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Measurement
Institute

Proficiency Test Final Report AQA 24-10 Organic Compounds in Potable Water

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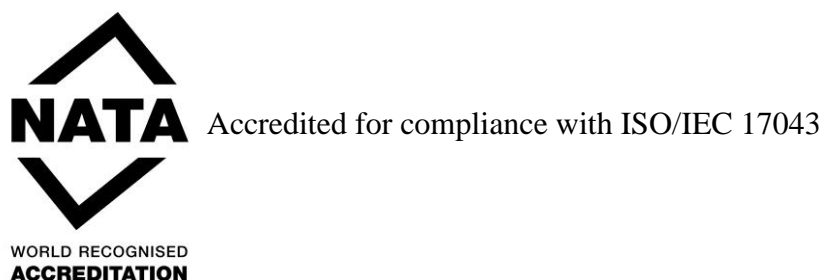


TABLE OF CONTENTS

SUMMARY	1
1 INTRODUCTION	3
1.1 NMI Proficiency Testing Program	3
1.2 Study Aims	3
1.3 Study Conduct	3
2 STUDY INFORMATION	4
2.1 Study Timetable	4
2.2 Participation and Laboratory Code	4
2.3 Selection of Analytes	4
2.4 Test Material Preparation	5
2.5 Homogeneity and Stability of Test Materials	5
2.6 Test Material Storage, Dispatch and Receipt	6
2.7 Instructions to Participants	6
2.8 Interim Report and Preliminary Report	6
3 PARTICIPANT LABORATORY INFORMATION	7
3.1 Participants' Test Methods	7
3.2 Basis of Participants' Measurement Uncertainty Estimates	7
3.3 Participants' Comments	9
4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS	11
4.1 Results Summary	11
4.2 Outliers and Extreme Outliers	11
4.3 Assigned Value	11
4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation	11
4.5 Performance Coefficient of Variation	11
4.6 Target Standard Deviation for Proficiency Assessment	12
4.7 z-Score	12
4.8 E _n -Score	12
4.9 Traceability and Measurement Uncertainty	12
5 TABLES AND FIGURES	13
6 DISCUSSION OF RESULTS	47
6.1 Assigned Value	47
6.2 Measurement Uncertainty Reported by Participants	48
6.3 z-Score	48
6.4 E _n -Score	50
6.5 Range of Organic Compounds Analysed by Participants	51
6.6 False Negatives	53
6.7 Reporting of Additional Analytes	53
6.8 Fitness for Purpose of Results – Australian Drinking Water Guidelines	55
6.9 Participants' Analytical Methods	60
6.10 Certified Reference Materials	68
6.11 Summary of Participants' Results and Performances	68
6.12 Comparison with Previous Organic Compounds in Potable Water PT Studies	71
7 REFERENCES	74

APPENDIX 1	SAMPLE PREPARATION	75
APPENDIX 2	ASSESSMENT OF HOMOGENEITY AND STABILITY	76
	A2.1 Homogeneity	76
	A2.2 Stability	79
APPENDIX 3	ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, z-SCORE AND E _n -SCORE CALCULATIONS	83
	A3.1 Robust Average and Associated Uncertainty	83
	A3.2 z-Score and E _n -Score Calculation	83
APPENDIX 4	PARTICIPANTS' TEST METHODS	84
APPENDIX 5	ACRONYMS AND ABBREVIATIONS	88

SUMMARY

AQA 24-10 Organic Compounds in Potable Water commenced in May 2024. Twenty-two laboratories registered to participate, and all participants submitted results.

The sample set consisted of three potable water samples and one reagent grade water sample. Samples were prepared in the NMI Sydney laboratory by spiking water with various analytes. Sample S1 was spiked with volatile organic compounds (VOCs), Sample S2 was spiked with polycyclic aromatic hydrocarbons (PAHs), Sample S3 was spiked with phenols, and Sample S4 was spiked with 17 β -estradiol.

Of a possible 347 results, 300 numeric results (86%) were submitted. Twenty-four results were a 'less than' value ($< x$) or Not Reported (NR), and 23 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 in potable water.*

Laboratories **2, 6, 7, 8, 10, 12, 13, 14, 17, 18, 19** and **21** reported numeric results for all 16 scored analytes.

Laboratories **1, 5, 11** and **16** did not report numeric results for analytes that they tested for and were present in the test samples (total of 19 results).

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

Of 297 z -scores, 262 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Of 289 E_n -scores, 241 (83%) 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 **7, 12, 14** and **18** achieved acceptable z -scores and E_n -scores across all 16 scored analytes.

Laboratories **11** and **15** did not achieve any acceptable z -scores or E_n -scores in this study; these participants may have reported their results in the incorrect units.

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

Of the 165 results assessed against the Australian Drinking Water Guidelines, 160 (97%) correctly reflected whether the sample exceeded the guideline(s) or not.

Laboratories **2, 6, 7, 8, 10, 12, 13, 14, 16, 17, 18, 19** and **21** returned the correct consequence for all nine analytes assessed.

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

Participants used a wide variety of methods across the different samples, and they were generally compatible with each other.

The most common methodology for Sample S1 VOCs was purge-and-trap GC-MS. The most common methodology for Samples S2 PAHs and S3 phenols was liquid-liquid extraction using dichloromethane, followed by analysis using GC-MS(/MS). All three participants reporting numeric results for Sample S4 17 β -estradiol used different methodologies from each other.

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

Of 300 numeric results, 277 (92%) were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 8.0% to 417%. 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 organic compounds in potable water;
- compare the performance of participants and assess their accuracy in the measurement of organic compounds in potable water;
- assess the consequence of participants' results for organic compounds in potable water against regulatory guidelines;
- evaluate the participants' methods for the measurement of organic compounds 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-two laboratories registered to participate in this study, and all participants were assigned a confidential laboratory code number for this study. All participants submitted results.

2.3 Selection of Analytes

When selecting analytes and spiked 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 Samples S1 volatile organic compounds (VOCs), S2 polycyclic aromatic hydrocarbons (PAHs) and S3 phenols are presented in Tables 1 to 3. Sample S4 was spiked with 17 β -estradiol.

Table 1 List of Possible Analytes for Sample S1

Benzene	1,2-dichloroethane	Toluene
Carbon tetrachloride	1,1-dichloroethene	Trichlorobenzenes (Total)
Chlorobenzene	1,2-dichloroethene	1,1,1-Trichloroethane
1,2-dichlorobenzene	Dichloromethane	Trichloroethylene
1,3-dichlorobenzene	Ethylbenzene	Trihalomethanes (Total)
1,4-dichlorobenzene	Styrene	Vinyl Chloride
1,1-dichloroethane	Tetrachloroethene	Xylenes

Table 2 List of Possible Analytes for Sample S2

Naphthalene	Phenanthrene	Benz[<i>a</i>]anthracene	Benzo[<i>a</i>]pyrene
Acenaphthylene	Anthracene	Chrysene	Indeno[1,2,3- <i>cd</i>]pyrene
Acenaphthene	Fluoranthene	Benzo[<i>b</i>]fluoranthene	Dibenz[<i>a,h</i>]anthracene
Fluorene	Pyrene	Benzo[<i>k</i>]fluoranthene	Benzo[<i>g,h,i</i>]perylene

Table 3 List of Possible Analytes for Sample S3

Phenol	2,4-Dimethylphenol	2,6-Dichlorophenol	2,3,4,6-Tetrachlorophenol
2-Chlorophenol	2-Nitrophenol	4-Chloro-3-methylphenol	2,4-Dinitrophenol
2-Methylphenol	4-Nitrophenol	2,4,6-Trichlorophenol	Pentachlorophenol
3 & 4-Methylphenols	2,4-Dichlorophenol	2,4,5-Trichlorophenol	

2.4 Test Material Preparation

Four test samples were prepared by adding analyte standard solution(s) to potable water (Samples S1, S2 and S3) and reagent grade water (Sample S4). The spiked values for the samples and corresponding ADWG values,⁵ are presented in Table 4.

Table 4 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (mg/L)	Uncertainty ^a (mg/L)	ADWG Health Guideline Value (mg/L)	ADWG Aesthetic Guideline Value (mg/L)
S1	1,2-Dichloroethane	0.200	0.010	0.003	-
	1,4-Dichlorobenzene	0.0776	0.0039	0.04	0.0003
	Carbon tetrachloride	0.100	0.005	0.003	-
	Dichloromethane	0.0157	0.0008	0.004	-
	Toluene	0.0500	0.0025	0.8	0.025
	Xylenes	0.200	0.010	0.6	0.02
S2	Benz[<i>a</i>]anthracene	0.00499	0.00025	-	-
	Benzo[<i>a</i>]pyrene	0.00403	0.00020	0.00001	-
	Chrysene	0.00299	0.00015	-	-
	Fluoranthene	0.00700	0.00035	-	-
	Phenanthrene	0.0100	0.0005	-	-
S3	2,4-Dichlorophenol	0.0139	0.0007	0.2	0.0003
	2,6-Dichlorophenol	0.00702	0.00035	-	-
	2-Methylphenol	0.0101	0.0005	-	-
	4-Methylphenol ^b	0.0120	0.0006	-	-
	Pentachlorophenol	0.0998	0.0050	0.01	-
S4	17 β -Estradiol	0.0000655	0.0000033	-	-

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

^b For Sample S3, participants were requested to report for 3 & 4-Methylphenols (total).

Additional sample preparation details are provided in Appendix 1.

2.5 Homogeneity and Stability of Test Materials

The samples were prepared, packaged and stored using a process that has been demonstrated to produce sufficiently homogeneous and stable samples in previous NMI PT studies with similar analytes and matrices. Homogeneity and stability testing was also conducted for Samples S3 and S4 in this study. For Sample S3, this testing was performed by an external provider, Envirolab Services Sydney Chemical Testing Laboratory.

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 68% to 134% of the spiked values, which is similar to ratios observed in previous NMI PT studies for similar analytes in water. Analytes were only scored when there was a reasonable consensus between participants' results.

Further homogeneity and stability information is provided in 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.
- 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 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 coefficient of variations, *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, with the exception that Sample S2 chrysene has now been set an assigned value, and participant results for this analyte have been scored.

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

Table 5 Basis of Measurement Uncertainty Estimate

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
1	VOC/ PAH/ Phenol	Top Down - precision and estimates of the method and laboratory bias k = 2	Duplicate analysis Instrument calibration	Recoveries of SS Standard purity	Eurachem/CITAC Guide
2	VOC/ PAH/ Phenol	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
3	VOC/ PAH/ Phenol	Coverage factor not reported			
4	VOC/ PAH/ Phenol	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
5	VOC	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS		ISO/GUM
	PAH/ Phenol	Coverage factor not reported			
6	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Instrument calibration	Instrument calibration Recoveries of SS Standard purity	ISO/GUM

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
7	VOC/ PAH/ Phenol	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
8	VOC/ PAH/ Phenol	Based on historical data Coverage factor not reported	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
9	VOC/ PAH/ Phenol	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - CRM		ISO/GUM
10	VOC/ PAH/ Phenol	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
11	VOC	k = 2	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	
	PAH/ Phenol	Coverage factor not reported			
12	VOC/ PAH/ Phenol	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - CRM	CRM Recoveries of SS	
13	VOC/ PAH/ Phenol	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
14	VOC/ PAH/ Phenol	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
15	VOC/ PAH/ Phenol	Top Down - reproducibility (standard deviation) from PT studies used directly Coverage factor not reported	Control samples - SS Duplicate analysis Instrument calibration		Eurachem/CITAC Guide

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
16	All	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
17	VOC/ PAH/ Phenol	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
18	VOC/ PAH/ Phenol	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS	Recoveries of SS	ISO/GUM
19	VOC/ PAH/ Phenol	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
20	VOC/ PAH/ Phenol	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) Coverage factor not reported	Control samples Duplicate analysis Instrument calibration	Laboratory bias from PT studies CRM Instrument calibration Recoveries of SS	
21	All	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
22	Phenol	Top Down - precision and estimates of the method and laboratory bias k = 2	Control samples - SS	Instrument calibration Recoveries of SS	ISO/GUM (DIN ISO 11352:2013)

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

Table 6 Participants' Comments

Lab. Code	Sample	Participant's Comments
8	S1	Total Trichlorobenzene includes 1,2,3-TCB, 1,2,4-TCB and 1,3,5-TCB. Total THM includes Bromodichloromethane, Bromoform, Chloroform and Dibromochloromethane. Xylenes include m&p-Xylene and o-Xylene.
	S2	Benzo[b]fluoranthene result also includes Benzo[j]fluoranthene.
11	All	Uncertainty: reported the range for THM; not collected adequate QC data to produce MU for BTEX
18	S1	Trihalomethanes (Total) only referring to chloroform, bromodichloromethane, dibromochloromethane, and bromoform. 1,2-Dichloroethene was analysed as cis and trans isomers, both below LOR.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 7 to 23 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), and other estimates of analyte concentration. Bar charts of results and performance scores are presented in Figures 2 to 18. An example chart with interpretation guide is shown in Figure 1.

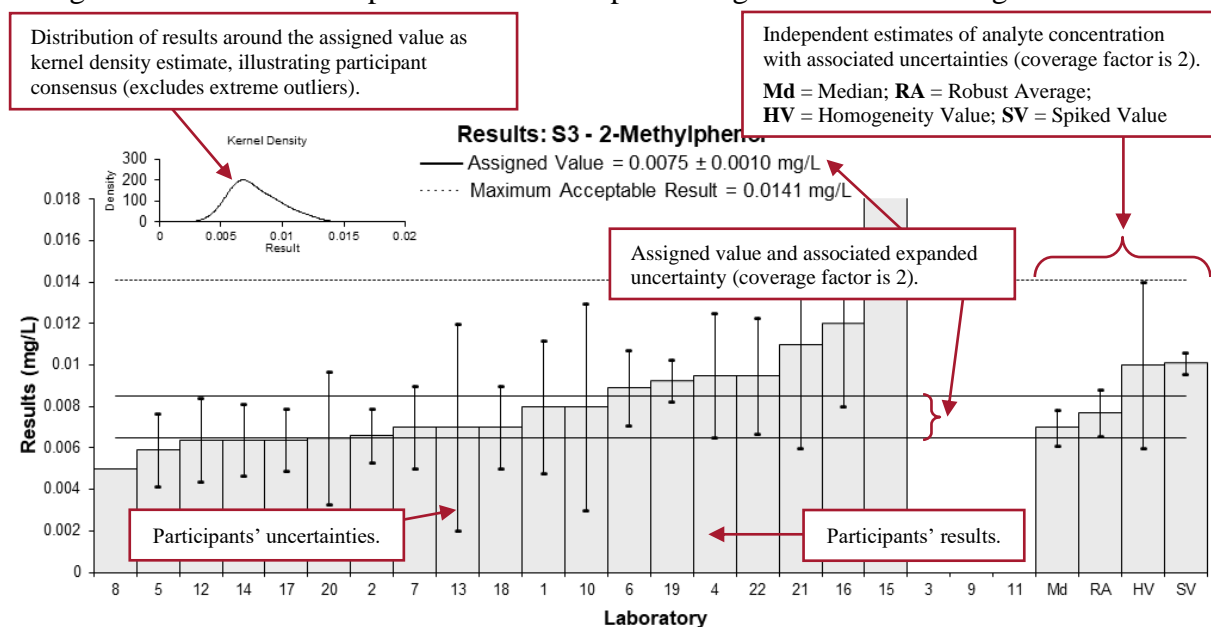


Figure 1 Guide to Presentation of Results

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.

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.

$$\sigma = X \times PCV \quad \text{Equation 1}$$

4.7 z-Score

For each participant result, a z-score is calculated according to Equation 2.

$$z = \frac{(\chi - X)}{\sigma} \quad \text{Equation 2}$$

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, 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.

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}} \quad \text{Equation 3}$$

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 7

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	1,2-Dichloroethane
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	NT	NT		
2	0.206	0.0169	-0.13	-0.19
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	0.173	0.055	-1.17	-0.65
7	0.193	0.058	-0.54	-0.29
8	0.189	0.065	-0.67	-0.32
9*	0.089	0.03	-3.84	-3.70
10	0.25	0.05	1.27	0.77
11	NR	NR		
12	0.232	0.08	0.70	0.27
13	0.21	0.05	0.00	0.00
14	0.224	0.0254	0.44	0.49
15**	170	51	5,390.16	3.33
16	0.23	NR	0.63	1.54
17	0.196	0.029	-0.44	-0.44
18	0.22	0.06	0.32	0.16
19	0.211	0.07	0.03	0.01
20	0.199	0.0792	-0.35	-0.14
21	0.21	0.05	0.00	0.00
22	NS	NS		

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.210	0.013
Spike Value	0.200	0.010
Robust Average	0.207	0.015
Median	0.210	0.013
Mean	0.202	
N	15	
Max	0.25	
Min	0.089	
Robust SD	0.023	
Robust CV	11%	

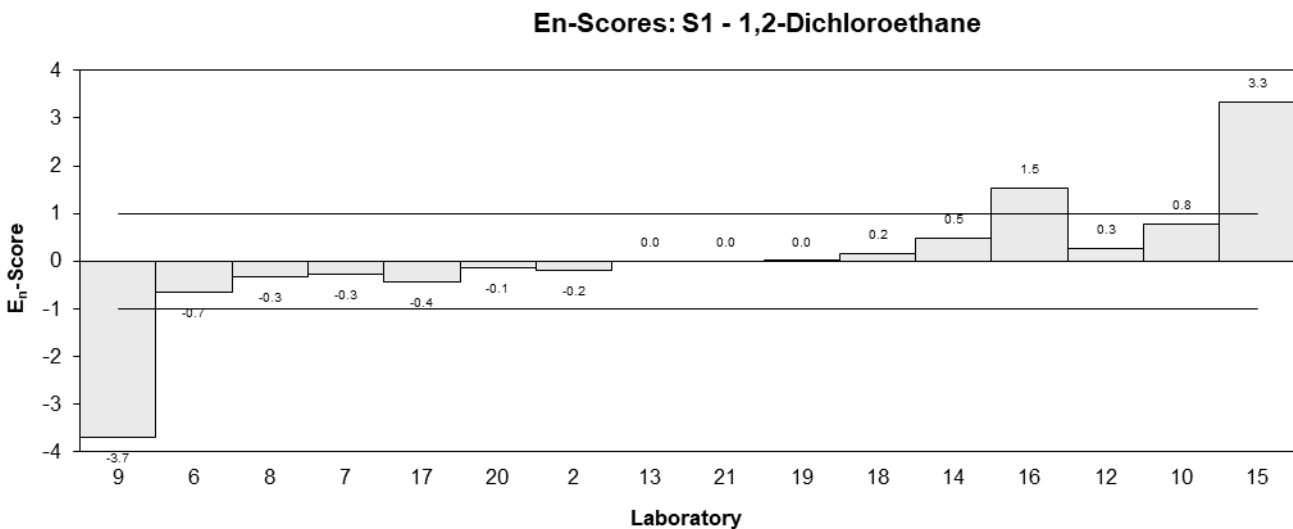
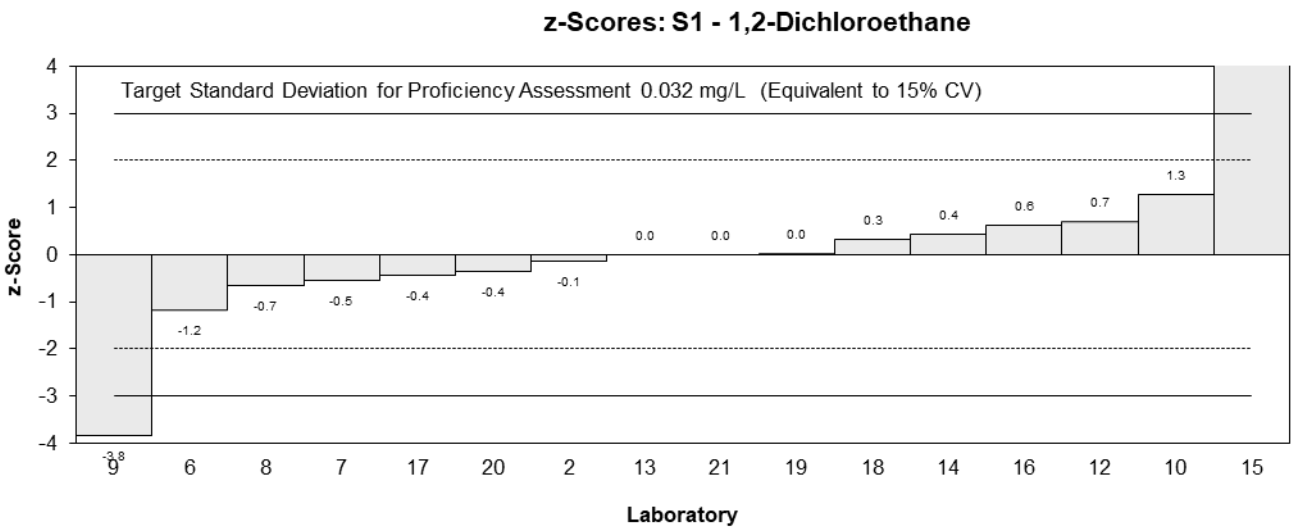
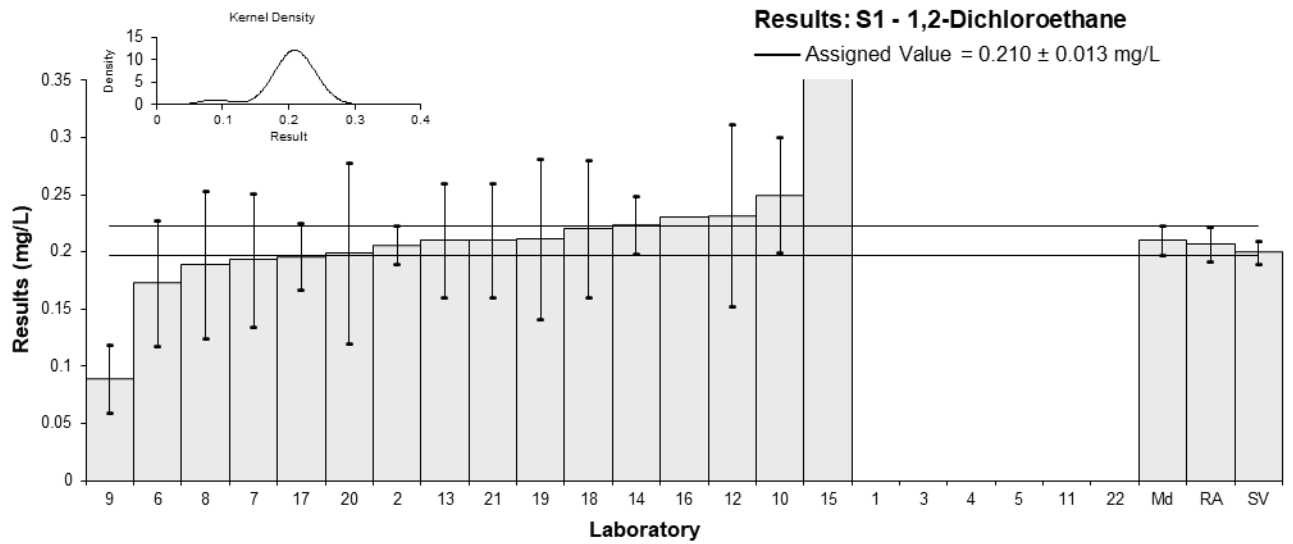


Figure 2

Table 8

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	1,4-Dichlorobenzene
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.072	0.014	0.03	0.02
2	0.0714	0.0081	-0.03	-0.03
3	0.075	NR	0.31	0.80
4	NT	NT		
5	NT	NT		
6	0.057	0.016	-1.37	-0.89
7	0.086	0.026	1.33	0.54
8	0.067	0.021	-0.44	-0.22
9	0.067	0.01	-0.44	-0.43
10	0.05	0.02	-2.02	-1.06
11	NR	NR		
12	0.0737	0.025	0.19	0.08
13	0.069	0.02	-0.25	-0.13
14	0.078	0.0103	0.59	0.57
15**	58.5	17.55	5,432.66	3.33
16	0.076	0.02	0.40	0.21
17	0.072	0.011	0.03	0.03
18	0.077	0.022	0.49	0.24
19	0.0782	0.02	0.60	0.32
20	0.074	0.0084	0.21	0.25
21	0.064	0.02	-0.72	-0.38
22	NS	NS		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.0717	0.0041
Spike Value	0.0776	0.0039
Robust Average	0.0717	0.0041
Median	0.0720	0.0045
Mean	0.0710	
N	17	
Max	0.086	
Min	0.05	
Robust SD	0.0068	
Robust CV	9.4%	

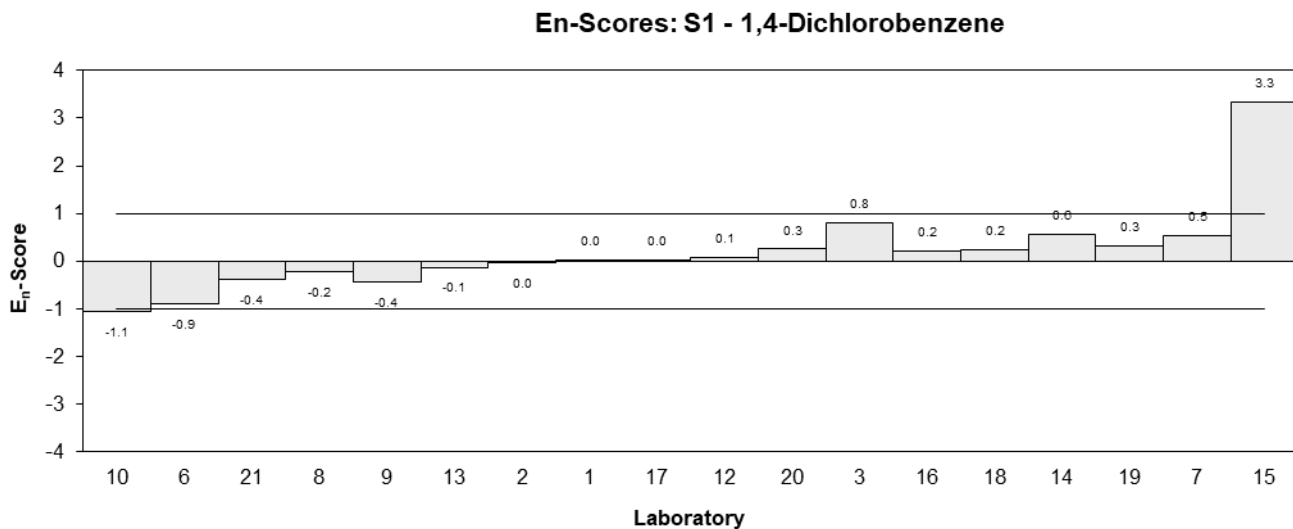
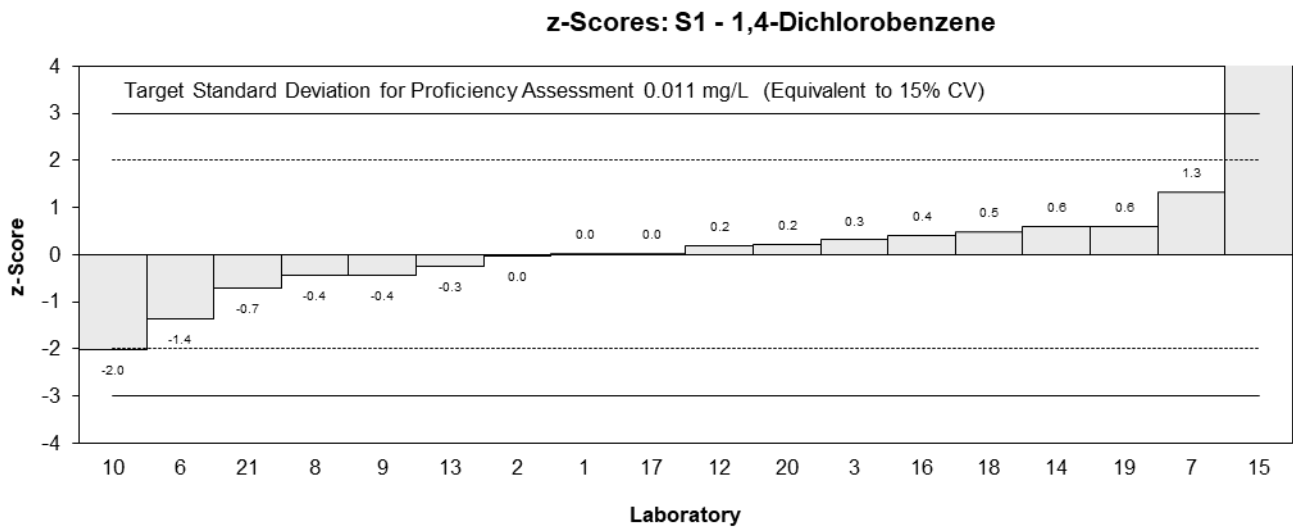
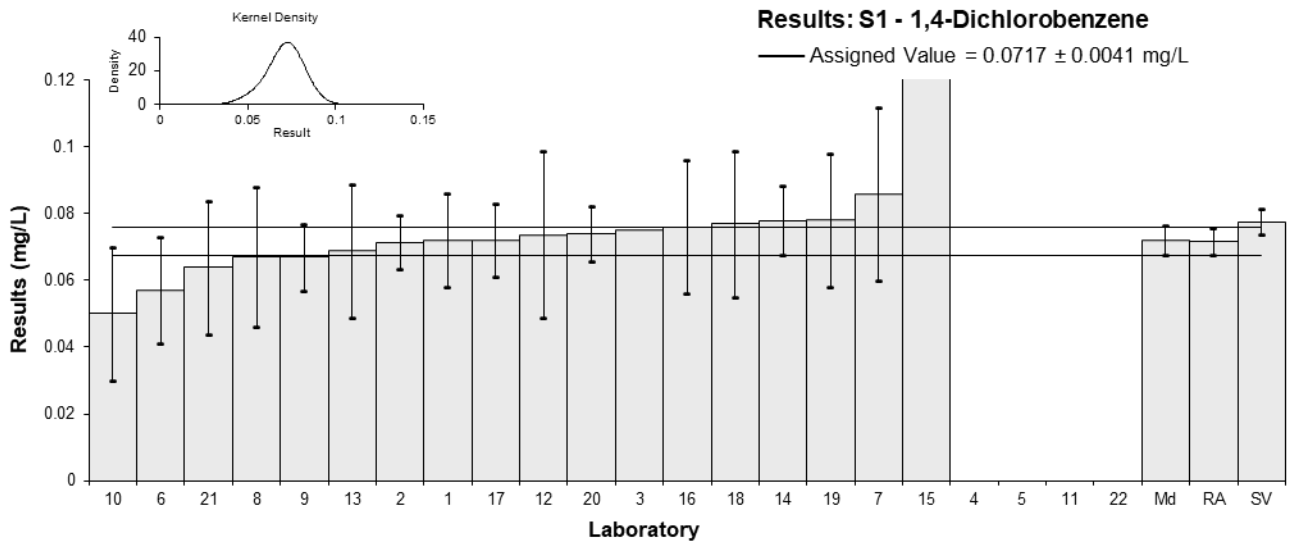


Figure 3

Table 9

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.12	0.024	1.75	0.95
2	0.084	0.0067	-0.77	-0.85
3	0.115	NR	1.40	1.82
4	NT	NT		
5	NT	NT		
6	0.089	0.028	-0.42	-0.20
7	0.086	0.026	-0.63	-0.32
8	0.083	0.03	-0.84	-0.38
9	0.083	0.02	-0.84	-0.53
10	0.13	0.05	2.46	0.68
11	NR	NR		
12	0.100	0.03	0.35	0.16
13	0.074	0.02	-1.47	-0.92
14	0.087	0.0128	-0.56	-0.47
15**	72	21.6	5,045.96	3.33
16	0.1	0.02	0.35	0.22
17	0.129	0.030	2.39	1.06
18	0.094	0.026	-0.07	-0.04
19	0.0779	0.022	-1.20	-0.70
20	0.099	0.0172	0.28	0.20
21	0.085	0.03	-0.70	-0.31
22	NS	NS		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.095	0.011
Spike Value	0.100	0.005
Robust Average	0.095	0.011
Median	0.0890	0.0090
Mean	0.0962	
N	17	
Max	0.13	
Min	0.074	
Robust SD	0.018	
Robust CV	19%	

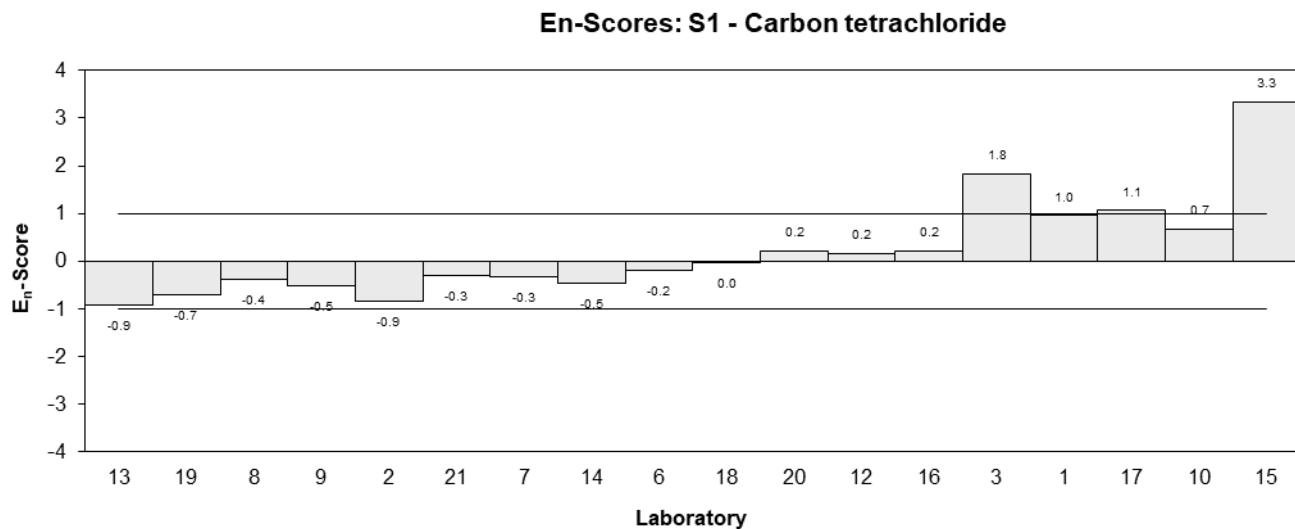
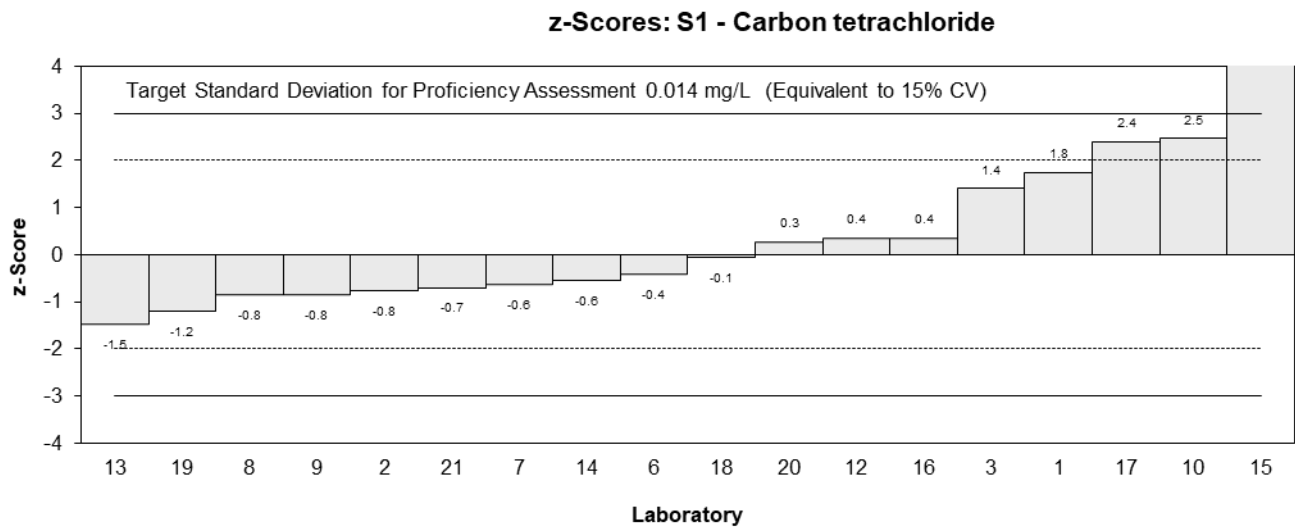
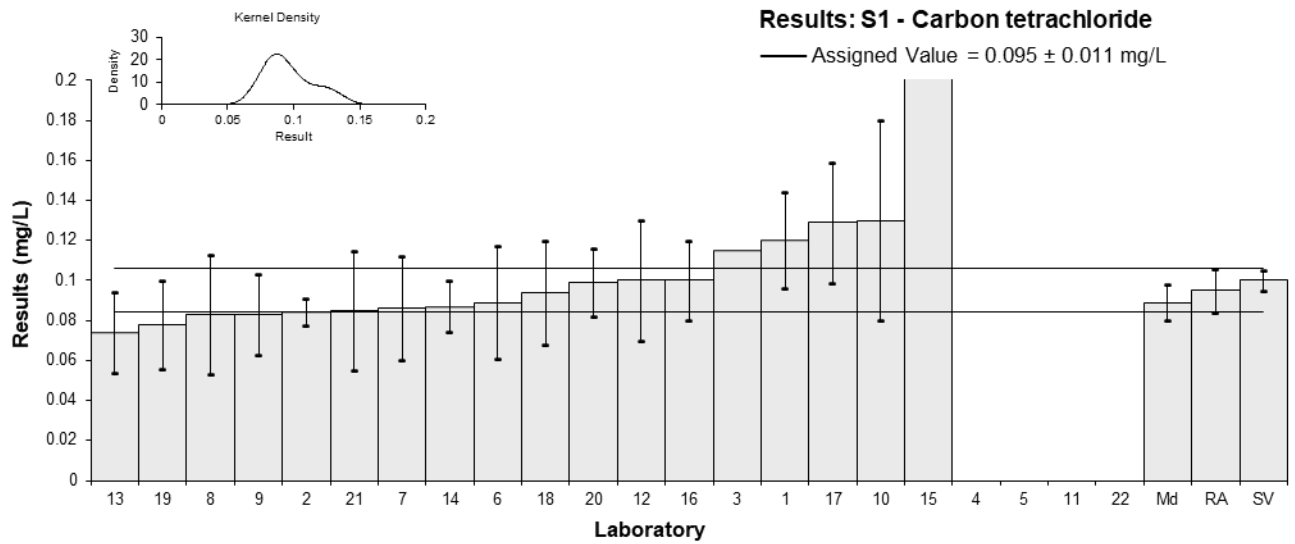


Figure 4

Table 10

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	<0.01	NR		
2	0.017	0.0037	-1.30	-0.86
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	0.018	0.003	-0.98	-0.73
7	0.023	0.007	0.60	0.25
8	0.0153	0.0076	-1.83	-0.71
9	NT	NT		
10	0.03	0.05	2.81	0.18
11	NR	NR		
12	0.0218	0.008	0.22	0.08
13	0.012	0.05	-2.88	-0.18
14	0.025	0.0034	1.23	0.86
15**	18	5.4	5,680.54	3.33
16	0.021	0.006	-0.03	-0.01
17	0.023	0.009	0.60	0.20
18	0.021	0.006	-0.03	-0.01
19	0.0235	0.005	0.76	0.41
20	NT	NT		
21	0.023	0.05	0.60	0.04
22	NS	NS		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.0211	0.0030
Spike Value	0.0157	0.0008
Robust Average	0.0211	0.0030
Median	0.0218	0.0017
Mean	0.0210	
N	13	
Max	0.03	
Min	0.012	
Robust SD	0.0044	
Robust CV	21%	

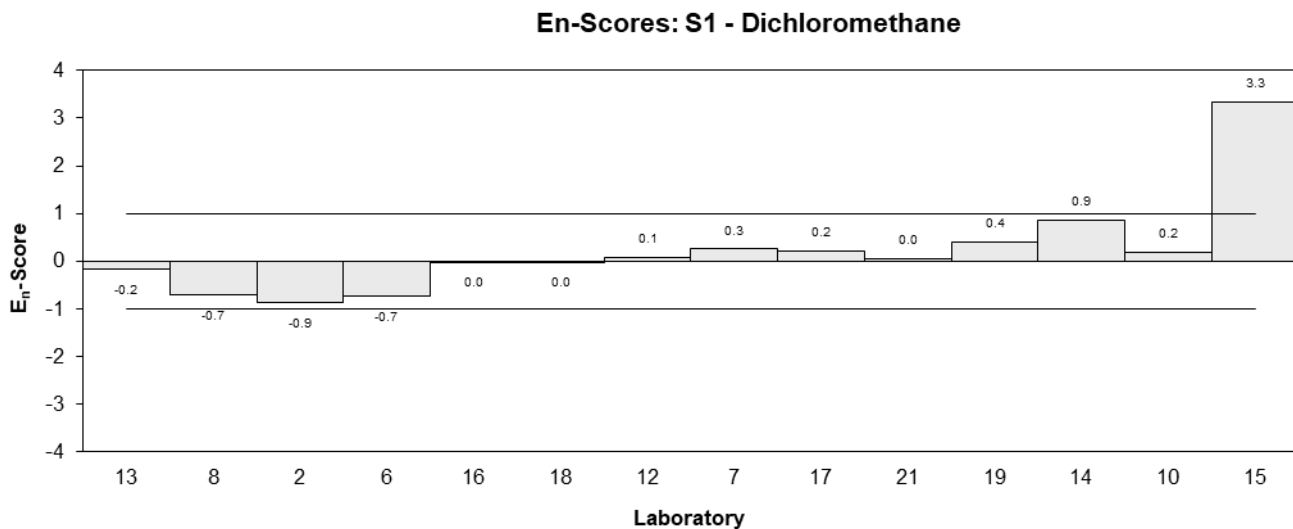
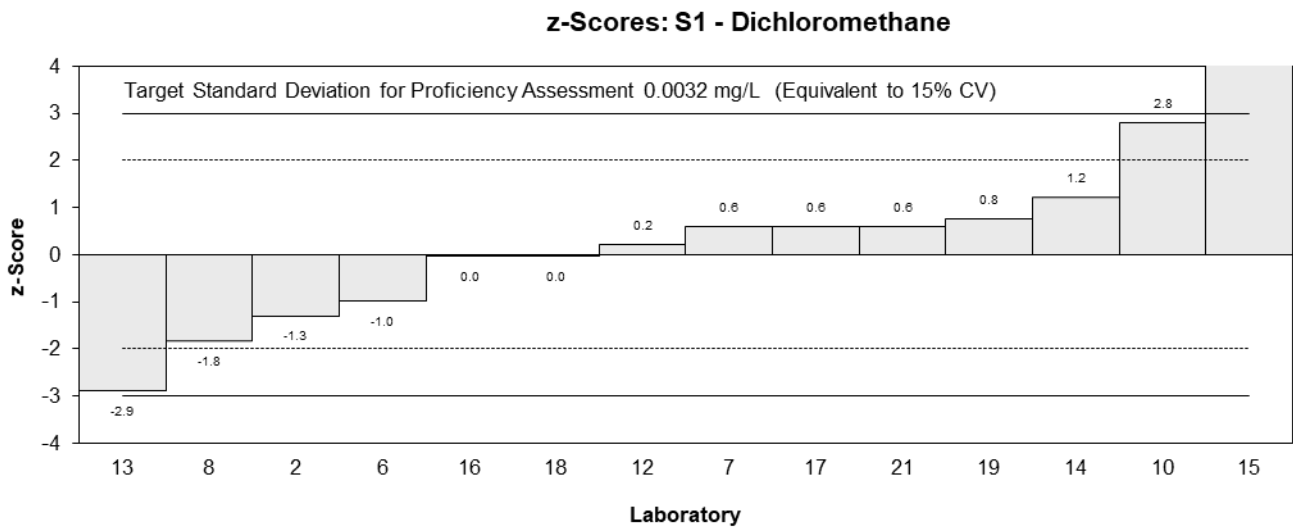
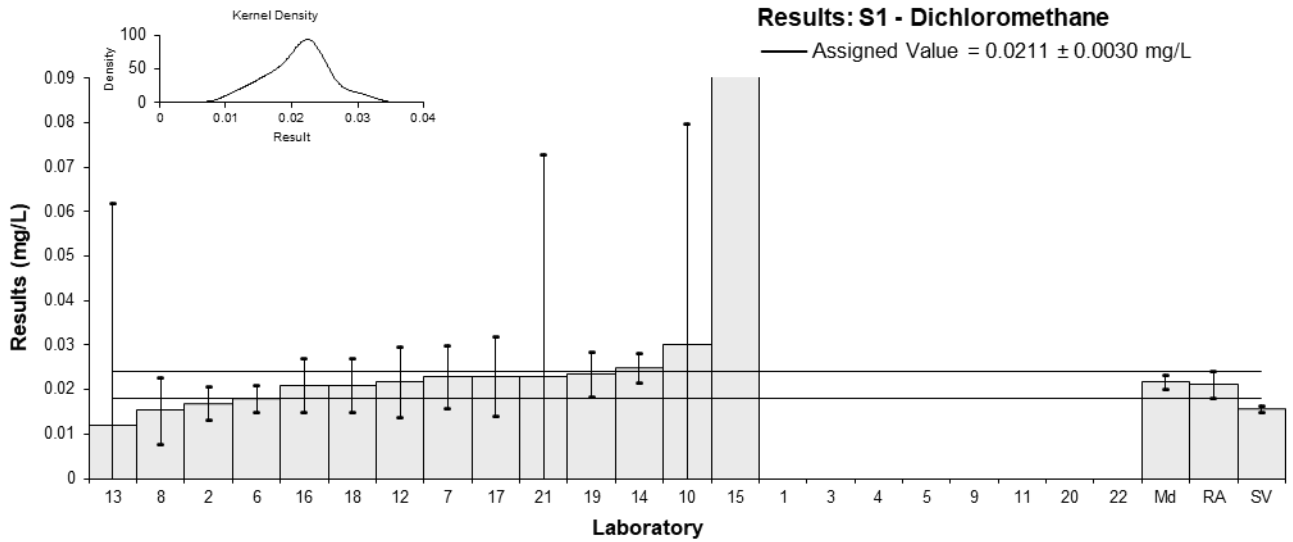


Figure 5

Table 11

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.062	0.012	1.19	0.75
2	0.047	0.0046	-0.71	-0.94
3	0.065	NR	1.57	3.26
4	0.054	0.016	0.18	0.09
5	0.0506	0.0101	-0.25	-0.19
6	0.043	0.023	-1.22	-0.41
7	0.050	0.015	-0.33	-0.17
8	0.046	0.015	-0.84	-0.43
9	0.061	0.02	1.06	0.41
10	0.064	0.03	1.44	0.38
11**	46.9	NR	5,937.57	12,328.26
12	0.0528	0.016	0.03	0.01
13	0.047	0.01	-0.71	-0.52
14	0.052	0.0071	-0.08	-0.07
15**	41	12.3	5,189.78	3.33
16	0.057	0.014	0.56	0.30
17	0.051	0.011	-0.20	-0.14
18	0.052	0.013	-0.08	-0.04
19	0.05	0.02	-0.33	-0.13
20	0.049	0.0061	-0.46	-0.50
21	0.05	0.02	-0.33	-0.13
22	NS	NS		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.0526	0.0038
Spike Value	0.0500	0.0025
Robust Average	0.0526	0.0038
Median	0.0510	0.0026
Mean	0.0528	
N	19	
Max	0.065	
Min	0.043	
Robust SD	0.0066	
Robust CV	13%	

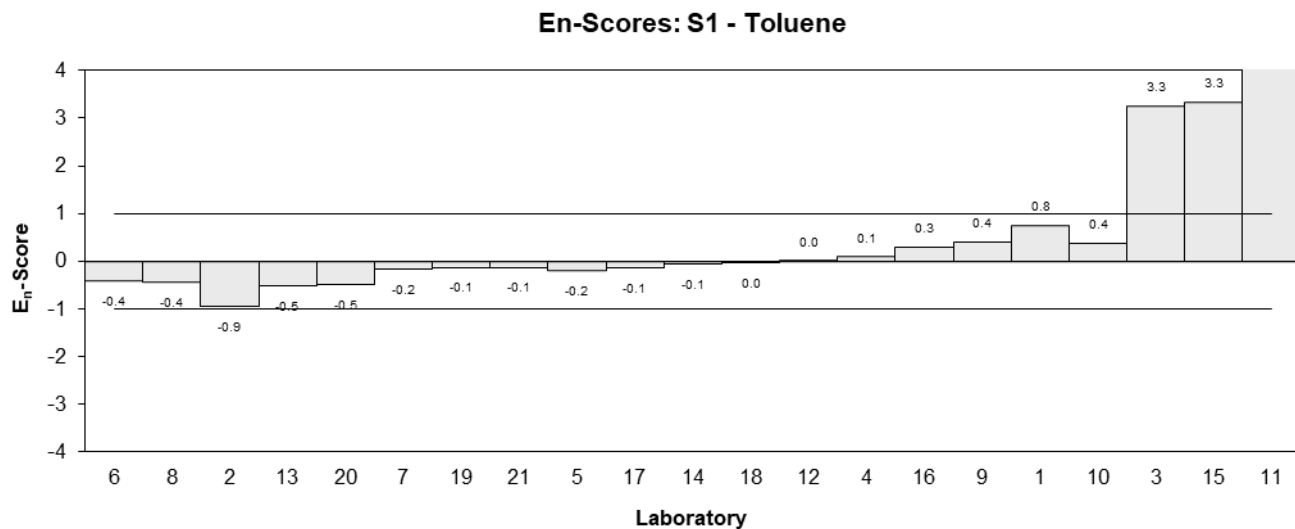
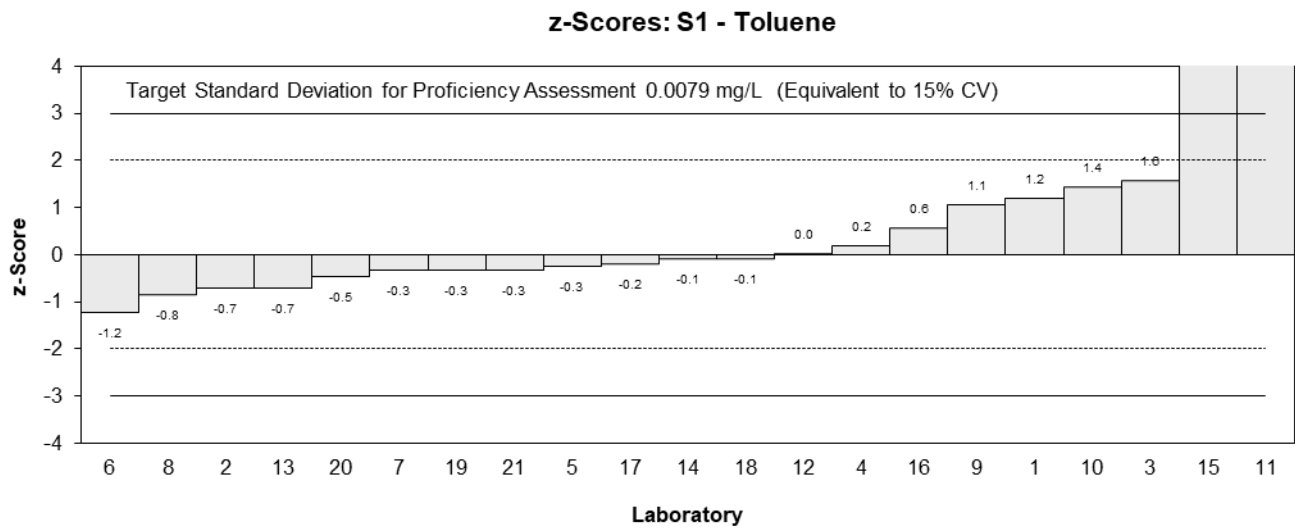
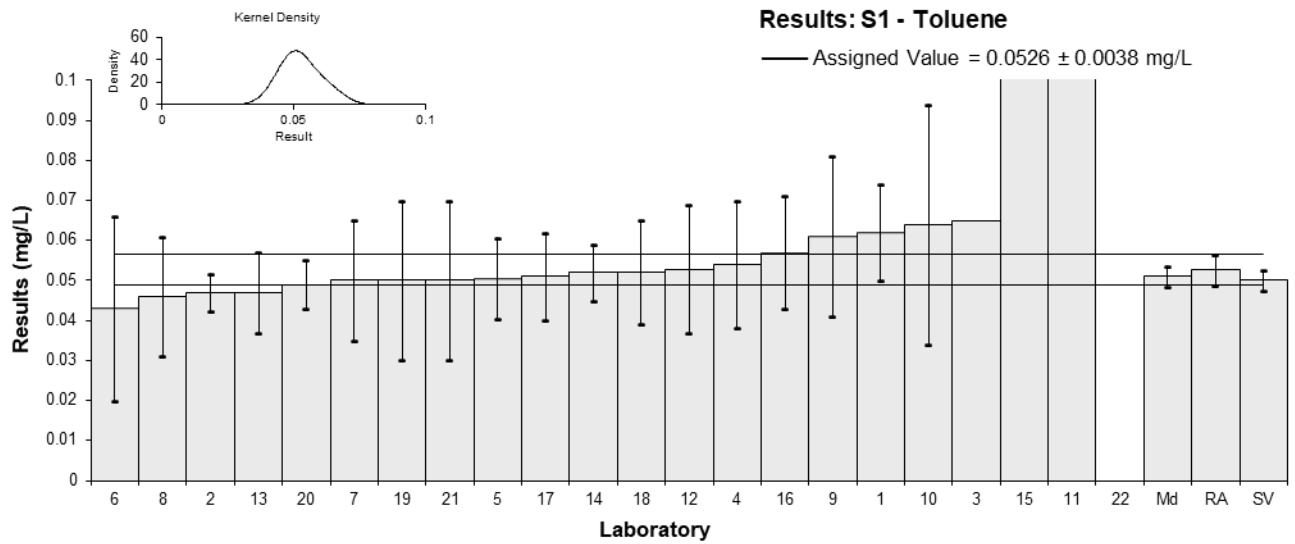


Figure 6

Table 12

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.17	0.034	0.99	0.61
2	0.132	0.0106	-0.72	-1.00
3	0.177	NR	1.31	2.42
4	0.13	0.04	-0.81	-0.43
5	0.1462	0.0292	-0.08	-0.06
6	0.122	NR	-1.17	-2.17
7	0.148	0.044	0.00	0.00
8	0.1318	0.0417	-0.73	-0.37
9	0.172	0.09	1.08	0.26
10	0.13	0.03	-0.81	-0.56
11**	143.0	NR	6,434.77	11,904.33
12	0.147	0.05	-0.05	-0.02
13	0.13	0.03	-0.81	-0.56
14	0.147	0.0201	-0.05	-0.04
15**	120	36	5,398.74	3.33
16	0.18	0.05	1.44	0.62
17	0.155	0.027	0.32	0.24
18	0.16	0.045	0.54	0.26
19	0.161	0.024	0.59	0.48
20	0.147	0.0195	-0.05	-0.04
21	0.13	0.04	-0.81	-0.43
22	NS	NS		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.148	0.012
Spike Value	0.200	0.010
Robust Average	0.148	0.012
Median	0.147	0.013
Mean	0.148	
N	19	
Max	0.18	
Min	0.122	
Robust SD	0.020	
Robust CV	14%	

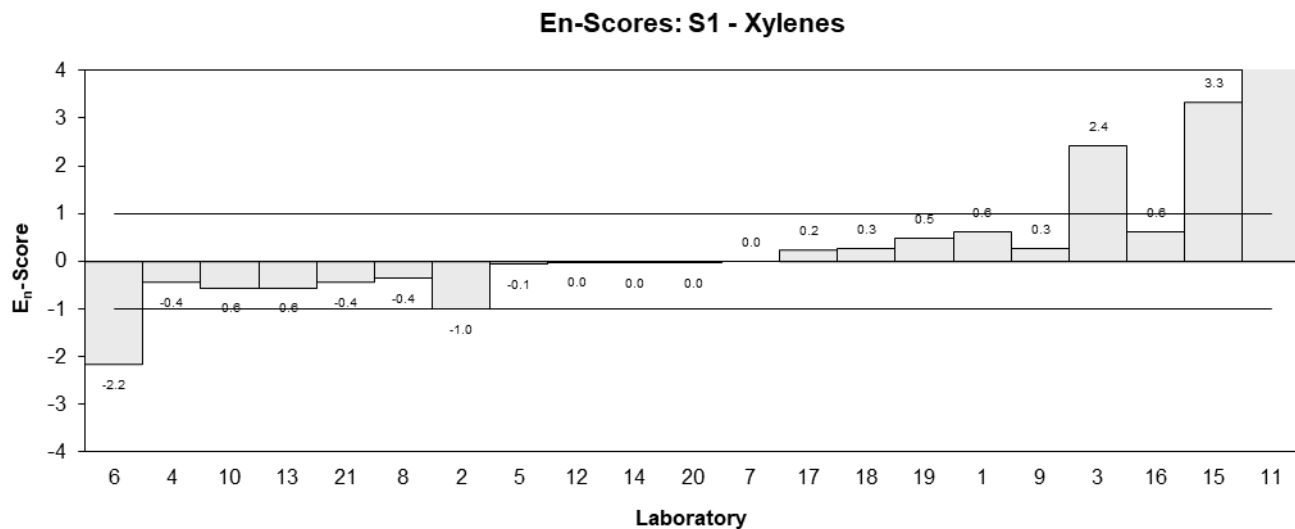
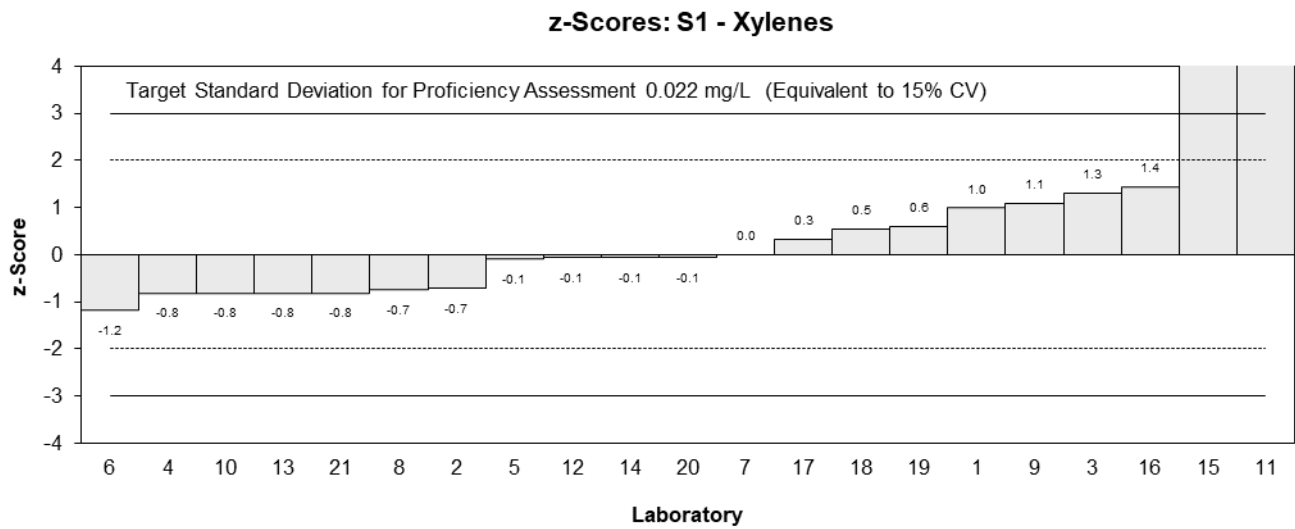
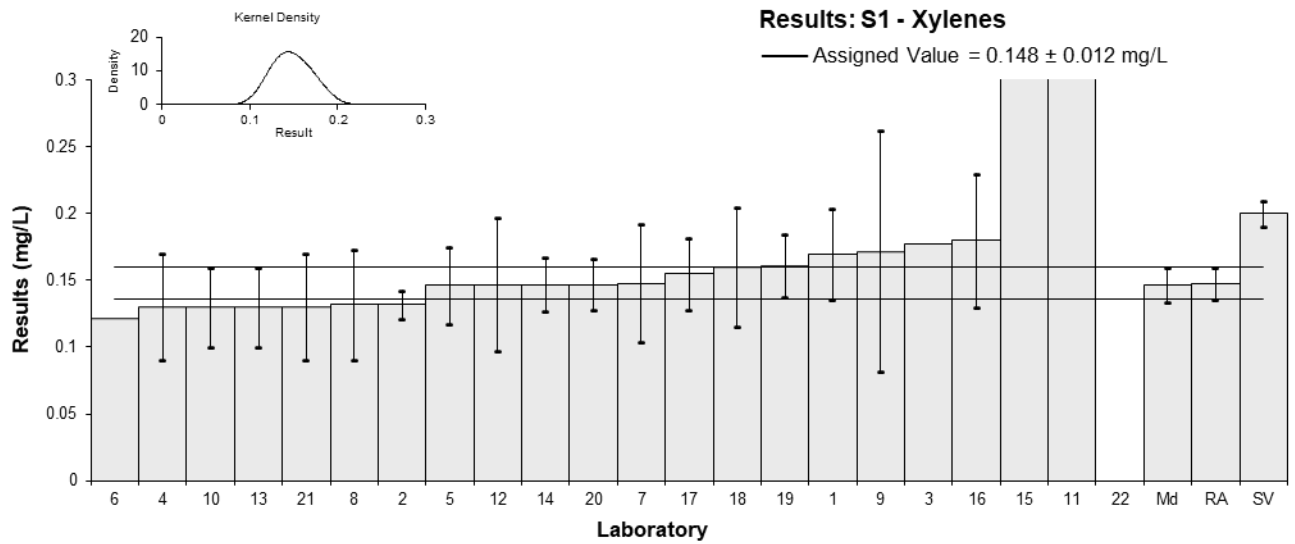


Figure 7

Table 13

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Benz[a]anthracene
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.0049	0.002	2.00 ▼	
2	0.0033	0.0007	-0.31	-0.20
3*	0.0062	NR	2.00 ▼	
4	0.0028	0.0008	-1.27	-0.74
5	0.0026	0.00078	-1.66	-0.99
6	0.0037	0.0009	0.46	0.24
7	0.003	0.001	-0.89	-0.43
8	0.0043	0.0014	1.62	0.58
9	NT	0.0004		
10	0.0038	0.001	0.66	0.32
11	NR	NR		
12	0.0034	0.0010	-0.12	-0.06
13	0.0033	0.001	-0.31	-0.15
14	0.0040	0.00098	1.04	0.51
15**	2.45	0.735	4,713.95	3.33
16	0.0038	0.0012	0.66	0.27
17	0.0030	0.0008	-0.89	-0.52
18	0.003	0.001	-0.89	-0.43
19	0.00372	0.001	0.50	0.24
20	0.0026	0.0021	-1.66	-0.40
21	0.004	0.002	1.04	0.27
22	NS	NS		

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

Statistics

Assigned Value	0.00346	0.00039
Spike Value	0.00499	0.00025
Robust Average	0.00353	0.00042
Max Acceptable Result	0.00649	
Median	0.00355	0.00044
Mean	0.00363	
N	18	
Max	0.0062	
Min	0.0026	
Robust SD	0.00072	
Robust CV	20%	

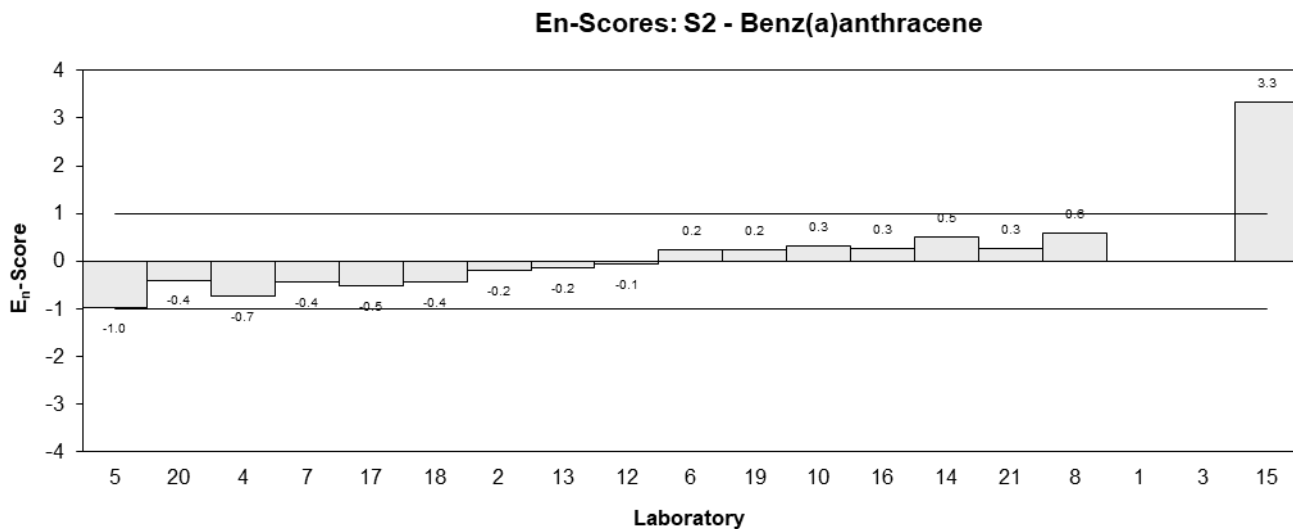
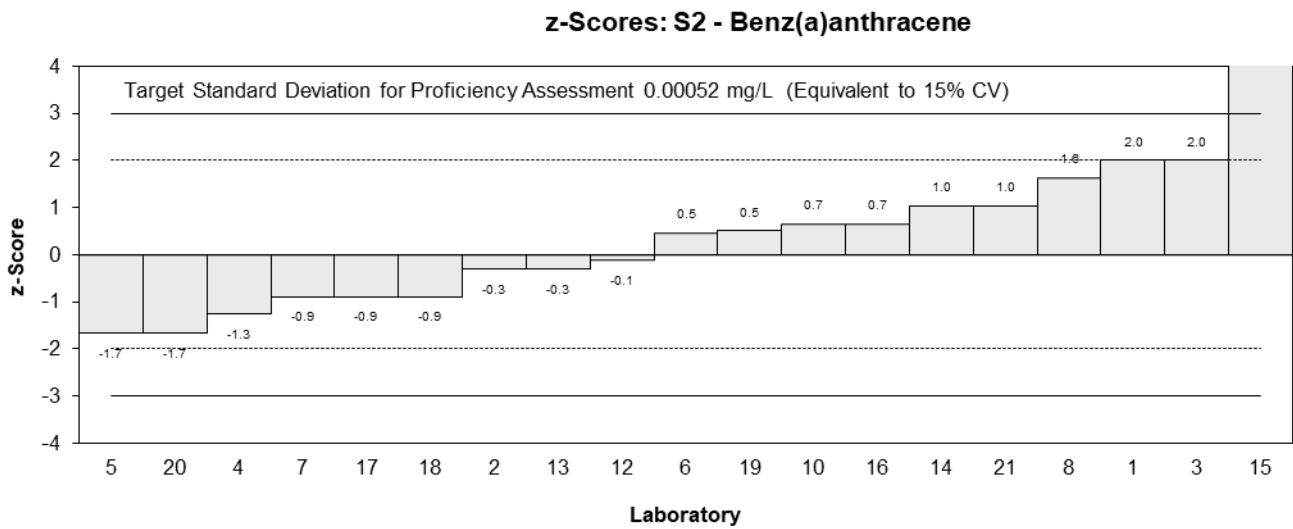
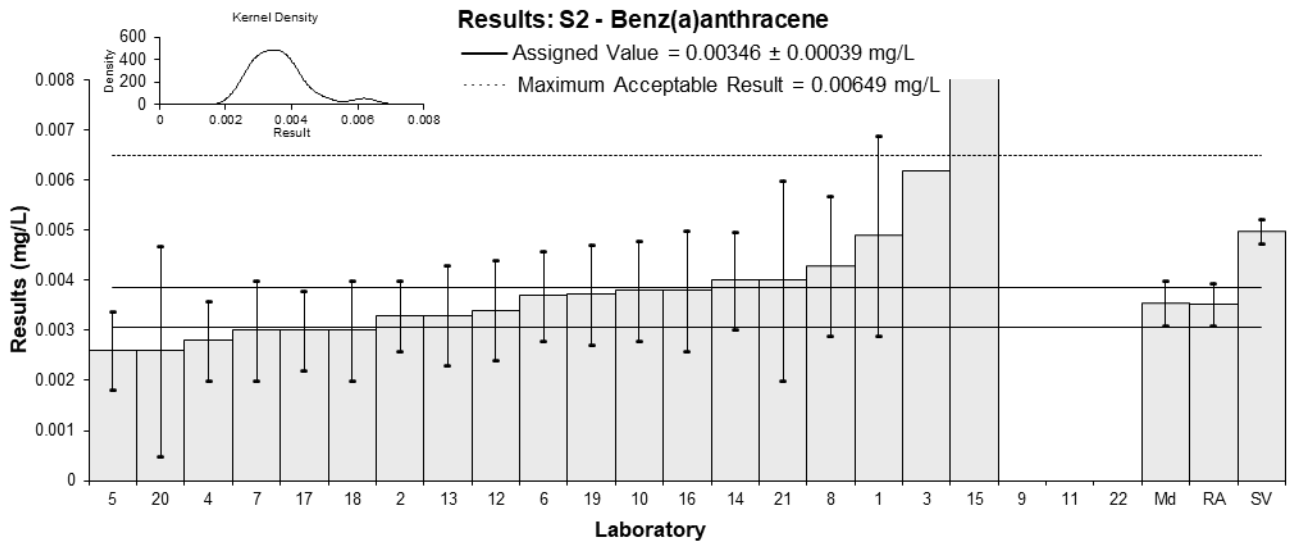


Figure 8

Table 14

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Benzo[a]pyrene
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1*	0.0062	0.0025	5.04	1.03
2	0.0033	0.0006	-0.43	-0.25
3	0.0054	NR	3.53	2.71
4	0.0027	0.0008	-1.57	-0.79
5	<0.001	NR		
6	0.0029	0.0007	-1.19	-0.64
7	0.004	0.001	0.89	0.39
8	0.0046	0.0022	2.02	0.46
9	NT	0.0003		
10	0.0042	0.001	1.27	0.55
11	NR	NR		
12	0.0040	0.0012	0.89	0.34
13	0.0027	0.001	-1.57	-0.68
14	0.0042	0.00098	1.27	0.56
15**	1.1	0.33	2,070.76	3.32
16	0.0047	0.0015	2.21	0.71
17	0.0028	0.0006	-1.38	-0.80
18	0.004	0.001	0.89	0.39
19	0.00329	0.001	-0.45	-0.20
20	0.0019	0.0012	-3.08	-1.18
21	0.002	0.002	-2.89	-0.72
22	NS	NS		

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00353	0.00069
Spike Value	0.00403	0.00020
Robust Average	0.00366	0.00074
Median	0.00400	0.00064
Mean	0.00370	
N	17	
Max	0.0062	
Min	0.0019	
Robust SD	0.0012	
Robust CV	33%	

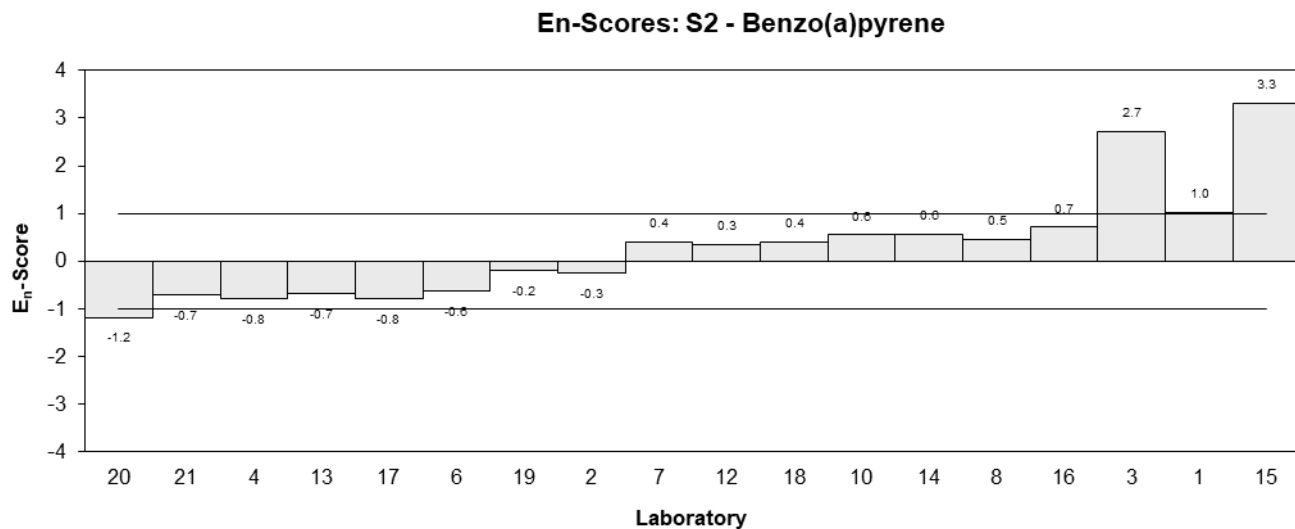
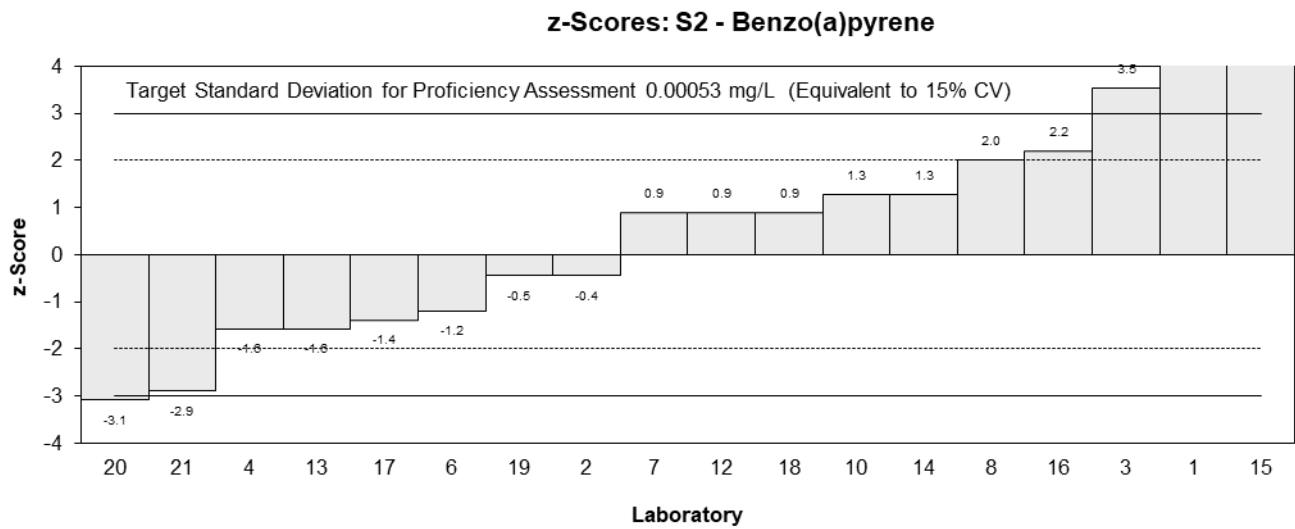
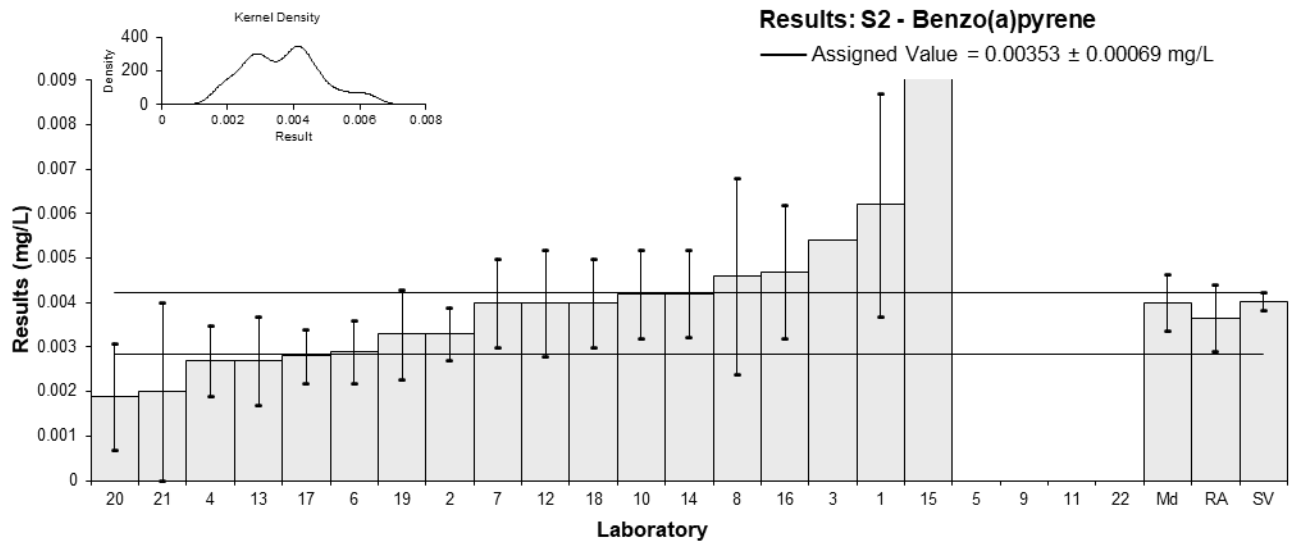


Figure 9

Table 15

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.0031	0.0012	2.00 ▼	
2	0.0017	0.0004	-1.84	-1.08
3	0.0035	NR	2.00 ▼	
4	0.0012	0.0004	-3.26	-1.91
5	<0.001	NR		
6	0.002	0.0005	-0.99	-0.52
7	0.002	0.001	-0.99	-0.32
8	0.0028	0.0011	1.28	0.38
9	0.0034	0.0006	2.00 ▼	
10	0.0019	0.001	-1.28	-0.41
11	NR	NR		
12	0.0021	0.0010	-0.71	-0.23
13	0.0019	0.001	-1.28	-0.41
14	0.0025	0.00065	0.43	0.19
15**	1.15	0.345	3,255.74	3.33
16	0.0033	0.0011	2.00 ▼	
17	0.0022	0.0005	-0.43	-0.22
18	0.002	0.001	-0.99	-0.32
19	0.00216	0.001	-0.54	-0.17
20	0.0016	0.0011	-2.13	-0.63
21	0.003	0.001	1.84	0.59
22	NS	NS		

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

Statistics

Assigned Value	0.00235	0.00045
Spike Value	0.00299	0.00015
Robust Average	0.00235	0.00045
Max Acceptable Result	0.00388	
Median	0.00213	0.00035
Mean	0.00235	
N	18	
Max	0.0035	
Min	0.0012	
Robust SD	0.00076	
Robust CV	32%	

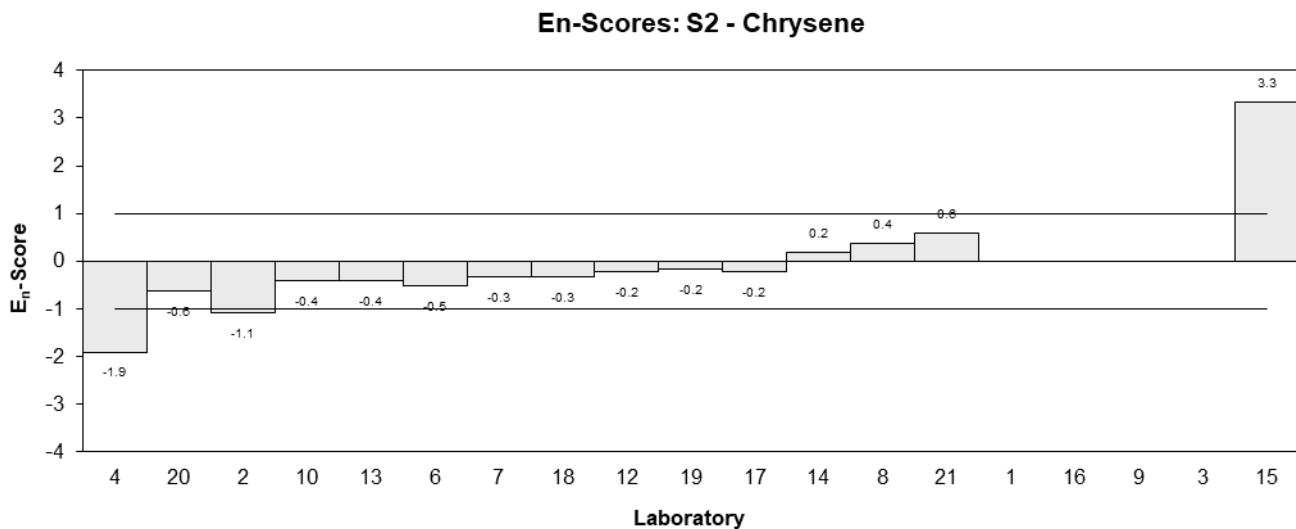
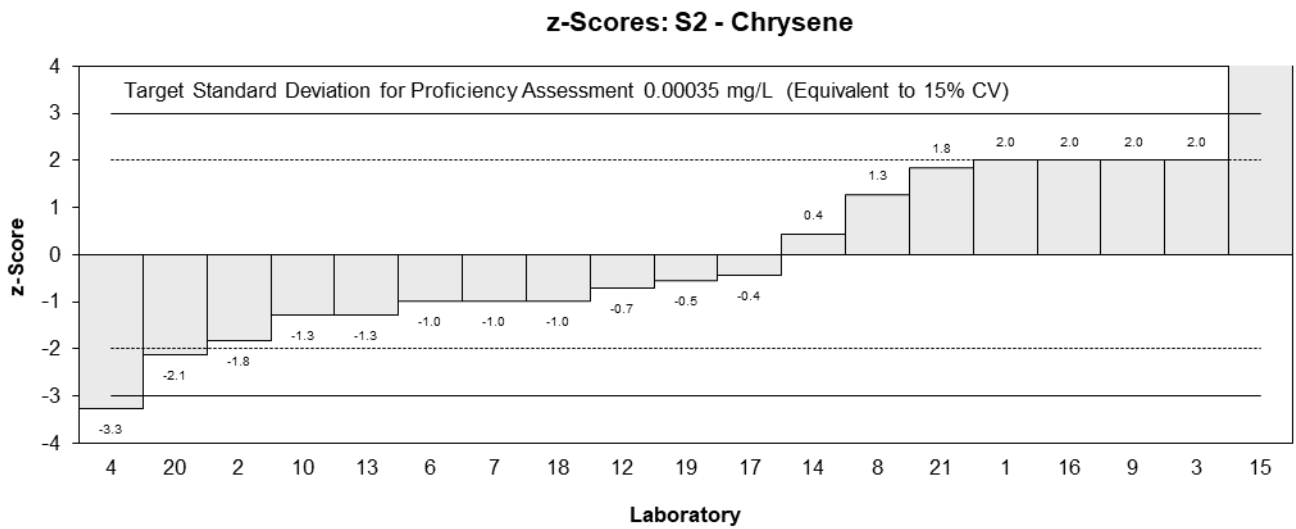
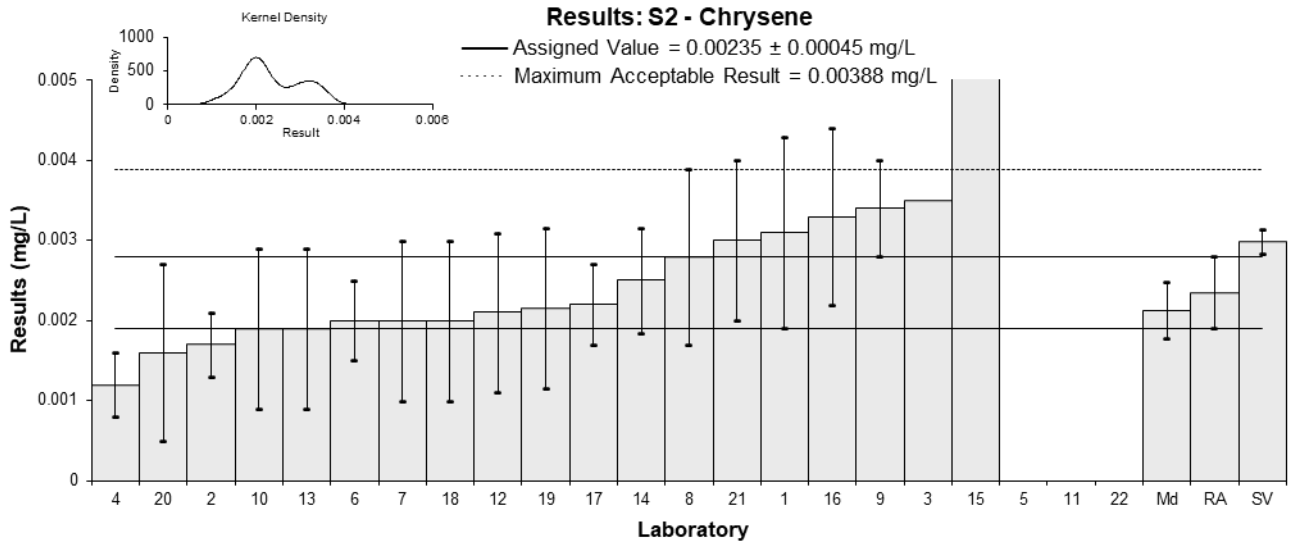


Figure 10

Table 16

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.0065	0.0026	0.79	0.26
2	0.0051	0.001	-0.81	-0.65
3	0.0068	NR	1.14	2.15
4	0.0068	0.002	1.14	0.48
5	0.0062	0.00186	0.45	0.20
6	0.0053	0.0013	-0.59	-0.37
7	0.006	0.002	0.22	0.09
8	0.006	0.0016	0.22	0.11
9	NT	0.0006		
10	0.0054	0.002	-0.47	-0.20
11	NR	NR		
12	0.0065	0.0020	0.79	0.34
13	0.0051	0.002	-0.81	-0.35
14	0.0054	0.00139	-0.47	-0.28
15**	5.75	1.725	6,591.15	3.33
16	0.0068	0.0022	1.14	0.44
17	0.0054	0.0009	-0.47	-0.41
18	0.006	0.002	0.22	0.09
19	0.00558	0.001	-0.26	-0.21
20	0.0044	0.0030	-1.62	-0.46
21	0.005	0.002	-0.93	-0.39
22	NS	NS		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00581	0.00046
Spike Value	0.00700	0.00035
Robust Average	0.00581	0.00046
Median	0.00579	0.00052
Mean	0.00579	
N	18	
Max	0.0068	
Min	0.0044	
Robust SD	0.00078	
Robust CV	13%	

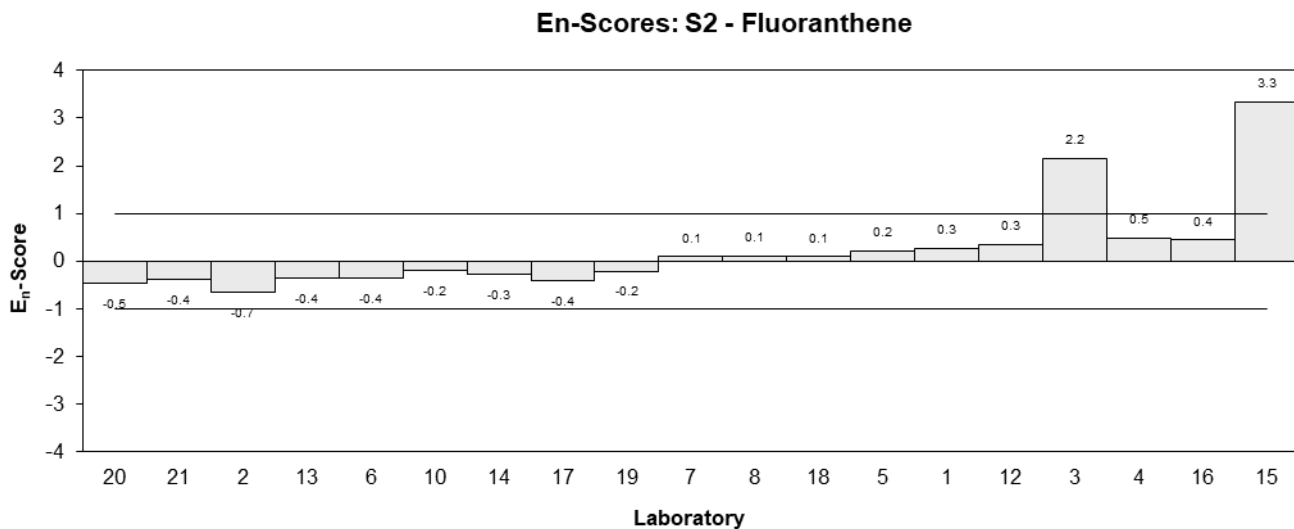
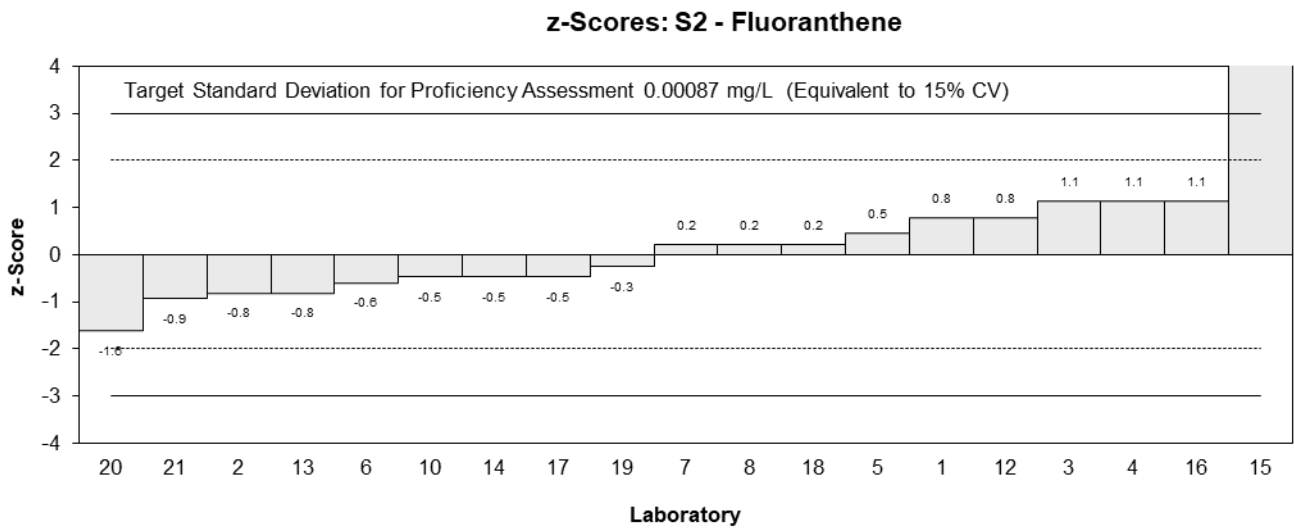
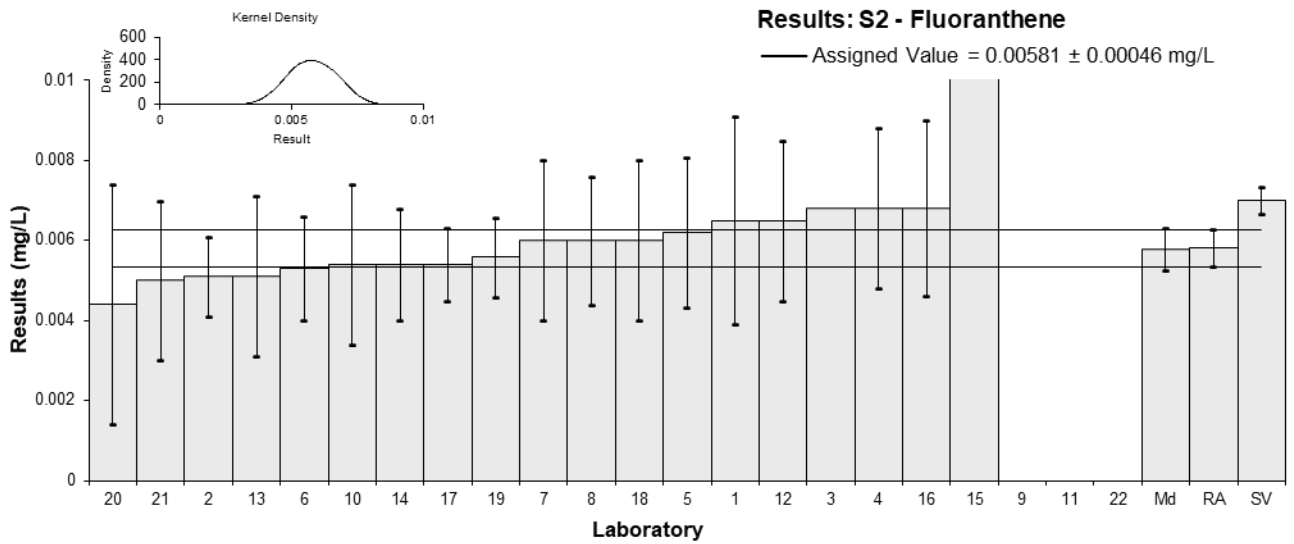


Figure 11

Table 17

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.0090	0.0036	0.79	0.26
2	0.0064	0.0017	-1.37	-0.86
3	0.0063	NR	-1.45	-1.92
4	0.0082	0.0025	0.12	0.06
5	0.012	0.0036	3.27	1.06
6	0.0076	0.0019	-0.37	-0.21
7	0.010	0.003	1.61	0.62
8	0.0087	0.0027	0.54	0.23
9	0.0065	0.002	-1.28	-0.71
10	0.0071	0.002	-0.79	-0.43
11	NR	NR		
12	0.0096	0.0029	1.28	0.51
13	0.0075	0.002	-0.46	-0.25
14	0.0086	0.00191	0.46	0.26
15**	9.2	2.76	7,612.38	3.33
16	0.0093	0.0029	1.04	0.41
17	0.0066	0.0010	-1.20	-1.07
18	0.01	0.004	1.61	0.48
19	0.00798	0.002	-0.06	-0.03
20	0.0062	0.0038	-1.53	-0.47
21	0.007	0.002	-0.87	-0.48
22	NS	NS		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00805	0.00091
Spike Value	0.0100	0.0005
Robust Average	0.00805	0.00091
Median	0.0080	0.0011
Mean	0.00814	
N	19	
Max	0.012	
Min	0.0062	
Robust SD	0.0016	
Robust CV	20%	

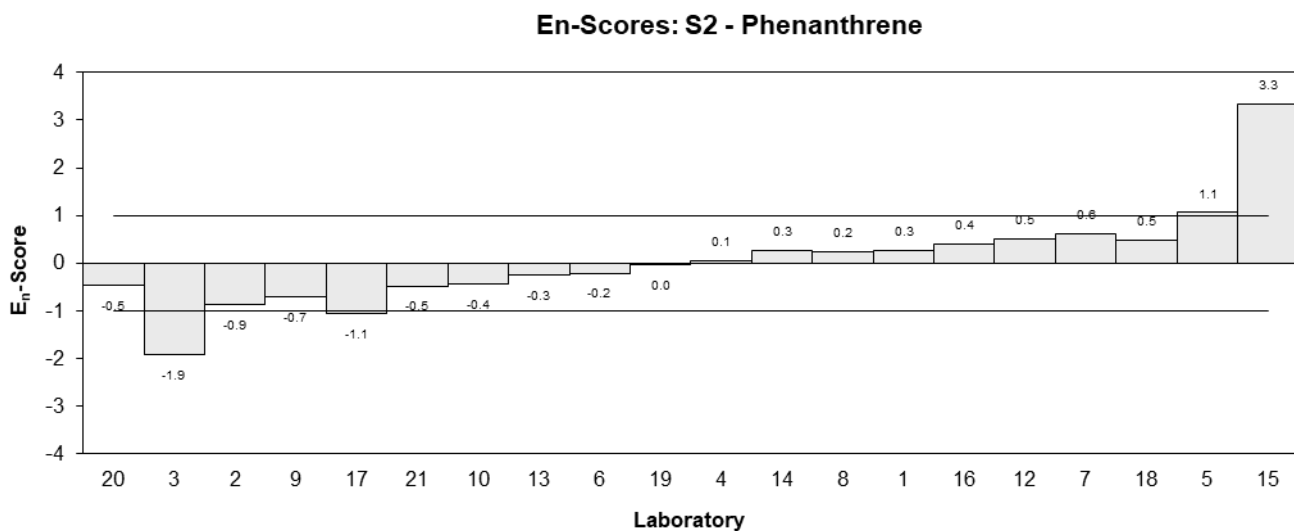
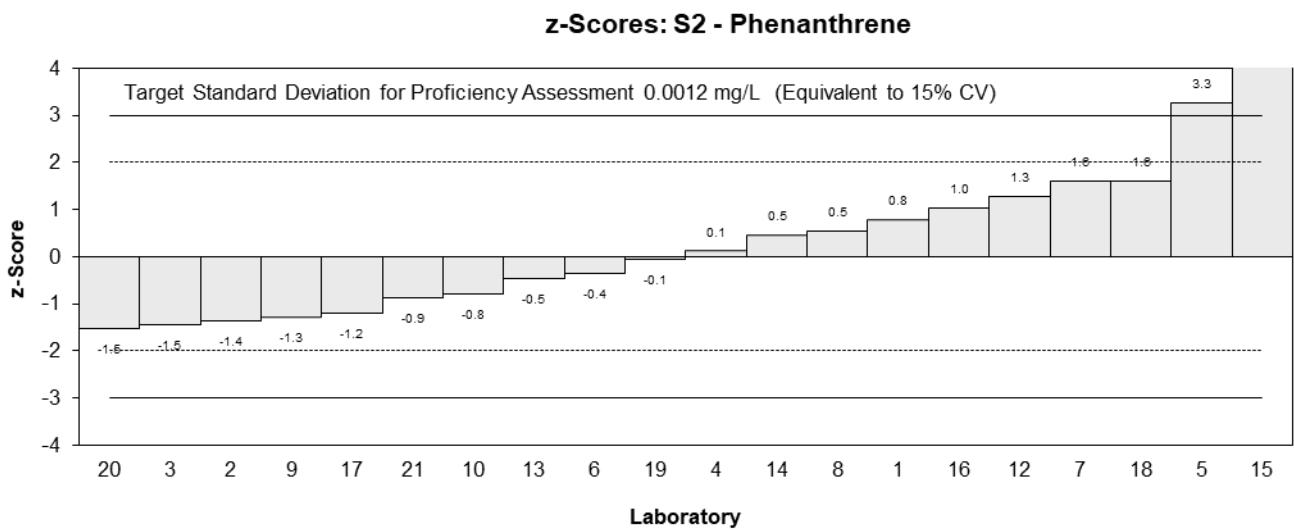
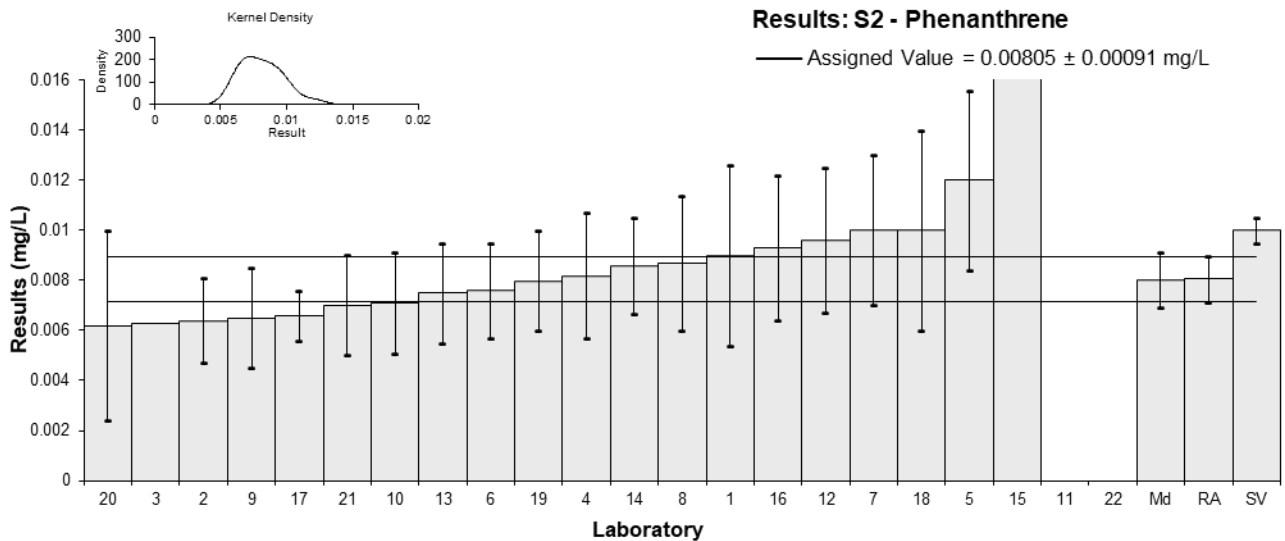


Figure 12

Table 18

Sample Details

Sample No.	S3
Matrix	Potable Water
Analyte	2,4-Dichlorophenol
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.013	0.0052	0.08	0.04
2	0.0111	0.0016	-0.66	-0.88
3	0.015	NR	0.86	2.00
4	0.011	0.003	-0.70	-0.56
5	0.0124	0.00372	-0.16	-0.10
6	0.013	0.003	0.08	0.06
7	0.013	0.004	0.08	0.05
8*	0.0038	NR	-3.52	-8.18
9	<0.03	NR		
10	0.012	0.005	-0.31	-0.16
11	NR	NR		
12	0.0111	0.004	-0.66	-0.41
13	0.013	0.003	0.08	0.06
14	0.01164	0.00316	-0.45	-0.35
15**	13	3.9	5,073.12	3.33
16	0.014	0.0048	0.47	0.24
17	0.0108	0.0021	-0.78	-0.84
18	0.014	0.006	0.47	0.20
19	0.015	0.003	0.86	0.69
20	0.0089	0.0049	-1.52	-0.78
21	0.015	0.005	0.86	0.43
22	0.01637	0.00231	1.39	1.40

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.0128	0.0011
Spike Value	0.0139	0.0007
Homogeneity Value	0.011	0.004
Robust Average	0.0126	0.0012
Median	0.0130	0.0016
Mean	0.0123	
N	19	
Max	0.01637	
Min	0.0038	
Robust SD	0.0021	
Robust CV	17%	

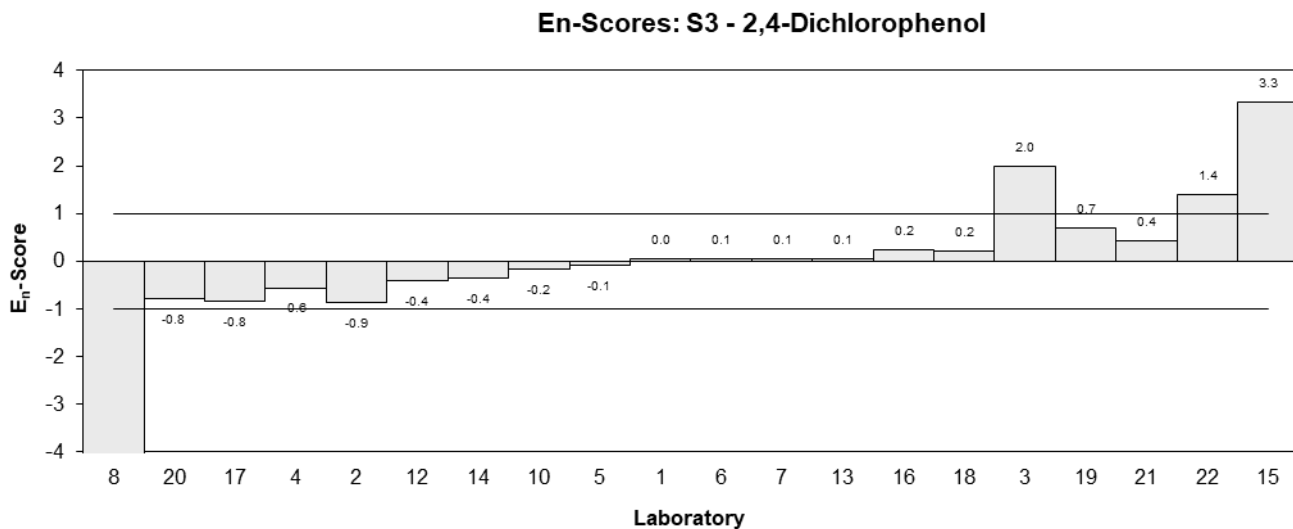
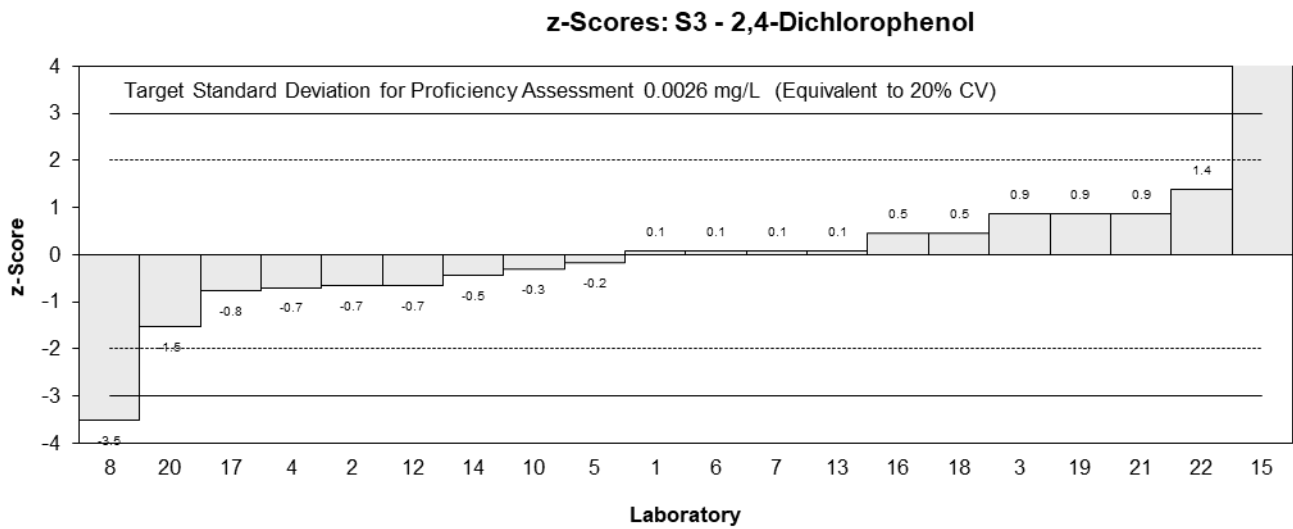
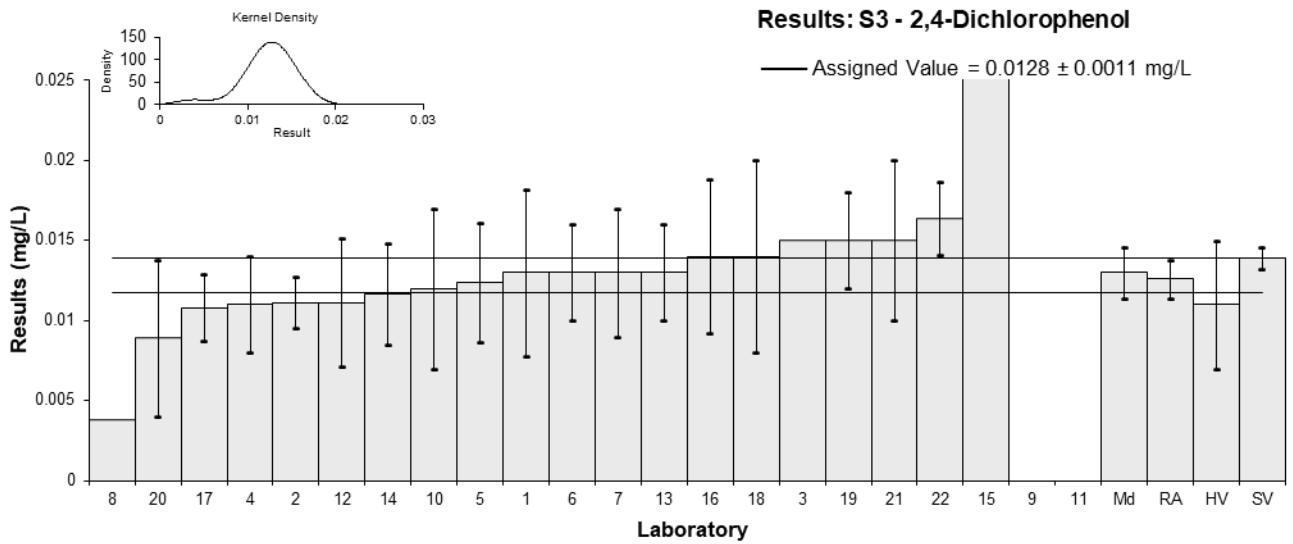


Figure 13

Table 19

Sample Details

Sample No.	S3
Matrix	Potable Water
Analyte	2,6-Dichlorophenol
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.0062	0.0025	-0.25	-0.12
2	0.005	0.0008	-1.17	-1.37
3	0.006	NR	-0.40	-0.68
4	0.0056	0.002	-0.71	-0.43
5	0.0086	0.00258	1.60	0.77
6	0.0065	0.001	-0.02	-0.02
7	0.007	0.001	0.37	0.38
8	0.0077	NR	0.90	1.53
9	<0.03	NR		
10	0.006	0.003	-0.40	-0.17
11	NR	NR		
12	0.0058	0.002	-0.55	-0.34
13	0.005	0.003	-1.17	-0.49
14	0.0055	0.00148	-0.78	-0.61
15**	6	1.8	4,596.23	3.33
16	0.0075	0.0024	0.75	0.39
17*	0.0032	0.0006	-2.55	-3.40
18	0.007	0.003	0.37	0.15
19	0.00737	0.001	0.65	0.67
20	0.0047	0.0021	-1.40	-0.81
21	0.008	0.003	1.13	0.48
22	0.00796	0.00112	1.10	1.06

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.00652	0.00077
Spike Value	0.00702	0.00035
Homogeneity Value	0.006	0.005
Robust Average	0.00640	0.00080
Median	0.00620	0.00100
Mean	0.00635	
N	19	
Max	0.0086	
Min	0.0032	
Robust SD	0.0014	
Robust CV	22%	

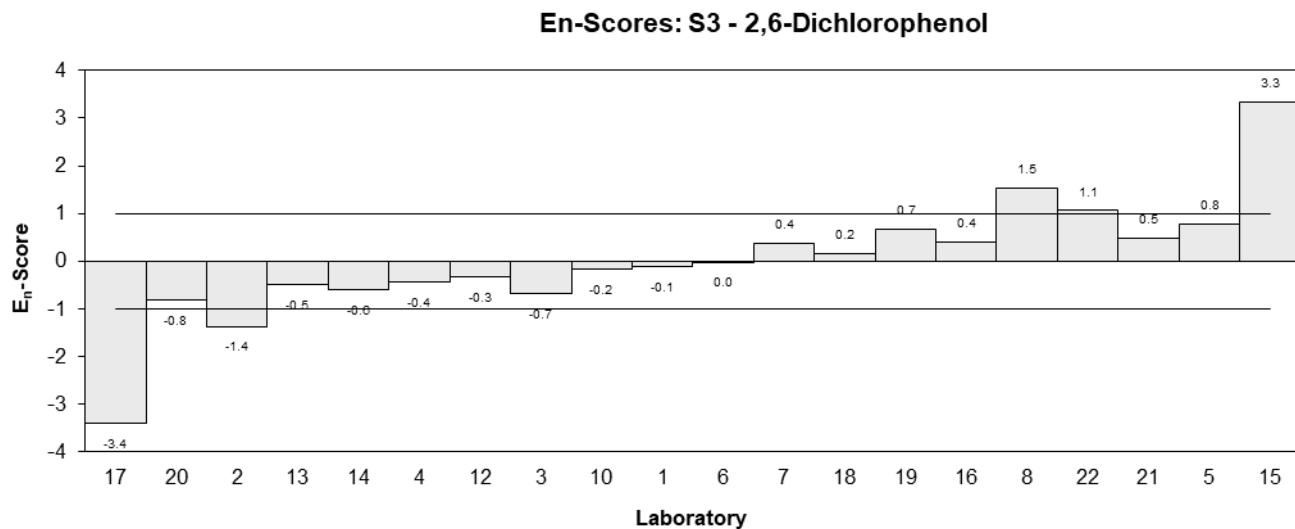
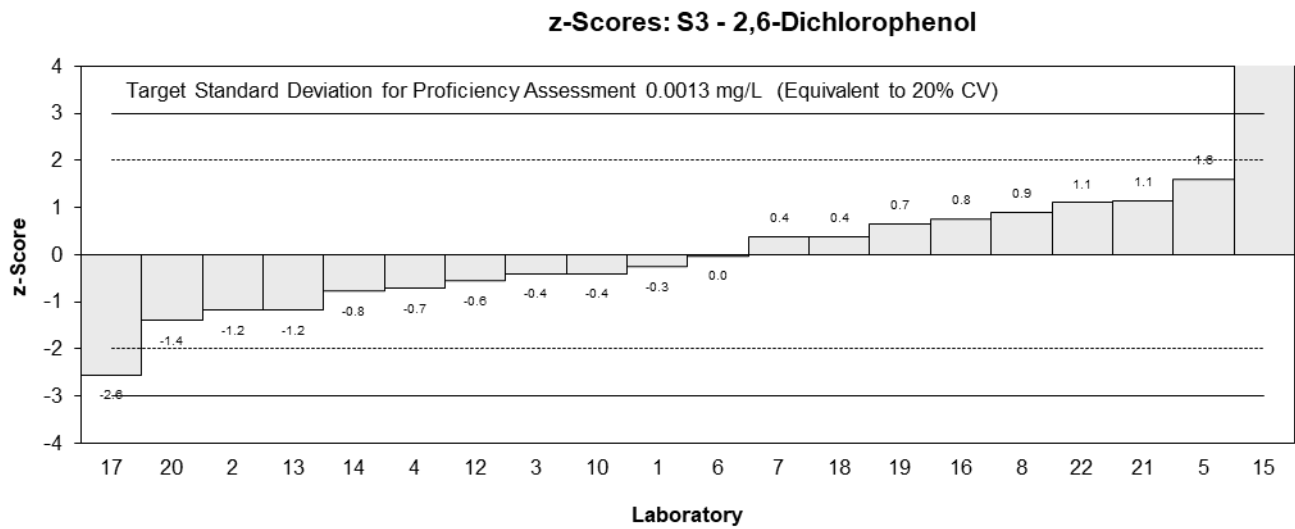
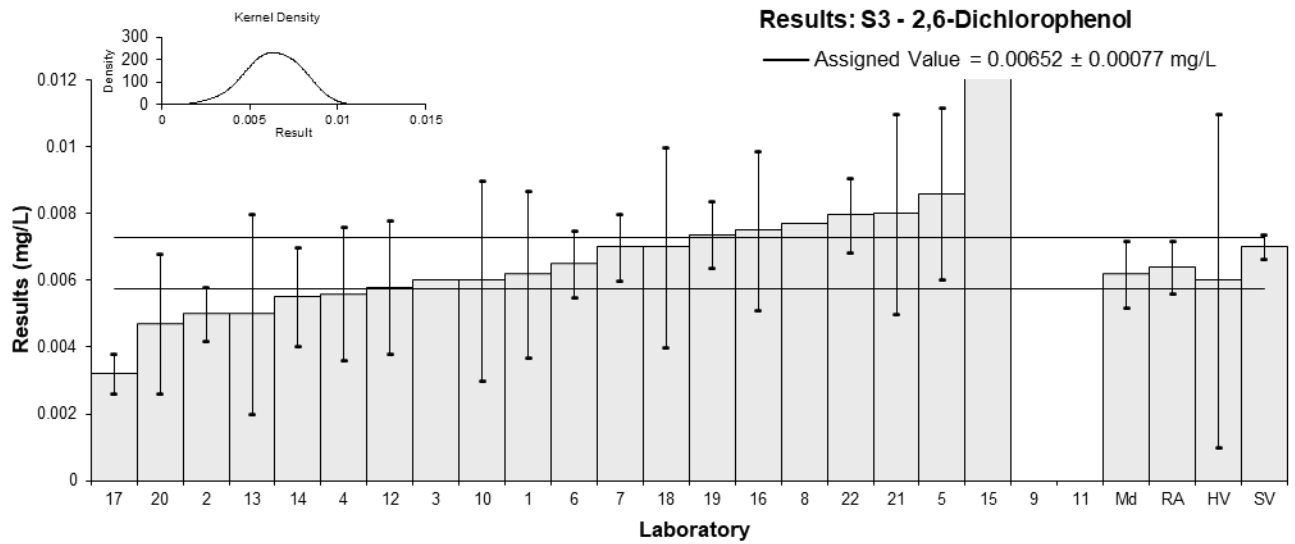


Figure 14

Table 20

Sample Details

Sample No.	S3
Matrix	Potable Water
Analyte	2-Methylphenol
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.0080	0.0032	0.33	0.15
2	0.0066	0.0013	-0.60	-0.55
3	NT	NT		
4	0.0095	0.003	1.33	0.63
5	0.0059	0.00177	-1.07	-0.79
6	0.0089	0.0018	0.93	0.68
7	0.007	0.002	-0.33	-0.22
8	0.005	NR	-1.67	-2.50
9	<0.03	NR		
10	0.008	0.005	0.33	0.10
11	NR	NR		
12	0.0064	0.002	-0.73	-0.49
13	0.007	0.005	-0.33	-0.10
14	0.0064	0.00172	-0.73	-0.55
15**	9.1	2.73	6,061.67	3.33
16*	0.012	0.004	2.00▼	
17	0.0064	0.0015	-0.73	-0.61
18	0.007	0.002	-0.33	-0.22
19	0.00927	0.001	1.18	1.25
20	0.0065	0.0032	-0.67	-0.30
21	0.011	0.005	2.00▼	
22	0.0095	0.0028	1.33	0.69

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

Statistics

Assigned Value	0.0075	0.0010
Spike Value	0.0101	0.0005
Homogeneity Value	0.010	0.004
Robust Average	0.0077	0.0011
Max Acceptable Result	0.0141	
Median	0.00700	0.00087
Mean	0.00780	
N	18	
Max	0.012	
Min	0.005	
Robust SD	0.0019	
Robust CV	24%	

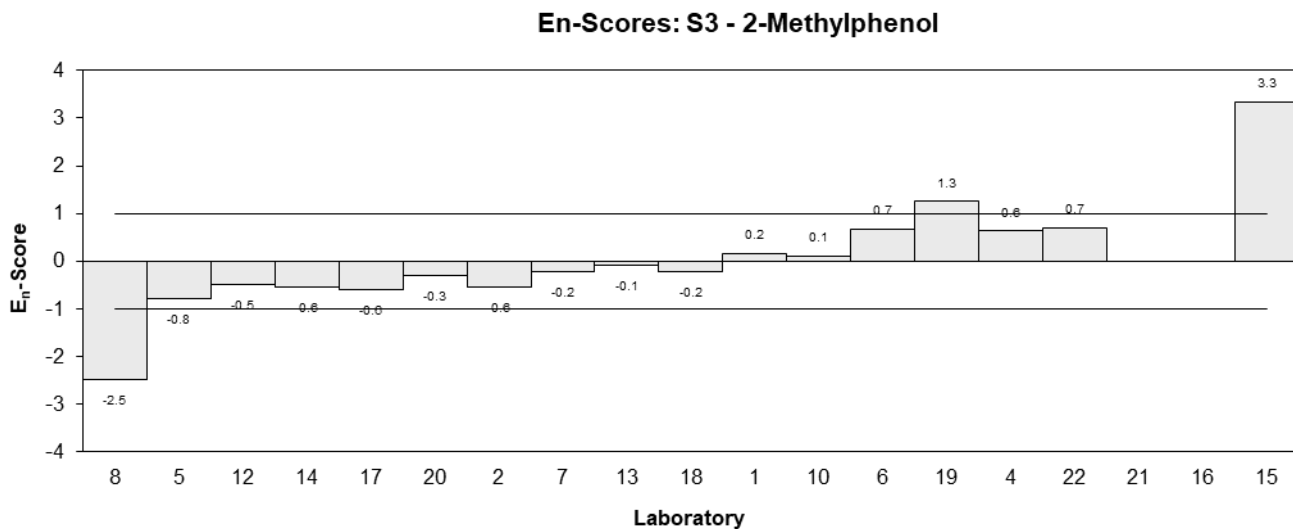
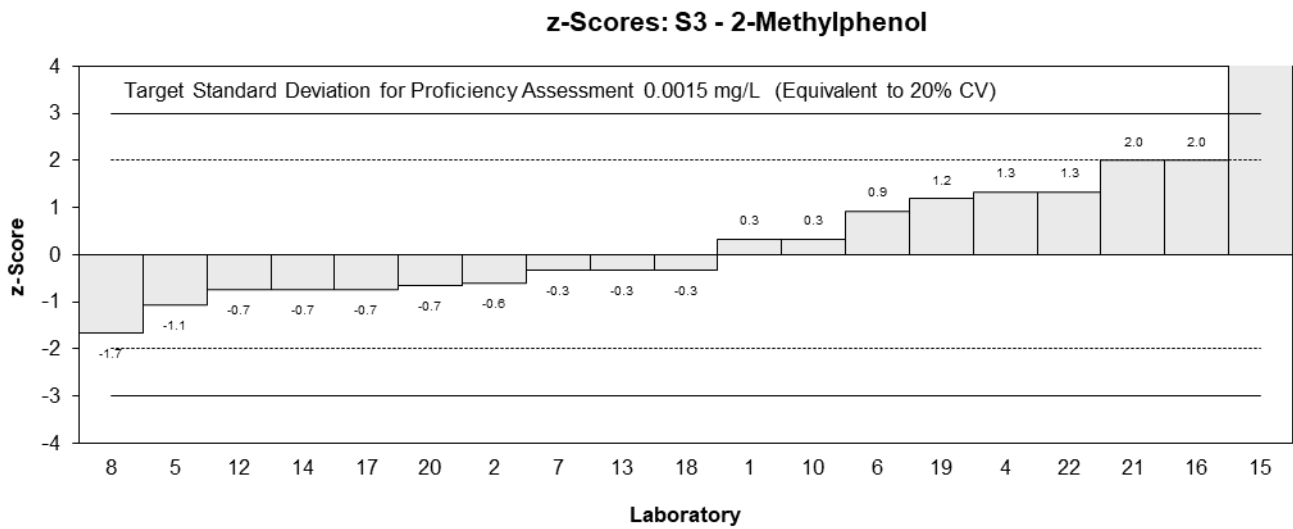
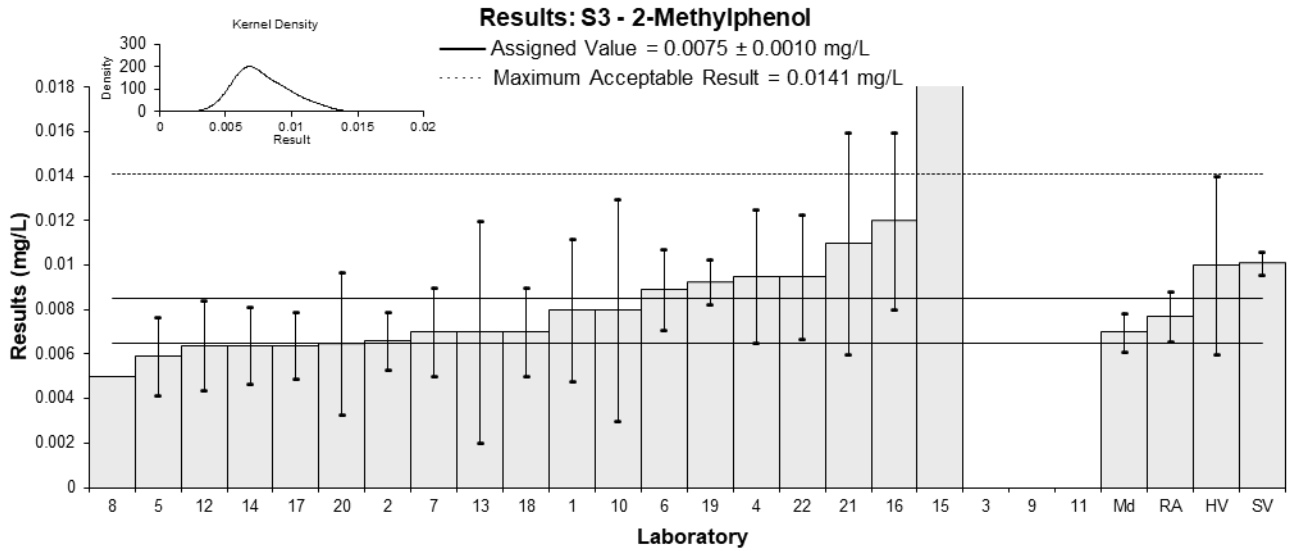


Figure 15

Table 21

Sample Details

Sample No.	S3
Matrix	Potable Water
Analyte	3 & 4-Methylphenols (total)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	0.0088	0.0035	0.37	0.16
2	0.0079	0.0013	-0.18	-0.16
3	NT	NT		
4	0.01	0.003	1.10	0.55
5	<0.006	NR		
6	0.01	0.002	1.10	0.75
7	0.007	0.002	-0.73	-0.50
8	0.0054	NR	-1.71	-2.15
9	<0.06	NR		
10	0.009	0.005	0.49	0.15
11	NR	NR		
12	0.0062	0.002	-1.22	-0.84
13	0.008	0.005	-0.12	-0.04
14	0.0067	0.00185	-0.91	-0.66
15	NT	NT		
16	<0.004	NR		
17	0.0067	0.0015	-0.91	-0.76
18	0.007	0.002	-0.73	-0.50
19	0.0104	0.002	1.34	0.92
20	0.0066	0.0045	-0.98	-0.34
21	0.011	0.005	1.71	0.54
22	0.01038	0.00332	1.33	0.61

Statistics

Assigned Value	0.0082	0.0013
Spike Value	0.0120	0.0006
Homogeneity Value	0.007	0.005
Robust Average	0.0082	0.0013
Median	0.0080	0.0012
Mean	0.00819	
N	16	
Max	0.011	
Min	0.0054	
Robust SD	0.0020	
Robust CV	24%	

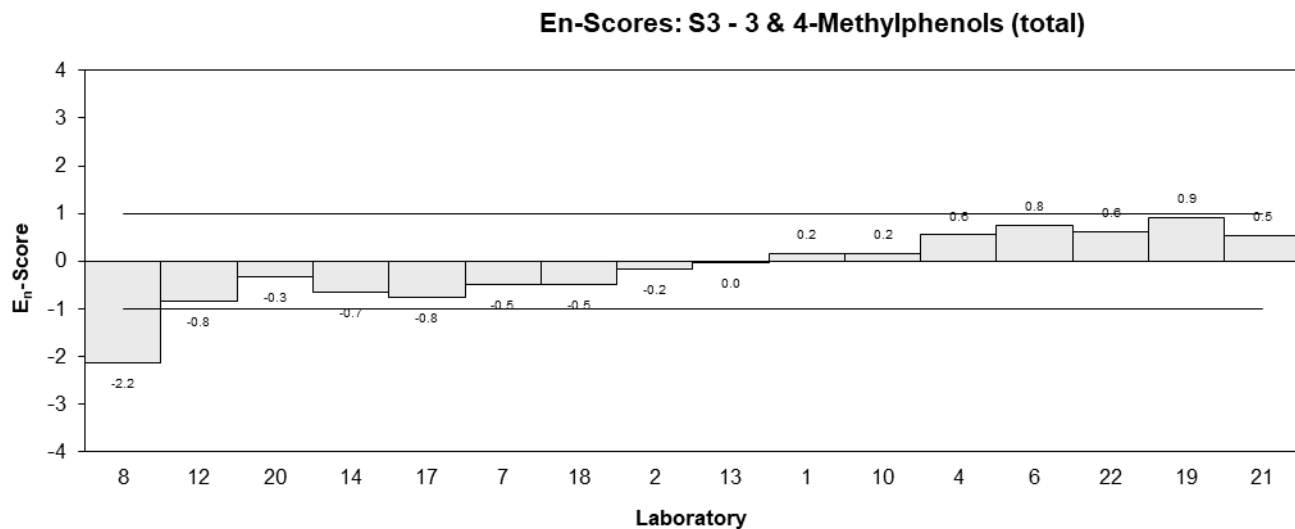
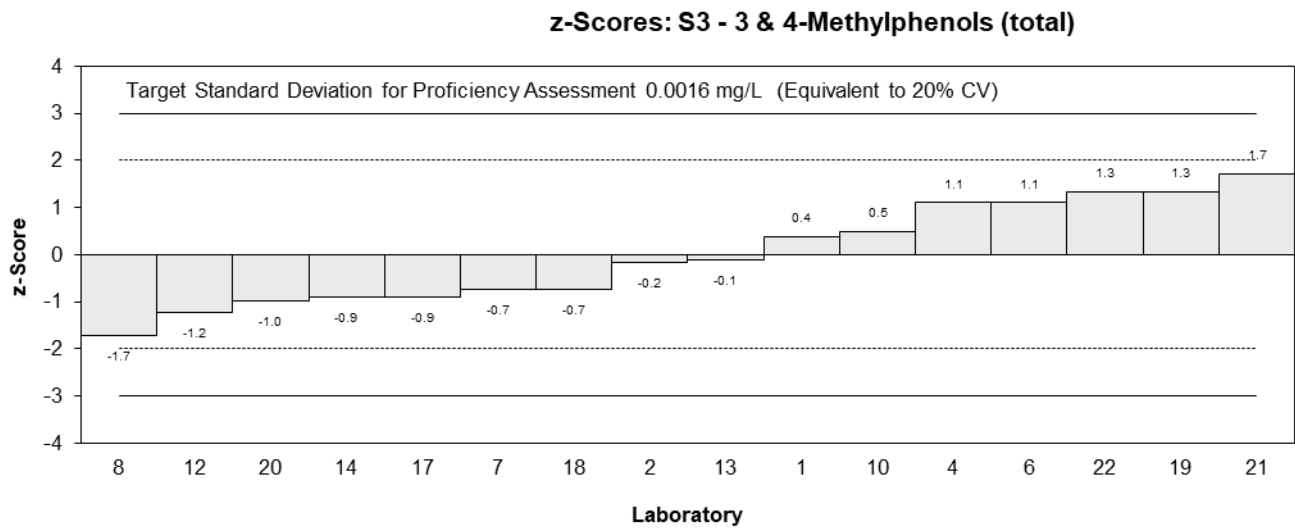
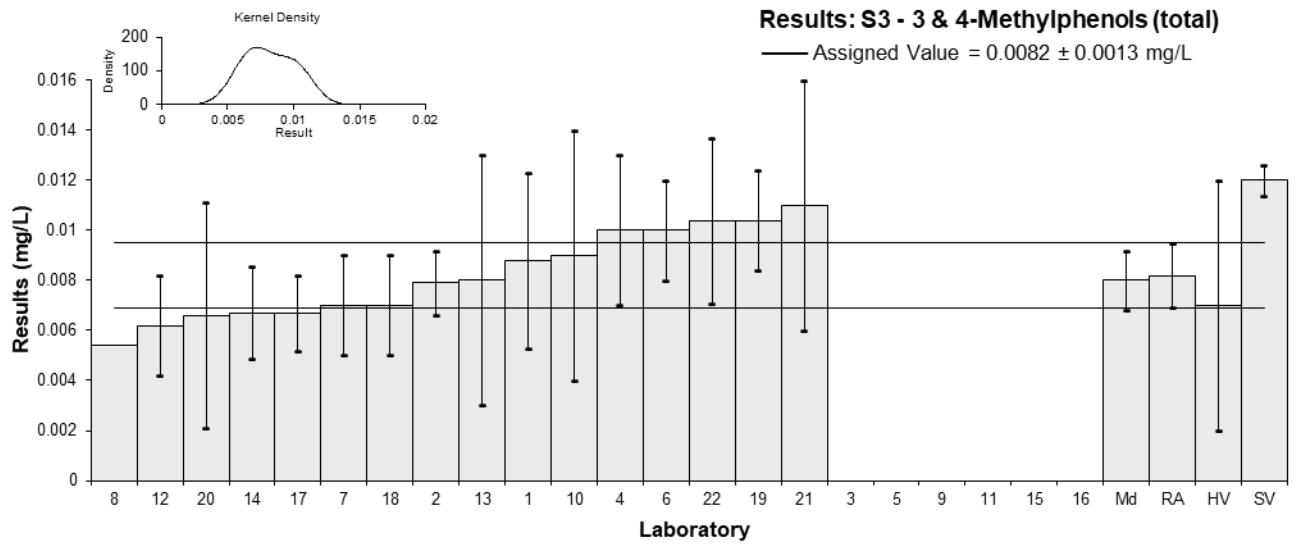


Figure 16

Table 22

Sample Details

Sample No.	S3
Matrix	Potable Water
Analyte	Pentachlorophenol
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	NT	NT		
2	0.066	NR	-1.41	-2.00
3	0.072	NR	-1.09	-1.54
4	0.11	0.033	0.98	0.51
5	0.1326	0.03978	2.21	0.97
6	0.093	0.019	0.05	0.04
7	0.113	0.023	1.14	0.79
8	0.06	NR	-1.74	-2.46
9	0.084	0.06	-0.43	-0.13
10	0.099	0.05	0.38	0.14
11	NR	NR		
12	0.102	0.032	0.54	0.29
13	0.075	0.05	-0.92	-0.33
14	0.0980	0.04763	0.33	0.12
15	NT	NT		
16	0.073	0.021	-1.03	-0.77
17*	0.0338	0.0212	-3.16	-2.34
18	0.106	0.053	0.76	0.26
19	0.0921	0.023	0.01	0.00
20	0.089	0.0860	-0.16	-0.03
21	0.072	0.02	-1.09	-0.84
22	0.12233	0.04869	1.65	0.60

* Outlier, see Section 4.2

Statistics

Assigned Value	0.092	0.013
Spike Value	0.0998	0.0050
Homogeneity Value	0.074	0.030
Robust Average	0.090	0.013
Median	0.092	0.015
Mean	0.089	
N	19	
Max	0.1326	
Min	0.0338	
Robust SD	0.023	
Robust CV	26%	

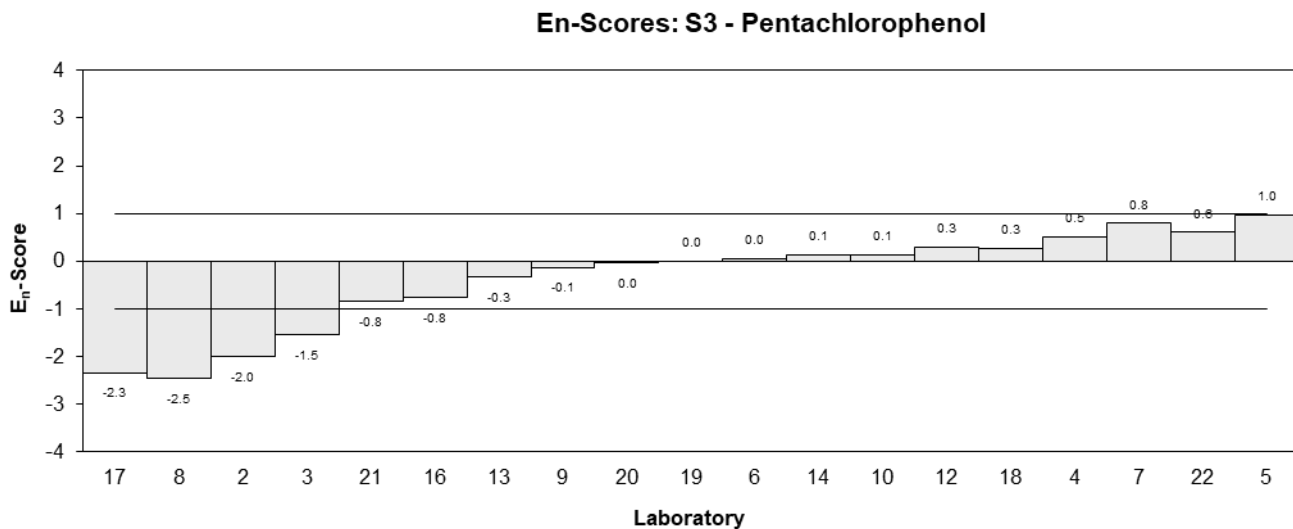
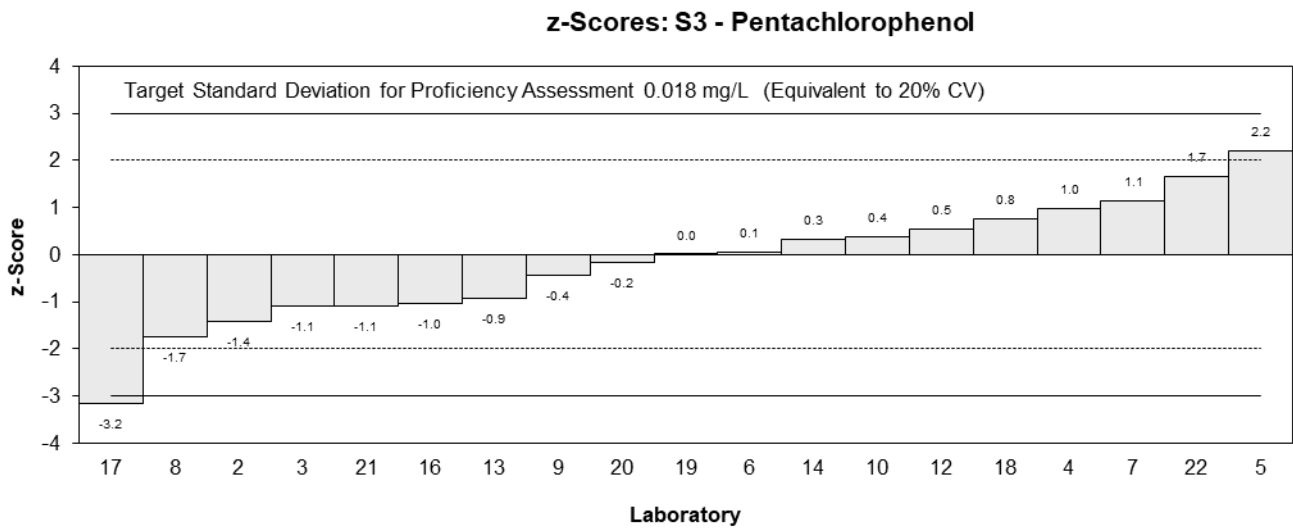
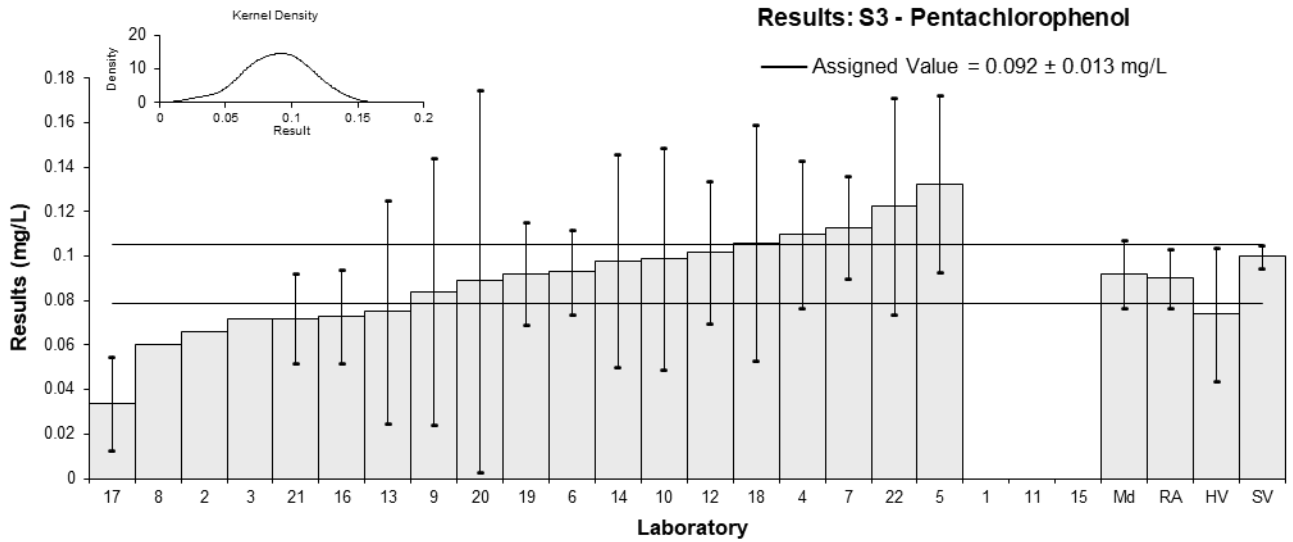


Figure 17

Table 23

Sample Details

Sample No.	S4
Matrix	Reagent Grade Water
Analyte	17 β -Estradiol
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty
1	NT	NT
2	NS	NS
3	NS	NS
4	NS	NS
5	NT	NT
6	0.00006	0.00002
7	NS	NS
8	NS	NS
9	NS	NS
10	NS	NS
11	NS	NS
12	NS	NS
13	NS	NS
14	NS	NS
15	NS	NS
16	0.00004	NR
17	NS	NS
18	NS	NS
19	NR	NR
20	NS	NS
21	0.00006	0.00002
22	NS	NS

Statistics

Assigned Value	Not Set	
Spike Value	0.0000655	0.0000033
Homogeneity Value	0.0000652	0.0000030
Robust Average	NA (N<6)	
Median	0.00006	
Mean	0.000053	
N	3	
Max	0.00006	
Min	0.00004	
Robust SD	NA (N<6)	
Robust CV	NA (N<6)	

Results: S4 - 17 β -Estradiol

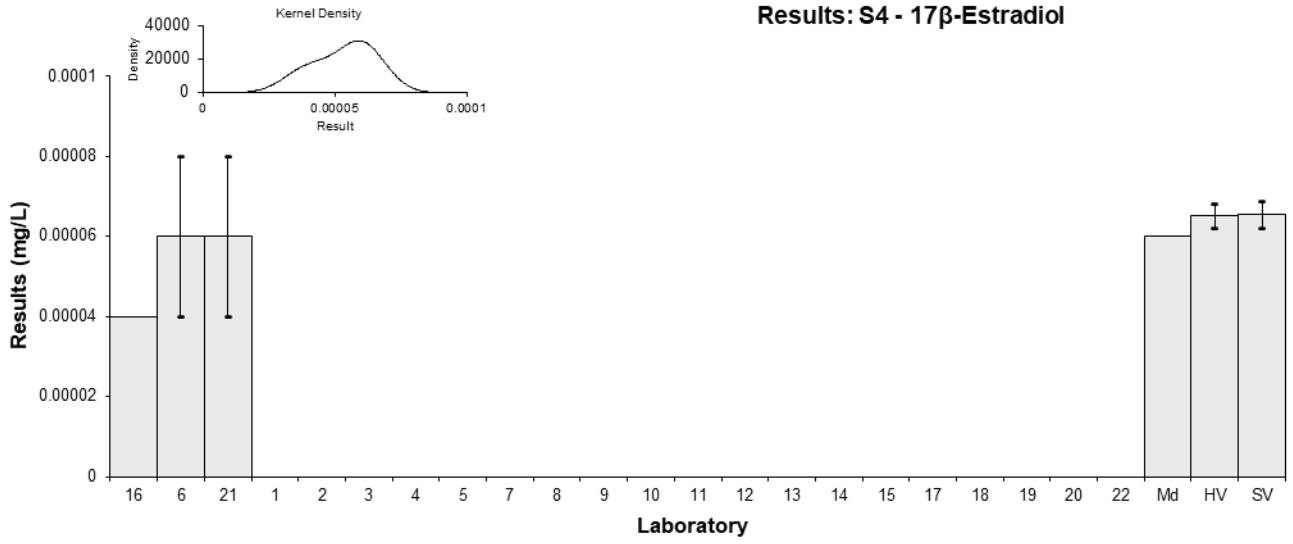


Figure 18

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 dichloromethane 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.

Sample S4 17 β -estradiol was a pilot study and so no assigned value was set. Participants may still compare their results with the descriptive statistics, homogeneity value 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 24. For scored analytes, assigned values were within the range of 68% to 134% of the spiked values, which is similar to ratios observed in previous NMI PT studies for organic compounds in water. Analytes have only been scored if there was reasonable consensus between participants' results.

Table 24 Comparison of Assigned Value (*Robust Average*) and Spiked Value

Sample	Analyte	Assigned Value (<i>Robust Average</i>) (mg/L)	Spiked Value (mg/L)	Assigned Value (<i>Robust Average</i>) / Spiked Value (%)
S1	1,2-Dichloroethane	0.210	0.200	105
	1,4-Dichlorobenzene	0.0717	0.0776	92
	Carbon tetrachloride	0.095	0.100	95
	Dichloromethane	0.0211	0.0157	134
	Toluene	0.0526	0.0500	105
	Xylenes	0.148	0.200	74
S2	Benz[<i>a</i>]anthracene	0.00346	0.00499	69
	Benzo[<i>a</i>]pyrene	0.00353	0.00403	88
	Chrysene	0.00235	0.00299	79
	Fluoranthene	0.00581	0.00700	83
	Phenanthrene	0.00805	0.0100	81
S3	2,4-Dichlorophenol	0.0128	0.0139	92
	2,6-Dichlorophenol	0.00652	0.00702	93
	2-Methylphenol	0.0075	0.0101	74
	3 & 4-Methylphenols (total)	0.0082	0.0120*	68
	Pentachlorophenol	0.092	0.0998	92
S4	17 β -Estradiol	(0.00006)	0.0000655	(92)

* Sample S3 was spiked with 4-methylphenol only.

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 300 numeric results submitted for the analytes of interest in this study, 277 (92%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 5).

Laboratories **3** and **11** did not report any uncertainties for their numeric results. Laboratory **8** did not report uncertainties for Sample S3 phenols, however they did report uncertainties for the other analytes. Laboratories **2** and **6** did not report an uncertainty for one of their numeric results each, however they did report uncertainties for all other results. All these participants reported they were accredited to ISO/IEC 17025 for all analyte types. Laboratory **16** did not report uncertainties for one Sample S1 analyte (for which they reported they were accredited to ISO/IEC 17025) and for Sample S4 17 β -estradiol (for which they reported they were not accredited).

Laboratory **22** reported relative uncertainty (as a percentage) instead of standard uncertainty (in units of mg/L); for consistency these uncertainties have been converted to standard uncertainty for this report.

The magnitude of reported uncertainties was within the range of 8.0% to 417% 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 277 MUs reported for this study, 23 were less than 15% relative, and 25 were greater than 50% relative; participants reporting these uncertainties may wish to reconsider if their MUs are realistic or fit-for-purpose.

Laboratories **10**, **13** and **21** reported extremely large relative uncertainties for Sample S1 dichloromethane (167%, 417% and 217% respectively).

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

Laboratory **9** attached estimates of MU to non-value results 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 0.1462 ± 0.0292 mg/L, it is better to report this as 0.146 ± 0.029 mg/L.⁹

6.3 z-Score

Target SDs equivalent to 15% PCV were used to calculate z -scores for Samples S1 VOCs and S2 PAHs. Target SDs equivalent to 20% PCV were used to calculate z -scores for Sample S3 phenols. Sample S4 17 β -estradiol was a pilot study and no z -scores were set.

CVs predicted by the Thompson-Horwitz equation,⁷ the between-laboratory CVs and target SDs (as PCV) obtained in this study are presented for comparison in Table 25.

Table 25 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	1,2-Dichloroethane	0.210	20	9.5	15
	1,4-Dichlorobenzene	0.0717	22	9.4	15
	Carbon tetrachloride	0.095	22	19	15
	Dichloromethane	0.0211	22	21	15
	Toluene	0.0526	22	13	15
	Xylenes	0.148	21	14	15
S2	Benz[<i>a</i>]anthracene	0.00346	22	19	15
	Benzo[<i>a</i>]pyrene	0.00353	22	31	15
	Chrysene	0.00235	22	32	15
	Fluoranthene	0.00581	22	13	15
	Phenanthrene	0.00805	22	20	15
S3	2,4-Dichlorophenol	0.0128	22	15	20
	2,6-Dichlorophenol	0.00652	22	20	20
	2-Methylphenol	0.0075	22	22	20
	3 & 4-Methylphenols (total)	0.0082	22	24	20
	Pentachlorophenol	0.092	22	24	20
S4	17 β -Estradiol	(0.00006)	22	-	Not Set

* 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 eight z -scores were adjusted across the following analytes: Sample S2 benz[*a*]anthracene and chrysene, and Sample S3 2-methylphenol. 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 297 results for which z -scores were calculated, 262 (88%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **2, 6, 7, 8, 10, 12, 13, 14, 17, 18, 19** and **21** reported numeric results for all 16 scored analytes. Of these participants, Laboratories **2, 6, 7, 12, 14, 18** and **19** returned acceptable z -scores for all analytes.

One participant received acceptable z -scores for all analytes they reported results for: Laboratory **22** (5).

Laboratories **11** and **15** returned unacceptable z -scores for all numeric results. These participants' results were all around 1000 times greater than the assigned value; they may have reported their results in units of $\mu\text{g/L}$ instead of mg/L as requested for this study.

The dispersal of z -scores is presented by laboratory in Figure 19, and by analyte in Figure 20.

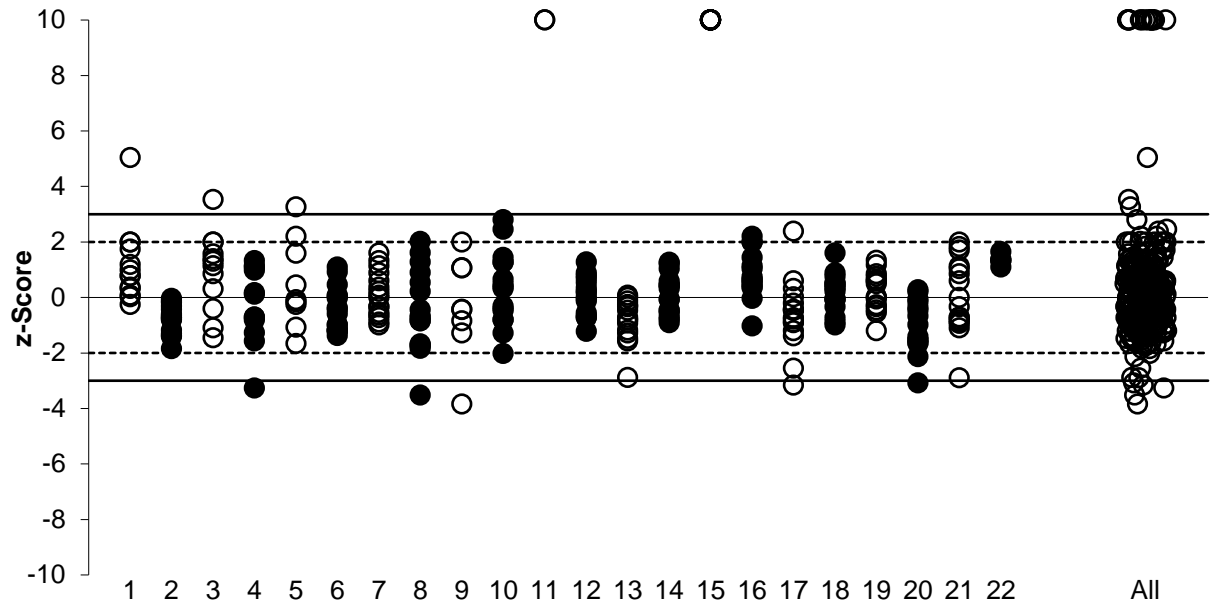


Figure 19 z-Score Dispersal by Laboratory

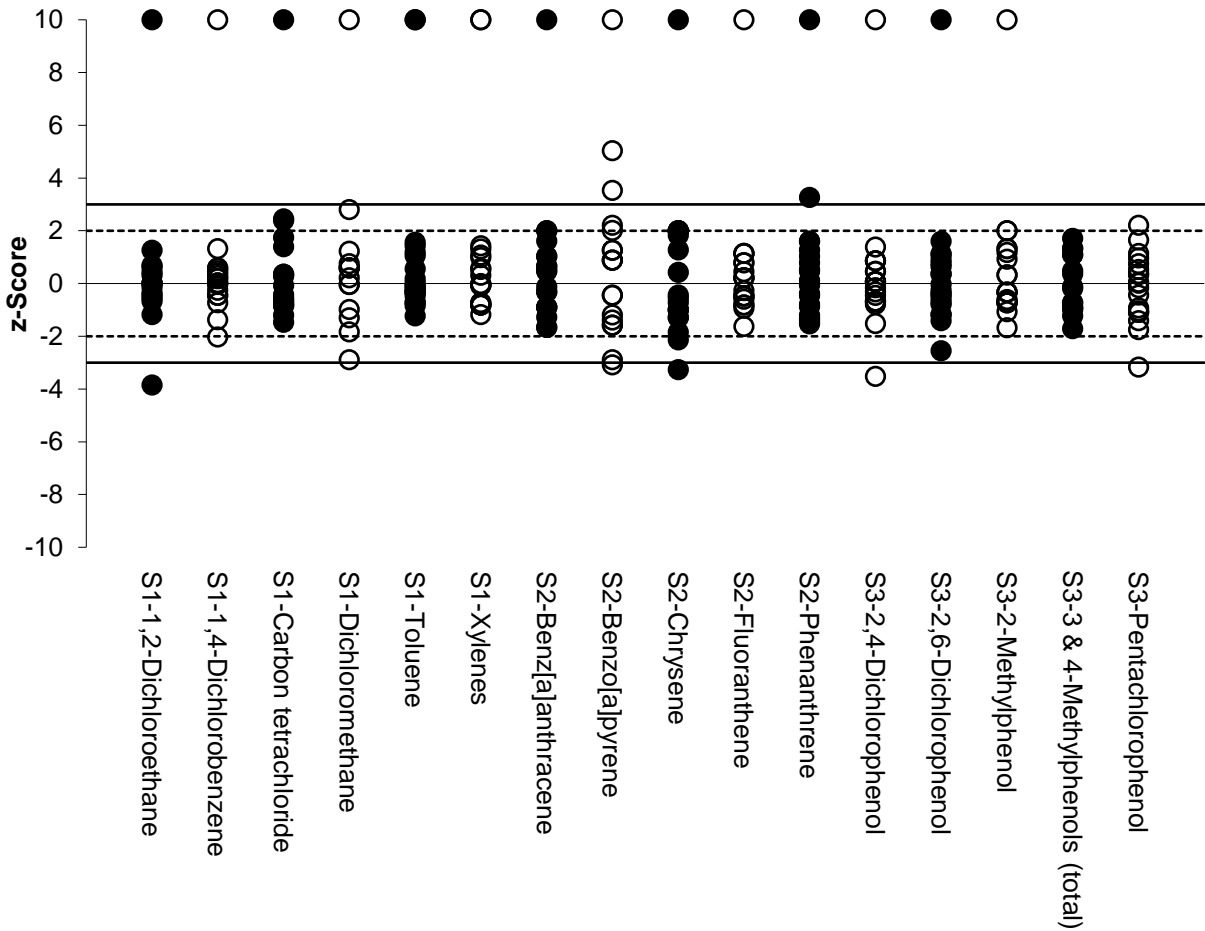


Figure 20 z-Score Dispersal by Laboratory

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.

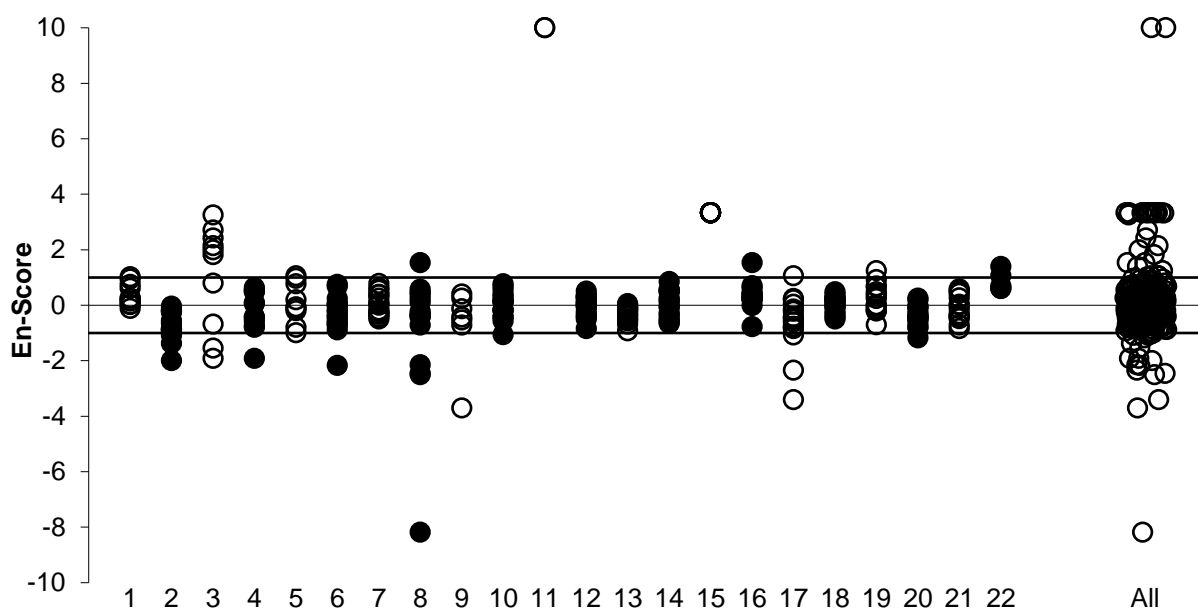
Of 289 results for which E_n -scores were calculated, 241 (83%) returned an acceptable score of $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories **7**, **12**, **13**, **14** and **18** returned acceptable E_n -scores for all 16 scored analytes.

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, Laboratory **21** received acceptable E_n -scores for all analytes that they reported results for and were scored (15).

Laboratories **11** and **15** returned unacceptable E_n -scores for all numeric results.

The dispersal of E_n -scores by laboratory is presented in Figure 21.



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

Figure 21 E_n -Score Dispersal by Laboratory

6.5 Range of Organic Compounds Analysed by Participants

Participants were provided with a list of potential organic compounds that could have been spiked into the samples, given in Tables 1 to 3 for Samples S1, S2 and S3, and Sample S4 was spiked with 17β -estradiol. Of these organic compounds, seventeen were spiked into the samples (Table 4). 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 26.

Laboratories **6**, **16** and **21** reported that they tested for all spiked analytes. Other than these participants, the proportion of organic compounds analysed by each participant ranged from 29% to 94%.

The proportion of participants analysing each organic compound in this study ranged from 14% (17β -estradiol) to 100% (2,4-dichlorophenol and 2,6-dichlorophenol).

Table 26 Summary of Organic Compounds Analysed by Participants*

Lab. Code Analyte	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	Proportion of Participants (%)	
1,2-Dichloroethane	NT	✓	NT	NT	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	77
1,4-Dichlorobenzene	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	86
Carbon tetrachloride	✓	✓	✓	NT	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	86
Dichloromethane	✓	✓	NT	NT	NT	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	73
Toluene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	95
Xylenes	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	95
Benz[<i>a</i>]anthracene	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	91
Benzo[<i>a</i>]pyrene	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	91
Chrysene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	95
Fluoranthene	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	91
Phenanthrene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	95
2,4-Dichlorophenol	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
2,6-Dichlorophenol	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	100
2-Methylphenol	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	95
3 & 4-Methylphenols	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	91
Pentachlorophenol	NT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	NT	✓	✓	✓	✓	✓	✓	✓	✓	91
17β-Estradiol	NT				NT	✓										✓			NT		✓			14
Proportion of Analytes (%)	82	94	71	71	71	100	94	94	71	94	94	94	94	94	82	100	94	94	94	88	100	29		

* If a participant did not receive the sample containing an analyte, the cell has been shaded. The proportion of analytes analysed is calculated as the proportion of total analytes spiked into this study.

6.6 False Negatives

Table 27 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 27 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (<i>Robust Average</i>) (mg/L)	Spiked Value (mg/L)	Result* (mg/L)
1	S1	Dichloromethane	0.0211	0.0157	<0.01
5	S2	Benzo[<i>a</i>]pyrene	0.00353	0.00403	<0.001
		Chrysene	0.00235	0.00299	<0.001
	S3	3 & 4-Methylphenols (total)	0.0082	0.0120	<0.006
11	S1	1,2-dichloroethane	0.210	0.200	NR
		1,4-dichlorobenzene	0.0717	0.0776	NR
		Carbon tetrachloride	0.095	0.100	NR
		Dichloromethane	0.0211	0.0157	NR
	S2	Benz[<i>a</i>]anthracene	0.00346	0.00499	NR
		Benzo[<i>a</i>]pyrene	0.00353	0.00403	NR
		Chrysene	0.00235	0.00299	NR
		Fluoranthene	0.00581	0.00700	NR
		Phenanthrene	0.00805	0.0100	NR
	S3	2,4-Dichlorophenol	0.0128	0.0139	NR
		2,6-Dichlorophenol	0.00652	0.00702	NR
		2-Methylphenol	0.0075	0.0101	NR
		3 & 4-Methylphenols (total)	0.0082	0.0120	NR
		Pentachlorophenol	0.092	0.0998	NR
16	S3	3 & 4-Methylphenols (total)	0.0082	0.0120	<0.004

* 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 28.

Table 28 Analytes Reported by Participants Not Spiked in the Test Samples

Lab. Code	Sample	Analyte	Result (mg/L)	Uncertainty (mg/L)
1	S1	Ethylbenzene	0.050	0.01
		Trihalomethanes (Total)	0.0030	0.0006
2	S1	Ethylbenzene	0.036	0.0032

Lab. Code	Sample	Analyte	Result (mg/L)	Uncertainty (mg/L)
	S1	Trihalomethanes (Total)	0.002	NR
3	S1	Ethylbenzene	0.051	NR
4	S1	Ethylbenzene	0.036	0.011
		Trihalomethanes (Total)	0.02	NR
	S3	2,3,4,6-Tetrachlorophenol	0.0014	0.0004
5	S1	Ethylbenzene	0.041	0.0082
6	S1	Ethylbenzene	0.034	0.008
		Trihalomethanes (Total)	0.002	NR
7	S1	Ethylbenzene	0.043	0.013
8	S1	Ethylbenzene	0.036	0.012
		Trihalomethanes (Total)	0.00202	0.00165
	S3	2,3,4,6-Tetrachlorophenol	0.00068	NR
9	S1	1,3-dichlorobenzene	0.071	0.01
		Ethylbenzene	0.046	0.01
	S2	Anthracene	0.0014	0.0004
10	S1	Ethylbenzene	0.036	0.01
		Trihalomethanes (Total)	0.0030	0.002
11	S1	Ethylbenzene	39.2	NR
12	S1	Ethylbenzene	0.0416	0.014
13	S1	Ethylbenzene	0.038	0.008
		Trihalomethanes (Total)	0.0024	0.0005
14	S1	Ethylbenzene	0.041	0.0054
		Trihalomethanes (Total)	0.003	0.0004
15	S1	Ethylbenzene	33	9.9
	S3	2,3,4,6-Tetrachlorophenol	1.2	0.36
16	S1	Ethylbenzene	0.046	0.012
		Trihalomethanes (Total)	0.0016	0.0005
17	S1	Ethylbenzene	0.044	0.008
		Trihalomethanes (Total)	0.002	0.001
18	S1	Ethylbenzene	0.043	0.01
19	S1	Ethylbenzene	0.0458	0.009
		Trihalomethanes (Total)	0.00245	0.0005
20	S1	Ethylbenzene	0.04	0.0052
21	S1	Ethylbenzene	0.039	0.01
		Trihalomethanes (Total)	0.002	0.002
22	S3	2,3,4,6-Tetrachlorophenol	0.0012	0.0002304

Many participants reported the presence of ethylbenzene and trihalomethanes (total) in Sample S1; these may have been incurred analytes in the original potable water matrix.

Participant results for these analytes are shown in Figures 22 and 23. While these analytes were not scored because they were not spiked, the study coordinator has suggested an ‘acceptable range’, defined as being within two target SDs (using 15% PCV) from the robust average of participants’ results.

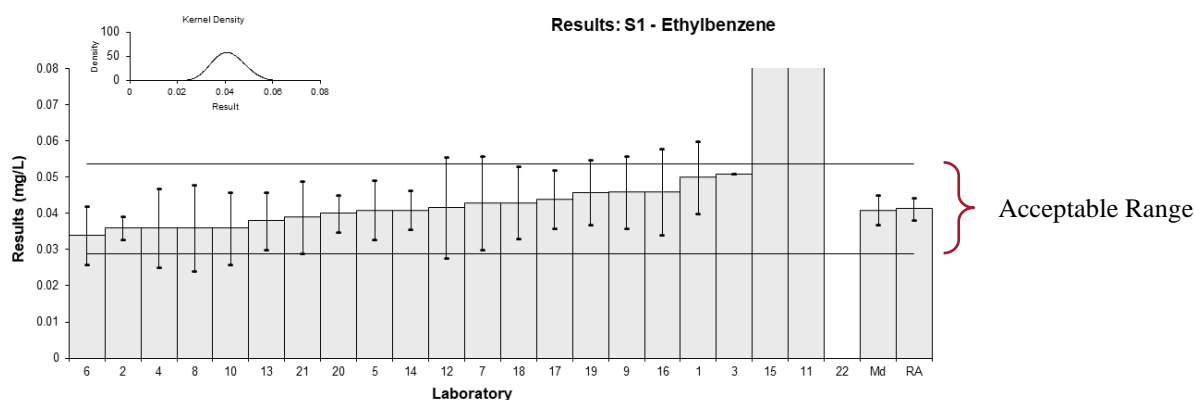


Figure 22 Participant Results for Ethylbenzene in Sample S1

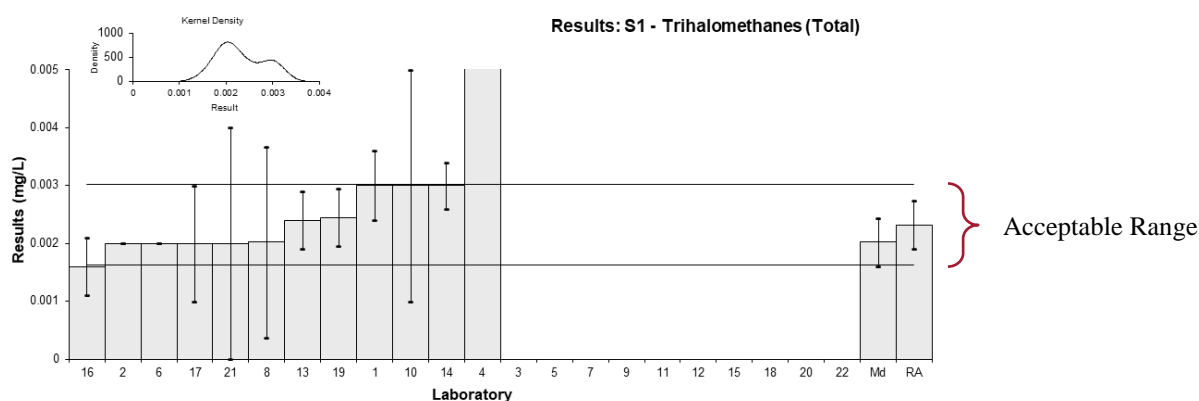


Figure 23 Participant Results for Trihalomethanes (Total) in Sample S1

6.8 Fitness for Purpose of Results – Australian Drinking Water Guidelines

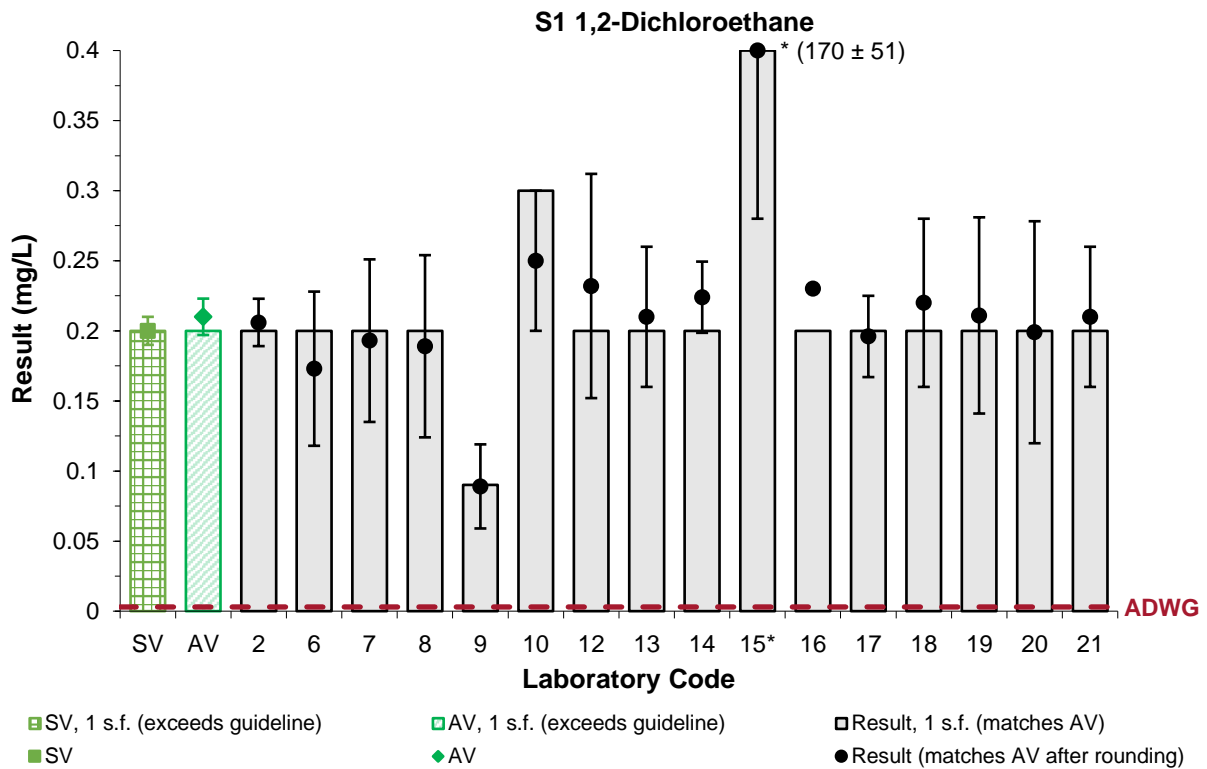
The ADWG specifies health-based and/or aesthetic guidelines for a number of water characteristics, including for organic compounds.⁵ Laboratories should be able to identify if a potable water sample exceeds the guideline or not. The ADWG specifies that comparison of results against the guideline value ‘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, nine spiked analytes had a health and/or aesthetic guideline.

Figures 24 to 32 show comparisons of the actual (with uncertainty) and rounded spiked value (SV), assigned value (AV) and participants’ results, as well as the guidelines (ADWG or ADWG (H) for health-based; ADWG (A) for aesthetic). Only numeric results have been included. Of 165 results assessed, 160 (97%) correctly reflected whether the sample exceeded the guideline(s) or not.

Laboratories **2, 6, 7, 8, 10, 12, 13, 14, 16, 17, 18, 19** and **21** returned the correct consequence for all analytes assessed. As results reported by Laboratories **11** and **15** were all extremely high, for all analytes below a guideline value, their results returned the incorrect consequence.

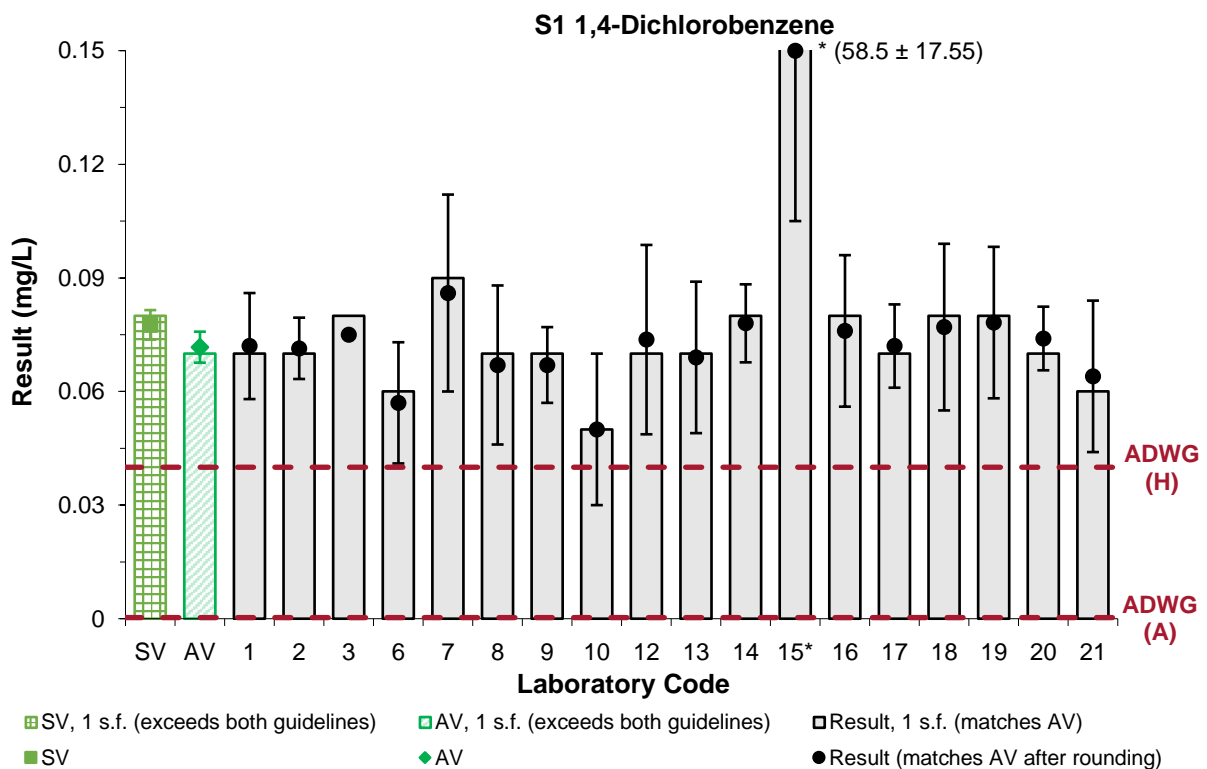
In some cases, a participant’s result returned the correct consequence, however had an uncertainty which spanned the guideline value(s). For this study, this occurred for results reported for S1 1,4-dichlorobenzene by Laboratory **10**, S1 dichloromethane by Laboratories

10, 13 and 21, S1 toluene by Laboratory 6, S2 benzo[a]pyrene by Laboratory 21 and S3 pentachlorophenol by Laboratory 20.



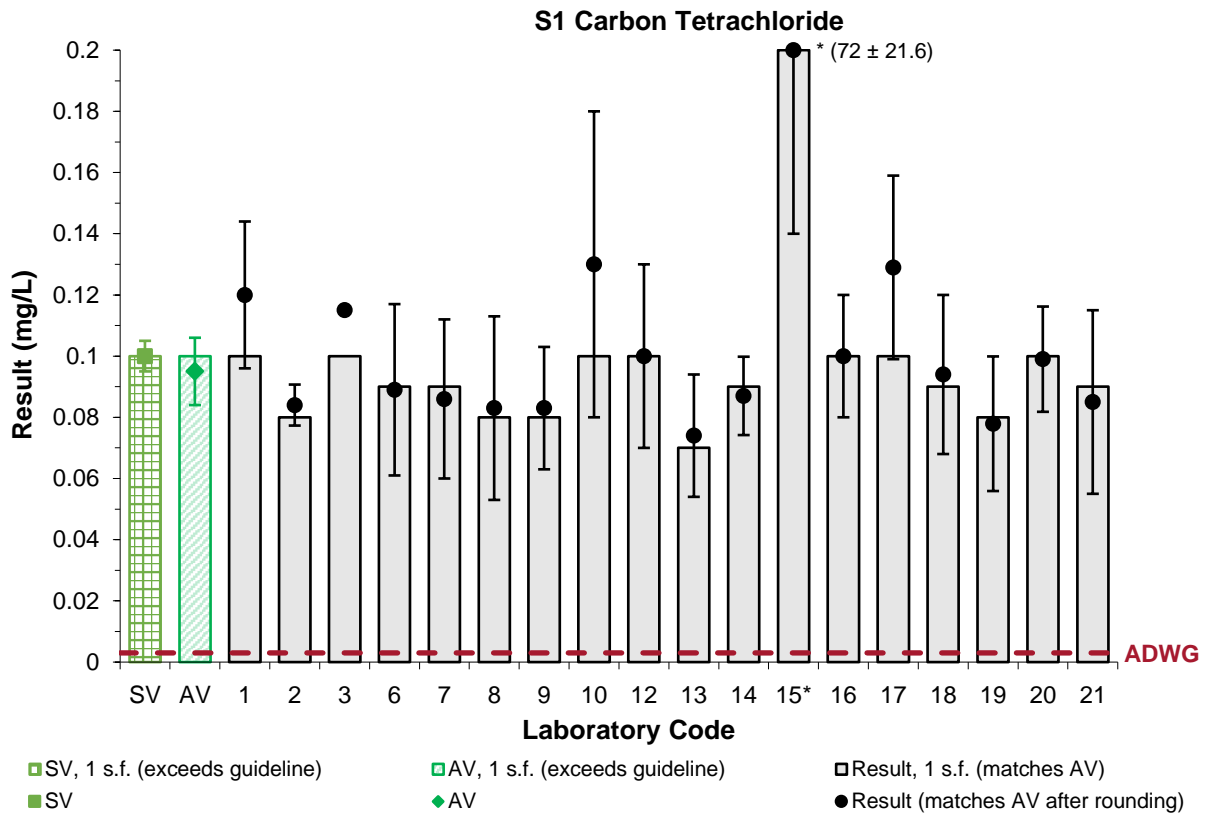
* Result from Laboratory 15 has been scaled to fit the chart; original result in parentheses.

Figure 24 Sample S1 1,2-Dichloroethane Spiked and Assigned Values, Participant Results and Guideline



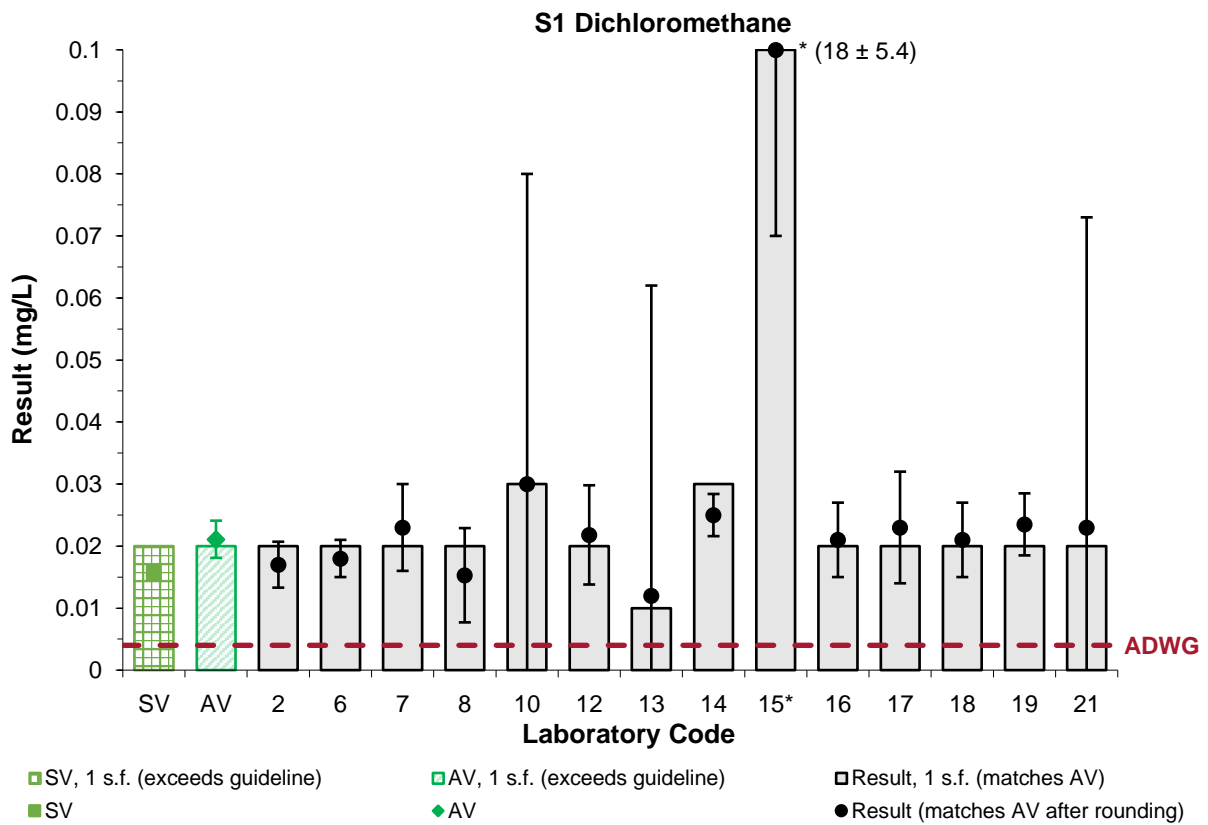
* Result from Laboratory 15 has been scaled to fit the chart; original result in parentheses.

Figure 25 Sample S1 1,4-Dichlorobenzene Spiked and Assigned Values, Participant Results and Guideline



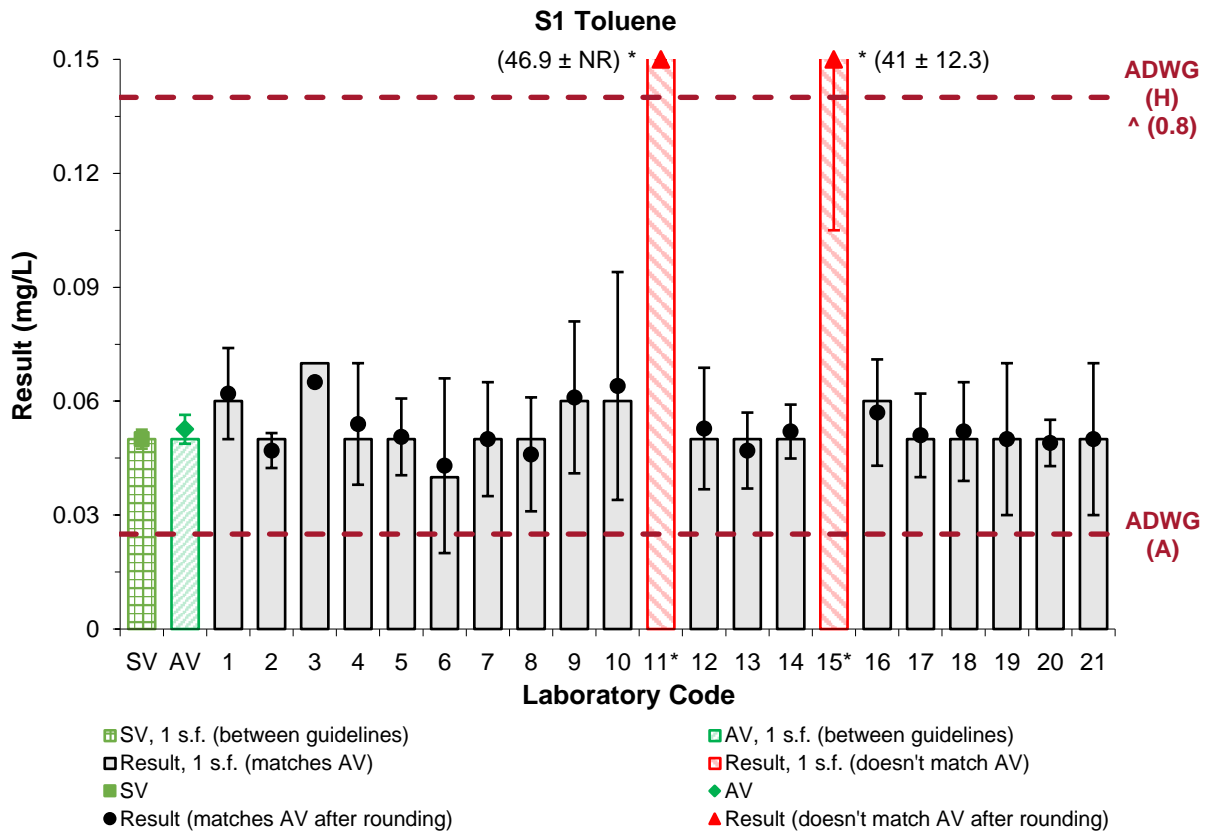
* Result from Laboratory **15** has been scaled to fit the chart; original result in parentheses.

Figure 26 Sample S1 Carbon Tetrachloride Spiked and Assigned Values, Participant Results and Guideline



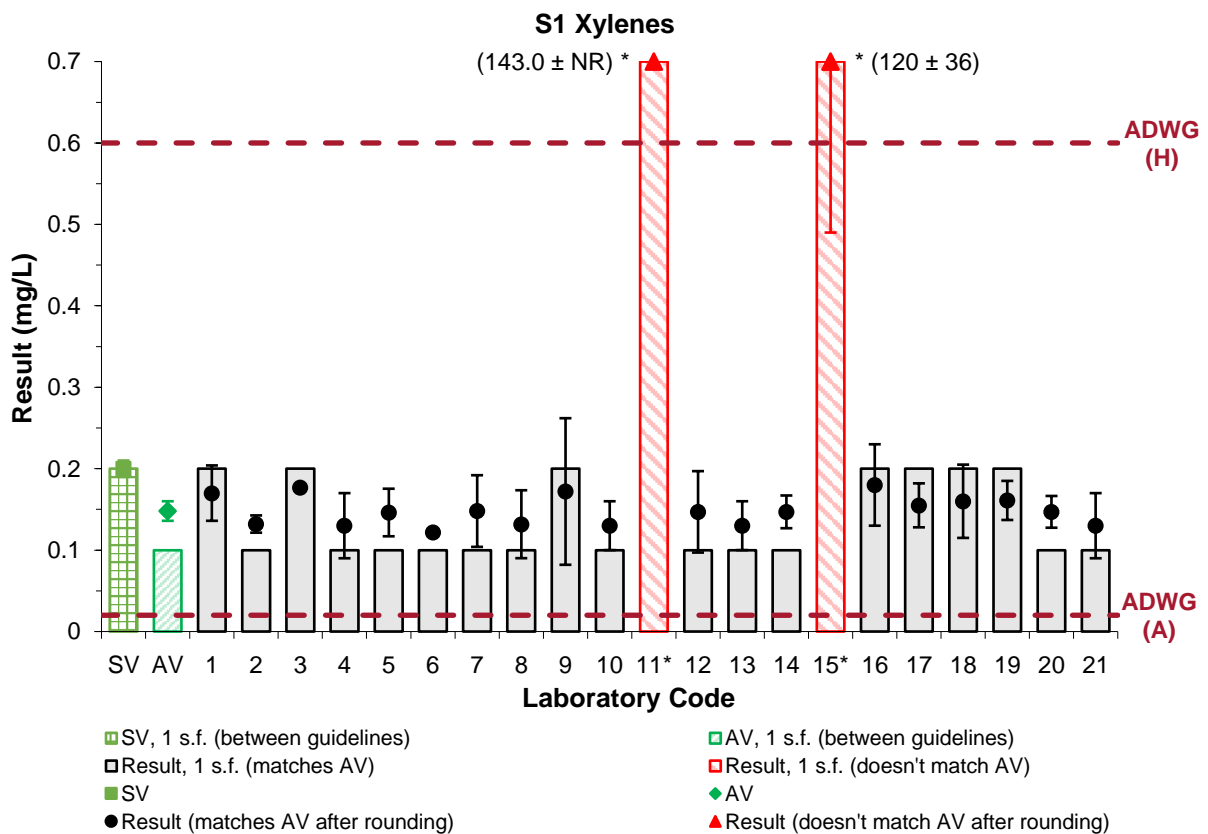
* Result from Laboratory **15** has been scaled to fit the chart; original result in parentheses.

Figure 27 Sample S1 Dichloromethane Spiked and Assigned Values, Participant Results and Guideline



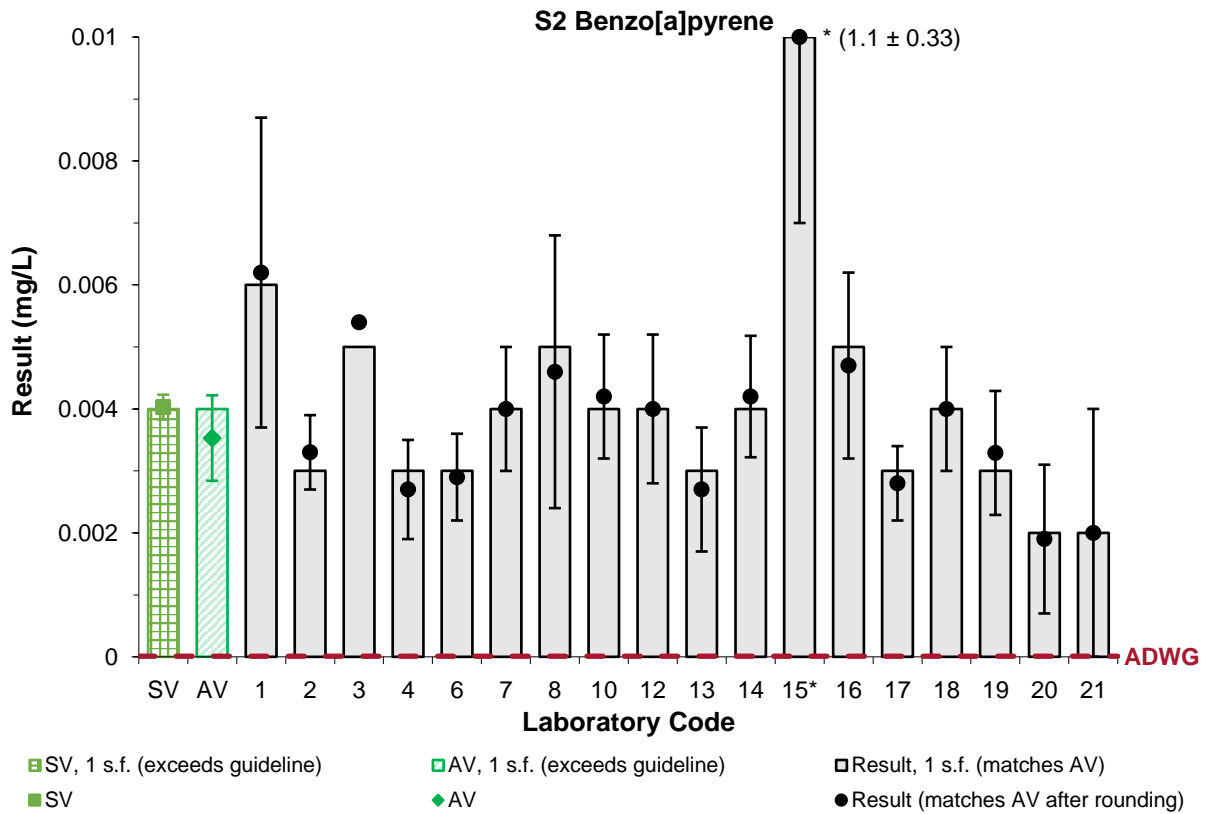
* Results from Laboratories **11** and **15** have been scaled to fit the chart; original results in parentheses.
 ^ ADWG (H) has been scaled to fit the chart; original value in parentheses.

Figure 28 Sample S1 Toluene Spiked and Assigned Values, Participant Results and Guideline



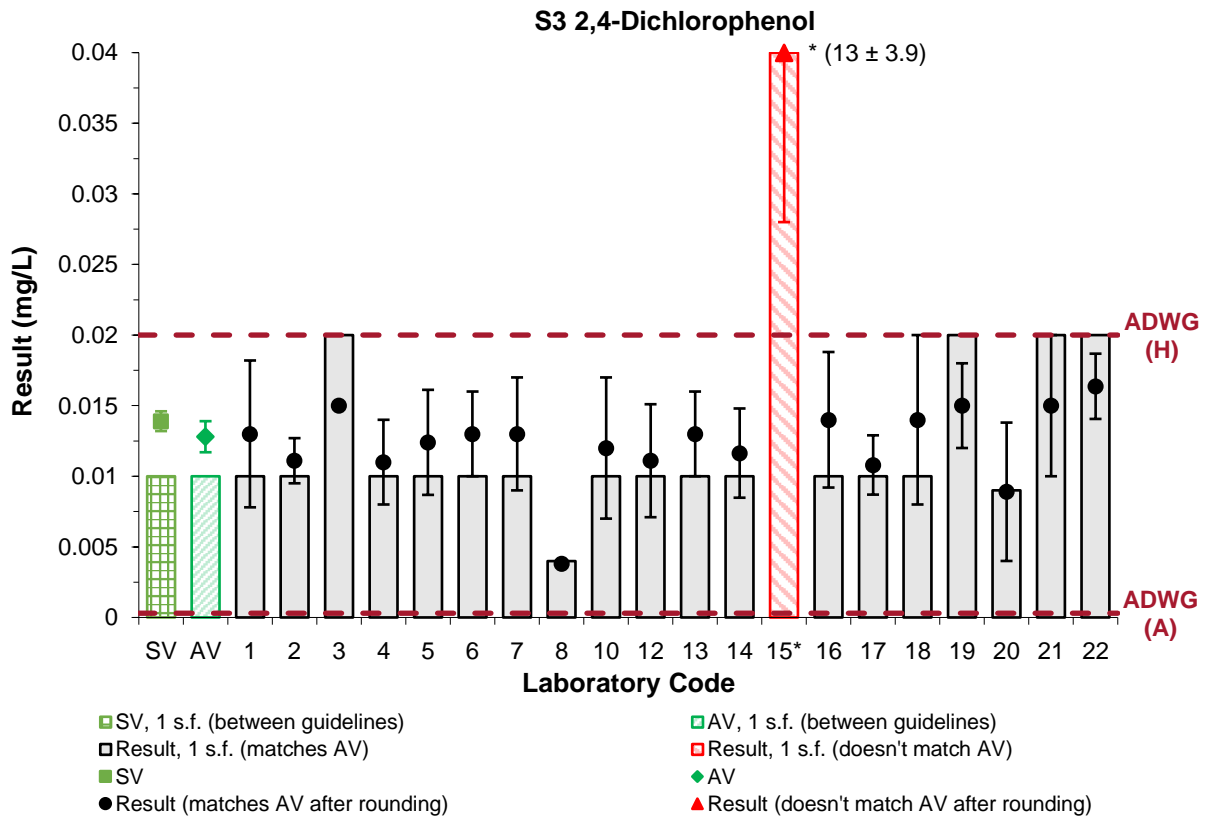
* Results from Laboratories **11** and **15** have been scaled to fit the chart; original results in parentheses.

Figure 29 Sample S1 Xylenes Spiked and Assigned Values, Participant Results and Guideline



* Result from Laboratory 15 have been scaled to fit the chart; original results in parentheses.

Figure 30 Sample S2 Benzo[a]pyrene Spiked and Assigned Values, Participant Results and Guideline



* Result from Laboratory 15 have been scaled to fit the chart; original results in parentheses.

Figure 31 Sample S3 2,4-Dichlorophenol Spiked and Assigned Values, Participant Results and Guideline

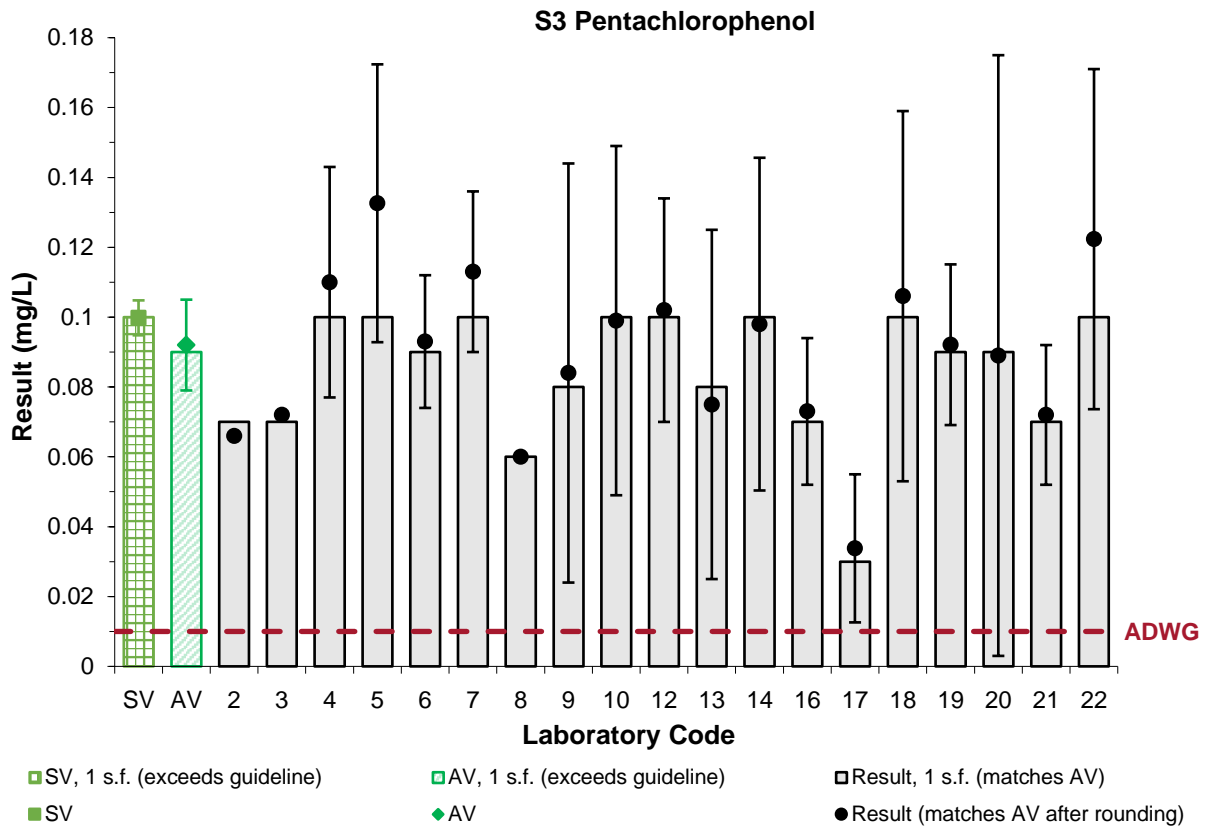


Figure 32 Sample S3 Pentachlorophenol Spiked and Assigned Values, Participant Results and Guideline

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).

Sample S1 VOCs

For Sample S1, participants were provided 2 x 42 mL vials. Participants reported test portions ranging from 5 mL to the whole vial. A comparison of z-scores and sample volume used for scored analytes is presented in Figure 33; there was no evident correlation observed.

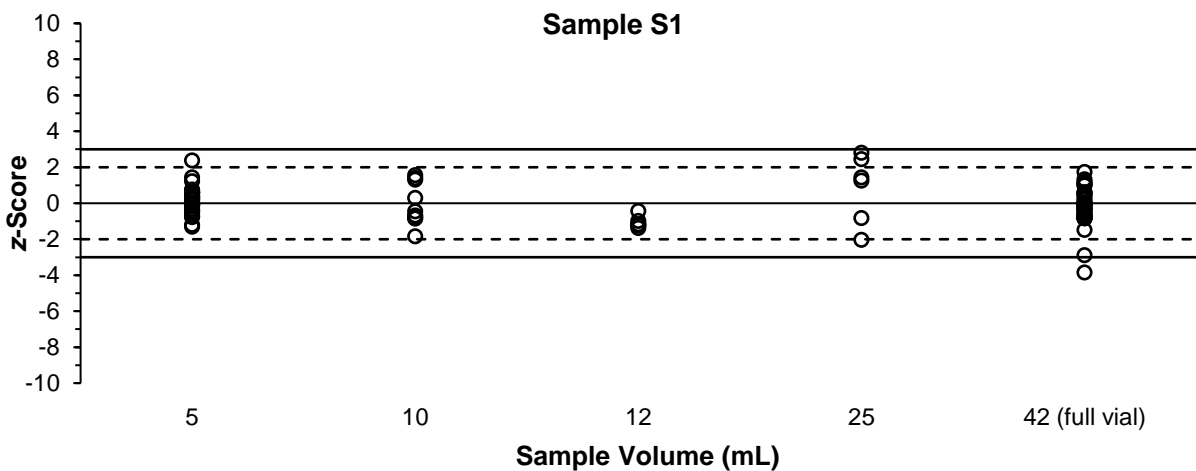


Figure 33 Sample S1 z-Score vs Sample Volume

Most participants either used purge-and-trap (P&T) gas chromatography (GC) coupled to mass spectrometry (MS) or tandem mass spectrometry (MS/MS), or headspace (HS) GC-MS. One participant used GC coupled to flame ionisation detection (FID). Four participants reported a liquid-liquid extraction (LLE) step as part of their preparation, with one of these participants reporting that they used methanol (MeOH) as the extraction solvent.

Plots of results reported and methodology used for Sample S1 are presented in Figures 34 to 39. 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.

The most common methodology used for Sample S1 was P&T GC-MS. There was no significant trend observed with regards to methodology used.

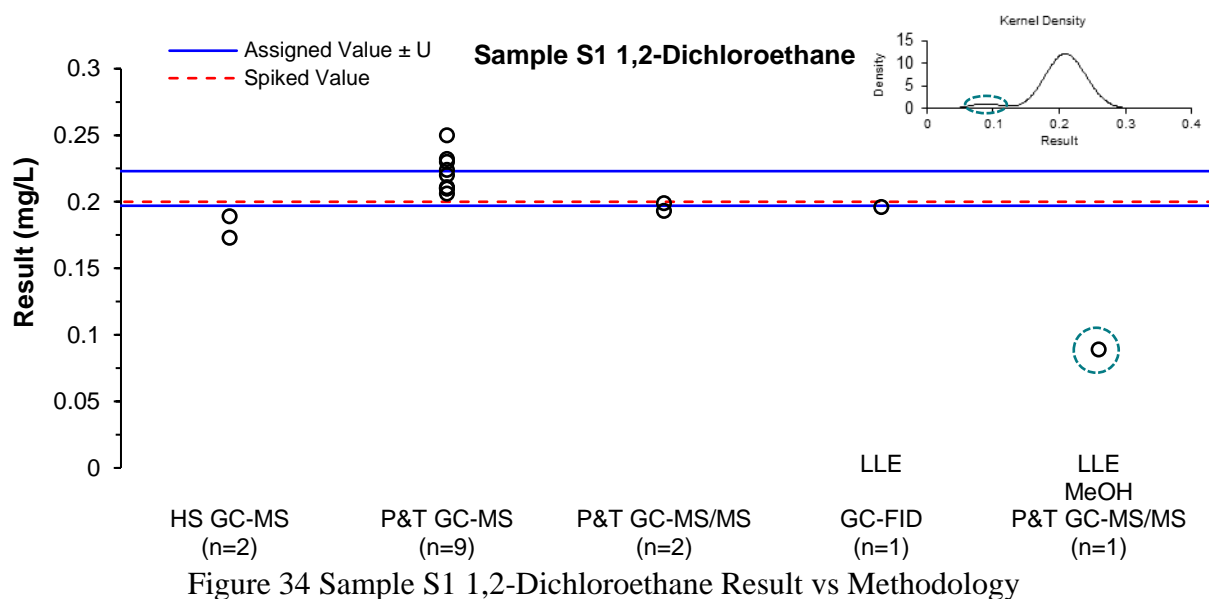


Figure 34 Sample S1 1,2-Dichloroethane Result vs Methodology

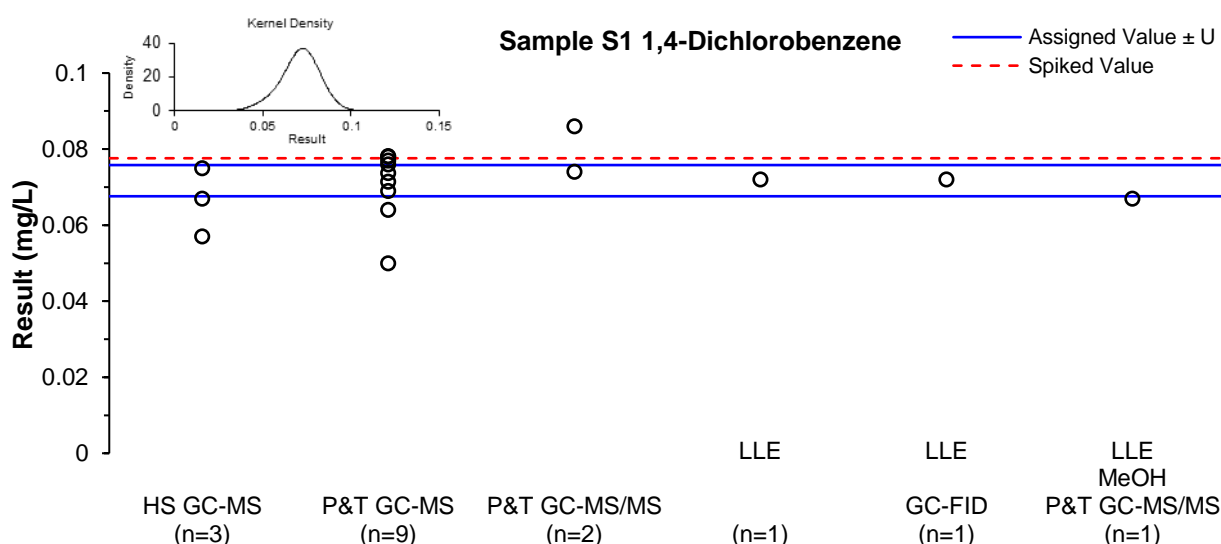


Figure 35 Sample S1 1,4-Dichlorobenzene Result vs Methodology

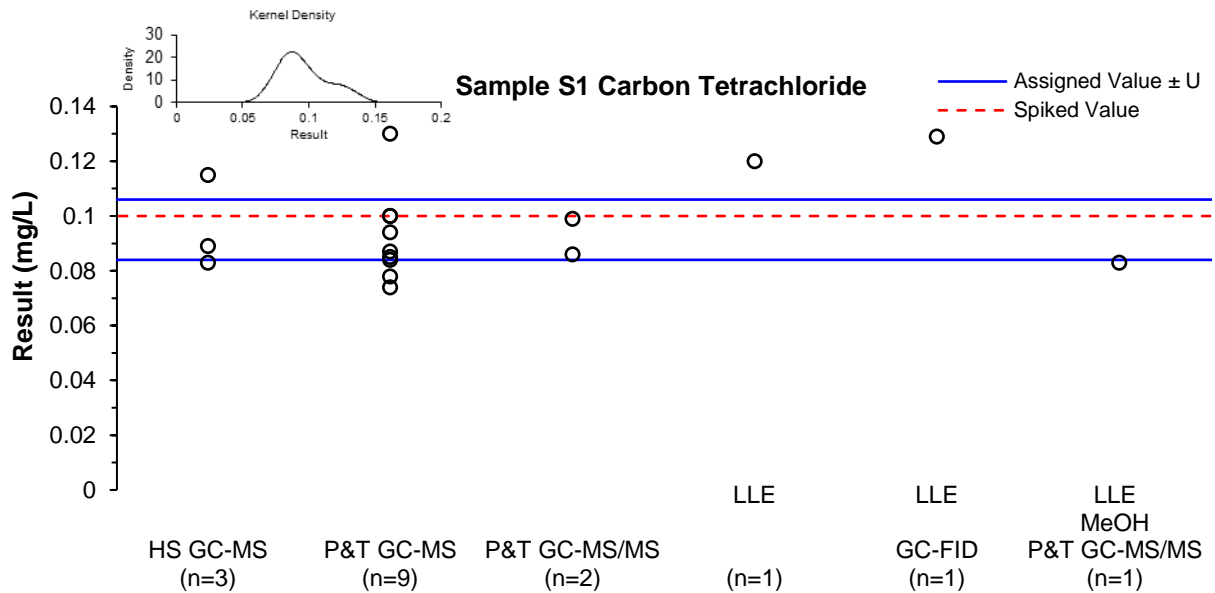


Figure 36 Sample S1 Carbon Tetrachloride Result vs Methodology

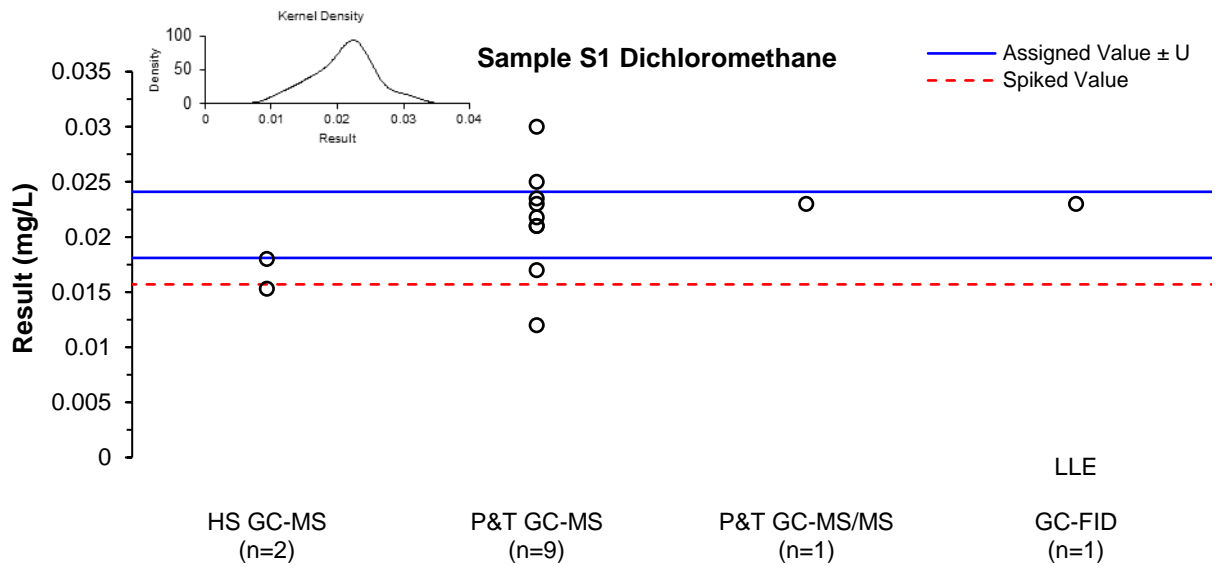


Figure 37 Sample S1 Dichloromethane Result vs Methodology

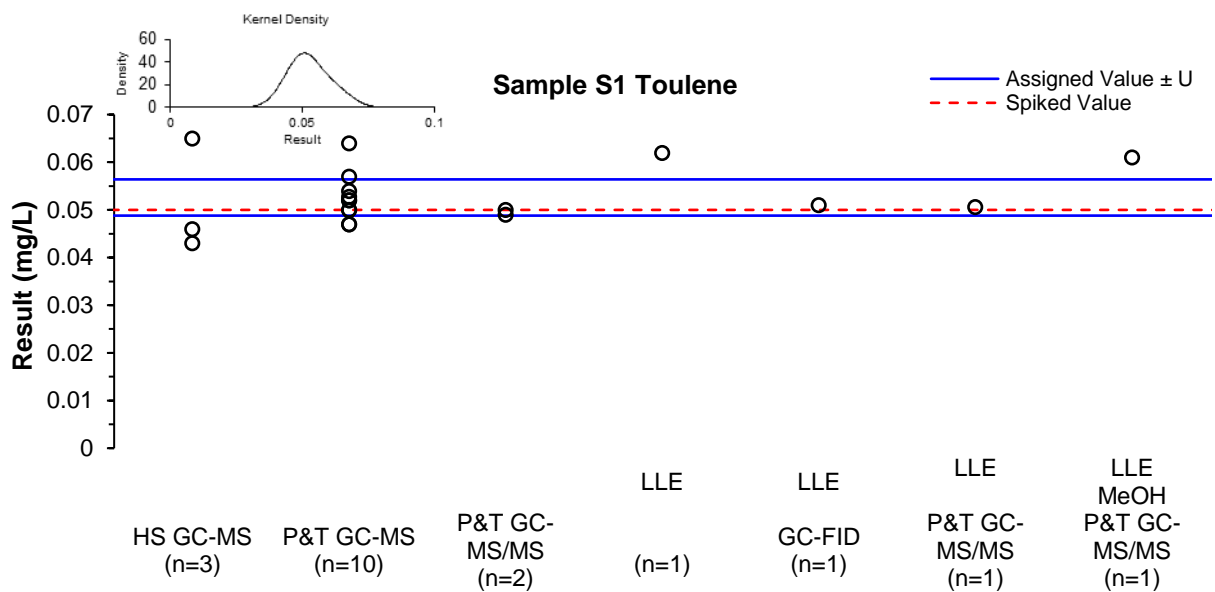


Figure 38 Sample S1 Toluene Result vs Methodology

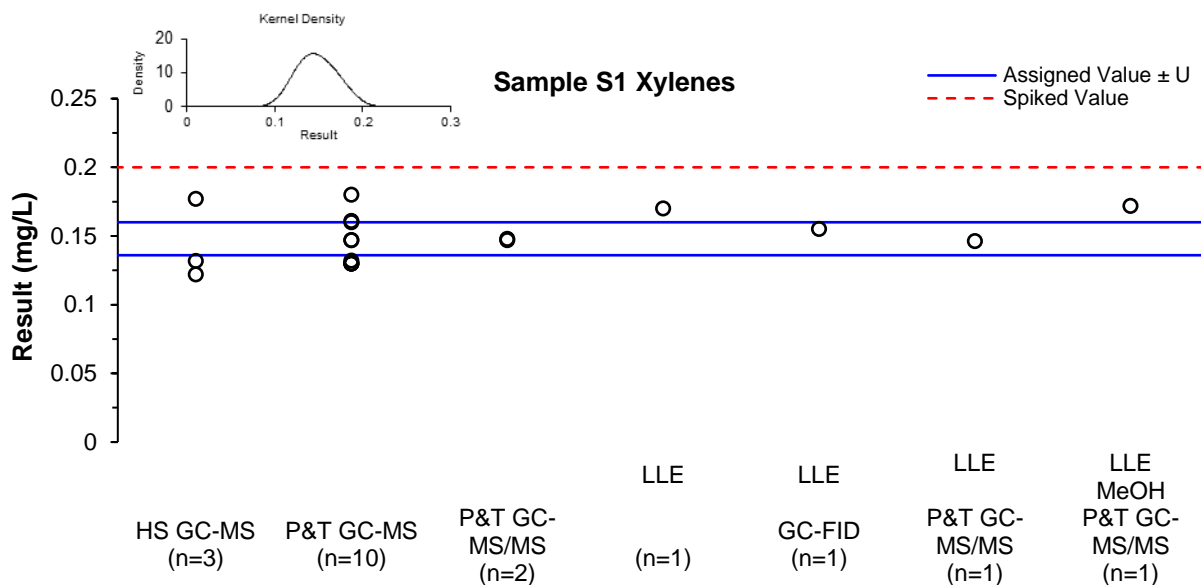


Figure 39 Sample S1 Xylenes Result vs Methodology

Sample S2 PAHs

For Sample S2, participants were given the choice of either 1 x 500 mL bottle or 3 x 100 mL bottles, depending on what suited their laboratory's method best. Participants reported test portions ranging from 35 mL to the whole bottle. A comparison of z -scores and sample volume used for scored analytes is presented in Figure 40; there was no evident correlation observed.

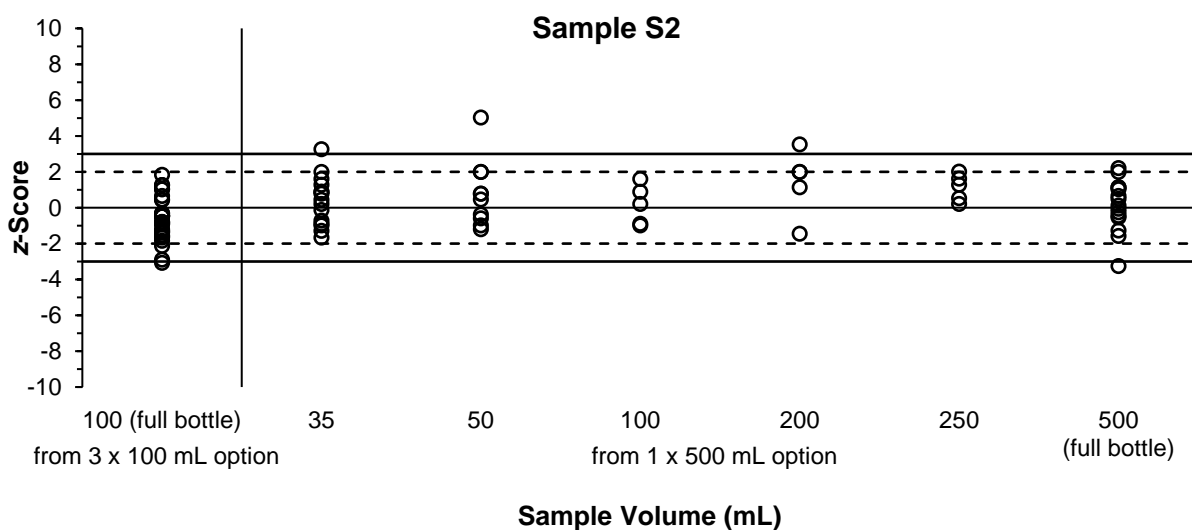


Figure 40 Sample S2 z -Score vs Sample Volume

The majority of participants used LLE, except for two participants who used solid-phase extraction (SPE) instead. Extraction solvents reported by participants were dichloromethane (DCM), hexane (HEX), or DCM / ethyl acetate (EtOAc) mixture. No participant reported a clean-up step. All participants used GC-MS(/MS) for their analysis.

Plots of results reported and methodology used for Sample S2 are presented in Figures 41 to 45. 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.

The most common methodology used for Sample S2 was LLE with DCM, and analysis using GC-MS(/MS). There was no significant trend observed with regards to methodology used.

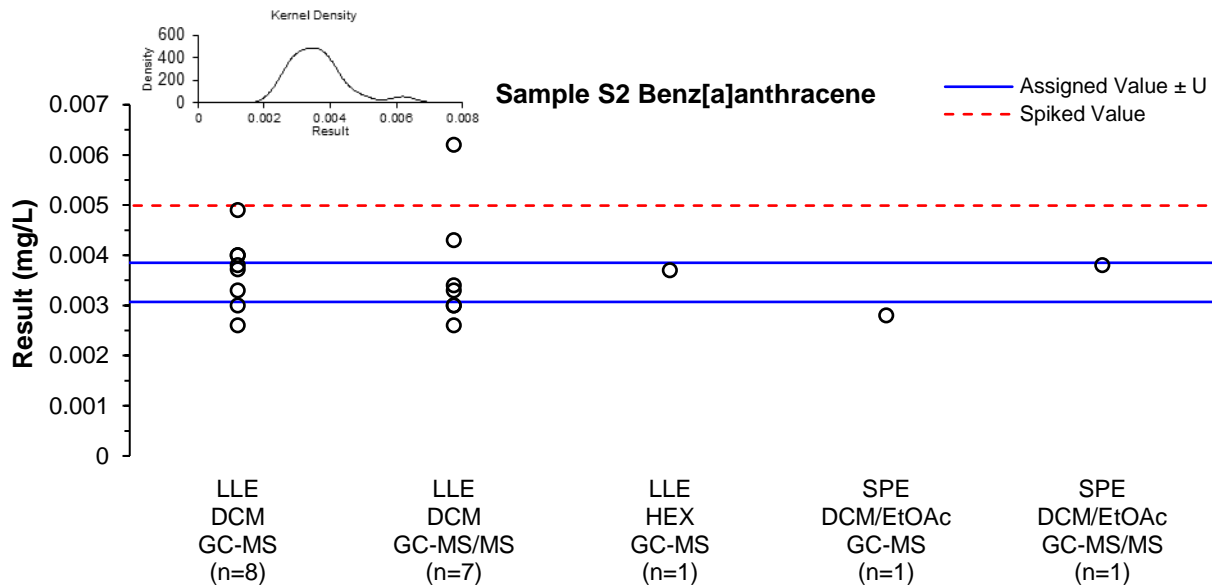


Figure 41 Sample S2 Benz[a]anthracene Result vs Methodology

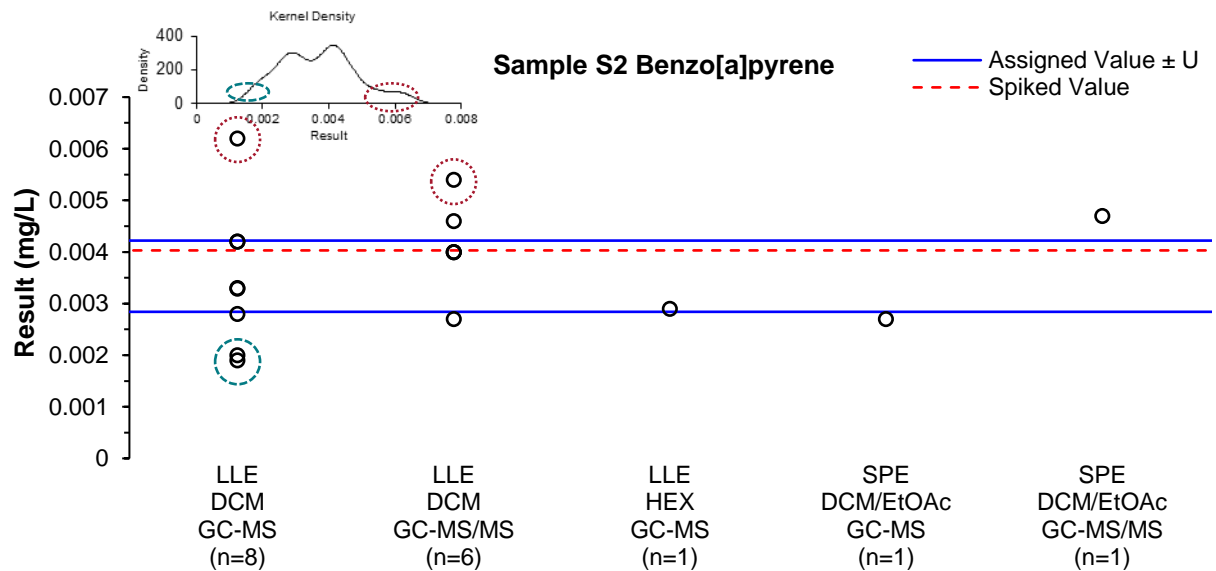


Figure 42 Sample S2 Benzo[a]pyrene Result vs Methodology

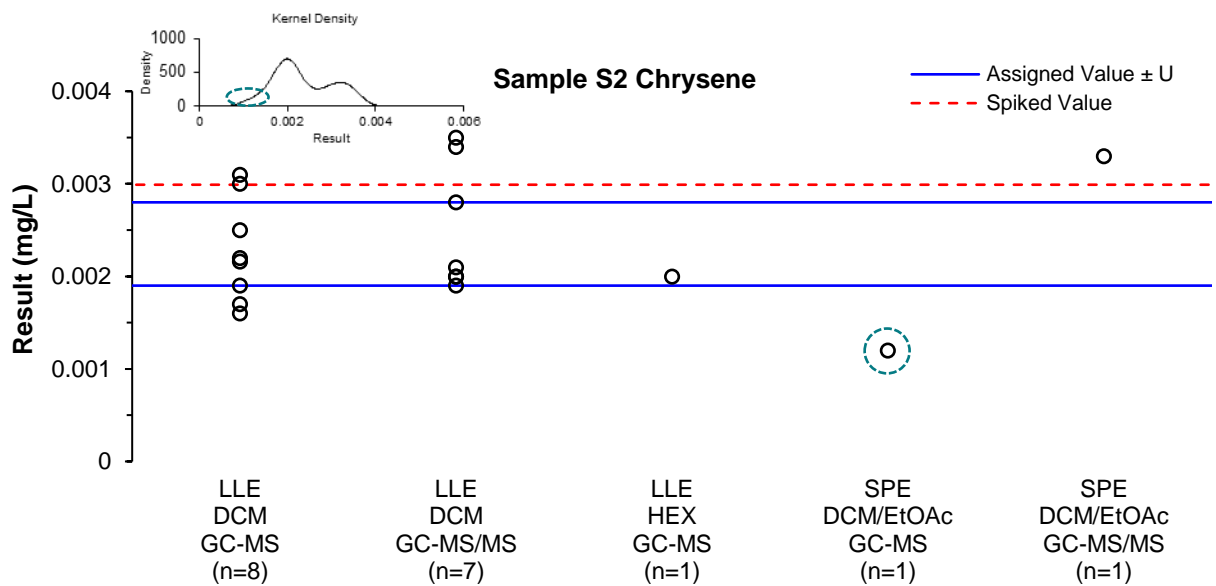


Figure 43 Sample S2 Chrysene Result vs Methodology

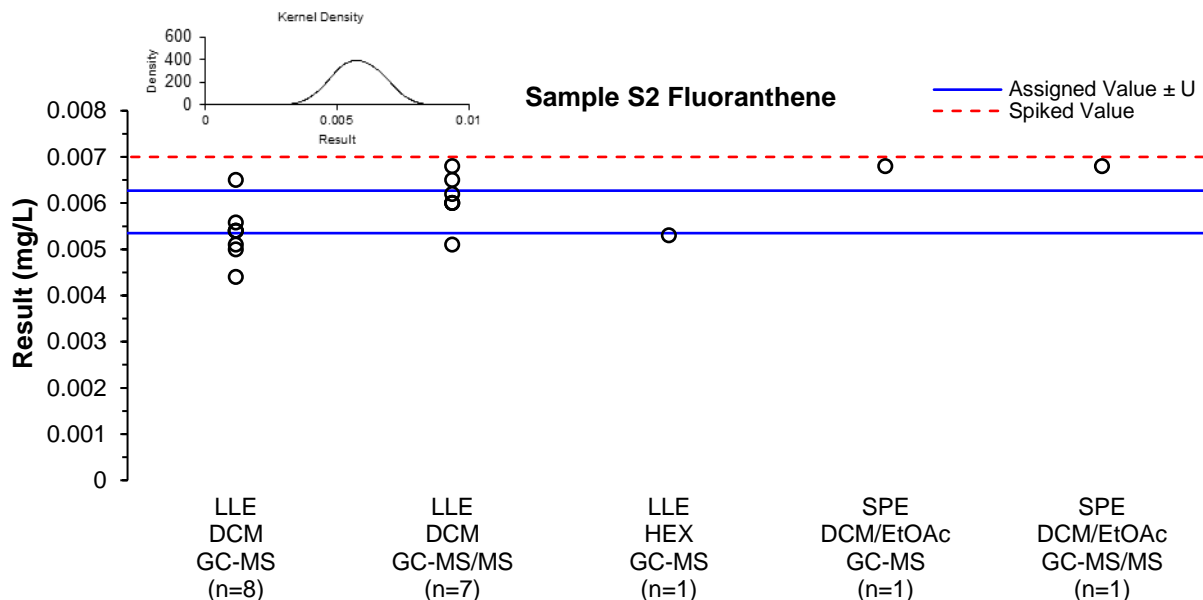


Figure 44 Sample S2 Fluoranthene Result vs Methodology

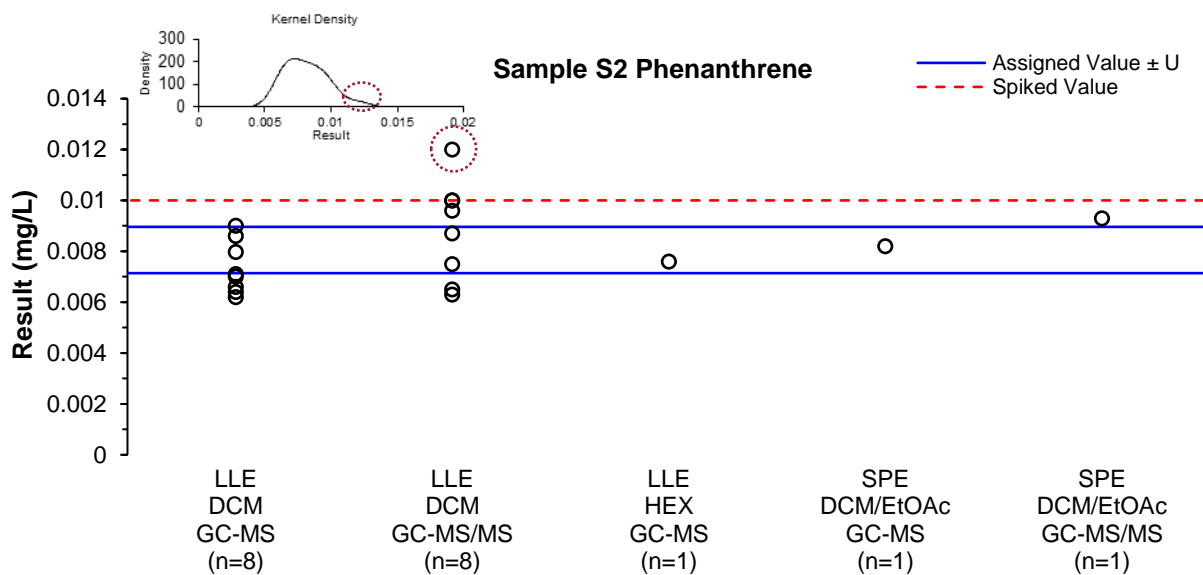


Figure 45 Sample S2 Phenanthrene Result vs Methodology

Sample S3 Phenols

For Sample S3, participants were provided 2 x 100 mL bottles. 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 46; there was no evident correlation observed.

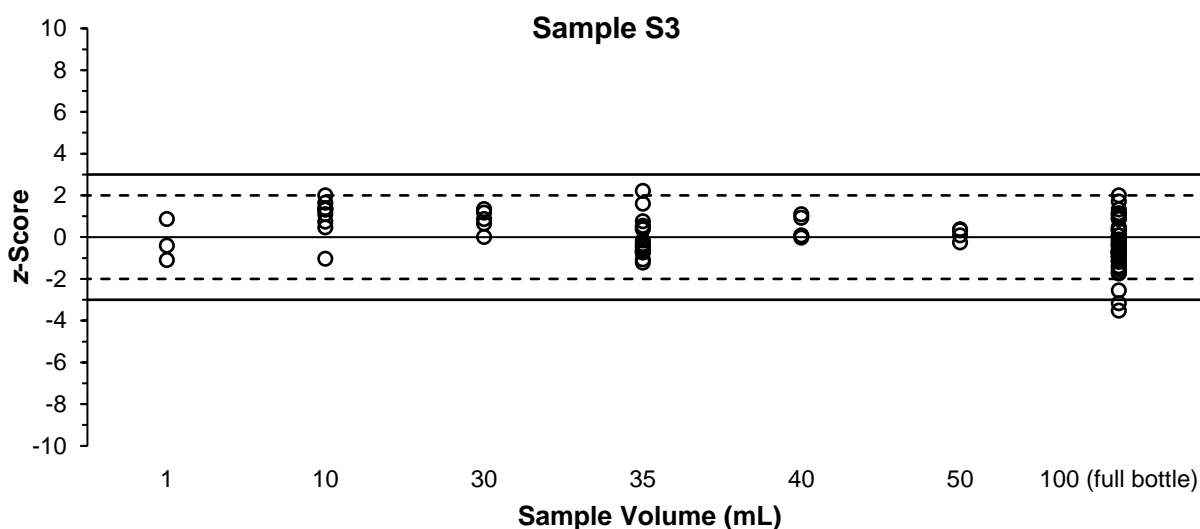


Figure 46 Sample S3 z-Score vs Sample Volume

The majority of participants used LLE, except for three participants that used either SPE, solid-phase microextraction (SPME) or no extraction. Extraction solvents reported by participants were DCM, HEX, DCM/EtOAc mixture or methyl tert-butyl ether (MTBE). No participant reported a clean-up step. Most participants used GC-MS(/MS), with only one participant using liquid chromatography (LC) coupled to MS/MS instead.

Plots of results reported and methodology used for Sample S3 are presented in Figures 47 to 51. 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.

The most common methodology used for Sample S3 was LLE with DCM, and analysis using GC-MS. There was no significant trend observed with regards to methodology used.

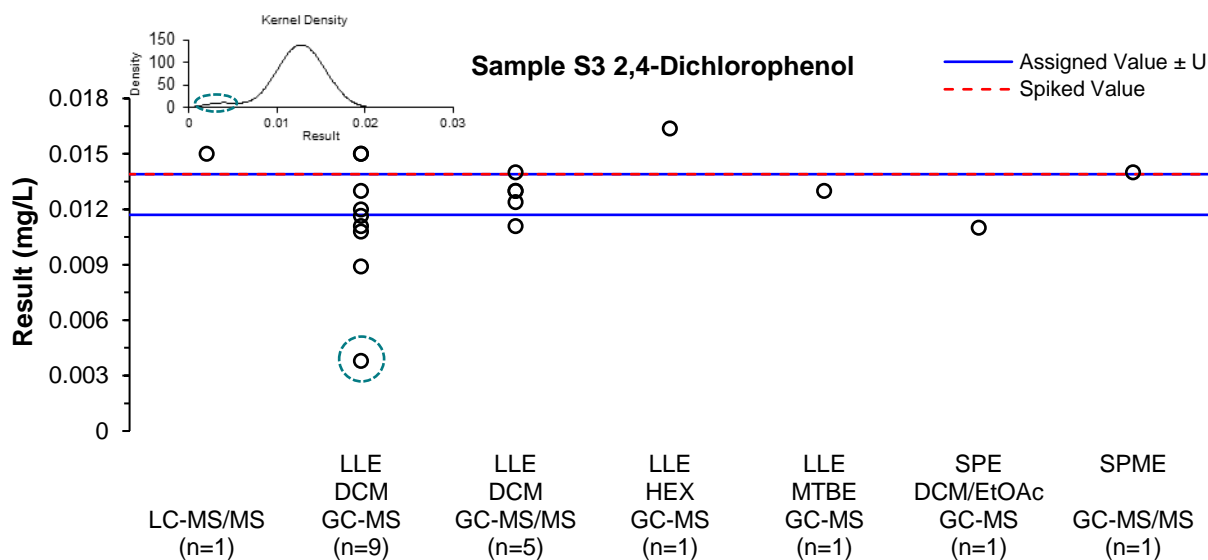


Figure 47 Sample S3 2,4-Dichlorophenol Result vs Methodology

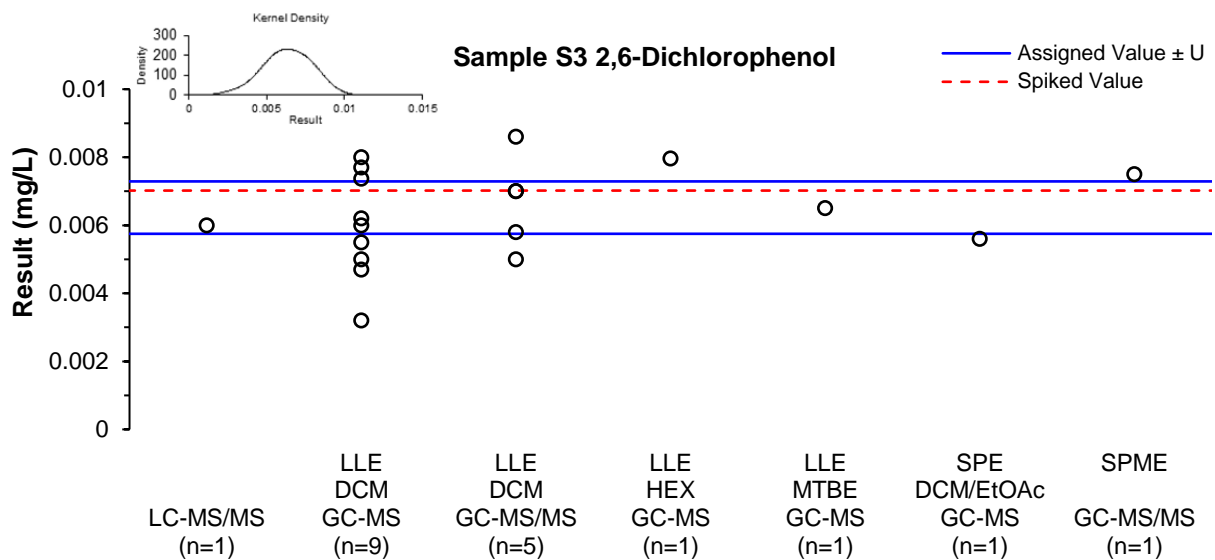


Figure 48 Sample S3 2,6-Dichlorophenol Result vs Methodology

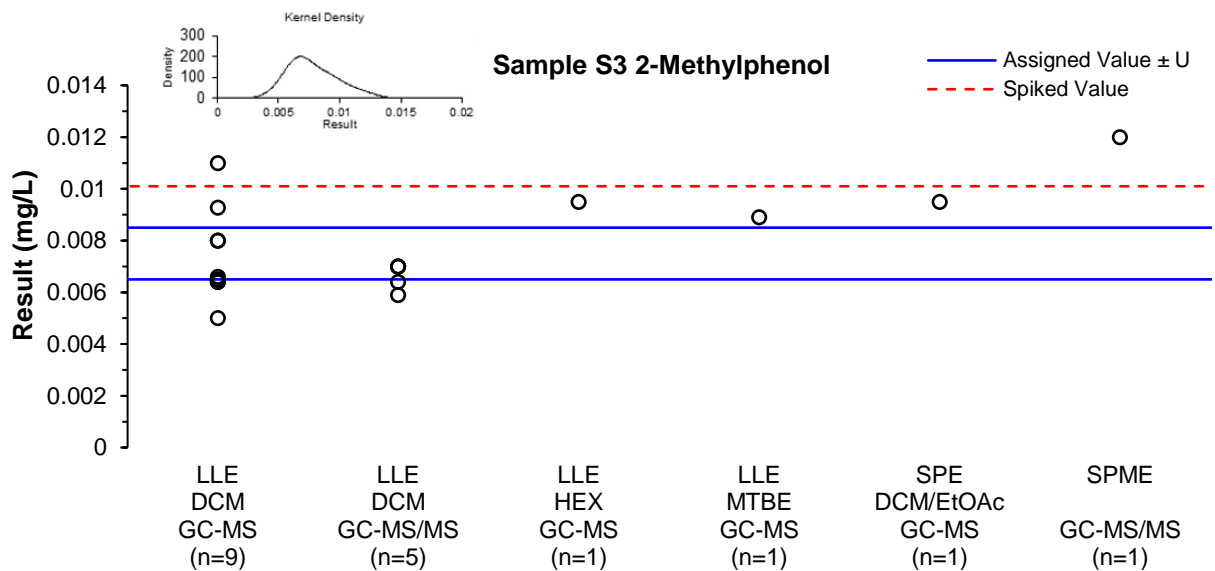


Figure 49 Sample S3 2-Methylphenol Result vs Methodology

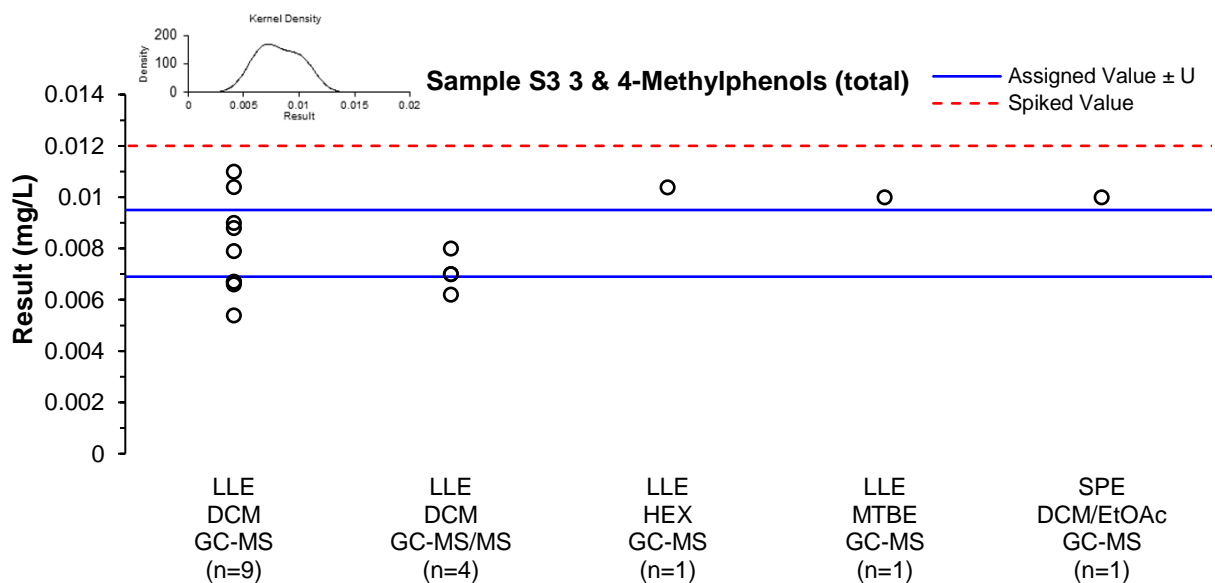


Figure 50 Sample S3 3 & 4-Methylphenols (total) Result vs Methodology

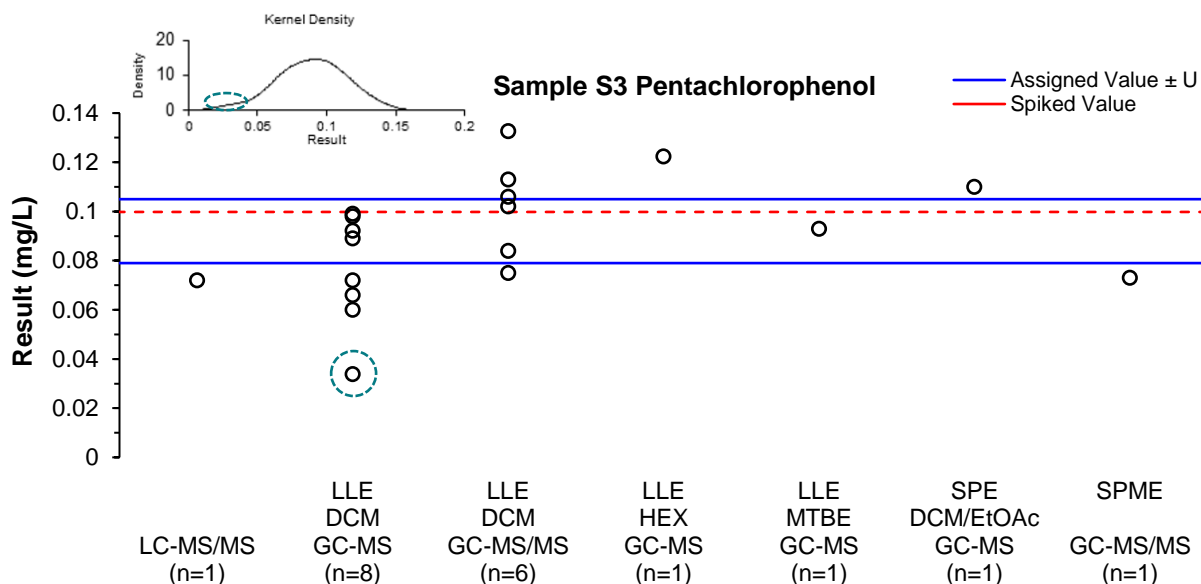


Figure 51 Sample S3 Pentachlorophenol Result vs Methodology

Sample S4 17β-Estradiol

17β-Estradiol was a pilot study. Three participants returned numeric results for this analyte. All participants used different extraction techniques (SPE with methanol, LLE with water/methanol, or direct injection onto instrument) but all used LC-MS/MS as the measurement instrument. Participants' results were generally compatible with each other, the spiked value and the NMI homogeneity value, taking into consideration expected variation.

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.

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

- Accustandard
- ERA
- o2Si
- Restek
- Sigma Aldrich
- ISO 17034 traceable 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'*¹⁰

6.11 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored results in this PT study are presented in Tables 29 to 31, and Figure 52.

Table 29 Summary of Participants' Results for Sample S1 Scored Analytes*

Lab. Code	1,2-dichloroethane	1,4-dichlorobenzene	Carbon tetrachloride	Dichloromethane	Toluene	Xylenes
AV	0.210	0.0717	0.095	0.0211	0.0526	0.148
SV	0.200	0.0776	0.100	0.0157	0.0500	0.200
1	NT	0.072	0.12	<0.01	0.062	0.17
2	0.206	0.0714	0.084	0.017	0.047	0.132
3	NT	0.075	0.115	NT	0.065	0.177
4	NT	NT	NT	NT	0.054	0.13
5	NT	NT	NT	NT	0.0506	0.1462
6	0.173	0.057	0.089	0.018	0.043	0.122
7	0.193	0.086	0.086	0.023	0.050	0.148
8	0.189	0.067	0.083	0.0153	0.046	0.1318
9	0.089	0.067	0.083	NT	0.061	0.172
10	0.25	0.05	0.13	0.03	0.064	0.13
11	NR	NR	NR	NR	46.9	143.0
12	0.232	0.0737	0.100	0.0218	0.0528	0.147
13	0.21	0.069	0.074	0.012	0.047	0.13
14	0.224	0.078	0.087	0.025	0.052	0.147
15	170	58.5	72	18	41	120
16	0.23	0.076	0.1	0.021	0.057	0.18
17	0.196	0.072	0.129	0.023	0.051	0.155
18	0.22	0.077	0.094	0.021	0.052	0.16
19	0.211	0.0782	0.0779	0.0235	0.05	0.161
20	0.199	0.074	0.099	NT	0.049	0.147
21	0.21	0.064	0.085	0.023	0.05	0.13
22	NS	NS	NS	NS	NS	NS

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

Table 30 Summary of Participants' Results for Sample S2 Scored Analytes*

Lab. Code	Benz[a]anthracene	Benzo[a]pyrene	Chrysene	Fluoranthene	Phenanthrene
AV	0.00346	0.00353	0.00235	0.00581	0.00805
SV	0.00499	0.00403	0.00299	0.00700	0.0100
1	0.0049	0.0062	0.0031	0.0065	0.0090
2	0.0033	0.0033	0.0017	0.0051	0.0064
3	0.0062	0.0054	0.0035	0.0068	0.0063
4	0.0028	0.0027	0.0012	0.0068	0.0082
5	0.0026	<0.001	<0.001	0.0062	0.012

Lab. Code	Benz[<i>a</i>]anthracene	Benzo[<i>a</i>]pyrene	Chrysene	Fluoranthene	Phenanthrene
6	0.0037	0.0029	0.002	0.0053	0.0076
7	0.003	0.004	0.002	0.006	0.010
8	0.0043	0.0046	0.0028	0.006	0.0087
9	NT	NT	0.0034	NT	0.0065
10	0.0038	0.0042	0.0019	0.0054	0.0071
11	NR	NR	NR	NR	NR
12	0.0034	0.0040	0.0021	0.0065	0.0096
13	0.0033	0.0027	0.0019	0.0051	0.0075
14	0.0040	0.0042	0.0025	0.0054	0.0086
15	2.45	1.1	1.15	5.75	9.2
16	0.0038	0.0047	0.0033	0.0068	0.0093
17	0.0030	0.0028	0.0022	0.0054	0.0066
18	0.003	0.004	0.002	0.006	0.01
19	0.00372	0.00329	0.00216	0.00558	0.00798
20	0.0026	0.0019	0.0016	0.0044	0.0062
21	0.004	0.002	0.003	0.005	0.007
22	NS	NS	NS	NS	NS

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

Table 31 Summary of Participants' Results for Sample S3 Scored Analytes*

Lab. Code	2,4-Dichlorophenol	2,6-Dichlorophenol	2-Methylphenol	3 & 4-Methylphenols (total)	Pentachlorophenol
AV	0.0128	0.00652	0.0075	0.0082	0.092
HV	0.011	0.006	0.010	0.007	0.074
SV	0.0139	0.00702	0.0101	0.0120	0.0998
1	0.013	0.0062	0.0080	0.0088	NT
2	0.0111	0.005	0.0066	0.0079	0.066
3	0.015	0.006	NT	NT	0.072
4	0.011	0.0056	0.0095	0.01	0.11
5	0.0124	0.0086	0.0059	<0.006	0.1326
6	0.013	0.0065	0.0089	0.01	0.093
7	0.013	0.007	0.007	0.007	0.113
8	0.0038	0.0077	0.005	0.0054	0.06
9	<0.03	<0.03	<0.03	<0.06	0.084
10	0.012	0.006	0.008	0.009	0.099
11	NR	NR	NR	NR	NR
12	0.0111	0.0058	0.0064	0.0062	0.102

Lab. Code	2,4-Dichlorophenol	2,6-Dichlorophenol	2-Methylphenol	3 & 4-Methylphenols (total)	Pentachlorophenol
13	0.013	0.005	0.007	0.008	0.075
14	0.01164	0.0055	0.0064	0.0067	0.0980
15	13	6	9.1	NT	NT
16	0.014	0.0075	0.012	<0.004	0.073
17	0.0108	0.0032	0.0064	0.0067	0.0338
18	0.014	0.007	0.007	0.007	0.106
19	0.015	0.00737	0.00927	0.0104	0.0921
20	0.0089	0.0047	0.0065	0.0066	0.089
21	0.015	0.008	0.011	0.011	0.072
22	0.01637	0.00796	0.0095	0.01038	0.12233

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

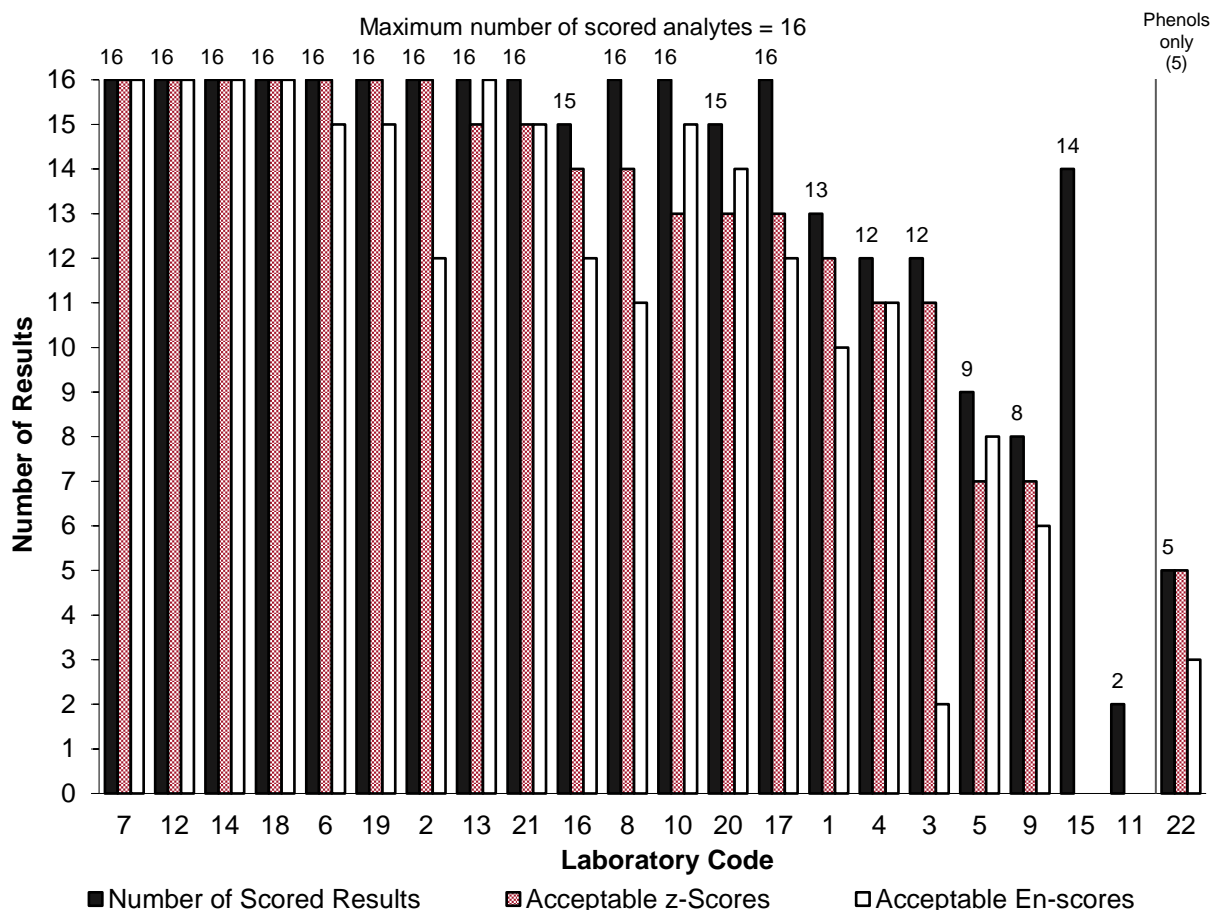


Figure 52 Summary of Participants' Performance

6.12 Comparison with Previous Organic Compounds in Potable Water PT Studies

AQA 24-10 is the second NMI PT study to include organic compounds in potable water. A summary of the participation and reported results rates in NMI Organic Compounds in Potable Water samples is presented in Figure 53. Participants reported a higher proportion of numeric results in this study as compared to the previous study, even with the increased number of analytes being assessed.

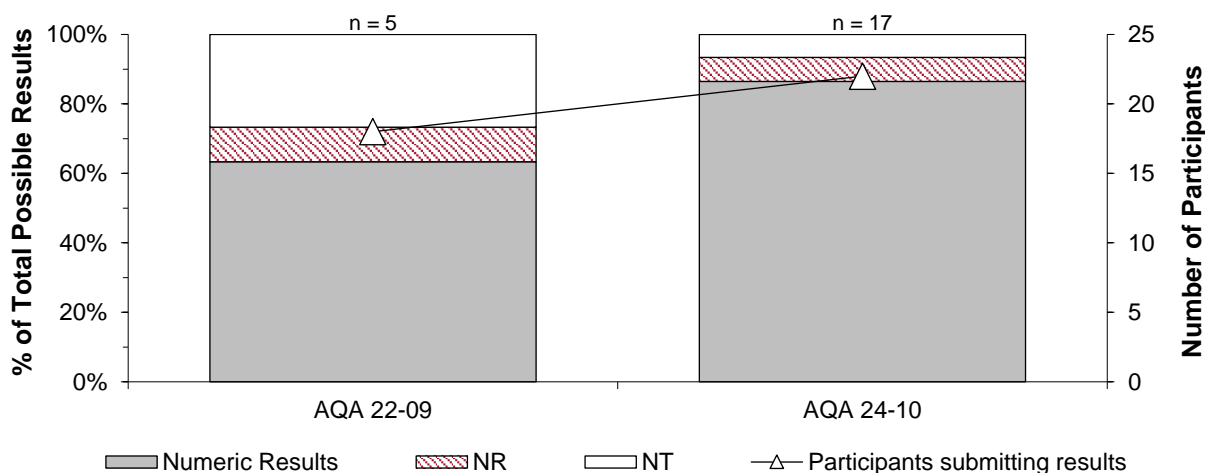


Figure 53 Summary of Participation and Reported Results in Organic Compounds in Potable Water PT Studies (n = number of spiked analytes)

A summary of the acceptable performance (presented as a percentage of the total number of scores) obtained by participants in NMI Organic Compounds in Potable Water samples is presented in Figure 54. Over this period, the average proportion of acceptable z -scores and E_n -scores was 94% and 83% respectively.

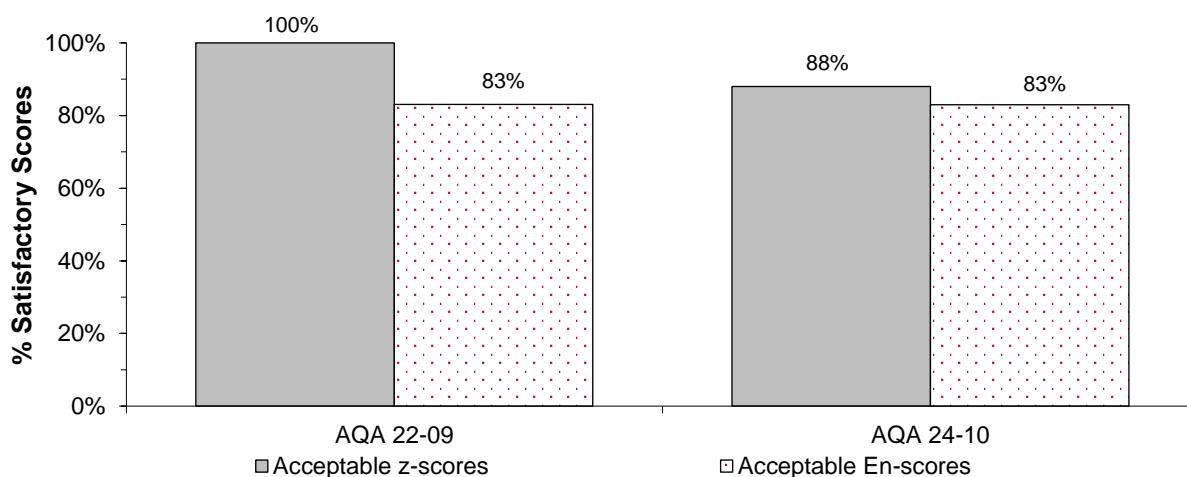


Figure 54 Acceptable z -Scores and E_n -Scores in Organic Compounds in Potable Water PT Studies

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 55 presents a summary of the relative uncertainties as reported by participants in NMI Organic Compounds in Potable Water samples. Over this time period, the vast majority of numeric results were reported with uncertainties (90%), with on average 94% 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 30% of relative uncertainties were outside this range, and may have been unrealistically small or too large and not fit-for-purpose.

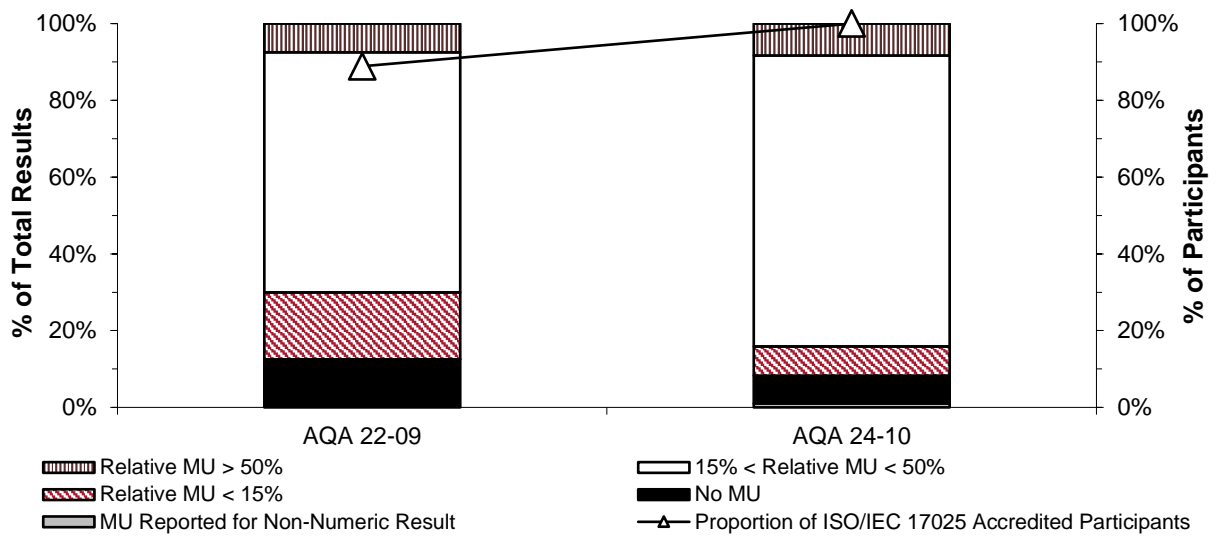


Figure 55 Summary of Participants' Relative Uncertainties for NMI Organic Compounds in Potable Water PT Studies

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] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd ed.
- [11] Fearn, T. and Thompson, M., 2001, ‘A new test for ‘sufficient homogeneity’’, *Analyst*, vol. 126, pp. 1414-1417.

APPENDIX 1 SAMPLE PREPARATION

Tap-water (potable water) was collected and autoclaved; this was used as the starting matrix for Samples S1, S2 and S3. Reagent grade water was used as the starting matrix for Sample S4.

Sample S1 VOCs

Autoclaved potable water (41.88 ± 0.05 g) was dispensed into headspace vials. All weighed vials were then placed in a refrigerator and the water allowed to cool. A composite spiking solution of the analytes was prepared in methanol. The composite spike solution (1 mL) was dispensed into each of the vials. The vials were then labelled, shrink-wrapped, and stored in a refrigerator at 4 °C until sample dispatch.

Sample S2 PAHs

Autoclaved potable water was collected in a stainless steel pot. The water was spiked with the individual analyte spiking solutions. 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 °C until sample dispatch.

Sample S3 Phenols

Autoclaved potable water (98.42 ± 0.05 g) was dispensed into amber glass bottles. All weighed bottles were then placed in a refrigerator and the water allowed to cool. A composite spiking solution of the analytes was prepared in methanol. The composite spike solution (1 mL) was dispensed into each of the bottles. The bottles were then labelled, shrink-wrapped, and stored in a refrigerator at 4 °C until sample dispatch.

Sample S4 17 β -Estradiol

Reagent grade water was collected in a Schott bottle and spiked with the analyte spiking solution. After at least two hours of continuous stirring, the spiked water was dispensed in aliquots of 250 mL into amber glass bottles. The bottles were then labelled, shrink-wrapped, and stored in a refrigerator at 4 °C until sample dispatch.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

The samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples.

Furthermore, homogeneity testing was conducted for Samples S3 and S4 in this study.

Sample S3 Homogeneity Testing

Homogeneity testing was conducted for all analytes in Sample S3. The testing was performed by an external provider, Envirolab Services Sydney Chemical Testing Laboratory, which holds third party (NATA) accreditation to ISO/IEC 17025 for these tests. Samples were analysed in duplicate under repeatability conditions.

The method used was LLE with DCM. Salt (approximately 10 g) was added to the sample (50 mL) and dissolved. The pH was adjusted to less than 2 using 10% H₂SO₄, and then extracted with DCM twice (10 mL, then 8 mL). The two collected volumes of DCM were then dried with sodium sulfate, and then concentrated to 1 mL. The solvent extract was then analysed by GC-MS/MS using instrument internal standards.

Homogeneity checks were based on that described by Thompson and Fearn,¹¹ which is also the procedure described in the International Harmonized Protocol,⁴ and these are presented in Tables 32 to 36. Samples were found to be sufficiently homogeneous for use in a PT study with a target SD (as PCV) of 20%.

Table 32 Homogeneity Testing for Sample S3 2,4-Dichlorophenol

Bottle Number	S3 2,4-Dichlorophenol (mg/L)	
	Replicate 1	Replicate 2
5	0.009	0.010
11	0.011	0.011
29	0.011	0.011
30	0.011	0.011
68	0.011	0.012
80	0.011	0.011
100	0.011	0.011
Average	0.011	
CV	5.9%	

Thompson and Fearn Homogeneity Tests¹¹

Test	Value	Critical	Result
Cochran	0.582	0.727	Pass
s_{an}/σ	0.198	0.500	Pass
s^2_{sam}	0.000	0.000	Pass

Table 33 Homogeneity Testing for Sample S3 2,6-Dichlorophenol

Bottle Number	S3 2,6-Dichlorophenol (mg/L)	
	Replicate 1	Replicate 2
5	0.0044	0.0052
11	0.0059	0.0058
29	0.0056	0.0056
30	0.0054	0.0058
68	0.0063	0.0060
80	0.0055	0.0052
100	0.0059	0.0055
Average	0.0056	
CV	8.3%	

Thompson and Fearn Homogeneity Tests¹¹

Test	Value	Critical	Result
Cochran	0.539	0.727	Pass
s_{an}/σ	0.252	0.500	Pass
s^2_{sam}	0.000	0.000	Pass

Table 34 Homogeneity Testing for Sample S3 2-Methylphenol

Bottle Number	S3 2-Methylphenol (mg/L)	
	Replicate 1	Replicate 2
5*	0.008	0.009
11	0.010	0.010
29	0.010	0.010
30	0.010	0.010
68	0.010	0.010
80	0.010	0.010
100	0.010	0.009
Average	0.010	
CV	6.8%	

Thompson and Fearn Homogeneity Tests¹¹

Test	Value	Critical	Result
Cochran	0.313	0.781	Pass
s_{an}/σ	0.095	0.500	Pass
s^2_{sam}	0.000	0.000	Pass

* Results for bottle 5 were not included in the test for homogeneity, being identified as Cochran outliers due to the difference between replicates.¹¹

Table 35 Homogeneity Testing for Sample S3 3 & 4-Methylphenols (total)

Bottle Number	S3 3 & 4-Methylphenols (total) (mg/L)	
	Replicate 1	Replicate 2
5*	0.0055	0.0062
11	0.0068	0.0069
29	0.0066	0.0067
30	0.0065	0.0068
68	0.0070	0.0070
80	0.0068	0.0066
100	0.0066	0.0065
Average	0.0066	
CV	6.0%	

Thompson and Fearn Homogeneity Tests¹¹

Test	Value	Critical	Result
Cochran	0.544	0.781	Pass
s_{an}/σ	0.092	0.500	Pass
s^2_{sam}	0.000	0.000	Pass

* Results for bottle 5 were not included in the test for homogeneity, being identified as Cochran outliers due to the difference between replicates.¹¹

Table 36 Homogeneity Testing for Sample S3 Pentachlorophenol

Bottle Number	S3 Pentachlorophenol (mg/L)	
	Replicate 1	Replicate 2
5	0.073	0.067
11	0.084	0.076
29	0.070	0.075
30	0.069	0.075
68	0.075	0.071
80	0.072	0.077
100	0.080	0.076
Average	0.074	
CV	6.3%	

Thompson and Fearn Homogeneity Tests¹¹

Test	Value	Critical	Result
Cochran	0.307	0.727	Pass
s_{an}/σ	0.274	0.500	Pass
s^2_{sam}	0.000	0.000	Pass

Sample S4 Homogeneity Testing

Homogeneity testing was conducted for 17 β -estradiol in Sample S4. The testing was performed by NMI Chemical Reference Values. Samples were analysed in duplicate under repeatability conditions.

Sample (3 mL) was spiked with ¹³C₃ 17 β -estradiol internal standard solution (153 ng/g, 37 μ L) before being briefly vortexed. SPE was performed using Waters Oasis HLB 3 cc (60 mg) extraction cartridges which were preconditioned by washing with methanol followed by Milli-Q water. Spiked samples were loaded then washed with Milli-Q water (1 mL) and eluted with methanol (1 mL). Extracts were reduced to dryness under nitrogen at 50 °C before being reconstituted in methanol (500 μ L) prior to analysis. Analysis was conducted on a Sciex Exion 2DLC chromatographic system coupled with a Sciex 7500 mass spectrometer.

Two-dimensional separation was performed via heart-cutting using Waters Acquity UPLC BEH C8 (1.7 μ m, 2.1 x 50 mm) and Waters Acquity UPLC HSS T3 (1.8 μ m, 2.1 x 50 mm) columns in the first and second dimensions respectively. A mobile phase consisting of water with 0.1% ammonium hydroxide and methanol was used in the first dimension. In the second dimension, a mobile phase consisting of water with 0.1 mM ammonium fluoride and methanol was used in the second dimension. The mass spectrometer was operated in multiple reaction monitoring MRM mode and calibrated using a seven-point calibration curve.

Calibration standards were prepared using a 17 β -estradiol solution prepared from NMIJ CRM 6004-a which was previously verified by comparison to other stock lines.

Homogeneity checks were performed as described above,^{4,11} and this is presented in Table 37. As this was a pilot study, no assigned value was set for this analyte and participants' results were not scored. Nevertheless, samples were found to be sufficiently homogeneous for use in a PT study with a target SD (as PCV) of 20%.

Table 37 Homogeneity Testing for Sample S4 17β-Estradiol

Bottle Number	S4 17β-Estradiol (mg/L)	
	Replicate 1	Replicate 2
3	0.0000657	0.0000616
5	0.0000662	0.0000667
16	0.0000661	0.0000692
20	0.0000634	0.0000638
25	0.0000626	0.0000672
32	0.0000659	0.0000670
34	0.0000648	0.0000628
Average	0.0000652	
CV	3.3%	

Thompson and Fearn Homogeneity Tests¹¹

Test	Value	Critical	Result
Cochran	0.391	0.727	Pass
s_{an}/σ	0.150	0.500	Pass
s^2_{sam}	0.000	0.000	Pass

A2.2 Stability

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 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks.

Furthermore, stability testing was conducted for Samples S3 and S4 in this study.

Sample S3 Stability Testing

Samples were taken from the refrigerator and packaged in the same way as the samples dispatched to participants. The samples were then stored at ambient conditions for the same amount of time as for the longest participant sample delivery time; for this study, this was nine days. The samples were then returned to the refrigerator, and samples were analysed after the study results due date ('Stability'). The results from these stability samples were compared against results from samples analysed at sample dispatch ('Initial'). Therefore, the stability samples reflect both transportation stability as well as stability over the course of the PT study at standard storage conditions.

Figures 56 to 60 present the spiked value (SV), initial and stability results, and the final assigned value (AV) for each analyte. Values were in agreement with each other within their respective uncertainties. The samples were shown to be adequately stable when assessed against the criteria specified in ISO 13528.⁷

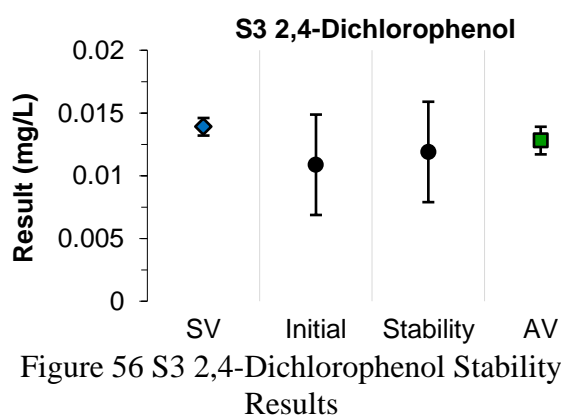


Figure 56 S3 2,4-Dichlorophenol Stability Results

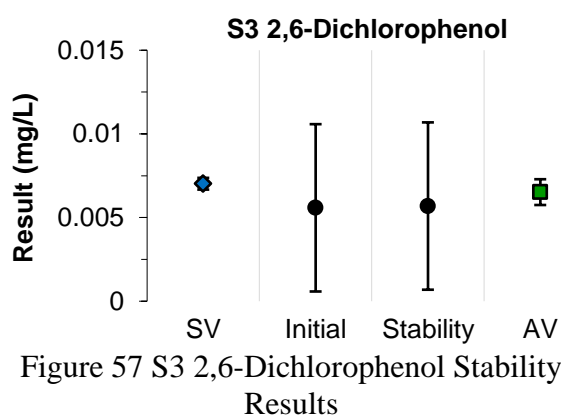


Figure 57 S3 2,6-Dichlorophenol Stability Results

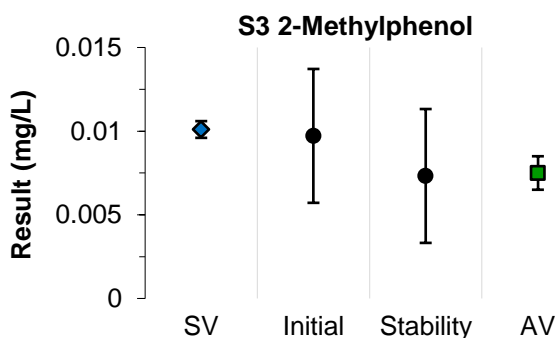


Figure 58 S3 2-Methylphenol Stability Results

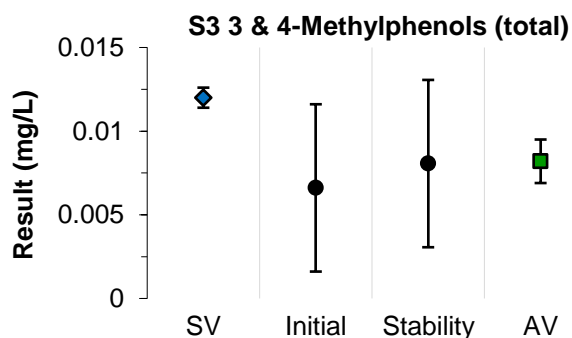


Figure 59 S3 3 & 4-Methylphenols (total) Stability Results

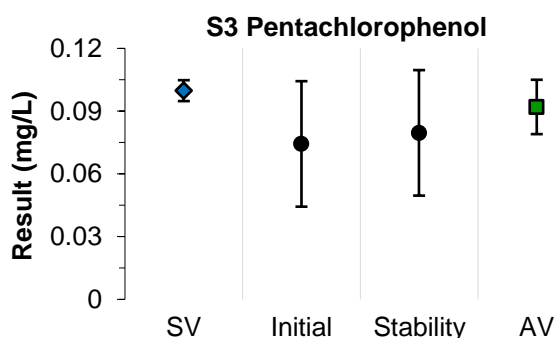


Figure 60 S3 Pentachlorophenol Stability Results

Sample S4 Stability Testing

Samples were taken from the refrigerator and packaged in the same way as the samples dispatched to participants. The samples were then stored at ambient conditions for seven days (beyond the longest sample delivery time for participants analysing this sample). The results from these stability samples ('Stability') were compared against results from samples which had been stored at $-80\text{ }^{\circ}\text{C}$ since sample production ('Initial'). Therefore, the stability samples reflect transportation stability.

Figure 61 presents the spiked value (SV), initial and stability results for 17β -estradiol. Values were in agreement with each other within their respective uncertainties. As this was a pilot study, no assigned value was set for this analyte and participants' results were not scored. Nevertheless, samples were found to be adequately stable when assessed against the criteria specified in ISO 13528.⁷

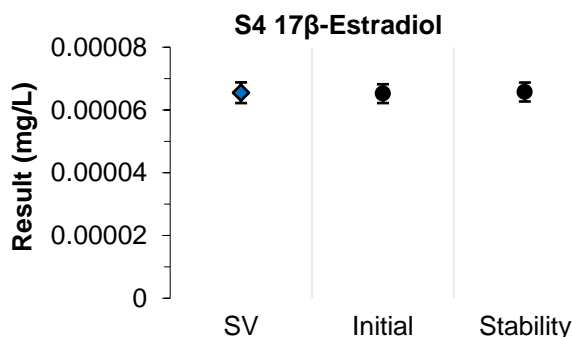


Figure 61 S4 17β-Estradiol Stability Results

Comparison of Participants' Results and Sample Transit Time

Comparisons of results to days spent in transit for scored analytes are presented in in Figures 62 to 77 (solid blue lines correspond to the assigned value $\pm U$ for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5).

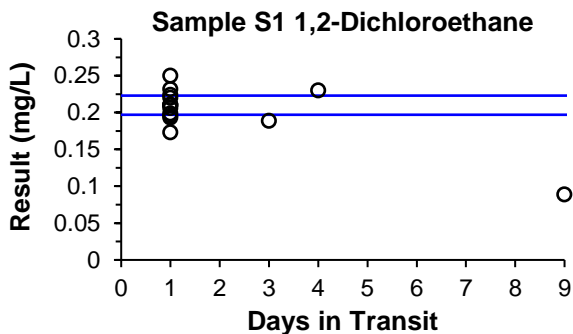


Figure 62 S1 1,2-Dichloroethane Result vs Transit Days

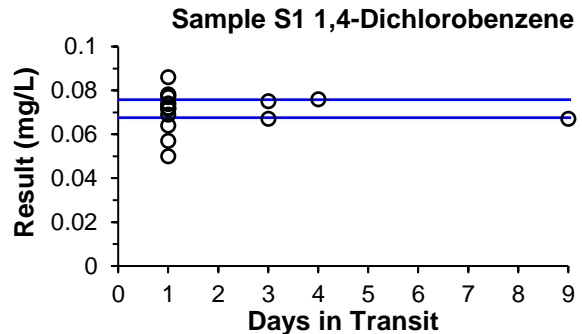


Figure 63 S1 1,4-Dichlorobenzene Result vs Transit Days

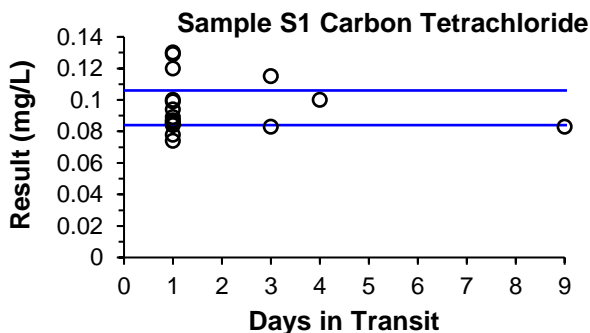


Figure 64 S1 Carbon Tetrachloride Result vs Transit Days

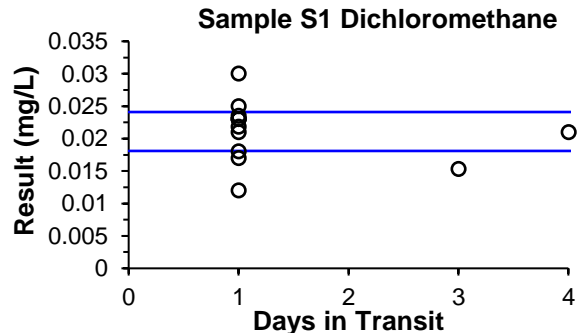


Figure 65 S1 Dichloromethane Results vs Transit Days

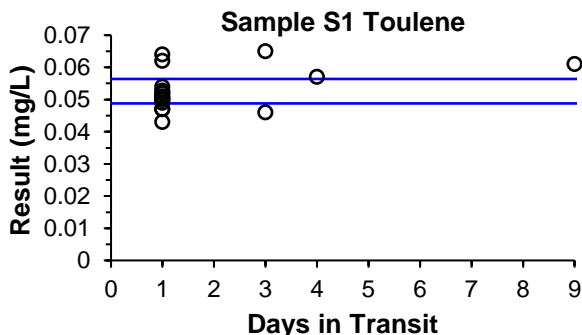


Figure 66 S1 Toluene Results vs Transit Days

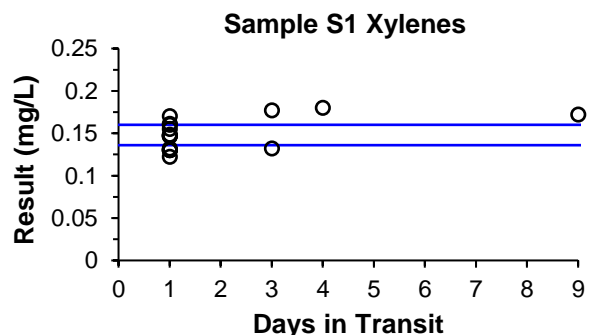


Figure 67 S1 Xylenes vs Transit Days

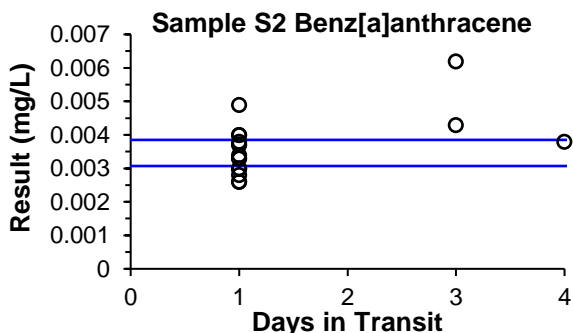


Figure 68 S2 Benz[a]anthracene vs Transit Days

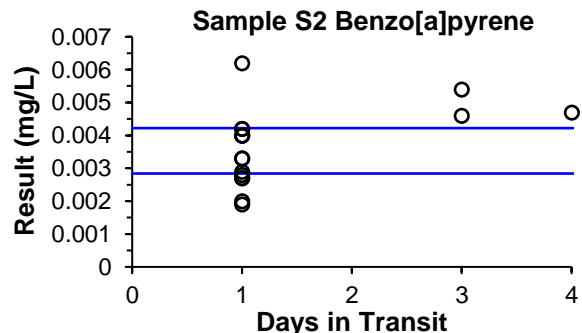


Figure 69 S2 Benzo[a]pyrene vs Transit Days

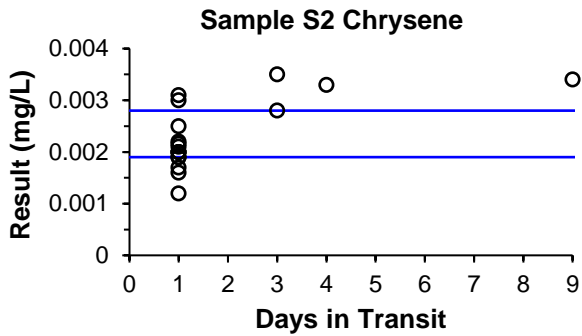


Figure 70 S2 Chrysene vs Transit Days

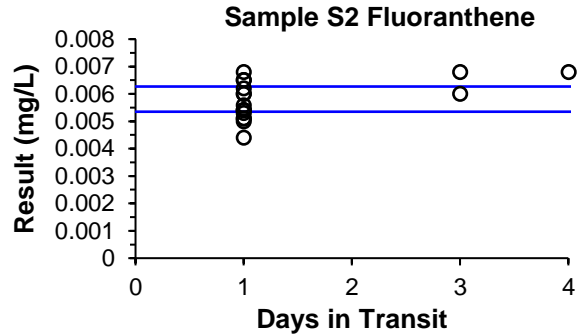


Figure 71 S2 Fluoranthene vs Transit Days

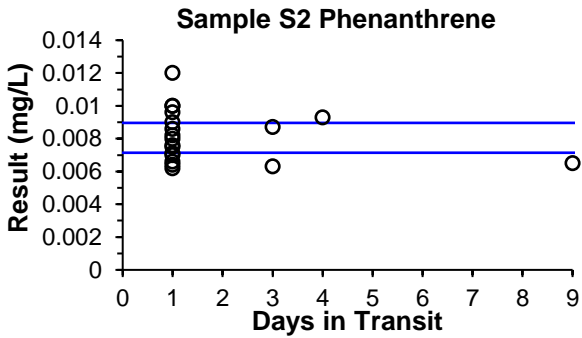


Figure 72 S2 Phenanthrene vs Transit Days

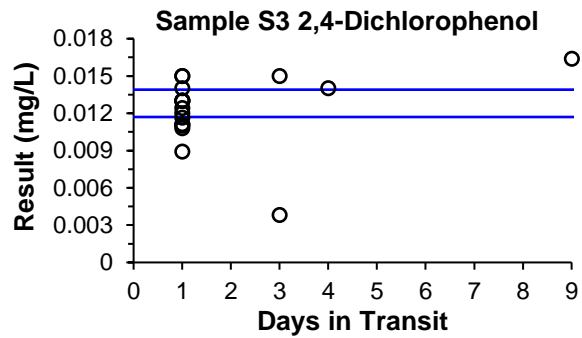


Figure 73 S3 2,4-Dichlorophenol vs Transit Days

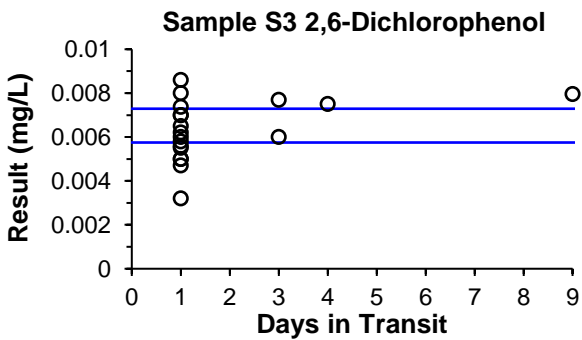


Figure 74 S3 2,6-Dichlorophenol vs Transit Days

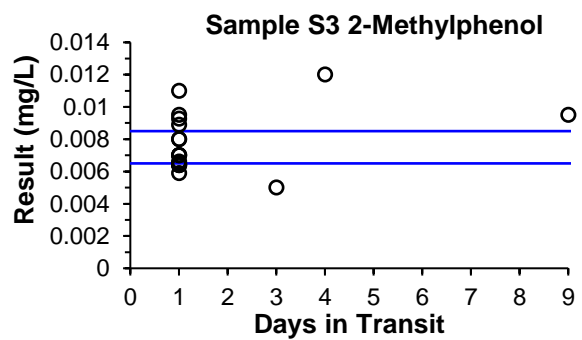


Figure 75 S3 2-Methylphenol vs Transit Days

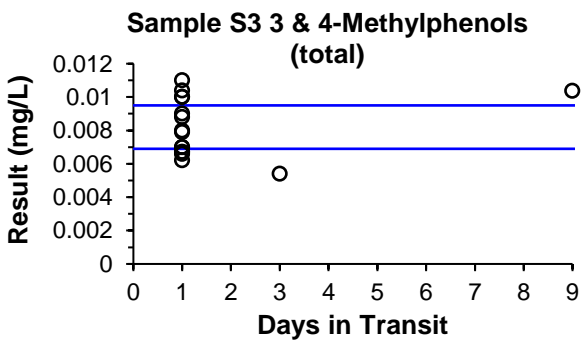


Figure 76 S3 3 & 4-Methylphenols (total) vs Transit Days

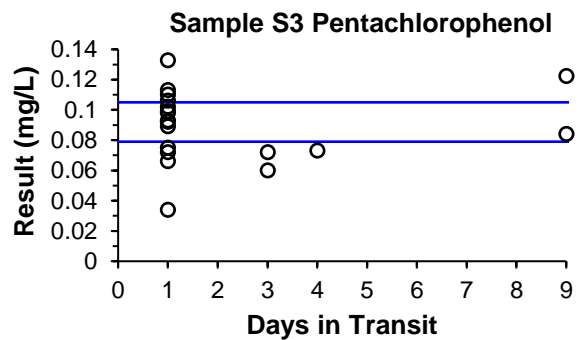


Figure 77 S3 Pentachlorophenol vs Transit Days

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.

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

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 38.

Table 38 Uncertainty of Robust Average for Sample S1 Dichloromethane

Number of results (p)	13
Robust Average	0.0211 mg/L
$S_{rob\ av}$	0.0044 mg/L
$u_{rob\ av}$	0.0015 mg/L
k	2
$U_{rob\ av}$	0.0030 mg/L

Therefore, the robust average for Sample S1 dichloromethane is 0.0211 ± 0.0030 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 39, using the result reported by Laboratory 2 for Sample S1 1,2-dichloroethane.

Table 39 z-Score and E_n-Score for Sample S1 1,2-Dichloroethane Result Reported by Laboratory 2

Participant Result (mg/L)	Assigned Value (mg/L)	Target Standard Deviation	z-Score	E _n -Score
0.206 ± 0.0169	0.210 ± 0.013	15% as PCV, or: $0.15 \times 0.210 =$ 0.0315 mg/L	$z = \frac{0.206 - 0.210}{0.0315}$ $= -0.13$	$E_n = \frac{0.206 - 0.210}{\sqrt{0.0169^2 + 0.013^2}}$ $= -0.19$

APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 40 to 43. Some responses may be modified so that the participant cannot be identified.

Table 40 Methodology – Sample S1 VOCs

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	42	Liquid-Liquid				
2	5	Purge and Trap	-	None	P&T GC-MS	USEPA 8260
3	10	Headspace	None	None	Headspace GC-MS	In-house method
4	40				P&T GC-MS	EPA 524.3
5	40	Liquid-Liquid		N/A	P&T GC-MS/MS	In-house method
6	12	Headspace			Headspace GC-MS	USEPA 8260 (In-House)
7	42	Purge & Trap	Nitrogen	None	P&T GC-MS/MS	USEPA 8260
8	10	Headspace	N/A	None	Headspace GC-MS	US EPA 8260 & 5021
9	40	Liquid-Liquid	Methanol	None	P&T GC-MS/MS	USEPA 8260
10	25	Purge & Trap	None	None	P&T GC-MS	USEPA 8260
11	42				P&T GC-MS	
12	5		NA		P&T GC-MS	
13	44	N/A	N/A	N/A	P&T GC-MS	USEPA 8260
14	5				P&T GC MS	
15	10				Headspace GC-MS	
16	5	Purge and trap			P&T GC-MS	USEPA 8260(mod)
17	5	Liquid-Liquid	n/a	None	GC-FID	USEPA SW846-8260
18	43	none	none	none	P&T GC-MS	USEPA 8260
19	5	NONE	NONE	NONE	P&T GC-MS	In-house method
20	5	NA	NA	None	P&T GC-MS/MS	
21	45	N/A	N/A	N/A	P&T GC-MS	USEPA 8260
22	NS					

Table 41 Methodology – Sample S2 PAHs

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	50	Liquid-Liquid	DCM	none	GC-MS	
2	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
3	200	Liquid-Liquid	DCM	None	GC-MS/MS	In-house method
4	500	SPE	DCM/EtOAc	None	GC-MS	EPA 525.3
5	35	Liquid-Liquid	DCM	N/A	GC-QQQ	In-house method
6	50	Liquid-Liquid	Hexane		GC-MS	USEPA 8272 (In-House)
7	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
8	250	Liquid-Liquid	DCM	None	GC-MS/MS	US EPA 8270
9	35	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8260
10	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
11	NR					
12	35	Liquid-Liquid	DCM		GC-MS/MS	
13	100	Liquid-Liquid	DCM	N/A	GC-MS/MS	USEPA 8270
14	100	Liquid-Liquid	DCM		GCMS	
15	40	Liquid-Liquid	Hexane	None	GC-MS	
16	500	SPE	DCM:EtOAc		GC-MS/MS	USEPA8270(mod)
17	100	Liquid-Liquid	DCM	None	GC-MS	USEPA SW846-8270
18	35	Liquid-Liquid	DCM	none	GC-MS/MS	USEPA 8260
19	513	Liquid-Liquid	DCM	NONE	GC-MS	In-house method
20	100	Liquid-Liquid	DCM	None	GC-MS	
21	100	Liquid-Liquid	DCM	N/A	GC-MS	USEPA 8270
22	NS					

Table 42 Methodology – Sample S3 Phenols

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	50	Liquid-Liquid	DCM	none	GC-MS	
2	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
3	1	None	None	None	LC-MS/MS	In-house method
4	100	SPE	DCM/EtOAc	None	GC-MS	EPA 525.3
5	35	Liquid-Liquid	DCM	N/A	GC-QQQ	In-house method
6	40	Liquid-Liquid	MTBE		GC-MS	USEPA 8270 (In-House)
7	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
8	100	Liquid-Liquid	DCM	None	GC-MS	US EPA 8270
9	35	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8260
10	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
11	NR					
12	35	Liquid-Liquid	DCM		GC-MS/MS	
13	100	Liquid-Liquid	DCM	N/A	GC-MS/MS	USEPA 8270
14	100	Liquid-Liquid	DCM		GCMS	
15	40	Liquid-Liquid	DCM	None	GC-MS	
16	10	SPME			GC-MS/MS	In house
17	100	Liquid-Liquid	DCM	None	GC-MS	USEPA SW846-8270
18	35	Liquid-Liquid	DCM	none	GC-MS/MS	USEPA 8260
19	30	Liquid-Liquid	DCM	NONE	GC-MS	In-house method
20	100	Liquid-Liquid	DCM	None	GC-MS	
21	100	Liquid-Liquid	DCM	N/A	GC-MS	USEPA 8270
22	10	Liquid-Liquid	Hexane	None	GC-MS	DIN 38407 F27 for Chlorophenols DIN EN 12673

Table 43 Methodology – Sample S4 17 β -Estradiol

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1						NT
2						NS
3						NS
4						NS
5						NT
6	100	SPE	Methanol		LC-MS/MS	USEPA 1694 (In-House)
7						NS
8						NS
9						NS
10						NS
11						NS
12						NS
13						NS
14						NS
15						NS
16	10	Direct Injection			LC-MS/MS	In house
17						NS
18						NS
19						NR
20						NS
21	100	Liquid-Liquid	Water:Methanol	N/A	LC-MS/MS	USEPA 539
22						NS

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

ADWG	Australian Drinking Water Guidelines
ADWG (A)	ADWG Aesthetic Guideline Value
ADWG (H)	ADWG Health-Based Guideline Value
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
DI	Direct Injection
EtOAc	Ethyl Acetate
FID	Flame Ionisation Detection
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
HEX	Hexane
HS	Headspace
HV	Homogeneity Value
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
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
NMIJ	National Metrology Institute of Japan

NR	Not Reported
NS	Not Supplied
NT	Not Tested
P&T	Purge-and-Trap
PAH	Polycyclic Aromatic Hydrocarbon
PCV	Performance Coefficient of Variation
PT	Proficiency Testing
RA	Robust Average
RM	Reference Material
s.f.	Significant Figures
SD	Standard Deviation
SI	International System of Units
SPE	Solid-Phase Extraction
SPME	Solid-Phase Microextraction
SS	Spiked Samples
SV	Spiked Value (or formulated concentration of a PT sample)
U	Expanded Uncertainty
VOC	Volatile Organic Compound

END OF REPORT