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Department of Industry, Science, Energy and Resources
National Measurement Institute

Proficiency Test Final Report AQA 20-15 Hydrocarbons in Water

March 2021

ACKNOWLEDGMENTS

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

I would like to thank the management and staff of the participating laboratories for supporting the study. It is only through widespread participation that we can provide an effective service to laboratories.

The assistance of the following NMI staff members in the planning, conduct and reporting of the study is acknowledged.

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SUMMARY

AQA 20-15 Hydrocarbons in Water commenced in November 2020. Twenty-three laboratories registered to participate and all participants submitted results.

The sample set consisted of four water samples. Samples were prepared in the North Ryde NMI laboratory using surface water from Browns Waterhole in Sydney. Participants measured total recoverable hydrocarbons (TRH) in Sample S1, volatile hydrocarbons (C6 to C10), benzene, toluene, ethylbenzene and xylenes (BTEX) in Sample S2 and polycyclic aromatic hydrocarbons (PAH) in Samples S3 and 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 petroleum hydrocarbon pollutants in water.*

Laboratories **1**, **2**, **3**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **17**, **18**, **22** and **23** reported results for all 22 analytes which were scored. For Sample S1, some participants reported hydrocarbon ranges outside of the recommended National Environment Protection Measure (NEPM) ranges.

One laboratory reported results for analytes not added to the test samples (total of 2 results).

Of 448 results for which z-scores were calculated, 399 (89%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Of 448 results for which E_n-scores were calculated, 352 (79%) 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 **1**, **9** and **18** returned satisfactory z-scores and E_n-scores for all 22 analytes for which scores were calculated. All results reported by Laboratories **5** (21), **20** (20), **16** (8) and **4** (1) also returned satisfactory z-scores and E_n-scores.

- *Evaluate the laboratories' test methods.*

For TRH analysis participants used liquid-liquid extraction, with various extraction solvents. GC-FID was the instrument of choice, though one participant reported using GC-MS.

For BTEX analysis, 14 participants used purge-and-trap while 5 participants used headspace. The majority of participants used GC-MS, except for one who reported using GC-FID.

For PAH analysis two participants used solid phase extraction, while all other participants used liquid-liquid extraction. A variety of extraction solvents were used. All participants used GC-MS(MS).

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

Of 466 numerical results, 445 (95%) were reported with an associated expanded measurement uncertainty.

Reported expanded uncertainties were within the range 1.6% to 77% relative.

- *Compare the performance of participants with past performance.*

Taken as a group, the performance for TRH has been improving over the last few studies. For BTEX, participants' performance has remained relatively good, with high proportions of satisfactory z-scores and E_n-scores. For PAH, participants' performance has also remained fairly consistent.

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

The test samples of this PT study are homogeneous and are well characterised. Surplus of these samples is 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: '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 and vegetables, water and soil;
- petroleum hydrocarbons in water and soil;
- PFAS in water, soil, biota and food;
- inorganic analytes in water, soil, food and pharmaceuticals;
- controlled drug assay 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 petroleum hydrocarbon pollutants in water;
- evaluate the laboratories' test methods;
- develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates;
- compare the performance of participants with past performance; 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[1] as a provider of proficiency testing schemes. This study falls within the scope of NMI's accreditation as a proficiency testing provider.

2 STUDY INFORMATION

2.1 Selection of Hydrocarbons

The hydrocarbons in this study, and their concentrations, were typical of those encountered by environmental testing laboratories monitoring 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 hydrocarbons 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]

A list of potential PAH for Samples S3 and S4 is presented in Table 1.

Table 1 List of Possible PAH for Samples S3 and S4

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

The actual spiked concentrations in each sample is presented in Table 2.

Table 2 Formulated Concentrations of Samples

Sample	Analyte	Spike (µg/L)	Uncertainty (µg/L)*
S1	TRH	3410	170
S2	Benzene	57.9	2.9
	Toluene	219	11
	Ethylbenzene	25.0	1.3
	Xylenes	188	9
	Total BTEX	489	24
S3	Anthracene	12.0	0.6
	Benzo(a)pyrene	5.00	0.25
	Chrysene	6.03	0.30
	Fluoranthene	5.85	0.29
	Fluorene	14.1	0.7
	Phenanthrene	2.02	0.10
	Pyrene	20.1	1.0
S4	Anthracene	7.06	0.35
	Benzo(a)pyrene	5.00	0.25
	Chrysene	15.1	0.8
	Fluoranthene	19.0	0.9
	Fluorene	17.0	0.8
	Phenanthrene	12.0	0.6
	Pyrene	6.43	0.32

* Estimated expanded uncertainty at approximately 95% confidence using a coverage factor of 2.

2.2 Study Timetable

The timetable of this study was:

Invitation issued	2 November 2020
Samples dispatched	26 November 2020
Results due	8 January 2021
Interim report issued	13 January 2021

2.3 Participation

Twenty-three laboratories registered to participate, and all participants submitted results.

2.4 Laboratory Code

All participants were assigned a confidential laboratory code number for this study.

2.5 Sample Preparation

Four test samples were prepared using water taken from the Browns Waterhole, Turramurra.

Sample S1 (TRH) was spiked with diesel fuel.

Sample S2 (BTEX) was spiked with unleaded petrol and diesel fuel.

Samples S3 and **S4 (PAH)** were spiked with differing amounts of anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.

Additional information on sample preparation is given in Appendix 1.

2.6 Homogeneity of Samples

All samples were prepared and packaged using a process that has been demonstrated to produce homogeneous samples in previous NMI Hydrocarbons in Water PT studies. No homogeneity testing was conducted for this study, and participants' results gave no reason to question the homogeneity of these samples.

2.7 Stability of Analytes

The storage stability of petroleum hydrocarbons spiked into water samples has been previously established.[6] No stability study was conducted for this study, and to assess possible instability, the results returned by participants were compared to the spiked concentration.

For Sample S1 TRH, the robust average was 57% of the spiked value. This is similar to values observed in previous Hydrocarbons in Water PT studies, and as there was also reasonable consensus between participants' results, an assigned value was set.

For Sample S2 BTEX, the robust averages of scored analytes were between 81 – 101% of the spiked values, providing good support for the stability of these analytes.

For Samples S3 and S4 PAH, the robust averages of scored analytes (excluding fluorene) were between 71 – 88%, providing good support for the stability of these analytes. For Samples S3 and S4 fluorene, the robust average was 57% and 55% of the spiked value respectively, but there was a good consensus between participants' results and so an assigned value was set.

2.8 Sample Storage, Dispatch and Receipt

The test samples were stored in a cool room at approximately 4°C prior to dispatch. Samples were dispatched on 26 November 2020.

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 e-mailed to participants.

2.9 Instructions to Participants

Participants were instructed as follows:

- Report results for the following:
  - S1: Semi-volatile hydrocarbons (>C10-C40). Australian NEPM fractions >C10-C16, >C16-C34, >C34-C40 are encouraged. The concentration range is between 200 – 10000 µg/L.
  - S2: Volatile Hydrocarbons (C6-C10), Benzene, Toluene, Ethylbenzene and Total Xylenes and Total BTEX. Individual BTEX components concentration is between 0.2 – 800 µg/L.
  - S3 and S4: Poly-aromatic hydrocarbons. The concentration range is between 0.05 – 50 µg/L.
- Report results on the electronic results sheet emailed to you.
- No limit of reporting has been set for this study. Report results as you would report them 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.
- Report semi-volatile hydrocarbons in Sample S1 using your laboratory's chosen quantitation range, and indicate what this range is. Use of the NEPM guideline ranges is encouraged.
- For each analyte in each sample, report the analytical results in units of µg/L together with an associated expanded uncertainty (e.g. 2000 ± 200 µg/L).
- Report your methodology information and the basis of your uncertainty estimates as requested on the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by e-mail (proficiency@measurement.gov.au).
- Please return results by 16 December 2020. Late results may not be included in the study report.

The results due date was extended to 8 January 2021 due to sample courier delivery delays and to account for end-of-year shutdown periods.

2.10 Interim Report

An interim report was emailed to all participants on 13 January 2021.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Participants' Test Methods

Participants were requested to provide information about their test methods. Responses are presented in Appendix 2.

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about their basis of measurement uncertainty. Responses are presented in Table 3.

Table 3 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	Professional judgment	Control samples - RM	CRM	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
2	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
3	All	Top Down - precision and estimates of the method and laboratory bias	Instrument calibration	CRM	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
4	TRH	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis Instrument calibration	CRM Instrument calibration	IANZ technical guide Measurement Uncertainty,precision and Limits of Detection
	BTEX / PAH	NT			
5	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
6	All	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
7	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
8	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
9	All	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS	Recoveries of SS	
10	All	control charts determine measurement uncertainty	Control samples - CRM	Recoveries of SS	ISO/GUM

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
11	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
12	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
13	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
14	TRH / PAH	Standard deviation of replicate analyses multiplied by 2 or 3		CRM Recoveries of SS	ISO/GUM
	BTEX		Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	
15	TRH / BTEX	NT			
	PAH		Control samples - CRM	CRM	
16	TRH / BTEX	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
	PAH	NT			
17	All	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples Duplicate analysis Instrument calibration	Laboratory bias from PT studies CRM Instrument calibration Recoveries of SS Standard purity	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
18	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	CRM Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
19	TRH / PAH	calculation of MU at each level	Duplicate analysis	Recoveries of SS	
	BTEX	NT			
20	All	Based on historical data	Duplicate analysis Instrument calibration	Instrument calibration Standard purity	Eurachem/CITAC Guide
21	All	Replicate data during validation			
22	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	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
23	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results

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

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, and the study coordinator's response (if applicable) are presented in Table 4.

Table 4 Additional Comments or Discussion of Results

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
3	S2	The samples had slight leakage before testing.	Sample receipt notification from your laboratory has marked the received samples as fit for analysis. Any problems with the samples should be reported as soon as possible and NMI will replace the sample if deemed necessary.
4	S1	Our Current range is C21 for test method but we did detect peaks greater than C21 but did not quantify these.	
14	S2	Average of duplicate analysis has been reported	
20	S2	C6-C9 result reported above.	
23	S2	Sample condition: "One BTEX vial broken"	Sample receipt notification from your laboratory has marked the samples as being received at ambient temperature, but no broken vials. Any problems with the samples should be reported as soon as possible and NMI will replace the sample if deemed necessary.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 29 with resultant summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max.), minimum (Min.), robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV).

Bar charts of results and performance scores are presented in Figures 2 to 24.

An example chart with interpretation guide is shown in Figure 1.

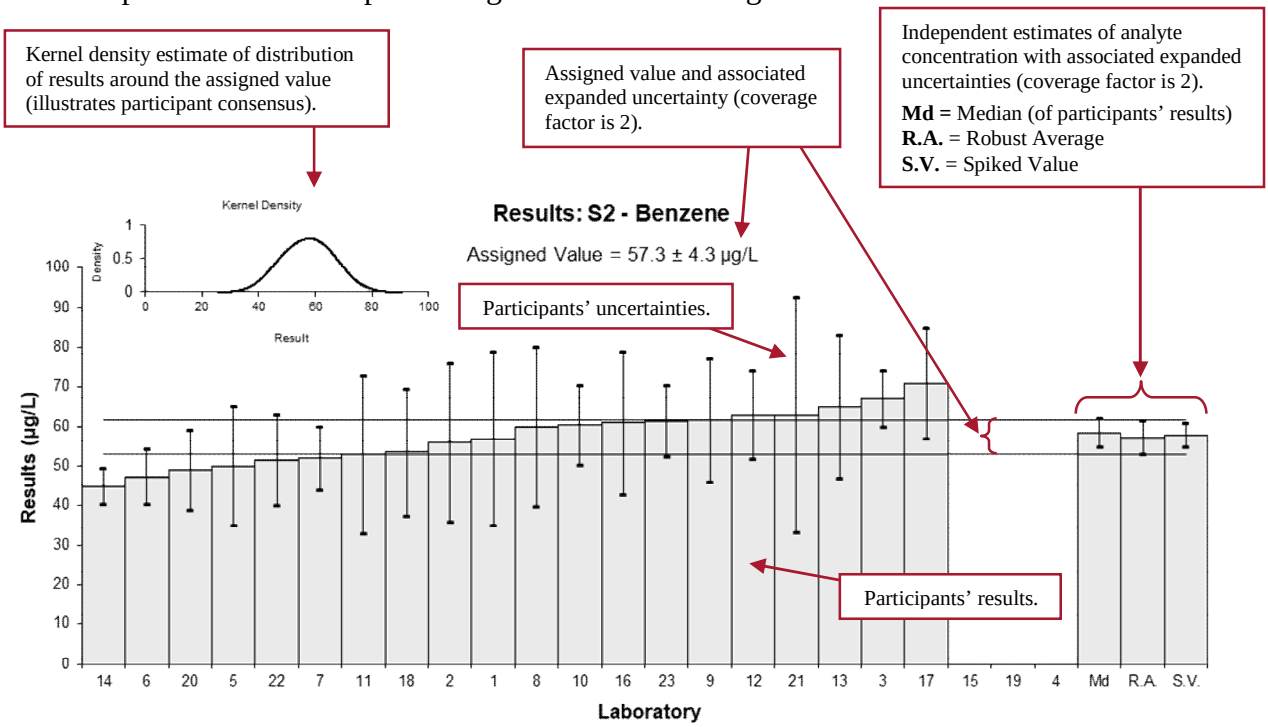


Figure 1 Guide to Presentation of Results

4.2 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).

4.3 Robust Average and Robust Between Laboratory Coefficient of Variation

The robust averages and associated expanded MUs, and robust CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528:2015.[7]

4.4 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a fixed measure of the between laboratory variation that in the judgement of the study organiser would be expected from participants, given the analyte concentrations. It is important to note that this is set by the study coordinator; it is not the CV of participants' results. The PCV 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' performance and can be compared from study to study.

4.5 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (X) and the PCV, as presented in Equation 1. This value is used in the calculation of z-scores.

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

4.6 z-Score

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

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

where:

z is z-score

χ is a participant's result

X is the assigned value

σ is the target standard deviation from Equation 1

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

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

4.7 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 satisfactory;
- $|E_n| > 1.0$ is unsatisfactory.

4.8 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 5

Sample Details

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

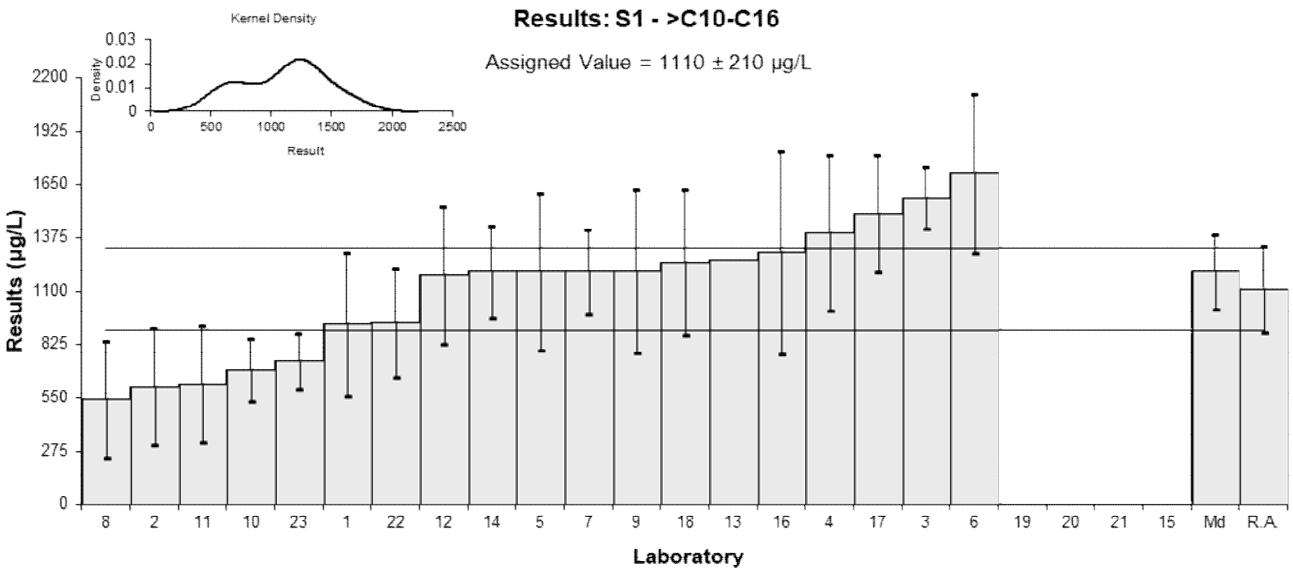
Participant Results

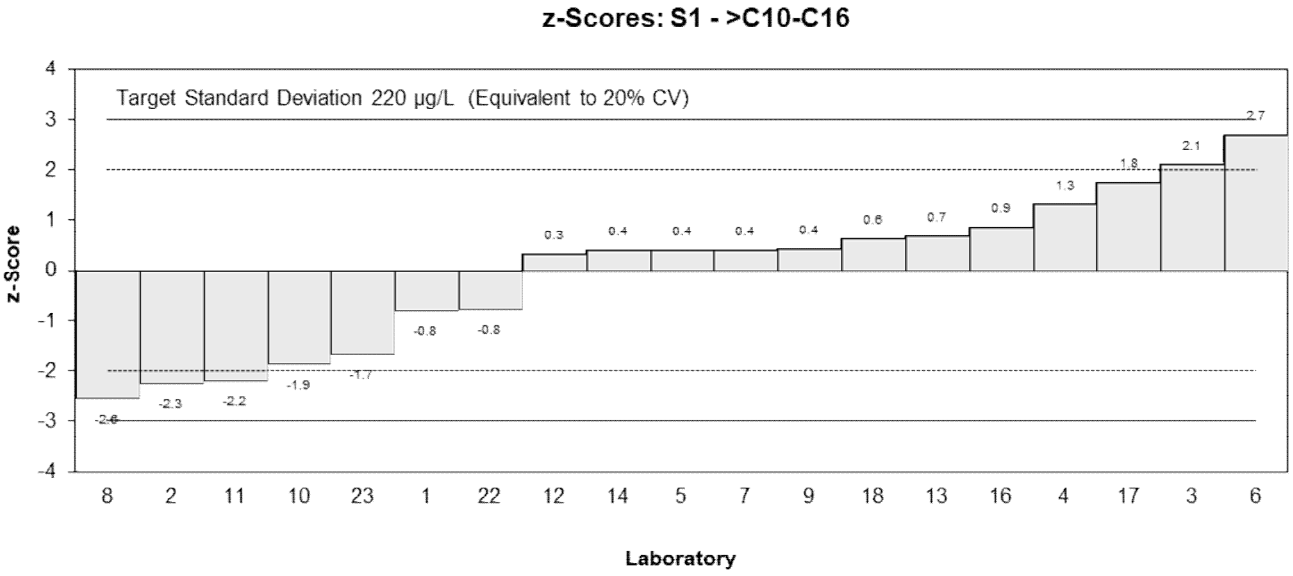
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	930	370	-0.81	-0.42
2	610	300	-2.25	-1.37
3	1580	158	2.12	1.79
4	1400	400	1.31	0.64
5	1200	400	0.41	0.20
6	1710	410	2.70	1.30
7	1200	220	0.41	0.30
8	540	300	-2.57	-1.56
9	1202.9	421.02	0.42	0.20
10	693	161	-1.88	-1.58
11	620	300	-2.21	-1.34
12	1182	355	0.32	0.17
13	1260	NR	0.68	0.71
14	1200	240	0.41	0.28
15	NT	NT		
16	1300	520	0.86	0.34
17	1500	300	1.76	1.07
18	1250	375	0.63	0.33
19	NR	NR		
20	NR	NR		
21	NR	NR		
22	938.1	281	-0.77	-0.49
23	740	140	-1.67	-1.47

Statistics

Assigned Value*	1110	210
Spike	Not Spiked	
Robust Average	1110	220
Median	1200	190
Mean	1110	
N	19	
Max.	1710	
Min.	540	
Robust SD	390	
Robust CV	35%	

* Robust average excluding Laboratories 6 and 8.


Results: S1 - >C10-C16
Kernel Density
Density
Result
Assigned Value = 1110 ± 210 µg/L
Results (µg/L)
Laboratory
8 2 11 10 23 1 22 12 14 5 7 9 18 13 16 4 17 3 6 19 20 21 15 Md R.A.


z-Scores: S1 - >C10-C16
Target Standard Deviation 220 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
8 2 11 10 23 1 22 12 14 5 7 9 18 13 16 4 17 3 6

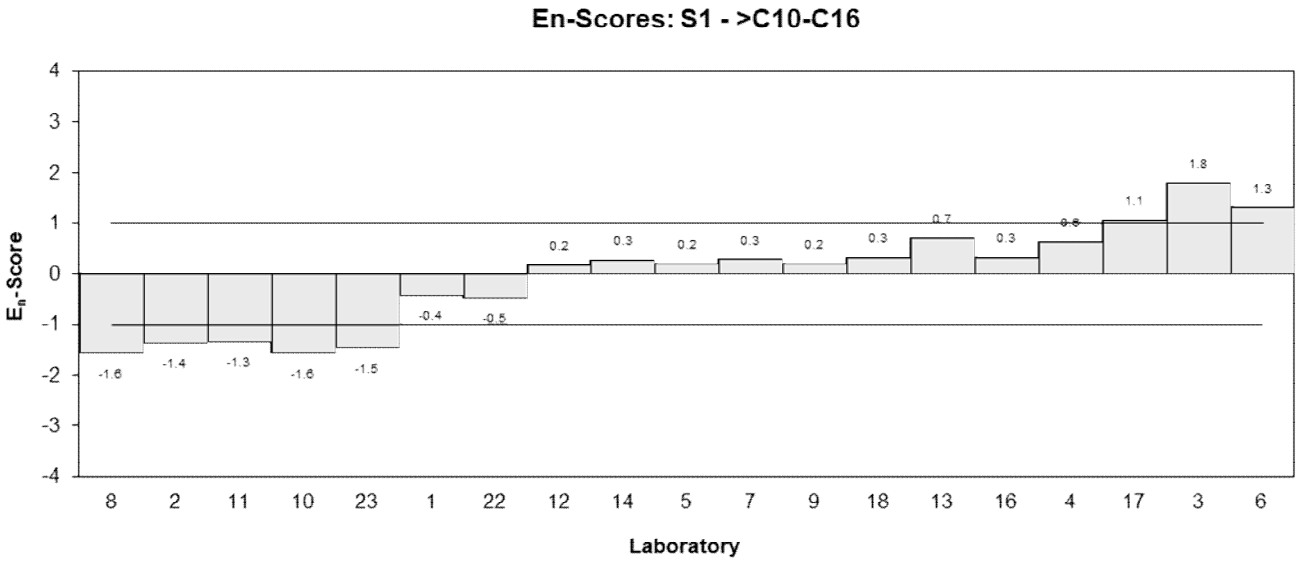

En-Scores: S1 - >C10-C16
En-Score
Laboratory
8 2 11 10 23 1 22 12 14 5 7 9 18 13 16 4 17 3 6

Figure 2

Table 6

Sample Details

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

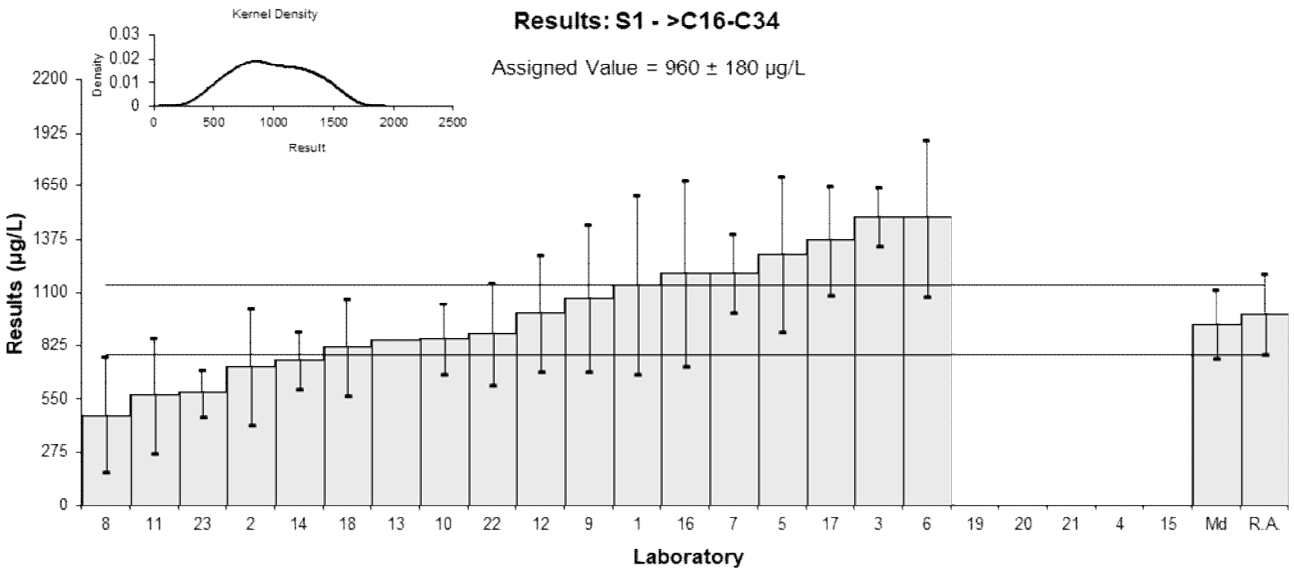
Participant Results

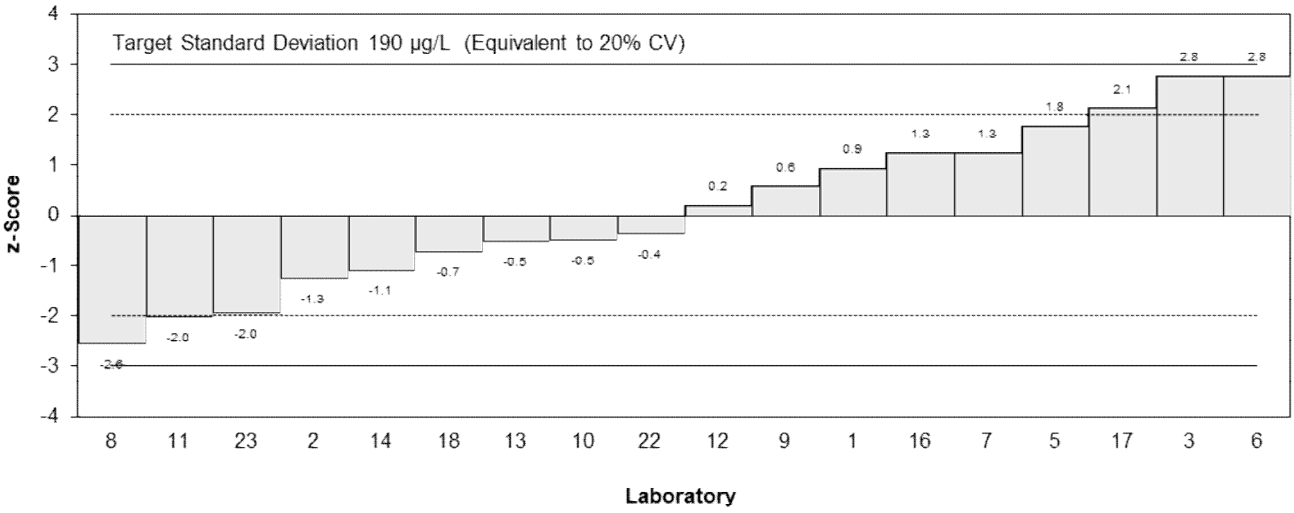
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1140	460	0.94	0.36
2	720	300	-1.25	-0.69
3	1490	149	2.76	2.27
4	NR	NR		
5	1300	400	1.77	0.78
6	1490	405	2.76	1.20
7	1200	200	1.25	0.89
8	470	300	-2.55	-1.40
9	1072.9	375.52	0.59	0.27
10	863	184	-0.51	-0.38
11	570	300	-2.03	-1.11
12	998.7	300	0.20	0.11
13	860	NR	-0.52	-0.56
14	750	150	-1.09	-0.90
15	NT	NT		
16	1200	480	1.25	0.47
17	1370	275	2.14	1.25
18	820	250	-0.73	-0.45
19	NR	NR		
20	NR	NR		
21	NR	NR		
22	888.2	266	-0.37	-0.22
23	584	120	-1.96	-1.74

Statistics

Assigned Value*	960	180
Spike	Not Spiked	
Robust Average	990	210
Median	940	180
Mean	990	
N	18	
Max.	1490	
Min.	470	
Robust SD	360	
Robust CV	36%	

* Robust average excluding Laboratories 3, 6 and 8.


Kernel Density
Density
Result
Results: S1 - >C16-C34
Assigned Value = 960 ± 180 µg/L
Results (µg/L)
Laboratory
8 11 23 2 14 18 13 10 22 12 9 1 16 7 5 17 3 6 19 20 21 4 15 Md R.A.


z-Scores: S1 - >C16-C34
Target Standard Deviation 190 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
8 11 23 2 14 18 13 10 22 12 9 1 16 7 5 17 3 6

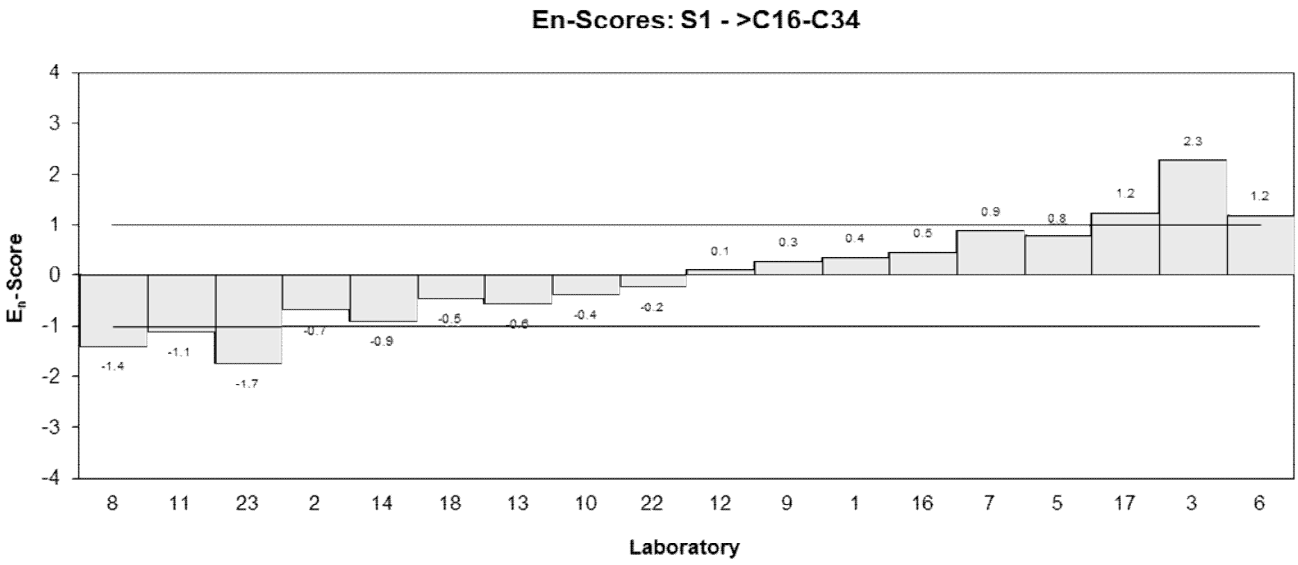

En-Scores: S1 - >C16-C34
En-Score
Laboratory
8 11 23 2 14 18 13 10 22 12 9 1 16 7 5 17 3 6

Figure 3

Table 7

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	<500	500
2	<100	NR
3	<100	NR
4	NR	NR
5	<500	NR
6	<200	NR
7	<100	NR
8	<100	NR
9	<100	30
10	250	54
11	<100	NR
12	< 100	10
13	<200	NR
14	< 100	NR
15	NT	NT
16	<100	NR
17	<100	NR
18	<100	NR
19	<50	50
20	NR	NR
21	NR	NR
22	< 100	30
23	<100	24

Statistics

Insufficient data to calculate statistics.

Table 8 Additional hydrocarbon ranges to those defined in Schedule B3 of the NEPM[5] reported by participants for Sample S1

Lab. Code	Range	Result (µg/L)	Uncertainty (µg/L)
4	>C16 – C21	1000	400
19	>C6 – C10	<10	10
	>C10 – C34	1250	100
20	C7 – C9	<100	67
	C10 – C14	490	160
	C15 – C36	1180	310
21	C7 – C9	<200	NR
	C10 – C14	700	189
	C15 – C36	1100	209

Table 9

Sample Details

Sample No.	S1
Matrix	Water
Analyte	TRH
Units	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	2070	NR	0.79	0.67
2	1330	NR	-1.87	-1.58
3**	3070	307	2.00	1.00
4	NT	NT		
5**	2500	800	2.00	0.75
6**	3200	NR	2.00	1.00
7	2400	420	1.98	1.03
8	1010	NR	-3.03	-2.55
9	2275.8	826.5	1.53	0.48
10	1806	400	-0.16	-0.08
11	1200	500	-2.34	-1.08
12	1320	360	-1.91	-1.09
13	2100	NR	0.90	0.76
14	1900	380	0.18	0.10
15	NT	NT		
16**	2500	1000	2.00	0.62
17**	2870	575	2.00	1.00
18	2070	620	0.79	0.31
19	1250	100	-2.16	-1.74
20	1690	360	-0.58	-0.33
21	1800	378	-0.18	-0.10
22	1826.3	548	-0.09	-0.04
23	1324	260	-1.90	-1.25

Statistics

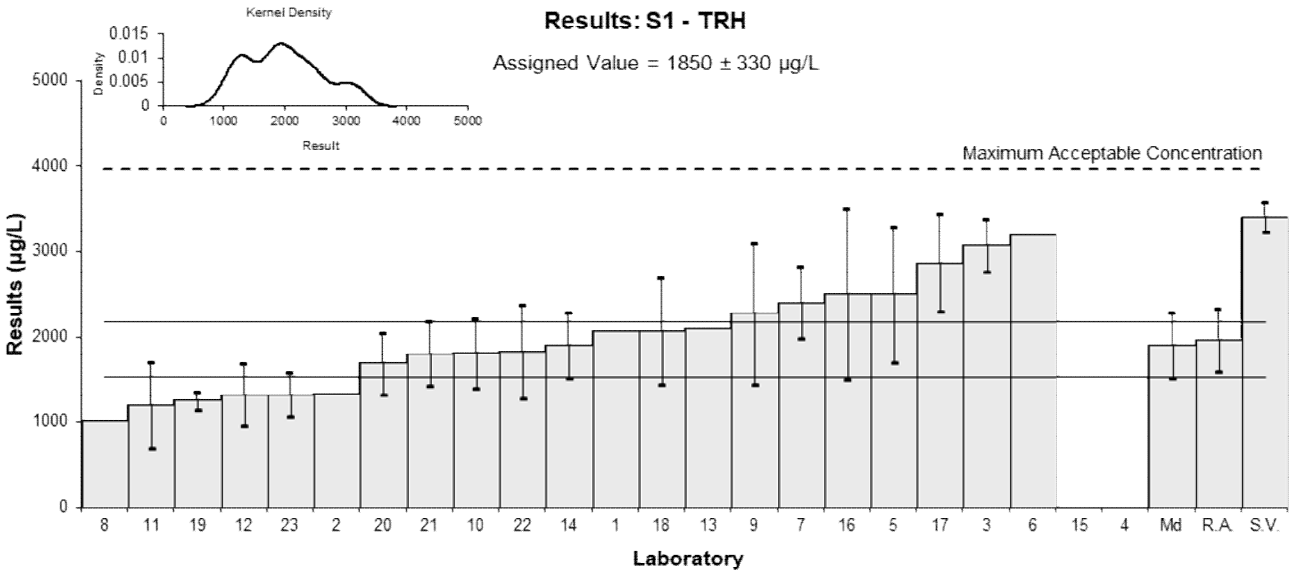
Assigned Value*	1850	330
Spike	3410	170
Max. Acceptable Conc.**	3970	
Robust Average	1960	370
Median	1900	380
Mean	1980	
N	21	
Max.	3200	
Min.	1010	
Robust SD	680	
Robust CV	35%	

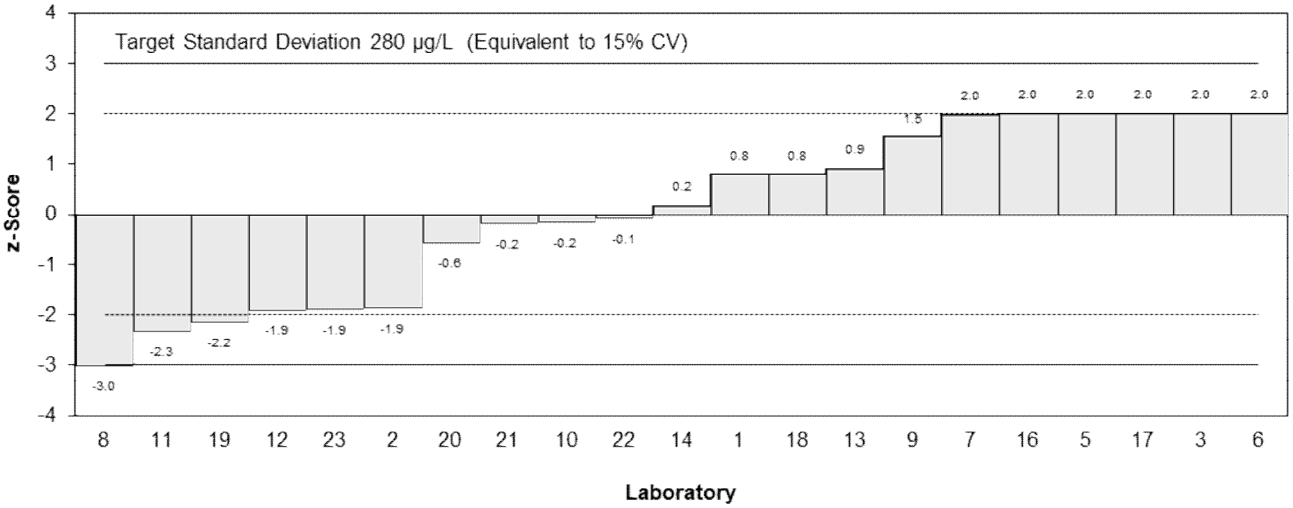
If a participant did not report a TRH value, the TRH result was calculated by the study coordinator by summing the individual hydrocarbon ranges reported, and no estimate of the uncertainty of the TRH result was made.

Laboratory 4 reported results up to C21 and noted that they detected but did not quantify peaks greater than C21; no TRH result was calculated for this participant by the study coordinator.

* Robust average excluding Laboratories 3 and 6.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S1 - TRH
Assigned Value = 1850 ± 330 µg/L
Maximum Acceptable Concentration
Results (µg/L)
Laboratory
8 11 19 12 23 2 20 21 10 22 14 1 18 13 9 7 16 5 17 3 6 15 4 Md R.A. S.V.


z-Scores: S1 - TRH
Target Standard Deviation 280 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
8 11 19 12 23 2 20 21 10 22 14 1 18 13 9 7 16 5 17 3 6

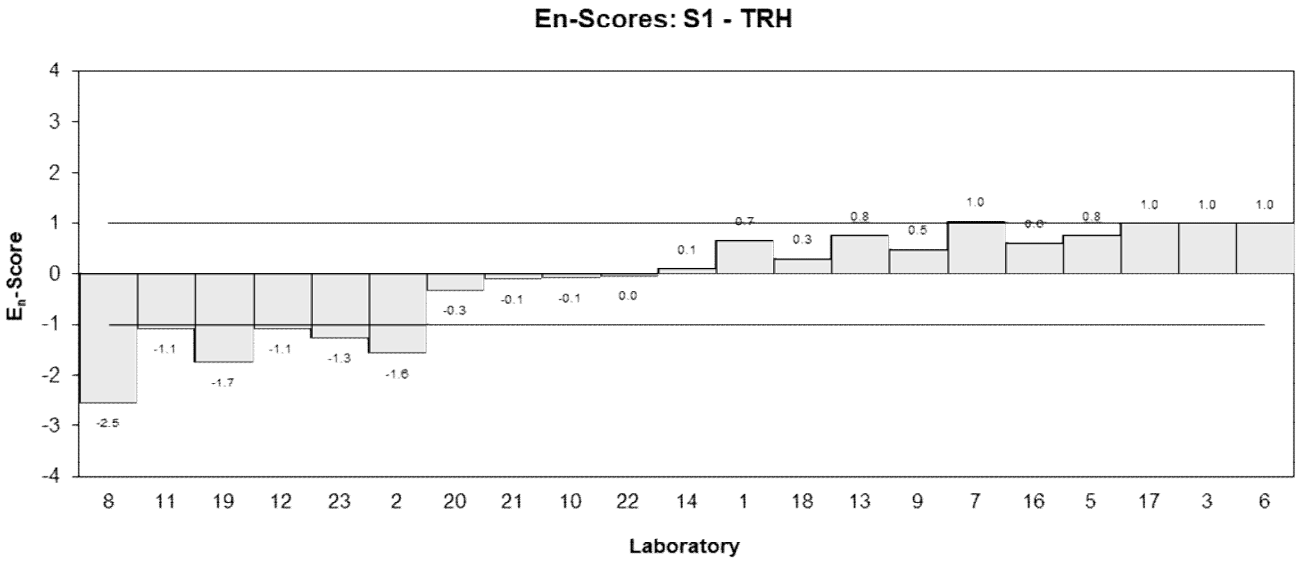

En-Scores: S1 - TRH
En-Score
Laboratory
8 11 19 12 23 2 20 21 10 22 14 1 18 13 9 7 16 5 17 3 6

Figure 4

Table 10

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	1000	400
2	1100	300
3	970	246
4	NT	NT
5	600	180
6	582	58
7	950	180
8	920	300
9	889.58	266.87
10	840	187
11	810	300
12	750	190
13	NT	NT
14	560	100
15	NT	NT
16	840	250
17	1170	235
18	907	281
19	NT	NT
20*	550	160
21	NT	NT
22	907	181
23	NT	NT

* C6 – C9 result reported.

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Robust Average	840	130
Median	890	61
Mean	844	
N	17	
Max.	1170	
Min.	550	
Robust SD	210	
Robust CV	25%	

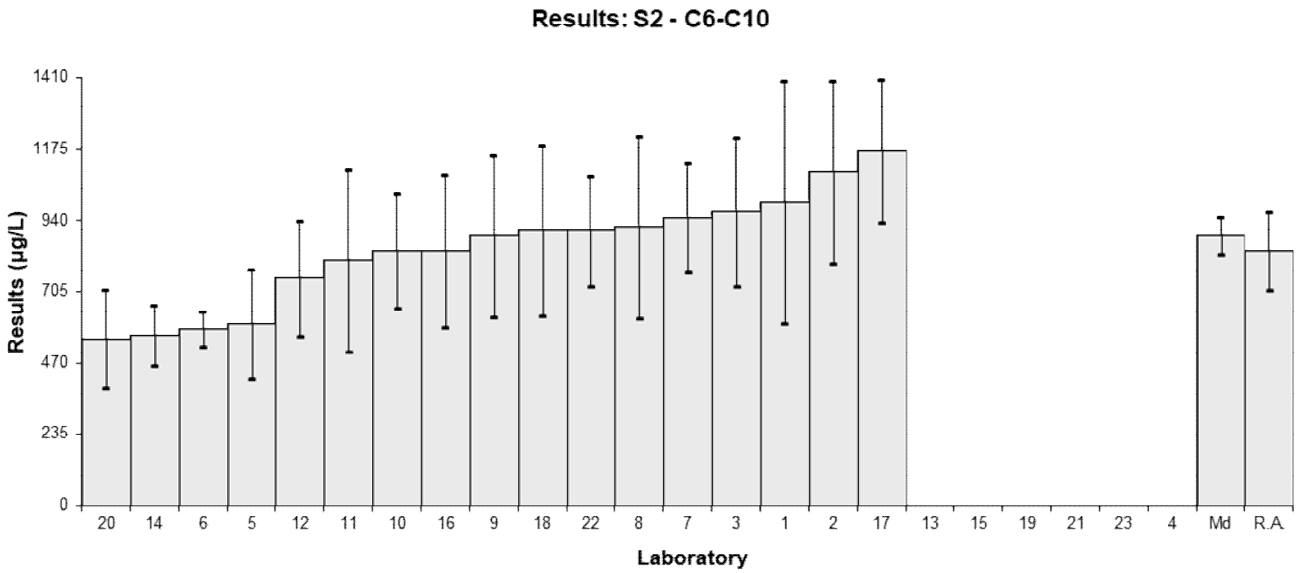

Results: S2 - C6-C10
Results (µg/L)
1410
1175
940
705
470
235
0
20
14
6
5
12
11
10
16
9
18
22
8
7
3
1
2
17
13
15
19
21
23
4
Md
R.A.
Laboratory

Figure 5

Table 11

Sample Details

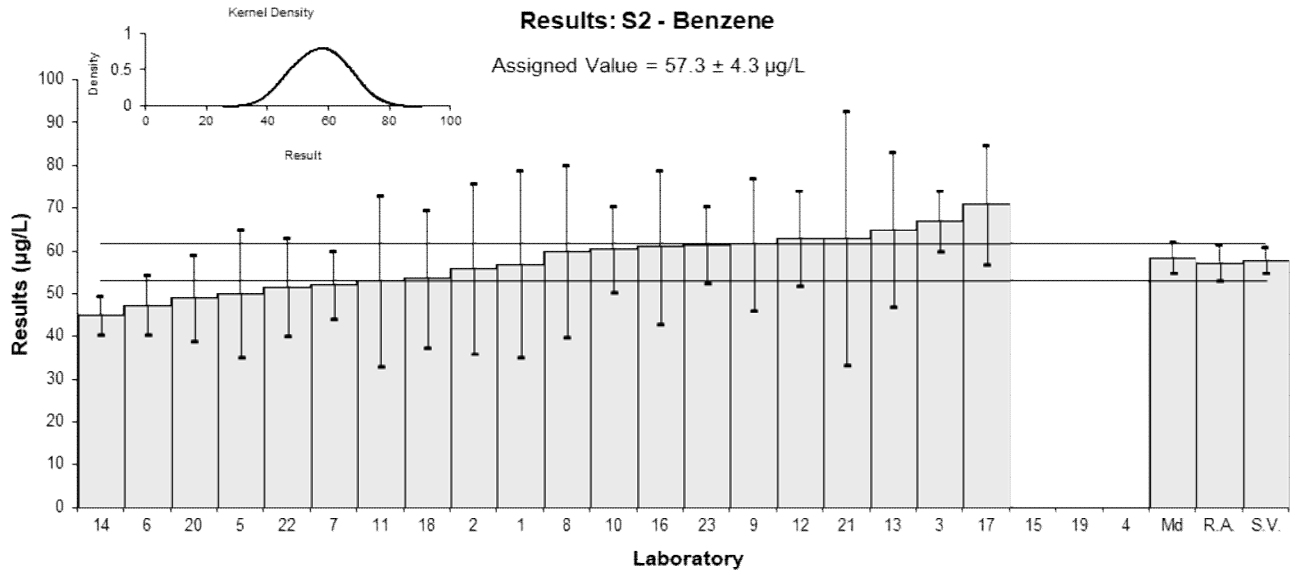
Sample No.	S2
Matrix	Water
Analyte	Benzene
Units	µg/L

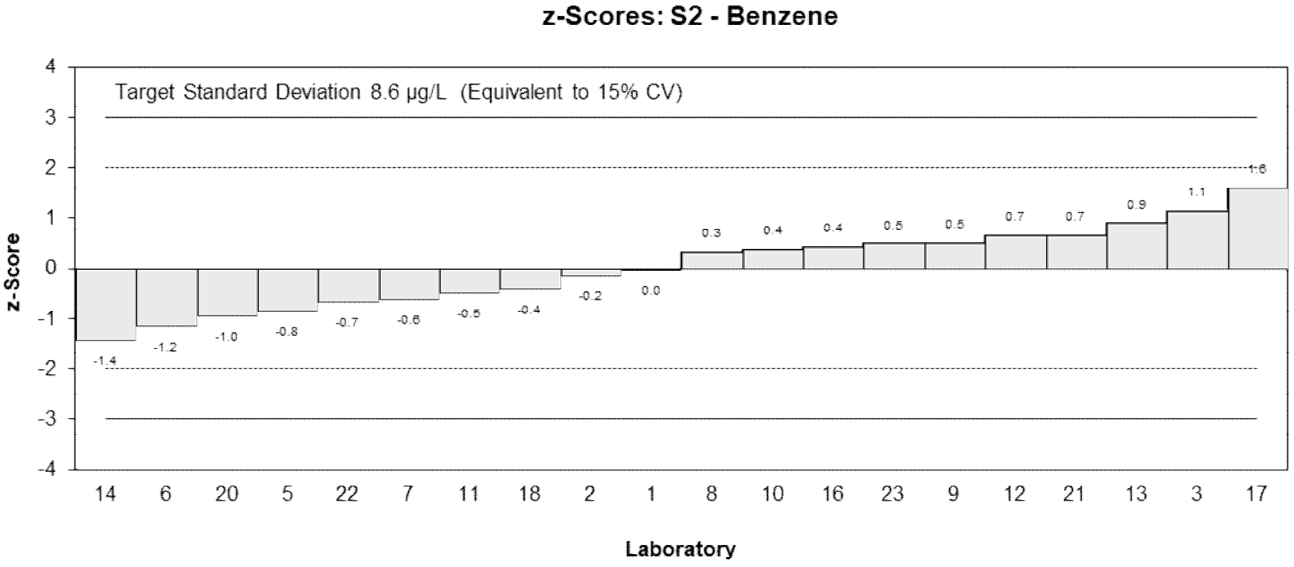
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	57	22	-0.03	-0.01
2	56	20	-0.15	-0.06
3	67	7	1.13	1.18
4	NT	NT		
5	50	15	-0.85	-0.47
6	47.4	6.8	-1.15	-1.23
7	52	8	-0.62	-0.58
8	60	20	0.31	0.13
9	61.66	15.42	0.51	0.27
10	60.5	10	0.37	0.29
11	53	20	-0.50	-0.21
12	63	11	0.66	0.48
13	65	18	0.90	0.42
14	45	4.4	-1.43	-2.00
15	NT	NT		
16	61	18	0.43	0.20
17	71	14	1.59	0.94
18	53.6	16.1	-0.43	-0.22
19	NT	NT		
20	49	10	-0.97	-0.76
21	63	29.61	0.66	0.19
22	51.6	11.3	-0.66	-0.47
23	61.5	8.9	0.49	0.42

Statistics

Assigned Value	57.3	4.3
Spike	57.9	2.9
Robust Average	57.3	4.3
Median	58.5	3.6
Mean	57.4	
N	20	
Max.	71	
Min.	45	
Robust SD	7.6	
Robust CV	13%	


Results: S2 - Benzene
Assigned Value = 57.3 ± 4.3 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
14 6 20 5 22 7 11 18 2 1 8 10 16 23 9 12 21 13 3 17 15 19 4 Md R.A. S.V.


z-Scores: S2 - Benzene
Target Standard Deviation 8.6 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 6 20 5 22 7 11 18 2 1 8 10 16 23 9 12 21 13 3 17

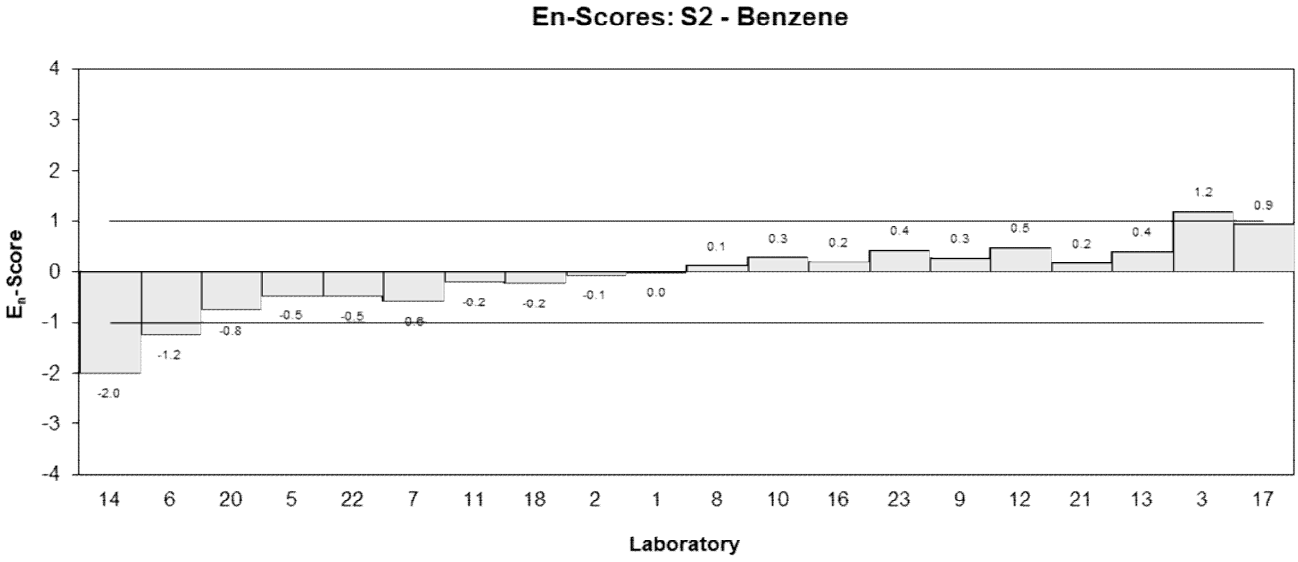

En-Scores: S2 - Benzene
En-Score
Laboratory
14 6 20 5 22 7 11 18 2 1 8 10 16 23 9 12 21 13 3 17

Figure 6

Table 12

Sample Details

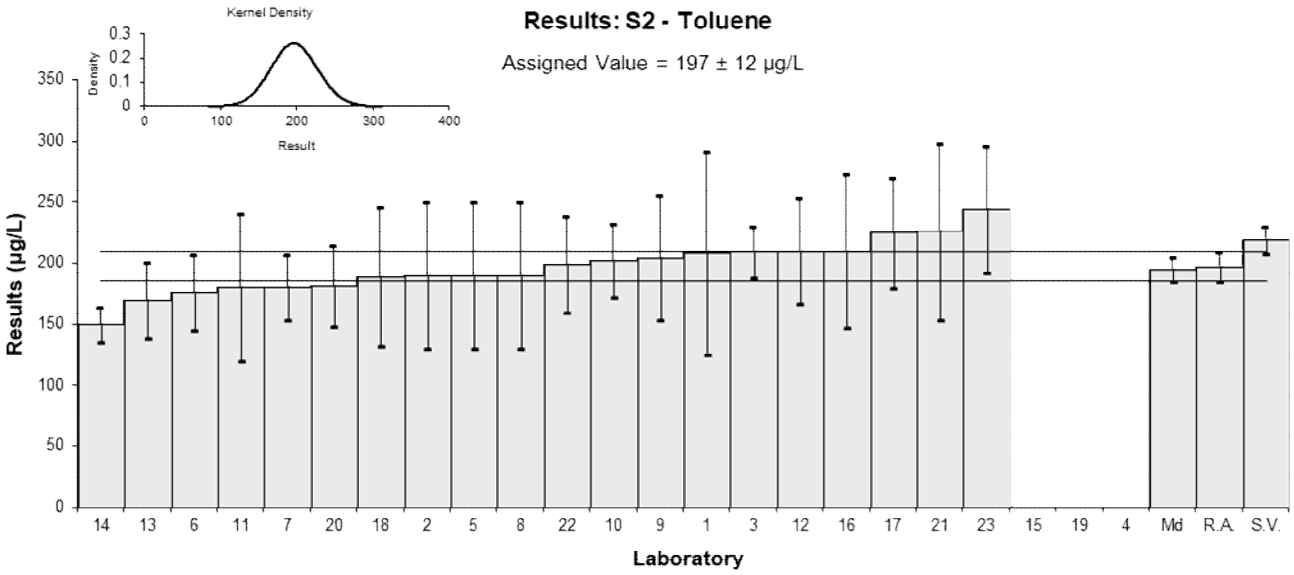
Sample No.	S2
Matrix	Water
Analyte	Toluene
Units	µg/L

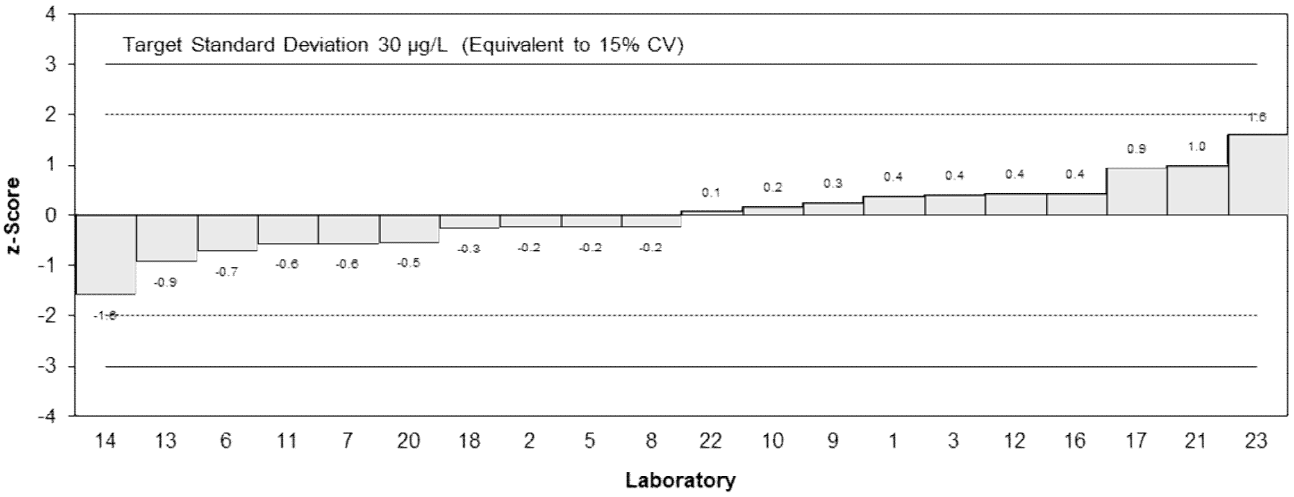
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	208	83	0.37	0.13
2	190	60	-0.24	-0.11
3	209	21	0.41	0.50
4	NT	NT		
5	190	60	-0.24	-0.11
6	176	31	-0.71	-0.63
7	180	27	-0.58	-0.58
8	190	60	-0.24	-0.11
9	204.51	51.13	0.25	0.14
10	202	30	0.17	0.15
11	180	60	-0.58	-0.28
12	210	43	0.44	0.29
13	170	31	-0.91	-0.81
14	150	14	-1.59	-2.55
15	NT	NT		
16	210	63	0.44	0.20
17	225	45	0.95	0.60
18	189	56.7	-0.27	-0.14
19	NT	NT		
20	181	33	-0.54	-0.46
21	226	72.32	0.98	0.40
22	199	39.8	0.07	0.05
23	244	52	1.59	0.88

Statistics

Assigned Value	197	12
Spike	219	11
Robust Average	197	12
Median	195	10
Mean	197	
N	20	
Max.	244	
Min.	150	
Robust SD	21	
Robust CV	11%	


Kernel Density
Density
Result
Results: S2 - Toluene
Assigned Value = 197 ± 12 µg/L
Results (µg/L)
Laboratory
14 13 6 11 7 20 18 2 5 8 22 10 9 1 3 12 16 17 21 23 15 19 4 Md R.A. S.V.


z-Scores: S2 - Toluene
Target Standard Deviation 30 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 13 6 11 7 20 18 2 5 8 22 10 9 1 3 12 16 17 21 23

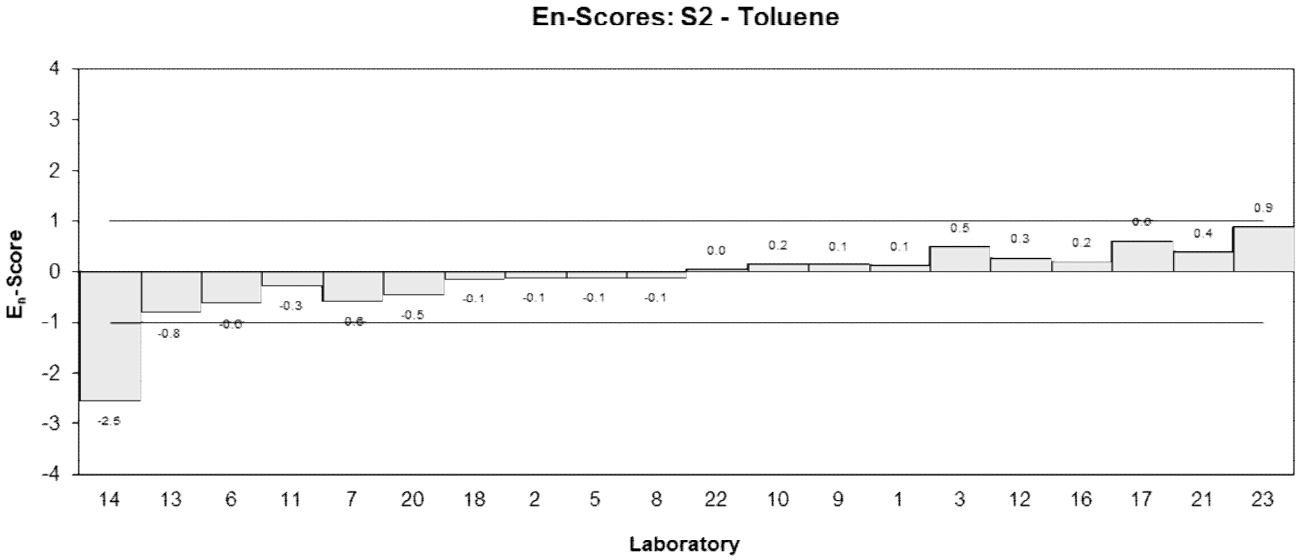

En-Scores: S2 - Toluene
En-Score
Laboratory
14 13 6 11 7 20 18 2 5 8 22 10 9 1 3 12 16 17 21 23

Figure 7

Table 13

Sample Details

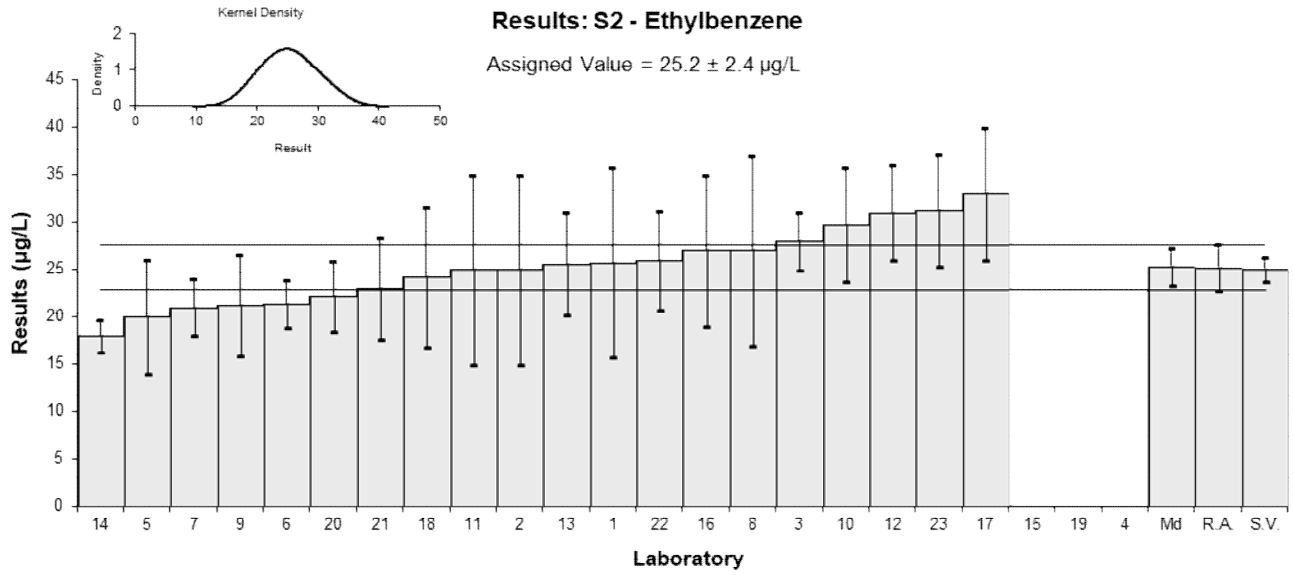
Sample No.	S2
Matrix	Water
Analyte	Ethylbenzene
Units	µg/L

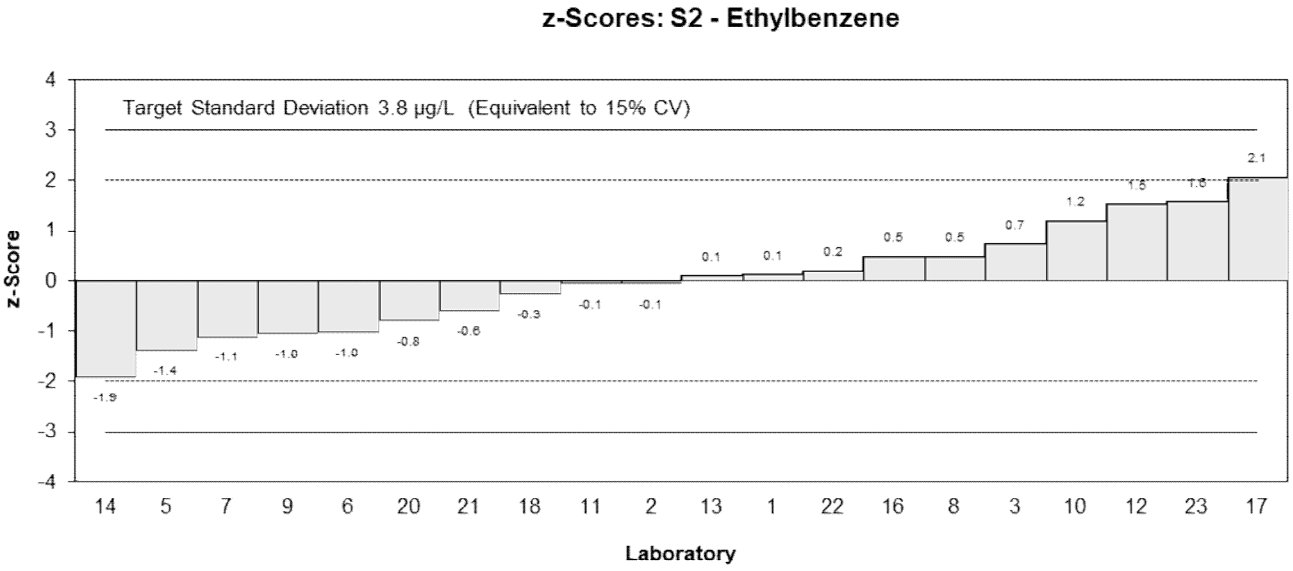
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	25.7	10	0.13	0.05
2	25	10	-0.05	-0.02
3	28	3	0.74	0.73
4	NT	NT		
5	20	6	-1.38	-0.80
6	21.3	2.5	-1.03	-1.13
7	21	3	-1.11	-1.09
8	27	10	0.48	0.18
9	21.28	5.32	-1.04	-0.67
10	29.7	6	1.19	0.70
11	25	10	-0.05	-0.02
12	31	5	1.53	1.05
13	25.6	5.4	0.11	0.07
14	18	1.7	-1.90	-2.45
15	NT	NT		
16	27	8.0	0.48	0.22
17	33	7	2.06	1.05
18	24.2	7.3	-0.26	-0.13
19	NT	NT		
20	22.2	3.7	-0.79	-0.68
21	23	5.29	-0.58	-0.38
22	26	5.2	0.21	0.14
23	31.2	5.9	1.59	0.94

Statistics

Assigned Value	25.2	2.4
Spike	25.0	1.3
Robust Average	25.2	2.4
Median	25.3	2.0
Mean	25.3	
N	20	
Max.	33	
Min.	18	
Robust SD	4.4	
Robust CV	17%	


Kernel Density
Density
Result
Results: S2 - Ethylbenzene
Assigned Value = 25.2 ± 2.4 µg/L
Results (µg/L)
Laboratory
14 5 7 9 6 20 21 18 11 2 13 1 22 16 8 3 10 12 23 17 15 19 4 Md R.A. S.V.


z-Scores: S2 - Ethylbenzene
Target Standard Deviation 3.8 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 5 7 9 6 20 21 18 11 2 13 1 22 16 8 3 10 12 23 17

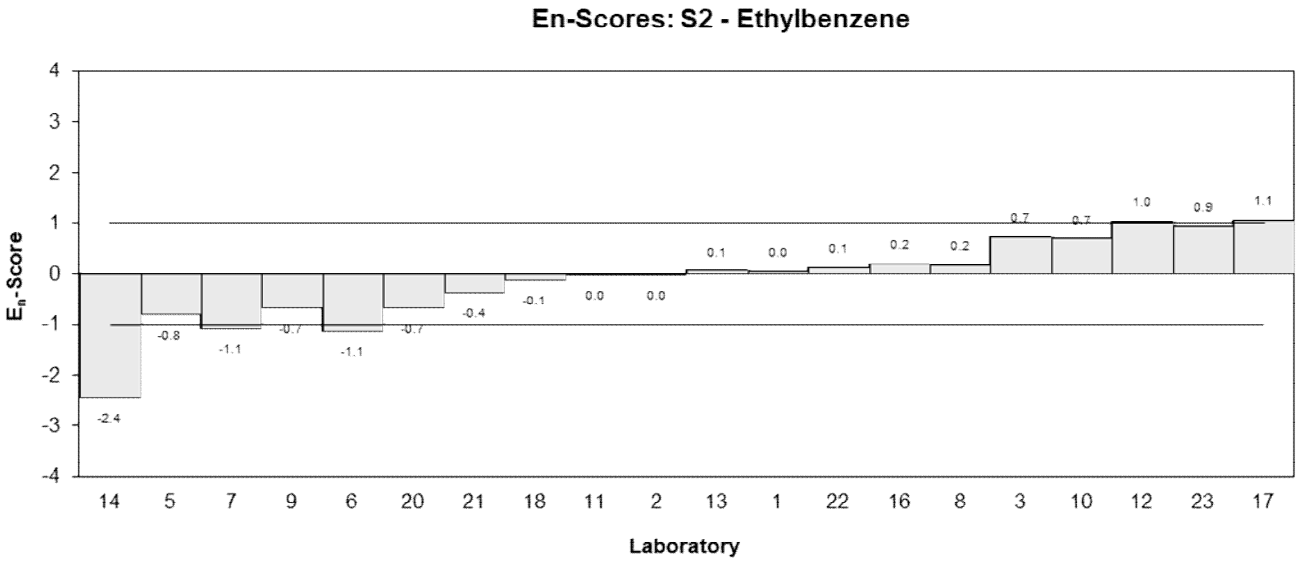

En-Scores: S2 - Ethylbenzene
En-Score
Laboratory
14 5 7 9 6 20 21 18 11 2 13 1 22 16 8 3 10 12 23 17

Figure 8

Table 14

Sample Details

Sample No.	S2
Matrix	Water
Analyte	Xylenes
Units	µg/L

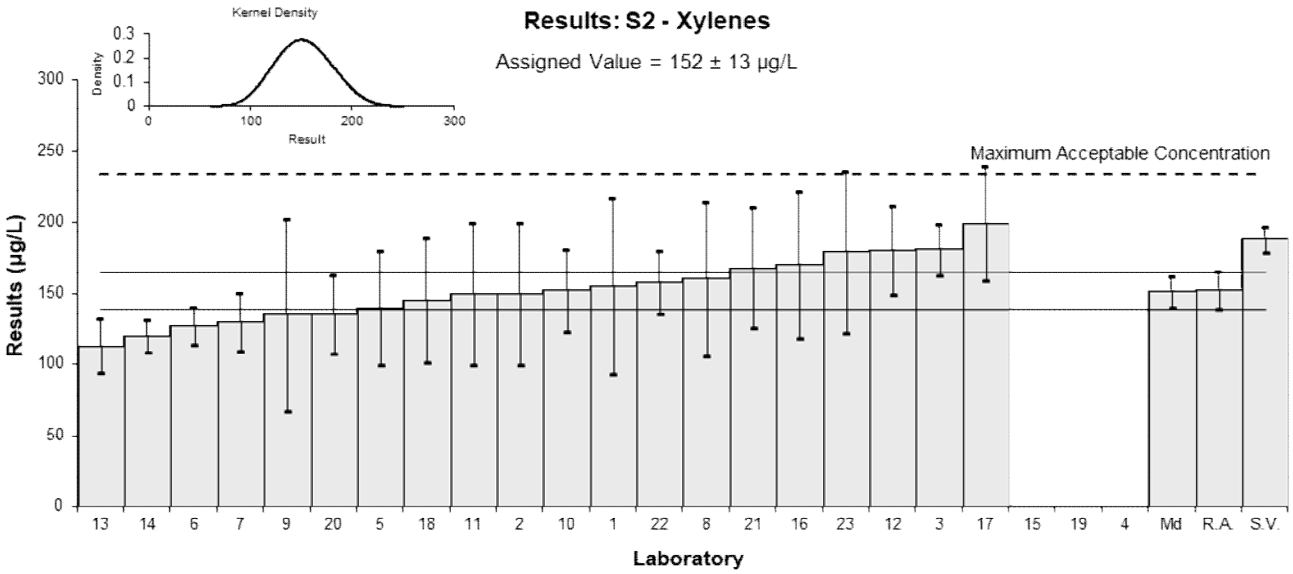
Participant Results

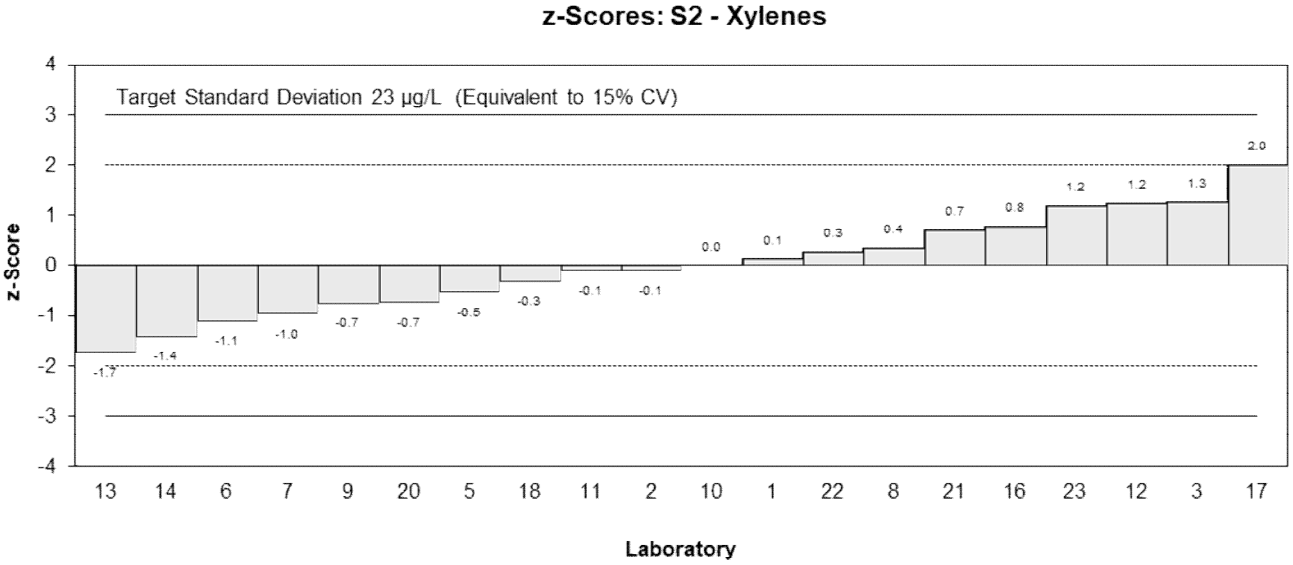
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	155	62	0.13	0.05
2	150	50	-0.09	-0.04
3	181	18	1.27	1.31
4	NT	NT		
5	140	40	-0.53	-0.29
6	127	13	-1.10	-1.36
7	130	20	-0.96	-0.92
8	160	54	0.35	0.14
9	135.11	67.56	-0.74	-0.25
10	152	29	0.00	0.00
11	150	50	-0.09	-0.04
12	180	31	1.23	0.83
13	113	19	-1.71	-1.69
14	120	11	-1.40	-1.88
15	NT	NT		
16	170	51	0.79	0.34
17*	199	40	2.00	1.00
18	145	43.6	-0.31	-0.15
19	NT	NT		
20	135.3	27.1	-0.73	-0.56
21	168	42	0.70	0.36
22	158	22.1	0.26	0.23
23	179	57	1.18	0.46

Statistics

Assigned Value	152	13
Spike	188	9
Max. Acceptable Conc.*	234	
Robust Average	152	13
Median	151	11
Mean	152	
N	20	
Max.	199	
Min.	113	
Robust SD	24	
Robust CV	16%	

* z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - Xylenes
Assigned Value = 152 ± 13 µg/L
Maximum Acceptable Concentration
Results (µg/L)
Laboratory
13 14 6 7 9 20 5 18 11 2 10 1 22 8 21 16 23 12 3 17 15 19 4 Md R.A. S.V.


z-Scores: S2 - Xylenes
Target Standard Deviation 23 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
13 14 6 7 9 20 5 18 11 2 10 1 22 8 21 16 23 12 3 17

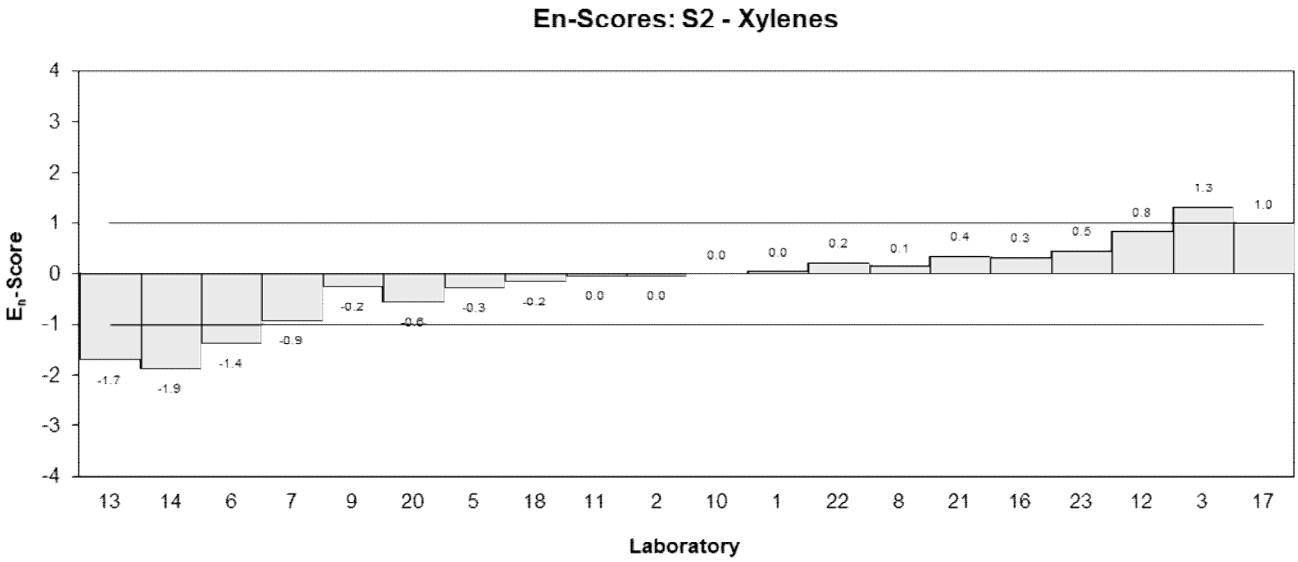

En-Scores: S2 - Xylenes
En-Score
Laboratory
13 14 6 7 9 20 5 18 11 2 10 1 22 8 21 16 23 12 3 17

Figure 9

Table 15

Sample Details

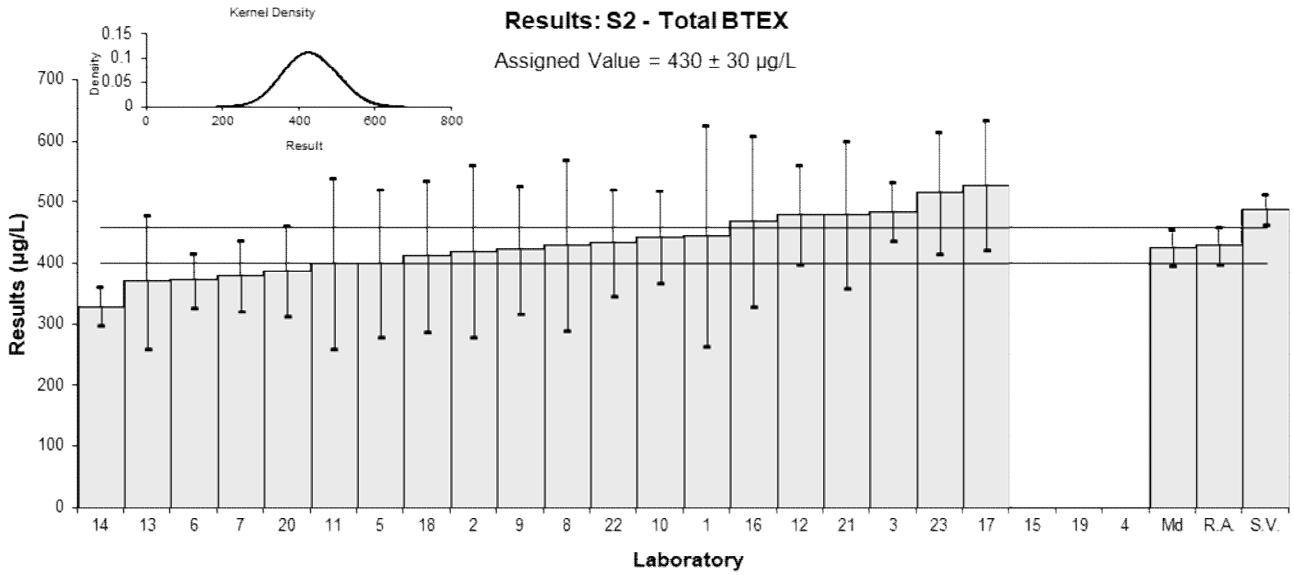
Sample No.	S2
Matrix	Water
Analyte	Total BTEX
Units	µg/L

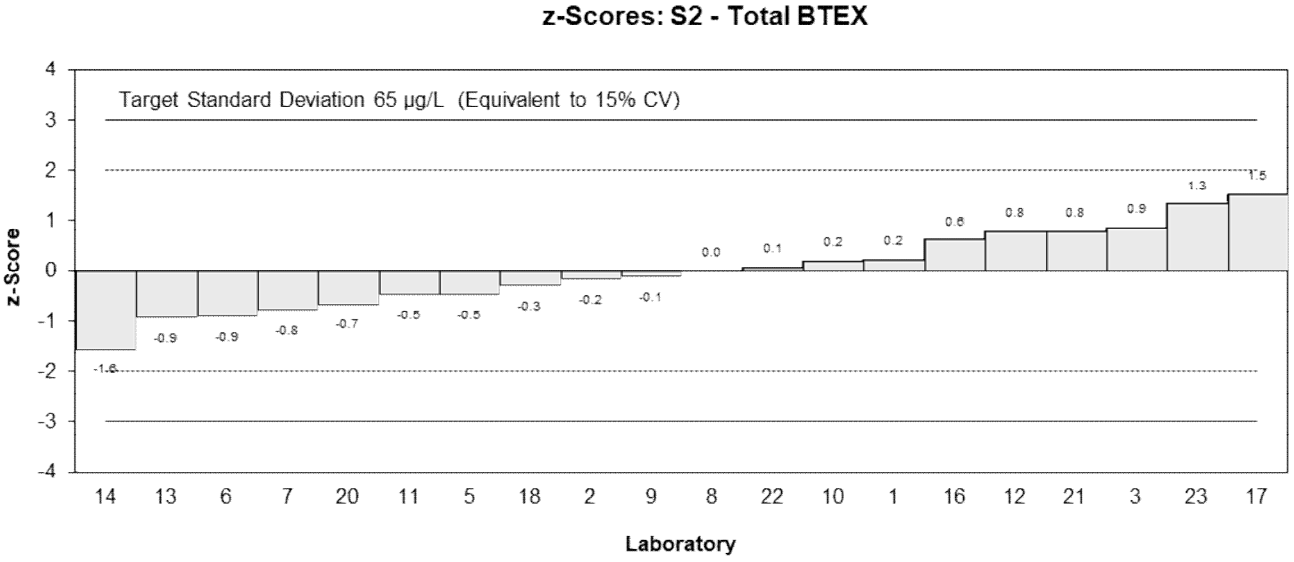
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	445	180	0.23	0.08
2	420	140	-0.16	-0.07
3	485	48	0.85	0.97
4	NT	NT		
5	400	120	-0.47	-0.24
6	372	45	-0.90	-1.07
7	380	58	-0.78	-0.77
8	430	140	0.00	0.00
9	422.6	105.63	-0.11	-0.07
10	443	75	0.20	0.16
11	400	140	-0.47	-0.21
12	480	80	0.78	0.59
13	370	110	-0.93	-0.53
14	330	31	-1.55	-2.32
15	NT	NT		
16	470	140	0.62	0.28
17	528	106	1.52	0.89
18	412	124	-0.28	-0.14
19	NT	NT		
20	387.5	73.8	-0.66	-0.53
21	480	120	0.78	0.40
22	434	86.8	0.06	0.04
23	516	100	1.33	0.82

Statistics

Assigned Value	430	30
Spike	489	24
Robust Average	430	30
Median	426	29
Mean	430	
N	20	
Max.	528	
Min.	330	
Robust SD	54	
Robust CV	13%	


Kernel Density
Density
Result
Results: S2 - Total BTEX
Assigned Value = 430 ± 30 µg/L
Results (µg/L)
Laboratory
14 13 6 7 20 11 5 18 2 9 8 22 10 1 16 12 21 3 23 17 15 19 4 Mid R.A. S.V.


z-Scores: S2 - Total BTEX
Target Standard Deviation 65 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 13 6 7 20 11 5 18 2 9 8 22 10 1 16 12 21 3 23 17

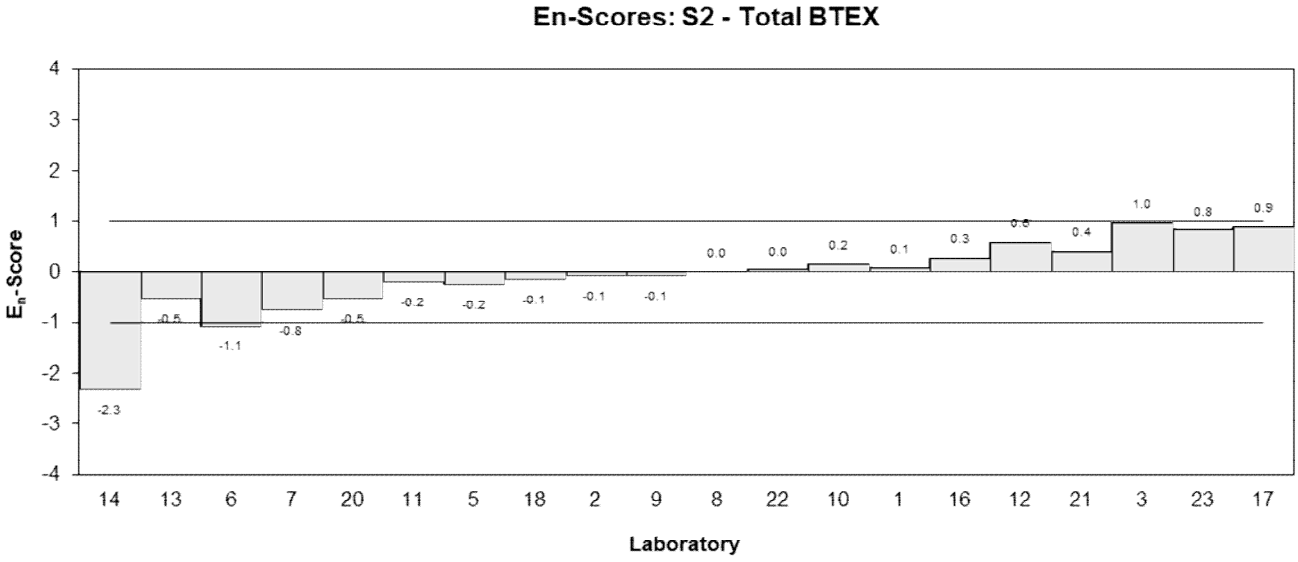

En-Scores: S2 - Total BTEX
En-Score
Laboratory
14 13 6 7 20 11 5 18 2 9 8 22 10 1 16 12 21 3 23 17

Figure 10

Table 16

Sample Details

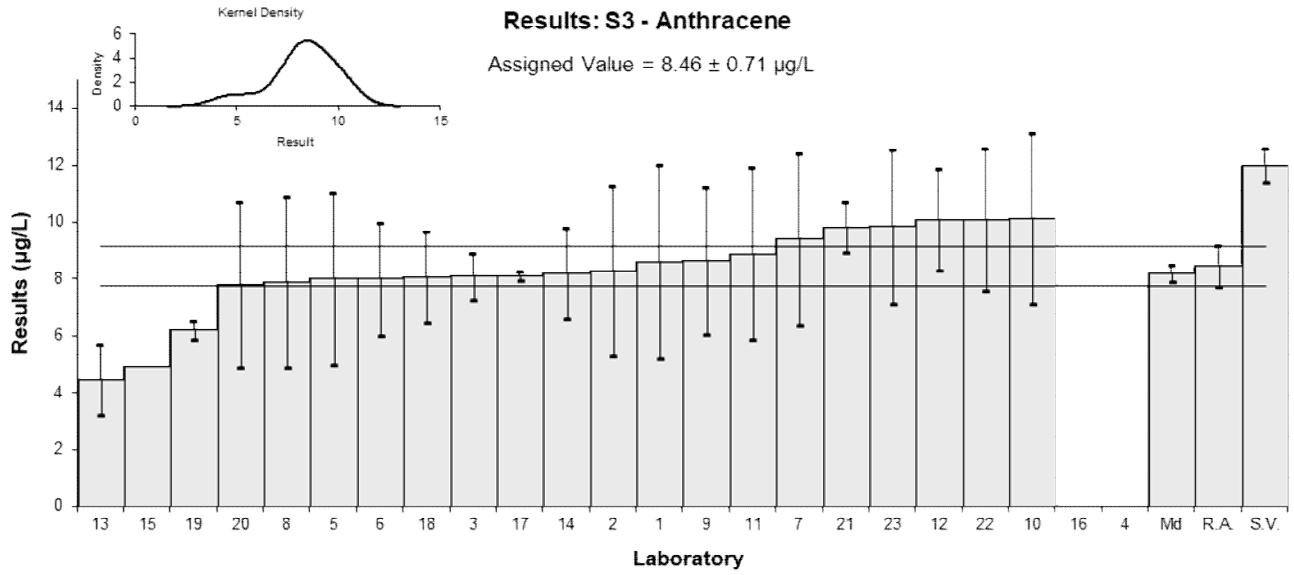
Sample No.	S3
Matrix	Water
Analyte	Anthracene
Units	µg/L

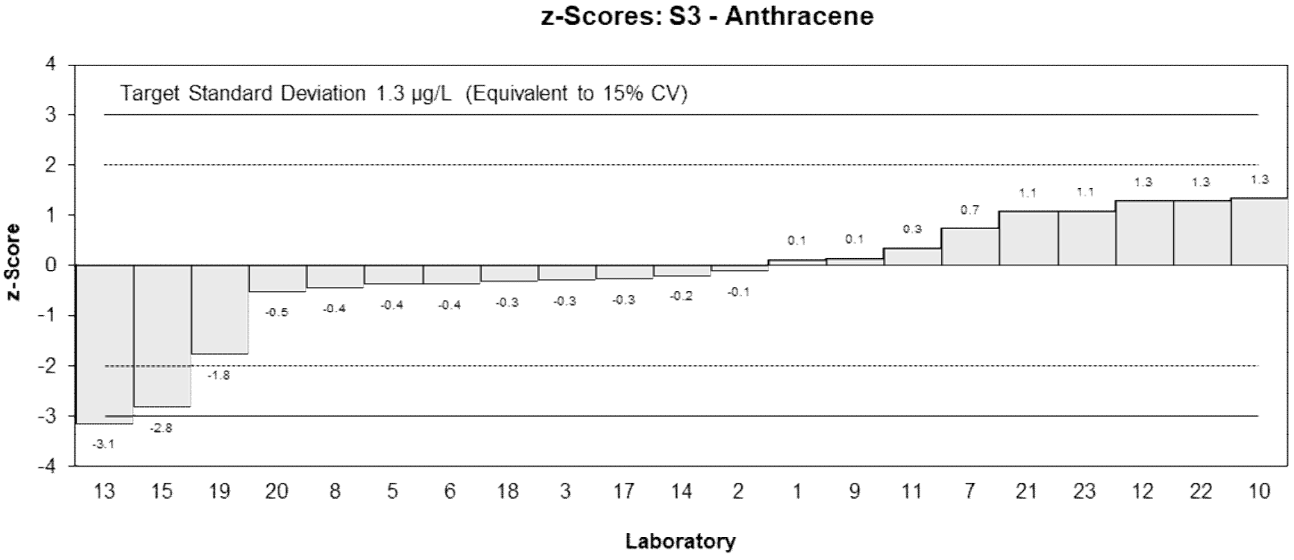
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	8.62	3.4	0.13	0.05
2	8.3	3	-0.13	-0.05
3	8.10	0.81	-0.28	-0.33
4	NT	NT		
5	8	3	-0.36	-0.15
6	8.0	2.0	-0.36	-0.22
7	9.4	3.0	0.74	0.30
8	7.9	3	-0.44	-0.18
9	8.64	2.59	0.14	0.07
10	10.15	3	1.33	0.55
11	8.9	3	0.35	0.14
12	10.1	1.77	1.29	0.86
13	4.47	1.25	-3.14	-2.78
14	8.2	1.6	-0.20	-0.15
15	4.8960	NR	-2.81	-5.02
16	NT	NT		
17	8.13	0.16	-0.26	-0.45
18	8.06	1.61	-0.32	-0.23
19	6.2	0.3	-1.78	-2.93
20	7.8	2.9	-0.52	-0.22
21	9.82	0.88	1.07	1.20
22	10.1	2.5	1.29	0.63
23	9.85	2.7	1.10	0.50

Statistics

Assigned Value	8.46	0.71
Spike	12.0	0.6
Robust Average	8.46	0.71
Median	8.20	0.30
Mean	8.27	
N	21	
Max.	10.15	
Min.	4.47	
Robust SD	1.3	
Robust CV	15%	


Kernel Density
Density
Result
Results: S3 - Anthracene
Assigned Value = 8.46 ± 0.71 µg/L
Results (µg/L)
13 15 19 20 8 5 6 18 3 17 14 2 1 9 11 7 21 23 12 22 10 16 4 Md R.A. S.V.
Laboratory


z-Scores: S3 - Anthracene
Target Standard Deviation 1.3 µg/L (Equivalent to 15% CV)
z-Score
13 15 19 20 8 5 6 18 3 17 14 2 1 9 11 7 21 23 12 22 10
Laboratory

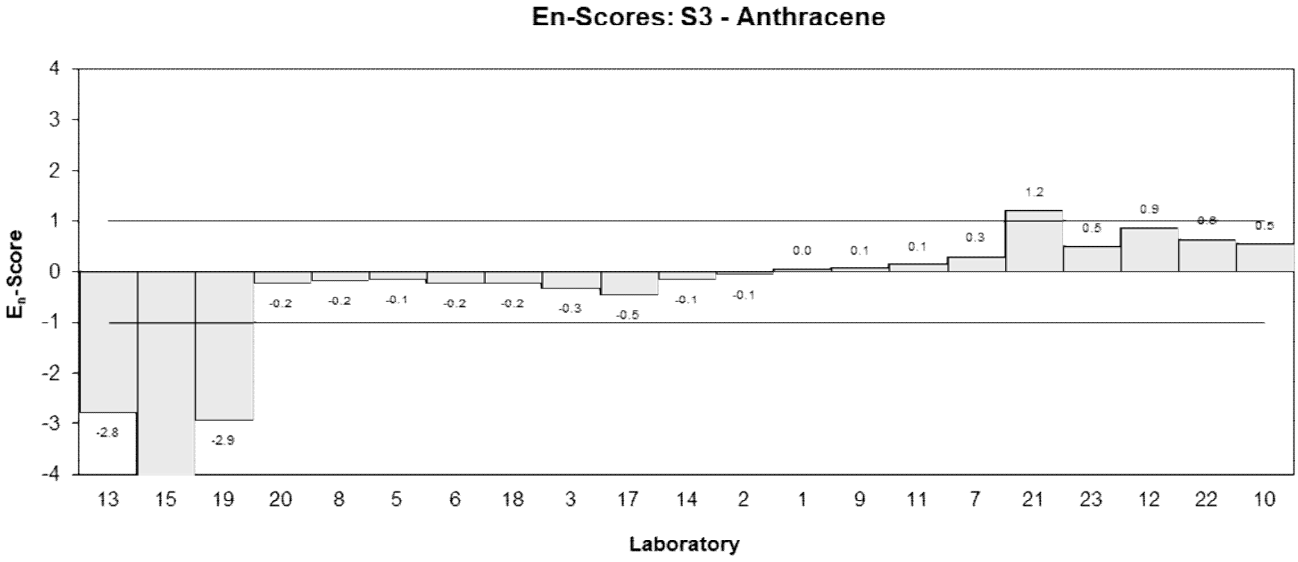

En-Scores: S3 - Anthracene
En-Score
13 15 19 20 8 5 6 18 3 17 14 2 1 9 11 7 21 23 12 22 10
Laboratory

Figure 11

Table 17

Sample Details

Sample No.	S3
Matrix	Water
Analyte	Benzo(a)pyrene
Units	µg/L

Participant Results

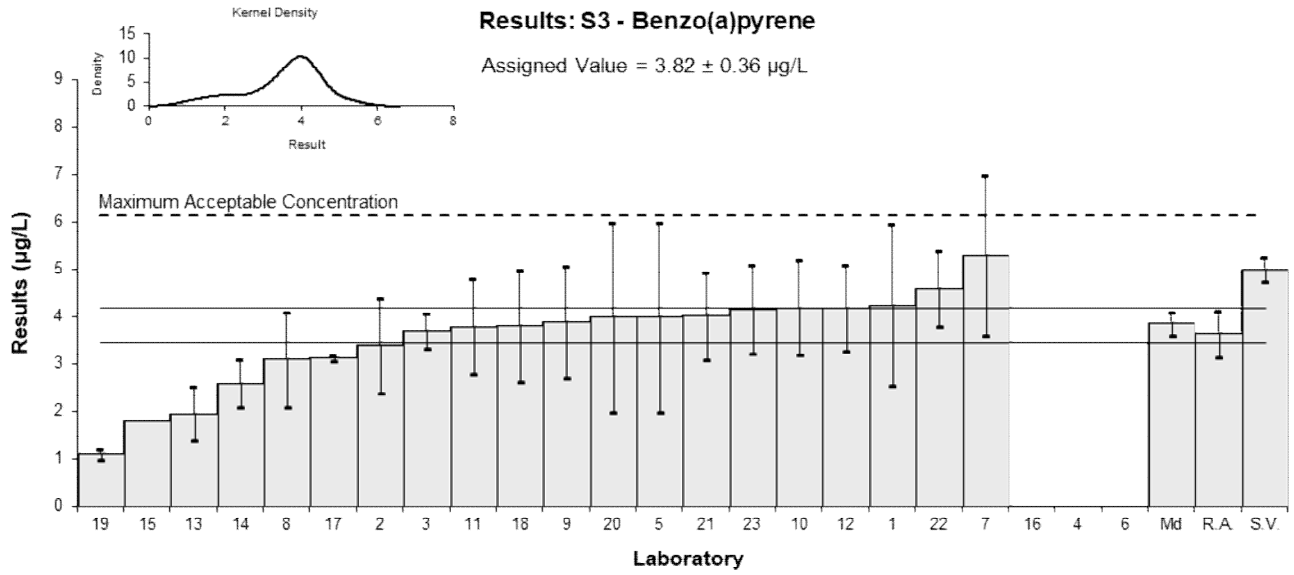
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	4.25	1.7	0.75	0.25
2	3.4	1	-0.73	-0.40
3	3.71	0.37	-0.19	-0.21
4	NT	NT		
5	4	2	0.31	0.09
6	NT	NT		
7**	5.3	1.7	2.00	0.85
8	3.1	1	-1.26	-0.68
9	3.9	1.17	0.14	0.07
10	4.2	1	0.66	0.36
11	3.8	1	-0.03	-0.02
12	4.2	0.9	0.66	0.39
13	1.96	0.57	-3.25	-2.76
14	2.6	0.5	-2.13	-1.98
15	1.8039	NR	-3.52	-5.60
16	NT	NT		
17	3.13	0.06	-1.20	-1.89
18	3.82	1.18	0.00	0.00
19	1.1	0.1	-4.75	-7.28
20	4	2	0.31	0.09
21	4.02	0.92	0.35	0.20
22	4.6	0.8	1.36	0.89
23	4.16	0.94	0.59	0.34

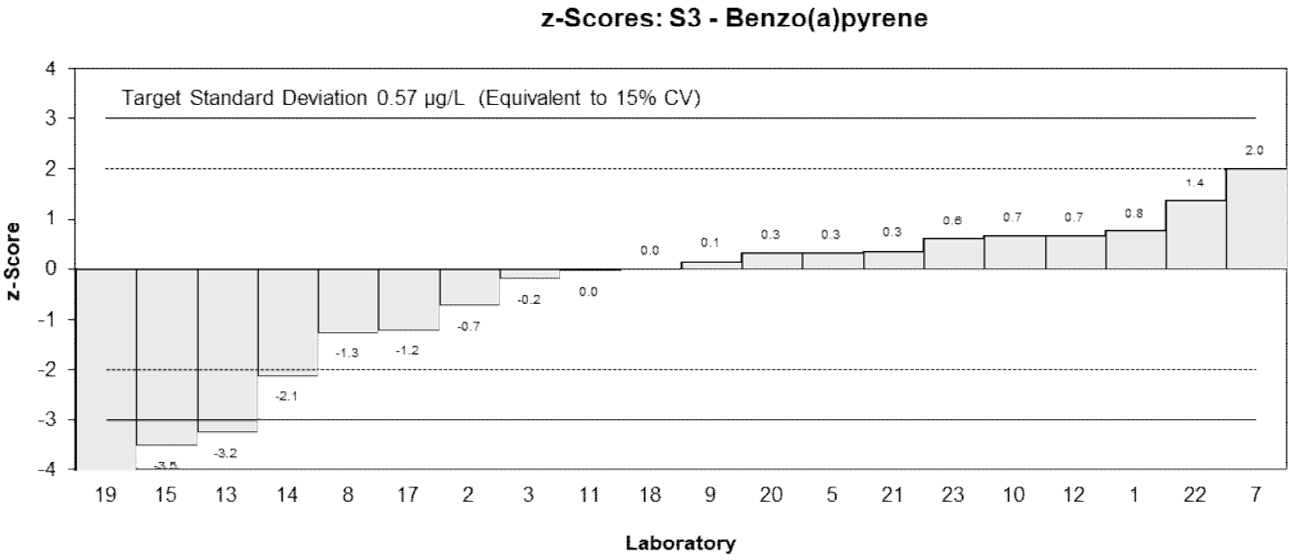
Statistics

Assigned Value*	3.82	0.36
Spike	5.00	0.25
Max. Acceptable Conc.**	6.15	
Robust Average	3.64	0.49
Median	3.86	0.25
Mean	3.55	
N	20	
Max.	5.3	
Min.	1.1	
Robust SD	0.87	
Robust CV	24%	

* Robust average excluding Laboratories 15 and 19.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S3 - Benzo(a)pyrene
Assigned Value = 3.82 ± 0.36 µg/L
Maximum Acceptable Concentration
Results (µg/L)
19 15 13 14 8 17 2 3 11 18 9 20 5 21 23 10 12 1 22 7 16 4 6 Md R.A. S.V.
Laboratory


z-Scores: S3 - Benzo(a)pyrene
Target Standard Deviation 0.57 µg/L (Equivalent to 15% CV)
z-Score
19 15 13 14 8 17 2 3 11 18 9 20 5 21 23 10 12 1 22 7
Laboratory

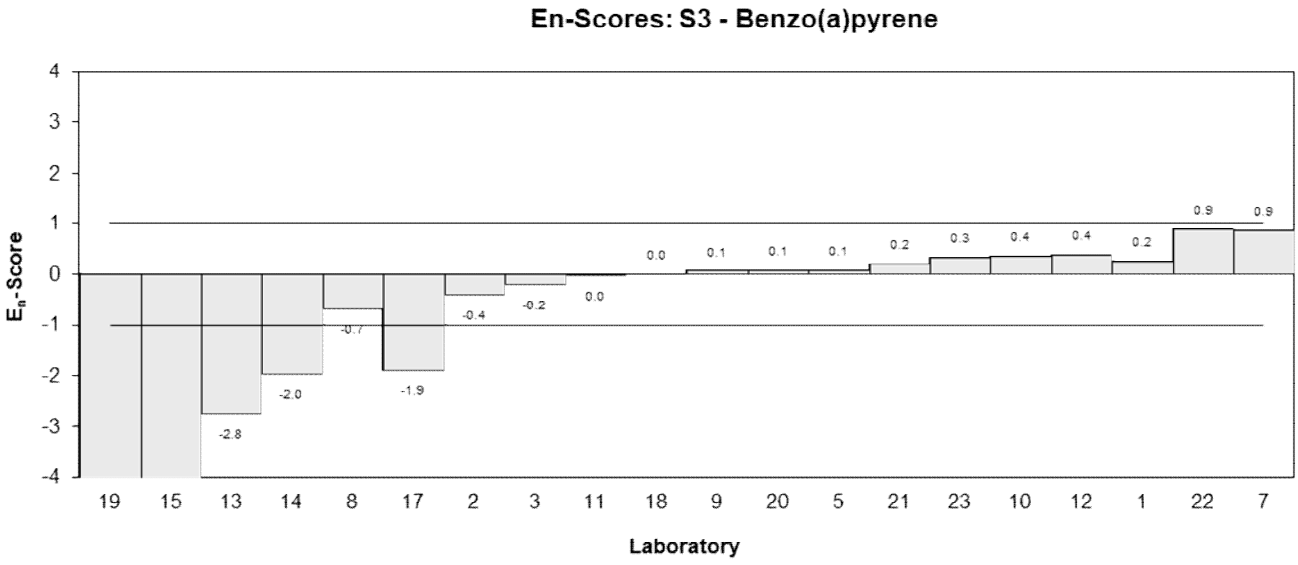

En-Scores: S3 - Benzo(a)pyrene
En-Score
19 15 13 14 8 17 2 3 11 18 9 20 5 21 23 10 12 1 22 7
Laboratory

Figure 12

Table 18

Sample Details

Sample No.	S3
Matrix	Water
Analyte	Chrysene
Units	µg/L

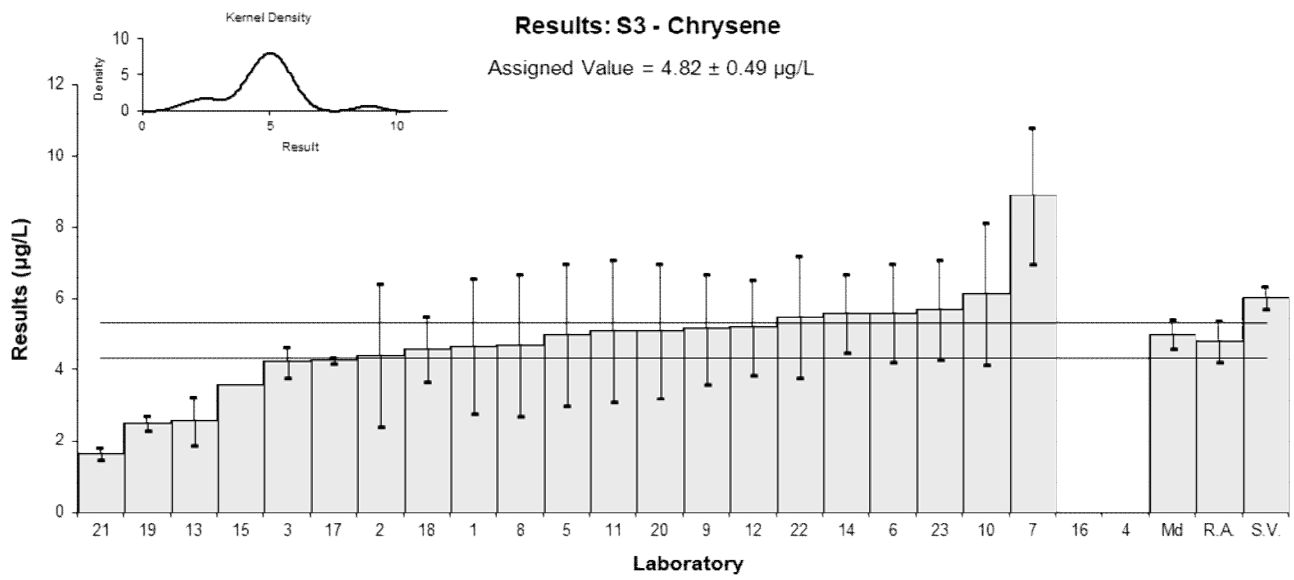
Participant Results

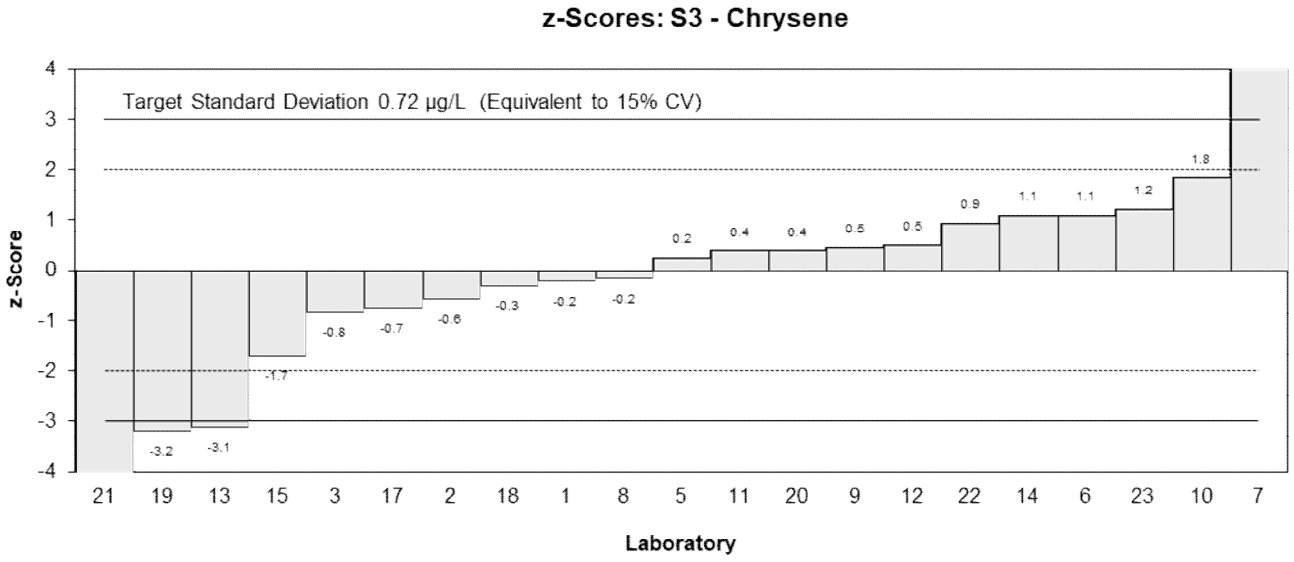
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	4.67	1.9	-0.21	-0.08
2	4.4	2	-0.58	-0.20
3	4.22	0.42	-0.83	-0.93
4	NT	NT		
5	5	2	0.25	0.09
6	5.6	1.4	1.08	0.53
7	8.9	1.9	5.64	2.08
8	4.7	2	-0.17	-0.06
9	5.15	1.55	0.46	0.20
10	6.15	2	1.84	0.65
11	5.1	2	0.39	0.14
12	5.19	1.33	0.51	0.26
13	2.56	0.67	-3.13	-2.72
14	5.6	1.1	1.08	0.65
15	3.5866	NR	-1.71	-2.52
16	NT	NT		
17	4.28	0.09	-0.75	-1.08
18	4.60	0.92	-0.30	-0.21
19	2.5	0.2	-3.21	-4.38
20	5.1	1.9	0.39	0.14
21	1.64	0.16	-4.40	-6.17
22	5.5	1.7	0.94	0.38
23	5.7	1.4	1.22	0.59

Statistics

Assigned Value*	4.82	0.49
Spike	6.03	0.30
Robust Average	4.79	0.57
Median	5.00	0.40
Mean	4.77	
N	21	
Max.	8.9	
Min.	1.64	
Robust SD	1.0	
Robust CV	22%	

* Robust average excluding Laboratories 7 and 21.


Kernel Density
Density
Result
Results: S3 - Chrysene
Assigned Value = 4.82 ± 0.49 µg/L
Results (µg/L)
21 19 13 15 3 17 2 18 1 8 5 11 20 9 12 22 14 6 23 10 7 16 4 Md R.A. S.V.
Laboratory


z-Scores: S3 - Chrysene
Target Standard Deviation 0.72 µg/L (Equivalent to 15% CV)
z-Score
21 19 13 15 3 17 2 18 1 8 5 11 20 9 12 22 14 6 23 10 7
Laboratory

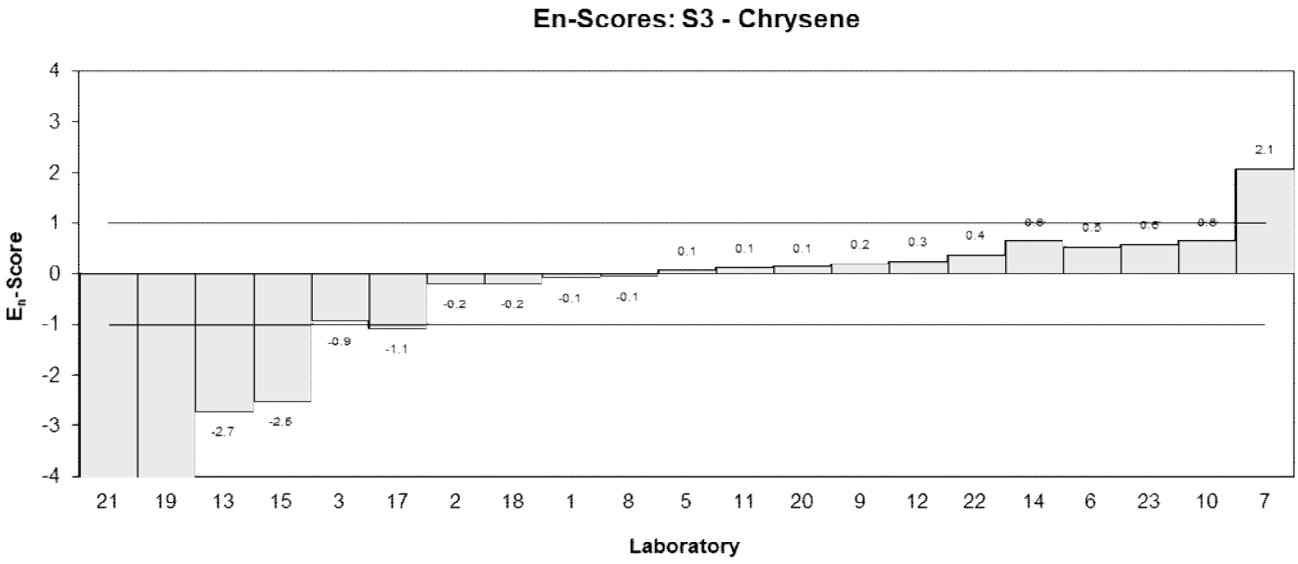

En-Scores: S3 - Chrysene
En-Score
21 19 13 15 3 17 2 18 1 8 5 11 20 9 12 22 14 6 23 10 7
Laboratory

Figure 13

Table 19

Sample Details

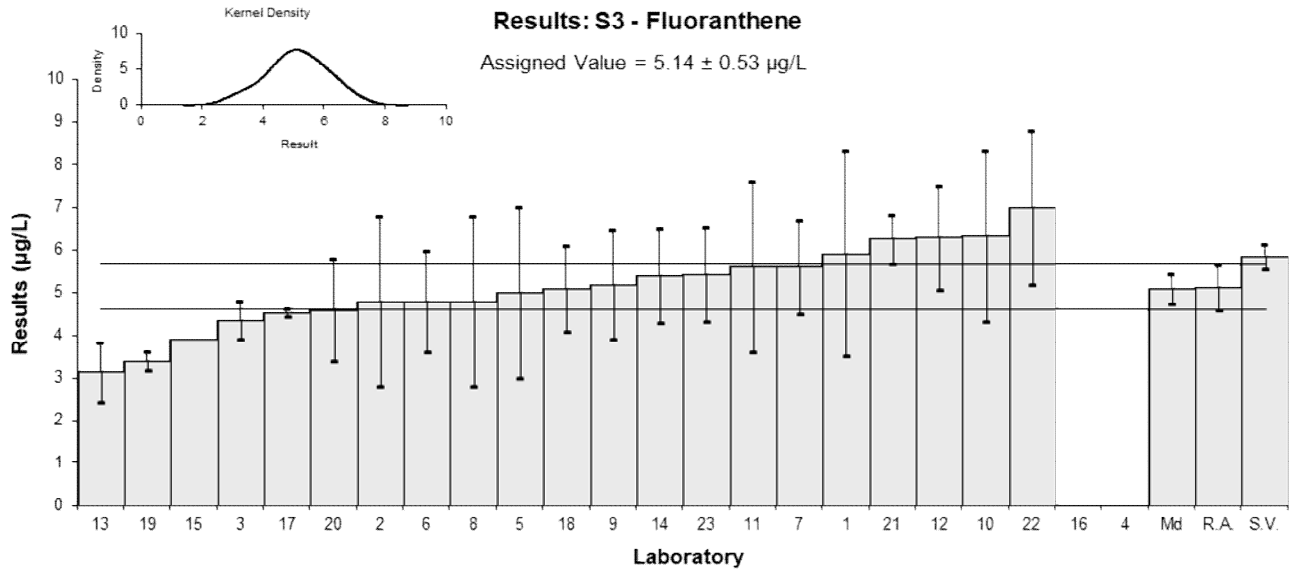
Sample No.	S3
Matrix	Water
Analyte	Fluoranthene
Units	µg/L

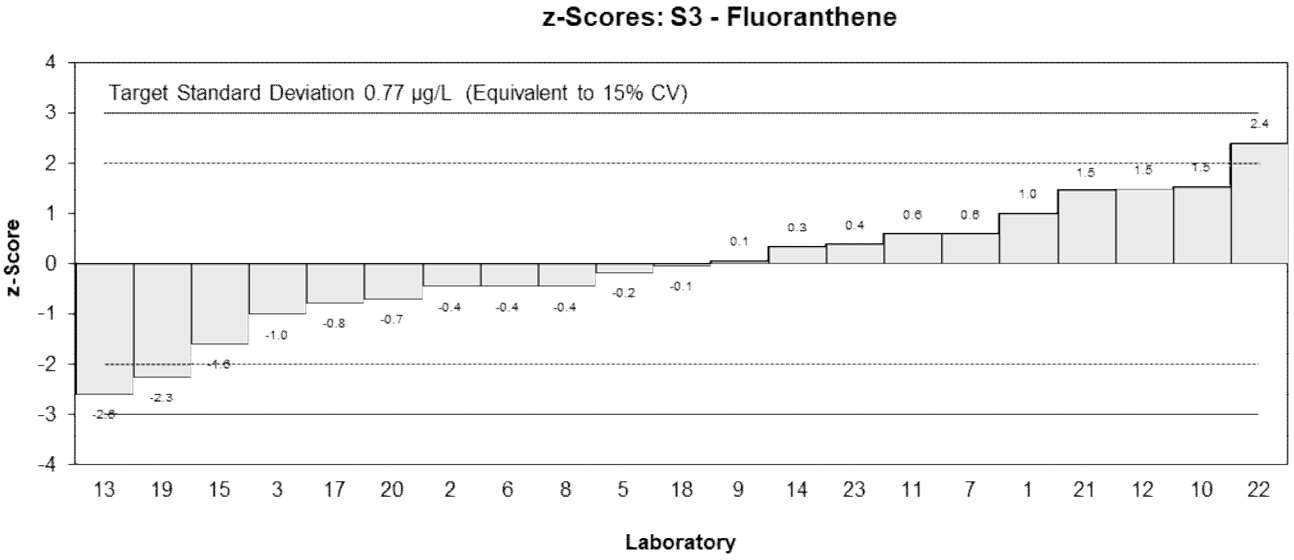
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	5.92	2.4	1.01	0.32
2	4.8	2	-0.44	-0.16
3	4.36	0.44	-1.01	-1.13
4	NT	NT		
5	5	2	-0.18	-0.07
6	4.8	1.2	-0.44	-0.26
7	5.6	1.1	0.60	0.38
8	4.8	2	-0.44	-0.16
9	5.19	1.29	0.06	0.04
10	6.33	2	1.54	0.58
11	5.6	2	0.60	0.22
12	6.29	1.21	1.49	0.87
13	3.14	0.69	-2.59	-2.30
14	5.4	1.1	0.34	0.21
15	3.9011	NR	-1.61	-2.34
16	NT	NT		
17	4.53	0.09	-0.79	-1.13
18	5.10	1.02	-0.05	-0.03
19	3.4	0.2	-2.26	-3.07
20	4.6	1.2	-0.70	-0.41
21	6.26	0.56	1.45	1.45
22	7.0	1.8	2.41	0.99
23	5.44	1.1	0.39	0.25

Statistics

Assigned Value	5.14	0.53
Spike	5.85	0.29
Robust Average	5.14	0.53
Median	5.10	0.34
Mean	5.12	
N	21	
Max.	7	
Min.	3.14	
Robust SD	0.97	
Robust CV	19%	


Kernel Density
Density
Result
Results: S3 - Fluoranthene
Assigned Value = 5.14 ± 0.53 µg/L
Results (µg/L)
13 19 15 3 17 20 2 6 8 5 18 9 14 23 11 7 1 21 12 10 22 16 4 Md R.A. S.V.
Laboratory


z-Scores: S3 - Fluoranthene
Target Standard Deviation 0.77 µg/L (Equivalent to 15% CV)
z-Score
13 19 15 3 17 20 2 6 8 5 18 9 14 23 11 7 1 21 12 10 22
Laboratory

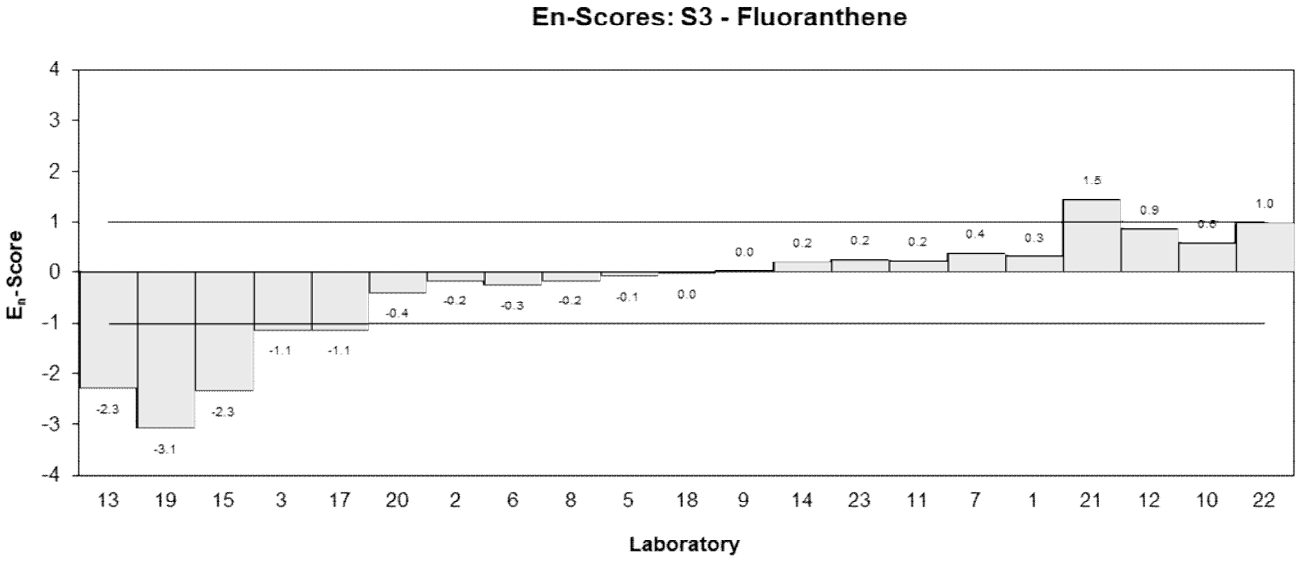

En-Scores: S3 - Fluoranthene
En-Score
13 19 15 3 17 20 2 6 8 5 18 9 14 23 11 7 1 21 12 10 22
Laboratory

Figure 14

Table 20

Sample Details

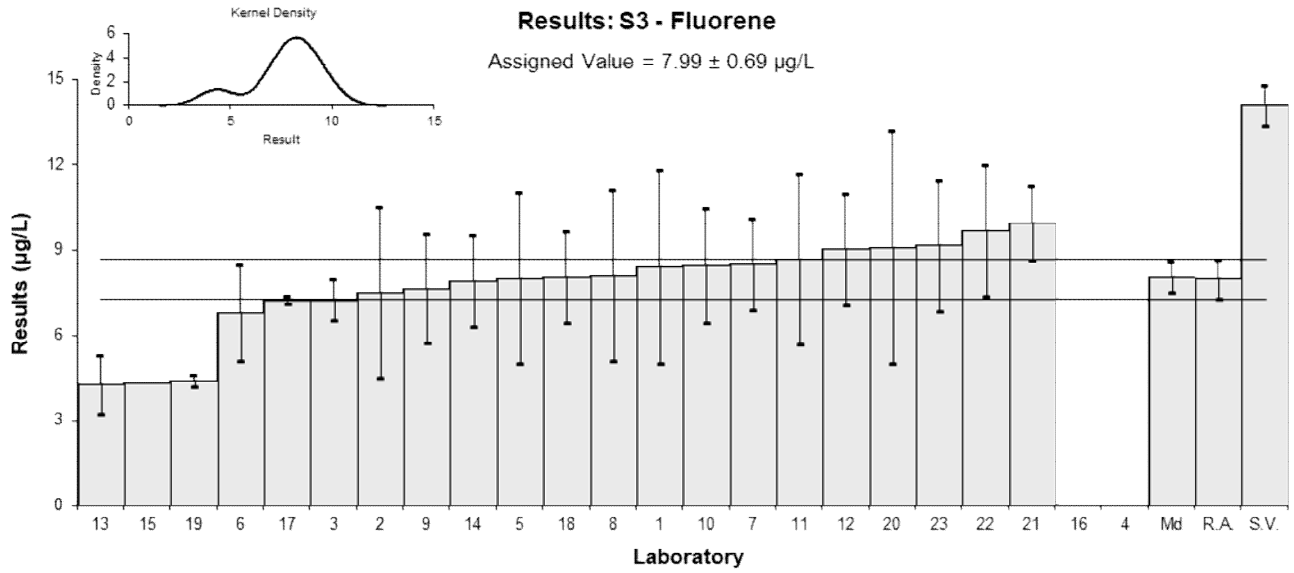
Sample No.	S3
Matrix	Water
Analyte	Fluorene
Units	µg/L

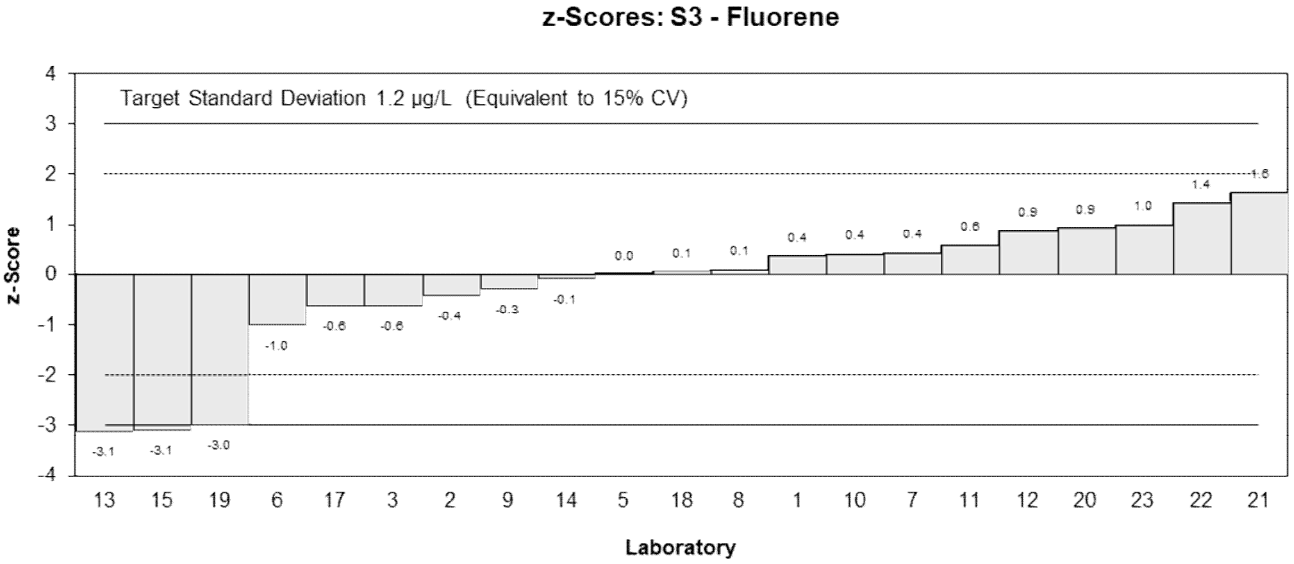
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	8.43	3.4	0.37	0.13
2	7.5	3	-0.41	-0.16
3	7.26	0.73	-0.61	-0.73
4	NT	NT		
5	8	3	0.01	0.00
6	6.8	1.7	-0.99	-0.65
7	8.5	1.6	0.43	0.29
8	8.1	3	0.09	0.04
9	7.64	1.91	-0.29	-0.17
10	8.47	2	0.40	0.23
11	8.7	3	0.59	0.23
12	9.03	1.95	0.87	0.50
13	4.26	1.02	-3.11	-3.03
14	7.9	1.6	-0.08	-0.05
15	4.2935	NR	-3.08	-5.36
16	NT	NT		
17	7.26	0.15	-0.61	-1.03
18	8.06	1.61	0.06	0.04
19	4.4	0.2	-3.00	-5.00
20	9.1	4.1	0.93	0.27
21	9.94	1.29	1.63	1.33
22	9.7	2.3	1.43	0.71
23	9.17	2.3	0.98	0.49

Statistics

Assigned Value	7.99	0.69
Spike	14.1	0.7
Robust Average	7.99	0.69
Median	8.06	0.54
Mean	7.74	
N	21	
Max.	9.94	
Min.	4.26	
Robust SD	1.3	
Robust CV	16%	


Kernel Density
Density
Result
Results: S3 - Fluorene
Assigned Value = 7.99 ± 0.69 µg/L
Results (µg/L)
13 15 19 6 17 3 2 9 14 5 18 8 1 10 7 11 12 20 23 22 21 16 4 Md R.A. S.V.
Laboratory


z-Scores: S3 - Fluorene
Target Standard Deviation 1.2 µg/L (Equivalent to 15% CV)
z-Score
-3.1 -3.1 -3.0 -1.0 -0.6 -0.6 -0.4 -0.3 -0.1 0.0 0.1 0.1 0.4 0.4 0.4 0.6 0.9 0.9 1.0 1.4 1.6
13 15 19 6 17 3 2 9 14 5 18 8 1 10 7 11 12 20 23 22 21
Laboratory

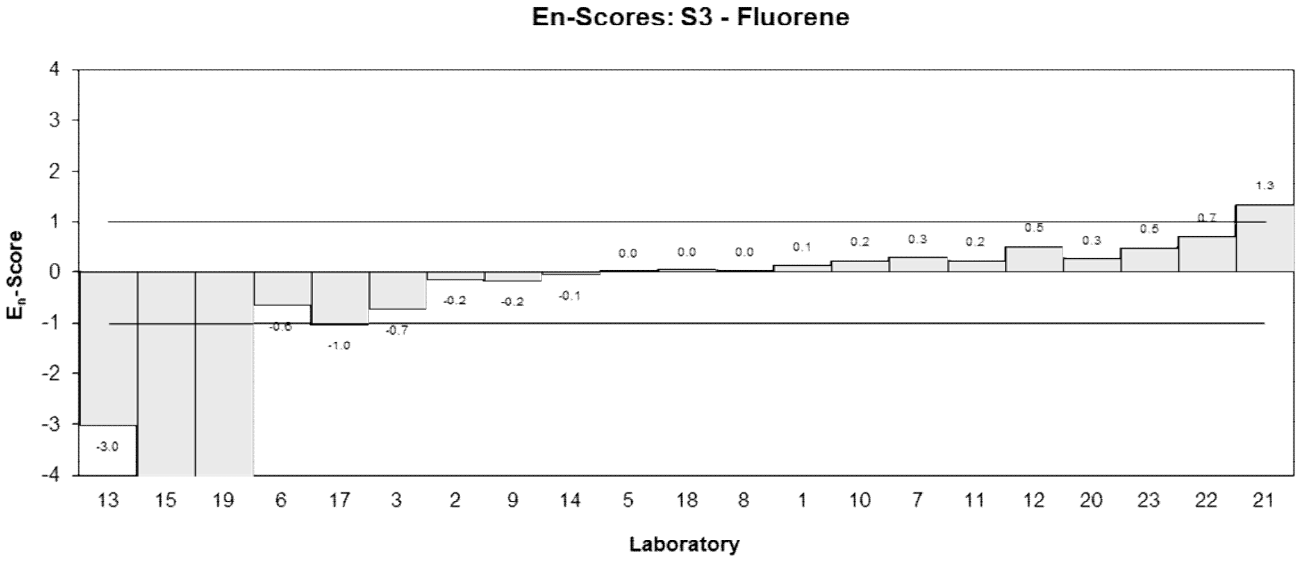

En-Scores: S3 - Fluorene
En-Score
-3.0 -0.6 -1.0 -0.7 -0.2 -0.2 -0.1 0.0 0.0 0.0 0.1 0.2 0.3 0.2 0.5 0.3 0.5 0.7 1.3
13 15 19 6 17 3 2 9 14 5 18 8 1 10 7 11 12 20 23 22 21
Laboratory

Figure 15

Table 21

Sample Details

Sample No.	S3
Matrix	Water
Analyte	Phenanthrene
Units	µg/L

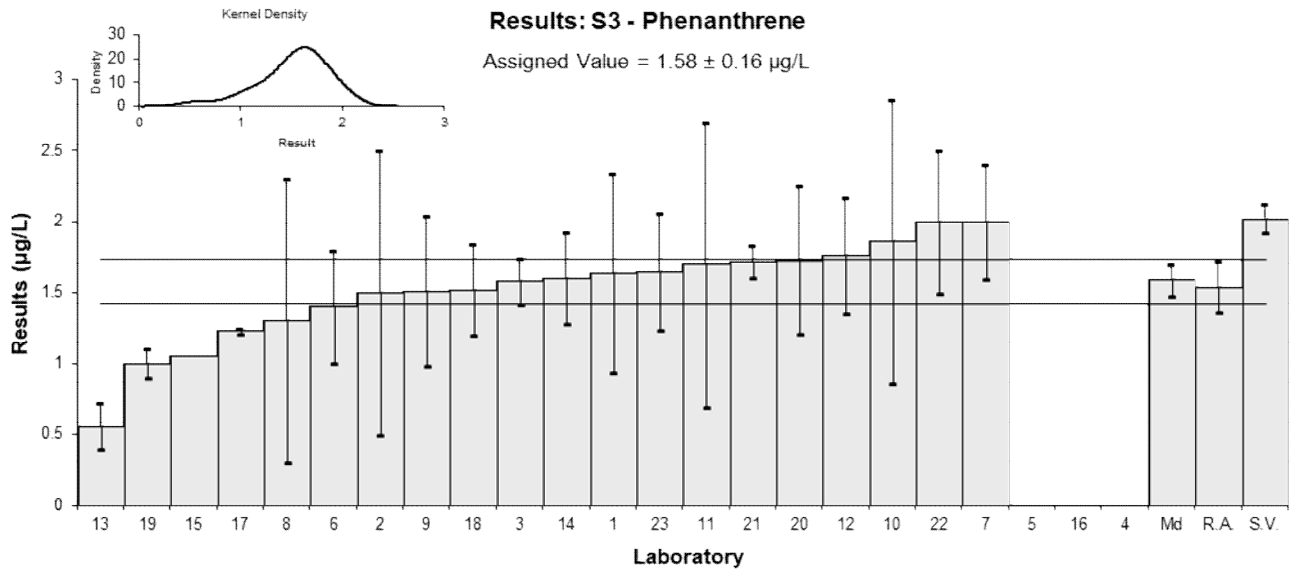
Participant Results

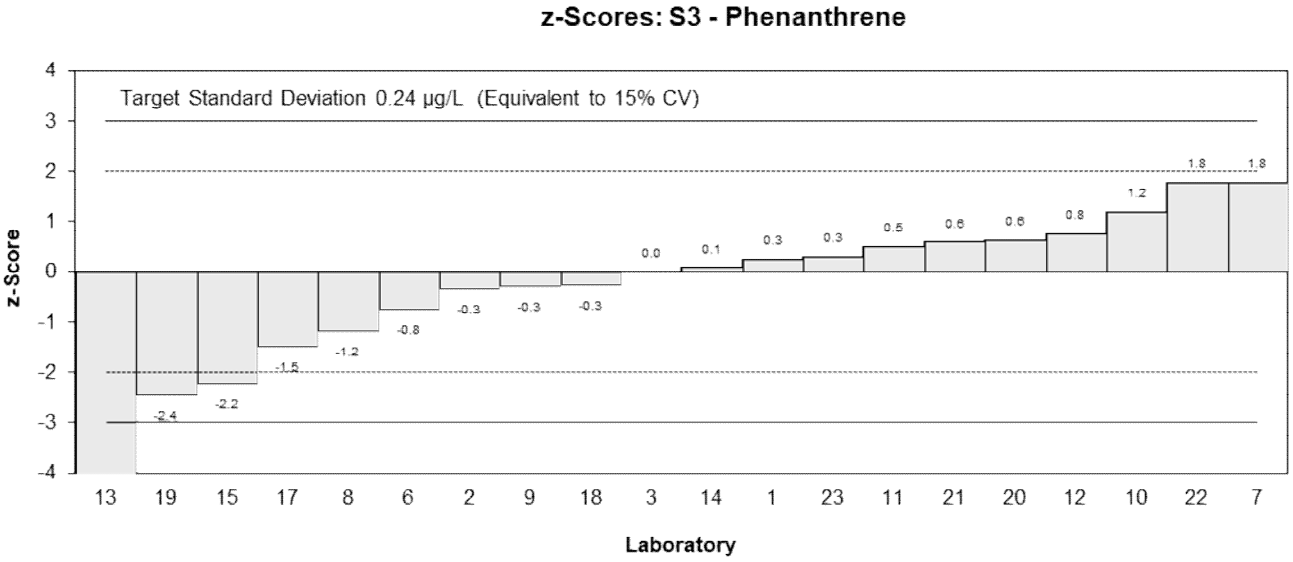
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.64	0.7	0.25	0.08
2	1.5	1	-0.34	-0.08
3	1.58	0.16	0.00	0.00
4	NT	NT		
5	<2	NR		
6	1.4	0.4	-0.76	-0.42
7	2.0	0.4	1.77	0.97
8	1.3	1	-1.18	-0.28
9	1.51	0.53	-0.30	-0.13
10	1.86	1	1.18	0.28
11	1.7	1	0.51	0.12
12	1.76	0.41	0.76	0.41
13	0.56	0.16	-4.30	-4.51
14	1.6	0.32	0.08	0.06
15	1.0532	NR	-2.22	-3.29
16	NT	NT		
17	1.23	0.02	-1.48	-2.17
18	1.52	0.32	-0.25	-0.17
19	1.0	0.1	-2.45	-3.07
20	1.73	0.52	0.63	0.28
21	1.72	0.11	0.59	0.72
22	2.0	0.5	1.77	0.80
23	1.65	0.41	0.30	0.16

Statistics

Assigned Value*	1.58	0.16
Spike	2.02	0.10
Robust Average	1.54	0.18
Median	1.59	0.11
Mean	1.52	
N	20	
Max.	2	
Min.	0.56	
Robust SD	0.33	
Robust CV	21%	

* Robust average excluding Laboratory 13.


Kernel Density
Density
Result
Results: S3 - Phenanthrene
Assigned Value = 1.58 ± 0.16 µg/L
Results (µg/L)
Laboratory
13 19 15 17 8 6 2 9 18 3 14 1 23 11 21 20 12 10 22 7 5 16 4 Md R.A. S.V.


z-Scores: S3 - Phenanthrene
Target Standard Deviation 0.24 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
13 19 15 17 8 6 2 9 18 3 14 1 23 11 21 20 12 10 22 7

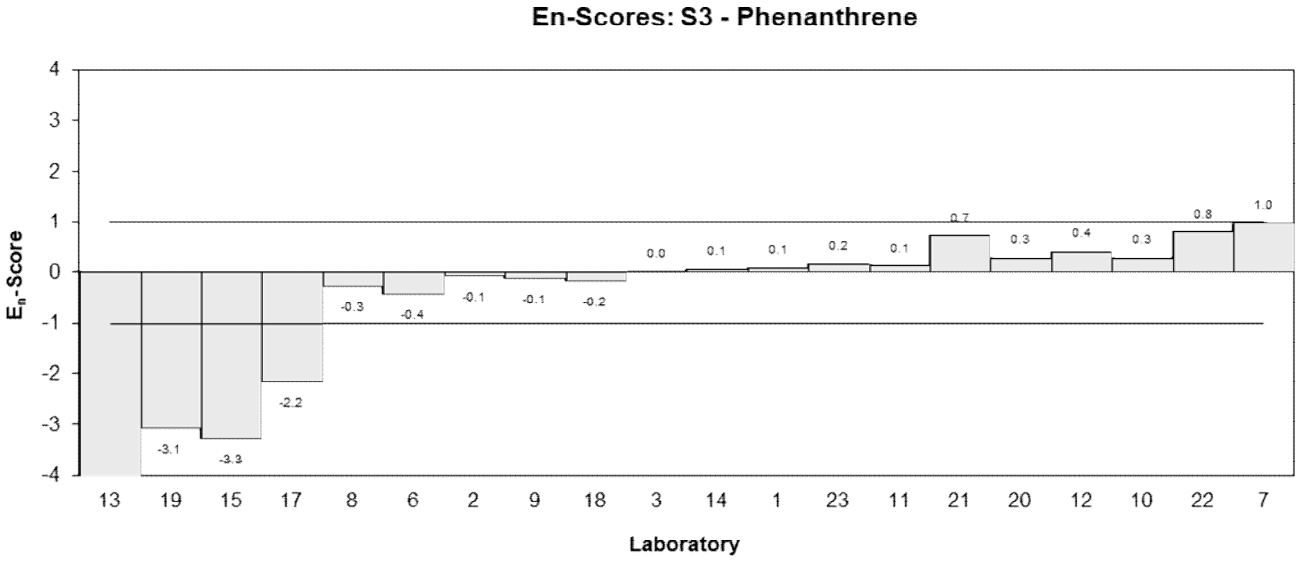

En-Scores: S3 - Phenanthrene
En-Score
Laboratory
13 19 15 17 8 6 2 9 18 3 14 1 23 11 21 20 12 10 22 7

Figure 16

Table 22

Sample Details

Sample No.	S3
Matrix	Water
Analyte	Pyrene
Units	µg/L

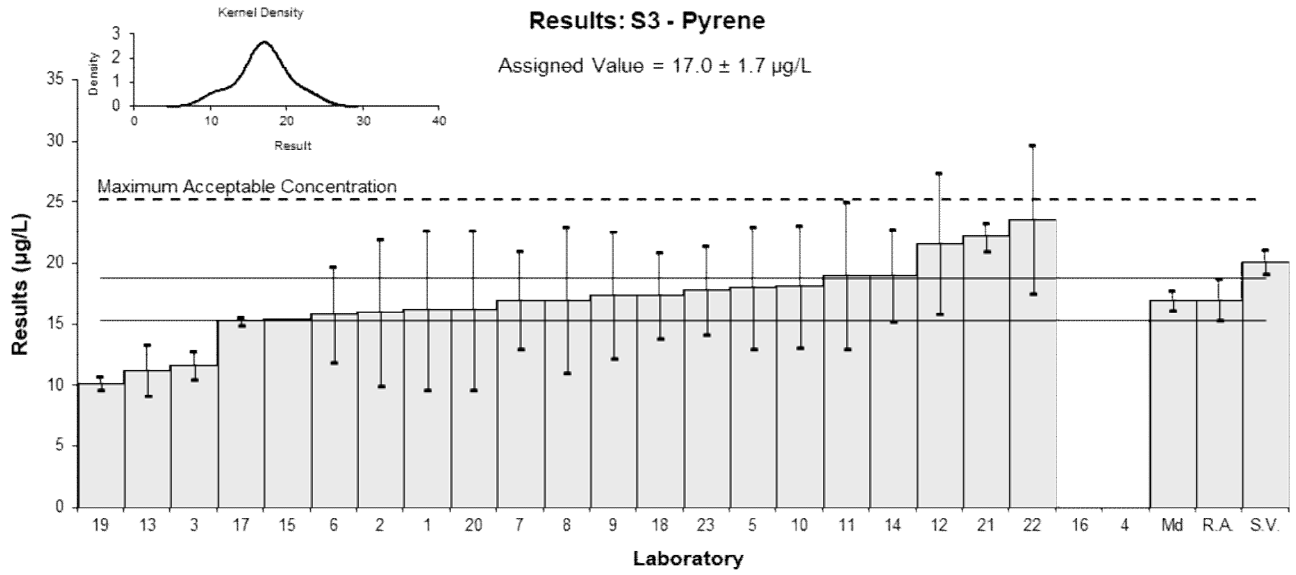
Participant Results

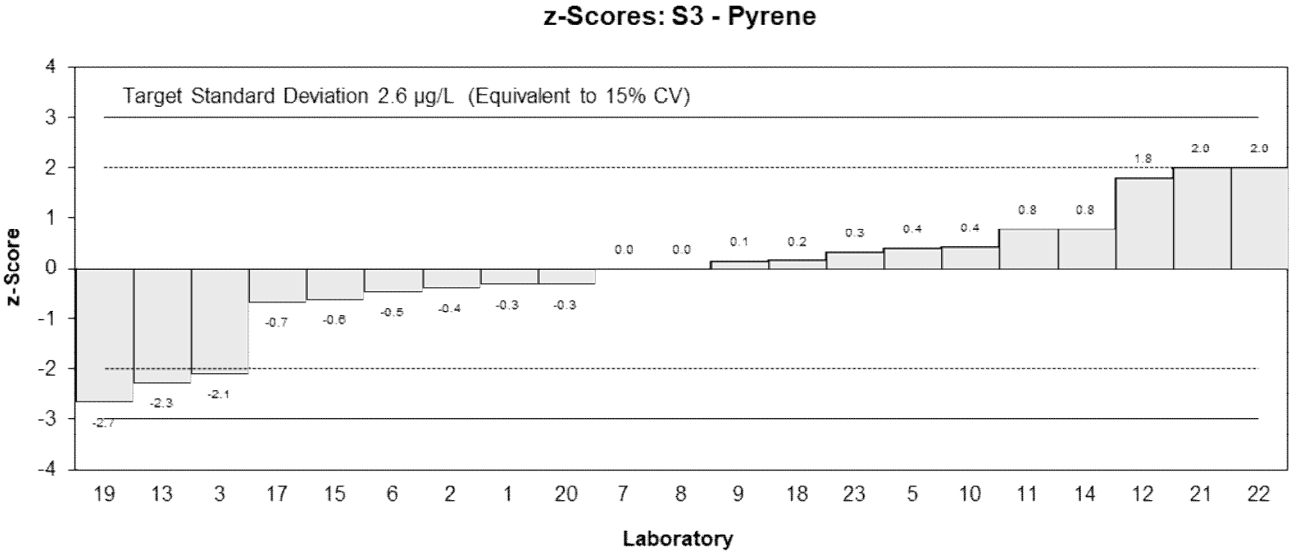
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	16.2	6.5	-0.31	-0.12
2	16	6	-0.39	-0.16
3	11.66	1.17	-2.09	-2.59
4	NT	NT		
5	18	5	0.39	0.19
6	15.8	3.9	-0.47	-0.28
7	17	4	0.00	0.00
8	17	6	0.00	0.00
9	17.36	5.21	0.14	0.07
10	18.1	5	0.43	0.21
11	19	6	0.78	0.32
12	21.6	5.76	1.80	0.77
13	11.2	2.1	-2.27	-2.15
14	19	3.8	0.78	0.48
15	15.3861	NR	-0.63	-0.95
16	NT	NT		
17	15.26	0.31	-0.68	-1.01
18	17.4	3.5	0.16	0.10
19	10.2	0.5	-2.67	-3.84
20	16.2	6.5	-0.31	-0.12
21*	22.17	1.12	2.00	1.00
22*	23.6	6.1	2.00	1.00
23	17.8	3.6	0.31	0.20

Statistics

Assigned Value	17.0	1.7
Spike	20.1	1.0
Max. Acceptable Conc.*	25.2	
Robust Average	17.0	1.7
Median	17.0	0.8
Mean	16.9	
N	21	
Max.	23.6	
Min.	10.2	
Robust SD	3.1	
Robust CV	18%	

* z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S3 - Pyrene
Assigned Value = 17.0 ± 1.7 µg/L
Maximum Acceptable Concentration
Results (µg/L)
Laboratory
19 13 3 17 15 6 2 1 20 7 8 9 18 23 5 10 11 14 12 21 22 16 4 Md R.A. S.V.


z-Scores: S3 - Pyrene
Target Standard Deviation 2.6 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
19 13 3 17 15 6 2 1 20 7 8 9 18 23 5 10 11 14 12 21 22

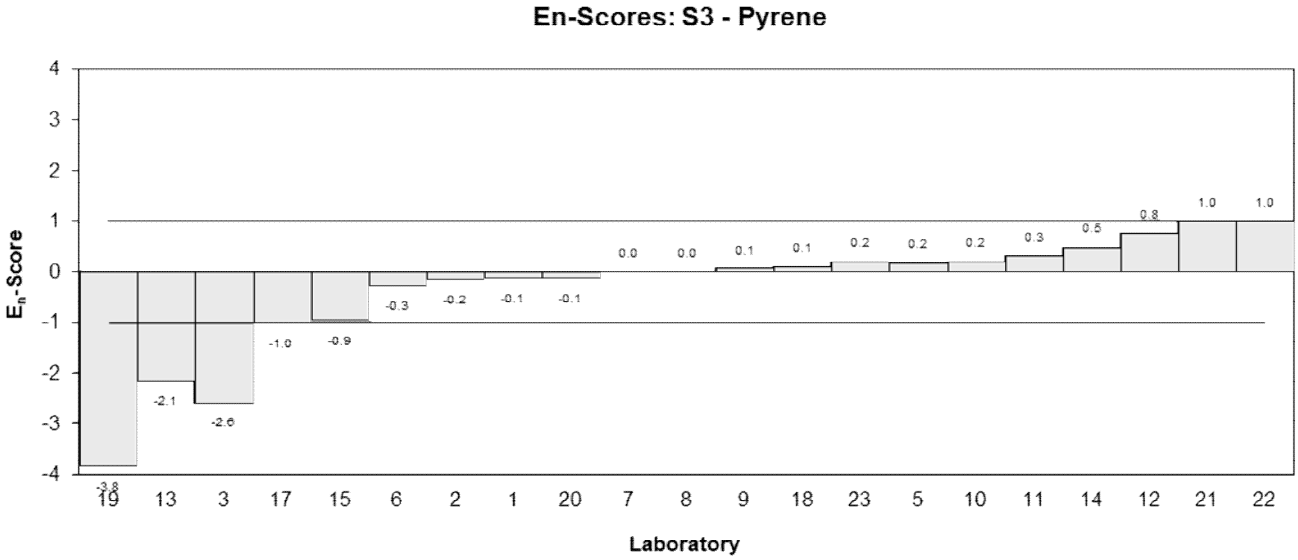

En-Scores: S3 - Pyrene
En-Score
Laboratory
19 13 3 17 15 6 2 1 20 7 8 9 18 23 5 10 11 14 12 21 22

Figure 17

Table 23

Sample Details

Sample No.	S4
Matrix	Water
Analyte	Anthracene
Units	µg/L

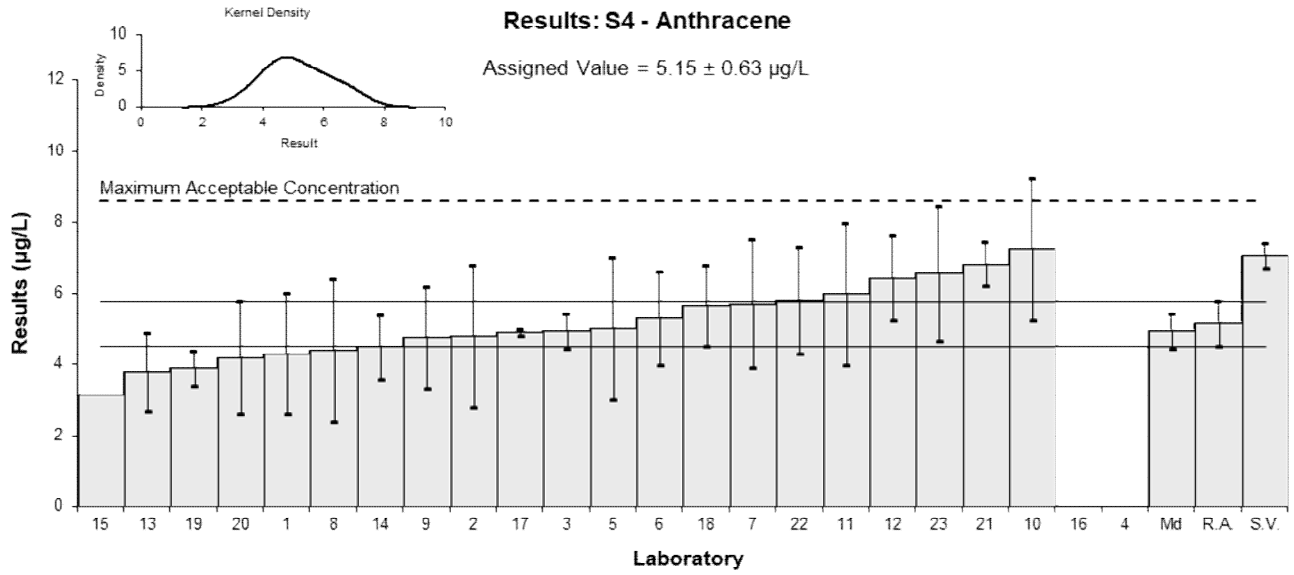
Participant Results

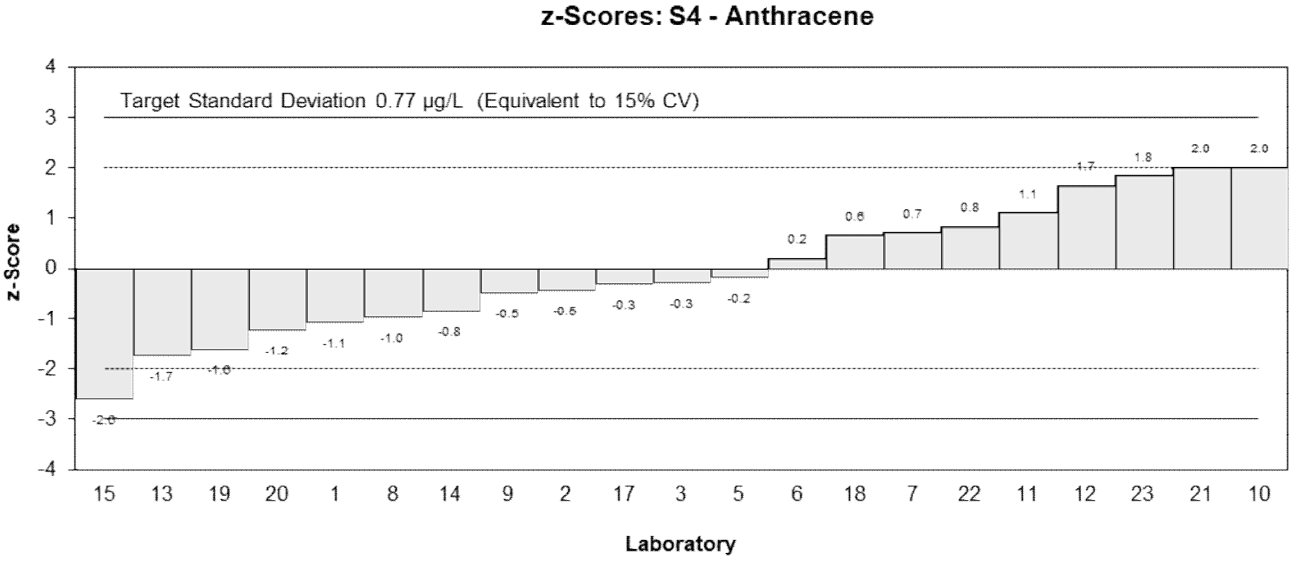
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	4.31	1.7	-1.09	-0.46
2	4.8	2	-0.45	-0.17
3	4.93	0.49	-0.28	-0.28
4	NT	NT		
5	5	2	-0.19	-0.07
6	5.3	1.3	0.19	0.10
7	5.7	1.8	0.71	0.29
8	4.4	2	-0.97	-0.36
9	4.77	1.43	-0.49	-0.24
10*	7.24	2	2.00	1.00
11	6.0	2	1.10	0.41
12	6.43	1.18	1.66	0.96
13	3.8	1.1	-1.75	-1.06
14	4.5	0.9	-0.84	-0.59
15	3.1318	NR	-2.61	-3.20
16	NT	NT		
17	4.91	0.1	-0.31	-0.38
18	5.65	1.13	0.65	0.39
19	3.9	0.5	-1.62	-1.55
20	4.2	1.6	-1.23	-0.55
21*	6.83	0.61	2.00	1.00
22	5.8	1.5	0.84	0.40
23	6.57	1.9	1.84	0.71

Statistics

Assigned Value	5.15	0.63
Spike	7.06	0.35
Max. Acceptable Conc.*	8.61	
Robust Average	5.15	0.63
Median	4.93	0.49
Mean	5.15	
N	21	
Max.	7.24	
Min.	3.1318	
Robust SD	1.1	
Robust CV	22%	

* z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S4 - Anthracene
Assigned Value = 5.15 ± 0.63 µg/L
Maximum Acceptable Concentration
Results (µg/L)
15 13 19 20 1 8 14 9 2 17 3 5 6 18 7 22 11 12 23 21 10 16 4 Md R.A. S.V.
Laboratory


z-Scores: S4 - Anthracene
Target Standard Deviation 0.77 µg/L (Equivalent to 15% CV)
z-Score
15 13 19 20 1 8 14 9 2 17 3 5 6 18 7 22 11 12 23 21 10
Laboratory

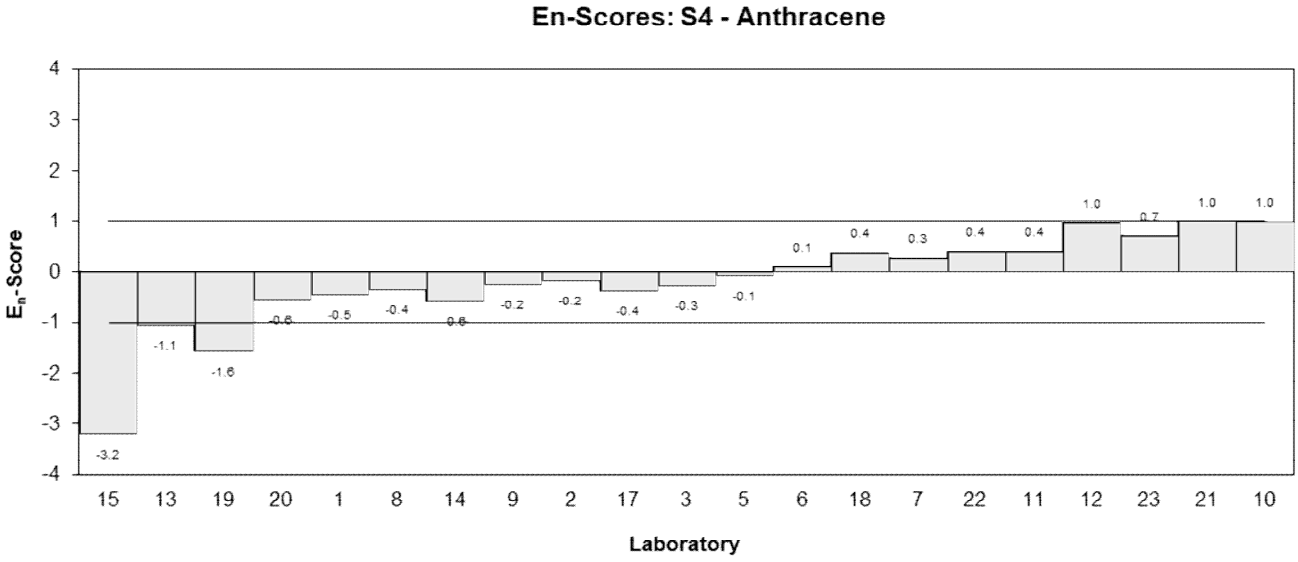

En-Scores: S4 - Anthracene
En-Score
15 13 19 20 1 8 14 9 2 17 3 5 6 18 7 22 11 12 23 21 10
Laboratory

Figure 18

Table 24

Sample Details

Sample No.	S4
Matrix	Water
Analyte	Benzo(a)pyrene
Units	µg/L

Participant Results

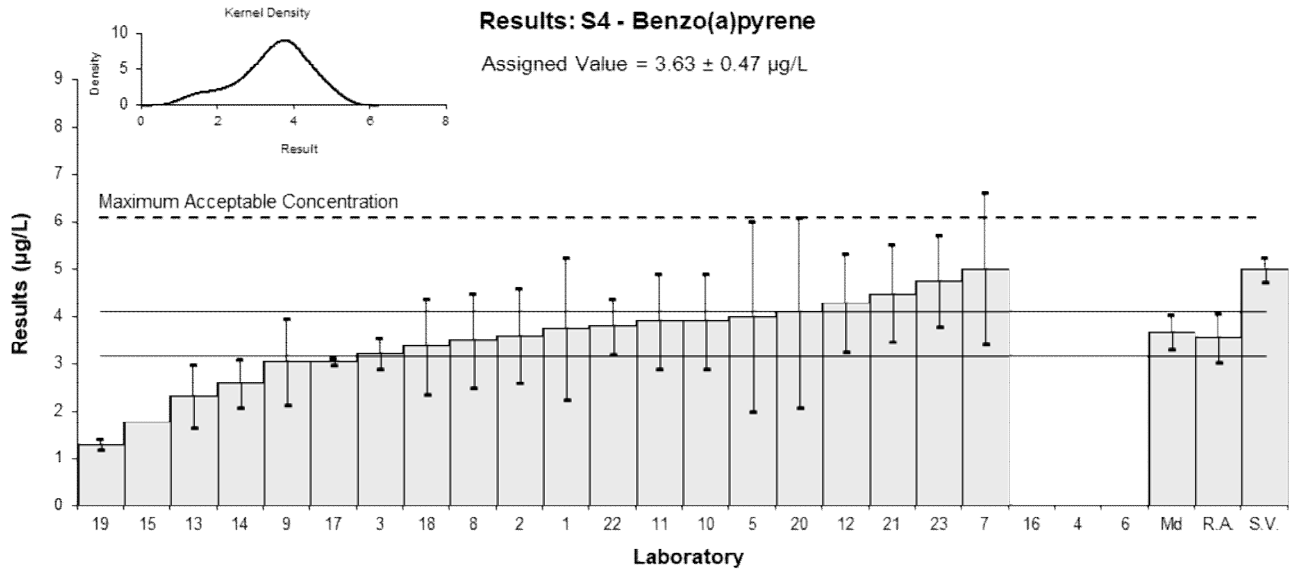
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	3.74	1.5	0.20	0.07
2	3.6	1	-0.06	-0.03
3	3.22	0.32	-0.75	-0.72
4	NT	NT		
5	4	2	0.68	0.18
6	NT	NT		
7**	5.0	1.6	2.00	0.82
8	3.5	1	-0.24	-0.12
9	3.04	0.91	-1.08	-0.58
10	3.91	1	0.51	0.25
11	3.9	1	0.50	0.24
12	4.29	1.05	1.21	0.57
13	2.32	0.67	-2.41	-1.60
14	2.6	0.5	-1.89	-1.50
15	1.7858	NR	-3.39	-3.92
16	NT	NT		
17	3.05	0.06	-1.07	-1.22
18	3.37	1.01	-0.48	-0.23
19	1.3	0.1	-4.28	-4.85
20	4.1	2	0.86	0.23
21	4.49	1.023	1.58	0.76
22	3.8	0.6	0.31	0.22
23**	4.75	0.95	2.00	1.00

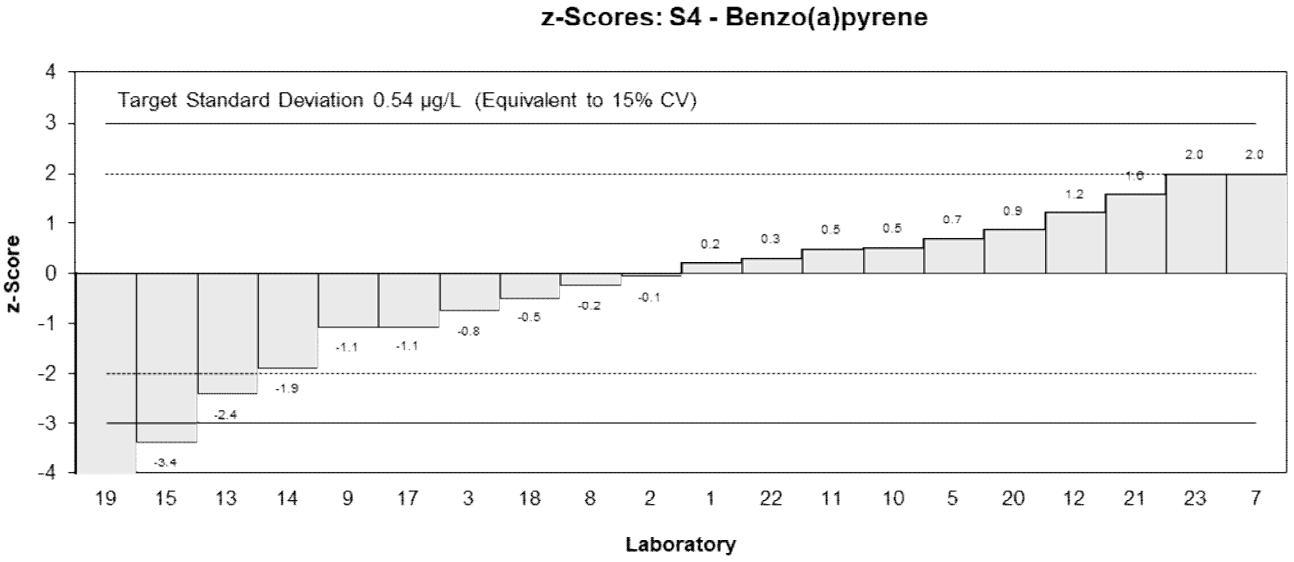
Statistics

Assigned Value*	3.63	0.47
Spike	5.00	0.25
Max. Acceptable Conc.**	6.09	
Robust Average	3.55	0.51
Median	3.67	0.37
Mean	3.49	
N	20	
Max.	5	
Min.	1.3	
Robust SD	0.92	
Robust CV	26%	

* Robust average excluding Laboratory 19.

** z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S4 - Benzo(a)pyrene
Assigned Value = 3.63 ± 0.47 µg/L
Maximum Acceptable Concentration
Results (µg/L)
19 15 13 14 9 17 3 18 8 2 1 22 11 10 5 20 12 21 23 7 16 4 6 Md R.A. S.V.
Laboratory


z-Scores: S4 - Benzo(a)pyrene
Target Standard Deviation 0.54 µg/L (Equivalent to 15% CV)
z-Score
19 15 13 14 9 17 3 18 8 2 1 22 11 10 5 20 12 21 23 7
Laboratory

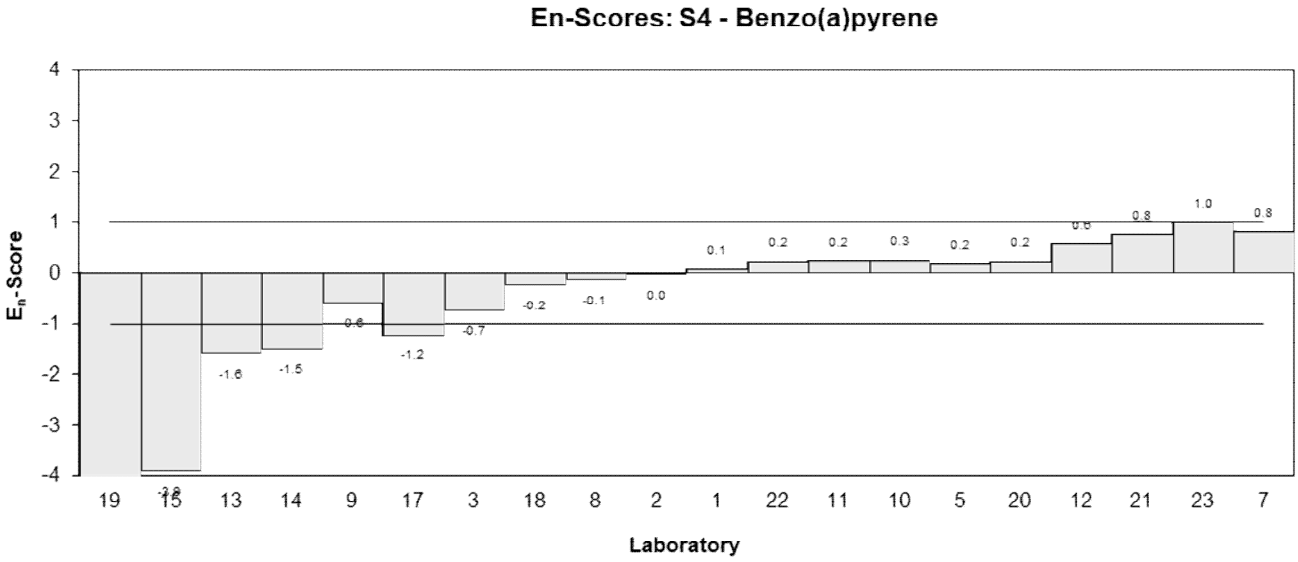

En-Scores: S4 - Benzo(a)pyrene
En-Score
19 15 13 14 9 17 3 18 8 2 1 22 11 10 5 20 12 21 23 7
Laboratory

Figure 19

Table 25

Sample Details

Sample No.	S4
Matrix	Water
Analyte	Chrysene
Units	µg/L

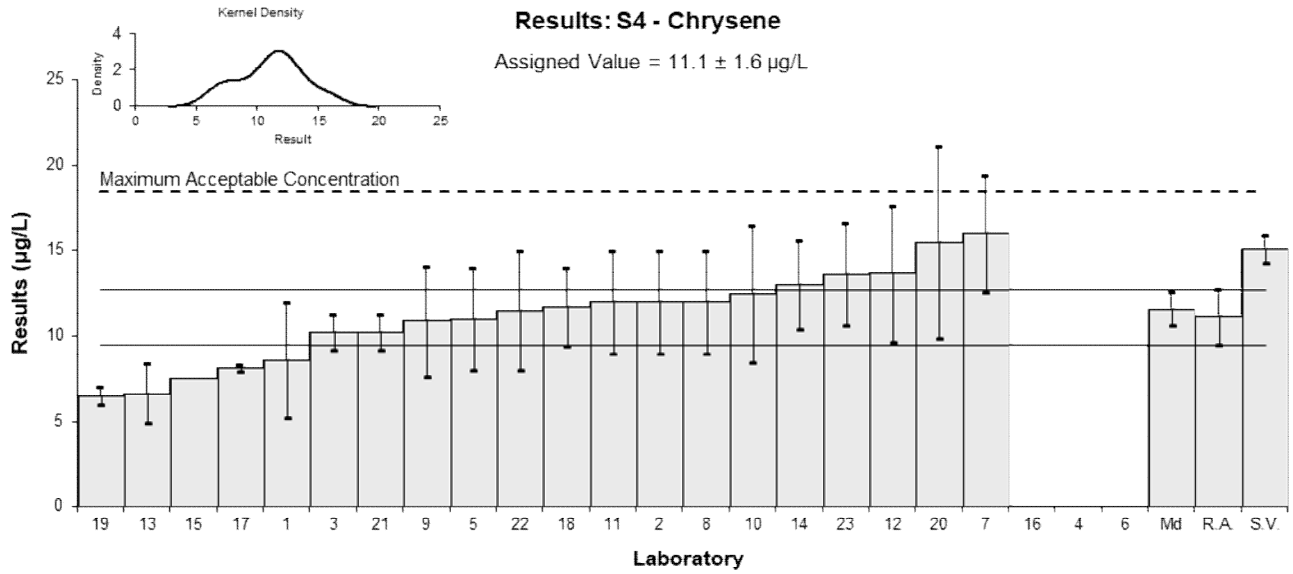
Participant Results

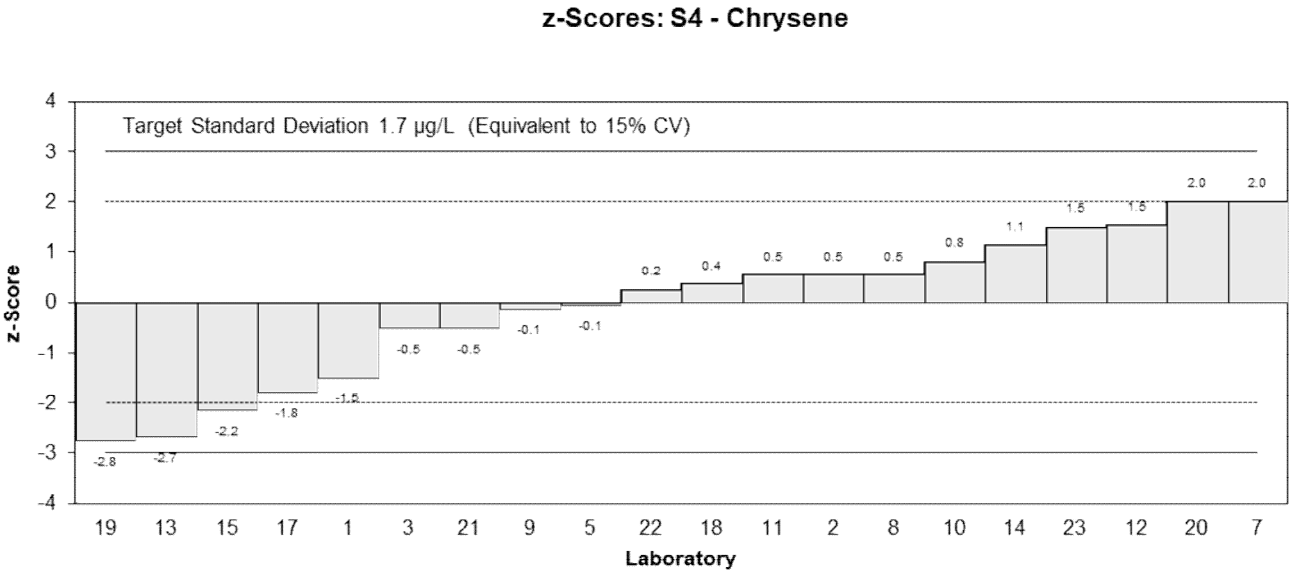
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	8.6	3.4	-1.50	-0.67
2	12	3	0.54	0.26
3	10.22	1.02	-0.53	-0.46
4	NT	NT		
5	11	3	-0.06	-0.03
6	NT	NT		
7*	16	3.4	2.00	1.00
8	12	3	0.54	0.26
9	10.86	3.26	-0.14	-0.07
10	12.45	4	0.81	0.31
11	12	3	0.54	0.26
12	13.65	3.97	1.53	0.60
13	6.63	1.74	-2.68	-1.89
14	13	2.6	1.14	0.62
15	7.5055	NR	-2.16	-2.25
16	NT	NT		
17	8.11	0.16	-1.80	-1.86
18	11.7	2.3	0.36	0.21
19	6.5	0.5	-2.76	-2.74
20*	15.5	5.6	2.00	0.76
21	10.23	1.02	-0.52	-0.46
22	11.5	3.5	0.24	0.10
23	13.6	3.0	1.50	0.74

Statistics

Assigned Value	11.1	1.6
Spike	15.1	0.8
Max. Acceptable Conc.*	18.4	
Robust Average	11.1	1.6
Median	11.6	1.0
Mean	11.2	
N	20	
Max.	16	
Min.	6.5	
Robust SD	2.9	
Robust CV	26%	

* z-Score adjusted to 2.00 (see Section 6.3).


Kernel Density
Density
Result
Results: S4 - Chrysene
Assigned Value = 11.1 ± 1.6 µg/L
Maximum Acceptable Concentration
Results (µg/L)
Laboratory
19 13 15 17 1 3 21 9 5 22 18 11 2 8 10 14 23 12 20 7 16 4 6 Md R.A. S.V.


z-Scores: S4 - Chrysene
Target Standard Deviation 1.7 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
19 13 15 17 1 3 21 9 5 22 18 11 2 8 10 14 23 12 20 7

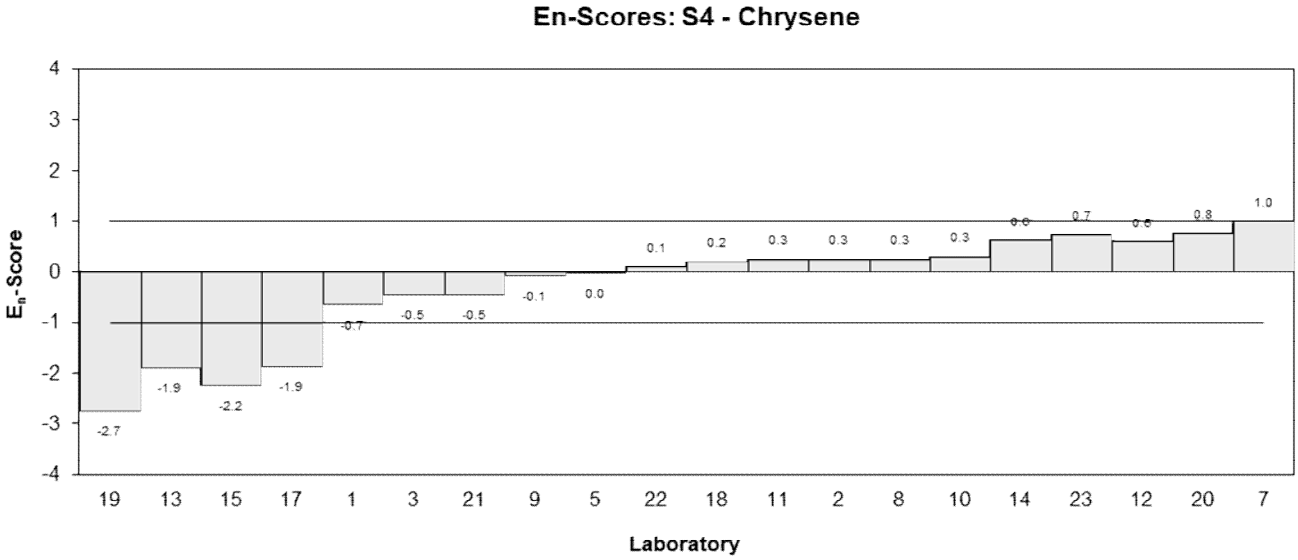

En-Scores: S4 - Chrysene
En-Score
Laboratory
19 13 15 17 1 3 21 9 5 22 18 11 2 8 10 14 23 12 20 7

Figure 20

Table 26

Sample Details

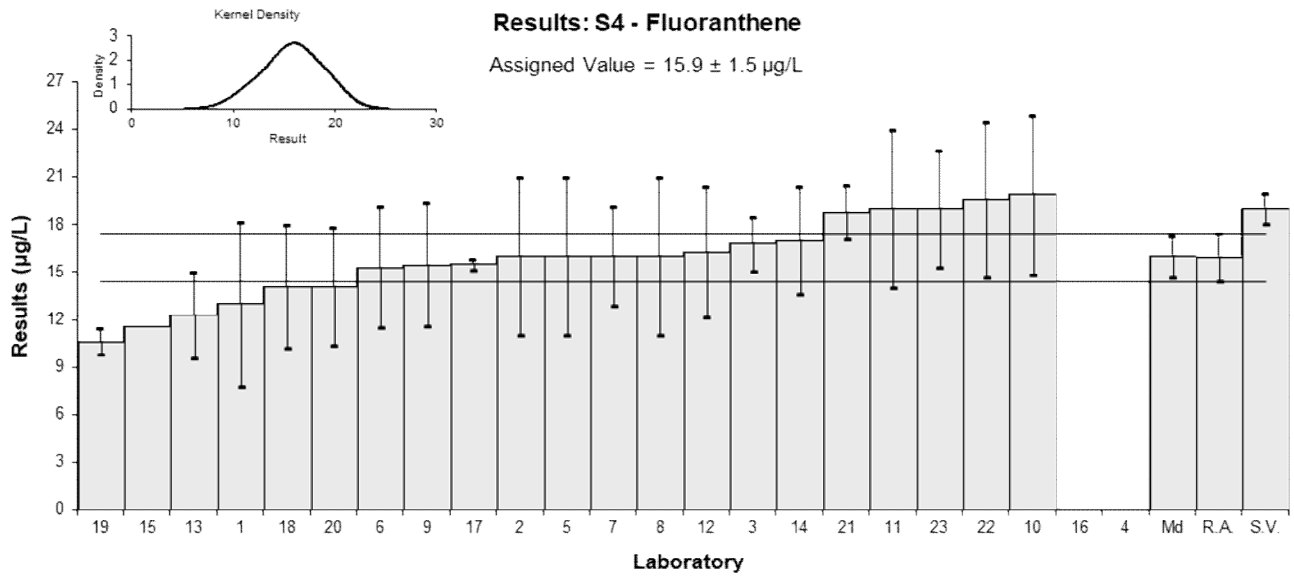
Sample No.	S4
Matrix	Water
Analyte	Fluoranthene
Units	µg/L

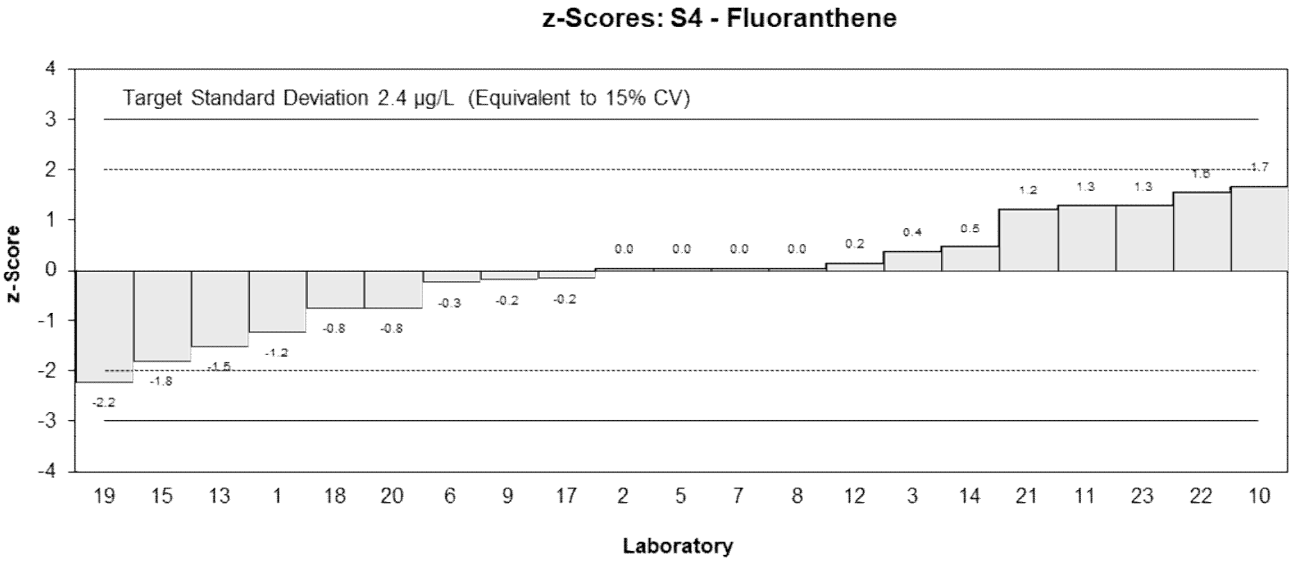
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	12.98	5.2	-1.22	-0.54
2	16	5	0.04	0.02
3	16.79	1.68	0.37	0.40
4	NT	NT		
5	16	5	0.04	0.02
6	15.3	3.8	-0.25	-0.15
7	16	3.1	0.04	0.03
8	16	5	0.04	0.02
9	15.47	3.87	-0.18	-0.10
10	19.87	5	1.66	0.76
11	19	5	1.30	0.59
12	16.26	4.12	0.15	0.08
13	12.29	2.7	-1.51	-1.17
14	17	3.4	0.46	0.30
15	11.5860	NR	-1.81	-2.88
16	NT	NT		
17	15.5	0.31	-0.17	-0.26
18	14.1	3.9	-0.75	-0.43
19	10.6	0.8	-2.22	-3.12
20	14.1	3.7	-0.75	-0.45
21	18.78	1.69	1.21	1.27
22	19.6	4.9	1.55	0.72
23	19.0	3.7	1.30	0.78

Statistics

Assigned Value	15.9	1.5
Spike	19.0	0.9
Robust Average	15.9	1.5
Median	16.0	1.3
Mean	15.8	
N	21	
Max.	19.87	
Min.	10.6	
Robust SD	2.8	
Robust CV	18%	


Kernel Density
Density
Result
Results: S4 - Fluoranthene
Assigned Value = 15.9 ± 1.5 µg/L
Results (µg/L)
Laboratory
19 15 13 1 18 20 6 9 17 2 5 7 8 12 3 14 21 11 23 22 10 16 4 Md R.A. S.V.


z-Scores: S4 - Fluoranthene
Target Standard Deviation 2.4 µg/L (Equivalent to 15% CV)
z-Score
-2.2 -1.8 -1.5 -1.2 -0.8 -0.8 -0.3 -0.2 -0.2 0.0 0.0 0.0 0.0 0.2 0.4 0.5 1.2 1.3 1.3 1.6 1.7
Laboratory
19 15 13 1 18 20 6 9 17 2 5 7 8 12 3 14 21 11 23 22 10

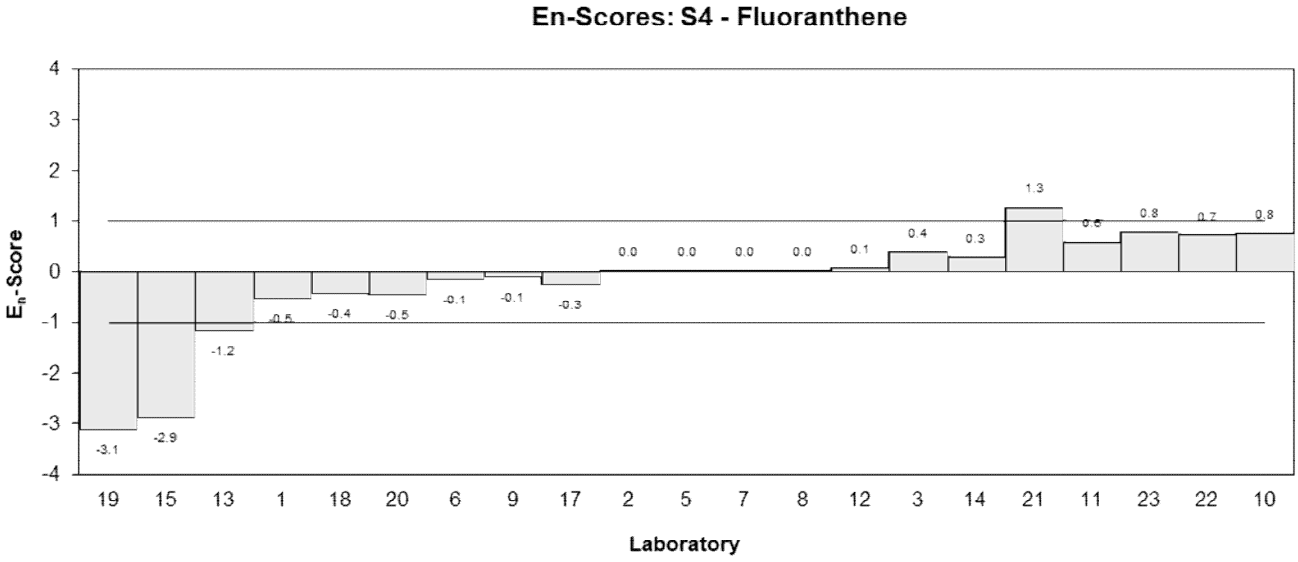

En-Scores: S4 - Fluoranthene
En-Score
-3.1 -2.9 -1.2 -0.5 -0.4 -0.5 -0.1 -0.1 -0.3 0.0 0.0 0.0 0.0 0.1 0.4 0.3 1.3 0.6 0.8 0.7 0.8
Laboratory
19 15 13 1 18 20 6 9 17 2 5 7 8 12 3 14 21 11 23 22 10

Figure 21

Table 27

Sample Details

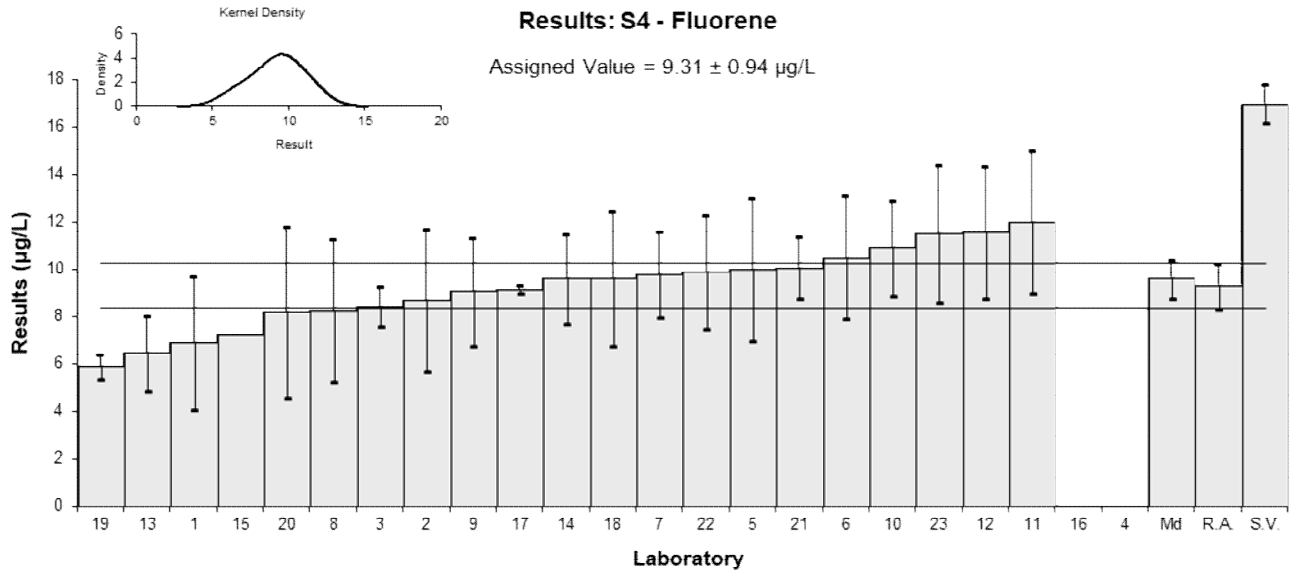
Sample No.	S4
Matrix	Water
Analyte	Fluorene
Units	µg/L

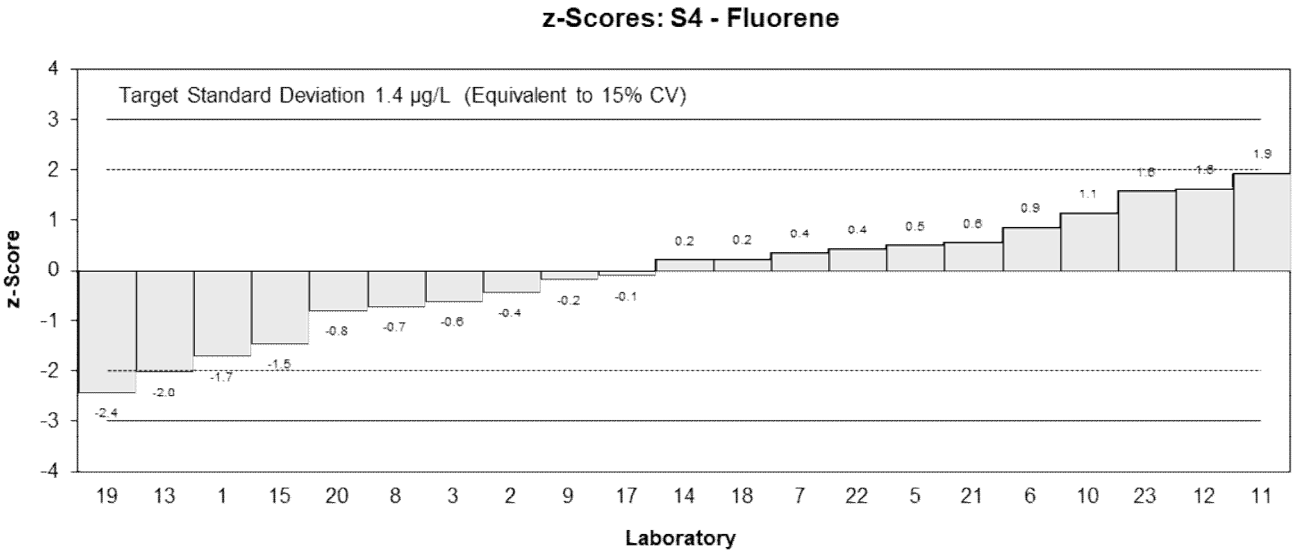
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	6.91	2.8	-1.72	-0.81
2	8.7	3	-0.44	-0.19
3	8.43	0.84	-0.63	-0.70
4	NT	NT		
5	10	3	0.49	0.22
6	10.5	2.6	0.85	0.43
7	9.8	1.8	0.35	0.24
8	8.3	3	-0.72	-0.32
9	9.06	2.27	-0.18	-0.10
10	10.9	2	1.14	0.72
11	12	3	1.93	0.86
12	11.58	2.8	1.63	0.77
13	6.47	1.55	-2.03	-1.57
14	9.6	1.9	0.21	0.14
15	7.2705	NR	-1.46	-2.17
16	NT	NT		
17	9.16	0.18	-0.11	-0.16
18	9.62	2.84	0.22	0.10
19	5.9	0.5	-2.44	-3.20
20	8.2	3.6	-0.79	-0.30
21	10.08	1.31	0.55	0.48
22	9.9	2.4	0.42	0.23
23	11.5	2.9	1.57	0.72

Statistics

Assigned Value	9.31	0.94
Spike	17.0	0.8
Robust Average	9.31	0.94
Median	9.60	0.79
Mean	9.23	
N	21	
Max.	12	
Min.	5.9	
Robust SD	1.7	
Robust CV	19%	


Kernel Density
Density
Result
Results: S4 - Fluorene
Assigned Value = 9.31 ± 0.94 µg/L
Results (µg/L)
19 13 1 15 20 8 3 2 9 17 14 18 7 22 5 21 6 10 23 12 11 16 4 Md R.A. S.V.
Laboratory


z-Scores: S4 - Fluorene
Target Standard Deviation 1.4 µg/L (Equivalent to 15% CV)
z-Score
19 13 1 15 20 8 3 2 9 17 14 18 7 22 5 21 6 10 23 12 11
Laboratory

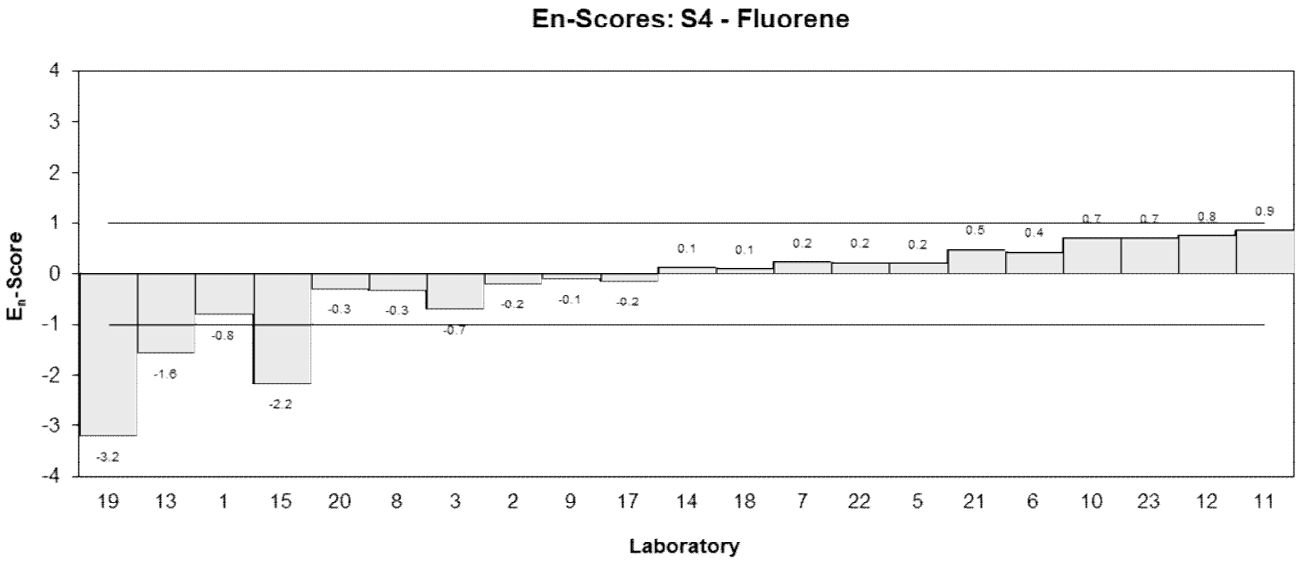

En-Scores: S4 - Fluorene
En-Score
19 13 1 15 20 8 3 2 9 17 14 18 7 22 5 21 6 10 23 12 11
Laboratory

Figure 22

Table 28

Sample Details

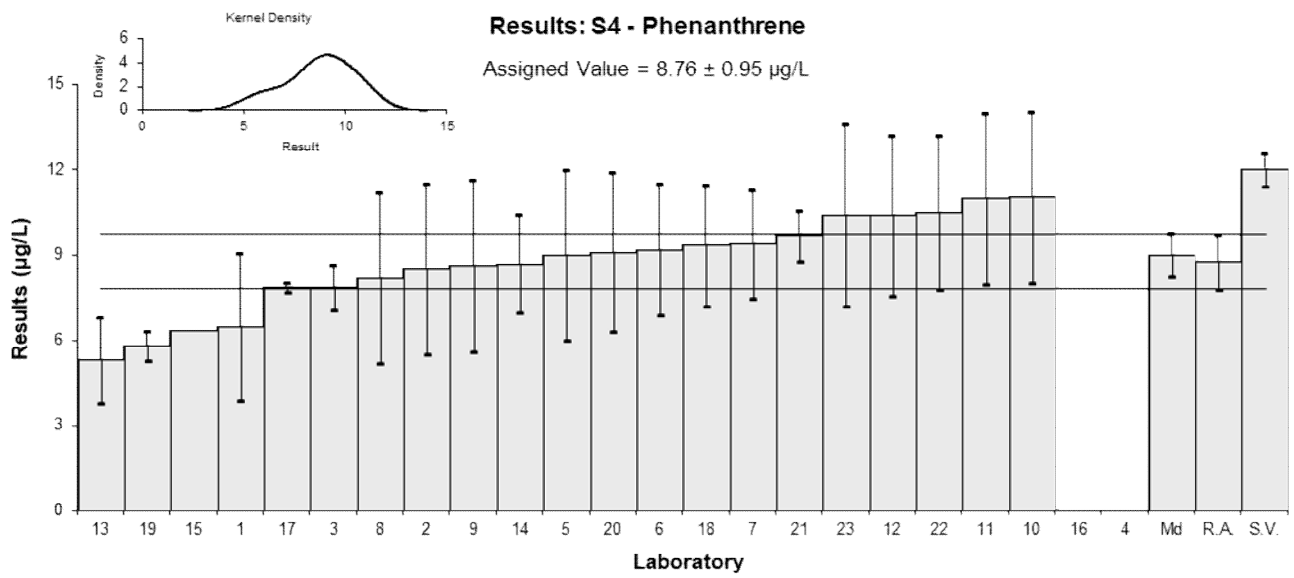
Sample No.	S4
Matrix	Water
Analyte	Phenanthrene
Units	µg/L

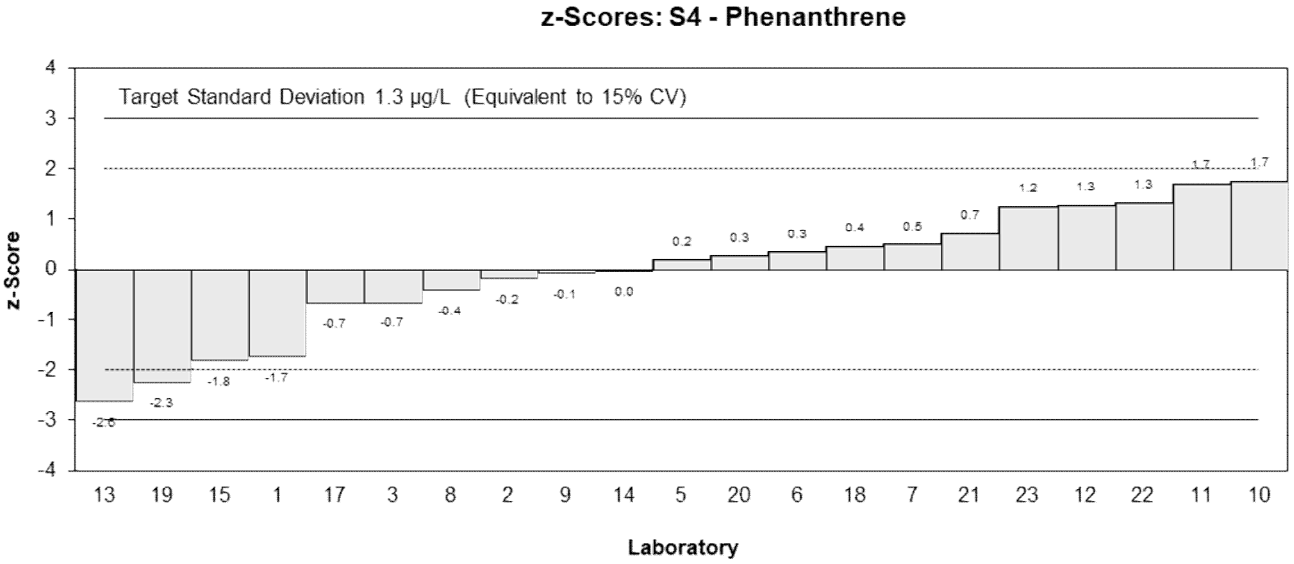
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	6.48	2.6	-1.74	-0.82
2	8.5	3	-0.20	-0.08
3	7.89	0.79	-0.66	-0.70
4	NT	NT		
5	9	3	0.18	0.08
6	9.2	2.3	0.33	0.18
7	9.4	1.9	0.49	0.30
8	8.2	3	-0.43	-0.18
9	8.63	3.02	-0.10	-0.04
10	11.05	3	1.74	0.73
11	11	3	1.70	0.71
12	10.41	2.82	1.26	0.55
13	5.29	1.51	-2.64	-1.95
14	8.7	1.7	-0.05	-0.03
15	6.3615	NR	-1.83	-2.52
16	NT	NT		
17	7.87	0.16	-0.68	-0.92
18	9.34	2.11	0.44	0.25
19	5.8	0.5	-2.25	-2.76
20	9.1	2.8	0.26	0.11
21	9.68	0.87	0.70	0.71
22	10.5	2.7	1.32	0.61
23	10.4	3.2	1.25	0.49

Statistics

Assigned Value	8.76	0.95
Spike	12.0	0.6
Robust Average	8.76	0.95
Median	9.00	0.75
Mean	8.70	
N	21	
Max.	11.05	
Min.	5.29	
Robust SD	1.7	
Robust CV	20%	


Kernel Density
Density
Result
Results: S4 - Phenanthrene
Assigned Value = 8.76 ± 0.95 µg/L
Results (µg/L)
13 19 15 1 17 3 8 2 9 14 5 20 6 18 7 21 23 12 22 11 10 16 4 Md R.A. S.V.
Laboratory


z-Scores: S4 - Phenanthrene
Target Standard Deviation 1.3 µg/L (Equivalent to 15% CV)
z-Score
13 19 15 1 17 3 8 2 9 14 5 20 6 18 7 21 23 12 22 11 10
Laboratory

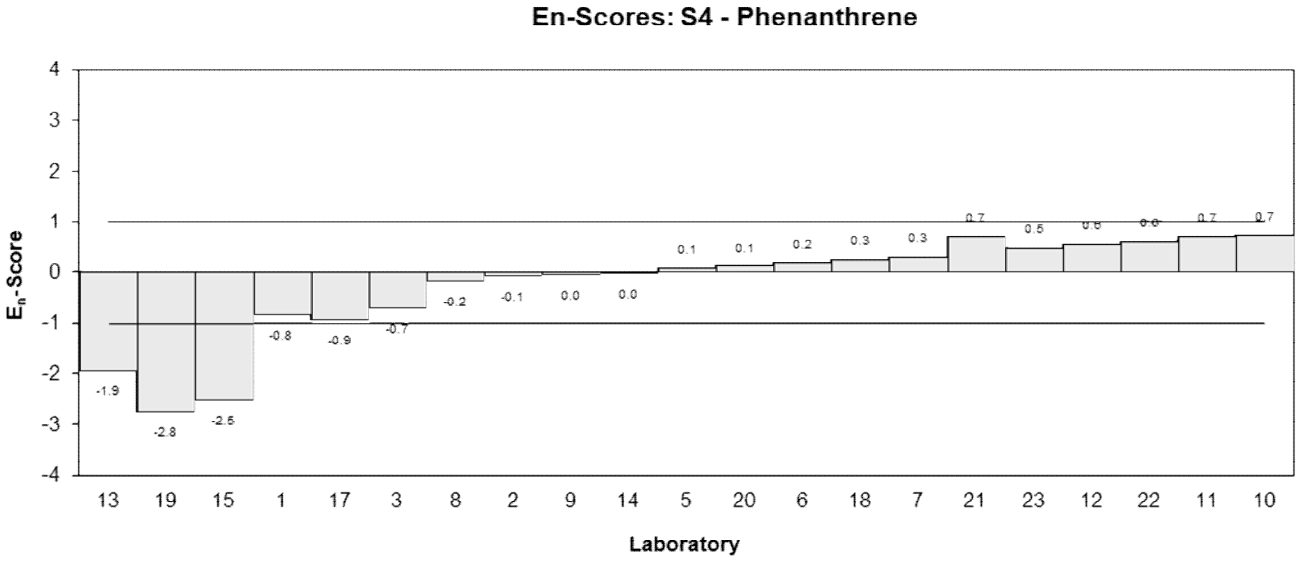

En-Scores: S4 - Phenanthrene
En-Score
13 19 15 1 17 3 8 2 9 14 5 20 6 18 7 21 23 12 22 11 10
Laboratory

Figure 23

Table 29

Sample Details

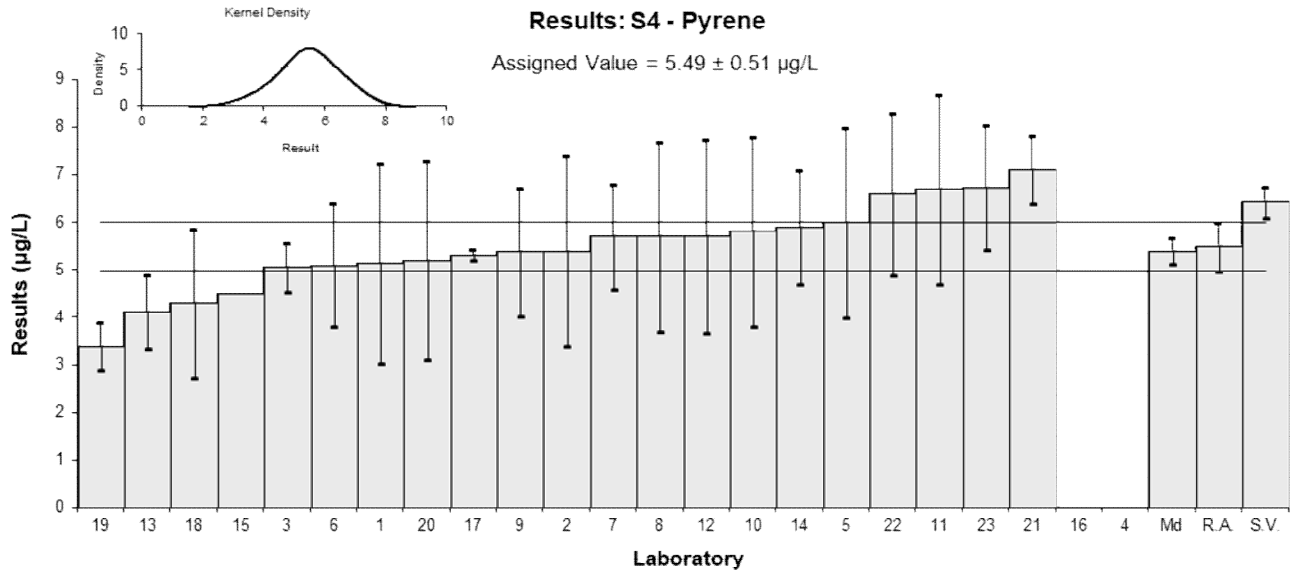
Sample No.	S4
Matrix	Water
Analyte	Pyrene
Units	µg/L

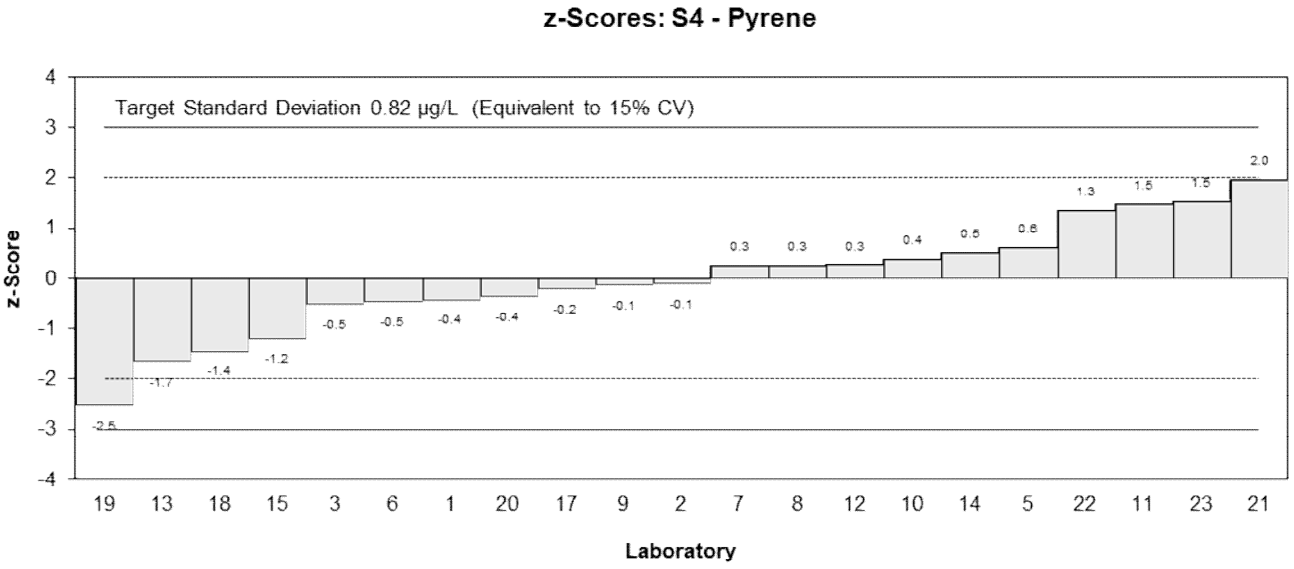
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	5.14	2.1	-0.43	-0.16
2	5.4	2	-0.11	-0.04
3	5.06	0.51	-0.52	-0.60
4	NT	NT		
5	6	2	0.62	0.25
6	5.1	1.3	-0.47	-0.28
7	5.7	1.1	0.26	0.17
8	5.7	2	0.26	0.10
9	5.38	1.35	-0.13	-0.08
10	5.81	2	0.39	0.16
11	6.7	2	1.47	0.59
12	5.71	2.04	0.27	0.10
13	4.12	0.77	-1.66	-1.48
14	5.9	1.2	0.50	0.31
15	4.4991	NR	-1.20	-1.94
16	NT	NT		
17	5.31	0.11	-0.22	-0.35
18	4.30	1.57	-1.45	-0.72
19	3.4	0.5	-2.54	-2.93
20	5.2	2.1	-0.35	-0.13
21	7.11	0.71	1.97	1.85
22	6.6	1.7	1.35	0.63
23	6.74	1.3	1.52	0.90

Statistics

Assigned Value	5.49	0.51
Spike	6.43	0.32
Robust Average	5.49	0.51
Median	5.40	0.28
Mean	5.47	
N	21	
Max.	7.11	
Min.	3.4	
Robust SD	0.94	
Robust CV	17%	


Kernel Density
Density
Result
Results: S4 - Pyrene
Assigned Value = 5.49 ± 0.51 µg/L
Results (µg/L)
19 13 18 15 3 6 1 20 17 9 2 7 8 12 10 14 5 22 11 23 21 16 4 Md R.A. S.V.
Laboratory


z-Scores: S4 - Pyrene
Target Standard Deviation 0.82 µg/L (Equivalent to 15% CV)
z-Score
19 13 18 15 3 6 1 20 17 9 2 7 8 12 10 14 5 22 11 23 21
Laboratory

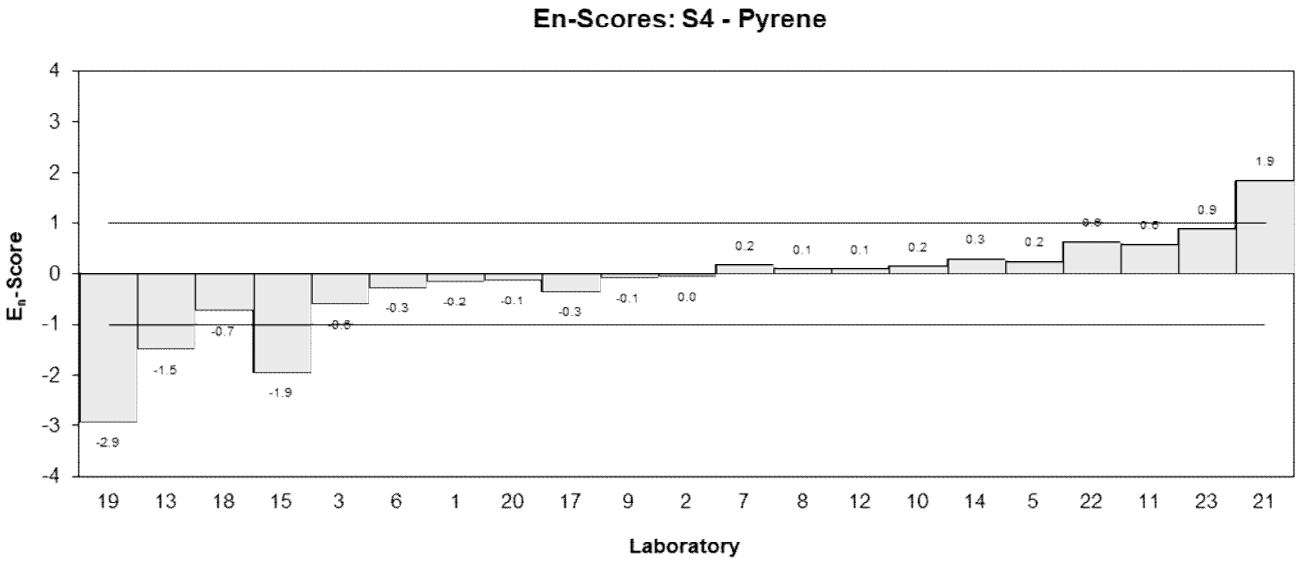

En-Scores: S4 - Pyrene
En-Score
19 13 18 15 3 6 1 20 17 9 2 7 8 12 10 14 5 22 11 23 21
Laboratory

Figure 24

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust average of participants' results was used as the assigned value for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2015.[7] Results less than 50% and greater than 150% of the robust average were removed before the calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using benzene in Sample S2 as an example.

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

No assigned values were set for the >C34-C40 range in Sample S1 as there were too few numerical results. Sample S2 C6-C10 range was also not scored; historically this has been due to its volatile nature and therefore data is provided for information only, though participants' CV in this study has improved as compared to previous Hydrocarbons in Water PT studies.

A comparison of the assigned values and the spiked values is presented in Table 30. Similar ratios of assigned value to spiked value have been observed in previous NMI Hydrocarbons in Water PT studies, and in this study assigned values were set if there was a reasonable consensus of participants' results.

Table 30 Comparison of Assigned Value and Spiked Value

Sample	Analyte	Assigned Value (µg/L)	Spiked Value (µg/L)	Assigned Value / Spiked Value (%)
S1	TRH	1850	3410	54%
S2	Benzene	57.3	57.9	99%
	Toluene	197	219	90%
	Ethylbenzene	25.2	25.0	101%
	Xylenes	152	188	81%
	Total BTEX	430	489	88%
S3	Anthracene	8.46	12.0	71%
	Benzo(a)pyrene	3.82	5.00	76%
	Chrysene	4.82	6.03	80%
	Fluoranthene	5.14	5.85	88%
	Fluorene	7.99	14.1	57%
	Phenanthrene	1.58	2.02	78%
	Pyrene	17.0	20.1	85%
S4	Anthracene	5.15	7.06	73%
	Benzo(a)pyrene	3.63	5.00	73%
	Chrysene	11.1	15.1	74%
	Fluoranthene	15.9	19.0	84%
	Fluorene	9.31	17.0	55%
	Phenanthrene	8.76	12.0	73%
	Pyrene	5.49	6.43	85%

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate. It is a requirement of ISO/IEC 17025 that laboratories have procedures to estimate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including when the client's instruction so requires.[9]

Of 466 numerical results submitted for analytes of interest in this study, 445 (95%) were reported with an associated uncertainty. Participants used a wide variety of procedures to estimate the expanded MU (Table 3).

Laboratory **13** did not report uncertainties for TRH results only, while Laboratory **15** reported PAH results only and did not report any uncertainties. Both participants reported being accredited to ISO/IEC 17025.

The magnitude of reported uncertainties was within the range of 1.6% to 77% relative. In general, an expanded measurement uncertainty of less than 10% relative is likely to be unrealistically small for the routine measurement of a hydrocarbon pollutant in water, while an expanded uncertainty of over 50% is likely to be too large. Of the 445 MUs, 50 were below 10% relative while 8 were greater than 50% relative. Participants reporting these uncertainties should consider if their MUs are suitable or fit-for-purpose.

Laboratories with results having a satisfactory z-score and an unsatisfactory E_n-score are likely to have underestimated the expanded uncertainty associated with that result.

An estimate of uncertainty expressed as a value should not be attached to a non-value result. Laboratories **1**, **9**, **12**, **19**, **20**, **22** and **23** attached an uncertainty to some of their non-value results reported.

In some cases the results were reported with an inappropriate number of significant figures. 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 4.49 ± 1.023 µg/L, it is better to report this as 4.5 ± 1.0 µg/L).[10]

6.3 z-Score

Target SDs equivalent to 15% and 20% PCV were used to calculate z-scores. CVs predicted by the Thompson-Horwitz equation,[8] target SDs (as PCV), and the between laboratories CVs obtained in this study are presented for comparison in Table 31.

Table 31 Comparison of Target SDs, Thompson-Horwitz CVs and Between Laboratories CVs

Sample	Analyte	Assigned Value (µg/L)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between Laboratories CV* (%)
S1	>C10-C16	1110	16	20	31
	>C16-C34	960	16	20	30
	TRH	1850	15	15	31
S2	Benzene	57.3	22	15	13
	Toluene	197	20	15	11
	Ethylbenzene	25.2	22	15	17
	Xylenes	152	21	15	16
	Total BTEX	430	18	15	13

Sample	Analyte	Assigned Value (µg/L)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between Laboratories CV* (%)
S3	Anthracene	8.46	22	15	15
	Benzo(a)pyrene	3.82	22	15	16
	Chrysene	4.82	22	15	18
	Fluoranthene	5.14	22	15	19
	Fluorene	7.99	22	15	16
	Phenanthrene	1.58	22	15	18
	Pyrene	17.0	22	15	18
S4	Anthracene	5.15	22	15	22
	Benzo(a)pyrene	3.63	22	15	23
	Chrysene	11.1	22	15	26
	Fluoranthene	15.9	22	15	18
	Fluorene	9.31	22	15	19
	Phenanthrene	8.76	22	15	20
	Pyrene	5.49	22	15	17

* Robust between laboratories CVs with outliers removed, if applicable.

To account for possible low bias in the consensus values due to laboratories using inefficient extraction or analytical techniques, a total of 15 z-scores were adjusted across the following analytes: Sample S1 TRH, Sample S2 xylenes, Sample S3 benzo(a)pyrene and pyrene, and Sample S4 anthracene, benzo(a)pyrene and chrysene. A maximum acceptable concentration was set to two target SDs more than the spiked value, and results lower than the maximum acceptable concentration but with a z-score greater than 2.0 had their z-score adjusted to 2.0. This ensured that laboratories reporting results close to the spiked value were not penalised. The z-scores for results higher than the maximum acceptable concentration were not adjusted, and z-scores less than 2.0 were left unaltered.

Of 448 results for which z-scores were calculated, 399 (89%) returned a satisfactory score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **1**, **2**, **3**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **17**, **18**, **22** and **23** reported results for all 22 analytes which were scored. Of these participants, Laboratories **1**, **9**, **10**, **12**, **18** and **23** returned satisfactory z-scores for all analytes.

Satisfactory z-scores were achieved for all scored analytes reported by Laboratories **5** (21), **20** (20), **16** (8) and **4** (1).

The dispersal of participants' z-scores is presented by laboratory in Figure 25 and by analyte in Figure 26.

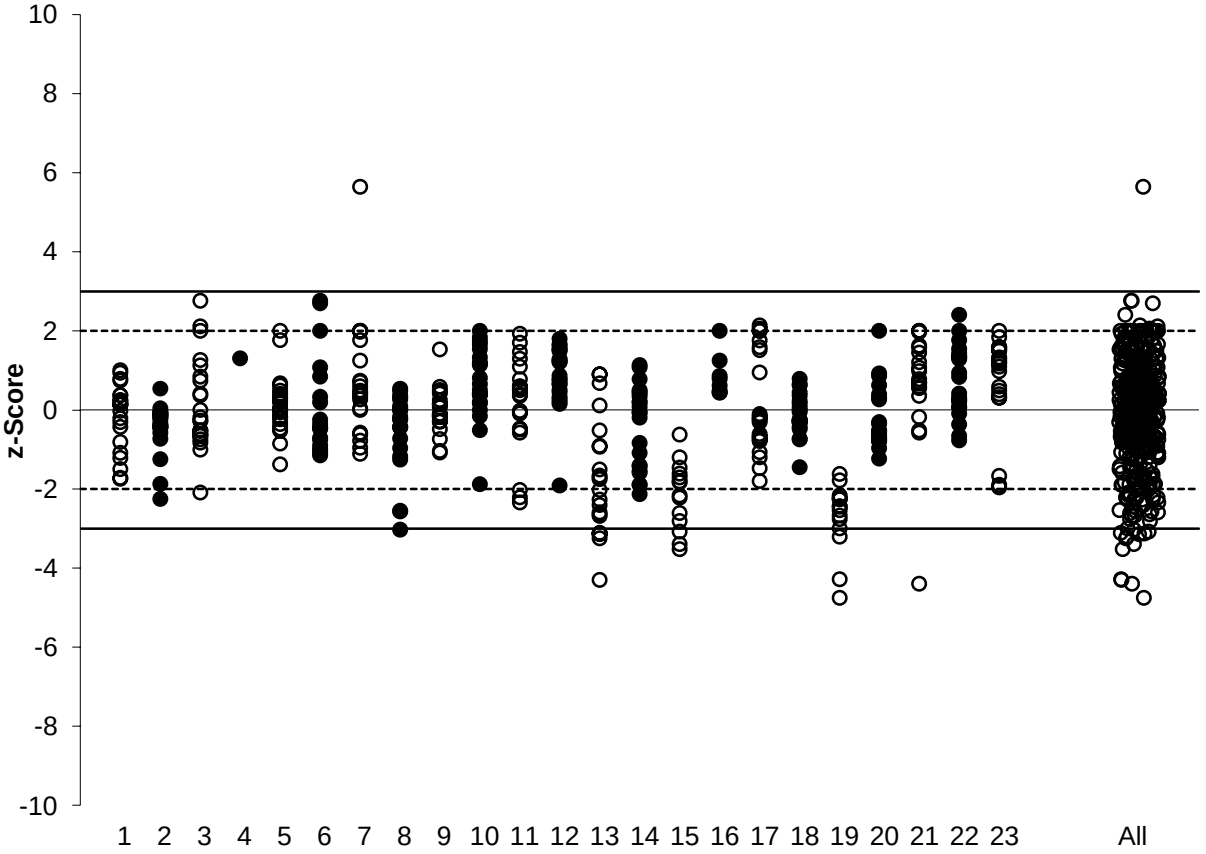


Figure 25 z-Score Dispersal by Laboratory

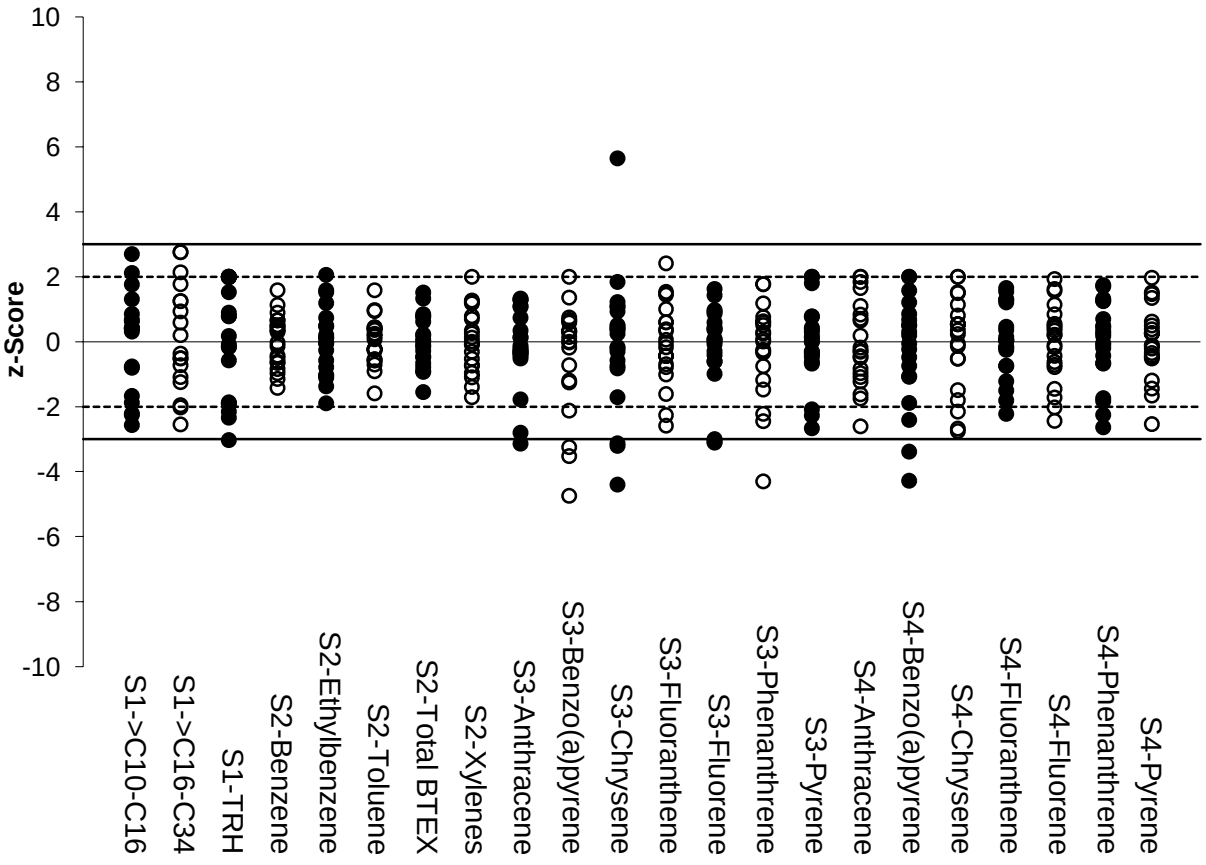


Figure 26 z-Score Dispersal by Sample and Analyte

Figure 27 presents participants' z-scores for Sample S1. Participants with a trend of z-scores below the zero line likely had an inefficient extraction process for TRH. As the ratio of the assigned value to the spiked value was 54% for TRH, participants reporting results with higher z-scores may have more efficient extraction methodologies.

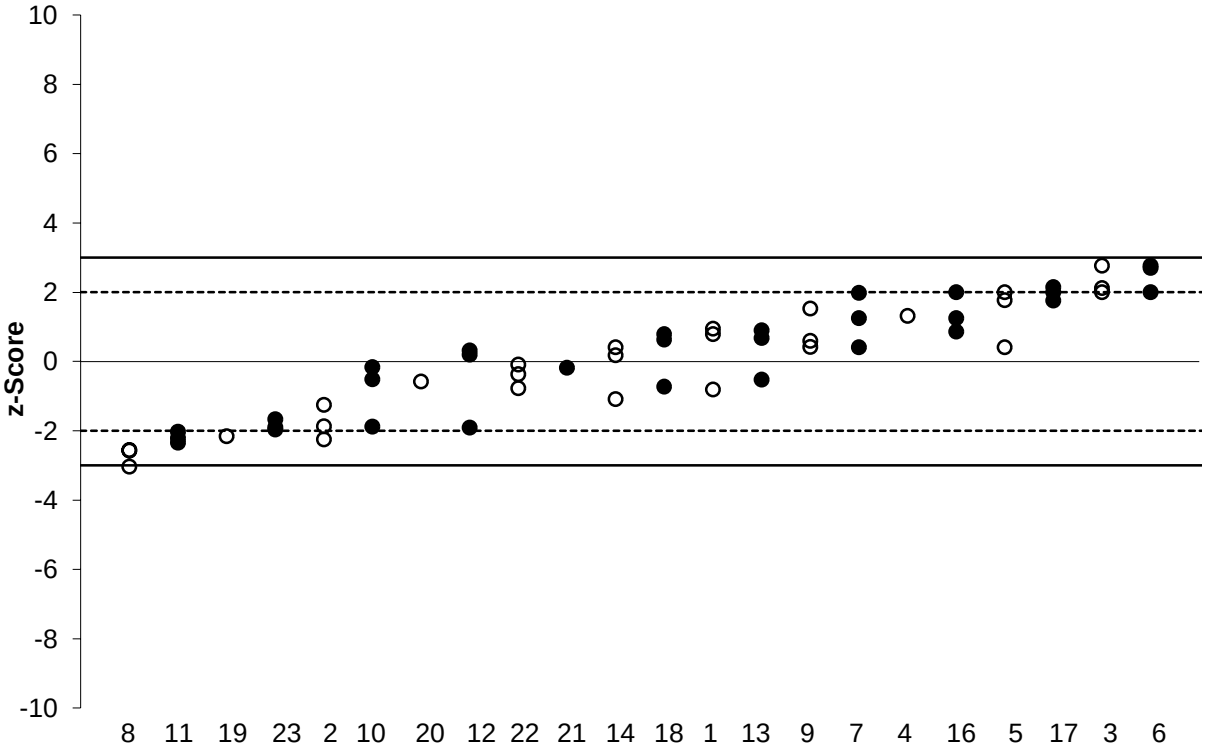


Figure 27 TRH (Sample S1) z-Score Dispersal by Laboratory

Figure 28 presents participants' z-scores for Sample S2 only. A trend of z-scores on one side of the zero line may indicate laboratory bias for BTEX analytes.

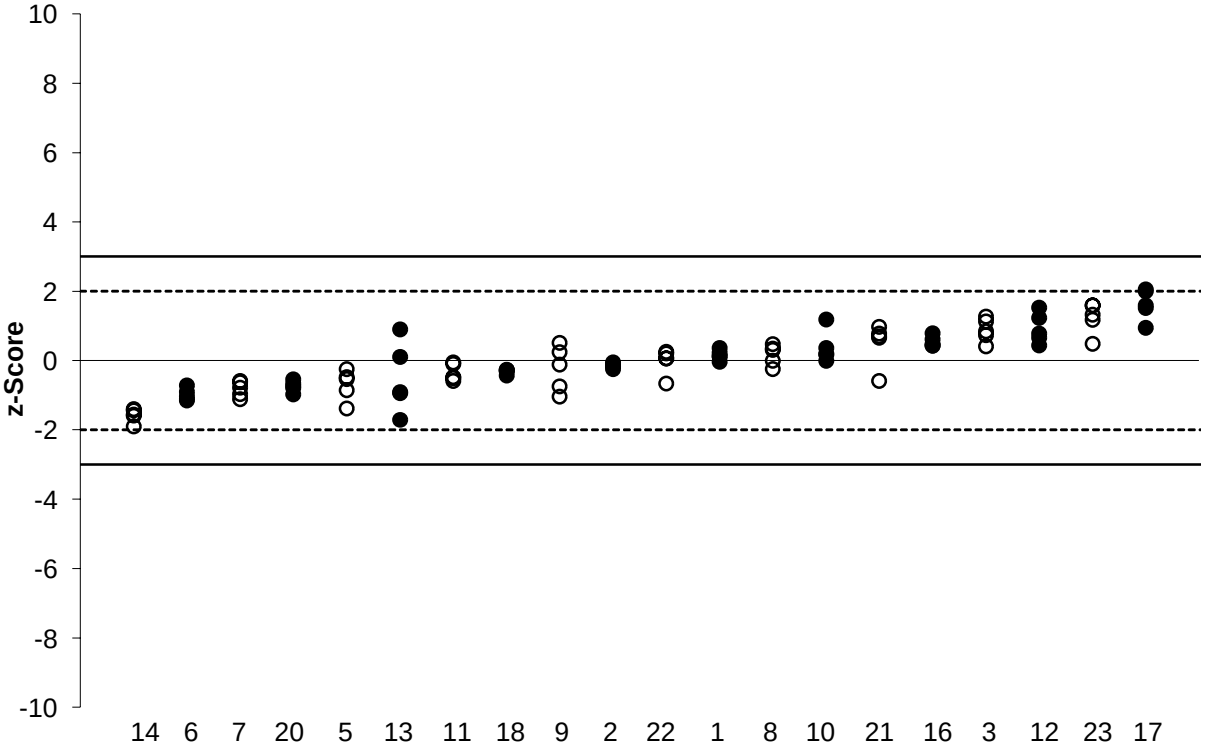


Figure 28 BTEX (Sample S2) z-Score Dispersal by Laboratory

Figure 29 presents participants' z-scores for Samples S3 and S4. Participants with a trend of z-scores below the zero line may have an inefficient extraction process for PAH analytes. As the ratio of the assigned value to the spiked value ranged from 55% – 88%, results with higher z-scores may correspond to the more efficient extraction of PAH analytes by participants.

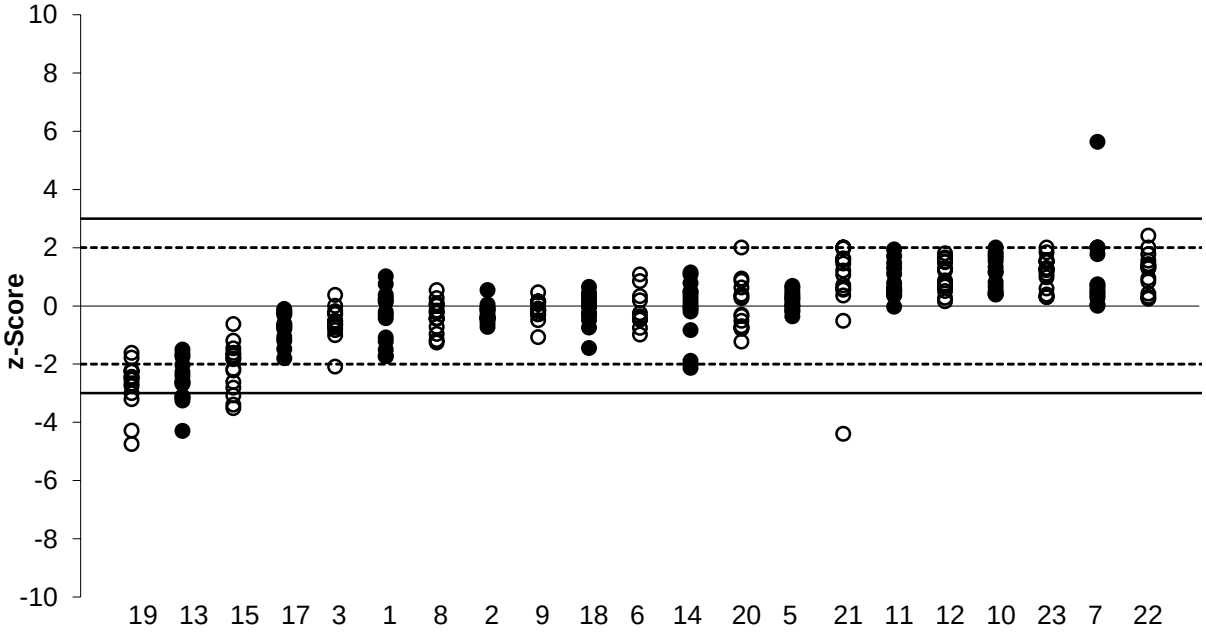


Figure 29 PAH (Samples S3 and S4) z-Score Dispersal by Laboratory

Scatter plots of z-scores for anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene in Samples S3 and S4 are presented in Figures 30 to 36. Scores are predominantly in the upper right and lower left quadrants, indicating that laboratory bias is the major contributor to the variability of results. Points close to the diagonal axis demonstrate excellent repeatability while points close to the zero demonstrate excellent repeatability and accuracy.

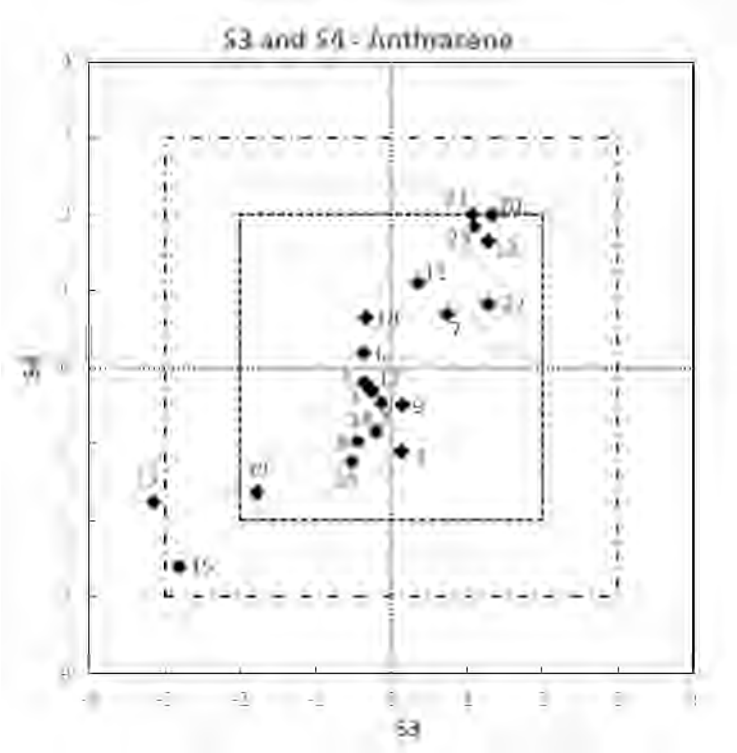
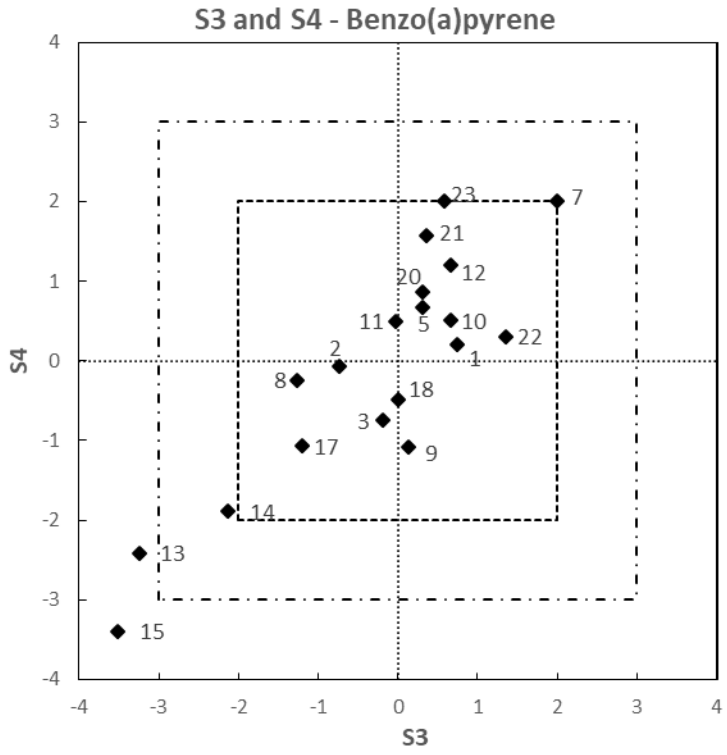
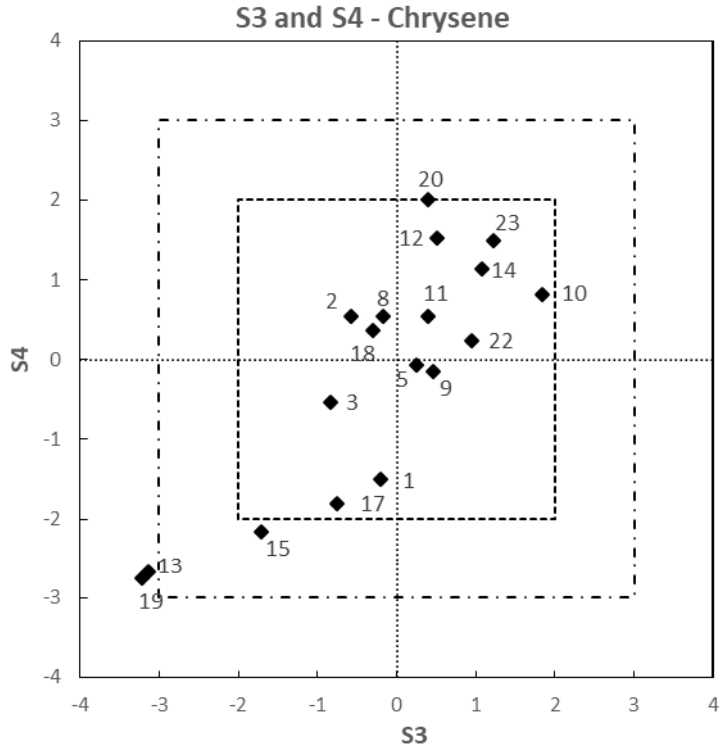


Figure 30 z-Score Scatter Plot – Anthracene



Laboratory 19 is off-scale.

Figure 31 z-Score Scatter Plot – Benzo(a)pyrene



Laboratories 7 and 21 are off-scale.

Figure 32 z-Score Scatter Plot – Chrysene

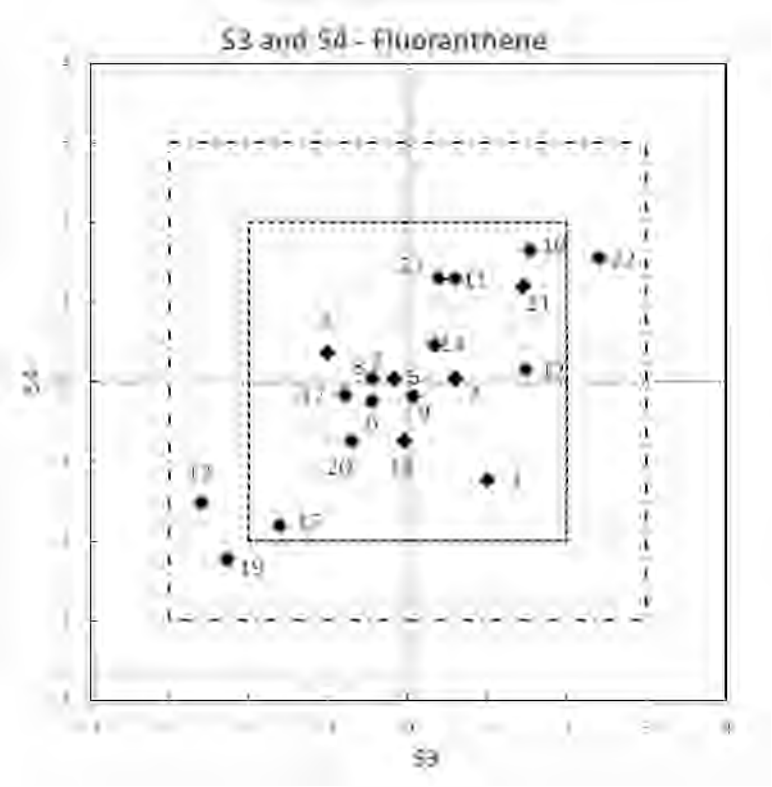


Figure 33 z-Score Scatter Plot – Fluoranthene

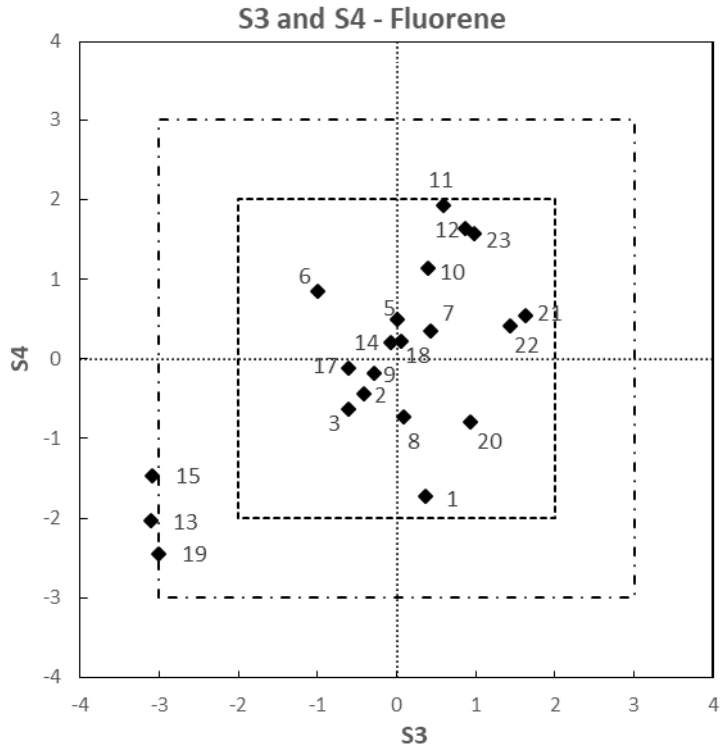
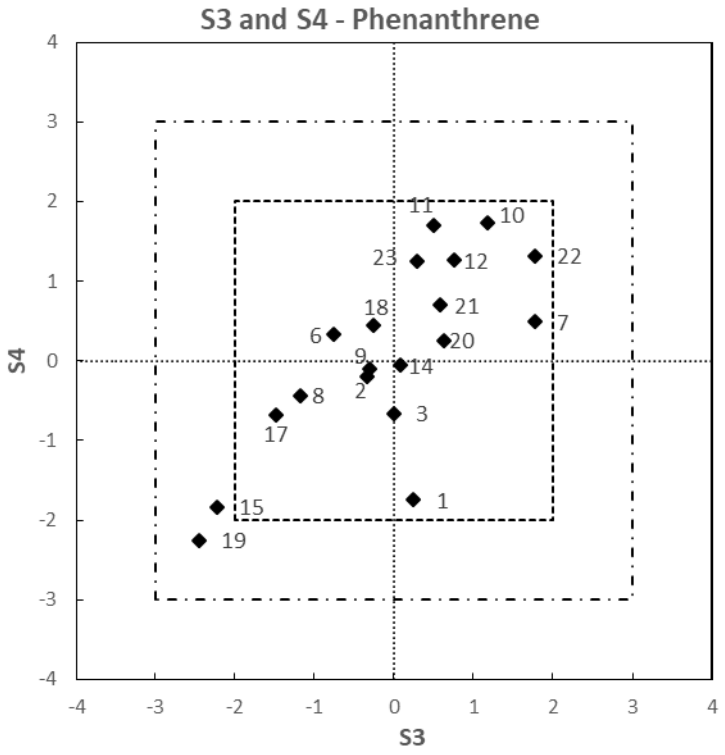


Figure 34 z-Score Scatter Plot – Fluorene



Laboratory 13 is off-scale.

Figure 35 z-Score Scatter Plot – Phenanthrene

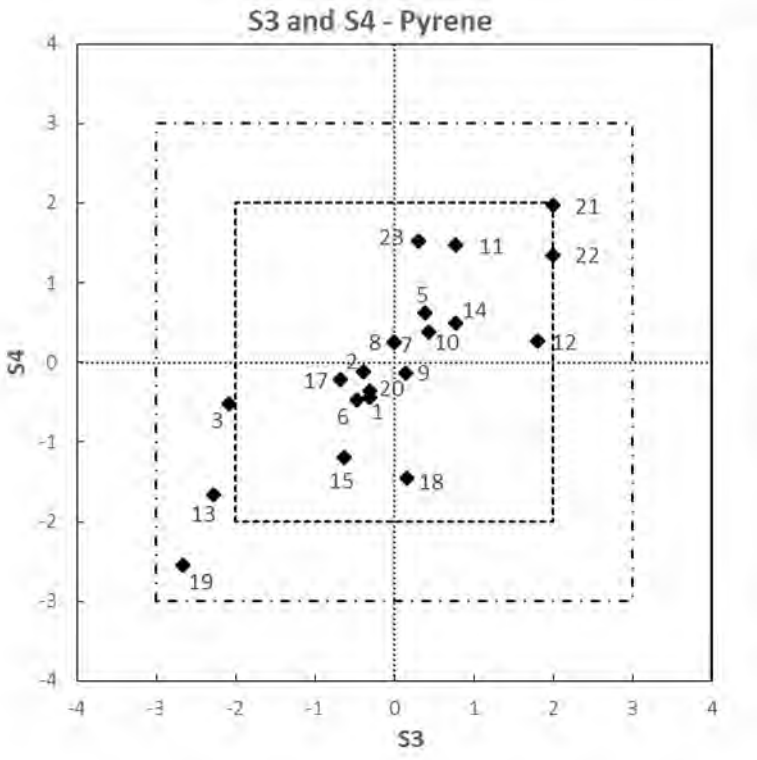


Figure 36 z-Score Scatter Plot – Pyrene

6.4 E_n-Score

Where a laboratory did not report a MU, 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-Scores, any E_n-scores greater than 1.0 were set to 1.0.

Of 448 results for which E_n-scores were calculated, 352 (79%) returned a satisfactory score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratories **1**, **9**, **18** and **22** returned satisfactory E_n-scores for all 22 analytes for which scores were calculated. All results reported by Laboratories **5** (21), **20** (20), **16** (8) and **4** (1) returned satisfactory E_n-scores.

Laboratory **19** returned unsatisfactory E_n-scores for all reported results (15).

A summary of E_n-score dispersal by laboratory is presented graphically in Figure 37.

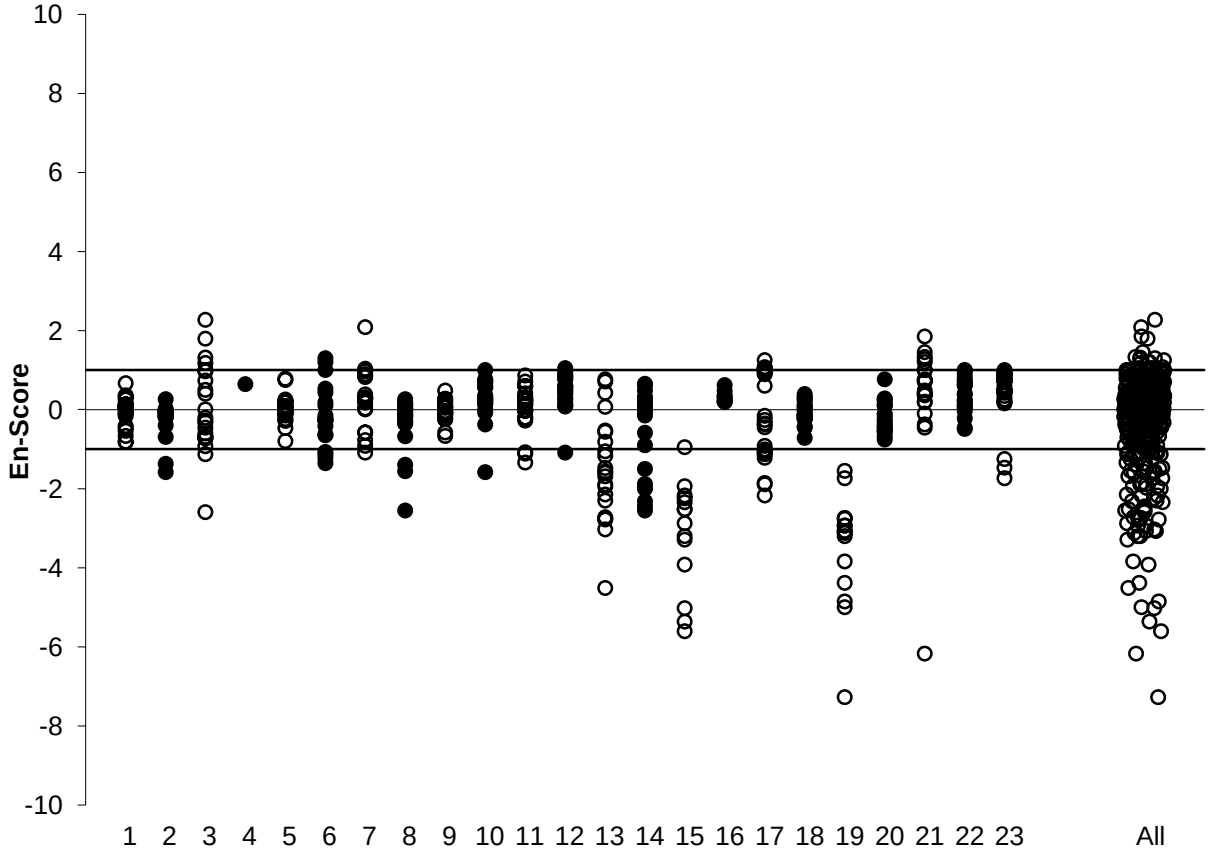


Figure 37 E_n-Score Dispersal by Laboratory

6.5 Reporting of Additional Analytes

One participant reported analytes that were not spiked into the test samples (total of 2 analytes). These are listed in Table 32.

Table 32 Analytes Reported by Participants Not Spiked into Samples

Lab. Code	Sample	Analyte	Result (µg/L)	Uncertainty (µg/L)
15	S3	Benz(a)anthracene	3.3322	NR
	S4	Benz(a)anthracene	6.8616	NR

6.6 Participants' Analytical Methods

TRH (Sample S1)

Eight participants reported taking 500 mL (i.e. the whole sample) for analysis, while the other participants reported sample test portions ranging from 35 – 490 mL. No trends were identified with consideration to whether the whole sample was used, or what volume was used (Figure 38).

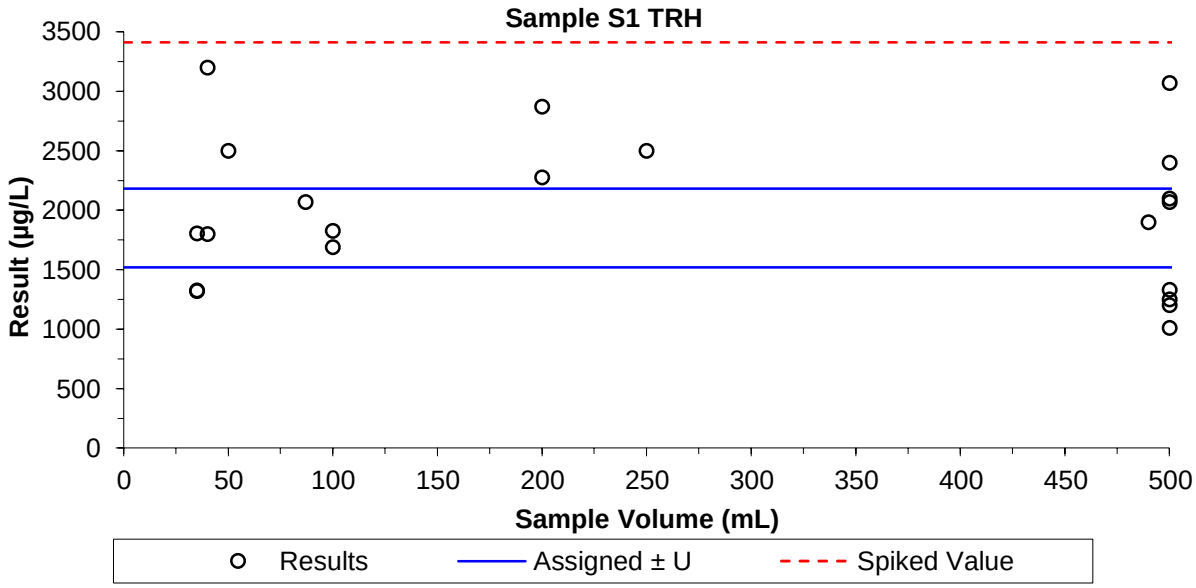


Figure 38 Sample S1 TRH Results vs Sample Volume

All participants reporting methodologies used liquid-liquid extraction, with dichloromethane, hexane, or a mixture of pentane and hexane as the solvent. Two participants reported an additional silica gel clean-up step for the samples. Most participants used GC-FID for analysis, except for one participant who used GC-MS instead. The most common methodology employed for TRH was liquid-liquid extraction with dichloromethane, and using GC-FID for analysis. A summary of results vs methodology is presented in Figure 39. No significant trends were identified.

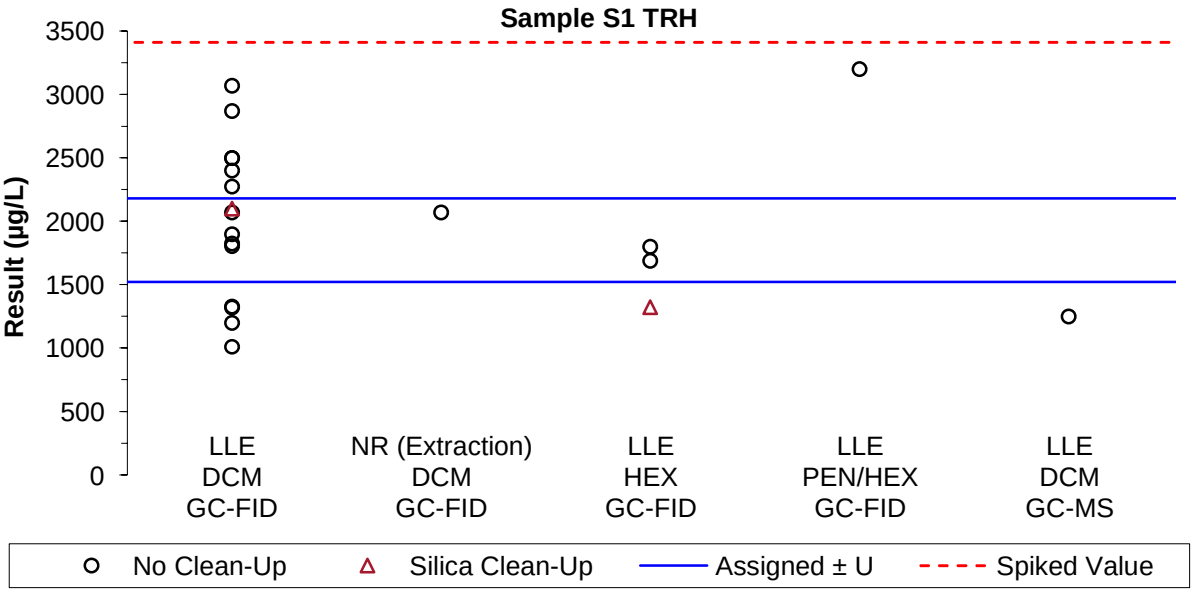


Figure 39 Sample S1 TRH Results vs Methodology

BTEX (Sample S2)

Nine participants reported taking the whole sample for analysis, while the other participants reported sample test portions ranging from 5 – 25 mL. For this study, it was observed that participants using the whole sample reported higher results on average than those who did not (Figure 40).

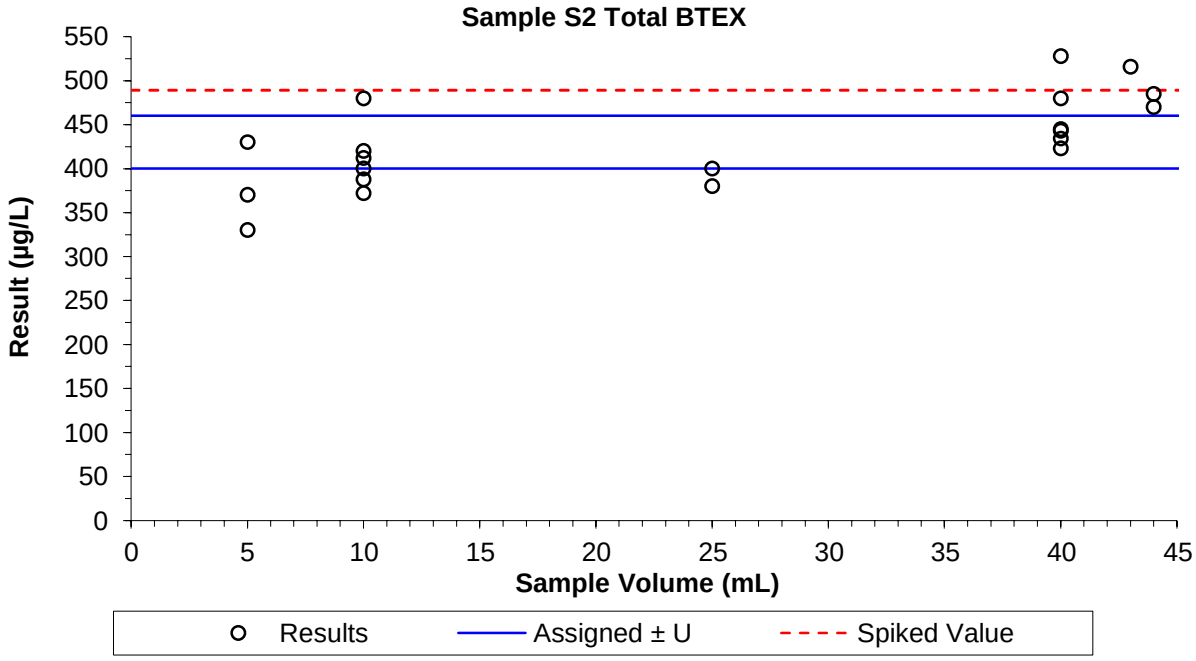


Figure 40 Sample S2 Total BTEX Results vs Sample Volume

For BTEX analysis, 13 participants reported using purge-and-trap GC-MS, 5 participants reported using headspace GC-MS, and 1 participant reported using purge-and-trap GC-FID. Three participants reported using methanol or water as the extraction solvent. A summary of results vs methodology is presented in Figure 41. No significant trends were identified.

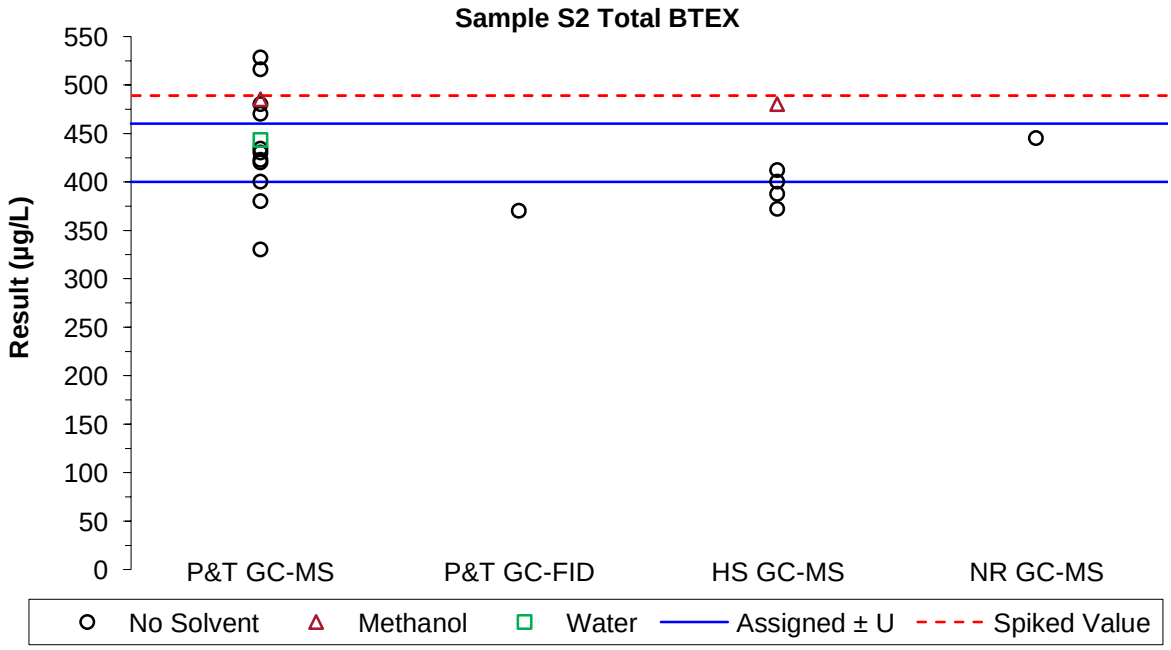


Figure 41 Sample S2 Total BTEX Results vs Methodology

PAHs (Samples S3 and S4)

Nine participants reported taking 500 mL (i.e. the whole sample) for analysis, while the other participants reported test portions ranging from 35 – 490 mL. Results as compared to the sample volume used is presented in Figure 42.

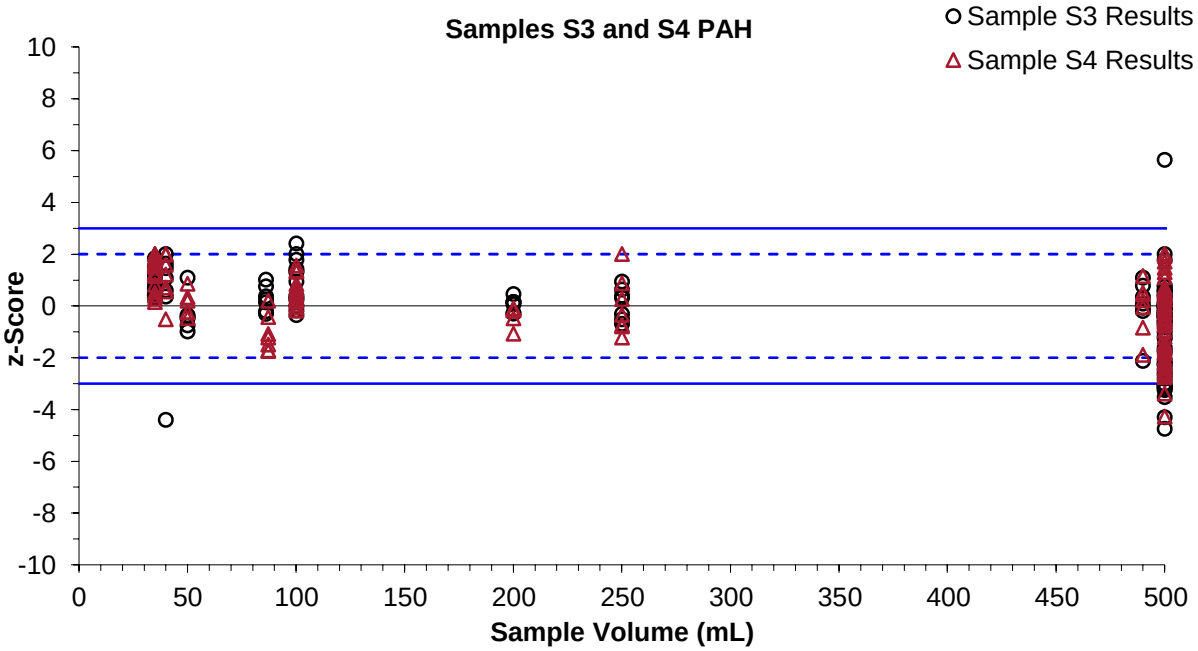


Figure 42 Samples S3 and S4 PAH z-Scores vs Sample Volume

The majority of participants used liquid-liquid extraction, except for 2 participants who used solid-phase extraction. Dichloromethane, hexane, and a mixture of dichloromethane and ethyl acetate were reported as extraction solvents. All participants used GC-MS or GC-MS/MS for analysis. The most common methodology employed for PAH was liquid-liquid extraction with dichloromethane, using GC-MS for analysis. A summary of results vs methodology is presented in Figure 43. The results reported by participants using solid-phase extraction were biased low compared to the assigned value.

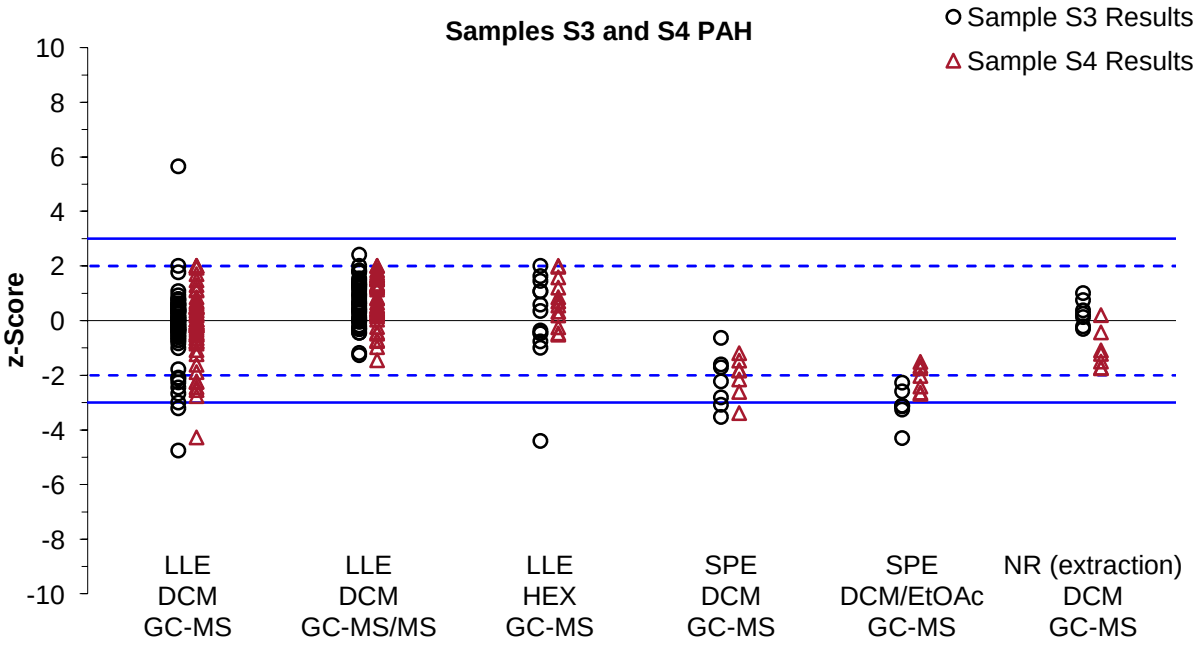


Figure 43 Samples S3 and S4 PAH z-Scores vs Methodology

6.7 Certified Reference Materials (CRM)

Participants were requested to report whether certified standards or matrix reference materials had been used as part of the quality assurance for the analysis. Nineteen laboratories reported using 'certified standards', from the following sources:

- NMI CRM
- AccuStandard
- Agilent
- ChemService
- Sigma-Aldrich / Merck
- Restek
- ISO 17034 standards

These materials 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]

6.8 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 44.

Table 33 Summary of Participants' Sample S1 and S2 Results for Scored Analytes (all values are in µg/L)*

Lab. Code	Sample S1			Sample S2				
	>C10-C16	>C16-C34	Total TRH	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX
A.V.	1110	960	1850	57.3	197	25.2	152	430
1	930	1140	2070	57	208	25.7	155	445
2	610	720	1330	56	190	25	150	420
3	1580	1490	3070	67	209	28	181	485
4	1400	NR	NT	NT	NT	NT	NT	NT
5	1200	1300	2500	50	190	20	140	400
6	1710	1490	3200	47.4	176	21.3	127	372
7	1200	1200	2400	52	180	21	130	380
8	540	470	1010	60	190	27	160	430
9	1202.9	1072.9	2275.8	61.66	204.51	21.28	135.11	422.6
10	693	863	1806	60.5	202	29.7	152	443
11	620	570	1200	53	180	25	150	400
12	1182	998.7	1320	63	210	31	180	480
13	1260	860	2100	65	170	25.6	113	370
14	1200	750	1900	45	150	18	120	330
15	NT	NT	NT	NT	NT	NT	NT	NT
16	1300	1200	2500	61	210	27	170	470
17	1500	1370	2870	71	225	33	199	528
18	1250	820	2070	53.6	189	24.2	145	412
19	NR	NR	1250	NT	NT	NT	NT	NT
20	NR	NR	1690	49	181	22.2	135.3	387.5
21	NR	NR	1800	63	226	23	168	480
22	938.1	888.2	1826.3	51.6	199	26	158	434
23	740	584	1324	61.5	244	31.2	179	516

* A.V. = Assigned Value. Shaded cells are results which returned a questionable or unsatisfactory z-score.

Table 34 Summary of Participants' Sample S3 and S4 Results for Scored Analytes (all values are in µg/L)*

Lab. Code	Sample S3							Sample S4						
	Anthracene	Benzo(a)pyrene	Chrysene	Fluoranthene	Fluorene	Phenanthrene	Pyrene	Anthracene	Benzo(a)pyrene	Chrysene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
A.V.	8.46	3.82	4.82	5.14	7.99	1.58	17.0	5.15	3.63	11.1	15.9	9.31	8.76	5.49
1	8.62	4.25	4.67	5.92	8.43	1.64	16.2	4.31	3.74	8.6	12.98	6.91	6.48	5.14
2	8.3	3.4	4.4	4.8	7.5	1.5	16	4.8	3.6	12	16	8.7	8.5	5.4
3	8.10	3.71	4.22	4.36	7.26	1.58	11.66	4.93	3.22	10.22	16.79	8.43	7.89	5.06
4	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
5	8	4	5	5	8	<2	18	5	4	11	16	10	9	6
6	8.0	NT	5.6	4.8	6.8	1.4	15.8	5.3	NT	NT	15.3	10.5	9.2	5.1
7	9.4	5.3	8.9	5.6	8.5	2.0	17	5.7	5.0	16	16	9.8	9.4	5.7
8	7.9	3.1	4.7	4.8	8.1	1.3	17	4.4	3.5	12	16	8.3	8.2	5.7
9	8.64	3.9	5.15	5.19	7.64	1.51	17.36	4.77	3.04	10.86	15.47	9.06	8.63	5.38
10	10.15	4.2	6.15	6.33	8.47	1.86	18.1	7.24	3.91	12.45	19.87	10.9	11.05	5.81
11	8.9	3.8	5.1	5.6	8.7	1.7	19	6.0	3.9	12	19	12	11	6.7
12	10.1	4.2	5.19	6.29	9.03	1.76	21.6	6.43	4.29	13.65	16.26	11.58	10.41	5.71
13	4.47	1.96	2.56	3.14	4.26	0.56	11.2	3.8	2.32	6.63	12.29	6.47	5.29	4.12
14	8.2	2.6	5.6	5.4	7.9	1.6	19	4.5	2.6	13	17	9.6	8.7	5.9
15	4.8960	1.8039	3.5866	3.9011	4.2935	1.0532	15.3861	3.1318	1.7858	7.5055	11.5860	7.2705	6.3615	4.4991
16	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	8.13	3.13	4.28	4.53	7.26	1.23	15.26	4.91	3.05	8.11	15.5	9.16	7.87	5.31
18	8.06	3.82	4.60	5.10	8.06	1.52	17.4	5.65	3.37	11.7	14.1	9.62	9.34	4.30
19	6.2	1.1	2.5	3.4	4.4	1.0	10.2	3.9	1.3	6.5	10.6	5.9	5.8	3.4
20	7.8	4	5.1	4.6	9.1	1.73	16.2	4.2	4.1	15.5	14.1	8.2	9.1	5.2
21	9.82	4.02	1.64	6.26	9.94	1.72	22.17	6.83	4.49	10.23	18.78	10.08	9.68	7.11
22	10.1	4.6	5.5	7.0	9.7	2.0	23.6	5.8	3.8	11.5	19.6	9.9	10.5	6.6
23	9.85	4.16	5.7	5.44	9.17	1.65	17.8	6.57	4.75	13.6	19.0	11.5	10.4	6.74

* A.V. = Assigned Value. Shaded cells are results which returned a questionable or unsatisfactory z-score.

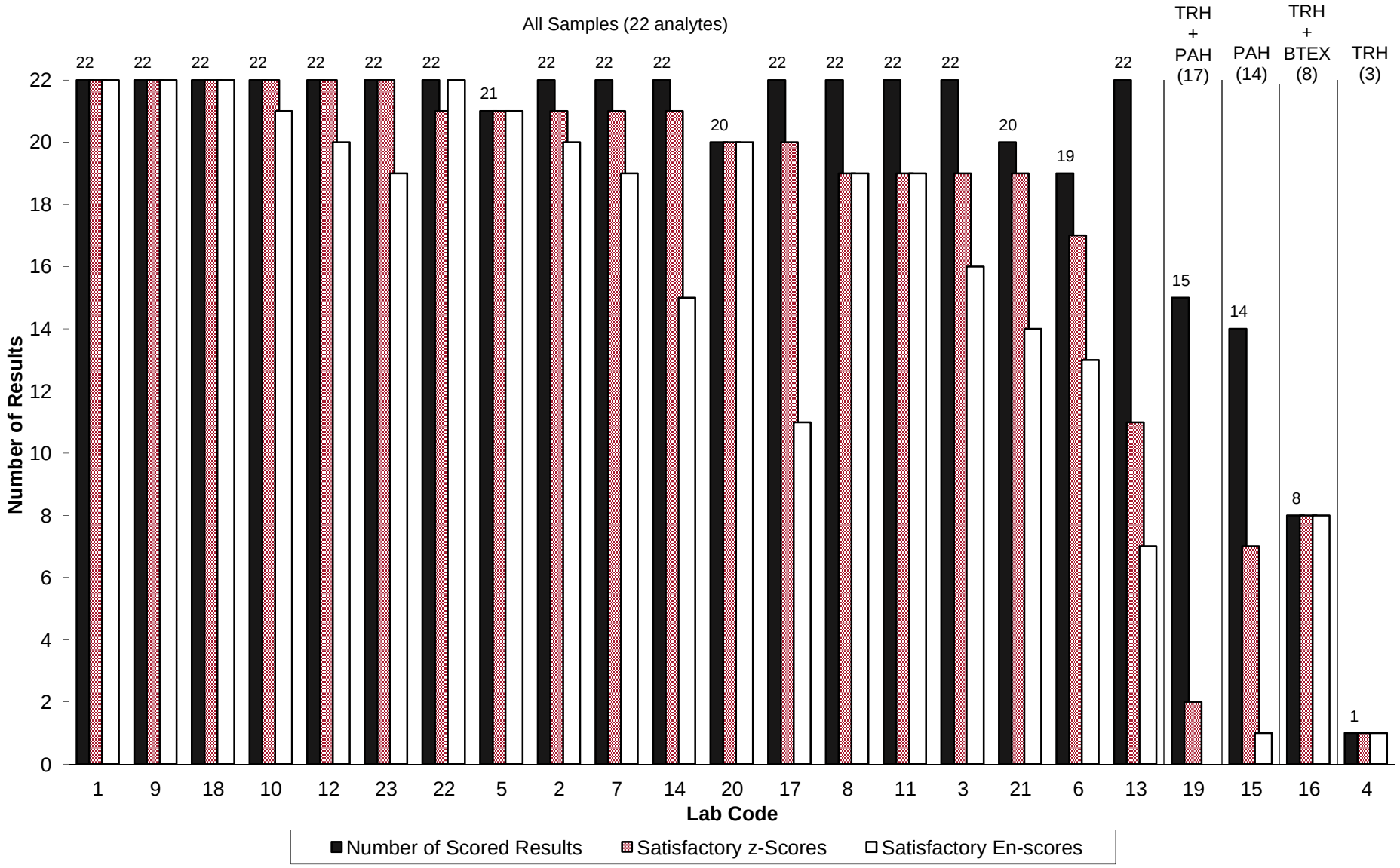


Figure 44 Summary of Participants' Performance

6.9 Comparison with Previous Studies

To enable direct comparison with previous studies, the target SD used to calculated z-scores has been kept constant between PT studies.

TRH

A summary of the 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 water over the last 10 studies (2012 – 2020) is presented in Figure 45. Over this period, the average proportion of satisfactory scores was 74% for z-scores and 64% for E_n-scores. While each PT study has a different group of participants, taken as a group, performance for TRH has improved over this period.

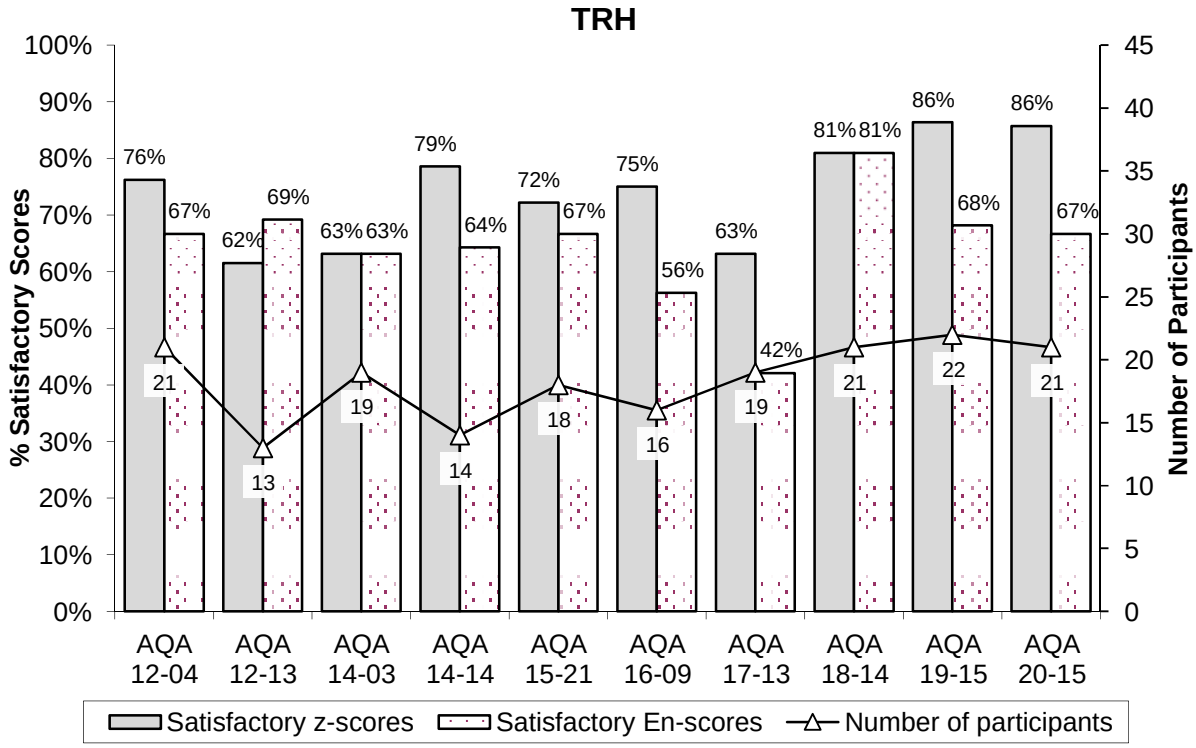


Figure 45 Summary of Satisfactory Scores for TRH (TPH for AQA 12-04 and 12-13) in Water PT Studies

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 water over the last 10 studies (2012 – 2020) is presented in Figure 46. Over this period, the proportion of satisfactory scores has remained high, with an average proportion of 93% and 88% for z-scores and E_n-scores respectively.

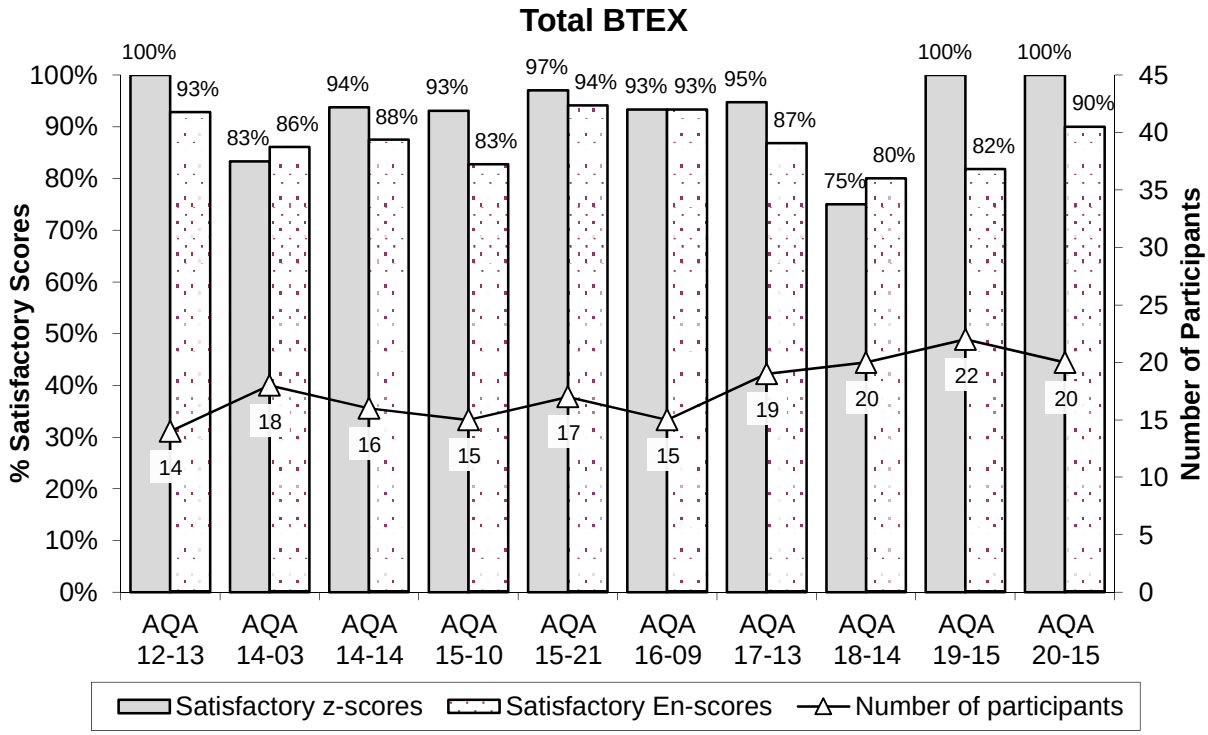


Figure 46 Summary of Satisfactory Scores for Total BTEX in Water PT Studies

PAH

NMI has run PAH in Water PT studies 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 PAH analytes in water over the last 6 studies (2015 – 2020) is presented in Figure 47. Over this period, the proportion of satisfactory scores has fairly consistent, with an average proportion of 86% and 79% for z-scores and E_n-scores respectively.

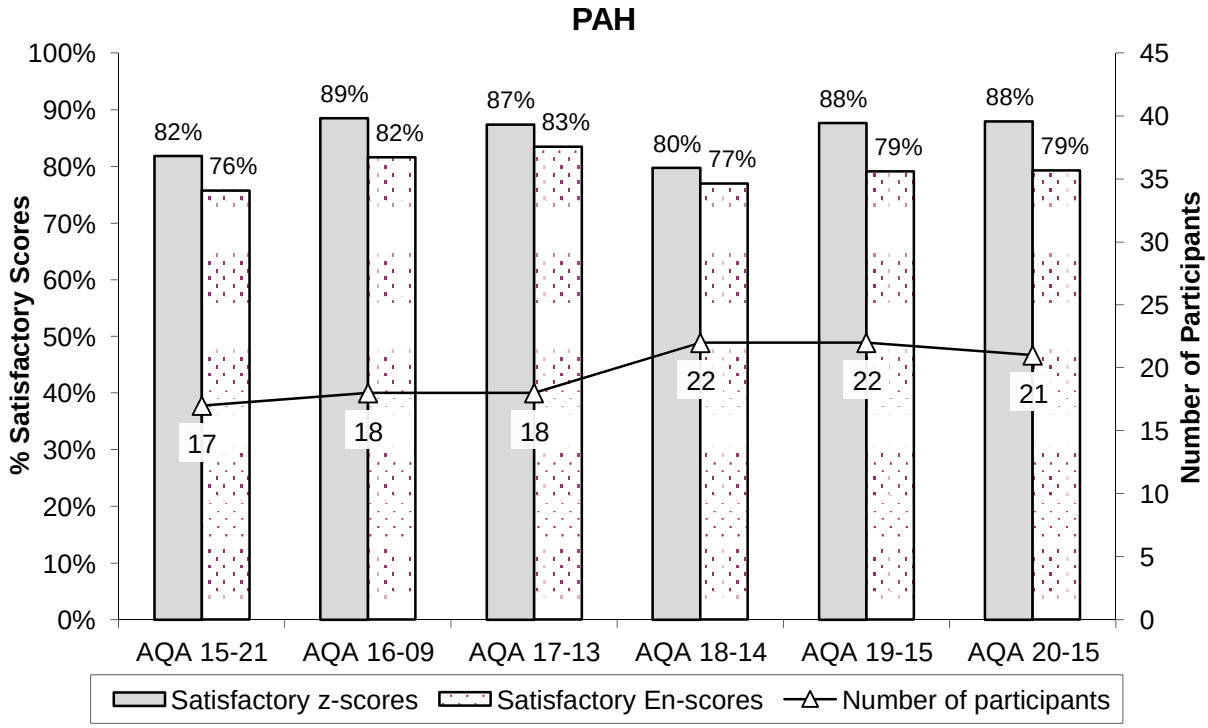


Figure 47 Summary of Satisfactory Scores for PAH Analytes in Water PT Studies

A plot of the assigned value, expressed as a percentage of the spiked value, for PAH in Water since 2015 is presented in Figure 48. On average, the recoveries of PAH in this PT study were similar to or slightly higher than the average of previous studies.

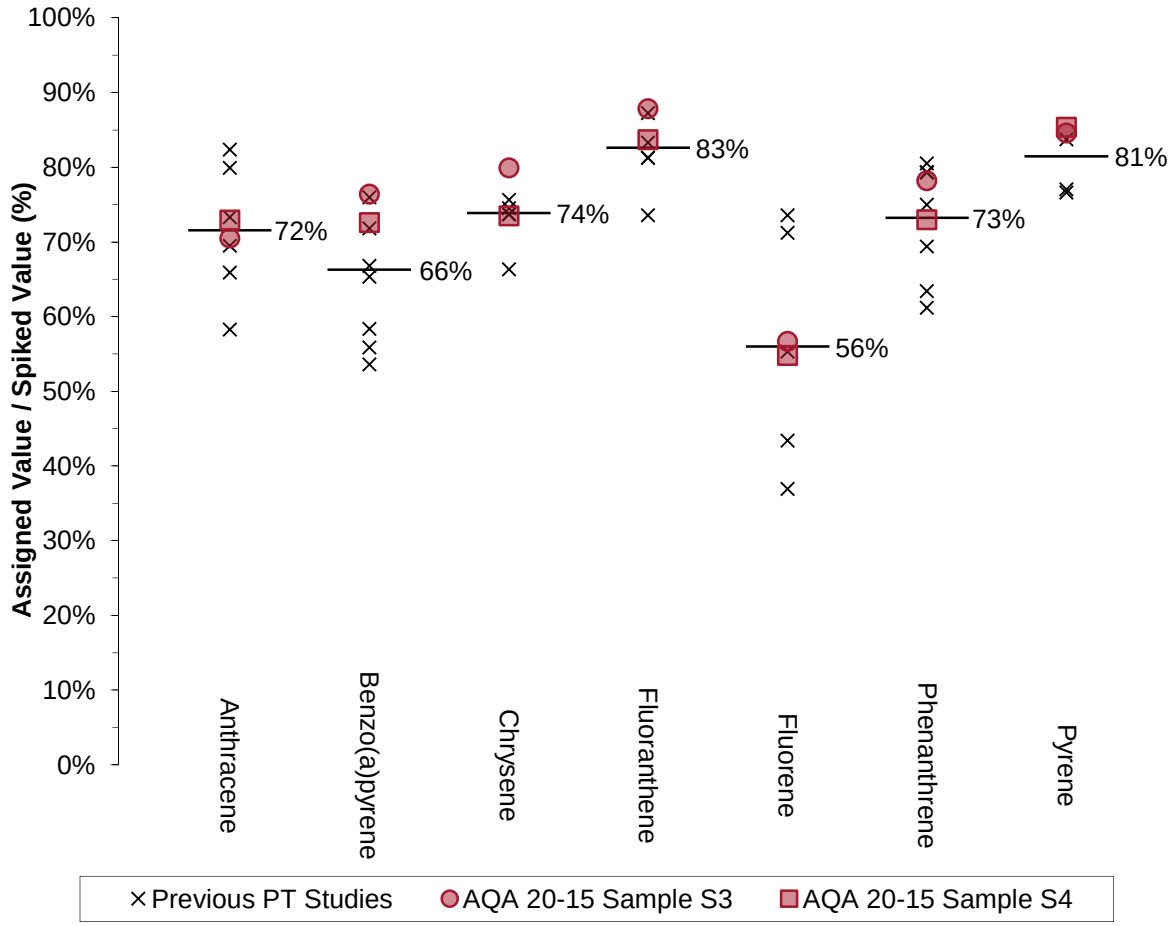


Figure 48 Comparison of Assigned Value / Spiked Value for PAH in Water with Previous PT Studies (the line indicates the average for each PAH).

7 REFERENCES

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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 PTs.

Water was sampled from Browns Waterhole, Turramurra. The water was filtered under vacuum through an Advantec 150 mm glass fibre filter. After filtration the water was placed in 10 L 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 acetone and dried. The cleaned bottles were placed in an air-conditioned room overnight. 498.5 ± 0.2 g of filtered autoclaved water (500 mL at 25°C) was weighed into the bottles. 1.70 mL of the methanol/diesel spiking solution 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

42 mL (41.88 ± 0.05 g) of filtered autoclaved water was weighed into Agilent vials. A composite spike solution was prepared by adding aliquots of diesel and unleaded petrol to methanol. One 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. Each vial was capped after spiking, and then labelled and shrink-wrapped.

Samples S3 and S4

The spiking solutions were prepared by dissolving each standard material in dichloromethane. 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 2 hours. The samples were then dispensed into 500 mL amber glass bottles which were labelled and shrink-wrapped.

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

APPENDIX 2 – TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 35 to 37. Some responses may be modified so that the participant cannot be identified.

Table 35 Sample S1 TRH Methodology

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Method
1	87		DCM		GC-FID	
2	500	Liquid-Liquid	DCM	none	GC-FID	USEPA 3510
3	500	Liquid-Liquid	DCM	None	GC-FID	USPEA 5015B
4	250	Liquid-Liquid	Hexane	None	GC-FID	Inhouse
5	250	Liquid-Liquid	DCM	None	GC-FID	USEPA 8260
6	40	Liquid-Liquid	Pentane/Hexane	None	GC-FID	In-House
7	500	Liquid-Liquid	DCM	none	GC-FID	NEPM 2013
8	500	Liquid-Liquid	DCM	None	GC-FID	USEPA 3510
9	200	Liquid-Liquid	DCM	None	GC-FID	In house
10	35	Liquid-Liquid	DCM	None	GC-FID	
11	500	Liquid-Liquid	DCM	None	GC-FID	USEPA 3510
12	35	Liquid-Liquid	DCM	None	GC-FID	In House
13	500	Liquid-Liquid	DCM	Silica	GC-FID	In house
14	490	Liquid-Liquid	DCM	None	GC-FID	In-house
15	NT					
16	50	Liquid-Liquid	DCM	None	GC-FID	USEPA3510
17	200	Liquid-Liquid	DCM	None	GC-FID	USEPA 8015B
18	500	Liquid-Liquid	DCM	None	GC-FID	NEPM B3
19	500	Liquid-Liquid	DCM	None	GC/MS	USEPA8260
20	100	Solvent extraction	Hexane	None	GC-FID	US EPA 8015
21	40	Liquid-Liquid	Hexane	None	GC-FID	USEPA 8015
22	100	Liquid-Liquid	DCM	None	GC-FID	In House
23	35	Liquid-Liquid	Hexane	Silica Gel	GC-FID	USEPA 3510

Table 36 Sample S2 BTEX Methodology

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Method
1	40		N/A		GC-MS	
2	10	Purge and Trap	N/A	none	P&T GC-MS	USEPA 3260
3	44	Purge and Trap	Methanol	None	GC-MS	USEPA 8260B
4	NT					
5	10	Headspace	N/A	None	GC-MS	USEPA 8260
6	10	Headspace	N/A	None	GC-MS	In-house
7	25	Purge and Trap	NA	none	GC-MS	NEPM 2013
8	5	Purge and Trap	N/A	None	P&T GC-MS	USEPA 8260
9	40	Purge and Trap	None	None	GC-MS	In house
10	40	Purge and Trap	Water	None	GC-MS	USEPA SW-846 Method 5030
11	25	Purge and Trap	None	None	P & T GCMS	USEPA 8260
12	40	Purge and Trap	None	None	GC-MS	USEPA 8260
13	5	Purge and Trap			GC-FID	USEPA8260
14	5 (purged)	Purge and Trap	NA	NA	GC-MS	USEPA 5030A
15	NT					
16	44	Purge and Trap	None	None	GC-MS	USEPA8260
17	40	Purge and Trap	None	None	GC-MS	USEPA 8260
18	10	Headspace	N/A	N/A	GC-MS	NEPM B3, US EPA 8260D
19	NT					
20	10	Headspace	-	-	GC-MS	US EPA 8260 & 5021
21	10	Headspace	Methanol	None	GC-MS	USEPA 5021A
22	40	Purge and Trap	None	None	GC-MS	USPEA 8260
23	43	Purge & Trap	N/A	N/A	GC-MS	USEPA 8260

Table 37 Samples S3 and S4 PAH Methodology

Lab. Code	Sample Volume (mL)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Method
1	86 & 87		DCM		GC-MS	
2	500	Liquid-Liquid	DCM	none	GC-MS	USEPA 8270
3	500	Liquid-Liquid	DCM	None	GC-MS	USPEA 8270C
4	NT					
5	100	Liquid-Liquid	DCM	None	GC-MS	USEPA 8260
6	50	Liquid-Liquid	Hexane	None	GC-MS	In-house
7	500	Liquid-Liquid	DCM	none	GC-MS	USEPA 8270D
8	500	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
9	200	Liquid-Liquid	DCM	None	GC-MS	In house
10	35	Liquid-Liquid	DCM	None	GC-MS/MS	
11	500	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270
12	35	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
13	500	SPE	DCM:EtOAc 1:1		GC-MS	USEPA8270
14	490	Liquid-Liquid	DCM	None	GC-MS	USEPA 8270D
15	500	SPE	DCM	None	GC-MS	USEPA 525.3
16	NT					
17						
18	500	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270E
19	500	Liquid-Liquid	DCM	None	GC/MS	USEPA8270
20	250	Liquid-Liquid	DCM	None	GC-MS	US EPA 8270
21	40	Liquid-Liquid	Hexane	None	GC-MS	USEPA 3500C 8270D
22	100	Liquid-Liquid	DCM	None	GC-MS/MS	USEPA 8270
23	35	Liquid-Liquid	DCM	N/A	GC-MS/MS	USEPA 8270

APPENDIX 3 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, Z-SCORE AND E_N-SCORE CALCULATIONS

A3.1 Robust Average and Associated Uncertainty

The robust average was calculated using the procedure described in ISO 13258:2015 Annex C.[7] The uncertainty for the robust average was estimated as:

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

where:

$u_{rob\ av}$ is the standard uncertainty of the robust average

$S_{rob\ av}$ is the standard deviation of the robust average

p is the number of results

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

A worked example is set out below in Table 38.

Table 38 Uncertainty of the Robust Average for Benzene in Sample S2

No. results (p)	20
Robust Average	57.348 µg/L
$S_{rob\ av}$	7.648 µg/L
$u_{rob\ av}$	2.138 µg/L
k	2
$U_{rob\ av}$	4.276 µg/L

Therefore, the robust average for benzene in Sample S2 is 57.3 ± 4.3 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.

A worked example for is set out below in Table 39.

Table 39 z-Score and E_n-Score for Sample S1 >C10-C16 Result Reported by Laboratory 1

Participant Result (µg/L)	Assigned Value (µg/L)	Target Standard Deviation	z-Score	E_n-Score
930 ± 370	1110 ± 210	20% as PCV, or: 0.2 × 1110 = 222 µg/L	z-Score = $\frac{930-1110}{222}$ = -0.81	E_n-score = $\frac{930-1110}{\sqrt{370^2+210^2}}$ = -0.42

APPENDIX 4 – ACRONYMS AND ABBREVIATIONS

BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
EtOAc	Ethyl Acetate
FID	Flame Ionisation Detector
GAG	General Accreditation Guidance (NATA)
GC	Gas Chromatography
GUM	Guide to the expression of Uncertainty in Measurement
HEX	Hexane
HS	Headspace
IANZ	International Accreditation New Zealand
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
Max.	Maximum value
Md	Median value
Min.	Minimum value
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
NATA	National Association of Testing Authorities (Australia)
NEPM	National Environmental Protection Measure
NMI	National Measurement Institute (Australia)
NR	Not Reported
NT	Not Tested
P&T	Purge and Trap
PAH	Polycyclic Aromatic Hydrocarbons
PCV	Performance Coefficient of Variation
PEN	Pentane
PT	Proficiency Test
R.A.	Robust Average
RM	Reference Material
S.V.	Spiked Value (or formulated concentration of a PT sample)

SD	Standard Deviation
SI	International System of Units
SPE	Solid Phase Extraction
SS	Spiked Samples
TPH	Total Petroleum Hydrocarbons
TRH	Total Recoverable Hydrocarbons
USEPA	United States Environmental Protection Agency

END OF REPORT