Australian Government
Department of Industry, Innovation and Science
National Measurement Institute

Proficiency Test Report
AQA 18-14
Hydrocarbons in Water

February 2019

ACKNOWLEDGMENTS

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

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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Accredited for compliance with ISO/IEC 17043

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SUMMARY

Proficiency test AQA 18-14 Petroleum Hydrocarbons in Water was conducted in September 2018, twenty-two laboratories submitted results.

Four sets of test samples were prepared at the NMI laboratory in Sydney. MilliQ water and river water collected from Browns Waterhole, Turramurra NSW filtered and autoclaved before use were used.

Sample S1 was prepared from river water to which was added artificially weathered diesel fuel. Each 500 mL test sample was individually spiked.

Sample S2 was river water to which was added methanol solution of unleaded petrol and diesel fuel. Each 42 mL test sample was individually spiked.

Samples S3 and S4 were milliQ water and river water, respectively. Both samples were spiked with similar amounts of anthracene, benzo(a)pyrene, chrysene, fluorene and phenanthrene. Sample S4 was spiked with additional PAHs, fluoranthene and pyrene. These samples were then dispensed in 500 mL brown bottles.

Participants measured total recoverable hydrocarbons (TRH) in Sample S1, volatile hydrocarbons (C6 to C10), benzene, toluene, ethylbenzene and xylene (BTEX) in Sample S2 and polycyclic aromatic hydrocarbons (PAHs) in Samples S3 and S4.

Assigned values were the consensus of participants' results, so although expressed in SI units, metrological traceability of the assigned values has not been established.

The outcomes of the study were assessed against the aims as follows:

> *To assess the performances of participant laboratories and their accuracy in the identification and measurement of petroleum hydrocarbon pollutants in water.*

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

Of 409 results for which z-scores were calculated, 330 (81%) returned a satisfactory score of $|z| \leq 2$.

Of 409 results for which E_n-scores were calculated, 316 (77%) returned a satisfactory score of $|E_n| \leq 1$.

Laboratories **1, 2, 7, 11, 14** and **16** returned satisfactory z and E_n-scores for all twenty analytes for which scores were calculated. Laboratory **21** reported results for 17 analytes and returned satisfactory z and E_n-scores.

Laboratories **4**, **6** and **8** are still reporting hydrocarbon ranges outside of the recommended NEPM fractions.

> *To develop the practical application of traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates.*

Of 427 numerical results, 422 (99%) were reported with an associated expanded uncertainty.

Expanded uncertainties were within the range 4.5% to 100% relative.

An expanded uncertainty of less than 10% relative is unrealistically small for the routine measurement of a hydrocarbon pollutant in water. Of the 422 expanded uncertainties, 5 were below 10% relative.

To evaluate the laboratories' test methods.

For the determination of TRH in Sample S1 participants used liquid-liquid extraction with either dichloromethane (DCM) or hexane as extraction solvent. All participants used GC-FID for analysis.

For the determination of PAHs in Samples S3 and S4 most participants used liquid-liquid extraction with DCM. One participant used hexane and one used solid phase extraction (SPE) with DCM/ethylacetate All laboratories used GC-MS(MS) for analysis.

Some participants used the whole sample for analysis, while others took a subsample. Laboratories did not report whether or not the sample container was rinsed to recover hydrocarbons adhering to the wall of the container. No trend with sample volume used for analysis emerged.

For BTEX analysis in Sample S2, three laboratories used headspace technique while all the other laboratories performed an extraction using purge-and-trap, followed by GC-MS.

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.

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 and biota;
- metals in water, soil, food and pharmaceuticals;
- controlled drug assay;
- allergens in food; and
- folic acid in flour.

1.2 Study Aims

The aims of the study were to:

- assess the performances of participant laboratories and their accuracy in the identification and measurement of petroleum hydrocarbon pollutants in water;
- develop the practical application of traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates; and
- evaluate the laboratories' test methods.

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 Chemical Proficiency Testing Study Protocol.[1] The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.[2] These documents have been prepared with reference to ISO Standard 17043[3] and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[4] 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 studied were selected as those typically encountered by laboratories monitoring water to assess the impact of transport fuels in the environment (for example through exhaust fumes emission or in the remediation of contaminated service station sites) or the contamination from industry that entails the use of wood, petroleum or coal to generate heat and power.

Four samples were prepared. One sample was water spiked with diesel fuel, one with unleaded petrol and diesel fuel and two samples were spiked with individual PAHs. The concentrations were typical of those encountered by environmental testing laboratories.

Investigation levels for the hydrocarbons studied are set out in Schedule B1 of the National Environmental Protection Measure (NEPM) as amended 2013.[5]

2.2 Study Timetable

The timetable of the study was:

Invitation issued:	04 September 2018
Samples dispatched:	03 October 2018
Results due:	07 November 2018
Interim report issued:	09 November 2018

2.3 Participation

Invited	66
Participated	22
Submitted results	22

2.4 Test Material Specification

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

Sample S1 (TRH) was river water spiked with diesel fuel.

Sample S2 (BTEX) was river water sample individually spiked with unleaded petrol and diesel fuel.

Sample S3 (PAH) and **Sample S4 (PAH)** were milli-Q and river water, respectively. Both samples were spiked with similar amounts of anthracene, benzo(a)pyrene, chrysene, fluorene and phenanthrene. Sample S4 was spiked with additional PAHs, fluoranthene and pyrene.

2.5 Laboratory Code

Participants were assigned a confidential code number.

2.6 Sample Preparation and Homogeneity Testing

The preparation of the study samples is described in Appendix 2.

No homogeneity testing was conducted. All samples were prepared and packaged using a process that has been demonstrated in the previous studies to produce homogeneous samples. The results of the study gave no reason to question the homogeneity of these samples.

2.7 Stability

The storage stability of petroleum hydrocarbons spiked into water samples has been previously established. [6] An allowance for any possible degradation was made in the uncertainties associated with the spiked concentrations.

No stability study was conducted, however results returned by participants gave no reason to question the stability of the samples.

2.8 Sample Storage, Dispatch and Receipt

The test samples were stored in a refrigerator at approximately 4°C prior to dispatch.

The samples were packaged into insulated styrene foam boxes and dispatched by courier on 03 October 2018.

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 electronic results sheet 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 to C10), Benzene, Toluene, Ethyl benzene and Xylenes. 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.
- For each analyte in each sample, report the analytical results in units of μg/L with an associated expanded uncertainty (eg 2000 ± 200 μg /L).
- Report the basis of your uncertainty estimates (eg 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 completed result sheet by 30 October 2018. Late results may not be included in the study report.**

2.10 Interim Report

An interim report tabling results and reported uncertainties was emailed to all participants on 9 November 2018.

3 PARTICIPANT LABORATORY INFORMATION

Table 1 Test Methods Sample S1 TRH

Lab. Code	Sample Volume (mL)	Extraction	Extraction solvent	Measurement	Method
1	200	Liquid-liquid extraction using dichloromethane. Solvent then concentrated to a final volume of 2mL.	DCM	GC-FID	In House
2	85	Liquid- Liquid Extraction	DCM	GC-FID	In House
3	400	Liquid-liquid	DCM	GC-FID	In house referenced to USEPA SW 846 8015A
4	100	Solvent extraction with pre-concentration	Hexane	GC-FID	US EPA 8015B
5	500	Liquid-Liquid extraction	DCM	GC-FID	In house based on US-EPA
6	400	Liquid-liquid	DCM	GC-FID	In House USEPA SW 846-8015A
7	100	Liquid-liquid	DCM	GC-FID	USEPA 3510
8	500	Liquid-liquid	DCM		Standard Methods for the Examination of Water and Wastewater online. Part 5520C.
9	100	Liquid-Liquid	DCM	GC-FID	USEPA
10	500	Liquid-liquid	DCM	GC-FID	USEPA Method 8015B
11	100	Liquid-liquid extraction using dichloromethane. Solvent is concentrated to a final volume of 1mL.	DCM	GC-FID	In house.
12	250	Liquid-Liquid separatory funnel extraction.	DCM	GC-FID.	In-house method based on US EPA 3510 & NEPM 2013.
13					
14	200	Liquid-Liquid	DCM	GC-FID	In house Method
15	100	Liquid-Liquid	DCM	GC-FID	USEPA 3510
16	200	Liquid-Liquid	DCM	GC-FID	USEPA Method 8015B
17	510	Liquid-liquid	DCM	GC-FID	USEPA 8000B / USEPA 8015B
18	500	Liquid-Liquid	DCM	GC-FID	USEPA 3510
19	500	Liquid-liquid	DCM	GC-FID	ORG007W - TRH by GC-FID
20	80	Liquid-Liquid	DCM	GC-FID	In House (based on USEPA 3510B, USEPA 8015B)
21	250	Liquid-liquid	DCM with solvent exchange to hexane	GC-FID	USEPA 3510
22	500	liquid-liquid	DCM	GC-FID	ma-30

Table 2 Test Methods Sample S2 BTEX

Lab. Code	Sample Volume (mL)	Extraction	Measurement	Method
1	40	Purge and Trap	GC-MS	In house method based on USEPA 8260
2	40	Purge and Trap	GC MS	In House method based on USEPA 8260
3	5	Purge and Trap	GCMS	In house method adapted from USEPA SW 846 8260B
4	10	Headspace	GC-MS	US EPA 8260B
5	10	Headspace	GC/MS	In House
6	5	Purge and Trap	GC-MS	In House USEPA SW846-8260B
7	25	Purge and Trap	GC-MS	USEPA 8260
8	5	Purge and Trap	GC-MS	APHA (online edition) 6200B
9	15	Purge and Trap	GC-MS	8260
10	40	Purge and Trap	GC-MS	USEPA 8260
11	5	Purge and Trap	GC-MS	In house method based on USEPA 8260
12	40	Purge and Trap	GCMS	In-house method based on US EPA 8260
13				
14	10	Purge and Trap	GC-MS	In house method based on USEPA 8260
15	44	Purge and Trap	GC-MS	USEPA 8260
16	40	Purge and Trap	GC-MS	USEPA 8260
17				
18	25	Purge and Trap	GC-MS	USEPA 8260
19	40	No extraction; direct inject analysis on purge and trap system	GCMS	ORG002W - VOCs in water by PTGCMS
20	39	Purge and Trap	GC-MS	USEPA 8260
21	10	Headspace	GC-MS	In-house method based on US EPA 8260
22	40	Purge and Trap	GC-MS	USEPA 8260

Table 3 Test Methods Samples S3 and S4 PAH

Lab. Code	Sample Volume (mL)	Extraction	Solvent	Measurement	Method
1	200	Liquid-liquid extraction using DCM, then concentrated to 2mL.	Dichloromethane	GC-MS	In-house based on USEPA 8270
2	80	Liquid-Liquid	DCM	GCMS	In-house method based on 8270C
3	400	Liquid-Liquid	DCM	GC-MS	In-house method - USEPA SW 846 - 8270D.
4	250	Liquid-Liquid	DCM	GC-MS SIM	
5	100	Liquid-Liquid	DCM	GCMS	In-house
6	400	Liquid-Liquid	DCM	GC-MS	In-house USEPA SW 846-8260B
7	100	Liquid-Liquid	DCM	GC-MS	USEPA 8270
8	500	SPE	DCM:EtOAc 1:1	GC-MS	Standard Methods for the Examination of Water and Wastewater online. Method 6410B
9	100	Liquid-Liquid	DCM	GC-MS	8270
10	500	Liquid-Liquid	DCM	GC-MS	USEPA 8270C
11	100	Liquid-liquid extraction using DCM. Solvent in concentrated to 1mL.	DCM	GC-MS	In-house based on USEPA 8270
12	250	Liquid-liquid separatory funnel extraction.	DCM	GCMS	In-house method based on US EPA 8270
13	40	Liquid-liquid with blow down	Hexane	GC-MS	In-house method based on US-EPA 8270C
14	100	Liquid-Liquid	DCM	GC-MS	In-house method referencing USEPA 8270
15	100	Liquid-Liquid	DCM	GC-MS	8270
16	200	Liquid-Liquid	DCM	GC-MS	USEPA 8270C
17	520	Liquid-Liquid	DCM	GC-MS	USEPA 8270C
18	500	Liquid-Liquid	DCM	GC-MS	USEPA 8270C
19	500	Liquid-Liquid	DCM	GC-MS-MS	in-house based on USEPA 8270D
20	80	Liquid-Liquid	DCM	GC-MS	In house (based on USEPA 3500C and 8270D)
21	100	Liquid-Liquid	DCM	GC-MS	In-house method, modified USEPA 8270d
22	500	Liquid-Liquid	DCM	GC MS MS	USEPA 8270C

Table 4 Basis of Expanded Uncertainty Estimate

Lab. Code	Basis of Uncertainty Estimate
1	Control charts
2	
3	
4	Based on historical data
5	Validation Data
6	QC DATA,
7	Top down approach based on precision and bias from QC samples.
8	Long term reproducibility
9	Top down approach based on precision and bias from QC samples.
10	Quality Control requirement
11	Control charts
12	Professional judgement.
13	
14	Control Charts
15	Top down approach based on precision and bias from QC samples.
16	Quality Control requirement
17	Repeatability Precision
18	The estimate is compliant with the "ISO Guide to the Uncertainty in Measurement" and is based on in-house validation and quality control data. A coverage factor of 2 is used to give a confidence level of approximately 95%.
19	Uncertainty of the calibration curve, precision, and method bias
20	Precision and estimates of the method and Laboratory bias
21	30%, uncertainty budget
22	Uncertainty based of ± 24% of ug/L result

Table 5 Additional Comment or Discussion of Results

Lab Code	Sample	Comment or Discussion
3	All S2 S3, S4	NMI to consider lowering sample volume. m&p and o-xylenes reported as xylenes Benzo(b+j)fluroranthene reported as Benzo(b)fluoranthene
4	S2	The above hydrocarbon result is C6-C9.
6	All	Samples were re-run to confirm results.
17	S3, S4	Traces of anthracene present
21	S3, S4	PAH results very close to method PQL.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 27 with resultant summary statistics: mean, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}).

Bar charts of results and performance scores are presented in Figures 2 to 22.

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

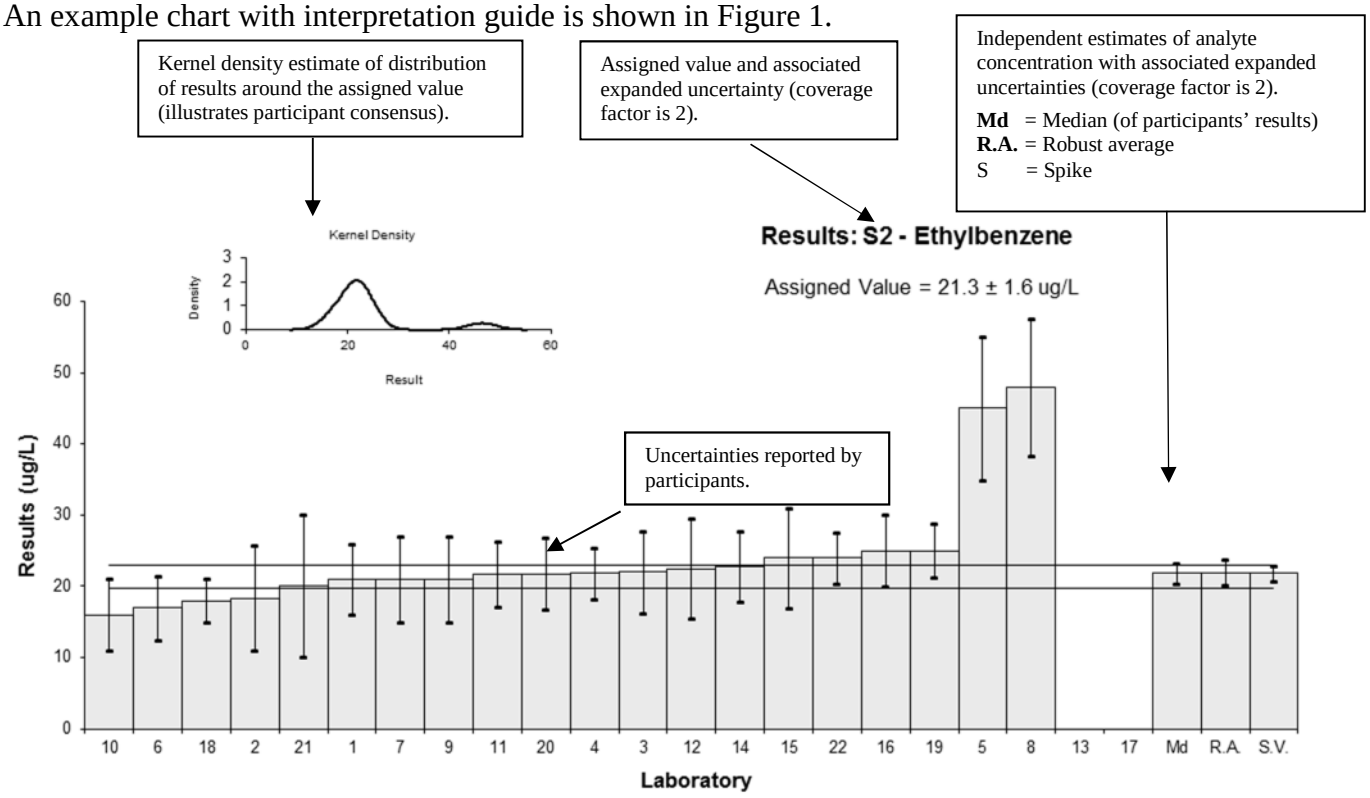


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

The assigned value is defined as: 'value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose.'[3]

For a proficiency test, the assigned value is the best available measurement of the true concentration of an analyte in the test sample.

4.3 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratory variation that in the judgement of the study organiser would be expected from participants given the sample concentration. It is important to note that this is a performance measure set by the study coordinator; it is not the coefficient of variation of participant results.

4.4 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (X) and the performance coefficient of variation (PCV). This value is used in the calculation of z-scores.

$$\sigma = X * PCV \qquad \text{Equation 1}$$

4.5 z-Score

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

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

where:

z is z-score
χ is the participant result
X is the study assigned value
σ is the target standard deviation from equation 1

A z-score with absolute value (|z|):

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

4.6 E_n-Score

The E_n-score is complementary to the z-score in assessment of laboratory performance. The E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

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

where:

E_n is the E_n-score
χ is the 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

An E_n-score with absolute value ($|E_n|$):

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

4.7 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017[7] must establish and demonstrate the traceability and measurement uncertainty associated with their test results.

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem /CITAC Guide.[8]

5 TABLES AND FIGURES

Table 6

Sample Details

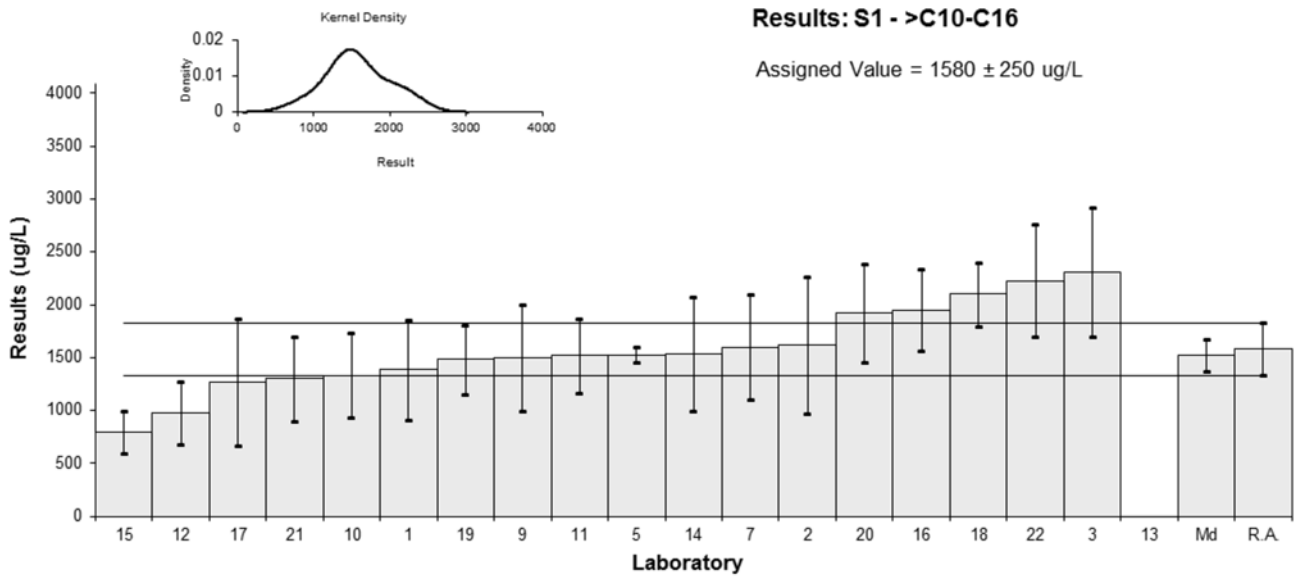
Sample No.	S1
Matrix.	Water
Analyte.	>C10-C16
Units	ug/L

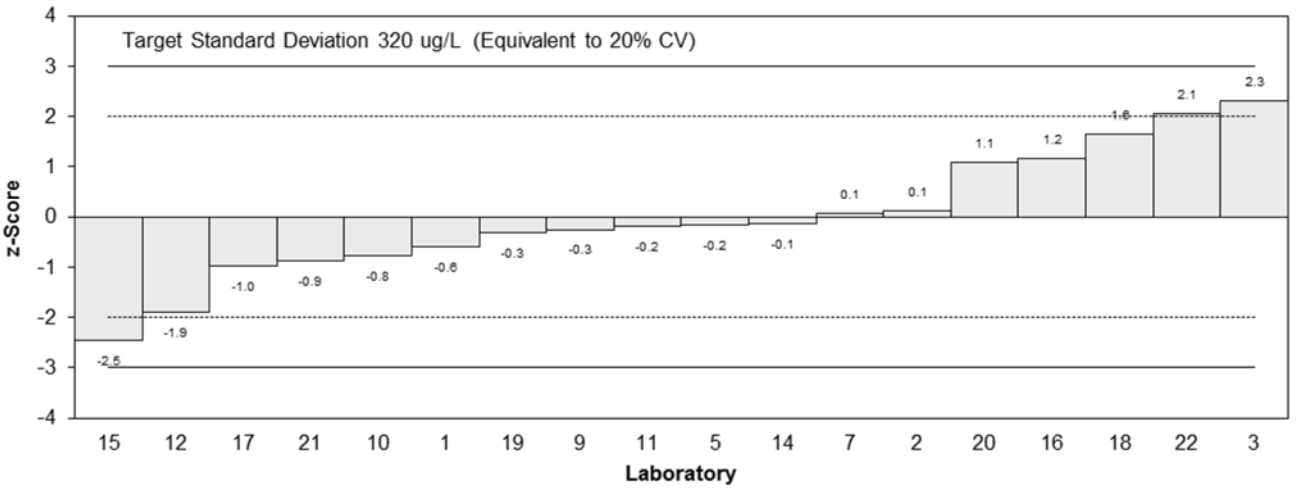
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1388	472	-0.61	-0.36
2	1619	650	0.12	0.06
3	2310	610	2.31	1.11
5	1527	69	-0.17	-0.20
7	1600	500	0.06	0.04
9	1500	500	-0.25	-0.14
10	1333	400	-0.78	-0.52
11	1520	350	-0.19	-0.14
12	980	294	-1.90	-1.55
13	NT	NT		
14	1537	537	-0.14	-0.07
15	800	200	-2.47	-2.44
16	1950	390	1.17	0.80
17	1270	600	-0.98	-0.48
18	2100	300	1.65	1.33
19	1482.3	326	-0.31	-0.24
20	1921	468.43	1.08	0.64
21	1300	400	-0.89	-0.59
22	2230	535.2	2.06	1.10

Statistics

Assigned Value	1580	250
Spike	Not Spiked	
Robust Average	1580	250
Median	1524	153
Mean	1576	
N	18	
Max.	2310	
Min.	800	
Robust SD	427	
Robust CV	27%	


Kernel Density
Density
Result
Results: S1 - >C10-C16
Assigned Value = 1580 ± 250 ug/L
Results (ug/L)
Laboratory
15 12 17 21 10 1 19 9 11 5 14 7 2 20 16 18 22 3 13 Md R.A.


z-Scores: S1 - >C10-C16
Target Standard Deviation 320 ug/L (Equivalent to 20% CV)
z-Score
Laboratory
15 12 17 21 10 1 19 9 11 5 14 7 2 20 16 18 22 3

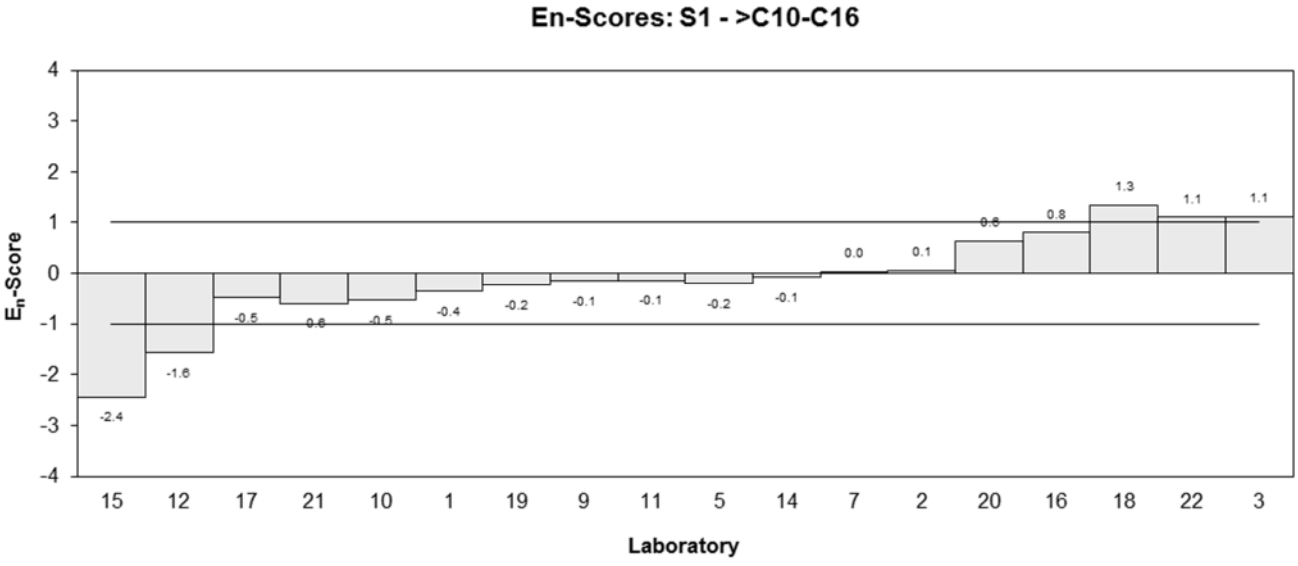

En-Scores: S1 - >C10-C16
En-Score
Laboratory
15 12 17 21 10 1 19 9 11 5 14 7 2 20 16 18 22 3

Figure 2

Table 7

Sample Details

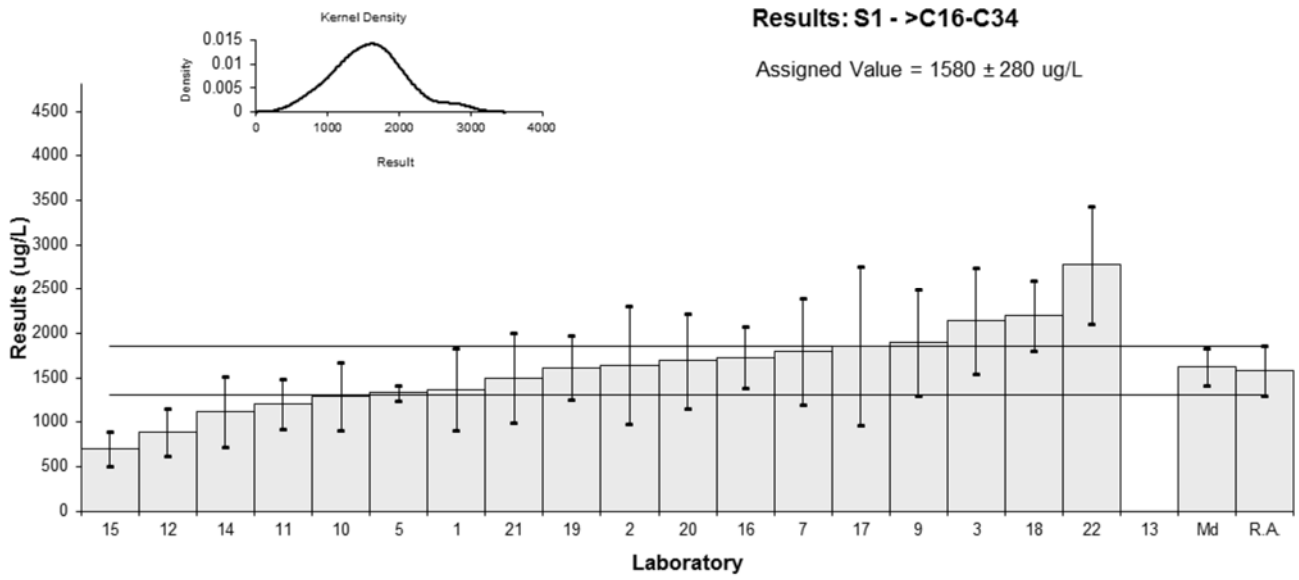
Sample No.	S1
Matrix.	Water
Analyte.	>C16-C34
Units	ug/L

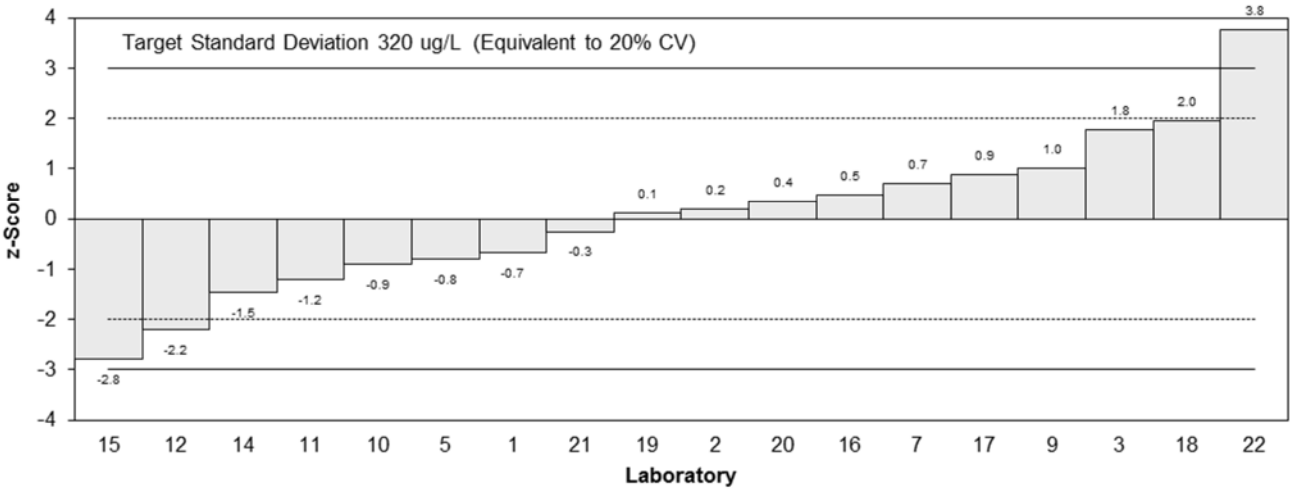
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1367	465	-0.67	-0.39
2	1642	660	0.20	0.09
3	2140	595	1.77	0.85
5	1328	82	-0.80	-0.86
7	1800	600	0.70	0.33
9	1900	600	1.01	0.48
10	1291	387	-0.91	-0.61
11	1200	280	-1.20	-0.96
12	886	266	-2.20	-1.80
13	NT	NT		
14	1119	391	-1.46	-0.96
15	700	200	-2.78	-2.56
16	1730	346	0.47	0.34
17	1860	900	0.89	0.30
18	2200	400	1.96	1.27
19	1615.6	355	0.11	0.08
20	1691	534.51	0.35	0.18
21	1500	500	-0.25	-0.14
22	2770	664.8	3.77	1.65

Statistics

Assigned Value	1580	280
Spike	Not Spiked	
Robust Average	1580	280
Median	1628	211
Mean	1597	
N	18	
Max.	2770	
Min.	700	
Robust SD	479	
Robust CV	30%	


Kernel Density
Density
Result
Results: S1 - >C16-C34
Assigned Value = 1580 ± 280 ug/L
Results (ug/L)
Laboratory
15 12 14 11 10 5 1 21 19 2 20 16 7 17 9 3 18 22 13 Md R.A.


z-Scores: S1 - >C16-C34
Target Standard Deviation 320 ug/L (Equivalent to 20% CV)
z-Score
Laboratory
15 12 14 11 10 5 1 21 19 2 20 16 7 17 9 3 18 22
-2.8 -2.2 -1.5 -1.2 -0.9 -0.8 -0.7 -0.3 0.1 0.2 0.4 0.5 0.7 0.9 1.0 1.8 2.0 3.8

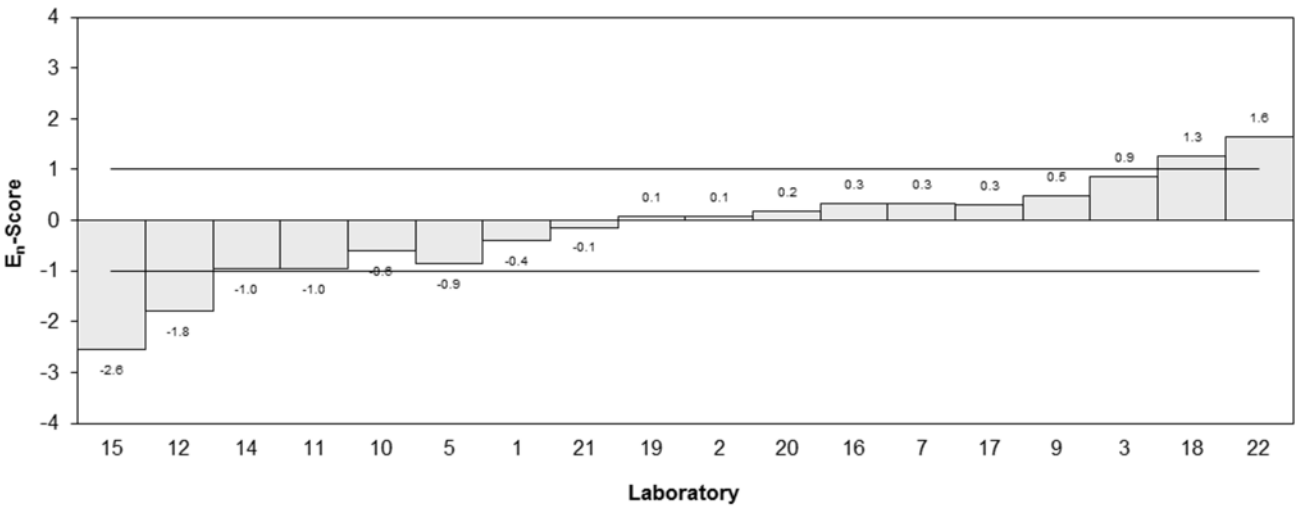

En-Scores: S1 - >C16-C34
En-Score
Laboratory
15 12 14 11 10 5 1 21 19 2 20 16 7 17 9 3 18 22
-2.6 -1.8 -1.0 -1.0 -0.6 -0.9 -0.4 -0.1 0.1 0.1 0.2 0.3 0.3 0.3 0.5 0.9 1.3 1.6

Figure 3

Table 8 Laboratories that reported for Sample S1 additional hydrocarbon ranges to those defined in Schedule B3 of the NEPM[5]

Lab Code	Range	Concentration (ug/L)	Uncertainty (ug/L)
4	C7-C9	<60	41
4	C10-C14	550	190
4	C15-C36	1570	420
6	Midpoint C9-10-Midpoint C14-15	700	396
6	Midpoint C14-15-Quarter interval C28-30	1950	696
6	Midpoint C28-30-Quarter interval C36-36	60	49
6	After C10 -Ending after C16	1350	676
6	After C15-Ending after C34	1330	425
6	After C34-Ending after C40	<100	50
8	>C7-C9	<400	80
8	>C10-C14	950	190
8	>C15-C36	1900	380

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Table 9

Sample Details

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

Participant Results

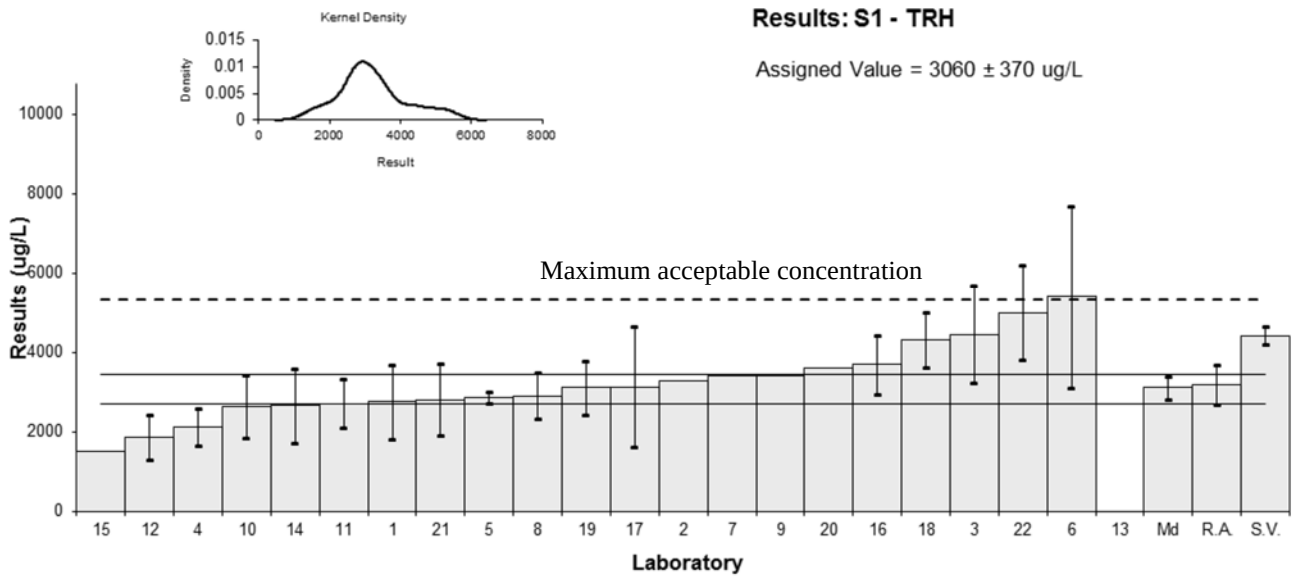
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2755	937	-0.66	-0.30
2	3261	NR	0.44	0.54
3**	4450	1237	2.00	1.00
4	2120	460	-2.05	-1.59
5	2855	151	-0.45	-0.51
6	5390	2292	5.08	1.00
7	3400	NR	0.74	0.92
8	2900	580	-0.35	-0.23
9	3400	NR	0.74	0.92
10	2624	787	-0.95	-0.50
11	2710	620	-0.76	-0.48
12	1866	560	-2.60	-1.78
13	NT	NT		
14	2656	929	-0.88	-0.40
15	1500	NR	-3.40	-4.22
16	3680	736	1.35	0.75
17	3130	1500	0.15	0.05
18**	4300	700	2.00	1.00
19	3098	681	0.08	0.05
20	3612	NR	1.20	1.49
21	2800	900	-0.57	-0.27
22**	5000	1200	2.00	1.00

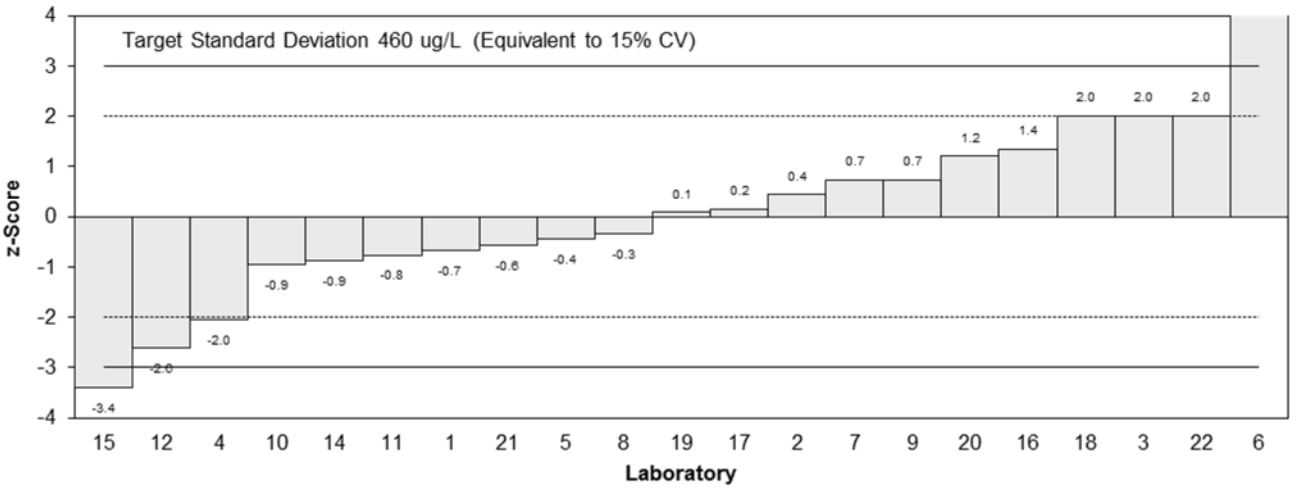
Statistics

Assigned Value*	3060	370
Spike	4420	220
Maximum acceptable conc.**	5338	
Robust Average	3170	505
Median	3098	298
Mean	3214	
N	21	
Max.	5390	
Min.	1500	
Robust SD	926	
Robust CV	29%	

*Robust average excluding laboratories 6, 15 and 22.

**z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S1 - TRH
Assigned Value = 3060 ± 370 ug/L
Maximum acceptable concentration
Results (ug/L)
Laboratory
15 12 4 10 14 11 1 21 5 8 19 17 2 7 9 20 16 18 3 22 6 13 Md R.A. S.V.


z-Scores: S1 - TRH
Target Standard Deviation 460 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
15 12 4 10 14 11 1 21 5 8 19 17 2 7 9 20 16 18 3 22 6

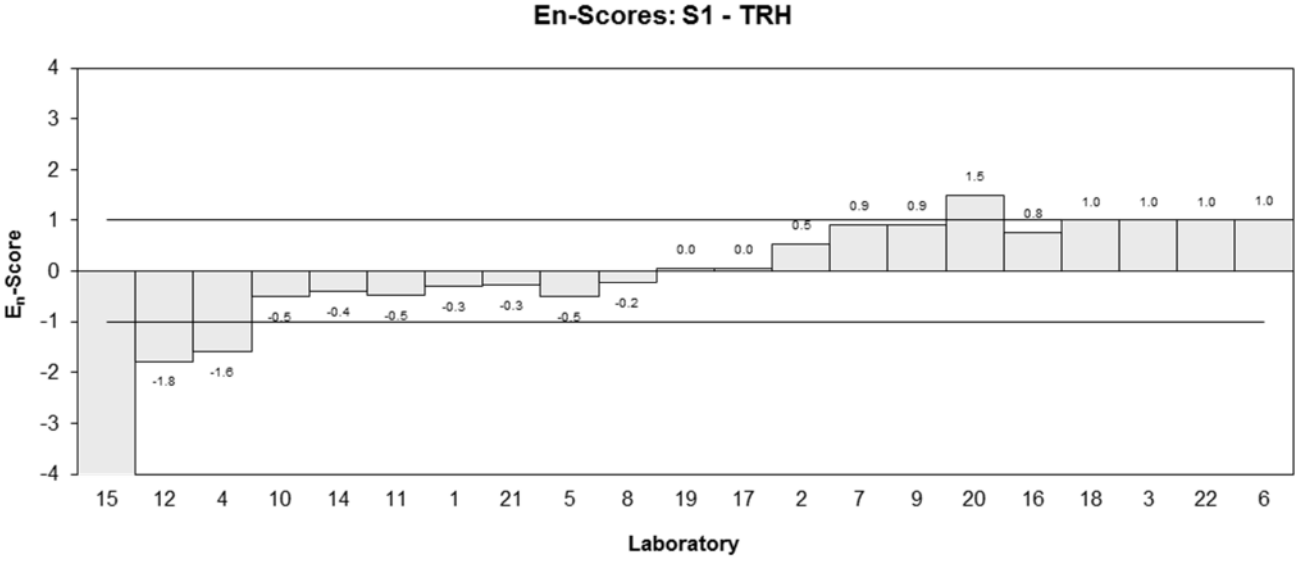

En-Scores: S1 - TRH
En-Score
Laboratory
15 12 4 10 14 11 1 21 5 8 19 17 2 7 9 20 16 18 3 22 6

Figure 4

Table 10

Sample Details

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

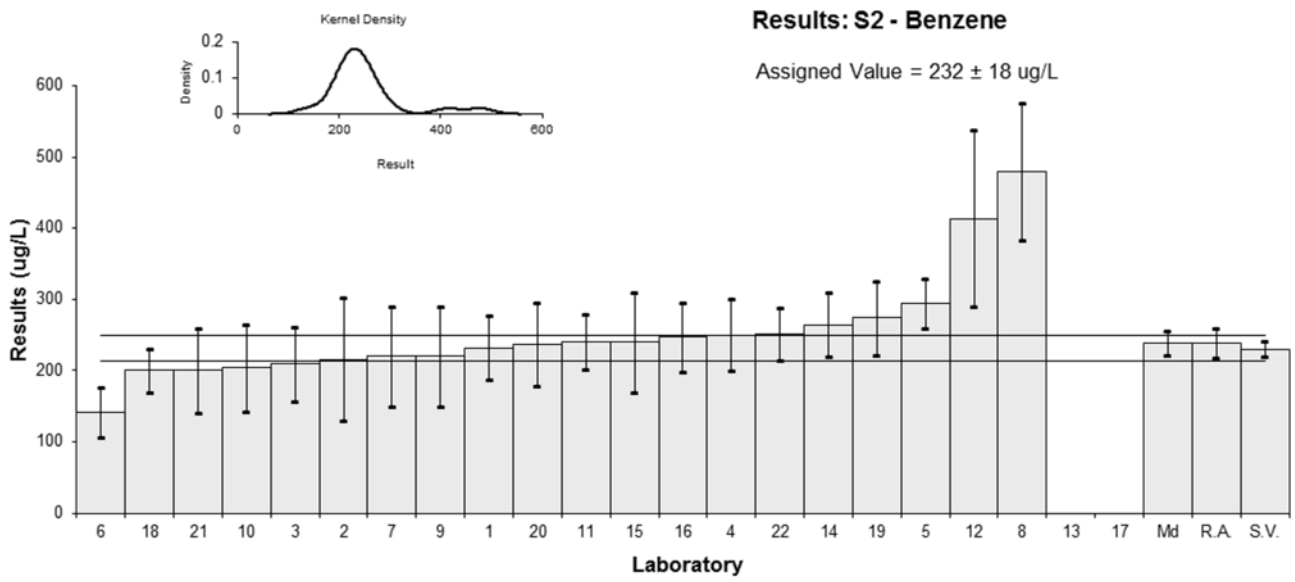
Participant Results

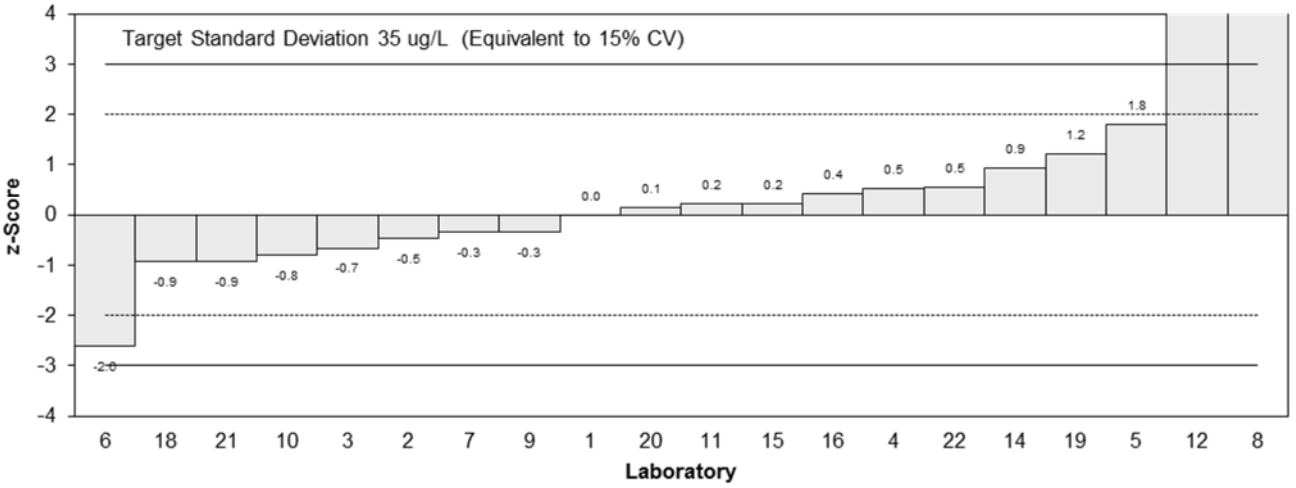
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	232	45	0.00	0.00
2	216	86	-0.46	-0.18
3	209	51.6	-0.66	-0.42
4	250	51	0.52	0.33
5	295	35	1.81	1.60
6	141	34.8	-2.61	-2.32
7	220	70	-0.34	-0.17
8	480	96	7.13	2.54
9	220	70	-0.34	-0.17
10	204	61	-0.80	-0.44
11	240	38.8	0.23	0.19
12	413.5	124	5.22	1.45
13	NT	NT		
14	264.3	44.5	0.93	0.67
15	240	70	0.23	0.11
16	247	48.4	0.43	0.29
17	NT	NT		
18	200	30	-0.92	-0.91
19	274	52	1.21	0.76
20	236.93	58.43	0.14	0.08
21	200	60	-0.92	-0.51
22	251	37.6	0.55	0.46

Statistics

Assigned Value*	232	18
Spike	230	11
Robust Average	239	21
Median	238	17
Mean	252	
N	20	
Max.	480	
Min.	141	
Robust SD	38	
Robust CV	16%	

*Robust average excluding laboratories 8 and 12.


Kernel Density
Density
Result
Results: S2 - Benzene
Assigned Value = 232 ± 18 ug/L
Results (ug/L)
Laboratory
6 18 21 10 3 2 7 9 1 20 11 15 16 4 22 14 19 5 12 8 13 17 Md R.A. S.V.


z-Scores: S2 - Benzene
Target Standard Deviation 35 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
6 18 21 10 3 2 7 9 1 20 11 15 16 4 22 14 19 5 12 8

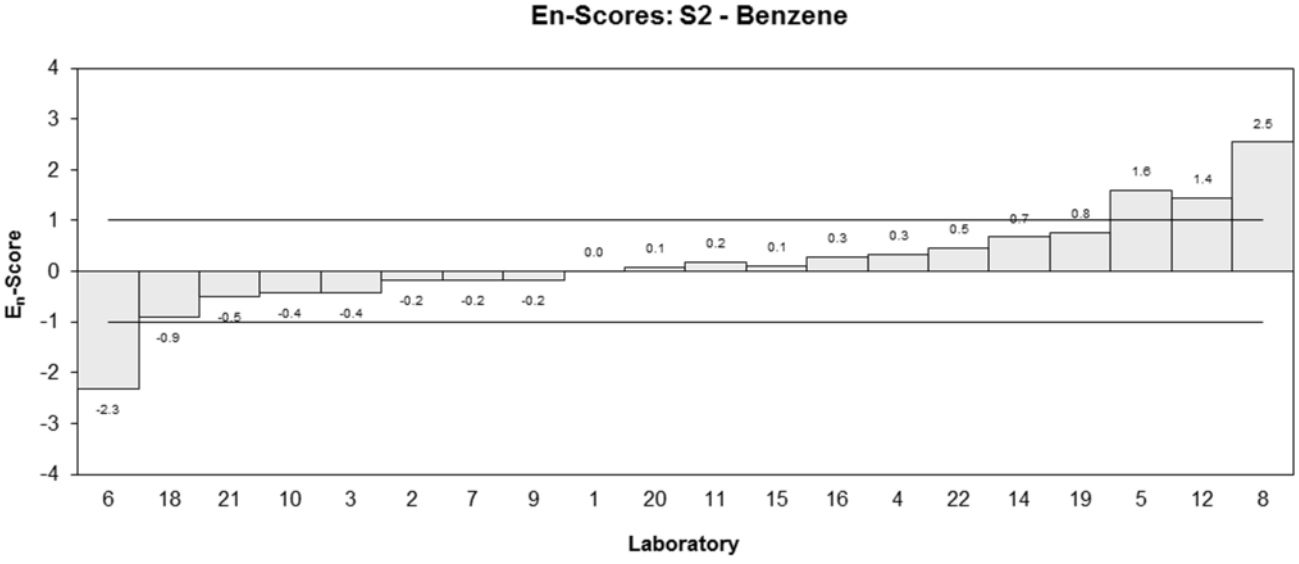

En-Scores: S2 - Benzene
En-Score
Laboratory
6 18 21 10 3 2 7 9 1 20 11 15 16 4 22 14 19 5 12 8

Figure 5

Table 11

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	1268	266
2	667	267
3	1080	409
4	1020	290
5	NT	NT
6	710	213
7	1300	400
8	NR	NR
9	1100	300
10	872	262
11	1370	360
12	1704	511
13	NT	NT
14	1490.4	352.9
15	1200	400
16	1300	260.0
17	NT	NT
18	810	150
19	1014	142
20	1703.58	511.07
21	1000	300
22	2356	353.4

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Robust Average	1190	220
Median	1150	136
Mean	1220	
N	18	
Max.	2356	
Min.	667	
Robust SD	375	
Robust CV	32%	

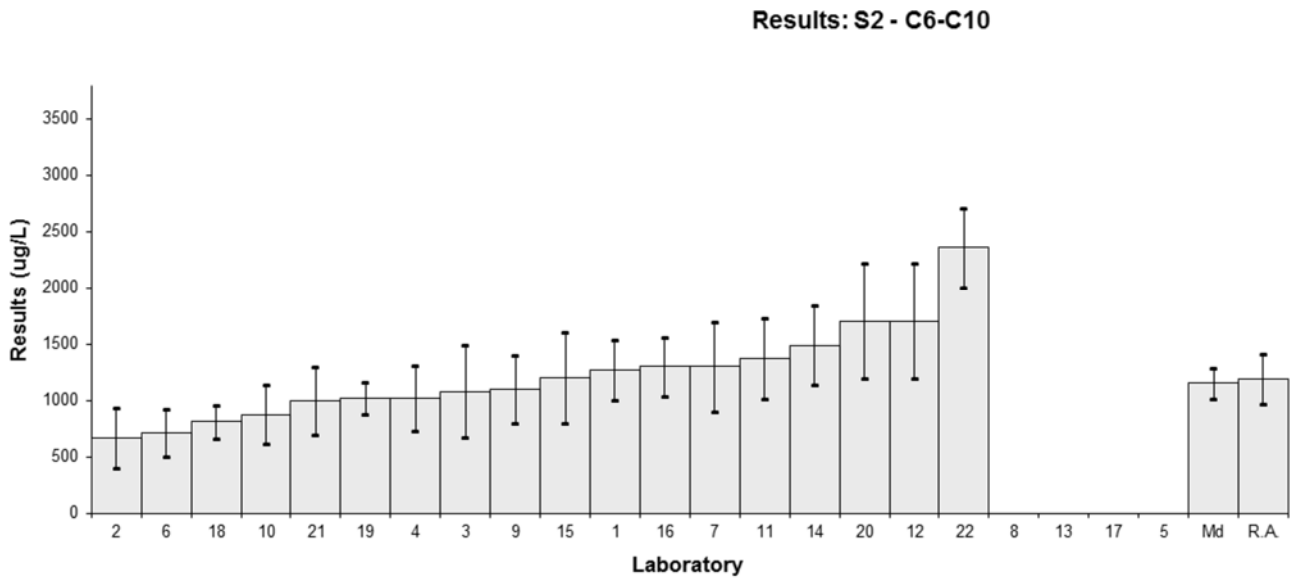

Results: S2 - C6-C10
Results (ug/L)
3500
3000
2500
2000
1500
1000
500
0
2
6
18
10
21
19
4
3
9
15
1
16
7
11
14
20
12
22
8
13
17
5
Md
R.A.
Laboratory

Figure 6

Table 12

Sample Details

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

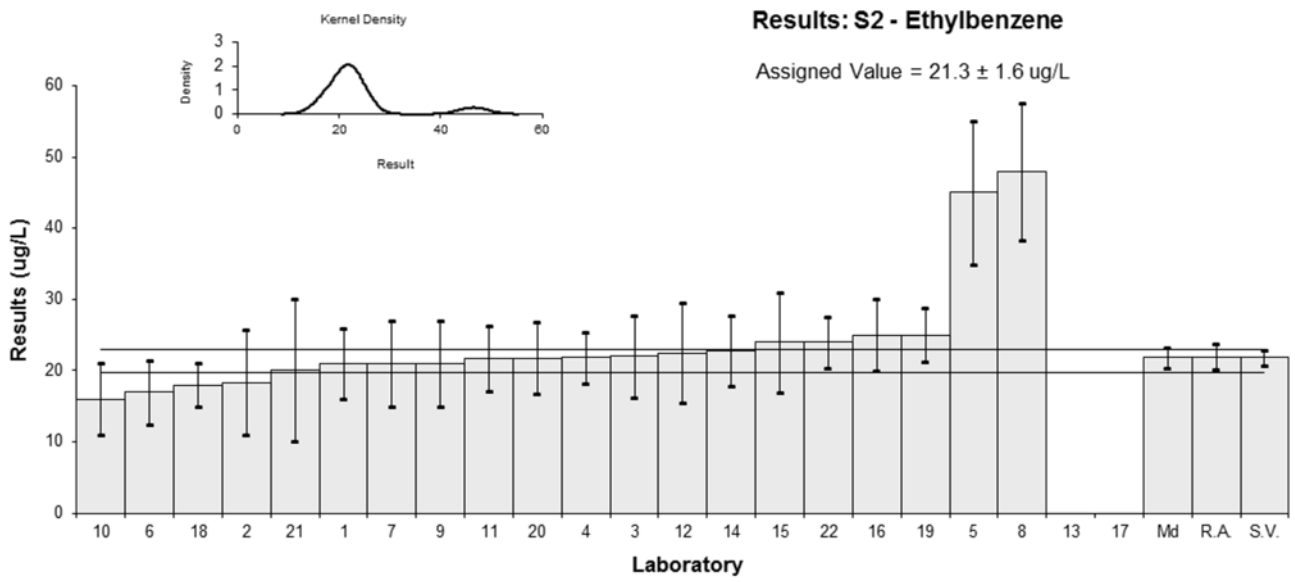
Participant Results

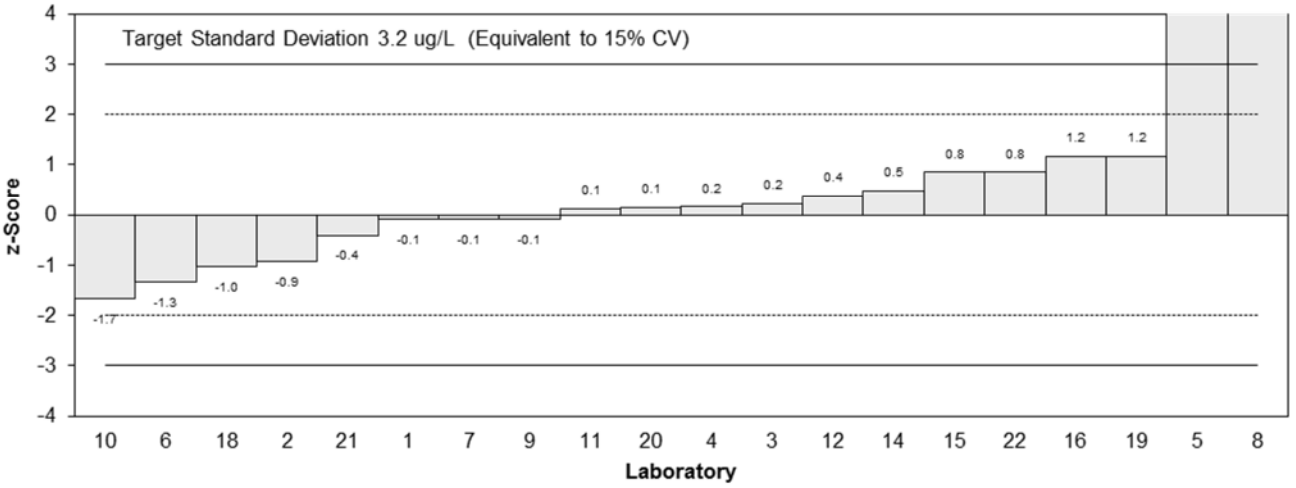
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	21	5	-0.09	-0.06
2	18.32	7.33	-0.93	-0.40
3	22	5.8	0.22	0.12
4	21.8	3.6	0.16	0.13
5	45	10	7.42	2.34
6	17	4.5	-1.35	-0.90
7	21	6	-0.09	-0.05
8	48	9.6	8.36	2.74
9	21	6	-0.09	-0.05
10	16	5	-1.66	-1.01
11	21.7	4.54	0.13	0.08
12	22.5	7	0.38	0.17
13	NT	NT		
14	22.8	4.9	0.47	0.29
15	24	7	0.85	0.38
16	25	5.0	1.16	0.70
17	NT	NT		
18	18	3	-1.03	-0.97
19	25	3.8	1.16	0.90
20	21.74	5.04	0.14	0.08
21	20	10	-0.41	-0.13
22	24	3.6	0.85	0.69

Statistics

Assigned Value*	21.3	1.6
Spike	21.8	1.1
Robust Average	21.9	1.8
Median	21.8	1.4
Mean	23.8	
N	20	
Max.	48	
Min.	16	
Robust SD	3.3	
Robust CV	15%	

*Robust average excluding laboratories 5 and 8.


Kernel Density
Density
Result
Results: S2 - Ethylbenzene
Assigned Value = 21.3 ± 1.6 ug/L
Results (ug/L)
Laboratory
10 6 18 2 21 1 7 9 11 20 4 3 12 14 15 22 16 19 5 8 13 17 Md R.A. S.V.


z-Scores: S2 - Ethylbenzene
Target Standard Deviation 3.2 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
10 6 18 2 21 1 7 9 11 20 4 3 12 14 15 22 16 19 5 8

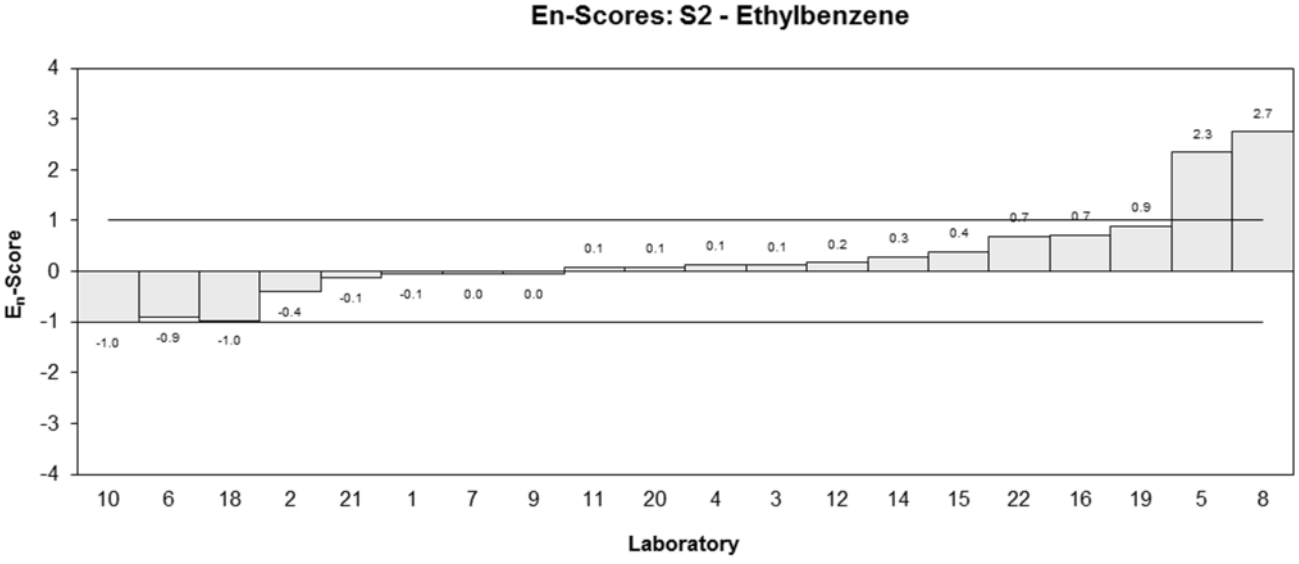

En-Scores: S2 - Ethylbenzene
En-Score
Laboratory
10 6 18 2 21 1 7 9 11 20 4 3 12 14 15 22 16 19 5 8

Figure 7

Table 13

Sample Details

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

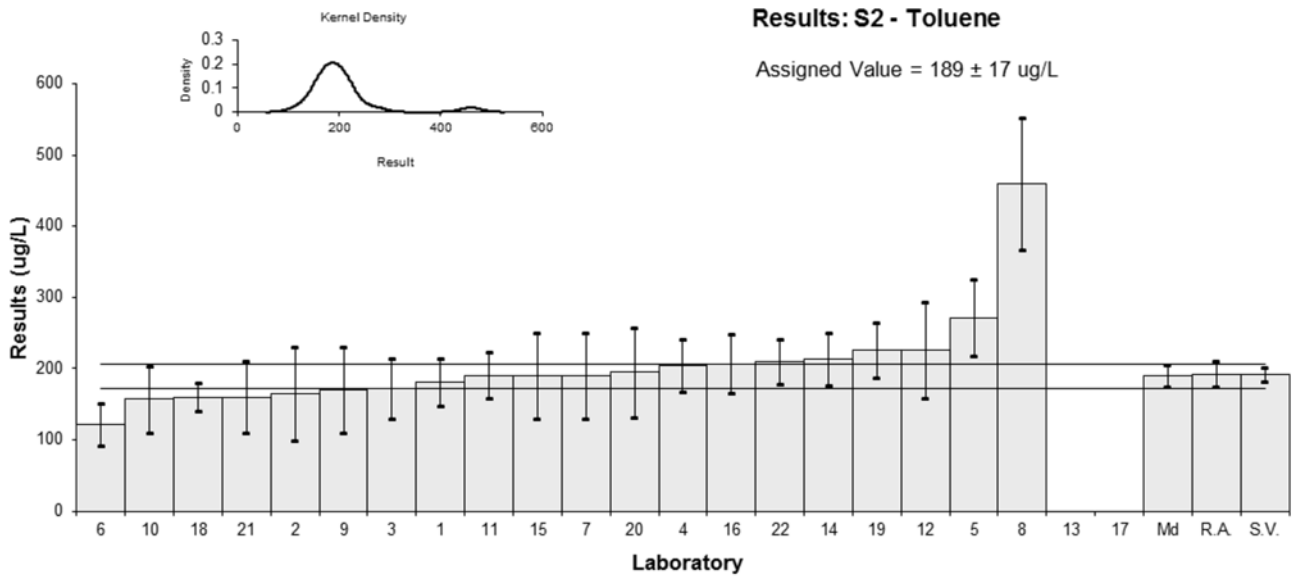
Participant Results

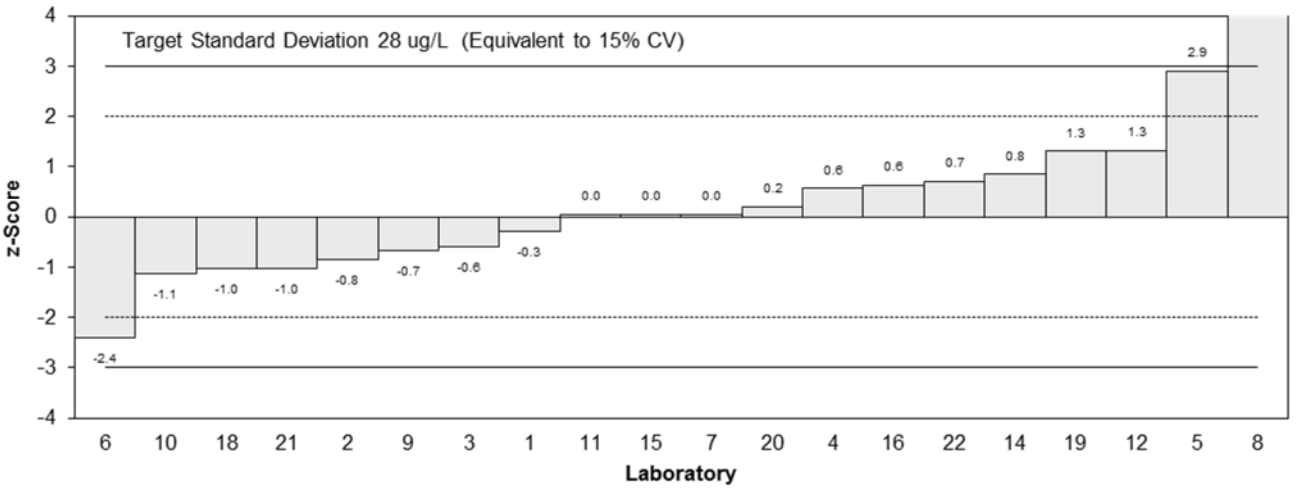
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	181	34	-0.28	-0.21
2	165	66	-0.85	-0.35
3	172	41.6	-0.60	-0.38
4	205	37	0.56	0.39
5	271	54	2.89	1.45
6	121	29.4	-2.40	-2.00
7	190	60	0.04	0.02
8	460	92	9.56	2.90
9	170	60	-0.67	-0.30
10	157	47	-1.13	-0.64
11	190	32.4	0.04	0.03
12	226.1	68	1.31	0.53
13	NT	NT		
14	213	37.4	0.85	0.58
15	190	60	0.04	0.02
16	207	41.4	0.63	0.40
17	NT	NT		
18	160	20	-1.02	-1.10
19	226	39	1.31	0.87
20	194.77	62.48	0.20	0.09
21	160	50	-1.02	-0.55
22	209	31.4	0.71	0.56

Statistics

Assigned Value*	189	17
Spike	191	10
Robust Average	192	18
Median	190	15
Mean	203	
N	20	
Max.	460	
Min.	121	
Robust SD	32	
Robust CV	17%	

*Robust average excluding laboratory 8.


Kernel Density
Density
Result
Results: S2 - Toluene
Assigned Value = 189 ± 17 ug/L
Results (ug/L)
Laboratory
6 10 18 21 2 9 3 1 11 15 7 20 4 16 22 14 19 12 5 8 13 17 Md R.A. S.V.


z-Scores: S2 - Toluene
Target Standard Deviation 28 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
6 10 18 21 2 9 3 1 11 15 7 20 4 16 22 14 19 12 5 8

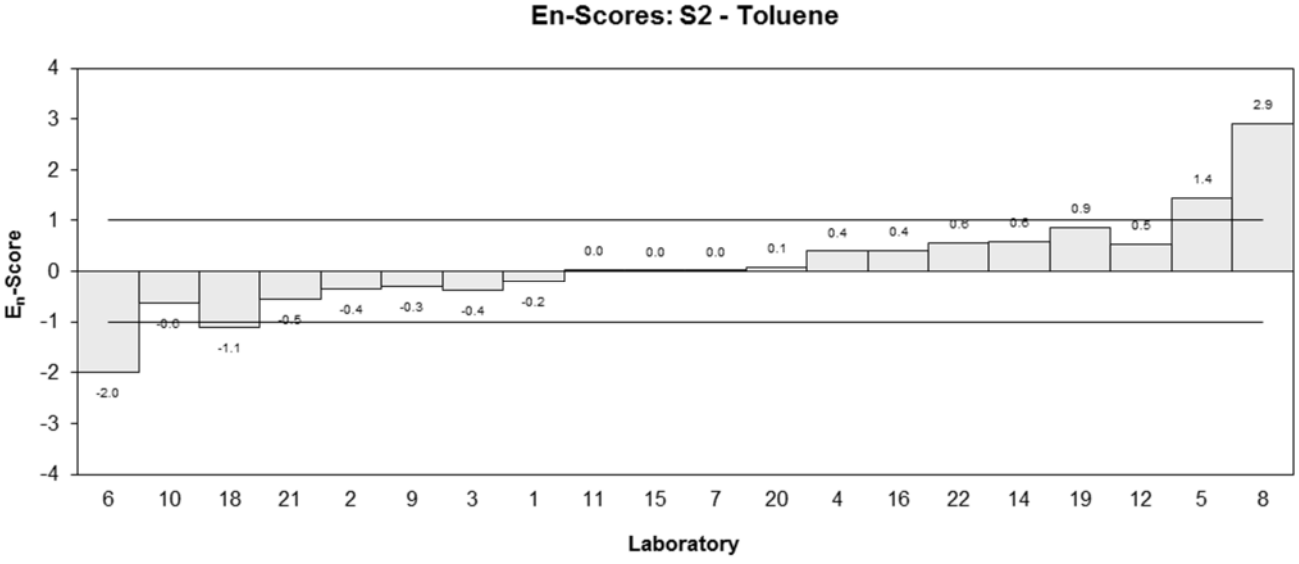

En-Scores: S2 - Toluene
En-Score
Laboratory
6 10 18 21 2 9 3 1 11 15 7 20 4 16 22 14 19 12 5 8

Figure 8

Table 14

Sample Details

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

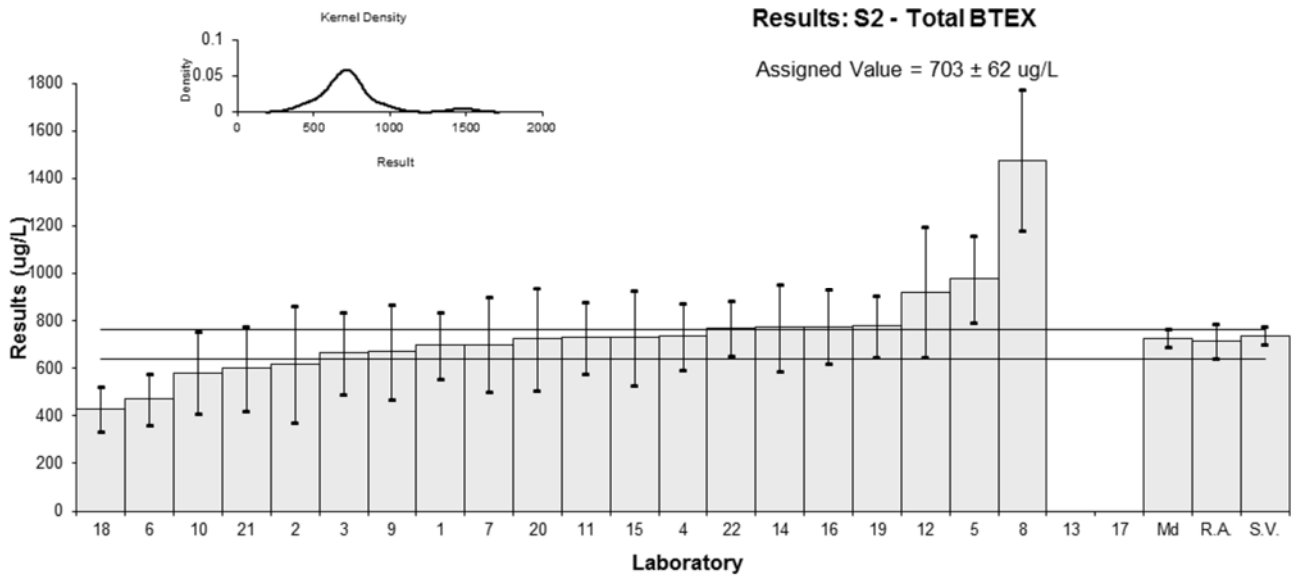
Participant Results

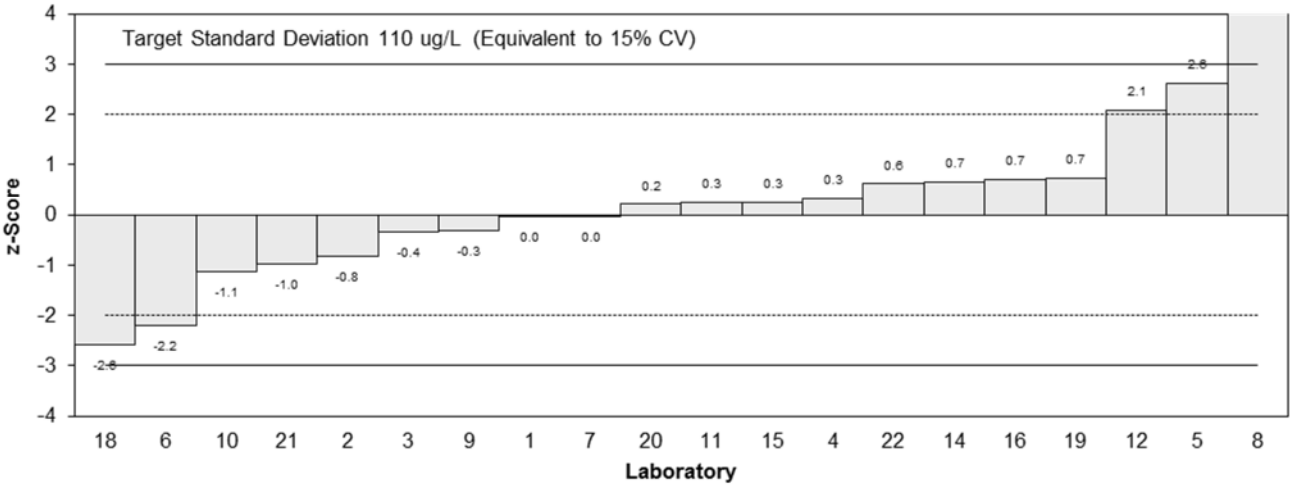
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	698	140	-0.05	-0.03
2	616.32	246	-0.82	-0.34
3	666	172	-0.35	-0.20
4	736	140	0.31	0.22
5	979	184	2.62	1.42
6	470	107	-2.21	-1.88
7	700	200	-0.03	-0.01
8	1478	295.6	7.35	2.57
9	670	200	-0.31	-0.16
10	583	175	-1.14	-0.65
11	730	150	0.26	0.17
12	922.9	277	2.09	0.77
13	NT	NT		
14	772.3	182.9	0.66	0.36
15	730	200	0.26	0.13
16	777	155.4	0.70	0.44
17	NT	NT		
18	430	93	-2.59	-2.44
19	779	130	0.72	0.53
20	724.74	217.42	0.21	0.10
21	600	180	-0.98	-0.54
22	768	115.2	0.62	0.50

Statistics

Assigned Value*	703	62
Spike	739	37
Robust Average	716	73
Median	727	38
Mean	742	
N	20	
Max.	1478	
Min.	430	
Robust SD	131	
Robust CV	18%	

*Robust average excluding laboratory 8.


Kernel Density
Density
Result
Results: S2 - Total BTEX
Assigned Value = 703 ± 62 ug/L
Results (ug/L)
Laboratory
18 6 10 21 2 3 9 1 7 20 11 15 4 22 14 16 19 12 5 8 13 17 Md R.A. S.V.


z-Scores: S2 - Total BTEX
Target Standard Deviation 110 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
18 6 10 21 2 3 9 1 7 20 11 15 4 22 14 16 19 12 5 8

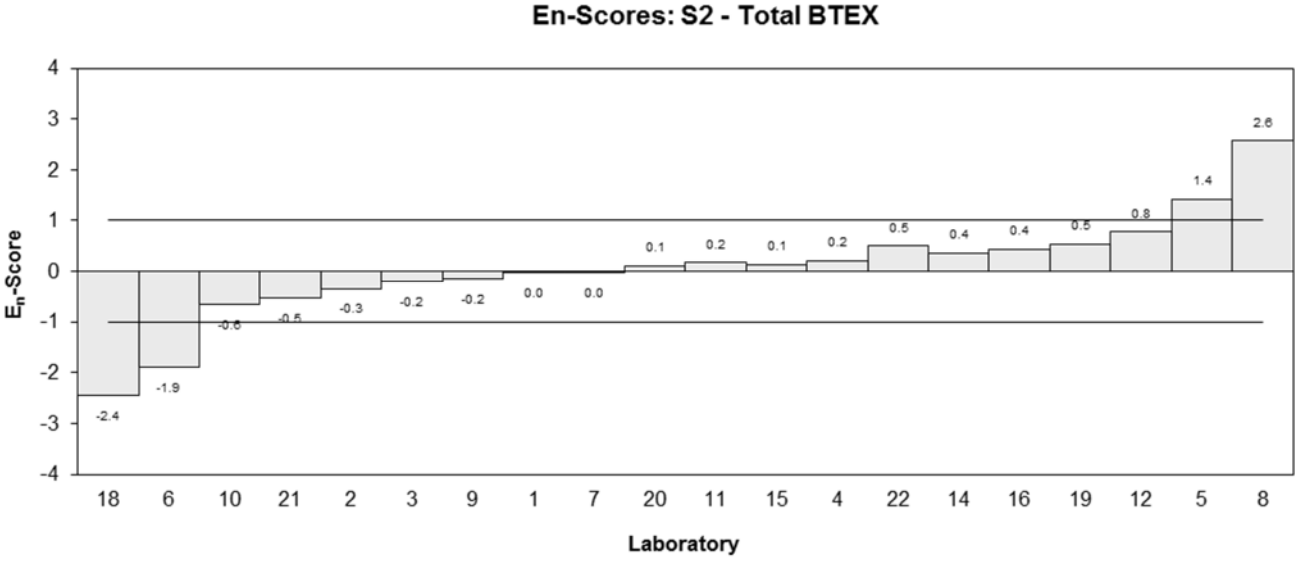

En-Scores: S2 - Total BTEX
En-Score
Laboratory
18 6 10 21 2 3 9 1 7 20 11 15 4 22 14 16 19 12 5 8

Figure 9

Table 15

Sample Details

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

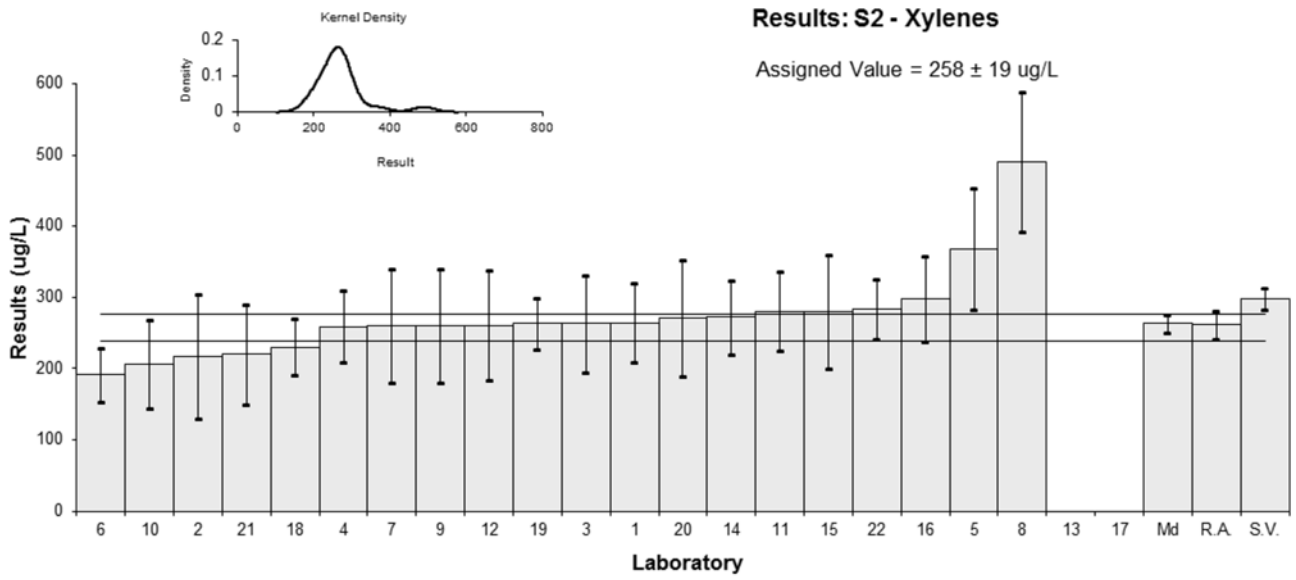
Participant Results

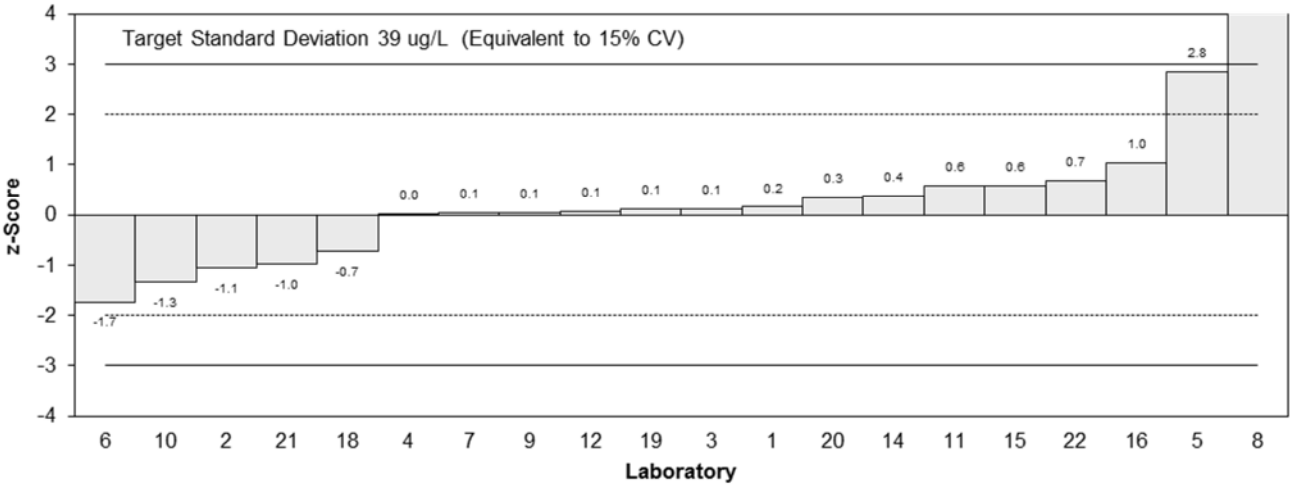
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	264	56	0.16	0.10
2	217	87	-1.06	-0.46
3	263	67.9	0.13	0.07
4	259	50	0.03	0.02
5	368	85	2.84	1.26
6	191	38.2	-1.73	-1.57
7	260	80	0.05	0.02
8	490	98	5.99	2.32
9	260	80	0.05	0.02
10	206	62	-1.34	-0.80
11	280	55.8	0.57	0.37
12	260.8	78	0.07	0.03
13	NT	NT		
14	272.1	52.7	0.36	0.25
15	280	80	0.57	0.27
16	298	59.6	1.03	0.64
17	NT	NT		
18	230	40	-0.72	-0.63
19	263	36	0.13	0.12
20	271.3	81.39	0.34	0.16
21	220	70	-0.98	-0.52
22	284	42.6	0.67	0.56

Statistics

Assigned Value*	258	19
Spike	298	15
Robust Average	261	20
Median	263	12
Mean	272	
N	20	
Max.	490	
Min.	191	
Robust SD	36	
Robust CV	14%	

*Robust average excluding laboratory 8.


Kernel Density
Density
Result
Results: S2 - Xylenes
Assigned Value = 258 ± 19 ug/L
Results (ug/L)
Laboratory
6 10 2 21 18 4 7 9 12 19 3 1 20 14 11 15 22 16 5 8 13 17 Md R.A. S.V.


z-Scores: S2 - Xylenes
Target Standard Deviation 39 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
6 10 2 21 18 4 7 9 12 19 3 1 20 14 11 15 22 16 5 8

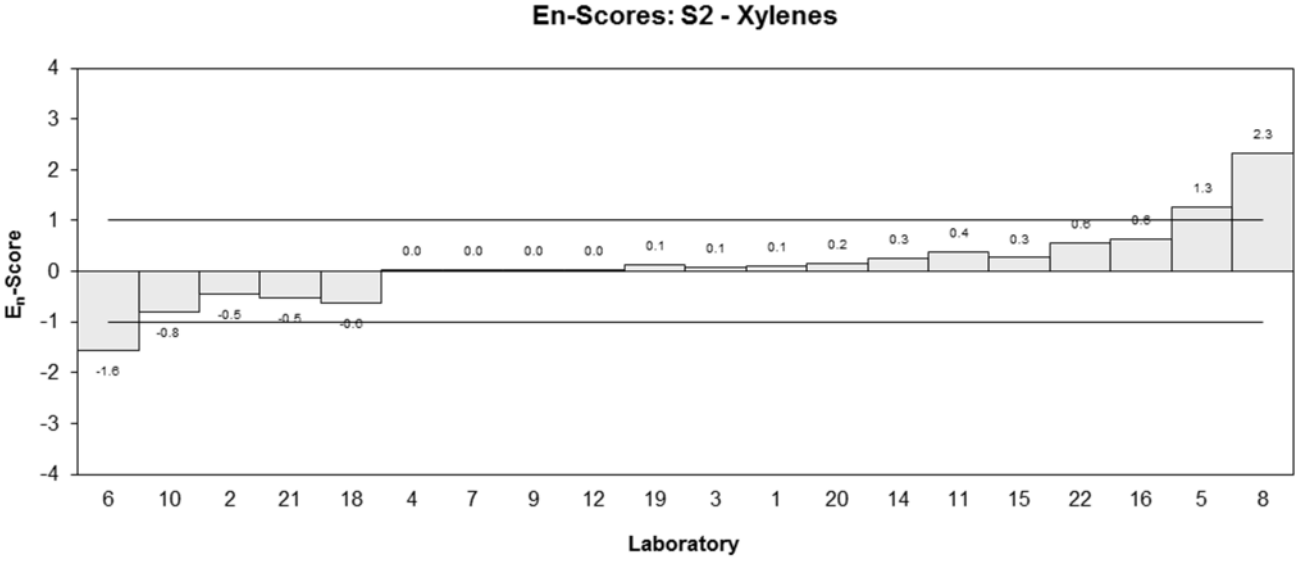

En-Scores: S2 - Xylenes
En-Score
Laboratory
6 10 2 21 18 4 7 9 12 19 3 1 20 14 11 15 22 16 5 8

Figure 10

Table 16

Sample Details

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

Participant Results

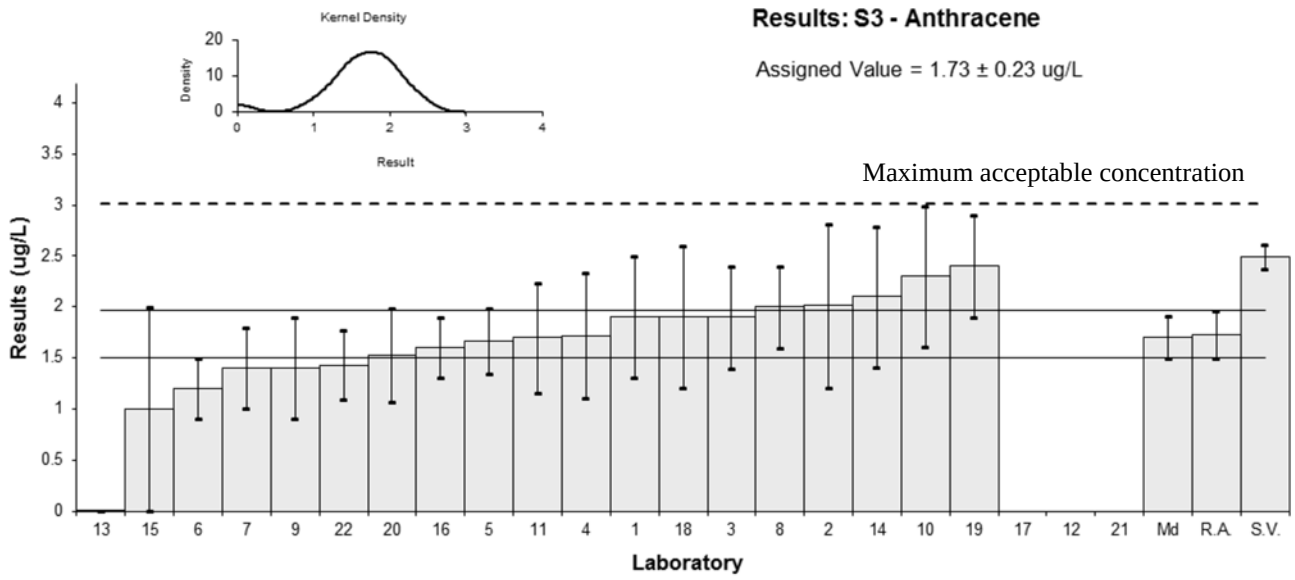
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.9	0.6	0.66	0.26
2	2.01	0.804	1.08	0.33
3	1.9	0.5	0.66	0.31
4	1.72	0.62	-0.04	-0.02
5	1.67	0.32	-0.23	-0.15
6	1.2	0.3	-2.04	-1.40
7	1.4	0.4	-1.27	-0.72
8	2.0	0.4	1.04	0.59
9	1.4	0.5	-1.27	-0.60
10**	2.3	0.69	2.00	0.78
11	1.7	0.54	-0.12	-0.05
12	<1	0.3		
13*	0.002476407	0.000495	-6.66	-7.51
14	2.1	0.69	1.43	0.51
15	1	1	-2.81	-0.71
16	1.6	0.3	-0.50	-0.34
17	<0.5	0.1		
18	1.9	0.7	0.66	0.23
19**	2.4	.5	2.00	1.00
20	1.53	0.46	-0.77	-0.39
21	<2	NR		
22	1.43	0.3432	-1.16	-0.73

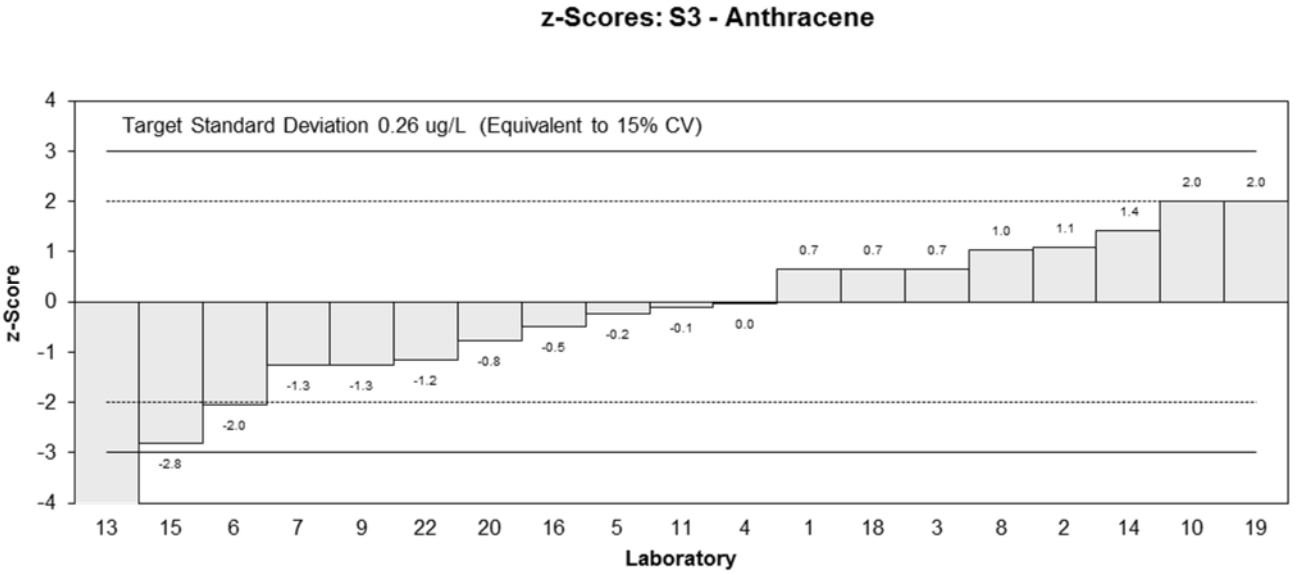
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

Statistics

Assigned Value	1.73	0.23
Spike	2.49	0.12
Maximum acceptable conc.***	3.01	
Robust Average	1.73	0.23
Median	1.70	0.21
Mean	1.73	
N	18	
Max.	2.4	
Min.	1	
Robust SD	0.39	
Robust CV	23%	

**z-score adjusted to 2 (see Section 6.3).


Kernel Density
Density
Result
Results: S3 - Anthracene
Assigned Value = 1.73 ± 0.23 ug/L
Maximum acceptable concentration
Results (ug/L)
13 15 6 7 9 22 20 16 5 11 4 1 18 3 8 2 14 10 19 17 12 21 Md R.A. S.V.
Laboratory


z-Scores: S3 - Anthracene
Target Standard Deviation 0.26 ug/L (Equivalent to 15% CV)
z-Score
13 15 6 7 9 22 20 16 5 11 4 1 18 3 8 2 14 10 19
Laboratory

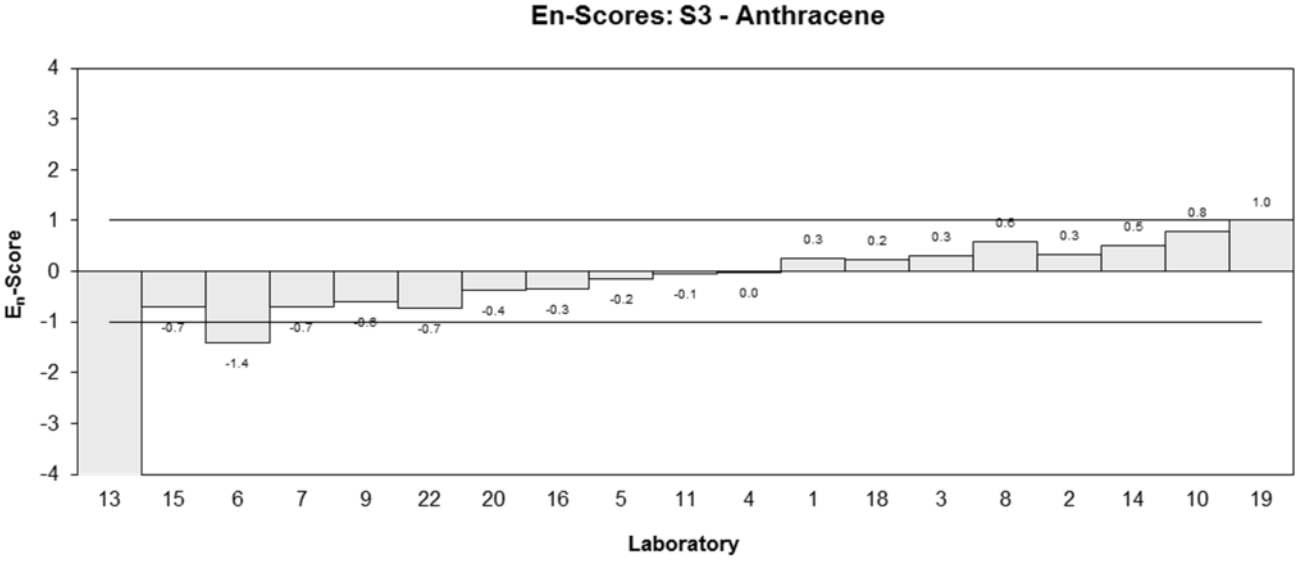

En-Scores: S3 - Anthracene
En-Score
13 15 6 7 9 22 20 16 5 11 4 1 18 3 8 2 14 10 19
Laboratory

Figure 11

Table 17

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.1	0.9	1.50	0.58
2	3.02	1.208	1.29	0.39
3* **	3.7	1.0	2.00	1.00
4	1.99	0.96	-1.42	-0.52
5	2.07	0.64	-1.21	-0.61
6	0.8	0.2	-4.56	-3.87
7	2.0	0.7	-1.40	-0.66
8	2.1	0.42	-1.13	-0.74
9	1.7	0.5	-2.19	-1.30
10	1.7	0.51	-2.19	-1.28
11	2.6	0.82	0.18	0.08
12	1.16	0.35	-3.61	-2.58
13*	0.003605537	0.000721	-6.66	-6.31
14	2.5	0.57	-0.08	-0.04
15	<1	NR		
16* **	3.4	0.7	2.00	1.00
17	2.6	0.5	0.18	0.11
18	3.1	1.0	1.50	0.53
19	8.5	1.7	15.73	3.42
20	2.04	1.27	-1.29	-0.37
21	3	1	1.24	0.44
22	2.49	0.5976	-0.11	-0.06

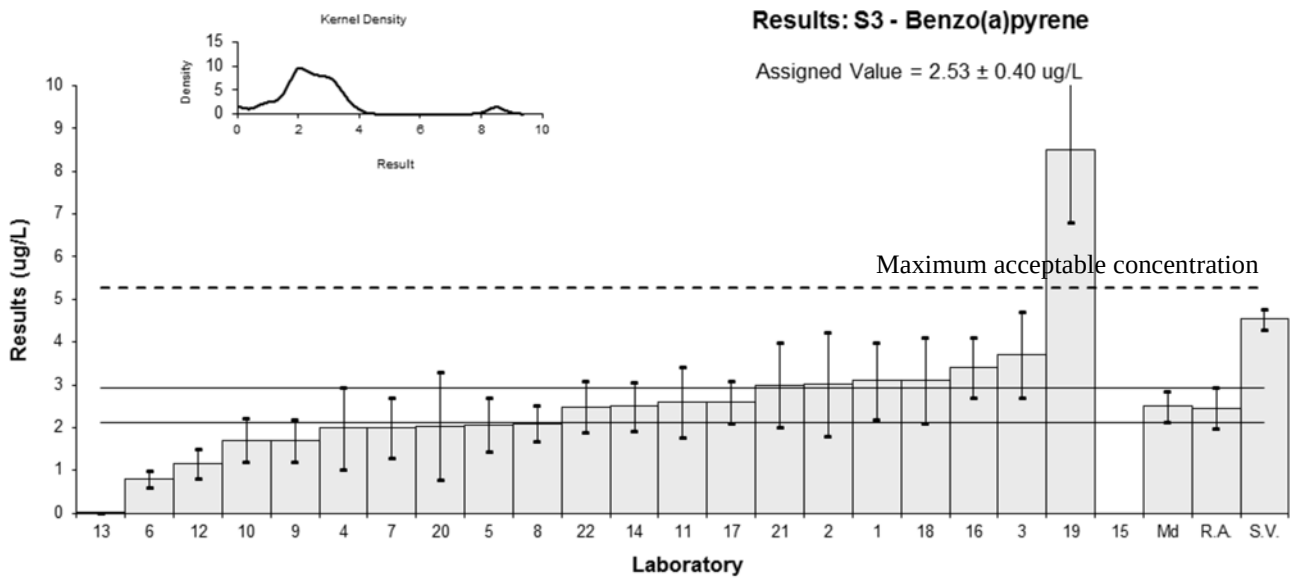
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

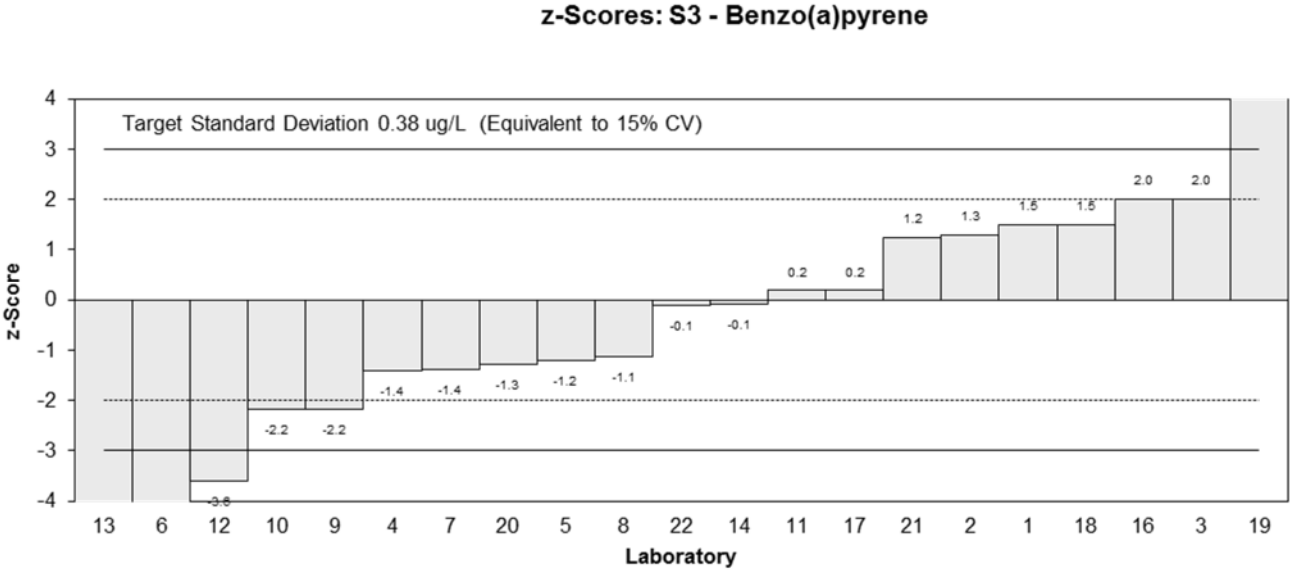
Statistics

Assigned Value**	2.53	0.40
Spike	4.53	0.23
Maximum acceptable conc.***	5.29	
Robust Average	2.46	0.48
Median	2.50	0.36
Mean	2.68	
N	20	
Max.	8.5	
Min.	0.8	
Robust SD	0.86	
Robust CV	35%	

**Robust average excluding laboratories 6, 12 and 19.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S3 - Benzo(a)pyrene
Assigned Value = 2.53 ± 0.40 ug/L
Maximum acceptable concentration
Results (ug/L)
13 6 12 10 9 4 7 20 5 8 22 14 11 17 21 2 1 18 16 3 19 15 Md R.A. S.V.
Laboratory


z-Scores: S3 - Benzo(a)pyrene
Target Standard Deviation 0.38 ug/L (Equivalent to 15% CV)
z-Score
13 6 12 10 9 4 7 20 5 8 22 14 11 17 21 2 1 18 16 3 19
Laboratory

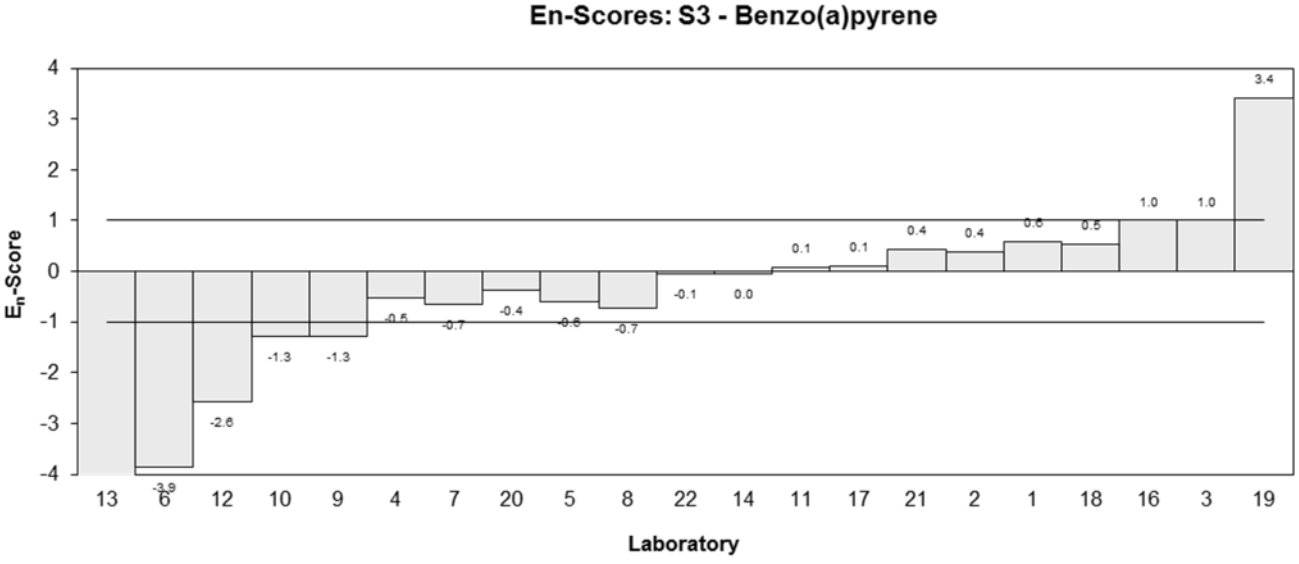

En-Scores: S3 - Benzo(a)pyrene
En-Score
13 6 12 10 9 4 7 20 5 8 22 14 11 17 21 2 1 18 16 3 19
Laboratory

Figure 12

Table 18

Sample Details

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

Participant Results

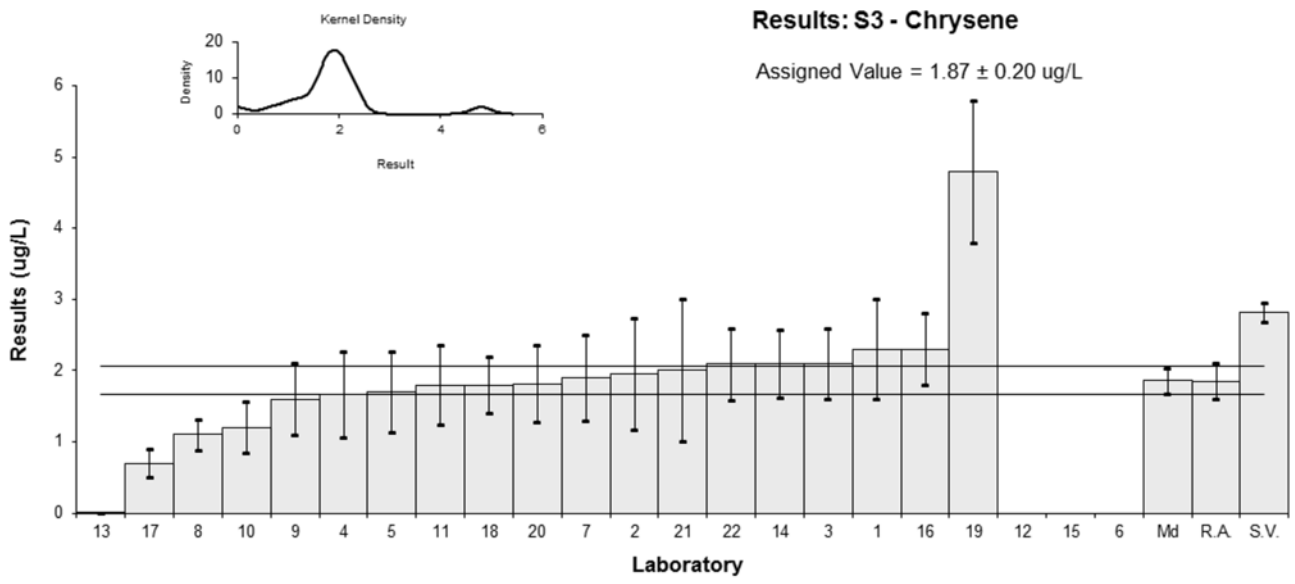
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.3	0.7	1.53	0.59
2	1.95	0.78	0.29	0.10
3	2.1	0.5	0.82	0.43
4	1.67	0.60	-0.71	-0.32
5	1.70	0.56	-0.61	-0.29
6	<1	0.3		
7	1.9	0.6	0.11	0.05
8	1.1	0.22	-2.75	-2.59
9	1.6	0.5	-0.96	-0.50
10	1.2	0.36	-2.39	-1.63
11	1.8	0.56	-0.25	-0.12
12	<1	0.3		
13*	0.001796309	0.000359	-6.66	-9.34
14	2.1	0.48	0.82	0.44
15	<1	NR		
16	2.3	0.5	1.53	0.80
17	0.7	0.2	-4.17	-4.14
18	1.8	0.4	-0.25	-0.16
19	4.8	1.0	10.45	2.87
20	1.81	0.54	-0.21	-0.10
21	2	1	0.46	0.13
22	2.09	0.5016	0.78	0.41

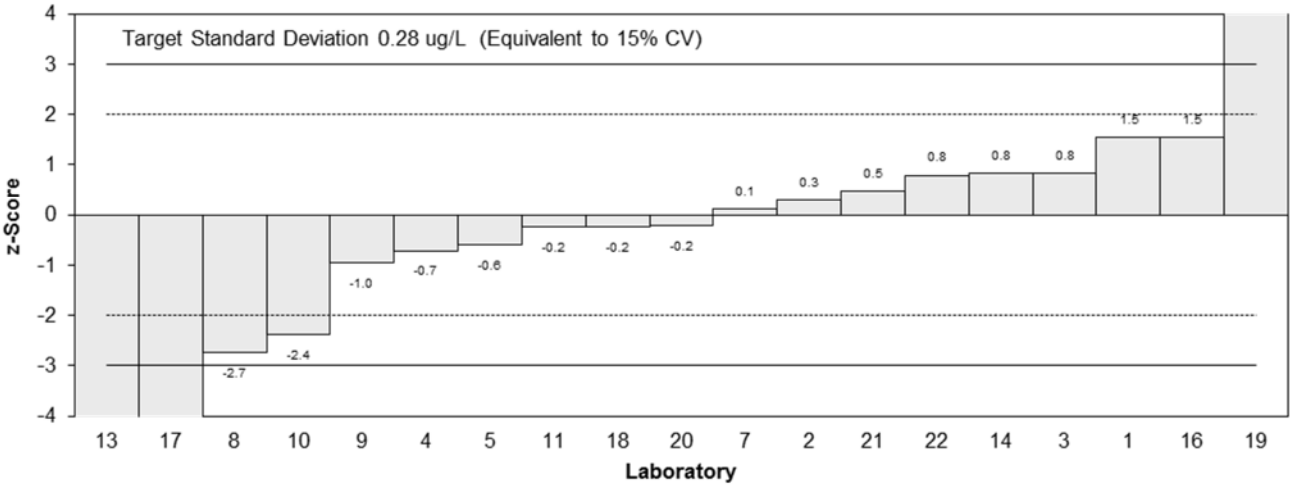
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

Statistics

Assigned Value**	1.87	0.20
Spike	2.82	0.14
Robust Average	1.85	0.25
Median	1.86	0.18
Mean	1.94	
N	18	
Max.	4.8	
Min.	0.7	
Robust SD	0.42	
Robust CV	28%	

**Robust average excluding laboratories 17 and 19.


Kernel Density
Density
Result
Results: S3 - Chrysene
Assigned Value = 1.87 ± 0.20 ug/L
Results (ug/L)
13 17 8 10 9 4 5 11 18 20 7 2 21 22 14 3 1 16 19 12 15 6 Md R.A. S.V.
Laboratory


z-Scores: S3 - Chrysene
Target Standard Deviation 0.28 ug/L (Equivalent to 15% CV)
z-Score
13 17 8 10 9 4 5 11 18 20 7 2 21 22 14 3 1 16 19
Laboratory

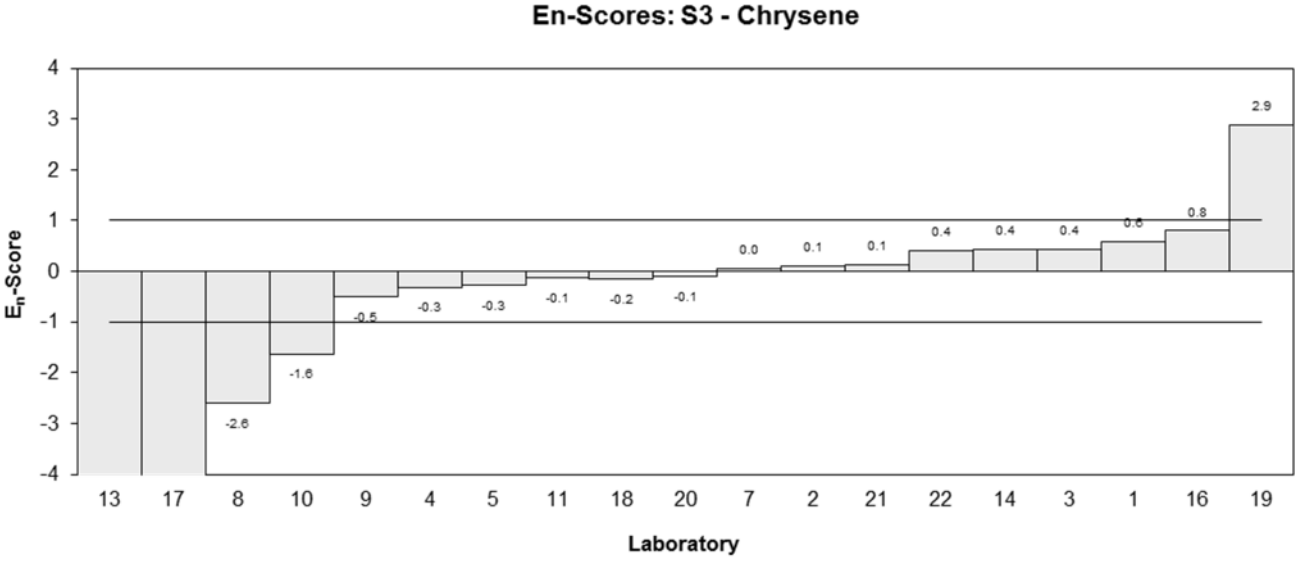

En-Scores: S3 - Chrysene
En-Score
13 17 8 10 9 4 5 11 18 20 7 2 21 22 14 3 1 16 19
Laboratory

Figure 13

Table 19

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.9	1.4	1.22	0.50
2	4.79	1.916	1.05	0.32
3	4.7	1.1	0.90	0.45
4* **	5.6	2.5	2.00	0.57
5* **	5.77	1.04	2.00	1.00
6	3.2	0.8	-1.51	-0.95
7	3.9	1	-0.39	-0.21
8	2.8	0.56	-2.16	-1.66
9	4.0	2	-0.23	-0.07
10	4.2	1.26	0.10	0.04
11	4.4	1.3	0.42	0.18
12	2.02	0.61	-3.41	-2.52
13*	0.006530067	0.001306	-6.66	-7.12
14	4.2	1.2	0.10	0.05
15	4	2	-0.23	-0.07
16	4.0	0.8	-0.23	-0.14
17	1.7	0.3	-3.93	-3.74
18	5.0	0.9	1.38	0.80
19	2.5	0.5	-2.64	-2.14
20	3.96	2.55	-0.29	-0.07
21	5	2	1.38	0.41
22	3.39	0.8136	-1.21	-0.75

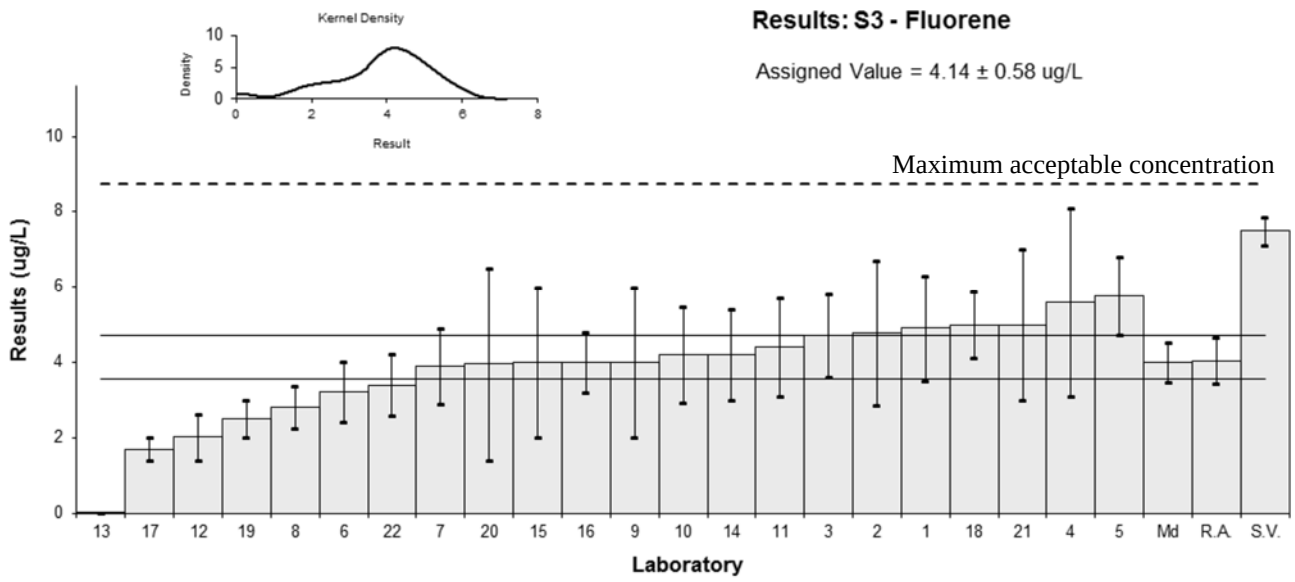
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

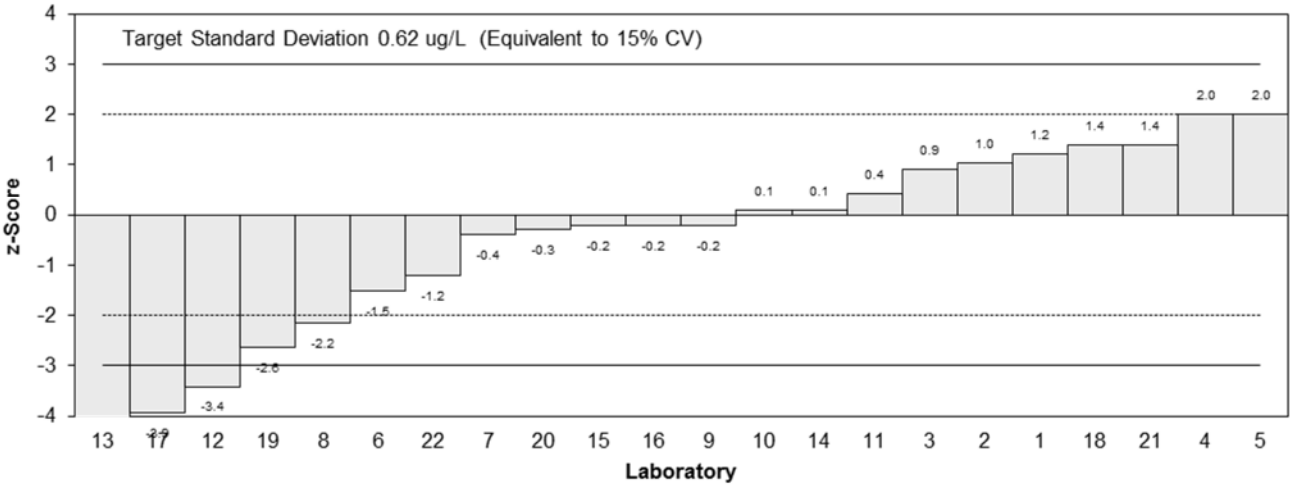
Statistics

Assigned Value**	4.14	0.58
Spike	7.49	0.37
Maximum acceptable conc.***	8.73	
Robust Average	4.04	0.62
Median	4.00	0.53
Mean	4.00	
N	21	
Max.	5.77	
Min.	1.7	
Robust SD	1.10	
Robust CV	27%	

**Robust average excluding laboratory 17.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S3 - Fluorene
Assigned Value = 4.14 ± 0.58 ug/L
Maximum acceptable concentration
Results (ug/L)
13 17 12 19 8 6 22 7 20 15 16 9 10 14 11 3 2 1 18 21 4 5 Md R.A. S.V.
Laboratory


z-Scores: S3 - Fluorene
Target Standard Deviation 0.62 ug/L (Equivalent to 15% CV)
z-Score
13 17 12 19 8 6 22 7 20 15 16 9 10 14 11 3 2 1 18 21 4 5
Laboratory

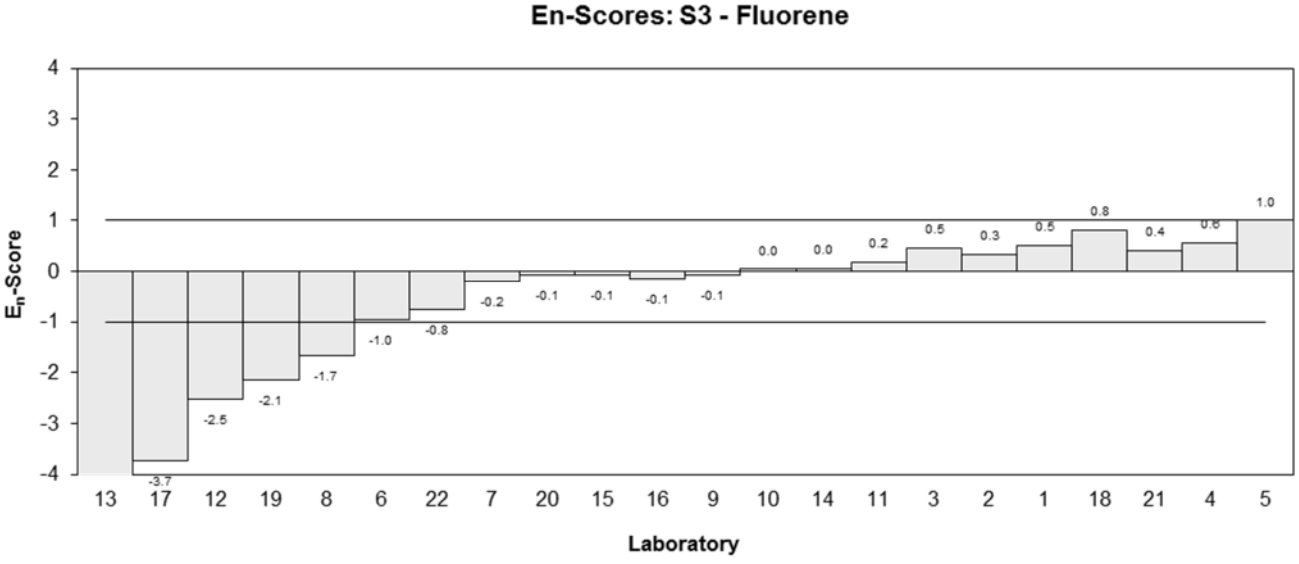

En-Scores: S3 - Fluorene
En-Score
13 17 12 19 8 6 22 7 20 15 16 9 10 14 11 3 2 1 18 21 4 5
Laboratory

Figure 14

Table 20

Sample Details

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

Participant Results

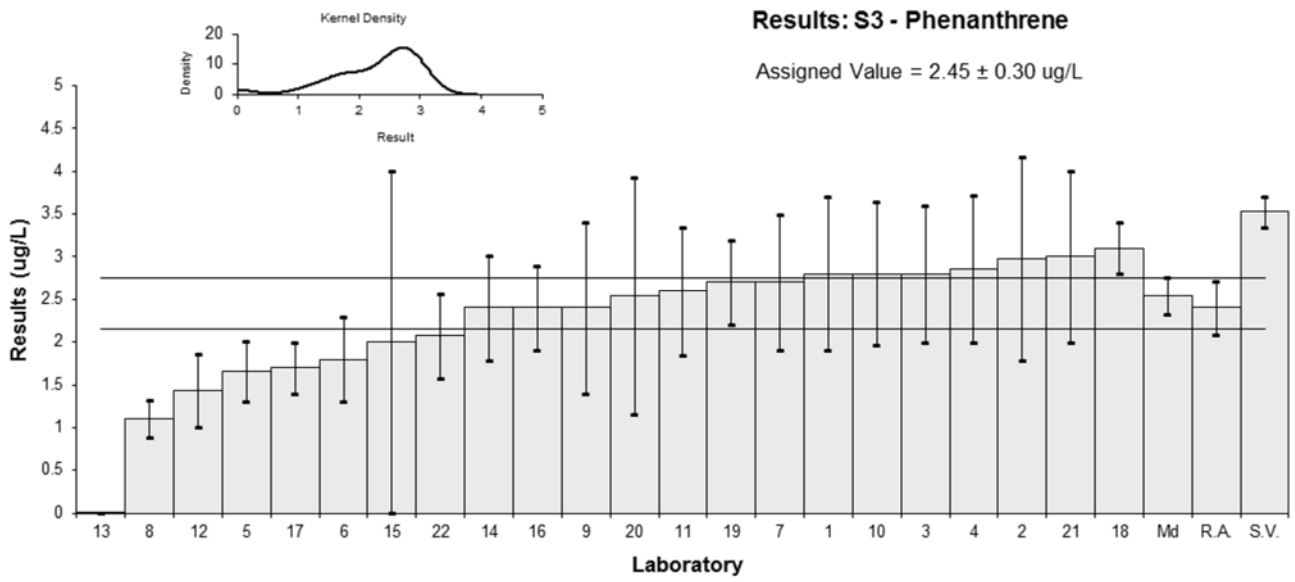
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.8	0.9	0.95	0.37
2	2.98	1.192	1.44	0.43
3	2.8	0.8	0.95	0.41
4	2.86	0.86	1.12	0.45
5	1.66	0.35	-2.15	-1.71
6	1.8	0.5	-1.77	-1.11
7	2.7	0.8	0.68	0.29
8	1.1	0.22	-3.67	-3.63
9	2.4	1	-0.14	-0.05
10	2.8	0.84	0.95	0.39
11	2.6	0.75	0.41	0.19
12	1.43	0.43	-2.78	-1.95
13*	0.003200544	0.00064	-6.66	-8.15
14	2.4	0.61	-0.14	-0.07
15	2	2	-1.22	-0.22
16	2.4	0.5	-0.14	-0.09
17	1.7	0.3	-2.04	-1.77
18	3.1	0.3	1.77	1.53
19	2.7	.5	0.68	0.43
20	2.54	1.39	0.24	0.06
21	3	1	1.50	0.53
22	2.07	0.4968	-1.03	-0.65

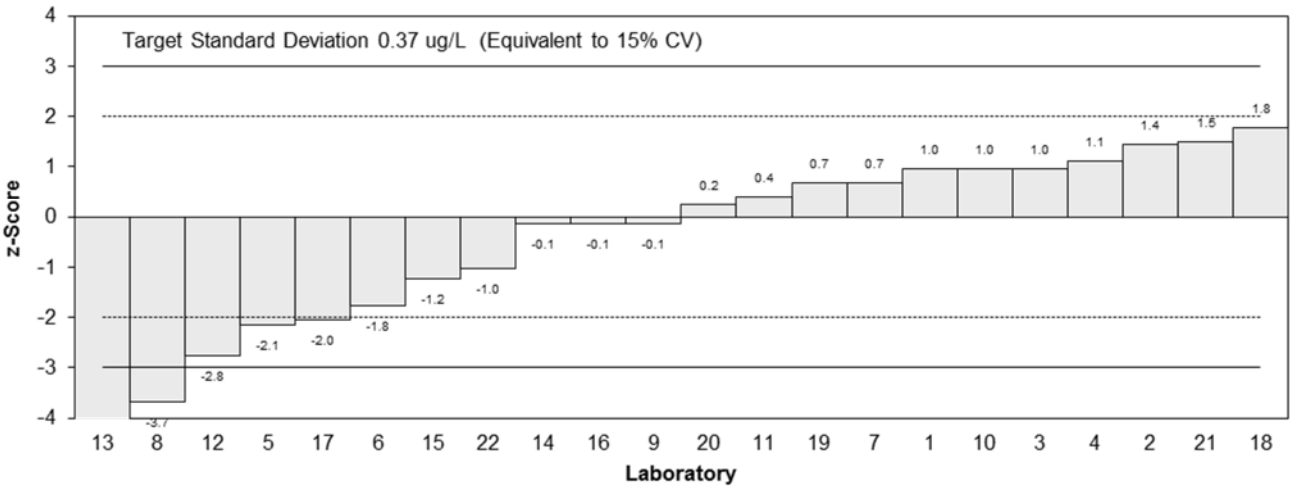
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

Statistics

Assigned Value**	2.45	0.30
Spike	3.53	0.18
Robust Average	2.40	0.32
Median	2.54	0.22
Mean	2.37	
N	21	
Max.	3.1	
Min.	1.1	
Robust SD	0.59	
Robust CV	25%	

**Robust average excluding laboratory 8.


Kernel Density
Density
Result
Results: S3 - Phenanthrene
Assigned Value = 2.45 ± 0.30 ug/L
Results (ug/L)
13 8 12 5 17 6 15 22 14 16 9 20 11 19 7 1 10 3 4 2 21 18 Md R.A. S.V.
Laboratory


z-Scores: S3 - Phenanthrene
Target Standard Deviation 0.37 ug/L (Equivalent to 15% CV)
z-Score
13 8 12 5 17 6 15 22 14 16 9 20 11 19 7 1 10 3 4 2 21 18
Laboratory

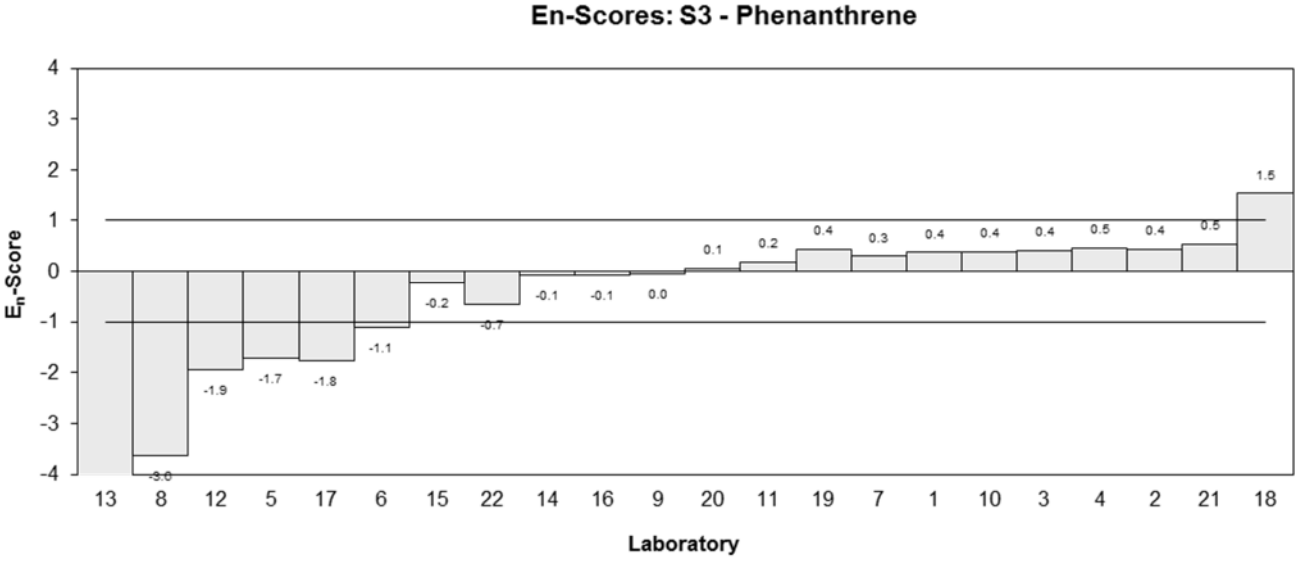

En-Scores: S3 - Phenanthrene
En-Score
13 8 12 5 17 6 15 22 14 16 9 20 11 19 7 1 10 3 4 2 21 18
Laboratory

Figure 15

Table 21

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.8	0.6	0.56	0.23
2	1.75	0.70	0.36	0.13
3	1.9	0.5	0.96	0.46
4	1.53	0.56	-0.52	-0.22
5	1.51	0.29	-0.60	-0.46
6	1.7	0.4	0.16	0.09
7	1.7	0.5	0.16	0.08
8	0.96	0.19	-2.81	-2.89
9	1.6	1	-0.24	-0.06
10	1.6	0.48	-0.24	-0.12
11	1.6	0.51	-0.24	-0.11
12	<1	0.3		
13*	0.00180843	0.000362	-6.66	-11.05
14	2.08	0.69	1.69	0.59
15	2	1	1.37	0.34
16	1.6	0.3	-0.24	-0.18
17	<0.5	0.1		
18	1.9	0.6	0.96	0.39
19***	2.7	.5	2.00	1.00
20	1.36	0.41	-1.20	-0.69
21	<2	NR		
22	1.35	0.324	-1.24	-0.87

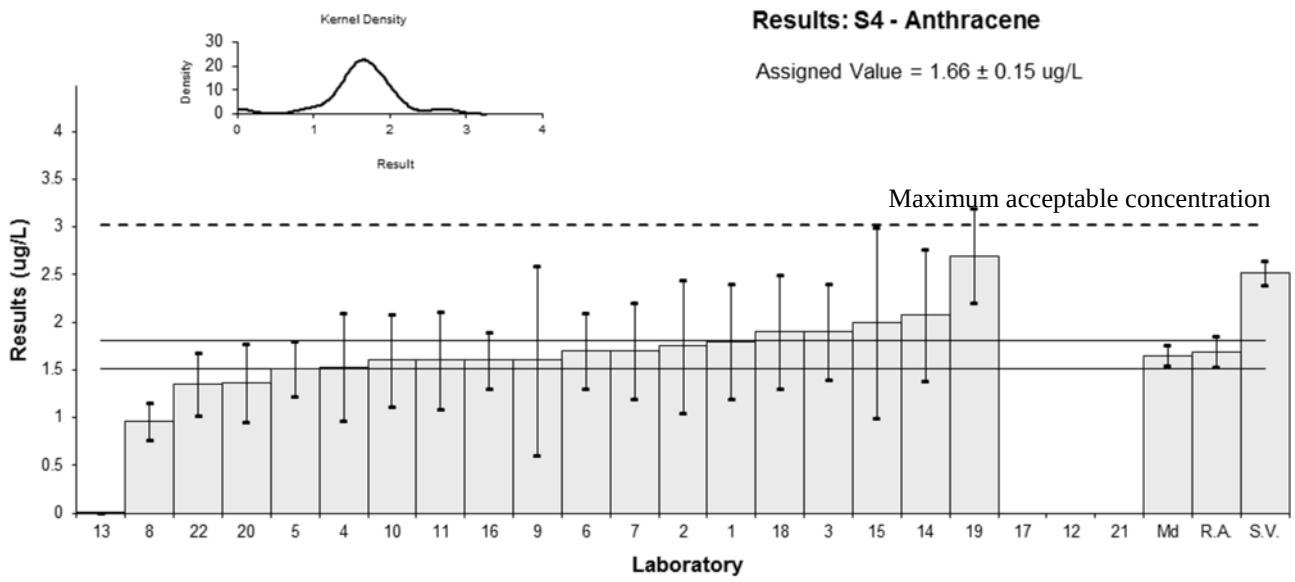
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

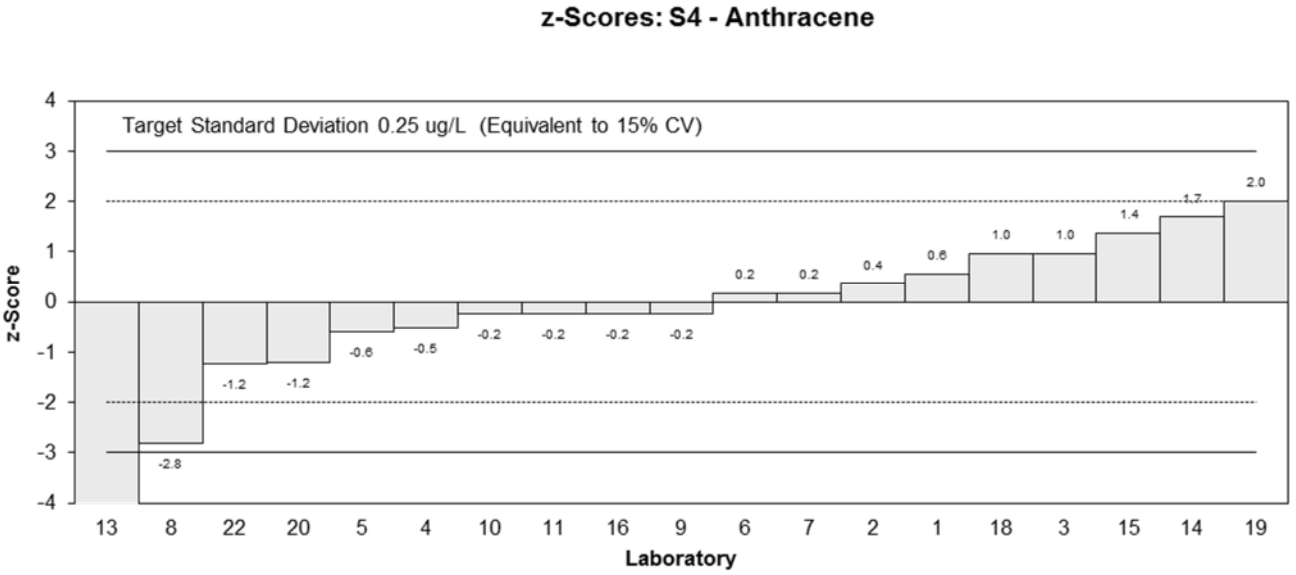
Statistics

Assigned Value**	1.66	0.15
Spike	2.52	0.13
Maximum acceptable conc.***	3.02	
Robust Average	1.69	0.16
Median	1.65	0.11
Mean	1.70	
N	18	
Max.	2.7	
Min.	0.96	
Robust SD	0.28	
Robust CV	17%	

**Robust average excluding laboratory 19.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S4 - Anthracene
Assigned Value = 1.66 ± 0.15 ug/L
Maximum acceptable concentration
Results (ug/L)
Laboratory
13 8 22 20 5 4 10 11 16 9 6 7 2 1 18 3 15 14 19 17 12 21 Md R.A. S.V.


z-Scores: S4 - Anthracene
Target Standard Deviation 0.25 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
13 8 22 20 5 4 10 11 16 9 6 7 2 1 18 3 15 14 19

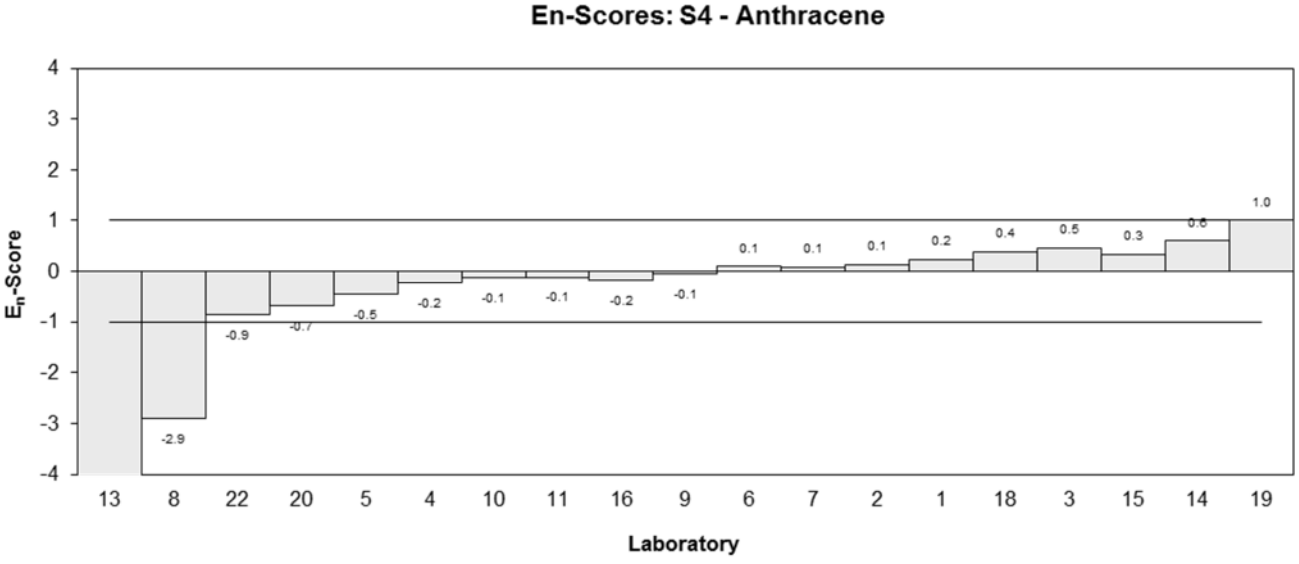

En-Scores: S4 - Anthracene
En-Score
Laboratory
13 8 22 20 5 4 10 11 16 9 6 7 2 1 18 3 15 14 19

Figure 16

Table 22

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.2	0.9	1.44	0.57
2* **	3.62	1.45	2.00	0.66
3* **	3.7	1.0	2.00	0.99
4	2.3	1.2	-0.84	-0.26
5	2.29	0.71	-0.86	-0.41
6	2.2	0.6	-1.09	-0.59
7	2.2	0.7	-1.09	-0.53
8	1.3	0.26	-3.37	-2.69
9	2.1	0.6	-1.34	-0.72
10	2.8	0.86	0.43	0.18
11	2.7	0.85	0.18	0.07
12	1.43	0.43	-3.04	-2.00
13*	0.004170247	0.000834	-6.66	-6.25
14	2.5	0.57	-0.33	-0.18
15	1	1	-4.13	-1.50
16* **	3.5	0.7	2.00	1.00
17	3.1	0.6	1.19	0.64
18	3.2	1.0	1.44	0.53
19	11.5	2.3	22.48	3.79
20	2.2	1.37	-1.09	-0.30
21	3	1	0.94	0.34
22	2.28	0.5472	-0.89	-0.51

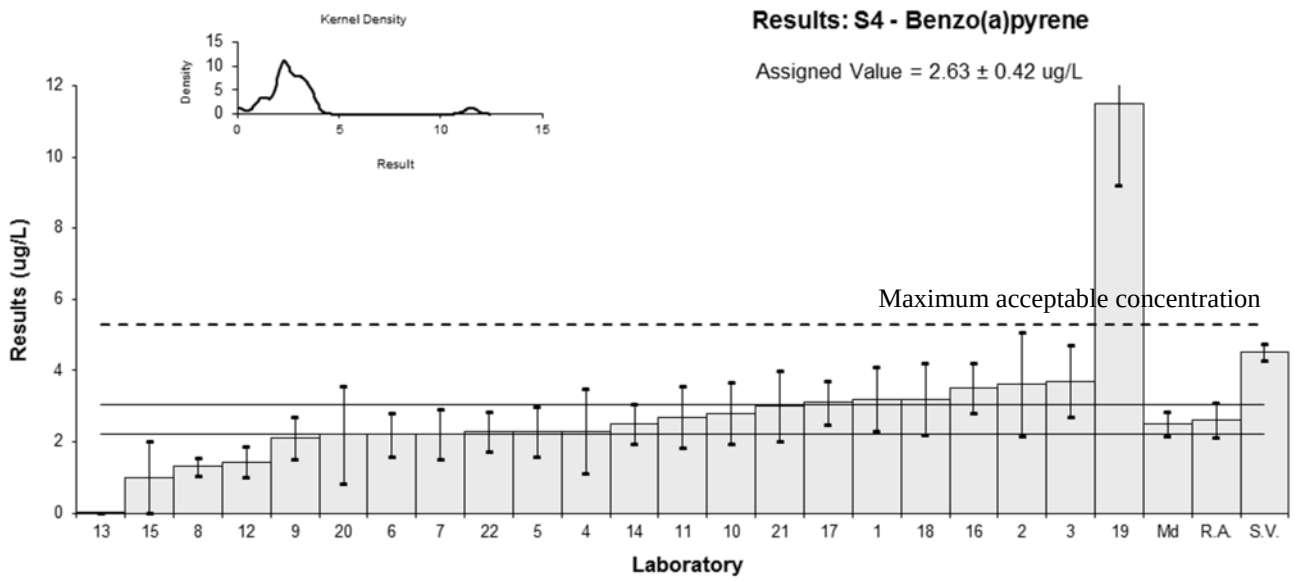
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

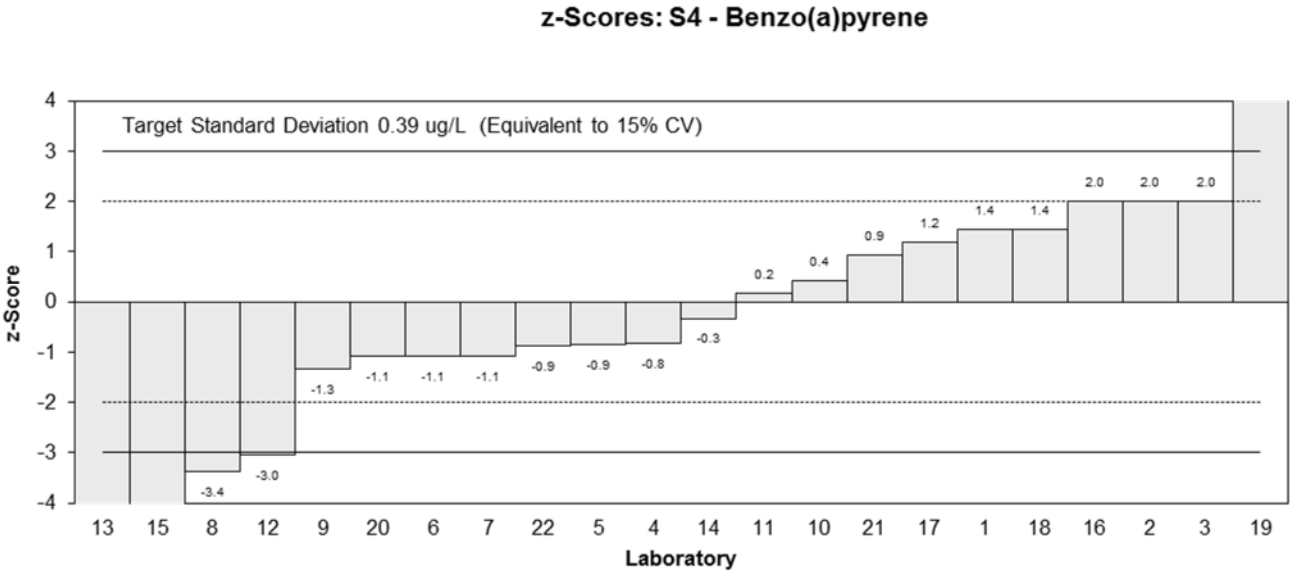
Statistics

Assigned Value**	2.63	0.42
Spike	4.51	0.23
Maximum acceptable conc.***	5.30	
Robust Average	2.61	0.47
Median	2.50	0.34
Mean	2.96	
N	21	
Max.	11.5	
Min.	1	
Robust SD	0.87	
Robust CV	33%	

**Robust average excluding laboratories 15 and 19.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S4 - Benzo(a)pyrene
Assigned Value = 2.63 ± 0.42 ug/L
Maximum acceptable concentration
Results (ug/L)
13 15 8 12 9 20 6 7 22 5 4 14 11 10 21 17 1 18 16 2 3 19 Md R.A. S.V.
Laboratory


z-Scores: S4 - Benzo(a)pyrene
Target Standard Deviation 0.39 ug/L (Equivalent to 15% CV)
z-Score
13 15 8 12 9 20 6 7 22 5 4 14 11 10 21 17 1 18 16 2 3 19
Laboratory

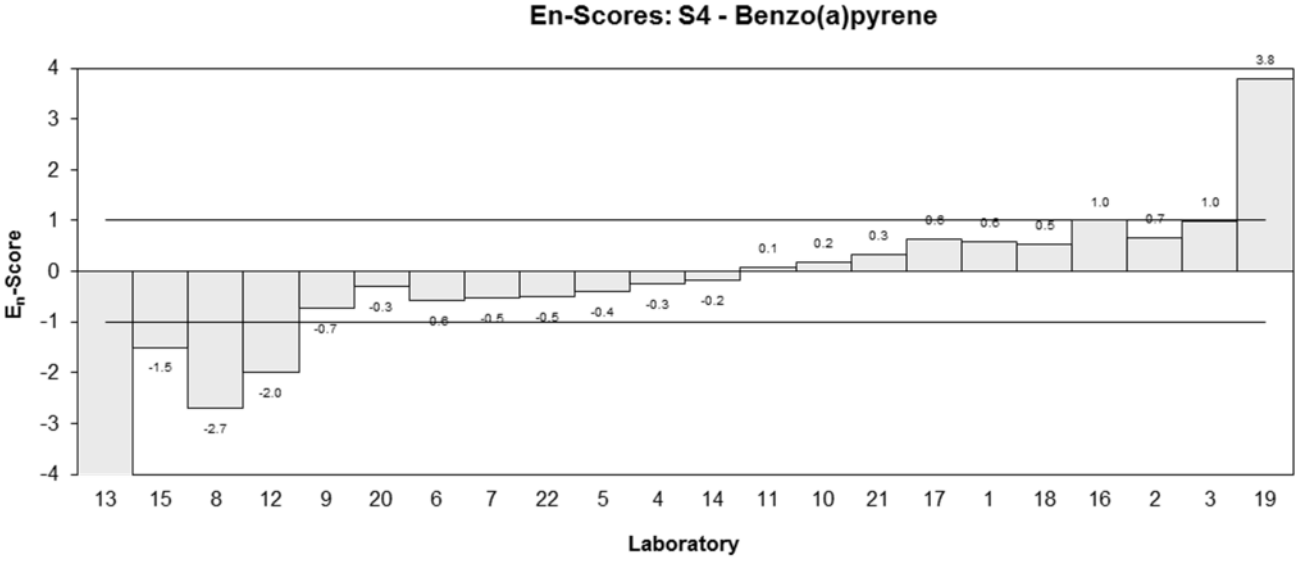

En-Scores: S4 - Benzo(a)pyrene
En-Score
13 15 8 12 9 20 6 7 22 5 4 14 11 10 21 17 1 18 16 2 3 19
Laboratory

Figure 17

Table 23

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.5	0.8	1.35	0.50
2	2.46	0.98	1.22	0.38
3	2.1	0.5	0.06	0.04
4	1.80	0.65	-0.90	-0.40
5	1.66	0.55	-1.35	-0.70
6	1.6	0.4	-1.54	-1.03
7	2.0	0.6	-0.26	-0.12
8	0.62	0.12	-4.68	-5.44
9	1.8	0.8	-0.90	-0.34
10	2.0	0.6	-0.26	-0.12
11	1.9	0.59	-0.58	-0.28
12	<1	0.3		
13*	0.00323938	0.000648	-6.66	-8.65
14	2.01	0.46	-0.22	-0.13
15***	3	2	2.00	0.46
16	2.5	0.5	1.35	0.76
17	0.6	0.1	-4.74	-5.69
18	2.0	0.5	-0.26	-0.14
19	7.1	1.4	16.09	3.53
20	1.78	0.53	-0.96	-0.52
21***	3	1	2.00	0.89
22	1.94	0.4656	-0.45	-0.27

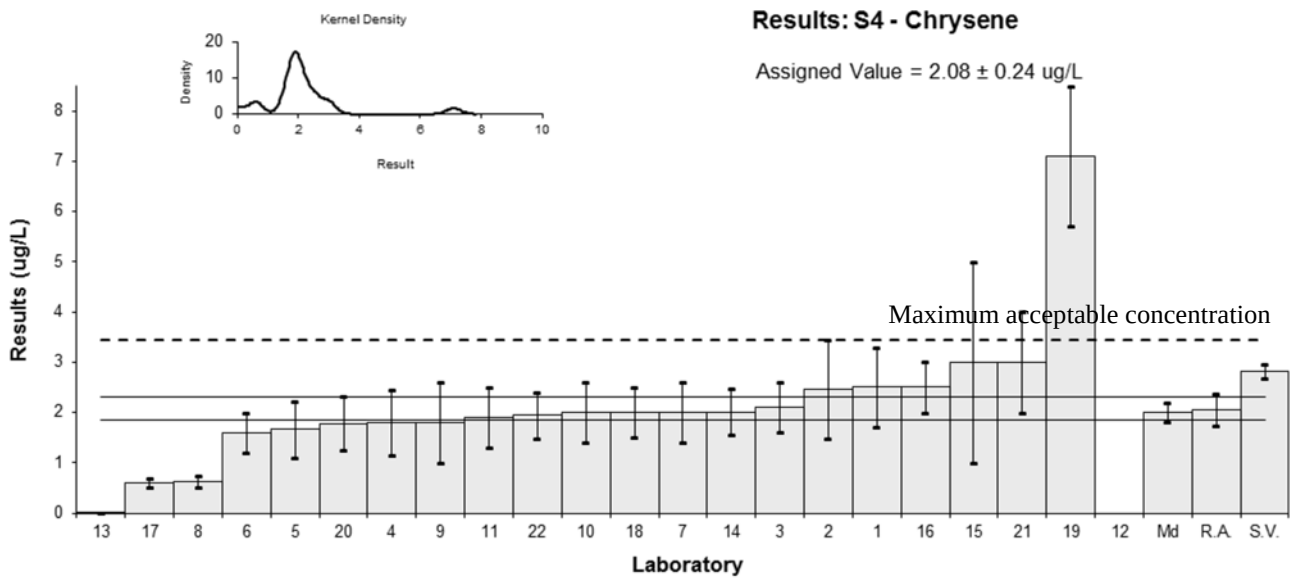
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

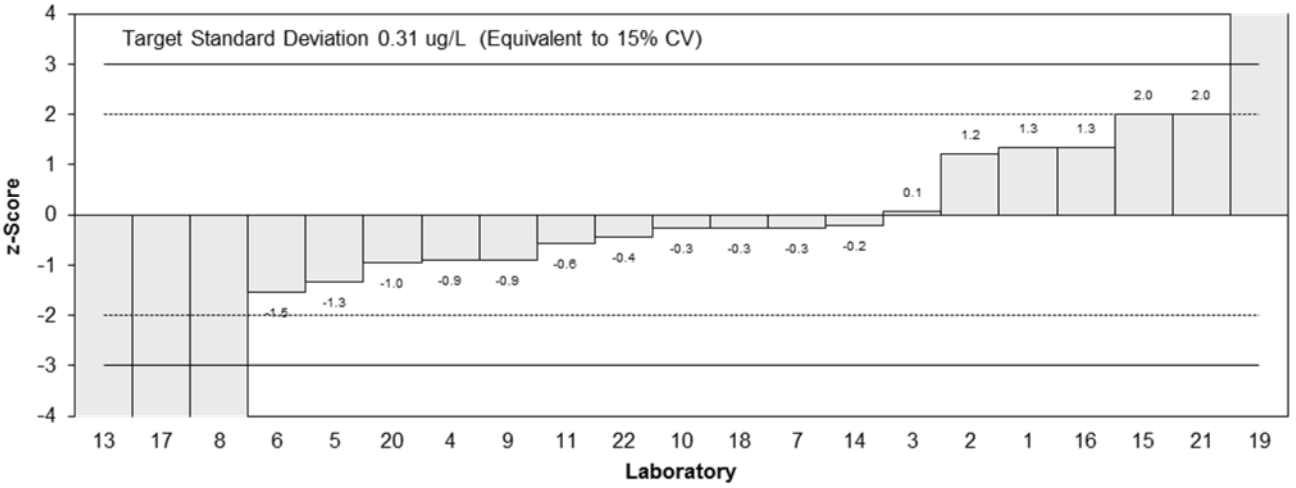
Statistics

Assigned Value**	2.08	0.24
Spike	2.82	0.14
Maximum acceptable conc.***	3.44	
Robust Average	2.06	0.32
Median	2.00	0.19
Mean	2.22	
N	20	
Max.	7.1	
Min.	0.6	
Robust SD	0.58	
Robust CV	28%	

**Robust average excluding laboratories 8, 17 and 19.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S4 - Chrysene
Assigned Value = 2.08 ± 0.24 ug/L
Maximum acceptable concentration
Results (ug/L)
Laboratory
13 17 8 6 5 20 4 9 11 22 10 18 7 14 3 2 1 16 15 21 19 12 Md R.A. S.V.


z-Scores: S4 - Chrysene
Target Standard Deviation 0.31 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
13 17 8 6 5 20 4 9 11 22 10 18 7 14 3 2 1 16 15 21 19

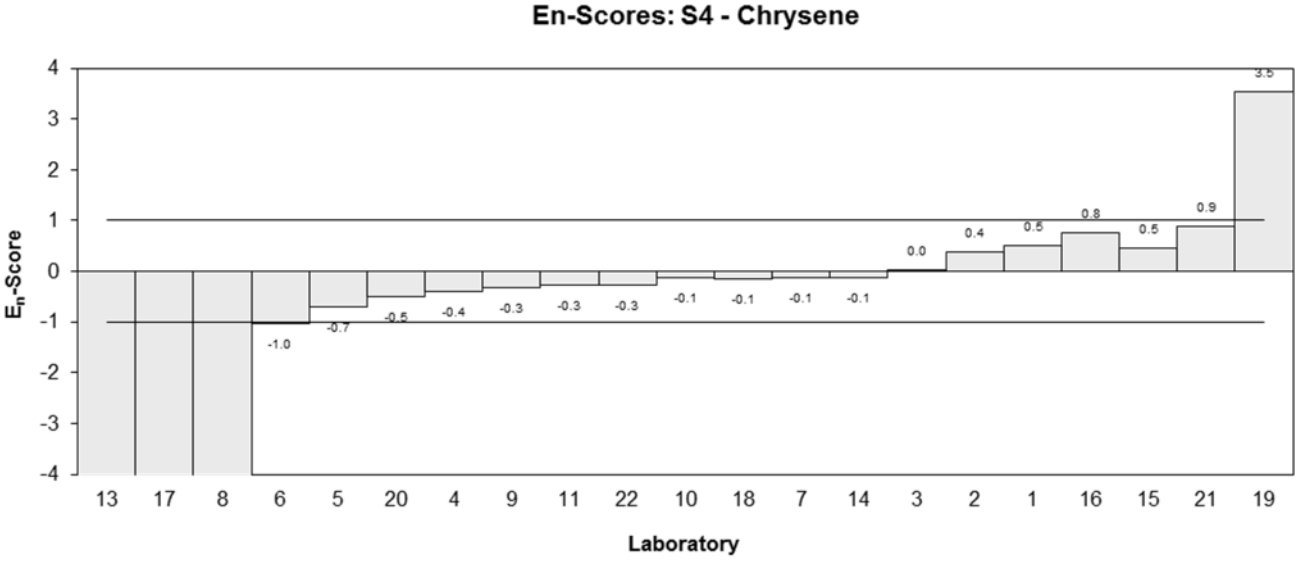

En-Scores: S4 - Chrysene
En-Score
Laboratory
13 17 8 6 5 20 4 9 11 22 10 18 7 14 3 2 1 16 15 21 19

Figure 18

Table 24

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.8	1.4	0.61	0.28
2	5.03	2.01	0.95	0.31
3	4.6	1.1	0.30	0.17
4	3.9	1.1	-0.76	-0.44
5	4.04	0.85	-0.55	-0.39
6	4.1	1	-0.45	-0.28
7	5.0	2	0.91	0.30
8	2.0	0.4	-3.64	-4.63
9	4.7	2	0.45	0.15
10* **	6.2	1.86	2.00	0.95
11	4.3	1.25	-0.15	-0.08
12	2.67	0.8	-2.62	-2.00
13*	0.005201104	0.00104	-6.66	-13.31
14	4.51	0.90	0.17	0.11
15	4	2	-0.61	-0.20
16	4.6	0.9	0.30	0.21
17	3.6	0.7	-1.21	-1.03
18	4.7	1.0	0.45	0.28
19	13.2	2.6	13.33	3.36
20	3.99	1.2	-0.62	-0.33
21	5	2	0.91	0.30
22	4	0.96	-0.61	-0.39

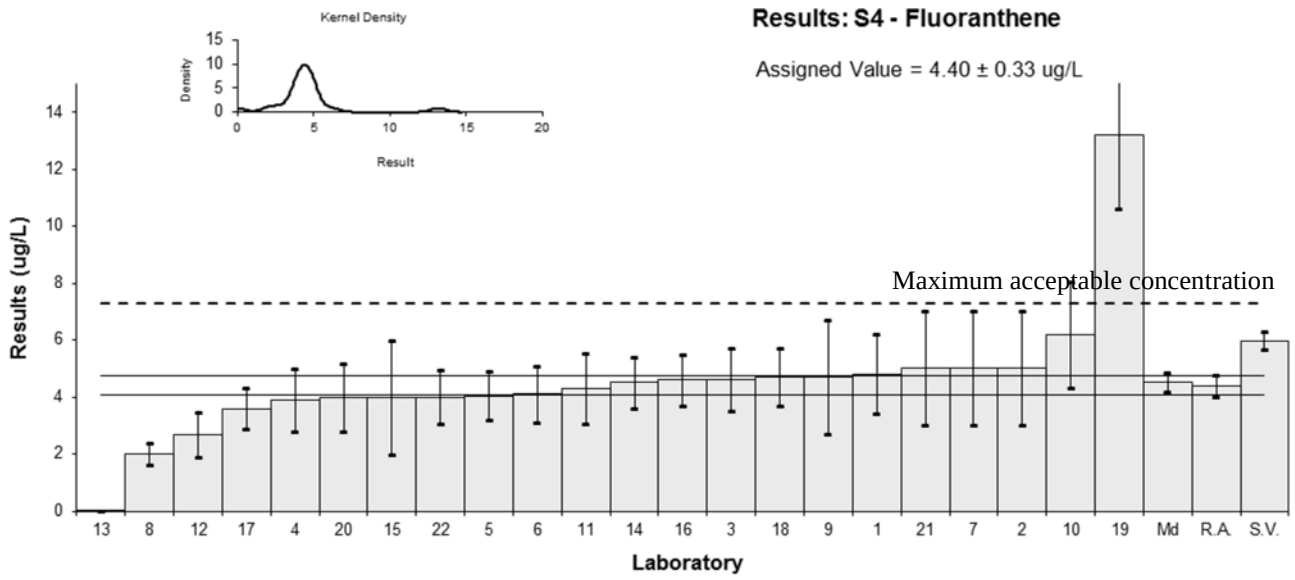
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

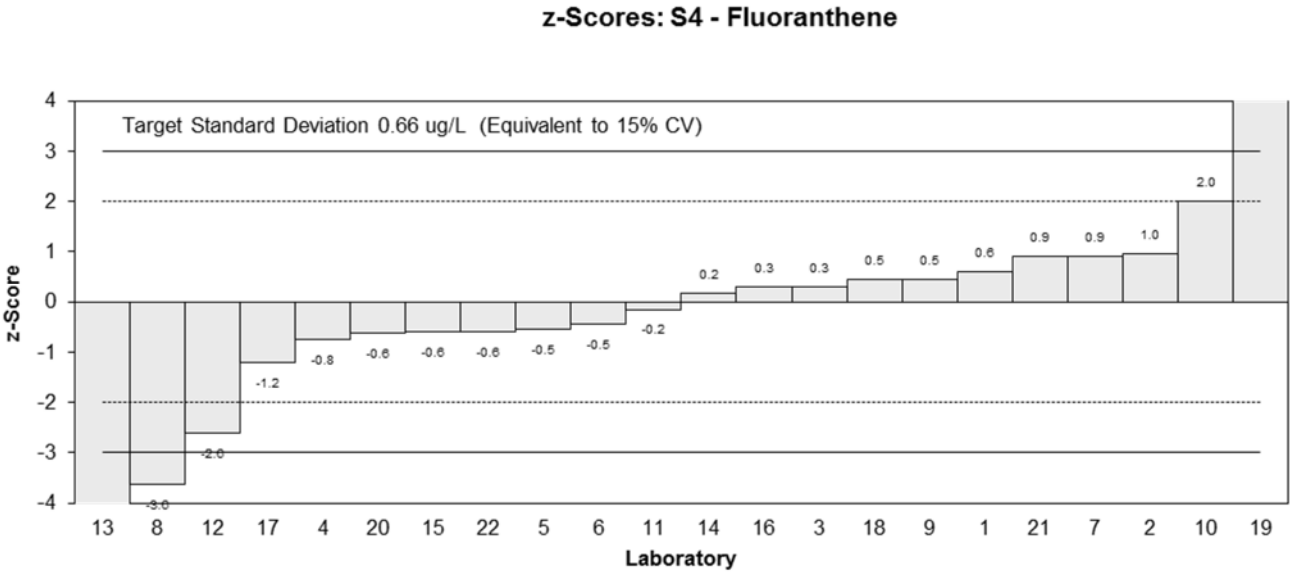
Statistics

Assigned Value**	4.40	0.33
Spike	5.98	0.30
Maximum acceptable conc.***	7.30	
Robust Average	4.40	0.38
Median	4.51	0.33
Mean	4.71	
N	21	
Max.	13.2	
Min.	2	
Robust SD	0.69	
Robust CV	16%	

**Robust average excluding laboratories 8 and 19.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S4 - Fluoranthene
Assigned Value = 4.40 ± 0.33 ug/L
Maximum acceptable concentration
Results (ug/L)
Laboratory
13 8 12 17 4 20 15 22 5 6 11 14 16 3 18 9 1 21 7 2 10 19 Md R.A. S.V.


z-Scores: S4 - Fluoranthene
Target Standard Deviation 0.66 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
13 8 12 17 4 20 15 22 5 6 11 14 16 3 18 9 1 21 7 2 10 19

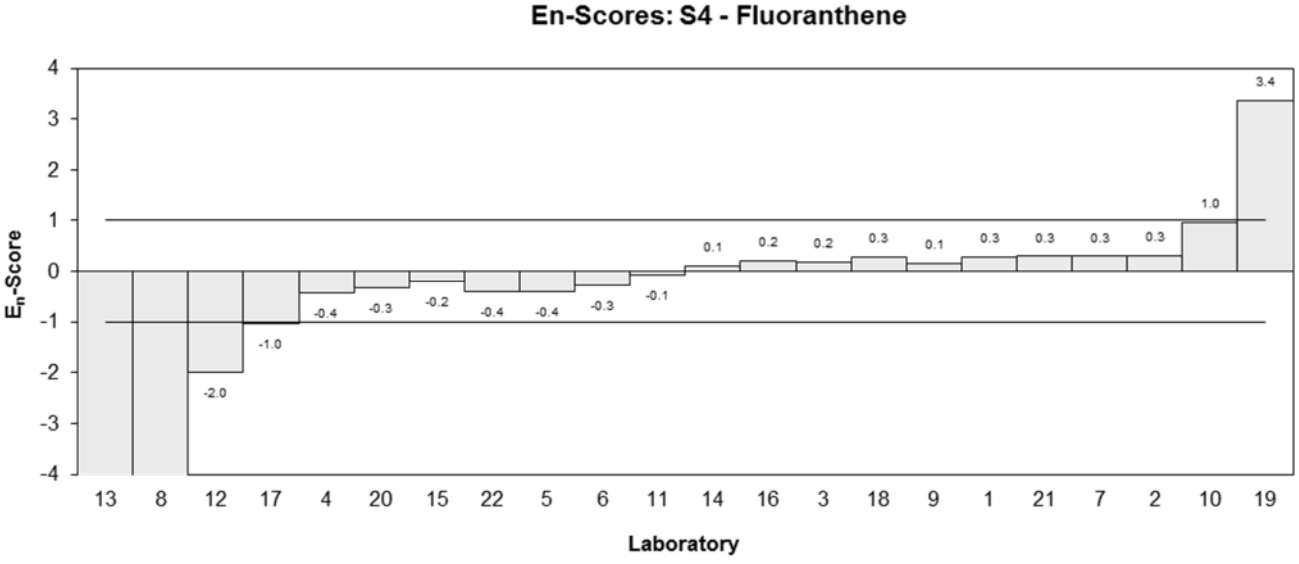

En-Scores: S4 - Fluoranthene
En-Score
Laboratory
13 8 12 17 4 20 15 22 5 6 11 14 16 3 18 9 1 21 7 2 10 19

Figure 19

Table 25

Sample Details

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

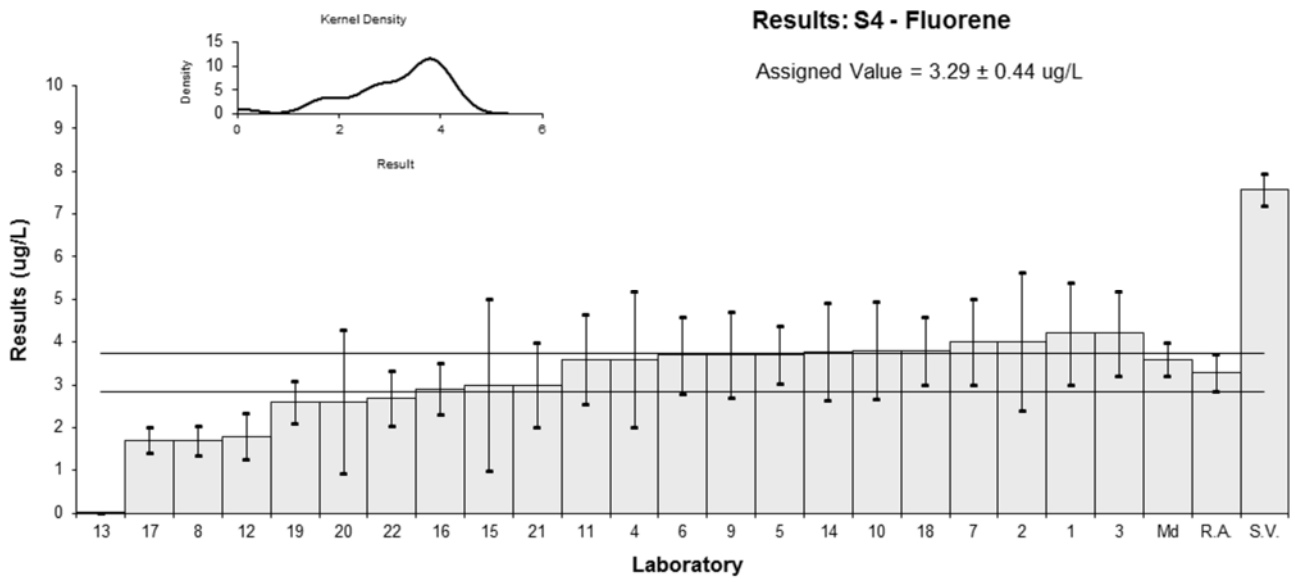
Participant Results

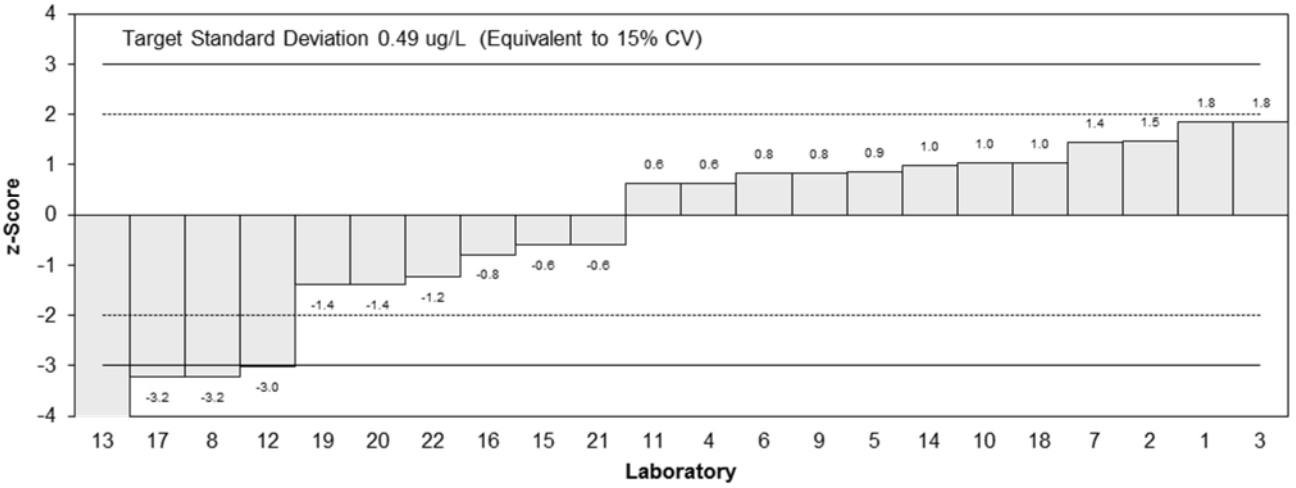
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.2	1.2	1.84	0.71
2	4.02	1.61	1.48	0.44
3	4.2	1.0	1.84	0.83
4	3.6	1.6	0.63	0.19
5	3.71	0.67	0.85	0.52
6	3.7	0.9	0.83	0.41
7	4.0	1	1.44	0.65
8	1.7	0.34	-3.22	-2.86
9	3.7	1	0.83	0.38
10	3.8	1.14	1.03	0.42
11	3.6	1.06	0.63	0.27
12	1.80	0.54	-3.02	-2.14
13*	0.003909338	0.000782	-6.66	-7.46
14	3.78	1.14	0.99	0.40
15	3	2	-0.59	-0.14
16	2.9	0.6	-0.79	-0.52
17	1.7	0.3	-3.22	-2.99
18	3.8	0.8	1.03	0.56
19	2.6	0.5	-1.40	-1.04
20	2.61	1.68	-1.38	-0.39
21	3	1	-0.59	-0.27
22	2.68	0.6432	-1.24	-0.78

* Laboratory 13 result was omitted from the statistical calculations (wrong units).

Statistics

Assigned Value	3.29	0.44
Spike	7.58	0.38
Robust Average	3.29	0.44
Median	3.60	0.40
Mean	3.24	
N	21	
Max.	4.2	
Min.	1.7	
Robust SD	0.81	
Robust CV	25%	


Kernel Density
Density
Result
Results: S4 - Fluorene
Assigned Value = 3.29 ± 0.44 ug/L
Results (ug/L)
13 17 8 12 19 20 22 16 15 21 11 4 6 9 5 14 10 18 7 2 1 3 Md R.A. S.V.
Laboratory


z-Scores: S4 - Fluorene
Target Standard Deviation 0.49 ug/L (Equivalent to 15% CV)
z-Score
13 17 8 12 19 20 22 16 15 21 11 4 6 9 5 14 10 18 7 2 1 3
Laboratory

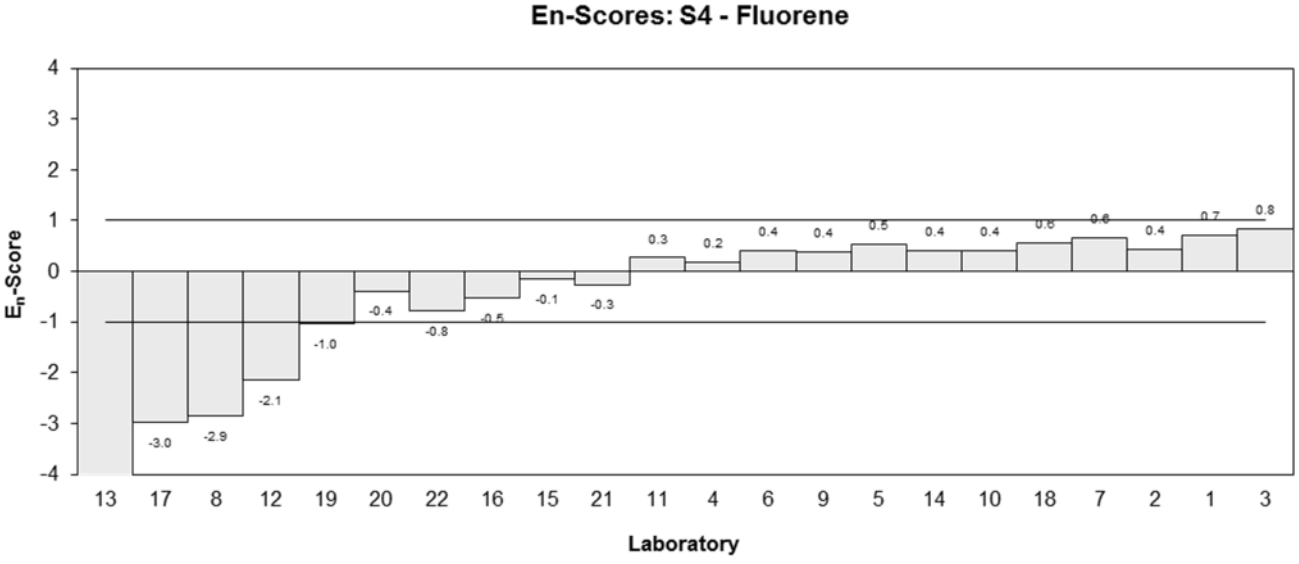

En-Scores: S4 - Fluorene
En-Score
13 17 8 12 19 20 22 16 15 21 11 4 6 9 5 14 10 18 7 2 1 3
Laboratory

Figure 20

Table 26

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.4	0.7	0.81	0.35
2	2.36	0.95	0.69	0.22
3	2.4	0.7	0.81	0.35
4	2.20	0.66	0.19	0.09
5	1.56	0.33	-1.81	-1.42
6	2.2	0.6	0.19	0.09
7	2.6	0.8	1.43	0.55
8	0.65	0.13	-4.64	-5.46
9	2.4	1	0.81	0.25
10	2.1	0.63	-0.12	-0.06
11	2.2	0.63	0.19	0.09
12	1.27	0.38	-2.71	-1.94
13*	0.002636924	0.000527	-6.66	-8.90
14	2.19	0.55	0.16	0.08
15	2	1	-0.44	-0.14
16	2.0	0.4	-0.44	-0.30
17	1.6	0.3	-1.68	-1.41
18	2.6	0.6	1.43	0.71
19***	2.9	.6	2.00	1.00
20	1.84	1.00	-0.93	-0.29
21	<2	NR		
22	1.74	0.4176	-1.25	-0.83

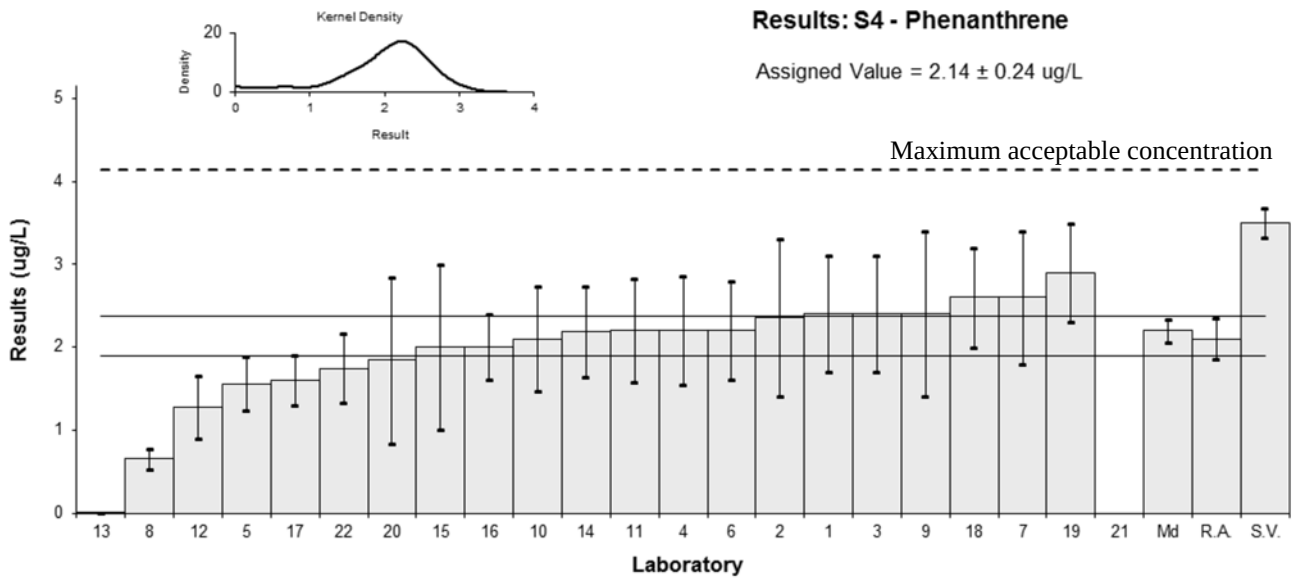
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

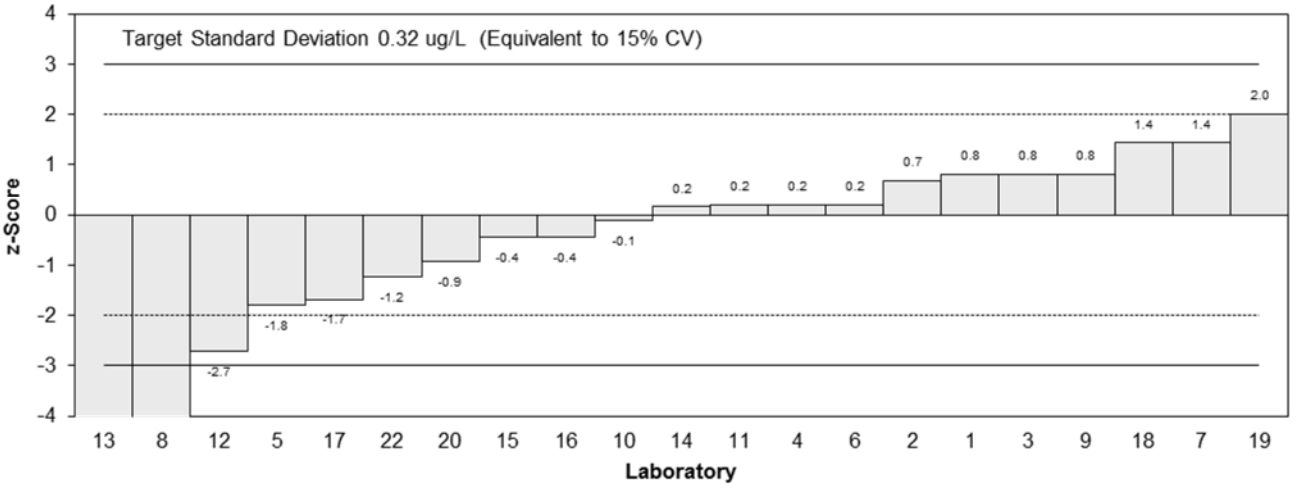
Statistics

Assigned Value	2.14	0.24
Spike	3.50	0.18
Maximum acceptable conc.***	4.14	
Robust Average	2.10	0.25
Median	2.20	0.14
Mean	2.06	
N	20	
Max.	2.9	
Min.	0.65	
Robust SD	0.45	
Robust CV	21%	

**Robust average excluding laboratory 8.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S4 - Phenanthrene
Assigned Value = 2.14 ± 0.24 ug/L
Maximum acceptable concentration
Results (ug/L)
Laboratory
13 8 12 5 17 22 20 15 16 10 14 11 4 6 2 1 3 9 18 7 19 21 Md R.A. S.V.


z-Scores: S4 - Phenanthrene
Target Standard Deviation 0.32 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
13 8 12 5 17 22 20 15 16 10 14 11 4 6 2 1 3 9 18 7 19

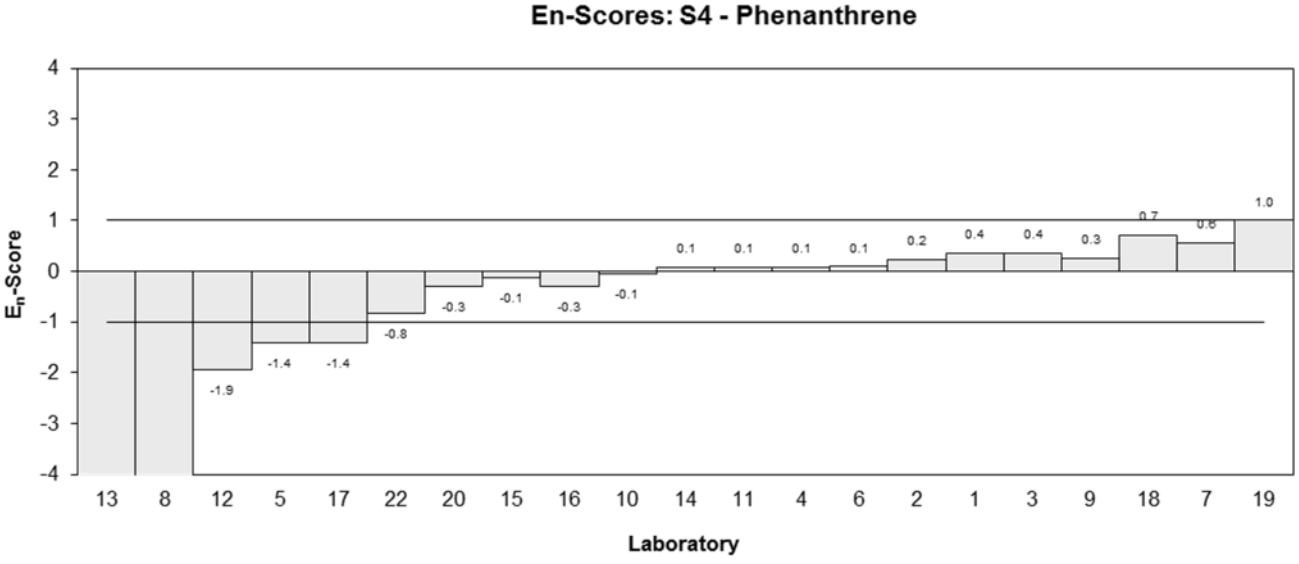

En-Scores: S4 - Phenanthrene
En-Score
Laboratory
13 8 12 5 17 22 20 15 16 10 14 11 4 6 2 1 3 9 18 7 19

Figure 21

Table 27

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.0	0.9	0.69	0.30
2	2.99	1.20	0.66	0.22
3	3.2	0.8	1.18	0.57
4	2.42	0.97	-0.74	-0.30
5	2.09	0.44	-1.54	-1.23
6	2.6	0.8	-0.29	-0.14
7	3.0	1	0.69	0.27
8	1.4	0.28	-3.24	-3.45
9	2.9	1	0.44	0.17
10* **	3.7	1	2.00	0.95
11	2.7	0.78	-0.05	-0.02
12	1.73	0.52	-2.43	-1.70
13*	0.003211909	0.000642	-6.66	-10.44
14	2.89	0.635	0.42	0.25
15	3	2	0.69	0.14
16	2.9	0.6	0.44	0.28
17	1.3	0.3	-3.48	-3.58
18	3.0	0.6	0.69	0.43
19	8.3	1.7	13.68	3.24
20	2.62	1.41	-0.25	-0.07
21	3	1	0.69	0.27
22	2.7	0.648	-0.05	-0.03

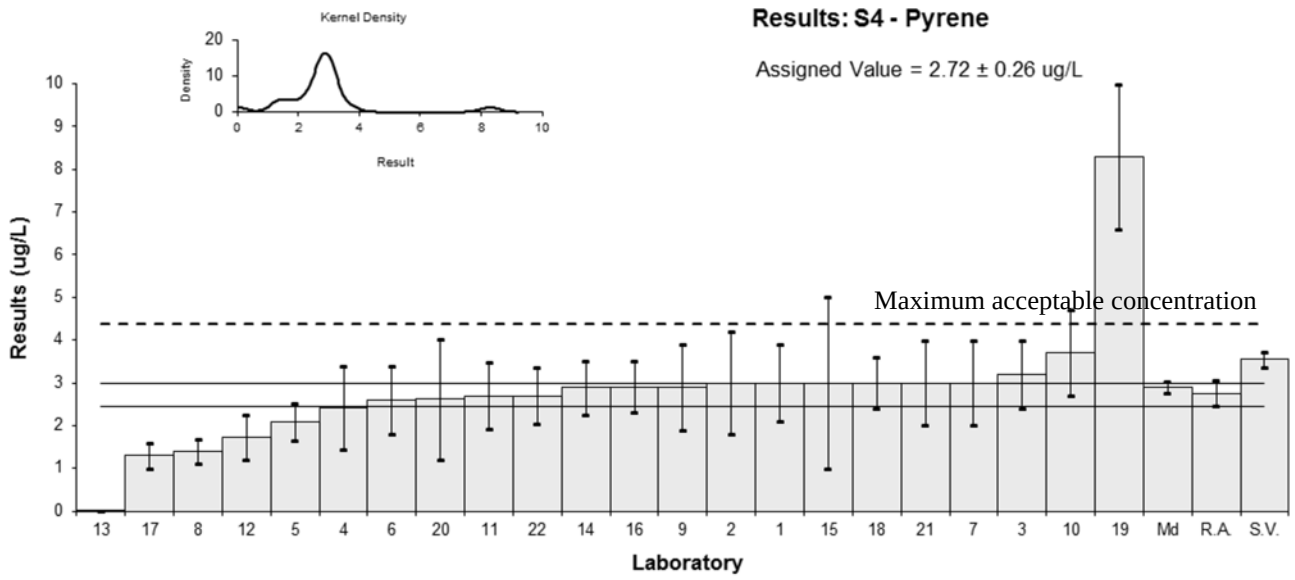
* Laboratory 13 result was omitted from the statistical calculations (wrong units).

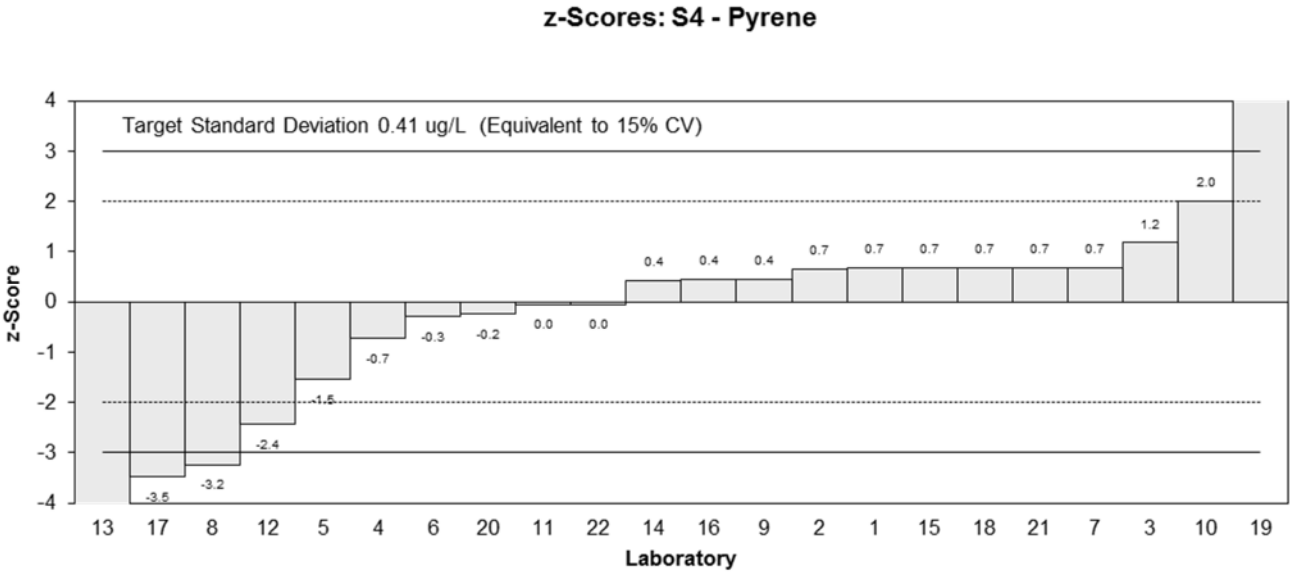
Statistics

Assigned Value**	2.72	0.26
Spike	3.55	0.18
Maximum acceptable conc.***	4.37	
Robust Average	2.76	0.29
Median	2.90	0.14
Mean	2.93	
N	21	
Max.	8.3	
Min.	1.3	
Robust SD	0.53	
Robust CV	19%	

**Robust average excluding laboratory 19.

***z-scores adjusted to 2 (see Section 6.3)


Kernel Density
Density
Result
Results: S4 - Pyrene
Assigned Value = 2.72 ± 0.26 ug/L
Maximum acceptable concentration
Results (ug/L)
Laboratory
13 17 8 12 5 4 6 20 11 22 14 16 9 2 1 15 18 21 7 3 10 19 Md R.A. S.V.


z-Scores: S4 - Pyrene
Target Standard Deviation 0.41 ug/L (Equivalent to 15% CV)
z-Score
Laboratory
13 17 8 12 5 4 6 20 11 22 14 16 9 2 1 15 18 21 7 3 10 19

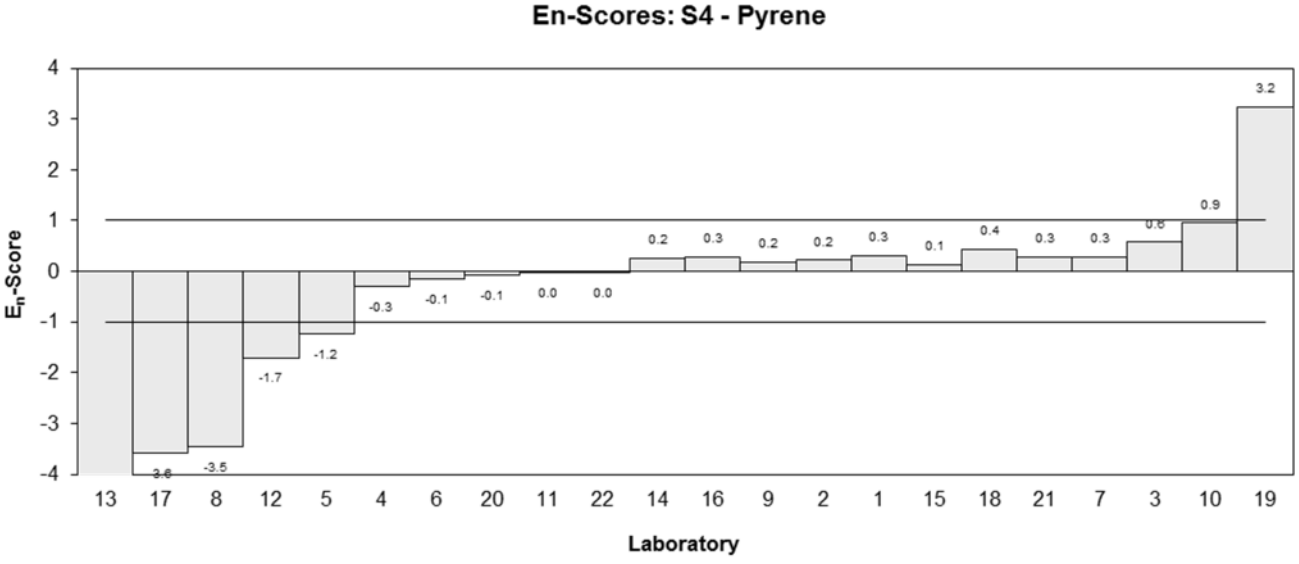
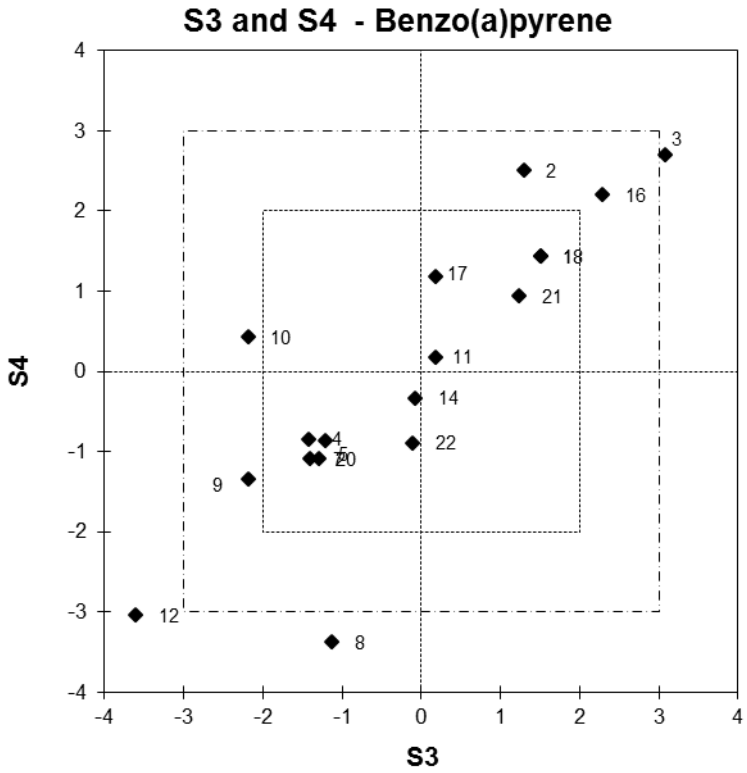
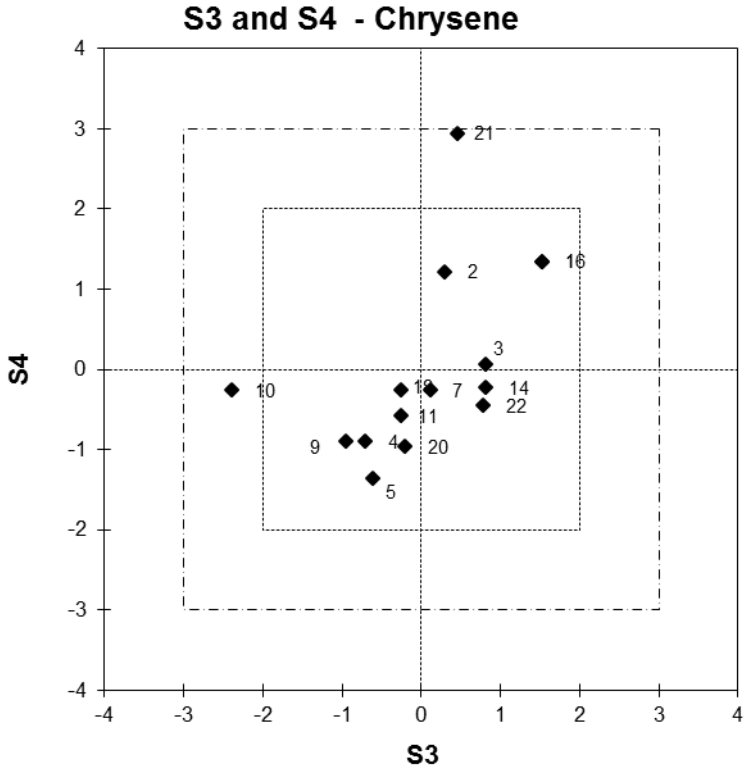

En-Scores: S4 - Pyrene
En-Score
Laboratory
13 17 8 12 5 4 6 20 11 22 14 16 9 2 1 15 18 21 7 3 10 19

Figure 22



Laboratories 6, 19 are off scale.

Figure 23 z-Score Scatter Plot: Benzo(a)pyrene in S3 and S4



Laboratories 8, 17 and 19 are off scale.

Figure 24 z-Score Scatter Plot: Chrysene in S3 and S4

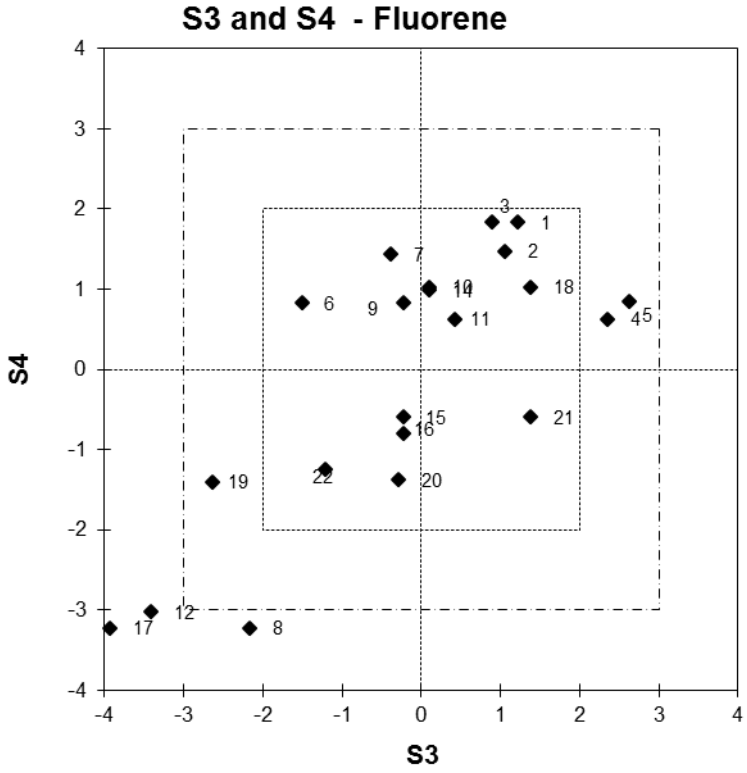
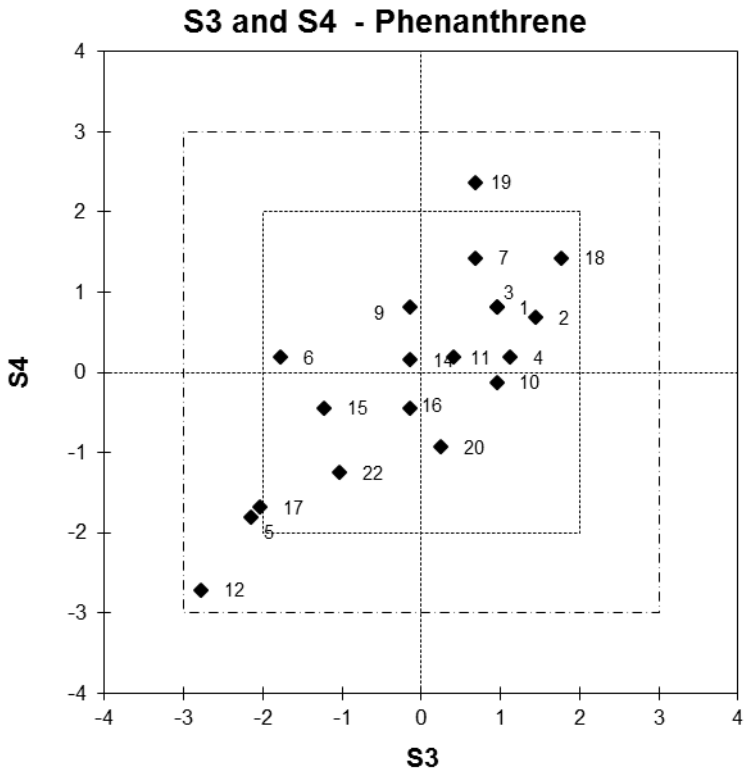
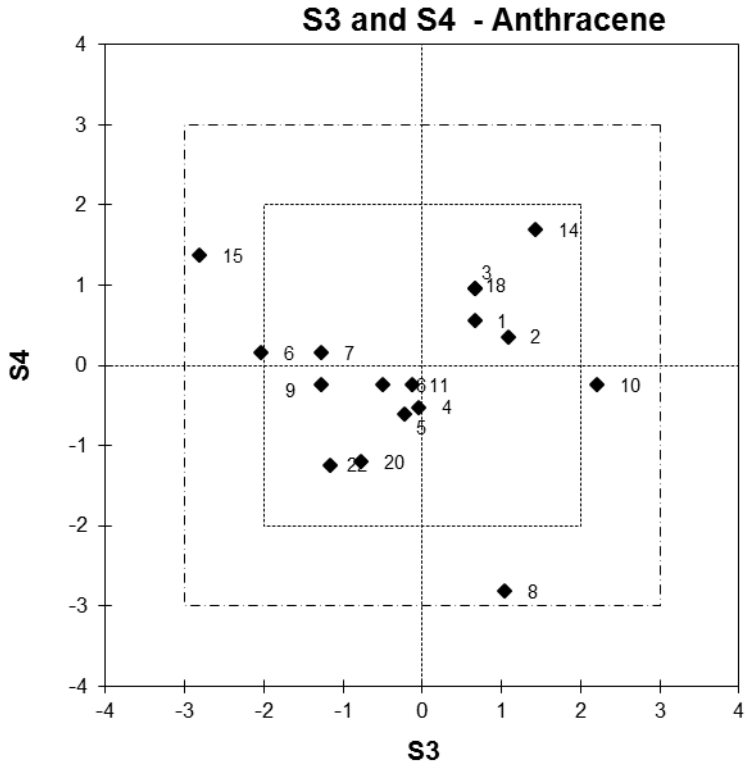


Figure 25 z-Score Scatter Plot: Fluorene in S3 and S4



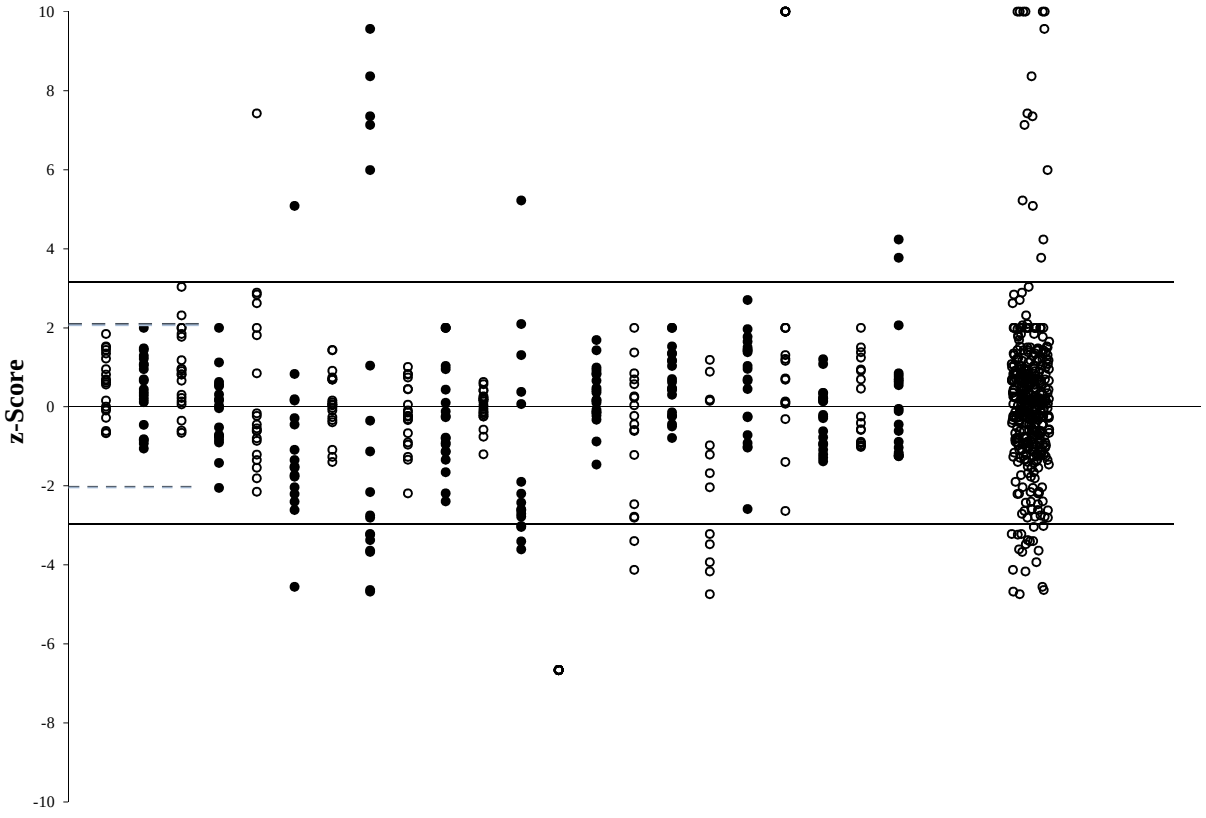
Laboratory 8 is off scale.

Figure 26 z-Score Scatter Plot: Phenanthrene in S3 and S4



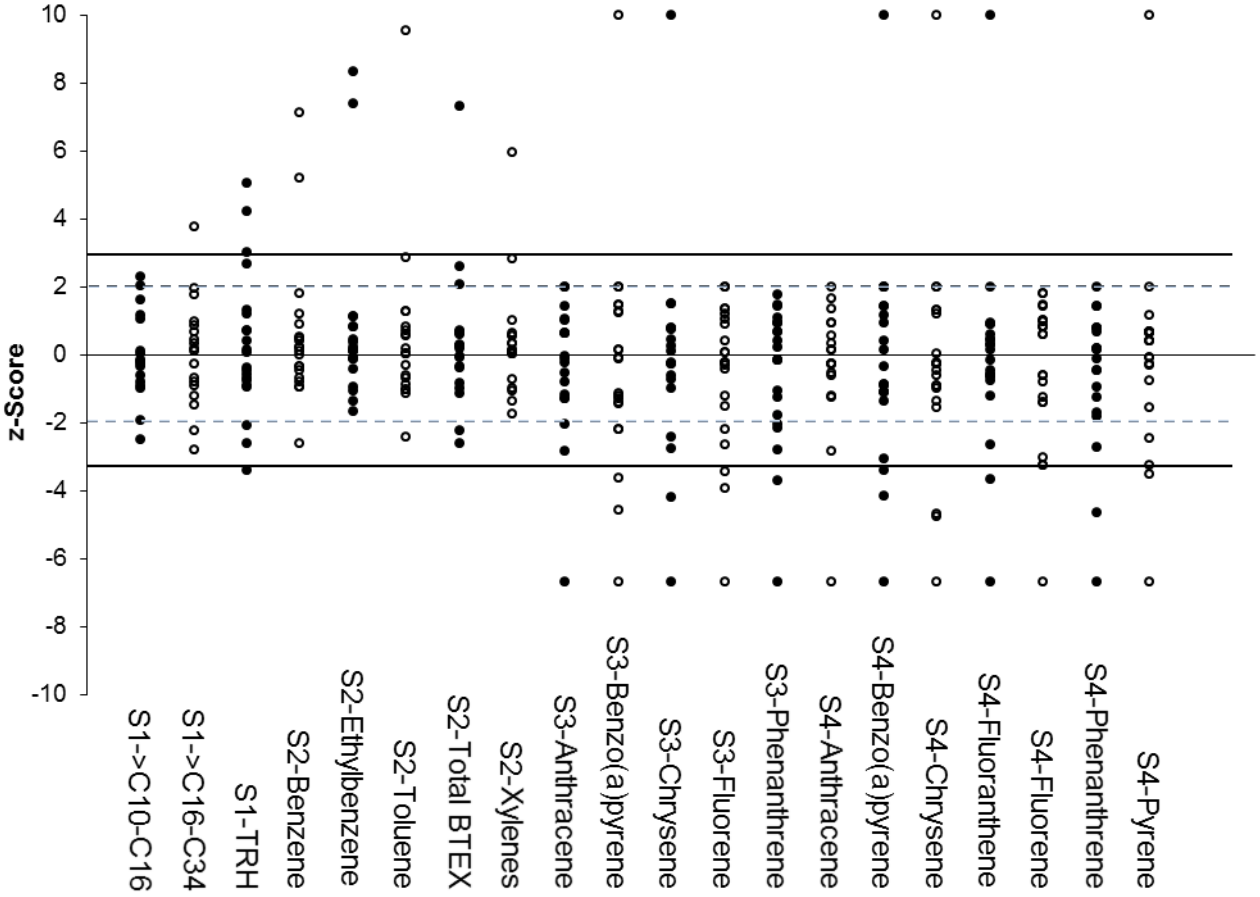
Laboratory 19 is off scale

Figure 27 z-Score Scatter Plot: Anthracene in S3 and S4



Scores >10 have been plotted as 10.

Figure 28 z-Score Dispersal by Laboratory



Scores >10 have been plotted as 10.

Figure 29 z-Score Dispersal by Sample and Analyte

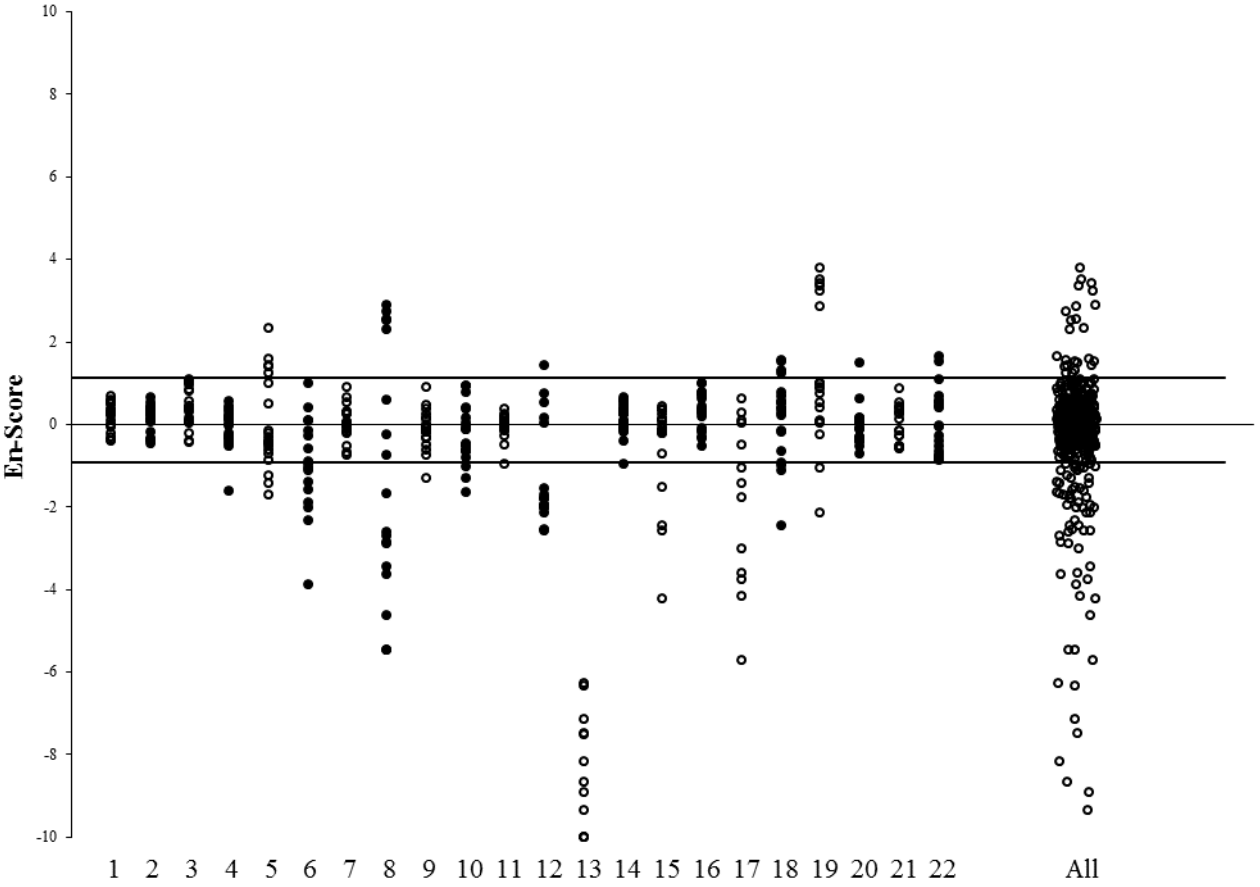


Figure 30 E_n-Score Dispersal by Laboratory

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Assigned values were the robust average of participants' results. The robust averages and associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'.[9] Results less than 50% and greater than 150% of the robust average were removed before calculation of the assigned value.

A comparison of the spiked concentration and the assigned values is presented in Table 28. The spiked concentration was the truest measure of the PAHs concentration in the water. However the robust average of participants' results was significantly lower (<75%) than the spiked concentration for most PAHs. This replicates what has been observed in previous NMI hydrocarbon in water studies. However, for all PAHs, there was a reasonable consensus (CVs between 16% to 35%) and an assigned value was set.

No assigned values were set for the C6-C10 range in Sample S2.

Appendix 3 sets out the calculation for the expanded uncertainty of the robust average of Toluene in Sample S2.

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.

Table 28 Comparison of Assigned Value (Robust Average) and Spiked Concentration.

Analyte	Spiked Concentration (µg/L)	Assigned Value (µg/L)	Assigned /spike (%)
S1 TRH	4420	3060	69
S2 Benzene	230	232	101
S2 Toluene	191	189	99
S2 Ethylbenzene	21.8	21.3	98
S2 Xylenes	298	258	87
S2 Total BTEX	739	703	95
S3 Anthracene	2.49	1.73	69
S3 Benzo(a)pyrene	4.53	2.53	56
S3 Chrysene	2.82	1.87	66
S3 Fluorene	7.49	4.14	55
S3 Phenanthrene	3.53	2.45	69
S4 Anthracene	2.52	1.66	66
S4 Benzo(a)pyrene	4.51	2.63	58
S4 Chrysene	2.82	2.08	74
S4 Fluoranthene	5.98	4.4	74
S4 Fluorene	7.58	3.29	43
S4 Phenanthrene	3.5	2.14	61
S4 Pyrene	3.55	2.72	77

6.2 Measurement Uncertainty Reported by Participants

It is a requirement of the ISO Standard 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.'

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate (Table 4). Where no TRH result was reported, then TRH was calculated by the study coordinator by summing the individual hydrocarbon ranges and no estimate of the uncertainty of the TRH result was made.

Of 427 numerical results, 422 (99%) were reported with an associated expanded uncertainty.

Expanded uncertainties were within the range 4.5% to 100% relative.

An expanded uncertainty of less than 10% relative is unrealistically small for the routine measurement of a hydrocarbon pollutant in water. Of the 422 expanded uncertainties, 5 were below 10% relative.

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

Some participants attached an estimate of the expanded measurement uncertainty to a result reported as less than their limit of detection.

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 1703.58 ± 511.07 µg/L better report 1700 ± 510 µg/L)[8].

6.3 z-Score

Target standard deviations equivalent to 15% CV were used to calculate z-scores. The between laboratory coefficient of variation predicted by the modified Horwitz equation[11] is presented for comparison in Table 31.

Table 29 Target standard deviations and modified Horwitz values

Sample	Analyte	Assigned value (µg/L)	Target SD (as PCV) (%)	Modified Horwitz CV (%)	Participants' SD (as CV) (%)
S1	<C10-C16	1580	15	15	27
S1	<C16-C34	1580	15	15	30
S1	TRH	3060	15	14	29
S2	Benzene	232	15	20	16
S2	Toluene	189	15	21	17
S2	Ethylbenzene	21.3	15	22	15
S2	Xylenes	258	15	20	14
S2	Total BTEX	703	15	17	18
S3	Anthracene	1.73	15	22	23
S3	Benzo(a)pyrene	2.53	15	22	35
S3	Chrysene	1.87	15	22	28
S3	Fluorene	4.14	15	22	27
S3	Phenanthrene	2.45	15	22	25

Sample	Analyte	Assigned value (µg/L)	Target SD (as PCV) (%)	Modified Horwitz CV (%)	Participants' SD (as CV) (%)
S4	Anthracene	1.66	15	22	17
S4	Benzo(a)pyrene	2.63	15	22	33
S4	Chrysene	2.08	15	22	28
S4	Fluoranthene	4.4	15	22	16
S4	Fluorene	3.29	15	22	25
S4	Phenanthrene	2.14	15	22	21
S4	Pyrene	2.72	15	22	19

To account for possible low bias in the consensus values due to laboratories using inefficient extraction techniques, some z-scores were adjusted so that a z-score greater than 2 was set at 2. A total of 15 z-scores were adjusted and included anthracene, benzo(a)pyrene and fluorene in Sample S3 and anthracene, benzo(a)pyrene, chrysene, fluoranthene, phenantrene and pyrene in Sample S4.

A maximum acceptable concentration was set to two target standard deviations more than the spiked level. This ensured that laboratories reporting results close to the spiked concentration were not penalised. For results higher than the maximum acceptable concentration z-scores were not adjusted. Scores of less than 2 were left unaltered.

Of 409 results for which z-scores were calculated, 330 (81%) returned a satisfactory score of $|z| \leq 2$.

Laboratories **1**, **2**, **7**, **11**, **14**, **16** and **20** returned satisfactory z-scores for all twenty analytes for which z-scores were calculated. Lab **21** reported results for 17 analytes and returned satisfactory z-scores for all of them.

Scatter plots of z-scores for benzo(a)pyrene, chrysene, fluorene, phenantrene and anthracene in Sample S3 and Sample S4 are presented in Figures 23 – 27. Summaries of z-scores by laboratory and by analyte are presented in Figures 28 and 29.

6.4 E_n-Score

Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

E_n-scores greater than 1 were set to 1 for participants for which z-scores were adjusted as discussed in Chapter 6.3 z-Scores.

Of 409 results for which E_n-scores were calculated, 316 (77%) returned a satisfactory score of $|E_n| \leq 1$.

Laboratories **1, 2, 7, 11, 14 and 16** returned satisfactory E_n-scores for all twenty analytes for which scores were calculated. Laboratory **21** return satisfactory E_n-scores for all seventeen results reported. A summary of E_n-scores by laboratory is presented in Figure 30.

6.5 Participants' Analytical Methods

TRH in Sample S1

All participants used liquid-liquid extraction for TRH in Sample S1. The extraction solvents reported were dichloromethane and hexane. All laboratories used GC-FID to measure hydrocarbons in the sample extract.

Seven laboratories reported taking 500 mL (ie the whole sample) for extraction while the other thirteen laboratories reported taking less than 500 mL, with test portions ranging from 80 – 400 mL. Laboratories did not report whether or not the sample container was rinsed to recover hydrocarbons adhering to the wall of the container.

BTEX in Sample S2

For BTEX analysis seventeen laboratories performed an extraction using purge-and-trap and three laboratories used headspace. All laboratories used GC-MS(MS) for analysis.

PAHs in Samples S3 and S4

Twenty-one participants used liquid-liquid extraction with DCM and one solid phase extraction (SPE). Twenty participants used DCM, one DCM and ethylacetate and one hexane. All laboratories used GC-MS(MS) to measure PAHs.

For extraction, sixteen laboratories reported taking less than 500 mL, with test portions ranging from 40 – 400 mL and six laboratories reported taking 500 mL (ie the whole sample). Laboratories did not report whether or not the sample container was rinsed to recover PAHs adhering to the wall of the container.

6.6 Certified Reference Materials (CRM)

Participants were requested to report whether certified or matrix reference materials (CRM) had been used as part of the quality assurance for the analysis. Twelve laboratories reported using 'certified' standards such as:

- AccuStandard
- Alkane standards
- Restek
- Supelco
- Dr Ehrenstorfer
- Sigma Aldrich
- Chemservice

These materials may not meet the internationally recognised definition of a Certified Reference Material:

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

6.7 Comparison with Previous Studies

TRH and total BTEX

The proportion of satisfactory z-scores for TRH and BTEX in water since 2008 is presented in Figures 31 and 32. On average the proportion of satisfactory z-scores was 76% for TRH and 89% for Total BTEX.

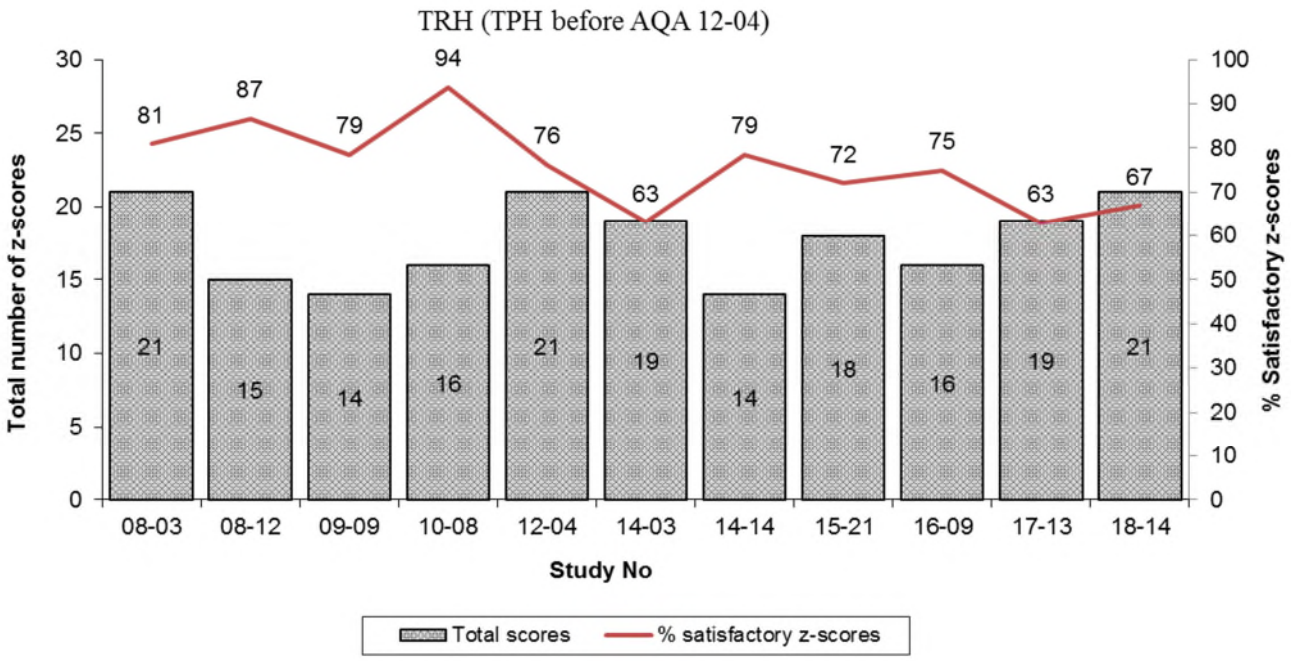


Figure 31 Percent satisfactory z-scores for TRH in NMI PTs of hydrocarbons in water

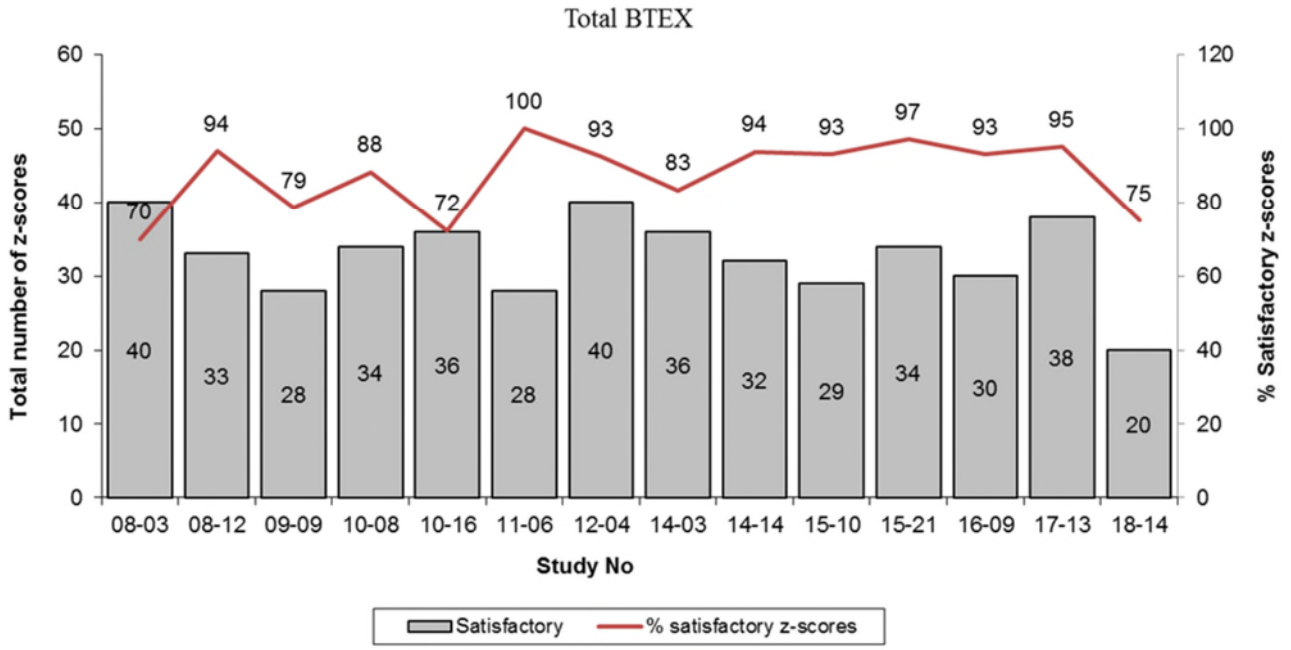


Figure 32 Percent satisfactory z-Scores for Total BTEX in NMI PTs of hydrocarbons in water

PAHs

A plot of the robust average, expressed as a percentage of the spiked concentration, for PAHs since 2015 is presented in Figure 33. The robust average of participants' results was significantly lower for fluorene (45%), benzo(a)pyrene (60%) and anthracene (67%). No trends were identified with the methods used by participants.

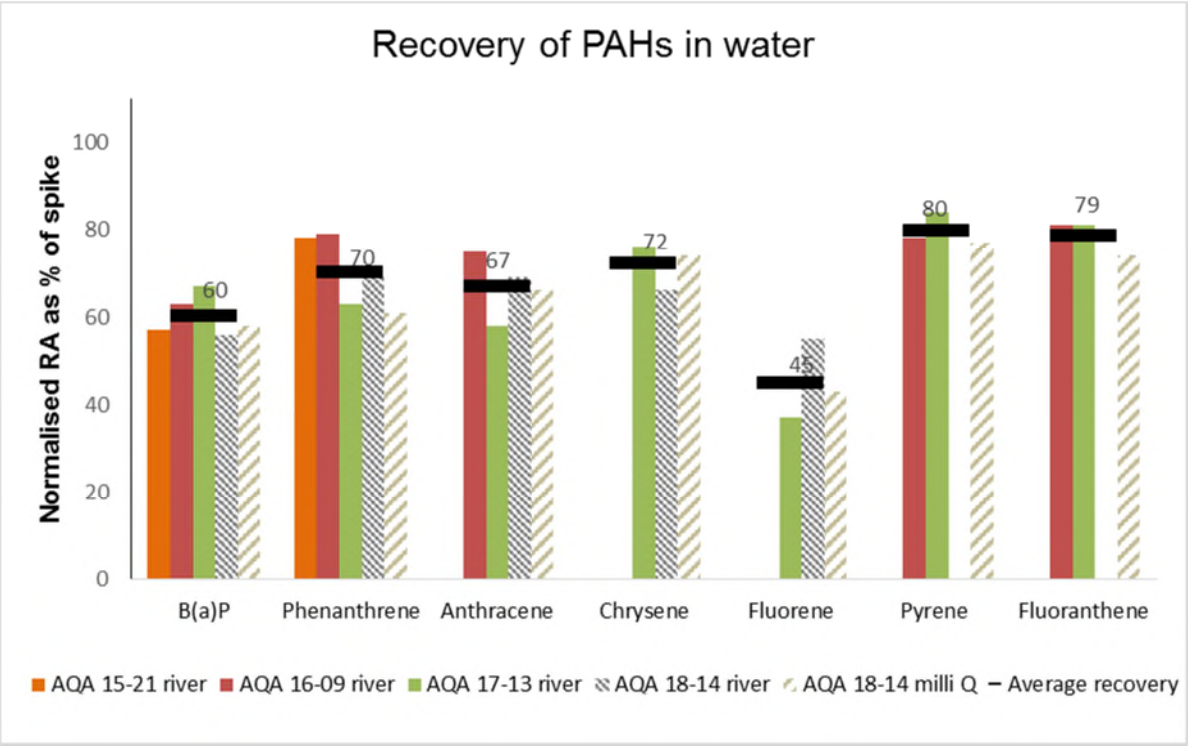


Figure 33 Robust average as % of spike level for PAHs since 2015

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[5] National Environment Protection Council (NEPC), National Environment Protection (Assessment of Site Contamination) Amendment Measure 2013, http://www.comlaw.gov.au/Details/F2013C00288 (Accessed September 2018).

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[8] EURACHEM/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed 20 September 2018, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[9] ISO/IEC 13528:2015, *Statistical methods for use in proficiency testing by interlaboratory comparisons*.

APPENDIX 1 - SAMPLE PREPARATION AND HOMOGENEITY TESTING

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 had been used in previous NMI Hydrocarbon PT studies.

Water was sampled from Browns Waterhole, Turramurra. The water was filtered under vacuum through an Advantec 150 mm glass fibre filter, placed in 10 litre Schott bottles and autoclaved. The autoclaved water was placed in a solvent rinsed 35.5 L stainless steel container and stirred to ensure homogeneity before being dispensed into the amber glass bottles.

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 water (500 mL @ 25ºC) was weighed into the bottles. 2.2 mL of the methanol/diesel spiking solution was added to each bottle. The bottles were immediately capped and inverted to mix the solution. Each bottle was then labelled and shrink-wrapped.

Sample S2

Forty-two mL of water was placed into Agilent vials. Composite spike solutions were prepared by adding aliquots of diesel and unleaded petrol to methanol and making up to volume. Composite spiking solution (1.0 mL) was added to each vial. Each vial was capped after spiking, labelled and shrink-wrapped.

Samples S3 &S4

The spike solutions were prepared by dissolving each standard material in DCM and diluting an aliquot of the first solution with acetone to give the spiking solutions. S3 was prepared using Milli-Q water and S4 was prepared using water from Brown's Waterhole that had been autoclaved. For each sample the water was placed in a stainless steel container. Both S3 and S4 were spiked with PAH standards at the same concentrations except for fluoranthene and pyrene which were added only in Sample S4. After spiking, the water was stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL amber glass bottles. Between preparation and dispatch the samples were stored in a coolroom at 4ºC.

Homogeneity Testing

The process used to prepare the samples was the same as previous NMI proficiency tests of pesticides in water. This process has been demonstrated to produce homogeneous samples and no homogeneity testing was conducted on these water samples.

APPENDIX 2 - ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY

The robust average was calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons – Annex C'[9] the uncertainty was estimated as:

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

where:

$u_{rob\ av}$	robust average standard uncertainty
$S_{rob\ av}$	robust average standard deviation
p	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 30.

Table 30 Uncertainty of the robust average for Toluene in Sample S2

No. results (p)	20
Robust Average	192.03 µg/L
$S_{rob\ av}$	32.46 µg/L
$u_{rob\ av}$	9.07 µg/L
k	2
$U_{rob\ av}$	18.14 µg/L

The robust average for Toluene in Sample S2 is 192 ± 18 µg/L.

APPENDIX 3 - ACRONYMS AND ABBREVIATIONS

BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
$\|E_n\|$	Absolute value of an E_n-score
GC-FID	Gas Chromatography Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometry
ISO	International Standards Organisation
Max	Maximum value in a set of results
Md	Median value in a set of results
Min	Minimum value in a set of results
NATA	National Association of Testing Authorities
NEPM	National Environmental Protection Measure
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
PAH	Polycyclic Aromatic Hydrocarbons
P & T	Purge and Trap
PT	Proficiency Test
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
Target SD	Target standard deviation
TPH	Total Petroleum Hydrocarbons.
TRH	Total Recoverable Hydrocarbons.
σ	Target standard deviation
$\|z\|$	Absolute value of a z-score

END of REPORT