Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

Proficiency Test Report AQA 19-04 Hydrocarbons in Soil

July 2019

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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Accredited for compliance with ISO/IEC 17043

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SUMMARY

Proficiency test AQA 19-04 Hydrocarbons in soil was conducted in March 2019, and seventeen laboratories submitted results. This is the fourth NMI PT study to include PAHs in soil.

Four sets of test samples were prepared at the NMI laboratory in Sydney using two different soils - garden soil from Randwick NSW and Menangle topsoil bought from a commercial supplier.

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 356 numeric results a total of 314 (88%) 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 284 results for which z-scores were calculated, 250 (88%) returned a satisfactory score of $|z| \leq 2$.

Of 284 results for which E_n-scores were calculated, 237 (83%) returned a satisfactory score of $|E_n| \leq 1$.

Laboratories **2**, **4**, **8**, **12** and **13** returned satisfactory z-scores and E_n-scores for all nineteen analytes for which scores were calculated.

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

Four PAHs were added to Sample S3 - chrysene, fluoranthene, fluorene, phenanthrene and seven to Sample S4 – anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene and pyrene.

Anthracene and benzo(a)pyrene presented the most difficulty for participant laboratories, especially when extracting from Sample S4 (Menangle topsoil).

Laboratories **9**, **11** and **15** did not report benzo(a)pyrene results (total of 3 false negatives).

Laboratory **7** reported PAHs that were not spiked into the test sample (a total of 2 false positives).

> *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 314 numeric results, 310 (99%) were reported with an associated expanded measurement uncertainty. The magnitude of these uncertainties was within the range 0 – 59% 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 participants used dichloromethane (DCM)/acetone in a 1:1 ratio, hexane/acetone in a 1:1 ratio, DCM alone and hexane alone. Three laboratories performed a clean-up procedure using silica. All laboratories used GC-FID to measure hydrocarbons in the sample extract. No trends with the extraction solvent or use of silica cleanup were evident

For BTEX and volatile fraction C6-C10 in Sample S2, all laboratories used methanol as the extraction solvent. For analysis, thirteen laboratories used purge-and-trap GC-MS and four laboratories used headspace with either GC-FID or GC-MS. No trends were evident with the test methods.

For PAHs, eleven participants used dichloromethane (DCM)/acetone in a 1:1 ratio, two used hexane/acetone (1:1) and two used DCM only. To facilitate extraction some participants used tumbling (3), sonication (3), ASE (1), mechanical shaking (1) and tumbling/sonication (1). Fourteen laboratories used GC-MS(MS) and one GC-FID. No trends were evident.

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 of 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]

2.2 Study Timetable

The timetable of the study was:

Invitation issued:	26/02/2019
Samples dispatched:	20/03/2019
Results due:	18/04/2019
Interim report issued:	26/04/2019

2.3 Participation

Participated	17
Submitted results	17

2.4 Test Material Specification

Four test samples were prepared.

Sample S1 (TRH) was prepared by spiking garden soil from Randwick NSW with diesel fuel and commercially purchased hydraulic oil.

Sample S2 (BTEX) was prepared by spiking garden soil from Randwick NSW with unleaded petrol and treated diesel fuel.

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

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

2.5 Laboratory Code

Participants were assigned a confidential code number.

2.6 Sample Preparation and Homogeneity

The preparation of the study samples is described in Appendix 1. Sample S1 was spiked with treated diesel fuel and hydraulic oil which was used for the first time. Homogeneity testing was conducted and Sample S1 had been demonstrated to be sufficiently homogeneous. All other samples were prepared using a validated preparation technique. No homogeneity testing was conducted, and results returned by participants gave no reason to question the homogeneity of the test samples.

2.7 Stability Testing

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

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 20 March 2019.

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.

PAH	
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 to proficiency@measurement.gov.au.
- **Please return completed result sheet by 18 April 2019. 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	Clean-up	Measurement
1	10	DCM	Silica	GC FID
2	10	DCM:Acetone 1:1		GC FID
3	10	Dichloromethane - Acetone		GC-FID
4	10	1:1 acetone/dcm	None	GC-FID
5	15	1:1 DCM:Hexane	Nil	GC-FID
6	10	DCM Acetone 50/50	None	GC-FID
7	5	Hexane / Acetone 1:1	Silica / Glass wool column	GC-FID
8	10	Dichloromethane: Acetone (1:1)		GC-FID
9	9.984	Dichloromethane / Acetone (1:1)	Filter through sodium sulfate and glass wool	GC-FID
10	10	DCM and Acetone	No	GC FID
11	5	Hexane:Acetone	Nil	GC-FID
12	10	50:50 Dichloromethane/ Acetone Mixture	None	GC-FID
13	10	1:1 Dichloromethane : Acetone	None	GC-FID
14	10	1:1 DCM:Acetone	None	GC-FID
15	10	Acetone:Dichloromethane (1:1)		GC-FID
16	10	Hexane:Acetone	Ni;	GC-FID
17	10	20 mL of Hexane	Silica gel for TPH fractions	GC-FID

Table 2 Test Methods Sample S2 BTEX

Lab. Code	Sample Mass. (g)	Extraction	Measurement
1	2	Methanol	Purge and trap GCMS
2	10	methanol	P&T GCMS
3	5	Methanol	P&T GC-MS
4	10	Methanol	P+T GC-MS
5	10	Methanol	P&T GC-MS
6	1		Headspace-GC-FID
7	10	Methanol	Thermo ISQ GC MS (Headspace)
8	10	Methanol	Purge & Trap GC-MS
9	9.934	Methanol	Purge & Trap GCMS
10	5		Purge and trap GC-MS
11	2	Methanol	Headspace GCMS
12	10	Methanol	P&T GC-MS
13	5	Methanol	Purge & Trap GCMS
14	14	Methanol	Headspace GC-MS
15	10	Methanol	Purge and Trap GC-MS
16	10	Methanol	Purge and Trap GCMS
17			

Table 3 Test Methods Sample S3/S4 PAHs

	Sample Mass (g)	Extraction	Solvent	Measurement	Method Reference
1	10	Accelerated solvent extractor(ASE)	DCM:acetone 1:1	GCMS SIM	In house based on 8270D
2	10	Liquid-solid	DCM:Acetone 1:1	GCMS	
3					
4	10	10g sample mixed with 20mL of solvent. Tumbled end-over-end for 1 hour.	1:1 acetone/DCM	GC-MS and GC-MS/MS	In house based on USEPA8270
5	15	Solid-Liquid Ultrasonic Bath	DCM	GC-MS	8270D
6	10	Solvent Extraction	DCM/Acetone	GC-FID	In house M012
7	5	Sonication	Hexane/Acetone 1:1	Thermo ISQ GC-MS (Liquid injection)	In house based on US EPA 8270D
8	10	Solid-liquid extraction	DCM/Acetone	GC-MS	USEPA 8270C
9	10	tumbling / sonication	DCM/Acetone (1:1)	GC MS	in house method based on USEPA 8270
10	10	Solid- Liquid extraction	DCM	GC-MS	In House USEPA SW 846-8260B
11	10	Solid:Liquid sonication	DCM:Acetone	GC-MS	In-house
12	5	solid-liquid	10ml of DCM:ACETONE 50:50 v/v	GCMS	In-house USEPA referenced method
13	10	Solvent extraction - end-over-end tumble	1:1 Dichloromethane : Acetone	GC-MS	In-house (referenced to 8270E)
14					
15	10	Solid-liquid extraction	DCM/Acetone	GC-MS	
16	10	Solid-Liquid extraction (mechanical shaking)	Hexane:Acetone	GCMS	8270D
17	10	Solid-liquid	20 mL of DCM/Acetone, 1/1, v/v	GC-MS/MS	In-house USEPA referenced method

Table 4 Basis of Expanded Uncertainty Estimate

Lab. Code	Basis of Uncertainty Estimate
1	Long term reproducibility
2	Control charts
3	S1 and S2 –Precision and estimates of the method and laboratory bias.
4	Control charts
5	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%.
6	Top down approach - bias associated with method precision.
7	Replicate precision
8	Quality control requirement
9	S1 and S2 – in house validation data, S3 and S4 in house methodology
10	QC DATA
11	Measurement of Uncertainty
12	Control Charts
13	Based on QC data
14	S1 and S2 Standard uncertainty based on historical data
15	Quality control requirement
16	Professional judgement
17	S1, S3 and S4 Reproducibility studies

Table 5 Additional Participants' Comments

Lab Code	Sample	Comment or Discussion
6	S1	Brackets calculated against C14, C28, C37
6	S2	C6-C10 bracket calculated against average of C6,C7,C8,C9,C10 saturated alkanes
9	S1	Matrix spike recoveries: >C10-16: 112%, >C16-34: 97%, >C34-40: 100%
9	S2	Soil spike recoveries: Benzene: 87%, Toluene: 85%, Ethylbenzene: 86%, Xylenes: 86%, C6 - C10: 97%.
10	S2, S3 and S4	Reruns and dilutions to confirm
11	S3	Sample contained both course and fine particles which can create an inhomogenous sample matrix.
14	S2	The result entered above for C6-C10 Hydrocarbons is a "C6-C9" result.
15	S3, S4	LOR= 0.5 mg/kg for all analytes
17	S1	TPH fractions for range 4, 5, 6, and 7.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 27 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 22.

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

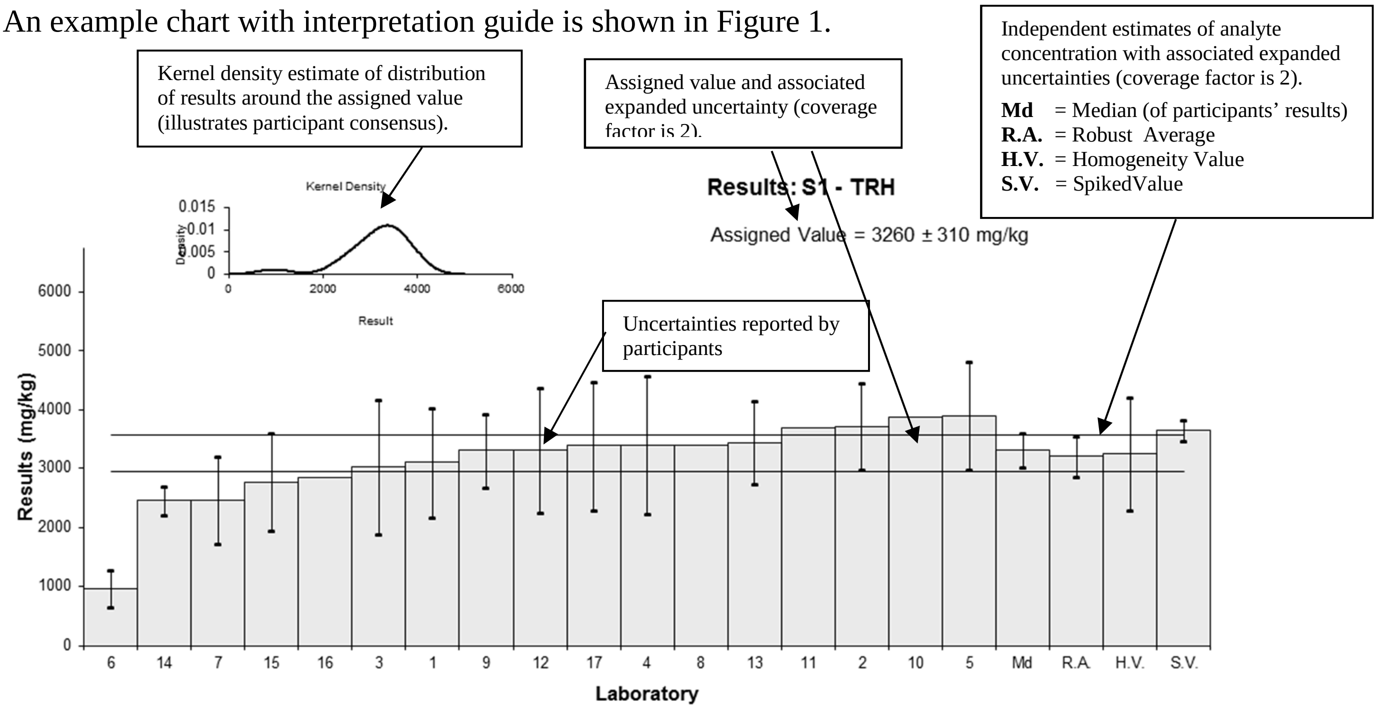


Figure 1 Guide to Presentation of Results

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. For this PT study the assigned values were the robust average of the participants' results.

4.3 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015'.[7]

4.4 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratories variation that in the judgement of the study organiser would be expected from participants given the sample concentration. It is important to note that this is a performance measure set by the study coordinator; it is not the coefficient of variation of participants' results.

4.5 Target Standard Deviation

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

$$\sigma = X * PCV \qquad \text{Equation 1}$$

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 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.

4.7 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 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.

4.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2015[7][8] 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.[9]

5 TABLES AND FIGURES

Table 6

Sample Details

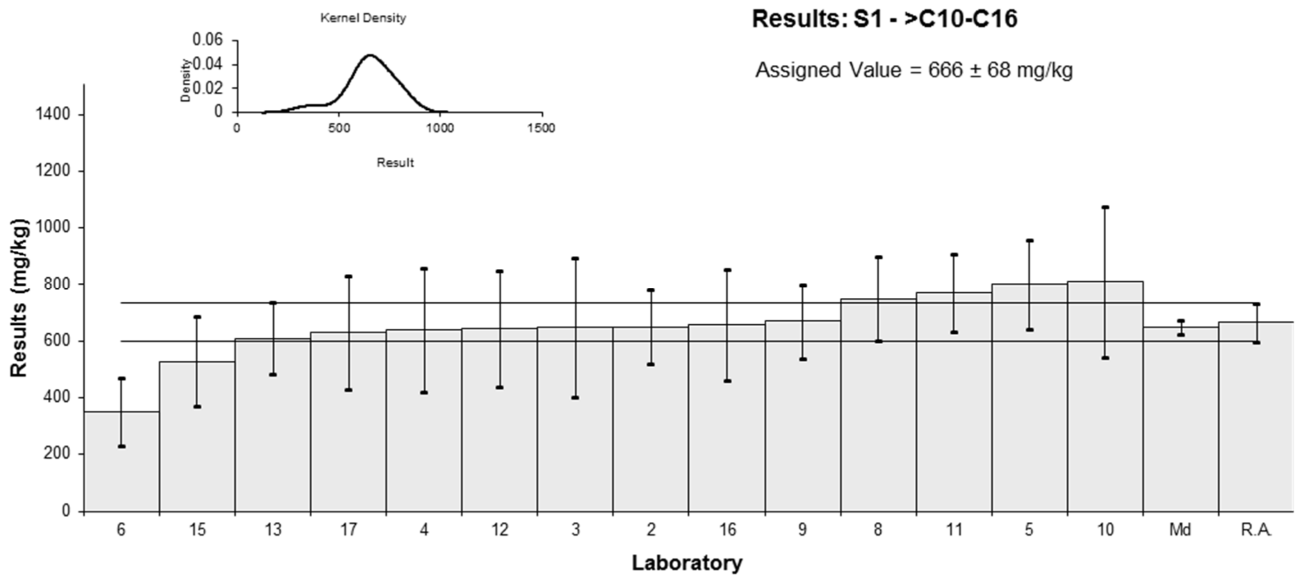
Sample No.	S1
Matrix.	Soil
Analyte.	>C10-C16
Units	mg/kg

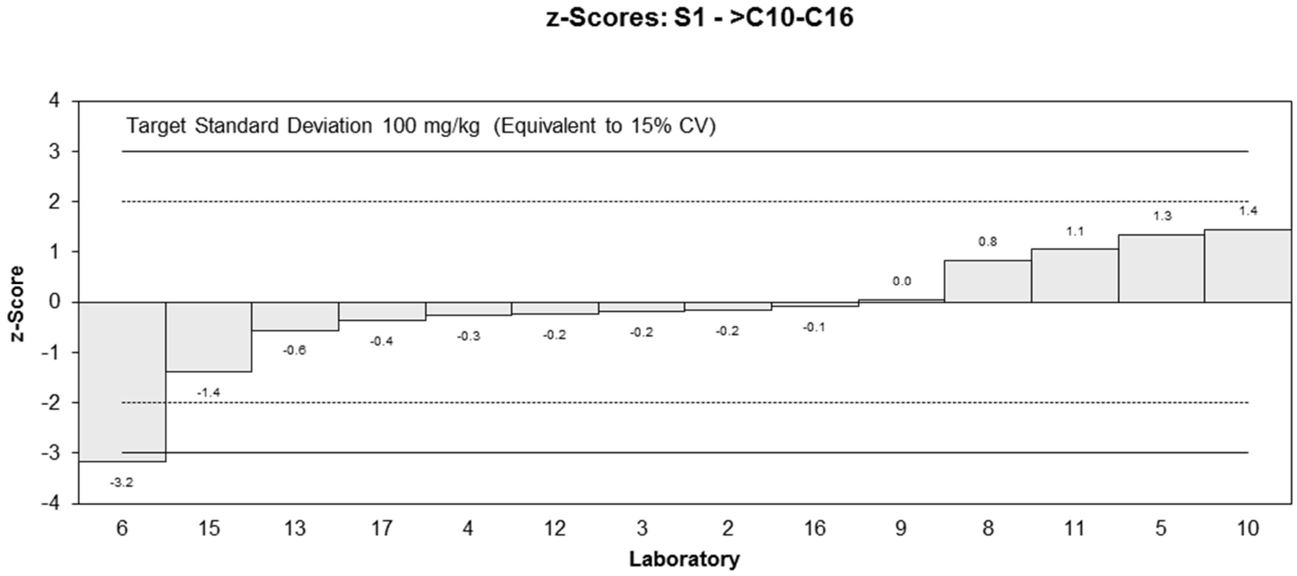
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
2	650	130	-0.16	-0.11
3	648	247.61	-0.18	-0.07
4	640	220	-0.26	-0.11
5	800	160	1.34	0.77
6	350	120	-3.16	-2.29
8	750	150	0.84	0.51
9	670	130	0.04	0.03
10	810	266	1.44	0.52
11	771	139	1.05	0.68
12	643	206	-0.23	-0.11
13	610	127	-0.56	-0.39
15	528	158	-1.38	-0.80
16	657	197	-0.09	-0.04
17	630	200	-0.36	-0.17

Statistics

Assigned Value	666	68
Spike	Not Spiked	
Robust Average	666	68
Median	649	26
Mean	654	
N	14	
Max.	810	
Min.	350	
Robust SD	100	
Robust CV	15%	


Results: S1 - >C10-C16
Assigned Value = 666 ± 68 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
6 15 13 17 4 12 3 2 16 9 8 11 5 10 Md R.A.
Laboratory


z-Scores: S1 - >C10-C16
Target Standard Deviation 100 mg/kg (Equivalent to 15% CV)
z-Score
-3.2 -1.4 -0.6 -0.4 -0.3 -0.2 -0.2 -0.2 -0.1 0.0 0.8 1.1 1.3 1.4
6 15 13 17 4 12 3 2 16 9 8 11 5 10
Laboratory

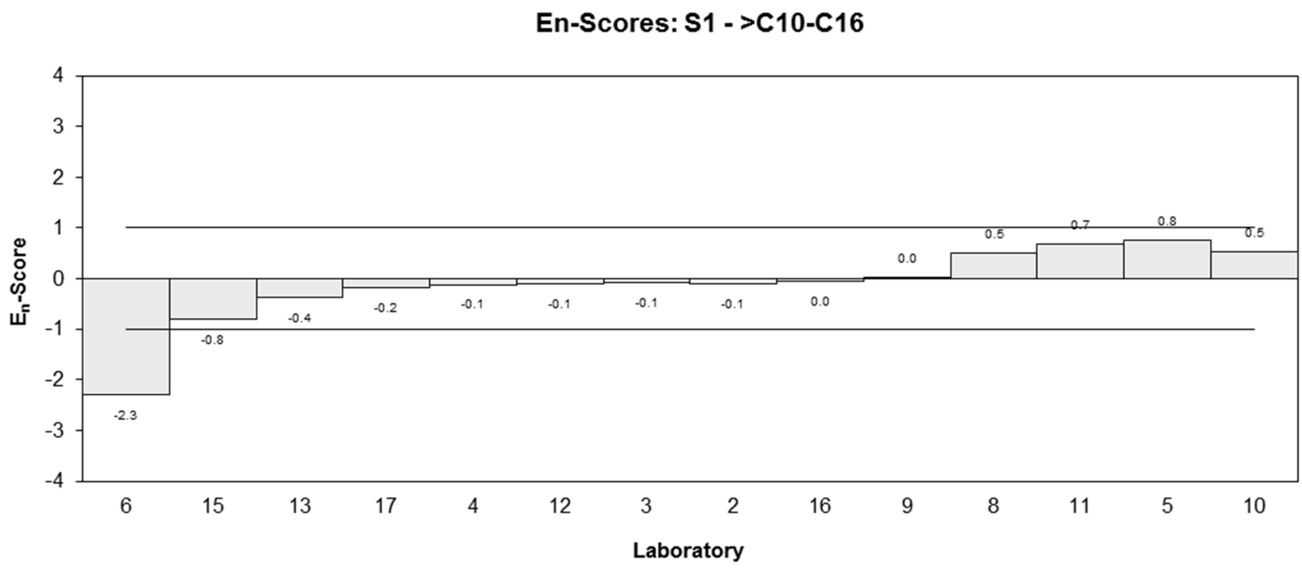

En-Scores: S1 - >C10-C16
En-Score
-2.3 -0.8 -0.4 -0.2 -0.1 -0.1 -0.1 -0.1 0.0 0.0 0.5 0.7 0.8 0.5
6 15 13 17 4 12 3 2 16 9 8 11 5 10
Laboratory

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
2	2500	500	0.84	0.53
3	1898	528.23	-0.97	-0.58
4	2180	760	-0.12	-0.05
5	2500	600	0.84	0.45
6	620	200	-4.80	-5.95
8	2200	440	-0.06	-0.04
9	2300	440	0.24	0.17
10	2440	803	0.66	0.27
11	2462	443	0.73	0.51
12	2047	655	-0.52	-0.25
13	2250	444	0.09	0.06
15	1826	548	-1.18	-0.68
16	2018	605	-0.61	-0.32
17	2169	690	-0.15	-0.07

Statistics

Assigned Value*	2220	180
Spike	Not Spiked	
Robust Average	2180	190
Median	2190	180
Mean	2100	
N	14	
Max.	2500	
Min.	620	
Robust SD	250	
Robust CV	12%	

*Robust average excluding laboratory 6.

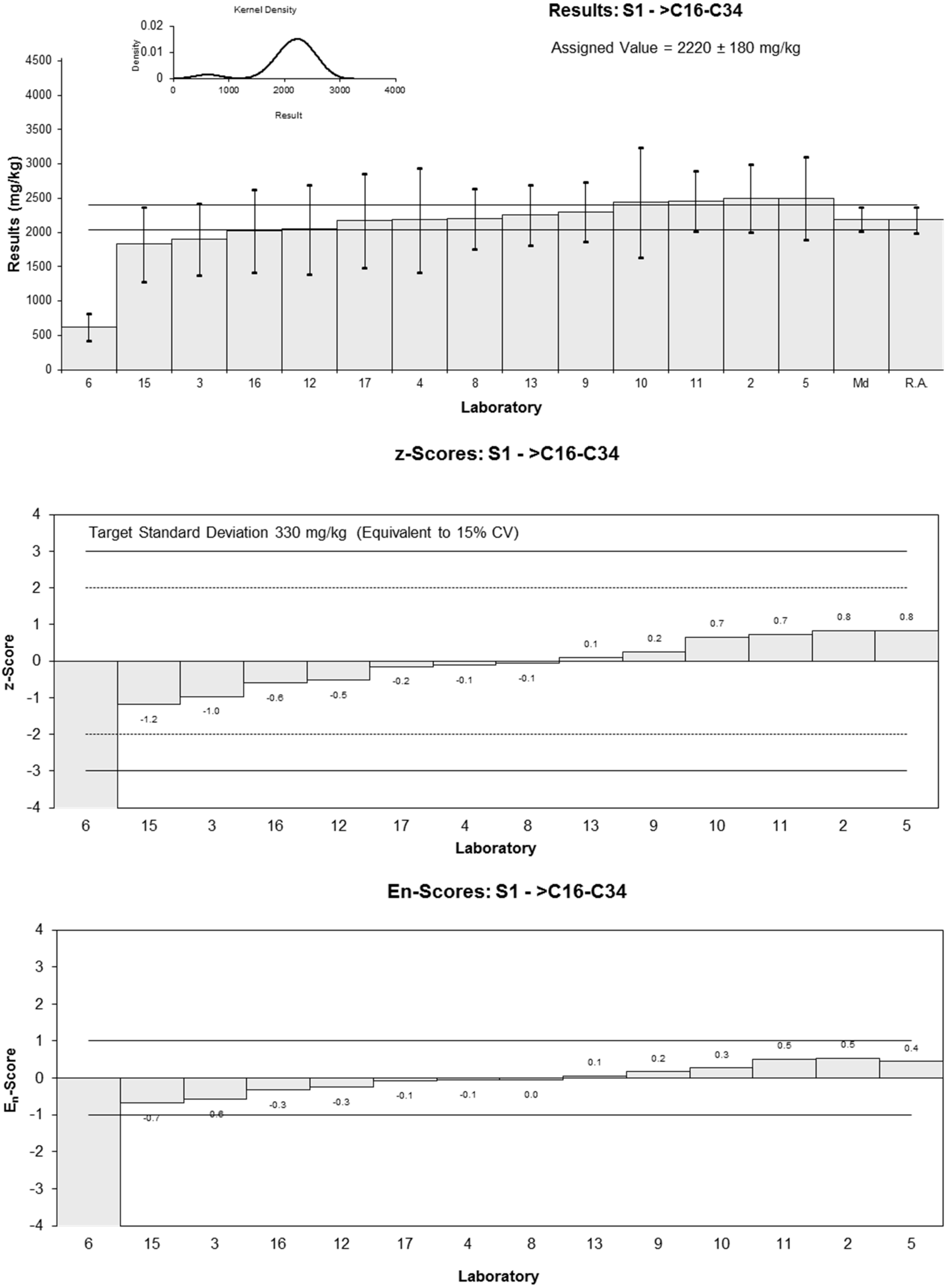

Results: S1 - >C16-C34
Assigned Value = 2220 ± 180 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 15 3 16 12 17 4 8 13 9 10 11 2 5 Md R.A.
z-Scores: S1 - >C16-C34
Target Standard Deviation 330 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - >C16-C34
E_n-Score
Laboratory

Figure 3

Table 8

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
2	560	110	0.44	0.27
3	479	167.58	-0.58	-0.25
4	580	200	0.70	0.26
5	570	160	0.57	0.26
6	<50	NR		
8	450	90	-0.95	-0.66
9	290	60	-2.98	-2.59
10	630	370	1.33	0.28
11	457	73	-0.86	-0.68
12	619	198	1.19	0.45
13	580	129	0.70	0.38
15	416	125	-1.38	-0.77
16	170	51	-4.51	-4.18
17	581	190	0.71	0.28

Statistics

Assigned Value*	525	68
Spike	Not Spiked	
Robust Average	510	81
Median	560	63
Mean	491	
N	13	
Max.	630	
Min.	170	
Robust SD	95	
Robust CV	19%	

*Robust average excluding laboratory 16.

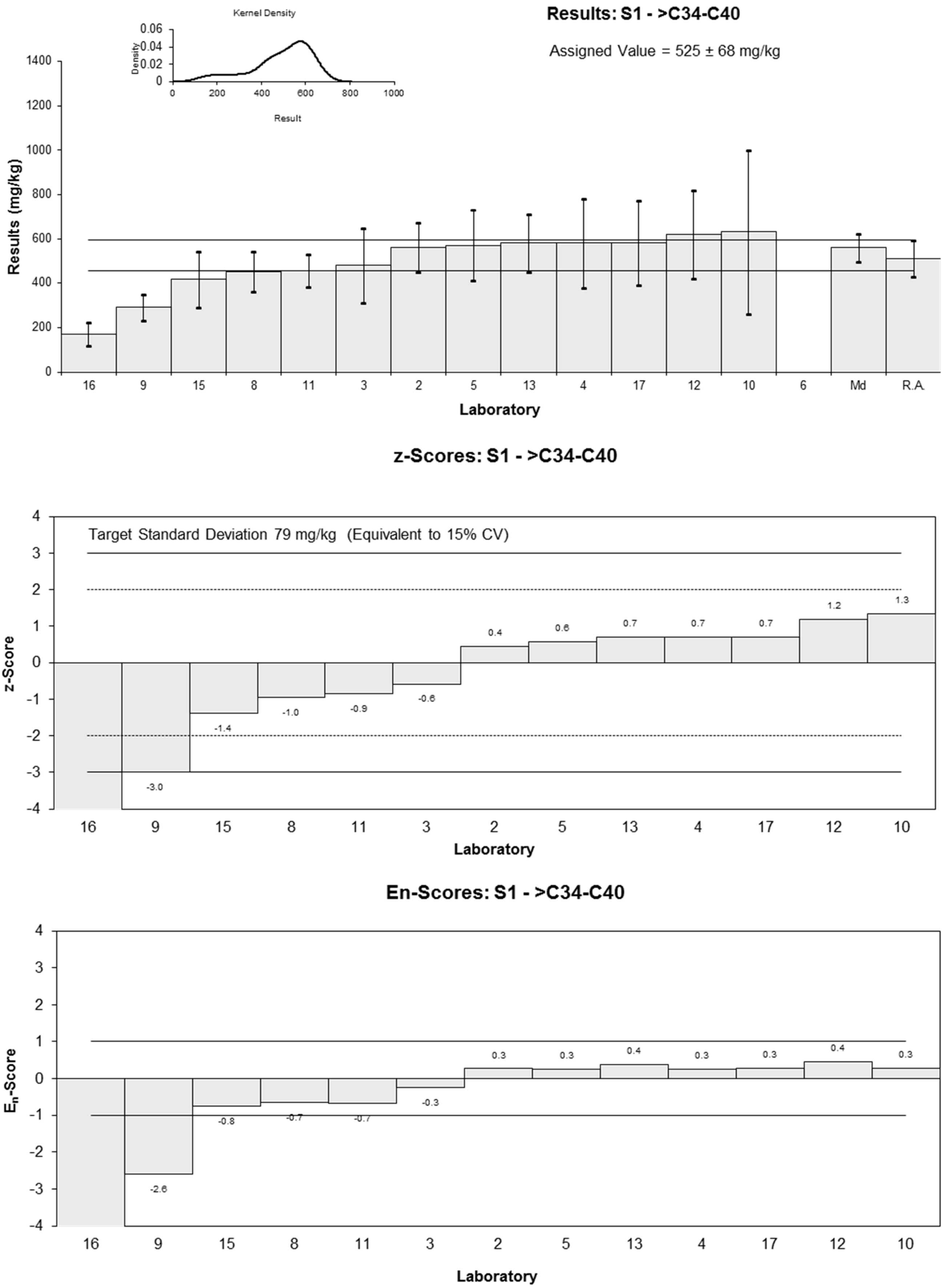

Results: S1 - >C34-C40
Assigned Value = 525 ± 68 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S1 - >C34-C40
Target Standard Deviation 79 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - >C34-C40
En-Score
Laboratory

Figure 4

Table 9 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)
1	C10-C14	290	80
1	C15-C36	2800	700
7	C7-C9	<10	3
7	C10-C14	206.25	61.875
7	C15-C36	2247.5	674.25
14	C7-C9	<8	5.4
14	C10-C14	171	39
14	C15-C36	2280	240
17*	C7-C9	<5	2
17	C10-C14	174	42
17	C15-C36	2656	580
17	C7-C36	2830	620

*Laboratory 17 also reported the hydrocarbons ranges as per Schedule B3 of the NEPM. These results were presented in Tables 6 to 8.

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Table 10

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1*	3100	930	-0.33	-0.16
2	3710	740	0.92	0.56
3	3025	1150	-0.48	-0.20
4	3400	1180	0.29	0.11
5	3900	920	1.31	0.66
6	960	320	-4.70	-5.16
7**	2453.75	736.125	-1.65	-1.01
8	3400	NR	0.29	0.45
9	3300	630	0.08	0.06
10	3880	NR	1.27	2.00
11	3690	NR	0.88	1.39
12	3309	1058	0.10	0.04
13	3440	700	0.37	0.24
14**	2450	240	-1.66	-2.07
15	2770	831	-1.00	-0.55
16	2845	NR	-0.85	-1.34
17	3381	1100	0.25	0.11

*TRH result cover the range from C10 to C36, not C10 to C40 as per NEPM.

**TRH result cover the range from C7 to C36, not C10-C40 as per NEPM.

Statistics

Assigned Value***	3260	310
Spike	3650	180
Homogeneity Value	3250	970
Robust Average	3200	340
Median	3310	290
Mean	3118	
N	17	
Max.	3900	
Min.	960	
Robust SD	500	
Robust CV	16%	

***Robust average excluding laboratory 6.

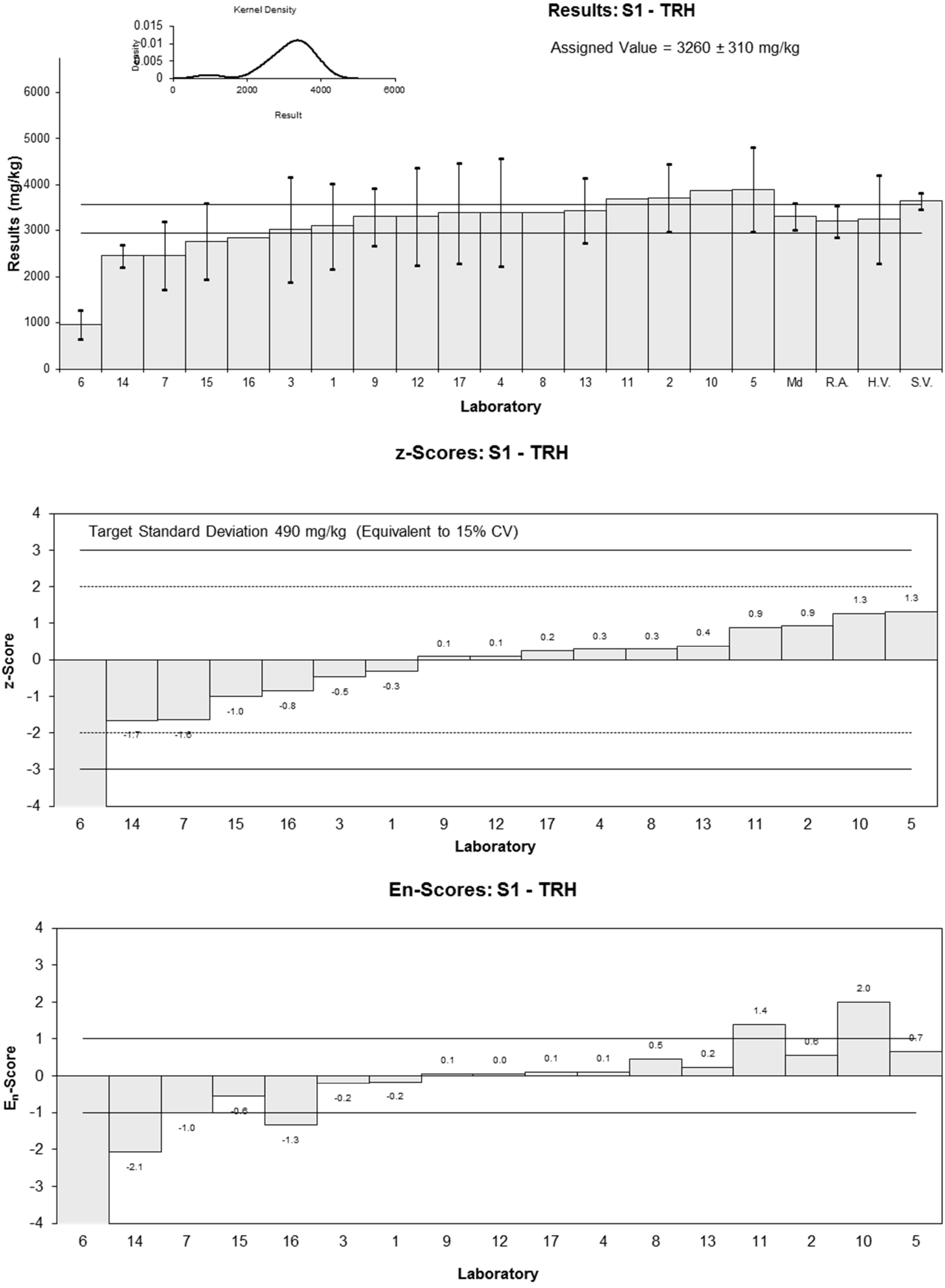

Results: S1 - TRH
Assigned Value = 3260 ± 310 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 14 7 15 16 3 1 9 12 17 4 8 13 11 2 10 5 Md R.A. H.V. S.V.
z-Scores: S1 - TRH
Target Standard Deviation 490 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - TRH
En-Score
Laboratory

Figure 5

Table 11

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	1.4	0.45
2	7.7	1.5
3	6.12	1.80
4	8.2	2
5	9.7	1.5
6	1.4	0.49
7	0.78	0.20
8	4.4	0.88
9	4.1	0.8
10	9.8	3.9
11	4.37	1.00
12	7.00	1.489
13	3.1	0.6
14	5.9	1.7
15	2.6	0.8
16	5.1	1.5
17	NT	NT

Statistics

Assigned Value	Not Set	
Spike	40.0	2.0
Robust Average	5.1	2.0
Median	4.8	1.7
Mean	5.1	
N	16	
Max.	9.8	
Min.	0.78	
Robust SD	1.90	
Robust CV	38%	

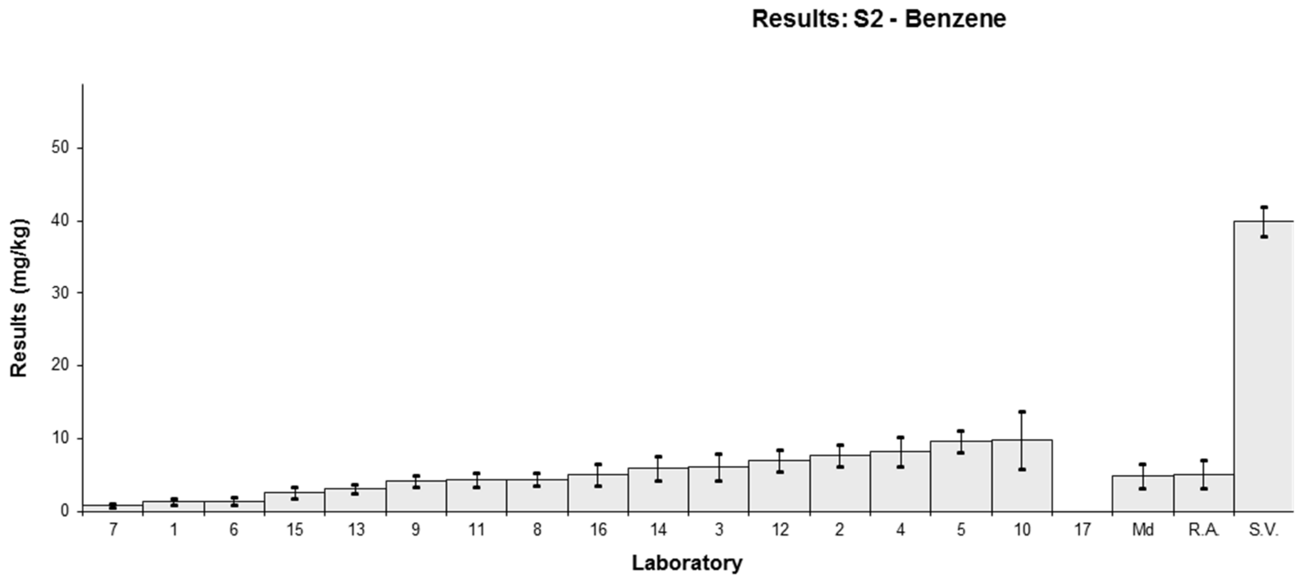

Results: S2 - Benzene
Results (mg/kg)
0
10
20
30
40
50
7
1
6
15
13
9
11
8
16
14
3
12
2
4
5
10
17
Md
R.A.
S.V.
Laboratory

Figure 6

Table 12

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	1600	320	.00	.00
3	1435.83	430.75	.00	.00
4	1350	380	.00	.00
5	1900	500	.00	.00
6	110	39	.00	.00
7	NT	NT		
8	1600	320	.00	.00
9	700	100	.00	.00
10	1480	608	.00	.00
11	1160	68.4	.00	.00
12	1388.996	321.872	.00	.00
13	1370	310	.00	.00
14*	830	390	.00	.00
15	2082.1	625	.00	.00
16	1090.7	327.2	.00	.00
17	NT	NT		

*Results are for the C6-C9 range.

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Robust Average	1330	310
Median	1380	190
Mean	1293	
N	14	
Max.	2082.1	
Min.	110	
Robust SD	360	
Robust CV	27%	

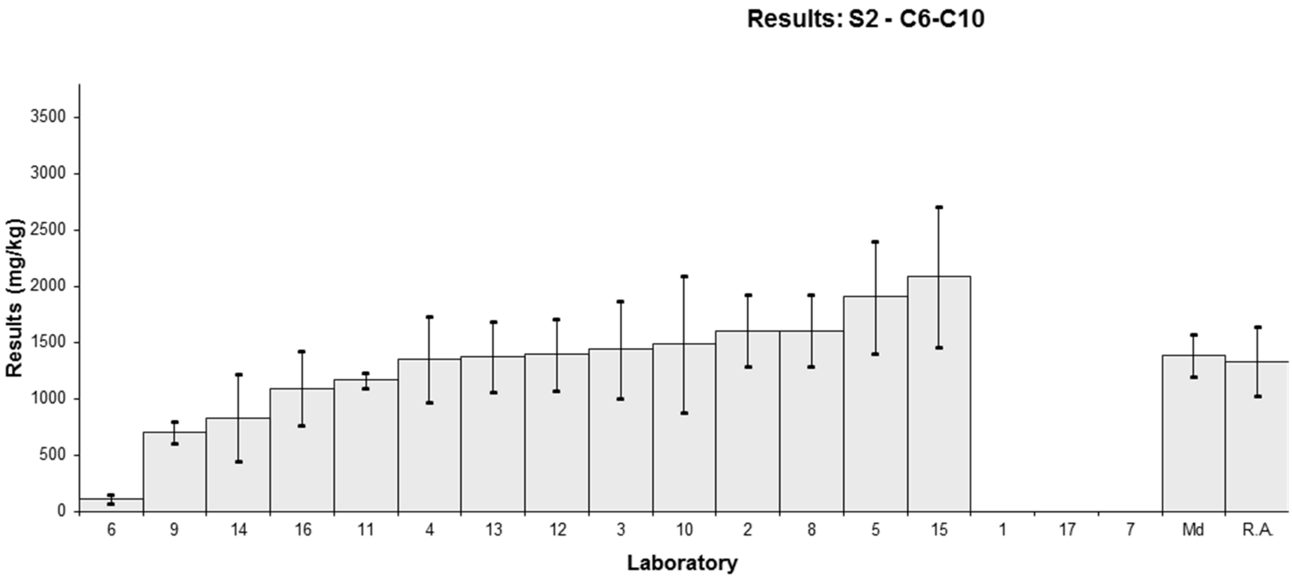

Results: S2 - C6-C10
Results (mg/kg)
3500
3000
2500
2000
1500
1000
500
0
6
9
14
16
11
4
13
12
3
10
2
8
5
15
1
17
7
Md
R.A.
Laboratory

Figure 7

Table 13

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	40	1.1	-1.28	-1.36
2	59	10	1.28	0.78
3	44.14	9.29	-0.72	-0.46
4	60	15	1.41	0.64
5	50	10	0.07	0.04
6	19	6.7	-4.11	-3.17
7	16.87	4.22	-4.39	-4.03
8	53	10.6	0.47	0.28
9	36	5.4	-1.82	-1.54
10*	65.2	18.3	2.00	0.80
11	50.9	25.4	0.19	0.05
12	55	11.294	0.74	0.42
13	54.5	9.5	0.67	0.43
14	46	13	-0.47	-0.24
15	45.1	13.5	-0.59	-0.29
16	27.3	8.2	-2.99	-2.07
17	NT	NT		

Statistics

Assigned Value**	49.5	6.9
Spike	81.0	4.1
Maximum acceptable conc	95.8	
Robust Average	46.0	8.9
Median	48.0	5.9
Mean	45.1	
N	16	
Max.	65.2	
Min.	16.87	
Robust SD	10.0	
Robust CV	22%	

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

**Robust average excluding laboratories 6 and 7.

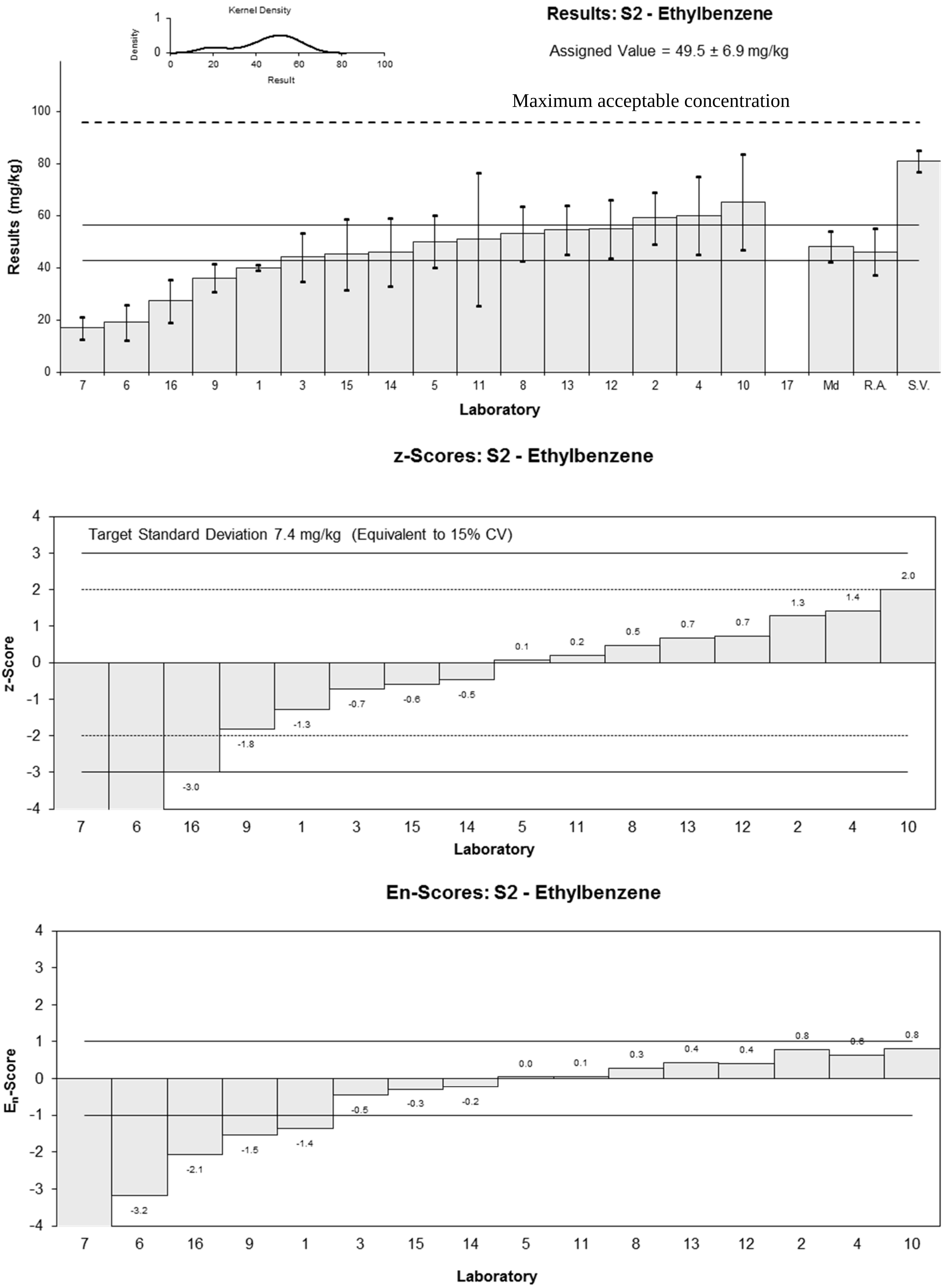

Kernel Density
Density
Result
Results: S2 - Ethylbenzene
Assigned Value = 49.5 ± 6.9 mg/kg
Maximum acceptable concentration
Results (mg/kg)
7 6 16 9 1 3 15 14 5 11 8 13 12 2 4 10 17 Md R.A. S.V.
Laboratory
z-Scores: S2 - Ethylbenzene
Target Standard Deviation 7.4 mg/kg (Equivalent to 15% CV)
z-Score
-3.0 -1.8 -1.3 -0.7 -0.6 -0.5 0.1 0.2 0.5 0.7 0.7 1.3 1.4 2.0
7 6 16 9 1 3 15 14 5 11 8 13 12 2 4 10
Laboratory
En-Scores: S2 - Ethylbenzene
E_n-Score
-3.2 -2.1 -1.5 -1.4 -0.5 -0.3 -0.2 0.0 0.1 0.3 0.4 0.4 0.8 0.6 0.8
7 6 16 9 1 3 15 14 5 11 8 13 12 2 4 10
Laboratory

Figure 8

Table 14

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	120	31	-3.57	-2.53
2	310	62	1.34	0.68
3	271.88	57.20	0.36	0.19
4*	350	80	2.00	1.00
5	290	30	0.83	0.59
6	91	32	-4.32	-3.02
7	87.08	21.77	-4.42	-3.42
8	241	48.2	-0.44	-0.26
9	160	27	-2.53	-1.87
10*	380	131	2.00	0.88
11	229	91.7	-0.75	-0.28
12	277	53.562	0.49	0.27
13	264	42	0.16	0.10
14	251	66	-0.18	-0.09
15	218.3	65.5	-1.03	-0.50
16	232.9	69.9	-0.65	-0.30
17	NT	NT		

Statistics

Assigned Value**	258	45
Spike	708	35
Maximum acceptable conc	786	
Robust Average	236	60
Median	246	30
Mean	236	
N	16	
Max.	380	
Min.	87.08	
Robust SD	68	
Robust CV	29%	

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

**Robust average excluding laboratories 6 and 7.

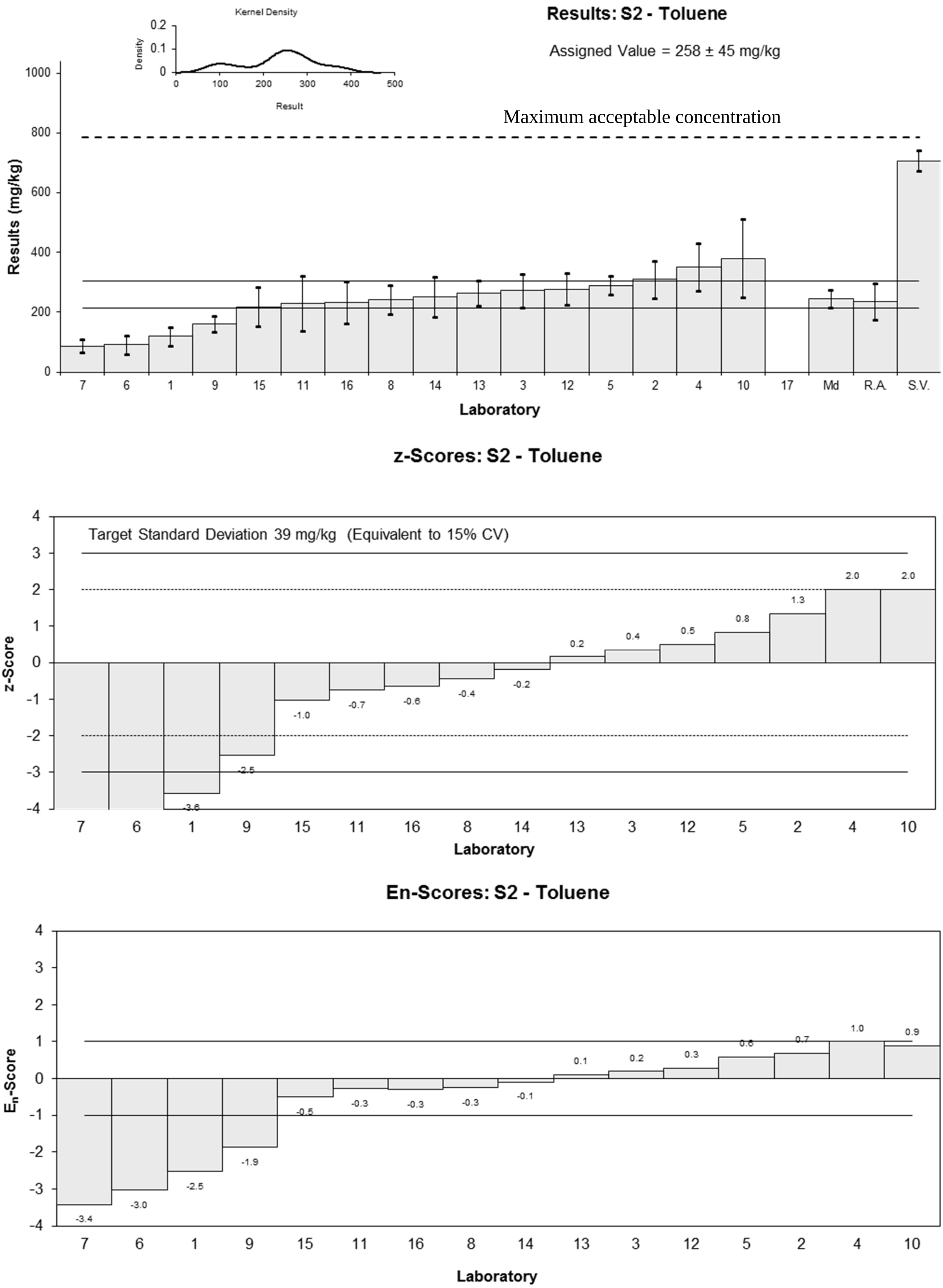

Results: S2 - Toluene
Assigned Value = 258 ± 45 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
Laboratory
7
6
1
9
15
11
16
8
14
13
3
12
5
2
4
10
17
Md
R.A.
S.V.
z-Scores: S2 - Toluene
Target Standard Deviation 39 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S2 - Toluene
En-Score
Laboratory

Figure 9

Table 15

Sample Details

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

Participant Results

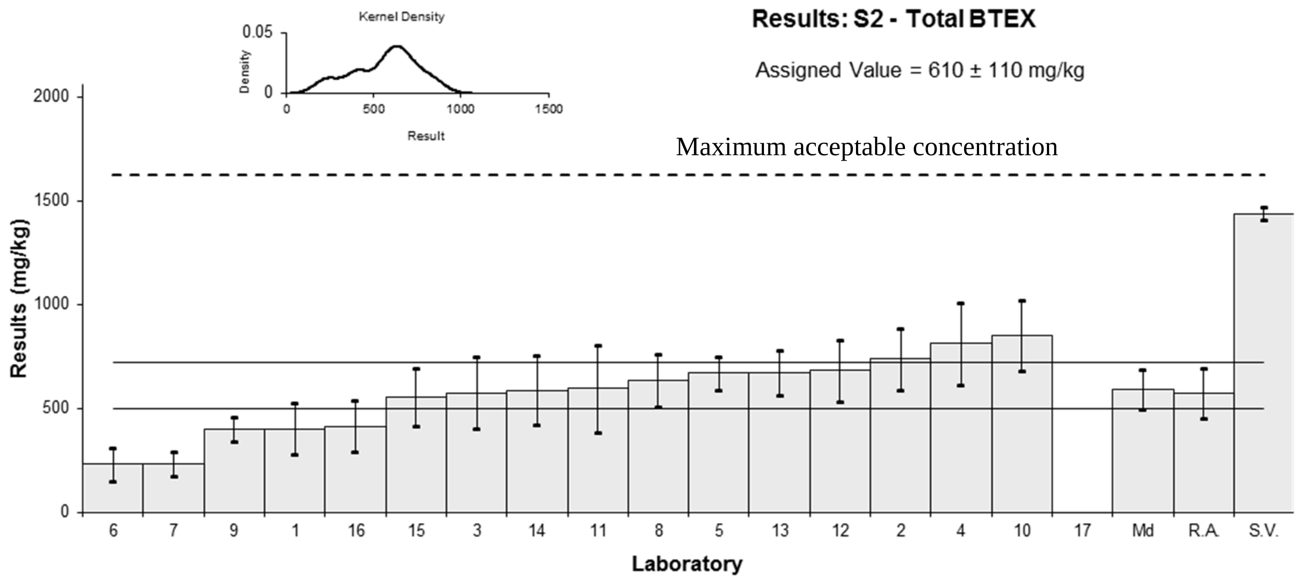
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	401	124	-2.28	-1.26
2	737	150	1.39	0.68
3	574.49	172.35	-0.39	-0.17
4*	810	200	2.00	0.88
5	670	80	0.66	0.44
6	230	80	-4.15	-2.79
7	230.88	57.72	-4.14	-3.05
8	633.4	126.68	0.26	0.14
9	400	60	-2.30	-1.68
10*	851	170	2.00	1.00
11	594	212	-0.17	-0.07
12	682	148.788	0.79	0.39
13	673	109	0.69	0.41
14	587	169	-0.25	-0.11
15	551.6	138	-0.64	-0.33
16	411.5	123.5	-2.17	-1.20
17	NT	NT		

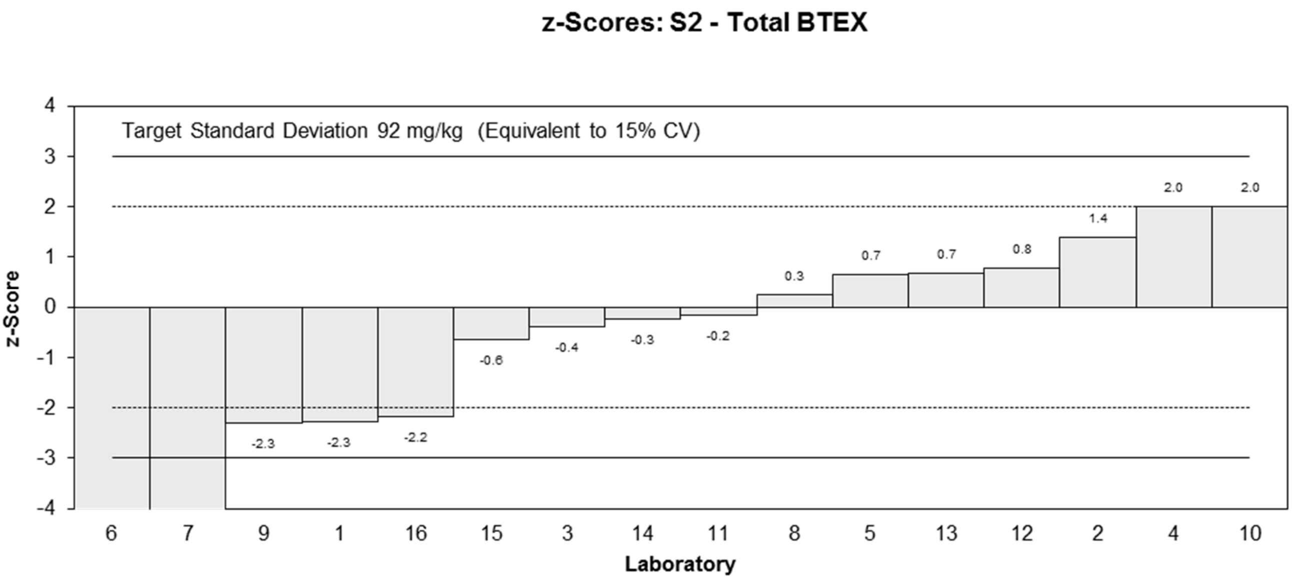
Statistics

Assigned Value**	610	110
Spike	1440	32
Maximum acceptable conc	1624	
Robust Average	570	120
Median	591	94
Mean	565	
N	16	
Max.	851	
Min.	230	
Robust SD	160	
Robust CV	28%	

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

**Robust average excluding laboratories 6 and 7.


Results: S2 - Total BTEX
Assigned Value = 610 ± 110 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
Laboratory
6 7 9 1 16 15 3 14 11 8 5 13 12 2 4 10 17 Md R.A. S.V.


z-Scores: S2 - Total BTEX
Target Standard Deviation 92 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 7 9 1 16 15 3 14 11 8 5 13 12 2 4 10
-2.3 -2.3 -2.2 -0.6 -0.4 -0.3 -0.2 0.3 0.7 0.7 0.8 1.4 2.0 2.0

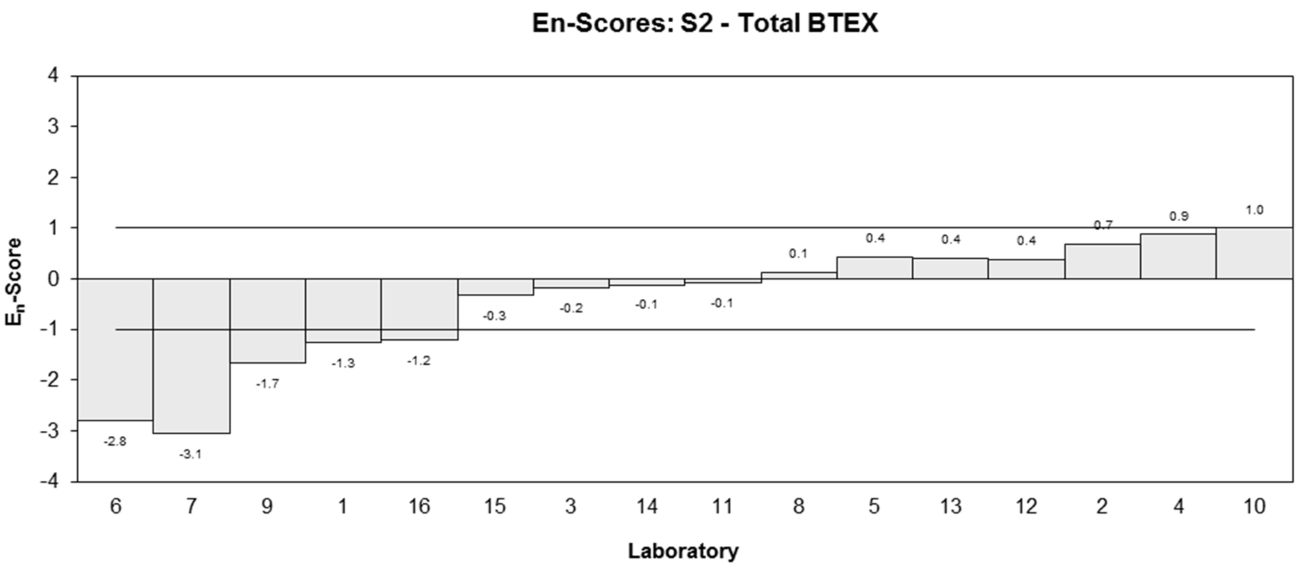

En-Scores: S2 - Total BTEX
E_n-Score
Laboratory
6 7 9 1 16 15 3 14 11 8 5 13 12 2 4 10
-2.8 -3.1 -1.7 -1.3 -1.2 -0.3 -0.2 -0.1 -0.1 0.1 0.4 0.4 0.4 0.7 0.9 1.0

Figure 10

Table 16

Sample Details

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

Participant Results

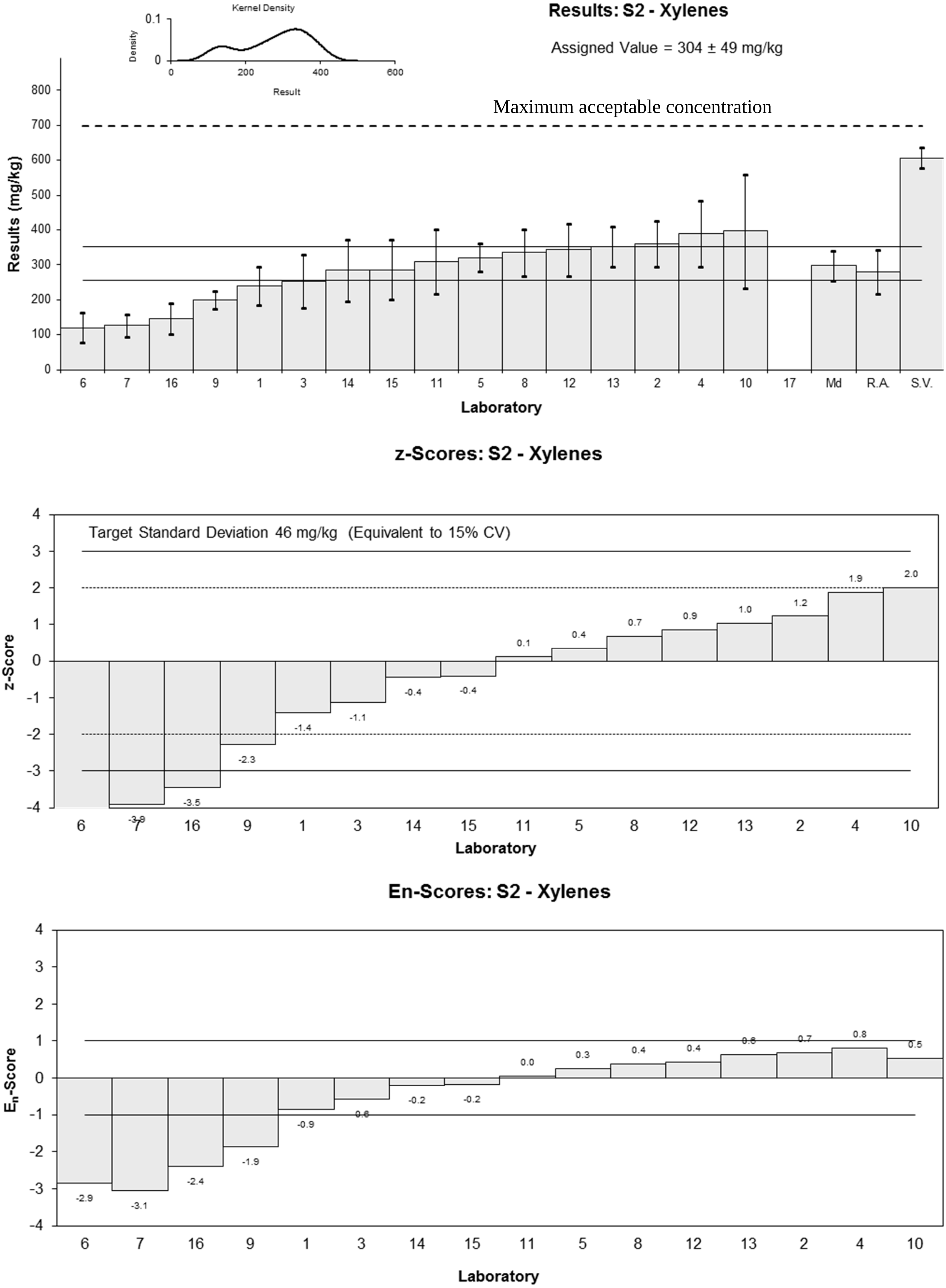
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	240	55	-1.40	-0.87
2	360	65	1.23	0.69
3	252.35	75.71	-1.13	-0.57
4	390	95	1.89	0.80
5	320	40	0.35	0.25
6	120	42	-4.04	-2.85
7	126.15	31.54	-3.90	-3.05
8	335	67	0.68	0.37
9	200	26	-2.28	-1.87
10*	396	163	2.00	0.54
11	309	93.5	0.11	0.05
12	343	74.853	0.86	0.44
13	351	57	1.03	0.63
14	284	88	-0.44	-0.20
15	285.5	85.7	-0.41	-0.19
16	146.2	43.9	-3.46	-2.40
17	NT	NT		

Statistics

Assigned Value**	304	49
Spike	607	30
Maximum acceptable conc	699	
Robust Average	279	63
Median	297	44
Mean	279	
N	16	
Max.	396	
Min.	120	
Robust SD	73	
Robust CV	26%	

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

**Robust average excluding laboratories 6 and 7.



Results: S2 - Xylenes
Assigned Value = 304 ± 49 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
Laboratory
6 7 16 9 1 3 14 15 11 5 8 12 13 2 4 10 17 Md R.A. S.V.
z-Scores: S2 - Xylenes
Target Standard Deviation 46 mg/kg (Equivalent to 15% CV)
z-Score
-3.5 -2.3 -1.4 -1.1 -0.4 -0.4 0.1 0.4 0.7 0.9 1.0 1.2 1.9 2.0
Laboratory
En-Scores: S2 - Xylenes
E_n-Score
-2.9 -3.1 -2.4 -1.9 -0.9 -0.2 -0.2 0.0 0.3 0.4 0.4 0.7 0.8 0.5
Laboratory

Figure 11

Table 17

Sample Details

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

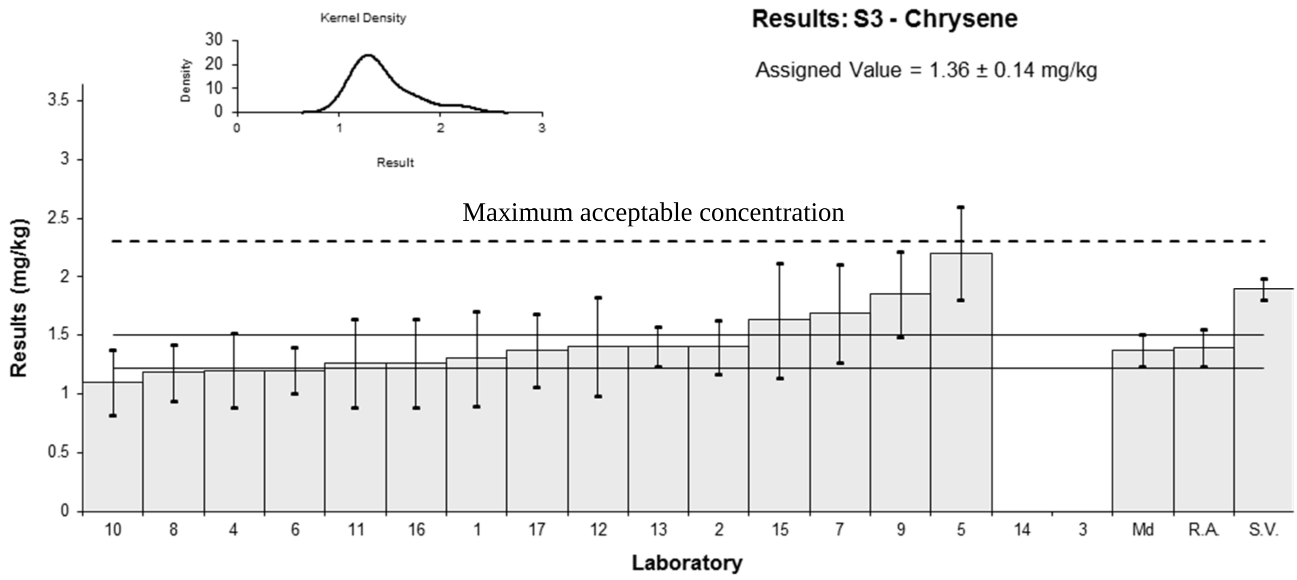
Participant Results

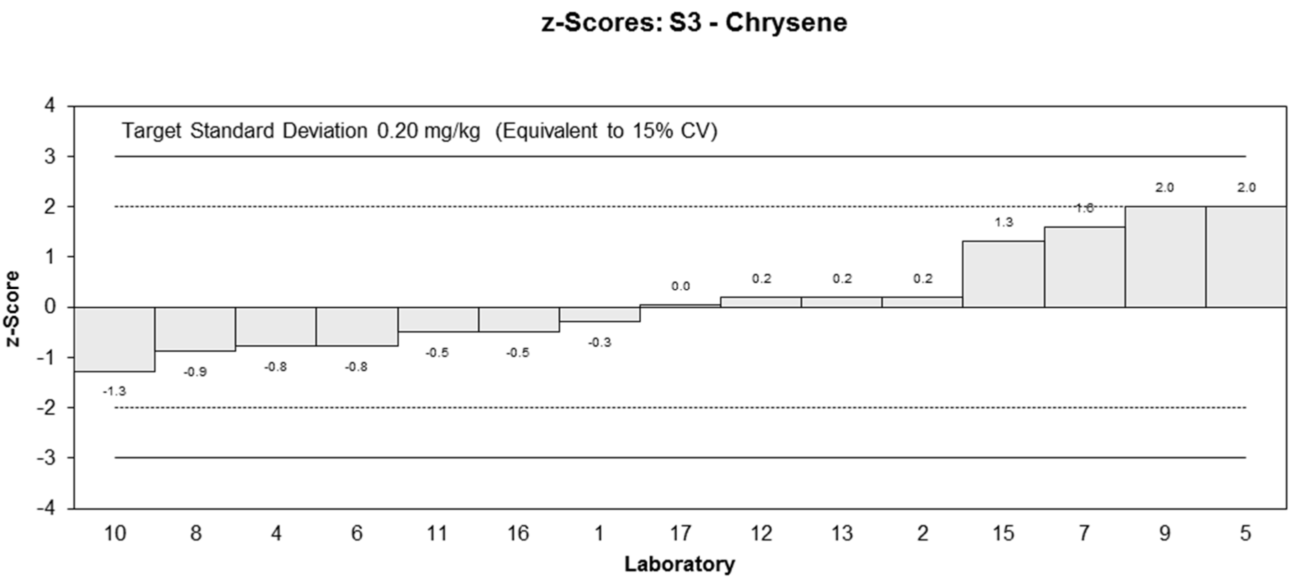
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.30	0.4	-0.29	-0.14
2	1.4	0.23	0.20	0.15
3	NT	NT		
4	1.2	0.32	-0.78	-0.46
5*	2.2	0.4	2.00	1.00
6	1.2	0.2	-0.78	-0.66
7	1.6875	0.42	1.61	0.74
8	1.18	0.24	-0.88	-0.65
9*	1.85	0.37	2.00	1.00
10	1.1	0.28	-1.27	-0.83
11	1.26	0.38	-0.49	-0.25
12	1.40	0.42	0.20	0.09
13	1.4	0.17	0.20	0.18
14	NT	NT		
15	1.63	0.49	1.32	0.53
16	1.26	0.378	-0.49	-0.25
17	1.37	0.31	0.05	0.03

Statistics

Assigned Value**	1.36	0.14
Spike	1.897	0.095
Maximum acceptable conc	2.297	
Robust Average	1.39	0.16
Median	1.37	0.14
Mean	1.43	
N	15	
Max.	2.2	
Min.	1.1	
Robust SD	0.21	
Robust CV	15%	

*z-score adjusted to 2 (see Section 6.3)
**Robust average excluding laboratory 5.


Results: S3 - Chrysene
Assigned Value = 1.36 ± 0.14 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
Laboratory
10 8 4 6 11 16 1 17 12 13 2 15 7 9 5 14 3 Md R.A. S.V.


z-Scores: S3 - Chrysene
Target Standard Deviation 0.20 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-1.3 -0.9 -0.8 -0.8 -0.5 -0.5 -0.3 0.0 0.2 0.2 0.2 1.3 1.6 2.0 2.0
10 8 4 6 11 16 1 17 12 13 2 15 7 9 5

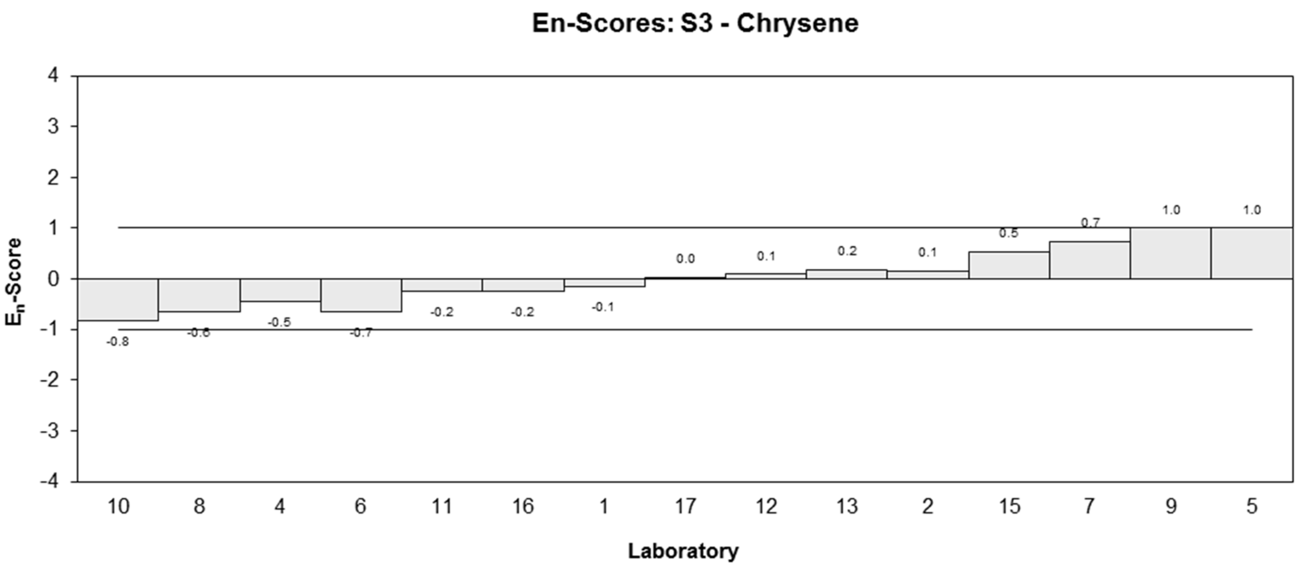

En-Scores: S3 - Chrysene
En-Score
Laboratory
-0.8 -0.6 -0.5 -0.7 -0.2 -0.2 -0.1 0.0 0.1 0.2 0.1 0.5 0.7 1.0 1.0
10 8 4 6 11 16 1 17 12 13 2 15 7 9 5

Figure 12

Table 18

Sample Details

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

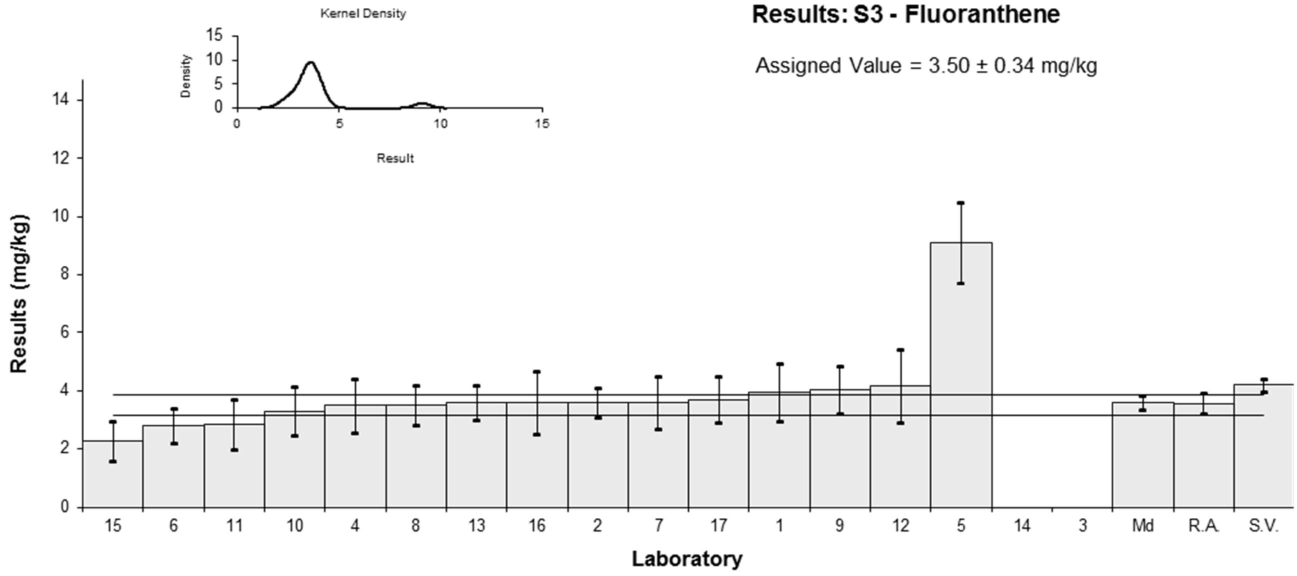
Participant Results

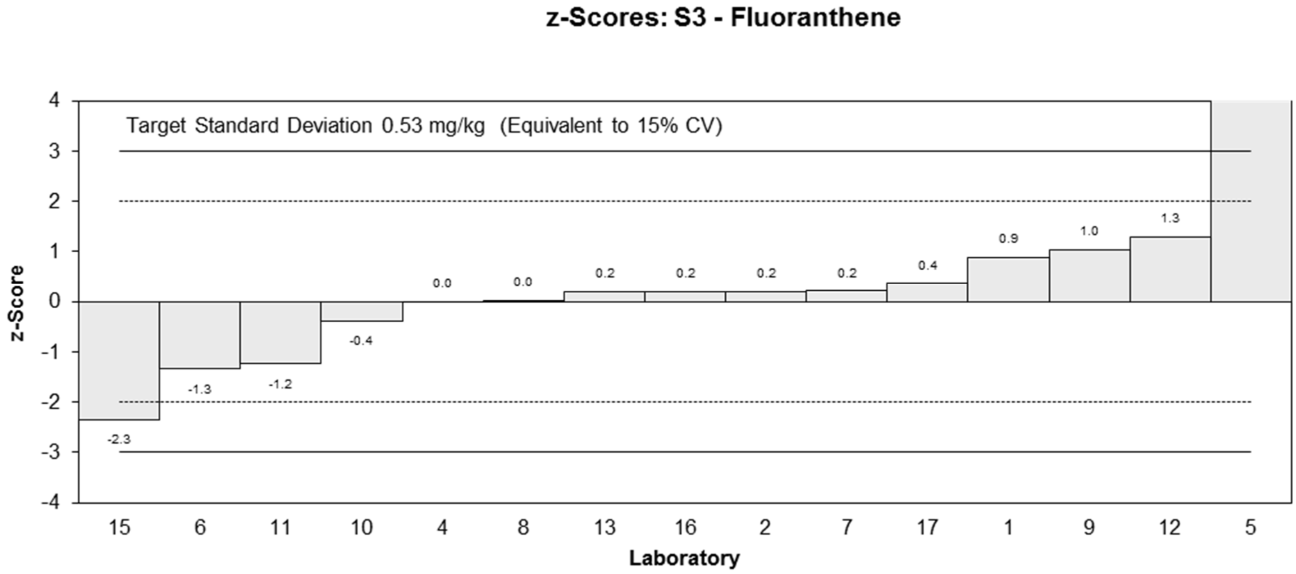
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.96	1.0	0.88	0.44
2	3.6	0.5	0.19	0.17
3	NT	NT		
4	3.5	0.93	0.00	0.00
5	9.1	1.4	10.67	3.89
6	2.8	0.6	-1.33	-1.02
7	3.61	0.90	0.21	0.11
8	3.51	0.70	0.02	0.01
9	4.04	0.81	1.03	0.61
10	3.3	0.83	-0.38	-0.22
11	2.85	0.85	-1.24	-0.71
12	4.18	1.25	1.30	0.52
13	3.6	0.61	0.19	0.14
14	NT	NT		
15	2.27	0.68	-2.34	-1.62
16	3.60	1.08	0.19	0.09
17	3.69	0.80	0.36	0.22

Statistics

Assigned Value*	3.50	0.34
Spike	4.20	0.21
Robust Average	3.56	0.36
Median	3.60	0.25
Mean	3.84	
N	15	
Max.	9.1	
Min.	2.27	
Robust SD	0.50	
Robust CV	14%	

*Robust average excluding laboratory 5.


Kernel Density
Results: S3 - Fluoranthene
Assigned Value = 3.50 ± 0.34 mg/kg
Results (mg/kg)
Laboratory
15
6
11
10
4
8
13
16
2
7
17
1
9
12
5
14
3
Md
R.A.
S.V.


z-Scores: S3 - Fluoranthene
Target Standard Deviation 0.53 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory

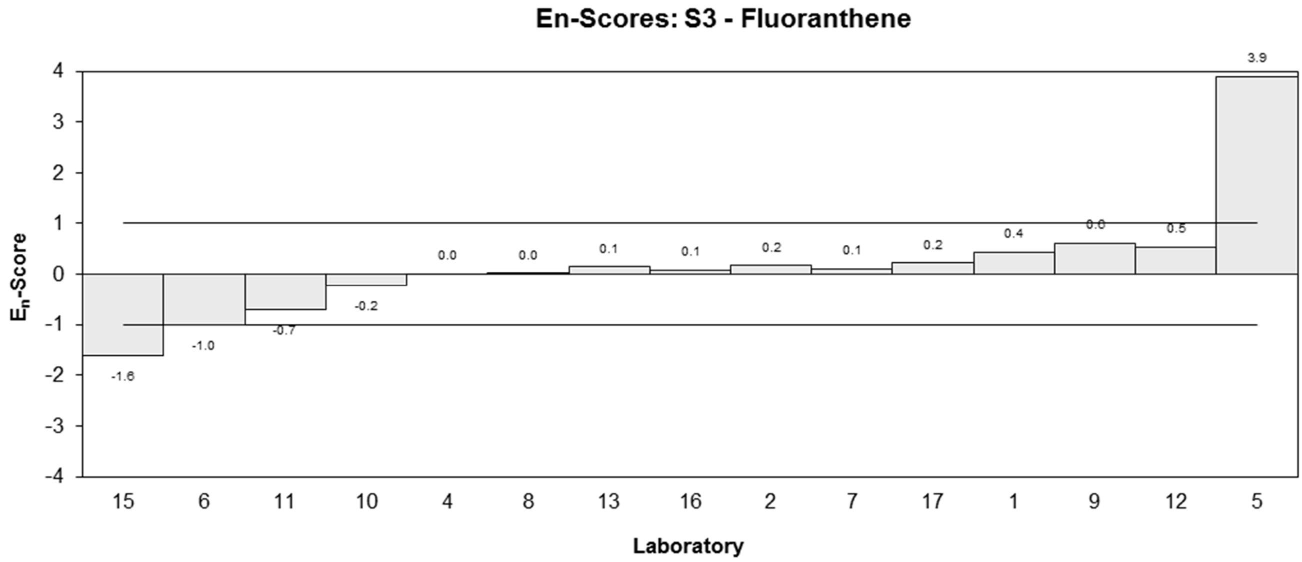

En-Scores: S3 - Fluoranthene
En-Score
Laboratory

Figure 13

Table 19

Sample Details

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

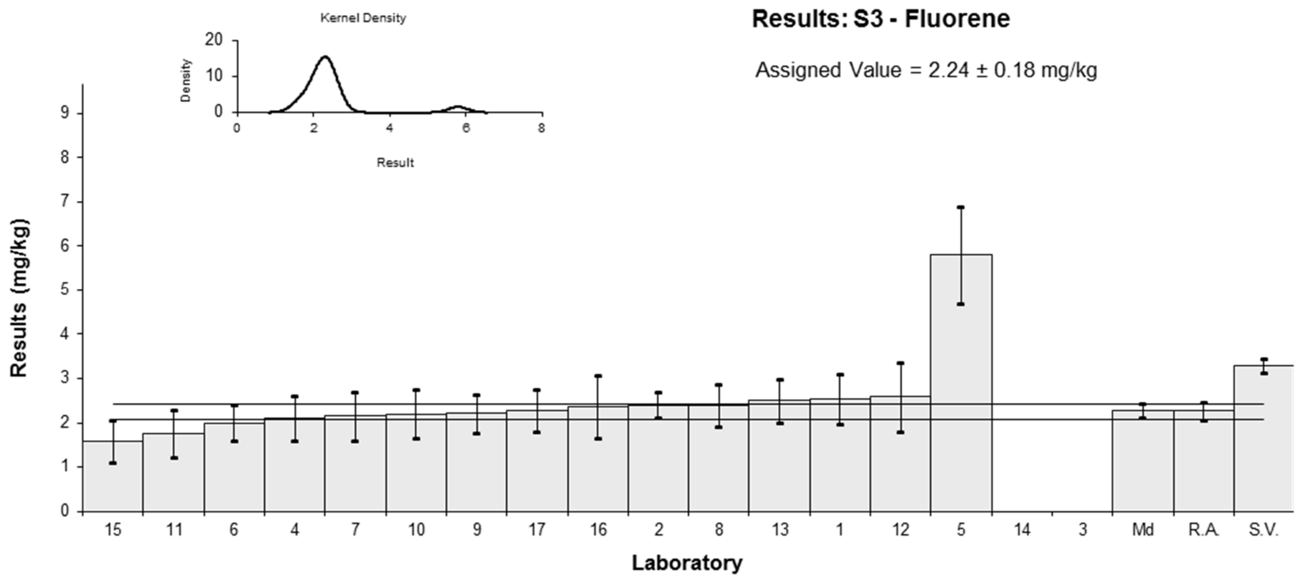
Participant Results

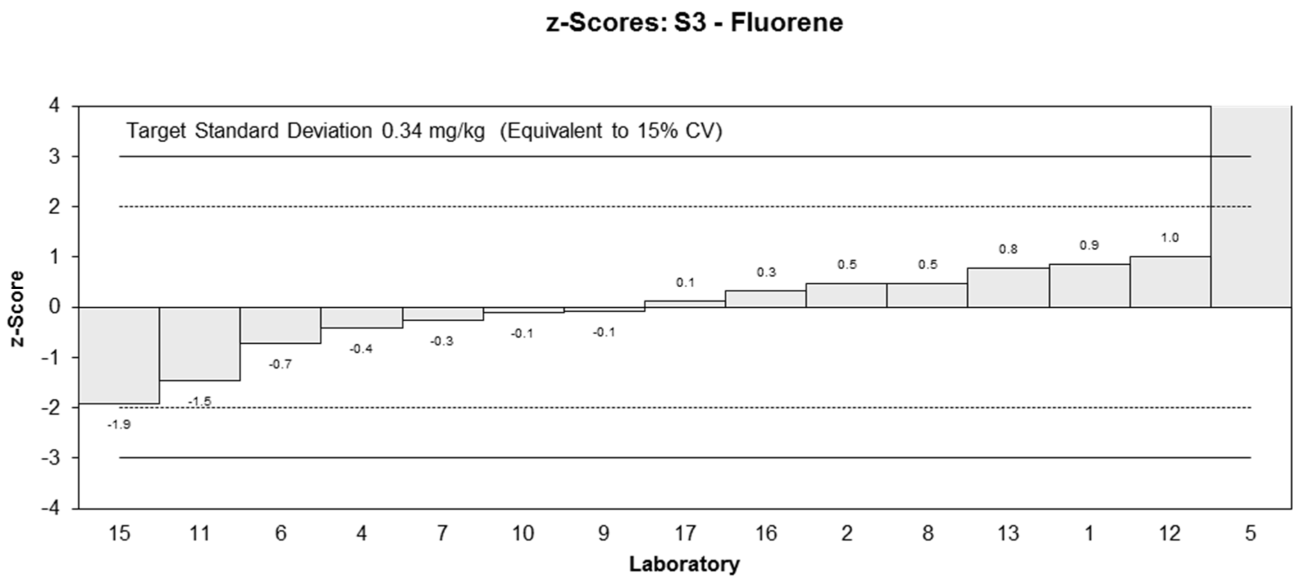
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.53	0.56	0.86	0.49
2	2.4	0.29	0.48	0.47
3	NT	NT		
4	2.1	0.51	-0.42	-0.26
5	5.8	1.1	10.60	3.19
6	2.0	0.4	-0.71	-0.55
7	2.1475	0.54	-0.28	-0.16
8	2.40	0.48	0.48	0.31
9	2.21	0.44	-0.09	-0.06
10	2.2	0.55	-0.12	-0.07
11	1.75	0.53	-1.46	-0.88
12	2.58	0.77	1.01	0.43
13	2.5	0.49	0.77	0.50
14	NT	NT		
15	1.59	0.48	-1.93	-1.27
16	2.35	0.71	0.33	0.15
17	2.28	0.47	0.12	0.08

Statistics

Assigned Value*	2.24	0.18
Spike	3.28	0.16
Robust Average	2.27	0.20
Median	2.28	0.15
Mean	2.46	
N	15	
Max.	5.8	
Min.	1.59	
Robust SD	0.27	
Robust CV	12%	

*Robust average excluding laboratory 5.


Results: S3 - Fluorene
Assigned Value = 2.24 ± 0.18 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 11 6 4 7 10 9 17 16 2 8 13 1 12 5 14 3 Md R.A. S.V.


z-Scores: S3 - Fluorene
Target Standard Deviation 0.34 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-1.9 -1.5 -0.7 -0.4 -0.3 -0.1 -0.1 0.1 0.3 0.5 0.5 0.8 0.9 1.0
15 11 6 4 7 10 9 17 16 2 8 13 1 12 5

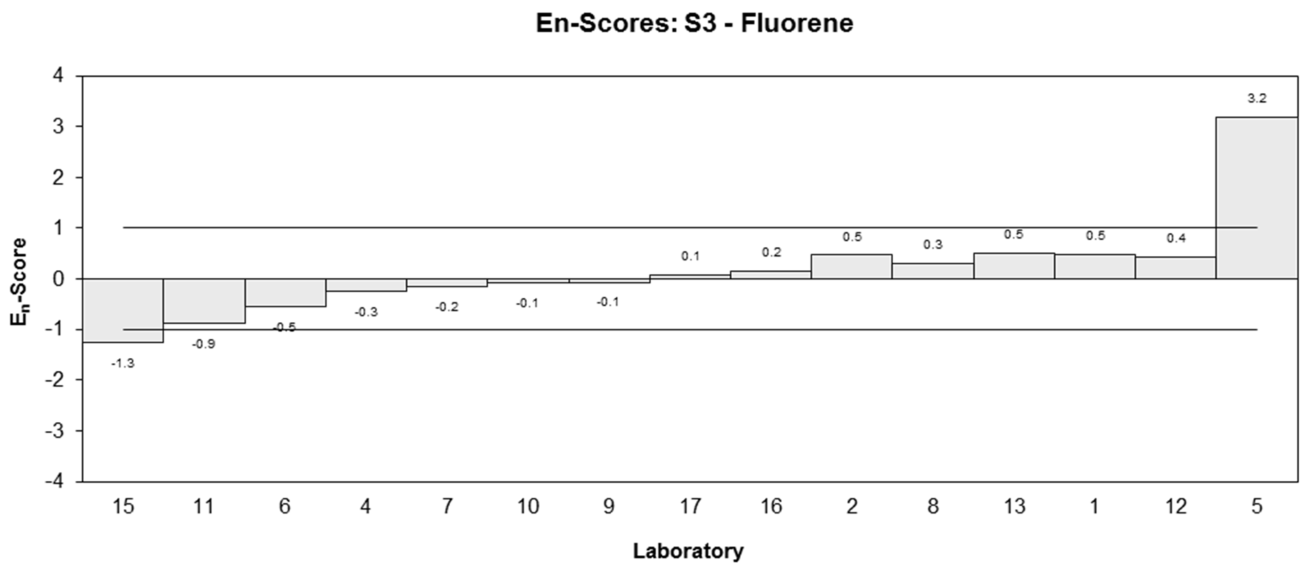

En-Scores: S3 - Fluorene
E_n-Score
Laboratory
-1.3 -0.9 -0.5 -0.3 -0.2 -0.1 -0.1 0.1 0.2 0.5 0.3 0.5 0.5 0.4 3.2
15 11 6 4 7 10 9 17 16 2 8 13 1 12 5

Figure 14

Table 20

Sample Details

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

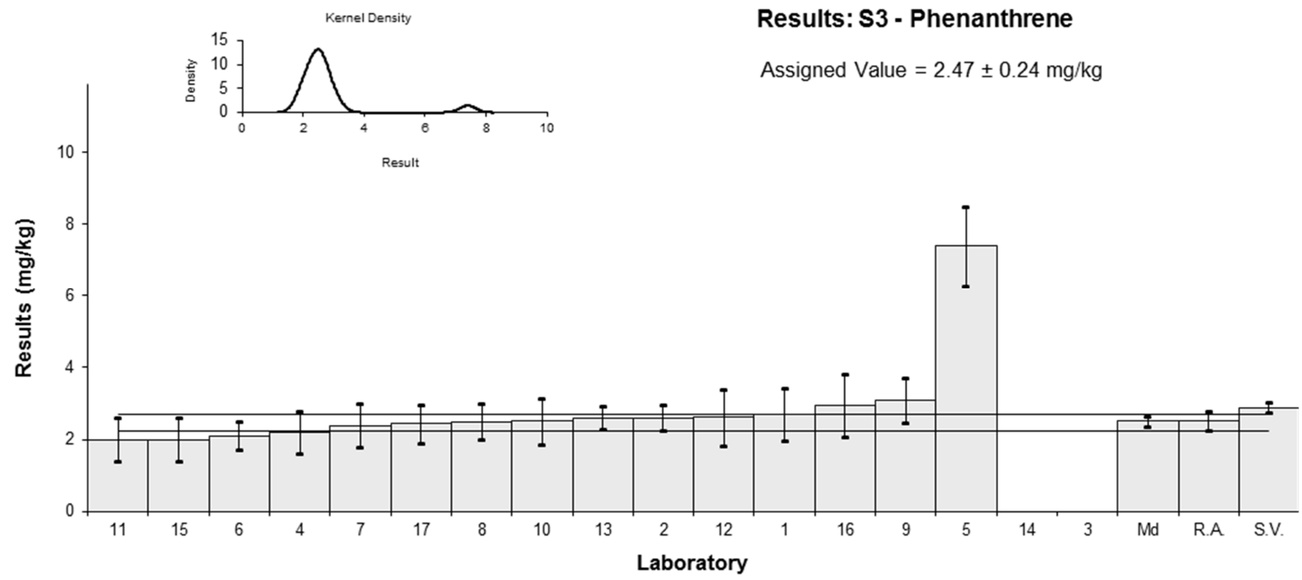
Participant Results

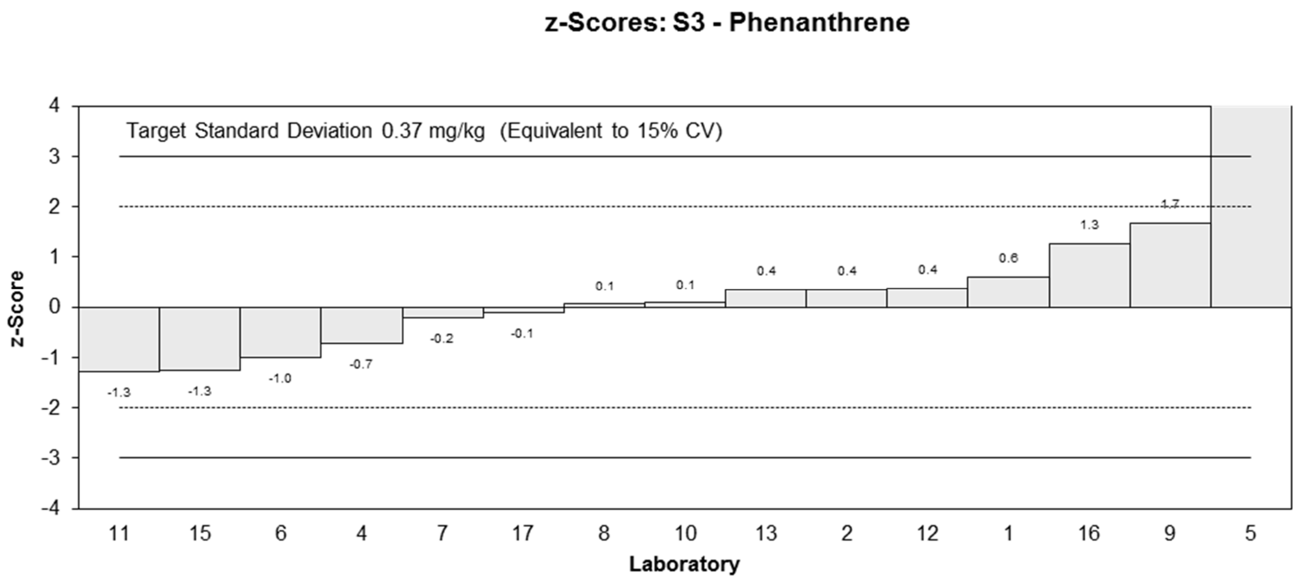
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.69	0.72	0.59	0.29
2	2.6	0.36	0.35	0.30
3	NT	NT		
4	2.2	0.58	-0.73	-0.43
5	7.4	1.1	13.31	4.38
6	2.1	0.4	-1.00	-0.79
7	2.3925	0.60	-0.21	-0.12
8	2.49	0.50	0.05	0.04
9	3.09	0.62	1.67	0.93
10	2.5	0.63	0.08	0.04
11	1.99	0.60	-1.30	-0.74
12	2.61	0.78	0.38	0.17
13	2.6	0.33	0.35	0.32
14	NT	NT		
15	2.00	0.6	-1.27	-0.73
16	2.94	0.88	1.27	0.52
17	2.43	0.53	-0.11	-0.07

Statistics

Assigned Value*	2.47	0.24
Spike	2.88	0.14
Robust Average	2.52	0.26
Median	2.50	0.16
Mean	2.80	
N	15	
Max.	7.4	
Min.	1.99	
Robust SD	0.35	
Robust CV	14%	

*Robust average excluding laboratory 5.


Results: S3 - Phenanthrene
Assigned Value = 2.47 ± 0.24 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 15 6 4 7 17 8 10 13 2 12 1 16 9 5 14 3 Md R.A. S.V.


z-Scores: S3 - Phenanthrene
Target Standard Deviation 0.37 mg/kg (Equivalent to 15% CV)
z-Score
-1.3 -1.3 -1.0 -0.7 -0.2 -0.1 0.1 0.1 0.4 0.4 0.4 0.6 1.3 1.7
11 15 6 4 7 17 8 10 13 2 12 1 16 9 5
Laboratory

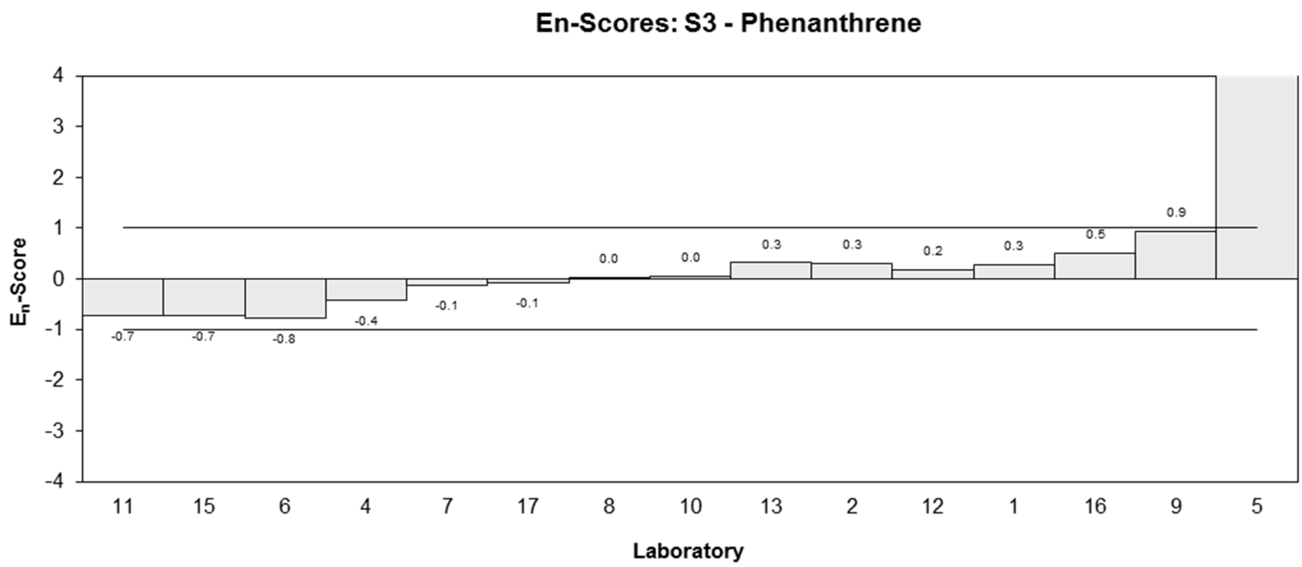

En-Scores: S3 - Phenanthrene
E_n-Score
-0.7 -0.7 -0.8 -0.4 -0.1 -0.1 0.0 0.0 0.3 0.3 0.2 0.3 0.5 0.9
11 15 6 4 7 17 8 10 13 2 12 1 16 9 5
Laboratory

Figure 15

Table 21

Sample Details

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

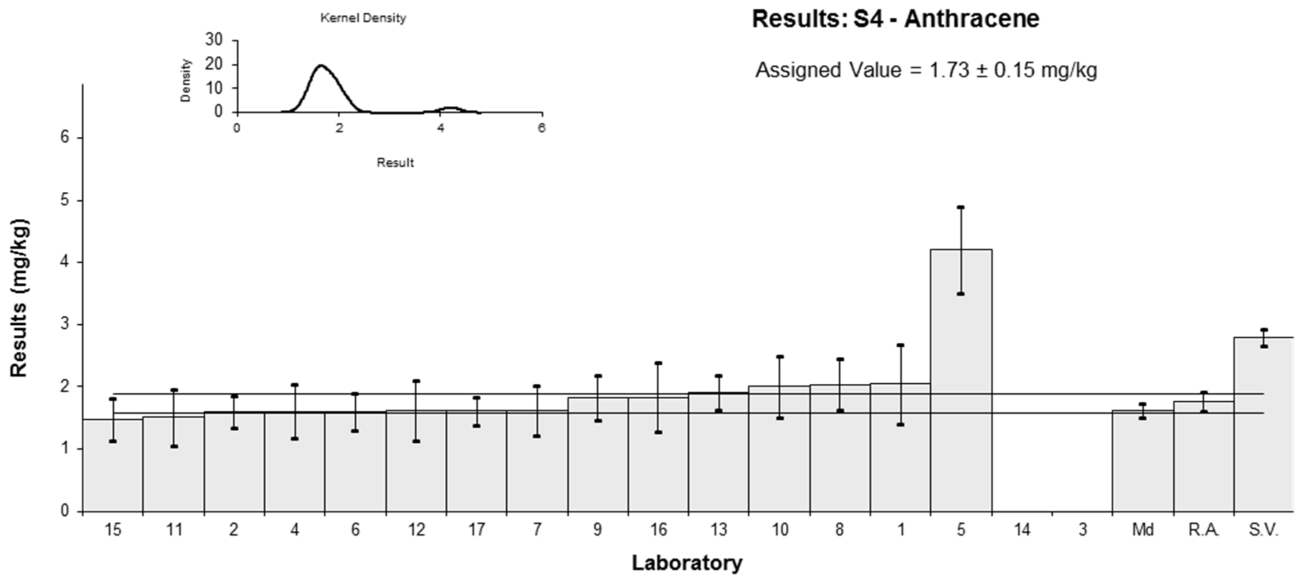
Participant Results

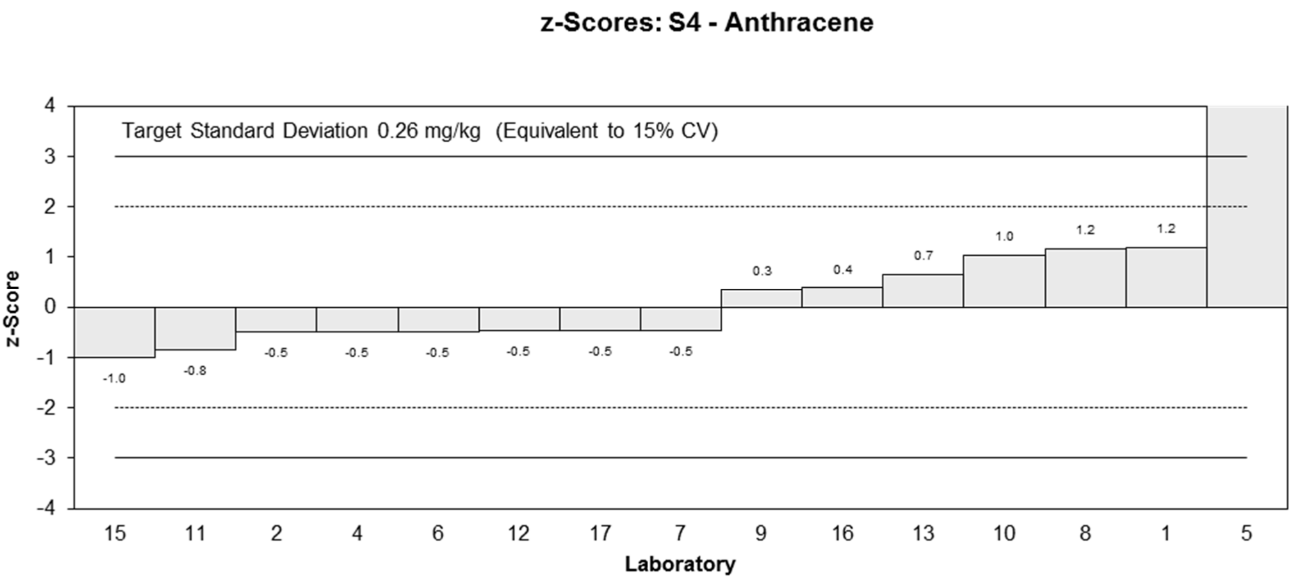
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.04	0.63	1.19	0.48
2	1.6	0.26	-0.50	-0.43
3	NT	NT		
4	1.6	0.43	-0.50	-0.29
5	4.2	0.7	9.52	3.45
6	1.6	0.3	-0.50	-0.39
7	1.61	0.40	-0.46	-0.28
8	2.03	0.41	1.16	0.69
9	1.82	0.36	0.35	0.23
10	2.0	0.5	1.04	0.52
11	1.51	0.45	-0.85	-0.46
12	1.61	0.48	-0.46	-0.24
13	1.9	0.28	0.66	0.54
14	NT	NT		
15	1.47	0.34	-1.00	-0.70
16	1.83	0.55	0.39	0.18
17	1.61	0.23	-0.46	-0.44

Statistics

Assigned Value*	1.73	0.15
Spike	2.79	0.14
Robust Average	1.76	0.16
Median	1.61	0.11
Mean	1.90	
N	15	
Max.	4.2	
Min.	1.47	
Robust SD	0.23	
Robust CV	13%	

*Robust average excluding laboratory 5.


Results: S4 - Anthracene
Assigned Value = 1.73 ± 0.15 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 11 2 4 6 12 17 7 9 16 13 10 8 1 5 14 3 Md R.A. S.V.


z-Scores: S4 - Anthracene
Target Standard Deviation 0.26 mg/kg (Equivalent to 15% CV)
z-Score
-1.0 -0.8 -0.5 -0.5 -0.5 -0.5 -0.5 -0.5 0.3 0.4 0.7 1.0 1.2 1.2
15 11 2 4 6 12 17 7 9 16 13 10 8 1 5
Laboratory

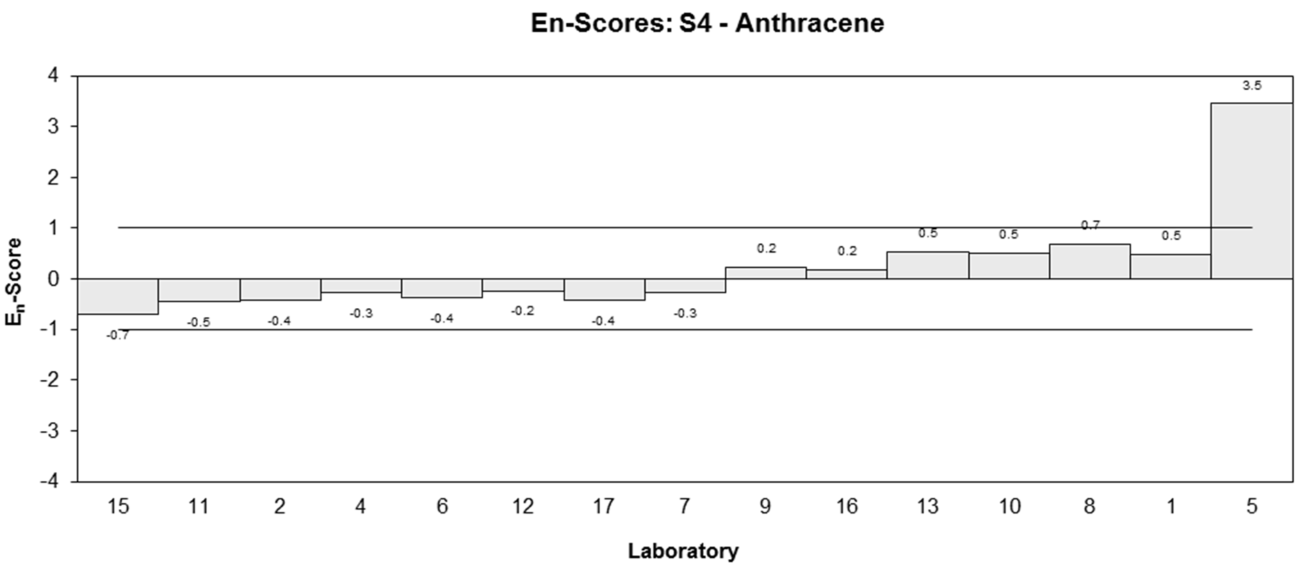

En-Scores: S4 - Anthracene
En-Score
-0.7 -0.5 -0.4 -0.3 -0.4 -0.2 -0.4 -0.3 0.2 0.2 0.5 0.5 0.7 0.5 3.5
15 11 2 4 6 12 17 7 9 16 13 10 8 1 5
Laboratory

Figure 16

Table 22

Sample Details

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

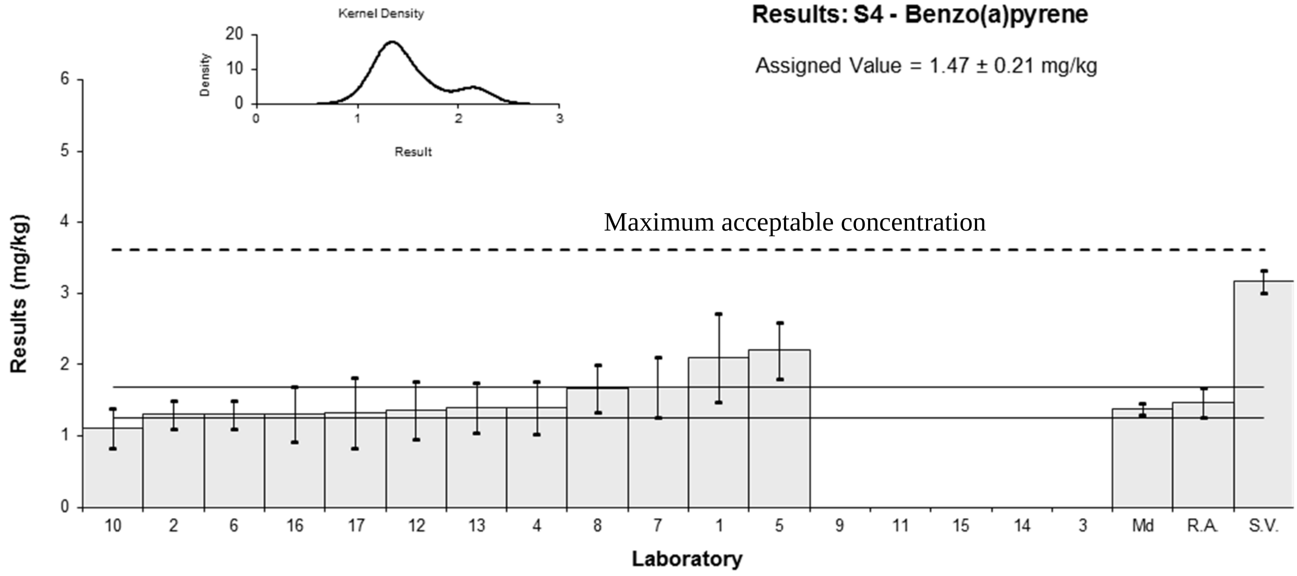
Participant Results

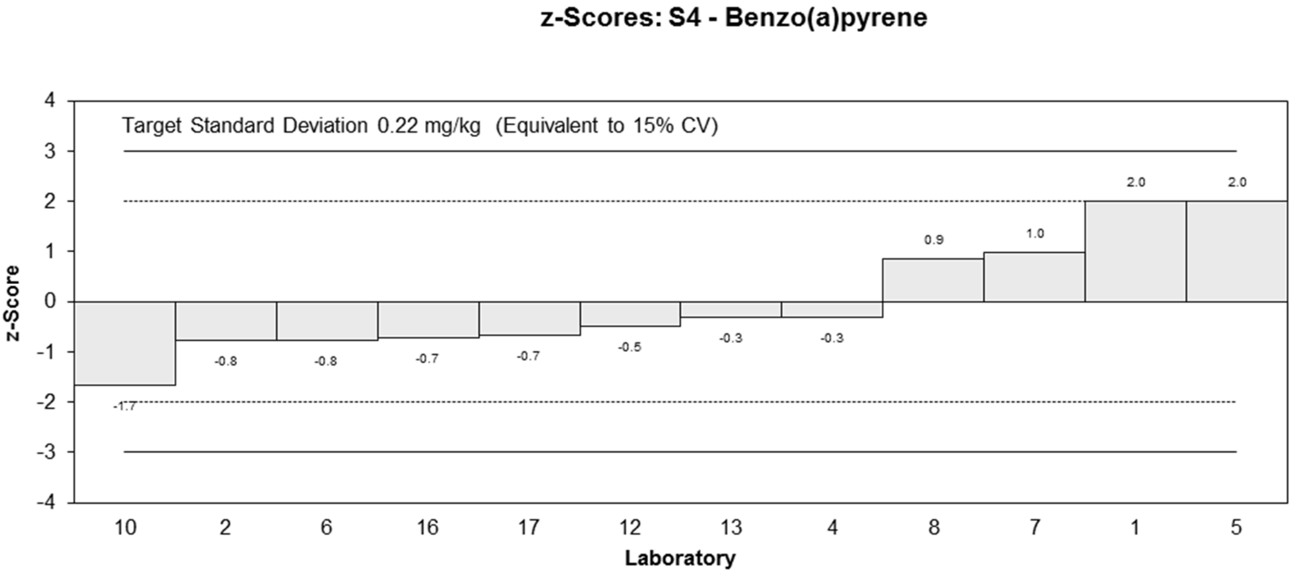
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1*	2.10	0.62	2.00	0.96
2	1.3	0.2	-0.77	-0.59
3	NT	NT		
4	1.4	0.37	-0.32	-0.16
5*	2.2	0.4	2.00	1.00
6	1.3	0.2	-0.77	-0.59
7	1.685	0.42	0.98	0.46
8	1.66	0.33	0.86	0.49
9	<0.01	NR		
10	1.1	0.28	-1.68	-1.06
11	<0.1	NR		
12	1.36	0.41	-0.50	-0.24
13	1.4	0.35	-0.32	-0.17
14	NT	NT		
15	<0.5	NR		
16	1.31	0.39	-0.73	-0.36
17	1.32	0.5	-0.68	-0.28

Statistics

Assigned Value	1.47	0.21
Spike	3.17	0.16
Maximum acceptable conc	3.61	
Robust Average	1.47	0.21
Median	1.38	0.08
Mean	1.51	
N	12	
Max.	2.2	
Min.	1.1	
Robust SD	0.29	
Robust CV	20%	

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


Results: S4 - Benzo(a)pyrene
Assigned Value = 1.47 ± 0.21 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
Laboratory
10 2 6 16 17 12 13 4 8 7 1 5 9 11 15 14 3 Md R.A. S.V.


z-Scores: S4 - Benzo(a)pyrene
Target Standard Deviation 0.22 mg/kg (Equivalent to 15% CV)
z-Score
-1.7 -0.8 -0.8 -0.7 -0.7 -0.5 -0.3 -0.3 0.9 1.0 2.0 2.0
10 2 6 16 17 12 13 4 8 7 1 5
Laboratory

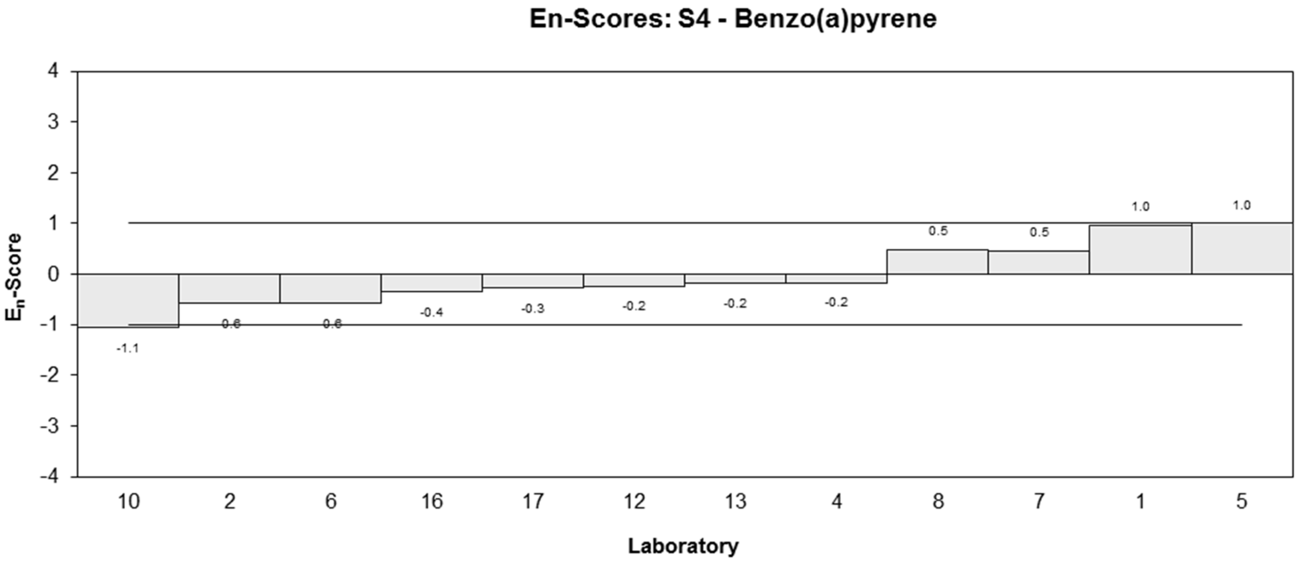

En-Scores: S4 - Benzo(a)pyrene
E_n-Score
-1.1 -0.6 -0.6 -0.4 -0.3 -0.2 -0.2 -0.2 0.5 0.5 1.0 1.0
10 2 6 16 17 12 13 4 8 7 1 5
Laboratory

Figure 17

Table 23

Sample Details

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

Participant Results

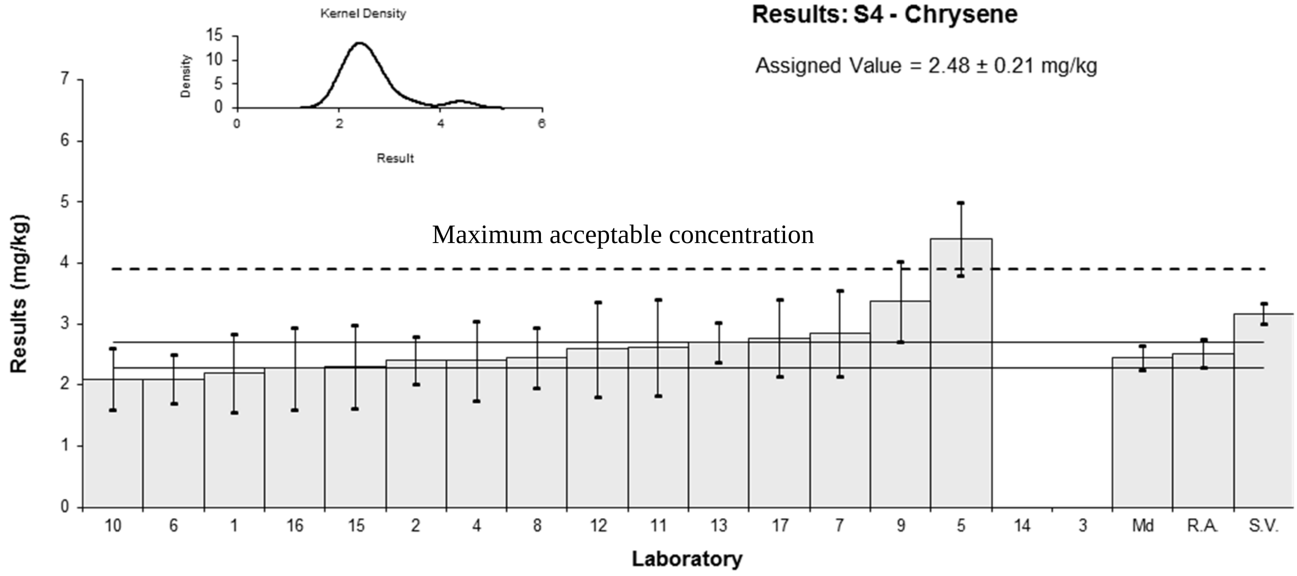
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.20	0.64	-0.75	-0.42
2	2.4	0.39	-0.22	-0.18
3	NT	NT		
4	2.4	0.65	-0.22	-0.12
5	4.4	0.6	5.16	3.02
6	2.1	0.4	-1.02	-0.84
7	2.8475	0.71	0.99	0.50
8	2.44	0.49	-0.11	-0.08
9*	3.37	0.67	2.00	1.00
10	2.1	0.5	-1.02	-0.70
11	2.62	0.79	0.38	0.17
12	2.59	0.78	0.30	0.14
13	2.7	0.33	0.59	0.56
14	NT	NT		
15	2.30	0.69	-0.48	-0.25
16	2.27	.68	-0.56	-0.30
17	2.77	0.63	0.78	0.44

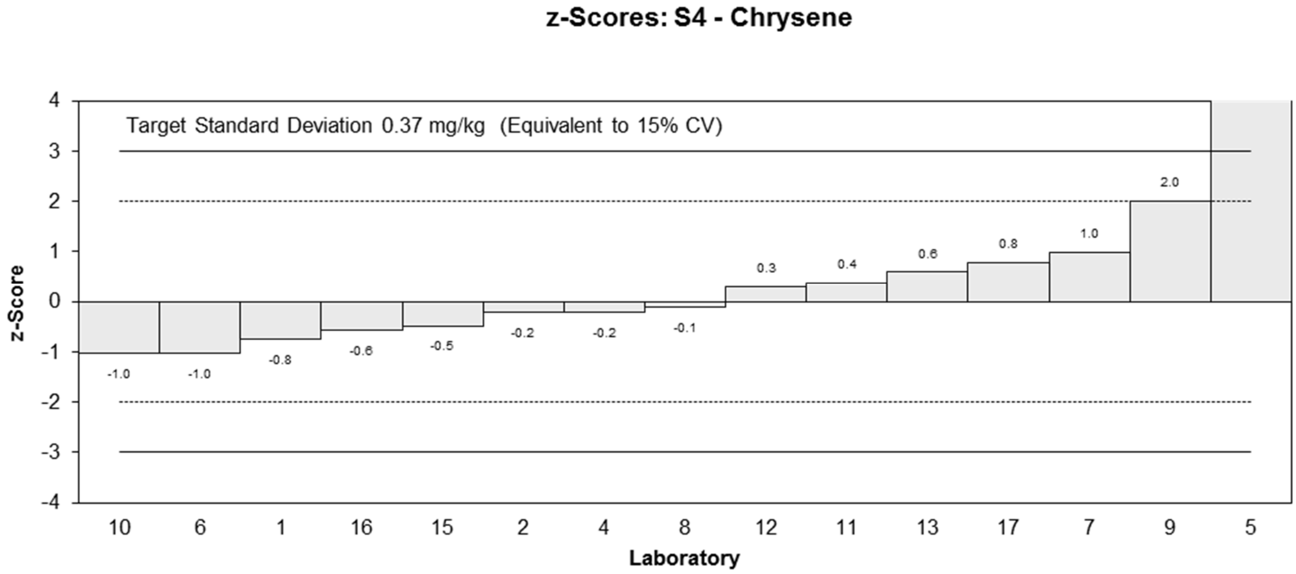
Statistics

Assigned Value**	2.48	0.21
Spike	3.17	0.16
Maximum acceptable conc	3.91	
Robust Average	2.52	0.23
Median	2.44	0.20
Mean	2.63	
N	15	
Max.	4.4	
Min.	2.1	
Robust SD	0.31	
Robust CV	12%	

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

**Robust average excluding laboratory 5.


Results: S4 - Chrysene
Assigned Value = 2.48 ± 0.21 mg/kg
Kernel Density
Density
Result
Maximum acceptable concentration
Results (mg/kg)
10
6
1
16
15
2
4
8
12
11
13
17
7
9
5
14
3
Md
R.A.
S.V.
Laboratory


z-Scores: S4 - Chrysene
Target Standard Deviation 0.37 mg/kg (Equivalent to 15% CV)
z-Score
-1.0
-1.0
-0.8
-0.6
-0.5
-0.2
-0.2
-0.1
0.3
0.4
0.6
0.8
1.0
2.0
10
6
1
16
15
2
4
8
12
11
13
17
7
9
5
Laboratory

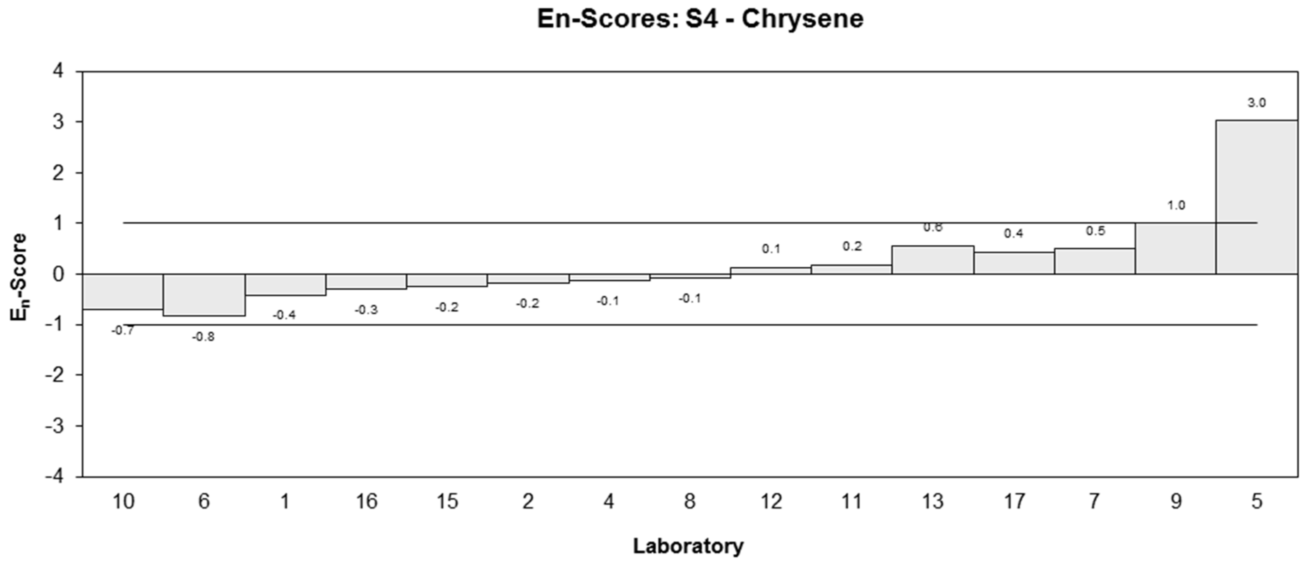

En-Scores: S4 - Chrysene
E_n-Score
-0.7
-0.8
-0.4
-0.3
-0.2
-0.2
-0.1
-0.1
0.1
0.2
0.6
0.4
0.5
1.0
3.0
10
6
1
16
15
2
4
8
12
11
13
17
7
9
5
Laboratory

Figure 18

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	2.90	0.73	0.74	0.38
2	2.5	0.4	-0.28	-0.24
3	NT	NT		
4	2.5	0.67	-0.28	-0.16
5	6.6	0.8	10.19	4.79
6	2.1	0.4	-1.30	-1.11
7	2.6	0.65	-0.03	-0.01
8	2.89	0.58	0.72	0.45
9	2.86	0.57	0.64	0.41
10	2.5	0.62	-0.28	-0.17
11	2.32	0.70	-0.74	-0.39
12	3.13	0.94	1.33	0.54
13	2.8	0.47	0.49	0.36
14	NT	NT		
15	1.70	0.51	-2.32	-1.63
16	2.61	0.78	0.00	0.00
17	2.78	0.53	0.43	0.29

Statistics

Assigned Value*	2.61	0.23
Spike	2.96	0.15
Robust Average	2.65	0.24
Median	2.61	0.21
Mean	2.85	
N	15	
Max.	6.6	
Min.	1.7	
Robust SD	0.35	
Robust CV	13%	

*Robust average excluding laboratory 5

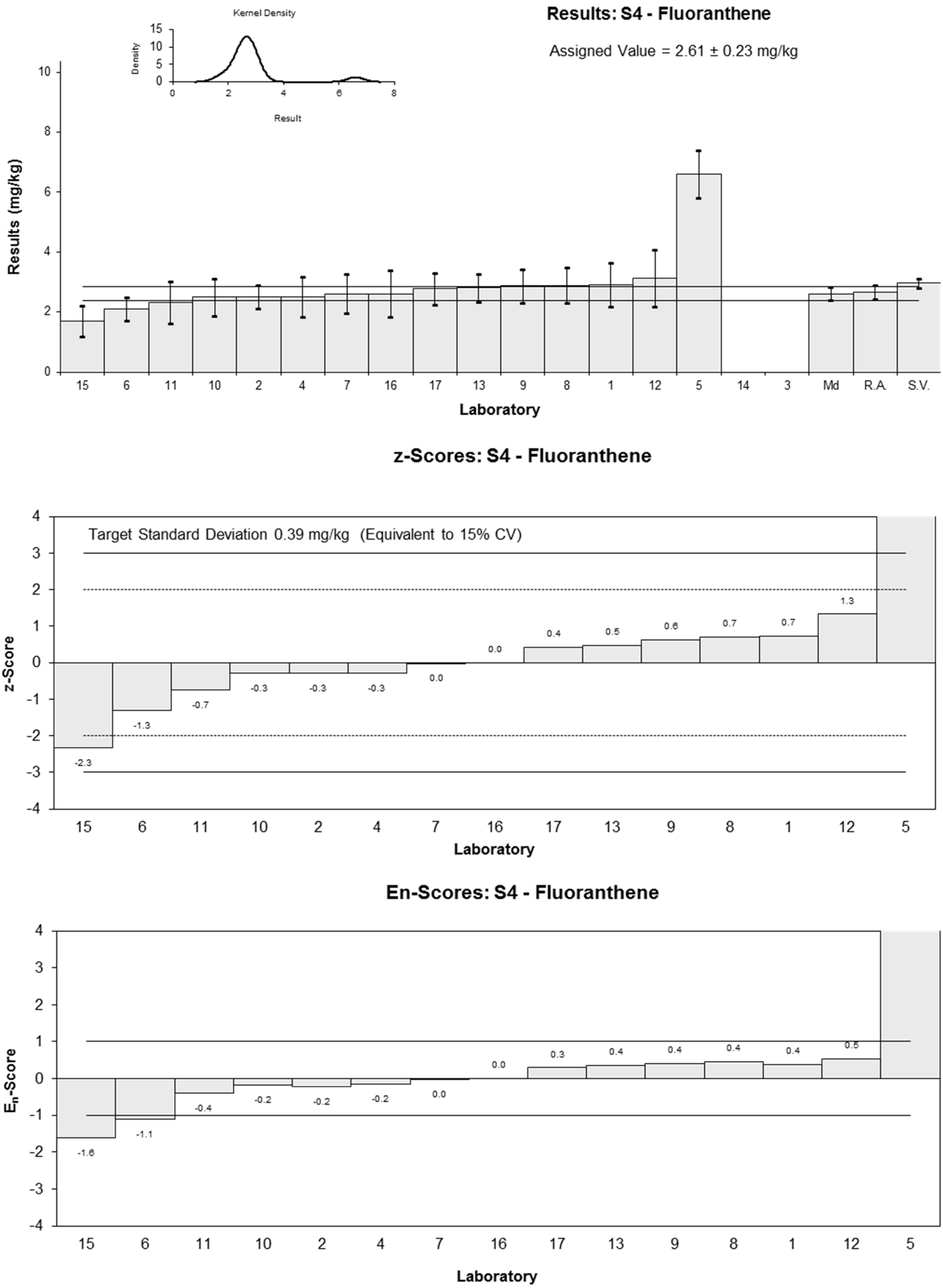

Results: S4 - Fluoranthene
Assigned Value = 2.61 ± 0.23 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
15 6 11 10 2 4 7 16 17 13 9 8 1 12 5 14 3 Md R.A. S.V.
Laboratory
z-Scores: S4 - Fluoranthene
Target Standard Deviation 0.39 mg/kg (Equivalent to 15% CV)
z-Score
-2.3 -1.3 -0.7 -0.3 -0.3 -0.3 0.0 0.0 0.4 0.5 0.6 0.7 0.7 1.3
15 6 11 10 2 4 7 16 17 13 9 8 1 12 5
Laboratory
En-Scores: S4 - Fluoranthene
E_n-Score
-1.6 -1.1 -0.4 -0.2 -0.2 -0.2 0.0 0.0 0.3 0.4 0.4 0.4 0.4 0.5
15 6 11 10 2 4 7 16 17 13 9 8 1 12 5
Laboratory

Figure 19

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	3.71	0.93	-0.42	-0.26
2	4.1	0.49	0.24	0.25
3	NT	NT		
4	3.8	0.93	-0.27	-0.16
5	11	3	11.85	2.34
6	3.5	0.7	-0.77	-0.61
7	3.77	0.94	-0.32	-0.19
8	4.44	0.89	0.81	0.51
9	3.65	0.73	-0.52	-0.39
10	3.8	0.95	-0.27	-0.16
11	3.87	1.16	-0.15	-0.08
12	4.41	1.32	0.76	0.33
13	4.8	0.94	1.41	0.85
14	NT	NT		
15	3.32	1.0	-1.08	-0.61
16	4.21	1.26	0.42	0.19
17	4.20	0.87	0.40	0.26

Statistics

Assigned Value*	3.96	0.29
Spike	4.85	0.24
Robust Average	4.02	0.32
Median	3.87	0.27
Mean	4.44	
N	15	
Max.	11	
Min.	3.32	
Robust SD	0.43	
Robust CV	11%	

*Robust average excluding laboratory 5

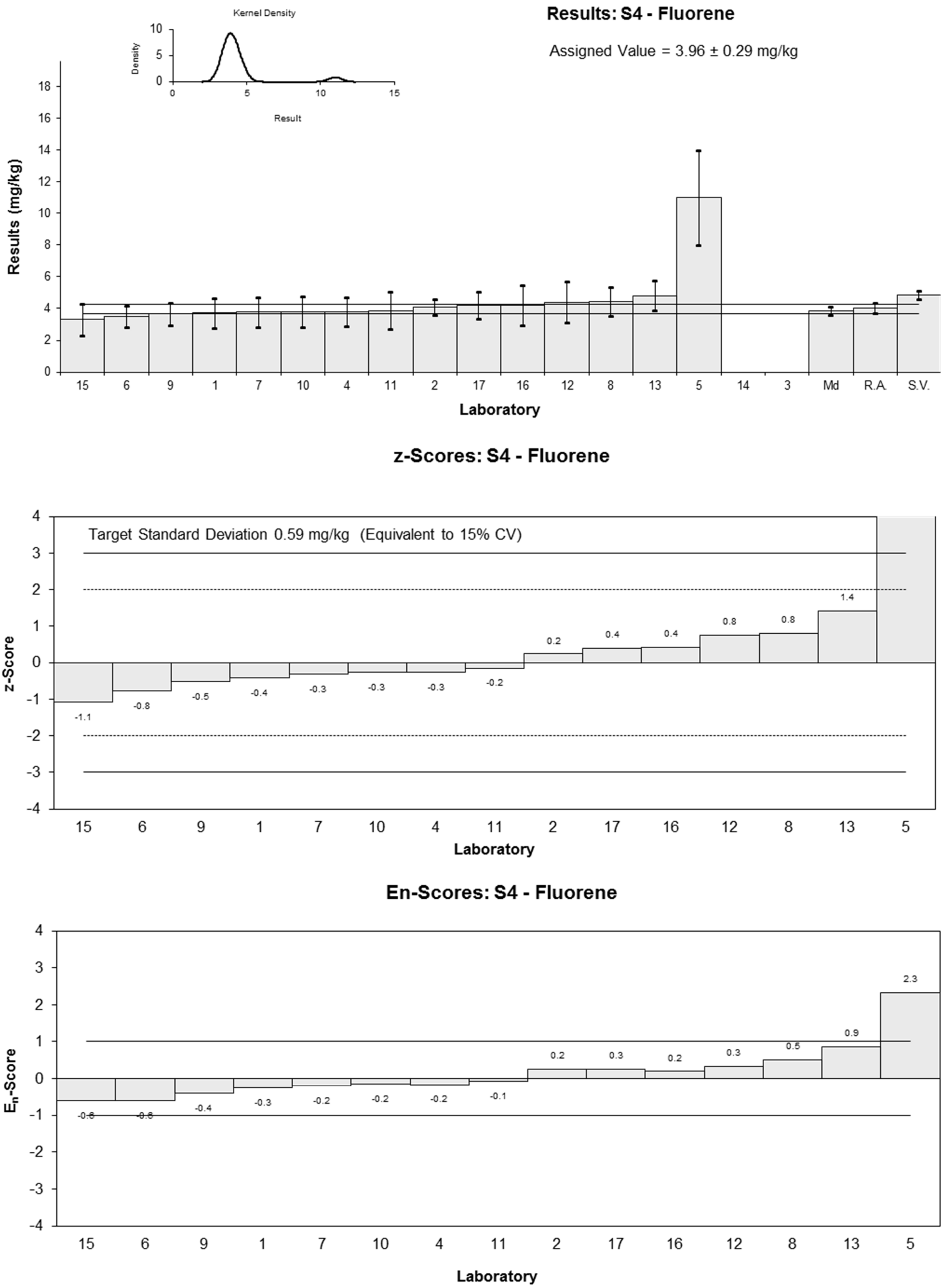

Results: S4 - Fluorene
Assigned Value = 3.96 ± 0.29 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 6 9 1 7 10 4 11 2 17 16 12 8 13 5 14 3 Md R.A. S.V.
z-Scores: S4 - Fluorene
Target Standard Deviation 0.59 mg/kg (Equivalent to 15% CV)
z-Score
-1.1 -0.8 -0.5 -0.4 -0.3 -0.3 -0.3 -0.2 0.2 0.4 0.4 0.8 0.8 1.4
Laboratory
15 6 9 1 7 10 4 11 2 17 16 12 8 13 5
En-Scores: S4 - Fluorene
En-Score
-0.6 -0.6 -0.4 -0.3 -0.2 -0.2 -0.2 -0.1 0.2 0.3 0.2 0.3 0.5 0.9 2.3
Laboratory
15 6 9 1 7 10 4 11 2 17 16 12 8 13 5

Figure 20

Table 26

Sample Details

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

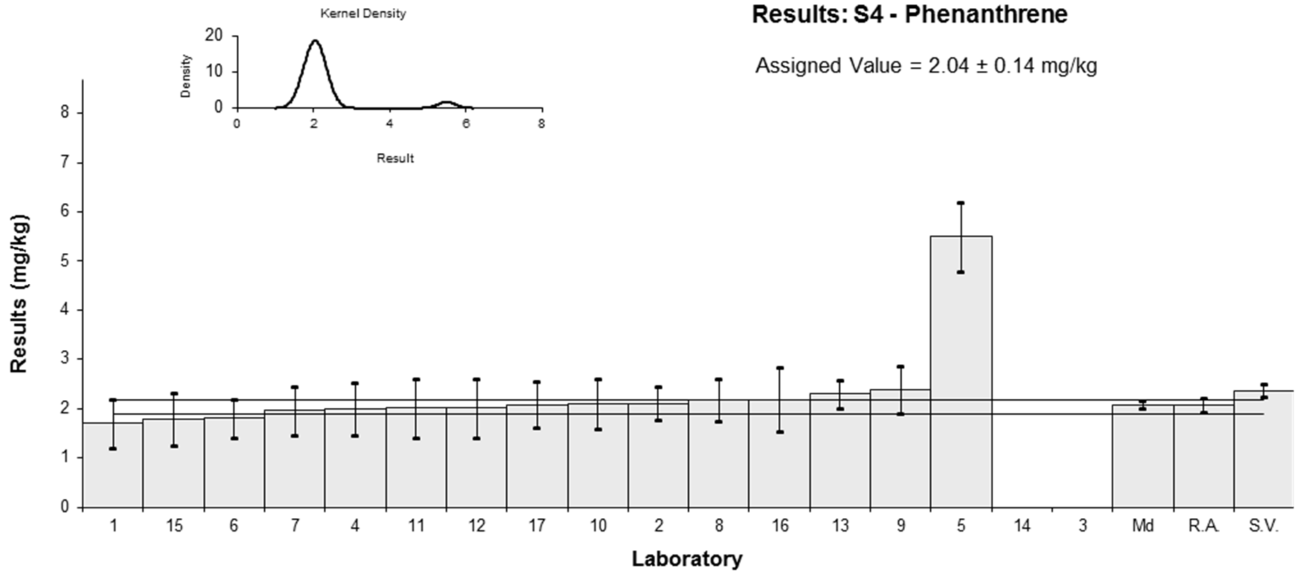
Participant Results

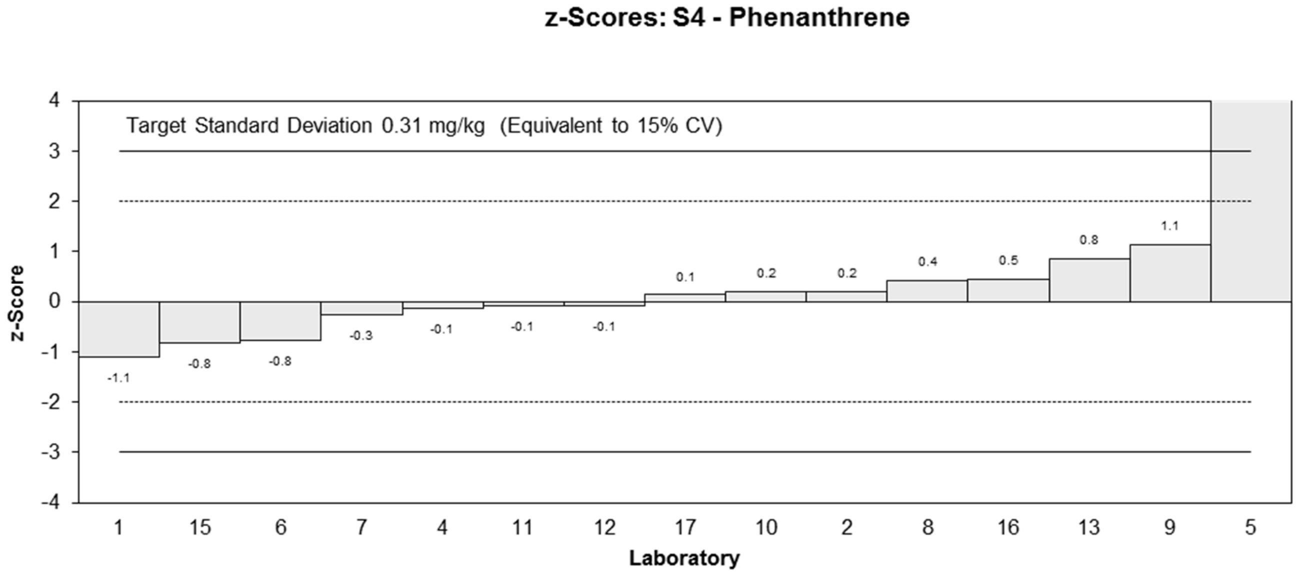
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.70	0.49	-1.11	-0.67
2	2.1	0.34	0.20	0.16
3	NT	NT		
4	2	0.53	-0.13	-0.07
5	5.5	0.7	11.31	4.85
6	1.8	0.4	-0.78	-0.57
7	1.9575	0.49	-0.27	-0.16
8	2.17	0.43	0.42	0.29
9	2.39	0.48	1.14	0.70
10	2.1	0.5	0.20	0.12
11	2.01	0.60	-0.10	-0.05
12	2.01	0.60	-0.10	-0.05
13	2.3	0.29	0.85	0.81
14	NT	NT		
15	1.79	0.54	-0.82	-0.45
16	2.18	0.65	0.46	0.21
17	2.08	0.46	0.13	0.08

Statistics

Assigned Value*	2.04	0.14
Spike	2.37	0.12
Robust Average	2.07	0.15
Median	2.08	0.08
Mean	2.27	
N	15	
Max.	5.5	
Min.	1.7	
Robust SD	0.21	
Robust CV	10%	

*Robust average excluding laboratory 5.


Results: S4 - Phenanthrene
Assigned Value = 2.04 ± 0.14 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
1 15 6 7 4 11 12 17 10 2 8 16 13 9 5 14 3 Md R.A. S.V.


z-Scores: S4 - Phenanthrene
Target Standard Deviation 0.31 mg/kg (Equivalent to 15% CV)
z-Score
-1.1 -0.8 -0.8 -0.3 -0.1 -0.1 -0.1 0.1 0.2 0.2 0.4 0.5 0.8 1.1
1 15 6 7 4 11 12 17 10 2 8 16 13 9 5
Laboratory

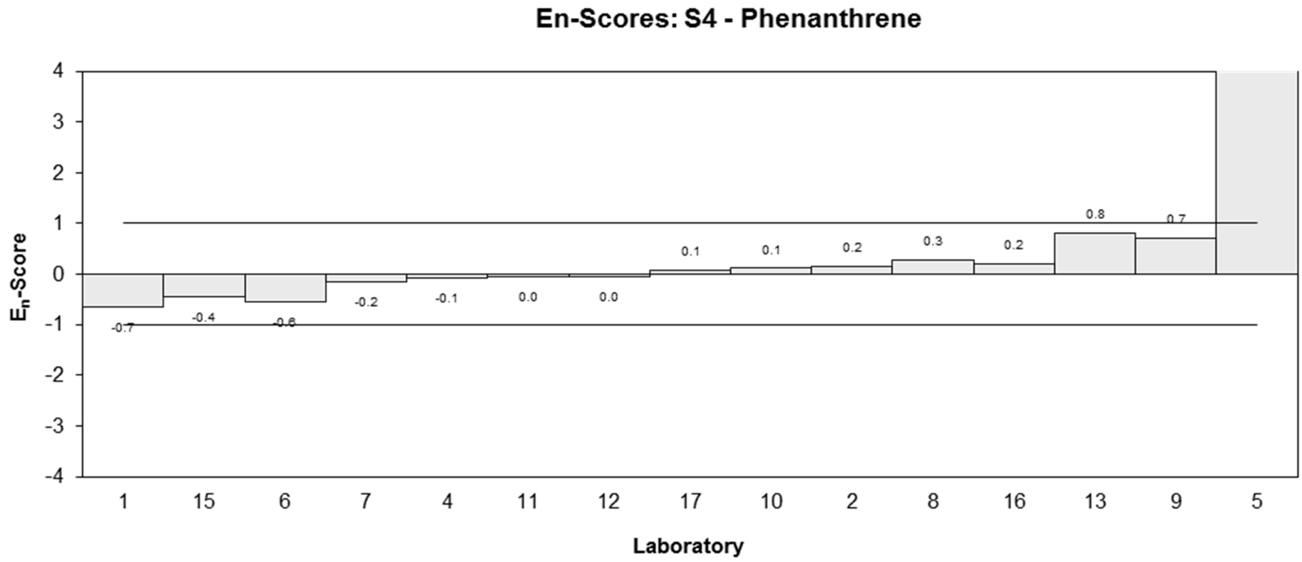

En-Scores: S4 - Phenanthrene
En-Score
-0.7 -0.4 -0.6 -0.2 -0.1 0.0 0.0 0.1 0.1 0.2 0.3 0.2 0.8 0.7
1 15 6 7 4 11 12 17 10 2 8 16 13 9 5
Laboratory

Figure 21

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	2.20	0.53	0.16	0.09
2	2.1	0.3	-0.16	-0.15
3	NT	NT		
4	2.1	0.59	-0.16	-0.08
5	5.3	0.8	9.77	3.86
6	1.8	0.3	-1.09	-1.03
7	2.0675	0.52	-0.26	-0.15
8	2.28	0.46	0.40	0.27
9	2.11	0.42	-0.12	-0.09
10	2.3	0.57	0.47	0.25
11	1.99	0.59	-0.50	-0.26
12	2.64	0.79	1.52	0.61
13	2.4	0.37	0.78	0.62
14	NT	NT		
15	1.29	0.39	-2.67	-2.04
16	2.10	0.63	-0.16	-0.08
17	2.36	0.45	0.65	0.44

Statistics

Assigned Value*	2.15	0.16
Spike	2.68	0.13
Robust Average	2.19	0.18
Median	2.11	0.14
Mean	2.34	
N	15	
Max.	5.3	
Min.	1.29	
Robust SD	0.24	
Robust CV	11%	

*Robust average excluding laboratory 5

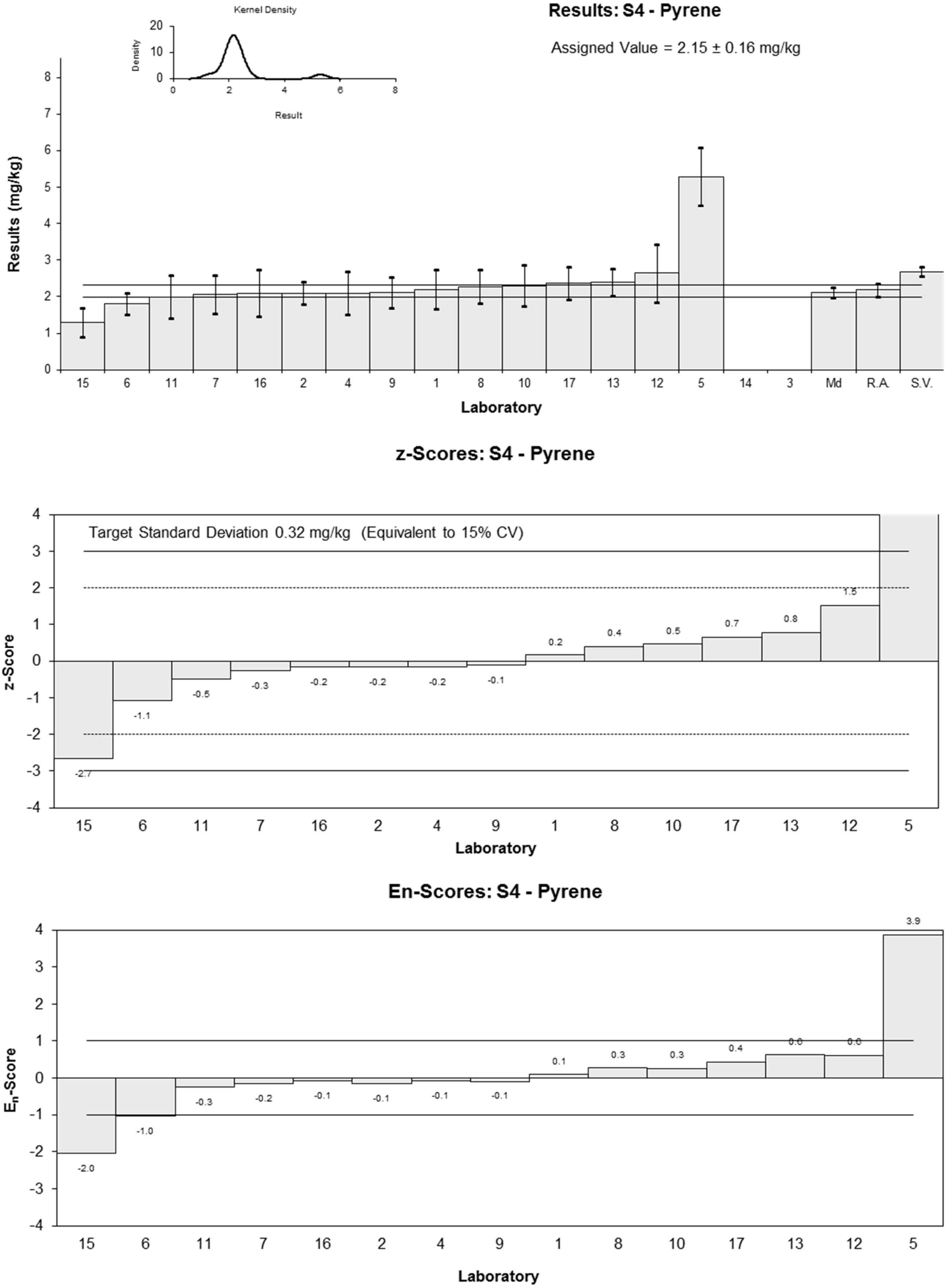

Kernel Density
Density
Result
Results: S4 - Pyrene
Assigned Value = 2.15 ± 0.16 mg/kg
Results (mg/kg)
15 6 11 7 16 2 4 9 1 8 10 17 13 12 5 14 3 Md R.A. S.V.
Laboratory
z-Scores: S4 - Pyrene
Target Standard Deviation 0.32 mg/kg (Equivalent to 15% CV)
z-Score
-2.7 -1.1 -0.5 -0.3 -0.2 -0.2 -0.2 -0.1 0.2 0.4 0.5 0.7 0.8 1.5
15 6 11 7 16 2 4 9 1 8 10 17 13 12 5
Laboratory
En-Scores: S4 - Pyrene
E_n-Score
-2.0 -1.0 -0.3 -0.2 -0.1 -0.1 -0.1 -0.1 0.1 0.3 0.3 0.4 0.6 0.6 3.9
15 6 11 7 16 2 4 9 1 8 10 17 13 12 5
Laboratory

Figure 22

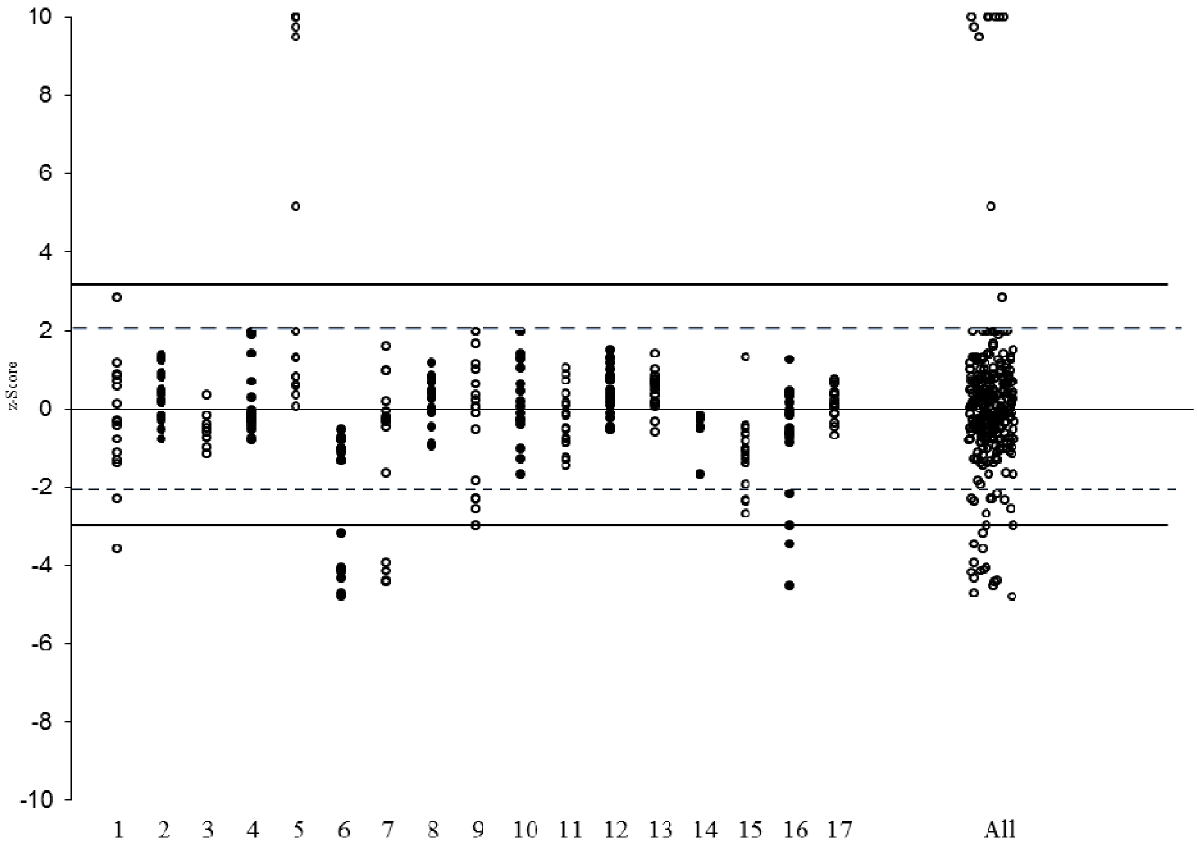


Figure 23 z-Score Dispersal by Laboratory

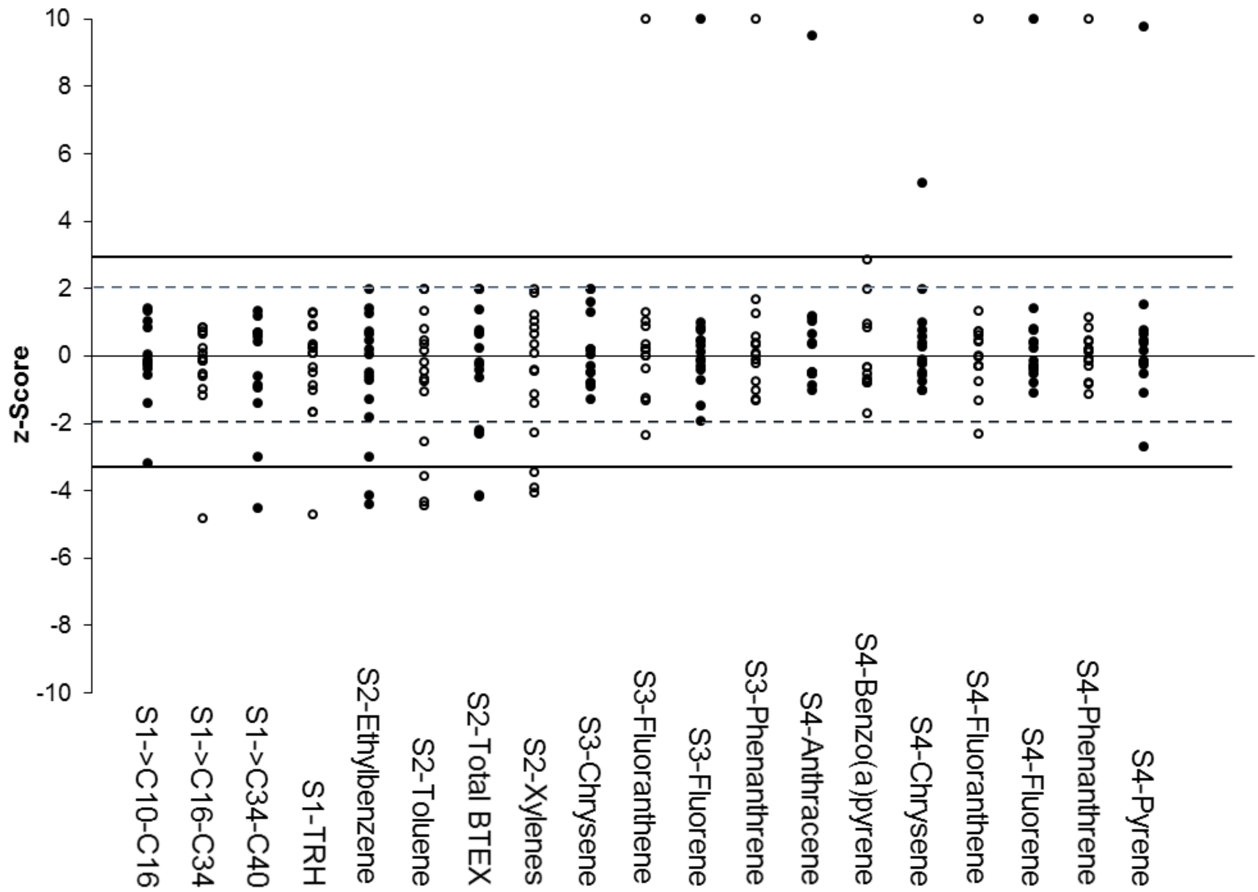


Figure 24 z-Score Dispersal by Sample and Analyte

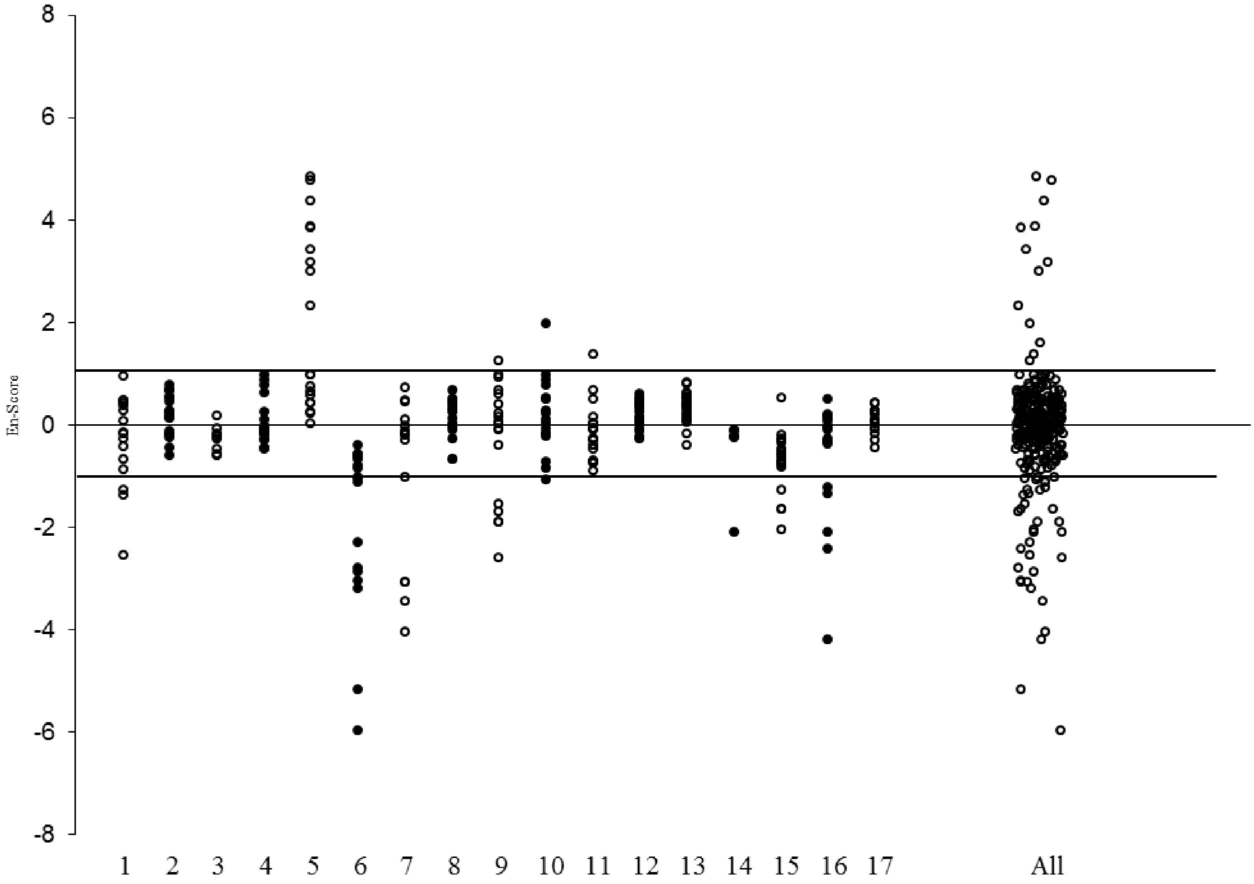


Figure 25 E_n-Score Dispersal by Laboratory

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'.[7] Appendix 2 sets out the calculation for the expanded uncertainty of the robust average of fluoranthene in Sample S4.

No assigned value was set for the C6-C10 range and benzene in Sample S2 because the submitted results were too variable or significantly lower than the spiked value.

The robust average of toluene, ethylbenzene, xylenes, Total BTEX in Sample S2 and benzo(a)pyrene in Sample S4 was lower than the spiked concentration, however there was a consensus of participants' results so an assigned value was set. A comparison of the assigned value and the spiked concentrations is presented in Table 28.

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 28 Comparison of Assigned Value and Spiked Concentration.

Sample	Analyte	Assigned concentration (mg/kg)	Spiked value (mg/kg)	Assigned/spike
S1	TRH	3260	3650	89%
S2	Ethylbenzene	49.5	81	61%
S2	Toluene	258	708	36%
S2	Total BTEX	610	1440	42%
S2	Xylenes	304	607	50%
S3	Chrysene	1.36	1.897	72%
S3	Fluoranthene	3.5	4.2	83%
S3	Fluorene	2.24	3.28	68%
S3	Phenanthrene	2.47	2.88	86%
S3	Anthracene	1.73	2.79	62%
S4	Benzo(a)pyrene	1.47	3.17	46%
S4	Chrysene	2.48	3.17	78%
S4	Fluoranthene	2.61	2.96	88%
S4	Fluorene	3.96	4.85	82%
S4	Phenanthrene	2.04	2.37	86%
S4	Pyrene	2.15	2.68	80%

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 314 numerical results, 310 were reported with an associated expanded uncertainty.

Expanded uncertainties were within the range 0% to 59% 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 310 expanded uncertainties, 25 were less than 15% relative. Some laboratories reported expanded uncertainties for analyte values that were below their limit of reporting/detection (e.g. $< 10 \pm 3$)

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 2.0675 ± 0.52 mg/kg is better to report 2.07 ±0.52 mg/kg and instead of 230.88 ± 57.72 mg/kg it is better to report 231 ± 58 mg/kg).[9]

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 284 results for which z-scores were calculated, 250 (88%) returned a satisfactory score of $|z| \leq 2$.

Laboratories **2**, **4**, **8**, **10**, **12** and **13** returned satisfactory z-scores for all nineteen analytes for which z-scores were calculated. Laboratories **3**, **11** and **17** returned satisfactory z-scores for all the analytes they reported.

Summaries of z-scores by laboratory and by analyte are presented in Figures 23 and 24.

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 284 results for which E_n-scores were calculated, 237 (83%) returned a satisfactory score of $|E_n| \leq 1$.

Laboratories **2**, **4**, **8**, **12** and **13** returned satisfactory E_n-scores for all nineteen analytes for which scores were calculated. Laboratories **3** and **17** returned satisfactory E_n-score for all the analytes they reported. A summary of E_n-scores by laboratory is presented in Figure 25.

6.5 Participants’ Analytical Methods

TRH in Sample S1

Participants used dichloromethane (DCM)/acetone in a 1:1 ratio, hexane/acetone in a 1:1 ratio, DCM alone and hexane alone. Three laboratories performed a clean-up procedure using silica. All laboratories used GC-FID to measure hydrocarbons in the sample extract. No trends with the extraction solvent or use of silica clean-up were evident (see Figure 26).

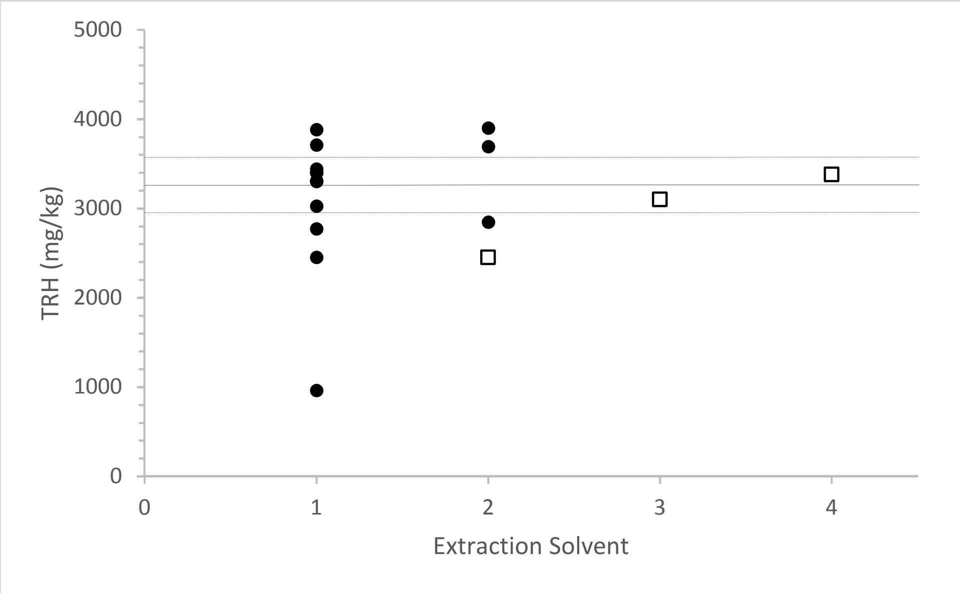


Figure 26 TRH results vs extraction solvent
1 = DCM/Acetone, 2 = Hexane/Acetone, 3 = DCM only, 4 = Hexane only
Open square = silica clean-up
Horizontal lines are the assigned value (solid) and its upper and lower 95% confidence interval.

BTEX in Sample S2

All laboratories used methanol as the extraction solvent.

For analysis, thirteen laboratories used purge-and-trap GC-MS and four laboratories used headspace with either GC-FID or GC-MS (Table 2). No trends were evident (Figure 27).

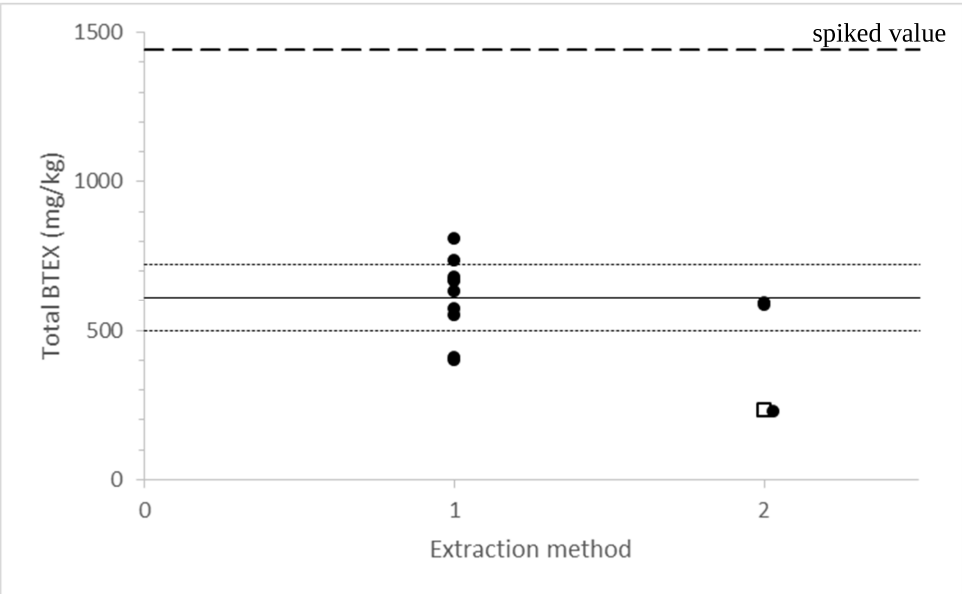


Figure 27 BTEX results vs extraction method
1 = Purge & trap, 2 = Headspace
Open square = GC-FID

Horizontal lines are the assigned value (solid) and its upper and lower 95% confidence interval.

Low recovery of benzene, toluene, ethylbenzene, xylenes and total BTEX in Sample S2 (13% to 61%) indicated that participants had difficulties with the extraction of these analytes. The soil used for preparation of Sample S2 was a new sandy soil from Randwick NSW.

NMI conducted a series of measurements of BTEX in the dried sandy Randwick soil and dried Menangle topsoil used in previous PT studies. BTEX recovery data in the two soils and the average recovery from PT studies in the last five years are presented in Figure 28. The recovery of BTEX was substantially affected by the nature of the sandy soil matrix collected from Randwick and used to prepare Sample S2.

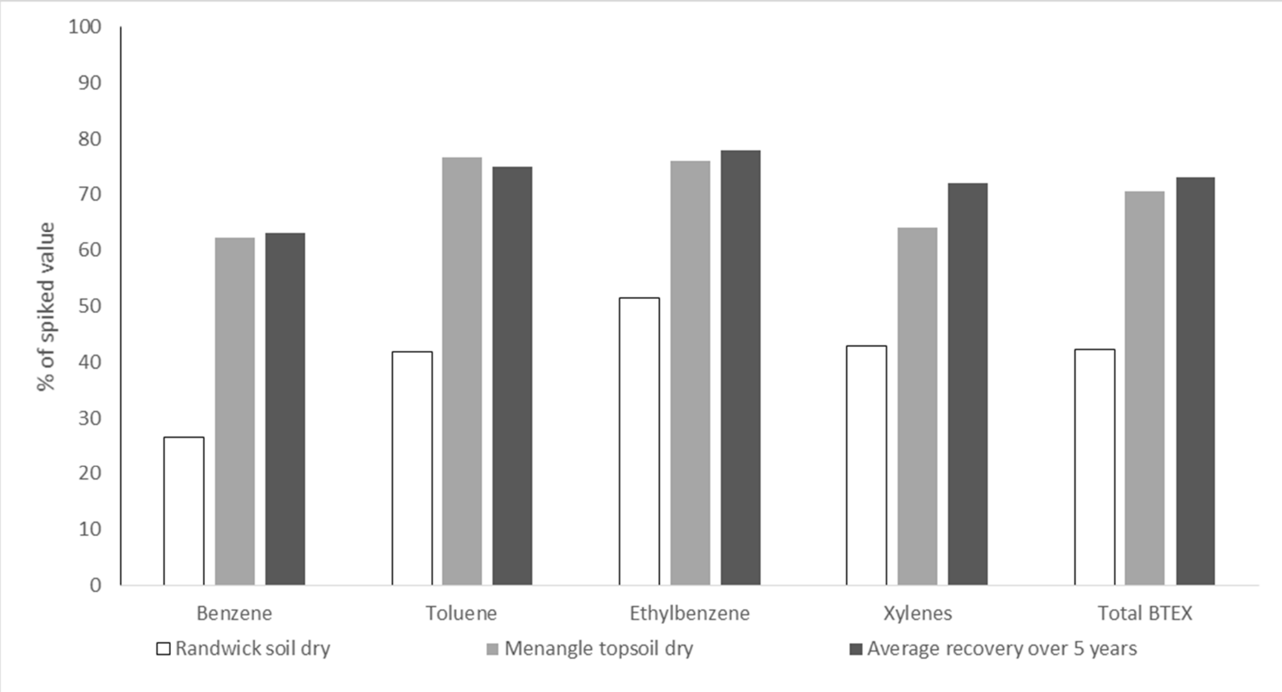


Figure 28 BTEX % spike recovery in dry Randwick sandy soil and Menangle topsoil vs the average recovery from PT studies in the last 5 years

PAHs in Sample S3/S4

Eleven participants used dichloromethane (DCM)/acetone in a 1:1 ratio, two used hexane/acetone (1:1) and two used DCM only. To facilitate extraction some participants used tumbling (3), sonication (3), ASE (1), mechanical shaking (1) and tumbling/sonication (1). Seven participants did not specify the extraction technique used.

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

Results vs extraction solvent and extraction technique were plotted. No trends were evident (Figures 29 to 35).

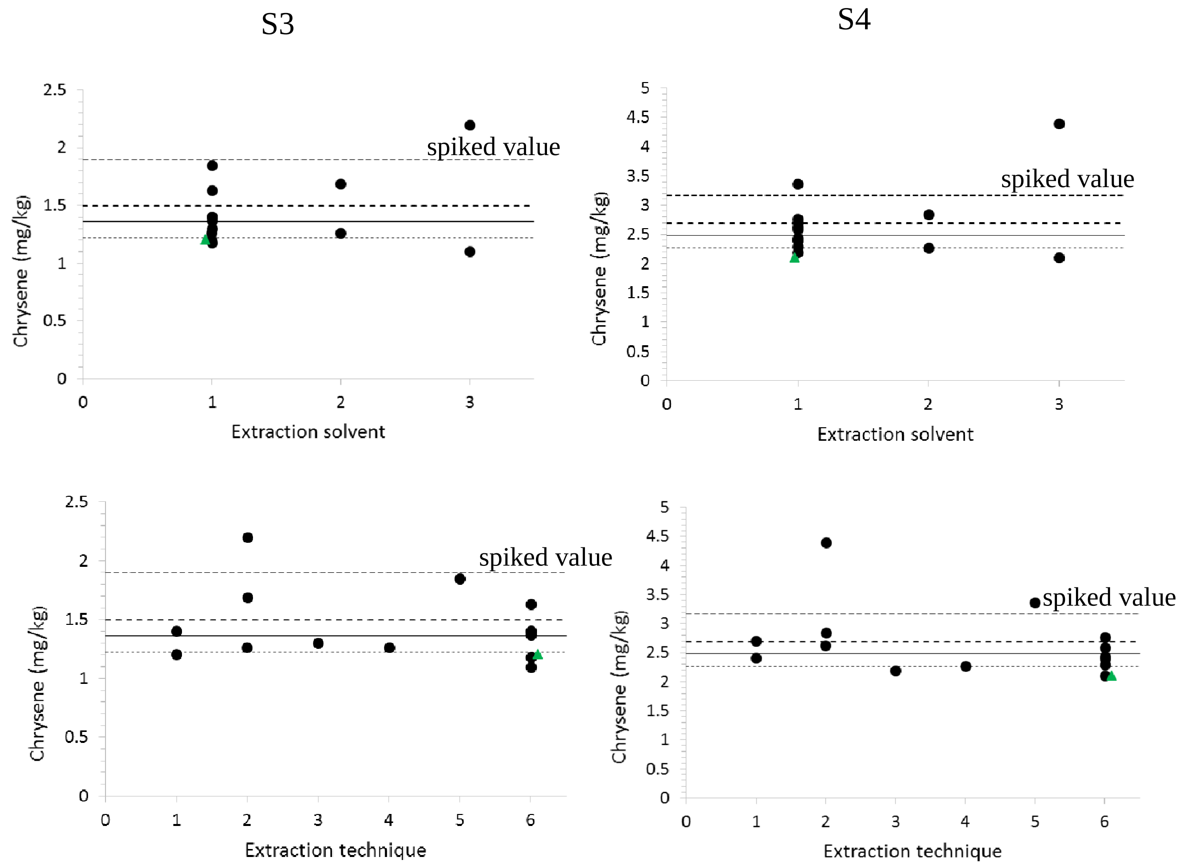


Figure 29 PAH results vs extraction solvent/technique (Chrysene)
Extraction Solvent: 1 = DCM/Acetone 2 = Hexane/Acetone 3 = DCM
Extraction Technique: 1 = tumbling 2 = sonication 3 = ASE 4 = mechanical shaking 5 = tumbling/sonication 6 = other/unspecified
black circle = GC-MS(MS); green triangle = GC-FID;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed).

S3 S4

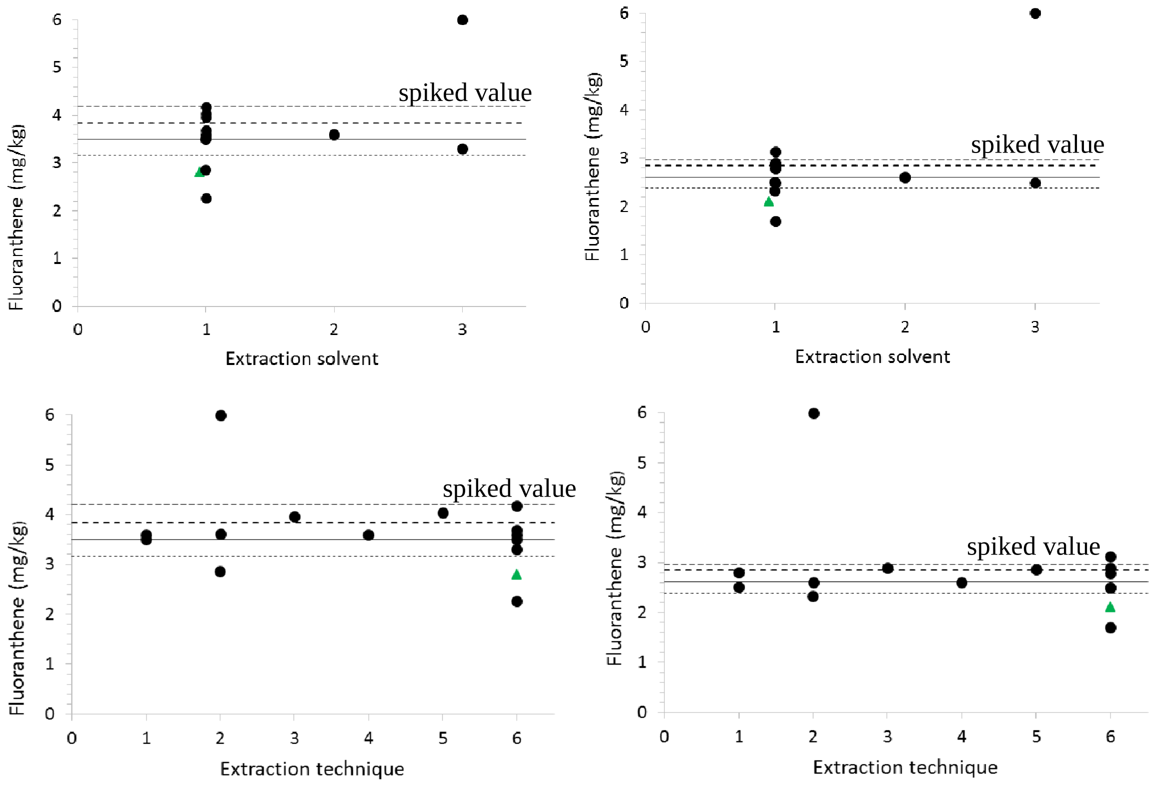


Figure 30 PAH results vs extraction solvent/technique (Fluoranthene)
Extraction Solvent: 1 = DCM/Acetone 2 = Hexane/Acetone 3 = DCM
Extraction Technique: 1 = tumbling 2 = sonication 3 = ASE 4 = mechanical shaking 5 = tumbling/sonication 6 = other/unspecified
black circle = GC-MS(MS); green triangle = GC-FID;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Results > 6 in Sample S4 have been plotted as 6

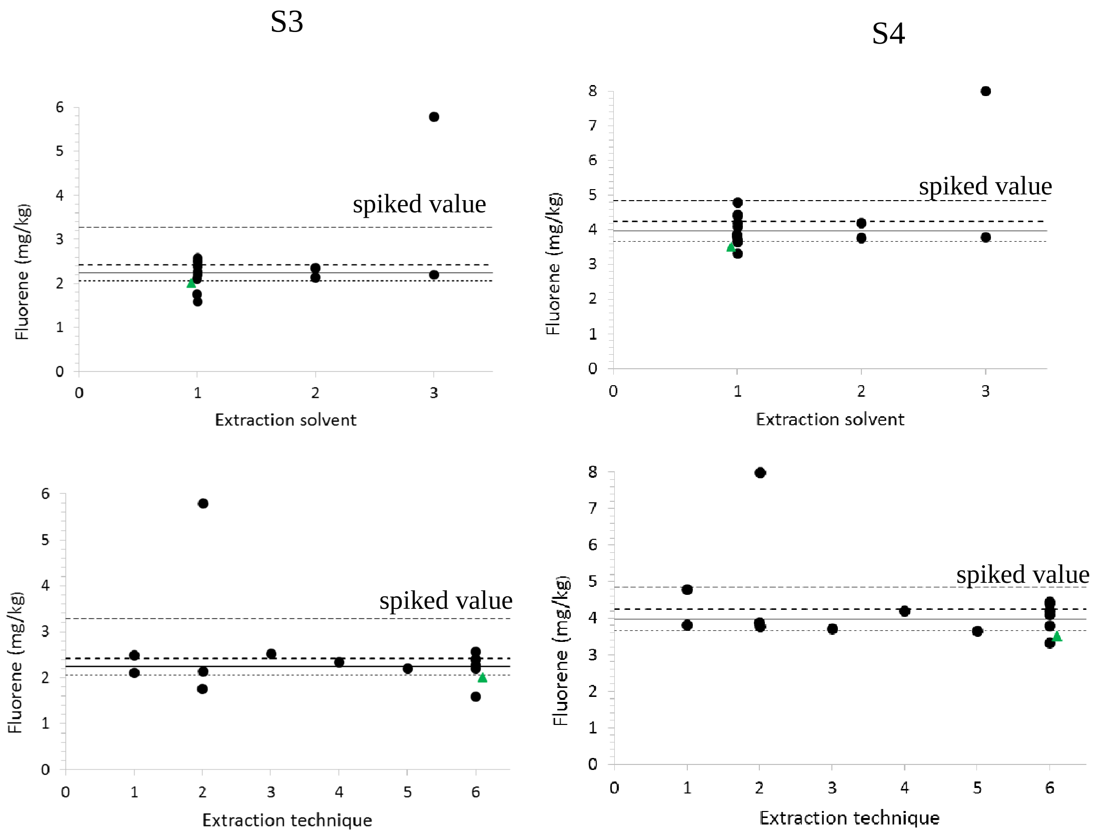


Figure 31 PAH results vs extraction solvent/technique (Fluorene)
Extraction Solvent: 1 = DCM/Acetone 2 = Hexane/Acetone 3 = DCM
Extraction Technique: 1 = tumbling 2 = sonication 3 = ASE 4 = mechanical shaking 5 = tumbling/sonication 6 = other/unspecified
black circle = GC-MS(MS); green triangle = GC-FID;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Results > 8 in Sample S4 have been plotted as 8

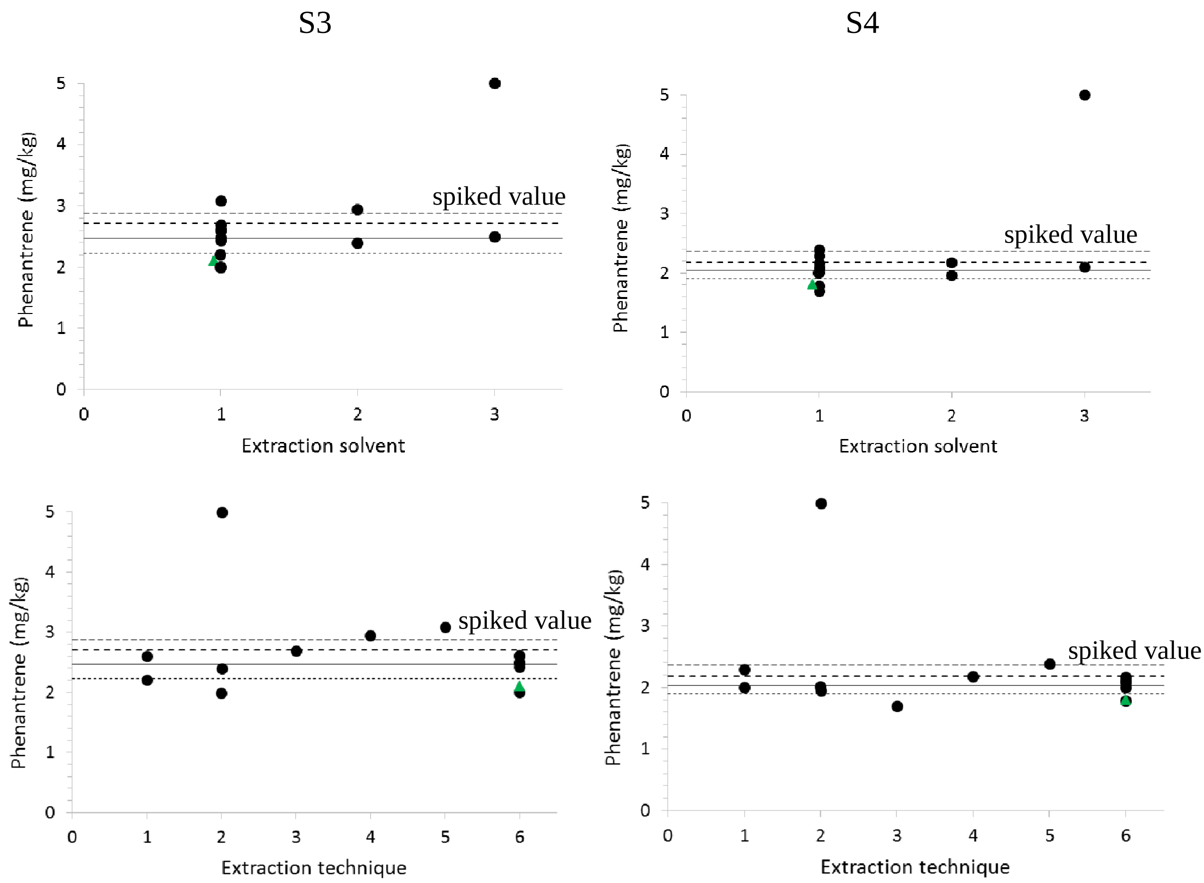


Figure 32 PAH results vs extraction solvent/technique (Phenanthrene)
Extraction Solvent: 1 = DCM/Acetone 2 = Hexane/Acetone 3 = DCM
Extraction Technique: 1 = tumbling 2 = sonication 3 = ASE 4 = mechanical shaking 5 = tumbling/sonication 6 = other/unspecified
black circle = GC-MS(MS); green triangle = GC-FID;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed). Results > 5 in Sample S4 have been plotted as 5

S4

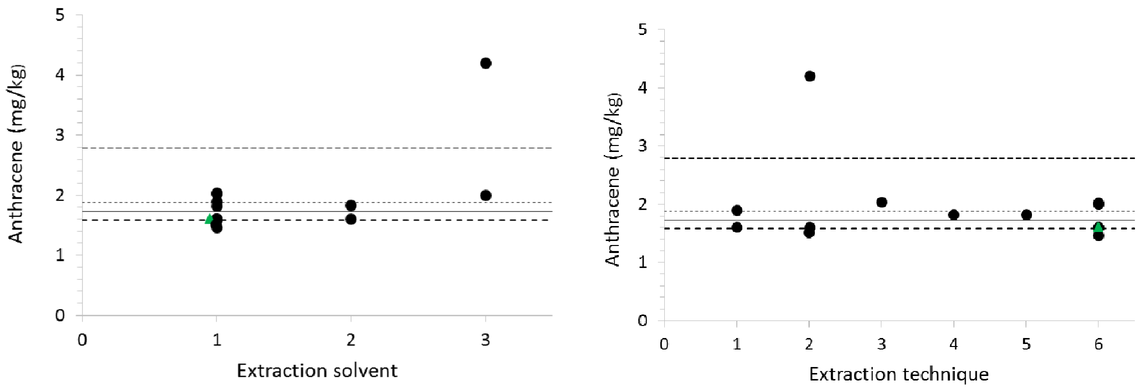


Figure 33 PAH results vs extraction solvent/technique (Anthracene)
Extraction Solvent: 1 = DCM/Acetone 2 = Hexane/Acetone 3 = DCM
Extraction Technique: 1 = tumbling 2 = sonication 3 = ASE 4 = mechanical shaking 5 = tumbling/sonication 6 = other/unspecified
black circle = GC-MS(MS); green triangle = GC-FID;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed).

S4

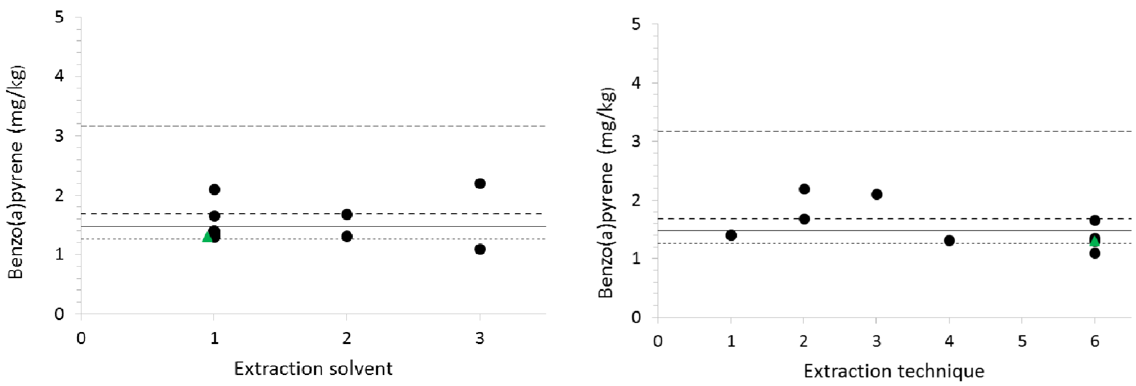


Figure 34 PAH results vs extraction solvent/technique (Benzo(a)pyrene)
Extraction Solvent: 1 = DCM/Acetone 2 = Hexane/Acetone 3 = DCM
Extraction Technique: 1 = tumbling 2 = sonication 3 = ASE 4 = mechanical shaking 5 = tumbling/sonication 6 = other/unspecified
black circle = GC-MS(MS); green triangle = GC-FID;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed).

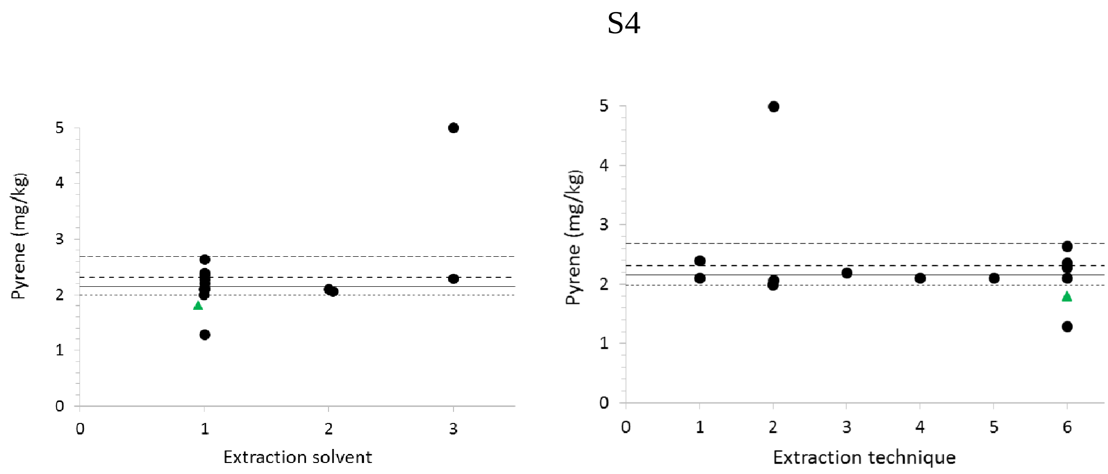


Figure 35 PAH results vs extraction solvent/technique (Pyrene)
Extraction Solvent: 1 = DCM/Acetone 2 = Hexane/Acetone 3 = DCM
Extraction Technique: 1 = tumbling 2 = sonication 3 = ASE 4 = mechanical shaking 5 = tumbling/sonication 6 = other/unspecified
black circle = GC-MS(MS); green triangle = GC-FID;
Horizontal lines are the assigned value (solid) and the upper and lower 95% confidence interval of the assigned value (small-dashed).

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

6.6 False negatives PAHs in Sample S4

When a laboratory reported a ‘<’ result and the assigned value was significantly higher than the < figure, the result was considered to be false negative. Laboratories 9, 11 and 15 reported benzo(a)pyrene as <0.01, <0.1 and <0.5 µg/L respectively, while the assigned value was 1.47 µg/L.

6.7 Reporting of PAHs Not Spiked Into Sample S3

One laboratory reported PAHs that were not spiked into the test samples. These are listed in Table 29. This laboratory should also revised its procedure for estimating the uncertainty of their measurement results. The reported uncertainty was with less significant figures than the measurement result. The recommended format to report uncertainty is presented in Section 6.2. The uncertainty of anthracene was reported as 0.00 which is not possible as all measurement results have a degree of uncertainty. As a simple rule of thumb, when the uncertainty estimate is smaller than 15% of the reported value or larger than 50% of the reported value then this should be reviewed as suspect.

Table 29 False Positives

Lab code	Analyte	Concentration (mg/kg)	Uncertainty (mg/kg)
7	Anthracene	0.015	0.00
7	Pyrene	0.0225	0.01

6.8 Accreditation

Laboratories **12** and **17** were not accredited. All other laboratories were accredited to ISO 17025.

6.9 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.

Four laboratories **2**, **9**, **12** and **17** 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
- N-alkanes

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*'[10]

6.10 Comparison with Previous Studies

Overall percentages of z-scores obtained by laboratories since 2009 for both TRH and BTEX are presented in Figures 36 and 37. 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 84% for TRH and 77% 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 for TRH.

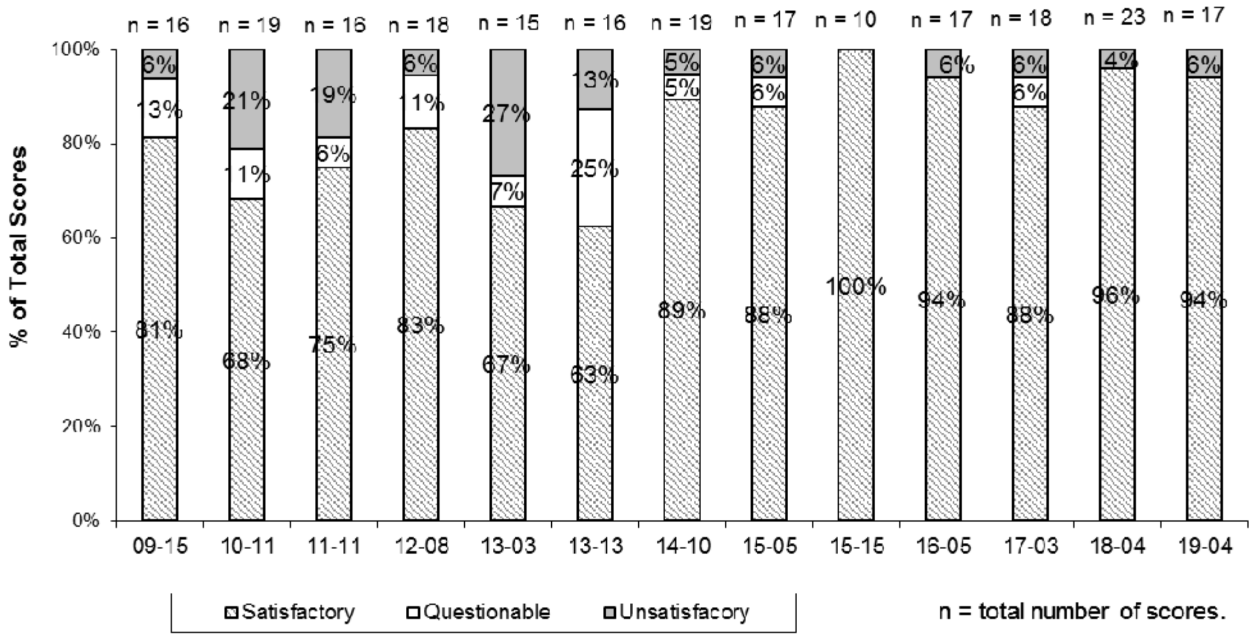


Figure 36 z-Scores for TRH (TPH before AQA 12-08) in NMI PTs of hydrocarbons in soil

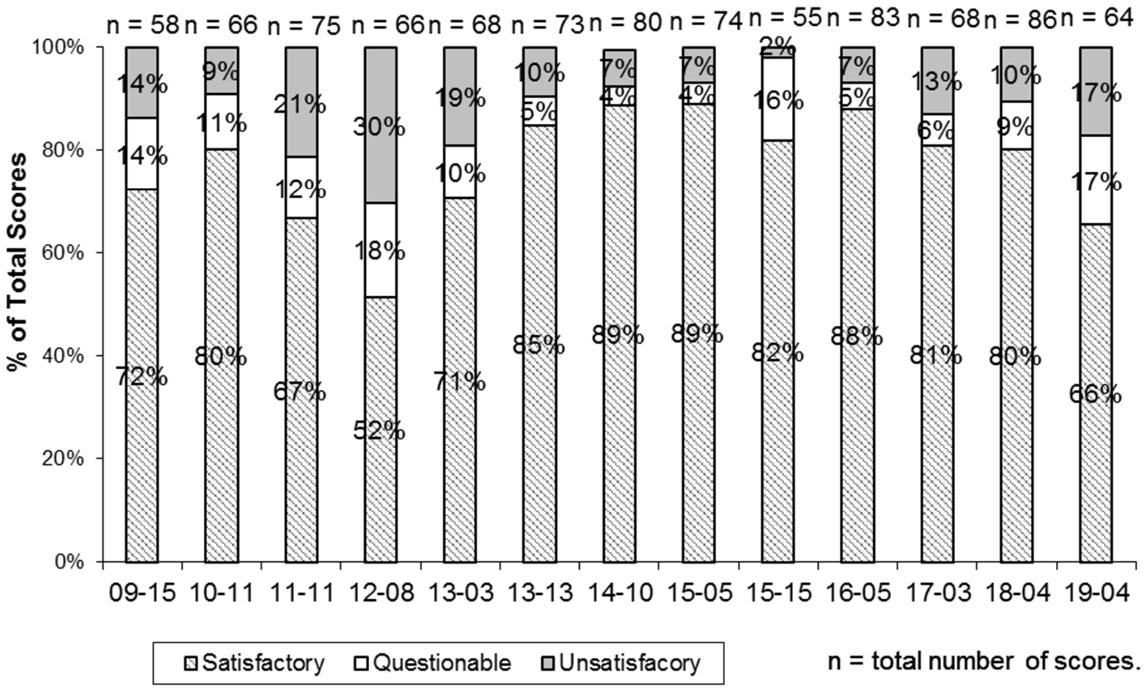


Figure 37 z-Scores for Total BTEX in NMI PTs of hydrocarbons in soil

7 REFERENCES

[1] NMI 2016, *Chemical Proficiency Testing Study Protocol*, viewed 3 May 2019, <http://www.measurement.gov.au>.

[2] NMI 2016, *Chemical Proficiency Testing Statistical Manual*, viewed 3 May 2019, <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] Worrall, R.D.,1996, 'Total Petroleum Hydrocarbons in Soil: Storage Stability Study', ACSL Public Interest Project, AGAL.

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

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

[9] Eurachem 2012, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed 10 May 2019, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

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

[11] National Measurement Institute, Method NGCMS_1112 – Determination of Semivolatile Total Recoverable Hydrocarbons in Soil and Water using GC-FID, 2014.

[12] Thompson, M. and Fearn, T. 2001. 'A new test for sufficient homogeneity', *Analyst*, vol. 126, pp 1414-1417.

APPENDIX 1 – SAMPLE PREPARATION AND HOMOGENEITY TESTING

A1.1 Diesel Fuel Preparation

Diesel fuel was purchased from a local retail outlet and treated to remove volatiles. Approximately 500 mL of diesel fuel was placed in a heated (80°C) open container and sparged with nitrogen. Treatment continued until the GC-FID chromatogram indicated that essentially all the hydrocarbons eluting before C_{10} had been removed. This same treated-diesel fuel was used in previous NMI Hydrocarbon PTs.

A1.2 Test Sample Preparation

Two soils were used in this study:

- Top-soil from Randwick, NSW, from a suburban garden for Samples S1 and S2.
- Uncontaminated soil described as Menangle topsoil bought from a Sydney supplier for Samples S3 and S4.

Soil was dried separately at 120ºC for two hours. The dried soil was sieved and the fraction between 355 – 850 µm was retained to prepare the samples.

Sample S1: 2207 g of Randwick soil was moistened with dichloromethane (DCM) and spiked with a 5.215 g of treated diesel fuel and 6.65 mL of commercially purchased hydraulic oil. The soil 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: 3004.2 g of dried, sieved Randwick soil 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, 11.42 g of un-leaded petrol and 4.02 g of sparged diesel were added to the soil. The drum was sealed and vigorously shaken. The sealed drum was then packed into another large drum and surrounded by cold gel-packs. The drums were then tumbled for 60 minutes on a hoop mixer. The soil was scooped into glass jars, tapped, topped up to minimise the vapour space and sealed. The process of filling the jars was conducted 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: Menangle topsoil (S3 1002.9 g, S4 1706.1 g) 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 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 unspiked soil (S3 1201.9 g, S4 1302.1 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 Sample S1 TRH

Seven bottles were selected at random from Sample S1. Duplicate test portions were taken from each bottle and TRH measured at the NMI North Ryde laboratory. Homogeneity testing was based on that described by Thomson and Fearn,[12] which is also the procedure described in the International Protocol.[4]

Measurements were made under repeatability conditions in random using NMI Method NGCMS_1112.[12] The analysis involved extraction by tumbling with 1:1 acetone/DCM and measurement by GC-FID. NMI holds third party (NATA) accreditation to ISO 17025 for these tests. Results of the homogeneity testing are presented in Table 30. The mean of the 14 measurements were used as the NMI homogeneity value. All samples were found to be sufficiently homogeneous for use in this PT study

Table 30 Sample S1, TRH homogeneity testing results

Bottle Fill Number	Chrysene mg/kg	
	Replicate 1	Replicate 2
3	2916	3088
15	2535	2916
19	2798	3372
21	3674	3619
24	3348	3266
35	3648	3645
39	3347	3282
Mean	3247	
CV	11%	

Thompson and Fearn[11] Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.64	0.73	**Pass**
S_{an}/σ	0.40	0.5	**Pass**
s^2_{sam}	95757	97837	**Pass**

No homogeneity testing was conducted on Samples S2, S3 and S4. The process used to prepare these PT 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 results from participants gave no reason to question the homogeneity of the samples.

APPENDIX 2 – 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'[7] 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 31.

Table 31 Uncertainty of robust average for fluoranthene in Sample S4

No. results (p)	15
Robust Average	2.653 mg/kg
$S_{rob\ av}$	0.3787 mg/kg
$u_{rob\ av}$	0.1222 mg/kg
K	2
$U_{rob\ av}$	0.244 mg/kg

The robust average for Fluoranthene in Sample S4 is 2.65 ± 0.24 mg/kg.

APPENDIX 3 – 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