Australian Government
Department of Industry, Science and Resources

National Measurement Institute

# Proficiency Test Final Report
# AQA 22-05
# Hydrocarbons in Soil

July 2022

## ACKNOWLEDGMENTS

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

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

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

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## SUMMARY

AQA 22-05 Hydrocarbons in Soil commenced in March 2022. Twenty-three laboratories enrolled to participate, and all participants submitted results.

Four test samples were prepared at the NMI laboratory in Sydney using topsoil bought from a commercial supplier. Participants were asked to report Total Recoverable Hydrocarbons (TRH) in Sample S1, benzene, toluene, ethylbenzene and xylenes (BTEX) and volatile hydrocarbons (C6 to C10) in Sample S2, and polycyclic aromatic hydrocarbons (PAHs) in Samples S3 and S4. The assigned values were the robust averages of participants' results for all scored analytes. The associated uncertainties were estimated from the robust standard deviation of participants' results.

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

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

- *Compare the performances of participants and assess their accuracy in the identification and measurement of hydrocarbon pollutants in soil.*

Laboratories **2**, **7**, **9**, **11**, **19**, **20** and **23** reported results for all scored analytes.

Six participants did not report results for analytes that they tested for and were present in the test samples (total of 6 results). One participant reported a result for an analyte that was not spiked into the test samples.

Of 402 *z* scores, 377 (94%) returned $|z| \le 2.0$, indicating a satisfactory performance.

Of 402 $E_n$ scores, 345 (86%) returned $|E_n| \le 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratory **19** returned satisfactory *z* scores and $E_n$ scores for all scored analytes.

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

For TRH, participants reported a variety of extraction techniques and solvents, though all used GC-FID for analysis. For BTEX, participants reported using a variety of extraction techniques, followed by headspace GC-FID or GC-MS(/MS), or purge and trap GC-MS(/MS) for analysis. For PAHs, all participants performed solid-liquid extraction with various extraction solvents, and then used GC-MS(/MS) for analysis.

- *Develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates.*

Of 437 numeric results, 403 results (92%) were reported with an associated expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 3.8% to 100% of the reported result.

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

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

# 1 INTRODUCTION

## 1.1 NMI Proficiency Testing Program

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

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

- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- inorganic analytes in soil, water, filters, food and pharmaceuticals;
- per- and polyfluoroalkyl substances in soil, water, biota and food;
- controlled drug assay, drugs in wipes, and clandestine laboratory; and
- allergens in food

## 1.2 Study Aims

The aims of the study were to:

- compare the performances of participants and assess their accuracy in the identification and measurement of hydrocarbon pollutants in soil;
- evaluate participants' methods for the measurement of hydrocarbon pollutants in soil;
- develop the practical application of traceability and measurement uncertainty, and provide participants with information that will be useful in assessing their uncertainty estimates; and
- produce materials that can be used in method validation and as control samples.

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

## 1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO/IEC 17043:2010 and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[1,4]

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

## 2 STUDY INFORMATION

### 2.1 Selection of Hydrocarbons

The hydrocarbons in this study, and their spiked levels, were typical of those encountered by environmental testing laboratories. Investigation levels for the hydrocarbons studied are set out in the National Environmental Protection (Assessment of Site Contamination) Measure (NEPM) Schedule B1 *Guideline on Investigation Levels for Soil and Groundwater*.[5]

Sample S1 assessed total recoverable hydrocarbons (TRH), Sample S2 assessed volatile hydrocarbons, and benzene, toluene, ethylbenzene and xylenes (BTEX), and Samples S3 and S4 assessed polycyclic aromatic hydrocarbons (PAHs). A list of potential PAHs for Samples S3 and S4 is presented in Table 1.

Table 1 List of Possible PAHs for Samples S3 and S4

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

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

Table 2 Spiked Values of Samples

| Sample | Analyte | Spiked Value (mg/kg) | Uncertainty (mg/kg)* |
|---|---|---|---|
| S1 | >C10-C16 | 1110 | 60 |
| | >C16-C34 | 1570 | 80 |
| | >C34-C40 | 174 | 9 |
| | TRH | 2860 | 140 |
| S2 | Benzene | 82.1 | 4.1 |
| | Toluene | 393 | 20 |
| | Ethylbenzene | 45.0 | 2.2 |
| | Xylenes | 337 | 17 |
| | Total BTEX | 858 | 43 |
| S3 | Anthracene | 1.29 | 0.06 |
| | Benzo[*a*]pyrene | 1.98 | 0.10 |
| | Chrysene | 0.699 | 0.035 |
| | Fluoranthene | 0.895 | 0.045 |
| | Fluorene | 2.18 | 0.11 |
| | Phenanthrene | 2.70 | 0.14 |
| | Pyrene | 1.29 | 0.06 |

| Sample | Analyte | Spiked Value (mg/kg) | Uncertainty (mg/kg)* |
|---|---|---|---|
| S4 | Anthracene | 1.60 | 0.08 |
| | Chrysene | 1.49 | 0.07 |
| | Fluoranthene | 2.19 | 0.11 |
| | Fluorene | 0.795 | 0.040 |
| | Phenanthrene | 1.30 | 0.07 |
| | Pyrene | 0.400 | 0.020 |

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

### 2.2 Study Timetable

The timetable of the study was:

| | |
|---|---|
| Invitation sent | 18/03/2022 |
| Samples dispatched | 19/04/2022 |
| Results due | 3/06/2022 |
| Interim report sent | 8/06/2022 |

### 2.3 Participation and Laboratory Code

Twenty-three laboratories enrolled to participate, and all participants were assigned a confidential laboratory code number for this study. All participants submitted results.

### 2.4 Sample Preparation

Soil purchased from a Sydney supplier was used as the starting material for all samples.

**Sample S1 (TRH)** was prepared by spiking the soil with treated diesel fuel and commercially purchased hydraulic oil.

**Sample S2 (BTEX)** was prepared by spiking the soil with unleaded petrol, treated diesel fuel and benzene.

**Samples S3 and S4 (PAHs)** was prepared by spiking the soil with varying amounts of anthracene, benzo[*a*]pyrene, chrysene, fluoranthene, fluorene, phenanthrene and/or pyrene.

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

### 2.5 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this PT study. The samples were prepared, packaged and stored using a process that has been demonstrated to produce homogeneous and stable samples in previous NMI Hydrocarbons in Soil PT studies. The storage stability of petroleum hydrocarbons in soil has also been previously established.[6]

Participants' results did not give reason to question the homogeneity or transport stability of the samples (Appendix 2). To further assess possible instability, participants' results were compared to the spiked values (Section 6.1). For TRH, assigned values were within 97% to 105% of the spiked value, providing good support for its stability. Assigned values for scored BTEX and PAHs were within the ranges of 60% to 86% and 51% to 88% of the spiked values respectively, which is similar to ratios observed in previous NMI Hydrocarbons in PT studies, and an assigned value was set if there was a reasonable consensus of participants' results.

## 2.6 Sample Storage, Dispatch and Receipt

Prior to dispatch, Samples S1, S3 and S4 were stored in a refrigerator at approximately 4 °C, and Sample S2 was stored in a freezer at approximately -20 °C. The samples were packaged in insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 19 April 2022.

The following items were also sent to participants:

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

An Excel spreadsheet for the electronic reporting of results was emailed to participants.

## 2.7 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- Do not test for volatile hydrocarbons (C6-C10) or BTEX components in Sample S1.
- Participants need not test for all listed analytes.
- Report results on as received basis in units of mg/kg for the following:
  - Sample S1: Semi-volatile hydrocarbons (>C10-C40) and TRH. Use your laboratory's chosen quantitation range, and indicate what this range is. Australian NEPM fractions >C10-C16, >C16-C34 and >C34-C40 are encouraged. The concentration range is between 1000 – 20000 mg/kg.
  - Sample S2: Volatile Hydrocarbons (C6-C10), Benzene, Toluene, Ethylbenzene, Xylenes and Total BTEX. Individual BTEX components concentration is between 50 – 5000 mg/kg.
  - Samples S3 and S4: PAHs from the list below. The concentration range is between 0.05 – 50 mg/kg.

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

- Report results as you would report to a client. This figure will be used in all statistical analysis in the study report.
- For each analyte, report the associated expanded uncertainty (e.g. 2000 ± 200 mg/kg).
- Report any listed analyte not tested as NT as the result.
- No limit of reporting has been set for this study. Report results as you would report them to a client, applying the limit of reporting of the method used for analysis.
- Report the basis of your uncertainty estimates as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).

- Complete the method details as requested in the results sheet.
- Return the completed results sheet by email (proficiency@measurement.gov.au).
- Please return the completed result sheet by 16 May 2022.

The results due date was extended to 3 June 2022 due to sample delivery delays to some international participants.

### 2.8 Interim Report

An interim report was emailed to all participants on 8 June 2022.

# 3 PARTICIPANT LABORATORY INFORMATION

## 3.1 Test Methods Reported by Participants

Participants were requested to provide information about their test methods. Responses received are presented in Appendix 3.

## 3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about their basis of measurement uncertainty (MU). Responses received are presented in Table 3. Some responses may be modified so that the participant cannot be identified.

Table 3 Basis of Expanded Uncertainty Estimate

| Lab. Code | Analyte | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|---|
| | | | Precision | Method Bias | |
| 1 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - CRM<br>Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Recoveries of SS | NATA General Accreditation Guidance Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 2 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | NATA General Accreditation Guidance Estimating and Reporting Measurement Uncertainty of Chemical Test Results |
| 3 | TRH | Top Down - precision and estimates of the method and laboratory bias | Control samples – SS<br>Duplicate analysis | Recoveries of SS | Eurachem/CITAC Guide |
| | BTEX/ PAHs | Top Down - precision and estimates of the method and laboratory bias | Control samples – SS<br>Duplicate analysis | CRM<br>Recoveries of SS | Eurachem/CITAC Guide |
| 4 | TRH/ BTEX | Standard uncertainty based on historical data | Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Standard purity | Eurachem/CITAC Guide |
| 5 | All | | Control samples<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | |
| 6 | All | Top Down - precision and estimates of the method and laboratory bias | Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration<br>Recoveries of SS | |

| Lab. Code | Analyte | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|---|
| | | | Precision | Method Bias | |
| 8 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - RM<br>Duplicate analysis<br>Instrument calibration | Laboratory bias from PT studies<br>CRM<br>Instrument calibration | Eurachem/CITAC Guide |
| 9 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS | Eurachem/CITAC Guide |
| 10 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | ISO/GUM |
| 11 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - RM<br>Duplicate analysis | Recoveries of SS | ISO/GUM |
| 12 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |
| 13 | All | | Control samples - SS<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | |
| 14 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | ISO/GUM |
| 15 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | | ISO/GUM |
| 16 | All | Standard deviation of replicate analyses multiplied by 2 or 3 | Duplicate analysis | | ISO/GUM |
| 17 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - CRM<br>Duplicate analysis<br>Instrument calibration | CRM<br>Instrument calibration | Eurachem/CITAC Guide |
| 18 | All | Top Down - precision and estimates of the method and laboratory bias | Duplicate analysis | Recoveries of SS | NMI Uncertainty Course |
| 19 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | NATA Technical Note 33 |

| Lab. Code | Analyte | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|---|
| | | | Precision | Method Bias | |
| 20 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | NATA Technical Note 33 |
| 22 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |
| 23 | All | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS | Recoveries of SS | NATA Technical Note 33 |

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

### 3.3 Participants’ Comments

Participants were invited to comment on the samples, this study, or future studies. Such feedback may be useful in improving future studies. Participants’ comments are presented in Table 4. Some comments may be modified so that the participant cannot be identified.

Table 4 Participants’ Comments

| Lab. Code | Sample | Participant's Comments |
|---|---|---|
| 3 | S3 and S4 | The laboratory reports Benzo(b&j)fluoranthene |
| 8 | All | Uncertainty: Laboratory Macro MU Calculation Pack based on QC Data |
| 12 | S2 | The BTEX concentration in Sample S2 was outside the working range of our method |

## 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 4.1 Results Summary

Participant results are listed in Tables 5 to 28 with summary statistics: robust average, median, mean, numeric results (N), maximum (Max.), minimum (Min.), robust standard deviation (robust SD) and robust coefficient of variation (robust CV). Bar charts of results and performance scores are presented in Figures 2 to 24. An example chart with interpretation guide is shown in Figure 1.

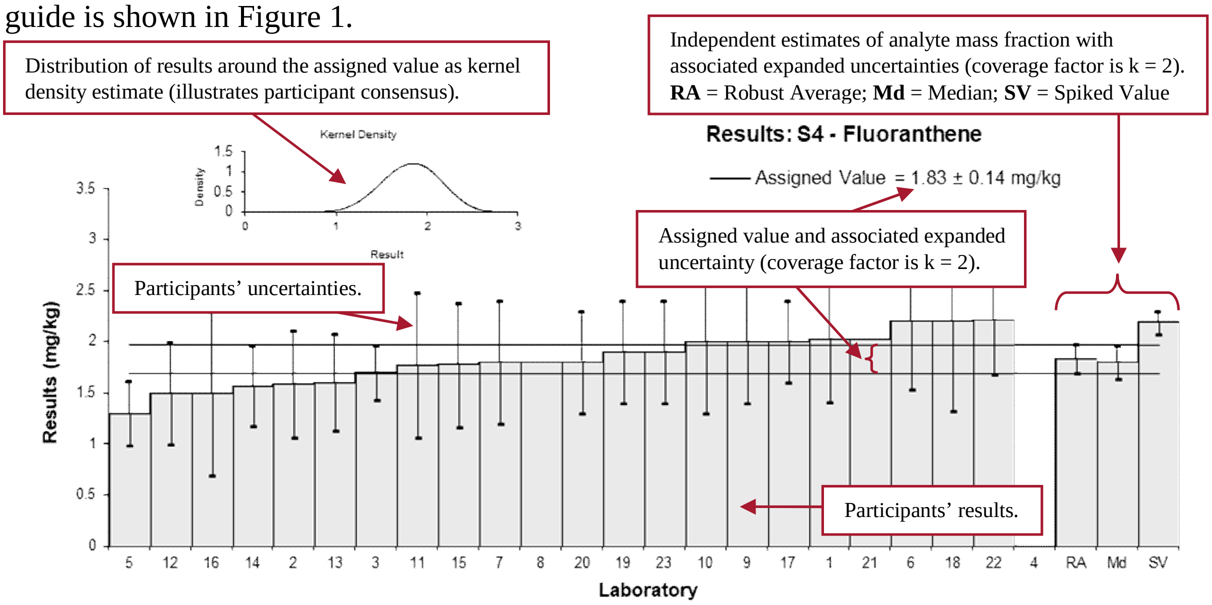


Figure 1 Guide to Presentation of Results

### 4.2 Outliers and Gross Errors

Outliers were any result less than 50% and greater than 150% of the robust average, and these were removed before the calculation of the assigned value.[3,4] Gross errors were any obvious blunders, e.g. results with incorrect units, or for a different analyte or sample, and such results were removed before the calculation of all summary statistics.[3]

### 4.3 Assigned Value

The assigned value is defined as the 'value attributed to a particular property of a proficiency test item'.[1] In this PT study, the property is the mass fraction of the analytes in the samples. Assigned values were the robust averages of participants' results, and the expanded uncertainties were estimated from the associated robust SDs (Appendix 4).

### 4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

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

### 4.5 Performance Coefficient of Variation

The performance coefficient of variation (PCV) is a fixed measure of the between-laboratory variation that in the judgement of the study coordinator would be expected from participants, given the levels of analytes present. The PCV is not the CV of participants' results; it is set by the study coordinator and is based on the mass fraction of the analytes and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[8] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performance and can be compared from study to study.

### 4.6 Target Standard Deviation

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

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

### 4.7 *z* Score

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

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

where:

$z$ is *z* score

$\chi$ is a participant's result

$X$ is the assigned value

$\sigma$ is the target standard deviation from Equation 1

To account for potential low bias in consensus value due to inefficient methodologies, scores may be adjusted for a 'maximum acceptable result' (see also Section 6.3).

For the absolute value of a *z* score:

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

### 4.8 $E_n$ Score

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

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

where:

$E_n$ is $E_n$ score

$\chi$ is a participant's result

$X$ is the assigned value

$U_\chi$ is the expanded uncertainty of the participant's result

$U_X$ is the expanded uncertainty of the assigned value

For the absolute value of an $E_n$ score:

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

### 4.9 Traceability and Measurement Uncertainty

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

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

## 5 TABLES AND FIGURES

Table 5

**Sample Details**

| | |
|---|---|
| **Sample** | S1 |
| **Analyte** | >C10-C16 |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1069 | 321 | -0.07 | -0.03 |
| **2** | 840 | 240 | -1.48 | -0.92 |
| **3** | 1020 | 194.5 | -0.37 | -0.27 |
| **4**** | NR | NR | | |
| **5** | 1150 | 396 | 0.43 | 0.17 |
| **6**** | NR | NR | | |
| **7** | 1190 | 357 | 0.68 | 0.30 |
| **8** | 980 | 122.5 | -0.62 | -0.63 |
| **9** | 1183 | 350 | 0.64 | 0.28 |
| **10** | 943.69 | 283.12 | -0.84 | -0.45 |
| **11** | 1330 | 530 | 1.54 | 0.46 |
| **12** | 860 | 260 | -1.36 | -0.79 |
| **13** | 860 | 260 | -1.36 | -0.79 |
| **14** | 1200 | 320 | 0.74 | 0.36 |
| **15** | 1129 | 339 | 0.30 | 0.14 |
| **16** | NT | NT | | |
| **17** | 1240 | 188 | 0.99 | 0.75 |
| **18*** | 470 | 140 | -3.77 | -3.55 |
| **19** | 1000 | 300 | -0.49 | -0.25 |
| **20** | 950 | 300 | -0.80 | -0.41 |
| **21** | 1260 | NR | 1.11 | 1.80 |
| **22**** | NR | NR | | |
| **23** | 1200 | 300 | 0.74 | 0.38 |

* Outlier

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1080 | 100 |
| **Spiked Value** | 1110 | 60 |
| **Robust Average** | 1060 | 100 |
| **Median** | 1070 | 110 |
| **Mean** | 1050 | 90 |
| **N** | 19 | |
| **Max** | 1330 | |
| **Min** | 470 | |
| **Robust SD** | 180 | |
| **Robust CV (%)** | 17 | |

** Laboratories 4, 6 and 22 reported results for non-NEPM hydrocarbon ranges for Sample S1, which are presented in Table 8.

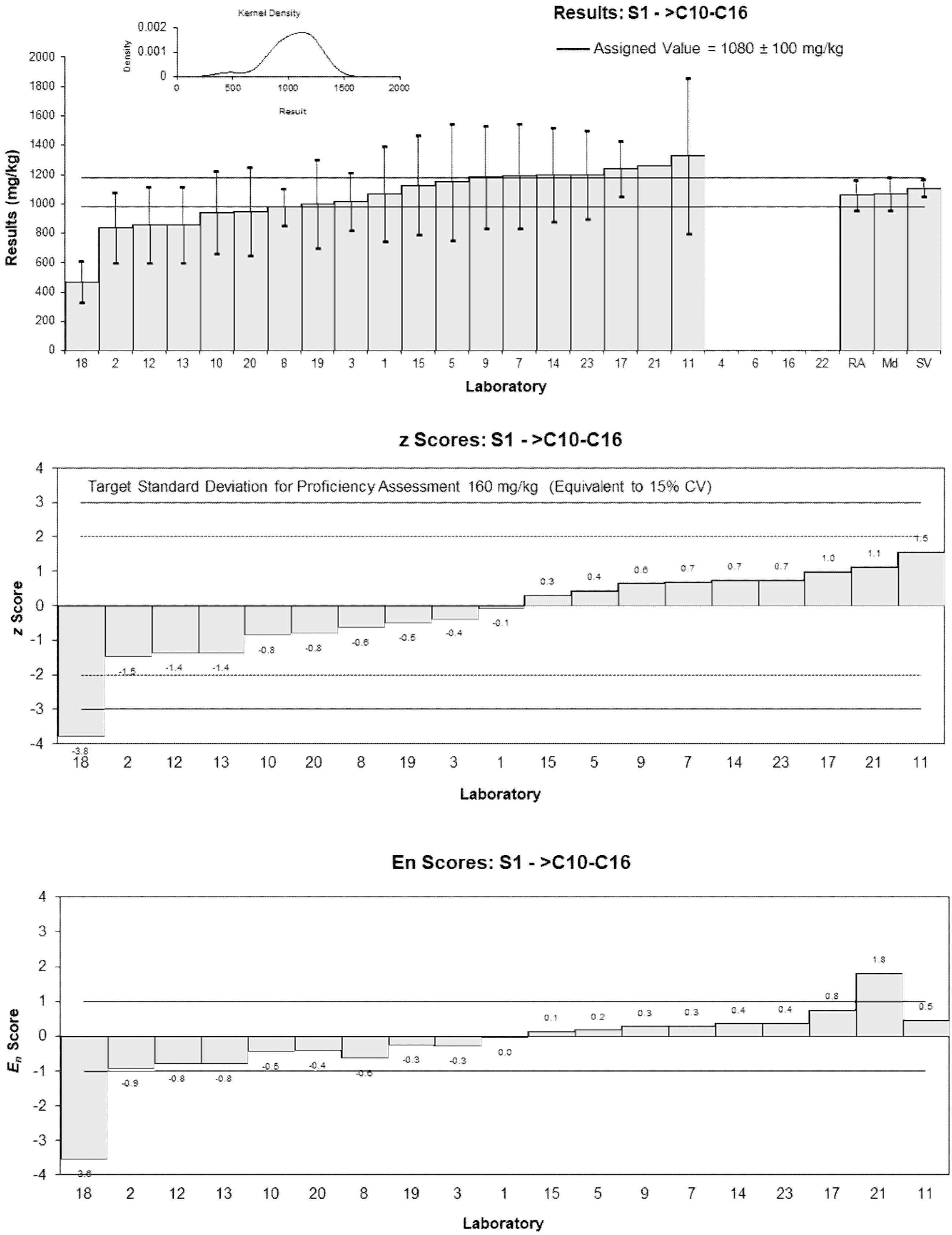
Results: S1 - >C10-C16
Assigned Value = 1080 ± 100 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
18 2 12 13 10 20 8 19 3 1 15 5 9 7 14 23 17 21 11 4 6 16 22 RA Md SV
z Scores: S1 - >C10-C16
Target Standard Deviation for Proficiency Assessment 160 mg/kg (Equivalent to 15% CV)
z Score
-3.8 -1.5 -1.4 -1.4 -0.8 -0.8 -0.6 -0.5 -0.4 -0.1 0.3 0.4 0.6 0.7 0.7 0.7 1.0 1.1 1.5
18 2 12 13 10 20 8 19 3 1 15 5 9 7 14 23 17 21 11
Laboratory
En Scores: S1 - >C10-C16
$E_n$ Score
-3.6 -0.9 -0.8 -0.8 -0.5 -0.4 -0.6 -0.3 -0.3 0.0 0.1 0.2 0.3 0.3 0.4 0.4 0.8 1.8 0.5
18 2 12 13 10 20 8 19 3 1 15 5 9 7 14 23 17 21 11
Laboratory

Figure 2

Table 6

**Sample Details**

| | |
|---|---|
| **Sample** | S1 |
| **Analyte** | >C16-C34 |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1537 | 461 | -0.22 | -0.11 |
| **2** | 1416 | 400 | -0.73 | -0.41 |
| **3** | 1490 | 291.2 | -0.42 | -0.31 |
| **4**** | NR | NR | | |
| **5** | 1660 | 673 | 0.29 | 0.10 |
| **6**** | NR | NR | | |
| **7** | 1488 | 446 | -0.43 | -0.22 |
| **8** | 1630 | 240.9 | 0.17 | 0.14 |
| **9** | 961 | 290 | -2.64 | -1.95 |
| **10** | 1498.1 | 449.4 | -0.39 | -0.20 |
| **11** | 1843 | 740 | 1.06 | 0.34 |
| **12** | 1400 | 400 | -0.80 | -0.45 |
| **13** | 1200 | 360 | -1.64 | -1.01 |
| **14** | 2040 | 540 | 1.89 | 0.81 |
| **15** | 1870 | 561 | 1.17 | 0.48 |
| **16** | NT | NT | | |
| **17** | 1620 | 272 | 0.13 | 0.10 |
| **18*** | 550 | 170 | -4.36 | -4.72 |
| **19** | 1600 | 400 | 0.04 | 0.02 |
| **20** | 1500 | 400 | -0.38 | -0.21 |
| **21** | 1850 | NR | 1.09 | 1.86 |
| **22**** | NR | NR | | |
| **23** | 1800 | 400 | 0.88 | 0.50 |

* Outlier

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1590 | 140 |
| **Spiked Value** | 1570 | 80 |
| **Robust Average** | 1560 | 160 |
| **Median** | 1540 | 100 |
| **Mean** | 1520 | 160 |
| **N** | 19 | |
| **Max** | 2040 | |
| **Min** | 550 | |
| **Robust SD** | 270 | |
| **Robust CV (%)** | 17 | |

** Laboratories 4, 6 and 22 reported results for non-NEPM hydrocarbon ranges for Sample S1, which are presented in Table 8.

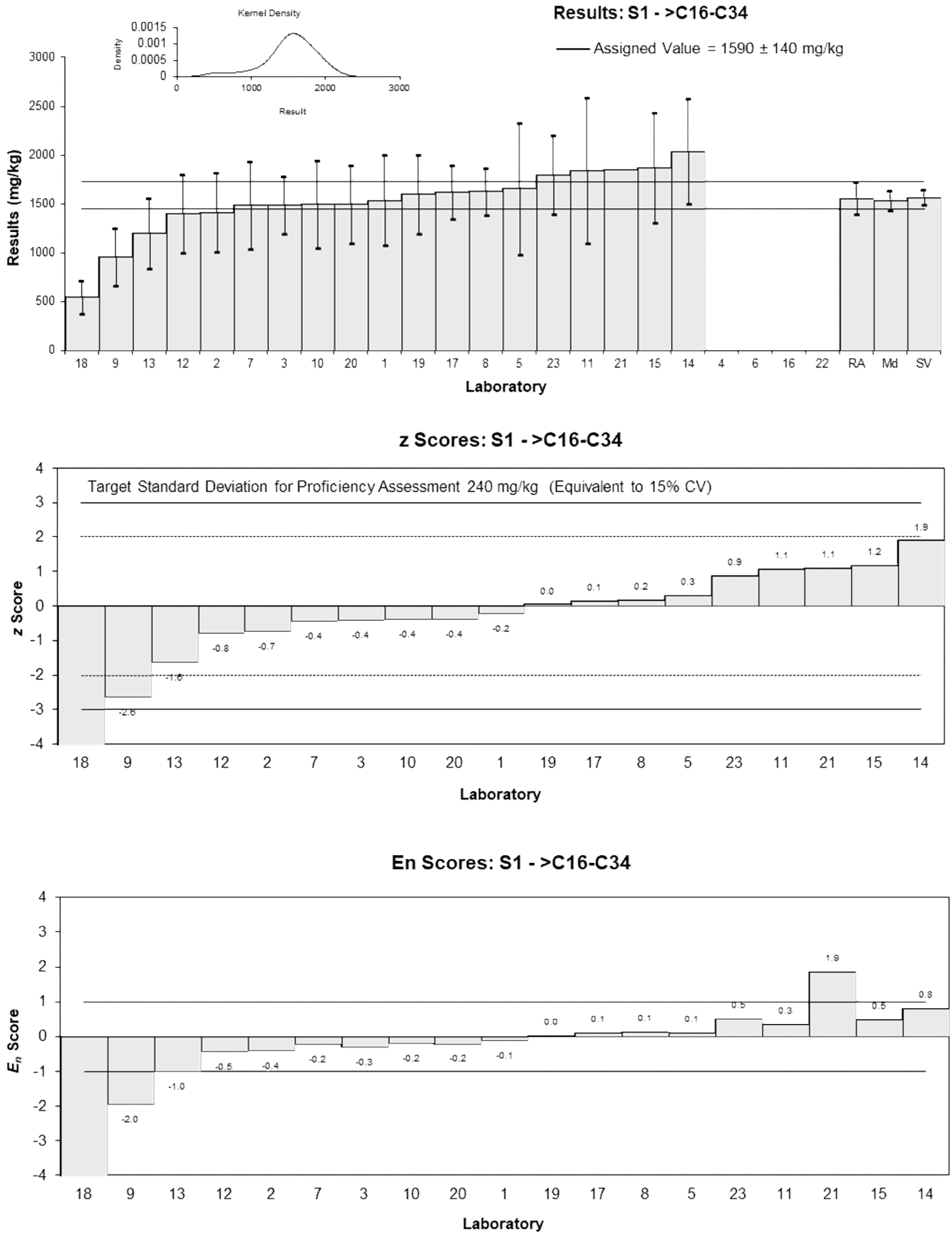
Results: S1 - >C16-C34
Assigned Value = 1590 ± 140 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
18 9 13 12 2 7 3 10 20 1 19 17 8 5 23 11 21 15 14 4 6 16 22 RA Md SV
z Scores: S1 - >C16-C34
Target Standard Deviation for Proficiency Assessment 240 mg/kg (Equivalent to 15% CV)
z Score
-2.6 -1.6 -0.8 -0.7 -0.4 -0.4 -0.4 -0.4 -0.2 0.0 0.1 0.2 0.3 0.9 1.1 1.1 1.2 1.9
Laboratory
18 9 13 12 2 7 3 10 20 1 19 17 8 5 23 11 21 15 14
En Scores: S1 - >C16-C34
$E_n$ Score
-2.0 -1.0 -0.5 -0.4 -0.2 -0.3 -0.2 -0.2 -0.1 0.0 0.1 0.1 0.1 0.5 0.3 1.9 0.5 0.8
Laboratory
18 9 13 12 2 7 3 10 20 1 19 17 8 5 23 11 21 15 14

Figure 3

Table 7

**Sample Details**

| | |
|---|---|
| **Sample** | S1 |
| **Analyte** | >C34-C40 |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 235 | 70 | 1.94 | 0.74 |
| **2** | 169 | 47 | -0.48 | -0.27 |
| **3** | 190 | 39.4 | 0.29 | 0.19 |
| **4**** | NR | NR | | |
| **5** | 170 | 107 | -0.44 | -0.11 |
| **6**** | NR | NR | | |
| **7** | 203 | 61 | 0.77 | 0.34 |
| **8** | 180 | 39.6 | -0.07 | -0.05 |
| **9*** | 72.8 | 21.8 | -4.00 | -4.21 |
| **10** | 159.55 | 47.865 | -0.82 | -0.45 |
| **11** | 169 | 68 | -0.48 | -0.19 |
| **12** | 160 | 50 | -0.81 | -0.42 |
| **13** | <100 | NR | | |
| **14** | 170 | 51 | -0.44 | -0.23 |
| **15** | 192 | 58 | 0.37 | 0.17 |
| **16** | NT | NT | | |
| **17** | 200 | 19 | 0.66 | 0.76 |
| **18*** | 70 | 20 | -4.10 | -4.59 |
| **19** | 200 | 100 | 0.66 | 0.18 |
| **20** | 100 | 100 | -3.00 | -0.81 |
| **21** | NR | NR | | |
| **22**** | NR | NR | | |
| **23** | 200 | 100 | 0.66 | 0.18 |

* Outlier

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 182 | 14 |
| **Spiked Value** | 174 | 9 |
| **Robust Average** | 174 | 21 |
| **Median** | 170 | 20 |
| **Mean** | 167 | 22 |
| **N** | 17 | |
| **Max** | 235 | |
| **Min** | 70 | |
| **Robust SD** | 34 | |
| **Robust CV (%)** | 20 | |

** Laboratories 4, 6 and 22 reported results for non-NEPM hydrocarbon ranges for Sample S1, which are presented in Table 8.

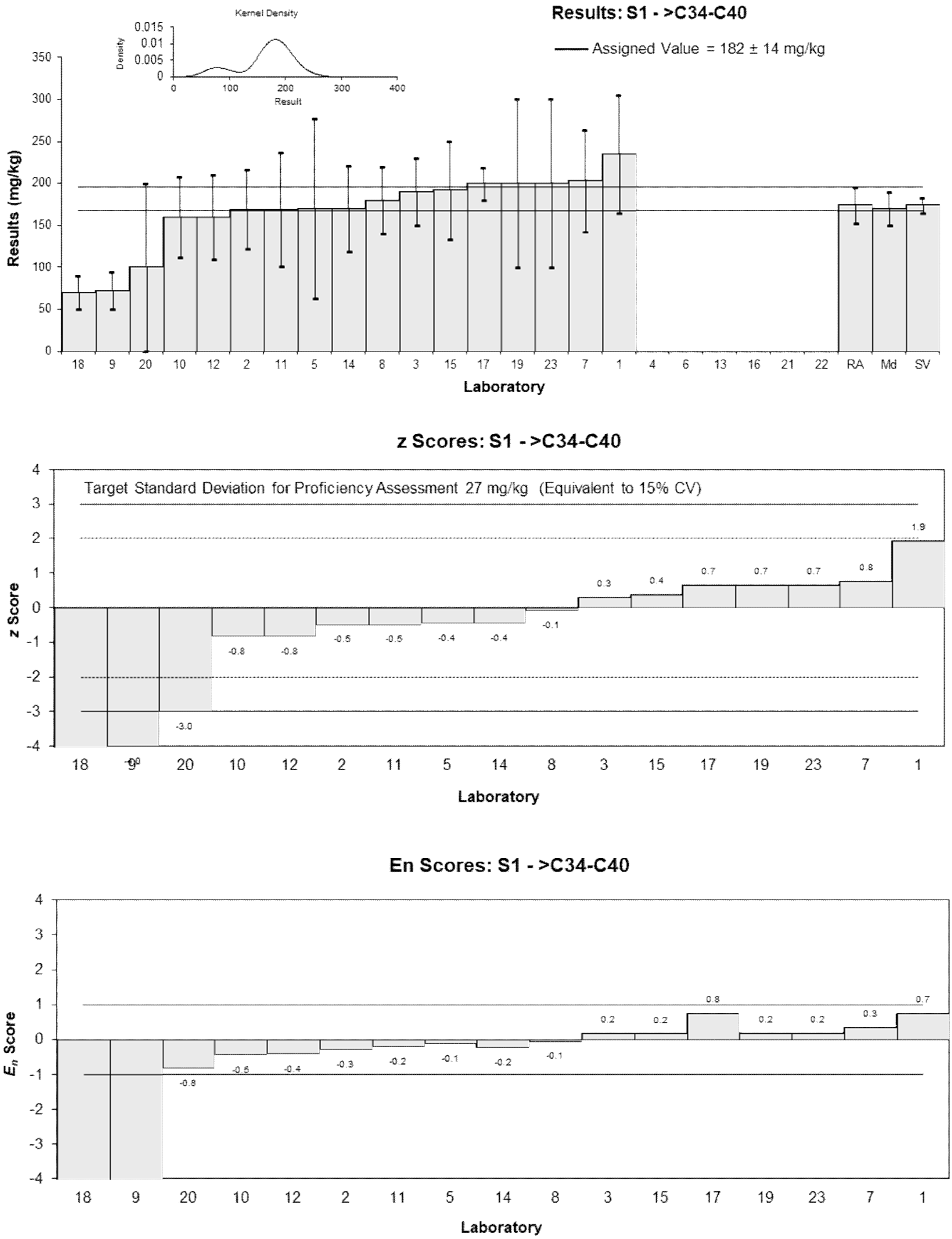
Kernel Density
Density
Result
Results: S1 - >C34-C40
Assigned Value = 182 ± 14 mg/kg
Results (mg/kg)
Laboratory
18 9 20 10 12 2 11 5 14 8 3 15 17 19 23 7 1 4 6 13 16 21 22 RA Md SV
z Scores: S1 - >C34-C40
Target Standard Deviation for Proficiency Assessment 27 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
18 9 20 10 12 2 11 5 14 8 3 15 17 19 23 7 1
En Scores: S1 - >C34-C40
$E_n$ Score
Laboratory
18 9 20 10 12 2 11 5 14 8 3 15 17 19 23 7 1

Figure 4

Table 8 Additional hydrocarbon ranges to those defined in NEPM,[5] reported by participants for Sample S1

| Lab. Code | Range | Result (mg/kg) | Uncertainty (mg/kg) |
|---|---|---|---|
| **4** | C7-C9 | <20 | 6.7 |
| | C10-C14 | 388 | 85 |
| | C15-C36 | 2070 | 330 |
| **6** | C9 | <10 | NR |
| | C10-C14 | 598 | 179.4 |
| | C15-C36 | 1873 | 561.9 |
| **22** | C7-C9 | <20 | NR |
| | C10-C14 | 670 | 200 |
| | C15-C36 | 2500 | 700 |

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Table 9

**Sample Details**

| | |
|---|---|
| **Sample** | S1 |
| **Analyte** | TRH |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2841 | 852 | 0.10 | 0.05 |
| **2** | 2425 | 687 | -0.89 | -0.52 |
| **3** | 2700 | 447.7 | -0.24 | -0.20 |
| **4** | 2460 | 340 | -0.81 | -0.83 |
| **5** | 2980 | NR | 0.43 | 0.78 |
| **6** | 2472 | 741.6 | -0.78 | -0.42 |
| **7** | 2881 | 864 | 0.19 | 0.09 |
| **8** | 2790 | NR | -0.02 | -0.04 |
| **9** | 2216.8 | NR | -1.39 | -2.54 |
| **10** | 2601.3 | 780.4 | -0.47 | -0.24 |
| **11** | 3342 | NR | 1.29 | 2.36 |
| **12** | 2400 | 700 | -0.95 | -0.54 |
| **13** | 2060 | NR | -1.76 | -3.22 |
| **14** | 3410 | 911 | 1.45 | 0.65 |
| **15** | 3191 | 958 | 0.93 | 0.40 |
| **16** | NT | NT | | |
| **17** | 3060 | 513 | 0.62 | 0.46 |
| **18*** | 1100 | 330 | -4.05 | -4.23 |
| **19** | 2800 | 800 | 0.00 | 0.00 |
| **20** | 2600 | 700 | -0.48 | -0.27 |
| **21** | 3110 | NR | 0.74 | 1.35 |
| **22** | 3170 | 950 | 0.88 | 0.38 |
| **23** | 3200 | NR | 0.95 | 1.74 |

* Outlier

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2800 | 230 |
| **Spiked Value** | 2860 | 140 |
| **Robust Average** | 2770 | 240 |
| **Median** | 2800 | 260 |
| **Mean** | 2720 | 220 |
| **N** | 22 | |
| **Max** | 3410 | |
| **Min** | 1100 | |
| **Robust SD** | 440 | |
| **Robust CV (%)** | 16 | |

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

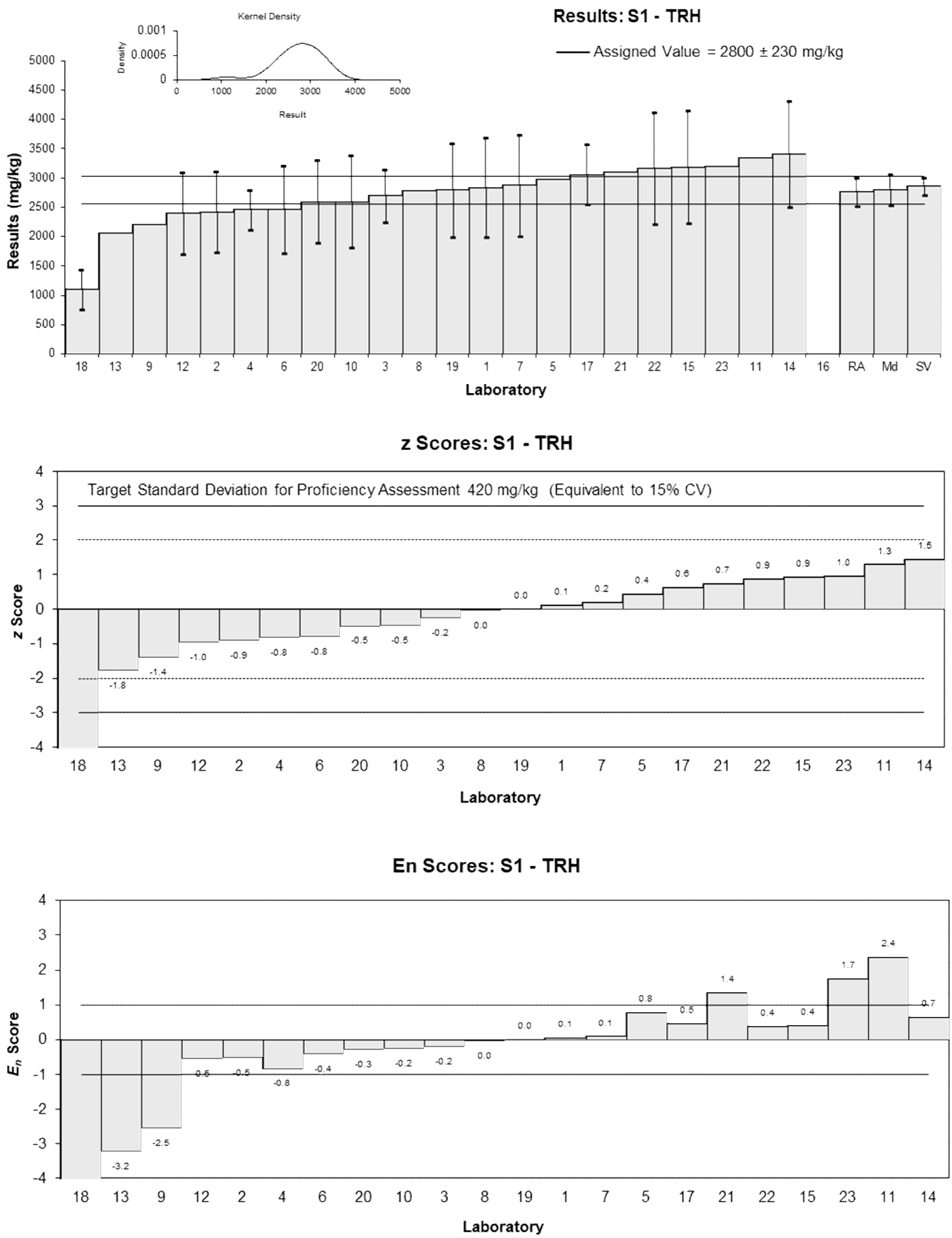

Results: S1 - TRH
Assigned Value = 2800 ± 230 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
18 13 9 12 2 4 6 20 10 3 8 19 1 7 5 17 21 22 15 23 11 14 16 RA Md SV
z Scores: S1 - TRH
Target Standard Deviation for Proficiency Assessment 420 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
18 13 9 12 2 4 6 20 10 3 8 19 1 7 5 17 21 22 15 23 11 14
En Scores: S1 - TRH
$E_n$ Score
Laboratory
18 13 9 12 2 4 6 20 10 3 8 19 1 7 5 17 21 22 15 23 11 14

Figure 5

Table 10

**Sample Details**

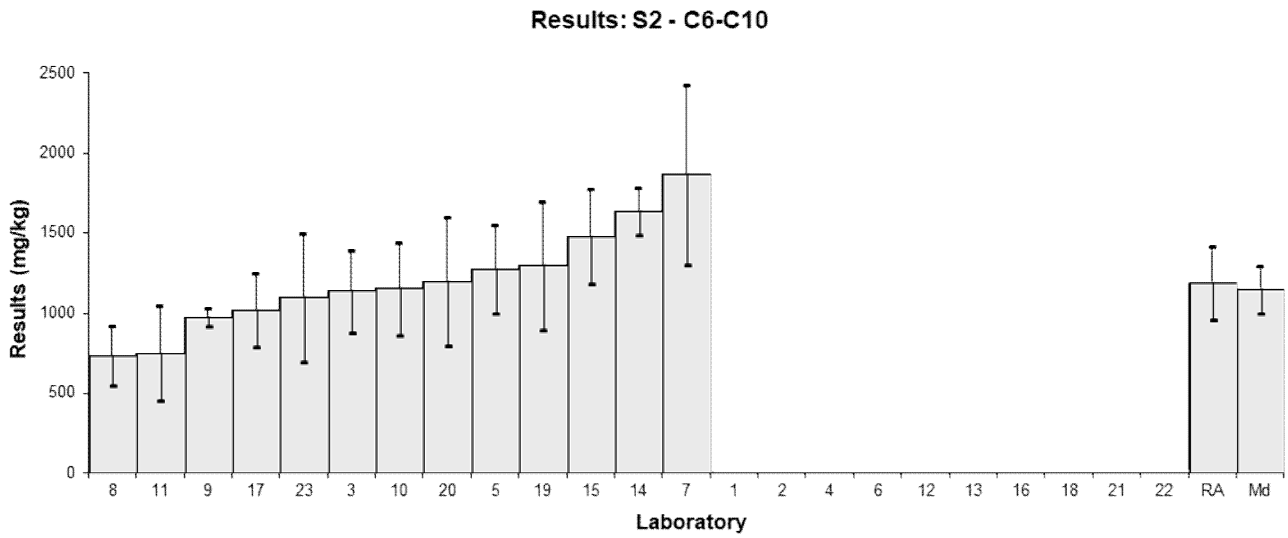
| | |
|---|---|
| **Sample** | S2 |
| **Analyte** | C6-C10 |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U |
|---|---|---|
| **1** | NT | NT |
| **2** | NT | NT |
| **3** | 1140 | 255.5 |
| **4** | NT | NT |
| **5** | 1280 | 277 |
| **6** | NT | NT |
| **7** | 1868 | 560 |
| **8** | 736 | 182 |
| **9** | 975 | 58 |
| **10** | 1153 | 288.3 |
| **11** | 752 | 300 |
| **12** | NT | NT |
| **13** | NT | NT |
| **14** | 1640 | 147 |
| **15** | 1478 | 296 |
| **16** | NT | NT |
| **17** | 1020 | 231 |
| **18** | NT | NT |
| **19** | 1300 | 400 |
| **20** | 1200 | 400 |
| **21** | NT | NT |
| **22** | NT | NT |
| **23** | 1100 | 400 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Robust Average** | 1190 | 230 |
| **Median** | 1150 | 150 |
| **Mean** | 1200 | 180 |
| **N** | 13 | |
| **Max** | 1868 | |
| **Min** | 736 | |
| **Robust SD** | 330 | |
| **Robust CV (%)** | 28 | |



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


Figure 6

Table 11

**Sample Details**

| | |
|---|---|
| **Sample** | S2 |
| **Analyte** | Benzene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U |
|---|---|---|
| **1** | NT | NT |
| **2** | 28.8 | 7.1 |
| **3** | 35.1 | 6.7 |
| **4** | 12.5 | 3.5 |
| **5** | 18.2 | 3.7 |
| **6*** | NR | NR |
| **7** | 52 | 16 |
| **8** | 40.3 | 8 |
| **9** | 22.9 | 5.3 |
| **10** | 20.98 | 5.245 |
| **11** | 28.8 | 12 |
| **12** | NT | NT |
| **13** | 14 | 4.0 |
| **14** | 31.1 | 7.8 |
| **15** | 41.1 | 8.2 |
| **16** | NT | NT |
| **17** | 22.4 | 3.9 |
| **18** | 37 | 11 |
| **19** | 15 | 5 |
| **20** | 39 | 10 |
| **21** | NT | NT |
| **22**** | 1.3 | 0.4 |
| **23** | 11 | 5 |

* Result changed from 0 to NR, ** Gross Error

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spiked Value** | 82.1 | 4.1 |
| **Robust Average** | 27.3 | 7.7 |
| **Median** | 28.8 | 9.2 |
| **Mean** | 27.7 | 5.8 |
| **N** | 17 | |
| **Max** | 52 | |
| **Min** | 11 | |
| **Robust SD** | 13 | |
| **Robust CV (%)** | 47 | |

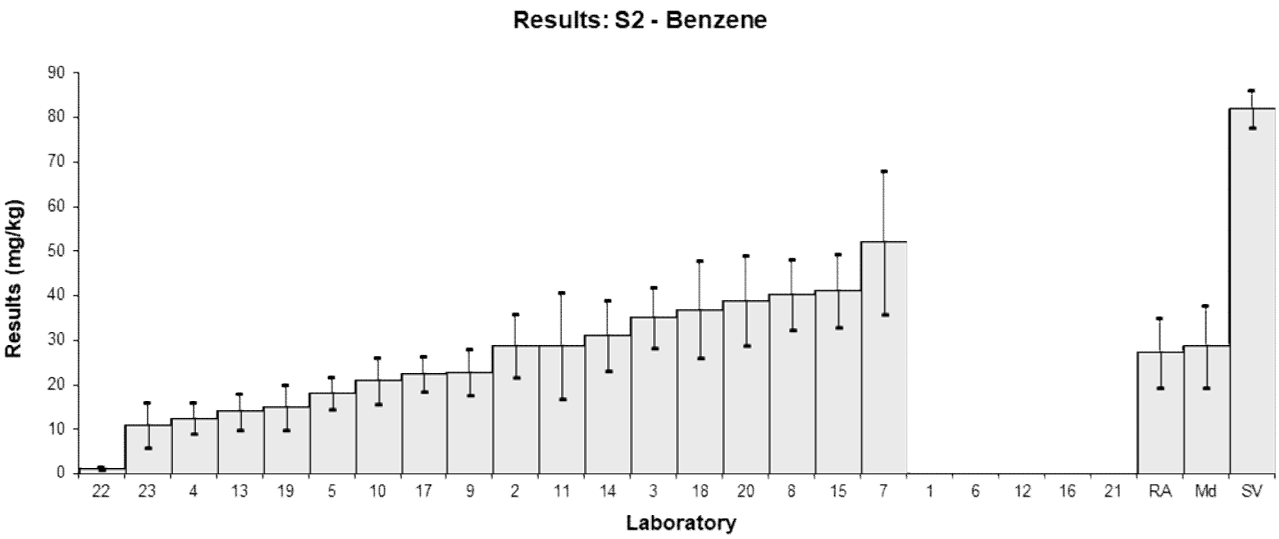

Results: S2 - Benzene
Results (mg/kg)
0
10
20
30
40
50
60
70
80
90
22
23
4
13
19
5
10
17
9
2
11
14
3
18
20
8
15
7
1
6
12
16
21
RA
Md
SV
Laboratory

Figure 7

Table 12

**Sample Details**

| | |
|---|---|
| **Sample** | S2 |
| **Analyte** | Toluene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 284 | 63 | 1.42 | 0.72 |
| **3** | 259 | 49.9 | 0.71 | 0.43 |
| **4** | 182 | 48 | -1.48 | -0.93 |
| **5** | 258 | 46.9 | 0.68 | 0.44 |
| **6**** | 19 | 5.7 | -6.13 | -7.27 |
| **7*** | 371 | 111 | 2.00▼ | 1.00▼ |
| **8** | 306 | 59.2 | 2.00▼ | 1.00▼ |
| **9** | 238 | 95 | 0.11 | 0.04 |
| **10** | 242.7 | 60.68 | 0.25 | 0.13 |
| **11** | 212 | 85 | -0.63 | -0.24 |
| **12** | NT | NT | | |
| **13** | 160 | 48 | -2.11 | -1.32 |
| **14** | 261 | 66 | 0.77 | 0.37 |
| **15** | 291 | 58 | 1.62 | 0.88 |
| **16** | NT | NT | | |
| **17** | 202 | 33 | -0.91 | -0.73 |
| **18** | 230 | 69 | -0.11 | -0.05 |
| **19** | 200 | 60 | -0.97 | -0.51 |
| **20** | 230 | 70 | -0.11 | -0.05 |
| **21** | NT | NT | | |
| **22*** | 79 | 23 | -4.42 | -4.19 |
| **23** | 190 | 60 | -1.25 | -0.66 |

* Outlier, ** Gross Error, ▼ Adjusted score

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 234 | 29 |
| **Spiked Value** | 393 | 20 |
| **Robust Average** | 234 | 32 |
| **Max Acceptable Result** | 464 | |
| **Median** | 234 | 29 |
| **Mean** | 233 | 30 |
| **N** | 18 | |
| **Max** | 371 | |
| **Min** | 79 | |
| **Robust SD** | 54 | |
| **Robust CV (%)** | 23 | |

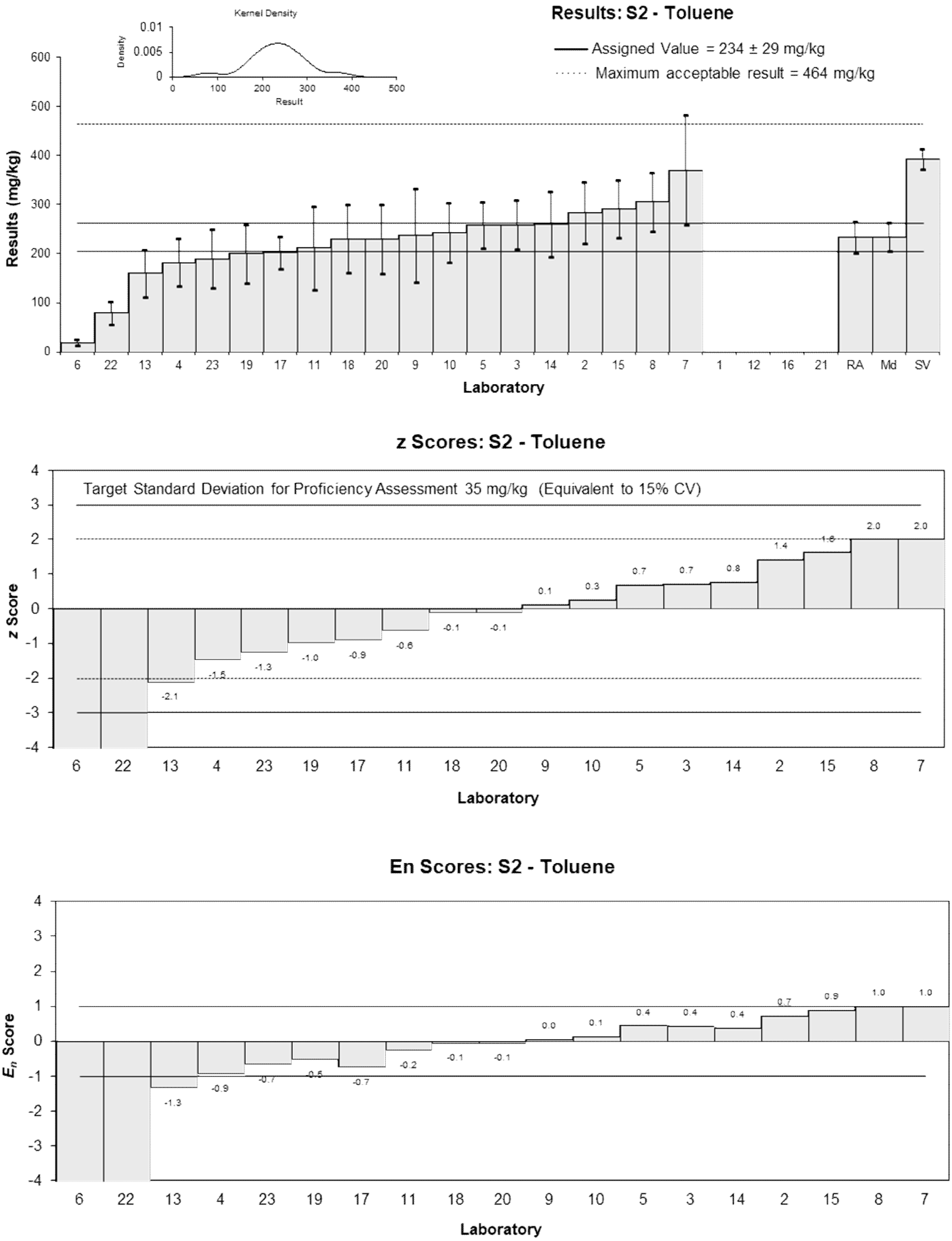

Results: S2 - Toluene
Assigned Value = 234 ± 29 mg/kg
Maximum acceptable result = 464 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
6 22 13 4 23 19 17 11 18 20 9 10 5 3 14 2 15 8 7 1 12 16 21 RA Md SV
Laboratory
z Scores: S2 - Toluene
Target Standard Deviation for Proficiency Assessment 35 mg/kg (Equivalent to 15% CV)
z Score
-2.1 -1.5 -1.3 -1.0 -0.9 -0.6 -0.1 -0.1 0.1 0.3 0.7 0.7 0.8 1.4 1.6 2.0 2.0
6 22 13 4 23 19 17 11 18 20 9 10 5 3 14 2 15 8 7
Laboratory
En Scores: S2 - Toluene
$E_n$ Score
-1.3 -0.9 -0.7 -0.5 -0.7 -0.2 -0.1 -0.1 0.0 0.1 0.4 0.4 0.4 0.7 0.9 1.0 1.0
6 22 13 4 23 19 17 11 18 20 9 10 5 3 14 2 15 8 7
Laboratory

Figure 8

Table 13

**Sample Details**

| | |
|---|---|
| **Sample** | S2 |
| **Analyte** | Ethylbenzene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

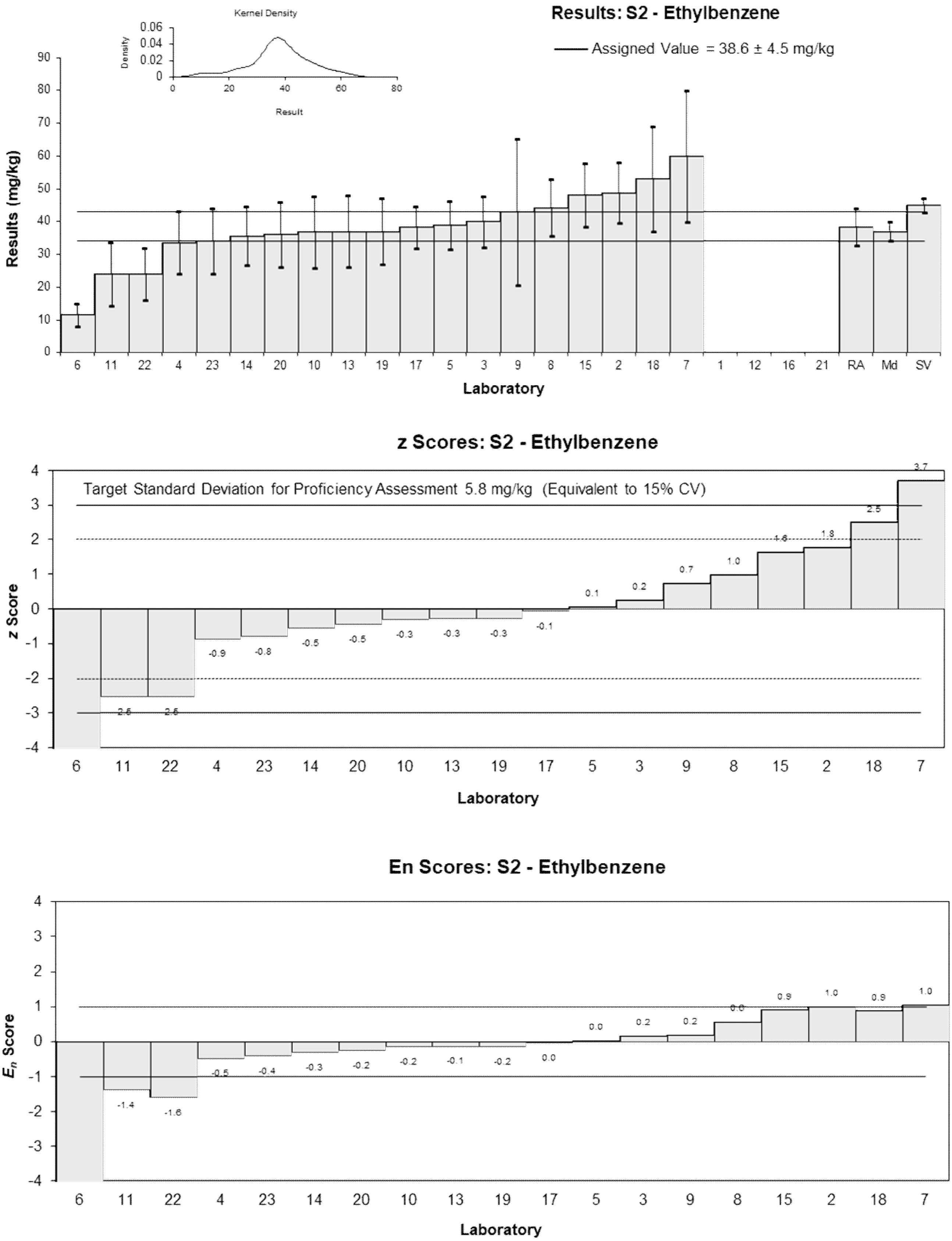
**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 48.8 | 9.2 | 1.76 | 1.00 |
| **3** | 40 | 7.8 | 0.24 | 0.16 |
| **4** | 33.6 | 9.4 | -0.86 | -0.48 |
| **5** | 38.9 | 7.3 | 0.05 | 0.03 |
| **6*** | 11.5 | 3.45 | -4.68 | -4.78 |
| **7*** | 60 | 20 | 3.70 | 1.04 |
| **8** | 44.2 | 8.7 | 0.97 | 0.57 |
| **9** | 42.9 | 22.3 | 0.74 | 0.19 |
| **10** | 36.8 | 11.04 | -0.31 | -0.15 |
| **11** | 24.0 | 9.6 | -2.52 | -1.38 |
| **12** | NT | NT | | |
| **13** | 37 | 11 | -0.28 | -0.13 |
| **14** | 35.5 | 8.9 | -0.54 | -0.31 |
| **15** | 48.1 | 9.6 | 1.64 | 0.90 |
| **16** | NT | NT | | |
| **17** | 38.3 | 6.3 | -0.05 | -0.04 |
| **18** | 53 | 16 | 2.49 | 0.87 |
| **19** | 37 | 10 | -0.28 | -0.15 |
| **20** | 36 | 10 | -0.45 | -0.24 |
| **21** | NT | NT | | |
| **22** | 24 | 8 | -2.52 | -1.59 |
| **23** | 34 | 10 | -0.79 | -0.42 |

* Outlier

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 38.6 | 4.5 |
| **Spiked Value** | 45.0 | 2.2 |
| **Robust Average** | 38.4 | 5.7 |
| **Median** | 37.0 | 2.9 |
| **Mean** | 38.1 | 5.0 |
| **N** | 19 | |
| **Max** | 60 | |
| **Min** | 11.5 | |
| **Robust SD** | 10.0 | |
| **Robust CV (%)** | 26 | |



Results: S2 - Ethylbenzene
Assigned Value = 38.6 ± 4.5 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 11 22 4 23 14 20 10 13 19 17 5 3 9 8 15 2 18 7 1 12 16 21 RA Md SV
z Scores: S2 - Ethylbenzene
Target Standard Deviation for Proficiency Assessment 5.8 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
6 11 22 4 23 14 20 10 13 19 17 5 3 9 8 15 2 18 7
En Scores: S2 - Ethylbenzene
$E_n$ Score
Laboratory
6 11 22 4 23 14 20 10 13 19 17 5 3 9 8 15 2 18 7


Figure 9

Table 14

**Sample Details**

| | |
|---|---|
| **Sample** | S2 |
| **Analyte** | Xylenes |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 304 | 59 | 1.85 | 1.01 |
| **3** | 265 | 59.4 | 0.76 | 0.41 |
| **4** | 207 | 65 | -0.87 | -0.44 |
| **5** | 272 | 54.4 | 0.95 | 0.56 |
| **6*** | 118.5 | 35.55 | -3.35 | -2.64 |
| **7*** | 358 | 107 | 2.00▼ | 1.00▼ |
| **8** | 264 | 50.6 | 0.73 | 0.45 |
| **9** | 252 | 82 | 0.39 | 0.16 |
| **10** | 215.5 | 64.65 | -0.63 | -0.32 |
| **11** | 183 | 73 | -1.54 | -0.70 |
| **12** | NT | NT | | |
| **13** | 200 | 60 | -1.06 | -0.57 |
| **14** | 241 | 61 | 0.08 | 0.04 |
| **15** | 308 | 62 | 1.96 | 1.03 |
| **16** | NT | NT | | |
| **17** | 236 | 42 | -0.06 | -0.04 |
| **18** | 280 | 84 | 1.18 | 0.47 |
| **19** | 230 | 70 | -0.22 | -0.11 |
| **20** | 210 | 70 | -0.78 | -0.37 |
| **21** | NT | NT | | |
| **22** | 161 | 37 | -2.16 | -1.66 |
| **23** | 210 | 70 | -0.78 | -0.37 |

* Outlier, ▼ Adjusted score

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 238 | 28 |
| **Spiked Value** | 337 | 17 |
| **Robust Average** | 238 | 31 |
| **Max Acceptable Result** | 409 | |
| **Median** | 236 | 25 |
| **Mean** | 238 | 26 |
| **N** | 19 | |
| **Max** | 358 | |
| **Min** | 118.5 | |
| **Robust SD** | 54 | |
| **Robust CV (%)** | 23 | |

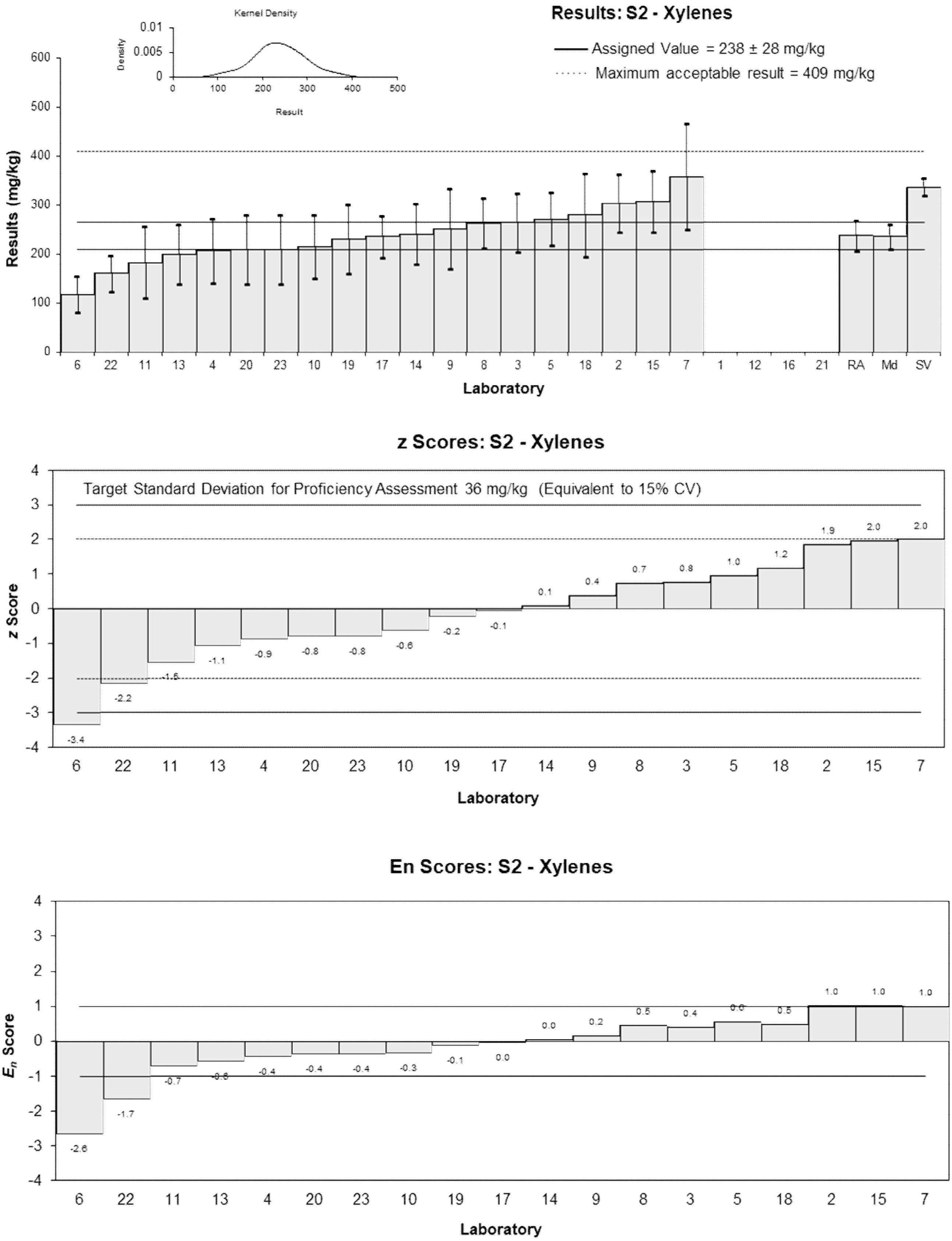

Results: S2 - Xylenes
Assigned Value = 238 ± 28 mg/kg
Maximum acceptable result = 409 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 22 11 13 4 20 23 10 19 17 14 9 8 3 5 18 2 15 7 1 12 16 21 RA Md SV
z Scores: S2 - Xylenes
Target Standard Deviation for Proficiency Assessment 36 mg/kg (Equivalent to 15% CV)
z Score
-3.4 -2.2 -1.5 -1.1 -0.9 -0.8 -0.8 -0.6 -0.2 -0.1 0.1 0.4 0.7 0.8 1.0 1.2 1.9 2.0 2.0
6 22 11 13 4 20 23 10 19 17 14 9 8 3 5 18 2 15 7
Laboratory
En Scores: S2 - Xylenes
$E_n$ Score
-2.6 -1.7 -0.7 -0.6 -0.4 -0.4 -0.4 -0.3 -0.1 0.0 0.0 0.2 0.5 0.4 0.6 0.5 1.0 1.0 1.0
6 22 11 13 4 20 23 10 19 17 14 9 8 3 5 18 2 15 7
Laboratory

Figure 10

Table 15

**Sample Details**

| | |
|---|---|
| **Sample** | S2 |
| **Analyte** | Total BTEX |
| **Matrix** | Soil |
| **Unit** | mg/kg |

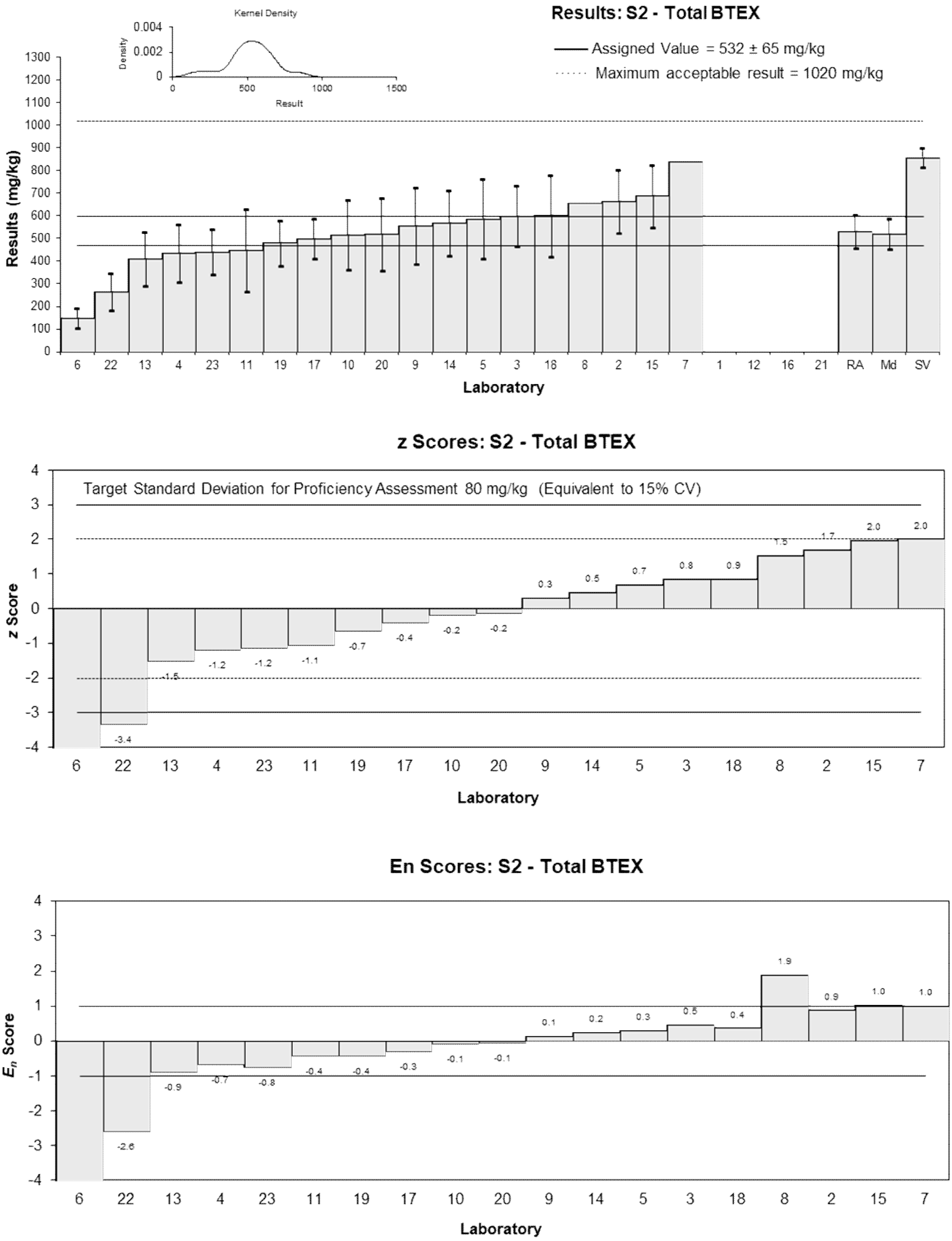
**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 666 | 140 | 1.68 | 0.87 |
| **3** | 599 | 134 | 0.84 | 0.45 |
| **4** | 435.1 | 125.9 | -1.21 | -0.68 |
| **5** | 587 | 176 | 0.69 | 0.29 |
| **6*** | 149 | 44.7 | -4.80 | -4.86 |
| **7*** | 841 | NR | 2.00▼ | 1.00▼ |
| **8** | 654 | NR | 1.53 | 1.88 |
| **9** | 556 | 167 | 0.30 | 0.13 |
| **10** | 515.9 | 154.8 | -0.20 | -0.10 |
| **11** | 447 | 180 | -1.07 | -0.44 |
| **12** | NT | NT | | |
| **13** | 410 | 120 | -1.53 | -0.89 |
| **14** | 569 | 144 | 0.46 | 0.23 |
| **15** | 688 | 138 | 1.95 | 1.02 |
| **16** | NT | NT | | |
| **17** | 499 | 88 | -0.41 | -0.30 |
| **18** | 600 | 180 | 0.85 | 0.36 |
| **19** | 480 | 100 | -0.65 | -0.44 |
| **20** | 520 | 160 | -0.15 | -0.07 |
| **21** | NT | NT | | |
| **22** | 265 | 80 | -3.35 | -2.59 |
| **23** | 440 | 100 | -1.15 | -0.77 |

* Outlier, ▼ Adjusted score

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 532 | 65 |
| **Spiked Value** | 858 | 43 |
| **Robust Average** | 530 | 73 |
| **Max Acceptable Result** | 1020 | |
| **Median** | 520 | 68 |
| **Mean** | 522 | 71 |
| **N** | 19 | |
| **Max** | 841 | |
| **Min** | 149 | |
| **Robust SD** | 130 | |
| **Robust CV (%)** | 24 | |



Results: S2 - Total BTEX
Assigned Value = 532 ± 65 mg/kg
Maximum acceptable result = 1020 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z Scores: S2 - Total BTEX
Target Standard Deviation for Proficiency Assessment 80 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
En Scores: S2 - Total BTEX
En Score
Laboratory


Figure 11

Table 16

**Sample Details**

| | |
|---|---|
| **Sample** | S3 |
| **Analyte** | Anthracene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.84 | 0.25 | -0.03 | -0.02 |
| **2** | 0.722 | 0.23 | -0.96 | -0.50 |
| **3** | 0.85 | 0.13 | 0.05 | 0.04 |
| **4** | NS | NS | | |
| **5** | 1 | 0.25 | 1.23 | 0.60 |
| **6** | 0.878 | 0.2634 | 0.27 | 0.12 |
| **7** | 0.7 | 0.2 | -1.14 | -0.68 |
| **8** | 1.0 | NR | 1.23 | 2.11 |
| **9** | 0.8 | 0.2 | -0.35 | -0.21 |
| **10** | 0.953 | 0.285 | 0.86 | 0.37 |
| **11** | 1 | 0.40 | 1.23 | 0.38 |
| **12** | 0.61 | 0.18 | -1.85 | -1.20 |
| **13** | 0.90 | 0.27 | 0.44 | 0.20 |
| **14** | 0.80 | 0.30 | -0.35 | -0.14 |
| **15** | 0.767 | 0.3 | -0.61 | -0.25 |
| **16** | 0.55 | 0.03 | -2.32 | -3.68 |
| **17** | 0.7 | 0.1 | -1.14 | -1.16 |
| **18*** | 1.5 | 0.6 | 2.00▼ | 1.00▼ |
| **19** | 0.9 | 0.3 | 0.44 | 0.18 |
| **20** | 1 | 0.3 | 1.23 | 0.50 |
| **21** | 0.781 | NR | -0.50 | -0.85 |
| **22** | 0.96 | 0.27 | 0.92 | 0.41 |
| **23** | 0.9 | 0.3 | 0.44 | 0.18 |

* Outlier, ▼ Adjusted score

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.844 | 0.074 |
| **Spiked Value** | 1.29 | 0.06 |
| **Robust Average** | 0.855 | 0.076 |
| **Max Acceptable Result** | 1.55 | |
| **Median** | 0.864 | 0.076 |
| **Mean** | 0.869 | 0.081 |
| **N** | 22 | |
| **Max** | 1.5 | |
| **Min** | 0.55 | |
| **Robust SD** | 0.14 | |
| **Robust CV (%)** | 17 | |

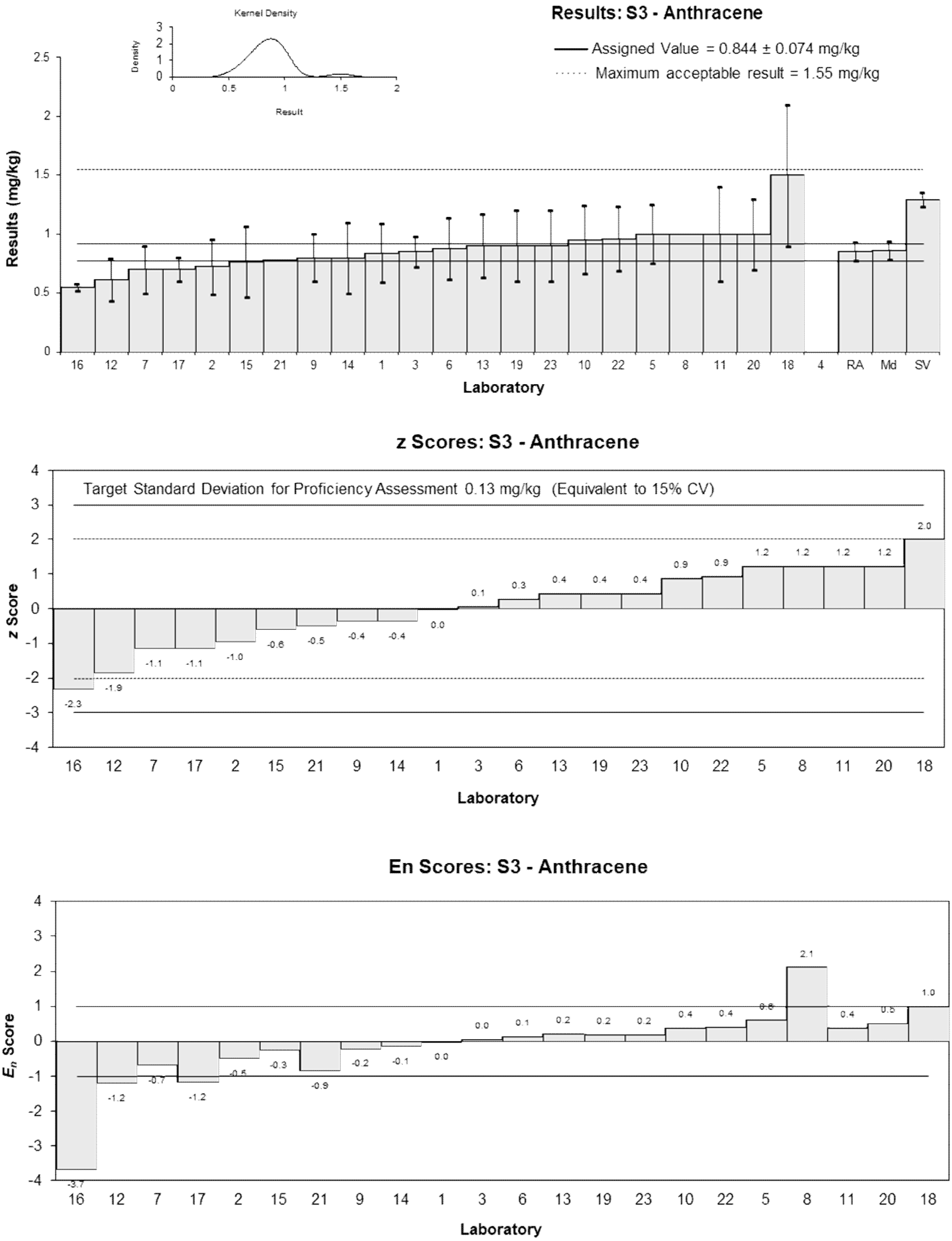

Results: S3 - Anthracene
Assigned Value = 0.844 ± 0.074 mg/kg
Maximum acceptable result = 1.55 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
16 12 7 17 2 15 21 9 14 1 3 6 13 19 23 10 22 5 8 11 20 18 4 RA Md SV
z Scores: S3 - Anthracene
Target Standard Deviation for Proficiency Assessment 0.13 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
16 12 7 17 2 15 21 9 14 1 3 6 13 19 23 10 22 5 8 11 20 18
-2.3 -1.9 -1.1 -1.1 -1.0 -0.6 -0.5 -0.4 -0.4 0.0 0.1 0.3 0.4 0.4 0.4 0.9 0.9 1.2 1.2 1.2 1.2 2.0
En Scores: S3 - Anthracene
En Score
Laboratory
16 12 7 17 2 15 21 9 14 1 3 6 13 19 23 10 22 5 8 11 20 18
-3.7 -1.2 -0.7 -1.2 -0.5 -0.3 -0.9 -0.2 -0.1 0.0 0.0 0.1 0.2 0.2 0.2 0.4 0.4 0.6 2.1 0.4 0.5 1.0

Figure 12

Table 17

**Sample Details**

| | |
|---|---|
| **Sample** | S3 |
| **Analyte** | Benzo[*a*]pyrene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

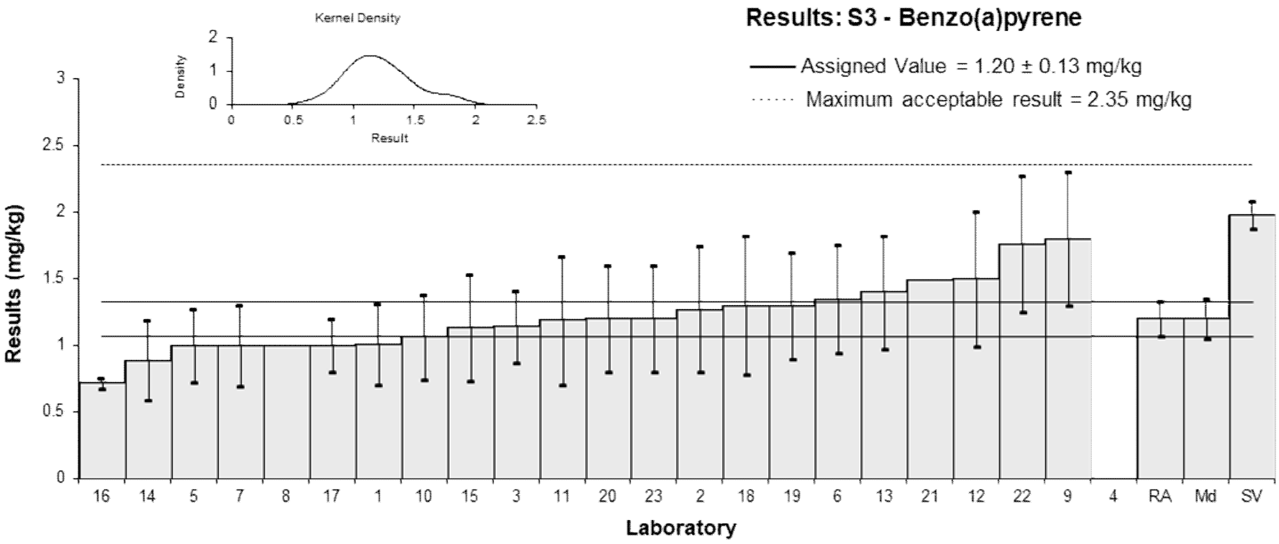
**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1.01 | 0.30 | -1.06 | -0.58 |
| **2** | 1.27 | 0.47 | 0.39 | 0.14 |
| **3** | 1.14 | 0.27 | -0.33 | -0.20 |
| **4** | NS | NS | | |
| **5** | 1 | 0.27 | -1.11 | -0.67 |
| **6** | 1.35 | 0.405 | 0.83 | 0.35 |
| **7** | 1 | 0.3 | -1.11 | -0.61 |
| **8** | 1.0 | NR | -1.11 | -1.54 |
| **9** | 1.8 | 0.5 | 2.00▼ | 1.00▼ |
| **10** | 1.065 | 0.319 | -0.75 | -0.39 |
| **11** | 1.19 | 0.48 | -0.06 | -0.02 |
| **12** | 1.5 | 0.5 | 1.67 | 0.58 |
| **13** | 1.4 | 0.42 | 1.11 | 0.45 |
| **14** | 0.89 | 0.30 | -1.72 | -0.95 |
| **15** | 1.133 | 0.4 | -0.37 | -0.16 |
| **16** | 0.72 | 0.04 | -2.67 | -3.53 |
| **17** | 1.0 | 0.2 | -1.11 | -0.84 |
| **18** | 1.3 | 0.52 | 0.56 | 0.19 |
| **19** | 1.3 | 0.4 | 0.56 | 0.24 |
| **20** | 1.2 | 0.4 | 0.00 | 0.00 |
| **21** | 1.489 | NR | 1.61 | 2.22 |
| **22** | 1.76 | 0.51 | 2.00▼ | 1.00▼ |
| **23** | 1.2 | 0.4 | 0.00 | 0.00 |

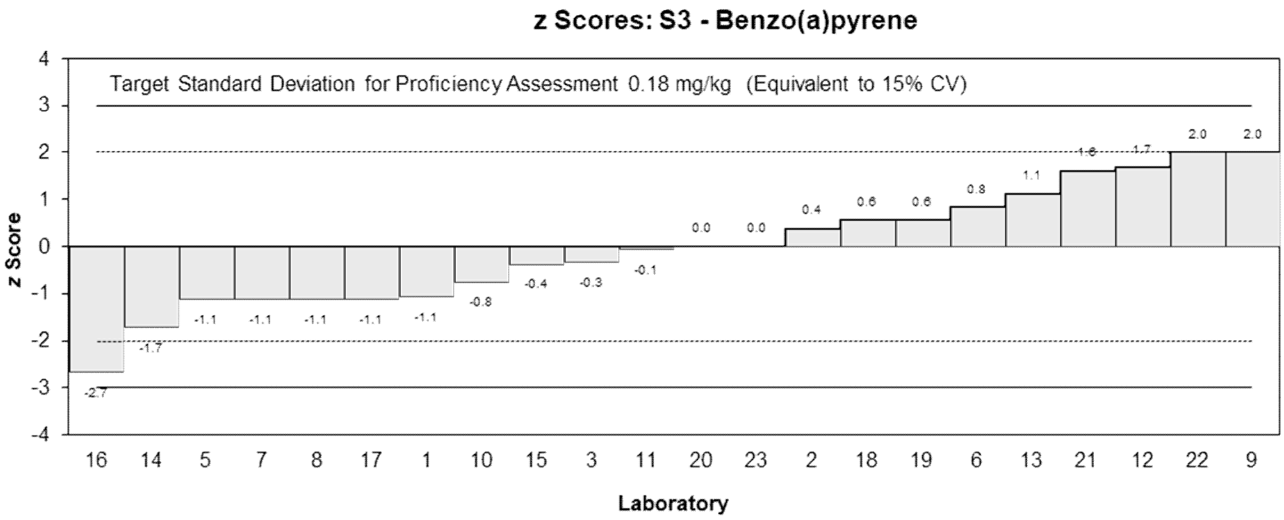
▼ Adjusted score

**Statistics**

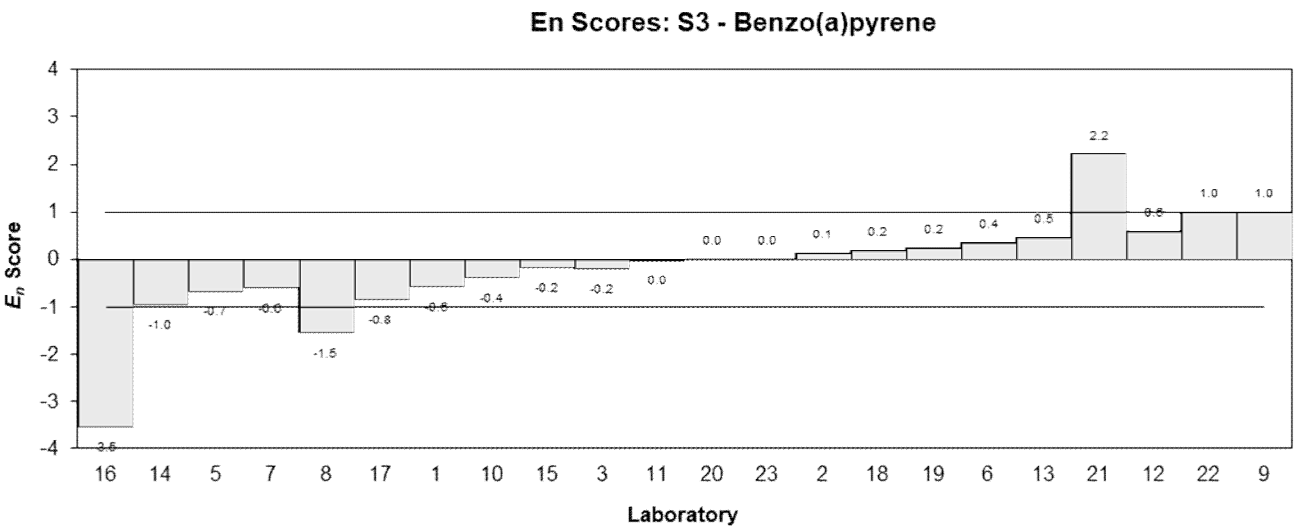
| | | |
|---|---|---|
| **Assigned Value** | 1.20 | 0.13 |
| **Spiked Value** | 1.98 | 0.10 |
| **Robust Average** | 1.20 | 0.13 |
| **Max Acceptable Result** | 2.35 | |
| **Median** | 1.20 | 0.15 |
| **Mean** | 1.21 | 0.11 |
| **N** | 22 | |
| **Max** | 1.8 | |
| **Min** | 0.72 | |
| **Robust SD** | 0.25 | |
| **Robust CV (%)** | 21 | |



Results: S3 - Benzo(a)pyrene
Assigned Value = 1.20 ± 0.13 mg/kg
Maximum acceptable result = 2.35 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
16 14 5 7 8 17 1 10 15 3 11 20 23 2 18 19 6 13 21 12 22 9 4 RA Md SV

z Scores: S3 - Benzo(a)pyrene
Target Standard Deviation for Proficiency Assessment 0.18 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
16 14 5 7 8 17 1 10 15 3 11 20 23 2 18 19 6 13 21 12 22 9
-2.7 -1.7 -1.1 -1.1 -1.1 -1.1 -1.1 -0.8 -0.4 -0.3 -0.1 0.0 0.0 0.4 0.6 0.6 0.8 1.1 1.6 1.7 2.0 2.0

En Scores: S3 - Benzo(a)pyrene
$E_n$ Score
Laboratory
16 14 5 7 8 17 1 10 15 3 11 20 23 2 18 19 6 13 21 12 22 9
-3.5 -1.0 -0.7 -0.6 -1.5 -0.8 -0.6 -0.4 -0.2 -0.2 0.0 0.0 0.0 0.1 0.2 0.2 0.4 0.5 2.2 0.6 1.0 1.0


Figure 13

Table 18

**Sample Details**

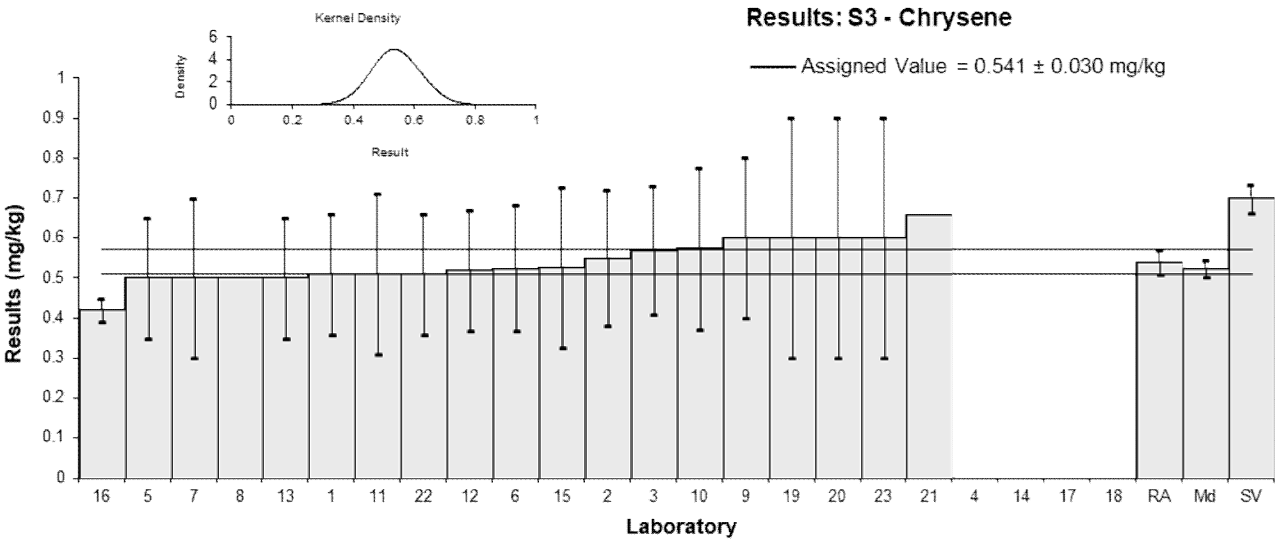
| | |
|---|---|
| **Sample** | S3 |
| **Analyte** | Chrysene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

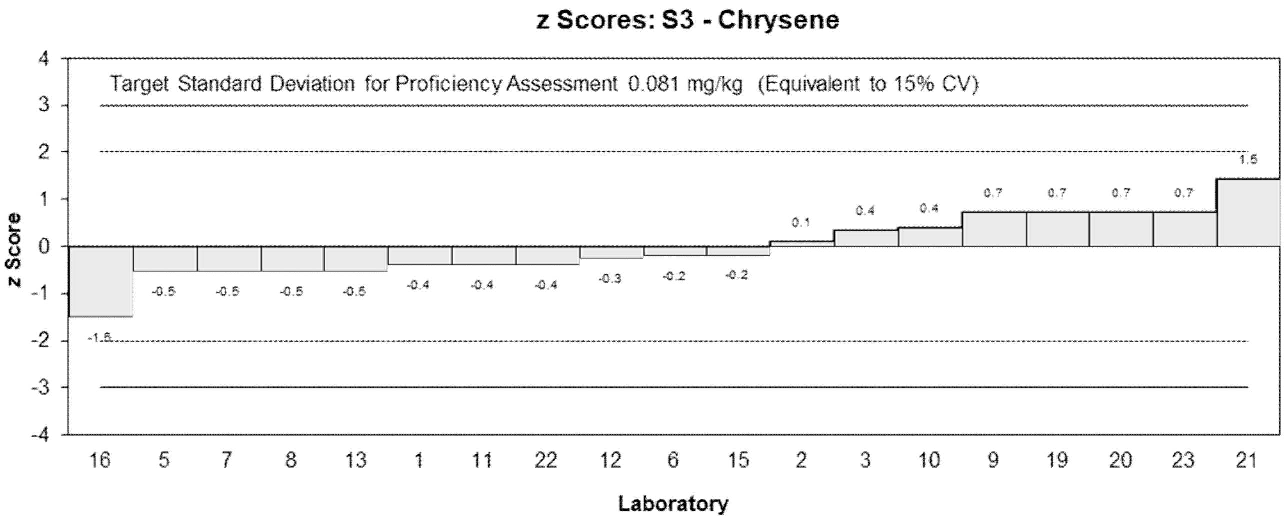
| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.51 | 0.15 | -0.38 | -0.20 |
| **2** | 0.551 | 0.17 | 0.12 | 0.06 |
| **3** | 0.57 | 0.16 | 0.36 | 0.18 |
| **4** | NS | NS | | |
| **5** | 0.5 | 0.15 | -0.51 | -0.27 |
| **6** | 0.525 | 0.1575 | -0.20 | -0.10 |
| **7** | 0.5 | 0.2 | -0.51 | -0.20 |
| **8** | 0.5 | NR | -0.51 | -1.37 |
| **9** | 0.6 | 0.2 | 0.73 | 0.29 |
| **10** | 0.574 | 0.201 | 0.41 | 0.16 |
| **11** | 0.51 | 0.2 | -0.38 | -0.15 |
| **12** | 0.52 | 0.15 | -0.26 | -0.14 |
| **13** | 0.50 | 0.15 | -0.51 | -0.27 |
| **14** | <0.5 | NR | | |
| **15** | 0.526 | 0.2 | -0.18 | -0.07 |
| **16** | 0.42 | 0.03 | -1.49 | -2.85 |
| **17** | <0.5 | NR | | |
| **18** | <1 | NR | | |
| **19** | 0.6 | 0.3 | 0.73 | 0.20 |
| **20** | 0.6 | 0.3 | 0.73 | 0.20 |
| **21** | 0.659 | NR | 1.45 | 3.93 |
| **22** | 0.51 | 0.15 | -0.38 | -0.20 |
| **23** | 0.6 | 0.3 | 0.73 | 0.20 |

**Statistics**

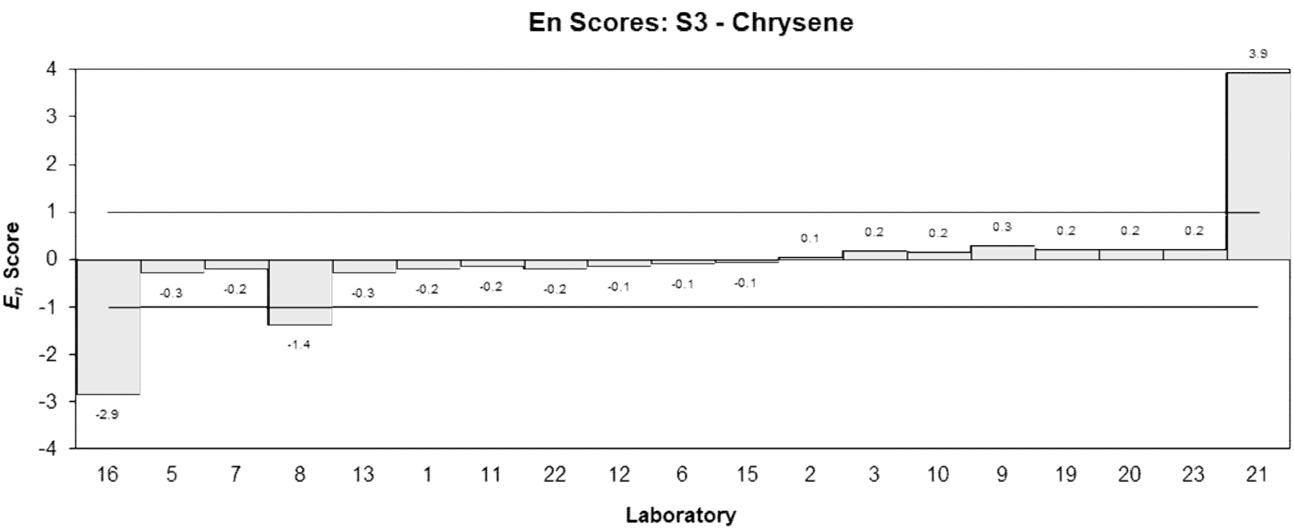
| | | |
|---|---|---|
| **Assigned Value** | 0.541 | 0.030 |
| **Spiked Value** | 0.699 | 0.035 |
| **Robust Average** | 0.541 | 0.030 |
| **Median** | 0.525 | 0.021 |
| **Mean** | 0.541 | 0.025 |
| **N** | 19 | |
| **Max** | 0.659 | |
| **Min** | 0.42 | |
| **Robust SD** | 0.053 | |
| **Robust CV (%)** | 9.8 | |



Results: S3 - Chrysene
Assigned Value = 0.541 ± 0.030 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
16 5 7 8 13 1 11 22 12 6 15 2 3 10 9 19 20 23 21 4 14 17 18 RA Md SV

z Scores: S3 - Chrysene
Target Standard Deviation for Proficiency Assessment 0.081 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
16 5 7 8 13 1 11 22 12 6 15 2 3 10 9 19 20 23 21
-1.5 -0.5 -0.5 -0.5 -0.5 -0.4 -0.4 -0.4 -0.3 -0.2 -0.2 0.1 0.4 0.4 0.7 0.7 0.7 0.7 1.5

En Scores: S3 - Chrysene
$E_n$ Score
Laboratory
16 5 7 8 13 1 11 22 12 6 15 2 3 10 9 19 20 23 21
-2.9 -0.3 -0.2 -1.4 -0.3 -0.2 -0.2 -0.2 -0.1 -0.1 -0.1 0.1 0.2 0.2 0.3 0.2 0.2 0.2 3.9


Figure 14

Table 19

**Sample Details**

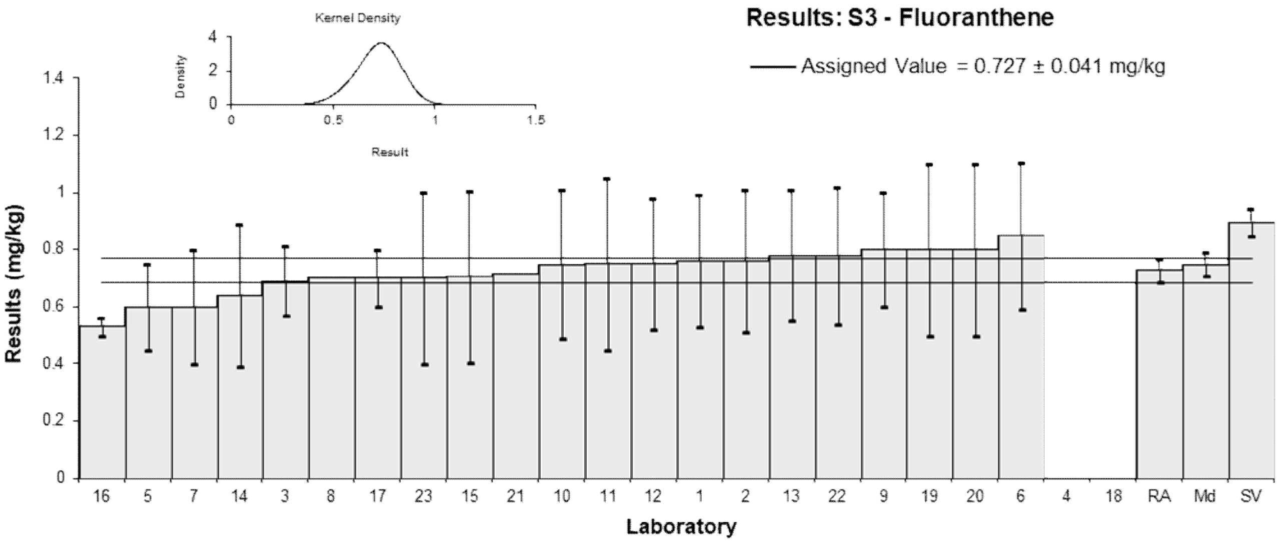
| | |
|---|---|
| **Sample** | S3 |
| **Analyte** | Fluoranthene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

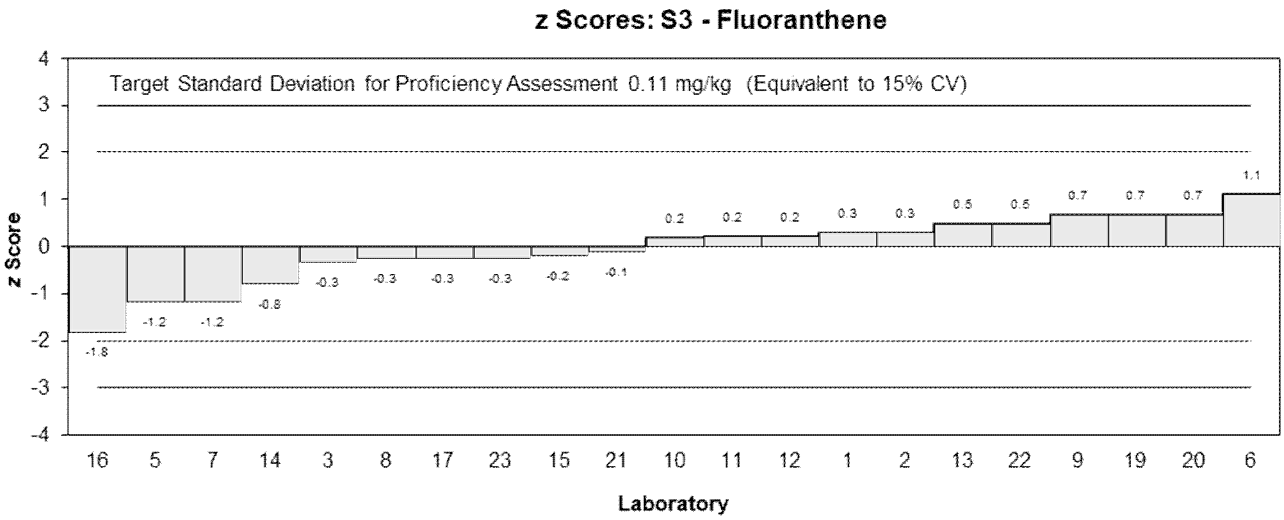
| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.76 | 0.23 | 0.30 | 0.14 |
| **2** | 0.76 | 0.25 | 0.30 | 0.13 |
| **3** | 0.69 | 0.12 | -0.34 | -0.29 |
| **4** | NS | NS | | |
| **5** | 0.6 | 0.15 | -1.16 | -0.82 |
| **6** | 0.848 | 0.2544 | 1.11 | 0.47 |
| **7** | 0.6 | 0.2 | -1.16 | -0.62 |
| **8** | 0.7 | NR | -0.25 | -0.66 |
| **9** | 0.8 | 0.2 | 0.67 | 0.36 |
| **10** | 0.749 | 0.262 | 0.20 | 0.08 |
| **11** | 0.75 | 0.30 | 0.21 | 0.08 |
| **12** | 0.75 | 0.23 | 0.21 | 0.10 |
| **13** | 0.78 | 0.23 | 0.49 | 0.23 |
| **14** | 0.64 | 0.25 | -0.80 | -0.34 |
| **15** | 0.705 | 0.3 | -0.20 | -0.07 |
| **16** | 0.53 | 0.03 | -1.81 | -3.88 |
| **17** | 0.7 | 0.1 | -0.25 | -0.25 |
| **18** | <1 | NR | | |
| **19** | 0.8 | 0.3 | 0.67 | 0.24 |
| **20** | 0.8 | 0.3 | 0.67 | 0.24 |
| **21** | 0.714 | NR | -0.12 | -0.32 |
| **22** | 0.78 | 0.24 | 0.49 | 0.22 |
| **23** | 0.7 | 0.3 | -0.25 | -0.09 |

**Statistics**

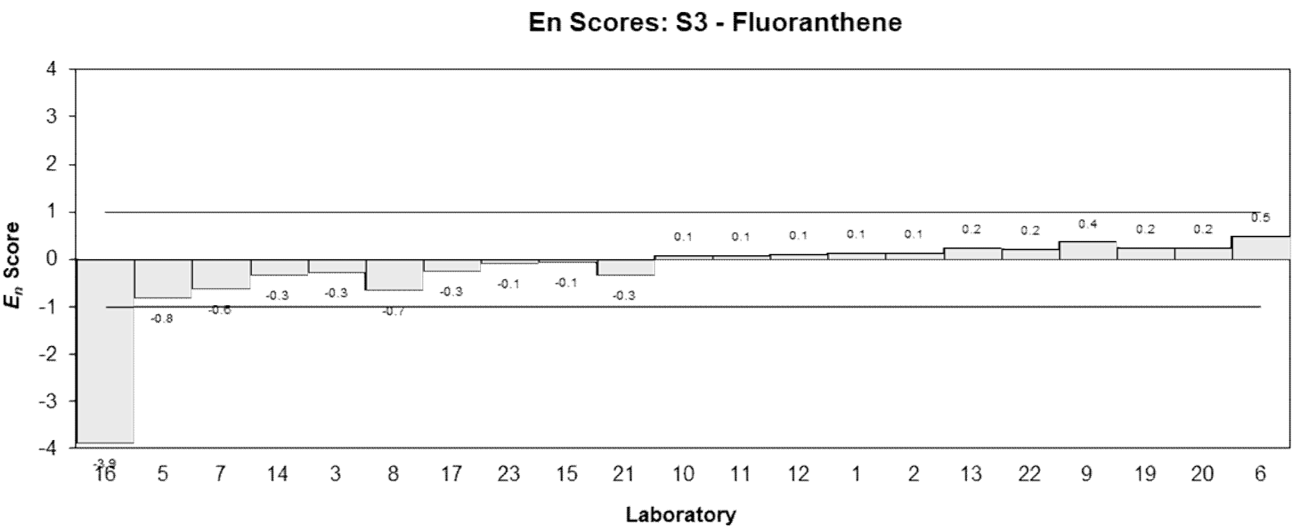
| | | |
|---|---|---|
| **Assigned Value** | 0.727 | 0.041 |
| **Spiked Value** | 0.895 | 0.045 |
| **Robust Average** | 0.727 | 0.041 |
| **Median** | 0.749 | 0.040 |
| **Mean** | 0.722 | 0.034 |
| **N** | 21 | |
| **Max** | 0.848 | |
| **Min** | 0.53 | |
| **Robust SD** | 0.075 | |
| **Robust CV (%)** | 10 | |



Results: S3 - Fluoranthene
Assigned Value = 0.727 ± 0.041 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
16 5 7 14 3 8 17 23 15 21 10 11 12 1 2 13 22 9 19 20 6 4 18 RA Md SV
Laboratory

z Scores: S3 - Fluoranthene
Target Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z Score
-1.8 -1.2 -1.2 -0.8 -0.3 -0.3 -0.3 -0.3 -0.2 -0.1 0.2 0.2 0.2 0.3 0.3 0.5 0.5 0.7 0.7 0.7 1.1
16 5 7 14 3 8 17 23 15 21 10 11 12 1 2 13 22 9 19 20 6
Laboratory

En Scores: S3 - Fluoranthene
$E_n$ Score
-3.9 -0.8 -0.6 -0.3 -0.3 -0.7 -0.3 -0.1 -0.1 -0.3 0.1 0.1 0.1 0.1 0.1 0.2 0.2 0.4 0.2 0.2 0.5
16 5 7 14 3 8 17 23 15 21 10 11 12 1 2 13 22 9 19 20 6
Laboratory


Figure 15

Table 20

**Sample Details**

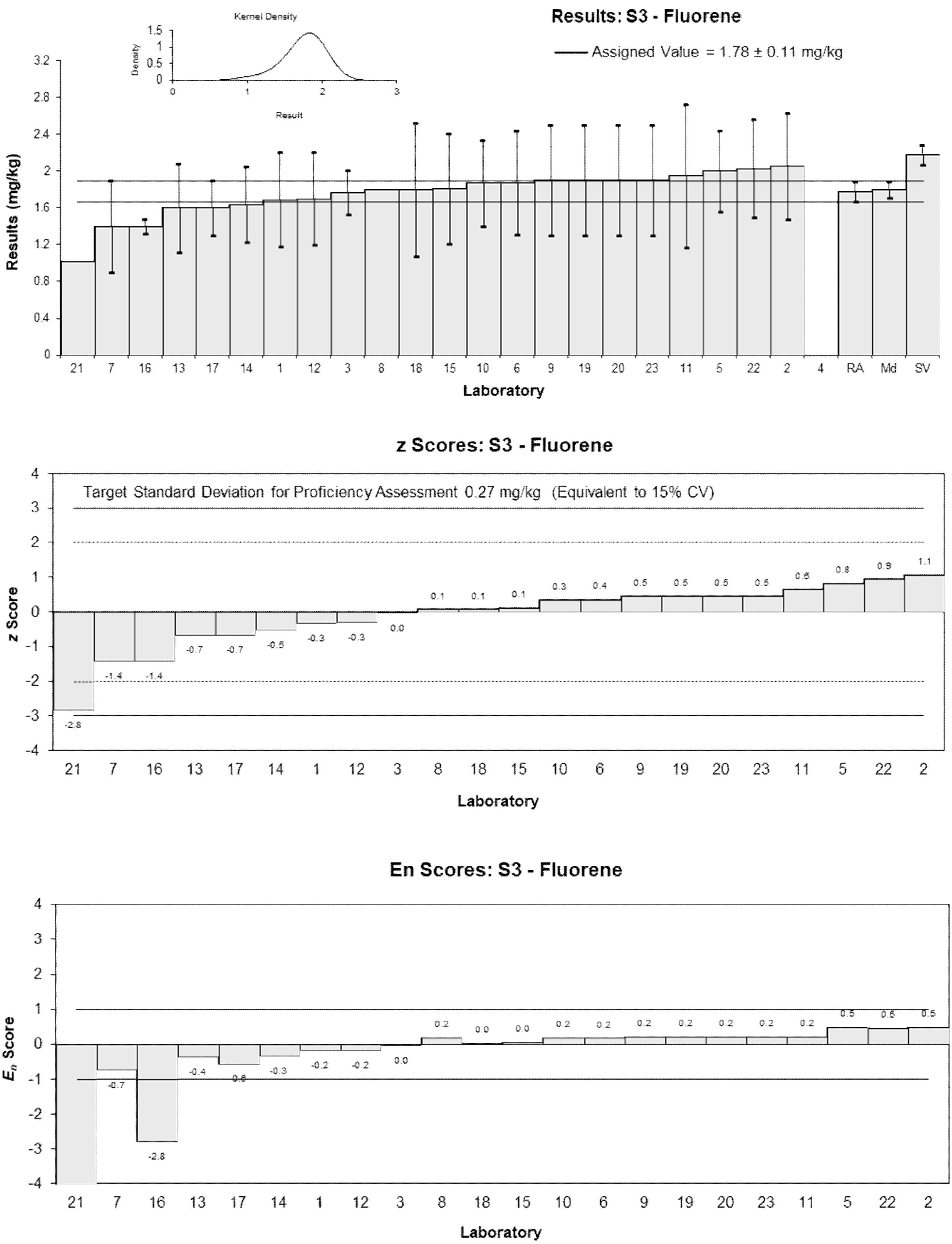
| | |
|---|---|
| **Sample** | S3 |
| **Analyte** | Fluorene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1.69 | 0.51 | -0.34 | -0.17 |
| **2** | 2.06 | 0.58 | 1.05 | 0.47 |
| **3** | 1.77 | 0.24 | -0.04 | -0.04 |
| **4** | NS | NS | | |
| **5** | 2 | 0.44 | 0.82 | 0.49 |
| **6** | 1.875 | 0.5625 | 0.36 | 0.17 |
| **7** | 1.4 | 0.5 | -1.42 | -0.74 |
| **8** | 1.8 | NR | 0.07 | 0.18 |
| **9** | 1.9 | 0.6 | 0.45 | 0.20 |
| **10** | 1.871 | 0.467 | 0.34 | 0.19 |
| **11** | 1.95 | 0.78 | 0.64 | 0.22 |
| **12** | 1.7 | 0.5 | -0.30 | -0.16 |
| **13** | 1.6 | 0.48 | -0.67 | -0.37 |
| **14** | 1.64 | 0.41 | -0.52 | -0.33 |
| **15** | 1.806 | 0.6 | 0.10 | 0.04 |
| **16** | 1.4 | 0.08 | -1.42 | -2.79 |
| **17** | 1.6 | 0.3 | -0.67 | -0.56 |
| **18** | 1.8 | 0.72 | 0.07 | 0.03 |
| **19** | 1.9 | 0.6 | 0.45 | 0.20 |
| **20** | 1.9 | 0.6 | 0.45 | 0.20 |
| **21** | 1.024 | NR | -2.83 | -6.87 |
| **22** | 2.03 | 0.53 | 0.94 | 0.46 |
| **23** | 1.9 | 0.6 | 0.45 | 0.20 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.78 | 0.11 |
| **Spiked Value** | 2.18 | 0.11 |
| **Robust Average** | 1.78 | 0.11 |
| **Median** | 1.80 | 0.09 |
| **Mean** | 1.76 | 0.10 |
| **N** | 22 | |
| **Max** | 2.06 | |
| **Min** | 1.024 | |
| **Robust SD** | 0.20 | |
| **Robust CV (%)** | 11 | |



Results: S3 - Fluorene
Assigned Value = 1.78 ± 0.11 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
21 7 16 13 17 14 1 12 3 8 18 15 10 6 9 19 20 23 11 5 22 2 4 RA Md SV
Laboratory
z Scores: S3 - Fluorene
Target Standard Deviation for Proficiency Assessment 0.27 mg/kg (Equivalent to 15% CV)
z Score
21 7 16 13 17 14 1 12 3 8 18 15 10 6 9 19 20 23 11 5 22 2
Laboratory
En Scores: S3 - Fluorene
$E_n$ Score
21 7 16 13 17 14 1 12 3 8 18 15 10 6 9 19 20 23 11 5 22 2
Laboratory


Figure 16

Table 21

**Sample Details**

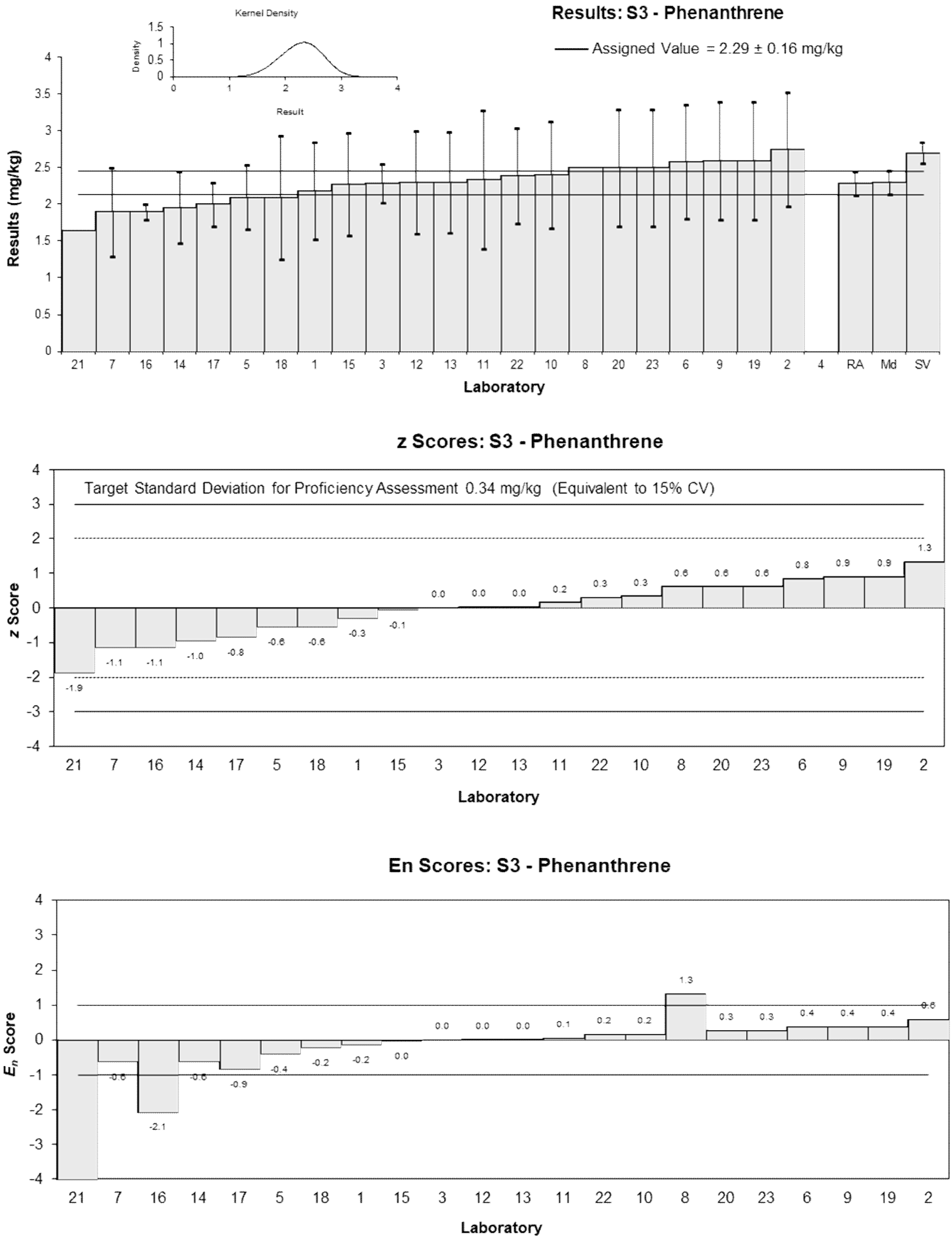
| | |
|---|---|
| **Sample** | S3 |
| **Analyte** | Phenanthrene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2.19 | 0.66 | -0.29 | -0.15 |
| **2** | 2.75 | 0.77 | 1.34 | 0.58 |
| **3** | 2.29 | 0.26 | 0.00 | 0.00 |
| **4** | NS | NS | | |
| **5** | 2.1 | 0.44 | -0.55 | -0.41 |
| **6** | 2.58 | 0.774 | 0.84 | 0.37 |
| **7** | 1.9 | 0.6 | -1.14 | -0.63 |
| **8** | 2.5 | NR | 0.61 | 1.31 |
| **9** | 2.6 | 0.8 | 0.90 | 0.38 |
| **10** | 2.406 | 0.721 | 0.34 | 0.16 |
| **11** | 2.34 | 0.94 | 0.15 | 0.05 |
| **12** | 2.3 | 0.7 | 0.03 | 0.01 |
| **13** | 2.3 | 0.68 | 0.03 | 0.01 |
| **14** | 1.96 | 0.49 | -0.96 | -0.64 |
| **15** | 2.271 | 0.7 | -0.06 | -0.03 |
| **16** | 1.9 | 0.1 | -1.14 | -2.07 |
| **17** | 2.0 | 0.3 | -0.84 | -0.85 |
| **18** | 2.1 | 0.84 | -0.55 | -0.22 |
| **19** | 2.6 | 0.8 | 0.90 | 0.38 |
| **20** | 2.5 | 0.8 | 0.61 | 0.26 |
| **21** | 1.645 | NR | -1.88 | -4.03 |
| **22** | 2.39 | 0.65 | 0.29 | 0.15 |
| **23** | 2.5 | 0.8 | 0.61 | 0.26 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.29 | 0.16 |
| **Spiked Value** | 2.70 | 0.14 |
| **Robust Average** | 2.29 | 0.16 |
| **Median** | 2.30 | 0.16 |
| **Mean** | 2.28 | 0.12 |
| **N** | 22 | |
| **Max** | 2.75 | |
| **Min** | 1.645 | |
| **Robust SD** | 0.29 | |
| **Robust CV (%)** | 13 | |



Results: S3 - Phenanthrene
Assigned Value = 2.29 ± 0.16 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
21 7 16 14 17 5 18 1 15 3 12 13 11 22 10 8 20 23 6 9 19 2 4 RA Md SV
z Scores: S3 - Phenanthrene
Target Standard Deviation for Proficiency Assessment 0.34 mg/kg (Equivalent to 15% CV)
z Score
-1.9 -1.1 -1.1 -1.0 -0.8 -0.6 -0.6 -0.3 -0.1 0.0 0.0 0.0 0.2 0.3 0.3 0.6 0.6 0.6 0.8 0.9 0.9 1.3
Laboratory
21 7 16 14 17 5 18 1 15 3 12 13 11 22 10 8 20 23 6 9 19 2
En Scores: S3 - Phenanthrene
En Score
-0.6 -2.1 -0.6 -0.9 -0.4 -0.2 -0.2 0.0 0.0 0.0 0.0 0.1 0.2 0.2 1.3 0.3 0.3 0.4 0.4 0.4 0.6
Laboratory
21 7 16 14 17 5 18 1 15 3 12 13 11 22 10 8 20 23 6 9 19 2


Figure 17

Table 22

**Sample Details**

| | |
|---|---|
| **Sample** | S3 |
| **Analyte** | Pyrene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1.15 | 0.35 | 0.43 | 0.20 |
| **2** | 1.21 | 0.42 | 0.80 | 0.31 |
| **3** | 1.01 | 0.2 | -0.43 | -0.34 |
| **4** | NS | NS | | |
| **5** | 0.7 | 0.22 | -2.35 | -1.67 |
| **6** | 1.25 | 0.375 | 1.05 | 0.45 |
| **7** | 0.8 | 0.3 | -1.73 | -0.92 |
| **8** | 1.1 | NR | 0.12 | 0.33 |
| **9** | 1.1 | 0.3 | 0.12 | 0.07 |
| **10** | 1.178 | 0.412 | 0.60 | 0.24 |
| **11** | 1.1 | 0.44 | 0.12 | 0.05 |
| **12** | 1.0 | 0.3 | -0.49 | -0.26 |
| **13** | 1.2 | 0.35 | 0.74 | 0.34 |
| **14** | 0.90 | 0.30 | -1.11 | -0.59 |
| **15** | 1.021 | 0.3 | -0.36 | -0.19 |
| **16** | <0.1 | 0.01 | | |
| **17** | 1.0 | 0.2 | -0.49 | -0.38 |
| **18** | 1.1 | 0.44 | 0.12 | 0.05 |
| **19** | 1.1 | 0.3 | 0.12 | 0.07 |
| **20** | 1.1 | 0.3 | 0.12 | 0.07 |
| **21** | 1.03 | NR | -0.31 | -0.83 |
| **22** | 1.2 | 0.3 | 0.74 | 0.39 |
| **23** | 1.1 | 0.3 | 0.12 | 0.07 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.08 | 0.06 |
| **Spiked Value** | 1.29 | 0.06 |
| **Robust Average** | 1.08 | 0.06 |
| **Median** | 1.10 | 0.06 |
| **Mean** | 1.06 | 0.06 |
| **N** | 21 | |
| **Max** | 1.25 | |
| **Min** | 0.7 | |
| **Robust SD** | 0.11 | |
| **Robust CV (%)** | 11 | |

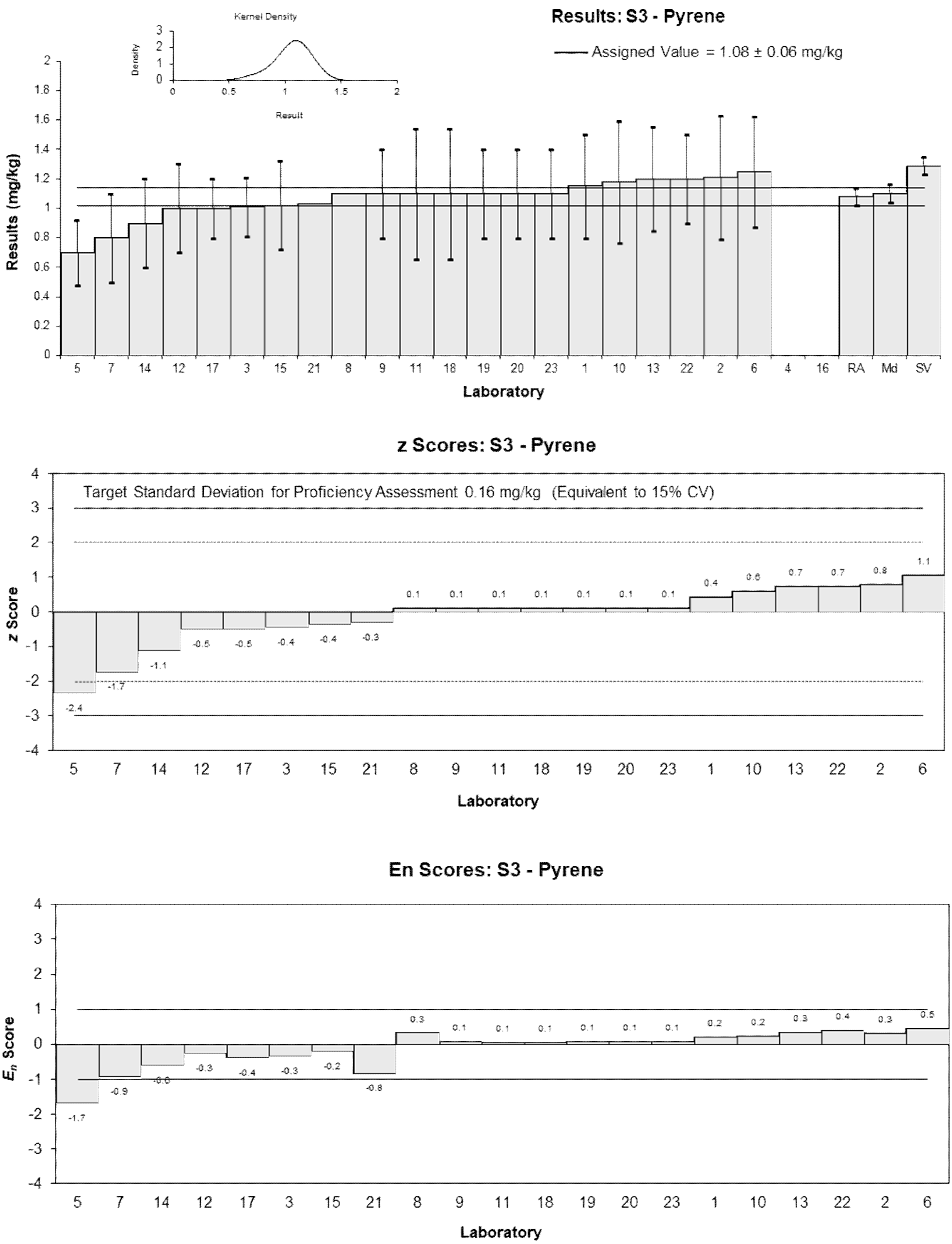

Results: S3 - Pyrene
Assigned Value = 1.08 ± 0.06 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5 7 14 12 17 3 15 21 8 9 11 18 19 20 23 1 10 13 22 2 6 4 16 RA Md SV
z Scores: S3 - Pyrene
Target Standard Deviation for Proficiency Assessment 0.16 mg/kg (Equivalent to 15% CV)
-2.4 -1.7 -1.1 -0.5 -0.5 -0.4 -0.4 -0.3 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.4 0.6 0.7 0.7 0.8 1.1
z Score
Laboratory
5 7 14 12 17 3 15 21 8 9 11 18 19 20 23 1 10 13 22 2 6
En Scores: S3 - Pyrene
-1.7 -0.9 -0.6 -0.3 -0.4 -0.3 -0.2 -0.8 0.3 0.1 0.1 0.1 0.1 0.1 0.1 0.2 0.2 0.3 0.4 0.3 0.5
$E_n$ Score
Laboratory
5 7 14 12 17 3 15 21 8 9 11 18 19 20 23 1 10 13 22 2 6

Figure 18

Table 23

**Sample Details**

| | |
|---|---|
| **Sample** | S4 |
| **Analyte** | Anthracene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

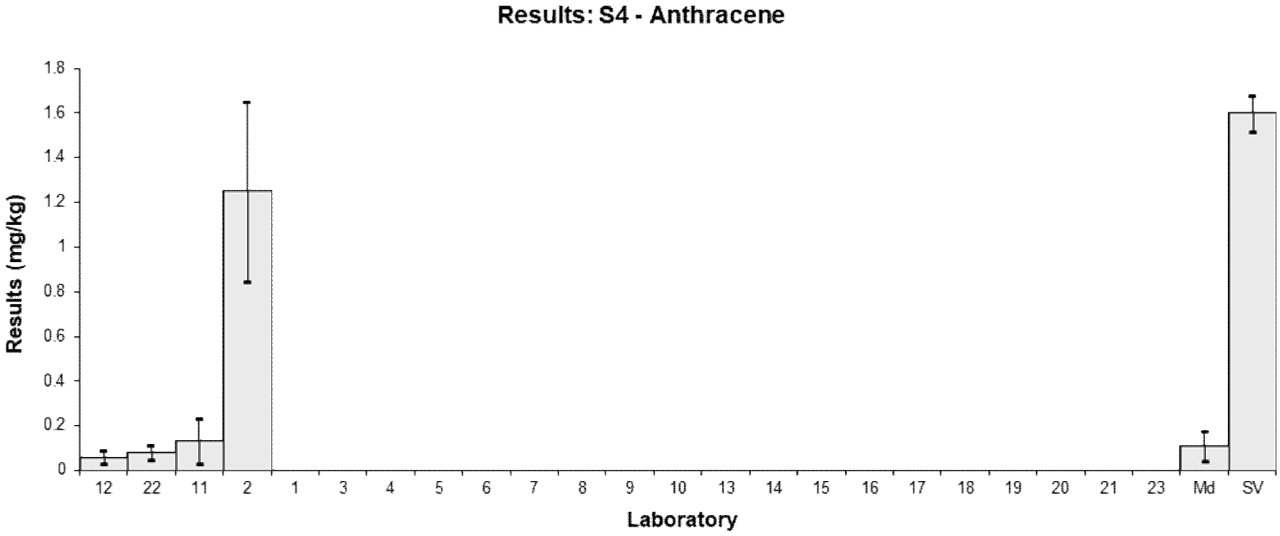
**Participant Results**

| Lab. Code | Result | U |
|---|---|---|
| **1** | < 0.5 | 1.5 |
| **2** | 1.25 | 0.4 |
| **3** | <0.5 | NR |
| **4** | NS | NS |
| **5** | <0.5 | 0.13 |
| **6*** | NR | NR |
| **7** | <0.1 | NR |
| **8** | <0.5 | NR |
| **9** | <0.1 | NR |
| **10** | <0.5 | 0.15 |
| **11** | 0.13 | 0.1 |
| **12** | 0.06 | 0.03 |
| **13** | <0.5 | NR |
| **14** | <0.5 | NR |
| **15** | < 0.5 | 0.2 |
| **16** | <0.1 | 0.01 |
| **17** | <0.5 | NR |
| **18** | <1 | NR |
| **19** | <0.1 | NR |
| **20** | <0.1 | NR |
| **21** | <0.05 | NR |
| **22** | 0.08 | 0.03 |
| **23** | <0.1 | NR |

* Result changed from 0 to NR

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spiked Value** | 1.60 | 0.08 |
| **Median** | 0.110 | 0.065 |
| **Mean** | 0.38 | 0.58 |
| **N** | 4 | |
| **Max** | 1.25 | |
| **Min** | 0.06 | |



Results: S4 - Anthracene
Results (mg/kg)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
12
22
11
2
1
3
4
5
6
7
8
9
10
13
14
15
16
17
18
19
20
21
23
Md
SV
Laboratory


Figure 19

Table 24

**Sample Details**

| | |
|---|---|
| **Sample** | S4 |
| **Analyte** | Chrysene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| 1 | 1.12 | 0.34 | -0.12 | -0.06 |
| 2 | 0.951 | 0.29 | -1.11 | -0.62 |
| 3 | 1.16 | 0.24 | 0.12 | 0.08 |
| 4 | NS | NS | | |
| 5 | 1.3 | 0.37 | 0.94 | 0.42 |
| 6 | 1.2 | 0.36 | 0.35 | 0.16 |
| 7 | 1.1 | 0.3 | -0.23 | -0.13 |
| 8 | 1.1 | NR | -0.23 | -0.40 |
| 9 | 1.6 | 0.5 | 2.00▼ | 0.90 |
| 10 | 1.353 | 0.473 | 1.25 | 0.44 |
| 11 | 1.09 | 0.44 | -0.29 | -0.11 |
| 12 | 0.94 | 0.29 | -1.17 | -0.65 |
| 13 | 1.0 | 0.30 | -0.82 | -0.44 |
| 14 | 0.93 | 0.30 | -1.23 | -0.66 |
| 15 | 1.181 | 0.4 | 0.24 | 0.10 |
| 16 | 0.95 | 0.05 | -1.11 | -1.70 |
| 17 | 1.1 | 0.3 | -0.23 | -0.13 |
| 18 | 1.0 | 0.4 | -0.82 | -0.34 |
| 19 | 1.3 | 0.3 | 0.94 | 0.51 |
| 20 | 1 | 0.3 | -0.82 | -0.44 |
| 21 | 1.452 | NR | 1.82 | 3.12 |
| 22 | 1.36 | 0.38 | 1.29 | 0.56 |
| 23 | 1.2 | 0.3 | 0.35 | 0.19 |

▼ Adjusted score

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.14 | 0.10 |
| **Spiked Value** | 1.49 | 0.07 |
| **Robust Average** | 1.14 | 0.10 |
| **Max Acceptable Result** | 1.83 | |
| **Median** | 1.11 | 0.09 |
| **Mean** | 1.15 | 0.08 |
| **N** | 22 | |
| **Max** | 1.6 | |
| **Min** | 0.93 | |
| **Robust SD** | 0.18 | |
| **Robust CV (%)** | 16 | |

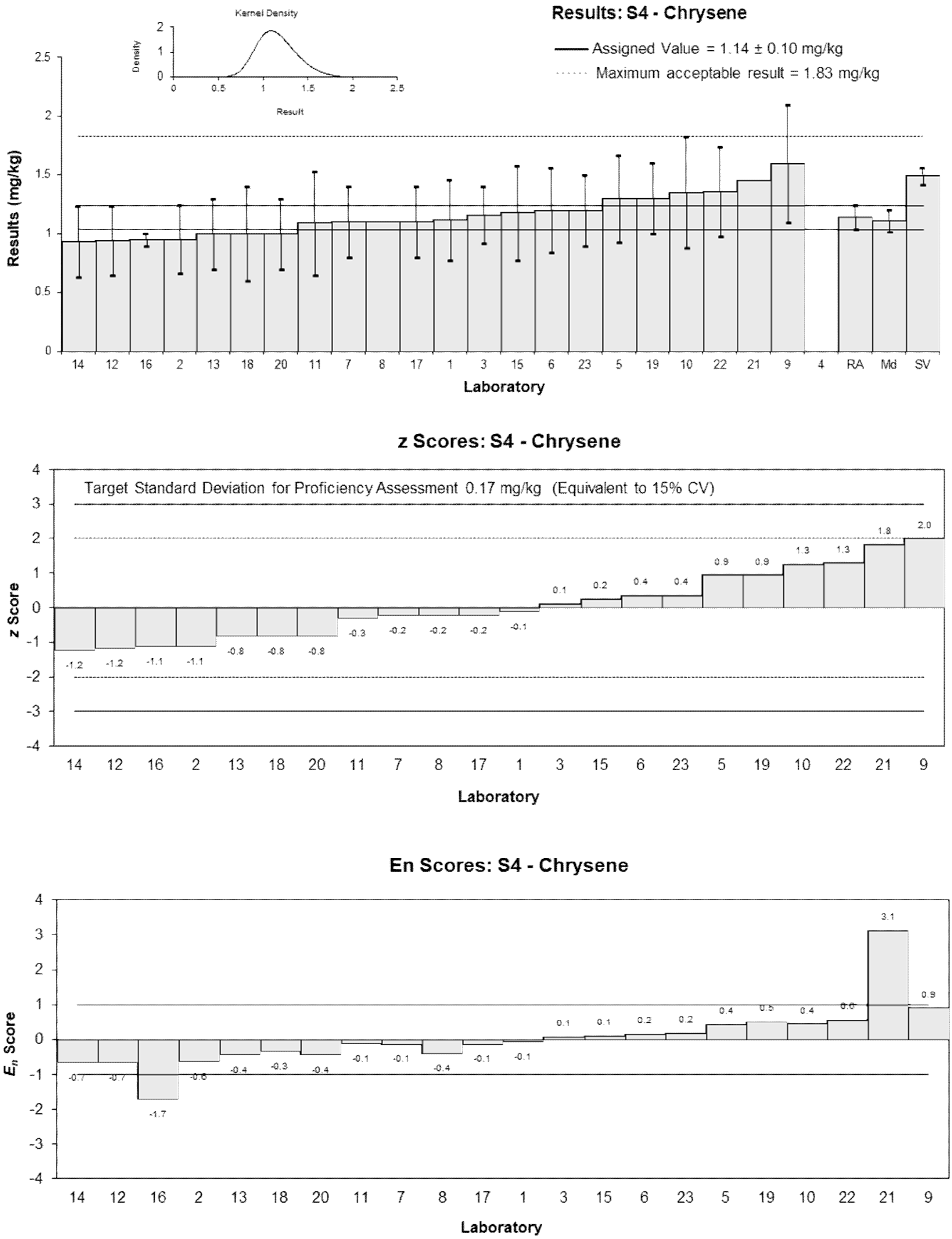

Results: S4 - Chrysene
Assigned Value = 1.14 ± 0.10 mg/kg
Maximum acceptable result = 1.83 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 12 16 2 13 18 20 11 7 8 17 1 3 15 6 23 5 19 10 22 21 9 4 RA Md SV
z Scores: S4 - Chrysene
Target Standard Deviation for Proficiency Assessment 0.17 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
14 12 16 2 13 18 20 11 7 8 17 1 3 15 6 23 5 19 10 22 21 9
En Scores: S4 - Chrysene
$E_n$ Score
Laboratory
14 12 16 2 13 18 20 11 7 8 17 1 3 15 6 23 5 19 10 22 21 9

Figure 20

Table 25

**Sample Details**

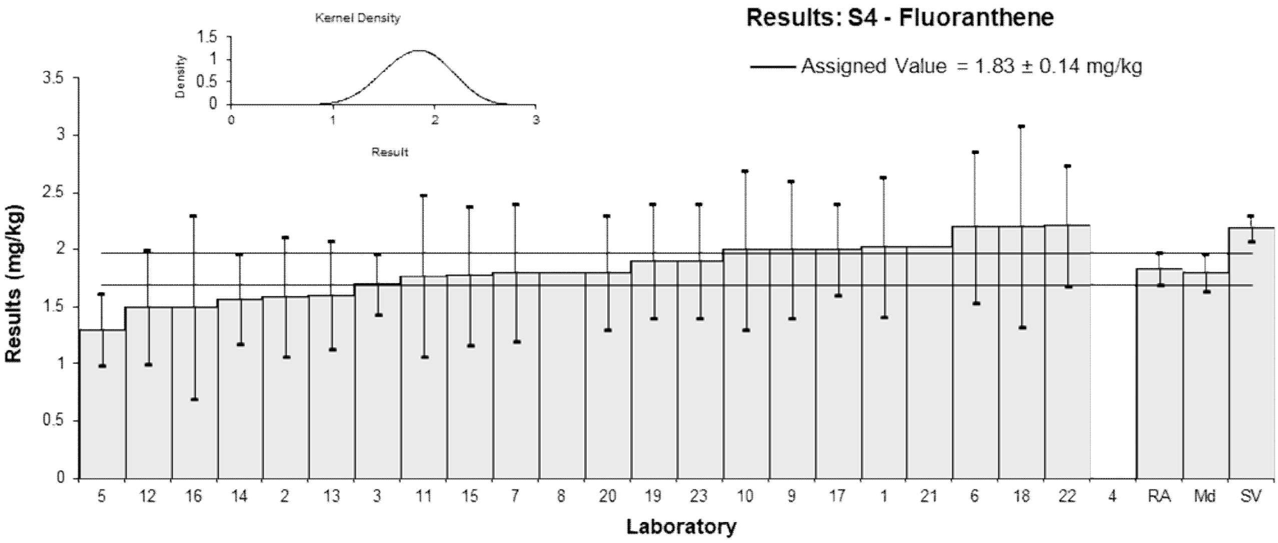
| | |
|---|---|
| **Sample** | S4 |
| **Analyte** | Fluoranthene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

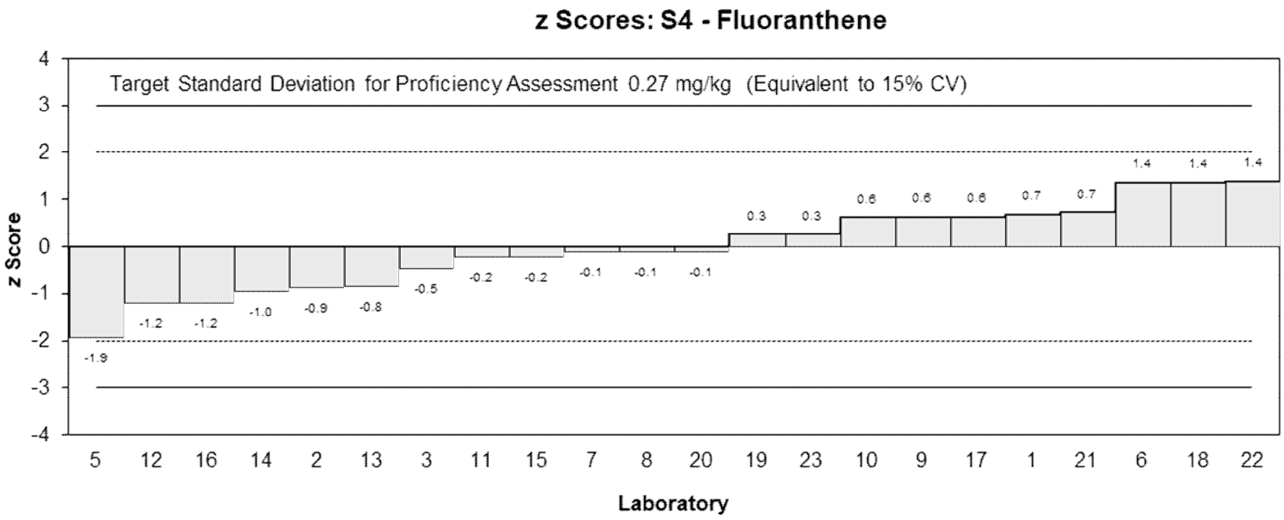
**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2.02 | 0.61 | 0.69 | 0.30 |
| **2** | 1.59 | 0.52 | -0.87 | -0.45 |
| **3** | 1.7 | 0.26 | -0.47 | -0.44 |
| **4** | NS | NS | | |
| **5** | 1.3 | 0.31 | -1.93 | -1.56 |
| **6** | 2.2 | 0.66 | 1.35 | 0.55 |
| **7** | 1.8 | 0.6 | -0.11 | -0.05 |
| **8** | 1.8 | NR | -0.11 | -0.21 |
| **9** | 2.0 | 0.6 | 0.62 | 0.28 |
| **10** | 1.997 | 0.698 | 0.61 | 0.23 |
| **11** | 1.77 | 0.71 | -0.22 | -0.08 |
| **12** | 1.5 | 0.5 | -1.20 | -0.64 |
| **13** | 1.6 | 0.47 | -0.84 | -0.47 |
| **14** | 1.57 | 0.39 | -0.95 | -0.63 |
| **15** | 1.772 | 0.6 | -0.21 | -0.09 |
| **16** | 1.5 | 0.8 | -1.20 | -0.41 |
| **17** | 2.0 | 0.4 | 0.62 | 0.40 |
| **18** | 2.2 | 0.88 | 1.35 | 0.42 |
| **19** | 1.9 | 0.5 | 0.26 | 0.13 |
| **20** | 1.8 | 0.5 | -0.11 | -0.06 |
| **21** | 2.029 | NR | 0.72 | 1.42 |
| **22** | 2.21 | 0.53 | 1.38 | 0.69 |
| **23** | 1.9 | 0.5 | 0.26 | 0.13 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.83 | 0.14 |
| **Spiked Value** | 2.19 | 0.11 |
| **Robust Average** | 1.83 | 0.14 |
| **Median** | 1.80 | 0.16 |
| **Mean** | 1.83 | 0.11 |
| **N** | 22 | |
| **Max** | 2.21 | |
| **Min** | 1.3 | |
| **Robust SD** | 0.27 | |
| **Robust CV (%)** | 15 | |


Results: S4 - Fluoranthene
Assigned Value = 1.83 ± 0.14 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5 12 16 14 2 13 3 11 15 7 8 20 19 23 10 9 17 1 21 6 18 22 4 RA Md SV


z Scores: S4 - Fluoranthene
Target Standard Deviation for Proficiency Assessment 0.27 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
5 12 16 14 2 13 3 11 15 7 8 20 19 23 10 9 17 1 21 6 18 22

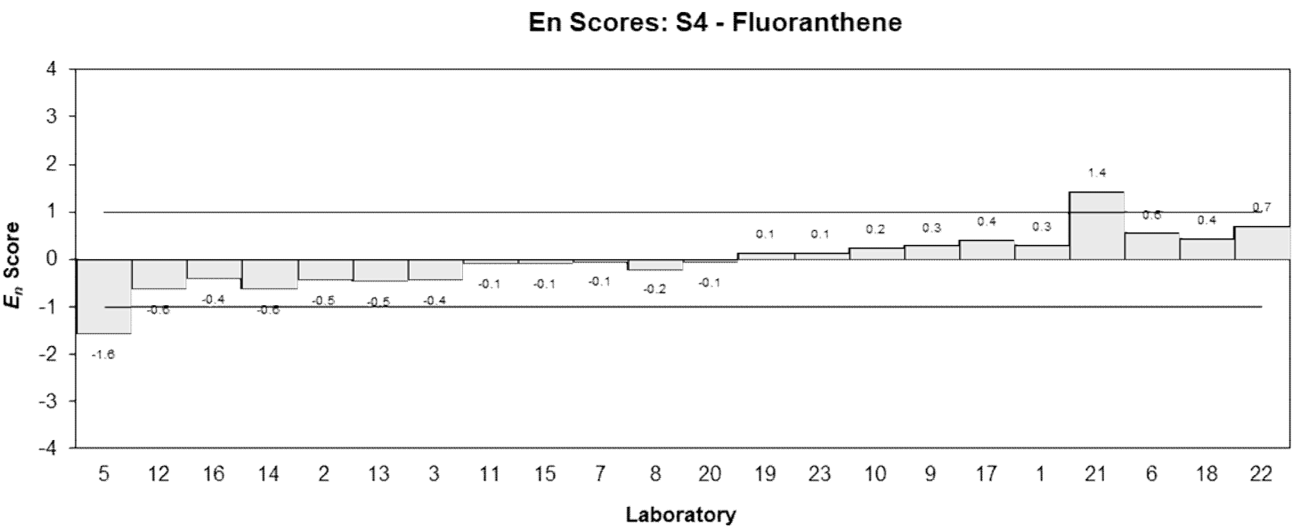

En Scores: S4 - Fluoranthene
$E_n$ Score
Laboratory
5 12 16 14 2 13 3 11 15 7 8 20 19 23 10 9 17 1 21 6 18 22

Figure 21

Table 26

**Sample Details**

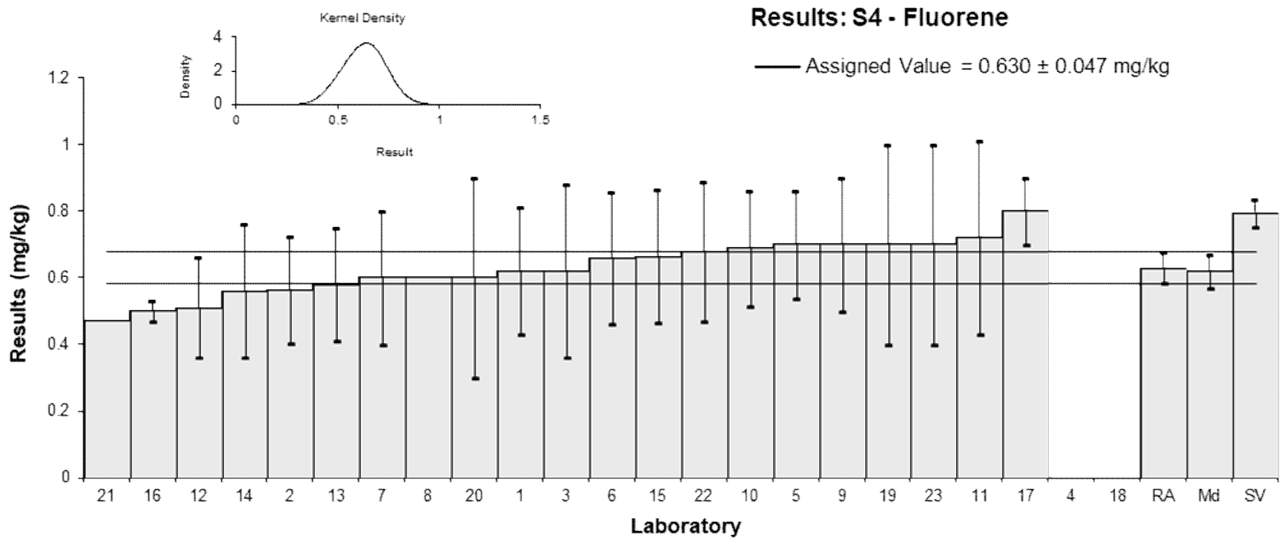
| | |
|---|---|
| **Sample** | S4 |
| **Analyte** | Fluorene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

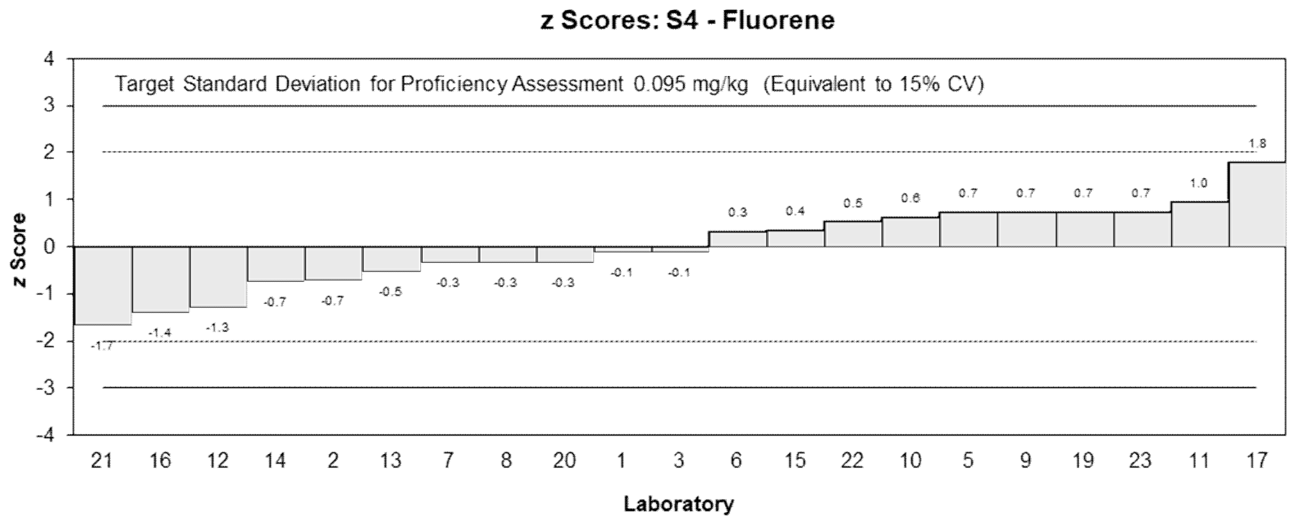
| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.62 | 0.19 | -0.11 | -0.05 |
| **2** | 0.564 | 0.16 | -0.70 | -0.40 |
| **3** | 0.62 | 0.26 | -0.11 | -0.04 |
| **4** | NS | NS | | |
| **5** | 0.7 | 0.16 | 0.74 | 0.42 |
| **6** | 0.66 | 0.198 | 0.32 | 0.15 |
| **7** | 0.6 | 0.2 | -0.32 | -0.15 |
| **8** | 0.6 | NR | -0.32 | -0.64 |
| **9** | 0.7 | 0.2 | 0.74 | 0.34 |
| **10** | 0.689 | 0.172 | 0.62 | 0.33 |
| **11** | 0.72 | 0.29 | 0.95 | 0.31 |
| **12** | 0.51 | 0.15 | -1.27 | -0.76 |
| **13** | 0.58 | 0.17 | -0.53 | -0.28 |
| **14** | 0.56 | 0.20 | -0.74 | -0.34 |
| **15** | 0.664 | 0.2 | 0.36 | 0.17 |
| **16** | 0.50 | 0.03 | -1.38 | -2.33 |
| **17** | 0.8 | 0.1 | 1.80 | 1.54 |
| **18** | <1 | NR | | |
| **19** | 0.7 | 0.3 | 0.74 | 0.23 |
| **20** | 0.6 | 0.3 | -0.32 | -0.10 |
| **21** | 0.472 | NR | -1.67 | -3.36 |
| **22** | 0.68 | 0.21 | 0.53 | 0.23 |
| **23** | 0.7 | 0.3 | 0.74 | 0.23 |

**Statistics**

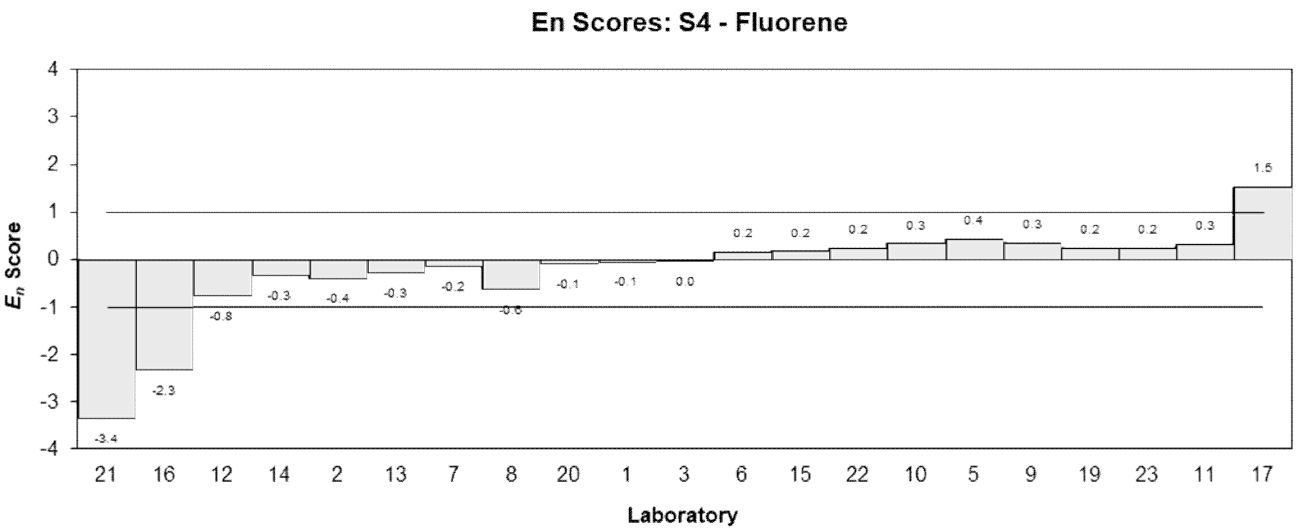
| | | |
|---|---|---|
| **Assigned Value** | 0.630 | 0.047 |
| **Spiked Value** | 0.795 | 0.040 |
| **Robust Average** | 0.630 | 0.047 |
| **Median** | 0.620 | 0.049 |
| **Mean** | 0.630 | 0.036 |
| **N** | 21 | |
| **Max** | 0.8 | |
| **Min** | 0.472 | |
| **Robust SD** | 0.086 | |
| **Robust CV (%)** | 14 | |



Results: S4 - Fluorene
Assigned Value = 0.630 ± 0.047 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
21 16 12 14 2 13 7 8 20 1 3 6 15 22 10 5 9 19 23 11 17 4 18 RA Md SV

z Scores: S4 - Fluorene
Target Standard Deviation for Proficiency Assessment 0.095 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
21 16 12 14 2 13 7 8 20 1 3 6 15 22 10 5 9 19 23 11 17

En Scores: S4 - Fluorene
$E_n$ Score
Laboratory
21 16 12 14 2 13 7 8 20 1 3 6 15 22 10 5 9 19 23 11 17


Figure 22

Table 27

**Sample Details**

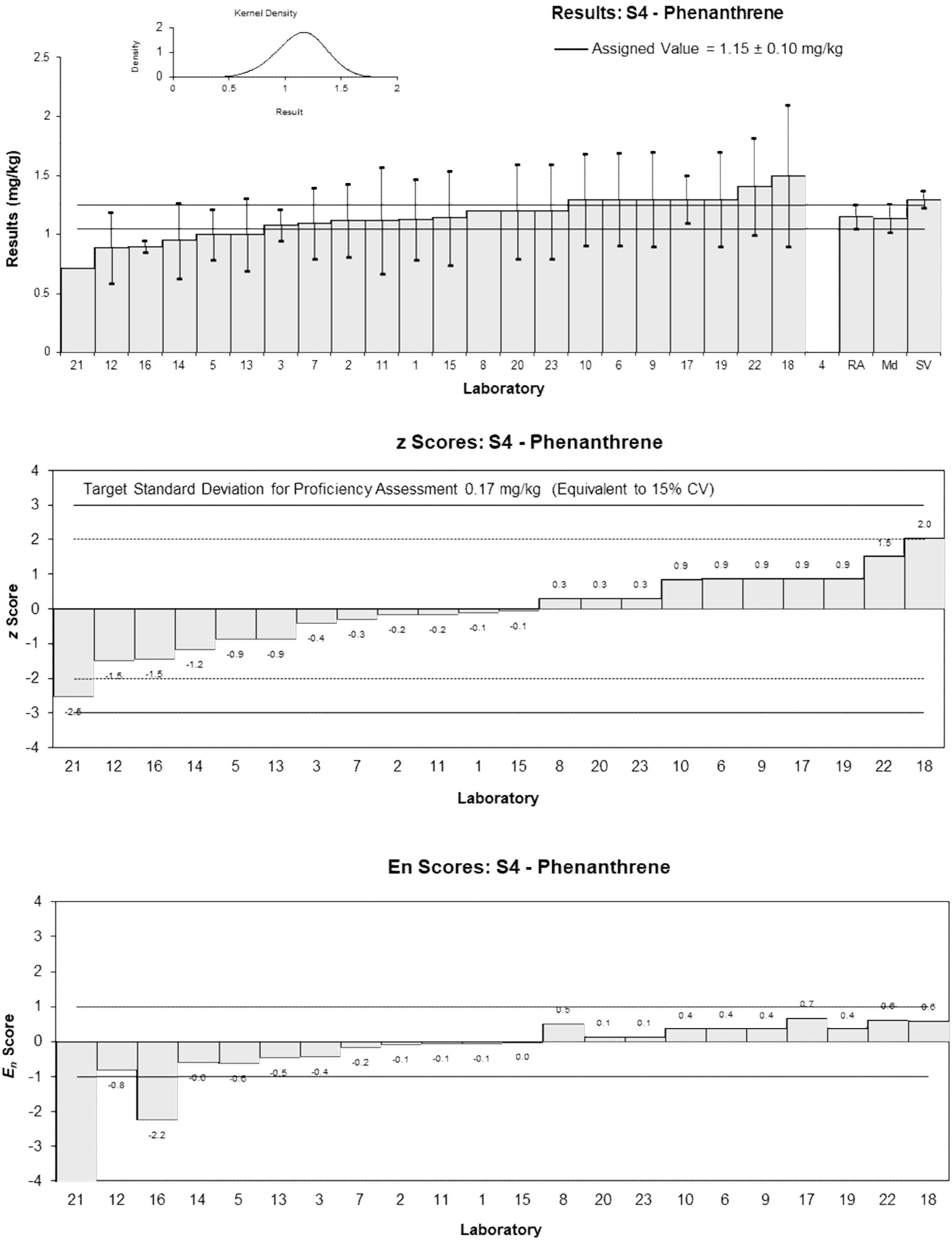
| | |
|---|---|
| **Sample** | S4 |
| **Analyte** | Phenanthrene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

**Participant Results**

| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1.13 | 0.34 | -0.12 | -0.06 |
| **2** | 1.12 | 0.31 | -0.17 | -0.09 |
| **3** | 1.08 | 0.13 | -0.41 | -0.43 |
| **4** | NS | NS | | |
| **5** | 1 | 0.21 | -0.87 | -0.64 |
| **6** | 1.3 | 0.39 | 0.87 | 0.37 |
| **7** | 1.1 | 0.3 | -0.29 | -0.16 |
| **8** | 1.2 | NR | 0.29 | 0.50 |
| **9** | 1.3 | 0.4 | 0.87 | 0.36 |
| **10** | 1.296 | 0.388 | 0.85 | 0.36 |
| **11** | 1.12 | 0.45 | -0.17 | -0.07 |
| **12** | 0.89 | 0.30 | -1.51 | -0.82 |
| **13** | 1.0 | 0.31 | -0.87 | -0.46 |
| **14** | 0.95 | 0.32 | -1.16 | -0.60 |
| **15** | 1.142 | 0.4 | -0.05 | -0.02 |
| **16** | 0.90 | 0.05 | -1.45 | -2.24 |
| **17** | 1.3 | 0.2 | 0.87 | 0.67 |
| **18** | 1.5 | 0.6 | 2.03 | 0.58 |
| **19** | 1.3 | 0.4 | 0.87 | 0.36 |
| **20** | 1.2 | 0.4 | 0.29 | 0.12 |
| **21** | 0.715 | NR | -2.52 | -4.35 |
| **22** | 1.41 | 0.41 | 1.51 | 0.62 |
| **23** | 1.2 | 0.4 | 0.29 | 0.12 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.15 | 0.10 |
| **Spiked Value** | 1.30 | 0.07 |
| **Robust Average** | 1.15 | 0.10 |
| **Median** | 1.14 | 0.12 |
| **Mean** | 1.14 | 0.08 |
| **N** | 22 | |
| **Max** | 1.5 | |
| **Min** | 0.715 | |
| **Robust SD** | 0.19 | |
| **Robust CV (%)** | 16 | |



Results: S4 - Phenanthrene
Assigned Value = 1.15 ± 0.10 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
21 12 16 14 5 13 3 7 2 11 1 15 8 20 23 10 6 9 17 19 22 18 4 RA Md SV
z Scores: S4 - Phenanthrene
Target Standard Deviation for Proficiency Assessment 0.17 mg/kg (Equivalent to 15% CV)
z Score
Laboratory
En Scores: S4 - Phenanthrene
$E_n$ Score
Laboratory


Figure 23

Table 28

**Sample Details**

| | |
|---|---|
| **Sample** | S4 |
| **Analyte** | Pyrene |
| **Matrix** | Soil |
| **Unit** | mg/kg |

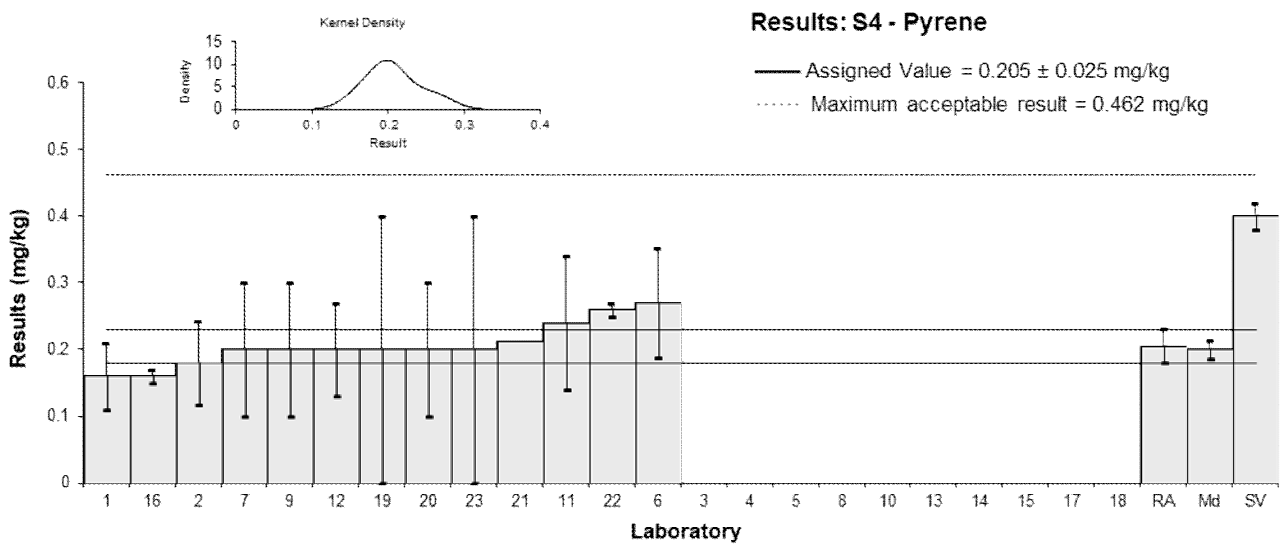
**Participant Results**

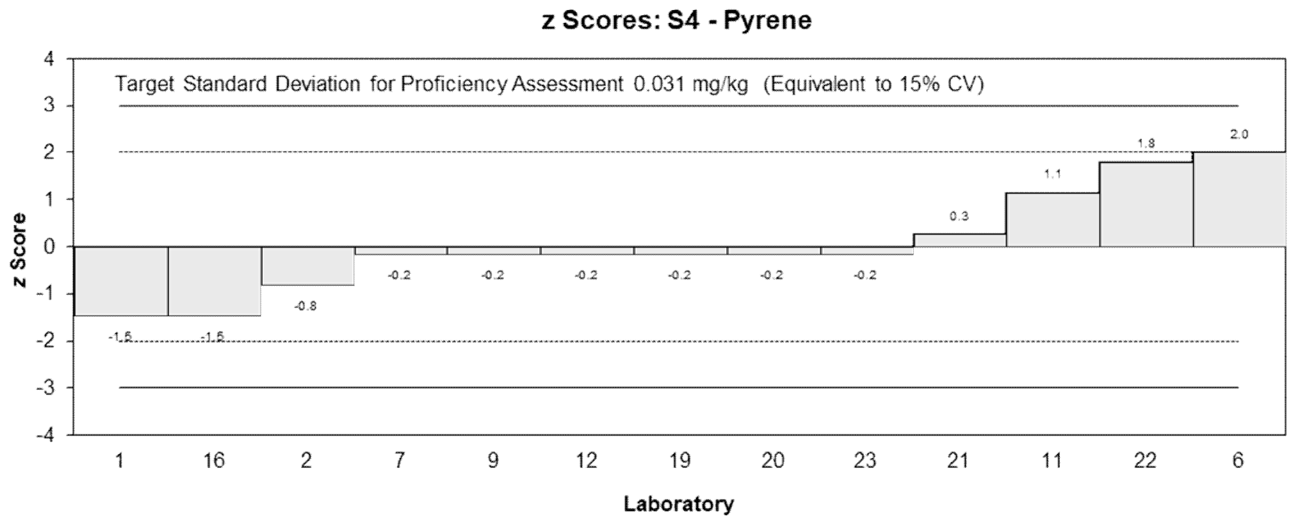
| Lab. Code | Result | U | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.16 | 0.05 | -1.46 | -0.80 |
| **2** | 0.18 | 0.063 | -0.81 | -0.37 |
| **3** | <0.5 | NR | | |
| **4** | NS | NS | | |
| **5** | <0.5 | 0.17 | | |
| **6** | 0.27 | 0.081 | 2.00▼ | 0.77 |
| **7** | 0.2 | 0.1 | -0.16 | -0.05 |
| **8** | <0.5 | NR | | |
| **9** | 0.2 | 0.1 | -0.16 | -0.05 |
| **10** | <0.5 | 0.15 | | |
| **11** | 0.24 | 0.1 | 1.14 | 0.34 |
| **12** | 0.20 | 0.07 | -0.16 | -0.07 |
| **13** | <0.5 | NR | | |
| **14** | <0.5 | NR | | |
| **15** | < 0.5 | 0.2 | | |
| **16** | 0.16 | 0.01 | -1.46 | -1.67 |
| **17** | <0.5 | NR | | |
| **18** | <1 | NR | | |
| **19** | 0.2 | 0.2 | -0.16 | -0.02 |
| **20** | 0.2 | 0.1 | -0.16 | -0.05 |
| **21** | 0.213 | NR | 0.26 | 0.32 |
| **22** | 0.26 | 0.01 | 1.79 | 2.04 |
| **23** | 0.2 | 0.2 | -0.16 | -0.02 |

▼ Adjusted score

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.205 | 0.025 |
| **Spiked Value** | 0.400 | 0.020 |
| **Robust Average** | 0.205 | 0.025 |
| **Max Acceptable Result** | 0.462 | |
| **Median** | 0.200 | 0.013 |
| **Mean** | 0.206 | 0.018 |
| **N** | 13 | |
| **Max** | 0.27 | |
| **Min** | 0.16 | |
| **Robust SD** | 0.036 | |
| **Robust CV (%)** | 17 | |


Results: S4 - Pyrene
Assigned Value = 0.205 ± 0.025 mg/kg
Maximum acceptable result = 0.462 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
1 16 2 7 9 12 19 20 23 21 11 22 6 3 4 5 8 10 13 14 15 17 18 RA Md SV
Laboratory


z Scores: S4 - Pyrene
Target Standard Deviation for Proficiency Assessment 0.031 mg/kg (Equivalent to 15% CV)
z Score
-1.5 -1.5 -0.8 -0.2 -0.2 -0.2 -0.2 -0.2 -0.2 0.3 1.1 1.8 2.0
1 16 2 7 9 12 19 20 23 21 11 22 6
Laboratory

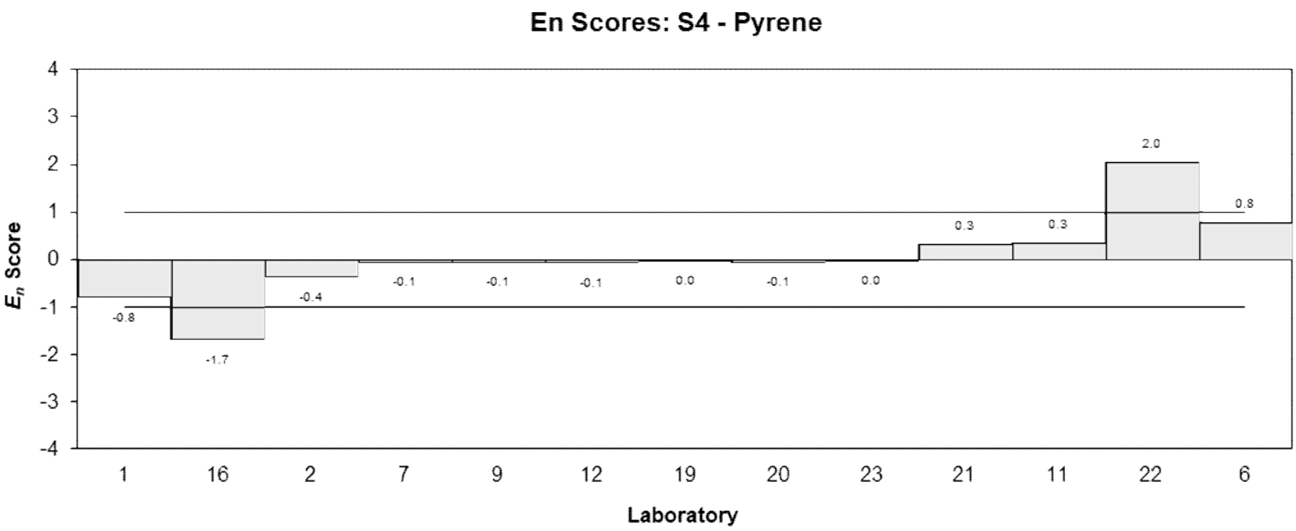

En Scores: S4 - Pyrene
En Score
-0.8 -1.7 -0.4 -0.1 -0.1 -0.1 0.0 -0.1 0.0 0.3 0.3 2.0 0.8
1 16 2 7 9 12 19 20 23 21 11 22 6
Laboratory

Figure 24

## 6 DISCUSSION OF RESULTS

### 6.1 Assigned Value

The robust averages of participants' results were used as the assigned values for all scored analytes. The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528:2015.[7] Results less than 50% and greater than 150% of the robust average were removed before calculation of the assigned value.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 4, using Sample S4 phenanthrene as an example.

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

No assigned values were set for Sample S2 benzene and Sample S4 anthracene as these analytes had poor recovery rates and the numeric results that were reported were highly variable. Sample S2 C6-C10 range was also not scored because of its volatile nature; participants' results have been provided for information only.

A comparison of the assigned values (or robust averages if no assigned value was set) and the spiked values is presented in Table 29. The assigned values for TRH were within the range of 97% to 105% of the spiked values, showing good consensus between the spiked and assigned values. The assigned values for scored BTEX and PAHs were within the ranges of 60% to 86% and 51% to 88% of the spiked values respectively. Similar ratios have been observed in previous PT studies, and an assigned value was set if there was a reasonable consensus of participants' results.

Table 29 Comparison of Assigned Value (or Robust Average) and Spiked Value

| Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Assigned Value *(Robust Average)* / Spiked Value (%) |
|---|---|---|---|---|
| S1 | >C10-C16 | 1080 | 1110 | 97 |
| | >C16-C34 | 1590 | 1570 | 101 |
| | >C34-C40 | 182 | 174 | 105 |
| | TRH | 2800 | 2860 | 98 |
| S2 | Benzene | *(27.3)* | 82.1 | *(33)* |
| | Toluene | 234 | 393 | 60 |
| | Ethylbenzene | 38.6 | 45.0 | 86 |
| | Xylenes | 238 | 337 | 71 |
| | Total BTEX | 532 | 858 | 62 |
| S3 | Anthracene | 0.844 | 1.29 | 65 |
| | Benzo[*a*]pyrene | 1.20 | 1.98 | 61 |
| | Chrysene | 0.541 | 0.699 | 77 |
| | Fluoranthene | 0.727 | 0.895 | 81 |
| | Fluorene | 1.78 | 2.18 | 82 |
| | Phenanthrene | 2.29 | 2.70 | 85 |
| | Pyrene | 1.08 | 1.29 | 84 |

| Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Assigned Value *(Robust Average)* / Spiked Value (%) |
|---|---|---|---|---|
| S4 | Anthracene | *(0.38)* | 1.60 | *(24)* |
| | Chrysene | 1.14 | 1.49 | 77 |
| | Fluoranthene | 1.83 | 2.19 | 84 |
| | Fluorene | 0.630 | 0.795 | 79 |
| | Phenanthrene | 1.15 | 1.30 | 88 |
| | Pyrene | 0.205 | 0.400 | 51 |

### 6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report estimates of the expanded uncertainty associated with their results. It is a requirement of ISO/IEC 17025:2017 that laboratories have procedures to estimate the uncertainty of chemical measurements and to report this uncertainty in specific circumstances, including when the client's instruction so requires.[9]

Of 437 numeric results, 403 results (92%) were reported with an associated expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 3). A number of participants reported using the NATA GAG Estimating and Reporting MU or Technical Note 33 as their guide; NATA no longer publishes these documents.[11]

Laboratories **7**, **8**, **21** did not report uncertainties for at least one of their reported numeric results; all of these participants reported being accredited to ISO/IEC 17025.

The magnitude of the reported expanded uncertainties was within the range 3.8% to 100% of the reported value. In general, an expanded uncertainty of less than 15% relative is likely to be unrealistically small for the routine measurement of a hydrocarbon pollutant in soil, while an expanded uncertainty of over 50% is likely too large. Of the 403 expanded MUs, 23 were less than 15% relative while 7 were greater than 50% relative.

Uncertainties associated with results returning a satisfactory *z* score but an unsatisfactory $E_n$ score may have been underestimated.

Laboratories **1**, **5**, **10**, **15** and **16** attached estimates of the expanded MU for results reported as less than their limit of reporting (LOR). An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[10]

In some cases the results were reported with an inappropriate number of significant figures. Including too many significant figures may inaccurately reflect the precision of measurements. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 943.69 ± 283.12 mg/kg, it is better to report this result as 940 ± 280 mg/kg.[10]

### 6.3 *z* Score

Target SDs equivalent to 15% CV were used to calculate *z* scores. CVs predicted by the Thompson-Horwitz equation,[8] target SDs (as PCV), and the between-laboratory CVs obtained in this study for scored analytes are presented for comparison in Table 30.

Table 30 Comparison of Thompson-Horwitz CVs, Target SDs, and Between-Laboratory CVs

| Sample | Analyte | Assigned Value (mg/kg) | Thompson-Horwitz CV (%) | Target SD (as PCV) (%) | Between-Laboratory CV* (%) |
|---|---|---|---|---|---|
| S1 | >C10-C16 | 1080 | 5.6 | 15 | 16 |
| | >C16-C34 | 1590 | 5.3 | 15 | 15 |
| | >C34-C40 | 182 | 7.3 | 15 | 12 |
| | TRH | 2800 | 4.8 | 15 | 15 |
| S2 | Toluene | 234 | 7.0 | 15 | 20 |
| | Ethylbenzene | 38.6 | 9.2 | 15 | 19 |
| | Xylenes | 238 | 7.0 | 15 | 19 |
| | Total BTEX | 532 | 6.2 | 15 | 20 |
| S3 | Anthracene | 0.844 | 16 | 15 | 16 |
| | Benzo[*a*]pyrene | 1.20 | 16 | 15 | 21 |
| | Chrysene | 0.541 | 18 | 15 | 9.8 |
| | Fluoranthene | 0.727 | 17 | 15 | 10 |
| | Fluorene | 1.78 | 15 | 15 | 11 |
| | Phenanthrene | 2.29 | 14 | 15 | 13 |
| | Pyrene | 1.08 | 16 | 15 | 11 |
| S4 | Chrysene | 1.14 | 16 | 15 | 16 |
| | Fluoranthene | 1.83 | 15 | 15 | 15 |
| | Fluorene | 0.630 | 17 | 15 | 14 |
| | Phenanthrene | 1.15 | 16 | 15 | 16 |
| | Pyrene | 0.205 | 20 | 15 | 17 |

* Robust between-laboratory CV with outliers removed, if applicable.

To account for possible low bias in the consensus values due to participants using inefficient analytical or extraction techniques, a total of nine *z* scores were adjusted across the following: Sample S2 toluene, xylenes and total BTEX, Sample S3 anthracene and benzo[*a*]pyrene, and Sample S4 chrysene and pyrene. A maximum acceptable result was set to two target SDs more than the spiked value, and results lower than the maximum acceptable result but with a *z* score greater than 2.0 had their *z* score adjusted to 2.0. This ensured that participants reporting results close to the spiked value were not penalised. *z* Scores for results higher than the maximum acceptable result were not adjusted, and *z* scores less than 2.0 were left unaltered.

Of 402 results for which *z* scores were calculated, 377 (94%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **2**, **7**, **9**, **11**, **19**, **20** and **23** reported results for all 20 analytes which were scored. Laboratories **2**, **19** and **23** returned satisfactory *z* scores for all of these scored analytes. Satisfactory *z* scores were achieved for all scored results reported by Laboratories **3** (19), **8** (19), **10** (19), **15** (19), **14** (18), and **17** (18).

Laboratories **1** and **12** analysed for TRH and PAHs only, and reported results for all 16 scored analytes. Both participants also returned satisfactory *z* scores for all of these scored analytes.

Laboratory **4** analysed for TRH and BTEX only, and achieved satisfactory *z* scores for all reported results that were scored (5).

The dispersal of participants' *z* scores is presented graphically by laboratory in Figure 25 and by analyte in Figure 26.

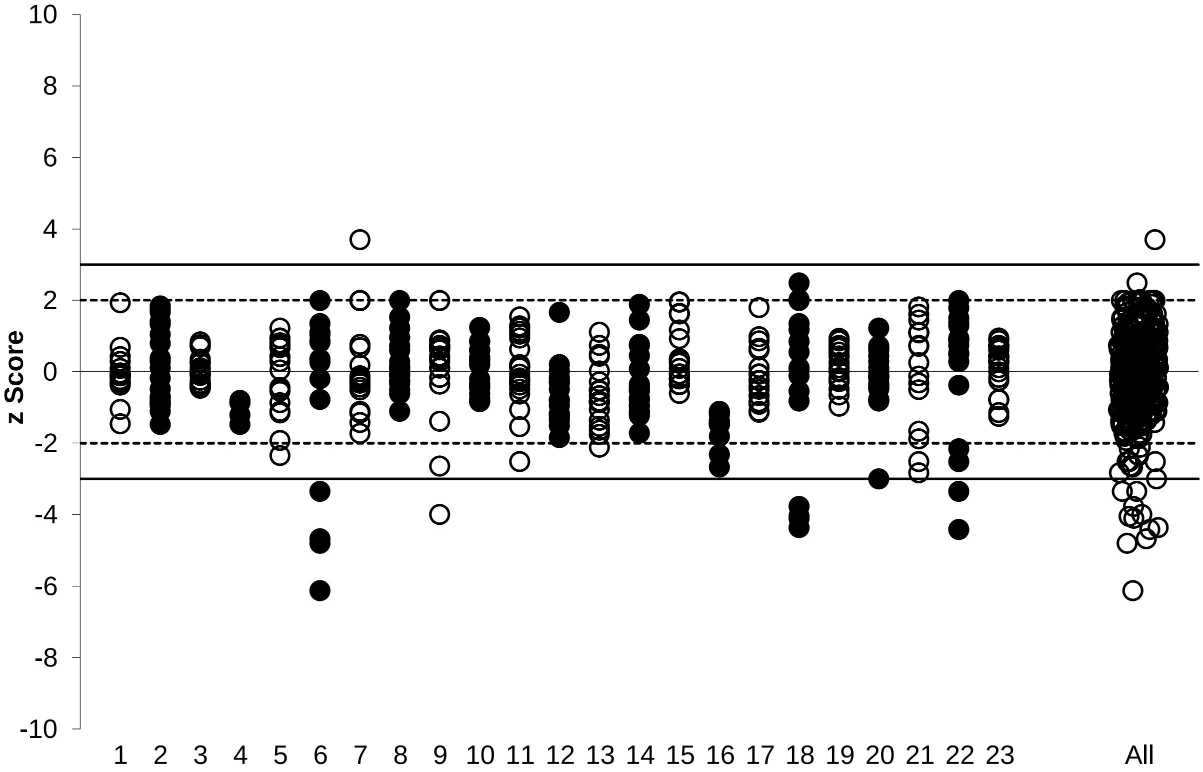



Figure 25 *z* Score Dispersal by Laboratory

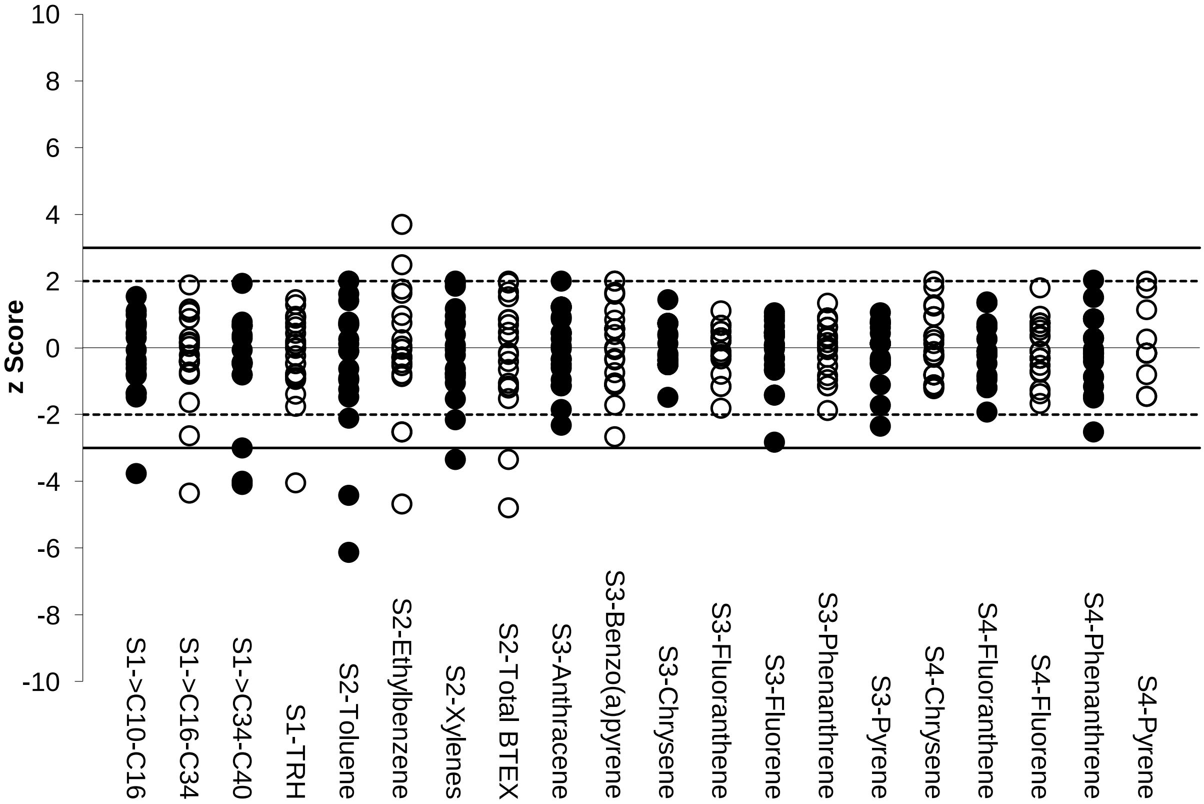



Figure 26 *z* Score Dispersal by Analyte

Participants' *z* scores for Sample S1 (TRH) only are presented in Figure 27. A trend of questionable or unsatisfactory *z* scores on one side of the zero line may indicate laboratory bias for TRH measurements.

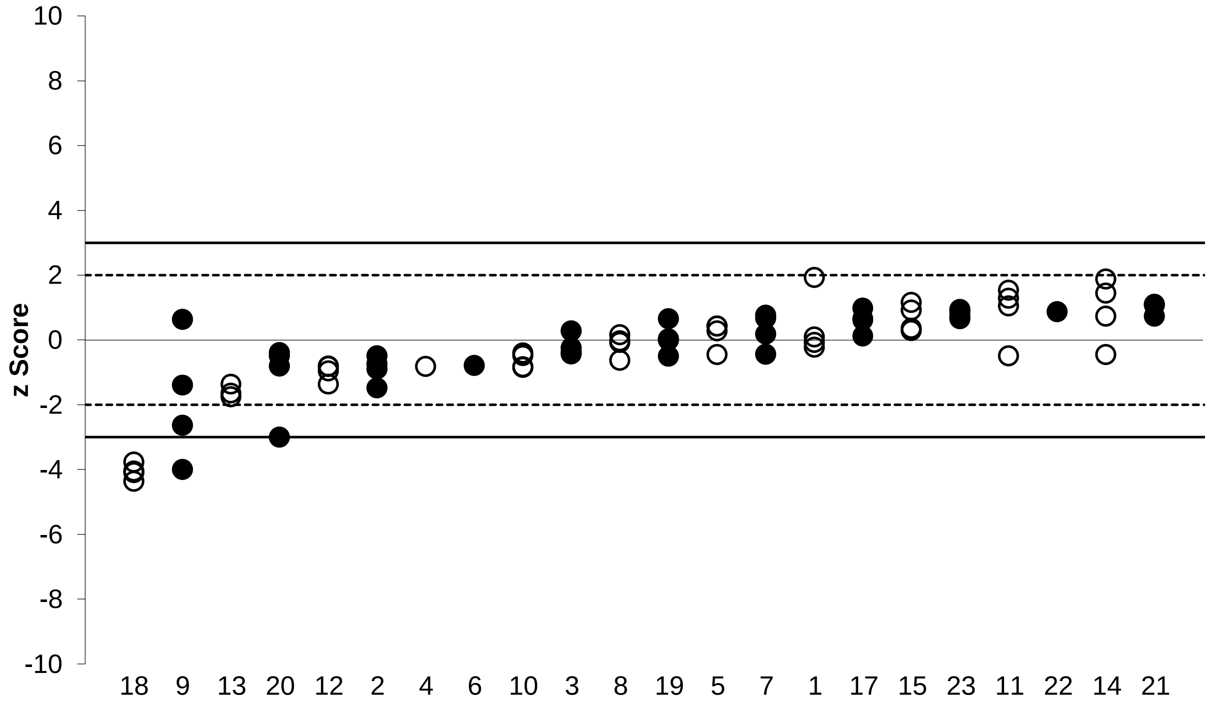



Figure 27 Sample S1 TRH *z* Score Dispersal by Laboratory

Participants' *z* scores for Sample S2 (BTEX) only are presented in Figure 28. Participants with a trend of questionable or unsatisfactory *z* scores below the zero line likely had an inefficient extraction process for BTEX. As the ratio of the assigned value to the spiked value was 62% for Total BTEX, participants reporting results with higher satisfactory *z* scores may have more efficient extraction methodologies.

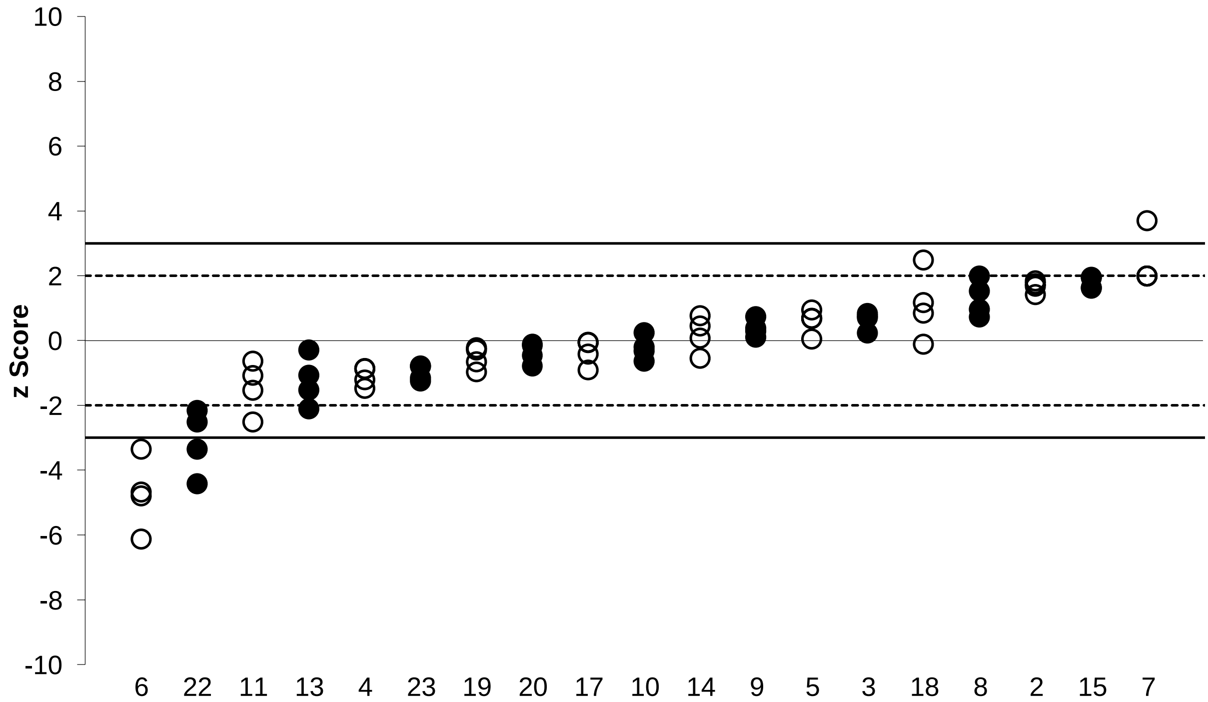



Figure 28 Sample S2 BTEX *z* Score Dispersal by Laboratory

Participants' *z* scores for Samples S3 and S4 (PAHs) only are presented in Figure 29. Participants with a trend of questionable or unsatisfactory *z* scores below the zero line likely had an inefficient extraction process for PAHs. As the ratios of the assigned values to the spiked values ranged from 51% to 88%, participants reporting results with higher satisfactory *z* scores may have more efficient extraction methodologies.

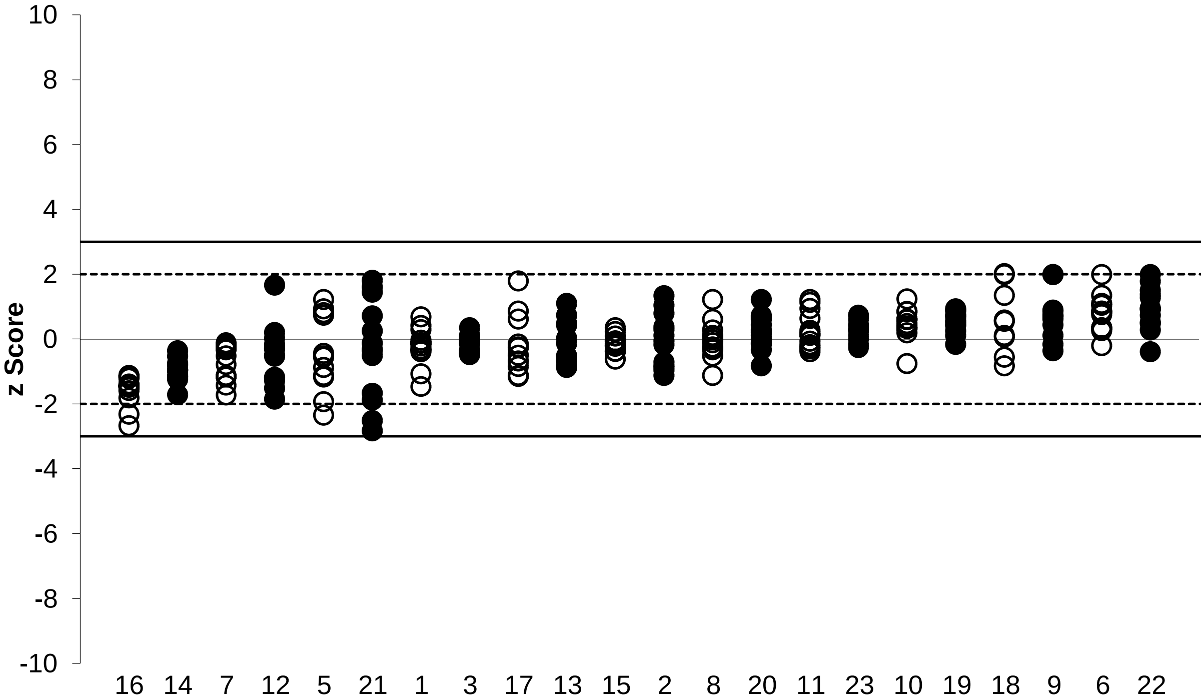



Figure 29 Samples S3 and S4 PAHs *z* Score Dispersal by Laboratory

Scatter plots of *z* scores for Samples S3 and S4 chrysene, fluoranthene, fluorene, phenanthrene and pyrene are presented in Figures 30 to 34. Scores are predominantly in the upper right and lower left quadrants, indicating that laboratory bias is the major contributor to the variability of results. Points close to the diagonal axis demonstrate excellent repeatability, while points close to the zero demonstrate excellent repeatability and accuracy.

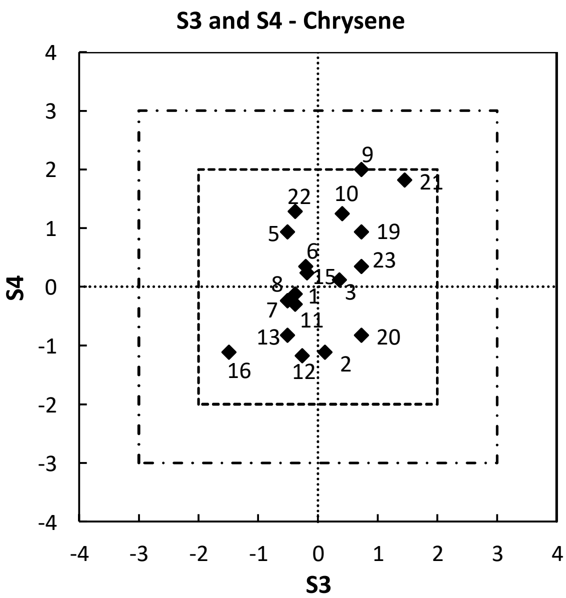



Figure 30 *z* Score Scatter Plot – Chrysene

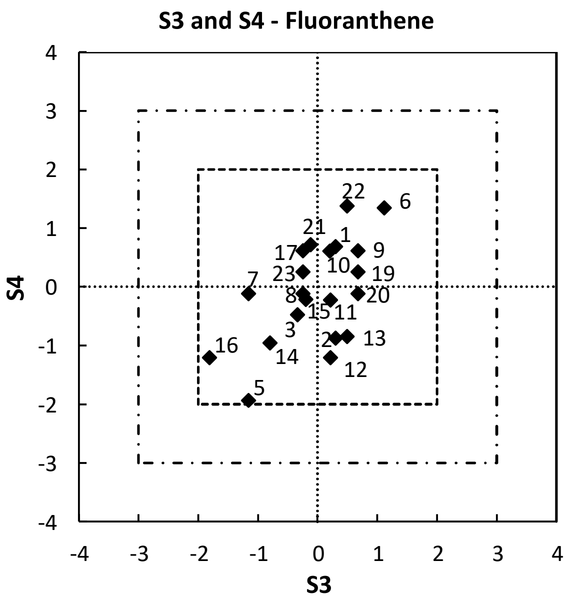



Figure 31 *z* Score Scatter Plot – Fluoranthene

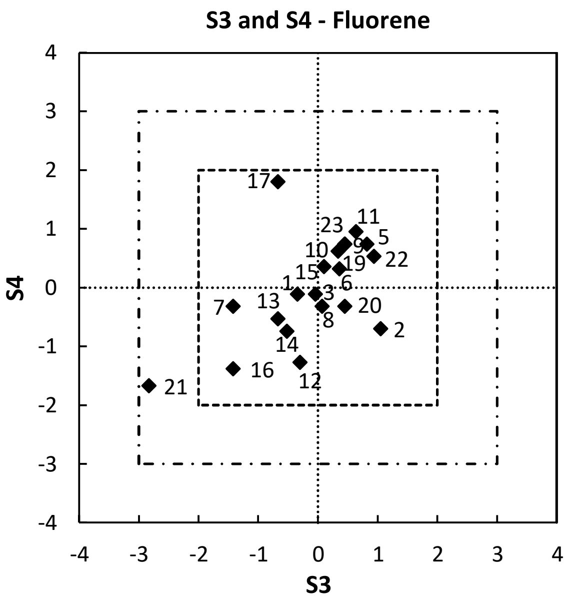



Figure 32 *z* Score Scatter Plot – Fluorene

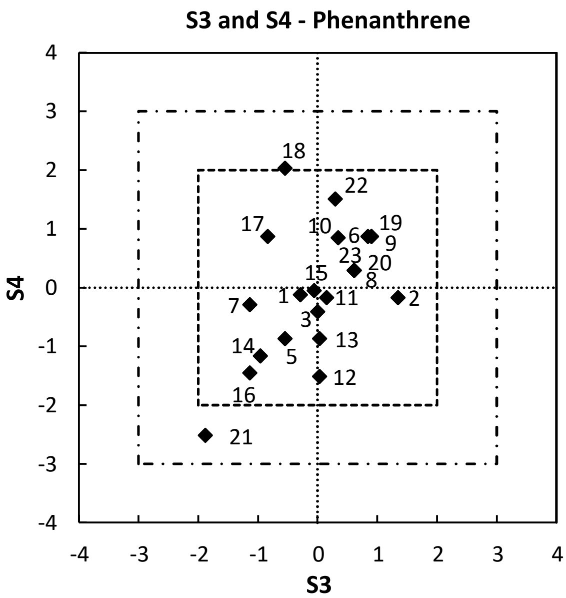



Figure 33 *z* Score Scatter Plot – Phenanthrene

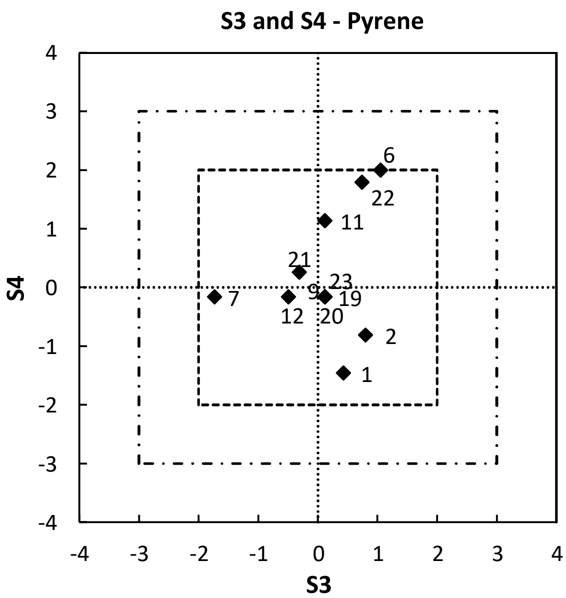



Figure 34 *z* Score Scatter Plot – Pyrene

### 6.4 $E_n$ Score

Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the $E_n$ score. For results for which *z* scores were adjusted as discussed in Section 6.3 *z* Score, $E_n$ scores greater than 1.0 were set to 1.0.

Of 402 results for which $E_n$ scores were calculated, 345 (86%) returned a satisfactory score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective uncertainties.

Laboratories **19** and **20** returned satisfactory $E_n$ scores for all 20 scored analytes. Satisfactory $E_n$ scores were achieved for all scored results reported by Laboratories **3** (19), **10** (19) and **14** (18).

Laboratory **1** returned satisfactory $E_n$ scores for all scored TRH and PAHs analytes (16).

Laboratory **4** achieved satisfactory *z* scores for all reported TRH and BTEX results that were scored (5).

The dispersal of participants' $E_n$ scores is presented graphically by laboratory in Figure 35.

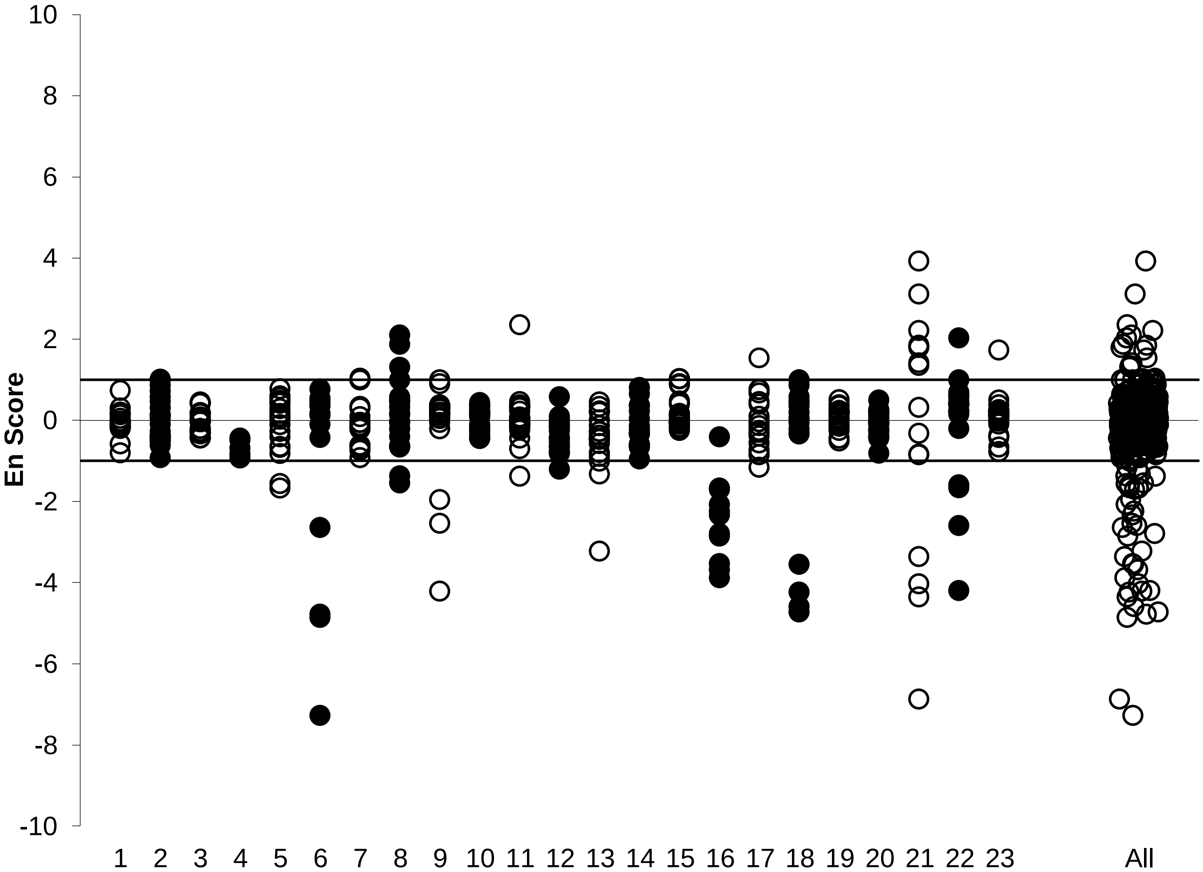



Figure 35 $E_n$ Score Dispersal by Laboratory

## 6.5 False Negatives

Table 31 presents false negative results. These are analytes present in the samples which a participant tested for but did not report a numeric result (for example, participants reporting a 'less-than' result (< *x*) when the assigned value was higher than their LOR, or laboratories that did not report anything). For analytes where no assigned value was set, results have only been considered to be false negatives when the robust average and spiked value were significantly higher than their LOR, or if no value was reported.

Table 31 False Negatives

| Lab. Code | Sample | Analyte | Assigned Value *(Robust Average)* (mg/kg) | Spiked Value (mg/kg) | Result (mg/kg) |
|---|---|---|---|---|---|
| 6 | S2 | Benzene | *(27.3)* | 82.1 | NR* |
| 13 | S1 | >C34-C40 | 182 | 174 | <100 |
| 14 | S3 | Chrysene | 0.541 | 0.699 | <0.5 |
| 16 | S3 | Pyrene | 1.08 | 1.29 | <0.1 |
| 17 | S3 | Chrysene | 0.541 | 0.699 | <0.5 |
| 21 | S1 | >C34-C40 | 182 | 174 | NR* |

* Result may or may not be a false negative, depending on the participant's actual LOR.

## 6.6 Reporting of Additional Analytes

One participant reported an analyte that was not spiked into the test samples. This result is presented in Table 32. Participants should take care to avoid any potential cross-contamination with other samples at their laboratory.

Table 32 Results Reported for Non-Spiked Analytes

| Lab. Code | Sample | Analyte | Result (mg/kg) | Uncertainty (mg/kg) |
|---|---|---|---|---|
| 18 | S4 | Benz[*a*]anthracene | 1.4 | 0.56 |

## 6.7 Participants' Analytical Methods

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

**TRH**

Participants used a sample size between 2 g and 15 g for TRH analysis, with the majority of participants using 10 g. A plot of results against sample mass used for analysis is presented in Figure 36.

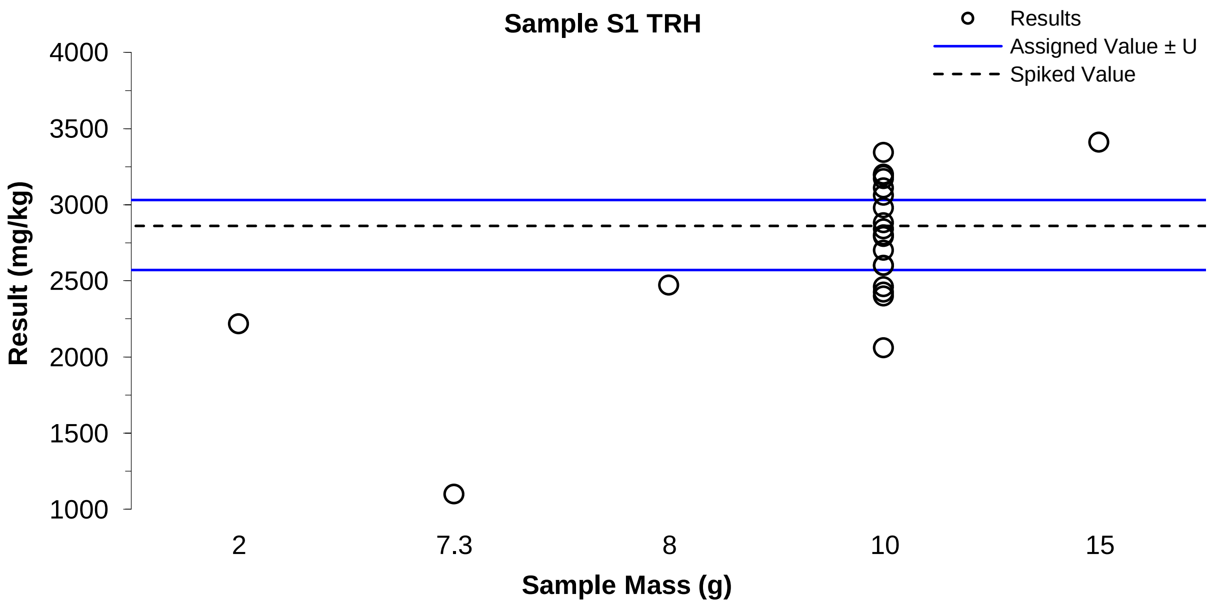



Figure 36 Sample S1 TRH Results vs Sample Mass Used for Analysis

Participants reported using either solid-liquid extraction (SLE) or sonication, with dichloromethane (DCM), acetone (ACE), hexane (HEX), and combinations of these as the extraction solvent(s). Five participants reported a clean-up step, and of these, four reported using silica. All participants used gas chromatography (GC) coupled to flame ionisation detection (FID) for analysis.

A plot of results and methodology for TRH in Sample S1 is presented in Figure 37. Methodologies are listed in order of extraction technique, extraction solvent, and instrument.

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

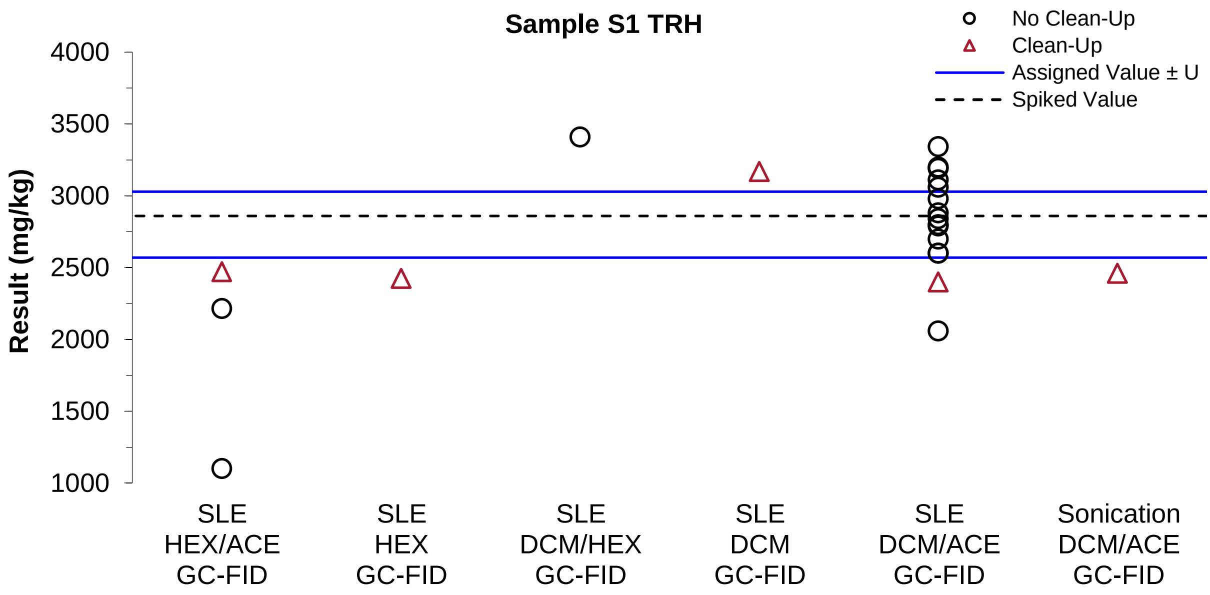



Figure 37 Sample S1 TRH Results vs Methodology

**BTEX**

Participants used a sample size between 0.26 g and 14 g for BTEX analysis, with the majority of participants using 10 g. A plot of results against sample mass used for analysis is presented in Figure 38.

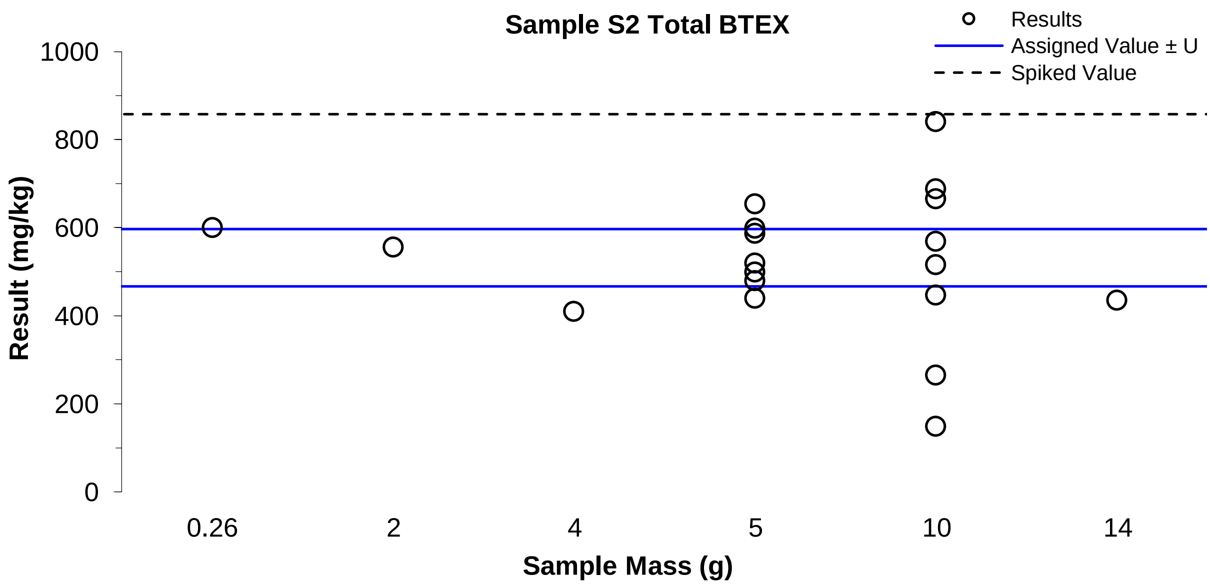



Figure 38 Sample S2 Total BTEX Results vs Sample Mass Used for Analysis

Extraction techniques reported by participants included SLE and sonication. One participant used DCM/ACE as their extraction solvent, while all other participants who reported an extraction solvent used methanol (MeOH). No participant reported a clean-up step. One participant used headspace (HS) GC-FID, while all other participants used purge and trap (P&T) or HS GC coupled to mass spectrometry (MS) or tandem mass spectrometry (MS/MS).

A plot of results and methodology for Total BTEX in Sample S2 is presented in Figure 39. Methodologies are listed in order of extraction technique, extraction solvent and instrument.

The most common methodology used to analyse BTEX in this study was SLE with MeOH, using P&T GC-MS for analysis.

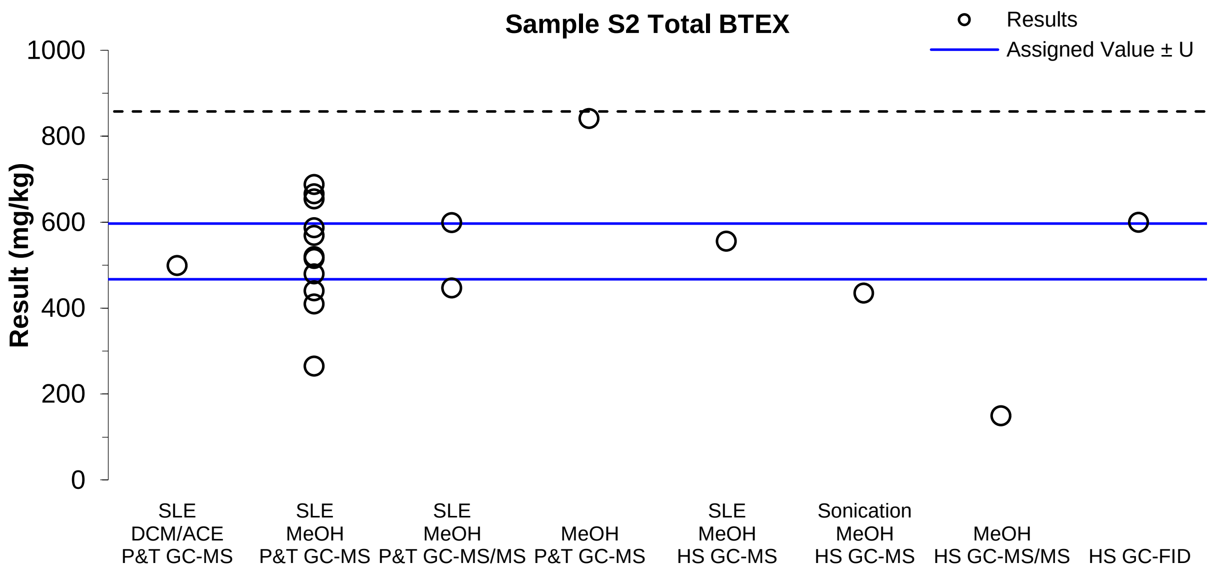



Figure 39 Sample S2 Total BTEX Results vs Methodology

**PAHs**

Participants used a sample size between 2 g and 15 g for PAHs analysis, with the majority of participants using 10 g. A plot of *z* scores against sample mass used for analysis is presented in Figure 40.

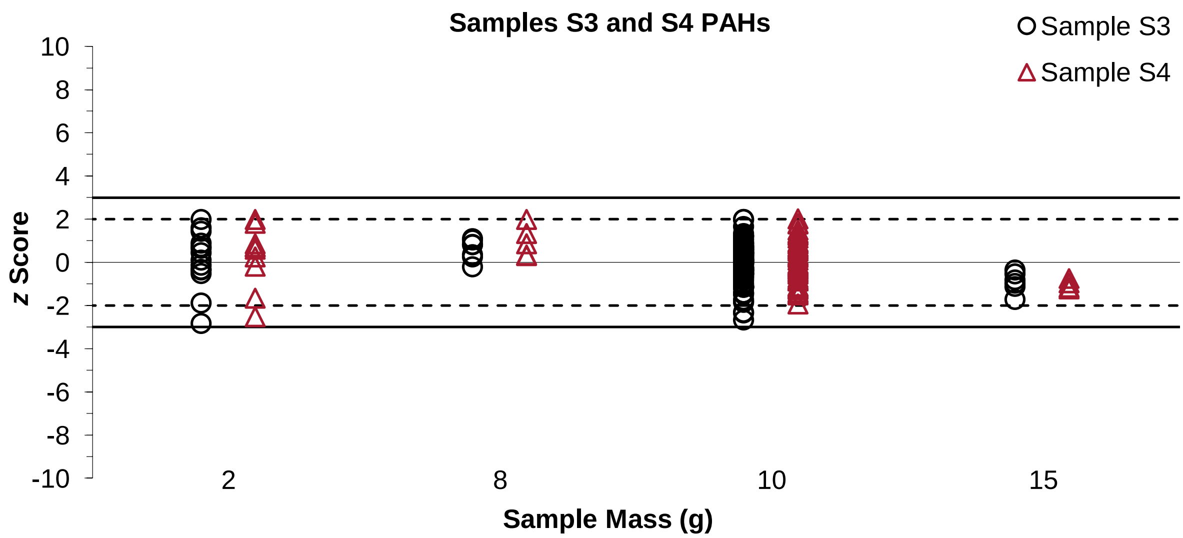



Figure 40 Samples S3 and S4 PAHs *z* Scores vs Sample Mass Used for Analysis

Participants reported using SLE, with DCM, ACE, HEX, ethyl acetate (EtOAc) and combinations of these as the extraction solvent. One participant reported using Florisil clean-up. All participants used GC-MS(/MS) for analysis.

A plot of *z* scores obtained and methodology used for the PAHs in Samples S3 and S4 is presented in Figure 41. Methodologies are listed in order of extraction technique, extraction solvent, clean-up (if applicable) and instrument.

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

In this study, it was seen that participants using just DCM as the extraction solvent reported results that were generally biased low (however still with satisfactory *z* scores).

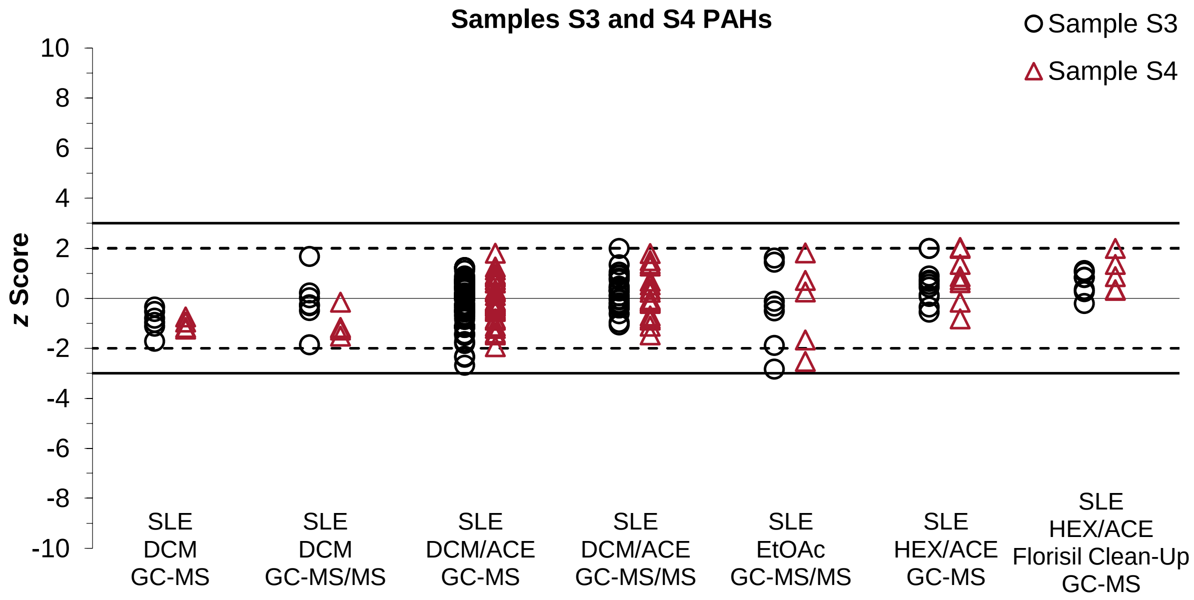



Figure 41 Samples S3 and S4 PAHs *z* Scores vs Methodology

## 6.8 Certified Reference Materials (CRM)

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

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

- NMI MX015
- Accustandard
- Sigma Aldrich, e.g. CRM352
- PM Separations
- ISO 17034 traceable standards
- ISO 17025 compliant standards

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

> '***reference material***, *accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures*'[12]

## 6.9 Summary of Participants' Results and Performances

Summaries of participants' results and performances for scored analytes in this PT study are presented in Tables 33 and 34, and Figure 42.

Table 33 Summary of Participants' Results (Samples S1 and S2)*

| Lab. Code | Sample S1 | | | | Sample S2 | | | |
|---|---|---|---|---|---|---|---|---|
| | >C10-C16 | >C16-C34 | >C34-C40 | TRH | Toluene | Ethylbenzene | Xylenes | Total BTEX |
| AV | 1080 | 1590 | 182 | 2800 | 234 | 38.6 | 238 | 532 |
| SV | 1110 | 1570 | 174 | 2860 | 393 | 45 | 337 | 858 |
| 1 | 1069 | 1537 | 235 | 2841 | NT | NT | NT | NT |
| 2 | 840 | 1416 | 169 | 2425 | 284 | 48.8 | 304 | 666 |
| 3 | 1020 | 1490 | 190 | 2700 | 259 | 40 | 265 | 599 |
| 4 | NR | NR | NR | 2460 | 182 | 33.6 | 207 | 435.1 |
| 5 | 1150 | 1660 | 170 | 2980 | 258 | 38.9 | 272 | 587 |
| 6 | NR | NR | NR | 2472 | 19 | 11.5 | 118.5 | 149 |
| 7 | 1190 | 1488 | 203 | 2881 | 371 | 60 | 358 | 841 |
| 8 | 980 | 1630 | 180 | 2790 | 306 | 44.2 | 264 | 654 |
| 9 | 1183 | 961 | 72.8 | 2216.8 | 238 | 42.9 | 252 | 556 |
| 10 | 943.69 | 1498.1 | 159.55 | 2601.3 | 242.7 | 36.8 | 215.5 | 515.9 |
| 11 | 1330 | 1843 | 169 | 3342 | 212 | 24.0 | 183 | 447 |
| 12 | 860 | 1400 | 160 | 2400 | NT | NT | NT | NT |
| 13 | 860 | 1200 | <100 | 2060 | 160 | 37 | 200 | 410 |
| 14 | 1200 | 2040 | 170 | 3410 | 261 | 35.5 | 241 | 569 |
| 15 | 1129 | 1870 | 192 | 3191 | 291 | 48.1 | 308 | 688 |
| 16 | NT | NT | NT | NT | NT | NT | NT | NT |
| 17 | 1240 | 1620 | 200 | 3060 | 202 | 38.3 | 236 | 499 |

| Lab. Code | Sample S1 | | | | Sample S2 | | | |
|---|---|---|---|---|---|---|---|---|
| | >C10-C16 | >C16-C34 | >C34-C40 | TRH | Toluene | Ethylbenzene | Xylenes | Total BTEX |
| 18 | 470 | 550 | 70 | 1100 | 230 | 53 | 280 | 600 |
| 19 | 1000 | 1600 | 200 | 2800 | 200 | 37 | 230 | 480 |
| 20 | 950 | 1500 | 100 | 2600 | 230 | 36 | 210 | 520 |
| 21 | 1260 | 1850 | NR | 3110 | NT | NT | NT | NT |
| 22 | NR | NR | NR | 3170 | 79 | 24 | 161 | 265 |
| 23 | 1200 | 1800 | 200 | 3200 | 190 | 34 | 210 | 440 |

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

Table 34 Summary of Participants' Results (Samples S3 and S4)*

| Lab. Code | Sample S3 | | | | | | | Sample S4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Anthracene | Benzo[*a*]pyrene | Chrysene | Fluoranthene | Fluorene | Phenanthrene | Pyrene | Chrysene | Fluoranthene | Fluorene | Phenanthrene | Pyrene |
| AV | 0.844 | 1.2 | 0.541 | 0.727 | 1.78 | 2.29 | 1.08 | 1.14 | 1.83 | 0.63 | 1.15 | 0.205 |
| SV | 1.29 | 1.98 | 0.699 | 0.895 | 2.18 | 2.7 | 1.29 | 1.49 | 2.19 | 0.795 | 1.3 | 0.4 |
| 1 | 0.84 | 1.01 | 0.51 | 0.76 | 1.69 | 2.19 | 1.15 | 1.12 | 2.02 | 0.62 | 1.13 | 0.16 |
| 2 | 0.722 | 1.27 | 0.551 | 0.76 | 2.06 | 2.75 | 1.21 | 0.951 | 1.59 | 0.564 | 1.12 | 0.18 |
| 3 | 0.85 | 1.14 | 0.57 | 0.69 | 1.77 | 2.29 | 1.01 | 1.16 | 1.7 | 0.62 | 1.08 | <0.5 |
| 4 | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| 5 | 1 | 1 | 0.5 | 0.6 | 2 | 2.1 | 0.7 | 1.3 | 1.3 | 0.7 | 1 | <0.5 |
| 6 | 0.878 | 1.35 | 0.525 | 0.848 | 1.875 | 2.58 | 1.25 | 1.2 | 2.2 | 0.66 | 1.3 | 0.27 |
| 7 | 0.7 | 1 | 0.5 | 0.6 | 1.4 | 1.9 | 0.8 | 1.1 | 1.8 | 0.6 | 1.1 | 0.2 |
| 8 | 1.0 | 1.0 | 0.5 | 0.7 | 1.8 | 2.5 | 1.1 | 1.1 | 1.8 | 0.6 | 1.2 | <0.5 |
| 9 | 0.8 | 1.8 | 0.6 | 0.8 | 1.9 | 2.6 | 1.1 | 1.6 | 2.0 | 0.7 | 1.3 | 0.2 |
| 10 | 0.953 | 1.065 | 0.574 | 0.749 | 1.871 | 2.406 | 1.178 | 1.353 | 1.997 | 0.689 | 1.296 | <0.5 |

| Lab. Code | Sample S3 | | | | | | | Sample S4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Anthracene | Benzo[*a*]pyrene | Chrysene | Fluoranthene | Fluorene | Phenanthrene | Pyrene | Chrysene | Fluoranthene | Fluorene | Phenanthrene | Pyrene |
| 11 | 1 | 1.19 | 0.51 | 0.75 | 1.95 | 2.34 | 1.1 | 1.09 | 1.77 | 0.72 | 1.12 | 0.24 |
| 12 | 0.61 | 1.5 | 0.52 | 0.75 | 1.7 | 2.3 | 1.0 | 0.94 | 1.5 | 0.51 | 0.89 | 0.20 |
| 13 | 0.90 | 1.4 | 0.50 | 0.78 | 1.6 | 2.3 | 1.2 | 1.0 | 1.6 | 0.58 | 1.0 | <0.5 |
| 14 | 0.80 | 0.89 | <0.5 | 0.64 | 1.64 | 1.96 | 0.90 | 0.93 | 1.57 | 0.56 | 0.95 | <0.5 |
| 15 | 0.767 | 1.133 | 0.526 | 0.705 | 1.806 | 2.271 | 1.021 | 1.181 | 1.772 | 0.664 | 1.142 | < 0.5 |
| 16 | 0.55 | 0.72 | 0.42 | 0.53 | 1.4 | 1.9 | <0.1 | 0.95 | 1.5 | 0.50 | 0.90 | 0.16 |
| 17 | 0.7 | 1.0 | <0.5 | 0.7 | 1.6 | 2.0 | 1.0 | 1.1 | 2.0 | 0.8 | 1.3 | <0.5 |
| 18 | 1.5 | 1.3 | <1 | <1 | 1.8 | 2.1 | 1.1 | 1.0 | 2.2 | <1 | 1.5 | <1 |
| 19 | 0.9 | 1.3 | 0.6 | 0.8 | 1.9 | 2.6 | 1.1 | 1.3 | 1.9 | 0.7 | 1.3 | 0.2 |
| 20 | 1 | 1.2 | 0.6 | 0.8 | 1.9 | 2.5 | 1.1 | 1 | 1.8 | 0.6 | 1.2 | 0.2 |
| 21 | 0.781 | 1.489 | 0.659 | 0.714 | 1.024 | 1.645 | 1.03 | 1.452 | 2.029 | 0.472 | 0.715 | 0.213 |
| 22 | 0.96 | 1.76 | 0.51 | 0.78 | 2.03 | 2.39 | 1.2 | 1.36 | 2.21 | 0.68 | 1.41 | 0.26 |
| 23 | 0.9 | 1.2 | 0.6 | 0.7 | 1.9 | 2.5 | 1.1 | 1.2 | 1.9 | 0.7 | 1.2 | 0.2 |

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

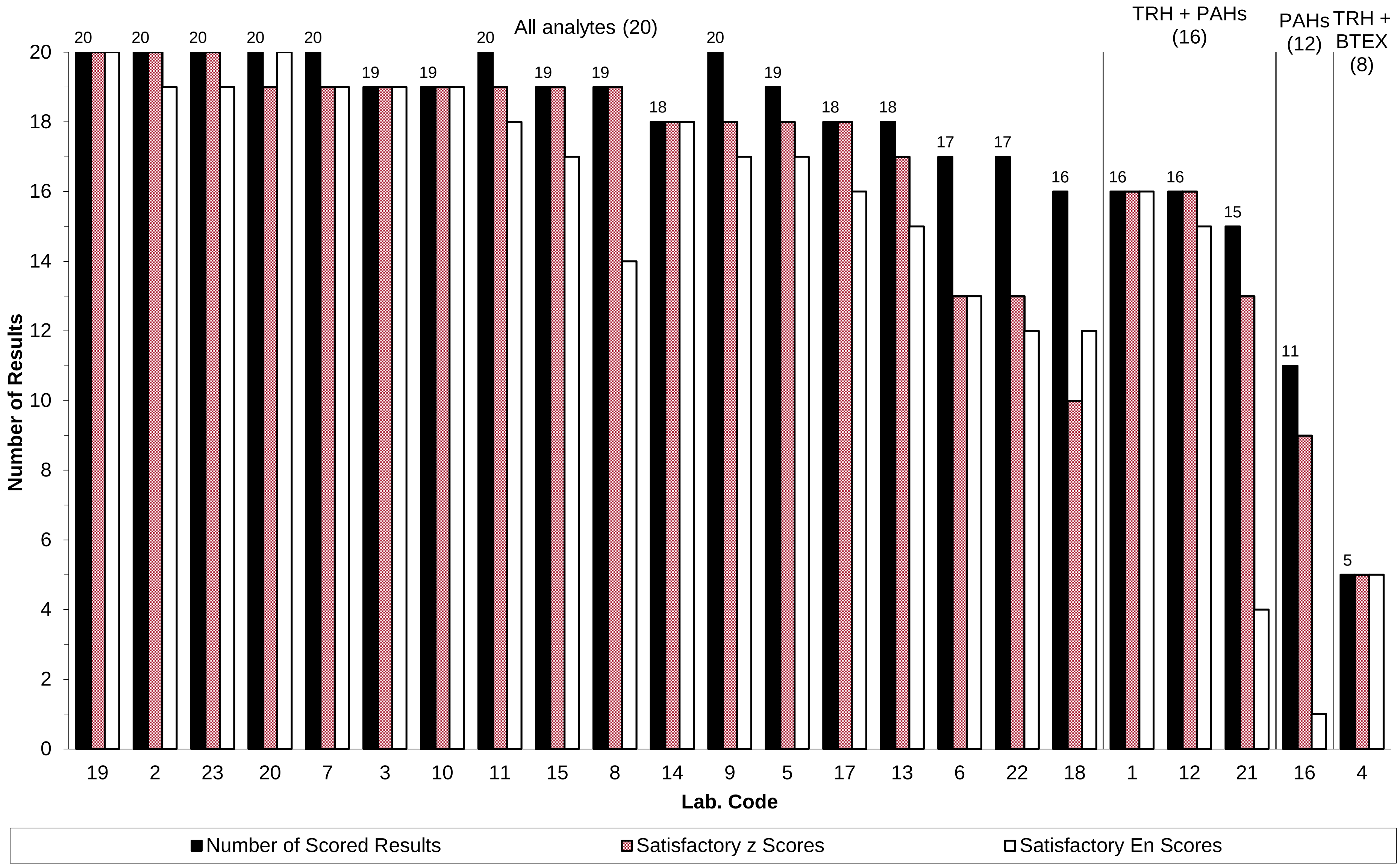



Figure 42 Summary of Participants' Performance

## 6.10 Comparison with Previous Hydrocarbons in Soil PT Studies

To enable direct comparison with results from previous Hydrocarbons in Soil PT studies, the target SD used to calculate *z* scores has been kept constant at 15% PCV.

Individual performance history reports are emailed to each participant at the end of each study; the consideration of *z* scores for an analyte over time provides much more useful information than a single *z* score. Over time, laboratories should expect at least 95% of their scores to lie within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ can occasionally occur, however, these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of *z* scores on one side of the zero line is an indication of method or laboratory bias.

**TRH**

A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by participants for TRH in soil over the last 10 studies (2014 – 2022) is presented in Figure 43. Over this period, the average proportion of satisfactory *z* scores was 93%, and the average proportion of satisfactory $E_n$ scores was 73%.

While each PT study has a different sample set and a different group of participants, taken as a group, the performance over this period remained relatively high for TRH.

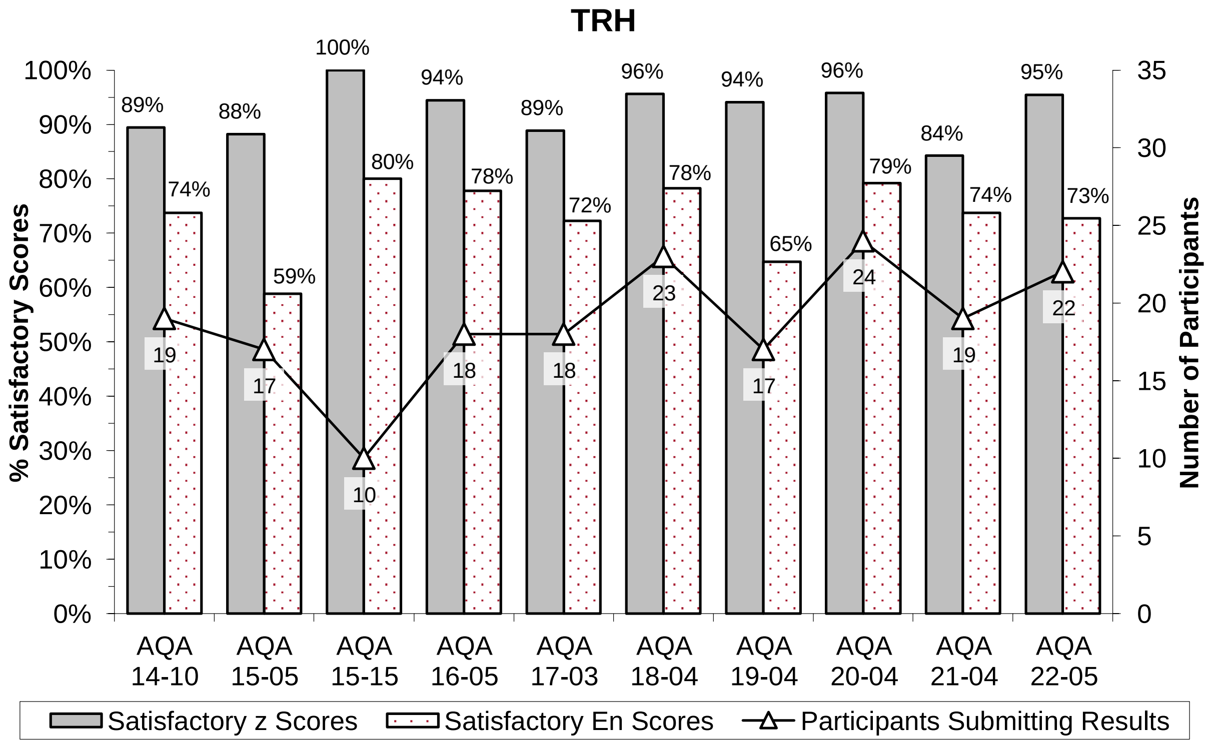



Figure 43 Participants' Performance for TRH in Hydrocarbons in Soil PT Studies

**Total BTEX**

A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by participants for Total BTEX in soil over the last 10 studies (2014 – 2022) is presented in Figure 44. Over this period, the average proportion of satisfactory *z* scores was 87%, and the average proportion of satisfactory $E_n$ scores was 81%.

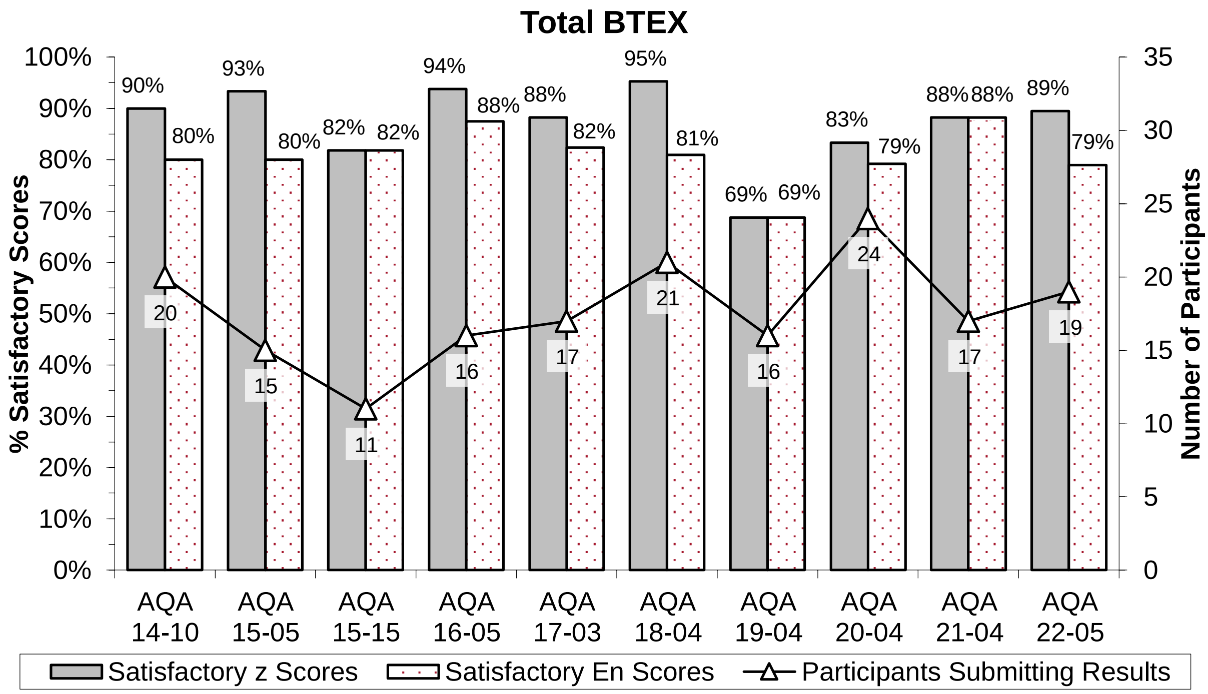



Figure 44 Participants' Performance for Total BTEX in Hydrocarbons in Soil PT Studies

**PAHs**

PAHs in soil was first introduced in NMI PT studies in 2016. A summary of the satisfactory performance (presented as a percentage of the total number of scores) obtained by participants for PAHs in soil over the last 7 studies (2016 – 2022) is presented in Figure 45. Over this period, the average proportion of satisfactory *z* scores was 92%, and the average proportion of satisfactory $E_n$ scores was 88%.

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

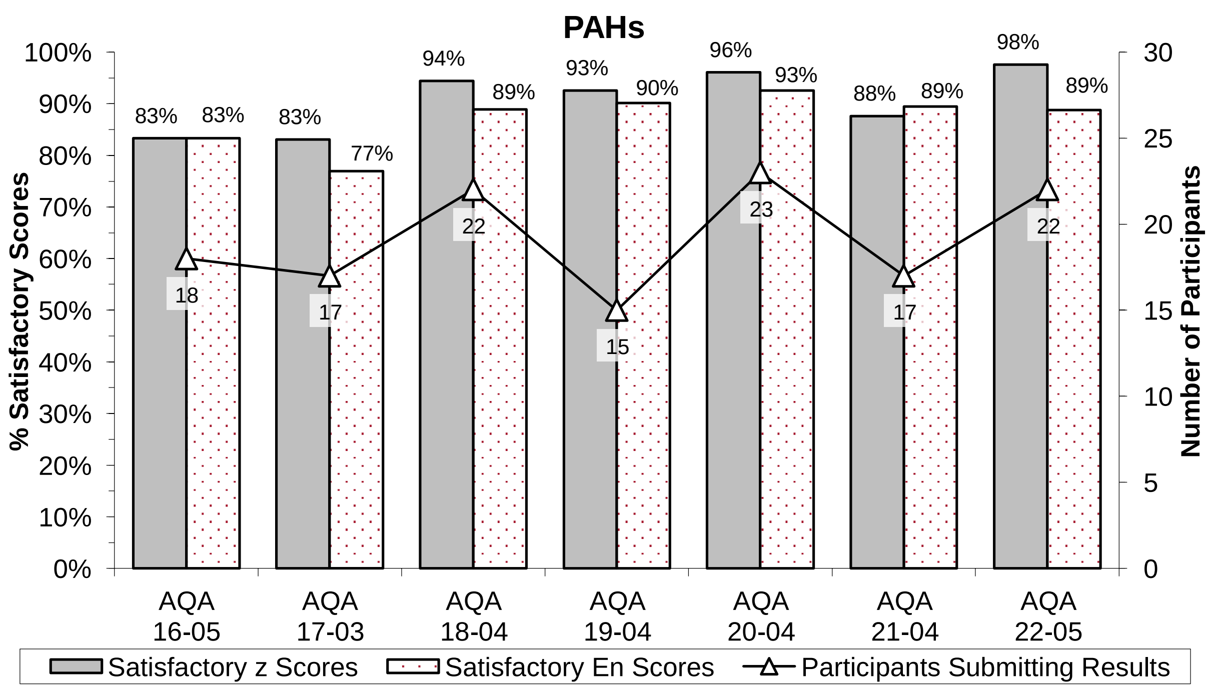



Figure 45 Participants' Performance for PAHs in Hydrocarbons in Soil PT Studies

A plot of the robust average expressed as a percentage of the spiked value for PAHs in topsoil since 2016 is presented in Figure 46. Results from samples with other soil matrices have not been included as it has been previously seen that the nature of the soil matrix can substantially affect the recovery of some analytes.[13]

For all spiked PAHs in this study, the robust averages were lower than the spiked values, consistent with previous studies. Throughout NMI Hydrocarbons in Soil PT studies, anthracene and benzo[*a*]pyrene have consistently had relatively low recoveries, averaging 46% and 43% respectively for the robust average to spiked value. Chrysene, fluoranthene, fluorene, phenanthrene and pyrene have had higher recoveries, with averages ranging from 74% to 86% for the robust average to spiked value.

For this study, anthracene and benzo[*a*]pyrene and returned higher recoveries than for previous studies. Sample S4 pyrene returned a low recovery in comparison to most previous studies; pyrene had been spiked at a much lower level in this sample than for previous studies.

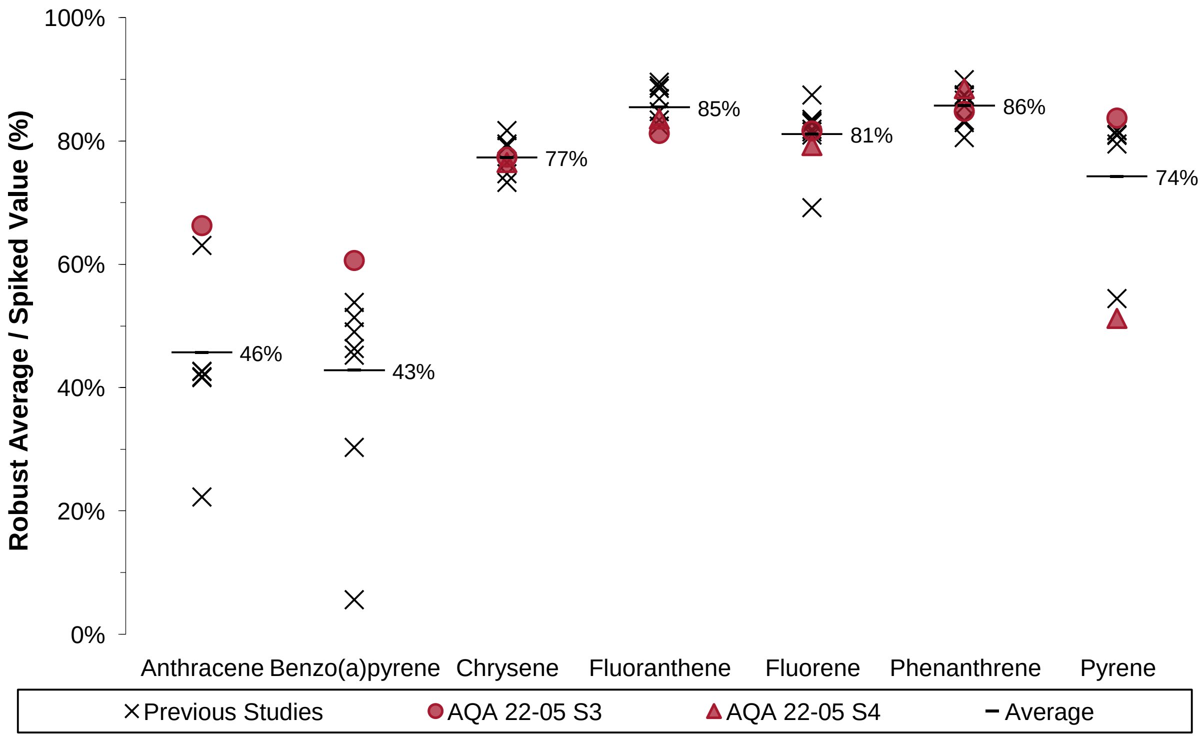



Figure 46 Recoveries of PAHs in Topsoil for Hydrocarbons in Soil PT Studies

## 7 REFERENCES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[13] NMI, 2018, *Proficiency Test Report AQA 18-04 Hydrocarbons in Soil*.

## APPENDIX 1 SAMPLE PREPARATION

### A1.1 Diesel Fuel Preparation

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

### A1.2 Test Sample Preparation

Uncontaminated soil described as Menangle topsoil bought from a Sydney supplier was used to prepare the samples. The soil was dried at 120 °C for at least two hours. The dried soil was sieved, and the fraction between 355 µm and 850 µm was used to prepare all samples.

**Sample S1**: Into a stainless steel pot, 2107.5 g of dried and sieved Menangle topsoil was placed. Dichloromethane was added to moisten the soil. A 6.312 g aliquot of sparged diesel was added by transferring 8 aliquots of 0.940 mL of diesel into the drum. The mass of diesel was calculated using a density of 0.83936 g/mL. In addition, 2.0 mL of PENRITE INDUS PRO HYDRAULIC 68 was added. The mixture was thoroughly stirred and the solvent was allowed to evaporate. The mixture was divided into 50 g portions using a Retsch PT 100 sample divider and packed into screw-capped glass jars, labelled and stored in a refrigerator.

**Sample S2**: Dried, sieved Menangle topsoil (3500.2 g) 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. Five aliquots of 0.840 mL of diesel (3.53 g using $\rho$ = 0.83936 g/mL) were added to the soil. Three aliquots of 80 µL of benzene (total of 0.240 mL) were added to the soil using a positive displacement pipette, followed by ten aliquots of 0.940 mL of unleaded gasoline (7.388 g using $\rho$ = 0.786 g/mL). The drum was sealed and vigorously shaken. The sealed drum was then packed into another large drum and surrounded by cold gel-packs. The drums were then tumbled for 60 minutes on a hoop mixer. The soil was scooped into glass jars, tapped, topped up to minimise the vapour space and sealed. The process of filling the jars was conducted with the drum in an open freezer in an attempt to minimise the loss of volatiles. The jars were labelled with the numbers representing the fill order. After the caps were sealed with Parafilm the jars were shrink-wrapped and stored in a freezer.

**Samples S3 and S4**: For Sample S3, 1004.9 g of dried and sieved Menangle topsoil was placed in a 3 L round bottom flask. Dichloromethane was then added to the soil to allow it to be suspended. Using a Gilson pipette, aliquots of the PAH 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. To minimise the creation of dust, 10 mL of Milli-Q water was added to the flask. The flask was shaken to mix. The solvent was then evaporated using a Büchi rotary evaporator. The bath temperature was set at ambient and gently increased to no more than 50 °C during the evaporation, the condenser temperature at 7 °C and less than 20 kPa of vacuum. After evaporating the dichloromethane, the soil was transferred to a V-mixer and diluted with 1102.4 g of clean soil. The total soil mass was 2107.3 g. The V-mixer was tumbled for two hours. After mixing the soil was divided using a Retsch PT100 sample divider into fifty samples of at least 50 g, placed in screw-capped glass jars, labelled and placed in a refrigerator.

The same procedure was used for Sample S4 except for the quantities of spike solutions, and masses of soil which were 1004.0 g into the 3 L flask and 1103.5 g of diluent soil, making a total of 2107.5 g of spiked soil.

## APPENDIX 2 ASSESSMENT OF HOMOGENEITY AND STABILITY

### A2.1 Homogeneity

No homogeneity testing was completed for this study as the samples were prepared using a process previously demonstrated to produce homogeneous samples. The results of this study also gave no reason to question the samples' homogeneity. Comparisons of the results obtained for all scored analytes to the bottle number analysed by participants are presented in Figures 47 to 50 (only known jar numbers, i.e. the participant received one jar only, have been included). No significant trend was observed.

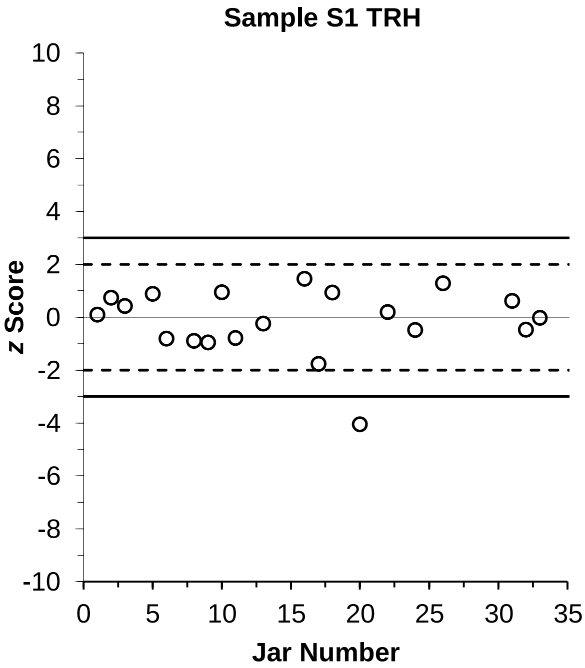


Figure 47 S1 TRH Results vs Jar Number

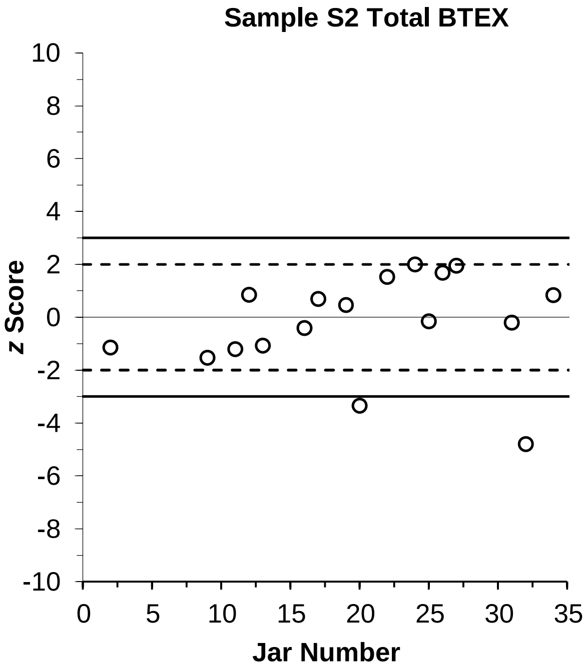


Figure 48 S2 Total BTEX Results vs Jar Number

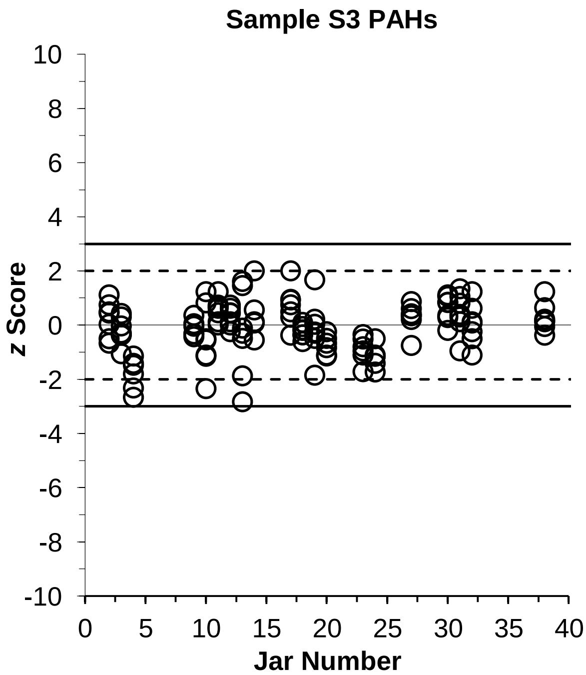


Figure 49 S3 PAHs *z* Scores vs Jar Number

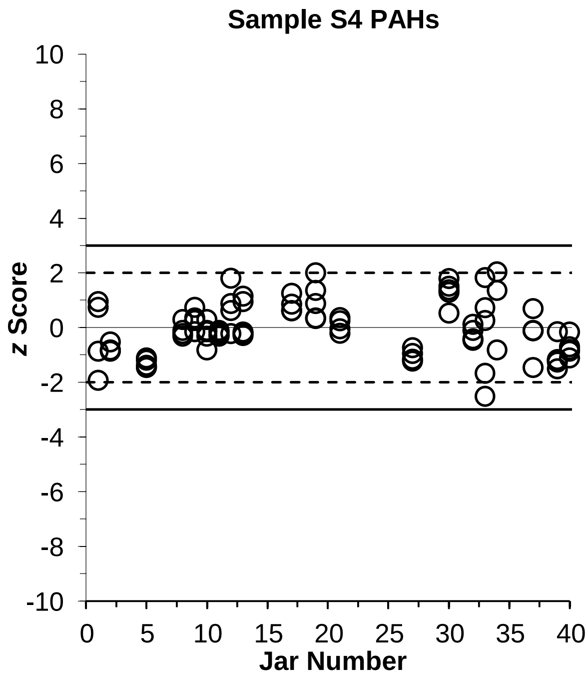


Figure 50 S4 PAHs *z* Scores vs Jar Number

### A2.2 Transportation Stability

No stability testing was conducted for this study, though results from previous NMI Hydrocarbons in Soil PT studies gave some assurance that the analytes were stable over similar transportation time frames. After preparation and before dispatch, Samples S1, S3 and S4 were stored in a refrigerator at approximately 4 °C, and Sample S2 was stored in a freezer at approximately -20 °C. For dispatch, samples were packaged into insulated polystyrene foam boxes with cooler bricks.

Comparisons of results obtained to days spent in transit for Sample S1 TRH, Sample S2 Total BTEX, and Samples S3 and S4 PAHs are presented in Figures 51 to 54.

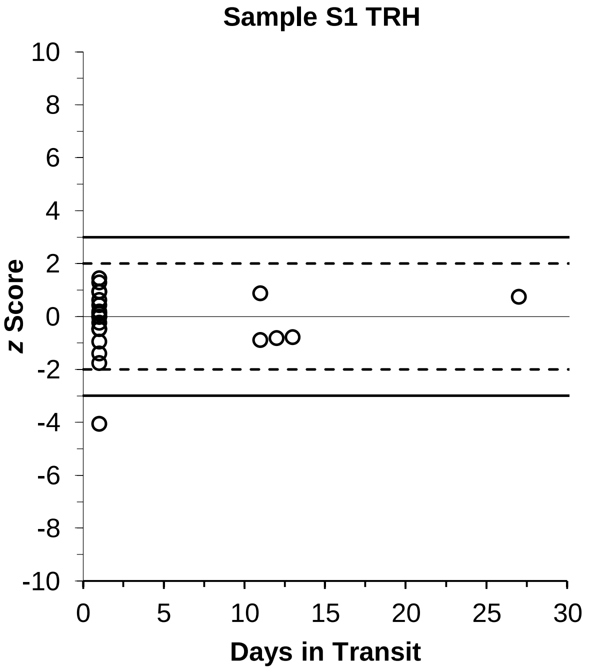


Figure 51 S1 TRH Results vs Days in Transit

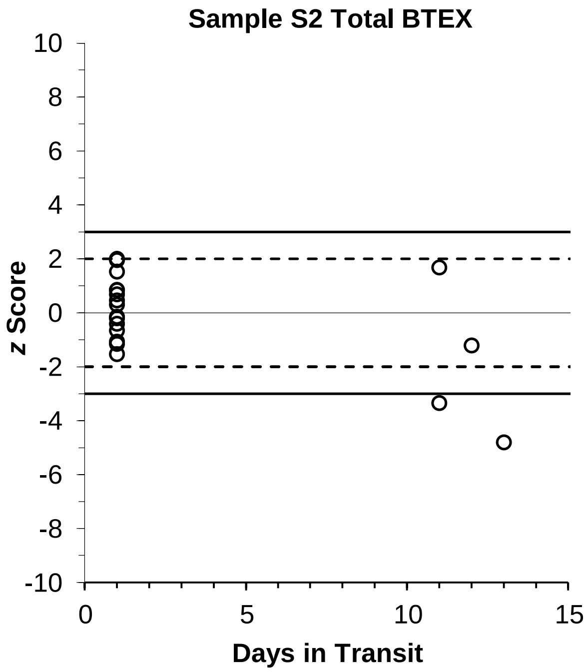


Figure 52 S2 Total BTEX Results vs Days in Transit

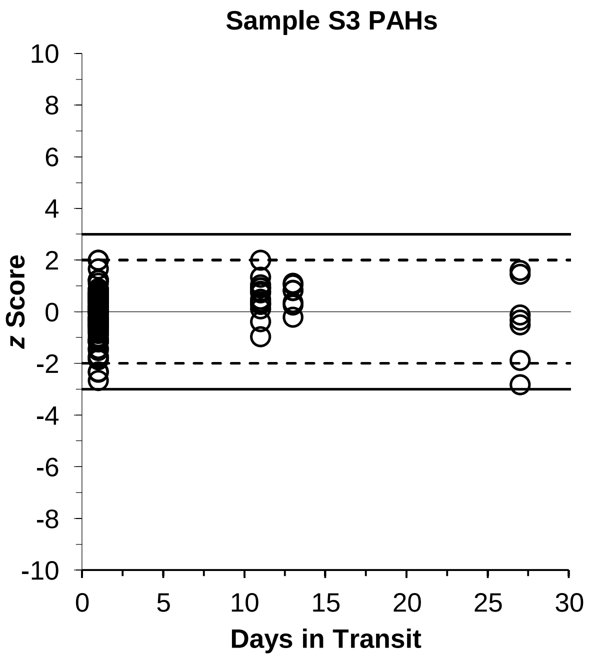


Figure 53 S3 PAHs *z* Scores vs Days in Transit

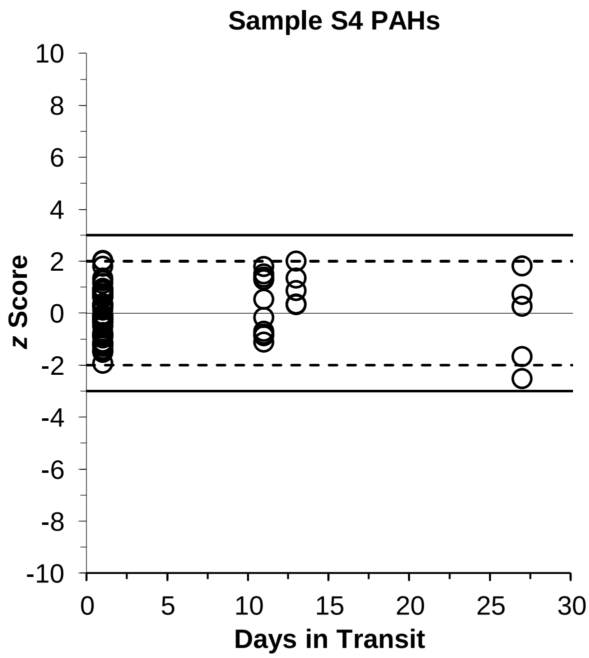


Figure 54 S4 PAHs *z* Scores vs Days in Transit

## APPENDIX 3 TEST METHODS REPORTED BY PARTICIPANTS

Participants were requested to provide information about their test methods. Responses are presented in Tables 35 to 37. Some responses may be modified so that the participant cannot be identified.

Table 35 Test Methods Sample S1 TRH

| Lab. Code | Sample Mass (g) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument | Method Reference |
|---|---|---|---|---|---|---|
| 1 | 10 | Solid-Liquid | DCM/ACETONE | | GC-FID | USEPA 8015 |
| 2 | 10 | Solid-Liquid | Hexane | Yes | GC-FID | USEPA |
| 3 | 10 | Solid-Liquid | DCM:Acetone | | GC-FID | In house |
| 4 | 10 | Sonication | DCM:Acetone 1:1 | Silica | GC-FID | USEPA 8015 |
| 5 | 10 | Solid-Liquid | DCM:Acetone | | GC-FID | |
| 6 | 8 | Solid-Liquid | Hexane:Acetone | Silica | GC-FID | |
| 7 | 10 | Solid-Liquid | DCM/Acetone | None | GC-FID | USEPA 8270C |
| 8 | 10 | Solid-Liquid | 1:1 DCM: ACETONE | | GC-FID | USEPA SW 846 - 8015 |
| 9 | 2 | Solid-Liquid | Hexane/Acetone | | GC-FID | Inhouse |
| 10 | 10 | Solid-Liquid | DCM:ACE | None | GC-FID | |
| 11 | 10g | Solid-Liquid | Ace/DCM | | GC-FID | USEPA8270 |
| 12 | 10 | Solid-Liquid | DCM/Acetone | Silica | GC-FID | NEPM Schedule B3 |
| 13 | 10 | Solid-Liquid | DCM/Acetone | | GC-FID | USEPA 3510 |
| 14 | 15 | Solid-Liquid | DCM/Hex | | GC-FID | USEPA 8015 |
| 15 | 10 | Solid-Liquid | DCM:Acetone | | GC-FID | In house |
| 16 | NT | | | | | |
| 17 | 10 | Solid-Liquid | Acetone:DCM | | GC-FID | USEPA SW846 8015 |
| 18 | 7.3 | Solid-Liquid | Hex:Acetone | no | GC-FID | In House |
| 19 | 10 | Solid-Liquid | DCM:Acetone | None | GC-FID | USEPA 3510 |

| Lab. Code | Sample Mass (g) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument | Method Reference |
|---|---|---|---|---|---|---|
| 20 | 10 | Solid-Liquid | DCM:Acetone | None | GC-FID | USEPA 3510 |
| 21 | 10 | Solid-Liquid | DCM/Acetone | NA | GC-FID | in-house |
| 22 | 10 | Solid-Liquid | DCM | Silica | GC-FID | In house |
| 23 | 10g | Solid-Liquid | DCM:Acetone | - | GC-FID | USEPA 3510 |

Table 36 Test Methods Sample S2 BTEX

| Lab. Code | Sample Mass (g) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument | Method Reference |
|---|---|---|---|---|---|---|
| 1 | NT | | | | | |
| 2 | 10 | Solid-Liquid | Methanol | No | P&T GC-MS | USEPA 8260 |
| 3 | 5 | Solid-Liquid | Methanol | | P&T GC-MS/MS | In house |
| 4 | 14 | Sonication | Methanol | Nil | Headspace GC-MS | USEPA 8260B |
| 5 | 5 | Solid-Liquid | Methanol | | P&T GC-MS | |
| 6 | 10 | | Methanol | N/A | Headspace GC-MS/MS | |
| 7 | 10 | Purge and Trap | Methanol | None | GC-MS | USEPA 8260B |
| 8 | 5 | Solid-Liquid | METHANOL | | P&T GC-MS | USEPA 8260 |
| 9 | 2 | Solid-Liquid | methanol | | Headspace GC-MS | Inhouse |
| 10 | 10 | Solid-Liquid | Methanol | None | P&T GC-MS | |
| 11 | 10g | Solid-Liquid | MeOH | | P&T GC-MS/MS | USEPA8260 |
| 12 | NT | | | | | |
| 13 | 4 | Solid-Liquid | Methanol | | P&T GCMS | USEPA 8260 |
| 14 | 10 | Solid-Liquid | Methanol | | P&T GC-MS | USEPA 8260 |
| 15 | 10 | Solid-Liquid | MeOH | | P&T GC-MS | USEPA 8260 |
| 16 | NT | | | | | |
| 17 | 5 | Solid-Liquid | Acetone:DCM | | P&T GC-MS | USEPA SW846 8260 |

| Lab. Code | Sample Mass (g) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument | Method Reference |
|---|---|---|---|---|---|---|
| 18 | 0.26 | | | no | headspace GC-FID | In House |
| 19 | 5 | Solid-Liquid | Methanol | None | P&T GC-MS | USEPA 8260 |
| 20 | 5 | Solid-Liquid | Methanol | None | P&T GC-MS | USEPA 8260 |
| 21 | NT | | | | | |
| 22 | 10 | Solid-Liquid | MeOH | None | P&T GC-MS | USEPA 8260 |
| 23 | 5g | Solid-Liquid | Methanol | - | P&T GC-MS | USEPA 8260 |

Table 37 Test Methods Samples S3 and S4 PAHs

| Lab. Code | Sample Mass (g) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument | Method Reference |
|---|---|---|---|---|---|---|
| 1 | 10 | Solid-Liquid | DCM/ACETONE | | GC-MS/MS | USEPA 8270 |
| 2 | 10 | Solid-Liquid | DCM/Acetone | No | GC-MS/MS | USEPA 8270 |
| 3 | 10 | Solid-Liquid | DCM:Acetone | | GC-MS | In house |
| 4 | NS | | | | | |
| 5 | 10 | Solid-Liquid | DCM:Acetone | | GC-MS | |
| 6 | 8 | Solid-Liquid | Hexane:Acetone | Florisil | GC-MS | In-house |
| 7 | 10 | Solid-Liquid | DCM/Acetone | None | GC-MS | USEPA 8270C |
| 8 | 10 | Solid-Liquid | 1:1 DCM: ACETONE | | GC-MS | USEPA 8270 |
| 9 | 2 | Solid-Liquid | Hexane/Acetone | | GC-MS | Inhouse |
| 10 | 10 | Solid-Liquid | DCM:ACE | None | GC-MS | |
| 11 | 10g | Solid-Liquid | Ace/DCM | | GC-MS | USEPA8270 |
| 12 | 10 | Solid-Liquid | DCM | Nil | GC-MS/MS | USEPA 8270 |
| 13 | 10 | Solid-Liquid | Acetone/DCM | | GC-MS | USEPA 8100 |
| 14 | 15 | Solid-Liquid | DCM | | GC-MS | USEPA 8270 |
| 15 | 10 | Solid-Liquid | DCM:Acetone | | GC-MS/MS | |

| Lab. Code | Sample Mass (g) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument | Method Reference |
|---|---|---|---|---|---|---|
| 16 | 10 | Solid-Liquid | DCM/Acetone | | GC-MS | USEPA 8270 |
| 17 | 10 | Solid-Liquid | Acetone:DCM | | GC-MS | USEPA SW846 8270 |
| 18 | 10 | Solid-Liquid | Hex:Acetone | no | GC-MS | In House |
| 19 | 10 | Solid-Liquid | DCM:Acetone | None | GC-MS | USEPA 8270 |
| 20 | 10 | Solid-Liquid | DCM:Acetone | None | GC-MS | USEPA 8270 |
| 21 | 2 | Solid-Liquid | Ethyl acetate | NA | GC-MS/MS | in-house |
| 22 | 10 | Solid-Liquid | DCM/acetone | None | GC-MS/MS | USEPA 8270 |
| 23 | 10g | Solid-Liquid | DCM:Acetone | - | GC-MS | USEPA 8270 |

## APPENDIX 4 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, *z* SCORE AND $E_n$ SCORE CALCULATIONS

### A4.1 Robust Average and Associated Uncertainty

The robust average was calculated using the procedure described in ISO 13528:2015.[7] The associated uncertainty was estimated as according to Equation 4.

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

where:

$u_{rob\ av}$ is the standard uncertainty of the robust average

$S_{rob\ av}$ is the standard deviation of the robust average

$p$ is the number of results

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

A worked example is set out below in Table 38.

Table 38 Uncertainty of the Robust Average for Sample S4 Phenanthrene

| | |
|---|---|
| No. Results (p) | 22 |
| Robust Average | 1.15 mg/kg |
| $S_{rob\ av}$ | 0.19 mg/kg |
| $u_{rob\ av}$ | 0.05 mg/kg |
| $k$ | 2 |
| $U_{rob\ av}$ | 0.10 mg/kg |

Therefore, the robust average for Sample S4 phenanthrene is 1.15 ± 0.10 mg/kg.

### A4.2 *z* Score and $E_n$ Score Calculations

For each participant's result, a *z* score and $E_n$ score are calculated according to Equations 2 and 3 respectively (Section 4).

A worked example is set out below in Table 39.

Table 39 *z* Score and $E_n$ Score Calculation for Sample S1 >C10-C16 Result Reported by Laboratory 1

| Participant Result (mg/kg) | Assigned Value (mg/kg) | Target SD | *z* Score | $E_n$ Score |
|---|---|---|---|---|
| 1069 ± 321 | 1080 ± 100 | 15% as PCV, or: 0.15 × 1080 = 162 mg/kg | $z$ Score $= \frac{1069-1080}{162}$ = -0.07 | $E_n$ Score $= \frac{1069-1080}{\sqrt{321^2+100^2}}$ = -0.03 |

## APPENDIX 5 ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| ACE | Acetone |
| AV | Assigned Value |
| BTEX | Benzene, Toluene, Ethylbenzene, Xylenes |
| CITAC | Cooperation on International Traceability in Analytical Chemistry |
| CRM | Certified Reference Material |
| CV | Coefficient of Variation |
| DCM | Dichloromethane |
| EtOAc | Ethyl Acetate |
| FID | Flame Ionisation Detection |
| GAG | General Accreditation Guidance (NATA) |
| GC | Gas Chromatography |
| GUM | Guide to the expression of Uncertainty in Measurement |
| HEX | Hexane |
| HS | Headspace (GC) |
| IEC | International Electrotechnical Commission |
| ISO | International Standards Organization |
| LOR | Limit Of Reporting |
| Max | Maximum value in a set of results |
| Md | Median value in a set of results |
| MeOH | Methanol |
| Min | Minimum value in a set of results |
| MS | Mass Spectrometry |
| MS/MS | Tandem Mass Spectrometry |
| MU | Measurement Uncertainty |
| N | Number of numeric results |
| NATA | National Association of Testing Authorities, Australia |
| NEPM | National Environmental Protection Measure |
| NMI | National Measurement Institute (Australia) |
| NR | Not Reported |
| NS | Not Supplied |
| NT | Not Tested |
| P&T | Purge and Trap (GC) |

| | |
|---|---|
| PAHs | Polycyclic Aromatic Hydrocarbons |
| PCV | Performance Coefficient of Variation |
| PT | Proficiency Testing |
| RA | Robust Average |
| RM | Reference Material |
| SD | Standard Deviation |
| SI | International System of Units |
| SLE | Solid-Liquid Extraction |
| SS | Spiked Samples |
| SV | Spiked Value, or formulated concentration of a PT sample |
| TRH | Total Recoverable Hydrocarbons |
| U | Expanded Uncertainty |
| US EPA | United States Environmental Protection Agency |

**END OF REPORT**