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Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 23-05 Hydrocarbons in Soil

July 2023

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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.

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NATA WORLD RECOGNISED ACCREDITATION

Accredited for compliance with ISO/IEC 17043

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SUMMARY

AQA 23-05 Hydrocarbons in Soil commenced in February 2023. Eighteen laboratories enrolled to participate, and seventeen participants submitted results.

Four test samples were prepared at the NMI laboratory in Sydney using topsoil bought from a commercial supplier. Participants were asked to report Total Recoverable Hydrocarbons (TRH) in Sample S1, benzene, toluene, ethylbenzene and xylenes (BTEX) and volatile hydrocarbons (C6 to C10) in Sample S2, and polycyclic aromatic hydrocarbons (PAHs) in Samples S3 and S4. The assigned values were the robust averages of participants' results for all scored analytes. The associated uncertainties were estimated from the robust standard deviation of participants' results.

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

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

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

Laboratories **4**, **5**, **6**, **7**, **8**, **10**, **12**, **14**, **15**, **17** and **18** reported numeric results for all 23 analytes which were scored.

Three participants did not report results for analytes that they tested for and were present in the test samples (total of seven results). Three participants reported results for analytes that was not spiked into the test samples (total of eight results).

Of 348 z-scores, 296 (85%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

Of 345 E_n-scores, 276 (80%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratories **10**, **12** and **17** returned satisfactory z-scores and E_n-scores for all scored analytes.

- *Evaluate participants' methods for the measurement of hydrocarbon pollutants in soil.*

For TRH, participants reported using solid-liquid extraction (SLE) or sonication with various extraction solvents, and all used GC-FID for analysis. For BTEX, participants reported using SLE or sonication with methanol, followed by headspace GC-MS(/MS), or purge and trap GC-MS(/MS) for analysis. For PAHs, all participants performed SLE with various extraction solvents, and then used GC-MS(/MS) for analysis.

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

Of 385 numeric results, 349 results (91%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 3.0% to 76% of the reported result.

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

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

NMI also has certified reference material MX015 Hydrocarbon-Contaminated Soil available for purchase.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

Proficiency testing (PT) is the 'evaluation of participant performance against pre-established criteria by means of inter-laboratory 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 PT studies in:

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

1.2 Study Aims

The aims of the study were to:

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

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

1.3 Study Conduct

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

NMI is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes.[1] This study is within the scope of NMI's accreditation.

2 STUDY INFORMATION

2.1 Selection of Hydrocarbons

The hydrocarbons in this study, and their spiked levels, were typical of those encountered by environmental testing laboratories. Investigation levels for the hydrocarbons studied are set out in the National Environmental Protection (Assessment of Site Contamination) Measure (NEPM) Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

Sample S1 assessed total recoverable hydrocarbons (TRH), Sample S2 assessed volatile hydrocarbons, and benzene, toluene, ethylbenzene and xylenes (BTEX), and Samples S3 and S4 assessed polycyclic aromatic hydrocarbons (PAHs). A list of potential PAHs for Samples S3 and S4 is presented in Table 1.

Table 1 List of Possible PAHs for Samples S3 and S4

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

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

Table 2 Spiked Values of Samples

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty (mg/kg)*
S1	>C10-C16	1150	60
	>C16-C34	1810	90
	>C34-C40	255	13
	TRH	3220	160
S2	Benzene	146	7
	Toluene	830	42
	Ethylbenzene	94.9	4.7
	Xylenes	712	36
	Total BTEX	1780	90
S3	Anthracene	3.18	0.16
	Benz[*a*]anthracene	1.69	0.08
	Benzo[*a*]pyrene	2.19	0.11
	Chrysene	0.897	0.045
	Fluoranthene	2.81	0.14
	Fluorene	1.00	0.05
	Phenanthrene	0.808	0.040
	Pyrene	1.71	0.09
S4	Anthracene	2.80	0.14
	Benz[*a*]anthracene	3.97	0.20
	Benzo[*a*]pyrene	3.96	0.20
	Chrysene	1.89	0.09

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty (mg/kg)*
	Fluoranthene	0.698	0.035
	Fluorene	3.50	0.18
	Phenanthrene	1.60	0.08
	Pyrene	1.19	0.06

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

2.2 Study Timetable

The timetable of the study was:

Invitations sent	27/02/2023
Samples sent	4/04/2023
Results due	12/05/2023
Interim Report	18/05/2023
Preliminary Report	24/05/2023

2.3 Participation and Laboratory Code

Eighteen laboratories enrolled to participate, and all participants were assigned a confidential laboratory code number for this study. Seventeen participants submitted results.

2.4 Sample Preparation

Soil purchased from a Sydney supplier was used as the starting material for all samples.

Sample S1 (TRH) was prepared by spiking the soil with treated diesel fuel and commercially purchased hydraulic oil.

Sample S2 (BTEX) was prepared by spiking the soil with unleaded petrol, treated diesel fuel and benzene.

Samples S3 and S4 (PAHs) was prepared by spiking the soil with varying amounts of anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.

Further information on the preparation of the samples is given in Appendix 1.

2.5 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this PT study. The samples were prepared, packaged, stored and dispatched using a process that has been demonstrated to produce homogeneous and stable samples in previous NMI Hydrocarbons in Soil PT studies. The storage stability of petroleum hydrocarbons in soil has also been previously established.[6]

Participants' results did not give reason to question the homogeneity or transport stability of the samples (Appendix 2). To further assess possible instability, participants' results were compared to the spiked values (Section 6.1). For TRH, assigned values were within 87% to 96% of the spiked value, providing good support for its stability. Assigned values for scored BTEX and PAHs were within the ranges of 49% to 77% and 58% to 92% of the spiked values respectively, which is similar to ratios observed in previous NMI Hydrocarbons in PT studies, and an assigned value was set for analytes in this study if there was a reasonable consensus of participants' results.

2.6 Sample Storage, Dispatch and Receipt

Prior to dispatch, Samples S1, S3 and S4 were stored in a refrigerator at approximately 4 °C, and Sample S2 was stored in a freezer at approximately -20 °C. The samples were packaged in insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 4 April 2023.

The following items were also sent to participants:

- a letter which included a description of the test samples and instructions for participants; and
- a form for participants to confirm the receipt and condition of the test samples.

An Excel spreadsheet for the electronic reporting of results was emailed to participants.

2.7 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- Do not test for volatile hydrocarbons (C6-C10) or BTEX components in Sample S1.
- Participants need not test for all listed analytes.
- Report results on as received basis in units of mg/kg for the following:
  - Sample S1: Semi-volatile hydrocarbons (>C10-C40) and TRH. Use your laboratory's chosen quantitation range, and indicate what this range is. Results will be assessed using Australian NEPM fractions >C10-C16, >C16-C34, >C34-C40 and TRH. The concentration range is between 1000 – 20000 mg/kg.
  - Sample S2: Volatile Hydrocarbons (C6-C10), Benzene, Toluene, Ethylbenzene, Xylenes and Total BTEX. Individual BTEX components concentration is between 50 – 5000 mg/kg.
  - Samples S3 and S4: PAHs from the list below. The concentration range is between 0.05 – 50 mg/kg.

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

- Report results as you would report to a client, i.e. corrected for recovery or not according to your standard procedure, and applying the limit of reporting of the method used for analysis (no limit of reporting has been set for this study).
- For each analyte, report the associated expanded uncertainty (e.g. 2000 ± 200 mg/kg).
- Report any listed analyte not tested as NT as the result.
- Report the basis of your uncertainty estimates as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- Please complete the method details as requested in the results sheet.
- Return the completed results sheet by email (proficiency@measurement.gov.au).

- Please return the completed result sheet by 1 May 2023. Late results may not be included in the study report.

The results due date was extended to 12 May 2023 due to sample delivery delays to some international participants.

2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 18 May 2023.

A Preliminary Report was emailed to all participants on 24 May 2023. This report included a summary of the results reported by laboratories, assigned values, performance coefficient of variations, *z*-scores and E_n-scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

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

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about their basis of measurement uncertainty (MU). Responses received are presented in Table 3. Some responses may be modified so that the participant cannot be identified.

Table 3 Basis of Expanded Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
1				
2	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	Instrument calibration	ISO/GUM
3	Standard uncertainty based on historical data	Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	Eurachem/CITAC Guide
4	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis Instrument calibration	Instrument calibration	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
6	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	ISO/GUM
7	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		ISO/GUM
8	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM	Laboratory bias from PT studies CRM Recoveries of SS	ISO/GUM
9	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	
11	Top Down - reproducibility (standard deviation) from PT studies used directly	Duplicate analysis	CRM Instrument calibration	
12	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
13	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	Laboratory bias from PT studies Instrument calibration	

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
			Recoveries of SS Standard purity	
14	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
15	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	NATA General Accreditation Guidance Estimating and Reporting Measurement Uncertainty of Chemical Test Results
17	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		ISO/GUM
18	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis Instrument calibration	CRM Recoveries of SS	NMI Uncertainty Course

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

3.3 Participants' Comments

Participants were invited to comment on the samples, this study, or future studies. Such feedback may be useful in improving future studies. Participants' comments are presented in Table 4. Some comments may be modified so that the participant cannot be identified.

Table 4 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
1	S3 and S4	Benzo[b]fluoranthene and Benzo[k]fluoranthene are reported as total of Benzo[b+k]fluoranthene under Benzo[b]fluoranthene.	
5	S1	SAMPLE JAR DIDN'T FILL TO FULL. ONLY 4/5 FULL.	Sample S1 containers were not prepared to be completely full. The samples were prepared using a process that has been demonstrated to produce sufficiently homogeneous and stable TRH in soil samples.
	S2	Benzene concentration detected is well out of the specified range in the paper.	There was poor recovery and highly variable results for Sample S2 benzene, likely due to its volatility. No assigned value was set in this study for this analyte.
9	S3	Dibenz(a,h)anthracene present at levels too low to produce gaussian peak.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 31 with summary statistics: robust average, median, mean, number of numeric results (N), maximum (Max), minimum (Min), robust standard deviation (robust SD) and robust coefficient of variation (robust CV). Bar charts of results and performance scores are presented in Figures 2 to 27. An example chart with interpretation guide is shown in Figure 1.

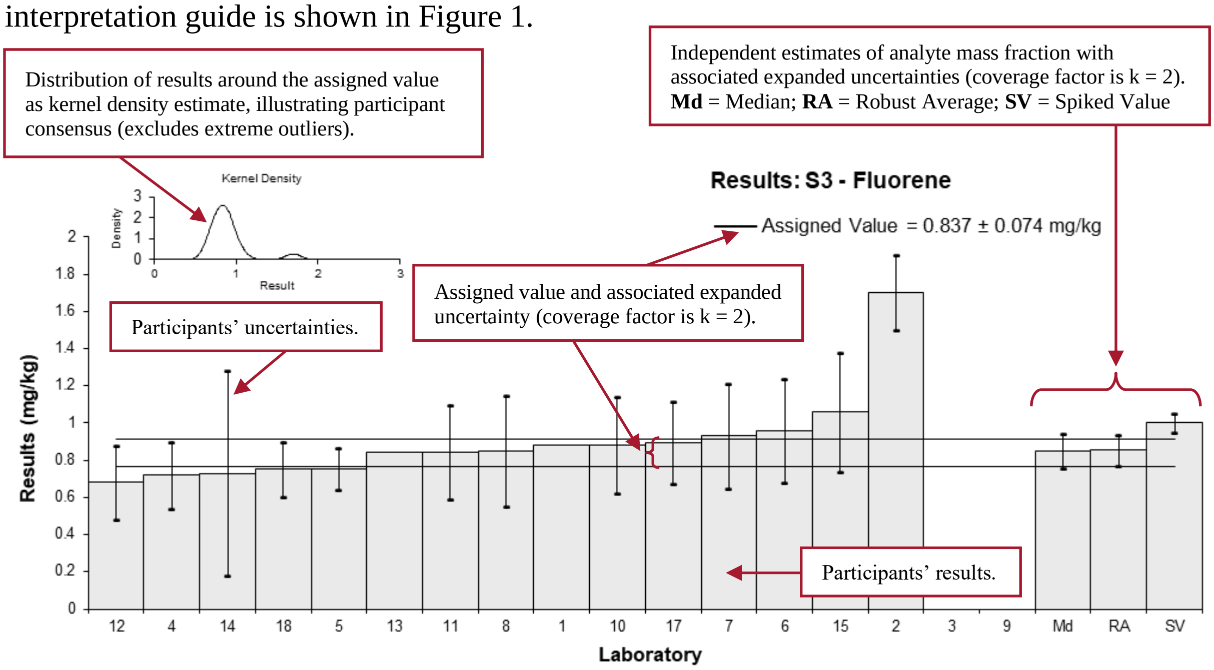


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

Outliers were any result less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value.[3,4] Extreme outliers were any obvious blunders, e.g. results with incorrect units, or for a different analyte or sample, and such results were removed before the calculation of all summary statistics.[3]

4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property of a proficiency test item'.[1] In this PT study, the property is the mass fraction of the analytes in the samples. Assigned values were the robust averages of participants' results, and the expanded uncertainties were estimated from the associated robust SDs (Appendix 3).

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

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

4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between-laboratory variation that in the judgement of the study coordinator would be expected from participants, given the levels of analytes present. The PCV is not the CV of participants' results; it is set by the study coordinator and is based on the mass fraction of the analytes and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[8] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performance and can be compared from study to study.

4.6 Target Standard Deviation for Proficiency Assessment

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

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

4.7 *z*-Score

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

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

where:

z is z-score

χ is a participant's result

X is the assigned value

σ is the target standard deviation from Equation 1

To account for potential low bias in consensus value due to inefficient methodologies, scores may be adjusted for a 'maximum acceptable result' (see also Section 6.3).

For the absolute value of a z-score:

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

4.8 *E_n*-Score

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

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

where:

E_n is E_n-score

χ is a participant's result

X is the assigned value

U_χ is the expanded uncertainty of the participant's result

U_X is the expanded uncertainty of the assigned value

For the absolute value of an E_n-score:

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

4.9 Traceability and Measurement Uncertainty

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

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

5 TABLES AND FIGURES

Table 5

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	>C10-C16
Unit	mg/kg

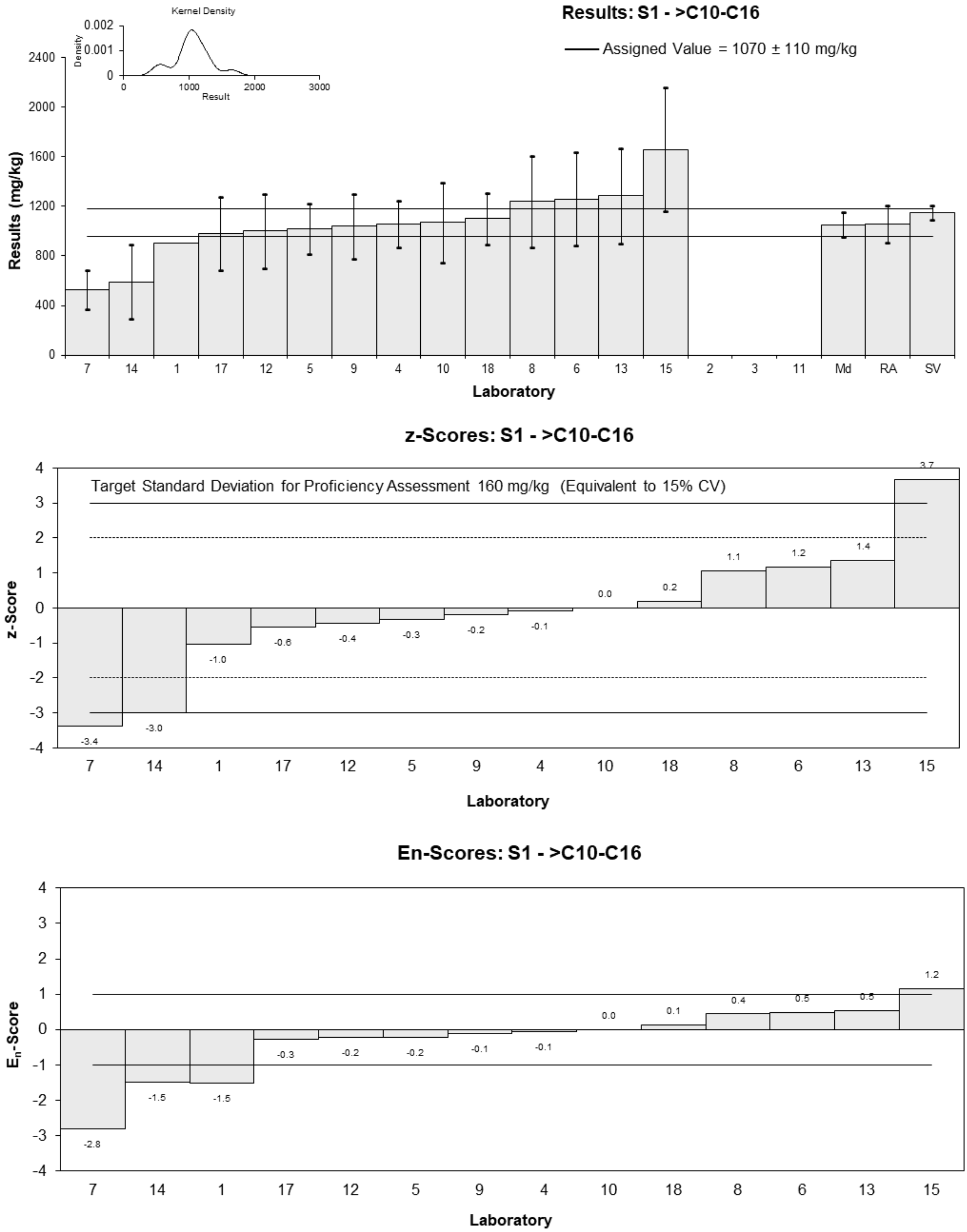
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	904	NR	-1.03	-1.51
2	NT	NT		
3	NR	NR		
4	1057	190	-0.08	-0.06
5	1016	203.2	-0.34	-0.23
6	1257.9	377.1	1.17	0.48
7*	527	158	-3.38	-2.82
8	1240	370	1.06	0.44
9	1040	260	-0.19	-0.11
10	1070	321	0.00	0.00
11	NR	NR		
12	1000	300	-0.44	-0.22
13	1286	386	1.35	0.54
14	590	300	-2.99	-1.50
15*	1659	498	3.67	1.15
17	982	295	-0.55	-0.28
18	1100	209	0.19	0.13

* Outlier, see Section 4.2

Statistics

Assigned Value	1070	110
Spike Value	1150	60
Robust Average	1060	150
Median	1050	100
Mean	1050	
N	14	
Max	1659	
Min	527	
Robust SD	220	
Robust CV	21%	



Results: S1 - >C10-C16
Assigned Value = 1070 ± 110 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
7 14 1 17 12 5 9 4 10 18 8 6 13 15 2 3 11 Md RA SV
z-Scores: S1 - >C10-C16
Target Standard Deviation for Proficiency Assessment 160 mg/kg (Equivalent to 15% CV)
z-Score
-3.4 -3.0 -1.0 -0.6 -0.4 -0.3 -0.2 -0.1 0.0 0.2 1.1 1.2 1.4 3.7
7 14 1 17 12 5 9 4 10 18 8 6 13 15
Laboratory
En-Scores: S1 - >C10-C16
En-Score
-2.8 -1.5 -1.5 -0.3 -0.2 -0.2 -0.1 -0.1 0.0 0.1 0.4 0.5 0.5 1.2
7 14 1 17 12 5 9 4 10 18 8 6 13 15
Laboratory

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	>C16-C34
Unit	mg/kg

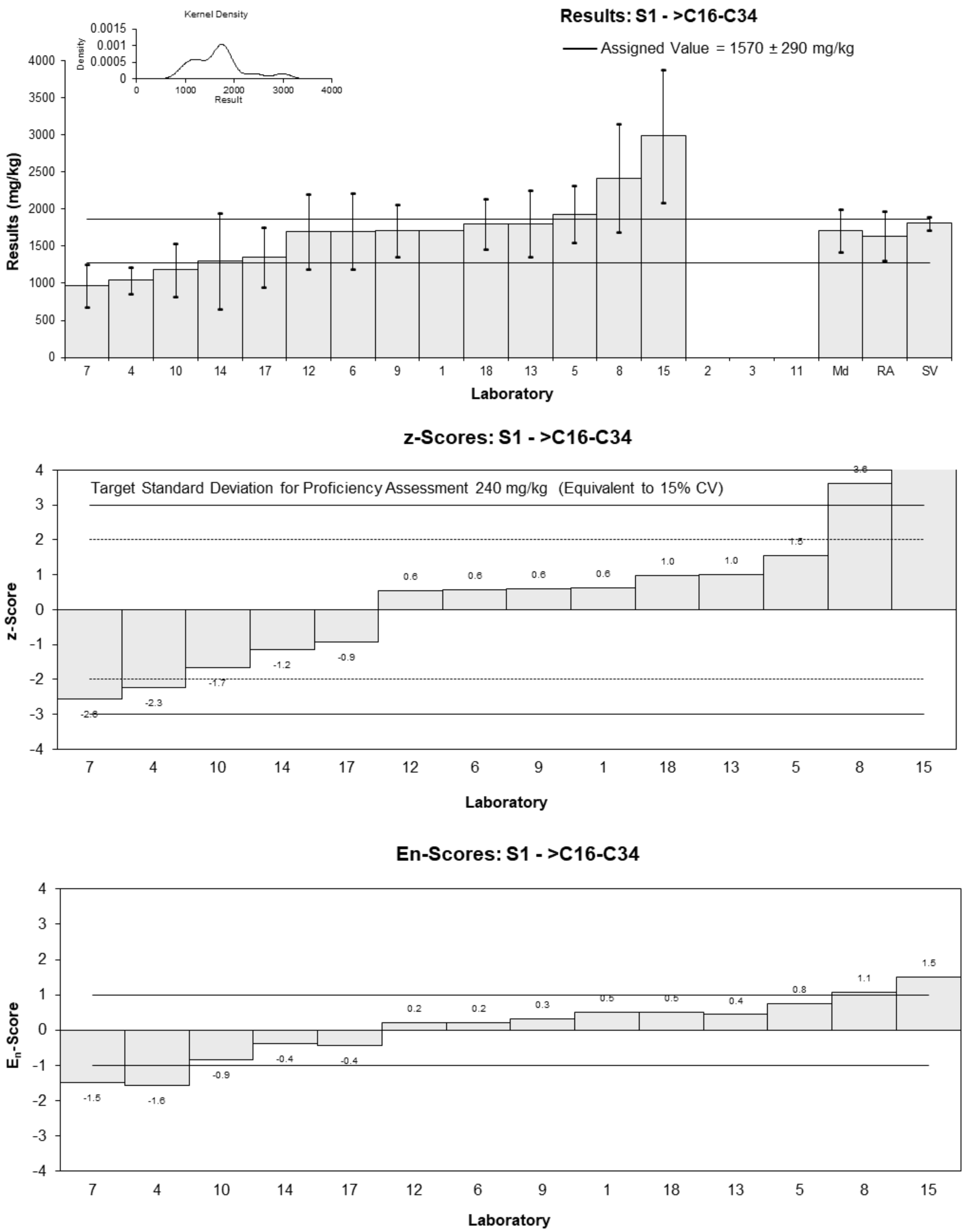
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1716	NR	0.62	0.50
2	NT	NT		
3	NR	NR		
4	1041	177	-2.25	-1.56
5	1933	386.6	1.54	0.75
6	1701.4	510.4	0.56	0.22
7	965	290	-2.57	-1.48
8	2420	730	3.61	1.08
9	1710	350	0.59	0.31
10	1180	354	-1.66	-0.85
11	NR	NR		
12	1700	510	0.55	0.22
13	1806	452	1.00	0.44
14	1300	650	-1.15	-0.38
15*	2990	897	6.03	1.51
17	1353	406	-0.92	-0.43
18	1800	342	0.98	0.51

* Outlier, see Section 4.2

Statistics

Assigned Value	1570	290
Spike Value	1810	90
Robust Average	1640	330
Median	1710	290
Mean	1690	
N	14	
Max	2990	
Min	965	
Robust SD	500	
Robust CV	30%	



Results: S1 - >C16-C34
Assigned Value = 1570 ± 290 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
7 4 10 14 17 12 6 9 1 18 13 5 8 15 2 3 11 Md RA SV
z-Scores: S1 - >C16-C34
Target Standard Deviation for Proficiency Assessment 240 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
7 4 10 14 17 12 6 9 1 18 13 5 8 15
En-Scores: S1 - >C16-C34
E_n-Score
Laboratory
7 4 10 14 17 12 6 9 1 18 13 5 8 15

Figure 3

Table 7

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	>C34-C40
Unit	mg/kg

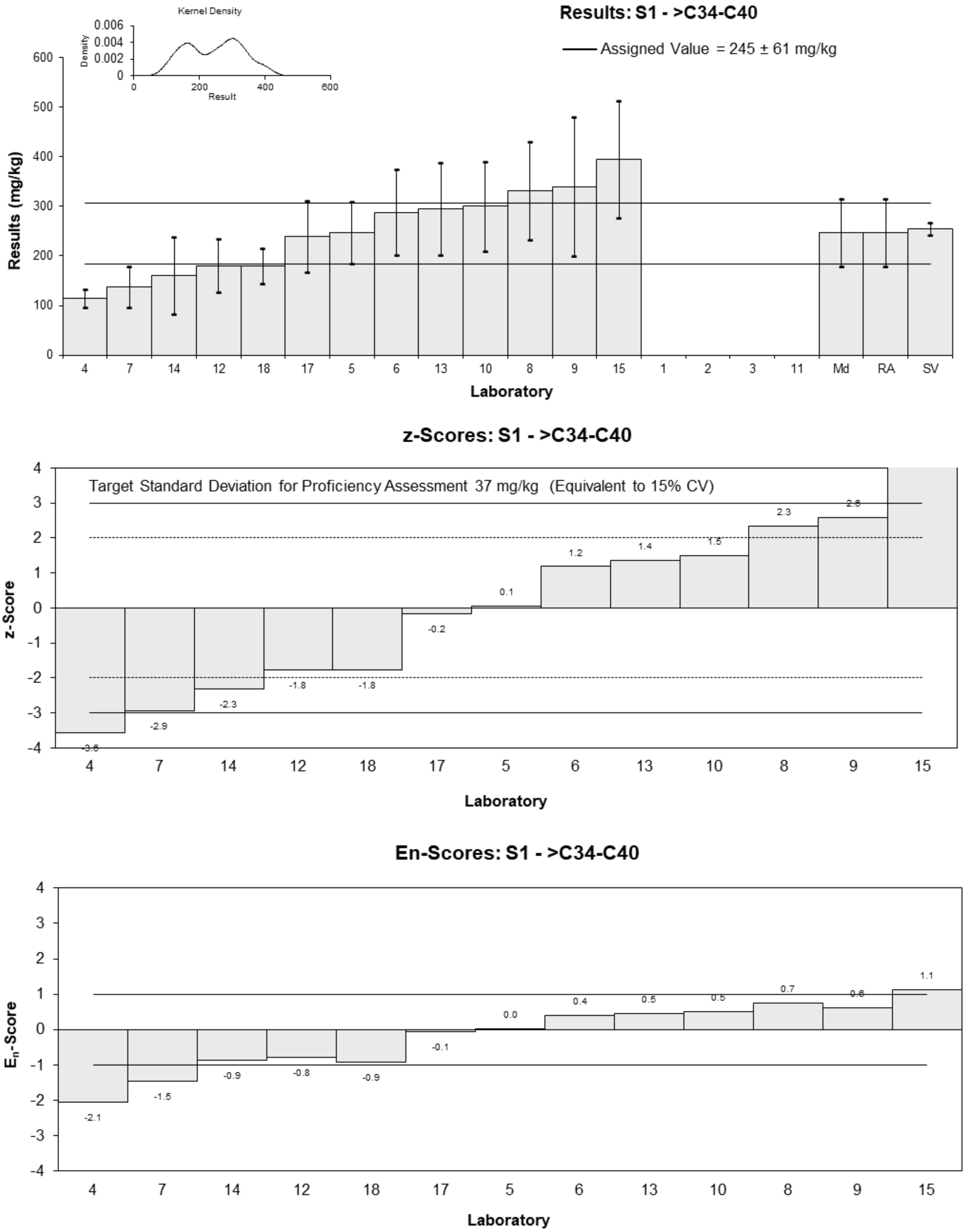
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	NT	NT		
3	NR	NR		
4*	114	18	-3.56	-2.06
5	247	61.75	0.05	0.02
6	288.3	86.5	1.18	0.41
7	137	41	-2.94	-1.47
8	331	99	2.34	0.74
9	340	140	2.59	0.62
10	300	90	1.50	0.51
11	NR	NR		
12	180	54	-1.77	-0.80
13	295	94	1.36	0.45
14	160	78	-2.31	-0.86
15*	395	119	4.08	1.12
17	239	72	-0.16	-0.06
18	180	36	-1.77	-0.92

* Outlier, see Section 4.2

Statistics

Assigned Value	245	61
Spike Value	255	13
Robust Average	247	68
Median	247	69
Mean	247	
N	13	
Max	395	
Min	114	
Robust SD	99	
Robust CV	40%	



Results: S1 - >C34-C40
Assigned Value = 245 ± 61 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4
7
14
12
18
17
5
6
13
10
8
9
15
1
2
3
11
Md
RA
SV
z-Scores: S1 - >C34-C40
Target Standard Deviation for Proficiency Assessment 37 mg/kg (Equivalent to 15% CV)
z-Score
-3.6
-2.9
-2.3
-1.8
-1.8
-0.2
0.1
1.2
1.4
1.5
2.3
2.6
Laboratory
En-Scores: S1 - >C34-C40
E_n-Score
-2.1
-1.5
-0.9
-0.8
-0.9
-0.1
0.0
0.4
0.5
0.5
0.7
0.6
1.1
Laboratory

Figure 4

Table 8 Non-NEPM Hydrocarbon Ranges Reported by Participants for Sample S1[5]

Lab. Code	Range	Result (mg/kg)	Uncertainty (mg/kg)
3	C7-C9	<20	6.7
	C10-C14	470	110
	C15-C36	2880	450

Table 9

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	TRH
Unit	mg/kg

Participant Results

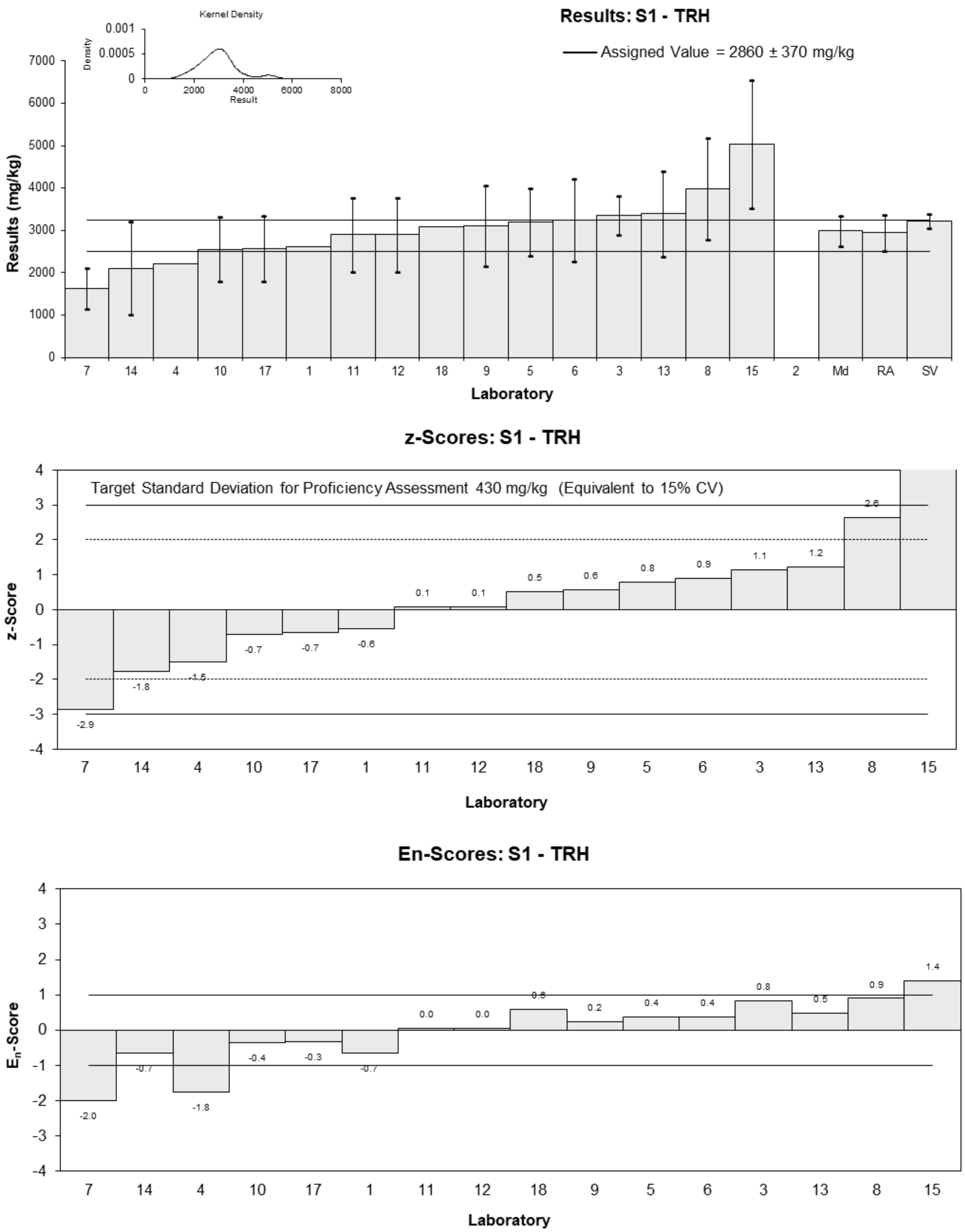
Lab. Code	Result	Uncertainty	z	E_n
1	2619	NR	-0.56	-0.65
2	NT	NT		
3	3350	460	1.14	0.83
4	2212	NR	-1.51	-1.75
5	3196	799	0.78	0.38
6	3247.6	974.3	0.90	0.37
7	1629	489	-2.87	-2.01
8	3991	1199	2.64	0.90
9	3100	950	0.56	0.24
10	2550	765	-0.72	-0.36
11	2896	868.8	0.08	0.04
12	2900	870	0.09	0.04
13	3387	1016	1.23	0.49
14	2100	1100	-1.77	-0.65
15*	5044	1513	5.09	1.40
17	2575	773	-0.66	-0.33
18	3080	NR	0.51	0.59

* Outlier, see Section 4.2

Statistics

Assigned Value	2860	370
Spike Value	3220	160
Robust Average	2940	420
Median	2990	360
Mean	2990	
N	16	
Max	5044	
Min	1629	
Robust SD	670	
Robust CV	23%	

Laboratories 4 and 18 did not report a TRH value. The study coordinator summed the individual hydrocarbon ranges, and no estimate of uncertainty of the TRH result was made.



Results: S1 - TRH
Assigned Value = 2860 ± 370 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S1 - TRH
Target Standard Deviation for Proficiency Assessment 430 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - TRH
En-Score
Laboratory

Figure 5

Table 10

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	C6-C10
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	NR	NR
2	NT	NT
3	NT	NT
4	1397	88
5	1873	374.6
6	2420	726
7	NT	NT
8	1620	540
9	NR	NR
10	1300	390
11	NT	NT
12	1600	480
13	NT	NT
14	NT	NT
15	1556	467
17	1306	340
18	1740	170

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Robust Average	1600	230
Median	1600	250
Mean	1650	
N	9	
Max	2420	
Min	1300	
Robust SD	280	
Robust CV	18%	

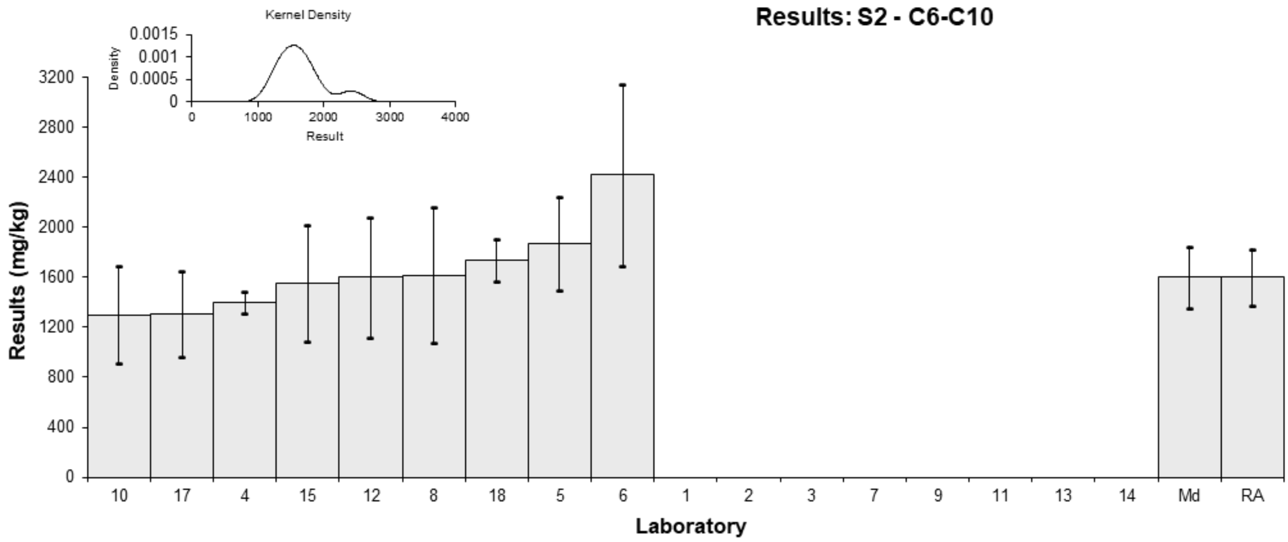

Kernel Density
0.0015
0.001
0.0005
0
Density
0
1000
2000
3000
4000
Result
Results: S2 - C6-C10
3200
2800
2400
2000
1600
1200
800
400
0
Results (mg/kg)
10
17
4
15
12
8
18
5
6
1
2
3
7
9
11
13
14
Md
RA
Laboratory

Figure 6

Table 11

Sample Details

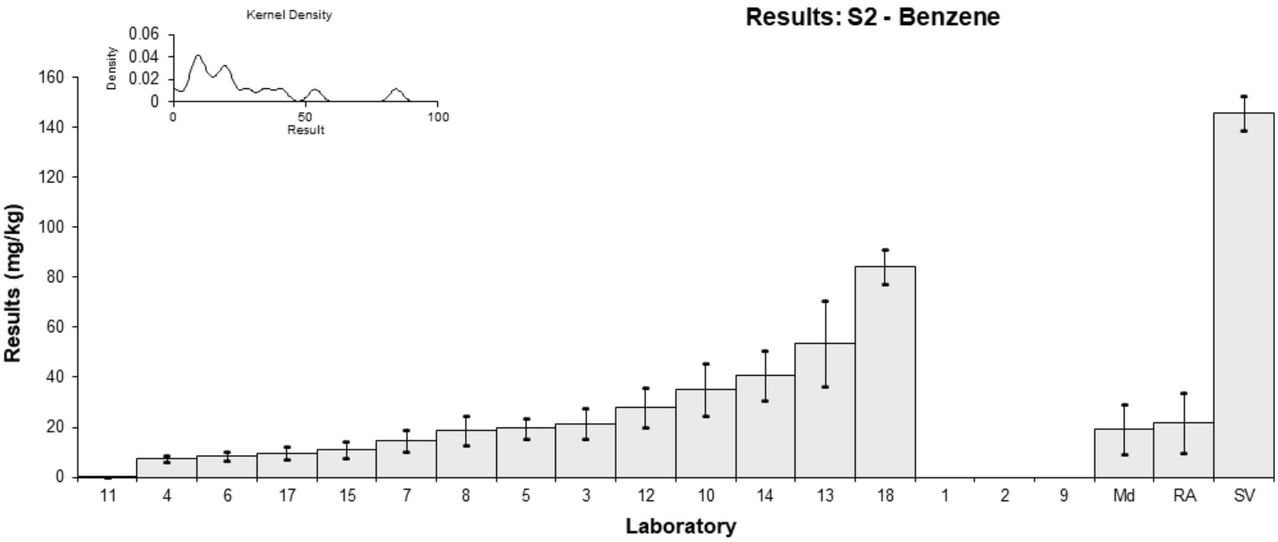
Sample No.	S2
Matrix	Soil
Analyte	Benzene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	NR	NR
2	NT	NT
3	21.5	6.1
4	7.6	1.3
5	19.5	4.29
6	8.5	1.7
7	14.6	4.4
8	18.6	6.0
9	NR	NR
10	34.9	10.5
11	0.062	0.0186
12	28	8
13	53.6	17.2
14	41	10
15	11	3.3
17	9.63	2.5
18	84.4	6.9

Statistics

Assigned Value	Not Set	
Spike Value	146	7
Robust Average	22	12
Median	19.1	9.9
Mean	25	
N	14	
Max	84.4	
Min	0.062	
Robust SD	18	
Robust CV	80%	



Results: S2 - Benzene
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11
4
6
17
15
7
8
5
3
12
10
14
13
18
1
2
9
Md
RA
SV

Figure 7

Table 12

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Toluene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	NR	NR
2	NT	NT
3	390	110
4	234	37
5	384	58.3
6	396	79.2
7	366	110
8	346	69
9	NR	NR
10	256	77
11**	29	8.7
12	400	120
13	437	79
14	430	110
15	260	78
17	292	76
18	620	77

** Gross Error, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	830	42
Robust Average	360	62
Median	384	47
Mean	370	
N	13	
Max	620	
Min	234	
Robust SD	90	
Robust CV	25%	

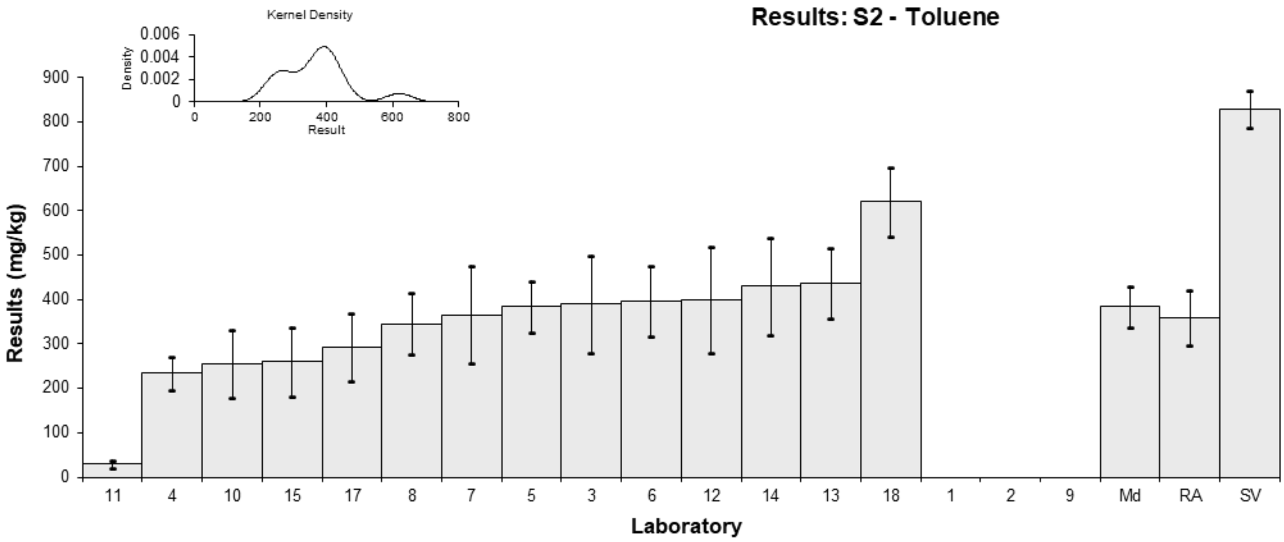

Kernel Density
0.006
0.004
0.002
0
Density
0
200
400
600
800
Result
Results: S2 - Toluene
900
800
700
600
500
400
300
200
100
0
Results (mg/kg)
11
4
10
15
17
8
7
5
3
6
12
14
13
18
1
2
9
Md
RA
SV
Laboratory

Figure 8

Table 13

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Ethylbenzene
Unit	mg/kg

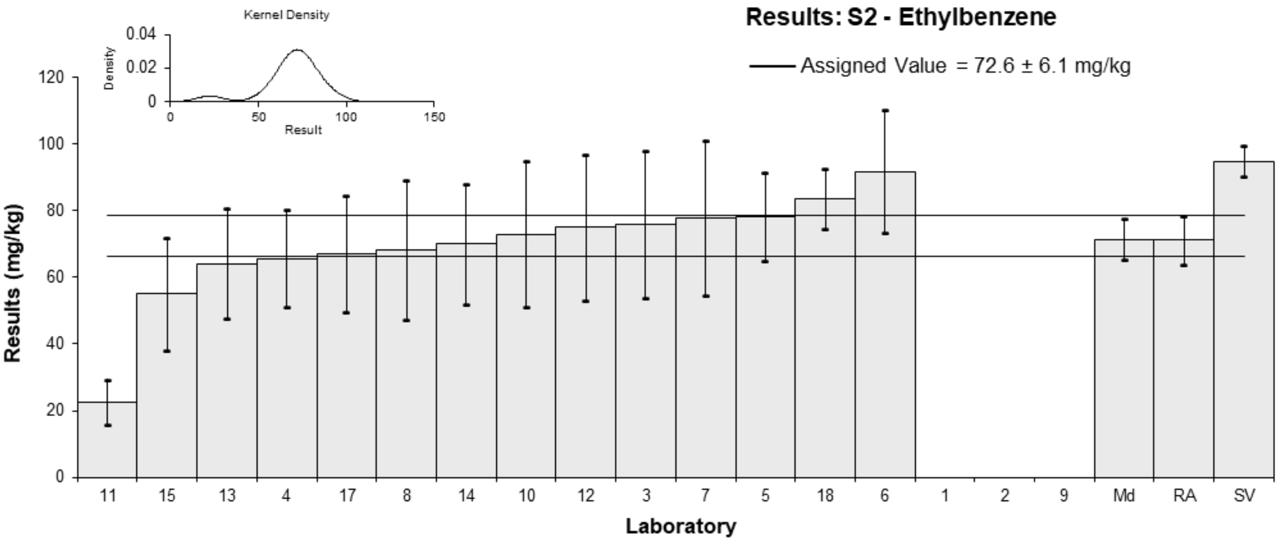
Participant Results

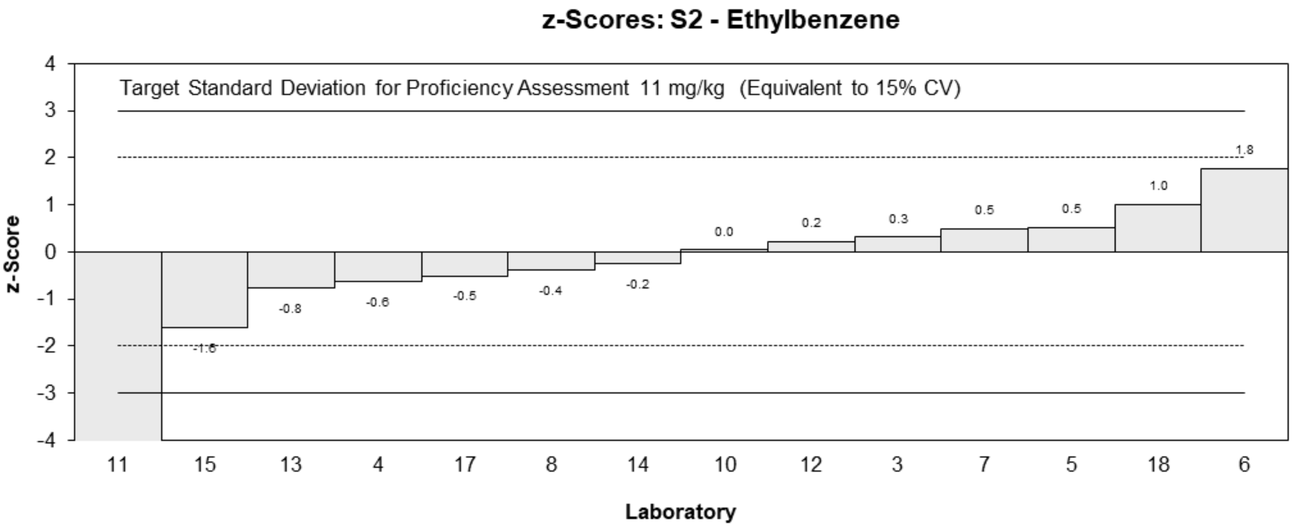
Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	NT	NT		
3	76	22	0.31	0.15
4	65.7	14.5	-0.63	-0.44
5	78.3	13.3	0.52	0.39
6	91.8	18.36	1.76	0.99
7	77.9	23.4	0.49	0.22
8	68.3	21.0	-0.39	-0.20
9	NR	NR		
10	73	22	0.04	0.02
11*	22.54	6.762	-4.60	-5.50
12	75	22	0.22	0.11
13	64.2	16.7	-0.77	-0.47
14	70	18	-0.24	-0.14
15	55	17	-1.62	-0.97
17	67.1	17.4	-0.51	-0.30
18	83.6	9.0	1.01	1.01

* Outlier, see Section 4.2

Statistics

Assigned Value	72.6	6.1
Spike Value	94.9	4.7
Robust Average	71.2	7.2
Median	71.5	6.0
Mean	69.2	
N	14	
Max	91.8	
Min	22.54	
Robust SD	11	
Robust CV	15%	


Results: S2 - Ethylbenzene
Assigned Value = 72.6 ± 6.1 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 15 13 4 17 8 14 10 12 3 7 5 18 6 1 2 9 Md RA SV


z-Scores: S2 - Ethylbenzene
Target Standard Deviation for Proficiency Assessment 11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
11 15 13 4 17 8 14 10 12 3 7 5 18 6
-1.6 -0.8 -0.6 -0.5 -0.4 -0.2 0.0 0.2 0.3 0.5 0.5 1.0 1.8

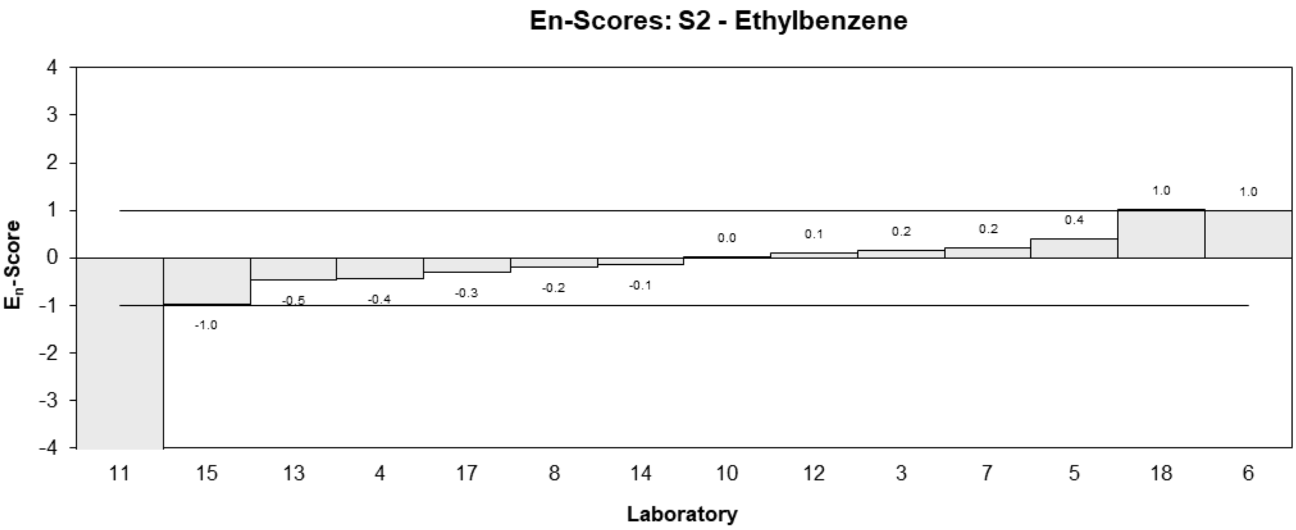

En-Scores: S2 - Ethylbenzene
En-Score
Laboratory
11 15 13 4 17 8 14 10 12 3 7 5 18 6
-1.0 -0.5 -0.4 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.2 0.4 1.0 1.0

Figure 9

Table 14

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Xylenes
Unit	mg/kg

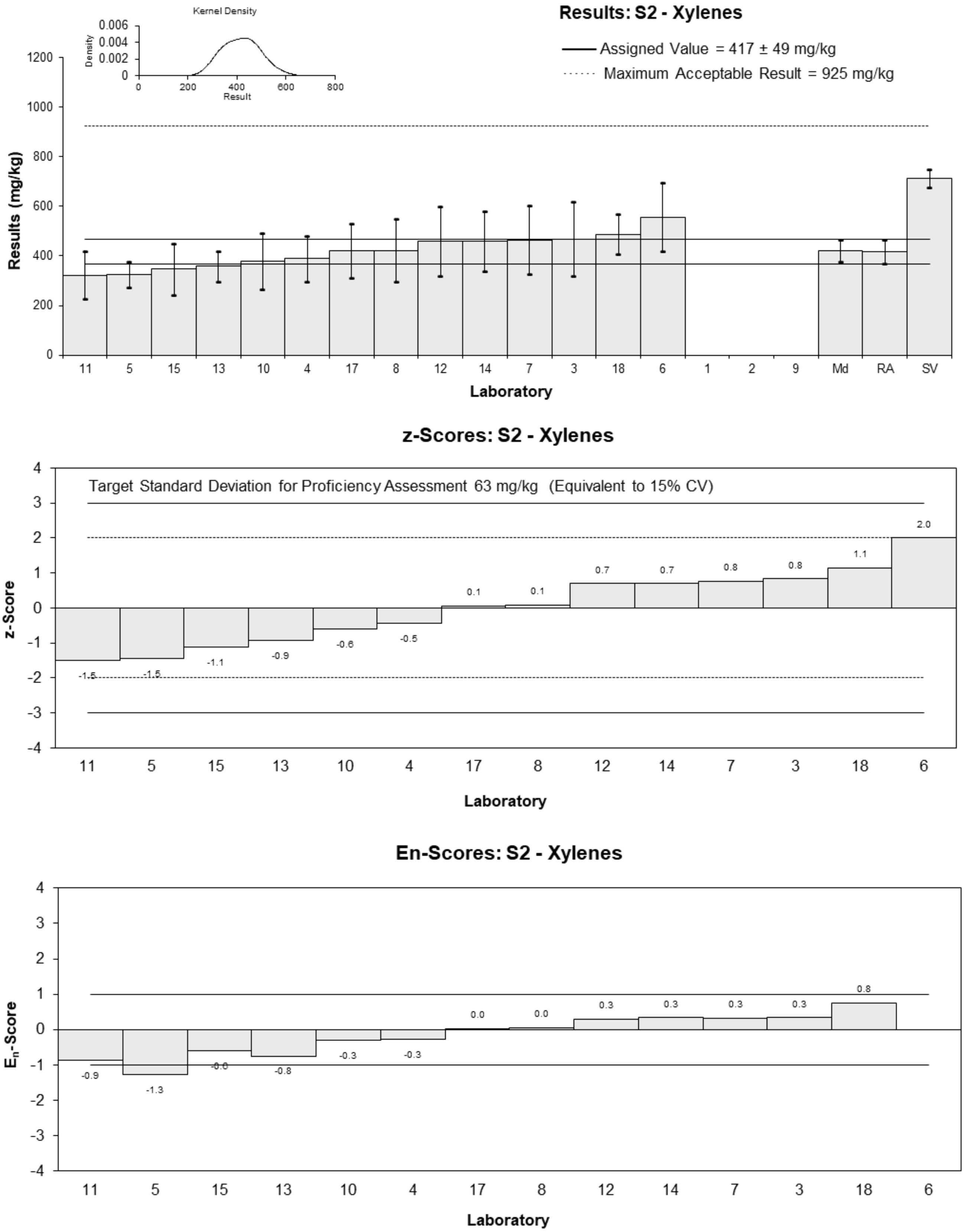
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	NT	NT		
3	469	149	0.83	0.33
4	389	93	-0.45	-0.27
5	326	52.16	-1.45	-1.27
6	557	139	2.00▼	
7	465	140	0.77	0.32
8	422	126	0.08	0.04
9	NR	NR		
10	379	114	-0.61	-0.31
11	322.5	96.75	-1.51	-0.87
12	460	140	0.69	0.29
13	358	61	-0.94	-0.75
14	460	120	0.69	0.33
15	347	104	-1.12	-0.61
17	421	109	0.06	0.03
18	488	81	1.14	0.75

▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	417	49
Spike Value	712	36
Robust Average	417	49
Max Acceptable Result	925	
Median	422	45
Mean	419	
N	14	
Max	557	
Min	322.5	
Robust SD	73	
Robust CV	17%	



Results: S2 - Xylenes
Assigned Value = 417 ± 49 mg/kg
Maximum Acceptable Result = 925 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 5 15 13 10 4 17 8 12 14 7 3 18 6 1 2 9 Md RA SV
z-Scores: S2 - Xylenes
Target Standard Deviation for Proficiency Assessment 63 mg/kg (Equivalent to 15% CV)
z-Score
-1.5 -1.5 -1.1 -0.9 -0.6 -0.5 0.1 0.1 0.7 0.7 0.8 0.8 1.1 2.0
11 5 15 13 10 4 17 8 12 14 7 3 18 6
Laboratory
En-Scores: S2 - Xylenes
En-Score
-0.9 -1.3 -0.6 -0.8 -0.3 -0.3 0.0 0.0 0.3 0.3 0.3 0.3 0.8
11 5 15 13 10 4 17 8 12 14 7 3 18 6
Laboratory

Figure 10

Table 15

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Total BTEX
Unit	mg/kg

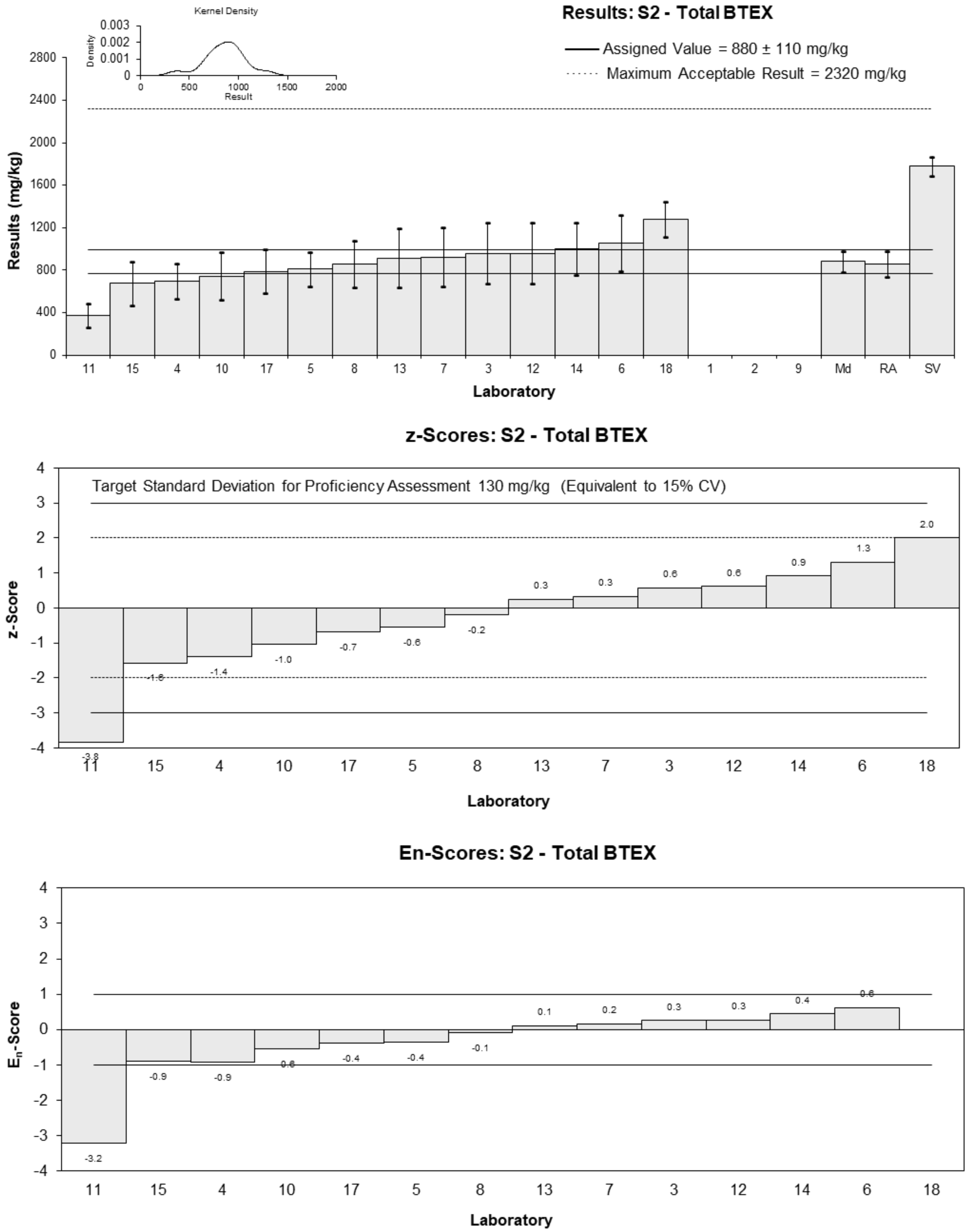
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	NT	NT		
3	957	287	0.58	0.25
4	696	167	-1.39	-0.92
5	808	161.6	-0.55	-0.37
6	1053.3	263	1.31	0.61
7	924	277	0.33	0.15
8	855	222	-0.19	-0.10
9	NR	NR		
10	742.9	223	-1.04	-0.55
11*	374.1	112.23	-3.83	-3.22
12	960	290	0.61	0.26
13	913	280	0.25	0.11
14	1000	250	0.91	0.44
15	673	202	-1.57	-0.90
17	789	205	-0.69	-0.39
18	1277	165	2.00▼	

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

Statistics

Assigned Value	880	110
Spike Value	1780	90
Robust Average	860	120
Max Acceptable Result	2320	
Median	880	100
Mean	860	
N	14	
Max	1277	
Min	374.1	
Robust SD	170	
Robust CV	20%	



Kernel Density
Density
Result
Results: S2 - Total BTEX
Assigned Value = 880 ± 110 mg/kg
Maximum Acceptable Result = 2320 mg/kg
Results (mg/kg)
Laboratory
z-Scores: S2 - Total BTEX
Target Standard Deviation for Proficiency Assessment 130 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S2 - Total BTEX
E_n-Score
Laboratory

Figure 11

Table 16

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Anthracene
Unit	mg/kg

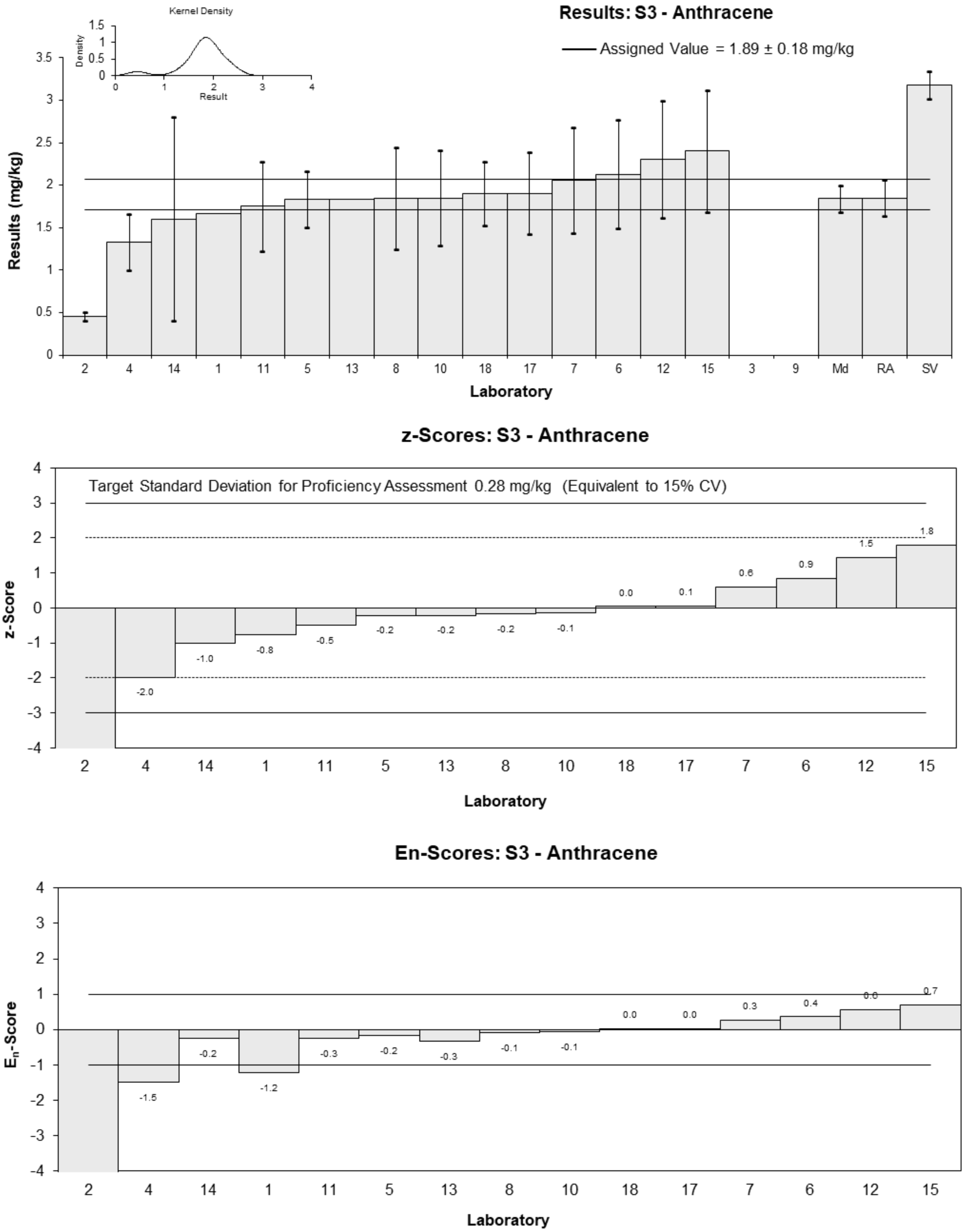
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.67	NR	-0.78	-1.22
2*	0.45	0.05	-5.08	-7.71
3	NS	NS		
4	1.33	0.33	-1.98	-1.49
5	1.83	0.33	-0.21	-0.16
6	2.13	0.64	0.85	0.36
7	2.06	0.62	0.60	0.26
8	1.84	0.60	-0.18	-0.08
9	NR	NR		
10	1.85	0.56	-0.14	-0.07
11	1.75	0.525	-0.49	-0.25
12	2.3	0.69	1.45	0.57
13	1.83	NR	-0.21	-0.33
14	1.6	1.2	-1.02	-0.24
15	2.40	0.72	1.80	0.69
17	1.905	0.48	0.05	0.03
18	1.9	0.38	0.04	0.02

* Outlier, see Section 4.2

Statistics

Assigned Value	1.89	0.18
Spike Value	3.18	0.16
Robust Average	1.85	0.21
Median	1.84	0.16
Mean	1.79	
N	15	
Max	2.4	
Min	0.45	
Robust SD	0.32	
Robust CV	18%	



Results: S3 - Anthracene
Assigned Value = 1.89 ± 0.18 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S3 - Anthracene
Target Standard Deviation for Proficiency Assessment 0.28 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S3 - Anthracene
En-Score
Laboratory

Figure 12

Table 17

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Benz[*a*]anthracene
Unit	mg/kg

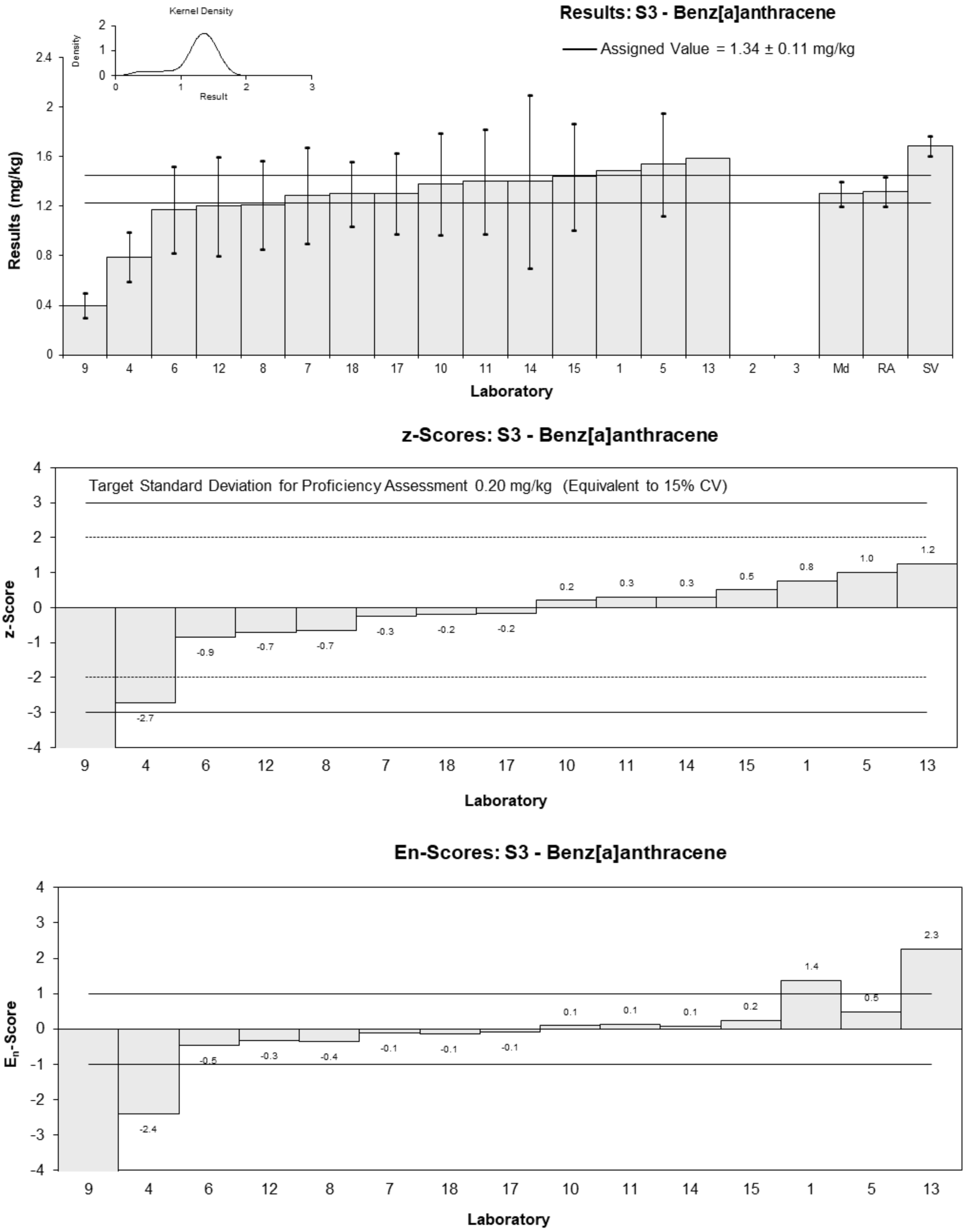
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.49	NR	0.75	1.36
2	<0.05	0.005		
3	NS	NS		
4	0.79	0.2	-2.74	-2.41
5	1.54	0.415	1.00	0.47
6	1.17	0.35	-0.85	-0.46
7	1.29	0.39	-0.25	-0.12
8	1.21	0.36	-0.65	-0.35
9*	0.40	0.10	-4.68	-6.32
10	1.38	0.41	0.20	0.09
11	1.4	0.42	0.30	0.14
12	1.2	0.4	-0.70	-0.34
13	1.59	NR	1.24	2.27
14	1.4	0.70	0.30	0.08
15	1.44	0.43	0.50	0.23
17	1.304	0.33	-0.18	-0.10
18	1.3	0.26	-0.20	-0.14

* Outlier, see Section 4.2

Statistics

Assigned Value	1.34	0.11
Spike Value	1.69	0.08
Robust Average	1.32	0.12
Median	1.30	0.10
Mean	1.26	
N	15	
Max	1.59	
Min	0.4	
Robust SD	0.19	
Robust CV	14%	



Results: S3 - Benz[a]anthracene
Assigned Value = 1.34 ± 0.11 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9 4 6 12 8 7 18 17 10 11 14 15 1 5 13 2 3 Md RA SV
z-Scores: S3 - Benz[a]anthracene
Target Standard Deviation for Proficiency Assessment 0.20 mg/kg (Equivalent to 15% CV)
z-Score
-2.7 -0.9 -0.7 -0.7 -0.3 -0.2 -0.2 0.2 0.3 0.3 0.5 0.8 1.0 1.2
Laboratory
En-Scores: S3 - Benz[a]anthracene
E_n-Score
-2.4 -0.5 -0.3 -0.4 -0.1 -0.1 -0.1 0.1 0.1 0.1 0.2 1.4 0.5 2.3
Laboratory

Figure 13

Table 18

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Benzo[*a*]pyrene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.20	NR	-0.32	-0.38
2*	0.53	0.07	-3.86	-4.18
3	NS	NS		
4	1.53	0.38	1.43	0.65
5	1.2	0.252	-0.32	-0.20
6	1.26	0.38	0.00	0.00
7	0.97	0.29	-1.53	-0.88
8	1.15	0.40	-0.58	-0.26
9*	0.40	0.10	-4.55	-4.56
10	1.23	0.37	-0.16	-0.07
11	1.45	0.435	1.01	0.41
12	1.1	0.32	-0.85	-0.45
13	1.57	NR	1.64	1.94
14	1.6	0.79	1.80	0.42
15	1.24	0.37	-0.11	-0.05
17	1.202	0.30	-0.31	-0.17
18	0.96	0.19	-1.59	-1.21

* Outlier, see Section 4.2

Statistics

Assigned Value	1.26	0.16
Spike Value	2.19	0.11
Robust Average	1.20	0.18
Median	1.20	0.15
Mean	1.16	
N	16	
Max	1.6	
Min	0.4	
Robust SD	0.29	
Robust CV	24%	

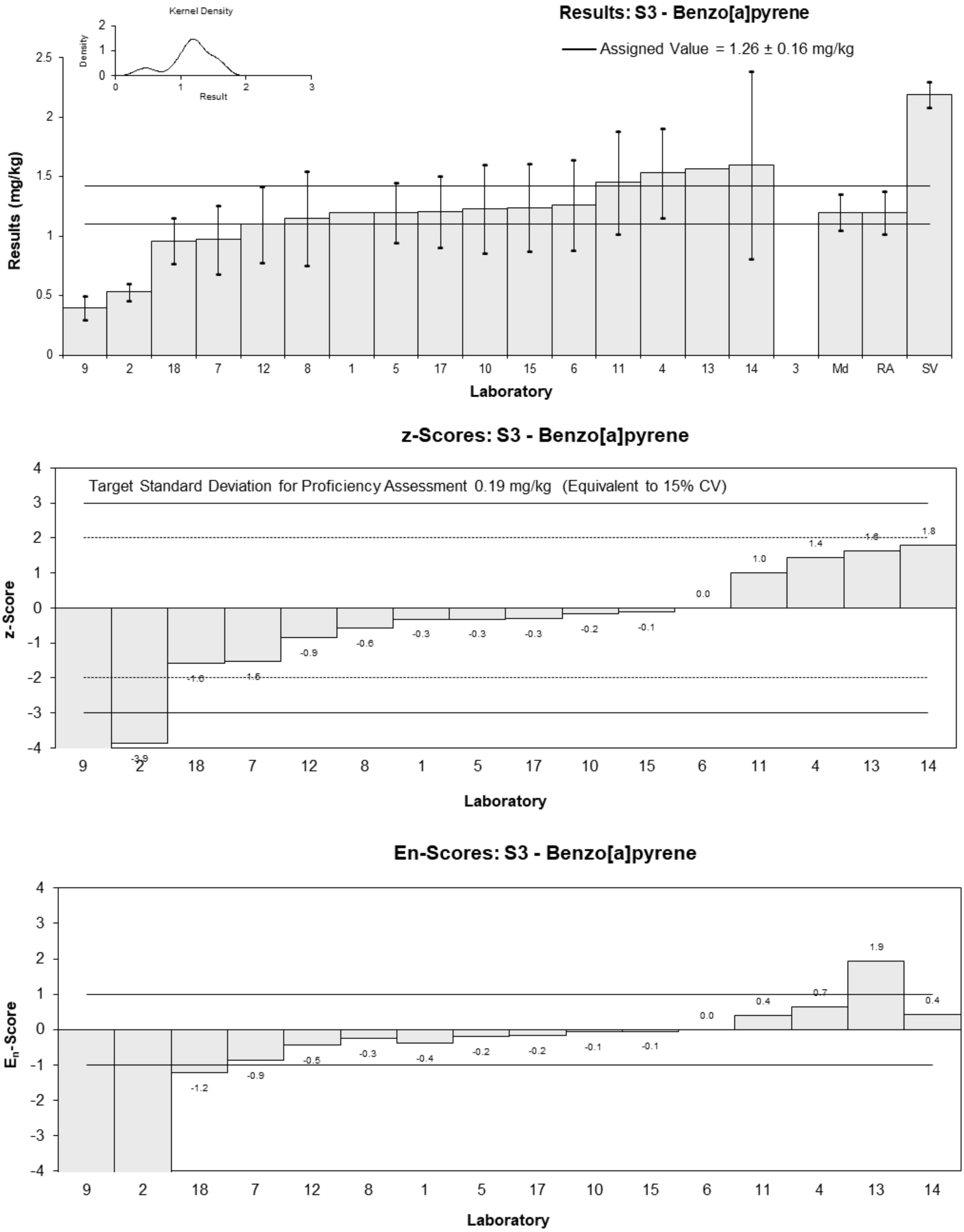

Results: S3 - Benzo[a]pyrene
Assigned Value = 1.26 ± 0.16 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9 2 18 7 12 8 1 5 17 10 15 6 11 4 13 14 3 Md RA SV
z-Scores: S3 - Benzo[a]pyrene
Target Standard Deviation for Proficiency Assessment 0.19 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
9 2 18 7 12 8 1 5 17 10 15 6 11 4 13 14
-3.9 -1.6 -1.5 -0.9 -0.6 -0.3 -0.3 -0.3 -0.2 -0.1 0.0 1.0 1.4 1.6 1.8
En-Scores: S3 - Benzo[a]pyrene
En-Score
Laboratory
9 2 18 7 12 8 1 5 17 10 15 6 11 4 13 14
-1.2 -0.9 -0.5 -0.3 -0.4 -0.2 -0.2 -0.1 -0.1 0.0 0.4 0.7 1.9 0.4

Figure 14

Table 19

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Chrysene
Unit	mg/kg

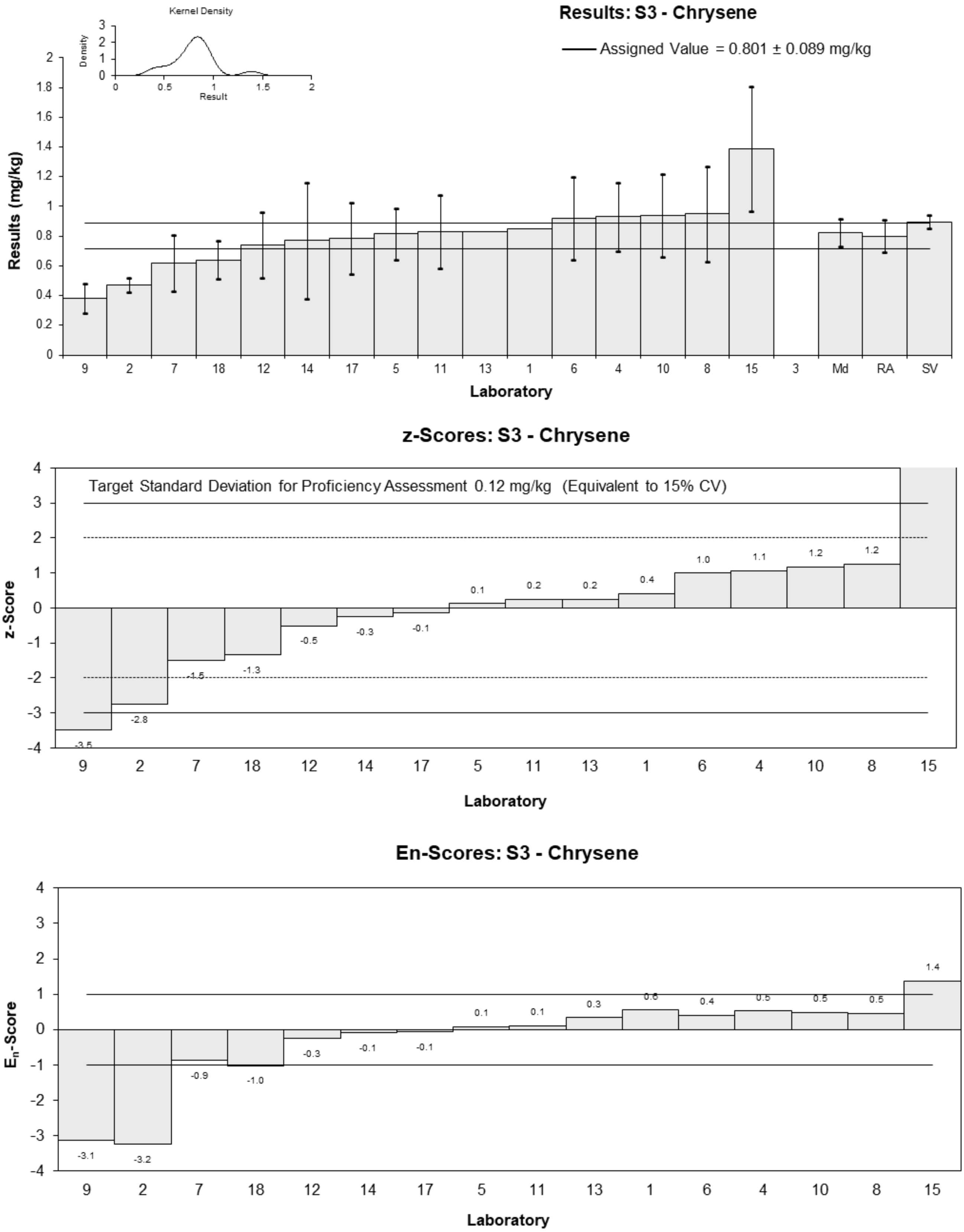
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.85	NR	0.41	0.55
2	0.47	0.05	-2.75	-3.24
3	NS	NS		
4	0.93	0.23	1.07	0.52
5	0.815	0.17115	0.12	0.07
6	0.92	0.28	0.99	0.41
7	0.62	0.19	-1.51	-0.86
8	0.95	0.32	1.24	0.45
9*	0.38	0.10	-3.50	-3.14
10	0.94	0.28	1.16	0.47
11	0.83	0.249	0.24	0.11
12	0.74	0.22	-0.51	-0.26
13	0.83	NR	0.24	0.33
14	0.77	0.39	-0.26	-0.08
15*	1.39	0.42	4.90	1.37
17	0.784	0.24	-0.14	-0.07
18	0.64	0.13	-1.34	-1.02

* Outlier, see Section 4.2

Statistics

Assigned Value	0.801	0.089
Spike Value	0.897	0.045
Robust Average	0.80	0.11
Median	0.823	0.095
Mean	0.80	
N	16	
Max	1.39	
Min	0.38	
Robust SD	0.17	
Robust CV	21%	



Kernel Density
Density
Result
Results: S3 - Chrysene
Assigned Value = 0.801 ± 0.089 mg/kg
Results (mg/kg)
Laboratory
9 2 7 18 12 14 17 5 11 13 1 6 4 10 8 15 3 Md RA SV
z-Scores: S3 - Chrysene
Target Standard Deviation for Proficiency Assessment 0.12 mg/kg (Equivalent to 15% CV)
z-Score
-3.5 -2.8 -1.5 -1.3 -0.5 -0.3 -0.1 0.1 0.2 0.2 0.4 1.0 1.1 1.2 1.2
Laboratory
9 2 7 18 12 14 17 5 11 13 1 6 4 10 8 15
En-Scores: S3 - Chrysene
E_n-Score
-3.1 -3.2 -0.9 -1.0 -0.3 -0.1 -0.1 0.1 0.1 0.3 0.6 0.4 0.5 0.5 0.5 1.4
Laboratory
9 2 7 18 12 14 17 5 11 13 1 6 4 10 8 15

Figure 15

Table 20

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Fluoranthene
Unit	mg/kg

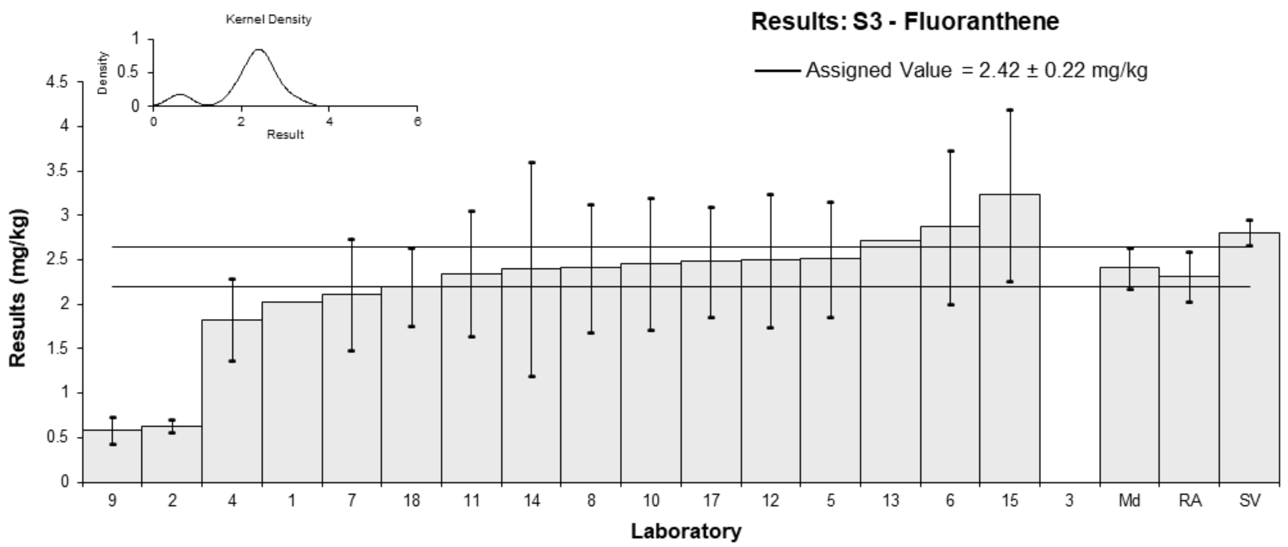
Participant Results

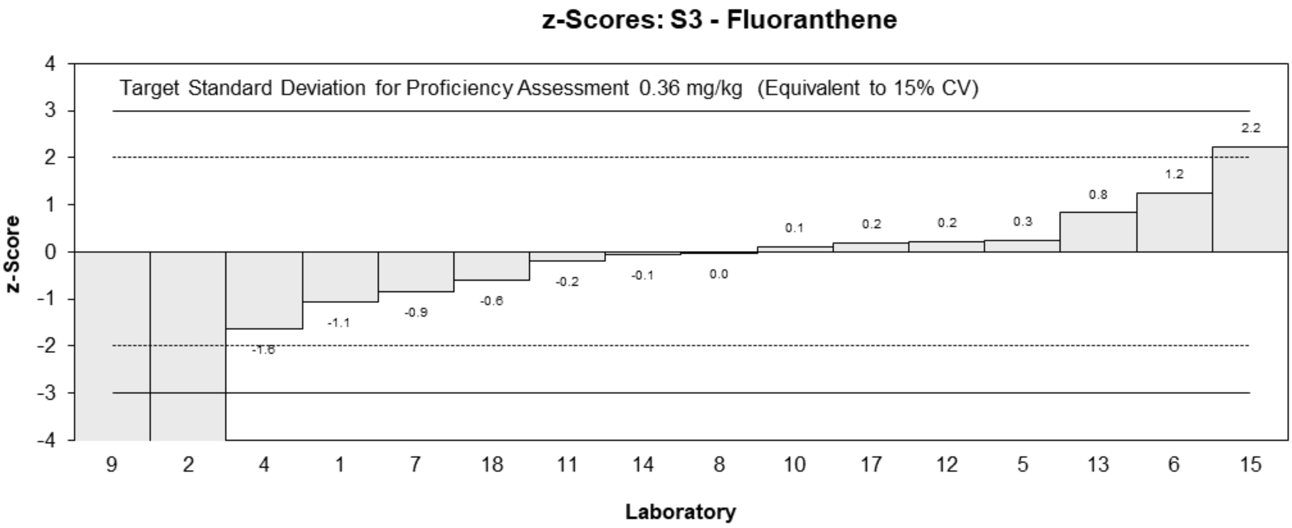
Lab. Code	Result	Uncertainty	z	E_n
1	2.03	NR	-1.07	-1.77
2*	0.63	0.07	-4.93	-7.75
3	NS	NS		
4	1.83	0.46	-1.63	-1.16
5	2.51	0.653	0.25	0.13
6	2.87	0.86	1.24	0.51
7	2.11	0.63	-0.85	-0.46
8	2.41	0.72	-0.03	-0.01
9*	0.58	0.15	-5.07	-6.91
10	2.46	0.74	0.11	0.05
11	2.35	0.705	-0.19	-0.09
12	2.5	0.75	0.22	0.10
13	2.72	NR	0.83	1.36
14	2.4	1.2	-0.06	-0.02
15	3.23	0.97	2.23	0.81
17	2.484	0.62	0.18	0.10
18	2.2	0.44	-0.61	-0.45

* Outlier, see Section 4.2

Statistics

Assigned Value	2.42	0.22
Spike Value	2.81	0.14
Robust Average	2.32	0.28
Median	2.41	0.23
Mean	2.21	
N	16	
Max	3.23	
Min	0.58	
Robust SD	0.44	
Robust CV	19%	


Results: S3 - Fluoranthene
Assigned Value = 2.42 ± 0.22 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9
2
4
1
7
18
11
14
8
10
17
12
5
13
6
15
3
Md
RA
SV


z-Scores: S3 - Fluoranthene
Target Standard Deviation for Proficiency Assessment 0.36 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
2.2
1.2
0.8
0.1
0.2
0.2
0.3
0.0
-0.1
-0.2
-0.6
-0.9
-1.1
-1.6

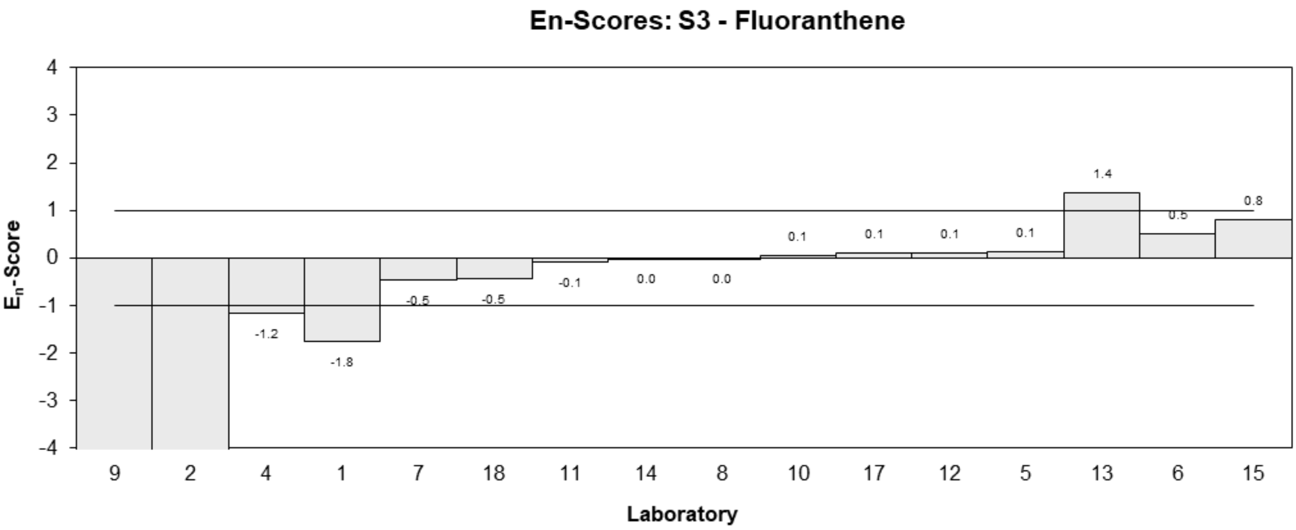

En-Scores: S3 - Fluoranthene
E_n-Score
Laboratory
1.4
0.8
0.5
0.1
0.1
0.1
0.1
0.0
0.0
-0.1
-0.5
-0.5
-1.2
-1.8

Figure 16

Table 21

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Fluorene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.88	NR	0.34	0.58
2*	1.70	0.2	6.87	4.05
3	NS	NS		
4	0.72	0.18	-0.93	-0.60
5	0.753	0.113	-0.67	-0.62
6	0.96	0.28	0.98	0.42
7	0.93	0.28	0.74	0.32
8	0.85	0.30	0.10	0.04
9	NR	NR		
10	0.88	0.26	0.34	0.16
11	0.845	0.2535	0.06	0.03
12	0.68	0.2	-1.25	-0.74
13	0.84	NR	0.02	0.04
14	0.73	0.55	-0.85	-0.19
15	1.06	0.32	1.78	0.68
17	0.893	0.22	0.45	0.24
18	0.75	0.15	-0.69	-0.52

* Outlier, see Section 4.2

Statistics

Assigned Value	0.837	0.074
Spike Value	1.00	0.05
Robust Average	0.854	0.083
Median	0.850	0.093
Mean	0.90	
N	15	
Max	1.7	
Min	0.68	
Robust SD	0.13	
Robust CV	15%	

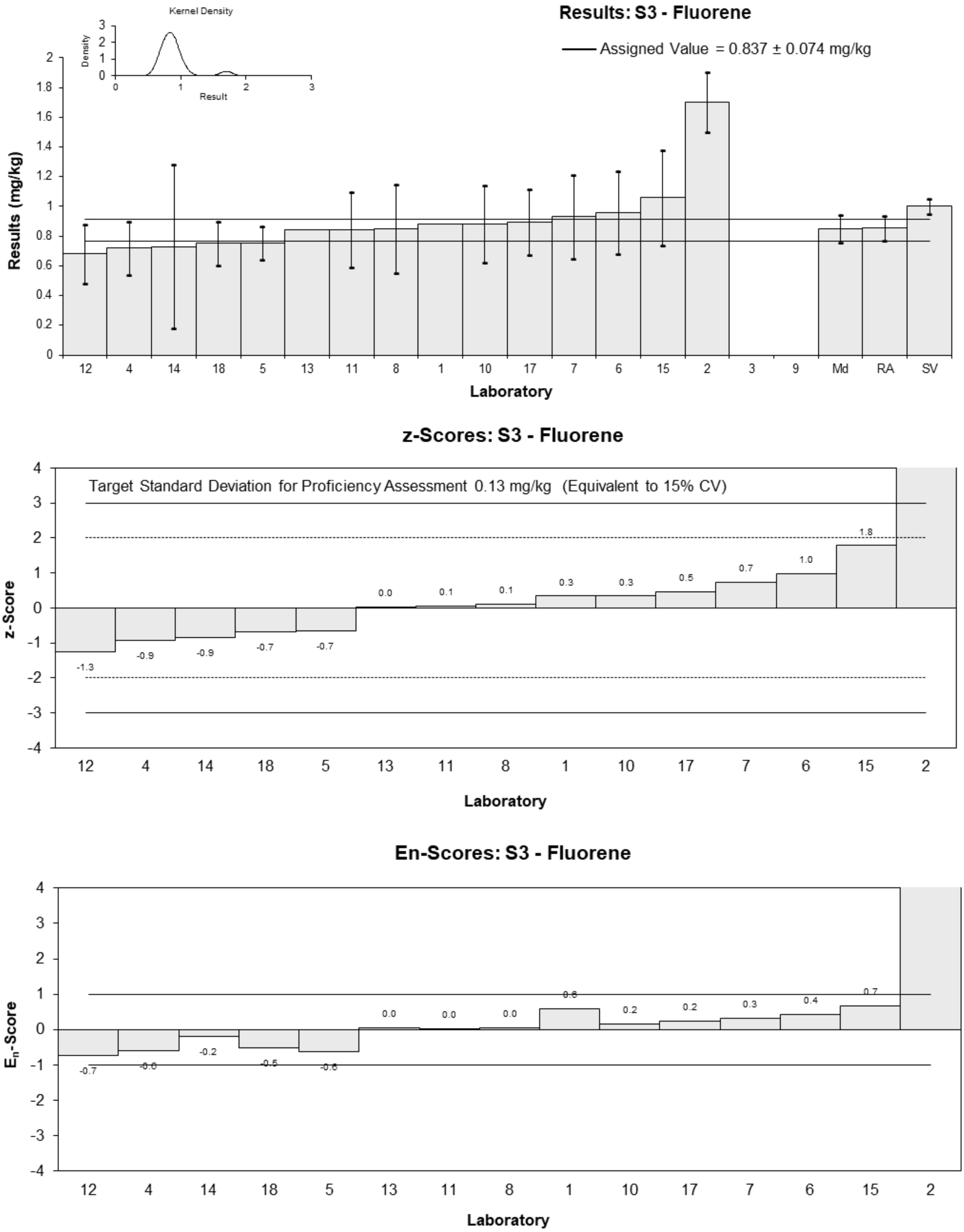

Results: S3 - Fluorene
Assigned Value = 0.837 ± 0.074 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
12 4 14 18 5 13 11 8 1 10 17 7 6 15 2 3 9 Md RA SV
Laboratory
z-Scores: S3 - Fluorene
Target Standard Deviation for Proficiency Assessment 0.13 mg/kg (Equivalent to 15% CV)
z-Score
-1.3 -0.9 -0.9 -0.7 -0.7 0.0 0.1 0.1 0.3 0.3 0.5 0.7 1.0 1.8
12 4 14 18 5 13 11 8 1 10 17 7 6 15 2
Laboratory
En-Scores: S3 - Fluorene
E_n-Score
-0.7 -0.2 0.0 0.0 0.0 0.2 0.2 0.3 0.4 0.7
12 4 14 18 5 13 11 8 1 10 17 7 6 15 2
Laboratory

Figure 17

Table 22

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Phenanthrene
Unit	mg/kg

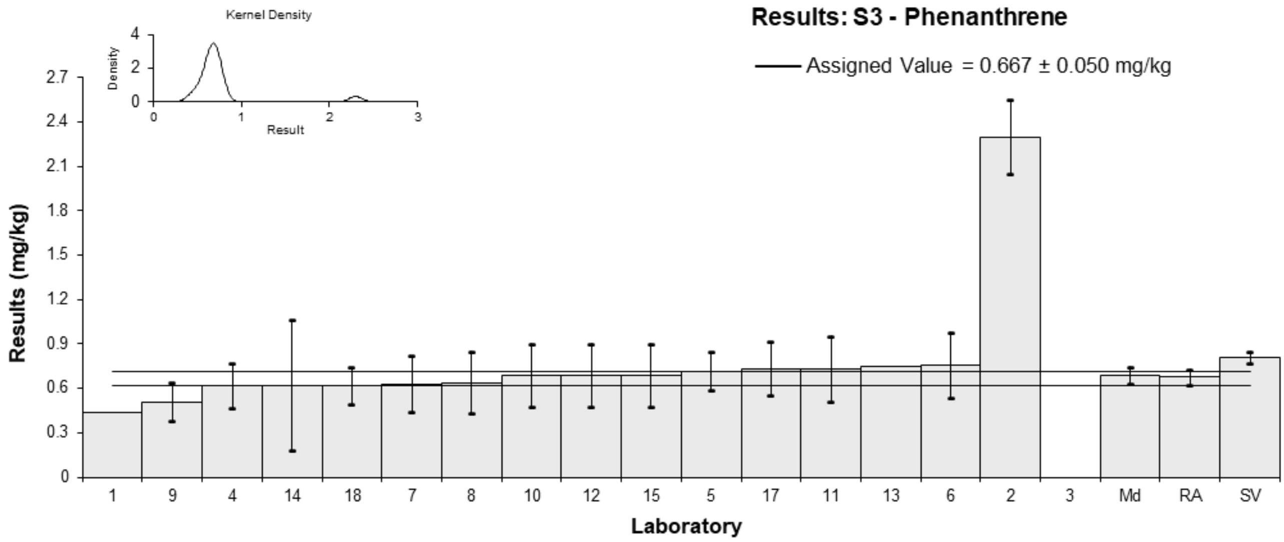
Participant Results

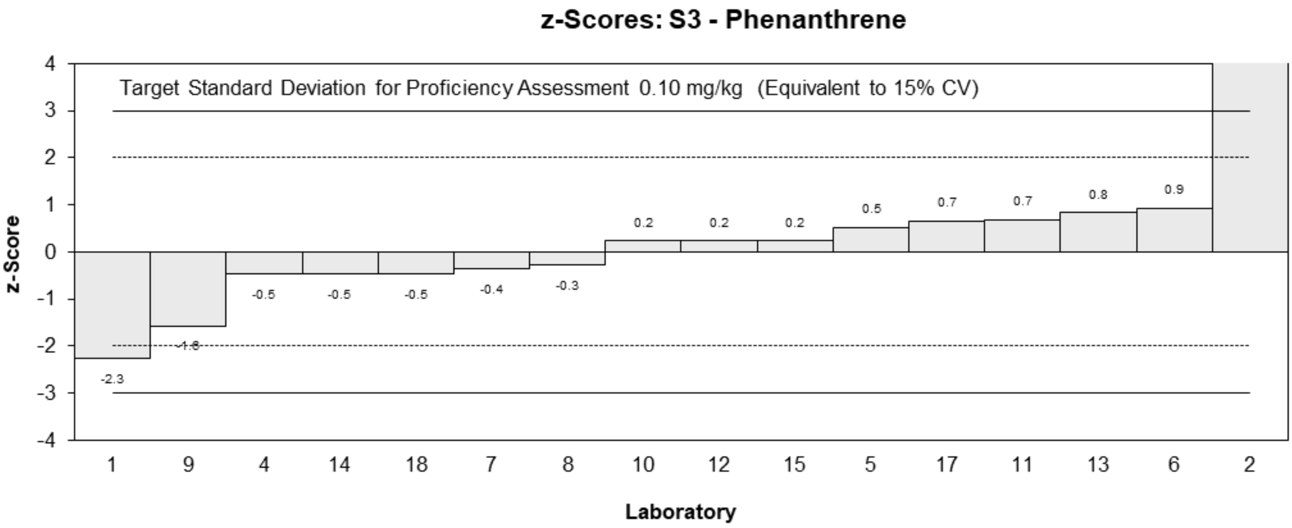
Lab. Code	Result	Uncertainty	z	E_n
1	0.44	NR	-2.27	-4.54
2*	2.3	0.25	16.32	6.41
3	NS	NS		
4	0.62	0.15	-0.47	-0.30
5	0.718	0.129	0.51	0.37
6	0.76	0.22	0.93	0.41
7	0.63	0.19	-0.37	-0.19
8	0.64	0.21	-0.27	-0.13
9	0.51	0.13	-1.57	-1.13
10	0.69	0.21	0.23	0.11
11	0.735	0.2205	0.68	0.30
12	0.69	0.21	0.23	0.11
13	0.75	NR	0.83	1.66
14	0.62	0.44	-0.47	-0.11
15	0.69	0.21	0.23	0.11
17	0.733	0.18	0.66	0.35
18	0.62	0.124	-0.47	-0.35

* Outlier, see Section 4.2

Statistics

Assigned Value	0.667	0.050
Spike Value	0.808	0.040
Robust Average	0.675	0.053
Median	0.690	0.056
Mean	0.76	
N	16	
Max	2.3	
Min	0.44	
Robust SD	0.084	
Robust CV	12%	


Kernel Density
Density
Result
Results: S3 - Phenanthrene
Assigned Value = 0.667 ± 0.050 mg/kg
Results (mg/kg)
Laboratory
1 9 4 14 18 7 8 10 12 15 5 17 11 13 6 2 3 Md RA SV


z-Scores: S3 - Phenanthrene
Target Standard Deviation for Proficiency Assessment 0.10 mg/kg (Equivalent to 15% CV)
z-Score
-2.3
-1.6
-0.5
-0.5
-0.5
-0.4
-0.3
0.2
0.2
0.2
0.5
0.7
0.7
0.8
0.9
1 9 4 14 18 7 8 10 12 15 5 17 11 13 6 2
Laboratory

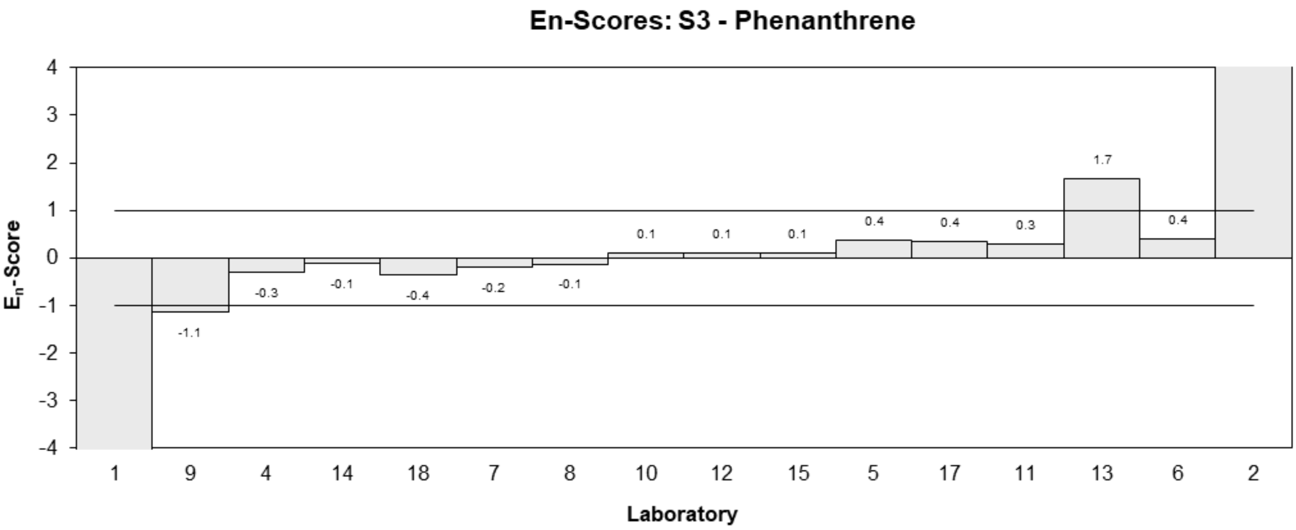

En-Scores: S3 - Phenanthrene
En-Score
-1.1
-0.3
-0.1
-0.4
-0.2
-0.1
0.1
0.1
0.1
0.4
0.4
0.3
1.7
0.4
1 9 4 14 18 7 8 10 12 15 5 17 11 13 6 2
Laboratory

Figure 18

Table 23

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Pyrene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.1	NR	2.73	3.21
2	1.1	0.1	-1.74	-1.82
3	NS	NS		
4	0.99	0.25	-2.24	-1.59
5	1.51	0.41	0.09	0.04
6	1.73	0.52	1.07	0.43
7	1.29	0.39	-0.89	-0.46
8	1.42	0.43	-0.31	-0.15
9*	0.53	0.14	-4.30	-4.07
10	1.54	0.46	0.22	0.10
11	1.4	0.42	-0.40	-0.20
12	1.7	0.5	0.94	0.39
13	1.6	NR	0.49	0.58
14	1.4	0.70	-0.40	-0.12
15	1.94	0.58	2.01	0.74
17	1.497	0.37	0.03	0.02
18	1.3	0.26	-0.85	-0.59

* Outlier, see Section 4.2

Statistics

Assigned Value	1.49	0.19
Spike Value	1.71	0.09
Robust Average	1.46	0.21
Median	1.46	0.15
Mean	1.44	
N	16	
Max	2.1	
Min	0.53	
Robust SD	0.33	
Robust CV	23%	

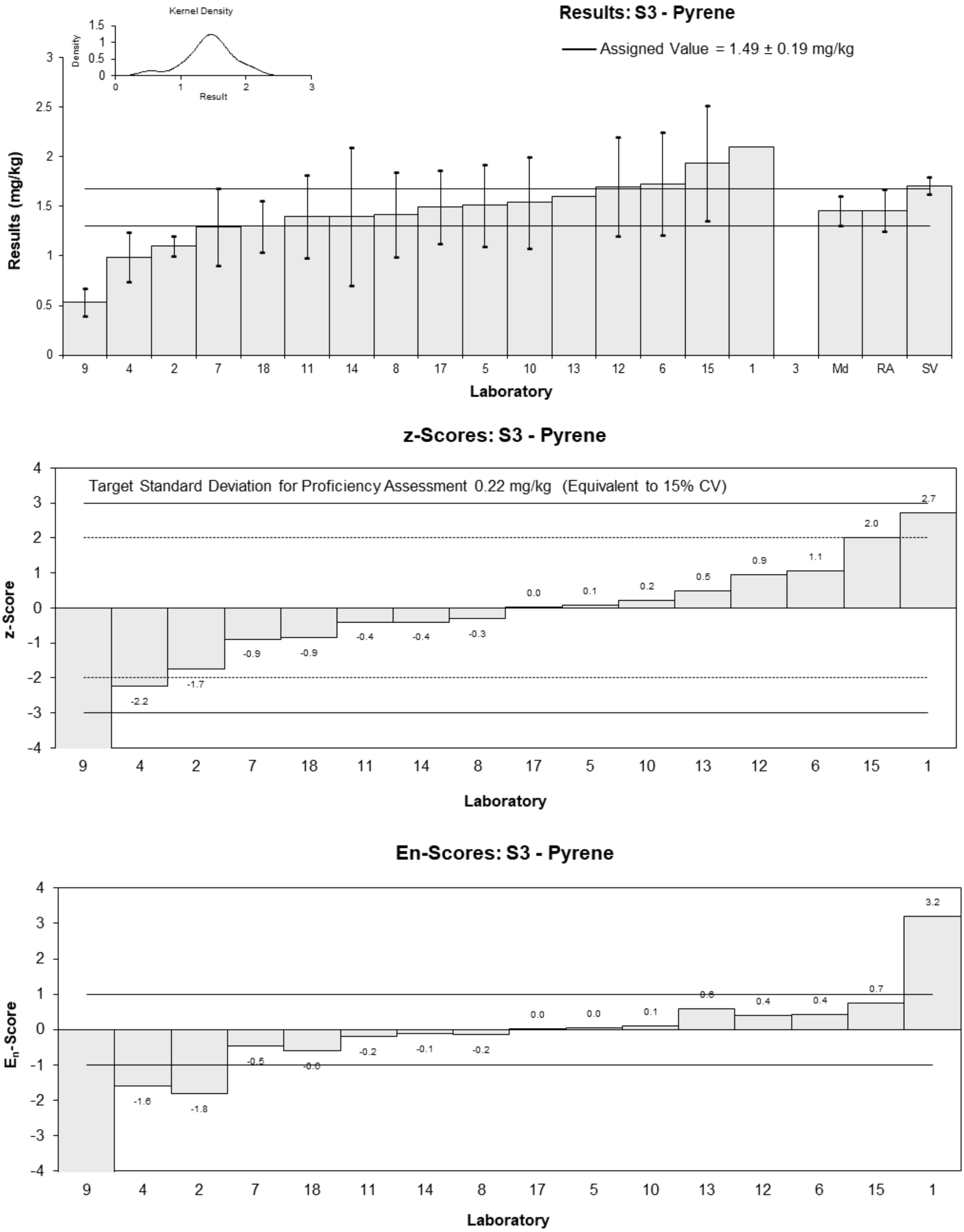

Results: S3 - Pyrene
Assigned Value = 1.49 ± 0.19 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
9 4 2 7 18 11 14 8 17 5 10 13 12 6 15 1 3 Md RA SV
Laboratory
z-Scores: S3 - Pyrene
Target Standard Deviation for Proficiency Assessment 0.22 mg/kg (Equivalent to 15% CV)
z-Score
-2.2 -1.7 -0.9 -0.9 -0.4 -0.4 -0.3 0.0 0.1 0.2 0.5 0.9 1.1 2.0 2.7
9 4 2 7 18 11 14 8 17 5 10 13 12 6 15 1
Laboratory
En-Scores: S3 - Pyrene
E_n-Score
-1.6 -1.8 -0.5 -0.6 -0.2 -0.1 -0.2 0.0 0.0 0.1 0.6 0.4 0.4 0.7 3.2
9 4 2 7 18 11 14 8 17 5 10 13 12 6 15 1
Laboratory

Figure 19

Table 24

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Anthracene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.70	NR	-0.41	-0.55
2	<0.05	0.005		
3	NS	NS		
4	1.32	0.33	-1.80	-1.27
5	1.84	0.3312	0.11	0.08
6	1.53	0.38	-1.03	-0.65
7	2.29	0.69	1.77	0.67
8	1.84	0.60	0.11	0.05
9*	0.58	0.15	-4.53	-4.92
10	1.84	0.55	0.11	0.05
11	1.6	0.48	-0.77	-0.40
12	2.2	0.7	1.44	0.54
13	1.83	NR	0.07	0.10
14	1.6	1.2	-0.77	-0.17
15	2.17	0.65	1.33	0.53
17	1.899	0.47	0.33	0.17
18	1.7	0.34	-0.41	-0.28

* Outlier, see Section 4.2

Statistics

Assigned Value	1.81	0.20
Spike Value	2.80	0.14
Robust Average	1.77	0.21
Median	1.83	0.22
Mean	1.73	
N	15	
Max	2.29	
Min	0.58	
Robust SD	0.33	
Robust CV	19%	

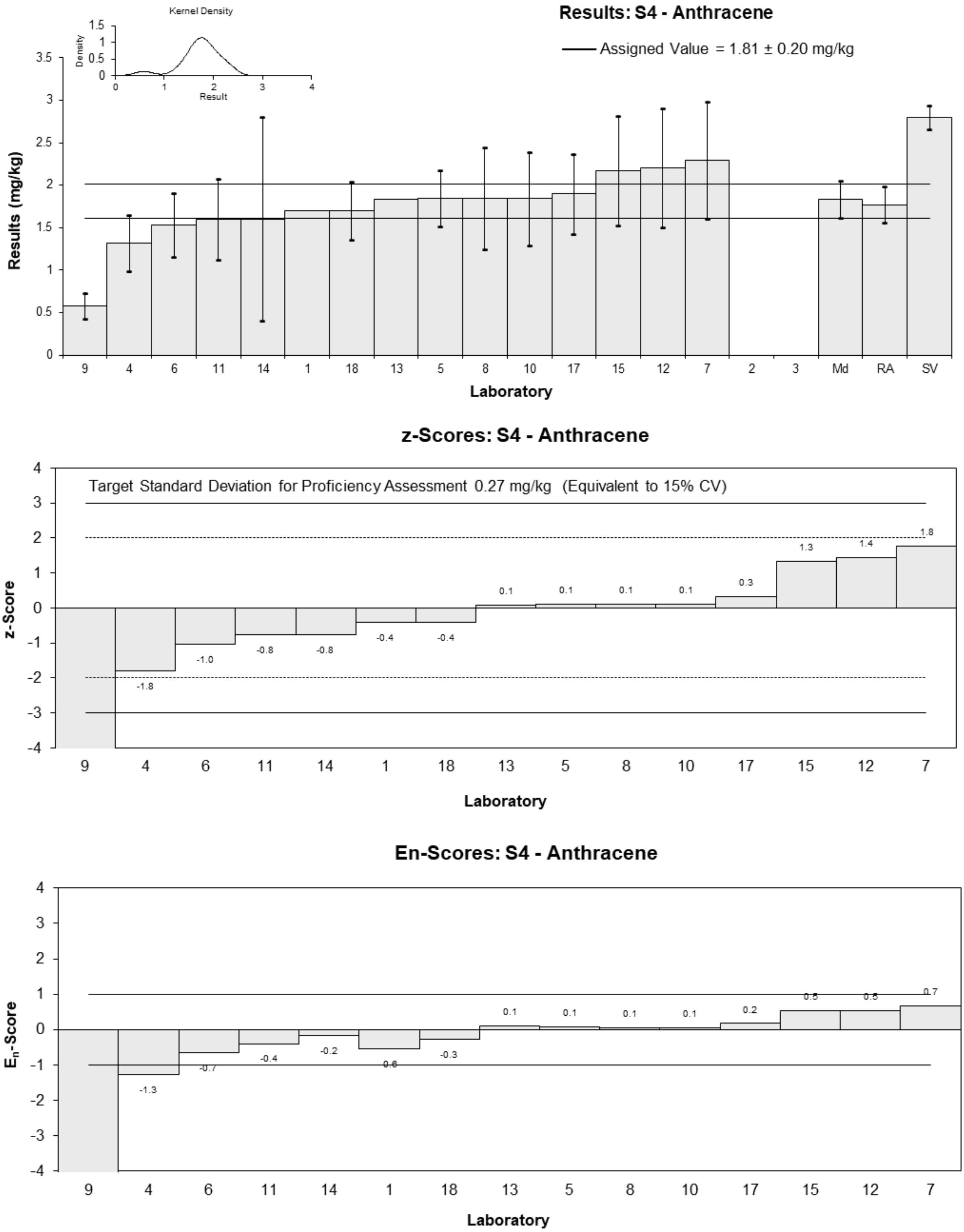

Results: S4 - Anthracene
Assigned Value = 1.81 ± 0.20 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9 4 6 11 14 1 18 13 5 8 10 17 15 12 7 2 3 Md RA SV
z-Scores: S4 - Anthracene
Target Standard Deviation for Proficiency Assessment 0.27 mg/kg (Equivalent to 15% CV)
z-Score
-1.8 -1.0 -0.8 -0.8 -0.4 -0.4 0.1 0.1 0.1 0.1 0.3 1.3 1.4 1.8
Laboratory
9 4 6 11 14 1 18 13 5 8 10 17 15 12 7
En-Scores: S4 - Anthracene
En-Score
-1.3 -0.7 -0.4 -0.2 -0.6 -0.3 0.1 0.1 0.1 0.1 0.2 0.5 0.5 0.7
Laboratory
9 4 6 11 14 1 18 13 5 8 10 17 15 12 7

Figure 20

Table 25

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Benz[*a*]anthracene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.19	NR	-0.30	-0.75
2	<0.05	0.005		
3	NS	NS		
4	2.12	0.53	-2.44	-2.15
5	3.72	1.004	0.76	0.37
6	3.71	1.11	0.74	0.33
7	3.92	1.18	1.16	0.48
8	3.26	0.98	-0.16	-0.08
9*	1.51	0.35	-3.65	-4.54
10	3.33	1	-0.02	-0.01
11	3.5	1.05	0.32	0.15
12	3.0	0.9	-0.68	-0.37
13	3.33	NR	-0.02	-0.05
14	3.4	1.7	0.12	0.04
15	3.25	0.98	-0.18	-0.09
17	3.276	0.82	-0.13	-0.08
18	3.1	0.62	-0.48	-0.37

* Outlier, see Section 4.2

Statistics

Assigned Value	3.34	0.20
Spike Value	3.97	0.20
Robust Average	3.29	0.23
Median	3.28	0.17
Mean	3.17	
N	15	
Max	3.92	
Min	1.51	
Robust SD	0.36	
Robust CV	11%	

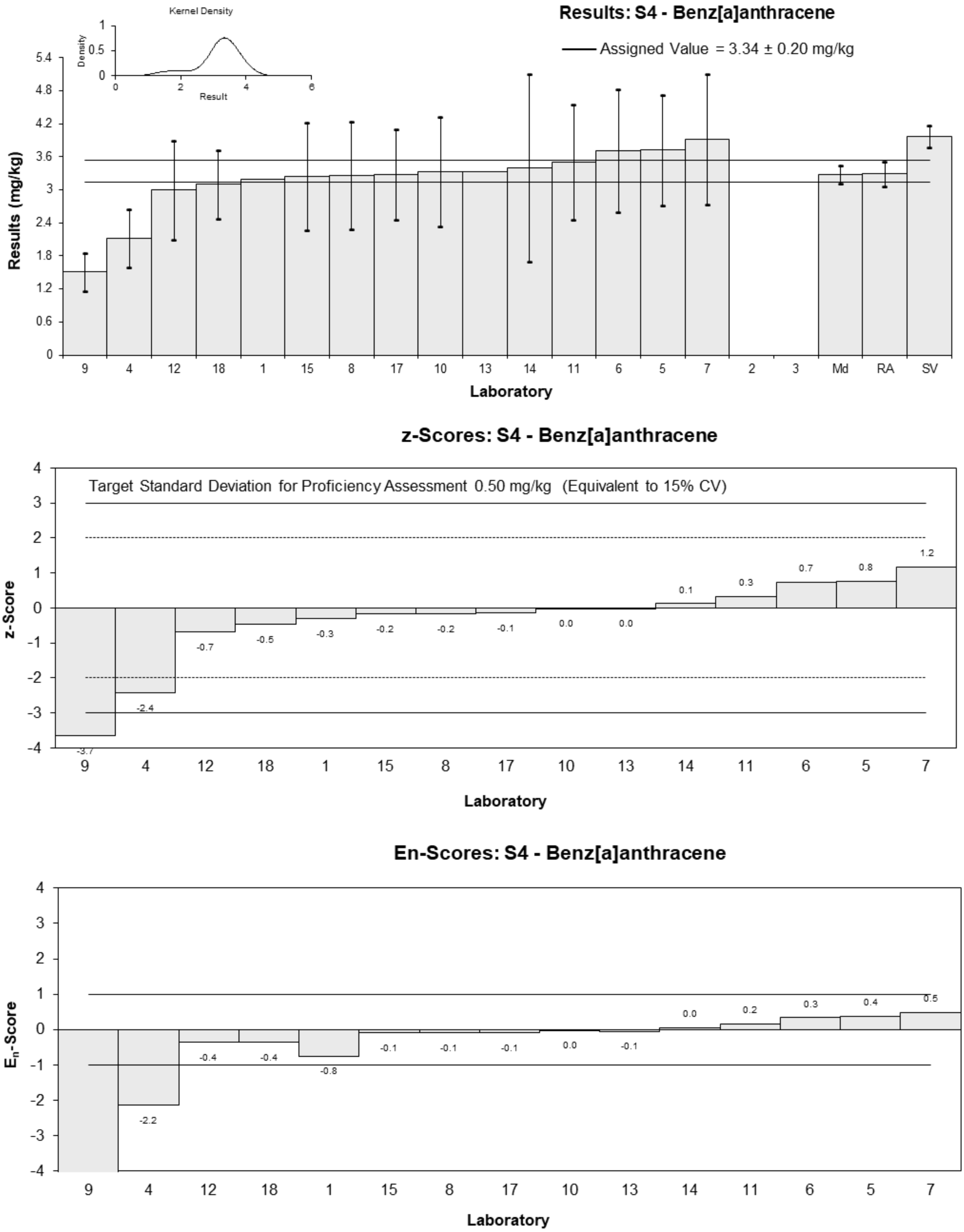

Results: S4 - Benz[a]anthracene
Assigned Value = 3.34 ± 0.20 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9 4 12 18 1 15 8 17 10 13 14 11 6 5 7 2 3 Md RA SV
z-Scores: S4 - Benz[a]anthracene
Target Standard Deviation for Proficiency Assessment 0.50 mg/kg (Equivalent to 15% CV)
z-Score
-3.7 -2.4 -0.7 -0.5 -0.3 -0.2 -0.2 -0.1 0.0 0.0 0.1 0.3 0.7 0.8 1.2
Laboratory
En-Scores: S4 - Benz[a]anthracene
E_n-Score
-2.2 -0.4 -0.4 -0.8 -0.1 -0.1 -0.1 0.0 -0.1 0.0 0.2 0.3 0.4 0.5
Laboratory

Figure 21

Table 26

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Benzo[*a*]pyrene
Unit	mg/kg

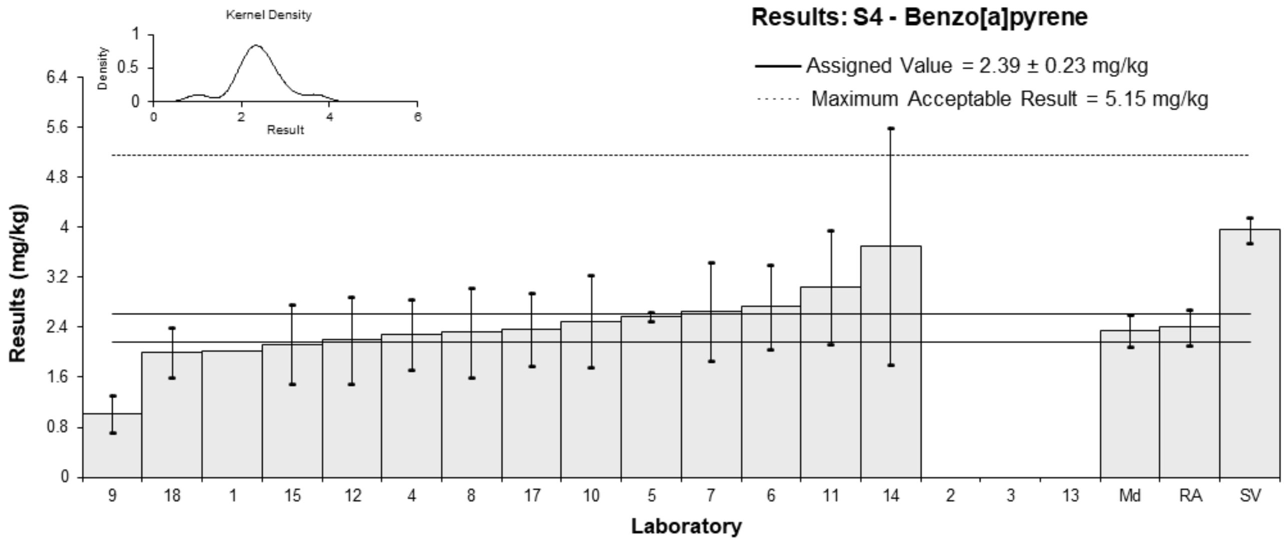
Participant Results

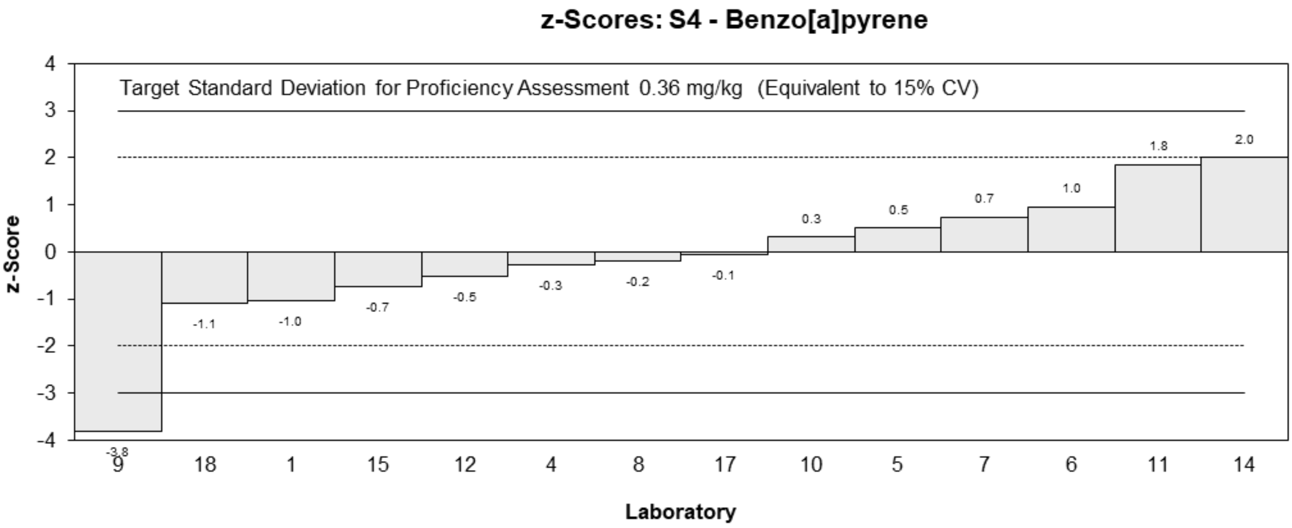
Lab. Code	Result	Uncertainty	z	E_n
1	2.02	NR	-1.03	-1.61
2	<0.05	0.005		
3	NS	NS		
4	2.29	0.57	-0.28	-0.16
5	2.57	0.077	0.50	0.74
6	2.73	0.68	0.95	0.47
7	2.65	0.79	0.73	0.32
8	2.32	0.71	-0.20	-0.09
9*	1.02	0.30	-3.82	-3.62
10	2.5	0.74	0.31	0.14
11	3.05	0.915	1.84	0.70
12	2.2	0.7	-0.53	-0.26
13	<0.05	NR		
14*	3.7	1.9	2.00▼	
15	2.13	0.64	-0.73	-0.38
17	2.373	0.59	-0.05	-0.03
18	2.0	0.4	-1.09	-0.85

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

Statistics

Assigned Value	2.39	0.23
Spike Value	3.96	0.20
Robust Average	2.40	0.29
Max Acceptable Result	5.15	
Median	2.35	0.26
Mean	2.40	
N	14	
Max	3.7	
Min	1.02	
Robust SD	0.44	
Robust CV	18%	


Results: S4 - Benzo[a]pyrene
Assigned Value = 2.39 ± 0.23 mg/kg
Maximum Acceptable Result = 5.15 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9 18 1 15 12 4 8 17 10 5 7 6 11 14 2 3 13 Md RA SV


z-Scores: S4 - Benzo[a]pyrene
Target Standard Deviation for Proficiency Assessment 0.36 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-3.8 -1.1 -1.0 -0.7 -0.5 -0.3 -0.2 -0.1 0.3 0.5 0.7 1.0 1.8 2.0
9 18 1 15 12 4 8 17 10 5 7 6 11 14

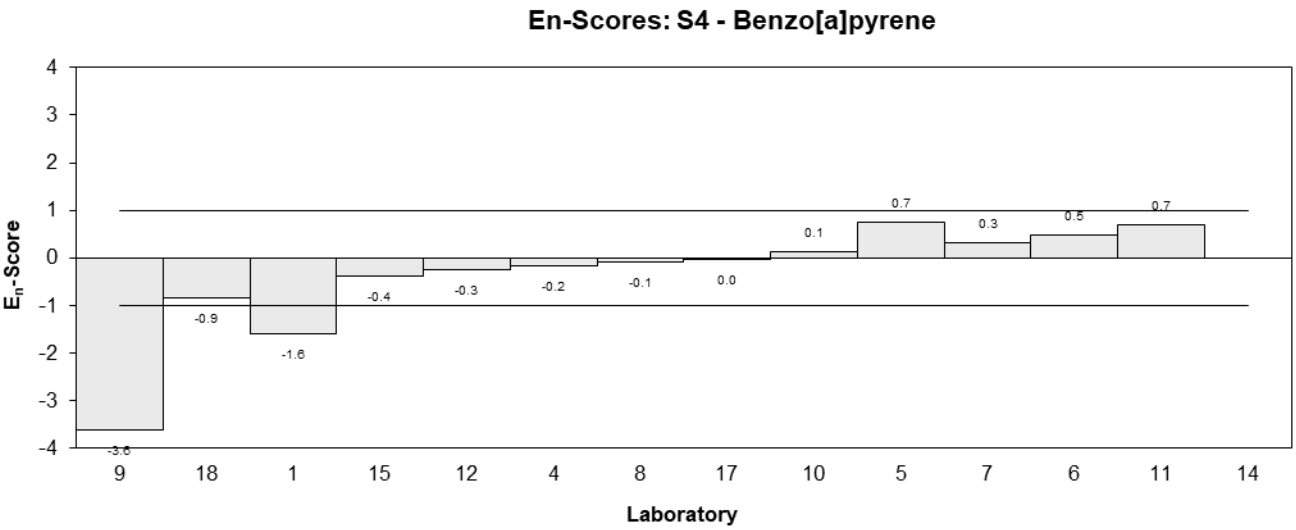

En-Scores: S4 - Benzo[a]pyrene
En-Score
Laboratory
-3.6 -0.9 -1.6 -0.4 -0.3 -0.2 -0.1 0.0 0.1 0.7 0.3 0.5 0.7
9 18 1 15 12 4 8 17 10 5 7 6 11 14

Figure 22

Table 27

Sample Details

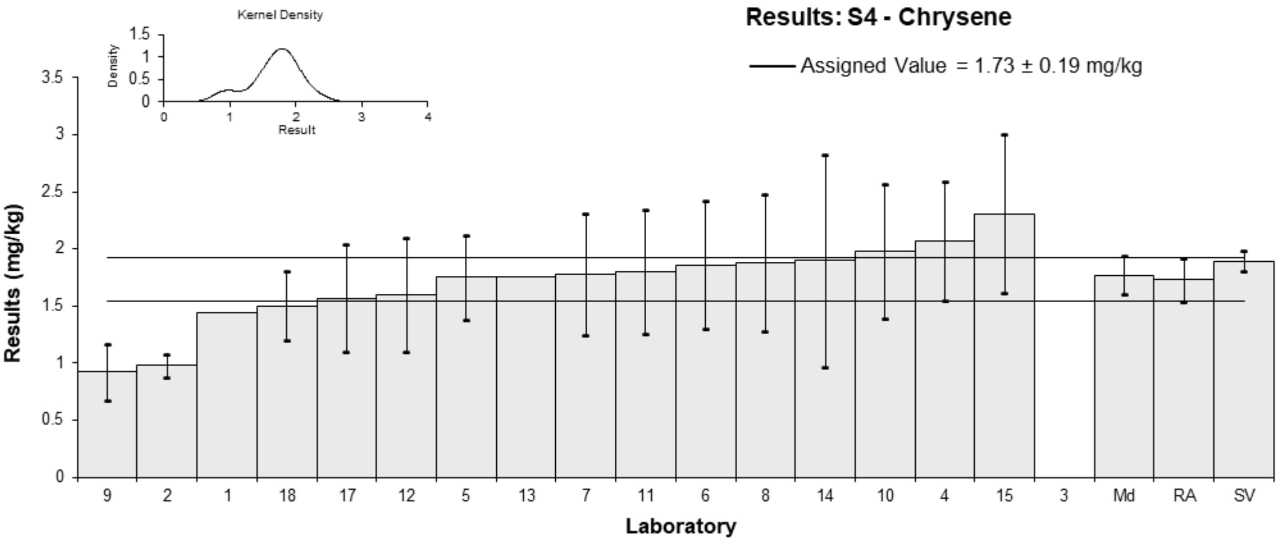
Sample No.	S4
Matrix	Soil
Analyte	Chrysene
Unit	mg/kg

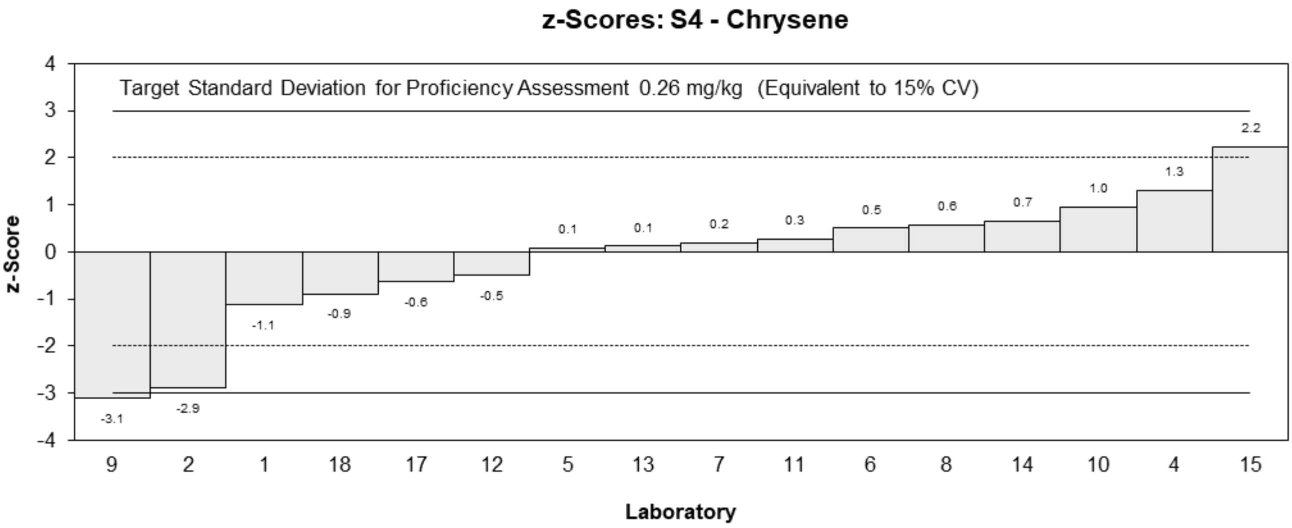
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.44	NR	-1.12	-1.53
2	0.98	0.1	-2.89	-3.49
3	NS	NS		
4	2.07	0.52	1.31	0.61
5	1.75	0.3675	0.08	0.05
6	1.86	0.56	0.50	0.22
7	1.78	0.53	0.19	0.09
8	1.88	0.60	0.58	0.24
9	0.92	0.25	-3.12	-2.58
10	1.98	0.59	0.96	0.40
11	1.8	0.54	0.27	0.12
12	1.6	0.5	-0.50	-0.24
13	1.76	NR	0.12	0.16
14	1.9	0.93	0.66	0.18
15	2.31	0.69	2.24	0.81
17	1.569	0.47	-0.62	-0.32
18	1.5	0.3	-0.89	-0.65

Statistics

Assigned Value	1.73	0.19
Spike Value	1.89	0.09
Robust Average	1.73	0.19
Median	1.77	0.17
Mean	1.69	
N	16	
Max	2.31	
Min	0.92	
Robust SD	0.30	
Robust CV	17%	


Results: S4 - Chrysene
Assigned Value = 1.73 ± 0.19 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9 2 1 18 17 12 5 13 7 11 6 8 14 10 4 15 3 Md RA SV


z-Scores: S4 - Chrysene
Target Standard Deviation for Proficiency Assessment 0.26 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
9 2 1 18 17 12 5 13 7 11 6 8 14 10 4 15
-3.1 -2.9 -1.1 -0.9 -0.6 -0.5 0.1 0.1 0.2 0.3 0.5 0.6 0.7 1.0 1.3 2.2

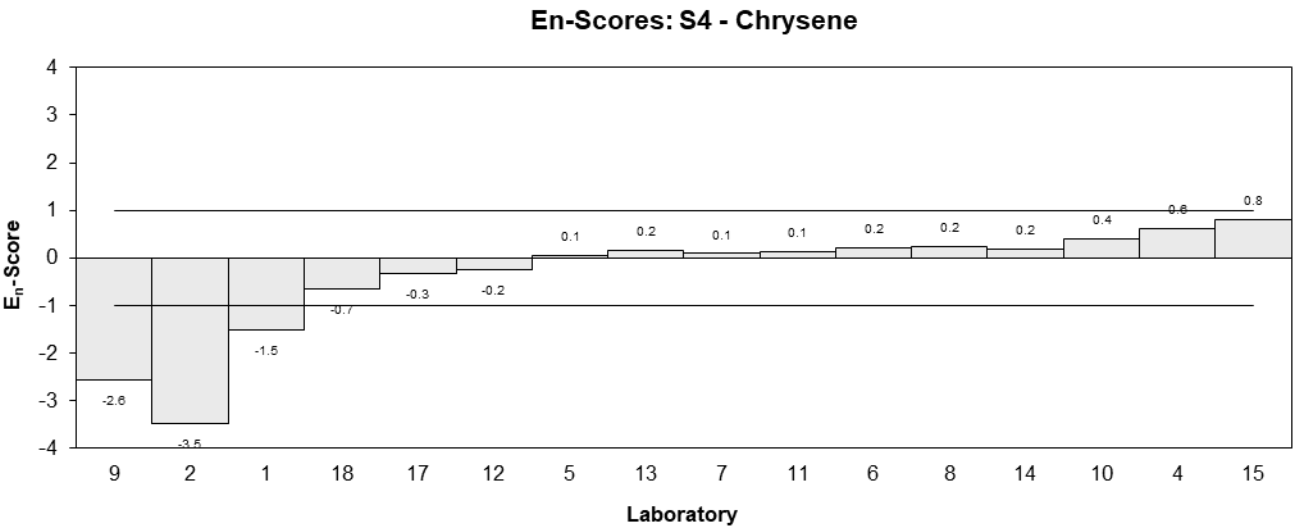

En-Scores: S4 - Chrysene
E_n-Score
Laboratory
9 2 1 18 17 12 5 13 7 11 6 8 14 10 4 15
-2.6 -3.5 -1.5 -0.7 -0.3 -0.2 0.1 0.2 0.1 0.1 0.2 0.2 0.2 0.4 0.6 0.8

Figure 23

Table 28

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Fluoranthene
Unit	mg/kg

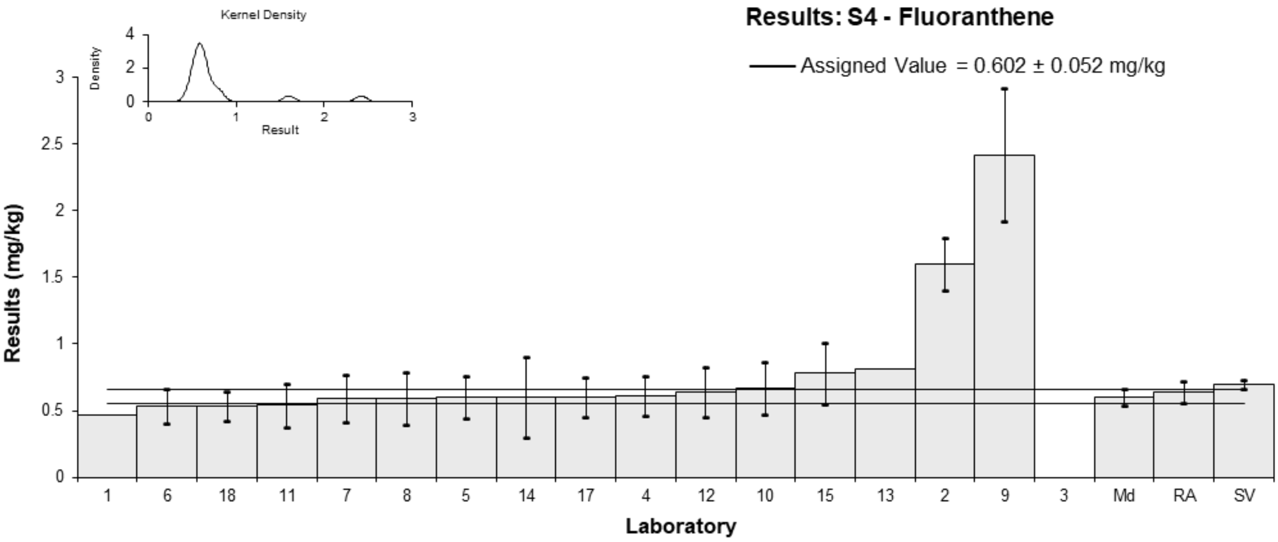
Participant Results

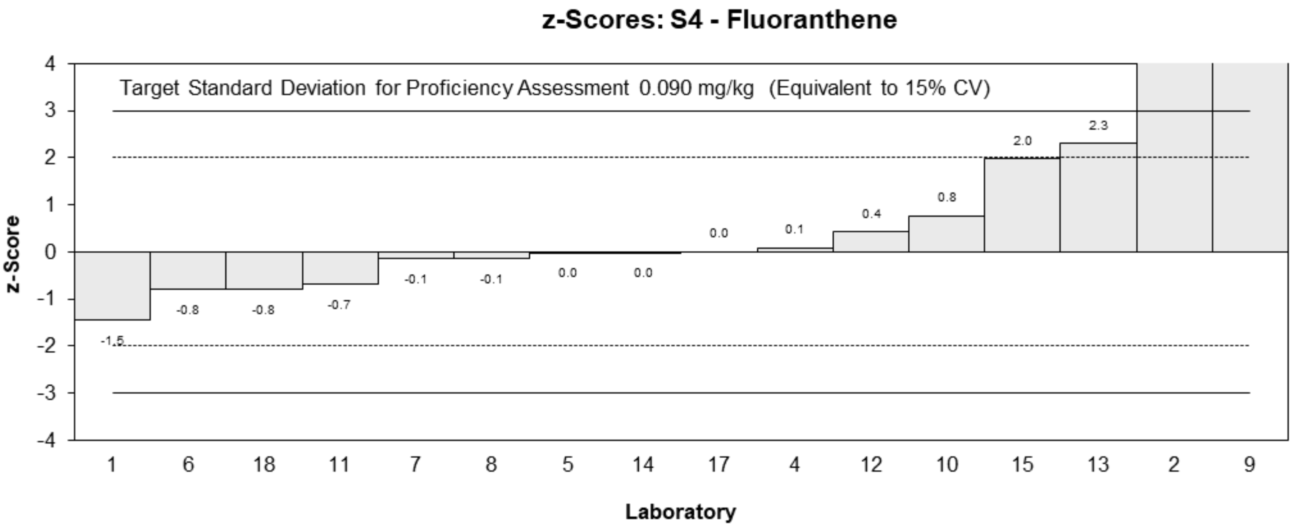
Lab. Code	Result	Uncertainty	z	E_n
1	0.47	NR	-1.46	-2.54
2*	1.6	0.2	11.05	4.83
3	NS	NS		
4	0.61	0.15	0.09	0.05
5	0.6	0.162	-0.02	-0.01
6	0.53	0.13	-0.80	-0.51
7	0.59	0.18	-0.13	-0.06
8	0.59	0.20	-0.13	-0.06
9*	2.42	0.50	20.13	3.62
10	0.67	0.2	0.75	0.33
11	0.54	0.162	-0.69	-0.36
12	0.64	0.19	0.42	0.19
13	0.81	NR	2.30	4.00
14	0.60	0.30	-0.02	-0.01
15	0.78	0.23	1.97	0.75
17	0.602	0.15	0.00	0.00
18	0.53	0.11	-0.80	-0.59

* Outlier, see Section 4.2

Statistics

Assigned Value	0.602	0.052
Spike Value	0.698	0.035
Robust Average	0.639	0.082
Median	0.601	0.060
Mean	0.79	
N	16	
Max	2.42	
Min	0.47	
Robust SD	0.13	
Robust CV	20%	


Results: S4 - Fluoranthene
Assigned Value = 0.602 ± 0.052 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
1
6
18
11
7
8
5
14
17
4
12
10
15
13
2
9
3
Md
RA
SV


z-Scores: S4 - Fluoranthene
Target Standard Deviation for Proficiency Assessment 0.090 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-1.5
-0.8
-0.8
-0.7
-0.1
-0.1
0.0
0.0
0.0
0.1
0.4
0.8
2.0
2.3
1
6
18
11
7
8
5
14
17
4
12
10
15
13
2
9

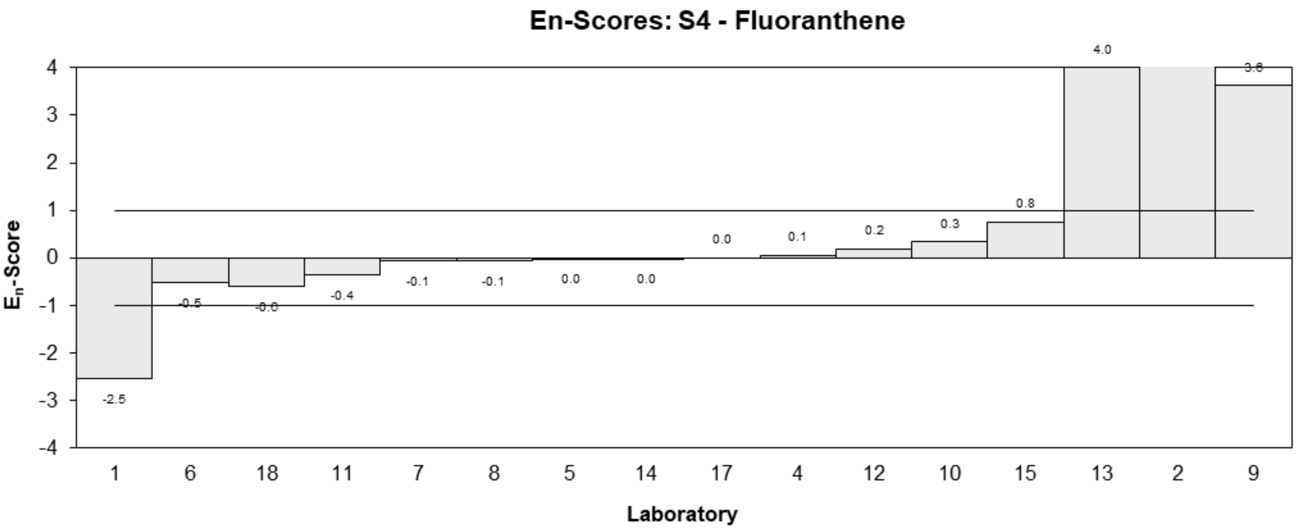

En-Scores: S4 - Fluoranthene
E_n-Score
Laboratory
-2.5
-0.5
-0.4
-0.1
-0.1
0.0
0.0
0.0
0.1
0.2
0.3
0.8
4.0
1
6
18
11
7
8
5
14
17
4
12
10
15
13
2
9

Figure 24

Table 29

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Fluorene
Unit	mg/kg

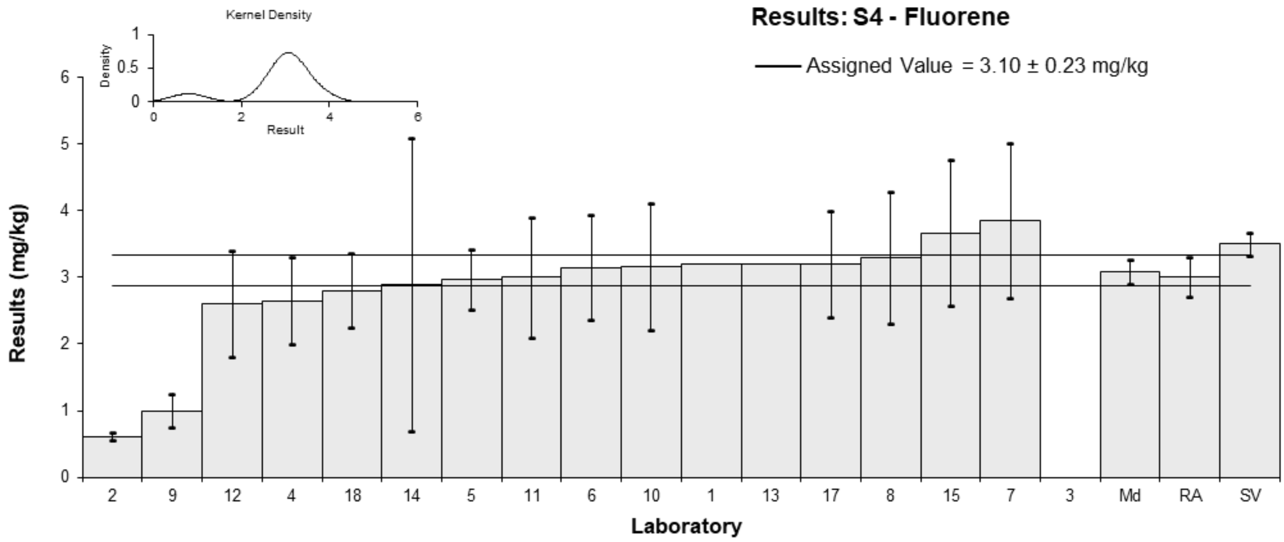
Participant Results

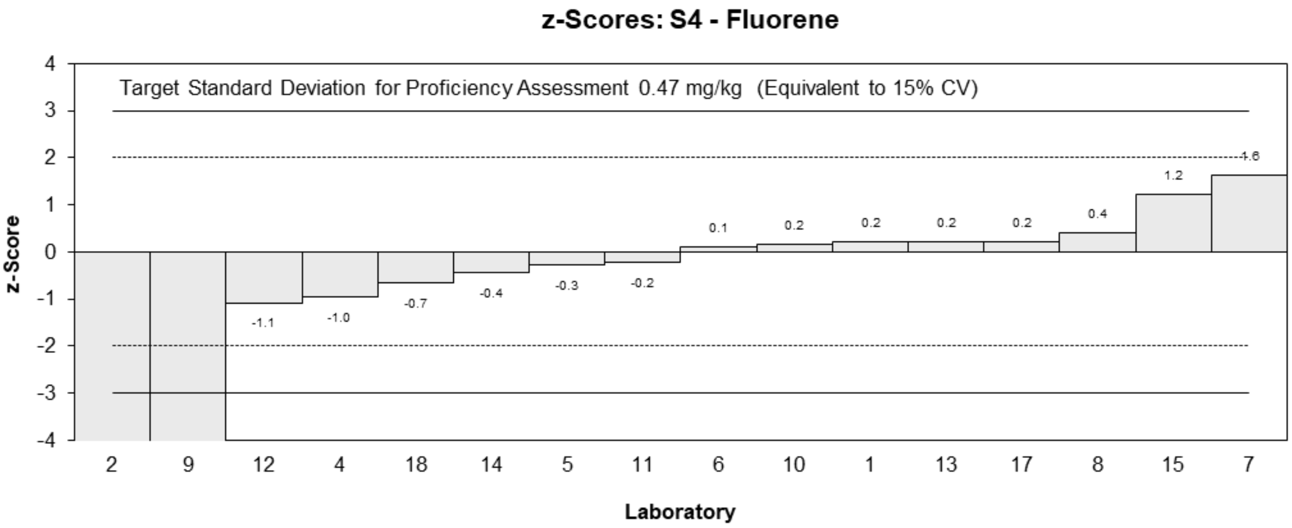
Lab. Code	Result	Uncertainty	z	E_n
1	3.20	NR	0.22	0.43
2*	0.61	0.06	-5.35	-10.48
3	NS	NS		
4	2.65	0.66	-0.97	-0.64
5	2.97	0.4455	-0.28	-0.26
6	3.15	0.79	0.11	0.06
7	3.86	1.16	1.63	0.64
8	3.29	0.99	0.41	0.19
9*	1.00	0.25	-4.52	-6.18
10	3.17	0.95	0.15	0.07
11	3	0.9	-0.22	-0.11
12	2.6	0.8	-1.08	-0.60
13	3.2	NR	0.22	0.43
14	2.9	2.2	-0.43	-0.09
15	3.67	1.10	1.23	0.51
17	3.202	0.80	0.22	0.12
18	2.8	0.56	-0.65	-0.50

* Outlier, see Section 4.2

Statistics

Assigned Value	3.10	0.23
Spike Value	3.50	0.18
Robust Average	3.01	0.29
Median	3.08	0.18
Mean	2.83	
N	16	
Max	3.86	
Min	0.61	
Robust SD	0.46	
Robust CV	15%	


Results: S4 - Fluorene
Assigned Value = 3.10 ± 0.23 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
2 9 12 4 18 14 5 11 6 10 1 13 17 8 15 7 3 Md RA SV


z-Scores: S4 - Fluorene
Target Standard Deviation for Proficiency Assessment 0.47 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
2 9 12 4 18 14 5 11 6 10 1 13 17 8 15 7
-1.1 -1.0 -0.7 -0.4 -0.3 -0.2 0.1 0.2 0.2 0.2 0.2 0.4 1.2 1.6

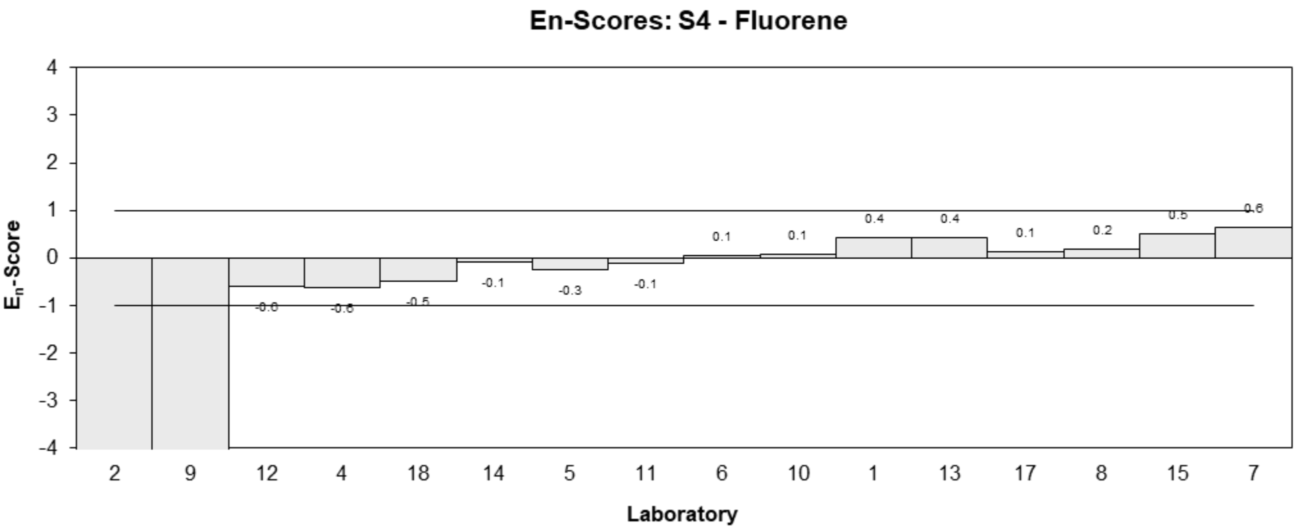

En-Scores: S4 - Fluorene
E_n-Score
Laboratory
2 9 12 4 18 14 5 11 6 10 1 13 17 8 15 7
-0.6 -0.6 -0.5 -0.1 -0.3 -0.1 0.1 0.1 0.4 0.4 0.1 0.2 0.5 0.6

Figure 25

Table 30

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Phenanthrene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.87	NR	-2.46	-6.37
2	1.1	0.1	-1.35	-2.19
3	NS	NS		
4	1.4	0.35	0.10	0.06
5	1.53	0.289	0.72	0.50
6	1.43	0.43	0.24	0.11
7	1.48	0.44	0.48	0.22
8	1.39	0.42	0.05	0.02
9	0.90	0.23	-2.32	-1.97
10	1.44	0.43	0.29	0.14
11	1.45	0.435	0.34	0.16
12	1.4	0.4	0.10	0.05
13	1.52	NR	0.68	1.75
14	1.3	0.82	-0.39	-0.10
15	1.38	0.41	0.00	0.00
17	1.462	0.37	0.40	0.22
18	1.3	0.26	-0.39	-0.29

Statistics

Assigned Value	1.38	0.08
Spike Value	1.60	0.08
Robust Average	1.38	0.08
Median	1.40	0.07
Mean	1.33	
N	16	
Max	1.53	
Min	0.87	
Robust SD	0.13	
Robust CV	9.7%	

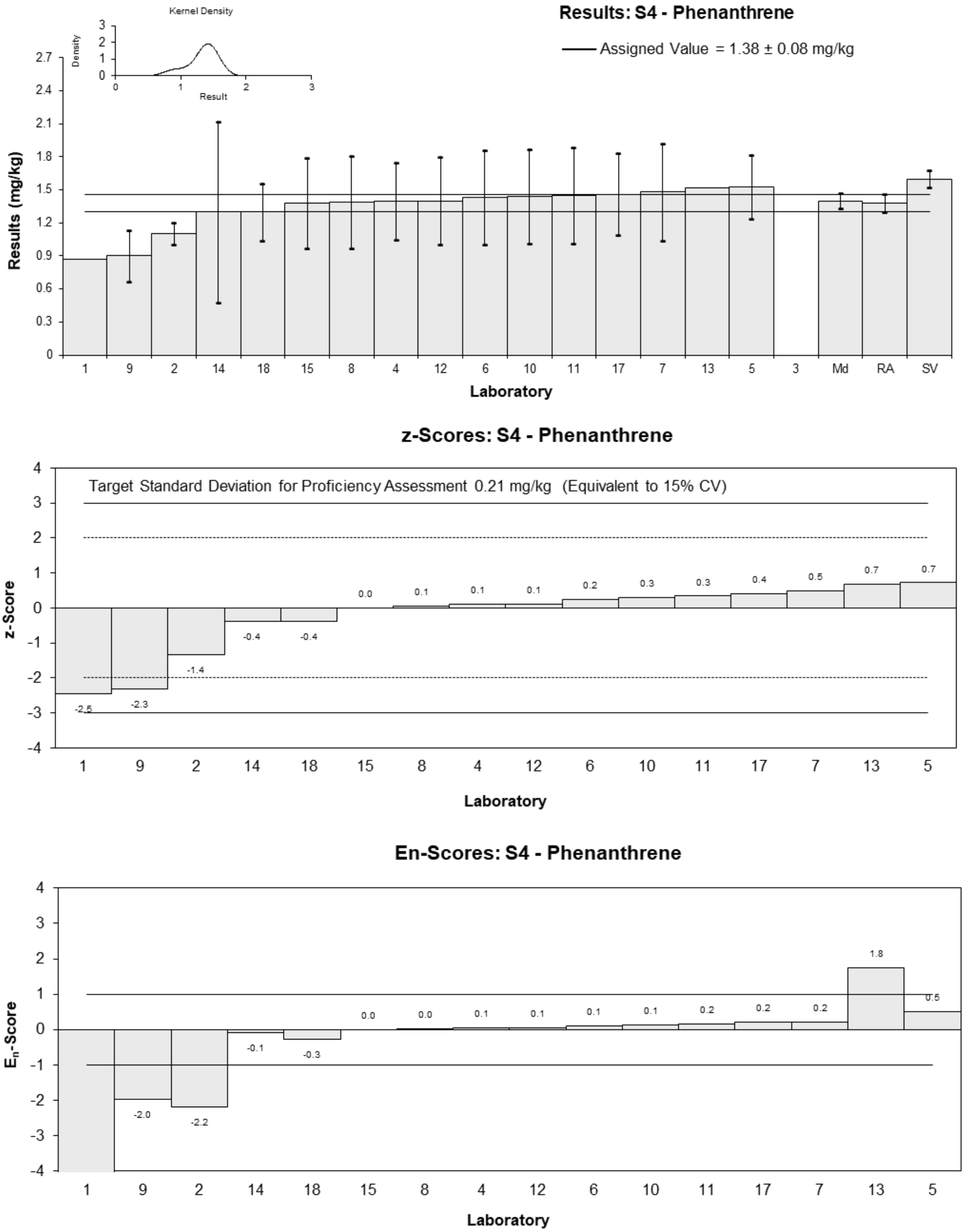

Results: S4 - Phenanthrene
Assigned Value = 1.38 ± 0.08 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
1 9 2 14 18 15 8 4 12 6 10 11 17 7 13 5 3 Md RA SV
z-Scores: S4 - Phenanthrene
Target Standard Deviation for Proficiency Assessment 0.21 mg/kg (Equivalent to 15% CV)
z-Score
-2.5 -2.3 -1.4 -0.4 -0.4 0.0 0.1 0.1 0.1 0.2 0.3 0.3 0.4 0.5 0.7 0.7
1 9 2 14 18 15 8 4 12 6 10 11 17 7 13 5
Laboratory
En-Scores: S4 - Phenanthrene
E_n-Score
-2.0 -2.2 -0.1 -0.3 0.0 0.0 0.1 0.1 0.1 0.1 0.2 0.2 0.2 1.8 0.5
1 9 2 14 18 15 8 4 12 6 10 11 17 7 13 5
Laboratory

Figure 26

Table 31

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Pyrene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.36	NR	1.65	2.25
2*	0.22	0.02	-5.32	-7.15
3	NS	NS		
4	0.99	0.25	-0.61	-0.36
5	1.07	0.2889	-0.12	-0.06
6	0.99	0.29	-0.61	-0.32
7	1.05	0.32	-0.24	-0.12
8	0.99	0.30	-0.61	-0.31
9	1.56	0.35	2.87	1.27
10	1.1	0.33	0.06	0.03
11	0.93	0.279	-0.98	-0.53
12	1.3	0.4	1.28	0.50
13	1.16	NR	0.43	0.58
14	0.93	0.57	-0.98	-0.27
15	1.25	0.38	0.98	0.40
17	1.039	0.26	-0.31	-0.18
18	0.88	0.18	-1.28	-0.97

* Outlier, see Section 4.2

Statistics

Assigned Value	1.09	0.12
Spike Value	1.19	0.06
Robust Average	1.07	0.12
Median	1.04	0.11
Mean	1.05	
N	16	
Max	1.56	
Min	0.22	
Robust SD	0.20	
Robust CV	18%	

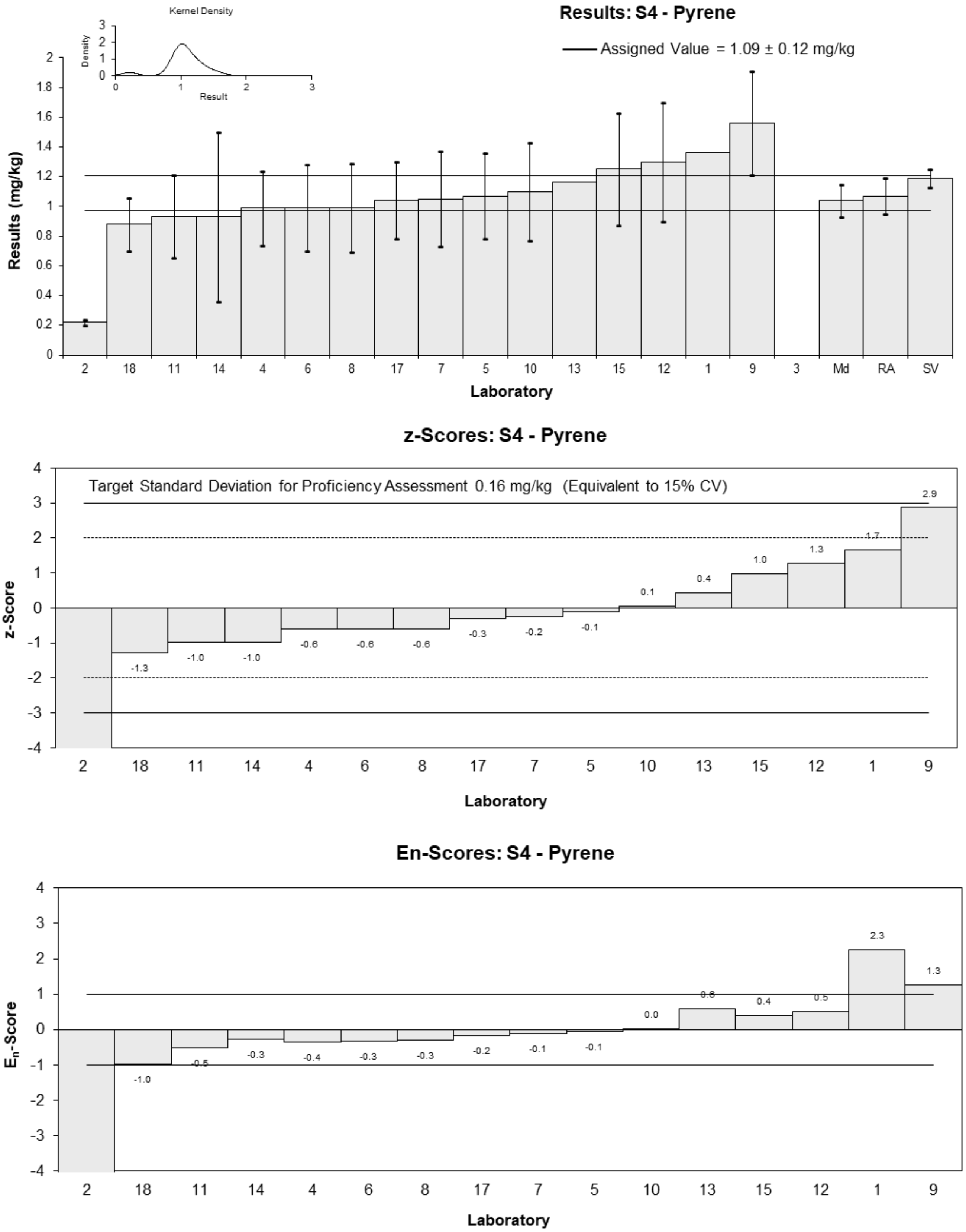

Results: S4 - Pyrene
Assigned Value = 1.09 ± 0.12 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
2 18 11 14 4 6 8 17 7 5 10 13 15 12 1 9 3 Md RA SV
z-Scores: S4 - Pyrene
Target Standard Deviation for Proficiency Assessment 0.16 mg/kg (Equivalent to 15% CV)
z-Score
-1.3 -1.0 -1.0 -0.6 -0.6 -0.6 -0.3 -0.2 -0.1 0.1 0.4 1.0 1.3 1.7 2.9
Laboratory
2 18 11 14 4 6 8 17 7 5 10 13 15 12 1 9
En-Scores: S4 - Pyrene
E_n-Score
-1.0 -0.5 -0.3 -0.4 -0.3 -0.3 -0.2 -0.1 -0.1 0.0 0.6 0.4 0.5 2.3 1.3
Laboratory
2 18 11 14 4 6 8 17 7 5 10 13 15 12 1 9

Figure 27

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages of participants' results were used as the assigned values for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[7] Results less than 50% and greater than 150% of the robust average were removed before calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S4 phenanthrene as an example.

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

No assigned values were set for Sample S2 benzene and toluene as these analytes had poor recovery rates, and the numeric results reported were highly variable; this may be due to the volatility of these compounds. Sample S2 C6-C10 range was also not scored because of its volatile nature and results have been provided for information only, though participants' results in this study were in good consensus with each other.

A comparison of the assigned values (or robust averages if no assigned value was set) and the spiked values is presented in Table 32. The assigned values for TRH were within the range of 87% to 96% of the spiked values, showing good consensus between the spiked and assigned values. The assigned values for scored BTEX and PAHs were within the ranges of 49% to 77% and 58% to 92% of the spiked values respectively. Similar ratios have been observed in previous PT studies, and an assigned value was set if there was a reasonable consensus of participants' results.

Table 32 Comparison of Assigned Value (or Robust Average) and Spiked Value

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Assigned Value *(Robust Average)* / Spiked Value (%)
S1	>C10-C16	1070	1150	93
	>C16-C34	1570	1810	87
	>C34-C40	245	255	96
	TRH	2860	3220	89
S2	Benzene	*(22)*	146	*(15)*
	Toluene	*(360)*	830	*(43)*
	Ethylbenzene	72.6	94.9	77
	Xylenes	417	712	59
	Total BTEX	880	1780	49
S3	Anthracene	1.89	3.18	59
	Benz[*a*]anthracene	1.34	1.69	79
	Benzo[*a*]pyrene	1.26	2.19	58
	Chrysene	0.801	0.897	89
	Fluoranthene	2.42	2.81	86
	Fluorene	0.837	1.00	84
	Phenanthrene	0.667	0.808	83
	Pyrene	1.49	1.71	87

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Assigned Value *(Robust Average)* / Spiked Value (%)
S4	Anthracene	1.81	2.80	65
	Benz[*a*]anthracene	3.34	3.97	84
	Benzo[*a*]pyrene	2.39	3.96	60
	Chrysene	1.73	1.89	92
	Fluoranthene	0.602	0.698	86
	Fluorene	3.10	3.50	89
	Phenanthrene	1.38	1.60	86
	Pyrene	1.09	1.19	92

6.2 Measurement Uncertainty Reported by Participants

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

Of 385 numeric results, 349 results (91%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3). Some participants reported using the NATA GAG Estimating and Reporting MU as their guide; NATA no longer publishes this document.[11]

Laboratory **1** reported results for Sample S1 TRH and Samples S3 and S4 PAHs, and did not report uncertainties for any results; this participant reported being accredited to ISO/IEC 17025. Laboratory **13** reported results for all samples, and did not report uncertainties for Samples S3 and S4 PAHs; this participant also reported being accredited to ISO/IEC 17025.

The magnitude of the reported expanded uncertainties was within the range 3.0% to 76% of the reported value. In general, an expanded uncertainty of less than 15% relative may be unrealistically small for the routine measurement of a hydrocarbon pollutant in soil, while an expanded uncertainty of over 50% may be too large and not fit-for-purpose. Of the 349 expanded MUs, 20 were less than 15% relative while 11 were greater than 50% relative.

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

Laboratories **2** and **3** attached estimates of the expanded MU for results reported as less than their limit of reporting (LOR). An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[10]

In some cases, the results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write 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 22.54 ± 6.762 mg/kg, it is better to report this result as 22.5 ± 6.8 mg/kg.[10]

6.3 *z*-Score

Target SDs equivalent to 15% CV were used to calculate *z*-scores. CVs predicted by the Thompson-Horwitz equation,[8] the between-laboratory CVs and target SDs (as PCV), obtained in this study for analytes in this study are presented for comparison in Table 33.

Table 33 Comparison of Thompson-Horwitz CVs, Between-Laboratory CVs, Target SDs

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Thompson-Horwitz CV[a] (%)	Between-Laboratory CV[b] (%)	Target SD (as PCV) (%)
S1	>C10-C16	1070	5.6	15	15
	>C16-C34	1570	5.3	27	15
	>C34-C40	245	7	33	15
	TRH	2860	4.8	20	15
S2	C6-C10	*(1600)*	*(5.3)*	18	Not Set
	Benzene	*(22)*	*(10)*	80	Not Set
	Toluene	*(360)*	*(6.6)*	25	Not Set
	Ethylbenzene	72.6	8.4	12	15
	Xylenes	417	6.5	17	15
	Total BTEX	880	5.8	18	15
S3	Anthracene	1.89	15	14	15
	Benz[*a*]anthracene	1.34	15	12	15
	Benzo[*a*]pyrene	1.26	15	18	15
	Chrysene	0.801	17	17	15
	Fluoranthene	2.42	14	14	15
	Fluorene	0.837	16	13	15
	Phenanthrene	0.667	17	12	15
	Pyrene	1.49	15	20	15
S4	Anthracene	1.81	15	16	15
	Benz[*a*]anthracene	3.34	13	9.2	15
	Benzo[*a*]pyrene	2.39	14	13	15
	Chrysene	1.73	15	17	15
	Fluoranthene	0.602	17	13	15
	Fluorene	3.10	13	11	15
	Phenanthrene	1.38	15	9.7	15
	Pyrene	1.09	16	16	15

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

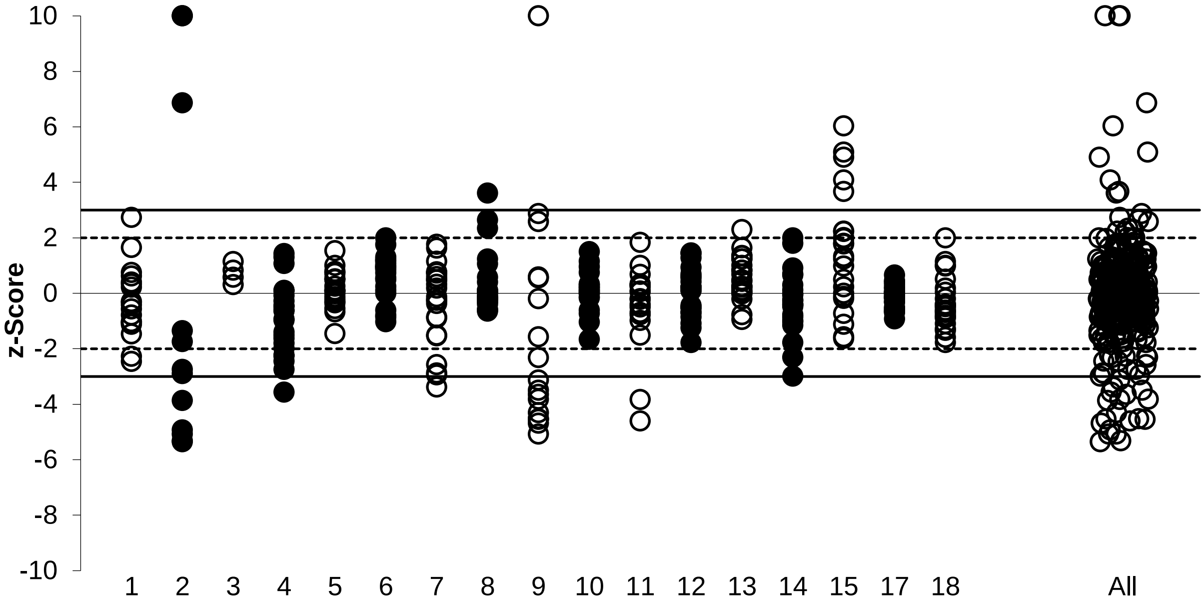
[b] Robust between-laboratory CV with outliers removed, if applicable.

To account for possible low bias in the consensus values due to participants using inefficient analytical or extraction techniques, a total of three *z*-scores were adjusted across the following: Sample S2 xylenes and total BTEX, and Sample S4 benzo[*a*]pyrene. A maximum acceptable result was set as the spiked value plus two target SDs of the spiked value. Results lower than the maximum acceptable result but with a *z*-score greater than 2.0 had their *z*-score adjusted to 2.0. This ensured that participants reporting results close to the spiked value were not penalised. *z*-Scores for results higher than the maximum acceptable result and *z*-scores less than 2.0 were left unaltered.

Of 348 results for which *z*-scores were calculated, 296 (85%) returned a score of |*z*| ≤ 2.0, indicating a satisfactory performance.

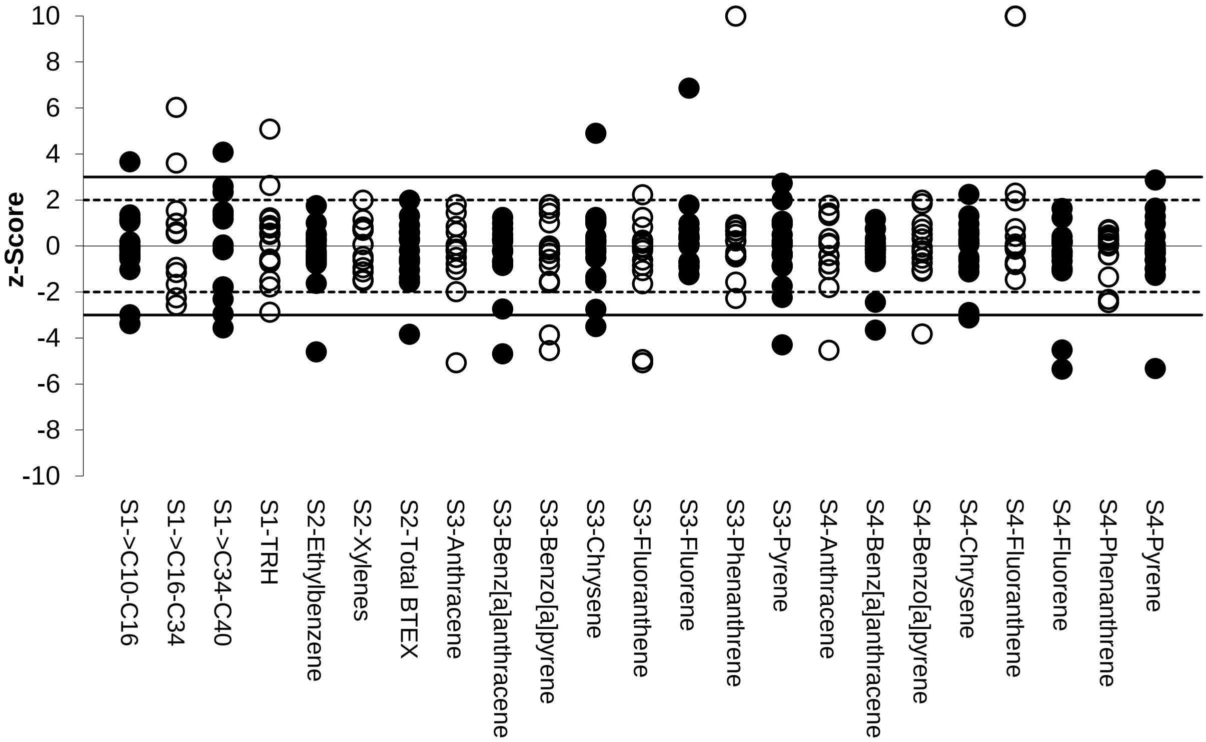
Laboratories **4**, **5**, **6**, **7**, **8**, **10**, **12**, **14**, **15**, **17** and **18** reported numeric results for all 23 scored analytes, and of these, Laboratories **5**, **6**, **10**, **12**, **17** and **18** returned satisfactory *z*-scores for all 23 scored analytes. One participant received satisfactory *z*-scores for all scored analytes they reported results for: Laboratory **3** (4).

The dispersal of participants' *z*-scores is presented graphically by laboratory in Figure 28 and by analyte in Figure 29.



z-Scores greater than 10.0 have been plotted at 10.0

Figure 28 *z*-Score Dispersal by Laboratory



z-Scores greater than 10.0 have been plotted at 10.0

Figure 29 *z*-Score Dispersal by Analyte

Participants’ *z*-scores for Sample S1 TRH only are presented in Figure 30. A trend of questionable or unsatisfactory *z*-scores on one side of the zero line may indicate laboratory bias for TRH measurements.

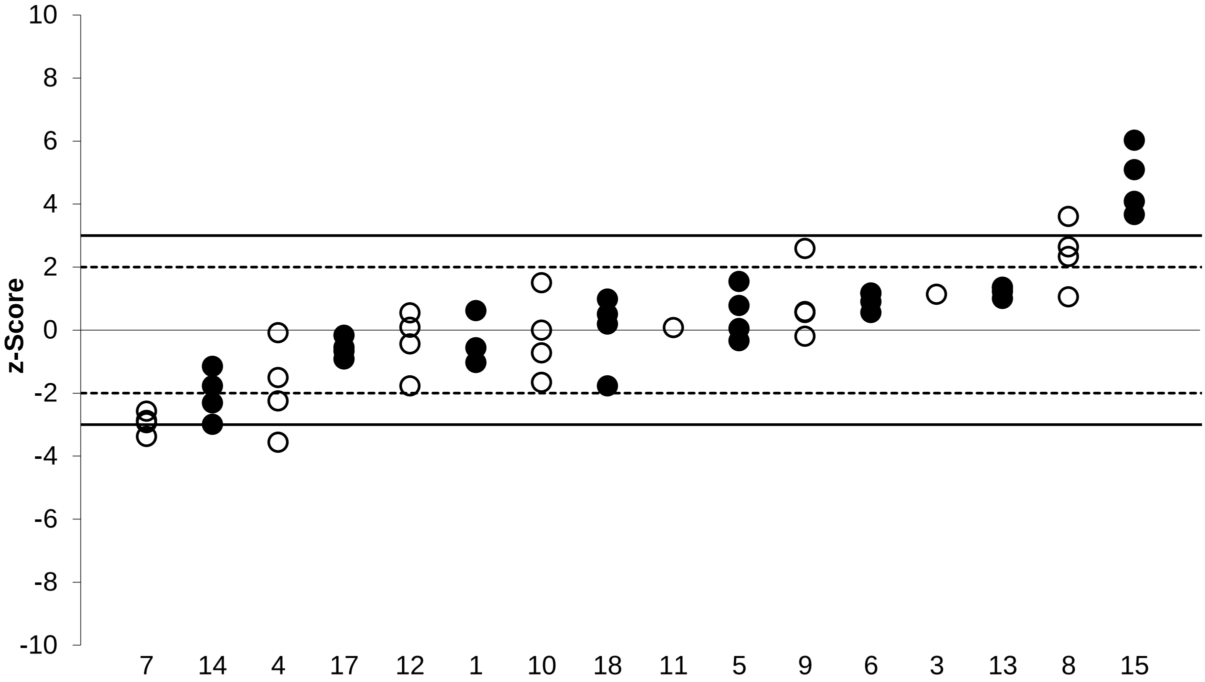


Figure 30 Sample S1 TRH *z*-Score Dispersal by Laboratory

Participants’ *z*-scores for Sample S2 BTEX only are presented in Figure 31. A trend of questionable or unsatisfactory *z*-scores on one side of the zero line may indicate laboratory bias for BTEX measurements; in particular, laboratories whose results consistently return questionable or unsatisfactory *z*-scores below the zero line likely have an inefficient extraction process for BTEX. As the ratio of the assigned value to the spiked value was 49% for Total BTEX, participants reporting results with higher satisfactory *z*-scores may have more efficient extraction methodologies.

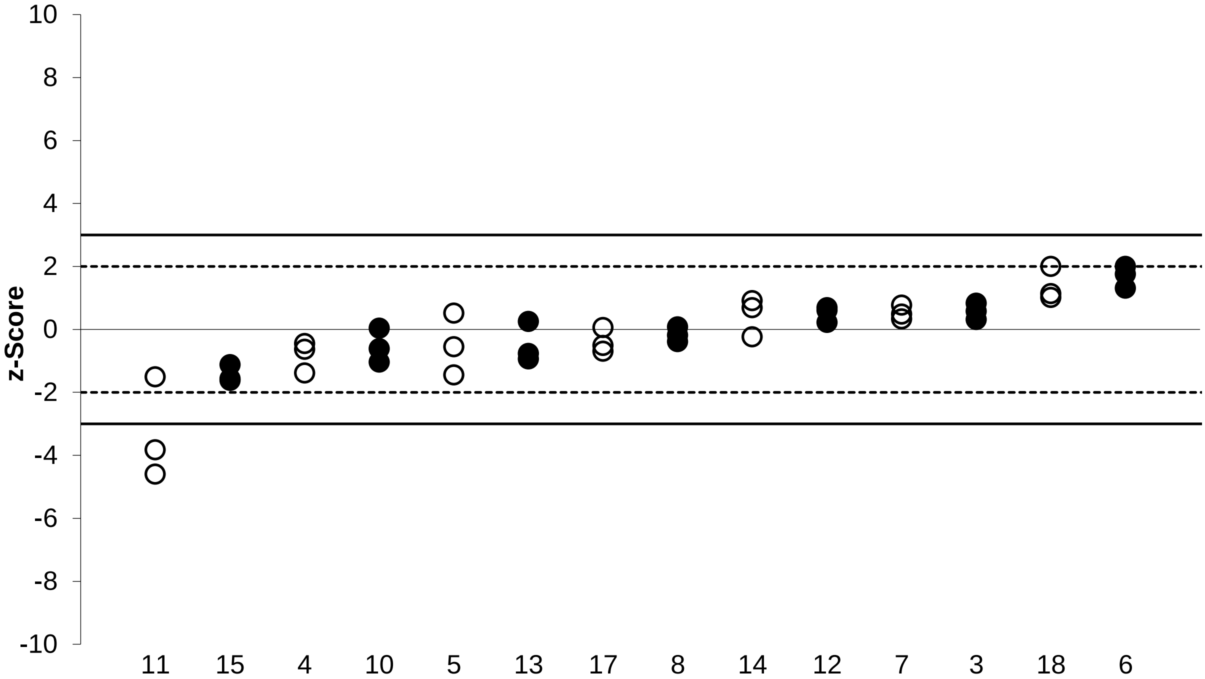
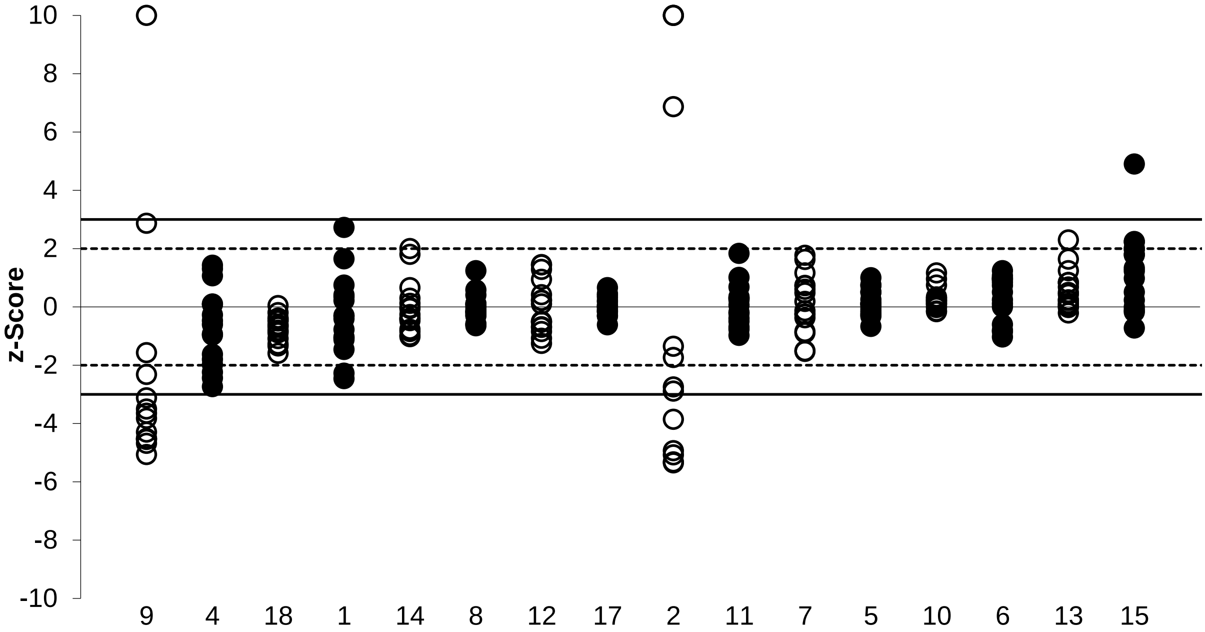


Figure 31 Sample S2 BTEX *z*-Score Dispersal by Laboratory

Participants' *z*-scores for Samples S3 and S4 PAHs only are presented in Figure 32. A trend of questionable or unsatisfactory *z*-scores on one side of the zero line may indicate laboratory bias for PAHs measurements; in particular, laboratories whose results consistently return questionable or unsatisfactory *z*-scores below the zero line likely have an inefficient extraction process for PAHs. As the ratios of the assigned values to the spiked values ranged from 58% to 92%, participants reporting results with higher satisfactory *z*-scores may have more efficient extraction methodologies.



z-Scores greater than 10.0 have been plotted at 10.0

Figure 32 Samples S3 and S4 PAHs *z*-Score Dispersal by Laboratory

Scatter plots of *z*-scores for Samples S3 and S4 anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene are presented in Figures 33 to 40. Scores are predominantly in the upper right and lower left quadrants, indicating that laboratory bias is the major contributor to the variability of results. Points close to the diagonal axis demonstrate excellent repeatability, while points close to the zero demonstrate excellent repeatability and accuracy.

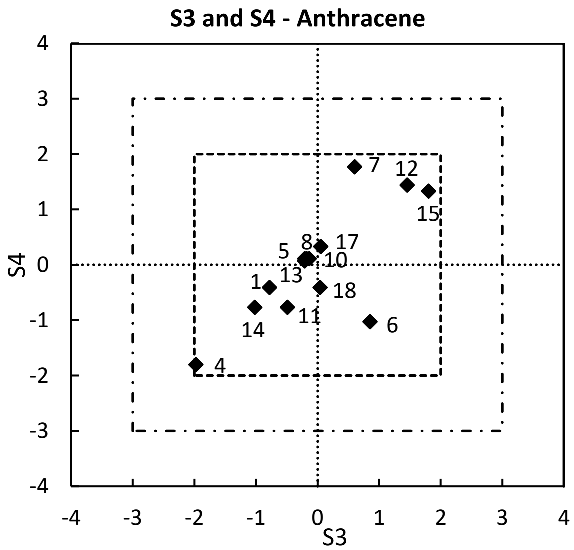
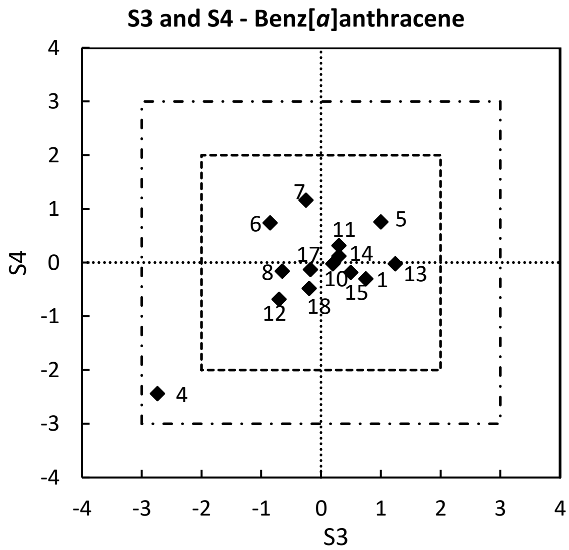
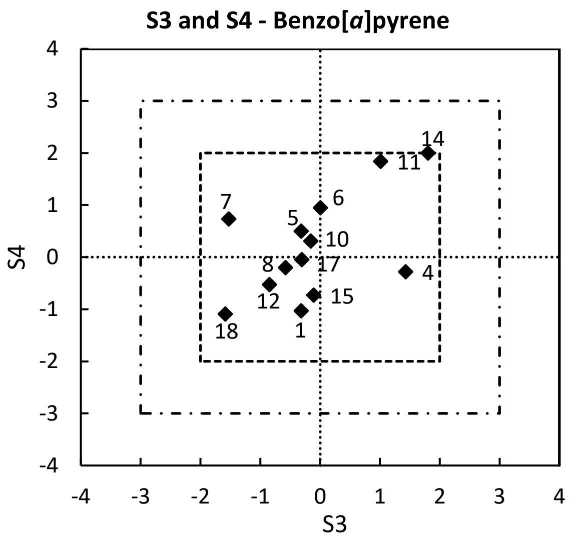


Figure 33 Anthracene *z*-Score Scatter Plot



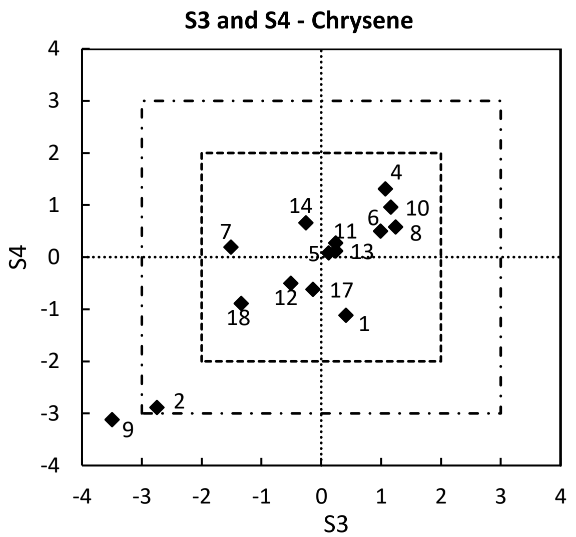
Laboratory **9** is off-scale.

Figure 34 Benz[*a*]anthracene *z*-Score Scatter Plot



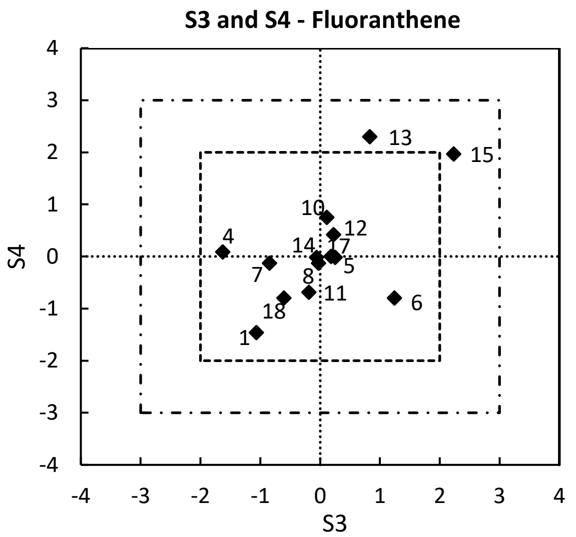
Laboratory **9** is off-scale.

Figure 35 Benzo[*a*]pyrene *z*-Score Scatter Plot



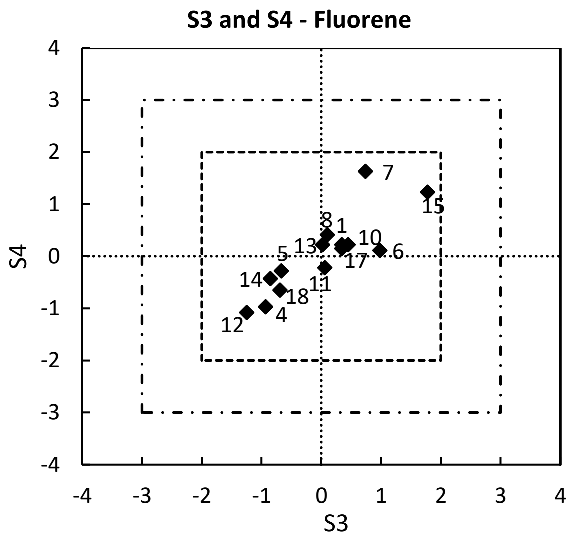
Laboratory **15** is off-scale.

Figure 36 Chrysene *z*-Score Scatter Plot



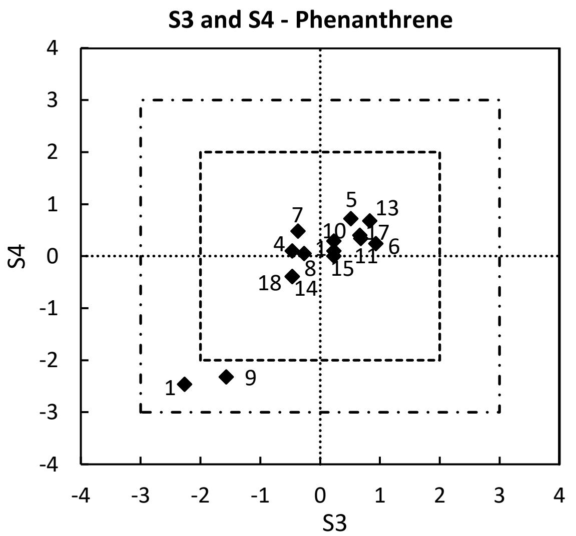
Laboratories **2** and **9** are off-scale.

Figure 37 Fluoranthene *z*-Score Scatter Plot



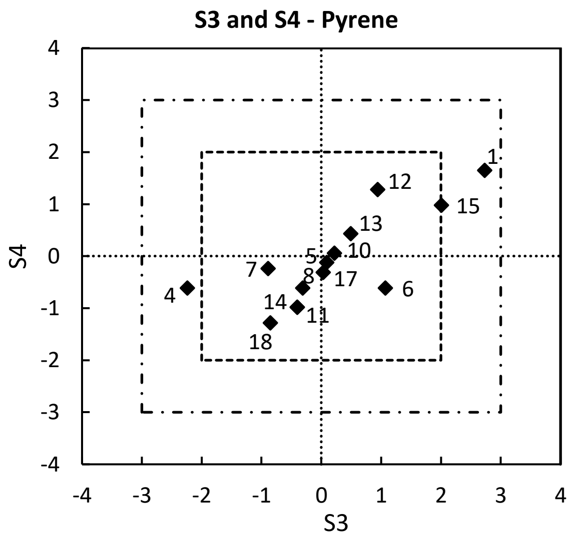
Laboratory **2** is off-scale.

Figure 38 Fluorene *z*-Score Scatter Plot



Laboratory **2** is off-scale.

Figure 39 Phenanthrene *z*-Score Scatter Plot



Laboratories **2** and **9** are off-scale.

Figure 40 Pyrene *z*-Score Scatter Plot

6.4 E_n-Score

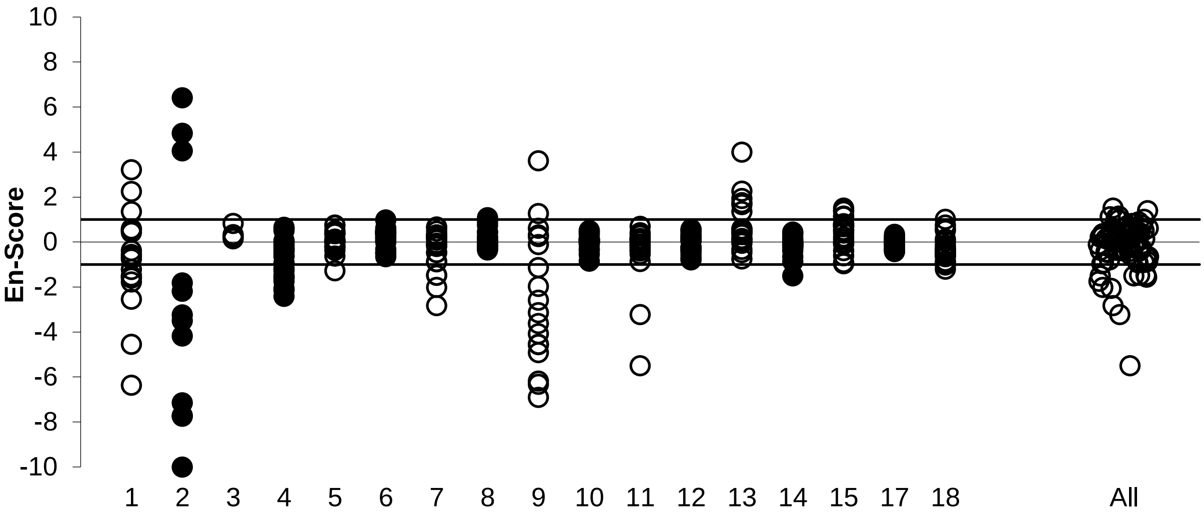
Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score. For results for which z-scores were adjusted as discussed in Section 6.3 z-Score, no E_n-score has been reported.

Of 345 results for which E_n-scores were calculated, 276 (80%) returned a satisfactory score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratories **10**, **12** and **17** returned satisfactory E_n-scores for all 23 scored analytes. One participant received satisfactory E_n-scores for all scored analytes they reported results for: Laboratory **3** (4).

Laboratory **2** did not return any satisfactory E_n-scores.

The dispersal of participants' E_n-scores is presented graphically by laboratory in Figure 41.



E_n-Scores greater than 10.0 have been plotted at 10.0

Figure 41 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 34 presents false negative results. These are analytes present in the samples which a participant tested for but did not report a numeric result; for example, participants reporting a 'less-than' result (< x) when the assigned value was higher than their LOR, or laboratories that did not report anything.

Table 34 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (mg/kg)	Spike Value (mg/kg)	Result* (mg/kg)
2	S3	Benz[*a*]anthracene	1.34	1.69	<0.05
	S4	Anthracene	1.81	2.80	<0.05
		Benz[*a*]anthracene	3.34	3.97	<0.05
		Benzo[*a*]pyrene	2.39	3.96	<0.05
9	S3	Anthracene	1.89	3.18	NR
		Fluorene	0.837	1.00	NR
13	S4	Benzo[*a*]pyrene	2.39	3.96	<0.05

* Result may or may not be a false negative, depending on the participant's actual LOR.

6.6 Reporting of Additional Analytes

Three participants reported analyte that were not spiked into the test samples. These results are presented in Table 35. Participants should take care to avoid any potential cross-contamination with other samples at their laboratory.

Table 35 Results Reported for Non-Spiked Analytes

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)
1	S3	Benzo[*b*+*k*]fluoranthene	1.058	NR
	S4	Benzo[*b*+*k*]fluoranthene	1.80	NR
9	S3	Acenaphthylene	0.43	0.11
		Benzo[*b*]fluoranthene	0.36	0.10
		Benzo[*k*]fluoranthene	0.21	0.05
		Indeno[1,2,3-*cd*]pyrene	0.45	0.12
		Benzo[*g*,*h*,*i*]perylene	0.25	0.07
13	S4	Benzo[*b*]fluoranthene	2.58	NR

6.7 Participants' Analytical Methods

A variety of analytical methods were used by participants in this study (Appendix 4).

TRH

Participants used a sample size between 4 g and 25 g for TRH analysis, with the majority of participants using 10 g. A plot of results against sample mass used for analysis is presented in Figure 42.

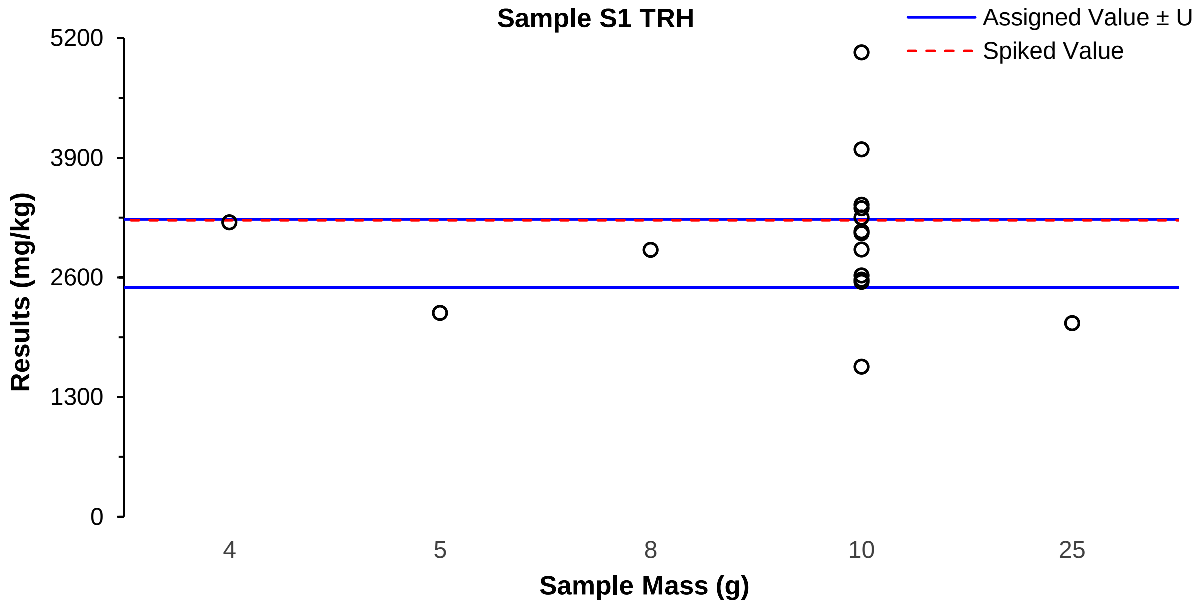


Figure 42 Sample S1 TRH Results vs Sample Mass Used for Analysis

Participants reported using either solid-liquid extraction (SLE) or sonication, with dichloromethane (DCM), acetone (ACE), hexane (HEX), or combinations of these as the extraction solvent(s). Four participants reported a silica clean-up step. All participants used gas chromatography (GC) coupled to flame ionisation detection (FID) for analysis.

A plot of results and methodology for TRH in Sample S1 is presented in Figure 43. Methodologies are listed in order of extraction technique, extraction solvent, clean-up and instrument.

The most common methodology used to analyse TRH in this study was SLE with DCM/ACE as the extraction solvent, with no clean-up and using GC-FID for analysis.

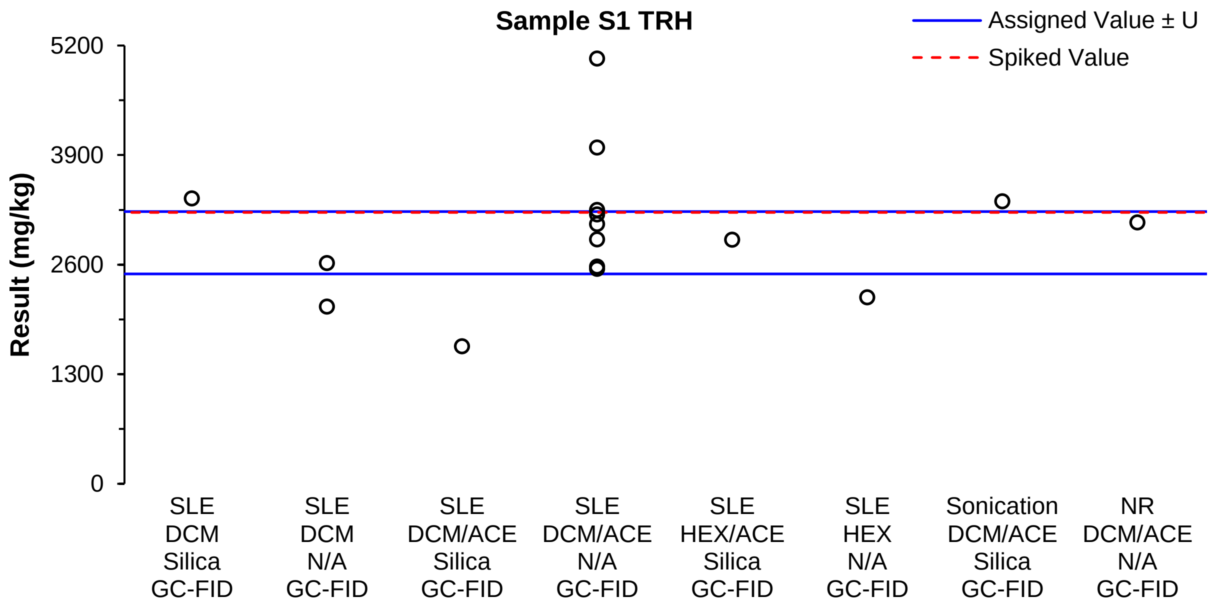


Figure 43 Sample S1 TRH Results vs Methodology

BTEX

Participants used a sample size between 2 g and 14 g for BTEX analysis, with the majority of participants using 10 g. A plot of results against sample mass used for analysis is presented in Figure 44.

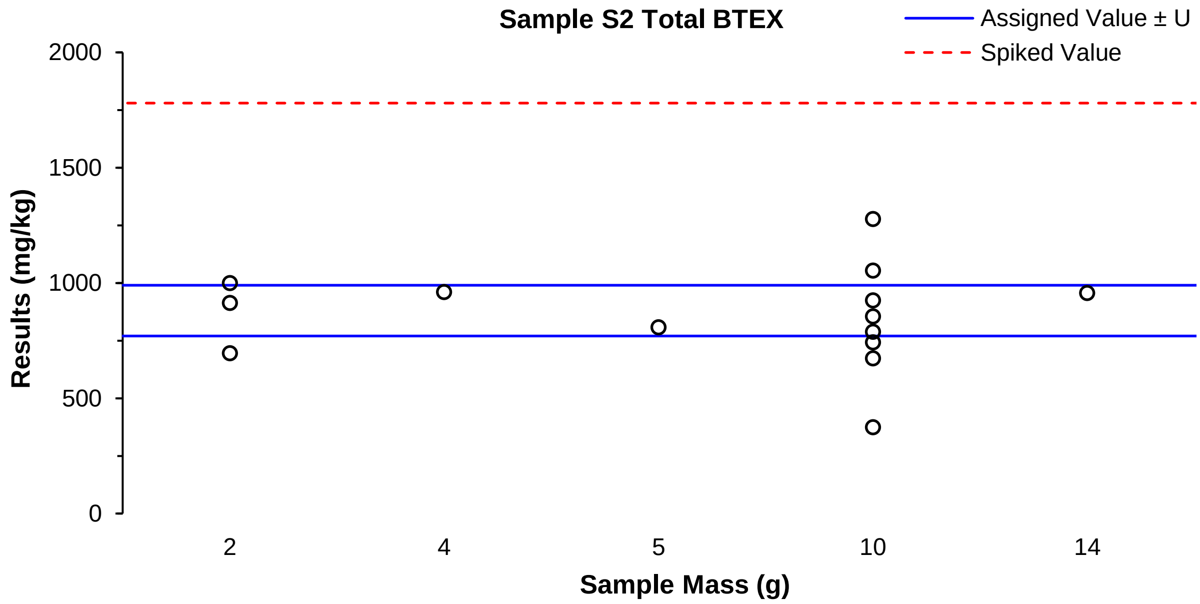


Figure 44 Sample S2 Total BTEX Results vs Sample Mass Used for Analysis

Extraction techniques reported by participants included SLE and sonication. All participants reported using methanol (MeOH) as their extraction solvent. No participant reported a clean-up step. Three participants used headspace (HS) GC coupled to mass spectrometry

(MS) or tandem mass spectrometry (MS/MS), while all other participants used purge and trap (P&T) GC-MS(/MS).

A plot of results and methodology for Total BTEX in Sample S2 is presented in Figure 45. Methodologies are listed in order of extraction technique, extraction solvent, clean-up and instrument.

The most common methodology used to analyse BTEX in this study was SLE with MeOH, using P&T GC-MS for analysis.

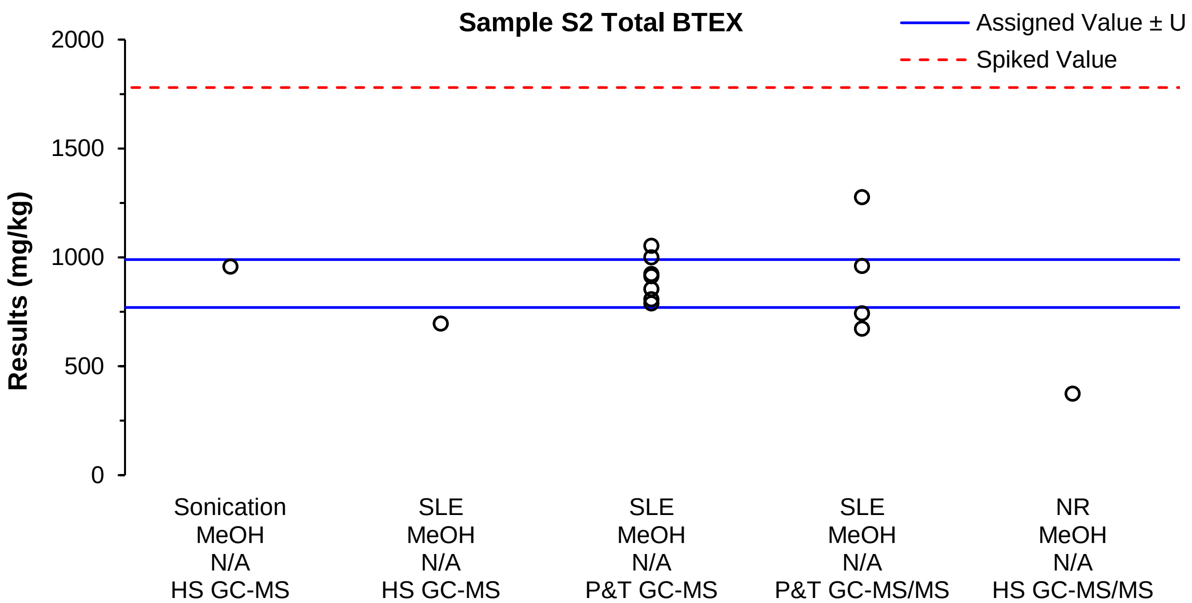
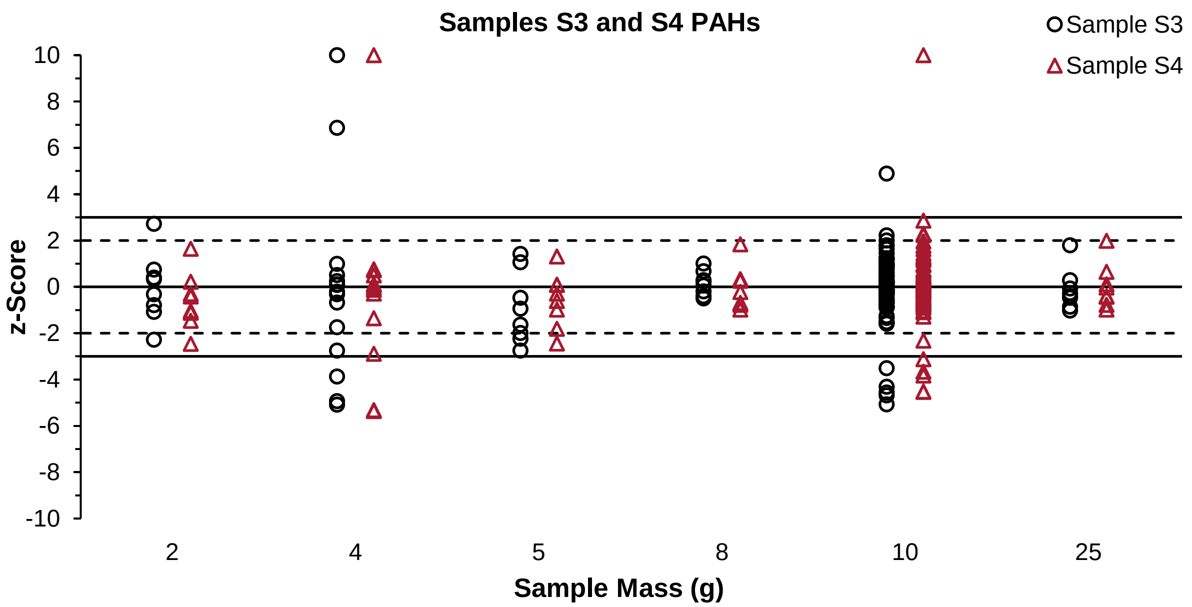


Figure 45 Sample S2 Total BTEX Results vs Methodology

PAHs

Participants used a sample size between 2 g and 25 g for PAHs analysis, with the majority of participants using 10 g. A plot of *z*-scores against sample mass used for analysis is presented in Figure 46.



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

Figure 46 Samples S3 and S4 PAHs *z*-Scores vs Sample Mass Used for Analysis

Participants reported using SLE, with DCM, ACE, HEX, ethyl acetate (EtOAc) and combinations of these as the extraction solvent. One participant reported using Florisil clean-up. All participants used GC-MS(/MS) for analysis.

A plot of *z*-scores obtained and methodology used for the PAHs in Samples S3 and S4 is presented in Figure 47. Methodologies are listed in order of extraction technique, extraction solvent, clean-up and instrument.

The most common methodology used to analyse PAHs in this study was SLE with DCM/ACE as the extraction solvent, with no clean-up and using GC-MS for analysis.

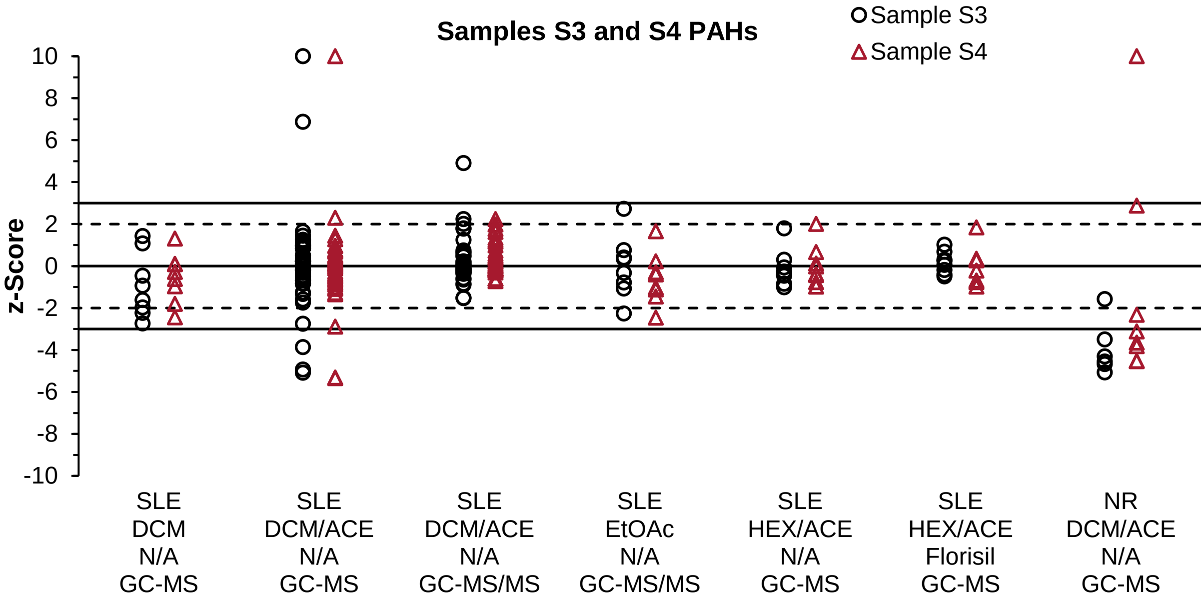


Figure 47 Samples S3 and S4 PAHs *z*-Scores vs Methodology

6.8 Certified Reference Materials (CRM)

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

Eight participants reported using certified standards and two participants reported using matrix reference materials. The following were reported by participants:

- NMI MX015
- Accustandard
- o2si
- Sigma Aldrich, e.g. CRM352

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

> '***reference material***, *accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures*'[12]

6.9 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 36 to 38, and Figure 48.

Table 36 Summary of Participants' Results (Samples S1 and S2)*

Lab. Code	Sample S1				Sample S2		
	>C10-C16	>C16-C34	>C34-C40	TRH	Ethylbenzene	Xylenes	Total BTEX
AV	1070	1570	245	2860	72.6	417	880
SV	1150	1810	255	3220	94.9	712	1780
1	904	1716	NR	2619	NR	NR	NR
2	NT	NT	NT	NT	NT	NT	NT
3	NR	NR	NR	3350	76	469	957
4	1057	1041	114	2212	65.7	389	696
5	1016	1933	247	3196	78.3	326	808
6	1257.9	1701.4	288.3	3247.6	91.8	557	1053.3
7	527	965	137	1629	77.9	465	924
8	1240	2420	331	3991	68.3	422	855
9	1040	1710	340	3100	NR	NR	NR
10	1070	1180	300	2550	73	379	742.9
11	NR	NR	NR	2896	22.54	322.5	374.1
12	1000	1700	180	2900	75	460	960
13	1286	1806	295	3387	64.2	358	913
14	590	1300	160	2100	70	460	1000
15	1659	2990	395	5044	55	347	673
17	982	1353	239	2575	67.1	421	789
18	1100	1800	180	3080	83.6	488	1277

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

Table 37 Summary of Participants' Results (Samples S3)*

Lab. Code	Sample S3							
	Anthracene	Benz[*a*]anthracene	Benzo[*a*]pyrene	Chrysene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
AV	1.89	1.34	1.26	0.801	2.42	0.837	0.667	1.49
SV	3.18	1.69	2.19	0.897	2.81	1.00	0.808	1.71
1	1.67	1.49	1.20	0.85	2.03	0.88	0.44	2.1
2	0.45	<0.05	0.53	0.47	0.63	1.70	2.3	1.1
3	NS	NS	NS	NS	NS	NS	NS	NS
4	1.33	0.79	1.53	0.93	1.83	0.72	0.62	0.99
5	1.83	1.54	1.2	0.815	2.51	0.753	0.718	1.51
6	2.13	1.17	1.26	0.92	2.87	0.96	0.76	1.73
7	2.06	1.29	0.97	0.62	2.11	0.93	0.63	1.29
8	1.84	1.21	1.15	0.95	2.41	0.85	0.64	1.42
9	NR	0.40	0.40	0.38	0.58	NR	0.51	0.53
10	1.85	1.38	1.23	0.94	2.46	0.88	0.69	1.54
11	1.75	1.4	1.45	0.83	2.35	0.845	0.735	1.4
12	2.3	1.2	1.1	0.74	2.5	0.68	0.69	1.7
13	1.83	1.59	1.57	0.83	2.72	0.84	0.75	1.6
14	1.6	1.4	1.6	0.77	2.4	0.73	0.62	1.4
15	2.40	1.44	1.24	1.39	3.23	1.06	0.69	1.94
17	1.905	1.304	1.202	0.784	2.484	0.893	0.733	1.497
18	1.9	1.3	0.96	0.64	2.2	0.75	0.62	1.3

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

Table 38 Summary of Participants' Results (Samples S4)*

Lab. Code	Sample S4							
	Anthracene	Benz[*a*]anthracene	Benzo[*a*]pyrene	Chrysene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
AV	1.81	3.34	2.39	1.73	0.602	3.10	1.38	1.09
SV	2.80	3.97	3.96	1.89	0.698	3.50	1.60	1.19
1	1.70	3.19	2.02	1.44	0.47	3.20	0.87	1.36
2	<0.05	<0.05	<0.05	0.98	1.6	0.61	1.1	0.22
3	NS	NS	NS	NS	NS	NS	NS	NS
4	1.32	2.12	2.29	2.07	0.61	2.65	1.4	0.99
5	1.84	3.72	2.57	1.75	0.6	2.97	1.53	1.07
6	1.53	3.71	2.73	1.86	0.53	3.15	1.43	0.99
7	2.29	3.92	2.65	1.78	0.59	3.86	1.48	1.05
8	1.84	3.26	2.32	1.88	0.59	3.29	1.39	0.99
9	0.58	1.51	1.02	0.92	2.42	1.00	0.90	1.56
10	1.84	3.33	2.5	1.98	0.67	3.17	1.44	1.1
11	1.6	3.5	3.05	1.8	0.54	3	1.45	0.93
12	2.2	3.0	2.2	1.6	0.64	2.6	1.4	1.3
13	1.83	3.33	<0.05	1.76	0.81	3.2	1.52	1.16
14	1.6	3.4	3.7	1.9	0.60	2.9	1.3	0.93
15	2.17	3.25	2.13	2.31	0.78	3.67	1.38	1.25
17	1.899	3.276	2.373	1.569	0.602	3.202	1.462	1.039
18	1.7	3.1	2.0	1.5	0.53	2.8	1.3	0.88

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

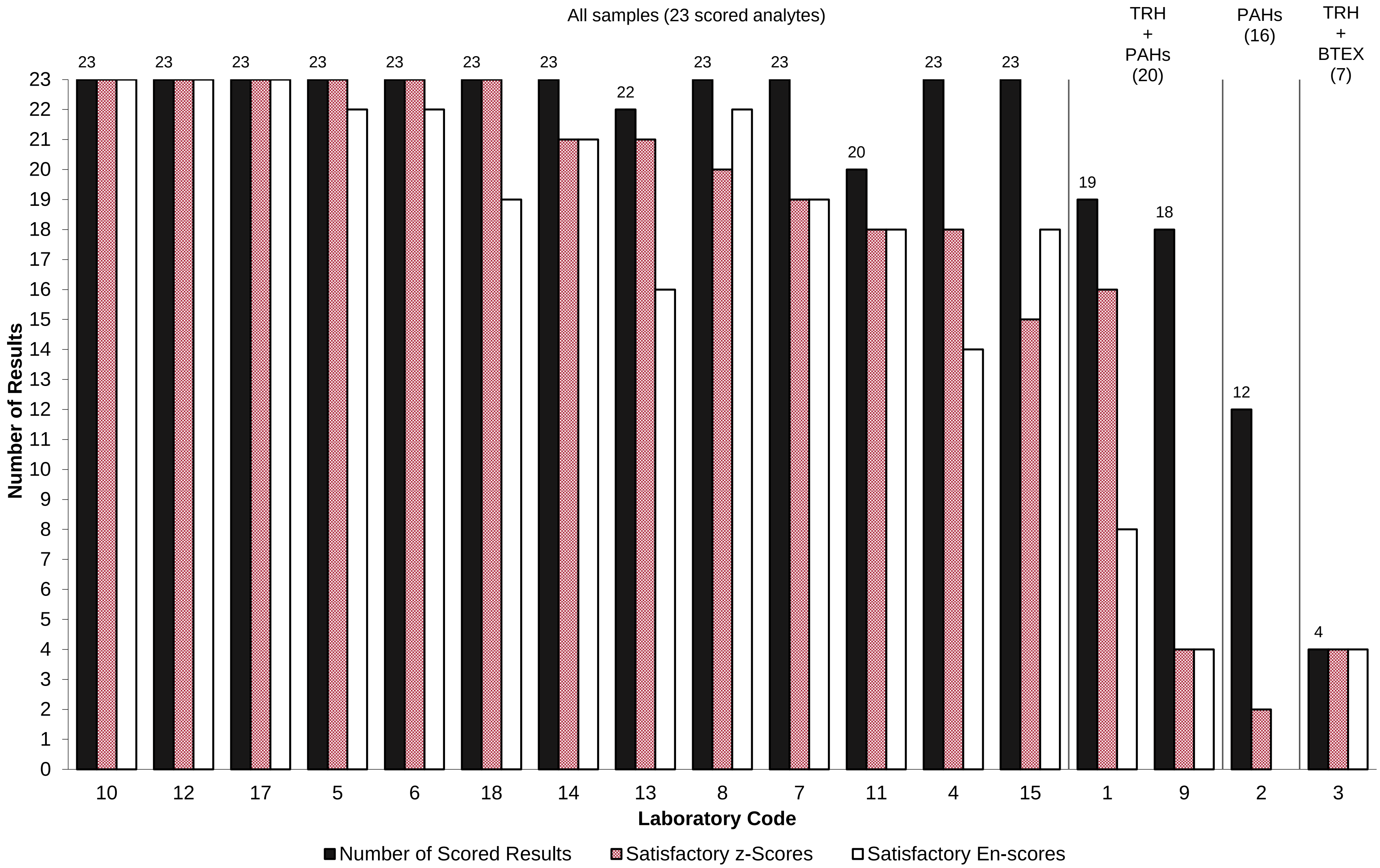


Figure 48 Summary of Participants' Performance

6.10 Comparison with Previous Hydrocarbons in Soil PT Studies

To enable direct comparison with results from previous Hydrocarbons in Soil PT studies, the target SD used to calculate *z*-scores has been kept constant at 15% PCV.

Individual performance history reports are emailed to each participant at the end of each study; the consideration of *z*-scores for an analyte over time provides much more useful information than a single *z*-score. Over time, laboratories should expect at least 95% of their scores to lie within the range $|z| \le 2.0$. Scores in the range $2.0 < |z| < 3.0$ can occasionally occur, however, these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of *z*-scores on one side of the zero line is an indication of method or laboratory bias.

TRH

A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by participants for TRH in soil over the last 10 studies (2015 – 2023) is presented in Figure 49. Over this period, the average proportion of satisfactory *z*-scores was 92%, and the average proportion of satisfactory E_n-scores was 74%.

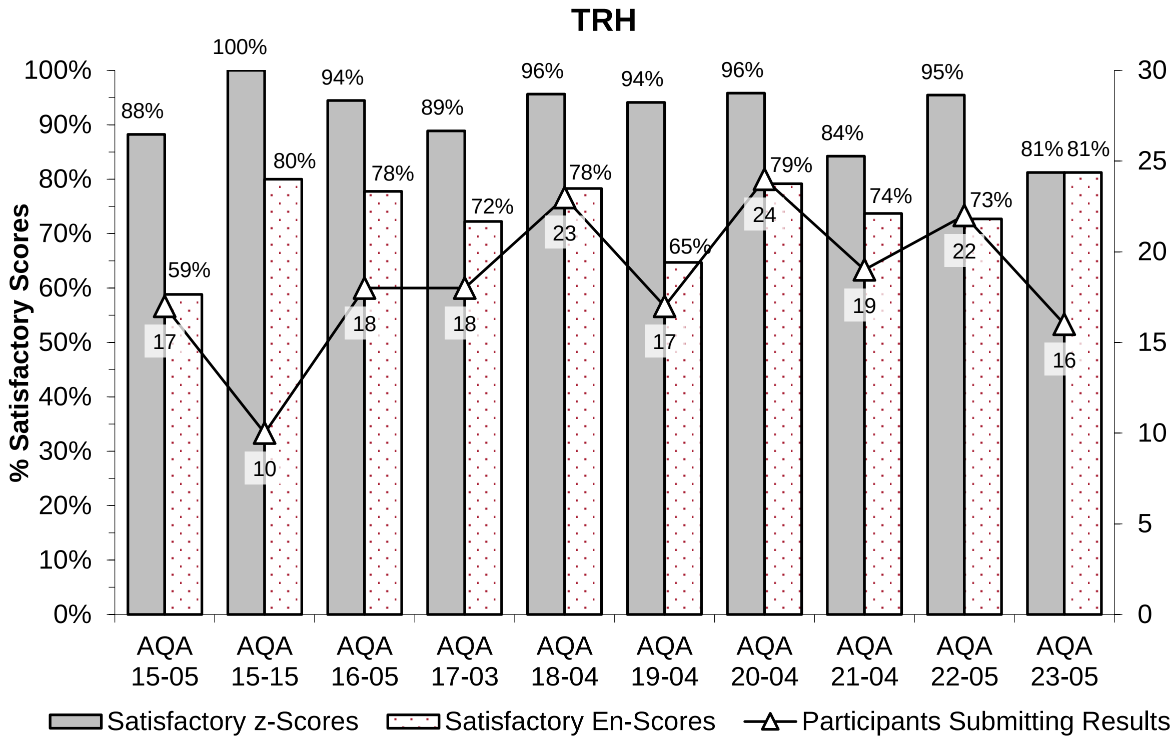


Figure 49 Participants' Performance for TRH in Hydrocarbons in Soil PT Studies

Total BTEX

A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by participants for Total BTEX in soil over the last 10 studies (2015 – 2023) is presented in Figure 50. Over this period, the average proportion of satisfactory *z*-scores was 88%, and the average proportion of satisfactory E_n-scores was 82%.

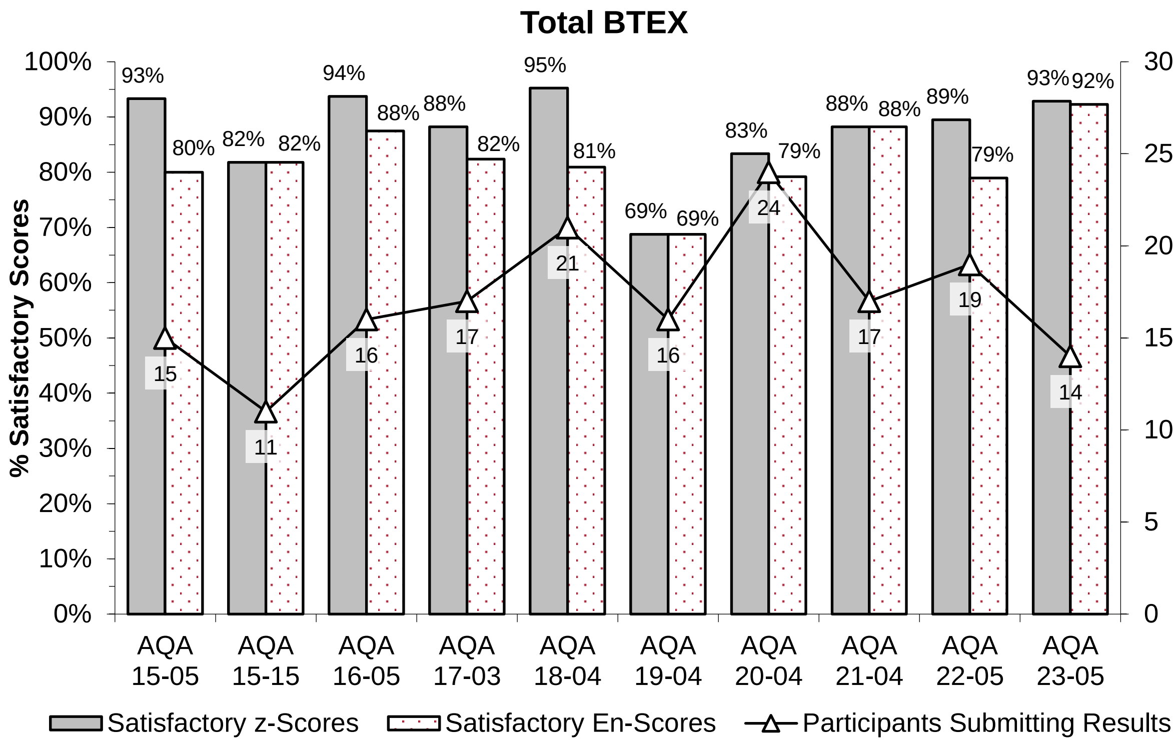


Figure 50 Participants' Performance for Total BTEX in Hydrocarbons in Soil PT Studies

PAHs

PAHs in soil was first introduced in NMI PT studies in 2016. A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by participants for PAHs in soil over the last 8 studies (2016 – 2023) is presented in Figure 51. Over this period, the average proportion of satisfactory *z*-scores was 90%, and the average proportion of satisfactory E_n-scores was 86%.

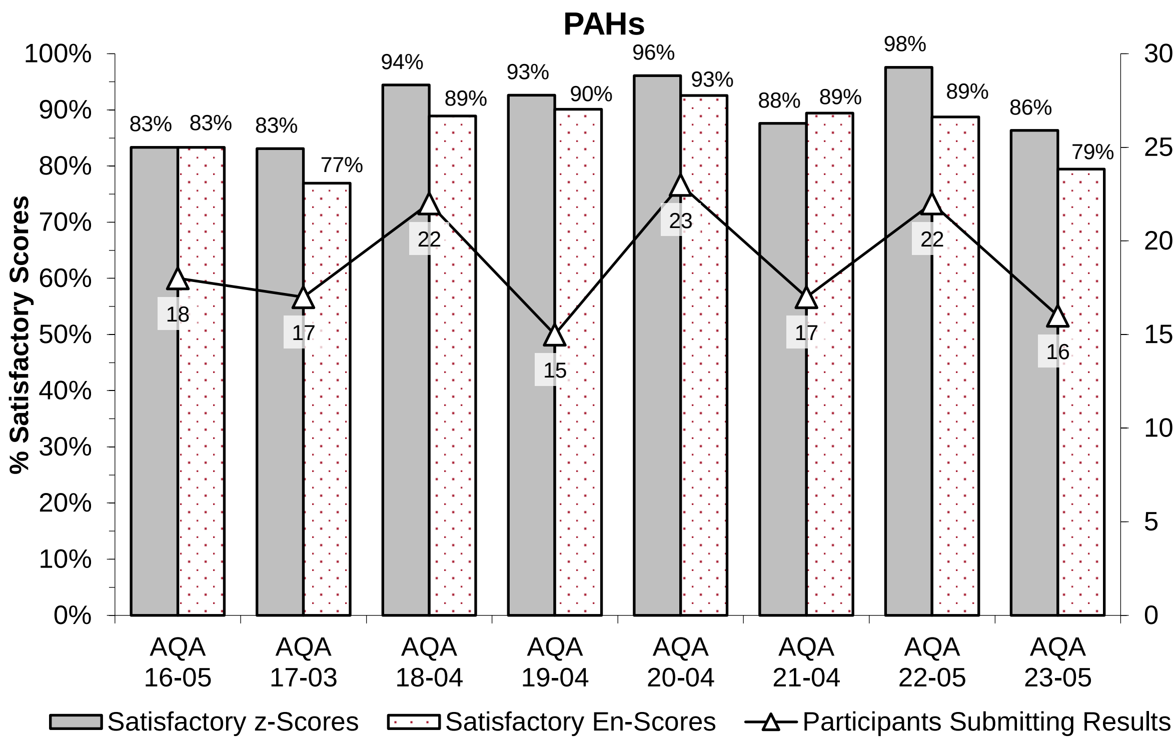


Figure 51 Participants' Performance for PAHs in Hydrocarbons in Soil PT Studies

A plot of the robust average expressed as a percentage of the spiked value for PAHs in topsoil since 2016 is presented in Figure 52. Results from samples with other soil matrices have not been included as it has been previously seen that the nature of the soil matrix can substantially affect the recovery of some analytes.[13]

This study was the first to include benz[*a*]anthracene as a spiked analyte.

For all spiked PAHs in this study, the robust averages were lower than the spiked values, consistent with previous studies. Throughout NMI Hydrocarbons in Soil PT studies, anthracene and benzo[*a*]pyrene have consistently had lower recoveries, averaging 49% and 46% respectively for the robust average to spiked value. Chrysene, fluoranthene, fluorene, phenanthrene and pyrene have had higher recoveries, with averages ranging from 77% to 86% for the robust average to spiked value.

For this study, anthracene, benzo[*a*]pyrene, chysene, fluorene and pyrene returned higher recoveries as compared to the average of previous studies.

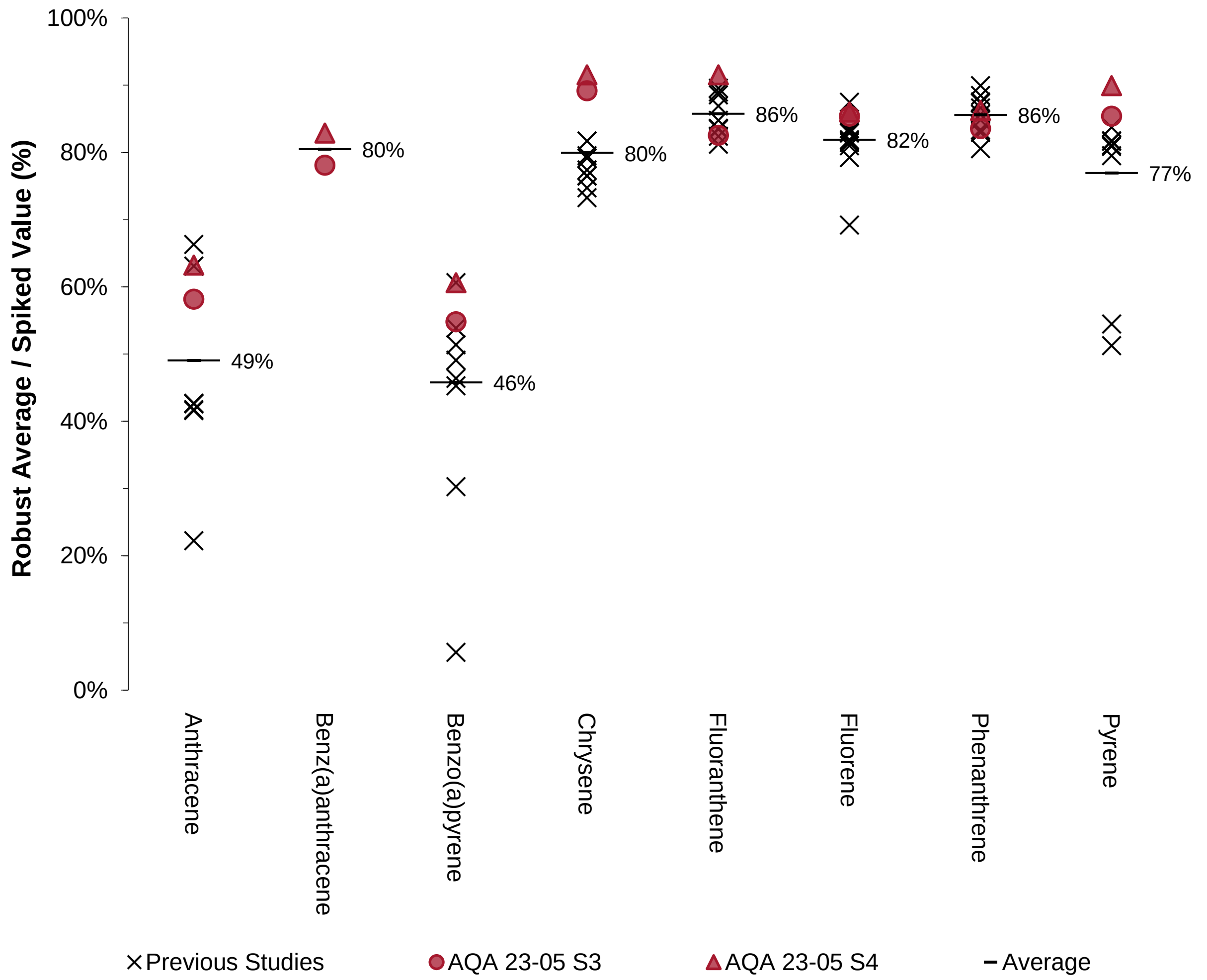


Figure 52 Recoveries of PAHs in Topsoil for Hydrocarbons in Soil PT Studies

7 REFERENCES

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

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

[13] NMI, 2018, *Proficiency Test Report AQA 18-04 Hydrocarbons in Soil*.

APPENDIX 1 SAMPLE PREPARATION

A1.1 Diesel Fuel 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 was used in previous NMI Hydrocarbon PTs.

A1.2 Test Sample Preparation

Uncontaminated soil described as Menangle topsoil bought from a Sydney supplier was used to prepare the samples. The soil was dried at 120 °C for at least two hours. The dried soil was sieved, and the fraction between 355 μm and 850 μm was used to prepare all samples.

Sample S1: Into a stainless steel pot, 2160.5 g of dried and sieved Menangle topsoil was placed. Dichloromethane was added to moisten the soil. A 6.715 g aliquot of sparged diesel was added by transferring 8 aliquots of 1.000 mL of diesel into the drum. The mass of diesel was calculated using a density of 0.83936 g/mL. In addition, 3.0 mL of PENRITE INDUS PRO HYDRAULIC 68 was added. The mixture was thoroughly stirred and the solvent was allowed to evaporate. The mixture was divided into 50 g portions using a Retsch PT 100 sample divider and packed into screw-capped glass jars, labelled and stored in a refrigerator.

Sample S2: Dried, sieved Menangle topsoil (3527.6 g) was placed in a 10 L stainless steel drum with a clamp-locked lid. The drum and soil were cooled in a freezer overnight. The drum containing the soil was removed from the freezer and the lid removed. Five aliquots of 0.840 mL of diesel (3.53 g using ρ = 0.83936 g/mL) were added to the soil. Four aliquots of 100 µL of benzene (total of 0.400 mL) were added to the soil using a positive displacement pipette, followed by two aliquots of 10 mL of unleaded gasoline (15.72 g using ρ = 0.786 g/mL). The drum was sealed and vigorously shaken. The sealed drum was then packed into another large drum and surrounded by cold gel-packs. The drums were then tumbled for 60 minutes on a hoop mixer. The soil was scooped into glass jars, tapped, topped up to minimise the vapour space and sealed. The process of filling the jars was conducted with the drum in an open freezer in an attempt to minimise the loss of volatiles. The jars were labelled, sealed with Parafilm, shrink-wrapped and stored in a freezer.

Samples S3 and S4: For Sample S3, 1000.3 g of dried and sieved Menangle topsoil was placed in a 3 L round bottom flask. Dichloromethane was then added to the soil to allow it to be suspended. Using a Gilson pipette, aliquots of the PAH standard solutions were added to the round bottom flask. The quantity of each standard was calculated using the target final mass of soil after the dilution of the contents of the round bottom flask. To minimise the creation of dust, 10 mL of Milli-Q water was added to the flask. The flask was shaken to mix. The solvent was then evaporated using a Büchi rotary evaporator. The bath temperature was set at ambient and gently increased to no more than 50 °C during the evaporation, the condenser temperature at 7 °C and less than 20 kPa of vacuum. After evaporating the dichloromethane, the soil was transferred to a V-mixer and diluted with 1099.8 g of clean soil. The total soil mass was 2100.1 g. The V-mixer was tumbled for two hours. After mixing the soil was divided using a Retsch PT100 sample divider into fifty samples of at least 50 g, placed in screw-capped glass jars, labelled and placed in a refrigerator.

The same procedure was used for Sample S4 except for the quantities of spike solutions, and masses of soil which were 1000.6 g into the 3 L flask and 1102.3 g of diluent soil, making a total of 2102.9 g of spiked soil.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce homogeneous samples. The results of this study also gave no reason to question the samples' homogeneity. Comparisons of results to bottle number for scored analytes are presented in Figures 53 to 70 (solid lines correspond to the assigned value ± U for each analyte). No significant fill order trend was observed.

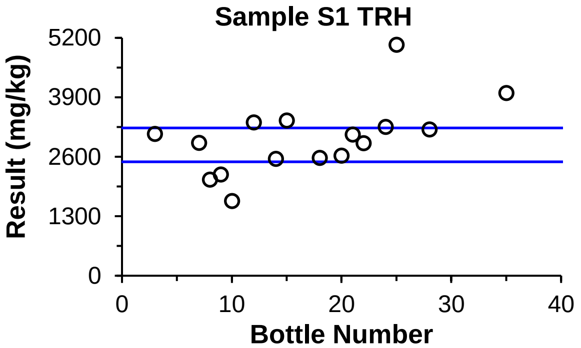

Figure 53 S1 TRH Results vs Bottle Number

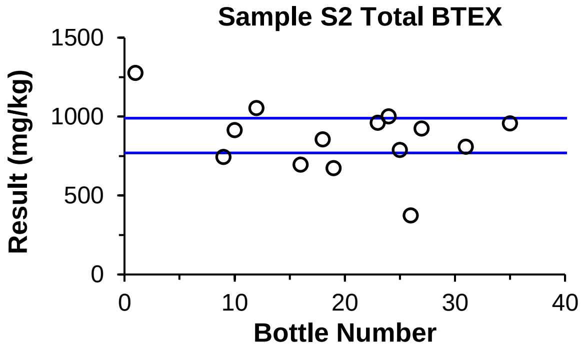

Figure 54 S2 Total BTEX Results vs Bottle Number

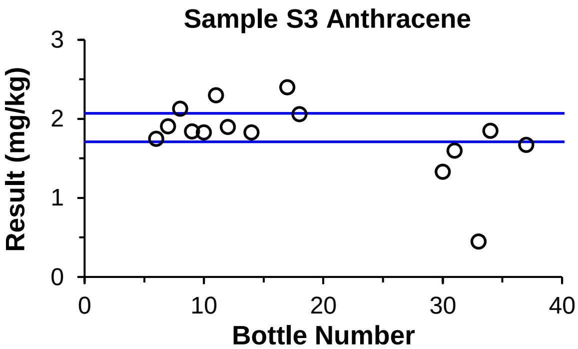

Figure 55 S3 Anthracene Results vs Bottle Number

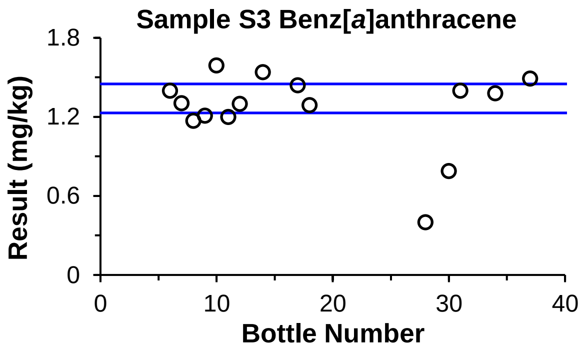

Figure 56 S3 Benz[*a*]anthracene Results vs Bottle Number

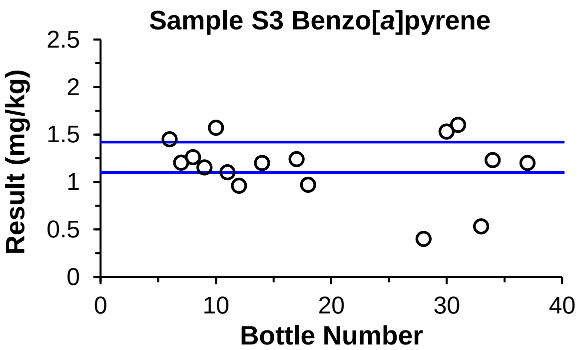

Figure 57 S3 Benzo[*a*]pyrene Results vs Bottle Number

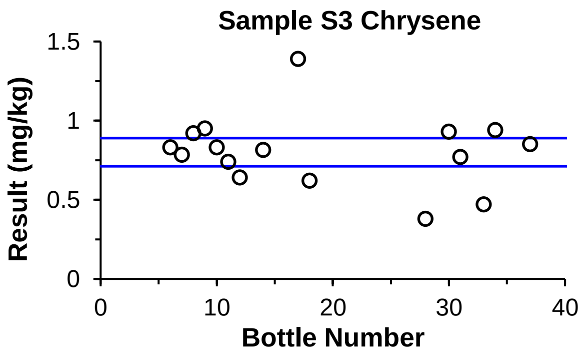

Figure 58 S3 Chrysene Results vs Bottle Number

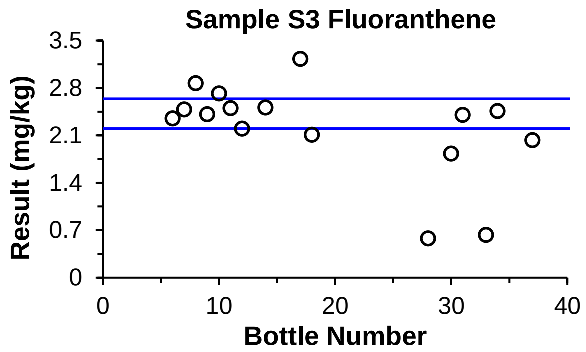

Figure 59 S3 Fluoranthene Results vs Bottle Number

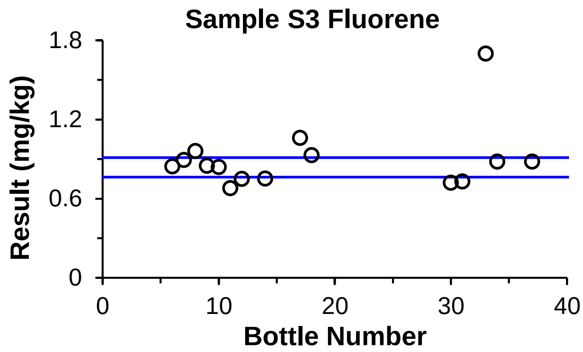

Figure 60 S3 Fluorene Results vs Bottle Number

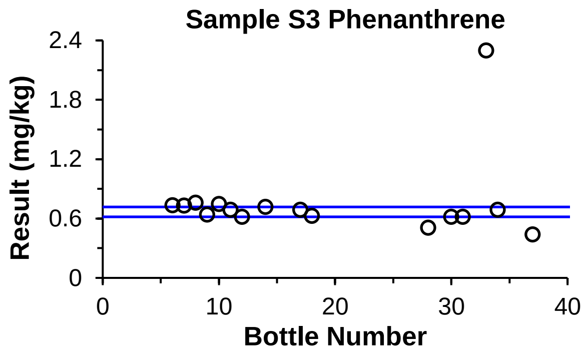

Figure 61 S3 Phenanthrene Results vs Bottle Number

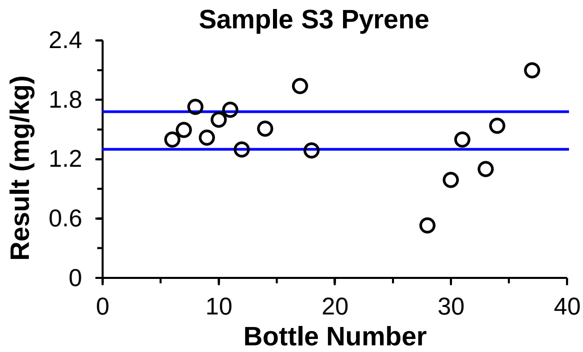

Figure 62 S3 Pyrene Results vs Bottle Number

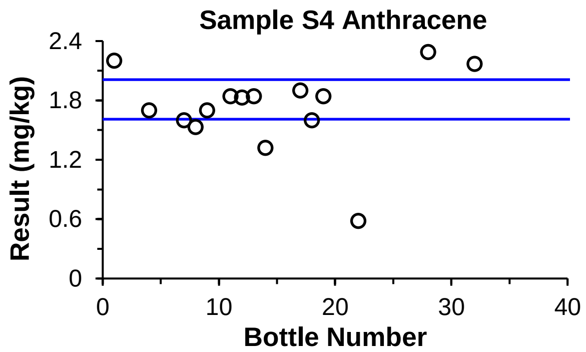

Figure 63 S4 Anthracene Results vs Bottle Number

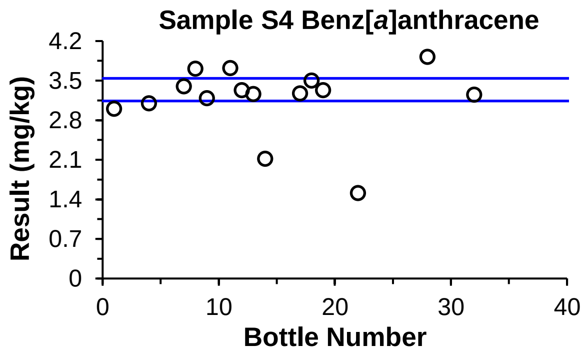

Figure 64 S4 Benz[*a*]anthracene Results vs Bottle Number

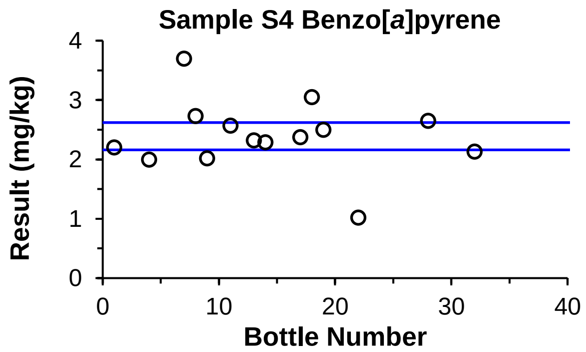

Figure 65 S4 Benzo[*a*]pyrene Results vs Bottle Number

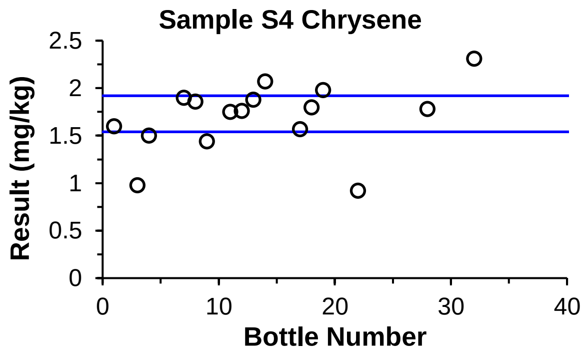

Figure 66 S4 Chrysene Results vs Bottle Number

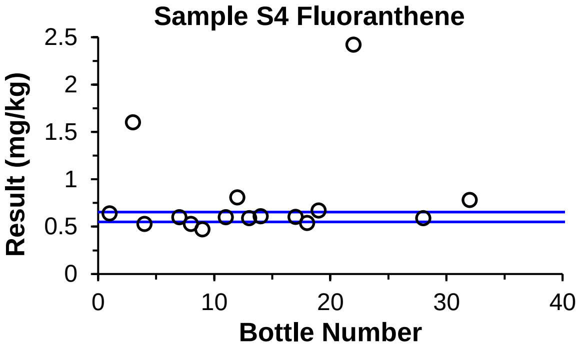

Figure 67 S4 Fluoranthene Results vs Bottle Number

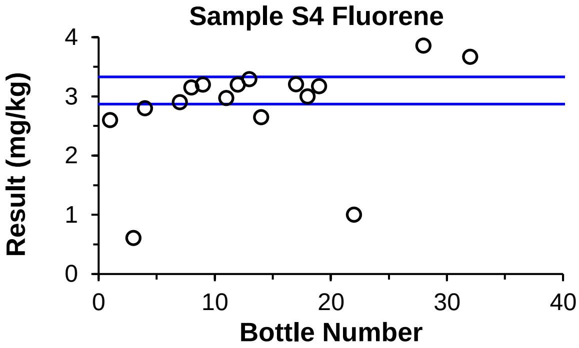

Figure 68 S4 Fluorene Results vs Bottle Number

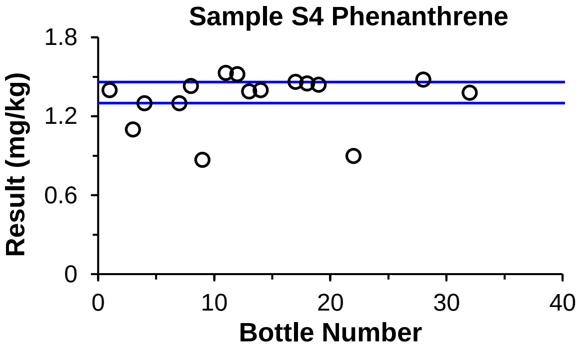

Figure 69 S4 Phenanthrene Results vs Bottle Number

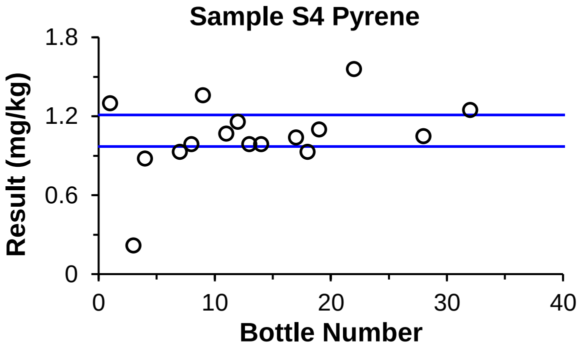

Figure 70 S4 Pyrene Results vs Bottle Number

A2.2 Transportation Stability

No stability testing was conducted for this study, though results from previous NMI Hydrocarbons in Soil PT studies gave some assurance that the analytes were stable over similar time frames. After preparation and before dispatch, Samples S1, S3 and S4 were stored in a refrigerator at approximately 4 °C, and Sample S2 was stored in a freezer at approximately -20 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks. Comparisons of results to days spent in transit for scored analytes are presented in Figures 71 to 88 (solid lines correspond to the assigned value ± U for each analyte). No significant trend was observed.

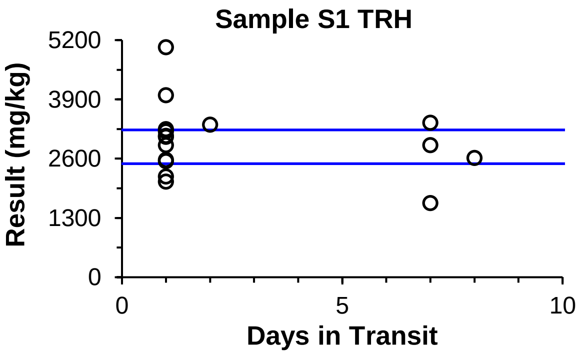

Figure 71 S1 TRH Results vs Transit Days

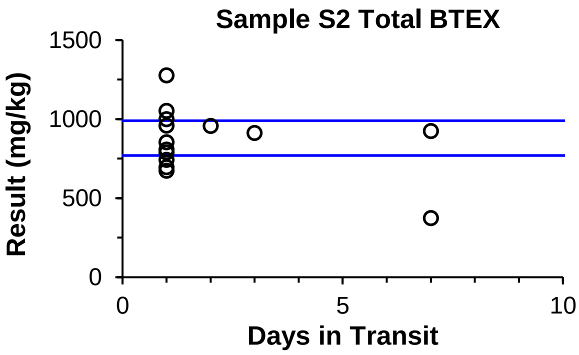

Figure 72 S2 Total BTEX Results vs Transit Days

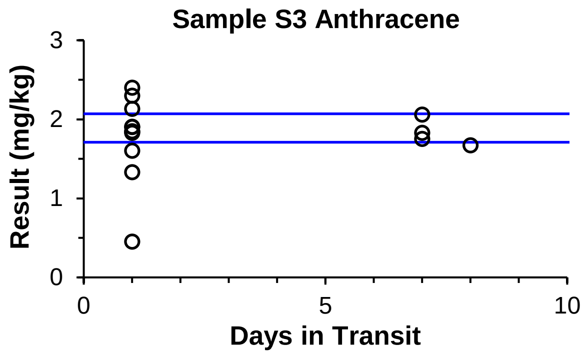

Figure 73 S3 Anthracene Results vs Transit Days

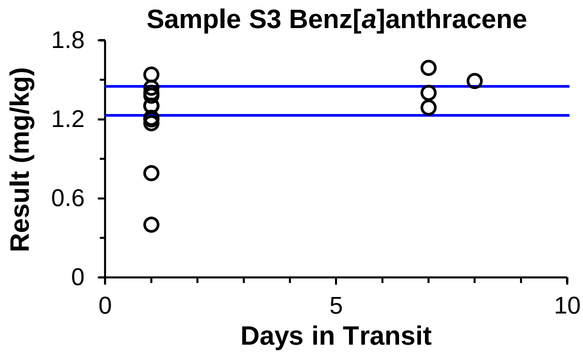

Figure 74 S3 Benz[*a*]anthracene Results vs Transit Days

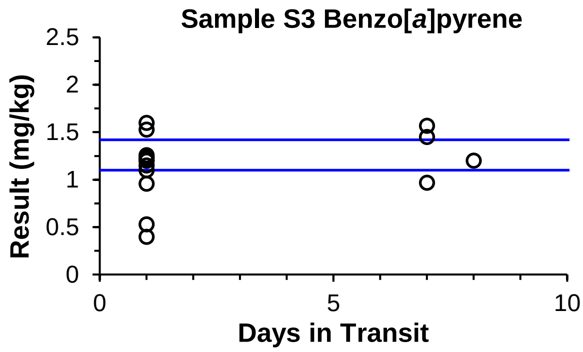

Figure 75 S3 Benzo[*a*]pyrene Results vs Transit Days

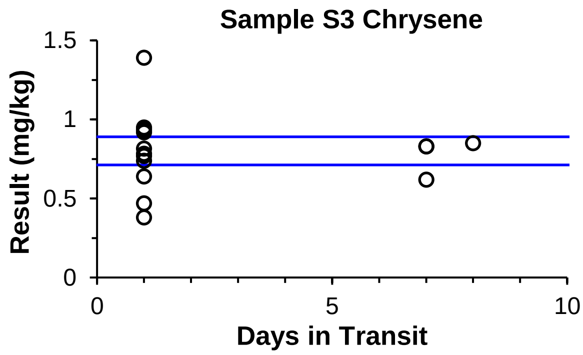

Figure 76 S3 Chrysene Results vs Transit Days

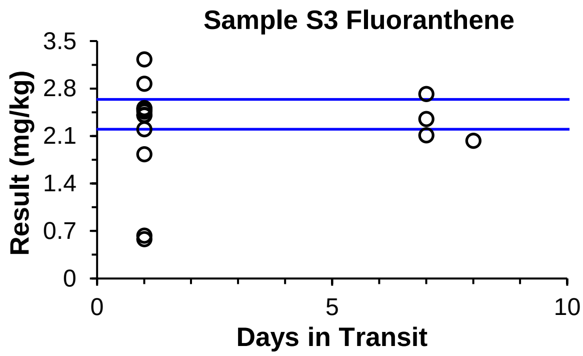

Figure 77 S3 Fluoranthene Results vs Transit Days

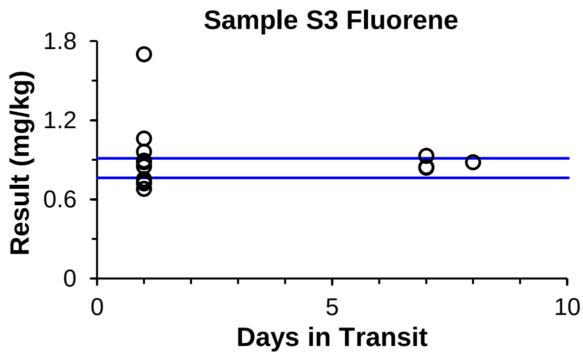

Figure 78 S3 Fluorene Results vs Transit Days

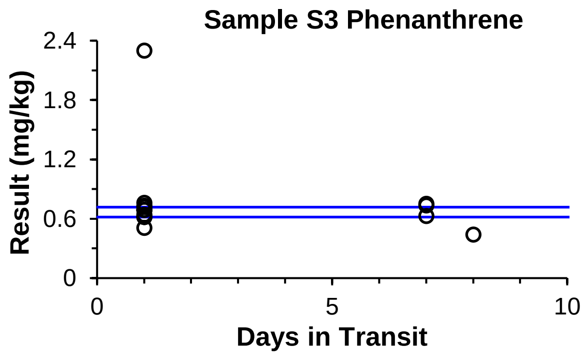

Figure 79 S3 Phenanthrene Results vs Transit Days

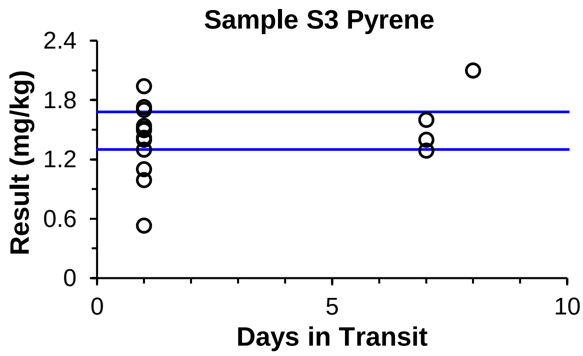

Figure 80 S3 Pyrene Results vs Transit Days

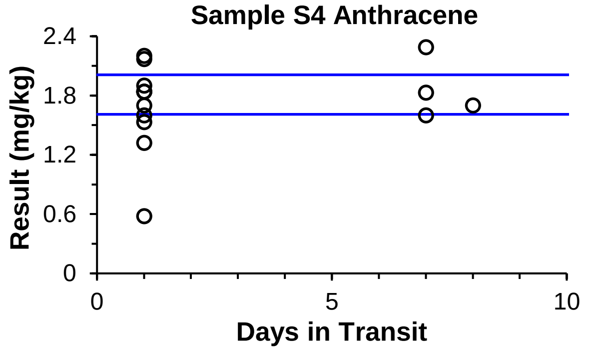

Figure 81 S4 Anthracene Results vs Transit Days

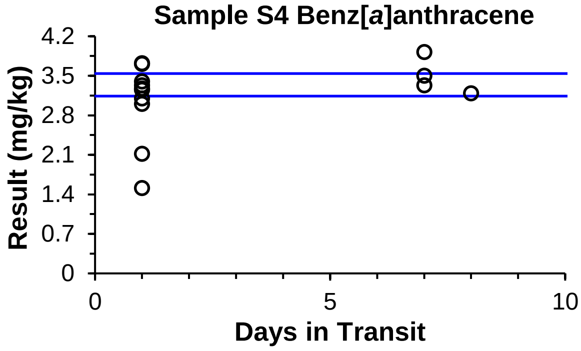

Figure 82 S4 Benz[*a*]anthracene Results vs Transit Days

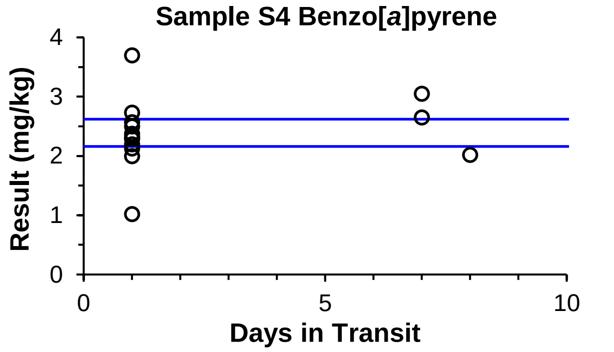

Figure 83 S4 Benzo[*a*]pyrene Results vs Transit Days

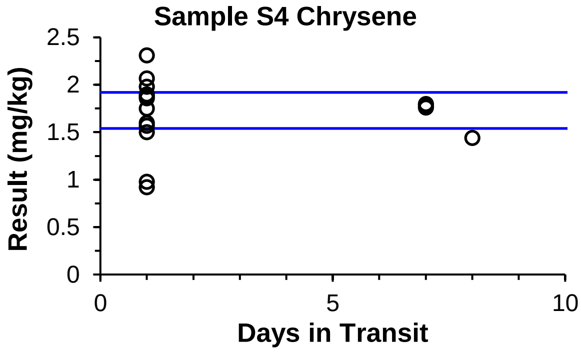

Figure 84 S4 Chrysene Results vs Transit Days

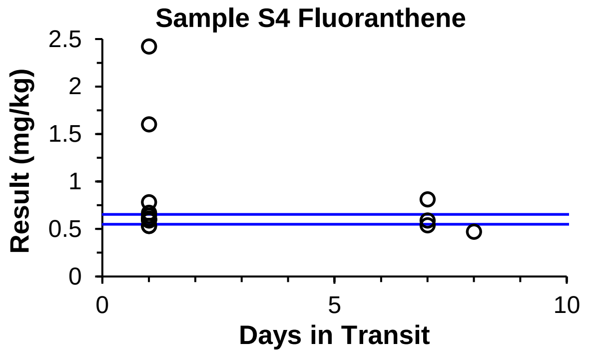

Figure 85 S4 Fluoranthene Results vs Transit Days

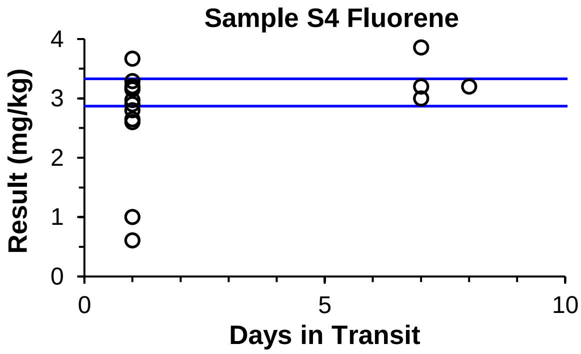

Figure 86 S4 Fluorene Results vs Transit Days

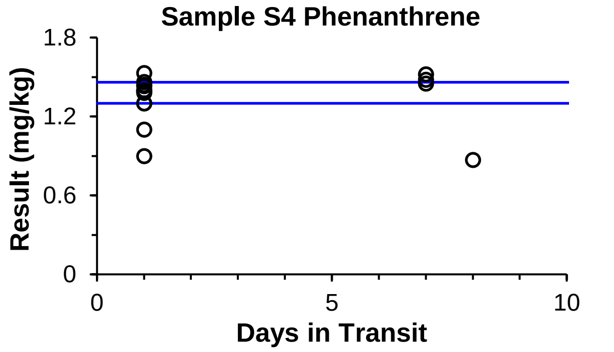

Figure 87 S4 Phenanthrene Results vs Transit Days

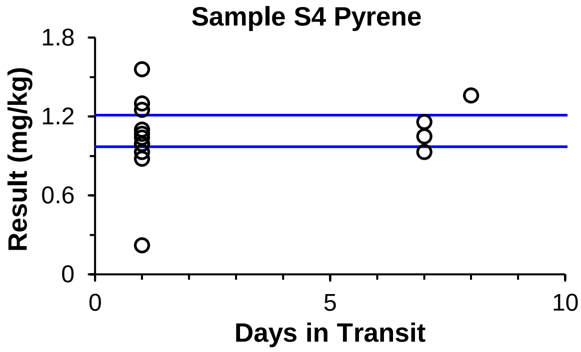

Figure 88 S4 Pyrene Results vs Transit Days

APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, *z* SCORE AND E_n SCORE CALCULATIONS

A3.1 Robust Average and Associated Uncertainty

The robust average was calculated using the procedure described in ISO 13528.[7] The associated uncertainty was estimated as according to Equation 4.

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

where:

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

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

A worked example is set out below in Table 39.

Table 39 Uncertainty of the Robust Average for Sample S4 Phenanthrene

No. Results (p)	16
Robust Average	1.38 mg/kg
$S_{rob\ av}$	0.13 mg/kg
$u_{rob\ av}$	0.04 mg/kg
k	2
$U_{rob\ av}$	0.08 mg/kg

Therefore, the robust average for Sample S4 phenanthrene is 1.38 ± 0.08 mg/kg.

A3.2 *z*-Score and E_n-Score Calculations

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

A worked example is set out below in Table 40.

Table 40 *z*-Score and E_n-Score Calculation for Sample S1 >C10-C16 Result Reported by Laboratory 1

Participant Result (mg/kg)	Assigned Value (mg/kg)	Target SD	*z*-Score	E_n-Score
904 ± NR	1070 ± 110	15% as PCV, or: 0.15 × 1070 = 160.5 mg/kg	$z\text{-Score} = \frac{904-1070}{160.5}$ = -1.03	$E_n\text{-Score} = \frac{904-1070}{\sqrt{0^2+110^2}}$ = -1.51

APPENDIX 4 TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 41 to 43. Some responses may be modified so that the participant cannot be identified.

Table 41 Test Methods Sample S1 TRH

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	10	Solid-Liquid	DCM		GC-FID	
2	NT					
3	10	Sonication	DCM:Acetone 1:1	Silica	GC-FID	USEPA 8015
4	5	Solid-Liquid	Hexane		GC-FID	Inhouse
5	4	Solid-Liquid	DCM/ACETONE	NIL	GC-FID	IN-HOUSE
6	10	Solid-Liquid	DCM:ACE	N/A	GC-FID	In-house
7	10	Solid-Liquid	DCM:Acetone	Silica	GC-FID	USEPA 8260
8	10	Solid-Liquid	DCM/Acetone	N/A	GC-FID	USEPA 8270
9	10		DCM:Acetone	None	GC-FID	USEPA 8015B
10	10	Solid-Liquid	DCM/Acetone	None	GC-FID	USEPA 8270C
11	8	Solid-Liquid	Hexane:Acetone	Silica	GC-FID	
12	10	Solid-Liquid	Acetone:DCM		GC-FID	2010 NEPM Schedule B3
13	10	Solid-Liquid	DCM	Silica	GC-FID	In house
14	25	Solid-Liquid	DCM	n/a	GC-FID	In-house
15	10	Solid-Liquid	DCM/ACETONE (1:1)		GC-FID	USEPA 8015
17	10	Solid-Liquid	DCM:Acetone		GC-FID	USEPA 8260
18	10	Solid-Liquid	DCM/Acetone		GC-FID	NEPM

Table 42 Test Methods Sample S2 BTEX

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	NT					
2	NT					
3	14	Sonication	Methanol	Nil	Headspace GC-MS	USEPA 8260
4	2	Solid-Liquid	Methanol		Headspace GC-MS	Inhouse
5	5	Solid-Liquid	METHANOL	NIL	PURGE&TRAP-GCMS	IN-HOUSE
6	10	Solid-Liquid	MeOH	N/A	P&T GC-MS	In-house
7	10	Solid-Liquid	Methanol	None	P&T GC-MS	USEPA 8260
8	10	Solid-Liquid	Methanol	N/A	P&T GC-MS	USEPA 8260
9	NT					

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
10	10	Solid-Liquid	Methanol	None	P&T GC-MS/MS	USEPA 8260B
11	10		Methanol	N/A	Headspace GC-MS/MS	
12	4	Solid-Liquid	Methanol		P&T GC-MS/MS	USEPA 8260
13	2	Solid-Liquid	MeOH		P&T GC-MS	USEPA 8260
14	2	Solid-Liquid	Methanol	n/a	P&T GC-MS	In-house
15	10	Solid-Liquid	METHANOL		P&T GC-MS/MS	USEPA 8260
17	10	Solid-Liquid	Methanol	None	P&T GC-MS	USEPA 8260
18	10	Solid-Liquid	Methanol		P&T GC-MS/MS	USEPA 8260

Table 43 Test Methods Samples S3 and S4 PAHs

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	2	Solid-Liquid	Ethyl acetate		GC-MS/MS	
2	4	Solid-Liquid	DCM/Acetone		GC-MS	USEPA 8270
3	NS					
4	5	Solid-Liquid	DCM		GC-MS	Inhouse
5	4	Solid-Liquid	DCM/ACETONE	NIL	GCMS	IN-HOUSE
6	10	Solid-Liquid	DCM:ACE	N/A	GC-MS	In-house
7	10	Solid-Liquid	DCM:Acetone		GC-MS/MS	USEPA 8260
8	10	Solid-Liquid	DCM/Acetone	N/A	GC-MS/MS	USEPA 8270
9	10		DCM:Acetone	None	GC-MS	USEPA 8270D
10	10	Solid-Liquid	DCM/Acetone	None	GC-MS	USEPA8270C
11	8	Solid-Liquid	Hexane:Acetone	Florisil	GC-MS	In-house
12	10	Solid-Liquid	Acetone:DCM		GC-MS	USEPA 8270
13	10	Solid-Liquid ASE extract	DCM/acetone	None	GC-MS	USEPA 8270
14	25	Solid-Liquid	Acetone/Hexane	n/a	GC-MS	In-house
15	10	Solid-Liquid	DCM/ACETONE (1:1)		GC-MS/MS	USEPA 8270
17	10	Solid-Liquid	DCM:Acetone		GC-MS/MS	USEPA 8260
18	10	Solid-Liquid	DCM/Acetone		GC-MS	USEPA 8270

APPENDIX 5 ACRONYMS AND ABBREVIATIONS

ACE	Acetone
AV	Assigned Value
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
EtOAc	Ethyl Acetate
FID	Flame Ionisation Detection
GAG	General Accreditation Guidance (NATA)
GC	Gas Chromatography
GUM	Guide to the expression of Uncertainty in Measurement
HEX	Hexane
HS	Headspace (GC)
IEC	International Electrotechnical Commission
ISO	International Standards Organization
LOR	Limit Of Reporting
Max	Maximum
Md	Median
MeOH	Methanol
Min	Minimum
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
MU	Measurement Uncertainty
N	Number of numeric results
NATA	National Association of Testing Authorities, Australia
NEPM	National Environmental Protection Measure
NMI	National Measurement Institute, Australia
NR	Not Reported
NS	Not Supplied
NT	Not Tested
P&T	Purge and Trap (GC)
PAHs	Polycyclic Aromatic Hydrocarbons
PCV	Performance Coefficient of Variation

PT	Proficiency Testing
RA	Robust Average
RM	Reference Material
SD	Standard Deviation
SI	International System of Units
SLE	Solid-Liquid Extraction
SS	Spiked Samples
SV	Spiked Value, or formulated concentration of a PT sample
TRH	Total Recoverable Hydrocarbons
U	Expanded Uncertainty
US EPA	United States Environmental Protection Agency

END OF REPORT