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Accredited for compliance with ISO/IEC 17043

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SUMMARY

AQA 25-04 Hydrocarbons in Soil commenced in March 2025. Seventeen laboratories enrolled to participate, and sixteen submitted results.

Three test samples were prepared at the NMIA laboratory in Sydney using soil from various sources. 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 Sample S3. The assigned values were the robust averages of participants' results for all scored analytes. The associated uncertainties were evaluated from the robust standard deviations of participants' results.

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

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

- *Compare participants' performances and assess their capabilities to identify and measure hydrocarbon pollutants in soil.*

Laboratories **3, 10, 13, 15** and **16** reported numeric results for all 18 scored analytes.

Laboratories **2, 4** and **9** reported false negatives ('less than' results where the assigned value was higher than their limit of reporting, or participants reporting NR; total of three results).

Two participants reported analytes that were not spiked into the test samples (total of two results).

Of 266 z -scores, 231 (87%) returned $|z| \leq 2.0$, indicating an acceptable performance.

Of 262 E_n -scores, 214 (82%) returned $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratories **10** and **15** returned acceptable z -scores and E_n -scores for all 18 scored analytes.

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

There was no significant trend observed between methodology used and results obtained for TRH, BTEX or PAHs, with excellent agreement generally between participants' results despite a range of methodologies being employed.

- *Develop the practical application of measurement uncertainty.*

Of 293 numeric results, 289 results (99%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 0.9% to 83% 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 well characterised. Surplus of these samples is available for purchase and can be used for quality control and method validation purposes.

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

1 INTRODUCTION

1.1 NMIA Proficiency Testing Program

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

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

- pesticide residues in soil, water, fruit, vegetables and herbs;
- hydrocarbons, phenols and volatile organic compounds in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, biosolid, water, biota and food;
- 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 participants' performances and assess their capabilities to identify and measure hydrocarbon pollutants in soil;
- evaluate participants' methods for the measurement of hydrocarbon pollutants in soil;
- develop the practical application of measurement uncertainty; 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 NMIA proficiency tests is described in the NMIA Study Protocol for Proficiency Testing.² The statistical methods used are described in the NMIA 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}

NMIA is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043:2023 as a provider of proficiency testing schemes.¹ This study is within the scope of NMIA's accreditation.

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitations sent	10/03/2025
Samples sent	7/04/2025
Results due	19/05/2025
Interim Report	21/05/2025
Preliminary Report	22/05/2025

2.2 Participation and Laboratory Code

Seventeen laboratories enrolled in this study, and all participants were assigned a confidential laboratory code number for this study. Of these, sixteen participants submitted results.

2.3 Selection of Analytes and Test Material Preparation

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 Environment Protection (Assessment of Site Contamination) Measure (NEPM) Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.⁵

Two soils were used as the starting materials in this study. Soil from a Victorian farm was used for Sample S1. Soil from a farm in New South Wales was used for Samples S2 and S3.

Sample S1 was prepared by spiking the soil with treated diesel fuel and commercially purchased hydraulic oil, and assessed NEPM fractions >C10-C16, >C16-C34, >C34-C40 and TRH.

Sample S2 was prepared by spiking the soil with unleaded petrol and treated diesel fuel, and assessed volatile hydrocarbons, and benzene, toluene, ethylbenzene, xylenes and Total BTEX.

Sample S3 was prepared by spiking the soil with various polycyclic aromatic hydrocarbons (PAHs). The spiked values for analytes in this sample are presented in Table 1.

Table 1 Spiked Values of Samples

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty (mg/kg)*
S3	Acenaphthene	1.89	0.09
	Anthracene	2.30	0.12
	Benz[<i>a</i>]anthracene	1.36	0.07
	Benzo[<i>a</i>]pyrene	1.68	0.08
	Benzo[<i>b</i>]fluoranthene	3.96	0.20
	Chrysene	1.15	0.06
	Fluoranthene	0.628	0.031
	Fluorene	0.421	0.021
	Phenanthrene	1.36	0.07
	Pyrene	0.736	0.037

*Evaluated expanded uncertainty at approximately 95% confidence using a coverage factor of 2. Stability was not considered and so the expanded uncertainty is related to the concentration at the time of spiking.

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

2.4 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 NMIA 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 where available (Section 6.1). Assigned values for Sample S3 PAHs were within the ranges of 54% to 83% of the spiked values, which is similar to ratios observed in previous NMIA Hydrocarbons in Soil PT studies.

2.5 Sample Storage, Dispatch and Receipt

Prior to dispatch, Samples S1 and S3 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 7 April 2025.

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.

2.6 Instructions to Participants

Participants were informed that Sample S1 was spiked with semi-volatile (>C10-C40) petroleum pollutants, Sample S2 was spiked with volatile petroleum pollutants (petrol and BTEX components), and Sample S3 was spiked with selected PAHs (the list of possible PAHs is presented in Table 2).

Table 2 List of Possible PAHs for Sample S3

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

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.
- Sample S3: PAHs. The concentration range is between 0.05 – 50 mg/kg.
- 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 in units of mg/kg (e.g. 2000 ± 200 mg/kg).
- Report any listed analyte not tested as NT as the result.
- Report the basis of your uncertainty evaluations 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 results by 5 May 2025. Late results may not be included in the study report.

The results due date was extended to 19 May 2025 for all participants due to sample delivery delays and to account for public holidays.

2.7 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 21 May 2025.

A Preliminary Report was emailed to all participants on 22 May 2025. 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 Evaluations

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 Evaluation

Lab. Code	Analyte	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
			Precision	Method Bias	
1	All	Top Down - reproducibility (standard deviation) from PT studies used directly Coverage factor not reported	Standard deviation from PT studies only		ISO/GUM
				CRM	
2	All	Top Down - precision and evaluations of the method and laboratory bias $k = 2$	Control samples - SS Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	NMIA Uncertainty Course
3	All	Top Down - precision and evaluations of the method and laboratory bias $k = 2$	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
4	All	Top Down - reproducibility (standard deviation) from PT studies used directly Coverage factor not reported	Duplicate analysis	CRM Instrument calibration	
5	All	Top Down - precision and evaluations of the method and laboratory bias $k = 2$	Control samples - SS Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
6	TRH/ PAHs	Top Down - precision and evaluations of the method and laboratory bias $k = 2$	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
7	All	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	

Lab. Code	Analyte	Approach to Evaluating MU	Information Sources for MU Evaluation*		Guide Document for Evaluating MU
			Precision	Method Bias	
8	All	Standard uncertainty based on historical data k = 2	Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	Eurachem/CITAC Guide
9	All	Coverage factor not reported			
10	All	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control samples - SS		Eurachem/CITAC Guide
11	All	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control samples - SS	Recoveries of SS	ISO/GUM
13	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Instrument calibration	CRM	ISO/GUM
14	All	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control samples - SS Duplicate analysis	Instrument calibration	
15	All	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control samples - SS	Recoveries of SS	Eurachem/CITAC Guide
16	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram) k = 2	Control samples	Recoveries of SS	ISO/GUM
17	All	Measurement uncertainty based upon in-house historical data. Coverage factor not reported	Control samples - CRM		

*CRM = Certified Reference Material; SS = Spiked Samples

3.3 Participants' Comments

Participants were invited to comment on this study or future studies. Such feedback may be useful in improving future studies. Participants' comments received 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
17	S3	Benzo[b]fluoranthene quoted as Benzo(b,k)fluoranthene

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 25 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), as well as other estimates of analyte mass fraction. Bar charts of results and performance scores are presented in Figures 2 to 21. An example chart with interpretation guide is shown in Figure 1.

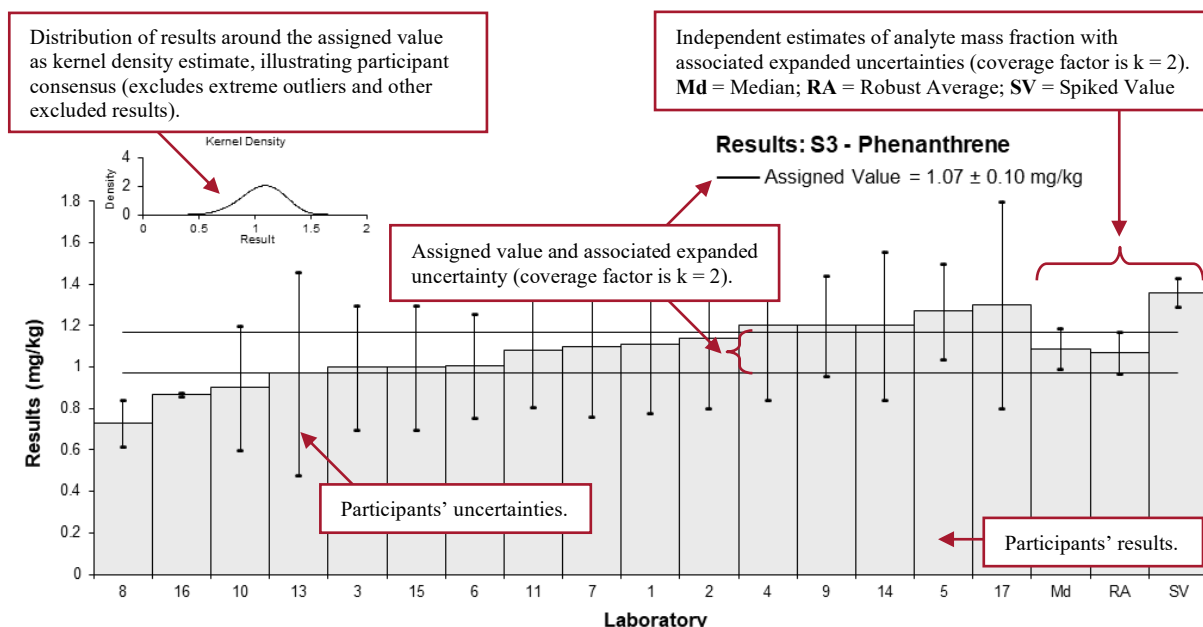


Figure 1 Guide to Presentation of Results

4.2 Outliers, Extreme Outliers and Other Excluded Results

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

The Sample S2 BTEX results for Laboratories 4, 8, 16 and 17 were consistently lower than the consensus value by approximately the same factor; this is an indication of laboratory or method bias. For Sample S3, Laboratory 17 reported that their result for Sample S3 benzo[*b*]fluoranthene was quoted as benzo[*b,k*]fluoranthene. To avoid unfair scoring, these results were also excluded from the calculation of all summary statistics, including the robust average calculations, as these would otherwise bias the assigned values.

4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property or characteristic 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 evaluated 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.

$$\sigma = X \times PCV \quad \text{Equation 1}$$

4.7 z-Score

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

$$z = \frac{(\chi - X)}{\sigma} \quad \text{Equation 2}$$

where:

z is z-score

χ is a participant's result

X is the assigned value

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

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

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.

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

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:

- $|E_n| < 1.0$ is acceptable; and
- $|E_n| \geq 1.0$ is unacceptable.

4.9 Traceability and Measurement Uncertainty

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

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

5 TABLES AND FIGURES

Table 5

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	759.19	227.76	-1.06	-0.60
2	933	289	0.22	0.10
3	960	300	0.42	0.18
4	NR	NR		
5	NR	NR		
6	998.5875	209.7034	0.71	0.43
7	960	210	0.42	0.26
8	NR	NR		
9	850	255	-0.39	-0.20
10	830	300	-0.54	-0.24
11	773	232	-0.96	-0.53
13	811	146	-0.68	-0.56
14	980	300	0.57	0.25
15	880	300	-0.17	-0.07
16	1089	45	1.37	2.17
17	940	273	0.27	0.13

Statistics

Assigned Value	903	73
Robust Average	903	73
Median	933	67
Mean	905	
N	13	
Max	1089	
Min	759.19	
Robust SD	110	
Robust CV	12%	

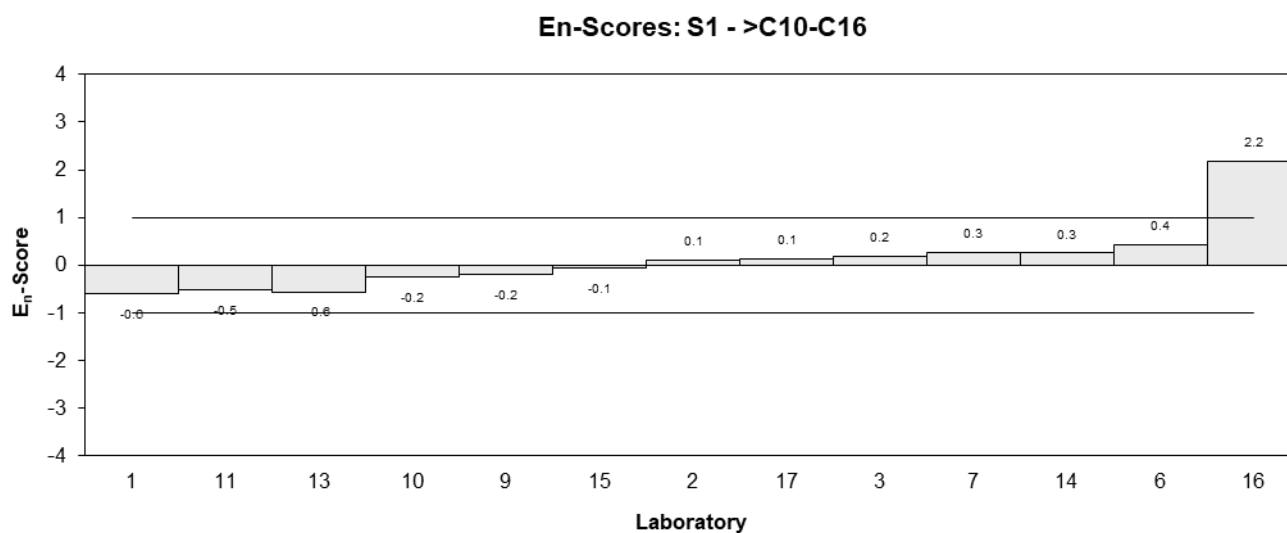
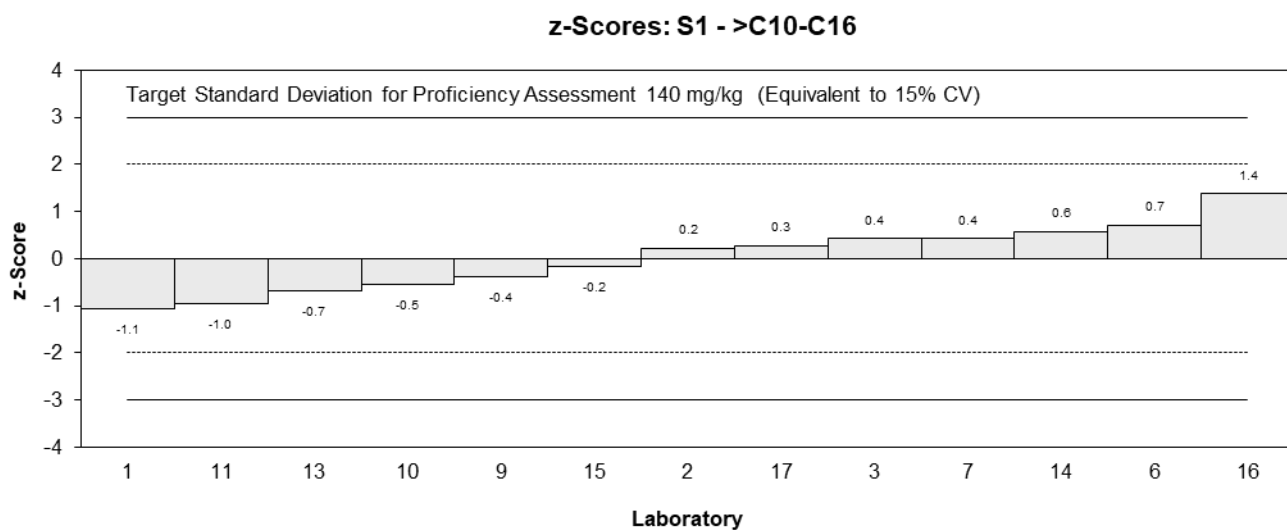
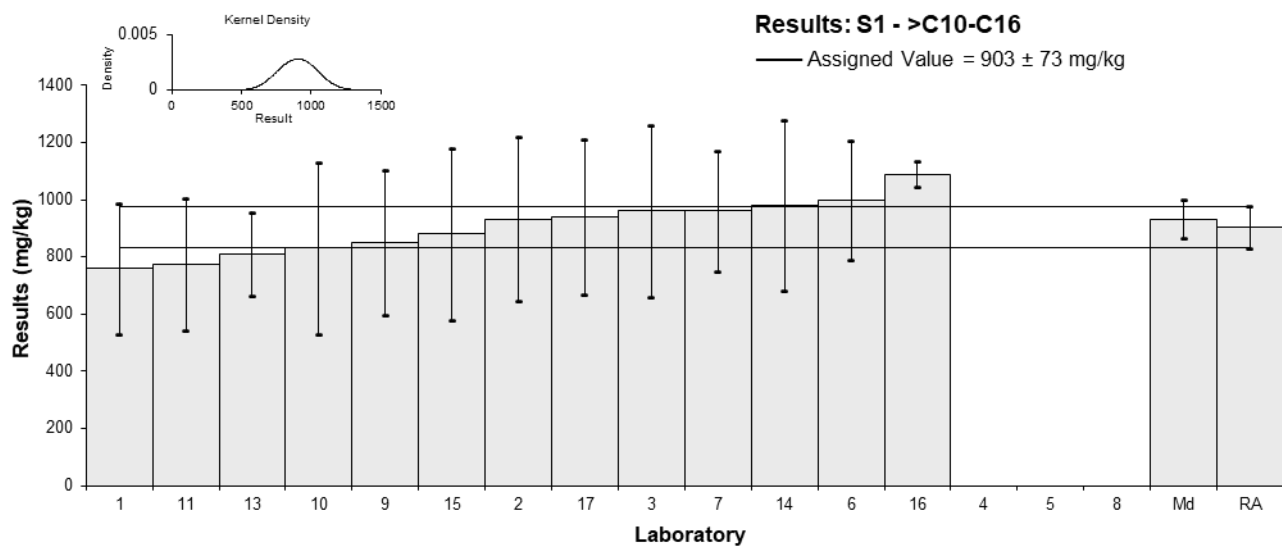


Figure 2

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	1722.70	516.81	0.99	0.41
2	1523	472	0.10	0.05
3	1700	500	0.89	0.38
4	NR	NR		
5	NR	NR		
6	1630.3125	440.1844	0.58	0.28
7	1500	380	0.00	0.00
8	NR	NR		
9	1180	354	-1.42	-0.82
10	1400	400	-0.44	-0.23
11	1391	417	-0.48	-0.24
13	1144	194	-1.58	-1.42
14	1800	540	1.33	0.53
15	1600	500	0.44	0.19
16	1597	85	0.43	0.54
17	1350	459	-0.67	-0.31

Statistics

Assigned Value	1500	160
Robust Average	1500	160
Median	1520	140
Mean	1500	
N	13	
Max	1800	
Min	1144	
Robust SD	230	
Robust CV	15%	

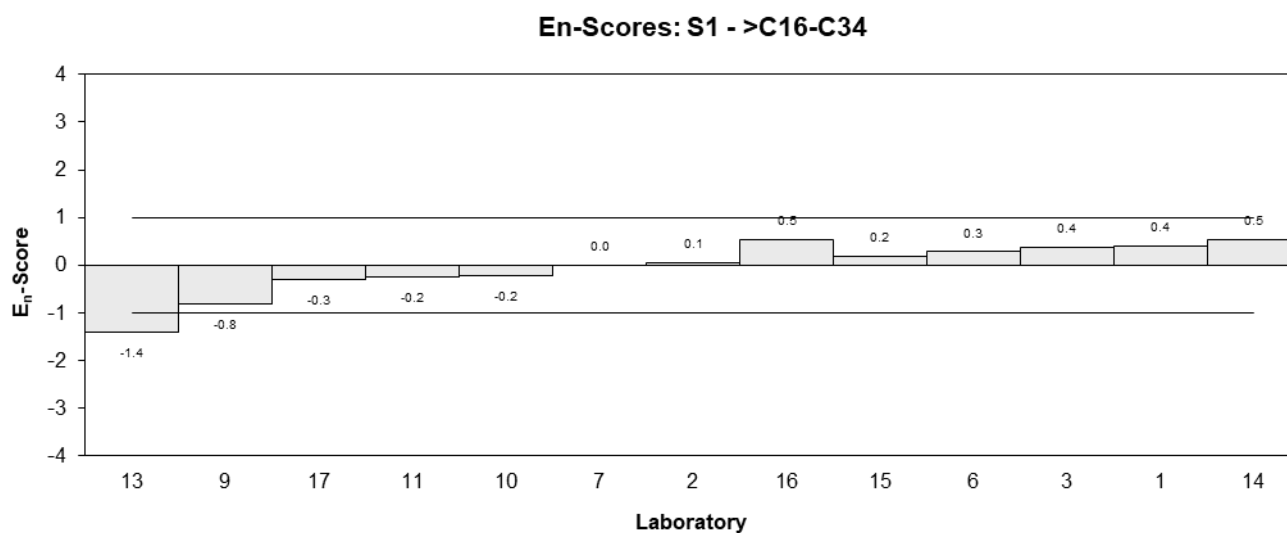
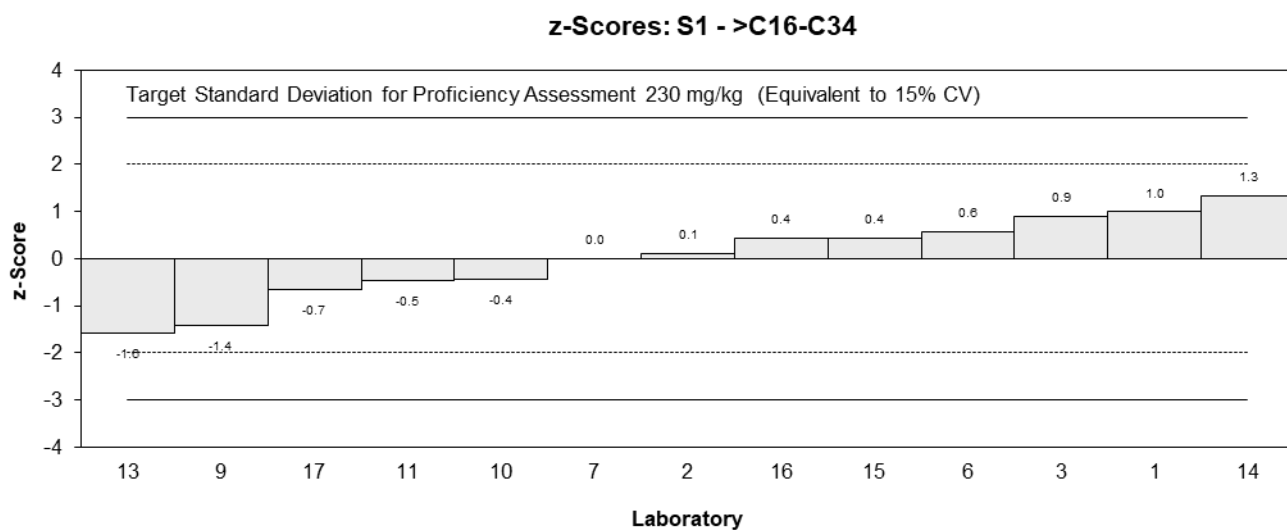
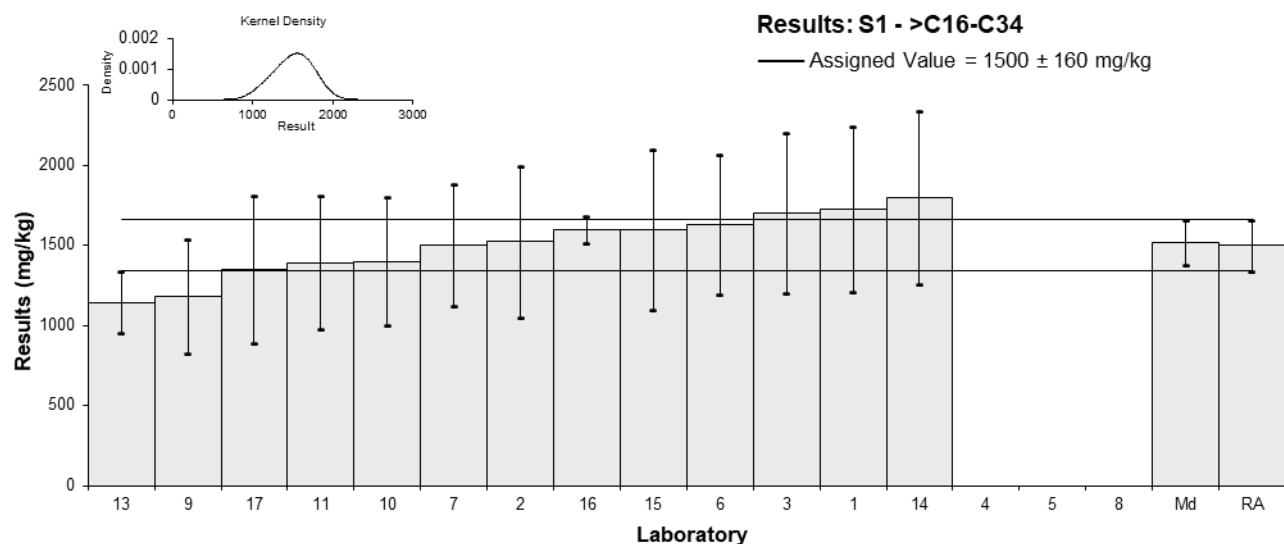


Figure 3

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	186.54	55.96	0.09	0.04
2	162	50	-0.80	-0.38
3	200	80	0.58	0.19
4	NR	NR		
5	NR	NR		
6	133.7250	33.4313	-1.82	-1.12
7	160	40	-0.87	-0.48
8	NR	NR		
9	<100	NR		
10	200	80	0.58	0.19
11	193	58	0.33	0.14
13	135	22	-1.78	-1.32
14	250	75	2.39	0.82
15	200	60	0.58	0.24
16	237	23	1.92	1.40
17	150	86	-1.23	-0.37

Statistics

Assigned Value	184	30
Robust Average	184	30
Median	190	31
Mean	184	
N	12	
Max	250	
Min	133.725	
Robust SD	41	
Robust CV	23%	

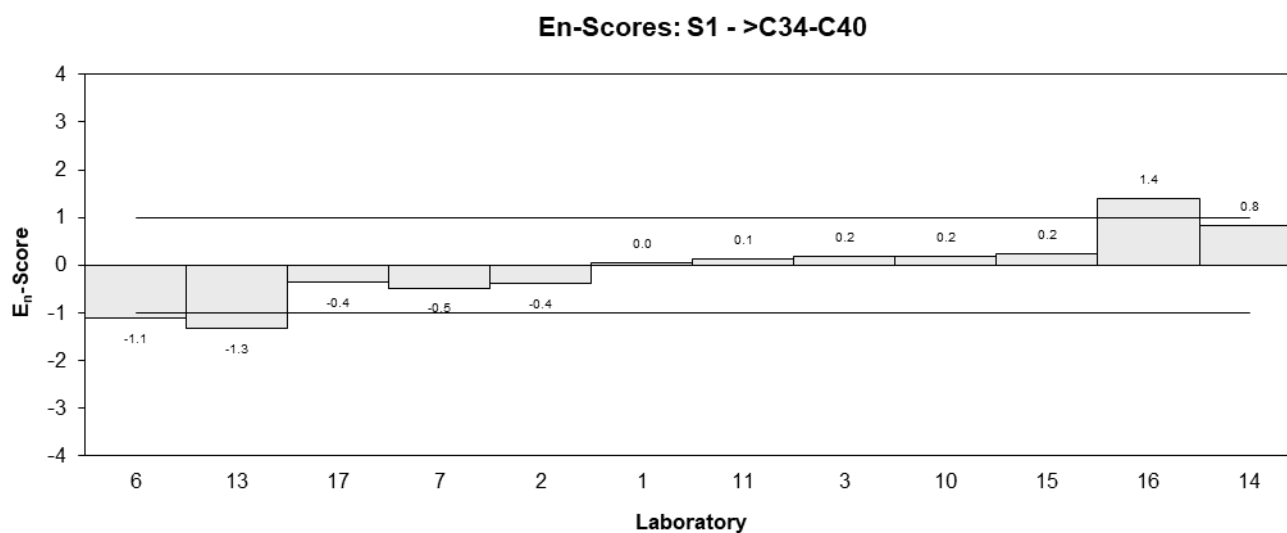
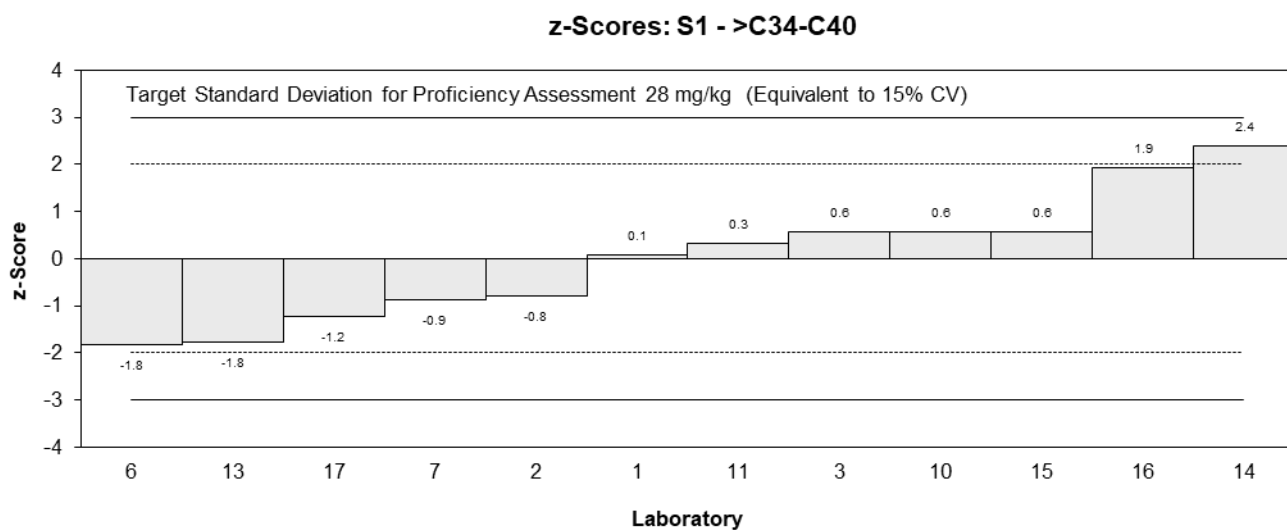
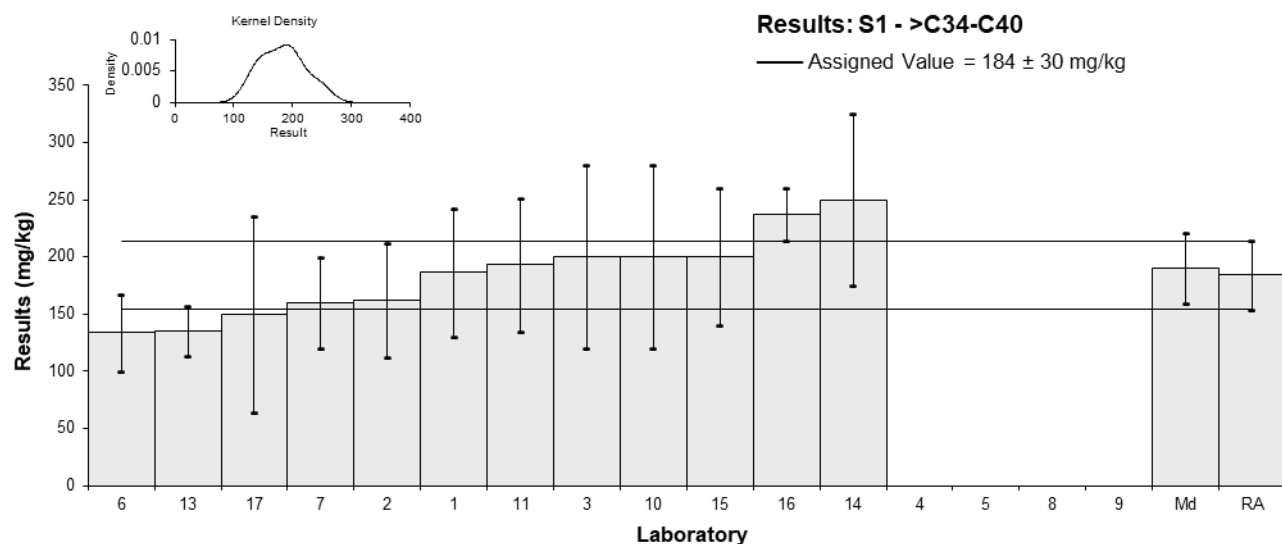


Figure 4

Table 8 Non-NEPM Hydrocarbon Ranges Reported by Participants for Sample S1⁵

Lab. Code	Range	Result (mg/kg)	Uncertainty (mg/kg)
5	C10-C14	530	159
	C15-C36	2600	730
8	C7-C9	<20	6.7
	C10-C14	310	67
	C15-C36	2380	360

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Table 9

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2668.43	800.53	0.00	0.00
2	2618	811	-0.13	-0.06
3	2900	900	0.57	0.25
4	2884.5	865.35	0.54	0.24
5	3200	990	1.32	0.52
6	2762.6250	690.6563	0.23	0.13
7	2600	780	-0.17	-0.09
8	2700	370	0.07	0.07
9	2030	NR	-1.60	-3.05
10	2500	800	-0.42	-0.21
11	2357	707	-0.78	-0.42
13	2090	NR	-1.45	-2.76
14	3100	910	1.07	0.46
15	2700	800	0.07	0.04
16	2923	NR	0.63	1.20
17	2440	586	-0.57	-0.37

Statistics

Assigned Value	2670	210
Robust Average	2670	210
Median	2680	190
Mean	2650	
N	16	
Max	3200	
Min	2030	
Robust SD	330	
Robust CV	13%	

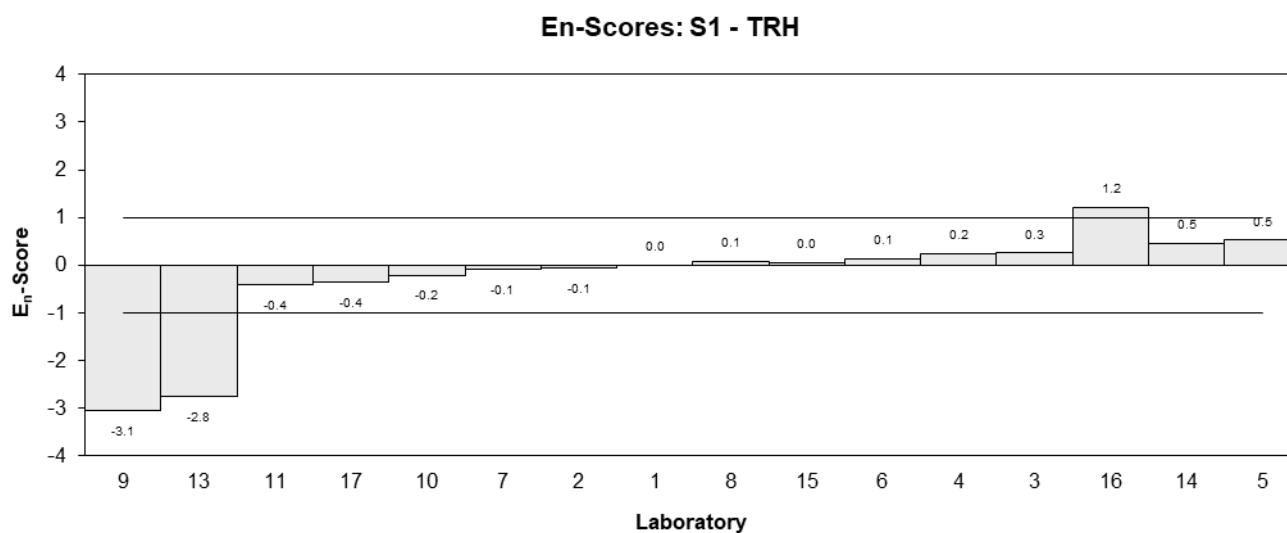
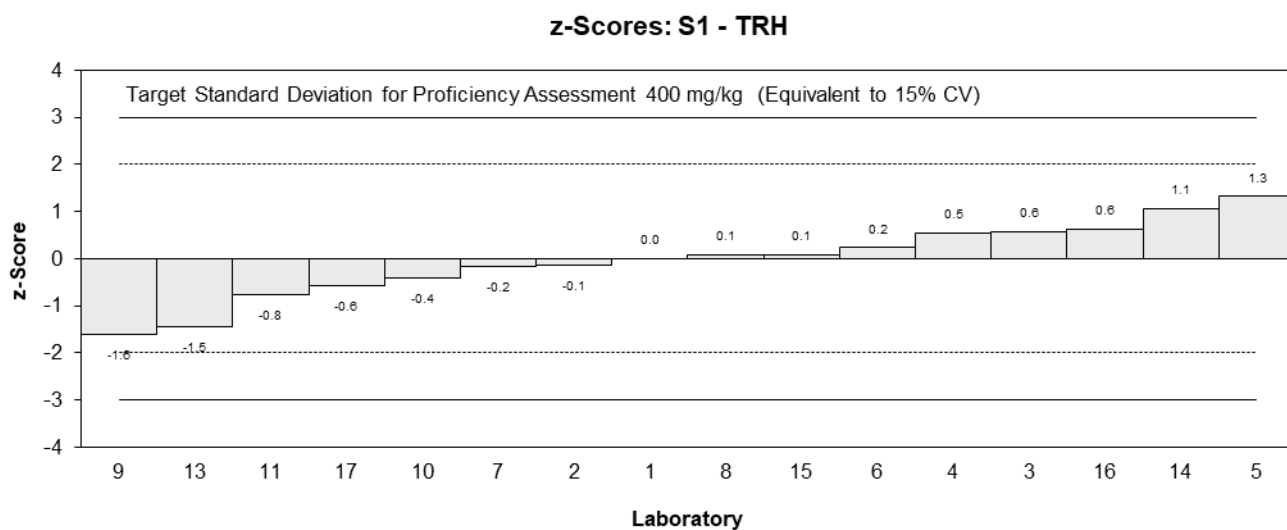
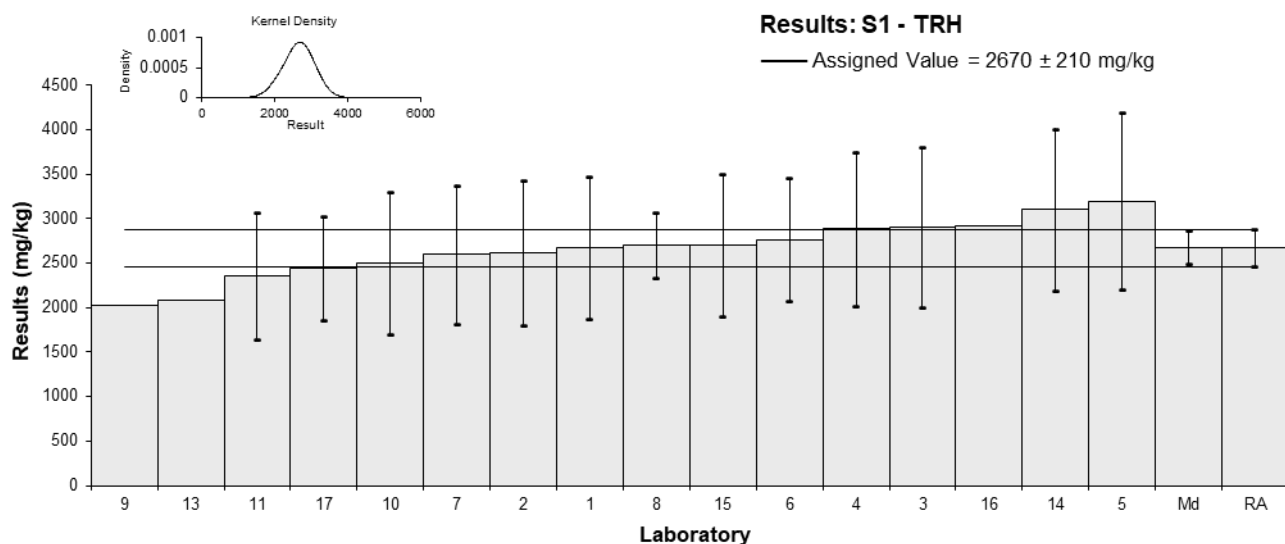


Figure 5

Table 10

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	4582.50	1374.75
2	4599	1380
3	7200	2500
4	NR	NR
5	NT	NT
6	NR	NR
7	4900	1500
8	NT	NT
9	6990	2097
10	4900	1000
11	4520	1250
13	2368	149
14	5000	1500
15	4700	1000
16**	347	6.5
17	5585	2402

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Robust Average	5050	790
Median	4900	350
Mean	5030	
N	11	
Max	7200	
Min	2368	
Robust SD	1100	
Robust CV	21%	

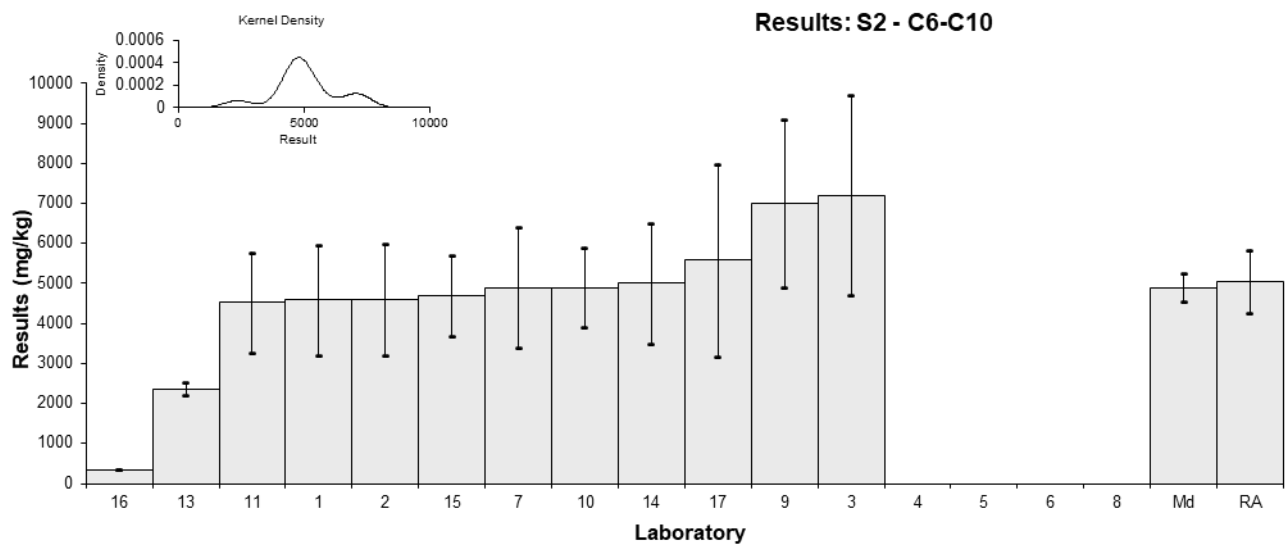


Figure 6

Table 11

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	35.90	10.77
2	31	9.3
3	37	10
4**	4.7	1.395
5	8.8	2.2
6	NR	NR
7	41	12
8**	9.45	0.87
9	17	5.1
10	37	10
11	36.7	10.5
13	14	3.3
14	7.5	2.3
15	35	10
16**	25	6.6
17**	3.8	1

** Excluded Result, see Section 4.2

Statistics

Assigned Value	Not Set	
Robust Average	27	11
Median	35.0	4.5
Mean	27.4	
N	11	
Max	41	
Min	7.5	
Robust SD	14	
Robust CV	53%	

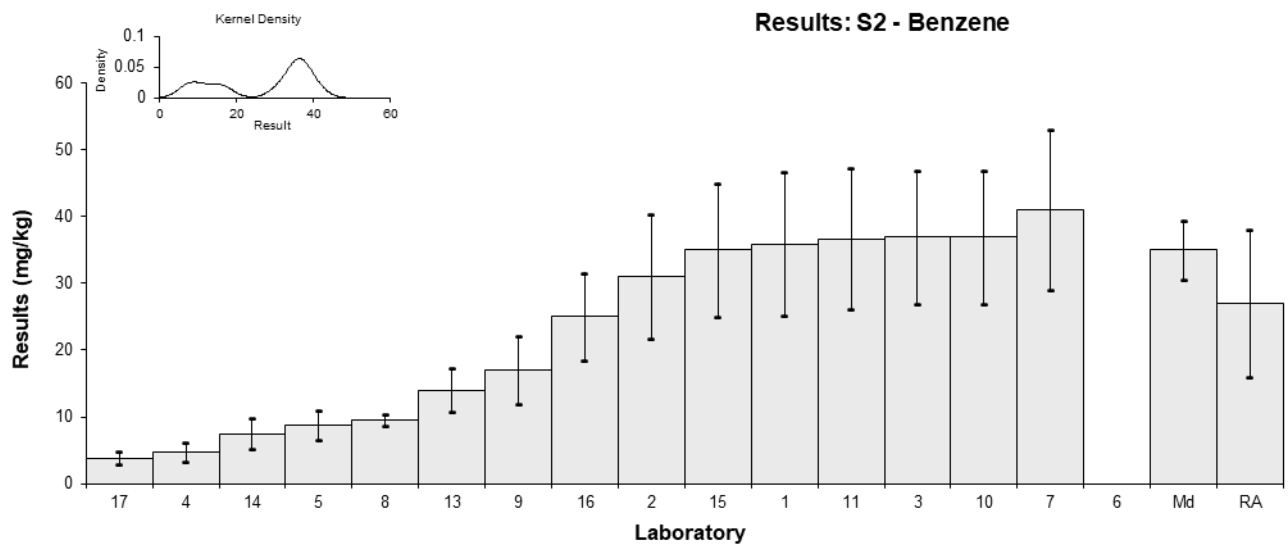


Figure 7

Table 12

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	457.30	137.19	-0.56	-0.27
2	437	131	-0.83	-0.42
3	670	200	2.28	0.81
4**	190	57	-4.13	-3.51
5	424	93	-1.00	-0.65
6	NR	NR		
7	530	159	0.41	0.18
8**	333	25	-2.22	-2.32
9*	810	243	4.15	1.23
10	600	100	1.35	0.84
11	519	146	0.27	0.12
13	420	168	-1.06	-0.44
14	440	130	-0.79	-0.40
15	540	200	0.55	0.19
16**	327	5.5	-2.30	-2.56
17**	229	55	-3.61	-3.11

* Outlier, ** Excluded Result, see Section 4.2

Statistics

Assigned Value	499	67
Robust Average	520	82
Median	519	91
Mean	532	
N	11	
Max	810	
Min	420	
Robust SD	110	
Robust CV	21%	

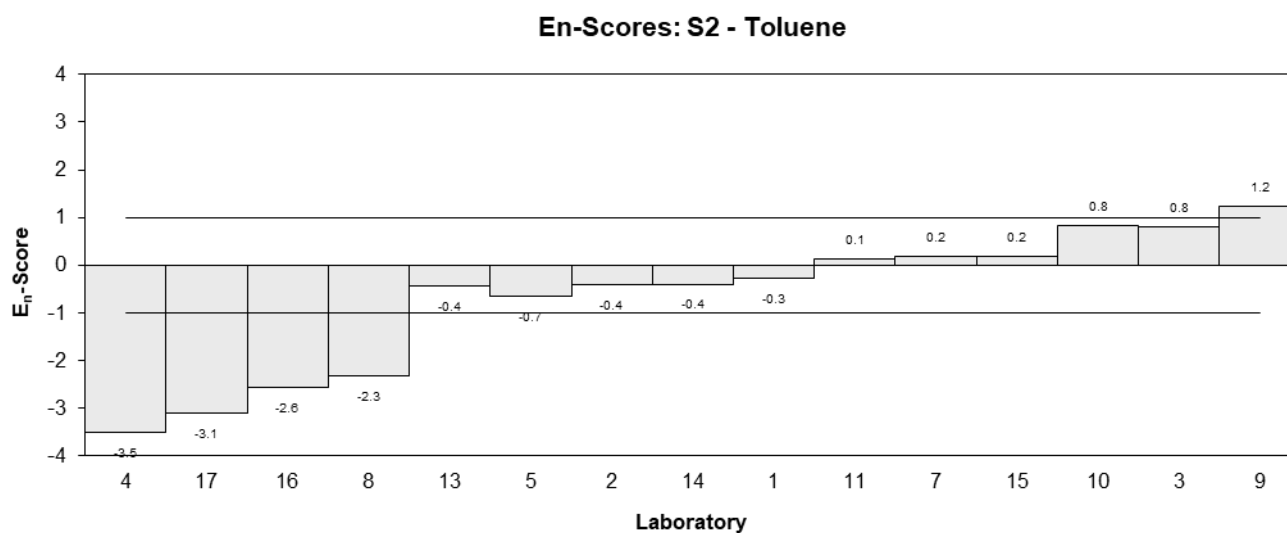
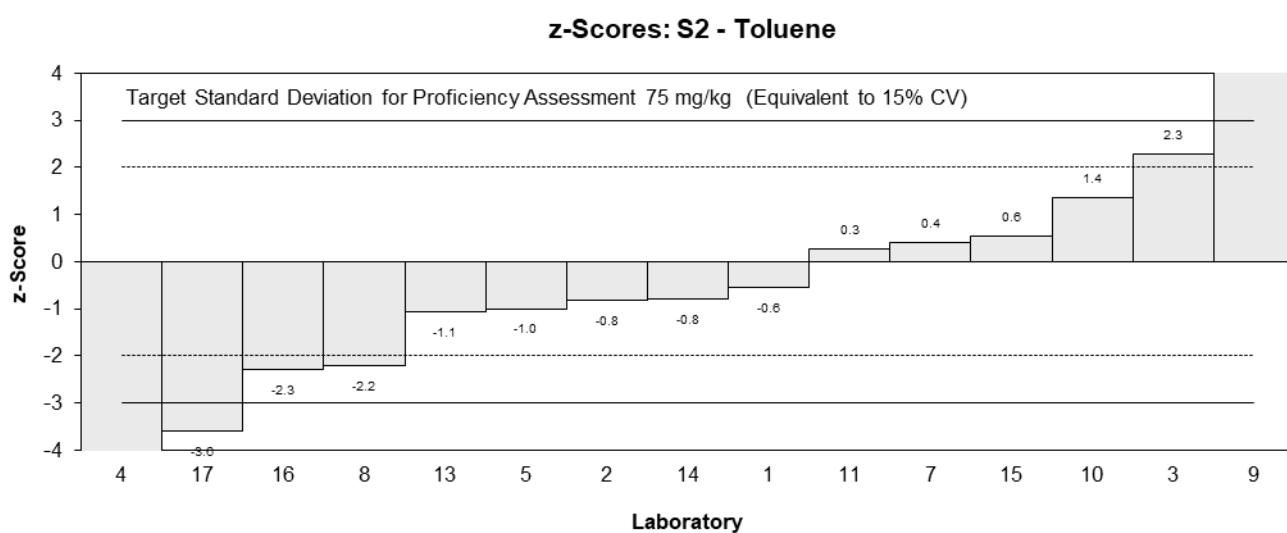
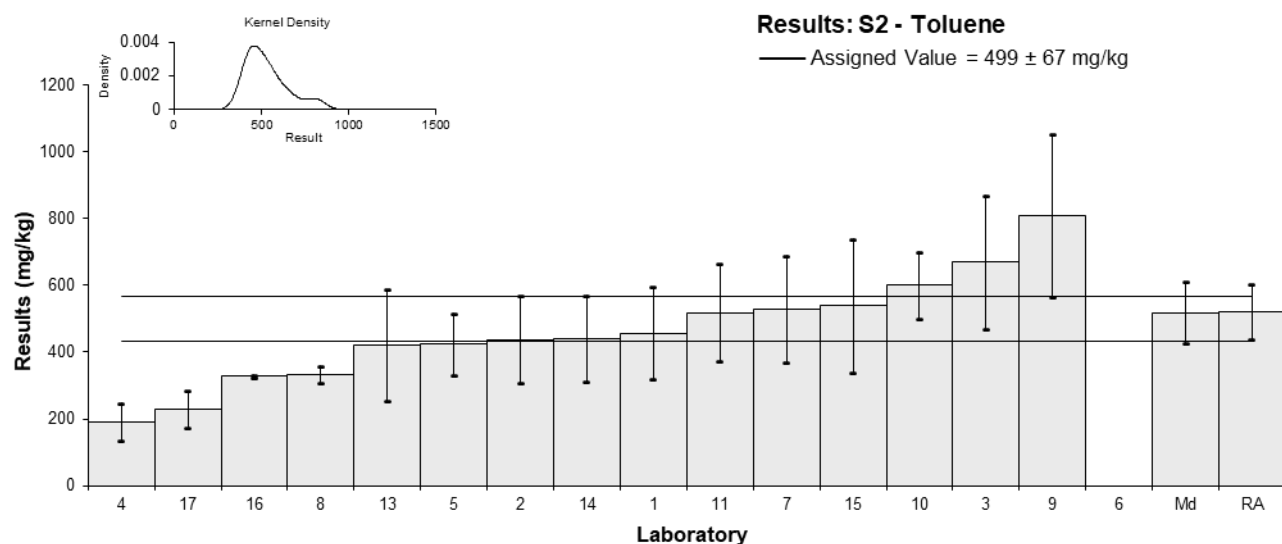


Figure 8

Table 13

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	139.60	41.88	-0.16	-0.08
2	133	40	-0.47	-0.23
3	200	60	2.66	0.91
4**	79	23.7	-2.98	-2.19
5	156	39	0.61	0.31
6	NR	NR		
7	140	42	-0.14	-0.07
8**	95.3	7.3	-2.22	-2.58
9	190	57	2.19	0.79
10	140	30	-0.14	-0.09
11	132	38	-0.51	-0.26
13	116	61	-1.26	-0.43
14	140	42	-0.14	-0.07
15	120	40	-1.07	-0.53
16**	81.5	5	-2.87	-3.47
17**	91	23	-2.42	-1.82

** Excluded Result, see Section 4.2

Statistics

Assigned Value	143	17
Robust Average	143	17
Median	140	9
Mean	146	
N	11	
Max	200	
Min	116	
Robust SD	22	
Robust CV	16%	

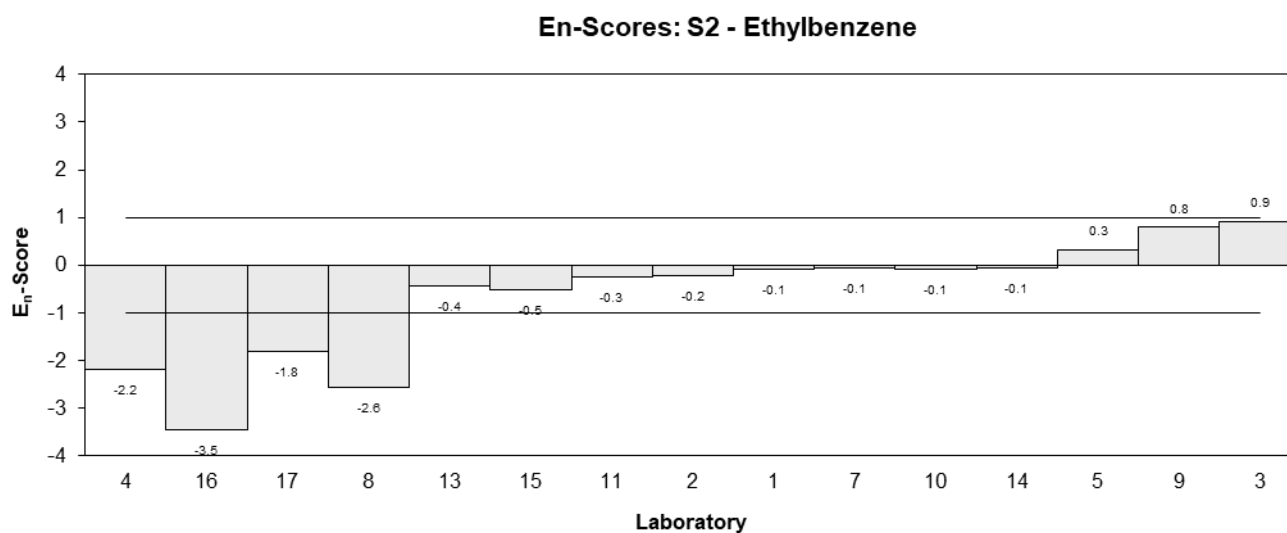
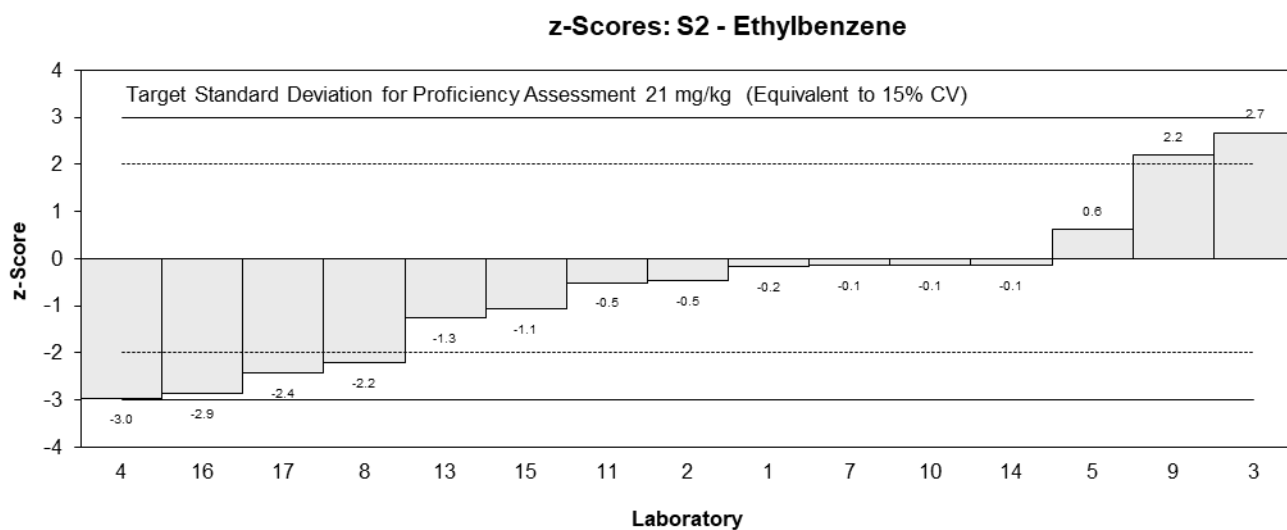
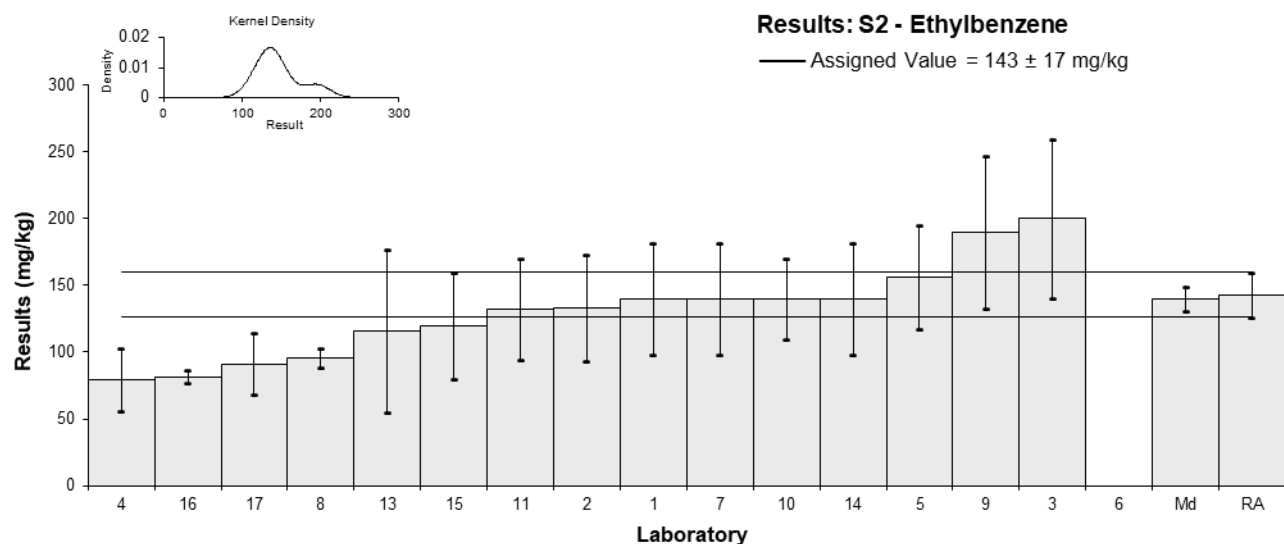


Figure 9

Table 14

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	679.20	203.76	0.10	0.05
2	609	183	-0.60	-0.30
3	820	250	1.50	0.57
4**	336	100.8	-3.32	-2.58
5	734	154	0.65	0.37
6	NR	NR		
7	620	190	-0.49	-0.24
8**	427	38	-2.41	-2.70
9	900	270	2.30	0.82
10	650	200	-0.19	-0.09
11	647	192	-0.22	-0.11
13	542	91	-1.27	-1.04
14	680	200	0.11	0.05
15	550	200	-1.19	-0.55
16**	326	17.5	-3.42	-4.14
17**	311	72	-3.57	-3.30

** Excluded Result, see Section 4.2

Statistics

Assigned Value	669	81
Robust Average	669	81
Median	650	46
Mean	676	
N	11	
Max	900	
Min	542	
Robust SD	110	
Robust CV	16%	

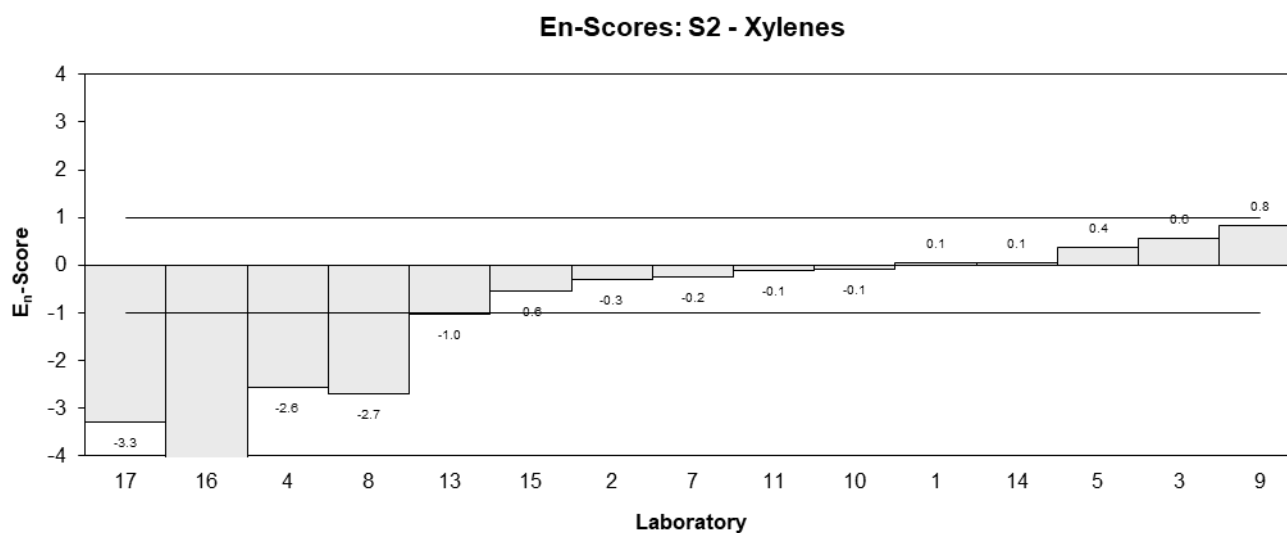
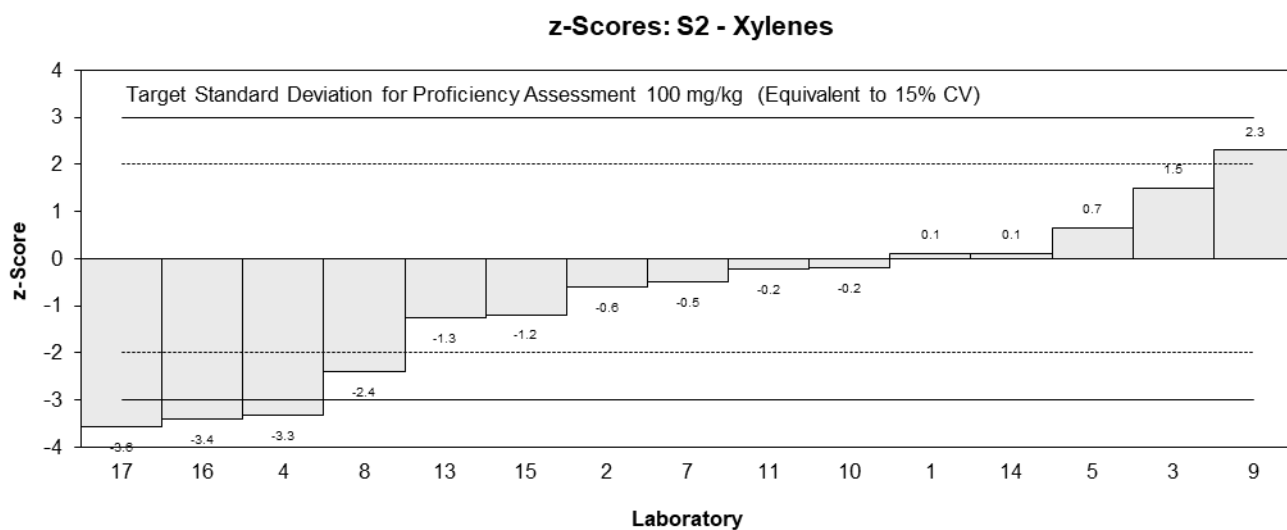
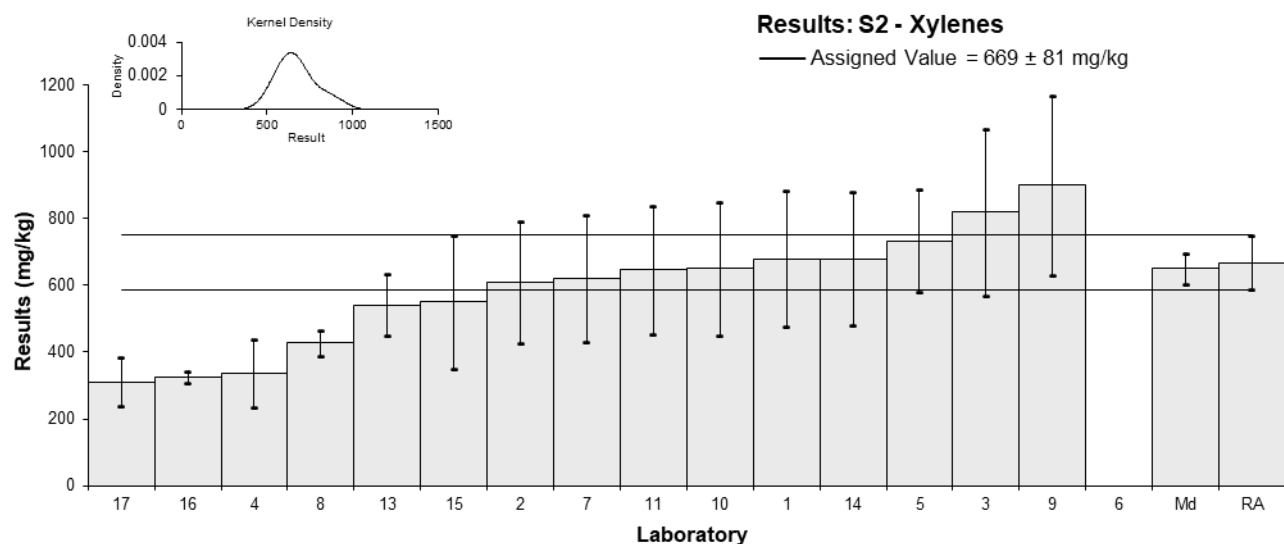


Figure 10

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	1312.70	393.81	-0.33	-0.16
2	1210	363	-0.82	-0.42
3	1700	500	1.55	0.61
4**	609.7	182.895	-3.72	-3.08
5	1320	356	-0.29	-0.15
6	NR	NR		
7	1500	450	0.58	0.25
8**	865	71	-2.49	-2.80
9	1920	576	2.61	0.90
10	1500	300	0.58	0.35
11	1330	386	-0.24	-0.12
13	1092	NR	-1.39	-1.69
14	1300	390	-0.39	-0.19
15	1200	300	-0.87	-0.52
16**	759.5	45	-3.00	-3.53
17**	635	150	-3.60	-3.29

** Excluded Result, see Section 4.2

Statistics

Assigned Value	1380	170
Robust Average	1380	170
Median	1320	130
Mean	1400	
N	11	
Max	1920	
Min	1092	
Robust SD	230	
Robust CV	17%	

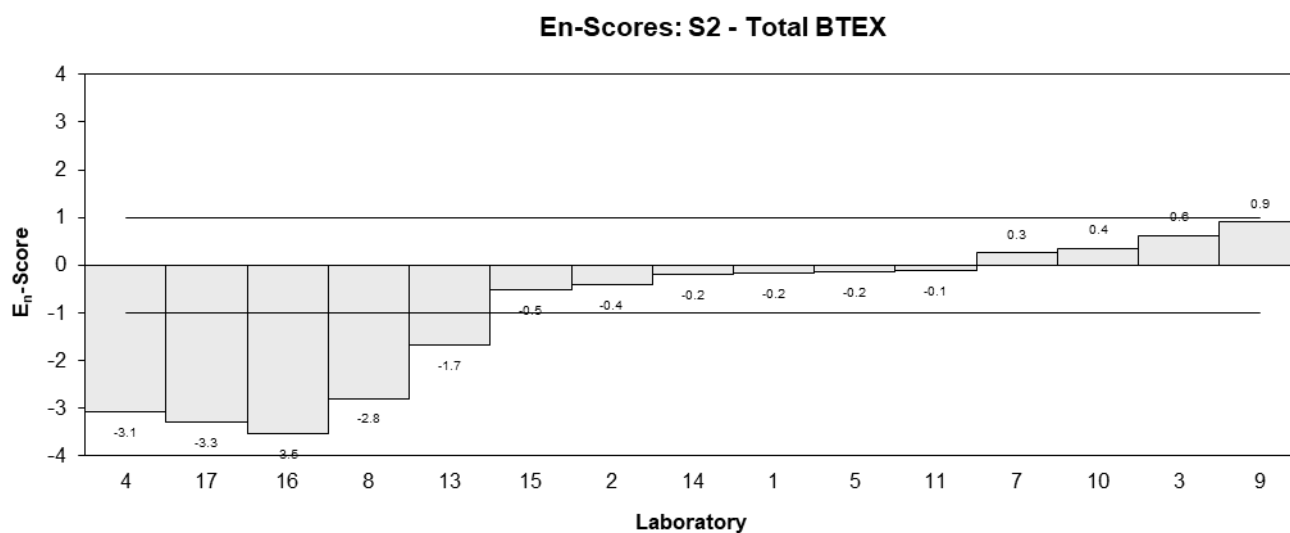
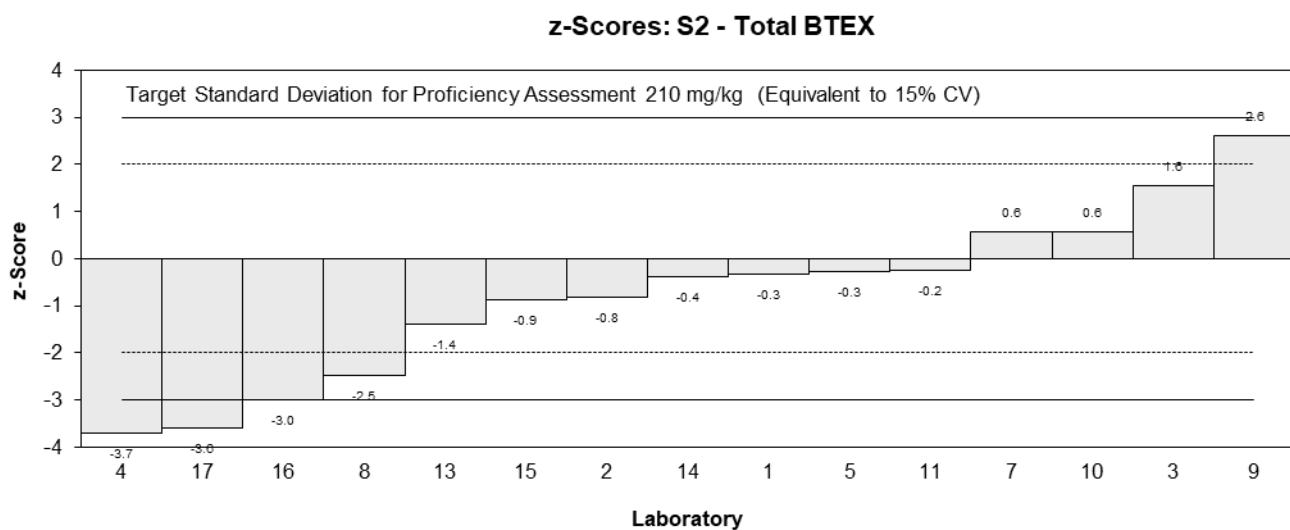
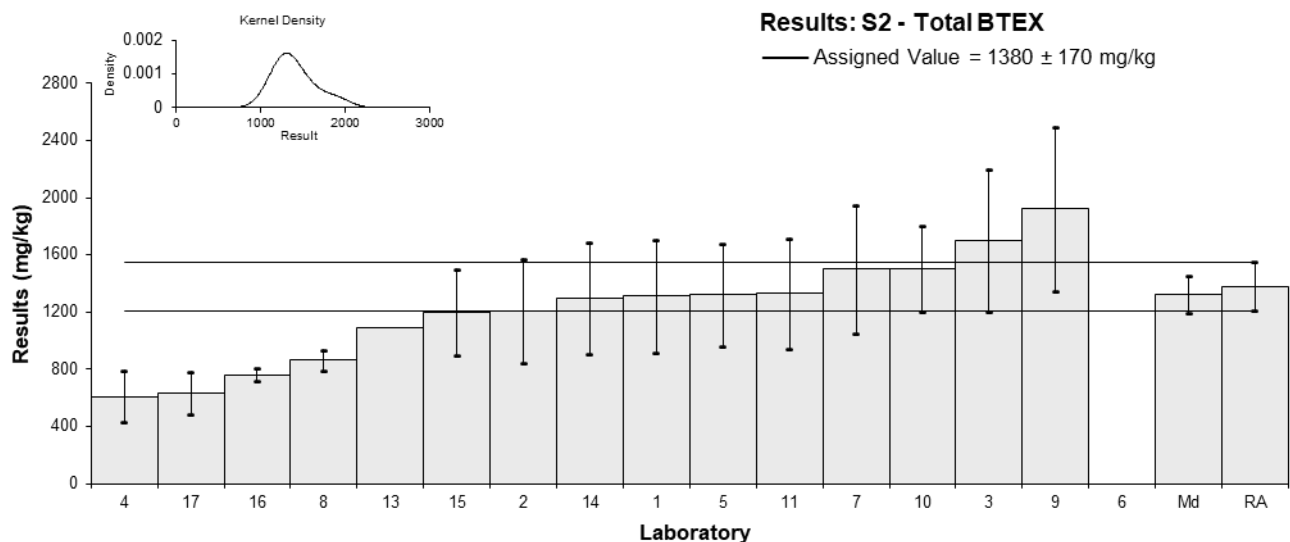


Figure 11

Table 16

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.45	0.44	0.24	0.11
2	1.48	0.44	0.38	0.18
3	1.3	0.5	-0.48	-0.19
4	1.45	0.435	0.24	0.11
5	1.62	0.31	1.05	0.66
6	1.3738	0.3434	-0.12	-0.07
7	1.4	0.42	0.00	0.00
8	1.09	0.32	-1.48	-0.91
9	1.3	0.38	-0.48	-0.25
10	1.2	0.5	-0.95	-0.39
11	1.46	0.37	0.29	0.15
13	1.38	0.69	-0.10	-0.03
14	1.6	0.48	0.95	0.40
15	1.5	0.5	0.48	0.19
16	1.13	0.01	-1.29	-2.24
17	1.7	0.5	1.43	0.58

Statistics

Assigned Value	1.40	0.12
Spike Value	1.89	0.09
Robust Average	1.40	0.12
Median	1.43	0.09
Mean	1.40	
N	16	
Max	1.7	
Min	1.09	
Robust SD	0.19	
Robust CV	13%	

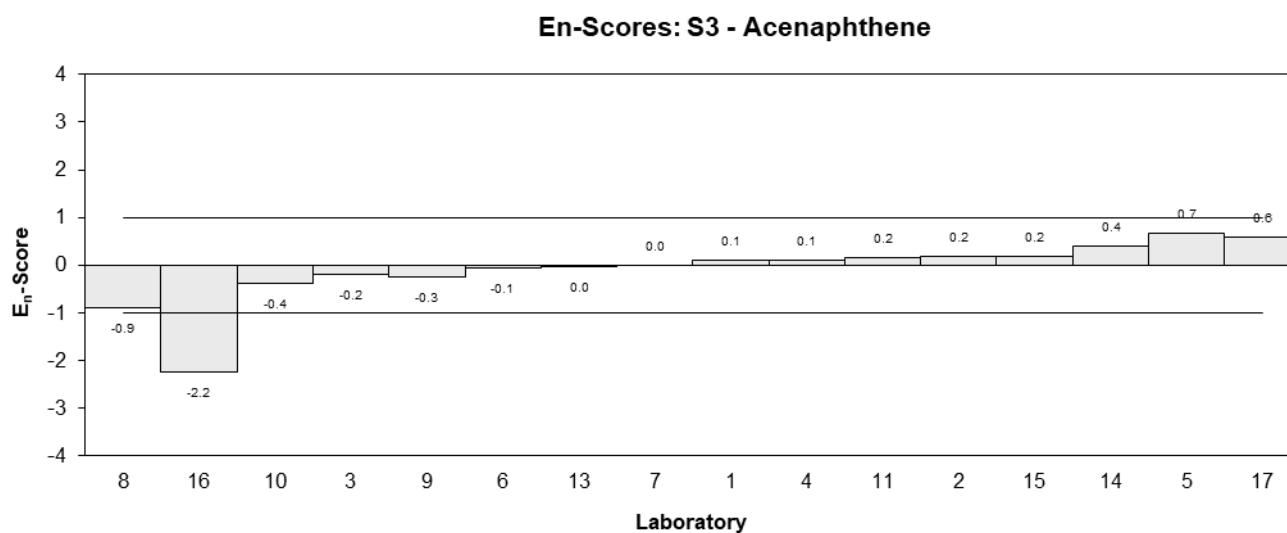
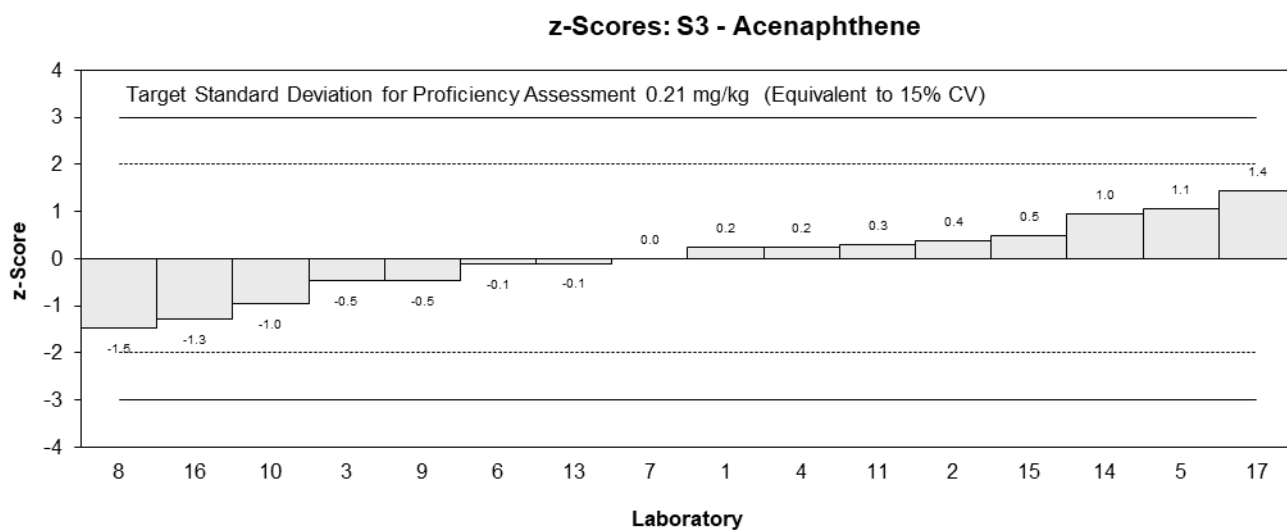
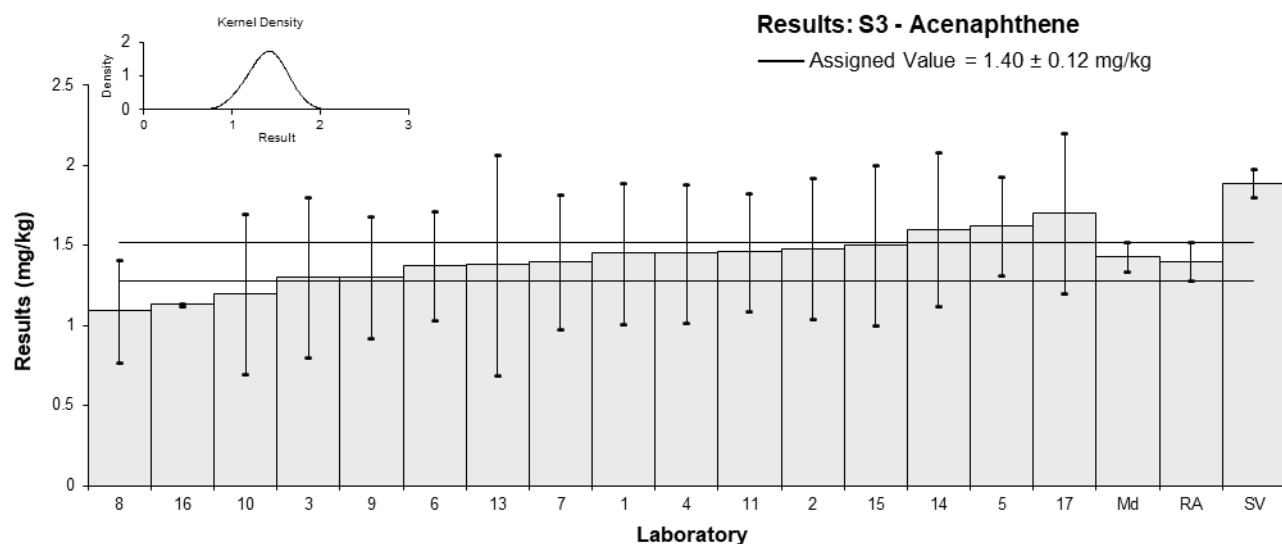


Figure 12

Table 17

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.22	0.37	-0.16	-0.08
2	1.01	0.3	-1.28	-0.72
3	1.1	0.4	-0.80	-0.35
4	1.5	0.45	1.33	0.53
5	1.48	0.41	1.23	0.53
6	1.1725	0.2931	-0.41	-0.24
7	1.4	0.45	0.80	0.32
8	0.85	0.26	-2.13	-1.33
9	1.3	0.27	0.27	0.16
10	1.1	0.3	-0.80	-0.45
11	1.28	0.32	0.16	0.08
13	1.18	0.59	-0.37	-0.11
14	1.5	0.45	1.33	0.53
15	1.3	0.4	0.27	0.12
16	0.97	0.019	-1.49	-1.85
17	1.6	0.5	1.87	0.67

Statistics

Assigned Value	1.25	0.15
Spike Value	2.30	0.12
Robust Average	1.25	0.15
Median	1.25	0.14
Mean	1.25	
N	16	
Max	1.6	
Min	0.85	
Robust SD	0.24	
Robust CV	19%	

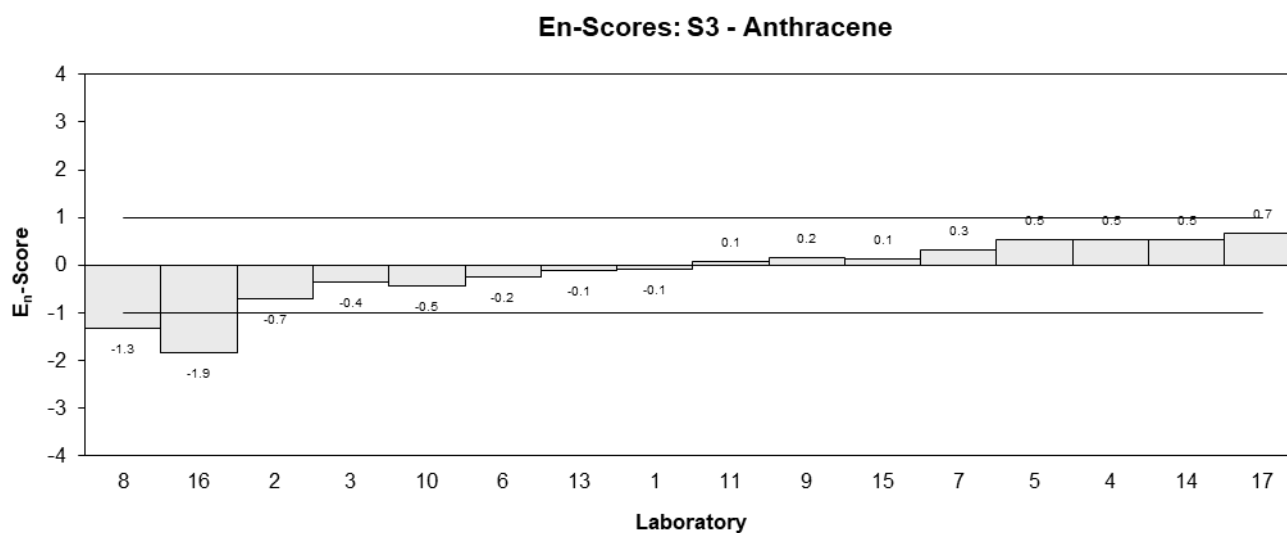
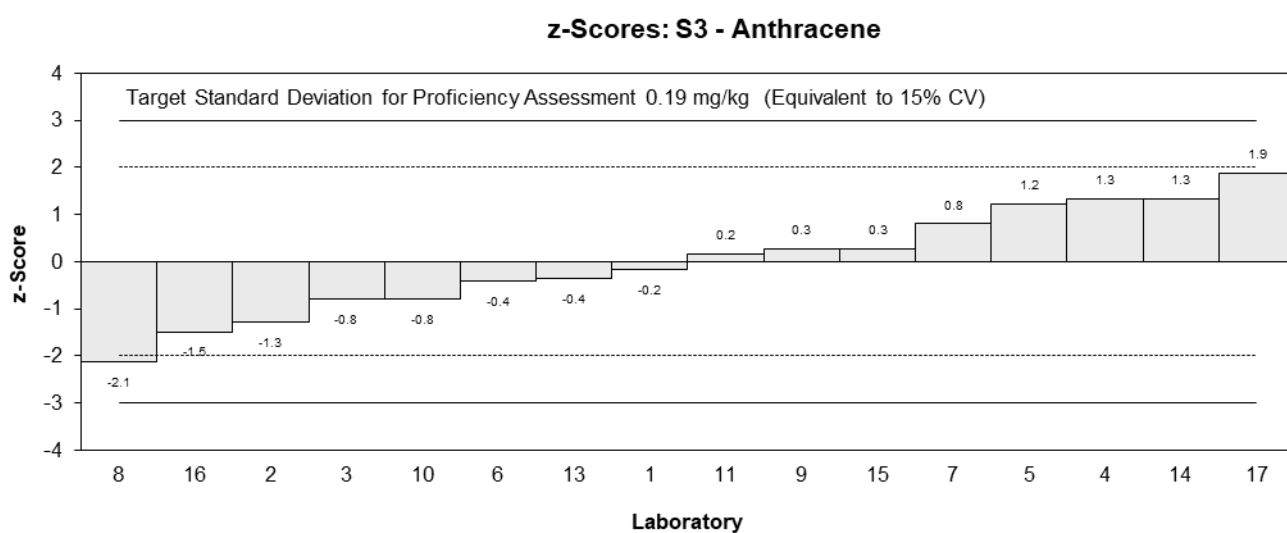
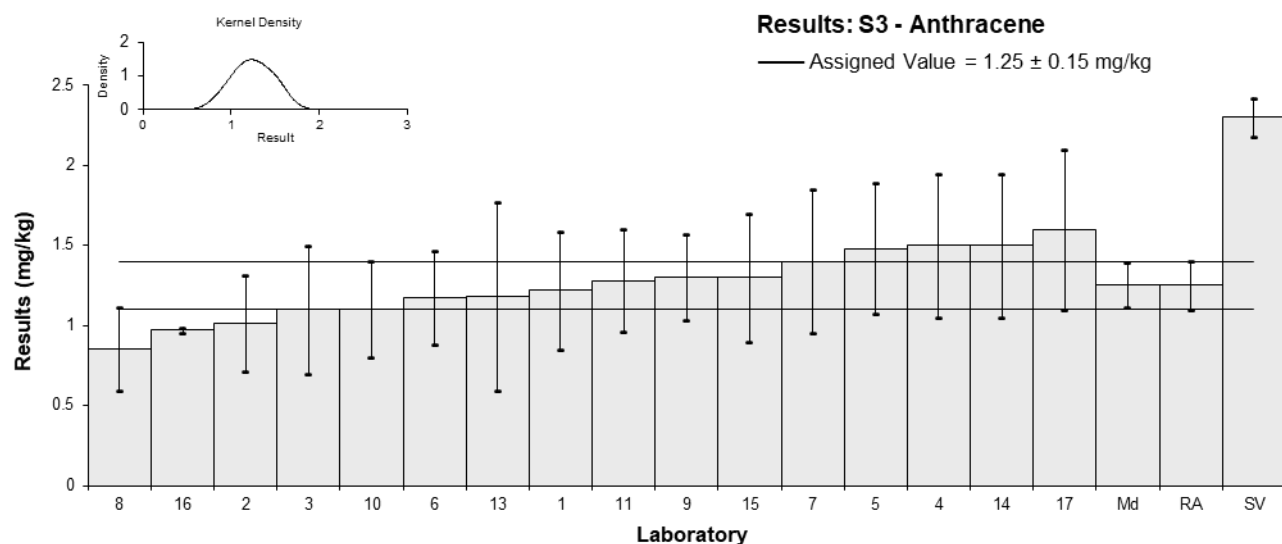


Figure 13

Table 18

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.95	0.29	-0.40	-0.20
2	1.05	0.31	0.26	0.13
3	0.9	0.3	-0.73	-0.36
4	1	0.3	-0.07	-0.03
5*	2.77	0.64	11.62	2.73
6	1.0313	0.2578	0.14	0.08
7	0.92	0.3	-0.59	-0.29
8	0.7	0.19	-2.05	-1.53
9	1.1	0.23	0.59	0.37
10	0.9	0.3	-0.73	-0.36
11	1.00	0.25	-0.07	-0.04
13	1.07	0.54	0.40	0.11
14	1.2	0.36	1.25	0.52
15	1.0	0.3	-0.07	-0.03
16	1.02	0.022	0.07	0.14
17	1.3	0.5	1.91	0.57

* Outlier, see Section 4.2

Statistics

Assigned Value	1.01	0.07
Spike Value	1.36	0.07
Robust Average	1.03	0.08
Median	1.01	0.07
Mean	1.12	
N	16	
Max	2.77	
Min	0.7	
Robust SD	0.13	
Robust CV	13%	

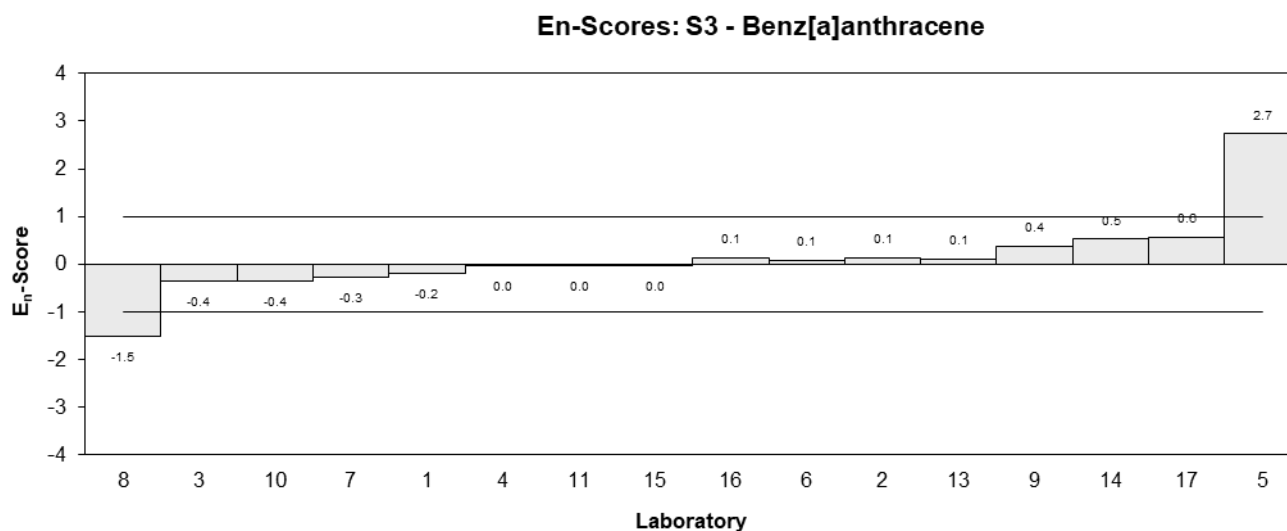
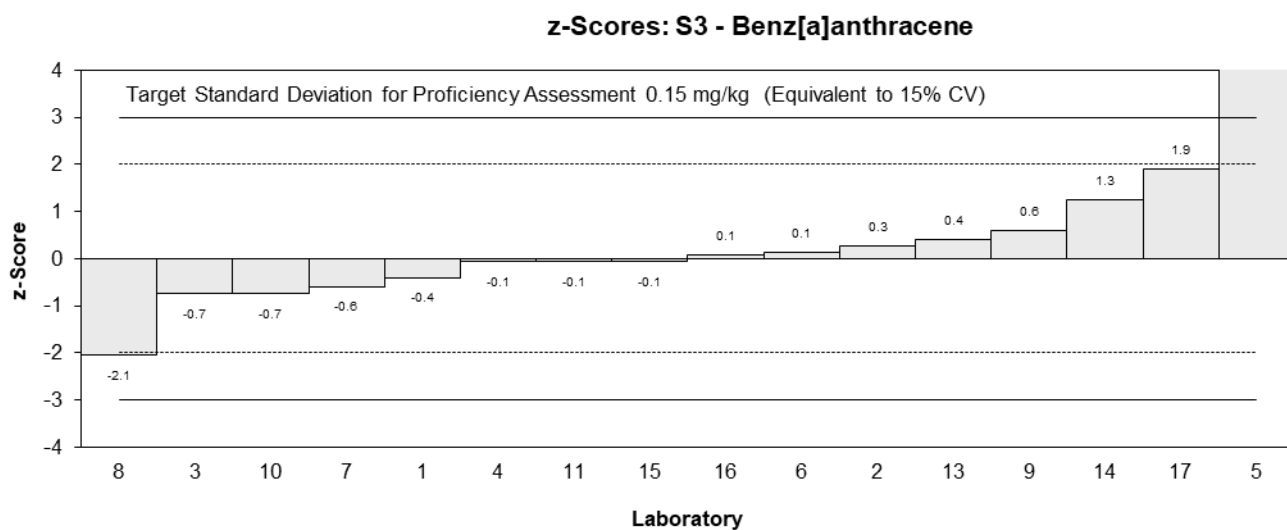
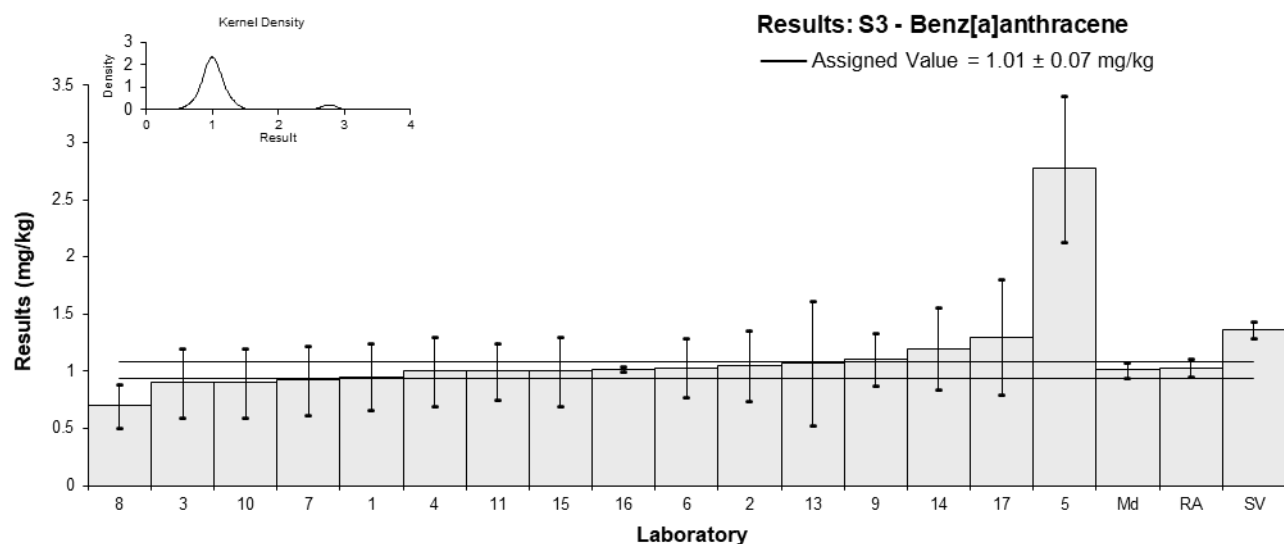


Figure 14

Table 19

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	1.02	0.31	-0.19	-0.09
2	< 0.5	0.29		
3	0.9	0.4	-0.95	-0.36
4	1.05	0.315	0.00	0.00
5*	2.8	0.98	11.11	1.78
6	1.0475	0.2619	-0.02	-0.01
7	1.1	0.29	0.32	0.16
8	0.841	0.065	-1.33	-1.75
9	1.2	0.24	0.95	0.58
10	0.98	0.4	-0.44	-0.17
11	0.99	0.30	-0.38	-0.19
13	1.01	0.51	-0.25	-0.08
14	1.6	0.48	2.00▼	
15	1.1	0.4	0.32	0.12
16	0.92	0.012	-0.83	-1.29
17	1.6	0.5	2.00▼	

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

Statistics

Assigned Value	1.05	0.10
Spike Value	1.68	0.08
Robust Average	1.09	0.13
Max Acceptable Result	2.18	
Median	1.05	0.06
Mean	1.21	
N	15	
Max	2.8	
Min	0.841	
Robust SD	0.21	
Robust CV	19%	

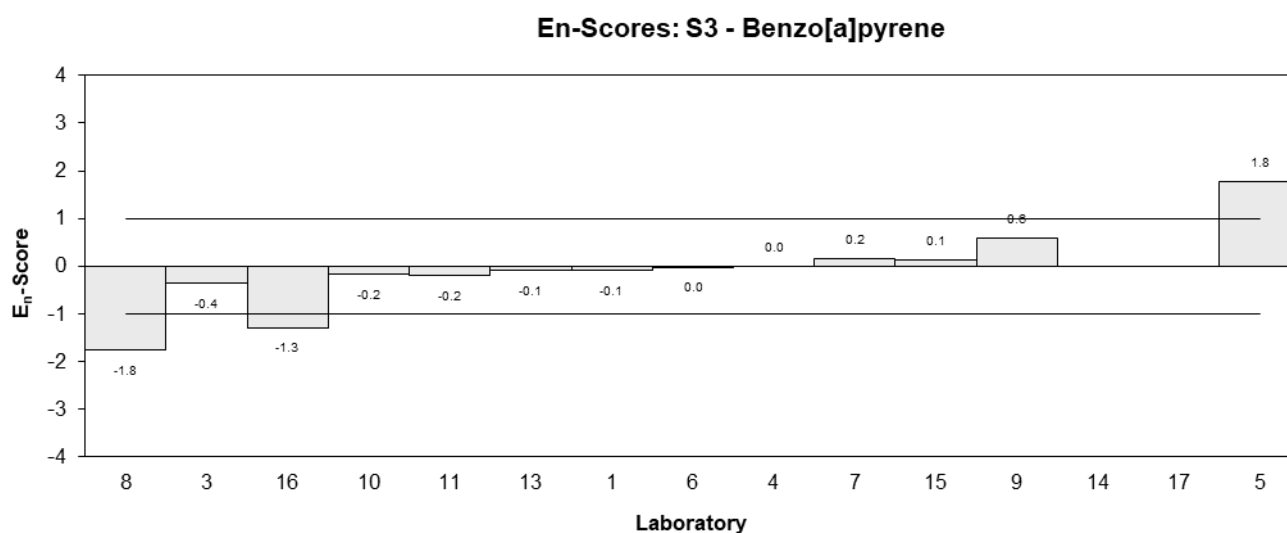
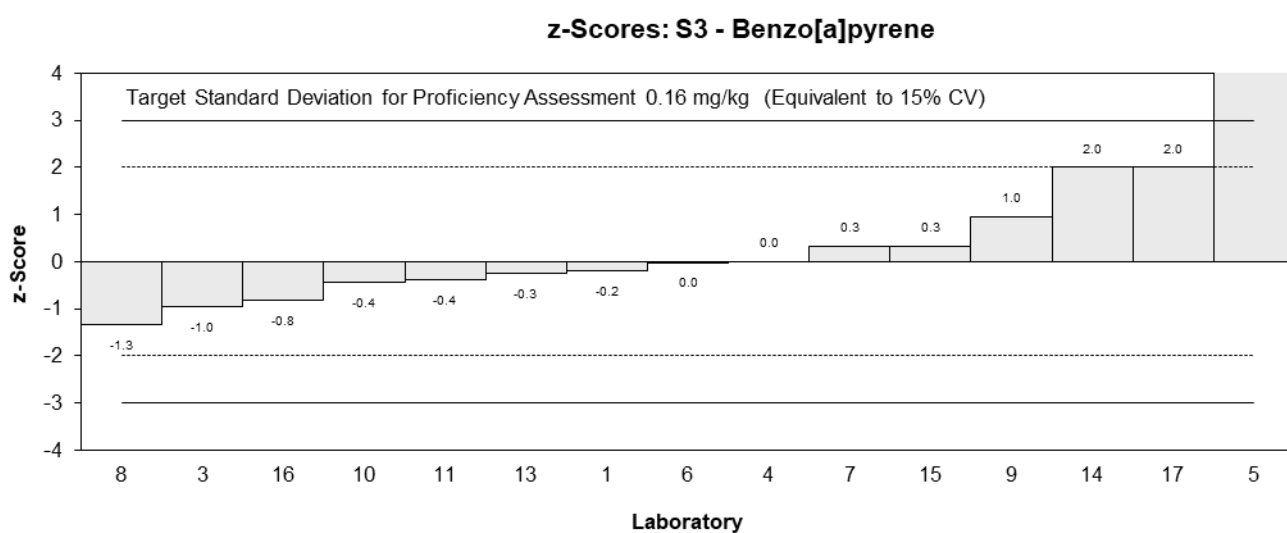
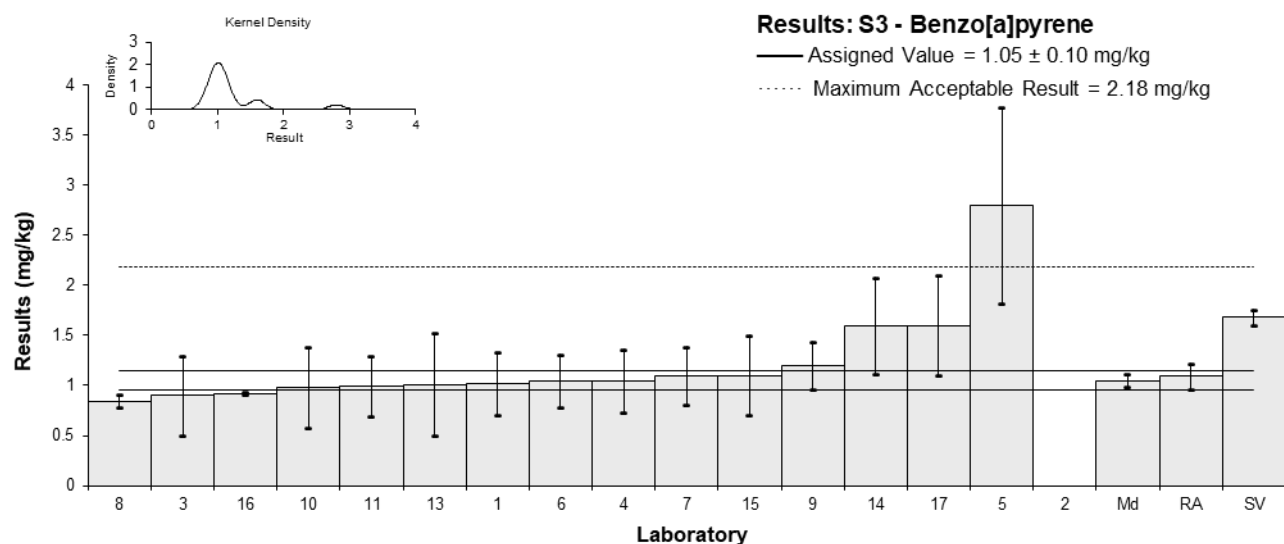


Figure 15

Table 20

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Benzo[<i>b</i>]fluoranthene
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.83	0.85	0.53	0.23
2	2.71	0.81	0.23	0.10
3	2.7	0.9	0.20	0.08
4	3.15	0.945	1.35	0.54
5*	7.14	2.71	11.50	1.66
6	2.7250	0.6813	0.27	0.14
7	2.9	0.91	0.71	0.29
8	2.12	0.44	-1.27	-0.95
9	1.4	0.42	-3.10	-2.39
10	2.5	0.8	-0.31	-0.14
11	2.94	0.735	0.81	0.40
13	2.65	1.32	0.08	0.02
14	NT	NT		
15	2.9	0.9	0.71	0.30
16	1.54	0.016	-2.75	-3.72
17**	7.9	4.3	13.44	1.23

* Outlier, ** Excluded Result, see Section 4.2

Statistics

Assigned Value	2.62	0.29
Spike Value	3.96	0.20
Robust Average	2.67	0.32
Median	2.72	0.20
Mean	2.87	
N	14	
Max	7.14	
Min	1.4	
Robust SD	0.48	
Robust CV	18%	

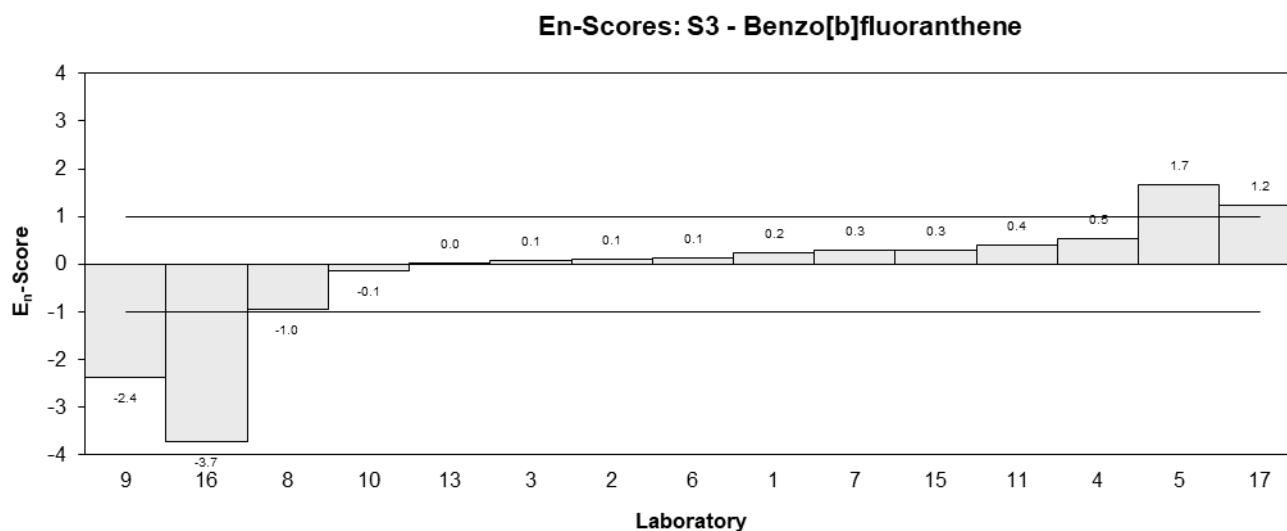
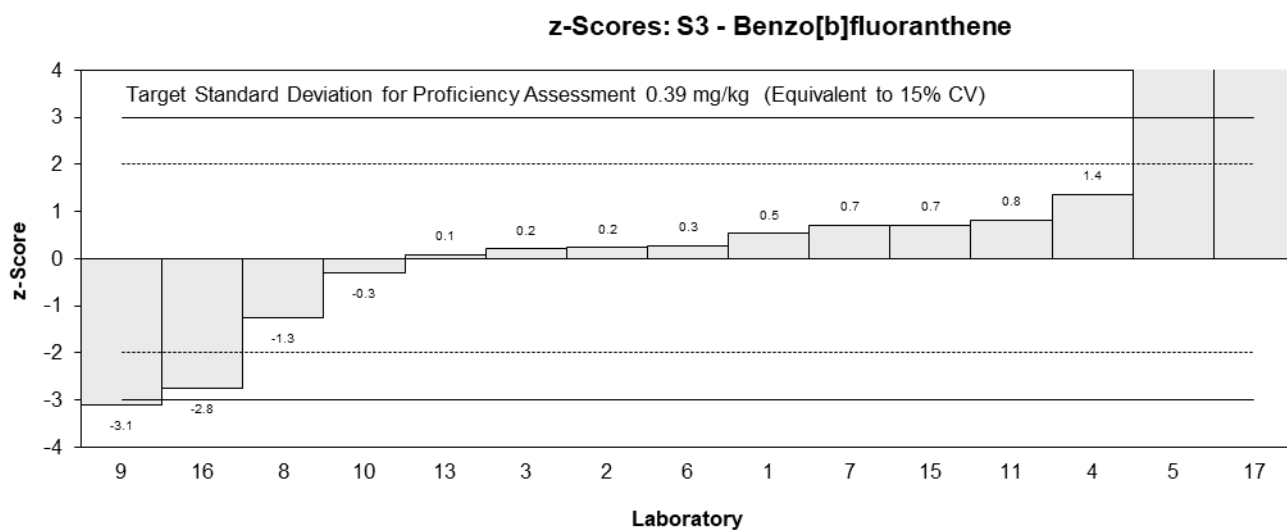
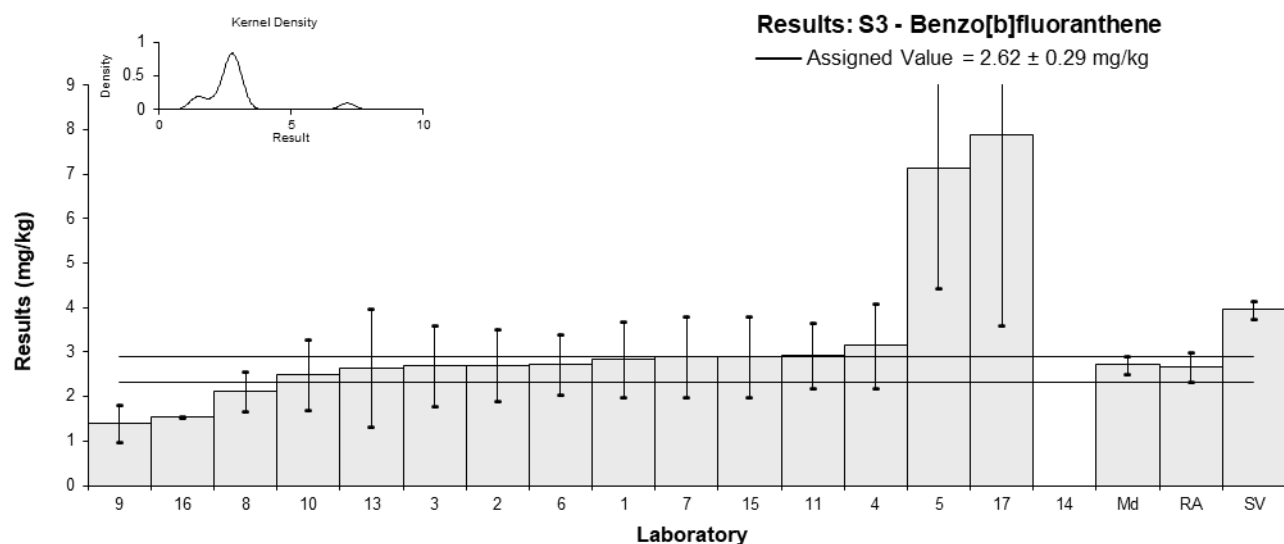


Figure 16

Table 21

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.84	0.25	0.32	0.15
2	0.92	0.28	0.98	0.41
3	0.7	0.3	-0.85	-0.33
4	0.845	0.2535	0.36	0.16
5*	2.36	0.94	12.95	1.65
6	0.7838	0.1959	-0.15	-0.09
7	0.81	0.25	0.07	0.03
8	0.563	0.084	-1.99	-2.13
9	0.94	0.2	1.15	0.65
10	0.8	0.3	-0.02	-0.01
11	0.78	0.20	-0.18	-0.10
13	0.67	0.33	-1.10	-0.39
14*	1.4	0.42	2.00▼	
15	0.8	0.3	-0.02	-0.01
16	0.74	0.024	-0.52	-0.80
17	1	0.5	1.65	0.39

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

Statistics

Assigned Value	0.802	0.074
Spike Value	1.15	0.06
Robust Average	0.835	0.093
Max Acceptable Result	1.50	
Median	0.805	0.079
Mean	0.93	
N	16	
Max	2.36	
Min	0.563	
Robust SD	0.15	
Robust CV	18%	

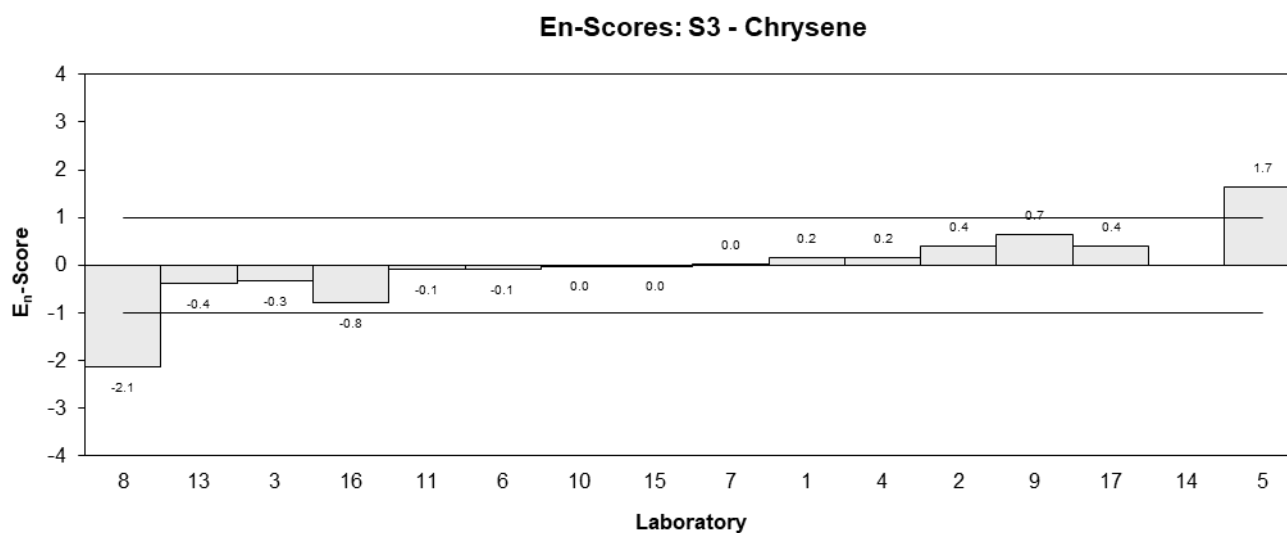
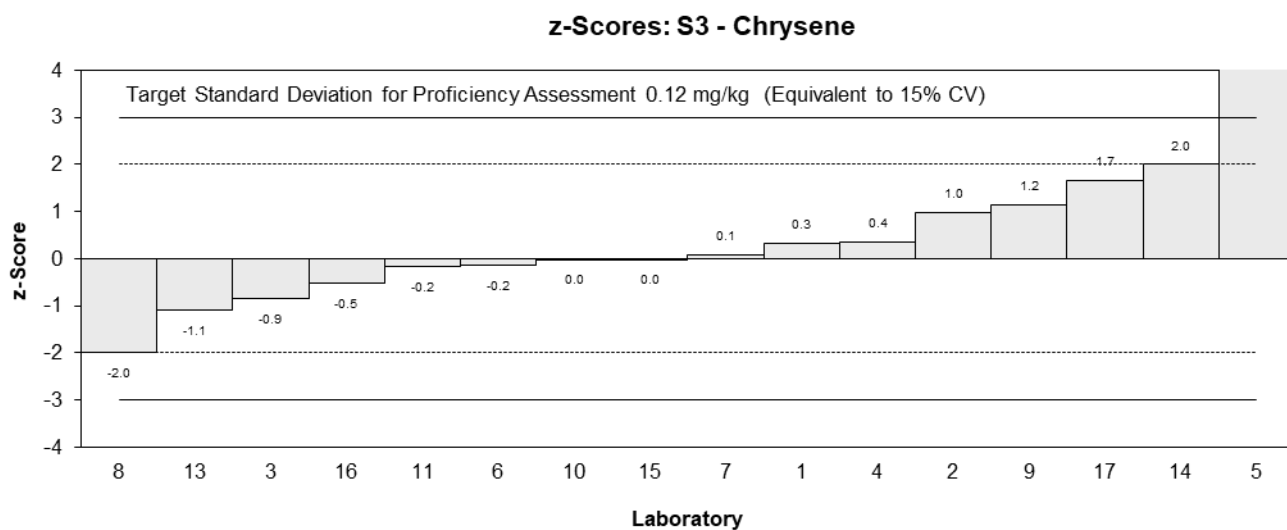
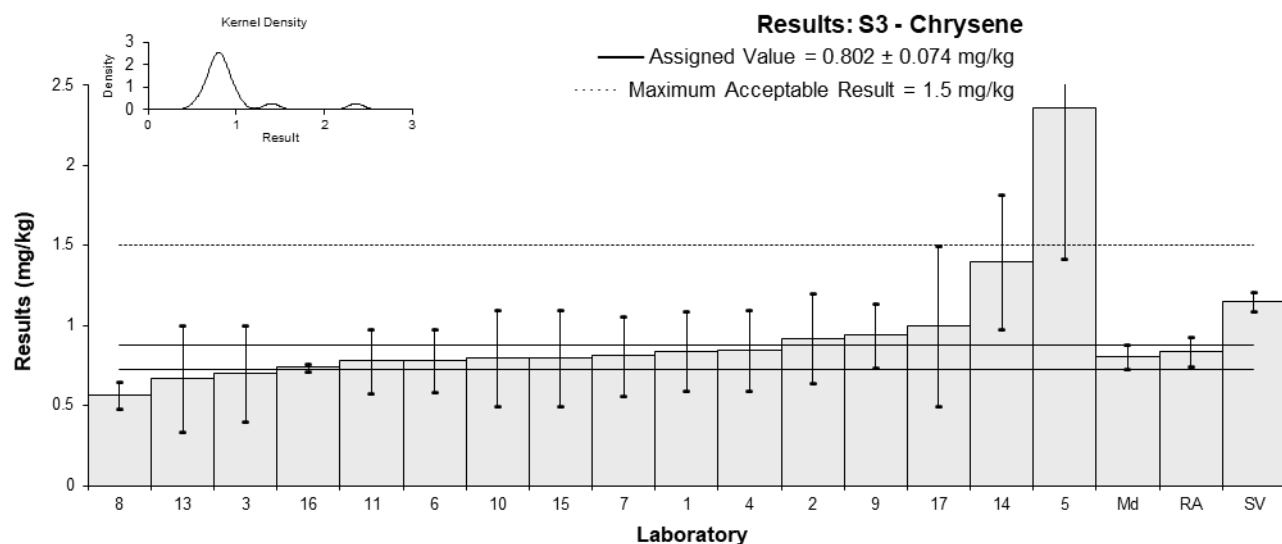


Figure 17

Table 22

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.56	0.17	0.57	0.24
2	0.58	0.17	0.83	0.36
3	0.4	0.2	-1.50	-0.56
4	0.57	0.171	0.70	0.30
5	0.63	0.16	1.47	0.67
6	0.4938	0.1234	-0.29	-0.16
7	0.53	0.16	0.18	0.08
8	0.352	0.036	-2.12	-2.37
9	0.62	0.14	1.34	0.68
10	0.4	0.2	-1.50	-0.56
11	0.54	0.14	0.31	0.16
13	0.5	0.25	-0.21	-0.06
14	0.56	0.17	0.57	0.24
15	0.5	0.2	-0.21	-0.08
16	0.4	0.009	-1.50	-1.94
17	0.6	0.5	1.09	0.17

Statistics

Assigned Value	0.516	0.059
Spike Value	0.628	0.031
Robust Average	0.516	0.059
Median	0.535	0.040
Mean	0.515	
N	16	
Max	0.63	
Min	0.352	
Robust SD	0.094	
Robust CV	18%	

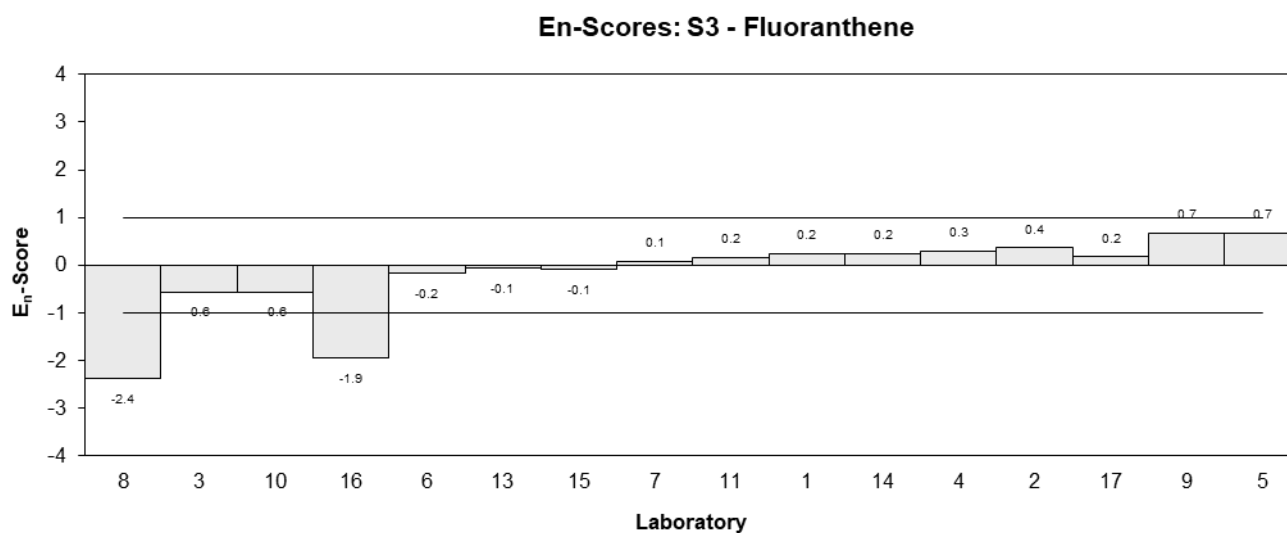
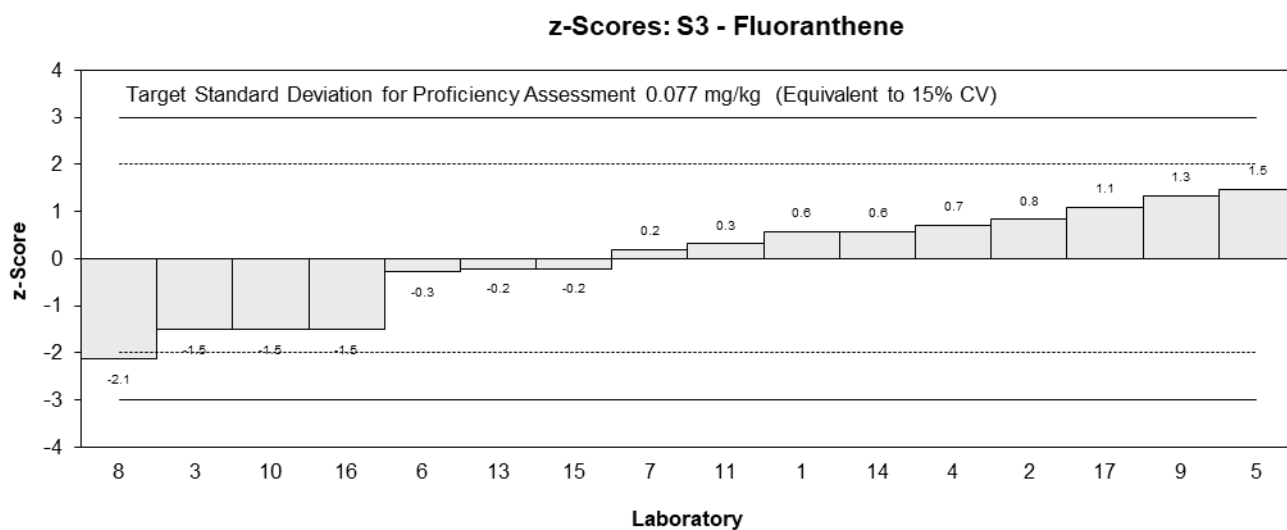
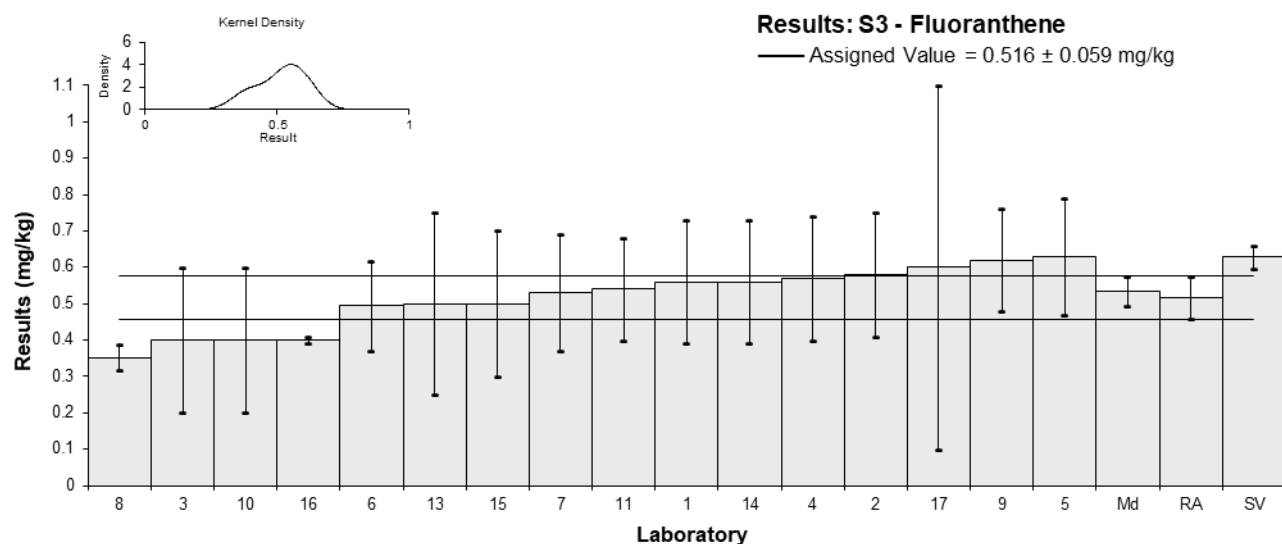


Figure 18

Table 23

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	<0.5	NR		
2	< 0.5	NR		
3	0.3	0.1	-0.46	-0.20
4	0.34	0.102	0.37	0.16
5	0.38	0.08	1.20	0.65
6	0.3275	0.0819	0.11	0.06
7	<0.5	NR		
8	0.237	0.029	-1.76	-1.72
9	0.44	0.11	2.00▼	
10	0.3	0.1	-0.46	-0.20
11	< 0.5	NR		
13	0.34	0.17	0.37	0.10
14	<0.5	NR		
15	0.3	0.1	-0.46	-0.20
16	0.29	0.009	-0.66	-0.78
17	<0.5	0.5		

▼ Adjusted Score, see Section 6.3

Statistics

Assigned Value	0.322	0.040
Spike Value	0.421	0.021
Robust Average	0.322	0.040
Max Acceptable Result	0.547	
Median	0.314	0.029
Mean	0.325	
N	10	
Max	0.44	
Min	0.237	
Robust SD	0.051	
Robust CV	16%	

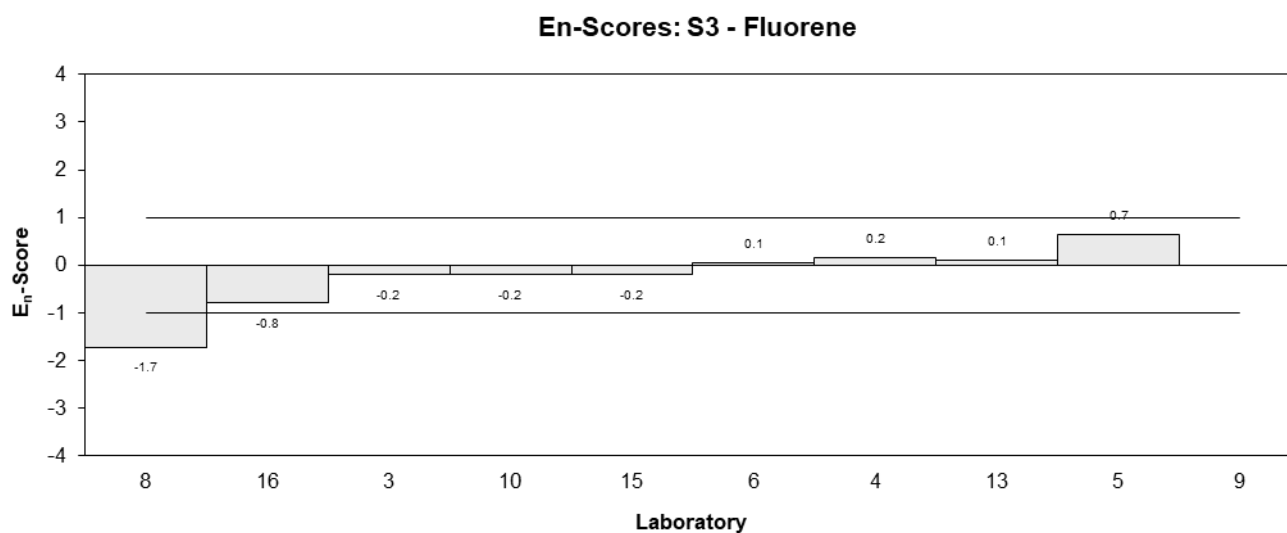
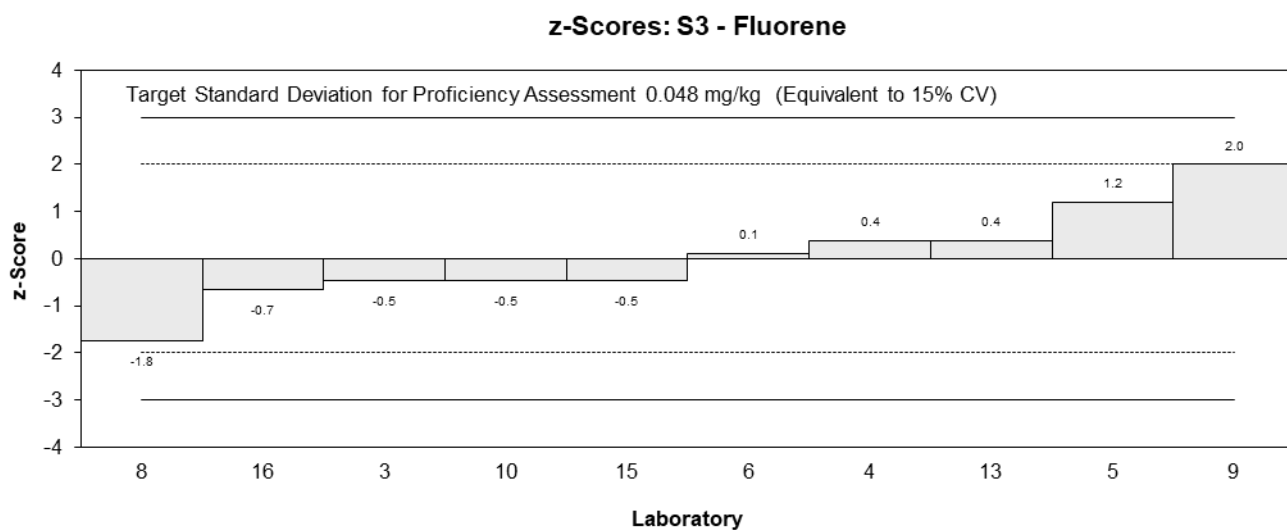
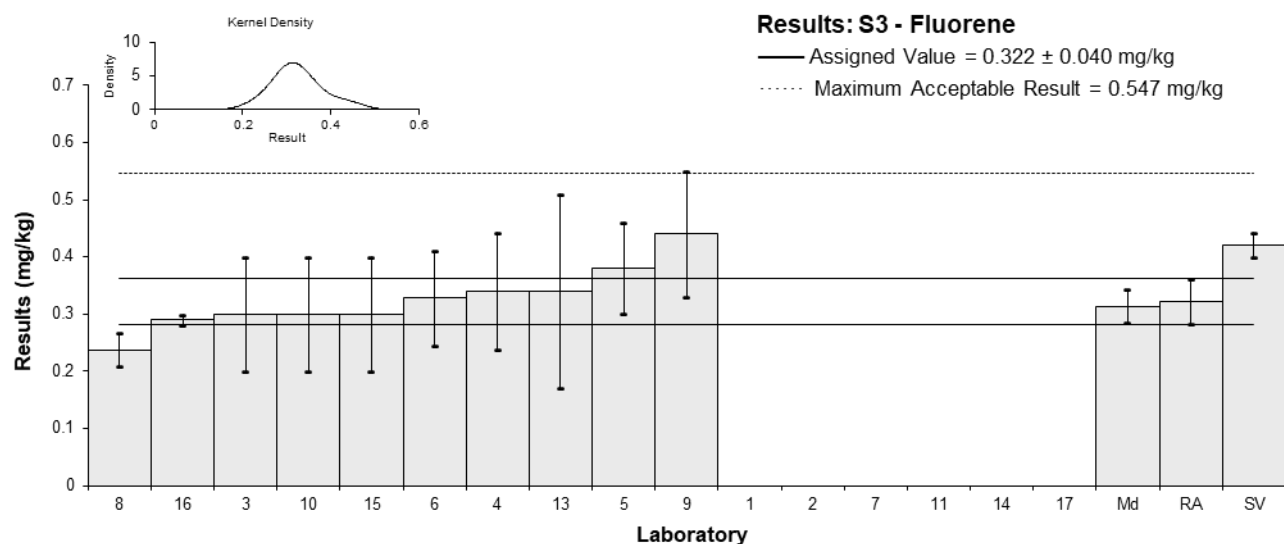


Figure 19

Table 24

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.11	0.33	0.25	0.12
2	1.14	0.34	0.44	0.20
3	1	0.3	-0.44	-0.22
4	1.2	0.36	0.81	0.35
5	1.27	0.23	1.25	0.80
6	1.0050	0.2513	-0.40	-0.24
7	1.1	0.34	0.19	0.08
8	0.73	0.11	-2.12	-2.29
9	1.2	0.24	0.81	0.50
10	0.9	0.3	-1.06	-0.54
11	1.08	0.27	0.06	0.03
13	0.97	0.49	-0.62	-0.20
14	1.2	0.36	0.81	0.35
15	1.0	0.3	-0.44	-0.22
16	0.87	0.008	-1.25	-1.99
17	1.3	0.5	1.43	0.45

Statistics

Assigned Value	1.07	0.10
Spike Value	1.36	0.07
Robust Average	1.07	0.10
Median	1.09	0.10
Mean	1.07	
N	16	
Max	1.3	
Min	0.73	
Robust SD	0.16	
Robust CV	15%	

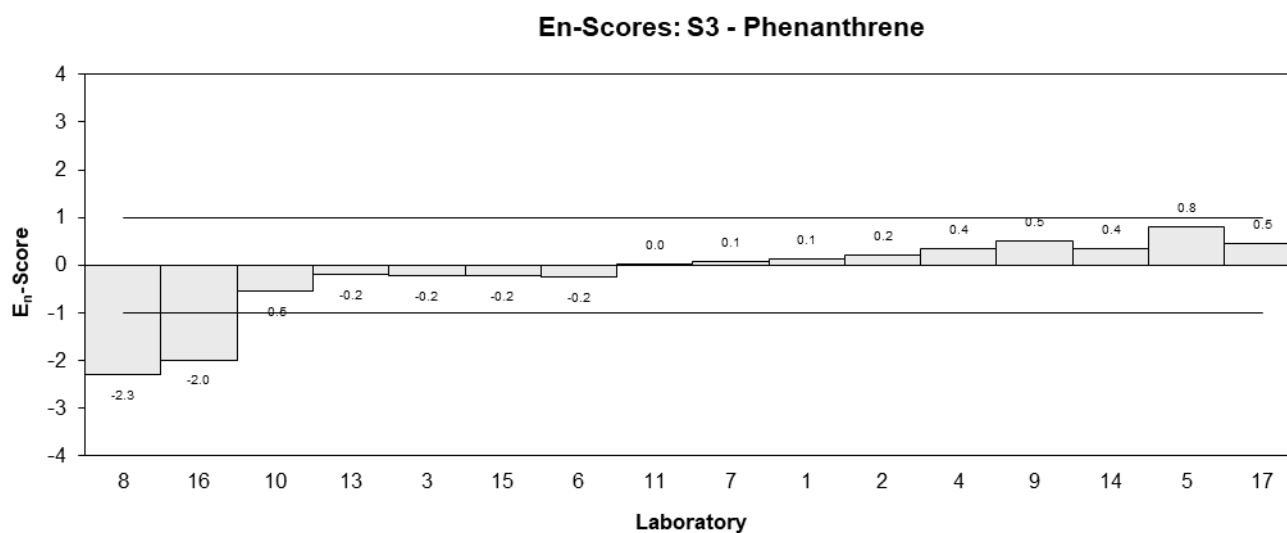
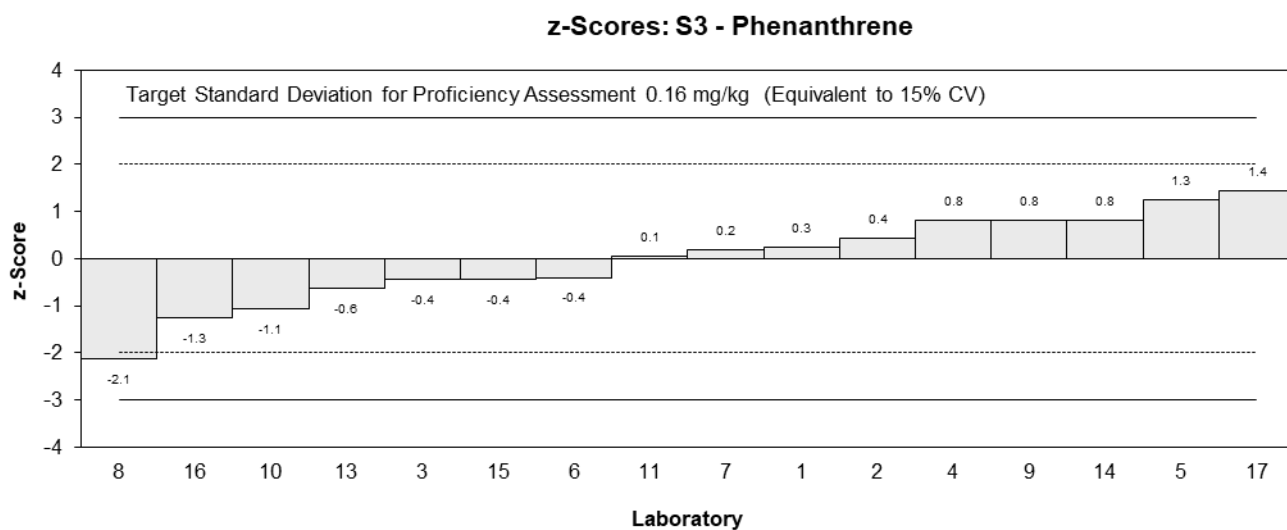
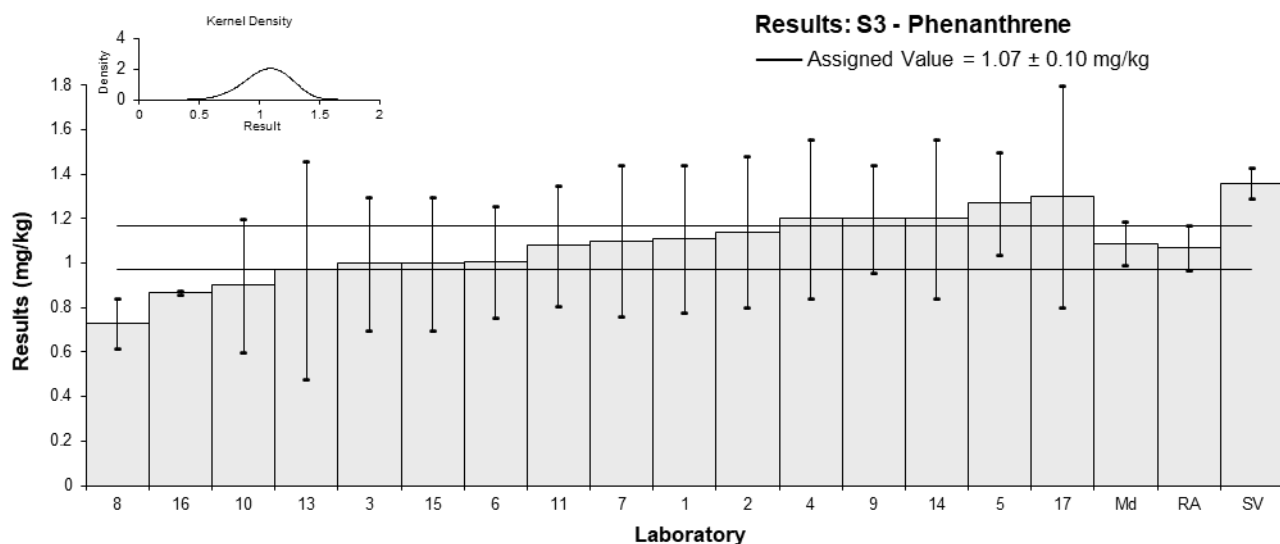


Figure 20

Table 25

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.68	0.20	0.78	0.34
2	0.66	0.2	0.56	0.24
3	0.5	0.2	-1.19	-0.52
4	0.68	0.204	0.78	0.33
5	0.72	0.21	1.22	0.51
6	0.5775	0.1444	-0.34	-0.20
7	0.65	0.19	0.45	0.21
8	0.42	0.055	-2.07	-2.30
9	0.67	0.15	0.67	0.38
10	0.5	0.2	-1.19	-0.52
11	0.63	0.16	0.23	0.12
13	0.57	0.28	-0.43	-0.14
14	0.67	0.20	0.67	0.29
15	0.6	0.2	-0.10	-0.04
16	0.47	0.02	-1.52	-2.17
17	0.7	0.5	1.00	0.18

Statistics

Assigned Value	0.609	0.061
Spike Value	0.736	0.037
Robust Average	0.609	0.061
Median	0.640	0.046
Mean	0.606	
N	16	
Max	0.72	
Min	0.42	
Robust SD	0.097	
Robust CV	16%	

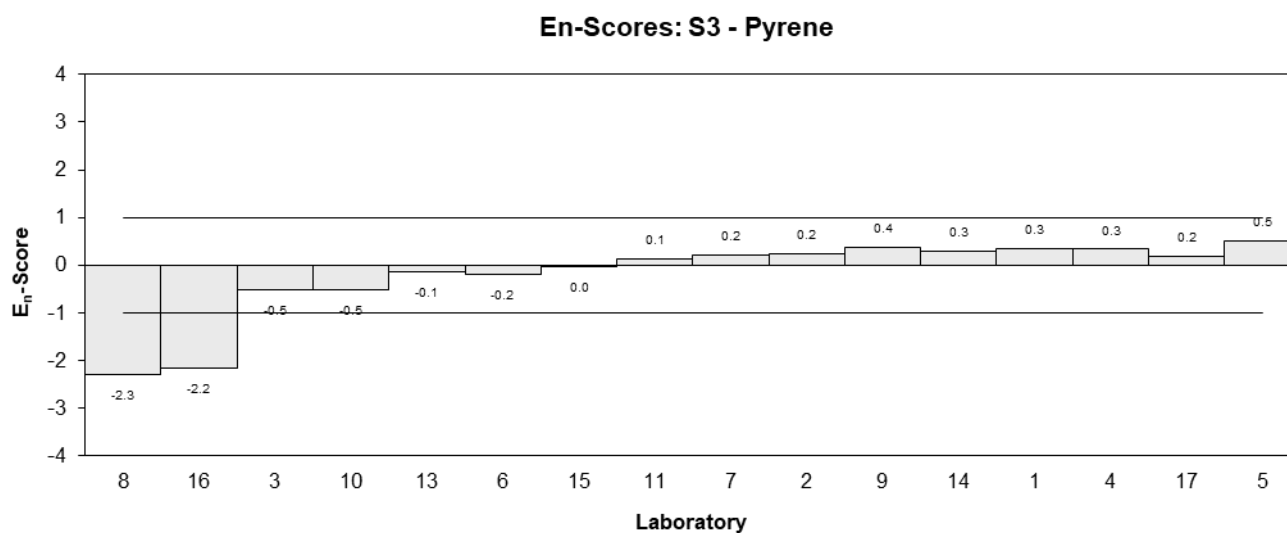
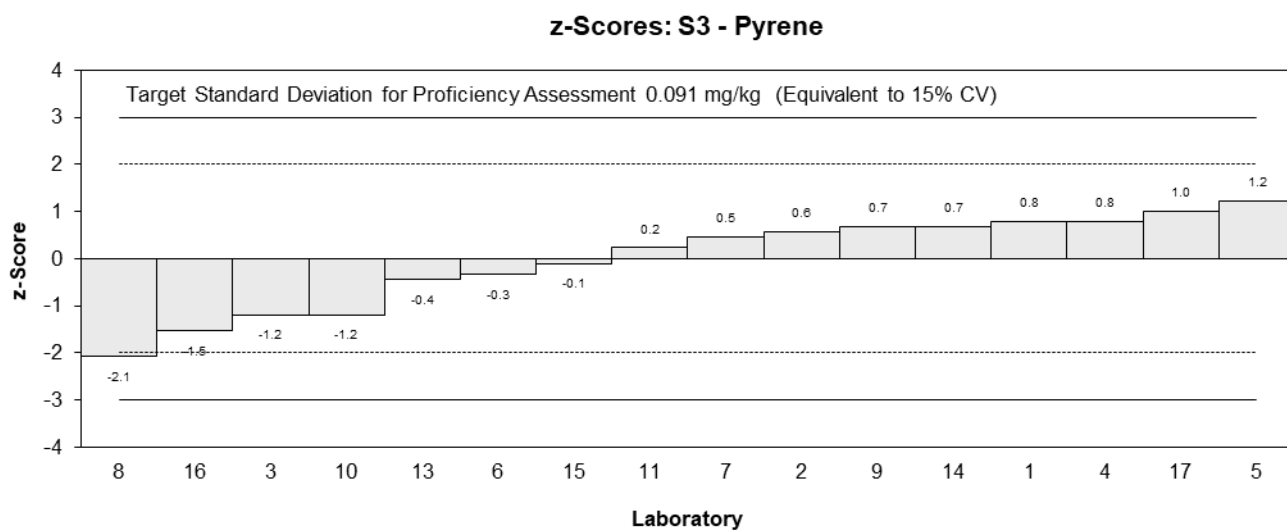
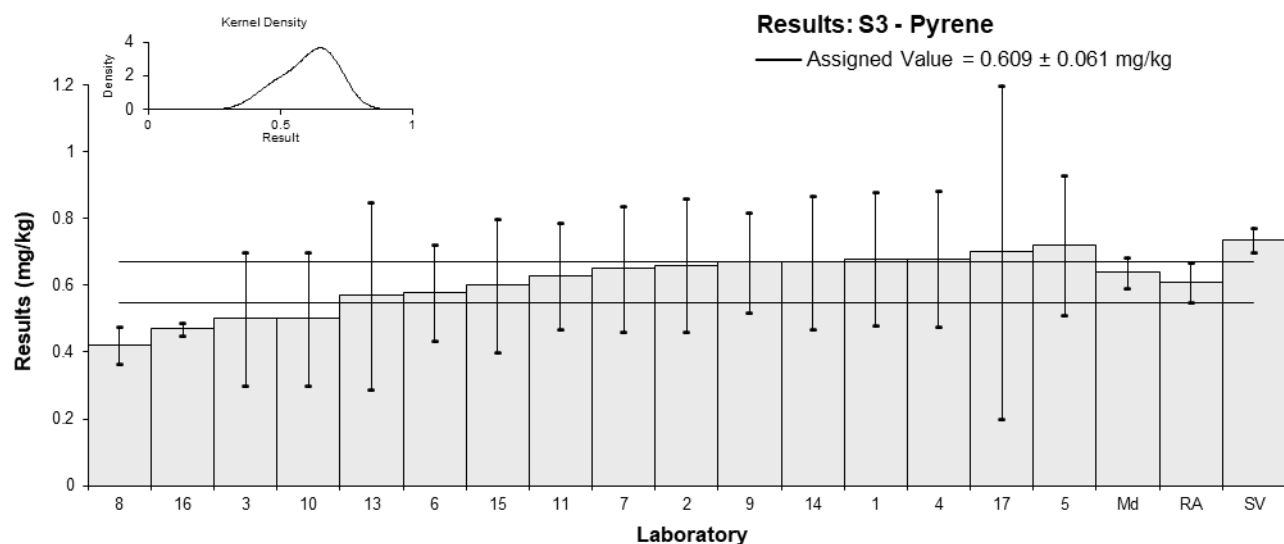


Figure 21

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The assigned values for all scored analytes were the robust averages of participants' results. If there were results less than 50% or greater than 150% of the robust average, these were excluded from the calculation of each assigned value.^{3,4} The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.⁷ The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S3 acenaphthene as an example.

For some of the analytes spiked in this study, a proportion of the analyte may be strongly bound to the soil, and so may not be readily extracted and measured. What laboratories measure may be described as 'extractable analyte', and the result may be influenced by the efficiency of the extraction process used. Therefore, the assigned value for some analytes may instead be the best estimate of the amount of 'extractable analyte'.

Samples S1 and S2 were spiked with commercially purchased products, and spiked values are not available. For Sample S3, a comparison of the assigned values and the spiked values is presented in Table 26. Assigned values were within the range of 54% to 83% of the spiked value, which is similar to ratios observed in previous NMIA Hydrocarbons in Soil PT studies. Assigned values were set if there was a reasonable consensus of participants' results.

Table 26 Comparison of Assigned Value and Spiked Value

Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Assigned Value / Spiked Value (%)
S3	Acenaphthene	1.40	1.89	74
	Anthracene	1.25	2.30	54
	Benz[a]anthracene	1.01	1.36	74
	Benzo[a]pyrene	1.05	1.68	63
	Benzo[b]fluoranthene	2.62	3.96	66
	Chrysene	0.802	1.15	70
	Fluoranthene	0.516	0.628	82
	Fluorene	0.322	0.421	76
	Phenanthrene	1.07	1.36	79
	Pyrene	0.609	0.736	83

No assigned value was set for Sample S2 benzene, as numeric results reported for this analyte were highly variable; this may be due to the volatility of this compound. Sample S2 C6-C10 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 reasonable consensus with each other.

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

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an evaluation of the expanded uncertainty associated with their results. It is a requirement of ISO/IEC 17025 that laboratories have procedures to

evaluate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including when the client's instruction so requires.⁹

Of 293 numeric results, 289 results (99%) were reported with an associated expanded MU. Participants used a wide variety of procedures to evaluate their uncertainty (Table 3). The magnitude of the reported expanded uncertainties was within the range 0.9% to 83% 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 to be fit-for-purpose. Of the 289 expanded MUs reported, 251 (87%) were within 15% and 50% relative, 30 were less than 15% relative while eight were greater than 50% relative.

Laboratory **13** did not report uncertainties for Sample S1 TRH and Sample S2 Total BTEX results (they did provide uncertainties for individual components). This participant reported being accredited to ISO/IEC 17025.

Sample S1 TRH results from Laboratories **9** and **16** had no uncertainties, as the results were calculated by the study coordinator by summing the individual hydrocarbon range results reported, and no evaluations of the uncertainty were made.

Most uncertainties reported by Laboratory **16** were less than 5% relative; not all sources of uncertainty may have been included in these uncertainties.

Participants were also requested to report the coverage factor associated with their uncertainties (Table 3). Nine participants reported a coverage factor of $k = 2$.

Uncertainties associated with results returning an acceptable z -score but an unacceptable E_n -score may have been underestimated.

Laboratories **2** and **17** attached evaluations of the expanded MU for results reported as less than their limit of reporting (LOR). An evaluation 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 1.1725 ± 0.2931 mg/kg, report 1.17 ± 0.29 mg/kg.¹⁰

6.3 z-Score

Target SDs for proficiency assessment 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 for proficiency assessment (as PCV) in this study are presented for comparison in Table 27.

Table 27 Comparison of Thompson-Horwitz CVs, Between-Laboratory CVs, Target SDs

Sample	Analyte	Assigned Value (mg/kg)	Thompson-Horwitz CV [†] (%)	Between-Laboratory CV [‡] (%)	Target SD (as PCV) (%)
S1	>C10-C16	903	5.7	12	15
	>C16-C34	1500	5.3	15	15
	>C34-C40	184	7.3	23	15
	TRH	2670	4.9	13	15
S2	C6-C10	5050*	4.4	21	Not Set
	Benzene	27*	9.7	53	Not Set

Sample	Analyte	Assigned Value (mg/kg)	Thompson-Horwitz CV [†] (%)	Between-Laboratory CV [‡] (%)	Target SD (as PCV) (%)
	Toluene	499	6.3	17	15
	Ethylbenzene	143	7.6	16	15
	Xylenes	669	6	16	15
	Total BTEX	1380	5.4	17	15
S3	Acenaphthene	1.40	15	13	15
	Anthracene	1.25	15	19	15
	Benz[<i>a</i>]anthracene	1.01	16	11	15
	Benzo[<i>a</i>]pyrene	1.05	16	14	15
	Benzo[<i>b</i>]fluoranthene	2.62	14	16	15
	Chrysene	0.802	17	14	15
	Fluoranthene	0.516	18	18	15
	Fluorene	0.322	19	16	15
	Phenanthrene	1.07	16	15	15
	Pyrene	0.609	17	16	15

*Robust Average (assigned value not set).

[†]Calculated from the assigned value.

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

To account for possible low bias in the consensus values due to participants using inefficient analytical or extraction techniques, a total of four *z*-scores were adjusted across the following: Sample S3 benzo[*a*]pyrene, chrysene and fluorene. 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 266 results for which *z*-scores were calculated, 231 (87%) returned a score of $|z| \leq 2.0$, indicating an acceptable performance.

Laboratories **3**, **10**, **13**, **15** and **16** reported numeric results for all 18 scored analytes. Of these participants, Laboratories **10**, **13** and **15** returned acceptable *z*-scores for all 18 scored analytes.

Five participants received acceptable *z*-scores for all scored analytes that they reported results for: Laboratories **1** (17), **7** (17), **11** (17), **2** (16) and **6** (14).

For Sample S3, Laboratory **5** reported four results that were significantly higher than the assigned value (*z*-scores were all greater than 10.0); the other six results reported by this participant for this sample returned acceptable *z*-scores. This participant may need to review if, for example, their calibrators were correctly prepared for those analytes with high unacceptable *z*-scores.

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

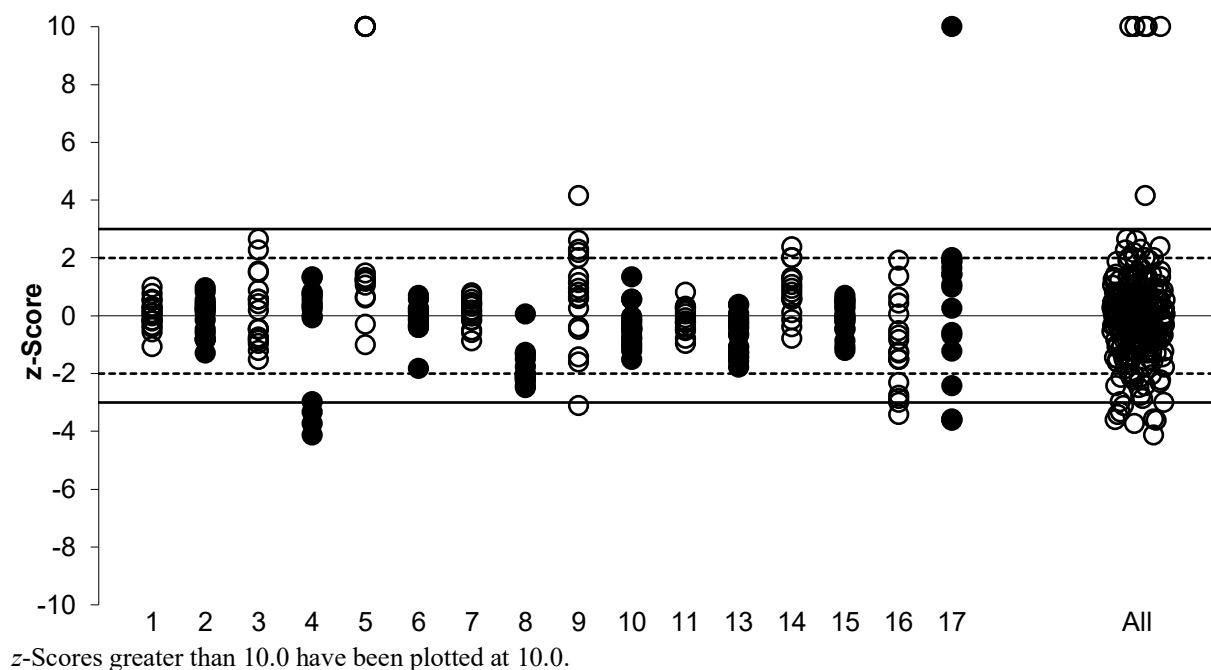


Figure 22 z-Score Dispersal by Laboratory

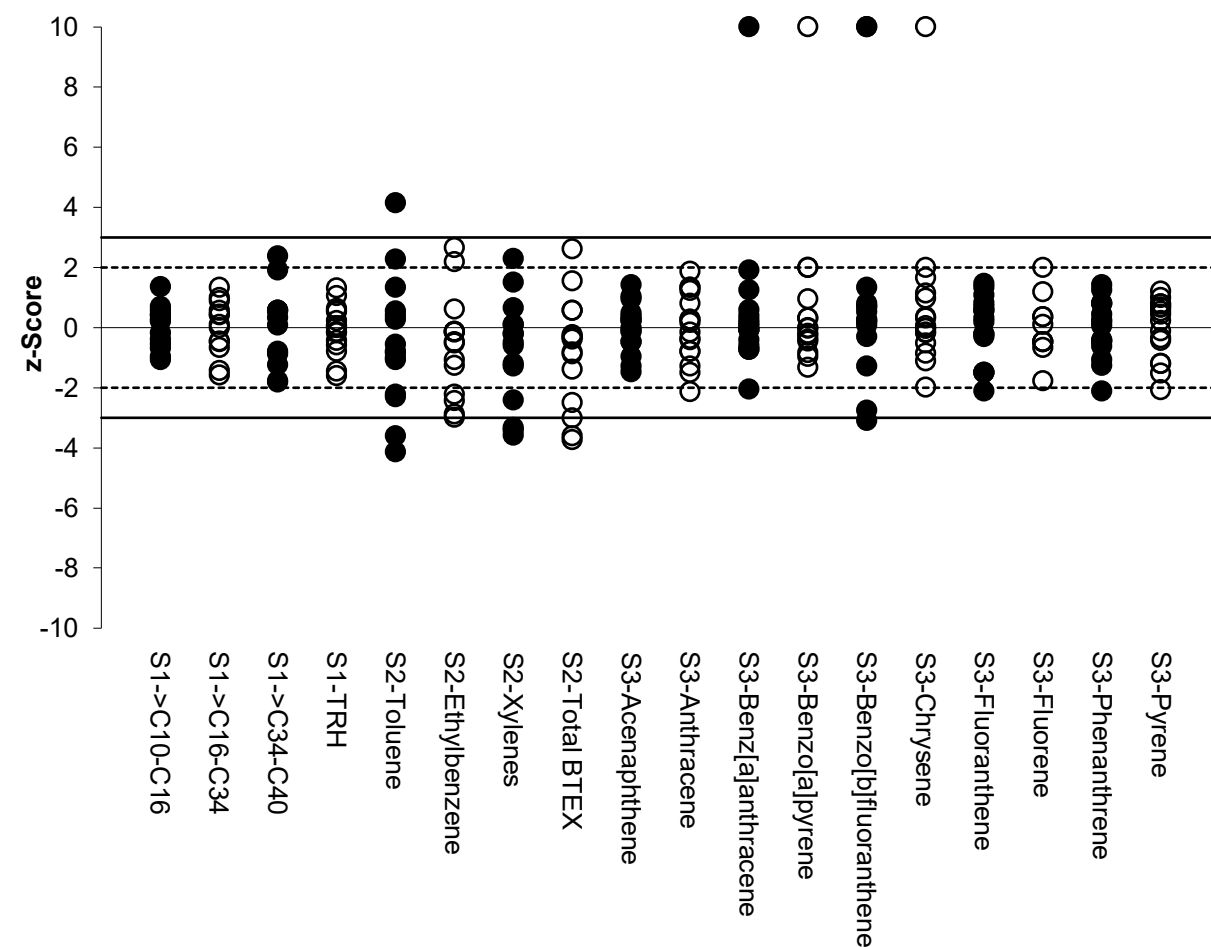


Figure 23 z-Score Dispersal by Analyte

Participants' z-scores for Sample S1 TRH only are presented in Figure 24. All except one result achieved acceptable z-scores for this sample.

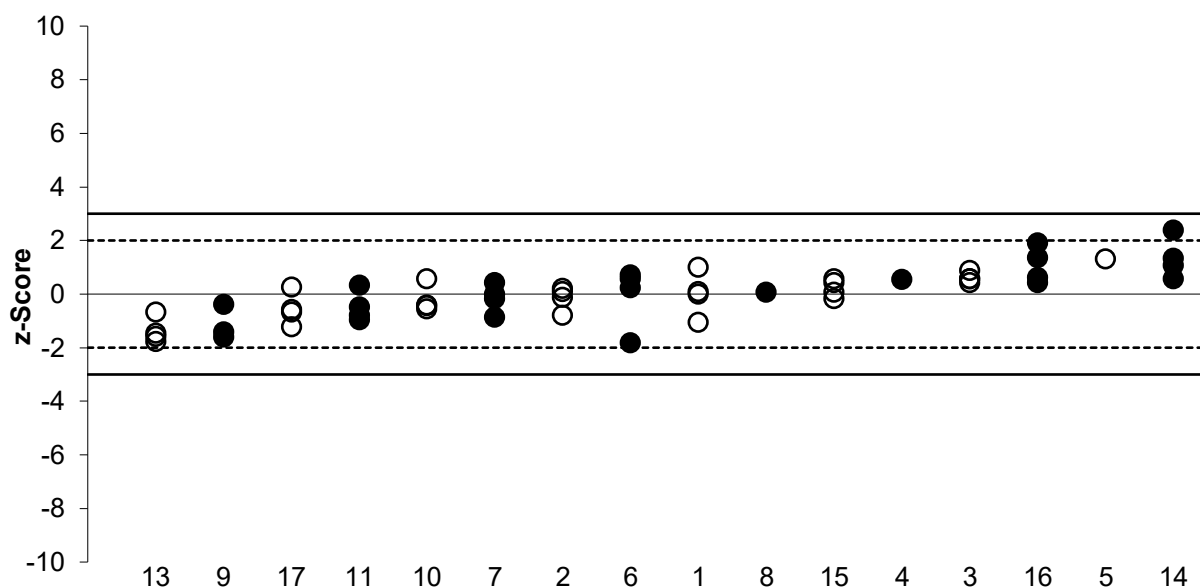


Figure 24 Sample S1 TRH z-Score Dispersal by Laboratory

Participants' z-scores for Sample S2 BTEX only are presented in Figure 25. A trend of questionable or unacceptable 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 unacceptable z-scores below the zero line may have an inefficient extraction process for BTEX.

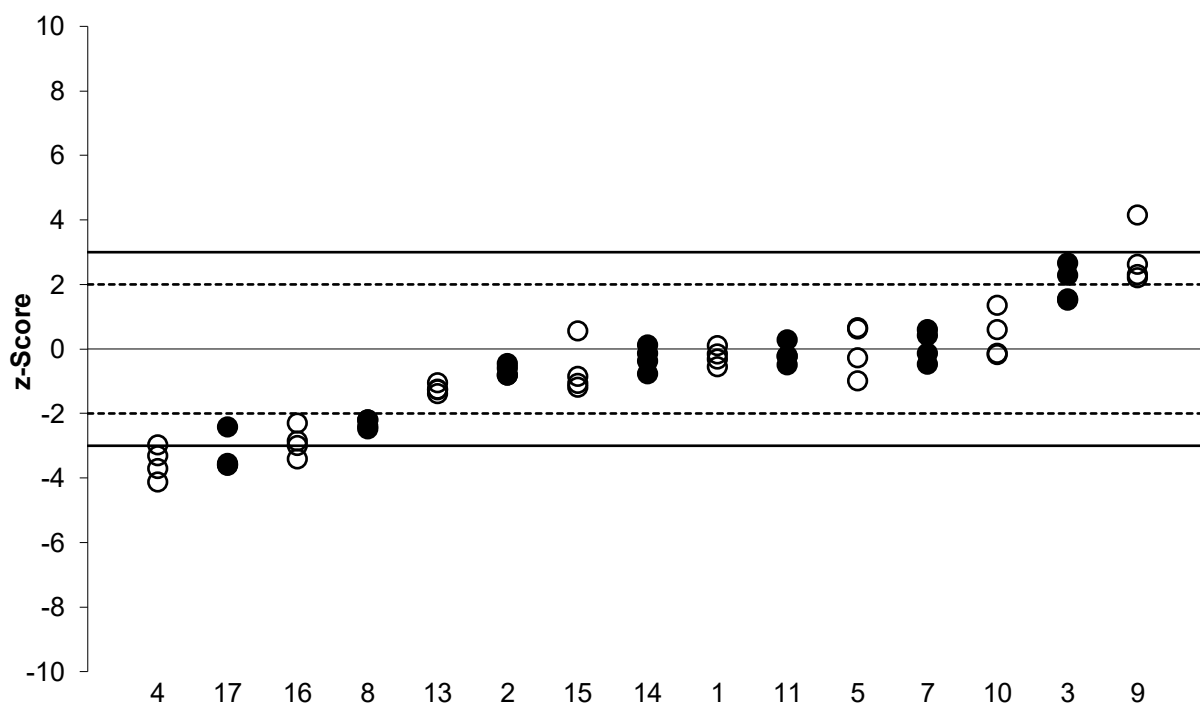
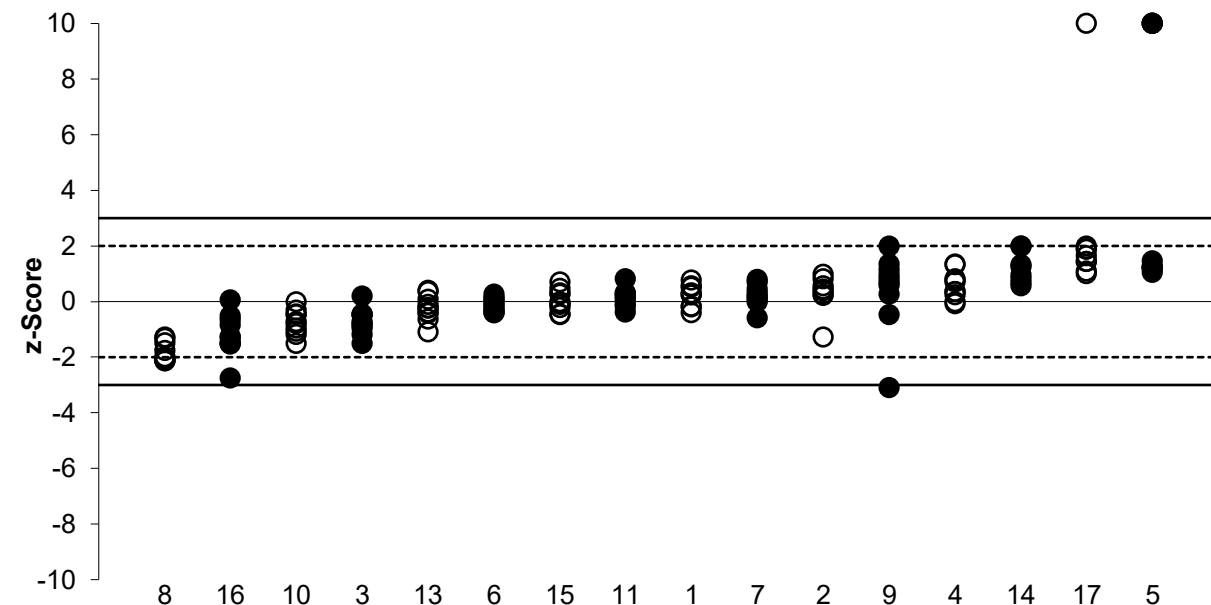


Figure 25 Sample S2 BTEX z-Score Dispersal by Laboratory

Participants' z-scores for Sample S3 PAHs only are presented in Figure 26. A trend of questionable or unacceptable z-scores on one side of the zero line may indicate laboratory bias for PAHs measurements. In particular, participants whose results consistently return questionable or unacceptable z-scores below the zero line may have an inefficient extraction

process for PAHs. As the ratios of the assigned values to the spiked values ranged from 54% to 83%, participants reporting results with higher acceptable z -scores may have more efficient methodologies.



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

Figure 26 Sample S3 PAHs z -Score Dispersal by Laboratory

6.4 E_n -Score

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

Of 262 results for which E_n -scores were calculated, 214 (82%) returned an acceptable score of $|E_n| < 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratories **3**, **10** and **15** returned acceptable E_n -scores for all 18 scored analytes.

Four participants received acceptable E_n -scores for all scored analytes they reported results for: Laboratories **1** (17), **7** (17), **11** (17) and **2** (16). Laboratory **14** had two results where no E_n -score was assigned as the associated results' z -scores were adjusted as described above; this participant returned acceptable E_n -scores for all other results (14).

The dispersal of participants' E_n -scores is presented graphically by laboratory in Figure 27.

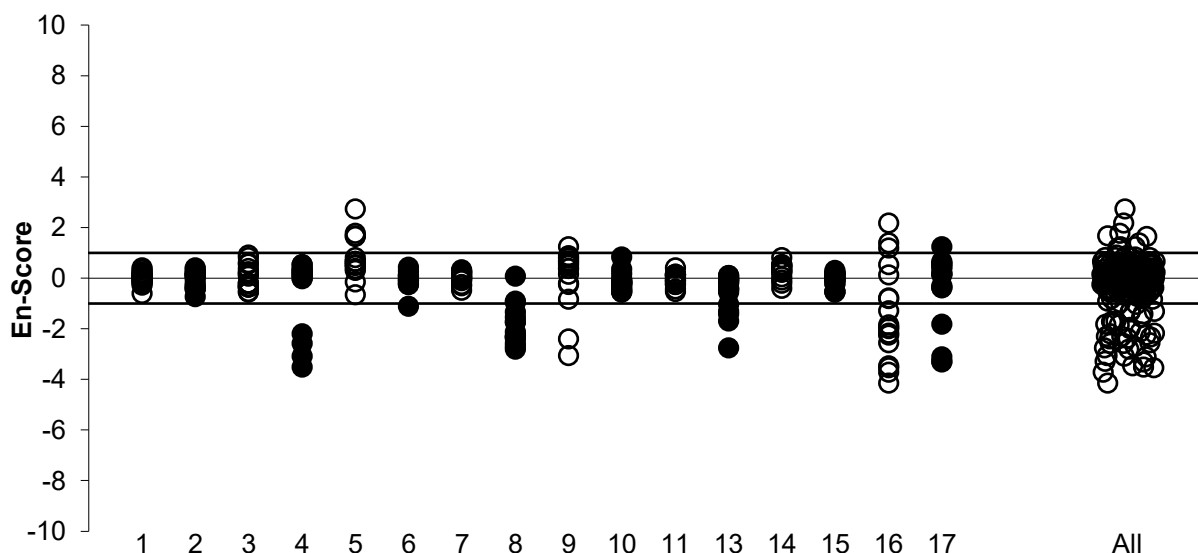


Figure 27 E_n -Score Dispersal by Laboratory

6.5 False Negatives

Three participants reported false negative results (Table 28). 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. For analytes where no assigned value was set, results have only been considered to be false negatives where the consensus value and spiked value (if applicable) were significantly higher than the participants’ LOR (i.e. the consensus value minus the expanded uncertainty, and the spiked value minus the expanded uncertainty, were both greater than the LOR), or if no value was reported.

Table 28 False Negatives

Lab. Code	Sample	Analyte	Assigned Value (mg/kg)	Spiked Value (mg/kg)	Result [†] (mg/kg)
2	S3	Benzo[a]pyrene	1.05	1.68	< 0.5
4	S2	C6 - C10 Hydrocarbons	5050*	-	NR
9	S1	>C34-C40	184	-	< 100

*Robust average (assigned value not set).

[†]Results reported as ‘NR’ may or may not be false negatives, depending on the participant’s actual LOR.

6.6 Reporting of Additional Analytes

Two participants reported additional analytes that were not spiked into the test samples by the study coordinator (Table 29). Sample S3 was spiked with benzo[b]fluoranthene, however Laboratories 9 and 16 reported the presence of benzo[k]fluoranthene also; these two analytes typically closely elute or coelute depending on chromatographic conditions.¹¹ Participants should take care with interpreting their analytical data. Both Laboratories 9 and 16 were biased low with their benzo[b]fluoranthene results, and this may have been affected by their reporting of benzo[k]fluoranthene results.

Table 29 Non-Spiked Analytes Reported by Participants

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
9	S3	Benzo[k]fluoranthene	0.69	0.15	NR
16	S3	Benzo[k]fluoranthene	1.53	0.02	NR

6.7 Participants' Analytical Methods

Results that were removed from all statistical calculations in Section 5 have also been removed from all discussion in this section. Where charts refer to $n = x$, this corresponds to x number of participants using that methodology.

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

TRH

Sample S1 was a 50 g soil sample. Participants used a sample size between 2 g and 10 g for TRH analysis, with most participants using 10 g. A plot of results against sample mass used for analysis is presented in Figure 28. The participant using 2 g returned a result that returned an acceptable z-score but was biased low; caution should be exercised when a small sample size is taken for analysis, as this may not be a suitable representation of the whole sample.

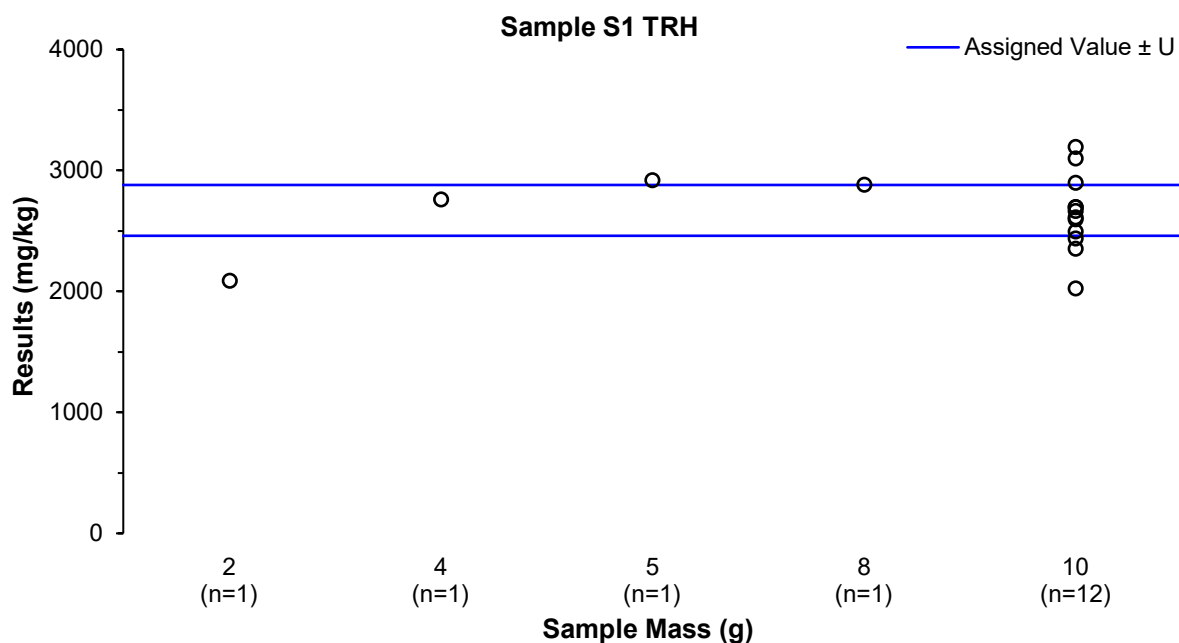


Figure 28 Sample S1 TRH Results vs Sample Mass Used for Analysis

All participants reported using solid-liquid extraction (SLE), with some participants specifying that they used mechanical agitation (MA) or sonication (S). Participants reported using dichloromethane (DCM), acetone (ACE), hexane (HEX), pentane (PENT) or combinations of these as the extraction solvent(s). Three 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 against methodology for Sample S1 TRH is presented in Figure 29. Methodologies are listed in order of reported extraction technique, extraction solvent(s), clean-up and instrument. The most common methodology used to analyse TRH in this study was SLE (MA) with DCM/ACE as the extraction solvent, with no clean-up and using GC-FID for analysis.

TRH analysis did not present a problem to laboratories' analytical techniques, with excellent agreement between reported results across a range of methodologies.

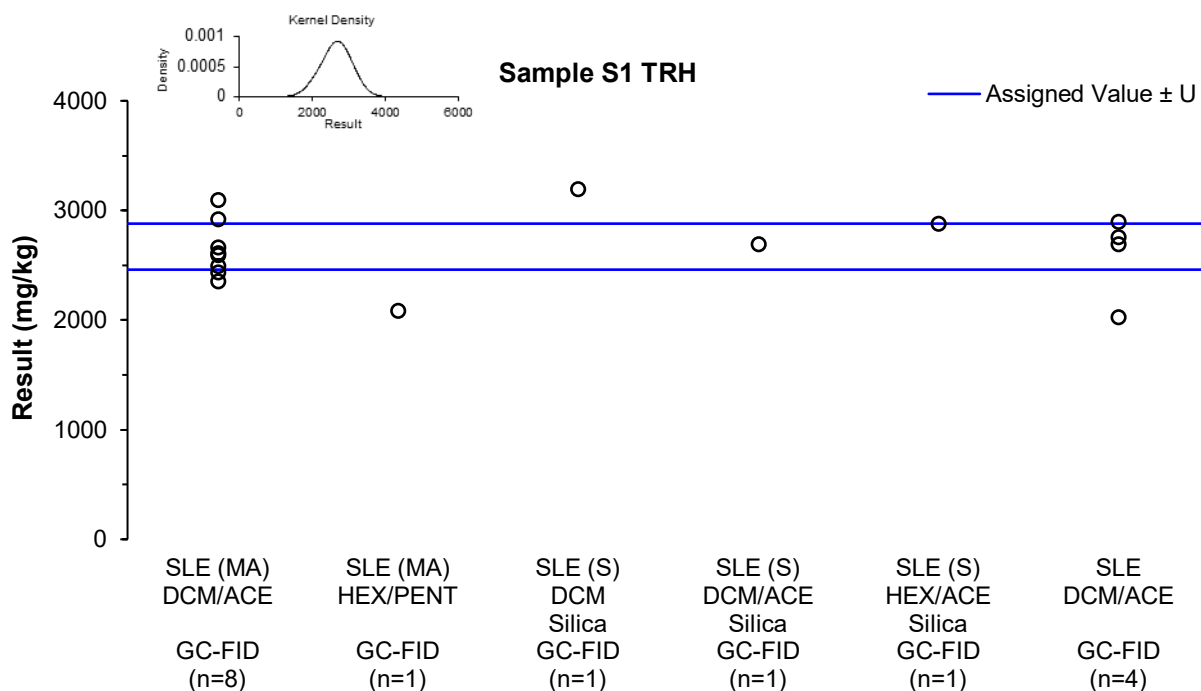


Figure 29 Sample S1 TRH Results vs Methodology

BTEX

Sample S2 was a 50 g soil sample. Participants used a sample size between 2 g and 10 g for BTEX analysis, with most participants using 5 g. A plot of results against sample mass used for analysis is presented in Figure 30. As with TRH, the participant using 2 g reported a result that returned an acceptable z-score but was biased low.

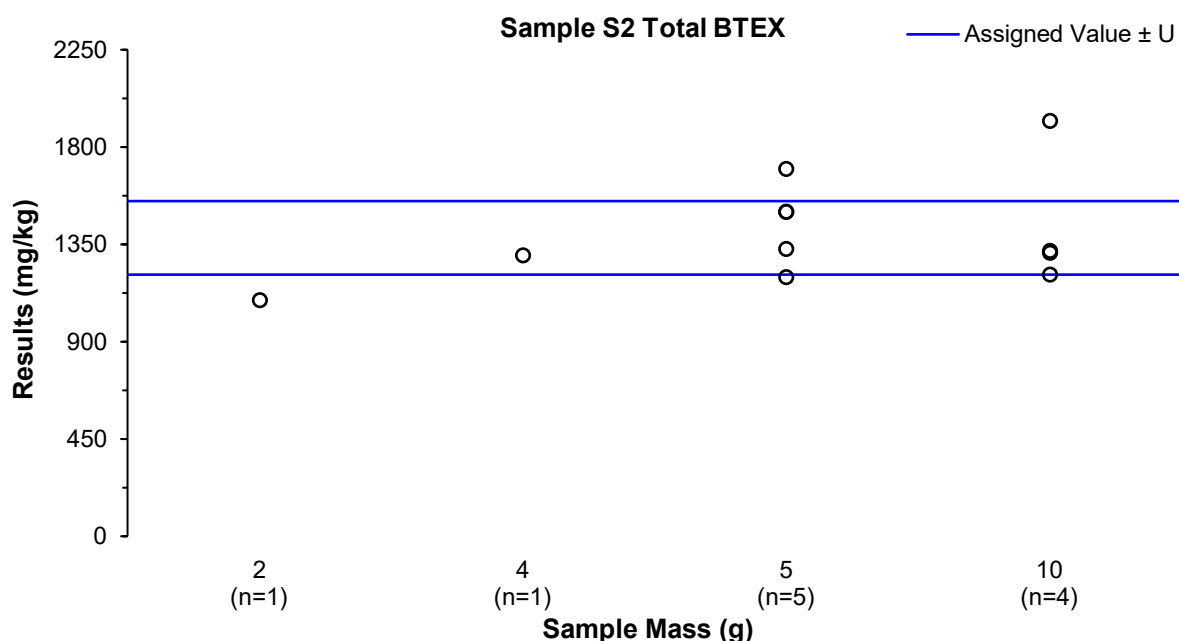


Figure 30 Sample S2 Total BTEX Results vs Sample Mass Used for Analysis

Participants used SLE, with some participants specifying that they used MA. All participants reporting numeric results for this sample reported using methanol (MeOH) as their extraction solvent, except for one participant who reported using DCM/ACE. No participant reported a clean-up step. One participant used headspace (HS) GC coupled to mass spectrometry (MS), while all other participants used purge and trap (P&T) GC-MS or GC-tandem mass spectrometry (MS/MS).

A plot of results and methodology for Total BTEX in Sample S2 is presented in Figure 31. Methodologies are listed in order of extraction technique, extraction solvent(s) and instrument. The most common methodology used to analyse BTEX in this study was SLE (MA) with MeOH, using P&T GC-MS for analysis.

Total BTEX analysis did not present a problem to laboratories' analytical techniques, with excellent agreement between reported results across a range of methodologies.

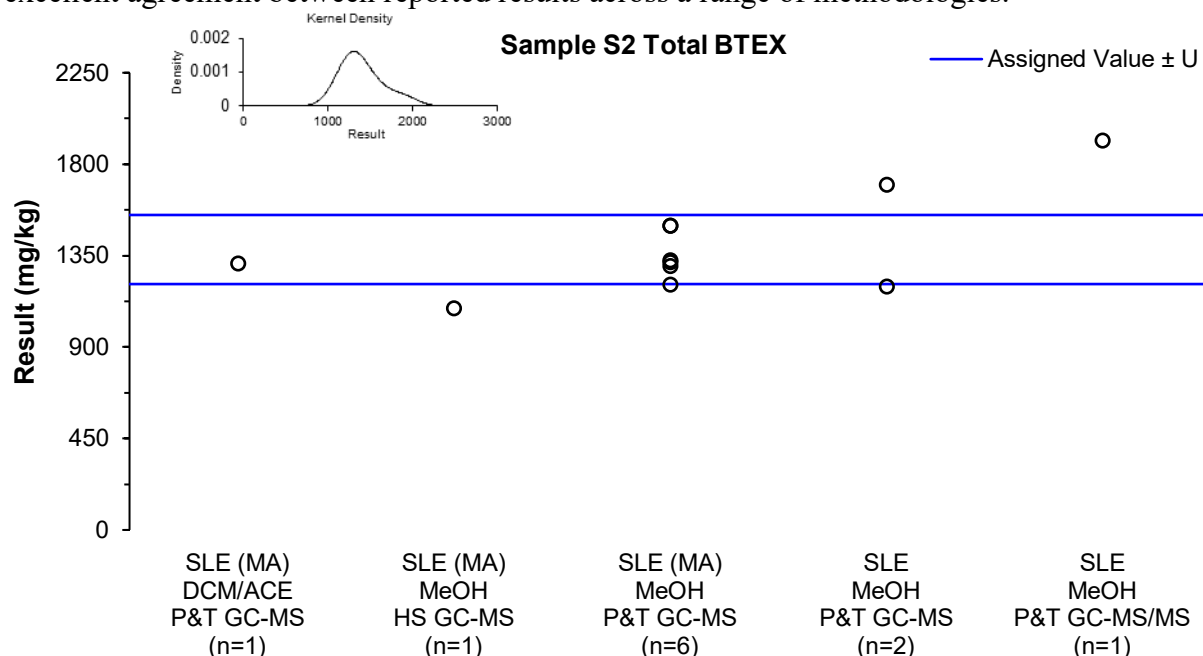
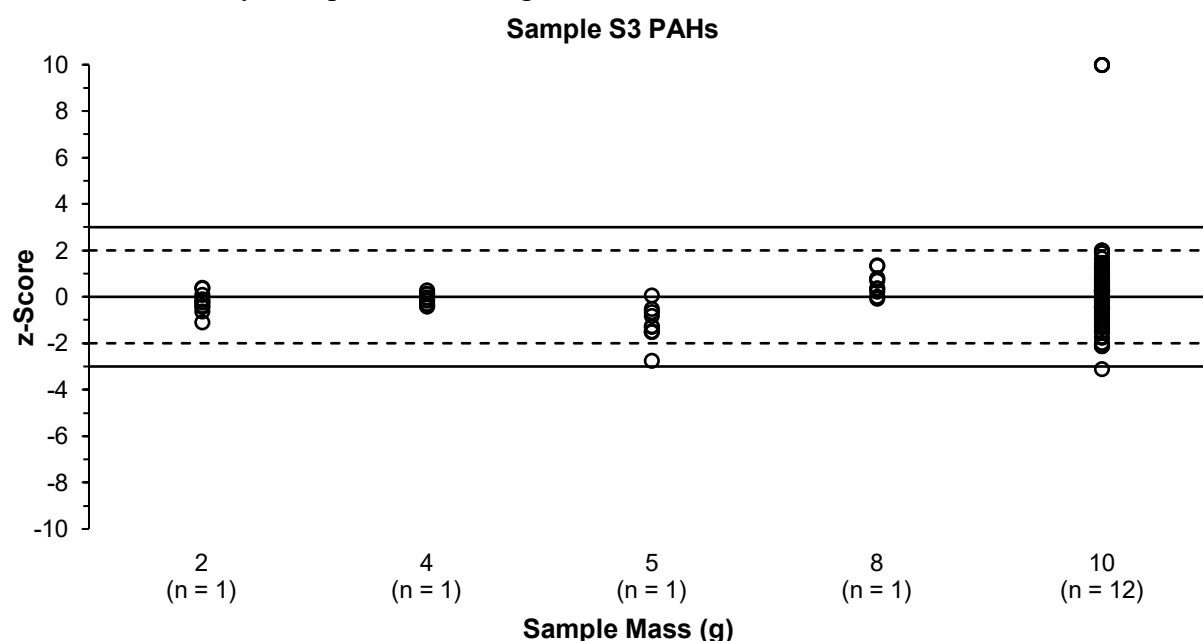


Figure 31 Sample S2 Total BTEX Results vs Methodology

PAHs

Sample S3 was a 50 g soil sample. Participants used a sample size between 2 g and 10 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 32.



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

Figure 32 Sample S3 PAHs z-Scores vs Sample Mass Used for Analysis

All participants reported using SLE, with some participants specifying that they used MA or S. Participants reported using DCM, ACE, HEX or combinations of these as the extraction solvent(s). One participant reported a silica clean-up step. All participants used GC-MS(/MS) for analysis.

A plot of z-scores obtained and methodology used for the PAHs in Sample S3 is presented in Figure 33. Methodologies are listed in order of extraction technique, extraction solvent(s), clean-up and instrument. The most common methodology used to analyse PAHs in this study was SLE (MA) with DCM/ACE as the extraction solvent, with no clean-up and using GC-MS/MS for analysis.

As discussed in Section 6.3, one participant reported four results that were significantly higher than the assigned value (z-scores were all greater than 10.0), whereas their other results returned acceptable z-scores. This participant may need to review if, for example, their calibrators were correctly prepared for those particular analytes with high unacceptable z-scores.

Generally, PAHs analysis did not present a problem to laboratories' analytical techniques, with excellent agreement between reported results across a range of methodologies.

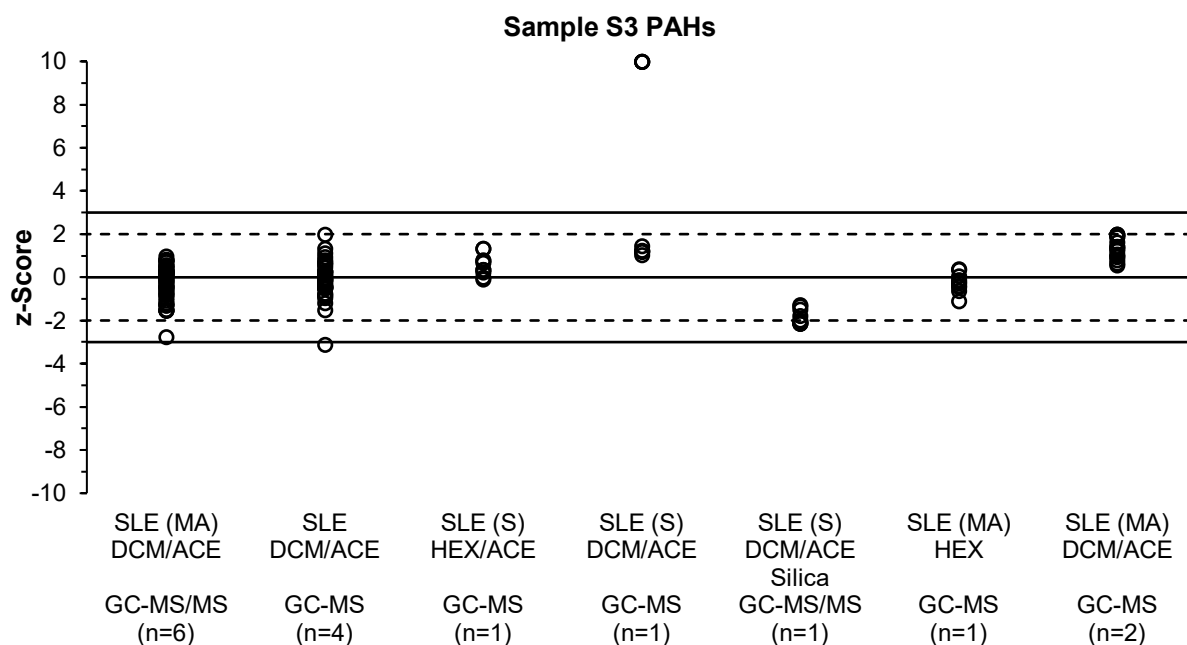


Figure 33 Sample S3 PAHs z-Scores vs Methodology

6.8 Certified Reference Materials

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

Nine participants reported using certified standards, one participant reported using matrix reference materials, and one participant reported using both. The following were reported by participants:

- NMIA MX015
- ERA, e.g. 727
- o2si
- Sigma Aldrich, e.g. CRM47993, CRM355, CRM143

- ISO 17034 traceable standards

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 30 and 31, and Figure 34.

Table 30 Summary of Participants' Results (Samples S1 and S2)*

Lab. Code	Sample S1				Sample S2			
	>C10-C16	>C16-C34	>C34-C40	TRH	Toluene	Ethylbenzene	Xylenes	Total BTEX
AV	903	1500	184	2670	499	143	669	1380
1	759.19	1722.70	186.54	2668.43	457.30	139.60	679.20	1312.70
2	933	1523	162	2618	437	133	609	1210
3	960	1700	200	2900	670	200	820	1700
4	NR	NR	NR	2884.5	190	79	336	609.7
5	NR	NR	NR	3200	424	156	734	1320
6	998.5875	1630.3125	133.7250	2762.6250	NR	NR	NR	NR
7	960	1500	160	2600	530	140	620	1500
8	NR	NR	NR	2700	333	95.3	427	865
9	850	1180	<100	2030	810	190	900	1920
10	830	1400	200	2500	600	140	650	1500
11	773	1391	193	2357	519	132	647	1330
13	811	1144	135	2090	420	116	542	1092
14	980	1800	250	3100	440	140	680	1300
15	880	1600	200	2700	540	120	550	1200
16	1089	1597	237	2923	327	81.5	326	759.5
17	940	1350	150	2440	229	91	311	635

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

Table 31 Summary of Participants' Results (Sample S3)*

Lab. Code	Sample S3									
	Acenaphthene	Anthracene	Benz[a]anthracene	Benzo[a]pyrene	Benzo[b]fluoranthene	Chrysene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
AV	1.40	1.25	1.01	1.05	2.62	0.802	0.516	0.322	1.07	0.609
SV	1.89	2.30	1.36	1.68	3.96	1.15	0.628	0.421	1.36	0.736
1	1.45	1.22	0.95	1.02	2.83	0.84	0.56	<0.5	1.11	0.68
2	1.48	1.01	1.05	< 0.5	2.71	0.92	0.58	< 0.5	1.14	0.66
3	1.3	1.1	0.9	0.9	2.7	0.7	0.4	0.3	1	0.5
4	1.45	1.5	1	1.05	3.15	0.845	0.57	0.34	1.2	0.68
5	1.62	1.48	2.77	2.8	7.14	2.36	0.63	0.38	1.27	0.72
6	1.3738	1.1725	1.0313	1.0475	2.7250	0.7838	0.4938	0.3275	1.0050	0.5775
7	1.4	1.4	0.92	1.1	2.9	0.81	0.53	<0.5	1.1	0.65
8	1.09	0.85	0.7	0.841	2.12	0.563	0.352	0.237	0.73	0.42
9	1.3	1.3	1.1	1.2	1.4	0.94	0.62	0.44	1.2	0.67
10	1.2	1.1	0.9	0.98	2.5	0.8	0.4	0.3	0.9	0.5
11	1.46	1.28	1.00	0.99	2.94	0.78	0.54	< 0.5	1.08	0.63
13	1.38	1.18	1.07	1.01	2.65	0.67	0.5	0.34	0.97	0.57
14	1.6	1.5	1.2	1.6	NT	1.4	0.56	<0.5	1.2	0.67
15	1.5	1.3	1.0	1.1	2.9	0.8	0.5	0.3	1.0	0.6
16	1.13	0.97	1.02	0.92	1.54	0.74	0.4	0.29	0.87	0.47
17	1.7	1.6	1.3	1.6	7.9	1	0.6	<0.5	1.3	0.7

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

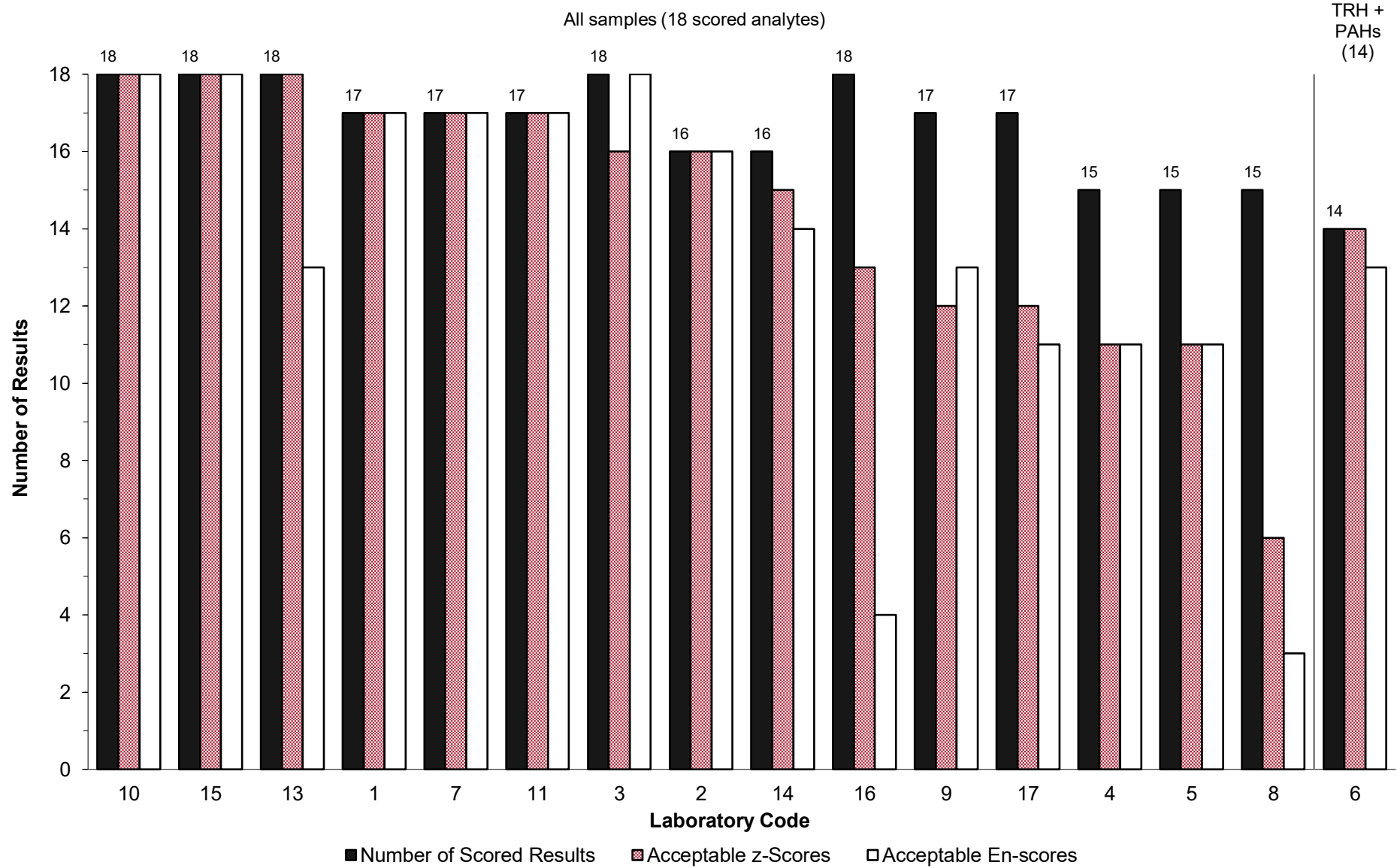


Figure 34 Summary of Participants' Performance

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 for proficiency assessment 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 $|z| \leq 2.0$. 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 acceptable performance (presented as a percentage of the total number of scores) obtained by participants for TRH in soil over the last 10 studies (2016 – 2025) is presented in Figure 35. Over this period, the average proportion of acceptable z -scores was 93%, and the average proportion of acceptable E_n -scores was 76%. For the last two studies, a high proportion of TRH results achieved acceptable z -scores, however the proportion of acceptable E_n -scores was lower; participants may need to review their uncertainties to ensure that they are not underestimating them.

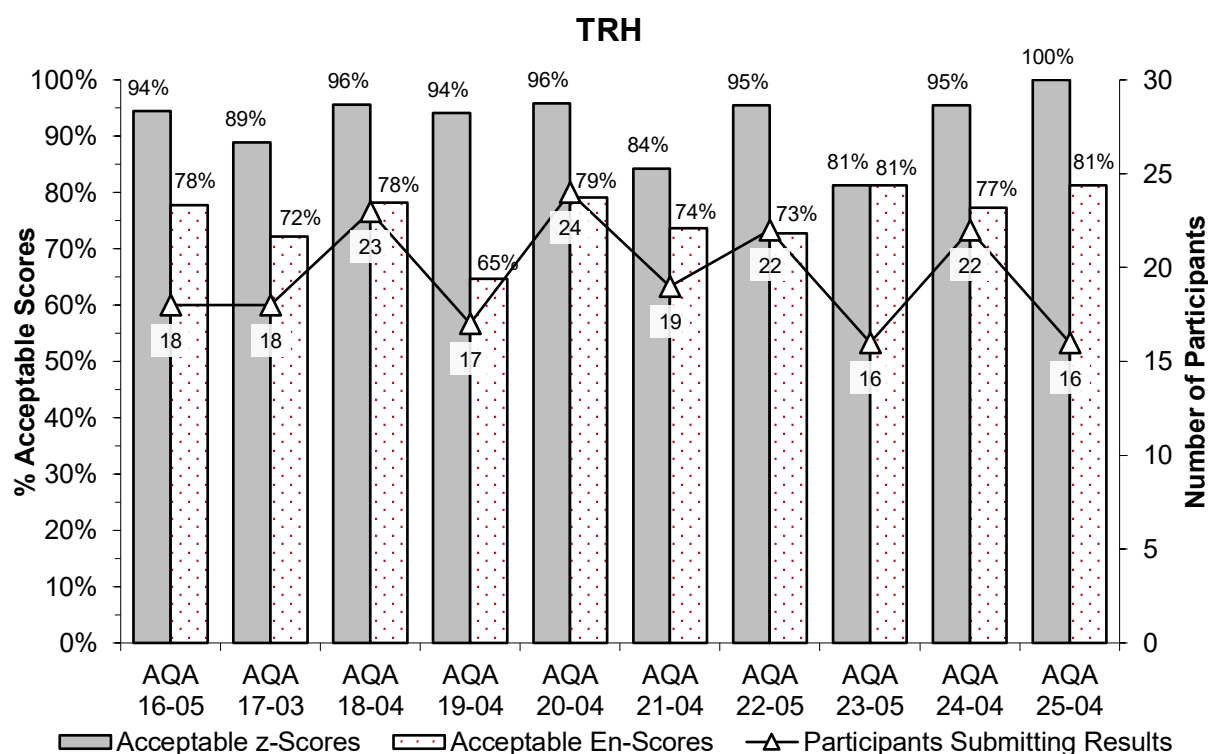


Figure 35 Participants' Performance for TRH in Hydrocarbons in Soil PT Studies

Total BTEX

A summary of the acceptable performance (presented as a percentage of the total number of scores) obtained by participants for Total BTEX in soil over the last 10 studies (2016 – 2025) is presented in Figure 36. Over this period, the average proportion of acceptable z -scores was 84%, and the average proportion of acceptable E_n -scores was 79%. Fewer participants returned acceptable z -scores and E_n -scores for this study as compared to previous studies.

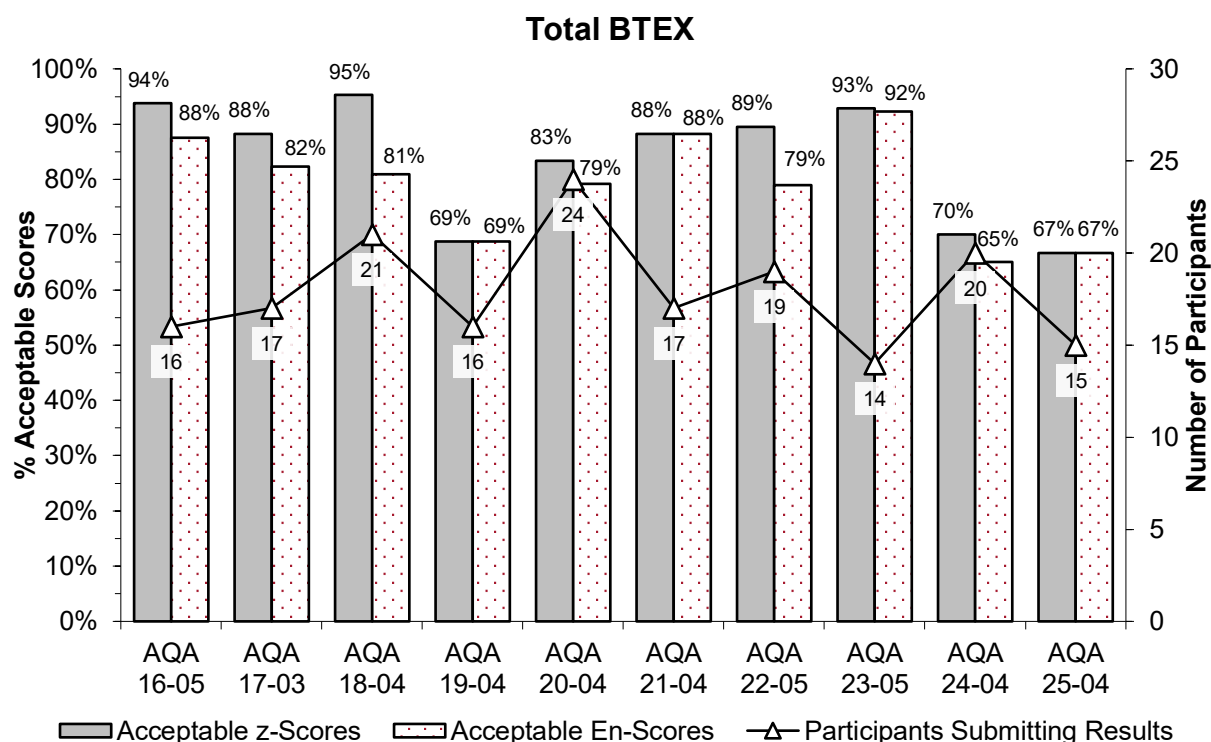


Figure 36 Participants' Performance for Total BTEX in Hydrocarbons in Soil PT Studies

PAHs

A summary of the acceptable performance (presented as a percentage of the total number of scores) obtained by participants for PAHs in soil over the last 10 studies (2016 – 2025) is presented in Figure 37. Over this period, the average proportion of acceptable z-scores was 91%, and the average proportion of acceptable E_n -scores was 86%.

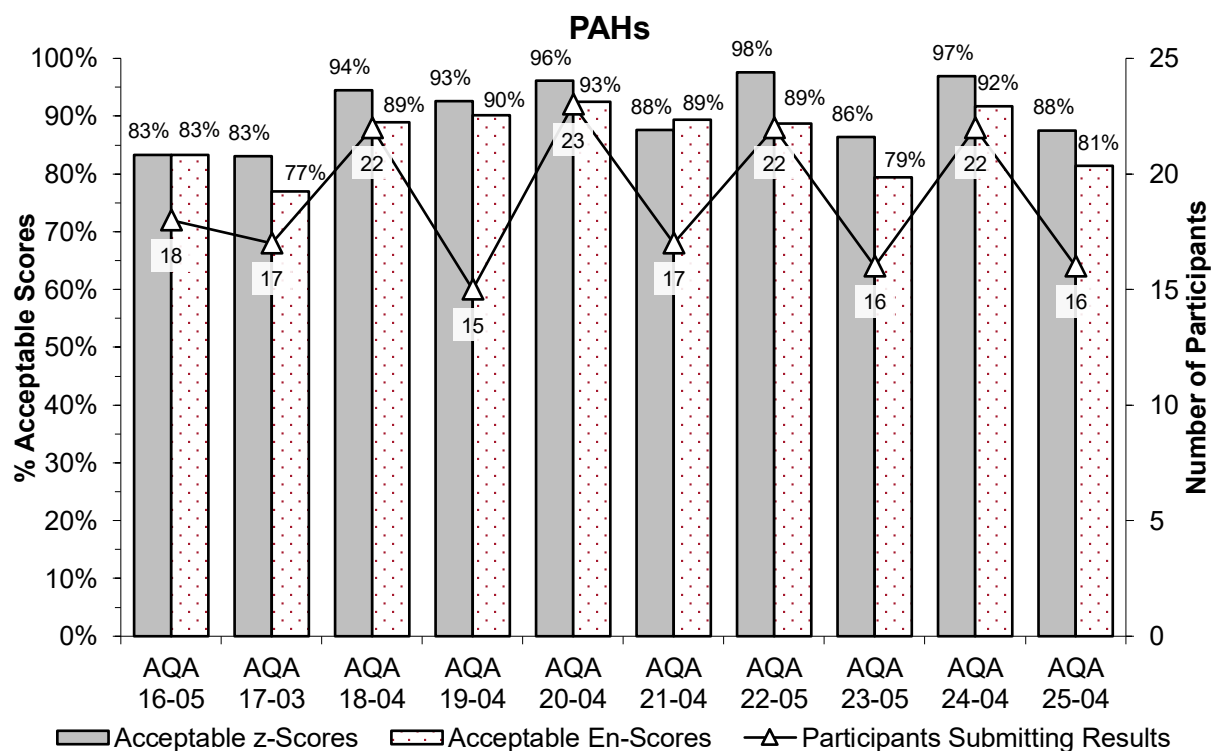


Figure 37 Participants' Performance for PAHs in Hydrocarbons in Soil PT Studies

A plot of the robust average expressed as a percentage of the spiked value for PAHs in garden soil (which was used for this study) and topsoil since 2016 is presented in Figure 38. Results from samples with other matrices have not been included as it has been previously seen that the nature of the matrix can substantially affect the recovery of some analytes.¹³

For all spiked PAHs in this study, the robust averages were lower than the spiked values, consistent with previous studies.

Throughout NMIA Hydrocarbons in Soil PT studies, anthracene and benzo[*a*]pyrene have consistently had lower results reported by participants as compared to the spiked values, averaging 51% and 49% respectively for the robust average to spiked value. A relatively high robust average to spiked value was achieved by participants in this study for benzo[*a*]pyrene (65%) as compared to previous studies.

This was the first study to include benzo[*b*]fluoranthene as a spiked analyte, and the robust average to spiked value ratio for this analyte was 67%.

For all other PAHs, the average of robust averages to spiked values for the other PAHs ranged from 76% to 85%.

The ratio of robust averages to spiked values were slightly lower than the average of previous studies for most analytes. This may have been affected by the garden soil matrix used.

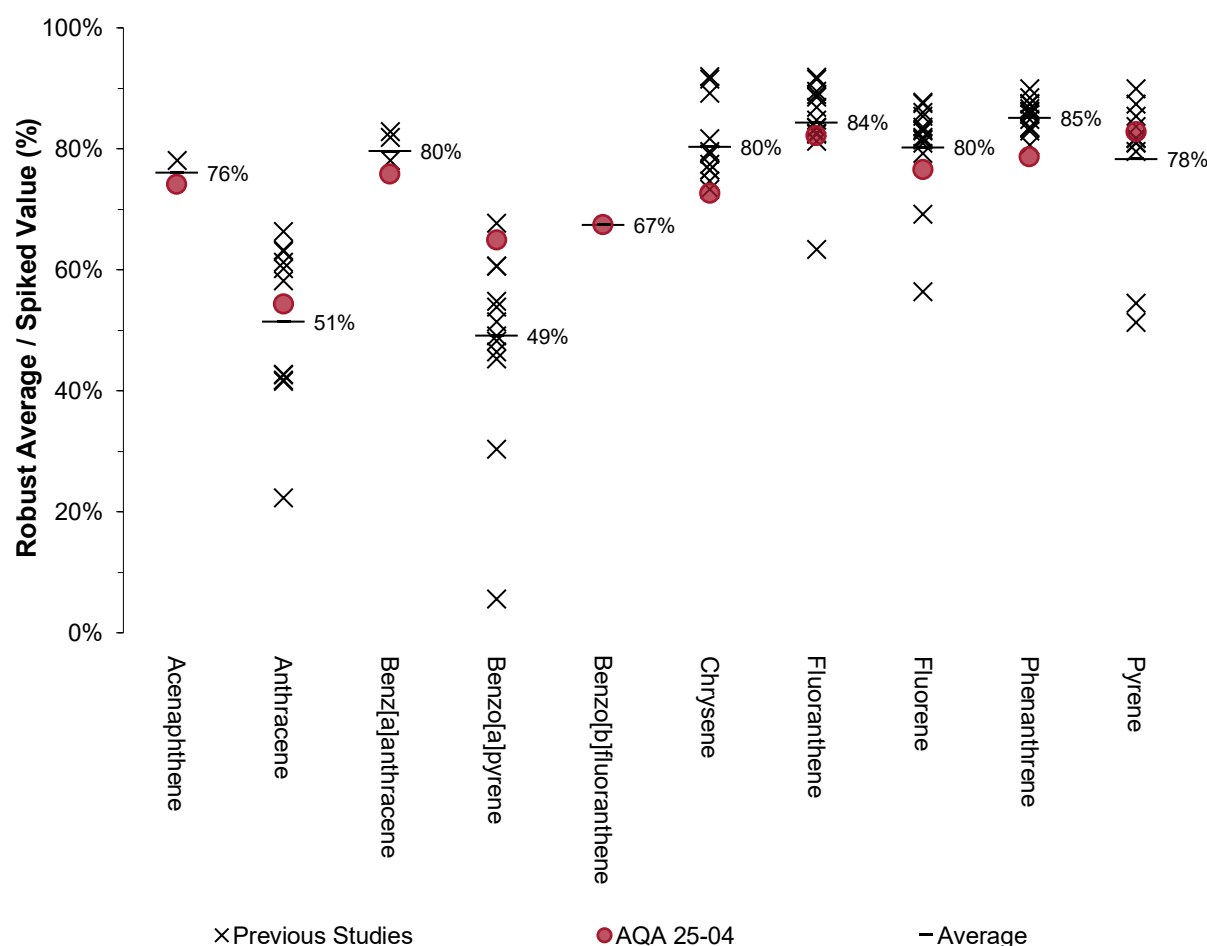


Figure 38 Recoveries of PAHs in Topsoil for Hydrocarbons in Soil PT Studies

As discussed in Section 6.2, it is a requirement of ISO/IEC 17025 that laboratories report their uncertainties.⁹ Figure 39 presents a summary of the relative uncertainties as reported by participants over the last 10 studies (2016 – 2025). Over this time, the vast majority of numeric results were reported with uncertainties (95%), with on average 92% of participants

reporting that they were accredited to ISO/IEC 17025. Most participants over this time period reported relative expanded uncertainties between 15% and 50%, however around 14% of relative uncertainties were outside this range, and may have been unrealistically small or too large to be fit-for-purpose.

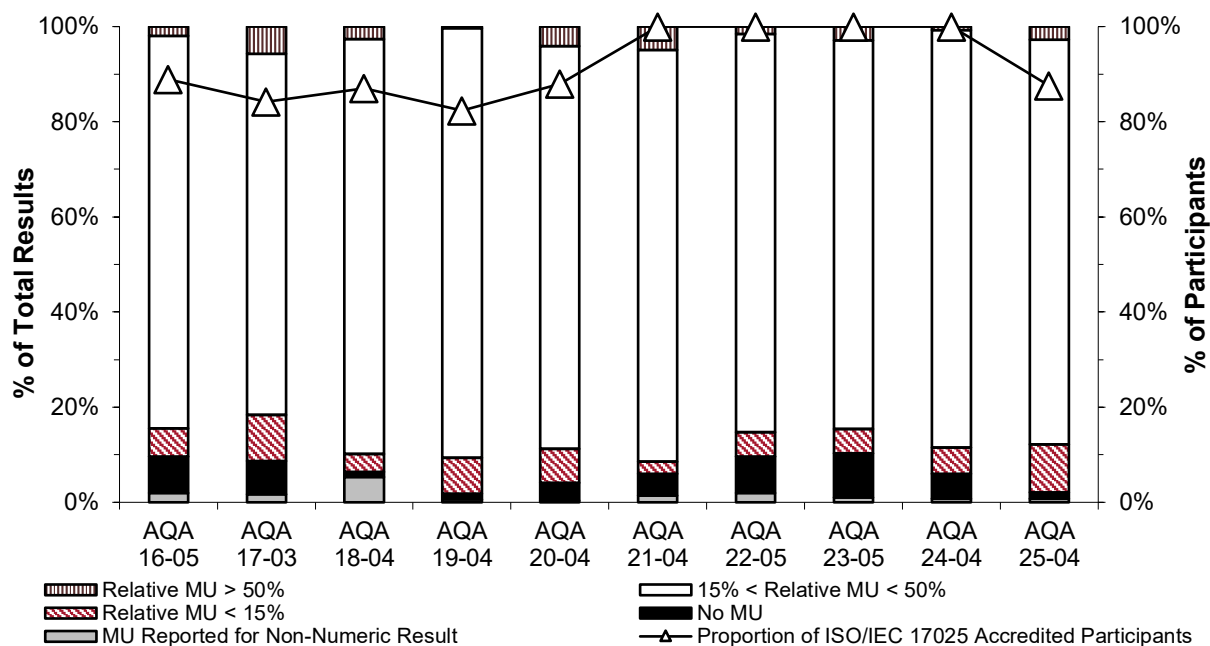


Figure 39 Summary of Participants' Relative Uncertainties for NMIA Hydrocarbons in Soil PT Studies

7 REFERENCES

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

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- [2] Commonwealth of Australia, Department of Industry, Science and Resources, NMIA, 2024, *Study Protocol for Proficiency Testing*, viewed July 2025, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.
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- [11] US EPA, 2018, *Method 8270E: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Revision 6, viewed July 2025, <https://www.epa.gov/sites/default/files/2020-10/documents/method_8270e_update_vi_06-2018_0.pdf>
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- [13] NMIA, 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. The diesel was analysed to confirm that essentially all the hydrocarbons eluting before C₁₀ had been removed. This same treated diesel fuel was used in previous NMI Hydrocarbon PTs.

A1.2 Test Sample Preparation

Two soils were used as the starting matrices in this study. For Sample S1, the soil used was from a Victorian farm which was ground and then sieved. For Samples S2 and S3, the soil used was from a farm in New South Wales which was dried and then sieved.

Sample S1: Soil was placed into a stainless-steel pot, suspended in solvent, spiked with sparged diesel and hydraulic fluid, and then mixed. After evaporation of the solvent, the spiked soil was divided into 40 samples and transferred into amber glass jars. Each sample was labelled, shrink-wrapped and stored in a refrigerator at 4 °C until dispatch.

Sample S2: Soil was placed in a stainless-steel drum with a clamp-locked lid and cooled in a freezer. The soil was spiked with unleaded petroleum and diesel and then tumbled. In an open freezer, the soil was scooped into glass jars and topped up to minimise the vapour space. Each sample was labelled, sealed with Parafilm, shrink-wrapped and stored in a freezer at -20 °C until dispatch.

Sample S3: Soil was placed into a round bottom flask, suspended in solvent, spiked with PAHs, and then mixed. After evaporation of the solvent, the soil was diluted with clean soil and then mixed. The soil was then divided into 40 samples and transferred into amber glass jars. Each sample was labelled, shrink-wrapped and stored in a refrigerator at 4 °C until dispatch.

APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce sufficiently homogeneous samples.

The results of this study also gave no reason to question the samples' homogeneity. Comparisons of results to container number for scored analytes are presented in Figures 40 to 51 (solid blue lines correspond to the assigned value \pm U for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5, or if that participant was sent more than one container for that sample). No significant fill order trend was observed.

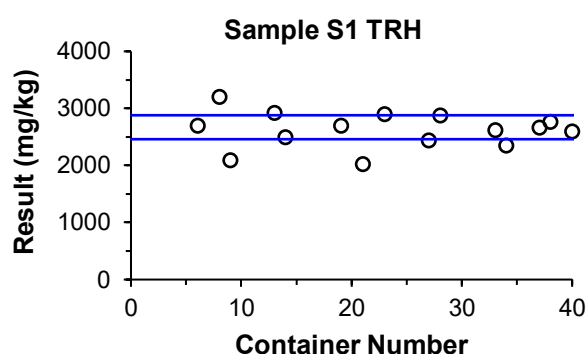


Figure 40 S1 TRH Results vs Container Number

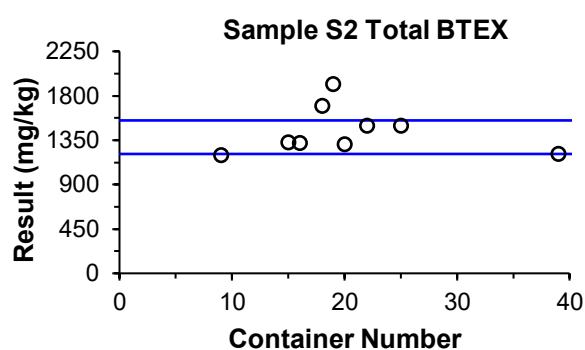


Figure 41 S2 Total BTEX Results vs Container Number

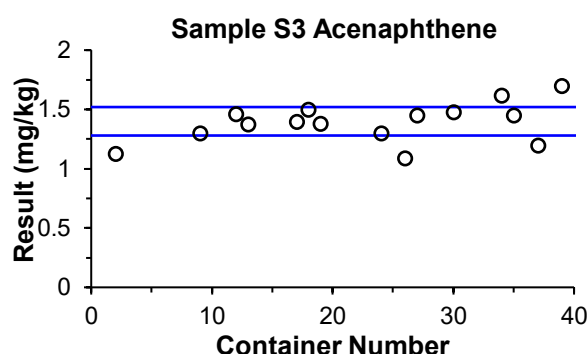


Figure 42 S3 Acenaphthene Results vs Container Number

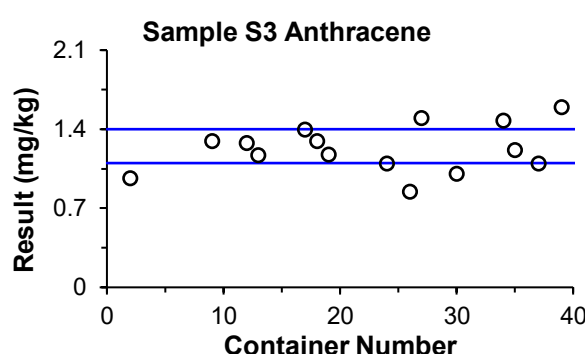


Figure 43 S3 Anthracene Results vs Container Number

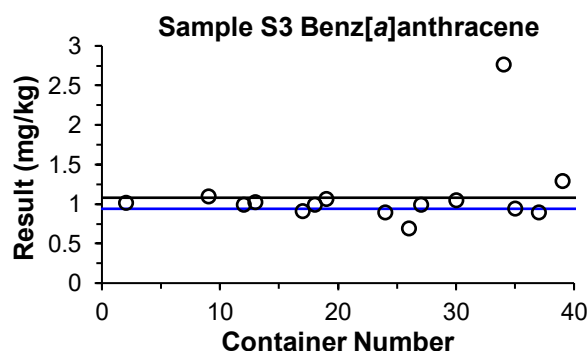


Figure 44 S3 Benz[a]anthracene Results vs Container Number

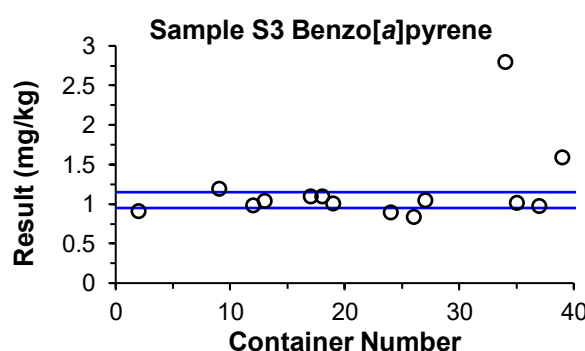


Figure 45 S3 Benzo[a]pyrene Results vs Container Number

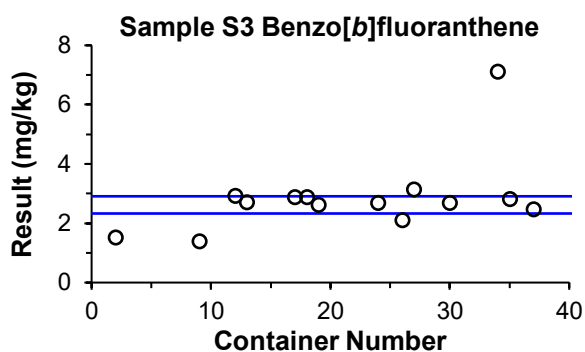


Figure 46 S3 Benzo[b]fluoranthene Results vs Container Number

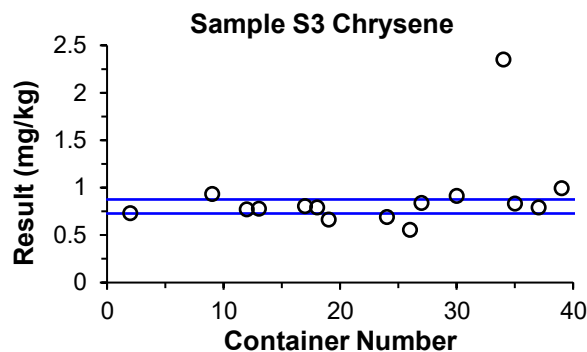


Figure 47 S3 Chrysene Results vs Container Number

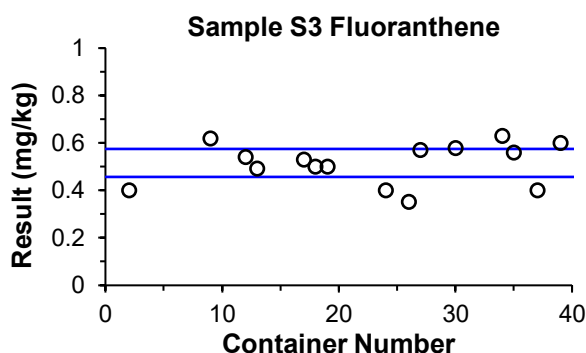


Figure 48 S3 Fluoranthene Results vs Container Number

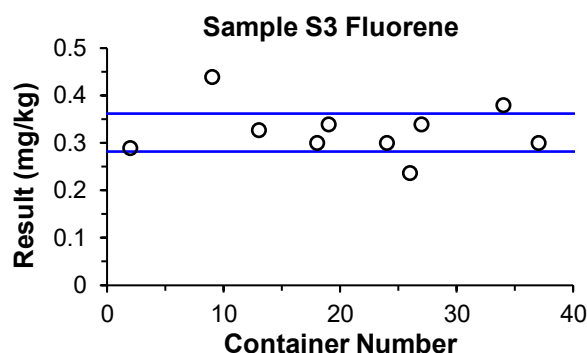


Figure 49 S3 Fluorene Results vs Container Number

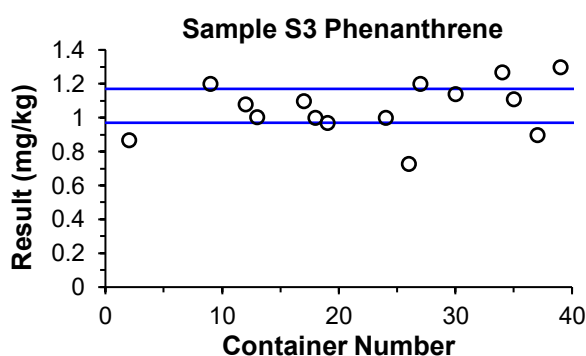


Figure 50 S3 Phenanthrene Results vs Container Number

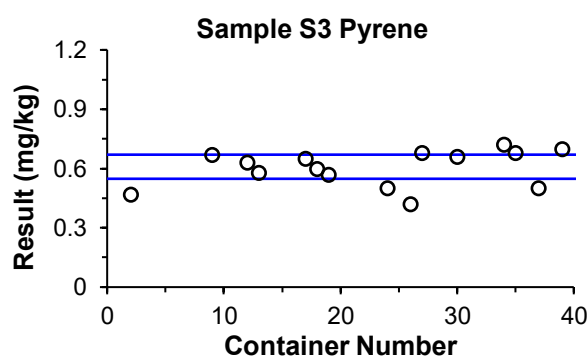


Figure 51 S3 Pyrene Results vs Container Number

A2.2 Stability

No stability testing was completed for this study as the samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples for similar analytes and matrices over a similar time frame. After preparation and before dispatch, Samples S1 and S3 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.

The results of this study also gave no reason to question the samples' transportation stability. Comparisons of results to days spent in transit for scored analytes are presented in Figures 52 to 63 (solid blue lines correspond to the assigned value \pm U for each analyte; results have not been included here if they were excluded from all statistical calculations in Section 5). No significant trend was observed.

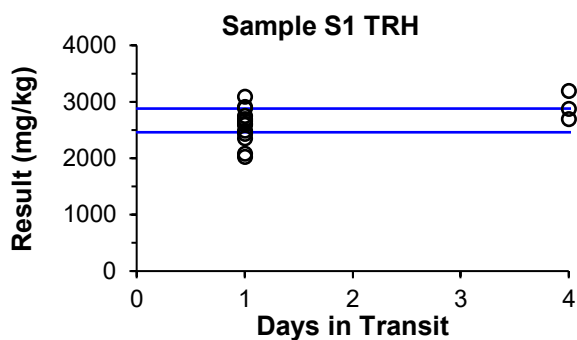


Figure 52 S1 TRH Results vs Transit Days

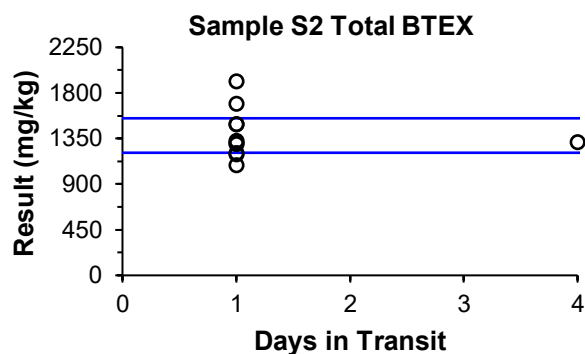


Figure 53 S2 Total BTEX Results vs Transit Days

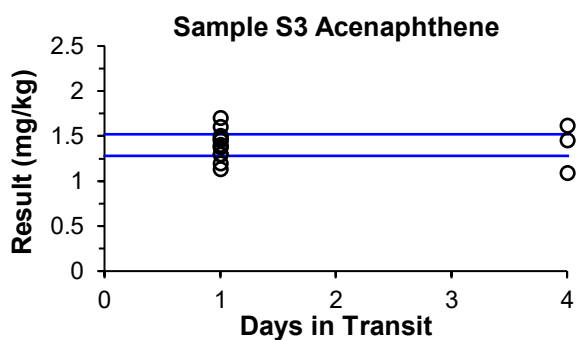


Figure 54 S3 Acenaphthene Results vs Transit Days

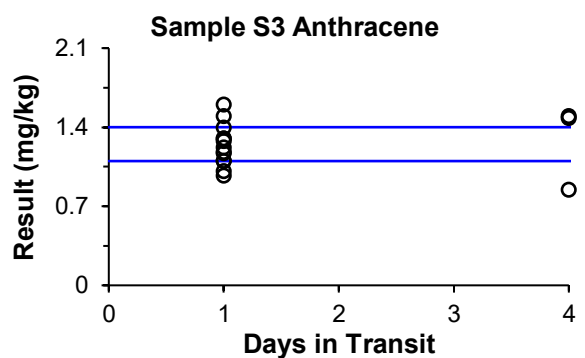


Figure 55 S3 Anthracene Results vs Transit Days

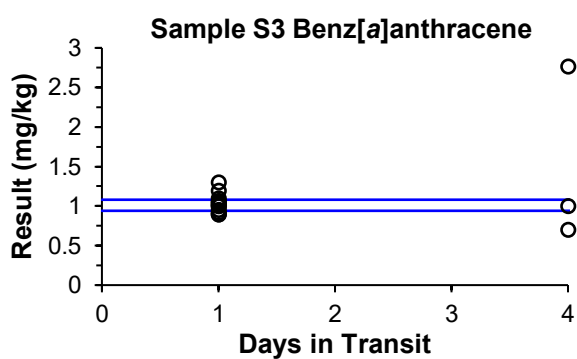


Figure 56 S3 Benz[a]anthracene Results vs Transit Days

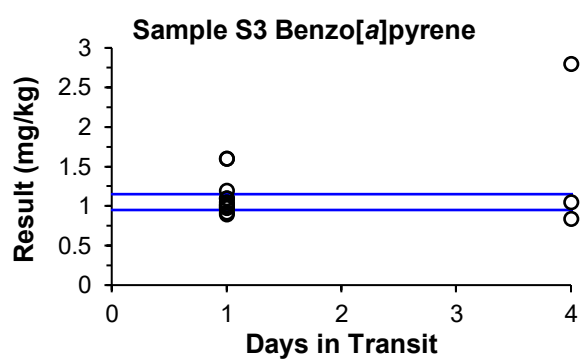


Figure 57 S3 Benzo[a]pyrene Results vs Transit Days

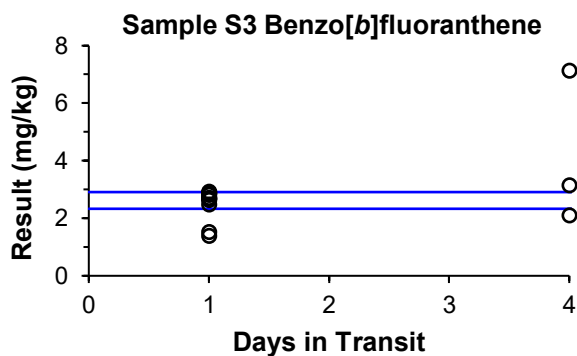


Figure 58 S3 Benzo[b]fluoranthene Results vs Transit Days

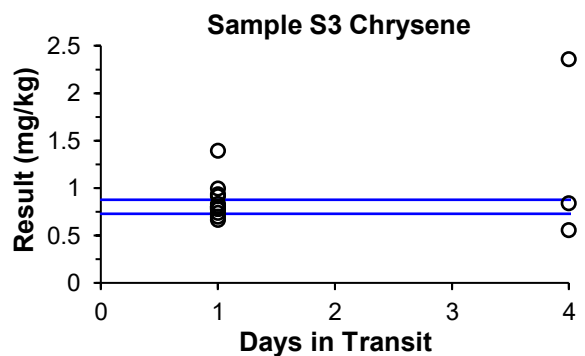


Figure 59 S3 Chrysene Results vs Transit Days

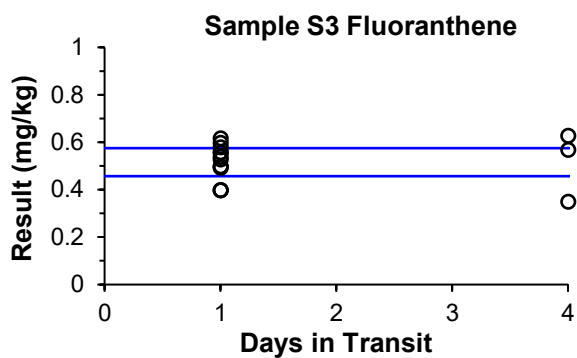


Figure 60 S3 Fluoranthene Results vs Transit Days

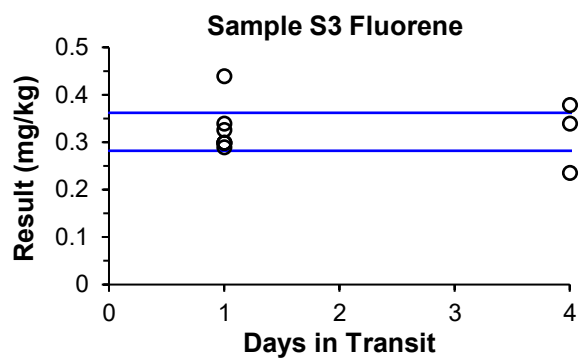


Figure 61 S3 Fluorene Results vs Transit Days

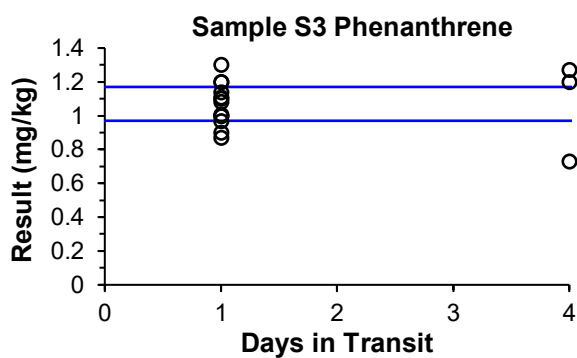


Figure 62 S3 Phenanthrene Results vs Transit Days

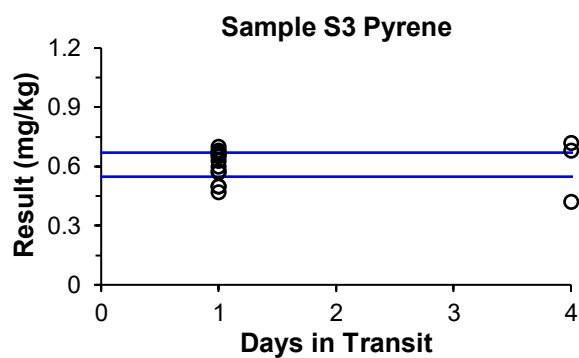


Figure 63 S3 Pyrene Results vs Transit Days

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 evaluated as according to Equation 4.

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

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 32.

Table 32 Uncertainty of the Robust Average for Sample S3 Acenaphthene

No. Results (p)	16
Robust Average	1.40 mg/kg
$S_{rob\ av}$	0.19 mg/kg
$u_{rob\ av}$	0.06 mg/kg
k	2
$U_{rob\ av}$	0.12 mg/kg

Therefore, the robust average for Sample S3 acenaphthene is 1.40 ± 0.12 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 33.

Table 33 z-Score and E_n -Score Calculation for Sample S3 Acenaphthene Result Reported by Laboratory 1

Participant Result (mg/kg)	Assigned Value (mg/kg)	Target SD	z-Score	E_n -Score
1.45 ± 0.44	1.40 ± 0.12	15% as PCV, or: $0.15 \times 1.40 =$ 0.21 mg/kg	$z = \frac{1.45 - 1.40}{0.21}$ $= 0.24$	$E_n = \frac{1.45 - 1.40}{\sqrt{0.44^2 + 0.12^2}}$ $= 0.11$

APPENDIX 4 TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 34 to 36. Some responses may be modified so that the participant cannot be identified.

Table 34 Test Methods Sample S1 TRH

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone	none	GC-FID	USEPA 8260
2	10	Solid-Liquid (Mechanical Agitation)	DCM/ACETONE	NO	GC-FID	USEPA 8015
3	10	Solid-Liquid	DCM:Acetone	None	GC-FID	USEPA 3510
4	8	Solid-Liquid (Sonication)	Hexane:Acetone	Silica	GC-FID	
5	10	Solid-Liquid (Sonication)	dcm	Silica	GC-FID	In house
6	4	Solid-Liquid	DCM/Acetone	NIL	GC-FID	In house
7	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone		GC-FID	
8	10	Solid-Liquid (Sonication)	DCM:Acetone 1:1	Silica	GC-FID	USEPA 8015
9	10	Solid-Liquid	DCM/Acetone	None	GC-FID	USEPA 8270C
10	10	Solid-Liquid (Mechanical Agitation)	DCM:Acetone	None	GC-FID	USEPA 8015
11	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone	None	GC-FID	USEPA 8260
13	2	Solid-Liquid (Mechanical Agitation)	Hexan:Pentane		GC-FID	NEPM
14	10	Solid-Liquid (Mechanical Agitation)	Acetone:DCM		GC-FID	NEPM schedule
15	10	Solid-Liquid	DCM:Acetone	None	GC-FID	USEPA 3510
16	5	Solid-Liquid (Mechanical Agitation)	DCM:Acetone	x	GC-FID	USEPA 8015
17	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone	None	GC-FID	NEPM

Table 35 Test Methods Sample S2 BTEX

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone	none	P&T GC-MS	USEPA 8260
2	10	Solid-Liquid (Mechanical Agitation)	METHANOL	NO	P&T GC-MS	USEPA 8260
3	5	Solid-Liquid	Methanol	None	P&T GC-MS	USEPA 8260
4	10		Methanol	N/A	Headspace GC-MS/MS	
5	10	Solid-Liquid (Mechanical Agitation)	MeOH	None	P&T GC-MS	USEPA 8260
6	5	Solid-Liquid	METHANOL	NIL	P&T GC-MS/MS	In house
7	5	Solid-Liquid (Mechanical Agitation)	Methanol		P&T GC-MS	USEPA 8260
8	14	Solid-Liquid (Sonication)	Methanol	Nil	Headspace GC-MS	USEPA 8260 & 5021
9	10	Solid-Liquid	Methanol	None	P&T GC-MS/MS	USEPA 8260B
10	5	Solid-Liquid (Mechanical Agitation)	Methanol	None	P&T GC-MS	USEPA 8260
11	5	Solid-Liquid (Mechanical Agitation)	MeOH	None	P&T GC-MS	USEPA 8260
13	2	Solid-Liquid (Mechanical Agitation)	Methanol		Headspace GC-MS	USEPA 8260
14	4	Solid-Liquid (Mechanical Agitation)	Methanol		P&T GC-MS	USEPA 8260
15	5	Solid-Liquid	Methanol	None	P&T GC-MS	USEPA 8260
16	5	Solid-Liquid (Mechanical Agitation)	Methanol	x	P&T GC-MS	USEPA 8260
17	10	Solid-Liquid (Mechanical Agitation)	Methanol	None	Headspace GC-MS	USEPA 8260B NEPM

Table 36 Test Methods Sample S3 PAHs

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone	none	GC-MS/MS	USEPA 8260
2	10	Solid-Liquid (Mechanical Agitation)	DCM/ACETONE	NO	GC-MS/MS	USEPA 8270
3	10	Solid-Liquid	DCM:Acetone	None	GC-MS	USEPA 8270
4	8	Solid-Liquid (Sonication)	Hexane:Acetone	N/A	GC-MS	In-house
5	10	Solid-Liquid (Sonication)	DCM/acetone	None	GC-MS	USEPA 8270
6	4	Solid-Liquid	DCM/Acetone	NIL	GC-MS	In house
7	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone		GC-MS/MS	USEPA 8310
8	10	Solid-Liquid (Sonication)	DCM:Acetone 1:1	Silica	GC-MS/MS	USEPA8270
9	10	Solid-Liquid	DCM/Acetone	None	GC-MS	USEPA8270C
10	10	Solid-Liquid (Mechanical Agitation)	DCM:Acetone	None	GC-MS/MS	USEPA 8270
11	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone	None	GC-MS/MS	USEPA 8260
13	2	Solid-Liquid (Mechanical Agitation)	Hexane		GC-MS	USEPA 8270
14	10	Solid-Liquid (Mechanical Agitation)	Acetone:DCM		GC-MS	USEPA 8270
15	10	Solid-Liquid	DCM:Acetone	None	GC-MS	USEPA 8270
16	5	Solid-Liquid (Mechanical Agitation)	DCM:Acetone	x	GC-MS/MS	USEPA 8270B
17	10	Solid-Liquid (Mechanical Agitation)	DCM/Acetone	None	GC-MS	USEPA 3550

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
FID	Flame Ionisation Detection
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
k	Coverage Factor
LOR	Limit Of Reporting
MA	Mechanical Agitation (SLE)
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
NMIA	National Measurement Institute Australia
NR	Not Reported
NT	Not Tested
P&T	Purge and Trap (GC)
PAH	Polycyclic Aromatic Hydrocarbon
PCV	Performance Coefficient of Variation
PENT	Pentane

PT	Proficiency Testing
RA	Robust Average
RM	Reference Material
S	Sonication (SLE)
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