Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 22-09 Organic Compounds and Pesticides in Potable Water

October 2022

ACKNOWLEDGMENTS

This study was conducted by the National Measurement Institute (NMI). Support funding was provided by the Australian Government Department of Industry, Science and Resources.

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.

Jenny Xu

Geoff Morschel

Luminita Antin

Hamish Lenton

Mark Lewin

Luke Baker

Raluca Iavetz

Manager, Chemical Reference Values

105 Delhi Rd, North Ryde, NSW 2113, Australia

Phone: +61 2 9449 0178

Email: raluca.iavetz@measurement.gov.au

NATA

WORLD RECOGNISED ACCREDITATION

Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

THIS PAGE IS INTENTIONALLY BLANK

SUMMARY

AQA 22-09 Organic Compounds and Pesticides in Potable Water commenced in June 2022. Nineteen laboratories registered to participate and eighteen 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 analytes.

Of a possible 162 results, 97 numeric results (60%) were submitted. Twelve results were a 'less than' value ($< x$) or Not Reported (NR), and 53 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 organic compounds and pesticides of interest in potable water.*

Laboratories **2**, **6**, **8**, **11**, **15**, **16**, **17** and **19** reported numeric results for all six scored analytes.

One participant did not report results for analytes which they tested for and were present in the test samples (total of six results). Six participants reported numeric results for analytes not spiked into the test samples (total of eight results).

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

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

Of 81 z scores, 77 (95%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Of 81 E_n scores, 70 (86%) returned a score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories **6**, **15** and **19** achieved satisfactory z and E_n scores across all six scored analytes.

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

Of the 14 results assessed against the Australian Drinking Water Guidelines, 78 (96%) correctly reflected whether the sample exceeded the guideline(s) or not.

Laboratories **2**, **6**, **11**, **15**, **16** and **19** returned correct consequences for all six analytes assessed.

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

Participants used a wide variety of methods for Sample S1 (pesticides). There was no evident correlation overall between the results obtained and method used.

For Sample S2 (volatile organic compounds), participants used either purge-and-trap or headspace GC-MS, with one participant reporting that they also used liquid-liquid extraction with methanol as part of their procedure. For this study, it was seen that results from headspace GC-MS were slightly biased low, while results from purge-and-trap GC-MS were slightly biased high.

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

Of 97 numeric results, 85 (88%) were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 0.04% to 425%. Participants used a wide variety of procedures to estimate their uncertainty.

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

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

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

The National Measurement Institute (NMI) is responsible for Australia's national measurement infrastructure, providing a range of services including a chemical proficiency testing program.

Proficiency testing (PT) is the 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparison'.[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMI offers studies in:

- pesticide residues in soil and water, fruit, vegetables and herbs;
- petroleum hydrocarbons and volatile organic compounds in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, water, biota and food;
- controlled drug assay, drugs in wipes and clandestine laboratory; and
- allergens in food.

1.2 Study Aims

The aims of the study were to:

- assess the ability of participants to correctly identify organic compounds and pesticides of interest in potable water;
- compare the performance of participants and assess their accuracy in the measurement of organic compounds and pesticides in potable water;
- assess the consequence of participants' results for organic compounds and pesticides in potable water against regulatory guidelines;
- evaluate the participants' methods for the measurement of organic compounds and 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 17043:2010,[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[4]

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

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitation sent 28/06/2022

Samples dispatched 26/07/2022

Results due 26/08/2022

Interim report sent 31/08/2022

2.2 Participation and Laboratory Code

Nineteen laboratories registered to participate in this study, and all participants were assigned a confidential laboratory code number for this study. Eighteen 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] and
- a variety of analytes amenable to gas and/or liquid chromatography.

The potential analytes spiked into the test samples are presented in Tables 1 and 2.

Table 1 List of Possible Analytes for Sample S1

Aldicarb	Dichlorvos	Omethoate
Aldrin	Dieldrin	Parathion
Atrazine	Dimethoate	Parathion-methyl
Azinphos-methyl	Diuron	Pendimethalin
Chlopyrifos	Endosulfan	Permethrin
Chlordane	Ethion	Picloram
Chlorfenvinphos	Fenthion	Piperonyl butoxide
Clopyralid	Glyphosate	Pirimicarb
Cyfluthrin	Heptachlor	Pirimphos-ethyl
Cypermethrin	Imazapyr	Pirimphos-methyl
2,4-D	Malathion	Propiconazole
DDT	MCPA	Simazine
Deltamethrin	Metolachlor	2,4,5-T
Diazinon	Metsulfuron-methyl	Tetrachlorvinphos

Table 2 List of Possible Analytes for Sample S2

Benzene	Dichloromethane	Trichloroethanes (Total)
Carbon tetrachloride	Ethylbenzene	Trichloroethylene
Chlorobenzene	Styrene	Trihalomethanes (Total)
Dichlorobenzenes (Total)	Tetrachloroethene	Vinyl Chloride
Dichloroethanes (Total)	Toluene	Xylenes (Total)
Dichloroethenes (Total)	Trichlorobenzenes (Total)	

2.4 Test Material Preparation

The test samples were prepared by spiking tap water with various analytes to obtain the concentrations listed in Table 3. Additional information on the preparation of the samples is given in Appendix 1.

Table 3 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/L)	Uncertainty[a] (mg/L)	Guideline Value[5] (mg/L)	
				Health	Aesthetic
S1	Aldicarb	0.00690	0.00034	0.004	-
	Atrazine	0.0242	0.0012	0.02	-
	2,4-D	0.0699	0.0035	0.03	-
	Glyphosate	0.651	0.033	1	-
S2	Chlorobenzene	0.251	0.013	0.3	0.01
	Dichlorobenzenes (Total)[b]	1.12	0.06	1.5	0.001
	Dichloromethane	0.00407	0.00020	0.004	-
	Toluene	0.0250	0.0012	0.8	0.025
	Trihalomethanes (Total)[c]	0.100	0.005	0.25	-

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

[b] Participants were requested to report for dichlorobenzenes (total). The sample was spiked with 1,2-dichlorobenzene only, and the guideline values are for 1,2-dichlorobenzene only.

[c] Participants were requested to report for trihalomethanes (total). The sample was spiked with chloroform only.

2.5 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this study. The samples were prepared, packaged and stored using a process that has been demonstrated to produce homogeneous and stable samples in previous NMI PT studies with similar analytes and matrices.

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

To further assess possible instability, the results returned by participants were compared to the spiked concentrations. For scored analytes other than Sample S2 toluene, assigned values were within the range of 80% to 97% of the spiked values, providing good support for the stability of these analytes. For Sample S2 toluene, the assigned value was 66% of the spiked value, however there was reasonable consensus between participants' results and so this analytes was also scored.

2.6 Test Material Storage and Dispatch

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 26 July 2022.

The following items were packaged with the samples:

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

An Excel spreadsheet for the electronic reporting of results was emailed to participants.

2.7 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- Participants need not test for all listed analytes.
- For each analyte in each sample, report a single result in units of mg/L expressed as if reporting to a client. 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. 0.50 ± 0.02 mg/L), if determined.
- Report any listed analyte not tested as NT.
- No limit of reporting has been set for this study. Report results as you would to a client, applying the limit of reporting of the method used for analysis.
- Give details of your methodology and basis of uncertainty estimate as requested by the results sheet emailed to you.
- Return the completed results sheet by 26 August 2022 by email to proficiency@measurement.gov.au.

2.8 Interim Report

An interim report was emailed to all participants on 31 August 2022.

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 4. Some responses were modified so that the participant cannot be identified.

Table 4 Basis of Measurement Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis	CRM Instrument calibration	Eurachem/CITAC Guide
2	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis Instrument calibration		Eurachem/CITAC Guide
3	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA Technical Note 33
6	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
8	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Instrument calibration Laboratory bias from PT studies Recoveries of SS	Eurachem/CITAC Guide
9	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration		
10	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	CRM Recoveries of SS	Eurachem/CITAC Guide
11	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	
12	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
13	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide
14	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS	Recoveries of SS	NMI Uncertainty Course
15	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
16	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration		Eurachem/CITAC Guide
17	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide
18		Control samples - SS	Recoveries of SS	
19	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide

* 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 5, along with the study coordinator's response where applicable. Some responses may be modified so that the participant cannot be identified.

Table 5 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
1	S2	Total Trihalomethanes reported as the sum of Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform at or above LOR.	
2	S1	Propazine reported as extra compound for sample 1.	
3	S1	Chlordane reported is sum of cis+trans-chlordane. Endosulfan is sum of Endosulfan I and II.	
4	All	microgram per litre units are preferred for reporting	Guideline values in the ADWG are expressed in units of mg/L.[5] Hence, participants in this study have been requested to report their results also in units of mg/L.
8	S2	Uncertainty was set to 25% based off previous proficiency trials, validation data and ongoing spike monitoring.	
	All	Uncertainty: Uncertainty set at 50%, unless validation indicates higher	

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
12	S1	The concentration of residue reported is an average of two determinations made on the same sample. The result of Atrazine in S1 is corrected for recovery at 71.11%. The LOQ for the method is at 0.0001 mg/l	
	All	There should be a separate PT study for pesticides in water only. Uncertainty: The reported uncertainty of result is an expanded uncertainty calculated using a coverage factor of 2 which gives a level of confidence of approximately 95%.	We organise new PT studies depending on interest from participants. If there is interest from others in having separate studies for pesticides and other organic compounds in potable water, we invite participants to let us know so that we can plan for future studies. We also currently run a separate pesticides in river water PT annually.
14	S2	Sample received 27th July but analysed on 16th August. Sample was run outside of hold time for VOCs.	
17	S1	A volume of 100mL was sub-sampled from the 500mL bottle.	
	All	The laboratory would like to request lower sample volumes to 100mL.	The sample volumes were selected based on experience with similar previous PT studies, as well as a survey conducted to our participants. If there is interest from others in having a lower sample volume, we invite participants to let us know so we can plan for future studies.
19	S1	DDT reported as Total DDT and Chlordane reported as Total Chlordane.	
	S2	Total Dichlorobenzenes include 1,2,Dichlorobenzene, 1,3-Dichlorobenzene and 1,4-Dichlorobenzene Total Dichloroethanes include 1,1-Dichloroethane and 1,2-Dichloroethane Total Dichloroethenes include 1,1-Dichloroethene, cis-1,2-Dichloroethene and trans-1,2-Dichloroethene Total Trichlorobenzenes include 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene and 1,3,5-Trichlorobenzene Total Trichloroethanes include 1,1,1-Trichloroethane and 1,1,2-Trichloroethane Total Trihalomethanes include Bromodichloromethane, Bromoform, Chloroform and Dibromochloromethane Total Xylenes include m&p-Xylene and o-Xylene	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 14 with summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max.), minimum (Min.), robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV). Bar charts of results and performance scores are presented in Figures 2 to 10. An example chart with interpretation guide is shown in Figure 1.

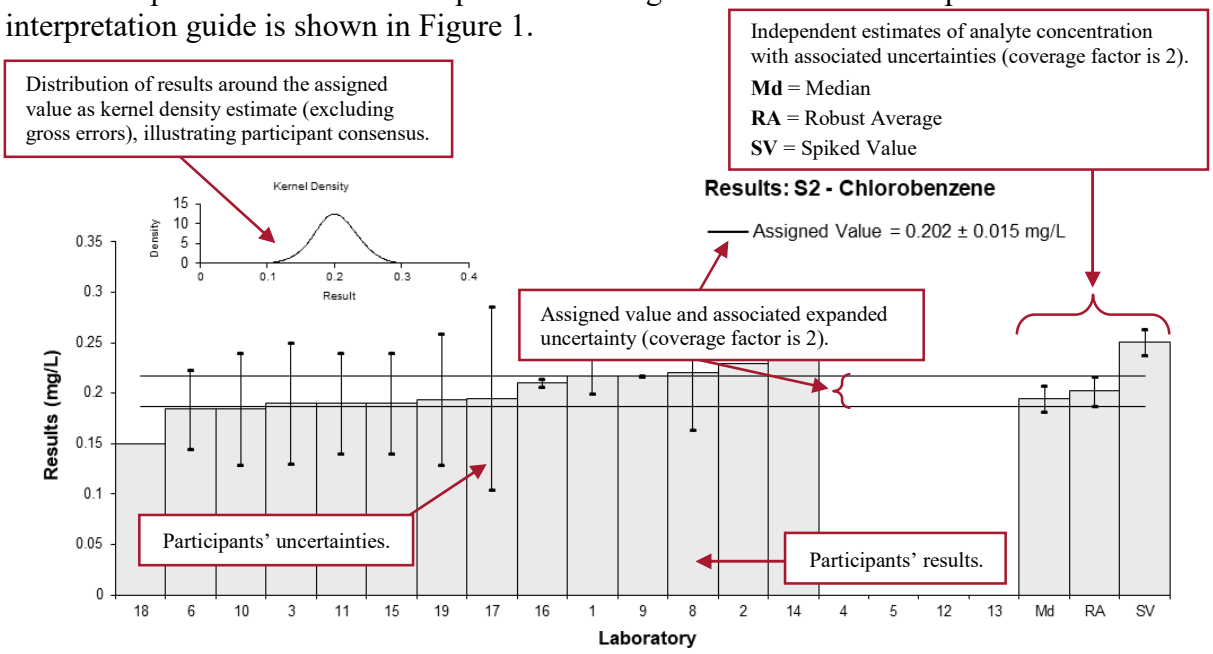


Figure 1 Guide to Presentation of Results

4.2 Outliers and Gross Errors

Outliers were results less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value.[3,4] Gross errors were obvious blunders, e.g. results reported with incorrect units or 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 of a proficiency test item'.[1] In this PT study, this property is the concentration of the analytes in the samples. Assigned values were the robust averages of participants' results, and the expanded uncertainties were estimated from the associated robust SDs (Appendix 3).

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded uncertainties, and robust CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528:2022.[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 from Equation 1

For the absolute value of a z score:

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

To account for potential low bias in the consensus value due to inefficient methodologies, 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:

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

4.9 Traceability and Measurement Uncertainty

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

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

5 TABLES AND FIGURES

Table 6

Sample Details

Sample	S1
Analyte	Aldicarb
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U
1	NT	NT
2	0.0058	NR
3	NT	NT
4	NT	NT
5	0.007	0.002
6	0.00593	0.00057
8	NT	NT
9	NR	NR
10	0.0063	0.0020
11**	0.055	0.015
12	NT	NT
13	NT	NT
14	NT	NT
15	NT	NT
16	0.0060	0.00012
17	NT	NT
18	NT	NT
19	NT	NT

** Gross Error

Statistics

Assigned Value	Not Set	
Spiked Value	0.00690	0.00034
Median	0.00600	0.00033
Mean	0.00621	0.00043
N	5	
Max	0.007	
Min	0.0058	
Robust SD	0.00054	
Robust CV	8.8%	

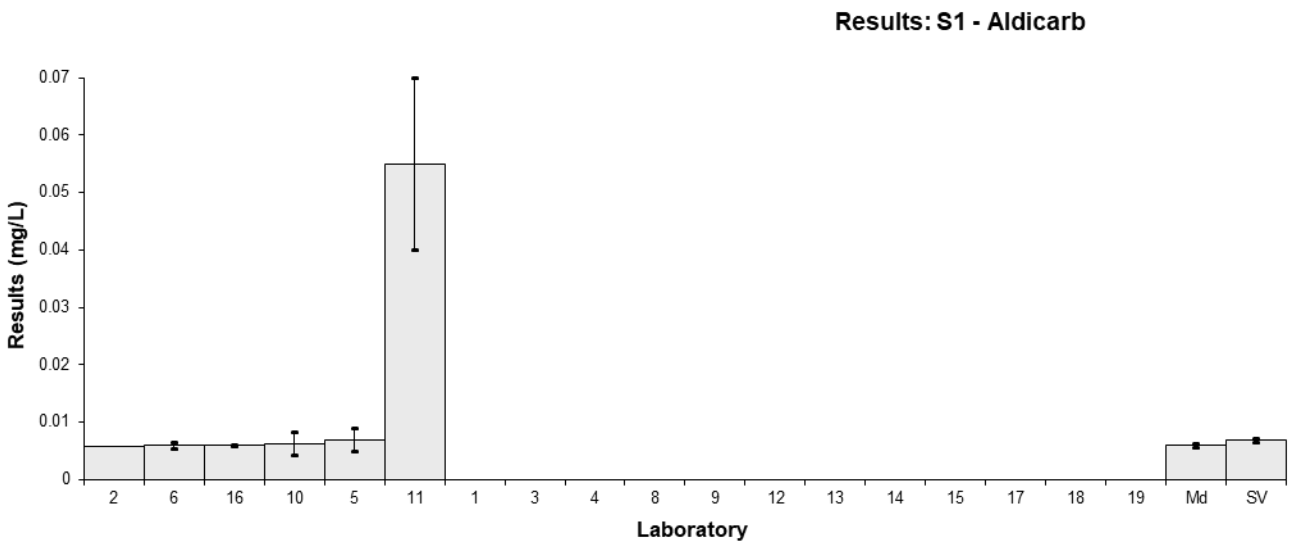

Results: S1 - Aldicarb
Results (mg/L)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
2
6
16
10
5
11
1
3
4
8
9
12
13
14
15
17
18
19
Md
SV
Laboratory

Figure 2

Table 7

Sample Details

Sample	S1
Analyte	Atrazine
Matrix	Potable Water
Unit	mg/L

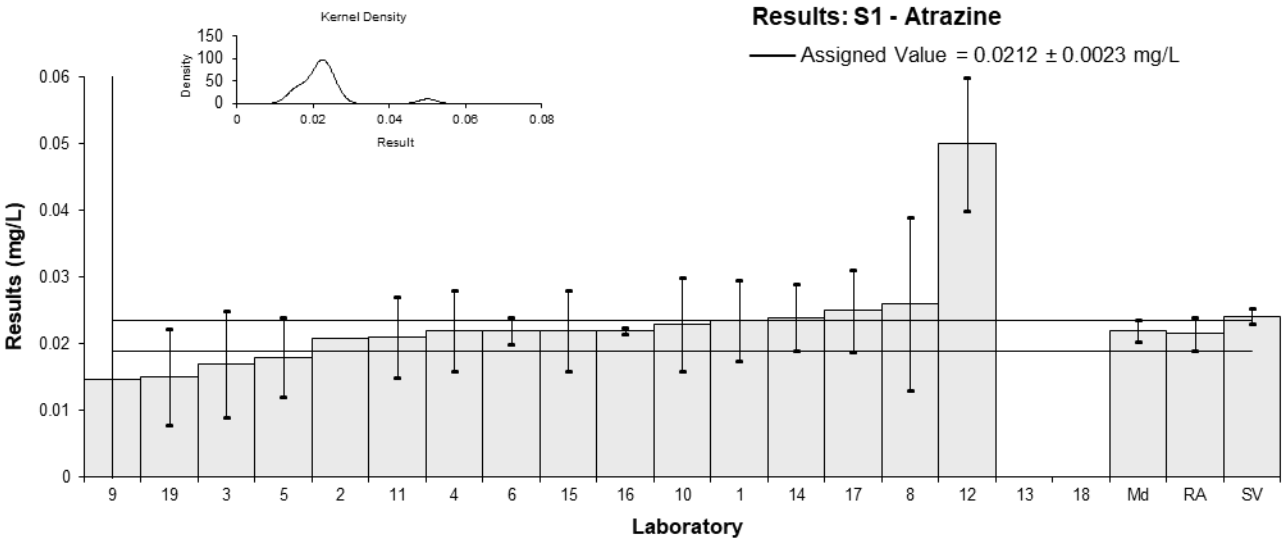
Participant Results

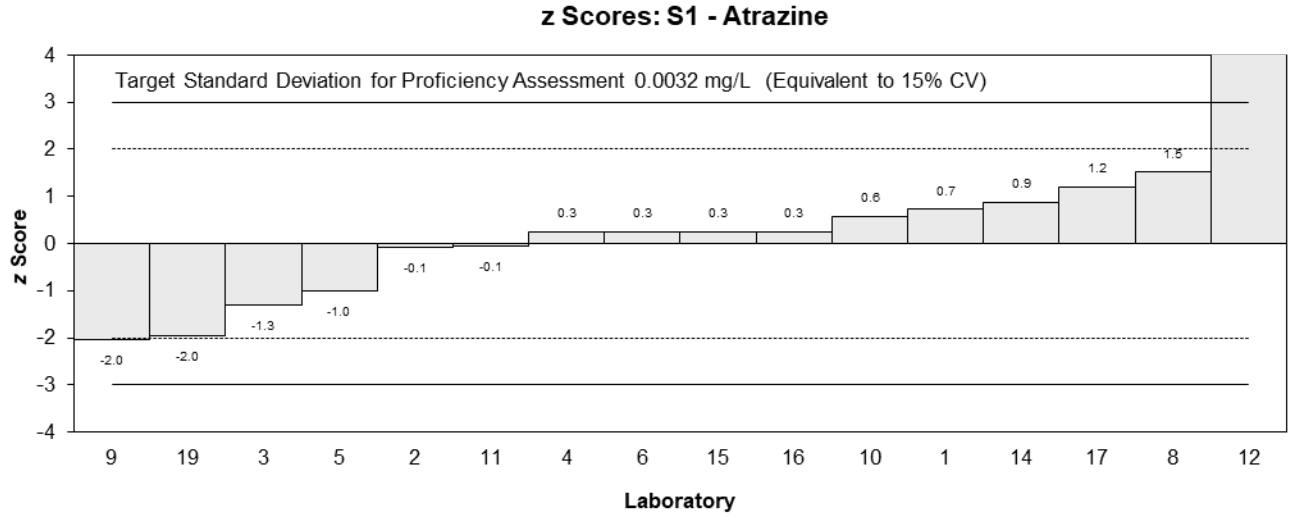
Lab. Code	Result	U	z	E_n
1	0.0235	0.0061	0.72	0.35
2	0.0209	NR	-0.09	-0.13
3	0.017	0.008	-1.32	-0.50
4	0.022	0.006	0.25	0.12
5	0.018	0.006	-1.01	-0.50
6	0.022	0.002	0.25	0.26
8	0.026	0.013	1.51	0.36
9	0.0147	0.0625	-2.04	-0.10
10	0.023	0.007	0.57	0.24
11	0.021	0.006	-0.06	-0.03
12*	0.05	0.01	9.06	2.81
13	NT	NT		
14	0.024	0.005	0.88	0.51
15	0.022	0.006	0.25	0.12
16	0.022	0.00044	0.25	0.34
17	0.025	0.0061	1.19	0.58
18	NT	NT		
19	0.015	0.0072	-1.95	-0.82

* Outlier

Statistics

Assigned Value	0.0212	0.0023
Spiked Value	0.0242	0.0012
Robust Average	0.0216	0.0025
Median	0.0220	0.0016
Mean	0.0229	0.0040
N	16	
Max	0.05	
Min	0.0147	
Robust SD	0.0040	
Robust CV	18%	


Kernel Density
Density
Result
Results: S1 - Atrazine
Assigned Value = 0.0212 ± 0.0023 mg/L
Results (mg/L)
Laboratory
9 19 3 5 2 11 4 6 15 16 10 1 14 17 8 12 13 18 Md RA SV


z Scores: S1 - Atrazine
Target Standard Deviation for Proficiency Assessment 0.0032 mg/L (Equivalent to 15% CV)
z Score
Laboratory
9 19 3 5 2 11 4 6 15 16 10 1 14 17 8 12

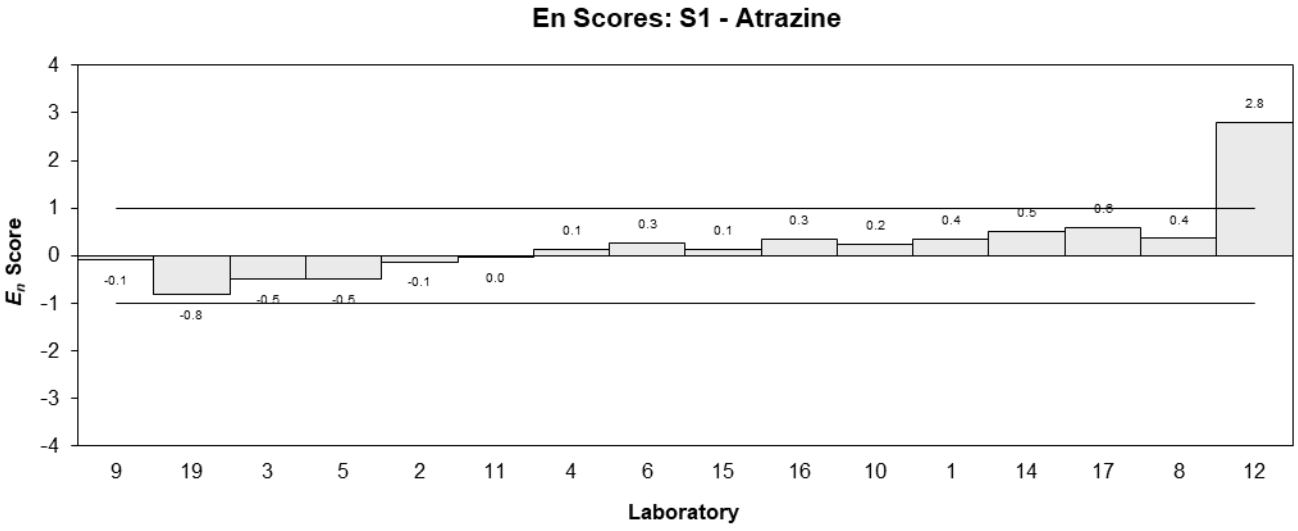

En Scores: S1 - Atrazine
En Score
Laboratory
9 19 3 5 2 11 4 6 15 16 10 1 14 17 8 12

Figure 3

Table 8

Sample Details

Sample	S1
Analyte	2,4-D
Matrix	Potable Water
Unit	mg/L

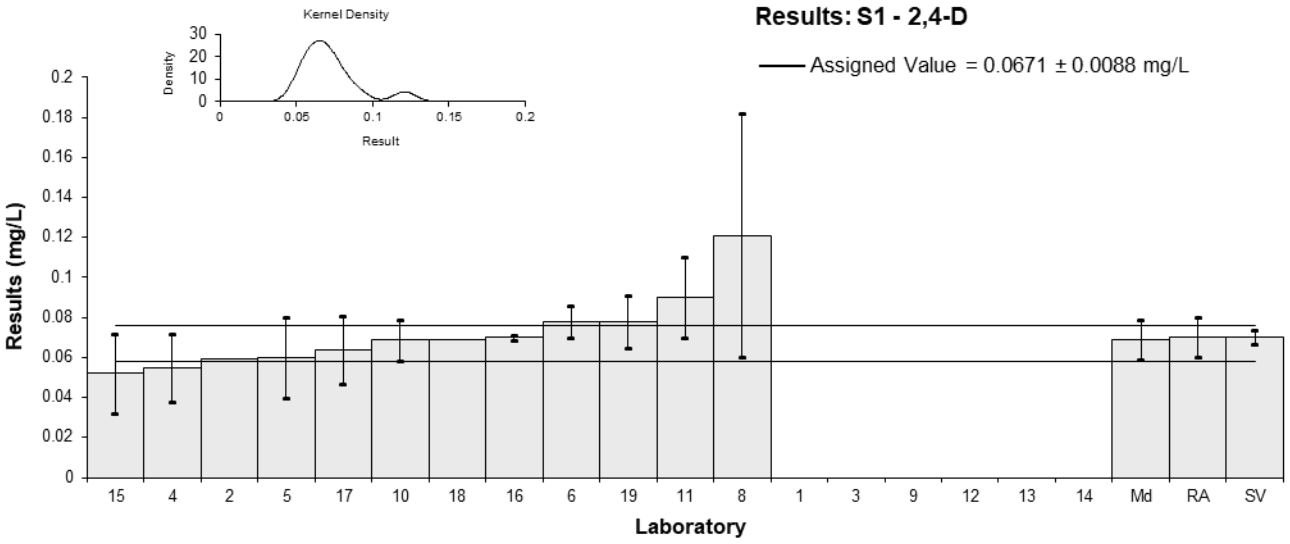
Participant Results

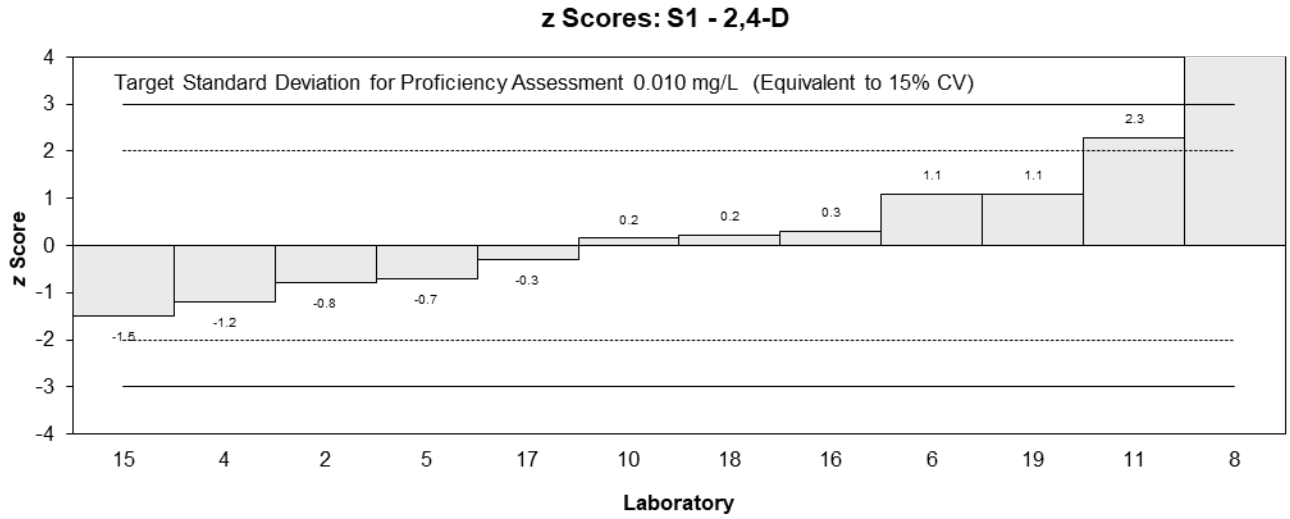
Lab. Code	Result	U	z	E_n
1	NT	NT		
2	0.059	NR	-0.80	-0.92
3	NT	NT		
4	0.055	0.017	-1.20	-0.63
5	0.060	0.02	-0.71	-0.32
6	0.078	0.008	1.08	0.92
8*	0.121	0.061	5.36	0.87
9	NR	NR		
10	0.0686	0.0104	0.15	0.11
11	0.09	0.02	2.28	1.05
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	0.052	0.02	-1.50	-0.69
16	0.070	0.0014	0.29	0.33
17	0.064	0.017	-0.31	-0.16
18	0.0692	NR	0.21	0.24
19	0.078	0.013	1.08	0.69

* Outlier

Statistics

Assigned Value	0.0671	0.0088
Spiked Value	0.0699	0.0035
Robust Average	0.070	0.010
Median	0.0689	0.0097
Mean	0.072	0.011
N	12	
Max	0.121	
Min	0.052	
Robust SD	0.014	
Robust CV	21%	


Kernel Density
Density
Result
Results: S1 - 2,4-D
Assigned Value = 0.0671 ± 0.0088 mg/L
Results (mg/L)
Laboratory
15 4 2 5 17 10 18 16 6 19 11 8 1 3 9 12 13 14 Md RA SV


z Scores: S1 - 2,4-D
Target Standard Deviation for Proficiency Assessment 0.010 mg/L (Equivalent to 15% CV)
z Score
Laboratory
15 4 2 5 17 10 18 16 6 19 11 8
-1.5 -1.2 -0.8 -0.7 -0.3 0.2 0.2 0.3 1.1 1.1 2.3

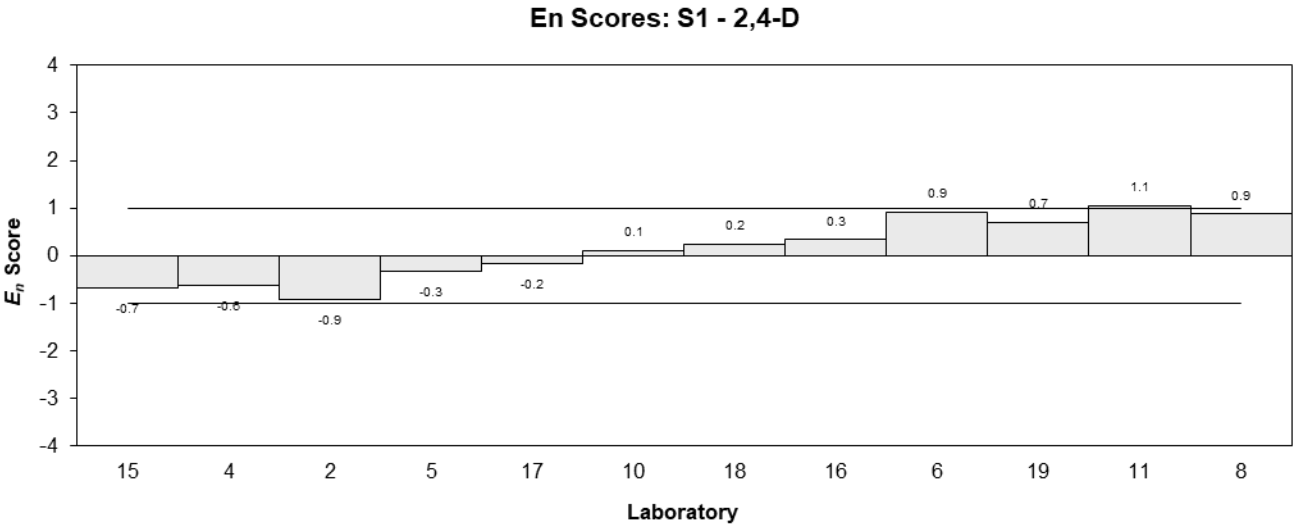

En Scores: S1 - 2,4-D
En Score
Laboratory
15 4 2 5 17 10 18 16 6 19 11 8
-0.7 -0.6 -0.9 -0.3 -0.2 0.1 0.2 0.3 0.9 0.7 1.1 0.9

Figure 4

Table 9

Sample Details

Sample	S1
Analyte	Glyphosate
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U
1	NT	NT
2	0.521	NR
3	NT	NT
4	NT	NT
5**	0.0006	0.0002
6	0.635	0.127
8	0.71	0.36
9	NR	NR
10	NT	NT
11	0.31	0.07
12	NT	NT
13	NT	NT
14	NT	NT
15	NT	NT
16	0.68	0.014
17	NT	NT
18	NT	NT
19	NT	NT

** Gross Error

Statistics

Assigned Value	Not Set	
Spiked Value	0.651	0.033
Median	0.64	0.12
Mean	0.57	0.15
N	5	
Max	0.71	
Min	0.31	
Robust SD	0.18	
Robust CV	32%	

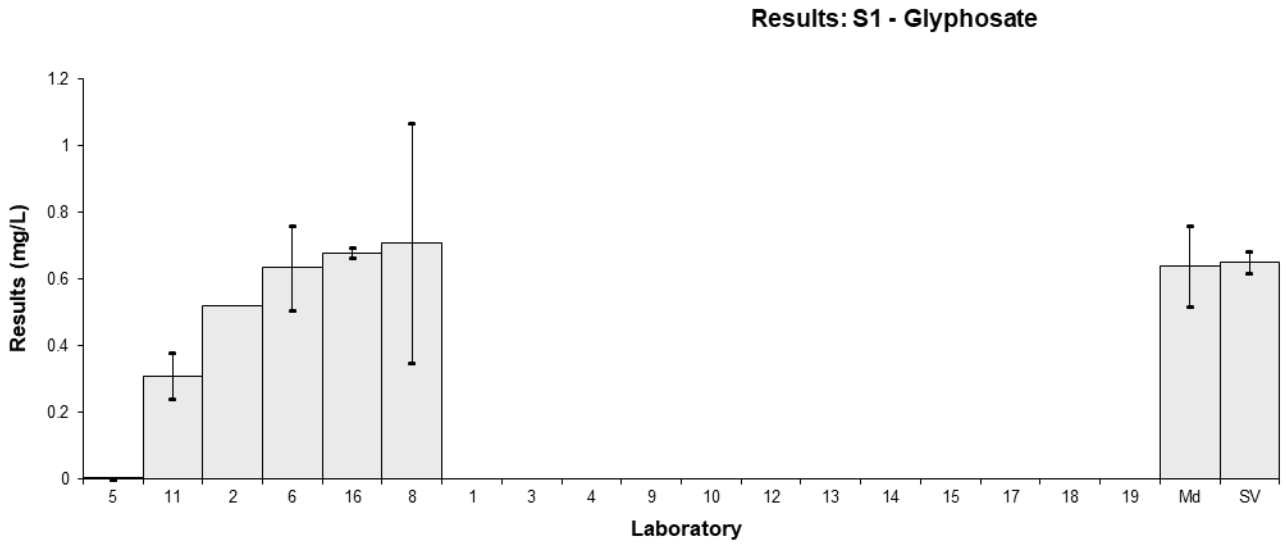

Results: S1 - Glyphosate
Results (mg/L)
1.2
1
0.8
0.6
0.4
0.2
0
5
11
2
6
16
8
1
3
4
9
10
12
13
14
15
17
18
19
Md
SV
Laboratory

Figure 5

Table 10

Sample Details

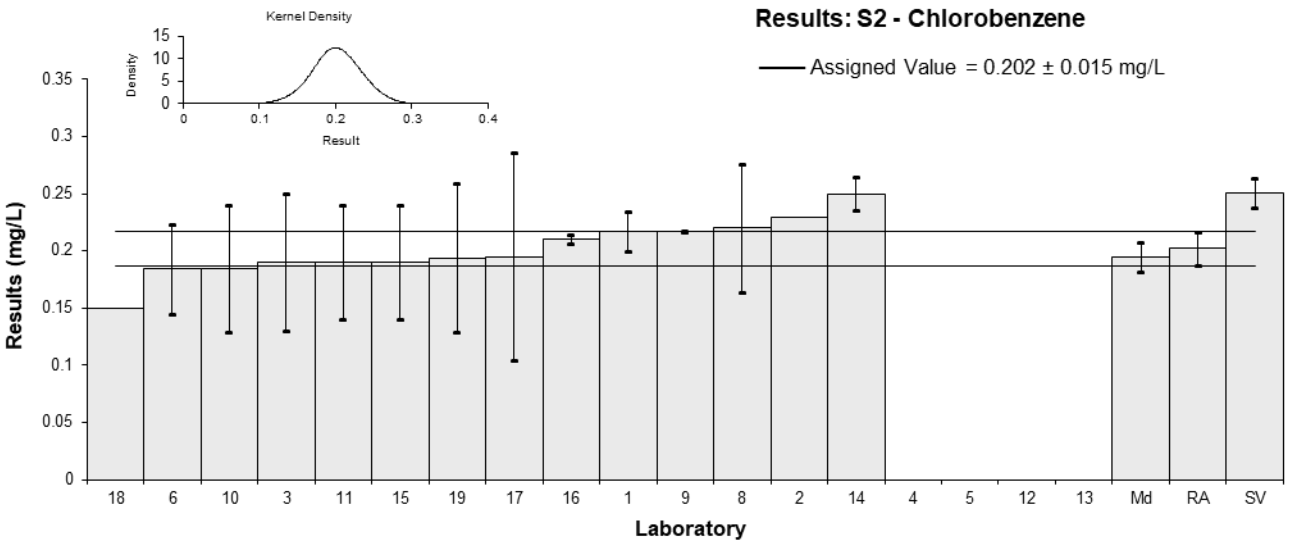
Sample	S2
Analyte	Chlorobenzene
Matrix	Potable Water
Unit	mg/L

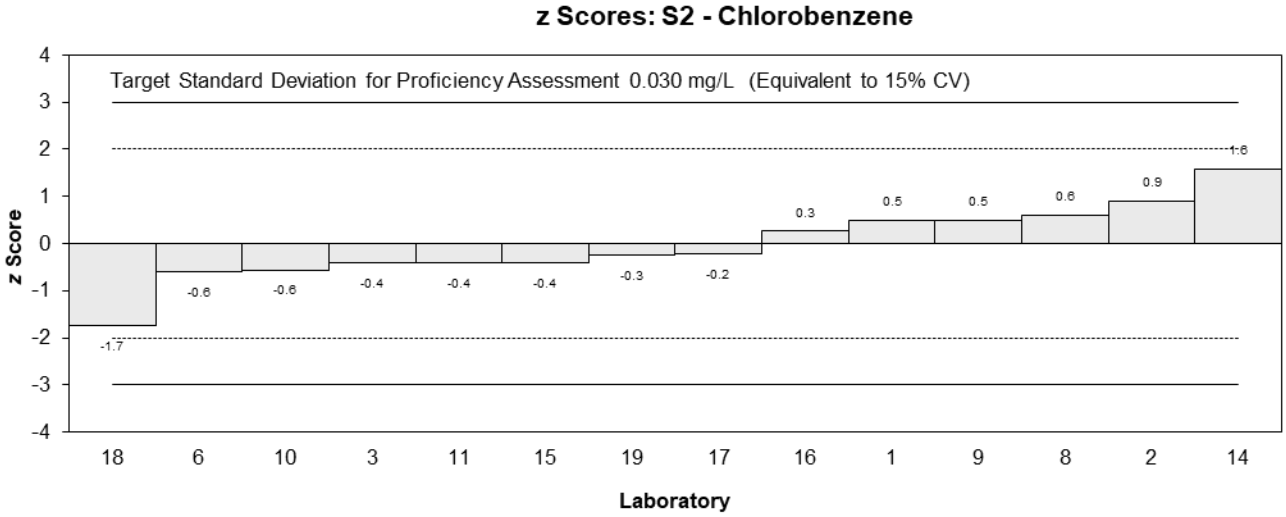
Participant Results

Lab. Code	Result	U	z	E_n
1	0.217	0.017	0.50	0.66
2	0.229	NR	0.89	1.80
3	0.19	0.06	-0.40	-0.19
4	NT	NT		
5	NT	NT		
6	0.184	0.039	-0.59	-0.43
8	0.22	0.056	0.59	0.31
9	0.217	0.00009	0.50	1.00
10	0.185	0.0555	-0.56	-0.30
11	0.19	0.05	-0.40	-0.23
12	NT	NT		
13	NT	NT		
14	0.25	0.015	1.58	2.26
15	0.19	0.05	-0.40	-0.23
16	0.21	0.0042	0.26	0.51
17	0.195	0.091	-0.23	-0.08
18	0.1493	NR	-1.74	-3.51
19	0.194	0.065	-0.26	-0.12

Statistics

Assigned Value	0.202	0.015
Spiked Value	0.251	0.013
Robust Average	0.202	0.015
Median	0.195	0.013
Mean	0.201	0.013
N	14	
Max	0.25	
Min	0.1493	
Robust SD	0.022	
Robust CV	11%	


Results: S2 - Chlorobenzene
Assigned Value = 0.202 ± 0.015 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
18 6 10 3 11 15 19 17 16 1 9 8 2 14 4 5 12 13 Md RA SV


z Scores: S2 - Chlorobenzene
Target Standard Deviation for Proficiency Assessment 0.030 mg/L (Equivalent to 15% CV)
z Score
Laboratory
18 6 10 3 11 15 19 17 16 1 9 8 2 14
-1.7 -0.6 -0.6 -0.4 -0.4 -0.4 -0.3 -0.2 0.3 0.5 0.5 0.6 0.9 1.6

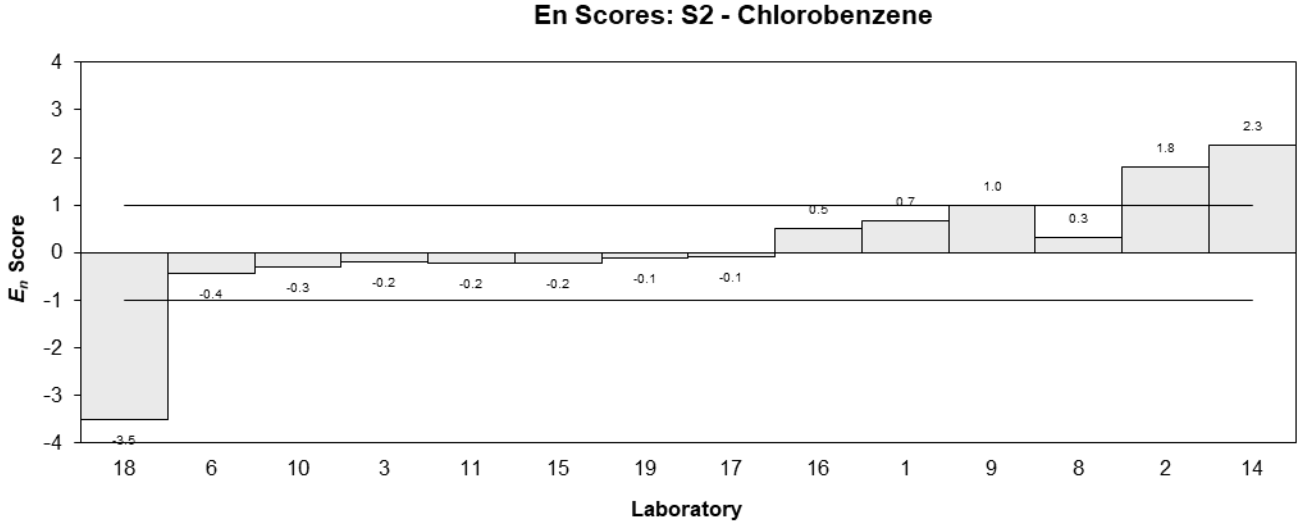

En Scores: S2 - Chlorobenzene
En Score
Laboratory
18 6 10 3 11 15 19 17 16 1 9 8 2 14
-3.5 -0.4 -0.3 -0.2 -0.2 -0.2 -0.1 -0.1 0.5 0.7 1.0 0.3 1.8 2.3

Figure 6

Table 11

Sample Details

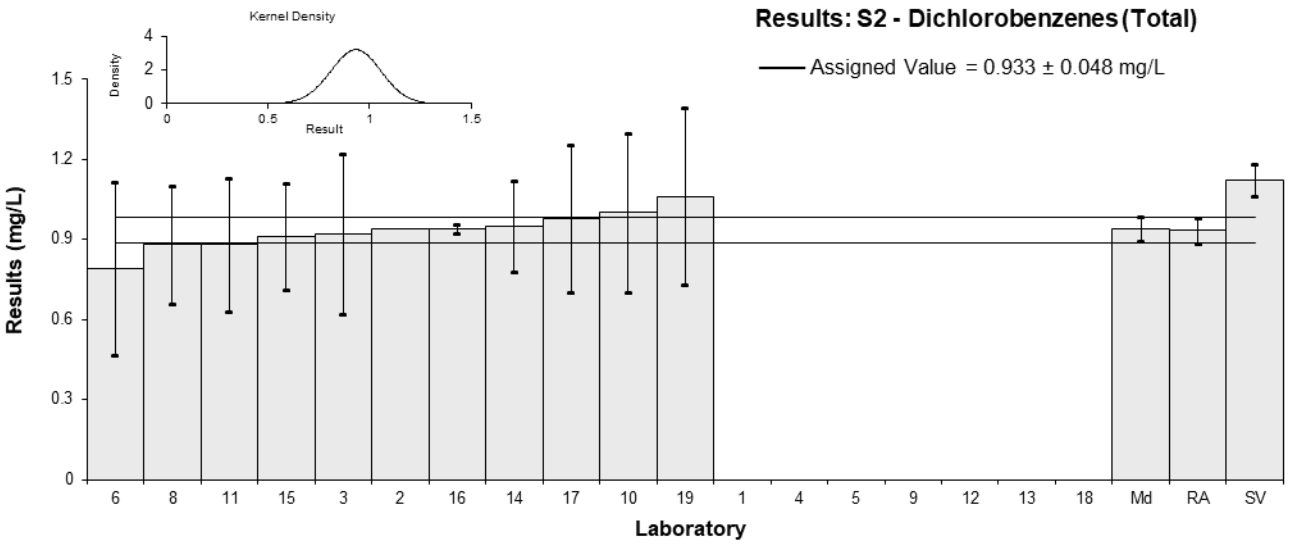
Sample	S2
Analyte	Dichlorobenzenes (Total)
Matrix	Potable Water
Unit	mg/L

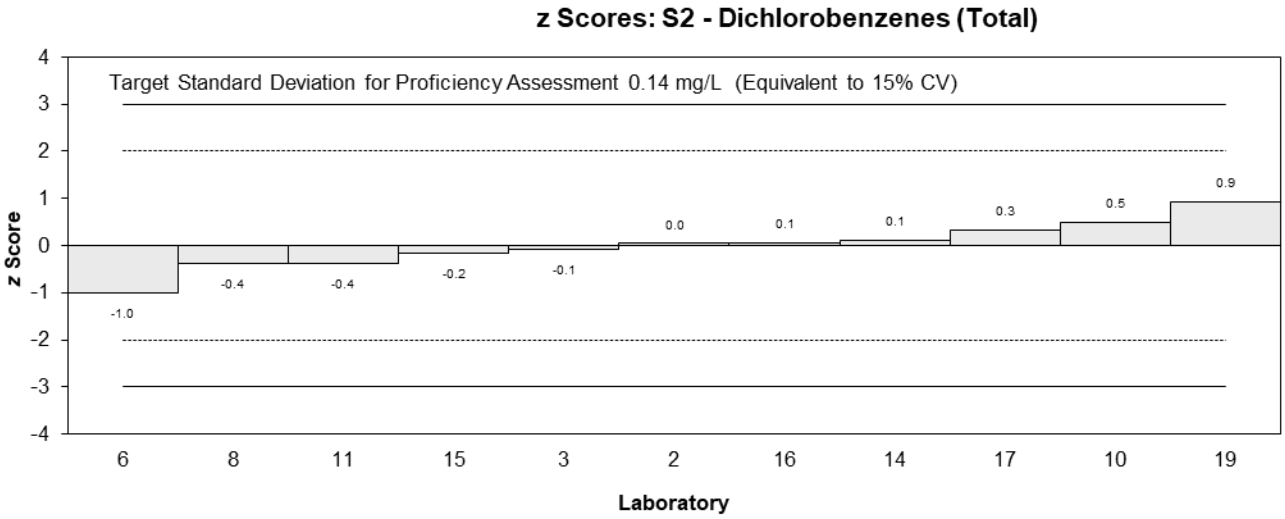
Participant Results

Lab. Code	Result	U	z	E_n
1	NT	NT		
2	0.939	NR	0.04	0.12
3	0.92	0.3	-0.09	-0.04
4	NT	NT		
5	NT	NT		
6	0.792	0.325	-1.01	-0.43
8	0.88	0.22	-0.38	-0.24
9	NR	NR		
10	1	0.3	0.48	0.22
11	0.88	0.25	-0.38	-0.21
12	NT	NT		
13	NT	NT		
14	0.95	0.17	0.12	0.10
15	0.91	0.2	-0.16	-0.11
16	0.94	0.0188	0.05	0.14
17	0.978	0.274	0.32	0.16
18	NT	NT		
19	1.062	0.331	0.92	0.39

Statistics

Assigned Value	0.933	0.048
Spiked Value	1.12	0.06
Robust Average	0.933	0.048
Median	0.939	0.044
Mean	0.932	0.043
N	11	
Max	1.062	
Min	0.792	
Robust SD	0.063	
Robust CV	6.8%	


Results: S2 - Dichlorobenzenes (Total)
Assigned Value = 0.933 ± 0.048 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6 8 11 15 3 2 16 14 17 10 19 1 4 5 9 12 13 18 Md RA SV


z Scores: S2 - Dichlorobenzenes (Total)
Target Standard Deviation for Proficiency Assessment 0.14 mg/L (Equivalent to 15% CV)
z Score
-1.0 -0.4 -0.4 -0.2 -0.1 0.0 0.1 0.1 0.3 0.5 0.9
Laboratory
6 8 11 15 3 2 16 14 17 10 19

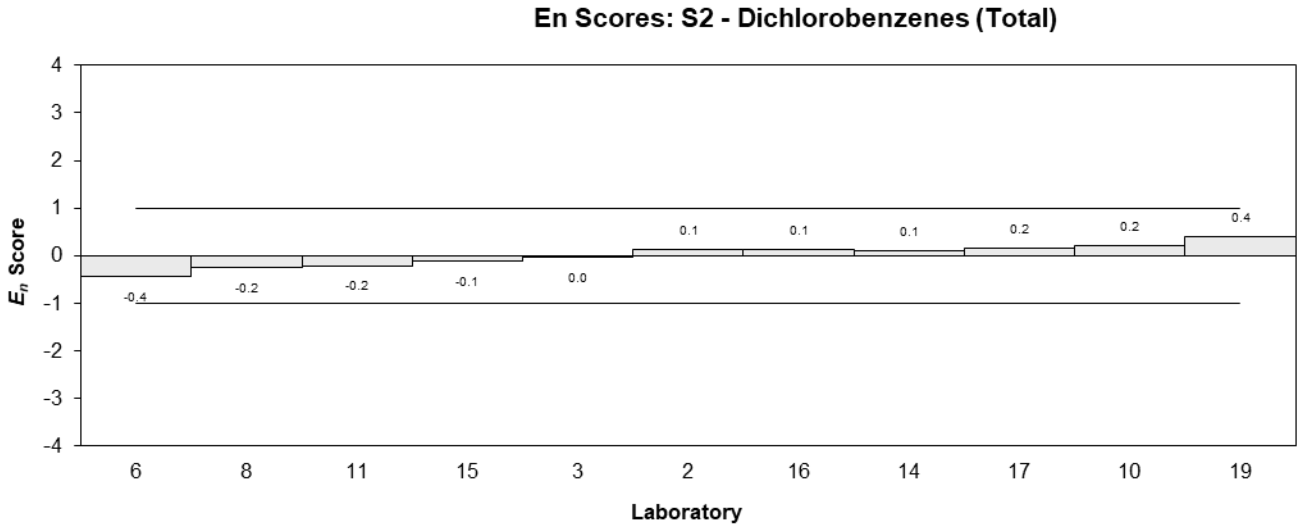

En Scores: S2 - Dichlorobenzenes (Total)
En Score
-0.4 -0.2 -0.2 -0.1 0.0 0.1 0.1 0.1 0.2 0.2 0.4
Laboratory
6 8 11 15 3 2 16 14 17 10 19

Figure 7

Table 12

Sample Details

Sample	S2
Analyte	Dichloromethane
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U
1	<0.005	NR
2	NT	NT
3	<0.004	NR
4	NT	NT
5	NT	NT
6	0.00347	0.0007
8**	0.0003	0.00006
9	NR	NR
10	NT	NT
11	0.006	0.002
12	NT	NT
13	NT	NT
14	0.004	0.0004
15	<0.01	NR
16	<0.005	NR
17	<0.005	NR
18	NT	NT
19	<0.010	0.0067

** Gross Error (after the interim report was released, the participant reported that the result should instead be 0.003).

Statistics

Assigned Value	Not Set	
Spiked Value	0.00407	0.00020
Median	0.0040	0.0011
Mean	0.0045	0.0015
N	3	
Max	0.006	
Min	0.00347	
Robust SD	0.0015	
Robust CV	34%	

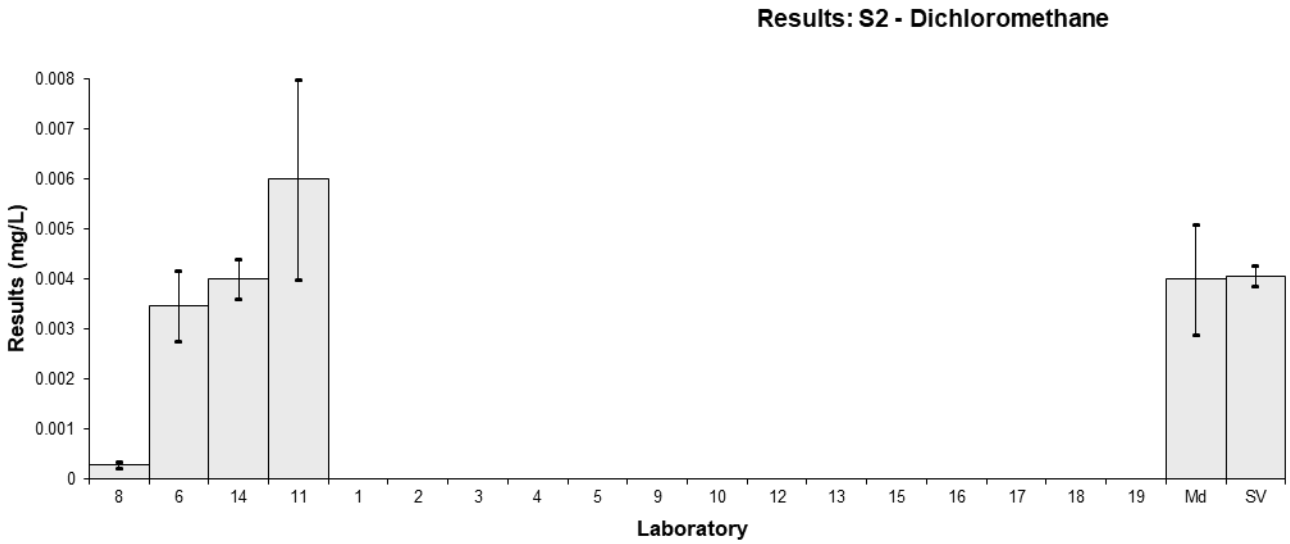

Results: S2 - Dichloromethane
Results (mg/L)
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
8
6
14
11
1
2
3
4
5
9
10
12
13
15
16
17
18
19
Md
SV
Laboratory

Figure 8

Table 13

Sample Details

Sample	S2
Analyte	Toluene
Matrix	Potable Water
Unit	mg/L

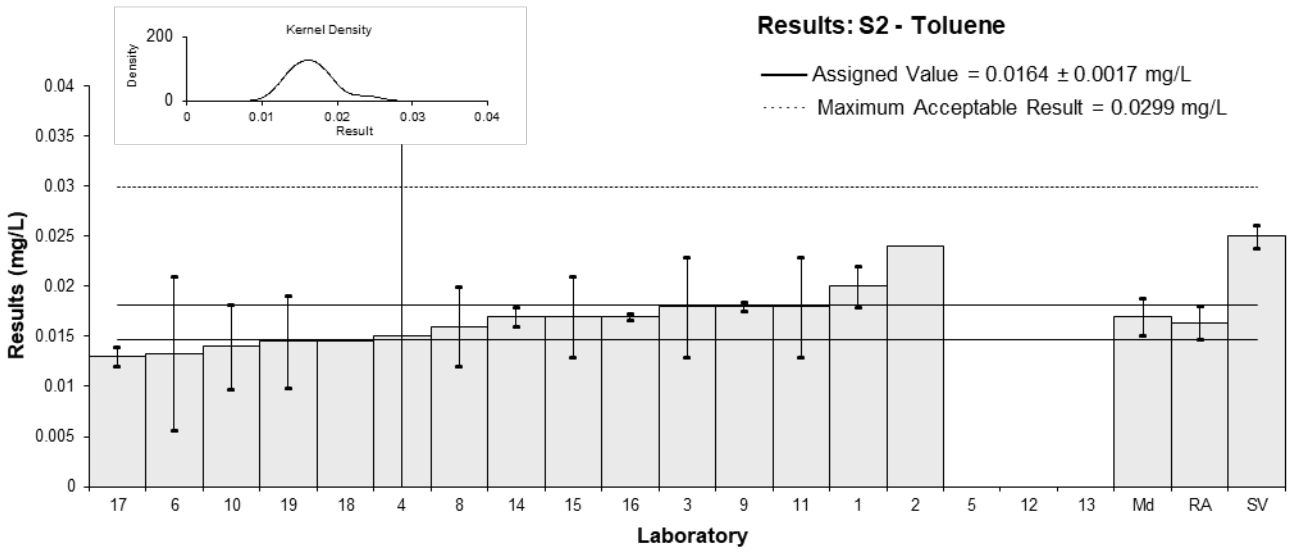
Participant Results

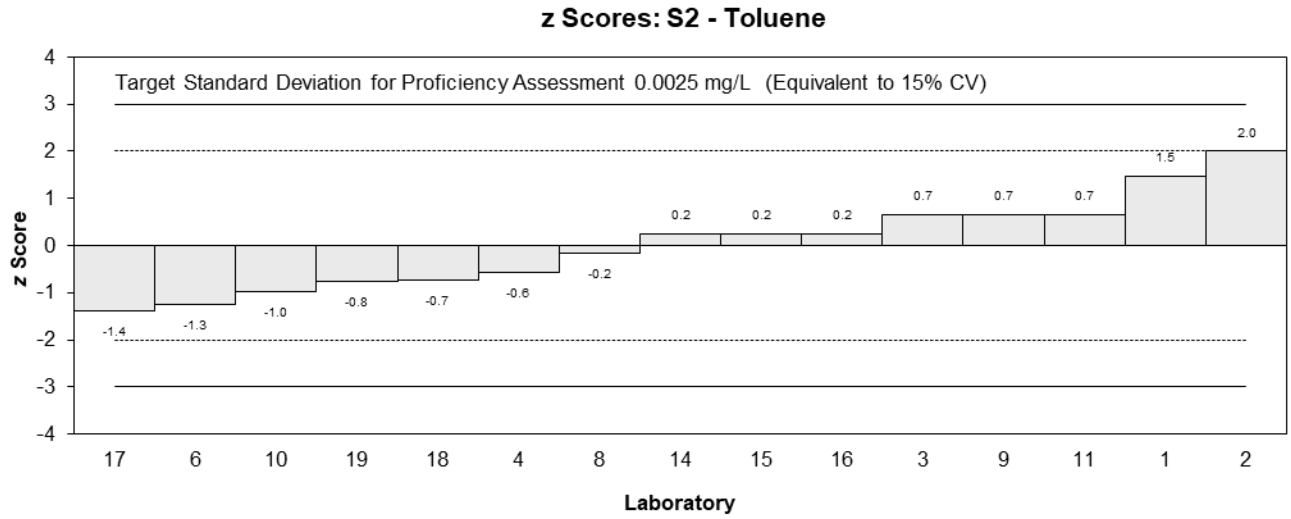
Lab. Code	Result	U	z	E_n
1	0.020	0.002	1.46	1.37
2	0.024	NR	2.00▼	1.00▼
3	0.018	0.005	0.65	0.30
4	0.015	0.05	-0.57	-0.03
5	NT	NT		
6	0.0133	0.0077	-1.26	-0.39
8	0.016	0.004	-0.16	-0.09
9	0.018	0.0005	0.65	0.90
10	0.014	0.0042	-0.98	-0.53
11	0.018	0.005	0.65	0.30
12	NT	NT		
13	NT	NT		
14	0.017	0.001	0.24	0.30
15	0.017	0.004	0.24	0.14
16	0.017	0.00034	0.24	0.35
17	0.013	0.001	-1.38	-1.72
18	0.0146	NR	-0.73	-1.06
19	0.0145	0.0046	-0.77	-0.39

▼ Adjusted score

Statistics

Assigned Value	0.0164	0.0017
Spiked Value	0.0250	0.0012
Robust Average	0.0164	0.0017
Max Acceptable Result	0.0299	
Median	0.0170	0.0019
Mean	0.0166	0.0015
N	15	
Max	0.024	
Min	0.013	
Robust SD	0.0026	
Robust CV	16%	


Results: S2 - Toluene
Assigned Value = 0.0164 ± 0.0017 mg/L
Maximum Acceptable Result = 0.0299 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17 6 10 19 18 4 8 14 15 16 3 9 11 1 2 5 12 13 Md RA SV


z Scores: S2 - Toluene
Target Standard Deviation for Proficiency Assessment 0.0025 mg/L (Equivalent to 15% CV)
z Score
Laboratory
17 6 10 19 18 4 8 14 15 16 3 9 11 1 2
-1.4 -1.3 -1.0 -0.8 -0.7 -0.6 -0.2 0.2 0.2 0.2 0.7 0.7 0.7 1.5 2.0

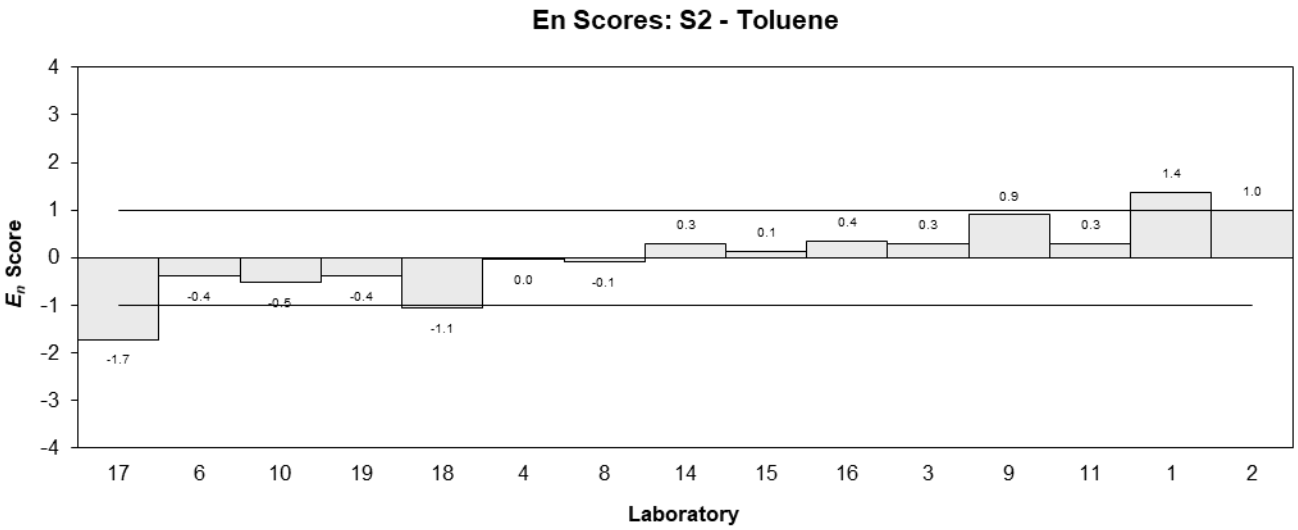

En Scores: S2 - Toluene
En Score
Laboratory
17 6 10 19 18 4 8 14 15 16 3 9 11 1 2
-1.7 -0.4 -0.5 -0.4 -1.1 0.0 -0.1 0.3 0.1 0.4 0.3 0.9 0.3 1.4 1.0

Figure 9

Table 14

Sample Details

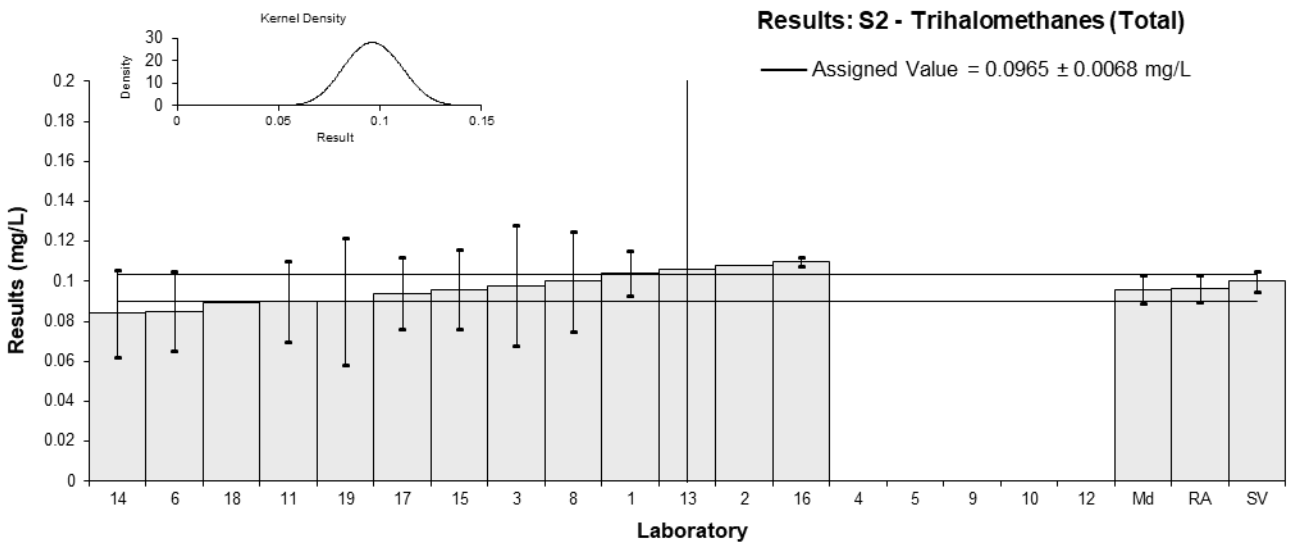
Sample	S2
Analyte	Trihalomethanes (Total)
Matrix	Potable Water
Unit	mg/L

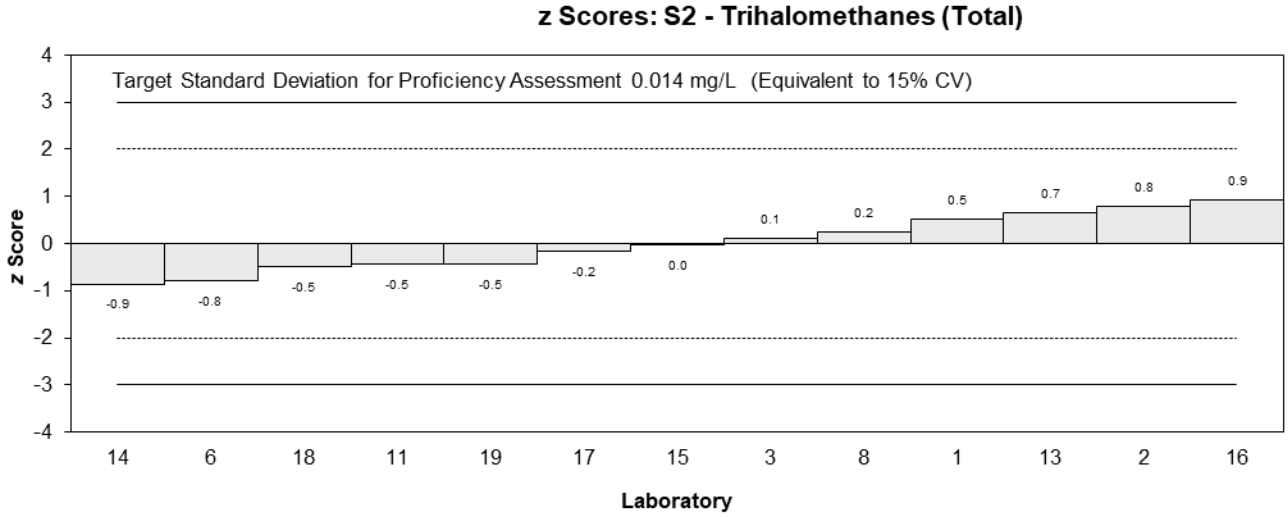
Participant Results

Lab. Code	Result	U	z	E_n
1	0.104	0.011	0.52	0.58
2	0.108	NR	0.79	1.69
3	0.098	0.03	0.10	0.05
4	NT	NT		
5	NT	NT		
6	0.085	0.02	-0.79	-0.54
8	0.1	0.025	0.24	0.14
9	NR	NR		
10	NT	NT		
11	0.09	0.02	-0.45	-0.31
12	NT	NT		
13	0.106	0.23	0.66	0.04
14	0.084	0.022	-0.86	-0.54
15	0.096	0.02	-0.03	-0.02
16	0.11	0.0022	0.93	1.89
17	0.094	0.018	-0.17	-0.13
18	0.0893	NR	-0.50	-1.06
19	0.09	0.032	-0.45	-0.20

Statistics

Assigned Value	0.0965	0.0068
Spiked Value	0.100	0.005
Robust Average	0.0965	0.0068
Median	0.0960	0.0069
Mean	0.0965	0.0048
N	13	
Max	0.11	
Min	0.084	
Robust SD	0.0099	
Robust CV	10%	


Results: S2 - Trihalomethanes (Total)
Assigned Value = 0.0965 ± 0.0068 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
14 6 18 11 19 17 15 3 8 1 13 2 16 4 5 9 10 12 Md RA SV


z Scores: S2 - Trihalomethanes (Total)
Target Standard Deviation for Proficiency Assessment 0.014 mg/L (Equivalent to 15% CV)
z Score
-0.9 -0.8 -0.5 -0.5 -0.5 -0.2 0.0 0.1 0.2 0.5 0.7 0.8 0.9
Laboratory
14 6 18 11 19 17 15 3 8 1 13 2 16

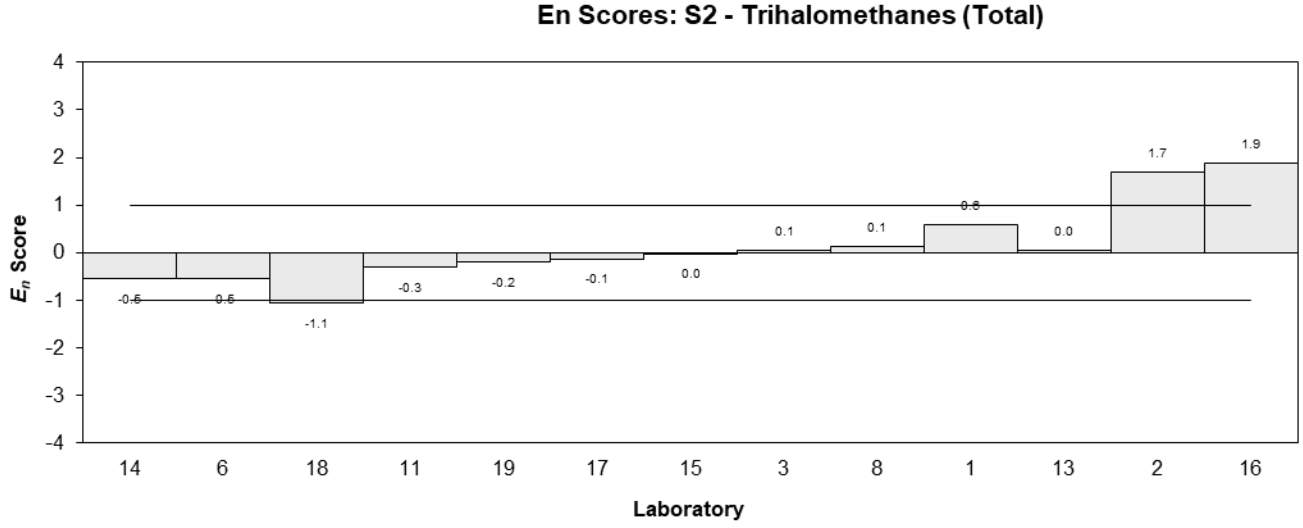

En Scores: S2 - Trihalomethanes (Total)
En Score
-0.5 -0.5 -1.1 -0.3 -0.2 -0.1 0.0 0.1 0.1 0.6 0.0 1.7 1.9
Laboratory
14 6 18 11 19 17 15 3 8 1 13 2 16

Figure 10

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages of participants' results were used as the assigned values for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2022.[6] Results less than 50% and greater than 150% of the robust average were removed before the calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using 2,4-D in Sample S1 as an example.

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

No assigned value was set for Sample S1 aldicarb and glyphosate, and Sample S2 dichloromethane, as there were too few reported numeric results. However, participants may still compare their results for these 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 15.

For scored analytes excluding Sample S2 toluene, assigned values were within the range of 80% to 97% of the spiked values, providing good support for the assigned values. For Sample S2 toluene, the assigned value was 66% of the spiked value, however there was reasonable consensus between participants' results and so this analyte was scored.

Table 15 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	Aldicarb	*(0.00621)*	0.00690	*(90)*
	Atrazine	0.0212	0.0242	88
	2,4-D	0.0671	0.0699	96
	Glyphosate	*(0.57)*	0.651	*(88)*
S2	Chlorobenzene	0.202	0.251	80
	Dichlorobenzenes (Total)	0.933	1.12	83
	Dichloromethane	*(0.0045)*	0.00407	*(111)*
	Toluene	0.0164	0.0250	66
	Trihalomethanes (Total)	0.0965	0.100	97

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 97 numeric results submitted for the analytes of interest in this study, 85 (88%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 4). One participant reported using the NATA Technical Note 33 as their guide; NATA no longer publishes this document.[10]

Laboratories **2** and **18** did not report uncertainties for any of their numeric results, despite reporting that they were accredited to ISO/IEC 17025.

The magnitude of reported uncertainties was within the range of 0.04% to 425% 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 85 MUs reported for this study, 20 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.

Laboratory **9** reported significantly different relative uncertainties for their numeric results, being 0.04%, 3% and 425%. Laboratories **4** and **13** both reported a result with a very large relative uncertainty (333% and 217% respectively). Participants should ensure that they have reported their uncertainties with the correct units.

Uncertainties associated with results returning a satisfactory *z* score but an unsatisfactory 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 1.062 ± 0.331 mg/L, it is better to report this as 1.06 ± 0.33 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 for scored analytes are presented for comparison in Table 16.

Table 16 Comparison of Thompson-Horwitz CV, Target SD and Between-Laboratory CV

Sample	Analyte	Assigned Value (mg/L)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between-Laboratory CV* (%)
S1	Atrazine	0.0212	22	15	17
	2,4-D	0.0671	22	15	17
S2	Chlorobenzene	0.202	20	15	11
	Dichlorobenzenes (Total)	0.933	16	15	6.8
	Toluene	0.0164	22	15	16
	Trihalomethanes (Total)	0.0965	22	15	10

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

To account for possible low bias in the consensus value due to participants using inefficient extraction or analytical techniques, one *z* score was adjusted in Sample S2 toluene. A maximum acceptable result was set to two target SDs more than the spiked value, and any result lower than the maximum acceptable result but with a *z* score greater than 2.0 had their *z* score adjusted to 2.0. This ensured that any participants reporting results close to the spiked value were not penalised. *z* Scores for results greater than the maximum acceptable result were not adjusted, and *z* scores less than 2.0 were left unaltered.

Of 81 results for which *z* scores were calculated, 77 (95%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **2**, **6**, **8**, **11**, **15**, **16**, **17** and **19** reported numeric results for all six scored analytes. Of these participants, Laboratories **2**, **6**, **15**, **16**, **17** and **19** returned satisfactory *z* scores for all analytes.

Satisfactory *z* scores were achieved for all scored analytes reported by Laboratories **3** (5), **10** (5), **14** (5), **1** (4), **18** (4), **4** (3), **5** (2) and **13** (1).

Laboratory **12** reported one numeric result and returned an unsatisfactory *z* score for this.

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

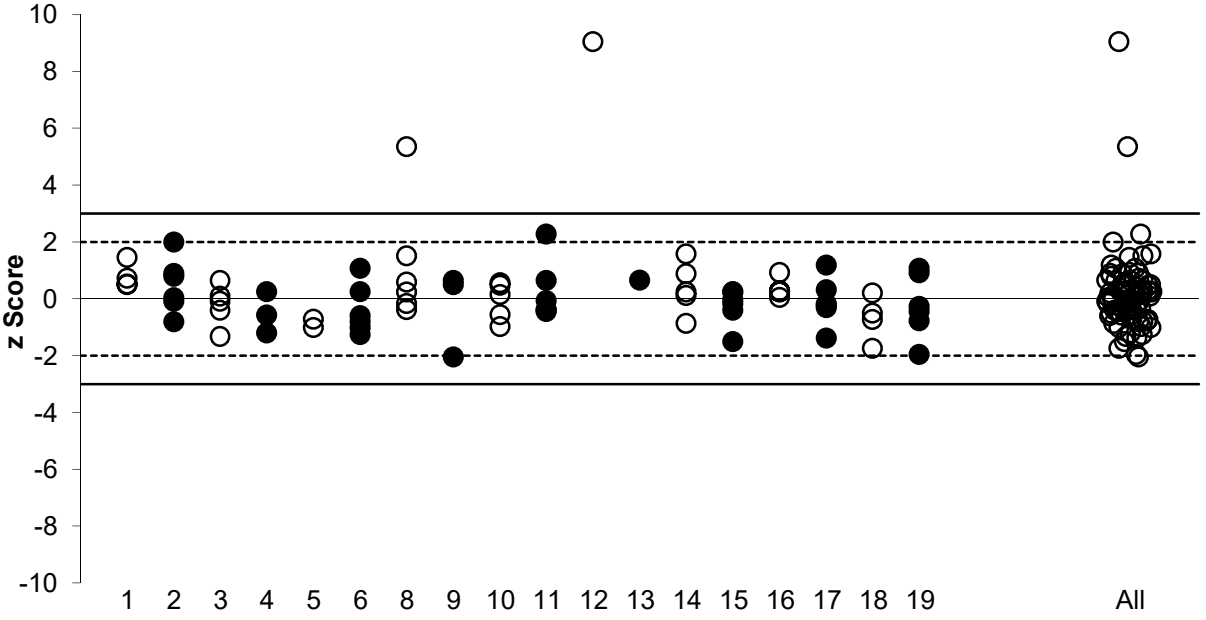


Figure 11 *z* Score Dispersal by Laboratory

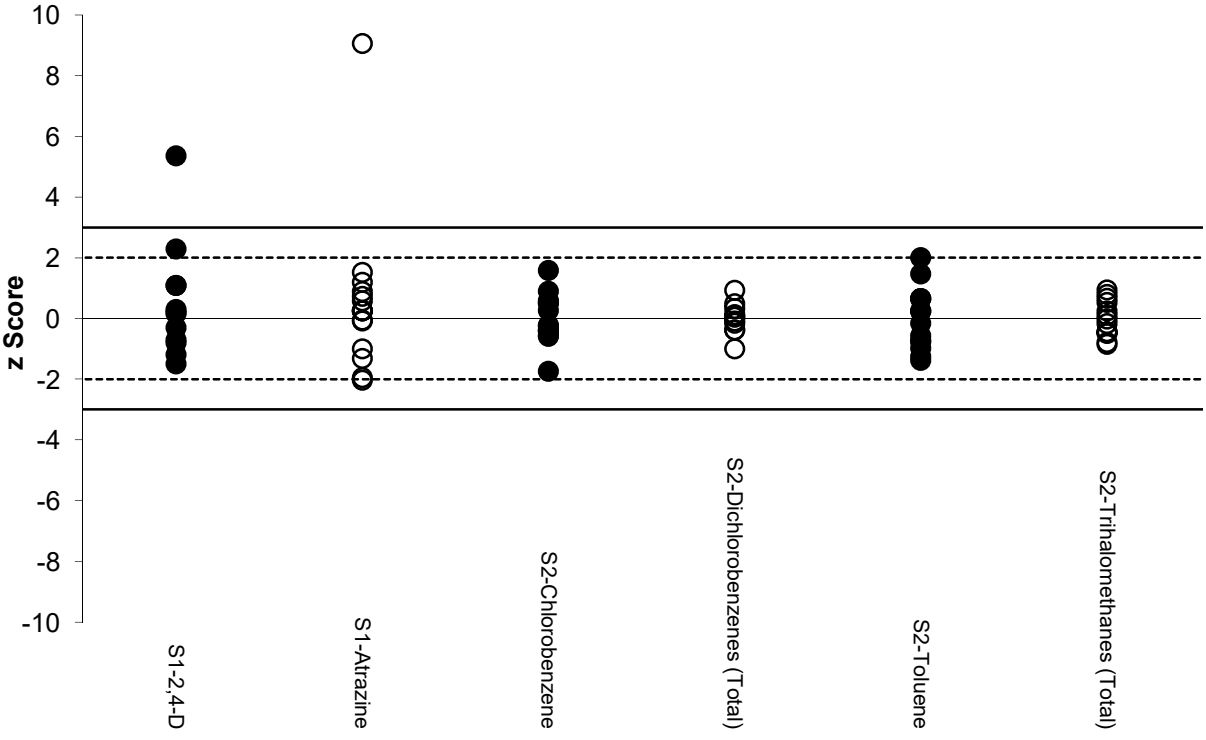


Figure 12 *z* Score Dispersal by Analyte

6.4 E_n Score

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

Of 81 results for which E_n scores were calculated, 70 (86%) returned a score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories **6**, **8**, **15** and **19** returned satisfactory E_n scores for all six scored analytes.

Satisfactory E_n scores were achieved for all scored analytes reported by Laboratories **3** (5), **10** (5), **4** (3), **9** (3), and **5** (2).

Laboratory **13** did return a satisfactory E_n score for their one numeric result reported, however this had an unrealistically large uncertainty (217% relative).

Laboratory **12** did not achieve a satisfactory E_n score.

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

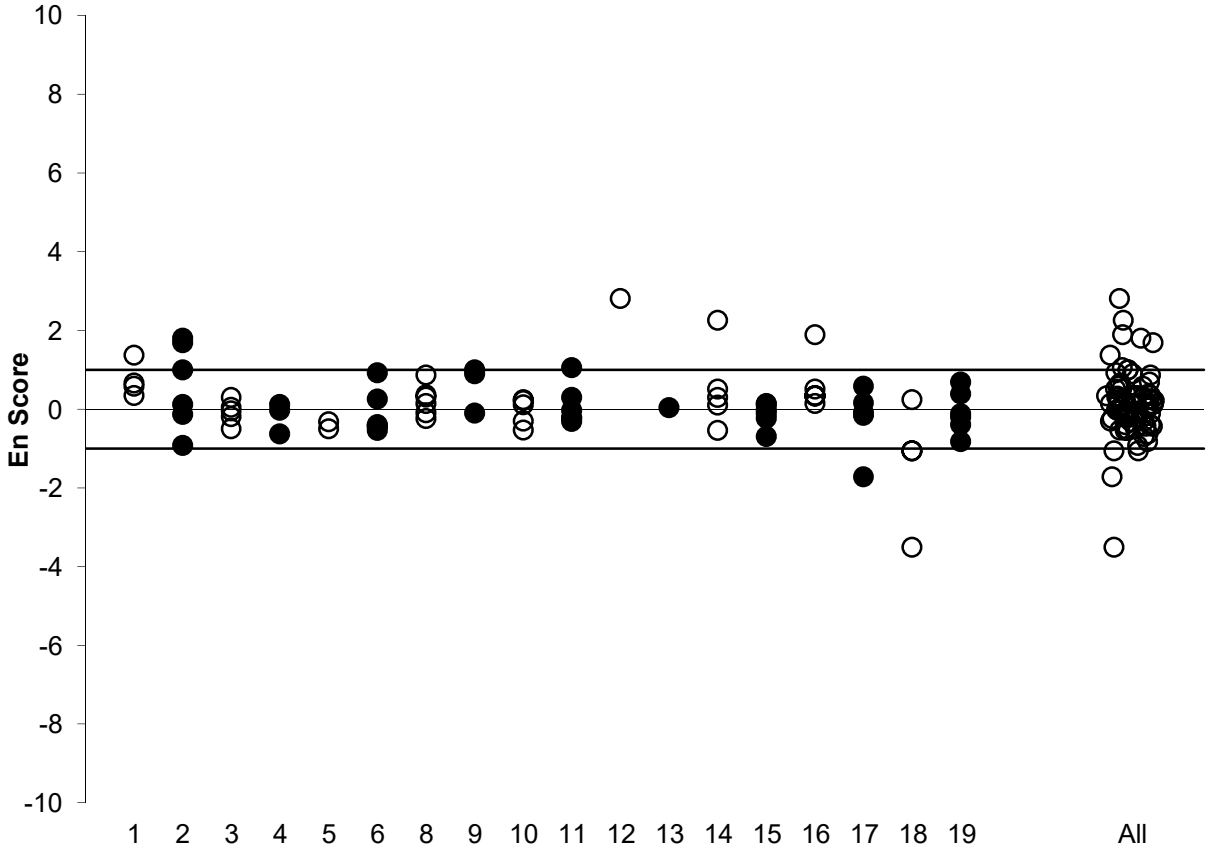


Figure 13 E_n Score Dispersal by Laboratory

6.5 False Negatives

Table 17 presents false negative results. These are analytes present in the samples which a participant tested for, but did not report a numeric result (for example, participants reporting a 'less than' result ($< x$) when the assigned value was higher than their limit of reporting (LOR), or participants that did not report anything). For analytes where no assigned value was set, results have only been considered to be false negatives where the robust average and spiked value were significantly higher than the participants' LOR, or if no value was reported.

Table 17 False Negatives

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (mg/L)	Spiked Value (mg/L)	Result* (mg/L)
9	S1	Aldicarb	*(0.00621)*	0.0069	NR
		2,4-D	0.0671	0.0699	NR
		Glyphosate	*(0.57)*	0.651	NR
	S2	Dichlorobenzenes (Total)	0.933	1.12	NR
		Dichloromethane	*(0.0045)*	0.00407	NR
		Trihalomethanes (Total)	0.0965	0.1	NR

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

6.6 Reporting of Additional Analytes

Analytes reported by participants which were not spiked into the test samples are presented in Table 18. In general, participants should take care to avoid any potential cross-contamination when analysing their samples.

Laboratories **2**, **8** and **11** reported simazine and/or propazine at low levels in Sample S1; these may have been trace impurities in the atrazine standard used to spike this sample.

Table 18 Analytes Reported by Participants Not Spiked in the Test Samples

Lab. Code	Sample	Analyte	Result (mg/L)	Uncertainty (mg/L)
2	S1	Simazine	0.00005	NR
		Propazine	0.00013	NR
8	S1	Simazine	0.00006	0.00003
11	S1	Propazine	0.00014	NR
	S2	Chloroform*	0.087	0.022
14	S2	Trichlorobenzenes (Total)	0.001	0.0001
18	S2	Benzene	0.0007	NR
19	S1	Endosulfan	0.00001	0.0000067
	S2	Trichlorobenzenes (Total)	0.0003	0.0009

* Sample S2 was spiked with chloroform, and participants were requested to report for trihalomethanes (total). Laboratory **11** reported for chloroform only also – this result is not an additional analyte, and has been presented here for information only.

6.7 Range of Organic Compounds and Pesticides Analysed by Participants

Participants were provided with a list of potential organic compounds and pesticides that could have been spiked into Samples S1 and S2, given in Tables 1 and 2 respectively. Of these, nine were spiked into the samples (Table 3). 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 19.

Laboratories **6**, **9**, **11** and **16** reported that they tested for all spiked analytes. All participants tested for at least one analyte spiked into the samples.

Of the spiked analytes in this study, atrazine was tested for by the highest proportion of participants (89%). The proportion of participants testing for each analyte in this study ranged from 39% to 89%.

Table 19 Summary of Participants' Analyses

Analyte \ Lab. Code	1	2	3	4	5	6	8	9	10	11	12	13	14	15	16	17	18	19	Proportion of Participants (%)
Aldicarb	NT	✓	NT	NT	✓	✓	NT	✓	✓	✓	NT	NT	NT	NT	✓	NT	NT	NT	39
Atrazine	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	NT	✓	89
2,4-D	NT	✓	NT	✓	✓	✓	✓	✓	✓	✓	NT	NT	NT	✓	✓	✓	✓	✓	72
Glyphosate	NT	✓	NT	NT	✓	✓	✓	✓	NT	✓	NT	NT	NT	NT	✓	NT	NT	NT	39
Chlorobenzene	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	78
Dichlorobenzenes (Total)	NT	✓	✓	NT	NT	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	✓	NT	✓	67
Dichloromethane	✓	NT	✓	NT	NT	✓	✓	✓	NT	✓	NT	NT	✓	✓	✓	✓	NT	✓	61
Toluene	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	83
Trihalomethanes (Total)	✓	✓	✓	NT	NT	✓	✓	✓	NT	✓	NT	✓	✓	✓	✓	✓	✓	✓	78
Proportion of Analytes (%)	56	89	67	33	44	100	89	100	67	100	11	11	67	78	100	78	44	78	67

6.8 Australian Drinking Water Guidelines – Organic Compounds and Pesticides

The ADWG specifies health and/or aesthetic guidelines for a number of water characteristics, including for organic compounds and pesticides.[5] Laboratories should be able to identify if a potable water sample exceeds the guideline or not. The ADWG also 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 equal to or less than the guideline value does not exceed the guideline, while any rounded value greater than the guideline value exceeds the guideline.[5] Therefore, the six analytes with assigned values in this study could be classified as either exceeding or not exceeding the relevant guideline(s).

Figures 14 to 19 show comparisons of the actual (with uncertainty) and rounded assigned value (AV) and participants' results, as well as the health (ADWG (H)) and aesthetic (ADWG (A)) guidelines where applicable. Where no numeric result or LOR was reported, and the participant did not report that the analyte was not tested for, these results have been excluded from consideration. Of the 81 results assessed, 78 (96%) correctly reflected whether the sample exceeded the guideline(s) or not. Laboratories **2**, **6**, **11**, **15**, **16** and **19** returned the correct consequence for all six analytes assessed, while Laboratories **3** (5), **10** (5), **14** (5), **1** (4), **18** (4), **4** (3), **9** (3), **5** (2) and **13** (1) returned the correct consequence for all assessed analytes they reported results for. In some cases, a participant's result returned the correct consequence, however had a very large uncertainty which spanned the guideline value.

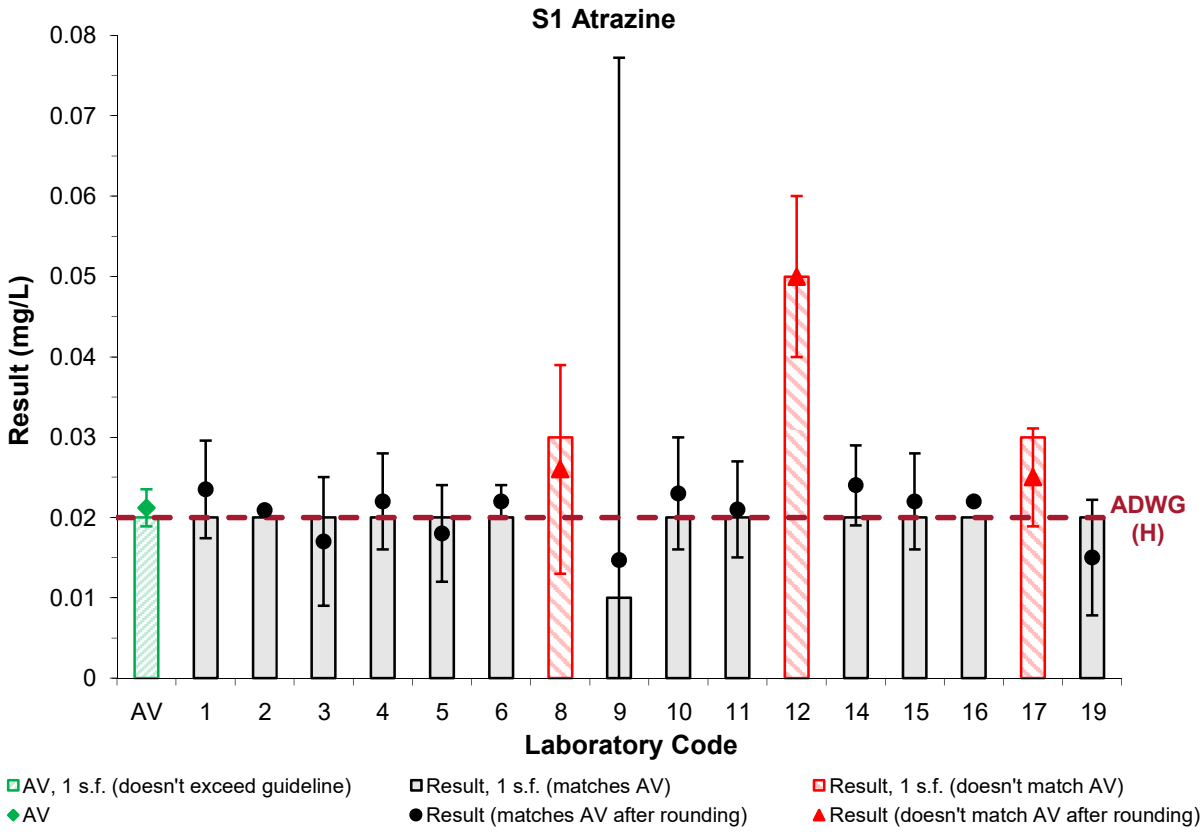


Figure 14 Sample S1 Atrazine Assigned Value, Participant Results and Guideline

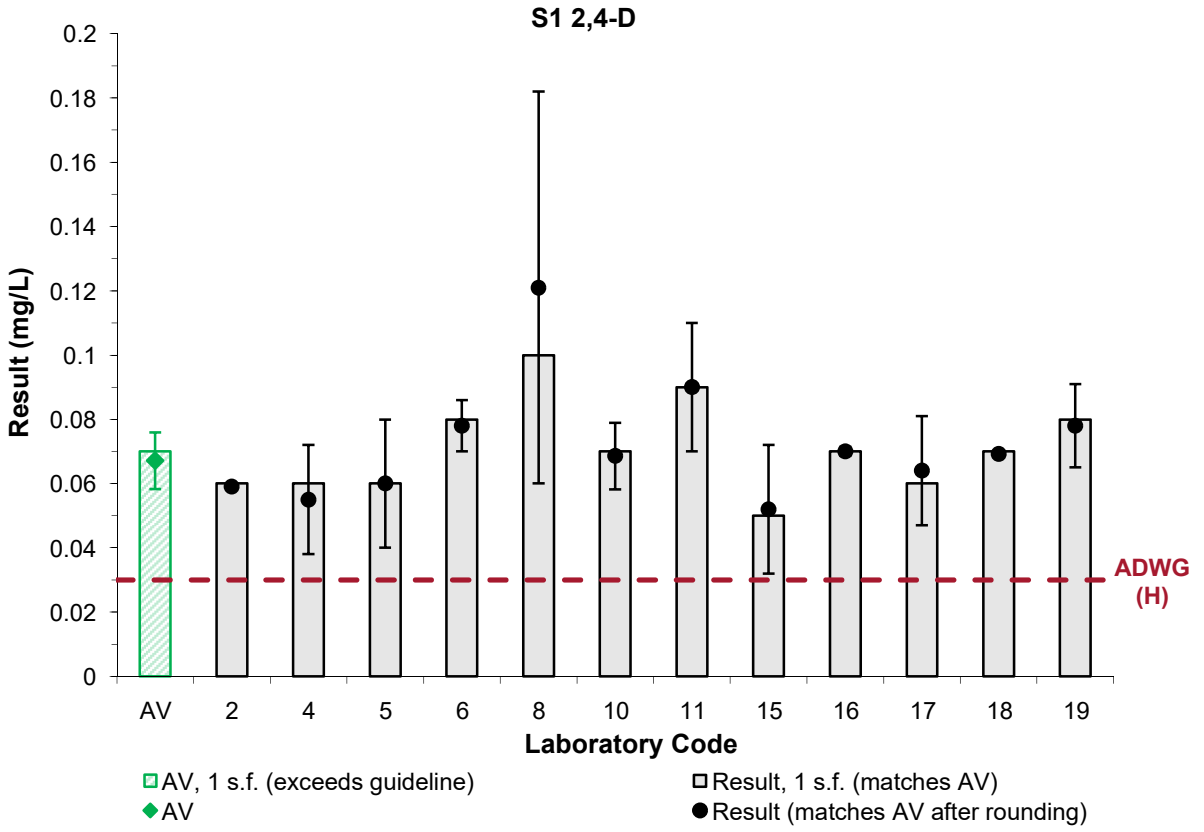


Figure 15 Sample S1 2,4-D Assigned Value, Participant Results and Guideline

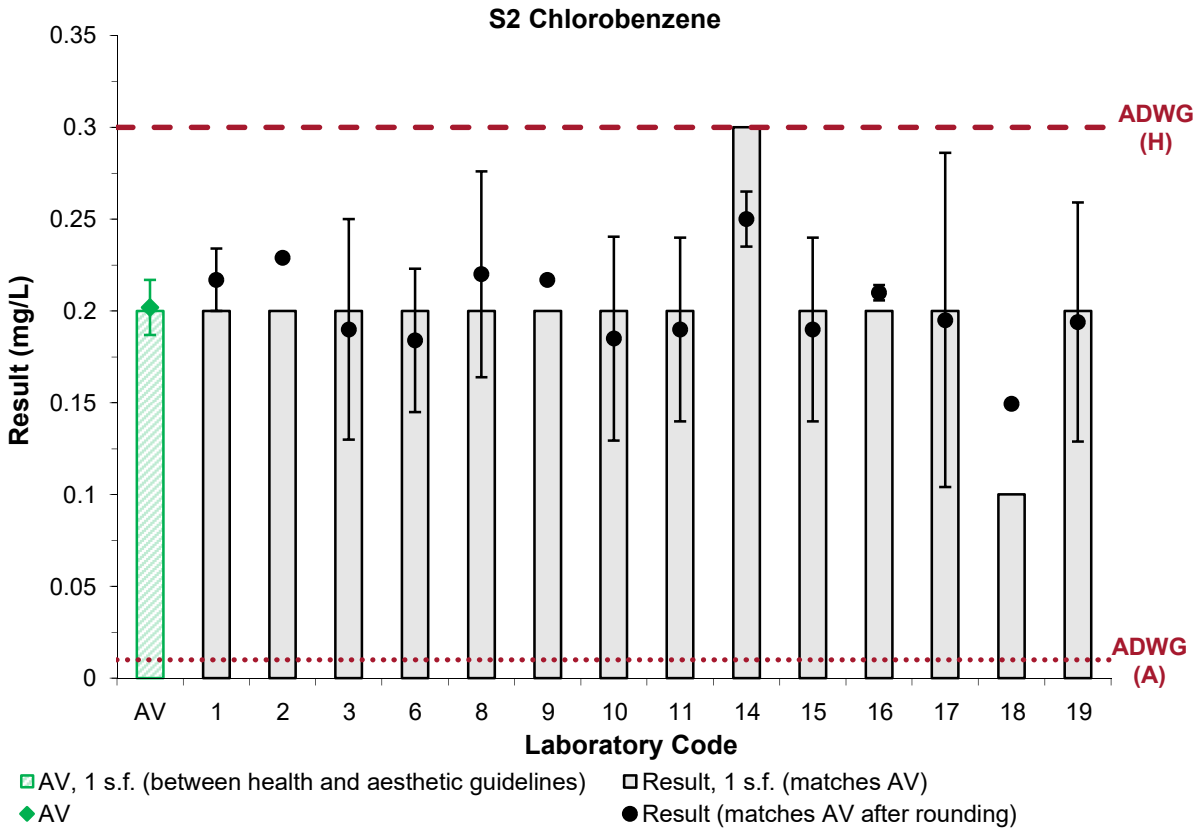
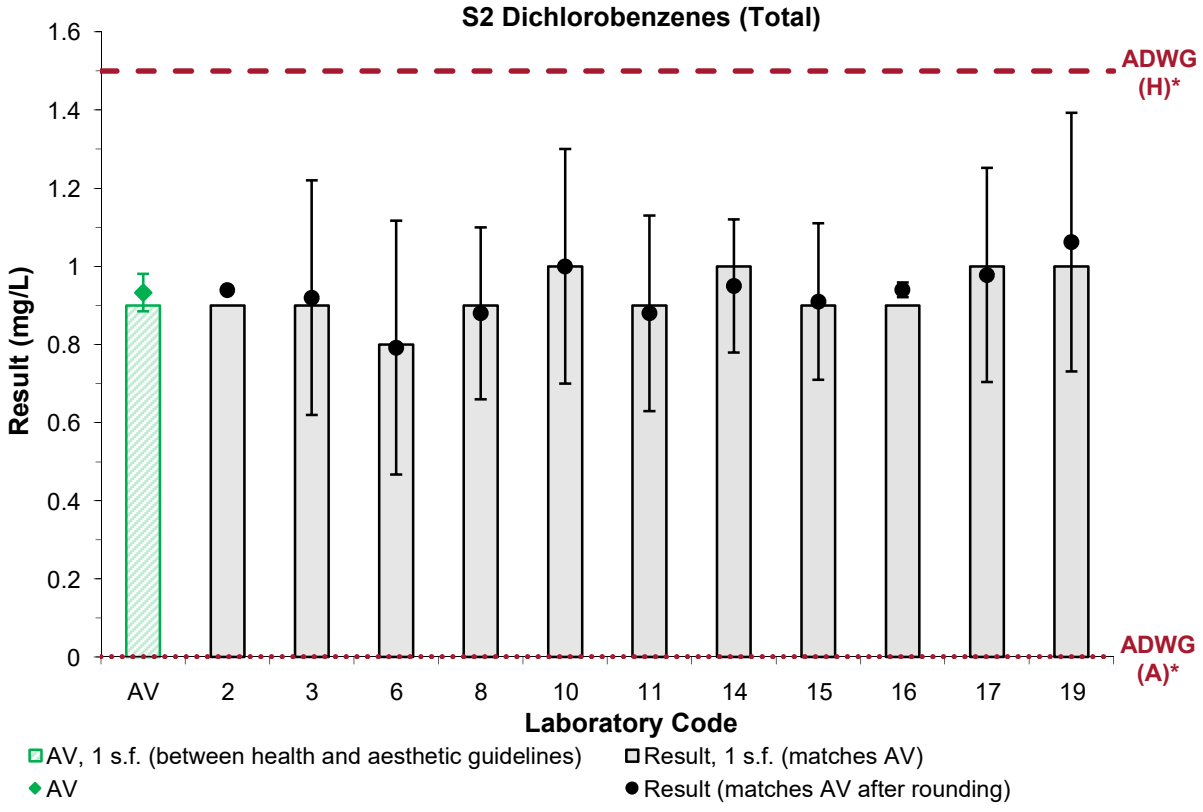
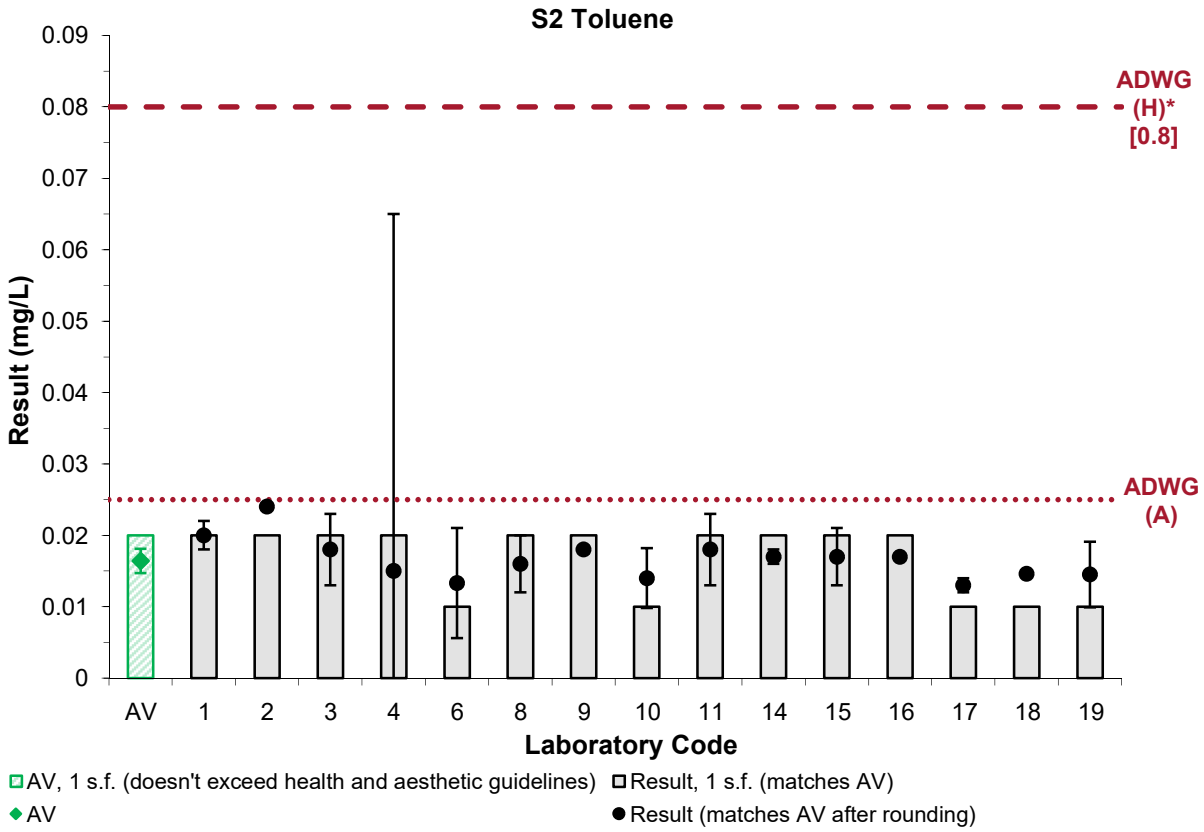


Figure 16 Sample S2 Chlorobenzene Assigned Value, Participant Results and Guideline



* Guideline levels are for 1,2-dichlorobenzene only, which Sample S2 was spiked with. Participants were requested to report dichlorobenzenes (total).

Figure 17 Sample S2 Dichlorobenzenes (Total) Assigned Value, Participant Results and Guideline



* Health guideline level has been scaled to fit on the chart, original result in brackets.

Figure 18 Sample S2 Toluene Assigned Value, Participant Results and Guideline

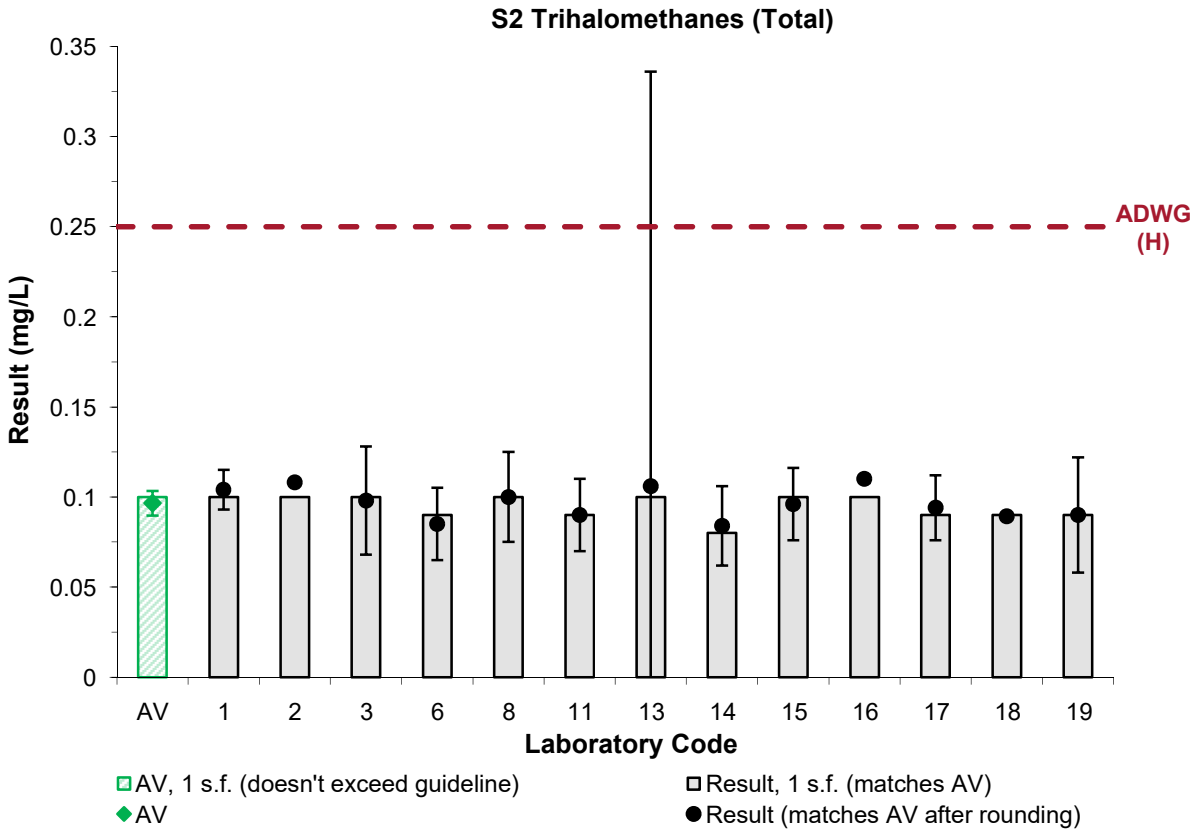


Figure 19 Sample S2 Trihalomethanes (Total) Assigned Value, Participant Results and Guideline

Sample S2 dichloromethane did not have an assigned value as there were too few numeric results returned by participants, with several participants reporting that the concentration of dichloromethane was below their LOR. The ADWG specifies a health guideline value of 0.004 mg/L for dichloromethane. Reported numeric results (excluding gross errors) ranged from 0.00347 to 0.006 mg/L, reflecting some participants' ability to analyse dichloromethane quantitatively around this concentration level. However, the reported LORs from other participants ranged from 0.004 to 0.01 mg/L, which may not be suitable for the purposes of assessing whether a sample exceeds or does not exceed the guideline value. Participants may need to review their methods to ensure that they are able to assess analytes in potable water samples at the levels specified by the relevant regulatory standards.

6.9 Participants' Analytical Methods

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

Sample S1

For Sample S1, participants were provided with 500 mL, and participants reported using test portions ranging from 0.5 mL to the whole bottle. There was no evident correlation overall between the results obtained and the reported sample volume used (comparison for scored analytes given in Figure 20).

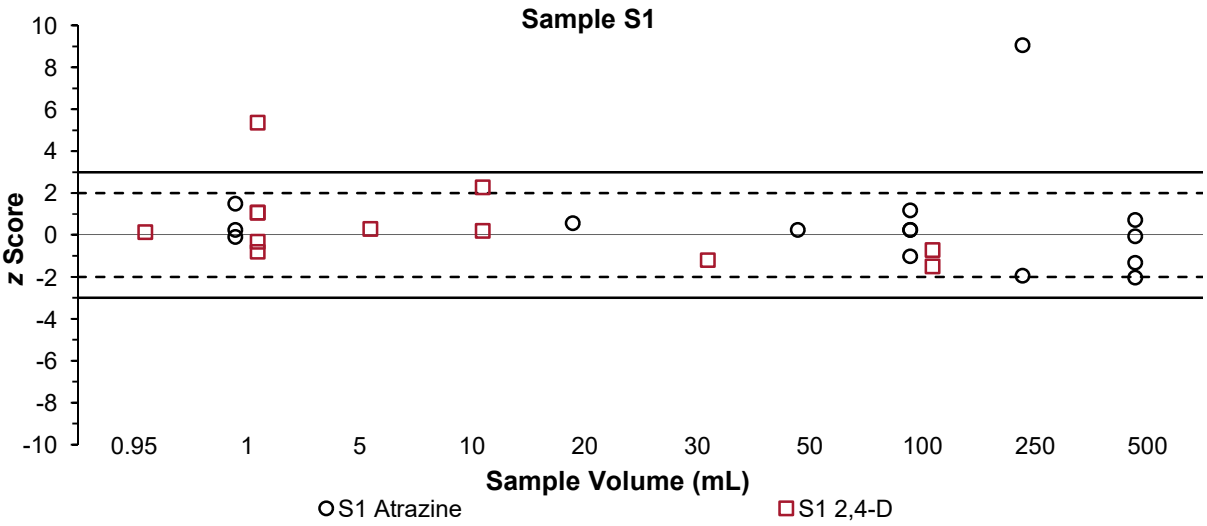


Figure 20 Sample S1 *z* Score vs Sample Volume

For the analytes in Samples S1, participants used direct injection (DI), or different extractions techniques such as liquid-liquid extraction (LLE), QuEChERS, and other solid phase extractions (SPE). For extraction solvents, participants used acetonitrile (ACN), dichloromethane (DCM), ethyl acetate (EtOAc), formic acid, methanol (MeOH), methyl *tert*-butyl ether (MTBE), toluene (TOL), or mixtures of these solvents. Several participants also reported a filtration and/or derivatisation steps for some analytes. Participants reported using liquid chromatography (LC) coupled with mass spectrometry (MS), tandem mass spectrometry (MS/MS) or fluorescence detection (FLD), and gas chromatography (GC) coupled with MS or MS/MS.

Plots of numeric results and methodology employed (extraction technique, extraction solvent and measurement instrument) for scored analytes are presented in Figures 21 and 22.

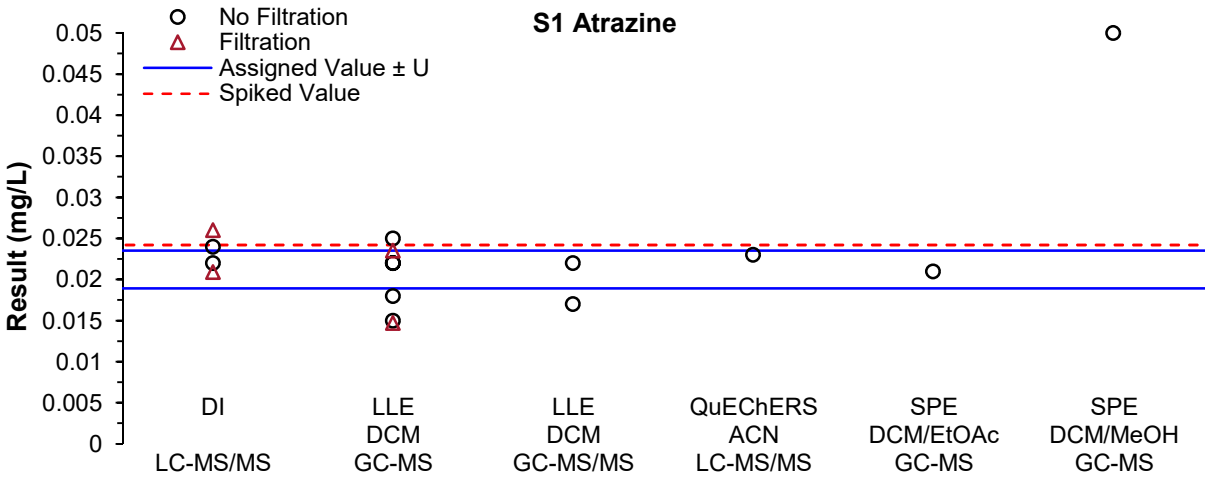


Figure 21 Sample S1 Atrazine Result vs Methodology

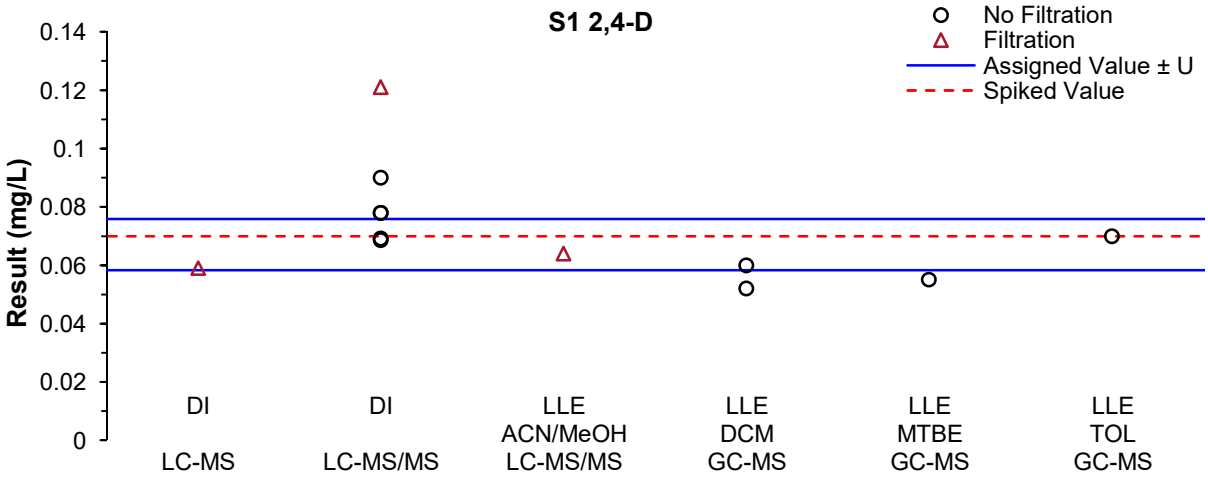


Figure 22 Sample S1 2,4-D Result vs Methodology

Sample S2

For Sample S2, participants were provided with 2 x 42 mL, and participants reported using test portions ranging from 5 mL to 25 mL. There was no evident correlation overall between the results obtained and the reported sample volume used (comparison for scored analytes given in Figure 23).

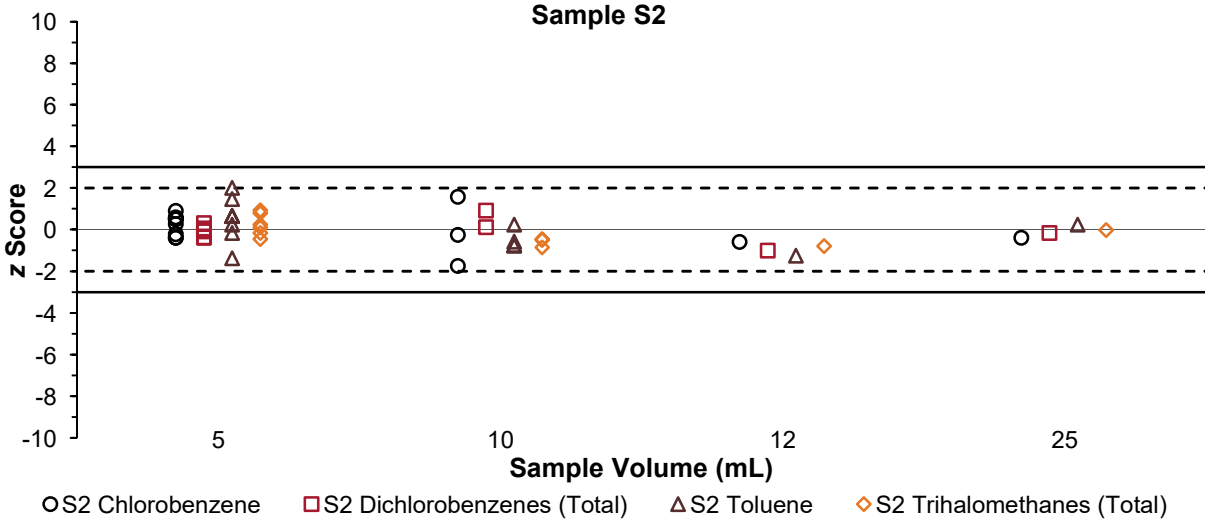


Figure 23 Sample S2 *z* Score vs Sample Volume

Participants used either purge-and-trap (P&T) GC-MS or headspace (HS) GC-MS. One participant reported LLE using methanol as the extraction solvent as part of their preparation. Plots of numeric results and methodology employed for scored analytes are presented in Figures 24 to 27.

In this study, it was observed for several Sample S2 analytes, results from participants using HS GC-MS were generally slightly biased low, while results from participants using P&T GC-MS were generally slightly biased high.

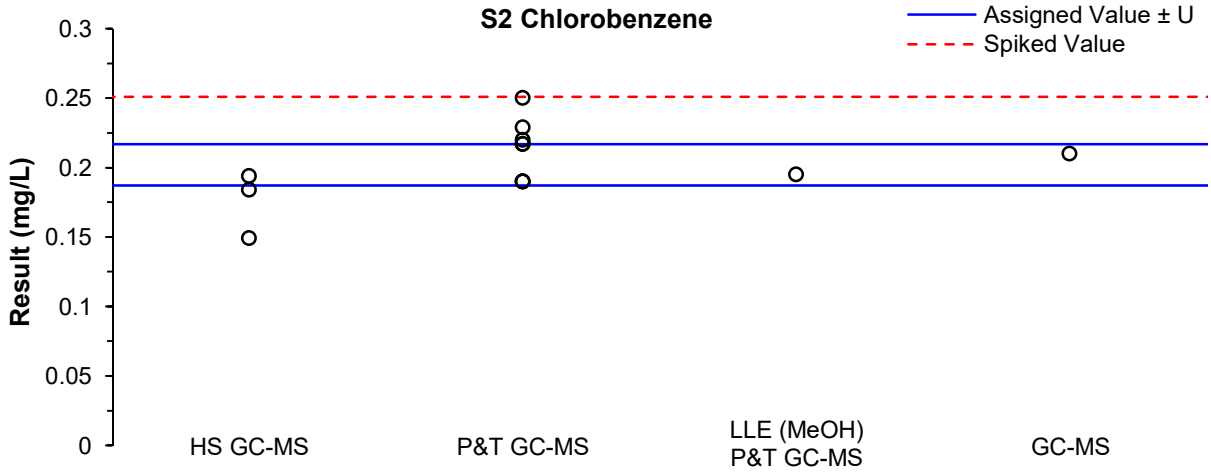


Figure 24 Sample S2 Chlorobenzene Result vs Methodology

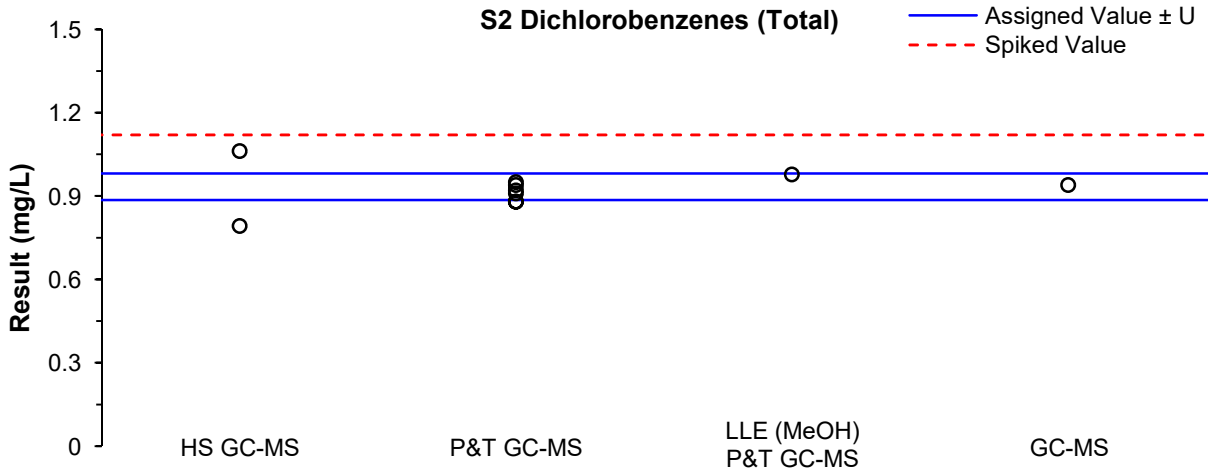


Figure 25 Sample S2 Dichlorobenzenes (Total) Result vs Methodology

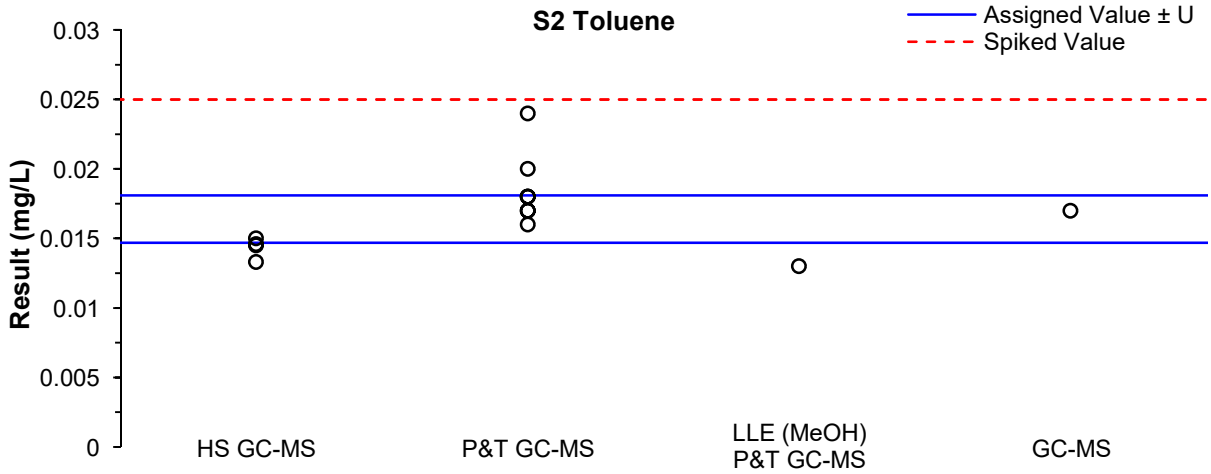


Figure 26 Sample S2 Toluene Result vs Methodology

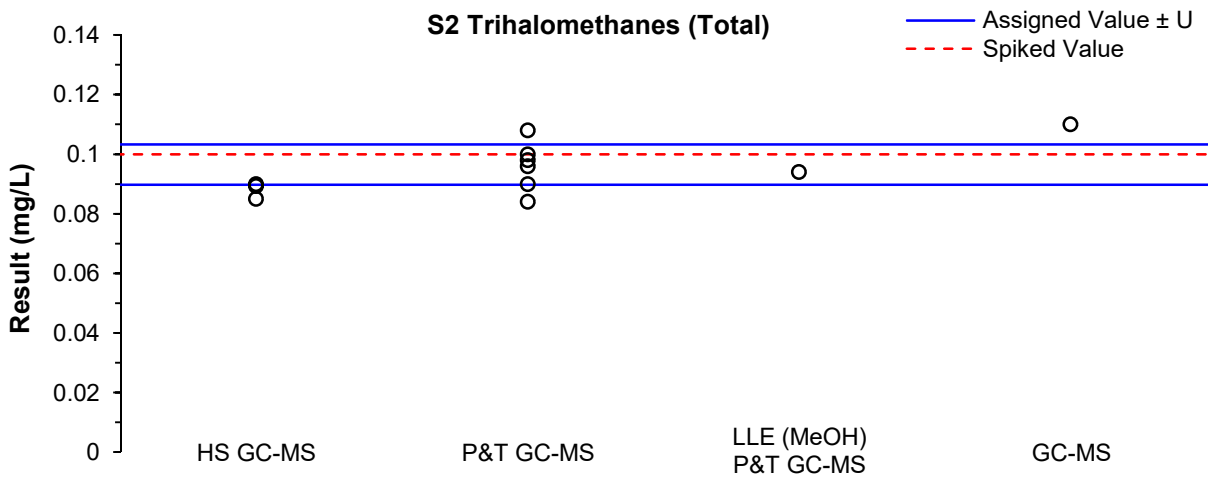


Figure 27 Sample S2 Trihalomethanes (Total) Result vs Methodology

Participants were requested to analyse the samples using their routine test method and to report a single result as they would to a client, that is, reported for recovery or not, according to their standard procedure. Results reported in this way reflect the true variability of results reported by laboratories to clients. Laboratories **8**, **12** and **18** 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.

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

- AccuStandard
- Chem-Lab
- HPC Standards
- o2si
- Restek
- Certified standards from local chemical supplier
- ISO 17034 compliant standards
- ISO 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*'[11]

6.11 Summary of Participants' Results and Performances

Summaries of participants' results and performances in this PT study are presented in Table 20 and Figure 28.

Table 20 Summary of Participants' Results for Scored Analytes*

Lab. Code	S1 Atrazine	S1 2,4-D	S2 Chlorobenzene	S2 Dichlorobenzenes (Total)	S2 Toluene	S2 Trihalomethanes (Total)
AV	0.0212	0.0671	0.202	0.933	0.0164	0.0965
SV	0.0242	0.0699	0.251	1.12	0.0250	0.100
1	0.0235	NT	0.217	NT	0.020	0.104
2	0.0209	0.059	0.229	0.939	0.024	0.108
3	0.017	NT	0.19	0.92	0.018	0.098
4	0.022	0.055	NT	NT	0.015	NT
5	0.018	0.060	NT	NT	NT	NT
6	0.022	0.078	0.184	0.792	0.0133	0.085
8	0.026	0.121	0.22	0.88	0.016	0.1
9	0.0147	NR	0.217	NR	0.018	NR
10	0.023	0.0686	0.185	1	0.014	NT
11	0.021	0.09	0.19	0.88	0.018	0.09
12	0.05	NT	NT	NT	NT	NT
13	NT	NT	NT	NT	NT	0.106
14	0.024	NT	0.25	0.95	0.017	0.084
15	0.022	0.052	0.19	0.91	0.017	0.096
16	0.022	0.070	0.21	0.94	0.017	0.11
17	0.025	0.064	0.195	0.978	0.013	0.094
18	NT	0.0692	0.1493	NT	0.0146	0.0893
19	0.015	0.078	0.194	1.062	0.0145	0.09

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

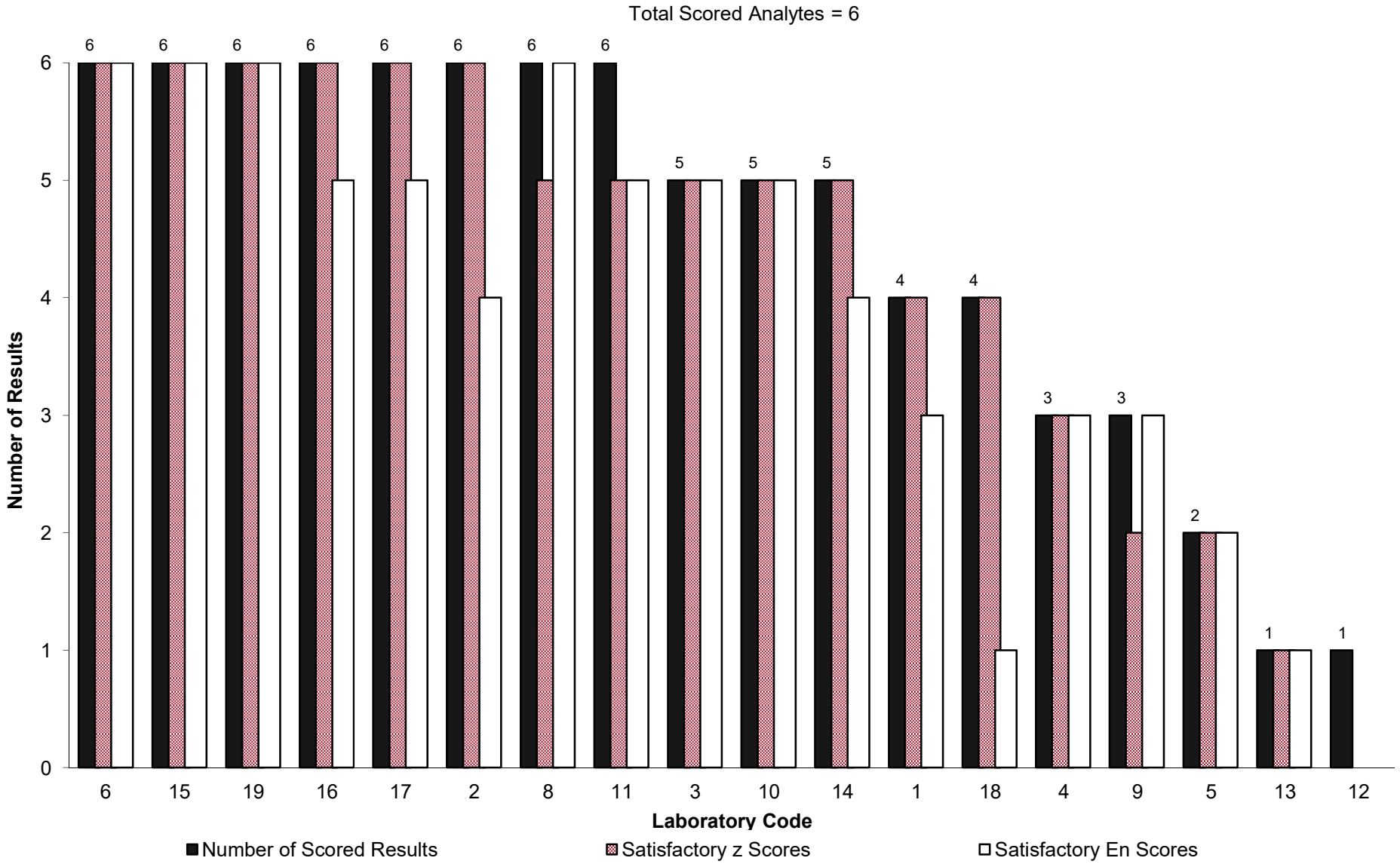


Figure 28 Summary of Participants' Performance

7 REFERENCES

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

[2] NMI, 2021, *Study Protocol for Proficiency Testing,* viewed September 2022, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>

[3] NMI, 2022, *Chemical Proficiency Testing Statistical Manual*, viewed September 2022, <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 13528:2022, *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] AS ISO/IEC 17025:2018, *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 September 2022, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>

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

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

APPENDIX 1 SAMPLE PREPARATION

Tap-water (potable water) was transferred into two 20 L Schott bottles using a beaker and funnel. The tap-water was then autoclaved.

Sample S1

After autoclaving, water was transferred into a pre-weighed 35 L stainless steel drum. The drum was stirred using the IKA stirrer and spiked. After stirring for two hours, the water was dispensed into solvent rinsed 500 mL amber glass bottles, labelled and shrink-wrapped.

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

Sample S2

Eighty headspace vials had 41.88 ± 0.05 g (42 mL) of autoclaved tap water weighed into each.

Standard solutions of dichloromethane and toluene were prepared by pipetting a calculated volume of each solvent into a 250 mL volumetric flask, and making up to volume with methanol. The chloroform standard was prepared by pipetting a calculated volume of chloroform into a 100 mL volumetric flask and making up to volume with methanol. The masses of analyte were calculated using densities from the CRC Handbook of Chemistry and Physics, 69th Edition.

Ampouled RESTEK standard solutions were used to spike the chlorobenzene and 1,2-dichlorobenzene when preparing the composite. Five ampoules of RESTEK 1,2-dichlorobenzene from two batches were used to prepare the composite.

The chloroform, dichloromethane and toluene were spiked using a pipette. The RESTEK standards were spiked into the composite flask in 0.1 mL aliquots using a pipette. The final composite solution was made up to 100 mL using Milli-Q water.

Aliquots (1 mL) of the composite solution were dispensed into each of the eighty headspace vials using a Hamilton ML620-DS Single Syringe Dispenser. The vials were labelled, shrink-wrapped and tumbled to mix.

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

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce homogeneous samples.

The results of this study also gave no reason to question the samples' homogeneity. Comparisons of *z* scores obtained for all scored analytes to bottle number analysed by participants are presented in Figures 29 to 34 (gross errors, if applicable, have been removed, and results have only been included when the participant was sent one sample set; for Sample S2, each participant was sent 2 bottles and these have both been graphed with the grey dotted line indicating results from the one participant).

Figure 29 S1 Atrazine *z* Score vs Bottle Number

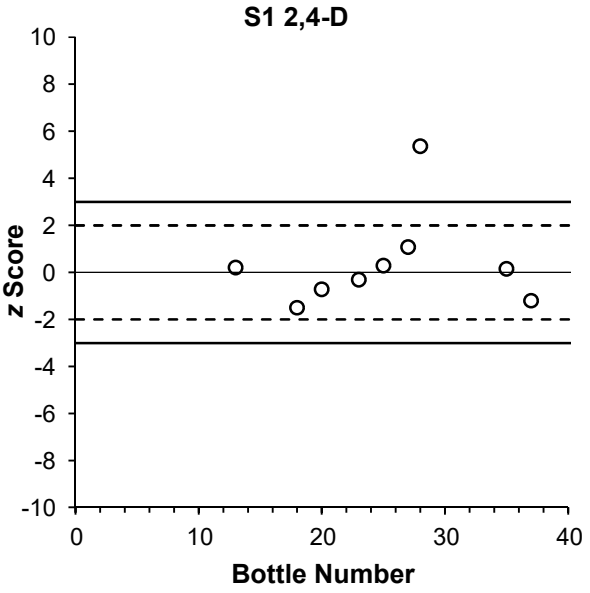


Figure 30 S1 2,4-D *z* Score vs Bottle Number

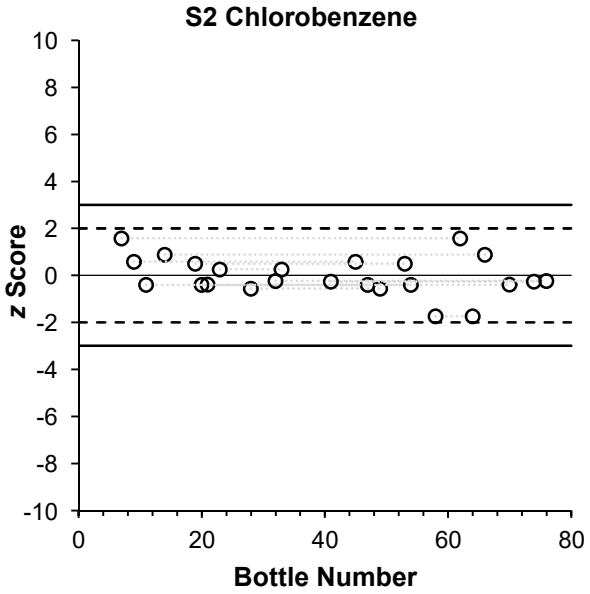


Figure 31 S2 Chlorobenzene *z* Score vs Bottle Number

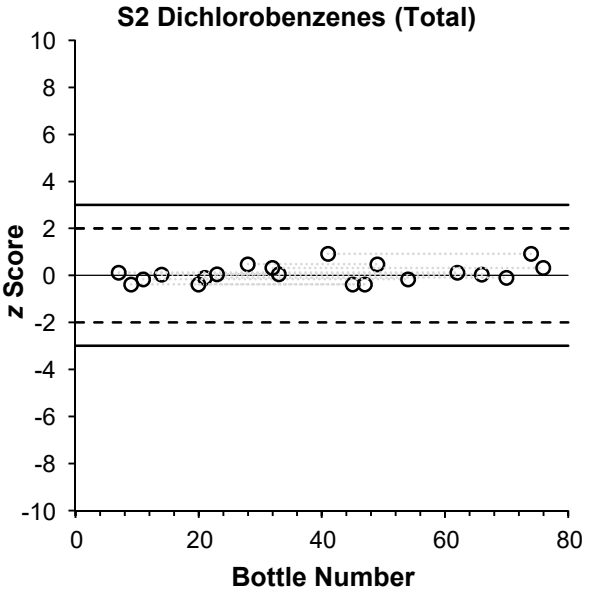


Figure 32 S2 Dichlorobenzenes (Total) *z* Score vs Bottle Number

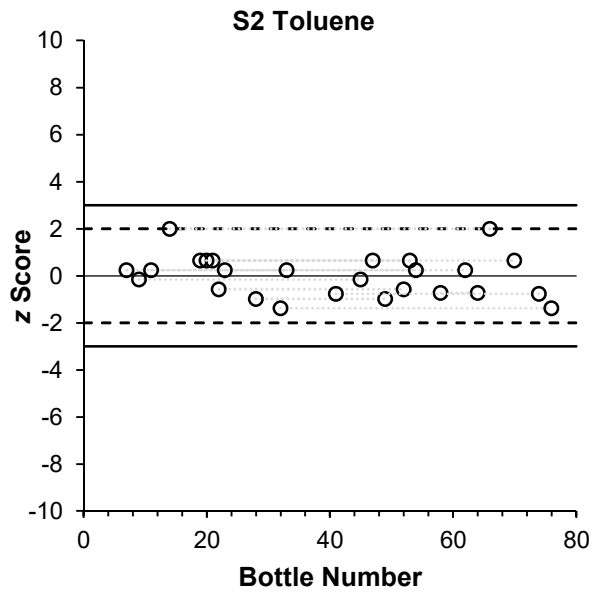


Figure 33 S2 Toluene *z* Score vs Bottle Number

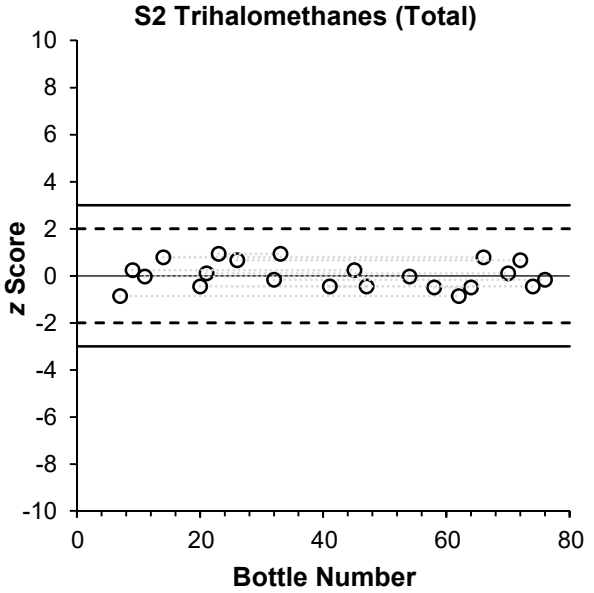


Figure 34 S2 Trihalomethanes (Total) *z* Score vs Bottle Number

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 stable samples for these and similar analytes in water (the samples were stored at 4 ºC after preparation and prior to dispatch, and the samples were packaged into insulated polystyrene foam boxes with cooler bricks for dispatch). Additionally, comparison between participant results and the spiked values gave some assurance that the analytes were stable.

No evidence of analyte degradation with respect to the amount of time spent in transit was observed. Comparisons of *z* scores obtained for all scored analytes to days spent in transit are presented in Figures 35 to 40 (gross errors, if applicable, have been removed).

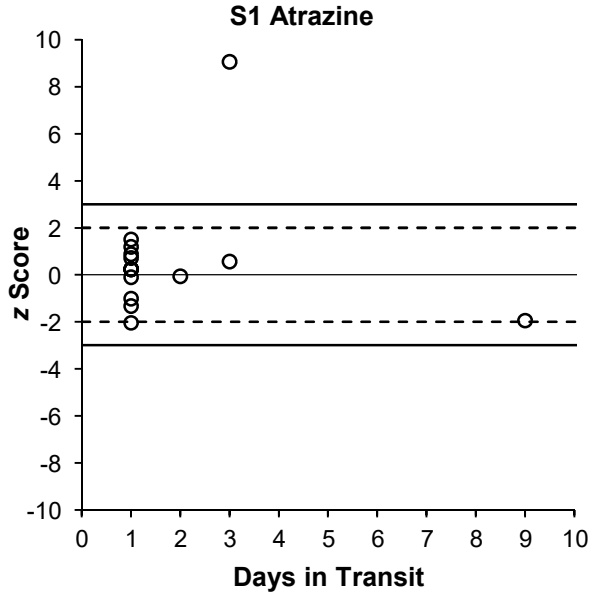


Figure 35 S1 Atrazine *z* Score vs Transit Time

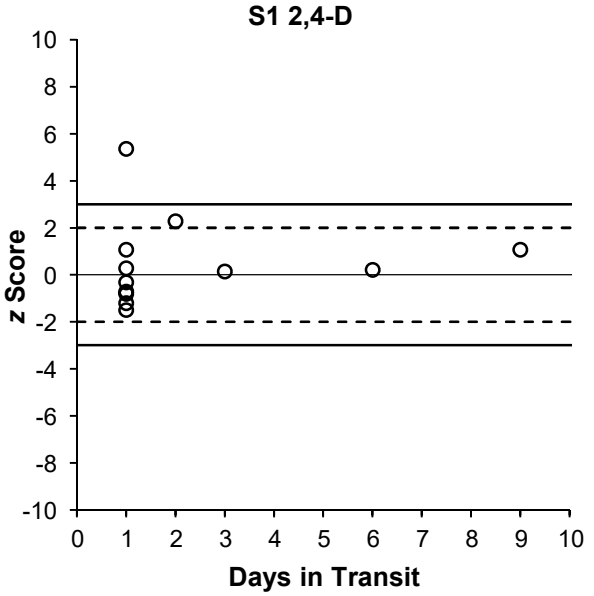


Figure 36 S1 2,4-D *z* Score vs Transit Time

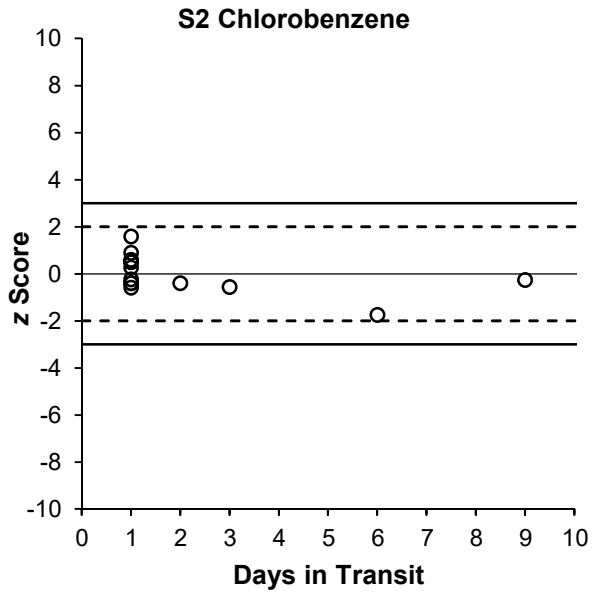


Figure 37 S2 Chlorobenzene *z* Score vs Transit Time

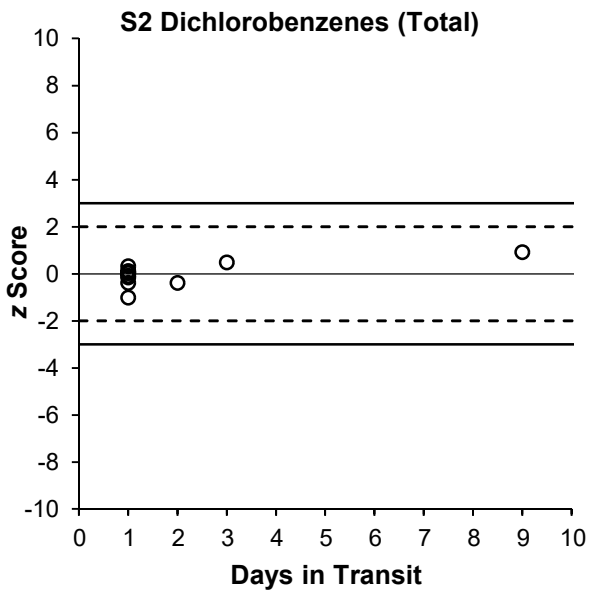


Figure 38 S2 Dichlorobenzenes (Total) *z* Score vs Transit Time

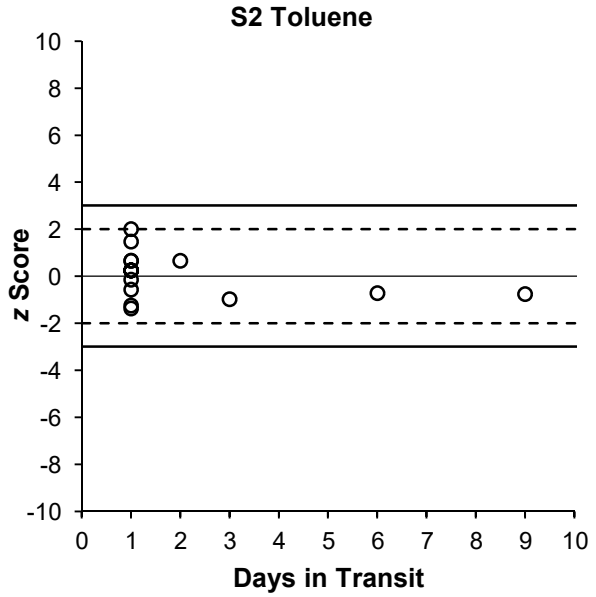


Figure 39 S2 Toluene *z* Score vs Transit Time

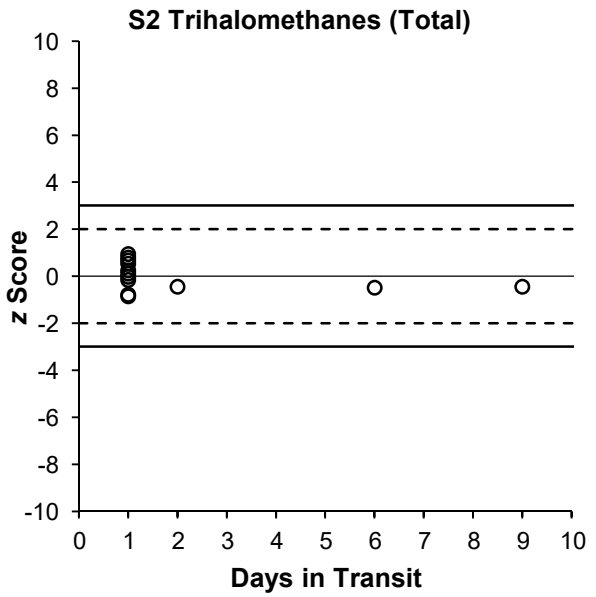


Figure 40 S2 Trihalomethanes (Total) *z* Score vs Transit Time

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

A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528:2022.[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 21.

Table 21 Uncertainty of Robust Average for Sample S1 2,4-D

Number of results (p)	12
Robust Average	0.070 mg/L
$S_{rob\ av}$	0.014 mg/L
$u_{rob\ av}$	0.005 mg/L
k	2
$U_{rob\ av}$	0.010 mg/L

Therefore, the robust average for Sample S1 2,4-D is 0.070 ± 0.010 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 22, using the result reported by Laboratory 1 for Sample S1 atrazine.

Table 22 *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
0.0235 ± 0.0061	0.0212 ± 0.0023	15% as PCV, or: 0.15 × 0.0212 = 0.00318 mg/L	z Score $= \frac{0.0235-0.0212}{0.00318}$ = 0.72	E_n Score $= \frac{0.0235-0.0212}{\sqrt{0.0061^2+0.0023^2}}$ = 0.35

APPENDIX 4 PARTICIPANTS' TEST METHODS

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

Table 23 Methodology – Sample S1 Aldicarb

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	NT				
2	1	Direct Injection	N/A	0.2um	LC-MS/MS
3	NT				
4	NT				
5	4	Direct Injection	N/A	N/A	LC-MS/MS
6	1	Direct injection			LC-MS/MS
8	NT				
9					
10	20	Quechers	acetonitrile	N	LC-MS/MS
11	10	Direct Injection			LC-MS/MS
12	NT				
13	NT				
14	NT				
15	NT				
16	<1	-	-		
17	NT				
18	NT				
19	NT				

Table 24 Methodology – Sample S1 Atrazine

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	500	Liquid-Liquid	DCM	Filtration	GC-MS
2	1	Direct Injection	N/A	0.2um	LC-MS/MS
3	500	Liquid-Liquid	DCM	None	GC-MS/MS
4	100	Liquid-Liquid	DCM		GC-MS/MS
5	100	Liquid-Liquid	DCM	N/A	GC-MS
6	1	Direct injection			LC-MS/MS
8	1	Direct Injection	nil	Filtration	LC-MS/MS
9	500	Liquid-Liquid	DCM	Filtration	GC-MS
10	20	Quechers	acetonitrile	N	LC-MS/MS
11	500	SPE	dcm:EtOAC 1:1		gcms
12	250	Oasis SPE	DCM-Methanol	SPE	GC-MS
13	NT				

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
14		Direct injection			LC-MS/MS
15	100	Liquid-Liquid	DCM	None	GC-MS
16	50	Liquid-Liquid	DCM		GC-MS
17	100	Liquid-Liquid	DCM	N/A	GC-MS
18	NT				
19	250	Liquid-Liquid	DCM	Nil	GC-MS

Table 25 Methodology – Sample S1 2,4-D

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	NT				
2	1	Direct Injection	N/A	0.2um	LC-MS
3	NT				
4	30	Liquid-Liquid	MtBE	Alkaline hydrolysis	GC-MS
5	100	Liquid-Liquid	DCM	Derivatisation	GC-MS
6	1	Direct injection			LC-MS/MS
8	1	Direct Injection	nil	Filtration	LC-MS/MS
9					
10	0.95	Direct Injection		n	LC-MS/MS
11	10	Direct Injection			LC-MS/MS
12	NT				
13	NT				
14	NT				
15	100	Liquid-Liquid	DCM	None	GC-MS
16	5	Liquid-Liquid	Toluene		GC-MS
17	1	Liquid-Liquid	Acetonitrile/Methanol	Filtration	LC-MS/MS
18	10	Direct Injection			LC-MS/MS
19	1	Direct Injection	Nil	Nil	LC-MS/MS

Table 26 Methodology – Sample S1 Glyphosate

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	NT				
2	10	Direct Injection	N/A	0.2um	LC-MS
3	NT				
4	NT				
5	4	Direct Injection	N/A	Pentane extraction	LC-FLD
6	1	Derivatisation			LC-MS/MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
8	0.5	Direct Injection (1:2 diluted with buffer)	0.1 Formic acid	Filtration	LC-MS/MS
9					
10	NT				
11	10	Direct Injection			LC-MS/MS
12	NT				
13	NT				
14	NT				
15	NT				
16	5	Liquid-Liquid			LC-MS/MS
17	NT				
18	NT				
19	NT				

Table 27 Methodology – Sample S2 Chlorobenzene

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	5	Purge & Trap	n/a	n/a	GC-MS
2	5	Direct Injection	N/A	N/A	P&T GC-MS
3	5	Purge and Trap	None	None	P&T GC-MS
4	NT				
5	NT				
6	12				Headspace GC-MS
8	5	On-trap concentration	Nil	Nil	P&T/GC-MS
9	5	Purge and trap			GC-MS
10					
11	5				P&T GC-MS
12	NT				
13	NT				
14	10 mL	via sparge tube			P&T GC-MS
15	25	Purge & Trap	None	None	P&T GC-MS
16	5	-	-	-	GC-MS
17	5	Liquid-Liquid	Methanol	N/A	P&T GC-MS
18	10	HS			Headspace GC-MS
19	10	Headspace	Nil	Nil	GC-MS

Table 28 Methodology – Sample S2 Dichlorobenzenes (Total)

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	NT				
2	5	Direct Injection	N/A	N/A	P&T GC-MS
3	5	Purge and Trap	None	None	P&T GC-MS
4	NT				
5	NT				
6	12				Headspace GC-MS
8	5	On-trap concentration	Nil	Nil	P&T/GC-MS
9					
10					
11	5				P&T GC-MS
12	NT				
13	NT				
14	10 mL	via sparge tube			P&T GC-MS
15	25	Purge & Trap	None	None	P&T GC-MS
16	5	-	-	-	GC-MS
17	5	Liquid-Liquid	Methanol	N/A	P&T GC-MS
18	NT				
19	10	Headspace	Nil	Nil	GC-MS

Table 29 Methodology – Sample S2 Dichloromethane

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	5	Purge & Trap	n/a	n/a	GC-MS
2	NT				
3	5	Purge and Trap	None	None	P&T GC-MS
4	NT				
5	NT				
6	12				Headspace GC-MS
8	5	On-trap concentration	Nil	Nil	P&T/GC-MS
9	5	Purge and trap			GC-MS
10	NT				
11	5				P&T GC-MS
12	NT				
13	NT				
14	10 mL	via sparge tube			P&T GC-MS
15	25	Purge & Trap	None	None	P&T GC-MS

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
16	5	-	-	-	GC-MS
17	5	Liquid-Liquid	Methanol	N/A	P&T GC-MS
18	NT				
19	10	Headspace	Nil	Nil	GC-MS

Table 30 Methodology – Sample S2 Toluene

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1	5	Purge & Trap	n/a	n/a	GC-MS
2	5	Direct Injection	N/A	N/A	P&T GC-MS
3	5	Purge and Trap	None	None	P&T GC-MS
4	10	Headspace	N/A		GC-MS
5	NT				
6	12				Headspace GC-MS
8	5	On-trap concentration	Nil	Nil	P&T/GC-MS
9	5	Purge and trap			GC-MS
10					
11	5				P&T GC-MS
12	NT				
13	NT				
14	10 mL	via sparge tube			P&T GC-MS
15	25	Purge & Trap	None	None	P&T GC-MS
16	5	-	-	-	GC-MS
17	5	Liquid-Liquid	Methanol	N/A	P&T GC-MS
18	10	HS			Headspace GC-MS
19	10	Headspace	Nil	Nil	GC-MS

Table 31 Methodology – Sample S2 Trihalomethanes (Total)

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
1					
2	5	Direct Injection	N/A	N/A	P&T GC-MS
3	5	Purge and Trap	None	None	P&T GC-MS
4	NT				
5	NT				
6	12				Headspace GC-MS
8	5	On-trap concentration	Nil	Nil	P&T/GC-MS
9					

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Instrument
10	NT				
11	5				P&T GC-MS
12	NT				
13					
14	10 mL	via sparge tube			P&T GC-MS
15	25	Purge & Trap	None	None	P&T GC-MS
16	5	-	-	-	GC-MS
17	5	Liquid-Liquid	Methanol	N/A	P&T GC-MS
18	10	HS			Headspace GC-MS
19	10	Headspace	Nil	Nil	GC-MS

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
2,4-D	2,4-Dichlorophenoxyacetic acid
ACN	Acetonitrile
ADWG	Australian Drinking Water Guidelines
ADWG (A)	Australian Drinking Water Guidelines Aesthetic Guideline Value
ADWG (H)	Australian Drinking Water Guidelines Health Guideline Value
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DI	Direct Injection
EtOAc	Ethyl Acetate
FLD	Fluorescence Detector
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
HS	Headspace
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOQ	Limit of Quantification
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
MTBE	Methyl *tert*-butyl ether
MU	Measurement Uncertainty
N	Number of numeric results

NATA	National Association of Testing Authorities, Australia
NMI	National Measurement Institute, Australia
NR	Not Reported
NT	Not Tested
P&T	Purge-and-Trap
PCV	Performance Coefficient of Variation
PT	Proficiency Testing
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe extraction method
RA	Robust Average
RM	Reference Material
SD	Standard Deviation
SI	International System of Units
SPE	Solid Phase Extraction
SS	Spiked Samples
SV	Spiked Value (or formulated concentration of a PT sample)
TOL	Toluene
U	Expanded Uncertainty
VOCs	Volatile Organic Compounds

END OF REPORT