Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Report
AQA 19-15
Hydrocarbons in Water

February 2020

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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Accredited for compliance with ISO/IEC 17043

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SUMMARY

AQA 19-15 was conducted in November 2019. Twenty-three laboratories submitted results.

The sample set consisted of four water samples. Samples were prepared in the NMI North Ryde laboratory using surface water from Browns Waterhole in the Turramurra area of Sydney.

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.

Traceability: 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 431 results for which z-scores were calculated, 380 (88%) returned a satisfactory score of $|z| \leq 2$.

Of 431 results for which E_n-scores were calculated, 334 (77%) returned a satisfactory score of $|E_n| \leq 1$.

Laboratories **1**, **8**, **12**, **14**, **21** and **22** returned satisfactory z-scores and E_n-scores for all 20 analytes for which scores were calculated.

Laboratories **4**, **6** and **16** reported hydrocarbon ranges outside of the recommended National Environment Protection Measure (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 452 numerical results, 427 (94%) were reported with an associated expanded uncertainty.

Expanded uncertainties were within the range 4.4% to 74% relative.

- *To evaluate the laboratories' test methods.*

For TRH analysis in Sample S1 participants used liquid-liquid extraction with either dichloromethane or hexane as the extraction solvent. All participants used GC-FID for analysis. Participants reported varying sample volumes used.

For BTEX analysis in Sample S2, four participants used a headspace technique, while the other participants performed an extraction using purge-and-trap, both followed by GC-MS.

For PAH analysis in Samples S3 and S4 one participant used solid phase extraction, while the other participants used liquid-liquid extraction. Extraction solvents reported included dichloromethane, hexane and dichloromethane/ethyl acetate. All laboratories used GC-MS(MS) for analysis. Participants reported varying sample volumes used.

No correlation between results and method was evident.

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 and biota;
- inorganic analytes 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.[2] The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.[3] These documents have been prepared with reference to ISO Standard 17043[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry 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 Environment Protection (Assessment of Site Contamination) Measure (NEPM) as amended 2013.[5]

2.2 Study Timetable

The timetable of the study was:

Invitation issued:	18 October 2019
Samples dispatched:	12 November 2019
Results due:	09 December 2019
Interim report issued:	14 January 2020

2.3 Participation

Invited:	78
Participated:	23
Submitted results:	23

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 spiked with unleaded petrol and diesel fuel.

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

2.5 Laboratory Code

Participants were assigned a confidential laboratory code number.

2.6 Sample Preparation and Homogeneity Testing

The preparation of the study samples is described in Appendix 1.

No homogeneity testing was conducted. All samples were prepared and packaged using a process that has been demonstrated in 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] 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 cool room at approximately 4°C prior to dispatch.

The samples were packaged into insulated styrene foam boxes and dispatched by courier on 12 November 2019.

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 – C10), Benzene, Toluene, Ethyl benzene, 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** with an associated expanded uncertainty (e.g. 2000 ± 200 µg/L).
- Report the basis of your uncertainty estimates (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.
- Please **complete the method details** as required in the Methodology sheet.
- Return the completed results sheet by e-mail (proficiency@measurement.gov.au).
- **Please return completed result sheet by 9 December 2019. 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 14 January 2020.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Participants' Test Method Summaries

Table 1 Test Methods Sample S1 TRH

Lab. Code	Sample Volume (mL)	Extraction	Extraction solvent	Measurement	Method*
1	200	Liquid-Liquid	DCM	GC-FID	USEPA Method 8015B
2	515	Liquid-liquid	DCM	GC-FID	USEPA 3510
3	250	Liquid-Liquid separatory funnel extraction	DCM	GC-FID	In-house method based on US EPA 3510 & NEPM 2013.
4	40	Liquid Liquid	Hexane	GC-FID	US EPA 8015
5	500	Liquid-liquid	DCM	GC-FID	In house
6	500	liquid/liquid	DCM	GC-FID	In house
7	400	Liquid-Liquid	Dichloromethane	GC-FID	In house
8	35	liquid-liquid	DCM	GC-FID	USEPA SW-846
9	200	Liquid-liquid	DCM	GC-FID	Inhouse method based on USEPA 3510
10	500	Liquid-Liquid extraction	DCM	Capillary GC/FID	USEPA SW 846 - 8015A
11	500	Liquid-Liquid	DCM	GC-FID	USEPA 3510C
12	35	Liquid-liquid	Hexane	GC-FID	In-house based off USEPA 3510
13					
14	400	Liquid-liquid	DCM	GC-FID	In house referenced to USEPA SW 846 8015A
15	400	Liquid - liquid	DCM	GC MS	In house
16	100	Solvent extraction with pre-concentration.	Hexane	GC-FID	US EPA 8015B
17	500	Liquid-liquid	DCM	GC-FID	USEPA Method 5015B
18	500	Liquid-liquid extraction	DCM	GC-FID	US EPA Method 8015
20	200	Liquid Liquid	DCM	GC FID	USEPA 8015C
21	100	Liquid-Liquid	DCM	GC-FID	Inhouse method based on USEPA 3510
22	100	Liquid-Liquid	DCM	GC-FID	Inhouse method based on USEPA 3510
23	500	Liquid - Liquid	DCM	GC-FID	In house
24	250	Liquid-liquid extraction	DCM	Shimadzu GC -FID.	In-house based on NEPM

Table 2 Test Methods Sample S2 BTEX

Lab. Code	Sample Volume (mL)	Extraction	Measurement	Method*
1	40	Purge and Trap	GC-MS	USEPA 8260
2	44	Purge and trap	GC-MS	USEPA 8260
3	40	Purge and Trap	GCMS	In-house method based on US EPA 8260
4	10	Solvent extraction, headspace injection	GC-MS	US EPA 5021A
5	40	No extraction; direct inject analysis on purge and trap system	GCMS	in house method (based on USEPA 5030 and 8020)
6	5	purge and trap	GCMS	epa 8260 modified
7	5	Purge and Trap	GC-MS	In-House based on USEPA 8260
8	43	purge and trap	GC-MS	USEPA SW-846 Method 5030
9	40	P&T	GC-MS	USEPA 8260
10	40	Purge and Trap	GC-MS	USEPA 8260B
11	5	Purge and Trap	GC-MS	USEPA 8260
12	5	Purge and trap	GC-MS	In-house based of USEPA 8260
13	12	Head Space	GC-MS	In House
14	5	Purge and Trap	Purge and Trap GCMS	In house method adapted from USEPA SW 846 8260B
15	400	Purge and Trap	GC-MS	In House adapted USEPA SW 846 8260D
16	10	Headspace	GC-MS	US EPA 8260B
17				
18	Entire full vial	Purge&trap	GC-MS	USEPA 5030B, 5035, 8260B
20	25	Purge and Trap	GC MS	USEPA 524.2
21	40	Purge and Trap	GC-MS	USEPA 8260
22	40	Purge and Trap	GC-MS	USEPA 8260
23	40	Purge and Trap	GC-MS	USEPA 8260
24	10	Static Headspace	Headspace GC-MS	In-house

Table 3 Test Methods Samples S3 and S4 PAH

Lab. Code	Sample Volume (mL)	Extraction	Solvent	Measurement	Method*
1	200	Liquid-liquid	DCM	GC-MS	USEPA 8270C, USEPA SW-846, USEPA 3500B
2					
3	250	Liquid-liquid separatory funnel extraction.	DCM	GCMS	In-house method based on US EPA 8270
4	40	Liquid liquid	Hexane	GC-MS	US EPA 3500C & 8270D
5	500	Liquid Liquid	DCM	GC-MS	USEPA 8270
6	500	SPE polymeric phase	DCM:ethyl acetate 1:1	GCMS	EPA 8270C modified
7	400	Liquid-Liquid	Dichloromethane	GC-MS	In-House
8	35	liquid-liquid	DCM	GC-MS QQQ	USEPA SW-846 METHOD 8100
9	200	Liquid-liquid	DCM	GC-MS	In-house method based on USEPA 8270
10	500	Liquid-Liquid extraction	DCM	GC-MS	USEPA 8270D
11	500	Liquid-Liquid	DCM	GC-MS	USEPA 8270D
12	35	Liquid-liquid	Dichloromethane	GC-MSMS	In-house based of USEPA 8270
13	50	Liquid-liquid extraction	Hexane	GC-MS	In-house method
14	400	Liquid-liquid	Dichloromethane (DCM)	GC-MS	In house method referenced to USEPA SW 846 - 8270D.
15	100	Liquid - liquid	DCM	GC-MS	In House based on USEPA SW-486 8270E
16	250	Liquid/liquid	DCM	GC-MS SIM	In-house
17	500	Liquid-liquid	DCM	GC-MS	USEPA 8270C
18	500	Liquid-liquid extraction	DCM	GC-MS	USEPA 8270E
20	100	Liquid-liquid	DCM	GC-MS	USEPA 3500B (Extraction and Preparation), USEPA 8270C
21	35	Liquid-Liquid	DCM	GC-MS/MS	In-house method based on USEPA 8270
22	35	Liquid-Liquid	DCM	GC MS/MS	In-house method based on USEPA 8270
23	500	Liquid-Liquid	DCM	GC-QQQ-MS	USEPA 8270D
24	200	Liquid-liquid extraction	DCM	GC-MS	In-house

*Some entries have been modified so that the participant cannot be identified.

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants' responses as received are listed in Table 4.

Table 4 Basis of Uncertainty Estimate

Lab. Code	Basis of Uncertainty Estimate
1	Quality Control requirement
2	S1 and S2: Top Down - precision and estimates of the method and laboratory bias
3	Standard deviation of replicate
4	S1: Replicate data S2, S3 and S4: Replicate data during validation
5	S1: uncertainty of the calibration curve, precision, and method bias S2, S3 and S4: in-house validation data
6	S1: longterm reporducibility matrix spikes S2, S3 and S4: Longterm reproducibility
7	Historical QC Data
8	
9	S1, S3 and S4: 20% S2: Control Charts
10	Top Down - precision and estimates of the method and laboratory bias
11	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%.
12	Control charts
13	S2, S3 and S4: Top Down – Precision and estimate of the method and laboratory bias
14	QC data
15	Quality Control Data
16	Based on historical data.
17	S1, S3 and S4: Quality Control requirement
18	S1: duplicates S2, S3 and S4: spiked recoveries and duplicates
20	
21	Control Charts
22	Control Charts
23	S1, S3 and S4: Uncertainty is based on ± 24% of ug/L result S2: Uncertainty based on ± 15% of ug/L results
24	Repeatability precision - based upon internal historical data

3.3 Participants' Comments

The study manager welcomes comments or suggestions from participants as it provides information which will improve future studies. All responses are listed as received in Table 5, along with the study manager's response, where appropriate.

Table 5 Additional Comment or Discussion of Results

Lab. Code	Sample	Comment or Discussion	Study Manager's Response
5	S2	A portion of the 40mL sample is purged and analysed.	
7	All	Please provide the option of 2x100mL bottles for analysis for future studies.	Thank you for your feedback, we will look into providing samples with lower volumes.
11	S2	Each of the 2 vials supplied gave vastly different results. Vial number 16 was about 10x lower than vial number 54. We have reported the higher of the two results.	The overall results from this study gave no indication of issues with homogeneity for BTEX.
14	S3, S4	Benzo(b+j) fluoranthene reported together as Benzo(b)fluoranthene.	
	All	If possible lower volumes to be made available as different options to select.	Thank you for your feedback, we will look into providing samples with lower volumes.
16	S2	The above Hydrocarbon result is for C6-C9.	
20	S2	1.2.4-Trimethylbenzene : 6 ug/L ±1.9ug/L 1.3.5-Trimethylbenzene: 21 ug/L ± 6.7ug/L (Note: these results are included in Total BTEX above;	
24	S3, S4	Benzo[b,k]fluroanthene reported as one result	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 28 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.

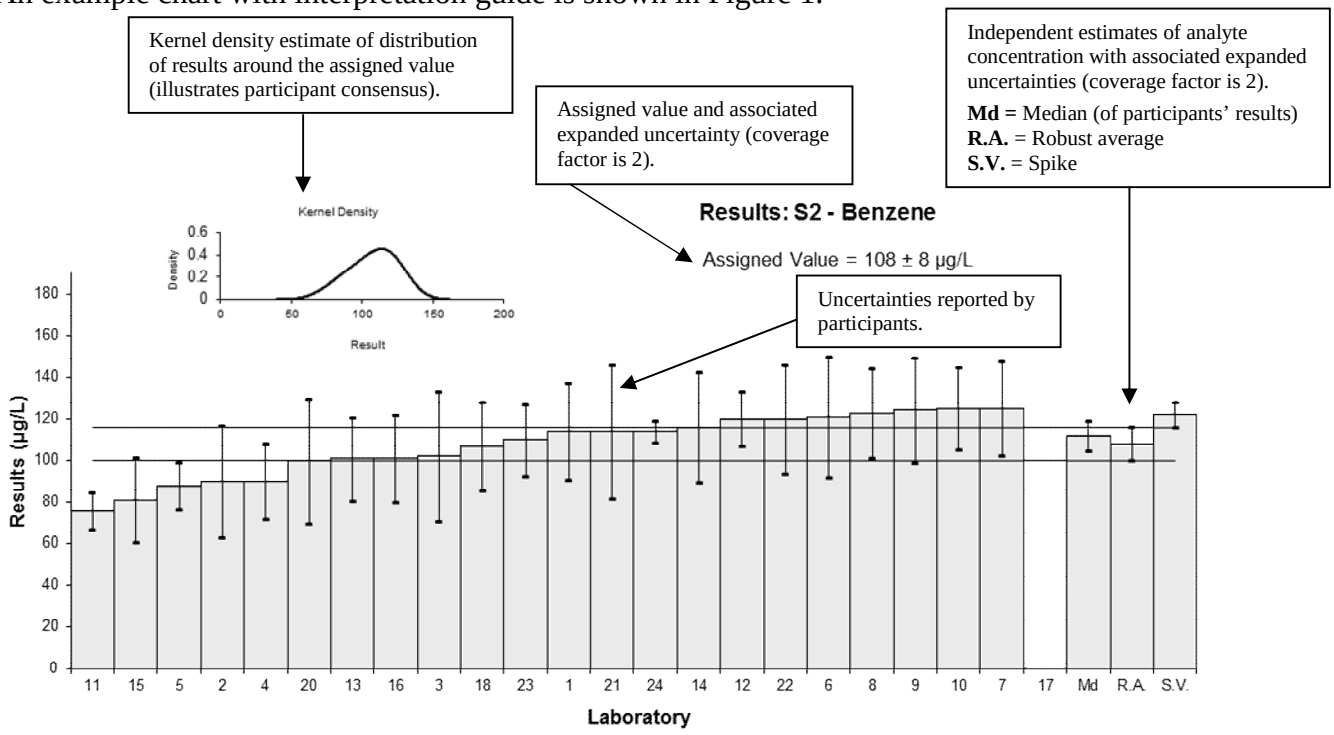


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

The assigned value is defined as the: 'value attributed to a particular property of a proficiency test item'.[1] In this study the property is the concentration of the analyte.

Assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations.

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), as presented in Equation 1. This value is used in the calculation of z-scores.

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

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 a participant's result

X is the assigned value

σ is the target standard deviation from Equation 1

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

- $|z| \leq 2$ is satisfactory;
- $2 < |z| < 3$ is questionable;
- $|z| \geq 3$ 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 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

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

- $|E_n| \leq 1$ is satisfactory;
- $|E_n| > 1$ is unsatisfactory.

4.7 Traceability and Measurement Uncertainty

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

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

4.8 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'ISO 13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparison'.[9]

5 TABLES AND FIGURES

Table 6

Sample Details

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

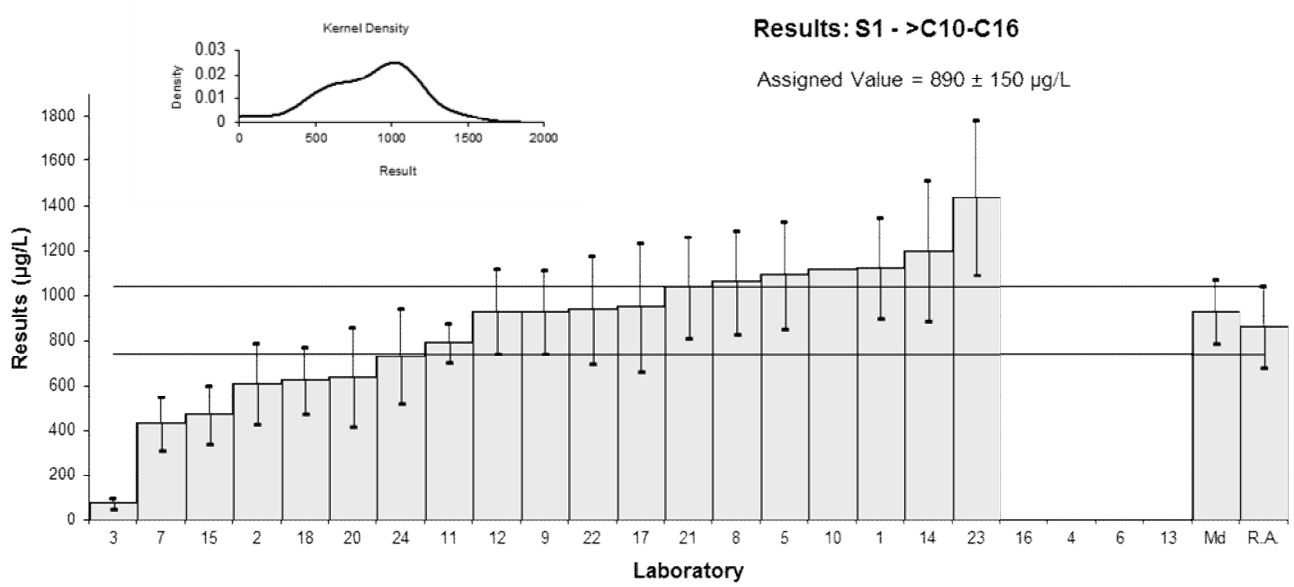
Participant Results

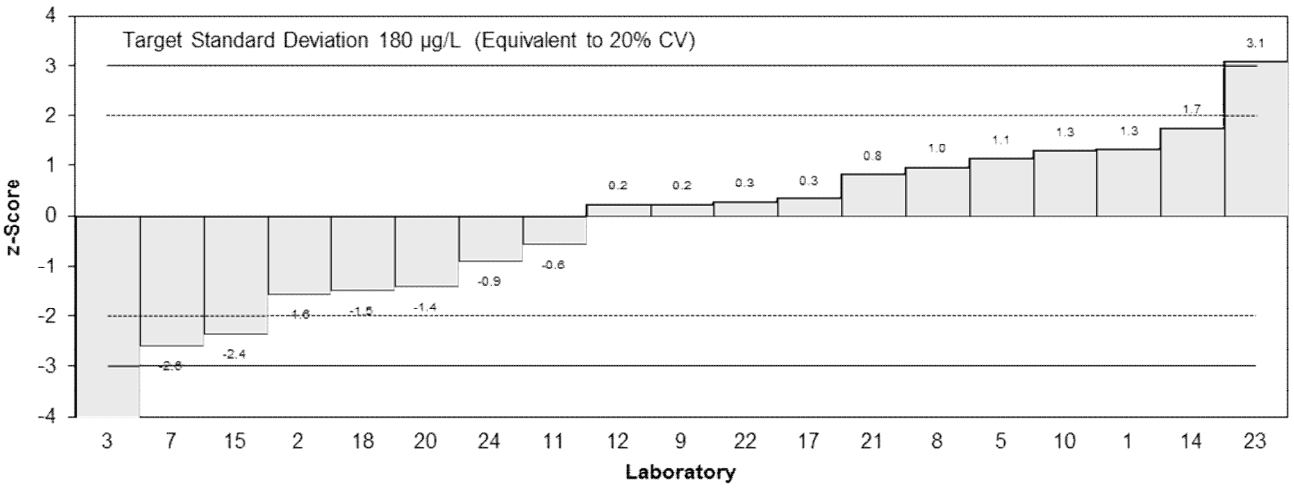
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1125	225	1.32	0.87
2	610	180	-1.57	-1.20
3	77	23	-4.57	-5.36
5	1092.7	240.4	1.14	0.72
7	430	117.6	-2.58	-2.41
8	1060.35	230.21	0.96	0.62
9	930.17	186	0.23	0.17
10	1120	NR	1.29	1.53
11	790	87	-0.56	-0.58
12	930	189	0.22	0.17
13	NT	NT		
14	1200	316	1.74	0.89
15	470	133	-2.36	-2.10
17	950	285	0.34	0.19
18	624	150	-1.49	-1.25
20	640	220	-1.40	-0.94
21	1036	225	0.82	0.54
22	940	240	0.28	0.18
23	1439.3	345.4	3.09	1.46
24	730	212	-0.90	-0.62

Statistics

Assigned Value*	890	150
Spike	Not Spiked	
Robust Average	860	180
Median	930	140
Mean	852	
N	19	
Max.	1439.3	
Min.	77	
Robust SD	240	
Robust CV	27%	

*Robust average excluding laboratories 3, 7 and 23.


Kernel Density
Density
Result
Results: S1 - >C10-C16
Assigned Value = 890 ± 150 µg/L
Results (µg/L)
Laboratory
3 7 15 2 18 20 24 11 12 9 22 17 21 8 5 10 1 14 23 16 4 6 13 Md R.A.


z-Scores: S1 - >C10-C16
Target Standard Deviation 180 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
3 7 15 2 18 20 24 11 12 9 22 17 21 8 5 10 1 14 23

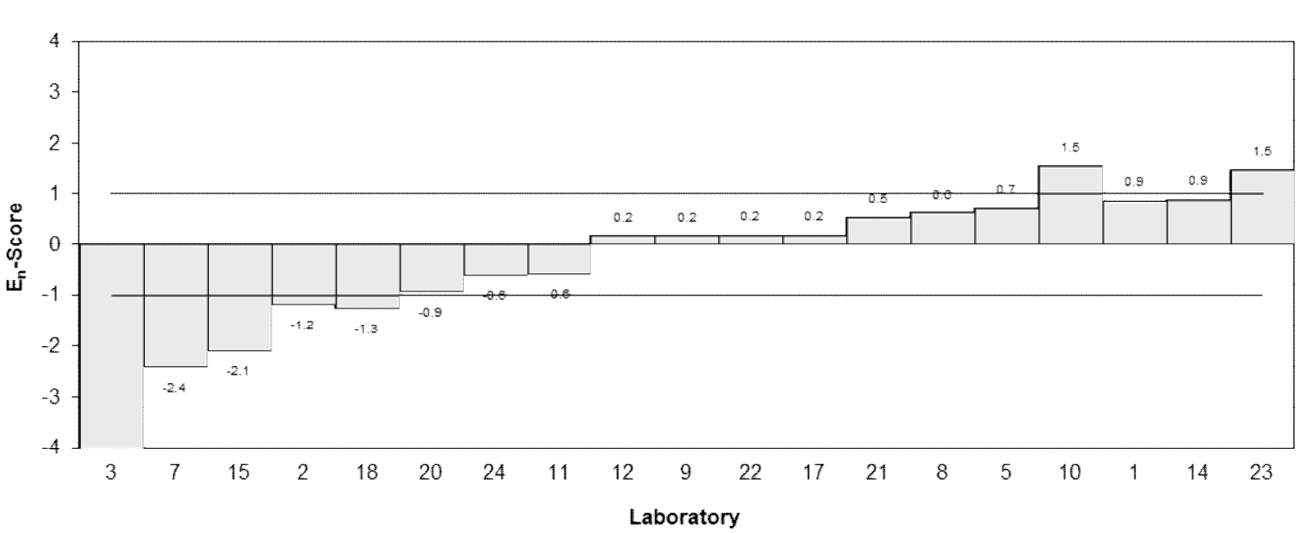

En-Scores: S1 - >C10-C16
En-Score
Laboratory
3 7 15 2 18 20 24 11 12 9 22 17 21 8 5 10 1 14 23

Figure 2

Table 7

Sample Details

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

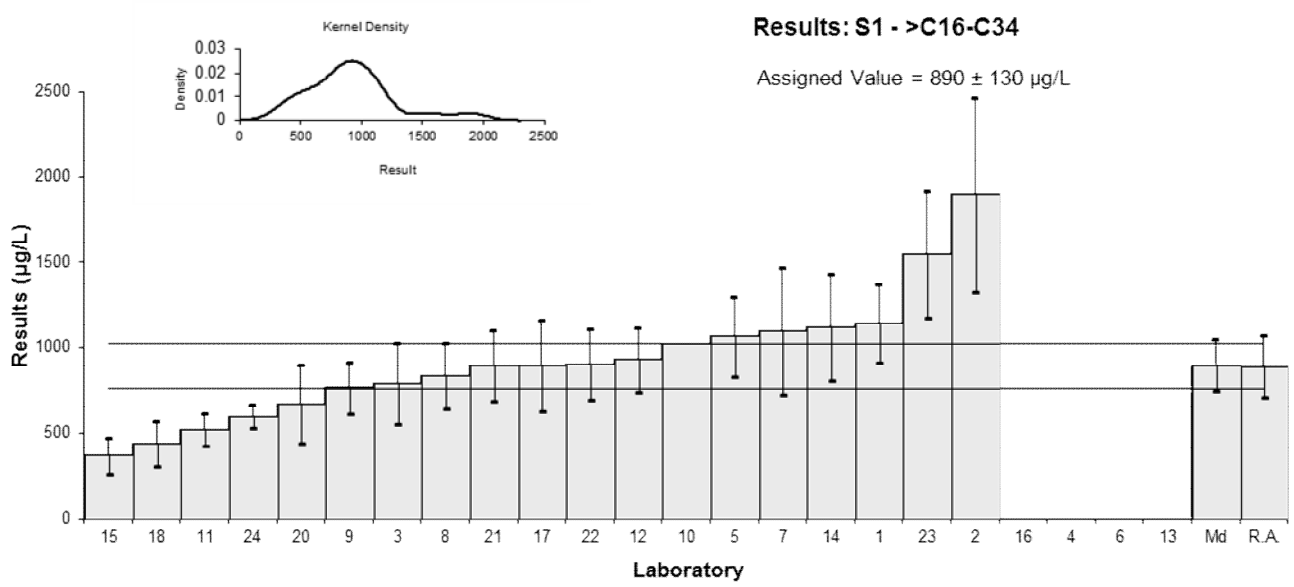
Participant Results

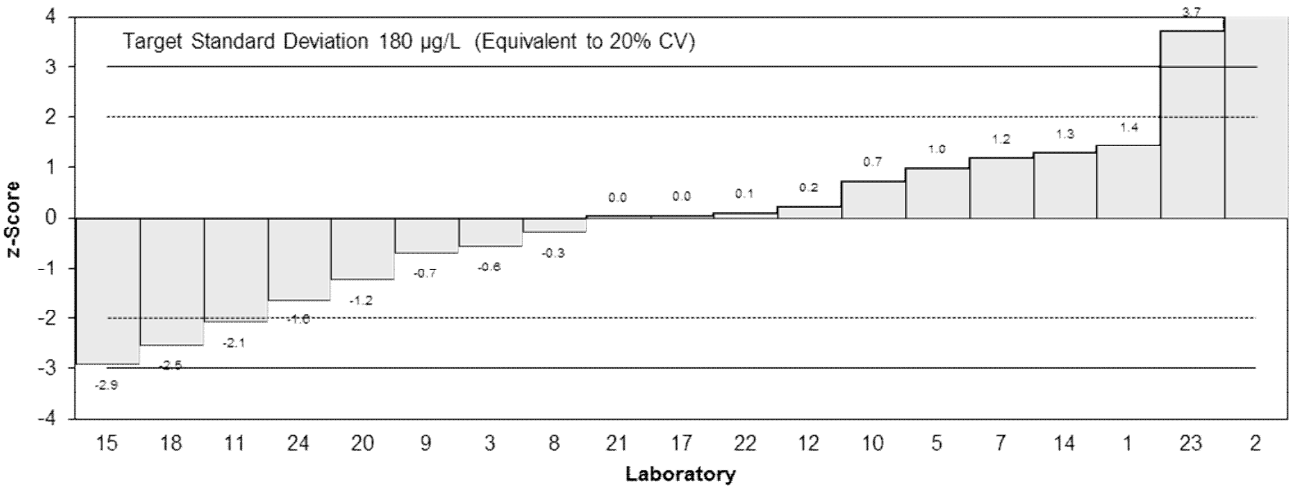
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1145	230	1.43	0.97
2	1900	570	5.67	1.73
3	789	237	-0.57	-0.37
5	1066.4	234.6	0.99	0.66
7	1100	369.9	1.18	0.54
8	837.93	192.86	-0.29	-0.22
9	765.62	153	-0.70	-0.62
10	1020	NR	0.73	1.00
11	520	92	-2.08	-2.32
12	931	189	0.23	0.18
13	NT	NT		
14	1120	311	1.29	0.68
15	370	106	-2.92	-3.10
17	897	269	0.04	0.02
18	438	130	-2.54	-2.46
20	670	230	-1.24	-0.83
21	895	206	0.03	0.02
22	906	206	0.09	0.07
23	1549.9	372.0	3.71	1.67
24	600	66	-1.63	-1.99

Statistics

Assigned Value*	890	130
Spike	Not Spiked	
Robust Average	890	180
Median	900	150
Mean	922	
N	19	
Max.	1900	
Min.	370	
Robust SD	210	
Robust CV	23%	

*Robust average excluding laboratories 2, 15, 18 and 23.


Kernel Density
Density
Result
Results: S1 - >C16-C34
Assigned Value = 890 ± 130 µg/L
Results (µg/L)
Laboratory
15 18 11 24 20 9 3 8 21 17 22 12 10 5 7 14 1 23 2 16 4 6 13 Md R.A.


z-Scores: S1 - >C16-C34
Target Standard Deviation 180 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
15 18 11 24 20 9 3 8 21 17 22 12 10 5 7 14 1 23 2

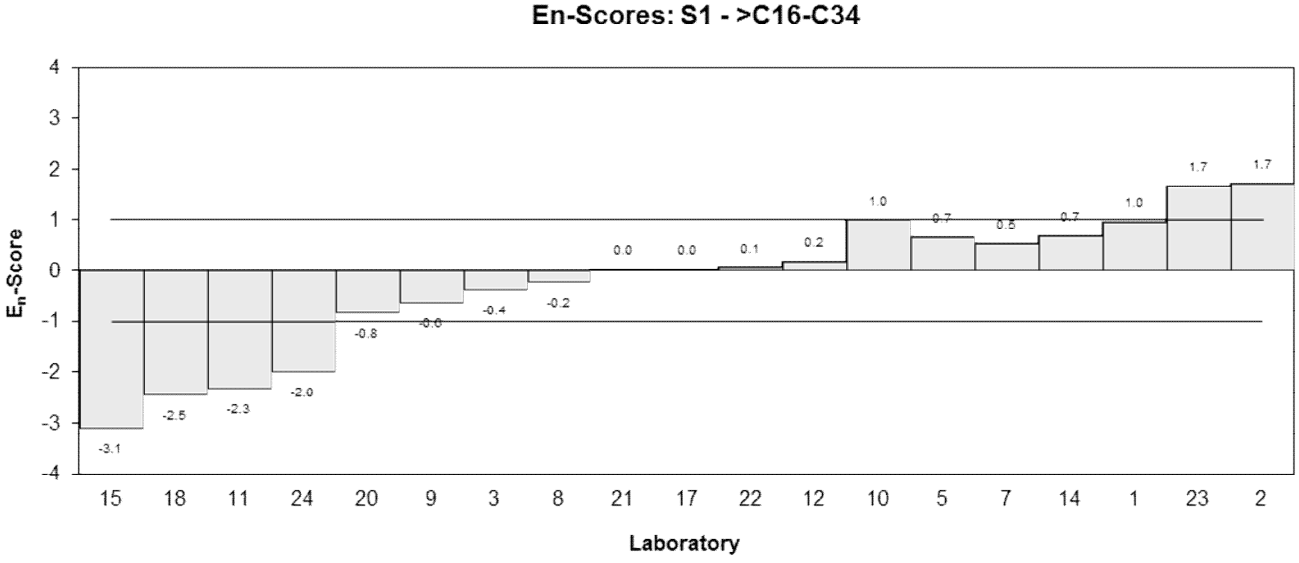

En-Scores: S1 - >C16-C34
En-Score
Laboratory
15 18 11 24 20 9 3 8 21 17 22 12 10 5 7 14 1 23 2

Figure 3

Table 8

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	<100	NR
2	<100	NR
3	433	130
5	<100	0
7	<50	5.6
8	<100	23
9	<100	20
10	<100	NR
11	<50	NR
12	< 100	20.3
13	NT	NT
14	<100	NR
15	<100	47
17	<100	NR
18	<100	NR
20	<50	22
21	< 100	23
22	<100	25
23*	NR	NR
24	<100	NR

*Result changed from 0 to NR.

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	

Table 9 Laboratories that reported additional hydrocarbon ranges to those defined in Schedule B3 of the NEPM[5] for Sample S1

Lab Code	Range	Concentration (µg/L)	Uncertainty (µg/L)
4	C7 - C9	<200	NR
	C10 - C14	600	150
	C15 - C36	1300	260
6	C7 - C9	<400	NR
	C10 - C14	860	270
	C15 - C36	2300	670
16	C7 - C9	<100	67
	C10 - C14	260	120
	C15 - C36	620	210

Table 10

Sample Details

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

Participant Results

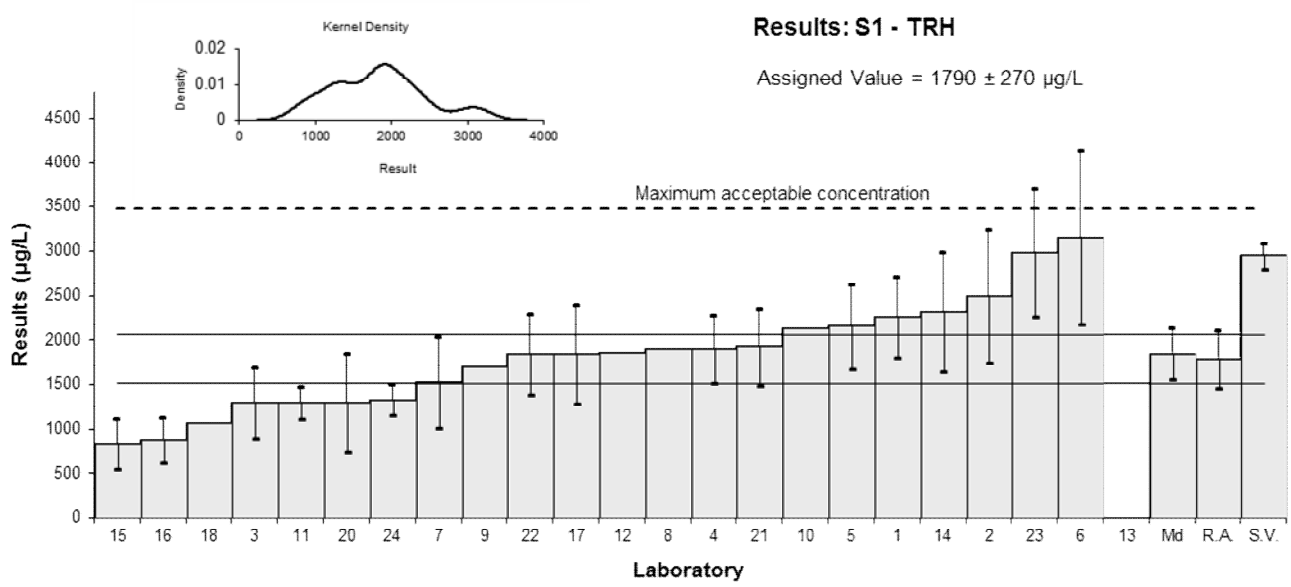
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2270	455	1.79	0.91
2**	2500	750	2.00	0.89
3	1299	390	-1.83	-1.04
4	1900	380	0.41	0.24
5	2159	472	1.37	0.68
6**	3160	980	2.00	1.00
7	1530	514.1	-0.97	-0.45
8	1898.28	NR	0.40	0.40
9	1695.79	NR	-0.35	-0.35
10	2140	NR	1.30	1.30
11	1300	180	-1.82	-1.51
12	1861	NR	0.26	0.26
13	NT	NT		
14	2320	668	1.97	0.74
15	840	286	-3.54	-2.42
16	880	250	-3.39	-2.47
17	1847	554	0.21	0.09
18	1062	NR	-2.71	-2.70
20	1300	560	-1.82	-0.79
21	1931	431	0.53	0.28
22	1846	460	0.21	0.10
23**	2989.2	717.4	2.00	1.00
24	1330	173	-1.71	-1.43

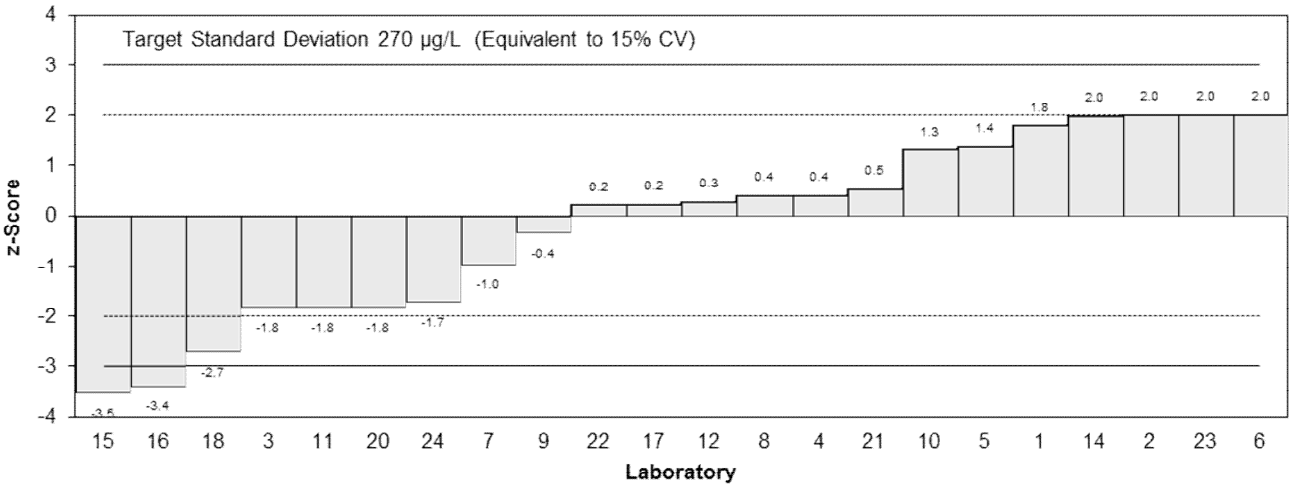
Statistics

Assigned Value*	1790	270
Spike	2950	150
Maximum acceptable conc.**	3490	
Robust Average	1790	330
Median	1850	290
Mean	1821	
N	22	
Max.	3160	
Min.	840	
Robust SD	460	
Robust CV	26%	

*Robust average excluding laboratories 6, 15, 16 and 23.

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


Kernel Density
Density
Result
Results: S1 - TRH
Assigned Value = 1790 ± 270 µg/L
Maximum acceptable concentration
Results (µg/L)
Laboratory
15 16 18 3 11 20 24 7 9 22 17 12 8 4 21 10 5 1 14 2 23 6 13 Md R.A. S.V.


z-Scores: S1 - TRH
Target Standard Deviation 270 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
15 16 18 3 11 20 24 7 9 22 17 12 8 4 21 10 5 1 14 2 23 6

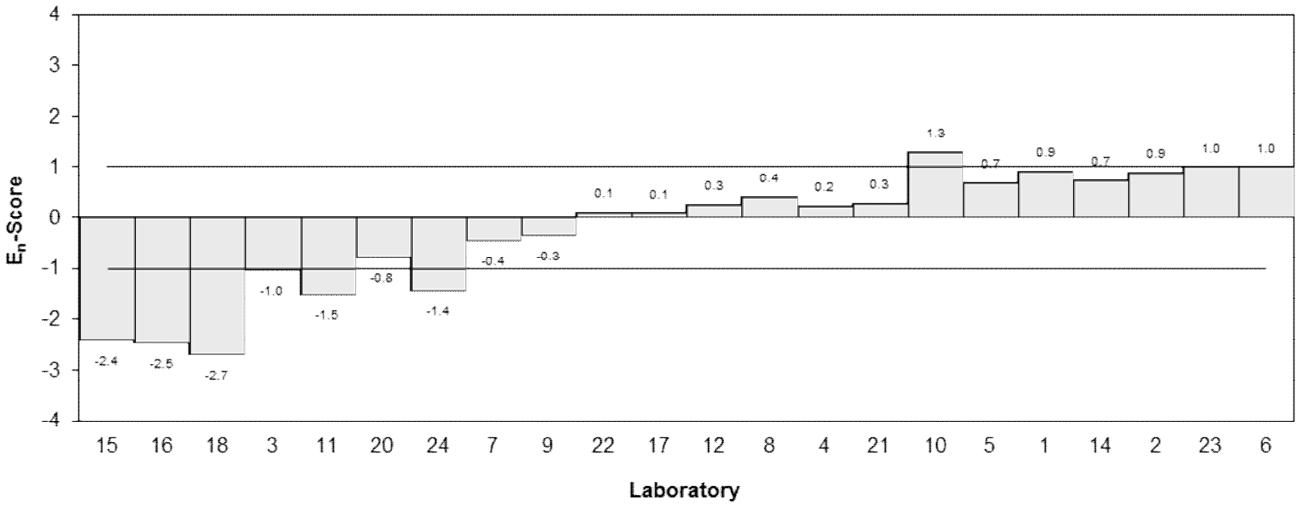

En-Scores: S1 - TRH
En-Score
Laboratory
15 16 18 3 11 20 24 7 9 22 17 12 8 4 21 10 5 1 14 2 23 6

Figure 4

Table 11

Sample Details

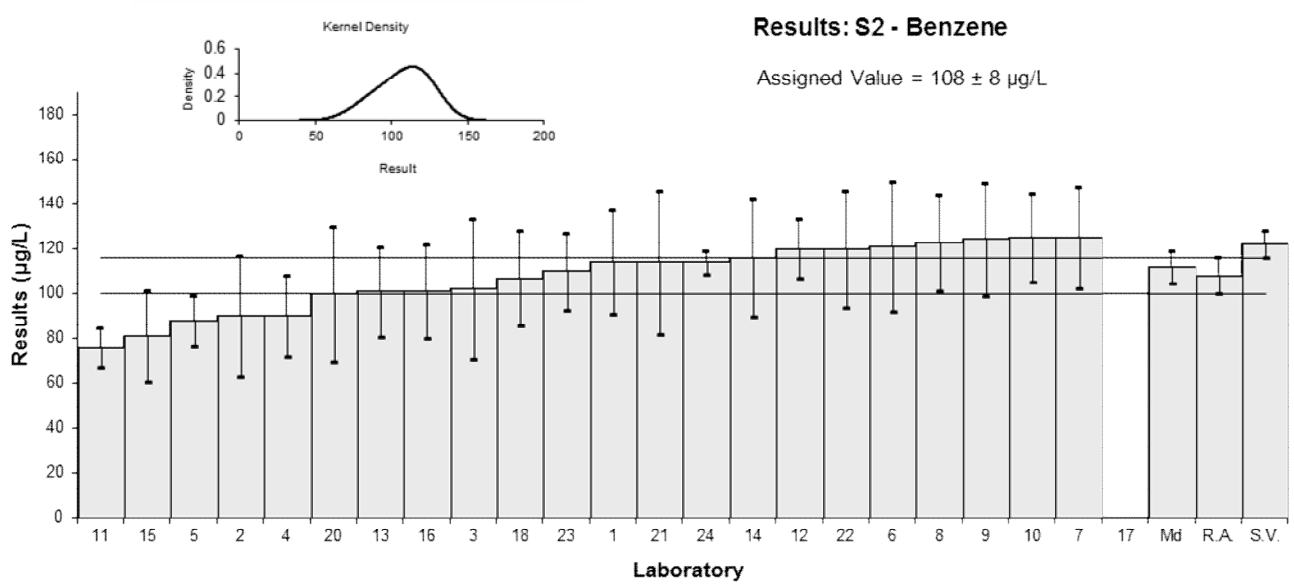
Sample No.	S2
Matrix.	Water
Analyte.	Benzene
Units	µg/L

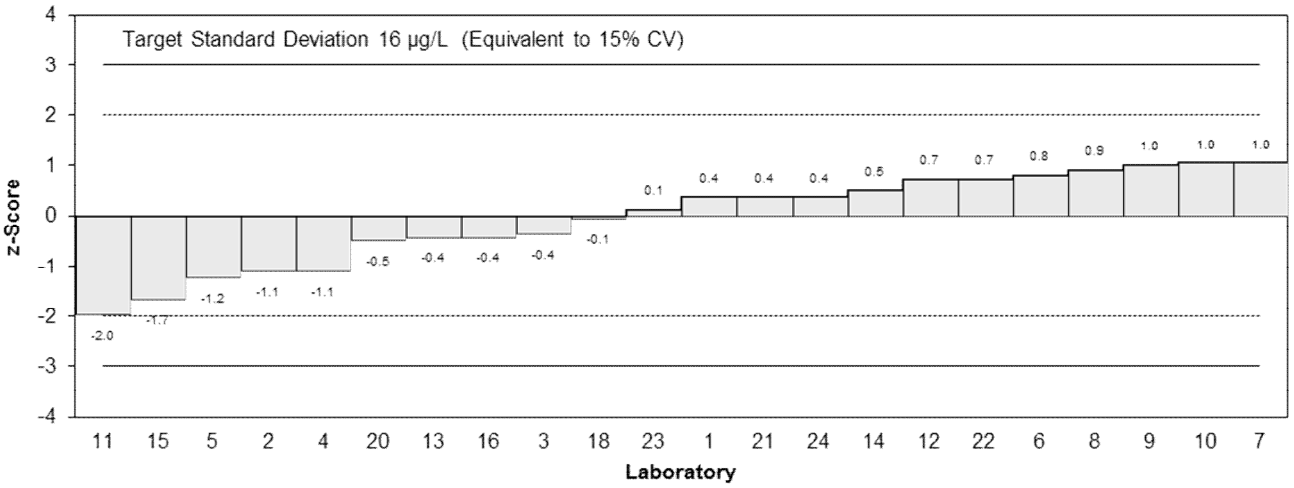
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	114	23	0.37	0.25
2	90.0	27	-1.11	-0.64
3	102	31	-0.37	-0.19
4	90	18	-1.11	-0.91
5	88	11	-1.23	-1.47
6	121.0	29.0	0.80	0.43
7	125	22.3	1.05	0.72
8	122.82	21.47	0.91	0.65
9	124.26	25	1.00	0.62
10	125	19.58	1.05	0.80
11	76	9	-1.98	-2.66
12	120	13	0.74	0.79
13	101	20	-0.43	-0.32
14	116	26.3	0.49	0.29
15	81	20.1	-1.67	-1.25
16	101	21	-0.43	-0.31
17	NT	NT		
18	107	21	-0.06	-0.04
20	100	30	-0.49	-0.26
21	114	32	0.37	0.18
22	120	26	0.74	0.44
23	110	17	0.12	0.11
24	114	5	0.37	0.64

Statistics

Assigned Value	108	8
Spike	122	6
Robust Average	108	8
Median	112	7
Mean	107	
N	22	
Max.	125	
Min.	76	
Robust SD	16	
Robust CV	15%	


Kernel Density
Density
Result
Results: S2 - Benzene
Assigned Value = 108 ± 8 µg/L
Results (µg/L)
Laboratory
11 15 5 2 4 20 13 16 3 18 23 1 21 24 14 12 22 6 8 9 10 7 17 Md R.A. S.V.


z-Scores: S2 - Benzene
Target Standard Deviation 16 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 15 5 2 4 20 13 16 3 18 23 1 21 24 14 12 22 6 8 9 10 7

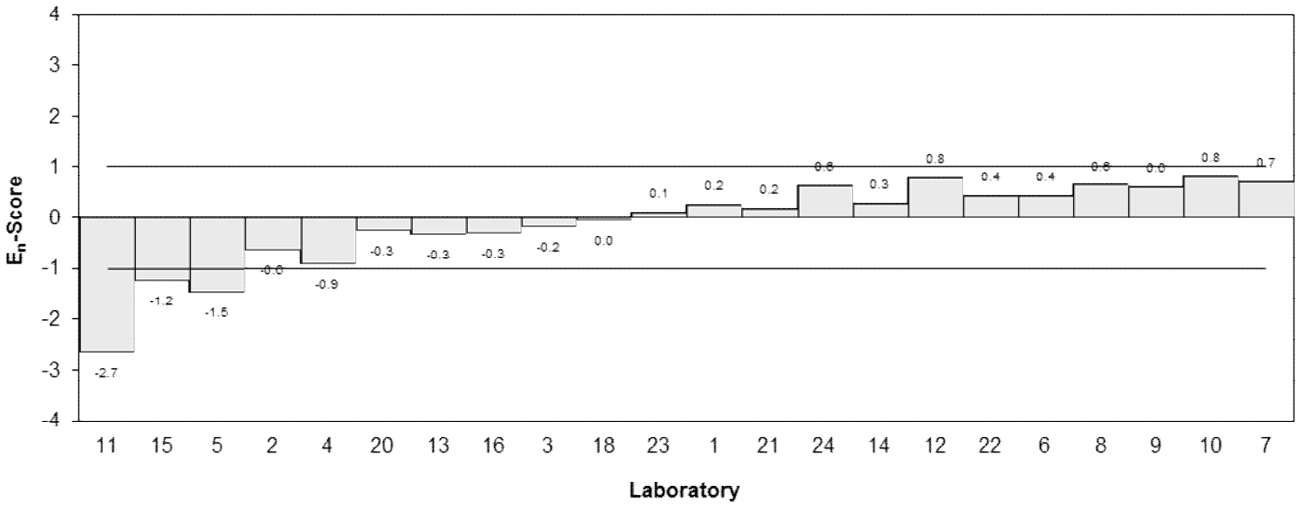

En-Scores: S2 - Benzene
En-Score
Laboratory
11 15 5 2 4 20 13 16 3 18 23 1 21 24 14 12 22 6 8 9 10 7

Figure 5

Table 12

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	730	145
2	320	97
3	588	176
4	NT	NT
5	360	61
6	NT	NT
7	600	152.5
8	723.16	172.91
9	729.39	109
10	640	127.01
11	390	70
12	NT	NT
13	496	50
14	610	220
15	320	122
16	490	150
17	NT	NT
18	644	130
20	410	NR
21	823	231
22	840	210
23	710	107
24	386	93

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Robust Average	570	110
Median	600	92
Mean	569	
N	19	
Max.	840	
Min.	320	
Robust SD	190	
Robust CV	34%	

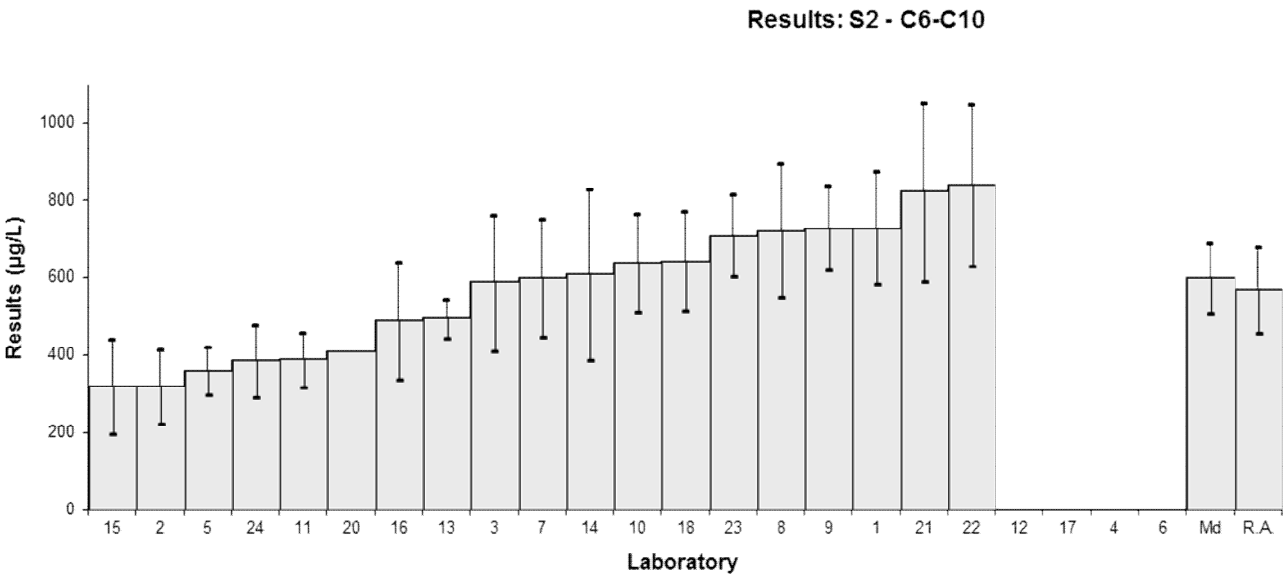

Results: S2 - C6-C10
Results (µg/L)
1000
800
600
400
200
0
15
2
5
24
11
20
16
13
3
7
14
10
18
23
8
9
1
21
22
12
17
4
6
Md
R.A.
Laboratory

Figure 6

Table 13

Sample Details

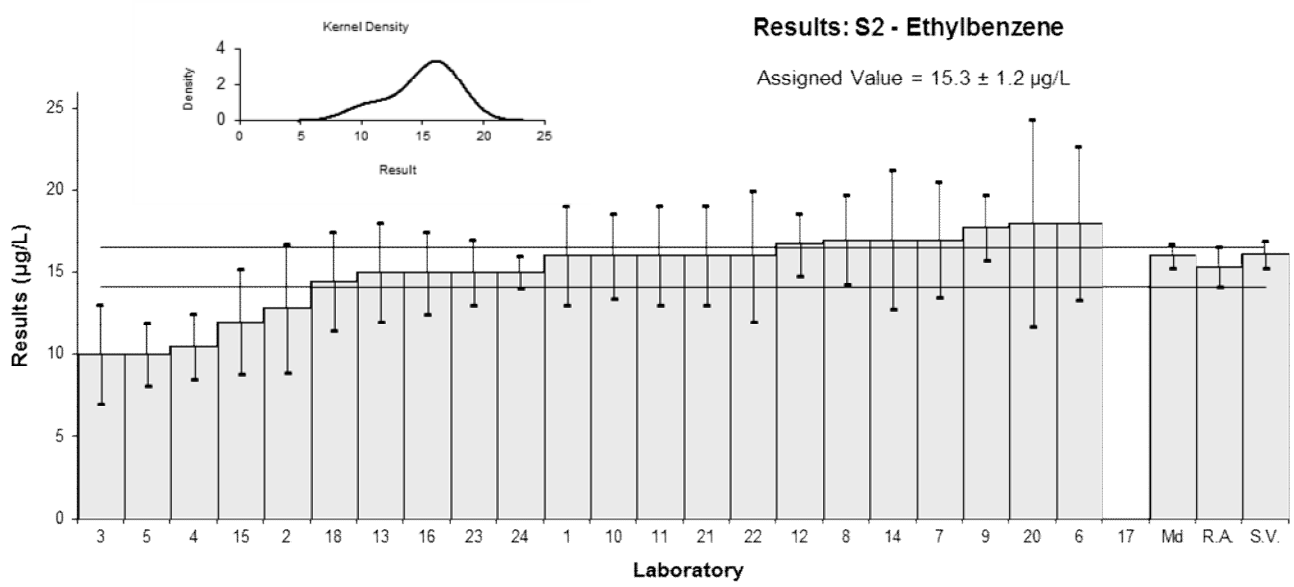
Sample No.	S2
Matrix.	Water
Analyte.	Ethylbenzene
Units	µg/L

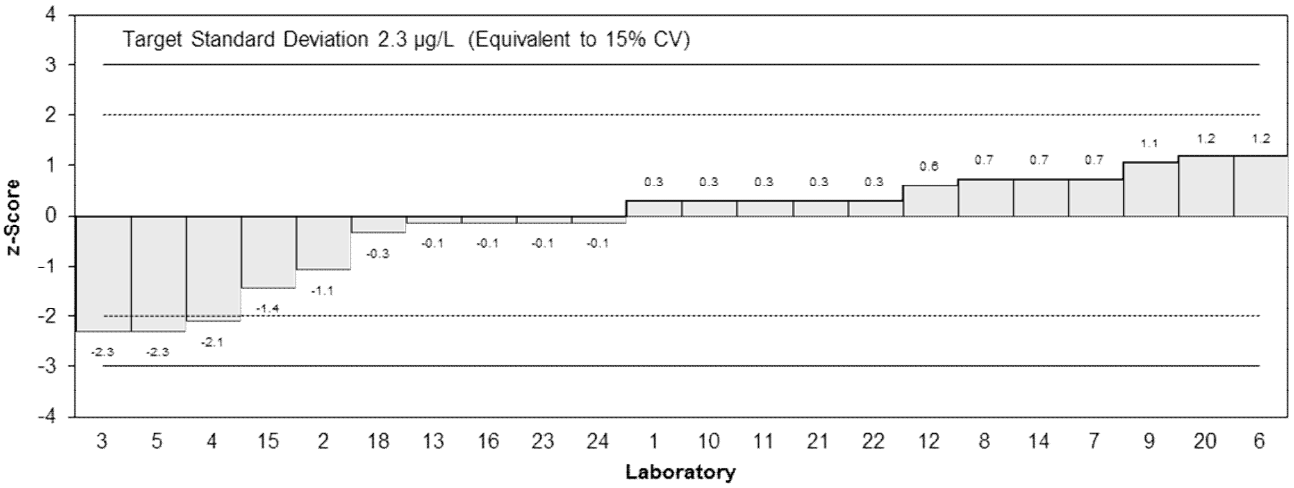
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	16	3	0.31	0.22
2	12.8	3.9	-1.09	-0.61
3	10	3	-2.31	-1.64
4	10.5	2	-2.09	-2.06
5	10	1.9	-2.31	-2.36
6	18.0	4.7	1.18	0.56
7	17	3.5	0.74	0.46
8	16.99	2.72	0.74	0.57
9	17.74	2	1.06	1.05
10	16	2.57	0.31	0.25
11	16	3	0.31	0.22
12	16.7	1.9	0.61	0.62
13	15	3	-0.13	-0.09
14	17	4.2	0.74	0.39
15	12	3.2	-1.44	-0.97
16	15	2.5	-0.13	-0.11
17	NT	NT		
18	14.5	3	-0.35	-0.25
20	18	6.3	1.18	0.42
21	16	3	0.31	0.22
22	16	4	0.31	0.17
23	15	2	-0.13	-0.13
24	15	1	-0.13	-0.19

Statistics

Assigned Value	15.3	1.2
Spike	16.1	0.8
Robust Average	15.3	1.2
Median	16.0	0.7
Mean	15.1	
N	22	
Max.	18	
Min.	10	
Robust SD	2.3	
Robust CV	15%	


Kernel Density
Density
Result
Results: S2 - Ethylbenzene
Assigned Value = 15.3 ± 1.2 µg/L
Results (µg/L)
Laboratory
3 5 4 15 2 18 13 16 23 24 1 10 11 21 22 12 8 14 7 9 20 6 17 Md R.A. S.V.


z-Scores: S2 - Ethylbenzene
Target Standard Deviation 2.3 µg/L (Equivalent to 15% CV)
z-Score
-2.3 -2.3 -2.1 -1.4 -1.1 -0.3 -0.1 -0.1 -0.1 -0.1 0.3 0.3 0.3 0.3 0.3 0.6 0.7 0.7 0.7 1.1 1.2 1.2
Laboratory
3 5 4 15 2 18 13 16 23 24 1 10 11 21 22 12 8 14 7 9 20 6

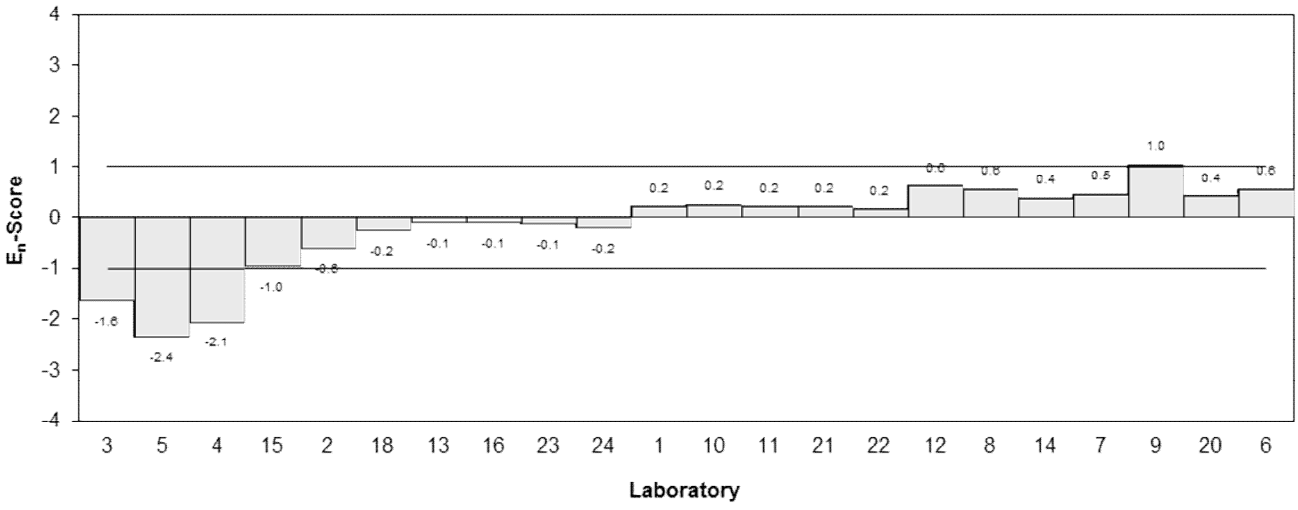

En-Scores: S2 - Ethylbenzene
En-Score
-1.6 -2.4 -2.1 -1.0 -0.6 -0.2 -0.1 -0.1 -0.1 -0.2 0.2 0.2 0.2 0.2 0.2 0.6 0.5 0.4 0.5 1.0 0.4 0.6
Laboratory
3 5 4 15 2 18 13 16 23 24 1 10 11 21 22 12 8 14 7 9 20 6

Figure 7

Table 14

Sample Details

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

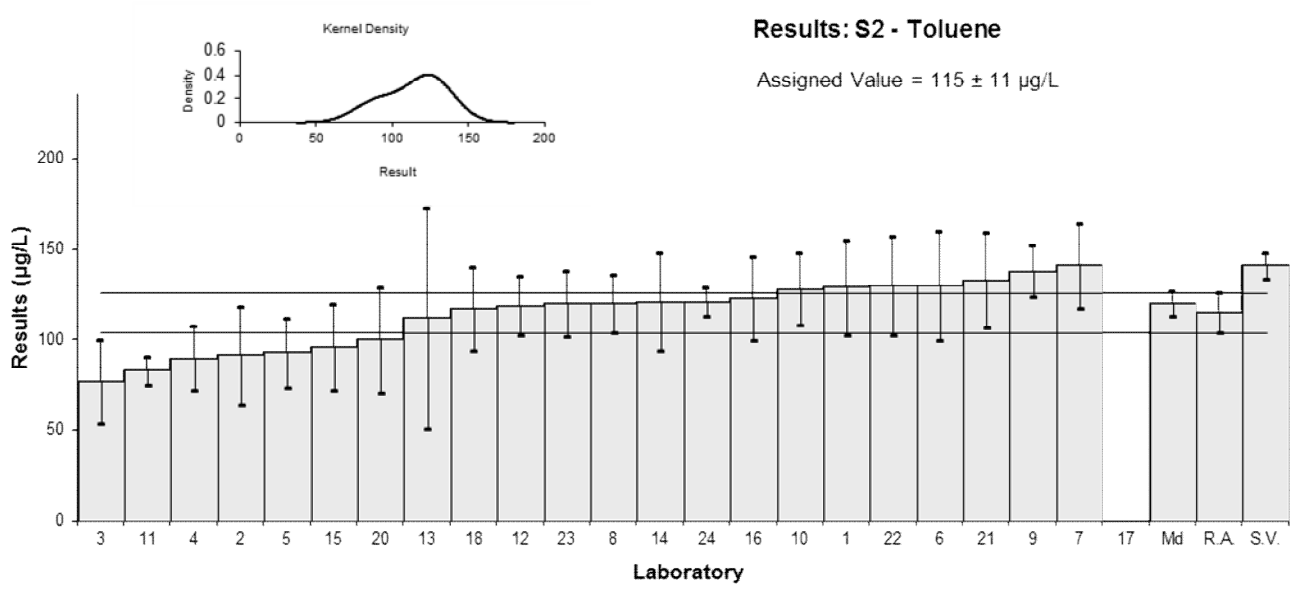
Participant Results

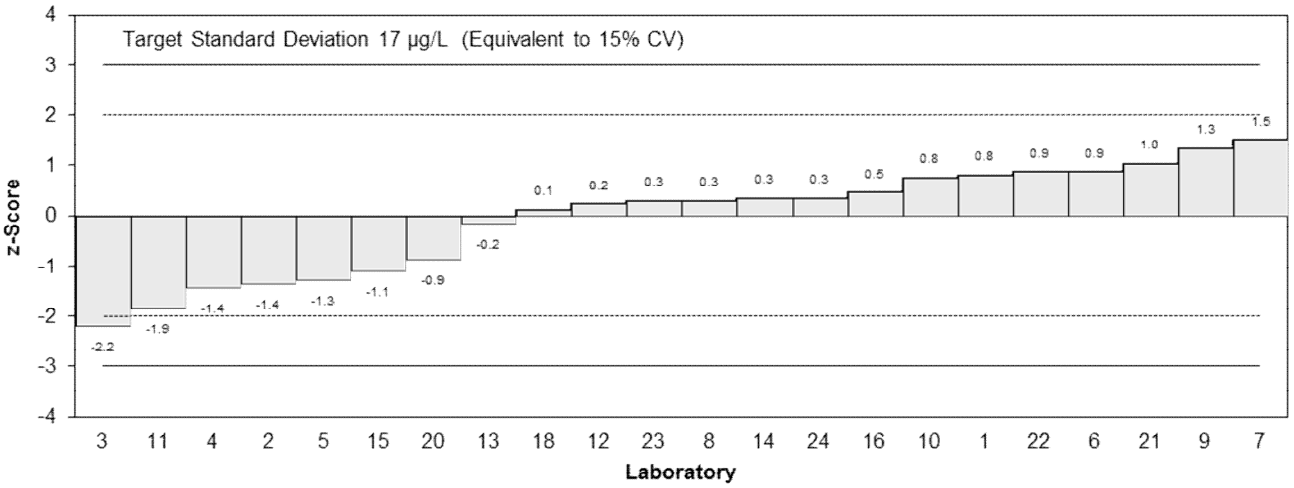
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	129	26	0.81	0.50
2	91.5	27	-1.36	-0.81
3	77	23	-2.20	-1.49
4	90	18	-1.45	-1.19
5*	93	19	-1.28	-1.00
6	130.0	29.9	0.87	0.47
7	141	23.4	1.51	1.01
8	120.12	15.92	0.30	0.26
9	138.03	14	1.34	1.29
10	128	19.73	0.75	0.58
11	83	8	-1.86	-2.35
12	119	16	0.23	0.21
13	112	61	-0.17	-0.05
14	121	26.9	0.35	0.21
15	96	23.4	-1.10	-0.73
16	123	23	0.46	0.31
17	NT	NT		
18	117	23	0.12	0.08
20	100	29	-0.87	-0.48
21	133	26	1.04	0.64
22	130	27	0.87	0.51
23	120	18	0.29	0.24
24	121	8	0.35	0.44

Statistics

Assigned Value	115	11
Spike	141	7
Robust Average	115	11
Median	120	7
Mean	114	
N	22	
Max.	141	
Min.	77	
Robust SD	20	
Robust CV	18%	

*Laboratory 5 has $|E_n| > 1$ when E_n is not rounded; this is an unsatisfactory E_n-score.


Kernel Density
Density
Result
Results: S2 - Toluene
Assigned Value = 115 ± 11 µg/L
Results (µg/L)
Laboratory
3 11 4 2 5 15 20 13 18 12 23 8 14 24 16 10 1 22 6 21 9 7 17 Md R.A. S.V.


z-Scores: S2 - Toluene
Target Standard Deviation 17 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
3 11 4 2 5 15 20 13 18 12 23 8 14 24 16 10 1 22 6 21 9 7

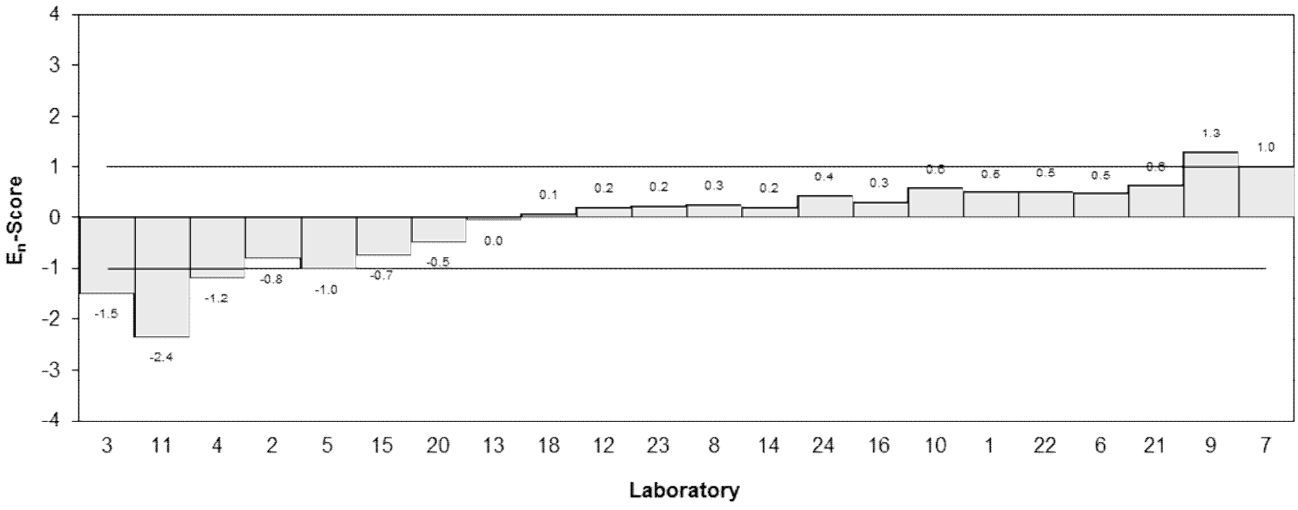

En-Scores: S2 - Toluene
En-Score
Laboratory
3 11 4 2 5 15 20 13 18 12 23 8 14 24 16 10 1 22 6 21 9 7

Figure 8

Table 15

Sample Details

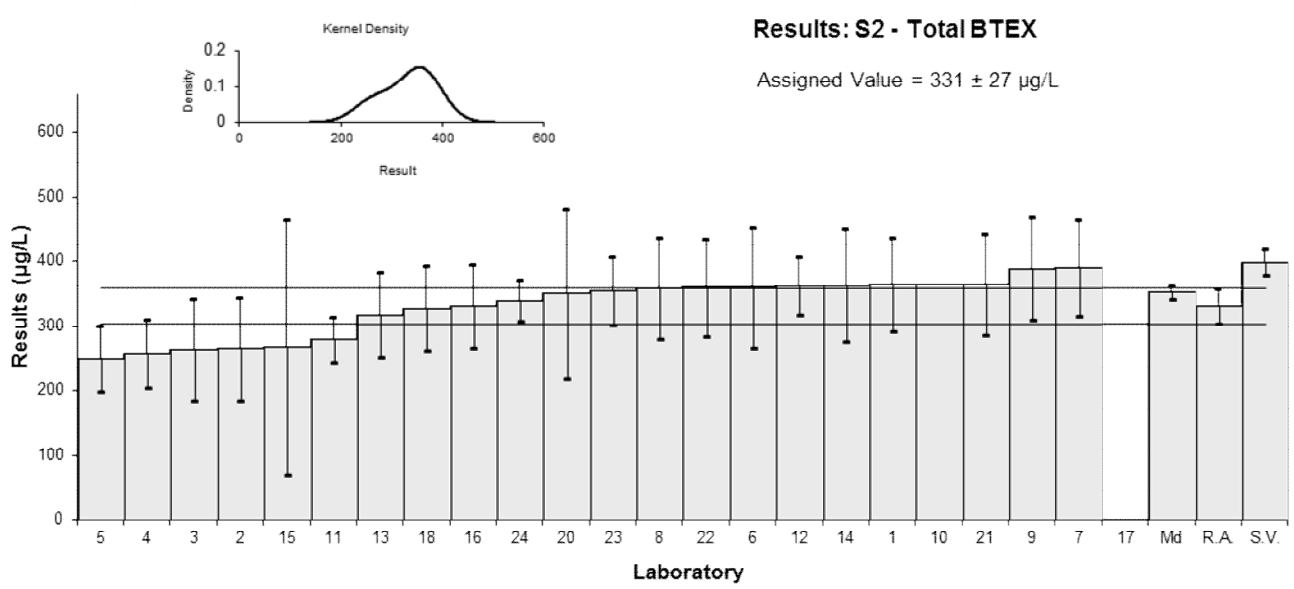
Sample No.	S2
Matrix.	Water
Analyte.	Total BTEX
Units	µg/L

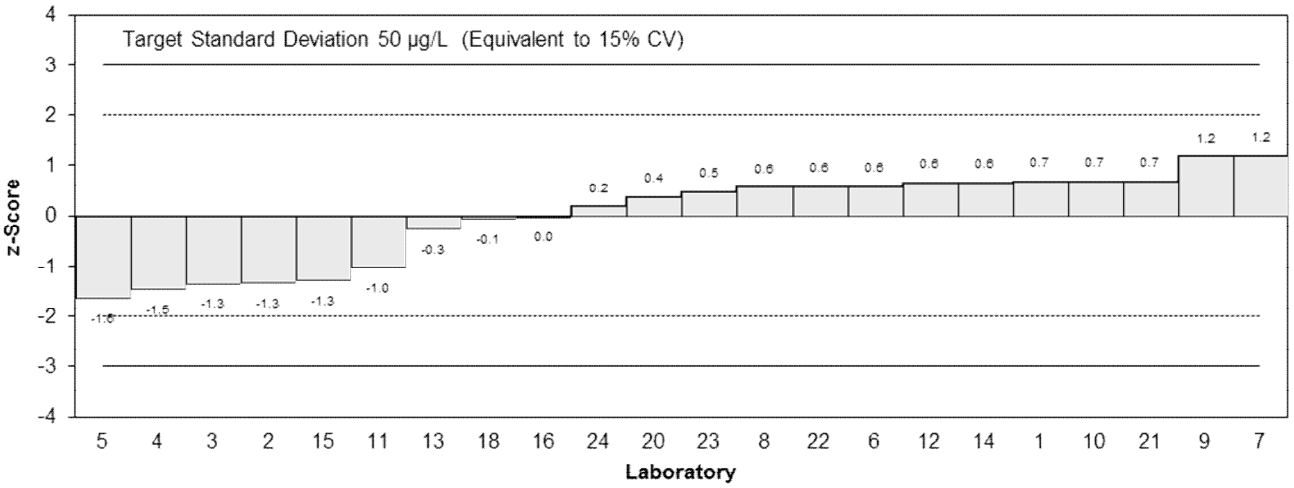
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	365	73	0.68	0.44
2	265	80	-1.33	-0.78
3	264	79	-1.35	-0.80
4	258	52	-1.47	-1.25
5	250	50	-1.63	-1.43
6	360	93.6	0.58	0.30
7	390	74.6	1.19	0.74
8	359	78.37	0.56	0.34
9	389.39	80	1.18	0.69
10	365	NR	0.68	1.26
11	280	35	-1.03	-1.15
12	363	44	0.64	0.62
13	318	66	-0.26	-0.18
14	363	87.3	0.64	0.35
15	267	197	-1.29	-0.32
16	330.4	64.5	-0.01	-0.01
17	NT	NT		
18	328	66	-0.06	-0.04
20	350	130	0.38	0.14
21	365	79	0.68	0.41
22	360	76	0.58	0.36
23	355	53	0.48	0.40
24	340	31	0.18	0.22

Statistics

Assigned Value	331	27
Spike	399	20
Robust Average	331	27
Median	353	11
Mean	331	
N	22	
Max.	390	
Min.	250	
Robust SD	51	
Robust CV	15%	


Kernel Density
Density
Result
Results: S2 - Total BTEX
Assigned Value = 331 ± 27 µg/L
Results (µg/L)
Laboratory
5 4 3 2 15 11 13 18 16 24 20 23 8 22 6 12 14 1 10 21 9 7 17 Md R.A. S.V.


z-Scores: S2 - Total BTEX
Target Standard Deviation 50 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
5 4 3 2 15 11 13 18 16 24 20 23 8 22 6 12 14 1 10 21 9 7

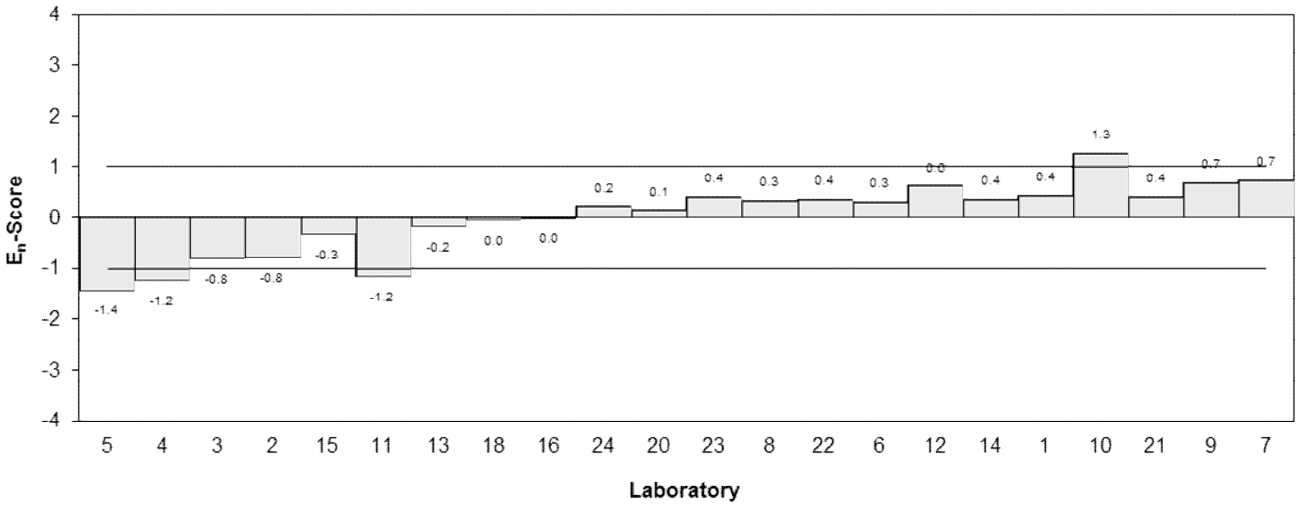

En-Scores: S2 - Total BTEX
En-Score
Laboratory
5 4 3 2 15 11 13 18 16 24 20 23 8 22 6 12 14 1 10 21 9 7

Figure 9

Table 16

Sample Details

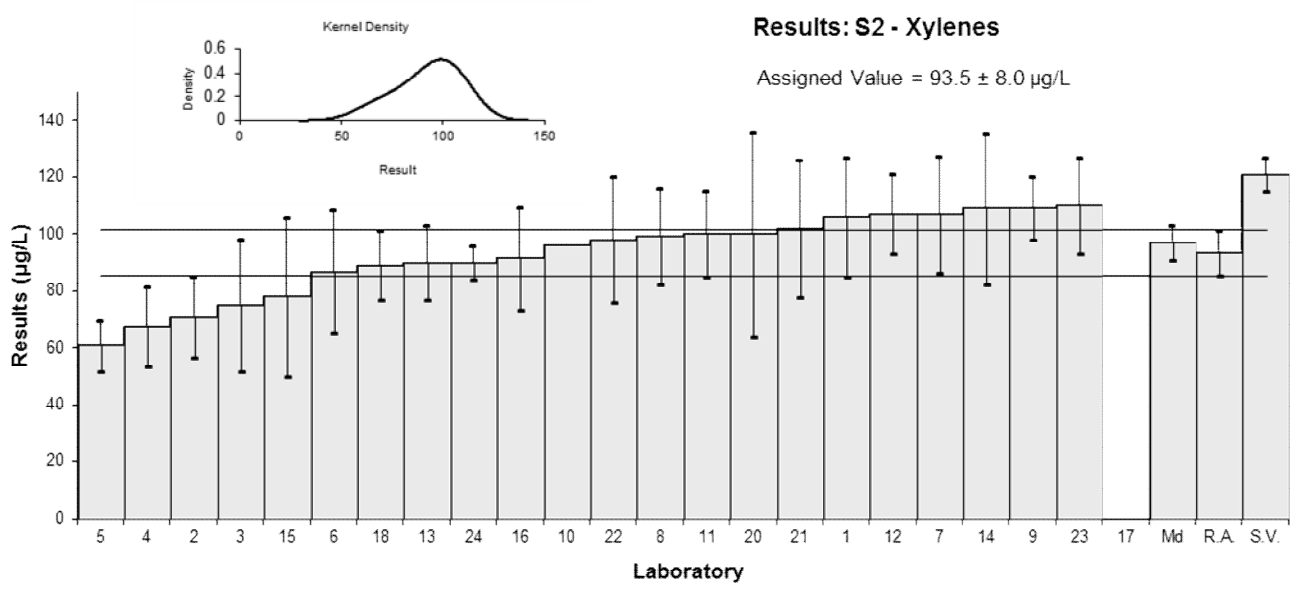
Sample No.	S2
Matrix.	Water
Analyte.	Xylenes
Units	µg/L

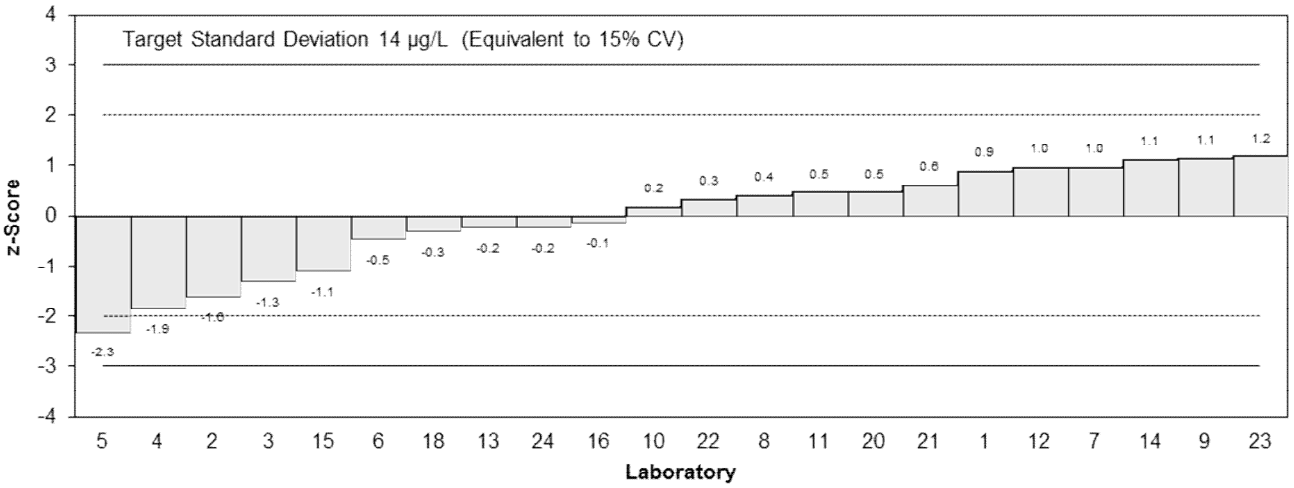
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	106	21	0.89	0.56
2	70.9	14	-1.61	-1.40
3	75	23	-1.32	-0.76
4	67.5	14	-1.85	-1.61
5	61	9	-2.32	-2.70
6	86.8	21.7	-0.48	-0.29
7	107	20.5	0.96	0.61
8	99.07	16.87	0.40	0.30
9	109.36	11	1.13	1.17
10	96	NR	0.18	0.31
11	100	15	0.46	0.38
12	107	14	0.96	0.84
13	90	13	-0.25	-0.23
14	109	26.4	1.11	0.56
15	78	28	-1.11	-0.53
16	91.4	18	-0.15	-0.11
17	NT	NT		
18	89.1	12	-0.31	-0.31
20	100	36	0.46	0.18
21	102	24	0.61	0.34
22	98	22	0.32	0.19
23	110	17	1.18	0.88
24	90	6	-0.25	-0.35

Statistics

Assigned Value	93.5	8.0
Spike	121	6
Robust Average	93.5	8.0
Median	97.0	6.2
Mean	92.9	
N	22	
Max.	110	
Min.	61	
Robust SD	15	
Robust CV	16%	


Kernel Density
Density
Result
Results: S2 - Xylenes
Assigned Value = 93.5 ± 8.0 µg/L
Results (µg/L)
Laboratory
5 4 2 3 15 6 18 13 24 16 10 22 8 11 20 21 1 12 7 14 9 23 17 Md R.A. S.V.


z-Scores: S2 - Xylenes
Target Standard Deviation 14 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
5 4 2 3 15 6 18 13 24 16 10 22 8 11 20 21 1 12 7 14 9 23

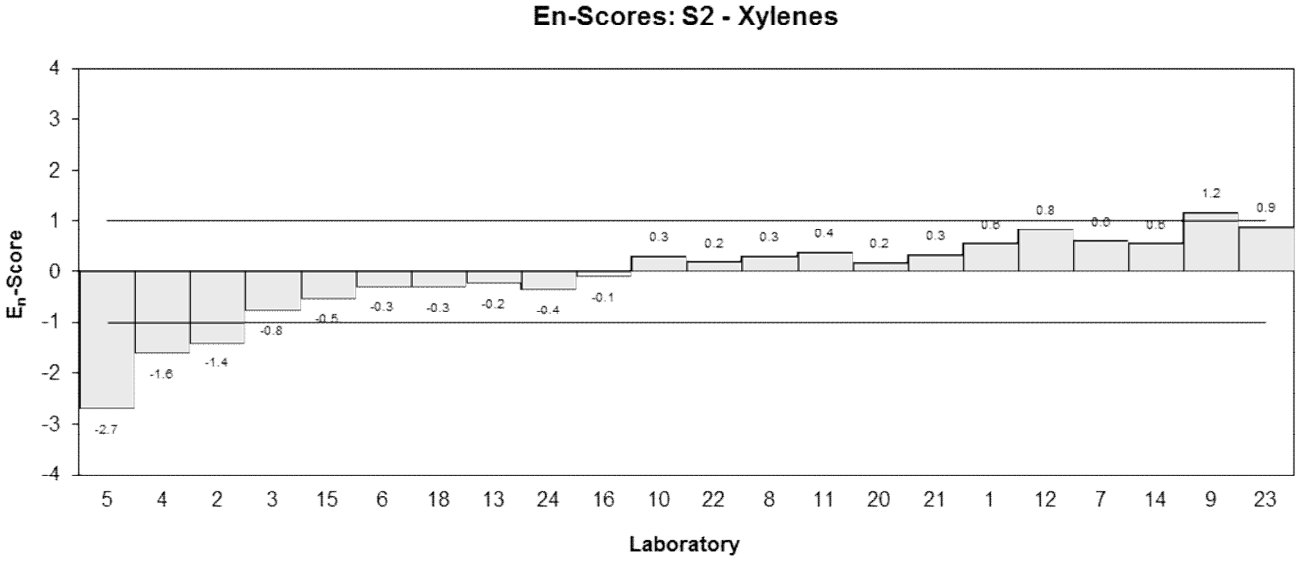

En-Scores: S2 - Xylenes
En-Score
Laboratory
5 4 2 3 15 6 18 13 24 16 10 22 8 11 20 21 1 12 7 14 9 23

Figure 10

Table 17

Sample Details

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

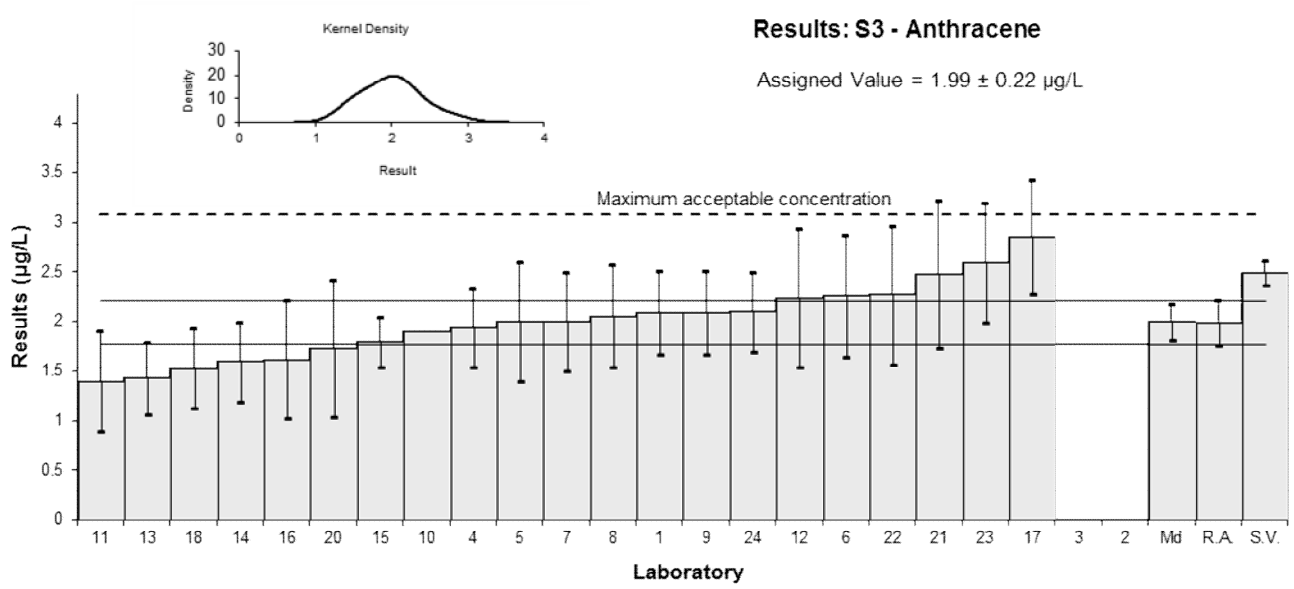
Participant Results

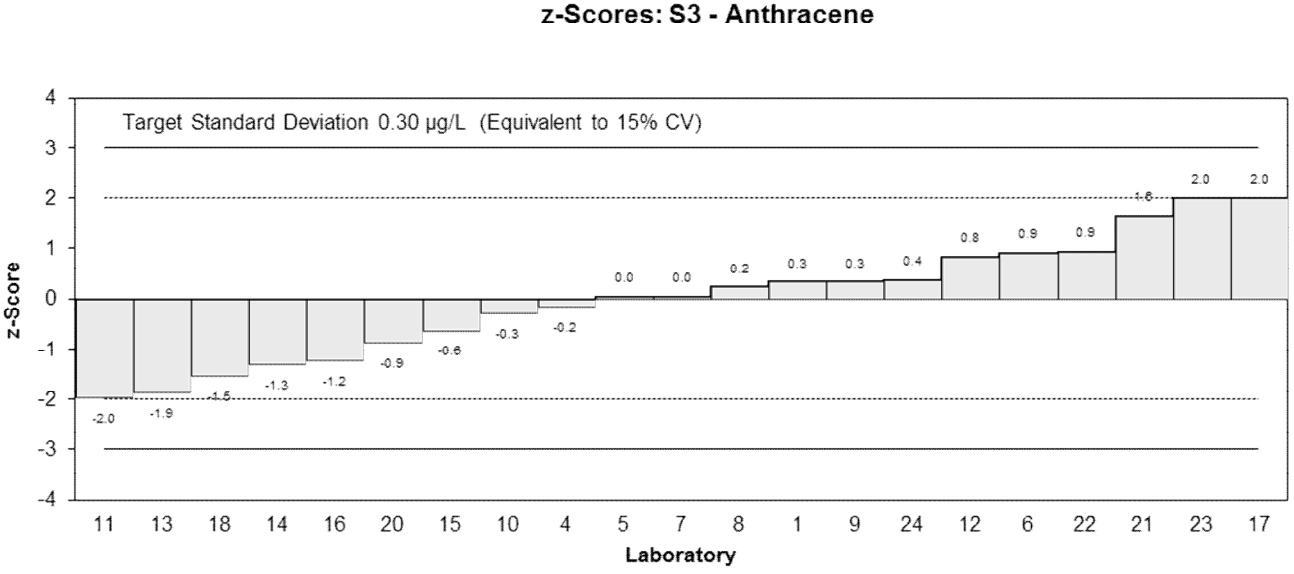
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.09	0.42	0.34	0.21
2	NT	NT		
3	<1	0.3		
4	1.94	0.39	-0.17	-0.11
5	2.0	0.6	0.03	0.02
6	2.26	0.61	0.90	0.42
7	2.0	0.5	0.03	0.02
8	2.06	0.52	0.23	0.12
9	2.09	0.42	0.34	0.21
10	1.9	NR	-0.30	-0.41
11	1.4	0.5	-1.98	-1.08
12	2.24	0.7	0.84	0.34
13	1.43	0.36	-1.88	-1.33
14	1.6	0.4	-1.31	-0.85
15	1.8	0.25	-0.64	-0.57
16	1.62	0.59	-1.24	-0.59
17*	2.855	0.571	2.00	1.00
18	1.53	0.4	-1.54	-1.01
20	1.73	0.69	-0.87	-0.36
21	2.48	0.74	1.64	0.63
22	2.27	0.7	0.94	0.38
23*	2.6	0.6	2.00	0.95
24	2.1	0.4	0.37	0.24

Statistics

Assigned Value	1.99	0.22
Spike	2.49	0.12
Maximum acceptable conc.*	3.09	
Robust Average	1.99	0.22
Median	2.00	0.18
Mean	2.00	
N	21	
Max.	2.855	
Min.	1.4	
Robust SD	0.40	
Robust CV	20%	

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


Kernel Density
Density
Result
Results: S3 - Anthracene
Assigned Value = 1.99 ± 0.22 µg/L
Maximum acceptable concentration
Results (µg/L)
Laboratory
11 13 18 14 16 20 15 10 4 5 7 8 1 9 24 12 6 22 21 23 17 3 2 Md R.A. S.V.


z-Scores: S3 - Anthracene
Target Standard Deviation 0.30 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 13 18 14 16 20 15 10 4 5 7 8 1 9 24 12 6 22 21 23 17
-2.0 -1.9 -1.5 -1.3 -1.2 -0.9 -0.6 -0.3 -0.2 0.0 0.0 0.2 0.3 0.3 0.4 0.8 0.9 0.9 1.6 2.0 2.0

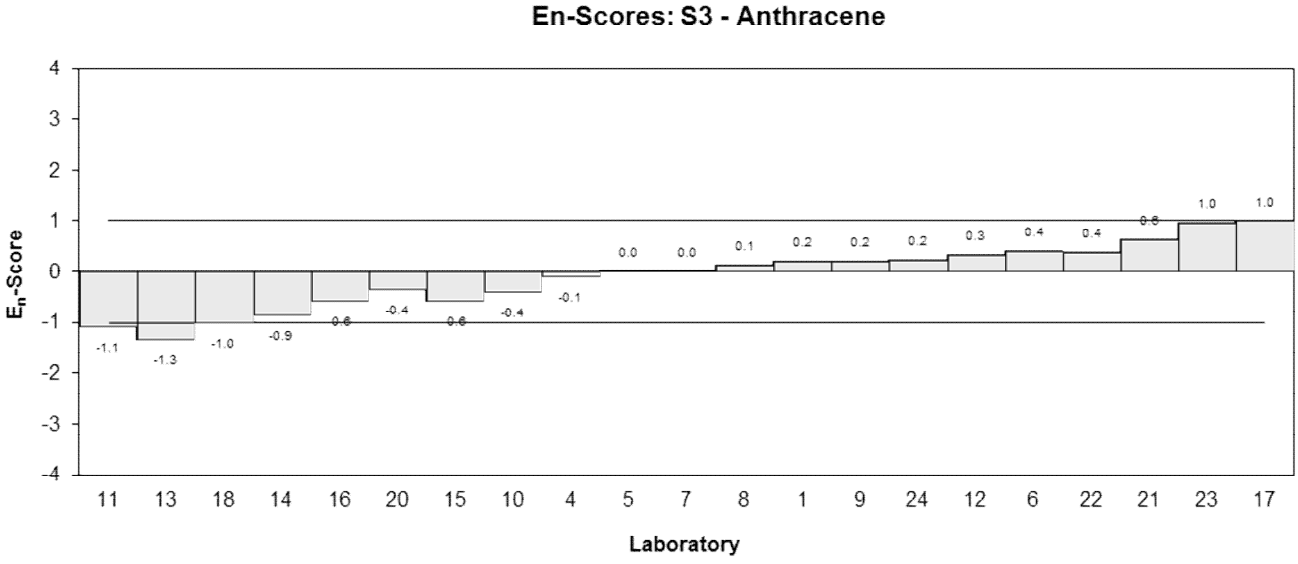

En-Scores: S3 - Anthracene
En-Score
Laboratory
11 13 18 14 16 20 15 10 4 5 7 8 1 9 24 12 6 22 21 23 17
-1.1 -1.3 -1.0 -0.9 -0.6 -0.4 -0.6 -0.4 -0.1 0.0 0.0 0.1 0.2 0.2 0.2 0.3 0.4 0.4 0.6 1.0 1.0

Figure 11

Table 18

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	3.21	0.64	-0.06	-0.04
2	NT	NT		
3	<1	0.3		
4	3.32	0.66	0.16	0.10
5	3.4	1.1	0.33	0.14
6	3.85	1.19	1.26	0.48
7	3.5	0.9	0.53	0.26
8	2.98	0.69	-0.53	-0.32
9	3.87	0.77	1.30	0.72
10	3.6	NR	0.74	0.86
11	1.7	0.5	-3.17	-2.36
12	3.27	1.1	0.06	0.03
13	0.77	0.19	-5.08	-5.36
14	4.2	1.1	1.98	0.82
15	2.2	0.5	-2.14	-1.59
16	2.3	1.1	-1.93	-0.80
17	3.765	0.753	1.08	0.61
18	2.61	0.7	-1.30	-0.77
20	2.5	0.72	-1.52	-0.89
21	3.31	0.99	0.14	0.07
22	3.23	0.98	-0.02	-0.01
23*	NR	NR		
24***	4.4	1.1	2.00	0.99

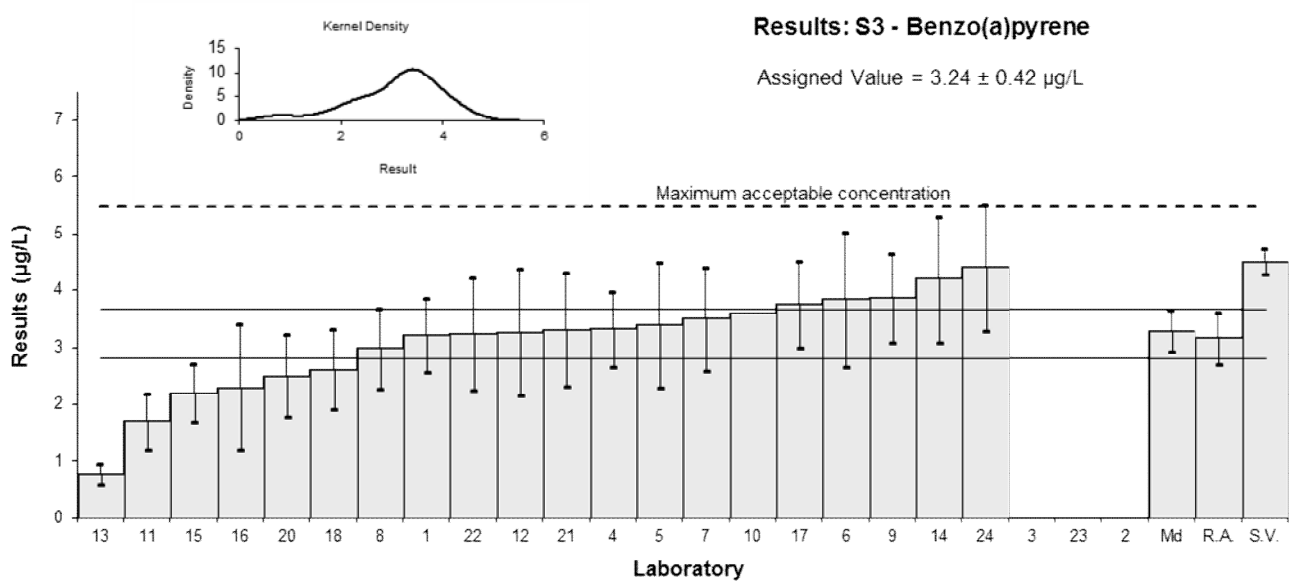
*Result changed from 0 to NR.

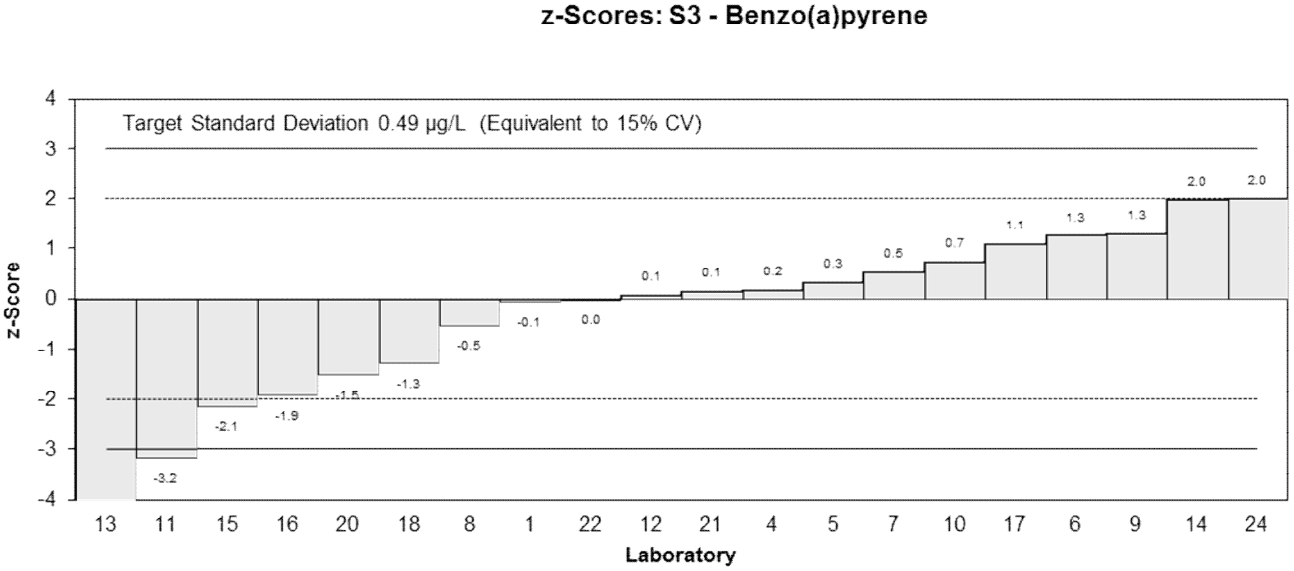
Statistics

Assigned Value**	3.24	0.42
Spike	4.51	0.23
Maximum acceptable conc.***	5.5	
Robust Average	3.17	0.45
Median	3.29	0.36
Mean	3.10	
N	20	
Max.	4.4	
Min.	0.77	
Robust SD	0.74	
Robust CV	23%	

**Robust average excluding laboratory 13.

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


Kernel Density
Density
Result
Results: S3 - Benzo(a)pyrene
Assigned Value = 3.24 ± 0.42 µg/L
Maximum acceptable concentration
Results (µg/L)
13 11 15 16 20 18 8 1 22 12 21 4 5 7 10 17 6 9 14 24 3 23 2 Md R.A. S.V.
Laboratory


z-Scores: S3 - Benzo(a)pyrene
Target Standard Deviation 0.49 µg/L (Equivalent to 15% CV)
z-Score
-3.2 -2.1 -1.9 -1.5 -1.3 -0.5 -0.1 0.0 0.1 0.1 0.2 0.3 0.5 0.7 1.1 1.3 1.3 2.0 2.0
13 11 15 16 20 18 8 1 22 12 21 4 5 7 10 17 6 9 14 24
Laboratory

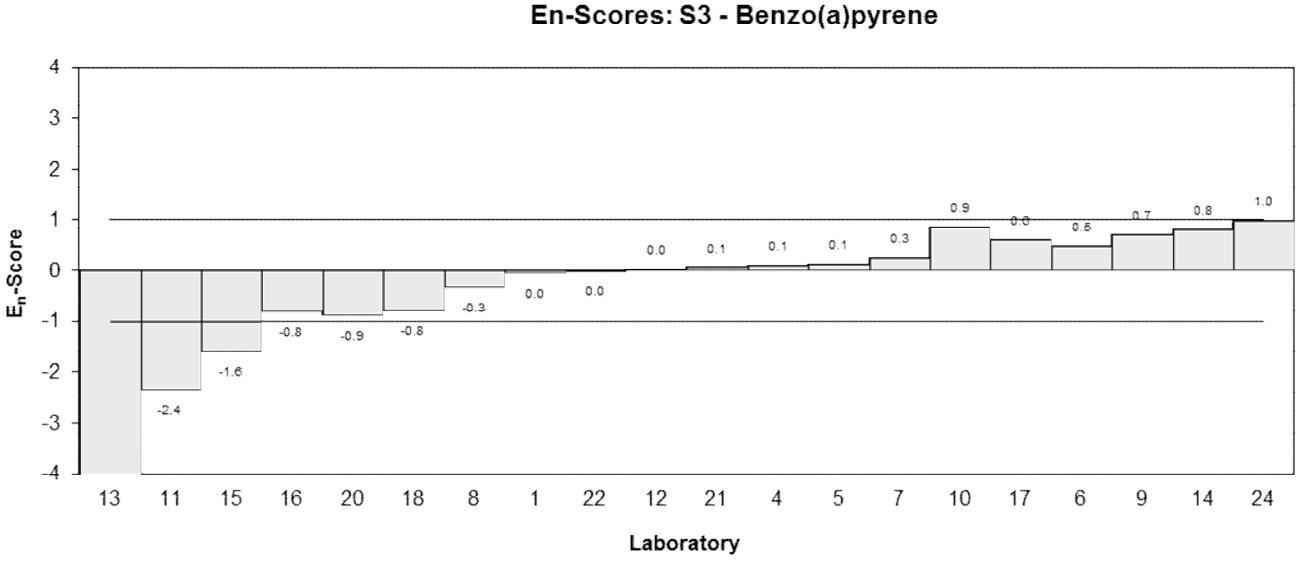

En-Scores: S3 - Benzo(a)pyrene
En-Score
-2.4 -1.6 -0.8 -0.9 -0.8 -0.3 0.0 0.0 0.0 0.1 0.1 0.1 0.3 0.9 0.6 0.5 0.7 0.8 1.0
13 11 15 16 20 18 8 1 22 12 21 4 5 7 10 17 6 9 14 24
Laboratory

Figure 12

Table 19

Sample Details

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

Participant Results

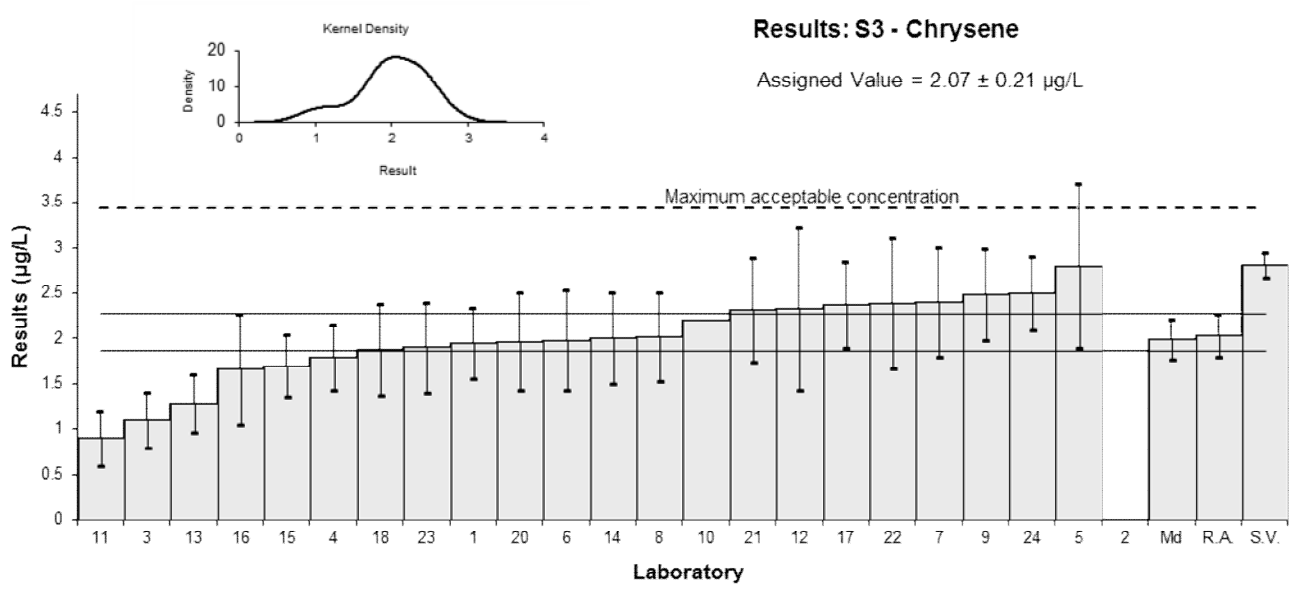
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.95	0.39	-0.39	-0.27
2	NT	NT		
3	1.1	0.3	-3.12	-2.65
4	1.80	0.36	-0.87	-0.65
5**	2.8	0.9	2.00	0.79
6	1.98	0.55	-0.29	-0.15
7	2.4	0.6	1.06	0.52
8	2.02	0.49	-0.16	-0.09
9	2.48	0.50	1.32	0.76
10	2.2	NR	0.42	0.62
11	0.9	0.3	-3.77	-3.20
12	2.33	0.9	0.84	0.28
13	1.29	0.32	-2.51	-2.04
14	2.0	0.5	-0.23	-0.13
15	1.7	0.34	-1.19	-0.93
16	1.66	0.60	-1.32	-0.64
17	2.368	0.474	0.96	0.57
18	1.88	0.5	-0.61	-0.35
20	1.97	0.53	-0.32	-0.18
21	2.32	0.57	0.81	0.41
22	2.39	0.72	1.03	0.43
23	1.9	0.5	-0.55	-0.31
24	2.5	0.4	1.38	0.95

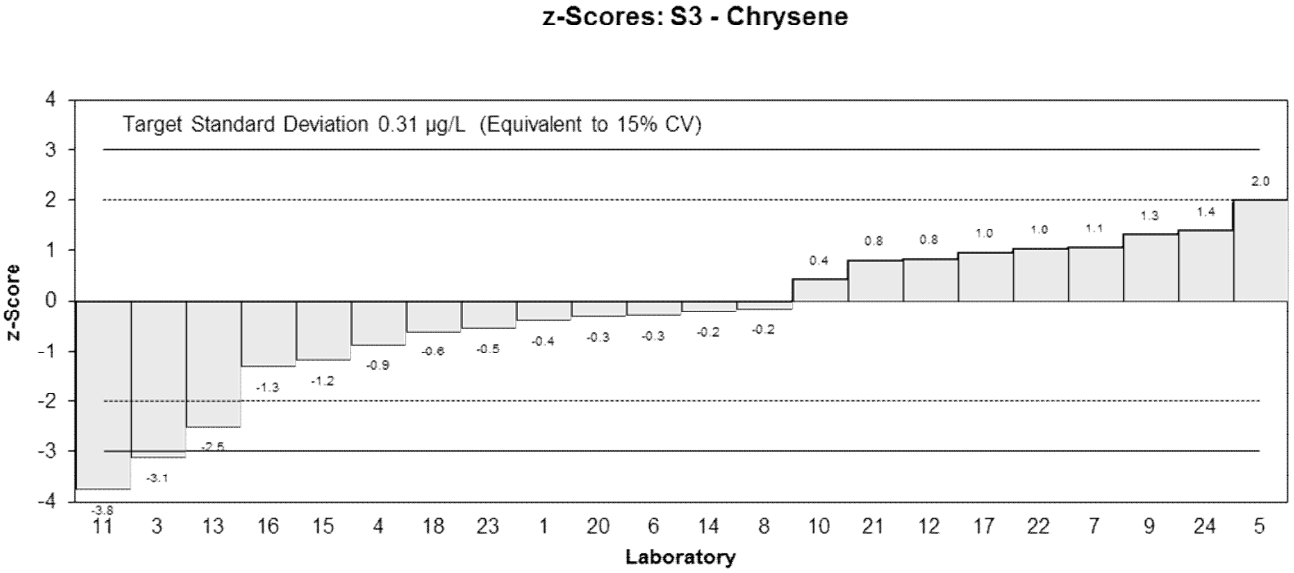
Statistics

Assigned Value*	2.07	0.21
Spike	2.81	0.14
Maximum acceptable conc.**	3.43	
Robust Average	2.03	0.23
Median	1.99	0.22
Mean	2.00	
N	22	
Max.	2.8	
Min.	0.9	
Robust SD	0.38	
Robust CV	18%	

*Robust average excluding laboratory 11.

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


Kernel Density
Density
Result
Results: S3 - Chrysene
Assigned Value = 2.07 ± 0.21 µg/L
Maximum acceptable concentration
Results (µg/L)
11 3 13 16 15 4 18 23 1 20 6 14 8 10 21 12 17 22 7 9 24 5 2 Md R.A. S.V.
Laboratory


z-Scores: S3 - Chrysene
Target Standard Deviation 0.31 µg/L (Equivalent to 15% CV)
z-Score
11 3 13 16 15 4 18 23 1 20 6 14 8 10 21 12 17 22 7 9 24 5
Laboratory

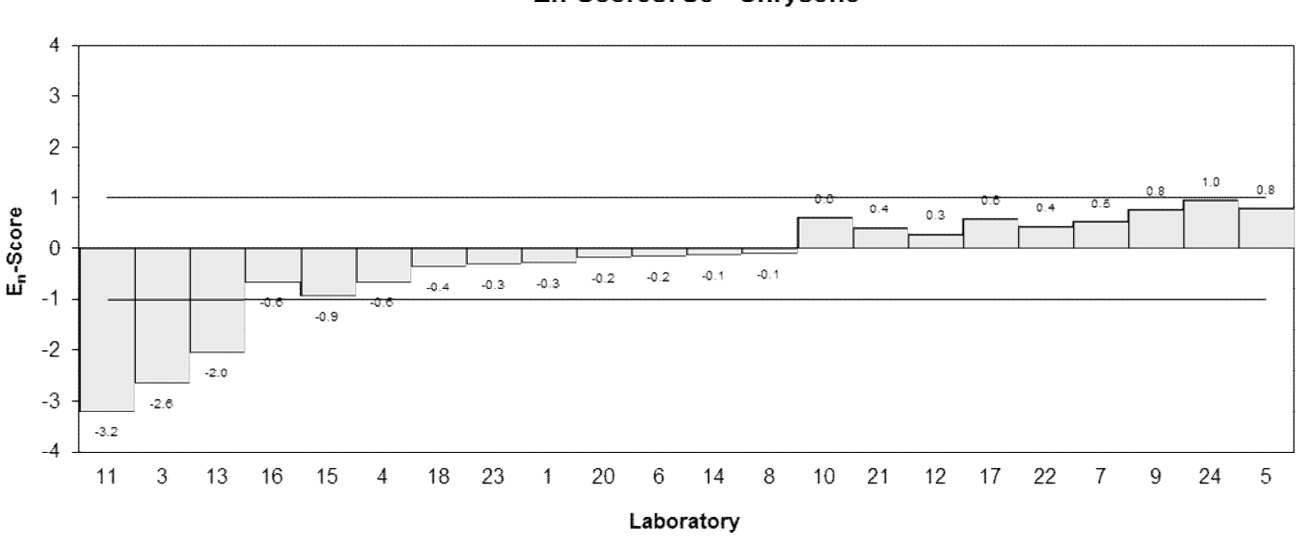

En-Scores: S3 - Chrysene
En-Score
11 3 13 16 15 4 18 23 1 20 6 14 8 10 21 12 17 22 7 9 24 5
Laboratory

Figure 13

Table 20

Sample Details

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

Participant Results

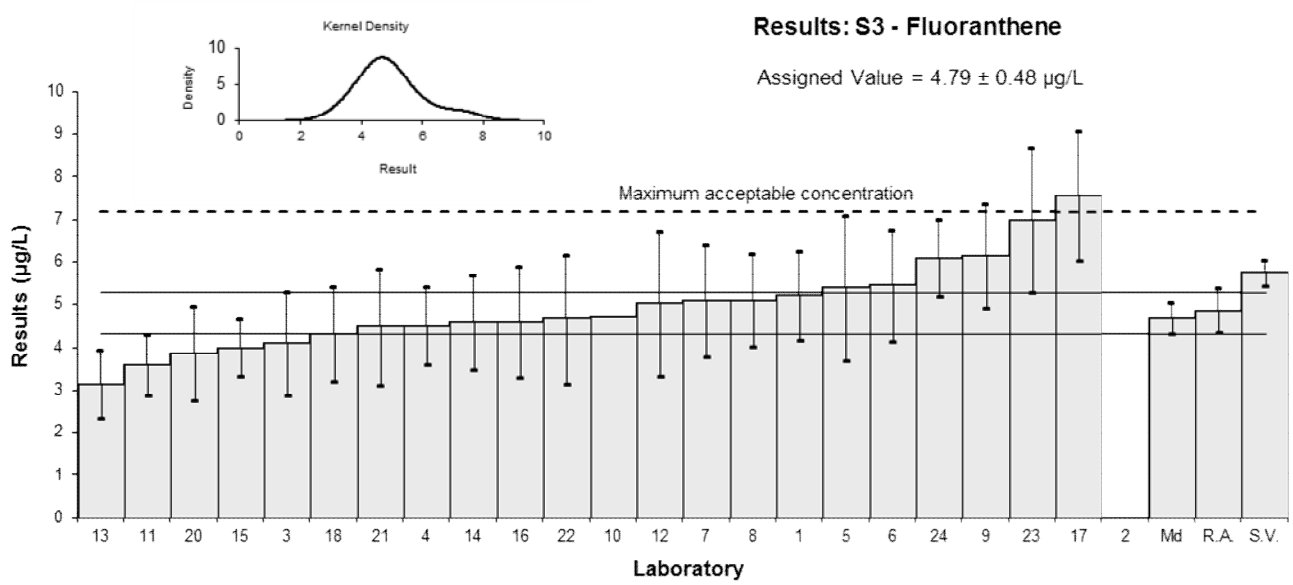
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5.22	1.04	0.60	0.38
2	NT	NT		
3	4.1	1.2	-0.96	-0.53
4	4.51	0.90	-0.39	-0.27
5	5.4	1.7	0.85	0.35
6	5.46	1.31	0.93	0.48
7	5.1	1.3	0.43	0.22
8	5.11	1.08	0.45	0.27
9	6.15	1.23	1.89	1.03
10	4.7	NR	-0.13	-0.19
11	3.6	0.7	-1.66	-1.40
12	5.03	1.7	0.33	0.14
13	3.15	0.79	-2.28	-1.77
14	4.6	1.1	-0.26	-0.16
15	4.0	0.67	-1.10	-0.96
16	4.6	1.3	-0.26	-0.14
17	7.571	1.514	3.87	1.75
18	4.33	1.1	-0.64	-0.38
20	3.86	1.1	-1.29	-0.77
21	4.49	1.35	-0.42	-0.21
22	4.67	1.51	-0.17	-0.08
23**	7.0	1.7	2.00	1.00
24	6.1	0.9	1.82	1.28

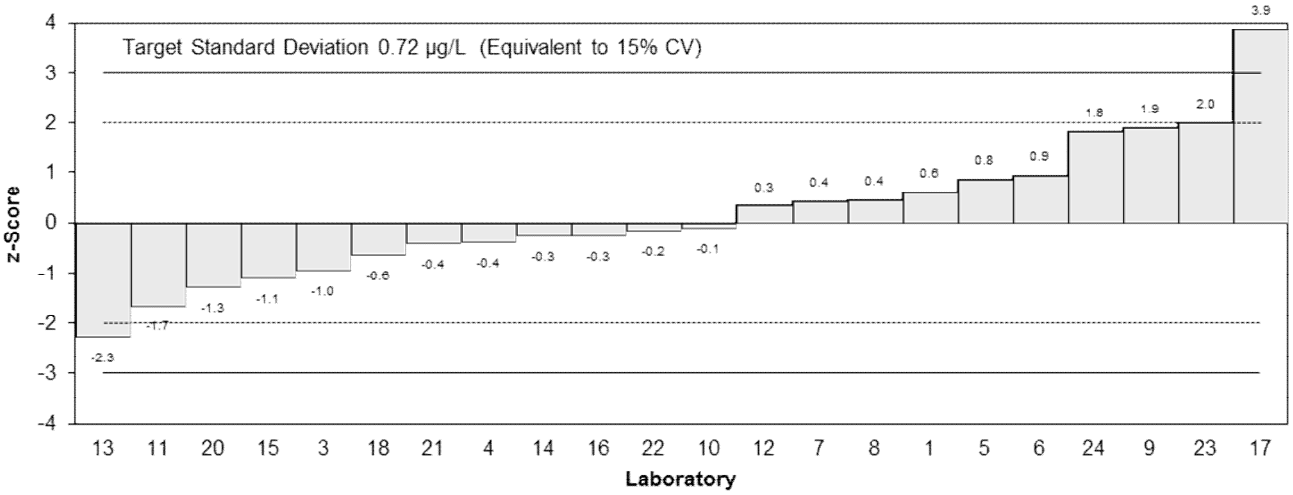
Statistics

Assigned Value*	4.79	0.48
Spike	5.75	0.29
Maximum acceptable conc.**	7.19	
Robust Average	4.87	0.51
Median	4.69	0.37
Mean	4.94	
N	22	
Max.	7.571	
Min.	3.15	
Robust SD	0.88	
Robust CV	18%	

*Robust average excluding laboratory 17.

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


Kernel Density
Density
Result
Results: S3 - Fluoranthene
Assigned Value = 4.79 ± 0.48 µg/L
Maximum acceptable concentration
Results (µg/L)
13 11 20 15 3 18 21 4 14 16 22 10 12 7 8 1 5 6 24 9 23 17 2 Md R.A. S.V.
Laboratory


z-Scores: S3 - Fluoranthene
Target Standard Deviation 0.72 µg/L (Equivalent to 15% CV)
z-Score
13 11 20 15 3 18 21 4 14 16 22 10 12 7 8 1 5 6 24 9 23 17
Laboratory

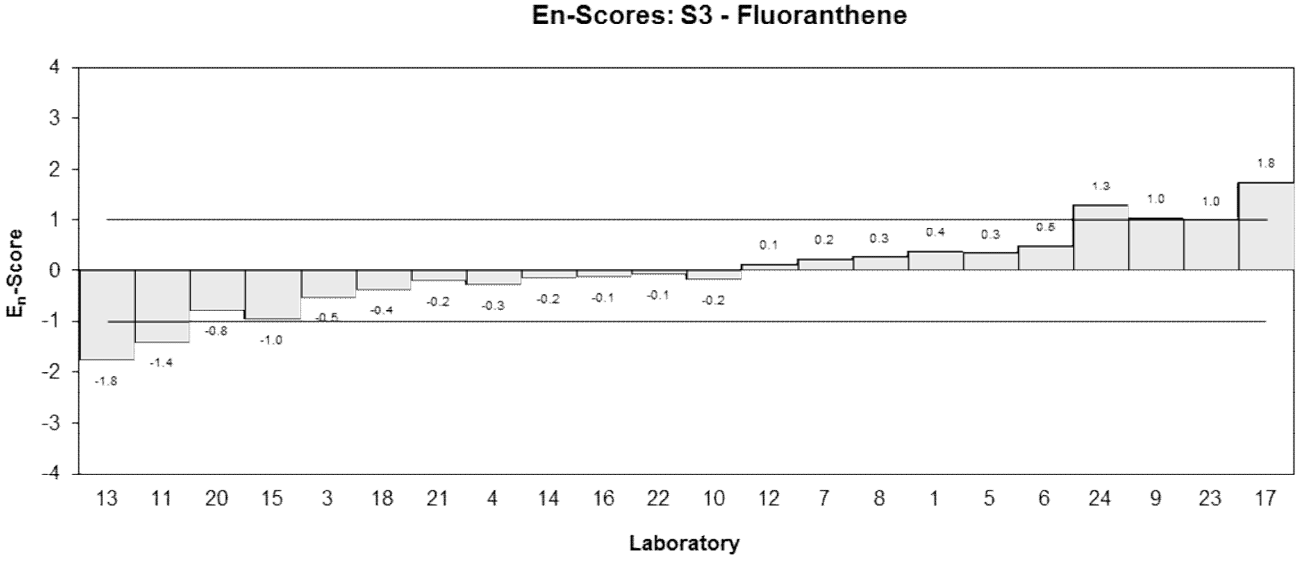

En-Scores: S3 - Fluoranthene
En-Score
13 11 20 15 3 18 21 4 14 16 22 10 12 7 8 1 5 6 24 9 23 17
Laboratory

Figure 14

Table 21

Sample Details

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

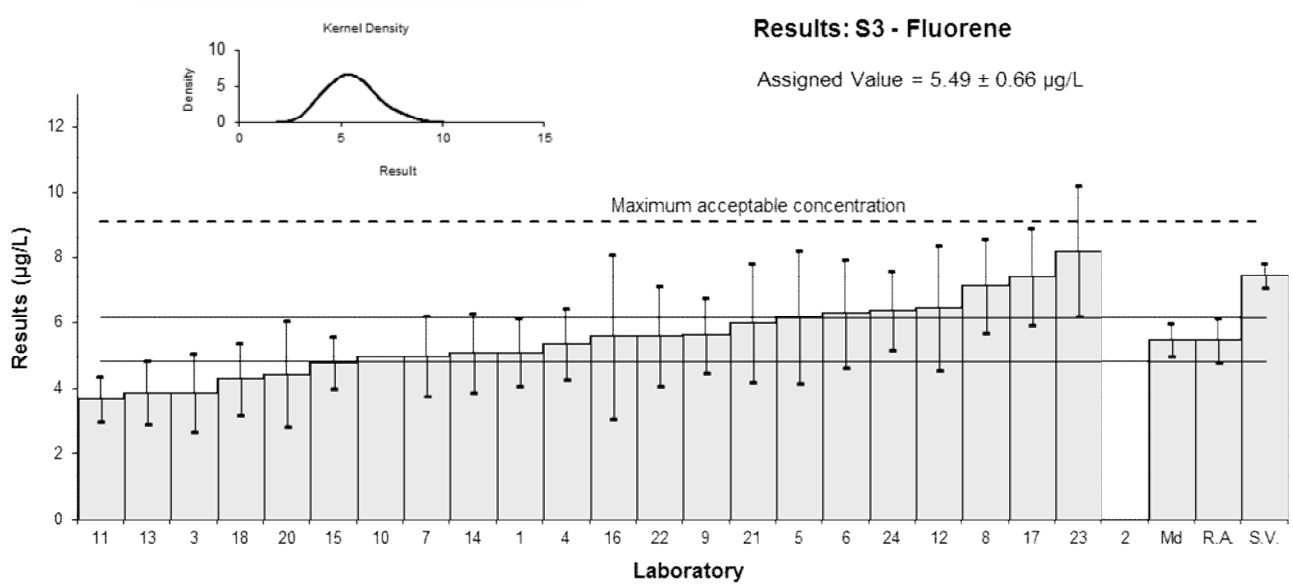
Participant Results

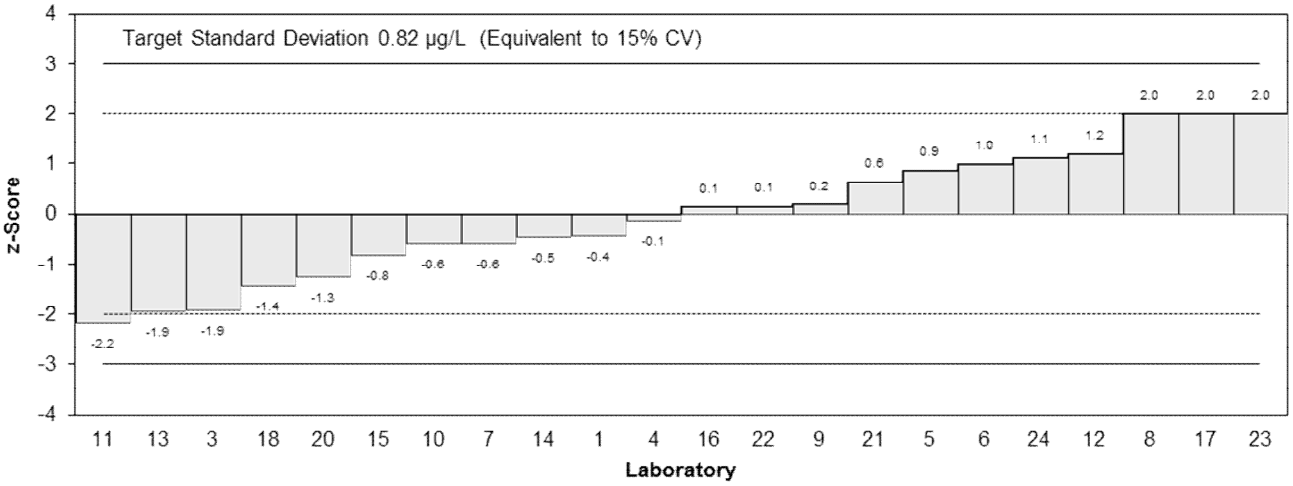
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5.12	1.02	-0.45	-0.30
2	NT	NT		
3	3.9	1.2	-1.93	-1.16
4	5.38	1.08	-0.13	-0.09
5	6.2	2.0	0.86	0.34
6	6.31	1.64	1.00	0.46
7	5.0	1.2	-0.60	-0.36
8*	7.14	1.44	2.00	1.00
9	5.64	1.13	0.18	0.11
10	5.0	NR	-0.60	-0.74
11	3.7	0.7	-2.17	-1.86
12	6.47	1.9	1.19	0.49
13	3.89	0.97	-1.94	-1.36
14	5.1	1.2	-0.47	-0.28
15	4.8	0.78	-0.84	-0.68
16	5.6	2.5	0.13	0.04
17*	7.415	1.483	2.00	1.00
18	4.31	1.1	-1.43	-0.92
20	4.45	1.6	-1.26	-0.60
21	6.01	1.80	0.63	0.27
22	5.61	1.52	0.15	0.07
23*	8.2	2.0	2.00	1.00
24	6.4	1.2	1.11	0.66

Statistics

Assigned Value	5.49	0.66
Spike	7.46	0.37
Maximum acceptable conc.*	9.1	
Robust Average	5.49	0.66
Median	5.49	0.50
Mean	5.53	
N	22	
Max.	8.2	
Min.	3.7	
Robust SD	1.2	
Robust CV	22%	

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


Kernel Density
Density
Result
Results: S3 - Fluorene
Assigned Value = 5.49 ± 0.66 µg/L
Maximum acceptable concentration
Results (µg/L)
11 13 3 18 20 15 10 7 14 1 4 16 22 9 21 5 6 24 12 8 17 23 2 Md R.A. S.V.
Laboratory


z-Scores: S3 - Fluorene
Target Standard Deviation 0.82 µg/L (Equivalent to 15% CV)
z-Score
11 13 3 18 20 15 10 7 14 1 4 16 22 9 21 5 6 24 12 8 17 23
Laboratory

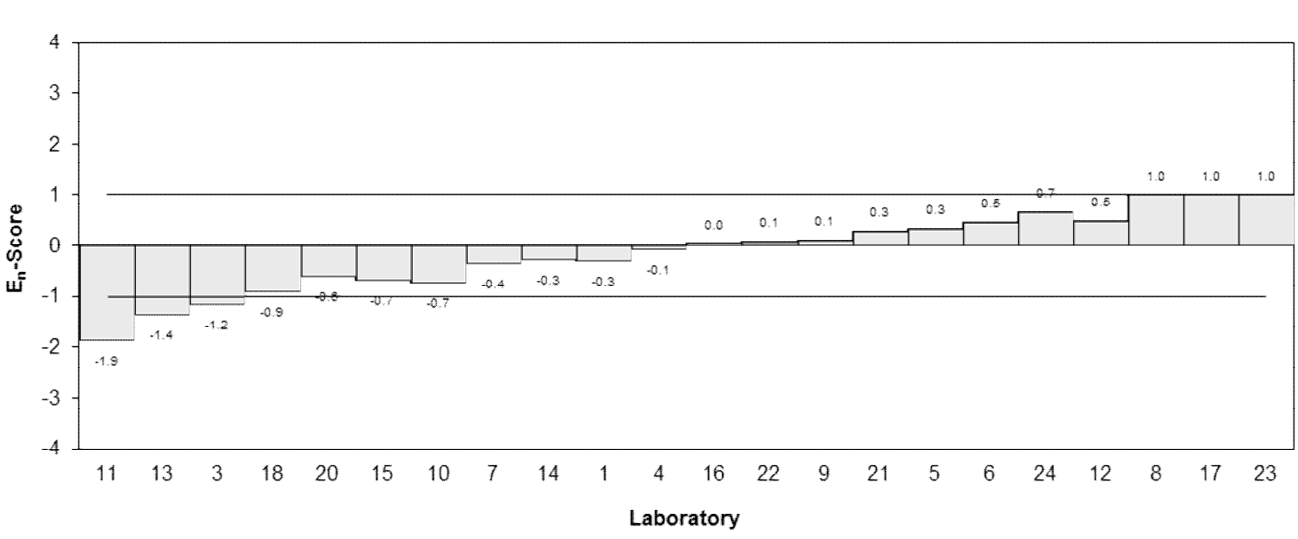

En-Scores: S3 - Fluorene
En-Score
11 13 3 18 20 15 10 7 14 1 4 16 22 9 21 5 6 24 12 8 17 23
Laboratory

Figure 15

Table 22

Sample Details

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

Participant Results

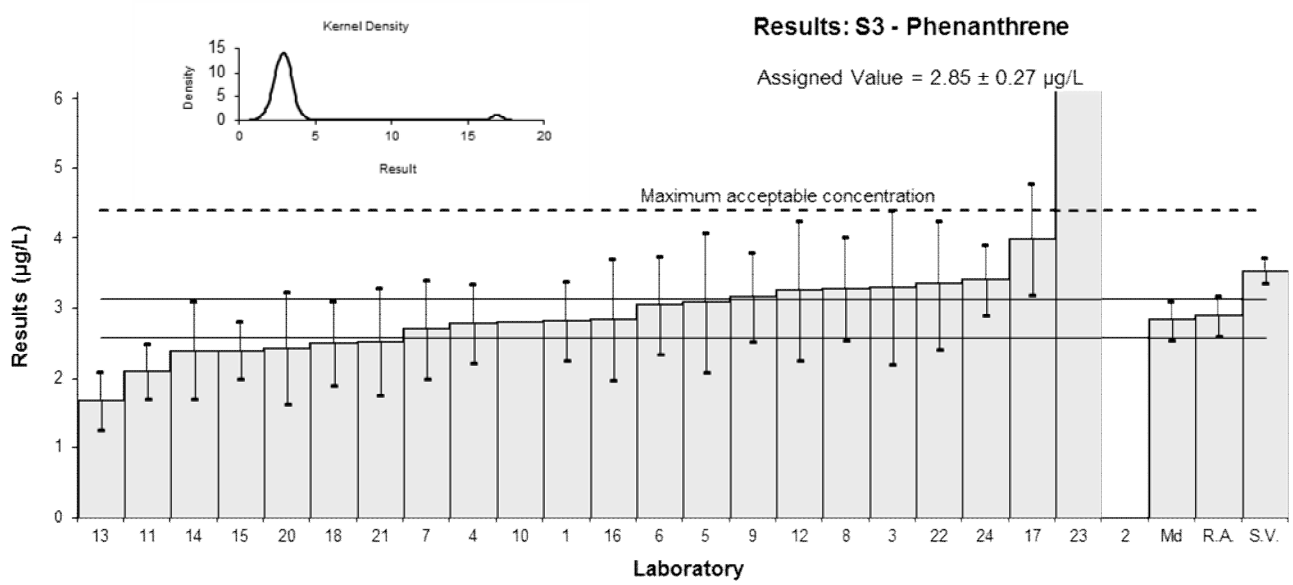
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.82	0.56	-0.07	-0.05
2	NT	NT		
3	3.3	1.1	1.05	0.40
4	2.78	0.56	-0.16	-0.11
5	3.1	1.0	0.58	0.24
6	3.05	0.70	0.47	0.27
7	2.7	0.7	-0.35	-0.20
8	3.28	0.73	1.01	0.55
9	3.16	0.63	0.73	0.45
10	2.8	NR	-0.12	-0.19
11	2.1	0.4	-1.75	-1.55
12	3.25	1.0	0.94	0.39
13	1.68	0.42	-2.74	-2.34
14	2.4	0.7	-1.05	-0.60
15	2.4	0.4	-1.05	-0.93
16	2.84	0.86	-0.02	-0.01
17**	3.987	0.797	2.00	1.00
18	2.51	0.6	-0.80	-0.52
20	2.43	0.8	-0.98	-0.50
21	2.52	0.76	-0.77	-0.41
22	3.34	0.91	1.15	0.52
23	16.9	4.1	32.87	3.42
24	3.4	0.5	1.29	0.97

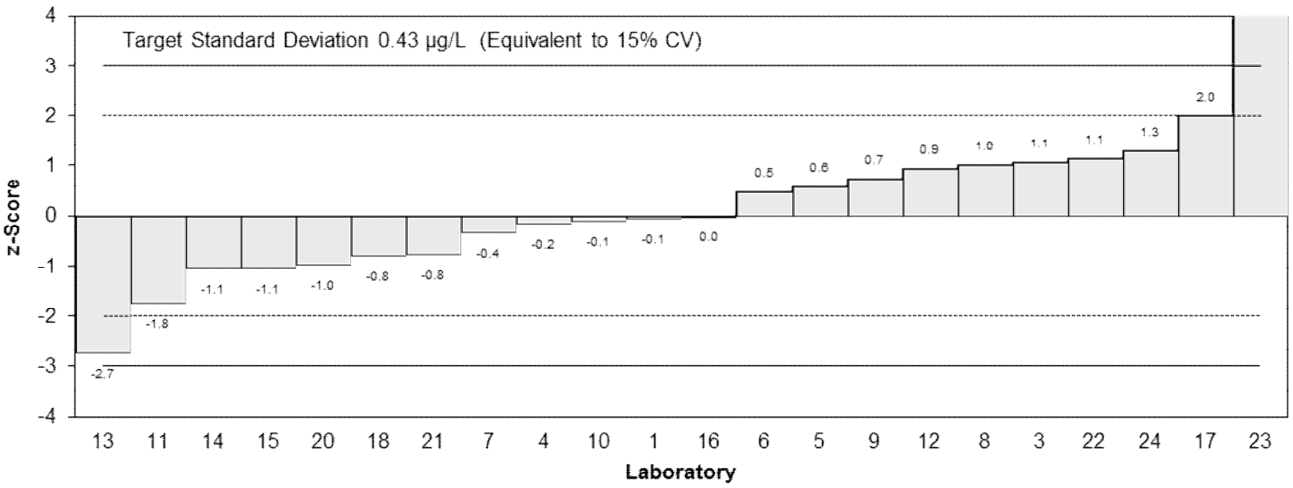
Statistics

Assigned Value*	2.85	0.27
Spike	3.54	0.18
Maximum acceptable conc.**	4.40	
Robust Average	2.89	0.28
Median	2.83	0.27
Mean	3.49	
N	22	
Max.	16.9	
Min.	1.68	
Robust SD	0.49	
Robust CV	17%	

*Robust average excluding laboratory 23.

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


Kernel Density
Density
Result
Results: S3 - Phenanthrene
Assigned Value = 2.85 ± 0.27 µg/L
Maximum acceptable concentration
Results (µg/L)
Laboratory
13 11 14 15 20 18 21 7 4 10 1 16 6 5 9 12 8 3 22 24 17 23 2 Md R.A. S.V.


z-Scores: S3 - Phenanthrene
Target Standard Deviation 0.43 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
13 11 14 15 20 18 21 7 4 10 1 16 6 5 9 12 8 3 22 24 17 23

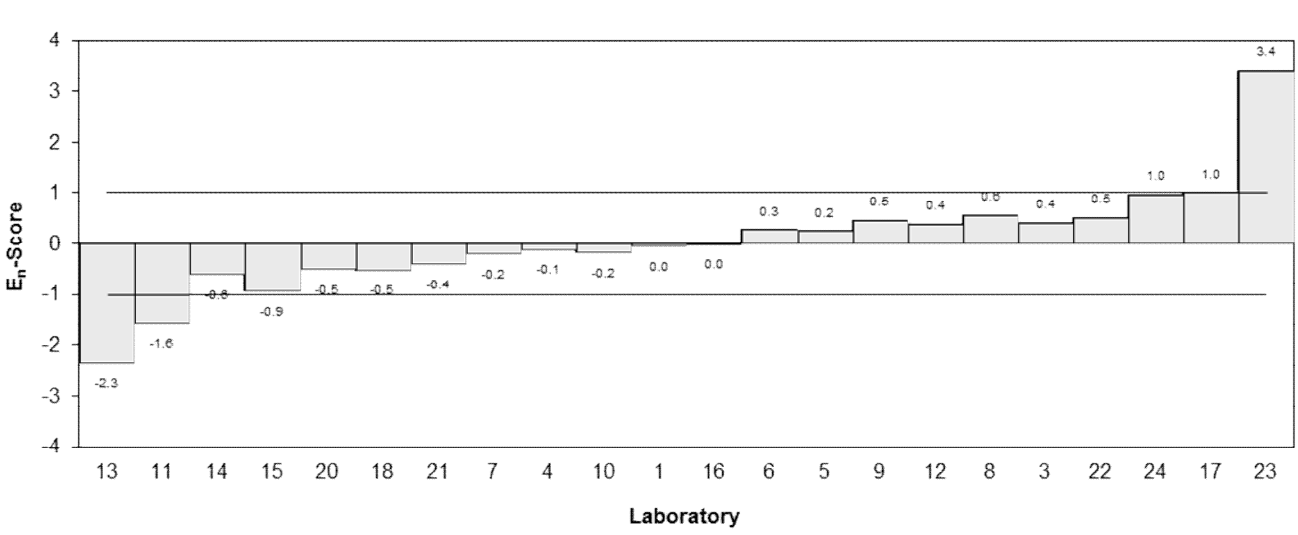

En-Scores: S3 - Phenanthrene
En-Score
Laboratory
13 11 14 15 20 18 21 7 4 10 1 16 6 5 9 12 8 3 22 24 17 23

Figure 16

Table 23

Sample Details

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

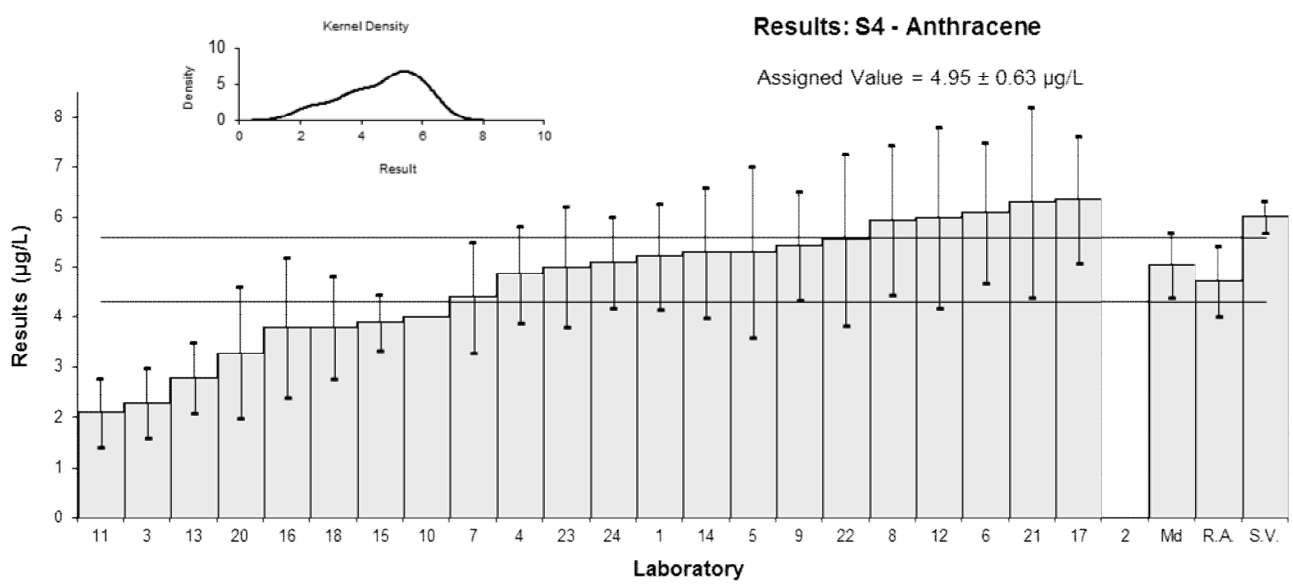
Participant Results

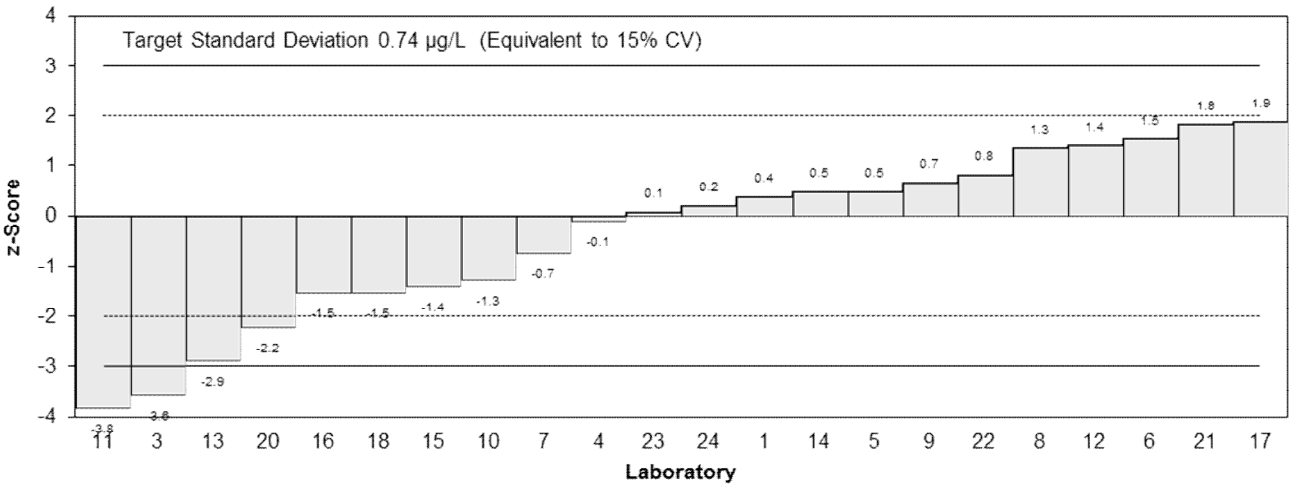
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5.22	1.04	0.36	0.22
2	NT	NT		
3	2.3	0.7	-3.57	-2.81
4	4.87	0.97	-0.11	-0.07
5	5.3	1.7	0.47	0.19
6	6.09	1.40	1.54	0.74
7	4.4	1.1	-0.74	-0.43
8	5.95	1.50	1.35	0.61
9	5.44	1.09	0.66	0.39
10	4.0	NR	-1.28	-1.51
11	2.1	0.7	-3.84	-3.03
12	5.99	1.8	1.40	0.55
13	2.80	0.7	-2.90	-2.28
14	5.3	1.3	0.47	0.24
15	3.9	0.54	-1.41	-1.27
16	3.8	1.4	-1.55	-0.75
17	6.345	1.269	1.88	0.98
18	3.80	1.0	-1.55	-0.97
20	3.3	1.3	-2.22	-1.14
21	6.3	1.9	1.82	0.67
22	5.55	1.72	0.81	0.33
23	5	1.2	0.07	0.04
24	5.1	0.9	0.20	0.14

Statistics

Assigned Value*	4.95	0.63
Spike	6.01	0.30
Robust Average	4.72	0.71
Median	5.05	0.65
Mean	4.68	
N	22	
Max.	6.345	
Min.	2.1	
Robust SD	1.1	
Robust CV	23%	

*Robust average excluding laboratories 3 and 11.


Kernel Density
Density
Result
Results: S4 - Anthracene
Assigned Value = 4.95 ± 0.63 µg/L
Results (µg/L)
Laboratory
11 3 13 20 16 18 15 10 7 4 23 24 1 14 5 9 22 8 12 6 21 17 2 Md R.A. S.V.


z-Scores: S4 - Anthracene
Target Standard Deviation 0.74 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 3 13 20 16 18 15 10 7 4 23 24 1 14 5 9 22 8 12 6 21 17

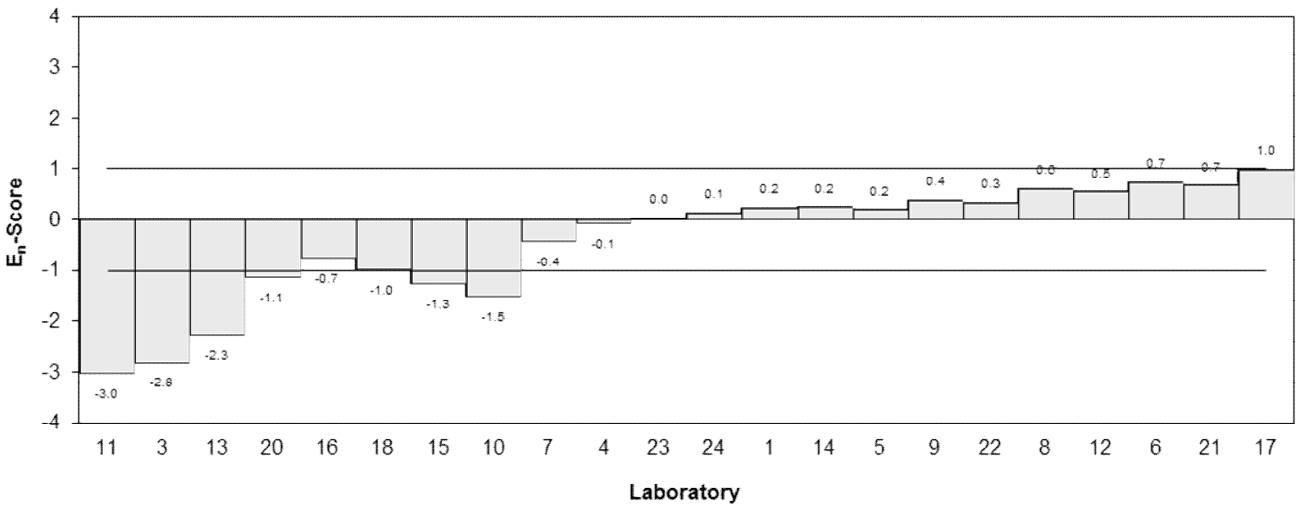

En-Scores: S4 - Anthracene
En-Score
Laboratory
11 3 13 20 16 18 15 10 7 4 23 24 1 14 5 9 22 8 12 6 21 17

Figure 17

Table 24

Sample Details

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

Participant Results

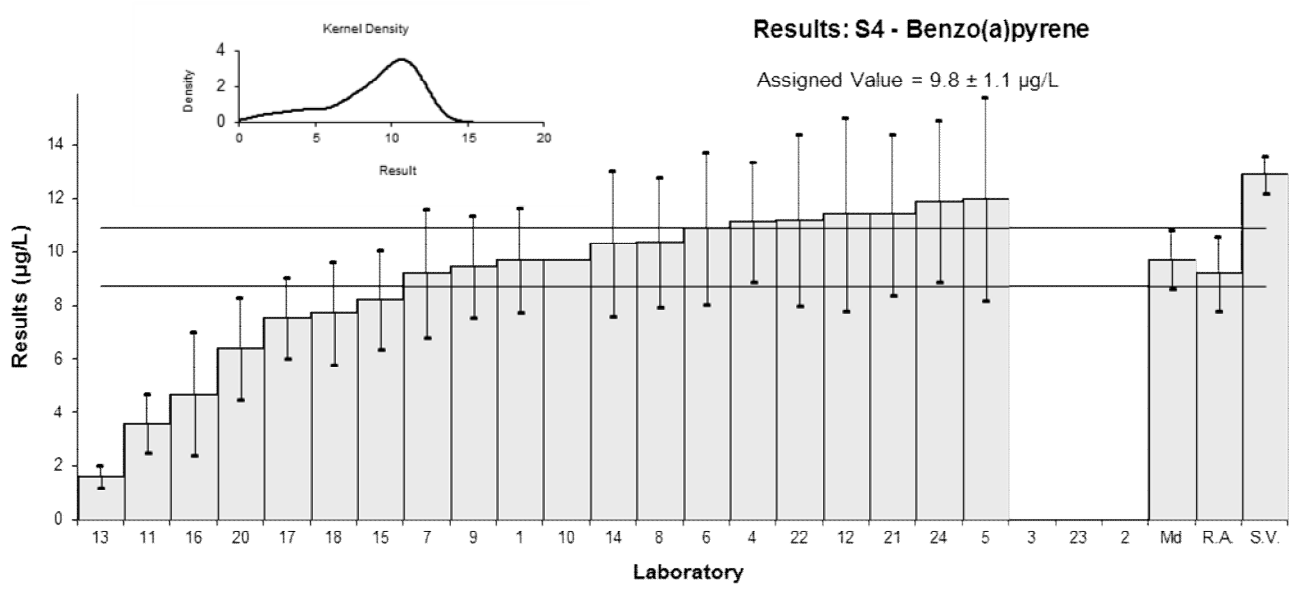
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	9.68	1.94	-0.08	-0.05
2	NT	NT		
3	<1	0.3		
4	11.11	2.22	0.89	0.53
5	12.0	3.8	1.50	0.56
6	10.91	2.84	0.76	0.36
7	9.2	2.4	-0.41	-0.23
8	10.36	2.40	0.38	0.21
9	9.46	1.89	-0.23	-0.16
10	9.7	NR	-0.07	-0.09
11	3.6	1.1	-4.22	-3.99
12	11.4	3.6	1.09	0.43
13	1.62	0.41	-5.56	-6.97
14	10.3	2.7	0.34	0.17
15	8.2	1.84	-1.09	-0.75
16	4.7	2.3	-3.47	-2.00
17	7.529	1.506	-1.54	-1.22
18	7.72	1.9	-1.41	-0.95
20	6.4	1.9	-2.31	-1.55
21	11.4	3.0	1.09	0.50
22	11.2	3.21	0.95	0.41
23*	NR	NR		
24	11.9	3.0	1.43	0.66

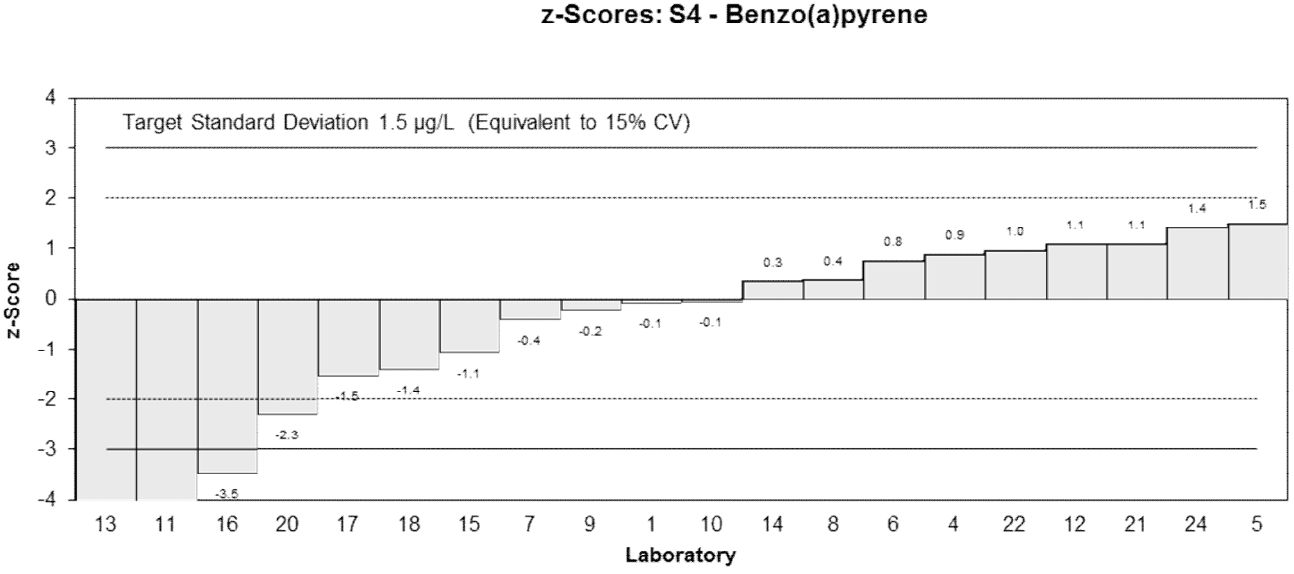
*Result changed from 0 to NR.

Statistics

Assigned Value**	9.8	1.1
Spike	12.9	0.7
Robust Average	9.2	1.4
Median	9.7	1.1
Mean	8.9	
N	20	
Max.	12	
Min.	1.62	
Robust SD	1.9	
Robust CV	20%	

**Robust average excluding laboratories 11 and 13.


Kernel Density
Density
Result
Results: S4 - Benzo(a)pyrene
Assigned Value = 9.8 ± 1.1 µg/L
Results (µg/L)
13 11 16 20 17 18 15 7 9 1 10 14 8 6 4 22 12 21 24 5 3 23 2 Md R.A. S.V.
Laboratory


z-Scores: S4 - Benzo(a)pyrene
Target Standard Deviation 1.5 µg/L (Equivalent to 15% CV)
z-Score
13 11 16 20 17 18 15 7 9 1 10 14 8 6 4 22 12 21 24 5
Laboratory

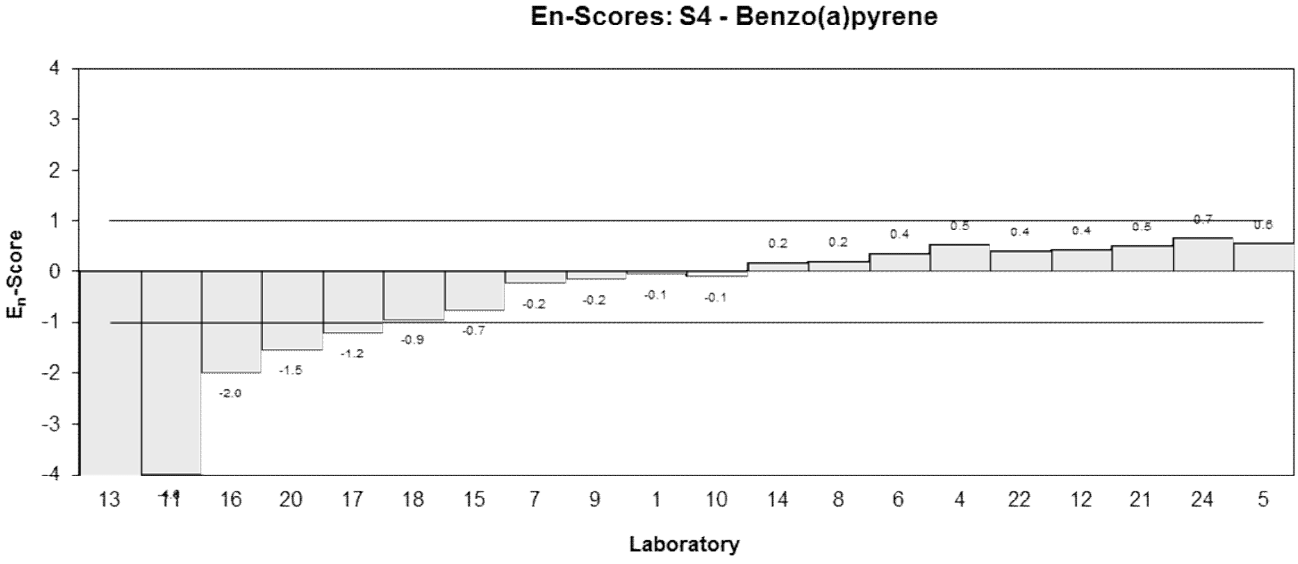

En-Scores: S4 - Benzo(a)pyrene
En-Score
13 11 16 20 17 18 15 7 9 1 10 14 8 6 4 22 12 21 24 5
Laboratory

Figure 18

Table 25

Sample Details

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

Participant Results

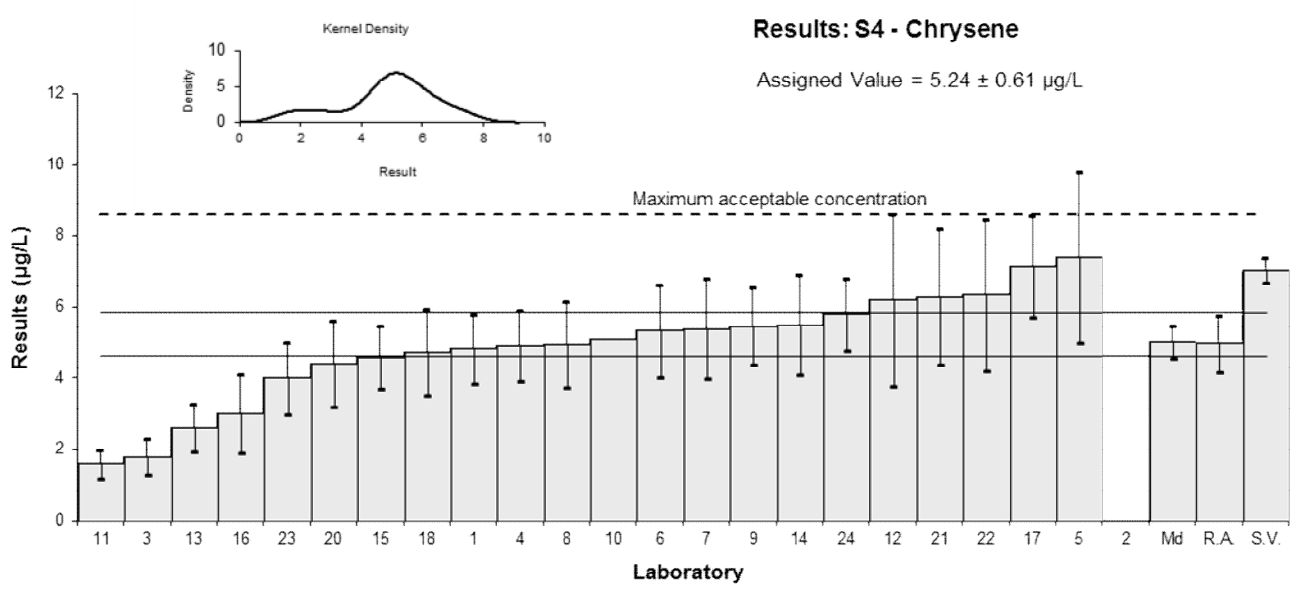
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.84	0.97	-0.51	-0.35
2	NT	NT		
3	1.8	0.5	-4.38	-4.36
4	4.92	0.98	-0.41	-0.28
5**	7.4	2.4	2.00	0.87
6	5.33	1.28	0.11	0.06
7	5.4	1.4	0.20	0.10
8	4.95	1.19	-0.37	-0.22
9	5.47	1.09	0.29	0.18
10	5.1	NR	-0.18	-0.23
11	1.6	0.4	-4.63	-4.99
12	6.20	2.4	1.22	0.39
13	2.62	0.66	-3.33	-2.92
14	5.5	1.4	0.33	0.17
15	4.6	0.89	-0.81	-0.59
16	3.0	1.1	-2.85	-1.78
17**	7.135	1.427	2.00	1.00
18	4.74	1.2	-0.64	-0.37
20	4.4	1.2	-1.07	-0.62
21	6.3	1.9	1.35	0.53
22	6.34	2.13	1.40	0.50
23	4	1.0	-1.58	-1.06
24	5.8	1.0	0.71	0.48

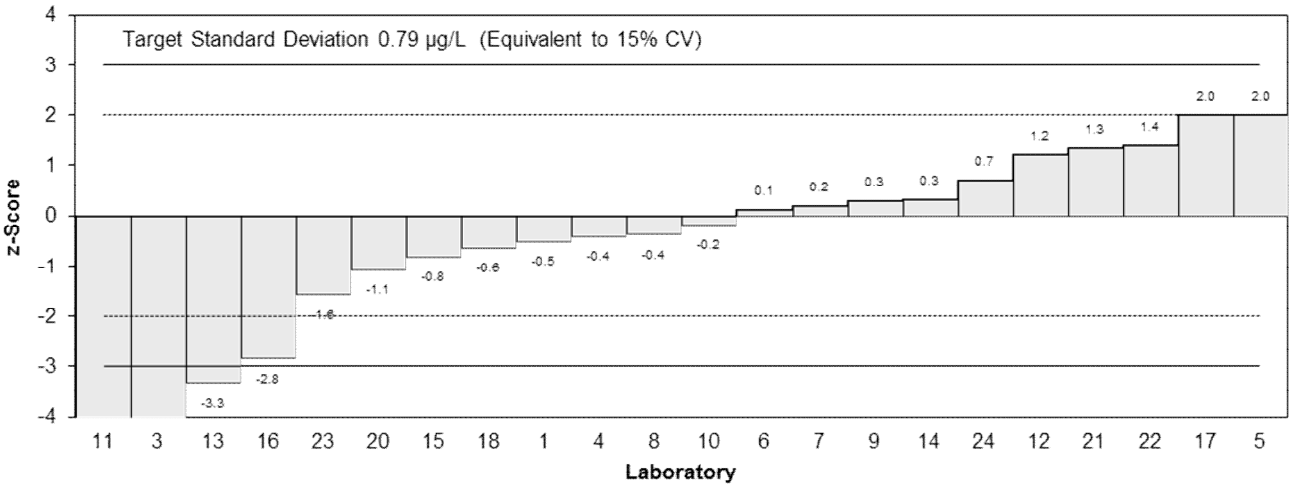
Statistics

Assigned Value*	5.24	0.61
Spike	7.03	0.35
Maximum acceptable conc.**	8.6	
Robust Average	4.97	0.80
Median	5.03	0.46
Mean	4.88	
N	22	
Max.	7.4	
Min.	1.6	
Robust SD	1.1	
Robust CV	21%	

*Robust average excluding laboratories 3 and 11.

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


Kernel Density
Density
Result
Results: S4 - Chrysene
Assigned Value = 5.24 ± 0.61 µg/L
Maximum acceptable concentration
Results (µg/L)
11 3 13 16 23 20 15 18 1 4 8 10 6 7 9 14 24 12 21 22 17 5 2 Md R.A. S.V.
Laboratory


z-Scores: S4 - Chrysene
Target Standard Deviation 0.79 µg/L (Equivalent to 15% CV)
z-Score
11 3 13 16 23 20 15 18 1 4 8 10 6 7 9 14 24 12 21 22 17 5
Laboratory

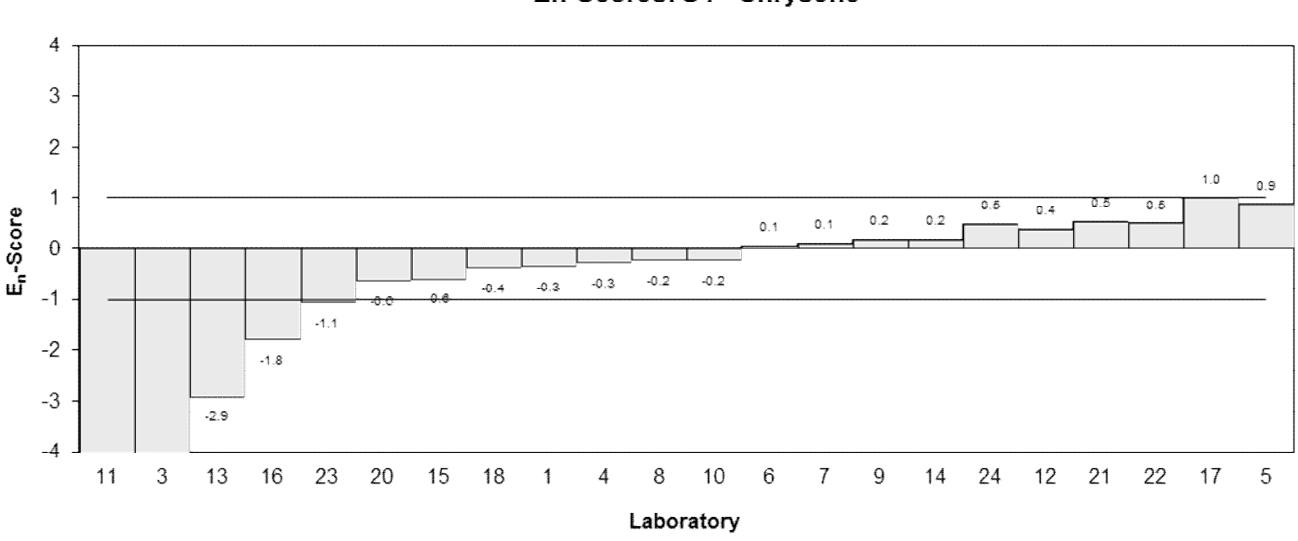

En-Scores: S4 - Chrysene
En-Score
11 3 13 16 23 20 15 18 1 4 8 10 6 7 9 14 24 12 21 22 17 5
Laboratory

Figure 19

Table 26

Sample Details

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

Participant Results

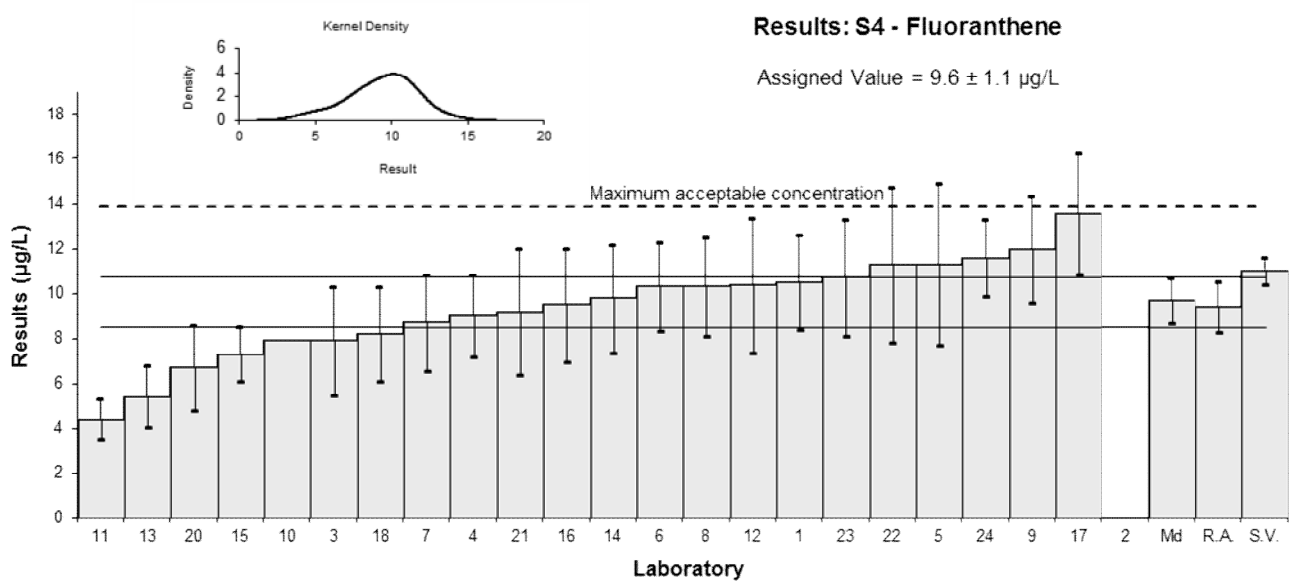
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	10.51	2.10	0.63	0.38
2	NT	NT		
3	7.9	2.4	-1.18	-0.64
4	9.02	1.80	-0.40	-0.27
5	11.3	3.6	1.18	0.45
6	10.31	1.96	0.49	0.32
7	8.7	2.1	-0.63	-0.38
8	10.31	2.18	0.49	0.29
9	11.97	2.37	1.65	0.91
10	7.9	NR	-1.18	-1.55
11	4.4	0.9	-3.61	-3.66
12	10.4	3.0	0.56	0.25
13	5.42	1.36	-2.90	-2.39
14	9.8	2.4	0.14	0.08
15	7.3	1.2	-1.60	-1.41
16	9.5	2.5	-0.07	-0.04
17**	13.571	2.714	2.00	1.00
18	8.20	2.1	-0.97	-0.59
20	6.7	1.9	-2.01	-1.32
21	9.2	2.8	-0.28	-0.13
22	11.3	3.46	1.18	0.47
23	10.7	2.6	0.76	0.39
24	11.6	1.7	1.39	0.99

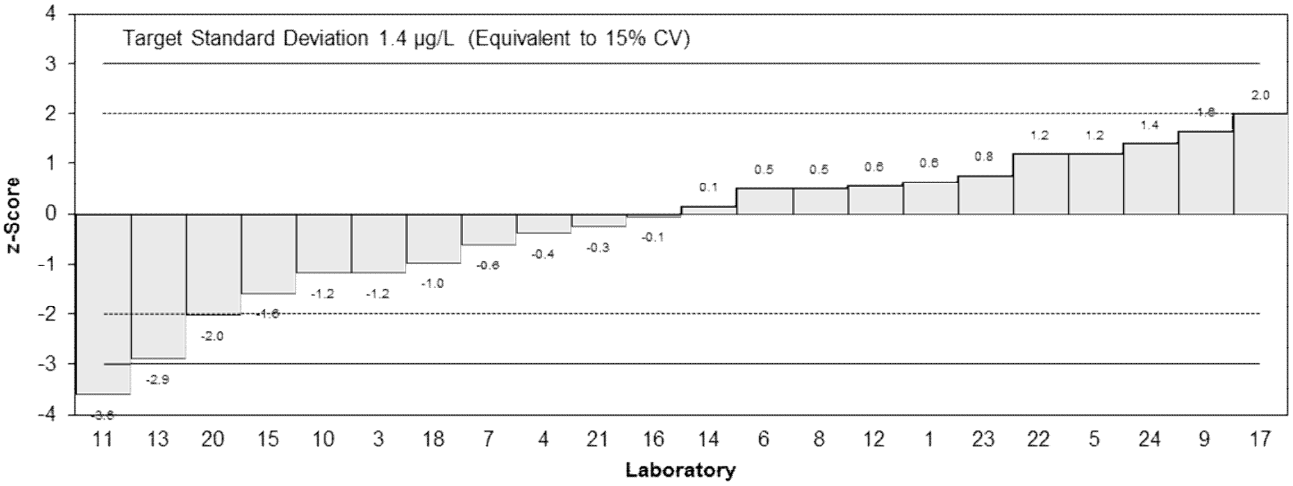
Statistics

Assigned Value*	9.6	1.1
Spike	11.0	0.6
Maximum acceptable conc.**	14	
Robust Average	9.4	1.1
Median	9.7	1.0
Mean	9.4	
N	22	
Max.	13.571	
Min.	4.4	
Robust SD	1.9	
Robust CV	20%	

*Robust average excluding laboratory 11.

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


Kernel Density
Density
Result
Results: S4 - Fluoranthene
Assigned Value = 9.6 ± 1.1 µg/L
Maximum acceptable concentration
Results (µg/L)
Laboratory
11 13 20 15 10 3 18 7 4 21 16 14 6 8 12 1 23 22 5 24 9 17 2 Md R.A. S.V.


z-Scores: S4 - Fluoranthene
Target Standard Deviation 1.4 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 13 20 15 10 3 18 7 4 21 16 14 6 8 12 1 23 22 5 24 9 17

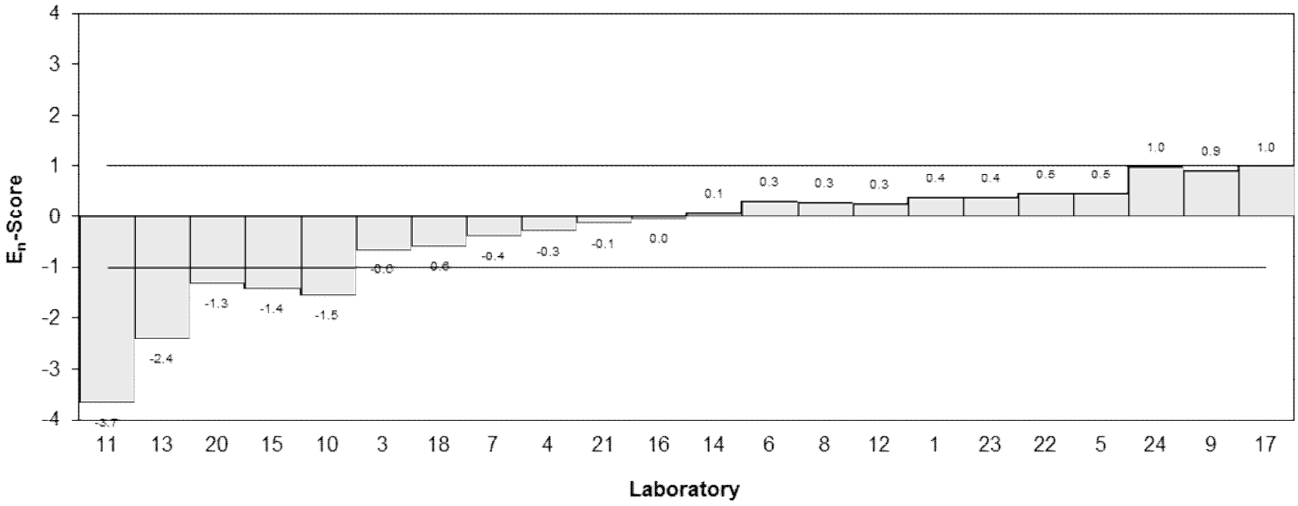

En-Scores: S4 - Fluoranthene
En-Score
Laboratory
11 13 20 15 10 3 18 7 4 21 16 14 6 8 12 1 23 22 5 24 9 17

Figure 20

Table 27

Sample Details

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

Participant Results

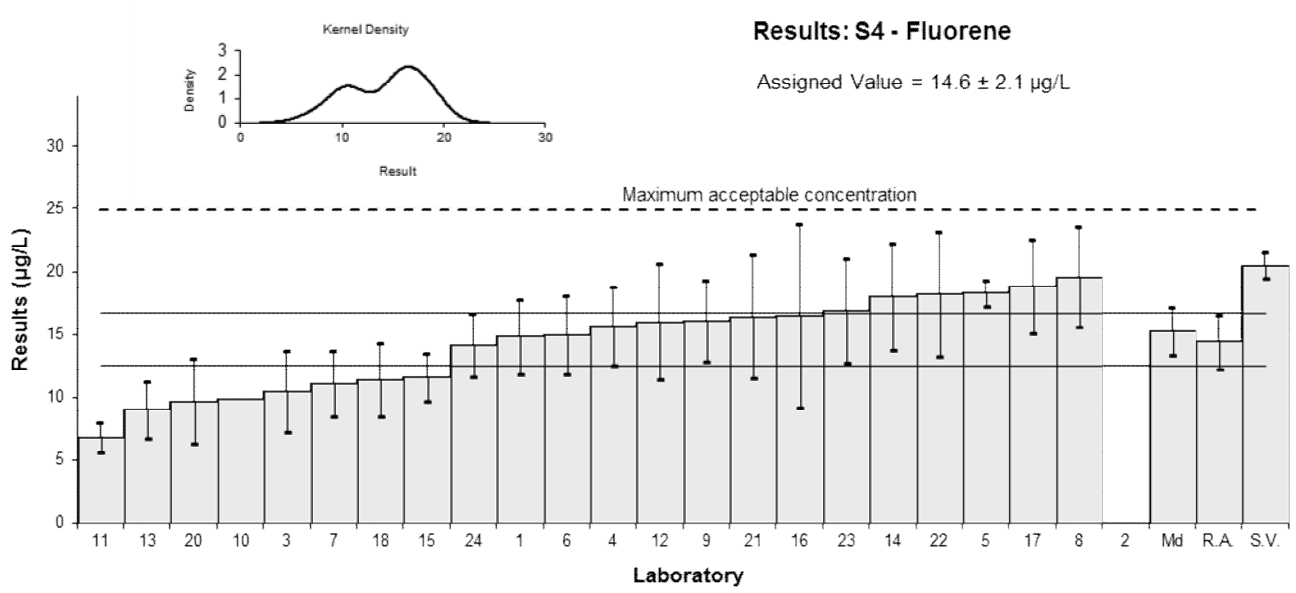
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	14.84	2.97	0.11	0.07
2	NT	NT		
3	10.5	3.2	-1.87	-1.07
4	15.67	3.13	0.49	0.28
5	18.3	1.0	1.69	1.59
6	14.95	3.14	0.16	0.09
7	11.1	2.6	-1.60	-1.05
8**	19.59	3.94	2.00	1.00
9	16.07	3.21	0.67	0.38
10	9.9	NR	-2.15	-2.24
11	6.8	1.2	-3.56	-3.22
12	16.0	4.6	0.64	0.28
13	9.02	2.26	-2.55	-1.81
14	18.0	4.2	1.55	0.72
15	11.6	1.89	-1.37	-1.06
16	16.5	7.3	0.87	0.25
17	18.829	3.766	1.93	0.98
18	11.4	2.9	-1.46	-0.89
20	9.7	3.4	-2.24	-1.23
21	16.4	4.9	0.82	0.34
22	18.2	4.95	1.64	0.67
23	16.9	4.1	1.05	0.50
24	14.1	2.5	-0.23	-0.15

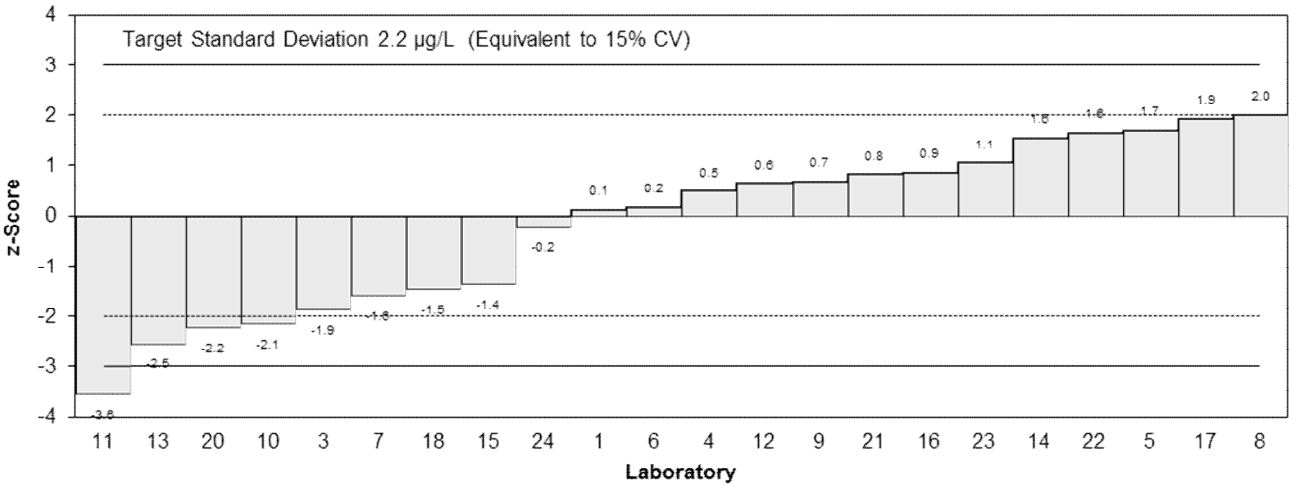
Statistics

Assigned Value*	14.6	2.1
Spike	20.5	1.0
Maximum acceptable conc.**	24.9	
Robust Average	14.4	2.1
Median	15.3	1.9
Mean	14.3	
N	22	
Max.	19.59	
Min.	6.8	
Robust SD	3.8	
Robust CV	26%	

*Robust average excluding laboratory 11.

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


Kernel Density
Density
Result
Results: S4 - Fluorene
Assigned Value = 14.6 ± 2.1 µg/L
Maximum acceptable concentration
Results (µg/L)
11 13 20 10 3 7 18 15 24 1 6 4 12 9 21 16 23 14 22 5 17 8 2 Md R.A. S.V.
Laboratory


z-Scores: S4 - Fluorene
Target Standard Deviation 2.2 µg/L (Equivalent to 15% CV)
z-Score
11 13 20 10 3 7 18 15 24 1 6 4 12 9 21 16 23 14 22 5 17 8
Laboratory

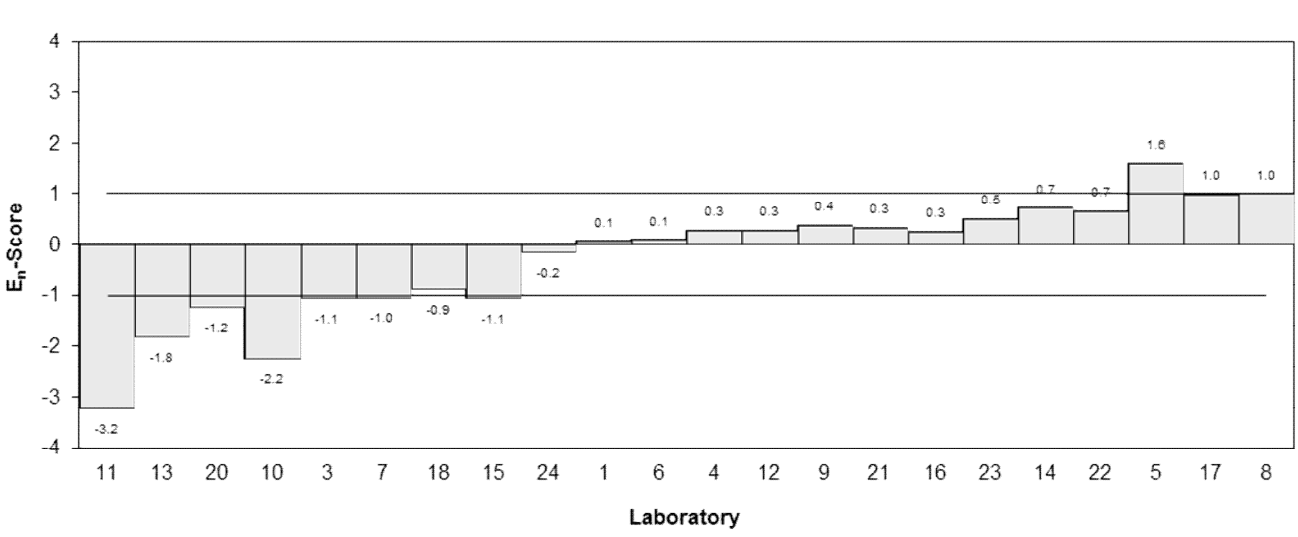

En-Scores: S4 - Fluorene
En-Score
11 13 20 10 3 7 18 15 24 1 6 4 12 9 21 16 23 14 22 5 17 8
Laboratory

Figure 21

Table 28

Sample Details

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

Participant Results

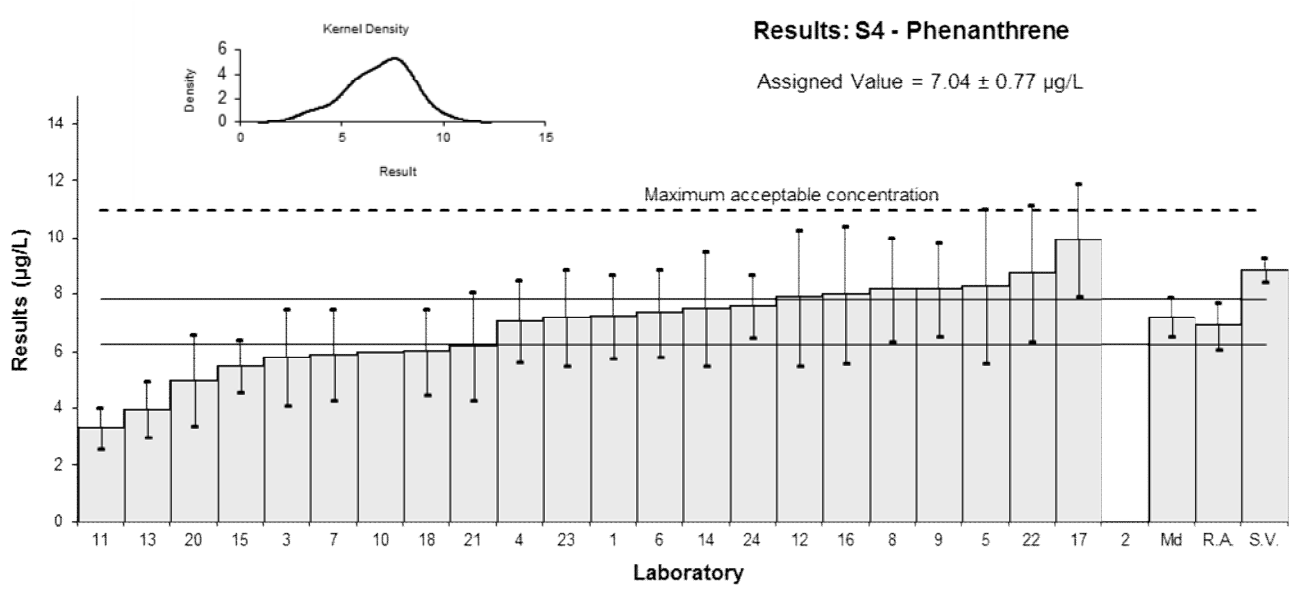
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.24	1.45	0.19	0.12
2	NT	NT		
3	5.8	1.7	-1.17	-0.66
4	7.06	1.41	0.02	0.01
5	8.3	2.7	1.19	0.45
6	7.36	1.54	0.30	0.19
7	5.9	1.6	-1.08	-0.64
8	8.19	1.82	1.09	0.58
9	8.19	1.64	1.09	0.63
10	6.0	NR	-0.98	-1.35
11	3.3	0.7	-3.54	-3.59
12	7.90	2.4	0.81	0.34
13	3.96	0.99	-2.92	-2.46
14	7.5	2.0	0.44	0.21
15	5.5	0.91	-1.46	-1.29
16	8.0	2.4	0.91	0.38
17**	9.935	1.987	2.00	1.00
18	6.01	1.5	-0.98	-0.61
20	5.0	1.6	-1.93	-1.15
21	6.2	1.9	-0.80	-0.41
22	8.77	2.39	1.64	0.69
23	7.2	1.7	0.15	0.09
24	7.6	1.1	0.53	0.42

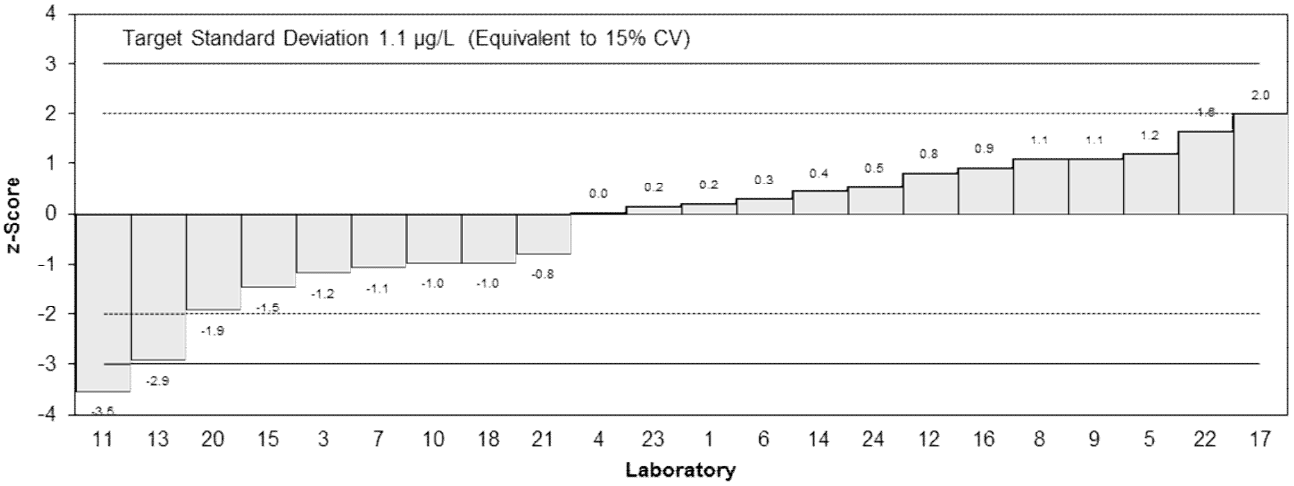
Statistics

Assigned Value*	7.04	0.77
Spike	8.87	0.44
Maximum acceptable conc.**	11.0	
Robust Average	6.92	0.81
Median	7.22	0.69
Mean	6.86	
N	22	
Max.	9.935	
Min.	3.3	
Robust SD	1.4	
Robust CV	20%	

*Robust average excluding laboratory 11.

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


Kernel Density
Density
Result
Results: S4 - Phenanthrene
Assigned Value = 7.04 ± 0.77 µg/L
Maximum acceptable concentration
Results (µg/L)
Laboratory
11 13 20 15 3 7 10 18 21 4 23 1 6 14 24 12 16 8 9 5 22 17 2 Md R.A. S.V.


z-Scores: S4 - Phenanthrene
Target Standard Deviation 1.1 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 13 20 15 3 7 10 18 21 4 23 1 6 14 24 12 16 8 9 5 22 17

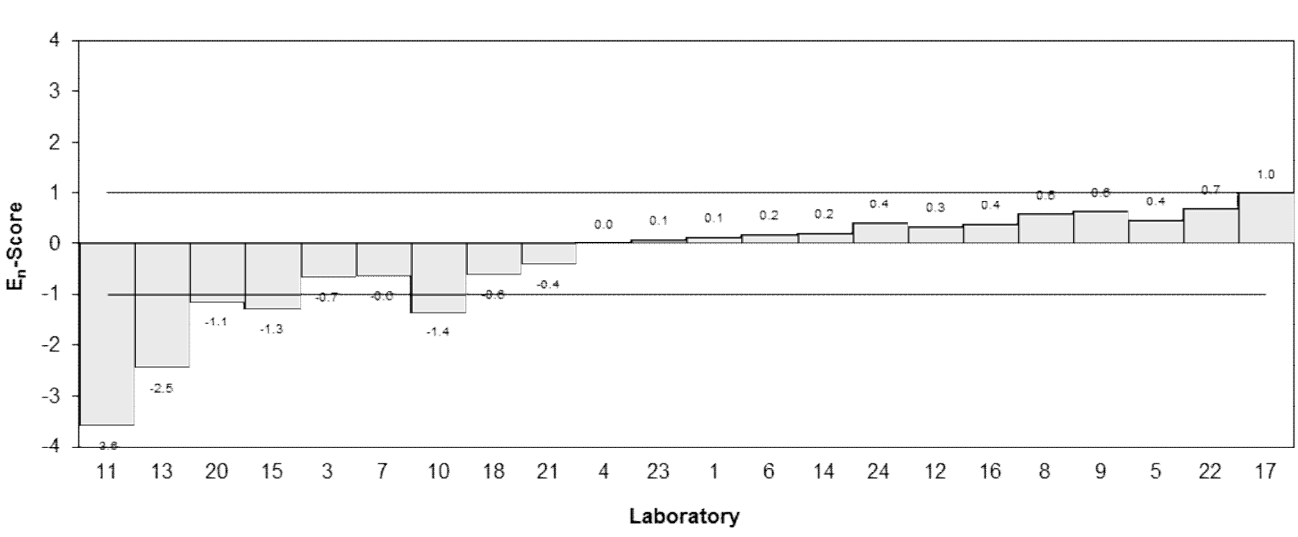
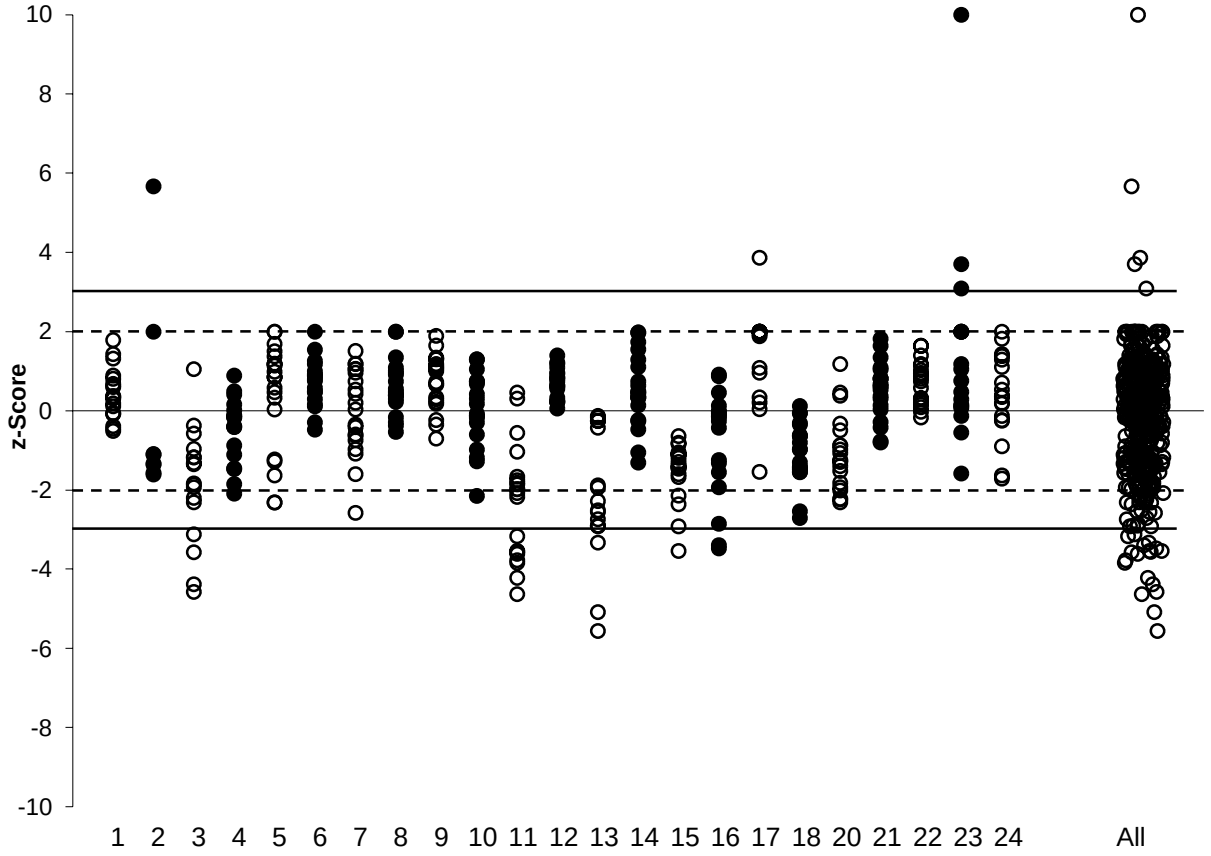
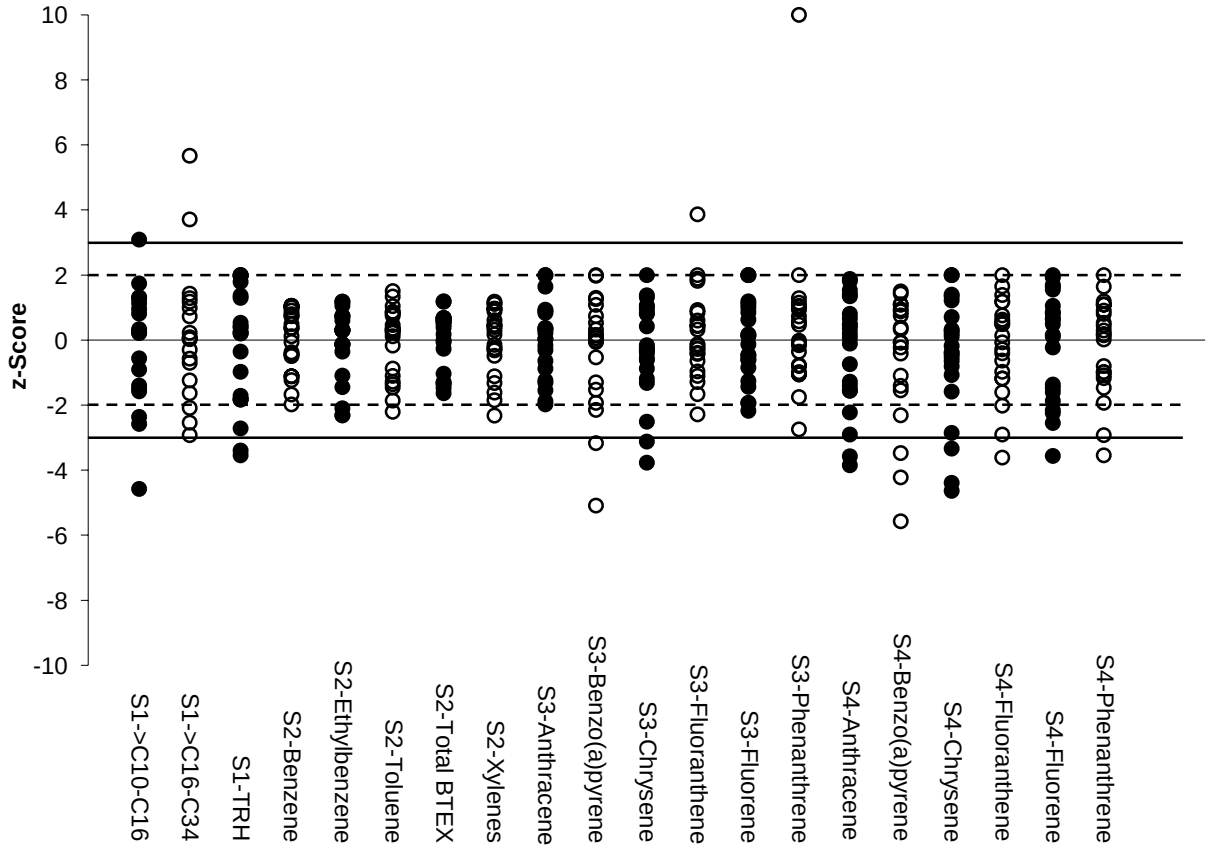

En-Scores: S4 - Phenanthrene
En-Score
Laboratory
11 13 20 15 3 7 10 18 21 4 23 1 6 14 24 12 16 8 9 5 22 17

Figure 22



Scores greater than 10 have been plotted as 10.

Figure 23 z-Score Dispersal by Laboratory



Scores greater than 10 have been plotted as 10.

Figure 24 z-Score Dispersal by Sample and Analyte

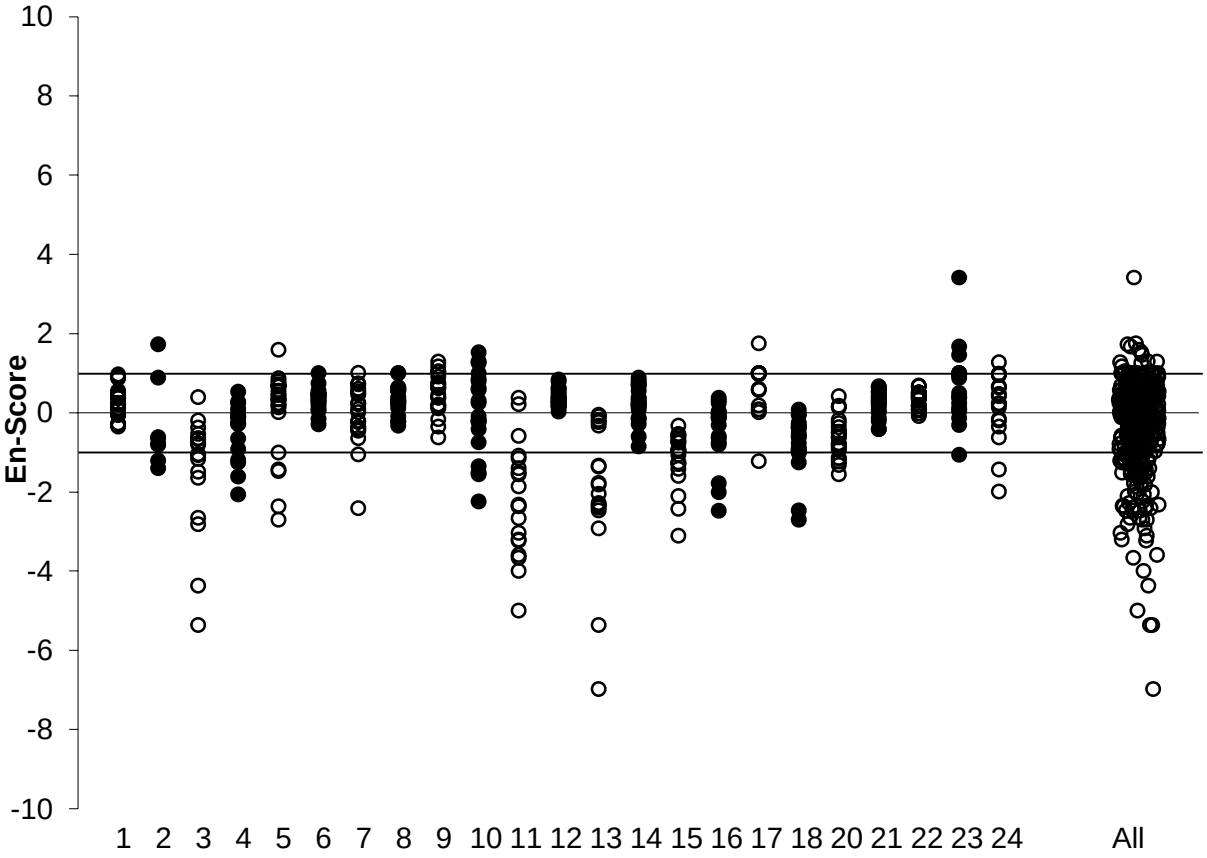


Figure 25 E_n-Score Dispersal by Laboratory

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 'ISO 13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparison'.[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 29. The spiked concentration was originally the truest measure of the PAH concentration in the water. However the robust average of participants' results was significantly lower (<75%) than the spiked concentration for several 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 17% to 26%) and an assigned value was set.

No assigned values were set for the >C34-C40 range in Sample S1 as there were too few results, and the C6-C10 range in Sample S2 as the results were too variable.

Appendix 2 sets out the calculation for the expanded uncertainty of the robust average of Ethylbenzene 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 29 Comparison of Assigned Value and Spiked Concentration.

Analyte	Spiked Concentration (µg/L)	Assigned Value (µg/L)	Assigned/Spike (%)
S1 TRH	2950	1790	61
S2 Benzene	122	108	89
S2 Ethylbenzene	16.1	15.3	95
S2 Toluene	141	115	82
S2 Total BTEX	399	331	83
S2 Xylenes	121	93.5	77
S3 Anthracene	2.49	1.99	80
S3 Benzo(a)pyrene	4.51	3.24	72
S3 Chrysene	2.81	2.07	74
S3 Fluoranthene	5.75	4.79	83
S3 Fluorene	7.46	5.49	74
S3 Phenanthrene	3.54	2.85	81
S4 Anthracene	6.01	4.95	82
S4 Benzo(a)pyrene	12.9	9.8	76
S4 Chrysene	7.03	5.24	75
S4 Fluoranthene	11.0	9.6	87
S4 Fluorene	20.5	14.6	71
S4 Phenanthrene	8.87	7.04	79

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.[7]

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, the TRH result 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 452 numerical results, 427 (94%) were reported with an associated expanded uncertainty.

Expanded uncertainties were within the range 4.4% to 74% relative.

An expanded uncertainty of less than 10% relative is unrealistically small for the routine measurement of a hydrocarbon pollutant in water. Of the 427 expanded uncertainties, 7 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. An estimate of uncertainty expressed as a value should not be attached to a result expressed as a range.

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 120.12 ± 15.92 µg/L, it is better to report this as 120 ± 16 µg/L).[8]

6.3 z-Score

Target standard deviations equivalent to 15% and 20% CV were used to calculate z-scores. The between laboratory coefficient of variation predicted by the modified Horwitz equation[10] is presented for comparison in Table 30.

Table 30 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	890	20	16	27
S1	>C16-C34	890	20	16	23
S1	TRH	1790	15	15	26
S2	Benzene	108	15	22	15
S2	Ethylbenzene	15.3	15	22	15
S2	Toluene	115	15	22	18
S2	Xylenes	93.5	15	22	16
S2	Total BTEX	331	15	19	15
S3	Anthracene	1.99	15	22	20
S3	Benzo(a)pyrene	3.24	15	22	23
S3	Chrysene	2.07	15	22	18
S3	Fluoranthene	4.79	15	22	18

Sample	Analyte	Assigned value (µg/L)	Target SD (as PCV) (%)	Modified Horwitz CV (%)	Participants' SD (as CV) (%)
S3	Fluorene	5.49	15	22	22
S3	Phenanthrene	2.85	15	22	17
S4	Anthracene	4.95	15	22	23
S4	Benzo(a)pyrene	9.8	15	22	20
S4	Chrysene	5.24	15	22	21
S4	Fluoranthene	9.6	15	22	20
S4	Fluorene	14.6	15	22	26
S4	Phenanthrene	7.04	15	22	20

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 17 z-scores were adjusted: TRH in Sample S1, anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene and phenanthrene in Sample S3, and chrysene, fluoranthene, fluorene and phenanthrene 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 431 results for which z-scores were calculated, 380 (88%) returned a satisfactory score of $|z| \leq 2$.

Laboratories **1**, **8**, **9**, **12**, **14**, **21**, **22** and **24** returned satisfactory z-scores for all 20 analytes for which z-scores were calculated.

Summaries of z-score dispersal by laboratory and by analyte are presented in Figures 23 and 24 respectively.

Scatter plots of z-scores for anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene and phenanthrene in Samples S3 and S4 are presented in Figures 26 to 31. Scores are predominantly in quadrants I and III, indicating that laboratory bias is the major contributor to the variability of results. The PAH (Samples S3 and S4) z-score dispersal by laboratory is also shown in Figure 32. Laboratories **11**, **13** and **3** reported low results for numerous PAHs.

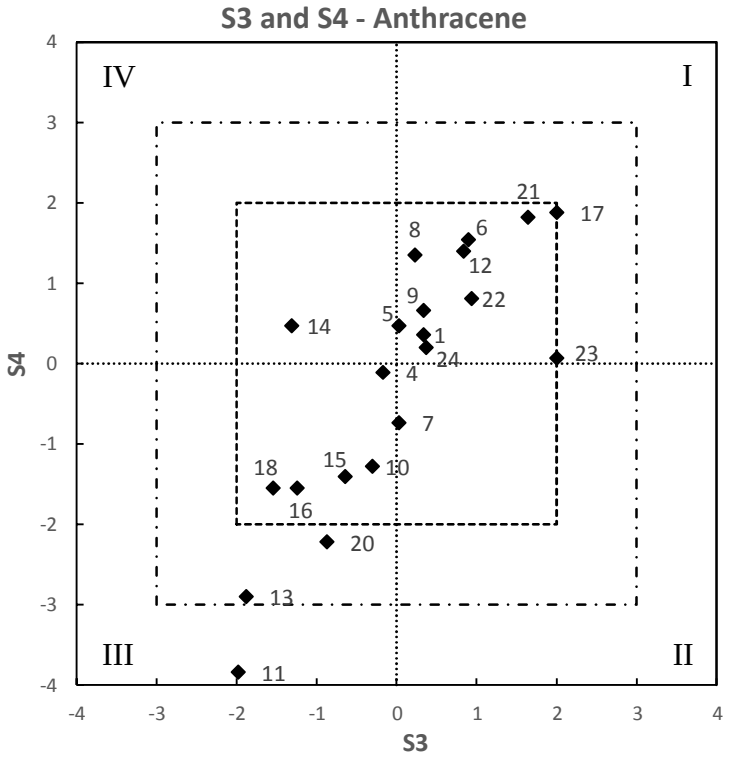
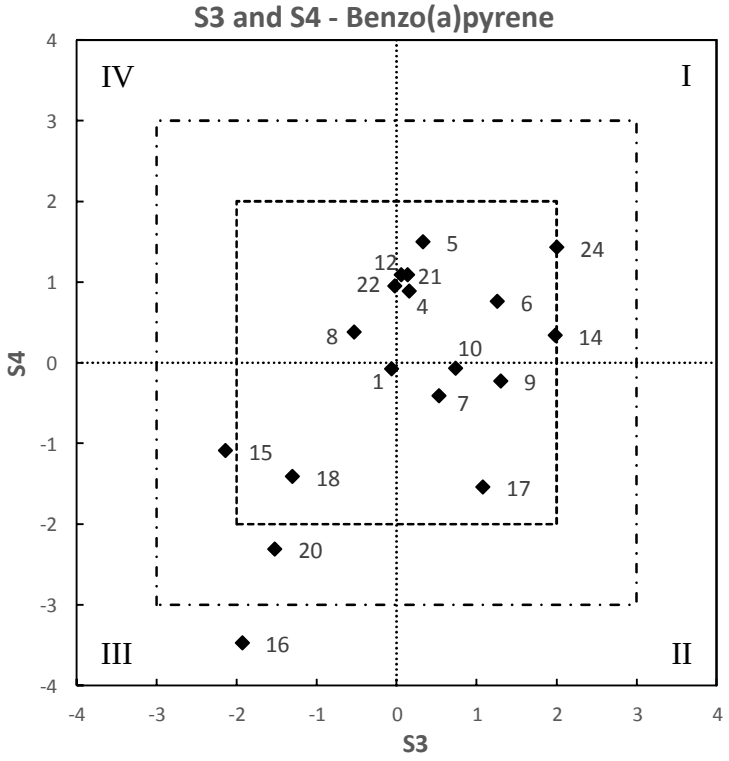
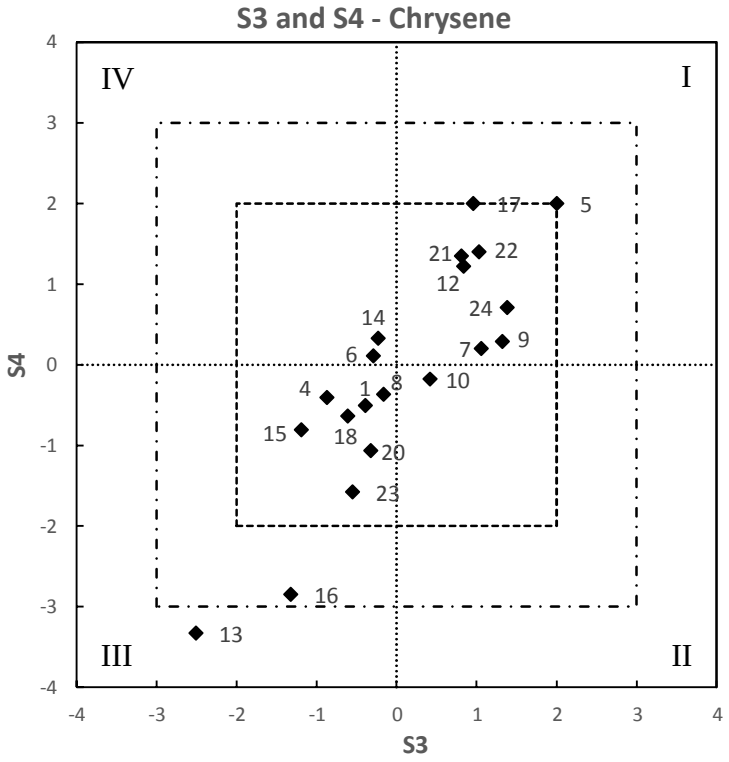


Figure 26 z-Score Scatter Plot: Anthracene in S3 and S4



Laboratories 11 and 13 are off scale.

Figure 27 z-Score Scatter Plot: Benzo(a)pyrene in S3 and S4



Laboratories 3 and 11 are off scale.

Figure 28 z-Score Scatter Plot: Chrysene in S3 and S4

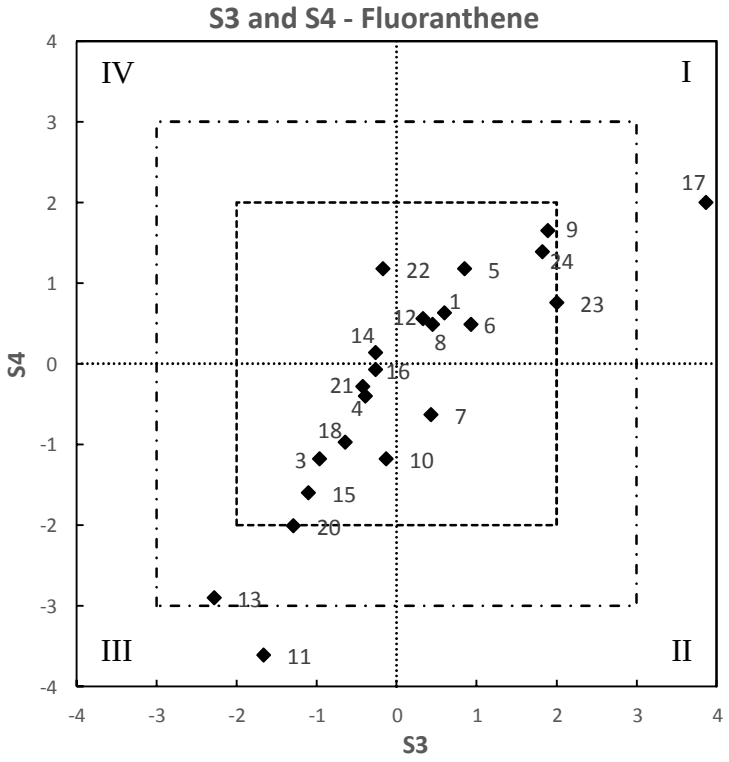


Figure 29 z-Score Scatter Plot: Fluoranthene in S3 and S4

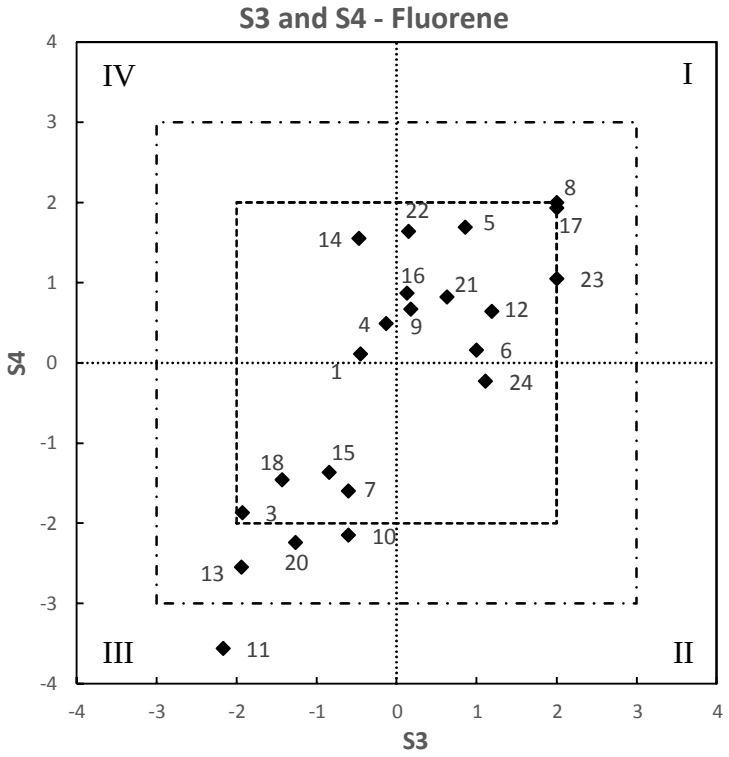
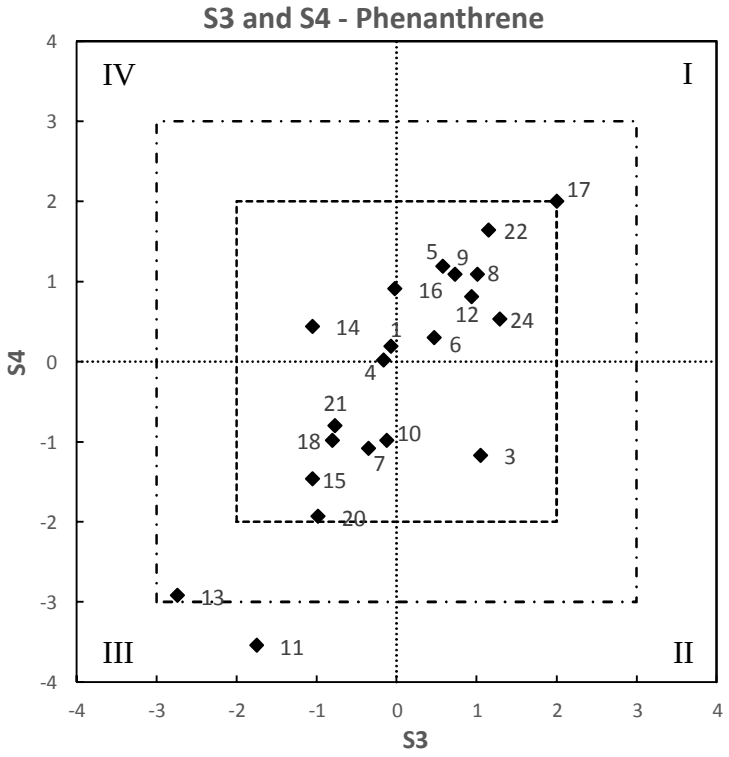
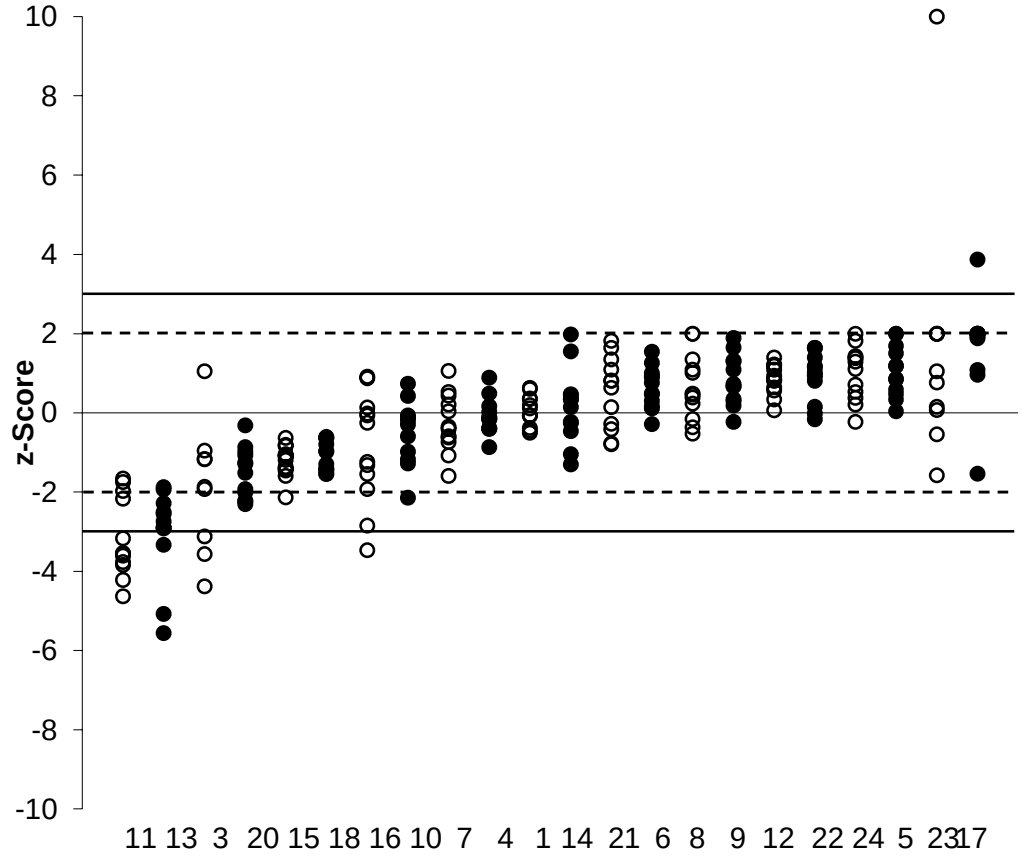


Figure 30 z-Score Scatter Plot: Fluorene in S3 and S4



Laboratory 23 is off scale.

Figure 31 z-Score Scatter Plot: Phenanthrene in S3 and S4



Scores greater than 10 have been plotted as 10.

Figure 32 PAH (Samples S3 and S4) z-Score Dispersal by Laboratory

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 analytes whose z-scores were adjusted as discussed in Section 6.3 z-Scores.

Of 431 results for which E_n-scores were calculated, 334 (77%) returned a satisfactory score of $|E_n| \leq 1$.

Laboratories **1**, **8**, **12**, **14**, **21** and **22** returned satisfactory E_n-scores for all 20 analytes for which scores were calculated.

A summary of E_n-score dispersal by laboratory is presented in Figure 25.

6.5 Participants' Analytical Methods

TRH in Sample S1

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

Eight laboratories reported taking 500 mL (i.e. the whole sample) for extraction, while the other laboratories reported sample test portions ranging from 35 – 400 mL. No trends were identified with consideration to whether the whole sample was used, or what volume was used (Figure 33). Laboratories did not report whether or not the sample container was rinsed to recover hydrocarbons adhering to the wall of the container.

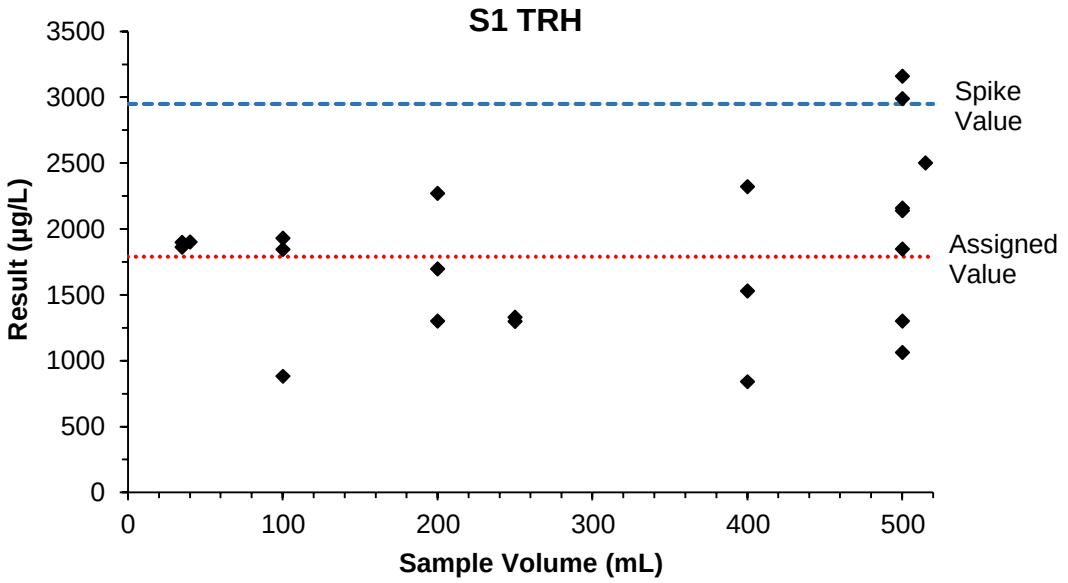


Figure 33 Results vs sample volume for TRH in Sample S1

BTEX in Sample S2

For BTEX analysis eighteen laboratories performed an extraction using purge-and-trap and four laboratories used headspace. All laboratories who analysed Sample S2 used GC-MS.

Eleven laboratories reported taking the whole sample for extraction, while the other laboratories reported sample test portions from 5 – 25 mL. No trends were identified with consideration to whether the whole sample was used, or what volume was used (Figure 34).

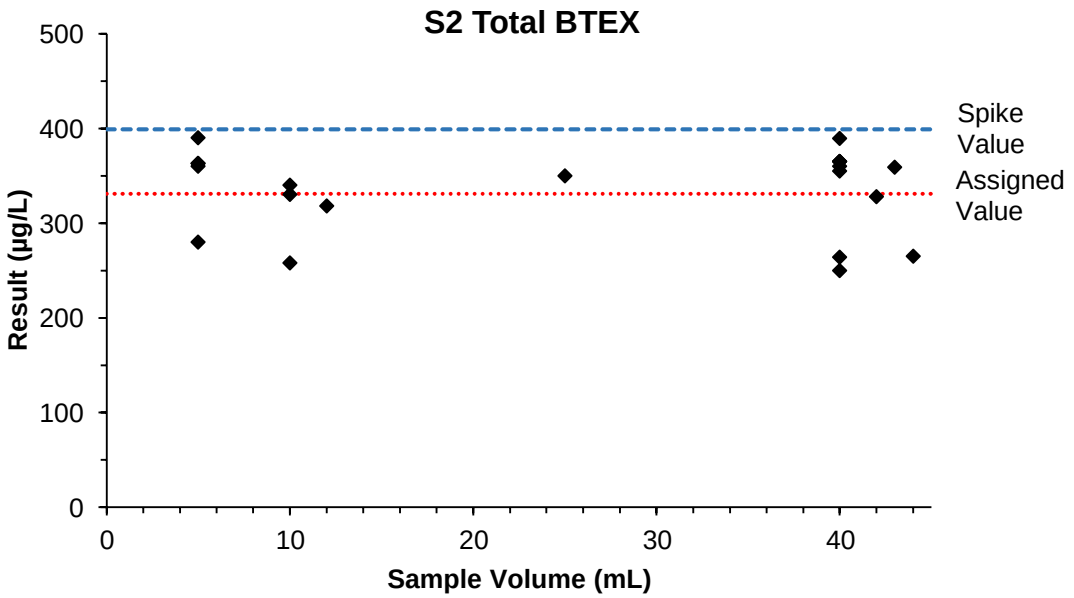
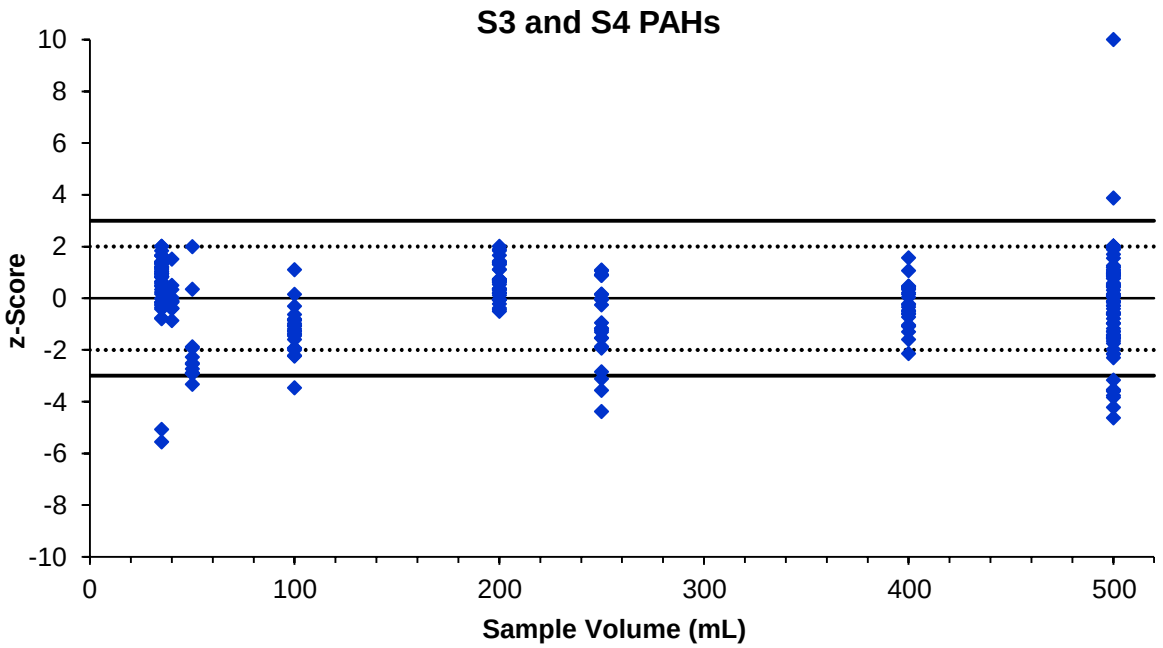


Figure 34 Results vs sample volume for Total BTEX in Sample S2

PAHs in Samples S3 and S4

For the laboratories analysing Samples S3 and S4, one participant used solid phase extraction and all other participants used liquid-liquid extraction. The extraction solvents reported were dichloromethane, hexane, and dichloromethane/ethyl acetate. All participants used GC-MS(MS) to measure PAHs.

Seven laboratories reported taking 500 mL (i.e. the whole sample) for extraction, while the other laboratories reported test portions ranging from 35 – 400 mL. No trends were identified with consideration to whether the whole sample was used, or what volume was used (Figure 35). Laboratories did not report whether or not the sample container was rinsed to recover PAHs adhering to the wall of the container.



Scores greater than 10 have been plotted as 10.

Figure 35 z-Score vs sample volume for PAHs in Samples S3 and S4

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. Sixteen laboratories reported using 'certified' standards such as:

- AccuStandard
- QC standards
- Alkane standards
- NMI CRM
- Novachem

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*'[11]

6.7 Comparison with Previous Studies

TRH

A summary of z-scores and E_n-scores obtained by laboratories for TRH in water since 2009 is presented in Figure 36. On average, the proportion of satisfactory z-scores was 75% and the proportion of satisfactory E_n-scores 65%.

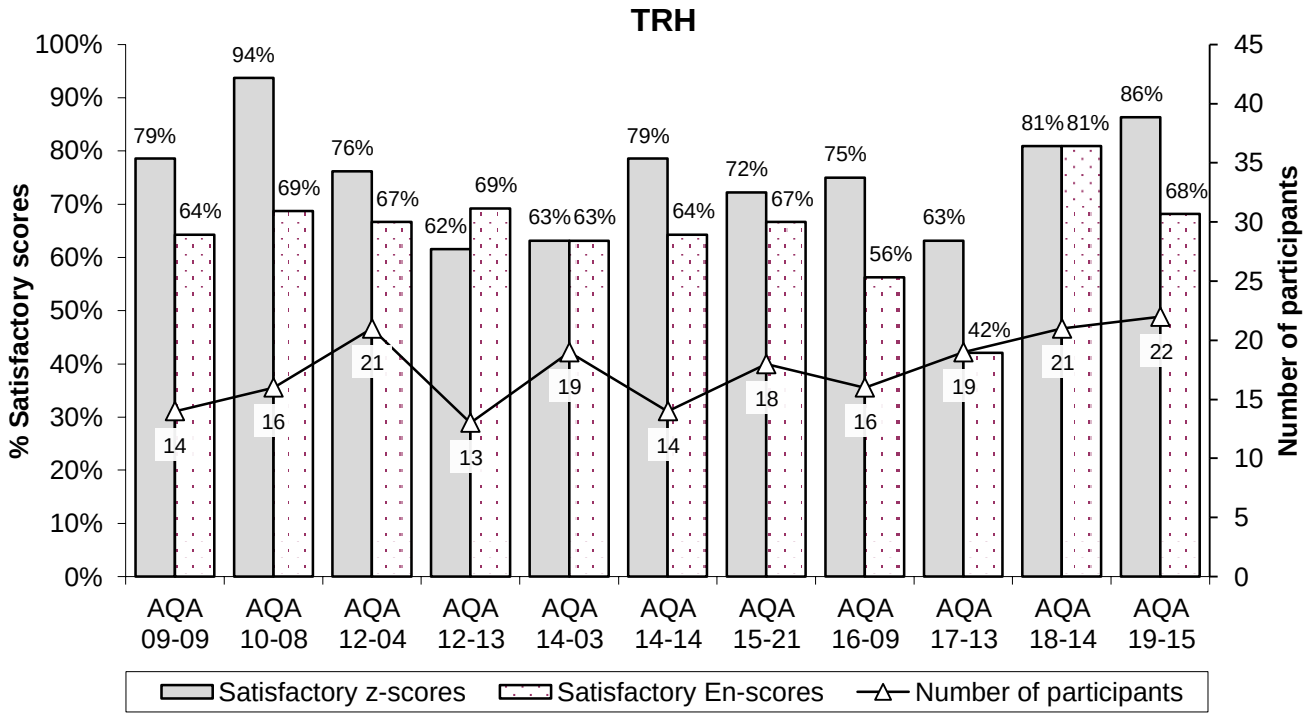


Figure 36 Summary of participants' performance for TRH (TPH for AQA 12-13 and previous studies) in water since 2009.

Total BTEX

A summary of z-scores and E_n-scores obtained by laboratories for Total BTEX in water since 2009 is presented in Figure 37. On average, the proportion of satisfactory z-scores was 90% and the proportion of satisfactory E_n-scores was 84%.

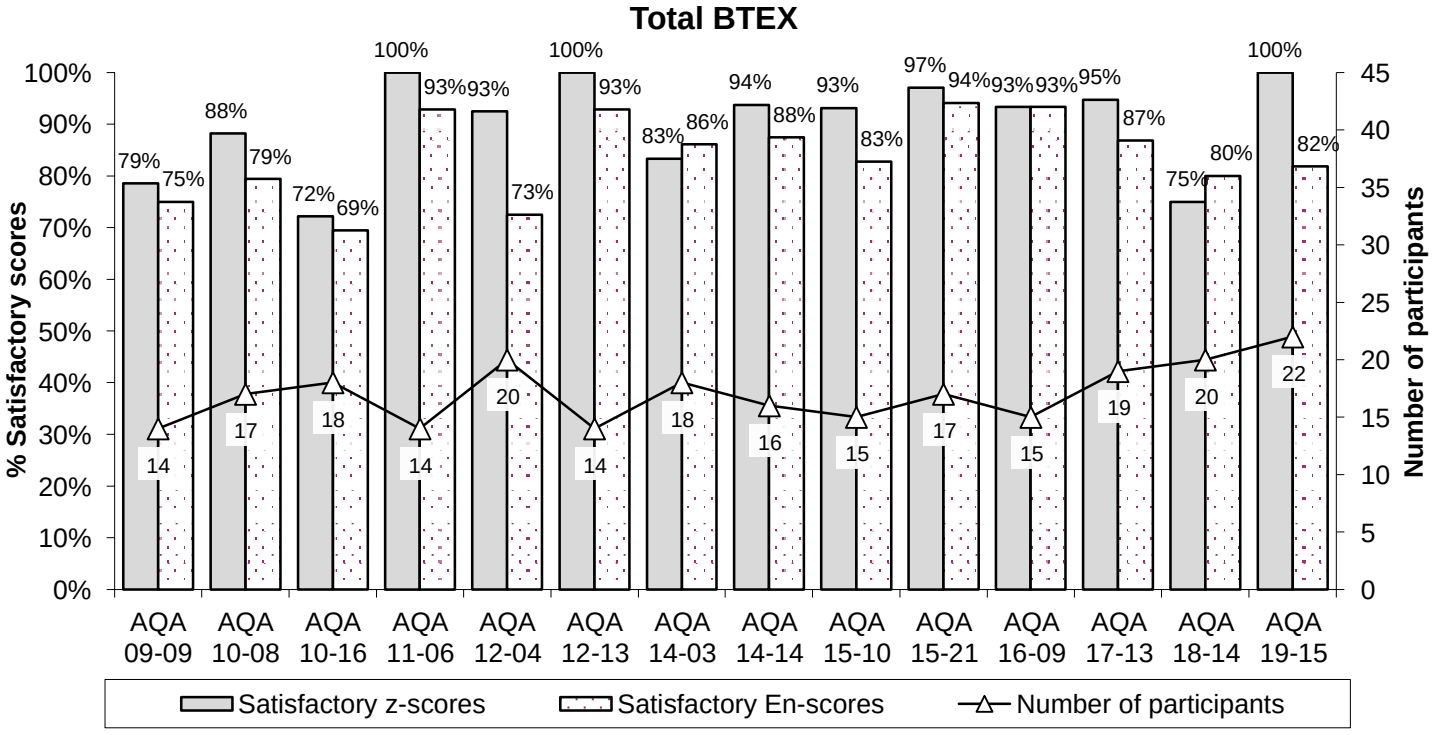


Figure 37 Summary of participants' performance for Total BTEX in water since 2009.

PAHs

A summary of z-scores and E_n-scores obtained by laboratories for all PAHs in water since 2015 is presented in Figure 38. On average, the proportion of satisfactory z-scores was 85% and the proportion of satisfactory E_n-scores was 79%.

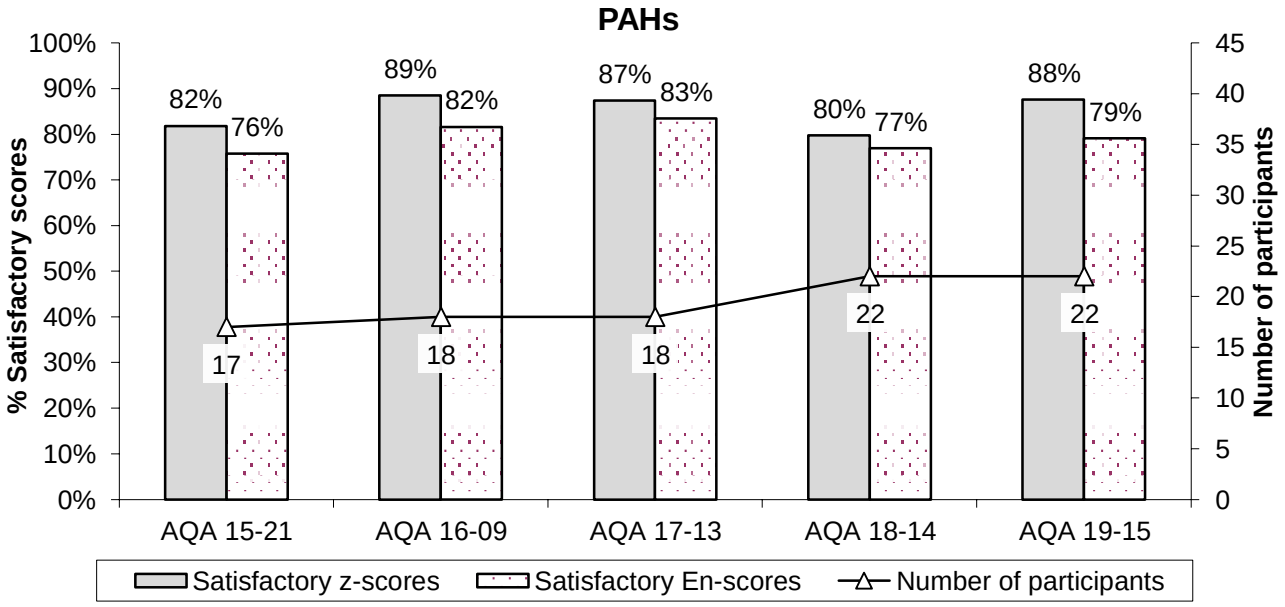


Figure 38 Summary of participants' performance for all PAHs in water since 2015.

A plot of the assigned value, expressed as a percentage of the spiked concentration, for PAHs since 2015 is presented in Figure 39. On average, the recovery of PAHs in this study was higher than in previous studies, however, the assigned values were still lower than the spike values for all analytes considered in this study.

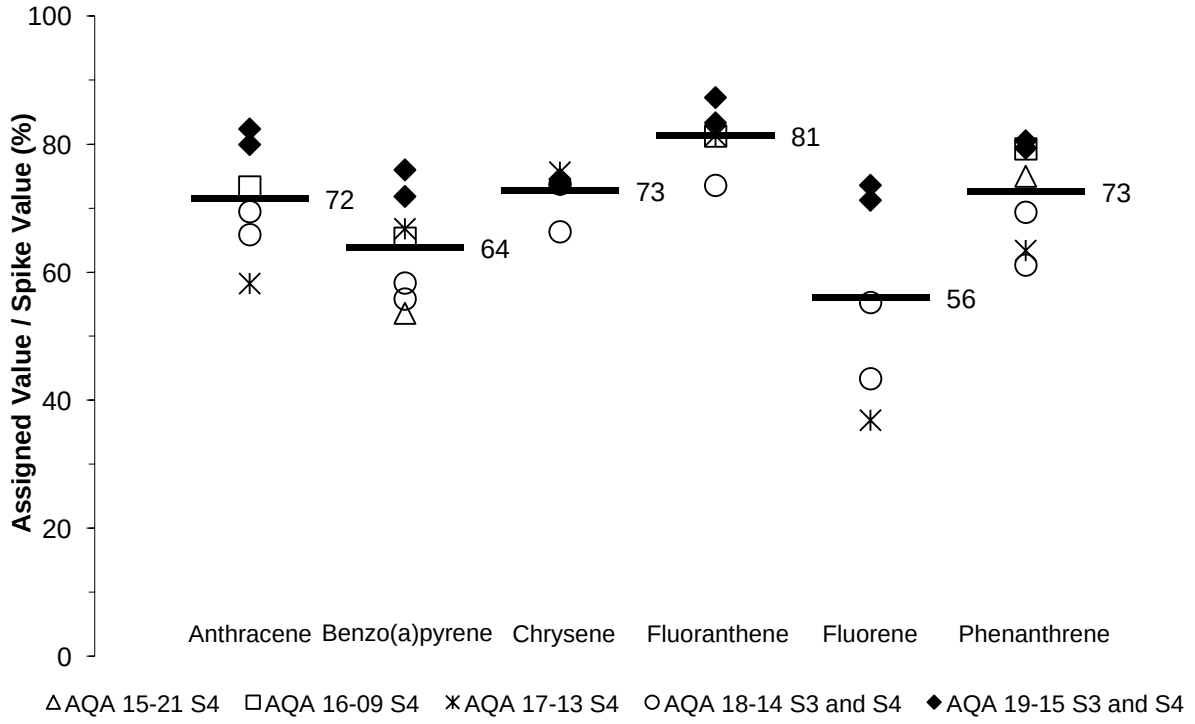


Figure 39 Assigned value as % of spike value for PAHs since 2015. The line indicates the average for each PAH.

7 REFERENCES

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[10] Thompson, M. and Lowthian, P.J. 1995, 'A Horwitz-like function describes precision in a proficiency test', *Analyst*, vol 120, pp 271-272.

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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 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 25ºC) was weighed into the bottles. 1.49 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

Forty-two millilitres (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. 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 spike solutions were prepared by dissolving each standard material in dichloromethane. The autoclaved water was placed in a stainless steel container. After spiking the water was stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL amber glass bottles.

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

Homogeneity Testing

The process used to prepare the samples was the same as previous NMI proficiency tests of hydrocarbons 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

When the robust average was calculated using the procedure described in 'ISO 13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparison – Annex C',[9] the uncertainty was estimated as:

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

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 31.

Table 31 Uncertainty of the robust average for Ethylbenzene in Sample S2

No. results (p)	22
Robust Average	15.3 µg/L
$S_{rob\ av}$	2.3 µg/L
$u_{rob\ av}$	0.6 µg/L
k	2
$U_{rob\ av}$	1.2 µg/L

The robust average for Ethylbenzene in Sample S2 is 15.3 ± 1.2 µg/L.

APPENDIX 3 - 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
$\|E_n\|$	Absolute value of an E_n-score
FID	Flame Ionisation Detector
GC	Gas Chromatography
IEC	International Electrotechnical Commission
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
MS	Mass Spectrometry
MSMS	Tandem Mass Spectrometry
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
PCV	Performance Coefficient of Variation
P&T	Purge and Trap
PT	Proficiency Test
R.A.	Robust Average
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
SI	International System of Units
S.V.	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