Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Final Report AQA 21-04 Hydrocarbons in Soil

August 2021

ACKNOWLEDGMENTS

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

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

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

Jenny Xu

Geoff Morschel

Beth Tully

Luminita Antin

Raluca Iavetz

Manager, Chemical Reference Values

105 Delhi Road, North Ryde, NSW 2113, Australia

Phone: +61 2 9449 0178

Email: raluca.iavetz@measurement.gov.au

Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

SUMMARY 1
1 INTRODUCTION 2
1.1 NMI Proficiency Testing Program 2
1.2 Study Aims 2
1.3 Study Conduct 2
2 STUDY INFORMATION 3
2.1 Selection of Hydrocarbons 3
2.2 Study Timetable 4
2.3 Participation and Laboratory Code 4
2.4 Sample Preparation 4
2.5 Homogeneity of Samples 4
2.6 Stability of Analytes 4
2.7 Sample Storage, Dispatch and Receipt 4
2.8 Instructions to Participants 5
2.9 Interim Report 5
3 PARTICIPANT LABORATORY INFORMATION 6
3.1 Test Methods Reported by Participants 6
3.2 Basis of Participants' Measurement Uncertainty Estimates 6
3.3 Participants' Comments 7
4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS 8
4.1 Results Summary 8
4.2 Outliers and Extreme Outliers 8
4.3 Assigned Value 8
4.4 Robust Average and Robust Between Laboratories Coefficient of Variation 8
4.5 Performance Coefficient of Variation 8
4.6 Target Standard Deviation 9
4.7 z-Score 9
4.8 E_n-Score 9
4.9 Traceability and Measurement Uncertainty 9
5 TABLES AND FIGURES 10
6 DISCUSSION OF RESULTS 56
6.1 Assigned Value 56
6.2 Measurement Uncertainty Reported by Participants 57
6.3 z-Score 57
6.4 E_n-Score 64
6.5 False Negatives 64
6.6 Reporting of Additional Analytes 65
6.7 Participants' Analytical Methods 65
6.8 Certified Reference Materials (CRM) 68
6.9 Summary of Participants' Results and Performances 69
6.10 Comparison with Previous Hydrocarbons in Soil PT Studies 72
7 REFERENCES 75
APPENDIX 1 – SAMPLE PREPARATION 76

A1.1 Diesel Fuel Preparation 76
A1.2 Test Sample Preparation 76
APPENDIX 2 – TRANSPORTATION STABILITY ASSESSMENT 77
APPENDIX 3 – TEST METHODS REPORTED BY PARTICIPANTS 78
APPENDIX 4 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, Z-SCORE AND E_N-SCORE CALCULATIONS 81
A4.1 Robust Average and Associated Uncertainty 81
A4.2 z-Score and E_n-Score Calculations 81
APPENDIX 5 – ACRONYMS AND ABBREVIATIONS 82

THIS PAGE IS INTENTIONALLY BLANK

SUMMARY

AQA 21-04 Hydrocarbons in Soil commenced in March 2021. Twenty-one laboratories enrolled to participate, and twenty participants submitted results.

Four test samples were prepared at the NMI laboratory in Sydney using Menangle 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. Assigned values were the robust averages of participants' results for all scored analytes. 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 **3**, **4**, **5**, **6**, **9**, **10**, **11**, **12**, **14** and **18** reported results for all scored analytes.

Six participants did not report results for analytes that they tested for and were present in the test samples (total of 7 results). One participant reported results for analytes that were not spiked into the test samples (total of 2 results).

Of 293 z-scores, 257 (88%) returned $|z| \leq 2.0$, indicating a satisfactory performance.

Of 293 E_n-scores, 257 (88%) returned $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratories **3**, **5**, **9** and **12** returned satisfactory z-scores and E_n-scores for all scored analytes.

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

For Sample S1 TRH, various extraction techniques and solvents were reported, and all participants used GC-FID for analysis. For Sample S2 BTEX, participants reported various extraction techniques, and headspace GC-MS(MS) or purge and trap GC-MS(MS) were used for analysis. For PAHs in Samples S3 and S4, various extraction techniques and solvents were reported, and participants used either GC-MS(MS) or GC-FID 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 346 numerical results, 330 results (95%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 5.9% to 77% of the reported value.

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

Taken as a group, the performance for TRH and PAHs has been improving over the last few studies. For BTEX, participants' performance has remained fairly good.

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

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

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

Proficiency testing (PT) is 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 and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- PFAS in soil, 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 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;
- compare the performance of participants with past performance; and
- produce materials that can be used in method validation and as control samples.

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

1.3 Study Conduct

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

A list of potential polycyclic aromatic hydrocarbons (PAHs) for Samples S3 and S4 is presented in Table 1.

Table 1 List of Possible PAHs for Samples S3 and S4

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

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

Table 2 Formulated Concentrations of Samples

Sample	Analyte	Spiked Value (mg/kg)	Uncertainty (mg/kg)*
S1	>C10-C16	759	38
	>C16-C34	1420	70
	>C34-C40	266	13
	TRH	2440	120
S2	Benzene	72.6	3.6
	Toluene	615	31
	Ethylbenzene	70.3	3.5
	Xylenes	527	26
	Total BTEX	1290	60
S3	Anthracene	0.797	0.040
	Benzo(a)pyrene	1.79	0.09
	Fluoranthene	3.05	0.15
	Fluorene	2.37	0.12
	Phenanthrene	3.07	0.15
	Pyrene	0.892	0.045
S4	Anthracene	2.30	0.12
	Benzo(a)pyrene	1.30	0.07
	Fluoranthene	0.798	0.040
	Fluorene	2.61	0.13
	Phenanthrene	0.904	0.045
	Pyrene	1.99	0.10

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

2.2 Study Timetable

The timetable of the study was:

Invitation issued	4 March 2021
Samples dispatched	6 April 2021
Results due	17 May 2021
Interim report issued	21 May 2021

2.3 Participation and Laboratory Code

Twenty-one laboratories participated, and all participants were assigned a confidential laboratory code number. Twenty 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, benzo(a)pyrene, fluoranthene, fluorene, phenanthrene and pyrene.

Additional sample preparation details are provided in Appendix 1.

2.5 Homogeneity of Samples

The samples were prepared and packaged using processes from previous NMI Hydrocarbons in Soil PTs that have been demonstrated to produce homogeneous samples. No homogeneity testing was conducted for this study, and the participants' results gave no reason to question the homogeneity of the test samples.

2.6 Stability of Analytes

The storage stability of petroleum hydrocarbons in soil has been previously established.[6] No stability testing was conducted for this study. To assess possible instability, the results returned by participants were compared to the spiked values (Section 6.1). A transportation stability assessment was also made (Appendix 2).

2.7 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 foam boxes with cooler bricks and dispatched by courier on 6 April 2021.

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.

2.8 Instructions to Participants

Participants were instructed as follows:

- Report results on as received basis in units of mg/kg for the following:
  - Sample S1: Semi-volatile hydrocarbons (>C10-C40) and Total Recoverable Hydrocarbons (TRH). Use your laboratory's chosen quantitation range, and indicate what this range is. Australian NEPM fractions >C10-C16, >C16-C34 and >C34-C40 are encouraged. 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: Poly-aromatic hydrocarbons (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. This figure will be used in all statistical analysis in the study report.
- 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.
- No limit of reporting has been set for this study. Report results as you would report them to a client, applying the limit of reporting of the method used for analysis.
- Report the basis of your uncertainty estimates as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- 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 3 May 2021.

The results due date was extended to 17 May 2021 due to sample delivery delays to some participants.

2.9 Interim Report

An interim report was emailed to all participants on 21 May 2021.

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 3.

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	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
1	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
2	TRH/ PAHs	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Recoveries of SS	
	BTEX	NT			
3	All	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS	Recoveries of SS	Nata Technical Note 33
5	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
6	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
7	TRH/ BTEX	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	CRM Recoveries of SS	ISO/GUM
	PAHs	NT			
8	TRH/ BTEX	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Recoveries of SS	
	PAHs	NT			
9	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS		
10	All	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples Duplicate analysis Instrument calibration		NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
12	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM	CRM Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results

Lab. Code	Analyte	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
			Precision	Method Bias	
13	All	Top Down - precision and estimates of the method and laboratory bias	Instrument calibration	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
14	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
15	TRH/ BTEX	NT			
	PAHs	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Recoveries of SS	NATA GAG Estimating and Reporting Measurement Uncertainty of Chemical Test Results
16	All	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	CRM Recoveries of SS	
17	All	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	
18	All	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	CRM	
20	All	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Laboratory bias from PT studies Recoveries of SS Standard purity	Eurachem/CITAC Guide
21	All	Standard uncertainty based on historical data.	Duplicate analysis Instrument calibration	CRM Instrument calibration Standard purity	Eurachem/CITAC Guide
	PAHs	NT			

* 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
14	S3 and S4	Benzo(b)fluoranthene and Benzo(k)fluoranthene analysed in conjunction with Benzo(f)fluoranthene and Benzo(j)fluoranthene.
16	S1	>C10-C16 = the integration of all area counts from the end of the nC10 peak to the end of the nC16 peak. >C16-C34 = the integration of all area counts from the end of the nC16 peak to the end of the nC34 peak. >C34-C40 = the integration of all area counts from the end of the nC34 peak to the end of the nC40 peak.
18	S4	spike recovery results: acenaphthene (79.6%)
21	S2	The result entered above for "C6-C10 Hydrocarbons", is a C6-C9 result.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 27 with summary statistics: robust average, median, mean, 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 23. An example chart with interpretation guide is shown in Figure 1.

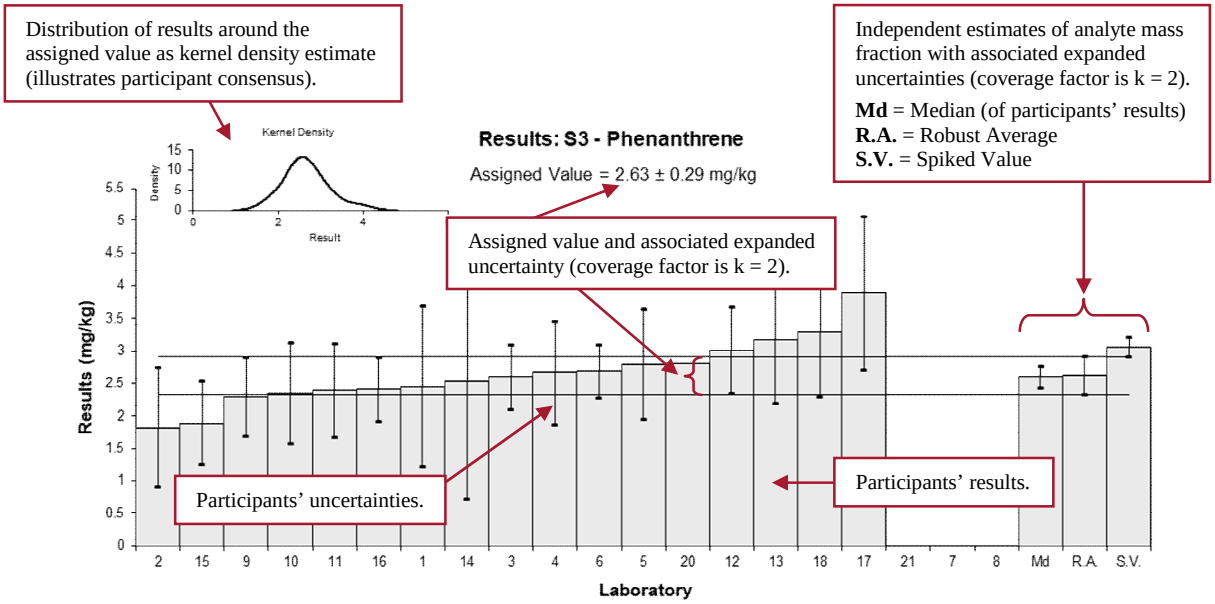


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

Outliers were results 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, if applicable, were obvious blunders, e.g. results with incorrect units, or for a different analyte or sample (gross errors), and such results were removed for 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 the participants' results and the expanded uncertainties were estimated from the associated robust standard deviations (Appendix 4).

4.4 Robust Average and Robust Between Laboratories Coefficient of Variation

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

4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between laboratories 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

The target standard deviation (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

For the absolute value of a z-score:

- $|z| \leq 2.0$ is satisfactory;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \geq 3.0$ 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;
- $|E_n| > 1.0$ 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
Units	mg/kg

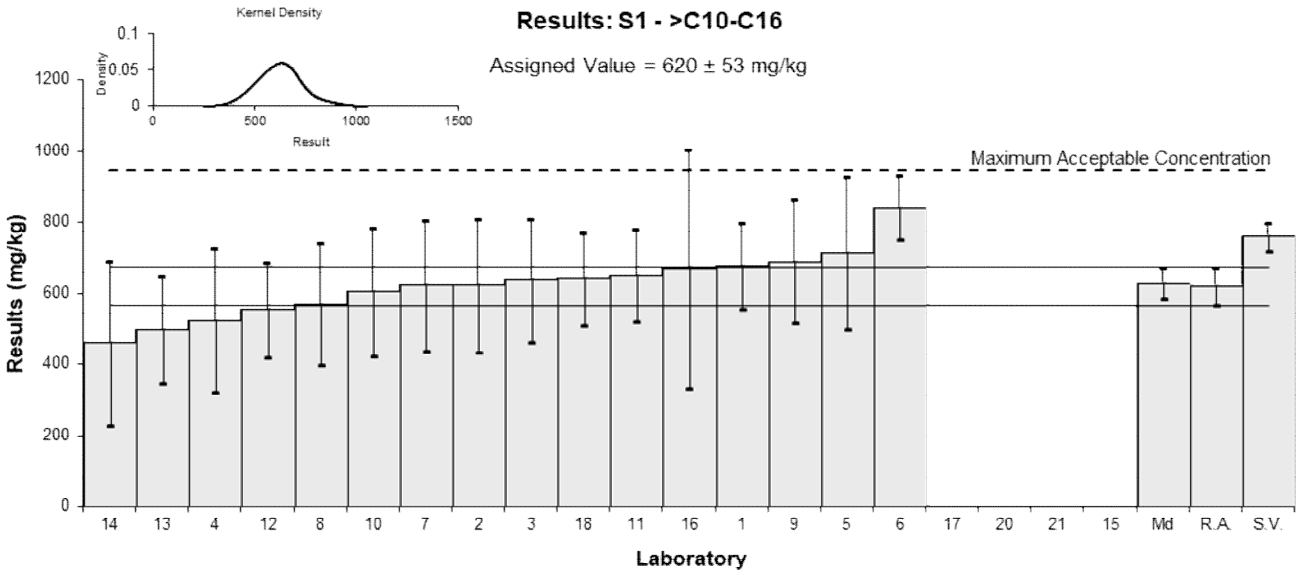
Participant Results

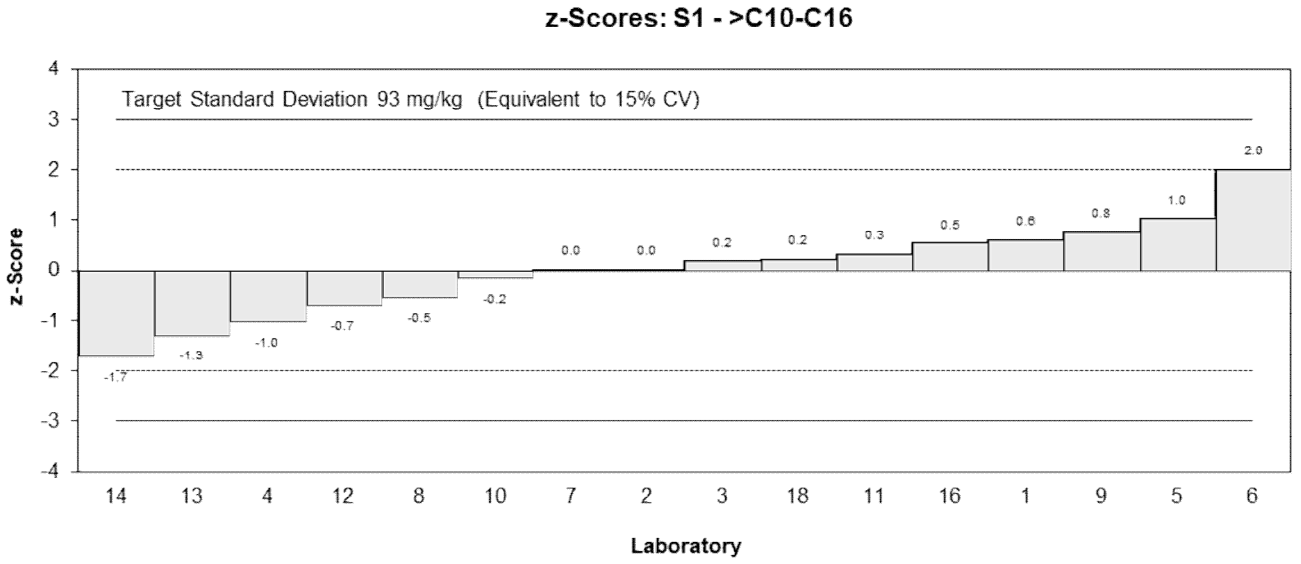
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	677	120	0.61	0.43
2	622.1	186.6	0.02	0.01
3	636.82	172	0.18	0.09
4	524	201	-1.03	-0.46
5	715	214	1.02	0.43
6*	840	90	2.00	1.00
7	622	185	0.02	0.01
8	570	171	-0.54	-0.28
9	690	173	0.75	0.39
10	604	181	-0.17	-0.08
11	650	130	0.32	0.21
12	554	133	-0.71	-0.46
13	499.18	149.75	-1.30	-0.76
14	460	230	-1.72	-0.68
15	NT	NT		
16	670	335	0.54	0.15
17	NR	NR		
18	640	128	0.22	0.14
20	NR	NR		
21	NR	NR		

Statistics

Assigned Value	620	53
Spike	759	38
Max. Acceptable Concentration*	945	
Robust Average	620	53
Median	629	42
Mean	623	
N	16	
Max.	840	
Min.	460	
Robust SD	85	
Robust CV	14%	

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


Kernel Density
Density
Result
Results: S1 - >C10-C16
Assigned Value = 620 ± 53 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
14 13 4 12 8 10 7 2 3 18 11 16 1 9 5 6 17 20 21 15 Md R.A. S.V.


z-Scores: S1 - >C10-C16
Target Standard Deviation 93 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 13 4 12 8 10 7 2 3 18 11 16 1 9 5 6
-1.7 -1.3 -1.0 -0.7 -0.5 -0.2 0.0 0.0 0.2 0.2 0.3 0.5 0.6 0.8 1.0 2.0

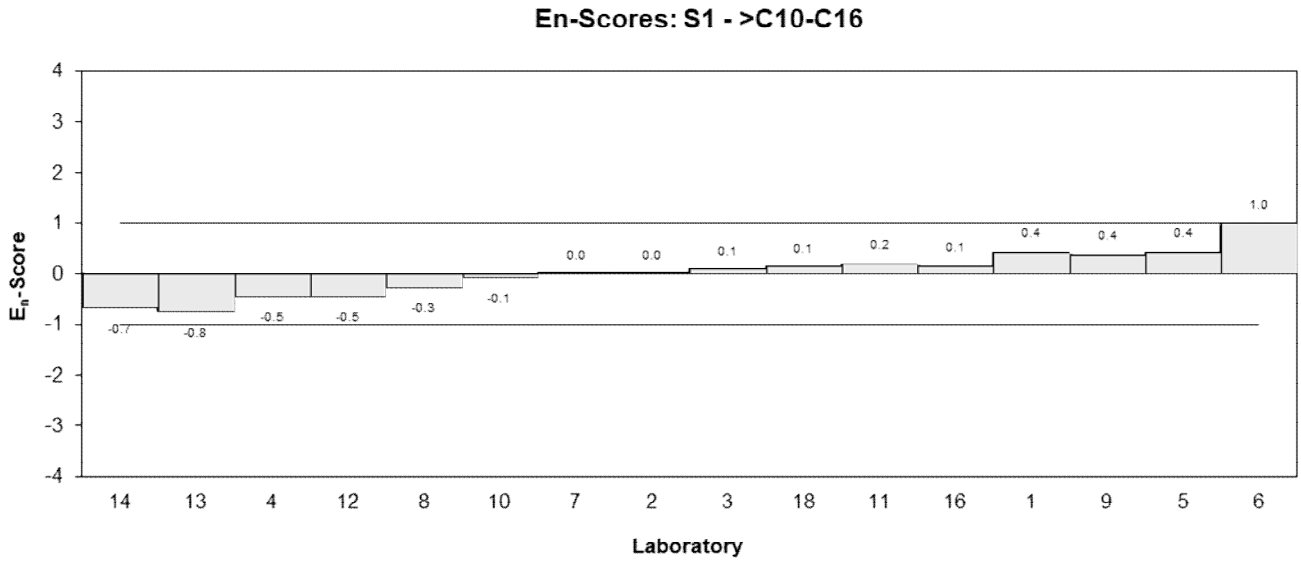

En-Scores: S1 - >C10-C16
En-Score
Laboratory
14 13 4 12 8 10 7 2 3 18 11 16 1 9 5 6
-0.7 -0.8 -0.5 -0.5 -0.3 -0.1 0.0 0.0 0.1 0.1 0.2 0.1 0.4 0.4 0.4 1.0

Figure 2

Table 6

Sample Details

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

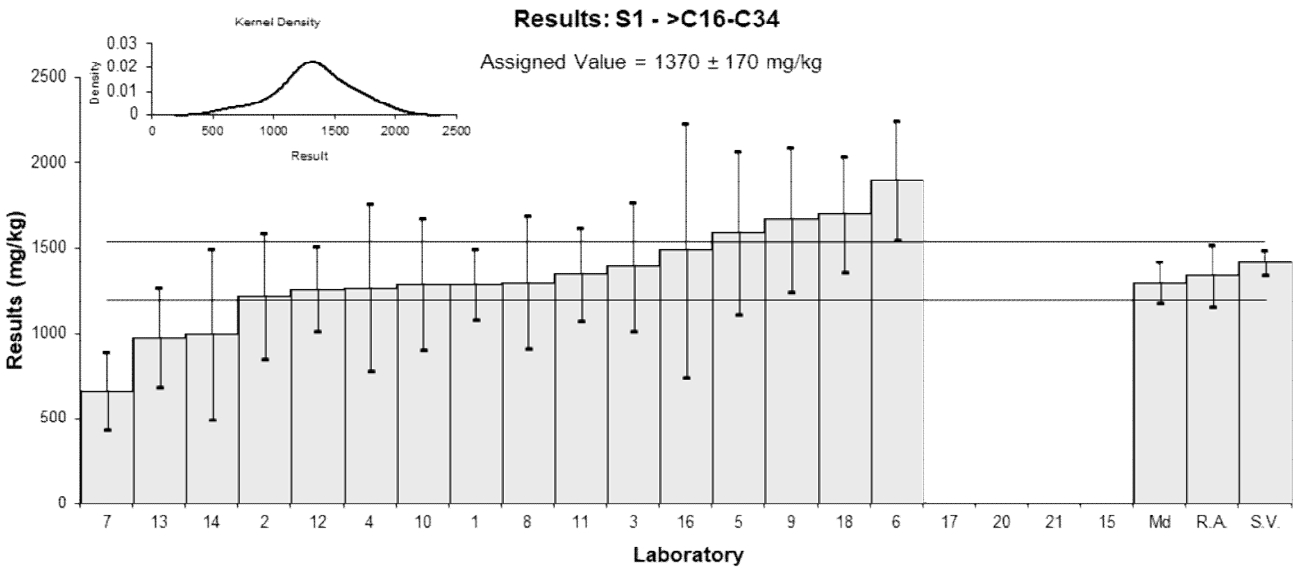
Participant Results

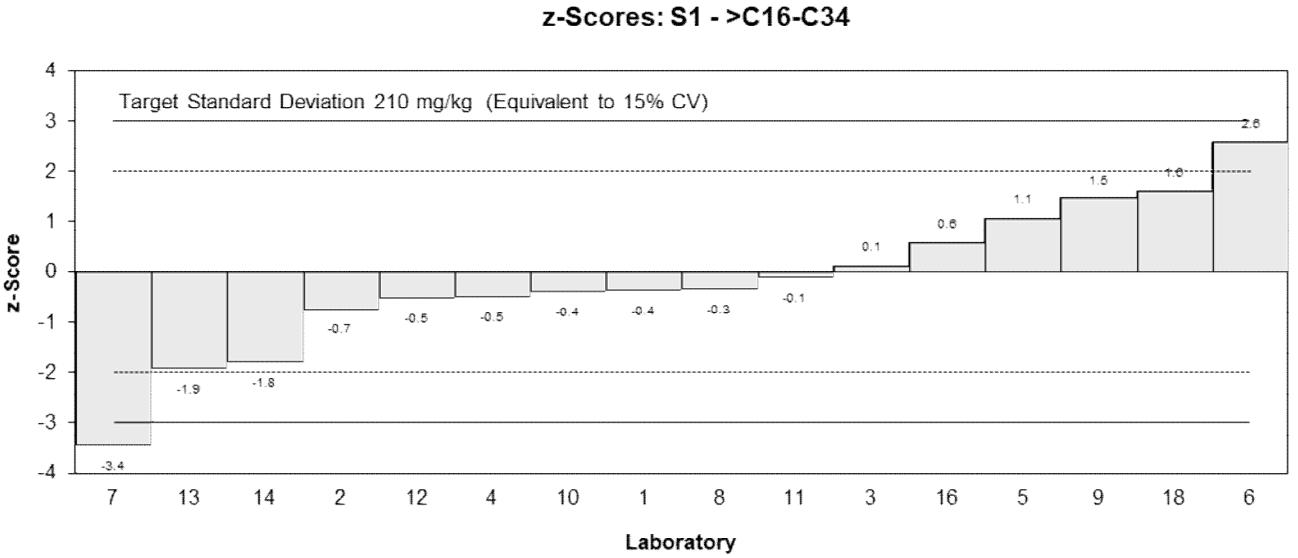
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1293	206	-0.37	-0.29
2	1218.8	365.6	-0.74	-0.38
3	1394.43	376	0.12	0.06
4	1270	488	-0.49	-0.19
5	1590	477	1.07	0.43
6	1900	350	2.58	1.36
7	662	225	-3.45	-2.51
8	1300	390	-0.34	-0.16
9	1670	418	1.46	0.66
10	1290	387	-0.39	-0.19
11	1348	269	-0.11	-0.07
12	1263	245	-0.52	-0.36
13	975.26	292.58	-1.92	-1.17
14	1000	500	-1.80	-0.70
15	NT	NT		
16	1490	745	0.58	0.16
17	NR	NR		
18	1700	340	1.61	0.87
20	NR	NR		
21	NR	NR		

Statistics

Assigned Value*	1370	170
Spike	1420	70
Robust Average	1340	180
Median	1300	120
Mean	1340	
N	16	
Max.	1900	
Min.	662	
Robust SD	290	
Robust CV	22%	

* Robust average excluding Laboratory 7.


Results: S1 - >C16-C34
Kernel Density
Density
Result
Assigned Value = 1370 ± 170 mg/kg
Results (mg/kg)
Laboratory
7 13 14 2 12 4 10 1 8 11 3 16 5 9 18 6 17 20 21 15 Md R.A. S.V.


z-Scores: S1 - >C16-C34
Target Standard Deviation 210 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
7 13 14 2 12 4 10 1 8 11 3 16 5 9 18 6
-3.4 -1.9 -1.8 -0.7 -0.5 -0.5 -0.4 -0.4 -0.3 -0.1 0.1 0.6 1.1 1.5 1.6 2.6

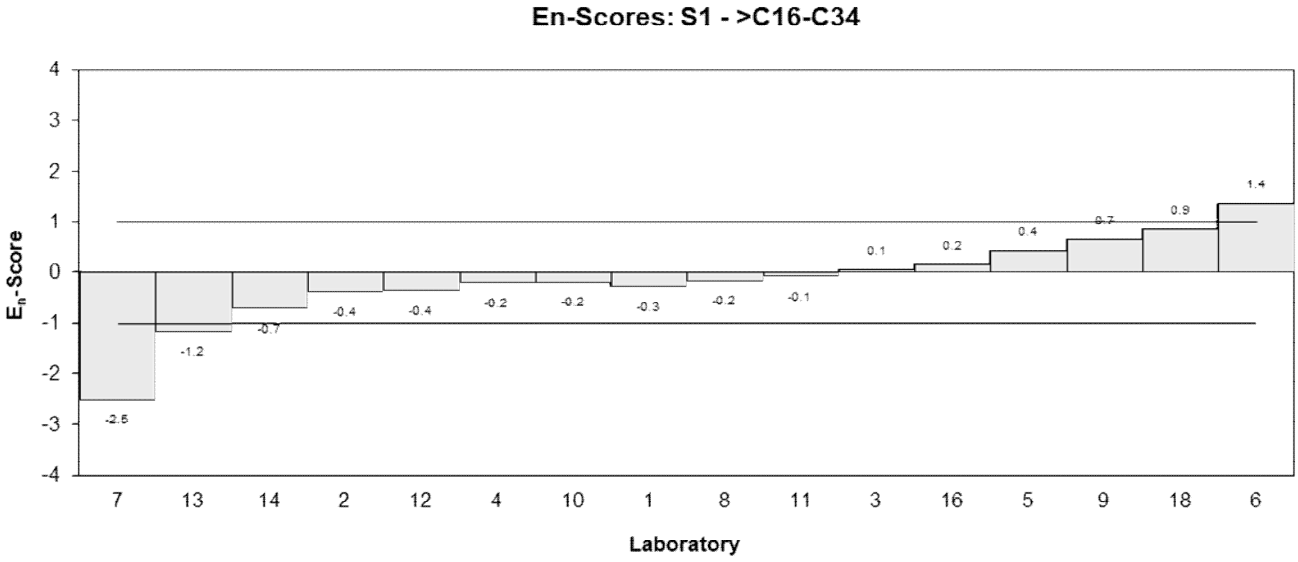

En-Scores: S1 - >C16-C34
En-Score
Laboratory
7 13 14 2 12 4 10 1 8 11 3 16 5 9 18 6
-2.5 -1.2 -0.7 -0.4 -0.4 -0.2 -0.2 -0.3 -0.2 -0.1 0.1 0.2 0.4 0.7 0.9 1.4

Figure 3

Table 7

Sample Details

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

Participant Results

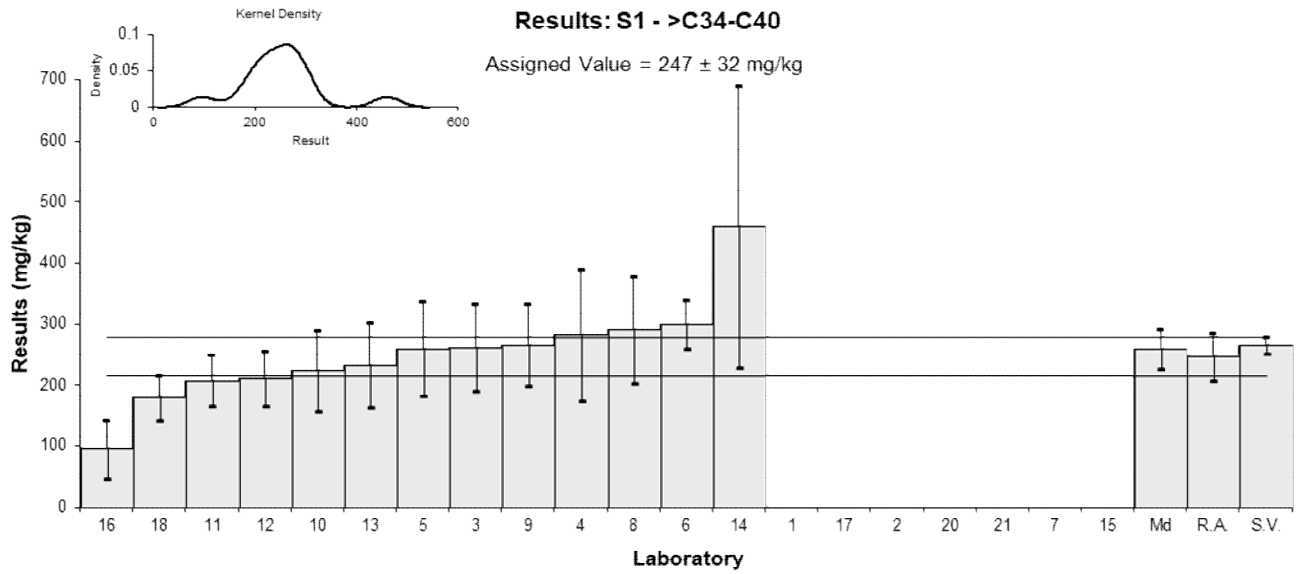
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	<50	NR		
2	NR	NR		
3	262.4	71	0.42	0.20
4	282	108	0.94	0.31
5	260	78	0.35	0.15
6	300	40	1.43	1.03
7*	NR	NR		
8	290	87.0	1.16	0.46
9	266	67	0.51	0.26
10	223	66	-0.65	-0.33
11	208	42	-1.05	-0.74
12	211	45	-0.97	-0.65
13	232.82	69.85	-0.38	-0.18
14	460	230	5.75	0.92
15	NT	NT		
16	95	48	-4.10	-2.63
17	NR	NR		
18	180	36	-1.81	-1.39
20	NR	NR		
21	NR	NR		

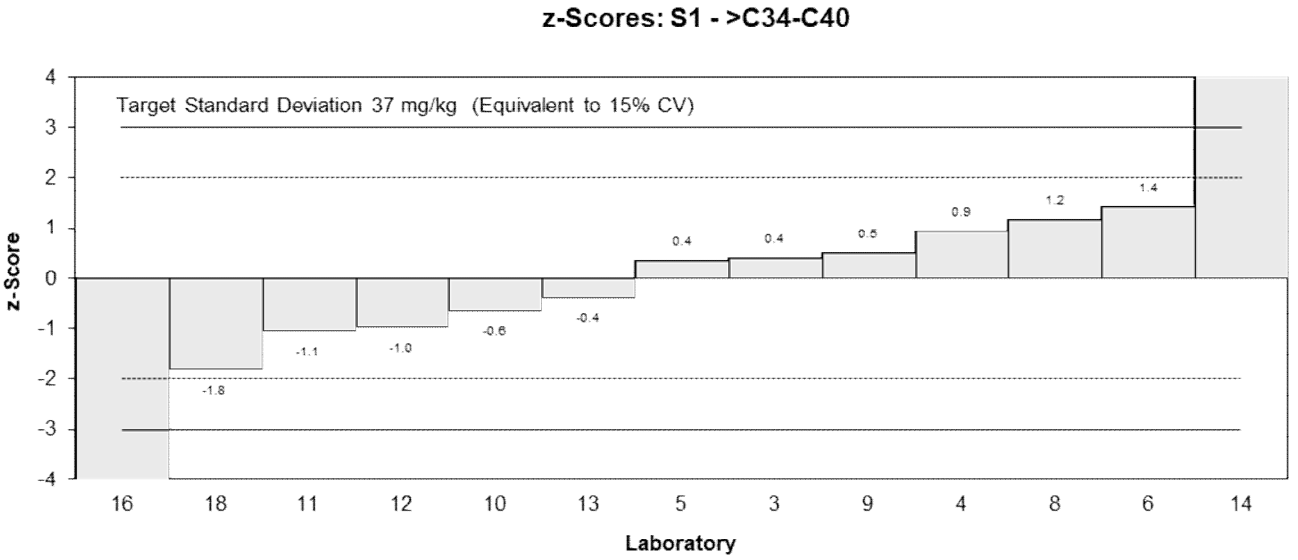
Statistics

Assigned Value**	247	32
Spike	266	13
Robust Average	247	38
Median	260	33
Mean	252	
N	13	
Max.	460	
Min.	95	
Robust SD	55	
Robust CV	22%	

* Result changed from 0 to NR for calculation of statistics.

** Robust average excluding Laboratories 14 and 16.


Kernel Density
Density
Result
Results: S1 - >C34-C40
Assigned Value = 247 ± 32 mg/kg
Results (mg/kg)
Laboratory
16 18 11 12 10 13 5 3 9 4 8 6 14 1 17 2 20 21 7 15 Md R.A. S.V.


z-Scores: S1 - >C34-C40
Target Standard Deviation 37 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
16 18 11 12 10 13 5 3 9 4 8 6 14

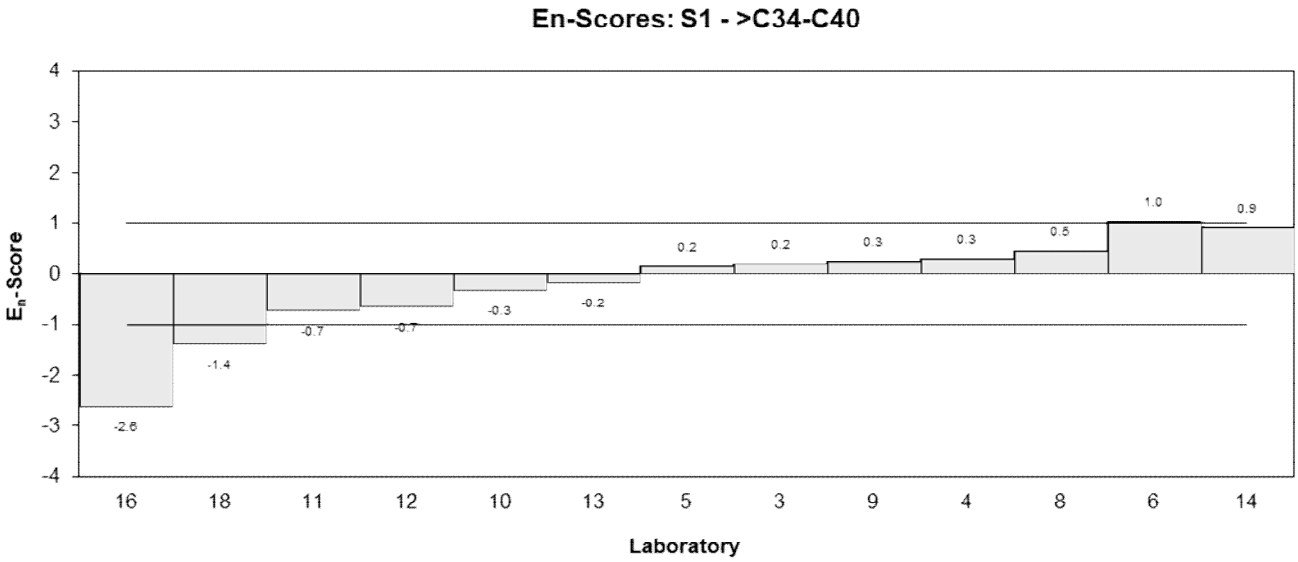

En-Scores: S1 - >C34-C40
En-Score
Laboratory
16 18 11 12 10 13 5 3 9 4 8 6 14

Figure 4

Table 8

Sample Details

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

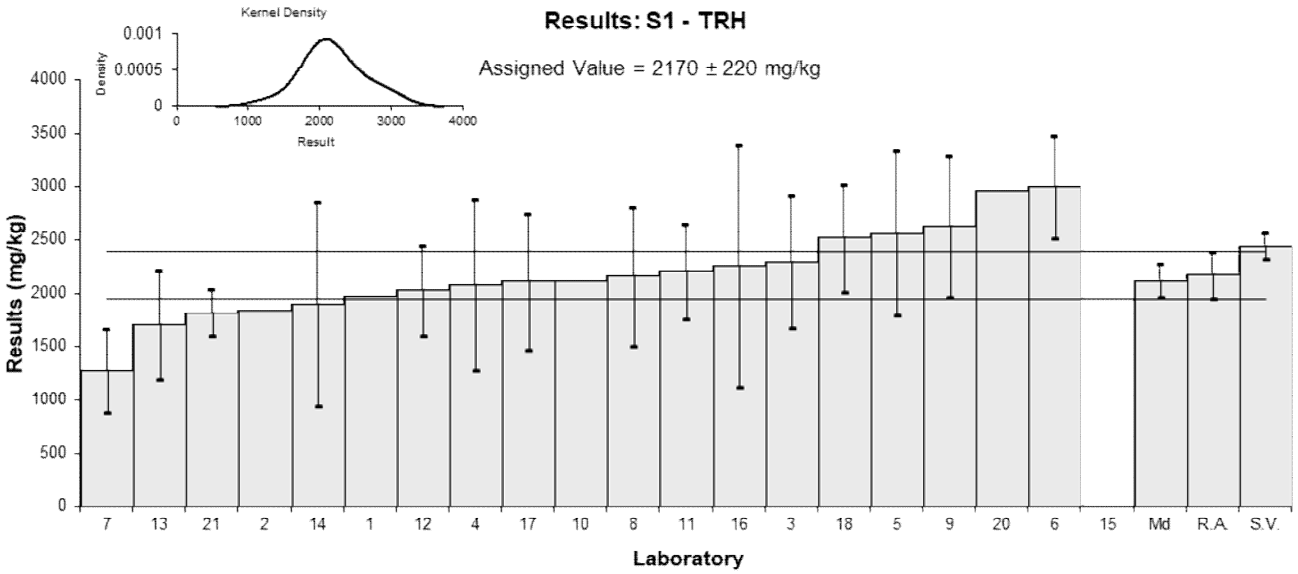
Participant Results

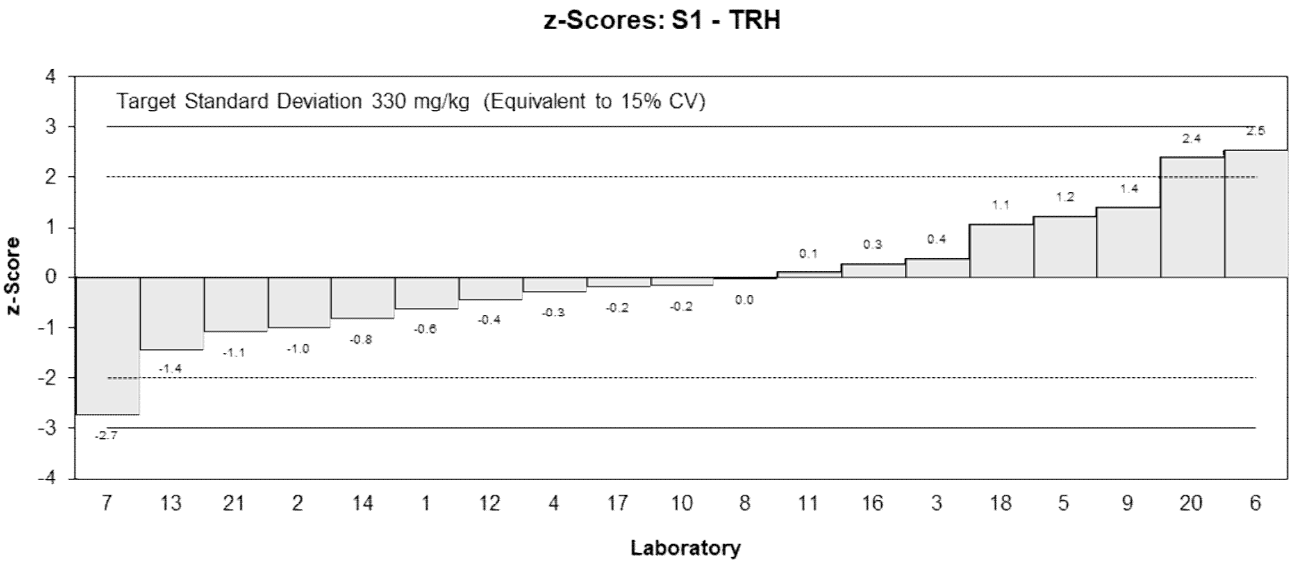
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1970	NR	-0.61	-0.91
2	1840.9	NR	-1.01	-1.50
3	2293.65	619	0.38	0.19
4	2076	797	-0.29	-0.11
5	2564	769	1.21	0.49
6	3000	480	2.55	1.57
7	1280	390	-2.73	-1.99
8	2160	648	-0.03	-0.01
9	2626	657	1.40	0.66
10	2117	NR	-0.16	-0.24
11	2206	441	0.11	0.07
12	2028	423	-0.44	-0.30
13	1707.25	512.18	-1.42	-0.83
14	1900	950	-0.83	-0.28
15	NT	NT		
16	2260	1130	0.28	0.08
17	2112	633.6	-0.18	-0.09
18	2520	504	1.08	0.64
20	2950	NR	2.40	3.55
21	1820	220	-1.08	-1.12

Statistics

Assigned Value	2170	220
Spike	2440	120
Robust Average	2170	220
Median	2120	160
Mean	2180	
N	19	
Max.	3000	
Min.	1280	
Robust SD	390	
Robust CV	18%	

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


Results: S1 - TRH
Kernel Density
Density
Result
Assigned Value = 2170 ± 220 mg/kg
Results (mg/kg)
Laboratory
7 13 21 2 14 1 12 4 17 10 8 11 16 3 18 5 9 20 6 15 Md R.A. S.V.


z-Scores: S1 - TRH
Target Standard Deviation 330 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
7 13 21 2 14 1 12 4 17 10 8 11 16 3 18 5 9 20 6

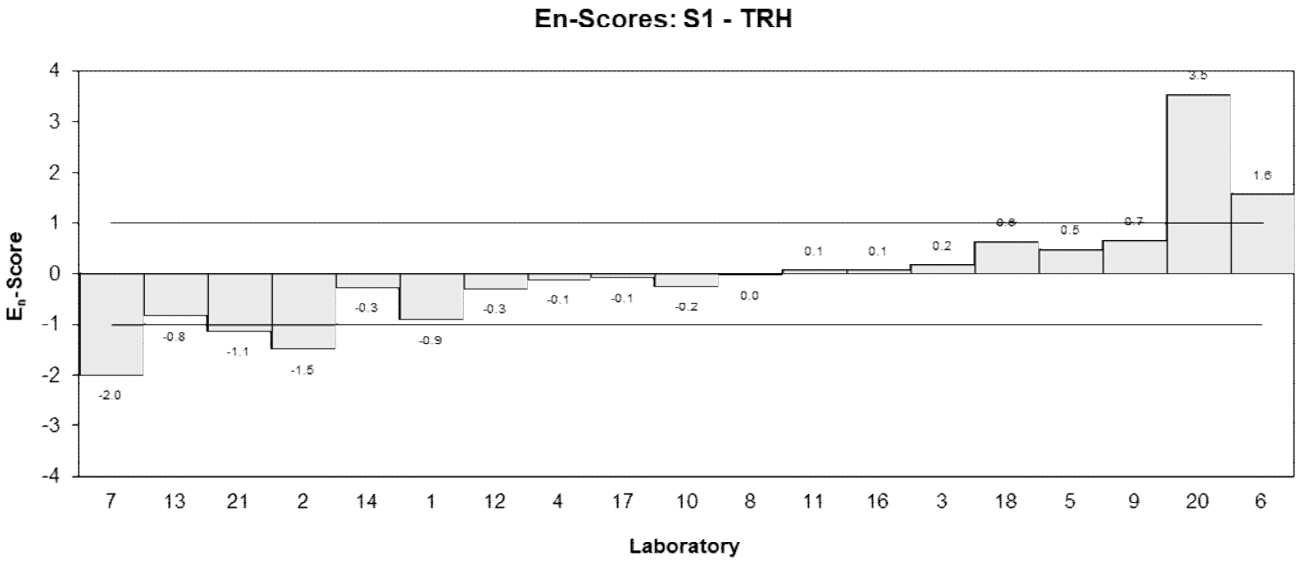

En-Scores: S1 - TRH
En-Score
Laboratory
7 13 21 2 14 1 12 4 17 10 8 11 16 3 18 5 9 20 6

Figure 5

Table 9 Additional hydrocarbon ranges to those defined in NEPM Schedule B3 *Guideline on Laboratory Analysis of Potentially Contaminated Soils*,[5] reported by participants for Sample S1

Lab. Code	Range	Result (mg/kg)	Uncertainty (mg/kg)
2	C34-C37	<200	NR
17	C7-C9	<10	NR
	C10-C14	448	134.4
	C15-C36	1664	499.2
20	C7-C9	<20	NR
	C10-C14	440	114
	C15-C36	2500	575
21	C7-C9	<8	5.4
	C10-C14	222	50
	C15-C36	1600	220

THIS PAGE IS INTENTIONALLY BLANK

Table 10

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	1210	70
2	NT	NT
3	1892.99	223
4	NT	NT
5	1914	574
6	2100	530
7	1160	450
8	1068	320
9	1727.5	519
10	1830	550
11	2057	617
12	1700	440
13	1504.85	451.45
14	NT	NT
15	NT	NT
16	NR	NR
17	NR	NR
18	1900	380
20	NT	NT
21*	1120	520

Statistics*

Assigned Value	Not Set	
Spike	Not Spiked	
Robust Average	1670	290
Median	1780	190
Mean	1670	
N	12	
Max.	2100	
Min.	1068	
Robust SD	400	
Robust CV	24%	

* Laboratory 21 reported results for the C6-C9 range; this result has been excluded from the calculation of all statistics.

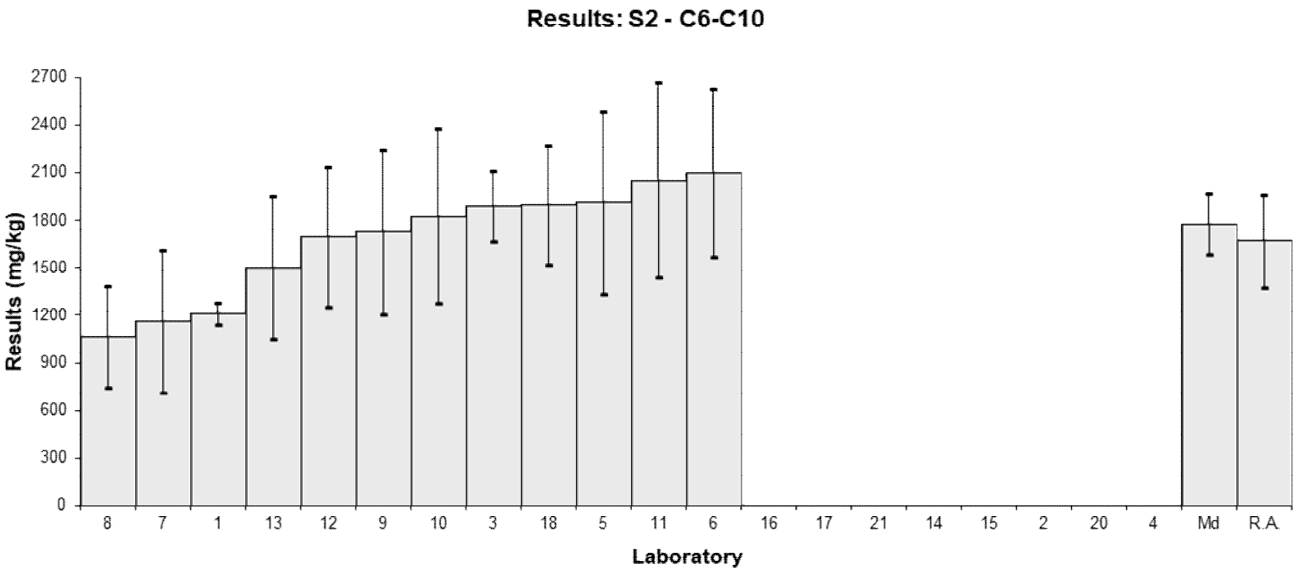

Results: S2 - C6-C10
Results (mg/kg)
2700
2400
2100
1800
1500
1200
900
600
300
0
8
7
1
13
12
9
10
3
18
5
11
6
16
17
21
14
15
2
20
4
Md
R.A.
Laboratory

Figure 6

Table 11

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	29.7	6.8
2	NT	NT
3	32.16	6
4	33.5	3.1
5	30.8	9.2
6	23	5
7	0.56	0.14
8	30.1	9.0
9	29.1	7.3
10	13.8	4.1
11	36.6	11
12	30	7
13	40.88	12.26
14	20	5
15	NT	NT
16	NR	NR
17	24	7.2
18	48	9.1
20	20	5
21	18.6	5.3

Statistics

Assigned Value	Not Set	
Spike	72.6	3.6
Robust Average	27.5	5.9
Median	29.7	5.1
Mean	27.1	
N	17	
Max.	48	
Min.	0.56	
Robust SD	9.8	
Robust CV	36%	

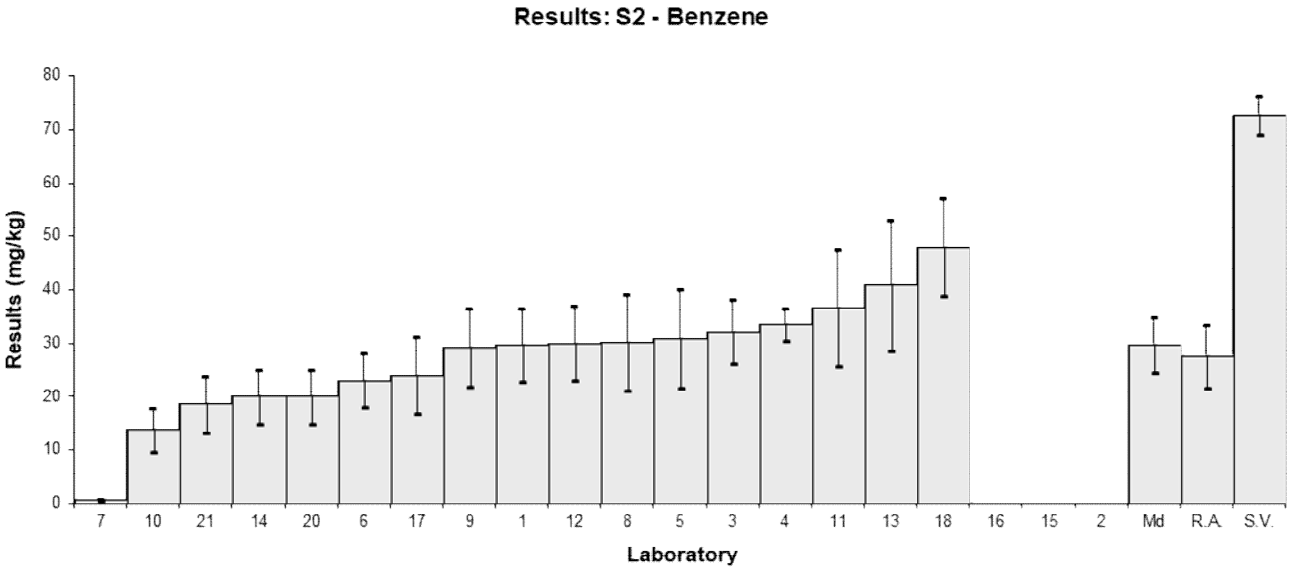

Results: S2 - Benzene
Results (mg/kg)
80
70
60
50
40
30
20
10
0
7
10
21
14
20
6
17
9
1
12
8
5
3
4
11
13
18
16
15
2
Md
R.A.
S.V.
Laboratory

Figure 7

Table 12

Sample Details

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

Participant Results

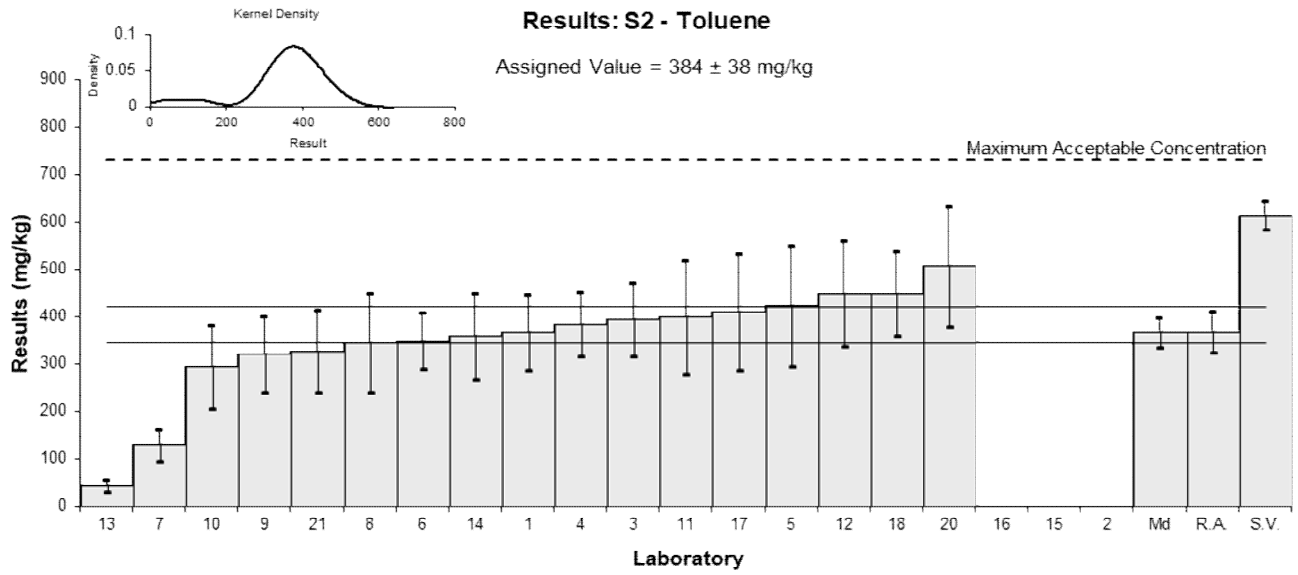
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	368	80	-0.28	-0.18
2	NT	NT		
3	395.87	77	0.21	0.14
4	385	67.8	0.02	0.01
5	424	127	0.69	0.30
6	350	60	-0.59	-0.48
7	130	33	-4.41	-5.05
8	345	104	-0.68	-0.35
9	321.4	80.4	-1.09	-0.70
10	294	88	-1.56	-0.94
11	400.4	120	0.28	0.13
12	450	110	1.15	0.57
13	43.12	12.94	-5.92	-8.49
14	360	90	-0.42	-0.25
15	NT	NT		
16	NR	NR		
17	410	123	0.45	0.20
18	450	90	1.15	0.68
20**	507	127	2.00	0.93
21	328	86	-0.97	-0.60

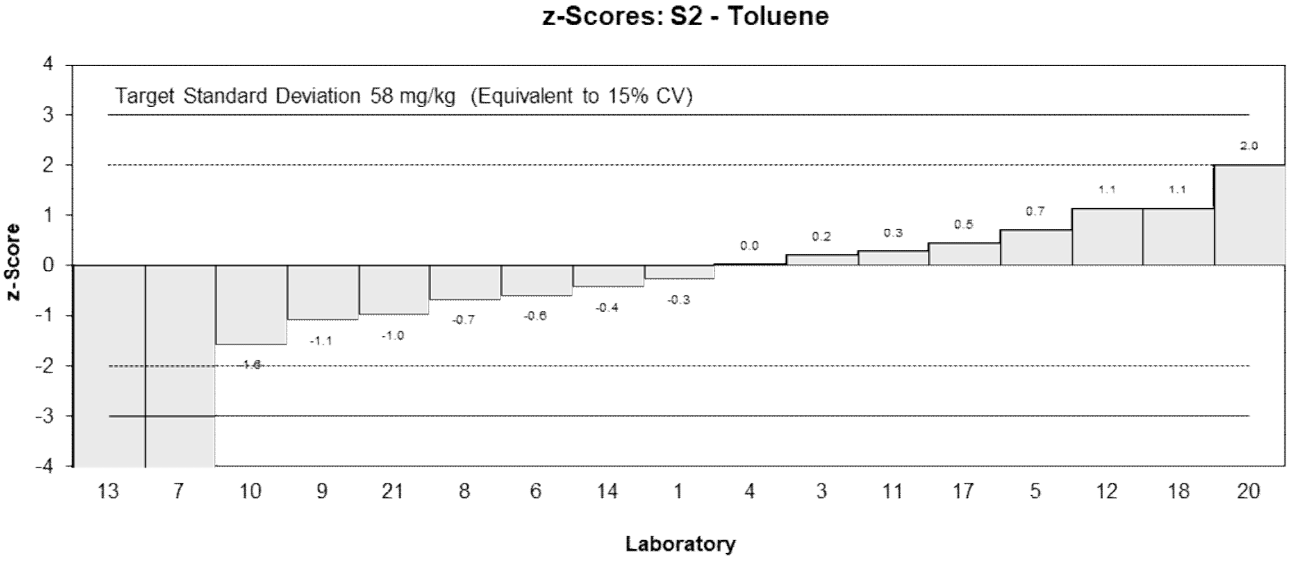
Statistics

Assigned Value*	384	38
Spike	615	31
Max. Acceptable Concentration**	730	
Robust Average	369	44
Median	368	32
Mean	351	
N	17	
Max.	507	
Min.	43.12	
Robust SD	73	
Robust CV	20%	

* Robust average excluding Laboratories 7 and 13.

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


Kernel Density
Density
Result
Results: S2 - Toluene
Assigned Value = 384 ± 38 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
13 7 10 9 21 8 6 14 1 4 3 11 17 5 12 18 20 16 15 2 Md R.A. S.V.


z-Scores: S2 - Toluene
Target Standard Deviation 58 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
13 7 10 9 21 8 6 14 1 4 3 11 17 5 12 18 20
-1.6 -1.1 -1.0 -0.7 -0.6 -0.4 -0.3 0.0 0.2 0.3 0.5 0.7 1.1 1.1 2.0

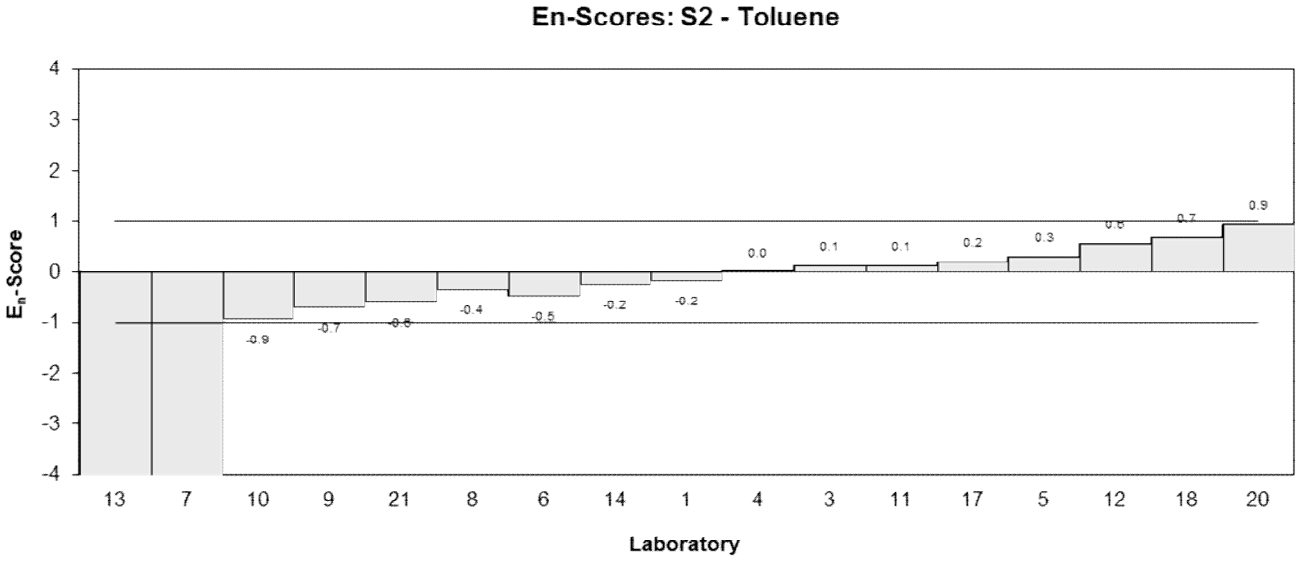

En-Scores: S2 - Toluene
En-Score
Laboratory
13 7 10 9 21 8 6 14 1 4 3 11 17 5 12 18 20
-0.9 -0.7 -0.6 -0.4 -0.5 -0.2 -0.2 0.0 0.1 0.1 0.2 0.3 0.5 0.7 0.9

Figure 8

Table 13

Sample Details

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

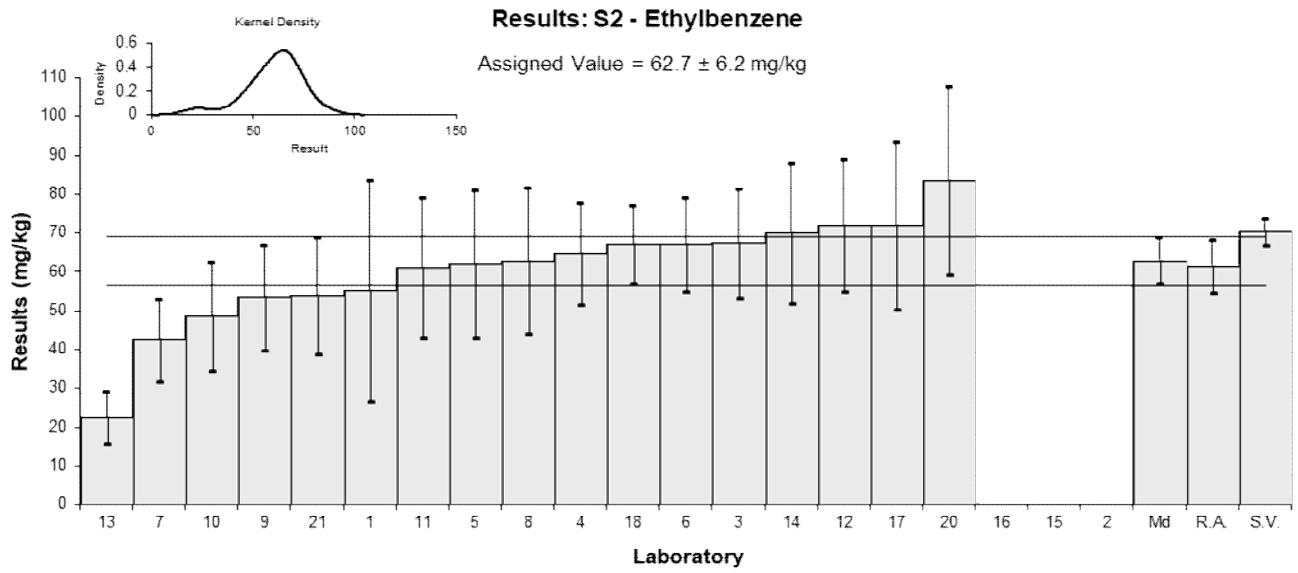
Participant Results

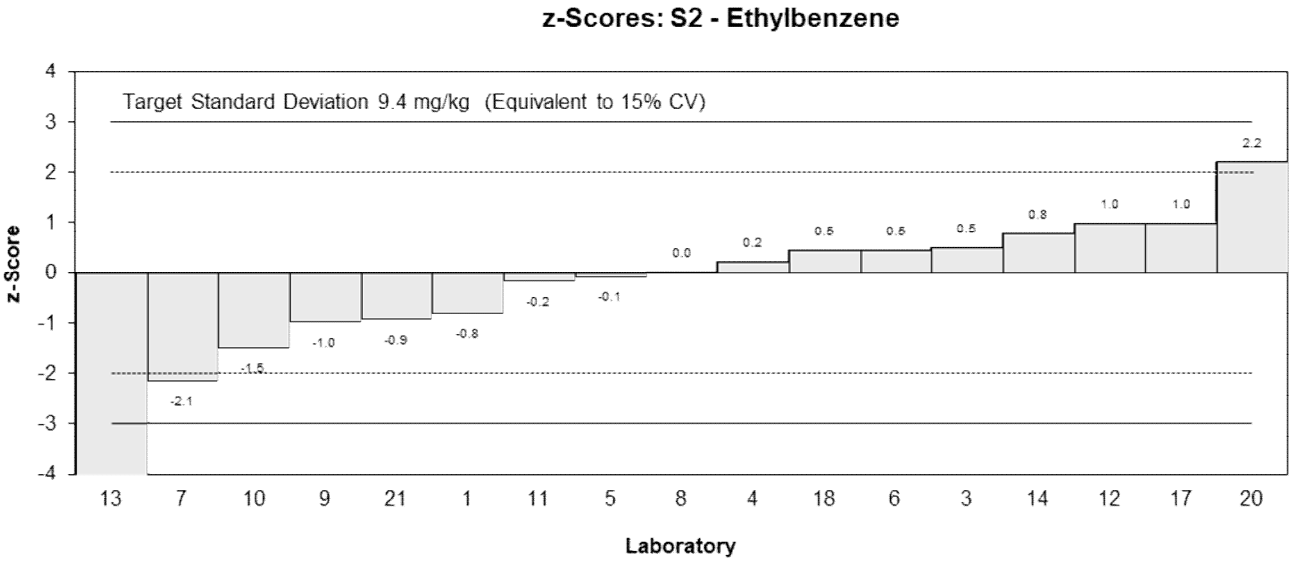
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	55.2	28.7	-0.80	-0.26
2	NT	NT		
3	67.37	14	0.50	0.31
4	64.7	13.1	0.21	0.14
5	62	19	-0.07	-0.04
6	67	12	0.46	0.32
7	42.5	10.6	-2.15	-1.64
8	62.9	18.9	0.02	0.01
9	53.4	13.4	-0.99	-0.63
10	48.6	14	-1.50	-0.92
11	61.2	18	-0.16	-0.08
12	72	17	0.99	0.51
13	22.62	6.79	-4.26	-4.36
14	70	18	0.78	0.38
15	NT	NT		
16	NR	NR		
17	72	21.6	0.99	0.41
18	67	10	0.46	0.37
20	83.5	24.2	2.21	0.83
21	54	15	-0.93	-0.54

Statistics

Assigned Value*	62.7	6.2
Spike	70.3	3.5
Robust Average	61.5	6.8
Median	62.9	5.9
Mean	60.4	
N	17	
Max.	83.5	
Min.	22.62	
Robust SD	11	
Robust CV	18%	

* Robust average excluding Laboratory 13.


Results: S2 - Ethylbenzene
Assigned Value = 62.7 ± 6.2 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
13 7 10 9 21 1 11 5 8 4 18 6 3 14 12 17 20 16 15 2 Md R.A. S.V.


z-Scores: S2 - Ethylbenzene
Target Standard Deviation 9.4 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
13 7 10 9 21 1 11 5 8 4 18 6 3 14 12 17 20
-2.1 -1.5 -1.0 -0.9 -0.8 -0.2 -0.1 0.0 0.2 0.5 0.5 0.5 0.8 1.0 1.0 2.2

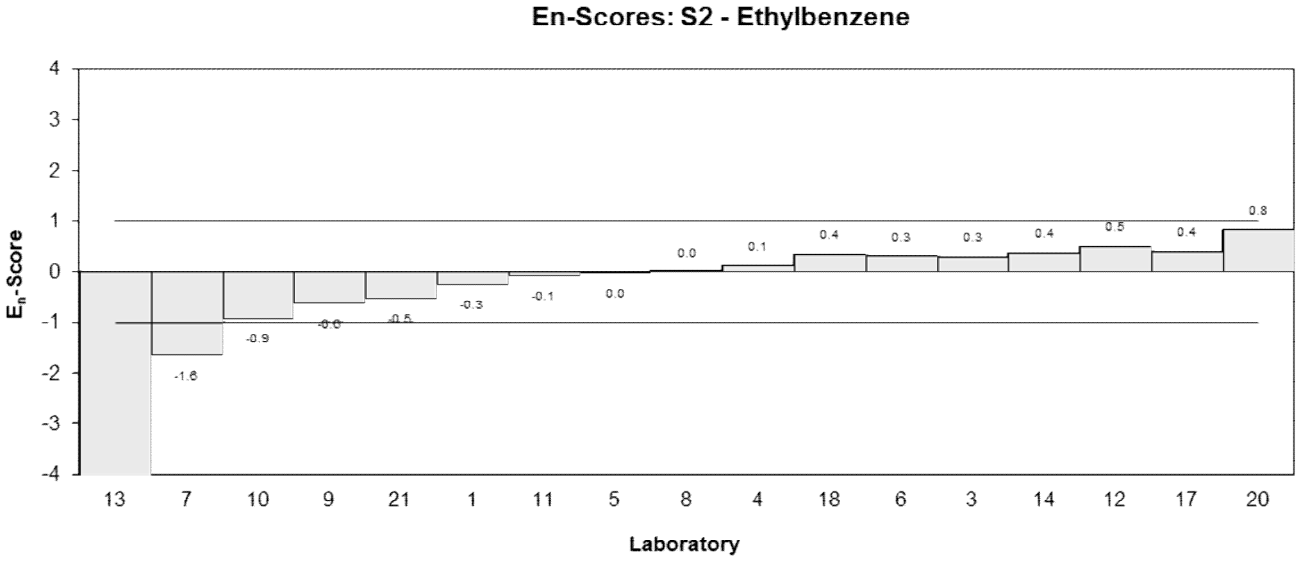

En-Scores: S2 - Ethylbenzene
En-Score
Laboratory
13 7 10 9 21 1 11 5 8 4 18 6 3 14 12 17 20
-1.6 -0.9 -0.6 -0.5 -0.3 -0.1 0.0 0.0 0.1 0.4 0.3 0.3 0.4 0.5 0.4 0.8

Figure 9

Table 14

Sample Details

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

Participant Results

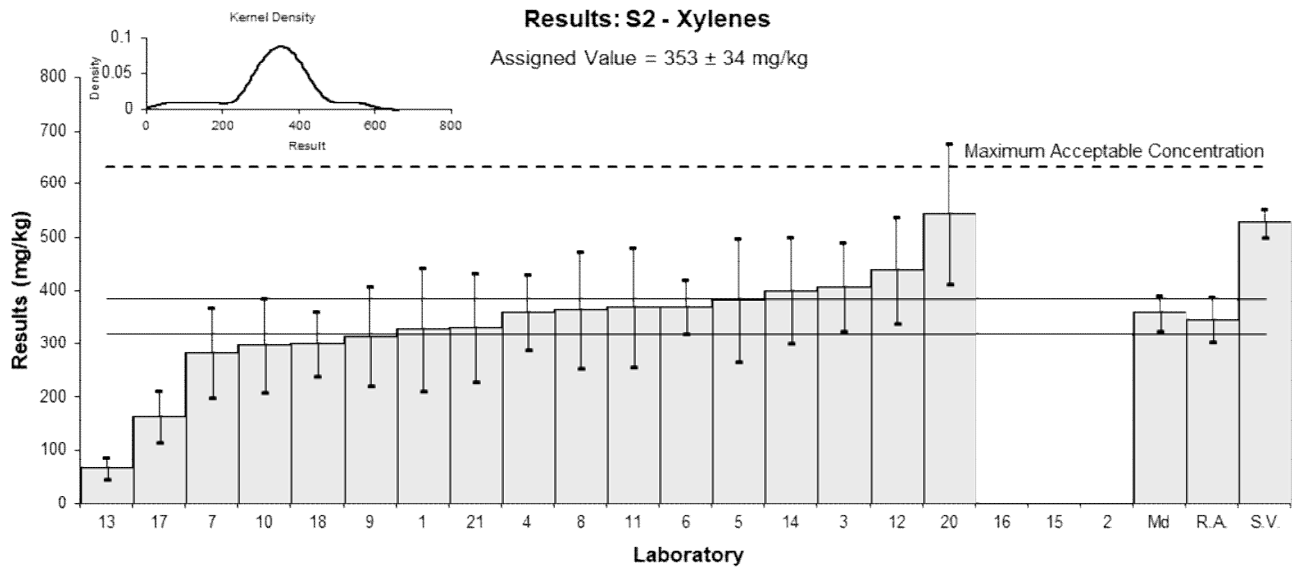
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	328	115	-0.47	-0.21
2	NT	NT		
3	408	83	1.04	0.61
4	359	71.1	0.11	0.08
5	383	115	0.57	0.25
6	370	50	0.32	0.28
7	284	85	-1.30	-0.75
8	364	109	0.21	0.10
9	315.2	94.6	-0.71	-0.38
10	298	89	-1.04	-0.58
11	369.9	111	0.32	0.15
12	440	100	1.64	0.82
13	67.11	20.13	-5.40	-7.24
14	400	100	0.89	0.44
15	NT	NT		
16	NR	NR		
17	164	49.2	-3.57	-3.16
18	300	60	-1.00	-0.77
20**	544	131	2.00	1.00
21	331	103	-0.42	-0.20

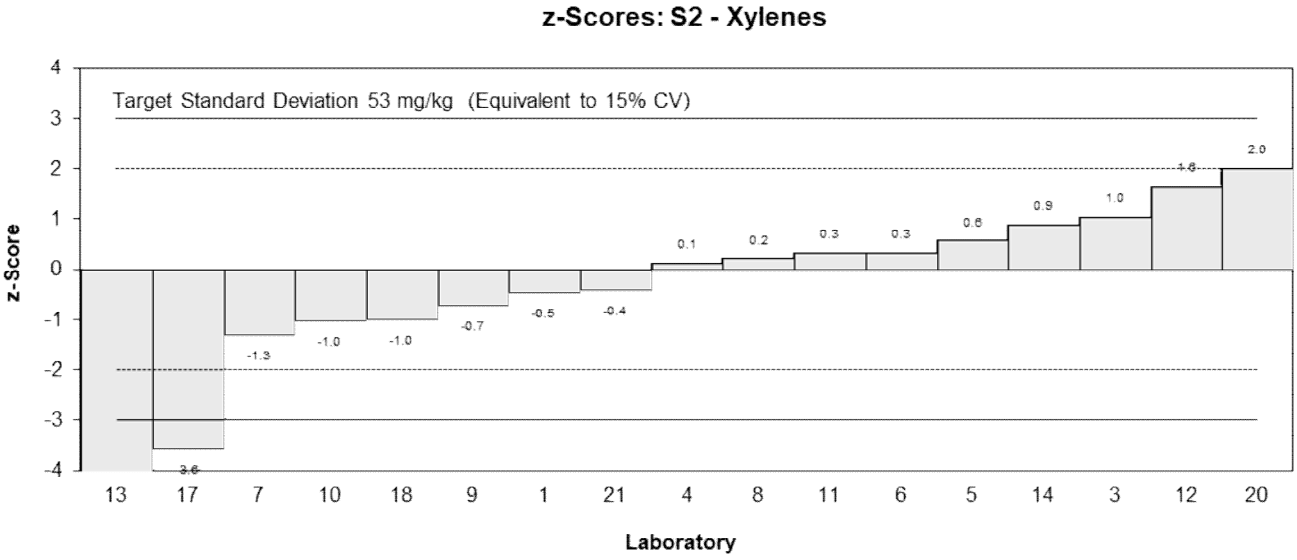
Statistics

Assigned Value*	353	34
Spike	527	26
Max. Acceptable Concentration**	633	
Robust Average	346	43
Median	359	33
Mean	337	
N	17	
Max.	544	
Min.	67.11	
Robust SD	71	
Robust CV	20%	

* Robust average excluding Laboratories 13, 17 and 20.

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


Results: S2 - Xylenes
Assigned Value = 353 ± 34 mg/kg
Kernel Density
Density
Result
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
13 17 7 10 18 9 1 21 4 8 11 6 5 14 3 12 20 16 15 2 Md R.A. S.V.


z-Scores: S2 - Xylenes
Target Standard Deviation 53 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
13 17 7 10 18 9 1 21 4 8 11 6 5 14 3 12 20

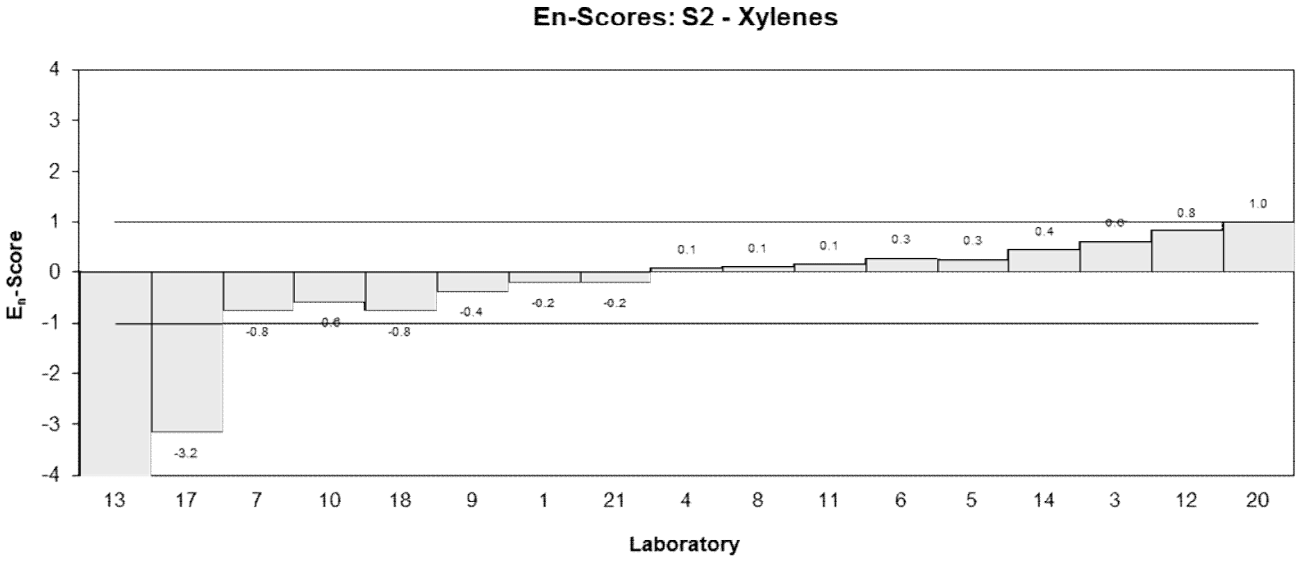

En-Scores: S2 - Xylenes
En-Score
Laboratory
13 17 7 10 18 9 1 21 4 8 11 6 5 14 3 12 20

Figure 10

Table 15

Sample Details

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

Participant Results

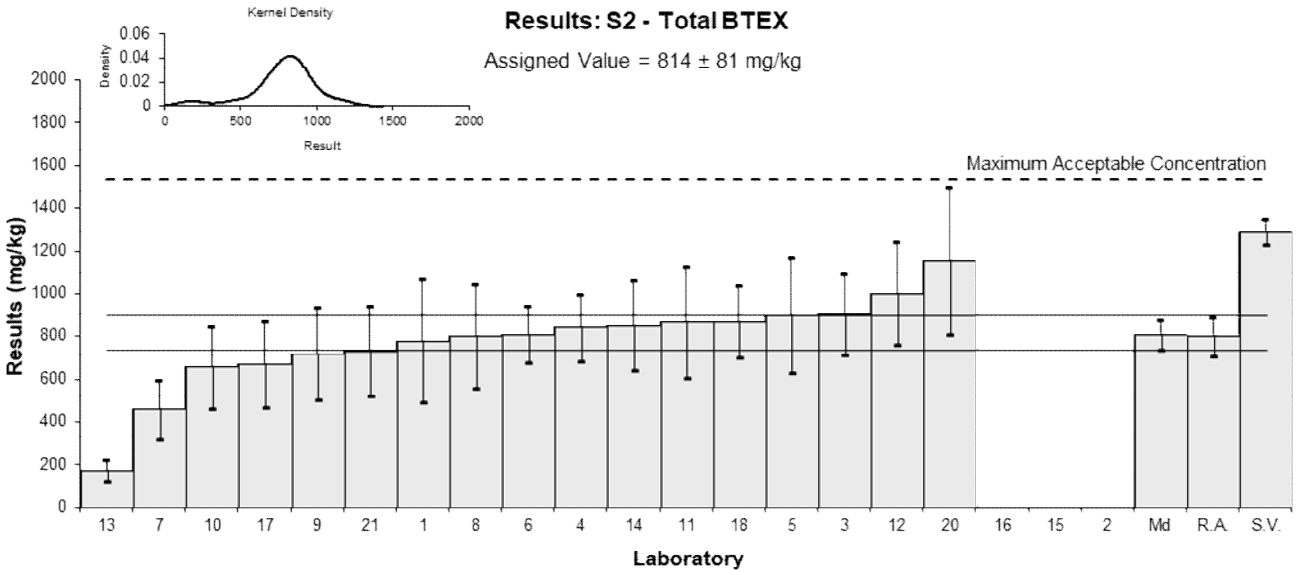
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	780	290	-0.28	-0.11
2	NT	NT		
3	903.4	191	0.73	0.43
4	842	155	0.23	0.16
5	900	270	0.70	0.31
6	810	130	-0.03	-0.03
7	458	137	-2.92	-2.24
8	802	241	-0.10	-0.05
9	719.1	215.7	-0.78	-0.41
10	655	190	-1.30	-0.77
11	868.1	260	0.44	0.20
12	1000	240	1.52	0.73
13	173.73	52.12	-5.24	-6.65
14	850	210	0.29	0.16
15	NT	NT		
16	NR	NR		
17	670	201	-1.18	-0.66
18	870	170	0.46	0.30
20**	1155	345	2.00	0.96
21	732	209	-0.67	-0.37

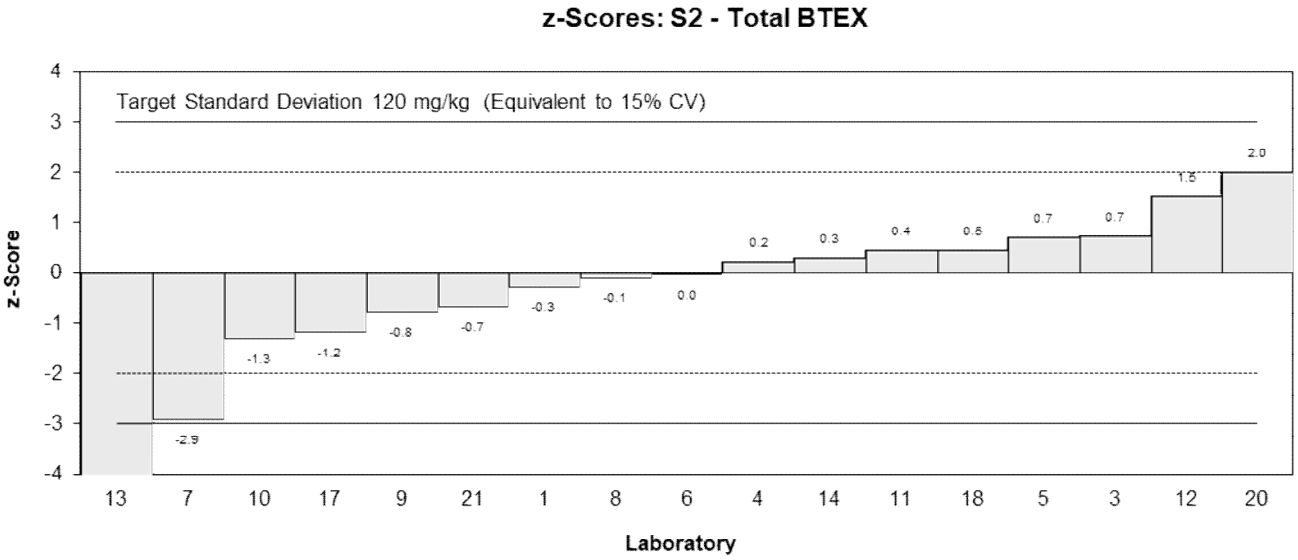
Statistics

Assigned Value*	814	81
Spike	1290	60
Max. Acceptable Concentration**	1530	
Robust Average	799	90
Median	810	69
Mean	776	
N	17	
Max.	1155	
Min.	173.73	
Robust SD	150	
Robust CV	19%	

* Robust average excluding Laboratory 13.

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


Kernel Density
Density
Result
Results: S2 - Total BTEX
Assigned Value = 814 ± 81 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
13 7 10 17 9 21 1 8 6 4 14 11 18 5 3 12 20 16 15 2 Md R.A. S.V.


z-Scores: S2 - Total BTEX
Target Standard Deviation 120 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
13 7 10 17 9 21 1 8 6 4 14 11 18 5 3 12 20
-2.9 -1.3 -1.2 -0.8 -0.7 -0.3 -0.1 0.0 0.2 0.3 0.4 0.5 0.7 0.7 1.5 2.0

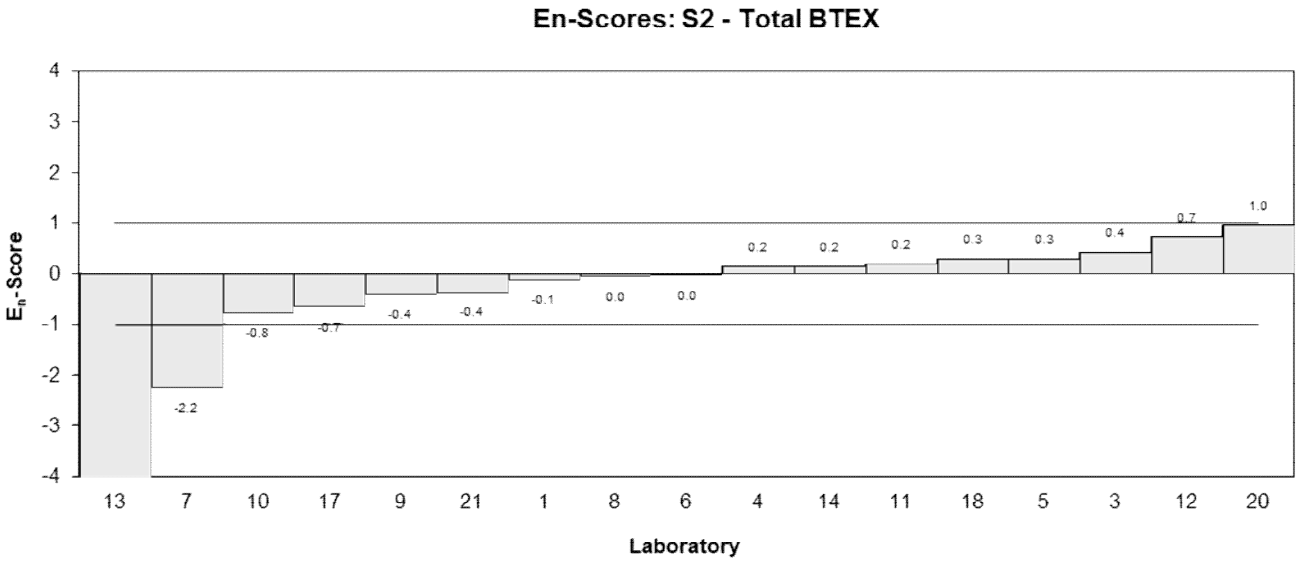

En-Scores: S2 - Total BTEX
En-Score
Laboratory
13 7 10 17 9 21 1 8 6 4 14 11 18 5 3 12 20
-2.2 -0.8 -0.7 -0.4 -0.4 -0.1 0.0 0.0 0.2 0.2 0.2 0.3 0.3 0.4 0.7 1.0

Figure 11

Table 16

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	0.20	0.10
2	NT	NT
3	<0.5	0.13
4	0.285	0.098
5	0.36	0.11
6	0.5	0.2
7	NT	NT
8	NT	NT
9	<0.5	0.1
10	<0.1	NR
11	<0.1	NR
12	< 0.5	0.2
13	0.48	0.14
14	0.3	0.23
15	<1	NR
16	0.16	0.04
17	0.43	0.129
18	0.41	0.12
20	0.28	NR
21	NT	NT

Statistics

Assigned Value	Not Set	
Spike	0.797	0.040
Robust Average	0.34	0.10
Median	0.330	0.095
Mean	0.341	
N	10	
Max.	0.5	
Min.	0.16	
Robust SD	0.13	
Robust CV	38%	

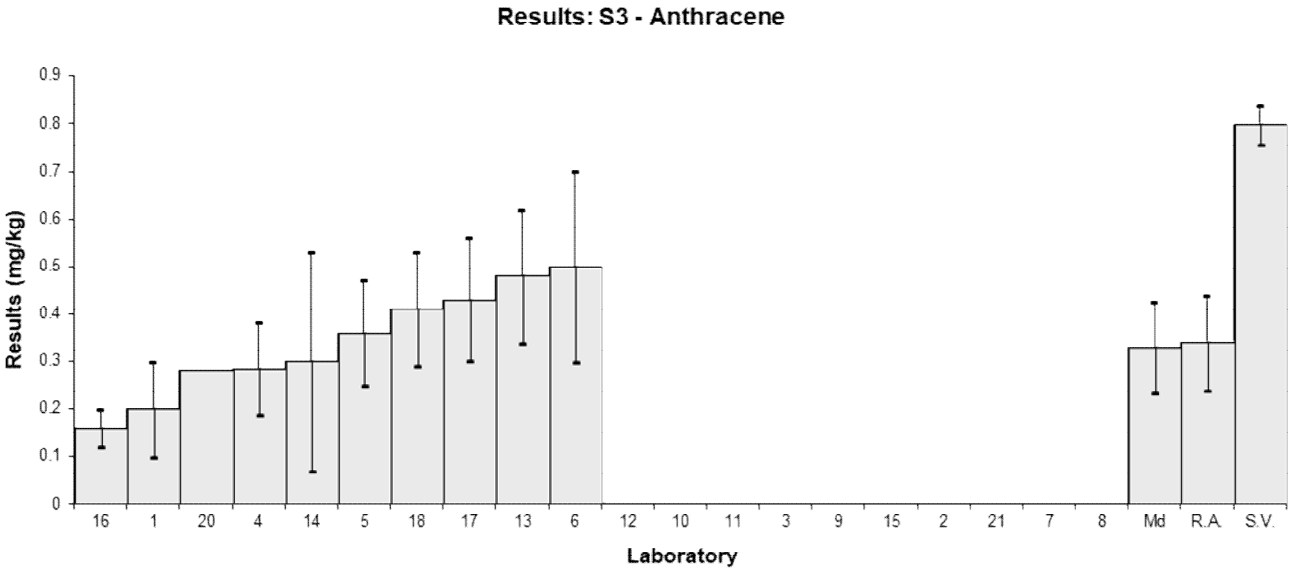

Results: S3 - Anthracene
Results (mg/kg)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
16
1
20
4
14
5
18
17
13
6
12
10
11
3
9
15
2
21
7
8
Md
R.A.
S.V.
Laboratory

Figure 12

Table 17

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Benzo(a)pyrene
Units	mg/kg

Participant Results

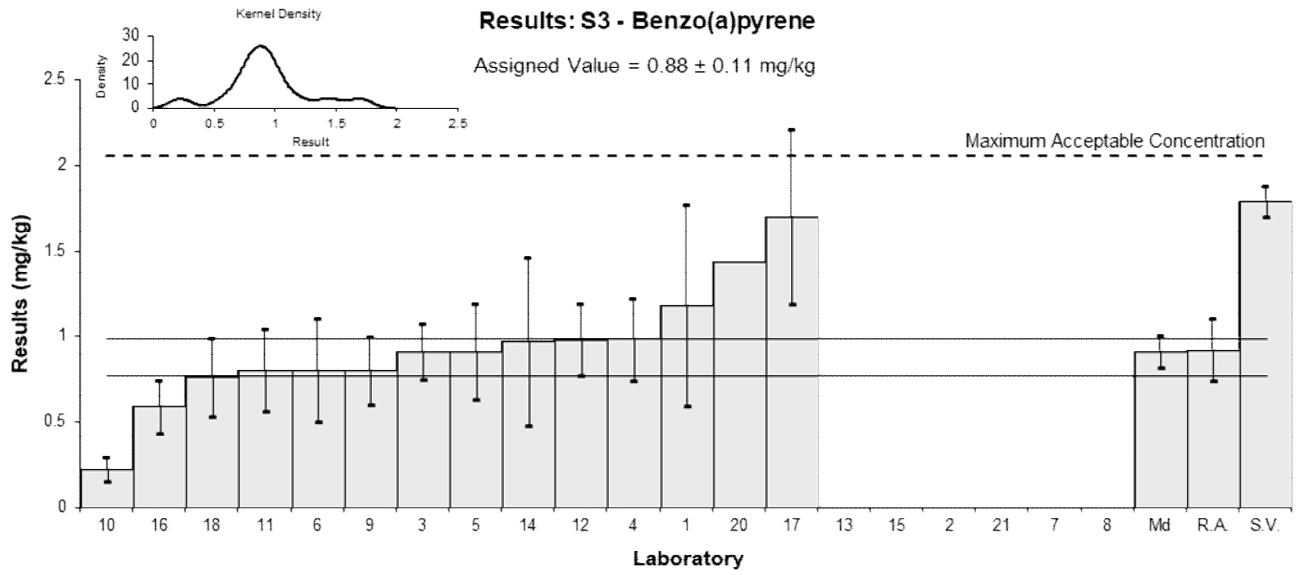
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1**	1.18	0.59	2.00	0.50
2	NT	NT		
3	0.91	0.16	0.23	0.15
4	0.984	0.242	0.79	0.39
5	0.91	0.28	0.23	0.10
6	0.8	0.3	-0.61	-0.25
7	NT	NT		
8	NT	NT		
9	0.8	0.2	-0.61	-0.35
10	0.223	0.07	-4.98	-5.04
11	0.8	0.24	-0.61	-0.30
12	0.98	0.21	0.76	0.42
13	<0.1	0.03		
14	0.97	0.49	0.68	0.18
15	<1	NR		
16	0.59	0.15	-2.20	-1.56
17**	1.7	0.51	2.00	1.00
18	0.76	0.23	-0.91	-0.47
20**	1.44	NR	2.00	1.00
21	NT	NT		

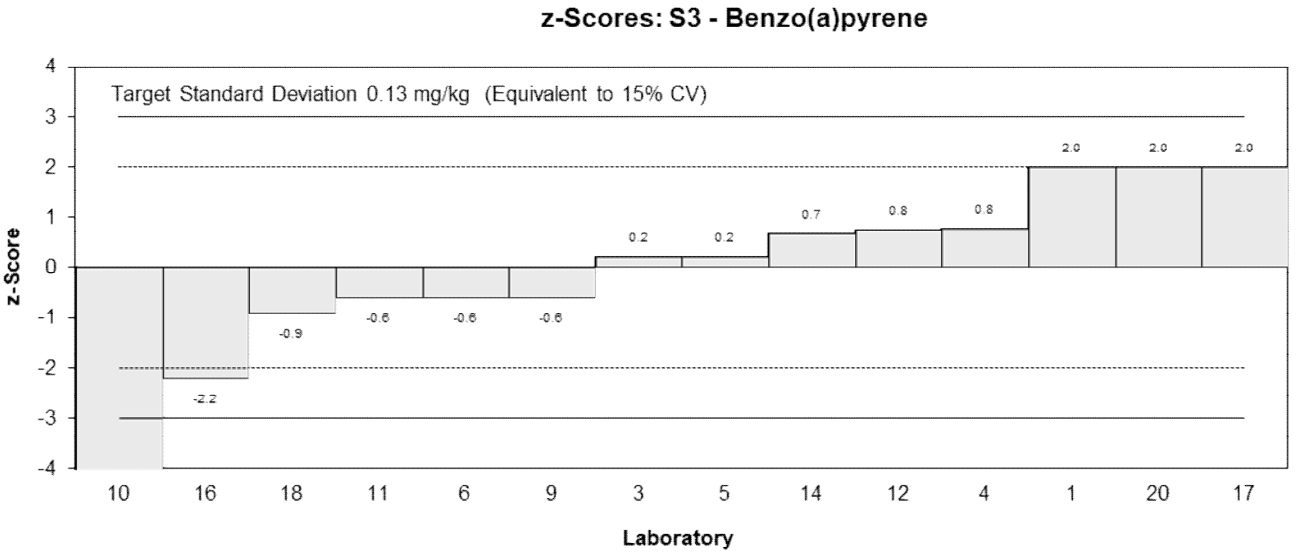
Statistics

Assigned Value*	0.88	0.11
Spike	1.79	0.09
Max. Acceptable Concentration**	2.05	
Robust Average	0.92	0.18
Median	0.910	0.094
Mean	0.932	
N	14	
Max.	1.7	
Min.	0.223	
Robust SD	0.27	
Robust CV	30%	

* Robust average excluding Laboratories 10, 17 and 20.

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


Kernel Density
Density
Result
Results: S3 - Benzo(a)pyrene
Assigned Value = 0.88 ± 0.11 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
10 16 18 11 6 9 3 5 14 12 4 1 20 17 13 15 2 21 7 8 Md R.A. S.V.


z-Scores: S3 - Benzo(a)pyrene
Target Standard Deviation 0.13 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
10 16 18 11 6 9 3 5 14 12 4 1 20 17
-2.2 -0.9 -0.6 -0.6 -0.6 0.2 0.2 0.7 0.8 0.8 2.0 2.0 2.0

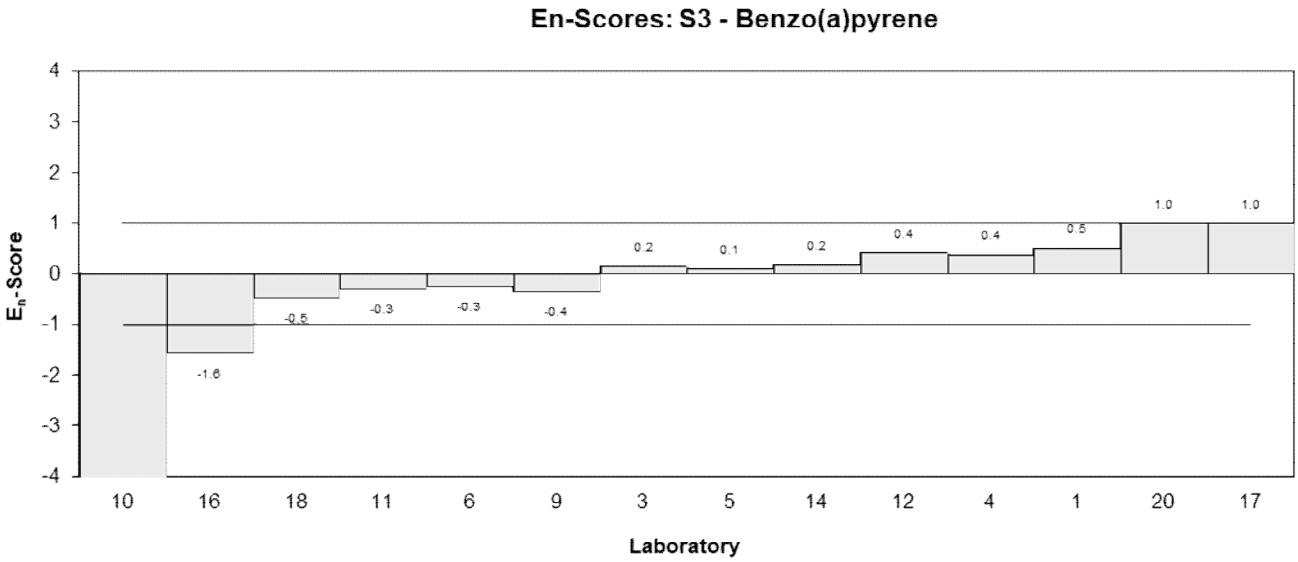

En-Scores: S3 - Benzo(a)pyrene
En-Score
Laboratory
10 16 18 11 6 9 3 5 14 12 4 1 20 17
-1.6 -0.5 -0.3 -0.3 -0.4 0.2 0.1 0.2 0.4 0.4 0.5 1.0 1.0

Figure 13

Table 18

Sample Details

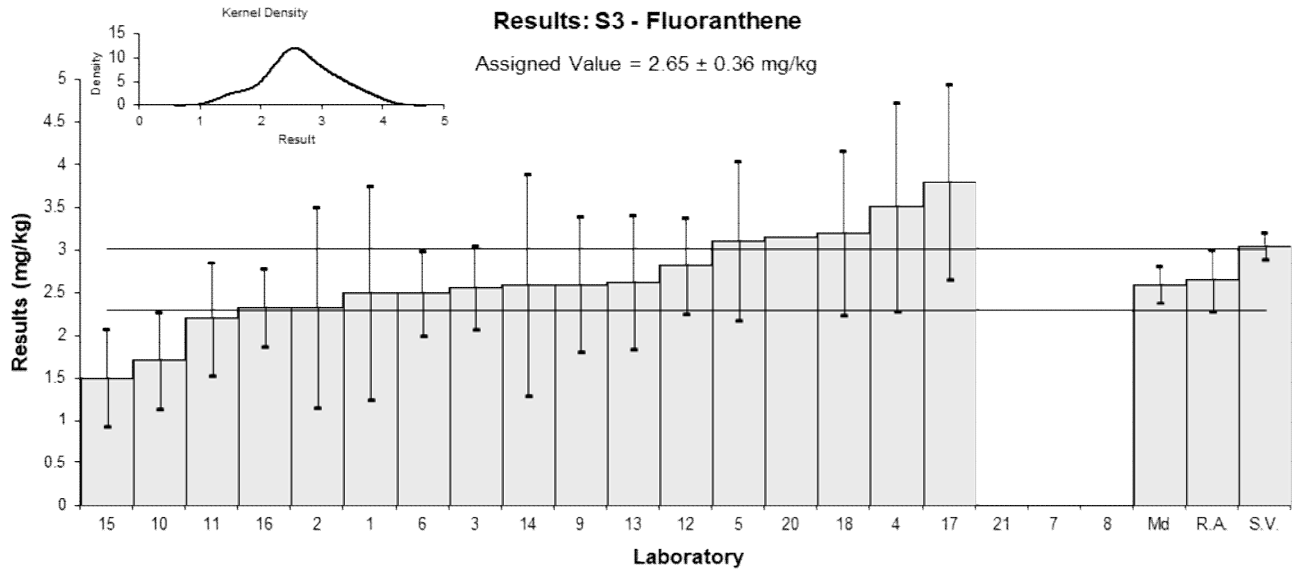
Sample No.	S3
Matrix	Soil
Analyte	Fluoranthene
Units	mg/kg

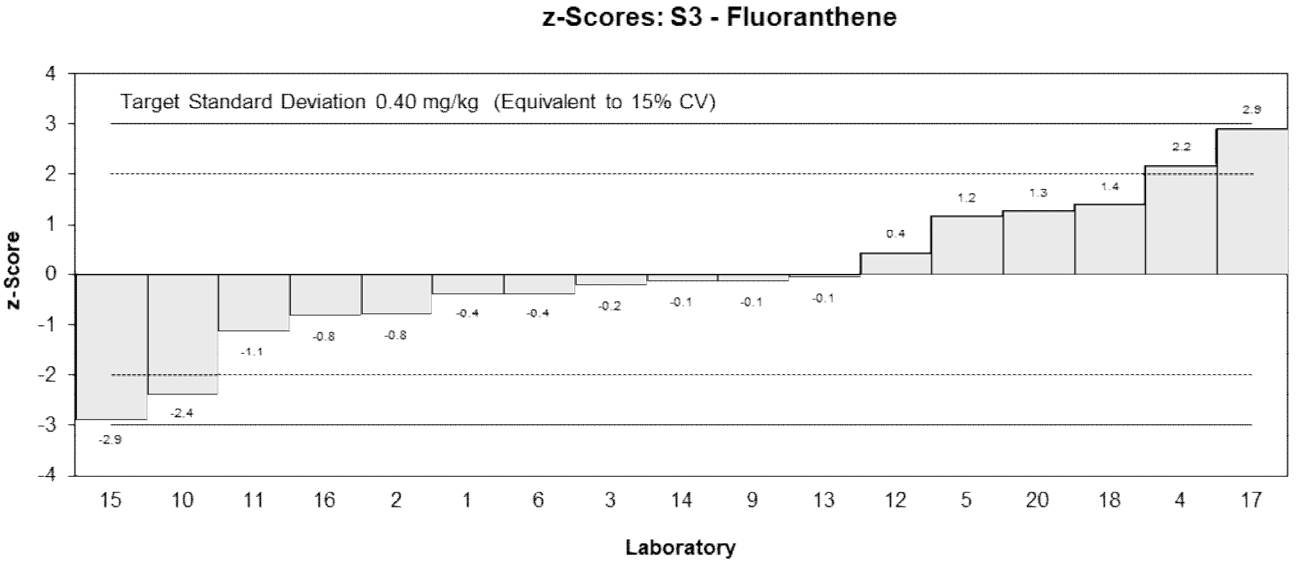
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	2.50	1.25	-0.38	-0.12
2	2.33	1.17	-0.81	-0.26
3	2.57	0.49	-0.20	-0.13
4	3.51	1.22	2.16	0.68
5	3.11	0.93	1.16	0.46
6	2.5	0.5	-0.38	-0.24
7	NT	NT		
8	NT	NT		
9	2.6	0.8	-0.13	-0.06
10	1.71	0.56	-2.36	-1.41
11	2.2	0.66	-1.13	-0.60
12	2.82	0.57	0.43	0.25
13	2.63	0.79	-0.05	-0.02
14	2.6	1.3	-0.13	-0.04
15	1.5	0.57	-2.89	-1.71
16	2.32	0.46	-0.83	-0.56
17	3.8	1.14	2.89	0.96
18	3.2	0.96	1.38	0.54
20	3.15	NR	1.26	1.39
21	NT	NT		

Statistics

Assigned Value	2.65	0.36
Spike	3.05	0.15
Robust Average	2.65	0.36
Median	2.60	0.21
Mean	2.65	
N	17	
Max.	3.8	
Min.	1.5	
Robust SD	0.59	
Robust CV	22%	


Kernel Density
Density
Result
Results: S3 - Fluoranthene
Assigned Value = 2.65 ± 0.36 mg/kg
Results (mg/kg)
Laboratory
15 10 11 16 2 1 6 3 14 9 13 12 5 20 18 4 17 21 7 8 Md R.A. S.V.


z-Scores: S3 - Fluoranthene
Target Standard Deviation 0.40 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
15 10 11 16 2 1 6 3 14 9 13 12 5 20 18 4 17
-2.9 -2.4 -1.1 -0.8 -0.8 -0.4 -0.4 -0.2 -0.1 -0.1 -0.1 0.4 1.2 1.3 1.4 2.2 2.9

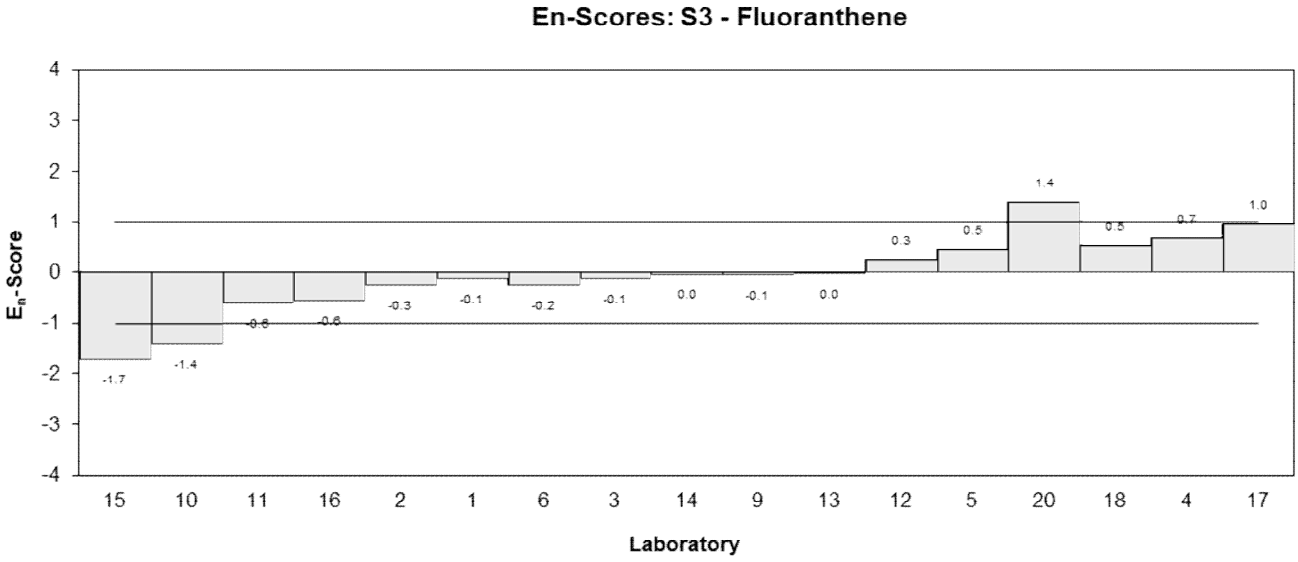

En-Scores: S3 - Fluoranthene
En-Score
Laboratory
15 10 11 16 2 1 6 3 14 9 13 12 5 20 18 4 17
-1.7 -1.4 -0.6 -0.6 -0.3 -0.1 -0.2 -0.1 0.0 -0.1 0.0 0.3 0.5 1.4 0.5 0.7 1.0

Figure 14

Table 19

Sample Details

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

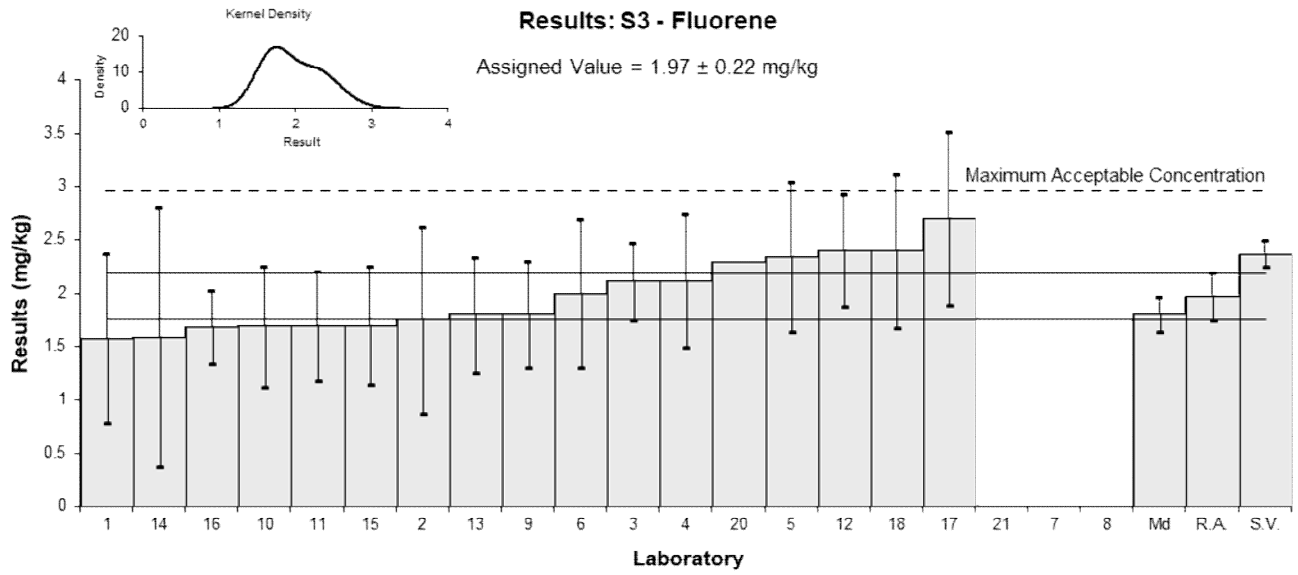
Participant Results

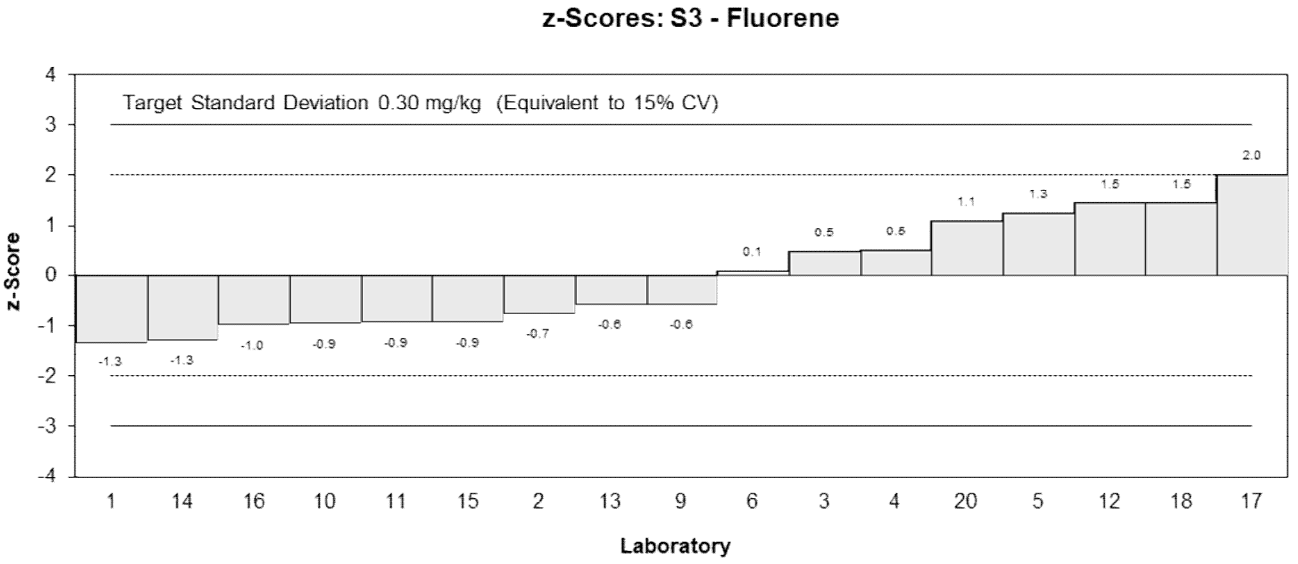
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.58	0.79	-1.32	-0.48
2	1.75	0.88	-0.74	-0.24
3	2.11	0.36	0.47	0.33
4	2.12	0.628	0.51	0.23
5	2.34	0.7	1.25	0.50
6	2.0	0.7	0.10	0.04
7	NT	NT		
8	NT	NT		
9	1.8	0.5	-0.58	-0.31
10	1.69	0.56	-0.95	-0.47
11	1.7	0.51	-0.91	-0.49
12	2.4	0.52	1.46	0.76
13	1.80	0.54	-0.58	-0.29
14	1.59	1.21	-1.29	-0.31
15	1.7	0.55	-0.91	-0.46
16	1.68	0.34	-0.98	-0.72
17*	2.7	0.81	2.00	0.87
18	2.4	0.72	1.46	0.57
20	2.29	NR	1.08	1.45
21	NT	NT		

Statistics

Assigned Value	1.97	0.22
Spike	2.37	0.12
Max. Acceptable Concentration*	2.96	
Robust Average	1.97	0.22
Median	1.80	0.16
Mean	1.98	
N	17	
Max.	2.7	
Min.	1.58	
Robust SD	0.37	
Robust CV	19%	

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


Results: S3 - Fluorene
Kernel Density
Density
Result
Assigned Value = 1.97 ± 0.22 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
1 14 16 10 11 15 2 13 9 6 3 4 20 5 12 18 17 21 7 8 Md R.A. S.V.


z-Scores: S3 - Fluorene
Target Standard Deviation 0.30 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 14 16 10 11 15 2 13 9 6 3 4 20 5 12 18 17
-1.3 -1.3 -1.0 -0.9 -0.9 -0.9 -0.7 -0.6 -0.6 0.1 0.5 0.6 1.1 1.3 1.5 1.5 2.0

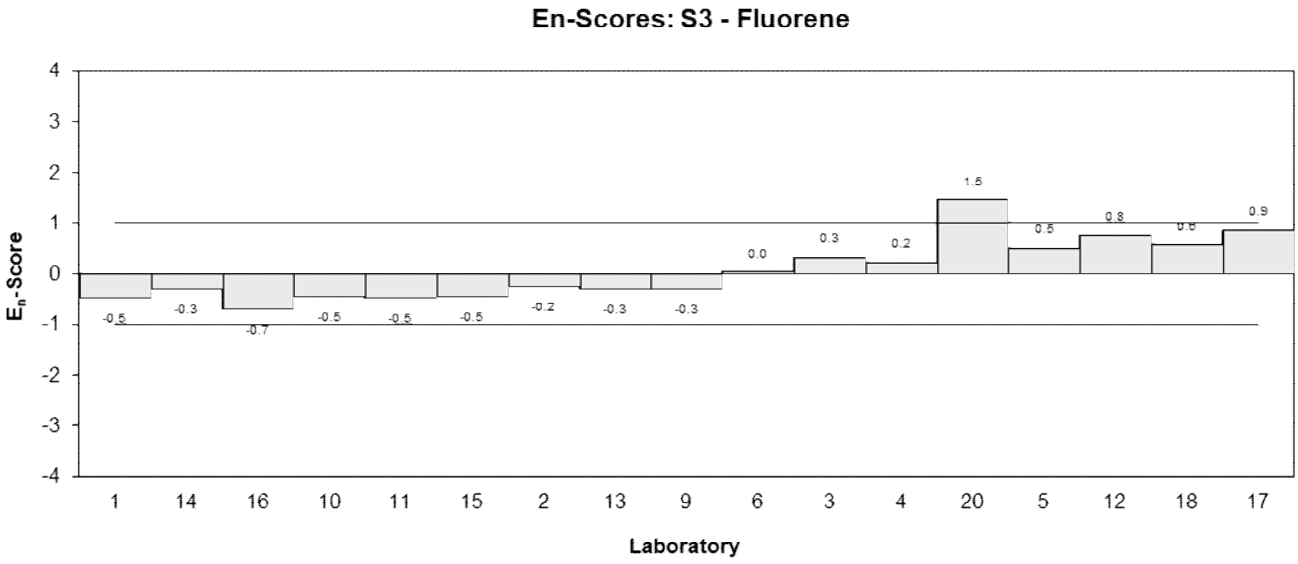

En-Scores: S3 - Fluorene
En-Score
Laboratory
1 14 16 10 11 15 2 13 9 6 3 4 20 5 12 18 17
-0.5 -0.3 -0.7 -0.5 -0.5 -0.5 -0.2 -0.3 -0.3 0.0 0.3 0.2 1.5 0.5 0.8 0.6 0.9

Figure 15

Table 20

Sample Details

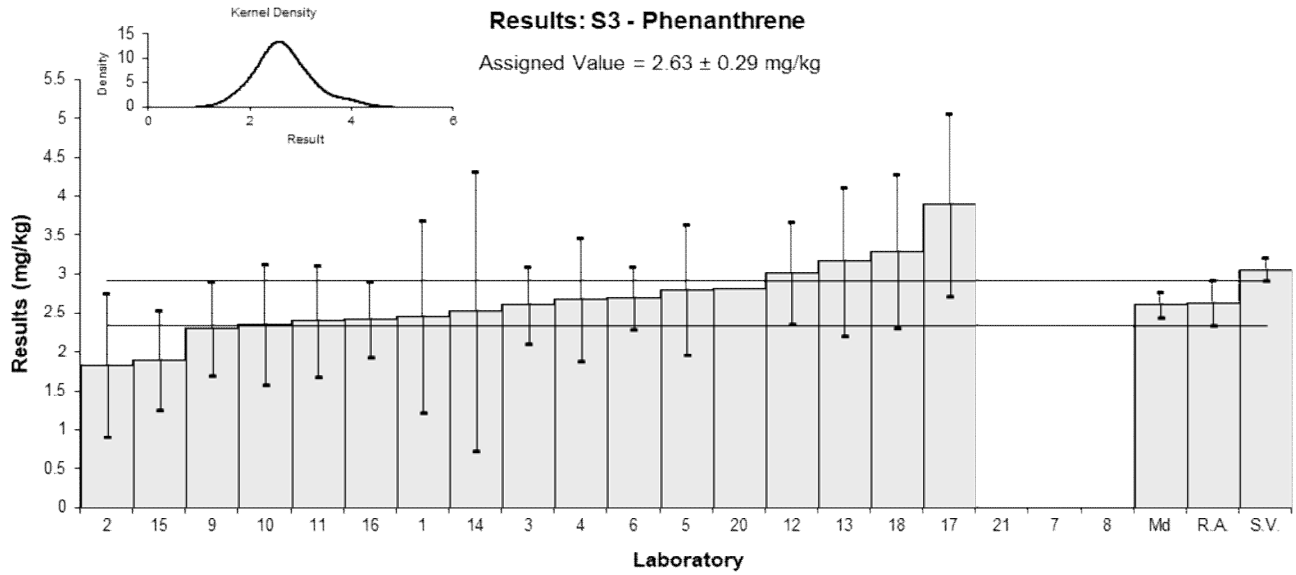
Sample No.	S3
Matrix	Soil
Analyte	Phenanthrene
Units	mg/kg

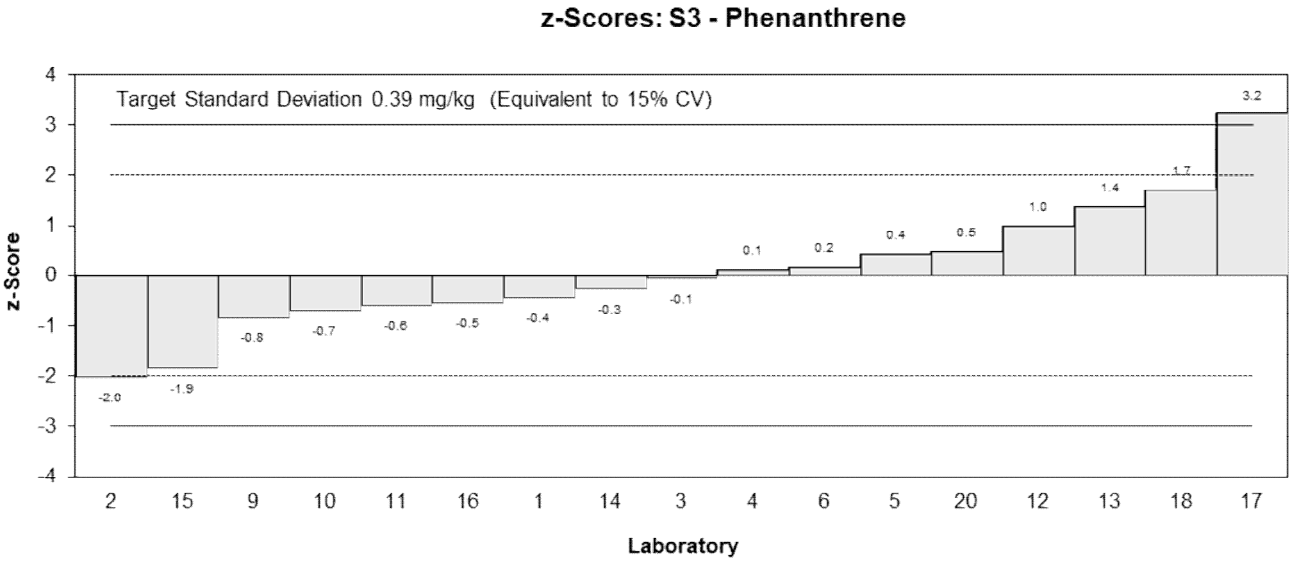
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	2.46	1.23	-0.43	-0.13
2	1.83	0.92	-2.03	-0.83
3	2.61	0.5	-0.05	-0.03
4	2.68	0.793	0.13	0.06
5	2.80	0.84	0.43	0.19
6	2.7	0.4	0.18	0.14
7	NT	NT		
8	NT	NT		
9	2.3	0.6	-0.84	-0.50
10	2.36	0.78	-0.68	-0.32
11	2.4	0.72	-0.58	-0.30
12	3.02	0.66	0.99	0.54
13	3.17	0.95	1.37	0.54
14	2.53	1.8	-0.25	-0.05
15	1.9	0.65	-1.85	-1.03
16	2.42	0.48	-0.53	-0.37
17	3.9	1.17	3.22	1.05
18	3.3	0.99	1.70	0.65
20	2.82	NR	0.48	0.66
21	NT	NT		

Statistics

Assigned Value	2.63	0.29
Spike	3.07	0.15
Robust Average	2.63	0.29
Median	2.61	0.16
Mean	2.66	
N	17	
Max.	3.9	
Min.	1.83	
Robust SD	0.47	
Robust CV	18%	


Kernel Density
Density
Result
Results: S3 - Phenanthrene
Assigned Value = 2.63 ± 0.29 mg/kg
Results (mg/kg)
Laboratory
2 15 9 10 11 16 1 14 3 4 6 5 20 12 13 18 17 21 7 8 Md R.A. S.V.


z-Scores: S3 - Phenanthrene
Target Standard Deviation 0.39 mg/kg (Equivalent to 15% CV)
z-Score
-2.0 -1.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3 -0.1 0.1 0.2 0.4 0.5 1.0 1.4 1.7 3.2
Laboratory
2 15 9 10 11 16 1 14 3 4 6 5 20 12 13 18 17

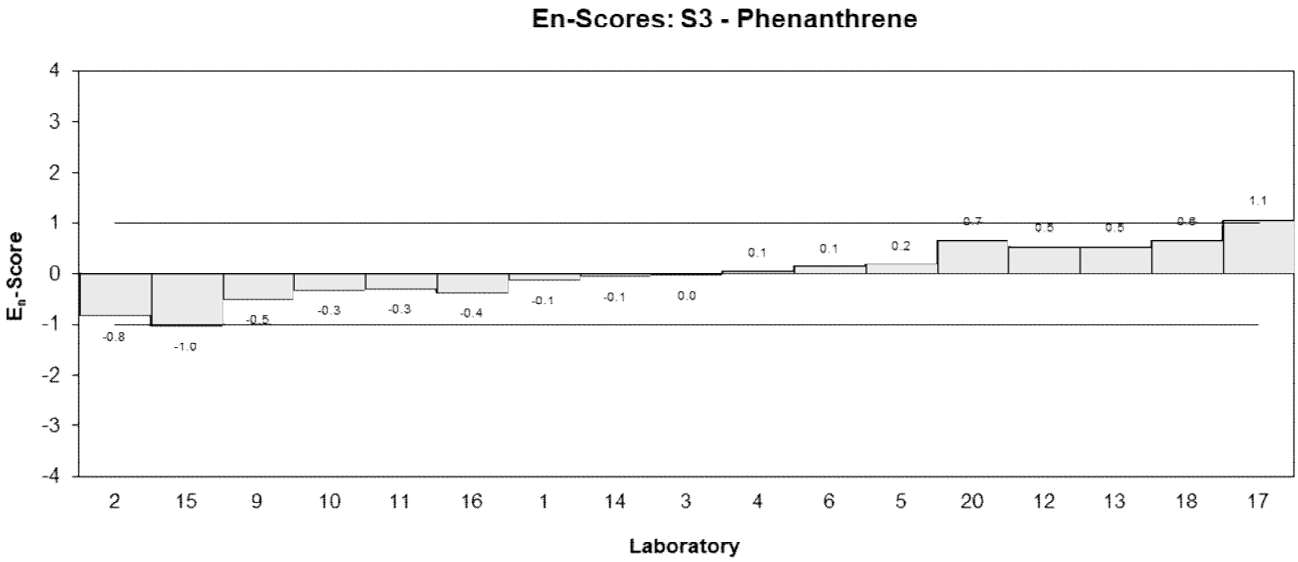

En-Scores: S3 - Phenanthrene
En-Score
-0.8 -1.0 -0.5 -0.3 -0.3 -0.4 -0.1 -0.1 0.0 0.1 0.1 0.2 0.7 0.5 0.5 0.6 1.1
Laboratory
2 15 9 10 11 16 1 14 3 4 6 5 20 12 13 18 17

Figure 16

Table 21

Sample Details

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

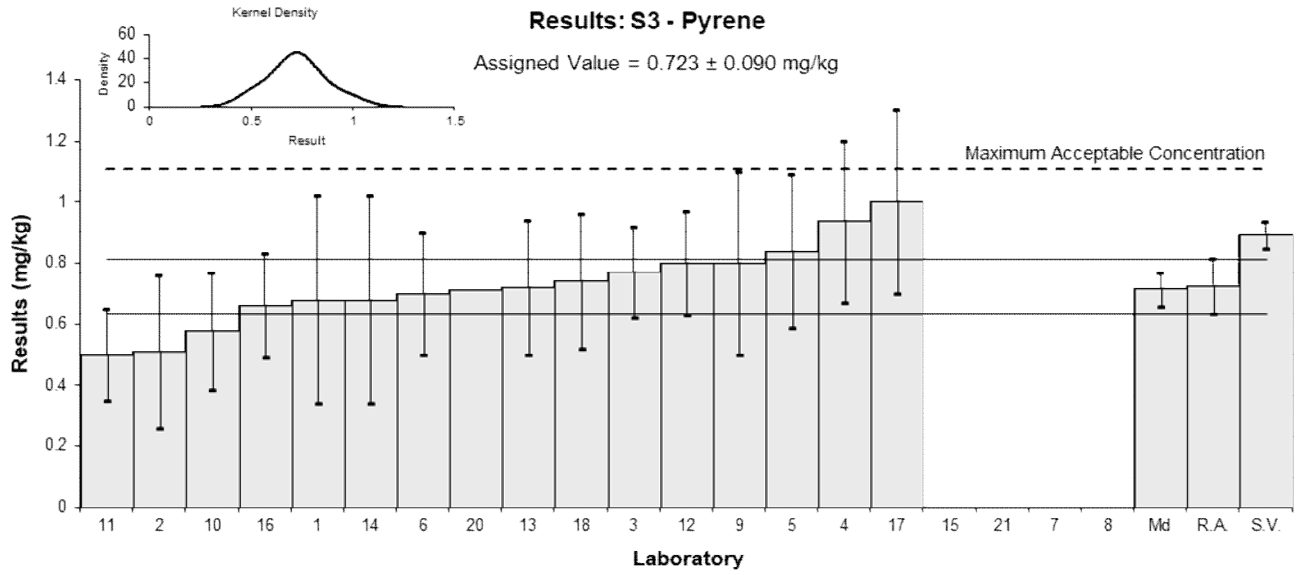
Participant Results

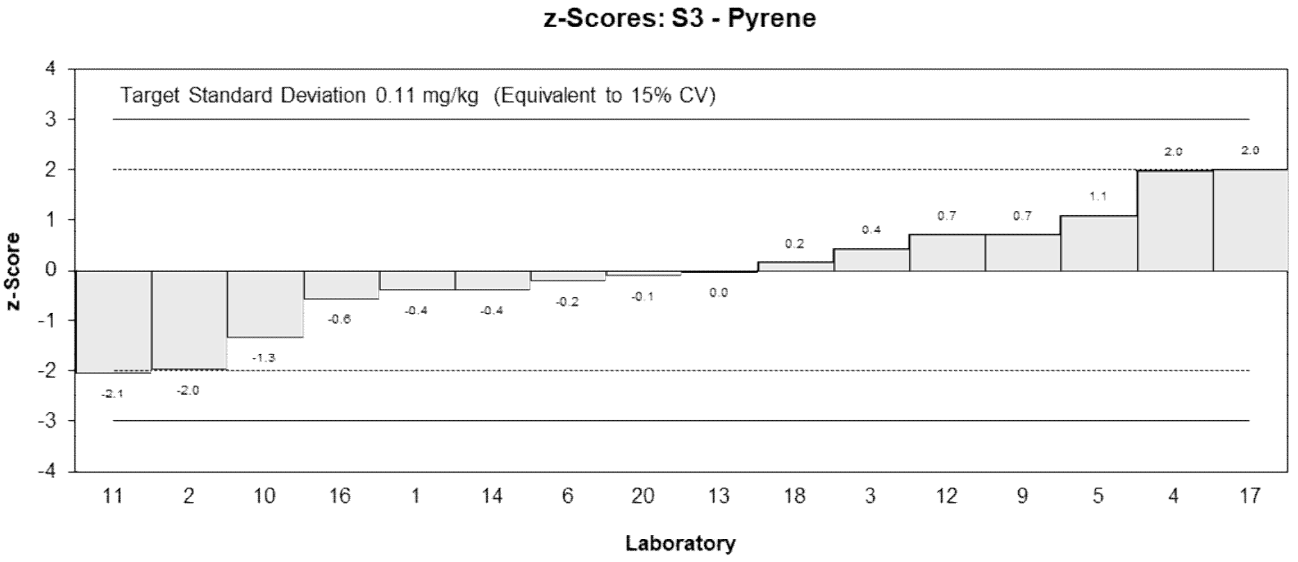
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	0.68	0.34	-0.40	-0.12
2	0.51	0.25	-1.96	-0.80
3	0.77	0.15	0.43	0.27
4	0.937	0.265	1.97	0.76
5	0.84	0.25	1.08	0.44
6	0.7	0.2	-0.21	-0.10
7	NT	NT		
8	NT	NT		
9	0.8	0.3	0.71	0.25
10	0.577	0.19	-1.35	-0.69
11	0.5	0.15	-2.06	-1.27
12	0.8	0.17	0.71	0.40
13	0.72	0.22	-0.03	-0.01
14	0.68	0.34	-0.40	-0.12
15	<1	NR		
16	0.66	0.17	-0.58	-0.33
17*	1	0.3	2.00	0.88
18	0.74	0.22	0.16	0.07
20	0.71	NR	-0.12	-0.14
21	NT	NT		

Statistics

Assigned Value	0.723	0.090
Spike	0.892	0.045
Max. Acceptable Concentration*	1.11	
Robust Average	0.723	0.090
Median	0.715	0.055
Mean	0.727	
N	16	
Max.	1	
Min.	0.5	
Robust SD	0.14	
Robust CV	20%	

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


Kernel Density
Density
Result
Results: S3 - Pyrene
Assigned Value = 0.723 ± 0.090 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
11 2 10 16 1 14 6 20 13 18 3 12 9 5 4 17 15 21 7 8 Md R.A. S.V.


z-Scores: S3 - Pyrene
Target Standard Deviation 0.11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
11 2 10 16 1 14 6 20 13 18 3 12 9 5 4 17
-2.1 -2.0 -1.3 -0.6 -0.4 -0.4 -0.2 -0.1 0.0 0.2 0.4 0.7 0.7 1.1 2.0 2.0

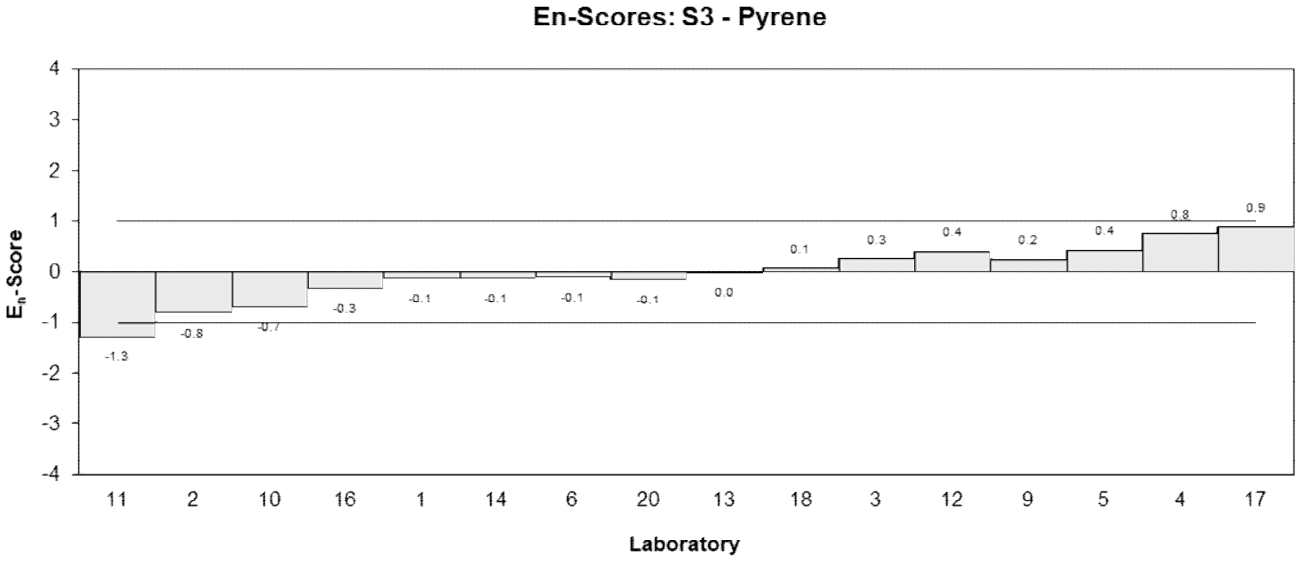

En-Scores: S3 - Pyrene
En-Score
Laboratory
11 2 10 16 1 14 6 20 13 18 3 12 9 5 4 17
-1.3 -0.8 -0.7 -0.3 -0.1 -0.1 -0.1 -0.1 0.0 0.1 0.3 0.4 0.2 0.4 0.8 0.9

Figure 17

Table 22

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	0.84	0.42
2	NT	NT
3	1.11	0.25
4	1.18	0.437
5	1.41	0.42
6	1.1	0.3
7	NT	NT
8	NT	NT
9	1.1	0.3
10	0.566	0.18
11	0.6	0.18
12	1.36	0.27
13	0.862	0.26
14	0.63	0.47
15	<1	NR
16	0.44	0.11
17	1.5	0.45
18	<0.01	NR
20	0.75	NR
21	NT	NT

Statistics

Assigned Value	Not Set	
Spike	2.30	0.12
Robust Average	0.96	0.26
Median	0.98	0.25
Mean	0.96	
N	14	
Max.	1.5	
Min.	0.44	
Robust SD	0.38	
Robust CV	40%	

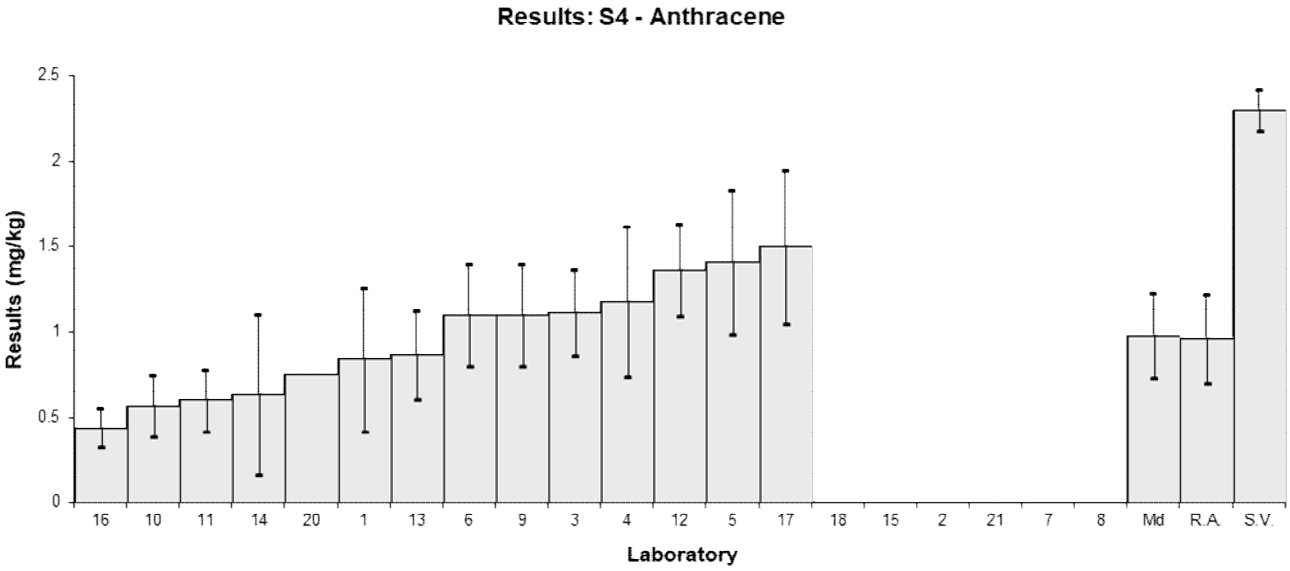

Results: S4 - Anthracene
Results (mg/kg)
2.5
2
1.5
1
0.5
0
16
10
11
14
20
1
13
6
9
3
4
12
5
17
18
15
2
21
7
8
Md
R.A.
S.V.
Laboratory

Figure 18

Table 23

Sample Details

Sample No.	S4
Matrix	Soil
Analyte	Benzo(a)pyrene
Units	mg/kg

Participant Results

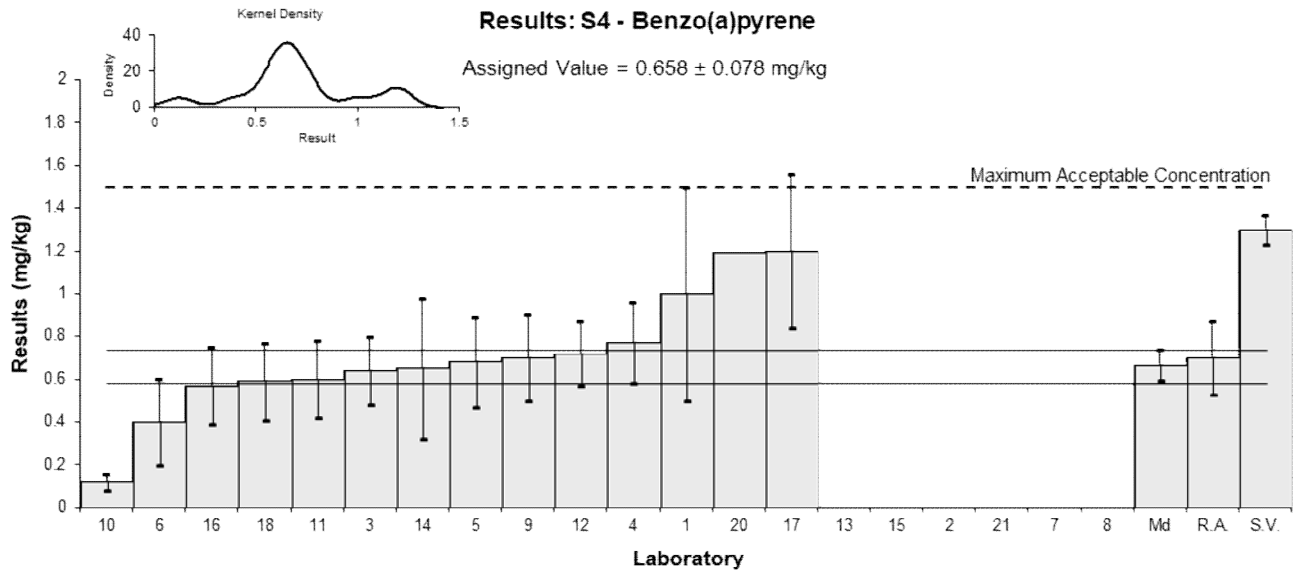
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1**	1.00	0.50	2.00	0.68
2	NT	NT		
3	0.64	0.16	-0.18	-0.10
4	0.772	0.190	1.16	0.56
5	0.68	0.21	0.22	0.10
6	0.4	0.2	-2.61	-1.20
7	NT	NT		
8	NT	NT		
9	0.7	0.2	0.43	0.20
10	0.119	0.039	-5.46	-6.18
11	0.6	0.18	-0.59	-0.30
12	0.72	0.15	0.63	0.37
13	<0.1	0.03		
14	0.65	0.33	-0.08	-0.02
15	<1	NR		
16	0.57	0.18	-0.89	-0.45
17**	1.2	0.36	2.00	1.00
18	0.59	0.18	-0.69	-0.35
20**	1.19	NR	2.00	1.00
21	NT	NT		

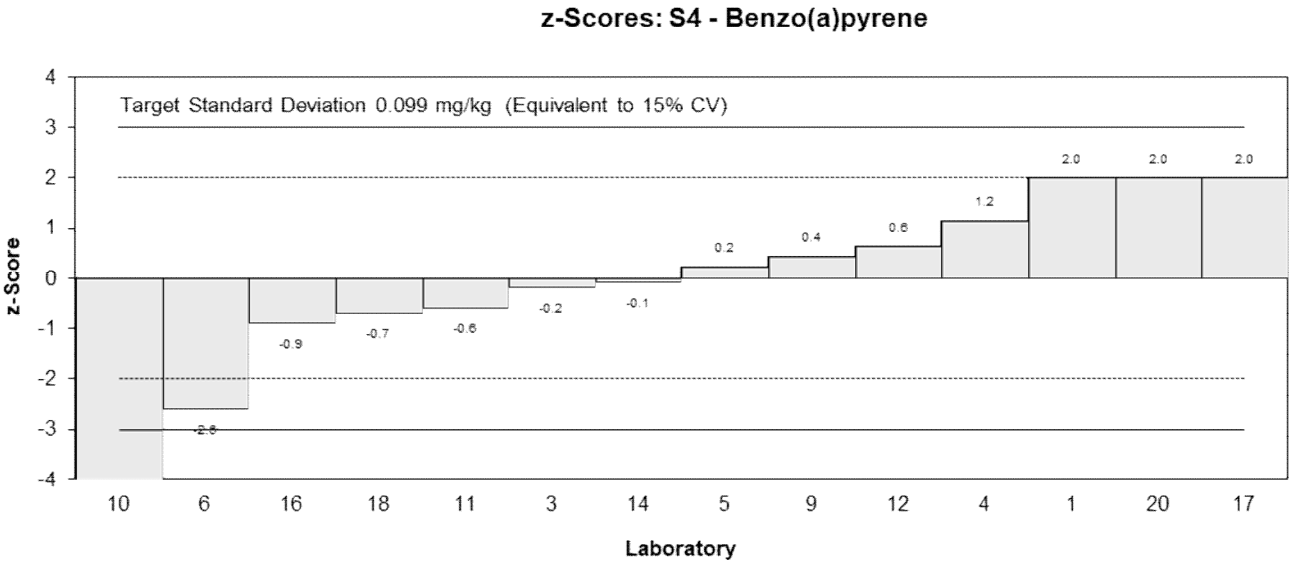
Statistics

Assigned Value*	0.658	0.078
Spike	1.30	0.07
Max. Acceptable Concentration**	1.50	
Robust Average	0.70	0.17
Median	0.665	0.073
Mean	0.702	
N	14	
Max.	1.2	
Min.	0.119	
Robust SD	0.26	
Robust CV	37%	

* Robust average excluding Laboratories 10, 17 and 20.

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


Kernel Density
Density
Result
Results: S4 - Benzo(a)pyrene
Assigned Value = 0.658 ± 0.078 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
10 6 16 18 11 3 14 5 9 12 4 1 20 17 13 15 2 21 7 8 Md R.A. S.V.


z-Scores: S4 - Benzo(a)pyrene
Target Standard Deviation 0.099 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
10 6 16 18 11 3 14 5 9 12 4 1 20 17

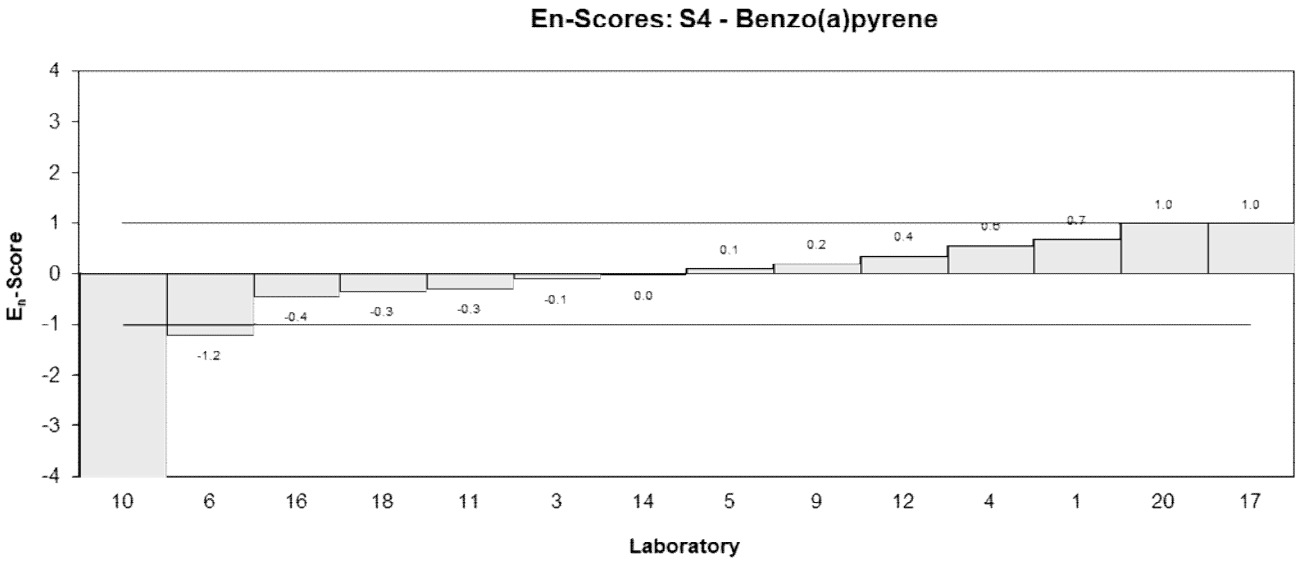

En-Scores: S4 - Benzo(a)pyrene
En-Score
Laboratory
10 6 16 18 11 3 14 5 9 12 4 1 20 17

Figure 19

Table 24

Sample Details

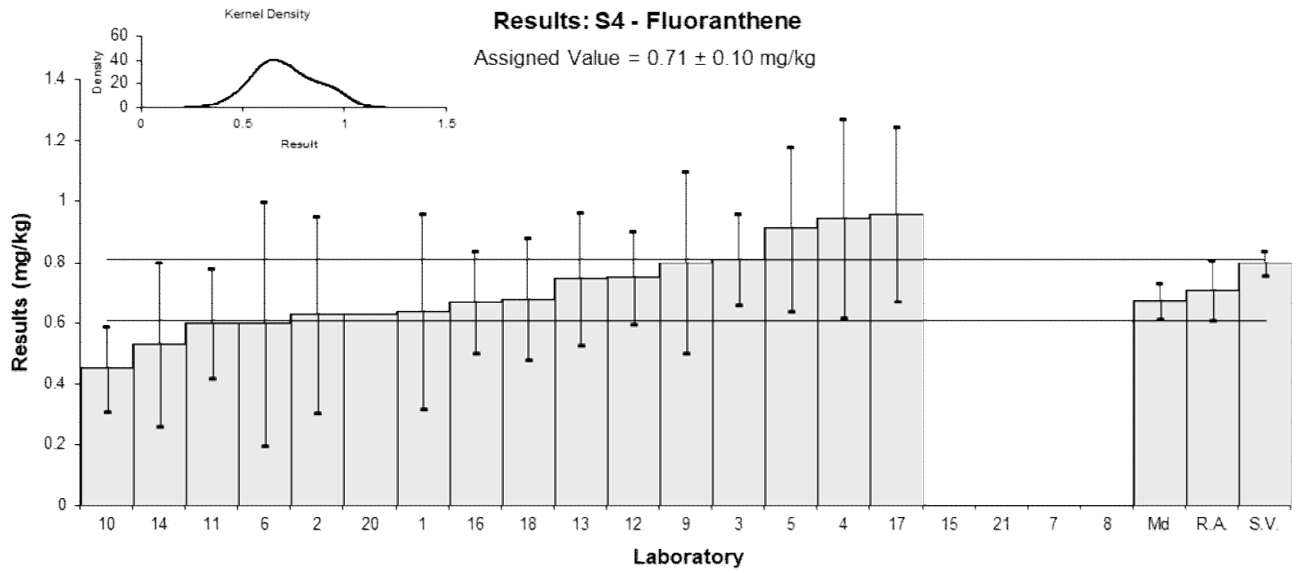
Sample No.	S4
Matrix	Soil
Analyte	Fluoranthene
Units	mg/kg

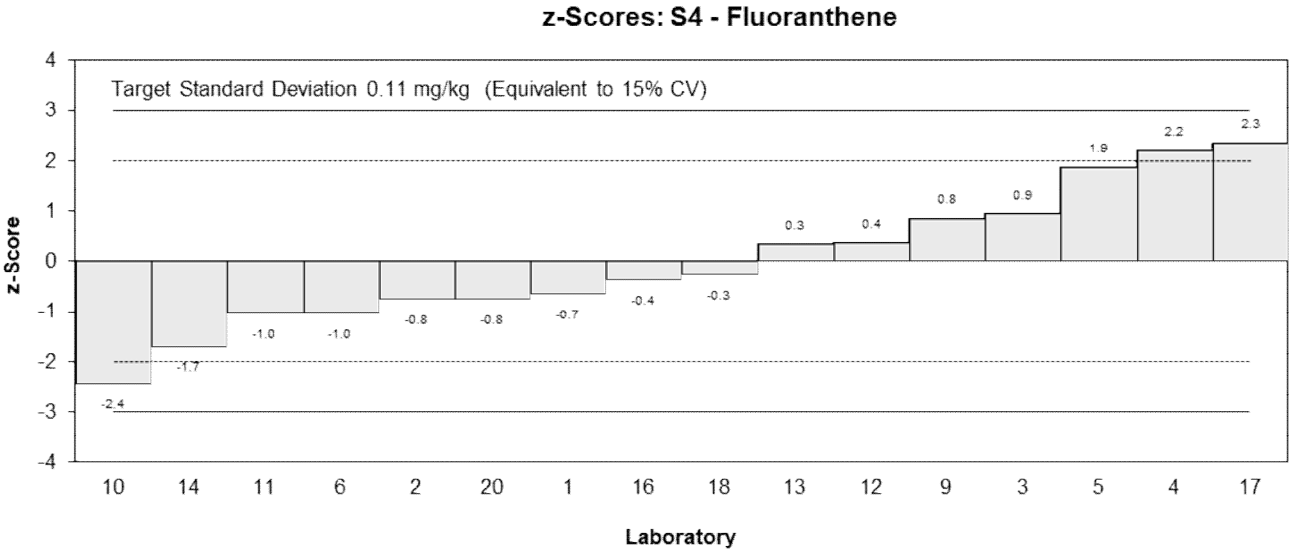
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	0.64	0.32	-0.66	-0.21
2	0.63	0.32	-0.75	-0.24
3	0.81	0.15	0.94	0.55
4	0.945	0.327	2.21	0.69
5	0.91	0.27	1.88	0.69
6	0.6	0.4	-1.03	-0.27
7	NT	NT		
8	NT	NT		
9	0.8	0.3	0.85	0.28
10	0.451	0.14	-2.43	-1.51
11	0.6	0.18	-1.03	-0.53
12	0.75	0.15	0.38	0.22
13	0.746	0.22	0.34	0.15
14	0.53	0.27	-1.69	-0.63
15	<1	NR		
16	0.67	0.17	-0.38	-0.20
17	0.96	0.288	2.35	0.82
18	0.68	0.2	-0.28	-0.13
20	0.63	NR	-0.75	-0.80
21	NT	NT		

Statistics

Assigned Value	0.71	0.10
Spike	0.798	0.040
Robust Average	0.71	0.10
Median	0.675	0.059
Mean	0.710	
N	16	
Max.	0.96	
Min.	0.451	
Robust SD	0.16	
Robust CV	23%	


Kernel Density
Density
Result
Results: S4 - Fluoranthene
Assigned Value = 0.71 ± 0.10 mg/kg
Results (mg/kg)
Laboratory
10 14 11 6 2 20 1 16 18 13 12 9 3 5 4 17 15 21 7 8 Md R.A. S.V.


z-Scores: S4 - Fluoranthene
Target Standard Deviation 0.11 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
10 14 11 6 2 20 1 16 18 13 12 9 3 5 4 17
-2.4 -1.7 -1.0 -1.0 -0.8 -0.8 -0.7 -0.4 -0.3 0.3 0.4 0.8 0.9 1.9 2.2 2.3

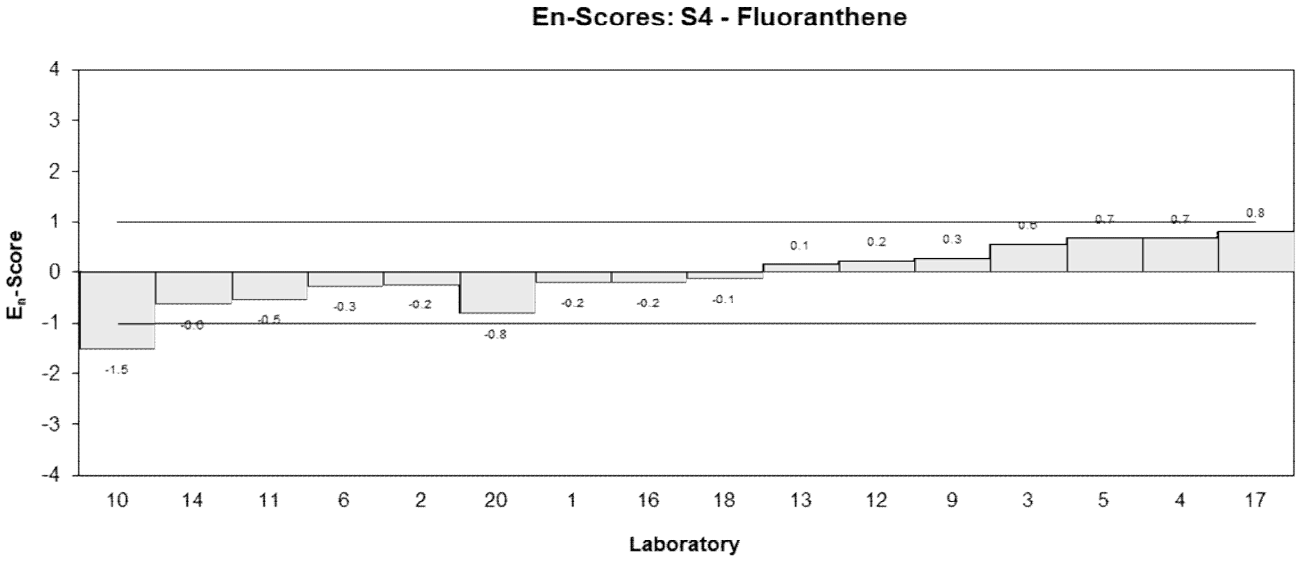

En-Scores: S4 - Fluoranthene
En-Score
Laboratory
10 14 11 6 2 20 1 16 18 13 12 9 3 5 4 17
-1.5 -0.6 -0.5 -0.3 -0.2 -0.8 -0.2 -0.2 -0.1 0.1 0.2 0.3 0.5 0.7 0.7 0.8

Figure 20

Table 25

Sample Details

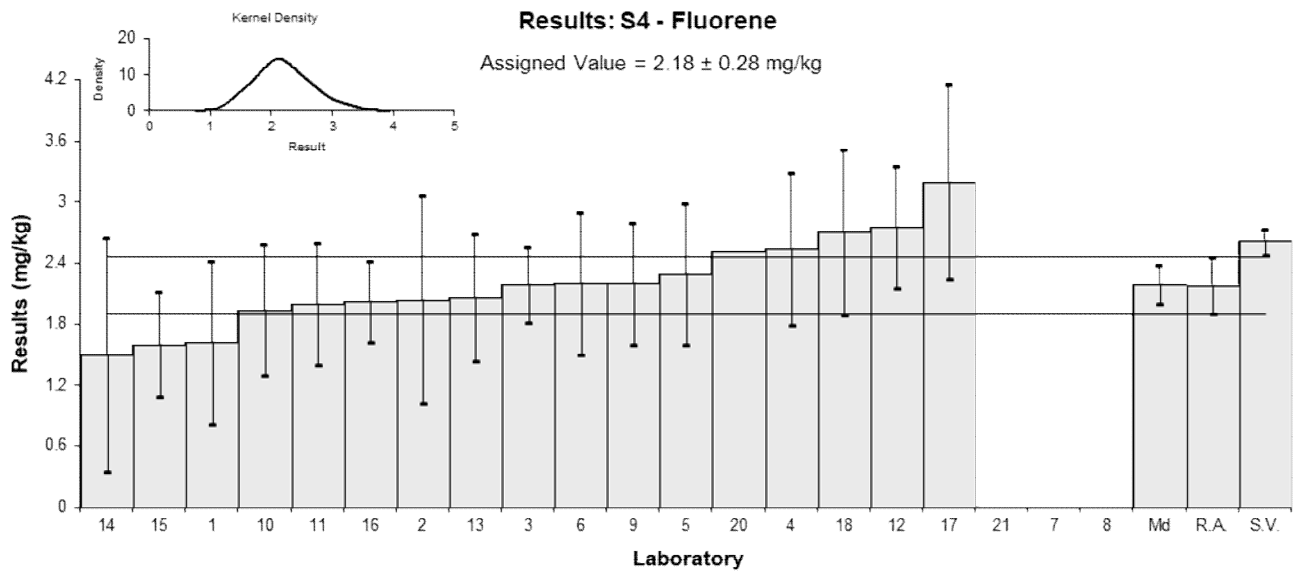
Sample No.	S4
Matrix	Soil
Analyte	Fluorene
Units	mg/kg

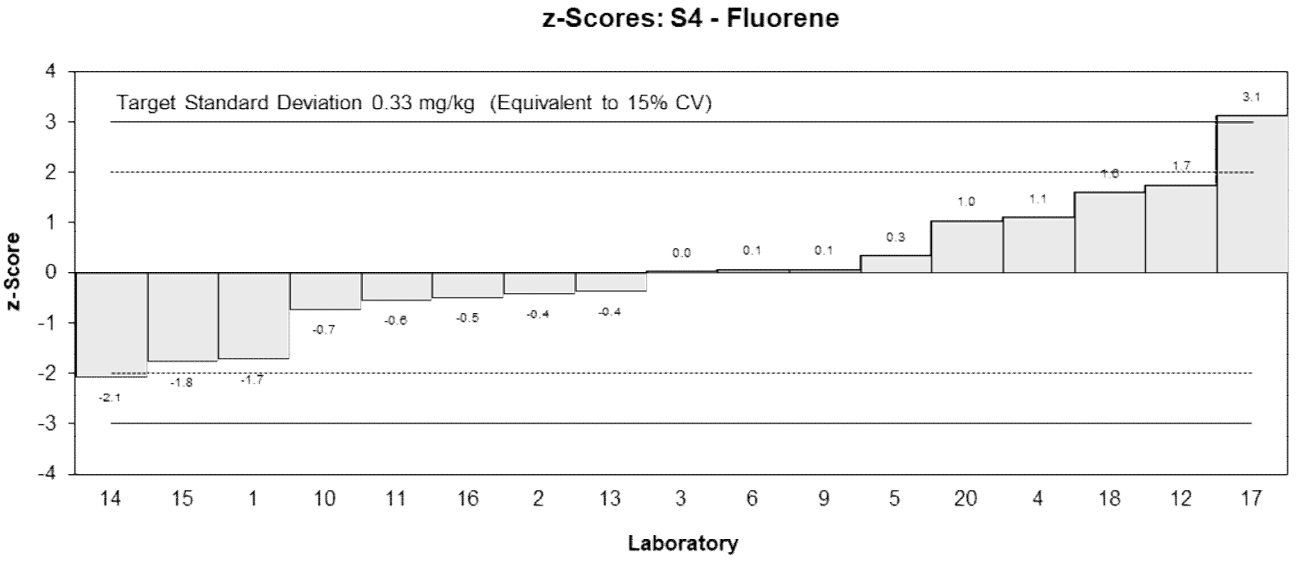
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.62	0.80	-1.71	-0.66
2	2.04	1.02	-0.43	-0.13
3	2.19	0.37	0.03	0.02
4	2.54	0.752	1.10	0.45
5	2.29	0.69	0.34	0.15
6	2.2	0.7	0.06	0.03
7	NT	NT		
8	NT	NT		
9	2.2	0.6	0.06	0.03
10	1.94	0.64	-0.73	-0.34
11	2	0.6	-0.55	-0.27
12	2.75	0.6	1.74	0.86
13	2.059	0.62	-0.37	-0.18
14	1.5	1.14	-2.08	-0.58
15	1.6	0.52	-1.77	-0.98
16	2.02	0.40	-0.49	-0.33
17	3.2	0.96	3.12	1.02
18	2.7	0.81	1.59	0.61
20	2.52	NR	1.04	1.21
21	NT	NT		

Statistics

Assigned Value	2.18	0.28
Spike	2.61	0.13
Robust Average	2.18	0.28
Median	2.19	0.19
Mean	2.20	
N	17	
Max.	3.2	
Min.	1.5	
Robust SD	0.46	
Robust CV	21%	


Results: S4 - Fluorene
Assigned Value = 2.18 ± 0.28 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 15 1 10 11 16 2 13 3 6 9 5 20 4 18 12 17 21 7 8 Md R.A. S.V.


z-Scores: S4 - Fluorene
Target Standard Deviation 0.33 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 15 1 10 11 16 2 13 3 6 9 5 20 4 18 12 17

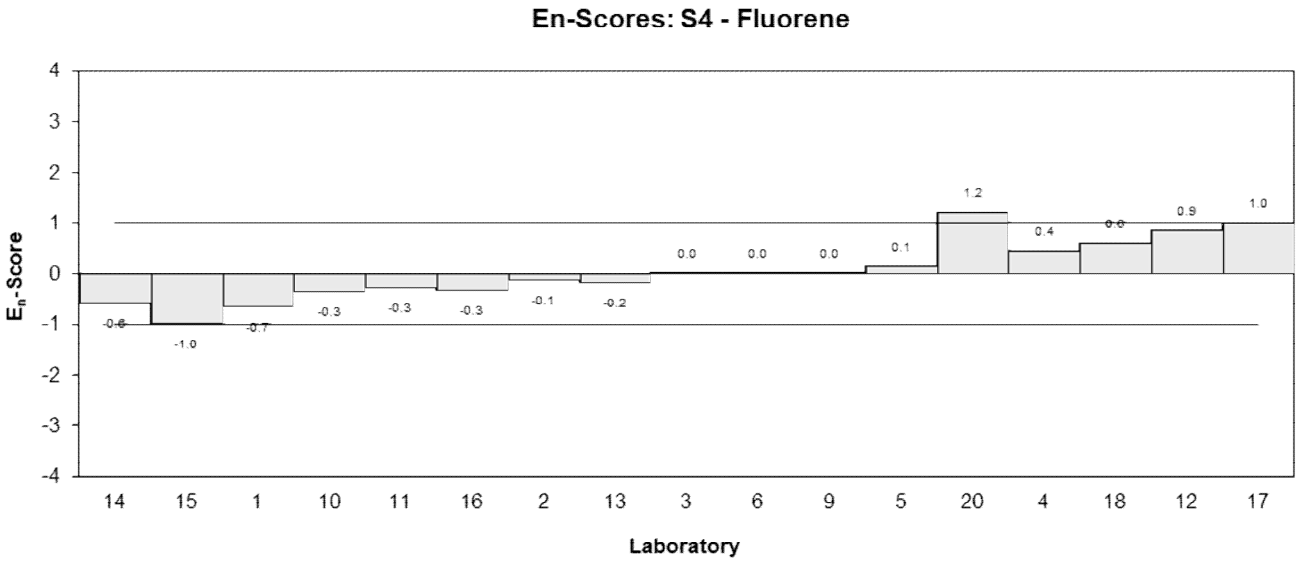

En-Scores: S4 - Fluorene
En-Score
Laboratory
14 15 1 10 11 16 2 13 3 6 9 5 20 4 18 12 17

Figure 21

Table 26

Sample Details

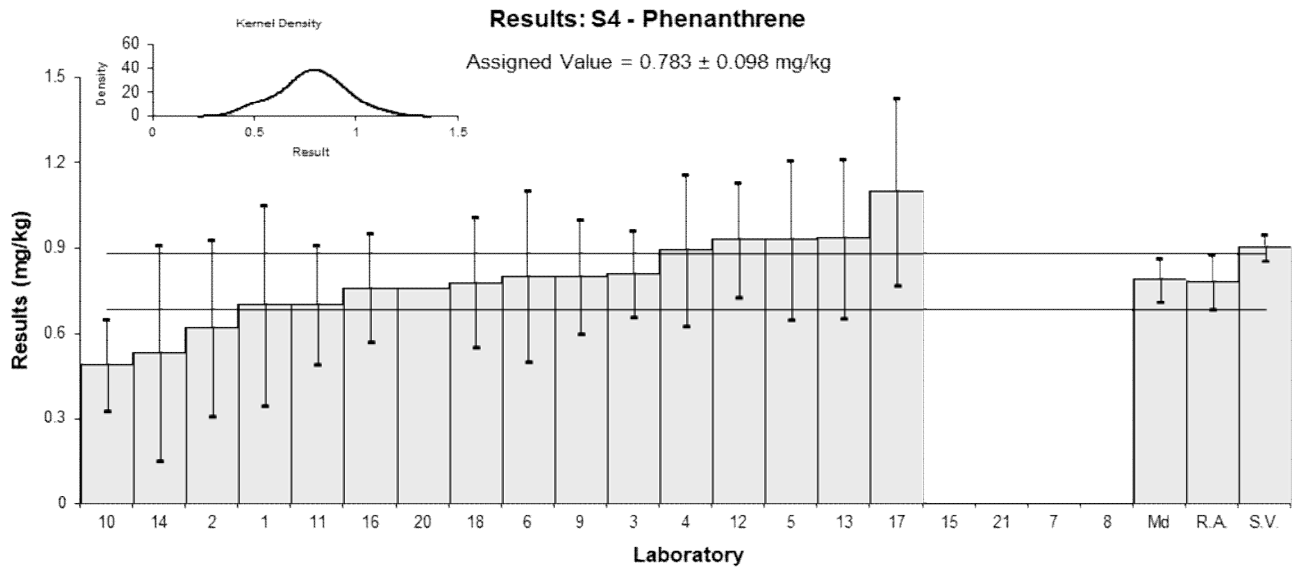
Sample No.	S4
Matrix	Soil
Analyte	Phenanthrene
Units	mg/kg

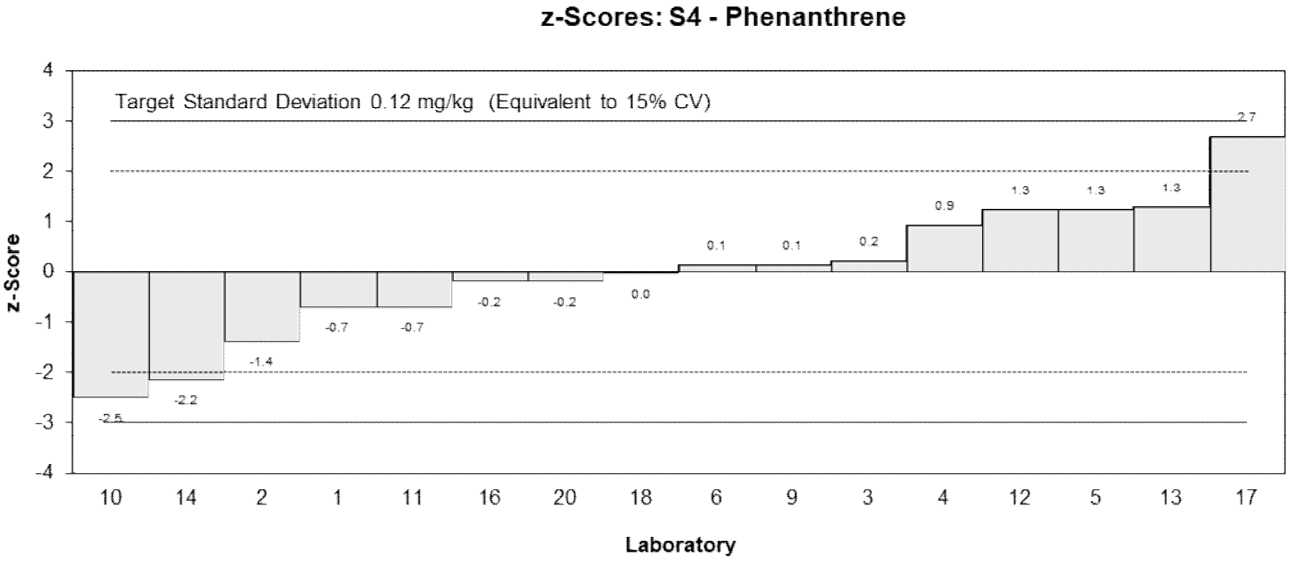
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	0.70	0.35	-0.71	-0.23
2	0.62	0.31	-1.39	-0.50
3	0.81	0.15	0.23	0.15
4	0.894	0.265	0.95	0.39
5	0.93	0.28	1.25	0.50
6	0.8	0.3	0.14	0.05
7	NT	NT		
8	NT	NT		
9	0.8	0.2	0.14	0.08
10	0.488	0.16	-2.51	-1.57
11	0.7	0.21	-0.71	-0.36
12	0.93	0.2	1.25	0.66
13	0.934	0.28	1.29	0.51
14	0.53	0.38	-2.15	-0.64
15	<1	NR		
16	0.76	0.19	-0.20	-0.11
17	1.1	0.33	2.70	0.92
18	0.78	0.23	-0.03	-0.01
20	0.76	NR	-0.20	-0.23
21	NT	NT		

Statistics

Assigned Value	0.783	0.098
Spike	0.904	0.045
Robust Average	0.783	0.098
Median	0.790	0.077
Mean	0.784	
N	16	
Max.	1.1	
Min.	0.488	
Robust SD	0.16	
Robust CV	20%	


Results: S4 - Phenanthrene
Kernel Density
Density
Result
Assigned Value = 0.783 ± 0.098 mg/kg
Results (mg/kg)
Laboratory
10 14 2 1 11 16 20 18 6 9 3 4 12 5 13 17 15 21 7 8 Md R.A. S.V.


z-Scores: S4 - Phenanthrene
Target Standard Deviation 0.12 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
10 14 2 1 11 16 20 18 6 9 3 4 12 5 13 17

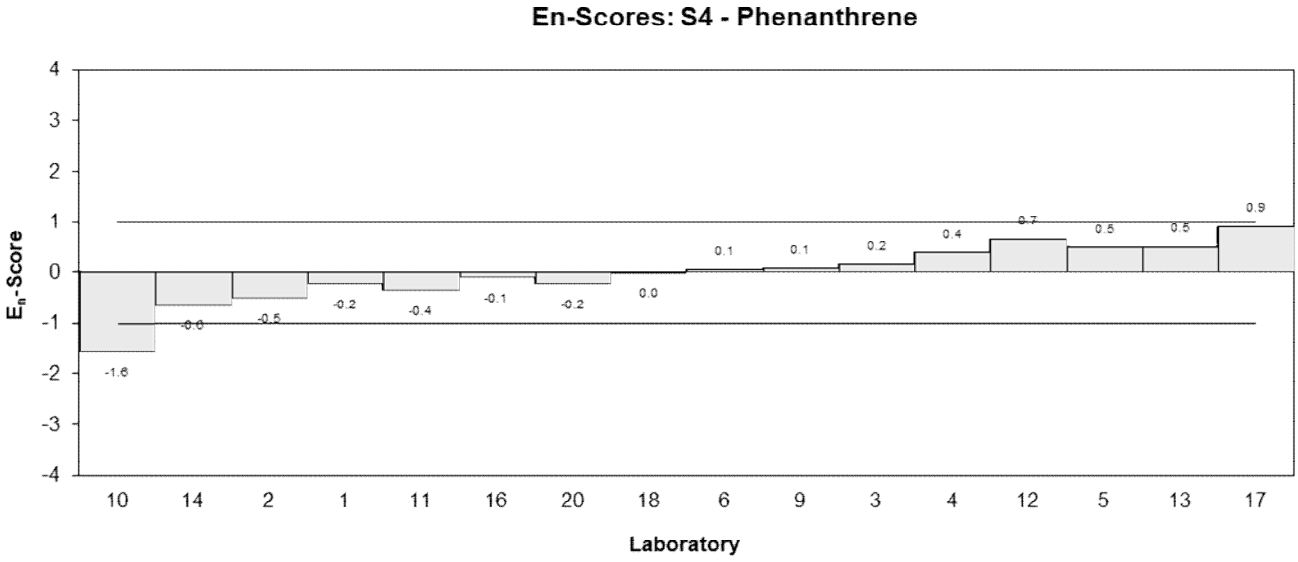

En-Scores: S4 - Phenanthrene
En-Score
Laboratory
10 14 2 1 11 16 20 18 6 9 3 4 12 5 13 17

Figure 22

Table 27

Sample Details

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

Participant Results

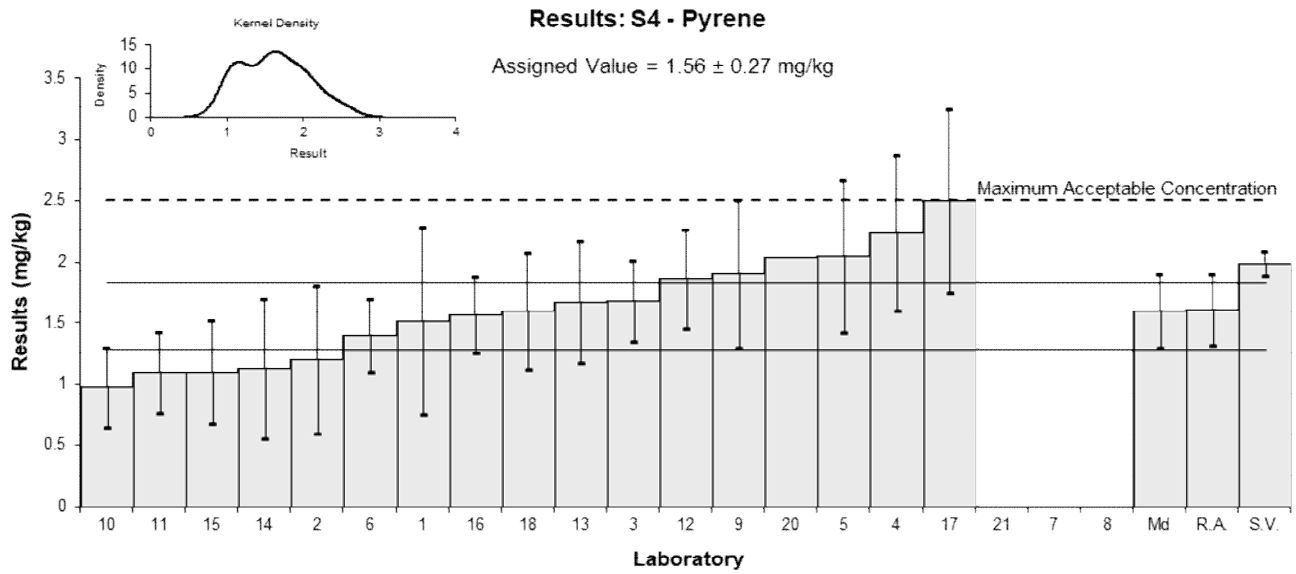
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.52	0.76	-0.17	-0.05
2	1.20	0.60	-1.54	-0.55
3	1.68	0.33	0.51	0.28
4**	2.24	0.633	2.00	0.99
5**	2.05	0.62	2.00	0.72
6	1.4	0.3	-0.68	-0.40
7	NT	NT		
8	NT	NT		
9	1.9	0.6	1.45	0.52
10	0.977	0.32	-2.49	-1.39
11	1.1	0.33	-1.97	-1.08
12	1.86	0.4	1.28	0.62
13	1.674	0.5	0.49	0.20
14	1.13	0.57	-1.84	-0.68
15	1.1	0.42	-1.97	-0.92
16	1.57	0.31	0.04	0.02
17**	2.5	0.75	2.00	1.00
18	1.6	0.48	0.17	0.07
20**	2.04	NR	2.00	1.00
21	NT	NT		

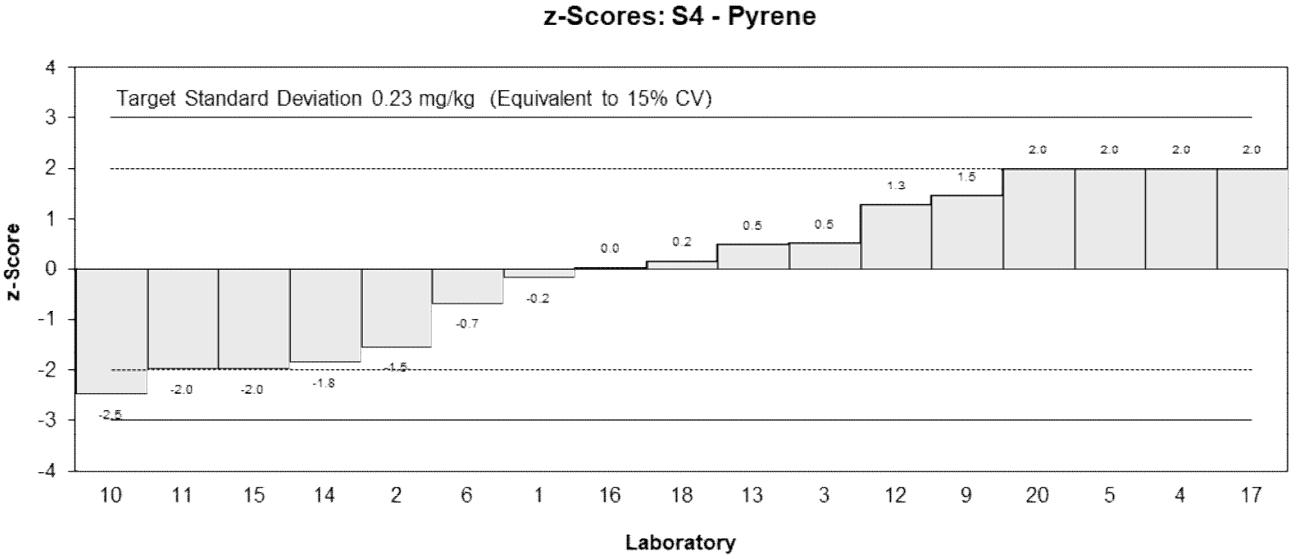
Statistics

Assigned Value*	1.56	0.27
Spike	1.99	0.10
Max. Acceptable Concentration**	2.5	
Robust Average	1.61	0.29
Median	1.60	0.30
Mean	1.62	
N	17	
Max.	2.5	
Min.	0.977	
Robust SD	0.48	
Robust CV	30%	

* Robust average excluding Laboratory 17.

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


Results: S4 - Pyrene
Kernel Density
Density
Result
Assigned Value = 1.56 ± 0.27 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
10 11 15 14 2 6 1 16 18 13 3 12 9 20 5 4 17 21 7 8 Md R.A. S.V.


z-Scores: S4 - Pyrene
Target Standard Deviation 0.23 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
10 11 15 14 2 6 1 16 18 13 3 12 9 20 5 4 17

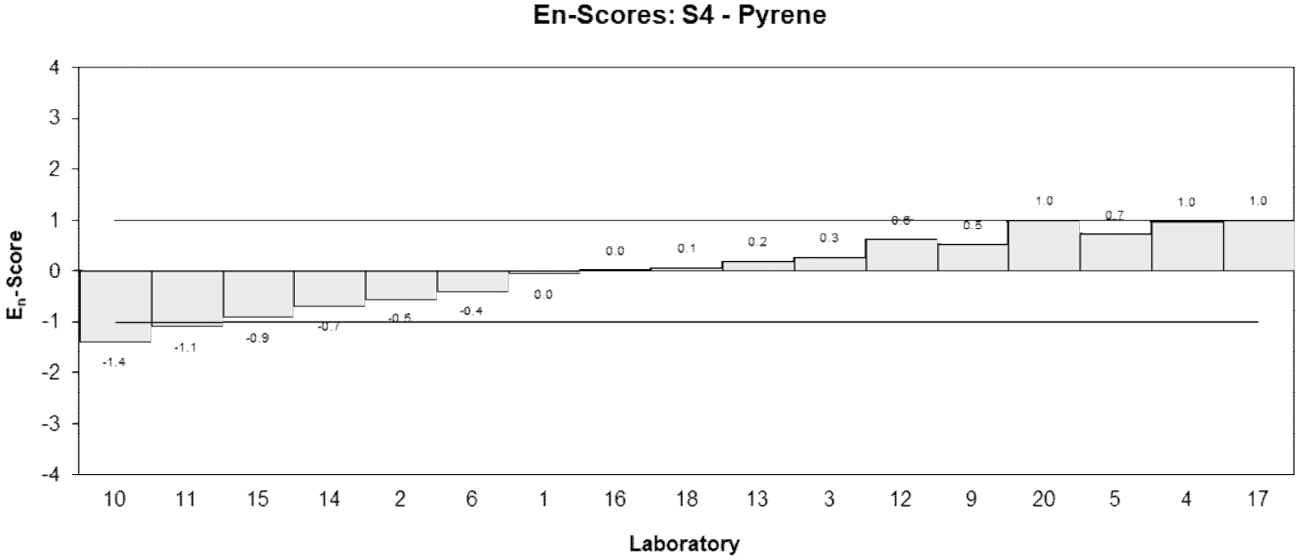

En-Scores: S4 - Pyrene
En-Score
Laboratory
10 11 15 14 2 6 1 16 18 13 3 12 9 20 5 4 17

Figure 23

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 13528:2015.[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 4, using fluoranthene in Sample S3 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, Sample S3 anthracene and Sample S4 anthracene as these analytes had poor recovery rates and reported results were highly variable. Sample S2 C6-C10 range was also not scored; historically this has been due to its volatile nature and therefore data is provided for information only, however the CV of participants' results in this study has improved as compared to previous Hydrocarbons in Soil PT studies.

A comparison of the assigned values (or robust averages if no assigned value was set) and the spiked values is presented in Table 28. The assigned values for TRH were within the range of 82% to 96% of the spiked values, showing good consensus between the spiked and assigned values. The assigned values for BTEX and PAHs were within the ranges of 62% to 89% and 49% to 89% of the spiked values respectively. Similar ratios have been observed in previous studies, and an assigned value was set if there was a reasonable consensus of results.

Table 28 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	620	759	82
	>C16-C34	1370	1420	96
	>C34-C40	247	266	93
	TRH	2170	2440	89
S2	Benzene	*(27.5)*	72.6	*(38)*
	Toluene	384	615	62
	Ethylbenzene	62.7	70.3	89
	Xylenes	353	527	67
	Total BTEX	814	1290	63
S3	Anthracene	*(0.34)*	0.797	*(43)*
	Benzo(a)pyrene	0.88	1.79	49
	Fluoranthene	2.65	3.05	87
	Fluorene	1.97	2.37	83
	Phenanthrene	2.63	3.07	86
	Pyrene	0.723	0.892	81
S4	Anthracene	*(0.96)*	2.30	*(42)*
	Benzo(a)pyrene	0.658	1.30	51

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Assigned Value *(Robust Average)* / Spiked Value (%)
	Fluoranthene	0.71	0.798	89
	Fluorene	2.18	2.61	84
	Phenanthrene	0.783	0.904	87
	Pyrene	1.56	1.99	78

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 17025:2017 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 346 numerical results, 330 results (95%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3).

The magnitude of the reported expanded uncertainties was within the range 5.9% to 77% of the reported value. In general, an expanded uncertainty of less than 15% relative is likely to be unrealistically small for the routine measurement of a hydrocarbon pollutant in soil, while an expanded uncertainty of over 50% is likely too large. Of the 330 expanded MUs, 9 were less than 15% relative while 17 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 **3**, **9**, **12** and **13** attached estimates of the expanded MU for results reported as less than their limit of detection. 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 499.18 ± 149.75 mg/kg, is better to report this result as 500 ± 150 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] target SDs (as PCV), and the between laboratories CVs obtained in this study for scored analytes are presented for comparison in Table 29.

Table 29 Comparison of Thompson-Horwitz CVs, Target SDs, and Between Laboratories CV

Sample	Analyte	Assigned Value (mg/kg)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between Laboratories CV* (%)
S1	>C10-C16	620	6.1	15	14
	>C16-C34	1370	5.4	15	20
	>C34-C40	247	7.0	15	17
	TRH	2170	5.0	15	18

Sample	Analyte	Assigned Value (mg/kg)	Thompson-Horwitz CV (%)	Target SD (as PCV) (%)	Between Laboratories CV* (%)
S2	Toluene	384	6.5	15	15
	Ethylbenzene	62.7	8.6	15	16
	Xylenes	353	6.6	15	14
	Total BTEX	814	5.8	15	16
S3	Benzo(a)pyrene	0.88	16	15	16
	Fluoranthene	2.65	14	15	22
	Fluorene	1.97	14	15	19
	Phenanthrene	2.63	14	15	18
	Pyrene	0.723	17	15	20
S4	Benzo(a)pyrene	0.658	17	15	16
	Fluoranthene	0.71	17	15	23
	Fluorene	2.18	14	15	21
	Phenanthrene	0.783	17	15	20
	Pyrene	1.56	15	15	28

* Robust between laboratories 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 16 z-scores were adjusted across the following analytes: Sample S1 >C10-C16, Sample S2 toluene, xylenes and total BTEX, Sample S3 benzo(a)pyrene, fluorene and pyrene, and Sample S4 benzo(a)pyrene and pyrene. A maximum acceptable concentration was set to two target SDs more than the spiked value, and results lower than the maximum acceptable concentration but with a z-score greater than 2.0 had their z-score adjusted to 2.0. This ensured that participants reporting results close to the spiked value were not penalised. z-Scores for results higher than the maximum acceptable concentration were not adjusted and z-scores less than 2.0 were left unaltered.

Of 293 results for which z-scores were calculated, 257 (88%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **3**, **4**, **5**, **6**, **9**, **10**, **11**, **12**, **14** and **18** reported results for all 18 analytes which were scored. Laboratories **3**, **5**, **9**, **12** and **18** returned satisfactory z-scores for all of these scored analytes.

Satisfactory z-scores were achieved for all scored results reported by Laboratories **1** (17), **8** (8) and **21** (5).

The dispersal of participants' z-scores is presented graphically by laboratory in Figure 24 and by analyte in Figure 25.

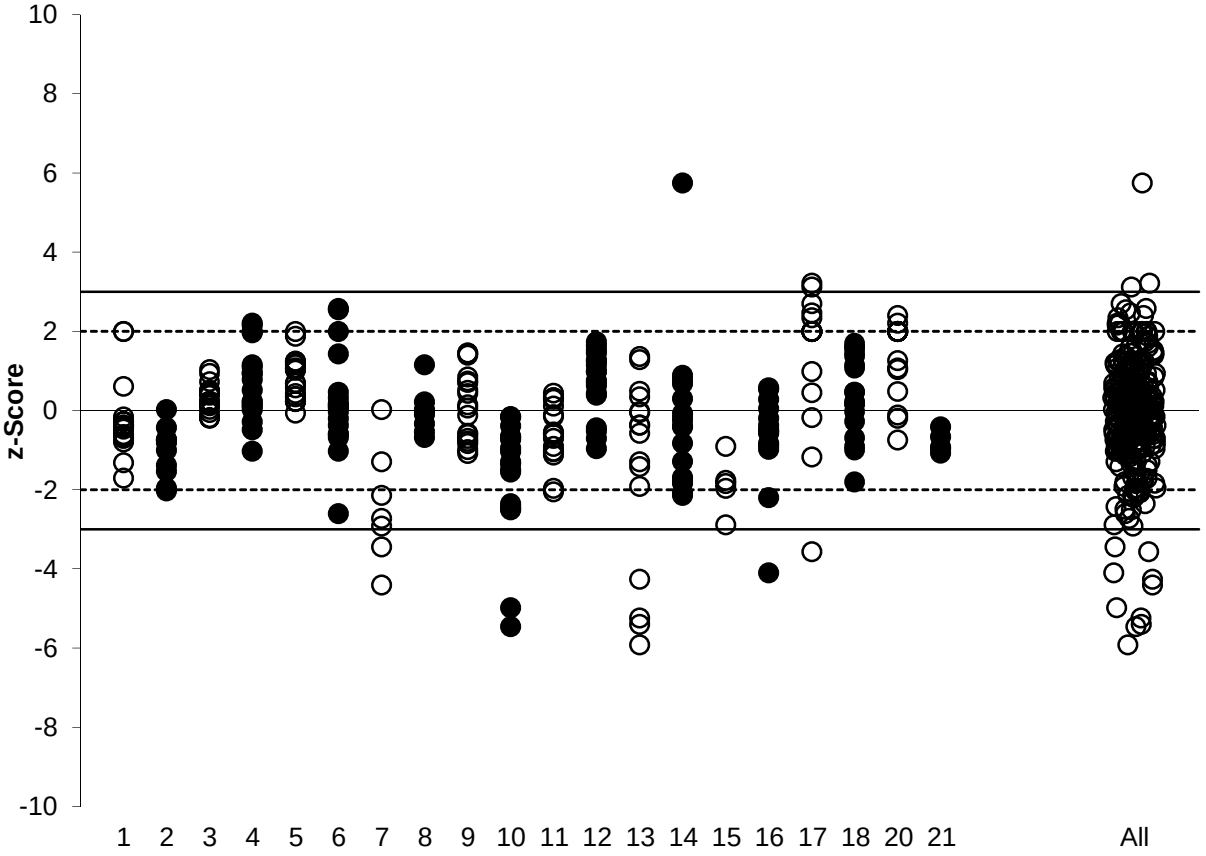


Figure 24 z-Score Dispersal by Laboratory

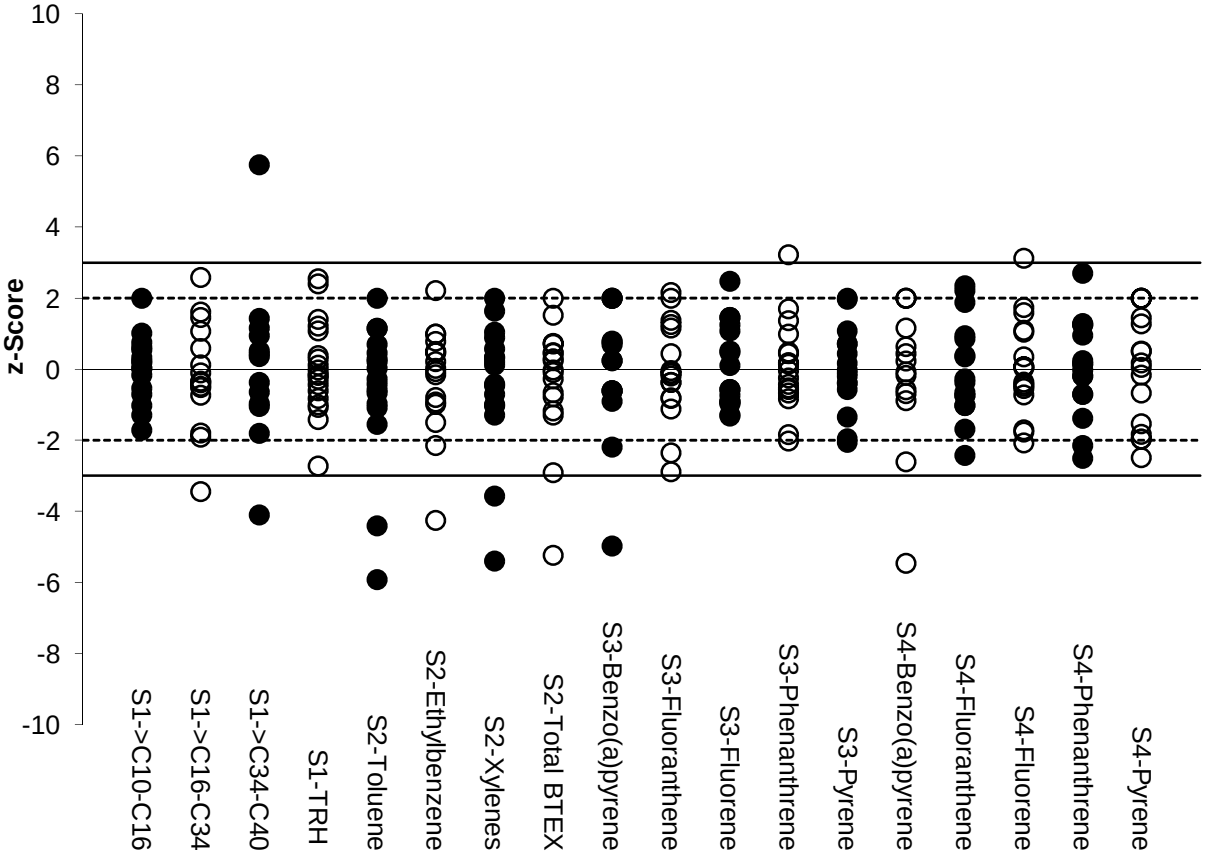


Figure 25 z-Score Dispersal by Analyte

Participants' z-scores for TRH (Sample S1), BTEX (Sample S2) and PAHs (Samples S3 and S4) are presented separately in Figures 26 to 28. A trend of z-scores on one side of the zero line may indicate laboratory bias for that analyte type.

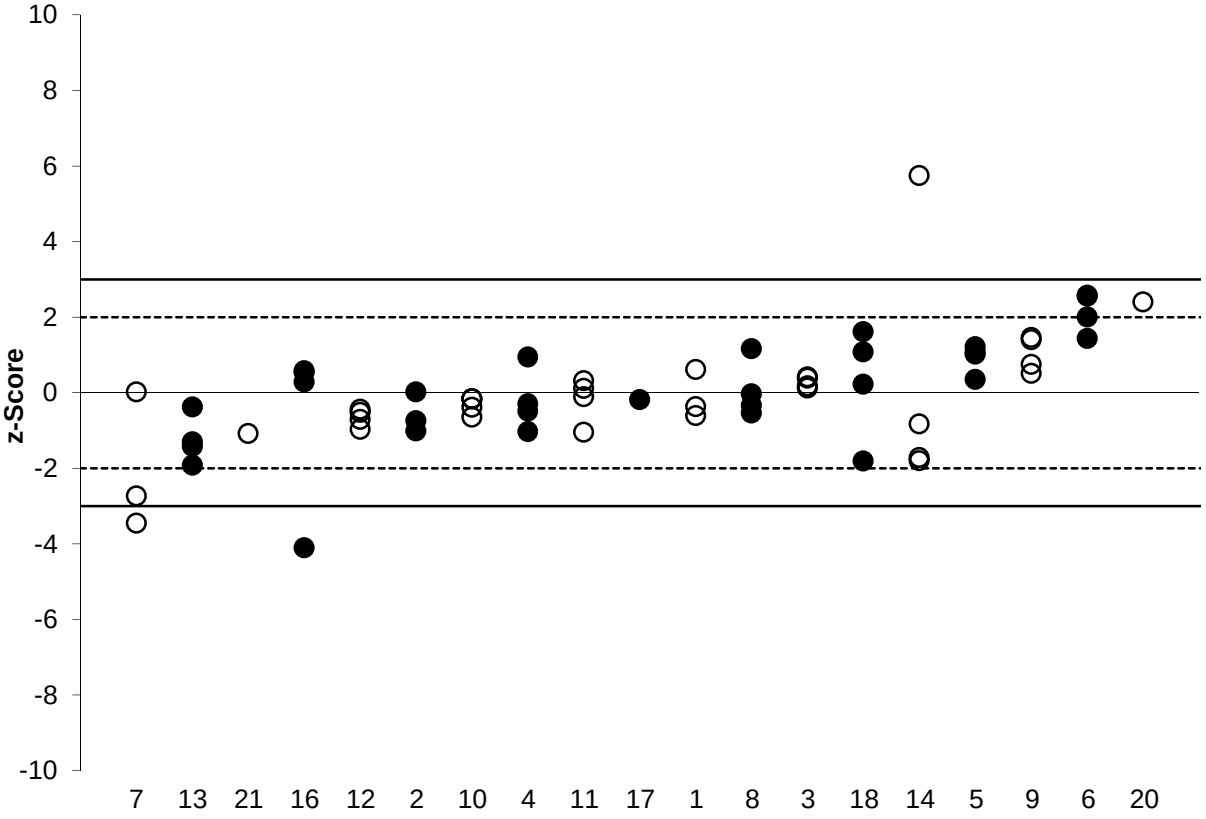


Figure 26 TRH (Sample S1) z-Score Dispersal by Laboratory

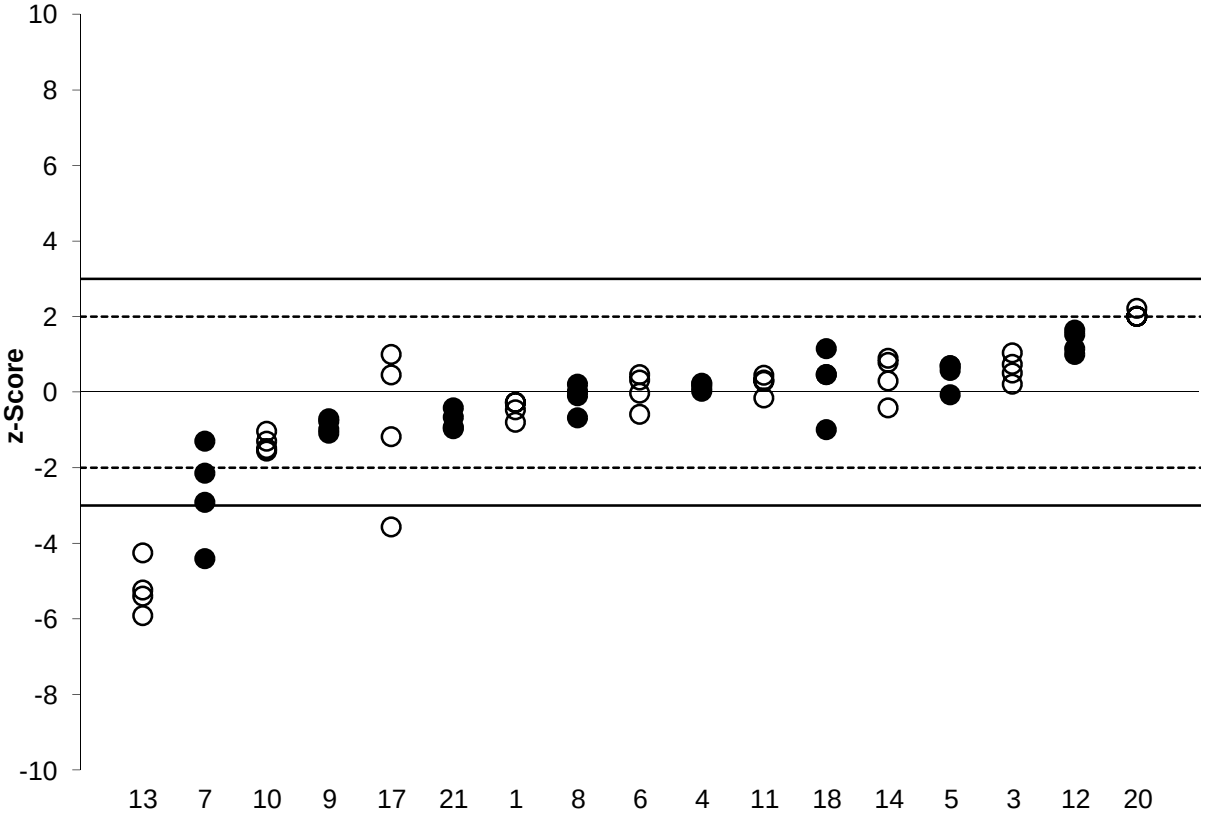


Figure 27 BTEX (Sample S2) z-Score Dispersal by Laboratory

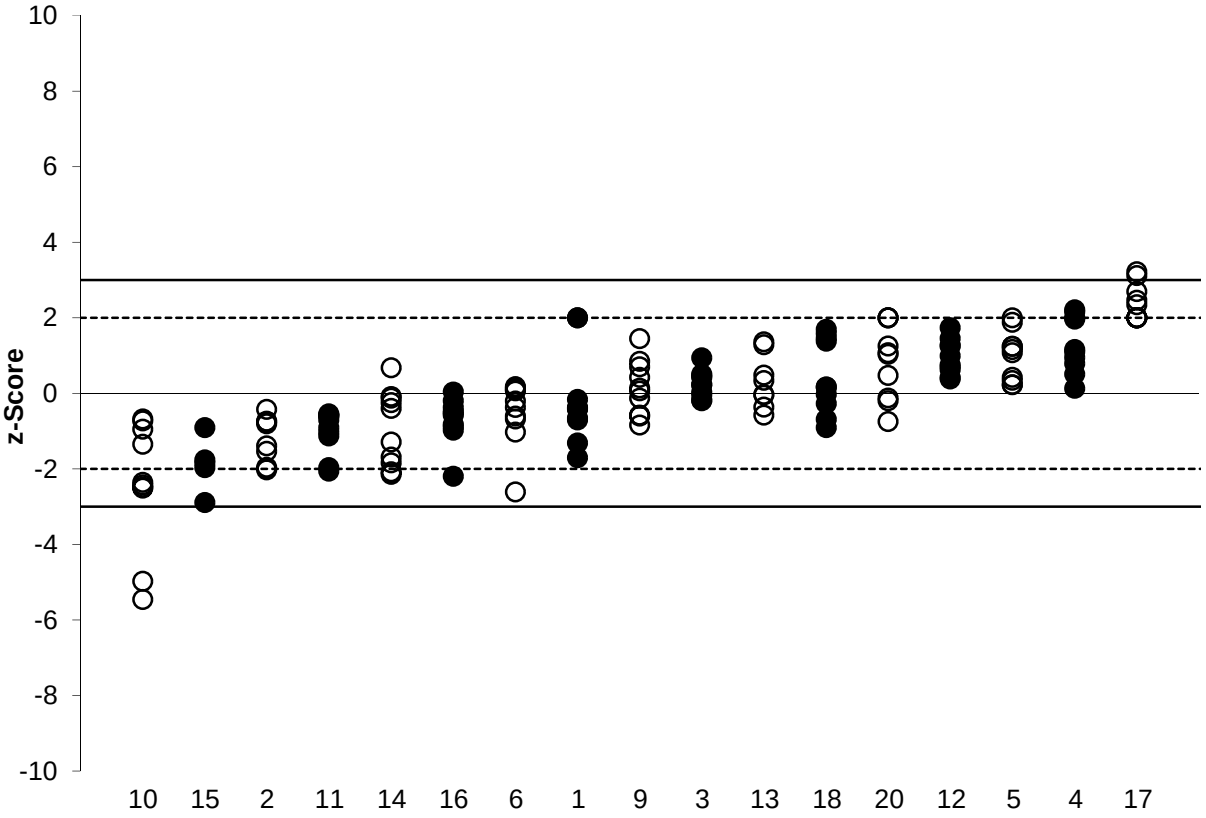
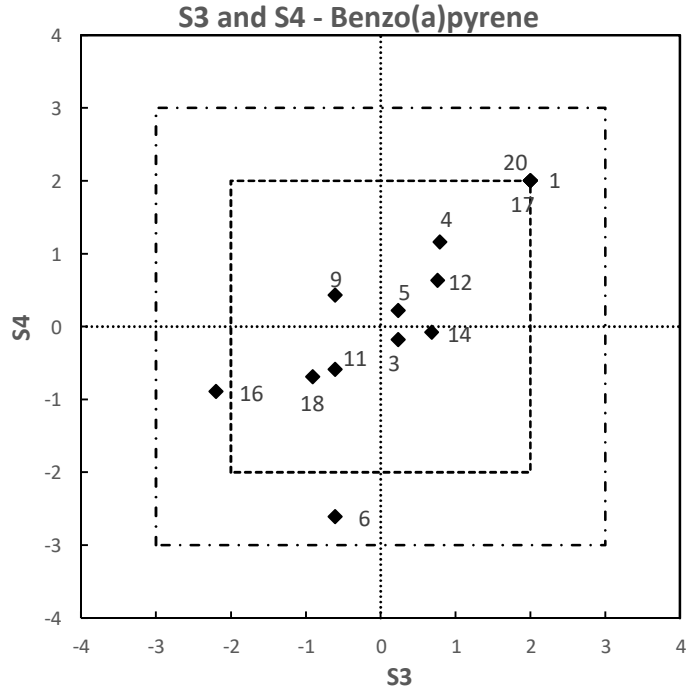


Figure 28 PAHs (Samples S3 and S4) z-Score Dispersal by Laboratory

Scatter plots of z-scores for benzo(a)pyrene, fluoranthene, fluorene, phenanthrene and pyrene in Samples S3 and S4 are presented in Figures 29 to 33. 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.



Laboratory 10 is off scale.

Figure 29 z-Score Scatter Plot – Benzo(a)pyrene

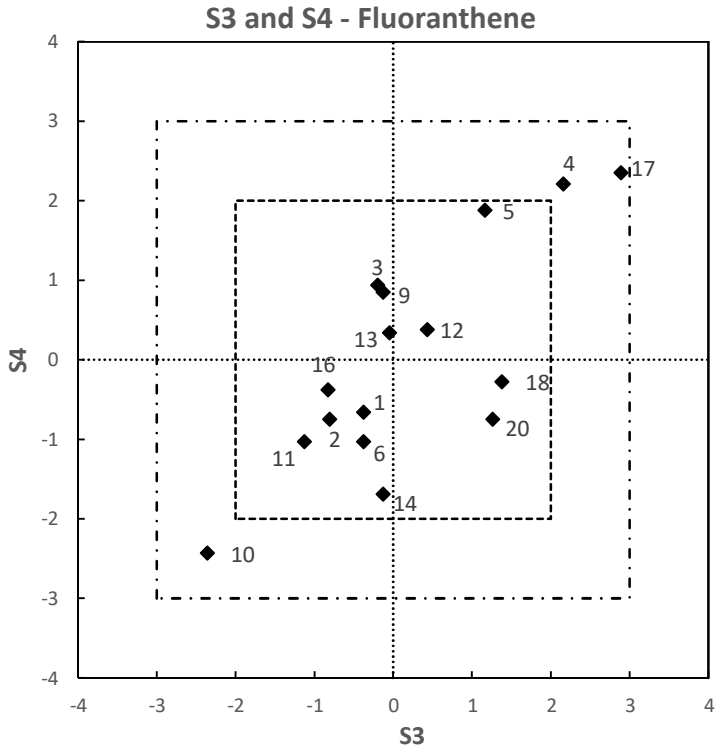


Figure 30 z-Score Scatter Plot – Fluoranthene

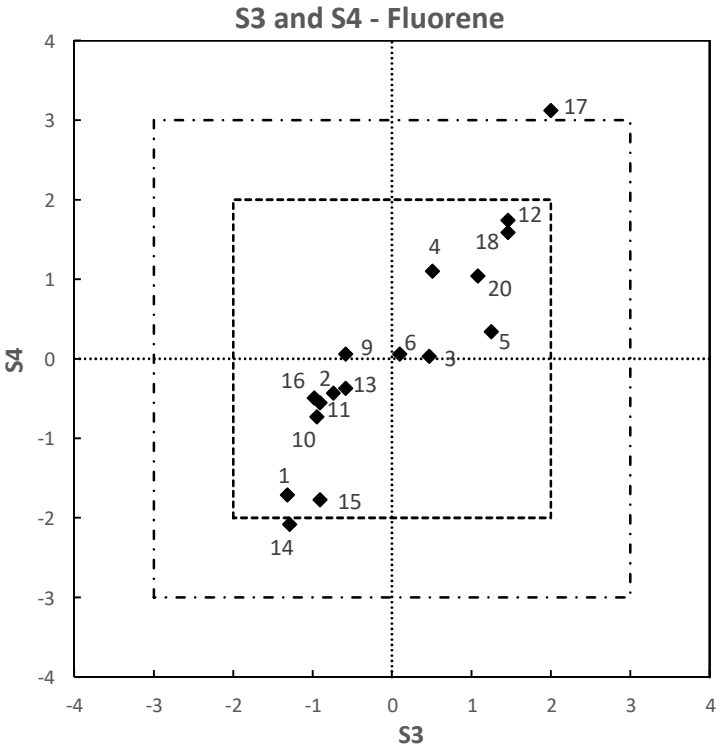


Figure 31 z-Score Scatter Plot – Fluorene

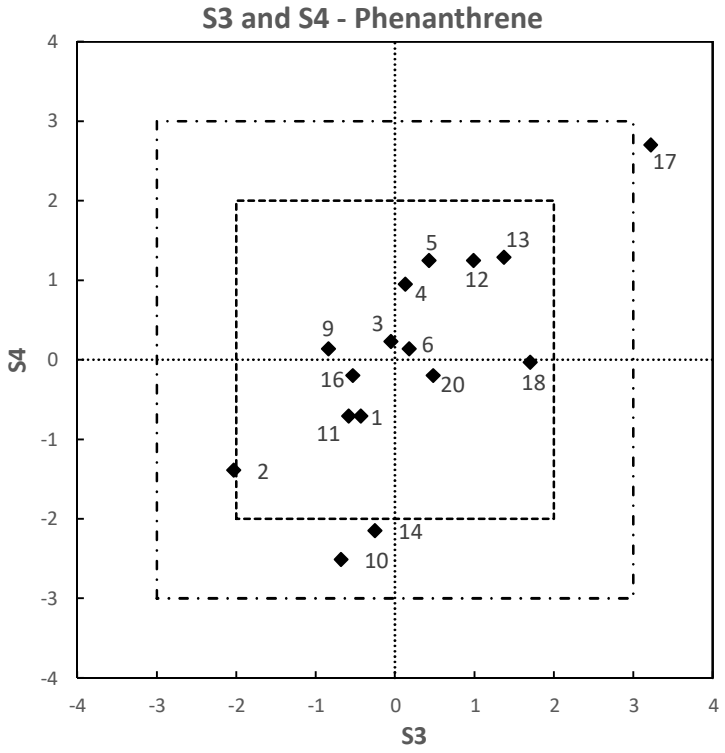


Figure 32 z-Score Scatter Plot – Phenanthrene

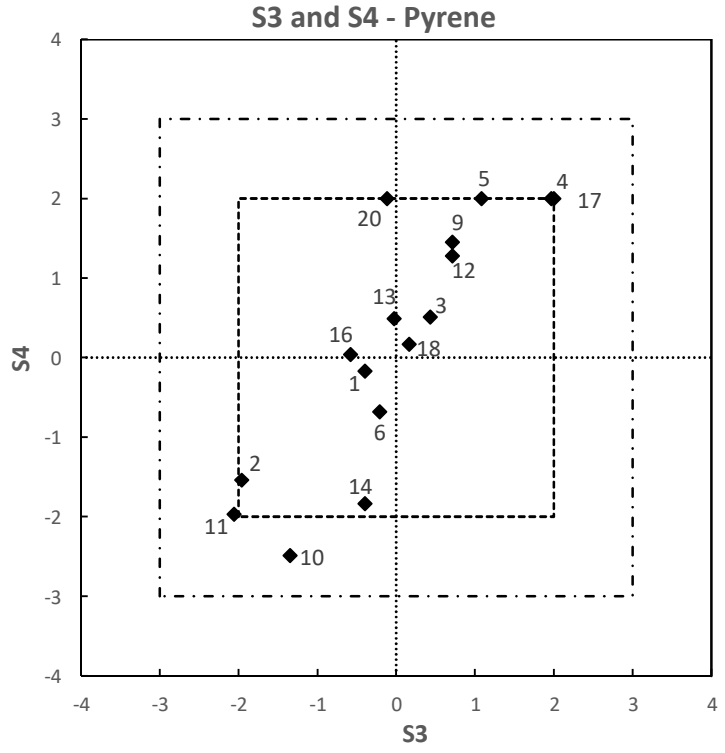


Figure 33 z-Score Scatter Plot – Pyrene

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-Scores, E_n-scores greater than 1.0 were set to 1.0.

Of 293 results for which E_n-scores were calculated, 257 (88%) 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 **3**, **4**, **5**, **9**, **12** and **14** returned satisfactory E_n-scores for all 18 scored analytes.

Satisfactory E_n-scores were achieved for all scored results reported by Laboratories **1** (17) and **8** (8).

The dispersal of participants' E_n-scores is presented graphically by laboratory in Figure 34.

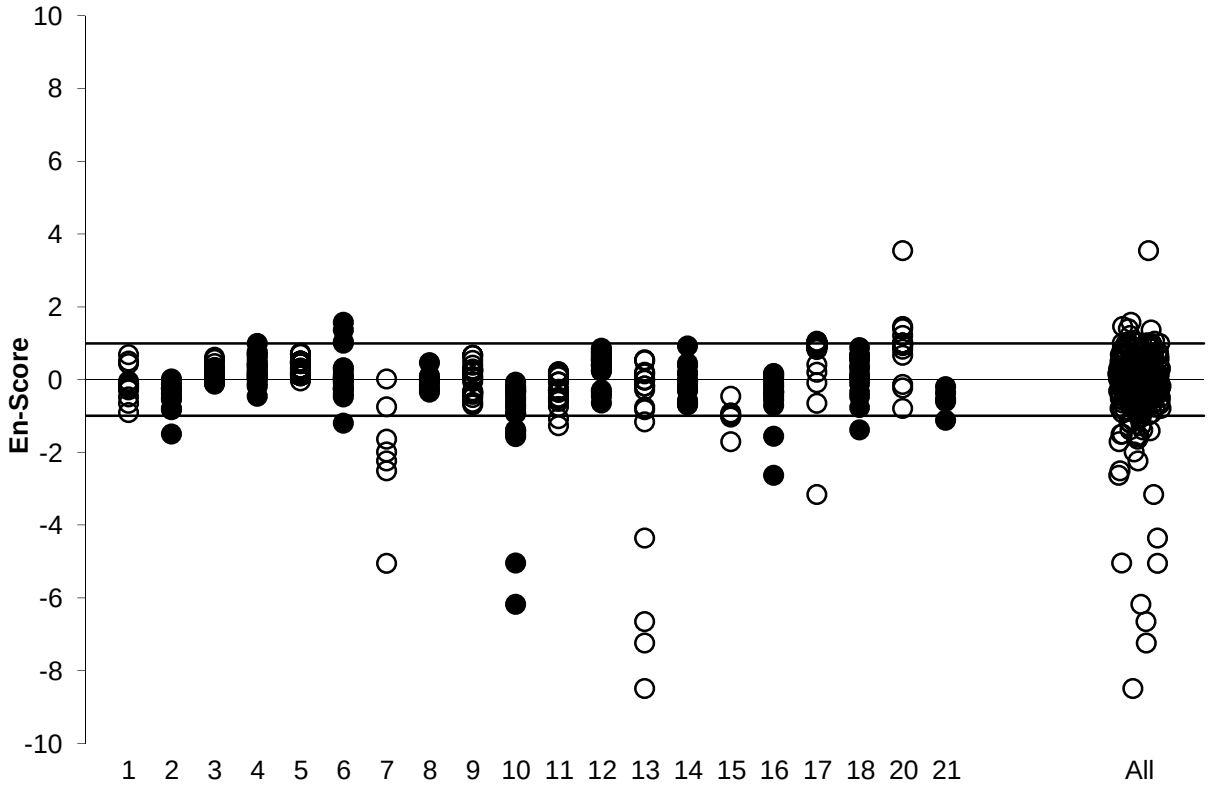


Figure 34 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 30 presents false negative results – analytes present in the samples which a participant tested for but did not report a result (for example, participants reporting a 'less-than' result (<*x*) when the assigned and spiked values were higher than their limit of reporting (LOR), or laboratories that didn't report any value). For analytes where no assigned value was set, results have only been considered to be false negatives when the robust average and spiked value were significantly higher than their LOR.

Table 30 False Negatives

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/mg)	Result (mg/kg)
1	S1	>C34-C40	247	266	<50
7	S1	>C34-C40	247	266	0

Lab. Code	Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/mg)	Result (mg/kg)
10	S3	Anthracene	*(0.34)*	0.797	<0.1
11	S3	Anthracene	*(0.34)*	0.797	<0.1
13	S3	Benzo(a)pyrene	0.88	1.79	<0.1
	S4	Benzo(a)pyrene	0.658	1.3	<0.1
18	S4	Anthracene	*(0.96)*	2.3	<0.01

6.6 Reporting of Additional Analytes

One participant reported analytes that were not spiked into the test samples. These results are presented in Table 31.

Table 31 Results Reported for Non-Spiked Analytes

Lab. Code	Sample	Analyte	Result (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
13	S3	Benz(a)anthracene	0.77	0.23	NR
	S4	Benz(a)anthracene	0.518	0.16	NR

6.7 Participants' Analytical Methods

A variety of analytical methods were used by participants in this study (Appendix 3).

TRH

Participants used a sample size between 2 g and 30 g for TRH analysis, with the majority of participants using 10 g. There was no evident correlation between the results obtained and the sample mass used for analysis (Figure 35).

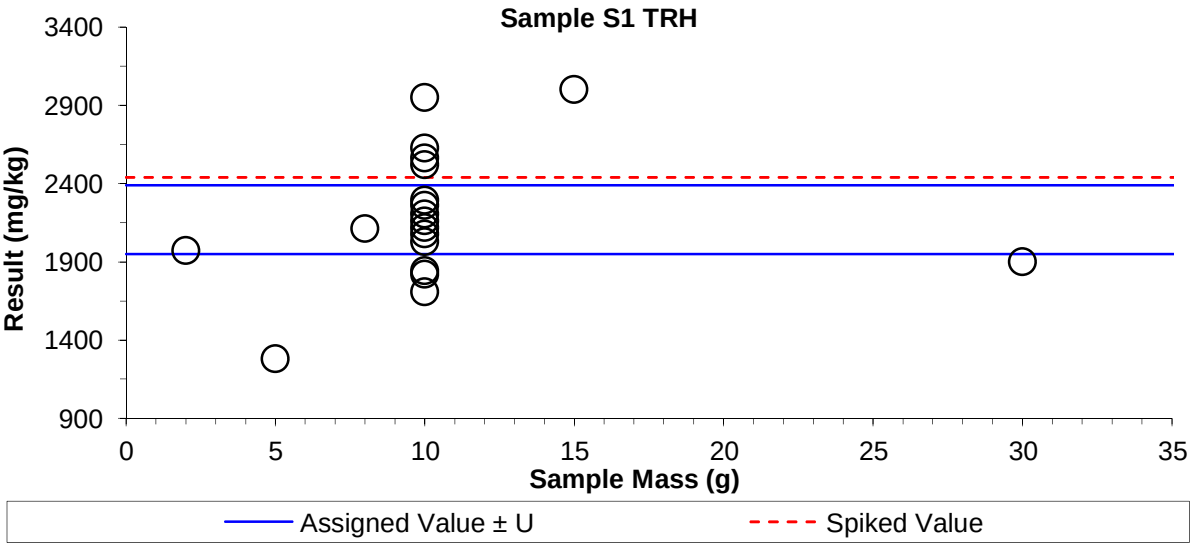


Figure 35 Sample S1 TRH Results vs Sample Mass Used for Analysis

Participants reported using either solid-liquid extraction or sonication, with dichloromethane, acetone, hexane, pentane, and combinations of these as the extraction solvent(s). Four participants reported a silica clean-up step and one participant reported a sodium sulfate clean-up step. All participants used GC-FID for analysis.

A plot of results and methodology for TRH in Sample S1 is presented in Figure 36. Methodologies are listed in order of extraction technique, extraction solvent, and instrument. Extraction method abbreviations used in the figure: SLE = Solid-Liquid Extraction. Solvent

abbreviations used in the figure: ACE = Acetone; DCM = Dichloromethane; HEX = Hexane; PEN = Pentane. Instrument abbreviations used in the figure: GC = Gas Chromatography; FID = Flame Ionisation Detector.

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

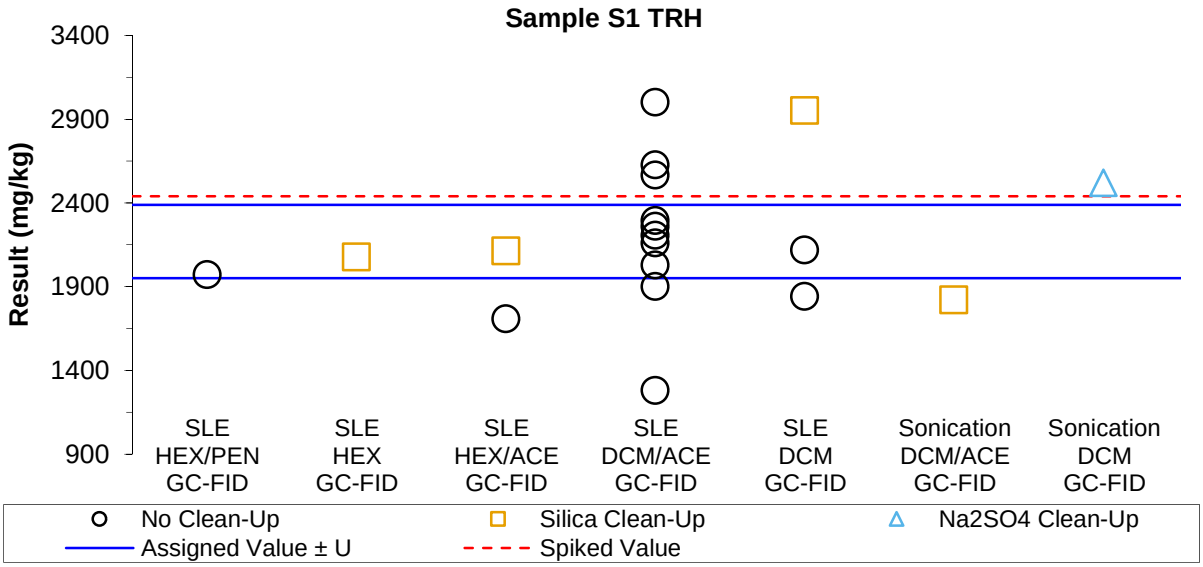


Figure 36 Sample S1 TRH Results vs Methodology

BTEX

Participants used a sample size between 0.3 g and 14 g for BTEX analysis, with the majority of participants using 10 g. There was no evident correlation between the results obtained and the sample mass used for analysis (Figure 37).

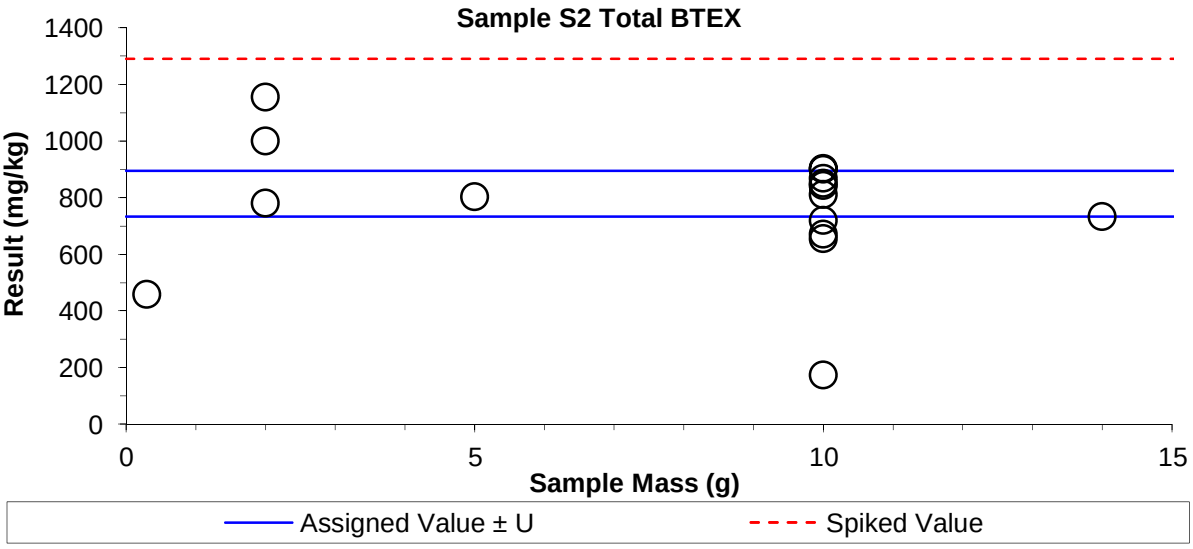


Figure 37 Sample S2 Total BTEX Results vs Sample Mass Used for Analysis

Extraction techniques reported by participants included solid-liquid extraction and sonication, and all participants reporting an extraction solvent used methanol. No participant reported a clean-up step. All participants used GC techniques, including purge and trap GC-MS(MS) or headspace GC-MS(MS).

A plot of results and methodology for Total BTEX in Sample S2 is presented in Figure 38. Methodologies are listed in order of extraction technique, extraction solvent and instrument. Extraction method abbreviations used in the figure: SLE = Solid-Liquid Extraction. Solvent abbreviations used in the figure: MeOH = Methanol. Instrument abbreviations used in the figure: HS = Headspace; P&T = Purge and Trap; GC = Gas Chromatography; MS = Mass Spectrometry; MS/MS = Tandem Mass Spectrometry.

The most common methodology used to analyse BTEX in this study was solid-liquid extraction with methanol, using purge and trap GC-MS for analysis.

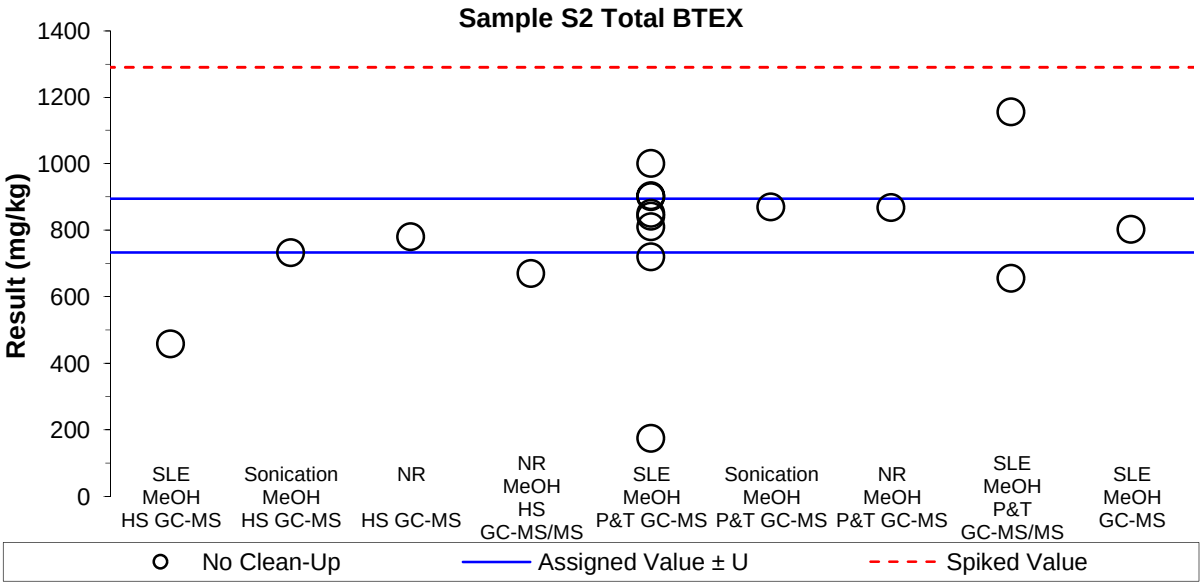


Figure 38 Sample S2 Total BTEX Results vs Methodology

PAHs

Participants used a sample size between 2 g and 30 g for PAHs analysis, with the majority of participants using 10 g (Figure 39).

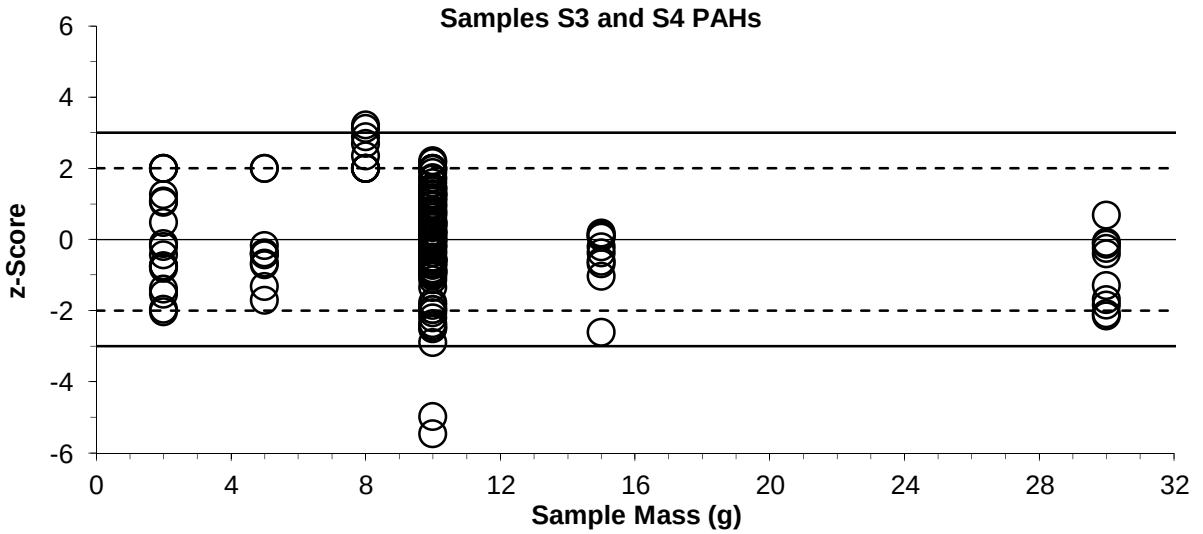


Figure 39 Samples S3 and S4 PAHs z-Scores vs Sample Mass Used for Analysis

Participants reported using solid-liquid extraction or sonication, using dichloromethane, acetone, hexane, ethyl acetate and combinations of these as the extraction solvent. One participant reported using Florisil and another participant reported using sodium sulfate for clean-up. Most participants used GC-MS(MS) for analysis, and one participant used GC-FID.

A plot of z-scores obtained and methodology for the various PAHs in Samples S3 and S4 is presented in Figure 40. Methodologies are listed in order of extraction technique, extraction solvent, clean-up (if applicable) and instrument. Extraction method abbreviations used in the figure: SLE = Solid-Liquid Extraction. Solvent abbreviations used in the figure: ACE = Acetone; DCM = Dichloromethane; EtOAc = Ethyl Acetate; HEX = Hexane. Instrument abbreviations used in the figure: GC = Gas Chromatography; FID = Flame Ionisation Detector; MS = Mass Spectrometry; MS/MS = Tandem Mass Spectrometry.

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

Participants who extracted using dichloromethane or ethyl acetate alone, with no clean-up, reported results that were generally biased low. The use of a dichloromethane/acetone extraction solvent mixture with GC-FID for analysis also gave results that were biased low.

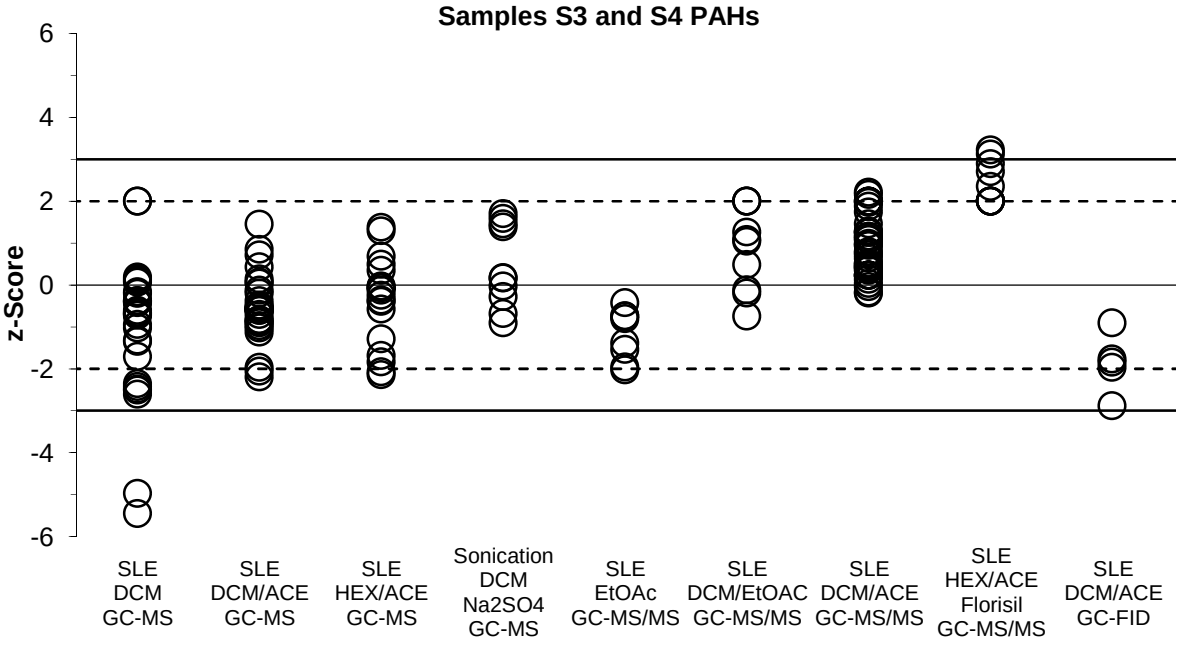


Figure 40 Samples S3 and S4 PAHs z-Scores vs Methodology

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.

Twelve participants reported using certified standards and three participants reported using matrix reference materials. The following were reported by participants:

- NMI (e.g. MX015)
- Sigma Aldrich (e.g. 49452-U, 47577-U)
- Accustandard (e.g. Z-014G-R, PS-CP-06A-1ML)
- Restek
- PM Separations
- o2Si
- RTC (e.g. CRM 356-100)
- 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*'[11]

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 32 and 33, and Figure 41.

Table 32 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
A.V.	620	1370	247	2170	384	62.7	353	814
S.V.	759	1420	266	2440	615	70.3	527	1290
1	677	1293	<50	1970	368	55.2	328	780
2	622.1	1218.8	NR	1840.9	NT	NT	NT	NT
3	636.82	1394.43	262.4	2293.65	395.87	67.37	408	903.4
4	524	1270	282	2076	385	64.7	359	842
5	715	1590	260	2564	424	62	383	900
6	840	1900	300	3000	350	67	370	810
7	622	662	NR	1280	130	42.5	284	458
8	570	1300	290	2160	345	62.9	364	802
9	690	1670	266	2626	321.4	53.4	315.2	719.1
10	604	1290	223	2117	294	48.6	298	655
11	650	1348	208	2206	400.4	61.2	369.9	868.1
12	554	1263	211	2028	450	72	440	1000
13	499.18	975.26	232.82	1707.25	43.12	22.62	67.11	173.73
14	460	1000	460	1900	360	70	400	850
15	NT	NT	NT	NT	NT	NT	NT	NT
16	670	1490	95	2260	NR	NR	NR	NR
17	NR	NR	NR	2112	410	72	164	670
18	640	1700	180	2520	450	67	300	870
20	NR	NR	NR	2950	507	83.5	544	1155
21	NR	NR	NR	1820	328	54	331	732

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

Table 33 Summary of Participants' Results (Samples S3 and S4)*

Lab. Code	Sample S3					Sample S4				
	Benzo(a)pyrene	Fluoranthene	Fluorene	Phenanthrene	Pyrene	Benzo(a)pyrene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
A.V.	0.88	2.65	1.97	2.63	0.723	0.658	0.71	2.18	0.783	1.56
S.V.	1.79	3.05	2.37	3.07	0.892	1.30	0.798	2.61	0.904	1.99
1	1.18	2.50	1.58	2.46	0.68	1.00	0.64	1.62	0.70	1.52
2	NT	2.33	1.75	1.83	0.51	NT	0.63	2.04	0.62	1.20
3	0.91	2.57	2.11	2.61	0.77	0.64	0.81	2.19	0.81	1.68
4	0.984	3.51	2.12	2.68	0.937	0.772	0.945	2.54	0.894	2.24
5	0.91	3.11	2.34	2.80	0.84	0.68	0.91	2.29	0.93	2.05
6	0.8	2.5	2.0	2.7	0.7	0.4	0.6	2.2	0.8	1.4
7	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
9	0.8	2.6	1.8	2.3	0.8	0.7	0.8	2.2	0.8	1.9
10	0.223	1.71	1.69	2.36	0.577	0.119	0.451	1.94	0.488	0.977
11	0.8	2.2	1.7	2.4	0.5	0.6	0.6	2	0.7	1.1
12	0.98	2.82	2.4	3.02	0.8	0.72	0.75	2.75	0.93	1.86
13	<0.1	2.63	1.80	3.17	0.72	<0.1	0.746	2.059	0.934	1.674
14	0.97	2.6	1.59	2.53	0.68	0.65	0.53	1.5	0.53	1.13
15	<1	1.5	1.7	1.9	<1	<1	<1	1.6	<1	1.1
16	0.59	2.32	1.68	2.42	0.66	0.57	0.67	2.02	0.76	1.57
17	1.7	3.8	2.7	3.9	1	1.2	0.96	3.2	1.1	2.5
18	0.76	3.2	2.4	3.3	0.74	0.59	0.68	2.7	0.78	1.6
20	1.44	3.15	2.29	2.82	0.71	1.19	0.63	2.52	0.76	2.04
21	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

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

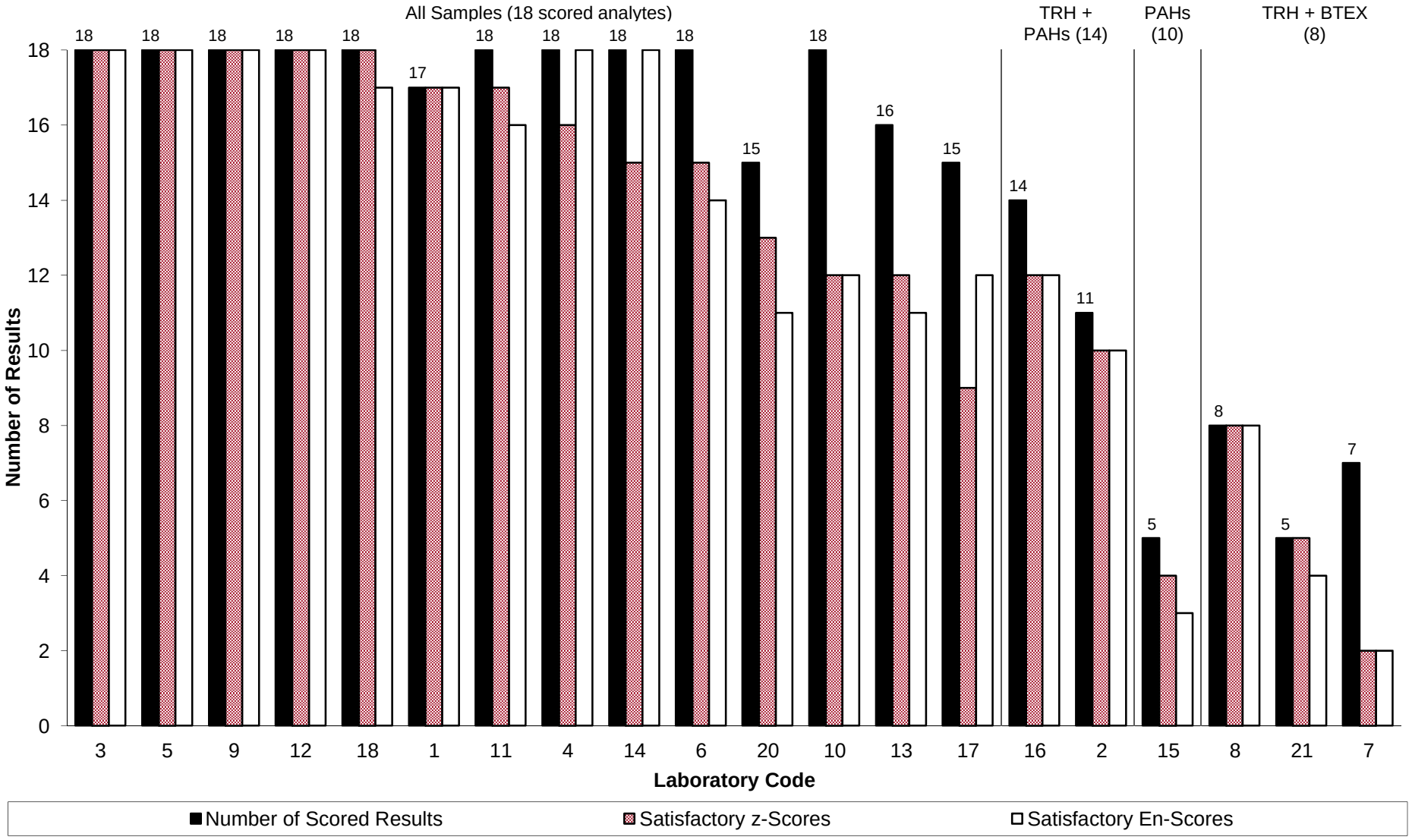


Figure 41 Summary of Participants' Performance

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 $|z| \leq 2.0$. 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 satisfactory performance (presented as a percentage of the total number of scores) obtained by participants for TRH in soil over the last 10 studies (2013 – 2020) is presented in Figure 42. Over this period, the average proportion of satisfactory z-scores was 89%, and the average proportion of satisfactory E_n-scores was 73%.

While each PT study has a different sample set and a different group of participant laboratories, taken as a group, the performance over this period has improved for TRH.

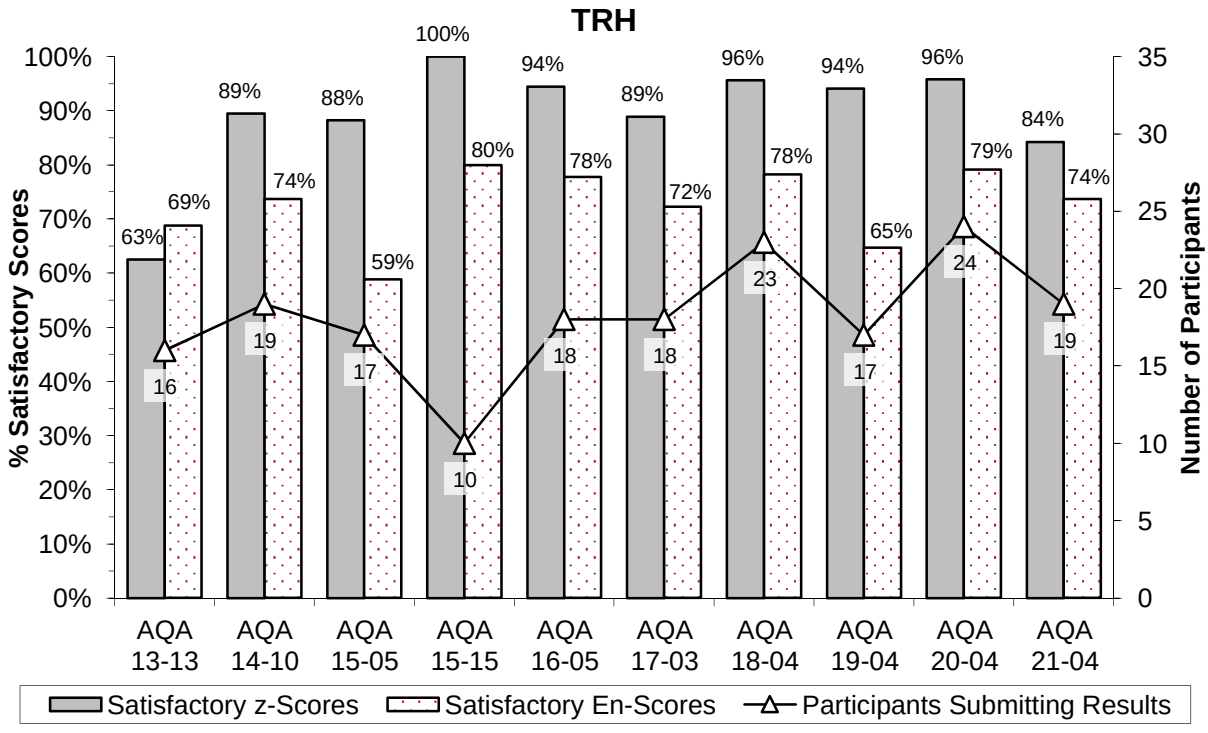


Figure 42 Participants' Performance for TRH in Hydrocarbons in Soil PT Studies

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 (2013 – 2020) is presented in Figure 43. Over this period, the average proportion of satisfactory z-scores was 87%, and the average proportion of satisfactory E_n-scores was 82%.

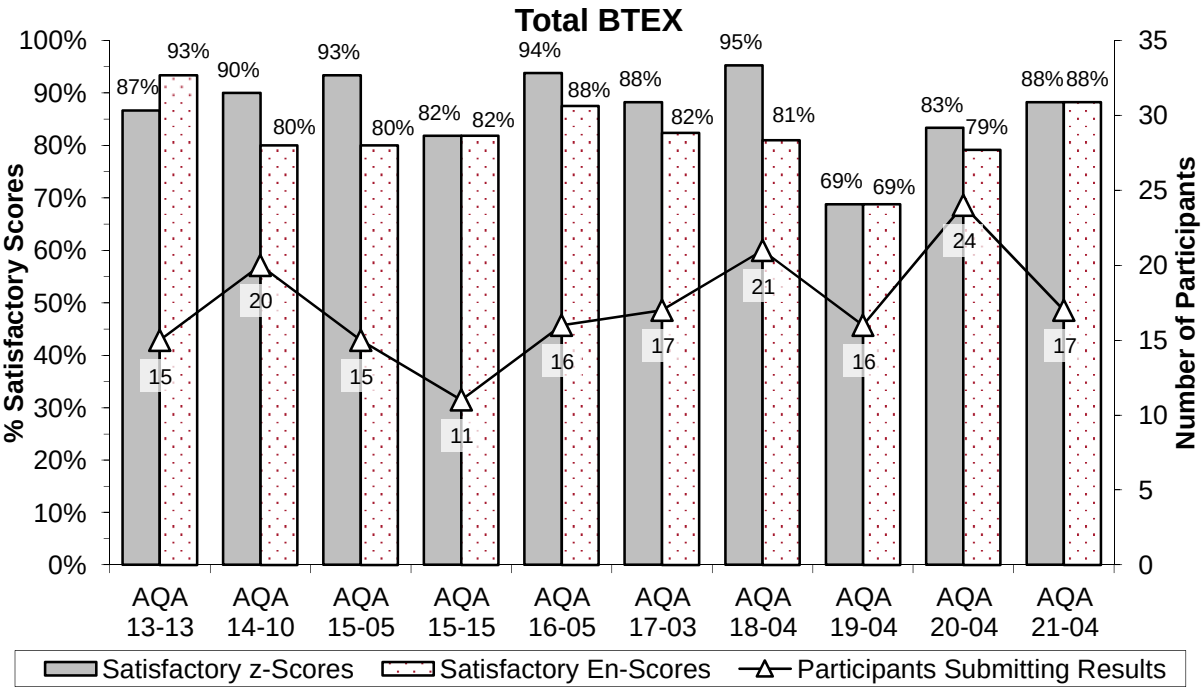


Figure 43 Participants' Performance for Total BTEX in Hydrocarbons in Soil PT Studies

PAHs

PAHs in soil was first introduced 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 6 studies (2016 – 2020) is presented in Figure 44. Over this period, the average proportion of satisfactory z-scores was 90%, and the average proportion of satisfactory E_n-scores was 87%.

While each PT study has a different sample set and a different group of participant laboratories, taken as a group, the performance over this period has improved for PAHs.

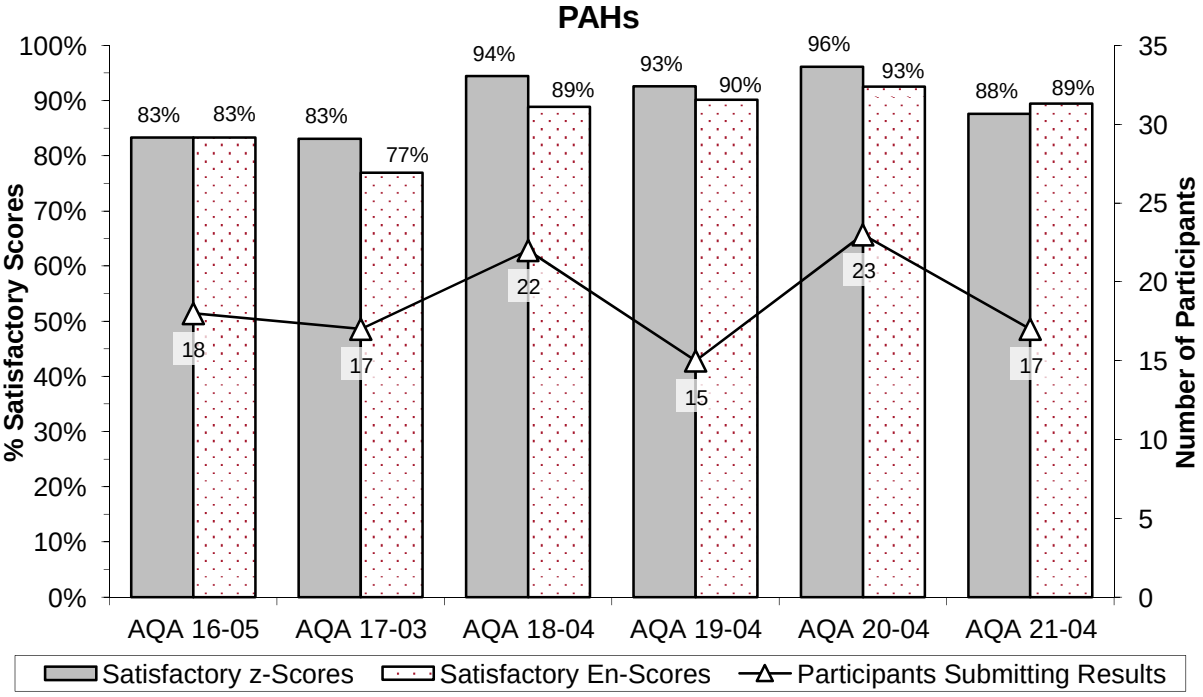


Figure 44 Participants' Performance for PAHs in Hydrocarbons in Soil PT Studies

A plot of the robust average expressed as a percentage of the spiked value, for PAHs in Menangle topsoil since 2016 is presented in Figure 45 (Samples S3 and S4 anthracene results from this study have been included in this chart, though they were not scored in this study due to the variability in participants' results). 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.[12]

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 had low recoveries, averaging 42% and 40% respectively for the robust average to spiked value. Fluoranthene, fluorene, phenanthrene and pyrene have had higher recoveries over this period, with averages in the range of 77% to 86% for the robust average to spiked value. For this study, benzo(a)pyrene and pyrene returned recoveries higher than the average of previous studies, while the other analytes returned recoveries similar to or very slightly higher than average of previous studies.

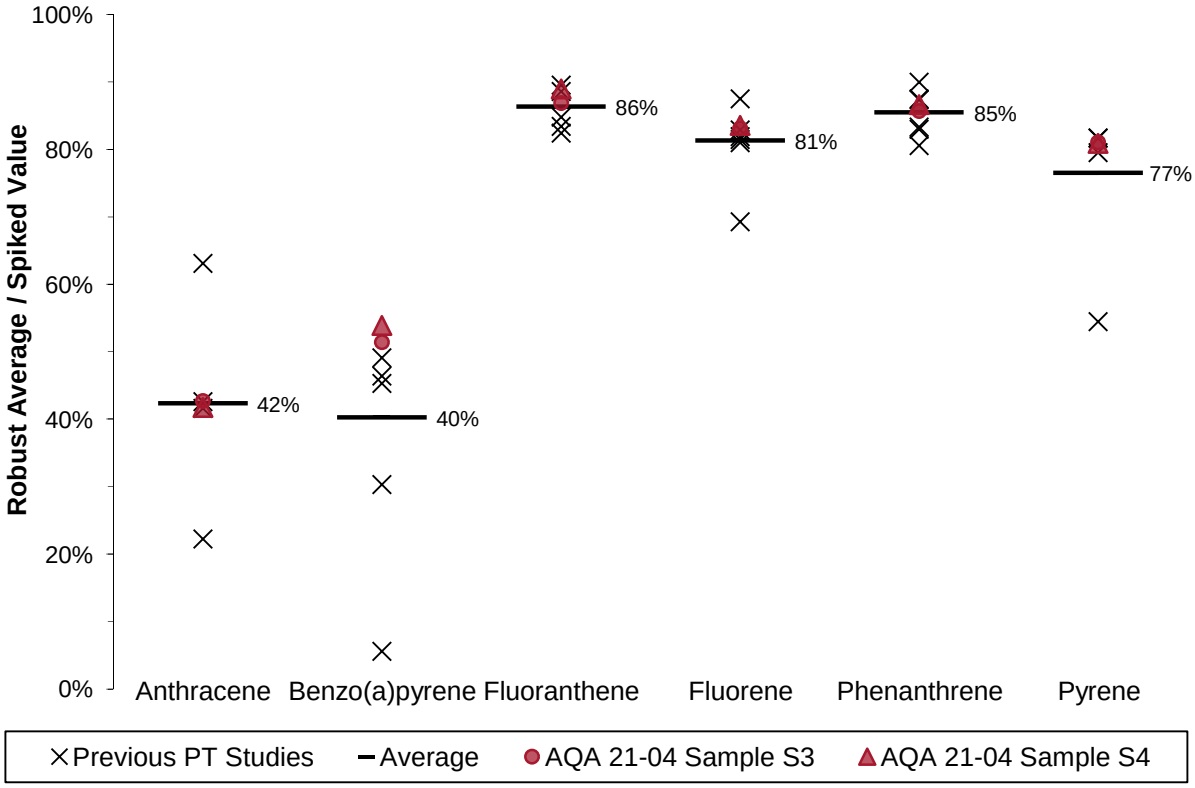


Figure 45 Recoveries of PAHs in Menangle Topsoil for Hydrocarbons in Soil PT Studies

7 REFERENCES

[1] ISO/IEC 17043:2010, *Conformity assessment – General requirements for proficiency testing.*

[2] NMI, 2020, *Study Protocol for Proficiency Testing*, viewed June 2021, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

[3] NMI, 2021, *Chemical Proficiency Testing Statistical Manual*, viewed June 2021, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

[4] Thompson, M., Ellison, S.L.R. & Wood, R. 2006. 'The International Harmonized Protocol For The Proficiency Testing Of Analytical Chemistry Laboratories', *Pure Appl. Chem.,* vol. 78, pp. 145-196.

[5] National Environmental Protection (Assessment of Site Contamination) Measure 1999 as amended 2013, viewed June 2021, <https://www.legislation.gov.au/Details/F2013C00288/Html/>.

[6] Worrall, R.D., 1996, 'Total Petroleum Hydrocarbons in Soil: Storage Stability Study', ACSL Public Interest Project, AGAL.

[7] ISO 13528:2015, *Statistical methods for use in proficiency testing by interlaboratory comparison*.

[8] Thompson, M., 2000, 'Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing', *Analyst*, vol. 125, pp. 385-386.

[9] ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories.*

[10] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed June 2021, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

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

[12] 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 two hours. The dried soil was sieved and the fraction between 355 μm and 850 μm was retained and used to prepare Samples S1, S2, S3 and S4.

Sample S1: Dried and sieved Menangle topsoil (2208.5 g) was placed into a stainless steel pot. Dichloromethane was added to moisten the soil. A 4.5085 g aliquot of sparged diesel was added. In addition, 3.2 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 in numeric fill order and stored in a refrigerator.

Sample S2: Dried and sieved Menangle topsoil (3000.5 g) was placed in a 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. Unleaded petrol (12.60 g) and benzene (0.130 mL) were added to a cooled beaker, and sparged diesel (3.07 g) was weighed into a second beaker. As quickly as possible, the contents of the beakers were added to the soil. 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 to minimise the loss of volatiles. The jars were labelled in numeric fill order. After the caps were sealed with Parafilm, the jars were shrink-wrapped and stored in a freezer.

Samples S3 & S4: For Sample S3, dried and sieved Menangle topsoil (1123.5 g) 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 six 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. 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 1100.8 g of clean soil. The total soil mass was 2224.3 g. The V-mixer was tumbled for about ninety minutes. After mixing, the soil was divided into fifty samples of at least 50 g, placed in glass jars, labelled in fill order 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 1107.4 g into the 3 L flask and 1100.8 g of diluent soil, making a total of 2208.2 g of spiked soil.

APPENDIX 2 – TRANSPORTATION STABILITY ASSESSMENT

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. Samples were packaged into insulated foam boxes with cooler bricks for dispatch.

Comparisons of results obtained to days spent in transit for Sample S1 TRH, Sample S2 Total BTEX, and Samples S3 and S4 PAHs are presented in Figures 46 to 48. No evidence of analyte degradation with respect to the amount of time spent in transit was observed.

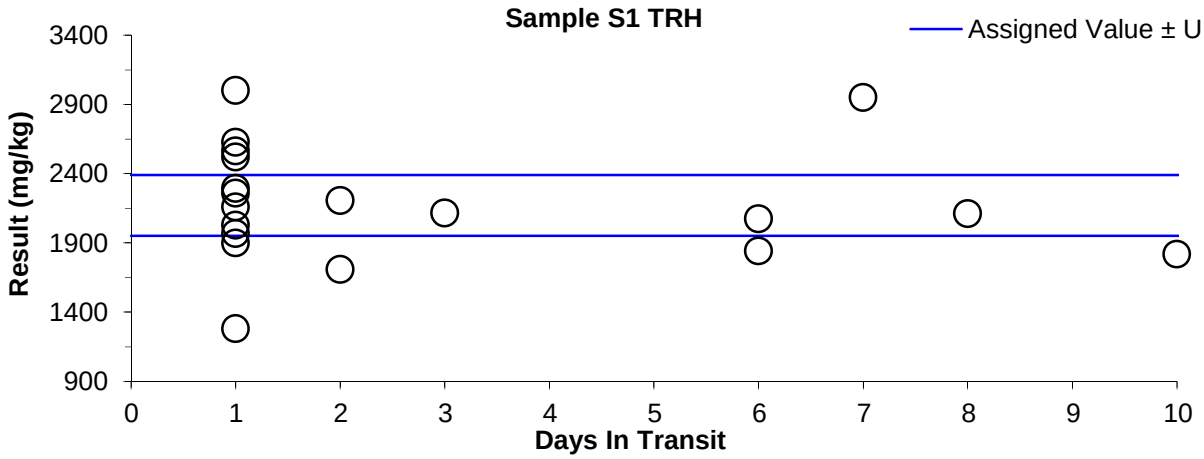


Figure 46 Sample S1 TRH Results vs Days in Transit

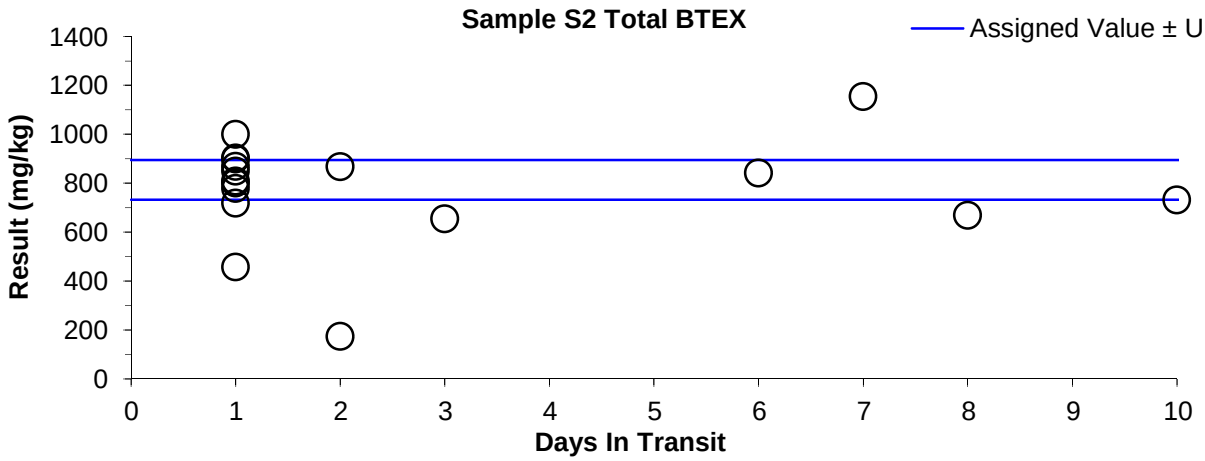


Figure 47 Sample S2 Total BTEX Results vs Days in Transit

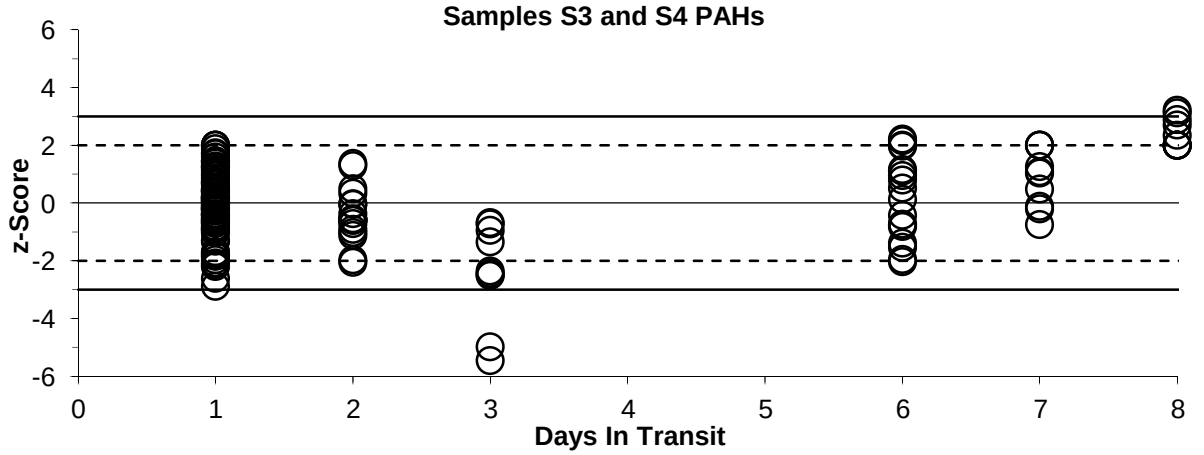


Figure 48 Samples S3 and S4 PAHs z-Scores vs Days in Transit

APPENDIX 3 – 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	Instrument	Method Reference
1	2	Solid-Liquid	Hexane:Pentane		GC-FID	In-house
2	10	Solid-Liquid	DCM		GC-FID	
3	10	Solid-Liquid	DCM/Acetone	N/A	GC-FID	USEPA SW-846
4	10	Solid-Liquid	Hexane	Silica	GC-FID	USEPA 3510
5	10	Solid-Liquid	DCM/ACE(1:1)	N/A	GC-FID	In-house
6	15	Solid-Liquid	DCM:Acetone	nil	GC-FID	USEPA 3550C
7	5	Solid-Liquid	1:1 DCM:Acetone	None	GC-FID	NEPM B3
8	10	Solid-Liquid	Acetone/DCM		GC-FID	USEPA 3510
9	10	Solid-Liquid	DCM:ACE		GC-FID	In house
10	10	Solid-Liquid	DCM	No	GC-FID	
11	10	Solid-Liquid	DCM/Acetone	None	GC-FID	USEPA 8270C
12	10g	Solid-Liquid	DCM/Acetone	None	GC-FID	In house
13	10	Solid-Liquid	Hexane:Acetone	None	GC-FID	USEPA 8270
14	30	Solid-Liquid	DCM/Acetone	Nil	GC-FID	
15	NT					
16	10	Solid-Liquid	1:1 DCM:Acetone	None	GC-FID	USEPA 8015B
17	8	Solid-Liquid	Hexane:Acetone	Silica	GC-FID	
18	10	sonication	DCM	NaSO4 through pasteur pipette	GC-FID	In house
20	10	Solid-Liquid	DCM	Silica	GC-FID	In house
21	10	Sonication	DCM:Acetone 1:1	Silica	GC-FID	USEPA 8015

Table 35 Test Methods Sample S2 BTEX

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Instrument	Method Reference
1	2	Head Space			GC-MS	In-house
2	NT					
3	10	Solid-Liquid	Methanol	N/A	P&T GC-MS	USEPA SW-846 Method 5030
4	10	Solid-Liquid	Methanol	/	P&T GC-MS	USEPA 8260
5	10	Solid-Liquid	MeOH	N/A	P&T GC-MS	In-house
6	10	Solid-Liquid	Methanol	NA	P&T GC-MS	USEPA 3550C
7	0.3	Solid-Liquid	Methanol	None	Headspace GC-MS	NEPM B3
8	5	Solid-Liquid	Methanol		GC-MS	USEPA 8260
9	10	Solid-Liquid	MeOH		P&T GC-MS	In house
10	10	Solid-Liquid	MEOH	No	P&T GC-MS/MS	
11	10	Purge and Trap	Methanol	None	GC-MS	USEPA 8260B
12	2g	Solid-Liquid	MeOH	None	P&T GC-MS	In house
13	10	Solid-Liquid	Methanol	None	P&T GC-MS	USEPA 8260
14	10	Solid-Liquid	Methanol	Nil	P&T GC-MS	
15	NT					
16						
17	10		Methanol	N/A	Headspace GC-MS/MS	
18		sonication	MeOH	None	P&T GC-MS	in house method based on USEPA 8260
20	2	Solid-Liquid	MeOH		P&T GC-MS/MS	USEPA8270
21	14	Sonication	Methanol	Nil	Headspace GC-MS	USEPA 8260B

Table 36 Test Methods Samples S3 and S4 PAHs

Lab. Code	Sample Mass (g)	Extraction Details	Extraction Solvent	Clean-Up	Instrument	Method Reference
1	5	Solid-Liquid	DCM		GC-MS	In-house
2	2	Solid-Liquid	EtAc		GC-MS/MS	
3	10	Solid-Liquid	DCM/Acetone	N/A	GC-MS/MS	USEPA SW-846 METHOD 8100
4	10	Solid-Liquid	DCM/Acetone	/	GC-MS/MS	USEPA 8270
5	10	Solid-Liquid	DCM/ACE(1:1)	N/A	GC-MS/MS	In-house
6	15	Solid-Liquid	DCM	NA	GC-MS	USEPA 3550C
7	NT					
8	NT					
9	10	Solid-Liquid	DCM:ACE		GC-MS	In house
10	10	Solid-Liquid	DCM	No	GC-MS	
11	10	Solid-Liquid	DCM/Acetone	None	GC-MS	USEPA 8270C
12	10g	Solid-Liquid	DCM/Acetone	None	GC-MS/MS	In house
13	10	Solid-Liquid	Hexane:Acetone	None	GC-MS	USEPA 8270
14	30	Solid-Liquid	Hexane/Acetone	Nil	GC-MS	
15	10	Solid-Liquid	ACE:DCM	Nil	GC-FID	In House
16	10	Solid-Liquid	1:1 DCM:Acetone	None	GC-MS	USEPA 8270D
17	8	Solid-Liquid	Hexane:Acetone	Florisil	GC-MS/MS	
18	10	sonication	DCM	NaSO4 through pasteur pipette	GC-MS	USPEA 8270
20	2	Solid-Liquid	DCM:ethyl acetate 1:1		GC-MS/MS	USEPA 8260
21	NT					

APPENDIX 4 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, Z-SCORE AND E_N-SCORE CALCULATIONS

A4.1 Robust Average and Associated Uncertainty

When the robust average was calculated using the procedure described in ISO 13528:2015,[7] the 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 37.

Table 37 Uncertainty of the Robust Average for Sample S3 Fluoranthene

No. Results (p)	17
Robust Average	2.65 mg/kg
$S_{rob\ av}$	0.59 mg/kg
$u_{rob\ av}$	0.18 mg/kg
k	2
$U_{rob\ av}$	0.36 mg/kg

Therefore, the robust average for Sample S3 fluoranthene is 2.65 ± 0.36 mg/kg.

A4.2 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.

A worked example is set out below in Table 38.

Table 38 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
677 ± 120	620 ± 53	15% as PCV, or: 0.15 × 620 = 93 mg/kg	z-Score = $\frac{677-620}{93}$ = 0.61	E_n-Score = $\frac{677-620}{\sqrt{120^2+53^2}}$ = 0.43

APPENDIX 5 – ACRONYMS AND ABBREVIATIONS

A.V.	Assigned Value
ACE	Acetone
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
EtOAc	Ethyl Acetate
FID	Flame Ionisation Detector
GAG	General Accreditation Guidance (NATA)
GC	Gas Chromatography
GUM	Guide to the expression of Uncertainty in Measurement
HEX	Hexane
HS	Headspace (GC)
IEC	International Electrotechnical Commission
ISO	International Standards Organization
LOR	Limit Of Reporting
Max.	Maximum value in a set of results
Md	Median value in a set of results
MeOH	Methanol
Min.	Minimum value in a set of results
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
NT	Not Tested
P&T	Purge and Trap (GC)
PAHs	Polycyclic Aromatic Hydrocarbons
PCV	Performance Coefficient of Variation
PEN	Pentane

PT	Proficiency Test
R.A.	Robust Average
RM	Reference Material
S.V.	Spiked Value, or formulated concentration of a PT sample
SD	Standard Deviation
SI	International System of Units
SLE	Solid-Liquid Extraction
SS	Spiked Samples
TRH	Total Recoverable Hydrocarbons
US EPA	United States Environmental Protection Agency

END OF REPORT