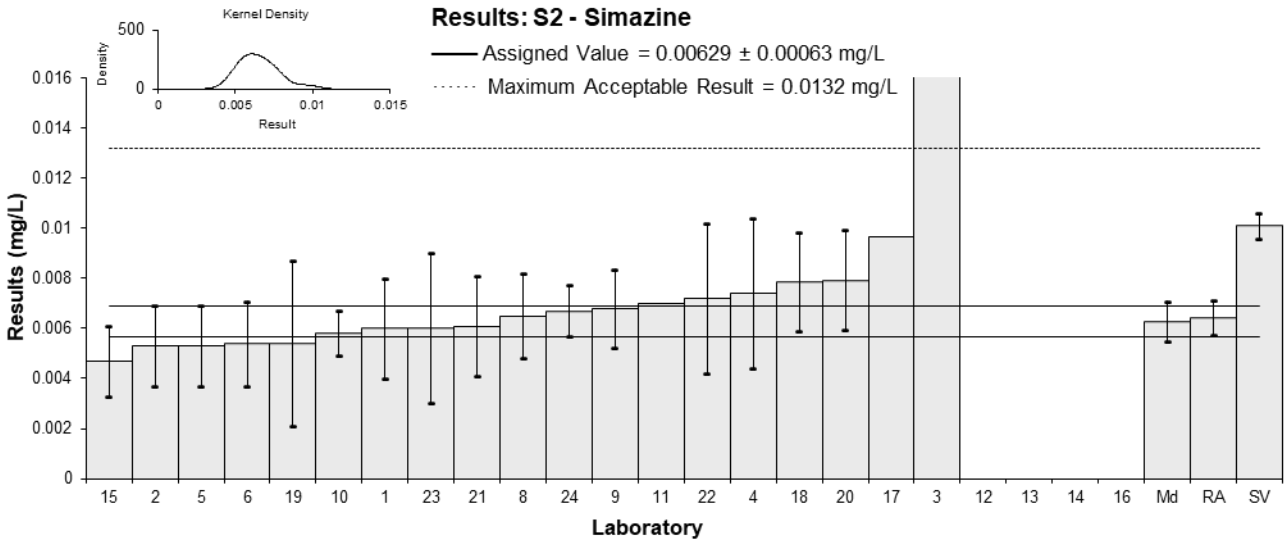
Participant Results

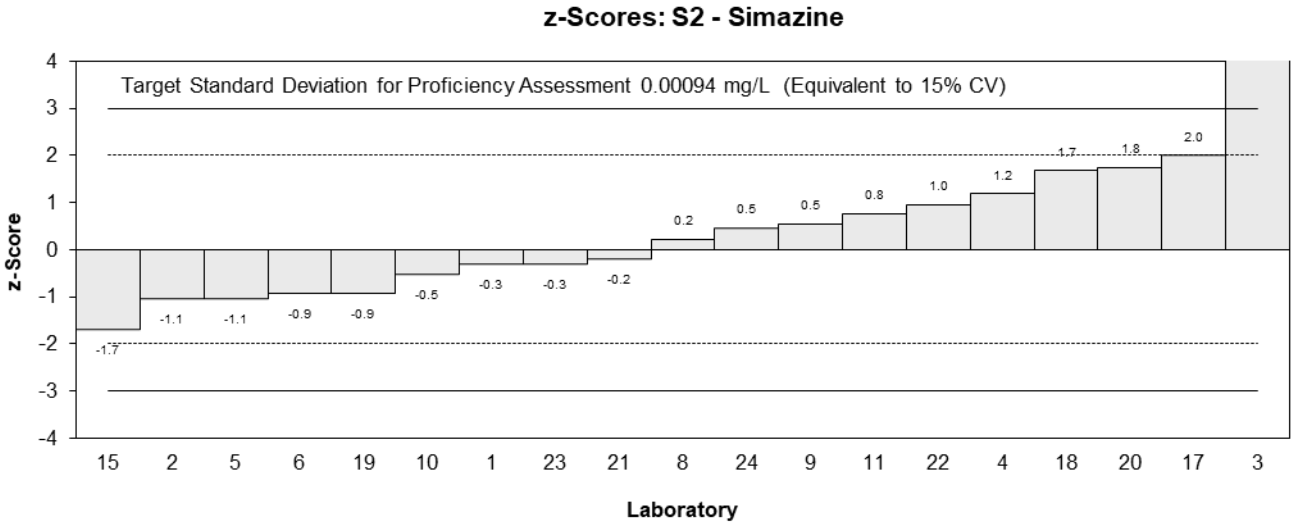
Lab. Code	Result	Uncertainty	Rec	z	E_n
1	0.006	0.002	82	-0.31	-0.14
2	0.0053	0.0016	NR	-1.05	-0.58
3**	7.3	2.19	NR	7,730.48	3.33
4	0.0074	0.0030	94	1.18	0.36
5	0.0053	0.0016	NR	-1.05	-0.58
6	0.0054	0.0017	74.2	-0.94	-0.49
8	0.0065	0.0017	NR	0.22	0.12
9	0.0068	0.00158	NR	0.54	0.30
10	0.0058	0.0009	NR	-0.52	-0.45
11	0.007	NR	98	0.75	1.13
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	0.0047	0.0014	81	-1.69	-1.04
16	NT	NT	NT		
17*	0.00967	NR	NR	2.00▼	
18	0.00787	0.00197	97	1.67	0.76
19	0.0054	0.0033	NR	-0.94	-0.26
20	0.00794	0.002	NR	1.75	0.79
21	0.0061	0.002	NR	-0.20	-0.09
22	0.0072	0.003	NR	0.96	0.30
23	0.006	0.003	80-120	-0.31	-0.09
24	0.00671	0.00101	NR	0.45	0.35

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

Statistics

Assigned Value	0.00629	0.00063
Spike Value	0.0101	0.0005
Robust Average	0.00642	0.00069
Max Acceptable Result	0.0132	
Median	0.00630	0.00079
Mean	0.00651	
N	18	
Max	0.00967	
Min	0.0047	
Robust SD	0.0012	
Robust CV	18%	


Kernel Density
Density
Result
Results: S2 - Simazine
Assigned Value = 0.00629 ± 0.00063 mg/L
Maximum Acceptable Result = 0.0132 mg/L
Results (mg/L)
Laboratory
15 2 5 6 19 10 1 23 21 8 24 9 11 22 4 18 20 17 3 12 13 14 16 Md RA SV


z-Scores: S2 - Simazine
Target Standard Deviation for Proficiency Assessment 0.00094 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
15 2 5 6 19 10 1 23 21 8 24 9 11 22 4 18 20 17 3

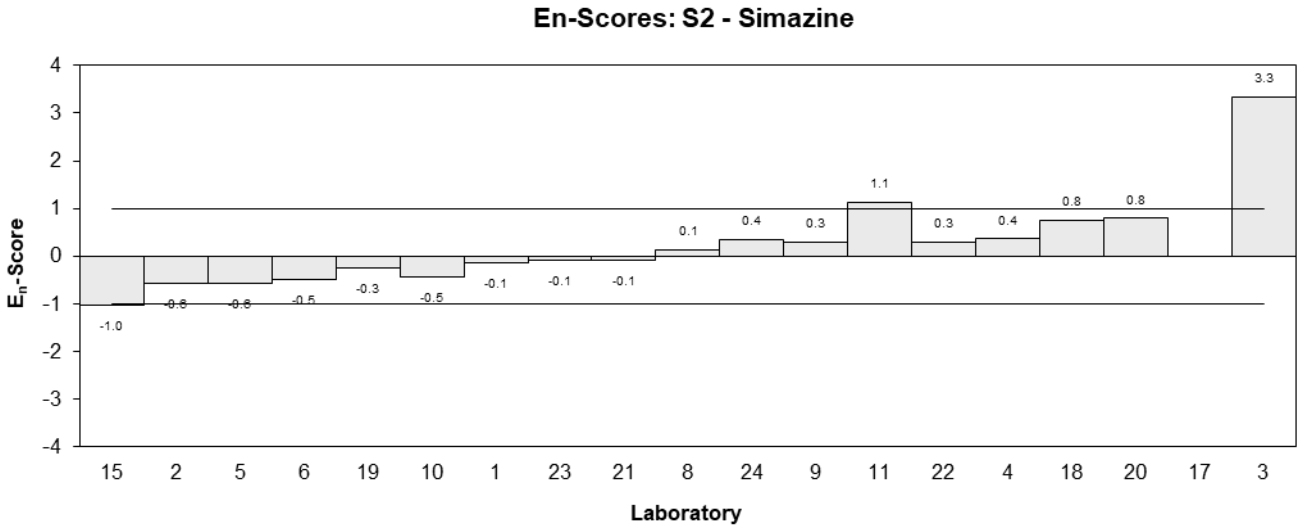

En-Scores: S2 - Simazine
En-Score
Laboratory
15 2 5 6 19 10 1 23 21 8 24 9 11 22 4 18 20 17 3

Figure 12

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The assigned values for all scored analytes were the robust averages of participants' results. If there were results less than 50% or greater than 150% of the robust average, these were excluded from the calculation of each assigned value.[3,4] The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[6] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using hexazinone in Sample S2 as an example.

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

No assigned values were set for Sample S1 chlorpyrifos and Sample S2 2,4-D as the consensus of participants' results were significantly lower than the spiked value; however, participants' results for both analytes were in reasonable agreement with each other. No assigned value was set for Sample S1 pirimicarb and Sample S2 MCPA and metsulfuron-methyl as reported results were too varied; however, the median of participants' results was very close to the spiked value for all three analytes. Participants may still compare their results for these non-scored analytes with the descriptive statistics and spiked value as presented in Section 5.

A comparison of the assigned values (or robust average if no assigned value was set) and spiked values is presented in Table 16. For scored analytes, assigned values were within the range of 61% to 100% of the spiked values, which is similar to ratios observed in previous NMI PT studies for pesticides in water. Analytes have only been scored if there was reasonable consensus between participants' results.

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

Sample	Analyte	Assigned Value *(Robust Average)* (mg/L)	Spiked Value (mg/L)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	Atrazine	0.00903	0.0100	90
	Chlorpyrifos	*(0.00176)*	0.00782	*(23)*
	Dieldrin	0.00899	0.00995	90
	Lindane	0.00504	0.00605	83
	Pirimicarb	*(0.000183)*	0.000181	*(101)*
S2	2,4-D	*(0.0291)*	0.0703	*(41)*
	Ethion	0.00123	0.00203	61
	Hexazinone	0.00200	0.00200	100
	MCPA	*(0.025)*	0.0301	*(83)*
	Metsulfuron-methyl	*(0.056)*	0.0603	*(93)*
	Simazine	0.00629	0.0101	62

For this study, Sample S1 was also spiked with aldicarb at 0.0238 ± 0.0012 mg/L, however this analyte was not detected by any participant. Aldicarb reacts with oxidising agents to form the sulfoxide.[10] As the original potable water matrix in this study was not autoclaved prior to spiking, the chlorine in the potable water may have reacted with the aldicarb resulting in non-detectable levels of this analyte.

The chlorpyrifos spiked into Sample S1 was also very unstable, with an extremely low robust average to spiked value ratio (23%). A similarly low ratio was observed previously for AQA 18-13 where chlorpyrifos was also spiked into potable water.[11] Generally, higher ratios have been observed when spiking chlorpyrifos into other water matrices such as river water or wastewater. Chlorpyrifos is unstable in the presence of copper.[10] Internal testing on the original potable water matrix indicated that the levels of copper were much higher as compared to other water matrices previously used, and so this may have contributed to the low robust average to spiked ratio of chlorpyrifos in this study.

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 165 numeric results submitted for the analytes of interest in this study, 147 (89%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3). One participant reported using the NATA as their guide; NATA no longer publishes uncertainty guidance documents.[12]

Laboratories **11** and **17** did not report uncertainties for any of their numeric results, despite reporting that they were accredited to ISO/IEC 17025. Laboratory **17** noted that they were currently re-evaluating their MU and that was why no uncertainties had been included for their results.

The magnitude of reported uncertainties was within the range of 6.4% to 62% relative to the result. In general, an expanded uncertainty of less than 15% relative is likely to be unrealistically small for routine analysis, while an uncertainty of greater than 50% relative is likely to be too large to be suitable. Of 147 MUs reported for this study, 10 were less than 15% relative and six were greater than 50% relative; participants reporting these uncertainties may wish to reconsider if their MUs are realistic or fit-for-purpose.

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

Laboratory **19** attached an estimate of MU to a non-value result reported. An estimate of uncertainty expressed as a value should not be attached to a non-value result.[9]

In some cases, the results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write the uncertainty to no more than two significant figures, and then write the result with the corresponding number of decimal places. For example, instead of 0.03531 ± 0.00883 mg/L, it is better to report this as 0.0353 ± 0.0088 mg/L.[9]

6.3 z-Score

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

Table 17 Comparison of Thompson-Horwitz CV, Between-Laboratory CV and Target SD

Sample	Analyte	Assigned Value *(Robust Average)* (mg/L)	Thompson-Horwitz CV (%)	Between-Laboratory CV* (%)	Target SD (as PCV) (%)
S1	Atrazine	0.00903	22	15	15
	Chlorpyrifos	*(0.00176)*	22	29	Not Set
	Dieldrin	0.00899	22	15	15
	Lindane	0.00504	22	13	15
	Pirimicarb	*(0.000183)*	22	35	Not Set
S2	2,4-D	*(0.0291)*	22	27	Not Set
	Ethion	0.00123	22	26	15
	Hexazinone	0.00200	22	12	15
	MCPA	*(0.025)*	22	59	Not Set
	Metsulfuron-methyl	*(0.056)*	22	34	Not Set
	Simazine	0.00629	22	16	15

* Robust between-laboratory CV (outliers removed where applicable).

To account for possible low bias in the consensus value due to participants using inefficient extraction or analytical techniques, a total of five *z*-scores were adjusted across the following analytes: S2 ethion and simazine. 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 participants reporting results close to the spiked value were not penalised. *z*-Scores for results higher than the maximum acceptable result and *z*-scores less than 2.0 were left unaltered.

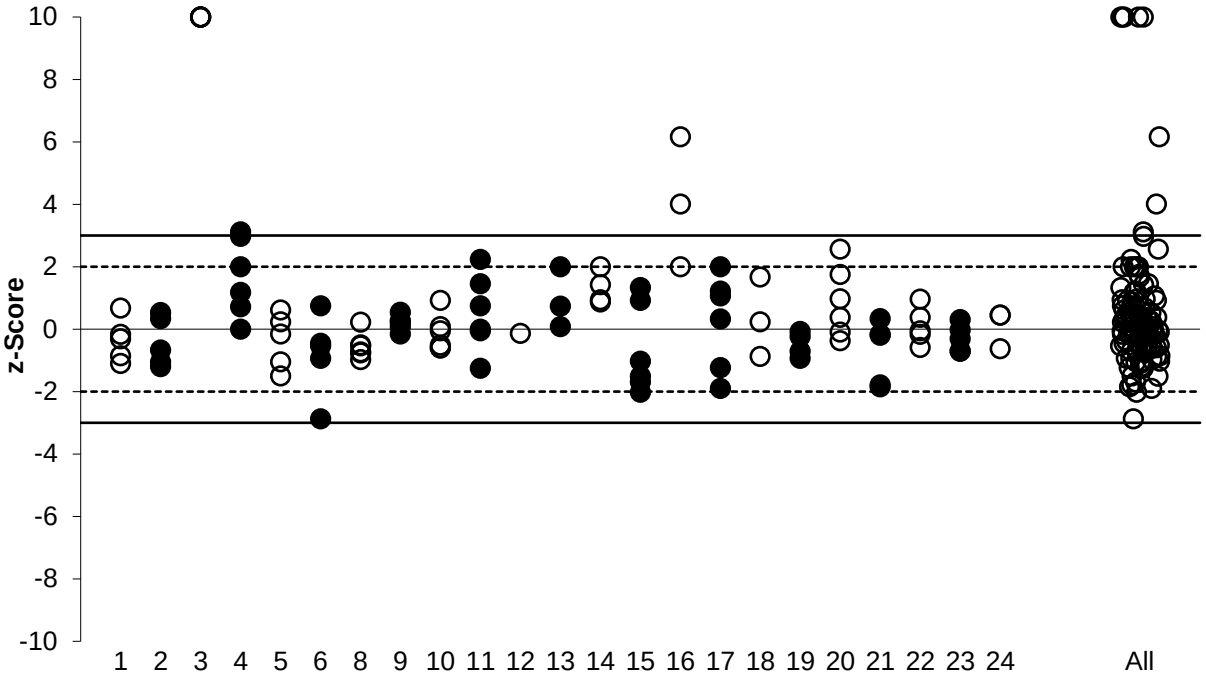
Of 108 results for which *z*-scores were calculated, 95 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **4**, **8**, **10**, **11**, **15**, **17** and **20** reported numeric results for all six scored analytes. Of these participants, Laboratories **8**, **10** and **17** returned acceptable *z*-scores for all analytes.

Thirteen participants received acceptable *z*-scores for all analytes they reported results for: Laboratories **1** (5), **2** (5), **5** (5), **9** (5), **21** (5), **22** (5), **23** (5), **14** (4), **19** (4), **13** (3), **18** (3), **24** (3) and **12** (1).

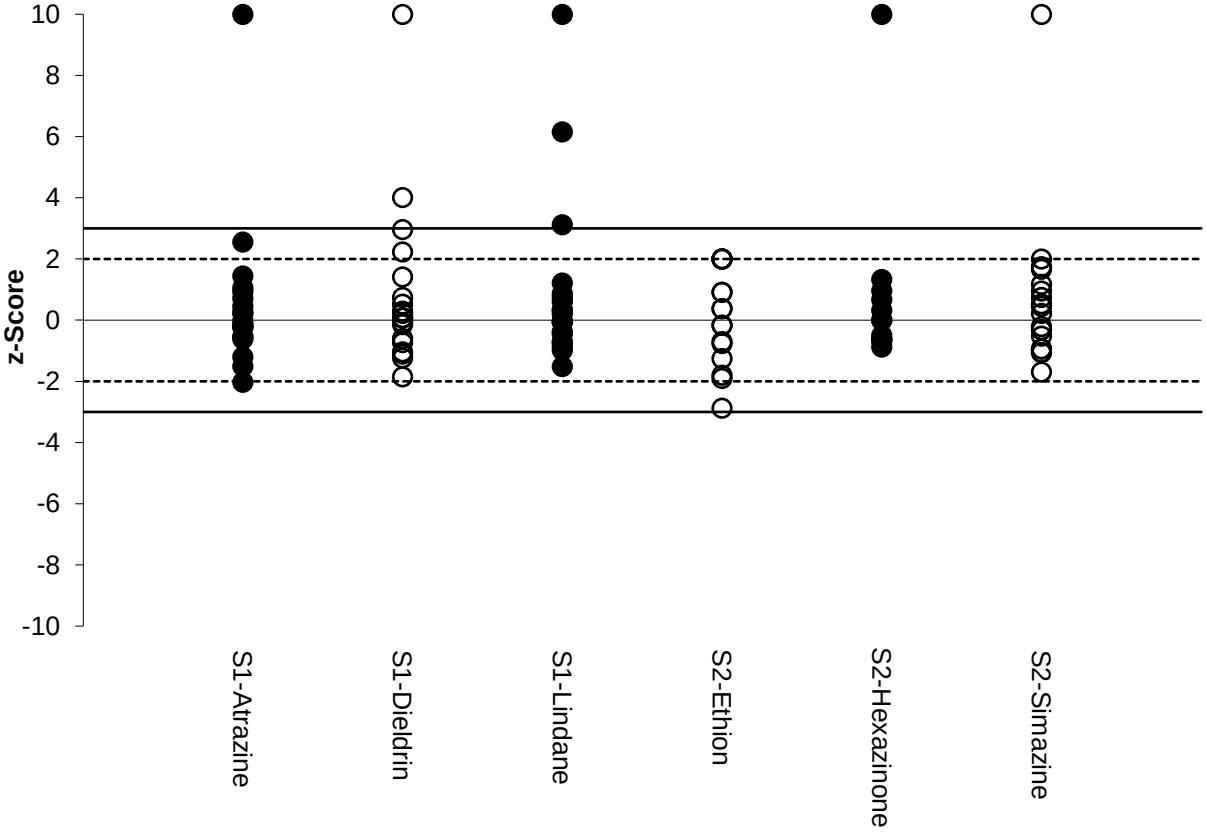
Laboratory **3** reported five numeric results and returned unacceptable *z*-scores for all results. This participant's results were all around 1000 times greater than the assigned value; this participant may have reported their results in units of µg/L instead of mg/L as requested for this study.

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



z-Scores greater than 10.0 have been plotted at 10.0.

Figure 13 *z*-Score Dispersal by Laboratory



z-Scores greater than 10.0 have been plotted at 10.0.

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 an inappropriate measurement, or uncertainty, or both. Where a participant did not report an uncertainty 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 reported.

Of 103 results for which E_n-scores were calculated, 81 (79%) returned an acceptable score of $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories **8** and **10** returned acceptable E_n-scores for all six scored analytes.

Ten participants received acceptable E_n-scores for all analytes they reported results for: Laboratories **1** (5), **2** (5), **5** (5), **9** (5), **22** (5), **23** (5), **19** (4), **18** (3), **24** (3) and **12** (1).

Some participants had results where the *z*-score was adjusted as described above, and so E_n-scores were only calculated for some of their results. Of these, two participants received acceptable E_n-scores for all analytes that were scored for them: Laboratories **4** (5) and **13** (2).

Laboratories **3** and **16** returned unacceptable E_n-scores for all reported results.

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

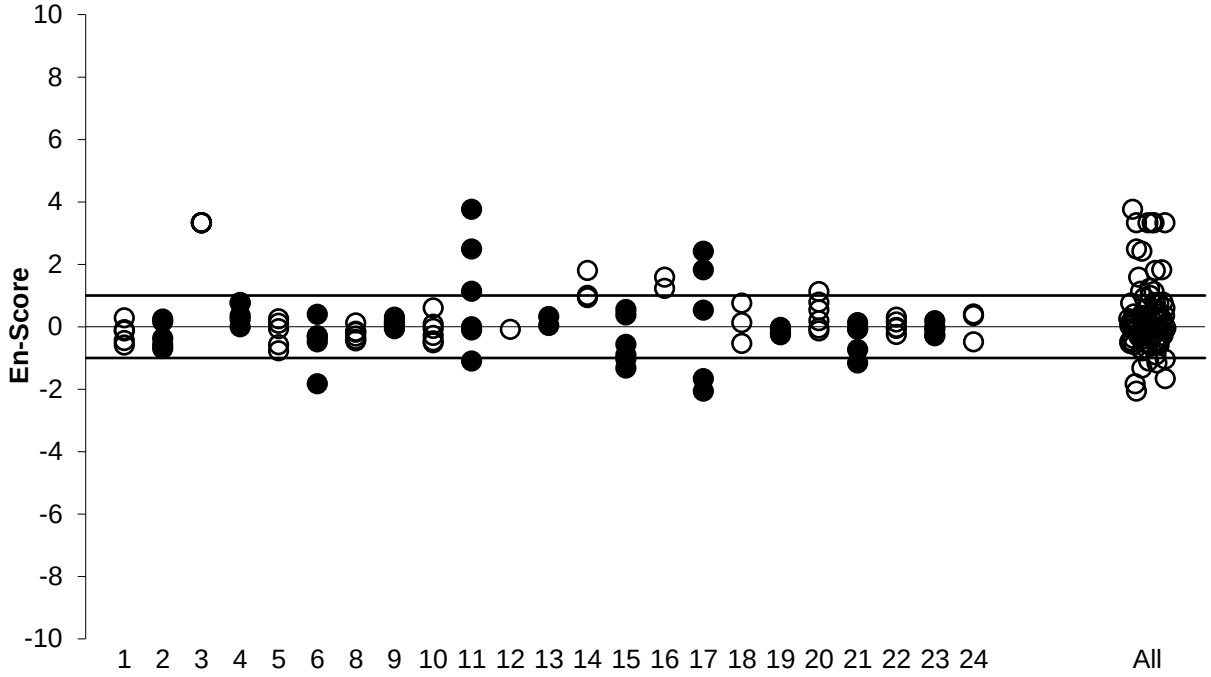


Figure 15 E_n-Score Dispersal by Laboratory

6.5 Range of Pesticides Analysed by Participants

Participants were provided with a list of potential pesticides that could have been spiked into the samples (Table 1). Of these, eleven were included in this study (Table 2). Participants were not required to test for all analytes 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 analytes is presented in Table 18.

Laboratories **4**, **5**, **10**, **17** and **22** reported that they tested for all spiked analytes. Other than these participants, the proportion of pesticides analysed by each participant ranged from 27% to 91%.

The proportion of participants analysing each pesticide in this study ranged from 35% (metsulfuron-methyl) to 96% (chlorpyrifos).

Table 18 Summary of Pesticides Analysed by Participants

Lab. Code / Analyte	1	2	3	4	5	6	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	Proportion of Participants (%)
Atrazine	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	87
Chlorpyrifos	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	96
2,4-D	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	NT	NT	NT	✓	✓	NT	✓	NT	✓	✓	NT	57
Dieldrin	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	NT	91
Ethion	NT	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	NT	83
Hexazinone	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	✓	NT	NT	✓	NT	✓	✓	NT	✓	✓	✓	✓	✓	74
Lindane	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	NT	87
MCPA	✓	✓	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	NT	NT	NT	✓	✓	NT	✓	NT	✓	✓	NT	57
Metsulfuron-methyl	✓	✓	NT	✓	✓	NT	NT	NT	✓	NT	NT	NT	NT	NT	NT	✓	✓	NT	NT	NT	✓	NT	NT	35
Pirimicarb	✓	NT	✓	✓	✓	NT	✓	NT	✓	✓	NT	NT	NT	NT	NT	✓	NT	NT	NT	NT	✓	NT	NT	39
Simazine	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	NT	NT	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	83
Proportion of Analytes (%)	91	91	82	100	100	55	91	55	100	91	36	36	45	64	36	100	64	55	82	64	100	82	27	

6.6 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. 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 (i.e. the robust average minus the expanded uncertainty, and the spiked value minus the expanded uncertainty, were both greater than the LOR), or if no value was reported.

Table 19 False Negatives

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (mg/L)	Spiked Value (mg/L)	Result* (mg/L)
4	S2	MCPA	*(0.025)*	0.0301	<0.001
10	S2	Metsulfuron-methyl	*(0.056)*	0.0603	<0.005
17	S2	Metsulfuron-methyl	*(0.056)*	0.0603	NR
19	S2	Ethion	0.00123	0.00203	<0.0005

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

6.7 Reporting of Additional Analytes

Analytes reported by participants which were not spiked into the test samples are presented in Table 20. In general, participants should take care to avoid any potential cross-contamination when analysing their samples.

Laboratories **1** and **17** reported simazine, propazine and/or desethylatrazine at low levels in Sample S1; these may have been trace impurities in the atrazine standard used to spike this sample.

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

Lab. Code	Sample	Analyte	Result (mg/L)	Uncertainty (mg/L)	Recovery (%)
1	S1	Simazine	0.00002	NR	NR
		propazine	0.00009	NR	NR
		desethylatrazine	0.00002	NR	NR
14	S1	Endosulfan	0.0023	0.0002	93
	S2	Endosulfan	0.0077	0.0005	93
17	S1	Propazine	0.00012	NR	NR
22	S2	Cypermethrin	0.0026	NR	NR
23	S2	Tetrachlorvinphos	0.006	NR	80-120

6.8 Fitness for Purpose of Results – Australian Drinking Water Guidelines

The ADWG specifies health and/or aesthetic guidelines for a number of water characteristics, including for pesticides.[5] Laboratories should be able to identify if a potable water sample exceeds the guideline or not. The ADWG specifies that comparison of results against the guideline value 'should occur at the level of one significant figure (s.f.)', and the consequence is that any rounded value less than or equal to the guideline value does not exceed the guideline, while any rounded value greater than the guideline value exceeds the guideline.[5] For this study, all spiked analytes only had a health guideline (no aesthetic guideline). The six

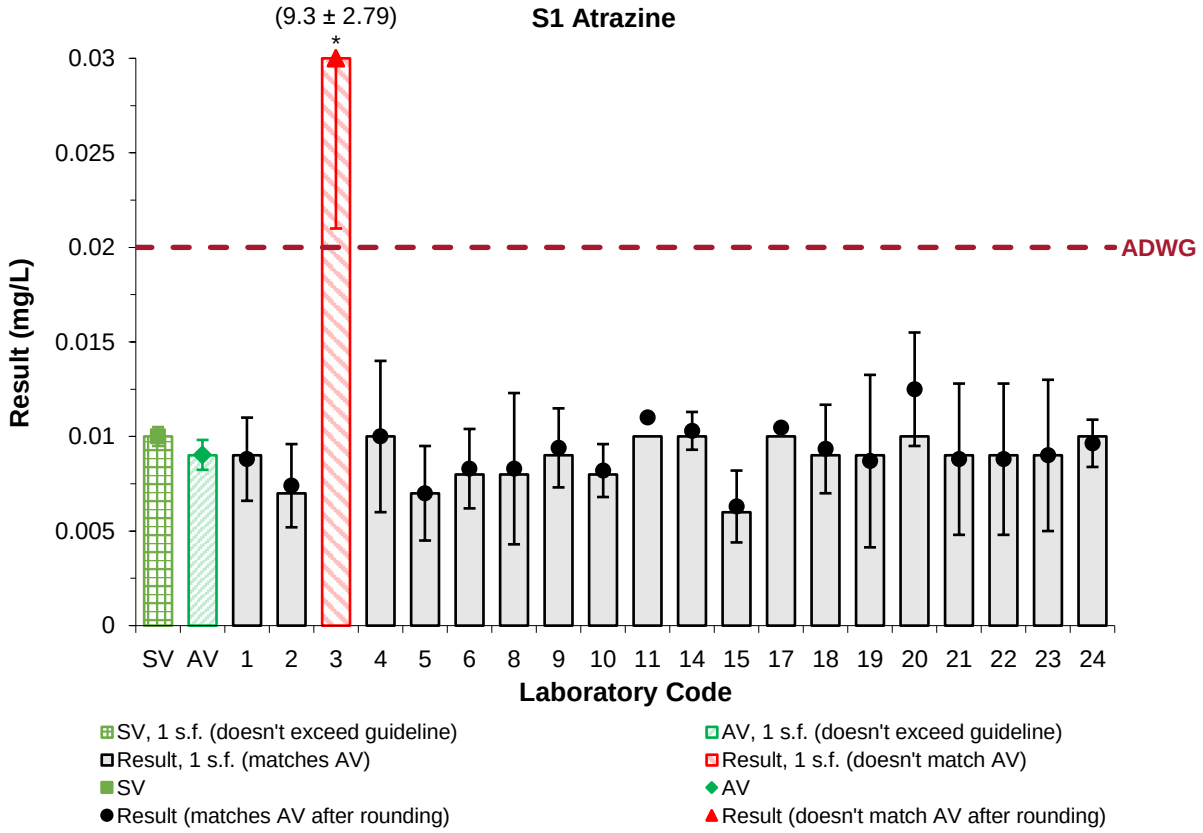
analytes with assigned values in this study could be classified as either exceeding or not exceeding the relevant guideline.

Figures 16 to 21 show comparisons of the actual (with uncertainty) and rounded spiked value (SV), assigned value (AV) and participants' results, as well as the guideline value (ADWG). Only numeric results have been included. Of 108 results assessed, 104 (96%) correctly reflected whether the sample exceeded the guideline or not.

Laboratories **4**, **8**, **10**, **11**, **15**, **17** and **20** returned the correct consequence for all six analytes assessed.

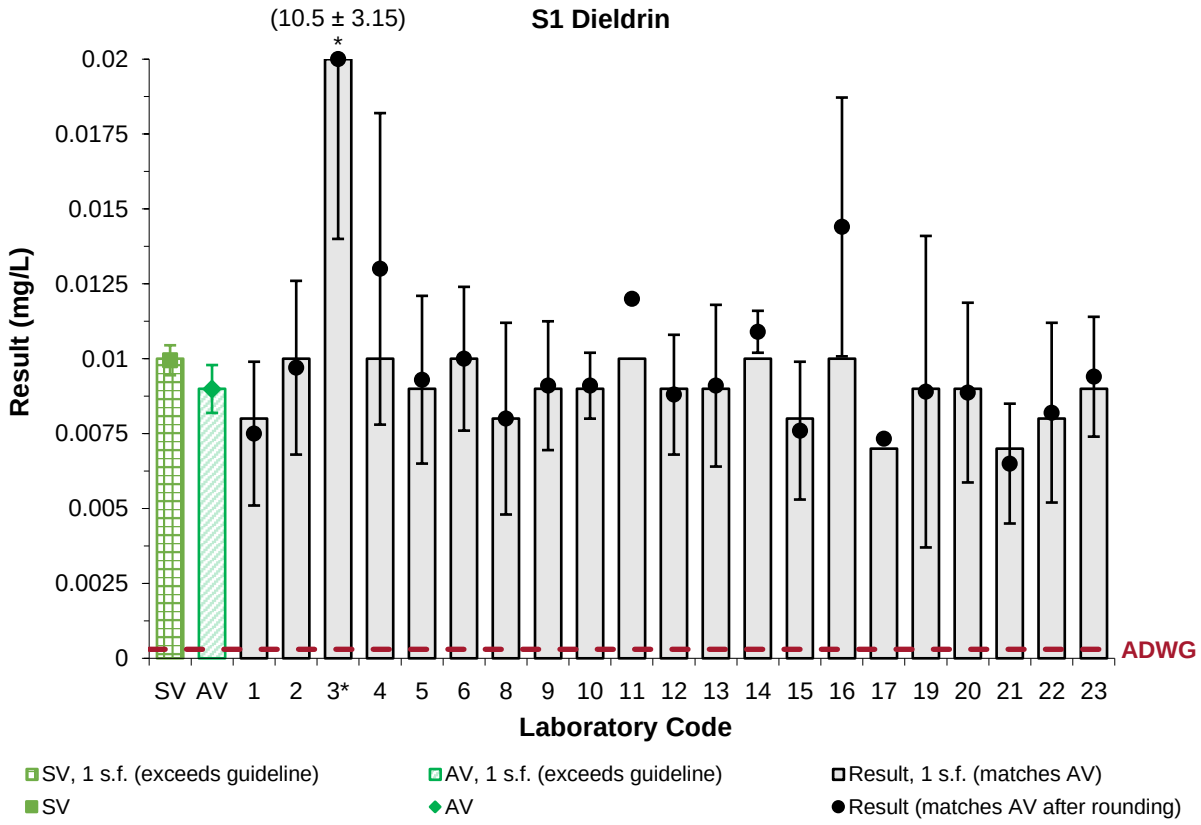
As results reported by Laboratory **3** were all extremely high, for all analytes below the guideline value, their result returned the incorrect consequence.

In some cases, a participant's result returned the correct consequence, however had an uncertainty which spanned the guideline value. For this study, this occurred for results reported by Laboratories **4** and **16** for Sample S1 lindane.



* Result from Laboratory **3** has been scaled to fit the chart; original result in parentheses.

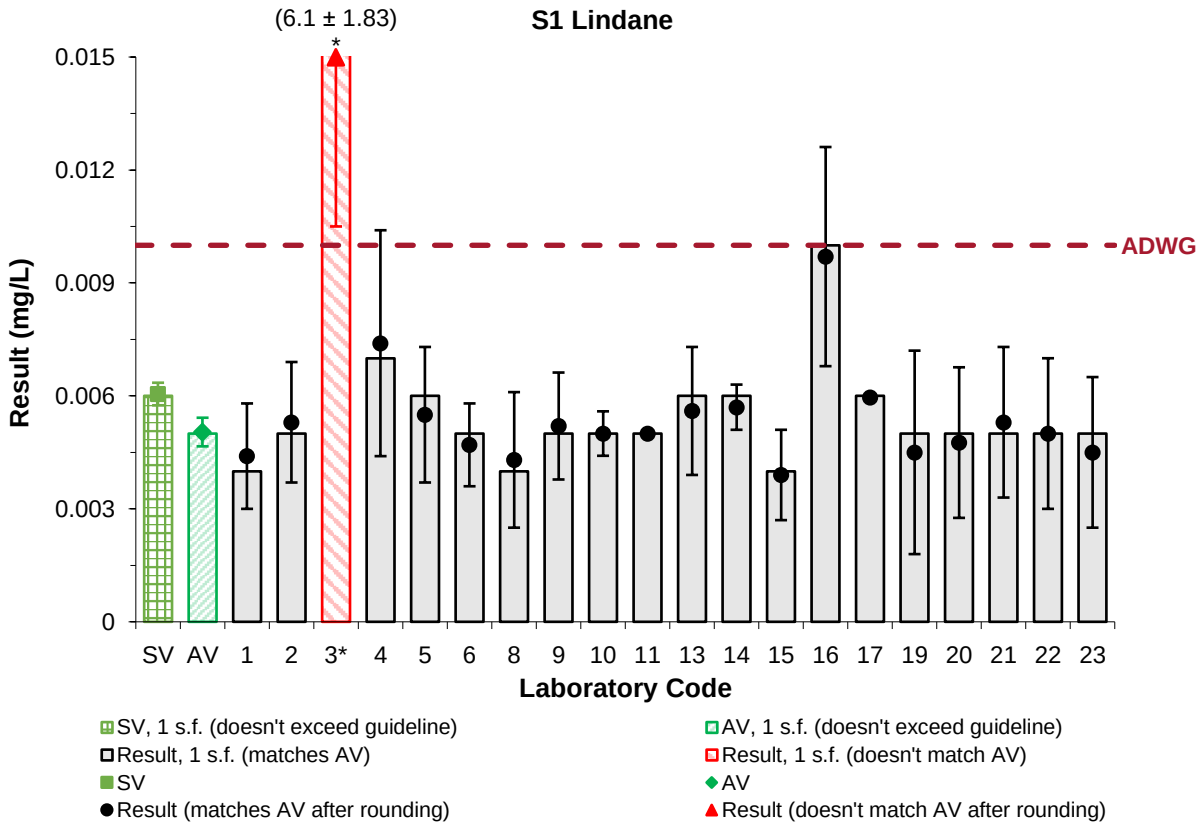
Figure 16 Sample S1 Atrazine Spiked and Assigned Values, Participant Results and Guideline



* Result from Laboratory **3** has been scaled to fit the chart; original result in parentheses.

The ADWG value is for aldrin and dieldrin combined. Sample S1 was spiked with dieldrin only.

Figure 17 Sample S1 Dieldrin Spiked and Assigned Values, Participant Results and Guideline



* Result from Laboratory **3** has been scaled to fit the chart; original result in parentheses.

Figure 18 Sample S1 Lindane Spiked and Assigned Values, Participant Results and Guideline

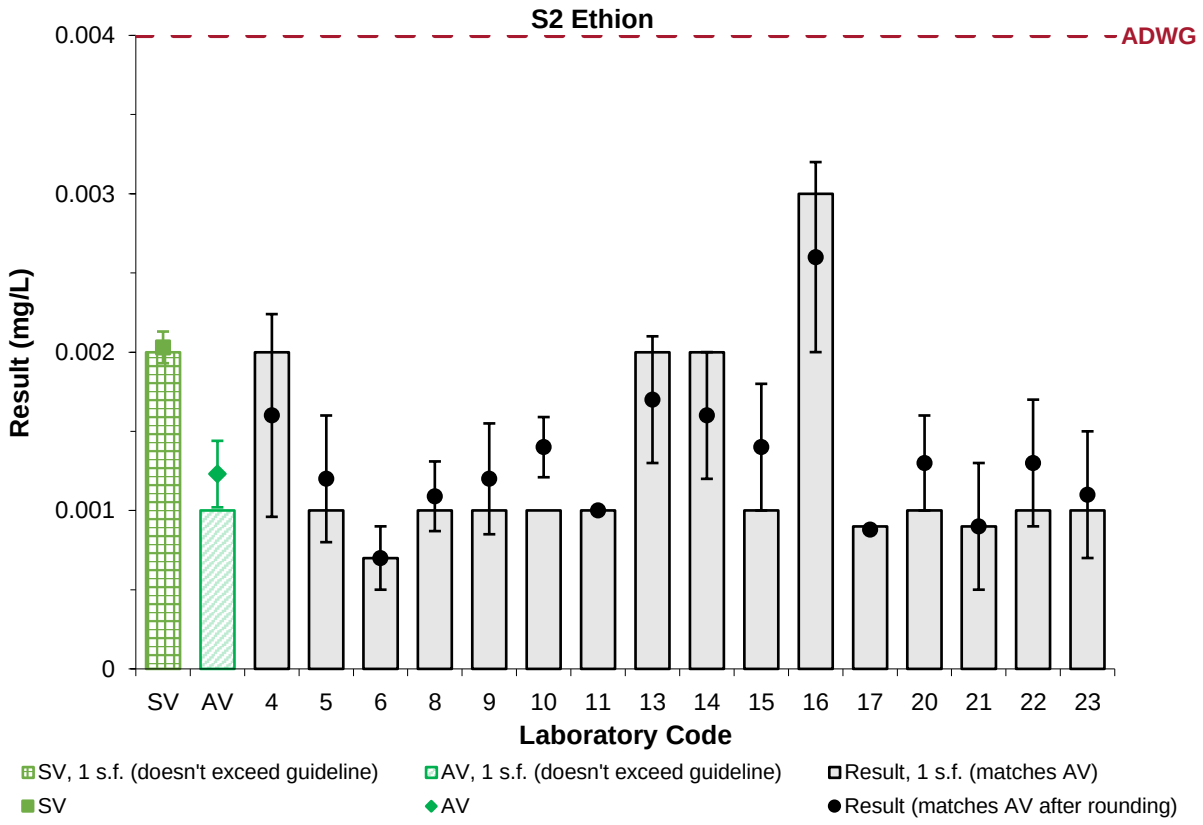
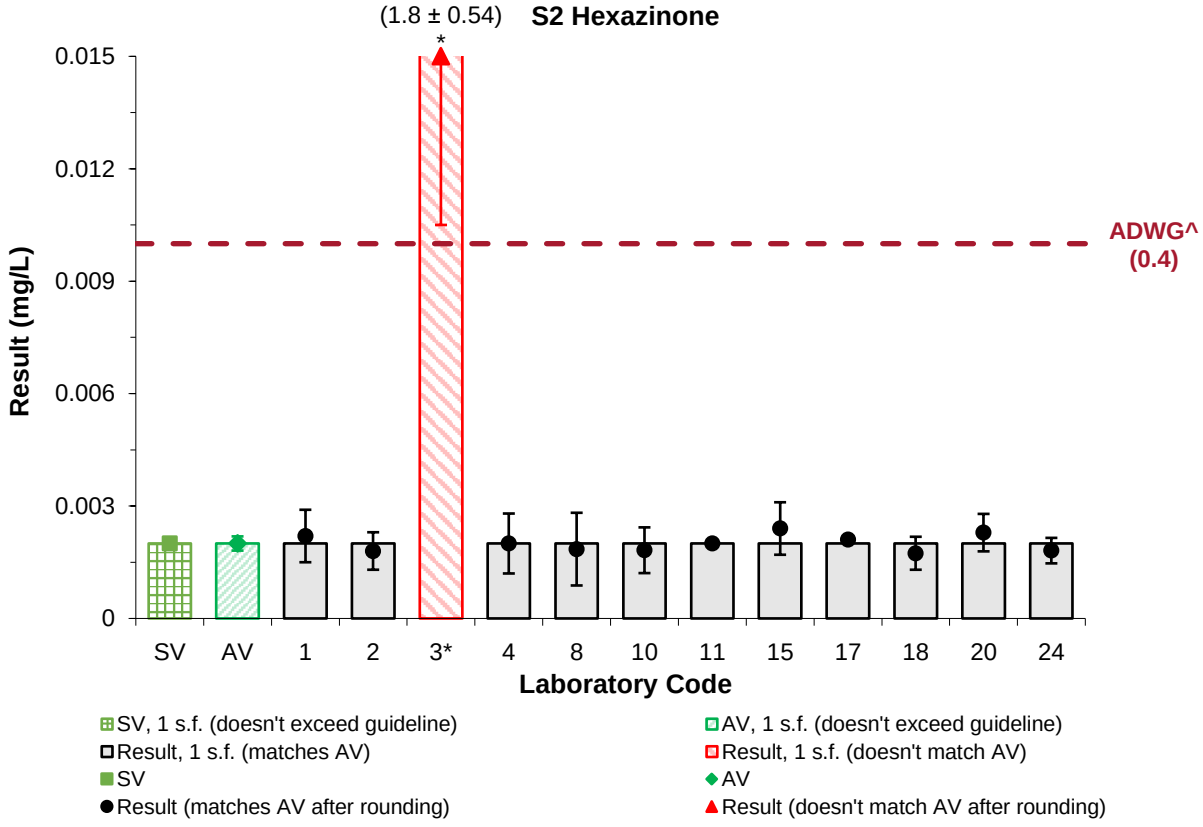
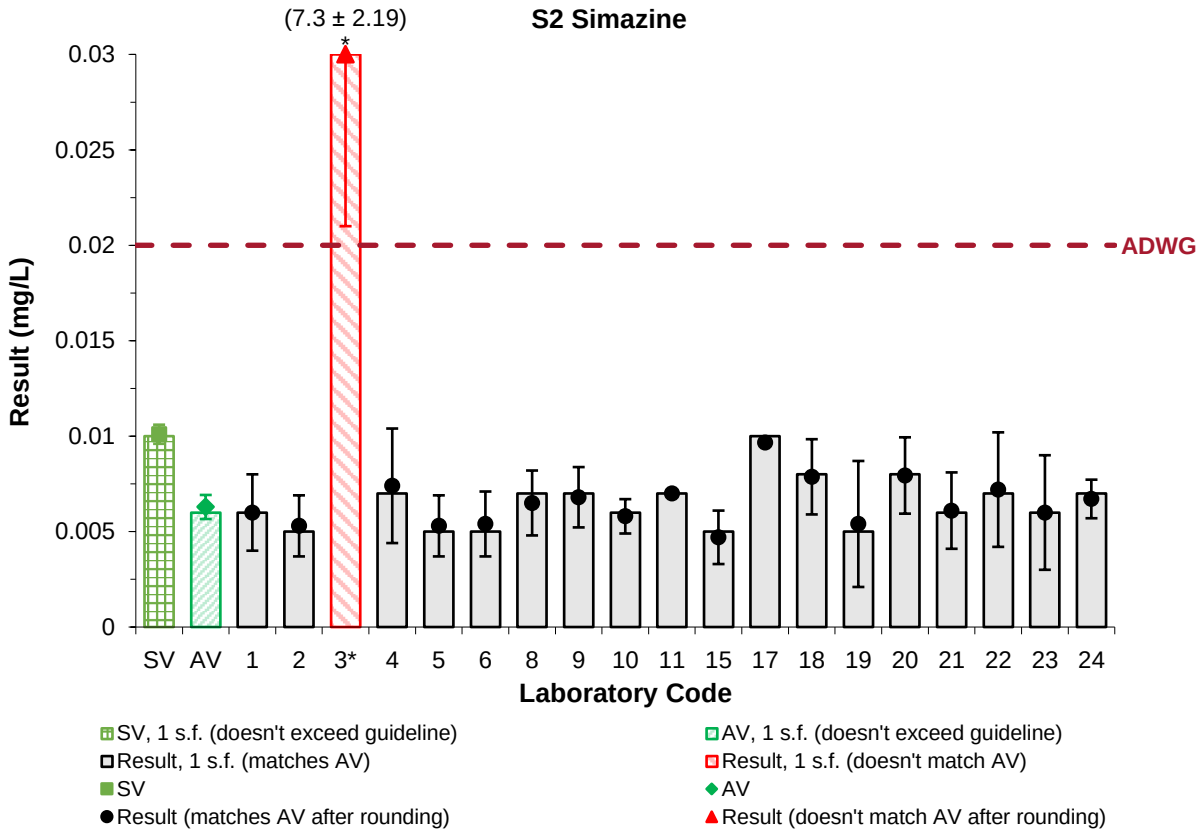


Figure 19 Sample S2 Ethion Spiked and Assigned Values, Participant Results and Guideline



* Result from Laboratory **3** has been scaled to fit the chart; original result in parentheses.
^ ADWG has been scaled to fit the chart; original value in parentheses.

Figure 20 Sample S2 Hexazinone Spiked and Assigned Values, Participant Results and Guideline

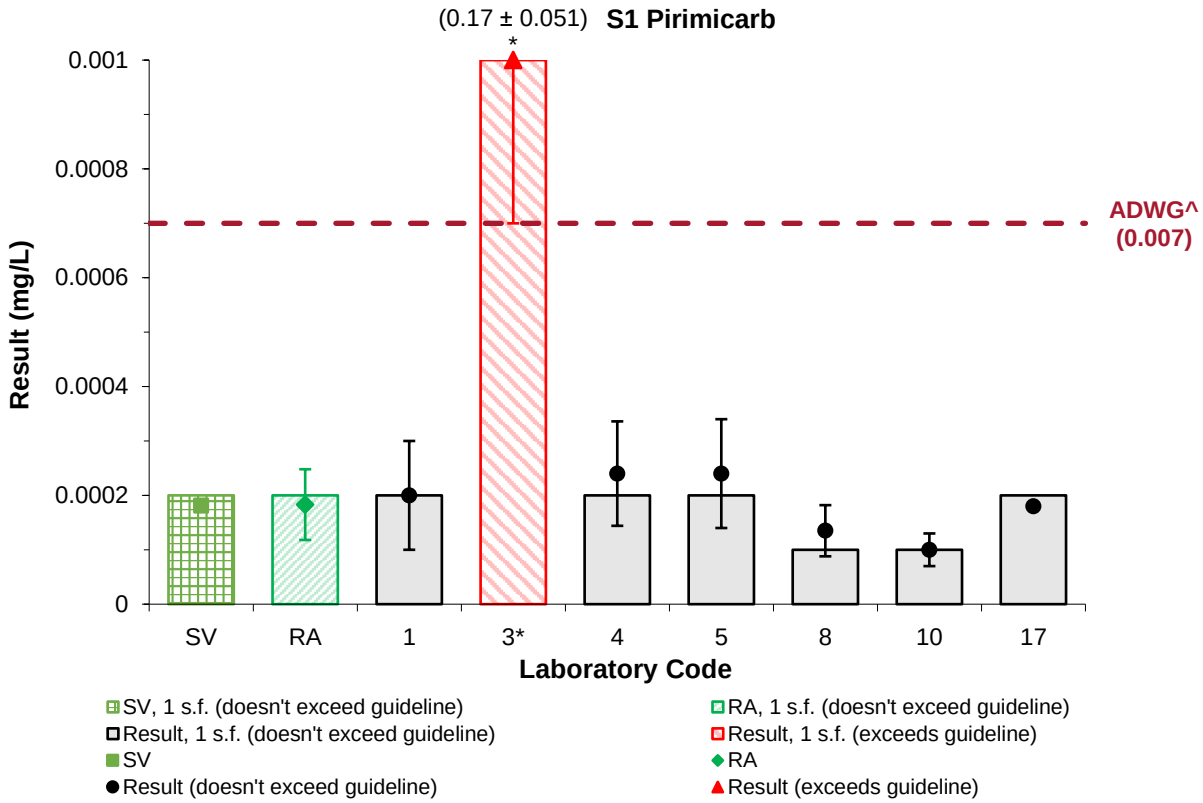


* Result from Laboratory **3** has been scaled to fit the chart; original result in parentheses.

Figure 21 Sample S2 Simazine Spiked and Assigned Values, Participant Results and Guideline

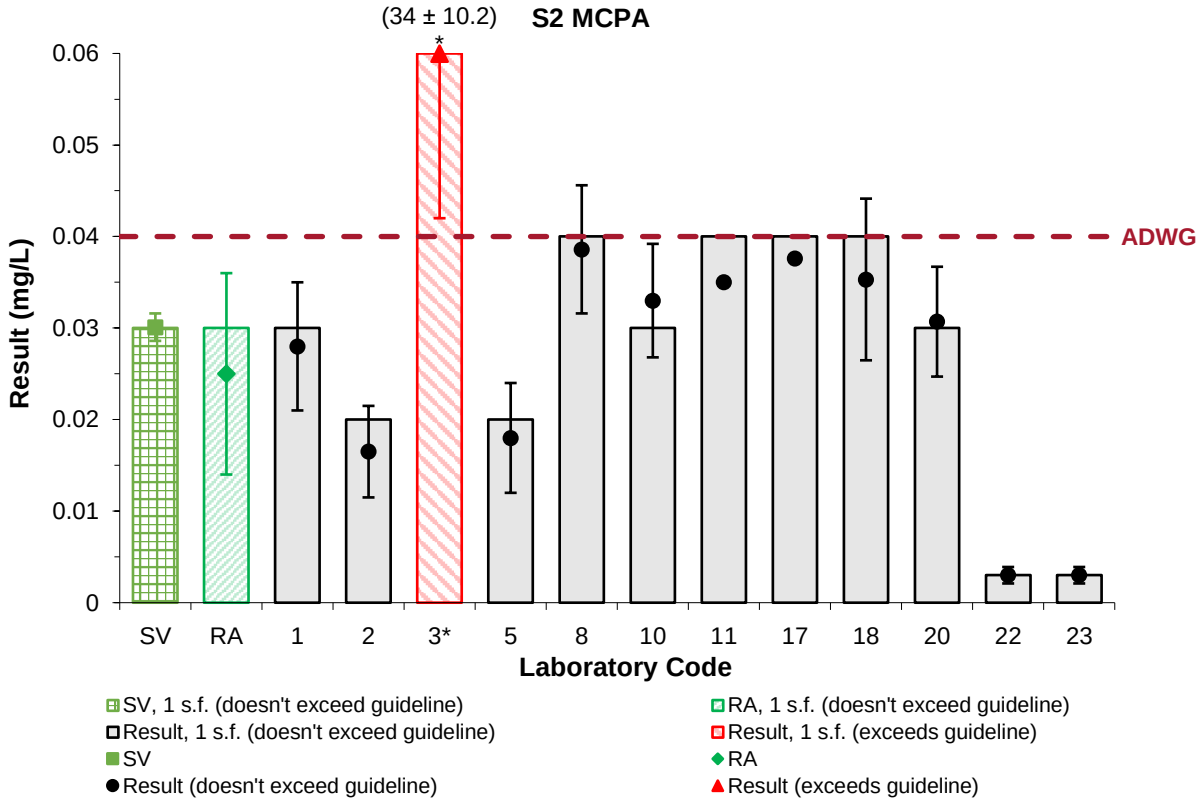
For Sample S1 pirimicarb and Sample S2 MCPA and metsulfuron-methyl, no assigned values were set, though consensus of participants' results were similar to spiked values. For information only, Figures 22 to 24 show comparisons of the actual (with uncertainty) and rounded spiked value (SV), robust average (RA) and participants' results, as well as the guideline value (ADWG). Only numeric results have been included.

The robust average of participants' results for these analytes matched the spiked value with regards to exceeding or not exceeding the ADWG. In most cases, participants' results also matched the spiked value for consequence, except for Laboratory **3** Sample S1 pirimicarb and Sample S2 MCPA (where the extremely high results returned the incorrect consequence when the analyte was below the guideline) as well as for Laboratories **1** and **5** for Sample S2 metsulfuron-methyl.



* Result from Laboratory **3** has been scaled to fit the chart; original result in parentheses.
^ ADWG has been scaled to fit the chart; original value in parentheses.

Figure 22 Sample S1 Pirimicarb Spiked Value and Robust Average, Participant Results and Guideline



* Result from Laboratory **3** has been scaled to fit the chart; original result in parentheses.

Figure 23 Sample S2 MCPA Spiked Value and Robust Average, Participant Results and Guideline

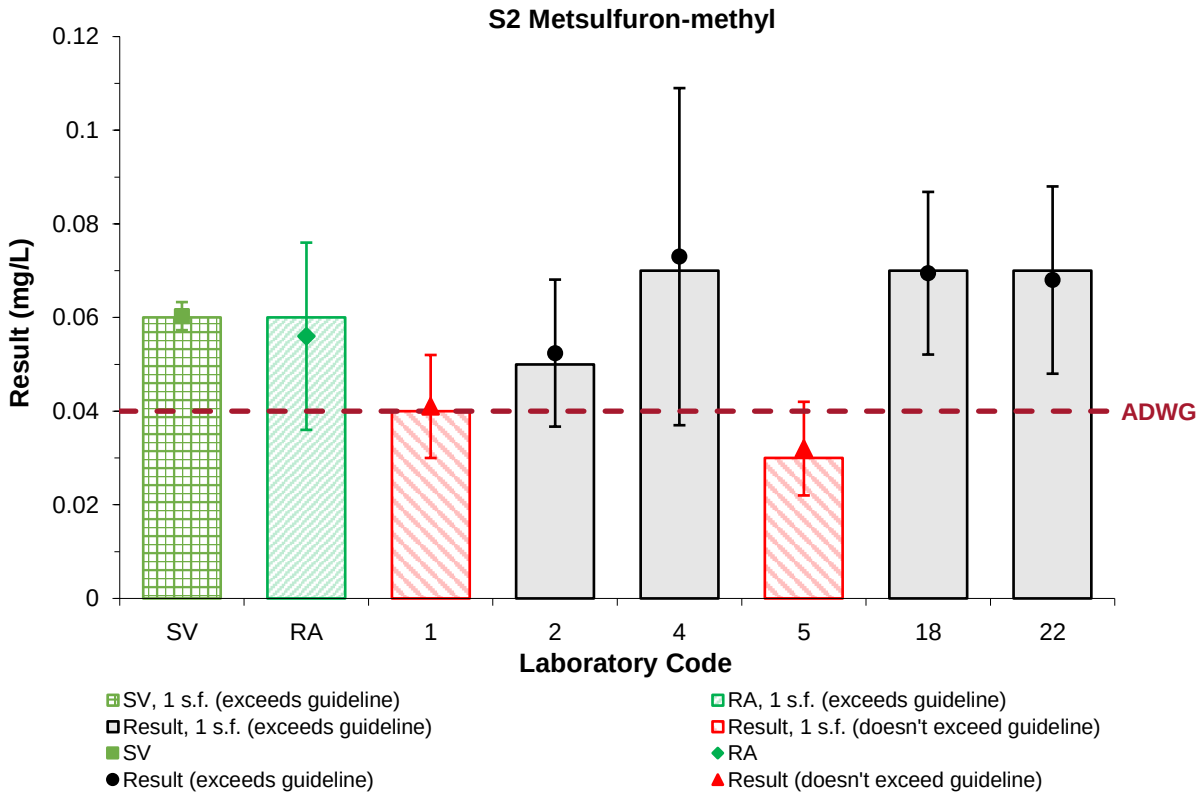


Figure 24 Sample S2 Metsulfuron-methyl Spiked Value and Robust Average, Participant Results and Guideline

6.9 Participants' Analytical Methods

Results that were removed from all statistical calculations in Section 5 have also been removed from all discussion in this section.

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 1 mL to the whole bottle. A comparison of *z*-scores and sample volume used for scored analytes is presented in Figure 25; there was no evident correlation observed in this study.

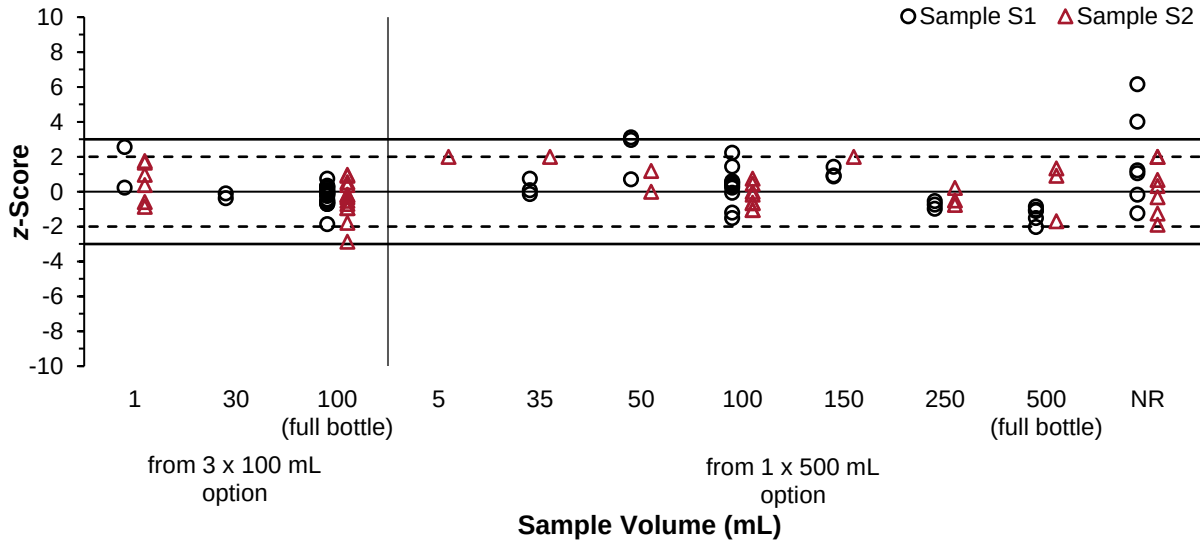


Figure 25 *z*-Score vs Sample Volume

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 acetone (ACE), acetonitrile (ACN), dichloromethane (DCM), ether, ethyl acetate (EtOAc), hexane (HEX), methanol (MeOH), toluene (TOL), or mixtures of these solvents. Some participants reported a filtration, centrifugation, dilution and/or derivatisation step as part of their analysis. Participants reported using liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS), gas chromatography (GC) coupled with mass spectrometry (MS), MS/MS, electron capture detection (ECD), flame photometric detection (FPD), or nitrogen-phosphorus detection (NPD), and high performance liquid chromatography (HPLC) coupled with diode array detection (DAD).

Plots of results reported and methodology used are presented in Figures 26 to 36. Methodologies are listed in order of reported extraction technique, extraction solvent(s) and instrument. If a participant did not report any methodology, this has been recorded as 'NR' (for 'Not Reported'). Where charts refer to n = *x*, this corresponds to *x* number of participants using that methodology. For scored analytes, participants' results yielding unacceptable *z*-scores ($|z| \geq 3.0$) have been circled for reference.

There was a wide variety of methodologies employed across the analytes in this study. The most common methodology used was LLE with DCM, followed by analysis using GC-MS.

For this study, while there was no assigned value set for Sample S2 MCPA, it was seen that participants using DI LC-MS/MS returned results much closer to the spiked value as compared to participants who used other methodologies and instruments.

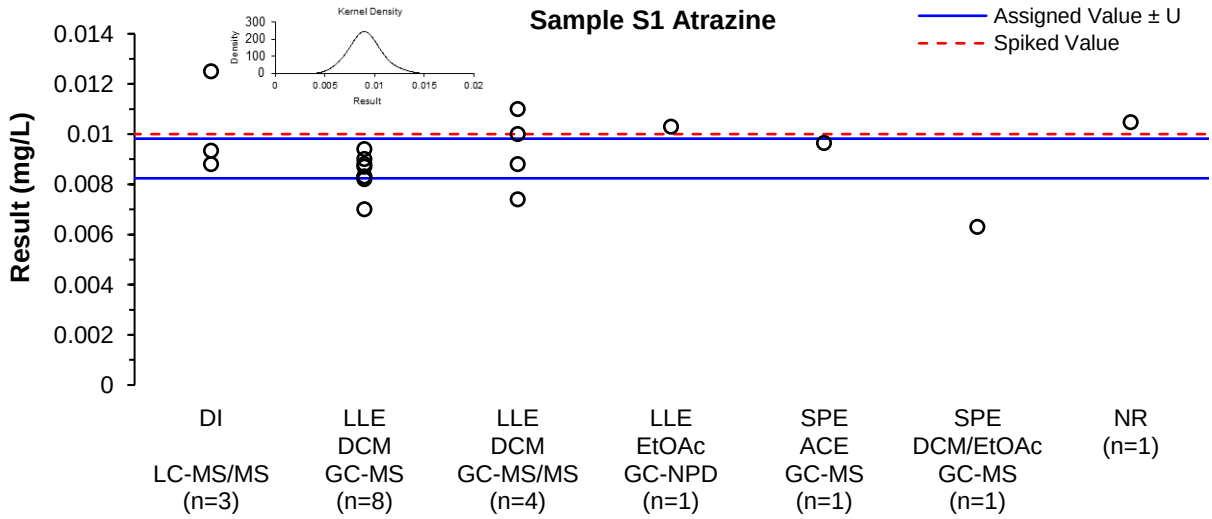


Figure 26 Sample S1 Atrazine Result vs Methodology

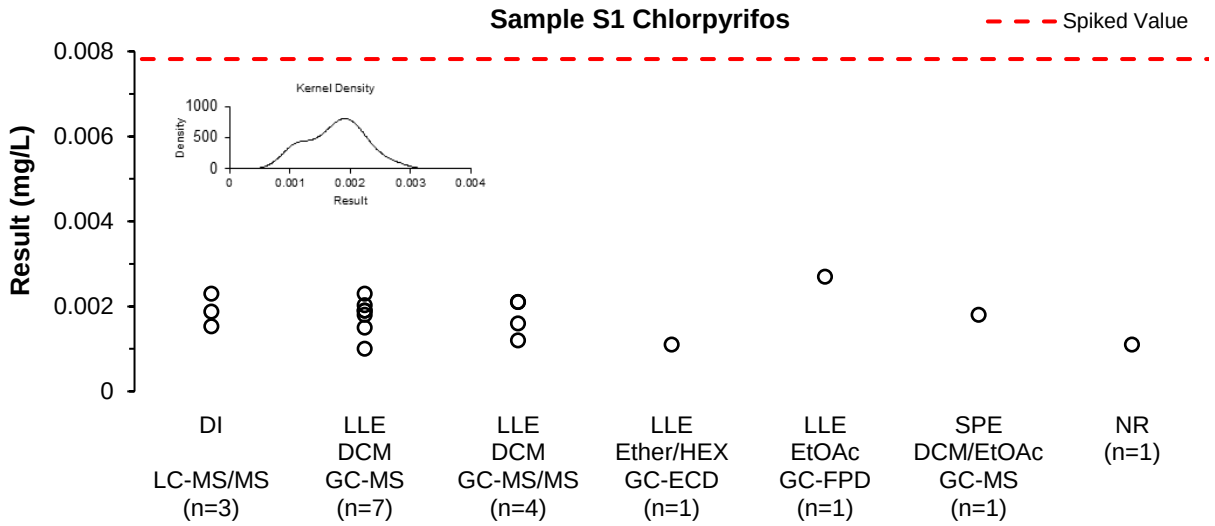


Figure 27 Sample S1 Chlorpyrifos Result vs Methodology

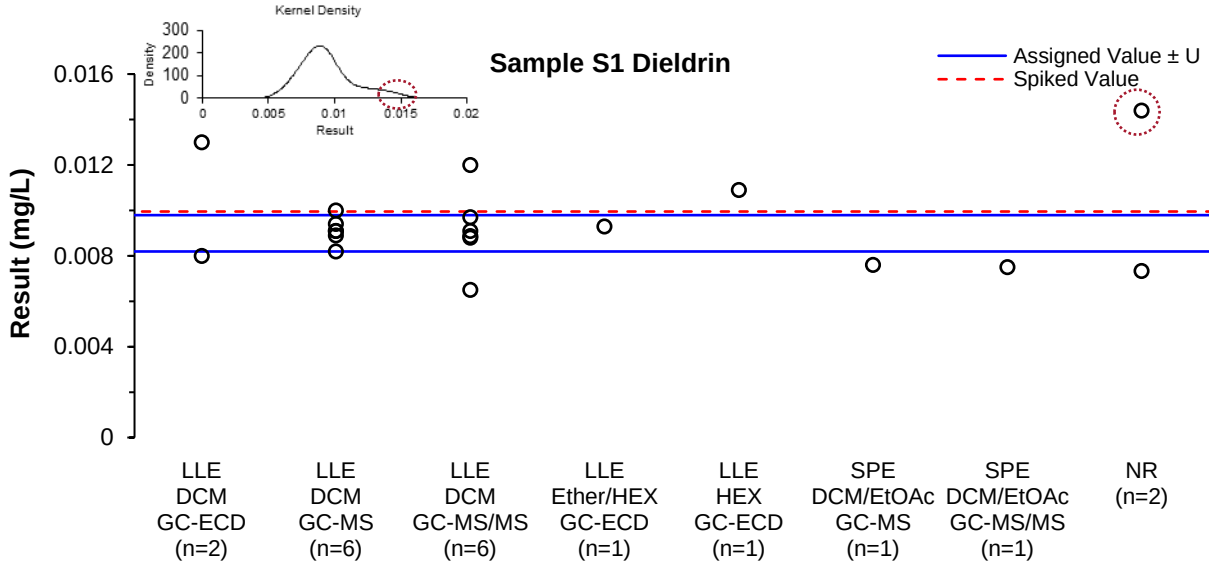


Figure 28 Sample S1 Dieldrin Result vs Methodology

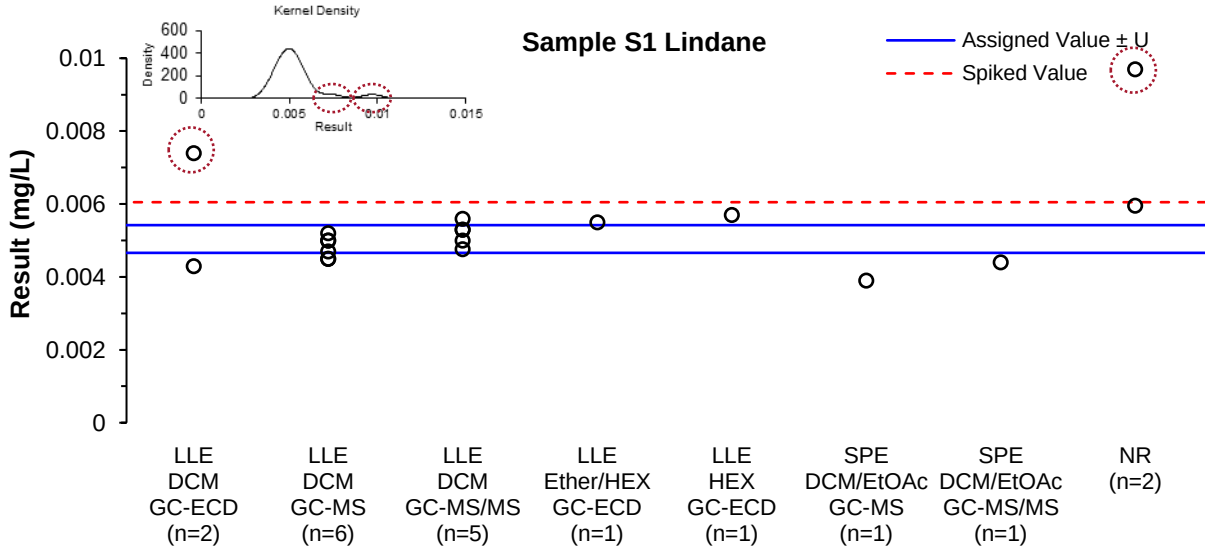


Figure 29 Sample S1 Lindane Result vs Methodology

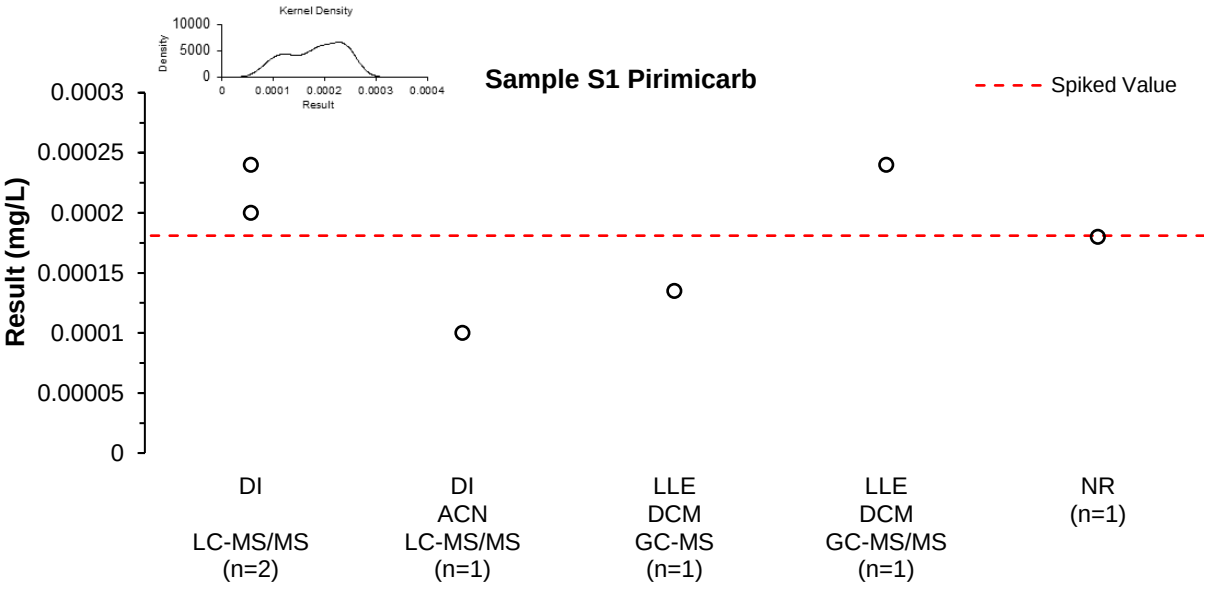


Figure 30 Sample S1 Pirimicarb Result vs Methodology

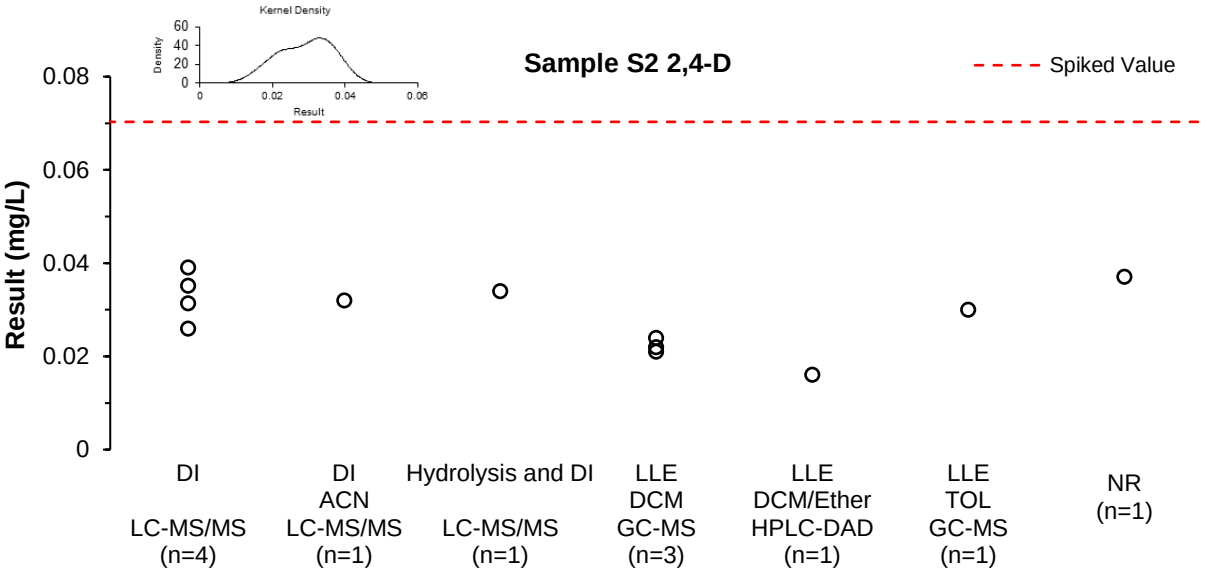


Figure 31 Sample S2 2,4-D Result vs Methodology

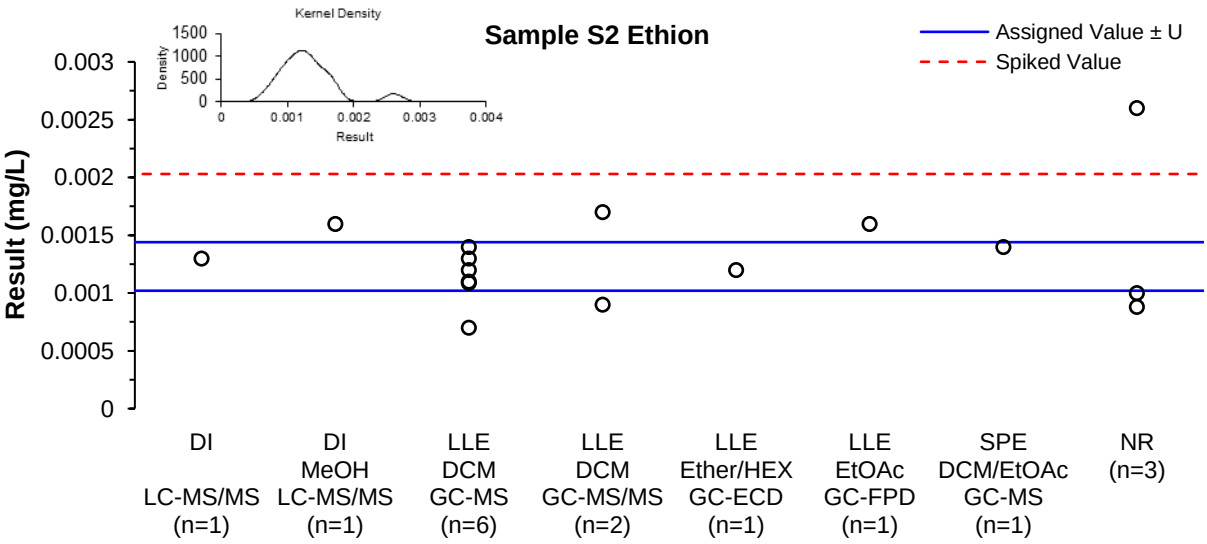


Figure 32 Sample S2 Ethion Result vs Methodology

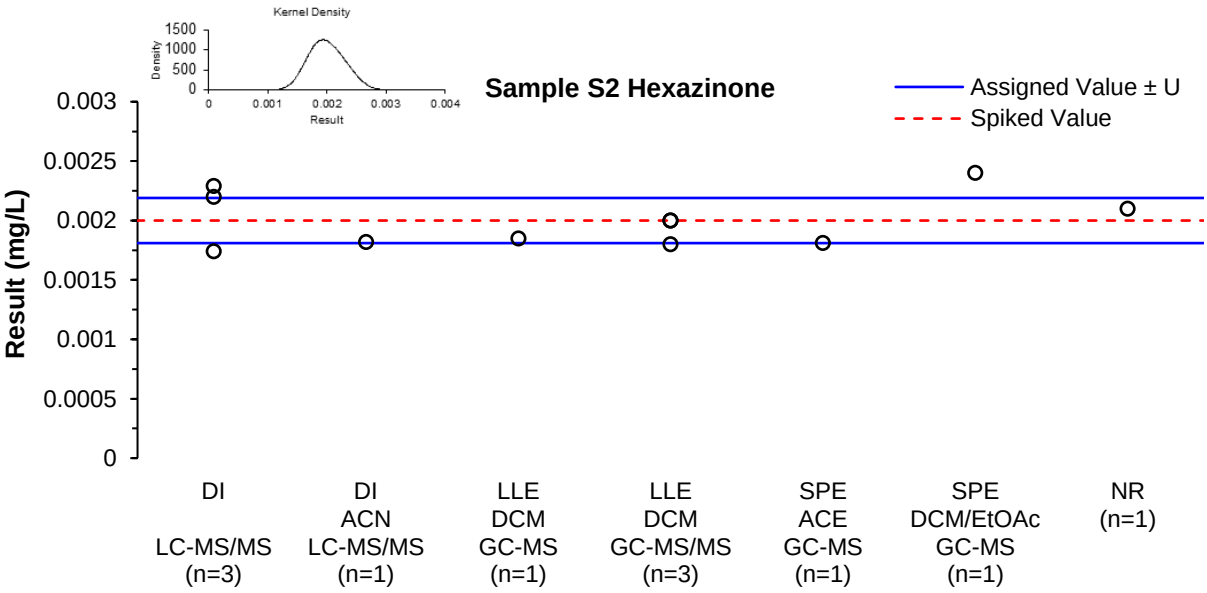


Figure 33 Sample S2 Hexazinone Result vs Methodology

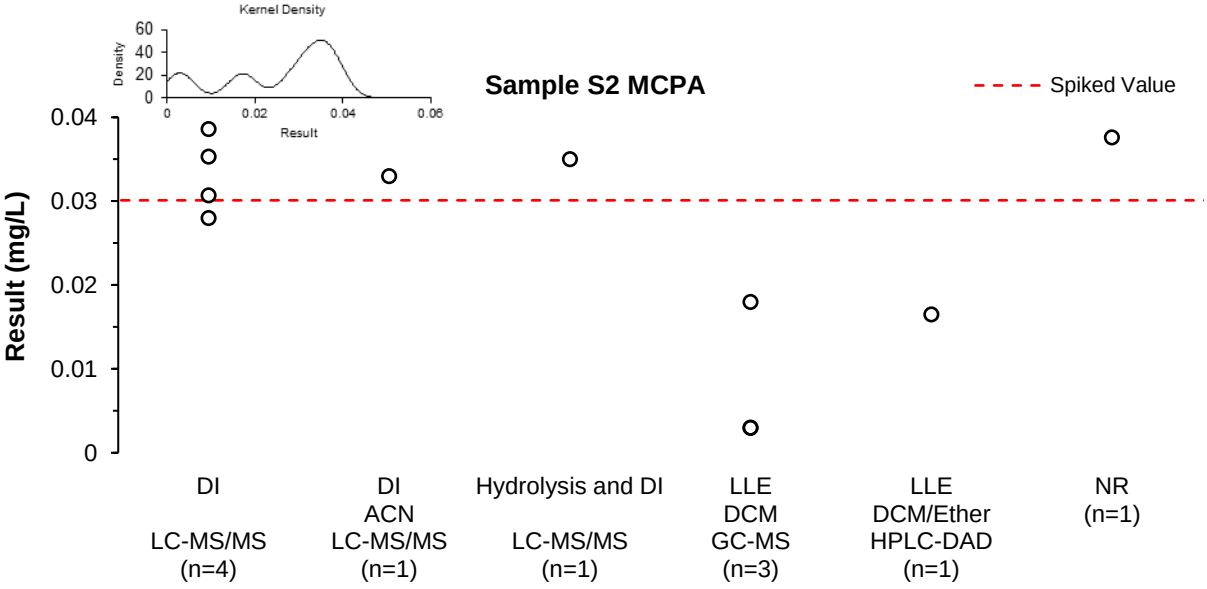


Figure 34 Sample S2 MCPA Result vs Methodology

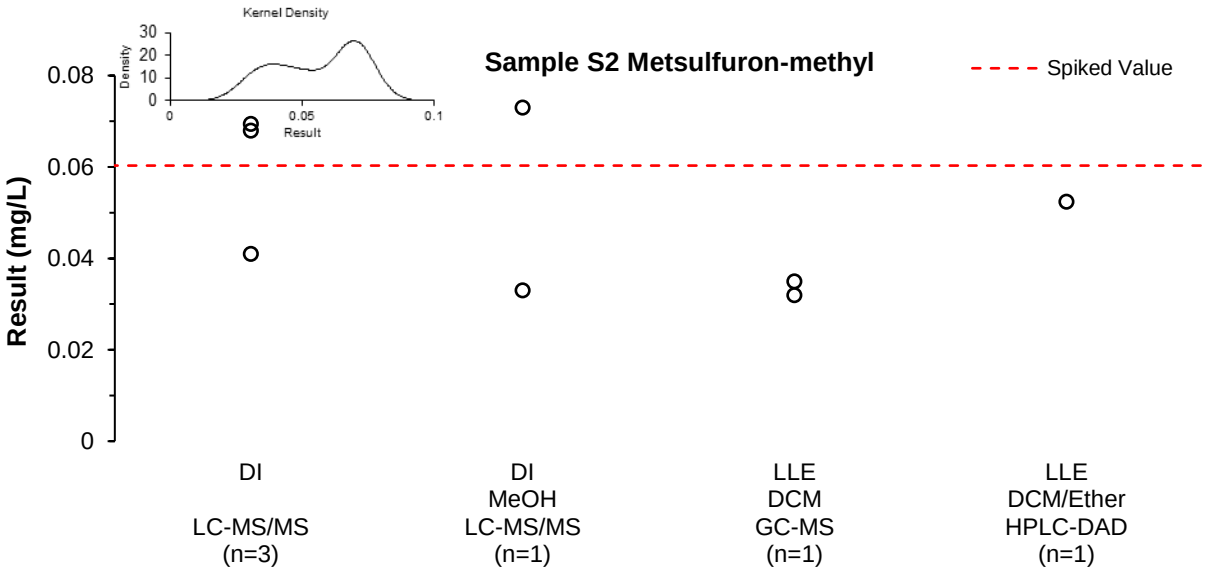


Figure 35 Sample S2 Metsulfuron-methyl Result vs Methodology

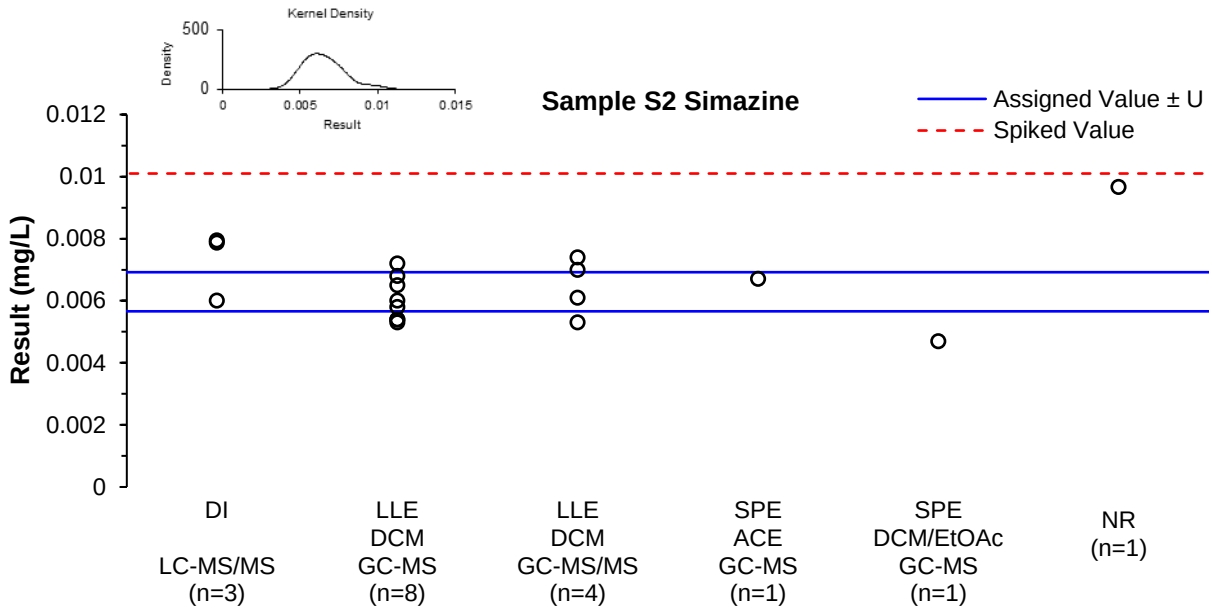


Figure 36 Sample S2 Simazine Result vs Methodology

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, corrected for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **1**, **4**, **6**, **11**, **14**, **15**, **18** and **23** reported recoveries for at least one analyte considered in this study, and the recoveries reported were in the range of 54% to 129%. No participant 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.

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

- AccuStandard
- Dr. Ehrenstorfer
- o2si
- PM Separations
- Sigma Aldrich (e.g. CRM48392)
- Certified reference materials
- ISO 17034 compliant standards
- ISO/IEC 17025 compliant 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 21 and Figure 37.

Table 21 Summary of Participants' Results for Scored Analytes*

Lab. Code	S1			S2		
	Atrazine	Dieldrin	Lindane	Ethion	Hexazinone	Simazine
AV	0.00903	0.00899	0.00504	0.00123	0.00200	0.00629
SV	0.0100	0.00995	0.00605	0.00203	0.00200	0.0101
1	0.0088	0.0075	0.0044	NT	0.0022	0.006
2	0.0074	0.0097	0.0053	< 0.002	0.0018	0.0053
3	9.3	10.5	6.1	NT	1.8	7.3
4	0.010	0.013	0.0074	0.0016	0.0020	0.0074
5	0.0070	0.0093	0.0055	0.0012	<0.002	0.0053
6	0.0083	0.0100	0.0047	0.0007	NT	0.0054
8	0.0083	0.008	0.0043	0.00109	0.00185	0.0065
9	0.0094	0.0091	0.0052	0.0012	NT	0.0068
10	0.0082	0.0091	0.005	0.0014	0.00182	0.0058
11	0.011	0.012	0.005	0.001	0.002	0.007
12	NT	0.0088	NT	<0.01	<0.002	NT
13	NT	0.0091	0.0056	0.0017	NT	NT
14	0.0103	0.0109	0.0057	0.0016	NT	NT
15	0.0063	0.0076	0.0039	0.0014	0.0024	0.0047
16	NT	0.0144	0.0097	0.0026	NT	NT
17	0.01047	0.00733	0.00596	0.00088	0.0021	0.00967
18	0.00934	NT	NT	NT	0.00174	0.00787
19	0.0087	0.0089	0.0045	<0.0005	NT	0.0054
20	0.0125	0.00887	0.00476	0.0013	0.00229	0.00794
21	0.0088	0.0065	0.0053	0.0009	<0.002	0.0061
22	0.0088	0.0082	0.005	0.0013	<0.002	0.0072
23	0.009	0.0094	0.0045	0.0011	<0.002	0.006
24	0.00964	NT	NT	NT	0.00181	0.00671

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

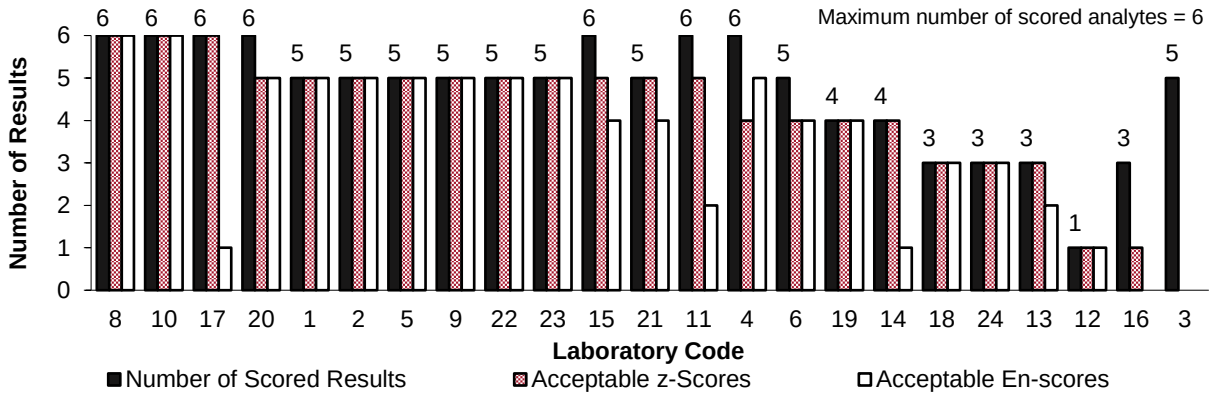


Figure 37 Summary of Participants' Performance

6.12 Comparison with Previous Pesticides in Potable Water PT Studies

NMI has included at least one pesticides in potable water sample in two previous studies: AQA 22-09 and AQA 18-13. AQA 24-09 is the first NMI PT study where all samples have been pesticides in potable water.

A summary of the participation and reported results rates in NMI Pesticides in Potable Water samples is presented in Figure 38. The proportion of pesticides being tested for by participants has remained relatively steady over these studies, even with the increased number of pesticides being assessed.

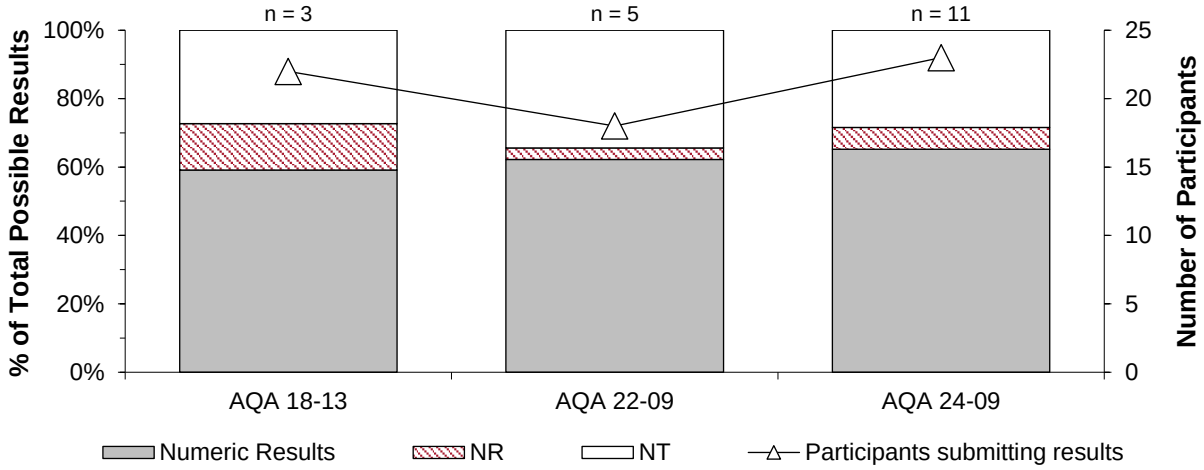


Figure 38 Summary of Participation and Reported Results in Pesticides in Potable Water PT Studies (n = number of spiked analytes)

A summary of the acceptable performance (presented as a percentage of the total number of scores) obtained by participants in NMI Pesticides in Potable Water samples is presented in Figure 39. 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 *z*-scores and E_n-scores was 86% and 82% respectively.

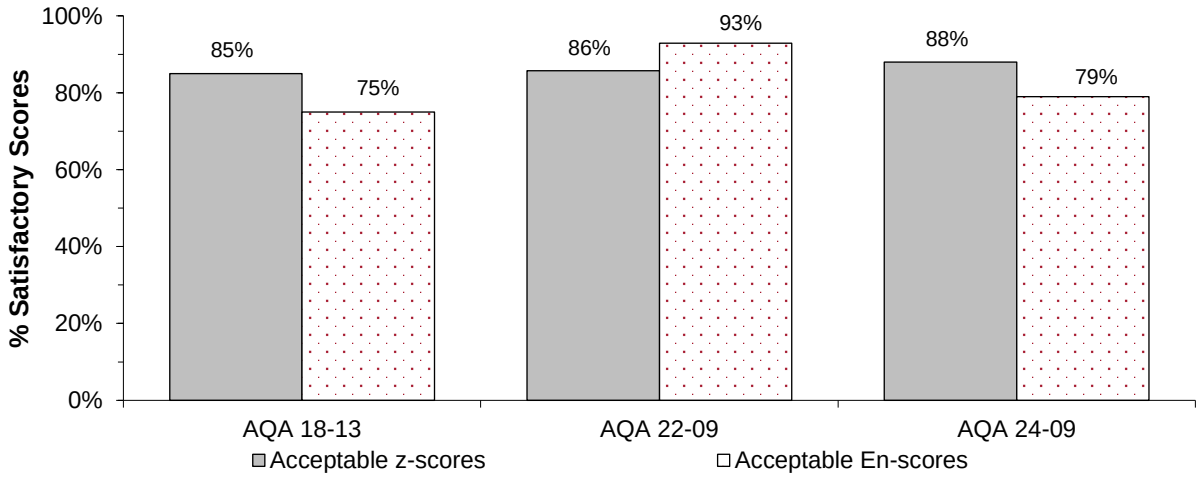


Figure 39 Acceptable *z*-Scores and E_n-Scores in Pesticides in Potable Water PT Studies

Individual performance history reports are emailed to participants at the end of each study; the consideration of *z*-scores over time provides much more useful information than a single score. Over time, laboratories should expect at least 95% of their 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 method or laboratory bias.

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties. Figure 40 presents a summary of the relative uncertainties as reported by participants in NMI Pesticides in Potable Water samples. Over this time period, the vast majority of numeric results were reported with uncertainties (92%), with on average 92% of participants in each study reporting that they were accredited to ISO/IEC 17025. Most participants over this time period reported relative expanded uncertainties between 15% and 50%, however around 28% of relative uncertainties were outside this range, and may have been unrealistically small or too large and not fit-for-purpose.

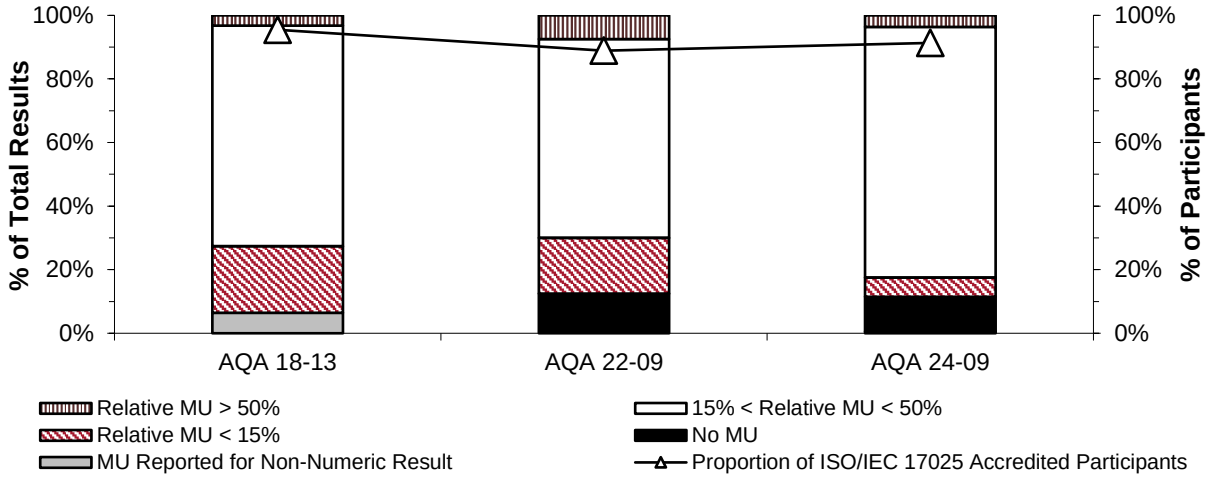


Figure 40 Summary of Participants' Relative Uncertainties for NMI Pesticides in Potable Water PT Studies

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 the competence of proficiency testing providers.*

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

[3] NMI, 2024, *Chemical Proficiency Testing Statistical Manual*, viewed August 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] NHMRC, 2022, *National Water Quality Management Strategy Australian Drinking Water Guidelines 6*, Version 3.8.

[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 August 2024, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>

[10] Tomlin, C.D.S., 2006, 'The Pesticide Manual, A World Compendium', 14th ed., British Crop Production Council.

[11] NMI, 2019, *Proficiency Test Report AQA 18-13 Pesticides in Water*, viewed August 2024, <https://www.industry.gov.au/sites/default/files/2019-06/aqa-18-13-pesticides-in-water-proficiency-test-final-report.pdf>

[12] NATA, 2020, Update to Measurement Uncertainty resources, viewed August 2024, <https://nata.com.au/news/update-to-measurement-uncertainty-resources/>

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

APPENDIX 1 SAMPLE PREPARATION

Tap water (potable water) was transferred into stainless steel pots. This was used as the starting matrix.

For both samples, the water in the pot was stirred using an IKA stirrer. While stirring, pesticide standard solutions were added. After at least two hours of continuous stirring, the spiked water was dispensed into 500 mL and 100 mL amber glass bottles (alternating between one 500 mL bottle and three 100 mL bottles).

The bottles were then labelled, shrink-wrapped, and stored in a refrigerator at 4 ºC until sample dispatch.

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 sufficiently homogeneous samples. The results of this study also gave no reason to question the samples' homogeneity.

A2.2 Stability

No stability testing was conducted for this study as the samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples for similar analytes and matrices over a similar time frame. After preparation and before dispatch, the samples were stored at 4 ºC. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks.

The results of this study also gave no reason to question the samples' transportation stability. Comparisons of results to days spent in transit for scored analytes are presented in Figures 41 to 46 (solid blue lines correspond to the assigned value ± U for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5). No significant trend was observed.

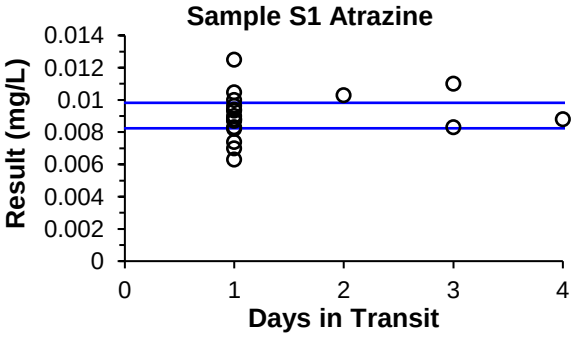


Figure 41 S1 Atrazine Results vs Transit Days

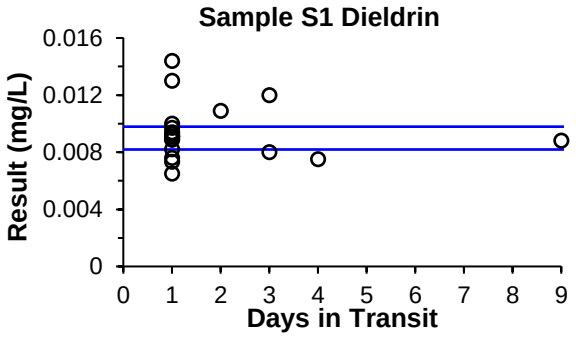


Figure 42 S1 Dieldrin Results vs Transit Days

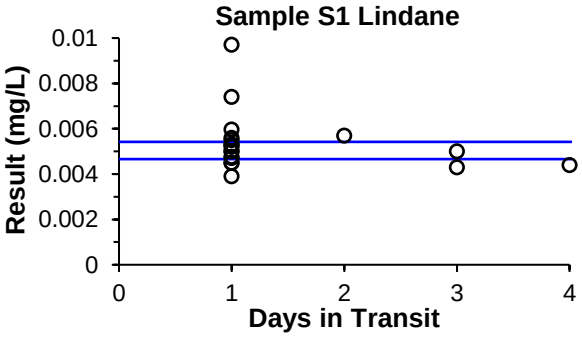


Figure 43 S1 Lindane Results vs Transit Days

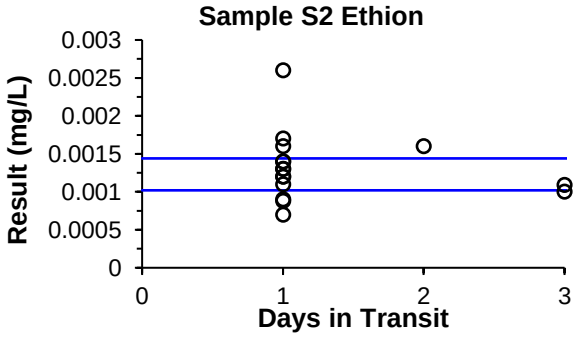


Figure 44 S2 Ethion Results vs Transit Days

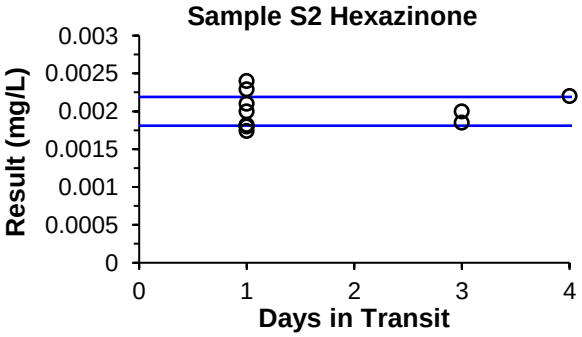


Figure 45 S2 Hexazinone Results vs Transit Days

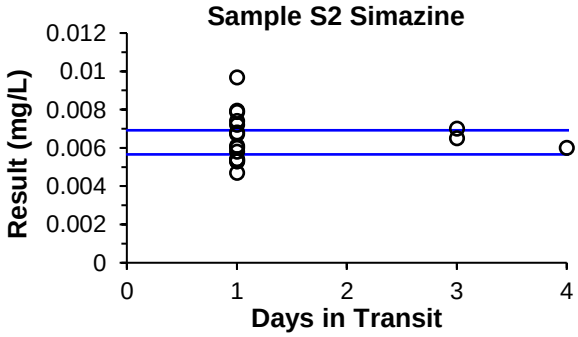


Figure 46 S2 Simazine Results vs Transit Days

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.

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

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 22.

Table 22 Uncertainty of Robust Average for Sample S2 Hexazinone

Number of results (p)	11
Robust Average	0.00200 mg/L
$S_{rob\ av}$	0.00025 mg/L
$u_{rob\ av}$	0.000094 mg/L
k	2
$U_{rob\ av}$	0.000188 mg/L

Therefore, the robust average for Sample S2 hexazinone is 0.00200 ± 0.00019 mg/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 23, using the result reported by Laboratory 1 for Sample S1 atrazine.

Table 23 z-Score and E_n-Score for Sample S1 Atrazine Result Reported by Laboratory 1

Participant Result (mg/L)	Assigned Value (mg/L)	Target Standard Deviation	z-Score	E_n-Score
0.0088 ± 0.0022	0.00903 ± 0.00079	15% as PCV, or: 0.15 × 0.00903 = 0.0013545 mg/L	$z = \frac{0.0088 - 0.00903}{0.0013545} = -0.17$	$E_n = \frac{0.0088 - 0.00903}{\sqrt{0.0022^2 + 0.00079^2}} = -0.10$

APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 24 to 34. Some responses may be modified so that the participant cannot be identified.

Table 24 Methodology – Atrazine

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS/MS
3	20	Quechers	acetonitrile	None	LC-MS/MS
4	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
5	100	Liquid-Liquid	DCM		GC-MS
6	100	Liquid-Liquid	DCM	None	GC-MS
8	250	Liquid-Liquid	DCM	Nil	GC-MS
9	100	Liquid-Liquid	DCM	None	GC-MS
10	100	Liquid-Liquid	DCM	NONE	GC-MS
11	100	Liquid-Liquid	DCM	None	GC-MS/MS
12	NT				
13	NT				
14	150	Liquid-Liquid	Ethyl acetate	None	GC-NPD
15	500	SPE	DCM/EtOAc		GC-MS
16	NT				
17	NR				
18	1	Direct Injection			LC-MS/MS
19	100	Liquid-Liquid	DCM	Filtration	GC-MS
20	1	Direct Injection	N/A	Centrifugation & dilution	LC-MS/MS
21	100	Liquid-Liquid	DCM	None	GC-MS/MS
22	100	Liquid-Liquid	DCM		GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	100	SPE	Acetone	None	GC-MS

Table 25 Methodology – Chlorpyrifos

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS/MS
3	20	Quechers	acetonitrile	None	LC-MS/MS
4	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
5	100	Liquid-Liquid	15%Ether/Hexane		GC-ECD

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
6	100	Liquid-Liquid	DCM	None	GC-MS
8	250	Liquid-Liquid	DCM	Nil	GC-MS
9	100	Liquid-Liquid	DCM	None	GC-MS
10	100	Liquid-Liquid	DCM	NONE	GC-MS
11	NR				
12	35	Liquid-Liquid	DCM	None	GC-MS/MS
13	35	Liquid-Liquid	DCM	None	GC-MS/MS
14	150	Liquid-Liquid	Ethyl acetate	None	GC-FPD
15	500	SPE	DCM/EtOAc		GC-MS
16	NR				
17	NR				
18	1	Direct Injection			LC-MS/MS
19	100	Liquid-Liquid	DCM	Filtration	GC-MS
20	1	Direct Injection	N/A	Centrifugation & dilution	LC-MS/MS
21	100	Liquid-Liquid	DCM	None	GC-MS/MS
22	100	Liquid-Liquid	DCM		GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	NT				

Table 26 Methodology – Dieldrin

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	500	SPE	DCM:EtOac		GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS/MS
3	40	Liquid-Liquid	Hexane	None	GC-MS/MS
4	50	Liquid-Liquid	DCM	N/A	GC-ECD
5	100	Liquid-Liquid	15%Ether/Hexane		GC-ECD
6	100	Liquid-Liquid	DCM	None	GC-MS
8	250	Liquid-Liquid	DCM	Nil	GC-ECD
9	100	Liquid-Liquid	DCM	None	GC-MS
10	100	Liquid-Liquid	DCM	NONE	GC-MS
11	100	Liquid-Liquid	DCM	None	GC-MS/MS
12	35	Liquid-Liquid	DCM	None	GC-MS/MS
13	35	Liquid-Liquid	DCM	None	GC-MS/MS
14	150	Liquid-Liquid	Hexane	None	GC-ECD
15	500	SPE	DCM/EtOAc		GC-MS
16	NR				

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
17	NR				
18	NT				
19	100	Liquid-Liquid	DCM	Filtration	GC-MS
20	30	Liquid-Liquid	DCM	N/A	GC-MS/MS
21	100	Liquid-Liquid	DCM	None	GC-MS/MS
22	100	Liquid-Liquid	DCM		GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	NT				

Table 27 Methodology – Lindane

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	500	SPE	DCM:EtOac		GC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS/MS
3	40	Liquid-Liquid	Hexane	None	GC-MS/MS
4	50	Liquid-Liquid	DCM	N/A	GC-ECD
5	100	Liquid-Liquid	15%Ether/Hexane		GC-ECD
6	100	Liquid-Liquid	DCM	None	GC-MS
8	250	Liquid-Liquid	DCM	Nil	GC-ECD
9	100	Liquid-Liquid	DCM	None	GC-MS
10	100	Liquid-Liquid	DCM	NONE	GC-MS
11	100	Liquid-Liquid	DCM	None	GC-MS/MS
12	NT				
13	35	Liquid-Liquid	DCM	None	GC-MS/MS
14	150	Liquid-Liquid	Hexane	None	GC-ECD
15	500	SPE	DCM/EtOAc		GC-MS
16	NR				
17	NR				
18	NT				
19	100	Liquid-Liquid	DCM	Filtration	GC-MS
20	30	Liquid-Liquid	DCM	N/A	GC-MS/MS
21	100	Liquid-Liquid	DCM	None	GC-MS/MS
22	100	Liquid-Liquid	DCM		GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	NT				

Table 28 Methodology – Pirimicarb

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	NT				
3	20	Quechers	acetonitrile	None	LC-MS/MS
4	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
5	1	Direct Injection			LC-MS/MS
6	NT				
8	250	Liquid-Liquid	DCM	Nil	GC-MS
9	NT				
10	1	Direct Injection	Acetonitrile	Filtration	LC-MS/MS
11	NR				
12	NT				
13	NT				
14	NT				
15	NT				
16	NT				
17	NR				
18	NT				
19	NT				
20	NT				
21	NT				
22	100	Liquid-Liquid	DCM		GC-MS
23	NT				
24	NT				

Table 29 Methodology – 2,4-D

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	100	Liquid-Liquid	DCM/Ether	None	HPLC DAD
3	1	Direct Injection	None	None	LC-MS/MS
4	5	Liquid-Liquid	Toluene	N/A	GC-MS
5	100	Liquid-Liquid	DCM		GC-MS
6	NT				
8	1	Direct Injection	Nil	Nil	LC-MS/MS
9	NT				
10	5	Direct Injection	Acetonitrile	Filtration	LC-MS/MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
11	10	Hydrolyse with base, then neutralise and direct injection	None	None	LC-MS/MS
12	NT				
13	NT				
14	NT				
15	NT				
16	NT				
17	NR				
18	1	Direct Injection			LC-MS/MS
19	NT				
20	1	Direct Injection	N/A	Filtration & dilution	LC-MS/MS
21	NT				
22	100	Liquid-Liquid	DCM	Derivatisation	GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	NT				

Table 30 Methodology – Ethion

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1	NT				
2	100	Liquid-Liquid	DCM	None	GC-MS/MS
3	NT				
4	5	Direct Injection	Methanol	N/A	LC-MS/MS
5	100	Liquid-Liquid	15%Ether/Hexane		GC-ECD
6	100	Liquid-Liquid	DCM	None	GC-MS
8	250	Liquid-Liquid	DCM	Nil	GC-MS
9	100	Liquid-Liquid	DCM	None	GC-MS
10	100	Liquid-Liquid	DCM	NONE	GC-MS
11	NR				
12	35	Liquid-Liquid	DCM	None	GC-MS/MS
13	35	Liquid-Liquid	DCM	None	GC-MS/MS
14	150	Liquid-Liquid	Ethyl acetate	None	GC-FPD
15	500	SPE	DCM/EtOAc		GC-MS
16	NR				
17	NR				
18	NT				
19	100	Liquid-Liquid	DCM	Filtration	GC-MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
20	1	Direct Injection	N/A	Centrifugation & dilution	LC-MS/MS
21	100	Liquid-Liquid	DCM	None	GC-MS/MS
22	100	Liquid-Liquid	DCM		GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	NT				

Table 31 Methodology – Hexazinone

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS/MS
3	20	Quechers	acetonitrile	None	LC-MS/MS
4	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
5	100	Liquid-Liquid	DCM		GC-MS
6	NT				
8	250	Liquid-Liquid	DCM	Nil	GC-MS
9	NT				
10	1	Direct Injection	Acetonitrile	Filtration	LC-MS/MS
11	100	Liquid-Liquid	DCM	None	GC-MS/MS
12	35	Liquid-Liquid	DCM	None	GC-MS/MS
13	NT				
14	NT				
15	500	SPE	DCM/EtOAc		GC-MS
16	NT				
17	NR				
18	1	Direct Injection			LC-MS/MS
19	NT				
20	1	Direct Injection	N/A	Centrifugation & dilution	LC-MS/MS
21	100	Liquid-Liquid	DCM	None	GC-MS/MS
22	100	Liquid-Liquid	DCM		GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	100	SPE	Acetone	None	GC-MS

Table 32 Methodology – MCPA

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	100	Liquid-Liquid	DCM/Ether	None	HPLC DAD
3	1	Direct Injection	None	None	LC-MS/MS
4	5	Liquid-Liquid	Toluene	N/A	GC-MS
5	100	Liquid-Liquid	DCM		GC-MS
6	NT				
8	1	Direct Injection	Nil	Nil	LC-MS/MS
9	NT				
10	5	Direct Injection	Acetonitrile	Filtration	LC-MS/MS
11	10	Hydrolyse with base, then neutralise and direct injection	None	None	LC-MS/MS
12	NT				
13	NT				
14	NT				
15	NT				
16	NT				
17	NR				
18	1	Direct Injection			LC-MS/MS
19	NT				
20	1	Direct Injection	N/A	Filtration & dilution	LC-MS/MS
21	NT				
22	100	Liquid-Liquid	DCM	Derivatisation	GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	NT				

Table 33 Methodology – Metsulfuron-methyl

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	100	Liquid-Liquid	DCM/Ether	None	HPLC DAD
3	NT				
4	5	Direct Injection	Methanol	N/A	LC-MS/MS
5	100	Liquid-Liquid	DCM		GC-MS
6	NT				
8	NT				
9	NT				

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
10	1	Direct Injection	Acetonitrile	Filtration	LC-MS/MS
11	NT				
12	NT				
13	NT				
14	NT				
15	NT				
16	NT				
17	NR				
18	1	Direct Injection			LC-MS/MS
19	NT				
20	NT				
21	NT				
22	10	Direct Injection	N/A		LC-MS/MS
23	NT				
24	NT				

Table 34 Methodology – Simazine

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
1		Direct Injection			LC-MS/MS
2	100	Liquid-Liquid	DCM	None	GC-MS/MS
3	20	Quechers	acetonitrile	None	LC-MS/MS
4	50	Liquid-Liquid	DCM	N/A	GC-MS/MS
5	100	Liquid-Liquid	DCM		GC-MS
6	100	Liquid-Liquid	DCM	None	GC-MS
8	250	Liquid-Liquid	DCM	Nil	GC-MS
9	100	Liquid-Liquid	DCM	None	GC-MS
10	100	Liquid-Liquid	DCM	NONE	GC-MS
11	100	Liquid-Liquid	DCM	None	GC-MS/MS
12	NT				
13	NT				
14	NT				
15	500	SPE	DCM/EtOAc		GC-MS
16	NT				
17	NR				
18	1	Direct Injection			LC-MS/MS
19	100	Liquid-Liquid	DCM	Filtration	GC-MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument
20	1	Direct Injection	N/A	Centrifugation & dilution	LC-MS/MS
21	100	Liquid-Liquid	DCM	None	GC-MS/MS
22	100	Liquid-Liquid	DCM		GC-MS
23	100	Liquid-Liquid	DCM	None	GC-MS
24	100	SPE	Acetone	None	GC-MS

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

2,4-D	2,4-Dichlorophenoxyacetic acid
ACE	Acetone
ACN	Acetonitrile
ADWG	Australian Drinking Water Guidelines
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DAD	Diode Array Detection
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DI	Direct Injection
ECD	Electron Capture Detection
EtOAc	Ethyl Acetate
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
k	Coverage Factor
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOR	Limit of Reporting
Max	Maximum
MCPA	2-methyl-4-chlorophenoxyacetic acid
Md	Median
MeOH	Methanol
Min	Minimum
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
N	Number of numeric results

NATA	National Association of Testing Authorities, Australia
NMI	National Measurement Institute, Australia
NPD	Nitrogen-Phosphorus Detection
NR	Not Reported
NT	Not Tested
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
s.f.	Significant Figures
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)
TOL	Toluene
U	Expanded Uncertainty

END OF REPORT