Australian Government
Department of Industry, Science and Resources

National Measurement Institute

# Proficiency Test Final Report AQA 23-10 Organic Compounds and Pesticides in Wastewater

October 2023

## 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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Gabriela Saveluc

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## SUMMARY

AQA 23-10 Organic Compounds and Pesticides in Wastewater commenced in June 2023. Twelve laboratories registered to participate, and eleven participants submitted results.

The sample set consisted of four wastewater samples. Samples were prepared in the NMI Sydney laboratory by spiking wastewater with various analytes.

Of a possible 253 results, 206 numeric results (81%) were submitted. Twenty-two results were a 'less than' value ($< x$) or Not Reported (NR), and 25 results were Not Tested (NT).

The assigned values for all scored analytes were the robust averages of participants' results. The associated uncertainties were estimated from the robust standard deviations of the 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:

- *Assess the ability of participants to correctly identify organic compounds and pesticides in wastewater.*

Laboratories **3**, **4**, **6**, **7** and **10** reported numeric results for all 16 scored analytes.

Two participants did not report numeric results for analytes which they tested for and were present in the test samples (total of two results). Three participants reported numeric results for analytes not spiked into the test samples (total of five results).

- *Compare the performance of participants and assess their accuracy in the measurement of organic compounds and pesticides in wastewater.*

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

Of 162 $z$-scores, 157 (97%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Of 151 $E_n$-scores, 128 (85%) returned a score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **4** achieved satisfactory $z$-and $E_n$-scores across all 16 scored analytes.

- *Evaluate the participants' methods for the measurement of organic compounds and pesticides in wastewater.*

For Sample S1 TRH, most participants used liquid-liquid extraction with dichloromethane, with analysis on GC-FID.

For Sample S2 BTEX, all participants used purge-and-trap GC-MS(/MS).

For Sample S3 PAHs, a wide variety of extraction techniques and solvents were used, however all participants used GC-MS(/MS) for analysis.

For Sample S4 Pesticides, a wide variety of procedures were employed by participants.

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

Of 206 numeric results, 201 (98%) were reported with an expanded measurement uncertainty. The magnitude of reported uncertainties was within the range of 1.3% to 50%. Participants used a wide variety of procedures to estimate their uncertainty.

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

The test samples of this study are homogeneous and are well characterised. Surplus samples are available for purchase from NMI 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 interlaboratory 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 studies in:

- pesticide residues in soil and water, fruit, vegetables and herbs;
- petroleum hydrocarbons and volatile organic compounds 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:

- assess the ability of participants to correctly identify organic compounds and pesticides in wastewater;
- compare the performance of participants and assess their accuracy in the measurement of organic compounds and pesticides in wastewater;
- evaluate the participants' methods for the measurement of organic compounds and pesticides in wastewater;
- 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 PT studies 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,[1] and The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.[4]

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

## 2 STUDY INFORMATION

### 2.1 Study Timetable

The timetable of the study was:

| | |
|---|---|
| Invitations sent | 13/06/2023 |
| Samples sent | 3/07/2023 |
| Results due | 7/08/2023 |
| Interim Report | 10/08/2023 |
| Preliminary Report | 12/09/2023 |

The release of the Preliminary Report was delayed due to an internal investigation relating to Sample S2 (see Section 2.8).

### 2.2 Participation and Laboratory Code

Twelve laboratories registered to participate in this study, and all participants were assigned a confidential laboratory code number for this study. Eleven participants submitted results.

### 2.3 Selection of Analytes

When selecting analytes and spiking values for this study, consideration was given to:

- a variety of analytes amenable to gas and/or liquid chromatography; and
- feedback and suggestions from participants and other stakeholders.

For Sample S1, participants were requested to measure semi-volatile hydrocarbons (>C10-C40) and total recoverable hydrocarbons (TRH). For Sample S2, participants were requested to measure volatile hydrocarbons (C6-C10), and benzene, toluene, ethylbenzene and xylenes (BTEX). For Sample S3, participants were provided with a list of potential poly-aromatic hydrocarbons (PAHs) that were spiked the sample (Table 1). For Sample S4, participants were provided with a list of potential pesticides that were spiked into the sample (Table 2).

Table 1 List of Possible PAHs for Sample S3

| | | | |
|---|---|---|---|
| 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 |

Table 2 List of Possible Pesticides for Sample S4

| | | |
|---|---|---|
| Aldicarb | Dicamba | Omethoate |
| Aldrin | Dieldrin | Parathion |
| Atrazine | Dimethoate | Parathion-methyl |
| Azinphos-methyl | Diuron | Pendimethalin |
| Chlorpyrifos | Endosulfan | Permethrin |
| Chlordane | Ethion | Picloram |
| Chlorfenvinphos | Fenthion | Piperonyl butoxide |
| Clopyralid | Heptachlor | Pirimicarb |

| | | |
|---|---|---|
| Cyfluthrin | Imazapyr | Pirimphos-ethyl |
| Cypermethrin | Lindane | Pirimphos-methyl |
| 2,4-D | Malathion | Propiconazole |
| DDT | MCPA | Simazine |
| Deltamethrin | Metolachlor | 2,4,5-T |
| Diazinon | Metsulfuron-methyl | Tetrachlorvinphos |

## 2.4 Test Material Preparation

The test samples were prepared by spiking processed wastewater with various analytes to obtain the concentrations listed in Table 3. Additional information on the preparation of the samples is given in Appendix 1.

Table 3 Spiked Values of Test Samples

| Sample | Analyte | Spiked Value (µg/L) | Uncertainty* (µg/L) |
|---|---|---|---|
| S1 | TRH | 2810 | 140 |
| S2 | Benzene | 69.2 | 3.5 |
| | Toluene | 261 | 13 |
| | Ethylbenzene | 29.0 | 1.5 |
| | Xylenes | 129 | 6 |
| | Total BTEX | 489 | 24 |
| S3 | Acenaphthene | 8.08 | 0.40 |
| | Acenaphthylene | 1.09 | 0.05 |
| | Benz[*a*]anthracene | 6.50 | 0.32 |
| | Benzo[*a*]pyrene | 3.62 | 0.18 |
| | Fluorene | 3.10 | 0.15 |
| | Phenanthrene | 1.95 | 0.10 |
| S4 | Atrazine | 11.6 | 0.6 |
| | Chlorpyrifos | 20.1 | 1.0 |
| | Dicamba | 7.49 | 0.37 |
| | Dieldrin | 5.01 | 0.25 |
| | Ethion | 3.99 | 0.20 |
| | Lindane | 10.0 | 0.5 |
| | Simazine | 5.05 | 0.25 |

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

## 2.5 Homogeneity and Stability of Test Materials

No homogeneity or stability testing was conducted for this study. The samples were prepared, packaged and stored using a process that has been demonstrated to produce sufficiently homogeneous and stable samples in previous NMI PT studies with similar analytes and matrices.

Participants' results gave no reason to question the homogeneity or transportation stability of the samples (Appendix 2). Assigned values were set if there was a reasonable consensus between participants' results.

### 2.6 Test Material Storage and Dispatch

After preparation, the samples were stored at 4 °C. Samples were packaged into insulated polystyrene foam boxes with cooler bricks and dispatched by courier on 3 July 2023.

The following items were packaged with the samples:

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

An 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.
- For each analyte in each sample, report a single result in units of µg/L expressed as if reporting to a client, applying the limit of reporting of the method used for analysis. This is the figure that will be used in all statistical analysis in the study report. Also, reported the associated expanded uncertainty in units of µg/L (e.g. 2000 ± 200 µg/L), if determined.
- If an analyte was not tested for, please report 'NT' as its result.
- Give details of your methodology and basis of uncertainty estimate as requested by the results sheet.
- Return the completed results sheet by 31 July 2023 by email to proficiency@measurement.gov.au.

The results due date was later extended to 7 August 2023 due to issues affecting some participants.

### 2.8 Interim Report and Preliminary Report

An Interim Report was emailed to all participants on 10 August 2023.

A Preliminary Report was emailed to all participants on 12 September 2023. The Preliminary Report included a summary of the results reported by participants, assigned values, performance coefficient of variations, *z*-scores and $E_n$-scores for each analyte in this study. No data from the Preliminary Report has been changed in the present Final Report.

The release of this Preliminary Report was delayed because of an internal investigation for Sample S2 ethylbenzene. This was due to a greater variability of participants' results as compared to the other BTEX analytes. This variability was also observed in the internal investigation, and so this analyte was not scored.

## 3 PARTICIPANT LABORATORY INFORMATION

### 3.1 Participants' Test Methods

Participants were requested to provide information about their test methods. Responses are presented in Appendix 4.

### 3.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their measurement uncertainty (MU) estimates. Responses are presented in Table 4. Some responses were modified so that the participant cannot be identified.

Table 4 Basis of Measurement Uncertainty Estimate

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation* | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 1 | Top Down - precision and estimates of the method and laboratory bias | Control samples - SS<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |
| 2 | 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 | Eurachem/CITAC Guide |
| 3 | Top Down - precision and estimates of the method and laboratory bias | Control samples - CRM | Recoveries of SS | Eurachem/CITAC Guide |
| 4 | Top Down - precision and estimates of the method and laboratory bias | Control samples - RM<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Recoveries of SS | ISO/GUM |
| 5 | 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 | Eurachem/CITAC Guide |
| 6 | Top Down - precision and estimates of the method and laboratory bias | Control samples - RM<br>Duplicate analysis | CRM<br>Instrument calibration | Eurachem/CITAC Guide |
| 7 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Control samples<br>Duplicate analysis<br>Instrument calibration | Instrument calibration<br>Laboratory bias from PT studies<br>Recoveries of SS | Eurachem/CITAC Guide |
| 8 | 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 |
| 10 | Top Down - reproducibility (standard deviation) from PT studies used directly | Control samples - SS<br>Duplicate analysis<br>Instrument calibration | | Eurachem/CITAC Guide |
| 11 | Top Down - precision and estimates of the method and laboratory bias | Control samples<br>Instrument calibration | Instrument calibration<br>Recoveries of SS<br>Standard purity | Eurachem/CITAC Guide |
| 12 | Bottom Up (ISO/GUM, fish bone/cause and effect diagram) | Duplicate analysis | | ISO/GUM |

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

### 3.3 Participants' Comments

Participants were invited to make comments or suggestions on the samples, this study, or possible future studies. Such feedback may be useful in improving future studies. Participants' comments received for this study are presented in Table 5, along with the study coordinator's response where applicable. Some responses may be modified so that the participant cannot be identified.

Table 5 Participants' Comments

| Lab. Code | Sample | Participant's Comments | Study Coordinator's Response |
|---|---|---|---|
| 3 | S1 | A 100mL aliquot was subsampled from the 500mL bottle and prepared as per procedure. | |
| | S2 | The laboratory had noted variations associated with the concentration of Ethylbenzene in this study. Each vial had a slightly different concentration to the next and confirmed on the same instrumentation. The laboratory obtained Ethylbenzene concentrations between 2.5 to 18.8 ug/L. A raised limit of report of 20 ug/L was used due to the high %RPD seen amongst each vial. | Further investigation was performed by NMI for this analyte, and some variability was observed. Therefore, no assigned value has been set for Sample S2 ethylbenzene to ensure participants were not negatively affected with regards to scoring. |
| | All | Please prepare more samples in the 100mL approach for SV analysis. | Thank you for your feedback. We are looking into providing 100 mL bottles as an option for other future PT studies. |
| 11 | S4 | Propazine detected at 0.05 ug/L | |

# 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

## 4.1 Results Summary

Participant results are listed in Tables 6 to 28 with summary statistics: robust average, median, mean, number of 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.

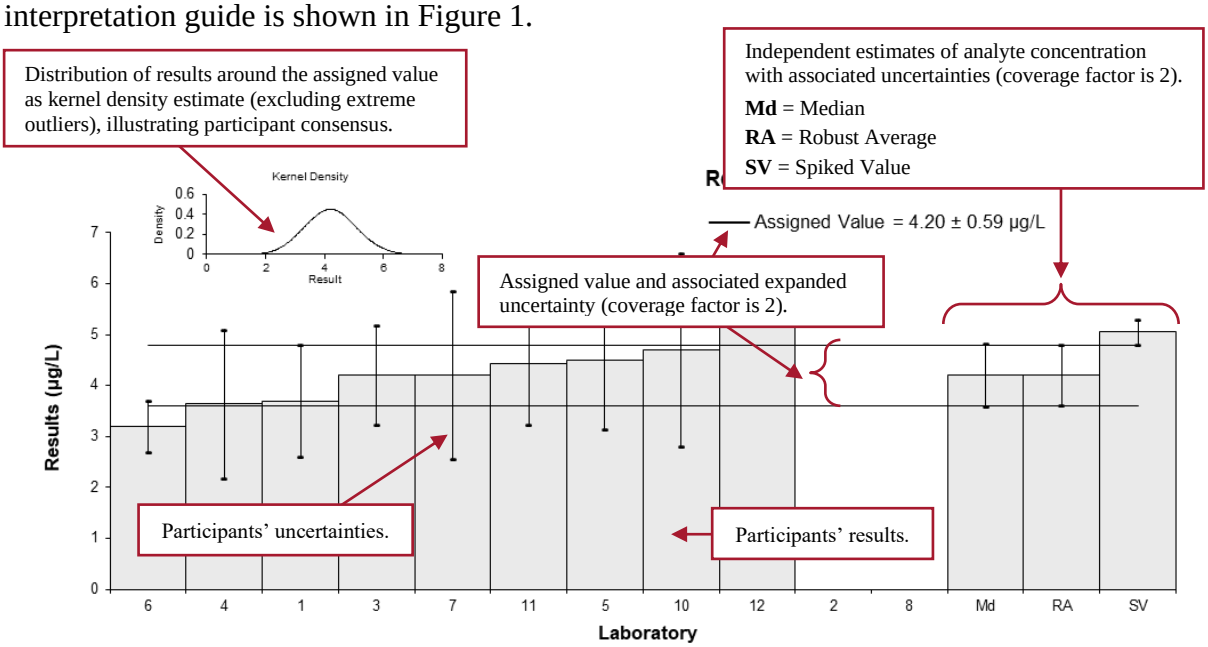



Figure 1 Guide to Presentation of Results

## 4.2 Outliers and Extreme Outliers

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

## 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, this property is the concentration 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 3).

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

The robust averages and associated expanded uncertainties, and robust CVs (a measure of the variability of participants' results) were calculated using the procedure described in ISO 13528.[5]

## 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 analyte concentrations. The PCV is not the CV of participants' results; it is set by the study coordinator and is based on the analyte concentrations and experience from previous studies, and is supported by mathematical models such as the Thompson-Horwitz equation.[6] By setting a fixed and realistic value for the PCV, a participant's performance does not depend on other participants' performances and can be compared from study to study.

### 4.6 Target Standard Deviation for Proficiency Assessment

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 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

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.

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

### 4.8 $E_n$-Score

The $E_n$-score is complementary to the *z*-score in the assessment of laboratory performance. The $E_n$-score includes expanded 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 MU associated with their test results.[7]

Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[8]

## 5 TABLES AND FIGURES

Table 6

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Wastewater |
| **Analyte** | >C10-C16 |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | 950 | 300 |
| **2** | 903 | 261.87 |
| **3** | 770 | 326 |
| **4** | 420 | 130 |
| **5** | 400 | 120 |
| **6** | 940 | 282 |
| **7** | 250 | 85 |
| **8** | 700 | 190 |
| **10** | 510 | 200 |
| **11** | 1056 | 296 |
| **12** | 705 | 20 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | Not Spiked | |
| **Robust Average** | 690 | 230 |
| **Median** | 710 | 260 |
| **Mean** | 690 | |
| **N** | 11 | |
| **Max** | 1056 | |
| **Min** | 250 | |
| **Robust SD** | 300 | |
| **Robust CV** | 43% | |

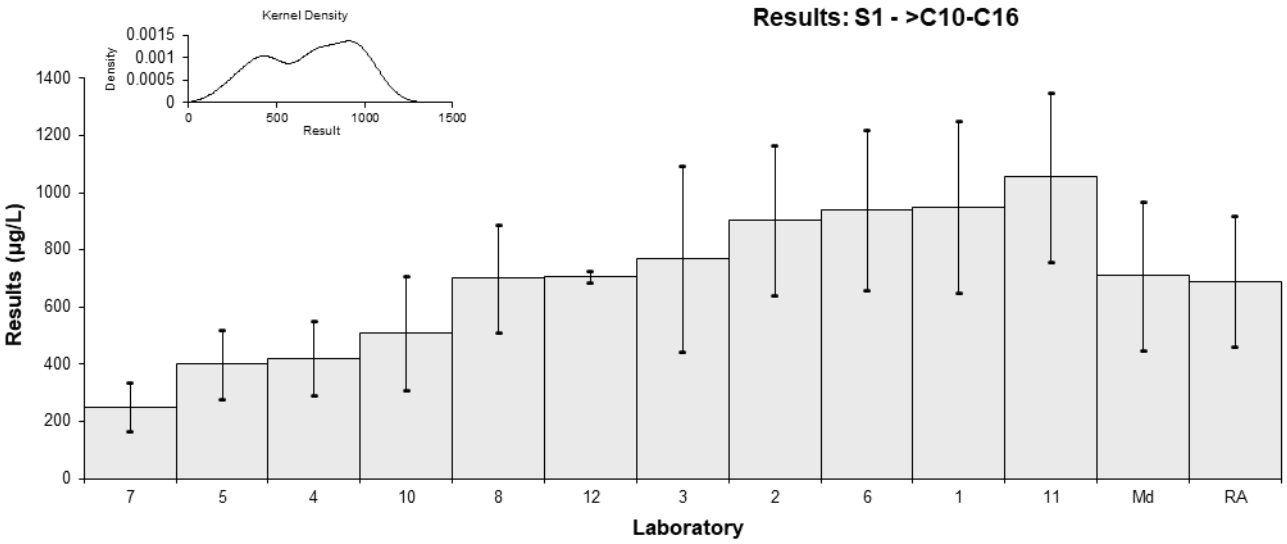

Results: S1 - >C10-C16
Kernel Density
Density
0.0015
0.001
0.0005
0
0
500
1000
1500
Result
Results (µg/L)
1400
1200
1000
800
600
400
200
0
7
5
4
10
8
12
3
2
6
1
11
Md
RA
Laboratory

Figure 2

Table 7

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Wastewater |
| **Analyte** | >C16-C34 |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | 840 | 300 |
| **2** | 1111 | 333.3 |
| **3** | 810 | 258 |
| **4** | 459 | 140 |
| **5** | <300 | NR |
| **6** | 890 | 270 |
| **7** | 310 | 120 |
| **8** | 790 | 300 |
| **10** | 350 | 140 |
| **11** | 1273 | 344 |
| **12** | 520 | 20 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | Not Spiked | |
| **Robust Average** | 740 | 290 |
| **Median** | 800 | 350 |
| **Mean** | 740 | |
| **N** | 10 | |
| **Max** | 1273 | |
| **Min** | 310 | |
| **Robust SD** | 360 | |
| **Robust CV** | 49% | |

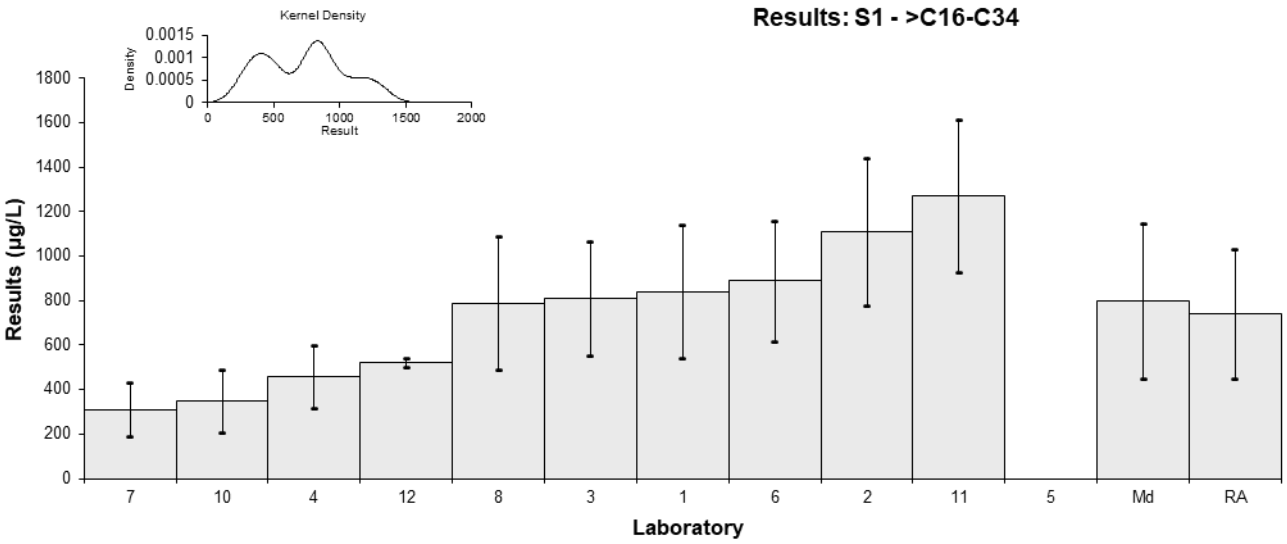

Results: S1 - >C16-C34
Kernel Density
Density
0.0015
0.001
0.0005
0
0
500
1000
1500
2000
Result
Results (µg/L)
1800
1600
1400
1200
1000
800
600
400
200
0
7
10
4
12
8
3
1
6
2
11
5
Md
RA
Laboratory

Figure 3

Table 8

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Wastewater |
| **Analyte** | >C34-C40 |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | <500 | NR |
| **2** | <200 | NR |
| **3** | <100 | NR |
| **4** | <50 | NR |
| **5** | <300 | NR |
| **6** | <100 | NR |
| **7** | <100 | 62 |
| **8** | <100 | NR |
| **10** | <100 | NR |
| **11** | 222 | 58 |
| **12** | <20 | 20 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | Not Spiked | |
| **Robust Average** | NA (N<6) | |
| **Median** | NA (N<3) | |
| **Mean** | NA (N<2) | |
| **N** | 1 | |
| **Max** | 222 | |
| **Min** | 222 | |
| **Robust SD** | NA (N<6) | |
| **Robust CV** | NA (N<6) | |

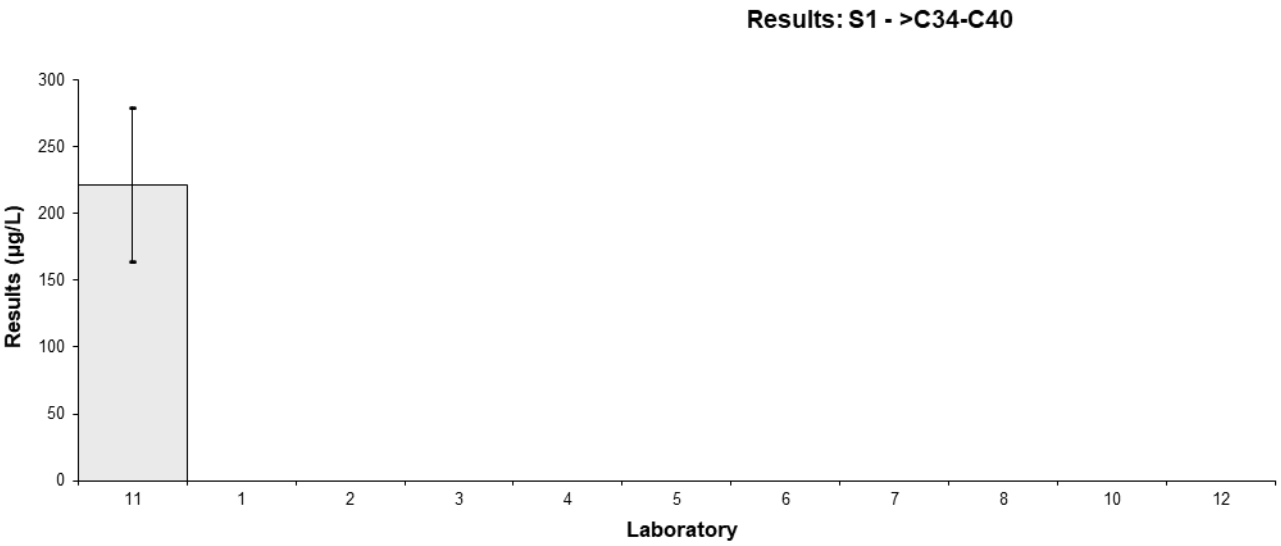

Results: S1 - >C34-C40
Results (µg/L)
300
250
200
150
100
50
0
11
1
2
3
4
5
6
7
8
10
12
Laboratory

Figure 4

Table 9

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Wastewater |
| **Analyte** | TRH |
| **Unit** | µg/L |

**Participant Results**

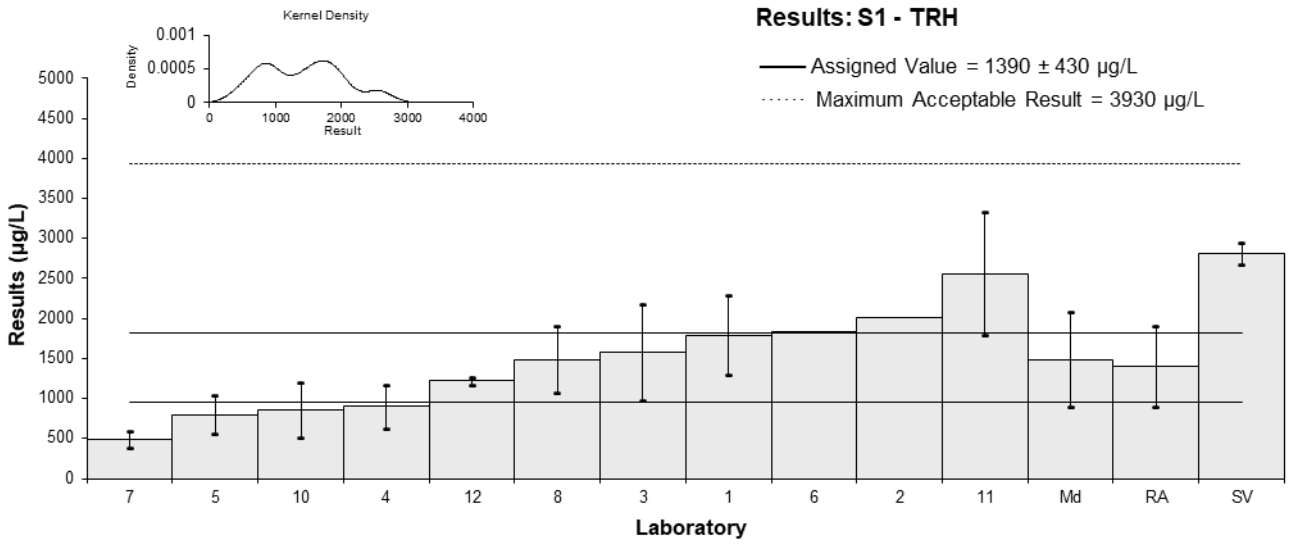
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1790 | 500 | 1.44 | 0.61 |
| **2** | 2014 | NR | 2.00▼ | |
| **3** | 1580 | 601 | 0.68 | 0.26 |
| **4** | 900 | 270 | -1.76 | -0.97 |
| **5** | 800 | 240 | -2.12 | -1.20 |
| **6** | 1830 | NR | 1.58 | 1.02 |
| **7*** | 490 | 98 | -3.24 | -2.04 |
| **8** | 1490 | 415 | 0.36 | 0.17 |
| **10** | 860 | 340 | -1.91 | -0.97 |
| **11*** | 2560 | 770 | 2.00▼ | |
| **12** | 1220 | 50 | -0.61 | -0.39 |

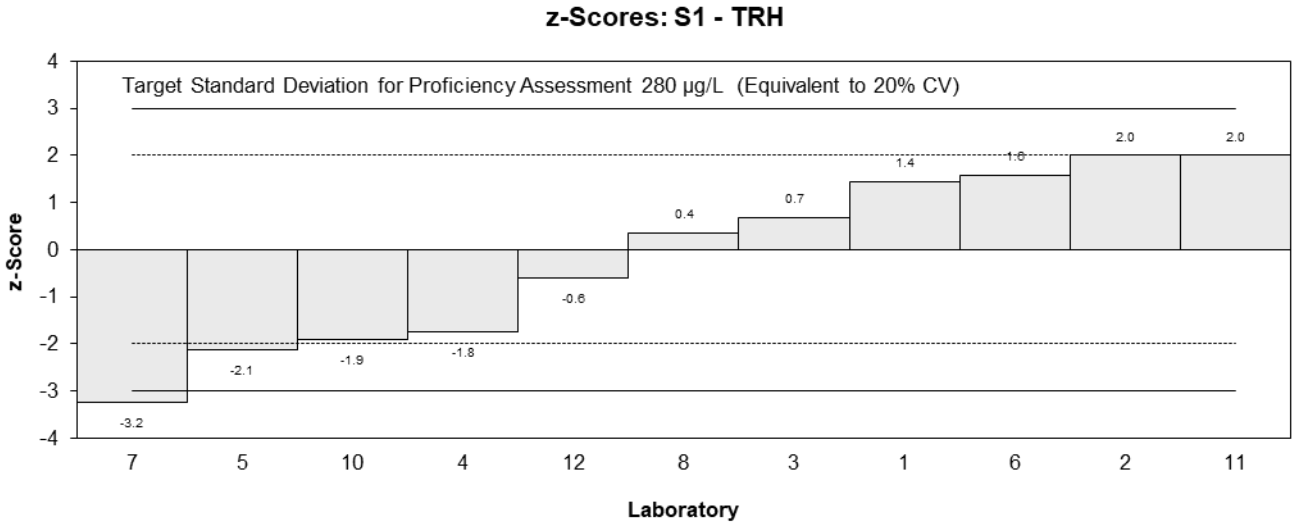
* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1390 | 430 |
| **Spike Value** | 2810 | 140 |
| **Robust Average** | 1400 | 510 |
| **Max Acceptable Result** | 3930 | |
| **Median** | 1490 | 590 |
| **Mean** | 1410 | |
| **N** | 11 | |
| **Max** | 2560 | |
| **Min** | 490 | |
| **Robust SD** | 670 | |
| **Robust CV** | 48% | |

Laboratory 2 did not report a TRH value. The study coordinator summed the individual hydrocarbon ranges, and no estimate of uncertainty of the TRH result was made.


Kernel Density
Density
Result
Results: S1 - TRH
Assigned Value = 1390 ± 430 µg/L
Maximum Acceptable Result = 3930 µg/L
Results (µg/L)
Laboratory
7
5
10
4
12
8
3
1
6
2
11
Md
RA
SV


z-Scores: S1 - TRH
Target Standard Deviation for Proficiency Assessment 280 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-3.2
-2.1
-1.9
-1.8
-0.6
0.4
0.7
1.4
1.6
2.0
2.0

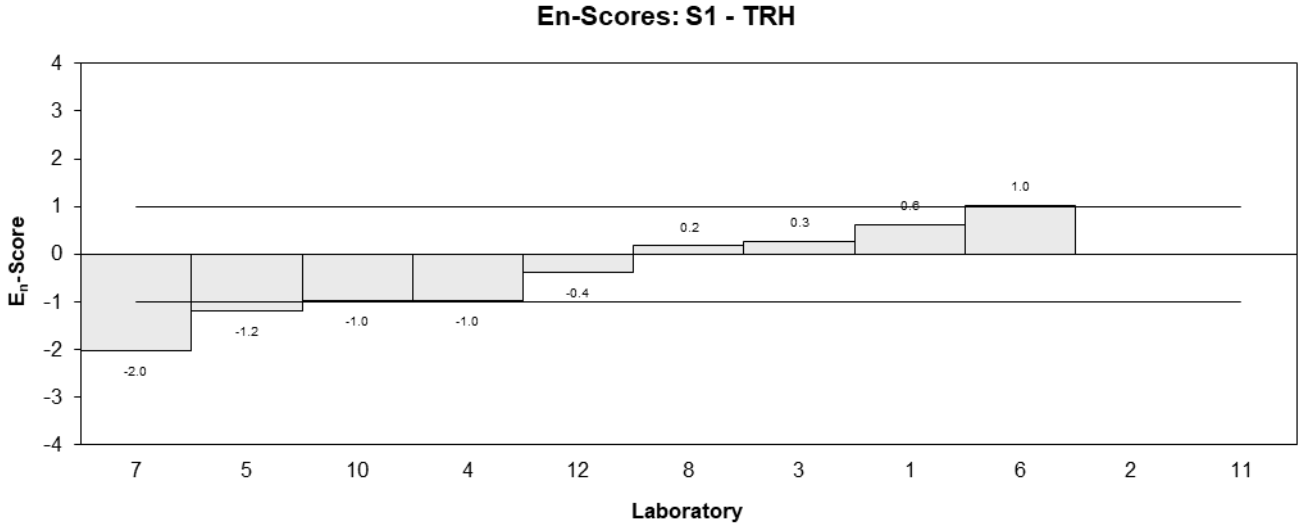

En-Scores: S1 - TRH
En-Score
Laboratory
-2.0
-1.2
-1.0
-1.0
-0.4
0.2
0.3
0.6
1.0

Figure 5

Table 10

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Wastewater |
| **Analyte** | C6-C10 |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | NT | NT |
| **2** | 1016 | 209.296 |
| **3** | 976 | 202.4 |
| **4** | 1190 | 360 |
| **5** | NT | NT |
| **6** | 970 | 191 |
| **7** | 1150 | 255 |
| **8** | 1060 | 237 |
| **10** | 580 | 240 |
| **11** | NT | NT |
| **12** | NT | NT |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | Not Spiked | |
| **Robust Average** | 1020 | 140 |
| **Median** | 1020 | 60 |
| **Mean** | 990 | |
| **N** | 7 | |
| **Max** | 1190 | |
| **Min** | 580 | |
| **Robust SD** | 140 | |
| **Robust CV** | 14% | |

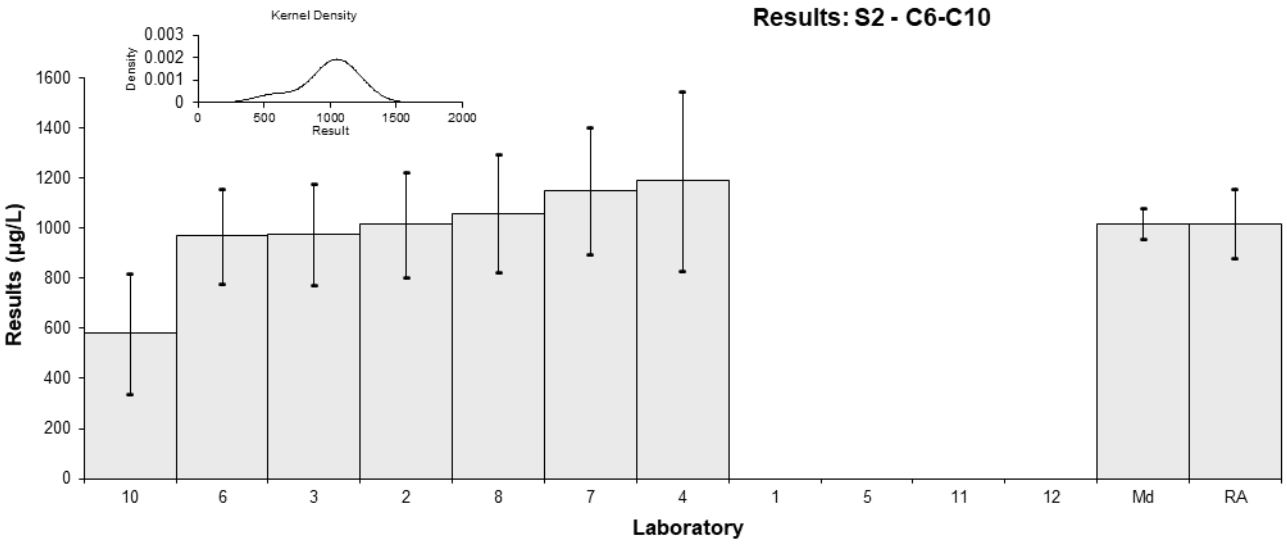

Results: S2 - C6-C10
Kernel Density
Density
0.003
0.002
0.001
0
0
500
1000
1500
2000
Result
Results (µg/L)
1600
1400
1200
1000
800
600
400
200
0
10
6
3
2
8
7
4
1
5
11
12
Md
RA
Laboratory

Figure 6

Table 11

**Sample Details**

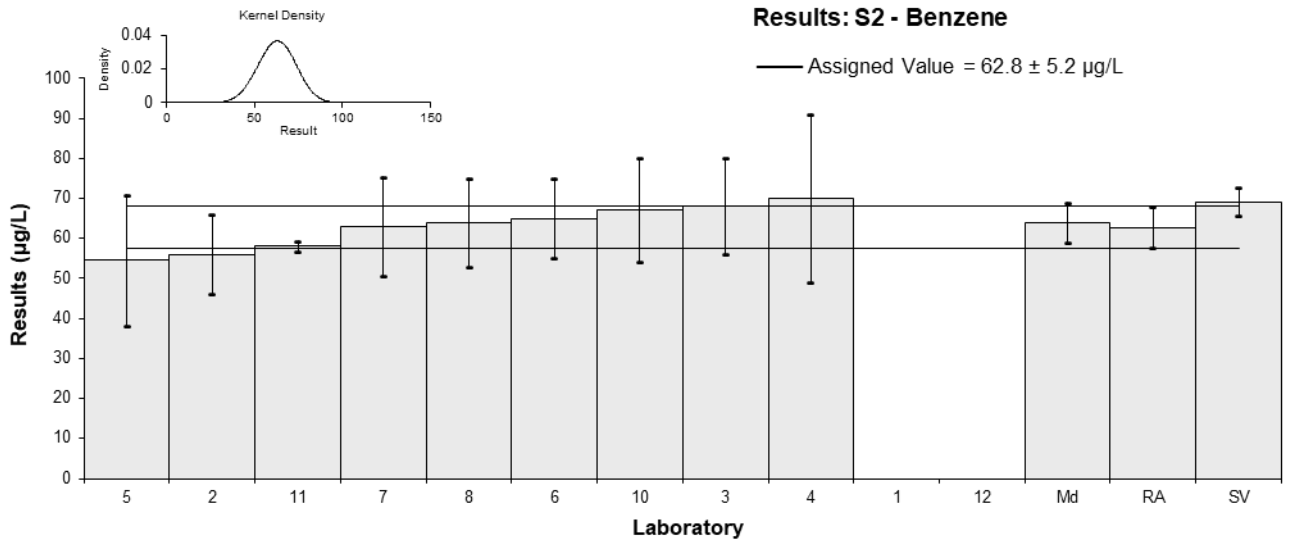
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Wastewater |
| **Analyte** | Benzene |
| **Unit** | µg/L |

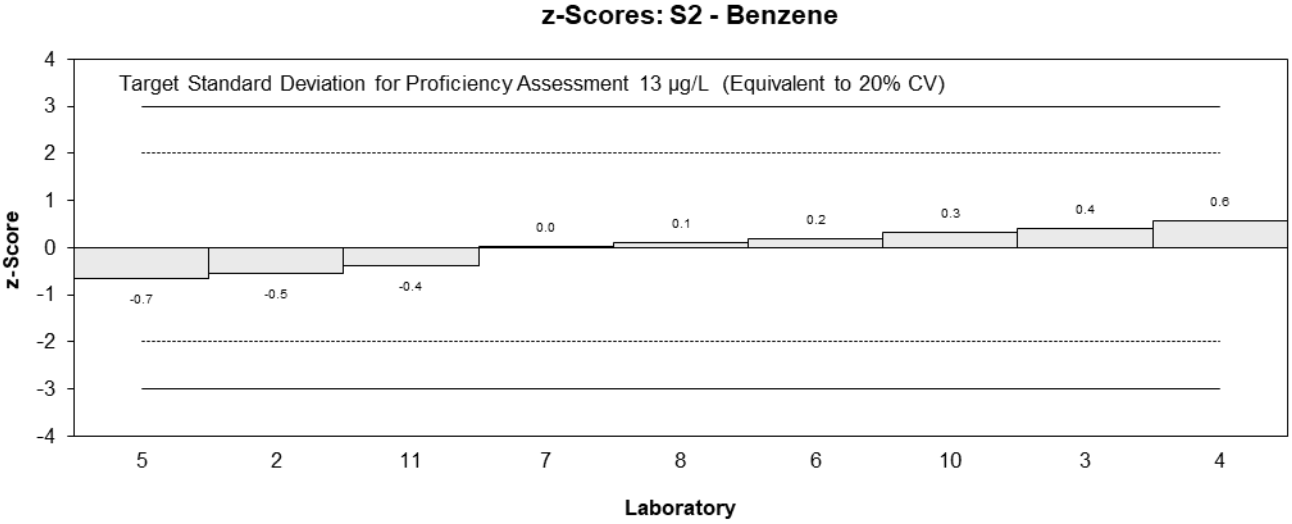
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 56 | 9.856 | -0.54 | -0.61 |
| **3** | 68 | 12 | 0.41 | 0.40 |
| **4** | 70.02 | 21 | 0.57 | 0.33 |
| **5** | 54.5 | 16.35 | -0.66 | -0.48 |
| **6** | 65 | 10 | 0.18 | 0.20 |
| **7** | 63 | 12.4 | 0.02 | 0.01 |
| **8** | 64 | 11 | 0.10 | 0.10 |
| **10** | 67 | 13 | 0.33 | 0.30 |
| **11** | 58 | 1.3 | -0.38 | -0.90 |
| **12** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 62.8 | 5.2 |
| **Spike Value** | 69.2 | 3.5 |
| **Robust Average** | 62.8 | 5.2 |
| **Median** | 64.0 | 4.9 |
| **Mean** | 62.8 | |
| **N** | 9 | |
| **Max** | 70.02 | |
| **Min** | 54.5 | |
| **Robust SD** | 6.2 | |
| **Robust CV** | 9.9% | |


Kernel Density
Density
Result
Results: S2 - Benzene
Assigned Value = 62.8 ± 5.2 µg/L
Results (µg/L)
Laboratory
5
2
11
7
8
6
10
3
4
1
12
Md
RA
SV


z-Scores: S2 - Benzene
Target Standard Deviation for Proficiency Assessment 13 µg/L (Equivalent to 20% CV)
z-Score
-0.7
-0.5
-0.4
0.0
0.1
0.2
0.3
0.4
0.6
Laboratory

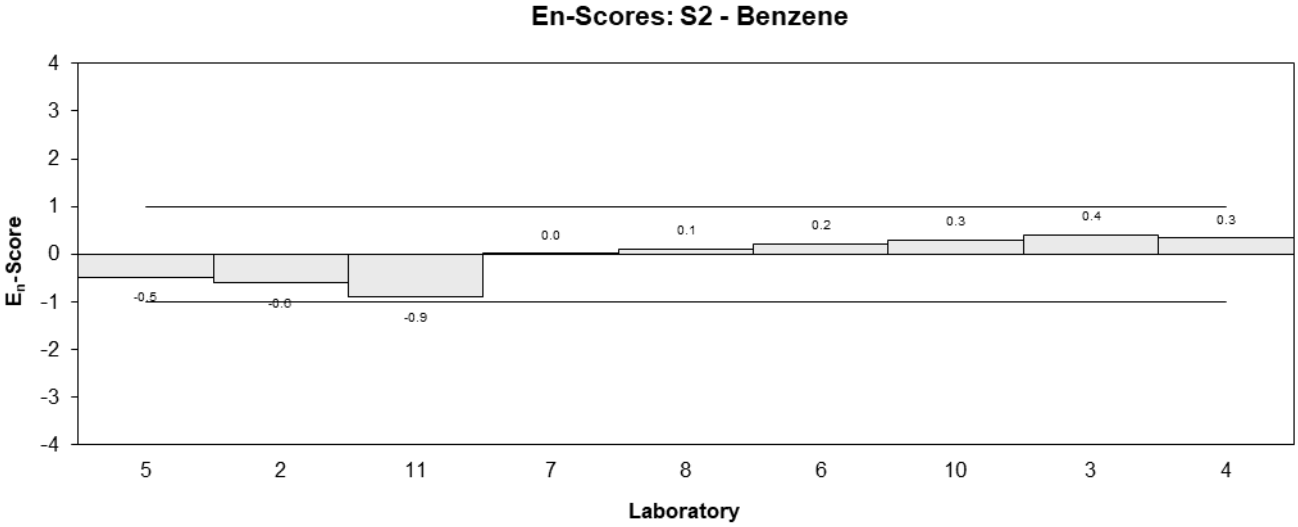

En-Scores: S2 - Benzene
En-Score
-0.5
-0.6
-0.9
0.0
0.1
0.2
0.3
0.4
0.3
Laboratory

Figure 7

Table 12

**Sample Details**

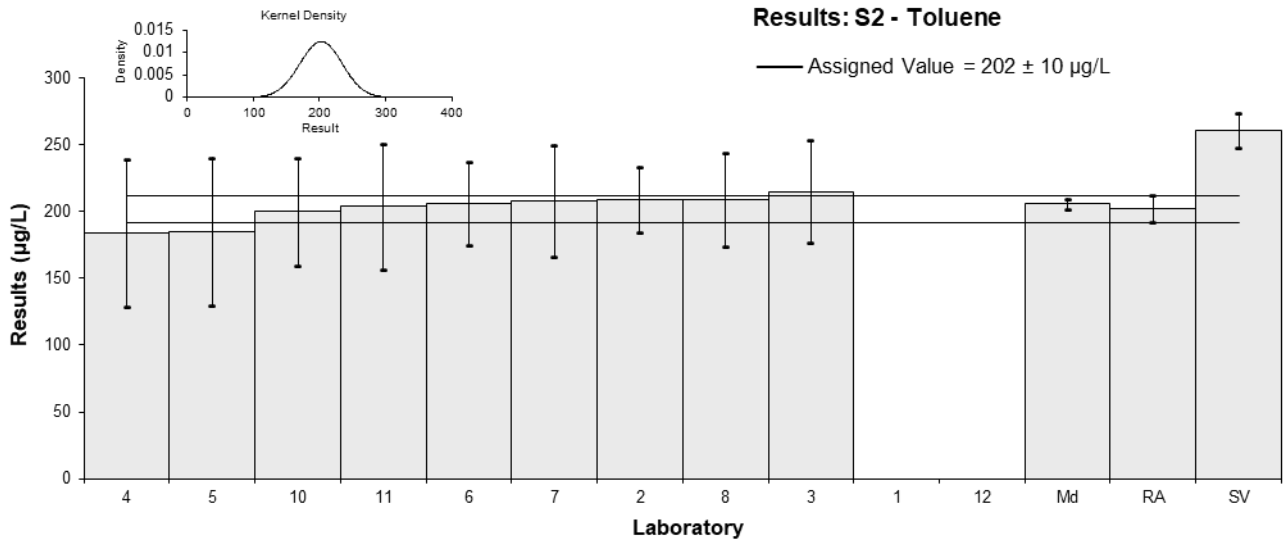
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Wastewater |
| **Analyte** | Toluene |
| **Unit** | µg/L |

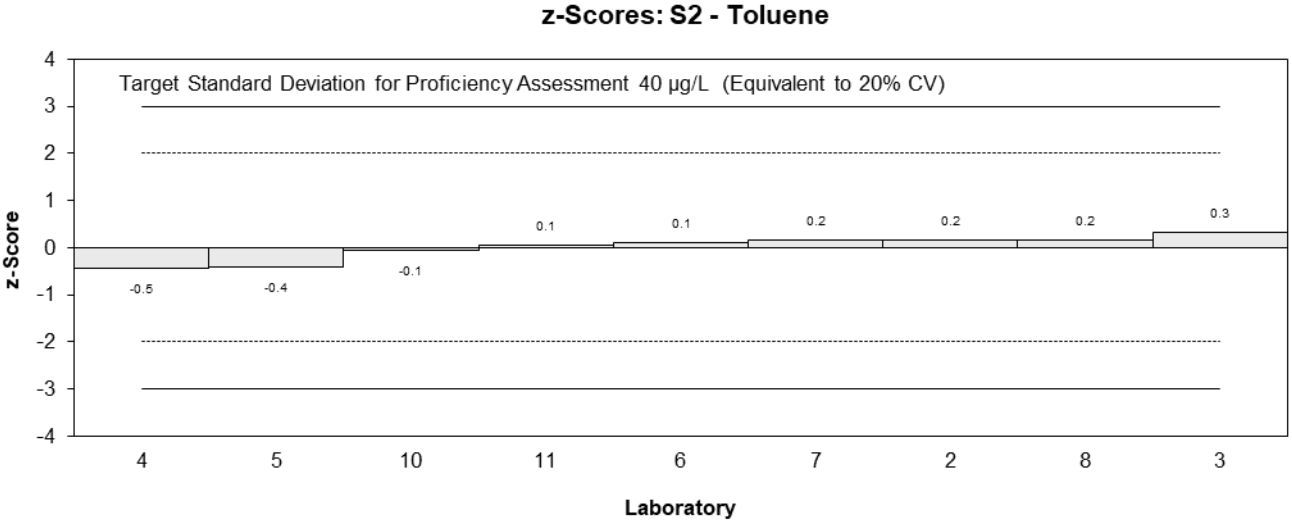
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 209 | 24.662 | 0.17 | 0.26 |
| **3** | 215 | 38.4 | 0.32 | 0.33 |
| **4** | 183.9 | 55 | -0.45 | -0.32 |
| **5** | 185 | 55.5 | -0.42 | -0.30 |
| **6** | 206 | 31 | 0.10 | 0.12 |
| **7** | 208 | 42 | 0.15 | 0.14 |
| **8** | 209 | 35 | 0.17 | 0.19 |
| **10** | 200 | 40 | -0.05 | -0.05 |
| **11** | 204 | 47 | 0.05 | 0.04 |
| **12** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 202 | 10 |
| **Spike Value** | 261 | 13 |
| **Robust Average** | 202 | 10 |
| **Median** | 206 | 4 |
| **Mean** | 202 | |
| **N** | 9 | |
| **Max** | 215 | |
| **Min** | 183.9 | |
| **Robust SD** | 12 | |
| **Robust CV** | 6.1% | |


Kernel Density
Density
Result
Results: S2 - Toluene
Assigned Value = 202 ± 10 µg/L
Results (µg/L)
Laboratory
4
5
10
11
6
7
2
8
3
1
12
Md
RA
SV


z-Scores: S2 - Toluene
Target Standard Deviation for Proficiency Assessment 40 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-0.5
-0.4
-0.1
0.1
0.1
0.2
0.2
0.2
0.3

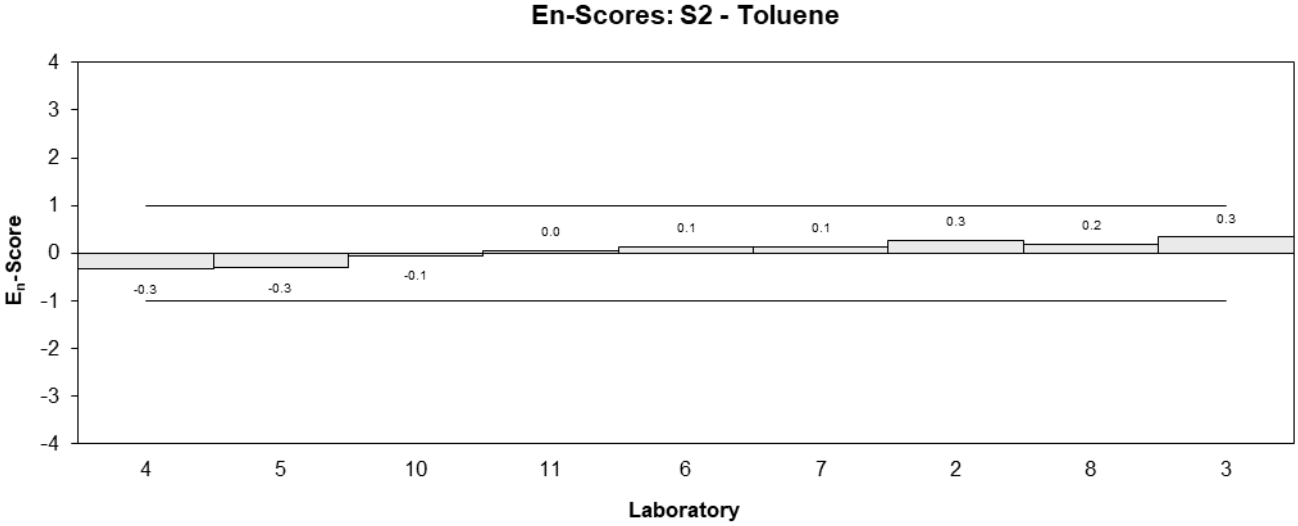

En-Scores: S2 - Toluene
En-Score
Laboratory
-0.3
-0.3
-0.1
0.0
0.1
0.1
0.3
0.2
0.3

Figure 8

Table 13

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Wastewater |
| **Analyte** | Ethylbenzene |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | NT | NT |
| **2** | <20 | NR |
| **3** | <20 | NR |
| **4** | 22.48 | 7 |
| **5** | 15.5 | 4.65 |
| **6** | 19 | 3 |
| **7** | 21 | 3.7 |
| **8**** | 2 | 0.6 |
| **10** | 17 | 3.4 |
| **11** | 11.2 | 3.6 |
| **12** | NT | NT |

** Extreme Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | 29.0 | 1.5 |
| **Robust Average** | 17.7 | 4.7 |
| **Median** | 18.0 | 4.2 |
| **Mean** | 17.7 | |
| **N** | 6 | |
| **Max** | 22.48 | |
| **Min** | 11.2 | |
| **Robust SD** | 4.6 | |
| **Robust CV** | 26% | |

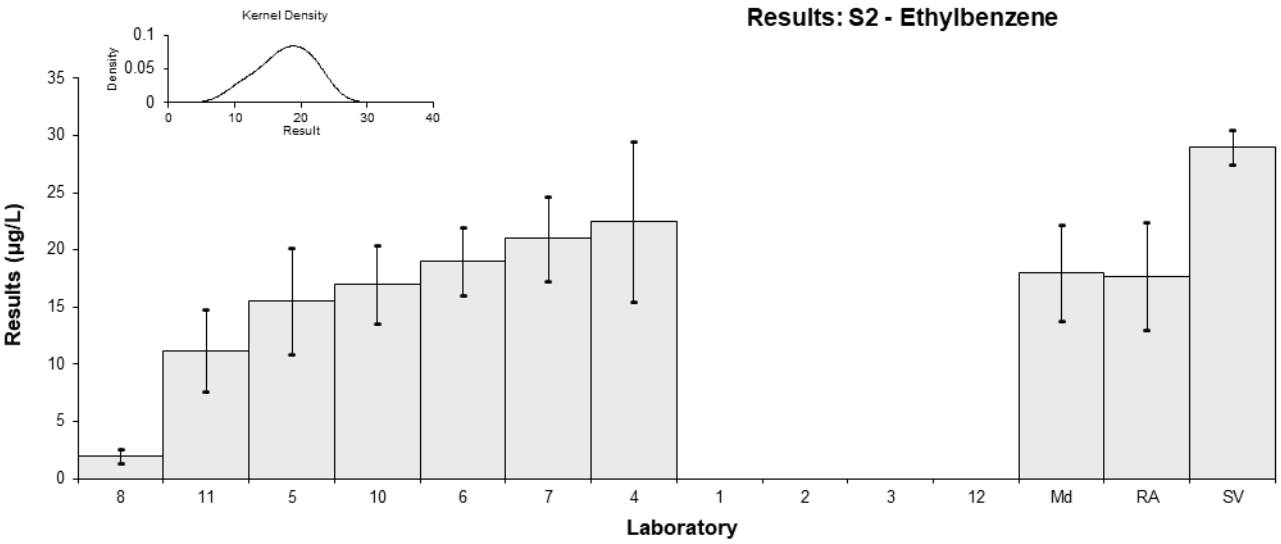

Results: S2 - Ethylbenzene
Kernel Density
Density
0.1
0.05
0
0
10
20
30
40
Result
Results (µg/L)
35
30
25
20
15
10
5
0
8
11
5
10
6
7
4
1
2
3
12
Md
RA
SV
Laboratory

Figure 9

Table 14

**Sample Details**

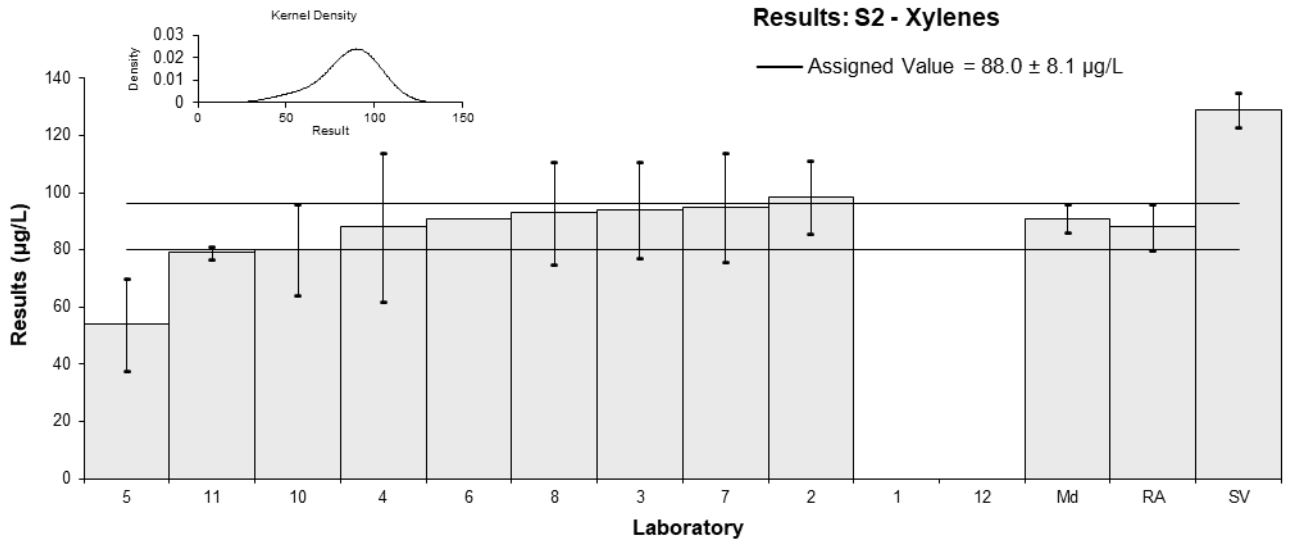
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Wastewater |
| **Analyte** | Xylenes |
| **Unit** | µg/L |

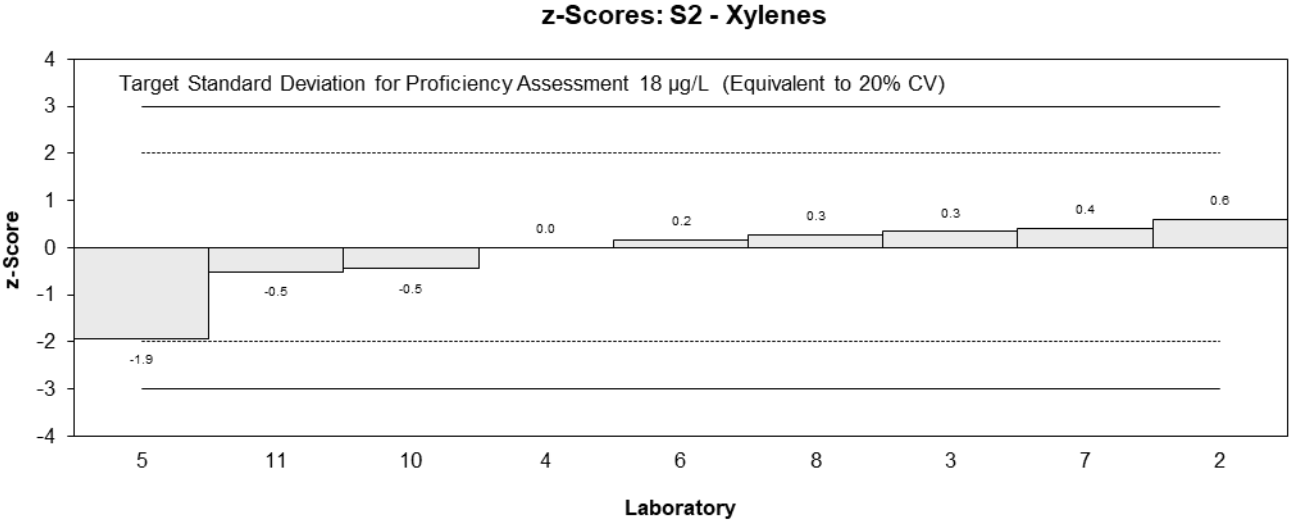
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 98.5 | 12.805 | 0.60 | 0.69 |
| **3** | 94 | 16.9 | 0.34 | 0.32 |
| **4** | 87.99 | 26 | 0.00 | 0.00 |
| **5** | 54 | 16.2 | -1.93 | -1.88 |
| **6** | 91 | NR | 0.17 | 0.37 |
| **7** | 95 | 19 | 0.40 | 0.34 |
| **8** | 93 | 18 | 0.28 | 0.25 |
| **10** | 80 | 16 | -0.45 | -0.45 |
| **11** | 79 | 2.1 | -0.51 | -1.08 |
| **12** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 88.0 | 8.1 |
| **Spike Value** | 129 | 6 |
| **Robust Average** | 88.0 | 8.1 |
| **Median** | 91.0 | 4.9 |
| **Mean** | 85.8 | |
| **N** | 9 | |
| **Max** | 98.5 | |
| **Min** | 54 | |
| **Robust SD** | 9.7 | |
| **Robust CV** | 11% | |


Kernel Density
Density
0.03
0.02
0.01
0
0
50
100
150
Result
Results: S2 - Xylenes
Assigned Value = 88.0 ± 8.1 µg/L
Results (µg/L)
140
120
100
80
60
40
20
0
5
11
10
4
6
8
3
7
2
1
12
Md
RA
SV
Laboratory


z-Scores: S2 - Xylenes
Target Standard Deviation for Proficiency Assessment 18 µg/L (Equivalent to 20% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.9
-0.5
-0.5
0.0
0.2
0.3
0.3
0.4
0.6
5
11
10
4
6
8
3
7
2
Laboratory

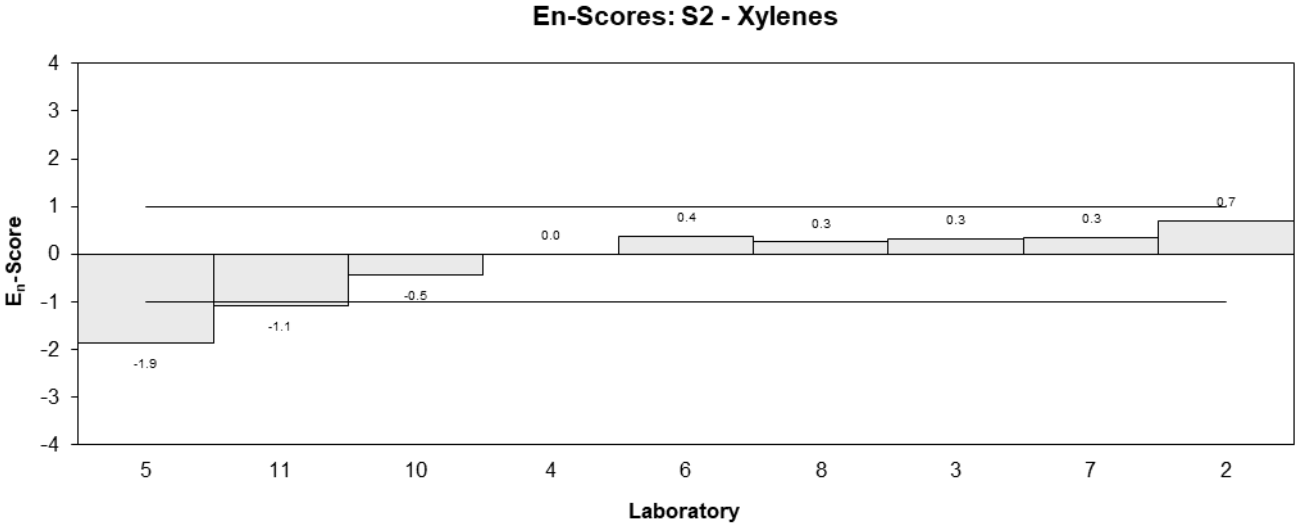

En-Scores: S2 - Xylenes
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.9
-1.1
-0.5
0.0
0.4
0.3
0.3
0.3
0.7
5
11
10
4
6
8
3
7
2
Laboratory

Figure 10

Table 15

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Wastewater |
| **Analyte** | Total BTEX |
| **Unit** | µg/L |

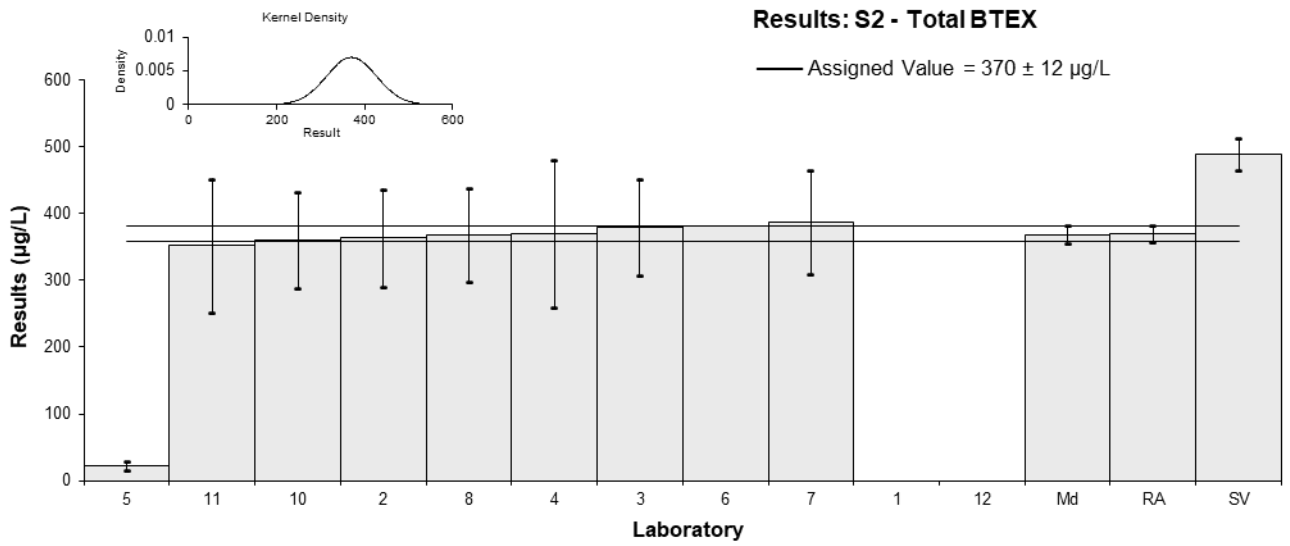
**Participant Results**

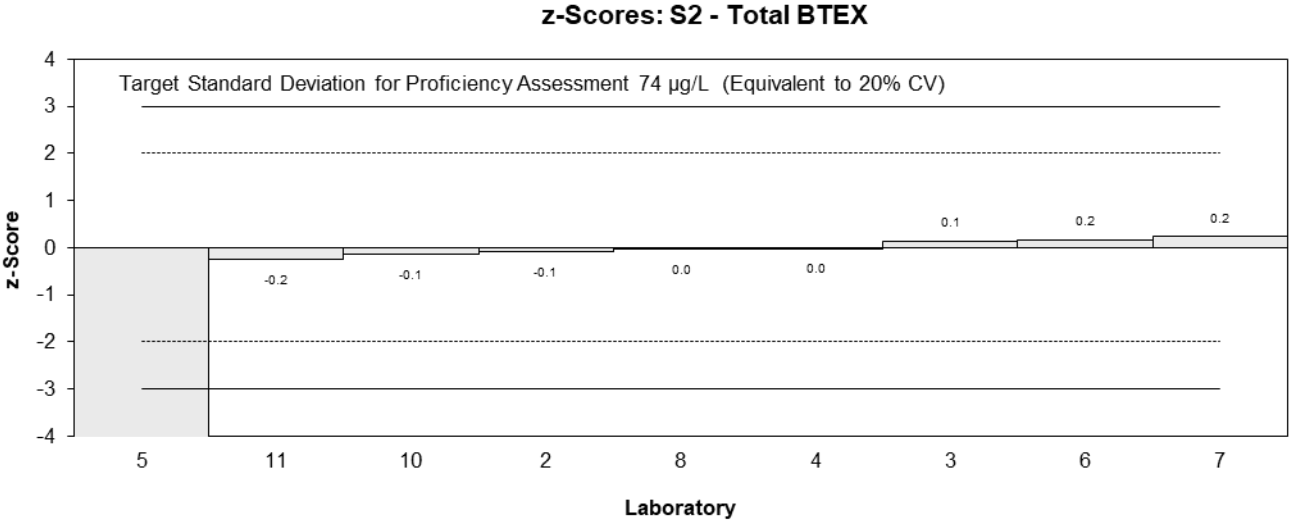
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | NT | NT | | |
| **2** | 364 | 72.8 | -0.08 | -0.08 |
| **3** | 380 | 71.9 | 0.14 | 0.14 |
| **4** | 369.63 | 111 | -0.01 | 0.00 |
| **5**** | 21.5 | 6.45 | -4.71 | -25.58 |
| **6** | 381 | NR | 0.15 | 0.92 |
| **7** | 387 | 77.4 | 0.23 | 0.22 |
| **8** | 368 | 70 | -0.03 | -0.03 |
| **10** | 360 | 72 | -0.14 | -0.14 |
| **11** | 352 | 100 | -0.24 | -0.18 |
| **12** | NT | NT | | |

** Extreme Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 370 | 12 |
| **Spike Value** | 489 | 24 |
| **Robust Average** | 370 | 12 |
| **Median** | 369 | 13 |
| **Mean** | 370 | |
| **N** | 8 | |
| **Max** | 387 | |
| **Min** | 352 | |
| **Robust SD** | 13 | |
| **Robust CV** | 3.6% | |


Kernel Density
Density
0.01
0.005
0
0
200
400
600
Result
Results: S2 - Total BTEX
Assigned Value = 370 ± 12 µg/L
Results (µg/L)
600
500
400
300
200
100
0
5
11
10
2
8
4
3
6
7
1
12
Md
RA
SV
Laboratory


z-Scores: S2 - Total BTEX
Target Standard Deviation for Proficiency Assessment 74 µg/L (Equivalent to 20% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.2
-0.1
-0.1
0.0
0.0
0.1
0.2
0.2
5
11
10
2
8
4
3
6
7
Laboratory

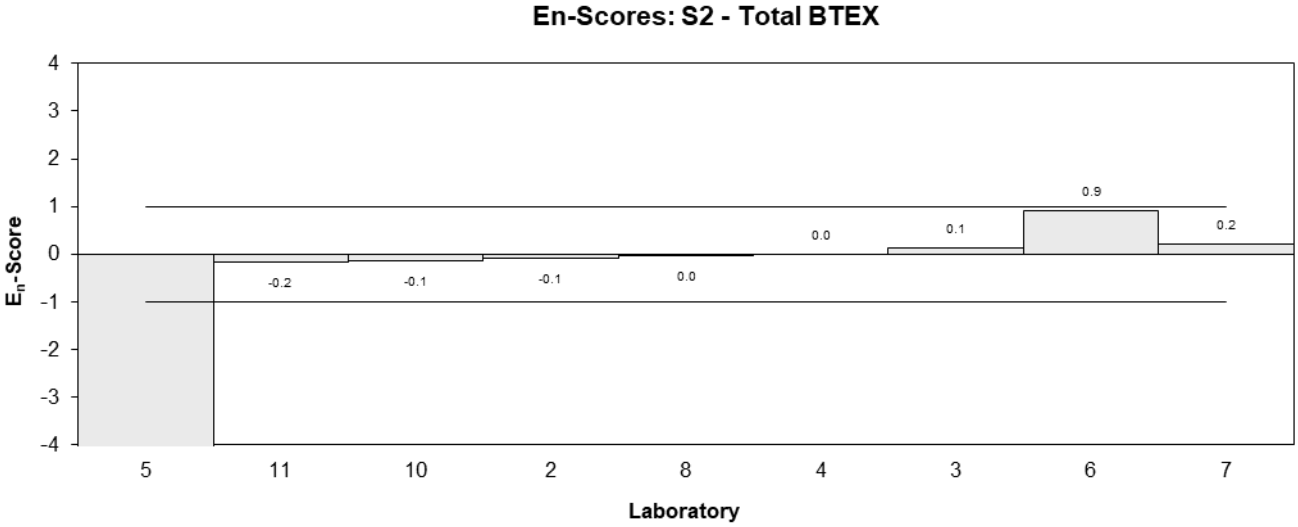

En-Scores: S2 - Total BTEX
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.2
-0.1
-0.1
0.0
0.0
0.1
0.9
0.2
5
11
10
2
8
4
3
6
7
Laboratory

Figure 11

Table 16

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Wastewater |
| **Analyte** | Acenaphthene |
| **Unit** | µg/L |

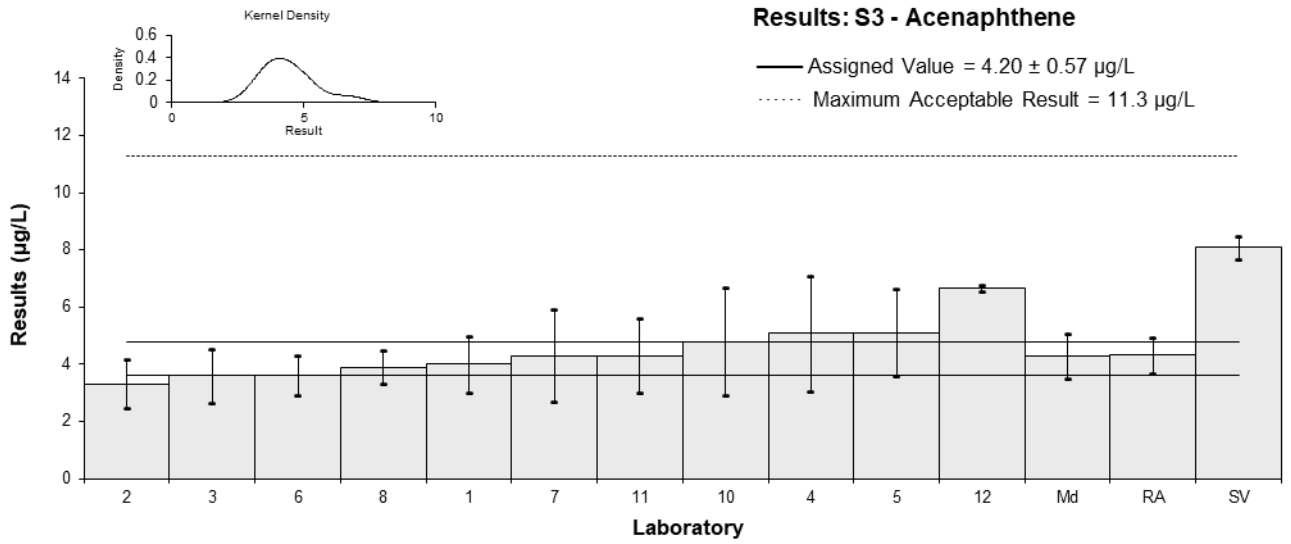
**Participant Results**

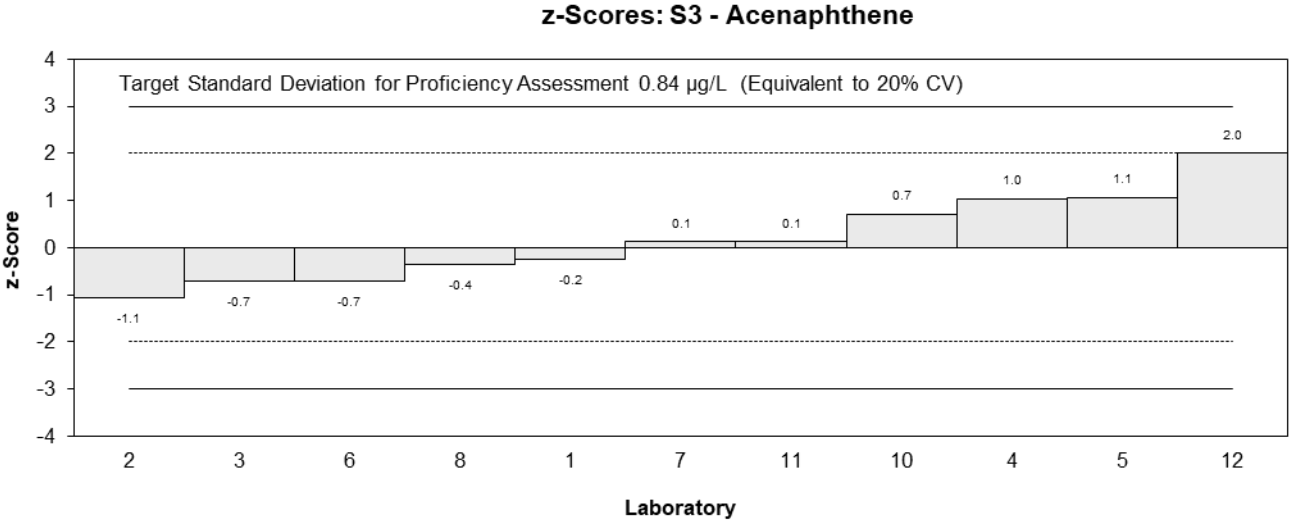
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 4 | 1 | -0.24 | -0.17 |
| **2** | 3.31 | 0.8606 | -1.06 | -0.86 |
| **3** | 3.6 | 0.94 | -0.71 | -0.55 |
| **4** | 5.07 | 2.03 | 1.04 | 0.41 |
| **5** | 5.1 | 1.53 | 1.07 | 0.55 |
| **6** | 3.6 | 0.7 | -0.71 | -0.66 |
| **7** | 4.3 | 1.6 | 0.12 | 0.06 |
| **8** | 3.9 | 0.6 | -0.36 | -0.36 |
| **10** | 4.8 | 1.9 | 0.71 | 0.30 |
| **11** | 4.3 | 1.3 | 0.12 | 0.07 |
| **12*** | 6.67 | 0.1 | 2.00▼ | |

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.20 | 0.57 |
| **Spike Value** | 8.08 | 0.40 |
| **Robust Average** | 4.32 | 0.62 |
| **Max Acceptable Result** | 11.3 | |
| **Median** | 4.30 | 0.78 |
| **Mean** | 4.42 | |
| **N** | 11 | |
| **Max** | 6.67 | |
| **Min** | 3.31 | |
| **Robust SD** | 0.82 | |
| **Robust CV** | 19% | |


Kernel Density
Density
Result
Results: S3 - Acenaphthene
Assigned Value = 4.20 ± 0.57 µg/L
Maximum Acceptable Result = 11.3 µg/L
Results (µg/L)
Laboratory
2
3
6
8
1
7
11
10
4
5
12
Md
RA
SV


z-Scores: S3 - Acenaphthene
Target Standard Deviation for Proficiency Assessment 0.84 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.1
-0.7
-0.7
-0.4
-0.2
0.1
0.1
0.7
1.0
1.1
2.0

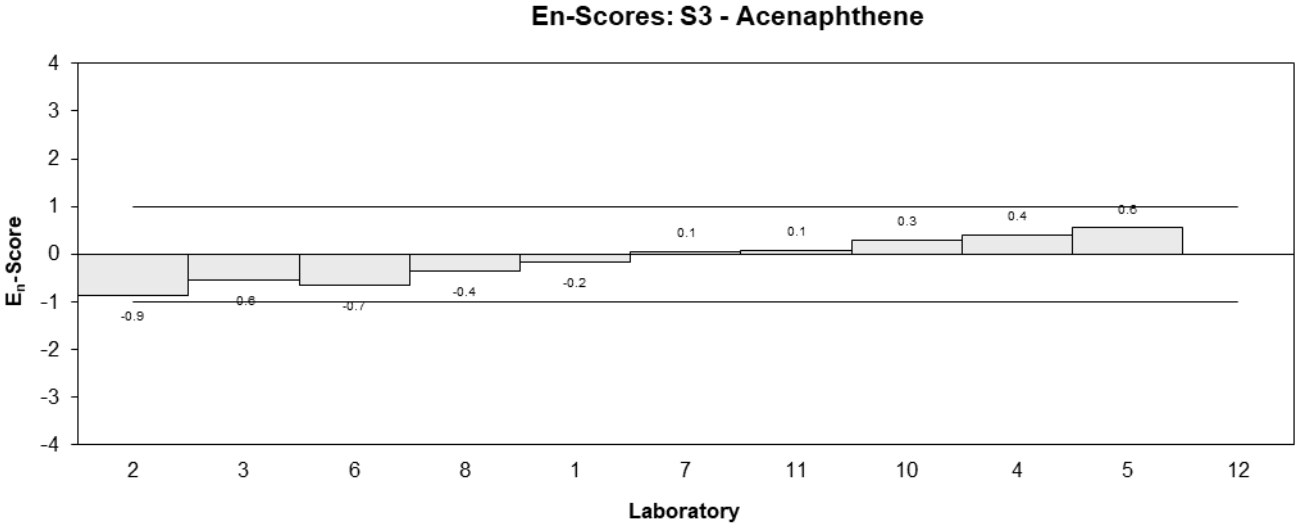

En-Scores: S3 - Acenaphthene
En-Score
Laboratory
-0.9
0.6
-0.7
-0.4
-0.2
0.1
0.1
0.3
0.4
0.6

Figure 12

Table 17

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Wastewater |
| **Analyte** | Acenaphthylene |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | <1 | NR |
| **2** | <1 | NR |
| **3** | <1 | NR |
| **4** | 0.68 | 0.27 |
| **5** | 0.8 | 0.24 |
| **6** | <1.0 | NR |
| **7** | <1 | 0.4 |
| **8** | <1.0 | NR |
| **10** | 0.73 | 0.29 |
| **11** | 1.66 | 0.43 |
| **12** | 0.92 | 0.05 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | 1.09 | 0.05 |
| **Robust Average** | NA (N<6) | |
| **Median** | 0.80 | 0.20 |
| **Mean** | 0.96 | |
| **N** | 5 | |
| **Max** | 1.66 | |
| **Min** | 0.68 | |
| **Robust SD** | NA (N<6) | |
| **Robust CV** | NA (N<6) | |

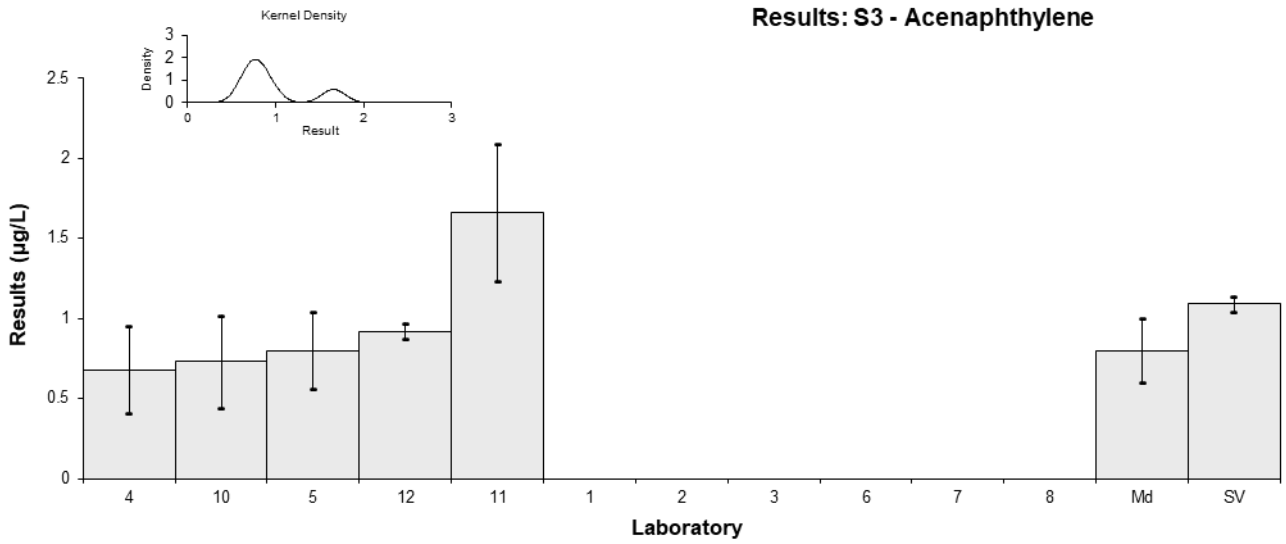

Results: S3 - Acenaphthylene
Kernel Density
Density
Result
Results (µg/L)
Laboratory
4
10
5
12
11
1
2
3
6
7
8
Md
SV

Figure 13

Table 18

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Wastewater |
| **Analyte** | Benz[*a*]anthracene |
| **Unit** | µg/L |

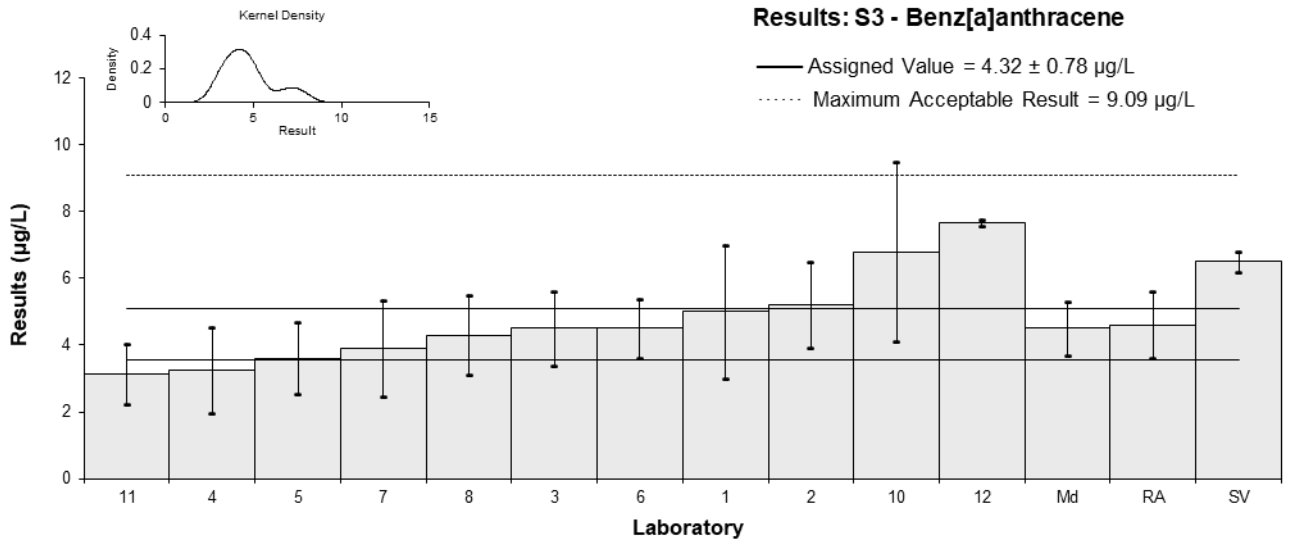
**Participant Results**

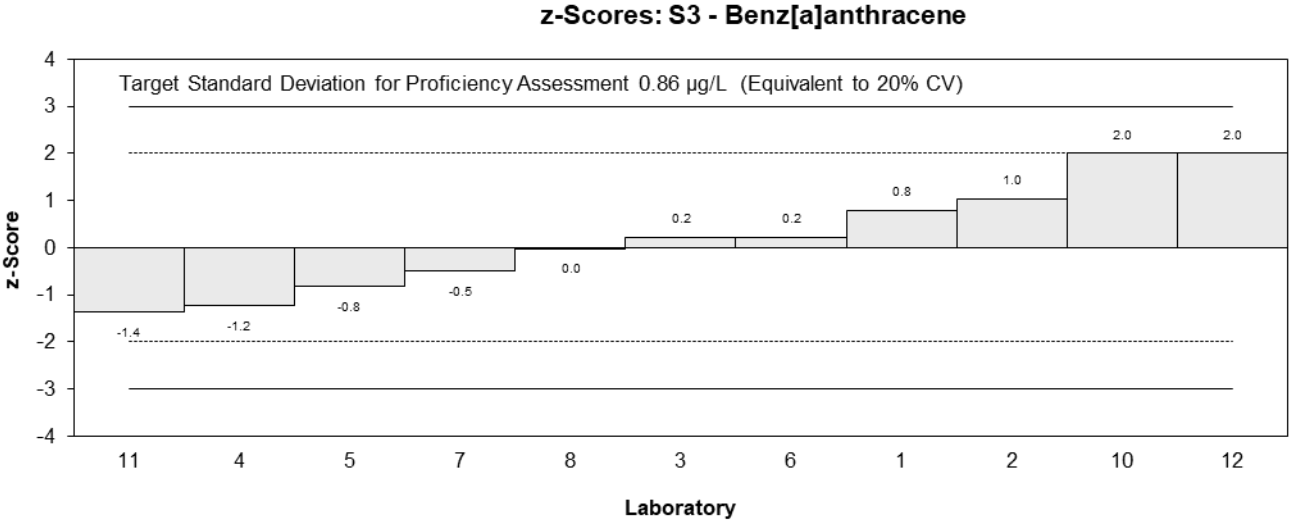
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 5 | 2 | 0.79 | 0.32 |
| **2** | 5.22 | 1.284 | 1.04 | 0.60 |
| **3** | 4.5 | 1.1 | 0.21 | 0.13 |
| **4** | 3.25 | 1.30 | -1.24 | -0.71 |
| **5** | 3.6 | 1.08 | -0.83 | -0.54 |
| **6** | 4.5 | 0.9 | 0.21 | 0.15 |
| **7** | 3.9 | 1.45 | -0.49 | -0.26 |
| **8** | 4.3 | 1.2 | -0.02 | -0.01 |
| **10** | 6.8 | 2.7 | 2.00▼ | |
| **11** | 3.14 | 0.9 | -1.37 | -0.99 |
| **12*** | 7.67 | 0.1 | 2.00▼ | |

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.32 | 0.78 |
| **Spike Value** | 6.50 | 0.32 |
| **Robust Average** | 4.6 | 1.0 |
| **Max Acceptable Result** | 9.09 | |
| **Median** | 4.50 | 0.80 |
| **Mean** | 4.72 | |
| **N** | 11 | |
| **Max** | 7.67 | |
| **Min** | 3.14 | |
| **Robust SD** | 1.4 | |
| **Robust CV** | 30% | |


Kernel Density
Density
Result
Results: S3 - Benz[a]anthracene
Assigned Value = 4.32 ± 0.78 µg/L
Maximum Acceptable Result = 9.09 µg/L
Results (µg/L)
Laboratory
11
4
5
7
8
3
6
1
2
10
12
Md
RA
SV


z-Scores: S3 - Benz[a]anthracene
Target Standard Deviation for Proficiency Assessment 0.86 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.4
-1.2
-0.8
-0.5
0.0
0.2
0.2
0.8
1.0
2.0
2.0

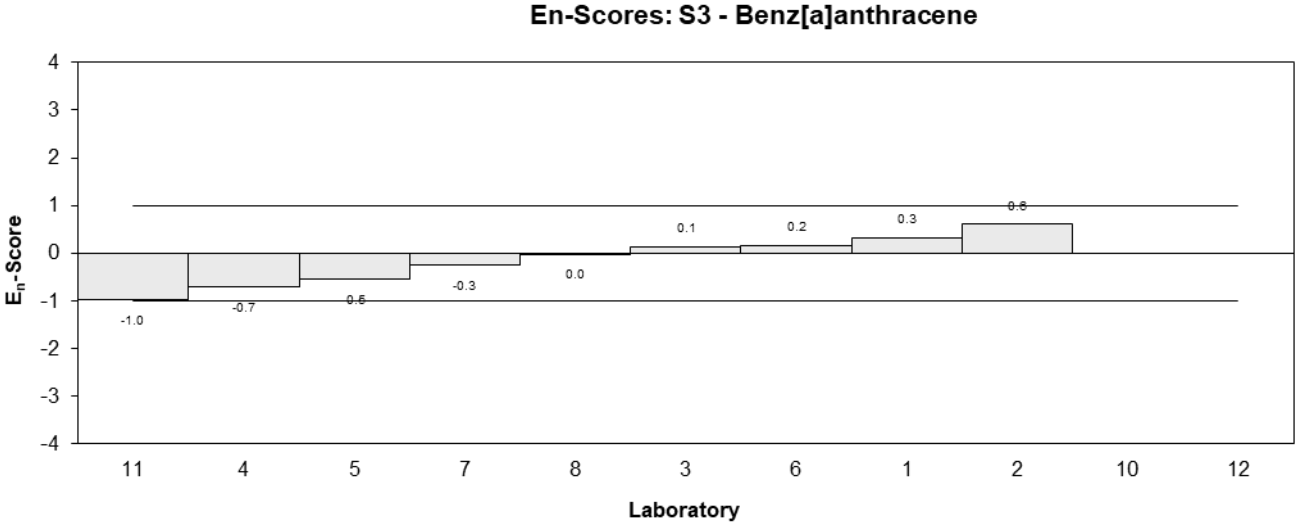

En-Scores: S3 - Benz[a]anthracene
En-Score
Laboratory
-1.0
-0.7
-0.5
-0.3
0.0
0.1
0.2
0.3
0.6

Figure 14

Table 19

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Wastewater |
| **Analyte** | Benzo[*a*]pyrene |
| **Unit** | µg/L |

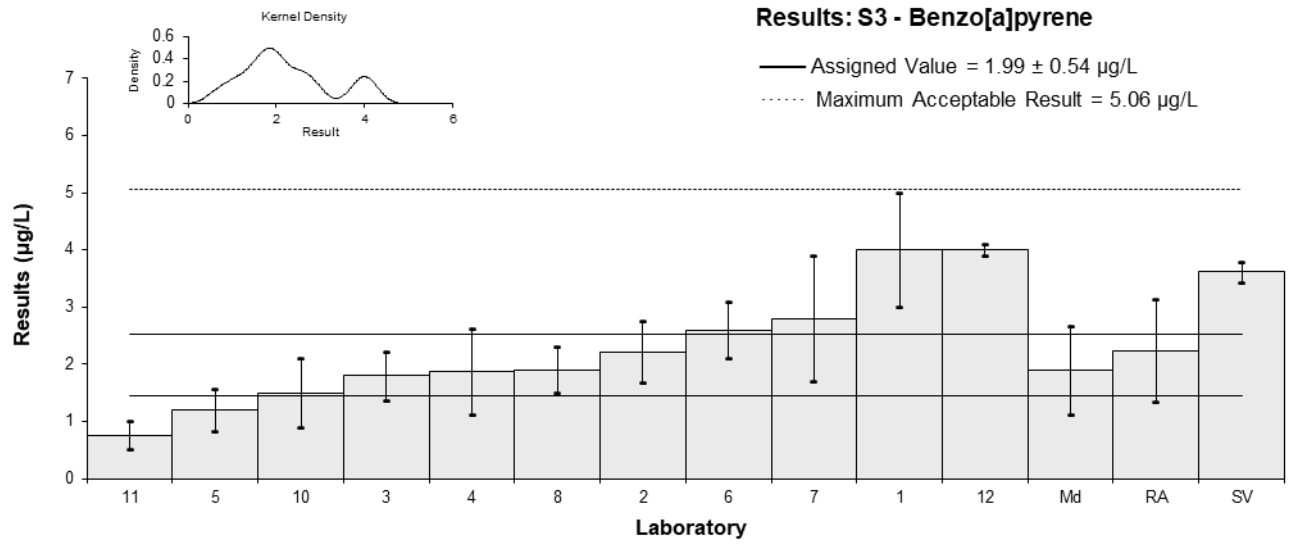
**Participant Results**

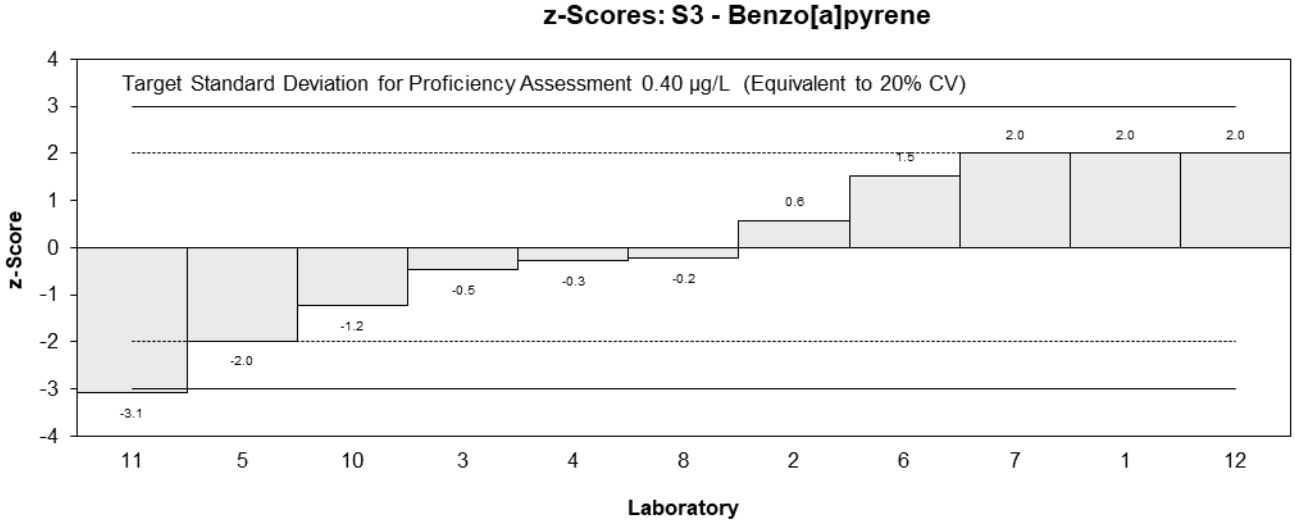
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1*** | 4 | 1 | 2.00▼ | |
| **2** | 2.22 | 0.5328 | 0.58 | 0.30 |
| **3** | 1.8 | 0.43 | -0.48 | -0.28 |
| **4** | 1.88 | 0.75 | -0.28 | -0.12 |
| **5** | 1.2 | 0.36 | -1.98 | -1.22 |
| **6** | 2.6 | 0.5 | 1.53 | 0.83 |
| **7** | 2.8 | 1.1 | 2.00▼ | |
| **8** | 1.9 | 0.4 | -0.23 | -0.13 |
| **10** | 1.5 | 0.60 | -1.23 | -0.61 |
| **11*** | 0.76 | 0.24 | -3.09 | -2.08 |
| **12*** | 4.00 | 0.1 | 2.00▼ | |

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.99 | 0.54 |
| **Spike Value** | 3.62 | 0.18 |
| **Robust Average** | 2.24 | 0.89 |
| **Max Acceptable Result** | 5.06 | |
| **Median** | 1.90 | 0.78 |
| **Mean** | 2.24 | |
| **N** | 11 | |
| **Max** | 4 | |
| **Min** | 0.76 | |
| **Robust SD** | 1.2 | |
| **Robust CV** | 53% | |


Kernel Density
Density
Result
Results: S3 - Benzo[a]pyrene
Assigned Value = 1.99 ± 0.54 µg/L
Maximum Acceptable Result = 5.06 µg/L
Results (µg/L)
11 5 10 3 4 8 2 6 7 1 12 Md RA SV
Laboratory


z-Scores: S3 - Benzo[a]pyrene
Target Standard Deviation for Proficiency Assessment 0.40 µg/L (Equivalent to 20% CV)
z-Score
-3.1 -2.0 -1.2 -0.5 -0.3 -0.2 0.6 1.5 2.0 2.0 2.0
11 5 10 3 4 8 2 6 7 1 12
Laboratory

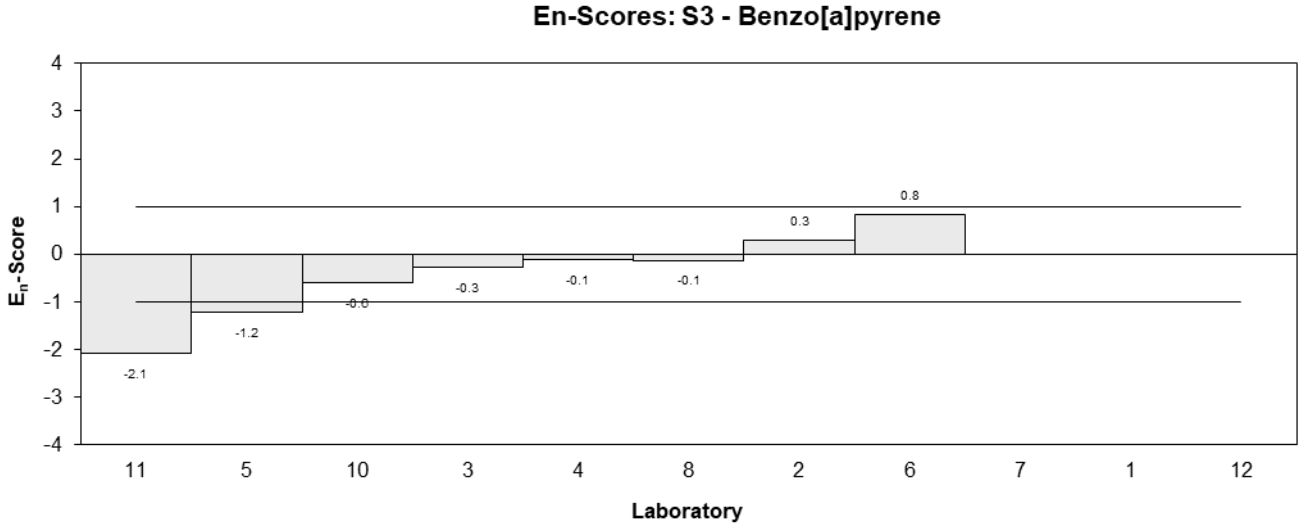

En-Scores: S3 - Benzo[a]pyrene
En-Score
-2.1 -1.2 -0.6 -0.3 -0.1 -0.1 0.3 0.8
11 5 10 3 4 8 2 6 7 1 12
Laboratory

Figure 15

Table 20

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Wastewater |
| **Analyte** | Fluorene |
| **Unit** | µg/L |

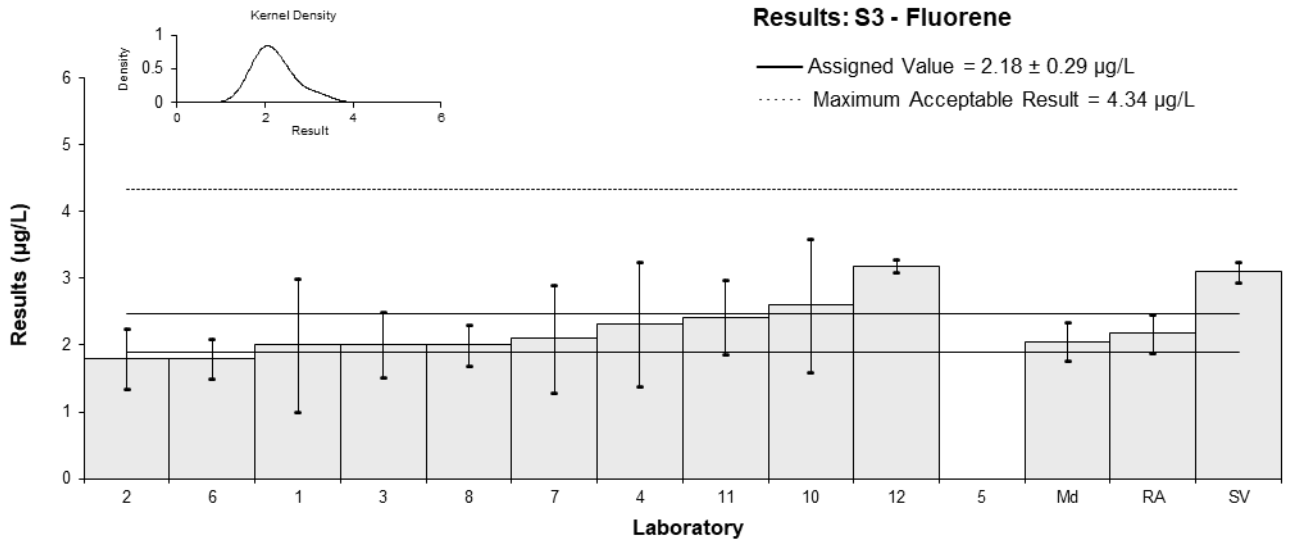
**Participant Results**

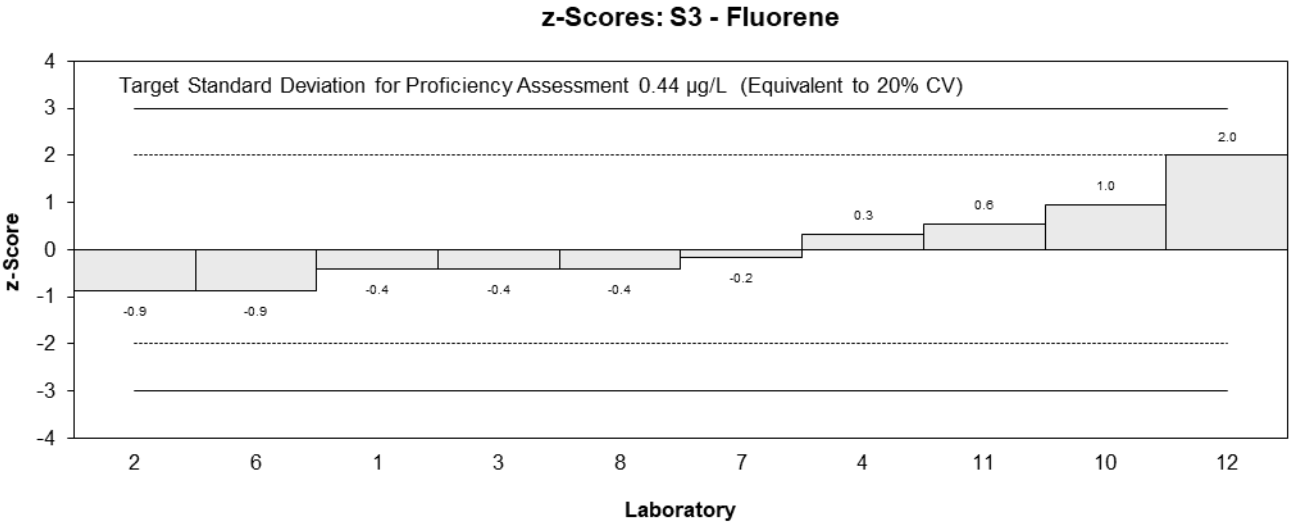
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2 | 1 | -0.41 | -0.17 |
| **2** | 1.8 | 0.45 | -0.87 | -0.71 |
| **3** | 2.0 | 0.49 | -0.41 | -0.32 |
| **4** | 2.32 | 0.93 | 0.32 | 0.14 |
| **5** | <0.02 | NR | | |
| **6** | 1.8 | 0.3 | -0.87 | -0.91 |
| **7** | 2.1 | 0.81 | -0.18 | -0.09 |
| **8** | 2.0 | 0.3 | -0.41 | -0.43 |
| **10** | 2.6 | 1.0 | 0.96 | 0.40 |
| **11** | 2.42 | 0.56 | 0.55 | 0.38 |
| **12** | 3.19 | 0.1 | 2.00▼ | |

▼ Adjusted Score, see Section 6.3

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.18 | 0.29 |
| **Spike Value** | 3.10 | 0.15 |
| **Robust Average** | 2.18 | 0.29 |
| **Max Acceptable Result** | 4.34 | |
| **Median** | 2.05 | 0.29 |
| **Mean** | 2.22 | |
| **N** | 10 | |
| **Max** | 3.19 | |
| **Min** | 1.8 | |
| **Robust SD** | 0.37 | |
| **Robust CV** | 17% | |


Kernel Density
Density
Result
Results: S3 - Fluorene
Assigned Value = 2.18 ± 0.29 µg/L
Maximum Acceptable Result = 4.34 µg/L
Results (µg/L)
Laboratory
2
6
1
3
8
7
4
11
10
12
5
Md
RA
SV


z-Scores: S3 - Fluorene
Target Standard Deviation for Proficiency Assessment 0.44 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-0.9
-0.9
-0.4
-0.4
-0.4
-0.2
0.3
0.6
1.0
2.0

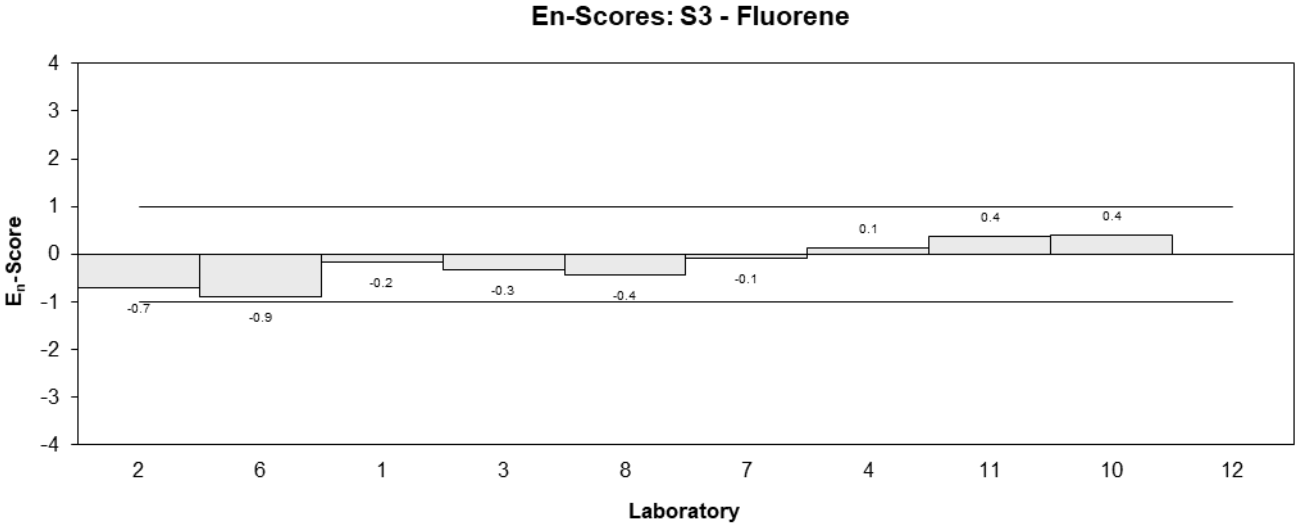

En-Scores: S3 - Fluorene
En-Score
Laboratory
-0.7
-0.9
-0.2
-0.3
-0.4
-0.1
0.1
0.4
0.4

Figure 16

Table 21

**Sample Details**

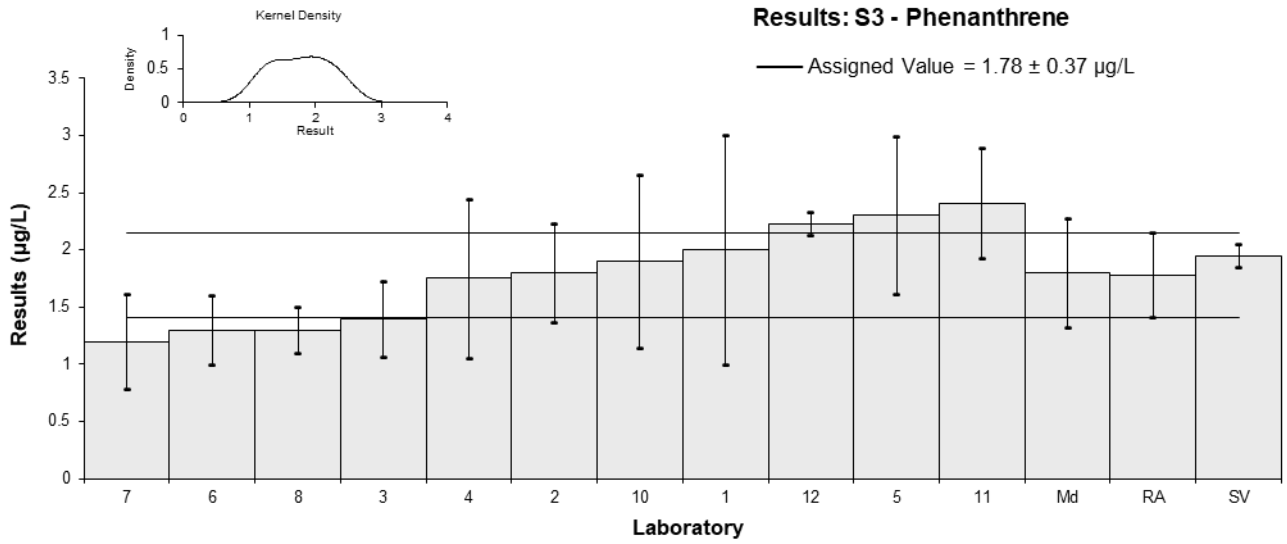
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | Wastewater |
| **Analyte** | Phenanthrene |
| **Unit** | µg/L |

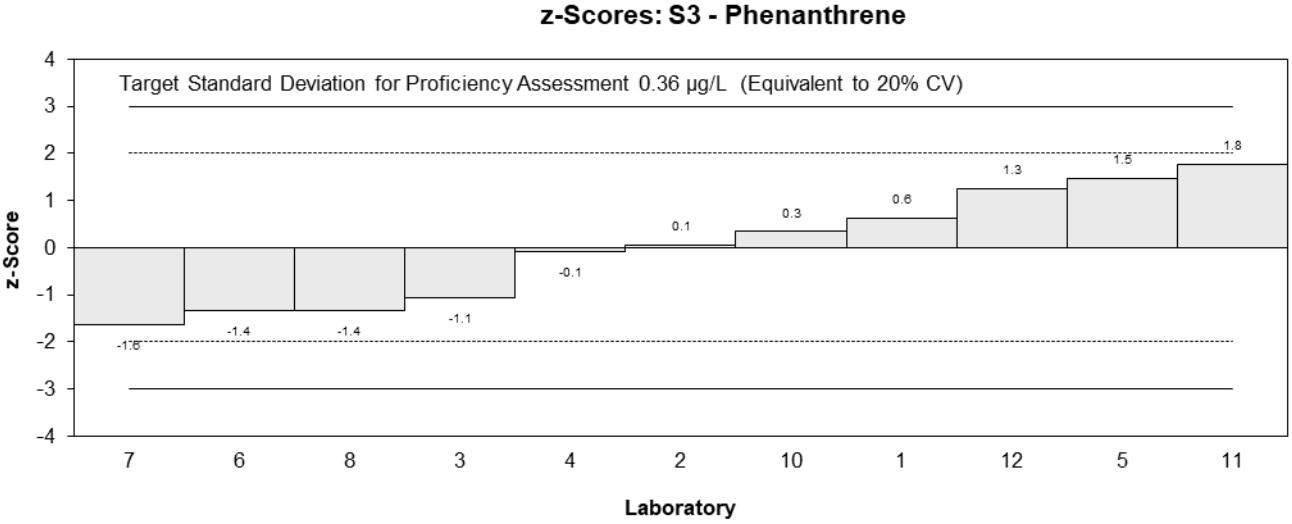
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2 | 1 | 0.62 | 0.21 |
| **2** | 1.8 | 0.432 | 0.06 | 0.04 |
| **3** | 1.4 | 0.33 | -1.07 | -0.77 |
| **4** | 1.75 | 0.70 | -0.08 | -0.04 |
| **5** | 2.3 | 0.69 | 1.46 | 0.66 |
| **6** | 1.3 | 0.3 | -1.35 | -1.01 |
| **7** | 1.2 | 0.41 | -1.63 | -1.05 |
| **8** | 1.3 | 0.2 | -1.35 | -1.14 |
| **10** | 1.9 | 0.76 | 0.34 | 0.14 |
| **11** | 2.41 | 0.48 | 1.77 | 1.04 |
| **12** | 2.23 | 0.1 | 1.26 | 1.17 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.78 | 0.37 |
| **Spike Value** | 1.95 | 0.10 |
| **Robust Average** | 1.78 | 0.37 |
| **Median** | 1.80 | 0.48 |
| **Mean** | 1.78 | |
| **N** | 11 | |
| **Max** | 2.41 | |
| **Min** | 1.2 | |
| **Robust SD** | 0.49 | |
| **Robust CV** | 28% | |


Kernel Density
Density
Result
Results: S3 - Phenanthrene
Assigned Value = 1.78 ± 0.37 µg/L
Results (µg/L)
Laboratory
7
6
8
3
4
2
10
1
12
5
11
Md
RA
SV


z-Scores: S3 - Phenanthrene
Target Standard Deviation for Proficiency Assessment 0.36 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.6
-1.4
-1.4
-1.1
-0.1
0.1
0.3
0.6
1.3
1.5
1.8

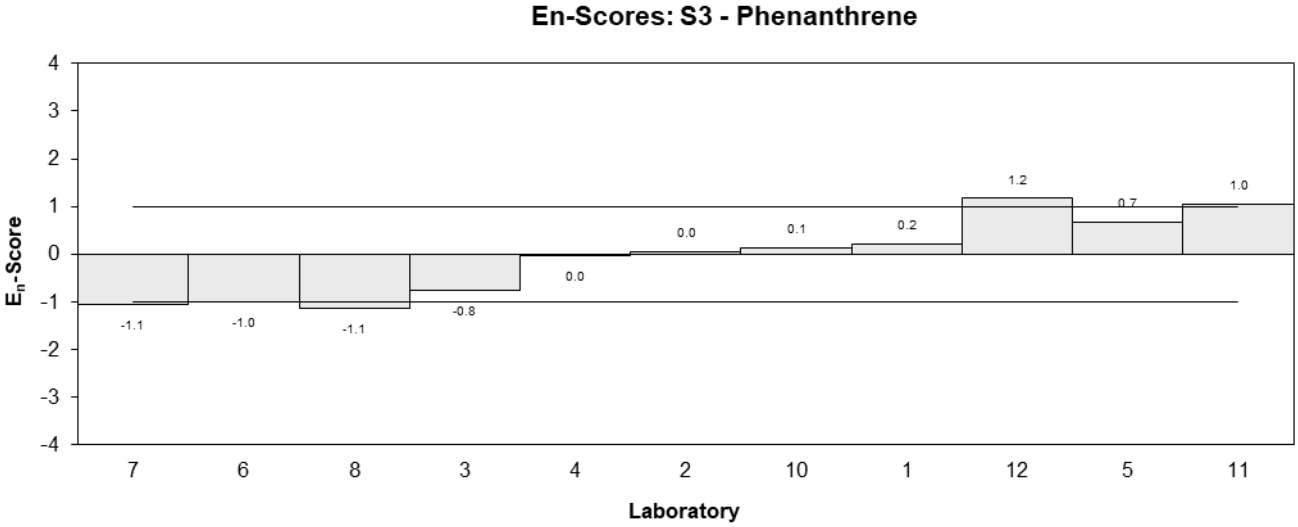

En-Scores: S3 - Phenanthrene
En-Score
Laboratory
-1.1
-1.0
-1.1
-0.8
0.0
0.0
0.1
0.2
1.2
0.7
1.0

Figure 17

Table 22

**Sample Details**

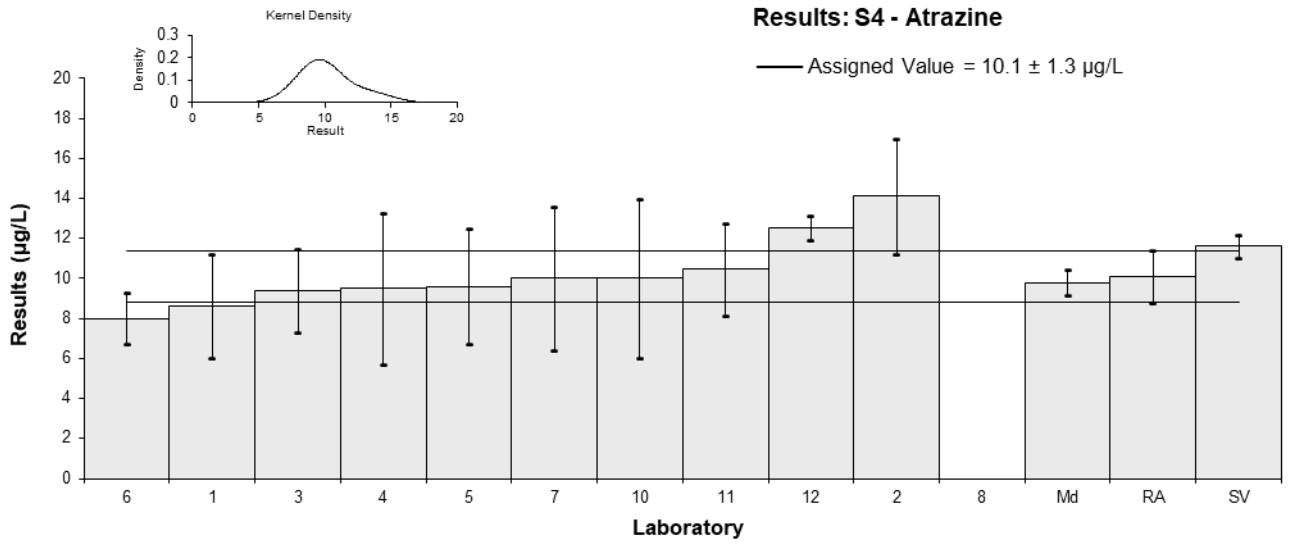
| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Wastewater |
| **Analyte** | Atrazine |
| **Unit** | µg/L |

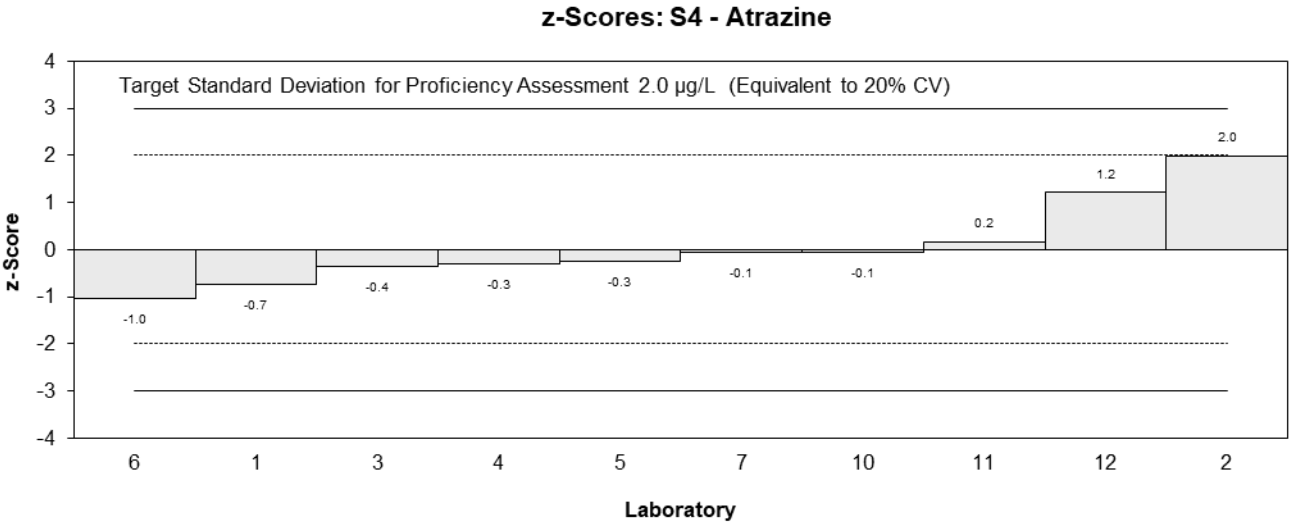
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 8.6 | 2.6 | -0.74 | -0.52 |
| **2** | 14.1 | 2.88 | 1.98 | 1.27 |
| **3** | 9.4 | 2.1 | -0.35 | -0.28 |
| **4** | 9.49 | 3.80 | -0.30 | -0.15 |
| **5** | 9.6 | 2.88 | -0.25 | -0.16 |
| **6** | 8 | 1.3 | -1.04 | -1.14 |
| **7** | 10 | 3.6 | -0.05 | -0.03 |
| **8** | NT | NT | | |
| **10** | 10 | 4.0 | -0.05 | -0.02 |
| **11** | 10.45 | 2.3 | 0.17 | 0.13 |
| **12** | 12.55 | 0.6 | 1.21 | 1.71 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 10.1 | 1.3 |
| **Spike Value** | 11.6 | 0.6 |
| **Robust Average** | 10.1 | 1.3 |
| **Median** | 9.80 | 0.62 |
| **Mean** | 10.2 | |
| **N** | 10 | |
| **Max** | 14.1 | |
| **Min** | 8 | |
| **Robust SD** | 1.7 | |
| **Robust CV** | 17% | |


Kernel Density
Density
Result
Results: S4 - Atrazine
Assigned Value = 10.1 ± 1.3 µg/L
Results (µg/L)
Laboratory
6
1
3
4
5
7
10
11
12
2
8
Md
RA
SV


z-Scores: S4 - Atrazine
Target Standard Deviation for Proficiency Assessment 2.0 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.0
-0.7
-0.4
-0.3
-0.3
-0.1
-0.1
0.2
1.2
2.0

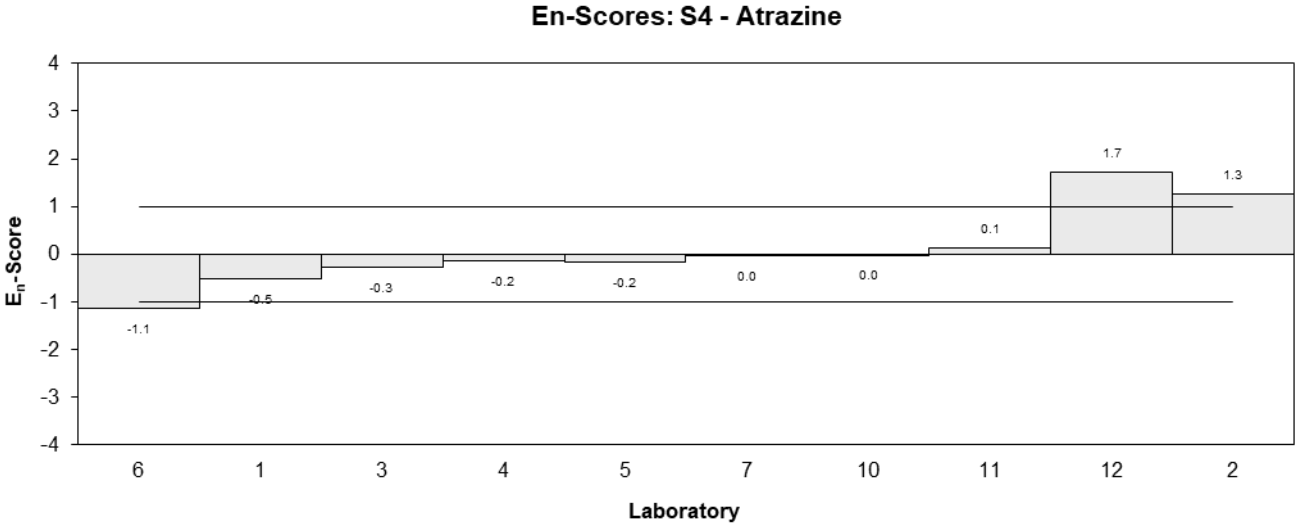

En-Scores: S4 - Atrazine
En-Score
Laboratory
-1.1
-0.5
-0.3
-0.2
-0.2
0.0
0.0
0.1
1.7
1.3

Figure 18

Table 23

**Sample Details**

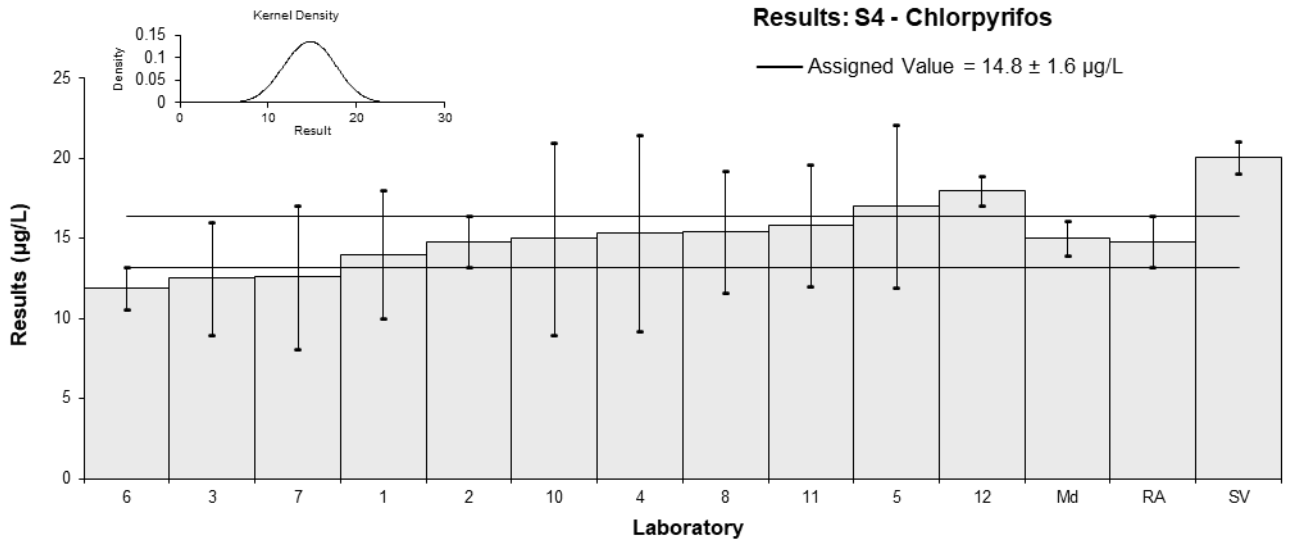
| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Wastewater |
| **Analyte** | Chlorpyrifos |
| **Unit** | µg/L |

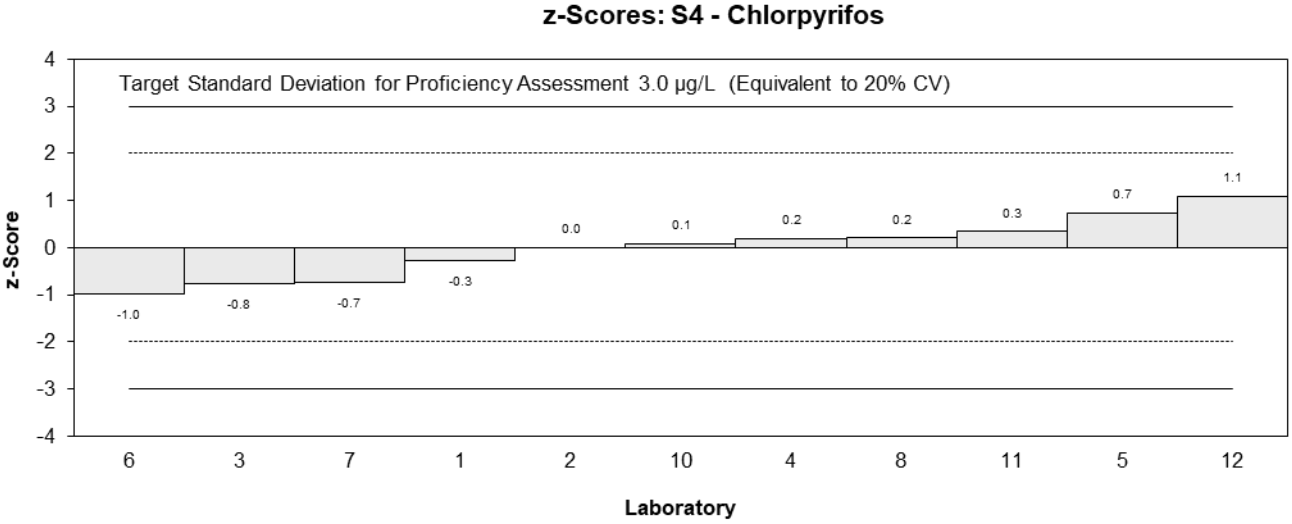
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 14 | 4 | -0.27 | -0.19 |
| **2** | 14.8 | 1.5836 | 0.00 | 0.00 |
| **3** | 12.5 | 3.54 | -0.78 | -0.59 |
| **4** | 15.34 | 6.13 | 0.18 | 0.09 |
| **5** | 17 | 5.1 | 0.74 | 0.41 |
| **6** | 11.9 | 1.3 | -0.98 | -1.41 |
| **7** | 12.6 | 4.5 | -0.74 | -0.46 |
| **8** | 15.4 | 3.8 | 0.20 | 0.15 |
| **10** | 15 | 6.0 | 0.07 | 0.03 |
| **11** | 15.8 | 3.8 | 0.34 | 0.24 |
| **12** | 18.00 | 0.9 | 1.08 | 1.74 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 14.8 | 1.6 |
| **Spike Value** | 20.1 | 1.0 |
| **Robust Average** | 14.8 | 1.6 |
| **Median** | 15.0 | 1.1 |
| **Mean** | 14.8 | |
| **N** | 11 | |
| **Max** | 18 | |
| **Min** | 11.9 | |
| **Robust SD** | 2.1 | |
| **Robust CV** | 15% | |


Results: S4 - Chlorpyrifos
Assigned Value = 14.8 ± 1.6 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
3
7
1
2
10
4
8
11
5
12
Md
RA
SV


z-Scores: S4 - Chlorpyrifos
Target Standard Deviation for Proficiency Assessment 3.0 µg/L (Equivalent to 20% CV)
z-Score
-1.0
-0.8
-0.7
-0.3
0.0
0.1
0.2
0.2
0.3
0.7
1.1
Laboratory

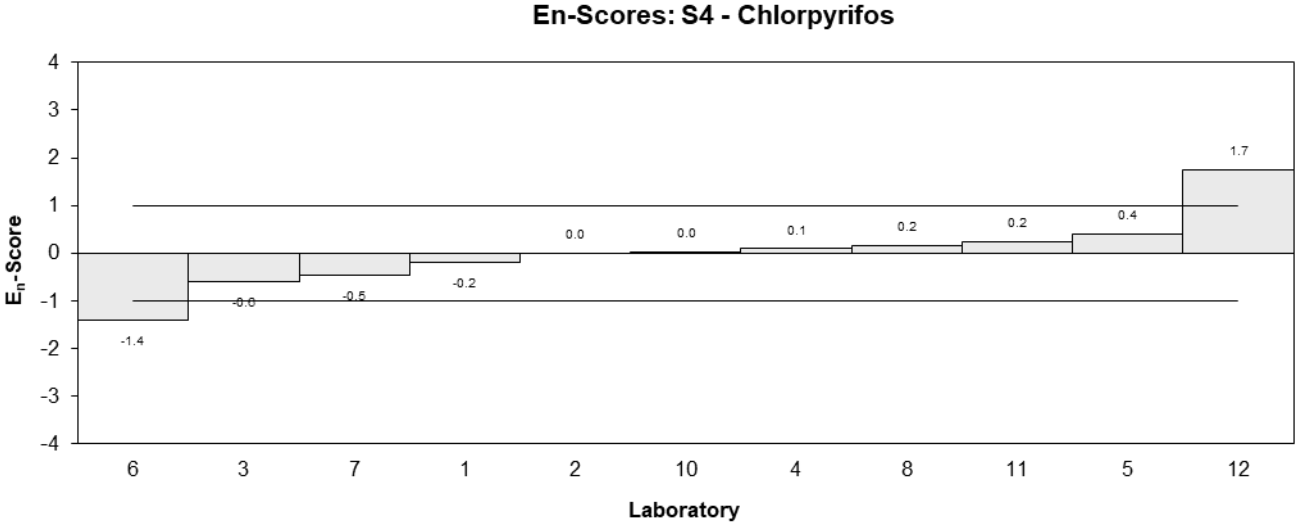

En-Scores: S4 - Chlorpyrifos
En-Score
-1.4
-0.6
-0.5
-0.2
0.0
0.0
0.1
0.2
0.2
0.4
1.7
Laboratory

Figure 19

Table 24

**Sample Details**

| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Wastewater |
| **Analyte** | Dicamba |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | NT | NT |
| **2** | 7.31 | 0.365 |
| **3** | NT | NT |
| **4** | NT | NT |
| **5** | NT | NT |
| **6** | <10 | NR |
| **7** | NT | NT |
| **8** | NT | NT |
| **10** | 6.5 | 1.6 |
| **11** | 4.66 | 1.4 |
| **12** | <0.05 | 0.05 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | 7.49 | 0.37 |
| **Robust Average** | NA (N<6) | |
| **Median** | 6.5 | 1.7 |
| **Mean** | 6.2 | |
| **N** | 3 | |
| **Max** | 7.31 | |
| **Min** | 4.66 | |
| **Robust SD** | NA (N<6) | |
| **Robust CV** | NA (N<6) | |

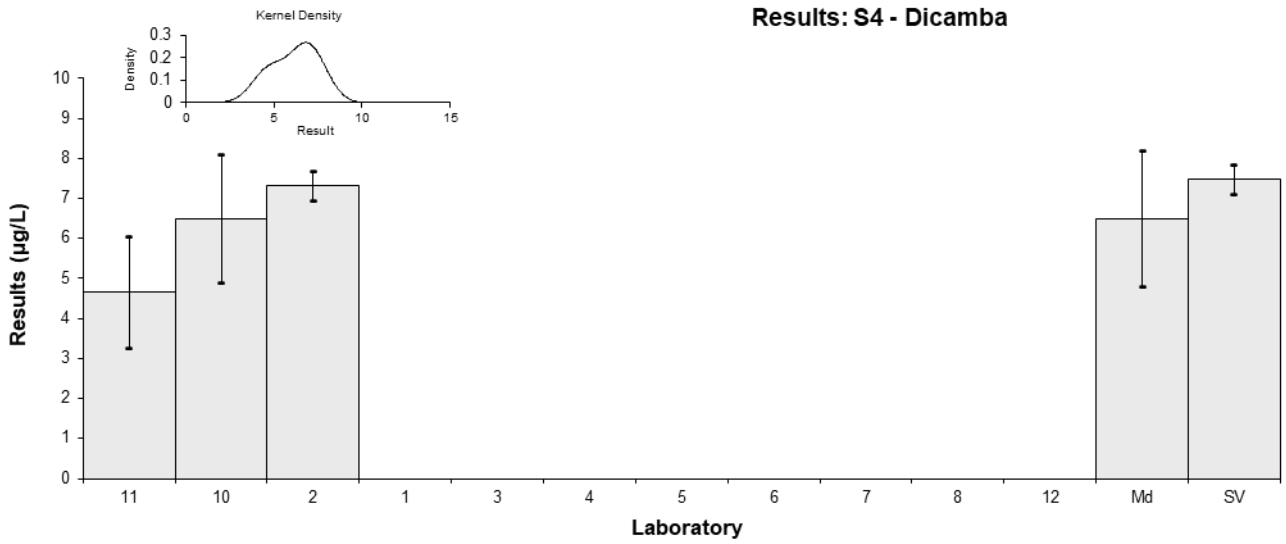

Results: S4 - Dicamba
Kernel Density
Density
Result
Results (µg/L)
Laboratory
11
10
2
1
3
4
5
6
7
8
12
Md
SV

Figure 20

Table 25

**Sample Details**

| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Wastewater |
| **Analyte** | Dieldrin |
| **Unit** | µg/L |

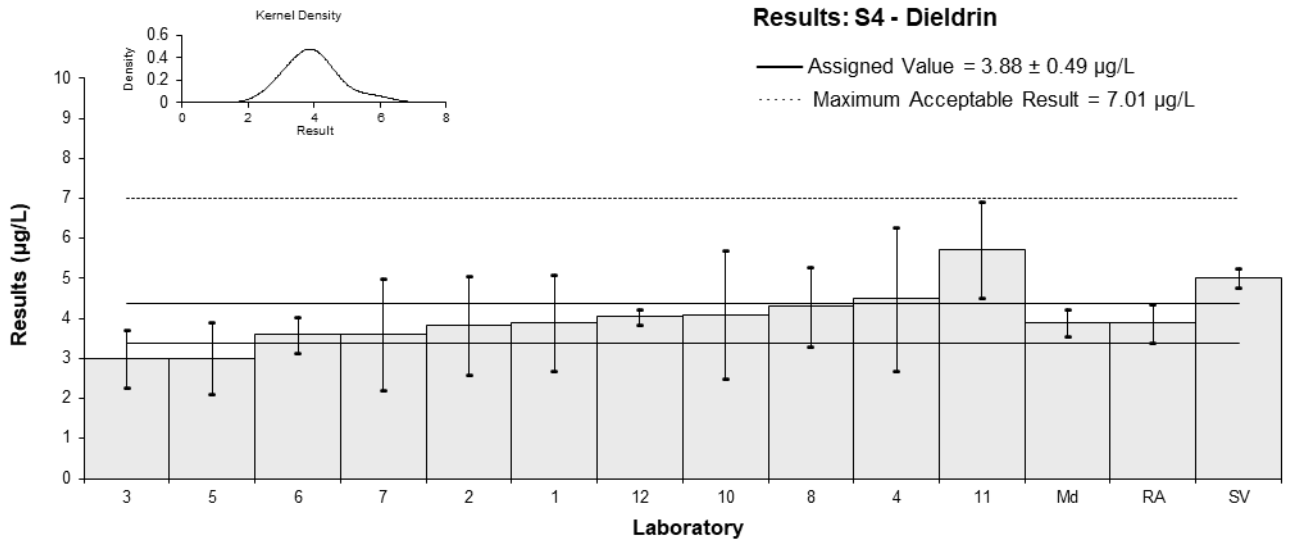
**Participant Results**

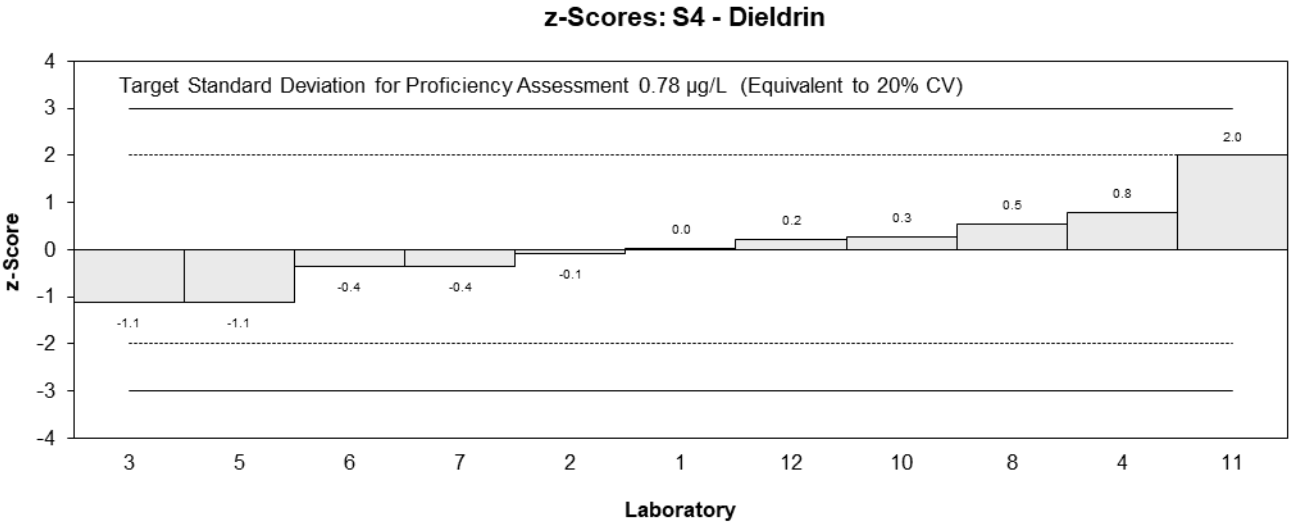
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 3.9 | 1.2 | 0.03 | 0.02 |
| **2** | 3.82 | 1.23 | -0.08 | -0.05 |
| **3** | 3.0 | 0.71 | -1.13 | -1.02 |
| **4** | 4.49 | 1.79 | 0.79 | 0.33 |
| **5** | 3 | 0.9 | -1.13 | -0.86 |
| **6** | 3.6 | 0.45 | -0.36 | -0.42 |
| **7** | 3.6 | 1.4 | -0.36 | -0.19 |
| **8** | 4.3 | 1.0 | 0.54 | 0.38 |
| **10** | 4.1 | 1.6 | 0.28 | 0.13 |
| **11** | 5.73 | 1.2 | 2.00▼ | |
| **12** | 4.04 | 0.2 | 0.21 | 0.30 |

▼ Adjusted Score, see Section 6.3

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 3.88 | 0.49 |
| **Spike Value** | 5.01 | 0.25 |
| **Robust Average** | 3.88 | 0.49 |
| **Max Acceptable Result** | 7.01 | |
| **Median** | 3.90 | 0.34 |
| **Mean** | 3.96 | |
| **N** | 11 | |
| **Max** | 5.73 | |
| **Min** | 3 | |
| **Robust SD** | 0.65 | |
| **Robust CV** | 17% | |


Kernel Density
Density
Result
Results: S4 - Dieldrin
Assigned Value = 3.88 ± 0.49 µg/L
Maximum Acceptable Result = 7.01 µg/L
Results (µg/L)
Laboratory
3 5 6 7 2 1 12 10 8 4 11 Md RA SV


z-Scores: S4 - Dieldrin
Target Standard Deviation for Proficiency Assessment 0.78 µg/L (Equivalent to 20% CV)
z-Score
-1.1 -1.1 -0.4 -0.4 -0.1 0.0 0.2 0.3 0.5 0.8 2.0
Laboratory
3 5 6 7 2 1 12 10 8 4 11

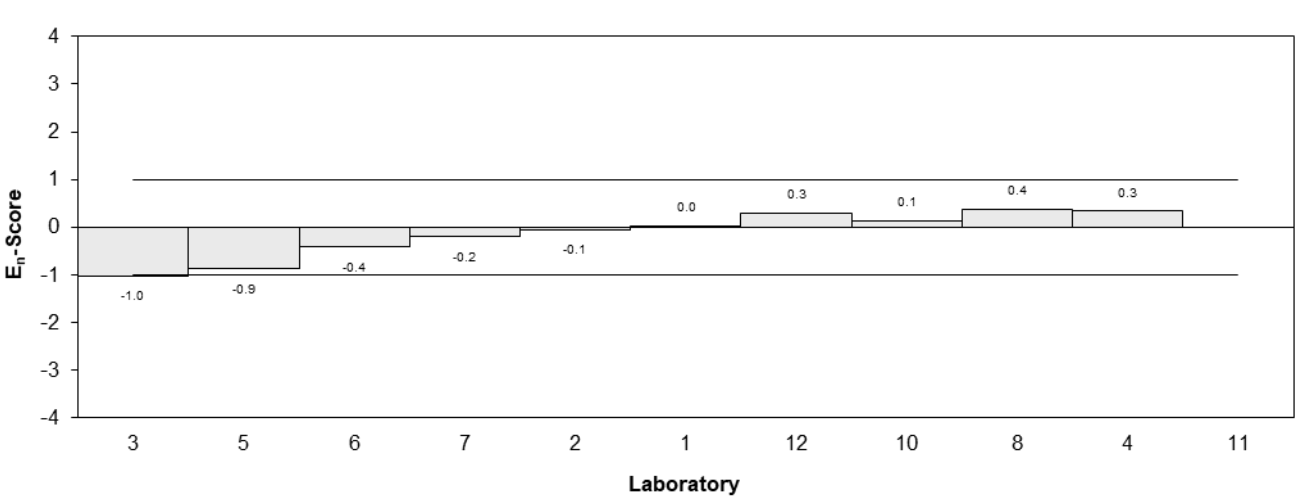

En-Scores: S4 - Dieldrin
En-Score
-1.0 -0.9 -0.4 -0.2 -0.1 0.0 0.3 0.1 0.4 0.3
Laboratory
3 5 6 7 2 1 12 10 8 4 11

Figure 21

Table 26

**Sample Details**

| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Wastewater |
| **Analyte** | Ethion |
| **Unit** | µg/L |

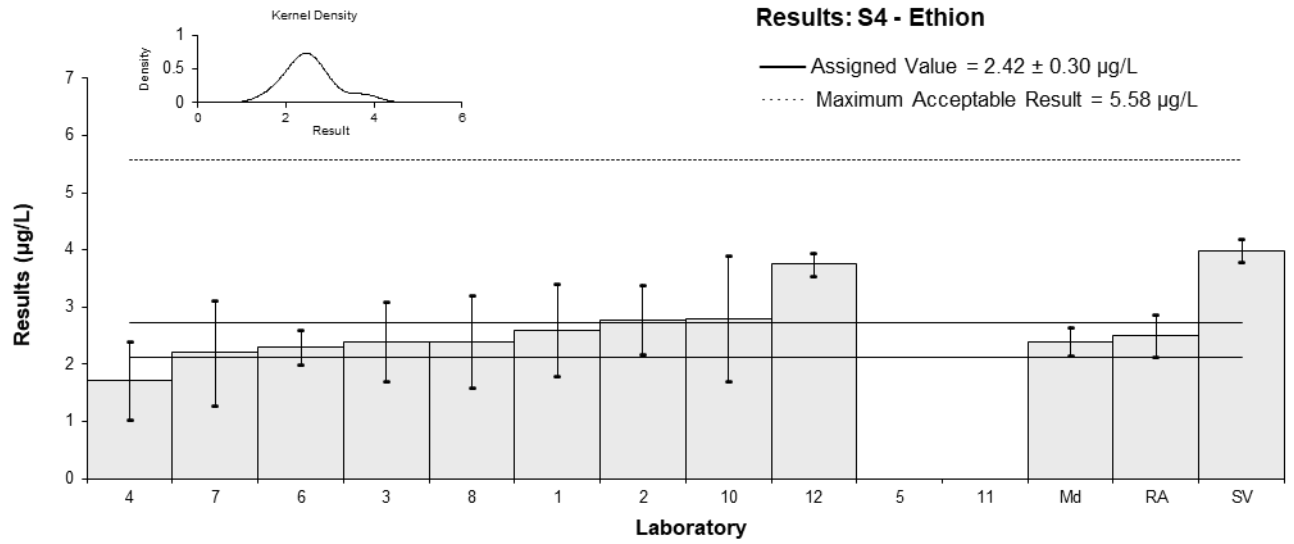
**Participant Results**

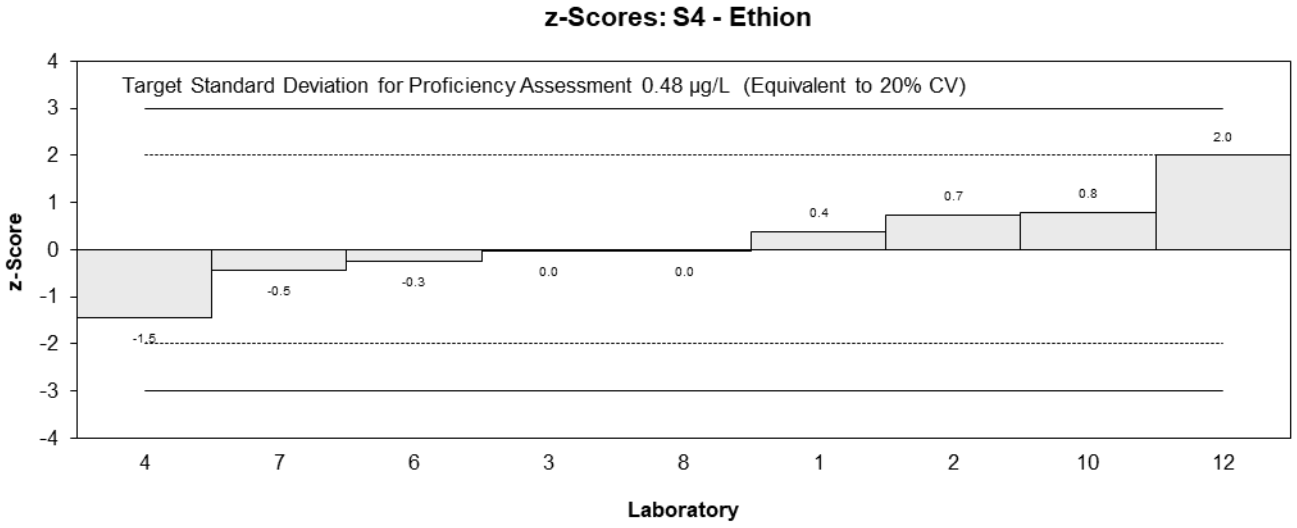
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2.6 | 0.8 | 0.37 | 0.21 |
| **2** | 2.78 | 0.6116 | 0.74 | 0.53 |
| **3** | 2.4 | 0.69 | -0.04 | -0.03 |
| **4** | 1.7183 | 0.68 | -1.45 | -0.94 |
| **5** | NT | NT | | |
| **6** | 2.3 | 0.3 | -0.25 | -0.28 |
| **7** | 2.2 | 0.91 | -0.45 | -0.23 |
| **8** | 2.4 | 0.8 | -0.04 | -0.02 |
| **10** | 2.8 | 1.1 | 0.79 | 0.33 |
| **11** | NT | NT | | |
| **12*** | 3.75 | 0.2 | 2.00▼ | |

* Outlier, see Section 4.2; ▼ Adjusted Score, see Section 6.3

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.42 | 0.30 |
| **Spike Value** | 3.99 | 0.20 |
| **Robust Average** | 2.50 | 0.36 |
| **Max Acceptable Result** | 5.58 | |
| **Median** | 2.40 | 0.25 |
| **Mean** | 2.55 | |
| **N** | 9 | |
| **Max** | 3.75 | |
| **Min** | 1.7183 | |
| **Robust SD** | 0.44 | |
| **Robust CV** | 17% | |


Kernel Density
Density
Result
Results: S4 - Ethion
Assigned Value = 2.42 ± 0.30 µg/L
Maximum Acceptable Result = 5.58 µg/L
Results (µg/L)
Laboratory
4 7 6 3 8 1 2 10 12 5 11 Md RA SV


z-Scores: S4 - Ethion
Target Standard Deviation for Proficiency Assessment 0.48 µg/L (Equivalent to 20% CV)
z-Score
-1.5
-0.5
-0.3
0.0
0.0
0.4
0.7
0.8
2.0
Laboratory
4 7 6 3 8 1 2 10 12

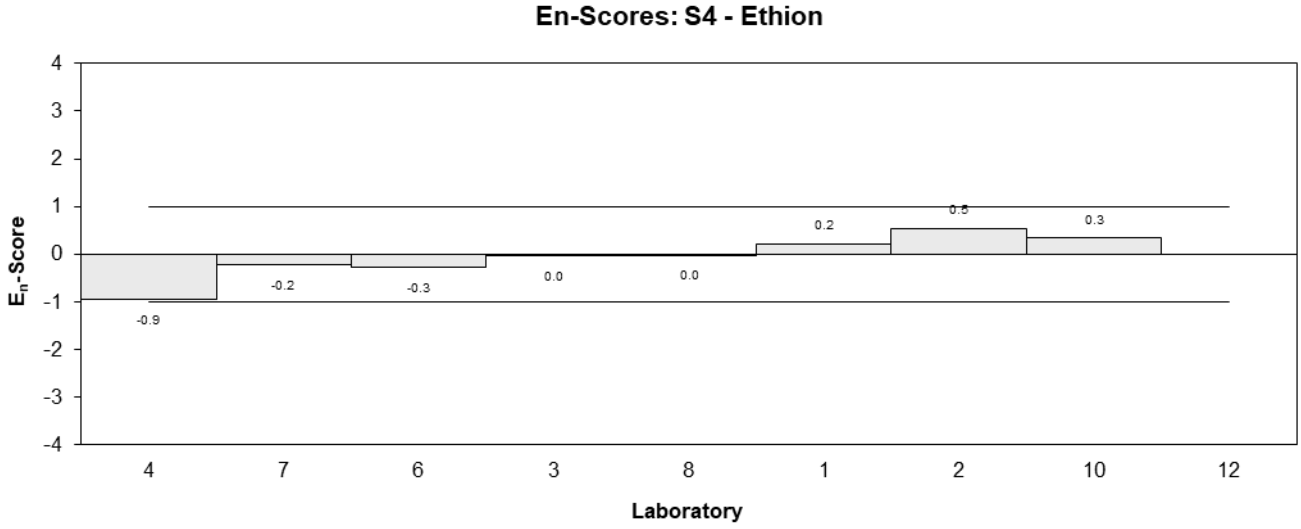

En-Scores: S4 - Ethion
En-Score
-0.9
-0.2
-0.3
0.0
0.0
0.2
0.5
0.3
Laboratory
4 7 6 3 8 1 2 10 12

Figure 22

Table 27

**Sample Details**

| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Wastewater |
| **Analyte** | Lindane |
| **Unit** | µg/L |

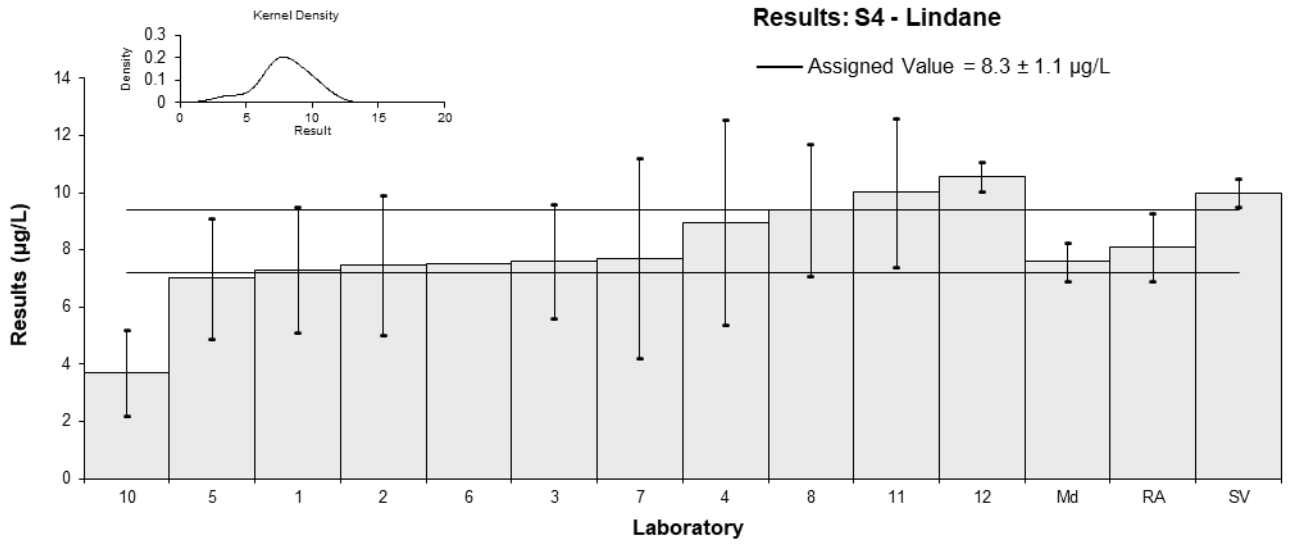
**Participant Results**

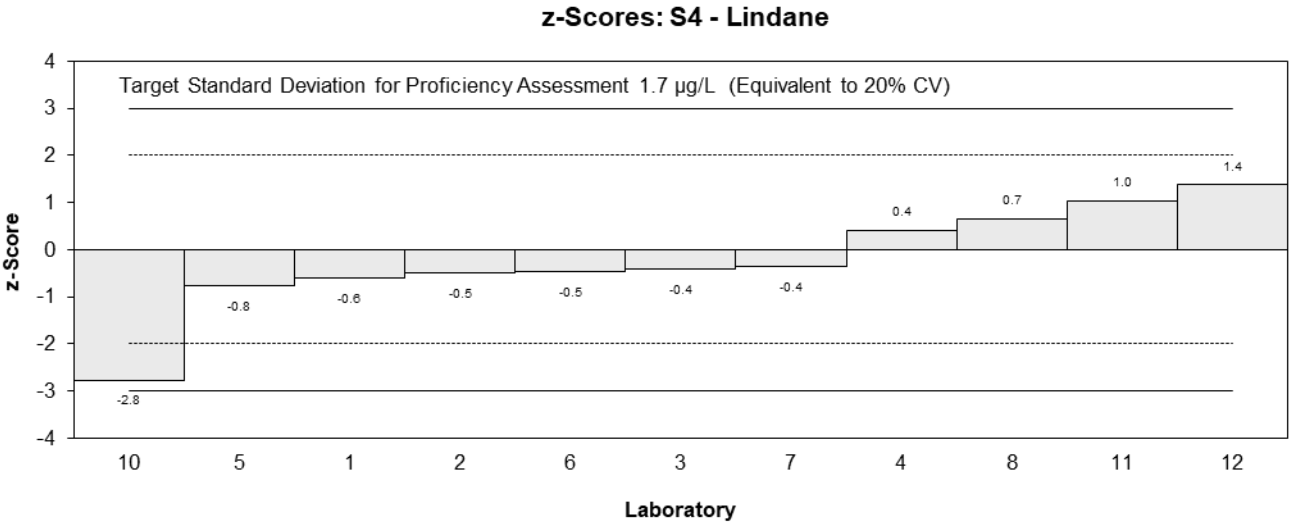
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 7.3 | 2.2 | -0.60 | -0.41 |
| **2** | 7.48 | 2.44 | -0.49 | -0.31 |
| **3** | 7.6 | 2 | -0.42 | -0.31 |
| **4** | 8.96 | 3.59 | 0.40 | 0.18 |
| **5** | 7 | 2.1 | -0.78 | -0.55 |
| **6** | 7.5 | NR | -0.48 | -0.73 |
| **7** | 7.7 | 3.5 | -0.36 | -0.16 |
| **8** | 9.4 | 2.3 | 0.66 | 0.43 |
| **10*** | 3.7 | 1.5 | -2.77 | -2.47 |
| **11** | 10.02 | 2.6 | 1.04 | 0.61 |
| **12** | 10.57 | 0.5 | 1.37 | 1.88 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 8.3 | 1.1 |
| **Spike Value** | 10.0 | 0.5 |
| **Robust Average** | 8.1 | 1.2 |
| **Median** | 7.60 | 0.67 |
| **Mean** | 7.9 | |
| **N** | 11 | |
| **Max** | 10.57 | |
| **Min** | 3.7 | |
| **Robust SD** | 1.7 | |
| **Robust CV** | 20% | |


Results: S4 - Lindane
Kernel Density
Density
Result
Assigned Value = 8.3 ± 1.1 µg/L
Results (µg/L)
Laboratory
10
5
1
2
6
3
7
4
8
11
12
Md
RA
SV


z-Scores: S4 - Lindane
Target Standard Deviation for Proficiency Assessment 1.7 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-2.8
-0.8
-0.6
-0.5
-0.5
-0.4
-0.4
0.4
0.7
1.0
1.4

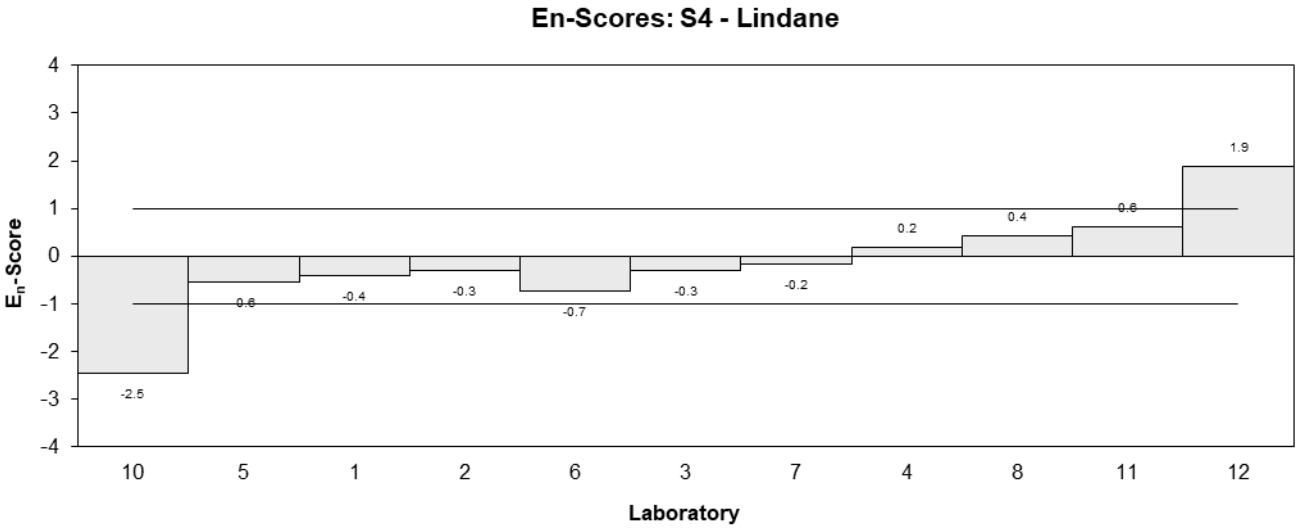

En-Scores: S4 - Lindane
En-Score
Laboratory
-2.5
-0.6
-0.4
-0.3
-0.7
-0.3
-0.2
0.2
0.4
0.6
1.9

Figure 23

Table 28

**Sample Details**

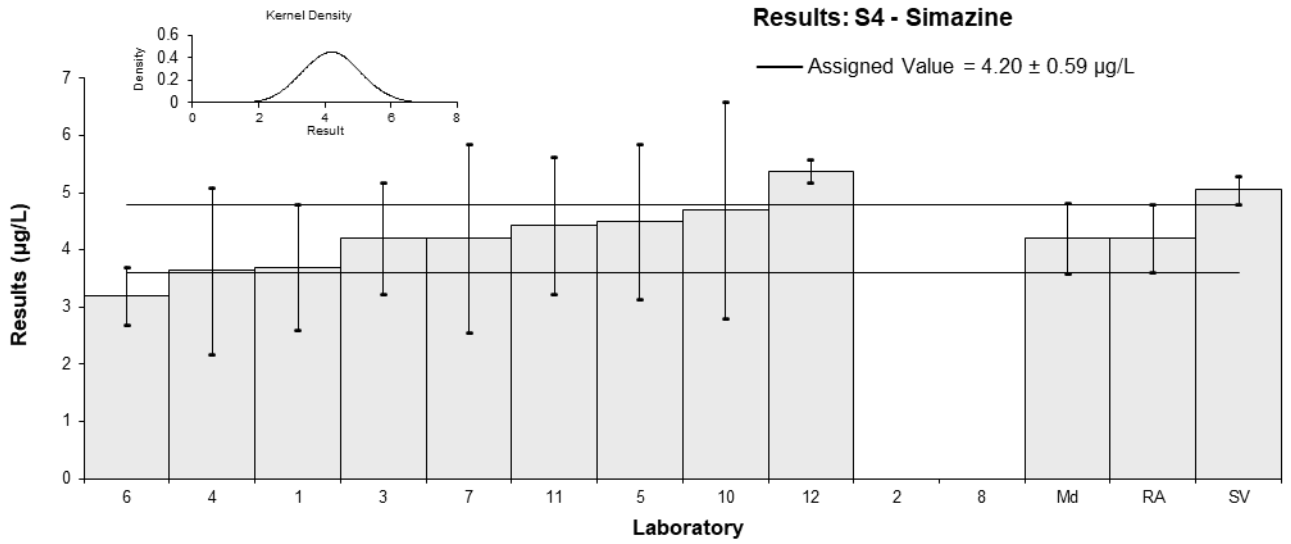
| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | Wastewater |
| **Analyte** | Simazine |
| **Unit** | µg/L |

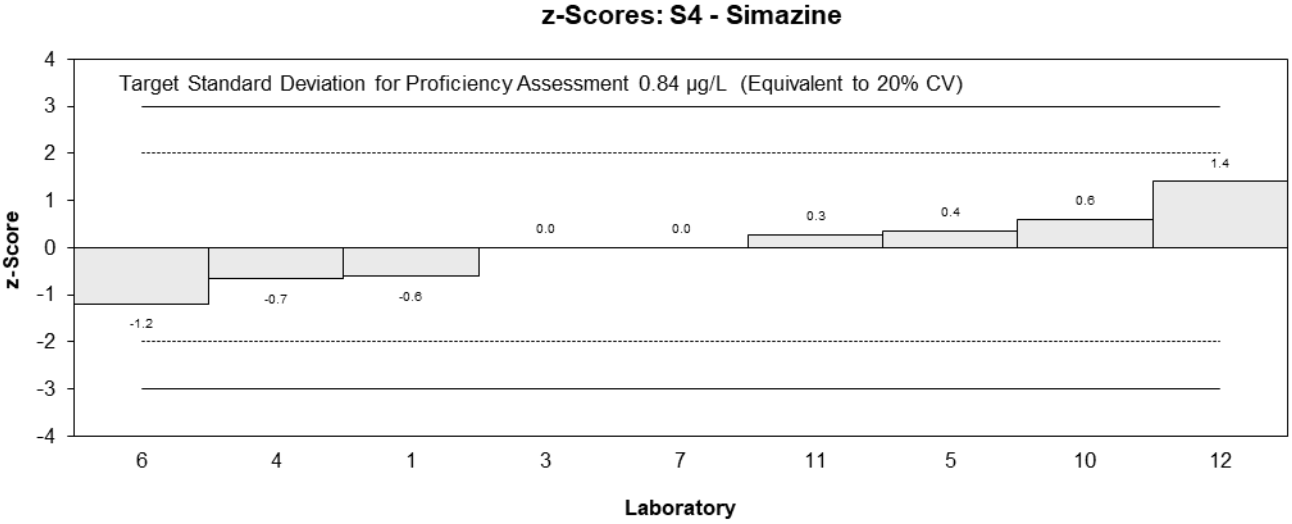
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 3.7 | 1.1 | -0.60 | -0.40 |
| **2** | NT | NT | | |
| **3** | 4.2 | 0.98 | 0.00 | 0.00 |
| **4** | 3.64 | 1.46 | -0.67 | -0.36 |
| **5** | 4.5 | 1.35 | 0.36 | 0.20 |
| **6** | 3.2 | 0.51 | -1.19 | -1.28 |
| **7** | 4.2 | 1.65 | 0.00 | 0.00 |
| **8** | NT | NT | | |
| **10** | 4.7 | 1.9 | 0.60 | 0.25 |
| **11** | 4.43 | 1.2 | 0.27 | 0.17 |
| **12** | 5.38 | 0.2 | 1.40 | 1.89 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.20 | 0.59 |
| **Spike Value** | 5.05 | 0.25 |
| **Robust Average** | 4.20 | 0.59 |
| **Median** | 4.20 | 0.62 |
| **Mean** | 4.22 | |
| **N** | 9 | |
| **Max** | 5.38 | |
| **Min** | 3.2 | |
| **Robust SD** | 0.70 | |
| **Robust CV** | 17% | |


Kernel Density
Density
Result
Results: S4 - Simazine
Assigned Value = 4.20 ± 0.59 µg/L
Results (µg/L)
Laboratory
6
4
1
3
7
11
5
10
12
2
8
Md
RA
SV


z-Scores: S4 - Simazine
Target Standard Deviation for Proficiency Assessment 0.84 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.2
-0.7
-0.6
0.0
0.0
0.3
0.4
0.6
1.4

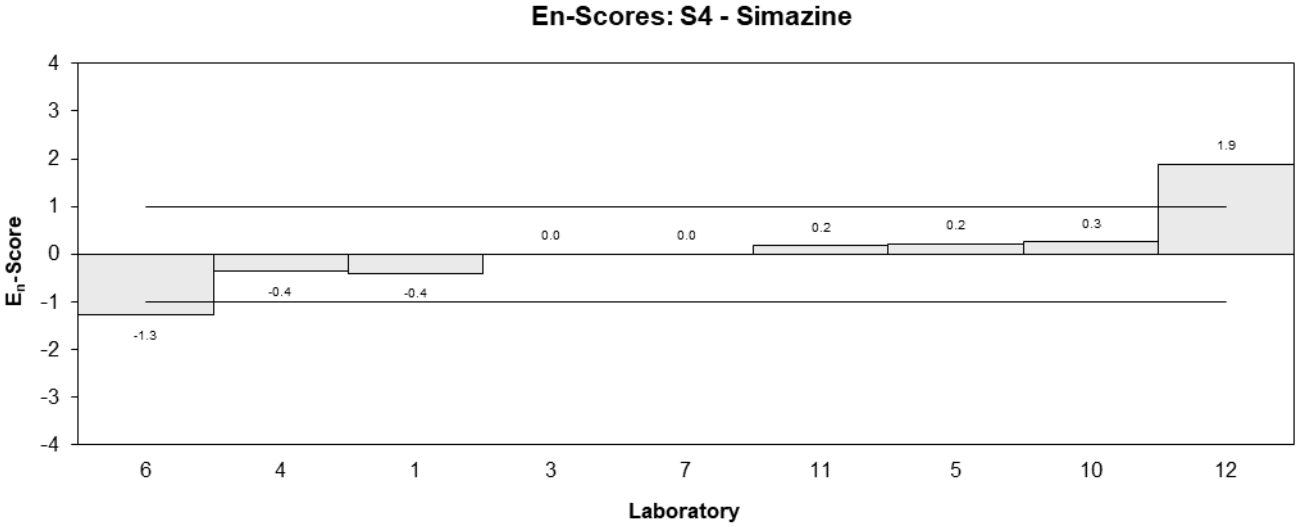

En-Scores: S4 - Simazine
En-Score
Laboratory
-1.3
-0.4
-0.4
0.0
0.0
0.2
0.2
0.3
1.9

Figure 24

# 6 DISCUSSION OF RESULTS

## 6.1 Assigned Value

The robust averages and associated expanded uncertainties were calculated using the procedure described in ISO 13528.[5] The assigned values for all scored analytes were the robust averages of participants' results, after results less than 50% and greater than 150% of the robust average had been removed.[3,4] The calculation of the expanded uncertainty for robust averages is presented in Appendix 3, using Sample S2 benzene 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.

For Sample S1, an assigned value was set only for TRH; no assigned values were set for the individual hydrocarbon ranges. No assigned value was set for Sample S2 ethylbenzene as there was greater variability of results between participants as compared to the other BTEX analytes, and this variability was also observed in a subsequent internal investigation. No assigned values were set for Sample S3 acenaphthylene and Sample S4 dicamba as there were too few reported numeric results. Sample S2 C6-C10 was also not scored; this was due to its volatile nature and therefore data has been provided for information only, though there was reasonable consensus between participants' results for this analyte in this study. For these analytes without assigned values, participants may still compare their results with the descriptive statistics and spiked values as presented in Section 5.

A comparison of the assigned values (or robust average if no assigned value was set) and spiked values is presented in Table 29.

In general, recoveries in this study were lower than previously observed for similar analytes in river water matrix, however, this may be due to the more complex wastewater matrix. Analytes have been scored if there was a reasonable consensus between participants' results.

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

| Sample | Analyte | Assigned Value *(Robust Average)* (µg/L) | Spiked Value (µg/L) | Assigned Value *(Robust Average)* / Spiked Value (%) |
|---|---|---|---|---|
| S1 | TRH | 1390 | 2810 | 49 |
| S2 | Benzene | 62.8 | 69.2 | 91 |
| | Toluene | 202 | 261 | 77 |
| | Ethylbenzene | *(17.7)* | 29.0 | *(61)* |
| | Xylenes | 88.0 | 129 | 68 |
| | Total BTEX | 370 | 489 | 76 |
| S3 | Acenaphthene | 4.20 | 8.08 | 52 |
| | Acenaphthylene | *(0.90)* | 1.09 | *(83)* |
| | Benz[*a*]anthracene | 4.32 | 6.50 | 66 |
| | Benzo[*a*]pyrene | 1.99 | 3.62 | 55 |
| | Fluorene | 2.18 | 3.10 | 70 |
| | Phenanthrene | 1.78 | 1.95 | 91 |
| S4 | Atrazine | 10.1 | 11.6 | 87 |
| | Chlorpyrifos | 14.8 | 20.1 | 74 |
| | Dicamba | *(6.2)* | 7.49 | *(83)* |

| Sample | Analyte | Assigned Value *(Robust Average)* (µg/L) | Spiked Value (µg/L) | Assigned Value *(Robust Average)* / Spiked Value (%) |
|---|---|---|---|---|
| | Dieldrin | 3.88 | 5.01 | 77 |
| | Ethion | 2.42 | 3.99 | 61 |
| | Lindane | 8.3 | 10.0 | 83 |
| | Simazine | 4.20 | 5.05 | 83 |

### 6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate. It is a requirement of ISO/IEC 17025 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.[7]

Of 206 numeric results submitted for the analytes of interest in this study, 201 (98%) were reported with an expanded MU. Participants used a wide variety of procedures to estimate their uncertainty (Table 4).

Laboratory **2** did not report a TRH result for Sample S1; the study coordinator summed the individual hydrocarbon ranges and no estimate of the uncertainty of the TRH result was made. Laboratory **6** did not report uncertainties for some of their numeric results; this participant reported that they were accredited to ISO/IEC 17025.

The magnitude of reported uncertainties was within the range of 1.3% to 50% relative to the result. In general, an expanded uncertainty of less than 15% relative is likely to be unrealistically small for routine analysis, while an uncertainty of greater than 50% relative is likely to be too large and not fit-for-purpose. Of 201 MUs reported for this study, 24 were less than 15% relative.

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

Laboratories **7** and **12** attached estimates of MU to non-value results reported. An estimate of uncertainty expressed as a value should not be attached to a non-value result.[8]

In some cases, the results and/or uncertainties 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 the uncertainty to no more than two significant figures, and then write the result with the corresponding number of decimal places. For example, instead of 3.31 ± 0.8606 µg/L, it is better to report this as 3.31 ± 0.86 µg/L.[8]

### 6.3 *z*-Score

Wastewater was a new water matrix for NMI PT studies, and so target SDs equivalent to 20% PCV were used to calculate *z*-scores. CVs predicted by the Thompson-Horwitz equation,[6] the between-laboratory CVs obtained in this study, and target SDs (as PCV) are presented for comparison in Table 30.

Table 30 Comparison of Thompson-Horwitz CV, Between-Laboratory CV and Target SD

| Sample | Analyte | Assigned Value *(Robust Average)* (µg/L) | Thompson-Horwitz CV[a] (%) | Between-Laboratory CV[b] (%) | Target SD (as PCV) (%) |
|---|---|---|---|---|---|
| S1 | >C10-C16 | *(690)* | 17 | 43 | Not Set |
| | >C16-C34 | *(740)* | 17 | 49 | Not Set |
| | >C34-C40 | N/A | N/A | N/A | Not Set |
| | TRH | 1390 | 15 | 38 | 20 |
| S2 | C6-C10 | *(1020)* | 16 | 14 | Not Set |
| | Benzene | 62.8 | 22 | 9.9 | 20 |
| | Toluene | 202 | 20 | 6.1 | 20 |
| | Ethylbenzene | *(17.7)* | 22 | 26 | Not Set |
| | Xylenes | 88.0 | 22 | 11 | 20 |
| | Total BTEX | 370 | 19 | 3.6 | 20 |
| S3 | Acenaphthene | 4.20 | 22 | 17 | 20 |
| | Acenaphthylene | *(0.90)* | 22 | 36 | Not Set |
| | Benz[*a*]anthracene | 4.32 | 22 | 23 | 20 |
| | Benzo[*a*]pyrene | 1.99 | 22 | 31 | 20 |
| | Fluorene | 2.18 | 22 | 17 | 20 |
| | Phenanthrene | 1.78 | 22 | 28 | 20 |
| S4 | Atrazine | 10.1 | 22 | 17 | 20 |
| | Chlorpyrifos | 14.8 | 22 | 15 | 20 |
| | Dicamba | *(6.2)* | 22 | 25 | Not Set |
| | Dieldrin | 3.88 | 22 | 17 | 20 |
| | Ethion | 2.42 | 22 | 14 | 20 |
| | Lindane | 8.3 | 22 | 17 | 20 |
| | Simazine | 4.20 | 22 | 17 | 20 |

[a] Calculated from the assigned value (robust average).

[b] Robust between-laboratory CV with outliers removed, if applicable.

To account for possible low bias in the consensus value due to participants using inefficient extraction or analytical techniques, 11 *z*-scores were adjusted across the following analytes: Sample S1 TRH, Sample S3 acenaphthene, benz[*a*]anthracene, benzo[*a*]pyrene and fluorene, and Sample S4 dieldrin and ethion. A maximum acceptable result was set as the spiked value plus two target SDs of the spiked value. 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 any participants reporting results close to the spiked value were not penalised. *z*-Scores for results greater than the maximum acceptable result, and *z*-scores less than 2.0, were left unaltered.

Of 162 results for which *z*-scores were calculated, 157 (97%) returned a score of $|z| \leq 2.0$, indicating a satisfactory performance.

Laboratories **3**, **4**, **6**, **7** and **10** reported numeric results for all 16 scored analytes. Of these participants, Laboratories **3**, **4** and **6** returned satisfactory *z*-scores for all analytes.

Four participants received satisfactory *z*-scores for all reported results that were scored: Laboratories **2** (15), **8** (14), **1** (12) and **12** (12).

The dispersal of *z*-scores is presented by laboratory in Figure 25, and by analyte in Figure 26.

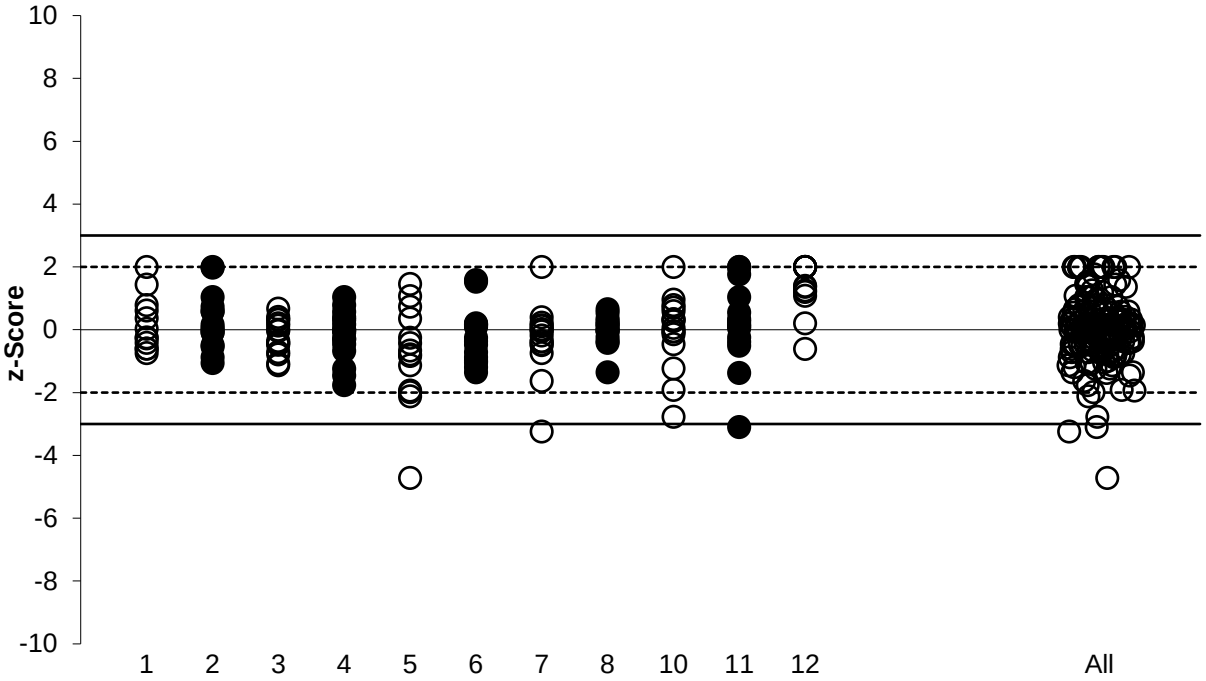



Figure 25 *z*-Score Dispersal by Laboratory

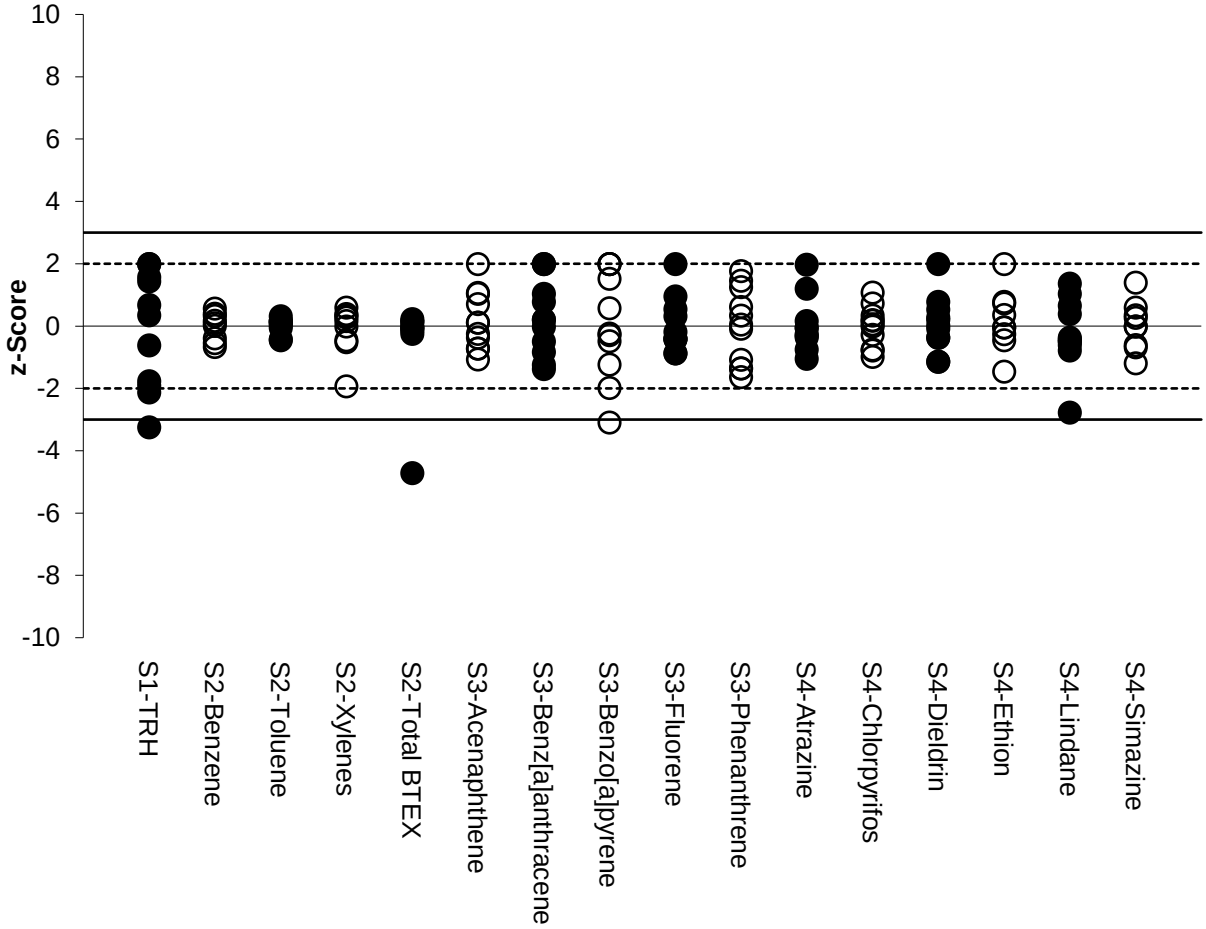



Figure 26 *z*-Score Dispersal by Analyte

## 6.4 $E_n$-Score

$E_n$-Scores can be interpreted in conjunction with *z*-scores, as an unsatisfactory $E_n$-score can either be caused by an inappropriate measurement or uncertainty, or both.

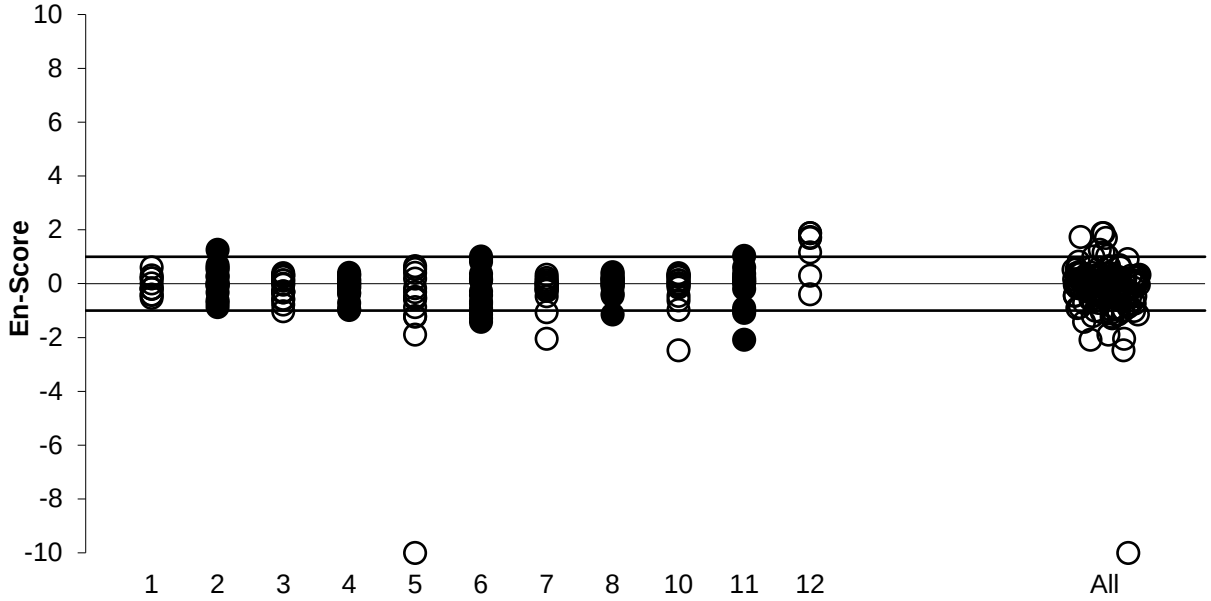
If a participant did not report an expanded MU with a result, an expanded uncertainty of zero (0) was used to calculate the $E_n$-score. For results whose *z*-scores were adjusted as discussed in Section 6.3 *z*-Score, no $E_n$-score has been calculated.

Of 151 results for which $E_n$-scores were calculated, 128 (85%) returned a score of $|E_n| \leq 1.0$, indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **4** returned satisfactory $E_n$-scores for all 16 scored analytes.

One participant received satisfactory $E_n$-scores for all reported results that were scored: Laboratory **1** (11).

The dispersal of $E_n$-scores by laboratory is presented in Figure 27.




$E_n$-scores less than -10.0 have plotted as -10.0.

Figure 27 $E_n$-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 limit of reporting (LOR), or participants that did not report anything. For analytes where no assigned value was set, results have only been considered to be false negatives where the robust average and spiked value were significantly higher than the participants' LOR (i.e. the robust average minus the expanded uncertainty, and the spiked value minus the expanded uncertainty, were both greater than the LOR), or if no value was reported.

Table 31 False Negatives

| Lab. Code | Sample | Analyte | Assigned Value *(Robust Average)* (µg/L) | Spiked Value (µg/L) | Result (µg/L) |
|---|---|---|---|---|---|
| 5 | S3 | Fluorene | 2.18 | 3.10 | <0.02 |
| 12 | S4 | Dicamba | *(6.2)* | 7.49 | <0.05 |

## 6.6 Reporting of Additional Analytes

Analytes reported by participants which were not spiked into the test samples are presented in Table 32. In general, participants should take care to avoid any potential cross-contamination when analysing their samples.

Laboratory **11** commented that they detected propazine at a low level (0.05 µg/L) in Sample S4; this may have been a trace impurity in the atrazine spiking standard used.

Table 32 Analytes Reported by Participants Not Spiked into the Test Samples

| Lab. Code | Sample | Analyte | Result (µg/L) | Uncertainty (µg/L) |
|---|---|---|---|---|
| 4 | S3 | Anthracene | 1.87 | 0.75 |
| | | Chrysene | 2.51 | 1.00 |
| | S4 | Malathion | 2.99 | 1.20 |
| 5 | S3 | Anthracene | 1.5 | 0.45 |
| 12 | S4 | Piperonyl butoxide | 0.06 | 0.02 |

## 6.7 Range of PAHs and Pesticides Analysed by Participants

Participants were provided with a list of potential PAHs (for Sample S3) and pesticides (for Sample S4) that could have been spiked into the samples, given in Tables 1 and 2 respectively. Of these, six PAHs and seven pesticides were spiked into the samples (Table 3). Participants were not required to test for all analytes, and were requested to report 'NT' (for 'Not Tested') for any that they did not analyse the samples for. A summary of participants' testing of the spiked analytes is presented in Table 33.

Laboratories **6**, **10** and **12** tested for all spiked analytes. The proportion of analytes each participant tested for ranged from 77% to 100%.

All participants tested for all the spiked PAHs. Of the spiked pesticides, all participants tested for chlorpyrifos, dieldrin and lindane. Only 4 participants (45%) tested for dicamba.

Table 33 Summary of Participants' Analyses

| Lab. Code / Analyte | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 12 | Proportion of Participants (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acenaphthene | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Acenaphthylene | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Benz[*a*]anthracene | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Benzo[*a*]pyrene | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Fluorene | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Phenanthrene | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Atrazine | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | 91 |
| Chlorpyrifos | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Dicamba | NT | ✓ | NT | NT | NT | ✓ | NT | NT | ✓ | ✓ | ✓ | 45 |
| Dieldrin | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Ethion | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | ✓ | NT | ✓ | 82 |
| Lindane | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | 100 |
| Simazine | ✓ | NT | ✓ | ✓ | ✓ | ✓ | ✓ | NT | ✓ | ✓ | ✓ | 82 |
| Proportion of Analytes (%) | 92 | 92 | 92 | 92 | 85 | 100 | 92 | 77 | 100 | 92 | 100 | |

### 6.8 Participants' Analytical Methods

Participants used a variety of analytical methods for the test samples (Appendix 4).

**Sample S1 TRH**

For Sample S1, participants were provided with 500 mL, and participants reported using test portions ranging from 40 mL to the whole bottle. A comparison of results and the sample volume used is presented in Figure 28. For this study, some participants using smaller sample volumes reported lower TRH results. Participants subsampling the bottle should ensure that the subsample taken is a suitable representation of the whole sample.

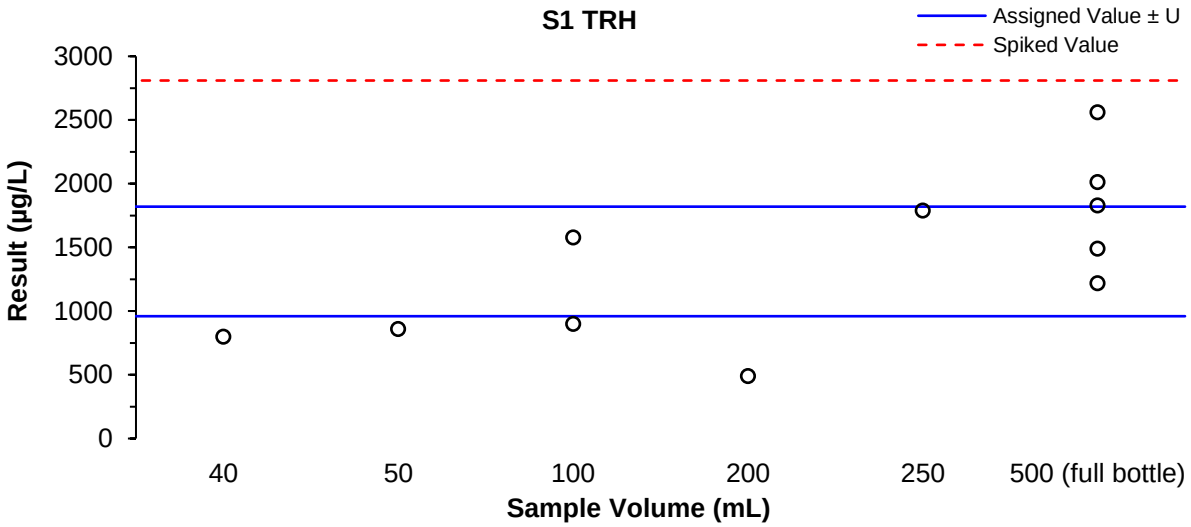



Figure 28 Sample S1 TRH Results vs Sample Volume

Most participants used liquid-liquid extraction (LLE), with one participant using solid phase extraction (SPE). For extraction solvents, participants used either dichloromethane (DCM) or hexane (HEX). Two participants reported a silica clean-up step, and one participant reported a filtration step. Most participants used gas chromatography (GC) coupled with flame ionisation detection (FID), with one participant using GC coupled with mass chromatography (MS) instead.

A plot of results against the methodology employed (extraction technique, extraction solvent and measurement instrument) is presented in Figure 29. In this study, the participants using hexane as the extraction solvent in general returned lower recoveries of TRH.

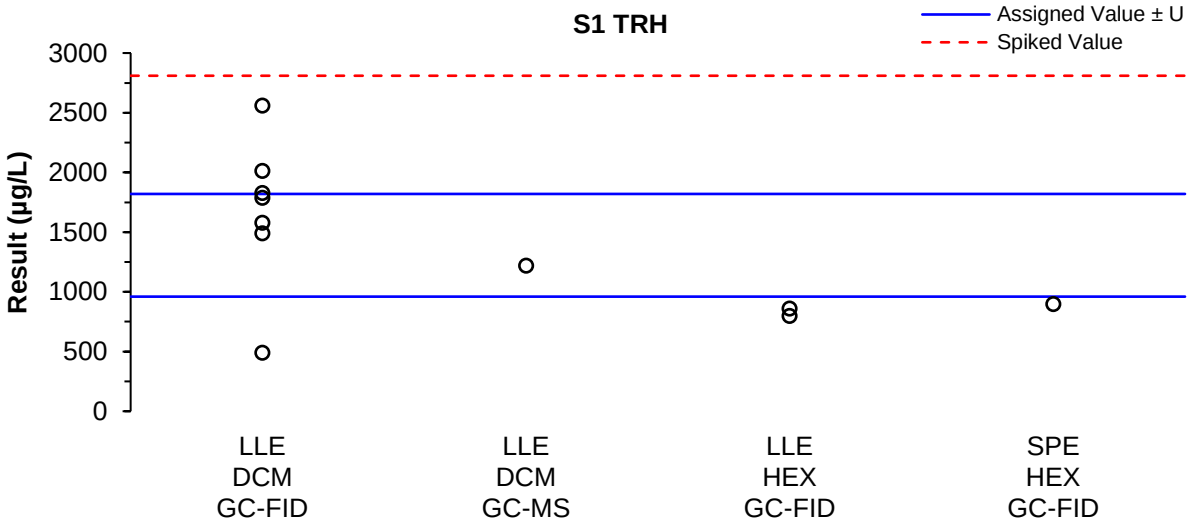



Figure 29 Sample S1 TRH Results vs Methodology

**Sample S2 BTEX**

For Sample S2 Total BTEX, Laboratory **5** reported a result of 21.5 µg/L, which was significantly lower than many of their individual BTEX analyte results. This result was therefore excluded from all statistical calculations as an extreme outlier, and has also been excluded from the following discussion.

For Sample S2, participants were provided with 2 x 42 mL (two vials were provided so that participants could repeat the measurement if required). Participants reported test portions of either 5 mL or the whole vial. A comparison of the results and sample volume used is presented in Figure 30; there was no evident correlation observed.

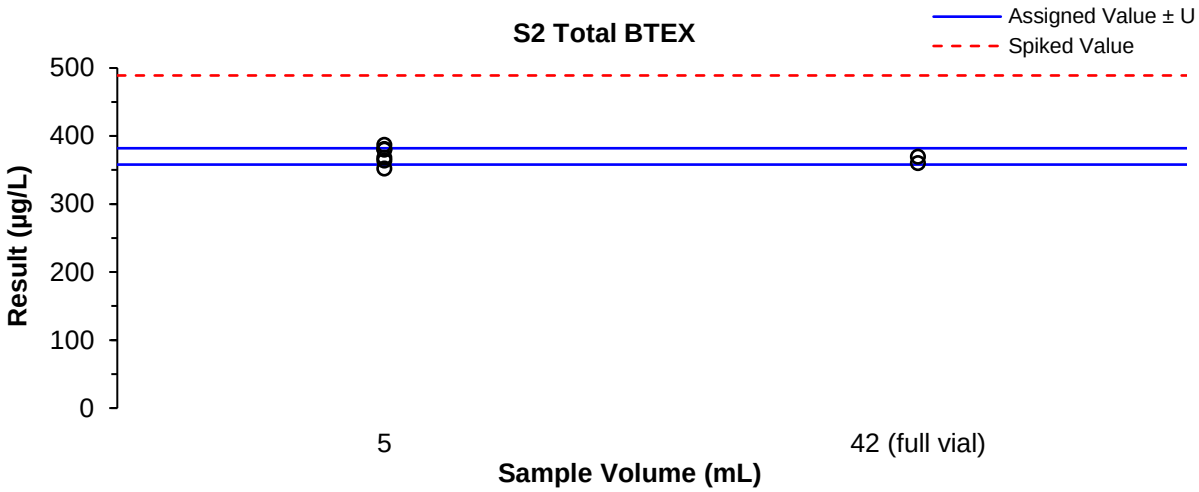



Figure 30 Sample S2 Total BTEX Results vs Sample Volume

All participants used purge-and-trap (P&T) GC-MS(/MS). One participant reported LLE using methanol (MeOH) as part of their preparation. A plot of results against methodology employed is presented in Figure 31.

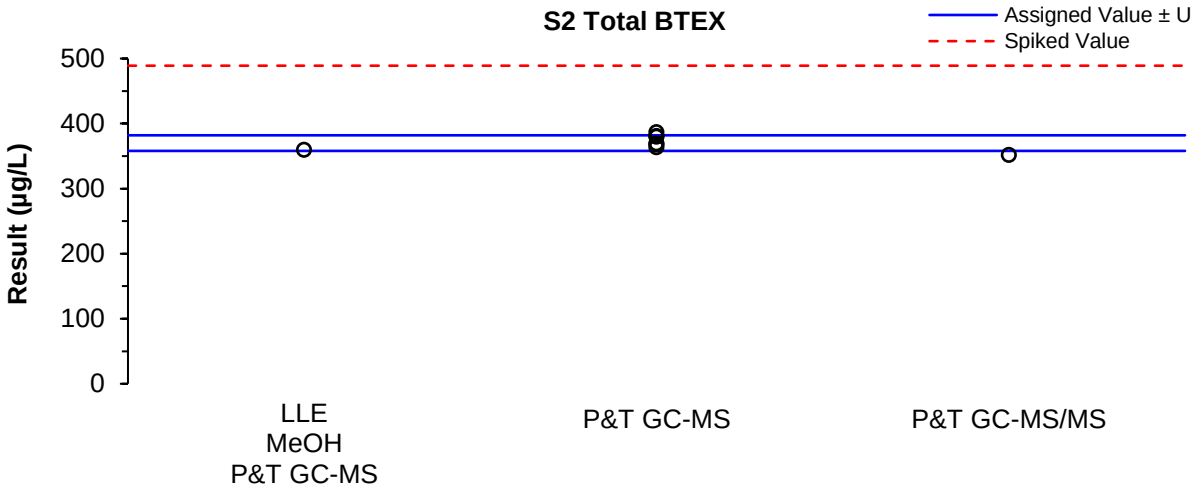



Figure 31 Sample S2 Total BTEX Results vs Methodology

**Sample S3 PAHs**

For Sample S3, participants were given the option of samples as 1 x 500 mL (3 participants) or as 3 x 100 mL (8 participants), depending on what suited their laboratory's method. Participants reported test portions ranging from 40 mL to 500 mL. A comparison of *z*-scores for scored analytes and sample volume used is presented in Figure 32; there was no evident correlation observed.

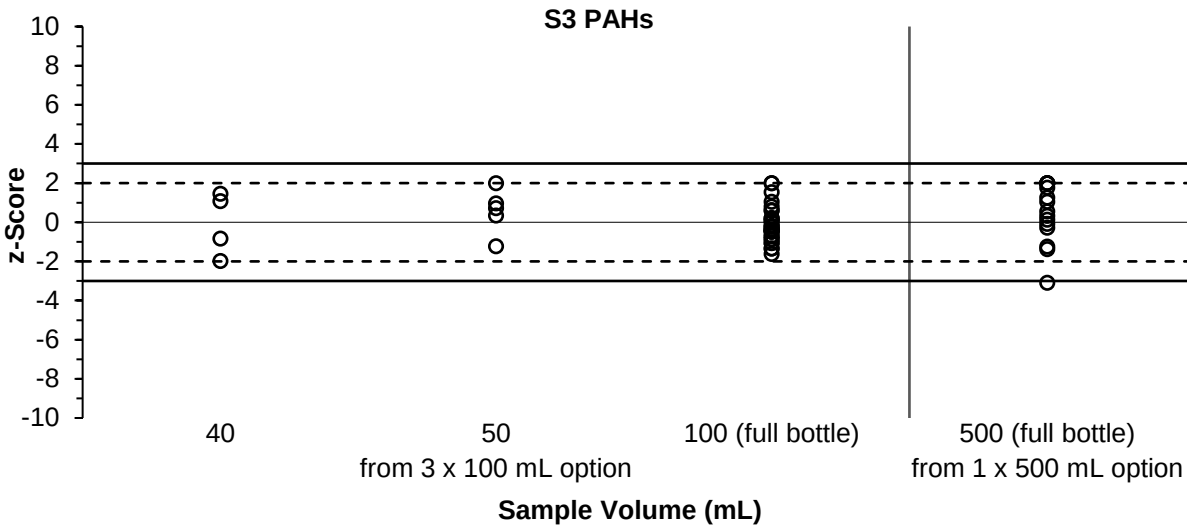



Figure 32 Sample S3 PAHs *z*-Scores vs Sample Volume

Participants reported using either LLE or SPE, with DCM, HEX or DCM/ethyl acetate (EtOAc) as the extraction solvent. One participant reported using a filtration step. All participants used GC-MS(/MS) for analysis. A plot of *z*-scores against methodology employed is presented in Figure 33; there was no evident correlation observed.

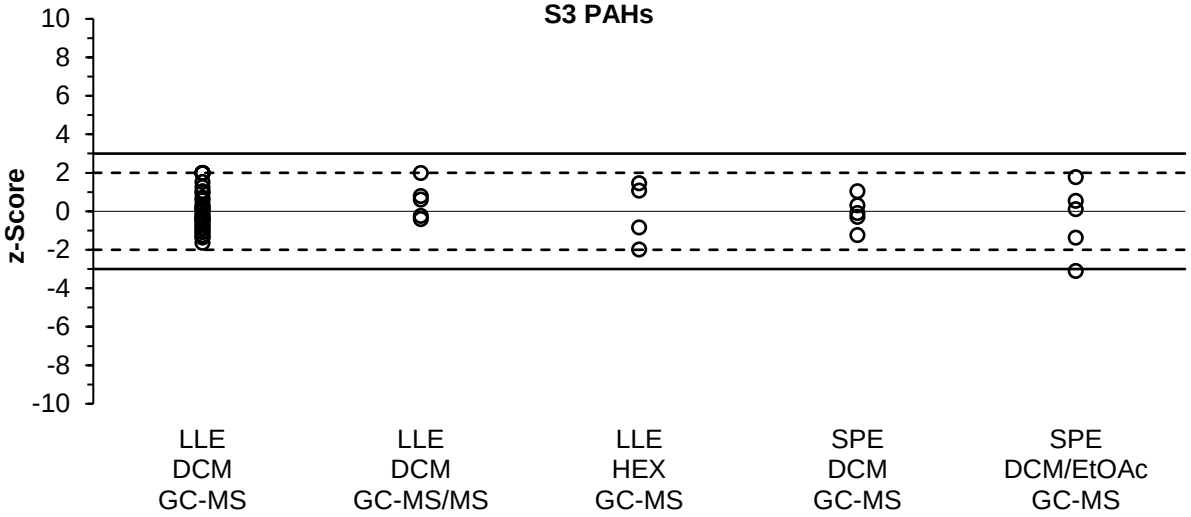



Figure 33 Sample S3 PAHs *z*-Scores vs Methodology

**Sample S4 Pesticides**

For Sample S4, participants were given the option of samples as 1 x 500 mL (3 participants) or as 3 x 100 mL (8 participants), depending on what suited their laboratory's method. Participants reported test portions ranging from 1 mL to 500 mL. A comparison of *z*-scores for scored analytes and sample volume used is presented in Figure 34 (if a participant did not report a volume, this has been marked as NR).

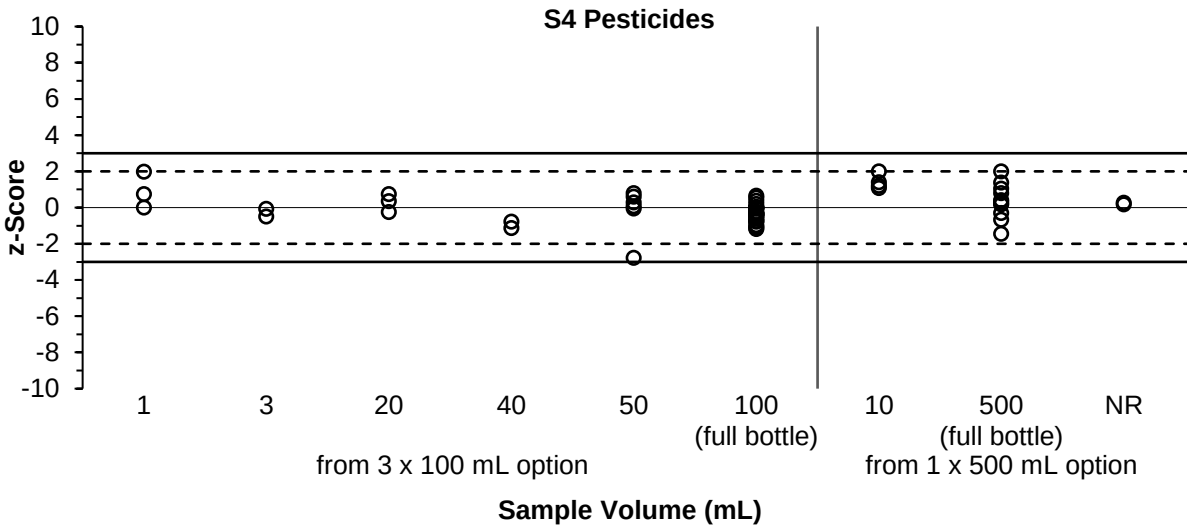



Figure 34 Sample S4 Pesticides *z*-Scores vs Sample Volume

Participants reported using LLE, QuEChERS, SPE, or direct injection (DI). Extraction solvents used included acetonitrile (ACN), DCM, DCM/EtOAc, HEX and toluene. Most participants did not use a clean-up step for their analysis, though a few participants reported a centrifugation, dilution and/or filtration step. Samples were analysed using GC coupled with electron capture detection (ECD), GC-MS(/MS) or liquid chromatography (LC) coupled with MS(/MS).

Figures 35 to 40 show comparisons of results and methodology employed for scored analytes. If a participant did not report part of their methodology, this has been marked as NR. A wide range of methodologies were employed, and there was no evident correlation observed.

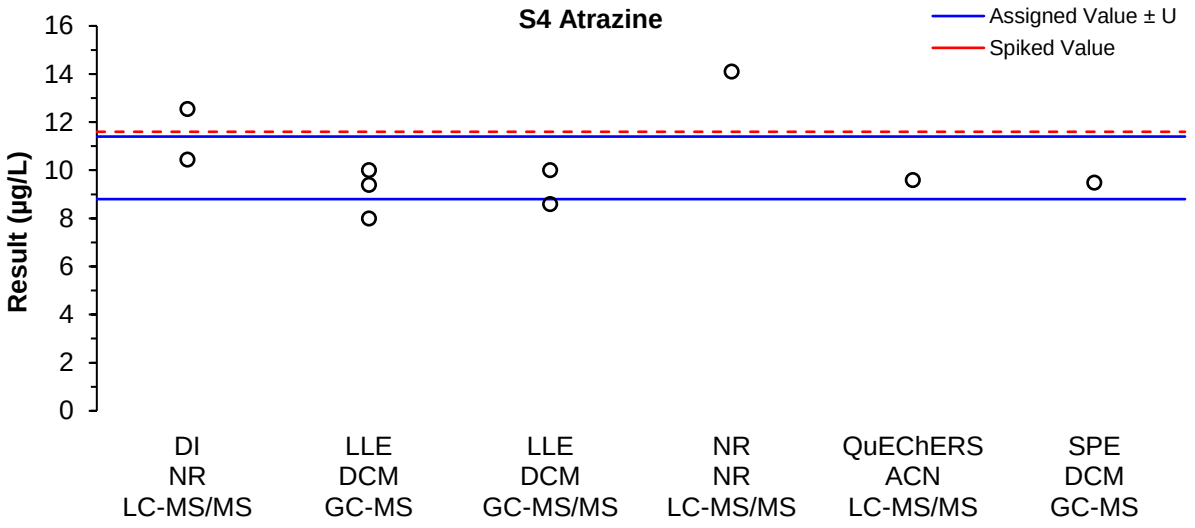



Figure 35 Sample S4 Atrazine Results vs Methodology

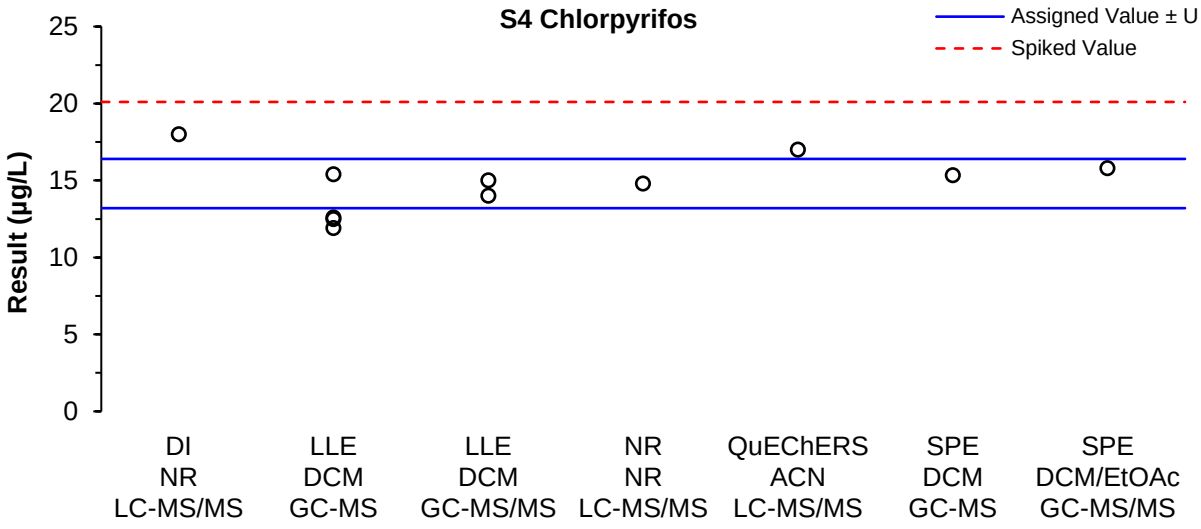



Figure 36 Sample S4 Chlorpyrifos Results vs Methodology

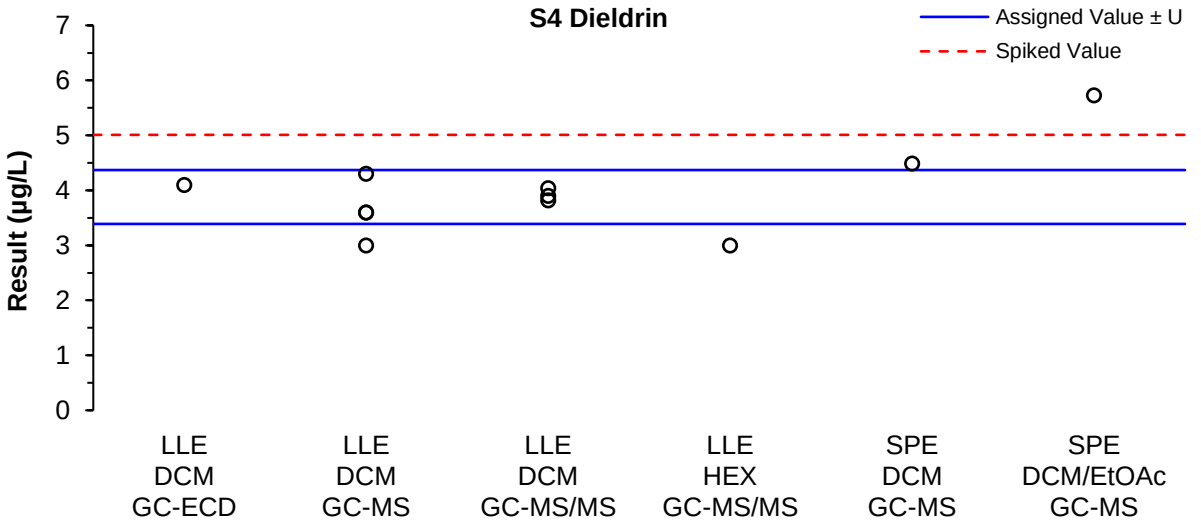



Figure 37 Sample S4 Dieldrin Results vs Methodology

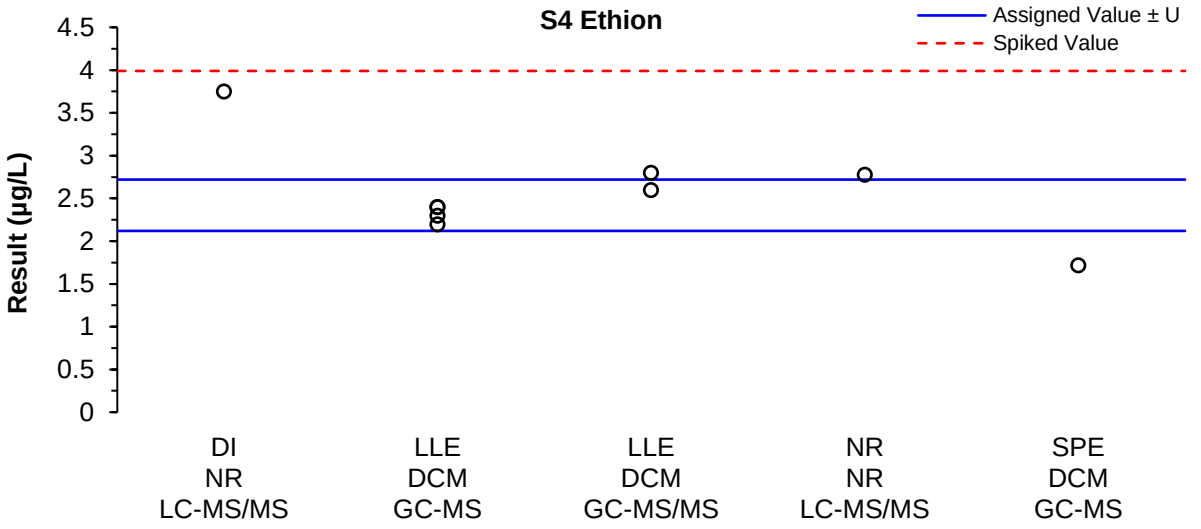



Figure 38 Sample S4 Ethion Results vs Methodology

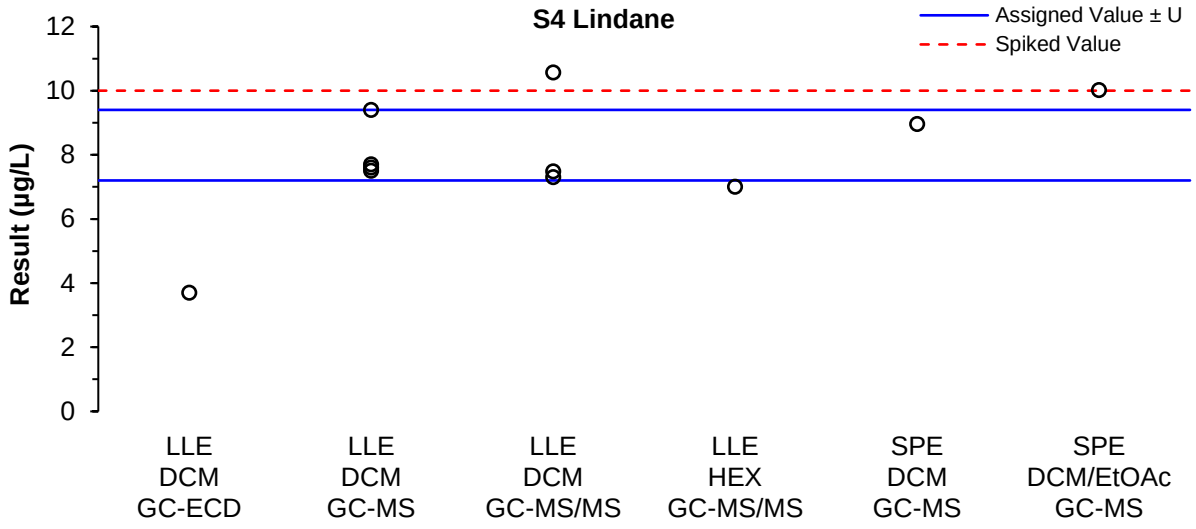



Figure 39 Sample S4 Lindane Results vs Methodology

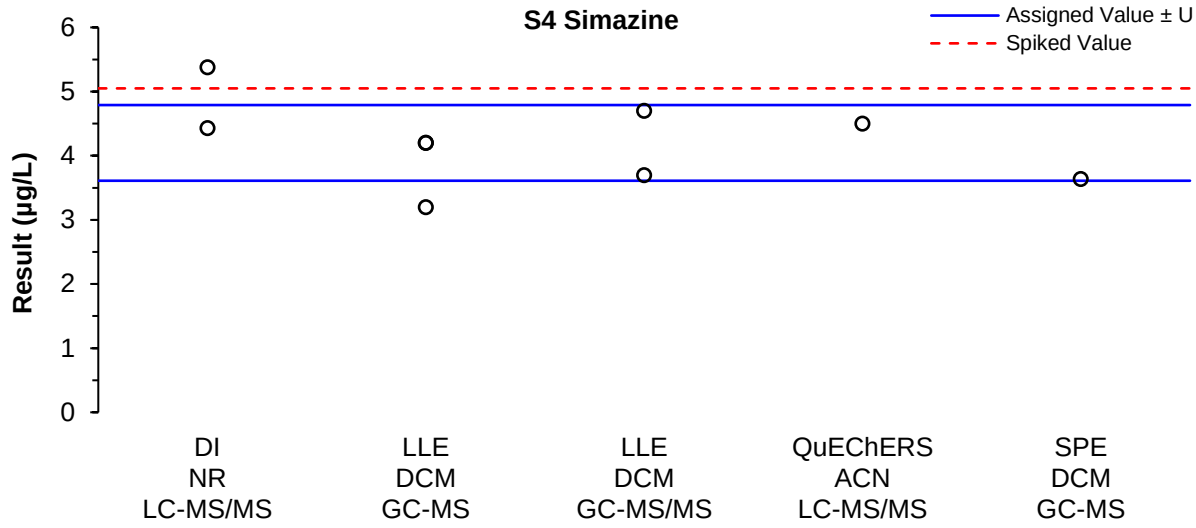



Figure 40 Sample S4 Simazine Results vs Methodology

### 6.9 Certified Reference Materials

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

Nine participants reported using certified standards. The following were listed:

- AccuStandard
- o2si
- ISO 17034 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*'[9]

### 6.10 Comparison with TRH and Total BTEX in River Water

This PT study was NMI's first study for organic compounds and pesticides in wastewater, however NMI currently runs annual studies for similar compounds in river water.

A comparison of TRH in wastewater, with TRH in river water for the last five studies (2018–2022), is shown in Figure 41. In river water, the recovery has remained relatively similar across the different studies and across different spiked levels, with an average recovery of 62%. For this study, the recovery in wastewater was lower, at 49%.

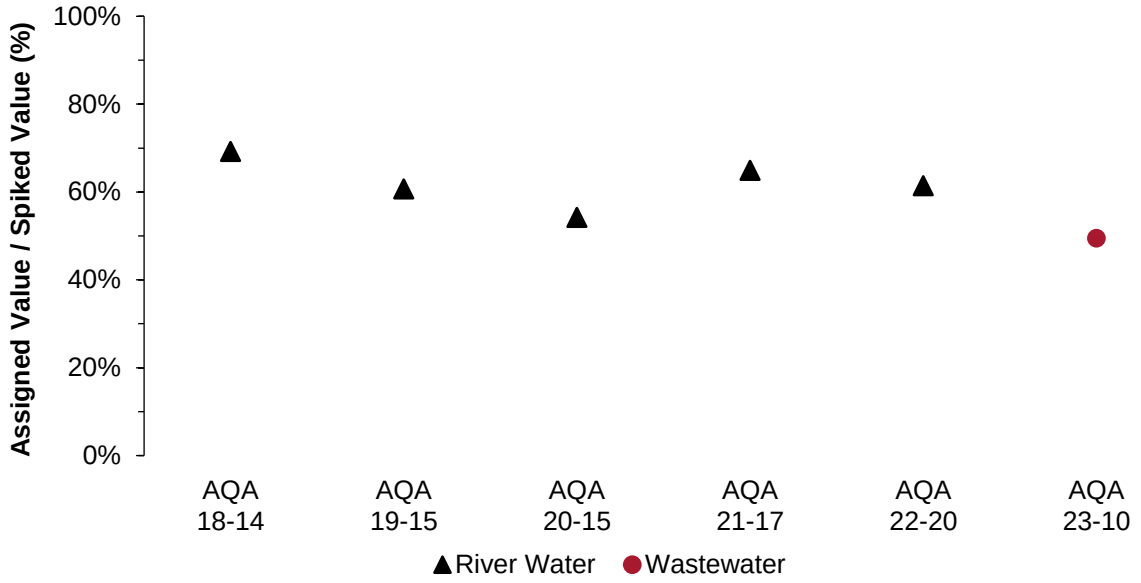



Figure 41 TRH Results in River Water and Wastewater

A comparison of total BTEX in wastewater, with total BTEX in river water for the last five studies (2018–2022), is shown in Figure 42. In river water, the recovery has remained relatively high across the different studies and across different spiked levels, with an average recovery of 89%. For this study, the recovery in wastewater was lower, at 76%.

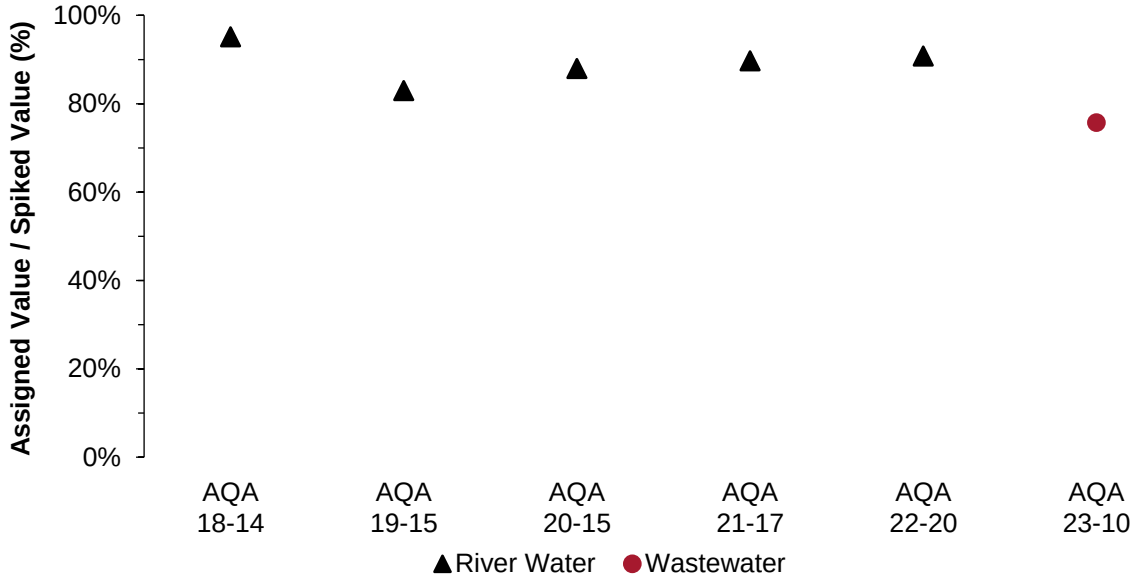



Figure 42 Total BTEX Results in River Water and Wastewater

The lower recoveries observed in the wastewater samples may be due to an increased complexity of the matrix.

### 6.11 Summary of Participants' Results and Performances

Summaries of participants' results and performances in this PT study for scored analytes are presented in Tables 34 to 36, and Figure 43.

Table 34 Summary of Participants' Results for Scored Analytes in Samples S1 and S2*

| Lab. Code | Sample S1 | Sample S2 | | | |
|---|---|---|---|---|---|
| | Total TRH | Benzene | Toluene | Xylenes | Total BTEX |
| AV | 1390 | 62.8 | 202 | 88.0 | 370 |
| SV | 2810 | 69.2 | 261 | 129 | 489 |
| 1 | 1790 | NT | NT | NT | NT |
| 2 | 2014 | 56 | 209 | 98.5 | 364 |
| 3 | 1580 | 68 | 215 | 94 | 380 |
| 4 | 900 | 70.02 | 183.9 | 87.99 | 369.63 |
| 5 | 800 | 54.5 | 185 | 54 | 21.5 |
| 6 | 1830 | 65 | 206 | 91 | 381 |
| 7 | 490 | 63 | 208 | 95 | 387 |
| 8 | 1490 | 64 | 209 | 93 | 368 |
| 10 | 860 | 67 | 200 | 80 | 360 |
| 11 | 2560 | 58 | 204 | 79 | 352 |
| 12 | 1220 | NT | NT | NT | NT |

* All values are in µg/L. Shaded cells are results which returned a questionable or unsatisfactory *z*-score. AV = Assigned Value, SV = Spiked Value.

Table 35 Summary of Participants' Results for Scored Analytes in Sample S3*

| Lab. Code | Sample S3 | | | | |
|---|---|---|---|---|---|
| | Acenaphthene | Benz[*a*]anthracene | Benzo[*a*]pyrene | Fluorene | Phenanthrene |
| AV | 4.20 | 4.32 | 1.99 | 2.18 | 1.78 |
| SV | 8.08 | 6.50 | 3.62 | 3.10 | 1.95 |
| 1 | 4 | 5 | 4 | 2 | 2 |
| 2 | 3.31 | 5.22 | 2.22 | 1.8 | 1.8 |
| 3 | 3.6 | 4.5 | 1.8 | 2.0 | 1.4 |
| 4 | 5.07 | 3.25 | 1.88 | 2.32 | 1.75 |
| 5 | 5.1 | 3.6 | 1.2 | <0.02 | 2.3 |
| 6 | 3.6 | 4.5 | 2.6 | 1.8 | 1.3 |
| 7 | 4.3 | 3.9 | 2.8 | 2.1 | 1.2 |
| 8 | 3.9 | 4.3 | 1.9 | 2.0 | 1.3 |
| 10 | 4.8 | 6.8 | 1.5 | 2.6 | 1.9 |
| 11 | 4.3 | 3.14 | 0.76 | 2.42 | 2.41 |
| 12 | 6.67 | 7.67 | 4.00 | 3.19 | 2.23 |

* All values are in µg/L. Shaded cells are results which returned a questionable or unsatisfactory *z*-score. AV = Assigned Value, SV = Spiked Value.

Table 36 Summary of Participants' Results for Scored Analytes in Sample S4*

| Lab. Code | Sample S4 | | | | | |
|---|---|---|---|---|---|---|
| | Atrazine | Chlorpyrifos | Dieldrin | Ethion | Lindane | Simazine |
| AV | 10.1 | 14.8 | 3.88 | 2.42 | 8.3 | 4.20 |
| SV | 11.6 | 20.1 | 5.01 | 3.99 | 10.0 | 5.05 |
| 1 | 8.6 | 14 | 3.9 | 2.6 | 7.3 | 3.7 |
| 2 | 14.1 | 14.8 | 3.82 | 2.78 | 7.48 | NT |
| 3 | 9.4 | 12.5 | 3.0 | 2.4 | 7.6 | 4.2 |
| 4 | 9.49 | 15.34 | 4.49 | 1.7183 | 8.96 | 3.64 |
| 5 | 9.6 | 17 | 3 | NT | 7 | 4.5 |
| 6 | 8 | 11.9 | 3.6 | 2.3 | 7.5 | 3.2 |
| 7 | 10 | 12.6 | 3.6 | 2.2 | 7.7 | 4.2 |
| 8 | NT | 15.4 | 4.3 | 2.4 | 9.4 | NT |
| 10 | 10 | 15 | 4.1 | 2.8 | 3.7 | 4.7 |
| 11 | 10.45 | 15.8 | 5.73 | NT | 10.02 | 4.43 |
| 12 | 12.55 | 18.00 | 4.04 | 3.75 | 10.57 | 5.38 |

* All values are in µg/L. Shaded cells are results which returned a questionable or unsatisfactory *z*-score. AV = Assigned Value, SV = Spiked Value.

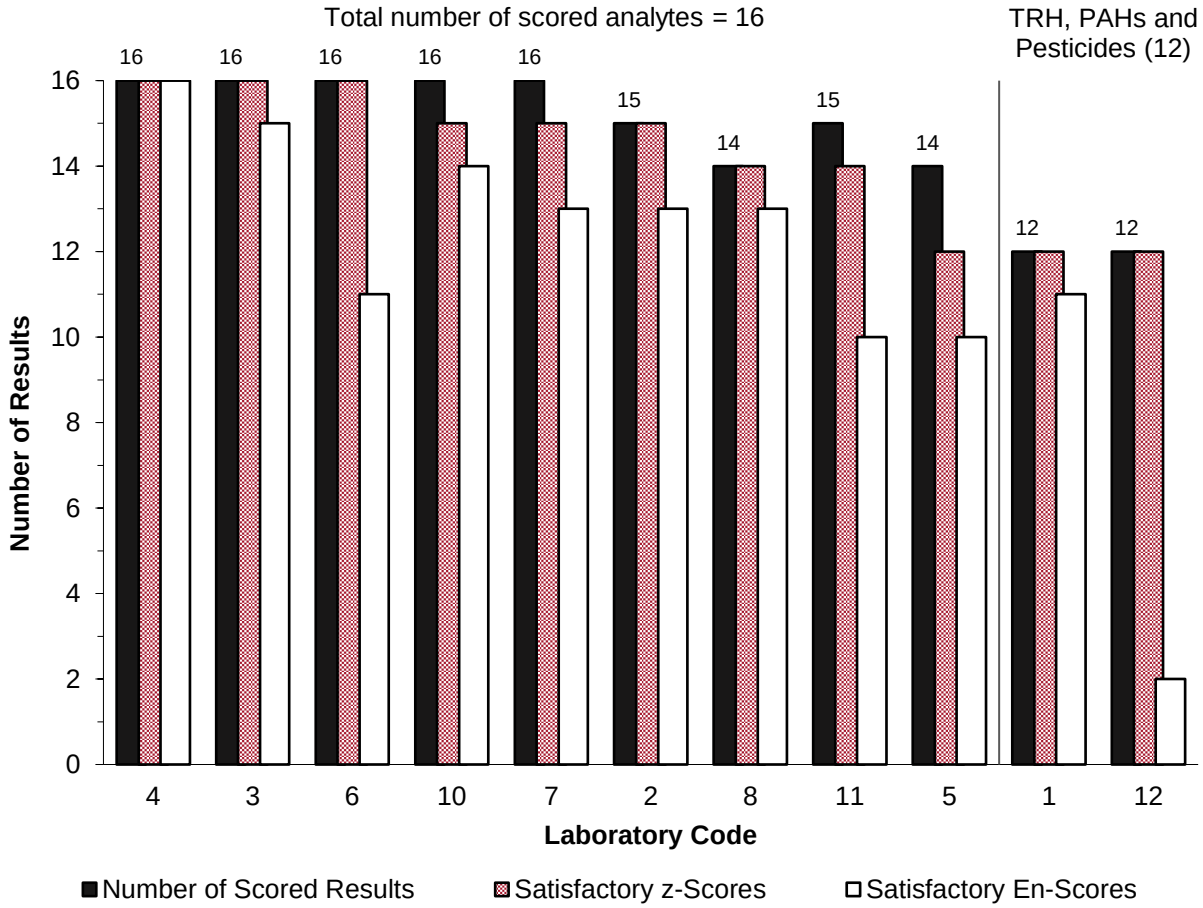



Figure 43 Summary of Participants' Performance

## 7 REFERENCES

Please note that for all undated references, the latest edition of the referenced document (including any amendments) applies.


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

[2] NMI, 2023, *Study Protocol for Proficiency Testing*, viewed September 2023, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>

[3] NMI, 2023, *Chemical Proficiency Testing Statistical Manual*, viewed September 2023, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>

[4] Thompson, M., Ellison, S.L.R. and Wood, R., 2006, 'The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem.*, vol 78, pp 145–196.

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

[6] Thompson, M., 2000, 'Recent Trends in Inter-laboratory Precision at ppb and sub-ppb Concentrations in Relation to Fitness for Purpose Criteria in Proficiency Testing', *Analyst*, vol 125, pp 385–386.

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

[8] Eurachem/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement,* 3rd ed., viewed September 2023, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>

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

## APPENDIX 1 SAMPLE PREPARATION

### A1.1 Diesel Fuel and Water 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 had been used in previous NMI Hydrocarbon PTs.

Wastewater was obtained from Sydney Water at West Ryde. It was filtered through an ADVANTEC GB140 Glass Filter and autoclaved.

### A1.2 Test Sample Preparation

**Sample S1**

A diesel spiking solution was prepared by weighing 0.51017 g of the treated diesel fuel into a 500 mL volumetric flask and making to volume with methanol. Amber glass bottles of approximately 500 mL capacity were rinsed with acetone and dried. The cleaned bottles were placed in an air-conditioned room overnight. Filtered, autoclaved water (538.4 ± 0.2 g, 540 mL at 25 °C) was weighed into each of the bottles. This amount of water was selected to minimise the headspace in the sample bottles after spiking. The methanol/diesel spiking solution (1.490 mL) was added to each bottle using a Hamilton dispenser. The bottles were immediately capped and inverted to mix the solution. Each bottle was then labelled and shrink-wrapped.

**Sample S2**

Filtered, autoclaved water (41.88 ± 0.05 g, 42 mL) was weighed into headspace vials. A composite spike solution was prepared by adding aliquots of diesel and unleaded petrol to methanol. Two of the BTEX compounds were fortified with additional laboratory solvent. The composite spiking solution was made up to volume with methanol. Composite spiking solution (1.0 mL) was added to each vial using a Hamilton dispenser. Each vial was capped after spiking, labelled and shrink-wrapped.

**Sample S3**

The PAH spike solutions were prepared by dissolving each standard material in dichloromethane. A 1:1 mix of Milli-Q water and filtered autoclaved wastewater (16045 g) was placed into a stainless steel container. After spiking, the water was stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL and 100 mL amber glass bottles which were labelled and shrink-wrapped.

**Sample S4**

The pesticide spike solutions were prepared by dissolving each standard material in acetone. A 1:1 mix of Milli-Q water and filtered autoclaved wastewater (15341 g) was placed into a stainless steel container. After spiking, the water was stirred using a top-driven impeller stirrer for at least two hours. The samples were then dispensed into 500 mL and 100 mL amber glass bottles which were labelled and shrink-wrapped.

For all samples, the samples were stored at 4 °C between preparation and dispatch.

## 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 sufficiently homogeneous samples.

Analytes were only set assigned values, and participants' results scored, if there was a reasonable consensus of participants' results.

### A2.2 Stability

Samples were stored at 4 ºC after preparation and prior to dispatch. For dispatch, the samples were packaged into insulated polystyrene foam boxes with cooler bricks, and all samples were delivered within two days of dispatch for this study. No stability testing was conducted for this study as the samples were prepared, stored and dispatched using a process previously demonstrated to produce sufficiently stable samples.

Comparisons of *z*-scores to days spent in transit for scored analytes are presented in Figures 44 to 56 (extreme outliers have been removed). No evidence of significant analyte degradation with respect to the amount of time spent in transit was observed.

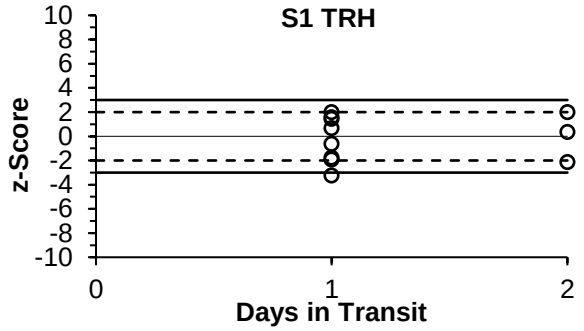



Figure 44 S1 TRH *z*-Score vs Transit Time

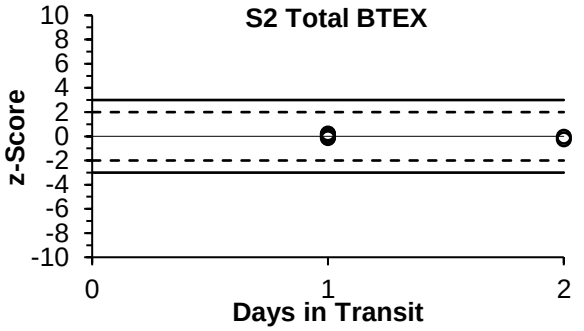



Figure 45 S2 Total BTEX *z*-Score vs Transit Time

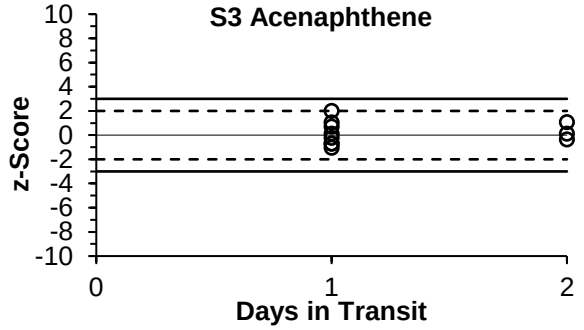



Figure 46 S3 Acenaphthene *z*-Score vs Transit Time

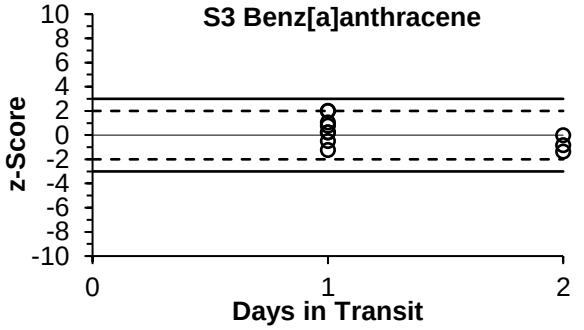



Figure 47 S3 Benz[*a*]anthracene *z*-Score vs Transit Time

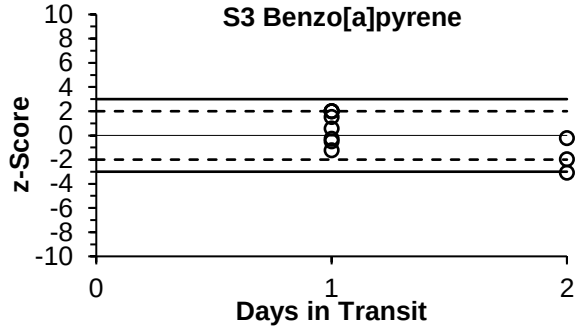



Figure 48 S3 Benzo[*a*]pyrene z-Score vs Transit Time

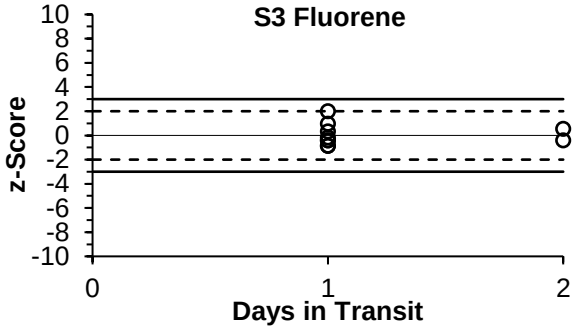



Figure 49 S3 Fluorene *z*-Score vs Transit Time

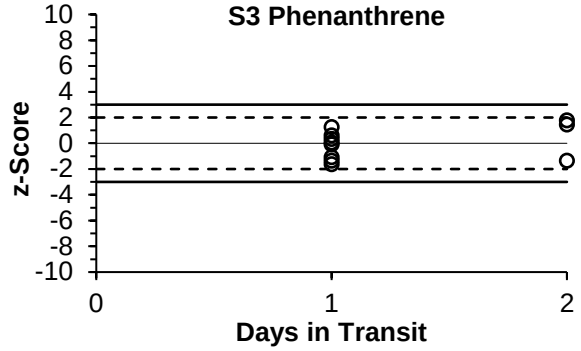



Figure 50 S3 Phenanthrene *z*-Score vs Transit Time

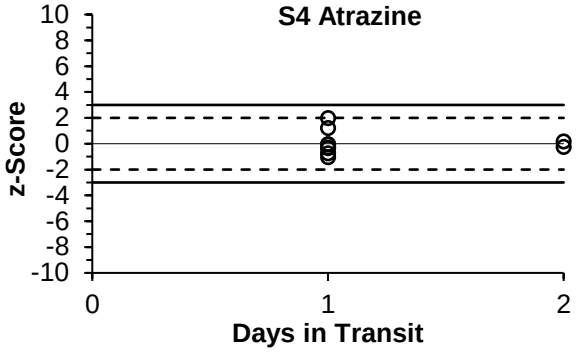



Figure 51 S4 Atrazine *z*-Score vs Transit Time

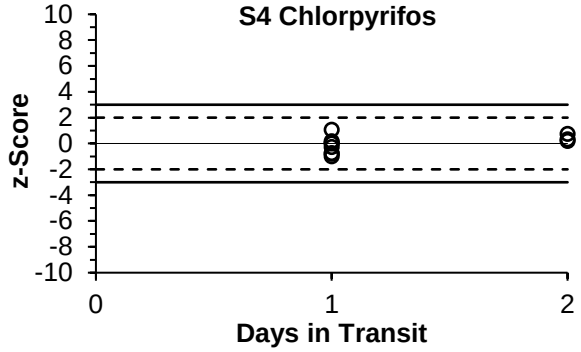



Figure 52 S4 Chlorpyrifos *z*-Score vs Transit Time

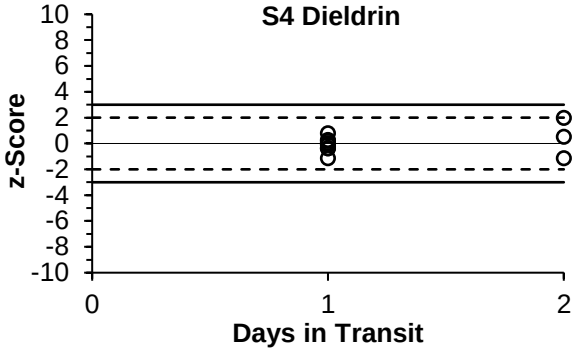



Figure 53 S4 Dieldrin *z*-Score vs Transit Time

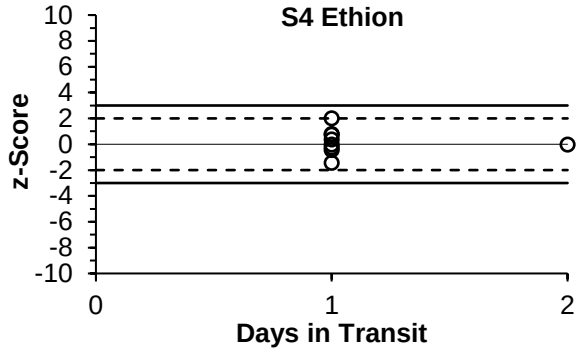



Figure 54 S4 Ethion *z*-Score vs Transit Time

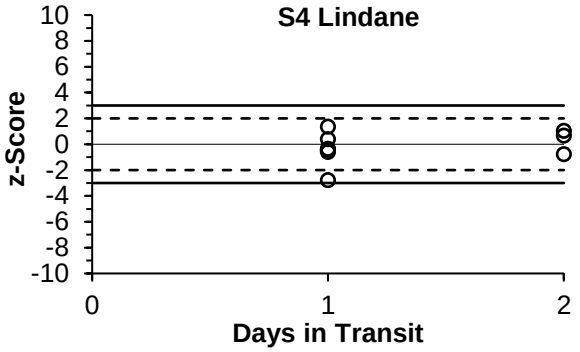



Figure 55 S4 Lindane *z*-Score vs Transit Time

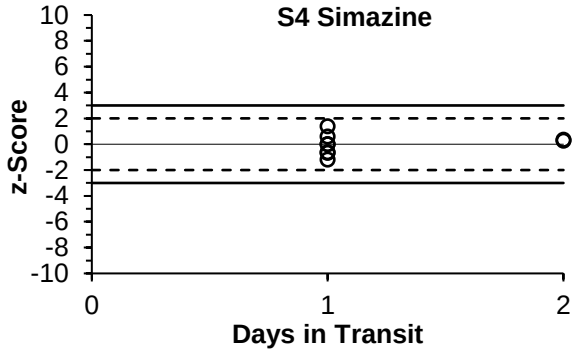



Figure 56 S4 Simazine *z*-Score vs Transit Time

## APPENDIX 3 ROBUST AVERAGE AND ASSOCIATED UNCERTAINTY, *z*-SCORE AND $E_n$-SCORE CALCULATIONS

### A3.1 Robust Average and Associated Uncertainty

Robust averages were calculated using the procedure described in ISO 13528.[5] The associated uncertainties were estimated as according to Equation 4.

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

where:

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

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

$p$ is the number of results

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

A worked example is set out below in Table 37.

Table 37 Uncertainty of Robust Average for Sample S2 Benzene

| | |
|---|---|
| Number of results ($p$) | 9 |
| Robust Average | 62.8 µg/L |
| $S_{rob\ av}$ | 6.2 µg/L |
| $u_{rob\ av}$ | 2.6 µg/L |
| $k$ | 2 |
| $U_{rob\ av}$ | 5.2 µg/L |

Therefore, the robust average for Sample S2 benzene is 62.8 ± 5.2 µg/L.

### A3.2 *z*-Score and $E_n$-Score Calculation

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 38, using the result reported by Laboratory 1 for Sample S1 TRH.

Table 38 *z*-Score and $E_n$-Score for Sample S1 TRH Result Reported by Laboratory 1

| Participant Result (µg/L) | Assigned Value (µg/L) | Target Standard Deviation | *z*-Score | $E_n$-Score |
|---|---|---|---|---|
| 1790 ± 500 | 1390 ± 430 | 20% as PCV, or: 0.2 × 1390 = 278 µg/L | $z = \frac{1790 - 1390}{278} = 1.44$ | $E_n = \frac{1790 - 1390}{\sqrt{500^2 + 430^2}} = 0.61$ |

## APPENDIX 4 PARTICIPANTS' TEST METHODS

Participants were requested to provide information about their test methods. Responses are presented in Tables 39 to 48. Some responses may be modified so that the participant cannot be identified.

Table 39 Methodology – Sample S1 TRH

| Lab. Code | Sample Volume (mL) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 250 | Liquid-Liquid | DCM | Silica Gel | GC-FID |
| 2 | 539 | Liquid-Liquid | DCM | None | GC-FID |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-FID |
| 4 | 100 | SPE | Hexane | None | GC-FID |
| 5 | 40 | Liquid-Liquid | Hexane | None | GC-FID |
| 6 | 530 | Liquid-Liquid | DCM | None | GC-FID |
| 7 | 200 | Liquid-Liquid | DCM | Filtration | GC-FID |
| 8 | 500 | Liquid-Liquid | DCM | None | GC-FID |
| 10 | 50 | Liquid-Liquid | Hexane | None | GC-FID |
| 11 | 500 | Liquid-Liquid | DCM | Silica | GC-FID |
| 12 | 500 | Liquid-Liquid | DCM | None | GC-MS |

Table 40 Methodology – Sample S2 BTEX

| Lab. Code | Sample Volume (mL) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | NT | | | | |
| 2 | 5 | Purge & Trap | None | None | P&T GC-MS |
| 3 | 5 | Purging | None | None | P&T GC-MS |
| 4 | 42 | Direct Injection | Water | None | P&T GC-MS |
| 5 | 10 | Direct Injection | | None | Headspace GC-MS |
| 6 | 5 | Direct Injection | None | None | P&T GC-MS |
| 7 | 5 | Purge and Trap | NA | NA | P&T GC-MS |
| 8 | 5 | Purge & Trap | n/a | None | GC-MS |
| 10 | 44 | Liquid-Liquid | MeOH | None | P&T GC-MS |
| 11 | 5 | Direct Injection | N/A | None | P&T GC-MS/MS |
| 12 | NT | | | | |

Table 41 Methodology – Sample S3 PAHs

| Lab. Code | Sample Volume (mL) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 100 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 2 | 102 | Liquid-Liquid | DCM | None | GC-MS |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-MS |

| Lab. Code | Sample Volume (mL) | Extraction Details | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 4 | 500 | SPE | DCM | None | GC-MS |
| 5 | 40 | Liquid-Liquid | Hexane | None | GC-MS |
| 6 | 116 | Liquid-Liquid | DCM | None | GC-MS |
| 7 | 100 | Liquid-Liquid | DCM | Filtration | GC-MS |
| 8 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 10 | 50 | Liquid-Liquid | DCM | None | GC-MS |
| 11 | 500 | SPE | DCM/ethyl acetate | None | GC-MS |
| 12 | 500 | Liquid-Liquid | DCM | None | GC-MS |

Table 42 Methodology – Sample S4 Atrazine

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 100 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 2 | 1 | | | Centrifugation & dilution | LC-MS/MS |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 4 | 500 | SPE | DCM | None | GC-MS |
| 5 | 20 | QuEChERS | acetonitrile | None | LC-MS/MS |
| 6 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 7 | 100 | Liquid-Liquid | DCM | Filtration | GC-MS |
| 8 | NT | | | | |
| 10 | 50 | Liquid-Liquid | DCM | N/A | GC-MS/MS |
| 11 | | Direct Injection | | | LC-MS/MS |
| 12 | 10 | Direct Injection | | Centrifuge | LC-MS/MS |

Table 43 Methodology – Sample S4 Chlorpyrifos

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 100 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 2 | 1 | | | Centrifugation & dilution | LC-MS/MS |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 4 | 500 | SPE | DCM | None | GC-MS |
| 5 | 20 | QuEChERS | acetonitrile | None | LC-MS/MS |
| 6 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 7 | 100 | Liquid-Liquid | DCM | Filtration | GC-MS |
| 8 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 10 | 50 | Liquid-Liquid | DCM | N/A | GC-MS/MS |
| 11 | 500 | SPE | DCM-EToAC | None | GC-MS/MS |
| 12 | 10 | Direct Injection | | Centrifuge | LC-MS/MS |

Table 44 Methodology – Sample S4 Dicamba

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | NT | | | | |
| 2 | 1 | | | Filtration & dilution | LC-MS/MS |
| 3 | NT | | | | |
| 4 | NT | | | | |
| 5 | NT | | | | |
| 6 | 10 | Direct Injection | NA | 0.2 micron Filter | LC-MS |
| 7 | NT | | | | |
| 8 | NT | | | | |
| 10 | 5 | Liquid-Liquid | Toluene | N/A | GC-MS |
| 11 | | Direct Injection | | | LC-MS/MS |
| 12 | 10 | Direct Injection | | Centrifuge | LC-MS/MS |

Table 45 Methodology – Sample S4 Dieldrin

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 100 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 2 | 3 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 4 | 500 | SPE | DCM | None | GC-MS |
| 5 | 40 | Liquid-Liquid | Hexane | None | GC-MS/MS |
| 6 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 7 | 100 | Liquid-Liquid | DCM | Filtration | GC-MS |
| 8 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 10 | 50 | Liquid-Liquid | DCM | N/A | GC-ECD |
| 11 | 500 | SPE | DCM-EToAC | None | GC-MS |
| 12 | 500 | Liquid-Liquid | DCM | None | GC-MS/MS |

Table 46 Methodology – Sample S4 Ethion

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 100 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 2 | 1 | | | Centrifugation & dilution | LC-MS/MS |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 4 | 500 | SPE | DCM | None | GC-MS |
| 5 | NT | | | | |
| 6 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 7 | 100 | Liquid-Liquid | DCM | Filtration | GC-MS |

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 8 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 10 | 50 | Liquid-Liquid | DCM | N/A | GC-MS/MS |
| 11 | NT | | | | |
| 12 | 10 | Direct Injection | | Centrifuge | LC-MS/MS |

Table 47 Methodology – Sample S4 Lindane

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 100 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 2 | 3 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 4 | 500 | SPE | DCM | None | GC-MS |
| 5 | 40 | Liquid-Liquid | Hexane | None | GC-MS/MS |
| 6 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 7 | 100 | Liquid-Liquid | DCM | Filtration | GC-MS |
| 8 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 10 | 50 | Liquid-Liquid | DCM | N/A | GC-ECD |
| 11 | 500 | SPE | DCM-EToAC | None | GC-MS |
| 12 | 500 | Liquid-Liquid | DCM | None | GC-MS/MS |

Table 48 Methodology – Sample S4 Simazine

| Lab. Code | Sample Volume (mL) | Extraction | Extraction Solvent | Clean-Up | Measurement Instrument |
|---|---|---|---|---|---|
| 1 | 100 | Liquid-Liquid | DCM | None | GC-MS/MS |
| 2 | NT | | | | |
| 3 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 4 | 500 | SPE | DCM | None | GC-MS |
| 5 | 20 | QuEChERS | acetonitrile | None | LC-MS/MS |
| 6 | 100 | Liquid-Liquid | DCM | None | GC-MS |
| 7 | 100 | Liquid-Liquid | DCM | Filtration | GC-MS |
| 8 | NT | | | | |
| 10 | 50 | Liquid-Liquid | DCM | N/A | GC-MS/MS |
| 11 | | Direct Injection | | | LC-MS/MS |
| 12 | 10 | Direct Injection | | Centrifuge | LC-MS/MS |

## APPENDIX 5 ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| 2,4,5-T | 2,4,5-Trichlorophenoxyacetic acid |
| 2,4-D | 2,4-Dichlorophenoxyacetic acid |
| ACN | Acetonitrile |
| AV | Assigned Value |
| BTEX | Benzene, Toluene, Ethylbenzene and Xylenes |
| CITAC | Cooperation on International Traceability in Analytical Chemistry |
| CRM | Certified Reference Material |
| CV | Coefficient of Variation |
| DCM | Dichloromethane |
| DDT | Dichlorodiphenyltrichloroethane |
| DI | Direct Injection |
| ECD | Electron Capture Detection |
| EtOAc | Ethyl Acetate |
| FID | Flame Ionisation Detection |
| GC | Gas Chromatography |
| GUM | Guide to the Expression of Uncertainty in Measurement |
| HEX | Hexane |
| IEC | International Electrotechnical Commission |
| ISO | International Organization for Standardization |
| LC | Liquid Chromatography |
| LLE | Liquid-Liquid Extraction |
| LOR | Limit of Reporting |
| Max | Maximum |
| MCPA | 2-methyl-4-chlorophenoxyacetic acid |
| Md | Median |
| MeOH | Methanol |
| Min | Minimum |
| MS | Mass Spectrometry |
| MS/MS | Tandem Mass Spectrometry |
| MU | Measurement Uncertainty |
| N | Number of numeric results |
| NA | Not Applicable |
| NATA | National Association of Testing Authorities, Australia |
| NMI | National Measurement Institute, Australia |

| | |
|---|---|
| NR | Not Reported |
| NT | Not Tested |
| P&T | Purge-and-Trap |
| PAH | Polycyclic Aromatic Hydrocarbon |
| PCV | Performance Coefficient of Variation |
| PT | Proficiency Testing |
| QuEChERS | Quick, Easy, Cheap, Effective, Rugged and Safe extraction method |
| RA | Robust Average |
| RM | Reference Material |
| SD | Standard Deviation |
| SI | International System of Units |
| SPE | Solid Phase Extraction |
| SS | Spiked Samples |
| SV | Spiked Value (or formulated concentration of a PT sample) |
| TRH | Total Recoverable Hydrocarbons |
| U | Expanded Uncertainty |

**END OF REPORT**