Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

Proficiency Test Report AQA 18-04 Hydrocarbons in Soil

June 2018

ACKNOWLEDGMENTS

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

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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SUMMARY

Proficiency test AQA 18-04 Hydrocarbons in soil was conducted in March/April 2018, and twenty-three laboratories submitted results. This is the third NMI PT study to include PAHs in soil.

Four sets of test samples were prepared at the NMI laboratory in Sydney using three different soils - Menangle topsoil bought from a Sydney supplier, clay from regional NSW and contaminated soil from a refinery.

Sample S1 was Menangle topsoil spiked with a diesel fuel extract of a contaminated soil from a refinery
Sample S2 was Menangle topsoil to which was added a mixture of unleaded petrol and diesel fuel.
Sample S3 was Menangle topsoil soil spiked with anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.
Sample S4 was clay spiked with anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.

Participants were asked to report Total Recoverable Hydrocarbons (TRH) (semivolatile components) in Sample S1; benzene, toluene, ethylbenzene and xylenes (BTEX) and volatile fraction C6-C10 in Sample S2 and polycyclic aromatic hydrocarbons (PAHs) in Samples S3 and S4.

The assigned values were the robust average of participants' results.

Of a possible 529 numeric results a total of 424 (80%) were submitted.

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

> *To compare the performances of participant laboratories and to assess their accuracy in the identification and measurement of petroleum hydrocarbon pollutants in soil;*

Laboratory performance was assessed using both z-scores and E_n-scores.

Of 348 results for which z-scores were calculated, 323 (93%) returned a satisfactory score of $|z| \le 2$.

Of 348 results for which E_n-scores were calculated, 299 (86%) returned a satisfactory score of $|E_n| \le 1$.

Laboratories **5**, **8**, **11**, **17**, **20** and **22** returned satisfactory z-scores and E_n-scores for all analytes for which scores were calculated.

> *To assess the ability of participant laboratories to correctly identify PAHs in soil;*

Seven PAHs were added to Samples S3 and S4 – anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluroene, phenanthrene and pyrene.

Anthracene, benzo(a)pyrene and pyrene presented the most difficulty for participants' laboratories, especially when extracting from Sample S4 (clay soil).

> *To develop the practical application of traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates;*

Of 424 numeric results, 419 (99%) were reported with an associated expanded measurement uncertainty. The magnitude of these uncertainties was within the range 0 – 200% relative.

Assigned values were the consensus of participants' results, so although expressed in SI units, metrological traceability of the assigned values has not been established.

To evaluate the laboratories' test methods.

For TRH (semi-volatile components) in Sample S1 and PAHs in Sample S3, participants used a variety of extraction solvents such as DCM/acetone, DCM only, toluene or hexane/acetone. Tumbling, sonication or ASE were used by some participants to facilitate extraction. Participants measured TRH using GC-FID and PAHs using GC-MS, GC-MS/MS or GC-FID.

For BTEX and volatile fraction C6-C10 in Sample S2 most participants used methanol extraction followed by purge-and-trap GC-MS measurement. Laboratories **4**, **6**, **9**, **13** and **21** used headspace with either GC-FID or GC-MS.

No trends were evident with the test methods.

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.

NMI PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMI offers studies in:

- pesticide residues in fruit and vegetables, 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;
- allergens in food and
- folic acid in flour.

1.2 Study Aims

The aims of the study were to:

- compare the performances of participant laboratories and to assess their accuracy in the identification and measurement of hydrocarbon pollutants in soil;
- assess the ability of participant laboratories to correctly identify PAHs in soil;
- develop the practical application of traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates; and
- evaluate the laboratories' test methods.

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

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.[1] The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.[2] These documents have been prepared with reference to ISO Standard 17043[3] and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[4] This study falls within the scope of NMI's accreditation as a proficiency testing provider.

2 STUDY INFORMATION

2.1 Selection of Hydrocarbons

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

Investigation levels for the hydrocarbons studied are set out in Schedule B1 of the National Environmental Protection Measure (NEPM) as amended 2013.[5]

2.1 Study Timetable

The timetable of the study was:

Invitation issued:	12/02/2018
Samples dispatched:	28/02/2018
Results due:	9/04/2018
Interim report issued:	18/04/2018

2.2 Participation

Participated	23
Submitted results	23

The laboratories that participated are listed in Appendix 1.

2.3 Test Material Specification

Four test samples were prepared:

Sample S1 (TRH) was prepared by spiking Menangle topsoil purchased from a Sydney supplier with diesel fuel extract of a contaminated soil from a refinery.

Sample S2 (BTEX) was prepared from Menangle topsoil purchased from a Sydney supplier spiked with unleaded petrol and treated diesel fuel.

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

Sample S4 (PAH) was prepared from clay sourced from regional NSW spiked with anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.

2.4 Laboratory Code

Participants were assigned a confidential code number.

2.5 Sample Preparation

The preparation of the study samples is described in Appendix 2.

2.6 Homogeneity and Stability Testing

Samples were prepared using a validated preparation technique. No homogeneity or stability testing was performed. Results returned by participants gave no reason to question the homogeneity or stability of these samples.

2.7 Sample Storage, Dispatch and Receipt

Prior to dispatch, Samples S1, S3 and S4 were stored in a refrigerator at approximately 4°C and Sample S2 was stored in a freezer at -18°C.

The samples were packaged into insulated styrene foam boxes and dispatched by courier on 28 February 2018.

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 faxback form for participants to confirm the receipt and condition of the test samples.

An electronic results sheet was e-mailed to participants.

2.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- Do not test for volatile hydrocarbons (≤ C10) or BTEX components in Sample S1.
- 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: Poly-aromatic hydrocarbons from the list below. The concentration range is between 0.05-50 mg/kg.

Naphthalene	Benz[a]anthracene
Acenaphthylene	Chrysene
Acenaphthene	Benzo[b]fluoranthene
Fluorene	Benzo[k]fluoranthene
Phenanthrene	Benzo[a]pyrene
Anthracene	Indeno[1,2,3-cd]pyrene
Fluoranthene	Dibenz[a,h]anthracene
Pyrene	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 (eg 2000 ± 200 mg/kg).
- Report the basis of your uncertainty estimates (eg 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 e-mail proficiency@measurement.gov.au).
- Please return completed result sheet by 9 April 2018. Late results may not be included in the study report.

3 PARTICIPANT LABORATORY INFORMATION

Table 1 Test Methods Sample S1 TRH

Lab. Code	Sample Mass (g)	Extraction	Cleanup	Measurement
1	10	DCM/Acetone		GC/FID
2	10	1:1 Hexane:Acetone		GC-FID
3	10	Dichloromethane		GC-FID
4	8	1:1 DCM:Acetone		GC-FID
5	10	DCM/ACETONE 1:1		GC-FID
6	10	50:50 Acetone Dichlormethane		GC-FID
7	15	1:1 DCM:Acetone		GC-FID
8	10	20mL 1:1 DCM:Acetone		GC-FID
9		Semi-volatiles (>C10-C40) sonication extraction in DCM:Acetone		GC-MS Headspace and GC-FID
10	6	1:1 DCM:Acetone		GC-FID
11	10	DCM:Acetone 1:1		GC-FID
12	10	DCM/ACETONE 1:1		GC-FID
13	7-9	Hexane Acetone 1:1	Silica	GC-FID
14	10	DCM/Acetone		GC-FID
15	5.1	DCM/Acetone (1:1)		GC-FID
16	10	DCM/Acetone		GC-FID
17	10	1:1 DCM:Acetone		GC-FID
18	10	DCM:acetone 1:1	Silica	GC-FID
19	10	Dichloromethane: Acetone (1:1)		GC-FID
20	10	50:50 DCM:Acetone		GC-FID
21	10	Dichloromethane:Acetone=1:1 (ASE)	Silica gel	GC/FID
22	9	1:1 DCM:Acetone		GC-FID
23	10	DCM/Acetone		GC-FID

Table 2 Test Methods Sample S2 BTEX

Lab. Code	Sample Mass. (g)	Extraction	Measurement
1	10	Methanol	GC/MS
2	10	Methanol	PT-GCMS
3	4	Methanol	GC-MS P&T
4	5	Methanol	HS-GCMS
5	5	Methanol	GC-MS Purge and Trap.
6	0.5		Headspace GC-FID
7	10	Methanol	GC-MS (purge and trap)
8	10	Methanol	GCMS P&T, DB-VRX column
9	2	Methanol	GC-MS Head space
10	14	Methanol	GCMS
11	5	Methanol	Purge and Trap GC-MS
12	5	Methanol	GC-MS Purge and Trap.
13	7-9	Methanol	Headspace GCMS
14	10	Methanol	GC-MS
15	12.682	Methanol	GCMS
16	5	Methanol	GCMS
17	10	Methanol	P&T-GC-MS
18	2	Methanol	Gc MS purge and trap
19	10	Methanol	Purge & Trap GC-MS
20	10	Methanol	purge and trap GCMS
21	2	Sodium chloride / phosphoric acid matrix modifying solution	GC/MS Headspace
22	4	Methanol	GC-P&T
23	5	Methanol	Purge and Trap- GC-MS

Table 3 Test Methods Sample S3/S4 PAHs

Lab. Code	Sample Mass (g)	Extraction	Solvent	Measurement	Method Reference
1	10	2hr tumbling with solvent	DCM/Acetone	GC/MS	In-house based on EPA8270C
2	10	Solid-Liquid	1:1 Hexane:Acetone	GC-MS	In-house based on US EPA 8270D
3	10	Solvent extraction	Dichloromethane	GC-MS	GCMS 11.11
4	5	Solvent extraction on whirly-gig	1:1 DCM:Acetone	GC-MS	
5	10		DCM/ACETONE 1:1	GC-MS	USEPA 8270
6	10	liquid-liquid	50:50 acetone dichlormethane	GC-FID	In house method
7	15	solid-liquid, ultrasonic	DCM	GC-MS	USEPA 8270C
8	10	solid –liquid	1:1 DCM:Acetone	GC-MS	In house based on USEPA 8270e.
9	10	Sonication	DCM and Acetone	GC-MS	In-house based on USEPA8270
11	10		DCM: Acetone 1:1	GC-MS	USEPA 8270C
12	10		DCM/ACETONE 1:1	GC-MS	USEPA 8270
13	7-9	Sonication	Hexane Acetone 1:1	GCMS SIM	In-house based on USEPA 8270C
14	10		DCM/Acetone	GC-MS	USEPA8270
15	10	tumbling / sonication	DCM/Acetone (1:1)	GC MS	in house based on USEPA 8270
16	10	DCM/Acetone	Toluene	GCMS	USEPA SW-846 method 8270D
17	10	20mL of 1:1 DCM:Acetone. 5g sodium sulphate was added, and the sample was tumbled end over end for 1 hour.	1:1 DCM:Acetone	GC-MS and GC-MS/MS	In house based on USEPA 8270e.
18	5	Accelerated Solvent Extractor (ASE)	DCM:acetone 1:1	GCMS	USEPA 8270C modified
19	10	Solid-liquid	DCM/Acetone	GC/MS	USEPA 8270C
20	10	solid –liquid	50:50 DCM:Acetone	GCMS	In house based on USEPA 8270e.
21	10	ASE	Dichloromethane:Acetone=1:1	GC-MS	In-house based on USEPA 8270D
22	9	solid-liquid	1:1 DCM:Acetone	GC-MS	USEPA 8270E
23	10	Solid-Liquid	DCM/Acetone	GC-MS	In house method

Table 4 Basis of Expanded Uncertainty Estimate

Lab. Code	Basis of Uncertainty Estimate
1	Long term standard precision
2	Professional judgement.
3	Top down approach. NATA technical note 33.
4	Tech Note 33
5	30% at >10*PQL
6	Spiking Recoveries
7	The estimate is compliant with the "ISO Guide to the Uncertainty in Measurement" and is based on in-house validation and quality control data. A coverage factor of 2 is used to give a confidence level of approximately 95%.
8	TRH/PAH: QC DATA – Control Charts BTEX: Estimation of MU from within-laboratory data on bias and precision has been calculated by using the procedures outlined in ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques
9	"bottom-up" approach
10	Standard uncertainty based on historical data.
11	30% at >10*PQL
12	30% at >10*PQL
13	Repeatability precision
14	40%
15	TRH: In-house validation data BTEX: Uncertainty based on precision data. Expanded Uncertainty presented, k = 2 PAH: in house methodology
16	QC Data
17	Control Charts
18	Longterm reproducibility
19	Quality Control Requirement
20	Control Charts
21	Uncertainty budget
22	Historical QC data.
23	Precision and estimate of the method and Laboratory bias

Table 5 Additional Participants' Comments

Lab Code	Sample	Comment or Discussion
21	S1	Sample analysed on an as-received basis
6	S2	Xylenes result the sum of m/p-xylene and o-xylene calculations
7	S2	Benzene, C6-C10 not reported. Sample was reanalysed but was out of holding time.
10	S2	The result entered above for "C6-C10 Hydrocarbons" is a C6-C9 result.
13	S2	The hydrocarbon band was measured for C6-C9 not C6-C10
18	S2	Benzene duplicates on different soil samples varied > 50%
21	S2	Concentrations exceeded the working range of the method
21	S3	Samples analysed on as-received basis
21	S4	Samples analysed on as-received basis

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 28 with resultant summary statistics: mean, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}).

Bar charts of results and performance scores are presented in Figures 2 to 23.

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

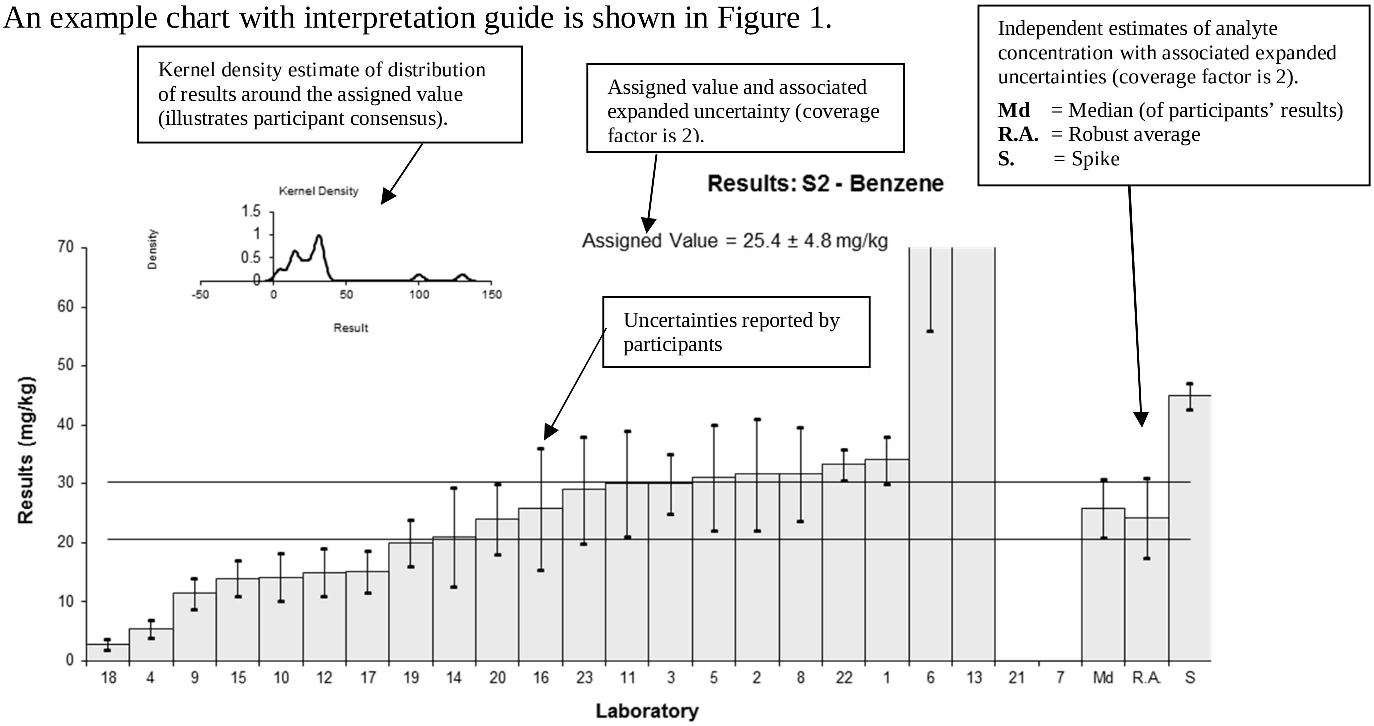


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

The assigned value is defined as: 'value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose.'[3]

For a proficiency test, the assigned value is the best available measurement of the true concentration of an analyte in the test sample.

4.3 Between-Laboratory Coefficient of Variation

The between laboratory coefficient of variation (CV) is a measure of the between laboratory variation that in the judgement of the study coordinator would be expected from participants given the analyte concentration. It is important to note this is not the coefficient of variation of participant results.

4.4 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (X) and the between-laboratory coefficient of variation (CV). This value is used for calculation of participant z-score.

$$\Sigma = X * CV \qquad \text{Equation 1}$$

4.5 z-Score

For each participant result a z-score is calculated according to Equation 2 below:

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

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|):

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

4.6 E_n-Score

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

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

where:

E_n is E_n-score
χ is a participant's result
X is the assigned value
U_χ is the expanded uncertainty of the participant's result
U_X is the expanded uncertainty of the assigned value

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

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

4.7 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2015[6] must establish and demonstrate the traceability and measurement uncertainty associated with their test results.

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[7]

5 TABLES AND FIGURES

Table 6

Sample Details

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

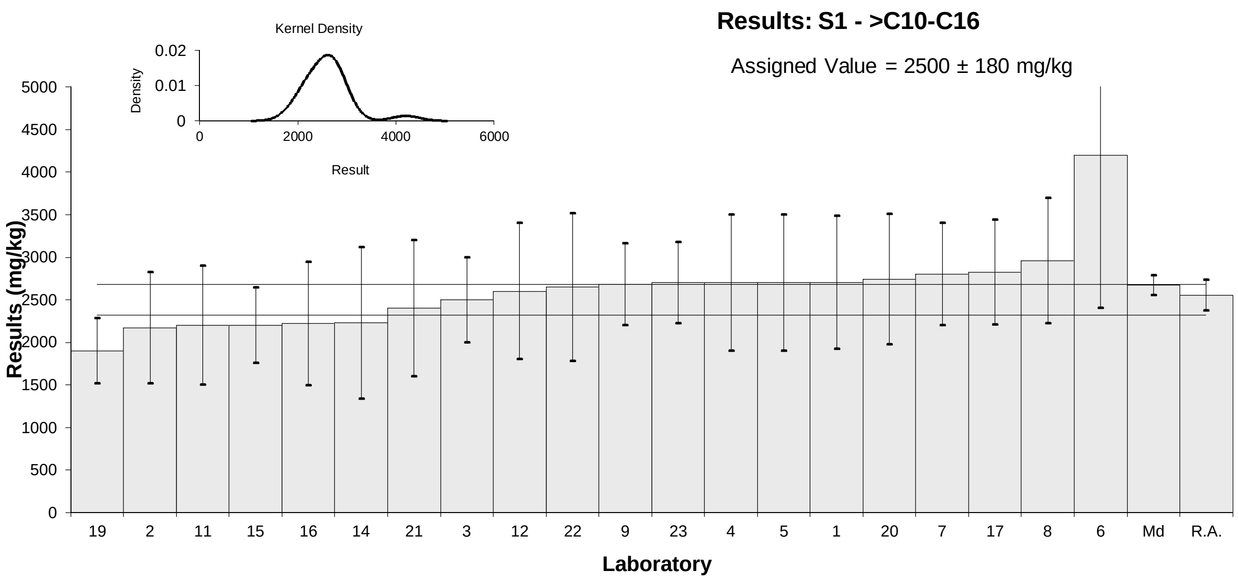
Participant Results

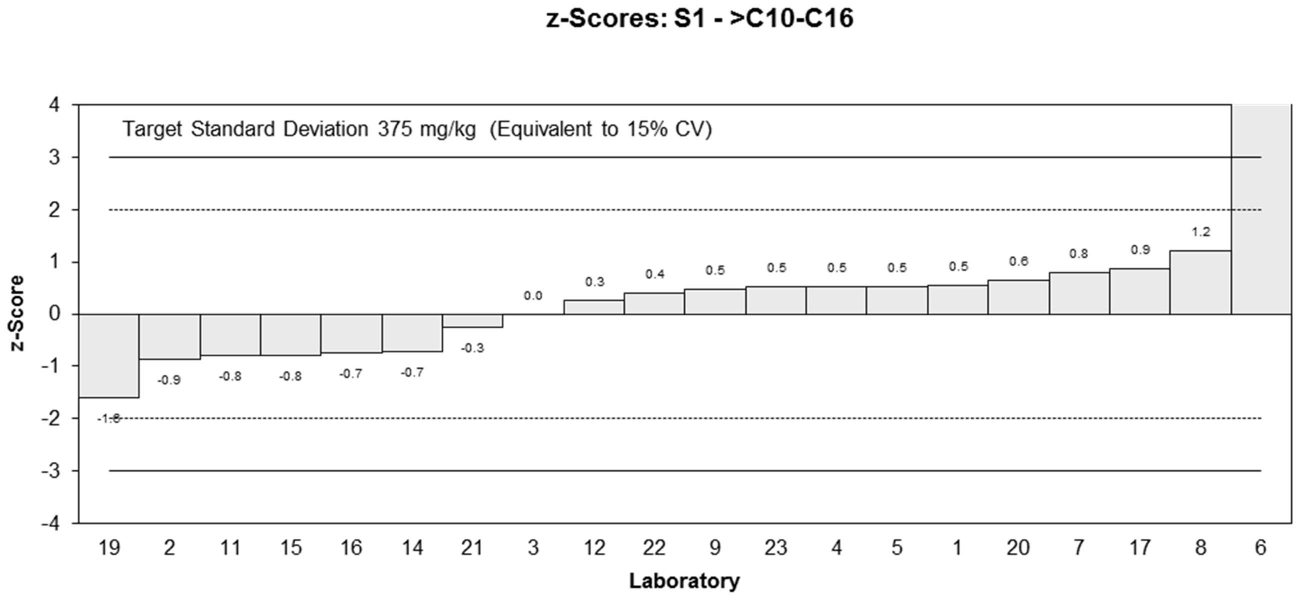
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2705	780	0.55	0.26
2	2171	651	-0.88	-0.49
3	2500	500	0.00	0.00
4	2700	800	0.53	0.24
5	2700	800	0.53	0.24
6	4200	1800	4.53	0.94
7	2800	600	0.80	0.48
8	2957	736	1.22	0.60
9	2680	482	0.48	0.35
11	2200	700	-0.80	-0.42
12	2600	800	0.27	0.12
14	2227	891	-0.73	-0.30
15	2200	440	-0.80	-0.63
16	2220	726.8	-0.75	-0.37
17	2827	616	0.87	0.51
19	1900	380	-1.60	-1.43
20	2742	768	0.65	0.31
21	2400	800	-0.27	-0.12
22	2650	867.2	0.40	0.17
23	2700	475	0.53	0.39

Statistics

Assigned Value*	2500	180
Spike	Not Spiked	
Robust Average	2550	180
Median	2670	113
Mean	2604	
N	20	
Max.	4200	
Min.	1900	
Robust SD	326	
Robust CV	13%	

*Robust average excluding laboratory 6.


Results: S1 - >C10-C16
Assigned Value = 2500 ± 180 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory


z-Scores: S1 - >C10-C16
Target Standard Deviation 375 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory

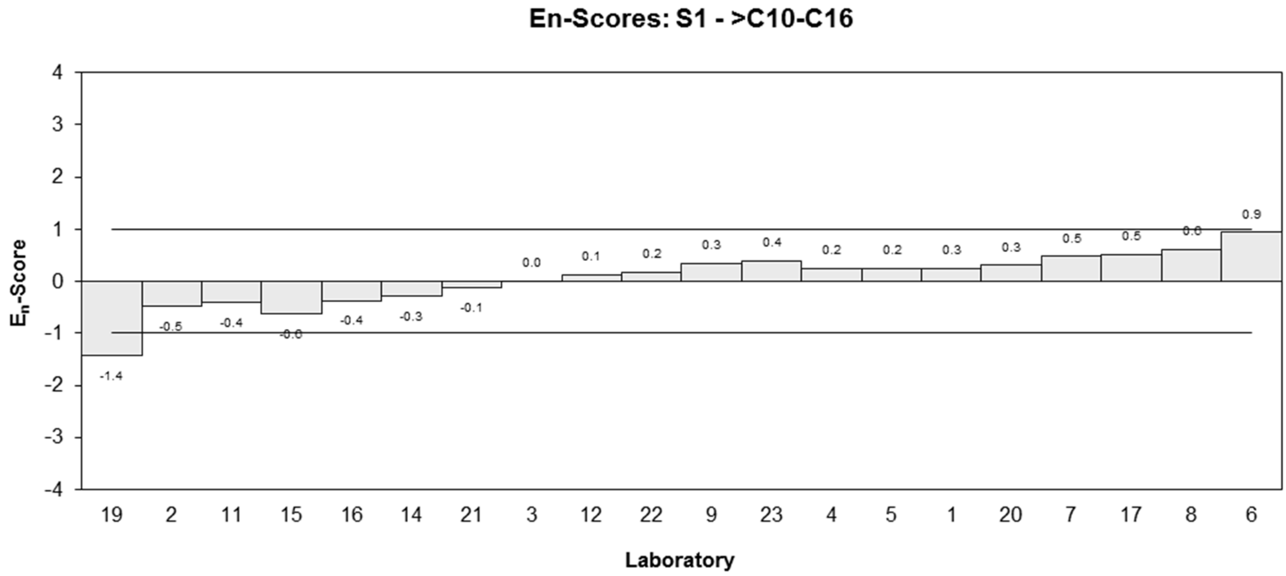

En-Scores: S1 - >C10-C16
En-Score
Laboratory

Figure 2

Table 7

Sample Details

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

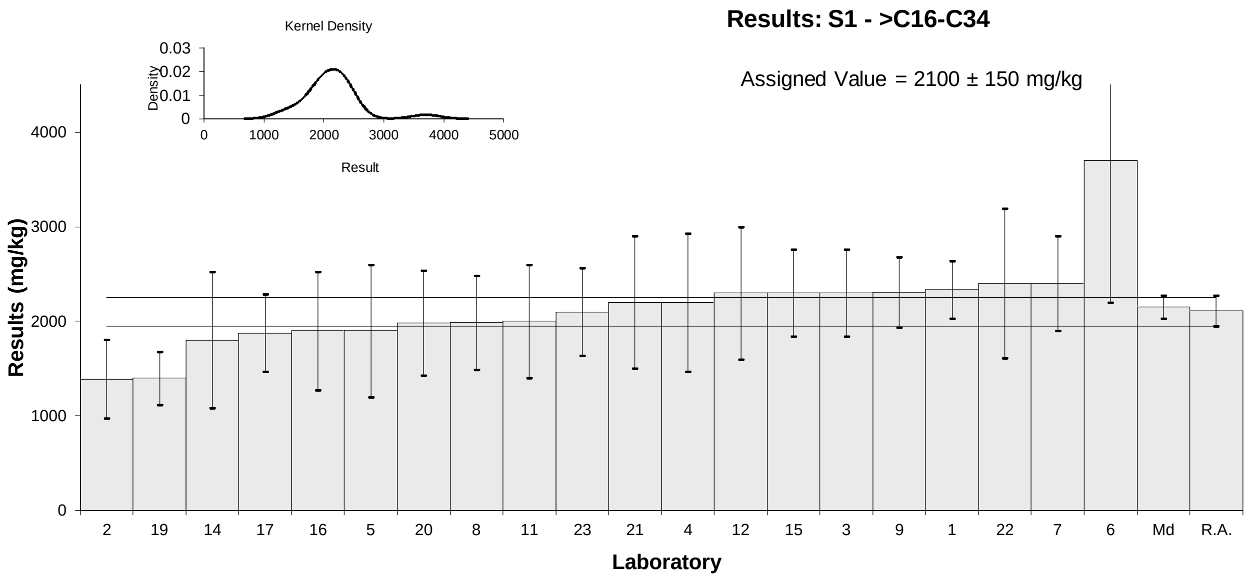
Participant Results

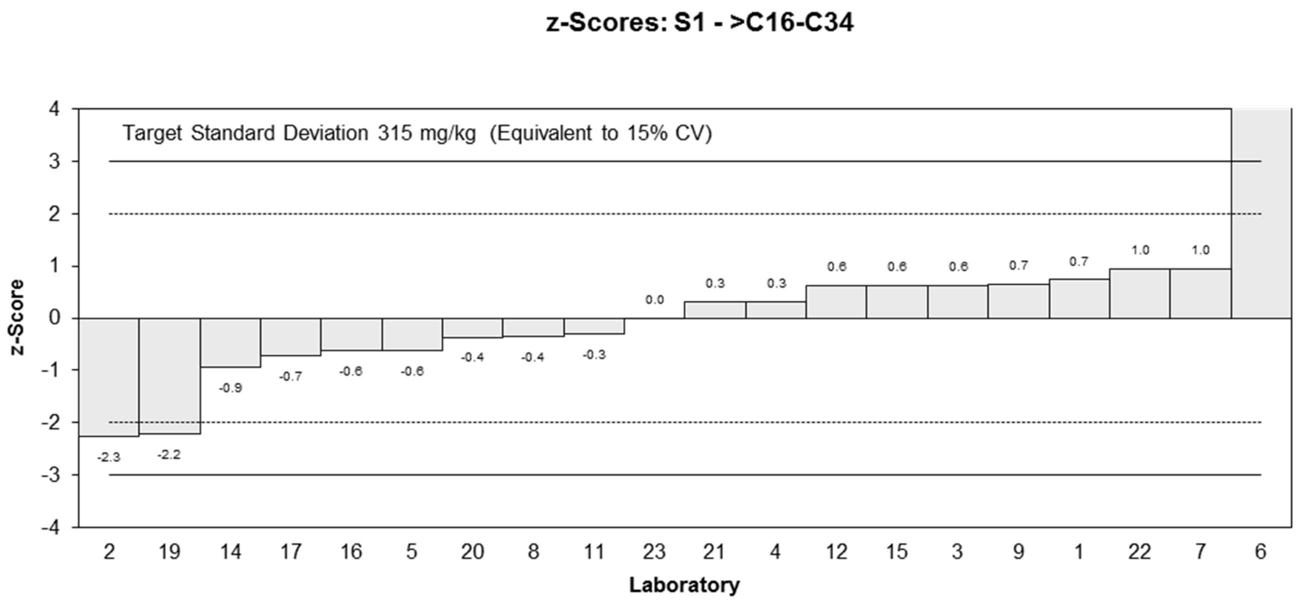
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2332	303	0.74	0.69
2	1389	417	-2.26	-1.60
3	2300	460	0.63	0.41
4	2200	730	0.32	0.13
5	1900	700	-0.63	-0.28
6	3700	1500	5.08	1.06
7	2400	500	0.95	0.57
8	1986	497	-0.36	-0.22
9	2307	369	0.66	0.52
11	2000	600	-0.32	-0.16
12	2300	700	0.63	0.28
14	1801	720	-0.95	-0.41
15	2300	460	0.63	0.41
16	1900	626.3	-0.63	-0.31
17	1875	409	-0.71	-0.52
19	1400	280	-2.22	-2.20
20	1984	556	-0.37	-0.20
21	2200	700	0.32	0.14
22	2400	790.1	0.95	0.37
23	2100	463	0.00	0.00

Statistics

Assigned Value*	2100	150
Spike	Not Spiked	
Robust Average	2109	161
Median	2150	120
Mean	2139	
N	20	
Max.	3700	
Min.	1389	
Robust SD	288	
Robust CV	14%	

*Robust average excluding laboratory 6.


Results: S1 - >C16-C34
Assigned Value = 2100 ± 150 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
2 19 14 17 16 5 20 8 11 23 21 4 12 15 3 9 1 22 7 6 Md R.A.


z-Scores: S1 - >C16-C34
Target Standard Deviation 315 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
2 19 14 17 16 5 20 8 11 23 21 4 12 15 3 9 1 22 7 6

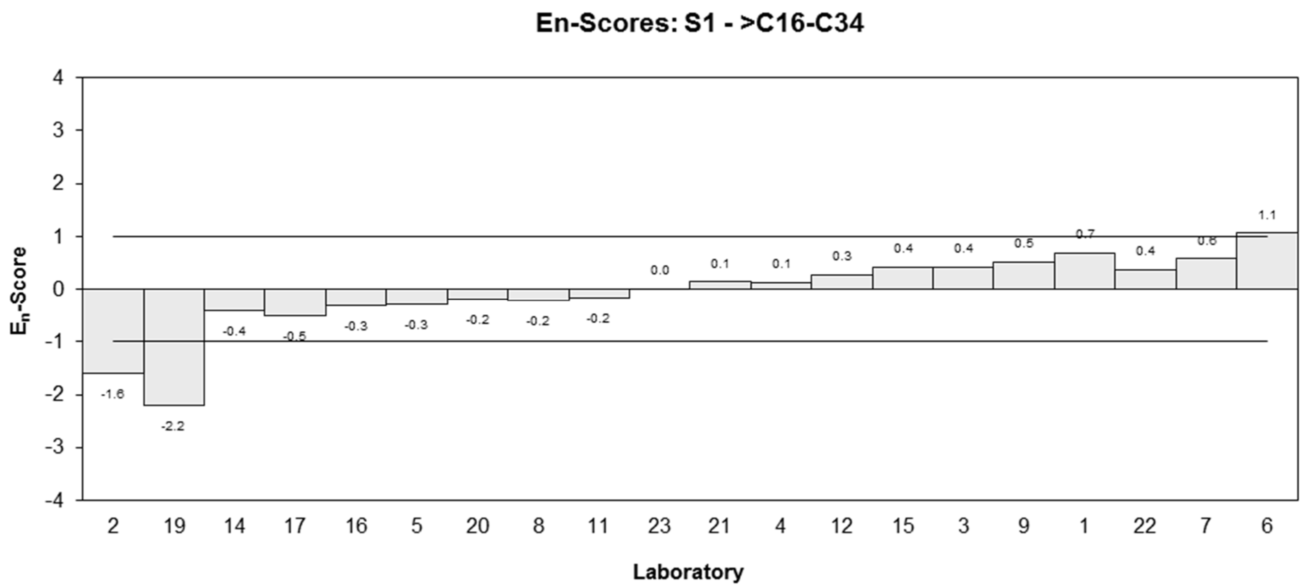

En-Scores: S1 - >C16-C34
En-Score
Laboratory
2 19 14 17 16 5 20 8 11 23 21 4 12 15 3 9 1 22 7 6

Figure 3

Table 8 Laboratories that reported for Sample S1 additional hydrocarbon ranges to those defined in Schedule B3 of the NEPM[5]

Lab Code	Range	Concentration (mg/kg)	Uncertainty (mg/kg)
10	C7-C9	<10	5.5
10	C10-C14	1190	250
10	C15-C36	3210	610
13	C10-C14	1295.96	388.79
13	C15-C33	2675.21	802.56
18	C10-C14	1540	480
18	C15-C36	3000	950

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Table 9

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5040	960	0.64	0.44
2	3560	1068	-1.51	-0.95
3	4800	960	0.29	0.20
4	4900	1900	0.43	0.16
5	4600	NR	0.00	0.00
6	8000	3300	4.93	1.03
7	5200	1100	0.87	0.53
8	4943	1236	0.50	0.27
9	4987	NR	0.56	1.55
10	4400	660	-0.29	-0.28
11	4200	1300	-0.58	-0.30
12	4900	NR	0.43	1.20
13	3971.18	1191.35	-0.91	-0.52
14	4028	NR	-0.83	-2.29
15	4500	NR	-0.14	-0.40
16	4120	726.8	-0.70	-0.62
17	4719	1029	0.17	0.11
18	4600	1500	0.00	0.00
19	3300	660	-1.88	-1.84
20	4726	1323	0.18	0.09
21	4600	1500	0.00	0.00
22	5050	1651.4	0.65	0.27
23	4800	950	0.29	0.20

Statistics

Assigned Value*	4600	250
Spike	Not Spiked	
Robust Average	4620	253
Median	4720	172
Mean	4693	
N	23	
Max.	8000	
Min.	3300	
Robust SD	486	
Robust CV	11%	

*Robust average excluding laboratory 6.

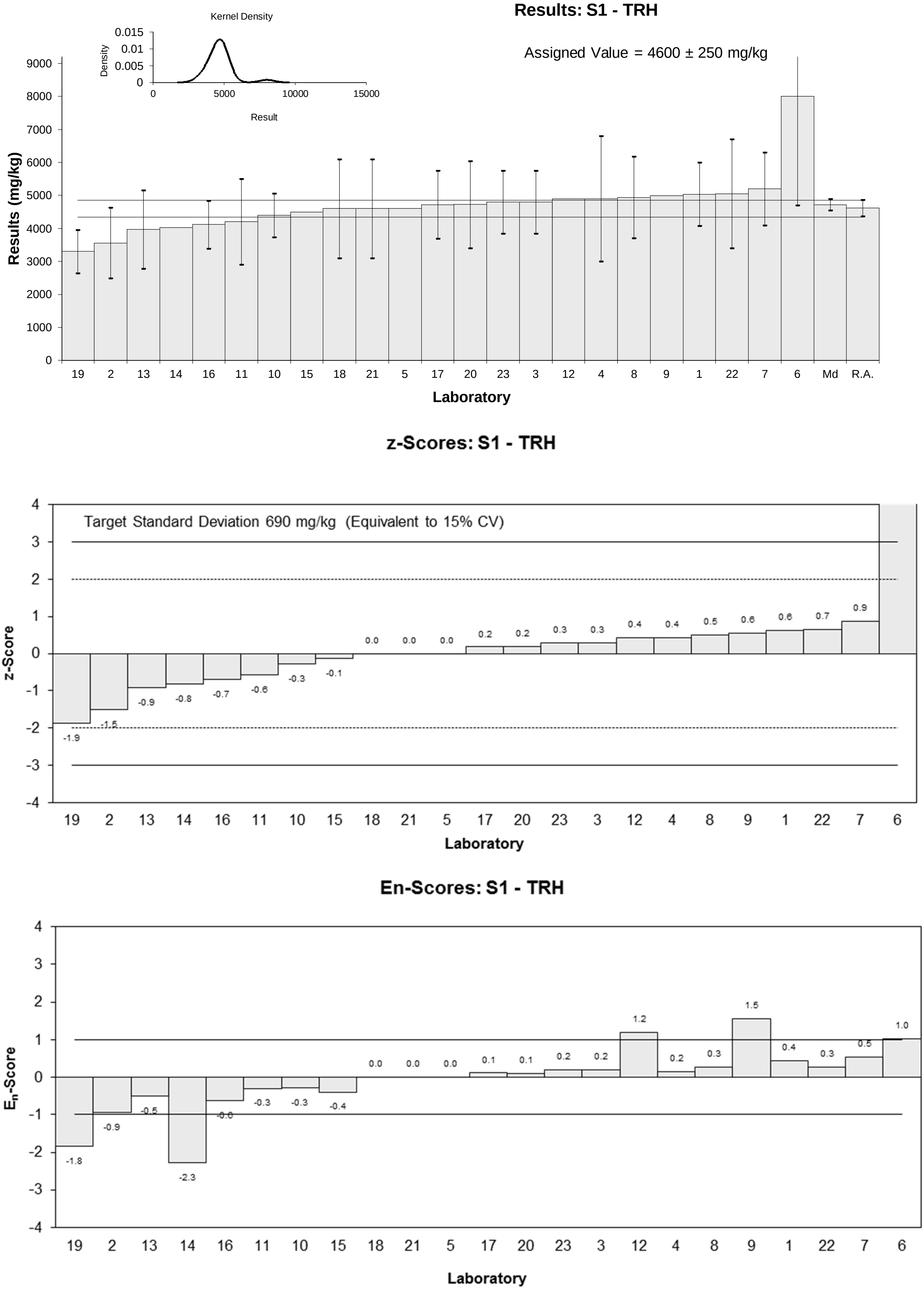

Results: S1 - TRH
Assigned Value = 4600 ± 250 mg/kg
Kernel Density
z-Scores: S1 - TRH
Target Standard Deviation 690 mg/kg (Equivalent to 15% CV)
En-Scores: S1 - TRH

Figure 4

Table 10

Sample Details

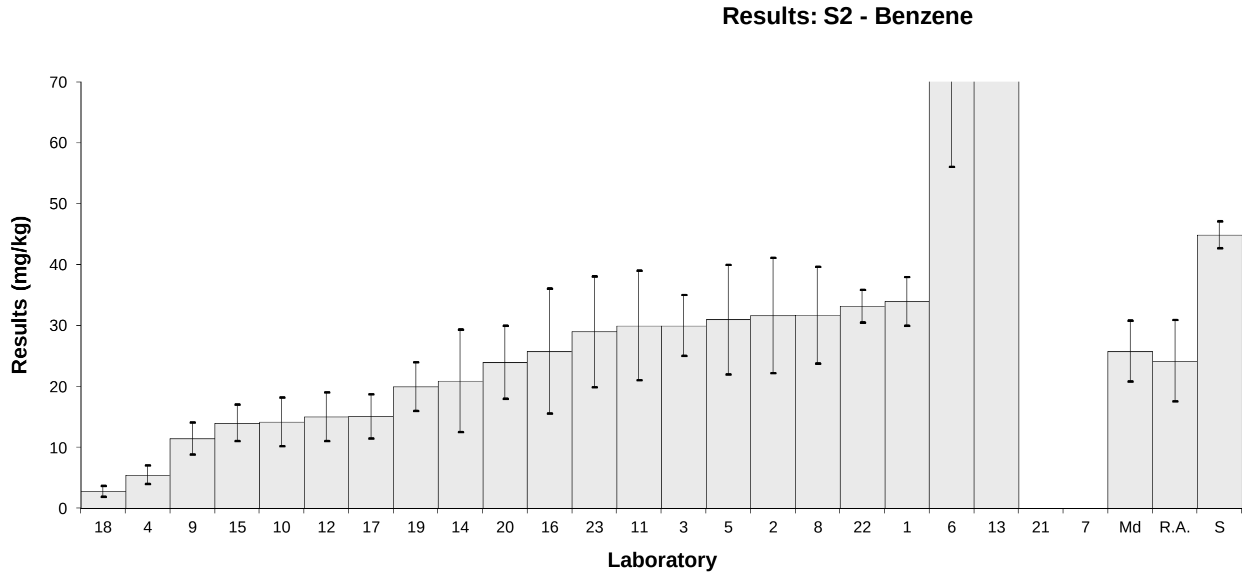
Sample No.	S2
Matrix.	Soil
Analyte.	Benzene
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty
1	34	4
2	31.65	9.50
3	30	5
4	5.5	1.5
5	31	9
6	100	44
7	NT	NT
8	31.7	7.9
9	11.410	2.624
10	14.2	4.0
11	30	9
12	15	4
13	129.69	25.94
14	20.93	8.4
15	14	3
16	25.8	10.3
17	15.1	3.6
18	2.8	0.90
19	20	4
20	24.0	6
21	NR	NR
22	33.2	2.68
23	29	9.1

Statistics

Assigned Value	Not set	
Spike	44.9	2.2
Robust Average	24.2	6.7
Median	25.8	5.0
Mean	30.9	
N	21	
Max.	129.69	
Min.	2.8	
Robust SD	12.3	
Robust CV	51%	



Results: S2 - Benzene
Results (mg/kg)
70
60
50
40
30
20
10
0
18
4
9
15
10
12
17
19
14
20
16
23
11
3
5
2
8
22
1
6
13
21
7
Md
R.A.
S
Laboratory

Figure 5

Table 11

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	2968	890
2	3906	1171.80
3	2600	390
4	1800	690
5	2300	700
6	1600	580
7	NT	NT
8	3447.8	925.5
9	2385	141
10*	1140	530
11	3000	900
12	2400	700
13*	8599.54	1719.91
14	2903	1161
15	1600	224
16	2940	1209
17	2789.0	742.9
18	NT	NT
19	2713	542.6
20	2734.6	684
21	NR	NR
22	2850	548.2
23	3000	1342.8

* Laboratories 10 and 13 reported C6-C9.

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Robust Average	2660	410
Median	2760	208
Mean	2884	
N	20	
Max.	8599.54	
Min.	1140	
Robust SD	740	
Robust CV	28%	

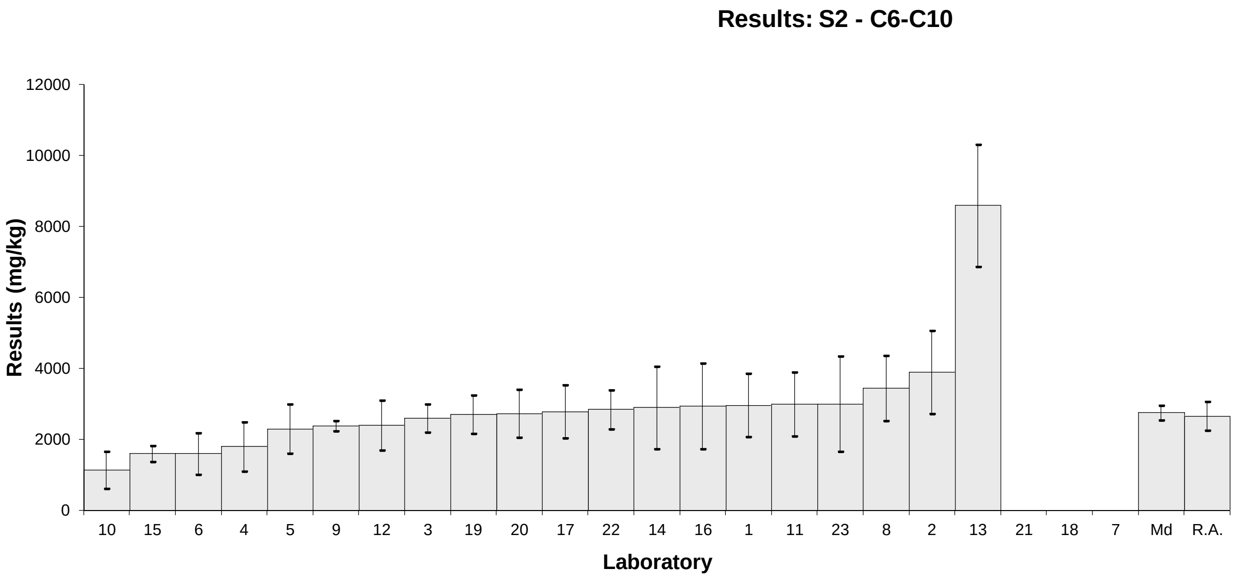

Results: S2 - C6-C10
Results (mg/kg)
12000
10000
8000
6000
4000
2000
0
10
15
6
4
5
9
12
3
19
20
17
22
14
16
1
11
23
8
2
13
21
18
7
Md
R.A.
Laboratory

Figure 6

Table 12

Sample Details

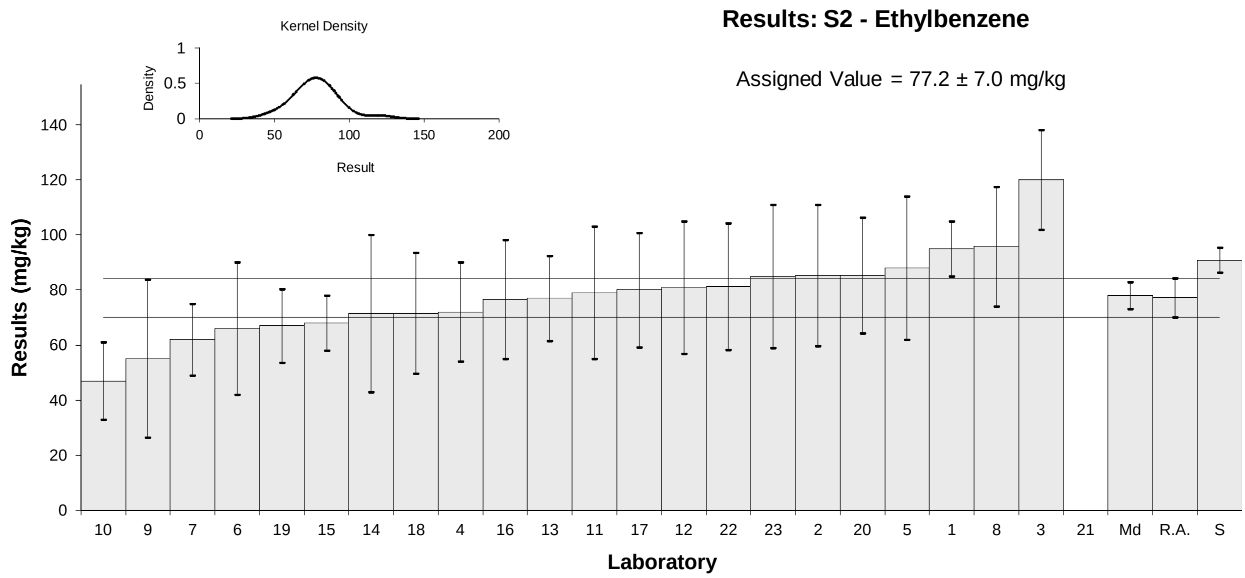
Sample No.	S2
Matrix.	Soil
Analyte.	Ethylbenzene
Units	mg/kg

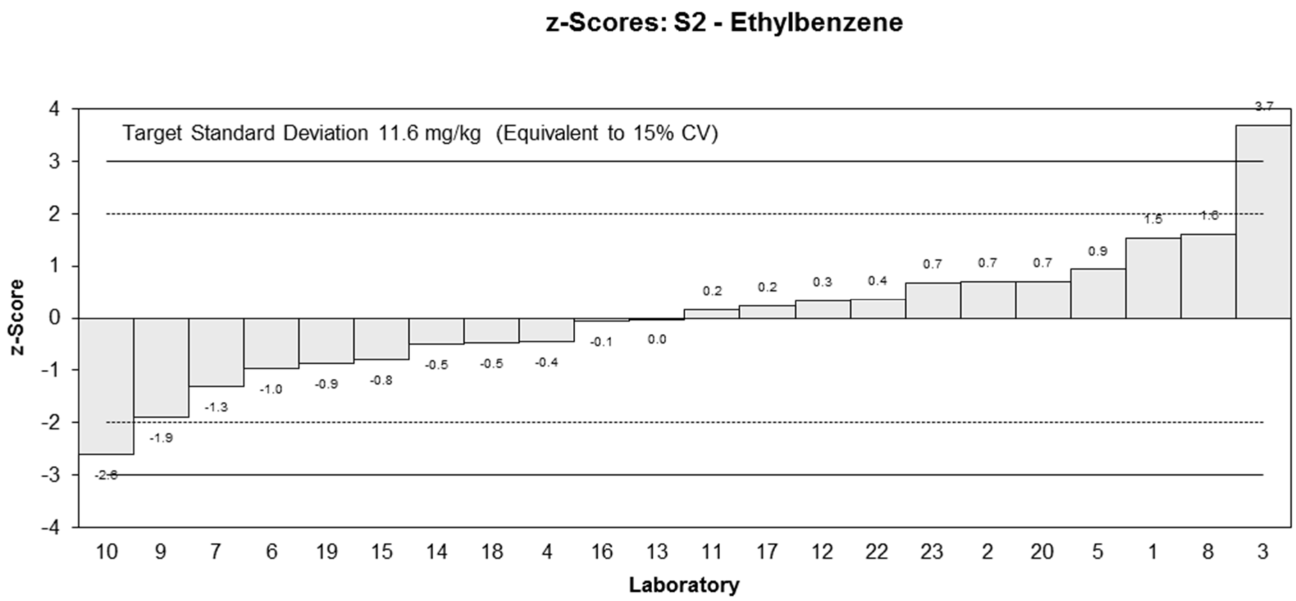
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	95	10	1.54	1.46
2	85.30	25.59	0.70	0.31
3	120	18	3.70	2.22
4	72	18	-0.45	-0.27
5	88	26	0.93	0.40
6	66	24	-0.97	-0.45
7	62	13	-1.31	-1.03
8	95.8	21.7	1.61	0.82
9	55.085	28.644	-1.91	-0.75
10	47	14	-2.61	-1.93
11	79	24	0.16	0.07
12	81	24	0.33	0.15
13	77.04	15.41	-0.01	-0.01
14	71.41	28.56	-0.50	-0.20
15	68	10	-0.79	-0.75
16	76.6	21.6	-0.05	-0.03
17	80.0	20.8	0.24	0.13
18	71.6	21.9	-0.48	-0.24
19	67	13.4	-0.88	-0.67
20	85.3	21	0.70	0.37
21	NR	NR		
22	81.3	22.91	0.35	0.17
23	85	26	0.67	0.29

Statistics

Assigned Value	77.2	7.0
Spike	90.8	4.5
Robust Average	77.2	7.0
Median	78.0	4.8
Mean	77.7	
N	22	
Max.	120	
Min.	47	
Robust SD	13.1	
Robust CV	17%	


Results: S2 - Ethylbenzene
Assigned Value = 77.2 ± 7.0 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
10 9 7 6 19 15 14 18 4 16 13 11 17 12 22 23 2 20 5 1 8 3 21 Md R.A. S


z-Scores: S2 - Ethylbenzene
Target Standard Deviation 11.6 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-2.6 -1.9 -1.3 -1.0 -0.9 -0.8 -0.5 -0.5 -0.4 -0.1 0.0 0.2 0.2 0.3 0.4 0.7 0.7 0.7 0.9 1.5 1.6 3.7
10 9 7 6 19 15 14 18 4 16 13 11 17 12 22 23 2 20 5 1 8 3

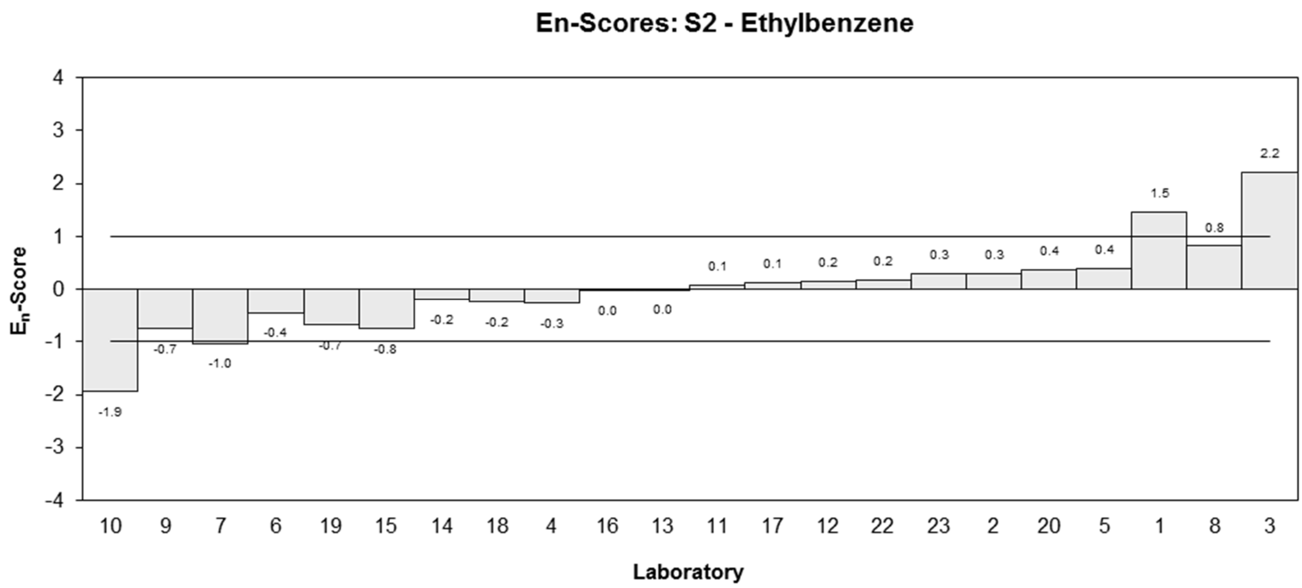

En-Scores: S2 - Ethylbenzene
E_n-Score
Laboratory
-1.9 -0.7 -1.0 -0.4 -0.7 -0.8 -0.2 -0.2 -0.3 0.0 0.0 0.1 0.1 0.2 0.2 0.3 0.3 0.4 0.4 1.5 0.8 2.2
10 9 7 6 19 15 14 18 4 16 13 11 17 12 22 23 2 20 5 1 8 3

Figure 7

Table 13

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1*	704	113	2.00	1.00
2	648.75	194.63	1.34	0.51
3	550	83	0.12	0.09
4	300	75	-2.96	-2.15
5	580	170	0.49	0.21
6*	740	280	2.00	0.68
7	160	34	-4.69	-4.24
8*	719.1	178.5	2.00	0.91
9	446.099	178.440	-1.16	-0.48
10	312	82	-2.81	-1.95
11	610	180	0.86	0.35
12	460	140	-0.99	-0.49
13	655.76	131.15	1.43	0.75
14	447.28	178.9	-1.14	-0.47
15	455	77	-1.05	-0.75
16	522	151.2	-0.22	-0.10
17	585.6	134.2	0.56	0.29
18	261	63	-3.44	-2.68
19	494	98.8	-0.57	-0.36
20	537.4	129	-0.03	-0.02
21	NR	NR		
22	614	213.1	0.91	0.32
23	980	299	5.43	1.42

Statistics

Assigned Value**	540	83
Spike	790	40
Maximum acceptable conc	952	
Robust Average	532	92
Median	544	64
Mean	536	
N	22	
Max.	980	
Min.	160	
Robust SD	172	
Robust CV	32%	

* z-score adjusted to 2 (see Section 6.3).

**Robust average excluding laboratories 7 and 23.

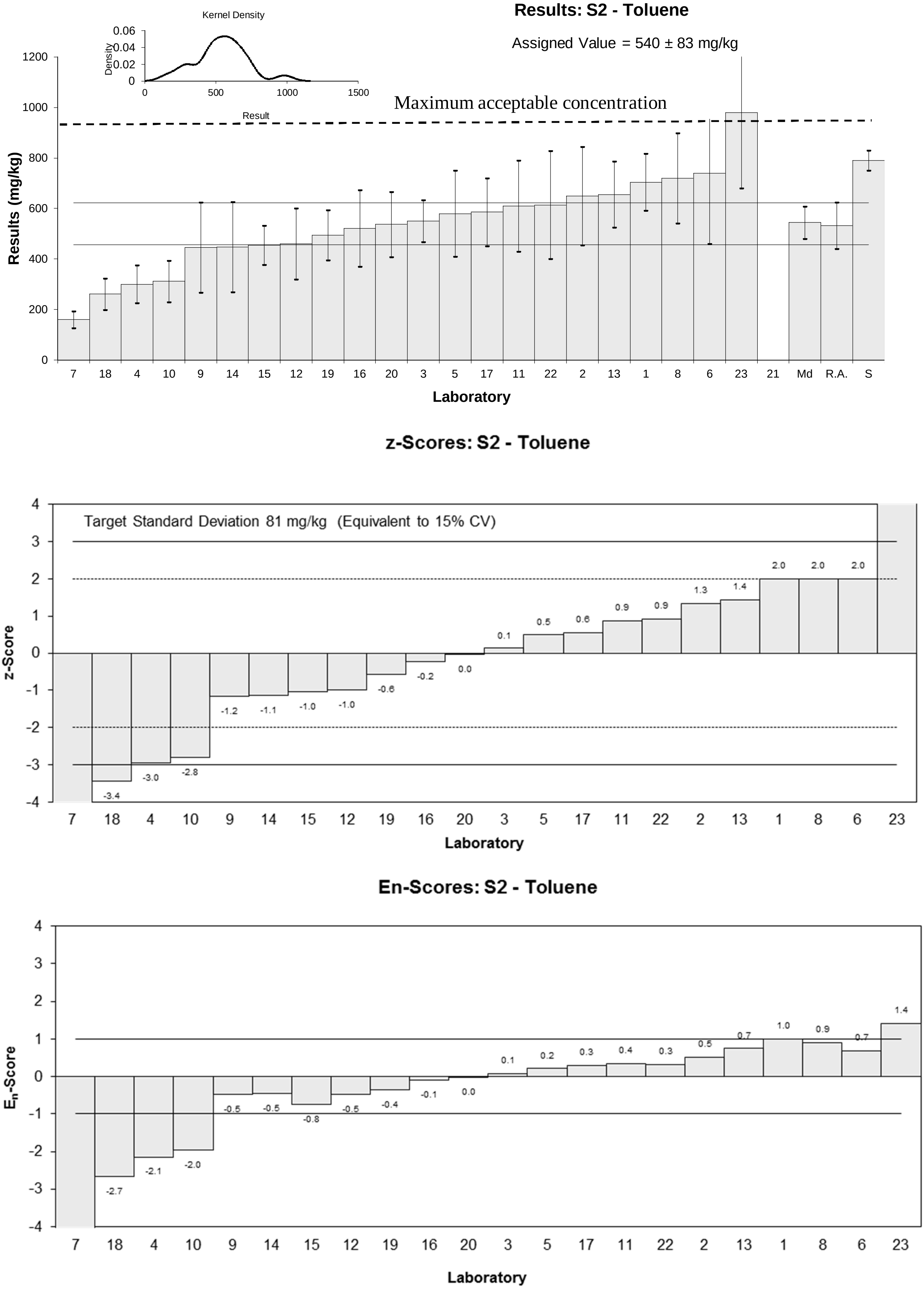

Results: S2 - Toluene
Assigned Value = 540 ± 83 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
Laboratory
7 18 4 10 9 14 15 12 19 16 20 3 5 17 11 22 2 13 1 8 6 23 21 Md R.A. S
z-Scores: S2 - Toluene
Target Standard Deviation 81 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S2 - Toluene
En-Score
Laboratory

Figure 8

Table 14

Sample Details

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

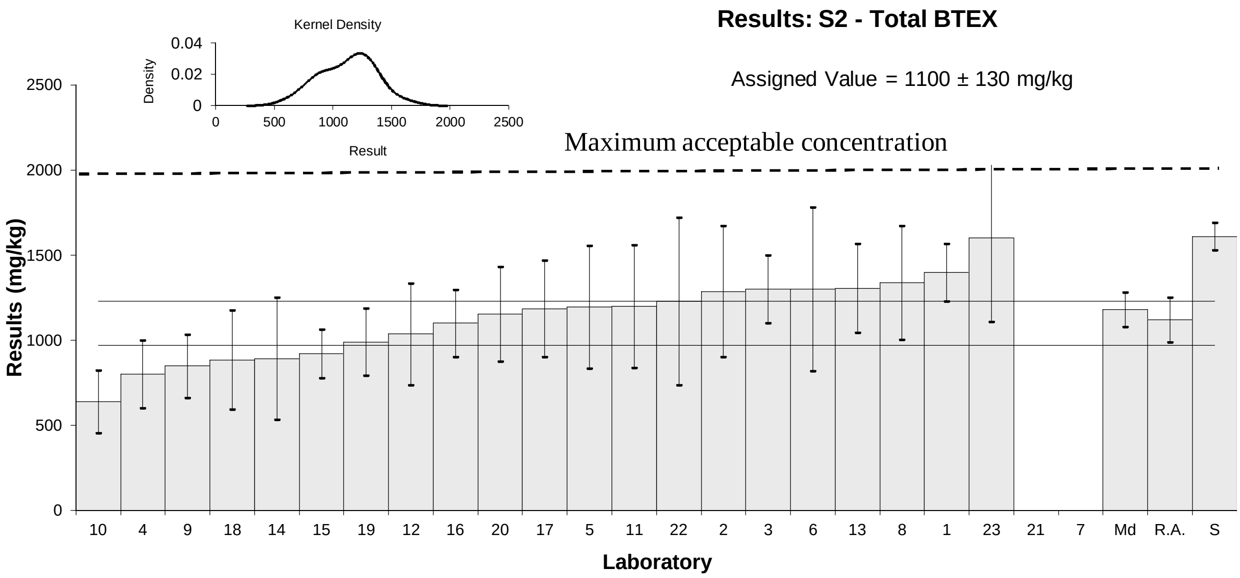
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1398	168	1.81	1.40
2	1286.80	386.04	1.13	0.46
3	1300	200	1.21	0.84
4	800	200	-1.82	-1.26
5	1194	360	0.57	0.25
6	1300	480	1.21	0.40
7	NT	NT		
8	1339.0	334.8	1.45	0.67
9	848.268	187.31	-1.53	-1.10
10	641	184	-2.78	-2.04
11	1200	360	0.61	0.26
12	1036	300	-0.39	-0.20
13	1305.03	261.01	1.24	0.70
14	892.73	357.09	-1.26	-0.55
15	921	142	-1.08	-0.93
16	1100	196.7	0.00	0.00
17	1184.7	283.7	0.51	0.27
18	885	292	-1.30	-0.67
19	990	198	-0.67	-0.46
20	1153.5	277	0.32	0.17
21	NR	NR		
22	1230	492.5	0.79	0.26
23*	1600	493	2.00	0.98

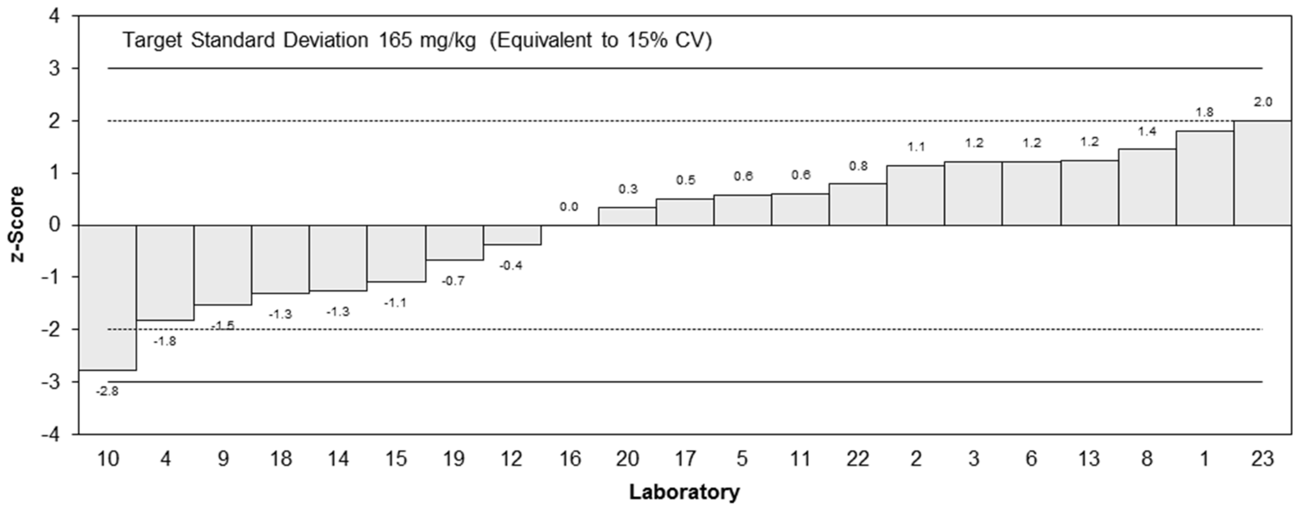
Statistics

Assigned Value	1100	130
Spike	1610	81
Maximum acceptable conc.	1940	
Robust Average	1120	130
Median	1180	100
Mean	1124	
N	21	
Max.	1600	
Min.	641	
Robust SD	238	
Robust CV	21%	

* z-score adjusted to 2 (see Section 6.3).



z-Scores: S2 - Total BTEX



En-Scores: S2 - Total BTEX

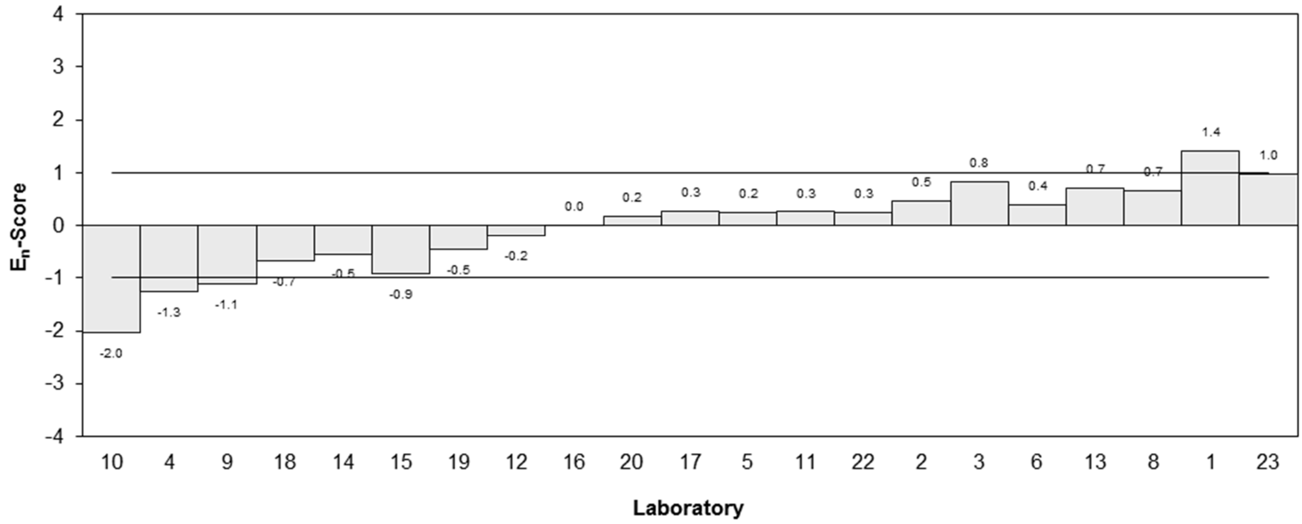


Figure 9

Table 15

Sample Details

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

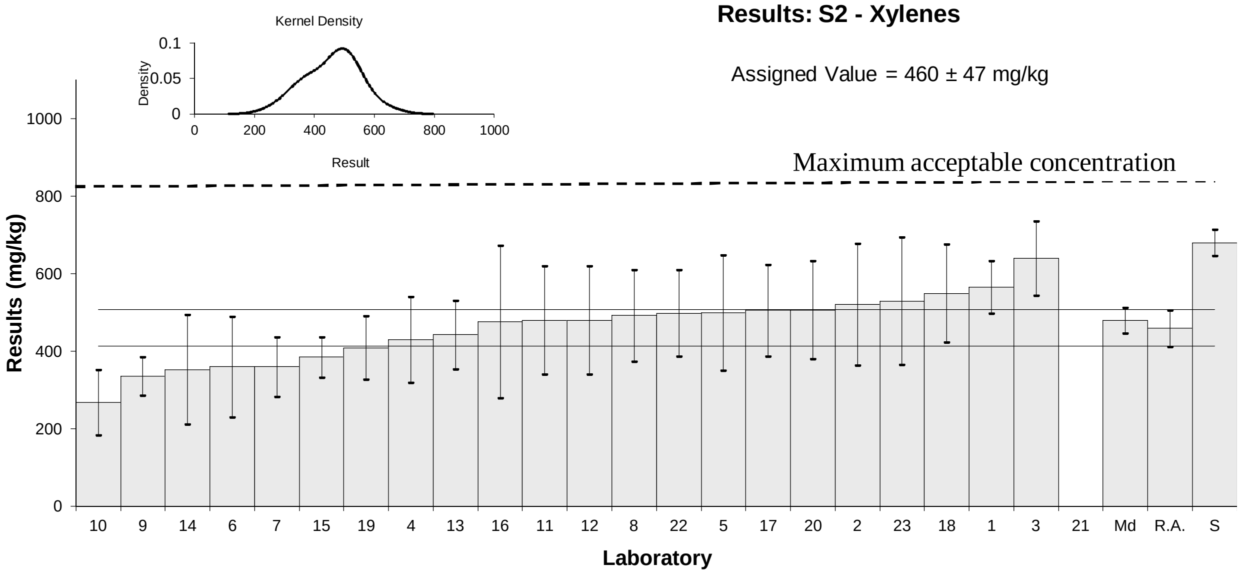
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	565	68	1.52	1.27
2	521.10	156.33	0.89	0.37
3*	640	96	2.00	1.00
4	430	110	-0.43	-0.25
5	500	149	0.58	0.26
6	360	130	-1.45	-0.72
7	360	77	-1.45	-1.11
8	492.4	118.0	0.47	0.26
9	335.674	49.167	-1.80	-1.83
10	268	84	-2.78	-1.99
11	480	140	0.29	0.14
12	480	140	0.29	0.14
13	442.55	88.51	-0.25	-0.17
14	353.11	141.24	-1.55	-0.72
15	385	52	-1.09	-1.07
16	477	196.7	0.25	0.08
17	505.7	117.8	0.66	0.36
18	549.5	126.4	1.30	0.66
19	409	81.8	-0.74	-0.54
20	506.8	127	0.68	0.35
21	NR	NR		
22	498	111.7	0.55	0.31
23	530	164	1.01	0.41

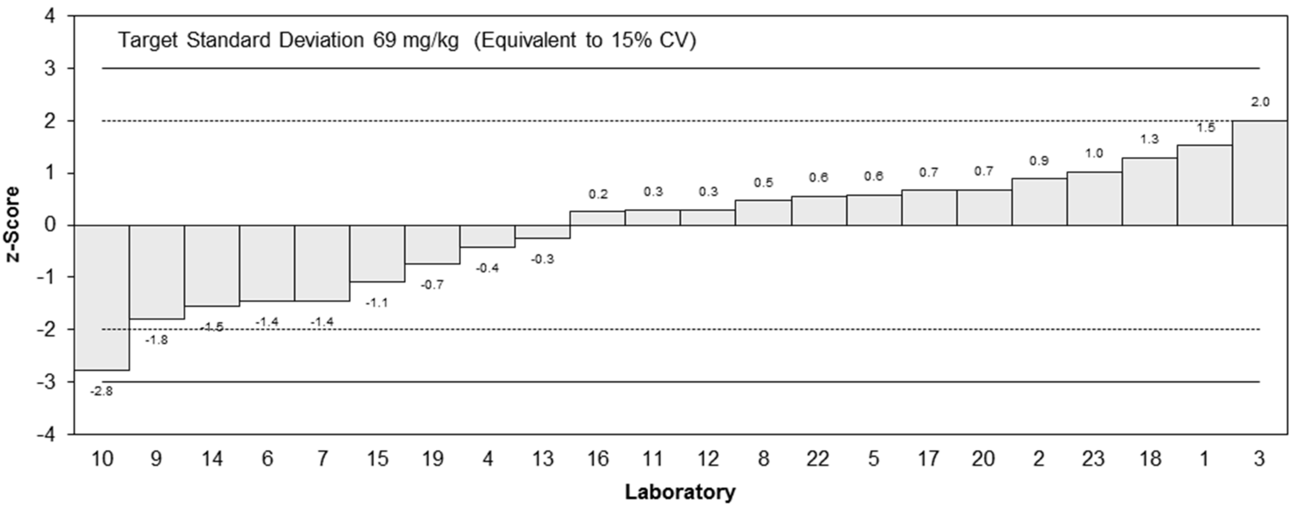
Statistics

Assigned Value	460	47
Spike	680	34
Maximum acceptable conc.	818	
Robust Average	460	47
Median	480	33
Mean	459	
N	22	
Max.	640	
Min.	268	
Robust SD	89	
Robust CV	19%	

* z-score adjusted to 2 (see Section 6.3).



z-Scores: S2 - Xylenes



En-Scores: S2 - Xylenes

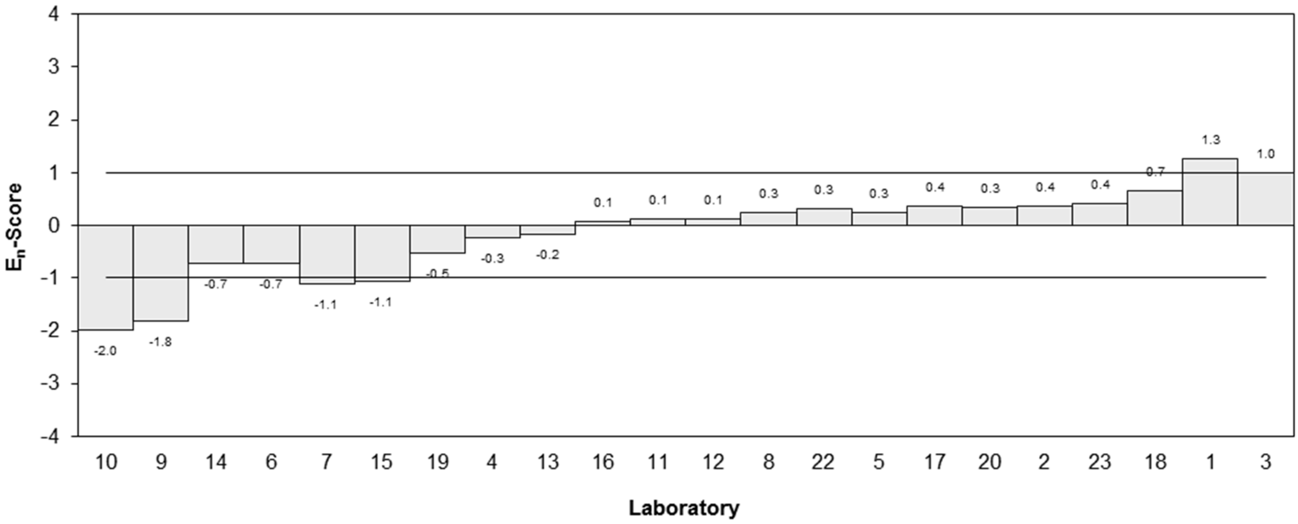


Figure 10

Table 16

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	0.8	0.2
2	0.87	0.26
3	0.78	0.16
4	0.71	0.18
5	0.81	0.3
6	1.2	0.23
7	1.1	0.3
8	0.82	0.20
9	0.613	0.306
10	NT	NT
11	0.7	0.3
12	0.6	0.3
13	0.82	0.21
14	0.8	0.32
15	0.48	0.10
16	0.9	0.64
17	0.72	0.21
18	0.74	0.22
19	0.8	0.2
20	0.7	0.18
21	0.72	0.22
22	0.9	0.64
23	0.7	0.21

Statistics

Assigned Value	Not Set	
Spike	3.49	0.17
Robust Average	0.776	0.063
Median	0.790	0.053
Mean	0.786	
N	22	
Max.	1.2	
Min.	0.48	
Robust SD	0.119	
Robust CV	15%	

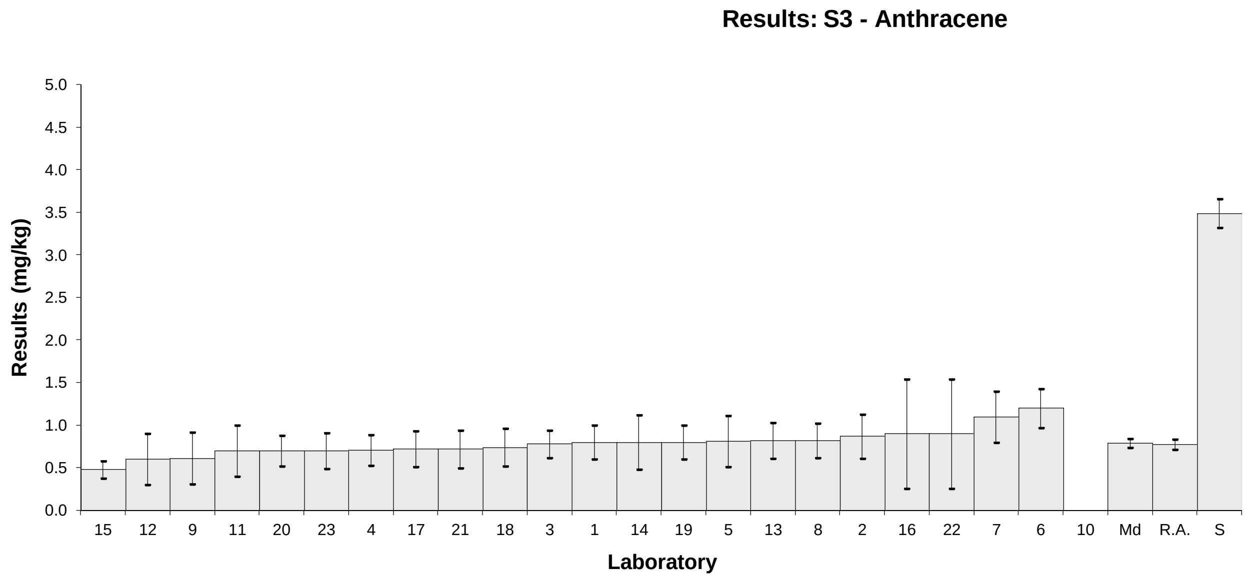

Results: S3 - Anthracene
Results (mg/kg)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
15 12 9 11 20 23 4 17 21 18 3 1 14 19 5 13 8 2 16 22 7 6 10 Md R.A. S
Laboratory

Figure 11

Table 17

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	<0.5	0.1
2	0.09	0.027
3	<1	NR
4	0.15	0.04
5	0.10	0.1
6	<1	NR
7	<0.2	NR
8	< 0.5	0.15
9	<0.100	NR
10	NT	NT
11	0.08	0.08
12	0.05	0.1
13	0.13	0.03
14	<0.1	NR
15	< 0.2	NR
16	<0.5	NR
17	< 0.5	0.1
18	0.27	0.09
19	1.0	0.2
20	< 0.5	0.2
21	0.16	0.05
22	<0.5	0.14
23	0.1	0.05

Statistics

Assigned Value	Not Set	
Spike	2.49	0.12
Robust Average	0.139	0.065
Median	0.115	0.037
Mean	0.213	
N	10	
Max.	1	
Min.	0.05	
Robust SD	0.080	
Robust CV	58%	

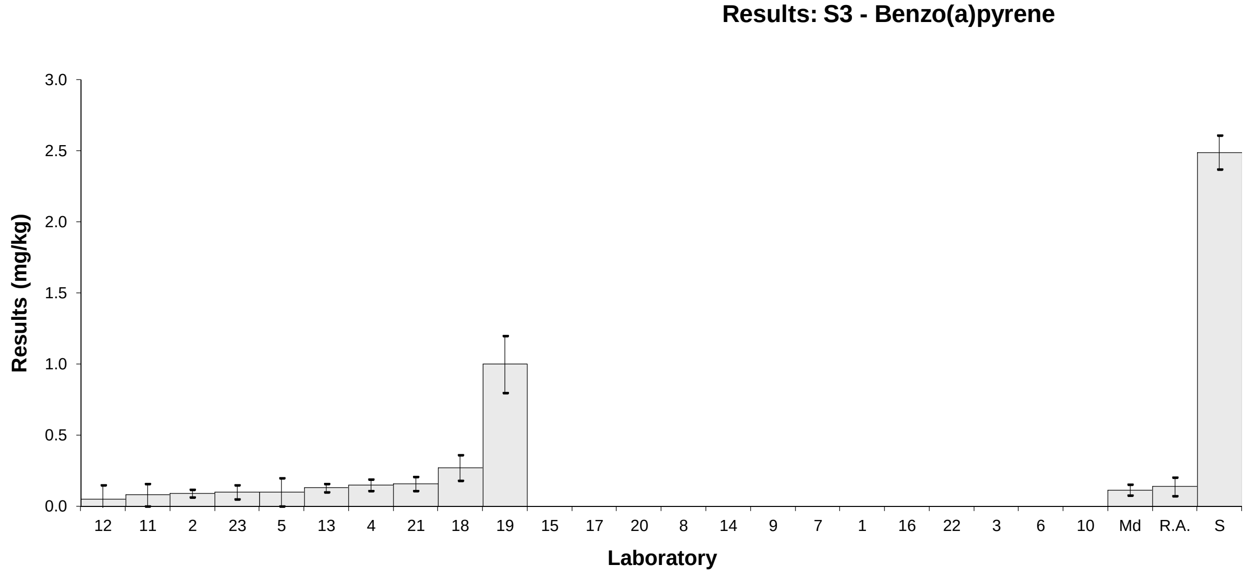

Results: S3 - Benzo(a)pyrene
Results (mg/kg)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
12
11
2
23
5
13
4
21
18
19
15
17
20
8
14
9
7
1
16
22
3
6
10
Md
R.A.
S
Laboratory

Figure 12

Table 18

Sample Details

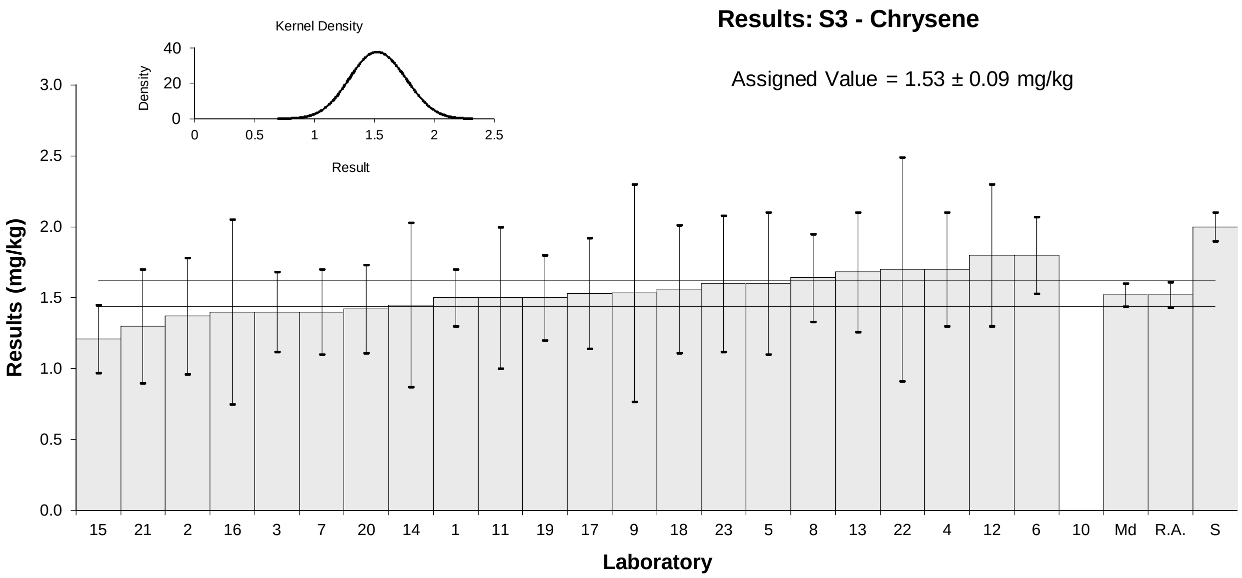
Sample No.	S3
Matrix.	Soil
Analyte.	Chrysene
Units	mg/kg

Participant Results

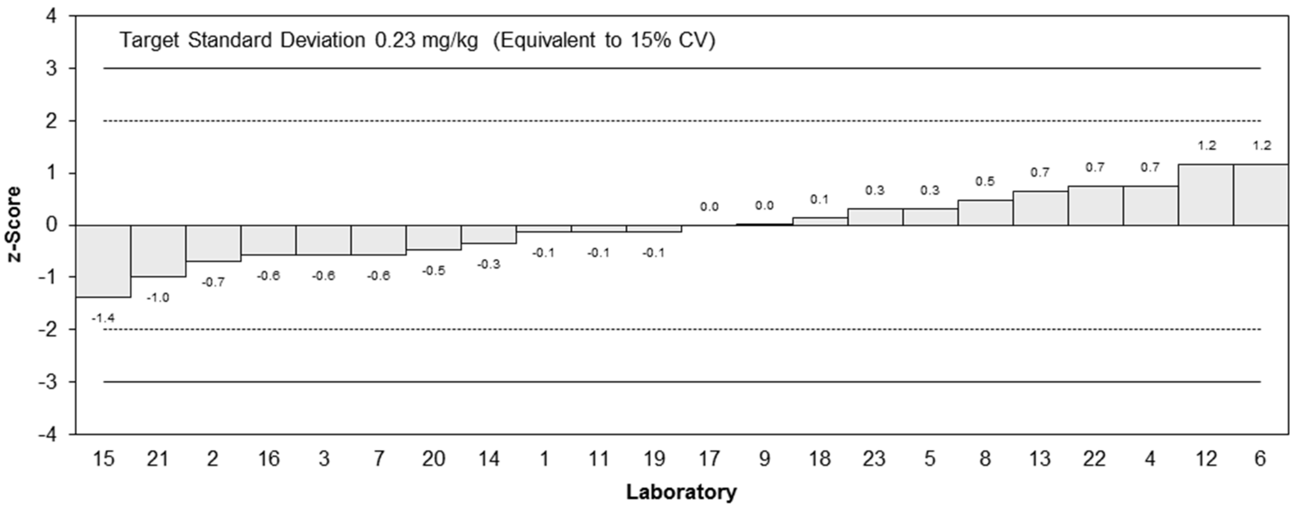
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.5	0.2	-0.13	-0.14
2	1.37	0.41	-0.70	-0.38
3	1.4	0.28	-0.57	-0.44
4	1.7	0.4	0.74	0.41
5	1.6	0.5	0.31	0.14
6	1.8	0.27	1.18	0.95
7	1.4	0.3	-0.57	-0.42
8	1.64	0.31	0.48	0.34
9	1.532	0.766	0.01	0.00
10	NT	NT		
11	1.5	0.5	-0.13	-0.06
12	1.8	0.5	1.18	0.53
13	1.68	0.42	0.65	0.35
14	1.45	0.58	-0.35	-0.14
15	1.21	0.24	-1.39	-1.25
16	1.4	0.65	-0.57	-0.20
17	1.53	0.39	0.00	0.00
18	1.56	0.45	0.13	0.07
19	1.5	0.3	-0.13	-0.10
20	1.42	0.31	-0.48	-0.34
21	1.3	0.4	-1.00	-0.56
22	1.7	0.79	0.74	0.21
23	1.6	0.48	0.31	0.14

Statistics

Assigned Value	1.53	0.09
Spike	2.00	0.10
Robust Average	1.53	0.09
Median	1.52	0.08
Mean	1.53	
N	22	
Max.	1.8	
Min.	1.21	
Robust SD	0.16	
Robust CV	11%	



z-Scores: S3 - Chrysene



En-Scores: S3 - Chrysene

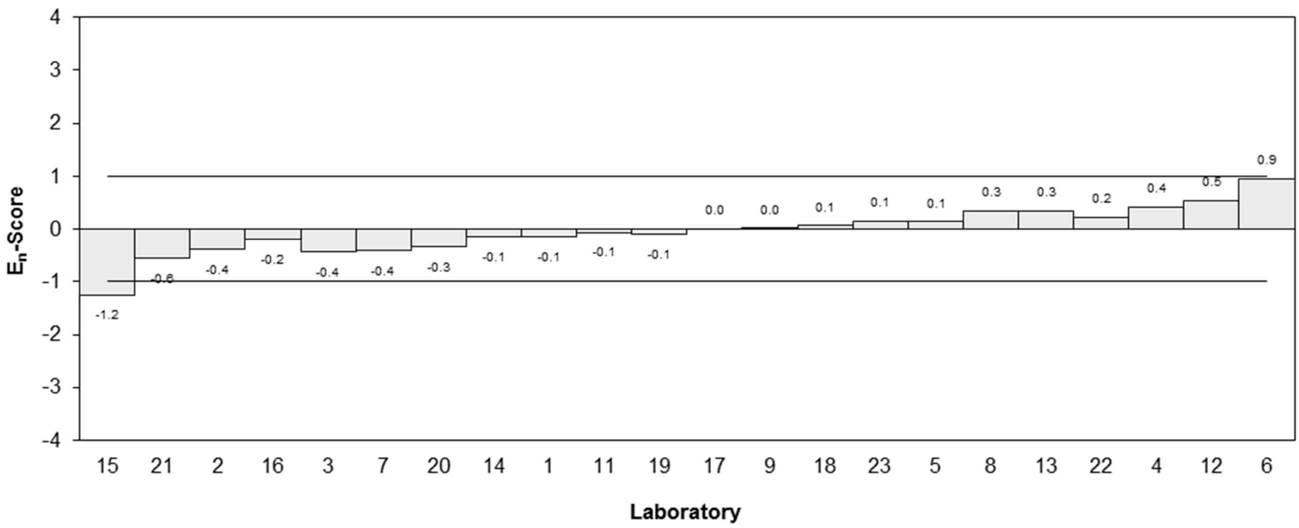


Figure 13

Table 19

Sample Details

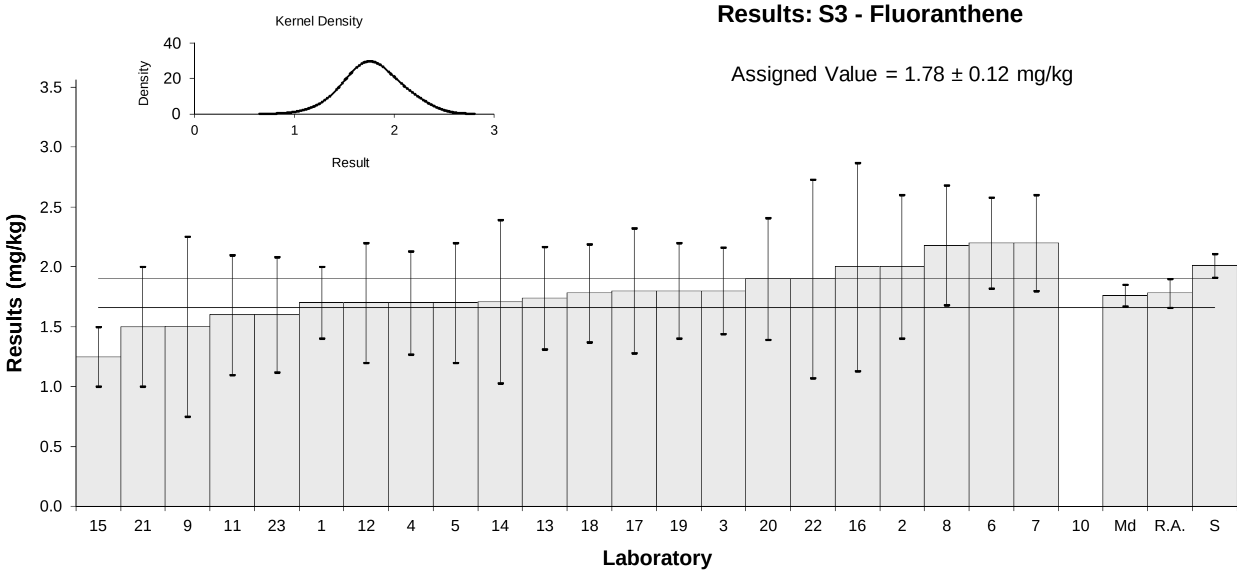
Sample No.	S3
Matrix.	Soil
Analyte.	Fluoranthene
Units	mg/kg

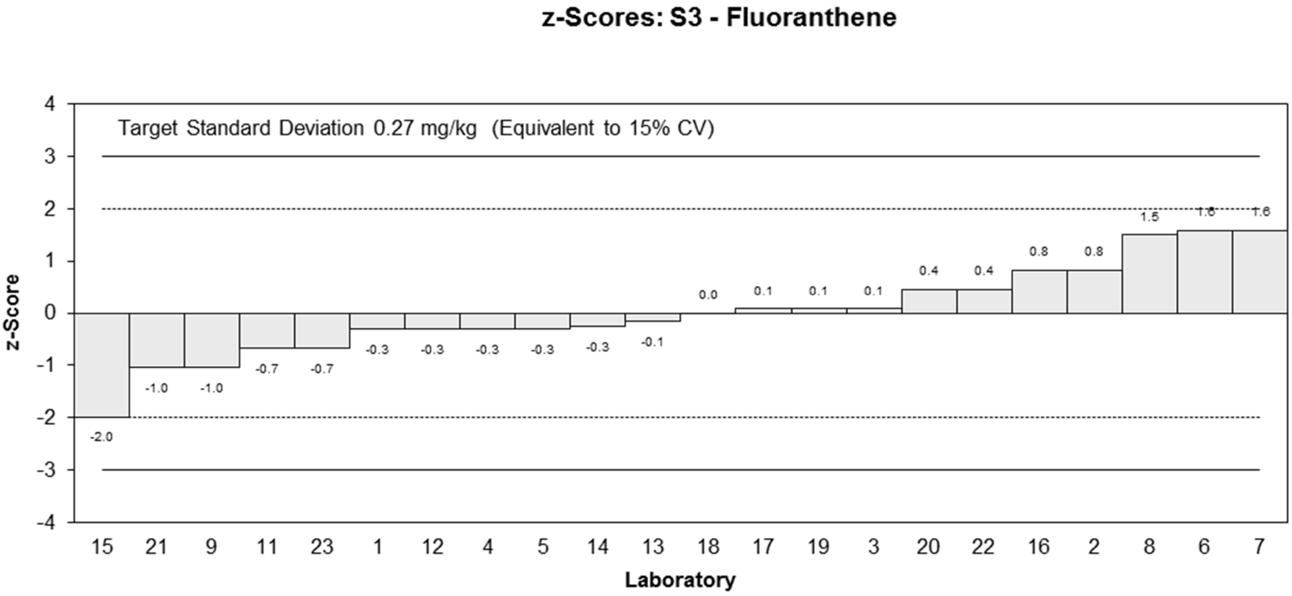
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.7	0.3	-0.30	-0.25
2	2.00	0.6	0.82	0.36
3	1.8	0.36	0.07	0.05
4	1.7	0.43	-0.30	-0.18
5	1.7	0.5	-0.30	-0.16
6	2.2	0.38	1.57	1.05
7	2.2	0.4	1.57	1.01
8	2.18	0.50	1.50	0.78
9	1.503	0.752	-1.04	-0.36
10	NT	NT		
11	1.6	0.5	-0.67	-0.35
12	1.7	0.5	-0.30	-0.16
13	1.74	0.43	-0.15	-0.09
14	1.71	0.68	-0.26	-0.10
15	1.25	0.25	-1.99	-1.91
16	2.0	0.87	0.82	0.25
17	1.8	0.52	0.07	0.04
18	1.78	0.41	0.00	0.00
19	1.8	0.4	0.07	0.05
20	1.9	0.51	0.45	0.23
21	1.5	0.5	-1.05	-0.54
22	1.9	0.83	0.45	0.14
23	1.6	0.48	-0.67	-0.36

Statistics

Assigned Value	1.78	0.12
Spike	2.01	0.10
Robust Average	1.78	0.12
Median	1.76	0.09
Mean	1.79	
N	22	
Max.	2.2	
Min.	1.25	
Robust SD	0.23	
Robust CV	13%	


Results: S3 - Fluoranthene
Assigned Value = 1.78 ± 0.12 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 21 9 11 23 1 12 4 5 14 13 18 17 19 3 20 22 16 2 8 6 7 10 Md R.A. S


z-Scores: S3 - Fluoranthene
Target Standard Deviation 0.27 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
15 21 9 11 23 1 12 4 5 14 13 18 17 19 3 20 22 16 2 8 6 7

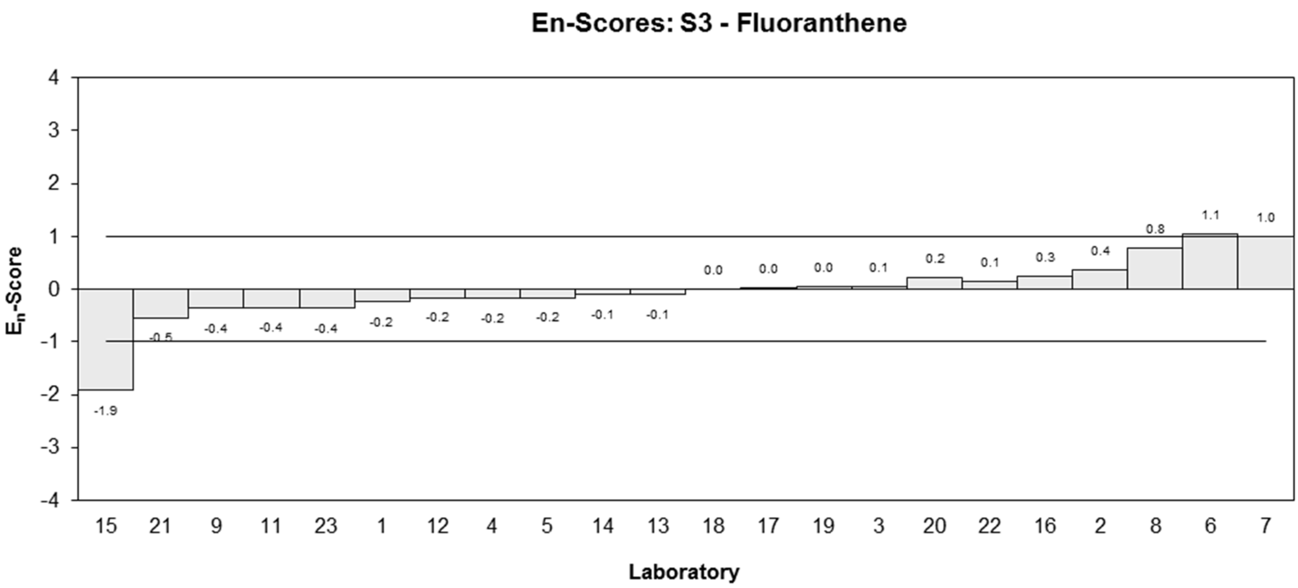

En-Scores: S3 - Fluoranthene
E_n-Score
Laboratory
15 21 9 11 23 1 12 4 5 14 13 18 17 19 3 20 22 16 2 8 6 7

Figure 14

Table 20

Sample Details

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

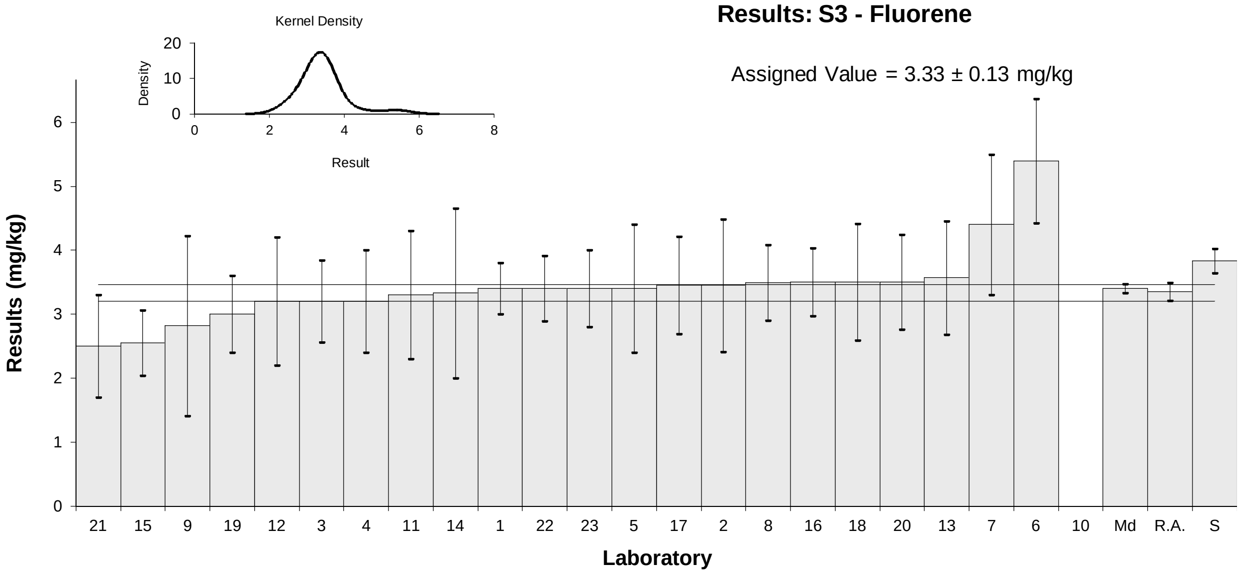
Participant Results

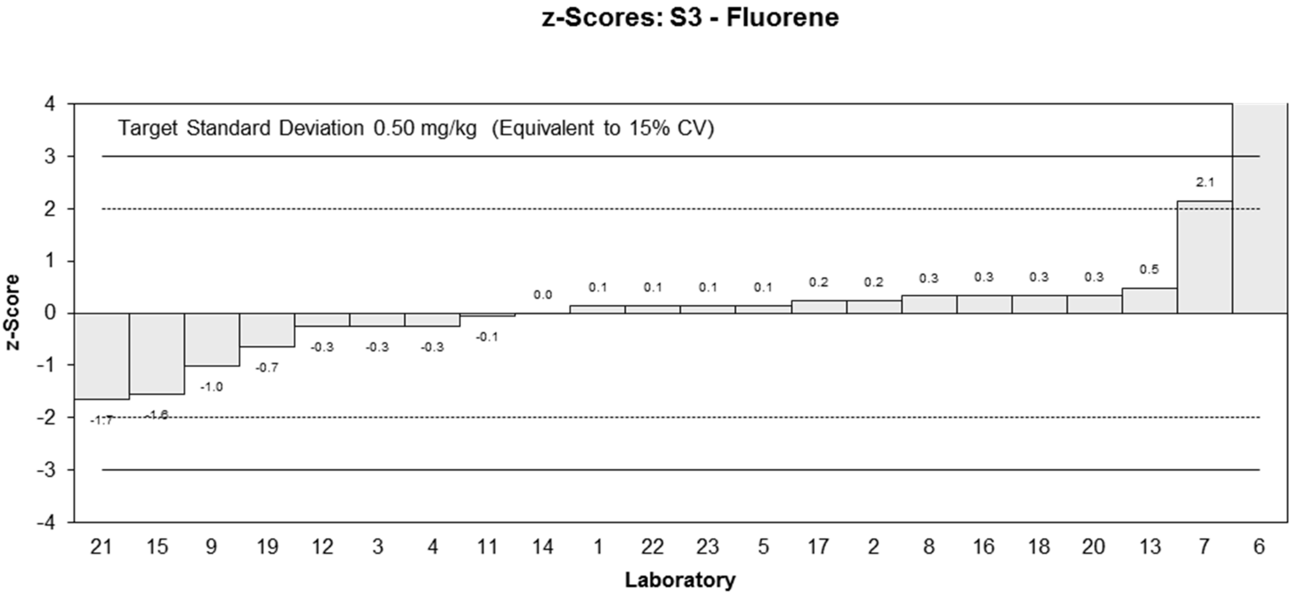
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.4	0.4	0.14	0.17
2	3.45	1.04	0.24	0.11
3	3.2	0.64	-0.26	-0.20
4	3.2	0.8	-0.26	-0.16
5	3.40	1	0.14	0.07
6	5.4	0.97	4.14	2.12
7	4.4	1.1	2.14	0.97
8	3.49	0.59	0.32	0.26
9	2.819	1.410	-1.02	-0.36
10	NT	NT		
11	3.3	1.0	-0.06	-0.03
12	3.2	1	-0.26	-0.13
13	3.57	0.89	0.48	0.27
14	3.33	1.33	0.00	0.00
15	2.55	0.51	-1.56	-1.48
16	3.5	0.53	0.34	0.31
17	3.45	0.76	0.24	0.16
18	3.50	0.91	0.34	0.18
19	3.0	0.6	-0.66	-0.54
20	3.50	0.74	0.34	0.23
21	2.5	0.8	-1.66	-1.02
22	3.4	0.51	0.14	0.13
23	3.4	0.6	0.14	0.11

Statistics

Assigned Value*	3.33	0.13
Spike	3.83	0.19
Robust Average	3.35	0.14
Median	3.40	0.07
Mean	3.41	
N	22	
Max.	5.4	
Min.	2.5	
Robust SD	0.27	
Robust CV	8.1%	

*Robust average excluding laboratory 6.


Results: S3 - Fluorene
Assigned Value = 3.33 ± 0.13 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
21 15 9 19 12 3 4 11 14 1 22 23 5 17 2 8 16 18 20 13 7 6 10 Md R.A. S
Laboratory


z-Scores: S3 - Fluorene
Target Standard Deviation 0.50 mg/kg (Equivalent to 15% CV)
z-Score
-1.7 -1.6 -1.0 -0.7 -0.3 -0.3 -0.3 -0.1 0.0 0.1 0.1 0.1 0.1 0.2 0.2 0.3 0.3 0.3 0.3 0.5 2.1
21 15 9 19 12 3 4 11 14 1 22 23 5 17 2 8 16 18 20 13 7 6
Laboratory

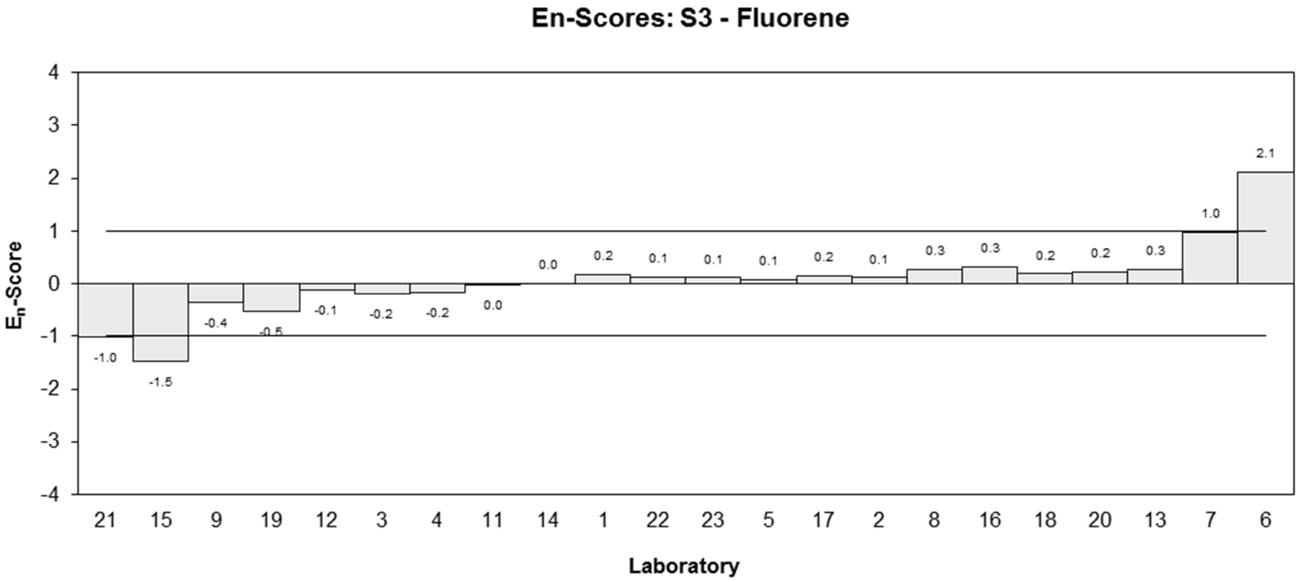

En-Scores: S3 - Fluorene
E_n-Score
-1.0 -1.5 -0.4 -0.5 -0.1 -0.2 -0.2 0.0 0.0 0.2 0.1 0.1 0.1 0.2 0.1 0.3 0.3 0.2 0.2 0.3 1.0 2.1
21 15 9 19 12 3 4 11 14 1 22 23 5 17 2 8 16 18 20 13 7 6
Laboratory

Figure 15

Table 21

Sample Details

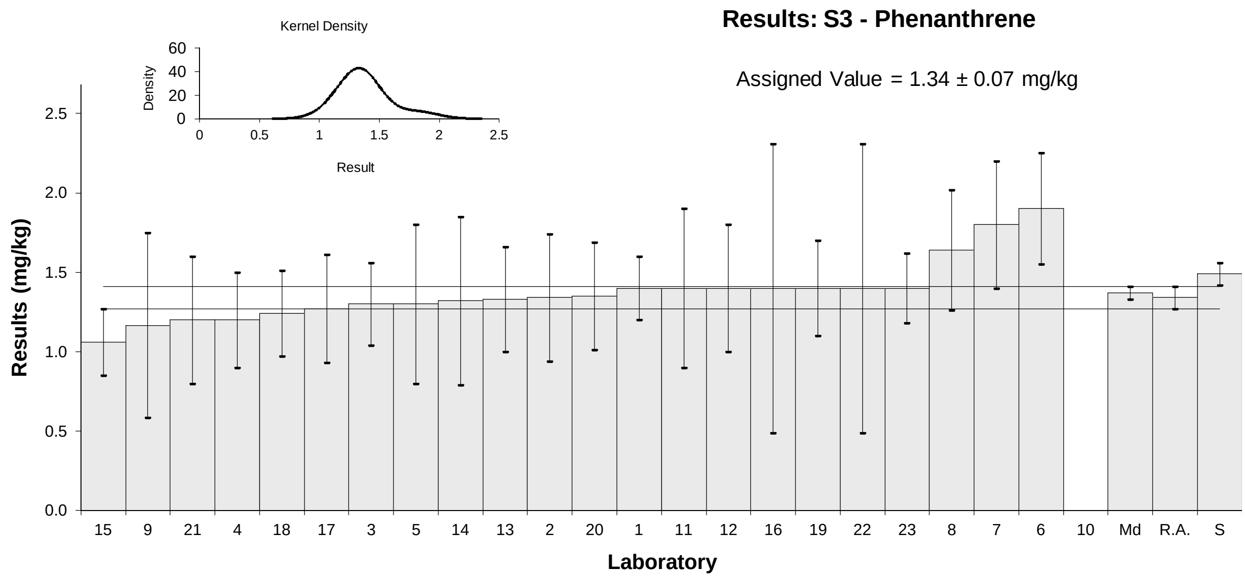
Sample No.	S3
Matrix.	Soil
Analyte.	Phenanthrene
Units	mg/kg

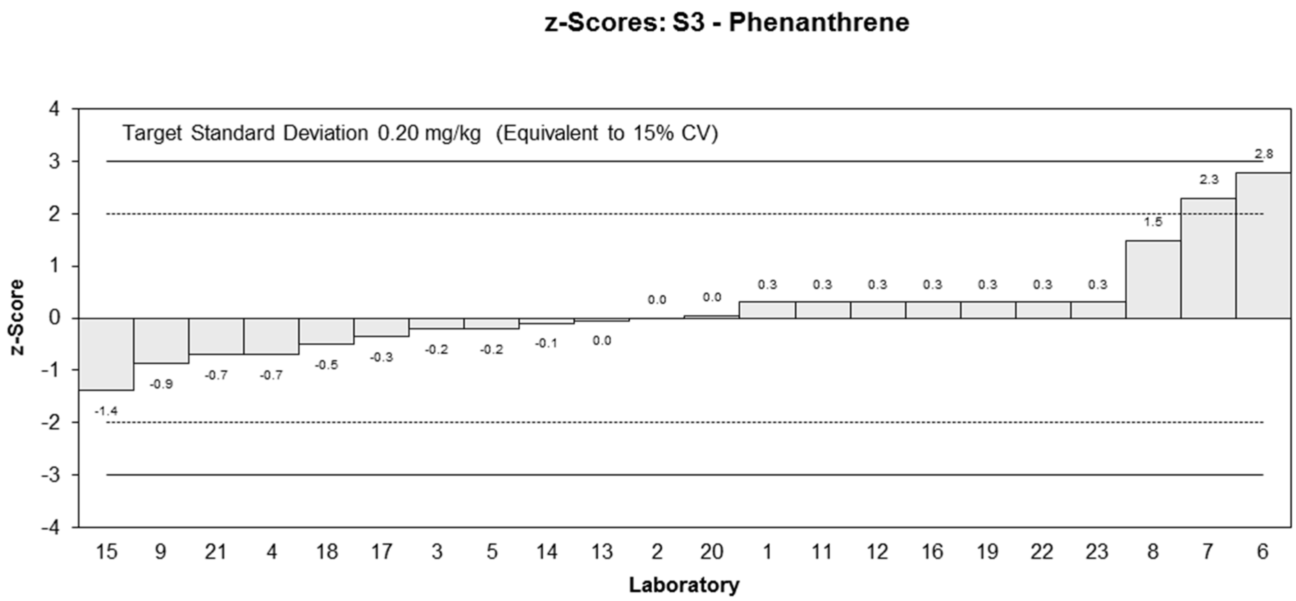
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.4	0.2	0.30	0.28
2	1.34	0.40	0.00	0.00
3	1.3	0.26	-0.20	-0.15
4	1.2	0.3	-0.70	-0.45
5	1.3	0.5	-0.20	-0.08
6	1.9	0.35	2.79	1.57
7	1.8	0.4	2.29	1.13
8	1.64	0.38	1.49	0.78
9	1.166	0.583	-0.87	-0.30
10	NT	NT		
11	1.4	0.5	0.30	0.12
12	1.4	0.4	0.30	0.15
13	1.33	0.33	-0.05	-0.03
14	1.32	0.53	-0.10	-0.04
15	1.06	0.21	-1.39	-1.26
16	1.4	0.91	0.30	0.07
17	1.27	0.34	-0.35	-0.20
18	1.24	0.27	-0.50	-0.36
19	1.4	0.3	0.30	0.19
20	1.35	0.34	0.05	0.03
21	1.2	0.4	-0.70	-0.34
22	1.4	0.91	0.30	0.07
23	1.4	0.22	0.30	0.26

Statistics

Assigned Value	1.34	0.07
Spike	1.49	0.07
Robust Average	1.34	0.07
Median	1.37	0.04
Mean	1.37	
N	22	
Max.	1.9	
Min.	1.06	
Robust SD	0.13	
Robust CV	9.7%	


Results: S3 - Phenanthrene
Assigned Value = 1.34 ± 0.07 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 9 21 4 18 17 3 5 14 13 2 20 1 11 12 16 19 22 23 8 7 6 10 Md R.A. S


z-Scores: S3 - Phenanthrene
Target Standard Deviation 0.20 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
15 9 21 4 18 17 3 5 14 13 2 20 1 11 12 16 19 22 23 8 7 6

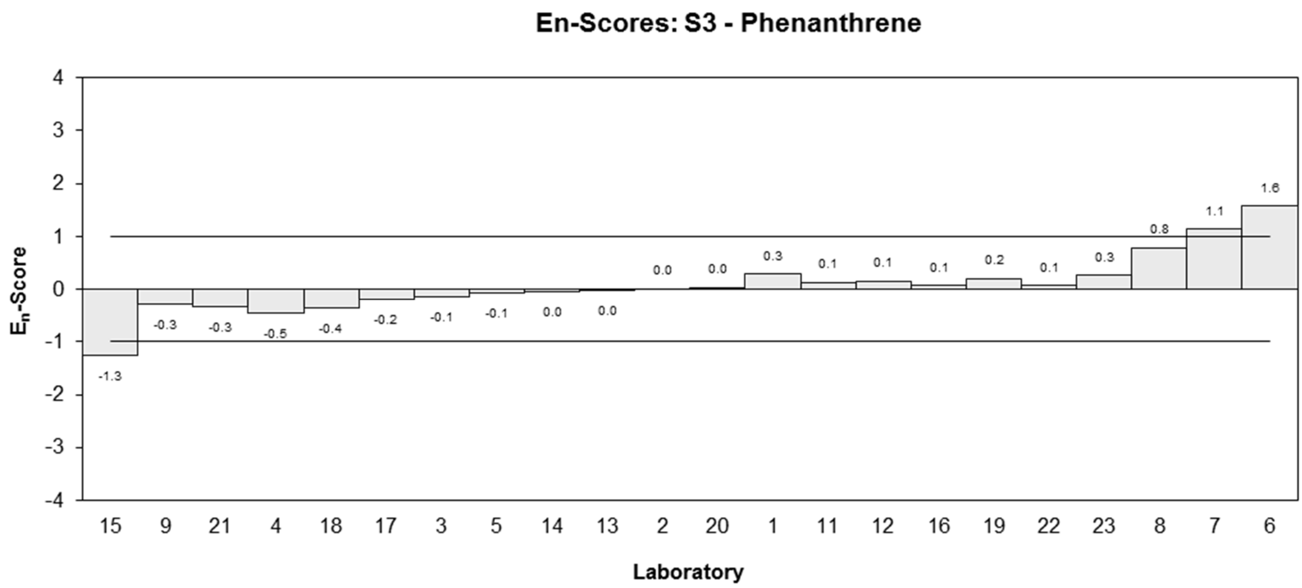

En-Scores: S3 - Phenanthrene
En-Score
Laboratory
15 9 21 4 18 17 3 5 14 13 2 20 1 11 12 16 19 22 23 8 7 6

Figure 16

Table 22

Sample Details

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

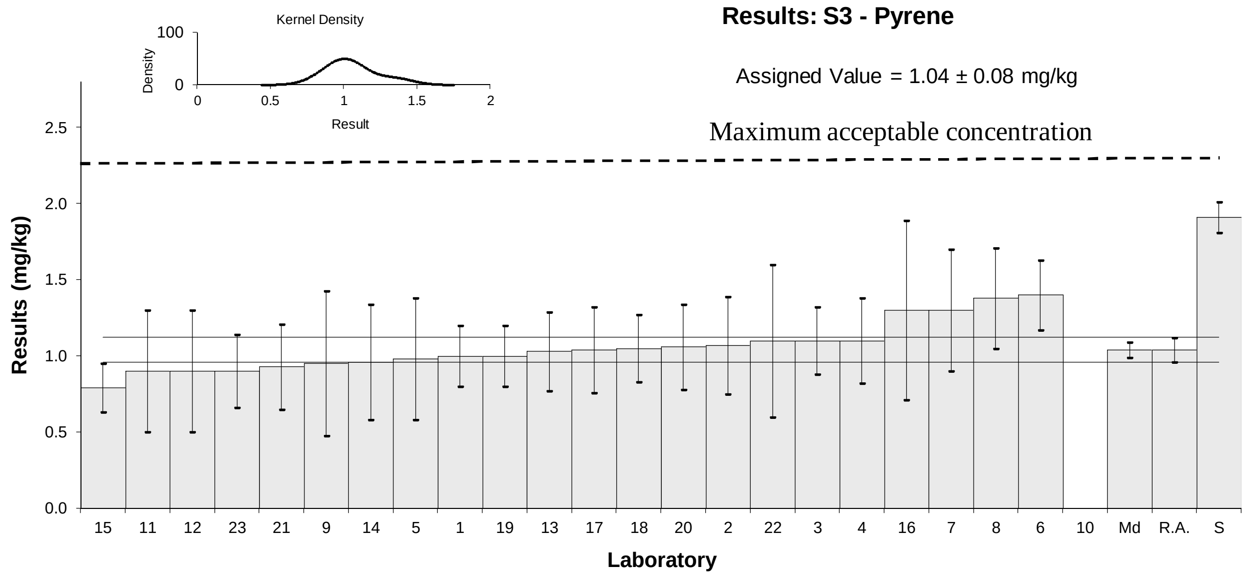
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.0	0.2	-0.26	-0.19
2	1.07	0.32	0.19	0.09
3	1.1	0.22	0.38	0.26
4	1.1	0.28	0.38	0.21
5	0.98	0.4	-0.38	-0.15
6*	1.4	0.23	2.00	1.00
7	1.3	0.4	1.67	0.64
8*	1.38	0.33	2.00	1.00
9	0.950	0.475	-0.58	-0.19
10	NT	NT		
11	0.9	0.4	-0.90	-0.34
12	0.9	0.4	-0.90	-0.34
13	1.03	0.26	-0.06	-0.04
14	0.96	0.38	-0.51	-0.21
15	0.79	0.16	-1.60	-1.40
16	1.3	0.59	1.67	0.44
17	1.04	0.28	0.00	0.00
18	1.05	0.22	0.06	0.04
19	1.0	0.2	-0.26	-0.19
20	1.06	0.28	0.13	0.07
21	0.93	0.28	-0.71	-0.38
22	1.1	0.50	0.38	0.12
23	0.9	0.24	-0.90	-0.55

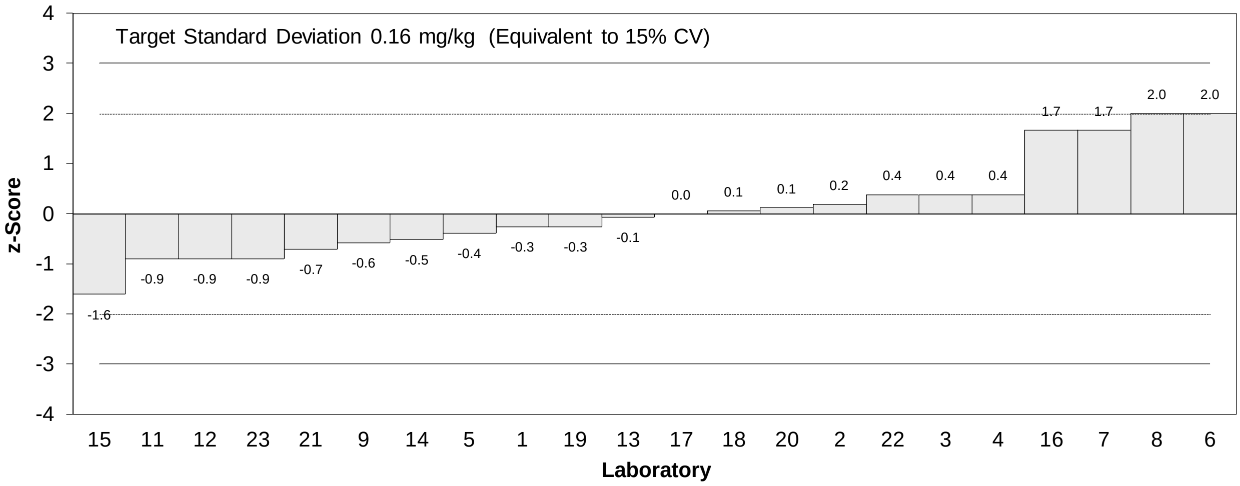
Statistics

Assigned Value	1.04	0.08
Spike	1.91	0.10
Maximum acceptable conc.	2.23	
Robust Average	1.04	0.08
Median	1.04	0.05
Mean	1.06	
N	22	
Max.	1.4	
Min.	0.79	
Robust SD	0.14	
Robust CV	14%	

* z-score adjusted to 2 (see Section 6.3).



z-Scores: S3 - Pyrene



En-Scores: S3 - Pyrene

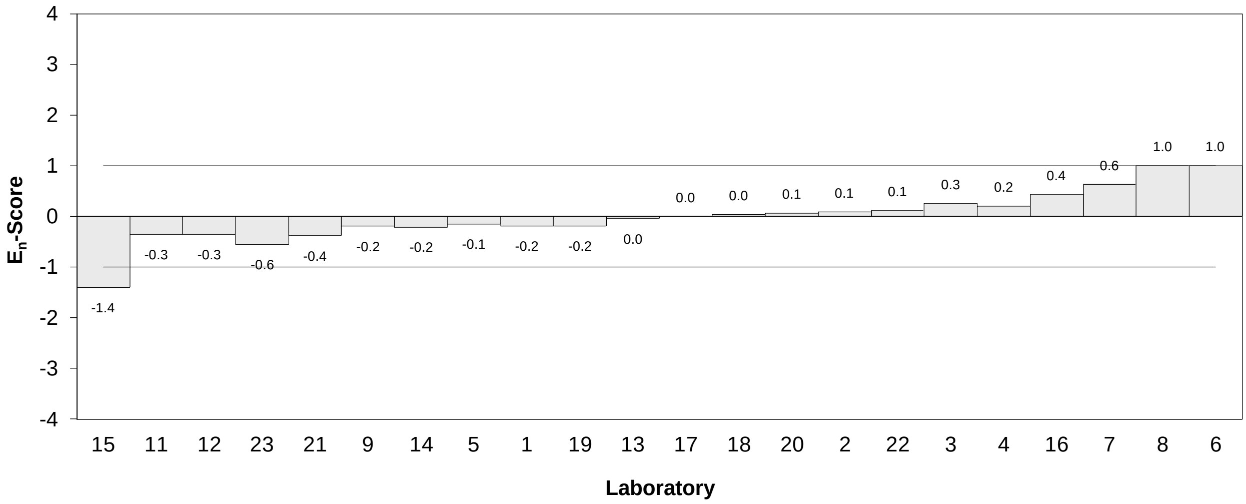


Figure 17

Table 23

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	<0.5	0.1
2	<0.05	0.015
3	<0.5	NR
4	NR	NR
5	<0.1	NR
6	<1	NR
7	<0.1	NR
8	< 0.5	0.12
9	<0.100	NR
10	NT	NT
11	<0.1	NR
12	<0.1	NR
13	0.06	0.01
14	<0.1	NR
15	< 0.2	NR
16	<0.5	NR
17	< 0.5	0.1
18	<0.05	NR
19	<0.1	NR
20	< 0.5	0.2
21	<0.04	NR
22	<0.5	0.35
23	<0.1	NR

Statistics

Assigned Value	Not Set	
Spike	3.50	0.17
N	1	

Table 24

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	<0.5	0.1
2	<0.05	0.015
3	<1	NR
4	NR	NR
5	<0.05	NR
6	<1	NR
7	<0.2	NR
8	< 0.5	0.15
9	<0.100	NR
10	NT	NT
11	<0.05	NR
12	<0.05	NR
13	0.02	0.00
14	<0.1	NR
15	< 0.2	NR
16	<0.5	NR
17	< 0.5	0.1
18	<0.05	NR
19	<0.1	NR
20	< 0.5	0.2
21	<0.04	NR
22	<0.5	0.14
23	<0.1	NR

Statistics

Assigned Value	Not Set	
Spike	2.49	0.12
N	1	

Table 25

Sample Details

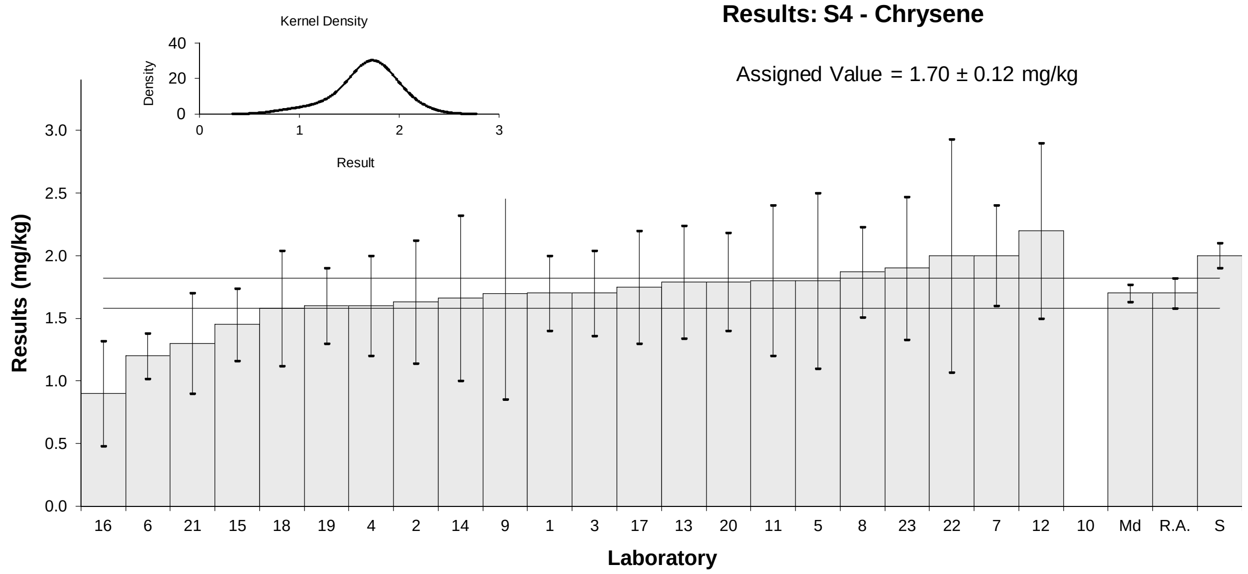
Sample No.	S4
Matrix.	Soil
Analyte.	Chrysene
Units	mg/kg

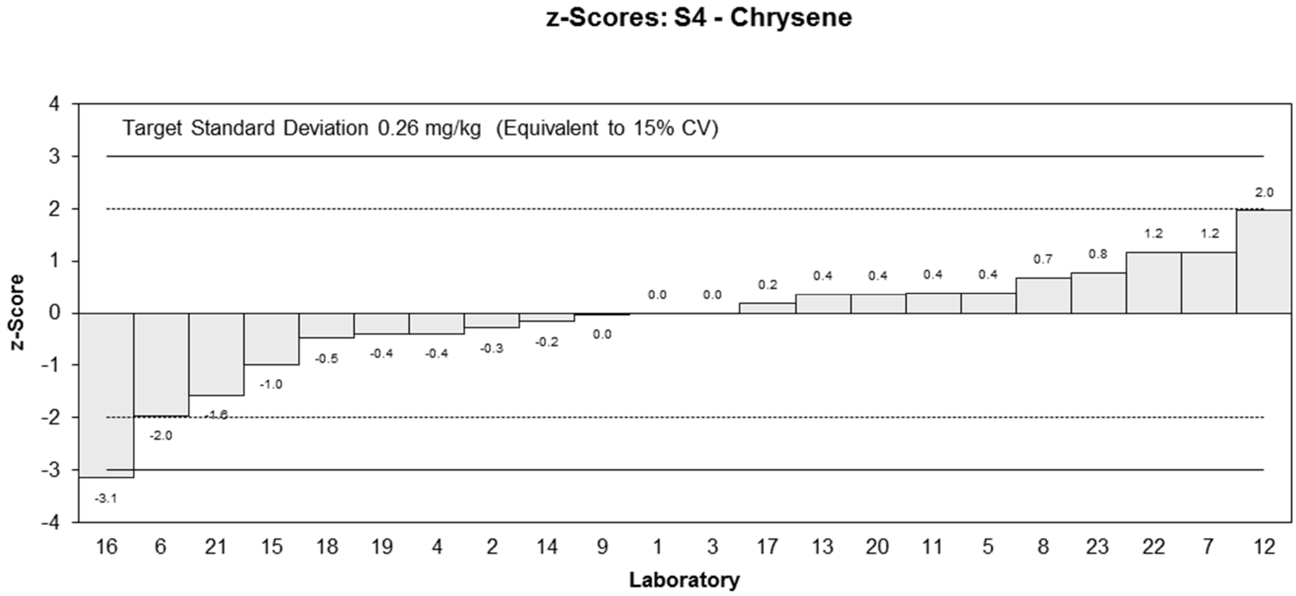
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.7	0.3	0.00	0.00
2	1.63	0.49	-0.27	-0.14
3	1.7	0.34	0.00	0.00
4	1.6	0.4	-0.39	-0.24
5	1.8	0.7	0.39	0.14
6	1.2	0.18	-1.96	-2.31
7	2.0	0.4	1.18	0.72
8	1.87	0.36	0.67	0.45
9	1.699	0.845	0.00	0.00
10	NT	NT		
11	1.8	0.6	0.39	0.16
12	2.2	0.7	1.96	0.70
13	1.79	0.45	0.35	0.19
14	1.66	0.66	-0.16	-0.06
15	1.45	0.29	-0.98	-0.80
16	0.9	0.42	-3.14	-1.83
17	1.75	0.45	0.20	0.11
18	1.58	0.46	-0.47	-0.25
19	1.6	0.3	-0.39	-0.31
20	1.79	0.39	0.35	0.22
21	1.3	0.4	-1.57	-0.96
22	2.0	0.93	1.18	0.32
23	1.9	0.57	0.78	0.34

Statistics

Assigned Value	1.70	0.12
Spike	2.00	0.10
Robust Average	1.70	0.12
Median	1.70	0.07
Mean	1.68	
N	22	
Max.	2.2	
Min.	0.9	
Robust SD	0.23	
Robust CV	14%	


Results: S4 - Chrysene
Assigned Value = 1.70 ± 0.12 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
16 6 21 15 18 19 4 2 14 9 1 3 17 13 20 11 5 8 23 22 7 12 10 Md R.A. S
Laboratory


z-Scores: S4 - Chrysene
Target Standard Deviation 0.26 mg/kg (Equivalent to 15% CV)
z-Score
-3.1 -2.0 -1.6 -1.0 -0.5 -0.4 -0.4 -0.3 -0.2 0.0 0.0 0.0 0.2 0.4 0.4 0.4 0.4 0.7 0.8 1.2 1.2 2.0
16 6 21 15 18 19 4 2 14 9 1 3 17 13 20 11 5 8 23 22 7 12
Laboratory

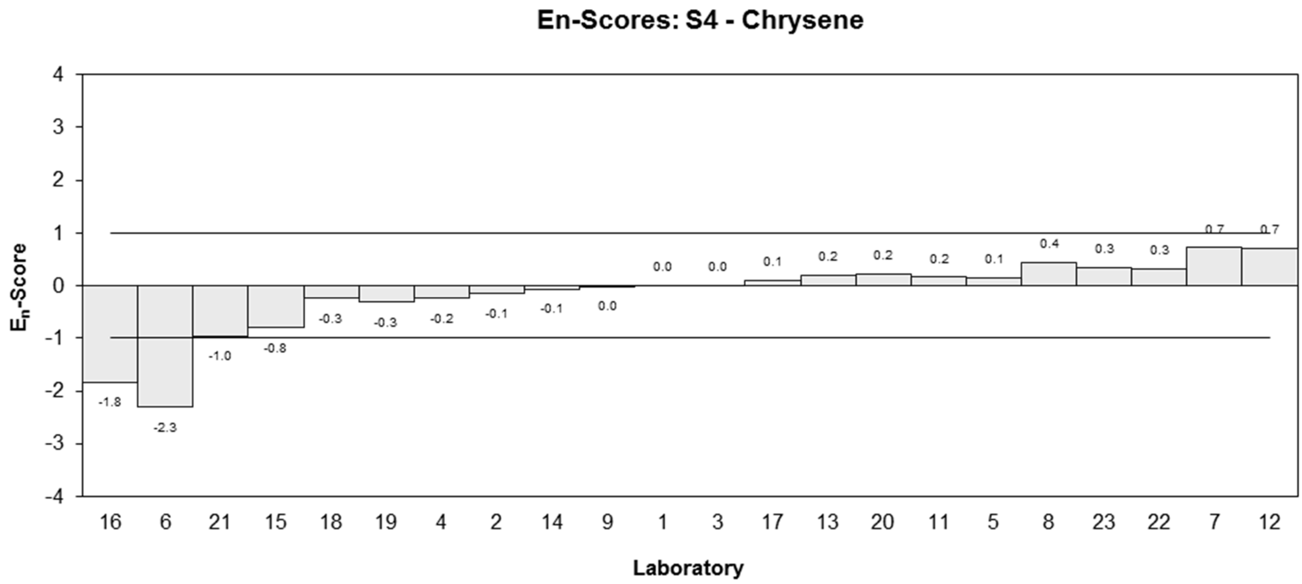

En-Scores: S4 - Chrysene
En-Score
-1.8 -2.3 -1.0 -0.8 -0.3 -0.3 -0.2 -0.1 -0.1 0.0 0.0 0.0 0.1 0.2 0.2 0.2 0.1 0.4 0.3 0.3 0.7 0.7
16 6 21 15 18 19 4 2 14 9 1 3 17 13 20 11 5 8 23 22 7 12
Laboratory

Figure 18

Table 26

Sample Details

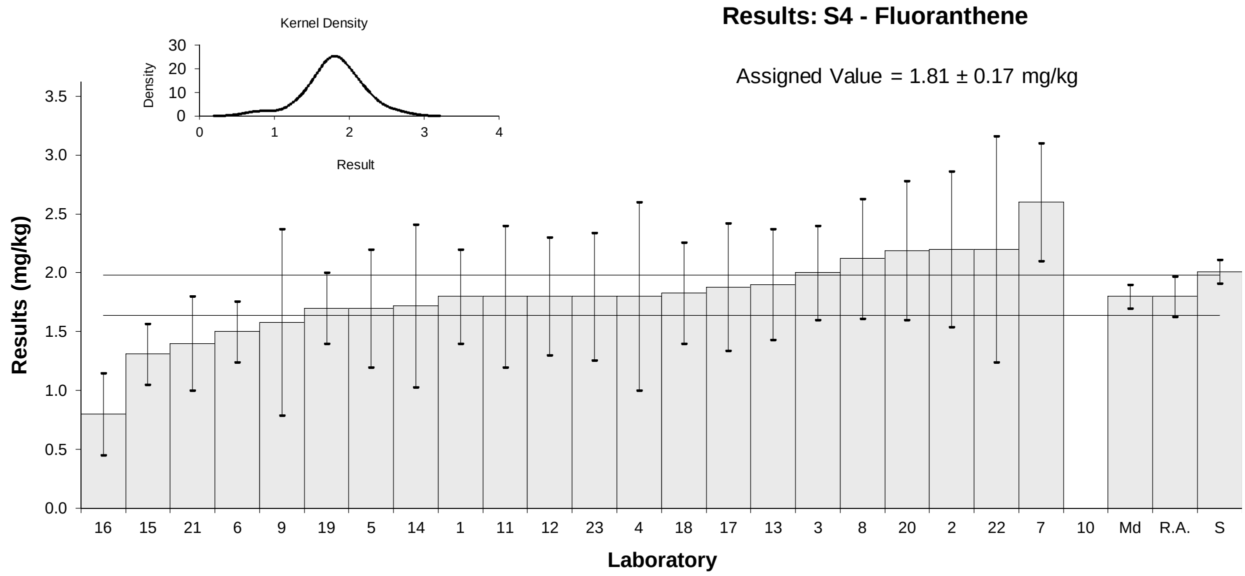
Sample No.	S4
Matrix.	Soil
Analyte.	Fluoranthene
Units	mg/kg

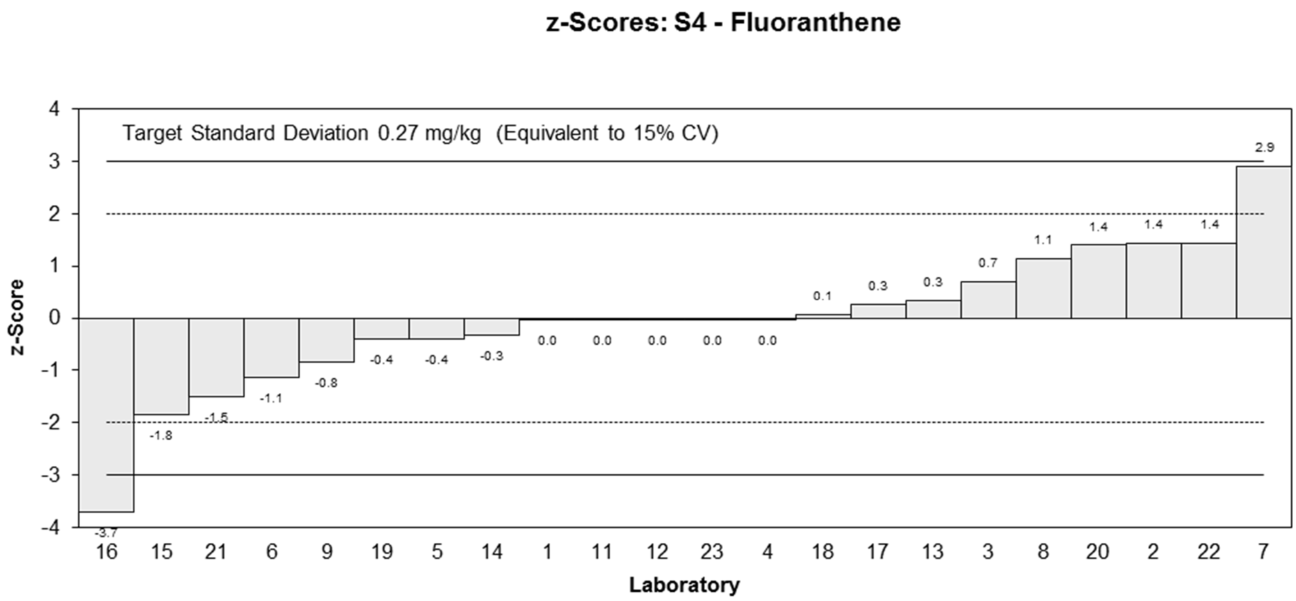
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.8	0.4	-0.04	-0.02
2	2.20	0.66	1.44	0.57
3	2.0	0.40	0.70	0.44
4	1.8	0.8	-0.04	-0.01
5	1.7	0.5	-0.41	-0.21
6	1.5	0.26	-1.14	-1.00
7	2.6	0.5	2.91	1.50
8	2.12	0.51	1.14	0.58
9	1.580	0.790	-0.85	-0.28
10	NT	NT		
11	1.8	0.6	-0.04	-0.02
12	1.8	0.5	-0.04	-0.02
13	1.90	0.47	0.33	0.18
14	1.72	0.69	-0.33	-0.13
15	1.31	0.26	-1.84	-1.61
16	0.8	0.35	-3.72	-2.60
17	1.88	0.54	0.26	0.12
18	1.83	0.43	0.07	0.04
19	1.7	0.3	-0.41	-0.32
20	2.19	0.59	1.40	0.62
21	1.4	0.4	-1.51	-0.94
22	2.2	0.96	1.44	0.40
23	1.8	0.54	-0.04	-0.02

Statistics

Assigned Value	1.81	0.17
Spike	2.01	0.10
Robust Average	1.81	0.17
Median	1.80	0.10
Mean	1.80	
N	22	
Max.	2.6	
Min.	0.8	
Robust SD	0.30	
Robust CV	17%	


Results: S4 - Fluoranthene
Assigned Value = 1.81 ± 0.17 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
16 15 21 6 9 19 5 14 1 11 12 23 4 18 17 13 3 8 20 2 22 7 10 Md R.A. S


z-Scores: S4 - Fluoranthene
Target Standard Deviation 0.27 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
16 15 21 6 9 19 5 14 1 11 12 23 4 18 17 13 3 8 20 2 22 7
-3.7 -1.8 -1.5 -1.1 -0.8 -0.4 -0.4 -0.3 0.0 0.0 0.0 0.0 0.0 0.1 0.3 0.3 0.7 1.1 1.4 1.4 1.4 2.9

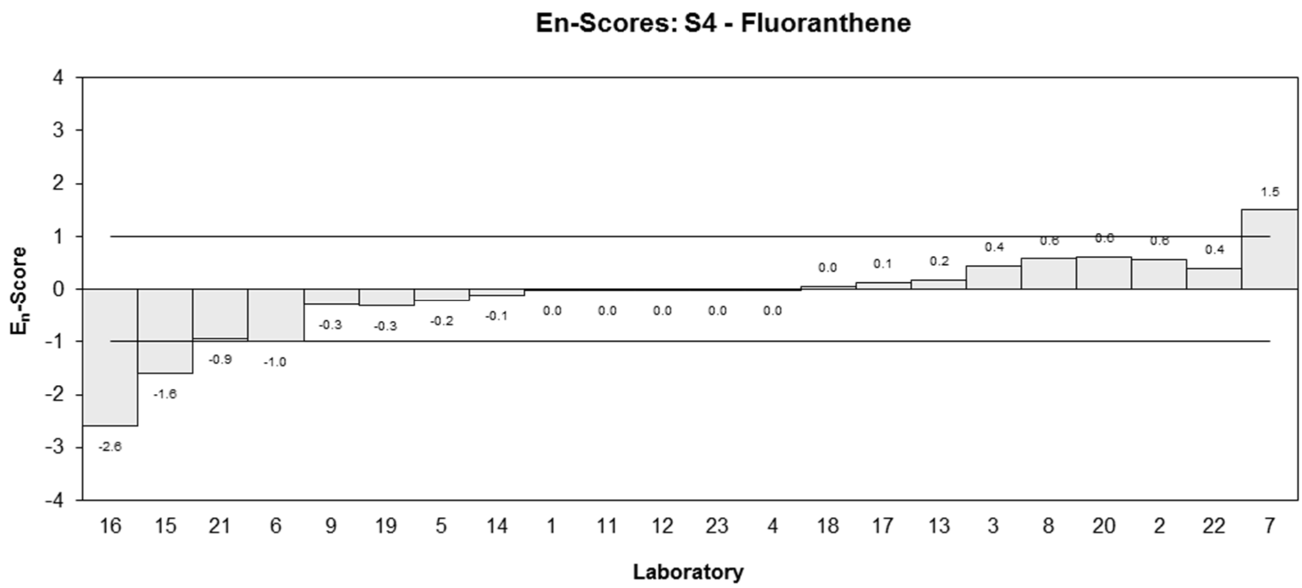

En-Scores: S4 - Fluoranthene
E_n-Score
Laboratory
16 15 21 6 9 19 5 14 1 11 12 23 4 18 17 13 3 8 20 2 22 7
-2.6 -1.6 -0.9 -1.0 -0.3 -0.3 -0.2 -0.1 0.0 0.0 0.0 0.0 0.0 0.0 0.1 0.2 0.4 0.6 0.6 0.6 0.4 1.5

Figure 19

Table 27

Sample Details

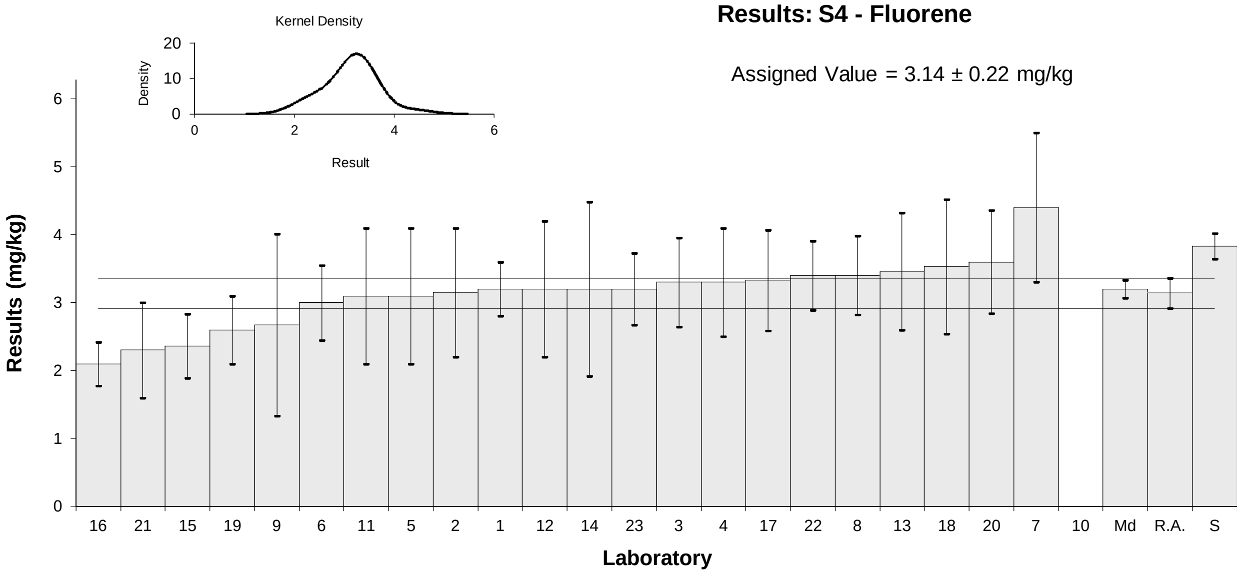
Sample No.	S4
Matrix.	Soil
Analyte.	Fluorene
Units	mg/kg

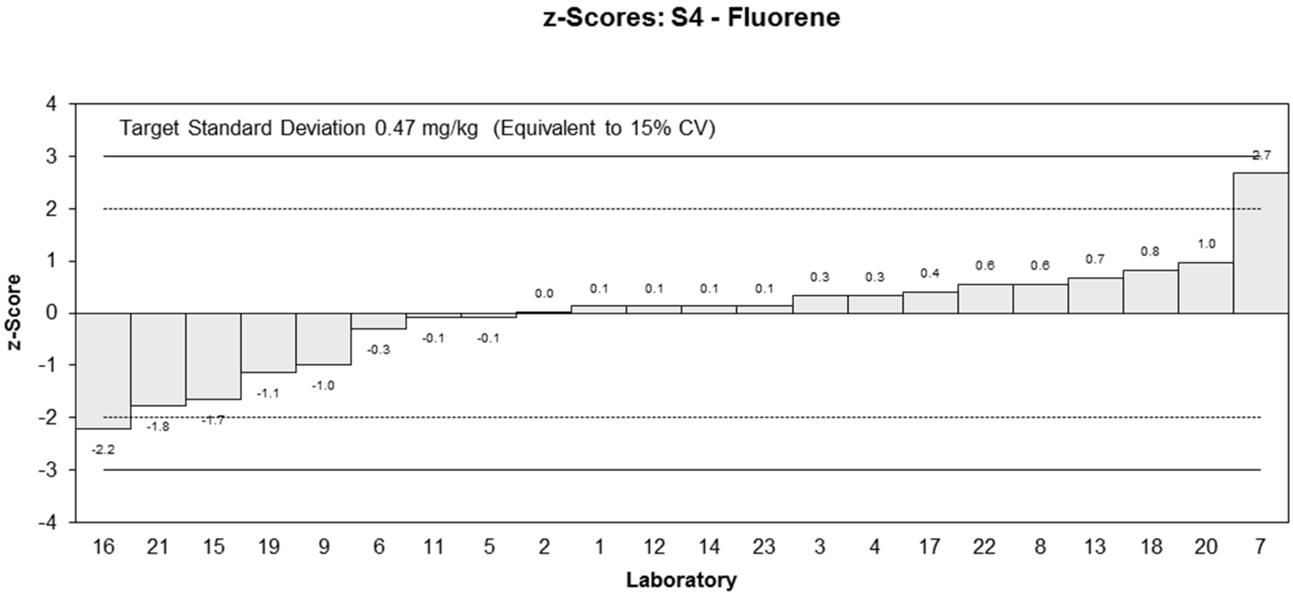
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.2	0.4	0.13	0.13
2	3.15	0.95	0.02	0.01
3	3.3	0.66	0.34	0.23
4	3.3	0.8	0.34	0.19
5	3.1	1	-0.08	-0.04
6	3.0	0.55	-0.30	-0.24
7	4.4	1.1	2.68	1.12
8	3.40	0.58	0.55	0.42
9	2.674	1.337	-0.99	-0.34
10	NT	NT		
11	3.1	1.0	-0.08	-0.04
12	3.2	1	0.13	0.06
13	3.46	0.86	0.68	0.36
14	3.2	1.28	0.13	0.05
15	2.36	0.47	-1.66	-1.50
16	2.1	0.32	-2.21	-2.68
17	3.33	0.74	0.40	0.25
18	3.53	0.99	0.83	0.38
19	2.6	0.5	-1.15	-0.99
20	3.60	0.76	0.98	0.58
21	2.3	0.7	-1.78	-1.14
22	3.4	0.51	0.55	0.47
23	3.2	0.53	0.13	0.10

Statistics

Assigned Value	3.14	0.22
Spike	3.83	0.19
Robust Average	3.14	0.22
Median	3.20	0.13
Mean	3.13	
N	22	
Max.	4.4	
Min.	2.1	
Robust SD	0.40	
Robust CV	13%	


Results: S4 - Fluorene
Assigned Value = 3.14 ± 0.22 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
16 21 15 19 9 6 11 5 2 1 12 14 23 3 4 17 22 8 13 18 20 7 10 Md R.A. S


z-Scores: S4 - Fluorene
Target Standard Deviation 0.47 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
16 21 15 19 9 6 11 5 2 1 12 14 23 3 4 17 22 8 13 18 20 7

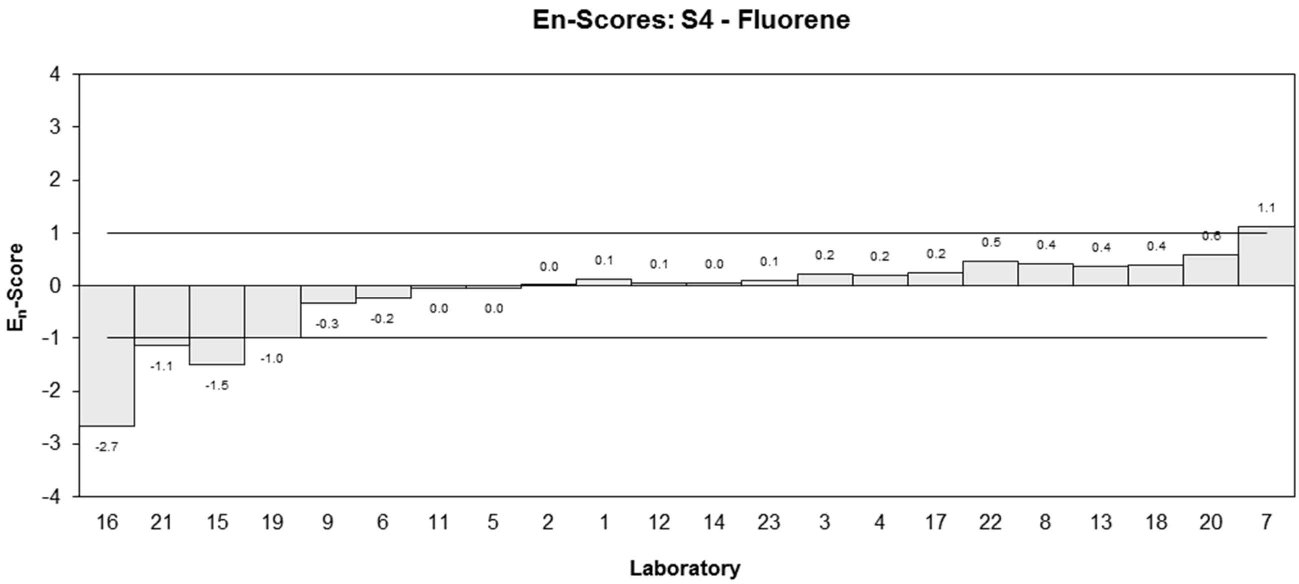

En-Scores: S4 - Fluorene
E_n-Score
Laboratory
16 21 15 19 9 6 11 5 2 1 12 14 23 3 4 17 22 8 13 18 20 7

Figure 20

Table 28

Sample Details

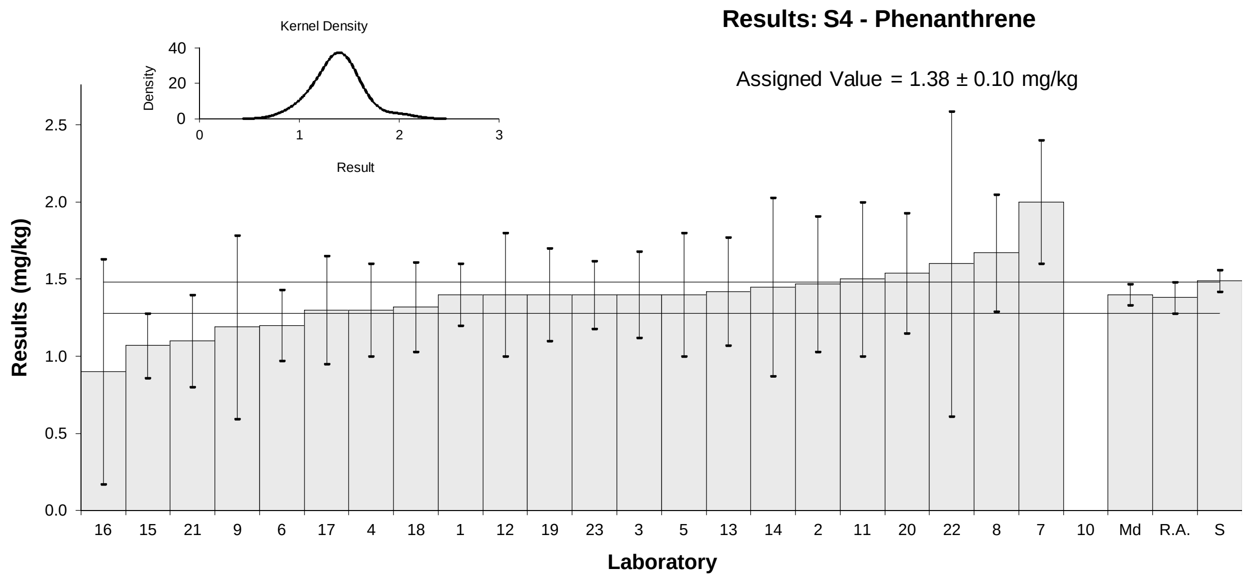
Sample No.	S4
Matrix.	Soil
Analyte.	Phenanthrene
Units	mg/kg

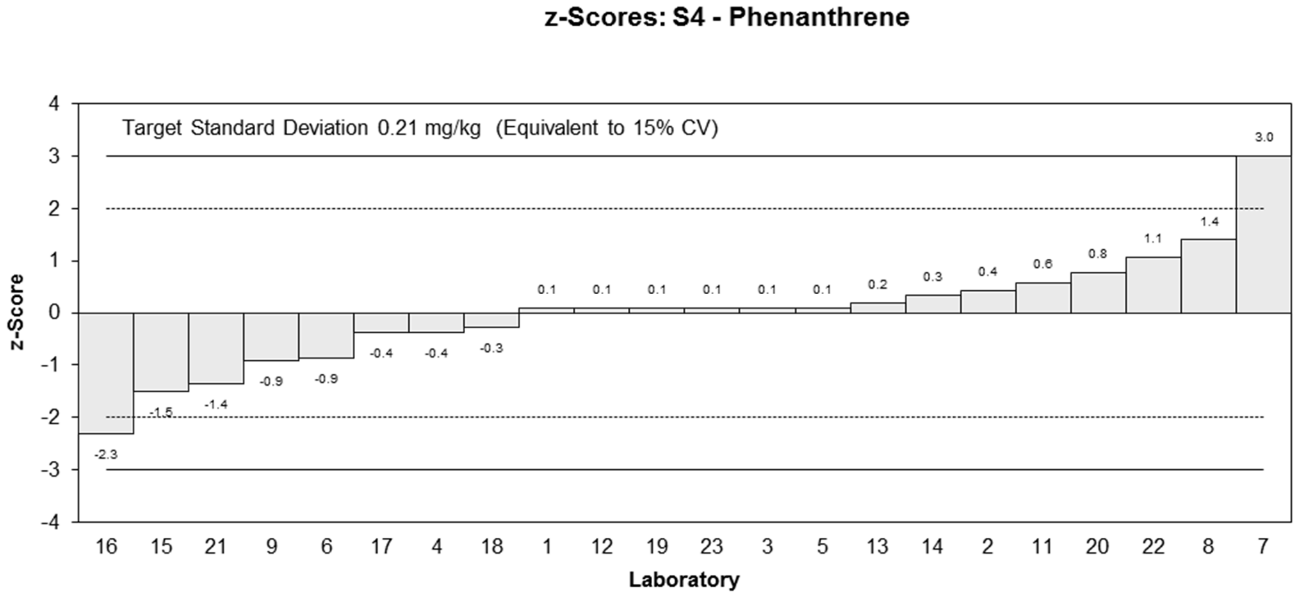
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.4	0.2	0.10	0.09
2	1.47	0.44	0.43	0.20
3	1.4	0.28	0.10	0.07
4	1.3	0.3	-0.39	-0.25
5	1.4	0.4	0.10	0.05
6	1.2	0.23	-0.87	-0.72
7	2.0	0.4	3.00	1.50
8	1.67	0.38	1.40	0.74
9	1.189	0.594	-0.92	-0.32
10	NT	NT		
11	1.5	0.5	0.58	0.24
12	1.4	0.4	0.10	0.05
13	1.42	0.35	0.19	0.11
14	1.45	0.58	0.34	0.12
15	1.07	0.21	-1.50	-1.33
16	0.9	0.73	-2.32	-0.65
17	1.3	0.35	-0.39	-0.22
18	1.32	0.29	-0.29	-0.20
19	1.4	0.3	0.10	0.06
20	1.54	0.39	0.77	0.40
21	1.1	0.3	-1.35	-0.89
22	1.6	0.99	1.06	0.22
23	1.4	0.22	0.10	0.08

Statistics

Assigned Value	1.38	0.10
Spike	1.49	0.07
Robust Average	1.38	0.10
Median	1.40	0.07
Mean	1.38	
N	22	
Max.	2	
Min.	0.9	
Robust SD	0.19	
Robust CV	14%	


Results: S4 - Phenanthrene
Assigned Value = 1.38 ± 0.10 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
16 15 21 9 6 17 4 18 1 12 19 23 3 5 13 14 2 11 20 22 8 7 10 Md R.A. S


z-Scores: S4 - Phenanthrene
Target Standard Deviation 0.21 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
16 15 21 9 6 17 4 18 1 12 19 23 3 5 13 14 2 11 20 22 8 7
-2.3 -1.5 -1.4 -0.9 -0.9 -0.4 -0.4 -0.3 0.1 0.1 0.1 0.1 0.1 0.1 0.2 0.3 0.4 0.6 0.8 1.1 1.4 3.0

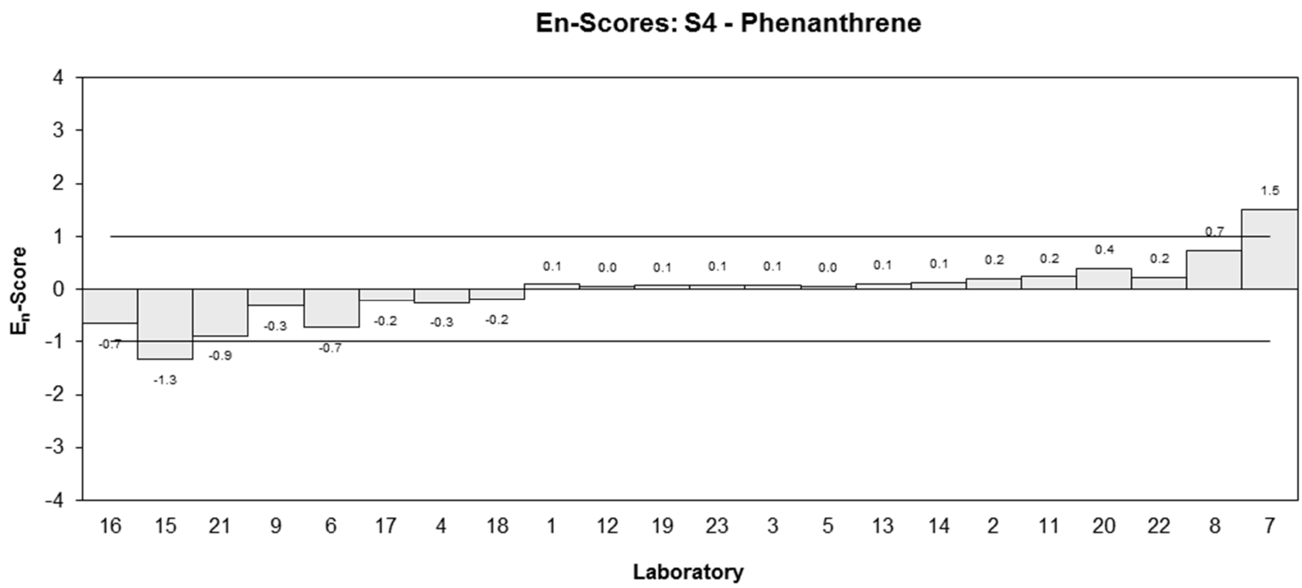

En-Scores: S4 - Phenanthrene
E_n-Score
Laboratory
16 15 21 9 6 17 4 18 1 12 19 23 3 5 13 14 2 11 20 22 8 7
-0.7 -1.3 -0.9 -0.3 -0.7 -0.2 -0.3 -0.2 0.1 0.0 0.1 0.1 0.1 0.0 0.1 0.1 0.2 0.2 0.4 0.2 0.7 1.5

Figure 21

Table 29

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	<0.5	0.1
2	<0.05	0.015
3	<0.5	NR
4	NR	NR
5	<0.1	NR
6	<1	NR
7	<0.1	NR
8	< 0.5	0.12
9	<0.100	NR
10	NT	NT
11	<0.1	NR
12	<0.1	NR
13	0.04	0.01
14	<0.1	NR
15	< 0.2	NR
16	<0.5	NR
17	< 0.5	0.1
18	<0.05	NR
19	<0.1	NR
20	< 0.5	0.2
21	<0.04	NR
22	<0.5	0.23
23	<0.1	NR

Statistics

Assigned Value	Not Set	
Spike	1.91	0.10
N	1	

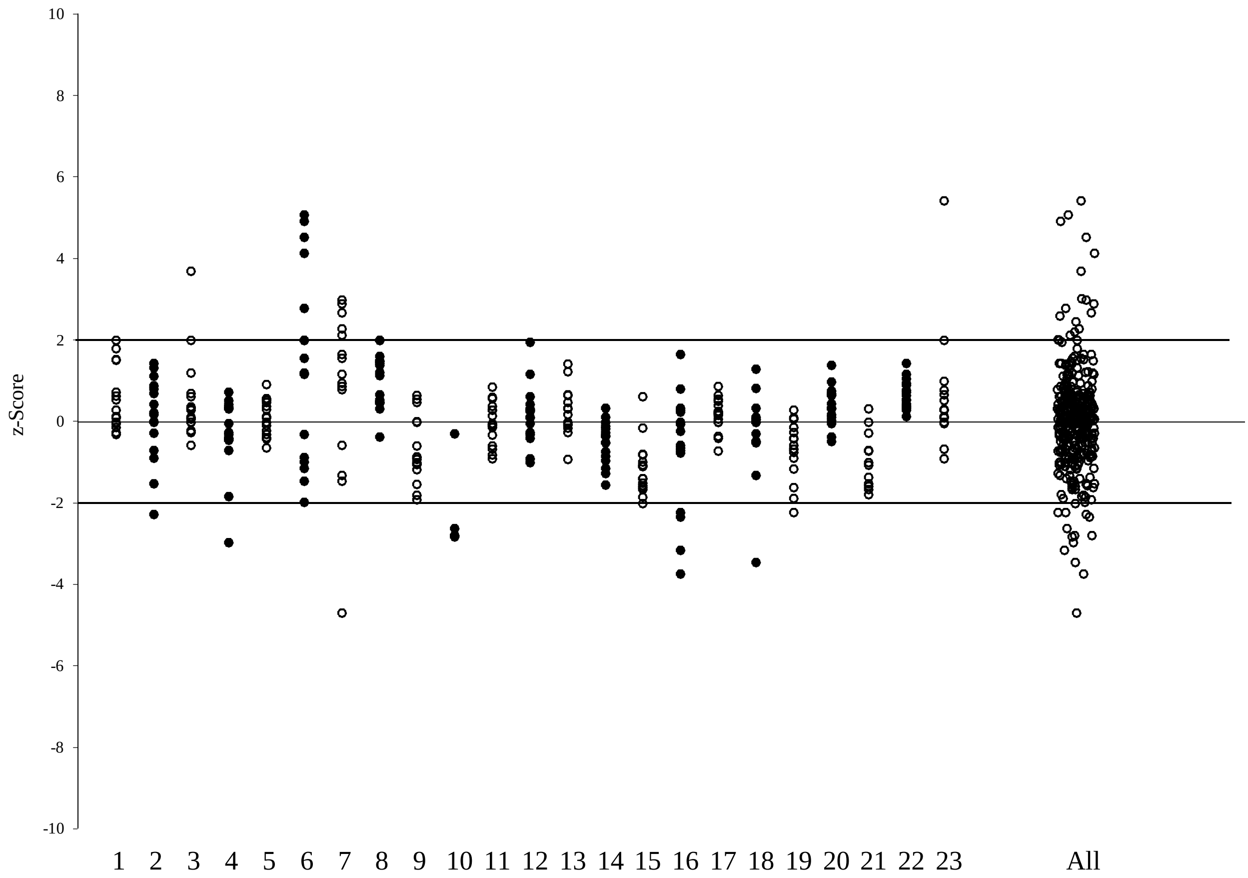


Figure 22 z-Score Dispersal by Laboratory

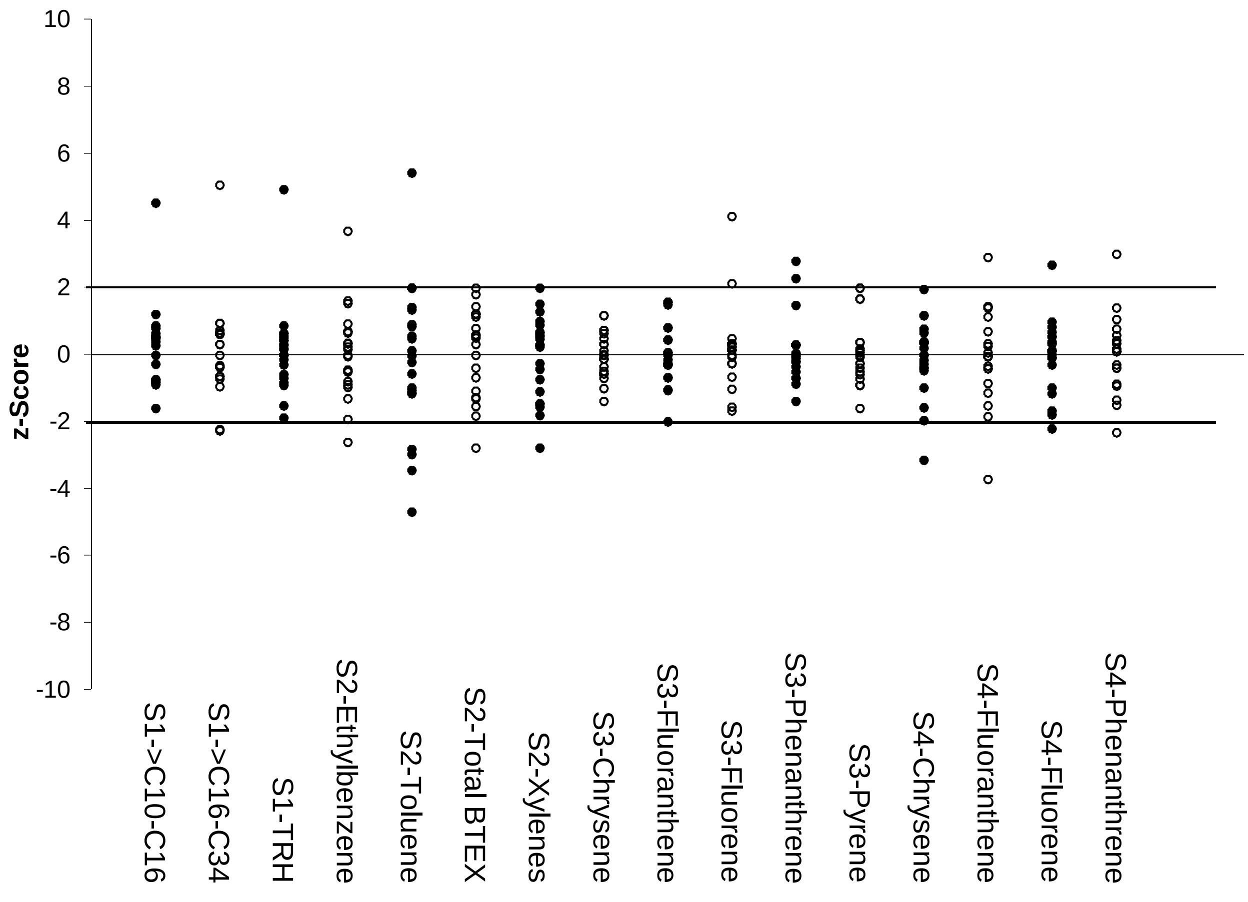


Figure 23 z-Score Dispersal by Sample and Analyte

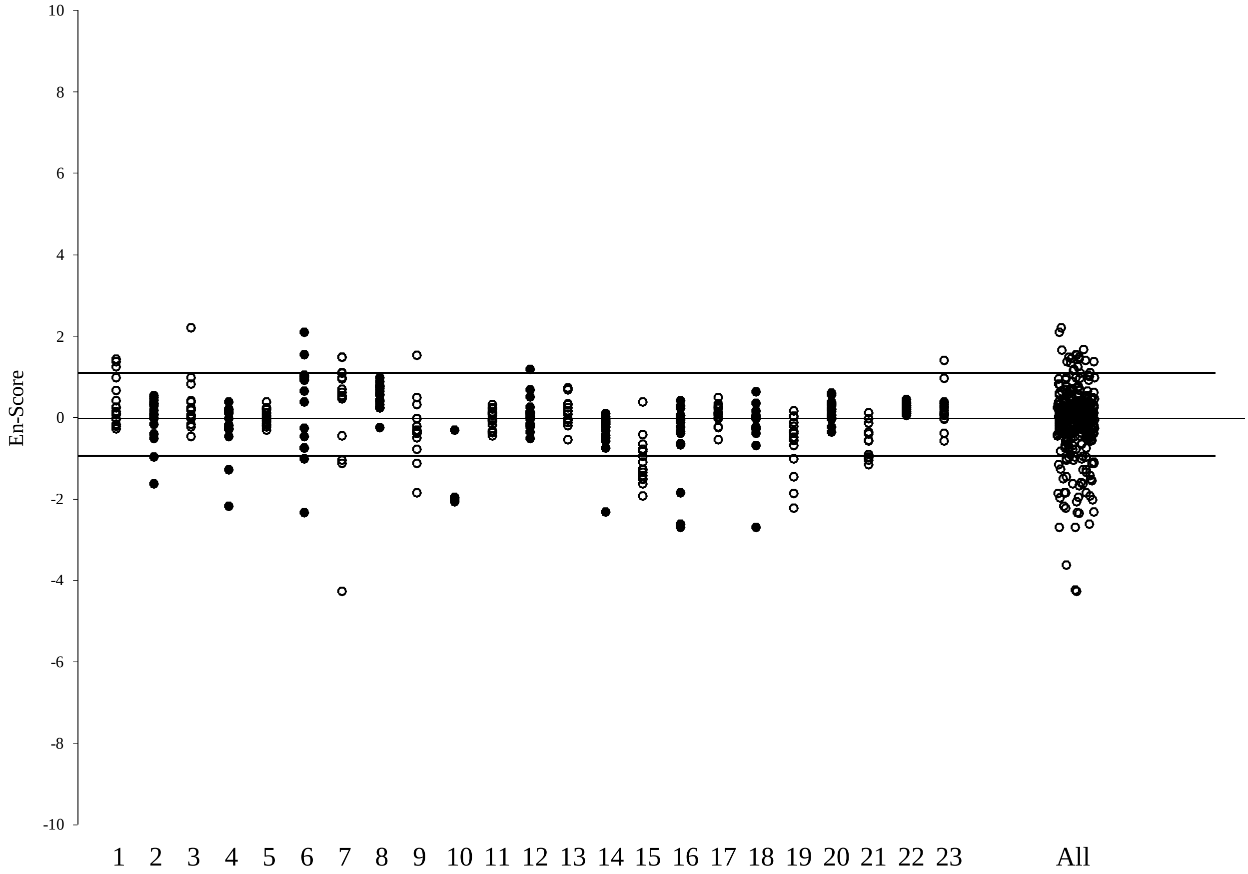


Figure 24 E_n-Score Dispersal by Laboratory

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust average of participants' results was used as the assigned value. The robust averages and associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015€, Statistical methods for use in proficiency testing by interlaboratory comparisons'.[8] Appendix 3 sets out the calculation for the expanded uncertainty of the robust average of Fluorene in Sample S3.

No assigned value was set for the C6-C10 range and benzene in Sample S2, benzo(a)pyrene and anthracene in Samples S3 and S4 and pyrene in Sample S4 because the submitted results were too variable or significantly lower than the spiked value.

In the case of pyrene in Sample S3, the assigned value was lower than the spiked concentration, however there was still a consensus of participants.

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

Table 30 Comparison of Assigned Value and Spiked Concentration.

Analyte	Assigned concentration (mg/kg)	Spiked value (mg/kg)	Assigned/spike
Ethylbenzene	77.2	90.8	85%
Toluene	540	790	68%
Total BTEX	1100	1610	68%
Xylenes	460	680	68%
Chrysene (S3)	1.53	2.00	77%
Fluoranthene (S3)	1.78	2.01	89%
Fluorene (S3)	3.33	3.83	87%
Phenanthrene (S3)	1.34	1.49	90%
Pyrene (S3)	1.04	1.91	54%
Chrysene (S4)	1.70	2.00	85%
Fluoranthene (S4)	1.81	2.01	90%
Fluorene (S4)	3.14	3.83	82%
Phenanthrene (S4)	1.38	1.49	93%

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 (Table 4).

It is a requirement of the ISO Standard 17025 that laboratories have procedures to estimate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including 'when the client's instruction so requires.' Of 424 numerical results, 419 (99%) were reported with an associated expanded uncertainty.

Expanded uncertainties were within the range 0% to 200% relative. An expanded uncertainty of less than 15% relative is likely to be unrealistically small for the routine measurement of a hydrocarbon pollutant in soil. Of the 419 expanded uncertainties, 17 were less than 15%

relative. Some laboratories reported expanded uncertainties for analyte values that were below their limit of reporting/detection (e.g. < 0.5 ± 0.1)

Laboratories having a satisfactory z-score and an unsatisfactory E_n-score are likely to have underestimated the expanded uncertainty associated with the result.

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 1695.7 ± 54.0 mg/kg it is better to report 1700 ± 54 mg/kg).[7]

6.3 z-Score

z-Scores were calculated using a target standard deviation equivalent to 15% CV.

To account for possible bias in the consensus values due to laboratories using inefficient analytical/extraction techniques, z-scores were adjusted for individual analytes in Sample S2 so that some z-scores greater than 2 were set at 2. A maximum acceptable concentration was set to two target standard deviations more than the spiked level. For results higher than the maximum acceptable concentration z-scores were not adjusted. This ensured that laboratories reporting results close to the spiked concentration were not penalised. Z-Scores of less than 2 were left unaltered.

Of 348 results for which z-scores were calculated, 323 (93%) returned a satisfactory score of $|z| \le 2$.

Laboratories **1**, **5**, **8, 11**, **12**, **14**, **15**, **17**, **20** and **22** returned satisfactory z-scores for all sixteen analytes for which z-scores were calculated.

Summaries of z-scores by laboratory and by analyte are presented in Figures 22 and 23.

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.

Of 348 results for which E_n-scores were calculated, 299 (86%) returned a satisfactory score of $|E_n| \le 1$.

Laboratories **5**, **8**, **11**, **17**, **20** and **22** returned satisfactory E_n-scores for all sixteen analytes for which scores were calculated. A summary of E_n-scores by laboratory is presented in Figure 24.

6.5 Participants' Analytical Methods

TRH in Sample S1

Twenty participants used dichloromethane (DCM)/acetone in a 1:1 ratio, one participant DCM only and two hexane/acetone in a 1:1 ratio. No trends with the extraction solvent were evident (see Figure 19). Three laboratories performed a clean-up procedure using silica. All laboratories used GC-FID to measure hydrocarbons in the sample extract (Table 1).

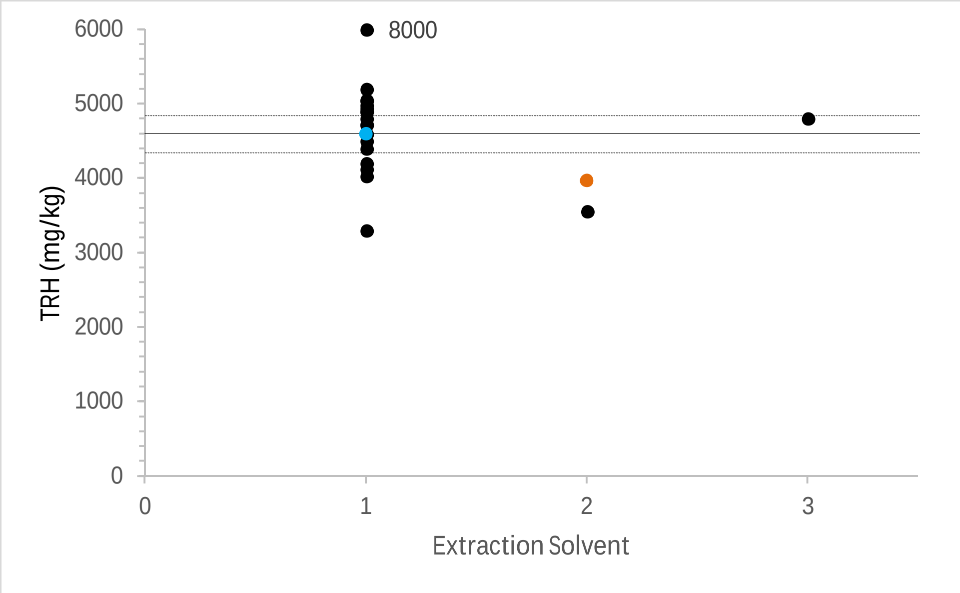


Figure 25 TRH results vs extraction solvent
1 = DCM/Acetone, 2 = Hexane/Acetone, 3 = DCM only
Blue = ASE + silica clean-up, Orange = silica clean-up
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (dashed). Results >6000 have been plotted as 6000

BTEX in Sample S2

Twenty-one laboratories used methanol as the extraction solvent. Laboratory 21 used sodium chloride / phosphoric acid matrix modifying solution for extraction, but did not report any results as the concentration exceeded the working range of the method.

For analysis, sixteen laboratories used purge-and-trap GC-MS, five laboratories used headspace with either GC-FID or GC-MS (Table 2) and one laboratory used GC-MS only. No trends were evident.

Low recovery of benzene in Sample S2 (56%) indicated that participants had difficulties with the extraction of this analyte. Literature suggests that hot methanol extraction using an ultrasonic bath/sonication prior to purge-and-trap is recommended to improve the recovery of benzene in soil samples.[10]

PAHs in Sample S3/S4

Seventeen participants used dichloromethane (DCM)/acetone in a 1:1 ratio, two used hexane/acetone (1:1), two used DCM only, and one used toluene. To facilitate extraction some participants used tumbling (2), whirly-gig (1), sonication (3), ASE (2), and tumbling/sonication (1). Thirteen participants did not specify the extraction technique used.

Twenty-one laboratories used GC-MS(MS) and one GC-FID (Table 3).

Results reported for chrysene, fluoranthene, fluorene and phenanthrene were in good agreement with the spiked value (77-90%) – Figures 26 to 29.

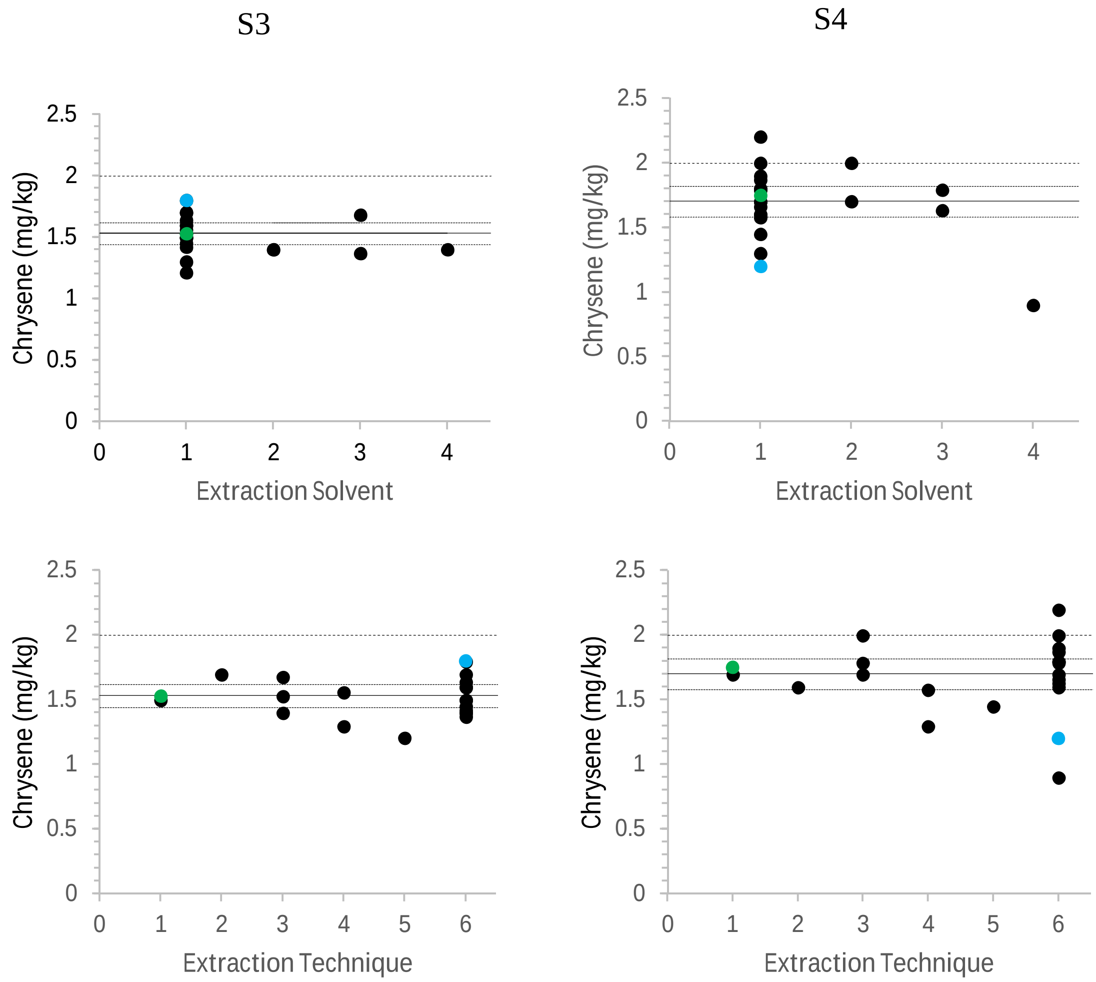


Figure 26 PAH results vs extraction solvent/technique (Chrysene)
Extraction Solvent: 1 = DCM/Acetone 2 = DCM 3 = Hexane/Acetone 4 = Toluene
Extraction Technique: 1 = tumbling 2 = whirly-gig 3 = sonication/ultrasonic 4 = ASE 5 = tumbling/sonication 6 = other/unspecified
black = GC-MS blue = GC-FID; green = GC-MS/MS;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Larger dashed lines are spike levels.

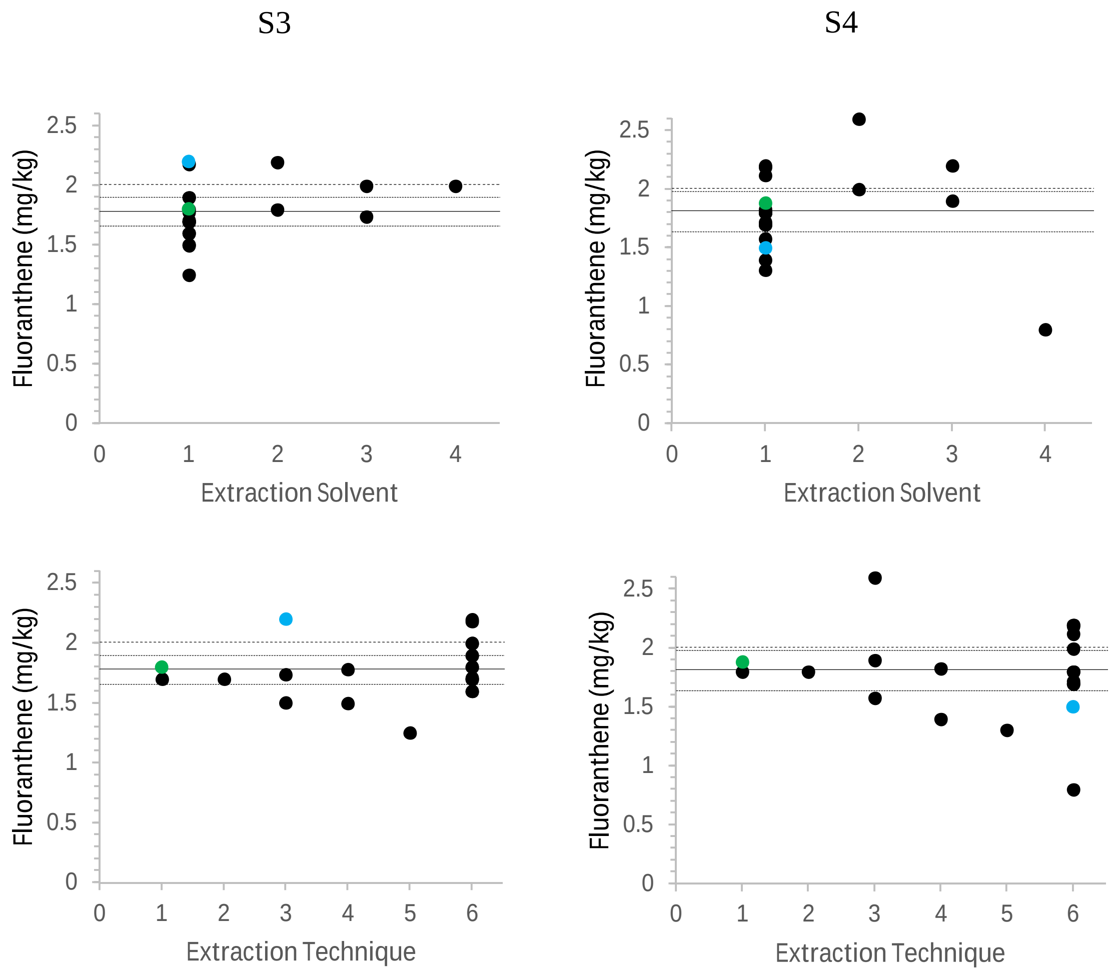


Figure 27 PAH results vs extraction solvent/technique (Fluoranthene)
Extraction Solvent: 1 = DCM/Acetone 2 = DCM 3 = Hexane/Acetone 4 = Toluene
Extraction Technique: 1 = tumbling 2 = whirly-gig 3 = sonication/ultrasonic 4 = ASE 5 = tumbling/sonication 6 = other/unspecified
black = GC-MS blue = GC-FID; green = GC-MS/MS;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Larger dashed lines are spike levels.

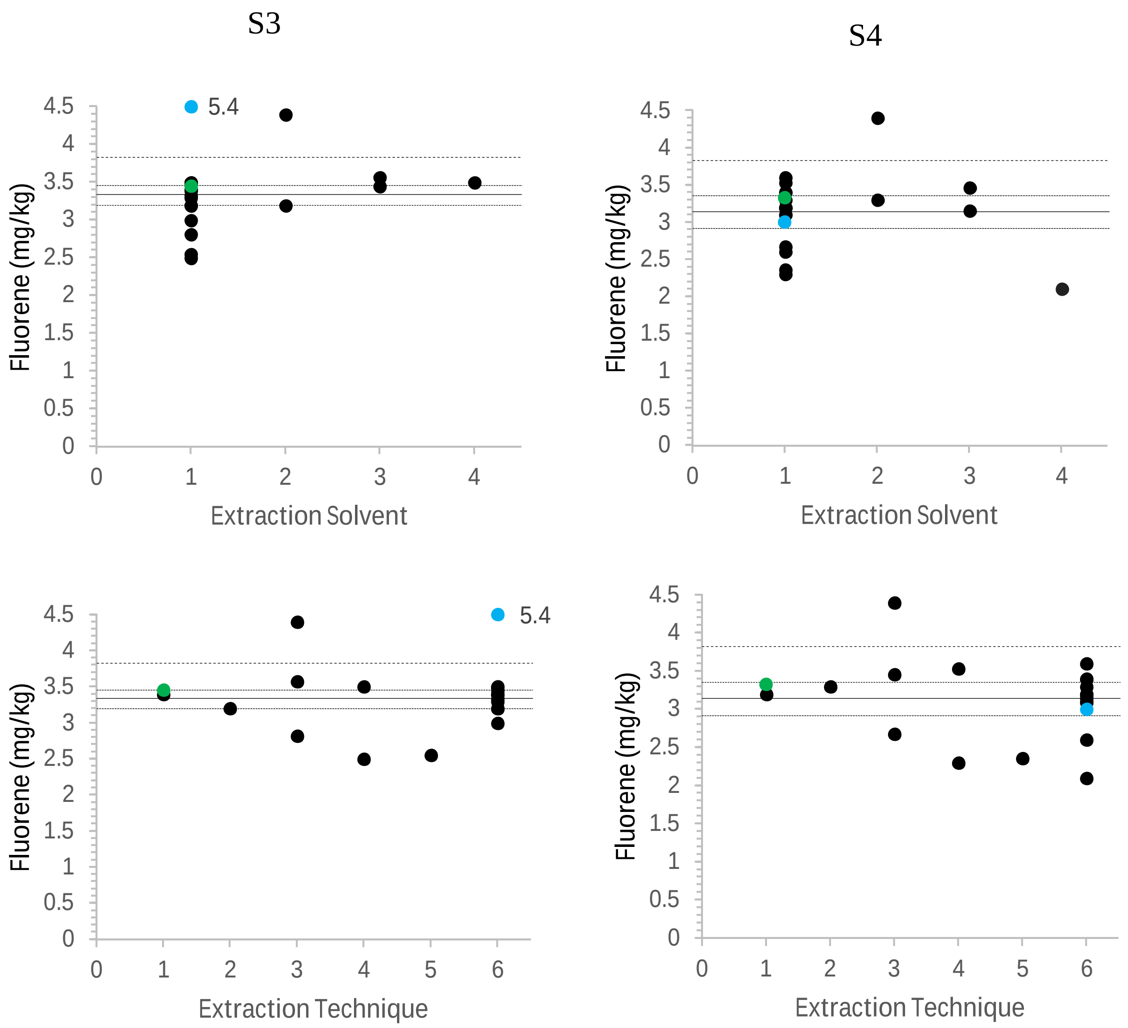


Figure 28 PAH results vs extraction solvent/technique (Fluorene)
Extraction Solvent: 1 = DCM/Acetone 2 = DCM 3 = Hexane/Acetone 4 = Toluene
Extraction Technique: 1 = tumbling 2 = whirly-gig 3 = sonication/ultrasonic 4 = ASE 5 = tumbling/sonication 6 = other/unspecified
black = GC-MS blue = GC-FID; green = GC-MS/MS;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Larger dashed lines are spike levels. Results > 4.5 have been plotted as 4.5

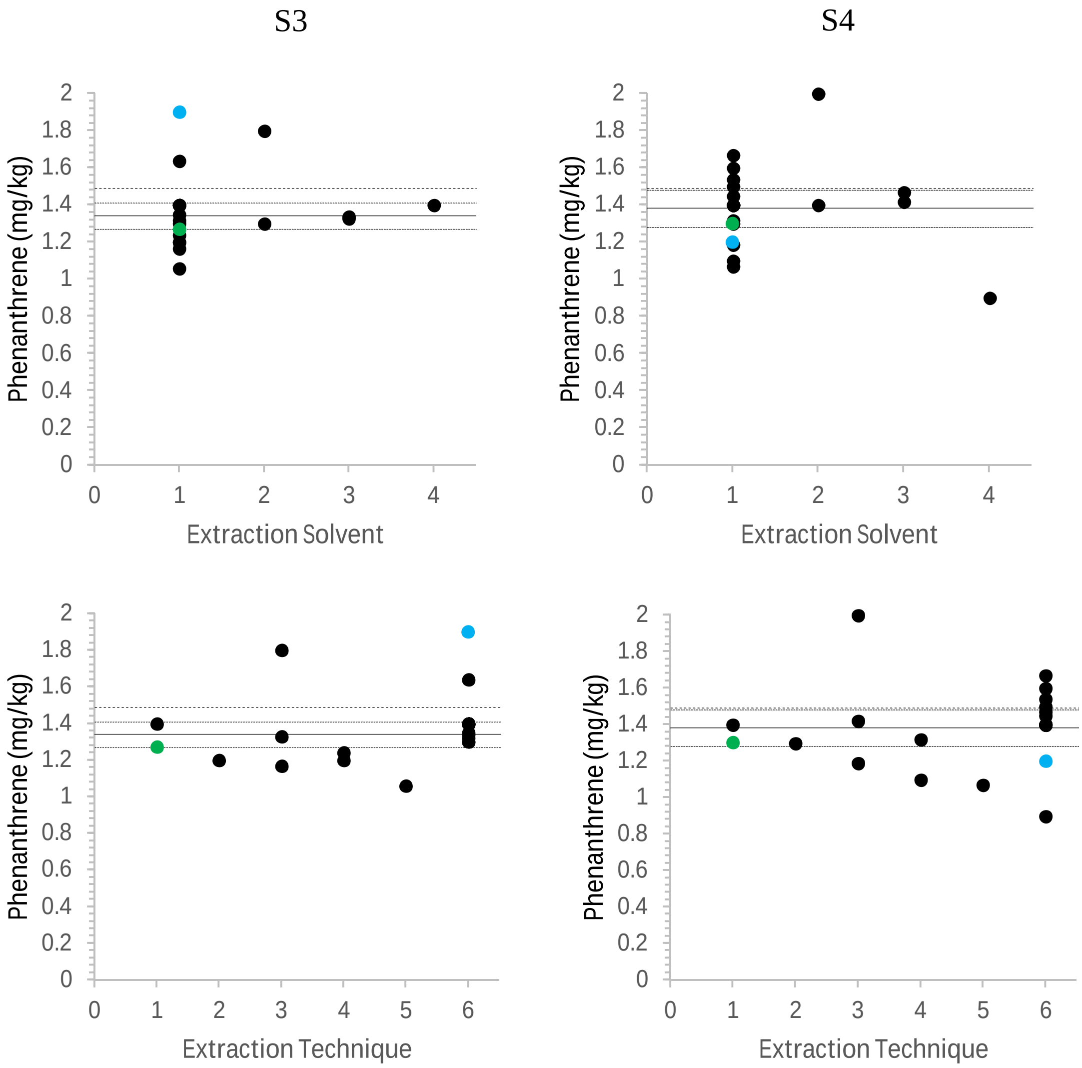
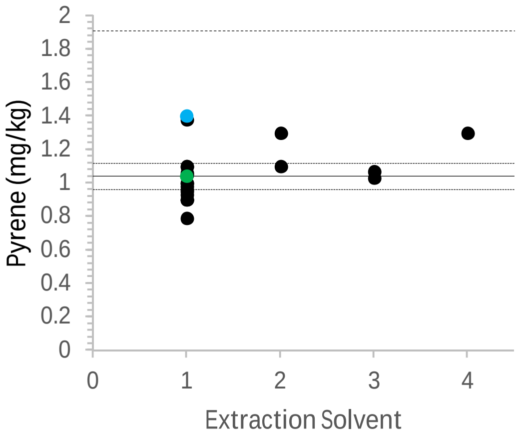


Figure 29 PAH results vs extraction solvent/technique (Phenanthrene)
Extraction Solvent: 1 = DCM/Acetone 2 = DCM 3 = Hexane/Acetone 4 = Toluene
Extraction Technique: 1 = tumbling 2 = whirly-gig 3 = sonication/ultrasonic 4 = ASE 5 = tumbling/sonication 6 = other/unspecified
black = GC-MS blue = GC-FID; green = GC-MS/MS;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Larger dashed lines are spike levels.

S3



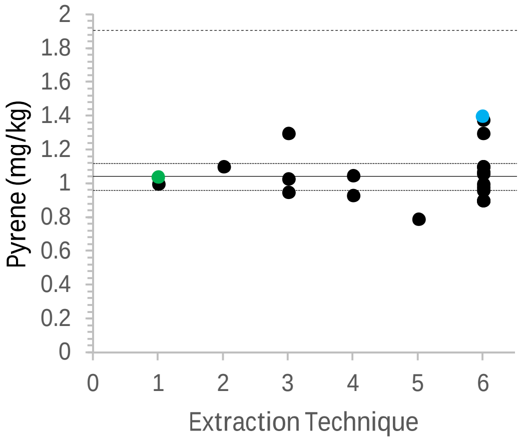


Figure 30 PAH results vs extraction solvent/technique (Pyrene)
Extraction Solvent: 1 = DCM/Acetone 2 = DCM 3 = Hexane/Acetone 4 = Toluene
Extraction Technique: 1 = tumbling 2 = whirly-gig 3 = sonication/ultrasonic 4 = ASE 5 = tumbling/sonication 6 = other/unspecified
black = GC-MS blue = GC-FID; green = GC-MS/MS;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Larger dashed lines are spike levels.

The nature of the soil matrix (S3-Menangle Topsoil and S4 – clay) substantially affected the recovery of benzo(a)pyrene, anthracene and pyrene – Figure 31. While recoveries of anthracene, benzo(a)pyrene and pyrene are lower than those of the other PAHs in Sample S3, there was a considerable decrease in recovery in Sample S4 clay (as highlighted by the red circles). None of the participants' methods were able to extract these three analytes from the clay soil sample in any appreciable amount.

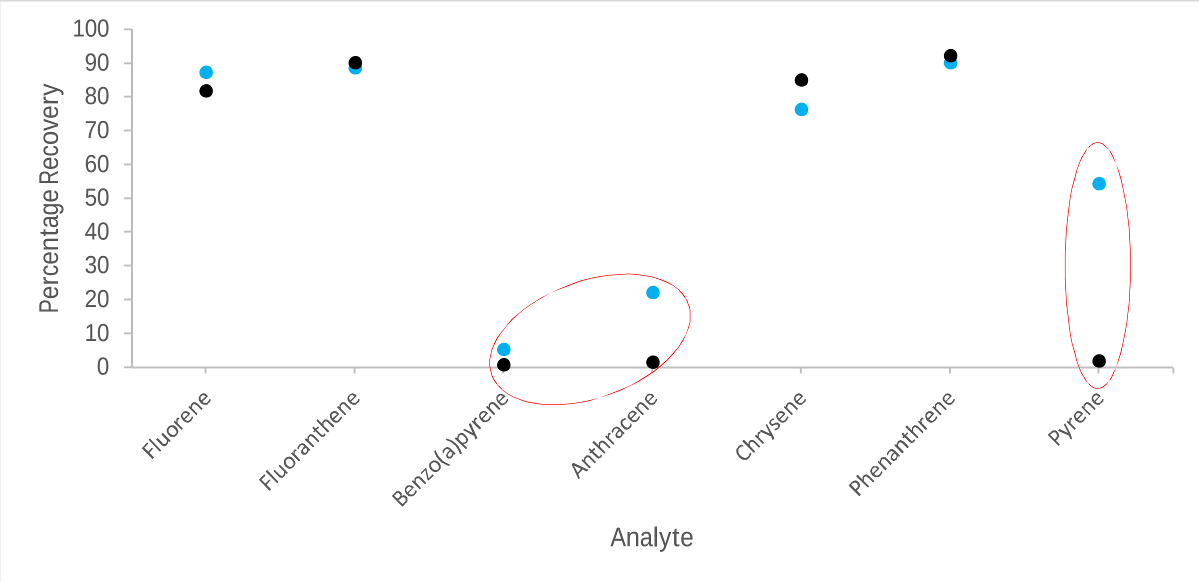


Figure 31 Percentage recoveries of PAHs in Menangle Topsoil (blue) and clay soil (black).

The study coordinator thanks laboratories for their time in reporting method details, which enhance the educational value of NMI PT.

6.6 Accreditation

Laboratory **1** was not accredited and laboratories **15** and **20** did not specify accreditation status. All other laboratories were accredited to ISO 17025.

6.7 Certified Reference Materials (CRM)

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

Three laboratories **8, 17** and **20** used MX-015, a certified reference material for TRH in soil. This material has been produced and certified by NMI Sydney and is available for purchase.

Sixteen laboratories reported using 'certified' standards such as:

- AccuStandard
- Supelco
- N-alkanes
- Restek
- CRM 356-100
- ChemService

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

> '***reference material***, *accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures*'[9]

6.8 Comparison with Previous Studies

Overall percentages of z-scores obtained by laboratories since 2009 for both TRH and BTEX are presented in Figures 32 and 33. To enable comparison, the target standard deviation used to calculate z-scores has been kept constant at 15% CV. The proportion of satisfactory z-scores over seven years on average is 83% for TRH and 78% for BTEX. 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.

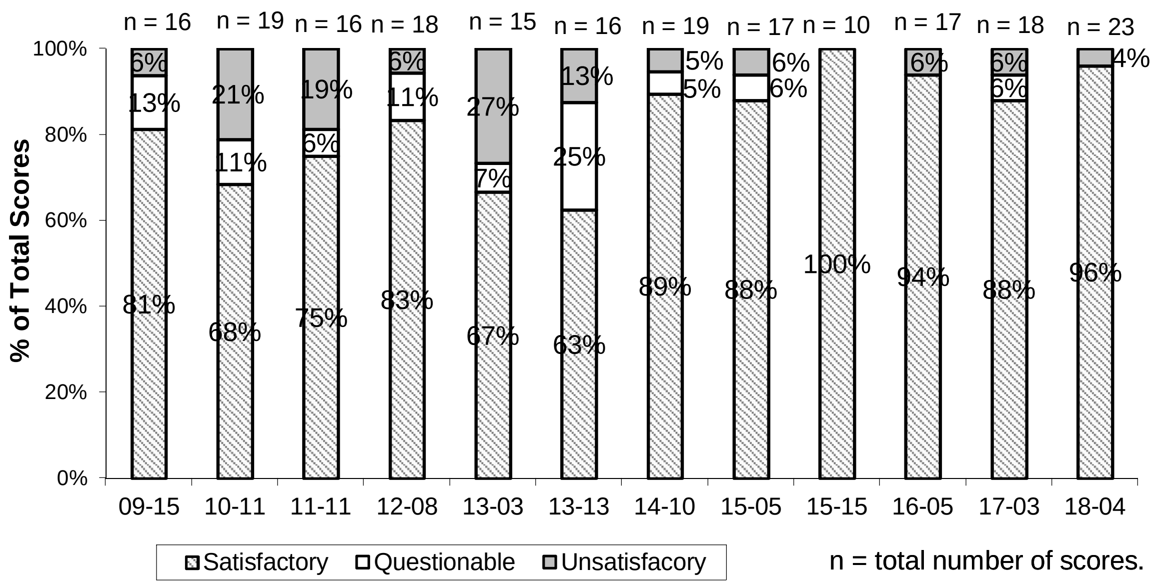


Figure 32 z-Scores for TRH (TPH before AQA 12-08) in NMI PTs of hydrocarbons in soil

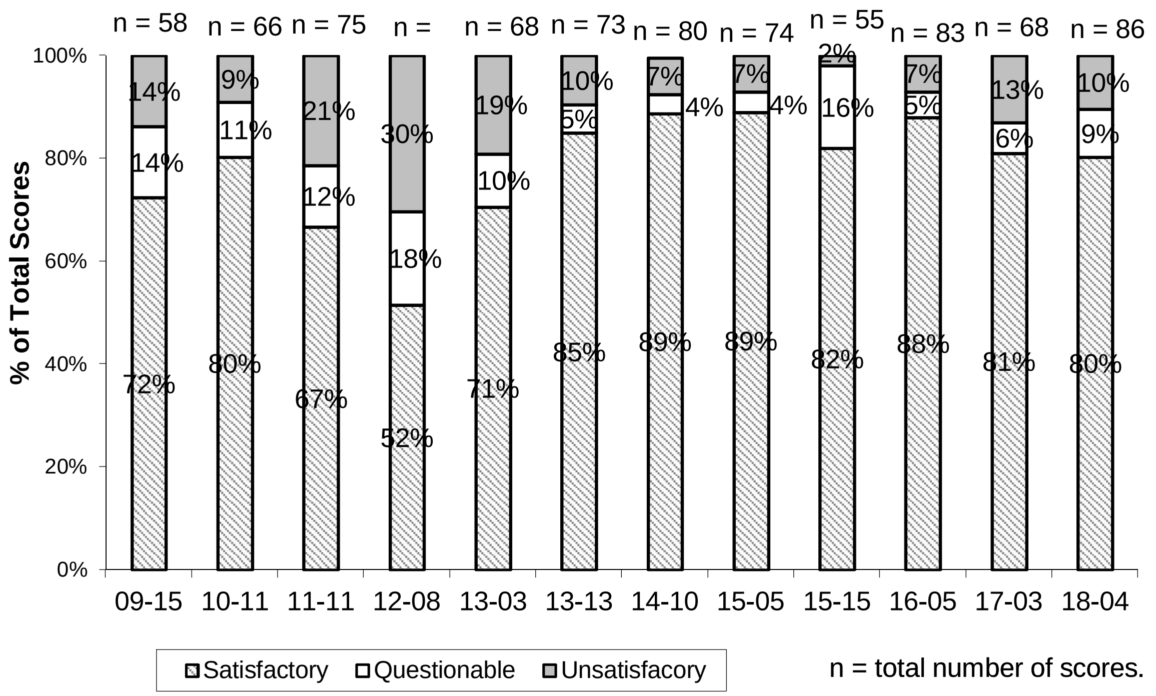


Figure 33 z-Scores for Total BTEX in NMI PTs of hydrocarbons in soil

7 REFERENCES

[1] NMI 2016, *Chemical Proficiency Testing Study Protocol,* viewed 3 May 2018, <http://www.measurement.gov.au>.

[2] NMI 2016, *Chemical Proficiency Testing Statistical Manual*, viewed 3 May 2018, <http://www.measurement.gov.au >.

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

[4] Thompson, M., Ellison, SLR. & Wood, R. 2006. 'The international harmonized protocol for proficiency testing of (chemical) analytical laboratories', *Pure Appl. Chem,* vol 78, pp 145-196.

[5] National Environmental Protection (Assessment of Site Contamination) Measure Vol 2: Schedule B1, 1999, *Guidelines on the Investigation Levels for Soil and Groundwater,* viewed 6 April 2017, <http://www.comlaw.gov.au/details/F2013C00288/html/volume_2>

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

[7] Eurachem 2012, *Quantifying Uncertainty in Analytical Measurement,* 3rd edition, viewed 10 May 2017, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[8] ISO/IEC 13528 2015, *Statistical methods for use in proficiency testing by interlaboratory comparisons.*

[9] JCGM 200:2008, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM),* 3rd edition.

[10] Askari, M. D.; Maskarinec, M. P.; Smith, S. M.; Beam, P. M.; Travis, C. C. 1996. 'Effectiveness of Purge-and-Trap for Measurement of Volatile Organic Compounds in Aged Soils', *Anal. Chem.*, vol 68, pp 3431-3433.

APPENDIX 1 – PARTICIPATING LABORATORIES

AMAL Analytical VIC	Analytica Laboratories Ltd, NEW ZEALAND
Analytical Reference Laboratory (WA) Pty Ltd, WA	Analytical Services Tasmania Dept of Primary Industry, Parks, Water and Environment, TAS
Australian Laboratory Services, QLD	Australian Laboratory Services, NSW
CHEMCENTRE WA	Envirolab Services VIC
Envirolab Services NSW	Eurofins mgt, QLD
Eurofins mgt, NSW	Eurofins mgt VIC
Hill Laboratories, New Zealand	MPL Laboratories (Envirolab Services WA), WA
National Measurement Institute NSW	Office of Environment and Heritage, Department of Premier and Cabinet Environmental Protection Science, NSW
SGS Environmental Services WA	SGS Environmental Services NSW
Sydney Environmental & Soil Laboratory NSW	Sydney Water Corporation NSW
Symbio Alliance QLD	Tweed Shire Council Tweed Laboratory Centre, NSW
Watercare Services Limited Laboratory Services, New Zealand	

APPENDIX 2 – SAMPLE PREPARATION AND HOMOGENEITY TESTING

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

Three different soils were used in this study. They were:

- Uncontaminated soil described as Menangle topsoil bought from a Sydney supplier.
- Contaminated soil from a NSW refinery.
- Clay from regional NSW.

Menangle topsoil and clay soil were dried separately at 120°C 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: 2306.6 g of Menangle topsoil was moistened with dichloromethane (DCM) and spiked with a 13.002 g of diesel extract of a contaminated soil from a NSW refinery. The spiked extract was prepared by tumbling diesel fuel and contaminated soil overnight followed by centrifugation.

The resulting top diesel layer was added to the DCM moistened soil and it was mixed thoroughly. The solvent was allowed to evaporate. The mixture was divided into 50 g portions using a Retsch PT 100 sample divider and packed into labelled screw-capped glass jars. These jars were labelled in numeric fill order and stored in a refrigerator.

Sample S2: 3748.4 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. As quickly as possible, 15.99 g of un-leaded petrol was added to a cooled beaker containing 4.21 g of sparged diesel. The contents of the beaker were then added to the soil. The drum was sealed and vigorously shaken. The sealed drum was then packed into another large drum and surrounded by cold gel-packs. The drums were then tumbled for 45 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 in a walk-in 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: Two different soils were used for these samples.

- **S3:** Menangle topsoil.
- **S4:** Clay from regional NSW.

Both S3 and S4 were spiked with the same analytes and concentrations.

For Sample S3 1000.9 g of dried and sieved Menangle topsoil was placed in a 3 litre 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 50ºC during the evaporation, the condenser temperature at 7ºC and less than 20 kPa of vacuum.

After evaporating the dichloromethane the soil was transferred to a V-mixer and diluted with 1304.8 g of clean soil. The total soil mass was 2305.7 g. The V-mixer was tumbled for about ninety minutes. After mixing the soil was divided into fifty samples of 50 g, placed in glass jars, labelled in fill order and placed in a refrigerator.

For Sample S4 999.8 g of dried and sieved clay was placed in a 3 litre 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 and gently increased to no more than 50ºC during the evaporation, the condenser temperature at 7ºC and less than 20 kPa of vacuum. The clay required significantly longer to dry than the Menangle topsoil. After evaporating the dichloromethane the soil was transferred to a V-mixer and diluted with 1300.9 g of clean soil. The total soil mass was 2300.7 g. The V-mixer was tumbled for about ninety minutes. After mixing the soil was divided into fifty samples of 50 g, placed in glass jars, labelled in fill order and placed in a refrigerator.

Homogeneity Testing

The process used to prepare the samples was the same as the one used in the previous NMI proficiency tests of hydrocarbons in soil. This process has been demonstrated to produce homogeneous samples and no homogeneity testing was conducted.

APPENDIX 3 – ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY

The robust average was calculated using the procedure described in 'ISO13258:2015€, Statistical methods for use in proficiency testing by interlaboratory comparisons – Annex C'[8] the uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 22.

Table 31 Uncertainty of robust average for Fluorene in Sample S3

No. results (p)	22
Robust Average	3.347 mg/kg
$S_{rob\ av}$	0.267 mg/kg
$u_{rob\ av}$	0.0711 mg/kg
k	2
$U_{rob\ av}$	0.142 mg/kg

The robust average for Fluorene in Sample S3 is 3.35 ± 0.14 mg/kg.

APPENDIX 4 – ACRONYMS AND ABBREVIATIONS

B(a)P	Benzo(a)pyrene
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
$\|E_n\|$	Absolute value of an E_n-score
GC-FID	Gas Chromatography Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometry
ISO	International Standards Organisation
Max	Maximum value in a set of results
Md	Median value in a set of results
Min	Minimum value in a set of results
NATA	National Association of Testing Authorities
NEPM	National Environmental Protection Measure
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
PAHs	Polycyclic Aromatic Hydrocarbons
P & T	Purge and Trap
PT	Proficiency Test
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
Target SD	Target standard deviation
TPH	Total Petroleum Hydrocarbons
TRH	Total Recoverable Hydrocarbons.
σ	Target standard deviation
$\|z\|$	Absolute value of a z-score

END OF REPORT