Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Report AQA 20-04 Hydrocarbons in Soil

July 2020

ACKNOWLEDGMENTS

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

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

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

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TABLE OF CONTENTS

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SUMMARY

AQA 20-04 Hydrocarbons in Soil commenced in March 2020. Twenty-five laboratories participated and all submitted results.

Four sets of 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 average of participants' results for all scored analytes. Associated uncertainties were estimated from the robust standard deviation of participants' results.

Of a possible 600 numeric results, a total of 538 numeric results (90%) were submitted. Fifteen results were submitted as a 'less than' value (<*x*) or Not Reported (NR), and forty-seven results were submitted as Not Tested (NT).

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 **2**, **4**, **5**, **6**, **7**, **9**, **11**, **14**, **15**, **18**, **19**, **21**, **22** and **23** reported numeric results for all analytes scored in this study.

Three laboratories did not report results for analytes that they tested for and were present in the test samples (Table 30, total of 3 results).

Of 494 z-scores, 455 (92%) returned a satisfactory score of $|z| \leq 2.0$.

Of 494 E_n-scores, 436 (88%) returned a satisfactory score of $|E_n| \leq 1.0$.

Laboratories **7**, **15** and **19** returned satisfactory z- and E_n-scores for all 22 scored analytes.

Laboratories **2**, **11** and **18** returned satisfactory z-scores for all 22 scored analytes.

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

For TRH in Sample S1, various extraction techniques and extraction solvents were reported. Three participants reported a clean-up step. All participants used GC-FID for analysis.

For BTEX in Sample S2, participants reported various extraction techniques and extraction solvents; some reported analysing samples without extraction. All participants used GC techniques, including purge and trap GC-MS or headspace GC-MS.

For PAHs in Samples S3 and S4, various extraction techniques and extraction solvents were reported. One participant reported a clean-up step. Participants used GC-FID or GC-MS(MS) for analysis.

No correlation between results and methodology was evident.

- *Develop the practical application of traceability and measurement uncertainty.*

Of 538 numeric results, 518 (96%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 5.9% to 100% of the reported value.

Metrological traceability of the assigned values has not been established as they were the consensus of participants' results.

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, food and pharmaceuticals;
- PFAS in soil, water and biota;
- controlled drug assay 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 the participants' methods for the measurement of hydrocarbon pollutants in soil; and
- develop the practical application of traceability and measurement uncertainty.

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 Statistical Manual.[3] These documents have been prepared with reference to ISO/IEC 17043[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[4]

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

2 STUDY INFORMATION

2.1 Selection of Hydrocarbons

The petroleum hydrocarbons and PAHs studied, and the spiked levels, were typical of those measured by environmental laboratories.

Investigation levels for the hydrocarbons studied are set out in the National Environmental Protection (Assessment of Site Contamination) Measure Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

2.2 Study Timetable

The timetable of the study was:

Invitation issued:	9 March 2020
Samples dispatched:	1 April 2020
Results due:	11 May 2020
Interim report issued:	14 May 2020

2.3 Participation

Twenty-five laboratories participated and all submitted results.

2.4 Laboratory Code

All participants were assigned a confidential laboratory code number.

2.5 Sample Preparation

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

Sample S2 (BTEX) was prepared by spiking soil purchased from a Sydney supplier with unleaded petrol and treated diesel fuel.

Sample S3 (PAHs) was prepared by spiking soil purchased from a Sydney supplier with anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.

Sample S4 (PAHs) was prepared by spiking soil purchased from a Sydney supplier with anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.

Further sample preparation details are provided in Appendix 1.

2.6 Homogeneity of Samples

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

2.7 Stability of Analytes

The storage stability of petroleum hydrocarbons in soil has been previously established.[6] No stability testing was conducted for this study.

2.8 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 -18°C.

The samples were packaged into insulated styrene foam boxes and dispatched by courier on 1 April 2020.

The following items were also sent to participants:

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

An electronic results sheet was e-mailed to participants.

2.9 Instructions to Participants

Participants were instructed as follows:

- Report results for the following:
  - S1: Semi-volatile hydrocarbons (>C10 – C40) (Australian NEPM fractions >C10 – C16, >C16 – C34 and >C34 – C40 are encouraged) and Total Recoverable Hydrocarbons (TRH). The concentration range is between 1000 – 20000 mg/kg.
  - S2: Volatile Hydrocarbons (C6 to C10), Benzene, Toluene, Ethylbenzene, Xylenes and Total BTEX. Individual BTEX components concentration is between 0.5 – 500 mg/kg.
  - S3 and S4: Poly-aromatic hydrocarbons from the list below. The concentration range is between 0.05 – 50 mg/kg.

PAHs			
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 on the electronic results sheet emailed to you.
- No limit of reporting has been set for this study. Report results as you would report them to a client, applying the limit of reporting of the method used for analysis. This is the figure that will be used in all statistical analysis in the study report.
- Report petroleum hydrocarbons by chain length groups and indicate the start/finish points for each hydrocarbon range. Use of NEPM guideline ranges is encouraged.
- For each analyte in each sample, report the analytical results in units of mg/kg together with an associated expanded uncertainty (e.g. 2000 ± 200 mg/kg).
- Report the basis of your uncertainty estimates (e.g. uncertainty budget, repeatability precision, long term result variability).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by email (proficiency@measurement.gov.au).
- **Please return completed result sheet by 27 April 2020.**

The results due date was extended to 11 May 2020 due to the exceptional national and international circumstances.

2.10 Interim Report

An interim report was emailed to participants on 14 May 2020.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses are presented in Appendix 2.

3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about their basis of measurement uncertainty. Responses are presented in Table 1.

Table 1 Basis of Expanded Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	ISO/GUM
2	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - SS	Recoveries of SS	Nata Technical Note 33
3	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide
4	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of SS	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
6	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	Instrument calibration Recoveries of SS Standard purity	ISO/GUM
7	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
8	Top Down - precision and estimates of the method and laboratory bias	Instrument calibration	Recoveries of SS	Nata Technical Note 33
9	Top Down - precision and estimates of the method and laboratory bias		CRM Instrument calibration Recoveries of SS Standard purity	Nata Technical Note 33
10	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples Duplicate analysis	Recoveries of SS	
11	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	
12	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis	CRM Recoveries of SS	Nata Technical Note 33

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
13	Standard uncertainty based on historical data.	Duplicate analysis Instrument calibration	CRM Instrument calibration	
14	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 January 2018 & NATA GAG Validation and verification of quantitative and qualitative test method January 2018
15		Control samples - RM	Instrument calibration Recoveries of SS	Control Charts
16	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control samples - CRM Duplicate analysis Instrument calibration	CRM Instrument calibration Laboratory bias from PT studies Recoveries of SS	
17	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis Instrument calibration	CRM Laboratory bias from PT studies Recoveries of SS	Nata Technical Note 33
18	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM Duplicate analysis	CRM	Eurachem/CITAC Guide
19	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
20	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate analysis	CRM	
21	Professional judgment	Duplicate analysis	CRM	Nata Technical Note 33
22	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Recoveries of SS	Nata Technical Note 33
23	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS	Instrument calibration Recoveries of SS Standard purity	Eurachem/CITAC Guide
24	Top Down - precision and estimates of the method and laboratory bias	Control samples - SS Duplicate analysis	Recoveries of SS	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation*		Guide Document for Estimating MU
		Precision	Method Bias	
25	Top Down - precision and estimates of the method and laboratory bias	Control samples - RM Duplicate analysis		Eurachem/CITAC Guide

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

3.3 Participants' Comments

Participants were invited to make any comments on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments are presented in Table 2.

Table 2 Participants' Comments

Lab. Code	Sample	Participant's Comments	Study Coordinator's Response
1	S3 and S4	Uncertainty for results below LOR (<0.5) left blank.	
7	S1	NEPM fractions reported	
13	S1	Please be aware that testing for TPH was performed outside of the sample holding time guideline of 14 days due to the COVID 19 lockdown.	
	S2	The result entered above for C6-C10 Hydrocarbons, is a C6-C9 result. Please be aware that testing for BTEX and C6-C9 was performed outside of the sample holding time guideline of 14 days due to the COVID 19 lockdown.	
14	S2	Soil (1g and 10g) extracted into methanol (purge and trap grade, 10 mL). Aliquots (1, 10, 100 uL) spiked into water (40 mL) for purge and trap GCMS. Reporting only 10 g of Soil & 10 uL of extract. 3 Analysts by 2 P&T GCMS systems - only reporting 1.	
	All	Some of the newer sections of this form, compared to AQA 16-05, such as STDs & Ref materials, Accreditation and Basis of Uncertainty Estimate might be different for each sample/analysis class S1, S2, S3 & S4. These samples are done in separate sections of our lab.	Thank you for your feedback, we will take this into consideration for future studies' results sheets.
15	S3	<0.5	
19	S1	NEPM Fractions reported	
20	S2	Soil spike recoveries: Benzene: 93%, Toluene: 90%, Ethylbenzene: 90%, Xylenes: 90%, C6 - C10: 83%.	
21	All	Uncertainty: 10g in 20mL solvent	
24	S2	Xylenes - Sum of meta & para Xylene and ortho Xylene	
	S3 and S4	Result for Benzo(b)fluoranthene is reported as Benzo(b)and Benzo (j) fluoranthene by the laboratory.	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 3 to 27 with resultant summary statistics: mean, median, maximum, minimum, 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 25.

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

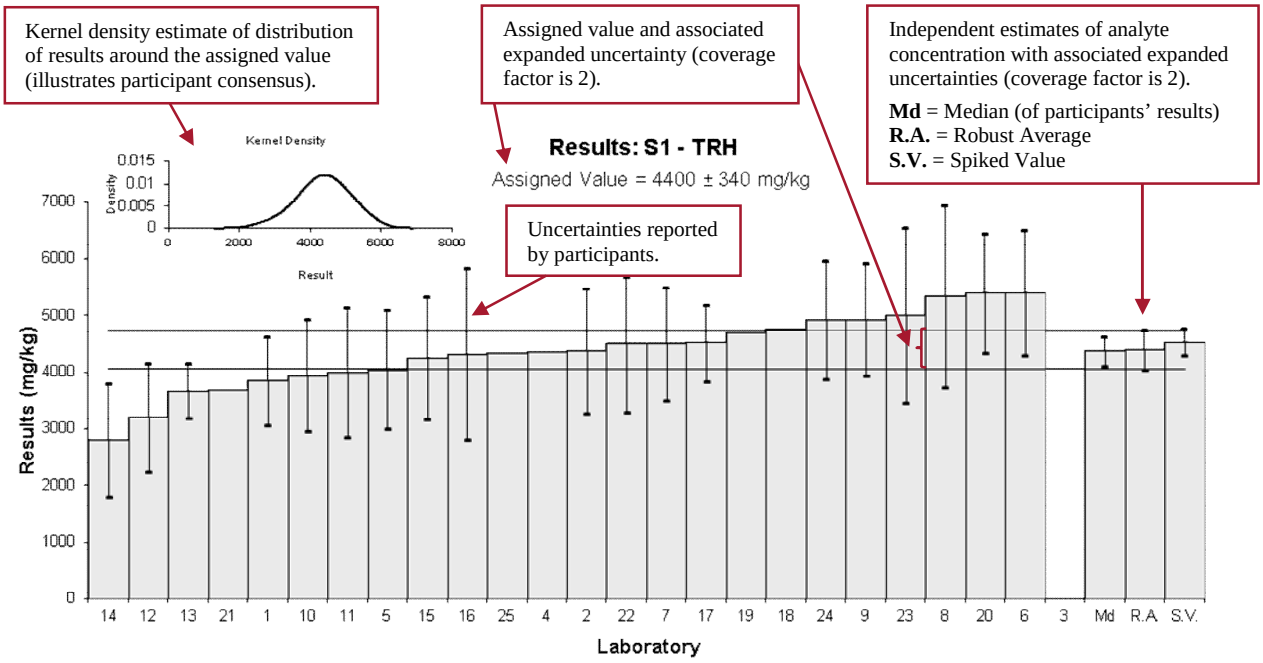


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

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

4.3 Robust Average and Robust Between Laboratory Coefficient of Variation

The robust averages and associated expanded measurement uncertainties, and robust between laboratory coefficient of variation (robust CV, a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528.[7]

4.4 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 organiser would be expected from participants given the levels of analytes present; it is not the CV of participants' results. The PCV is based on the mass fraction level of the analytes and experience from previous studies, and is backed up 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 and against achievable performance.

4.5 Target Standard Deviation

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

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

This value is used for calculation of participant z-score.

4.6 z-Score

For each participant 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 participant result

X is the study assigned value

σ is the target standard deviation from equation 1

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

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

4.7 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

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

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

4.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC 17025:2017 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 3

Sample Details

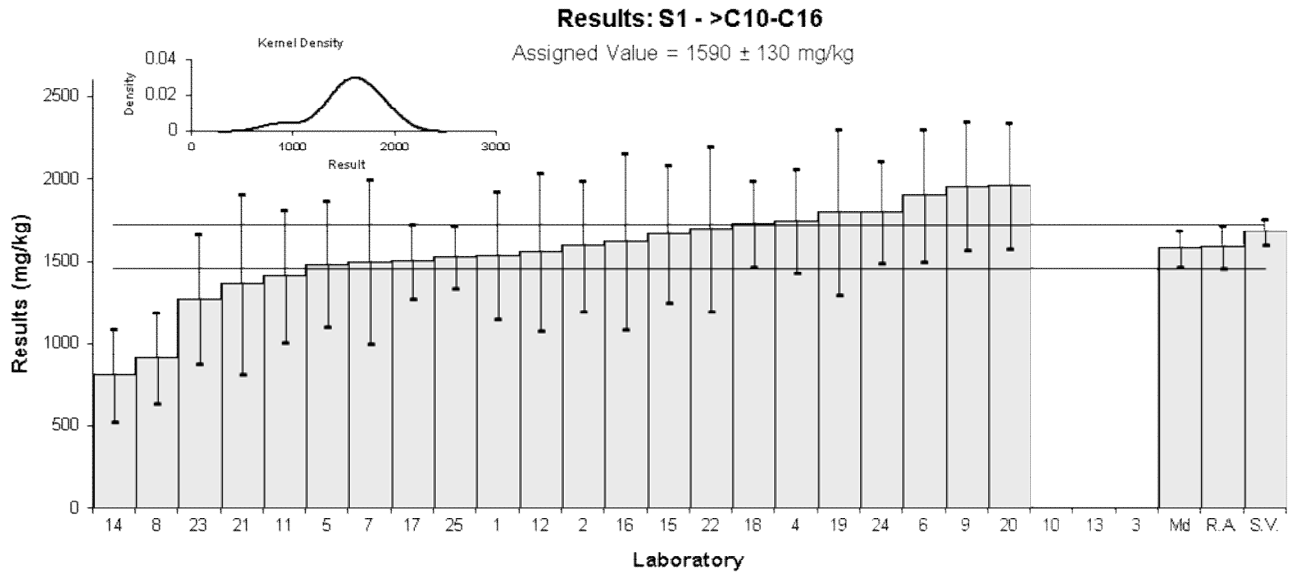
Sample No.	S1
Matrix	Soil
Analyte	>C10-C16
Units	mg/kg

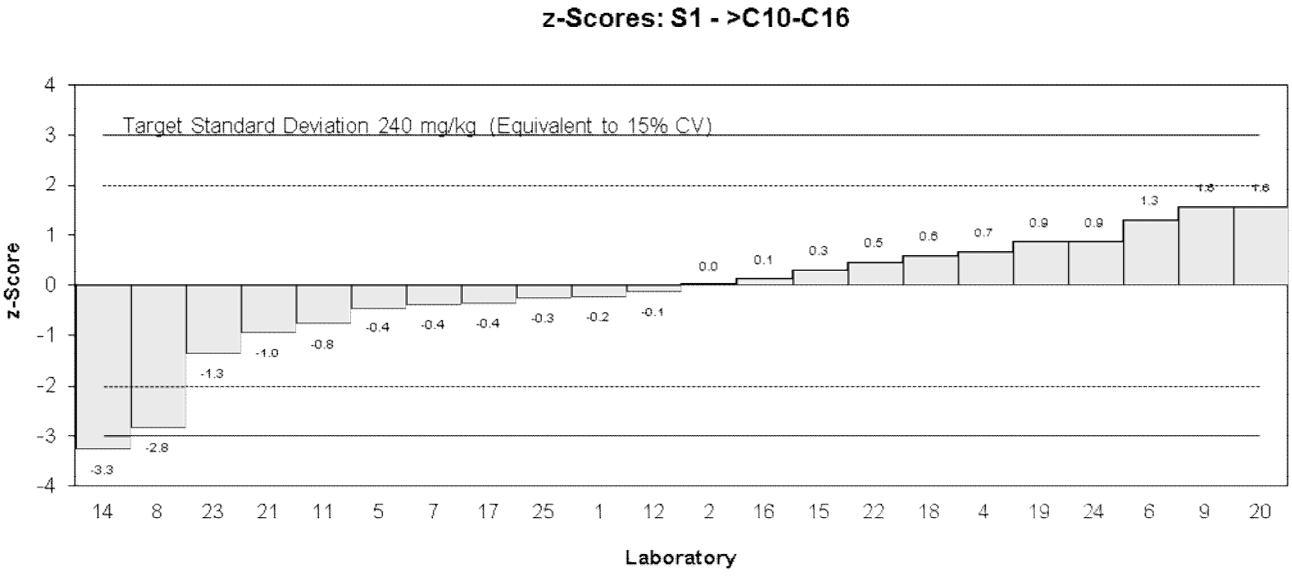
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1535	383.75	-0.23	-0.14
2	1594.42	399	0.02	0.01
3	NT	NT		
4	1747	314	0.66	0.46
5	1484	382	-0.44	-0.26
6	1900	400	1.30	0.74
7	1500	500	-0.38	-0.17
8	914.06	274.22	-2.83	-2.23
9	1960	392	1.55	0.90
10	NR	NR		
11	1408	401	-0.76	-0.43
12	1560	480	-0.13	-0.06
13	NR	NR		
14	810	280	-3.27	-2.53
15	1666	416	0.32	0.17
16	1620	531	0.13	0.05
17	1504	226	-0.36	-0.33
18	1730	262.7	0.59	0.48
19	1800	500	0.88	0.41
20	1962.24	382	1.56	0.92
21	1363	545	-0.95	-0.41
22	1700	500	0.46	0.21
23	1270	394	-1.34	-0.77
24	1800	305	0.88	0.63
25	1530	191.3	-0.25	-0.26

Statistics

Assigned Value	1590	130
Spike	1680	80
Robust Average	1590	130
Median	1580	110
Mean	1562	
N	22	
Max.	1962.24	
Min.	810	
Robust SD	250	
Robust CV	16%	


Results: S1 - >C10-C16
Assigned Value = 1590 ± 130 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 8 23 21 11 5 7 17 25 1 12 2 16 15 22 18 4 19 24 6 9 20 10 13 3 Md R.A. S.V.


z-Scores: S1 - >C10-C16
Target Standard Deviation 240 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 8 23 21 11 5 7 17 25 1 12 2 16 15 22 18 4 19 24 6 9 20

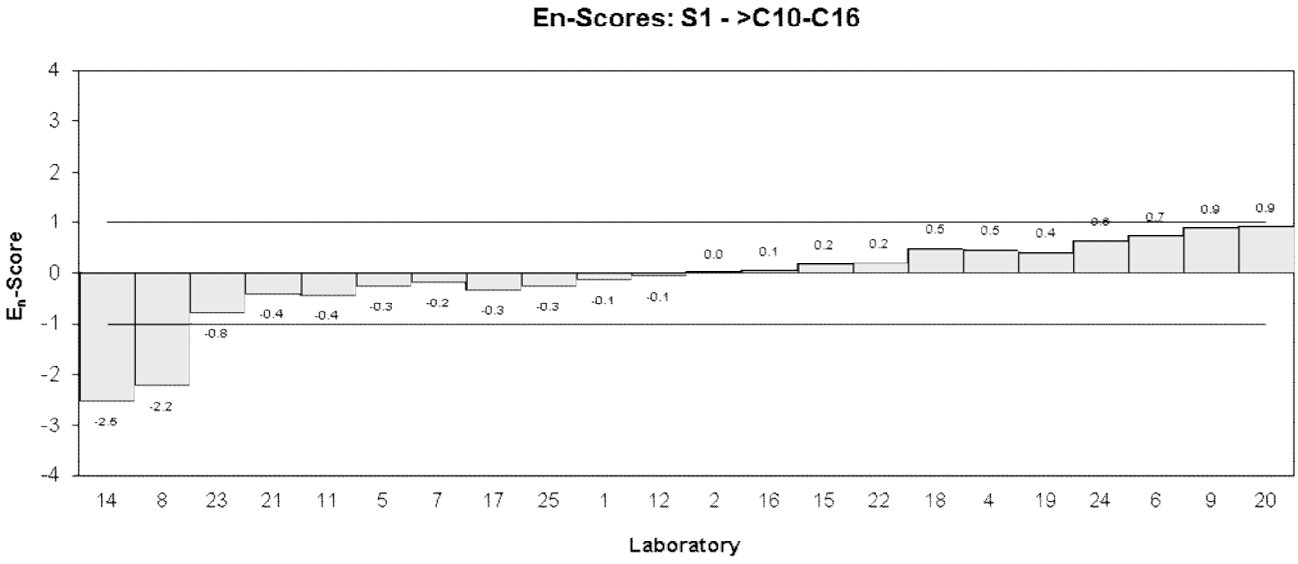

En-Scores: S1 - >C10-C16
En-Score
Laboratory
14 8 23 21 11 5 7 17 25 1 12 2 16 15 22 18 4 19 24 6 9 20

Figure 2

Table 4

Sample Details

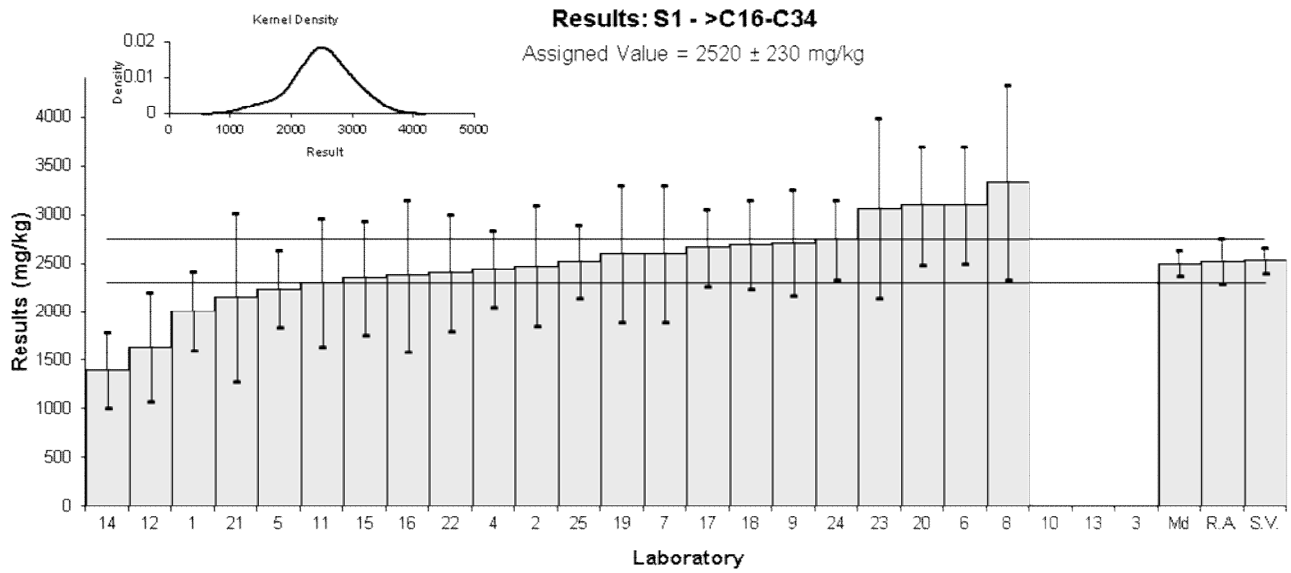
Sample No.	S1
Matrix	Soil
Analyte	>C16-C34
Units	mg/kg

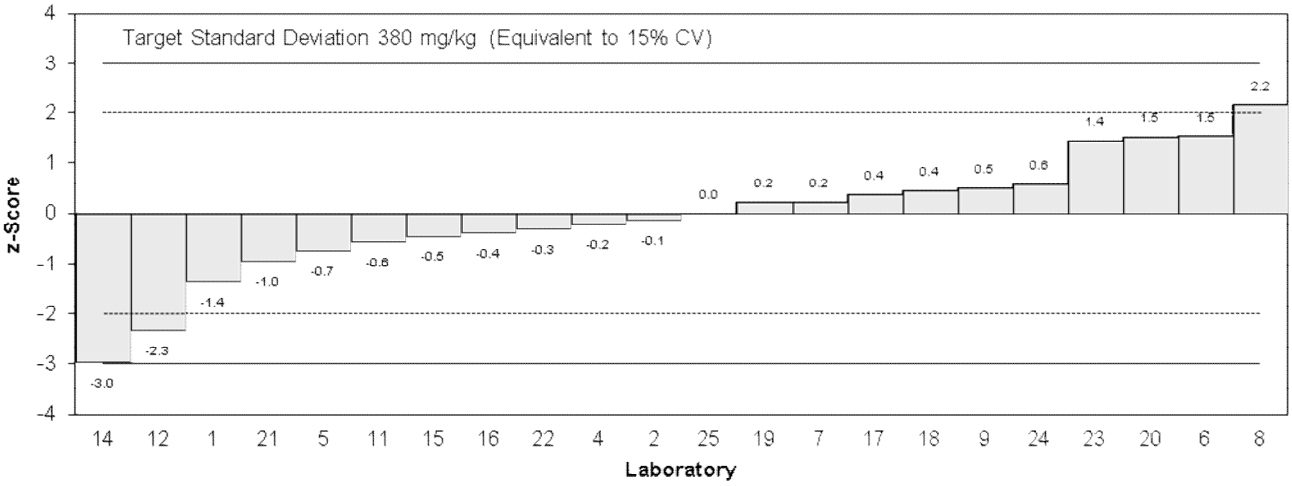
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	2002	400.4	-1.37	-1.12
2	2470.97	618	-0.13	-0.07
3	NT	NT		
4	2442	390	-0.21	-0.17
5	2237	396	-0.75	-0.62
6	3100	600	1.53	0.90
7	2600	700	0.21	0.11
8	3334.41	1000.32	2.15	0.79
9	2710	542	0.50	0.32
10	NR	NR		
11	2303	657	-0.57	-0.31
12	1640	560	-2.33	-1.45
13	NR	NR		
14	1400	390	-2.96	-2.47
15	2347	587	-0.46	-0.27
16	2370	780	-0.40	-0.18
17	2660	399	0.37	0.30
18	2690	451.1	0.45	0.34
19	2600	700	0.21	0.11
20	3097.537448	605	1.53	0.89
21	2156	862	-0.96	-0.41
22	2400	600	-0.32	-0.19
23	3064	919	1.44	0.57
24	2740	410	0.58	0.47
25	2520	372.5	0.00	0.00

Statistics

Assigned Value	2520	230
Spike	2530	130
Robust Average	2520	230
Median	2500	130
Mean	2495	
N	22	
Max.	3334.41	
Min.	1400	
Robust SD	420	
Robust CV	17%	


Results: S1 - >C16-C34
Assigned Value = 2520 ± 230 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 12 1 21 5 11 15 16 22 4 2 25 19 7 17 18 9 24 23 20 6 8 10 13 3 Md R.A. S.V.


z-Scores: S1 - >C16-C34
Target Standard Deviation 380 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 12 1 21 5 11 15 16 22 4 2 25 19 7 17 18 9 24 23 20 6 8
-3.0 -2.3 -1.4 -1.0 -0.7 -0.6 -0.5 -0.4 -0.3 -0.2 -0.1 0.0 0.2 0.2 0.4 0.4 0.5 0.6 1.4 1.5 1.5 2.2

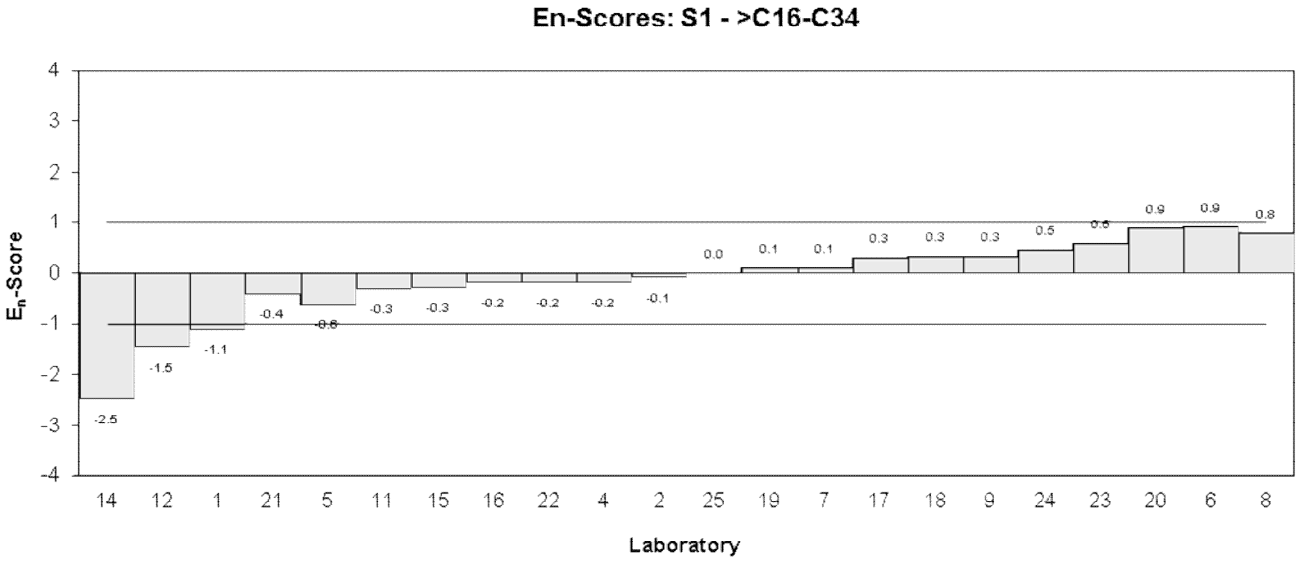

En-Scores: S1 - >C16-C34
En-Score
Laboratory
14 12 1 21 5 11 15 16 22 4 2 25 19 7 17 18 9 24 23 20 6 8
-2.5 -1.5 -1.1 -0.4 -0.6 -0.3 -0.3 -0.2 -0.2 -0.2 -0.1 0.0 0.1 0.1 0.3 0.3 0.3 0.5 0.6 0.9 0.9 0.8

Figure 3

Table 5

Sample Details

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

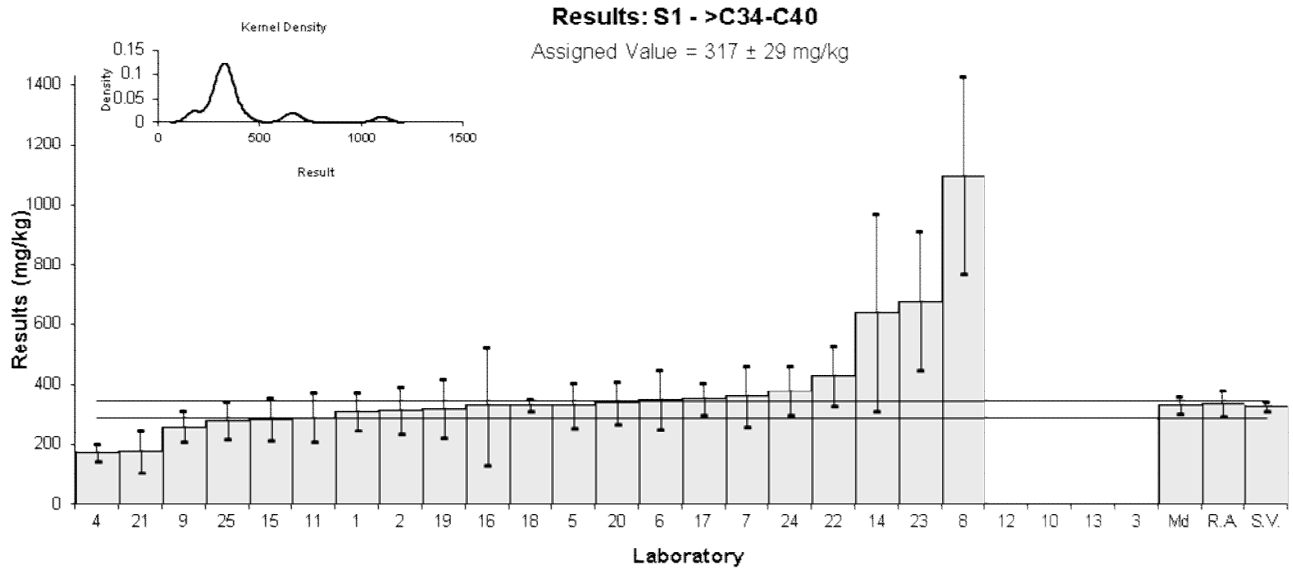
Participant Results

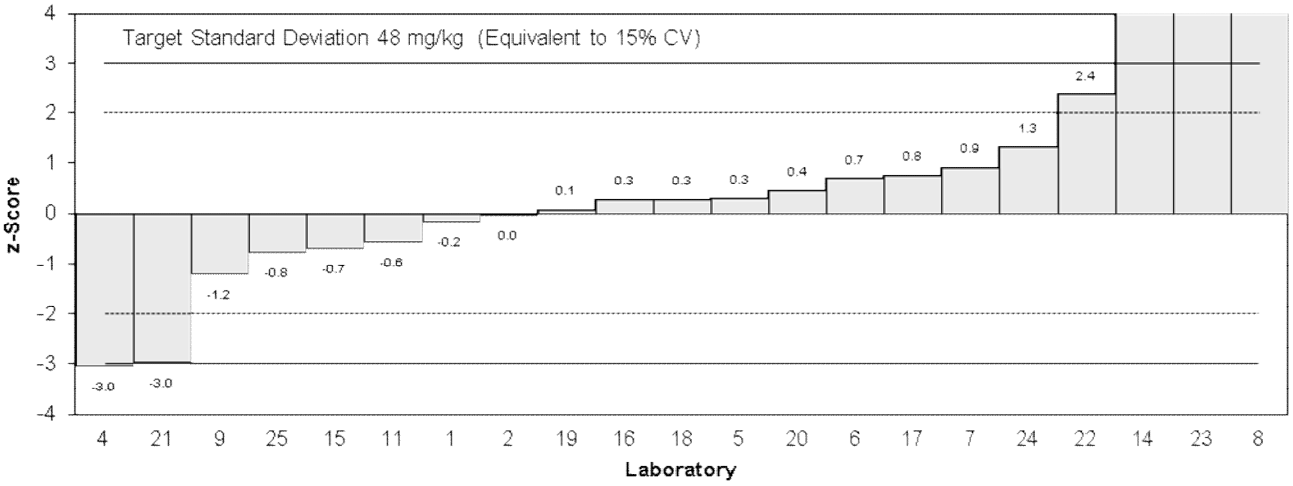
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	309	61.8	-0.17	-0.12
2	314.81	79	-0.05	-0.03
3	NT	NT		
4	172	27	-3.05	-3.66
5	331	76	0.29	0.17
6	350	100	0.69	0.32
7	360	100	0.90	0.41
8	1099.26	329.78	16.45	2.36
9	260	52	-1.20	-0.96
10	NR	NR		
11	290	82.8	-0.57	-0.31
12	<100	NR		
13	NR	NR		
14	640	330	6.79	0.98
15	284	71	-0.69	-0.43
16	330	196	0.27	0.07
17	353	53	0.76	0.60
18	330	19.5	0.27	0.37
19	320	100	0.06	0.03
20	338.2821391	71	0.45	0.28
21	176	70	-2.97	-1.86
22	430	100	2.38	1.09
23	680	231	7.63	1.56
24	380	80.9	1.32	0.73
25	280	61.6	-0.78	-0.54

Statistics

Assigned Value*	317	29
Spike	328	16
Robust Average	336	43
Median	330	27
Mean	382	
N	21	
Max.	1099.26	
Min.	172	
Robust SD	49	
Robust CV	16%	

* Robust average excluding laboratories 8, 14 and 23.


Results: S1 - >C34-C40
Assigned Value = 317 ± 29 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4 21 9 25 15 11 1 2 19 16 18 5 20 6 17 7 24 22 14 23 8 12 10 13 3 Md R.A S.V.


z-Scores: S1 - >C34-C40
Target Standard Deviation 48 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 21 9 25 15 11 1 2 19 16 18 5 20 6 17 7 24 22 14 23 8

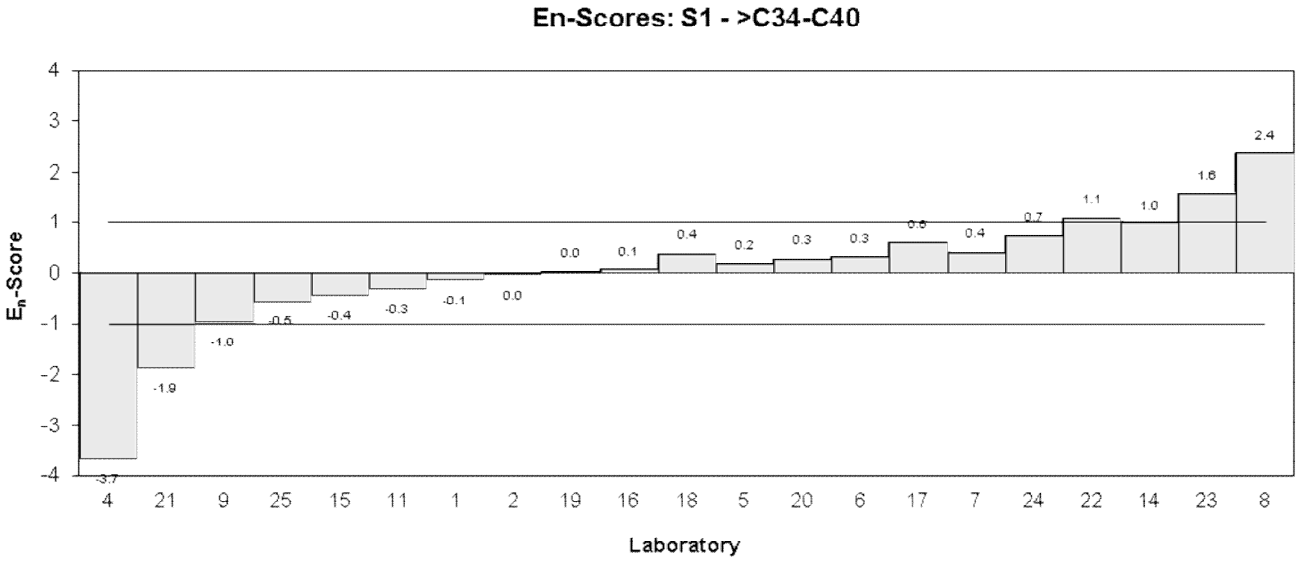

En-Scores: S1 - >C34-C40
En-Score
Laboratory
4 21 9 25 15 11 1 2 19 16 18 5 20 6 17 7 24 22 14 23 8

Figure 4

Table 6 Additional hydrocarbon ranges to those defined in Schedule B3 of the NEPM[5] reported for Sample S1

Range	Lab. Code	Result (mg/kg)	Uncertainty (mg/kg)
C7 - C9	**10**	<10	NR
	13	<8	5.4
C10 - C14	**10**	621.6	155.4
	13	600	130
C15 - C36	**10**	3325.2	831.3
	13	3070	460

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Table 7

Sample Details

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

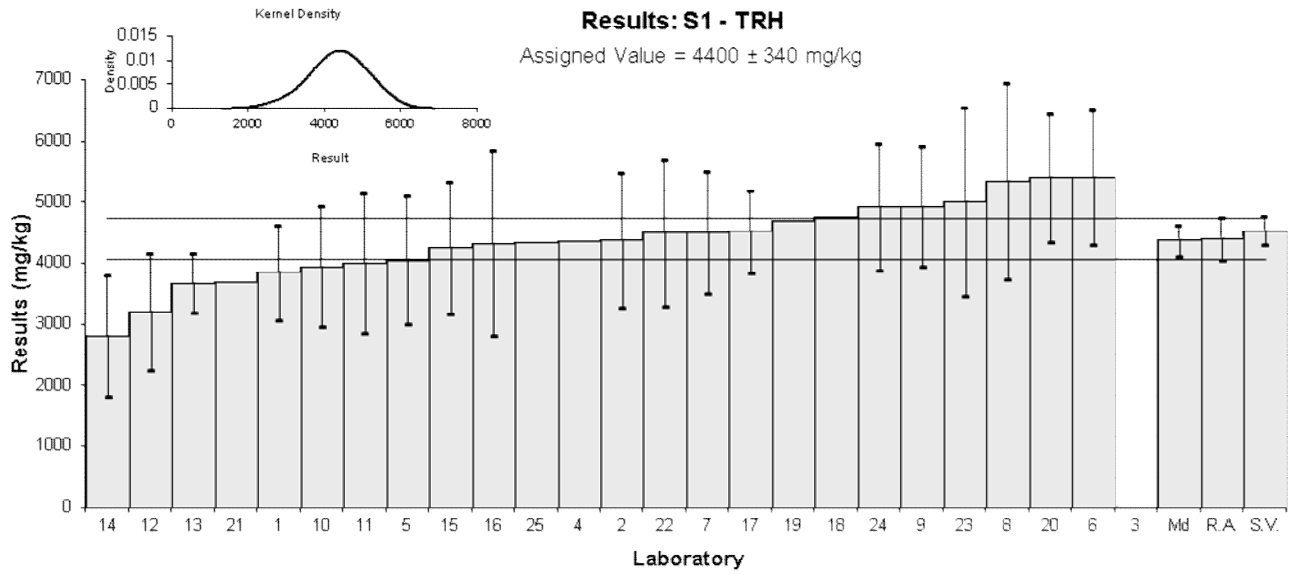
Participant Results

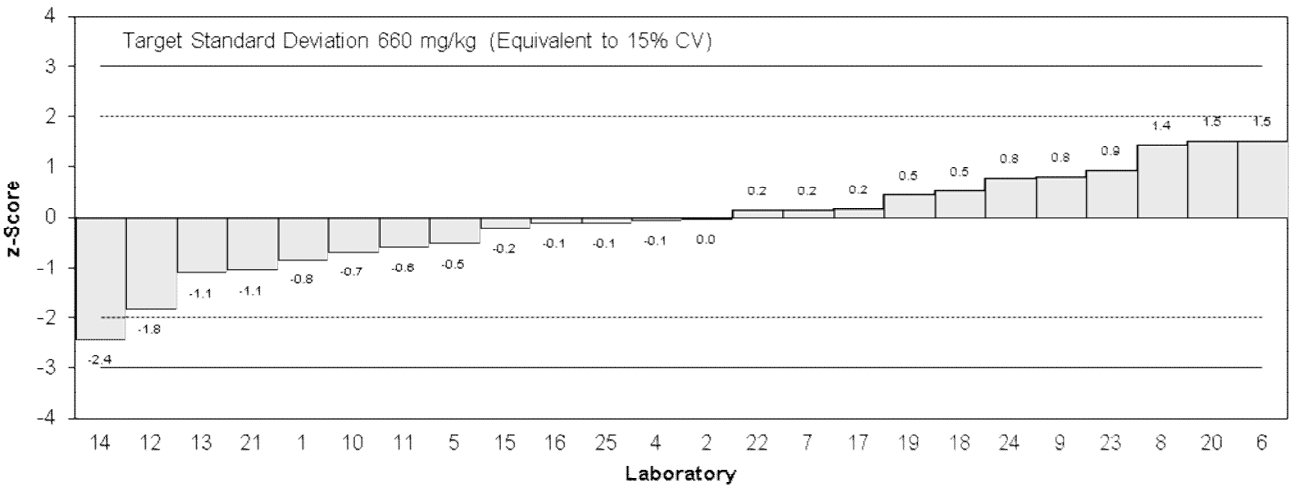
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	3846	769.2	-0.84	-0.66
2	4380.2	1096	-0.03	-0.02
3	NT	NT		
4	4361	NR	-0.06	-0.11
5	4051	1043	-0.53	-0.32
6	5400	1100	1.52	0.87
7	4500	1000	0.15	0.09
8	5347.73	1604.3	1.44	0.58
9	4930	986	0.80	0.51
10	3946.9	986.7	-0.69	-0.43
11	4001	1141	-0.60	-0.34
12	3200	960	-1.82	-1.18
13	3670	480	-1.11	-1.24
14	2800	1000	-2.42	-1.51
15	4257	1074	-0.22	-0.13
16	4320	1510	-0.12	-0.05
17	4517	678	0.18	0.15
18	4750	NR	0.53	1.03
19	4700	NR	0.45	0.88
20	5398.059598	1058	1.51	0.90
21	3695	NR	-1.07	-2.07
22	4500	1200	0.15	0.08
23	5010	1550	0.92	0.38
24	4920	1043	0.79	0.47
25	4330	NR	-0.11	-0.21

Statistics

Assigned Value	4400	340
Spike	4530	230
Robust Average	4400	340
Median	4370	250
Mean	4368	
N	24	
Max.	5400	
Min.	2800	
Robust SD	660	
Robust CV	15%	

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


Kernel Density
Density
Result
Results: S1 - TRH
Assigned Value = 4400 ± 340 mg/kg
Results (mg/kg)
Laboratory
14 12 13 21 1 10 11 5 15 16 25 4 2 22 7 17 19 18 24 9 23 8 20 6 3 Md R.A S.V.


z-Scores: S1 - TRH
Target Standard Deviation 660 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 12 13 21 1 10 11 5 15 16 25 4 2 22 7 17 19 18 24 9 23 8 20 6

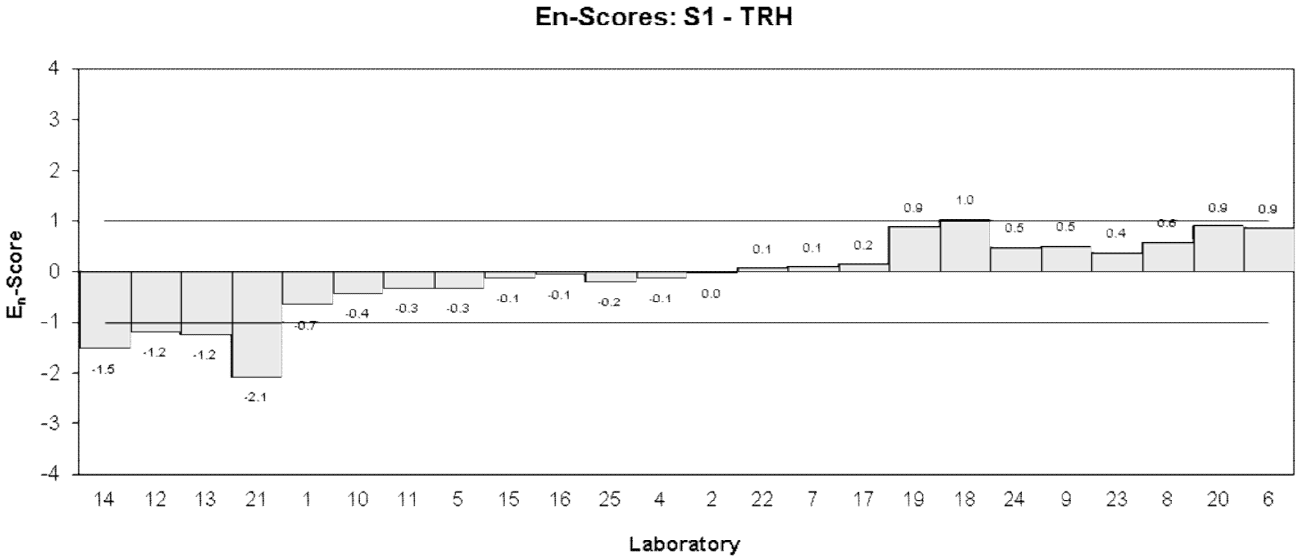

En-Scores: S1 - TRH
En-Score
Laboratory
14 12 13 21 1 10 11 5 15 16 25 4 2 22 7 17 19 18 24 9 23 8 20 6

Figure 5

Table 8

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	19.6	4.9
2	24.75	5
3	NT	NT
4	25.830	5.940
5	36	8
6	30	5
7	28	10
8	25.25	7.6
9	13	2.6
10	14.41005	3.6
11	7.57	1.9
12	14	4
13	15.6	4.4
14	36	9.0
15	25	7
16	30.9	12.3
17	16	3.2
18	30.4	5.32
19	35	10
20	37	7.0
21	19.09	7.64
22	37	10
23	1.05	0.27
24	38.6	7.1
25	27.2	5.46

Statistics

Assigned Value	Not Set	
Spike	59.4	3.0
Robust Average	24.8	5.5
Median	25.5	5.9
Mean	24.5	
N	24	
Max.	38.6	
Min.	1.05	
Robust SD	10.7	
Robust CV	43%	

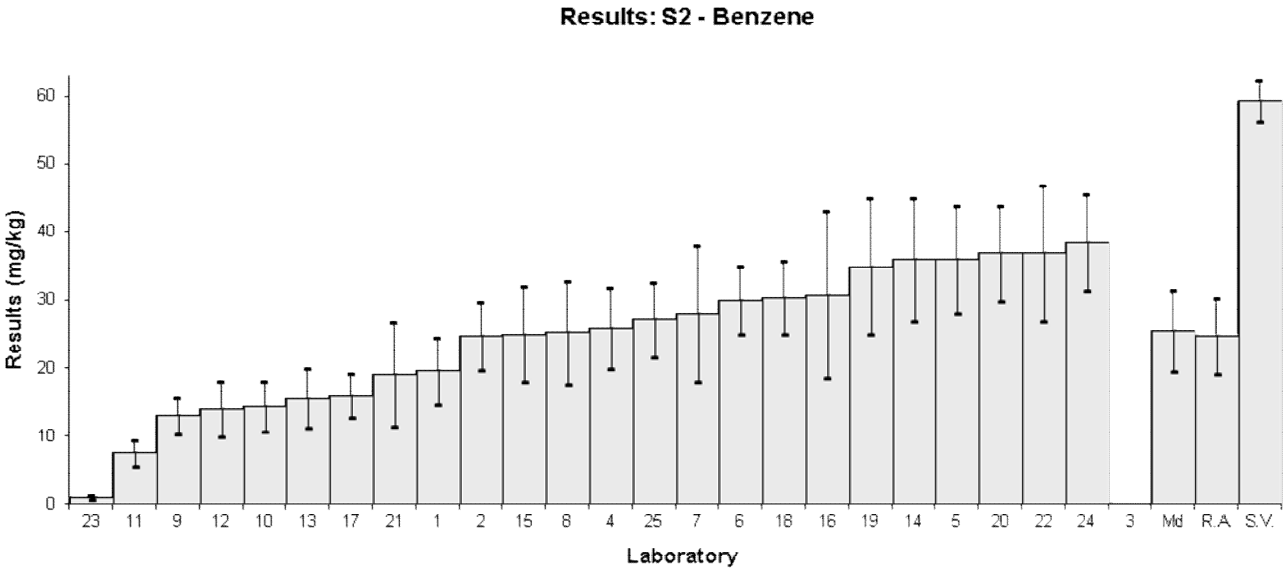

Results: S2 - Benzene
Results (mg/kg)
0
10
20
30
40
50
60
23
11
9
12
10
13
17
21
1
2
15
8
4
25
7
6
18
16
19
14
5
20
22
24
3
Md
R.A.
S.V.
Laboratory

Figure 6

Table 9

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	1565.3	469.6
2	2166.38	542
3	NT	NT
4	1407.279	83.02
5	1600	400
6	1700	430
7	1700	600
8	862.49	258.7
9	830	166
10	NT	NT
11	NT	NT
12	1030	400
13*	910	420
14	NT	NT
15	2145	515
16	1280	530
17	1212	242
18	1720	389.2
19	1700	600
20	1500	210
21	1135	454
22	1700	600
23	NT	NT
24	1750	385
25	1600	392.51

* Results are for the C6-C9 range.

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Robust Average	1470	240
Median	1580	120
Mean	1476	
N	20	
Max.	2166.38	
Min.	830	
Robust SD	430	
Robust CV	29%	

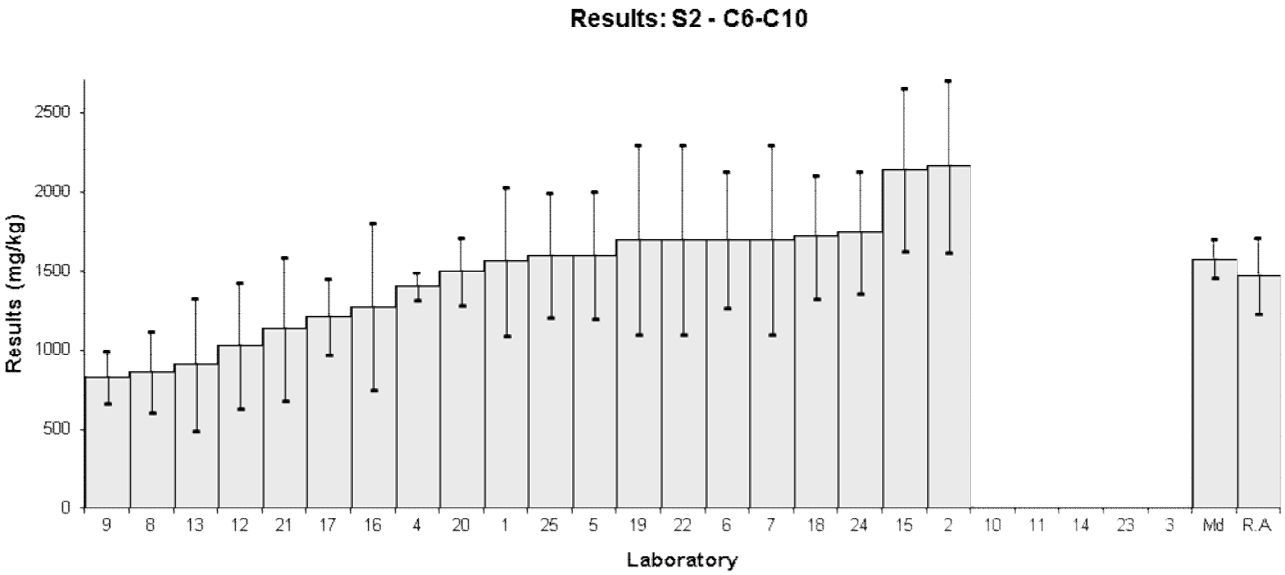

Results: S2 - C6-C10
Results (mg/kg)
2500
2000
1500
1000
500
0
9
8
13
12
21
17
16
4
20
1
25
5
19
22
6
7
18
24
15
2
10
11
14
23
3
Md
R.A
Laboratory

Figure 7

Table 10

Sample Details

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

Participant Results

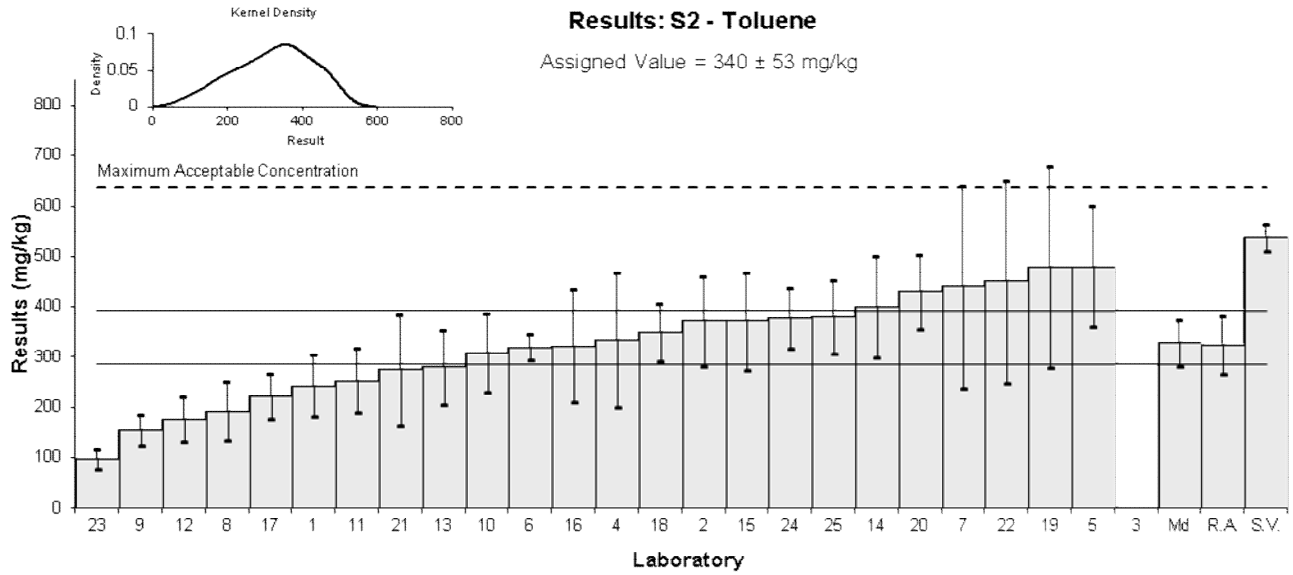
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	243.7	60.9	-1.89	-1.19
2	371.95	89	0.63	0.31
3	NT	NT		
4	334.660	133.86	-0.10	-0.04
5**	480	120	2.00	1.00
6	320	25	-0.39	-0.34
7	440	200	1.96	0.48
8	192.61	57.8	-2.89	-1.88
9	155	31	-3.63	-3.01
10	309.13945	77.28	-0.61	-0.33
11	254	64	-1.69	-1.03
12	177	44	-3.20	-2.37
13	280	73	-1.18	-0.67
14	400	100	1.18	0.53
15	372	97	0.63	0.29
16	322	112	-0.35	-0.15
17	222	44	-2.31	-1.71
18	350	57.8	0.20	0.13
19**	480	200	2.00	0.68
20	430	73	1.76	1.00
21	274.55	110	-1.28	-0.54
22**	450	200	2.00	0.53
23	97.3	19.5	-4.76	-4.30
24	378	59.9	0.75	0.48
25	380	73.57	0.78	0.44

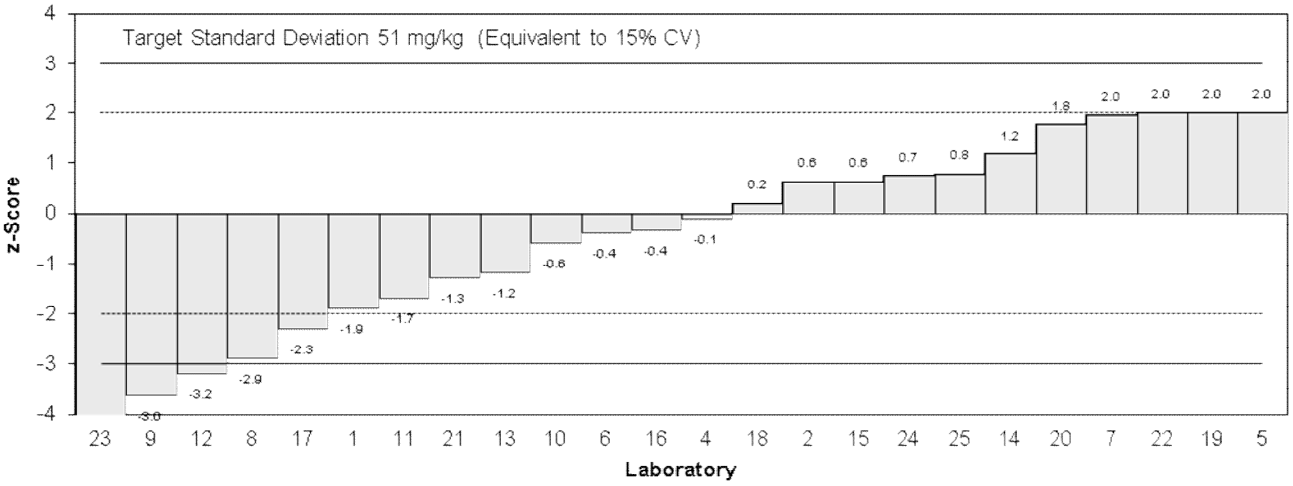
Statistics

Assigned Value*	340	53
Spike	537	27
Max. Acceptable Conc.**	639	
Robust Average	324	58
Median	328	46
Mean	321	
N	24	
Max.	480	
Min.	97.3	
Robust SD	100	
Robust CV	29%	

* Robust average excluding laboratories 9 and 23.

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


Kernel Density
Density
Result
Results: S2 - Toluene
Assigned Value = 340 ± 53 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
23 9 12 8 17 1 11 21 13 10 6 16 4 18 2 15 24 25 14 20 7 22 19 5 3 Md R.A S.V.


z-Scores: S2 - Toluene
Target Standard Deviation 51 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
23 9 12 8 17 1 11 21 13 10 6 16 4 18 2 15 24 25 14 20 7 22 19 5

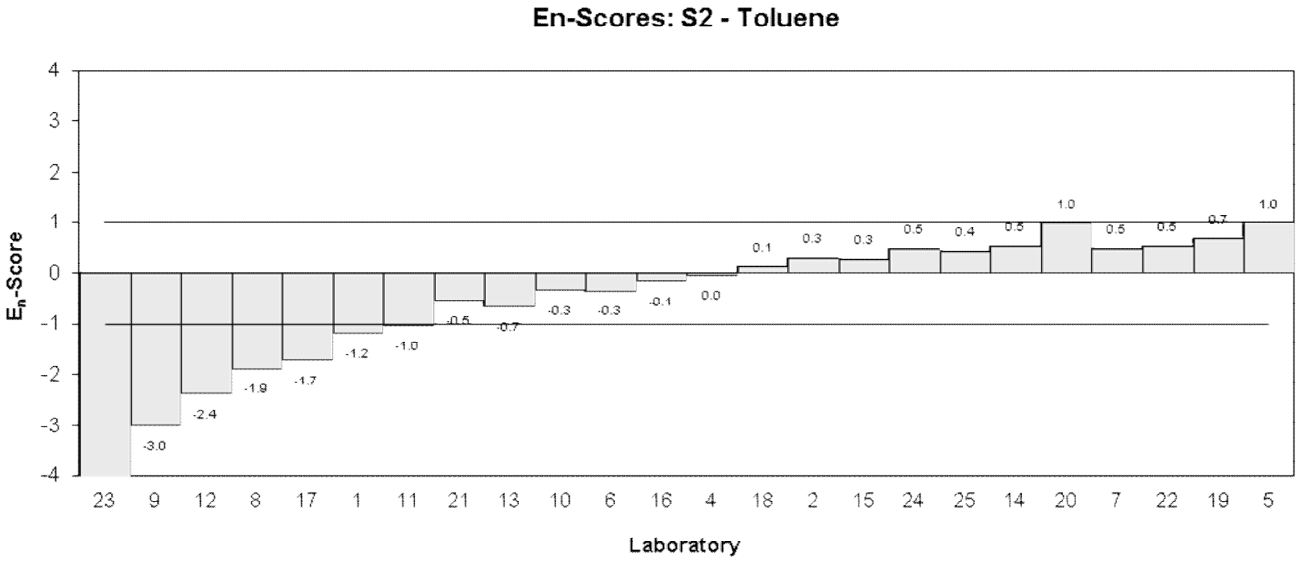

En-Scores: S2 - Toluene
En-Score
Laboratory
23 9 12 8 17 1 11 21 13 10 6 16 4 18 2 15 24 25 14 20 7 22 19 5

Figure 8

Table 11

Sample Details

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

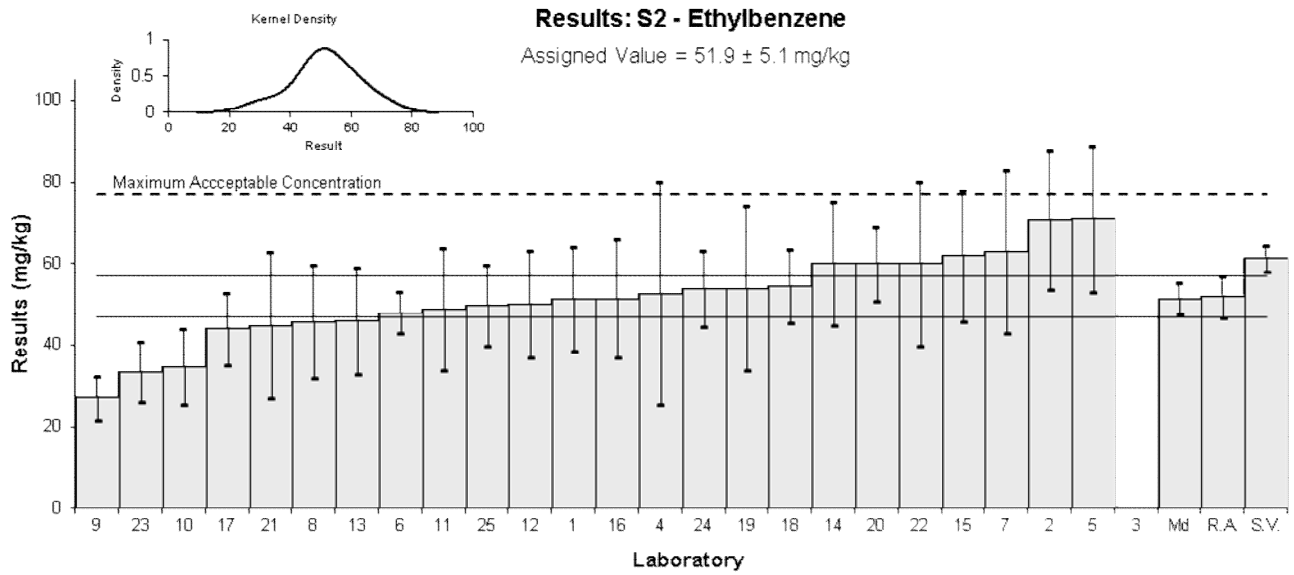
Participant Results

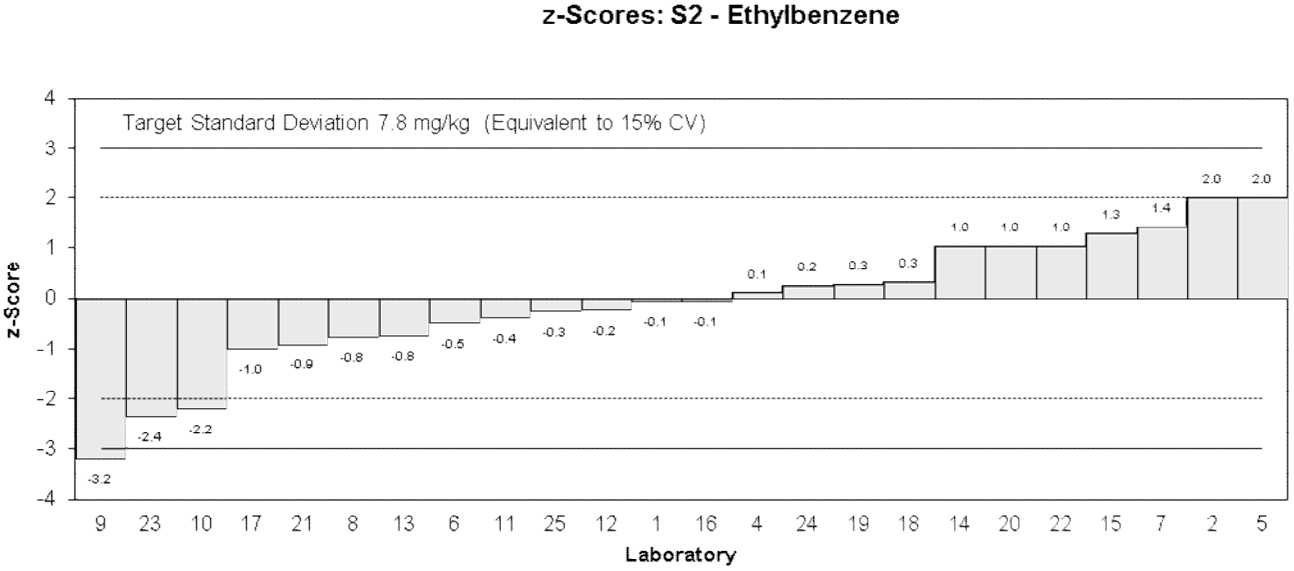
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	51.4	12.8	-0.06	-0.04
2*	70.70	17	2.00	1.00
3	NT	NT		
4	52.738	27.42	0.11	0.03
5*	71	18	2.00	1.00
6	48	5	-0.50	-0.55
7	63	20	1.43	0.54
8	45.83	13.7	-0.78	-0.42
9	27	5.4	-3.20	-3.35
10	34.752325	9.23	-2.20	-1.63
11	48.9	15	-0.39	-0.19
12	50	13	-0.24	-0.14
13	46	13	-0.76	-0.42
14	60	15	1.04	0.51
15	62	16	1.30	0.60
16	51.5	14.5	-0.05	-0.03
17	44	8.8	-1.01	-0.78
18	54.4	8.93	0.32	0.24
19	54	20	0.27	0.10
20	60	9.0	1.04	0.78
21	44.76	17.9	-0.92	-0.38
22	60	20	1.04	0.39
23	33.5	7.4	-2.36	-2.05
24	53.8	9.3	0.24	0.18
25	49.8	9.87	-0.27	-0.19

Statistics

Assigned Value	51.9	5.1
Spike	61.3	3.1
Max. Acceptable Conc.*	76.9	
Robust Average	51.9	5.1
Median	51.5	3.9
Mean	51.5	
N	24	
Max.	71	
Min.	27	
Robust SD	9.9	
Robust CV	19%	

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


Results: S2 - Ethylbenzene
Assigned Value = 51.9 ± 5.1 mg/kg
Kernel Density
Density
Result
Maximum Accceptable Concentration
Results (mg/kg)
Laboratory
9 23 10 17 21 8 13 6 11 25 12 1 16 4 24 19 18 14 20 22 15 7 2 5 3 Md R.A S.V.


z-Scores: S2 - Ethylbenzene
Target Standard Deviation 7.8 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
9 23 10 17 21 8 13 6 11 25 12 1 16 4 24 19 18 14 20 22 15 7 2 5

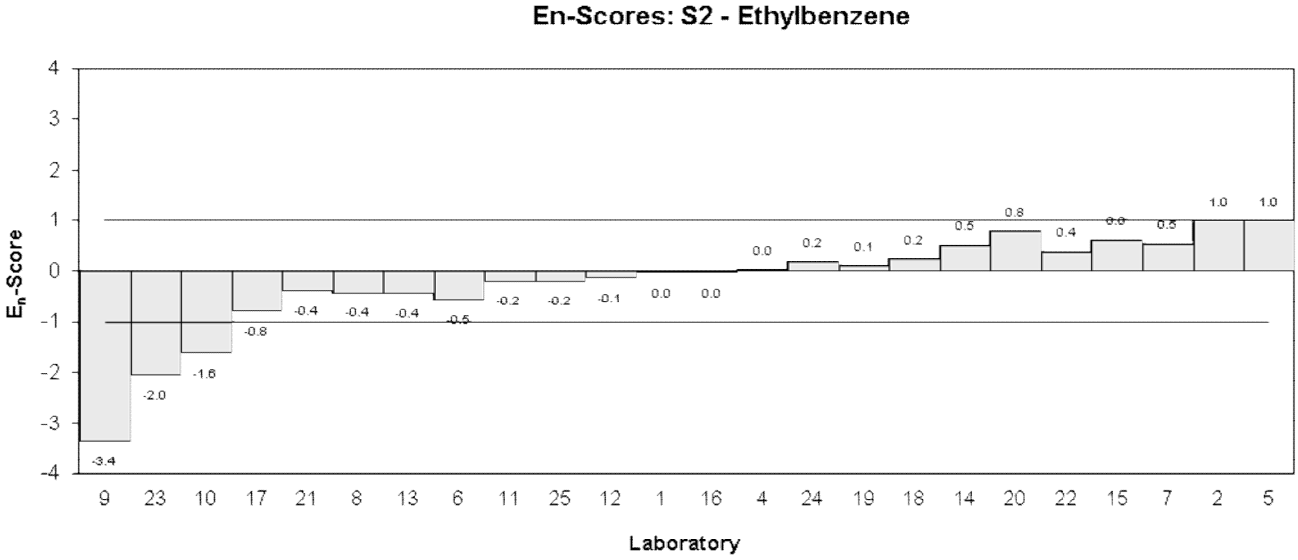

En-Scores: S2 - Ethylbenzene
En-Score
Laboratory
9 23 10 17 21 8 13 6 11 25 12 1 16 4 24 19 18 14 20 22 15 7 2 5

Figure 9

Table 12

Sample Details

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

Participant Results

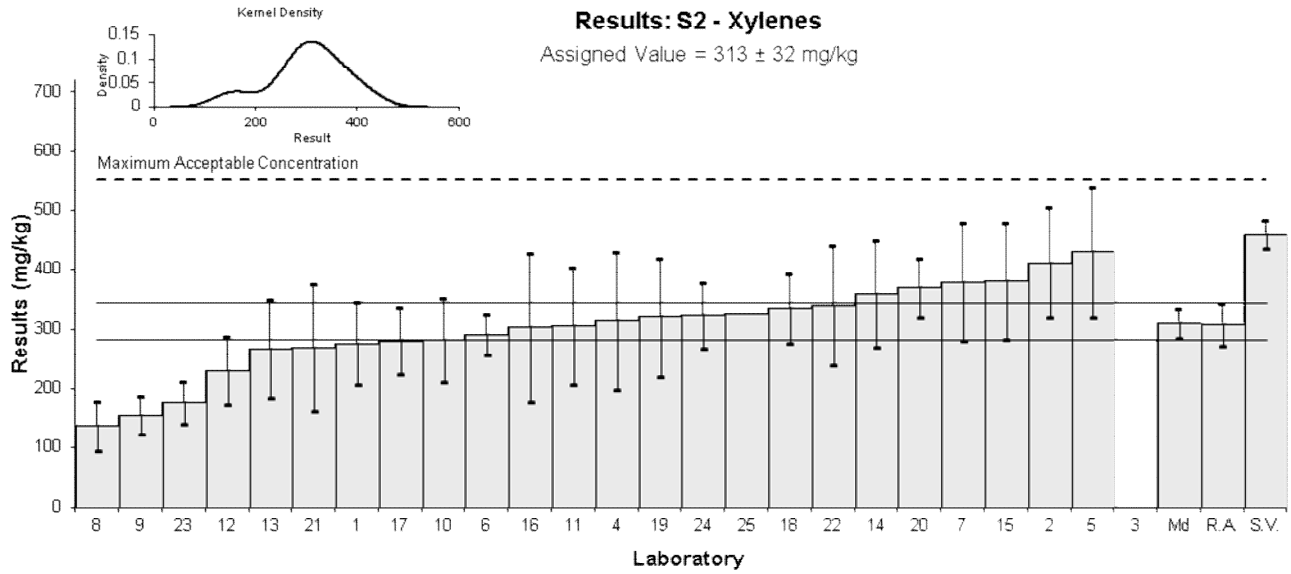
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	275.7	68.9	-0.79	-0.49
2**	412.38	92	2.00	1.00
3	NT	NT		
4	314.361	116.31	0.03	0.01
5**	430	110	2.00	1.00
6	290	33	-0.49	-0.50
7	380	100	1.43	0.64
8	136.54	41	-3.76	-3.39
9	154	31	-3.39	-3.57
10	281.6482	70.41	-0.67	-0.41
11	306	98	-0.15	-0.07
12	230	58	-1.77	-1.25
13	266	83	-1.00	-0.53
14	360	90	1.00	0.49
15	381	99	1.45	0.65
16	303	125	-0.21	-0.08
17	280	56	-0.70	-0.51
18	335	59.0	0.47	0.33
19	320	100	0.15	0.07
20	370	50	1.21	0.96
21	268.38	107	-0.95	-0.40
22	340	100	0.58	0.26
23	176.8	35.4	-2.90	-2.85
24	323.2	54.5	0.22	0.16
25	326	NR	0.28	0.41

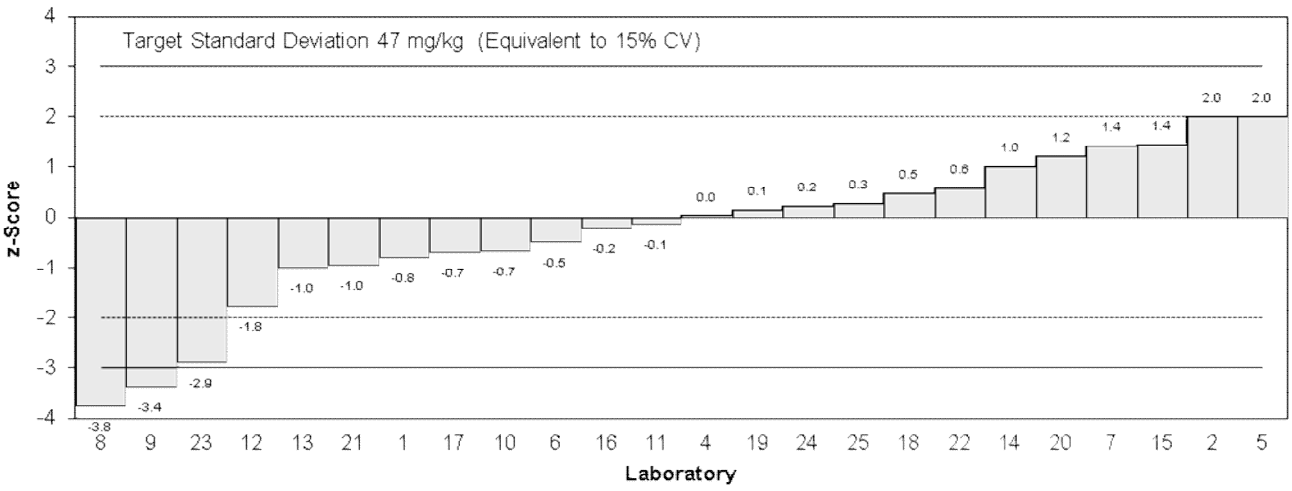
Statistics

Assigned Value*	313	32
Spike	460	23
Max. Acceptable Conc.**	554	
Robust Average	308	35
Median	310	24
Mean	303	
N	24	
Max.	430	
Min.	136.54	
Robust SD	62	
Robust CV	20%	

* Robust average excluding laboratory 8.

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


Kernel Density
Density
Result
Results: S2 - Xylenes
Assigned Value = 313 ± 32 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
8 9 23 12 13 21 1 17 10 6 16 11 4 19 24 25 18 22 14 20 7 15 2 5 3 Md R.A S.V.


z-Scores: S2 - Xylenes
Target Standard Deviation 47 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
8 9 23 12 13 21 1 17 10 6 16 11 4 19 24 25 18 22 14 20 7 15 2 5

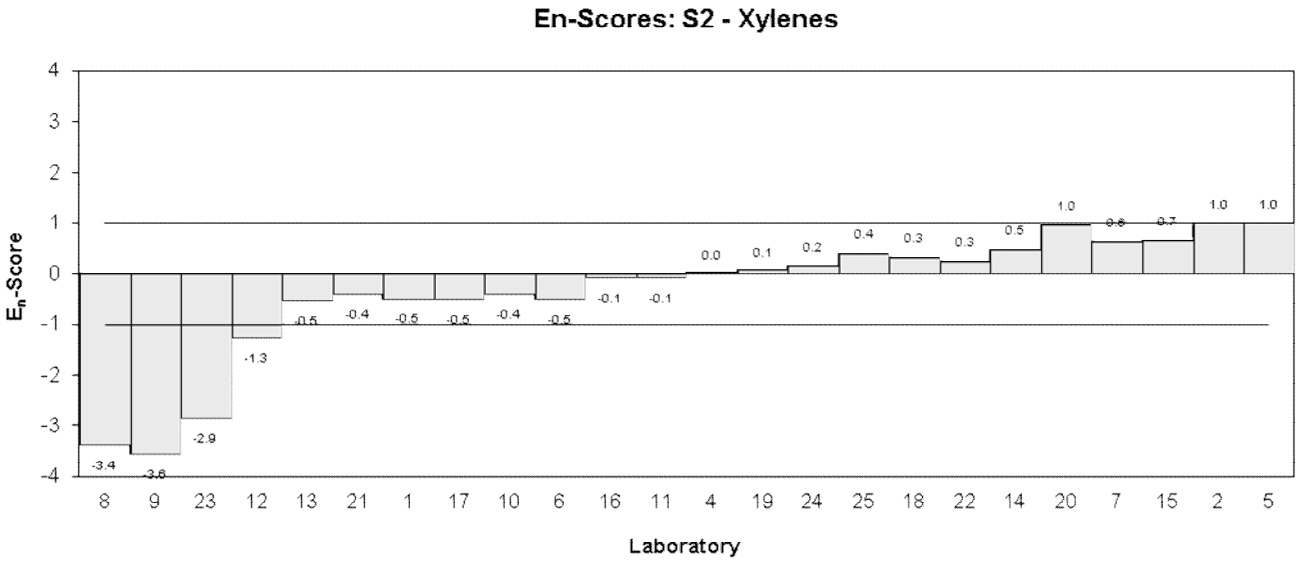

En-Scores: S2 - Xylenes
En-Score
Laboratory
8 9 23 12 13 21 1 17 10 6 16 11 4 19 24 25 18 22 14 20 7 15 2 5

Figure 10

Table 13

Sample Details

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

Participant Results

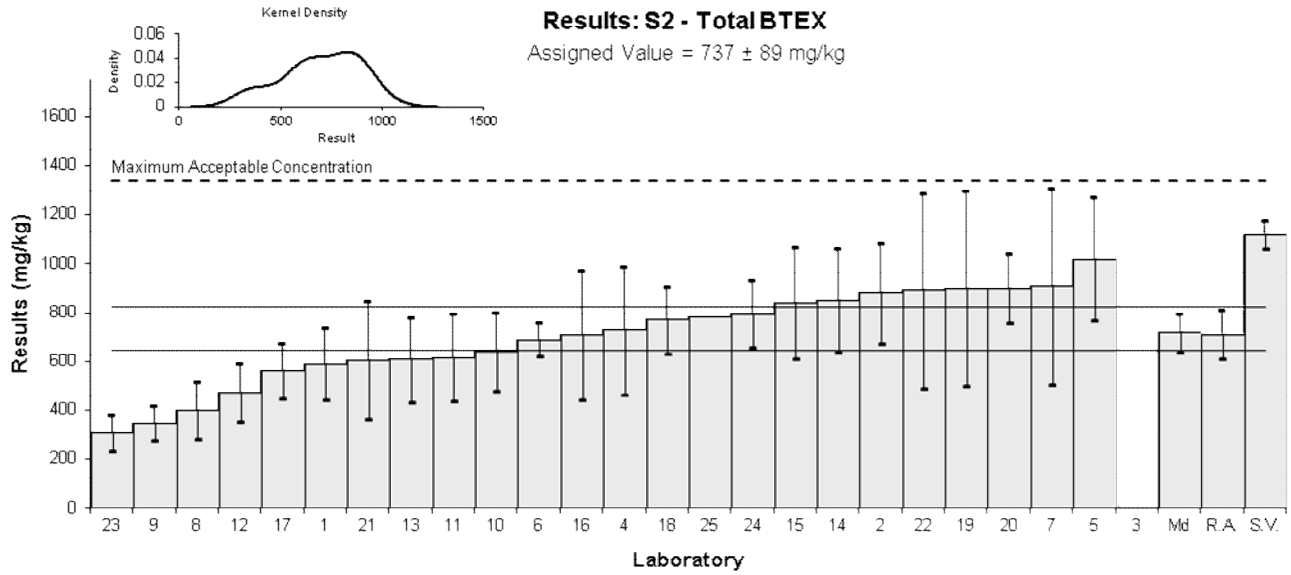
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	590.37	147.6	-1.33	-0.85
2	879.77	203	1.29	0.64
3	NT	NT		
4	727.589	263.38	-0.09	-0.03
5**	1020	250	2.00	1.00
6	690	68	-0.43	-0.42
7	910	400	1.56	0.42
8	400.23	120.1	-3.05	-2.25
9	349	70	-3.51	-3.43
10	639.95	160.0	-0.88	-0.53
11	616	179	-1.09	-0.61
12	472	118	-2.40	-1.79
13	607.6	173.4	-1.17	-0.66
14	850	210	1.02	0.50
15	840	227	0.93	0.42
16	707	264	-0.27	-0.11
17	562	112	-1.58	-1.22
18	770	135.6	0.30	0.20
19	900	400	1.47	0.40
20	900	140	1.47	0.98
21	606.78	242.7	-1.18	-0.50
22	890	400	1.38	0.37
23	309	74	-3.87	-3.70
24	794	137	0.52	0.35
25	783	NR	0.42	0.52

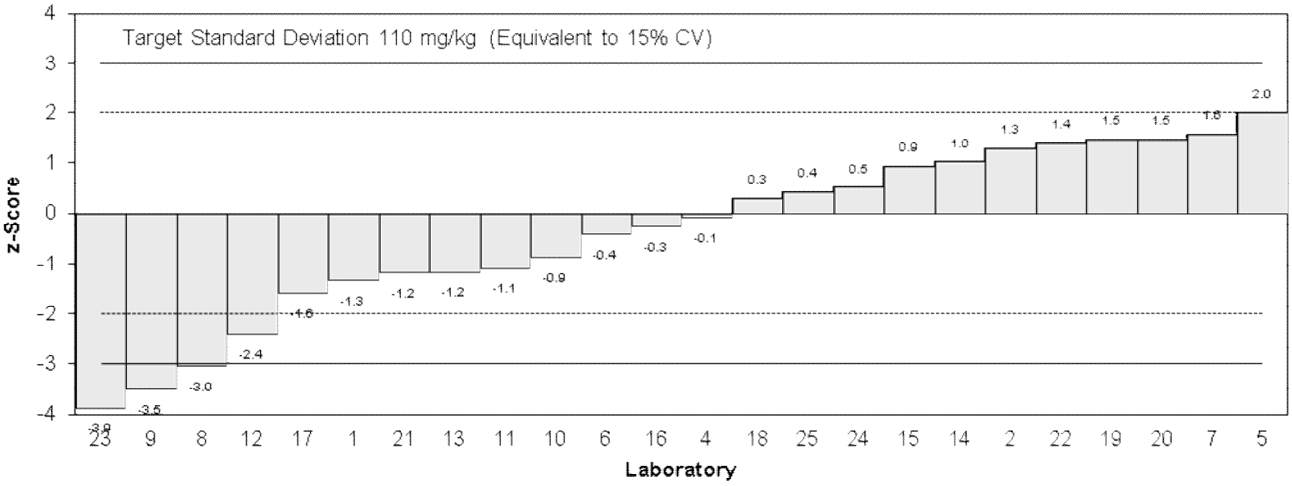
Statistics

Assigned Value*	737	89
Spike	1120	60
Max. Acceptable Conc.**	1340	
Robust Average	710	100
Median	717	81
Mean	701	
N	24	
Max.	1020	
Min.	309	
Robust SD	170	
Robust CV	23%	

* Robust average excluding laboratories 9 and 23.

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


Kernel Density
Density
Result
Results: S2 - Total BTEX
Assigned Value = 737 ± 89 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
23 9 8 12 17 1 21 13 11 10 6 16 4 18 25 24 15 14 2 22 19 20 7 5 3 Md R.A S.V.


z-Scores: S2 - Total BTEX
Target Standard Deviation 110 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
23 9 8 12 17 1 21 13 11 10 6 16 4 18 25 24 15 14 2 22 19 20 7 5

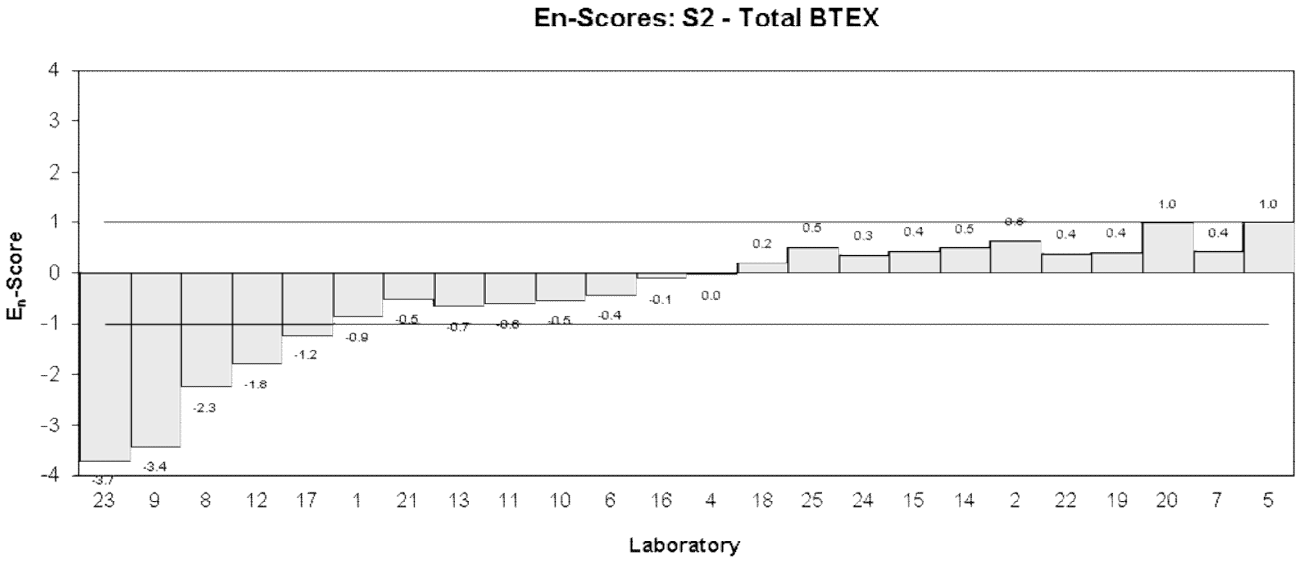

En-Scores: S2 - Total BTEX
En-Score
Laboratory
23 9 8 12 17 1 21 13 11 10 6 16 4 18 25 24 15 14 2 22 19 20 7 5

Figure 11

Table 14

Sample Details

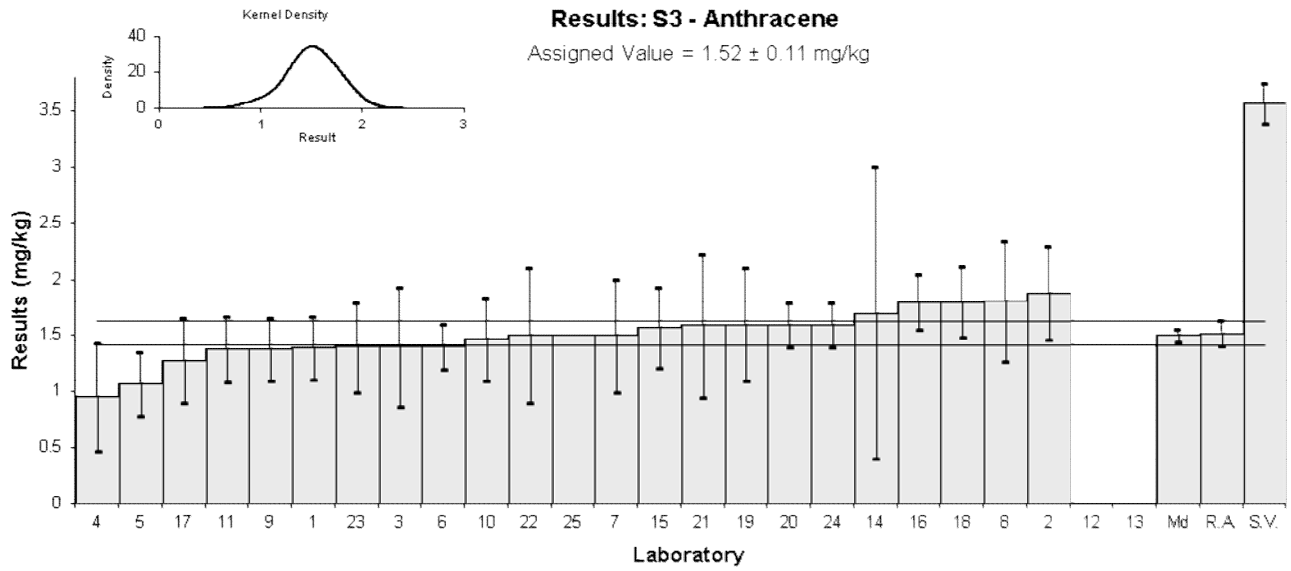
Sample No.	S3
Matrix	Soil
Analyte	Anthracene
Units	mg/kg

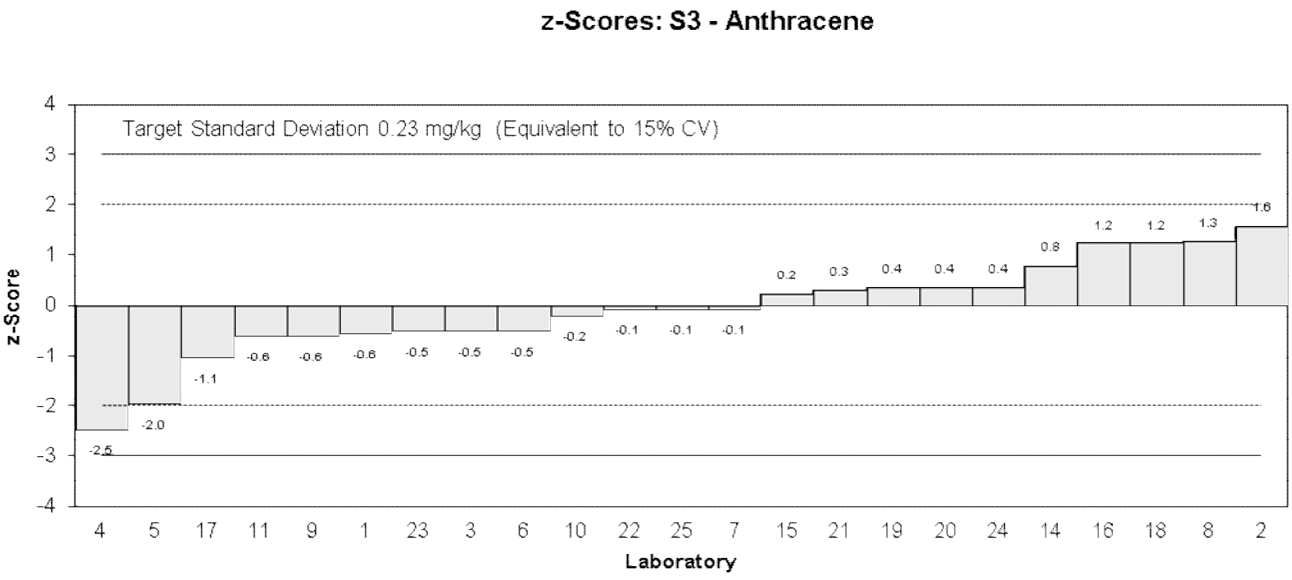
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.39	0.278	-0.57	-0.43
2	1.88	0.42	1.58	0.83
3	1.4	0.53	-0.53	-0.22
4	0.954	0.48	-2.48	-1.15
5	1.07	0.28	-1.97	-1.50
6	1.4	0.2	-0.53	-0.53
7	1.5	0.5	-0.09	-0.04
8	1.807	0.54	1.26	0.52
9	1.38	0.28	-0.61	-0.47
10	1.47	0.37	-0.22	-0.13
11	1.38	0.29	-0.61	-0.45
12	NT	NT		
13	NT	NT		
14	1.7	1.3	0.79	0.14
15	1.57	0.36	0.22	0.13
16	1.8	0.25	1.23	1.03
17	1.28	0.38	-1.05	-0.61
18	1.8	0.31	1.23	0.85
19	1.6	0.5	0.35	0.16
20	1.6	0.2	0.35	0.35
21	1.59	0.64	0.31	0.11
22	1.5	0.6	-0.09	-0.03
23	1.4	0.4	-0.53	-0.29
24	1.6	0.2	0.35	0.35
25	1.5	NR	-0.09	-0.18

Statistics

Assigned Value	1.52	0.11
Spike	3.57	0.18
Robust Average	1.52	0.11
Median	1.50	0.06
Mean	1.50	
N	23	
Max.	1.88	
Min.	0.954	
Robust SD	0.21	
Robust CV	14%	


Kernel Density
Density
Result
Results: S3 - Anthracene
Assigned Value = 1.52 ± 0.11 mg/kg
Results (mg/kg)
Laboratory
4 5 17 11 9 1 23 3 6 10 22 25 7 15 21 19 20 24 14 16 18 8 2 12 13 Md R.A. S.V.


z-Scores: S3 - Anthracene
Target Standard Deviation 0.23 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 5 17 11 9 1 23 3 6 10 22 25 7 15 21 19 20 24 14 16 18 8 2

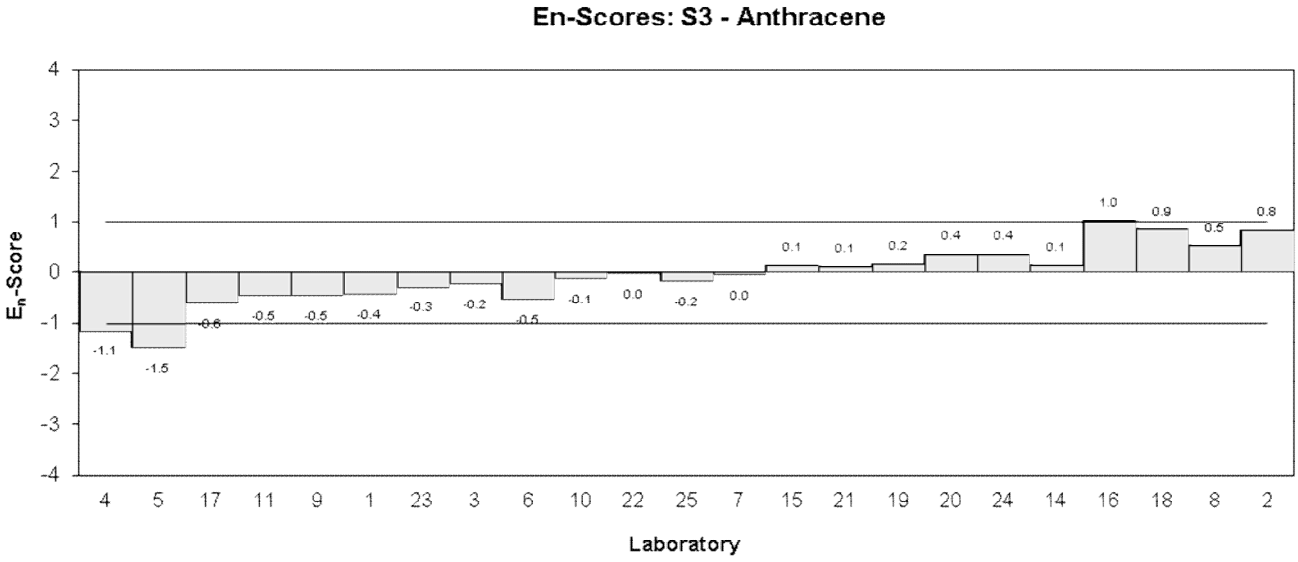

En-Scores: S3 - Anthracene
En-Score
Laboratory
4 5 17 11 9 1 23 3 6 10 22 25 7 15 21 19 20 24 14 16 18 8 2

Figure 12

Table 15

Sample Details

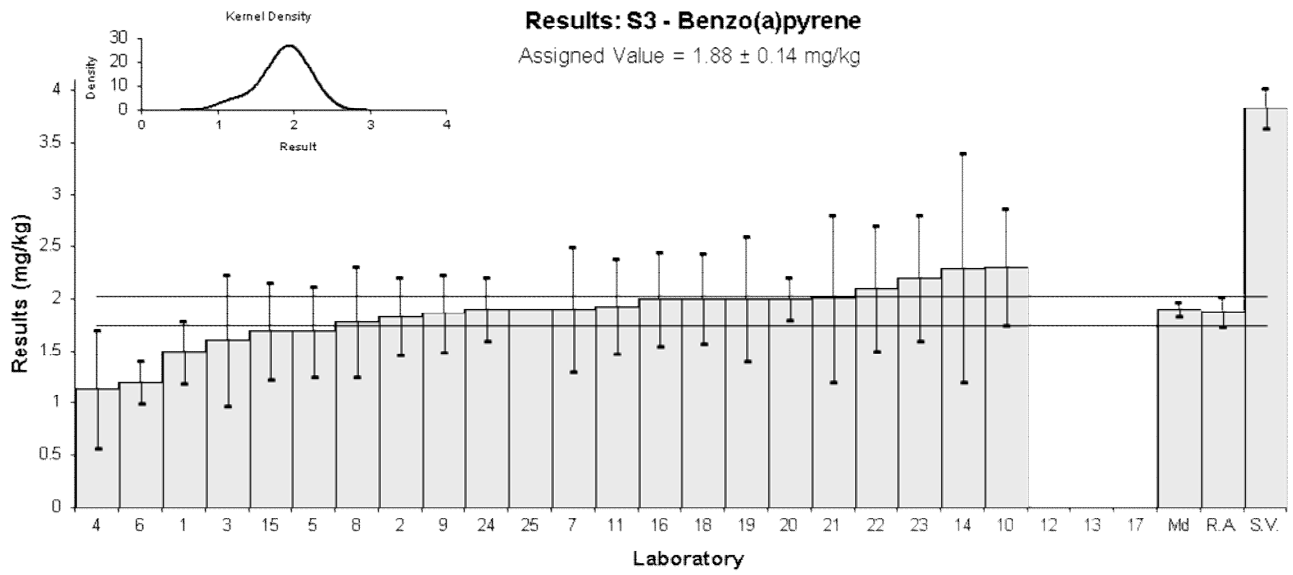
Sample No.	S3
Matrix	Soil
Analyte	Benzo(a)pyrene
Units	mg/kg

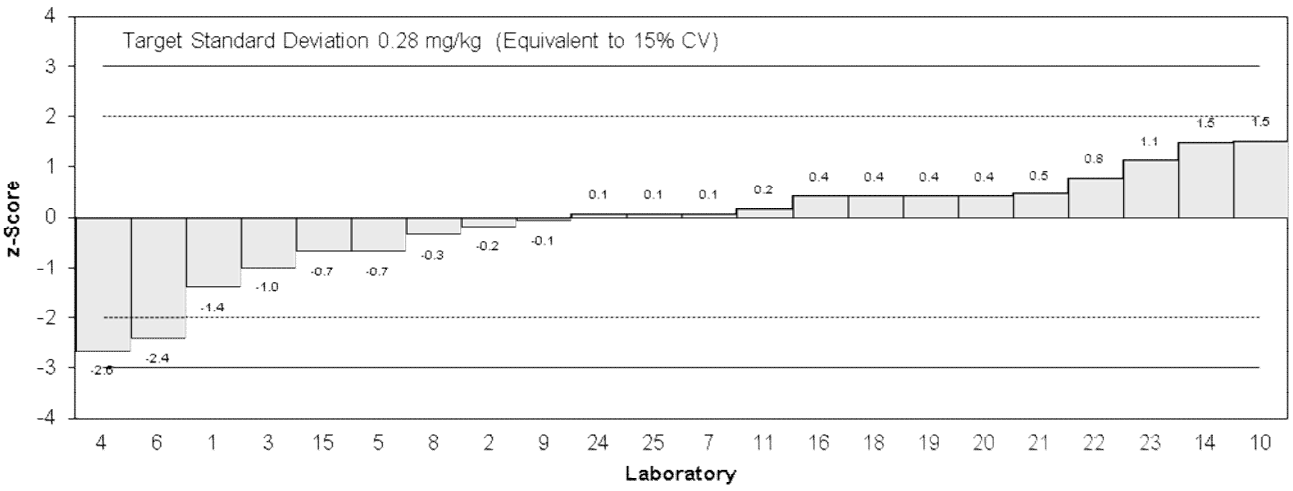
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.49	0.298	-1.38	-1.18
2	1.83	0.37	-0.18	-0.13
3	1.6	0.63	-0.99	-0.43
4	1.133	0.57	-2.65	-1.27
5	1.69	0.43	-0.67	-0.42
6	1.2	0.2	-2.41	-2.79
7	1.9	0.6	0.07	0.03
8	1.782	0.53	-0.35	-0.18
9	1.86	0.37	-0.07	-0.05
10	2.31	0.56	1.52	0.74
11	1.93	0.45	0.18	0.11
12	NT	NT		
13	NT	NT		
14	2.3	1.1	1.49	0.38
15	1.69	0.46	-0.67	-0.40
16	2.0	0.45	0.43	0.25
17	NT	NT		
18	2.0	0.43	0.43	0.27
19	2	0.6	0.43	0.19
20	2.0	0.2	0.43	0.49
21	2.01	0.8	0.46	0.16
22	2.1	0.6	0.78	0.36
23	2.2	0.6	1.13	0.52
24	1.9	0.3	0.07	0.06
25	1.9	NR	0.07	0.14

Statistics

Assigned Value	1.88	0.14
Spike	3.83	0.19
Robust Average	1.88	0.14
Median	1.90	0.07
Mean	1.86	
N	22	
Max.	2.31	
Min.	1.133	
Robust SD	0.27	
Robust CV	14%	


Kernel Density
Density
Result
Results: S3 - Benzo(a)pyrene
Assigned Value = 1.88 ± 0.14 mg/kg
Results (mg/kg)
Laboratory
4 6 1 3 15 5 8 2 9 24 25 7 11 16 18 19 20 21 22 23 14 10 12 13 17 Md R.A S.V.


z-Scores: S3 - Benzo(a)pyrene
Target Standard Deviation 0.28 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 6 1 3 15 5 8 2 9 24 25 7 11 16 18 19 20 21 22 23 14 10
-2.6 -2.4 -1.4 -1.0 -0.7 -0.7 -0.3 -0.2 -0.1 0.1 0.1 0.1 0.2 0.4 0.4 0.4 0.4 0.5 0.8 1.1 1.5 1.5

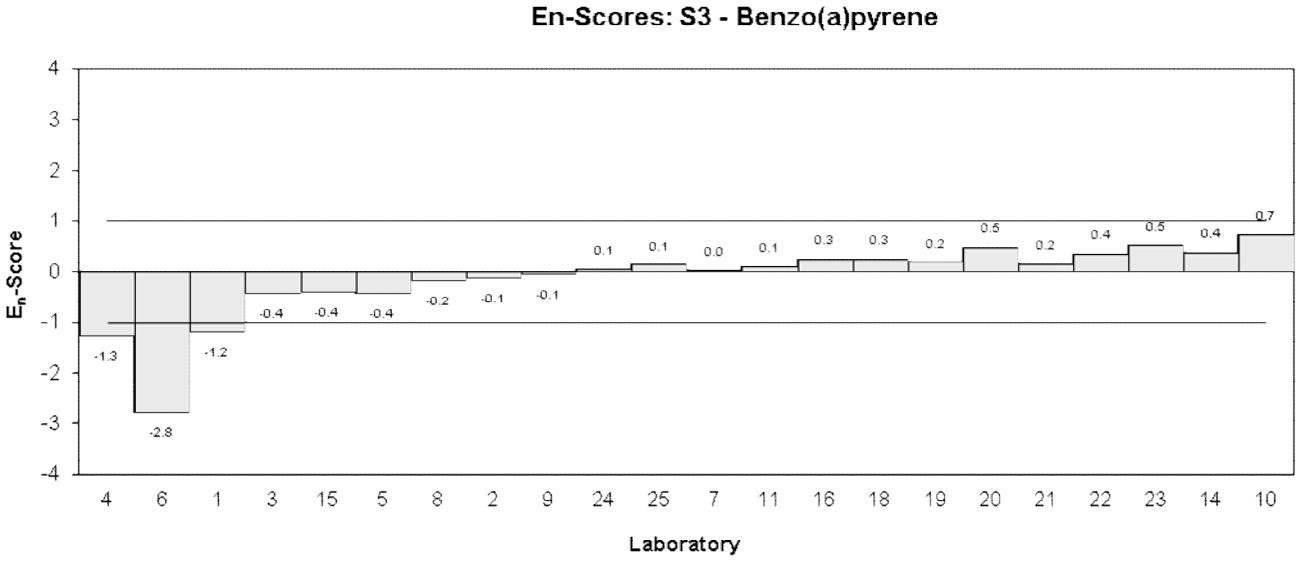

En-Scores: S3 - Benzo(a)pyrene
En-Score
Laboratory
4 6 1 3 15 5 8 2 9 24 25 7 11 16 18 19 20 21 22 23 14 10
-1.3 -2.8 -1.2 -0.4 -0.4 -0.4 -0.2 -0.1 -0.1 0.1 0.1 0.0 0.1 0.3 0.3 0.2 0.5 0.2 0.4 0.5 0.4 0.7

Figure 13

Table 16

Sample Details

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

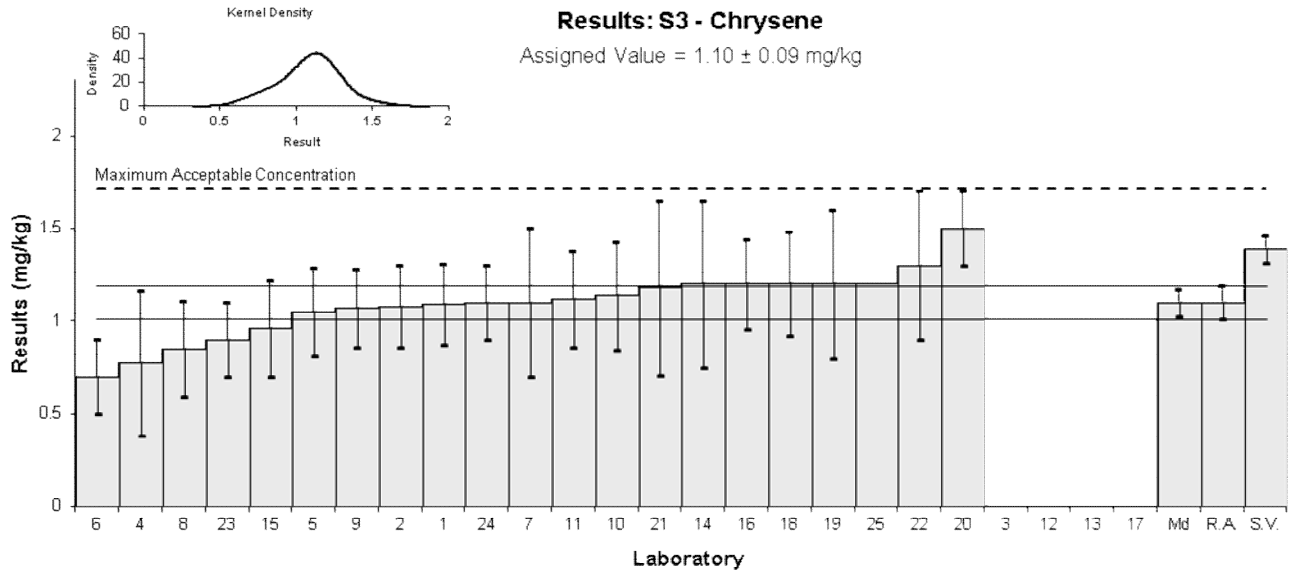
Participant Results

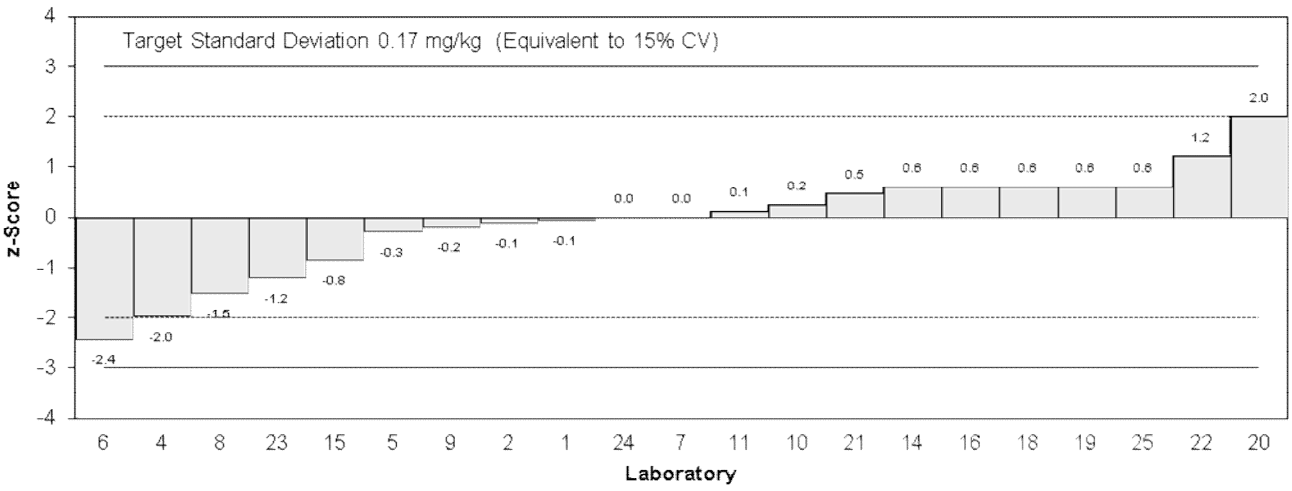
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.09	0.218	-0.06	-0.04
2	1.08	0.22	-0.12	-0.08
3	<1	NR		
4	0.774	0.39	-1.98	-0.81
5	1.05	0.24	-0.30	-0.20
6	0.7	0.2	-2.42	-1.82
7	1.1	0.4	0.00	0.00
8	0.85	0.26	-1.52	-0.91
9	1.07	0.21	-0.18	-0.13
10	1.14	0.29	0.24	0.13
11	1.12	0.26	0.12	0.07
12	NT	NT		
13	NT	NT		
14	1.2	0.45	0.61	0.22
15	0.96	0.26	-0.85	-0.51
16	1.2	0.24	0.61	0.39
17	NT	NT		
18	1.2	0.28	0.61	0.34
19	1.2	0.4	0.61	0.24
20*	1.5	0.2	2.00	1.00
21	1.18	0.47	0.48	0.17
22	1.3	0.4	1.21	0.49
23	0.9	0.2	-1.21	-0.91
24	1.1	0.2	0.00	0.00
25	1.2	NR	0.61	1.11

Statistics

Assigned Value	1.10	0.09
Spike	1.39	0.07
Max. Acceptable Conc.*	1.7	
Robust Average	1.10	0.09
Median	1.10	0.07
Mean	1.09	
N	21	
Max.	1.5	
Min.	0.7	
Robust SD	0.16	
Robust CV	14%	

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


Kernel Density
Density
Result
Results: S3 - Chrysene
Assigned Value = 1.10 ± 0.09 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
6 4 8 23 15 5 9 2 1 24 7 11 10 21 14 16 18 19 25 22 20 3 12 13 17 Md R.A S.V.


z-Scores: S3 - Chrysene
Target Standard Deviation 0.17 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 4 8 23 15 5 9 2 1 24 7 11 10 21 14 16 18 19 25 22 20

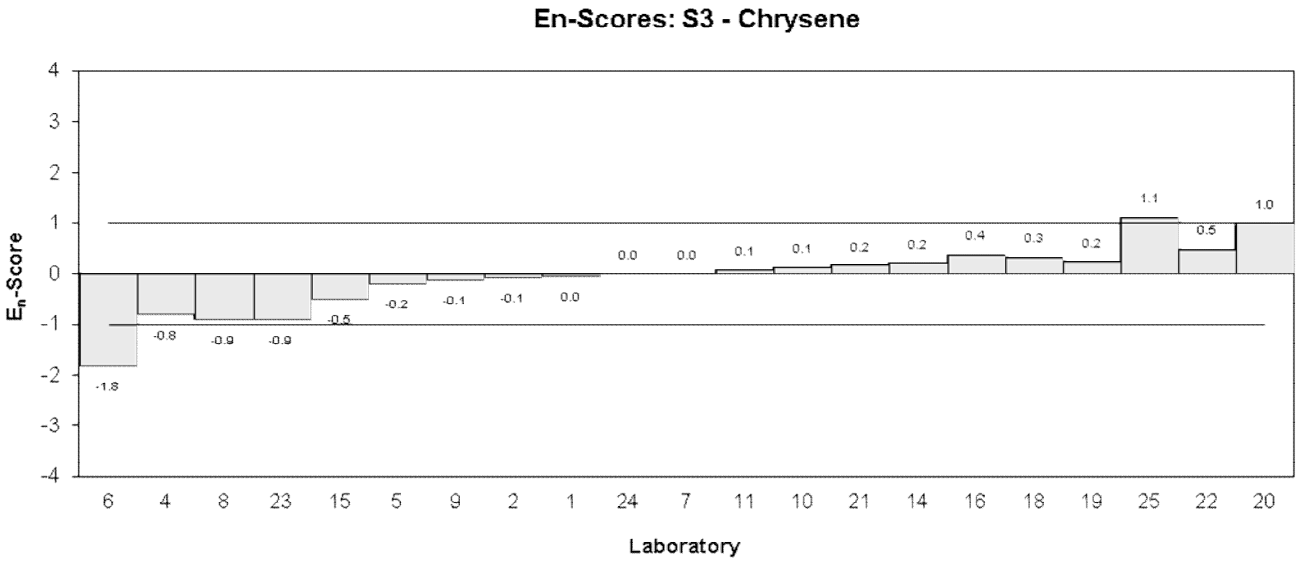

En-Scores: S3 - Chrysene
En-Score
Laboratory
6 4 8 23 15 5 9 2 1 24 7 11 10 21 14 16 18 19 25 22 20

Figure 14

Table 17

Sample Details

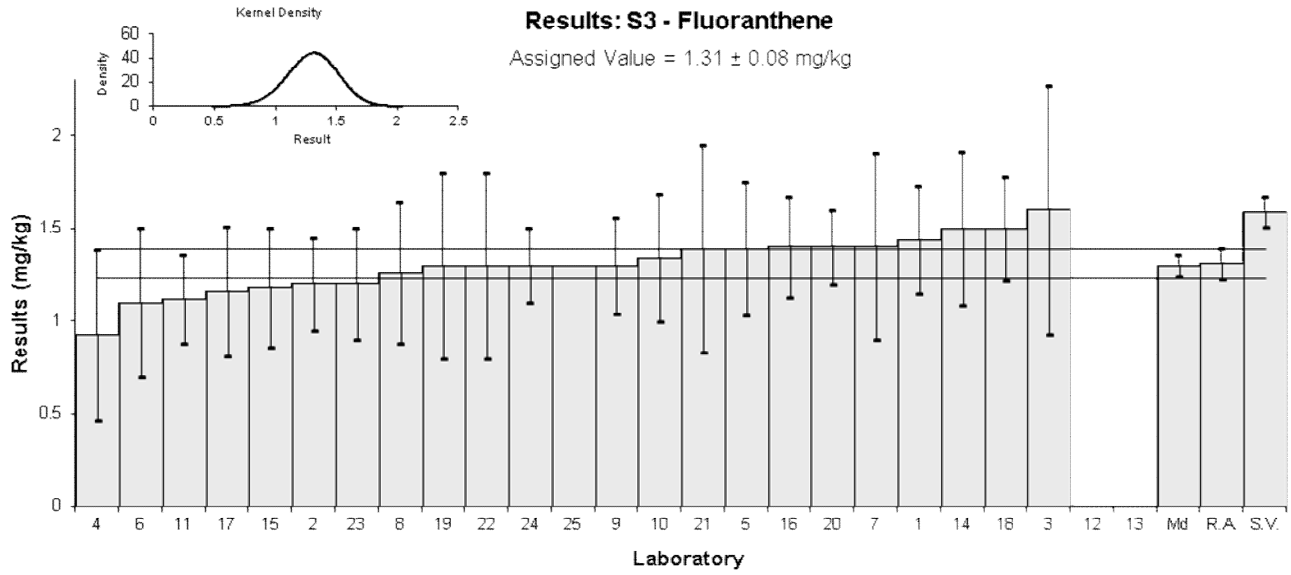
Sample No.	S3
Matrix	Soil
Analyte	Fluoranthene
Units	mg/kg

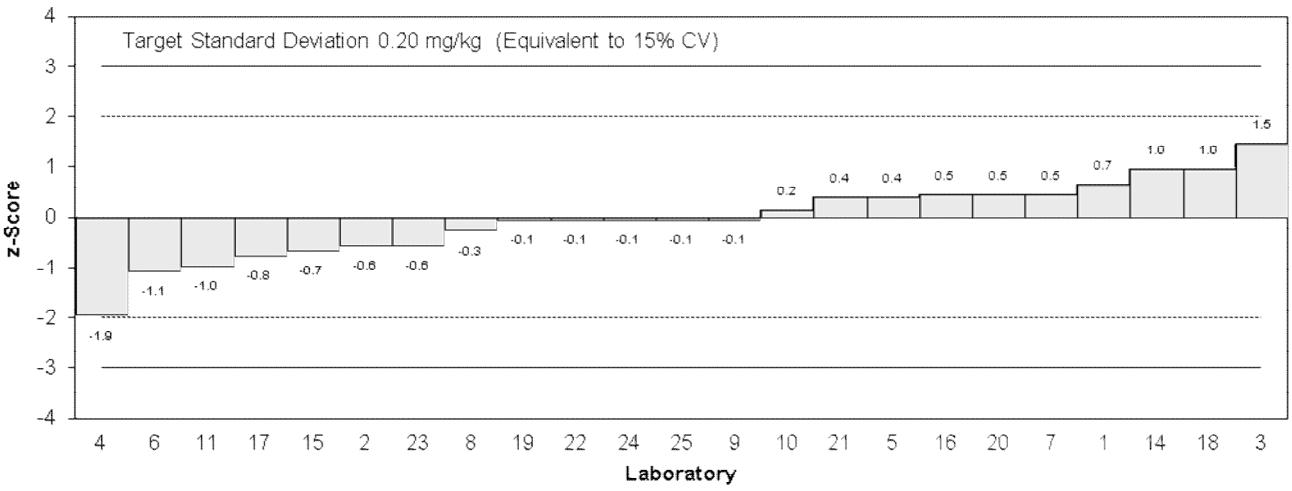
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.44	0.288	0.66	0.43
2	1.20	0.25	-0.56	-0.42
3	1.6	0.67	1.48	0.43
4	0.928	0.46	-1.94	-0.82
5	1.39	0.36	0.41	0.22
6	1.1	0.4	-1.07	-0.51
7	1.4	0.5	0.46	0.18
8	1.258	0.38	-0.26	-0.13
9	1.30	0.26	-0.05	-0.04
10	1.34	0.34	0.15	0.09
11	1.12	0.24	-0.97	-0.75
12	NT	NT		
13	NT	NT		
14	1.5	0.41	0.97	0.45
15	1.18	0.32	-0.66	-0.39
16	1.4	0.27	0.46	0.32
17	1.16	0.35	-0.76	-0.42
18	1.5	0.28	0.97	0.65
19	1.3	0.5	-0.05	-0.02
20	1.4	0.2	0.46	0.42
21	1.39	0.56	0.41	0.14
22	1.3	0.5	-0.05	-0.02
23	1.2	0.3	-0.56	-0.35
24	1.3	0.2	-0.05	-0.05
25	1.3	NR	-0.05	-0.13

Statistics

Assigned Value	1.31	0.08
Spike	1.59	0.08
Robust Average	1.31	0.08
Median	1.30	0.06
Mean	1.30	
N	23	
Max.	1.6	
Min.	0.928	
Robust SD	0.15	
Robust CV	11%	


Kernel Density
Density
Result
Results: S3 - Fluoranthene
Assigned Value = 1.31 ± 0.08 mg/kg
Results (mg/kg)
Laboratory
4 6 11 17 15 2 23 8 19 22 24 25 9 10 21 5 16 20 7 1 14 18 3 12 13 Md R.A S.V.


z-Scores: S3 - Fluoranthene
Target Standard Deviation 0.20 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 6 11 17 15 2 23 8 19 22 24 25 9 10 21 5 16 20 7 1 14 18 3
-1.9 -1.1 -1.0 -0.8 -0.7 -0.6 -0.6 -0.3 -0.1 -0.1 -0.1 -0.1 -0.1 0.2 0.4 0.4 0.5 0.5 0.5 0.7 1.0 1.0 1.5

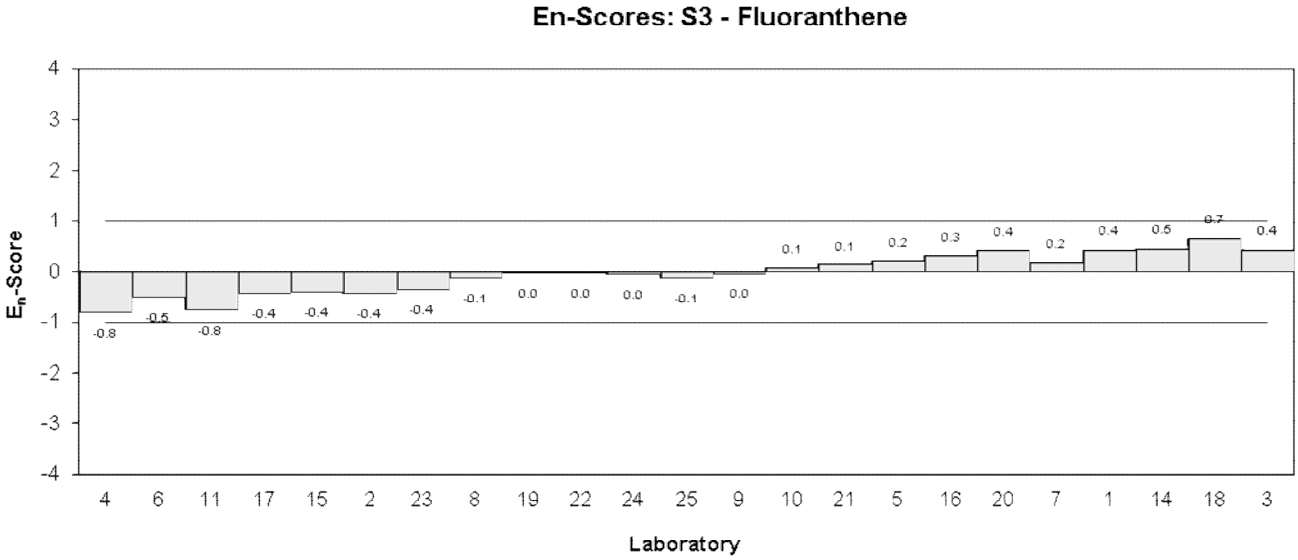

En-Scores: S3 - Fluoranthene
En-Score
Laboratory
4 6 11 17 15 2 23 8 19 22 24 25 9 10 21 5 16 20 7 1 14 18 3
-0.8 -0.5 -0.8 -0.4 -0.4 -0.4 -0.4 -0.1 0.0 0.0 0.0 -0.1 0.0 0.1 0.1 0.2 0.3 0.4 0.2 0.4 0.5 0.7 0.4

Figure 15

Table 18

Sample Details

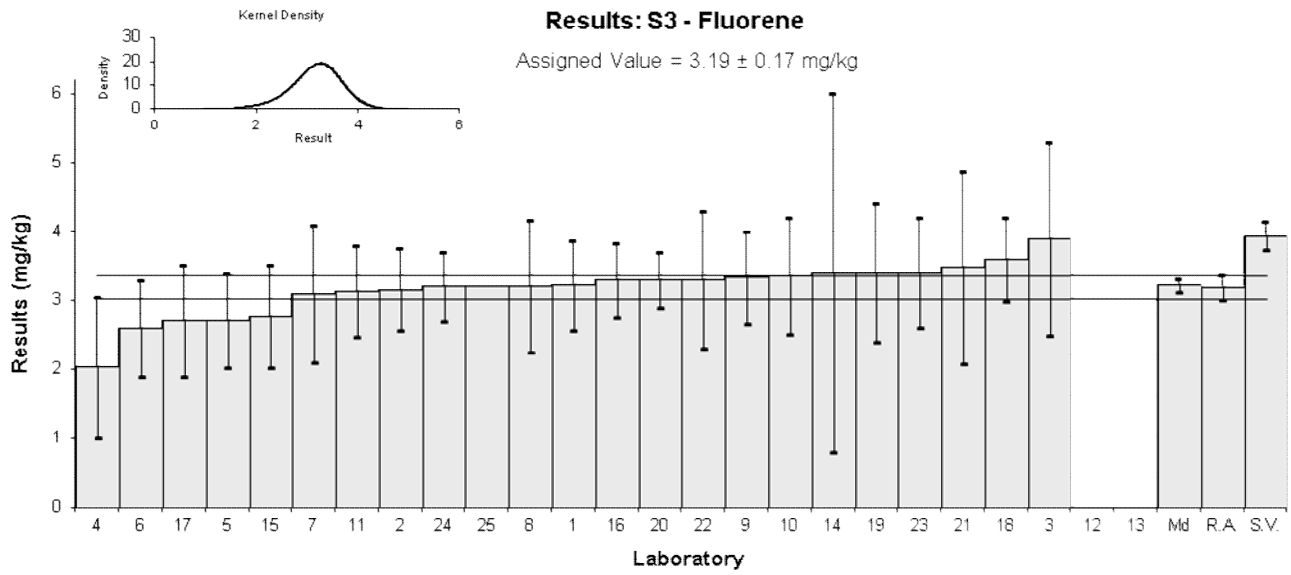
Sample No.	S3
Matrix	Soil
Analyte	Fluorene
Units	mg/kg

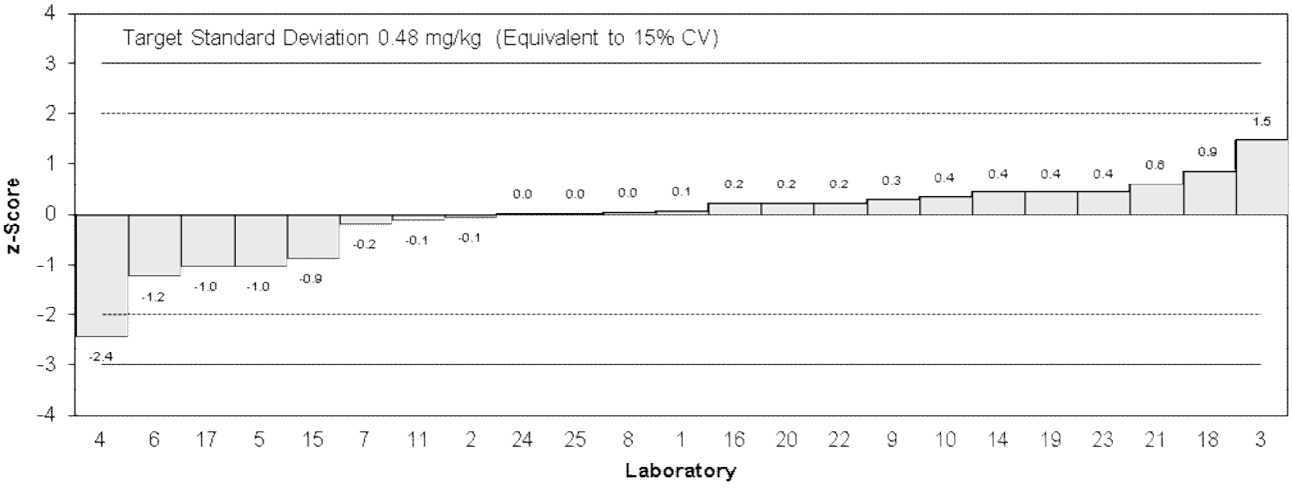
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	3.22	0.644	0.06	0.05
2	3.16	0.60	-0.06	-0.05
3	3.9	1.4	1.48	0.50
4	2.030	1.02	-2.42	-1.12
5	2.70	0.68	-1.02	-0.70
6	2.6	0.7	-1.23	-0.82
7	3.1	1	-0.19	-0.09
8	3.207	0.96	0.04	0.02
9	3.33	0.67	0.29	0.20
10	3.36	0.84	0.36	0.20
11	3.14	0.66	-0.10	-0.07
12	NT	NT		
13	NT	NT		
14	3.4	2.6	0.44	0.08
15	2.77	0.75	-0.88	-0.55
16	3.3	0.54	0.23	0.19
17	2.70	0.81	-1.02	-0.59
18	3.6	0.60	0.86	0.66
19	3.4	1	0.44	0.21
20	3.3	0.4	0.23	0.25
21	3.48	1.39	0.61	0.21
22	3.3	1	0.23	0.11
23	3.4	0.8	0.44	0.26
24	3.2	0.5	0.02	0.02
25	3.2	NR	0.02	0.06

Statistics

Assigned Value	3.19	0.17
Spike	3.94	0.20
Robust Average	3.19	0.17
Median	3.22	0.09
Mean	3.17	
N	23	
Max.	3.9	
Min.	2.03	
Robust SD	0.33	
Robust CV	10%	


Results: S3 - Fluorene
Assigned Value = 3.19 ± 0.17 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4 6 17 5 15 7 11 2 24 25 8 1 16 20 22 9 10 14 19 23 21 18 3 12 13 Md R.A S.V.


z-Scores: S3 - Fluorene
Target Standard Deviation 0.48 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 6 17 5 15 7 11 2 24 25 8 1 16 20 22 9 10 14 19 23 21 18 3
-2.4 -1.2 -1.0 -1.0 -0.9 -0.2 -0.1 -0.1 0.0 0.0 0.0 0.1 0.2 0.2 0.2 0.3 0.4 0.4 0.4 0.4 0.6 0.9 1.5

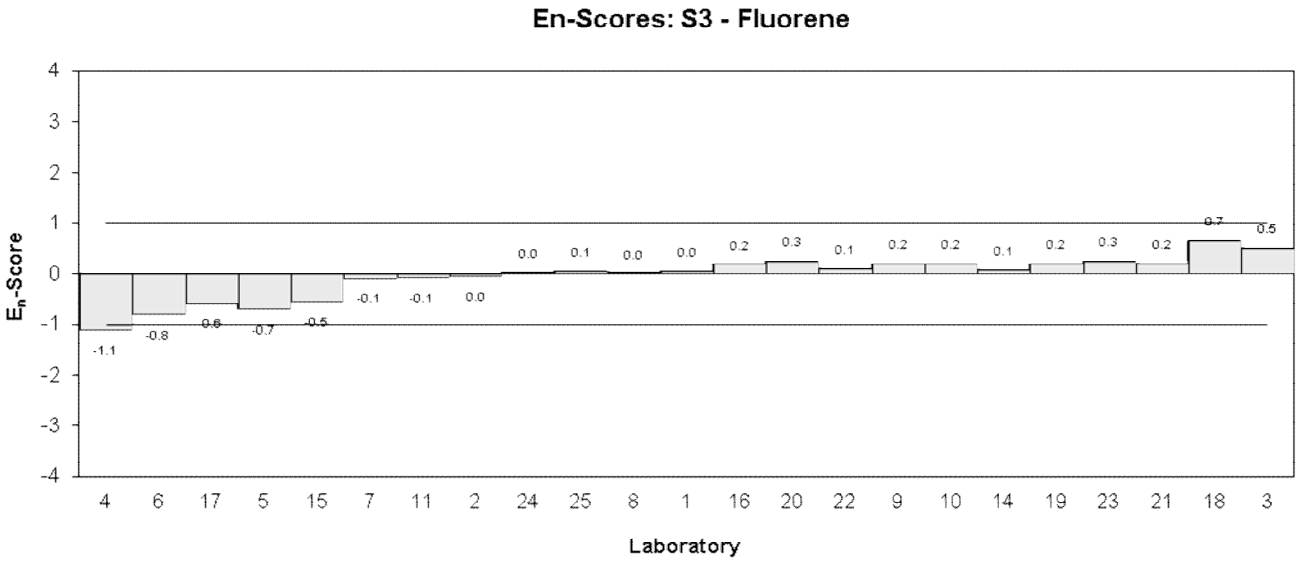

En-Scores: S3 - Fluorene
En-Score
Laboratory
4 6 17 5 15 7 11 2 24 25 8 1 16 20 22 9 10 14 19 23 21 18 3
-1.1 -0.8 -0.6 -0.7 -0.5 -0.1 -0.1 0.0 0.0 0.1 0.0 0.0 0.2 0.3 0.1 0.2 0.2 0.1 0.2 0.3 0.2 0.7 0.5

Figure 16

Table 19

Sample Details

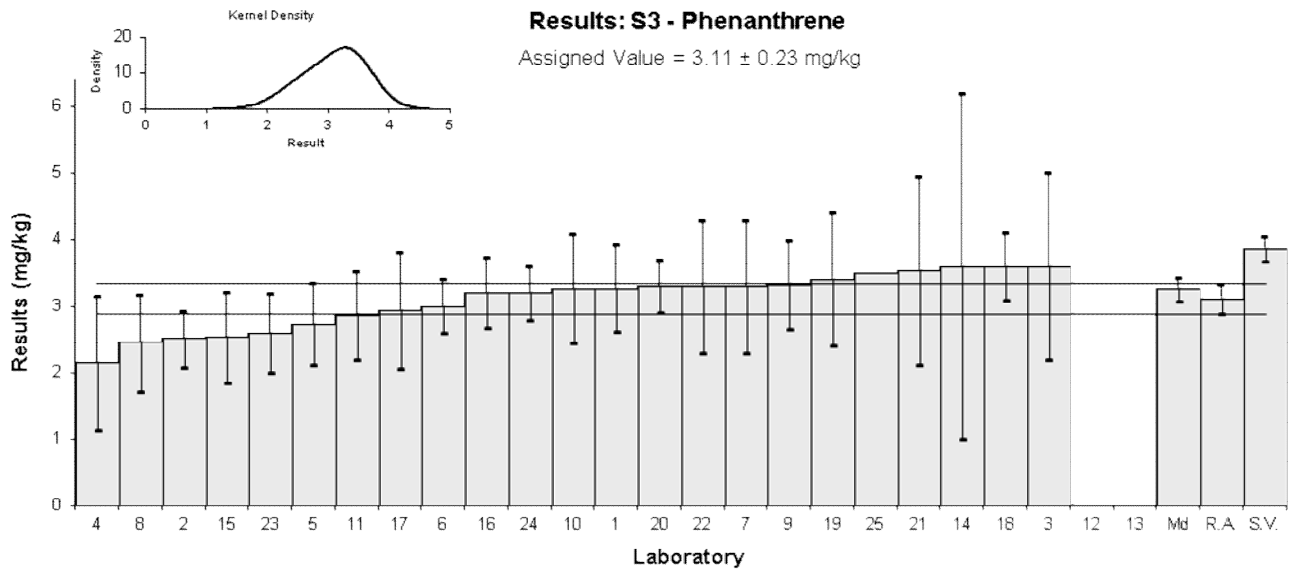
Sample No.	S3
Matrix	Soil
Analyte	Phenanthrene
Units	mg/kg

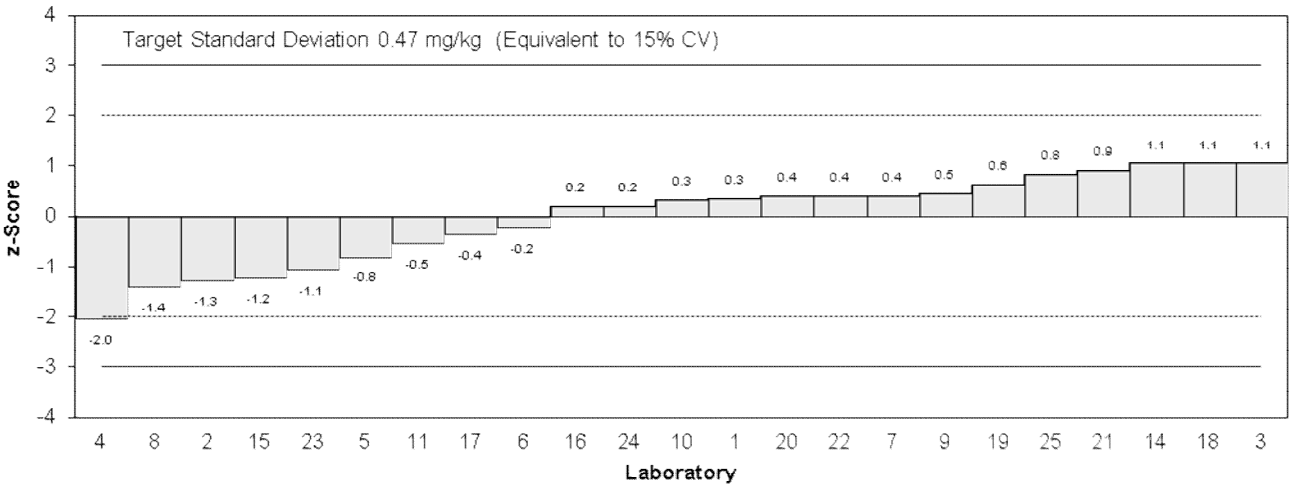
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	3.27	0.654	0.34	0.23
2	2.51	0.42	-1.29	-1.25
3	3.6	1.4	1.05	0.35
4	2.156	1.01	-2.05	-0.92
5	2.73	0.62	-0.81	-0.57
6	3.0	0.4	-0.24	-0.24
7	3.3	1	0.41	0.19
8	2.449	0.73	-1.42	-0.86
9	3.32	0.66	0.45	0.30
10	3.26	0.82	0.32	0.18
11	2.86	0.67	-0.54	-0.35
12	NT	NT		
13	NT	NT		
14	3.6	2.6	1.05	0.19
15	2.53	0.68	-1.24	-0.81
16	3.2	0.53	0.19	0.16
17	2.94	0.88	-0.36	-0.19
18	3.6	0.50	1.05	0.89
19	3.4	1	0.62	0.28
20	3.3	0.4	0.41	0.41
21	3.53	1.41	0.90	0.29
22	3.3	1	0.41	0.19
23	2.6	0.6	-1.09	-0.79
24	3.2	0.4	0.19	0.20
25	3.5	NR	0.84	1.70

Statistics

Assigned Value	3.11	0.23
Spike	3.86	0.19
Robust Average	3.11	0.23
Median	3.26	0.17
Mean	3.09	
N	23	
Max.	3.6	
Min.	2.156	
Robust SD	0.45	
Robust CV	14%	


Kernel Density
Density
Result
Results: S3 - Phenanthrene
Assigned Value = 3.11 ± 0.23 mg/kg
Results (mg/kg)
Laboratory
4 8 2 15 23 5 11 17 6 16 24 10 1 20 22 7 9 19 25 21 14 18 3 12 13 Md R.A S.V.


z-Scores: S3 - Phenanthrene
Target Standard Deviation 0.47 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 8 2 15 23 5 11 17 6 16 24 10 1 20 22 7 9 19 25 21 14 18 3

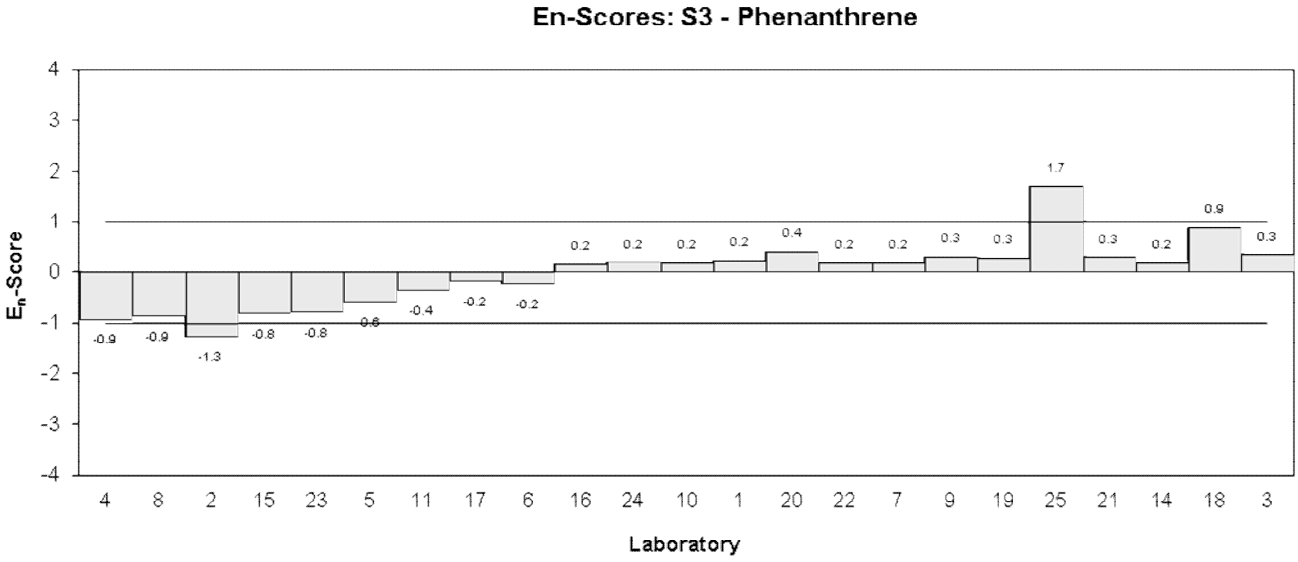

En-Scores: S3 - Phenanthrene
En-Score
Laboratory
4 8 2 15 23 5 11 17 6 16 24 10 1 20 22 7 9 19 25 21 14 18 3

Figure 17

Table 20

Sample Details

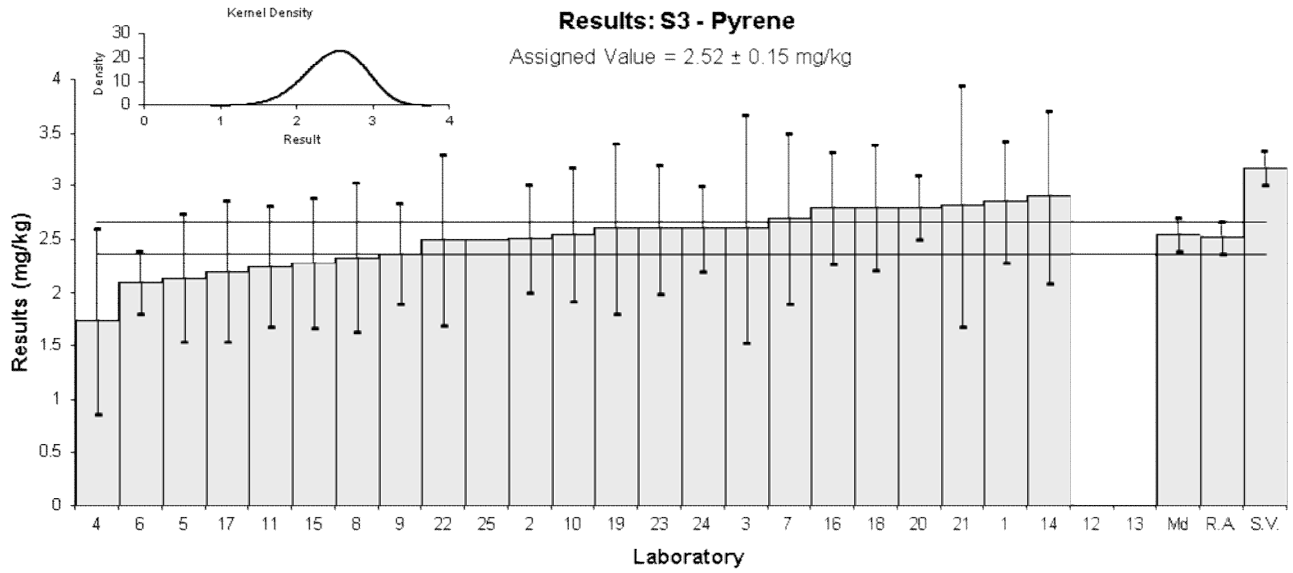
Sample No.	S3
Matrix	Soil
Analyte	Pyrene
Units	mg/kg

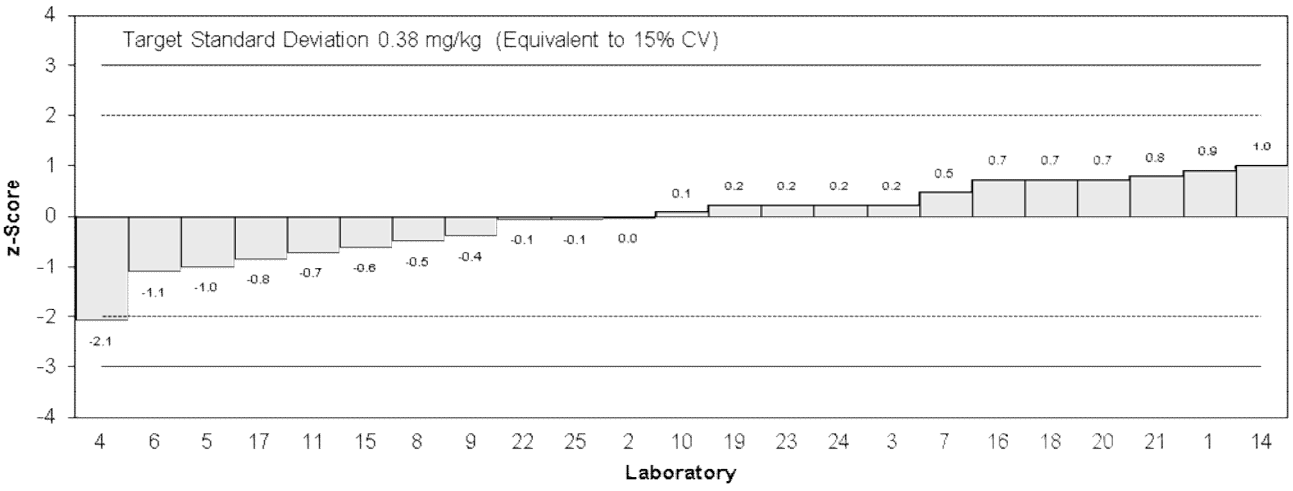
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	2.86	0.572	0.90	0.57
2	2.51	0.5	-0.03	-0.02
3	2.6	1.07	0.21	0.07
4	1.734	0.87	-2.08	-0.89
5	2.14	0.6	-1.01	-0.61
6	2.1	0.3	-1.11	-1.25
7	2.7	0.8	0.48	0.22
8	2.333	0.7	-0.49	-0.26
9	2.37	0.47	-0.40	-0.30
10	2.55	0.63	0.08	0.05
11	2.25	0.56	-0.71	-0.47
12	NT	NT		
13	NT	NT		
14	2.9	0.81	1.01	0.46
15	2.28	0.61	-0.63	-0.38
16	2.8	0.52	0.74	0.52
17	2.20	0.66	-0.85	-0.47
18	2.8	0.59	0.74	0.46
19	2.6	0.8	0.21	0.10
20	2.8	0.3	0.74	0.83
21	2.82	1.13	0.79	0.26
22	2.5	0.8	-0.05	-0.02
23	2.6	0.6	0.21	0.13
24	2.6	0.4	0.21	0.19
25	2.5	NR	-0.05	-0.13

Statistics

Assigned Value	2.52	0.15
Spike	3.17	0.16
Robust Average	2.52	0.15
Median	2.55	0.16
Mean	2.50	
N	23	
Max.	2.9	
Min.	1.734	
Robust SD	0.29	
Robust CV	12%	


Kernel Density
Density
Result
Results: S3 - Pyrene
Assigned Value = 2.52 ± 0.15 mg/kg
Results (mg/kg)
Laboratory
4 6 5 17 11 15 8 9 22 25 2 10 19 23 24 3 7 16 18 20 21 1 14 12 13 Md R.A. S.V.


z-Scores: S3 - Pyrene
Target Standard Deviation 0.38 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 6 5 17 11 15 8 9 22 25 2 10 19 23 24 3 7 16 18 20 21 1 14
-2.1 -1.1 -1.0 -0.8 -0.7 -0.6 -0.5 -0.4 -0.1 -0.1 0.0 0.1 0.2 0.2 0.2 0.2 0.5 0.7 0.7 0.7 0.8 0.9 1.0

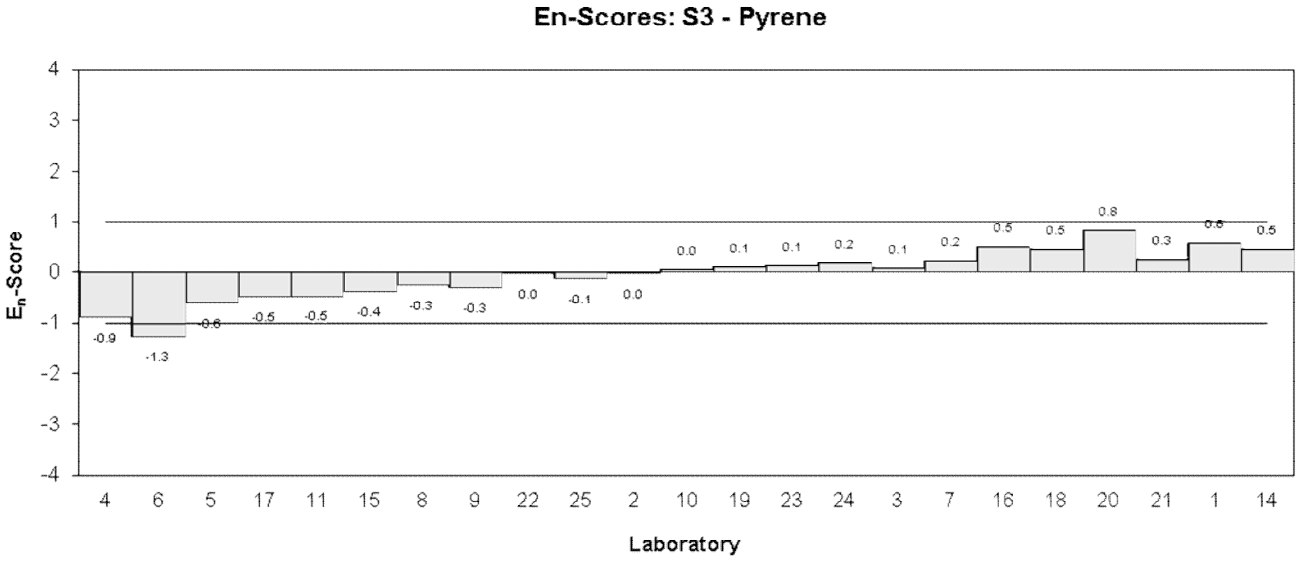

En-Scores: S3 - Pyrene
En-Score
Laboratory
4 6 5 17 11 15 8 9 22 25 2 10 19 23 24 3 7 16 18 20 21 1 14
-0.9 -1.3 -0.6 -0.5 -0.5 -0.4 -0.3 -0.3 0.0 -0.1 0.0 0.0 0.1 0.1 0.2 0.1 0.2 0.5 0.5 0.8 0.3 0.6 0.5

Figure 18

Table 21

Sample Details

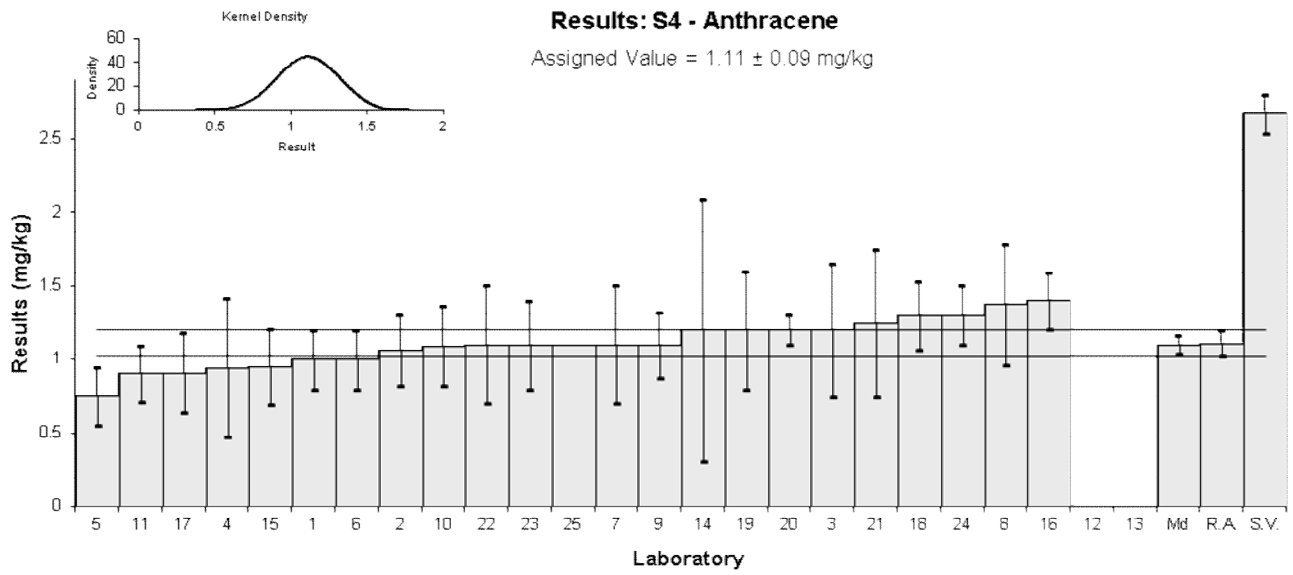
Sample No.	S4
Matrix	Soil
Analyte	Anthracene
Units	mg/kg

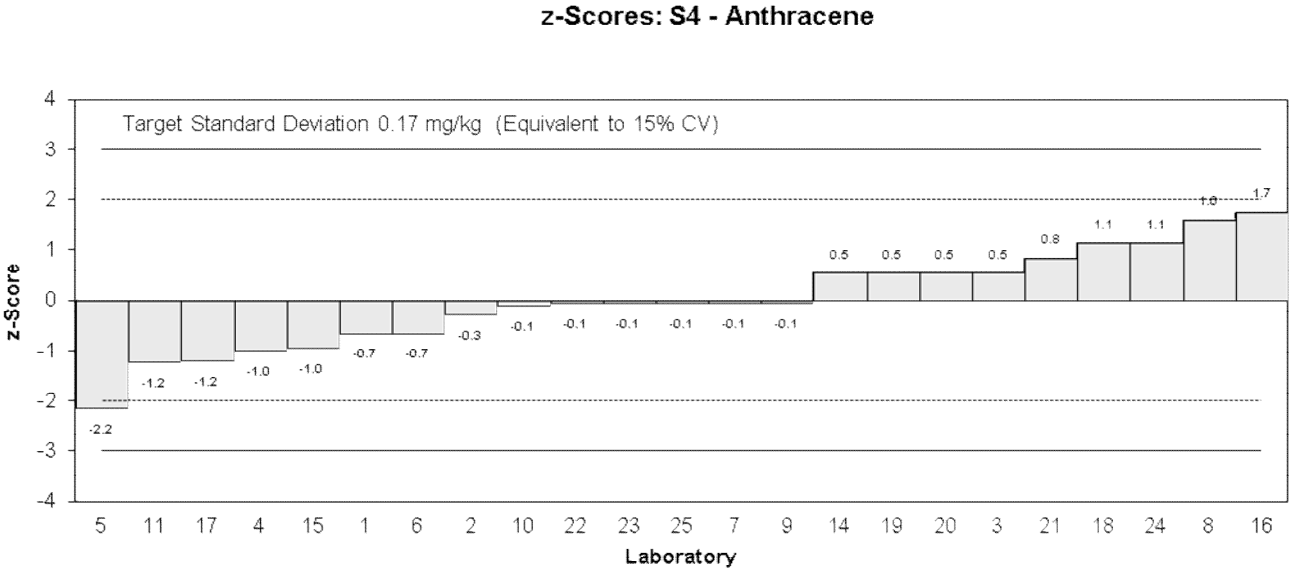
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.00	0.2	-0.66	-0.50
2	1.06	0.24	-0.30	-0.20
3	1.2	0.45	0.54	0.20
4	0.943	0.47	-1.00	-0.35
5	0.75	0.2	-2.16	-1.64
6	1.0	0.2	-0.66	-0.50
7	1.1	0.4	-0.06	-0.02
8	1.375	0.41	1.59	0.63
9	1.10	0.22	-0.06	-0.04
10	1.09	0.27	-0.12	-0.07
11	0.903	0.19	-1.24	-0.98
12	NT	NT		
13	NT	NT		
14	1.2	0.89	0.54	0.10
15	0.95	0.26	-0.96	-0.58
16	1.4	0.19	1.74	1.38
17	0.91	0.27	-1.20	-0.70
18	1.3	0.23	1.14	0.77
19	1.2	0.4	0.54	0.22
20	1.2	0.1	0.54	0.67
21	1.25	0.5	0.84	0.28
22	1.1	0.4	-0.06	-0.02
23	1.1	0.3	-0.06	-0.03
24	1.3	0.2	1.14	0.87
25	1.1	NR	-0.06	-0.11

Statistics

Assigned Value	1.11	0.09
Spike	2.67	0.13
Robust Average	1.11	0.09
Median	1.10	0.06
Mean	1.11	
N	23	
Max.	1.4	
Min.	0.75	
Robust SD	0.17	
Robust CV	15%	


Kernel Density
Density
Result
Results: S4 - Anthracene
Assigned Value = 1.11 ± 0.09 mg/kg
Results (mg/kg)
Laboratory
5 11 17 4 15 1 6 2 10 22 23 25 7 9 14 19 20 3 21 18 24 8 16 12 13 Md R.A. S.V.


z-Scores: S4 - Anthracene
Target Standard Deviation 0.17 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
5 11 17 4 15 1 6 2 10 22 23 25 7 9 14 19 20 3 21 18 24 8 16

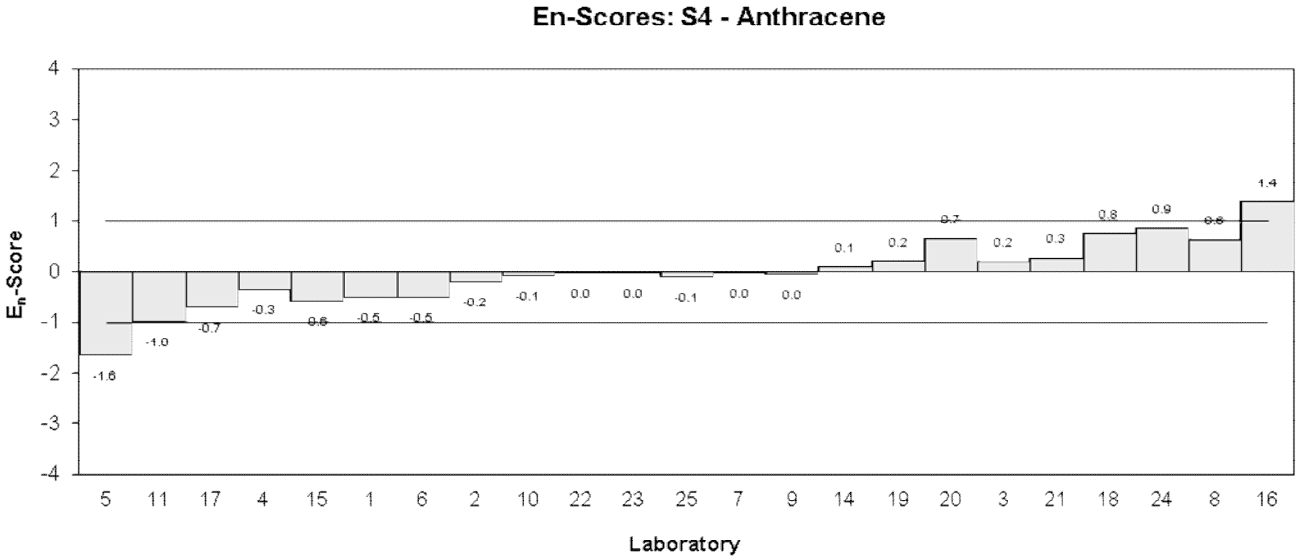

En-Scores: S4 - Anthracene
En-Score
Laboratory
5 11 17 4 15 1 6 2 10 22 23 25 7 9 14 19 20 3 21 18 24 8 16

Figure 19

Table 22

Sample Details

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

Participant Results

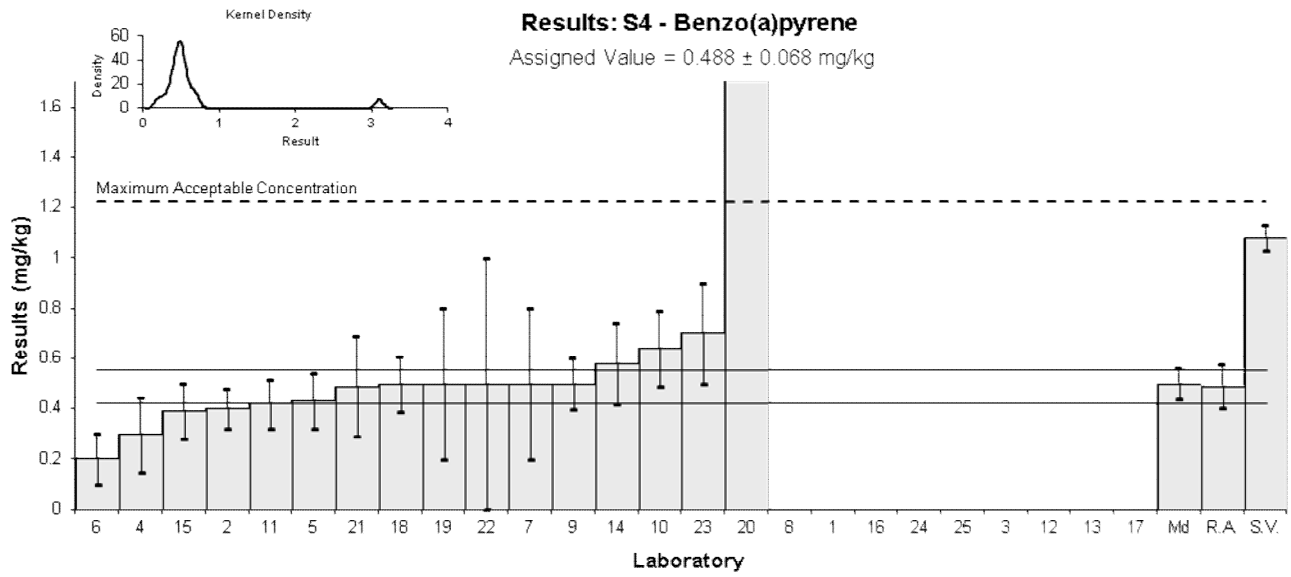
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	<0.5	NR		
2	0.40	0.08	-1.20	-0.84
3	<1	NR		
4	0.297	0.15	-2.61	-1.16
5	0.43	0.11	-0.79	-0.45
6	0.2	0.1	-3.93	-2.38
7	0.5	0.3	0.16	0.04
8	<0.1	0.03		
9	0.50	0.1	0.16	0.10
10**	0.64	0.15	2.00	0.92
11	0.42	0.097	-0.93	-0.57
12	NT	NT		
13	NT	NT		
14	0.58	0.16	1.26	0.53
15	0.39	0.11	-1.34	-0.76
16	<0.5	0.1		
17	NT	NT		
18	0.5	0.11	0.16	0.09
19	0.5	0.3	0.16	0.04
20	3.1	0.3	35.68	8.49
21	0.49	0.2	0.03	0.01
22	0.5	0.5	0.16	0.02
23**	0.7	0.2	2.00	1.00
24	<0.5	NR		
25	<0.5	NR		

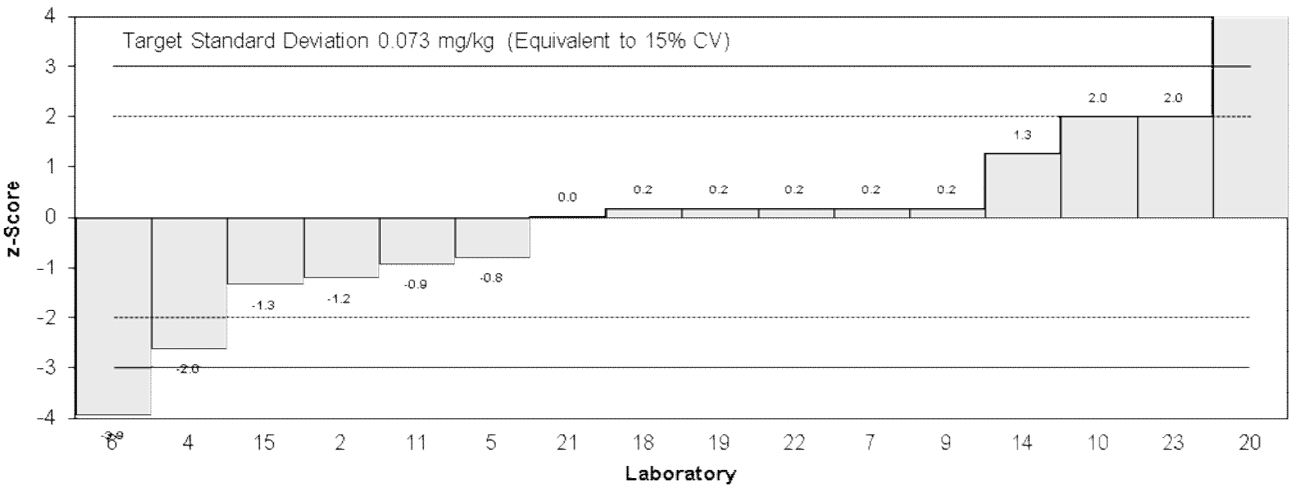
Statistics

Assigned Value*	0.488	0.068
Spike	1.08	0.05
Max. Acceptable Conc.**	1.226	
Robust Average	0.489	0.086
Median	0.500	0.063
Mean	0.634	
N	16	
Max.	3.1	
Min.	0.2	
Robust SD	0.10	
Robust CV	21%	

* Robust average excluding laboratories 6 and 20.

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


Kernel Density
Density
Result
Results: S4 - Benzo(a)pyrene
Assigned Value = 0.488 ± 0.068 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
6 4 15 2 11 5 21 18 19 22 7 9 14 10 23 20 8 1 16 24 25 3 12 13 17 Md R.A S.V.


z-Scores: S4 - Benzo(a)pyrene
Target Standard Deviation 0.073 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 4 15 2 11 5 21 18 19 22 7 9 14 10 23 20

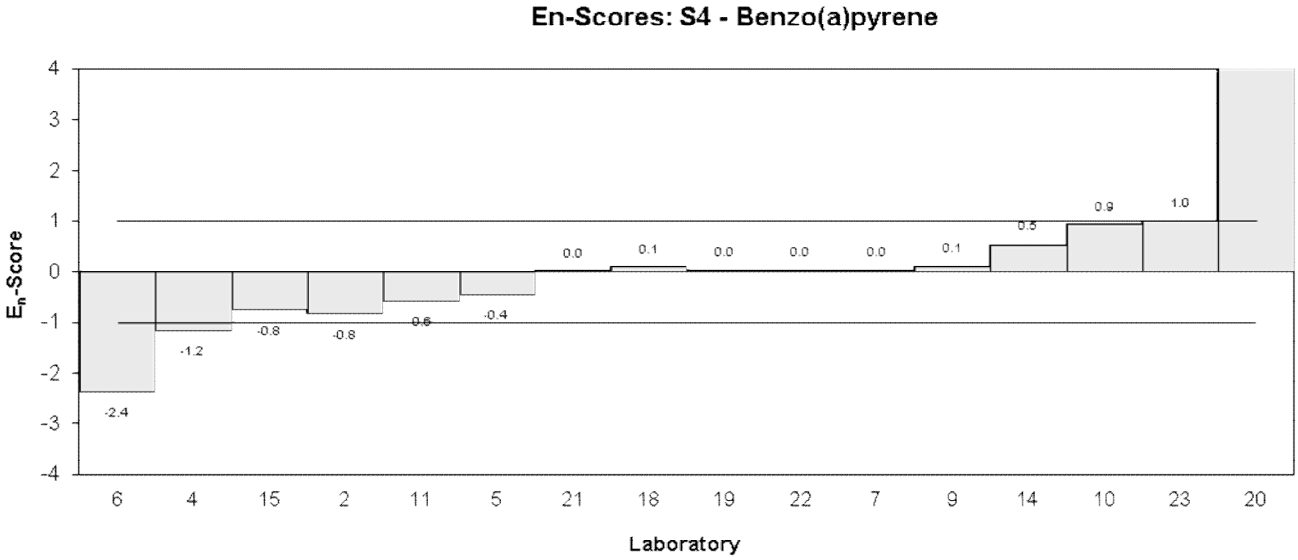

En-Scores: S4 - Benzo(a)pyrene
En-Score
Laboratory
6 4 15 2 11 5 21 18 19 22 7 9 14 10 23 20

Figure 20

Table 23

Sample Details

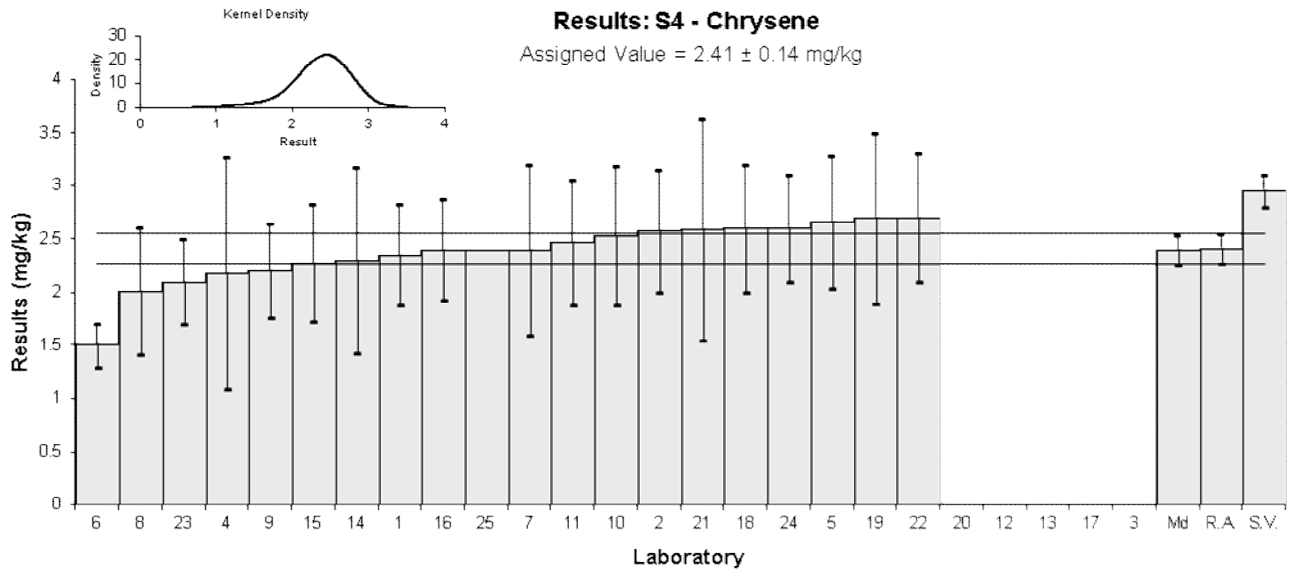
Sample No.	S4
Matrix	Soil
Analyte	Chrysene
Units	mg/kg

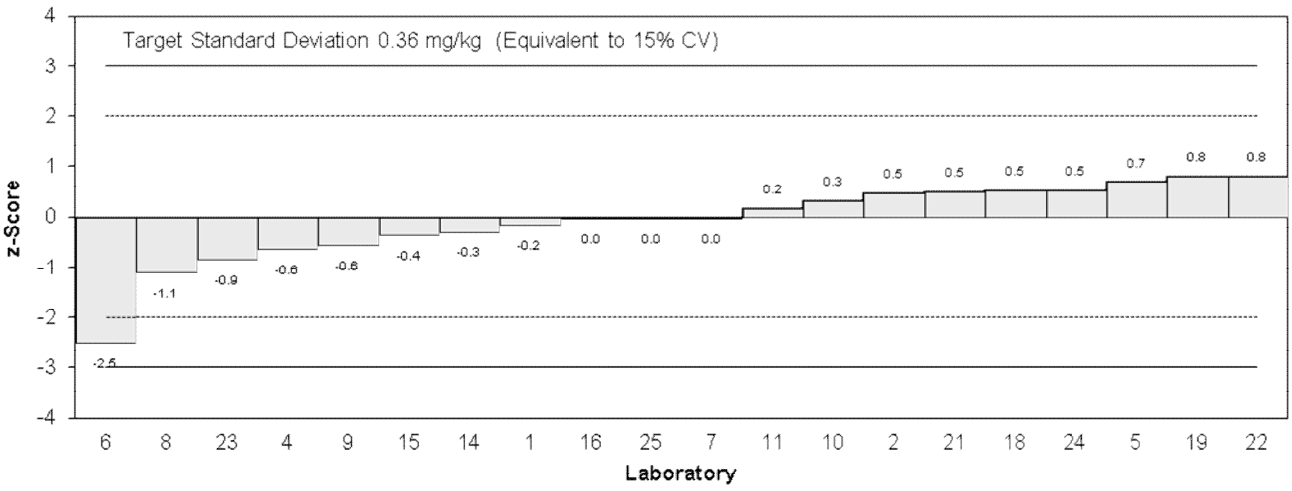
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	2.35	0.47	-0.17	-0.12
2	2.58	0.57	0.47	0.29
3	NT	NT		
4	2.178	1.09	-0.64	-0.21
5	2.66	0.62	0.69	0.39
6	1.5	0.2	-2.52	-3.73
7	2.4	0.8	-0.03	-0.01
8	2.01	0.6	-1.11	-0.65
9	2.20	0.44	-0.58	-0.45
10	2.53	0.65	0.33	0.18
11	2.47	0.58	0.17	0.10
12	NT	NT		
13	NT	NT		
14	2.3	0.87	-0.30	-0.12
15	2.28	0.55	-0.36	-0.23
16	2.4	0.47	-0.03	-0.02
17	NT	NT		
18	2.6	0.60	0.53	0.31
19	2.7	0.8	0.80	0.36
20	<0.5	NR		
21	2.59	1.04	0.50	0.17
22	2.7	0.6	0.80	0.47
23	2.1	0.4	-0.86	-0.73
24	2.6	0.5	0.53	0.37
25	2.4	NR	-0.03	-0.07

Statistics

Assigned Value	2.41	0.14
Spike	2.95	0.15
Robust Average	2.41	0.14
Median	2.40	0.14
Mean	2.38	
N	20	
Max.	2.7	
Min.	1.5	
Robust SD	0.24	
Robust CV	10%	


Kernel Density
Density
Result
Results: S4 - Chrysene
Assigned Value = 2.41 ± 0.14 mg/kg
Results (mg/kg)
Laboratory
6 8 23 4 9 15 14 1 16 25 7 11 10 2 21 18 24 5 19 22 20 12 13 17 3 Md R.A. S.V.


z-Scores: S4 - Chrysene
Target Standard Deviation 0.36 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 8 23 4 9 15 14 1 16 25 7 11 10 2 21 18 24 5 19 22
-2.5 -1.1 -0.9 -0.6 -0.6 -0.4 -0.3 -0.2 0.0 0.0 0.0 0.2 0.3 0.5 0.5 0.5 0.5 0.7 0.8 0.8

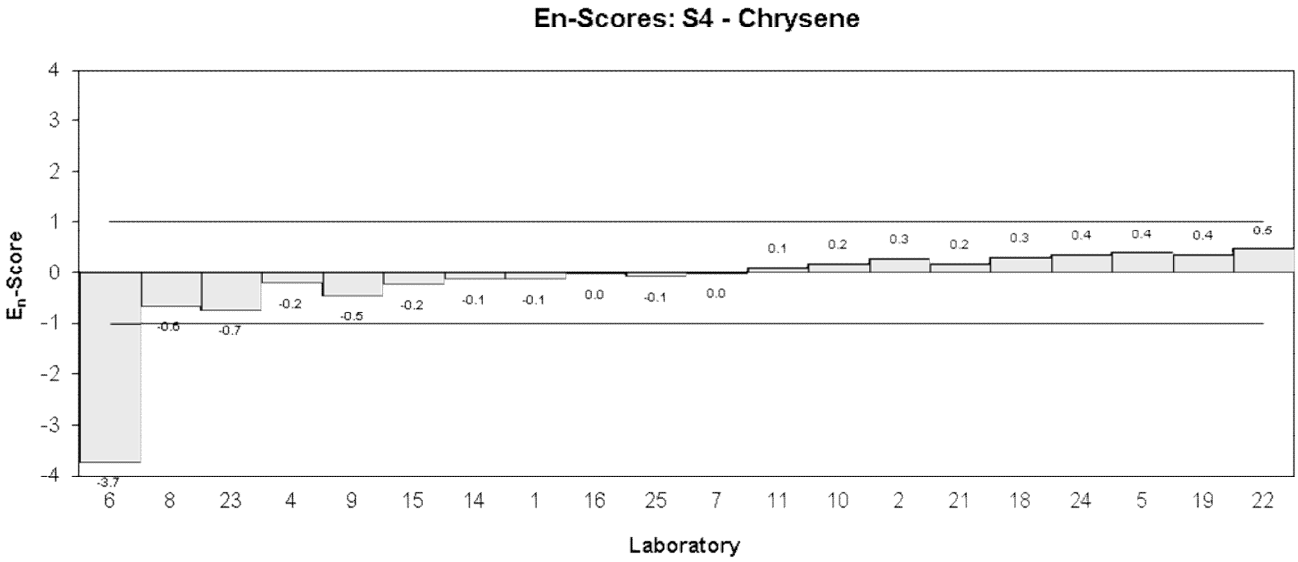

En-Scores: S4 - Chrysene
En-Score
Laboratory
6 8 23 4 9 15 14 1 16 25 7 11 10 2 21 18 24 5 19 22
-3.7 -0.6 -0.7 -0.2 -0.5 -0.2 -0.1 -0.1 0.0 -0.1 0.0 0.1 0.2 0.3 0.2 0.3 0.4 0.4 0.4 0.5

Figure 21

Table 24

Sample Details

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

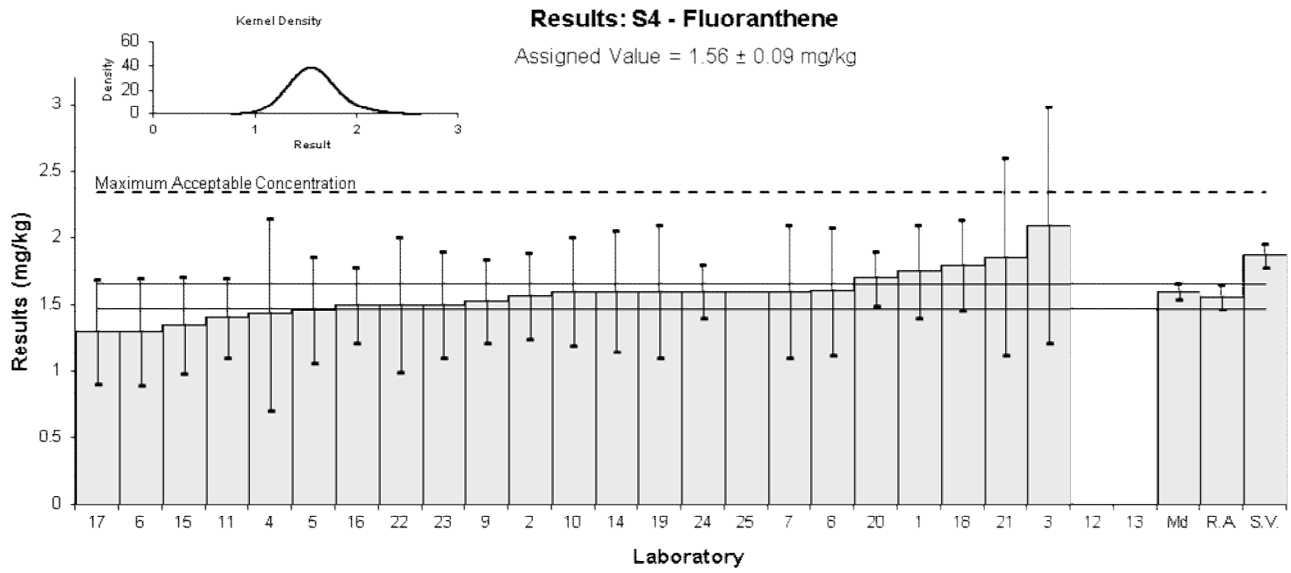
Participant Results

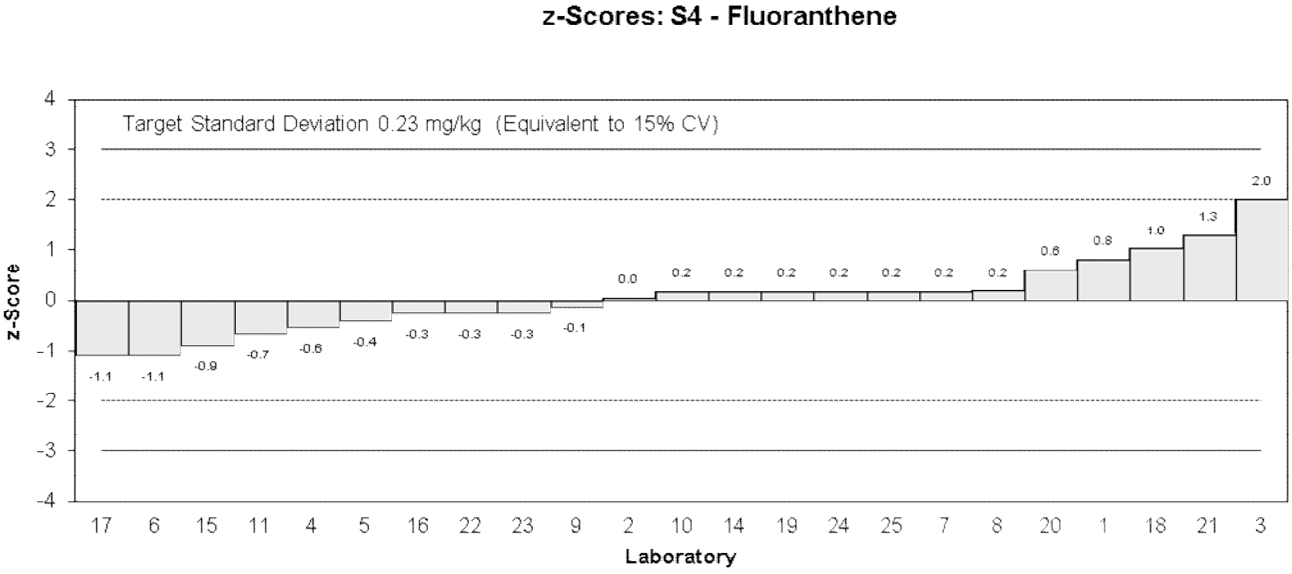
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.75	0.35	0.81	0.53
2	1.57	0.32	0.04	0.03
3*	2.1	0.88	2.00	0.61
4	1.430	0.72	-0.56	-0.18
5	1.46	0.40	-0.43	-0.24
6	1.3	0.4	-1.11	-0.63
7	1.6	0.5	0.17	0.08
8	1.603	0.48	0.18	0.09
9	1.53	0.31	-0.13	-0.09
10	1.60	0.4	0.17	0.10
11	1.4	0.3	-0.68	-0.51
12	NT	NT		
13	NT	NT		
14	1.6	0.45	0.17	0.09
15	1.35	0.36	-0.90	-0.57
16	1.5	0.28	-0.26	-0.20
17	1.30	0.39	-1.11	-0.65
18	1.8	0.34	1.03	0.68
19	1.6	0.5	0.17	0.08
20	1.7	0.2	0.60	0.64
21	1.86	0.74	1.28	0.40
22	1.5	0.5	-0.26	-0.12
23	1.5	0.4	-0.26	-0.15
24	1.6	0.2	0.17	0.18
25	1.6	NR	0.17	0.44

Statistics

Assigned Value	1.56	0.09
Spike	1.87	0.09
Max. Acceptable Conc.*	2.3	
Robust Average	1.56	0.09
Median	1.60	0.06
Mean	1.58	
N	23	
Max.	2.1	
Min.	1.3	
Robust SD	0.17	
Robust CV	11%	

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


Results: S4 - Fluoranthene
Assigned Value = 1.56 ± 0.09 mg/kg
Kernel Density
Density
Result
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
17 6 15 11 4 5 16 22 23 9 2 10 14 19 24 25 7 8 20 1 18 21 3 12 13 Md R.A S.V.


z-Scores: S4 - Fluoranthene
Target Standard Deviation 0.23 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
17 6 15 11 4 5 16 22 23 9 2 10 14 19 24 25 7 8 20 1 18 21 3

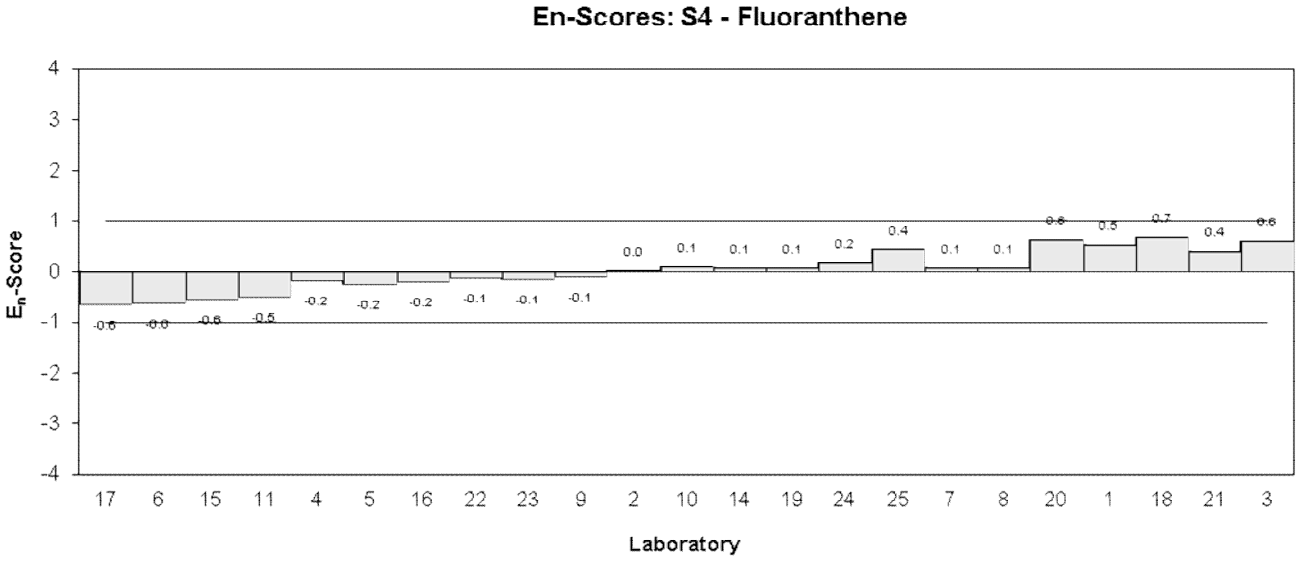

En-Scores: S4 - Fluoranthene
En-Score
Laboratory
17 6 15 11 4 5 16 22 23 9 2 10 14 19 24 25 7 8 20 1 18 21 3

Figure 22

Table 25

Sample Details

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

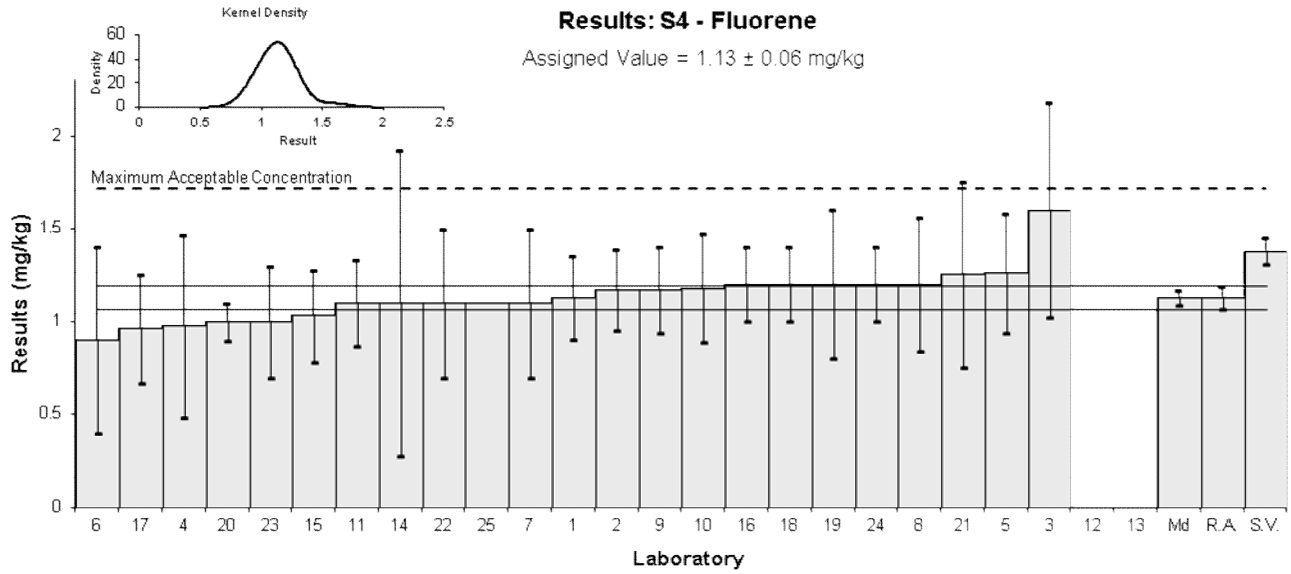
Participant Results

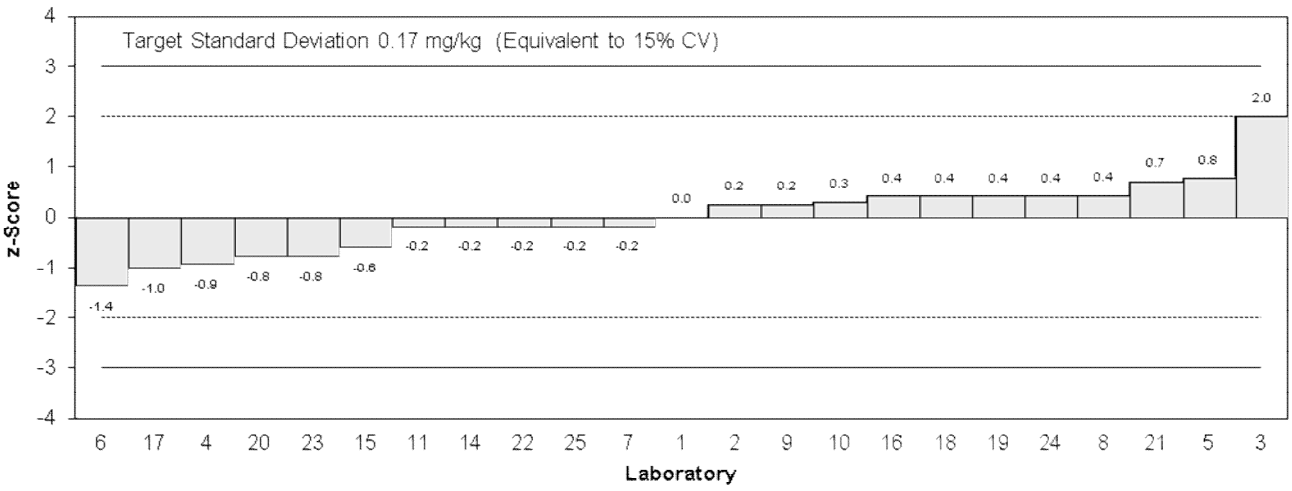
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.13	0.226	0.00	0.00
2	1.17	0.22	0.24	0.18
3*	1.6	0.58	2.00	0.81
4	0.974	0.49	-0.92	-0.32
5	1.26	0.32	0.77	0.40
6	0.9	0.5	-1.36	-0.46
7	1.1	0.4	-0.18	-0.07
8	1.201	0.36	0.42	0.19
9	1.17	0.23	0.24	0.17
10	1.18	0.29	0.29	0.17
11	1.1	0.23	-0.18	-0.13
12	NT	NT		
13	NT	NT		
14	1.1	0.82	-0.18	-0.04
15	1.03	0.25	-0.59	-0.39
16	1.2	0.2	0.41	0.34
17	0.96	0.29	-1.00	-0.57
18	1.2	0.20	0.41	0.34
19	1.2	0.4	0.41	0.17
20	1.0	0.1	-0.77	-1.11
21	1.25	0.5	0.71	0.24
22	1.1	0.4	-0.18	-0.07
23	1.0	0.3	-0.77	-0.42
24	1.2	0.2	0.41	0.34
25	1.1	NR	-0.18	-0.50

Statistics

Assigned Value	1.13	0.06
Spike	1.38	0.07
Max. Acceptable Conc.*	1.72	
Robust Average	1.13	0.06
Median	1.13	0.04
Mean	1.14	
N	23	
Max.	1.6	
Min.	0.9	
Robust SD	0.11	
Robust CV	10%	

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


Kernel Density
Density
Result
Results: S4 - Fluorene
Assigned Value = 1.13 ± 0.06 mg/kg
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
6 17 4 20 23 15 11 14 22 25 7 1 2 9 10 16 18 19 24 8 21 5 3 12 13 Md R.A. S.V.


z-Scores: S4 - Fluorene
Target Standard Deviation 0.17 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 17 4 20 23 15 11 14 22 25 7 1 2 9 10 16 18 19 24 8 21 5 3

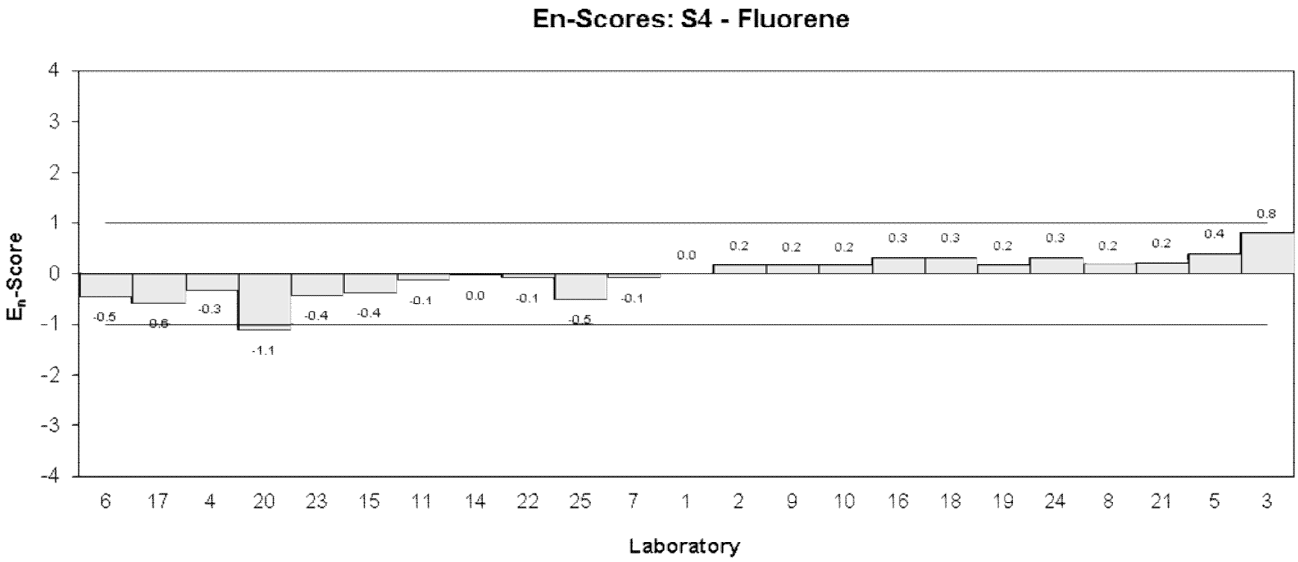

En-Scores: S4 - Fluorene
En-Score
Laboratory
6 17 4 20 23 15 11 14 22 25 7 1 2 9 10 16 18 19 24 8 21 5 3

Figure 23

Table 26

Sample Details

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

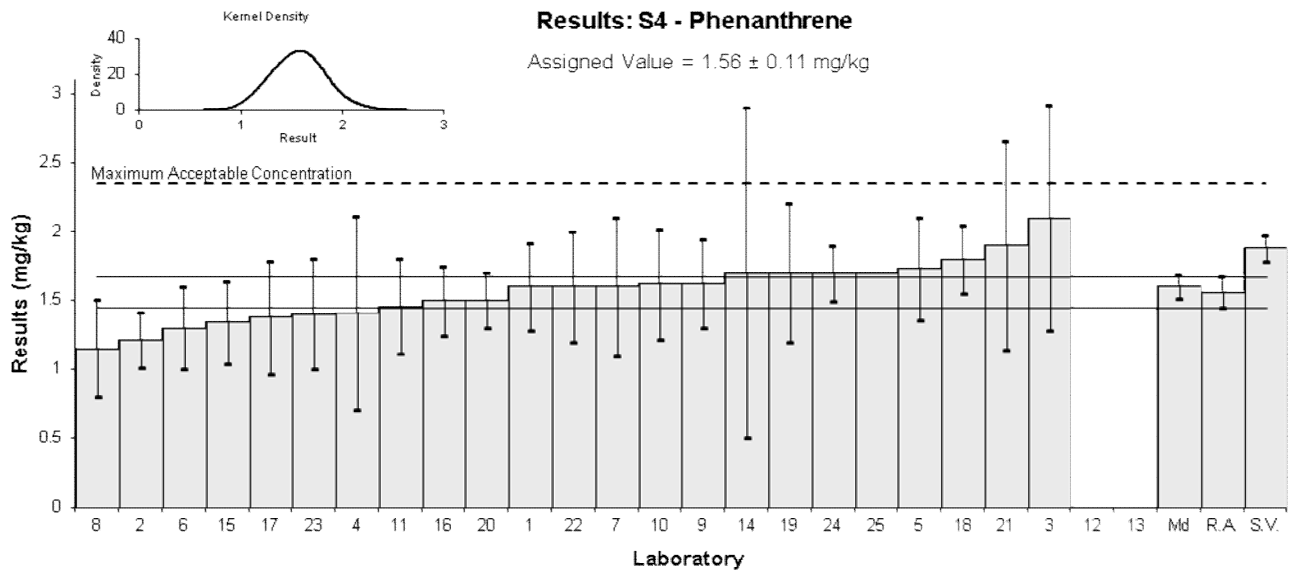
Participant Results

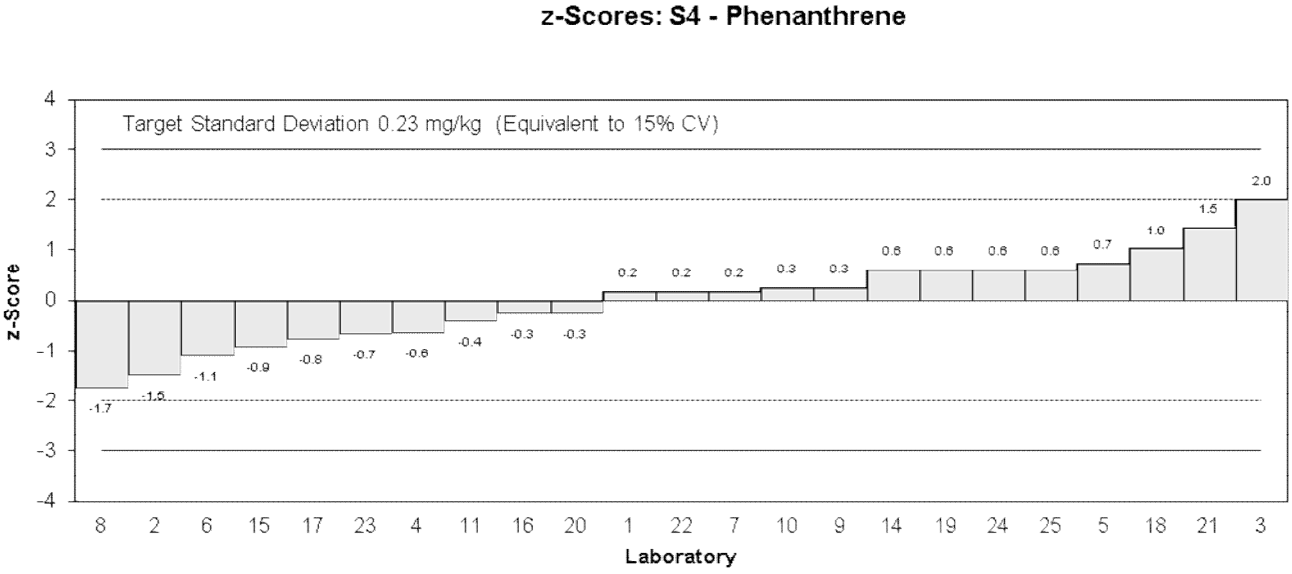
Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	1.60	0.32	0.17	0.12
2	1.21	0.20	-1.50	-1.53
3*	2.1	0.82	2.00	0.65
4	1.410	0.70	-0.64	-0.21
5	1.73	0.37	0.73	0.44
6	1.3	0.3	-1.11	-0.81
7	1.6	0.5	0.17	0.08
8	1.153	0.35	-1.74	-1.11
9	1.62	0.32	0.26	0.18
10	1.62	0.4	0.26	0.14
11	1.46	0.34	-0.43	-0.28
12	NT	NT		
13	NT	NT		
14	1.7	1.2	0.60	0.12
15	1.34	0.30	-0.94	-0.69
16	1.5	0.25	-0.26	-0.22
17	1.38	0.41	-0.77	-0.42
18	1.8	0.25	1.03	0.88
19	1.7	0.5	0.60	0.27
20	1.5	0.2	-0.26	-0.26
21	1.9	0.76	1.45	0.44
22	1.6	0.4	0.17	0.10
23	1.4	0.4	-0.68	-0.39
24	1.7	0.2	0.60	0.61
25	1.7	NR	0.60	1.27

Statistics

Assigned Value	1.56	0.11
Spike	1.88	0.09
Max. Acceptable Conc.*	2.3	
Robust Average	1.56	0.11
Median	1.60	0.08
Mean	1.57	
N	23	
Max.	2.1	
Min.	1.153	
Robust SD	0.22	
Robust CV	14%	

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


Results: S4 - Phenanthrene
Assigned Value = 1.56 ± 0.11 mg/kg
Kernel Density
Density
Result
Maximum Acceptable Concentration
Results (mg/kg)
Laboratory
8 2 6 15 17 23 4 11 16 20 1 22 7 10 9 14 19 24 25 5 18 21 3 12 13 Md R.A S.V.


z-Scores: S4 - Phenanthrene
Target Standard Deviation 0.23 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
8 2 6 15 17 23 4 11 16 20 1 22 7 10 9 14 19 24 25 5 18 21 3

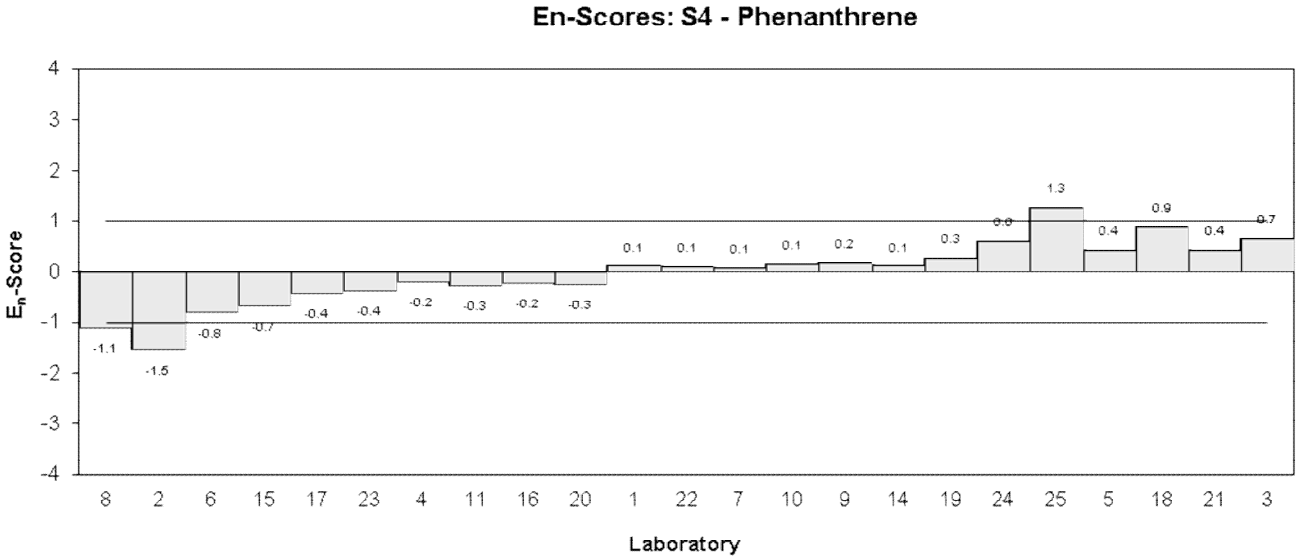

En-Scores: S4 - Phenanthrene
En-Score
Laboratory
8 2 6 15 17 23 4 11 16 20 1 22 7 10 9 14 19 24 25 5 18 21 3

Figure 24

Table 27

Sample Details

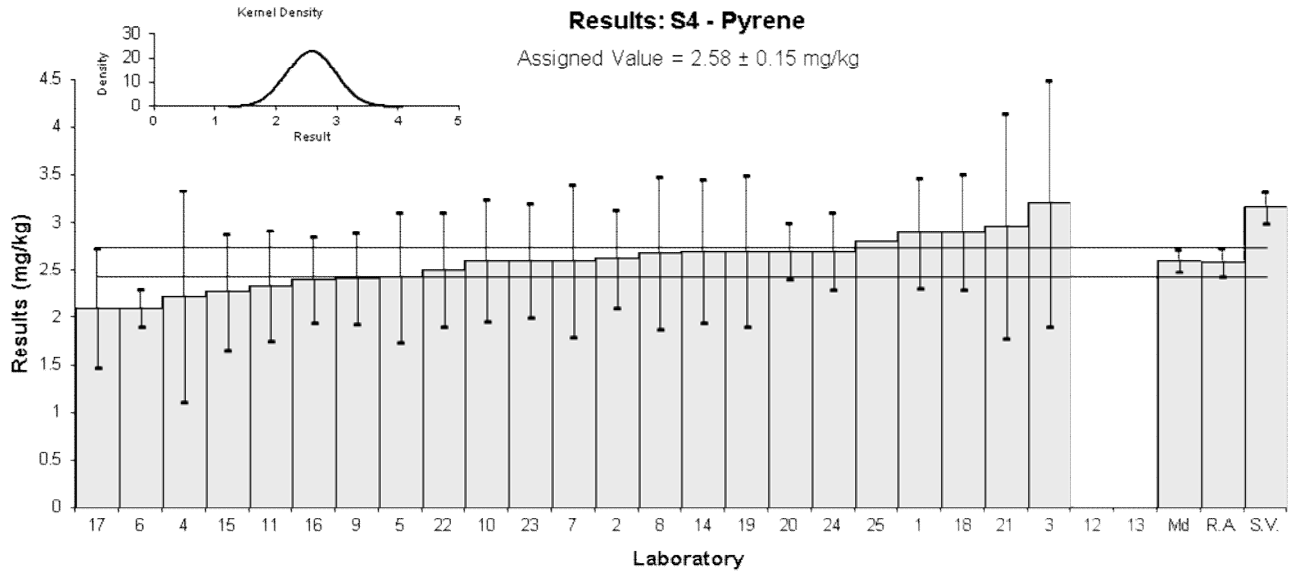
Sample No.	S4
Matrix	Soil
Analyte	Pyrene
Units	mg/kg

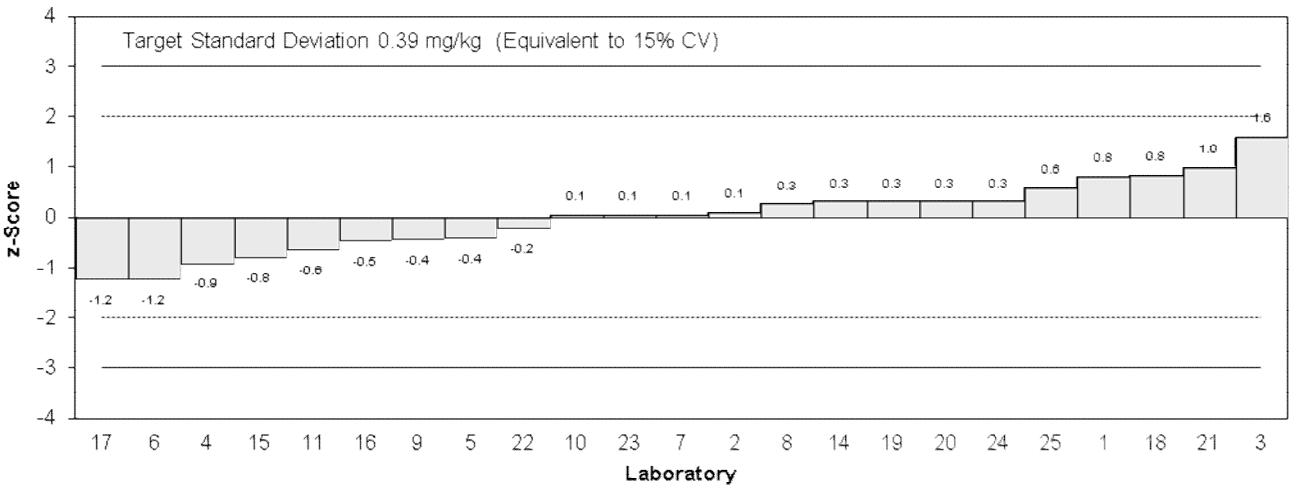
Participant Results

Lab. Code	Result	Uncertainty	z-Score	E_n-Score
1	2.89	0.578	0.80	0.52
2	2.62	0.51	0.10	0.08
3	3.2	1.3	1.60	0.47
4	2.225	1.11	-0.92	-0.32
5	2.42	0.68	-0.41	-0.23
6	2.1	0.2	-1.24	-1.92
7	2.6	0.8	0.05	0.02
8	2.681	0.8	0.26	0.12
9	2.41	0.48	-0.44	-0.34
10	2.60	0.64	0.05	0.03
11	2.33	0.58	-0.65	-0.42
12	NT	NT		
13	NT	NT		
14	2.7	0.75	0.31	0.16
15	2.27	0.61	-0.80	-0.49
16	2.4	0.45	-0.47	-0.38
17	2.10	0.63	-1.24	-0.74
18	2.9	0.61	0.83	0.51
19	2.7	0.8	0.31	0.15
20	2.7	0.3	0.31	0.36
21	2.96	1.18	0.98	0.32
22	2.5	0.6	-0.21	-0.13
23	2.6	0.6	0.05	0.03
24	2.7	0.4	0.31	0.28
25	2.8	NR	0.57	1.47

Statistics

Assigned Value	2.58	0.15
Spike	3.16	0.16
Robust Average	2.58	0.15
Median	2.60	0.12
Mean	2.58	
N	23	
Max.	3.2	
Min.	2.1	
Robust SD	0.28	
Robust CV	11%	


Kernel Density
Density
Result
Results: S4 - Pyrene
Assigned Value = 2.58 ± 0.15 mg/kg
Results (mg/kg)
Laboratory
17 6 4 15 11 16 9 5 22 10 23 7 2 8 14 19 20 24 25 1 18 21 3 12 13 Md R.A S.V.


z-Scores: S4 - Pyrene
Target Standard Deviation 0.39 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
17 6 4 15 11 16 9 5 22 10 23 7 2 8 14 19 20 24 25 1 18 21 3

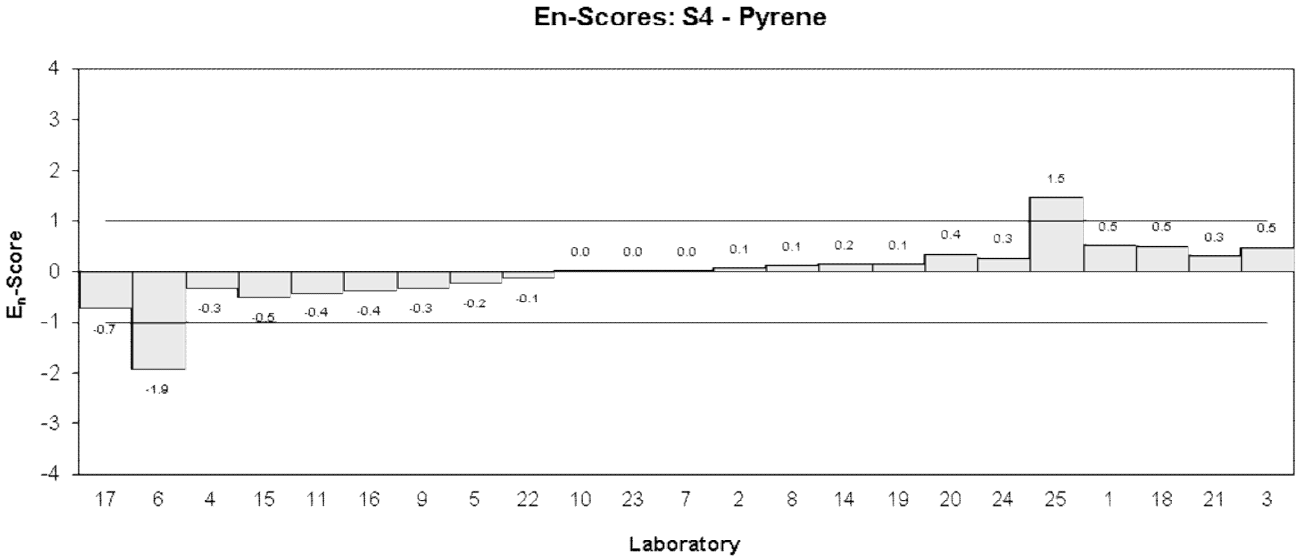

En-Scores: S4 - Pyrene
En-Score
Laboratory
17 6 4 15 11 16 9 5 22 10 23 7 2 8 14 19 20 24 25 1 18 21 3

Figure 25

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust average of participants' results was used as the assigned value 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 3, using pyrene in Sample S4 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 value was set for C6-C10 and benzene in Sample S2 because the reported numeric results were too variable.

A comparison of the assigned value (or robust average if no assigned value was set) and the spiked value is presented in Table 28. In this study, the assigned values for TRH were within the range of 95% to 100% 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 63% to 85% and 42% to 83% of the spiked values respectively. Similar ratios have been observed in previous Hydrocarbons in Soil PT studies, and in this study an assigned value was set where there was a consensus of participants' results (robust CVs for scored BTEX analytes were between 19% to 29%, and robust CVs for scored PAHs analytes were between 10% to 21%).

Table 28 Comparison of Assigned Value (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	1590	1680	95
	>C16-C34	2520	2530	100
	>C34-C40	317	328	97
	TRH	4400	4530	97
S2	Benzene	*(24.8)*	59.4	*(42)*
	Toluene	340	537	63
	Ethylbenzene	51.9	61.3	85
	Xylenes	313	460	68
	Total BTEX	737	1120	66
S3	Anthracene	1.52	3.57	43
	Benzo(a)pyrene	1.88	3.83	49
	Chrysene	1.10	1.39	79
	Fluoranthene	1.31	1.59	82
	Fluorene	3.19	3.94	81
	Phenanthrene	3.11	3.86	81
	Pyrene	2.52	3.17	79

Sample	Analyte	Assigned Value *(Robust Average)* (mg/kg)	Spiked Value (mg/kg)	Assigned Value *(Robust Average)* / Spiked Value (%)
S4	Anthracene	1.11	2.67	42
	Benzo(a)pyrene	0.488	1.08	45
	Chrysene	2.41	2.95	82
	Fluoranthene	1.56	1.87	83
	Fluorene	1.13	1.38	82
	Phenanthrene	1.56	1.88	83
	Pyrene	2.58	3.16	82

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate. 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 538 numerical results, 518 results (96%) were reported with an associated expanded measurement uncertainty. Participants used a wide variety of procedures to estimate the expanded measurement uncertainty (Table 1).

The magnitude of the reported expanded uncertainties was within the range 5.9% to 100% 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 518 expanded measurement uncertainties, 39 were less than 15% relative while 22 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 **8**, **13** and **16** attached estimates of the expanded measurement uncertainty 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. 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 1099.26 ± 329.78 mg/kg, is better to report this as 1100 ± 330 mg/kg).[10]

6.3 z-Score

Target SDs equivalent to 15% CV were used to calculate z-scores. Target SDs (as PCV), CVs predicted by the Thompson-Horwitz equation,[8] and the between laboratories CVs obtained in this study for scored analytes are presented for comparison in Table 29.

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

Sample	Analyte	Assigned value (mg/kg)	Target SD (as PCV) (%)	Thompson-Horwitz CV (%)	Between Laboratories CV (%)
S1	>C10-C16	1590	15	5.3	16
	>C16-C34	2520	15	4.9	17
	>C34-C40	317	15	6.7	16
	TRH	4400	15	4.5	15
S2	Toluene	340	15	6.7	29
	Ethylbenzene	51.9	15	8.8	19
	Xylenes	313	15	6.7	20
	Total BTEX	737	15	5.9	23
S3	Anthracene	1.52	15	15	14
	Benzo(a)pyrene	1.88	15	15	14
	Chrysene	1.10	15	16	14
	Fluoranthene	1.31	15	15	11
	Fluorene	3.19	15	13	10
	Phenanthrene	3.11	15	13	14
	Pyrene	2.52	15	14	12
S4	Anthracene	1.11	15	16	15
	Benzo(a)pyrene	0.488	15	18	21
	Chrysene	2.41	15	14	10
	Fluoranthene	1.56	15	15	11
	Fluorene	1.13	15	16	10
	Phenanthrene	1.56	15	15	14
	Pyrene	2.58	15	14	11

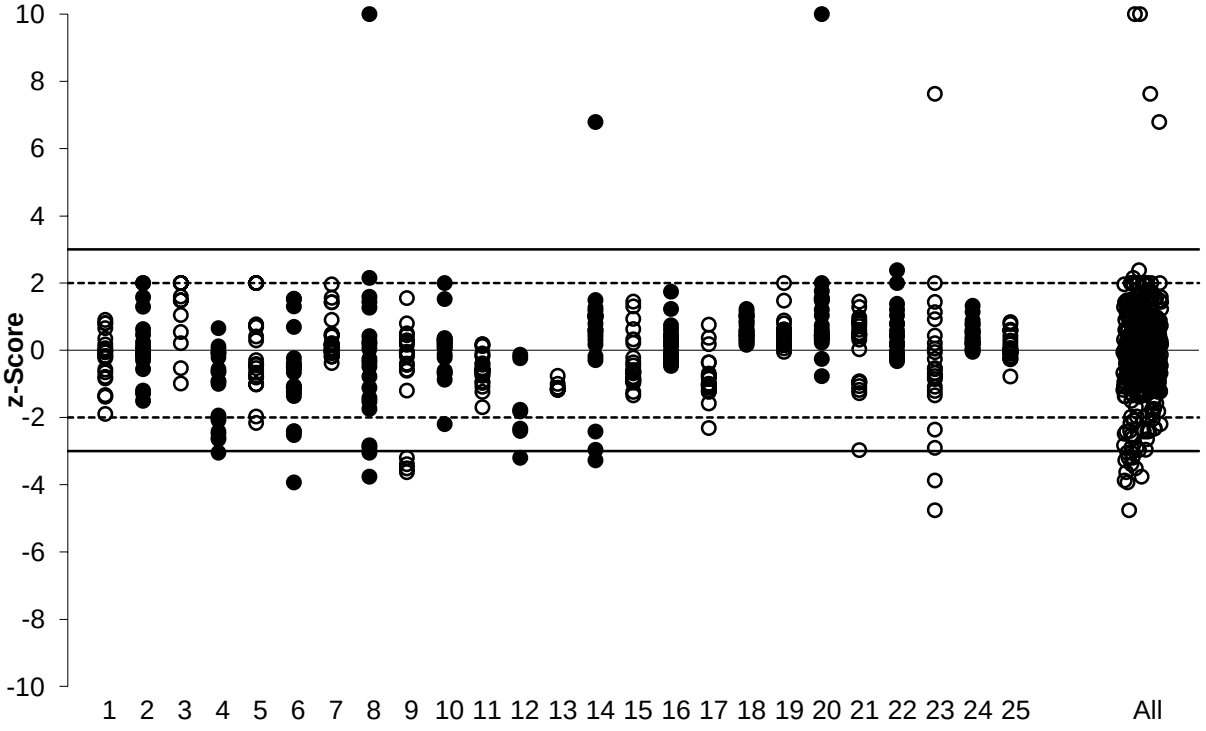
To account for possible low bias in the consensus values due to laboratories using inefficient analytical or extraction techniques, a total of 14 z-scores were adjusted across the following analytes: toluene, ethylbenzene, xylenes and total BTEX in Sample S2, chrysene in Sample S3, and benzo(a)pyrene, fluoranthene, fluorene and phenanthrene in Sample S4. 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 had their z-score adjusted to 2. This ensured that laboratories reporting results close to the spiked concentration were not penalised. The z-scores for results higher than the maximum acceptable concentration were not adjusted. z-Scores less than 2 were left unaltered.

The dispersal of participants' z-scores is presented graphically by laboratory in Figure 26 and by analyte in Figure 27.

Of 494 results for which z-scores were calculated, 455 (92%) returned a satisfactory score of $|z| \leq 2.0$.

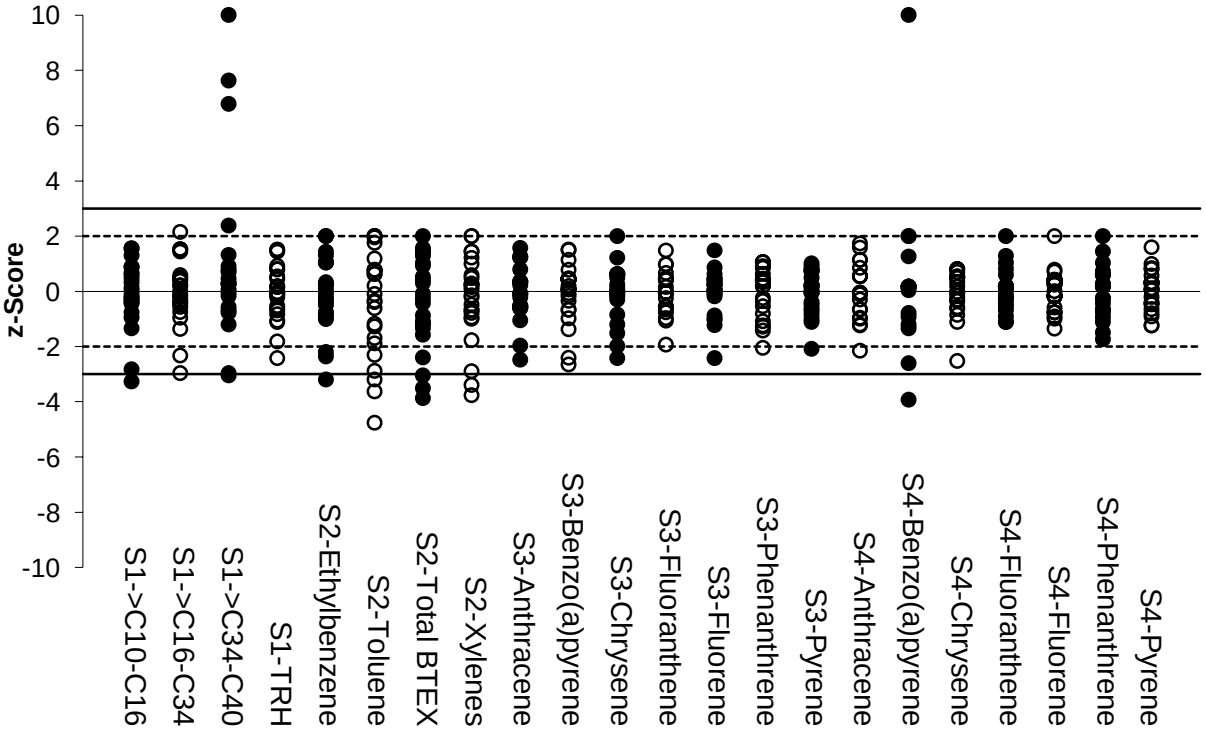
Laboratories **2**, **4**, **5**, **6**, **7**, **9**, **11**, **14**, **15**, **18**, **19**, **21**, **22** and **23** reported results for all 22 analytes which were scored. Laboratories **2**, **7**, **11**, **15**, **18**, **19** returned satisfactory z-scores for all 22 scored analytes.

Satisfactory z-scores were achieved for all scored analytes reported by laboratories **1** (21), **16** (21), **24** (21), **25** (21), **3** (11) and **13** (5).



Scores greater than 10 have been plotted as 10.

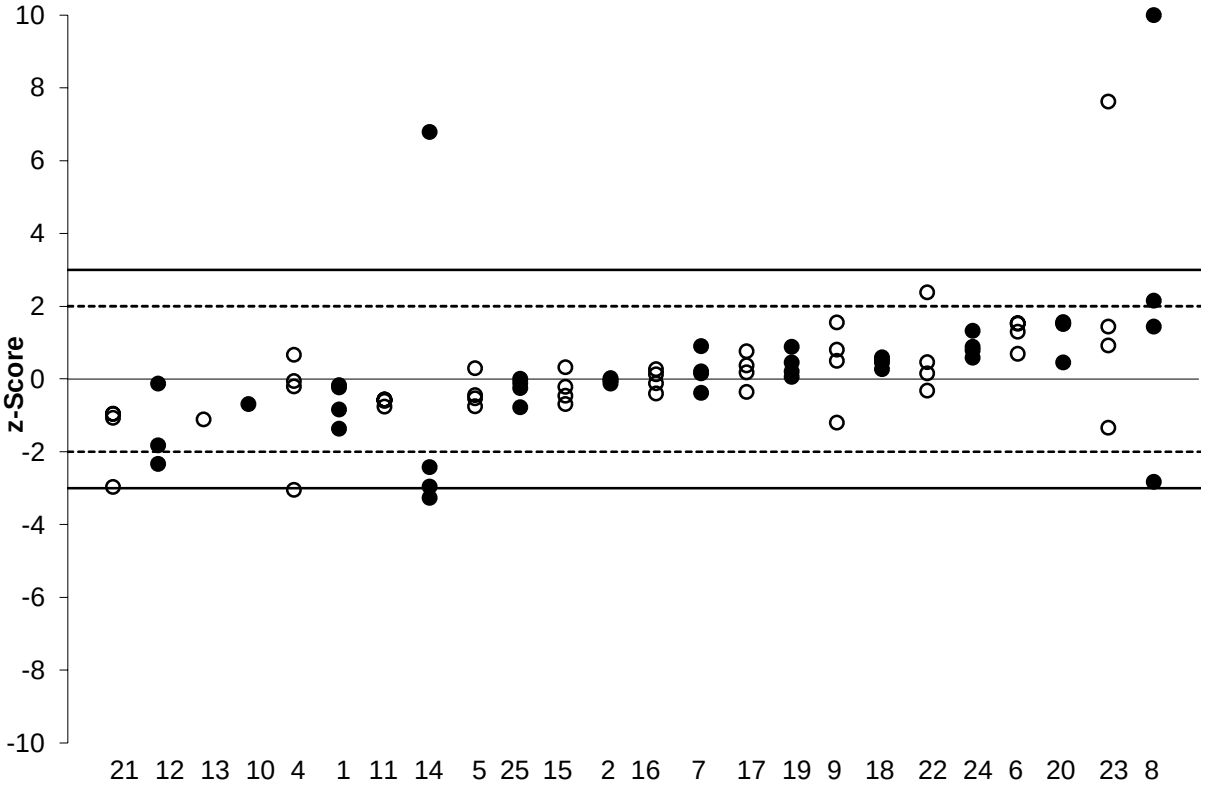
Figure 26 z-Score Dispersal by Laboratory



Scores greater than 10 have been plotted as 10.

Figure 27 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 28 to 30. A trend of z-scores on one side of the zero line may indicate laboratory bias for that analyte type.



Scores greater than 10 have been plotted at 10.

Figure 28 TRH (Sample S1) z-Score Dispersal by Laboratory

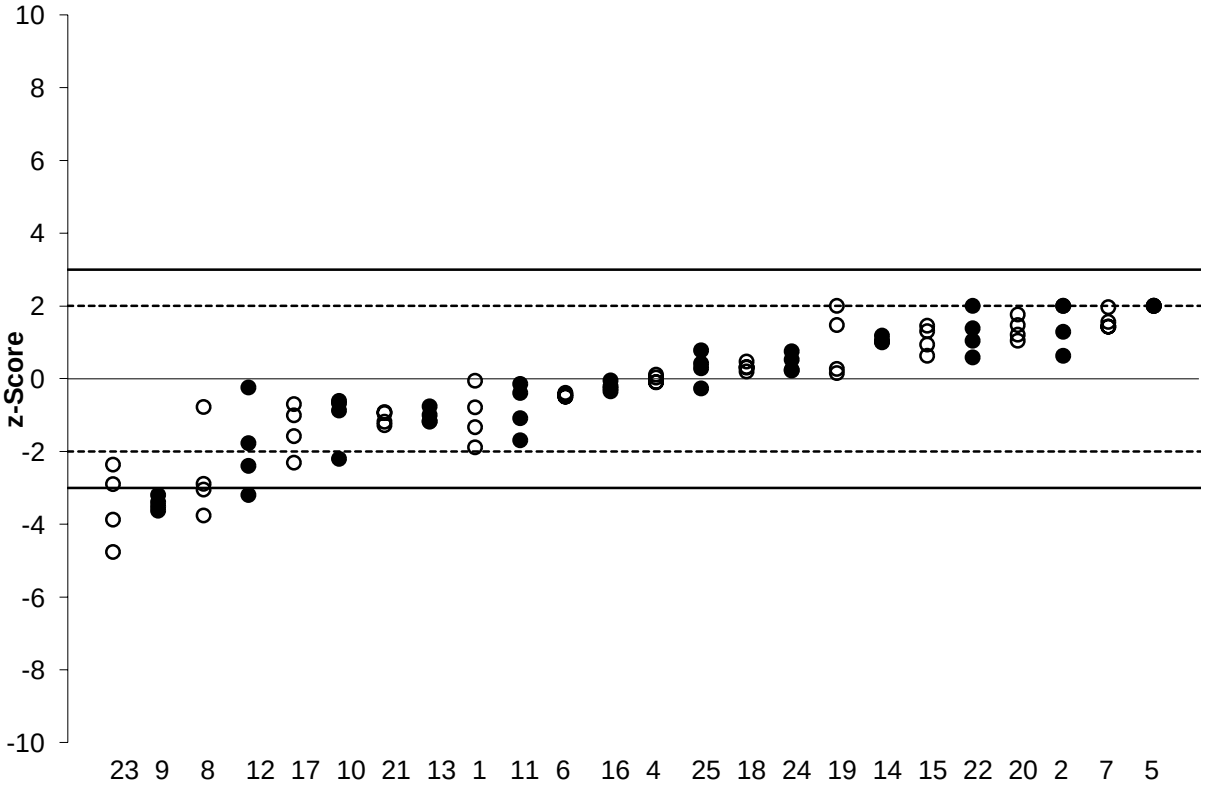
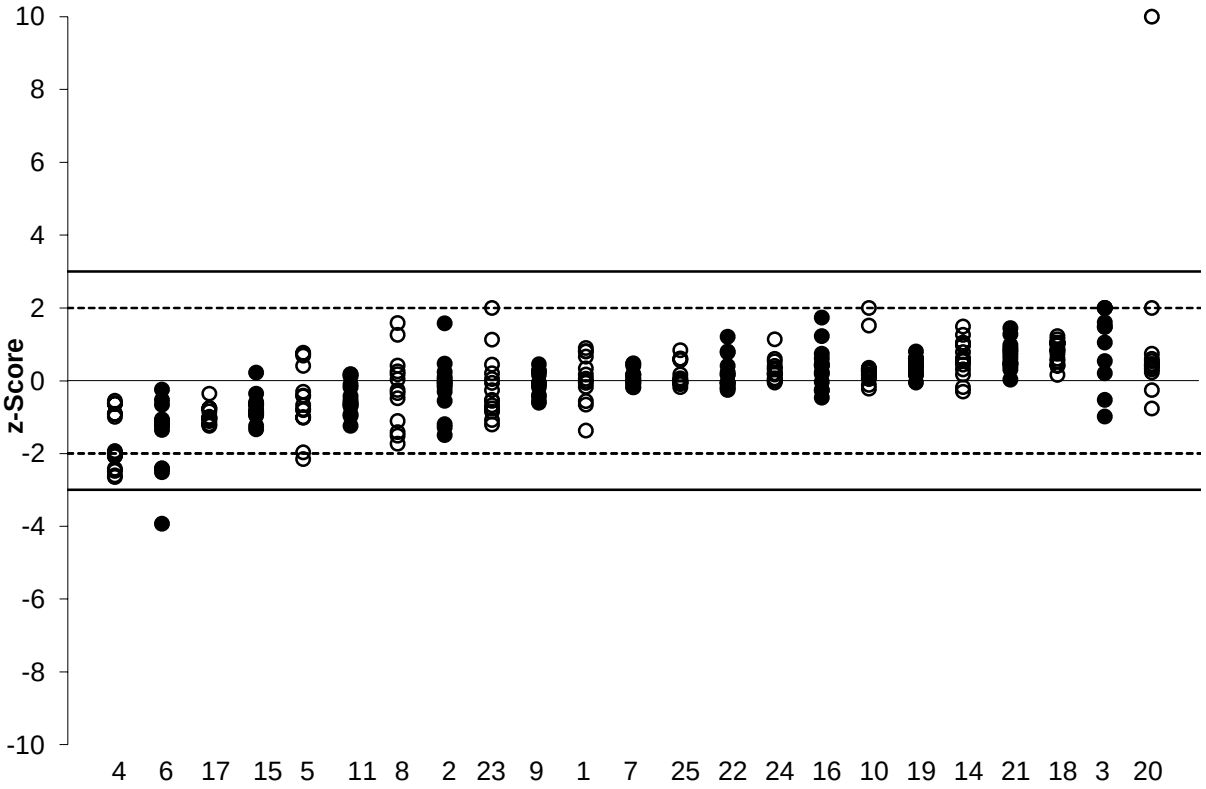


Figure 29 BTEX (Sample S2) z-Score Dispersal by Laboratory



Scores greater than 10 have been plotted at 10.

Figure 30 PAHs (Samples S3 and S4) z-Score Dispersal by Laboratory

Scatter plots of z-scores for anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene in Samples S3 and S4 are presented in Figures 31 to 37. Scores are predominantly in quadrants I and III, indicating that laboratory bias is the major contributor to the variability of results.

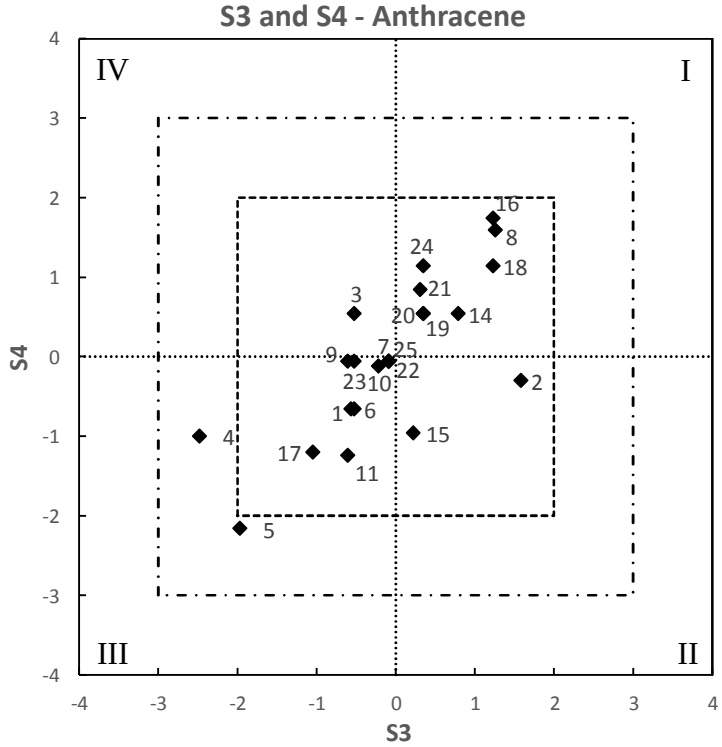
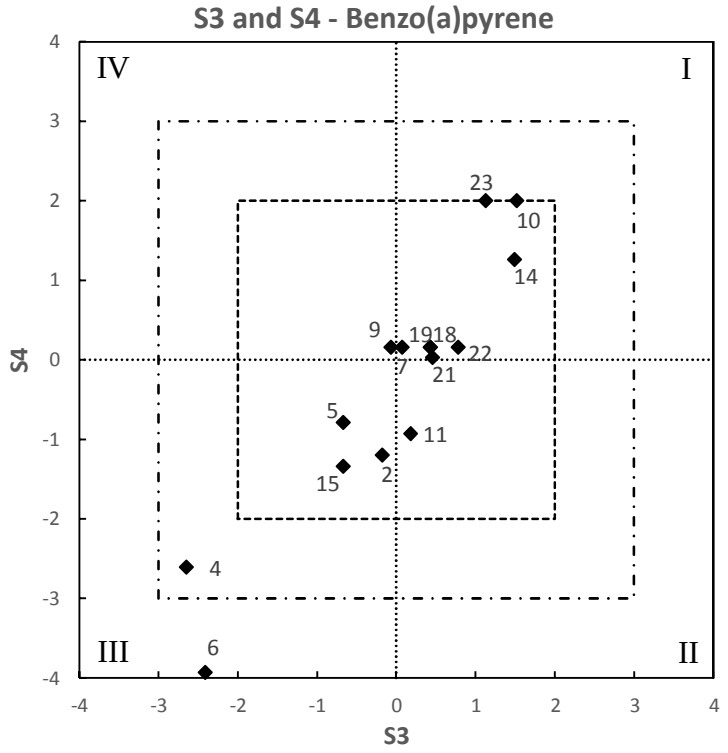


Figure 31 z-Score Scatter Plot – Anthracene in S3 and S4



Laboratory 20 is off scale.

Figure 32 z-Score Scatter Plot – Benzo(a)pyrene in S3 and S4

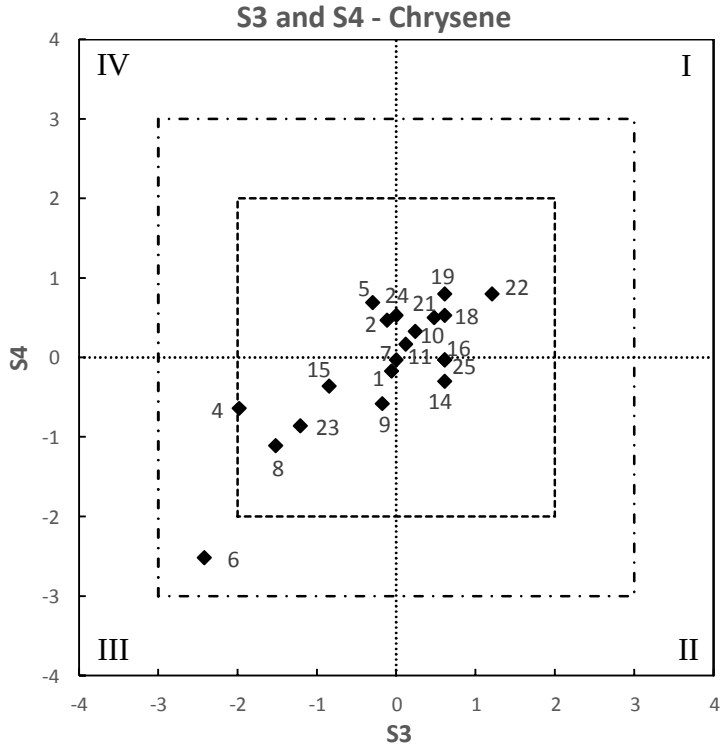


Figure 33 z-Score Scatter Plot – Chrysene in S3 and S4

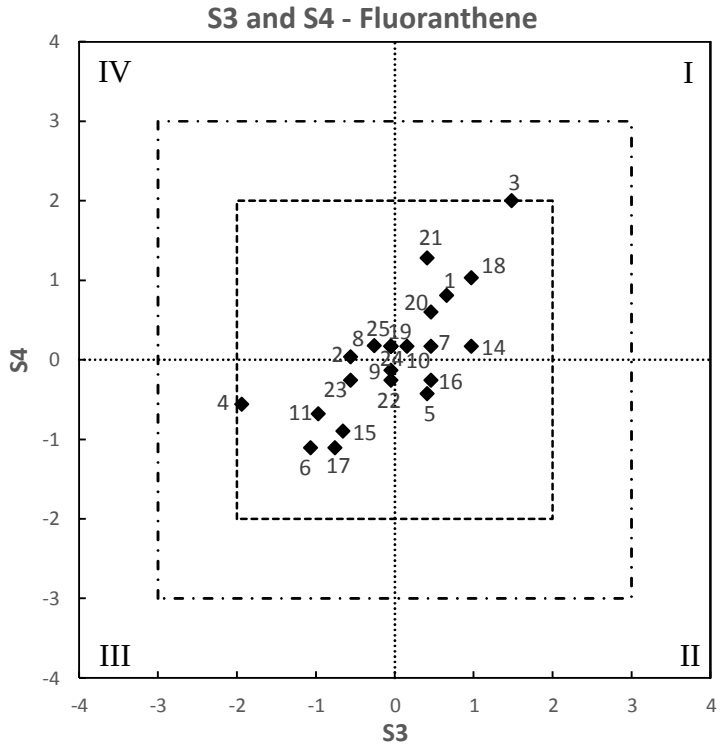


Figure 34 z-Score Scatter Plot – Fluoranthene in S3 and S4

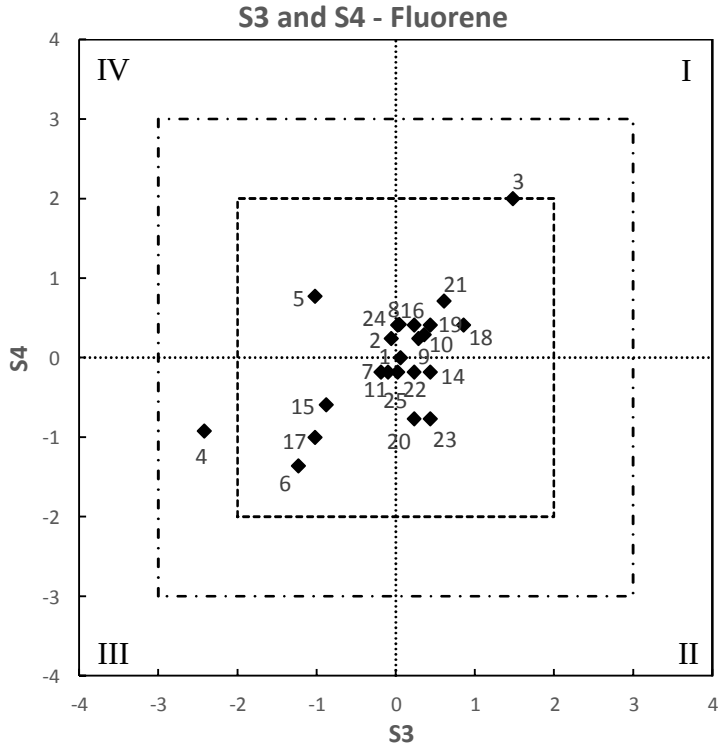


Figure 35 z-Score Scatter Plot – Fluorene in S3 and S4

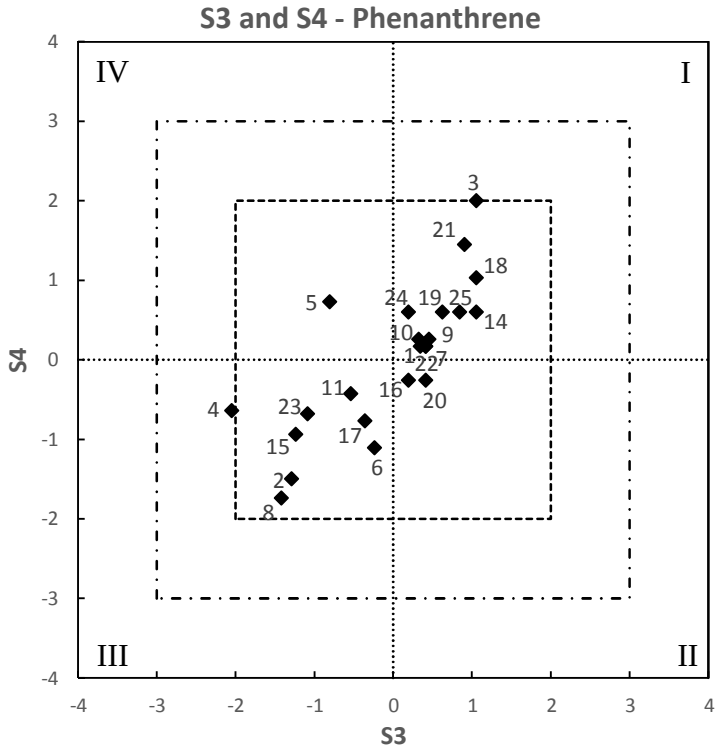


Figure 36 z-Score Scatter Plot – Phenanthrene in S3 and S4

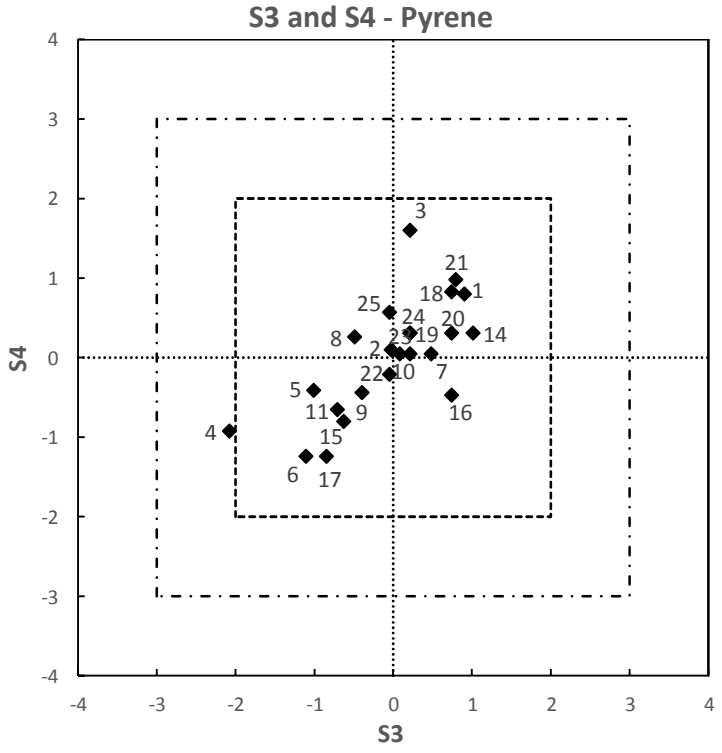


Figure 37 z-Score Scatter Plot – Pyrene in S3 and S4

6.4 E_n-Score

Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score. E_n-scores greater than 1 were set to 1 for results for which z-scores were adjusted as discussed in Section 6.3 z-Scores.

Of 494 results for which E_n-scores were calculated, 436 (88%) returned a satisfactory score of $|E_n| \leq 1.0$.

Laboratories **7**, **15** and **19** returned satisfactory E_n-scores for all 22 scored analytes.

Satisfactory E_n-scores were achieved for all scored analytes reported by laboratories **24** (21) and **3** (11).

The dispersal of participants' E_n-scores by laboratory is presented in Figure 38.

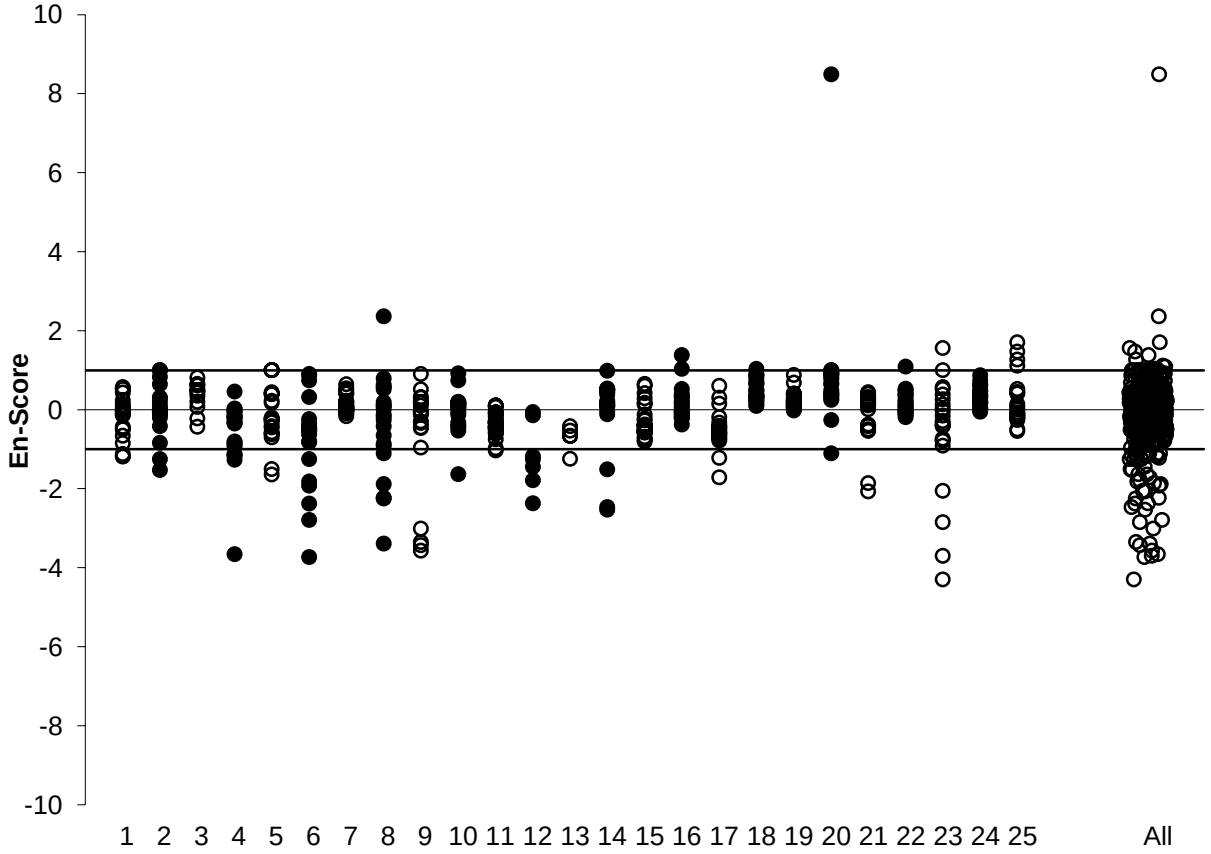


Figure 38 E_n-Score Dispersal by Laboratory

6.5 False Negatives

Table 30 lists false negative results – an analyte present for which a laboratory tested but did not report a result (e.g. laboratories reporting a '<' or NR result when the assigned and spiked value was higher than the participants' reporting limit, or laboratories that left the result cell blank).

Table 30 False Negatives

Lab. Code	Sample	Pesticide
3	S3	Chrysene
8	S4	Benzo(a)pyrene
20	S4	Chrysene

6.6 Participants' Analytical Methods

A variety of analytical methods were used by participants in this PT study (Tables 33 to 35).

TRH

Participants used a sample size between 5 g and 50 g for TRH analysis, with the majority of participants using around 10 g. There was no evident correlation overall between the results obtained and the sample mass used for analysis (Figure 39).

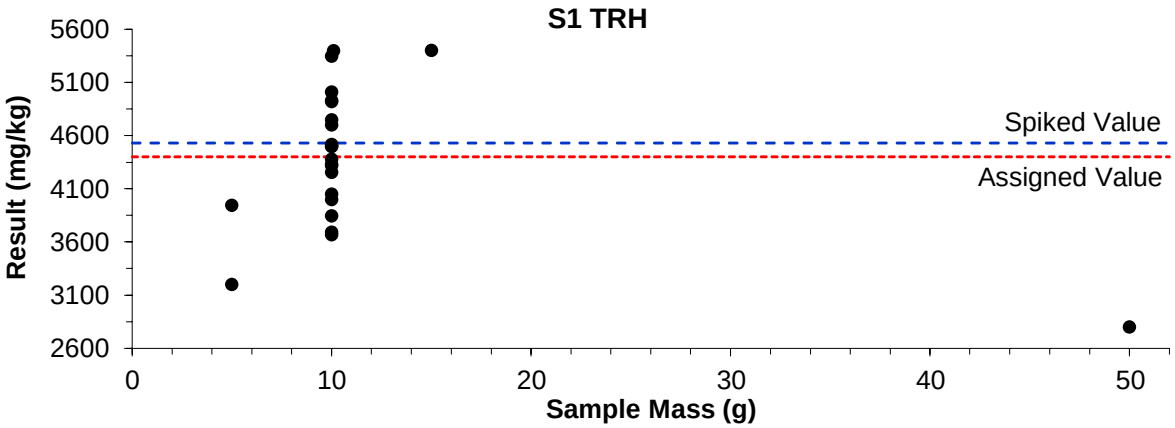


Figure 39 S1 TRH Result vs Sample Mass Used for Analysis

Participants reported using a variety of extraction techniques including solid-liquid extraction, liquid-liquid extraction and sonication, with dichloromethane, acetone, hexane, pentane and combinations of these as the extraction solvent. Three participants reported a clean-up step; these participants used silica/glass wool and sodium sulfate for the clean-up. All participants used GC-FID for analysis.

A plot of results reported and method used for TRH in Sample S1 is presented in Figure 40. Test methods are listed in order of extraction technique, extraction solvent, clean-up, and instrument. Solvent abbreviations used in the figure: DCM = Dichloromethane; ACE = Acetone; HEX = Hexane; PEN = Pentane. Extraction method abbreviations used in the figure: SLE = Solid-Liquid Extraction; LLE = Liquid-Liquid Extraction.

The most common methodology used to analysis 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.

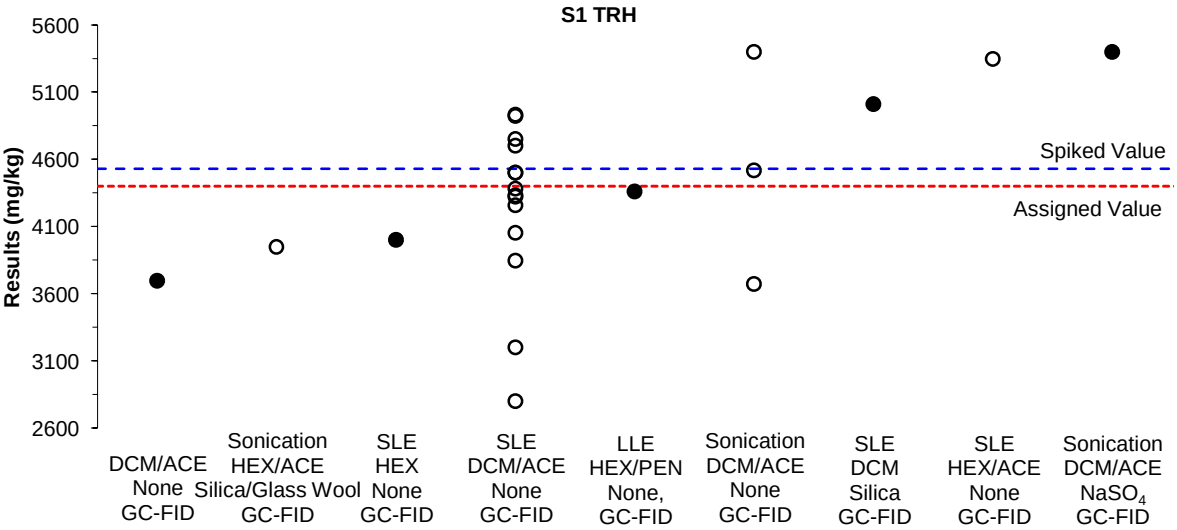


Figure 40 S1 TRH Result vs Test Method

BTEX

Participants used a sample size between 2 g and 14 g for BTEX analysis. There was no evident correlation overall between the results obtained and the sample mass used for analysis (Figure 41).

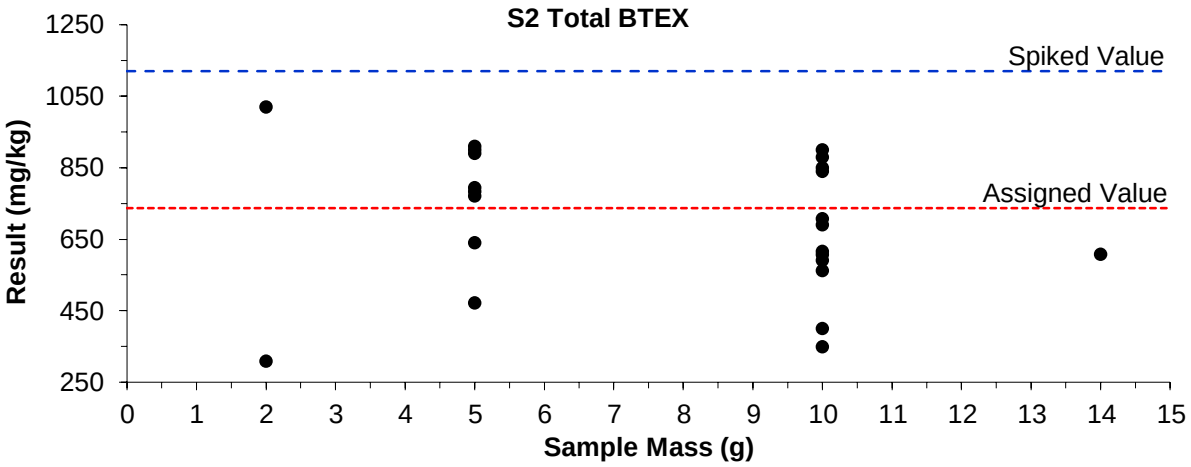


Figure 41 S2 Total BTEX Result vs Sample Mass Used for Analysis

Extraction techniques reported by participants included solid-liquid extraction and sonication extraction techniques, though not all participants used an extraction method. Methanol was the main extraction solvent used, with one participant using dichloromethane/acetone. No participant reported a clean-up step. All participants used GC techniques, including purge and trap GC-MS or headspace GC-MS.

A plot of results reported and method used for BTEX in Sample S2 is presented in Figure 42. Test methods are listed in order of extraction technique, extraction solvent, clean-up, and instrument. Solvent abbreviations used in the figure: DCM = Dichloromethane; ACE = Acetone; MeOH = Methanol. Extraction method abbreviations used in the figure: SLE = Solid-Liquid Extraction. Instrument abbreviations used in the figure: P&T = Purge and Trap; HS = Headspace

The most common methodology used to analyse BTEX in this study was purge and trap GC-MS with methanol as the extraction solvent.

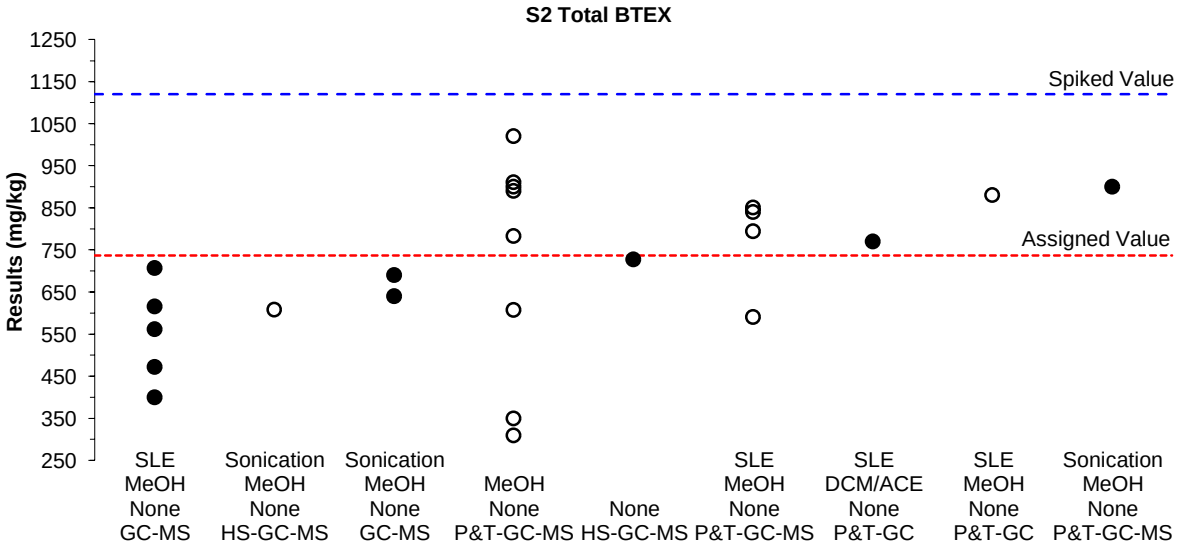
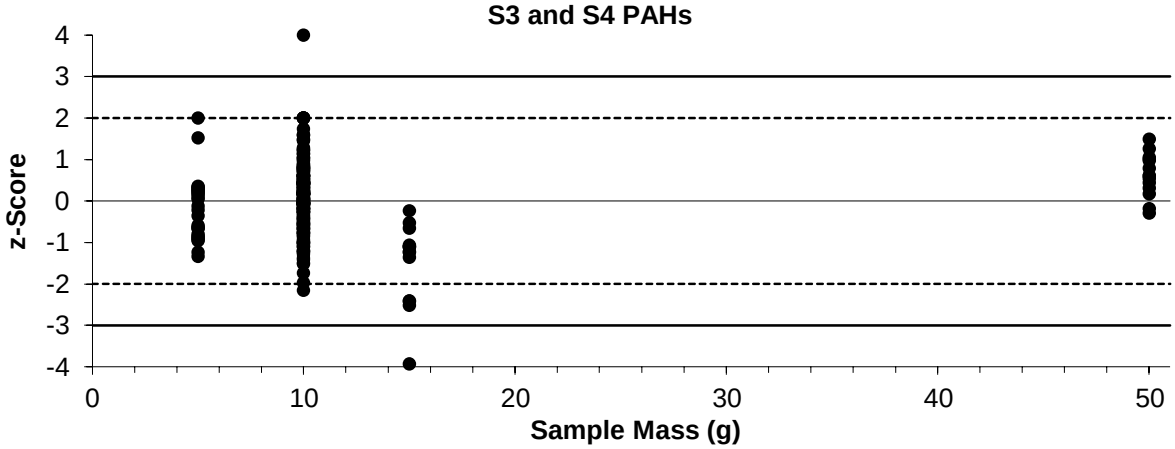


Figure 42 S2 Total BTEX Result vs Test Method

PAHs

Participants used a sample size between 5 g and 50 g for PAH analysis, with the majority of participants using 10 g. There was no evident correlation overall between the results obtained and the sample mass used for analysis (Figure 43).



Scores greater than 4 have been plotted as 4.

Figure 43 S3 and S4 PAHs z-Score vs Sample Mass Used for Analysis

Participants reported using a variety of extraction techniques including solid-liquid extraction, liquid-liquid extraction and sonication, with dichloromethane, acetone, hexane and combinations of these as the extraction solvent. One participants reported using silica/glass wool as a clean-up step. Participants used GC-FID and GC-MS(MS) for analysis.

A plot of z-scores obtained and method used for the various PAHs in Samples S3 and S4 are presented in Figures 44 to 50. Results for Sample S3 are represented as circles and results for Sample S4 are represented as triangles. Test methods are listed in order of extraction technique, extraction solvent, clean-up, and instrument. Solvent abbreviations used in the figure: DCM = Dichloromethane; ACE = Acetone; HEX = Hexane. Extraction method abbreviations used in the figure: SLE = Solid-Liquid Extraction, LLE = Liquid-Liquid Extraction.

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 for analysis.

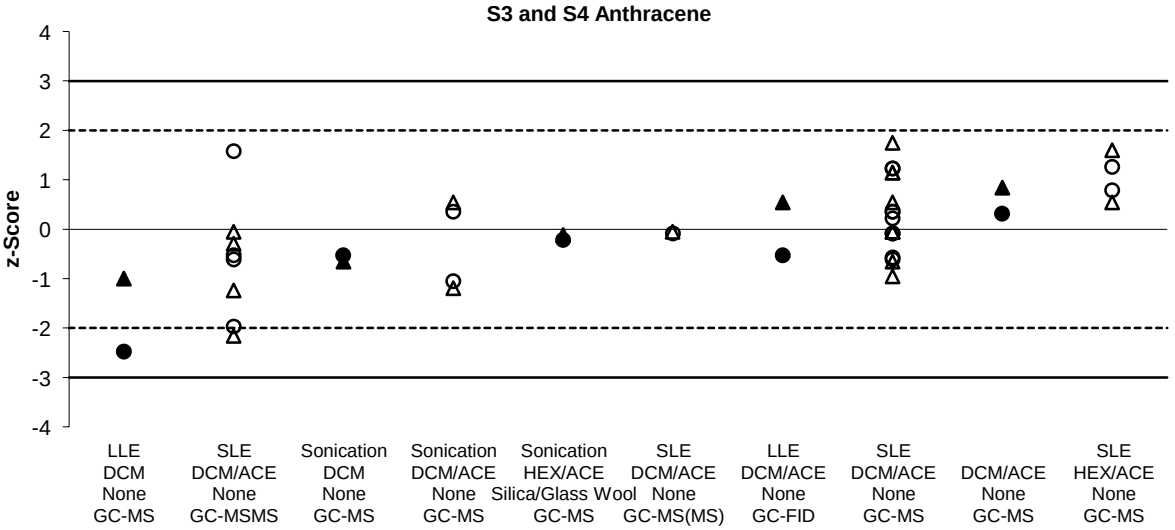
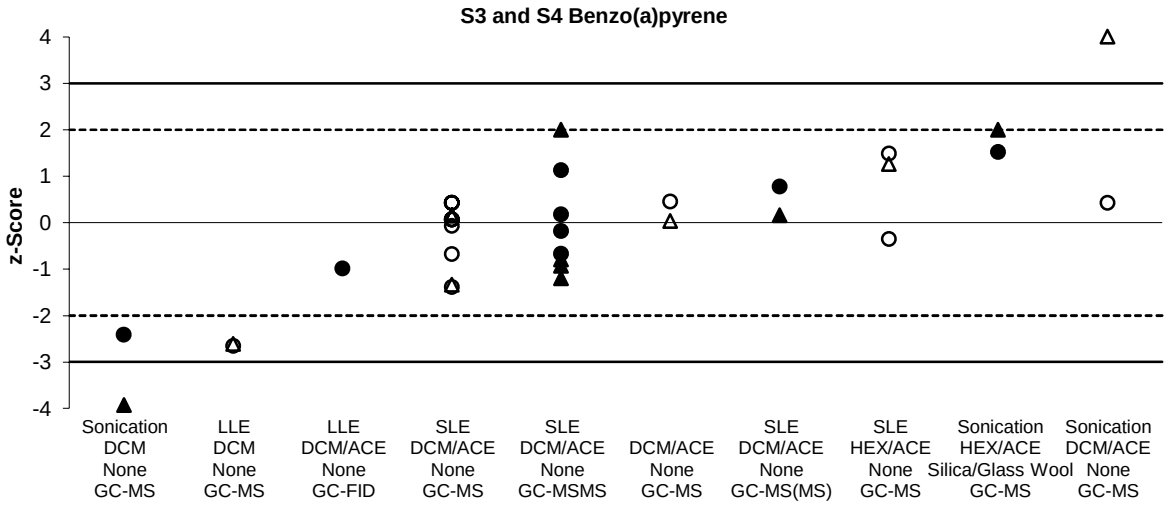


Figure 44 S3 and S4 Anthracene z-Score vs Test Method



Scores greater than 4 have been plotted as 4.

Figure 45 S3 and S4 Benzo(a)pyrene z-Score vs Test Method

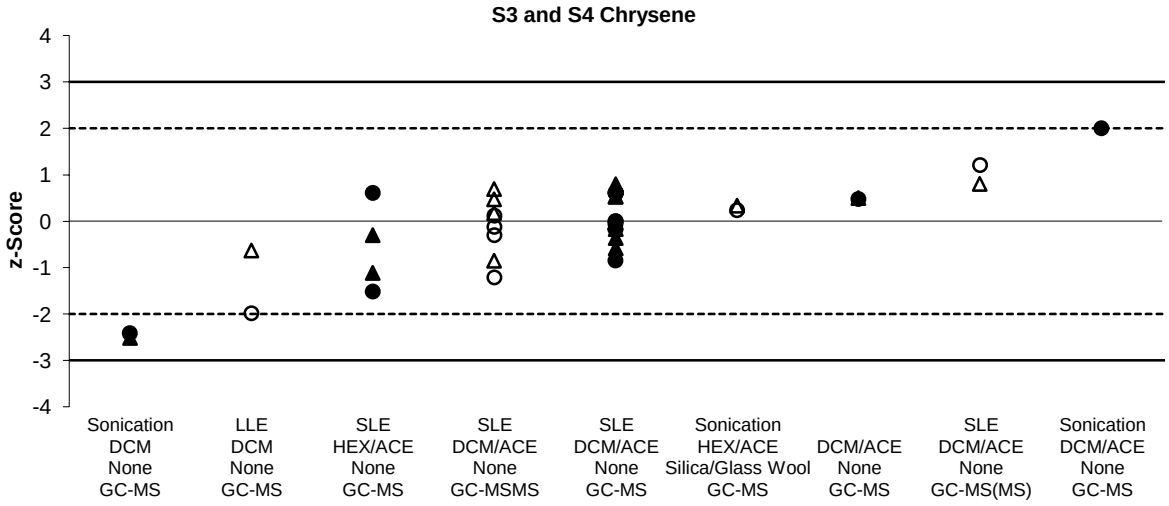


Figure 46 S3 and S4 Chrysene z-Score vs Test Method

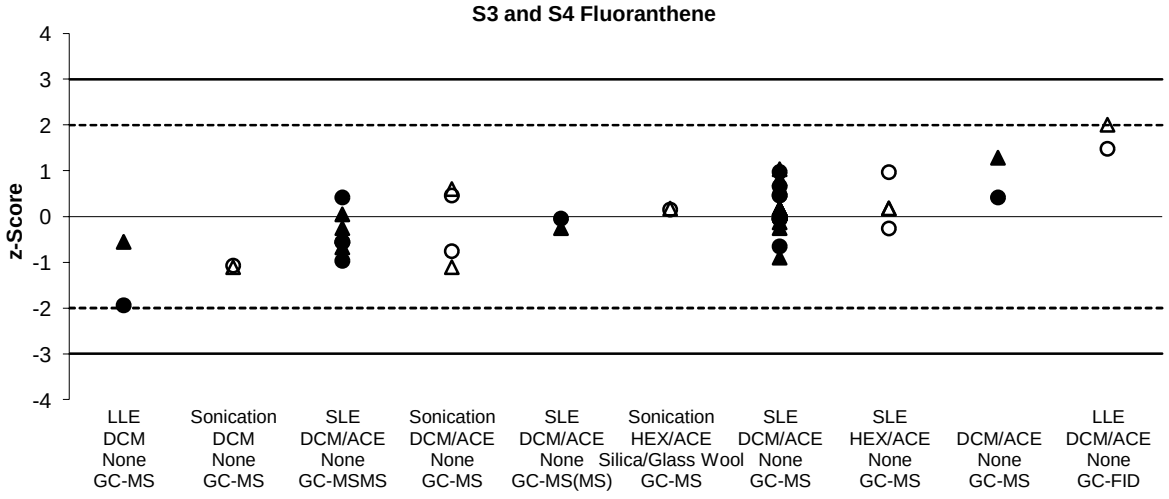


Figure 47 S3 and S4 Fluoranthene z-Score vs Test Method

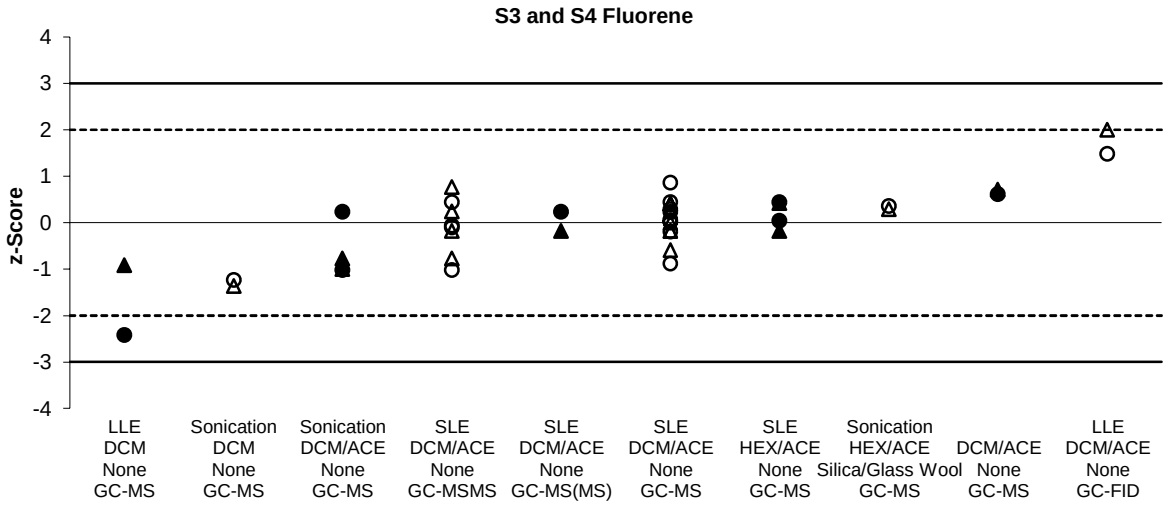


Figure 48 S3 and S4 Fluorene z-Score vs Test Method

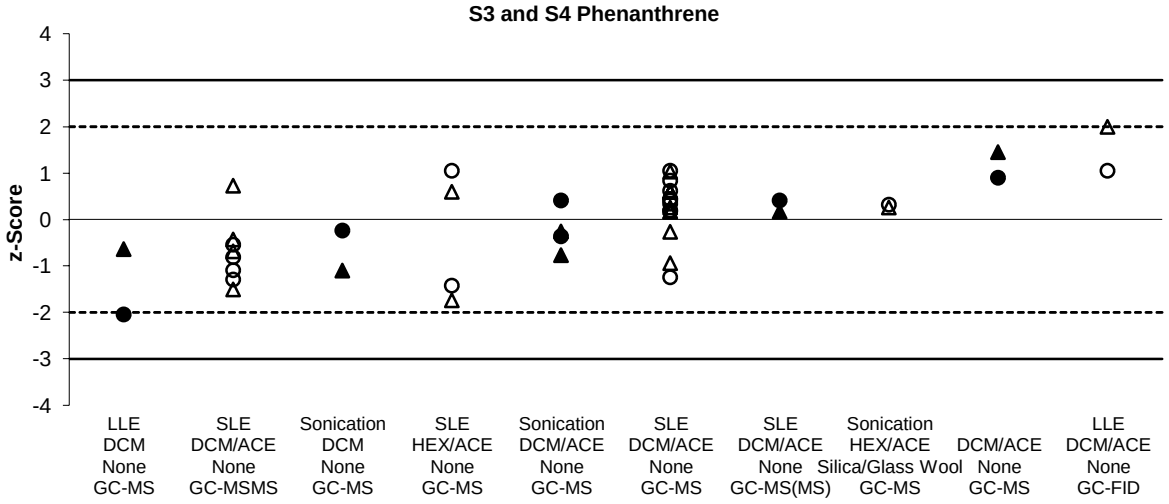


Figure 49 S3 and S4 Phenanthrene z-Score vs Test Method

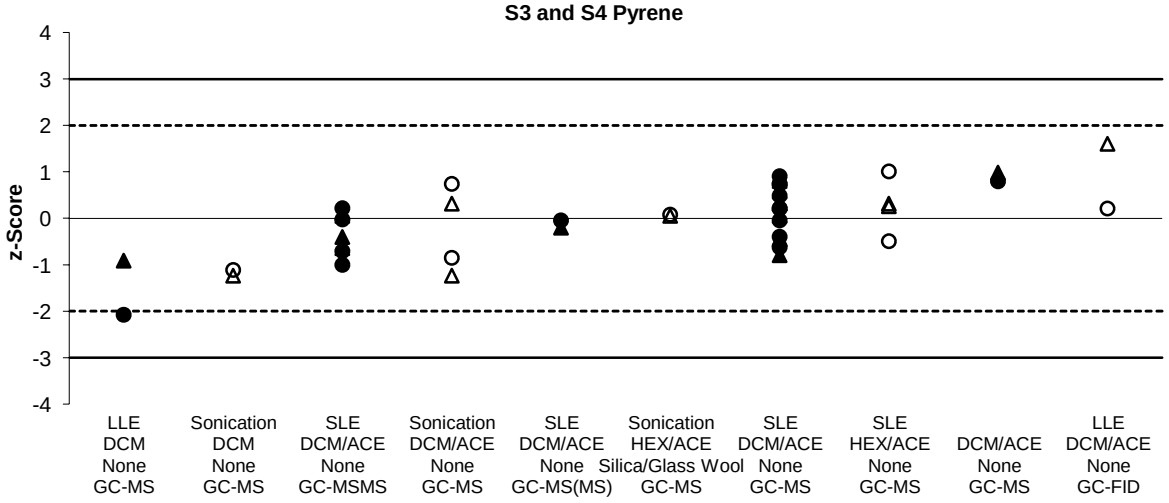


Figure 50 S3 and S4 Pyrene z-Score vs Test Method

6.7 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 the analysis.

Twenty-three participants reported using certified standards and one participant reported using matrix reference materials, including:

- 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
- ChemService
- ISO Guide 34 / ISO 17034 traceable standards
- CRM 356-100

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]

6.8 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 31 and 32, and Figure 51.

Table 31 Summary of Participants' Results (Samples S1 and S2)*

Lab. Code	S1 >C10-C16 (mg/kg)	S1 >C16-C34 (mg/kg)	S1 >C34-C40 (mg/kg)	S1 TRH (mg/kg)	S2 Toluene (mg/kg)	S2 Ethylbenzene (mg/kg)	S2 Xylenes (mg/kg)	S2 Total BTEX (mg/kg)
A.V.	1590	2520	317	4400	340	51.9	313	737
S.V.	1680	2530	328	4530	537	61.3	460	1120
1	1535	2002	309	3846	243.7	51.4	275.7	590.37
2	1594.42	2470.97	314.81	4380.2	371.95	70.7	412.38	879.77
3	NT	NT	NT	NT	NT	NT	NT	NT
4	1747	2442	172	4361	334.660	52.738	314.361	727.589
5	1484	2237	331	4051	480	71	430	1020
6	1900	3100	350	5400	320	48	290	690
7	1500	2600	360	4500	440	63	380	910
8	914.06	3334.41	1099.26	5347.73	192.61	45.83	136.54	400.23
9	1960	2710	260	4930	155	27	154	349
10	NR	NR	NR	3946.9	309.13945	34.752325	281.6482	639.95
11	1408	2303	290	4001	254	48.9	306	616
12	1560	1640	<100	3200	177	50	230	472
13	NR	NR	NR	3670	280	46	266	607.6
14	810	1400	640	2800	400	60	360	850
15	1666	2347	284	4257	372	62	381	840
16	1620	2370	330	4320	322	51.5	303	707
17	1504	2660	353	4517	222	44	280	562
18	1730	2690	330	4750	350	54.4	335	770
19	1800	2600	320	4700	480	54	320	900
20	1962.24	3097.537448	338.2821391	5398.059598	430	60	370	900
21	1363	2156	176	3695	274.55	44.76	268.38	606.78
22	1700	2400	430	4500	450	60	340	890
23	1270	3064	680	5010	97.3	33.5	176.8	309
24	1800	2740	380	4920	378	53.8	323.2	794
25	1530	2520	280	4330	380	49.8	326	783

* Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value; S.V. = Spiked Value

Table 32 Summary of Participants' Results (Samples S3 and S4)*

Lab. Code	S3 Anthracene (mg/kg)	S3 Benzo[a]pyrene (mg/kg)	S3 Chrysene (mg/kg)	S3 Fluoranthene (mg/kg)	S3 Fluorene (mg/kg)	S3 Phenanthrene (mg/kg)	S3 Pyrene (mg/kg)	S4 Anthracene (mg/kg)	S4 Benzo[a]pyrene (mg/kg)	S4 Chrysene (mg/kg)	S4 Fluoranthene (mg/kg)	S4 Fluorene (mg/kg)	S4 Phenanthrene (mg/kg)	S4 Pyrene (mg/kg)
A.V.	1.52	1.88	1.1	1.31	3.19	3.11	2.52	1.11	0.488	2.41	1.56	1.13	1.56	2.58
S.V.	3.57	3.83	1.39	1.59	3.94	3.86	3.17	2.67	1.08	2.95	1.87	1.38	1.88	3.16
1	1.39	1.49	1.09	1.44	3.22	3.27	2.86	1.00	<0.5	2.35	1.75	1.13	1.60	2.89
2	1.88	1.83	1.08	1.20	3.16	2.51	2.51	1.06	0.40	2.58	1.57	1.17	1.21	2.62
3	1.4	1.6	<1	1.6	3.9	3.6	2.6	1.2	<1	NT	2.1	1.6	2.1	3.2
4	0.954	1.133	0.774	0.928	2.03	2.156	1.734	0.943	0.297	2.178	1.430	0.974	1.410	2.225
5	1.07	1.69	1.05	1.39	2.70	2.73	2.14	0.75	0.43	2.66	1.46	1.26	1.73	2.42
6	1.4	1.2	0.7	1.1	2.6	3.0	2.1	1.0	0.2	1.5	1.3	0.9	1.3	2.1
7	1.5	1.9	1.1	1.4	3.1	3.3	2.7	1.1	0.5	2.4	1.6	1.1	1.6	2.6
8	1.807	1.782	0.85	1.258	3.207	2.449	2.333	1.375	<0.1	2.01	1.603	1.201	1.153	2.681
9	1.38	1.86	1.07	1.30	3.33	3.32	2.37	1.10	0.50	2.20	1.53	1.17	1.62	2.41
10	1.47	2.31	1.14	1.34	3.36	3.26	2.55	1.09	0.64	2.53	1.60	1.18	1.62	2.60
11	1.38	1.93	1.12	1.12	3.14	2.86	2.25	0.903	0.42	2.47	1.4	1.1	1.46	2.33
12	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	1.7	2.3	1.2	1.5	3.4	3.6	2.9	1.2	0.58	2.3	1.6	1.1	1.7	2.7
15	1.57	1.69	0.96	1.18	2.77	2.53	2.28	0.95	0.39	2.28	1.35	1.03	1.34	2.27
16	1.8	2.0	1.2	1.4	3.3	3.2	2.8	1.4	<0.5	2.4	1.5	1.2	1.5	2.4
17	1.28	NT	NT	1.16	2.70	2.94	2.20	0.91	NT	NT	1.30	0.96	1.38	2.10
18	1.8	2.0	1.2	1.5	3.6	3.6	2.8	1.3	0.5	2.6	1.8	1.2	1.8	2.9
19	1.6	2	1.2	1.3	3.4	3.4	2.6	1.2	0.5	2.7	1.6	1.2	1.7	2.7
20	1.6	2.0	1.5	1.4	3.3	3.3	2.8	1.2	3.1	<0.5	1.7	1.0	1.5	2.7
21	1.59	2.01	1.18	1.39	3.48	3.53	2.82	1.25	0.49	2.59	1.86	1.25	1.9	2.96
22	1.5	2.1	1.3	1.3	3.3	3.3	2.5	1.1	0.5	2.7	1.5	1.1	1.6	2.5
23	1.4	2.2	0.9	1.2	3.4	2.6	2.6	1.1	0.7	2.1	1.5	1.0	1.4	2.6
24	1.6	1.9	1.1	1.3	3.2	3.2	2.6	1.3	<0.5	2.6	1.6	1.2	1.7	2.7
25	1.5	1.9	1.2	1.3	3.2	3.5	2.5	1.1	<0.5	2.4	1.6	1.1	1.7	2.8

* Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value; S.V. = Spiked Value

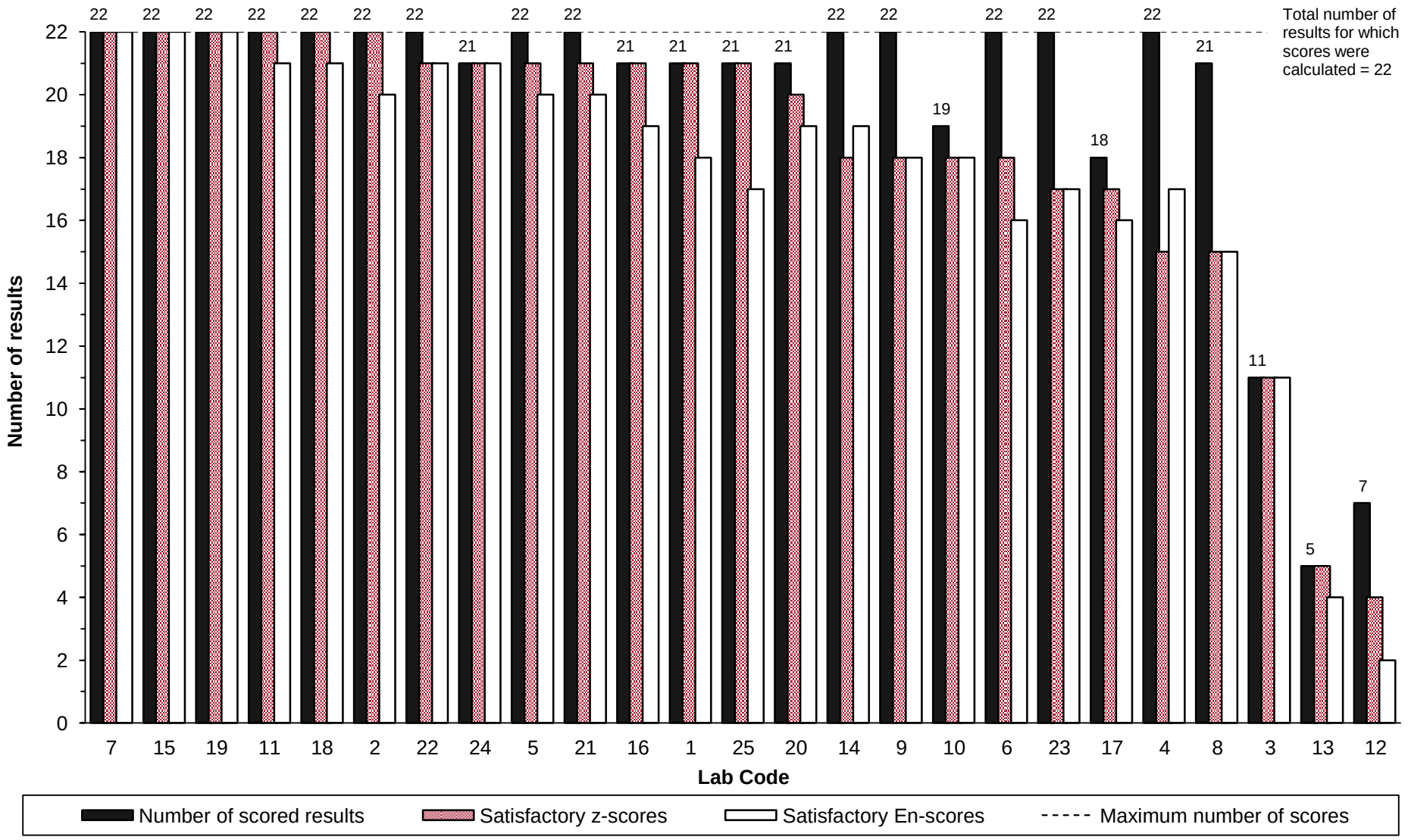


Figure 51 Summary of Participants' Performance

6.9 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 the 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 laboratories for TRH in soil over the last 10 studies (2013 – 2020) are presented in Figure 52. Over this period, the average proportion of satisfactory z-scores was 88%, and the average proportion of satisfactory E_n-scores was 71%.

While each proficiency testing 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.

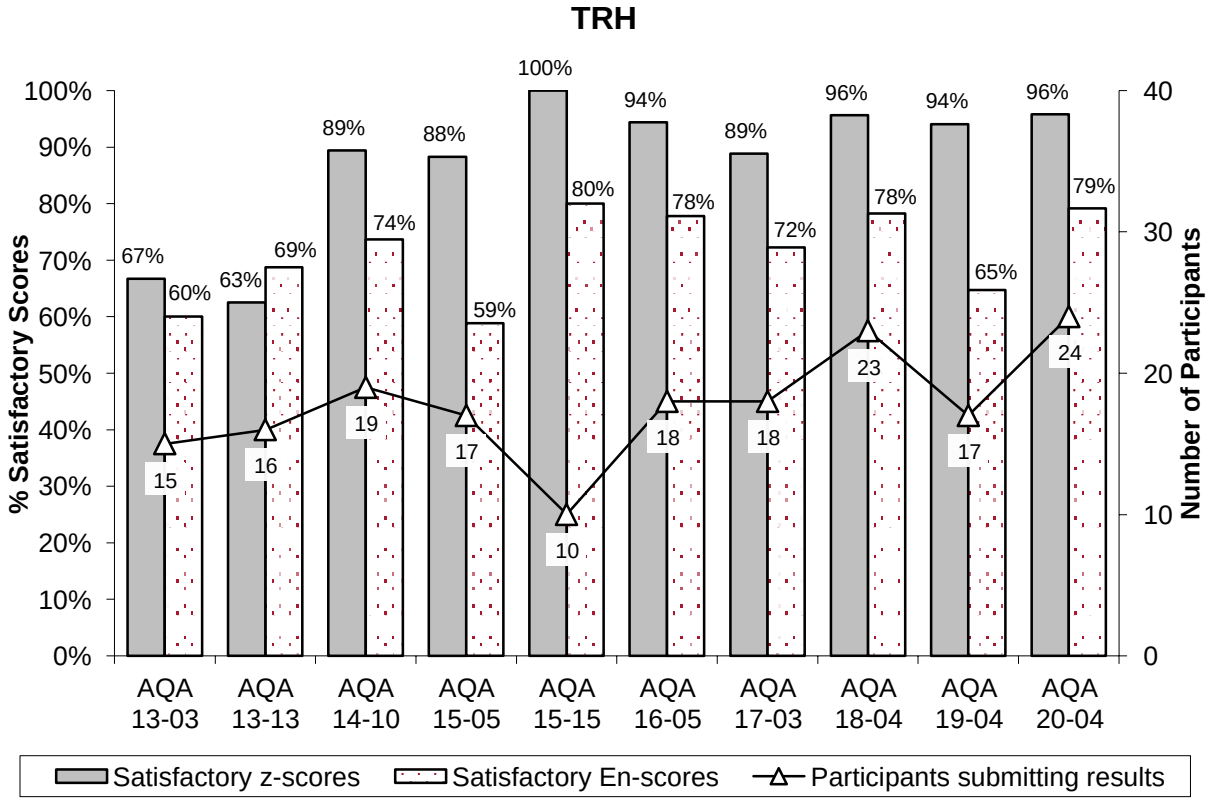


Figure 52 Summary of participants' performance for TRH (TPH for AQA 13-03 and previous studies) in Hydrocarbons in Soil PT studies

Total BTEX

A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by laboratories for Total BTEX in soil over the last 10 studies (2013 – 2020) are presented in Figure 53. Over this period, the average proportion of satisfactory z-scores was 85%, and the average proportion of satisfactory E_n-scores was 79%.

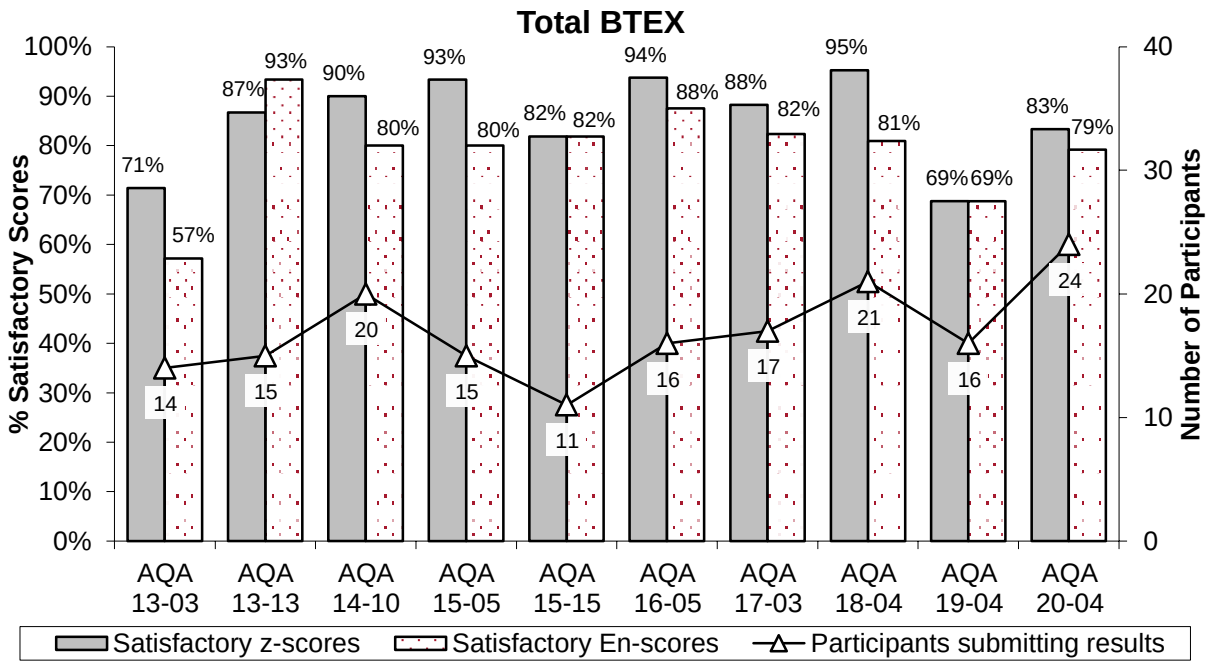


Figure 53 Summary of participants' performance for Total BTEX in Hydrocarbons in Soil PT studies

PAHs

PAHs in soil was first introduced in AQA 16-05. A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by laboratories for PAHs in soil over the last 5 studies (2016 – 2020) are presented in Figure 54. Over this period, the average proportion of satisfactory z-scores was 90%, and the average proportion of satisfactory E_n-scores was 86%.

While each proficiency testing 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.

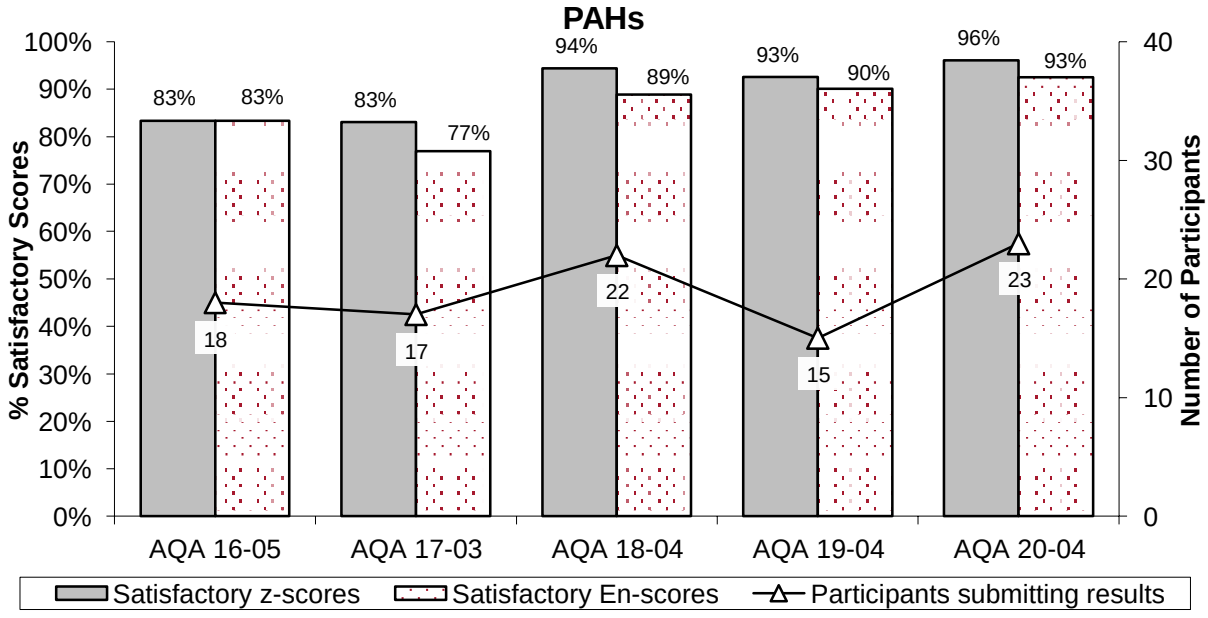


Figure 54 Summary of participants' performance for PAHs in Hydrocarbons in Soil PT studies

A plot of the robust average, expressed as a percentage of the spiked concentration, for PAHs in Menangle topsoil since 2016 is presented in Figure 55. 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 PAH analytes considered in this study, the robust averages were lower than the spiked values, consistent with previous studies. Throughout NMI PT studies, anthracene and benzo(a)pyrene have had particularly low recoveries, averaging 42% and 35% respectively for the robust average to spiked value. Chrysene, fluoranthene, fluorene, phenanthrene and pyrene have had higher recoveries over this period, with averages in the range of 74% to 86% for the robust average to spiked value.

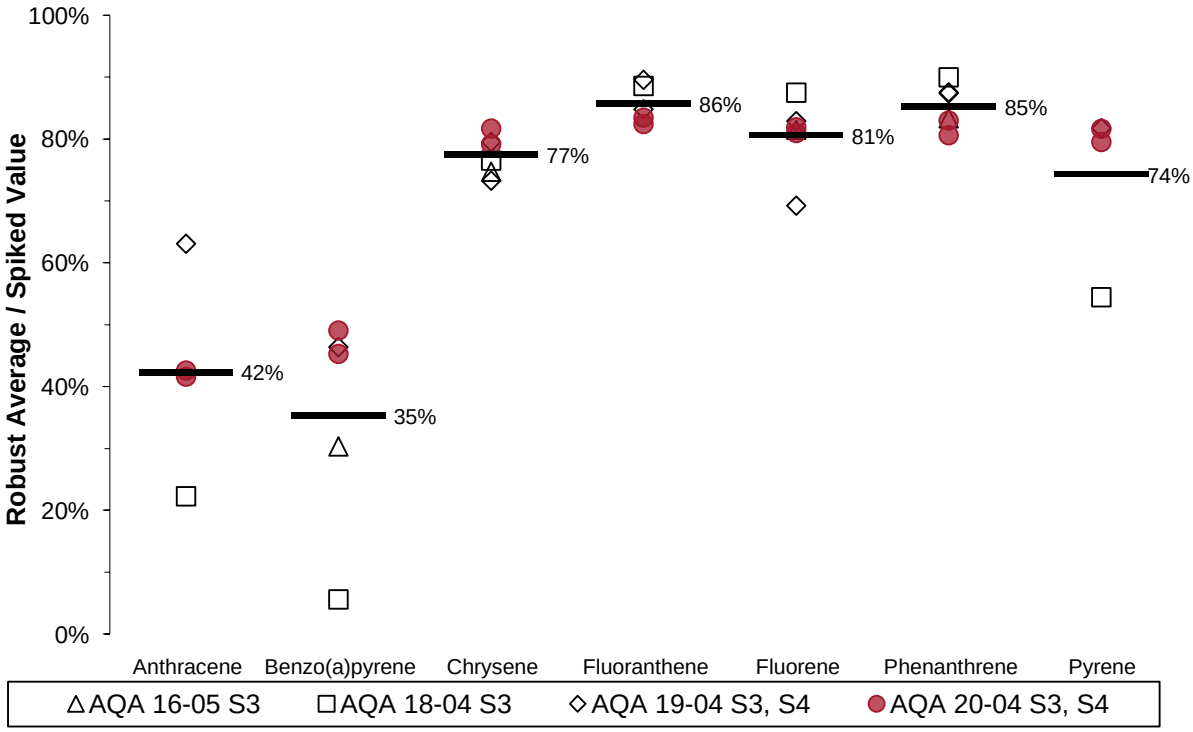


Figure 55 Robust Average as % of Spiked Value for PAHs in Menangle Topsoil (line indicates average)

7 REFERENCES

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APPENDIX 1 – SAMPLE PREPARATION

A2.1 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.

A2.2 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 120ºC for two hours. The dried soil was sieved and the fraction between 355 – 850 μm was retained and used to prepare Samples S1, S2, S3 and S4.

Sample S1: Into a stainless steel pot 3001.4 g of dried and sieved Menangle topsoil was placed. Dichloromethane was added to moisten the soil. A 10.09 g aliquot of sparged diesel was added. In addition 4.0 mL of PENRITE INDUS PRO HYDRAULIC 68 was added. The mixture was thoroughly stirred and the solvent was allowed to evaporate. The mixture was divided into 50 g portions using a Retsch PT 100 sample divider and packed into screw-capped glass jars, labelled in numeric fill order and stored in a refrigerator.

Sample S2: 3001.4 g of dried, sieved Menangle topsoil was placed in a 10 L stainless steel drum with a clamp-locked lid. The drum and soil were cooled in a freezer overnight. The drum containing the soil was removed from the freezer and the lid removed. 8.264 g of unleaded petrol was added to a cooled beaker and 3.00 g of sparged diesel was weighed into a second beaker. The contents of the beakers were added to the soil as quickly as possible. The drum was sealed and vigorously shaken. The sealed drum was then packed into another large drum and surrounded by cold gel-packs. The drums were then tumbled for 60 minutes on a hoop mixer. The soil was scooped into glass jars, tapped, topped up to minimise the vapour space and sealed. The process of filling the jars was conducted with the drum in an open freezer in an attempt to minimise the loss of volatiles. The jars were labelled with the numbers representing the fill order. After the caps were sealed with Parafilm the jars were shrink-wrapped and stored in a freezer.

Samples S3 & S4: Both Samples S3 and S4 were prepared using dried and sieved Menangle topsoil from Australian Native Landscapes. For Sample S3, 1104.9 g of dried and sieved Menangle topsoil was placed in a 3 L round bottom flask. Dichloromethane was then added to the soil to allow it to be suspended. Using a Gilson pipette aliquots of the seven 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 temperature 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 1120.1 g of clean soil. The total soil mass was 2225.0 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 1107.9 g into the 3 litre flask, 1119.1 g of diluent soil making a total of 2227.0 g of spiked soil.

APPENDIX 2 – TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 33 to 35.

Table 33 Test Methods Sample S1 TRH

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference*
1	10	Solid-Liquid	DCM:ACETONE (1:1)	None	GC-FID	
2	10	Solid-Liquid	DCM/Acetone	None	GC-FID	USEPA SW-846
3	NT					
4		Liquid-Liquid	Hexane:Pentane		GC-FID	In-house
5	10	Solid-Liquid	DCM:Acetone	None	GC-FID	In house
6	15	Sonication	1:1 DCM:Acetone	nil	GC-FID	NEPM 2013
7	10	Solid-Liquid	DCM:Acetone 50:50	None	GC-FID	USEPA 3510
8	10	Solid-Liquid	Hexane:Acetone	None	GCFID	USEPA 8270
9	10	Solid-Liquid	DCM/Acetone	None	GC-FID	USEPA 8270C
10	5	Sonication	Hexane,Acetone 1:1	Silica/glass wool column	GC-FID	US EPA 3550C
11	10	Solid-Liquid	Hexane	None	GC-FID	USPEA 3510
12	5	Solid-Liquid	1:1 DCM:acetone	None	GC-FID	NEPM B3 2013
13	10	Sonication	DCM:Acetone 1:1	None	GC-FID	USEPA 8015
14	50	Solid-Liquid	Acetone/DCM	None	GC-FID	USEPA 8015 Revision D
15	10	Solid-Liquid	10ml of DCM:ACETONE 50:50 v/v		GC-FID	USEPA3510
16	10	Solid-Liquid	DCM/Acetone	None	GC-FID	
17	10	Sonication	Acetone:Dichloromethane (1:1)	None	GC-FID	USPEA 8270C
18	10	Solid-Liquid	DCM/Acetone	None	GC-FID	USEPA 8015
19	10	Solid-liquid	DCM:Acetone	none	GC-FID	USEPA 3510
20	10.1053	Sonication	DCM:ACE	NaSO4 through pastur pipette	GC-FID	In house
21	10	inhouse method	DCM/ACETONE	None	GC -FID	NEPM 1999
22	10	Solid-Liquid	DCM:Acetone (50:50)	None	GC-FID	USEPA 3510
23	10	Solid-Liquid	DCM	silica	GC-FID	In house
24	10	Solid-Liquid	DCM/Acetone	None	GC-FID	In House
25	10	Solid-Liquid	DCM/ACE	None	GD-FID	USEPA8015MOD

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

Table 34 Test Methods Sample S2 BTEX

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	10	Solid-Liquid	Methanol		P&T GC-MS	
2	10	Solid-Liquid	Methanol	None	GC-Purge and trap	USEPA SW-846 Method 5030
3	NT					
4		Head Space			GC-MS	In-house
5	2	Purge and Trap	MeOH	None	GC-MS	In house
6	10	Sonication	Methanol	nil	GC-MS	NEPM 2013
7	5	Purge and Trap	P&T Methanol	None	P&T GC-MS	USEPA 8260
8	10	Solid-Liquid	Methanol	None	GCMS	USEPA 8260
9	10	Purge and Trap	Methanol	None	GC-MS	USEPA 8260B
10	5	Sonication	Methanol	None	GC-MS-ISQ	US EPA 5021A
11	10	Solid-Liquid	Methanol	None	GC-MS	USPEA 8260
12	5	Solid-Liquid	Methanol	None	GC-MS	NEPM B3 2013
13	14	Sonication	Methanol	None	GC-MS Headspace	USEPA 8260B
14	10	Solid-Liquid	Methanol	None	P&T GCMS	
15	10	Solid-Liquid	Methanol	None	P&T GCMS	USEPA 8260
16	10	Solid-Liquid	Methanol	None	GC-MS	
17	10	Solid-Liquid	Methanol	None	GC-MS	USEPA 8260B
18	5	Solid-Liquid	DCM/Acetone	None	GC-P&T	USEPA 8260
19	5	Purge and Trap	P&T Methanol	none	P&T GCMS	USEPA 8260
20	10	Sonication	MeOH	None	P&T GC MS	in house method based on USEPA 8260
21	10	Purge and Trap	MEOH	None	GC MS	USEPA 8260
22	5	Purge and Trap	Methanol	None	P&T GC-MS	USPEA 8260
23	2	Purge and Trap	methanol	None	Gc-MS	USEPA8260
24	5	Solid-Liquid	Methanol	None	GC-MS P&T	USEPA 8260
25	5	Purge and Trap	MEOH	None	GC-MS	USEPA 8260D

Table 35 Test Methods Samples S3 and S4 PAHs

Lab. Code	Sample Mass (g)	Extraction	Extraction Solvent	Clean-Up	Measurement Instrument	Method Reference
1	10	Solid-Liquid	DCM:ACETONE (1:1)	None	GC-MS	
2	10	Solid-Liquid	DCM/Acetone	None	GC-QQQ	USEPA SW-846 METHOD 8100
3	10	Liquid-Liquid	DCM:ACE	None	GC-FID	In House
4		Liquid-Liquid	DCM	None	GC-MS	In-house
5	10	Solid-Liquid	DCM:Acetone	None	GC-MS/MS	In house
6	15	Sonication	DCM	nil	GC-MS	USEPA 3550C
7	10	Solid-Liquid	DCM:Acetone 50:50	None	GC-MS	USEPA 8270
8	10	Solid-Liquid	Hexane:Acetone	None	GCMS	USEPA 8270
9	10	Solid-Liquid	DCM/Acetone	None	GC-MS	USEPA 8270C
10	5	Sonication	Hexane,Acetone 1:1	Silica/glass wool column	GC-MS-ISQ	US EPA 3550C
11	10	Solid-Liquid	DCM/Acetone	None	GC-MS/MS	USPEA 8270
12	NT					
13	NT					
14	50	Solid-Liquid	Acetone/Hexane	None	GCMS	AOAC 15th Edition 1990
15	5	Solid-Liquid	10ml of DCM:ACETONE 50:50 v/v		GC-MS	in- house USEPA referenced Method
16	10	Solid-Liquid	DCM/Acetone	None	GC-MS	
17	10	Sonication	Acetone:Dichloromethane (1:1)	None	GC-MS	USEPA 8270C
18	10	Solid-Liquid	DCM/Acetone	None	GC-MS	USEPA 8270
19	10	Solid-Liquid	DCM:Acetone	none	GCMS	USEPA 8270
20	10	Sonication	DCM:ACE	None	GC MS	USPEA 8270
21	10	inhouse method	DCM/ACETONE	None	GC MS	USEPA 8270
22	10	Solid-Liquid	DCM:Acetone (50:50)	None	GC-MS/ GC-MS-MS	USEPA 8270
23	10	Solid-Liquid	DCM:acetone	None	GC-QQQ	In house
24	10	Solid-Liquid	DCM/Acetone	None	GC-MS	USEPA 8270
25	10	Solid-Liquid	DCM/ACE	None	GC-MS	USEPA 8270E

APPENDIX 3 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY

When the robust average was calculated using the procedure described in ISO 13258:2015 'Statistical methods for use in proficiency testing by interlaboratory comparisons – Annex C',[7] the uncertainty was estimated as according to Equation 4.

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

where:

$u_{rob\ av}$	is robust average standard uncertainty
$S_{rob\ av}$	is robust average standard deviation
p	is 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 36.

Table 36 Uncertainty of robust average for pyrene in Sample S4

No. results (p)	23
Robust Average	2.582 mg/kg
$S_{rob\ av}$	0.282 mg/kg
$u_{rob\ av}$	0.074 mg/kg
k	2
$U_{rob\ av}$	0.148 mg/kg

The robust average for pyrene in Sample S4 is 2.58 ± 0.15 mg/kg.

APPENDIX 4 – 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
FID	Flame Ionization Detector
GC	Gas Chromatography Flame
HEX	Hexane
HS	Headspace
IEC	International Electrotechnical Commission
ISO	International Standards Organisation
LLE	Liquid-Liquid Extraction
Max.	Maximum value in a set of results
Md	Median value in a set of results
Min.	Minimum value in a set of results
MS	Mass Spectrometry
MSMS	Tandem Mass Spectrometry
NATA	National Association of Testing Authorities
NEPM	National Environmental Protection Measure
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
P&T	Purge and Trap
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
SLE	Solid-Liquid Extraction
SS	Spiked Samples
TPH	Total Petroleum Hydrocarbons
TRH	Total Recoverable Hydrocarbons

END OF REPORT