Proficiency Test Final Report AQA 23-21 Hydrocarbons and Phenols in River Water

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ACKNOWLEDGMENTS

Raluca Iavetz

Manager, Chemical Reference Values

105 Delhi Road, North Ryde, NSW 2113, Australia

Phone: +61 2 9449 0178

Email: raluca.iavetz@measurement.gov.au

Accredited for compliance with ISO/IEC 17043, except for all Sample S4 analytes (phenols in water) which are outside the scope of NMI's accreditation.

TABLE OF CONTENTS

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SUMMARY

AQA 23-21 Hydrocarbons and Phenols in River Water commenced in October 2023. Twenty-nine laboratories registered to participate, and 28 participants submitted results.

The sample set consisted of four water samples. Samples were prepared in the Sydney NMI laboratory using river water. Participants measured total recoverable hydrocarbons (TRH) in Sample S1, volatile hydrocarbons (C6 to C10), benzene, toluene, ethylbenzene and xylenes (BTEX) in Sample S2, polycyclic aromatic hydrocarbons (PAHs) in Sample S3 and phenols in Sample S4.

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 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:

- *Compare the performances of participants and assess their accuracy in the identification and measurement of hydrocarbon and phenol pollutants in river water.*

Laboratories **1**, **2**, **4**, **6**, **10**, **17**, **18**, **19**, **20**, **22**, **24**, **26**, **28** and **29** reported results for all 17 scored analytes.

Five participants did not report results for analytes that they tested for and were present in the samples (total of eight results). Five participants reported numeric results for analytes that were not spiked into the samples (total of five results).

Of 414 z-scores, 371 (90%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Of 393 E_n-scores, 323 (82%) returned a score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories **18** and **29** returned satisfactory z-scores and E_n-scores for all 17 scored analytes.

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

Of 482 numeric results, 454 (94%) were reported with an associated expanded measurement uncertainty. Reported expanded uncertainties were within the range of 4.8% to 66% relative.

Participants reported a wide range of procedures for estimating their uncertainty.

- *Evaluate the laboratories' test methods.*

For TRH analysis, the most common methodology was liquid-liquid extraction with dichloromethane, and analysis using GC-FID.

For BTEX analysis, the majority of participants used purge-and-trap GC-MS.

For both PAHs and phenols analysis, the most common methodology was liquid-liquid extraction with dichloromethane, and analysis using GC-MS, followed closely by the same extraction procedure with analysis using GC-MS/MS instead.

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

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

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

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

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

1.2 Study Aims

The aims of the study were to:

- compare the performances of participants and assess their accuracy in the identification and measurement of hydrocarbon and phenol pollutants in river water;
- develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates;
- evaluate the laboratories' test methods; and
- produce materials that can be used in method validation and as control samples.

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

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO/IEC 17043,[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[4]

NMI is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes.[1] This study falls within the scope of NMI's accreditation, except for all Sample S4 analytes (phenols in water) which are outside the scope of NMI's accreditation.

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of this study was:

Invitations sent	17/10/2023
Samples sent	13/11/2023
Results due	12/12/2023
Interim Report	15/12/2023
Preliminary Report	18/12/2023

2.2 Participation

Twenty-nine laboratories registered to participate, and all participants were assigned a confidential laboratory code number for this study. Twenty-eight participants submitted results.

2.3 Selection of Analytes

The analytes and their concentrations in this study were typical of those encountered by environmental testing laboratories monitoring river water to assess the impact of transport fuels in the environment, or the contamination from industry that entails the use of wood, petroleum or coal to generate heat and power. Investigation levels for the analytes studied are set out in the National Environmental Protection (Assessment of Site Contamination) Measure, Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

For Sample S1, participants were requested to measure semi-volatile hydrocarbons (>C10-C40) and total recoverable hydrocarbons (TRH). For Sample S2, participants were requested to measure volatile hydrocarbons (C6-C10), and benzene, toluene, ethylbenzene and xylenes (BTEX). Participants were provided with a list of potential poly-aromatic hydrocarbons (PAHs) spiked into Sample S3 (Table 1) and potential phenols spiked into Sample S4 (Table 2).

Table 1 Possible Spiked PAHs in Sample S3

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

Table 2 Possible Spiked Phenols in Sample S4

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

2.4 Test Material Preparation

Four test samples were prepared by spiking river water with various analytes to obtain the concentrations listed in Table 3. Sample S1 was spiked with diesel fuel, Sample S2 was spiked with unleaded petrol and diesel fuel, Samples S3 was spiked with different amounts of acenaphthene, acenaphthylene, benz[*a*]anthacene, benzo[*a*]pyrene, fluorene, phenanthrene

and pyrene, and Sample S4 was spiked with differing amounts of 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,4-dichlorophenol, and 2,6-dichlorophenol. Additional information on sample preparation is given in Appendix 1.

Table 3 Spiked Values of Test Samples

Sample	Analyte	Spiked Value (µg/L)	Uncertainty[a] (µg/L)
S1	TRH	3200	160
S2	Benzene	69.2	3.5
	Toluene	261	13
	Ethylbenzene	29.0	1.5
	Xylenes	129	6
	Total BTEX	489	24
S3	Acenaphthene	8.01	0.40
	Acenaphthylene	2.99	0.15
	Benz[a]anthracene	6.51	0.33
	Benzo[a]pyrene	3.57	0.18
	Fluorene	3.14	0.16
	Phenanthrene	1.93	0.10
	Pyrene	2.85	0.14
S4	2-Methylphenol	10.0	0.5
	3 & 4-Methylphenols (total)[b]	12.1	0.6
	2,4-Dichlorophenol	14.0	0.7
	2,6-Dichlorophenol	14.0	0.7

[a] Estimated expanded uncertainty at approximately 95% confidence using a coverage factor of 2. Stability was not considered and so the expanded uncertainty is related to the concentration at the time of spiking.
[b] Sample S4 was spiked with both 3-methylphenol and 4-methylphenol. Participants were requested to report for the total of 3 & 4-methylphenols.

2.5   Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted on these test materials before the samples were sent. The samples were prepared, stored and dispatched using a process that has been demonstrated to produce sufficiently homogeneous and stable samples in previous similar NMI PT studies. Additionally, the storage stability of petroleum hydrocarbons in water has been previously established.[6] A preliminary trial for the homogeneity and stability of phenols in water was also performed prior to this study, and results indicated that the preparation, storage and dispatch processes used would produce samples suitable for this PT study.

Participants' results also gave no reason to question the homogeneity or stability of these samples (Appendix 2). Analytes have only been scored if there was a reasonable consensus between participants' results, and if the assigned value to spiked value ratio was similar to those observed in previous NMI studies.

2.6   Test Material Storage, Dispatch and Receipt

The test samples were stored at approximately 4 °C prior to dispatch. Samples were dispatched on 13 November 2023.

The following items were also sent to participants:

- 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.

- Do not test for volatile hydrocarbons (C6-C10) or BTEX components in Sample S1.

- Participants need not test for all listed analytes.

- If analyses cannot be commenced on the day of receipt, please store the samples chilled.

- For each analyte in each sample, report a single result in units of µg/L expressed as if reporting to a client, applying the limit of reporting of the method used for analysis. This is the figure that will be used in all statistical analysis in the study report.

- For each analyte in each sample, report the associated expanded uncertainty in units of µg/L (e.g. 2000 ± 200 µg/L), if determined.

- Report results for the following:

    o Sample S1: Semi-volatile hydrocarbons (>C10-C40) and Total Recoverable Hydrocarbons (TRH). Use your laboratory's chosen quantitation range, and indicate what this range is. Australian NEPM fractions >C10-C16, >C16-C34, >C34-C40 are encouraged. The concentration range is between $200 – 10000$ µg/L.

    o Sample S2: Volatile Hydrocarbons (C6-C10), Benzene, Toluene, Ethylbenzene, Total Xylenes and Total BTEX. Individual BTEX components concentration is between $10 – 2500$ µg/L.

    o Sample S3: PAHs. The concentration range is between $1 – 50$ µg/L.

    o Sample S4: Phenols. The concentration range is between $1 – 50$ µg/L.

- 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 December 2023 by email to proficiency@measurement.gov.au.

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

2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 15 December 2023.

A Preliminary Report was emailed to all participants on 18 December 2023. This report included a summary of the results reported by participants, assigned values, performance coefficients of variation (PCVs), z-scores and E_n-scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Participants' Test Methods

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

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about their basis of measurement uncertainty (MU). Responses are presented in Table 4. Some responses may be modified so that the participant cannot be identified.

Table 4 Basis of Uncertainty Estimate

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
1	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	ISO/GUM
2	TRH / BTEX / Phenols	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	CRM	
	PAH	Top Down - reproducibility (standard deviation) from PT studies used directly	Duplicate analysis Instrument calibration	CRM	
3	All	Based on historical data	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
4	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
5	All	Repeatability precision - based upon internal historical data	Control samples - CRM	Laboratory bias from PT studies CRM	
6	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
7	All				

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
8	PAHs	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Recoveries of SS	ISO/GUM
9	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
10	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM	CRM	ISO/GUM
12	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Recoveries of SS	ISO/GUM
13	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
14	BTEX	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - CRM	CRM	ISO/GUM
15	TRH / PAHs / Phenols	Standard deviation of replicate analyses multiplied by 2 or 3			
16	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis	CRM Recoveries of SS	ISO/GUM
17	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	Laboratory bias from PT studies CRM Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
18	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS Standard purity	NMI Uncertainty Course
19	TRH / BTEX	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis		Eurachem/CITAC Guide
	PAHs / Phenols		Control samples		

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
20	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
21	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Laboratory bias from PT studies Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
22	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis		Eurachem/CITAC Guide
23	All				
24	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	CRM Recoveries of SS	ISO/GUM
25	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
26	All	Top Down - reproducibility (standard deviation) from PT studies used directly	Control samples - SS Duplicate analysis	Instrument calibration Recoveries of SS	
27	BTEX	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	CRM	NMI Uncertainty Course
28	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration	Eurachem/CITAC Guide
29	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	ISO/GUM

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

Participants were also requested to report their coverage factor. Reported coverage factors are presented in Table 5.

Table 5 Coverage Factors

Lab. Code	TRH Coverage Factor	BTEX Coverage Factor	PAHs Coverage Factor	Phenols Coverage Factor
5	2	2	2	2
8	NS	NS	2	NT
10	2	2	2	2
16	2	2	2	2
18	2.26	2.26	2.26	2.26
21	2	2	2	2
24	2.3	2.4	2.3	2.3
27	NT	0.2	NS	NS
28	2	2	2	2

3.3 Participants' Comments

Participants were invited to make any comments or suggestions on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies.
Participants' comments 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	Study Coordinator's Response
3	S4	There is no uncertainty of measurement for the above Phenol analytes.	
5	S3	Benzo[b,k]fluoranthene reported as one result	
	S4	4-Methylphenol only reported for '3 & 4-Methylphenols, total'.	
20	All	Request the 100mL option for sample volume to be made available for TPH(SV).	Thank you for your suggestion. The current sample preparation procedure requires all bottles for the sample to be the same size, and therefore in this study we only offered participants the 500 mL bottle option for Sample S1. We aim to investigate providing different bottle size options in future.
24	S4	3 & 4 - MethylPhenols is recovered and reported as 4 - MethylPhenols.	
25	S1	TRH - extract spilled during extraction.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 7 to 28 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), along with other estimates of analyte concentration. Bar charts of results and performance scores are presented in Figures 2 to 21. An example chart with interpretation guide is shown in Figure 1.
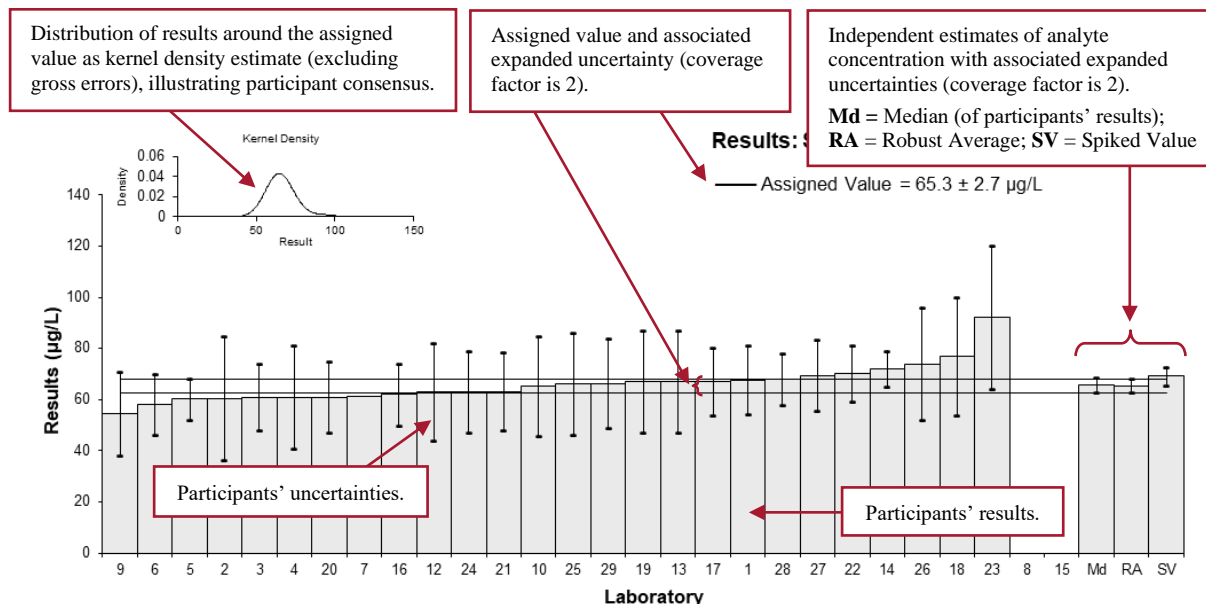
Figure 1 Guide to Presentation of Results

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 were obvious blunders, e.g. results reported with incorrect units or basis, and such results were removed for the calculation of all summary statistics.[3,4]

4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property of a proficiency test item'.[1] In this PT study, the 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 between-laboratory CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528.[7]

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 concentration of the analytes and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[8] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performances and can be compared from study to study.

4.6　Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment (σ) is the product of the assigned value (X) and the PCV, as presented in Equation 1.

$$\sigma = X \times PCV \qquad \textit{Equation 1}$$

4.7　*z*-Score

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

$$z = \frac{(\chi - X)}{\sigma} \qquad \textit{Equation 2}$$

where:

　　z　　is *z*-score

　　χ　　is a participant's result

　　X　　is the assigned value

　　σ　　is the target standard deviation for proficiency assessment from Equation 1

For the absolute value of a *z*-score ($|z|$):

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

To account for potential low bias in consensus value due to inefficient methodologies, scores may be adjusted for a 'maximum acceptable result'. Additional information is given in Section 6.3.

4.8　*E$_n$*-Score

The *E$_n$*-score is complementary to the *z*-score in assessment of laboratory performance. *E$_n$*-score includes measurement uncertainty and is calculated according to Equation 3.

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

where:

　　E_n　　is *E$_n$*-score

　　χ　　is a participant's result

　　X　　is the assigned value

　　U_χ　　is the expanded uncertainty of the participant's result

　　U_X　　is the expanded uncertainty of the assigned value

For the absolute value of an *E$_n$*-score ($|E_n|$):

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

4.9　Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025 must establish and demonstrate the traceability and measurement uncertainty associated with their test results.[9]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[10]

5 TABLES AND FIGURES

Table 7

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	>C10-C16
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	En
1	704.9	282	-0.95	-0.50
2	814	326	-0.32	-0.15
3	NR	NR		
4	1100	300	1.32	0.67
5*	1419	341	3.16	1.44
6	590	180	-1.61	-1.13
7	564	NR	-1.76	-1.80
8	NS	NS		
9	NR	NR		
10	640	192	-1.32	-0.90
12	NR	NR		
13	760	400	-0.63	-0.25
14	NR	NR		
15*	330	30	-3.10	-3.13
16*	1600	480	4.20	1.43
17	920	541	0.29	0.09
18	654	196	-1.24	-0.83
19*	431	86.2	-2.52	-2.30
20	1260	491	2.24	0.75
21	NR	NR		
22*	1480	437	3.51	1.30
23	1070	320	1.15	0.55
24	1300	650	2.47	0.64
25	NR	NR		
26	1100	220	1.32	0.83
27	NT	NT		
28	890	243	0.11	0.07
29	768.3	230.5	-0.58	-0.36

* Outlier, see Section 4.2

Statistics

Assigned Value	870	170
Spike Value	Not Spiked	
Robust Average	920	220
Median	850	210
Mean	920	
N	20	
Max	1600	
Min	330	
Robust SD	400	
Robust CV	43%	
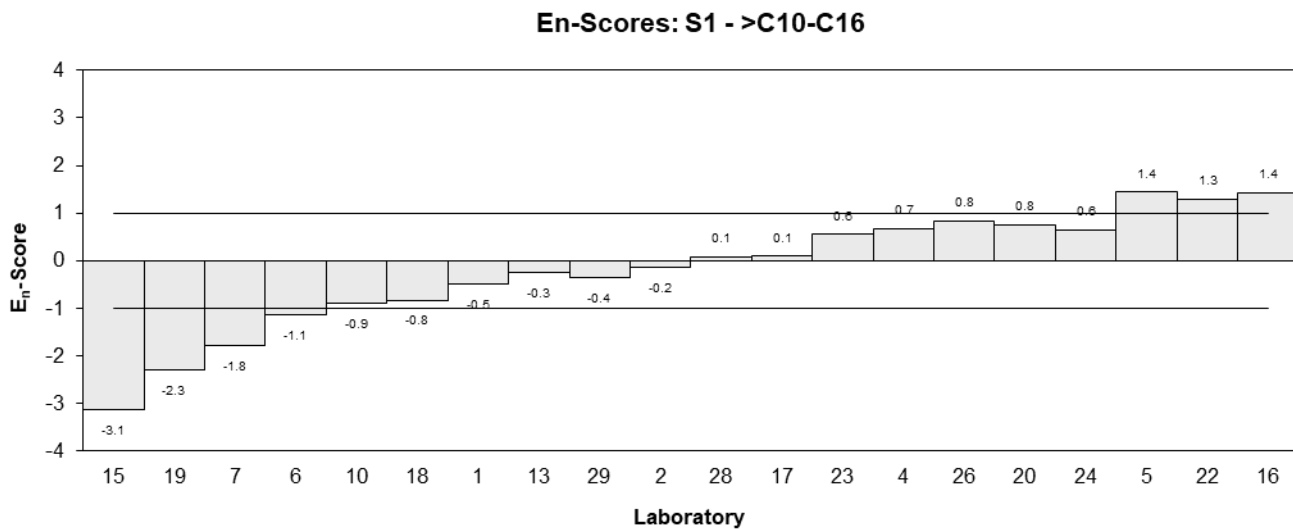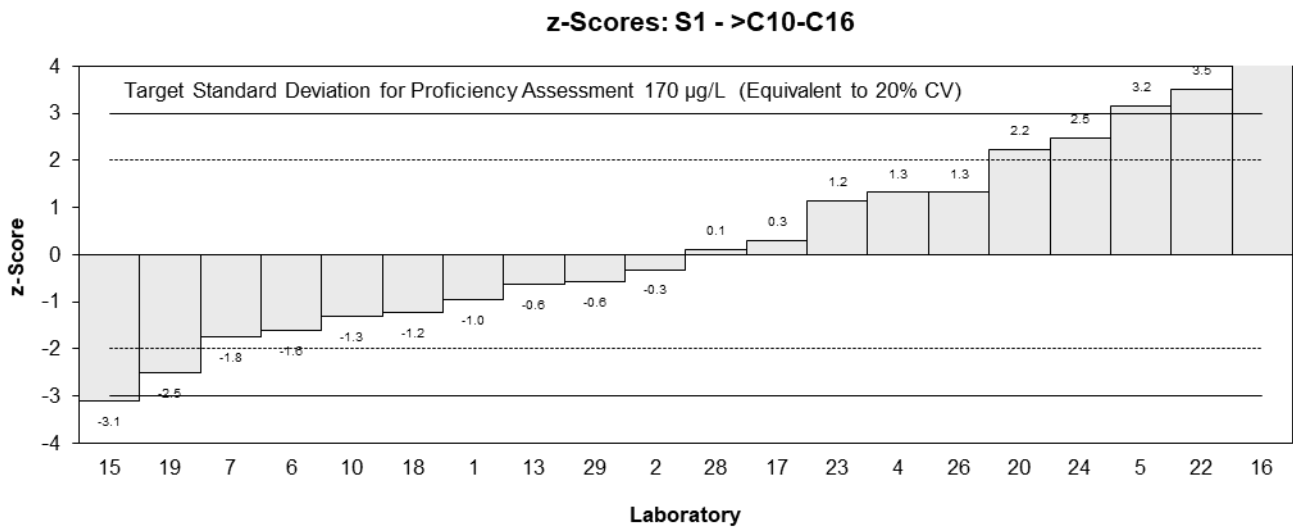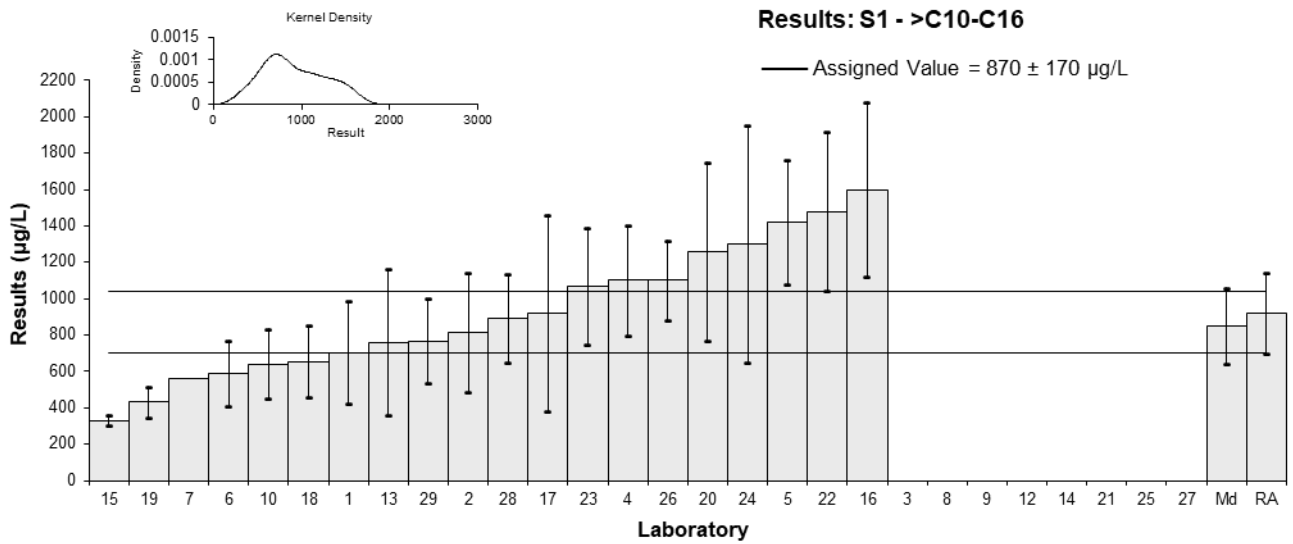
Figure 2

Table 8

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	>C16-C34
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	763.5	305.4	-0.29	-0.14
2	711	284	-0.61	-0.32
3	NR	NR		
4	960	300	0.93	0.46
5	1271	368	2.85	1.18
6	530	160	-1.73	-1.36
7	525	NR	-1.76	-2.19
8	NS	NS		
9	NR	NR		
10	560	168	-1.54	-1.18
12	NR	NR		
13	920	400	0.68	0.26
14	NR	NR		
15*	125	15	-4.23	-5.23
16*	1350	405	3.33	1.27
17	810	365	0.00	0.00
18	590	177	-1.36	-1.00
19*	388	116.4	-2.60	-2.42
20	1030	324	1.36	0.63
21	NR	NR		
22*	1360	385	3.40	1.35
23	910	270	0.62	0.33
24*	1400	700	3.64	0.83
25	908	300	0.60	0.30
26	990	200	1.11	0.75
27	NT	NT		
28	900	251	0.56	0.32
29	693.3	208	-0.72	-0.48

* Outlier, see Section 4.2

Statistics

Assigned Value	810	130
Spike Value	Not Spiked	
Robust Average	850	190
Median	900	170
Mean	840	
N	21	
Max	1400	
Min	125	
Robust SD	350	
Robust CV	42%	
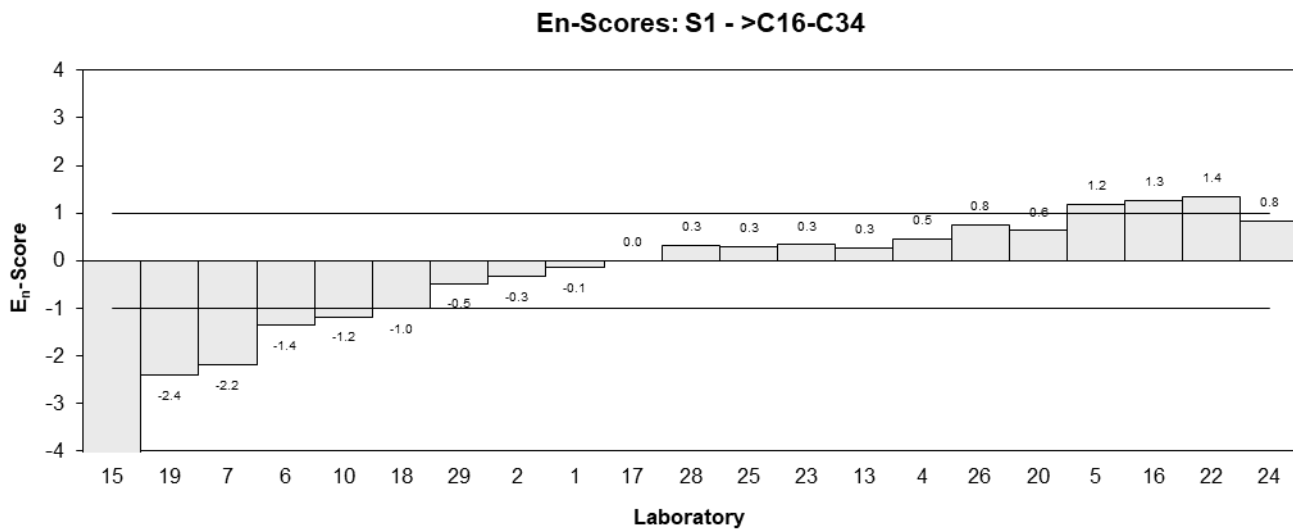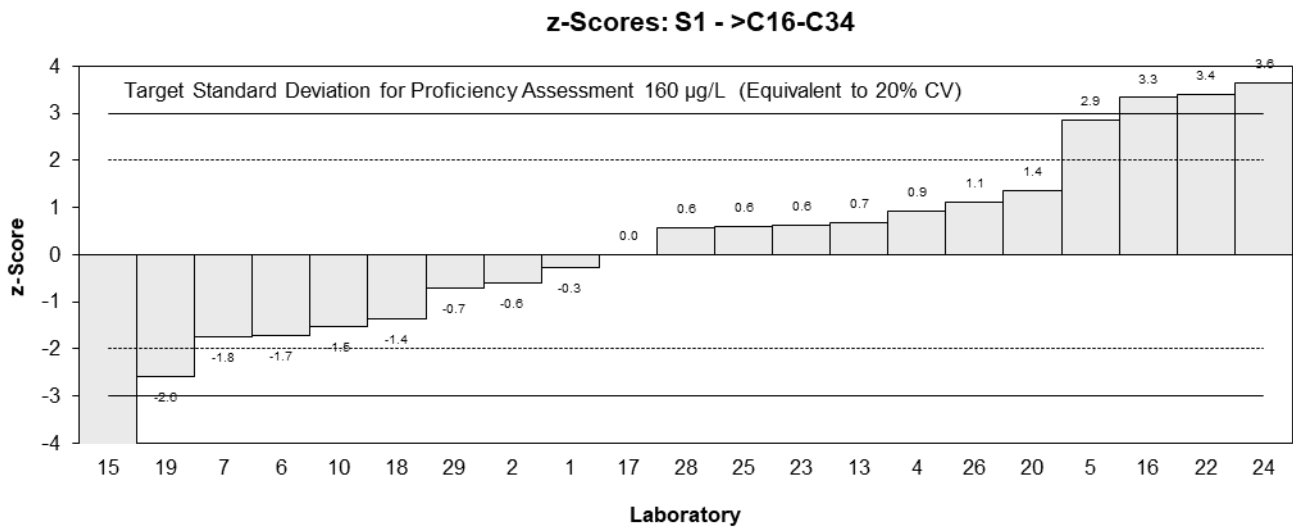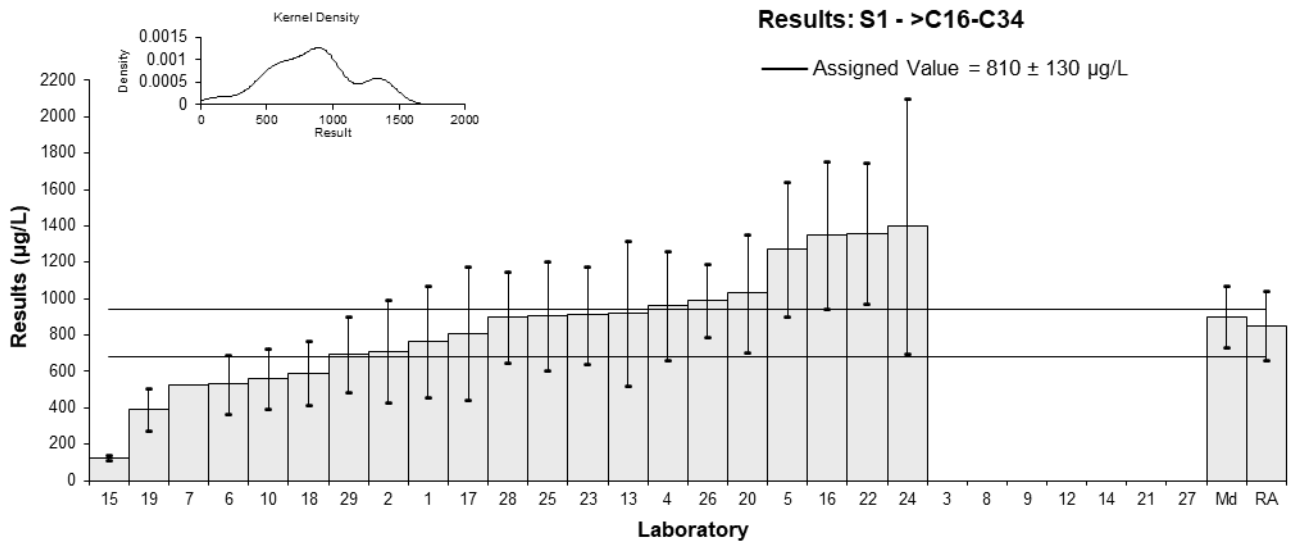
Figure 3

Table 9

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	>C34-C40
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty
1	<100	NR
2	<500	NR
3	NR	NR
4	<100	NR
5	<100	100
6	NR	NR
7	<0.1	NR
8	NS	NS
9	NR	NR
10	< 100	NR
12	NR	NR
13	<100	NR
14	NR	NR
15	<50	15
16	<50	NR
17	<100	66
18	< 100	NR
19	<100	NR
20	<100	NR
21	NR	NR
22	<100	NR
23	<100	NR
24	< 100	NR
25	<100	NR
26	<100	NR
27	NT	NT
28	<100	NR
29	< 100	NR

Statistics

Insufficient data to calculate statistics.

Table 10 Non-NEPM Hydrocarbon Ranges Reported by Participants for Sample S1

Lab. Code	Range	Result (μg/L)	Uncertainty (μg/L)
3	C7-C9	<100	67
	C10-C14	330	140
	C15-C36	780	240
9	>C10-C14	<200	NR
	>C15-C36	<300	NR
12	C7-C9	<100	NR
	C10-C14	320	96
	C15-C36	850	260
21	C10-C14	400	116
	C15-C36	560	151
25	>C9-C16	NR	NR
	C10-C14	NR	NR
	C15-C28	110	40

Table 11

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1494	597.6	-0.16	-0.05
2	1525	NR	-0.02	-0.02
3	1120	280	-1.79	-1.04
4	2060	NR	2.00▼	
5*	2690	619	2.00▼	
6	1100	330	-1.87	-0.99
7	1088	NR	-1.93	-1.58
8	NS	NS		
9	<500	NR		
10	1200	360	-1.44	-0.72
12	1200	360	-1.44	-0.72
13	1680	NR	0.65	0.54
14	NR	NR		
15*	460	80	-4.66	-3.67
16*	2950	885	2.00▼	
17	1730	1145	0.87	0.17
18	1244	373	-1.25	-0.61
19*	819	NR	-3.10	-2.54
20	2290	848	2.00▼	
21	960	288	-2.48	-1.42
22*	2840	NR	2.00▼	
23	1980	590	1.96	0.69
24*	2700	1350	2.00▼	
25	NR	NR		
26	2090	420	2.00▼	
27	NT	NT		
28	1790	499	1.13	0.45
29	1461.6	438.5	-0.30	-0.13

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

Statistics

Assigned Value	1530	280	Laboratories 2, 4, 13 and 19 did not report a TRH value. The study coordinator summed the individual hydrocarbon ranges, and no estimate of uncertainty of the TRH result was made.
Spike Value	3200	160	
Robust Average	1670	390	
Max Acceptable Result	4160		
Median	1530	340	
Mean	1670		
N	23		
Max	2950		
Min	460		
Robust SD	750		
Robust CV	45%		
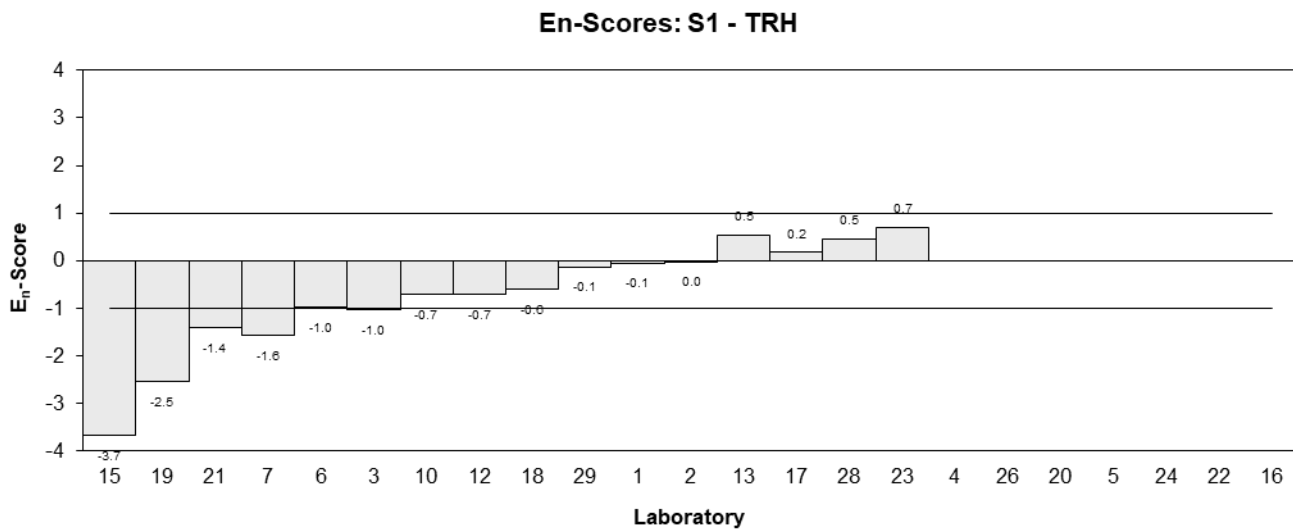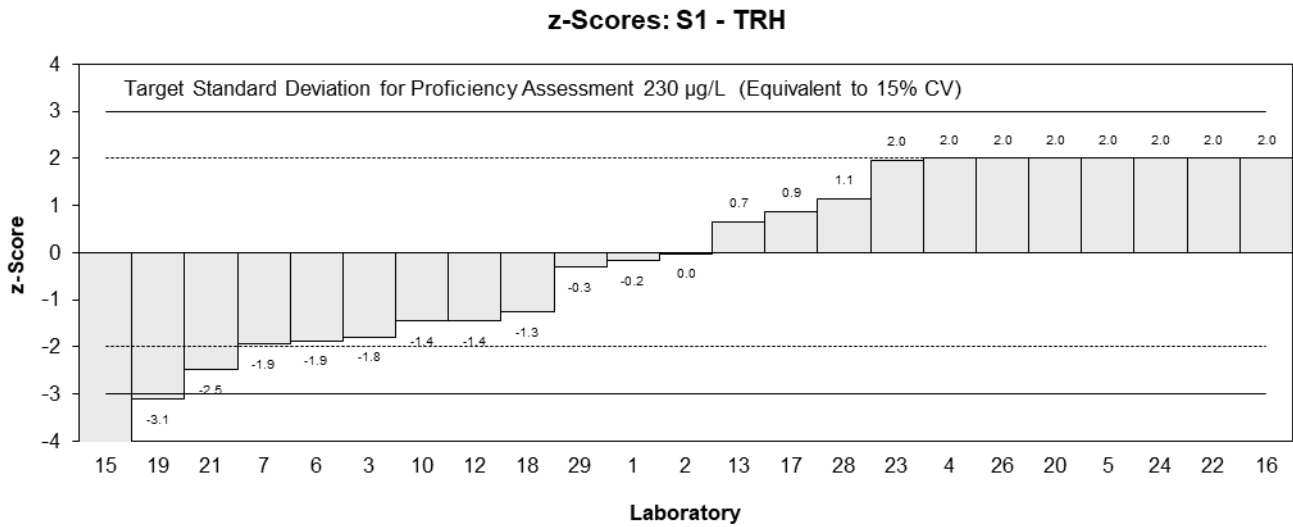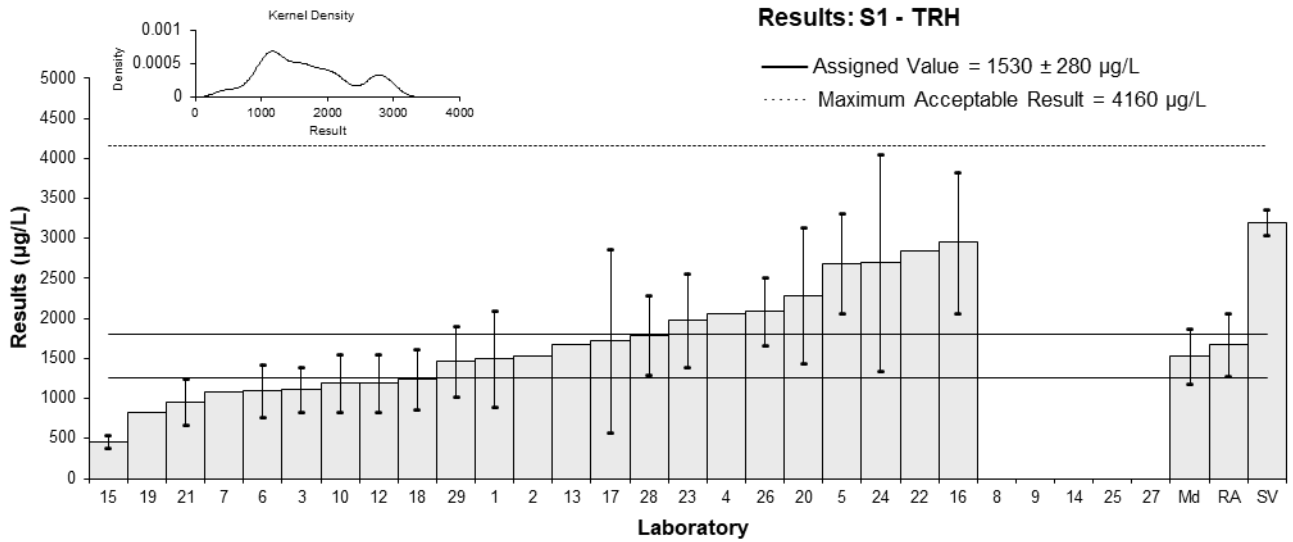
Figure 4

Table 12

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	C6-C10
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty
1	1011	202.2
2	1322	529
3	NT	NT
4	1100	300
5	851.6	119
6	1100	330
7	NT	NT
8	NS	NS
9	NT	NT
10	1100	330
12	NT	NT
13	990	300
14	NT	NT
15	NT	NT
16	1217	425
17	1040	231
18	1109	333
19	773	159
20	870	200
21	NT	NT
22	870	171
23	1150	345
24	NT	NT
25	980	300
26	640	190
27	NT	NT
28	990	191
29	1090	286

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Robust Average	1020	90
Median	1030	70
Mean	1010	
N	18	
Max	1322	
Min	640	
Robust SD	160	
Robust CV	16%	
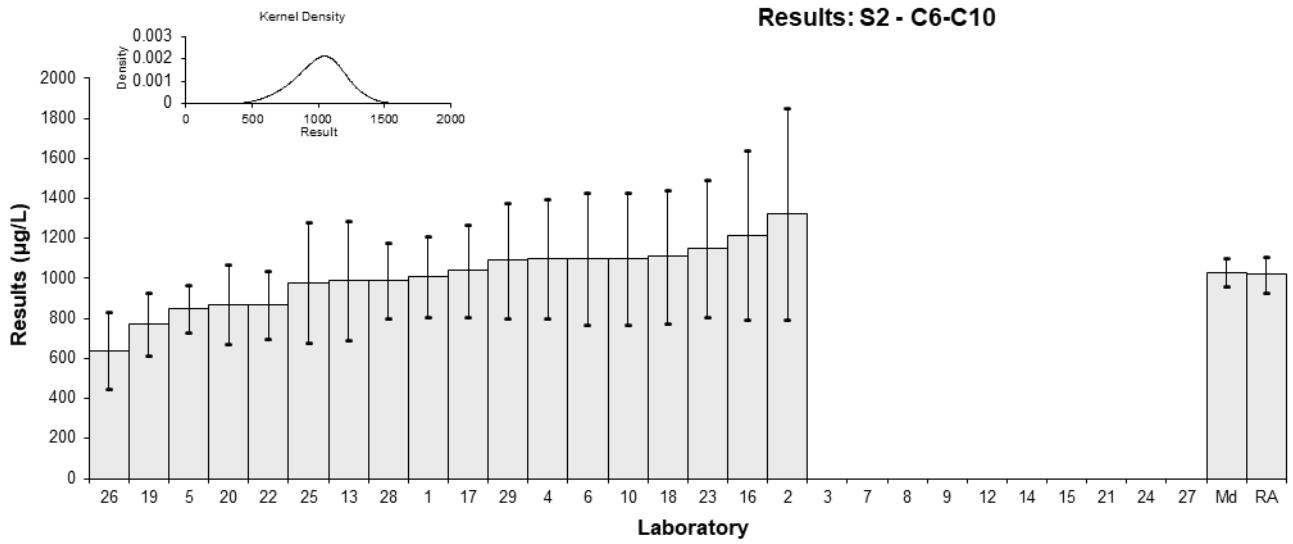
Figure 5

Table 13

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	67.651	13.53	0.24	0.17
2	60.4	24.2	-0.50	-0.20
3	61	13	-0.44	-0.32
4	61	20	-0.44	-0.21
5	60.2	8	-0.52	-0.60
6	58	12	-0.75	-0.59
7	61.1	NR	-0.43	-1.56
8	NS	NS		
9	54.5	16.35	-1.10	-0.65
10	65.1	19.5	-0.02	-0.01
12	63.0	19	-0.23	-0.12
13	67	20	0.17	0.08
14	72	7	0.68	0.89
15	NT	NT		
16	62	12	-0.34	-0.27
17	67	13.2	0.17	0.13
18	77	23	1.19	0.51
19	66.9	20	0.16	0.08
20	61	13.7	-0.44	-0.31
21	63.2	15.2	-0.21	-0.14
22	70	11	0.48	0.41
23	92	28	2.73	0.95
24	63	16	-0.23	-0.14
25	66	20	0.07	0.03
26	74	22	0.89	0.39
27	69.4	13.9	0.42	0.29
28	68	10	0.28	0.26
29	66.3	17.6	0.10	0.06

Statistics

Assigned Value	65.3	2.7
Spike Value	69.2	3.5
Robust Average	65.3	2.7
Median	65.6	3.0
Mean	66.0	
N	26	
Max	92	
Min	54.5	
Robust SD	5.4	
Robust CV	8.3%	

Results: S2 - Benzene

Assigned Value = 65.3 ± 2.7 µg/L

z-Scores: S2 - Benzene

Target Standard Deviation for Proficiency Assessment 9.8 µg/L (Equivalent to 15% CV)

En-Scores: S2 - Benzene
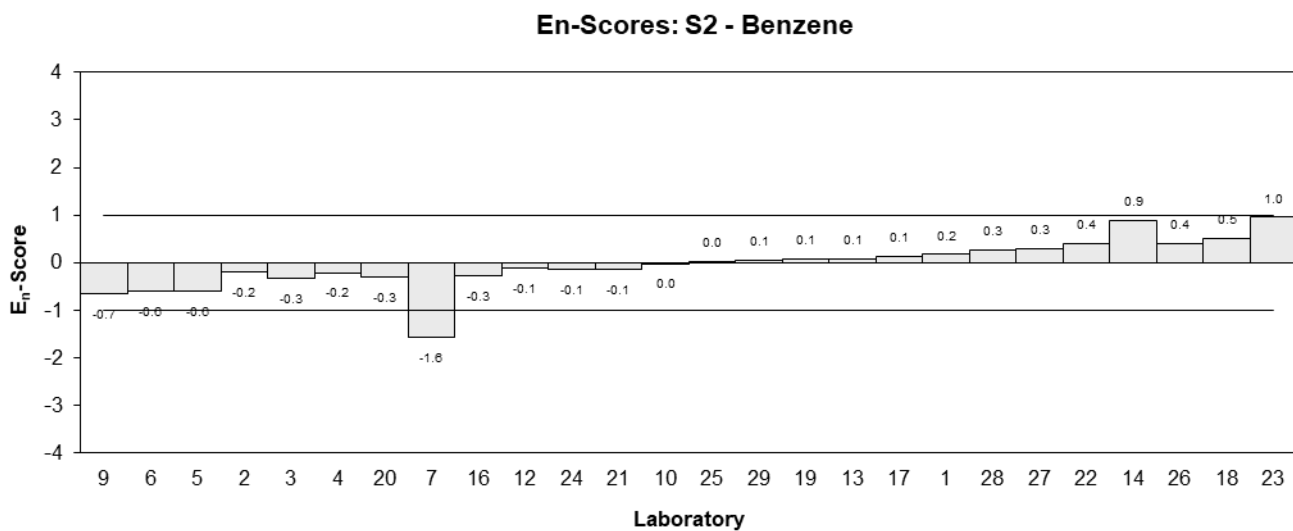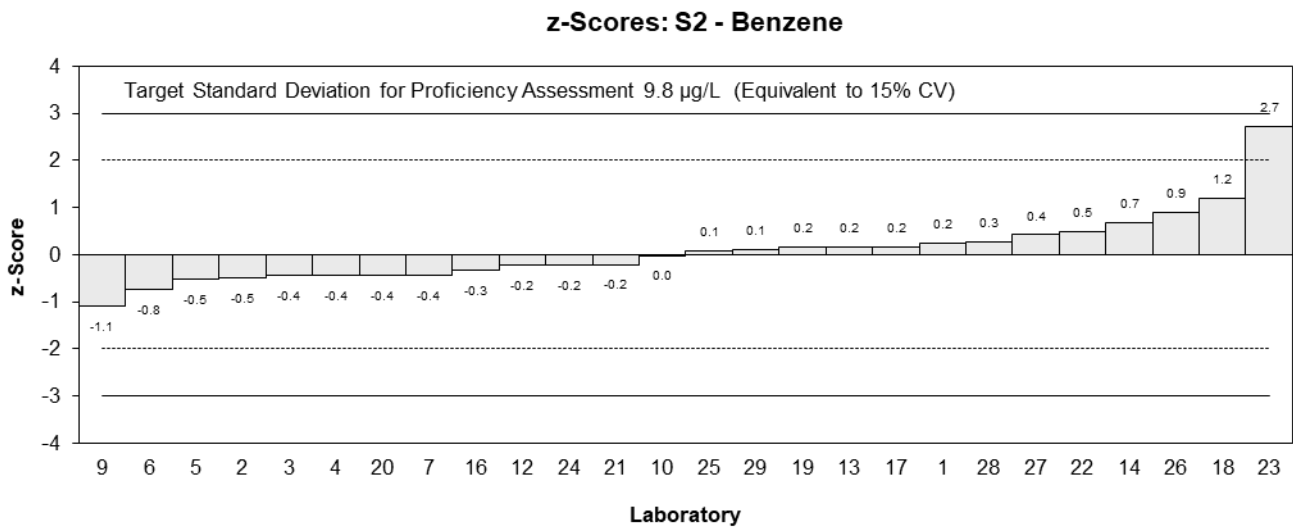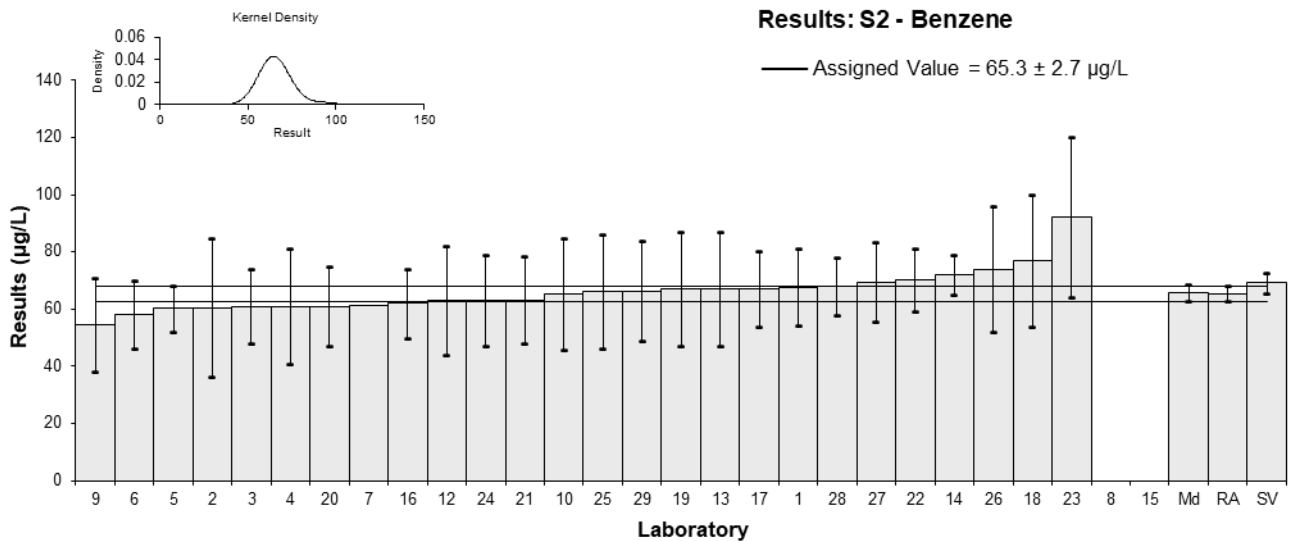
Figure 6

Table 14

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	240.1	48.02	0.38	0.26
2	187.7	75	-1.15	-0.51
3	209	38	-0.53	-0.44
4	210	50	-0.50	-0.33
5	192.1	27	-1.02	-1.13
6	210	42	-0.50	-0.38
7**	26.7	NR	-5.88	-13.35
8	NS	NS		
9	170	51	-1.67	-1.07
10	249	75	0.65	0.29
12	253	91	0.76	0.28
13	220	50	-0.21	-0.13
14	280	21	1.56	2.05
15	NT	NT		
16	275	55	1.41	0.84
17	231	46.6	0.12	0.08
18	295	89	2.00	0.75
19	210	71.4	-0.50	-0.23
20	214	40.9	-0.38	-0.30
21	234.4	46.9	0.22	0.15
22	184	28	-1.26	-1.35
23	220	66	-0.21	-0.10
24	230	58	0.09	0.05
25	240	70	0.38	0.18
26	220	66	-0.21	-0.10
27	258	51.6	0.91	0.58
28	216	33	-0.32	-0.30
29	246	62	0.56	0.30

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	227	15
Spike Value	261	13
Robust Average	227	15
Median	220	15
Mean	228	
N	25	
Max	295	
Min	170	
Robust SD	31	
Robust CV	14%	

Results: S2 - Toluene

Assigned Value = 227 ± 15 µg/L

z-Scores: S2 - Toluene

En-Scores: S2 - Toluene
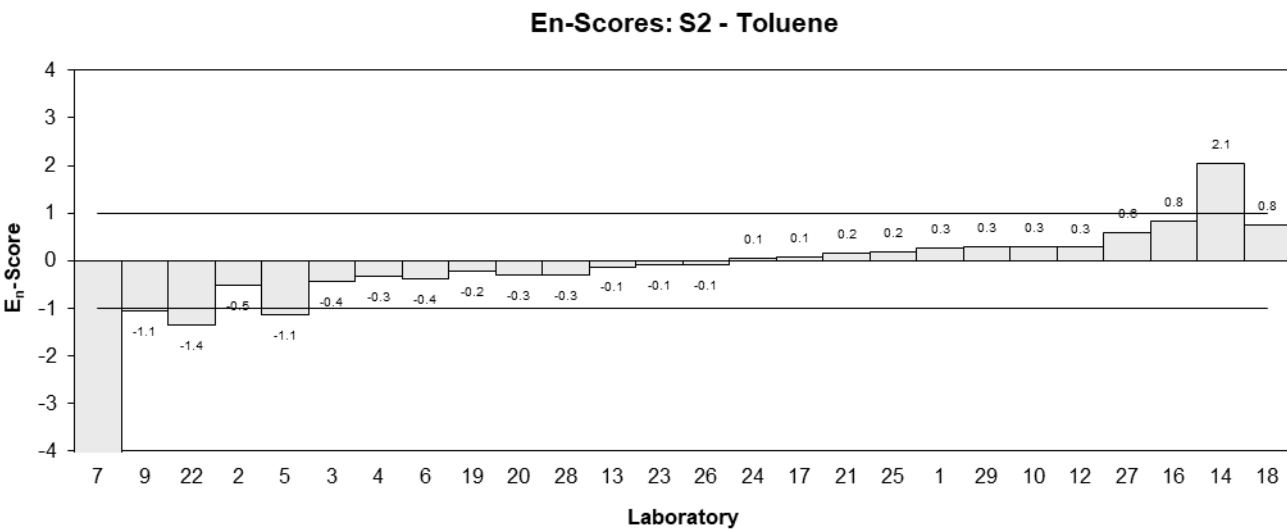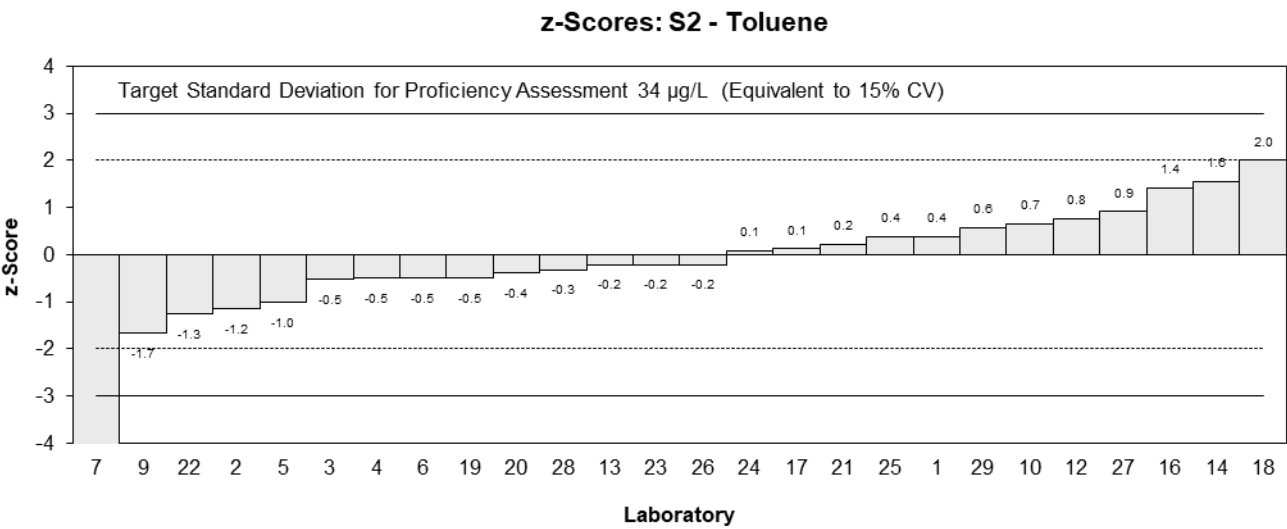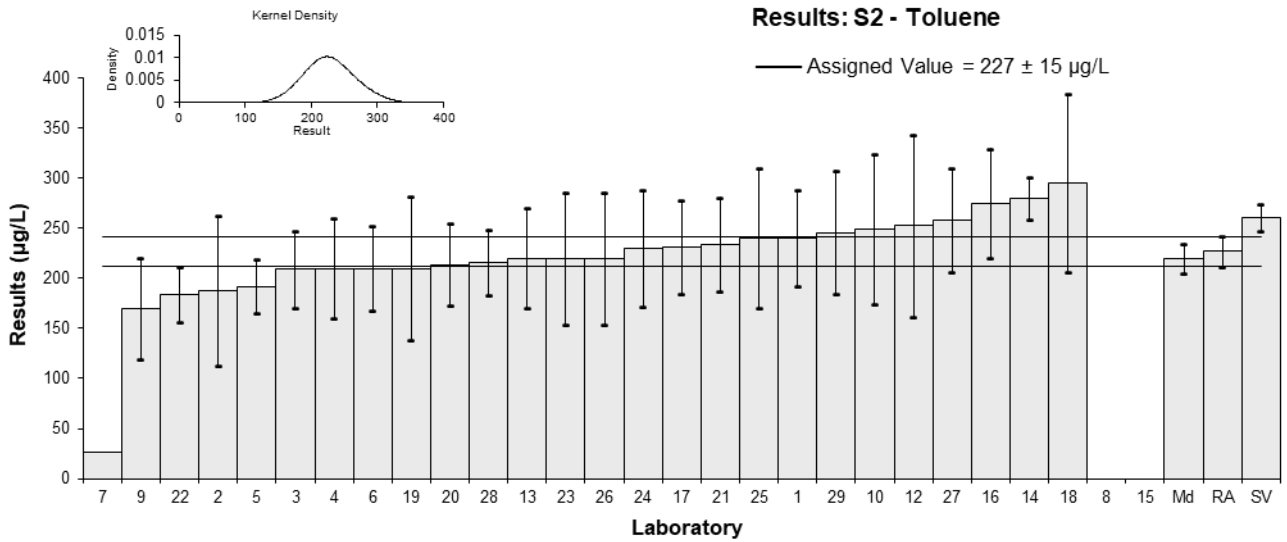
Figure 7

Table 15

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	21.64	4.328	0.07	0.05
2	21.9	8.8	0.16	0.06
3	18.8	3.1	-0.81	-0.79
4	23	7	0.50	0.23
5	19.8	3	-0.50	-0.50
6	21	4	-0.12	-0.10
7*	45.2	NR	7.41	21.64
8	NS	NS		
9	19.5	5.85	-0.59	-0.32
10	19.7	5.9	-0.53	-0.28
12	23.5	9	0.65	0.23
13	21	7	-0.12	-0.06
14	32	3	2.00▼	
15	NT	NT		
16	25	5	1.12	0.70
17	24	4.2	0.81	0.60
18	18	5	-1.06	-0.66
19	20.1	4.02	-0.40	-0.31
20	19	3.8	-0.75	-0.61
21	21.9	5.7	0.16	0.09
22	19	3	-0.75	-0.75
23	22	7	0.19	0.08
24	22	5.5	0.19	0.11
25	23	7	0.50	0.23
26	20	6	-0.44	-0.23
27	22.5	4.5	0.34	0.24
28	23	3	0.50	0.50
29	21.1	5.8	-0.09	-0.05

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

Statistics

Assigned Value	21.4	1.1
Spike Value	29.0	1.5
Robust Average	21.6	1.1
Max Acceptable Result	37.7	
Median	21.8	1.2
Mean	22.6	
N	26	
Max	45.2	
Min	18	
Robust SD	2.3	
Robust CV	11%	

Results: S2 - Ethylbenzene

—— Assigned Value = 21.4 ± 1.1 µg/L
······ Maximum Acceptable Result = 37.7 µg/L

z-Scores: S2 - Ethylbenzene

En-Scores: S2 - Ethylbenzene
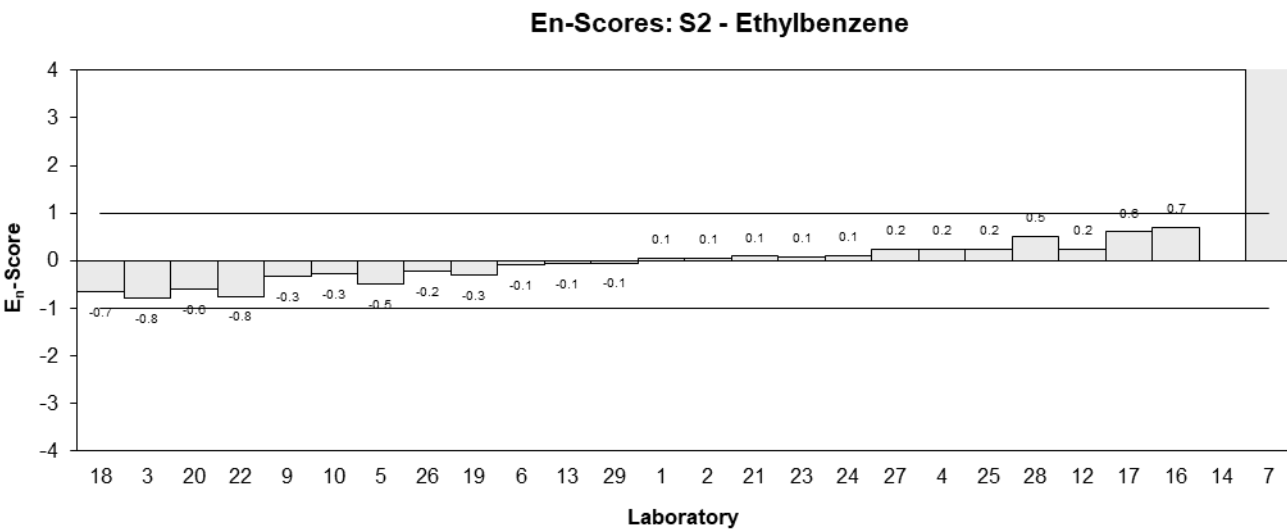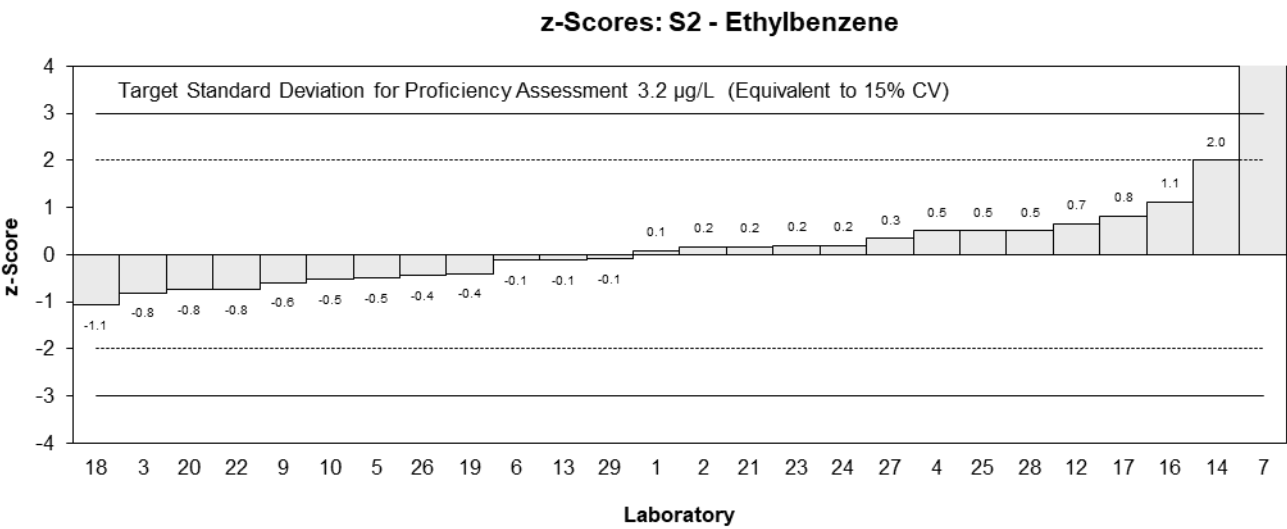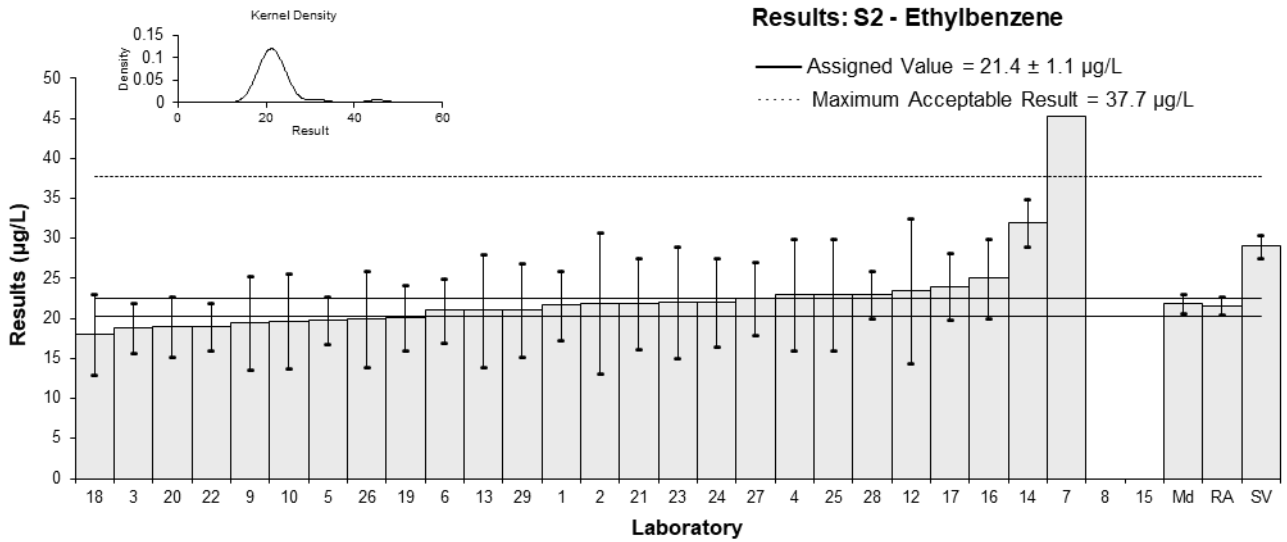
Figure 8

Table 16

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	95.1	19.02	0.09	0.06
2	97.4	39	0.25	0.09
3	83	16.4	-0.77	-0.62
4	100	30	0.43	0.20
5	88	11	-0.42	-0.47
6	80	16	-0.99	-0.81
7	139.8	NR	2.00▼	
8	NS	NS		
9	82.5	24.75	-0.81	-0.45
10	88	26	-0.42	-0.22
12	76.1	26	-1.26	-0.67
13	98	30	0.29	0.13
14	77	4	-1.20	-2.34
15	NT	NT		
16	110	22	1.14	0.71
17	109	19.9	1.07	0.73
18	112	34	1.29	0.52
19	93.2	14	-0.05	-0.05
20	83	18	-0.77	-0.57
21	88.2	20.3	-0.40	-0.27
22	89	NR	-0.35	-0.82
23	110	33	1.14	0.48
24	95	24	0.08	0.04
25	99	30	0.36	0.17
26	94	28	0.01	0.00
27	85.4	17.1	-0.60	-0.47
28	101	25	0.50	0.28
29	95.6	23.9	0.12	0.07

▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	93.9	6.0
Spike Value	129	6
Robust Average	93.9	6.0
Max Acceptable Result	168	
Median	94.5	4.7
Mean	95.0	
N	26	
Max	139.8	
Min	76.1	
Robust SD	12	
Robust CV	13%	
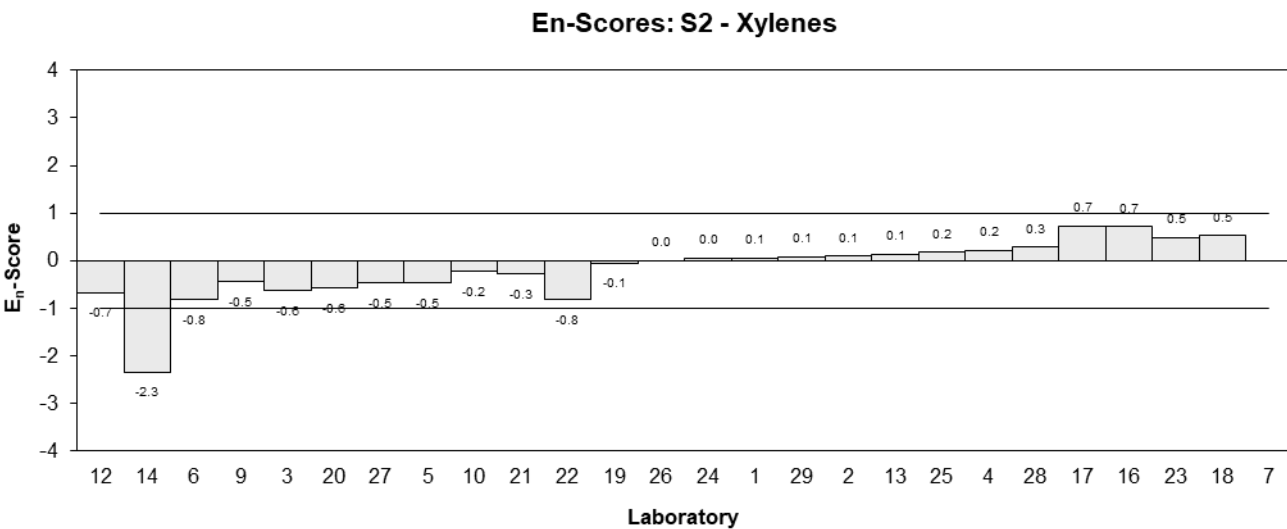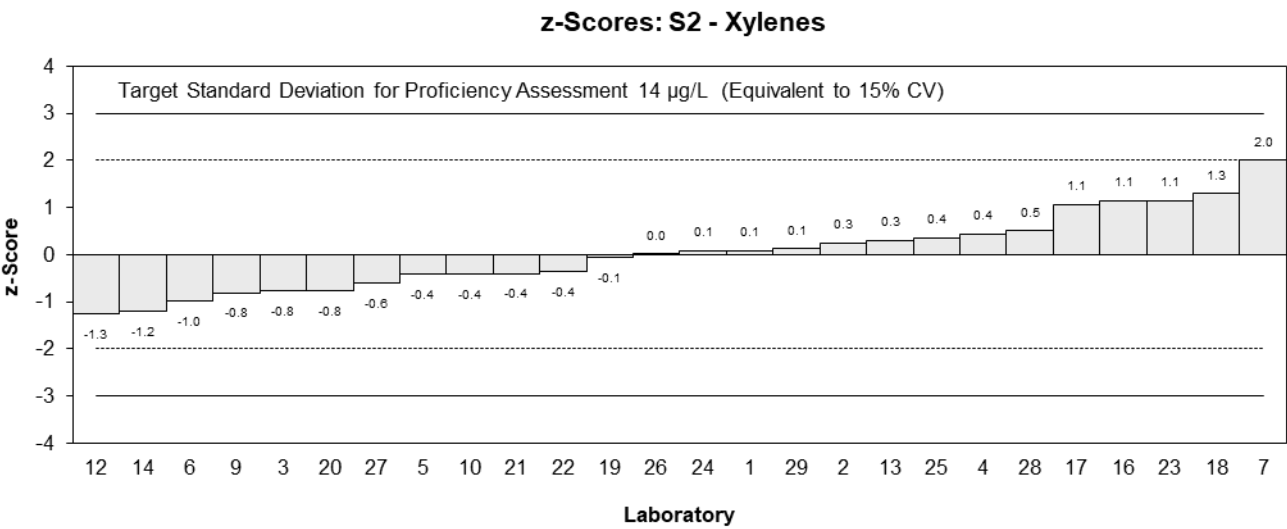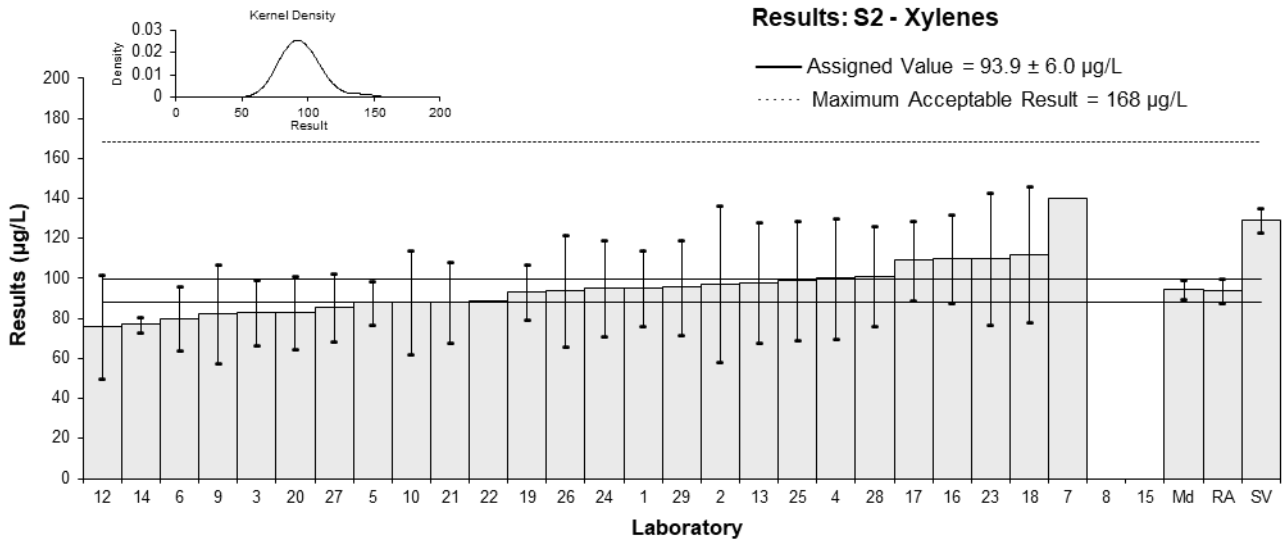
Figure 9

Table 17

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	424	84.8	0.31	0.22
2	367.4	147	-0.62	-0.25
3	371.8	70.5	-0.55	-0.45
4	390	100	-0.25	-0.15
5	360.1	50	-0.74	-0.83
6	360	72	-0.74	-0.60
7	272.8	NR	-2.18	-6.61
8	NS	NS		
9	326.5	97.95	-1.29	-0.79
10	421.8	126.4	0.28	0.13
12	416	158	0.18	0.07
13	410	100	0.08	0.05
14	461	22	0.92	1.88
15	NT	NT		
16	472	94	1.10	0.70
17	431	86.2	0.43	0.29
18	502	151	1.60	0.64
19	390.2	78	-0.24	-0.18
20	377	89	-0.46	-0.31
21	408	106	0.05	0.03
22	362	NR	-0.71	-2.15
23	444	133	0.64	0.29
24	410	100	0.08	0.05
25	430	100	0.41	0.25
26	410	120	0.08	0.04
27	435	87	0.49	0.34
28	408	161	0.05	0.02
29	429	107	0.40	0.22

Statistics

Assigned Value	405	20
Spike Value	489	24
Robust Average	405	20
Median	410	17
Mean	403	
N	26	
Max	502	
Min	272.8	
Robust SD	41	
Robust CV	10%	
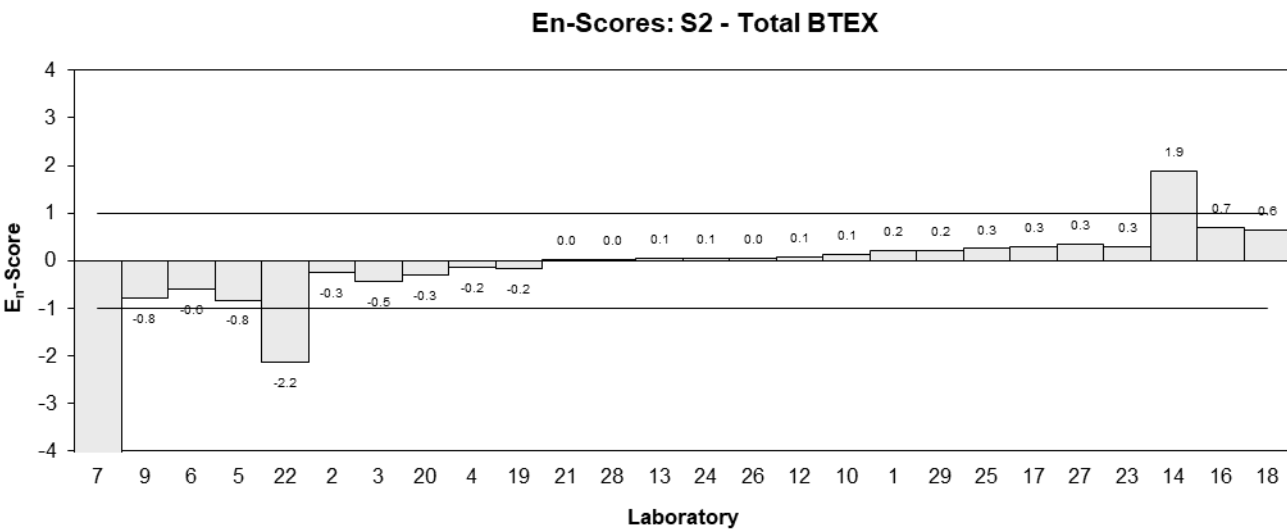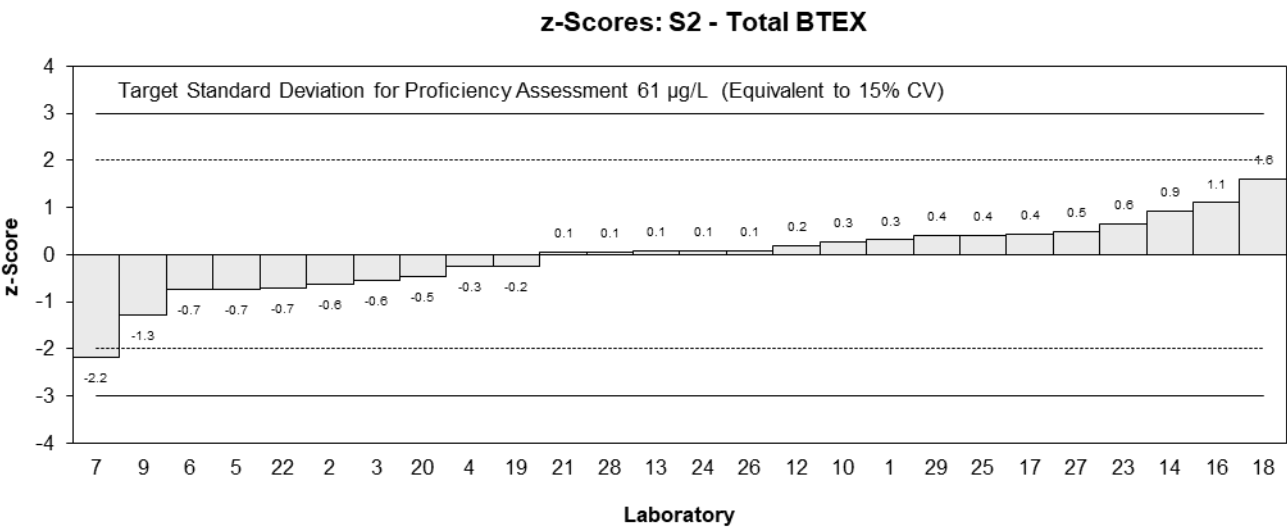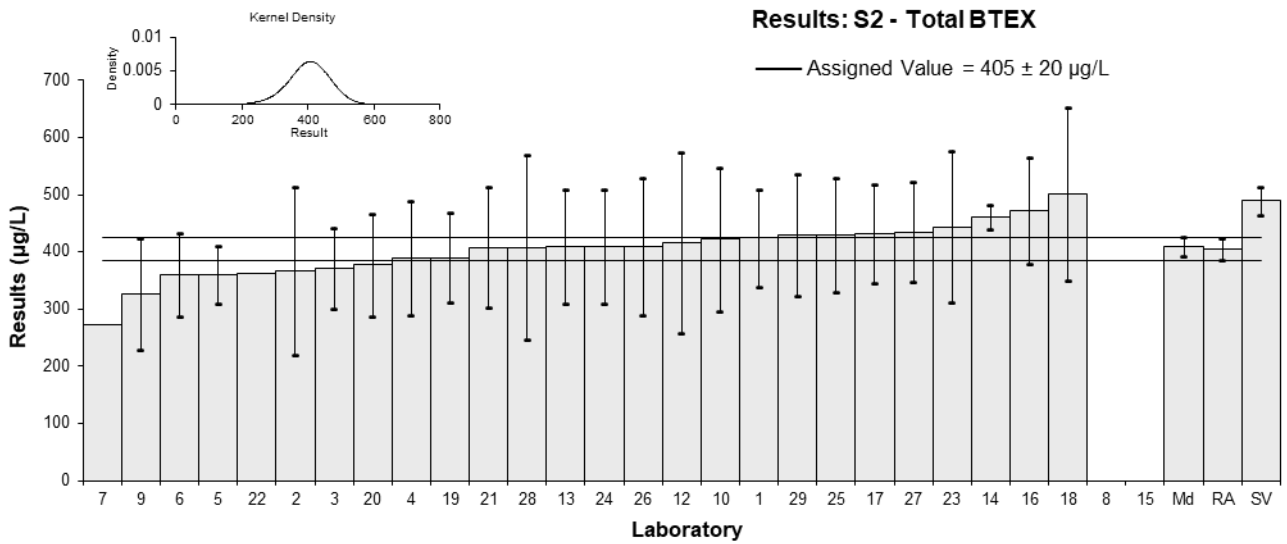
Figure 10

Table 18

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	4.0082	1.403
2	2.78	1.1
3	3.8	1.9
4	2.7	0.6
5	2.9	0.9
6	2.8	0.84
7	2.6	NR
8	2.1	0.4
9	1.9	0.57
10	3.81	1.14
12	3.96	1.4
13	3.8	1
14	NS	NS
15	3.9	0.5
16	1	0.3
17	2.6	0.97
18	4.12	1.24
19	3	0.75
20	2.9	0.76
21	3.6	0.9
22	3.1	0.66
23	2.34	0.7
24	2.5	1.3
25	3.2	1
26	3.5	0.7
27	NS	NS
28	2.2	0.3
29	3.501	1.23

Statistics

Assigned Value	Not Set	
Spike Value	8.01	0.40
Robust Average	3.06	0.38
Median	2.95	0.42
Mean	3.02	
N	26	
Max	4.12	
Min	1	
Robust SD	0.78	
Robust CV	26%	
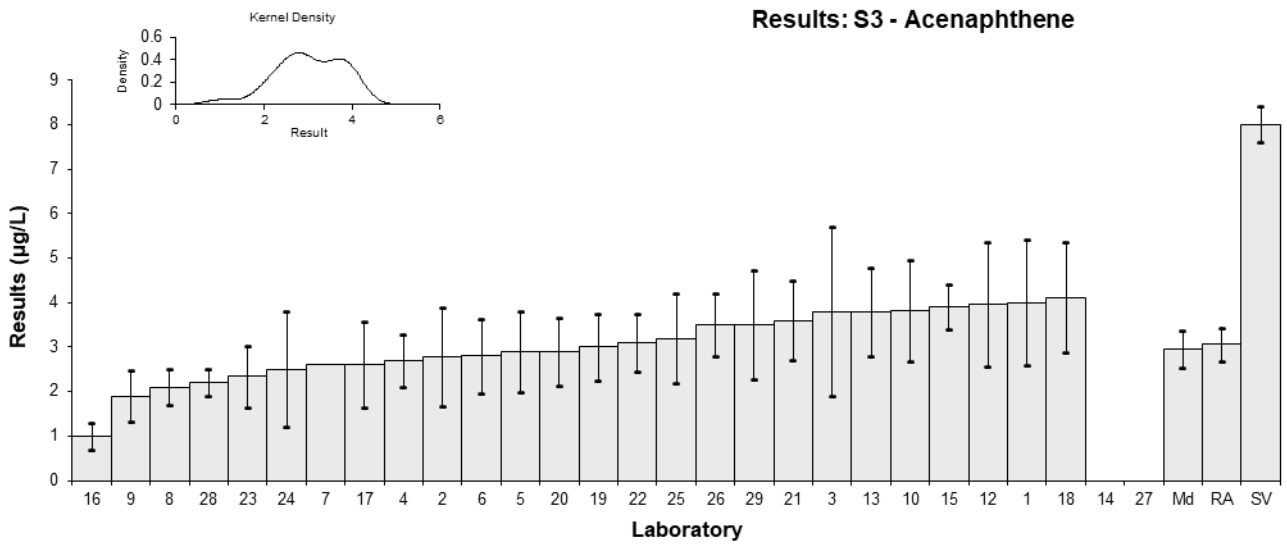
Figure 11

Table 19

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	1.692	0.6768
2	0.68	0.3
3	1.63	0.88
4	1.2	0.4
5	1.3	0.4
6	1.1	0.33
7	0.9	NR
8	0.8	0.2
9	0.915	0.2745
10	1.49	0.45
12	1.80	0.7
13	1.7	0.5
14	NS	NS
15	1.1	0.2
16	<1	NR
17	1.3	0.52
18	1.83	0.55
19	1.27	0.32
20	1.3	0.35
21	2.5	0.7
22	1.3	0.25
23	<1	NR
24	1.3	0.65
25	1.5	0.5
26	1.5	0.3
27	NS	NS
28	1.1	0.3
29	1.424	0.43

Statistics

Assigned Value	Not Set	
Spike Value	2.99	0.15
Robust Average	1.34	0.18
Median	1.30	0.15
Mean	1.36	
N	24	
Max	2.5	
Min	0.68	
Robust SD	0.36	
Robust CV	27%	
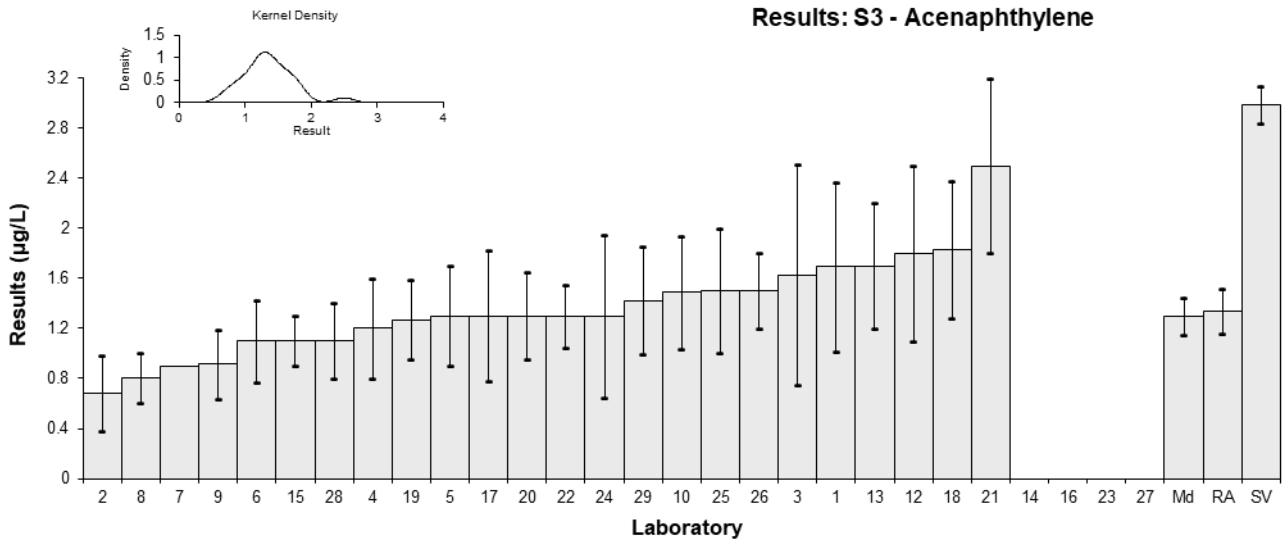
Figure 12

Table 20

Sample Details

Sample No.	S3
Matrix	River Water
Analyte	Benz[a]anthracene
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	2.082	0.8328	-3.96	-3.24
2	5.2	2.1	0.09	0.03
3	4.9	1.6	-0.30	-0.14
4	5.1	2	-0.04	-0.01
5	6.4	2.6	1.65	0.48
6*	2	0.6	-4.07	-4.21
7	3.8	NR	-1.73	-3.02
8	5.9	1.3	1.00	0.56
9*	1.5	0.45	-4.72	-5.77
10	4.51	1.35	-0.81	-0.44
12	4.64	1.6	-0.64	-0.30
13	4.7	1	-0.56	-0.39
14	NS	NS		
15	<1	NR		
16	4	1.2	-1.47	-0.88
17	4.6	1.71	-0.69	-0.30
18	4.68	1.40	-0.58	-0.31
19	5.94	1.5	1.05	0.52
20	5.4	1.31	0.35	0.20
21*	7.6	1.7	2.00▼	
22	5.3	1.1	0.22	0.14
23	4.95	1.49	-0.23	-0.12
24	6.1	3.1	1.26	0.31
25	5.8	2	0.87	0.33
26	6.4	1.3	1.65	0.93
27	NS	NS		
28	4.8	1.3	-0.43	-0.24
29	4.682	1.4	-0.58	-0.31

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

Statistics

Assigned Value	5.13	0.44
Spike Value	6.51	0.33
Robust Average	4.98	0.54
Max Acceptable Result	8.46	
Median	4.90	0.37
Mean	4.84	
N	25	
Max	7.6	
Min	1.5	
Robust SD	1.1	
Robust CV	22%	

Results: S3 - Benz[a]anthracene

Assigned Value = 5.13 ± 0.44 µg/L
Maximum Acceptable Result = 8.46 µg/L

z-Scores: S3 - Benz[a]anthracene

En-Scores: S3 - Benz[a]anthracene
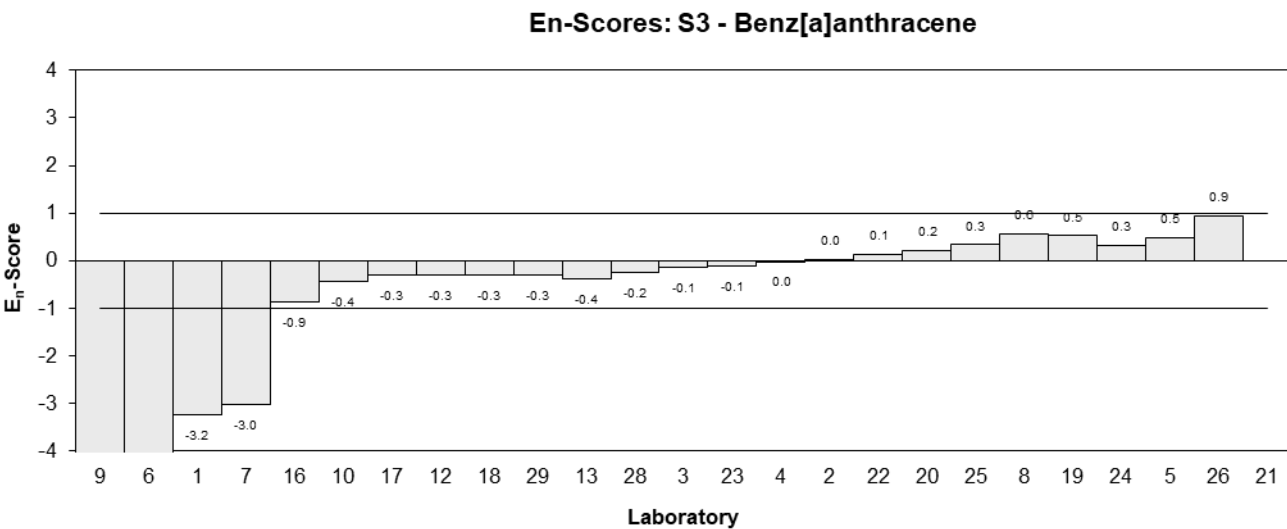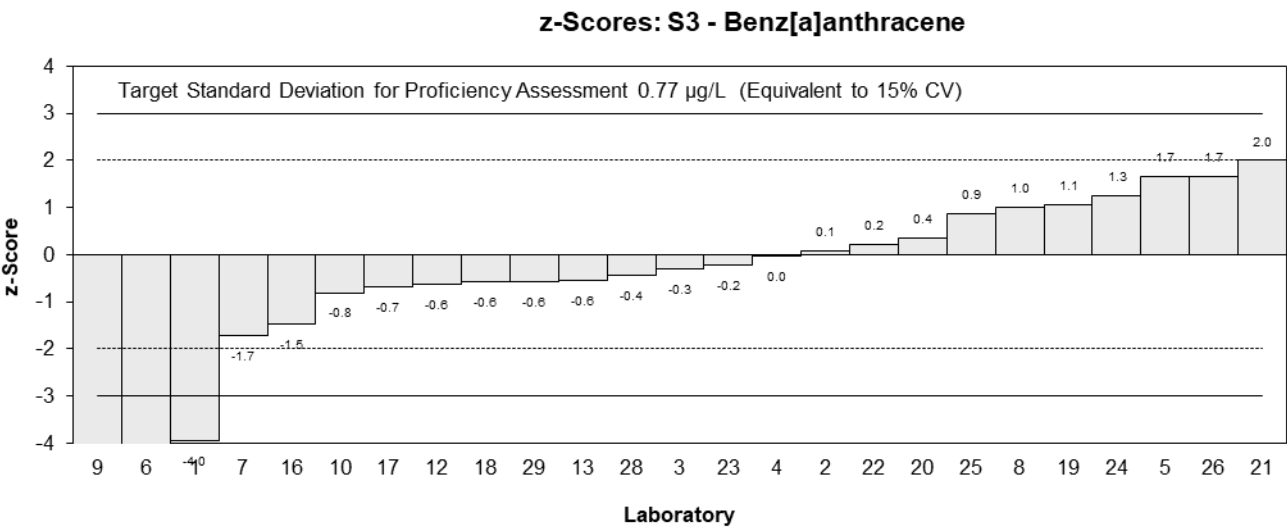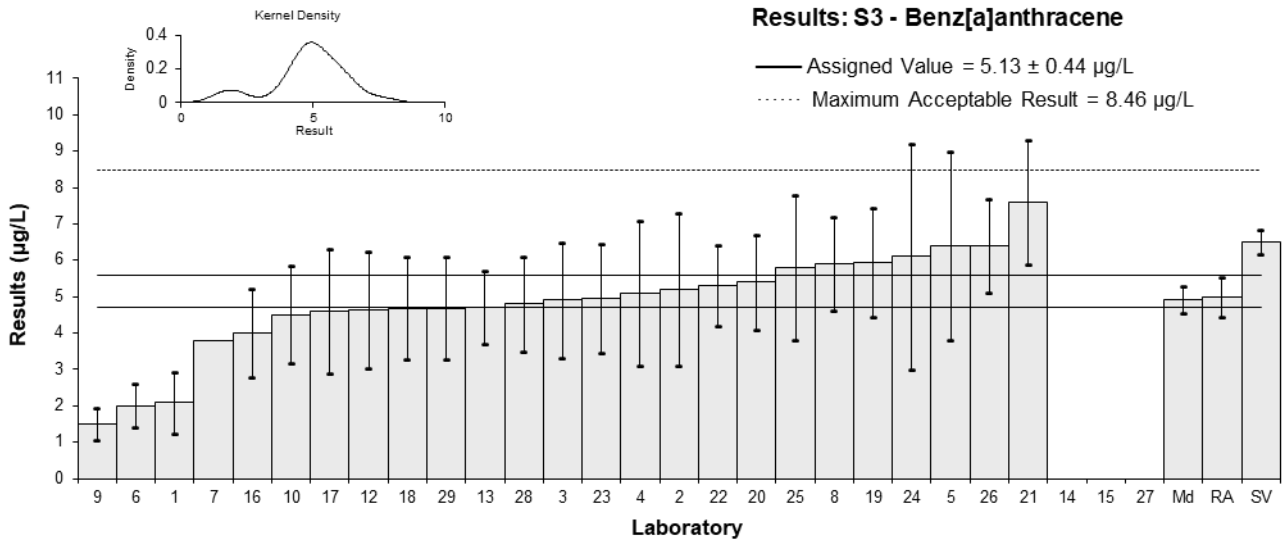
Figure 13

Table 21

Sample Details

Sample No.	S3
Matrix	River Water
Analyte	Benzo[a]pyrene
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.316	0.9264	0.17	0.06
2	2.41	0.96	0.44	0.15
3	1.97	0.95	-0.86	-0.30
4	2.3	0.6	0.12	0.06
5	2.3	1.1	0.12	0.04
6*	0.99	0.3	-3.75	-3.79
7*	0.9	NR	-4.01	-9.07
8	2.8	0.9	1.59	0.59
9**	0.31	0.093	-5.75	-11.05
10	2.04	0.61	-0.65	-0.35
12	2.00	0.6	-0.77	-0.42
13	2.0	0.6	-0.77	-0.42
14	NS	NS		
15	2.2	0.4	-0.18	-0.14
16	2	0.6	-0.77	-0.42
17	2.1	0.8	-0.47	-0.20
18	2.07	0.62	-0.56	-0.30
19	2.63	0.6	1.09	0.60
20	2.4	0.57	0.41	0.24
21	2.8	0.9	1.59	0.59
22	2.6	0.54	1.00	0.61
23	2	0.6	-0.77	-0.42
24	2.5	1.3	0.71	0.18
25	2.3	1	0.12	0.04
26	2.5	0.5	0.71	0.46
27	NS	NS		
28	2.1	0.4	-0.47	-0.37
29	1.896	0.57	-1.07	-0.62

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.26	0.15
Spike Value	3.57	0.18
Robust Average	2.22	0.16
Median	2.20	0.15
Mean	2.16	
N	25	
Max	2.8	
Min	0.9	
Robust SD	0.32	
Robust CV	15%	

Results: S3 - Benzo[a]pyrene

Assigned Value = 2.26 ± 0.15 µg/L

z-Scores: S3 - Benzo[a]pyrene

En-Scores: S3 - Benzo[a]pyrene
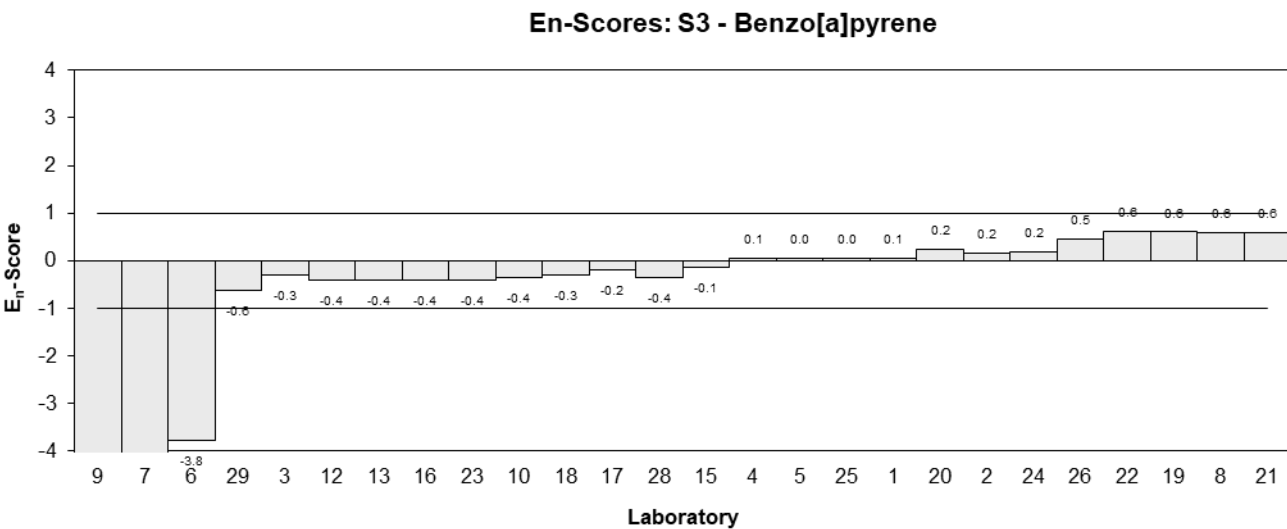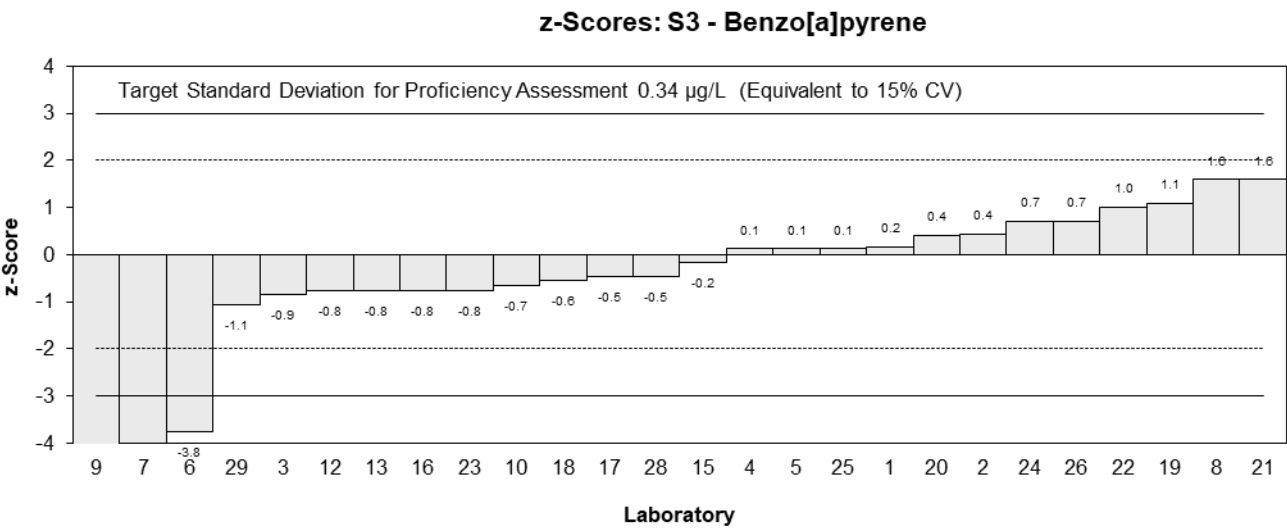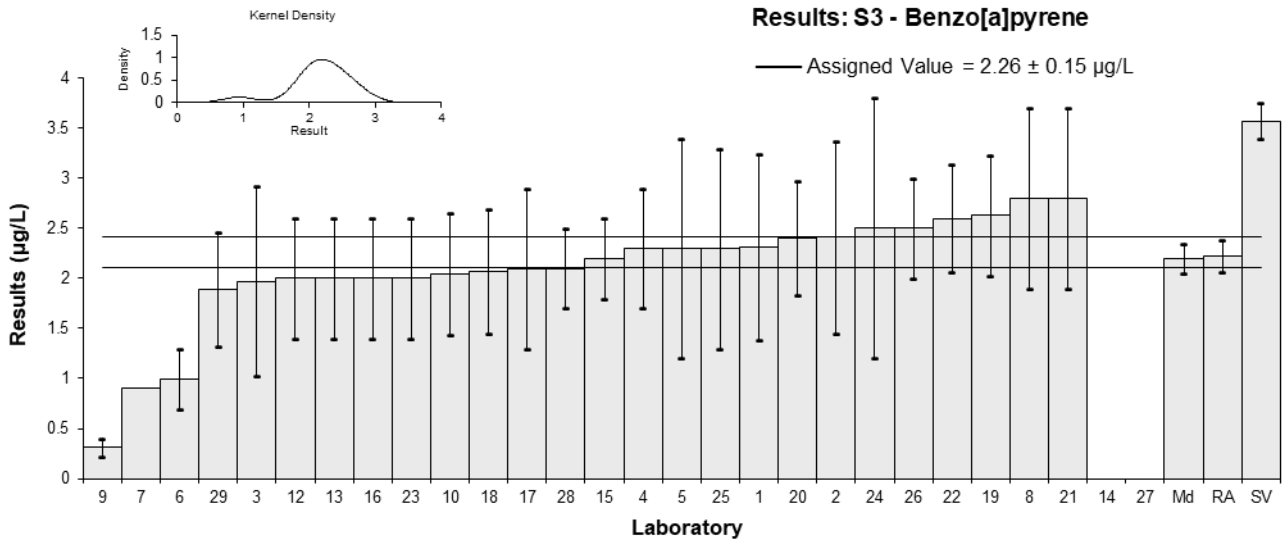
Figure 14

Table 22

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.083	0.7291	1.22	0.44
2	1.65	0.7	-0.42	-0.15
3	2.12	0.94	1.36	0.38
4	1.5	0.5	-0.98	-0.50
5	1.8	0.5	0.15	0.08
6	1.6	0.47	-0.61	-0.33
7	1.8	NR	0.15	0.29
8	1.6	0.3	-0.61	-0.48
9	1.1	0.33	-2.50	-1.84
10	1.97	0.59	0.80	0.35
12	1.83	0.7	0.27	0.10
13	2.0	0.6	0.91	0.39
14	NS	NS		
15	2	0.3	0.91	0.72
16	<1	NR		
17	1.4	0.55	-1.36	-0.63
18	2.06	0.62	1.14	0.47
19	1.79	0.45	0.11	0.06
20	1.6	0.4	-0.61	-0.38
21	2.2	0.6	1.67	0.71
22	1.7	0.37	-0.23	-0.15
23	1.47	0.44	-1.10	-0.63
24	1.6	0.8	-0.61	-0.20
25	1.8	0.6	0.15	0.06
26	1.9	0.37	0.53	0.35
27	NS	NS		
28	1.4	0.2	-1.36	-1.47
29	1.888	0.66	0.48	0.19

Statistics

Assigned Value	1.76	0.14
Spike Value	3.14	0.16
Robust Average	1.76	0.14
Median	1.80	0.15
Mean	1.75	
N	25	
Max	2.2	
Min	1.1	
Robust SD	0.27	
Robust CV	16%	

Results: S3 - Fluorene

Assigned Value = 1.76 ± 0.14 µg/L

z-Scores: S3 - Fluorene

Target Standard Deviation for Proficiency Assessment 0.26 µg/L (Equivalent to 15% CV)

En-Scores: S3 - Fluorene
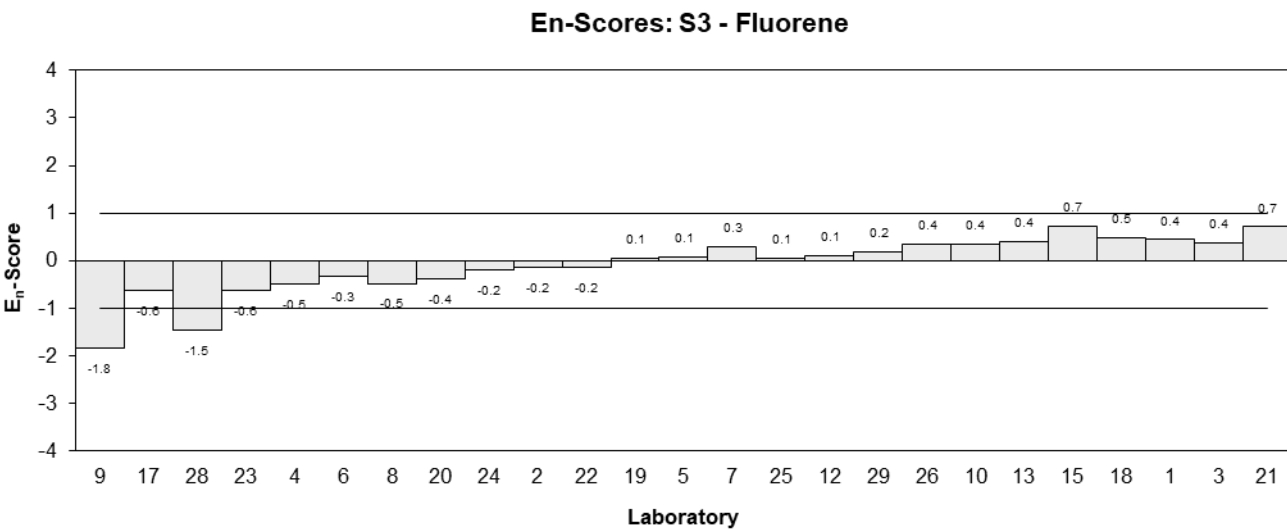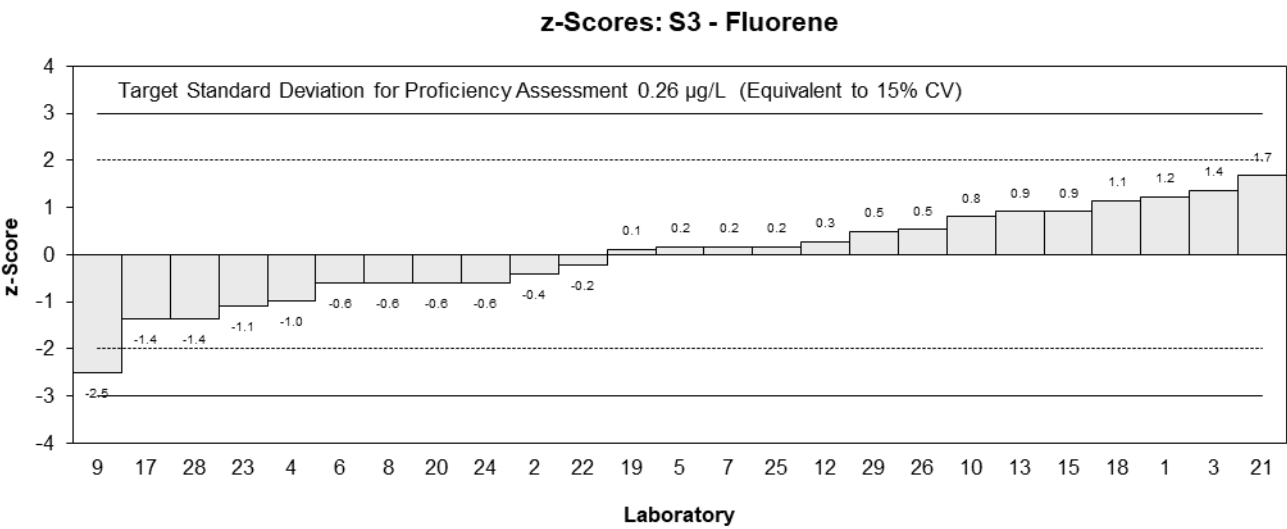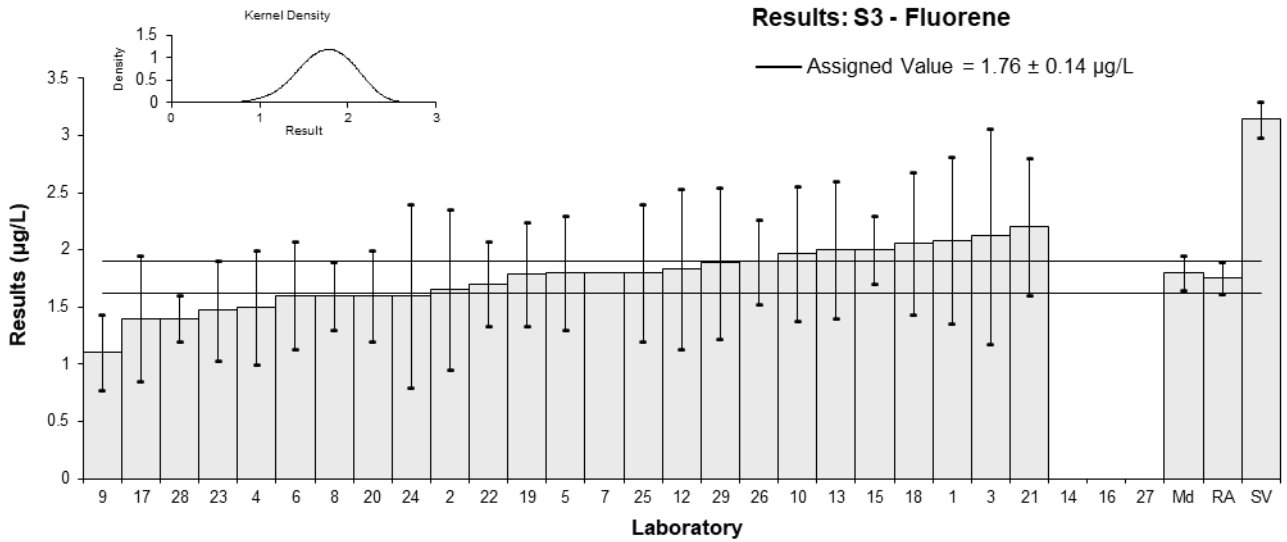
Figure 15

Table 23

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.604	0.5614	1.43	0.50
2	1.24	0.5	-0.40	-0.16
3	1.43	0.44	0.56	0.24
4	1.4	0.5	0.40	0.16
5	1.5	0.6	0.91	0.30
6	1.1	0.32	-1.11	-0.66
7	1.2	NR	-0.61	-1.33
8	1.2	0.3	-0.61	-0.38
9	0.99	0.297	-1.67	-1.06
10	1.46	0.44	0.71	0.31
12	1.25	0.6	-0.35	-0.12
13	1.4	0.5	0.40	0.16
14	NS	NS		
15	1.5	0.2	0.91	0.82
16	1	0.3	-1.62	-1.02
17	1.2	0.41	-0.61	-0.29
18	1.52	0.46	1.01	0.43
19	1.43	0.36	0.56	0.30
20	1.4	0.33	0.40	0.23
21*	2.3	0.6	2.00▼	
22	1.3	0.36	-0.10	-0.05
23	1.17	0.35	-0.76	-0.42
24	1.3	0.65	-0.10	-0.03
25	1.3	0.5	-0.10	-0.04
26	1.7	0.34	1.92	1.08
27	NS	NS		
28	1.2	0.2	-0.61	-0.55
29	1.217	0.43	-0.52	-0.23

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

Statistics

Assigned Value	1.32	0.09
Spike Value	1.93	0.10
Robust Average	1.33	0.10
Max Acceptable Result	2.50	
Median	1.30	0.08
Mean	1.36	
N	26	
Max	2.3	
Min	0.99	
Robust SD	0.19	
Robust CV	15%	
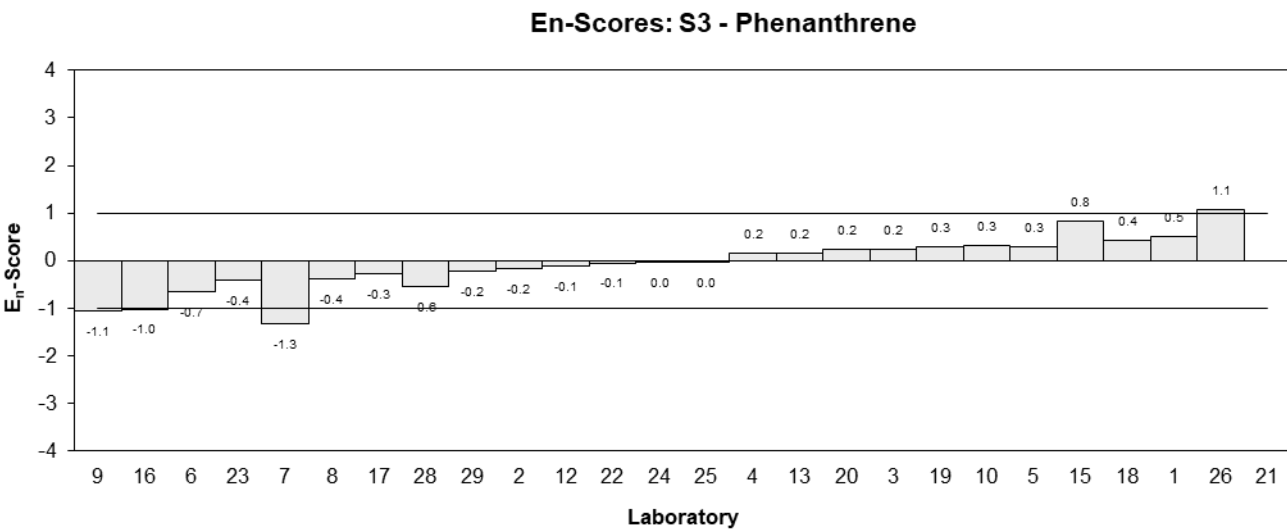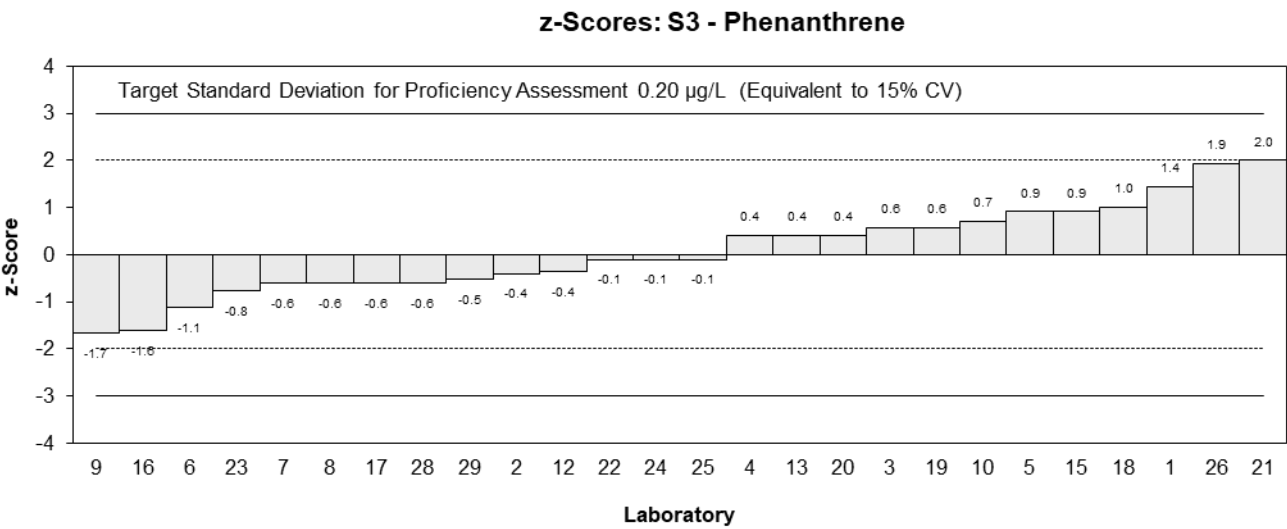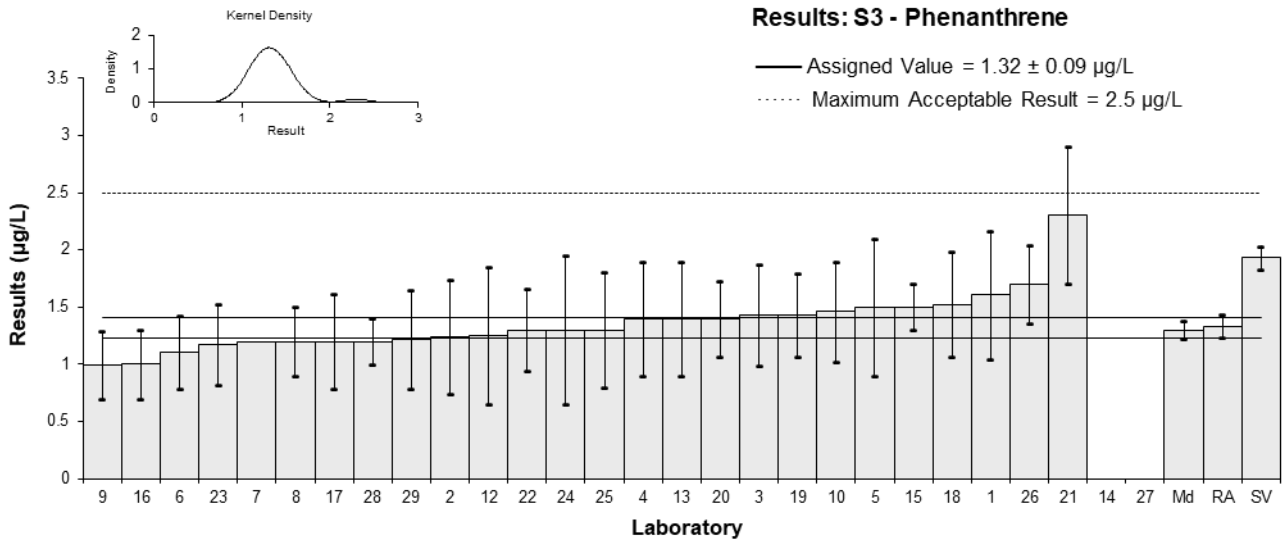
Figure 16

Table 24

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.756	1.1024	1.29	0.40
2	2.36	0.9	0.14	0.05
3	2.35	0.95	0.12	0.04
4	2.3	0.6	-0.03	-0.02
5	2.5	0.9	0.55	0.21
6	1.8	0.55	-1.47	-0.90
7	3.2	NR	2.57	6.36
8	2.2	0.4	-0.32	-0.26
9	1.6	0.48	-2.05	-1.42
10	2.26	0.68	-0.14	-0.07
12	2.50	0.8	0.55	0.23
13	2.3	0.7	-0.03	-0.01
14	NS	NS		
15	2.2	0.3	-0.32	-0.33
16	2	0.6	-0.89	-0.50
17	2.1	1.32	-0.61	-0.16
18	2.23	0.67	-0.23	-0.12
19	2.42	0.6	0.32	0.18
20	2.4	0.68	0.26	0.13
21	3	0.7	1.99	0.97
22	2.4	0.53	0.26	0.16
23	2.2	0.66	-0.32	-0.16
24	2.1	1.1	-0.61	-0.19
25	1.9	0.5	-1.18	-0.79
26	2.7	0.54	1.13	0.70
27	NS	NS		
28	2.2	0.5	-0.32	-0.21
29	2.386	0.84	0.22	0.09

Statistics

Assigned Value	2.31	0.14
Spike Value	2.85	0.14
Robust Average	2.31	0.14
Median	2.30	0.08
Mean	2.32	
N	26	
Max	3.2	
Min	1.6	
Robust SD	0.29	
Robust CV	12%	

Results: S3 - Pyrene

Assigned Value = 2.31 ± 0.14 µg/L

z-Scores: S3 - Pyrene

Target Standard Deviation for Proficiency Assessment 0.35 µg/L (Equivalent to 15% CV)

En-Scores: S3 - Pyrene
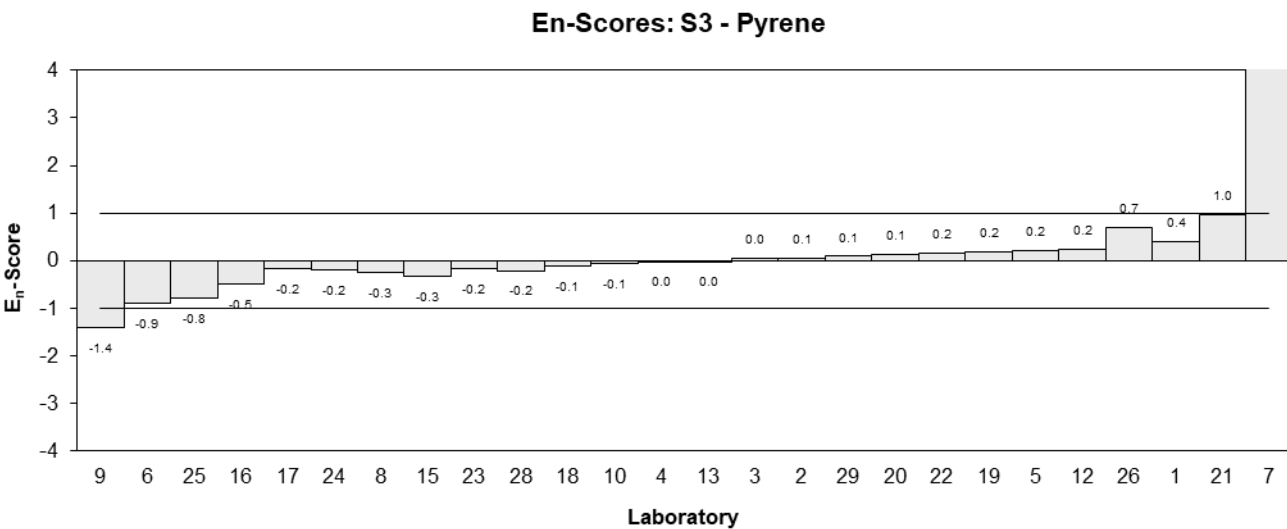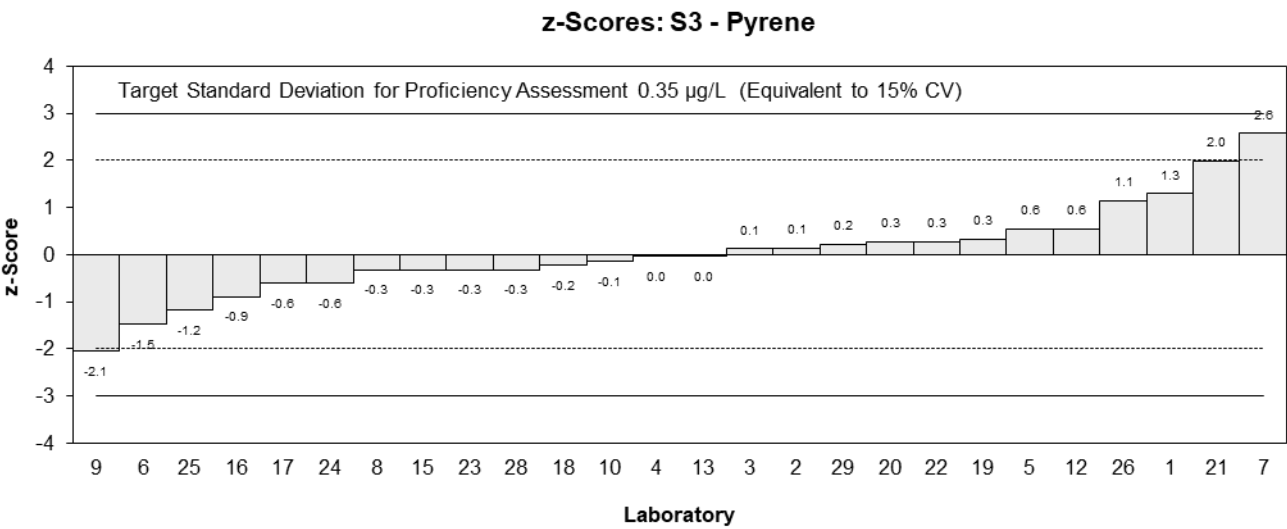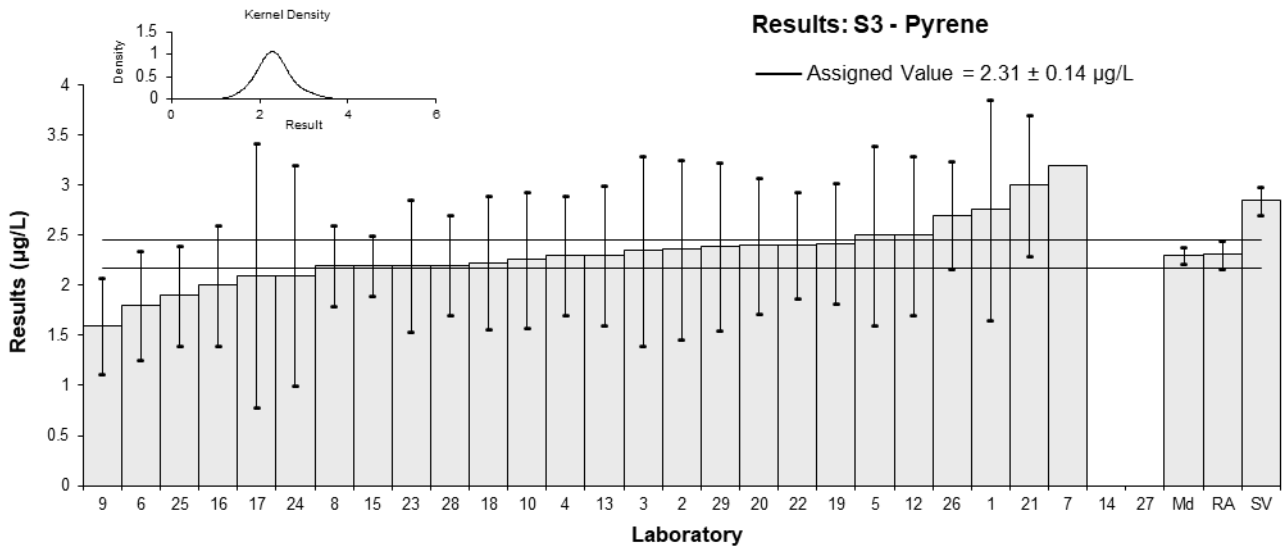
Figure 17

Table 25

Sample Details

Sample No.	S4
Matrix	River Water
Analyte	2-Methylphenol
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	En
1	6.9	3.105	-0.13	-0.06
2	7.47	2.9	0.28	0.13
3	4.7	NR	-1.68	-2.90
4	8	4	0.65	0.23
5	8.3	2.2	0.86	0.52
6	6.9	2.1	-0.13	-0.08
7	NT	NT		
8	NT	NT		
9	9.95	2.985	2.00▼	
10	7.14	2.14	0.04	0.03
12	8.39	3.4	0.93	0.37
13	<5	NR		
14	NS	NS		
15	8.8	0.8	1.21	1.50
16	6	1.8	-0.76	-0.55
17	4.9	2.42	-1.54	-0.85
18	7.23	2.17	0.11	0.06
19	9.97	1.34	2.00▼	
20	6.0	1.62	-0.76	-0.59
21*	15.7	4.1	6.09	2.06
22	5.7	1.14	-0.97	-0.98
23	<10	NR		
24	6	3	-0.76	-0.35
25	8	4	0.65	0.23
26	6.5	1.3	-0.41	-0.38
27	NS	NS		
28	6.0	1.4	-0.76	-0.67
29	7.037	1.76	-0.03	-0.02

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

Statistics

Assigned Value	7.08	0.82
Spike Value	10.0	0.5
Robust Average	7.20	0.86
Max Acceptable Result	14.0	
Median	7.09	0.86
Mean	7.53	
N	22	
Max	15.7	
Min	4.7	
Robust SD	1.6	
Robust CV	22%	
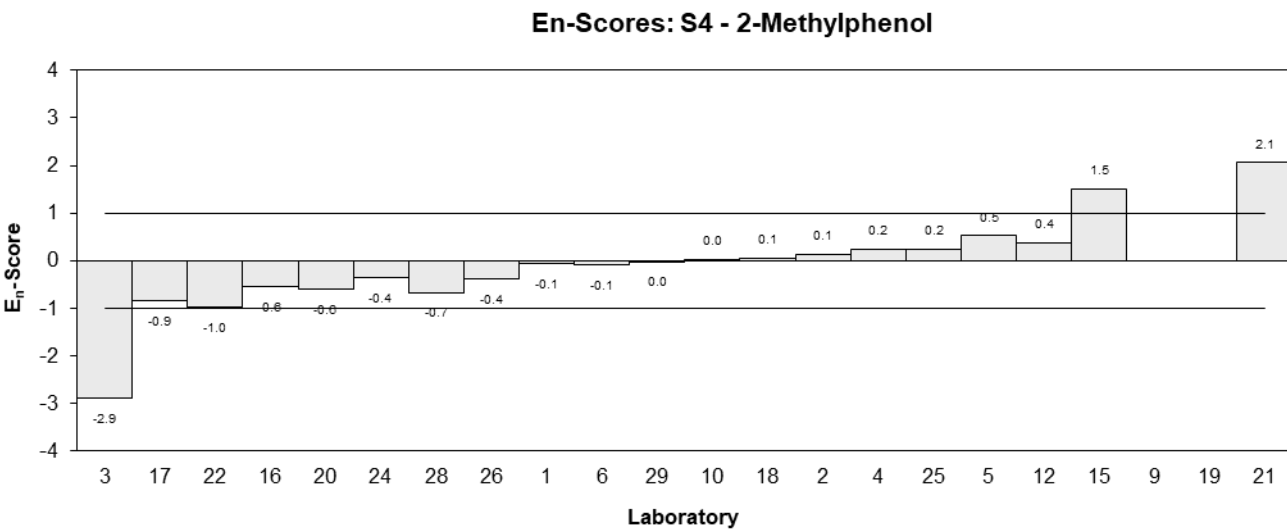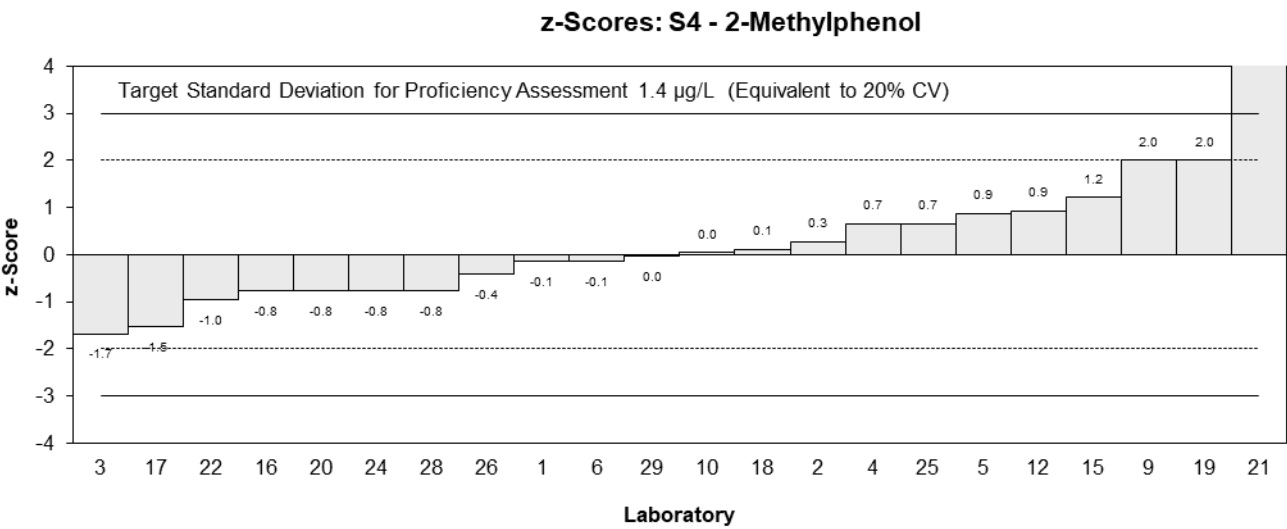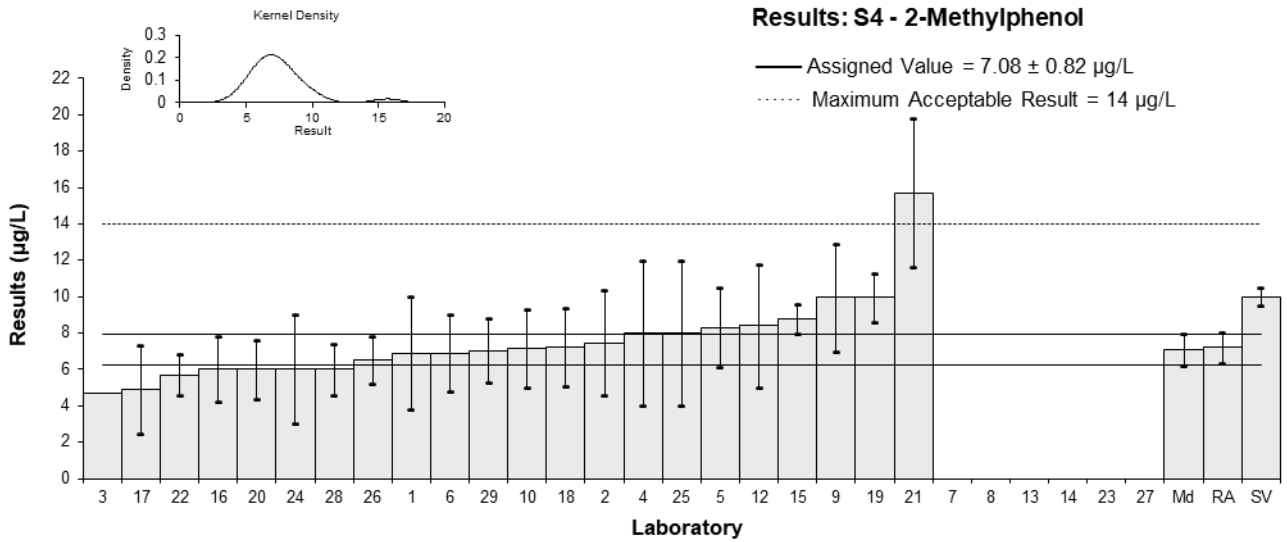
Figure 18

Table 26

Sample Details

Sample No.	S4
Matrix	River Water
Analyte	3 & 4-Methylphenols (total)
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	7.676	3.454	-0.08	-0.03
2	4.62	1.8	-2.04	-1.47
3	5.7	NR	-1.35	-1.75
4	9	4	0.77	0.29
5	8.9	2.5	0.71	0.40
6	8.2	2.5	0.26	0.14
7	NT	NT		
8	NT	NT		
9	11.5	3.45	2.00▼	
10	8.52	2.56	0.46	0.25
12	5.55	2.2	-1.44	-0.90
13	8	4	0.13	0.05
14	NS	NS		
15	10.6	1	1.79	1.79
16	4	1.2	-2.44	-2.24
17	5.9	3.23	-1.22	-0.55
18	9.94	2.98	1.37	0.67
19	11.8	1.8	2.00▼	
20	6.5	1.79	-0.83	-0.60
21*	23.6	5.9	10.13	2.62
22	6.6	1.16	-0.77	-0.72
23	<20	NR		
24	9	4.5	0.77	0.26
25	8	4	0.13	0.05
26	7.7	1.5	-0.06	-0.05
27	NS	NS		
28	6.2	1.4	-1.03	-0.87
29	7.969	1.99	0.11	0.07

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

Statistics

Assigned Value	7.8	1.2
Spike Value	12.1	0.6
Robust Average	8.0	1.3
Max Acceptable Result	16.9	
Median	8.0	1.2
Mean	8.5	
N	23	
Max	23.6	
Min	4	
Robust SD	2.4	
Robust CV	30%	

Results: S4 - 3 & 4-Methylphenols (total)

——— Assigned Value = 7.8 ± 1.2 µg/L

- - - - Maximum Acceptable Result = 16.9 µg/L

z-Scores: S4 - 3 & 4-Methylphenols (total)

En-Scores: S4 - 3 & 4-Methylphenols (total)
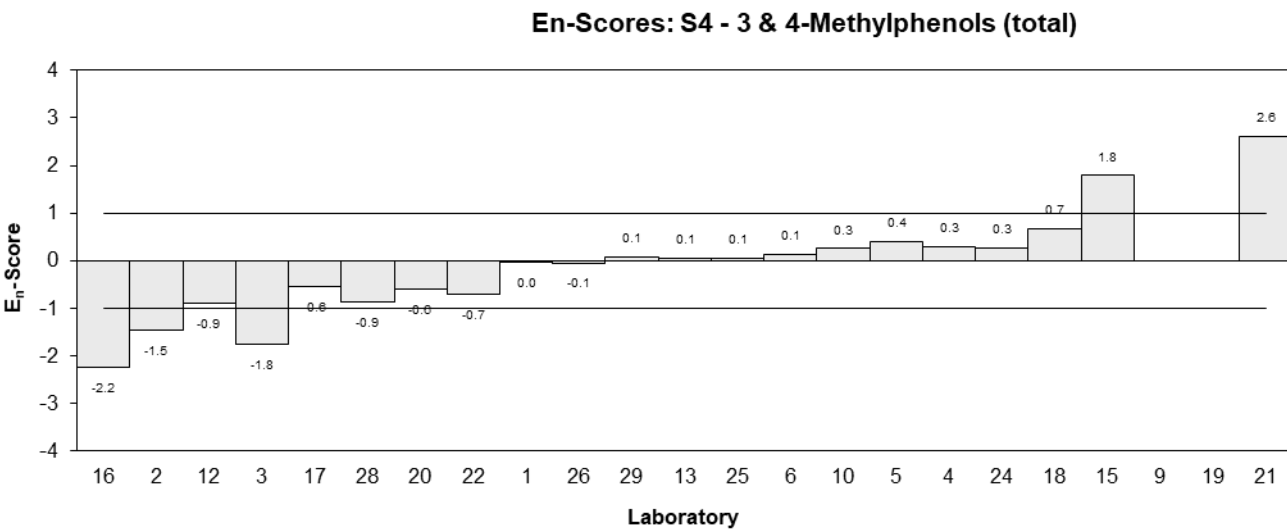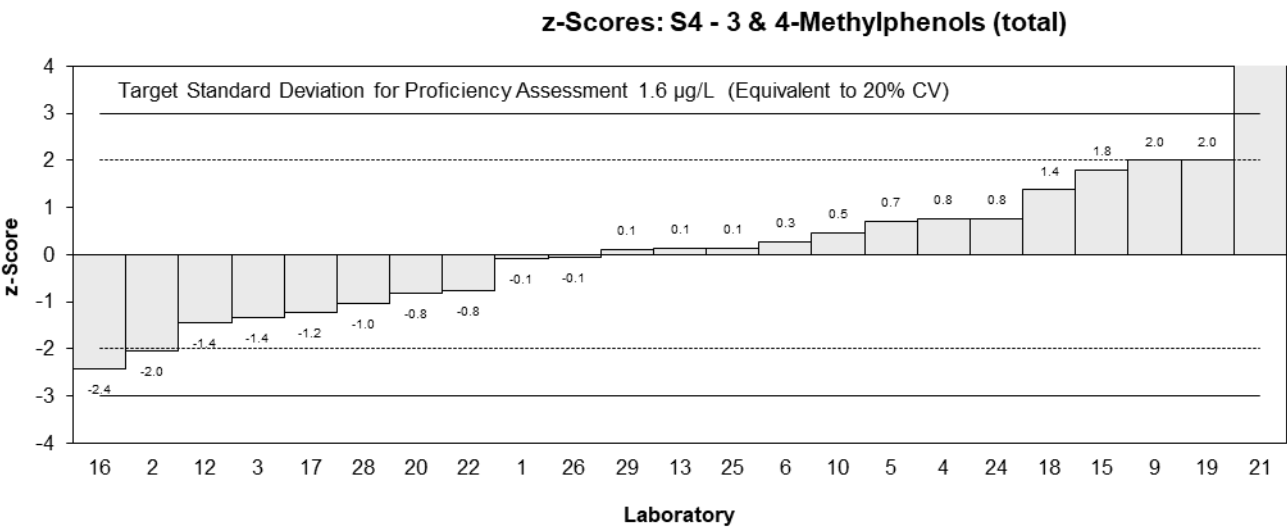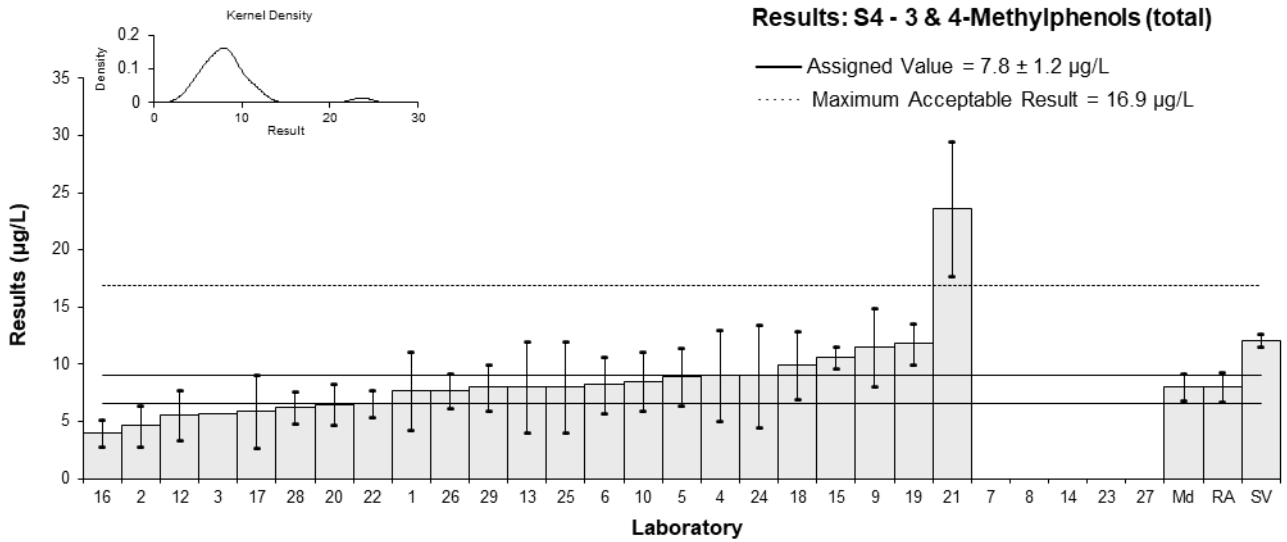
Figure 19

Table 27

Sample Details

Sample No.	S4
Matrix	River Water
Analyte	2,4-Dichlorophenol
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	9.529	4.288	-0.37	-0.17
2	12.1	4.8	0.87	0.35
3	7.1	NR	-1.55	-1.88
4	12	4	0.83	0.39
5	12.7	3.6	1.17	0.60
6	8.6	2.6	-0.83	-0.55
7*	21.5	NR	5.44	6.59
8	NT	NT		
9	14.5	4.35	2.00▼	
10	9.25	2.78	-0.51	-0.32
12	9.99	2.5	-0.15	-0.10
13	12	5	0.83	0.32
14	NS	NS		
15	14.5	1.4	2.00▼	
16	6	1.8	-2.09	-1.74
17*	5.2	2.39	-2.48	-1.74
18	9.38	2.81	-0.45	-0.28
19	13.9	2.6	1.75	1.16
20	7.1	1.94	-1.55	-1.24
21*	16.9	4.1	2.00▼	
22	7.8	1.15	-1.21	-1.22
23	<10	NR		
24*	19	9.5	2.00▼	
25	12	4	0.83	0.39
26	7.5	1.5	-1.36	-1.24
27	NS	NS		
28	8.4	1.6	-0.92	-0.81
29	11.938	4.18	0.80	0.36

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

Statistics

Assigned Value	10.3	1.7
Spike Value	14.0	0.7
Robust Average	10.9	2.0
Max Acceptable Result	19.7	
Median	11.0	2.1
Mean	11.2	
N	24	
Max	21.5	
Min	5.2	
Robust SD	3.9	
Robust CV	36%	

Results: S4 - 2,4-Dichlorophenol

Assigned Value = 10.3 ± 1.7 µg/L
Maximum Acceptable Result = 19.7 µg/L

z-Scores: S4 - 2,4-Dichlorophenol

Target Standard Deviation for Proficiency Assessment 2.1 µg/L (Equivalent to 20% CV)

En-Scores: S4 - 2,4-Dichlorophenol
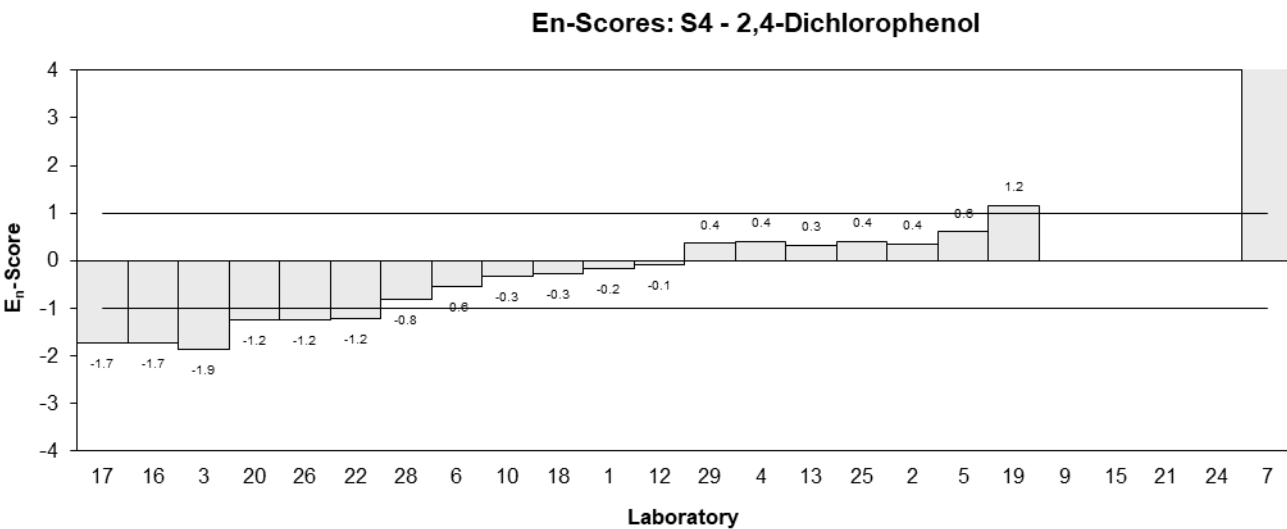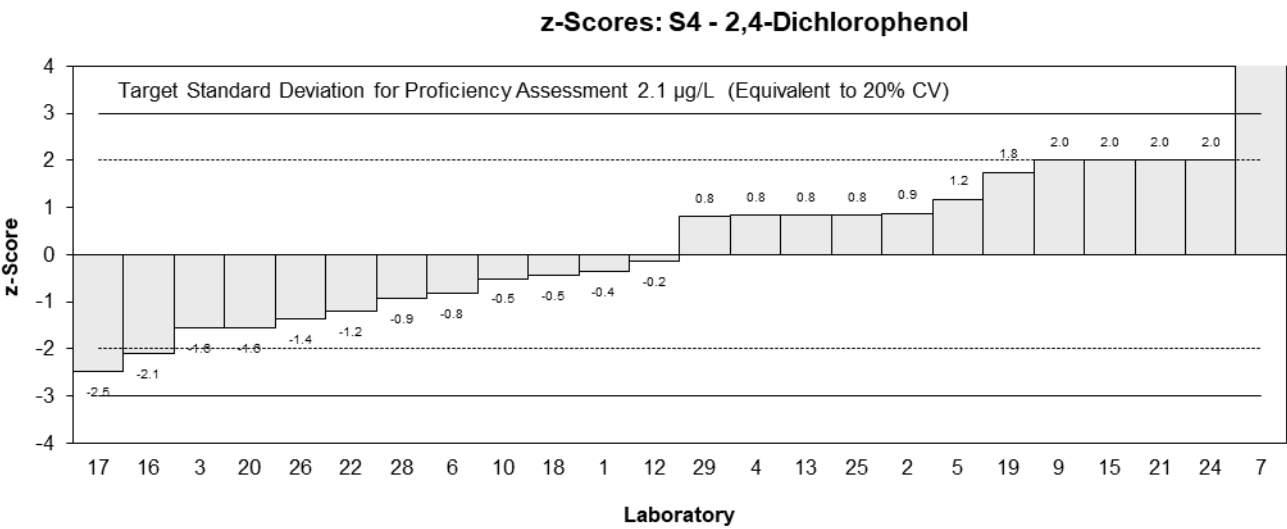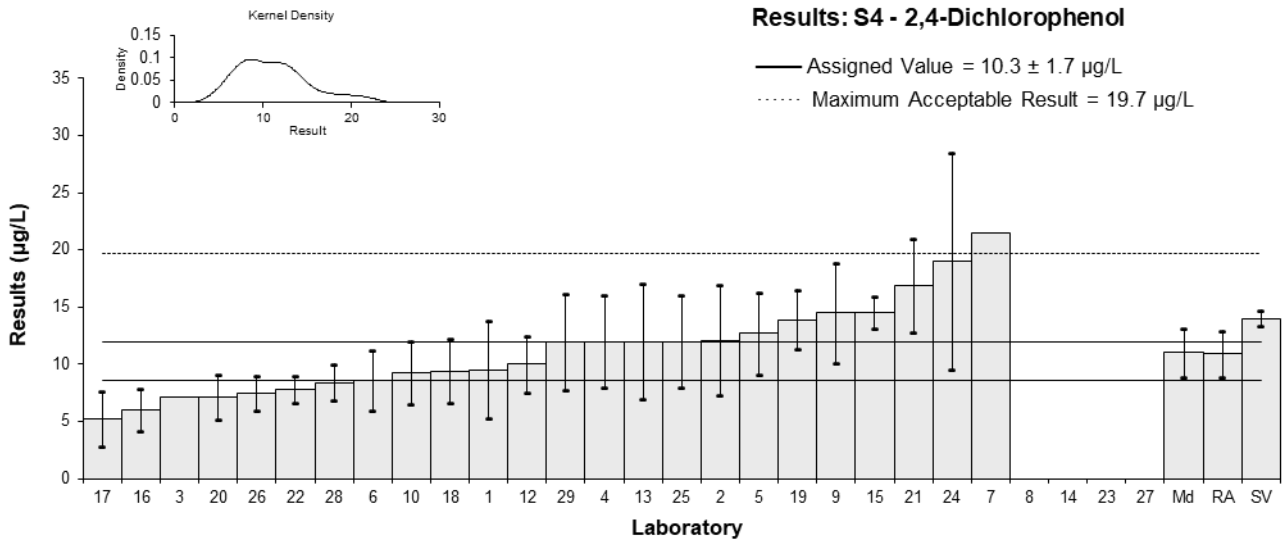
Figure 20

Table 28

Sample Details

Sample No.	S4
Matrix	River Water
Analyte	2,6-Dichlorophenol
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	11.78	5.301	0.31	0.12
2	9.18	3.7	-0.86	-0.47
3	7.1	NR	-1.80	-2.22
4	12	4	0.41	0.21
5	NT	NT		
6	8.7	2.6	-1.08	-0.76
7*	16.6	NR	2.00▼	
8	NT	NT		
9	14	4.2	1.31	0.63
10	8.75	2.62	-1.06	-0.74
12	11.6	2.4	0.23	0.17
13	13	5	0.86	0.36
14	NS	NS		
15	14.8	1.5	1.67	1.58
16	6	1.8	-2.30	-2.00
17*	2.5	1.1	-3.87	-4.08
18	9.98	2.99	-0.50	-0.32
19	14	2.5	1.31	0.94
20*	2.5	0.68	-3.87	-4.47
21*	19.6	4.5	2.00▼	
22*	3.2	0.55	-3.56	-4.20
23	<10	NR		
24*	21	11	4.46	0.89
25	12	4	0.41	0.21
26*	2.9	0.58	-3.69	-4.34
27	NS	NS		
28*	3.3	0.6	-3.51	-4.11
29	12.265	4.29	0.52	0.25

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

Statistics

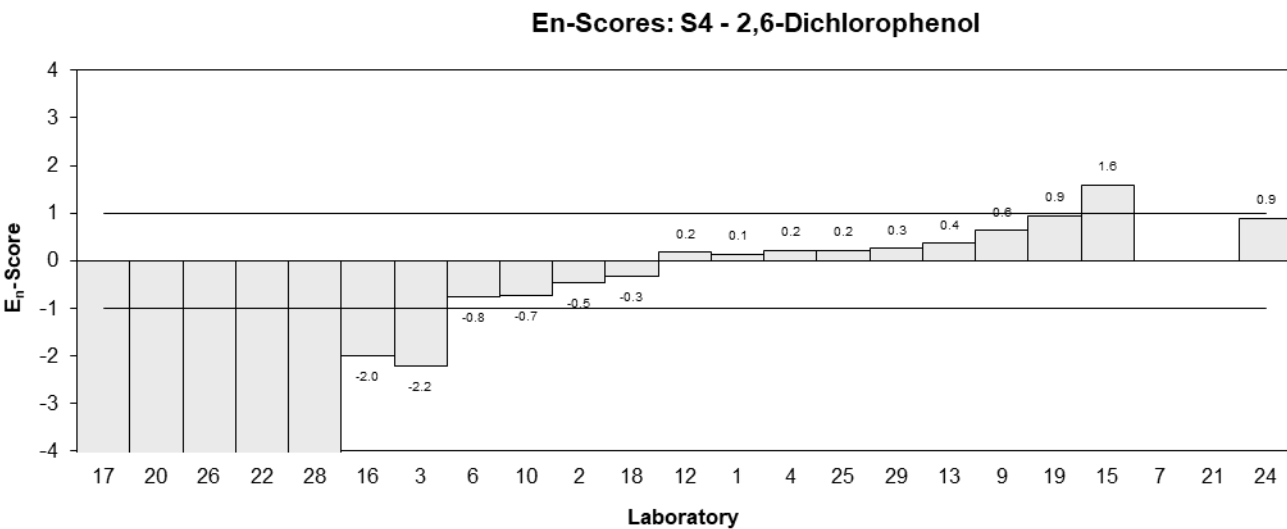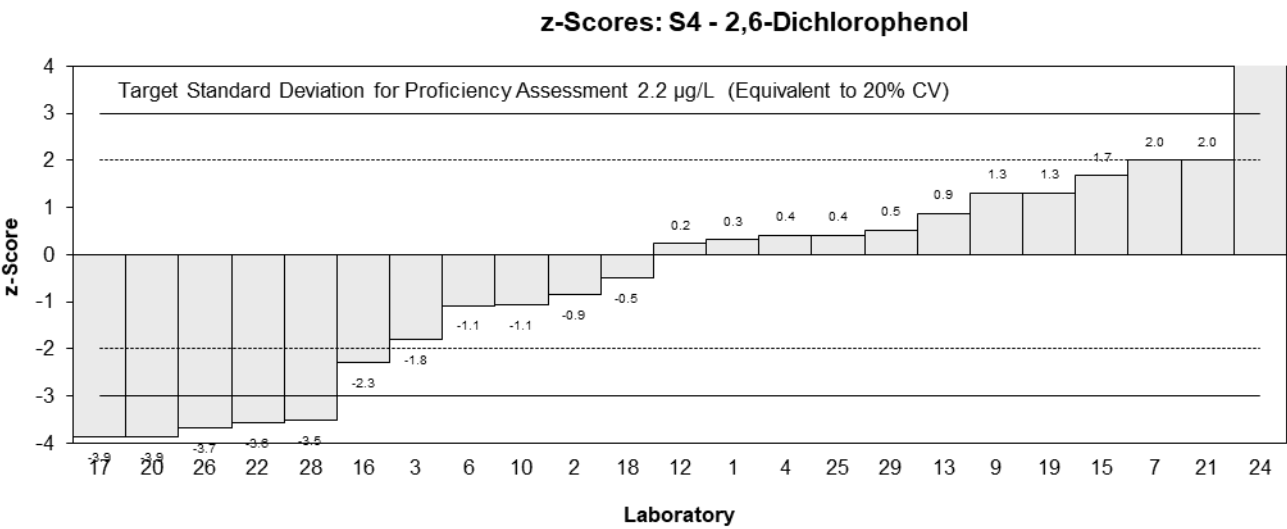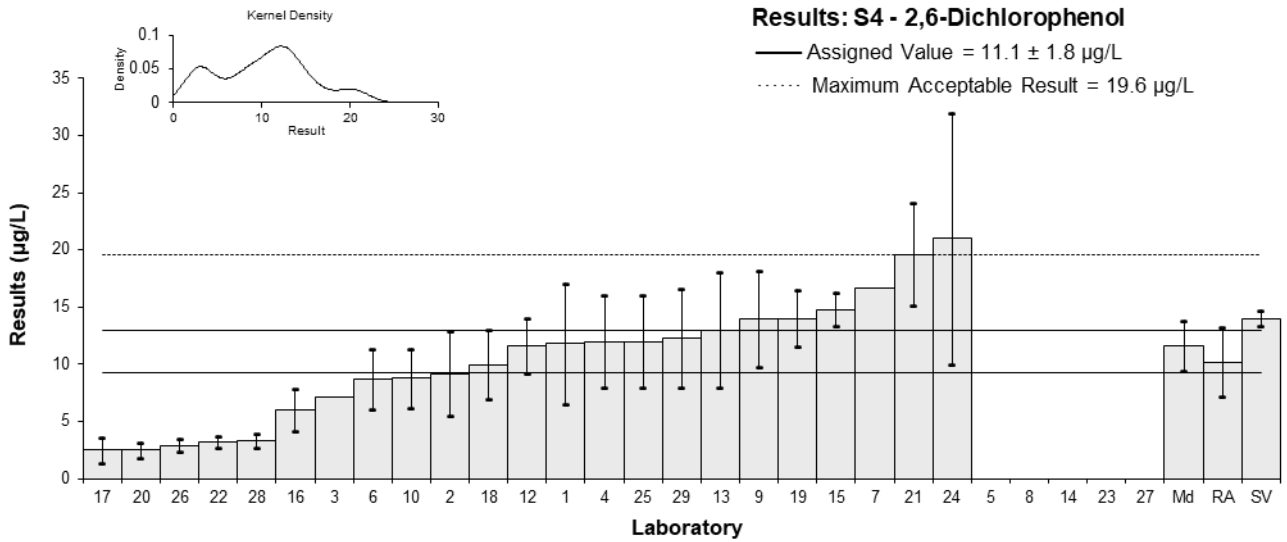| Assigned Value	11.1	1.8
Spike Value	14.0	0.7
Robust Average	10.2	3.0
Max Acceptable Result	19.6	
Median	11.6	2.2
Mean	10.3	
N	23	
Max	21	
Min	2.5	
Robust SD	5.7	
Robust CV	56%	

Figure 21

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[7] The assigned values for all scored analytes were the robust averages of participants' results, after results less than 50% and greater than 150% of the robust average had been removed.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S3 fluorene as an example.

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

No assigned value was set for Sample S1 >C34-C40 as there were no numeric results reported. No assigned values were set for Sample S3 acenaphthene and acenaphthylene as the consensus value was significantly lower than the spiked value, though there was a reasonable consensus between participants' results for these analytes. Sample S2 C6-C10 range was also not scored; historically this has been due to its volatile nature and therefore data has been provided for information only, though participants' results were in good agreement with each other for this study. For these analytes which were not scored, participants may still compare their results with the descriptive statistics and spiked values as presented in Section 5.

A comparison of the assigned values (or robust average if no assigned value was set) and the spiked values is presented in Table 29. Assigned values were set where the consensus value to spiked value ratio was similar to those observed in previous NMI PT studies, and if there was a reasonable consensus of participants' results.

Table 29 Comparison of Assigned Value (*Robust Average*) and Spiked Value

Sample	Analyte	Assigned Value (*Robust Average*) (µg/L)	Spiked Value (µg/L)	Assigned Value (*Robust Average*) / Spiked Value (%)
S1	TRH	1530	3200	48
S2	Benzene	65.3	69.2	94
	Toluene	227	261	87
	Ethylbenzene	21.4	29.0	74
	Xylenes	93.9	129	73
	Total BTEX	405	489	83
S3	Acenaphthene	*(3.06)*	8.01	*(38)*
	Acenaphthylene	*(1.34)*	2.99	*(45)*
	Benz[*a*]anthracene	5.13	6.51	79
	Benzo[*a*]pyrene	2.26	3.57	63
	Fluorene	1.76	3.14	56
	Phenanthrene	1.32	1.93	68
	Pyrene	2.31	2.85	81
S4	2-Methylphenol	7.08	10.0	71
	3 & 4-Methylphenol (total)	7.8	12.1	64
	2,4-Dichlorophenol	10.3	14.0	74
	2,6-Dichlorophenol	11.1	14.0	79

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report the expanded uncertainty estimates associated with their results and the basis of this uncertainty. 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.[9]

Of 482 numeric results submitted for analytes of interest in this study, 454 (94%) were reported with an associated uncertainty. Participants used a wide variety of procedures to estimate their expanded MU (Table 4).

Laboratory **3** did not report uncertainties for their Sample S4 phenols results only, Laboratory **22** did not report uncertainties for Sample S1 TRH and Sample S2 xylenes and total BTEX only, and Laboratory **7** did not report any uncertainties across all samples. These participants reported being accredited to ISO/IEC 17025 across all analyte types.

Sample S1 TRH results from Laboratories **2**, **4**, **13** and **19** had no uncertainties, as the results were calculated by the study coordinator by summing the individual hydrocarbon range results reported.

The magnitude of reported uncertainties was within the range of 4.8% to 66% relative. In general, an expanded measurement uncertainty of less than 10% relative is likely to be unrealistically small for the routine measurement of hydrocarbons and phenols in river water, while an expanded uncertainty of over 50% is likely to be too large and not fit-for-purpose. Of 454 MUs, nine were below 10% relative, while 11 were greater than 50% relative.

Participants were requested to report the coverage factor associated with their uncertainty (Table 5). Most participants reporting coverage factors reported the same coverage factor across all analyte types, though one participant reported a different coverage factor for BTEX as compared to the other analytes. Coverage factors ranged from 2 to 2.4, except for Laboratory **27** who reported a coverage factor of 0.2 for BTEX, which was an extremely small coverage factor and may have been reported incorrectly.

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

An estimate of uncertainty expressed as a value should not be attached to a non-value result.[10] Laboratories **5**, **15** and **17** attached an uncertainty to at least one of their non-value results.

In some cases, results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the measurement precision. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 67.651 ± 13.53 µg/L, it is better to report this as 68 ± 14 µg/L.[10]

6.3 z-Score

Target SDs equivalent to 20% PCV were used to calculate z-scores for the individual hydrocarbon ranges in Sample S1, as well as for Sample S4 phenols (which were a new analyte type introduced in this study). Target SDs equivalent to 15% PCV were used to calculate z-scores for all other analytes. CVs predicted by the Thompson-Horwitz equation,[8] the between-laboratory CVs obtained and target SDs (as PCV) for this study are presented for comparison in Table 30.

Table 30 Comparison of Thompson-Horwitz CV, Between-Laboratory CV and Target SD

Sample	Analyte	Assigned Value *(Robust Average)* (µg/L)	Thompson-Horwitz CV[a] (%)	Between-Laboratory CV[b] (%)	Target SD (as PCV) (%)
S1	>C10-C16	870	16	31	20
	>C16-C34	810	17	27	20
	TRH	1530	15	30	15
S2	C6-C10	*(1020)*	16	16	Not Set
	Benzene	65.3	22	8.3	15
	Toluene	227	20	14	15
	Ethylbenzene	21.4	22	9.8	15
	Xylenes	93.9	22	13	15
	Total BTEX	405	18	10	15
S3	Acenaphthene	*(3.06)*	22	26	Not Set
	Acenaphthylene	*(1.34)*	22	27	Not Set
	Benz[*a*]anthracene	5.13	22	16	15
	Benzo[*a*]pyrene	2.26	22	13	15
	Fluorene	1.76	22	16	15
	Phenanthrene	1.32	22	14	15
	Pyrene	2.31	22	12	15
S4	2-Methylphenol	7.08	22	21	20
	3 & 4-Methylphenol (total)	7.8	22	28	20
	2,4-Dichlorophenol	10.3	22	29	20
	2,6-Dichlorophenol	11.1	22	26	20

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

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

To account for possible low bias in the consensus values due to laboratories using inefficient extraction or analytical techniques, a total of 21 *z*-scores were adjusted across the following analytes: Sample S1 TRH, Sample S2 ethylbenzene and xylenes, Sample S3 benz[*a*]anthracene, phenanthrene, and Sample S4 2-methylphenol, 3 & 4-methylphenols (total), 2,4-dichlorophenol and 2,6-dichlorophenol. For these analytes, 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 greater than the maximum acceptable result, and *z*-scores less than 2.0, were left unaltered.

Of 414 results for which *z*-scores were calculated, 371 (90%) returned an acceptable score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **1**, **2**, **4**, **6**, **10**, **17**, **18**, **19**, **20**, **22**, **24**, **26**, **28** and **29** reported results for all 17 scored analytes. Of these participants, Laboratories **4**, **10**, **18** and **29** returned acceptable *z*-scores for all scored analytes.

Four other participants received acceptable *z*-scores for all reported results that were scored: Laboratories **13** (16), **3** (15), **12** (15) and **25** (15).

Laboratories **14** and **27** analysed Sample S2 BTEX only, and returned acceptable *z*-scores for all five scored analytes. Laboratory **8** analysed Sample S3 PAHs only, and returned acceptable *z*-scores for all five scored analytes.

A summary of participants' *z*-scores dispersal is presented by laboratory in Figure 22 and by analyte in Figure 23.
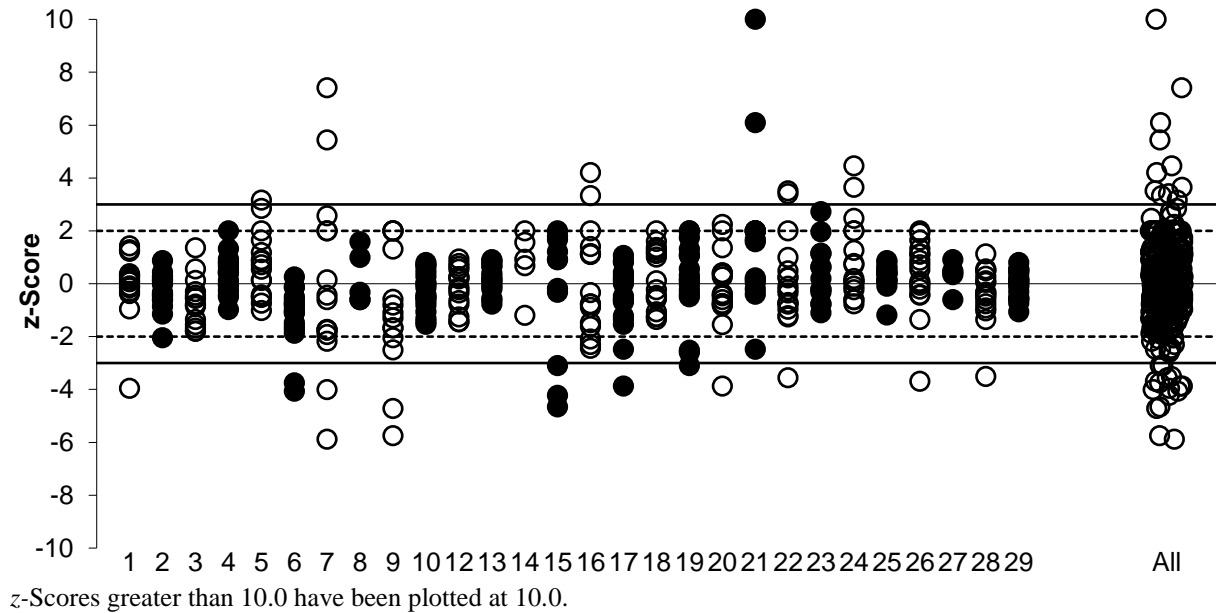

z-Scores greater than 10.0 have been plotted at 10.0.

Figure 22 *z*-Score Dispersal by Laboratory

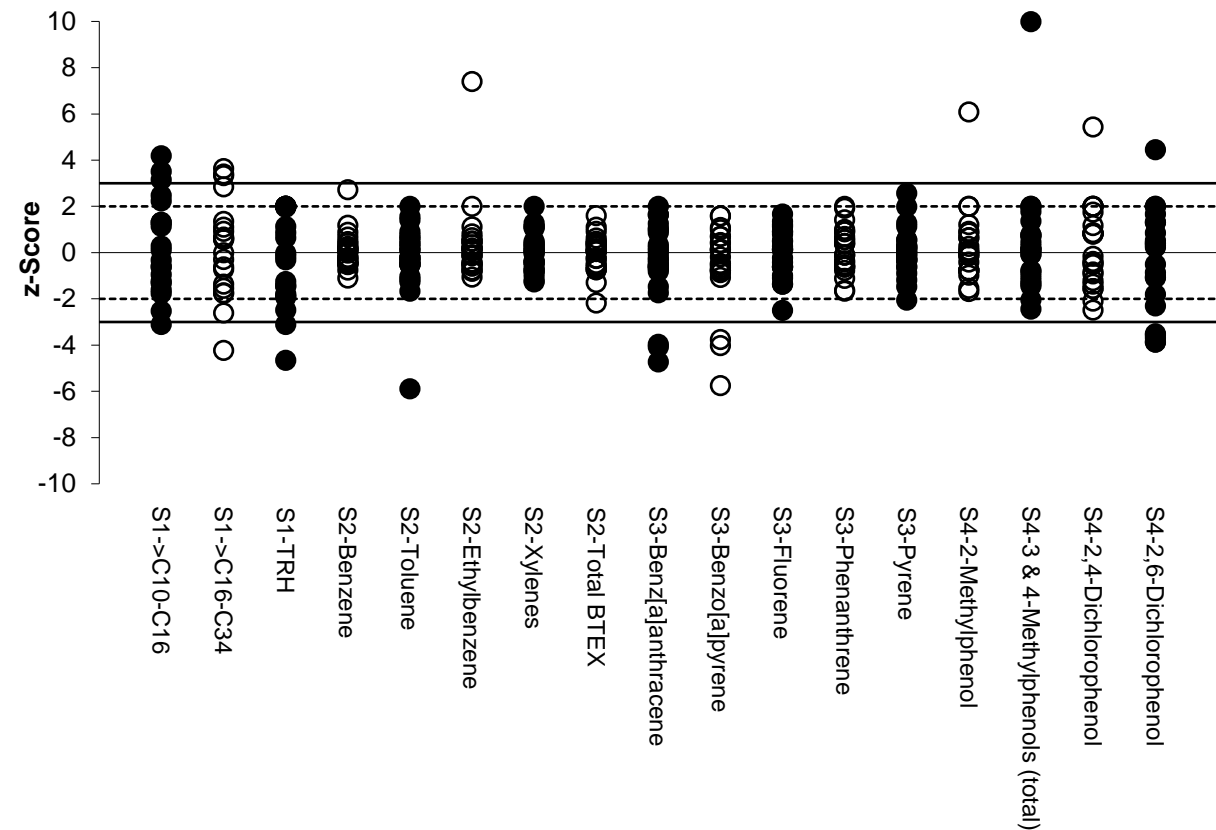*z*-Scores greater than 10.0 have been plotted at 10.0.

Figure 23 *z*-Score Dispersal by Sample and Analyte

Figure 24 presents participants' *z*-scores for Sample S1 (TRH) only. Participants with a trend of *z*-scores below the zero line possibly had an inefficient extraction process for TRH. As the ratio of the assigned value to the spiked value was 48% for TRH, participants reporting results with higher satisfactory *z*-scores may have more efficient extraction methodologies.
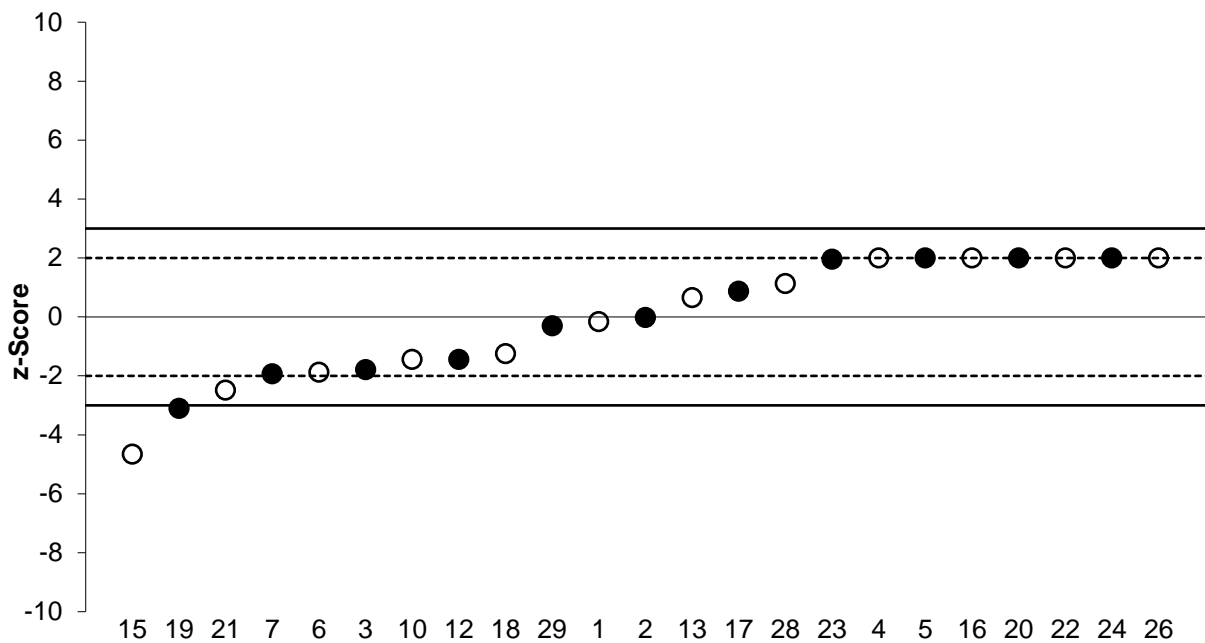

Figure 24 Sample S1 (TRH) *z*-Score Dispersal by Laboratory

Figure 25 presents participants' *z*-scores for Sample S2 (BTEX) only. Participants with a trend of *z*-scores below the zero line possibly had an inefficient extraction process for BTEX. As the ratio of the assigned value to the spiked value was 83% for total BTEX, participants reporting results with higher satisfactory *z*-scores may have more efficient extraction methodologies.

BTEX results from Laboratory **7** were extremely varied. Their result for ethylbenzene was significantly higher than the assigned value (211%) and their result for toluene was significantly lower than the assigned value (12%).
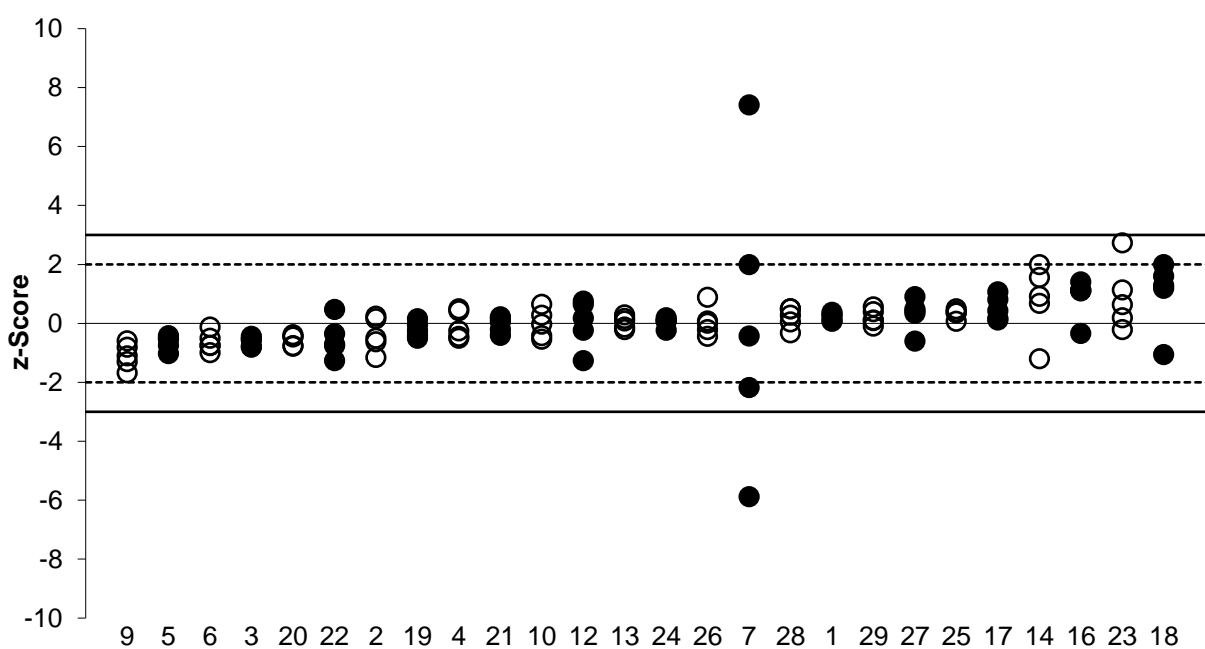

Figure 25 Sample S2 (BTEX) *z*-Score Dispersal by Laboratory

Figure 26 presents participants' *z*-scores for Samples S3 (PAHs) only. Participants with a trend of *z*-scores below the zero line may have an inefficient extraction process for PAHs. As the ratio of the assigned values to the spiked values ranged from 56% to 81%, results with higher satisfactory *z*-scores may correspond to the more efficient extraction of PAHs.
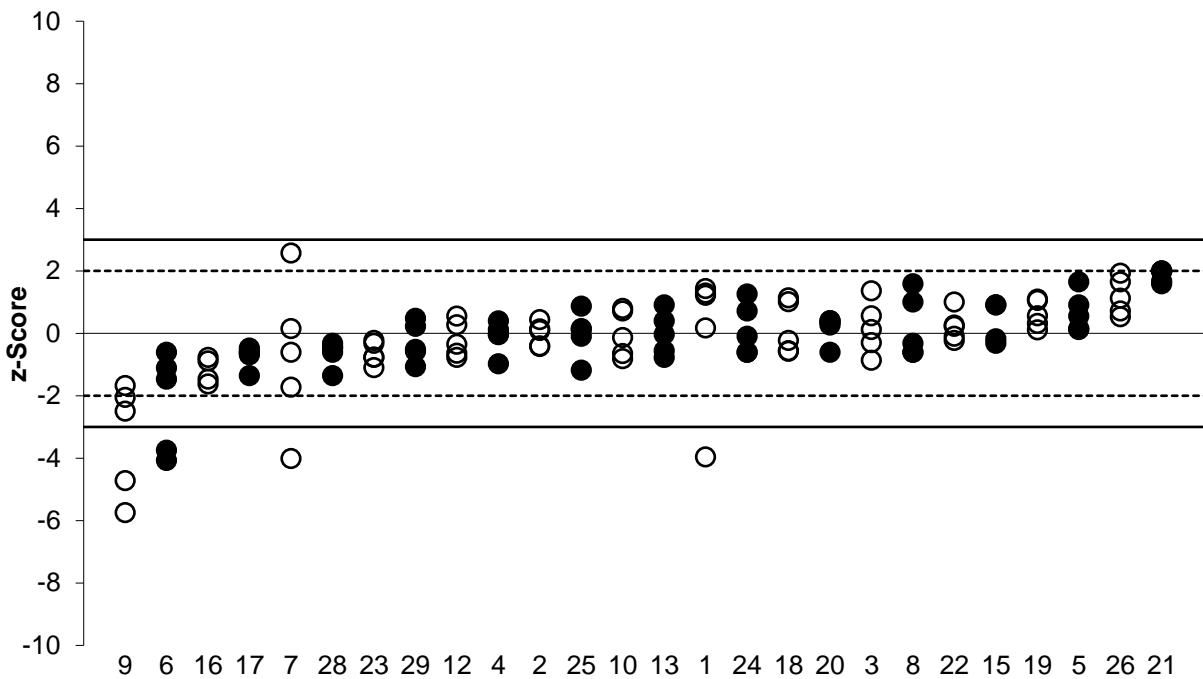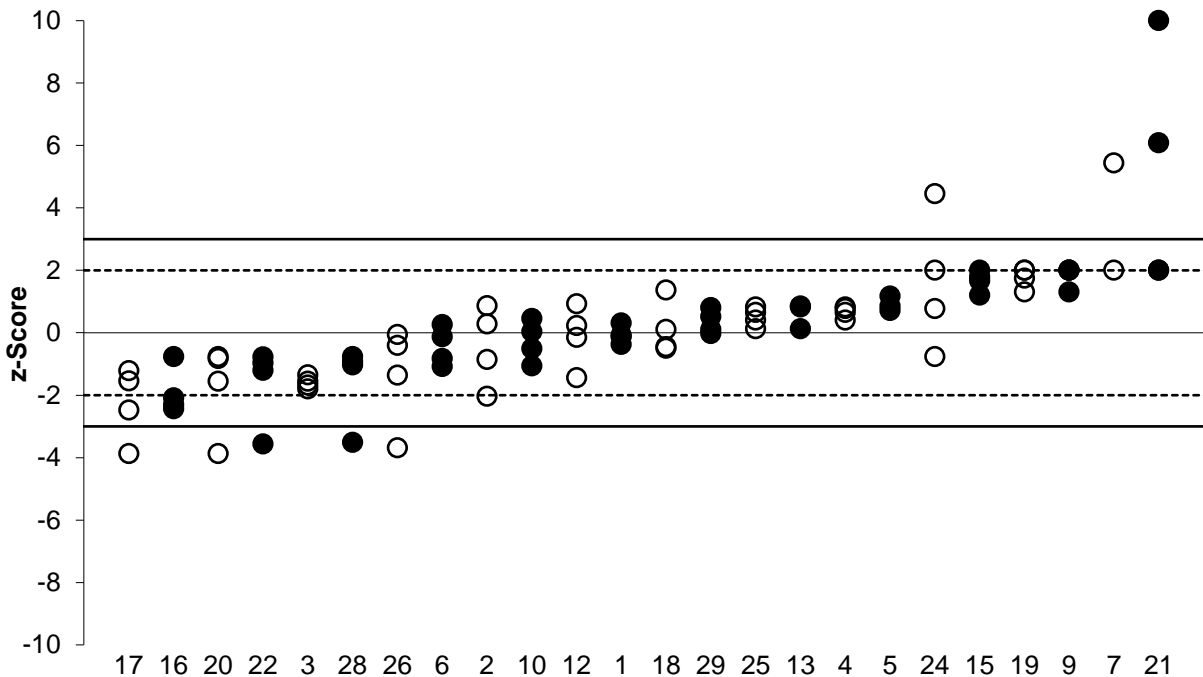

Figure 26 Sample S3 (PAHs) *z*-Score Dispersal by Laboratory

Figure 27 presents participants' *z*-scores for Sample S4 (Phenols) only. Participants with a trend of *z*-scores below the zero line may have an inefficient extraction process for phenols. As the ratio of the assigned values to the spiked values ranged from 64% to 79%, results with higher satisfactory *z*-scores may correspond to the more efficient extraction of phenols.

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

Figure 27 Sample S4 (Phenols) *z*-Score Dispersal by Laboratory

6.4 En-Score

E_n-scores can be interpreted in conjunction with z-scores, as an unsatisfactory E_n-score can either be caused by issues with measurement, or uncertainty, or both. If a participant did not report any 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-scores were assigned.

Of 393 results for which E_n-scores were calculated, 323 (82%) returned an acceptable score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratories **18** and **29** returned acceptable E_n-scores for all 17 scored analytes. Six other participants received acceptable E_n-scores for all reported results that were scored: Laboratories **4** (16), **13** (16), **12** (15), **24** (15), **25** (15) and **23** (13).

Laboratory **27** analysed Sample S2 BTEX only, and returned acceptable E_n-scores for all five scored analytes. Laboratory **8** analysed Sample S3 PAHs only, and returned acceptable E_n-scores for all five scored analytes.

A summary of E_n-score dispersal by laboratory is presented in Figure 28.
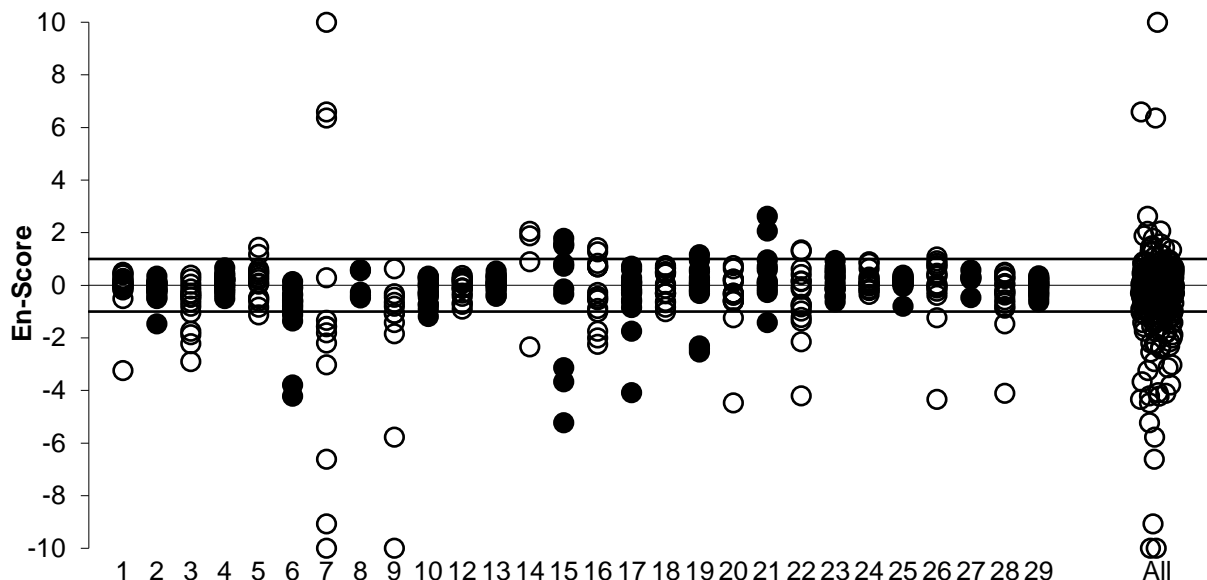
E_n-Scores greater than 10.0 have been plotted at 10.0. E_n-Scores less than -10.0 have been plotted at -10.0.

Figure 28 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 31 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, when participants reported a 'less than' result ($< x$) when the assigned value was greater than their limit of reporting (LOR), or if no value was reported. 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 31 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (Robust Average) (µg/L)	Spiked Value (µg/L)	Result (µg/L)
9	S1	Total TRH	1530	3200	<500
13	S4	2-Methylphenol	7.08	10.0	<5
15	S3	Benz[a]anthracene	5.13	6.51	<1
16	S3	Acenaphthylene	(1.34)	2.99	<1
		Fluorene	1.76	3.14	<1
23	S3	Acenaphthylene	(1.34)	2.99	<1
	S4	2,4-Dichlorophenol	10.3	14.0	<10
		2,6-Dichlorophenol	11.1	14.0	<10

6.6 Reporting of Additional Analytes

Table 32 presents analytes reported by participants that were not spiked into the test samples by the study coordinator. In general, participants should take care to avoid any potential cross-contamination when analysing their samples.

Table 32 Non-Spiked Analytes Reported by Participants

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)
3	S3	Fluoranthene	0.0261	0.0075
9	S3	Chrysene	1.45	0.435
13	S4	2,4-Dimethylphenol	9	4
15	S3	Chrysene	5.2	0.8
24	S3	Fluoranthene	0.03	0.02

6.7 Participants' Analytical Methods

Sample S1 TRH

Of participants reporting numeric results, eleven participants reported taking the whole sample for analysis, while others reported sample test portions ranging from 35 mL to 450 mL. In this study there was no evident correlation between the results obtained and the reported sample volume used (Figure 29).
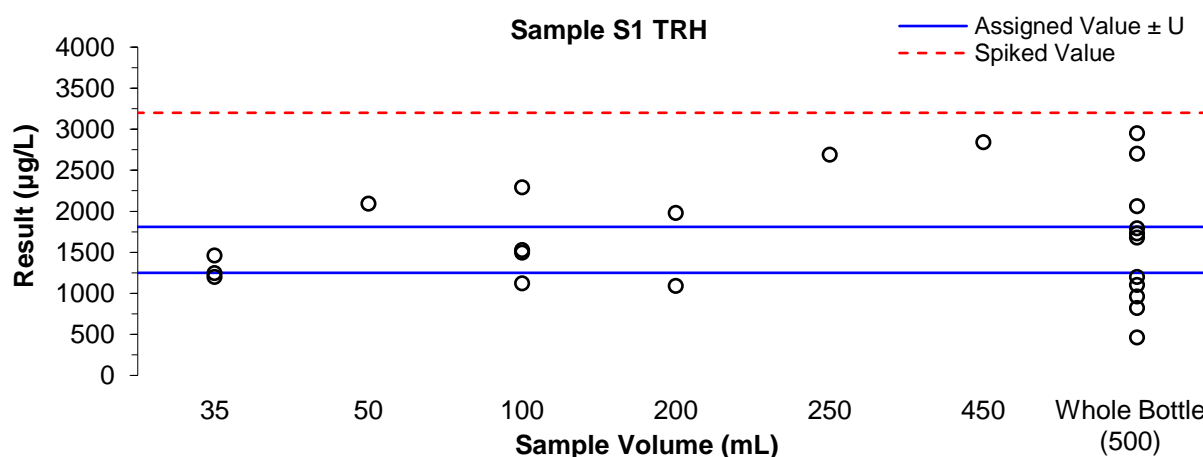

Figure 29 Sample S1 TRH Results vs Sample Volume

One participant reported using solid-phase extraction (SPE) with hexane (HEX) as the extraction solvent, while all other participants used liquid-liquid extraction (LLE) with a mixture of acetone (ACE) / dichloromethane (DCM), DCM only or HEX only as the solvent. One participant reported using a silica clean-up step, and another participant reported using a clean-up step but did not specify the process used. One participant reported using gas chromatography (GC) coupled with mass spectrometry (MS), and all other participants reported using GC coupled with flame ionisation detection (FID).

The most common methodology employed in this study was LLE with DCM, with no clean-up, and using GC-FID for analysis. A summary of results compared to methodology is presented in Figure 30. No significant trend was observed.
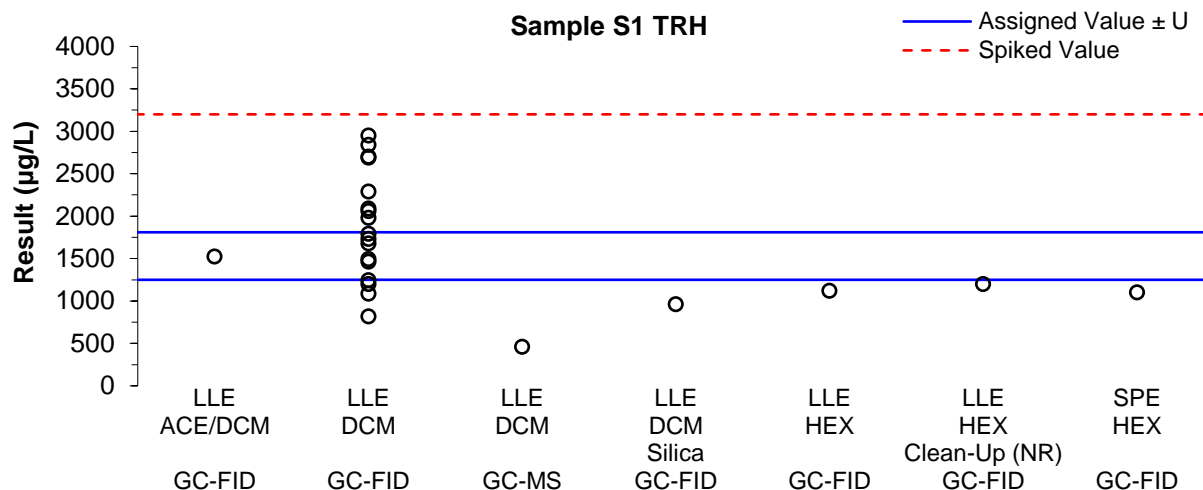

Figure 30 Sample S1 TRH Results vs Methodology

BTEX (Sample S2)

Eleven participants reported taking the whole sample (42 mL) for analysis, while others reported sample test portions ranging from 5 mL to 25 mL (Figure 31). In this study, participants using 10 mL were generally biased low, though these participants all used similar methodologies and their low bias may be also related to their methodology (see below).
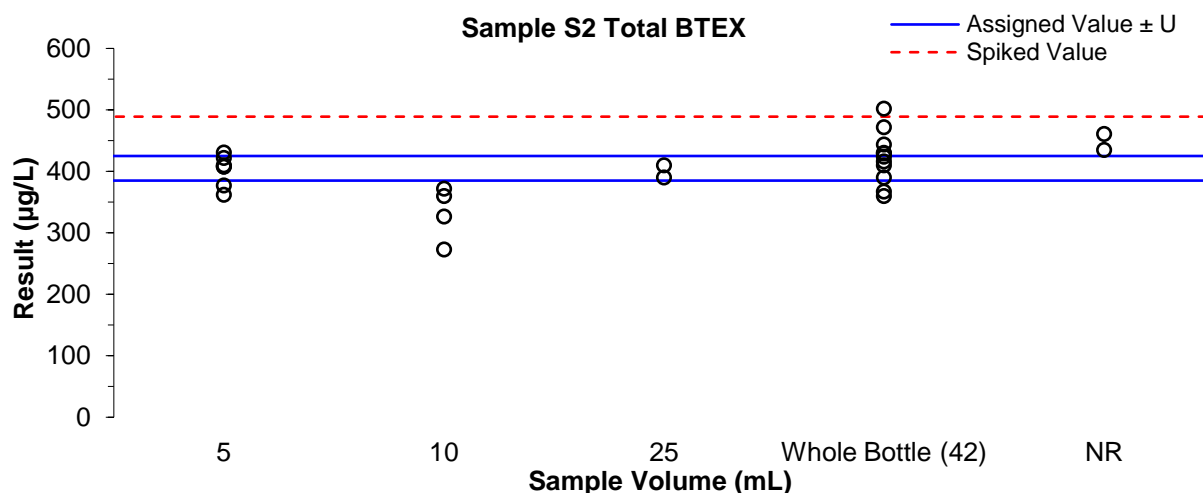

Figure 31 Sample S2 Total BTEX Results vs Sample Volume

For BTEX analysis, participants used either purge-and-trap (P&T) GC-MS or GC coupled to tandem mass spectrometry (MS/MS), or headspace (HS) GC-MS(/MS). Three participants reported LLE and one participant reported SPE as part of their preparation. The most common

methodology was P&T GC-MS. A summary of results compared to methodology is presented in Figure 32.

Most participants using HS GC-MS (including all participants who used 10 mL as their sample volume for testing) reported results that were biased low.
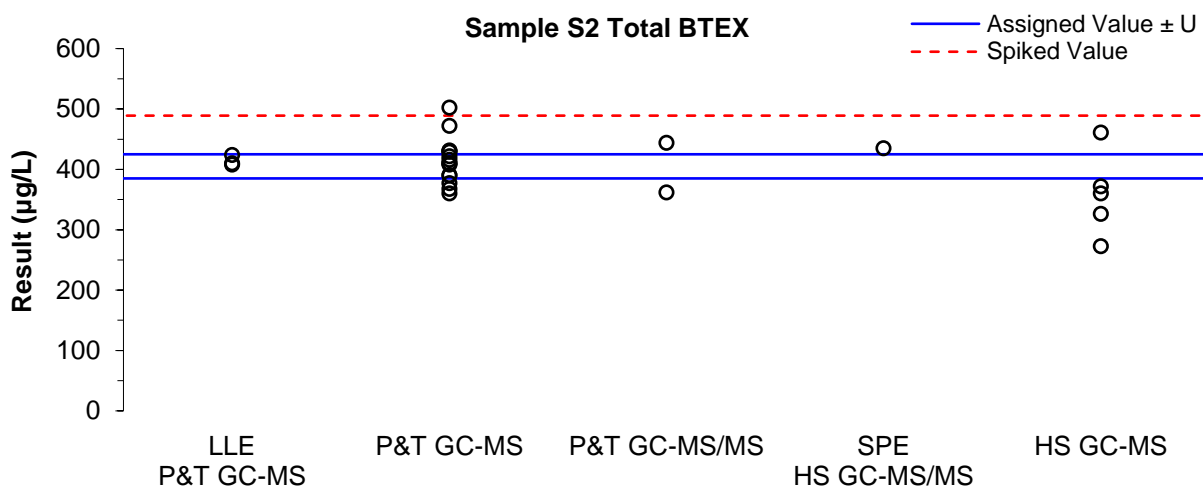

Figure 32 Sample S2 Total BTEX Results vs Methodology

PAHs (Sample S3)

For this study, participants were given the option of either analysing 1 x 500 mL bottle (15 participants) or 3 x 100 mL bottles (11 participants), depending on which best suited their laboratory's method. Participants reported test portions ranging from 35 mL to 500 mL. z-Scores obtained as compared to the sample volume used is presented in Figure 33. In this study, one participant using 40 mL from the 100 mL bottle option reported results that were generally biased low; their methodology was different compared to the other participants which may have also contributed to this bias (see below).
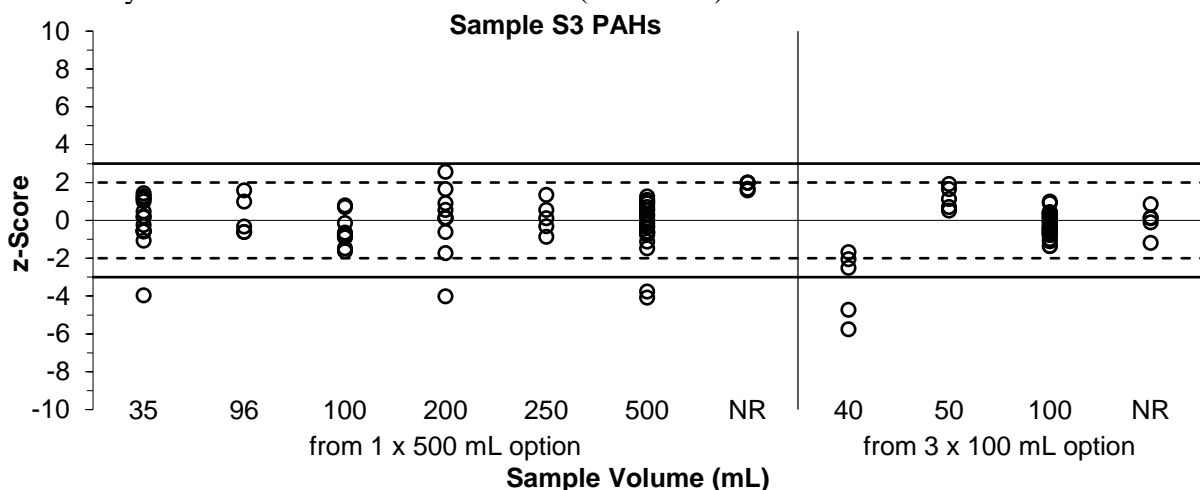
Figure 33 Sample S3 PAHs z-Scores vs Sample Volume

The majority of participants used LLE, except for two participants who used SPE. DCM, a mixture of DCM/ACE, HEX only or a mixture of DCM/ethyl acetate (EtOAc) were reported as extraction solvents. All participants used GC-MS(/MS) for analysis. No participant reported a clean-up step.

The most common methodology employed for PAHs was LLE with DCM, no clean-up, and using GC-MS for analysis. A summary of results compared to methodology is presented in

Figure 34. In this study, one participant used hexane as their extraction solvent; in general, their results were biased low.

Sample S3 PAHs

Figure 34 Samples S3 PAHs *z*-Scores vs Methodology

Phenols (Sample S4)

Participants were provided with 2 x 100 mL bottles for this sample. Participants reported sample test portions ranging from 1 mL to the full bottle (100 mL), with some participants reporting that they used both bottles as part of their analyses (200 mL), see Figure 35. Participants analysing small volumes in this study had quite varied results; participants should ensure that the aliquot taken is a suitable representation of the whole sample.
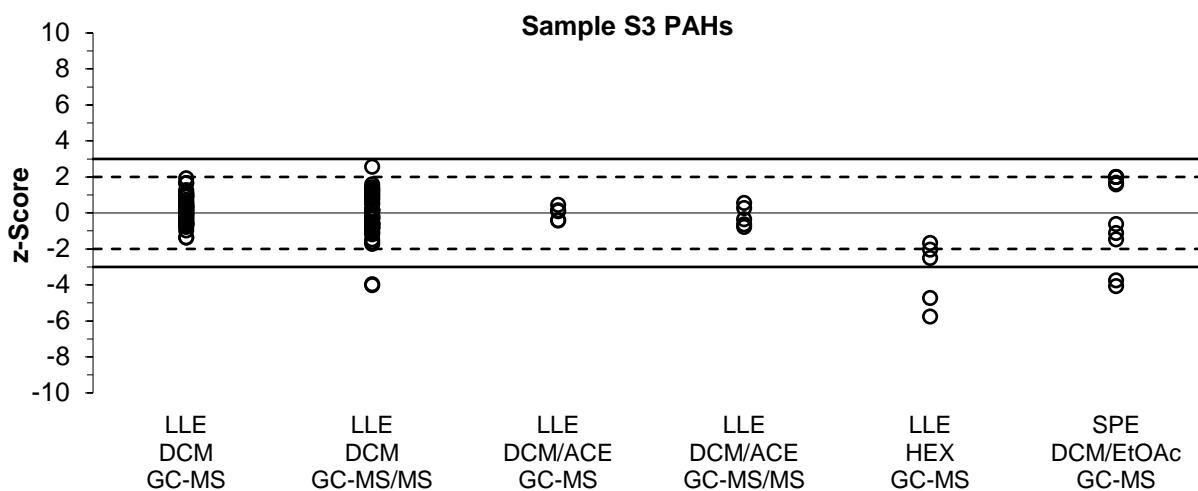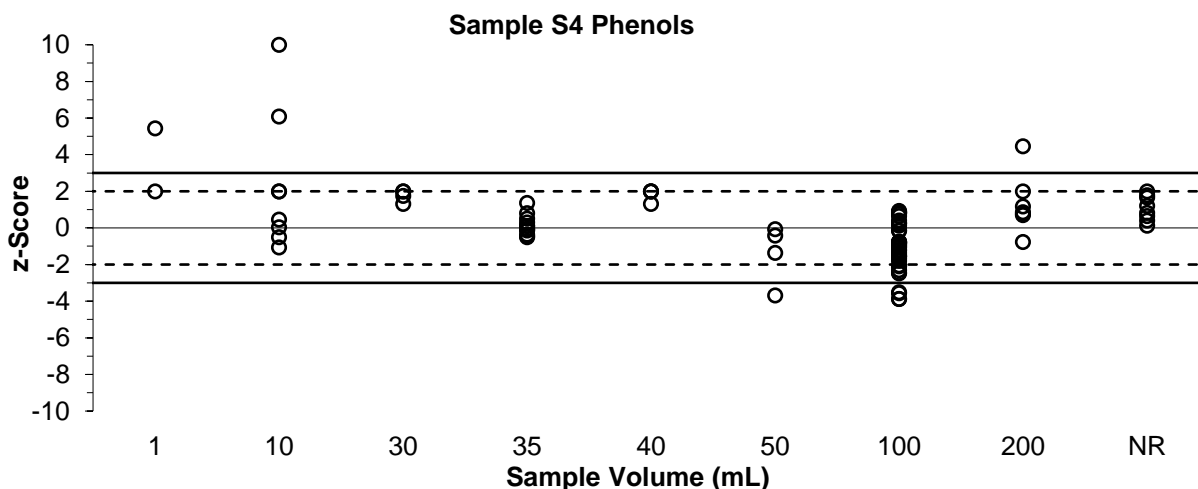
Sample S4 Phenols

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

Figure 35 Sample S4 Phenols *z*-Scores vs Sample Volume

For phenols analysis, participants used either LLE, SPE or solid phase microextraction (SPME) for extraction, or direct injection (DI). Extraction solvents reported were DCM, DCM/ACE, DCM/EtOAc or HEX. One participant used liquid chromatography (LC) coupled to MS/MS, while all other participants used GC-MS(/MS) for analyses. No participant reported a clean-up step. The most common methodology employed for phenols was LLE with DCM, no clean-up, and using GC-MS for analysis.

A summary of results compared to methodology is presented in Figure 36. In this study, both the participant using direct injection onto LC-MS/MS and the participant using SPME and GC-MS reported results biased high.
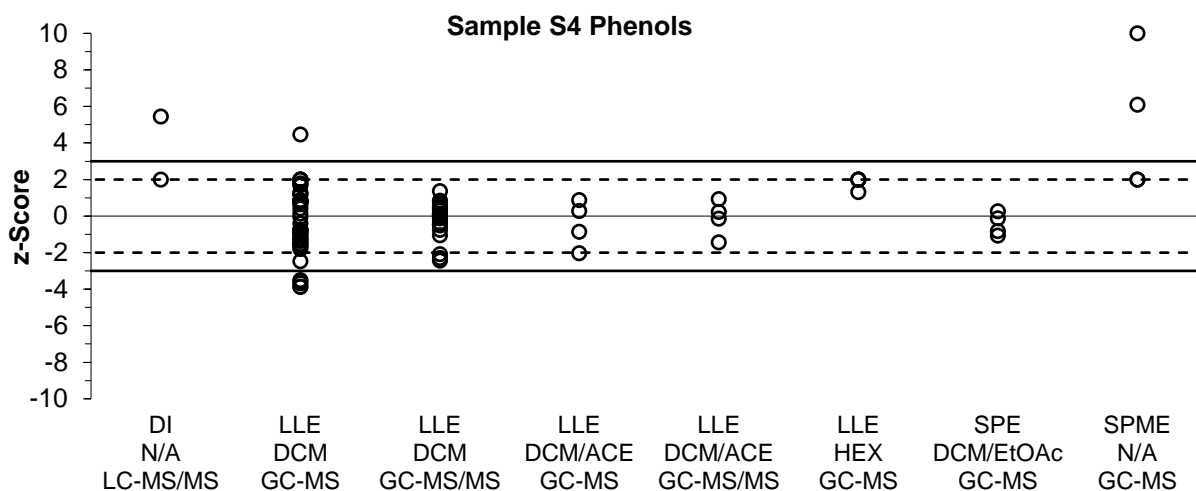
z-Scores greater than 10.0 have been plotted at 10.0.

Figure 36 Sample S4 Phenols z-Scores vs Methodology

6.8 Certified Reference Materials

Participants were requested to report whether certified standards or matrix reference materials had been used as part of the quality assurance for the analysis.

Twenty-two participants reported using certified standards and two participants reported using both certified standards and matrix reference materials. The following were reported:

- NMI standards

- AccuStandard (e.g. DRH-004S-R1-5X)

- o2si

- Sigma-Aldrich (e.g. CRM47505)

- ISO 17034 standards

These materials may or may not meet the internationally recognised definition of a CRM:

> '***reference material***, *accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures*'[11]

6.9 Summary of Participants' Performance

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 33 and 34, and Figure 37.

Table 33 Summary of Participants' Samples S1 and S2 Results for Scored Analytes*

Lab. Code	S1 TRH			S2 BTEX				
	>C10-C16	>C16-C34	Total TRH	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX
AV	870	810	1530	65.3	227	21.4	93.9	405
SV	-	-	3200	69.2	261	29.0	129	489
1	704.9	763.5	1494	67.651	240.1	21.64	95.1	424
2	814	711	1525	60.4	187.7	21.9	97.4	367.4
3	NR	NR	1120	61	209	18.8	83	371.8
4	1100	960	2060	61	210	23	100	390
5	1419	1271	2690	60.2	192.1	19.8	88	360.1
6	590	530	1100	58	210	21	80	360
7	564	525	1088	61.1	26.7	45.2	139.8	272.8
8	NS	NS	NS	NS	NS	NS	NS	NS
9	NR	NR	<500	54.5	170	19.5	82.5	326.5
10	640	560	1200	65.1	249	19.7	88	421.8
12	NR	NR	1200	63.0	253	23.5	76.1	416
13	760	920	1680	67	220	21	98	410
14	NR	NR	NR	72	280	32	77	461
15	330	125	460	NT	NT	NT	NT	NT
16	1600	1350	2950	62	275	25	110	472
17	920	810	1730	67	231	24	109	431
18	654	590	1244	77	295	18	112	502
19	431	388	819	66.9	210	20.1	93.2	390.2

Lab. Code	S1 TRH			S2 BTEX				
	>C10-C16	>C16-C34	Total TRH	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX
20	1260	1030	2290	61	214	19	83	377
21	NR	NR	960	63.2	234.4	21.9	88.2	408
22	1480	1360	2840	70	184	19	89	362
23	1070	910	1980	92	220	22	110	444
24	1300	1400	2700	63	230	22	95	410
25	NR	908	NR	66	240	23	99	430
26	1100	990	2090	74	220	20	94	410
27	NT	NT	NT	69.4	258	22.5	85.4	435
28	890	900	1790	68	216	23	101	408
29	768.3	693.3	1461.6	66.3	246	21.1	95.6	429

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

Table 34 Summary of Participants' Samples S3 and S4 Results for Scored Analytes*

Lab. Code	S3 PAHs					S4 Phenols			
	Benz[*a*]anthracene	Benzo[*a*]pyrene	Fluorene	Phenanthrene	Pyrene	2-Methylphenol	3 & 4-Methylphenols (total)	2,4-Dichlorophenol	2,6-Dichlorophenol
AV	5.13	2.26	1.76	1.32	2.31	7.08	7.8	10.3	11.1
SV	6.51	3.57	3.14	1.93	2.85	10.0	12.1	14.0	14.0
1	2.082	2.316	2.083	1.604	2.756	6.9	7.676	9.529	11.78
2	5.2	2.41	1.65	1.24	2.36	7.47	4.62	12.1	9.18
3	4.9	1.97	2.12	1.43	2.35	4.7	5.7	7.1	7.1
4	5.1	2.3	1.5	1.4	2.3	8	9	12	12
5	6.4	2.3	1.8	1.5	2.5	8.3	8.9	12.7	NT
6	2	0.99	1.6	1.1	1.8	6.9	8.2	8.6	8.7

Lab. Code	S3 PAHs					S4 Phenols			
	Benz[a]anthracene	Benzo[a]pyrene	Fluorene	Phenanthrene	Pyrene	2-Methylphenol	3 & 4-Methylphenols (total)	2,4-Dichlorophenol	2,6-Dichlorophenol
7	3.8	0.9	1.8	1.2	3.2	NT	NT	21.5	16.6
8	5.9	2.8	1.6	1.2	2.2	NT	NT	NT	NT
9	1.5	0.31	1.1	0.99	1.6	9.95	11.5	14.5	14
10	4.51	2.04	1.97	1.46	2.26	7.14	8.52	9.25	8.75
12	4.64	2.00	1.83	1.25	2.50	8.39	5.55	9.99	11.6
13	4.7	2.0	2.0	1.4	2.3	<5	8	12	13
14	NS	NS	NS	NS	NS	NS	NS	NS	NS
15	<1	2.2	2	1.5	2.2	8.8	10.6	14.5	14.8
16	4	2	<1	1	2	6	4	6	6
17	4.6	2.1	1.4	1.2	2.1	4.9	5.9	5.2	2.5
18	4.68	2.07	2.06	1.52	2.23	7.23	9.94	9.38	9.98
19	5.94	2.63	1.79	1.43	2.42	9.97	11.8	13.9	14
20	5.4	2.4	1.6	1.4	2.4	6.0	6.5	7.1	2.5
21	7.6	2.8	2.2	2.3	3	15.7	23.6	16.9	19.6
22	5.3	2.6	1.7	1.3	2.4	5.7	6.6	7.8	3.2
23	4.95	2	1.47	1.17	2.2	<10	<20	<10	<10
24	6.1	2.5	1.6	1.3	2.1	6	9	19	21
25	5.8	2.3	1.8	1.3	1.9	8	8	12	12
26	6.4	2.5	1.9	1.7	2.7	6.5	7.7	7.5	2.9
27	NS	NS	NS	NS	NS	NS	NS	NS	NS
28	4.8	2.1	1.4	1.2	2.2	6.0	6.2	8.4	3.3
29	4.682	1.896	1.888	1.217	2.386	7.037	7.969	11.938	12.265

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

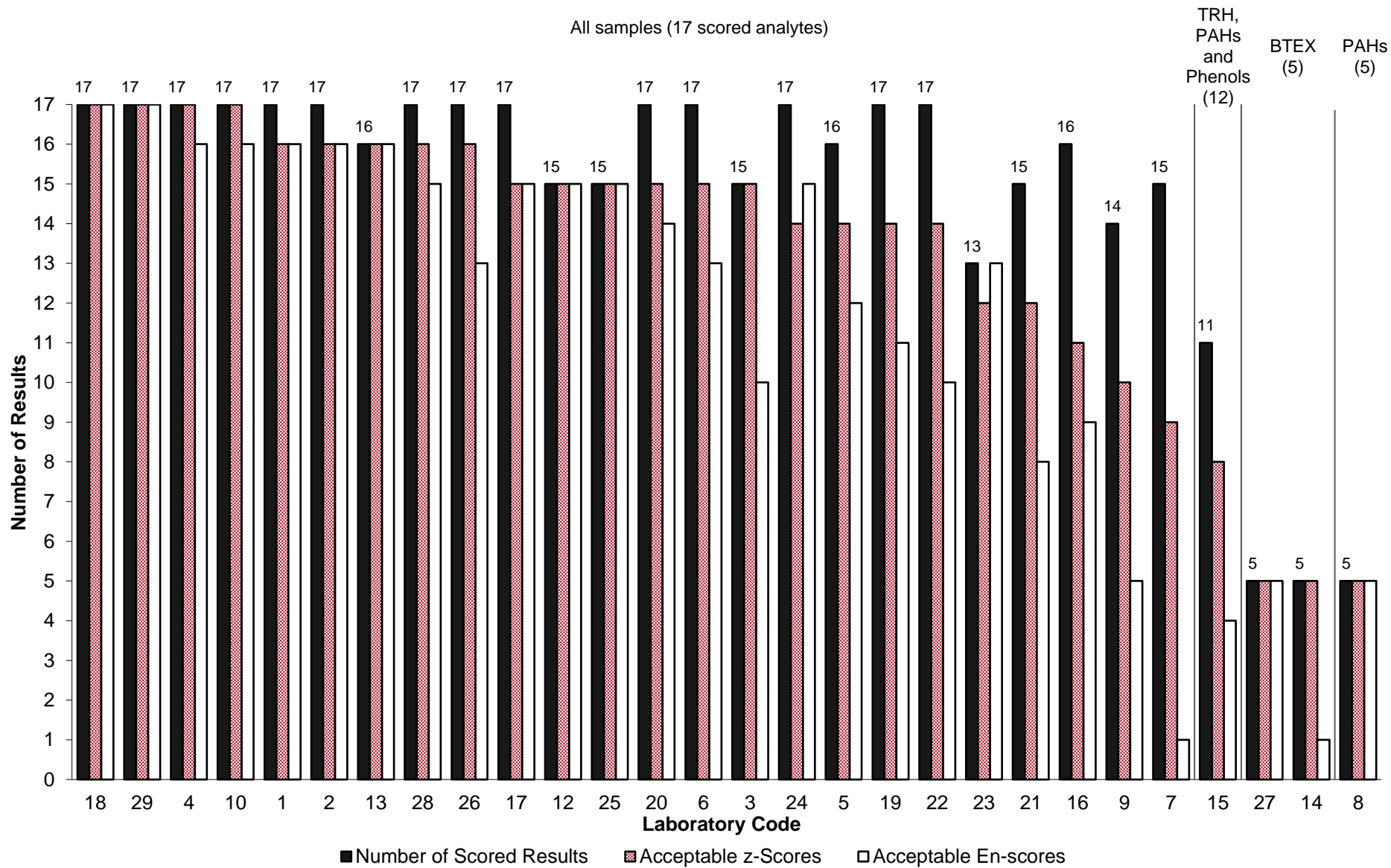AQA 23-21 Hydrocarbons and Phenols in River Water

Figure 37 Summary of Participants' Performance

6.10 Comparison with Previous Studies

Comparisons with previous studies are provided for TRH, BTEX and PAHs, as this study was the first time phenols in river water was run by NMI.

TRH

A summary of z-scores and E_n-scores, presented as a percentage of the total number of scores for each study, obtained by participants for TRH in river water over the last 10 studies where this was scored (2014–2023) is presented in Figure 38. Over this period, the average proportion of acceptable scores was 77% for z-scores and 65% for E_n-scores.
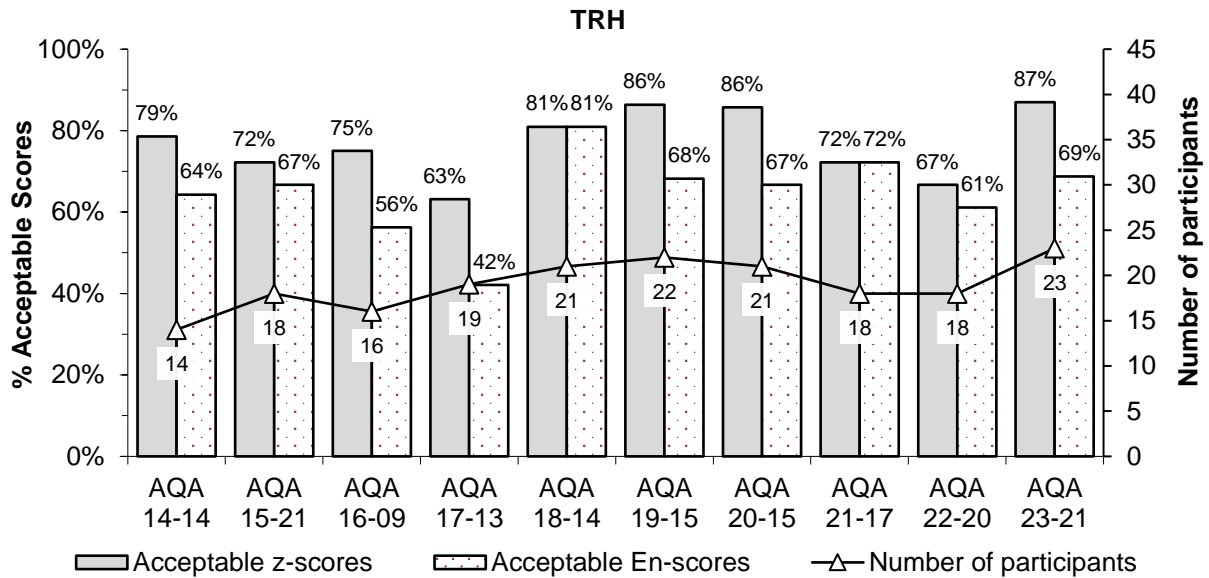

Figure 38 Summary of Acceptable Scores for NMI TRH in River Water PT Studies

Total BTEX

A summary of z-scores and E_n-scores, presented as a percentage of the total number of scores for each study, obtained by participants for total BTEX in river water over the last 10 studies where this was scored (2015–2023) is presented in Figure 39. Over this period, the proportion of acceptable scores has remained high, with an average proportion of 94% and 88% for z-scores and E_n-scores respectively.
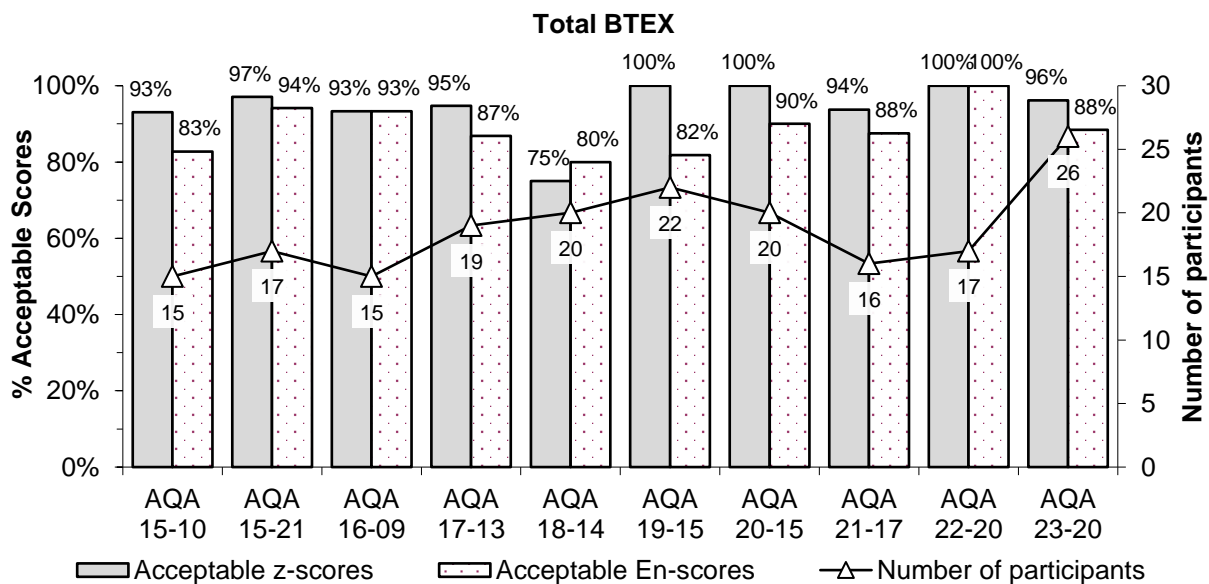

Figure 39 Summary of Acceptable Scores for Total BTEX in River Water PT Studies

PAHs

NMI has included PAHs in river water as PT samples since 2015. A summary of z-scores and E_n-scores, presented as a percentage of the total number of scores for each study, obtained by participants for PAHs in river water over the last 9 studies (2015–2023) is presented in Figure 40. Over this period, the proportion of acceptable scores has remained fairly consistent, with an average proportion of 87% and 82% for z-scores and E_n-scores respectively.
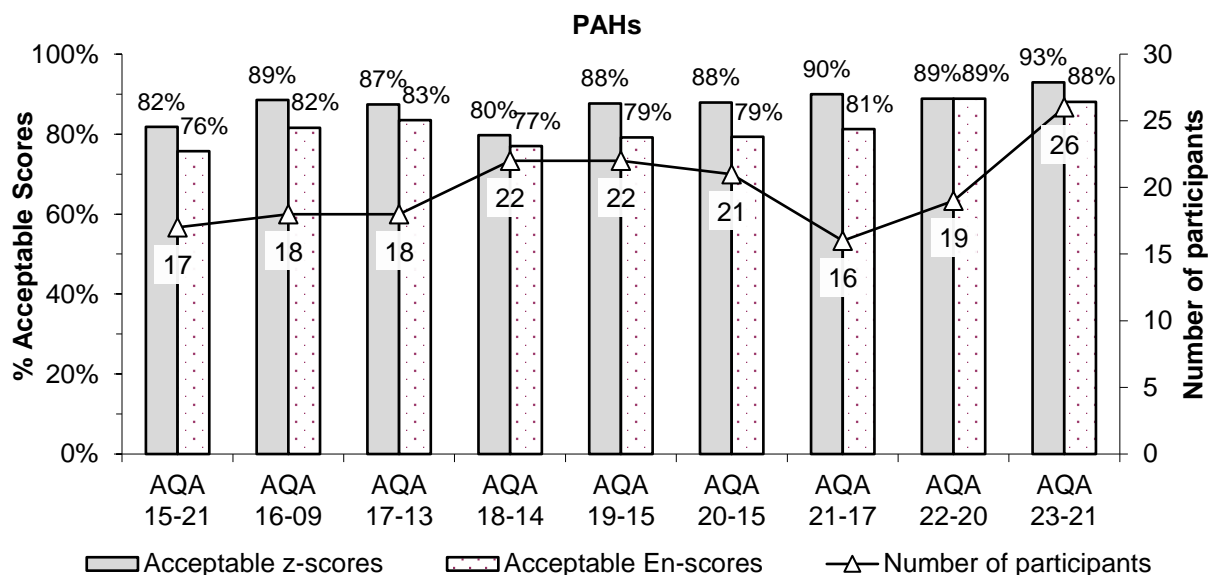

Figure 40 Summary of Acceptable Scores for PAHs in River Water PT Studies

A plot of the assigned value, expressed as a percentage of the spiked value, for PAHs in river water since 2015 is presented in Figure 41 for analytes scored in this PT study. In this study, the ratio of assigned value to spiked value for all scored analytes were similar to the averages observed across previous studies.
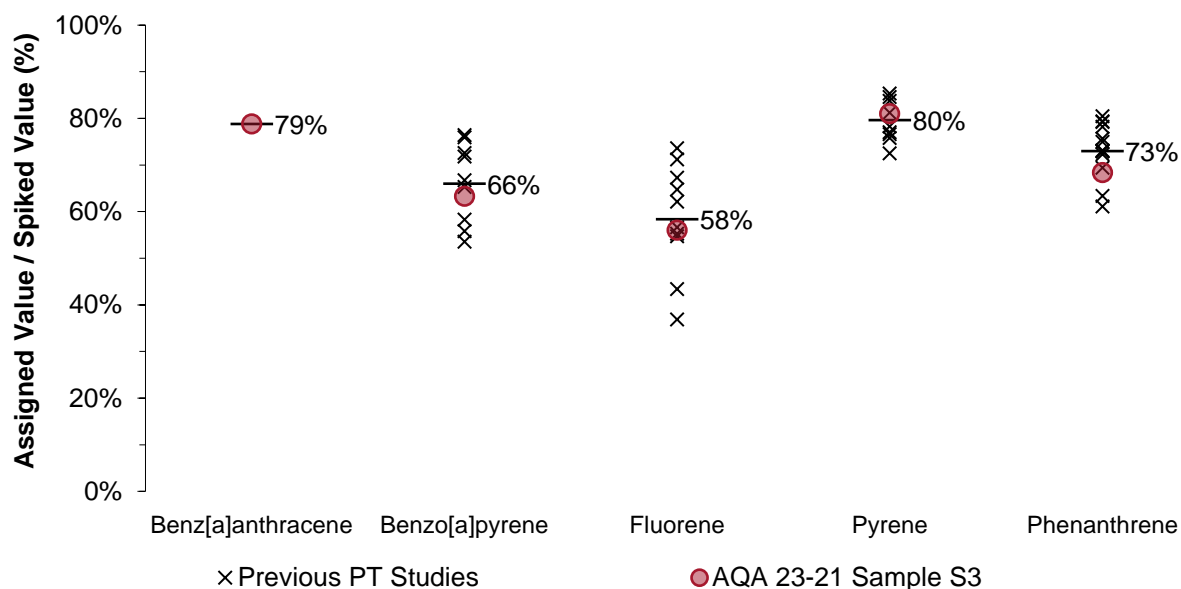
Lines indicate the average for each PAH.

Figure 41 Ratio of Assigned Value to Spiked Value for PAHs in River Water PT Studies

Measurement Uncertainties

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties.[9] Figure 42 presents a summary of the relative uncertainties as reported by

participants over the last 10 studies (2015–2023). Over this time period, 90% of participants reported that they were accredited to ISO/IEC 17025. The vast majority (96%) of numeric results were reported with uncertainties. Additionally, most results (89%) were reported with relative uncertainties between 10% and 50%; in the last two studies, a greater proportion of results had relative uncertainties within this range as compared to the previous few studies.
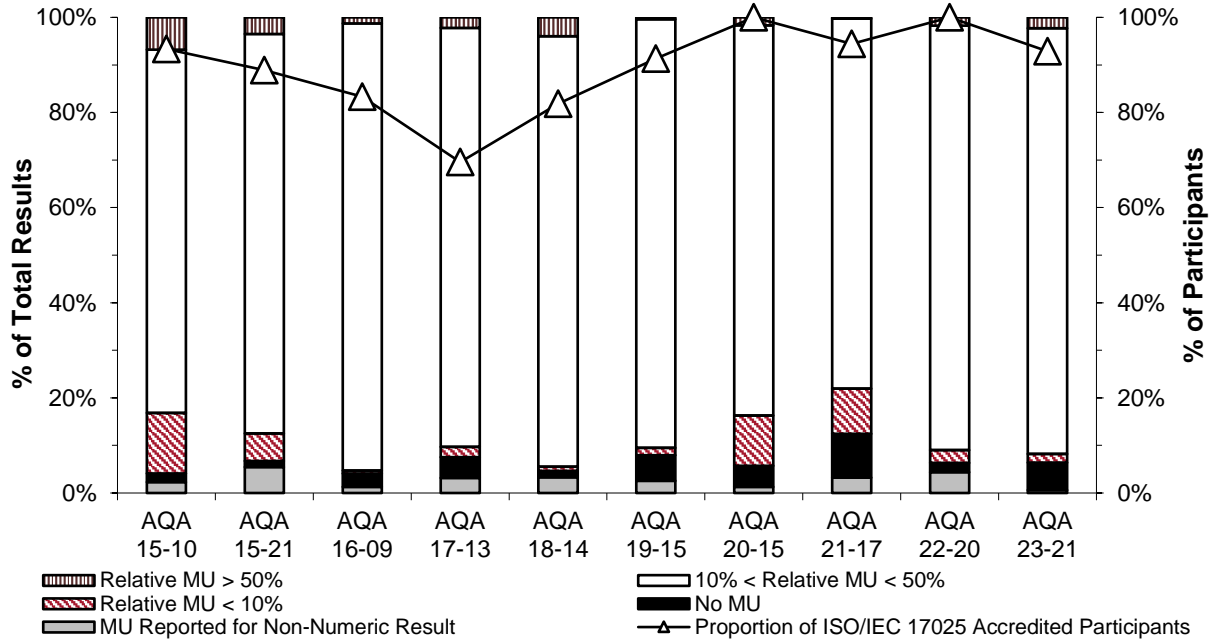

Figure 42 Summary of Participants' Relative Uncertainties for NMI Hydrocarbons and Phenols in River Water PT Studies

7   REFERENCES

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

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

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

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

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

[5]   National Environment Protection Council, National Environment Protection (Assessment of Site Contamination) Measure 1999 Amendment Measure 2013, viewed January 2024, <https://www.legislation.gov.au/F2008B00713/latest/text/12>

[6]   La Greca, B., 1996, 'Storage Stability Study: Petrol BTEX Residues in Water', *ACSL Public Interest Project*, AGAL.

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

[8]   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.

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

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

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

APPENDIX 1 SAMPLE PREPARATION

A1.1 Diesel Fuel and River Water Preparation

Diesel fuel was purchased from a local retail outlet and treated to remove volatiles. Approximately 500 mL of diesel fuel was placed in a heated (80 °C) open container and sparged with nitrogen. Treatment continued until the GC-FID chromatogram indicated that essentially all the hydrocarbons eluting before C_{10} had been removed. This same treated diesel fuel has been used in previous NMI Hydrocarbon PT studies.

Water was sampled from Wingecarribee River at Burradoo. The water was filtered under vacuum through an Advantec 150 mm glass fibre filter. After filtration, the water was placed in Schott bottles and autoclaved.

A1.2 Test Sample Preparation

Sample S1

A diesel spiking solution was prepared by weighing a portion of the treated diesel fuel into a 500 mL volumetric flask and making to volume with methanol. Amber glass bottles of approximately 500 mL capacity were rinsed with 70% ethanol : 30% reagent grade water and oven dried. The cleaned bottles were placed in an air-conditioned room overnight. Filtered autoclaved river water (498.5 ± 0.2 g, or 500 mL at 25 °C) was weighed into the bottles. The water was pumped into the vials through a Sartorius filter capsule using a peristaltic pump. Methanol/diesel spiking solution (2 mL) was added to each bottle using a Hamilton dispenser. The bottles were immediately capped and inverted to mix the solution. Each bottle was then labelled and shrink-wrapped.

Sample S2

Filtered autoclaved river water (41.88 ± 0.05 g, or 42 mL at 25 °C) was weighed into Agilent vials. The water was pumped into the vials through a Sartorius filter capsule using a peristaltic pump. A composite spike solution was prepared by adding aliquots of diesel and unleaded petrol to methanol. Two of the BTEX compounds was fortified with additional laboratory solvent. The composite spiking solution was made up to volume with methanol. Composite spiking solution (1.0 mL) was added to each vial using a Hamilton dispenser. Each vial was capped after spiking, and then labelled and shrink-wrapped.

Sample S3

The spiking solutions were prepared by dissolving each standard material in DCM. Diluted spiking solutions were prepared using acetone. The autoclaved water was placed in a stainless steel container. After spiking the water was stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL and 100 mL amber glass bottles which were then labelled and shrink-wrapped.

Sample S4

Filtered autoclaved river water (98.42 ± 0.05 g, or 99 mL at 25 °C) was weighed into 100 mL amber glass bottles using a peristaltic pump and Sartorius filter. A composite spiking solution was prepared using the phenol stock solutions previously prepared. Composite spiking solution (1 mL) was dispensed into each bottle using a Hamilton dispenser. The bottles were vigorously shaken for 15 seconds, then labelled in fill order and shrink-wrapped.

Between preparation and dispatch, all samples were stored in a cool room at 4 °C.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples for similar analytes and matrices. A preliminary trial for the homogeneity of phenols in water was performed prior to this study, and results indicated that the preparation processes used would produce samples suitable for this PT study.

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

A2.2 Stability

No stability testing was conducted for this study as the samples were stored and dispatched using a process previously demonstrated to produce sufficiently stable samples for similar analytes and matrices. A preliminary trial for the stability of phenols in water was performed prior to this study, and results indicated that the storage and dispatch processes used would produce samples suitable for this PT study.

The results of this study also gave no reason to question the samples' transportation stability. Comparisons of z-scores to days in transit are presented in Figures 43 to 53 for scored analytes.
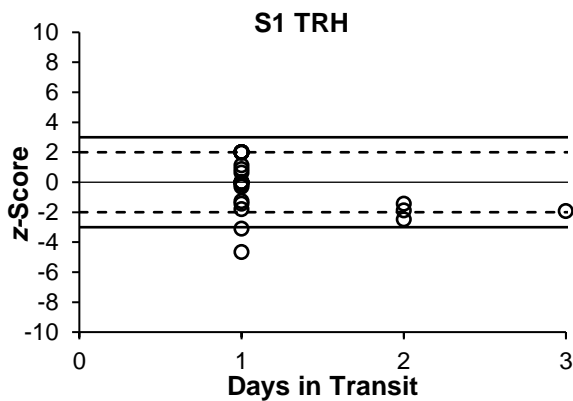
Figure 43 S1 TRH vs Transit Days
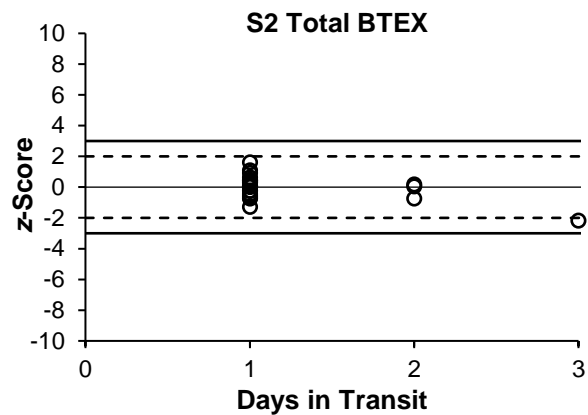
Figure 44 S2 Total BTEX vs Transit Days
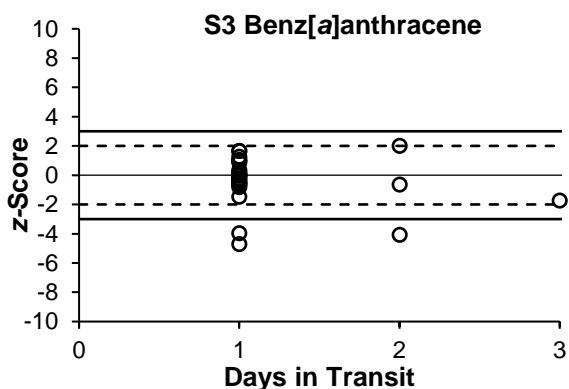
Figure 45 S3 Benz[*a*]anthracene vs Transit Days

Figure 46 S3 Benzo[*a*]pyrene vs Transit Days
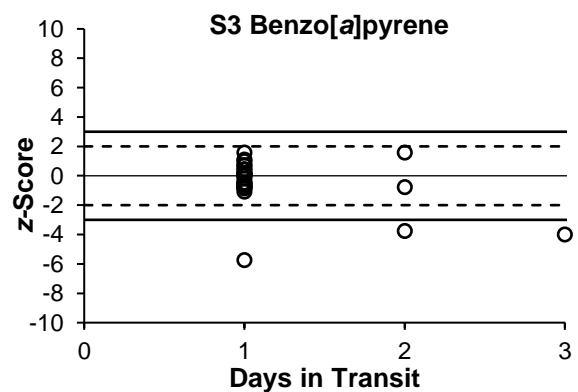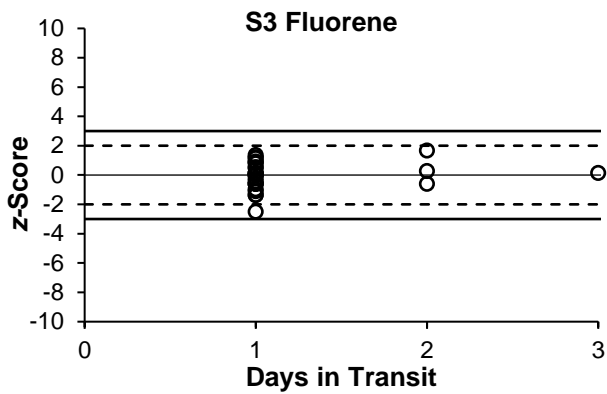
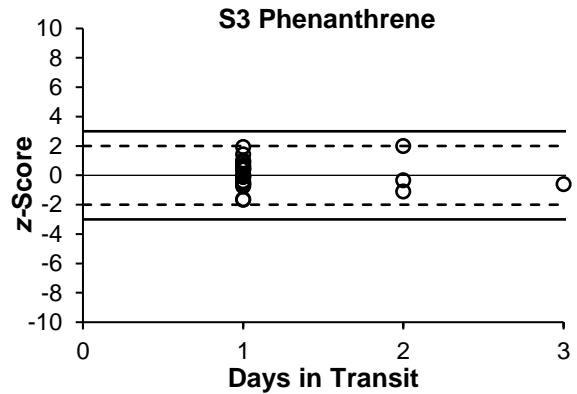Figure 47 S3 Fluorene vs Transit Days

Figure 48 S3 Phenanthrene vs Transit Days
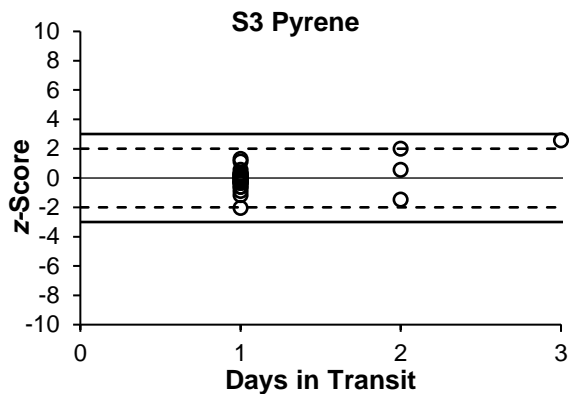
Figure 49 S3 Pyrene vs Transit Days
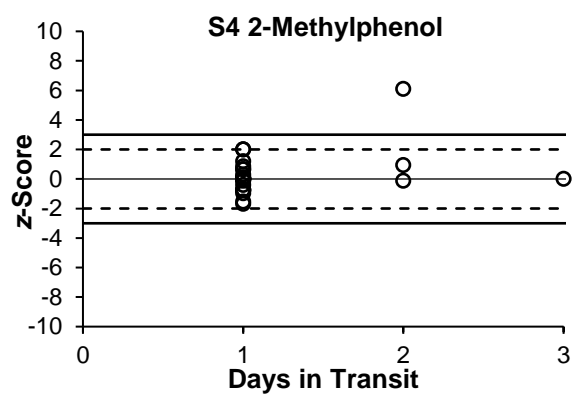
Figure 50 S4 2-Methylphenol vs Transit Days
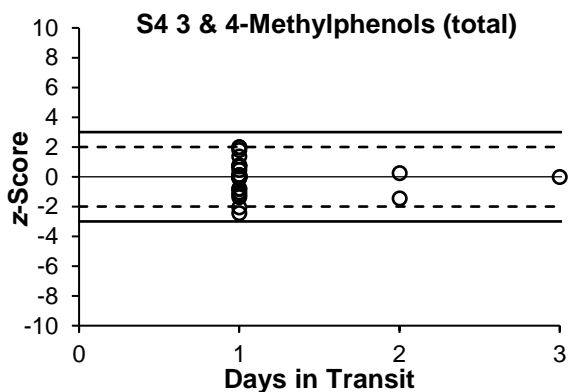
Figure 51 S4 3 & 4-Methylphenol (total) vs Transit Days
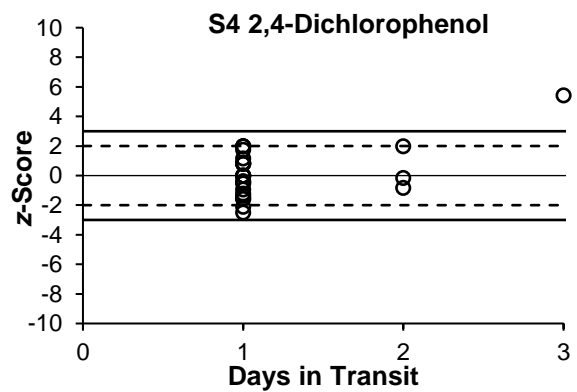
Figure 52 S4 2,4-Dichlorophenol vs Transit Days
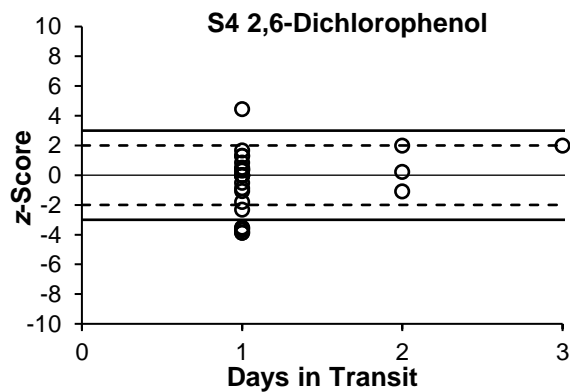
Figure 53 S4 2,6-Dichlorophenol vs Transit Days

AQA 23-21 Hydrocarbons and Phenols in River Water

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.[7] The associated uncertainties were estimated as according to Equation 4.

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

where:

$u_{rob\ av}$	is the standard uncertainty of the robust average
$S_{rob\ av}$	is the standard deviation of the robust average
p	is the number of results

The expanded uncertainty ($U_{rob\ av}$) is the standard uncertainty multiplied by a coverage factor of 2 at approximately 95% confidence level.

A worked example is set out below in Table 35.

Table 35 Uncertainty of the Robust Average for Sample S3 Fluorene

Number of results (p)	25
Robust Average	1.76 µg/L
$S_{rob\ av}$	0.27 µg/L
$u_{rob\ av}$	0.07 µg/L
k	2
$U_{rob\ av}$	0.14 µg/L

Therefore, the robust average for fluorene in Sample S3 is 1.76 ± 0.14 µg/L.

A3.2 z-Score and E_n-Score Calculation

For each participant's result, a *z*-score and E_n-score are calculated according to Equations 2 and 3 respectively (Section 4).

A worked example is set out below in Table 36.

Table 36 *z*-Score and E_n-Score for Sample S1 >C16-C34 Result Reported by Laboratory 13

Participant Result (µg/L)	Assigned Value (µg/L)	Target Standard Deviation	*z*-Score	E_n-Score
920 ± 400	810 ± 130	20% as PCV, or: $0.2 \times 810 = 162$ µg/L	$z = \dfrac{920 - 810}{162}$ $= 0.68$	$E_n = \dfrac{920 - 810}{\sqrt{400^2 + 130^2}}$ $= 0.26$

APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 37 to 40. Some responses may be modified so that the participant cannot be identified.

Table 37 Methodology – Sample S1 TRH

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	100	Liquid-Liquid	DCM		GC-FID	In-house Method
2	100	Liquid-Liquid	Ace/DCM	None	GC-FID	USEPA 8270
3	100	Solvent extraction	Hexane	None	GC-FID	USEPA 8015
4	500	Liquid-Liquid	DCM	None	GC-FID	USEPA 3510
5	250	Liquid-Liquid	DCM	None	GC-FID	In-house based in USEPA 8000B & NEPM
6	500	SPE	Hexane	None	GC-FID	USEPA 8015D
7	200	Liquid-Liquid	DCM	None	GC-FID	In-house Method
8	NS					
9	40	Liquid-Liquid	Hexane	None	GC-FID	USEPA 8015D
10	35	Liquid-Liquid	DCM	None	GC-FID	USEPA 8015
12	500	Liquid-Liquid	Hexane	Yes	GC-FID	In-house Method
13	500	Liquid-Liquid	DCM	None	GC-FID	USEPA 3510
14						
15	500	Liquid-Liquid	DCM	None	GC-MS	
16	500	Liquid-Liquid	DCM	None	GC-FID	USEPA 8260
17	500	Liquid-Liquid	DCM	None	GC-FID	
18	35	Liquid-Liquid	DCM	None	GC-FID	USEPA 8015
19	500	Liquid-Liquid	DCM	None	GC-FID	In-house Method
20	100	Liquid-Liquid	DCM	None	GC-FID	In-house Method
21	500	Liquid-Liquid	DCM	Silica	GC-FID	In-house Method

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
22	450	Liquid-Liquid	DCM	None	GC-FID	USEPA 8015
23	200	Liquid-Liquid	DCM	None	GC-FID	USEPA 8260
24	500	Liquid-Liquid	DCM	None	GC-FID	In-house Method
25	500	Liquid-Liquid	DCM	None	GC-FID	USEPA 3510
26	50	Liquid-Liquid	DCM	None	GC-FID	
27	NT					
28	500	Liquid-Liquid	DCM	None	GC-FID	USEPA SW846-8015
29	35	Liquid-Liquid	DCM	None	GC-FID	USEPA8260

Table 38 Methodology – Sample S2 BTEX

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	40	Liquid-Liquid	NONE		P&T GC-MS	In-house Method
2	44	Direct inject	NA	None	P&T GC-MS	USEPA 8260
3	10	Headspace	-	-	Headspace GC-MS	USEPA 8260 & 5021
4	25	Purge and Trap	None	None	P&T GC-MS	USEPA 8260
5	10	Headspace	MEOH	None	Headspace GC-MS	In-house based in USEPA 8000B & 8260B
6	40	Direct Injection	None	None	P&T GC-MS	USEPA 524.3
7	10	Headspace	None	None	Headspace GC-MS	In-house Method
8	NS					
9	10	Headspace	None	None	Headspace GC-MS	USEPA 5021A
10	5	N/A		None	P&T GC-MS	USEPA 8260
12	42			None	P&T GC-MS	In-house Method
13	25	Purge and Trap	None	None	P&T GC-MS	USEPA 8260
14		None	None	None	Headspace GC-MS	USEPA 8260B

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
15						
16	40	N/A	N/A	None	P&T GC-MS	USEPA 8260
17	5	N/A	N/A	None	P&T GC-MS	
18	43	Liquid-Gas	Nitrogen Gas	None	P&T GC-MS	USEPA 8260
19	40	Purge & Trap		None	P&T GC-MS	In-house Method
20	5	None	None	None	P&T GCMS	USEPA 8260
21	5	None		None	P&T GC-MS	USEPA 8260
22	5				P&T GC-MS/MS	USEPA 8260
23	44				P&T GC-MS/MS	USEPA 8260
24	5	P&T	Helium	None	P&T GCMS	In-house method
25	44	Purge and Trap	None	None	P&T GC-MS	USEPA 8260
26	44	Liquid-Liquid	Methanol	None	P&T GC-MS	
27		SPE			Headspace GC-MS/MS	USEPA 524.2
28	5	Liquid-Liquid	N/A	None	P&T GC-MS	USEPA SW846-8260
29	43				P&T GC-MS	USEPA8260

Table 39 Methodology – Sample S3 PAHs

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	35	Liquid-Liquid	DCM		GC-MS/MS	In-house Method
2	100	Liquid-Liquid	Ace/DCM	None	GC-MS	USEPA 8270
3	250	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
4	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
5	200	Liquid-Liquid	DCM	None	GC-MS	In-house based on USEPA 3550, 3510 & 8270C
6	500	SPE	DCM/EtOAc	None	GC-MS	USEPA 525.3

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
7	200	Liquid-Liquid	DCM	None	GC-MS/MS	In-house Method
8	96	Liquid-Liquid	DCM	N/A	GC-MS/MS	USEPA 8270D
9	40	Liquid-Liquid	Hexane	None	GC-MS	USEPA8270D
10	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
12	500	Liquid-Liquid	DCM/Acetone	None	GC-MS/MS	In-house Method
13	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
14	NS					
15	500	Liquid-Liquid	DCM	None	GC-MS	
16	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
17	100	Liquid-Liquid	DCM	None	GC-MS	
18	35	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
19	500	Liquid-Liquid	DCM	None	GC-MS	In-house Method
20	100	Liquid-Liquid	DCM	None	GCMS	USEPA 8270
21		SPE	DCM/EtOAc	None	GC-MS	USEPA 8270
22	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
23	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
24	500	Liquid-Liquid	DCM	None	GC-MS	In-house Method
25	500	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
26	50	Liquid-Liquid	DCM	None	GC-MS	
27	NS					
28	100	Liquid-Liquid	DCM	None	GC-MS	USEPA SW846-8270
29	35	Liquid-Liquid	DCM		GC-MS/MS	USEPA8260

Table 40 Methodology – Sample S4 Phenols

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	35	Liquid-Liquid	DCM		GC-MS/MS	In-house Method
2	100	Liquid-Liquid	Ace/DCM	None	GC-MS	USEPA 8270
3	100	Liquid-Liquid	DCM	None	GC-MS	US EPA 8270
4	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
5	200	Liquid-Liquid	DCM	None	GC-MS	In-house based on USEPA 3550, 3510 & 8270C
6	100	SPE	DCM/EtOAc	None	GC-MS	USEPA 525.3
7	1	direct injection	None	None	LC-MS/MS	In-house Method
8	NS					
9	40	Liquid-Liquid	Hexane	None	GC-MS	USEPA 8270D
10	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
12	100	Liquid-Liquid	DCM/ Acetone	None	GC-MS/MS	In-house Method
13	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
14	NS					
15	500	Liquid-Liquid	DCM	None	GC-MS	
16	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
17	100	Liquid-Liquid	DCM	None	GC-MS	
18	35	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
19	30	Liquid-Liquid	DCM	None	GC-MS	In-house Method
20	100	Liquid-Liquid	DCM	None	GCMS	USEPA 8270
21	10	SPME	None	None	GC-MS	In-house Method
22	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
23	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
24	200	Liquid-Liquid	DCM	None	GC-MS	In-house Method

Lab. Code	Sample Volume (mL)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
25	500	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
26	50	Liquid-Liquid	DCM	None	GC-MS	
27	NS					
28	100	Liquid-Liquid	DCM	None	GC-MS	USEPA SW846-8270
29	35	Liquid-Liquid	DCM		GC-MS/MS	USEPA8260

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

ACE	Acetone
AV	Assigned Value
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
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
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
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
MU	Measurement Uncertainty
N	Number of numeric results
NATA	National Association of Testing Authorities, Australia
NEPM	National Environmental Protection Measure
NMI	National Measurement Institute, Australia
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
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)
TRH	Total Recoverable Hydrocarbons
USEPA	United States Environmental Protection Agency

END OF REPORT