Australian Government
Department of Industry, Science and Resources

National Measurement Institute

# Proficiency Test Final Report AQA 22-17 Trace Elements in Sea Water and River Water

February 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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Accredited for compliance with ISO/IEC 17043

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## SUMMARY

This report presents the results of the proficiency test AQA 22-17, Trace Elements in Sea Water and River Water. The study focused on the measurement of dissolved Ag, Al, As, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Sb, Se, Sn, Tl, U, V and Zn in sea water and of dissolved Ag, Al, As, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, U, V and Zn in river water.

The assigned values were the robust averages of participants' results. The associated uncertainties were estimated from the robust standard deviation of participants' results.

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

i. *compare the performance of participant laboratories and assess their accuracy;*

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

Of 468 scored results, 441 (94%) returned a satisfactory score of $|z| \leq 2.0$.

Of 468 scored results, 405 (87%) returned a satisfactory score of $|E_n| \leq 1.0$.

**Laboratory 7** reported results for all 40 tests and all returned satisfactory z-scores and $E_n$-scores.

ii. *evaluate the laboratories' methods used in determination of inorganic analytes in sea water and river water;*

The results reported for trace elements in the sea water sample were more variable and had more unsatisfactory results than in the fresh water sample. Arsenic and selenium in sea water were the tests which most challenged participants' analytical techniques when compared to the river water sample.

For As measurements in sea water participants reported using ICP-MS in collision or reaction mode with He or $O_2$ as collision/reaction gases. For Se measurements participants used ICP-MS in collision mode with He or HEHe or in reaction mode with $O_2$, $H_2$ or $NH_3$.

Chromium results in the river water sample were more variable than those in sea water. The high carbon content in the river water may explain the discrepancy.

A limited number of laboratories reported results for P in sea water.

Low level P and Se in sea water were the tests which presented the most analytical difficulty to participating laboratories with CVs of 27% and 22% respectively.

iii. *compare the performance of participant laboratories with their past performance;*

AQA 22-17 is the 31$^{st}$ NMI proficiency study of metals in water. Over last 10 years, the average proportion of satisfactory scores was 91% for z-scores and 83% for $E_n$-scores..

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

Of 468 numerical results, 462 (99%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 1% to 208% of the reported value. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 3.

v. *produce materials that can be used in method validation and as control samples.*

Surplus test samples from the present study are available for sale.

A certified reference material for metals in sea water (MX014) with reference values traceable to SI is also available for sale from NMI.

# 1 INTRODUCTION

## 1.1 NMI Proficiency Testing Program

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

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

- inorganic analytes in soil, water, food and pharmaceuticals;
- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- PFAS in water, soil, biota and food;
- controlled drug assay; and
- folic acid in flour.

AQA 22-17 is the 31st NMI proficiency study of metals in water.

## 1.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories methods used in determination of inorganic analytes in river and sea water;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

## 1.3 Study Conduct

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

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

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

# 2 STUDY INFORMATION

## 2.1 Selection of Matrices and Inorganic Analytes

The 40 tests were selected from those for which an investigation level is published in Australian and New Zealand Guidelines for Fresh and Marine Water Quality[5] and are commonly measured by water testing laboratories.

## 2.2 Participation

Eighteen laboratories participated and seventeen submitted results.

The timetable of the study was:

| | |
|---|---|
| Invitation issued: | 14 October 2022 |
| Samples dispatched: | 14 November 2022 |
| Results due: | 16 December 2022 |
| Interim report issued: | 21 December 2022 |

### 2.3 Test Material Specification

Two samples were provided for analysis:

**Sample S1** was 100 mL of filtered sea water preserved by adding 2% (v/w) nitric acid; and

**Sample S2** was 100 mL of filtered river water preserved by adding 2% (v/w) nitric acid and 0.01% (v/w) hydrochloric acid.

### 2.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

### 2.5 Sample Preparation, Analysis and Homogeneity Testing

A partial homogeneity test was conducted in this study. The same validated preparation procedure was followed as in previous studies.[2] Test samples from previous studies were demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. The results from the partial homogeneity test are reported in this study as the homogeneity values. No homogeneity testing was conducted for Al in S1.

The preparation and analysis are described in Appendices 1 and 3.

### 2.6 Stability of Analytes

No stability study was carried out for Samples S1 and S2. Stability studies conducted for similar previous studies of metals in river and sea water including the MX014 certification found no significant changes in any of the analytes' concentration.

### 2.7 Sample Storage, Dispatch and Receipt

Samples S1 and S2 were refrigerated before dispatch.

The samples were dispatched by courier on 14 November 2022.

A description of the test samples, instructions for participants, and a form for participants to confirm the receipt of the test samples, were sent with the samples.

An Excel spreadsheet for the electronic reporting of results was e-mailed to participants.

### 2.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- Participants are asked to report results in units of µg/L for:

| **SAMPLE S1 sea water** | | **SAMPLE S2 river water** | |
|---|---|---|---|
| **Test DISSOLVED** | **Approximate Conc. Range µg/L** | **Test DISSOLVED** | **Approximate Conc. Range µg/L** |
| Ag | <10 | Ag | <10 |
| Al | <50 | Al | <250 |
| As | <10 | As | <10 |

| | | | |
|---|---|---|---|
| Be | <10 | Be | <50 |
| Cd | <10 | Cd | <10 |
| Cr | <10 | Co | <10 |
| Cu | <50 | Cr | <10 |
| Fe | <250 | Cu | <250 |
| Hg | <2 | Fe | <2000 |
| Mn | <50 | Hg | <2 |
| Ni | <10 | Mn | <250 |
| P | <250 | Mo | <50 |
| Pb | <10 | Ni | <10 |
| Sb | <10 | Pb | <10 |
| Se | <10 | Sb | <50 |
| Sn | <10 | Se | <10 |
| Tl | <10 | Tl | <10 |
| U | <10 | U | <10 |
| V | <10 | V | <10 |
| Zn | <50 | Zn | <250 |

- Report results using the electronic results sheet emailed to you.
- Report results as you would report to a client. For each analyte in each sample, report the expanded measurement uncertainty associated with your analytical result (e.g. 5.23 ± 0.51 µg/L).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.

### 2.9 Interim Report

An interim report was emailed to participants on 21 December 2022.

## 3 PARTICIPANT LABORATORY INFORMATION

### 3.1 Methodology for Dissolved Elements

Summaries of test methods are transcribed in Tables 1 and 2. The instruments and settings reported by participants are presented in Appendix 5.

Table 1 Methodology for Total Elements

| Lab. Code | Method Reference | Sample Volume (mL) | Temp. (°C) | Time (min) | $HNO_3$ (mL) | HCl (mL) | $HNO_3$ (1:1) (mL) | .HCl (1:1) (mL) | $H_2O_2$ (mL) | Other (mL) |
|---|---|---|---|---|---|---|---|---|---|---|
| 2* | USEPA 200.8 & 245, APHA 3125 | | | | | | | | | |
| 6 | In house W32 and W32a referencing APHA 3125 | | | | | | | | | |
| 7 | Inhouse method with reference to USEPA6020 | 14 | 95 | 90 | 0.28 | 0.42 | | | | |
| 8 | APHA | 20 | 95 | 120 | 1 | 0.5 | | | | |
| 10 | | 30 | 95-100 | 90 | 2 | | | | | |
| 11 | | 20 | 100 | 60 | 0.5 | 0.5 | | | | |
| 12 | In House, US EPA 6020B | | | | | | | | | |
| 13* | APHA 3125 | 5 | 95 | 120 | 2 | 1 | | | | |
| 14* | EPA6020 and APHA3112 | 10 | 95 | 120 | 0.25 | | | | | 0.5 ($H_2SO_4$) |
| 15 | analysed as received | | | | | | | | | |
| 16 | APHA 3125 B | | | | | | | | | |
| 18 | In-house test method | | | | | | | | | |

*Additional Information in Table 2.

### 3.2 Additional Information

Participants had the option to report additional information for each sample analysed. These are transcribed in Table 2.

Table 2 Additional information

| Lab Code | Additional Information |
|---|---|
| 2 | Methodology: Not digested |
| 13 | Sample S1: We are not accredited for Sea Water and ordered this sample by mistake |
| 14 | Methodology: 1.5 mL KMNO4 and 1 mL K2S2O8 also added into digestion tube<br>Instrument Techniques: Collision/Reaction Cell with Kinetic Energy Discrimination |

### 3.3 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 3).

Table 3 Basis of Uncertainty Estimate

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation[a] | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 1 | Top Down - precision and estimates of the method and laboratory bias | Control Samples - CRM<br>Duplicate Analysis | CRM<br>Recoveries of SS | Eurachem/CITAC Guide |

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation[a] | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 2 | Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) | Control Samples - CRM<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration<br>Recoveries of SS | ISO/GUM |
| 4 | Standard deviation of replicate analyses multiplied by 2 or 3 | Control Samples - SS<br>Duplicate Analysis | | |
| 5 | Top Down - precision and estimates of the method and laboratory bias | Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration<br>Recoveries of SS | NMI Uncertainty Course |
| 6 | Top Down - precision and estimates of the method and laboratory bias | Control Samples<br>Duplicate Analysis | CRM | Nordtest Report TR537 |
| 7 | Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) | Control Samples - SS<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration<br>Recoveries of SS | Eurachem/CITAC Guide |
| 8 | Top Down - precision and estimates of the method and laboratory bias | Control Samples<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration<br>Recoveries of SS | Eurachem/CITAC Guide |
| 9 | 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 | ISO/GUM |
| 10 | Top Down - precision and estimates of the method and laboratory bias | Control Samples - CRM<br>Duplicate Analysis | CRM<br>Recoveries of SS | Nordtest Report TR537 |
| 11 | Control charts | Control Samples - CRM | CRM<br>Instrument Calibration<br>Recoveries of SS | ASTM E2554-13 |
| 12 | Top Down - precision and estimates of the method and laboratory bias | Control Samples - SS | Recoveries of SS | ISO/GUM |
| 13 | Top Down - precision and estimates of the method and laboratory bias | Control samples - CRM | CRM<br>Instrument Calibration | Eurachem/CITAC Guide |
| 14 | Professional judgment | Control Samples - CRM | CRM<br>Recoveries of SS | Inhouse Method |
| 15 | Standard deviation of replicate analyses multiplied by 2 or 3 | Duplicate Analysis | CRM | |
| 16 | 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 |
| 18 | Top Down - precision and estimates of the method and laboratory bias | Duplicate Analysis | CRM | Eurachem/CITAC Guide |

[a] RM = Reference Material, CRM = Certified Reference Material, SS =Spiked samples.

### 3.4 Participant Comments on this PT Study or Suggestions for Future Studies

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Such feedback may be useful in improving future studies.

There were no participants' comments reported in this study.

## 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 4.1 Results Summary

Participant results are listed in Tables 4 to 43 with results' summary statistics: robust average, median, maximum, minimum, robust standard deviation ($SD_{rob}$) and robust coefficient of variation ($CV_{rob}$). Bar charts of results and performance scores are presented in Figures 2 to 41. An example chart with an interpretation guide is shown in Figure 1.

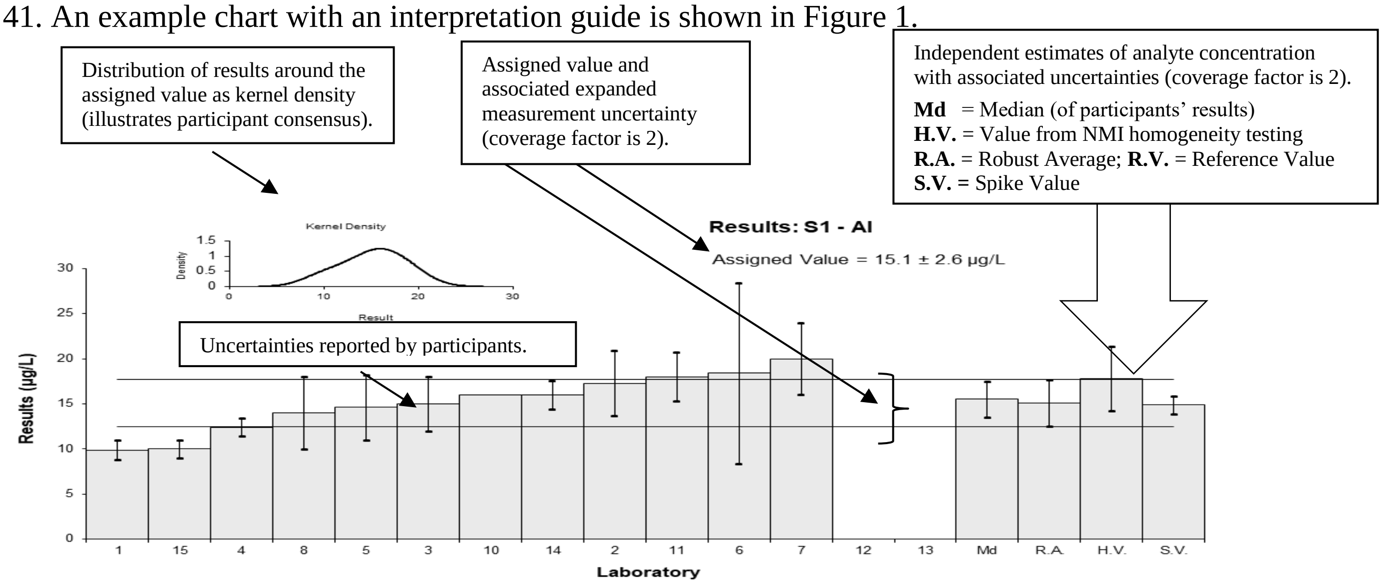


Figure 1 Guide to Presentation of Results

### 4.2 Outliers and Extreme Outliers

Outliers were results less than 50% and greater than 150% of the robust average and were removed before assigned value calculation. Extreme outliers (gross errors) were obvious blunders, such as those with incorrect units, decimal errors, or results from a different proficiency test item and were removed for calculation of summary statistics.[3, 4,6]

### 4.3 Assigned Value

An example of the assigned value calculation using data from the present study is given in Appendix 2. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'[1] In this study, the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, outliers removed; the expanded uncertainties were estimated from the associated robust standard deviations.[4, 6]

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

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by inter-laboratory comparisons, ISO13528:2022'.[6] The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528:2022.[6]

### 4.5 Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment (σ) is the product of the assigned value *(X)* and the performance coefficient of variation (PCV). This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value.

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

It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation.[7]

### 4.6 z-Score

An example of z-score calculation using data from the present study is given in Appendix 2. For each participants' result a z-score is calculated according to Equation 2 below:

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

where:

- $z$ is z-score;
- $\chi$ is participants' result;
- $X$ is the study assigned value;
- $\sigma$ is the target standard deviation.

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

- |z| ≤ 2.0 is satisfactory;
- 2.0 < |z| < 3.0 is questionable;
- |z| ≥ 3.0 is unsatisfactory.

### 4.7 $E_n$-Score

An example of $E_n$-score calculation using data from the present study is given in Appendix 2. The $E_n$-score is complementary to the z-score in assessment of laboratory performance. $E_n$-score includes measurement uncertainty and is calculated according to Equation 3 below:

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

where:

- $E_n$ is $E_n$-score;
- $\chi$ is participants' result;
- $X$ is the assigned value;
- $U_\chi$ is the expanded uncertainty of the participants' result;
- $U_X$ is the expanded uncertainty of the assigned value.

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

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

### 4.8 Traceability and Measurement Uncertainty

Laboratories accredited to AS ISO/IEC Standard 17025:2018[8] must establish and demonstrate the traceability and measurement uncertainty associated with their test results. Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[9]

## 5 TABLES AND FIGURES

Table 4

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Ag |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1**** | 24.1 | 2.61 | 100.44 | 8.64 |
| **2** | 1.6 | 0.5 | 0.44 | 0.19 |
| **3** | 1.57 | 0.16 | 0.31 | 0.32 |
| **4** | 1.45 | 0.19 | -0.22 | -0.21 |
| **5** | NR | NR | | |
| **6** | 1.3 | 0.26 | -0.89 | -0.67 |
| **7** | 1.91 | 0.45 | 1.82 | 0.86 |
| **8** | NT | NT | | |
| **9** | < 5 | 1 | | |
| **10** | 1.5 | 0.30 | 0.00 | 0.00 |
| **11** | 1.63 | 0.25 | 0.58 | 0.45 |
| **12** | <5 | <1.5 | | |
| **13** | NT | NT | | |
| **14** | 1.01 | 0.5 | -2.18 | -0.94 |
| **15** | 1.53 | 0.07 | 0.13 | 0.18 |
| **16** | 1.4 | NR | -0.44 | -0.67 |
| **18** | NT | NT | | |

** Gross Error, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.50 | 0.15 |
| **Spike Value** | 1.53 | 0.09 |
| **Homogeneity Value** | 1.40 | 0.17 |
| **Robust Average** | 1.50 | 0.15 |
| **Median** | 1.52 | 0.12 |
| **Mean** | 1.49 | |
| **N** | 10 | |
| **Max** | 1.91 | |
| **Min** | 1.01 | |
| **Robust SD** | 0.18 | |
| **Robust CV** | 12% | |

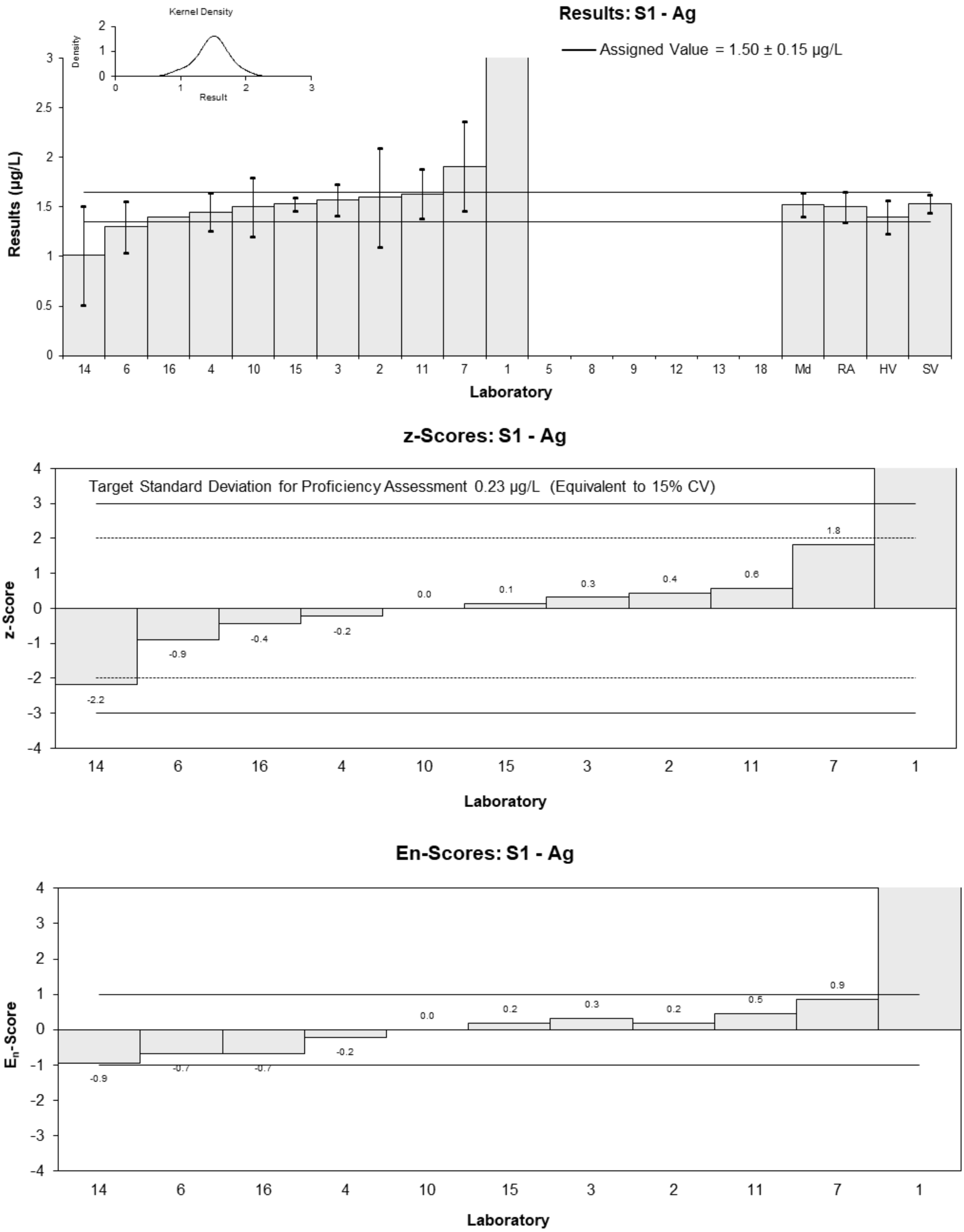

Results: S1 - Ag
Assigned Value = 1.50 ± 0.15 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
14 6 16 4 10 15 3 2 11 7 1 5 8 9 12 13 18 Md RA HV SV
z-Scores: S1 - Ag
Target Standard Deviation for Proficiency Assessment 0.23 µg/L (Equivalent to 15% CV)
z-Score
-2.2 -0.9 -0.4 -0.2 0.0 0.1 0.3 0.4 0.6 1.8
14 6 16 4 10 15 3 2 11 7 1
Laboratory
En-Scores: S1 - Ag
$E_n$-Score
-0.9 -0.7 -0.7 -0.2 0.0 0.2 0.3 0.2 0.5 0.9
14 6 16 4 10 15 3 2 11 7 1
Laboratory

Figure 2

Table 5

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Al |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <50 | NR | | |
| **2** | 26 | 8 | -0.24 | -0.13 |
| **3** | 32 | 3.2 | 0.86 | 0.75 |
| **4** | 23.5 | 4.7 | -0.70 | -0.53 |
| **5** | NR | NR | | |
| **6** | 21 | 4.2 | -1.15 | -0.92 |
| **7** | 28.4 | 6.0 | 0.20 | 0.14 |
| **8** | NT | NT | | |
| **9** | < 50 | 10 | | |
| **10** | 27 | 5.4 | -0.05 | -0.04 |
| **11** | 18.6 | 3.7 | -1.59 | -1.33 |
| **12** | <50 | <15 | | |
| **13** | NT | NT | | |
| **14** | 35 | 17.5 | 1.41 | 0.42 |
| **15** | 40.0 | 3.40 | 2.33 | 1.99 |
| **16** | 24 | NR | -0.60 | -0.61 |
| **18** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 27.3 | 5.4 |
| **Spike Value** | Not Spiked | |
| **Robust Average** | 27.3 | 5.4 |
| **Median** | 26.5 | 5.0 |
| **Mean** | 27.6 | |
| **N** | 10 | |
| **Max** | 40 | |
| **Min** | 18.6 | |
| **Robust SD** | 6.9 | |
| **Robust CV** | 25% | |

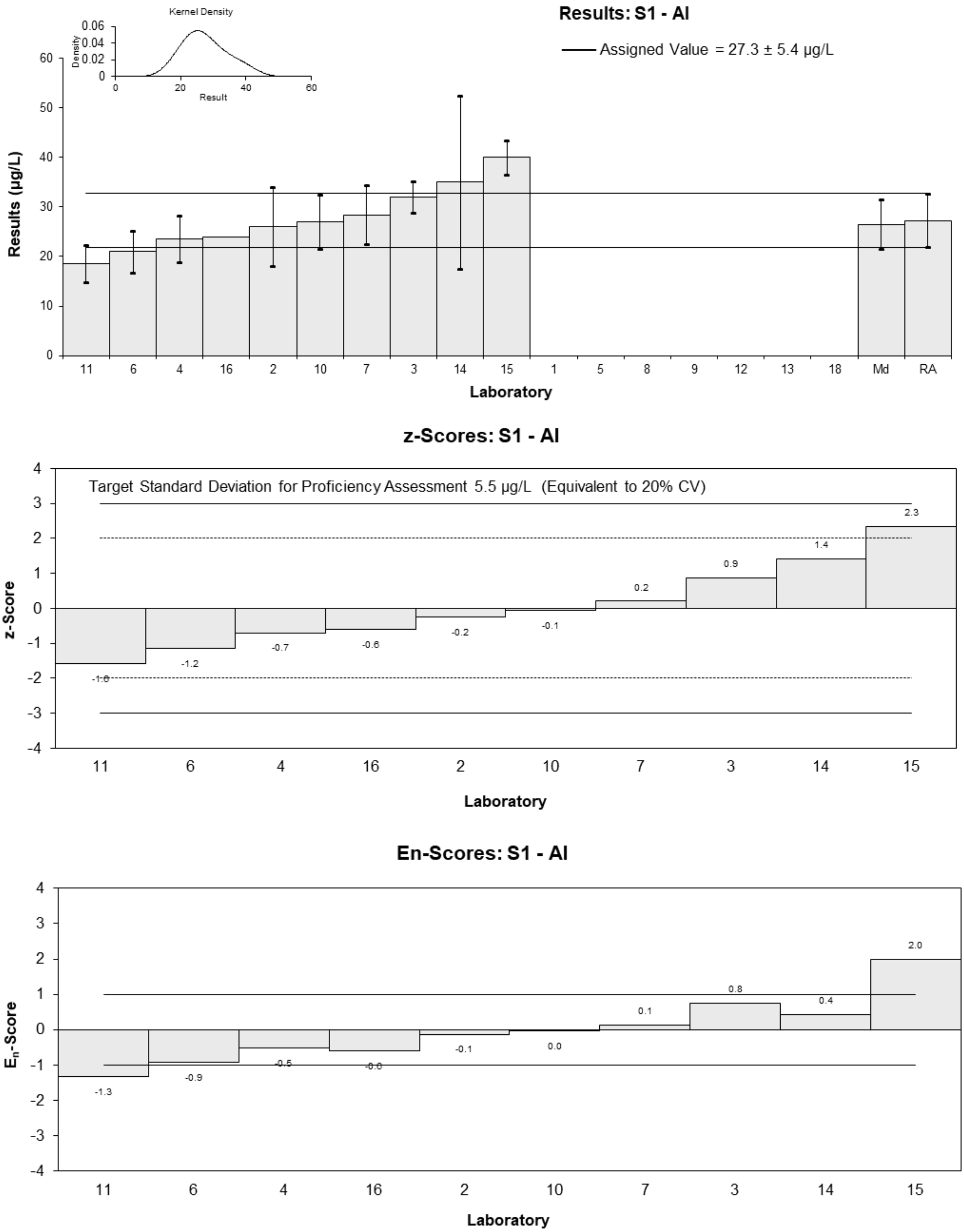

Results: S1 - Al
Assigned Value = 27.3 ± 5.4 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
11 6 4 16 2 10 7 3 14 15 1 5 8 9 12 13 18 Md RA
z-Scores: S1 - Al
Target Standard Deviation for Proficiency Assessment 5.5 µg/L (Equivalent to 20% CV)
z-Score
-1.6 -1.2 -0.7 -0.6 -0.2 -0.1 0.2 0.9 1.4 2.3
Laboratory
11 6 4 16 2 10 7 3 14 15
En-Scores: S1 - Al
$E_n$-Score
-1.3 -0.9 -0.5 -0.6 -0.1 0.0 0.1 0.8 0.4 2.0
Laboratory
11 6 4 16 2 10 7 3 14 15

Figure 3

Table 6

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | As |
| **Unit** | µg/L |

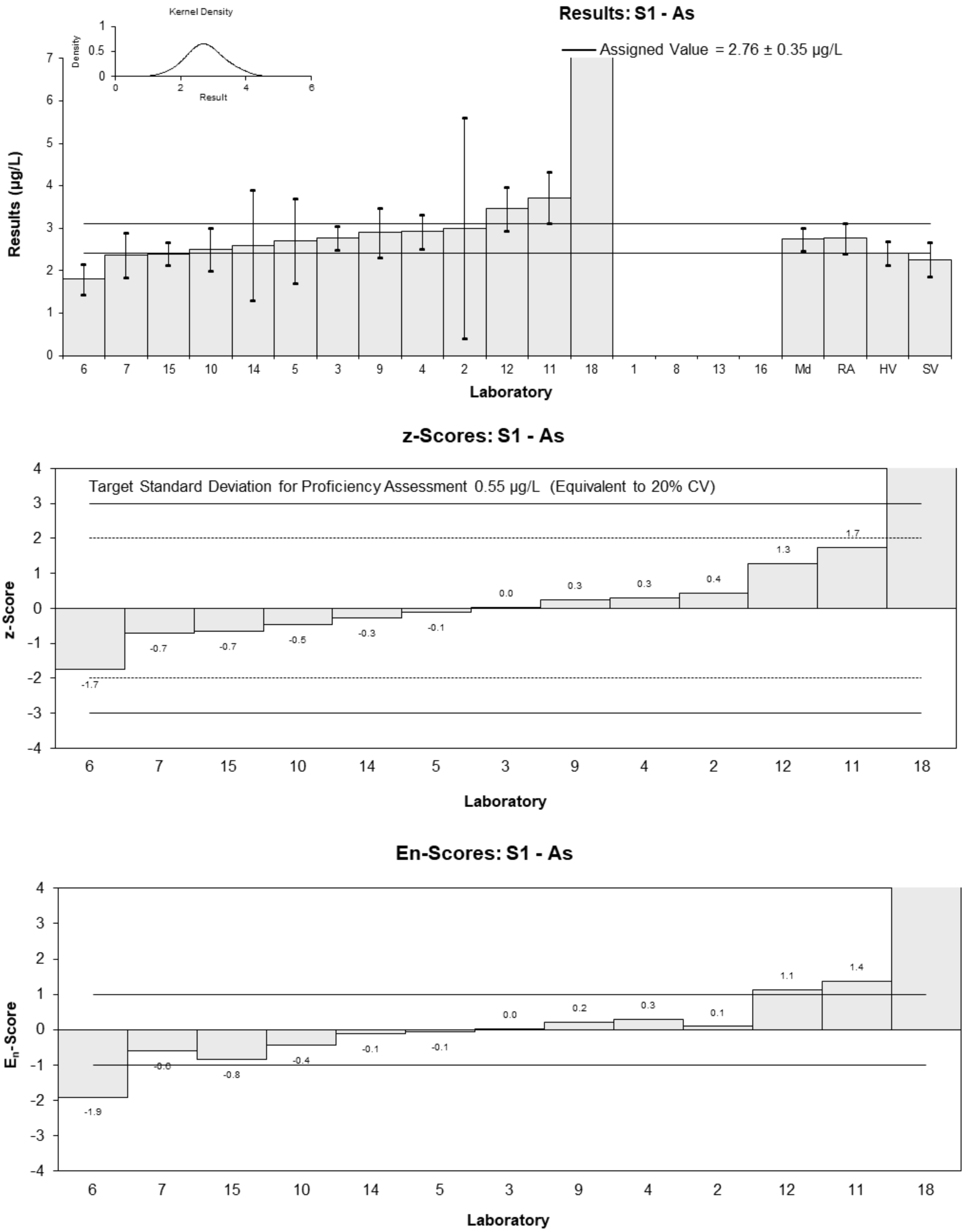
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <5 | NR | | |
| **2** | 3.0 | 2.6 | 0.43 | 0.09 |
| **3** | 2.77 | 0.28 | 0.02 | 0.02 |
| **4** | 2.92 | 0.41 | 0.29 | 0.30 |
| **5** | 2.7 | 1 | -0.11 | -0.06 |
| **6** | 1.8 | 0.36 | -1.74 | -1.91 |
| **7** | 2.37 | 0.53 | -0.71 | -0.61 |
| **8** | NT | NT | | |
| **9** | 2.9 | 0.58 | 0.25 | 0.21 |
| **10** | 2.5 | 0.50 | -0.47 | -0.43 |
| **11** | 3.72 | 0.60 | 1.74 | 1.38 |
| **12** | 3.46 | 0.519 | 1.27 | 1.12 |
| **13** | NT | NT | | |
| **14** | 2.6 | 1.3 | -0.29 | -0.12 |
| **15** | 2.39 | 0.27 | -0.67 | -0.84 |
| **16** | <4 | NR | | |
| **18**** | 24.5 | 2.1 | 39.38 | 10.21 |

** Gross Error, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.76 | 0.35 |
| **Spike Value** | 2.26 | 0.40 |
| **Homogeneity Value** | 2.41 | 0.29 |
| **Robust Average** | 2.76 | 0.35 |
| **Median** | 2.74 | 0.27 |
| **Mean** | 2.76 | |
| **N** | 12 | |
| **Max** | 3.72 | |
| **Min** | 1.8 | |
| **Robust SD** | 0.49 | |
| **Robust CV** | 18% | |



Results: S1 - As
Assigned Value = 2.76 ± 0.35 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6 7 15 10 14 5 3 9 4 2 12 11 18 1 8 13 16 Md RA HV SV
z-Scores: S1 - As
Target Standard Deviation for Proficiency Assessment 0.55 µg/L (Equivalent to 20% CV)
z-Score
-1.7 -0.7 -0.7 -0.5 -0.3 -0.1 0.0 0.3 0.3 0.4 1.3 1.7
6 7 15 10 14 5 3 9 4 2 12 11 18
Laboratory
En-Scores: S1 - As
En-Score
-1.9 -0.6 -0.8 -0.4 -0.1 -0.1 0.0 0.2 0.3 0.1 1.1 1.4
6 7 15 10 14 5 3 9 4 2 12 11 18
Laboratory


Figure 4

Table 7

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Be |
| **Unit** | µg/L |

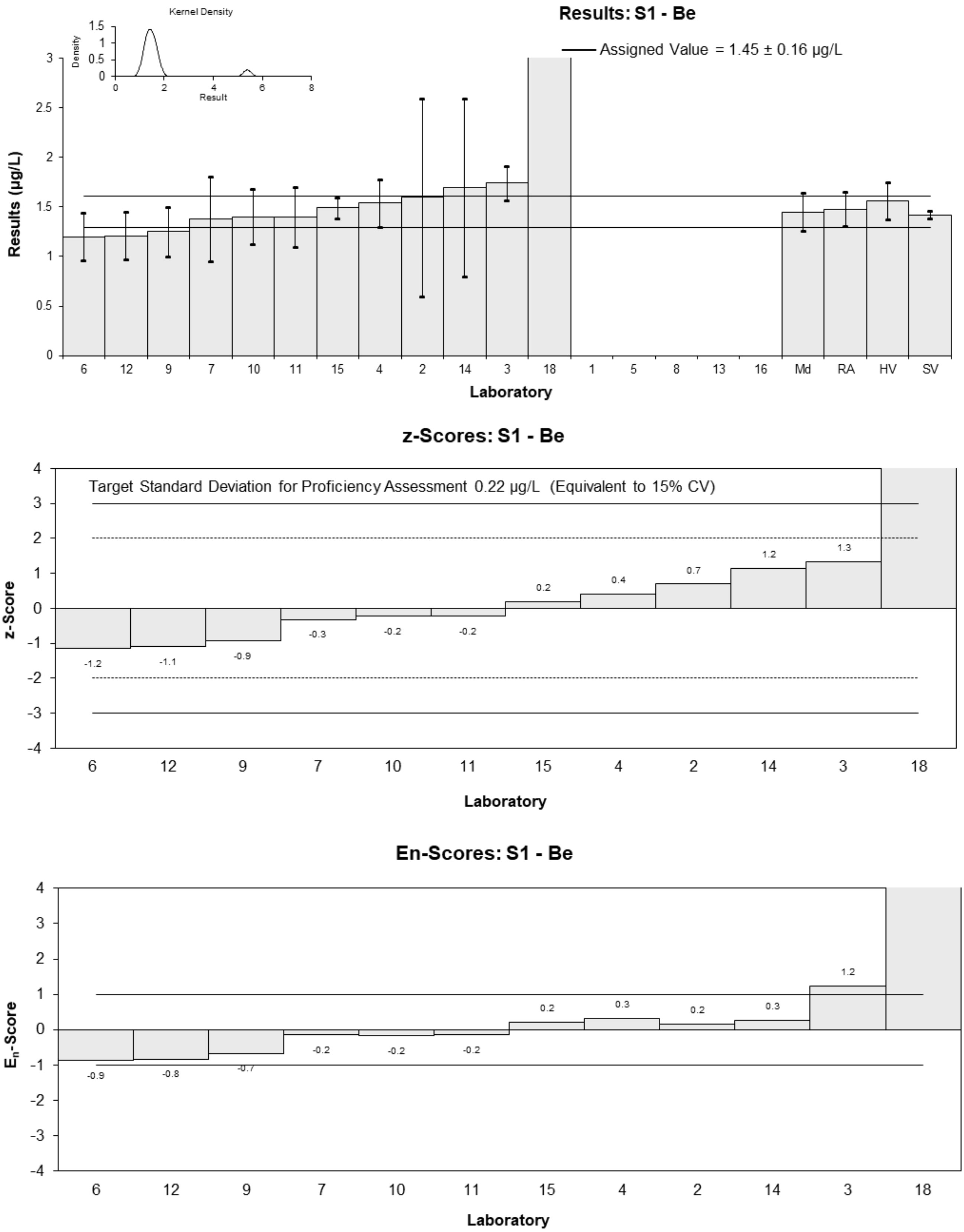
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| 1 | <5 | NR | | |
| 2 | 1.6 | 1.0 | 0.69 | 0.15 |
| 3 | 1.74 | 0.17 | 1.33 | 1.24 |
| 4 | 1.54 | 0.24 | 0.41 | 0.31 |
| 5 | NR | NR | | |
| 6 | 1.2 | 0.24 | -1.15 | -0.87 |
| 7 | 1.38 | 0.43 | -0.32 | -0.15 |
| 8 | NT | NT | | |
| 9 | 1.25 | 0.25 | -0.92 | -0.67 |
| 10 | 1.4 | 0.28 | -0.23 | -0.16 |
| 11 | 1.4 | 0.30 | -0.23 | -0.15 |
| 12 | 1.21 | 0.242 | -1.10 | -0.83 |
| 13 | NT | NT | | |
| 14 | 1.7 | 0.9 | 1.15 | 0.27 |
| 15 | 1.49 | 0.11 | 0.18 | 0.21 |
| 16 | NT | NT | | |
| 18* | 5.39 | 0.16 | 18.11 | 17.41 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.45 | 0.16 |
| **Spike Value** | 1.42 | 0.04 |
| **Homogeneity Value** | 1.56 | 0.19 |
| **Robust Average** | 1.48 | 0.17 |
| **Median** | 1.45 | 0.19 |
| **Mean** | 1.78 | |
| **N** | 12 | |
| **Max** | 5.39 | |
| **Min** | 1.2 | |
| **Robust SD** | 0.24 | |
| **Robust CV** | 16% | |



Results: S1 - Be
Assigned Value = 1.45 ± 0.16 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
12
9
7
10
11
15
4
2
14
3
18
1
5
8
13
16
Md
RA
HV
SV
z-Scores: S1 - Be
Target Standard Deviation for Proficiency Assessment 0.22 µg/L (Equivalent to 15% CV)
z-Score
-1.2
-1.1
-0.9
-0.3
-0.2
-0.2
0.2
0.4
0.7
1.2
1.3
Laboratory
En-Scores: S1 - Be
En-Score
-0.9
-0.8
-0.7
-0.2
-0.2
-0.2
0.2
0.3
0.2
0.3
1.2
Laboratory


Figure 5

Table 8

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Cd |
| **Unit** | µg/L |

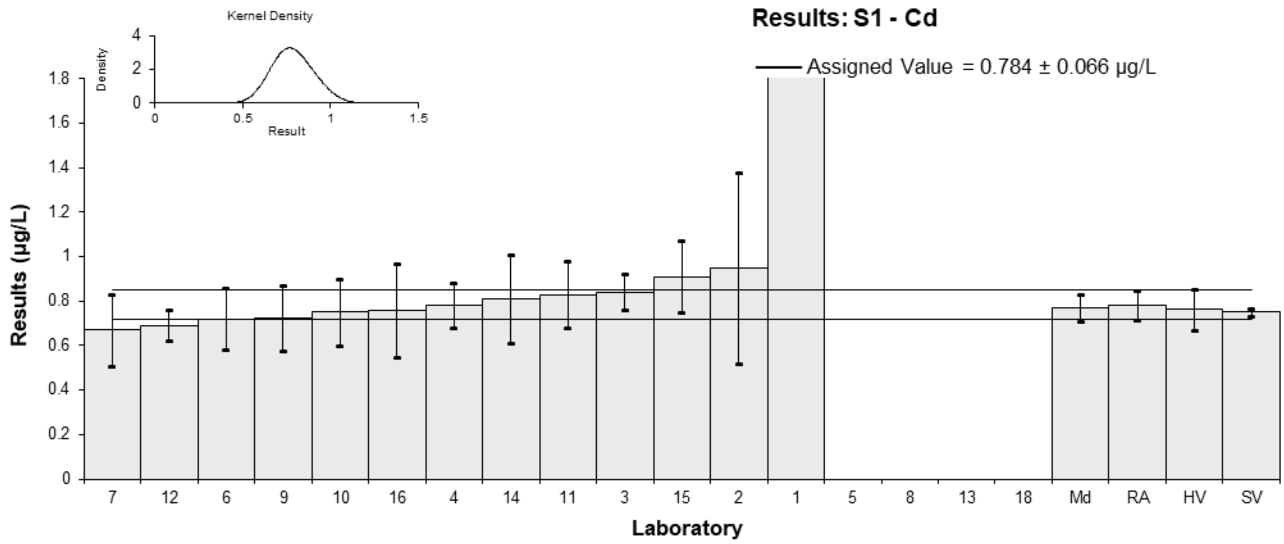
**Participant Results**

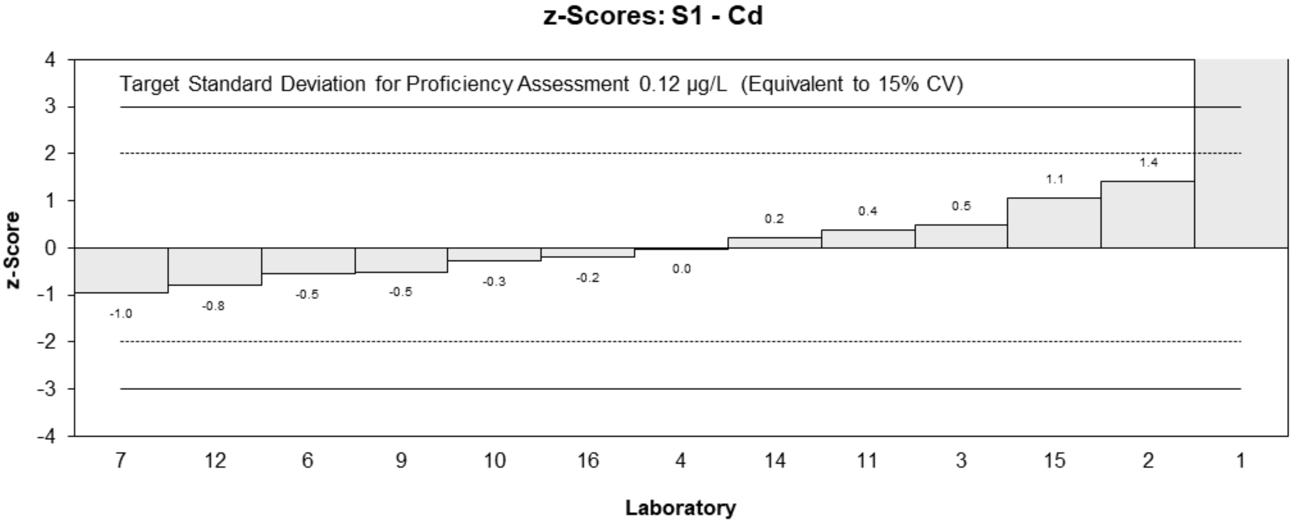
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1**** | 8 | 0.77 | 61.36 | 9.34 |
| **2** | 0.95 | 0.43 | 1.41 | 0.38 |
| **3** | 0.84 | 0.08 | 0.48 | 0.54 |
| **4** | 0.782 | 0.102 | -0.02 | -0.02 |
| **5** | NR | NR | | |
| **6** | 0.72 | 0.14 | -0.54 | -0.41 |
| **7** | 0.67 | 0.16 | -0.97 | -0.66 |
| **8** | NT | NT | | |
| **9** | 0.724 | 0.145 | -0.51 | -0.38 |
| **10** | 0.75 | 0.15 | -0.29 | -0.21 |
| **11** | 0.83 | 0.15 | 0.39 | 0.28 |
| **12** | 0.69 | 0.069 | -0.80 | -0.98 |
| **13** | NT | NT | | |
| **14** | 0.81 | 0.2 | 0.22 | 0.12 |
| **15** | 0.91 | 0.16 | 1.07 | 0.73 |
| **16** | 0.76 | 0.21 | -0.20 | -0.11 |
| **18** | NT | NT | | |

** Gross Error, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.784 | 0.066 |
| **Spike Value** | 0.750 | 0.020 |
| **Homogeneity Value** | 0.762 | 0.091 |
| **Robust Average** | 0.784 | 0.066 |
| **Median** | 0.771 | 0.059 |
| **Mean** | 0.786 | |
| **N** | 12 | |
| **Max** | 0.95 | |
| **Min** | 0.67 | |
| **Robust SD** | 0.092 | |
| **Robust CV** | 12% | |


Results: S1 - Cd
Assigned Value = 0.784 ± 0.066 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
12
6
9
10
16
4
14
11
3
15
2
1
5
8
13
18
Md
RA
HV
SV


z-Scores: S1 - Cd
Target Standard Deviation for Proficiency Assessment 0.12 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.0
-0.8
-0.5
-0.5
-0.3
-0.2
0.0
0.2
0.4
0.5
1.1
1.4
7
12
6
9
10
16
4
14
11
3
15
2
1

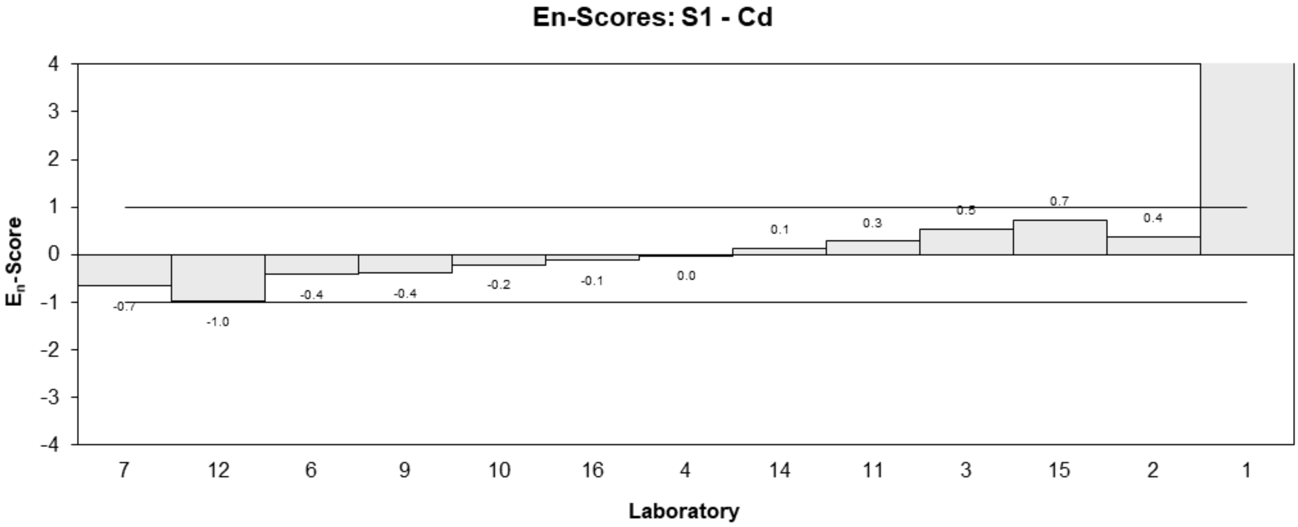

En-Scores: S1 - Cd
En-Score
Laboratory
-0.7
-1.0
-0.4
-0.4
-0.2
-0.1
0.0
0.1
0.3
0.5
0.7
0.4
7
12
6
9
10
16
4
14
11
3
15
2
1

Figure 6

Table 9

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Cr |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <5 | NR | | |
| **2** | 2.0 | 1.0 | 0.39 | 0.11 |
| **3** | 1.89 | 0.19 | 0.00 | 0.00 |
| **4** | 1.88 | 0.29 | -0.04 | -0.03 |
| **5** | NR | NR | | |
| **6** | 1.8 | 0.36 | -0.32 | -0.24 |
| **7** | 1.93 | 0.50 | 0.14 | 0.08 |
| **8** | NT | NT | | |
| **9** | 1.75 | 0.35 | -0.49 | -0.39 |
| **10** | 1.9 | 0.38 | 0.04 | 0.03 |
| **11** | 1.95 | 0.30 | 0.21 | 0.19 |
| **12** | 1.3 | 0.195 | -2.08 | -2.75 |
| **13** | NT | NT | | |
| **14** | 1.8 | 0.9 | -0.32 | -0.10 |
| **15** | 1.98 | 0.14 | 0.32 | 0.54 |
| **16** | 2.17 | 0.76 | 0.99 | 0.37 |
| **18*** | 5.5 | 2.0 | 12.73 | 1.80 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.89 | 0.09 |
| **Spike Value** | 1.99 | 0.07 |
| **Homogeneity Value** | 1.92 | 0.23 |
| **Robust Average** | 1.91 | 0.11 |
| **Median** | 1.90 | 0.10 |
| **Mean** | 2.14 | |
| **N** | 13 | |
| **Max** | 5.5 | |
| **Min** | 1.3 | |
| **Robust SD** | 0.16 | |
| **Robust CV** | 8.4% | |

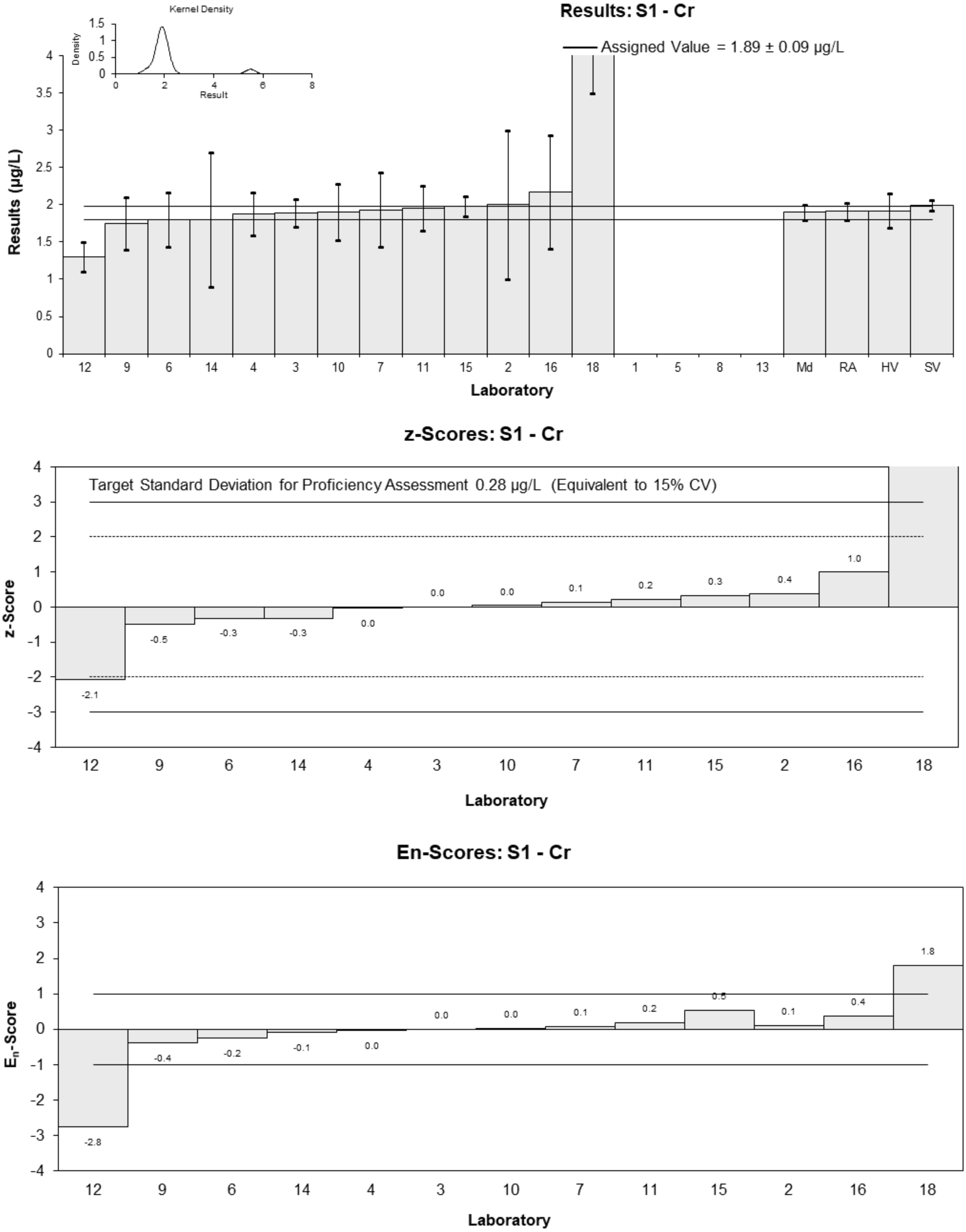

Kernel Density
Density
Result
Results: S1 - Cr
Assigned Value = 1.89 ± 0.09 µg/L
Results (µg/L)
Laboratory
12 9 6 14 4 3 10 7 11 15 2 16 18 1 5 8 13 Md RA HV SV
z-Scores: S1 - Cr
Target Standard Deviation for Proficiency Assessment 0.28 µg/L (Equivalent to 15% CV)
z-Score
-2.1 -0.5 -0.3 -0.3 0.0 0.0 0.0 0.1 0.2 0.3 0.4 1.0
Laboratory
12 9 6 14 4 3 10 7 11 15 2 16 18
En-Scores: S1 - Cr
En-Score
-2.8 -0.4 -0.2 -0.1 0.0 0.0 0.0 0.1 0.2 0.5 0.1 0.4 1.8
Laboratory
12 9 6 14 4 3 10 7 11 15 2 16 18

Figure 7

Table 10

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Cu |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 10.72 | 0.85 | -0.29 | -0.41 |
| **2** | 12 | 3 | 0.48 | 0.26 |
| **3** | 12.7 | 1.30 | 0.89 | 0.98 |
| **4** | 12.4 | 2.2 | 0.71 | 0.51 |
| **5** | NR | NR | | |
| **6** | 11 | 2.2 | -0.12 | -0.09 |
| **7** | 10.7 | 2.5 | -0.30 | -0.19 |
| **8** | NT | NT | | |
| **9** | 9.44 | 1.89 | -1.05 | -0.86 |
| **10** | 11 | 2.2 | -0.12 | -0.09 |
| **11** | 11.1 | 1.7 | -0.06 | -0.05 |
| **12** | 8.65 | 1.73 | -1.52 | -1.34 |
| **13** | NT | NT | | |
| **14** | 11 | 2.7 | -0.12 | -0.07 |
| **15** | 12.2 | 1.02 | 0.60 | 0.77 |
| **16** | 11.6 | 2.9 | 0.24 | 0.13 |
| **18**** | 140 | 19 | 76.67 | 6.77 |

** Gross Error, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 11.2 | 0.8 |
| **Spike Value** | 11.0 | 0.8 |
| **Homogeneity Value** | 12.6 | 1.5 |
| **Robust Average** | 11.2 | 0.8 |
| **Median** | 11.0 | 0.6 |
| **Mean** | 11.1 | |
| **N** | 13 | |
| **Max** | 12.7 | |
| **Min** | 8.65 | |
| **Robust SD** | 1.1 | |
| **Robust CV** | 10% | |

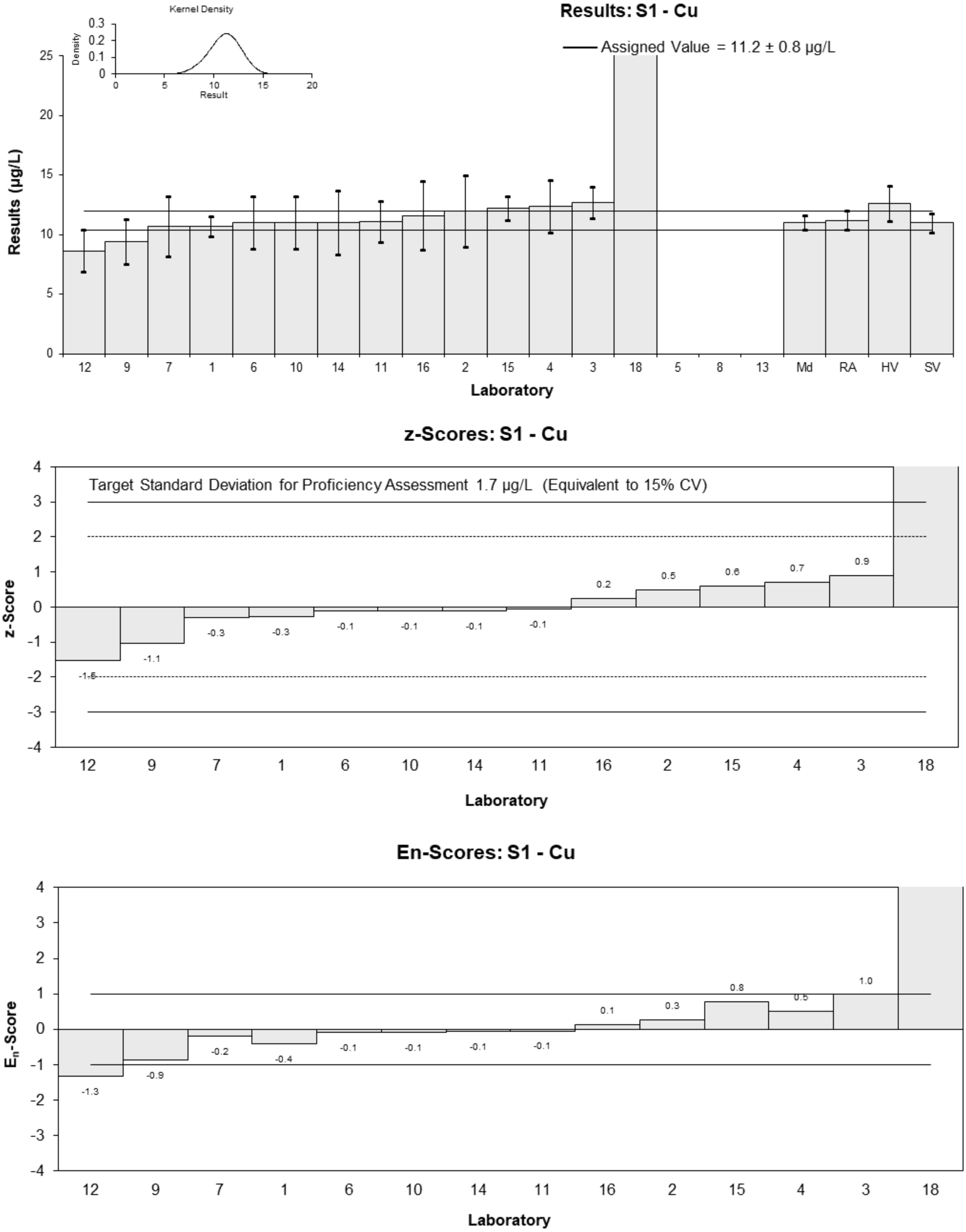

Results: S1 - Cu
Assigned Value = 11.2 ± 0.8 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12 9 7 1 6 10 14 11 16 2 15 4 3 18 5 8 13 Md RA HV SV
z-Scores: S1 - Cu
Target Standard Deviation for Proficiency Assessment 1.7 µg/L (Equivalent to 15% CV)
z-Score
-1.5 -1.1 -0.3 -0.3 -0.1 -0.1 -0.1 -0.1 0.2 0.5 0.6 0.7 0.9
12 9 7 1 6 10 14 11 16 2 15 4 3 18
Laboratory
En-Scores: S1 - Cu
En-Score
-1.3 -0.9 -0.2 -0.4 -0.1 -0.1 -0.1 -0.1 0.1 0.3 0.8 0.5 1.0
12 9 7 1 6 10 14 11 16 2 15 4 3 18
Laboratory

Figure 8

Table 11

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Fe |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <50 | NR | | |
| **2** | 41 | 9 | -0.19 | -0.12 |
| **3** | 51 | 5.1 | 1.39 | 1.38 |
| **4** | 38.0 | 6.1 | -0.66 | -0.58 |
| **5** | NR | NR | | |
| **6** | 35 | 7.0 | -1.14 | -0.90 |
| **7** | 40.9 | 14.5 | -0.21 | -0.09 |
| **8** | NT | NT | | |
| **9** | < 50 | 10 | | |
| **10** | 44 | 8.8 | 0.28 | 0.19 |
| **11** | 47.5 | 7.1 | 0.84 | 0.66 |
| **12** | <50 | <15 | | |
| **13** | NT | NT | | |
| **14** | 42 | 11 | -0.03 | -0.02 |
| **15** | 40.3 | 1.97 | -0.30 | -0.44 |
| **16** | 43.7 | 5.9 | 0.24 | 0.21 |
| **18** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 42.2 | 3.8 |
| **Spike Value** | 39.5 | 1.2 |
| **Homogeneity Value** | 43.2 | 5.2 |
| **Robust Average** | 42.2 | 3.8 |
| **Median** | 41.5 | 2.8 |
| **Mean** | 42.3 | |
| **N** | 10 | |
| **Max** | 51 | |
| **Min** | 35 | |
| **Robust SD** | 4.8 | |
| **Robust CV** | 11% | |

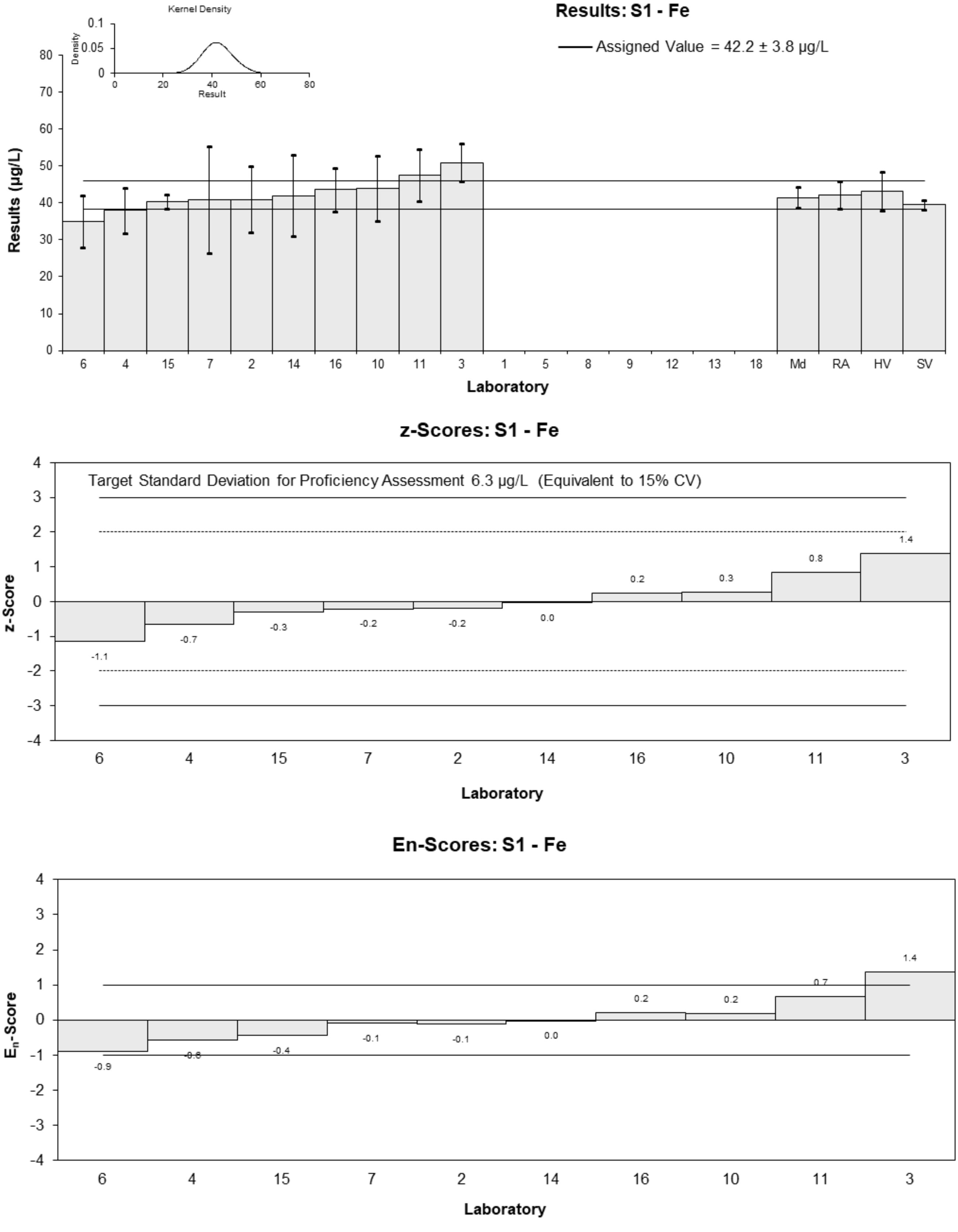

Results: S1 - Fe
Assigned Value = 42.2 ± 3.8 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
z-Scores: S1 - Fe
Target Standard Deviation for Proficiency Assessment 6.3 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - Fe
$E_n$-Score
Laboratory

Figure 9

Table 12

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Hg |
| **Unit** | μg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.33 | 0.057 | 0.30 | 0.21 |
| **2** | 0.36 | 0.05 | 0.93 | 0.73 |
| **3*** | 1.25 | 0.13 | 19.70 | 6.96 |
| **4** | 0.336 | 0.078 | 0.42 | 0.24 |
| **5** | 0.3 | 0.05 | -0.34 | -0.27 |
| **6** | <0.5 | NR | | |
| **7** | 0.34 | 0.07 | 0.51 | 0.31 |
| **8** | NT | NT | | |
| **9** | 0.31 | 0.062 | -0.13 | -0.09 |
| **10** | 0.30 | 0.06 | -0.34 | -0.23 |
| **11** | 0.4 | 0.10 | 1.77 | 0.80 |
| **12** | 0.259 | 0.0518 | -1.20 | -0.93 |
| **13** | NT | NT | | |
| **14** | 0.26 | 0.07 | -1.18 | -0.72 |
| **15** | NR | NR | | |
| **16** | 0.299 | 0.064 | -0.36 | -0.24 |
| **18** | NT | NT | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.316 | 0.033 |
| **Spike Value** | 0.360 | 0.010 |
| **Homogeneity Value** | 0.363 | 0.044 |
| **Robust Average** | 0.325 | 0.038 |
| **Median** | 0.320 | 0.022 |
| **Mean** | 0.395 | |
| **N** | 12 | |
| **Max** | 1.25 | |
| **Min** | 0.259 | |
| **Robust SD** | 0.053 | |
| **Robust CV** | 16% | |

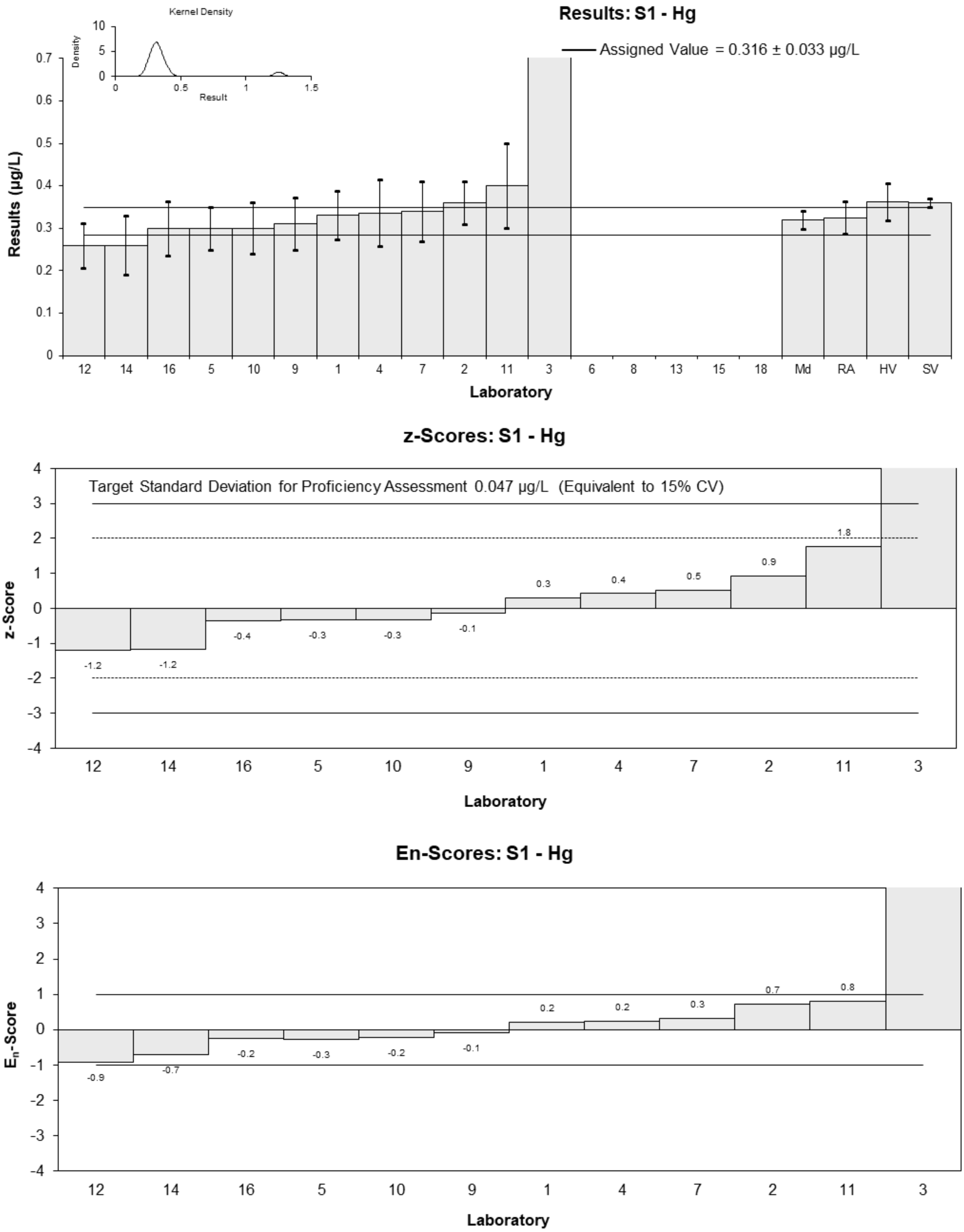

Results: S1 - Hg
Assigned Value = 0.316 ± 0.033 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12
14
16
5
10
9
1
4
7
2
11
3
6
8
13
15
18
Md
RA
HV
SV
z-Scores: S1 - Hg
Target Standard Deviation for Proficiency Assessment 0.047 µg/L (Equivalent to 15% CV)
z-Score
-1.2
-1.2
-0.4
-0.3
-0.3
-0.1
0.3
0.4
0.5
0.9
1.8
En-Scores: S1 - Hg
En-Score
-0.9
-0.7
-0.2
-0.3
-0.2
-0.1
0.2
0.2
0.3
0.7
0.8

Figure 10

Table 13

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Mn |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 5.28 | 0.46 | -0.27 | -0.35 |
| **2** | 5.4 | 4.0 | -0.12 | -0.02 |
| **3** | 6.64 | 0.66 | 1.38 | 1.46 |
| **4** | 5.42 | 0.82 | -0.10 | -0.09 |
| **5** | NR | NR | | |
| **6** | 4.8 | 0.96 | -0.85 | -0.67 |
| **7** | 5.64 | 1.55 | 0.17 | 0.09 |
| **8** | NT | NT | | |
| **9** | 5.02 | 1.00 | -0.58 | -0.44 |
| **10** | 5.5 | 1.1 | 0.00 | 0.00 |
| **11** | 6.55 | 1.0 | 1.27 | 0.97 |
| **12** | <5 | <1.5 | | |
| **13** | NT | NT | | |
| **14** | 5.3 | 1.3 | -0.24 | -0.15 |
| **15** | 5.79 | 0.34 | 0.35 | 0.54 |
| **16** | 4.70 | 0.70 | -0.97 | -0.98 |
| **18** | 5.9 | 1.3 | 0.48 | 0.29 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 5.50 | 0.42 |
| **Spike Value** | 6.17 | 0.24 |
| **Homogeneity Value** | 6.24 | 0.75 |
| **Robust Average** | 5.50 | 0.42 |
| **Median** | 5.42 | 0.38 |
| **Mean** | 5.53 | |
| **N** | 13 | |
| **Max** | 6.64 | |
| **Min** | 4.7 | |
| **Robust SD** | 0.60 | |
| **Robust CV** | 11% | |

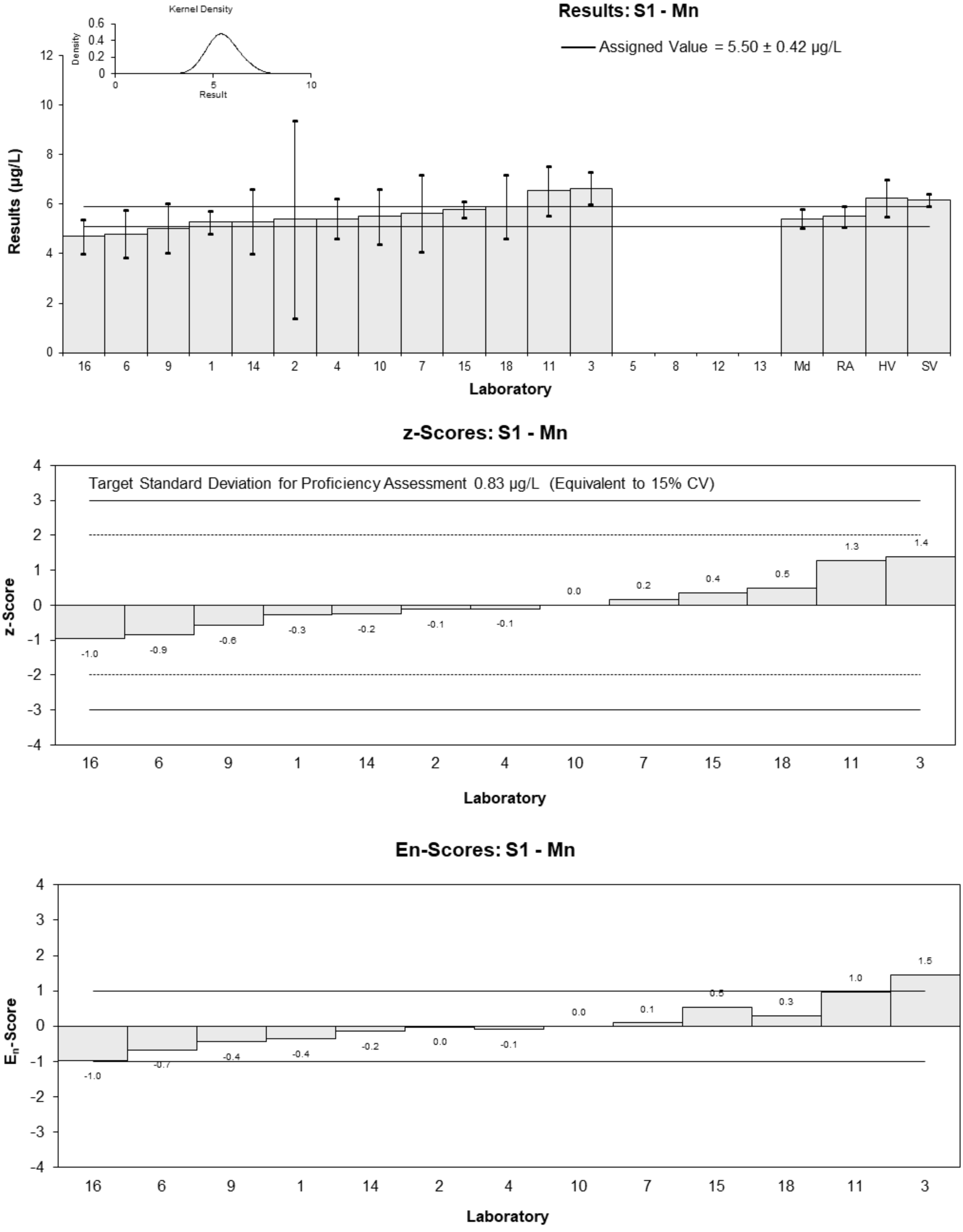

Results: S1 - Mn
Assigned Value = 5.50 ± 0.42 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
16 6 9 1 14 2 4 10 7 15 18 11 3 5 8 12 13 Md RA HV SV
z-Scores: S1 - Mn
Target Standard Deviation for Proficiency Assessment 0.83 µg/L (Equivalent to 15% CV)
z-Score
-1.0 -0.9 -0.6 -0.3 -0.2 -0.1 -0.1 0.0 0.2 0.4 0.5 1.3 1.4
16 6 9 1 14 2 4 10 7 15 18 11 3
Laboratory
En-Scores: S1 - Mn
En-Score
-1.0 -0.7 -0.4 -0.4 -0.2 0.0 -0.1 0.0 0.1 0.5 0.3 1.0 1.5
16 6 9 1 14 2 4 10 7 15 18 11 3
Laboratory

Figure 11

Table 14

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Ni |
| **Unit** | µg/L |

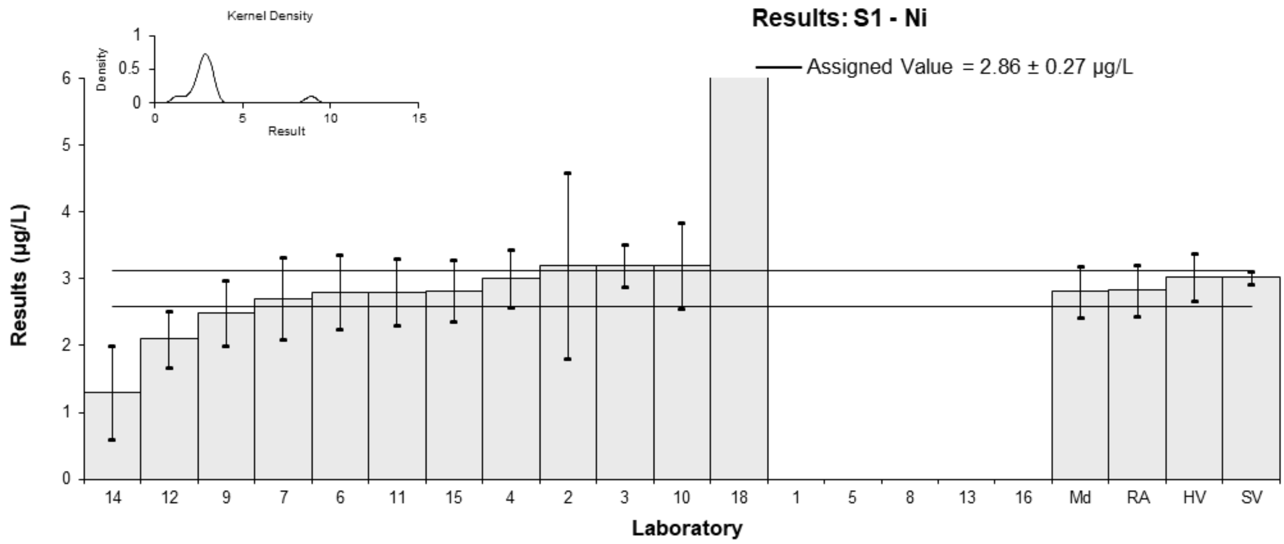
**Participant Results**

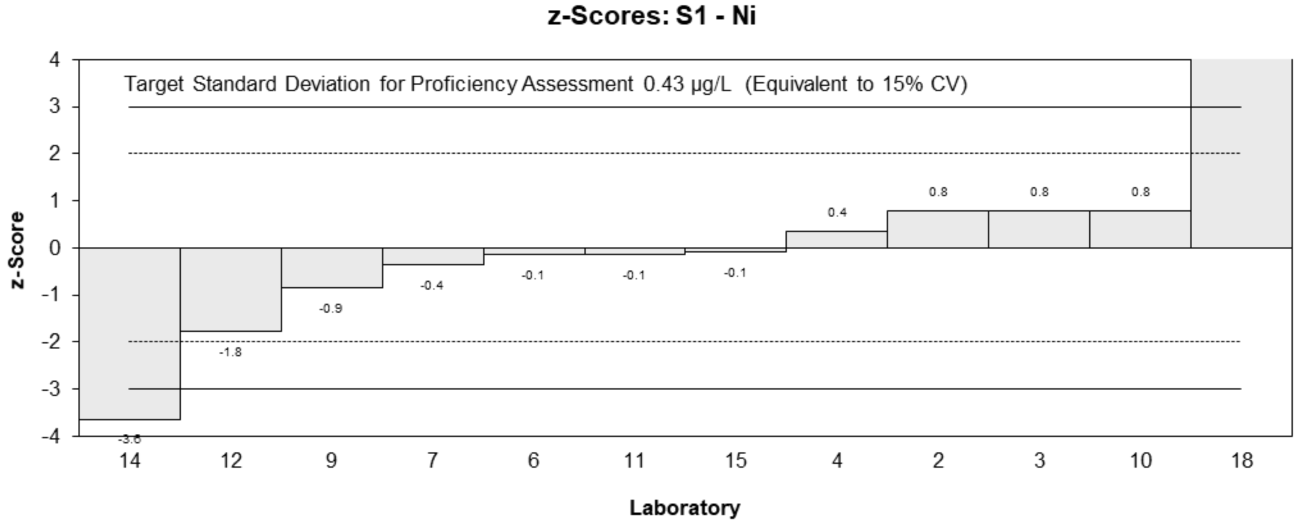
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <5 | NR | | |
| **2** | 3.2 | 1.4 | 0.79 | 0.24 |
| **3** | 3.2 | 0.32 | 0.79 | 0.81 |
| **4** | 3.01 | 0.43 | 0.35 | 0.30 |
| **5** | NR | NR | | |
| **6** | 2.8 | 0.56 | -0.14 | -0.10 |
| **7** | 2.71 | 0.61 | -0.35 | -0.22 |
| **8** | NT | NT | | |
| **9** | 2.49 | 0.498 | -0.86 | -0.65 |
| **10** | 3.2 | 0.64 | 0.79 | 0.49 |
| **11** | 2.8 | 0.50 | -0.14 | -0.11 |
| **12** | 2.1 | 0.42 | -1.77 | -1.52 |
| **13** | NT | NT | | |
| **14*** | 1.3 | 0.7 | -3.64 | -2.08 |
| **15** | 2.82 | 0.46 | -0.09 | -0.07 |
| **16** | <7 | NR | | |
| **18*** | 8.9 | 1.6 | 14.08 | 3.72 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.86 | 0.27 |
| **Spike Value** | 3.02 | 0.10 |
| **Homogeneity Value** | 3.03 | 0.36 |
| **Robust Average** | 2.83 | 0.38 |
| **Median** | 2.81 | 0.38 |
| **Mean** | 3.21 | |
| **N** | 12 | |
| **Max** | 8.9 | |
| **Min** | 1.3 | |
| **Robust SD** | 0.52 | |
| **Robust CV** | 18% | |


Results: S1 - Ni
Assigned Value = 2.86 ± 0.27 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
14 12 9 7 6 11 15 4 2 3 10 18 1 5 8 13 16 Md RA HV SV


z-Scores: S1 - Ni
Target Standard Deviation for Proficiency Assessment 0.43 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-3.6 -1.8 -0.9 -0.4 -0.1 -0.1 -0.1 0.4 0.8 0.8 0.8
14 12 9 7 6 11 15 4 2 3 10 18

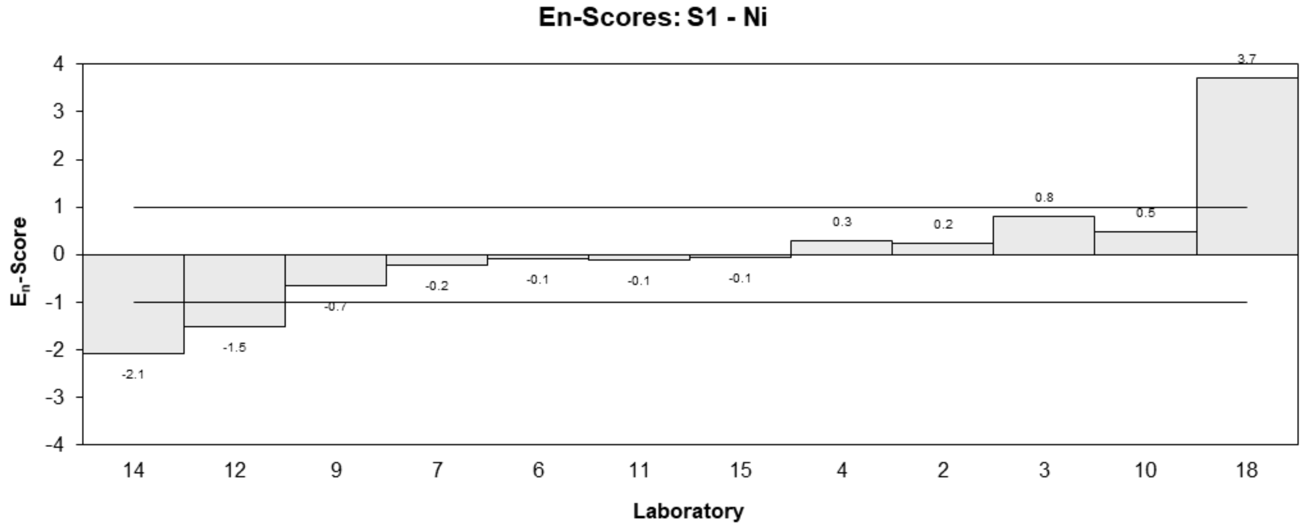

En-Scores: S1 - Ni
En-Score
Laboratory
-2.1 -1.5 -0.7 -0.2 -0.1 -0.1 -0.1 0.3 0.2 0.8 0.5 3.7
14 12 9 7 6 11 15 4 2 3 10 18

Figure 12

Table 15

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | P |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <1000 | NR | | |
| **2** | 100 | 50 | -0.90 | -0.37 |
| **3** | 119 | 12 | -0.12 | -0.09 |
| **4*** | 216 | 31 | 3.85 | 2.11 |
| **5** | NT | NT | | |
| **6** | NT | NT | | |
| **7** | 120 | 38 | -0.08 | -0.04 |
| **8** | NT | NT | | |
| **9** | 158 | 31.6 | 1.48 | 0.80 |
| **10** | 120 | 24 | -0.08 | -0.05 |
| **11** | NT | NT | | |
| **12** | NT | NT | | |
| **13** | NT | NT | | |
| **14** | 160 | 80 | 1.56 | 0.44 |
| **15** | 77.6 | 6.3 | -1.82 | -1.36 |
| **16** | NT | NT | | |
| **18** | NT | NT | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 122 | 32 |
| **Spike Value** | 95.0 | 3.6 |
| **Homogeneity Value** | 100 | 12 |
| **Robust Average** | 131 | 38 |
| **Median** | 120 | 38 |
| **Mean** | 134 | |
| **N** | 8 | |
| **Max** | 216 | |
| **Min** | 77.6 | |
| **Robust SD** | 43 | |
| **Robust CV** | 32% | |

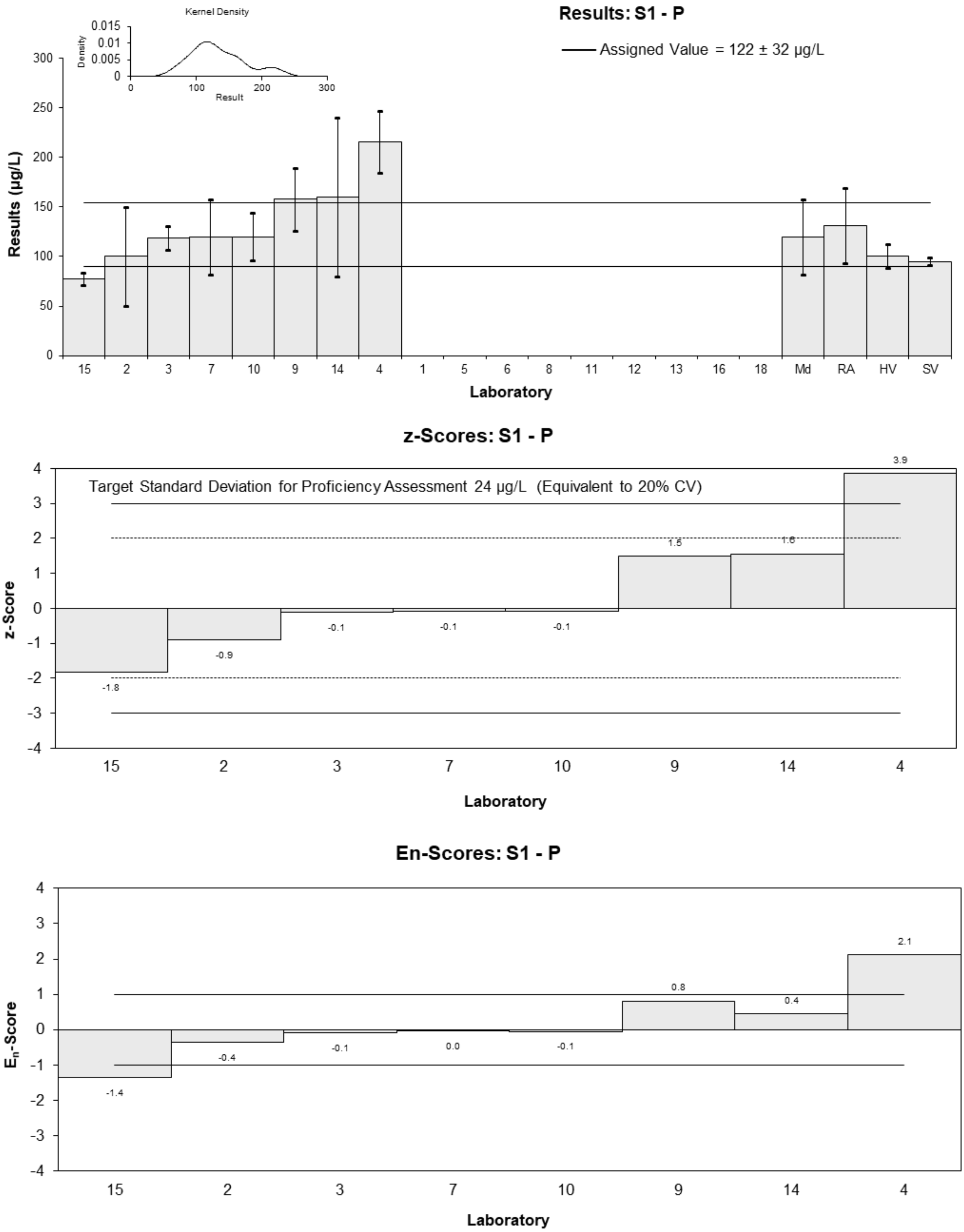

Kernel Density
Density
Result
Results: S1 - P
Assigned Value = 122 ± 32 µg/L
Results (µg/L)
15 2 3 7 10 9 14 4 1 5 6 8 11 12 13 16 18 Md RA HV SV
Laboratory
z-Scores: S1 - P
Target Standard Deviation for Proficiency Assessment 24 µg/L (Equivalent to 20% CV)
z-Score
-1.8 -0.9 -0.1 -0.1 -0.1 1.5 1.6 3.9
15 2 3 7 10 9 14 4
Laboratory
En-Scores: S1 - P
$E_n$-Score
-1.4 -0.4 -0.1 0.0 -0.1 0.8 0.4 2.1
15 2 3 7 10 9 14 4
Laboratory

Figure 13

Table 16

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Pb |
| **Unit** | µg/L |

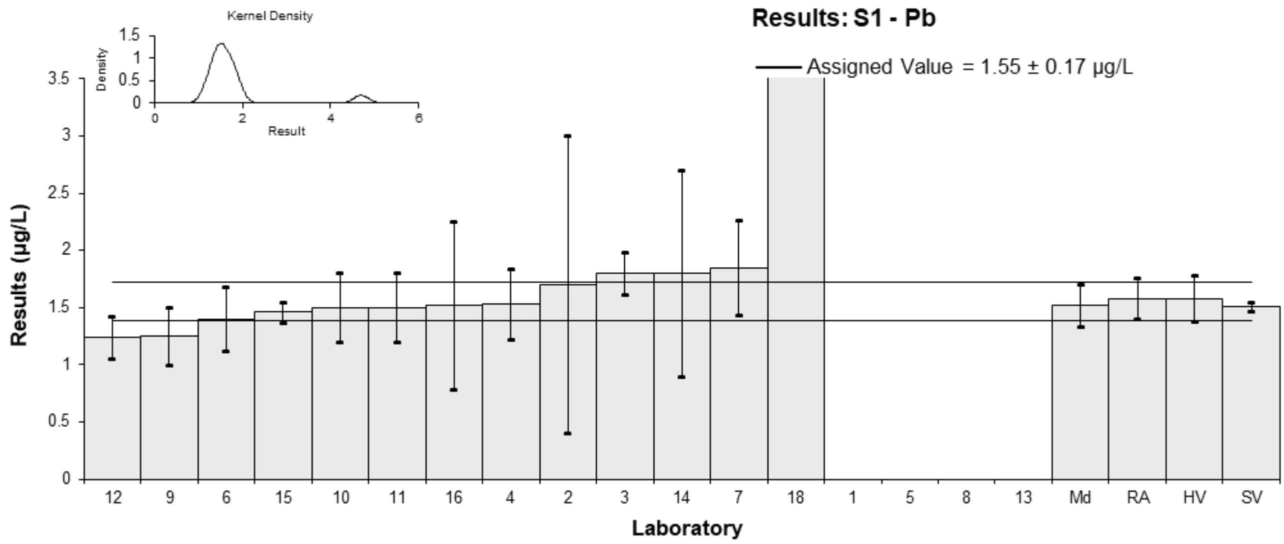
**Participant Results**

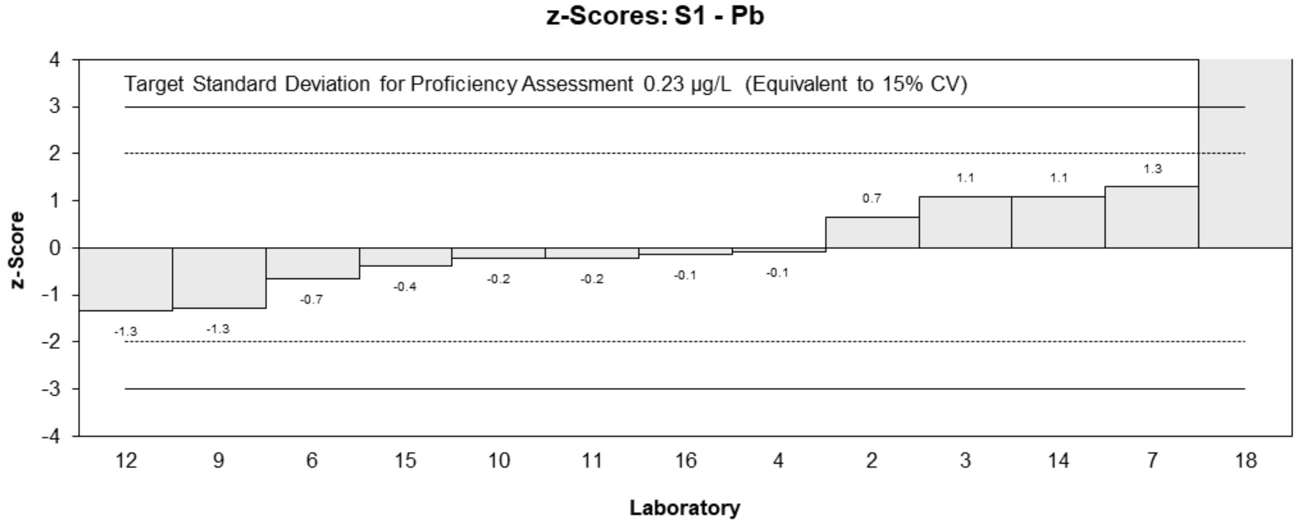
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <5 | NR | | |
| **2** | 1.7 | 1.3 | 0.65 | 0.11 |
| **3** | 1.80 | 0.18 | 1.08 | 1.01 |
| **4** | 1.53 | 0.31 | -0.09 | -0.06 |
| **5** | NR | NR | | |
| **6** | 1.4 | 0.28 | -0.65 | -0.46 |
| **7** | 1.85 | 0.41 | 1.29 | 0.68 |
| **8** | NT | NT | | |
| **9** | 1.25 | 0.25 | -1.29 | -0.99 |
| **10** | 1.5 | 0.30 | -0.22 | -0.15 |
| **11** | 1.5 | 0.30 | -0.22 | -0.15 |
| **12** | 1.24 | 0.186 | -1.33 | -1.23 |
| **13** | NT | NT | | |
| **14** | 1.8 | 0.9 | 1.08 | 0.27 |
| **15** | 1.46 | 0.09 | -0.39 | -0.47 |
| **16** | 1.52 | 0.73 | -0.13 | -0.04 |
| **18*** | 4.7 | 0.6 | 13.55 | 5.05 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.55 | 0.17 |
| **Spike Value** | 1.51 | 0.04 |
| **Homogeneity Value** | 1.58 | 0.20 |
| **Robust Average** | 1.58 | 0.18 |
| **Median** | 1.52 | 0.19 |
| **Mean** | 1.79 | |
| **N** | 13 | |
| **Max** | 4.7 | |
| **Min** | 1.24 | |
| **Robust SD** | 0.26 | |
| **Robust CV** | 16% | |


Results: S1 - Pb
Assigned Value = 1.55 ± 0.17 µg/L
Kernel Density
Density
Result
Results (µg/L)
12
9
6
15
10
11
16
4
2
3
14
7
18
1
5
8
13
Md
RA
HV
SV
Laboratory


z-Scores: S1 - Pb
Target Standard Deviation for Proficiency Assessment 0.23 µg/L (Equivalent to 15% CV)
z-Score
-1.3
-1.3
-0.7
-0.4
-0.2
-0.2
-0.1
-0.1
0.7
1.1
1.1
1.3
12
9
6
15
10
11
16
4
2
3
14
7
18
Laboratory

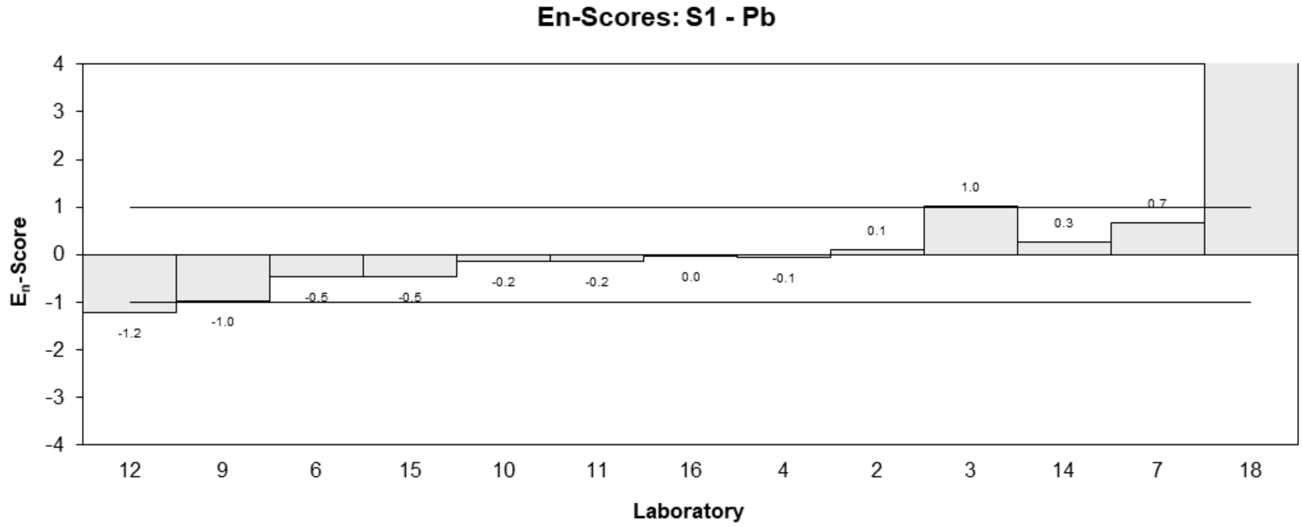

En-Scores: S1 - Pb
En-Score
-1.2
-1.0
-0.5
-0.5
-0.2
-0.2
0.0
-0.1
0.1
1.0
0.3
0.7
12
9
6
15
10
11
16
4
2
3
14
7
18
Laboratory

Figure 14

Table 17

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Sb |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1*** | 8.85 | 1.02 | 3.65 | 2.91 |
| **2** | 6.2 | 0.9 | 0.56 | 0.50 |
| **3** | 5.70 | 0.57 | -0.02 | -0.03 |
| **4** | 5.54 | 1.17 | -0.21 | -0.15 |
| **5** | NR | NR | | |
| **6** | NT | NT | | |
| **7** | 5.54 | 1.22 | -0.21 | -0.14 |
| **8** | NT | NT | | |
| **9** | < 5 | 1 | | |
| **10** | 5.3 | 1.1 | -0.49 | -0.36 |
| **11** | 6.51 | 1.0 | 0.92 | 0.75 |
| **12** | 5.74 | 0.861 | 0.02 | 0.02 |
| **13** | NT | NT | | |
| **14** | 5.4 | 1.4 | -0.37 | -0.22 |
| **15** | 5.26 | 0.19 | -0.54 | -1.18 |
| **16** | 6.3 | NR | 0.68 | 1.71 |
| **18** | 5.53 | 0.31 | -0.22 | -0.41 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 5.72 | 0.34 |
| **Spike Value** | 5.32 | 0.27 |
| **Homogeneity Value** | 6.17 | 0.74 |
| **Robust Average** | 5.80 | 0.39 |
| **Median** | 5.62 | 0.29 |
| **Mean** | 5.99 | |
| **N** | 12 | |
| **Max** | 8.85 | |
| **Min** | 5.26 | |
| **Robust SD** | 0.54 | |
| **Robust CV** | 9.3% | |

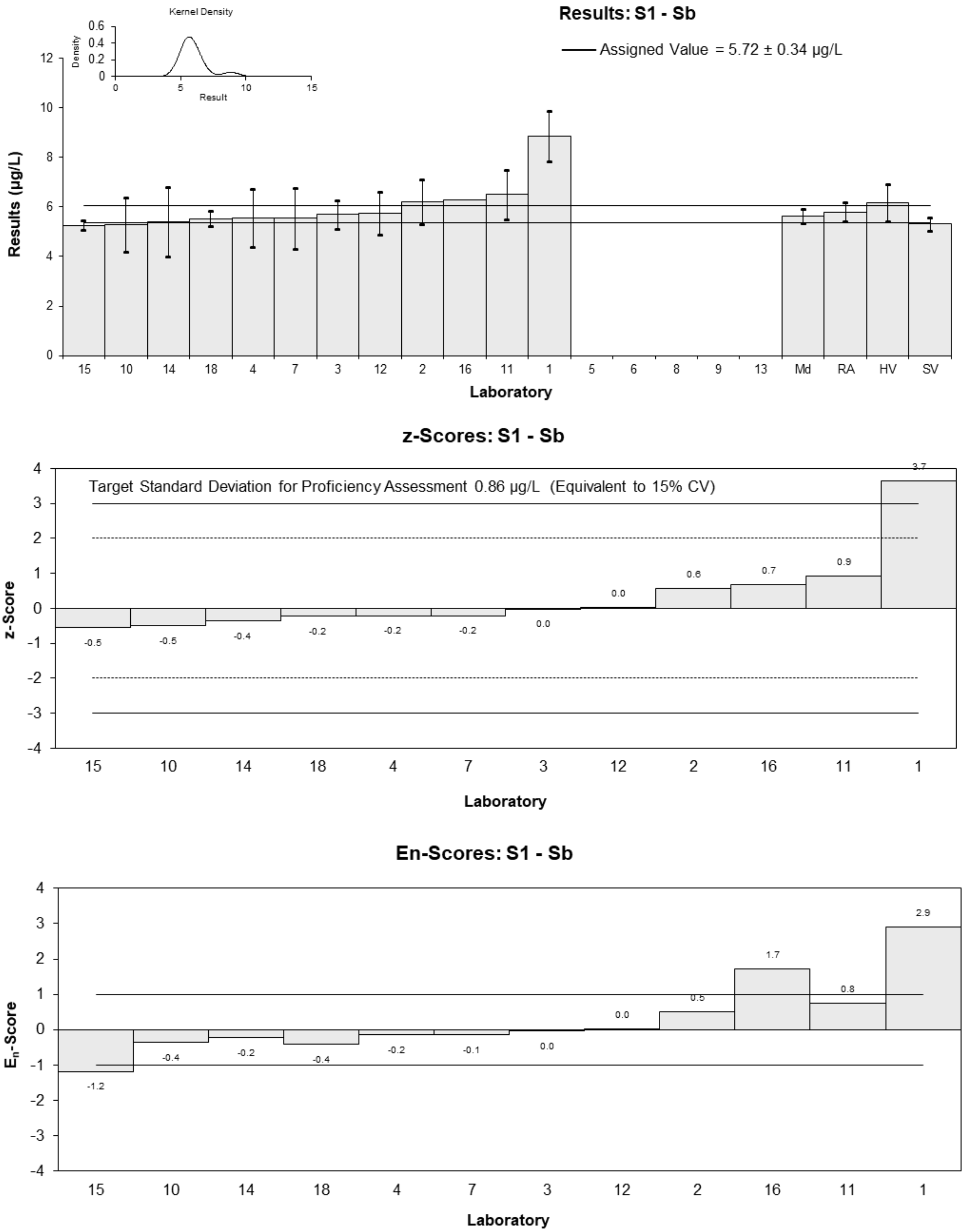

Results: S1 - Sb
Assigned Value = 5.72 ± 0.34 µg/L
Kernel Density
Density
Result
Results (µg/L)
15 10 14 18 4 7 3 12 2 16 11 1 5 6 8 9 13 Md RA HV SV
Laboratory
z-Scores: S1 - Sb
Target Standard Deviation for Proficiency Assessment 0.86 µg/L (Equivalent to 15% CV)
z-Score
-0.5 -0.5 -0.4 -0.2 -0.2 -0.2 0.0 0.0 0.6 0.7 0.9 3.7
15 10 14 18 4 7 3 12 2 16 11 1
Laboratory
En-Scores: S1 - Sb
En-Score
-1.2 -0.4 -0.2 -0.4 -0.2 -0.1 0.0 0.0 0.5 1.7 0.8 2.9
15 10 14 18 4 7 3 12 2 16 11 1
Laboratory

Figure 15

Table 18

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Se |
| **Unit** | µg/L |

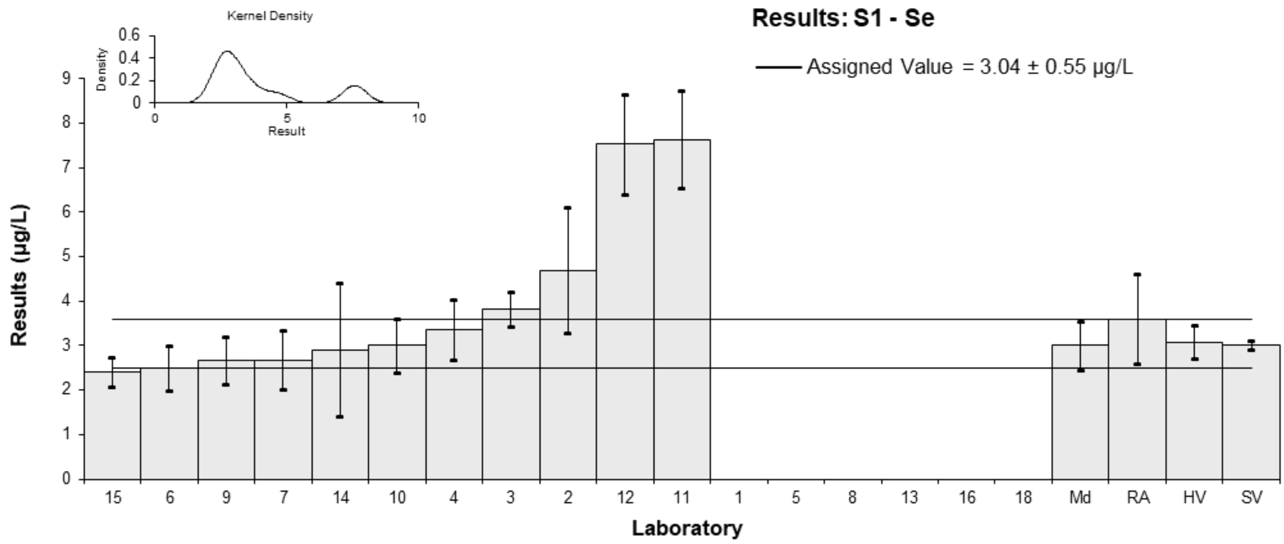
**Participant Results**

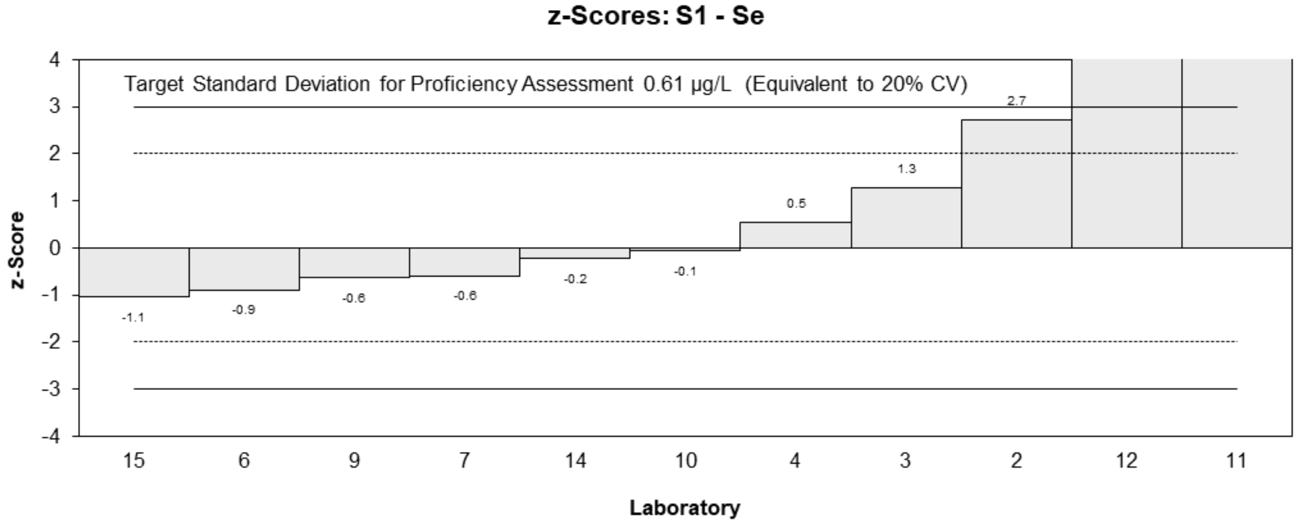
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <50 | NR | | |
| **2** | 4.7 | 1.4 | 2.73 | 1.10 |
| **3** | 3.82 | 0.40 | 1.28 | 1.15 |
| **4** | 3.37 | 0.68 | 0.54 | 0.38 |
| **5** | NR | NR | | |
| **6** | 2.5 | 0.50 | -0.89 | -0.73 |
| **7** | 2.68 | 0.66 | -0.59 | -0.42 |
| **8** | NT | NT | | |
| **9** | 2.66 | 0.532 | -0.62 | -0.50 |
| **10** | 3.0 | 0.60 | -0.07 | -0.05 |
| **11*** | 7.64 | 1.1 | 7.57 | 3.74 |
| **12*** | 7.53 | 1.1295 | 7.38 | 3.57 |
| **13** | NT | NT | | |
| **14** | 2.9 | 1.5 | -0.23 | -0.09 |
| **15** | 2.40 | 0.33 | -1.05 | -1.00 |
| **16** | <4 | 2.7 | | |
| **18** | NT | NT | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 3.04 | 0.55 |
| **Spike Value** | 3.01 | 0.10 |
| **Homogeneity Value** | 3.08 | 0.37 |
| **Robust Average** | 3.6 | 1.0 |
| **Median** | 3.00 | 0.56 |
| **Mean** | 3.9 | |
| **N** | 11 | |
| **Max** | 7.64 | |
| **Min** | 2.4 | |
| **Robust SD** | 1.4 | |
| **Robust CV** | 39% | |


Kernel Density
Density
Result
Results: S1 - Se
Assigned Value = 3.04 ± 0.55 µg/L
Results (µg/L)
15 6 9 7 14 10 4 3 2 12 11 1 5 8 13 16 18 Md RA HV SV
Laboratory


z-Scores: S1 - Se
Target Standard Deviation for Proficiency Assessment 0.61 µg/L (Equivalent to 20% CV)
z-Score
-1.1 -0.9 -0.6 -0.6 -0.2 -0.1 0.5 1.3 2.7
15 6 9 7 14 10 4 3 2 12 11
Laboratory

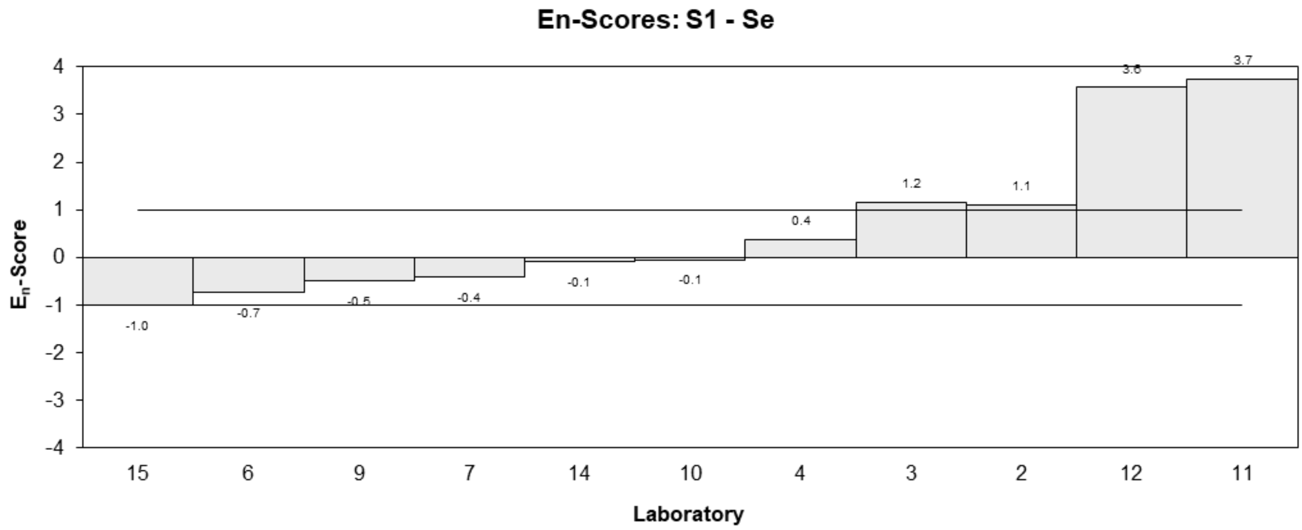

En-Scores: S1 - Se
En-Score
-1.0 -0.7 -0.5 -0.4 -0.1 -0.1 0.4 1.2 1.1 3.6 3.7
15 6 9 7 14 10 4 3 2 12 11
Laboratory

Figure 16

Table 19

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Sn |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <5 | NR | | |
| **2** | 4.2 | 0.7 | -0.03 | -0.03 |
| **3** | 4.36 | 0.44 | 0.22 | 0.28 |
| **4** | 4.43 | 0.93 | 0.33 | 0.22 |
| **5** | NR | NR | | |
| **6** | NT | NT | | |
| **7** | 3.79 | 0.93 | -0.68 | -0.45 |
| **8** | NT | NT | | |
| **9** | < 5 | 1 | | |
| **10** | 4.2 | 0.84 | -0.03 | -0.02 |
| **11** | 4.26 | 0.65 | 0.06 | 0.06 |
| **12** | <5 | <1.5 | | |
| **13** | NT | NT | | |
| **14** | 4.2 | 1.1 | -0.03 | -0.02 |
| **15** | 3.90 | 0.27 | -0.51 | -0.87 |
| **16** | 5.5 | NR | 2.02 | 5.12 |
| **18** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.22 | 0.25 |
| **Spike Value** | 4.02 | 0.11 |
| **Homogeneity Value** | 3.82 | 0.46 |
| **Robust Average** | 4.22 | 0.25 |
| **Median** | 4.20 | 0.20 |
| **Mean** | 4.32 | |
| **N** | 9 | |
| **Max** | 5.5 | |
| **Min** | 3.79 | |
| **Robust SD** | 0.30 | |
| **Robust CV** | 7.1% | |

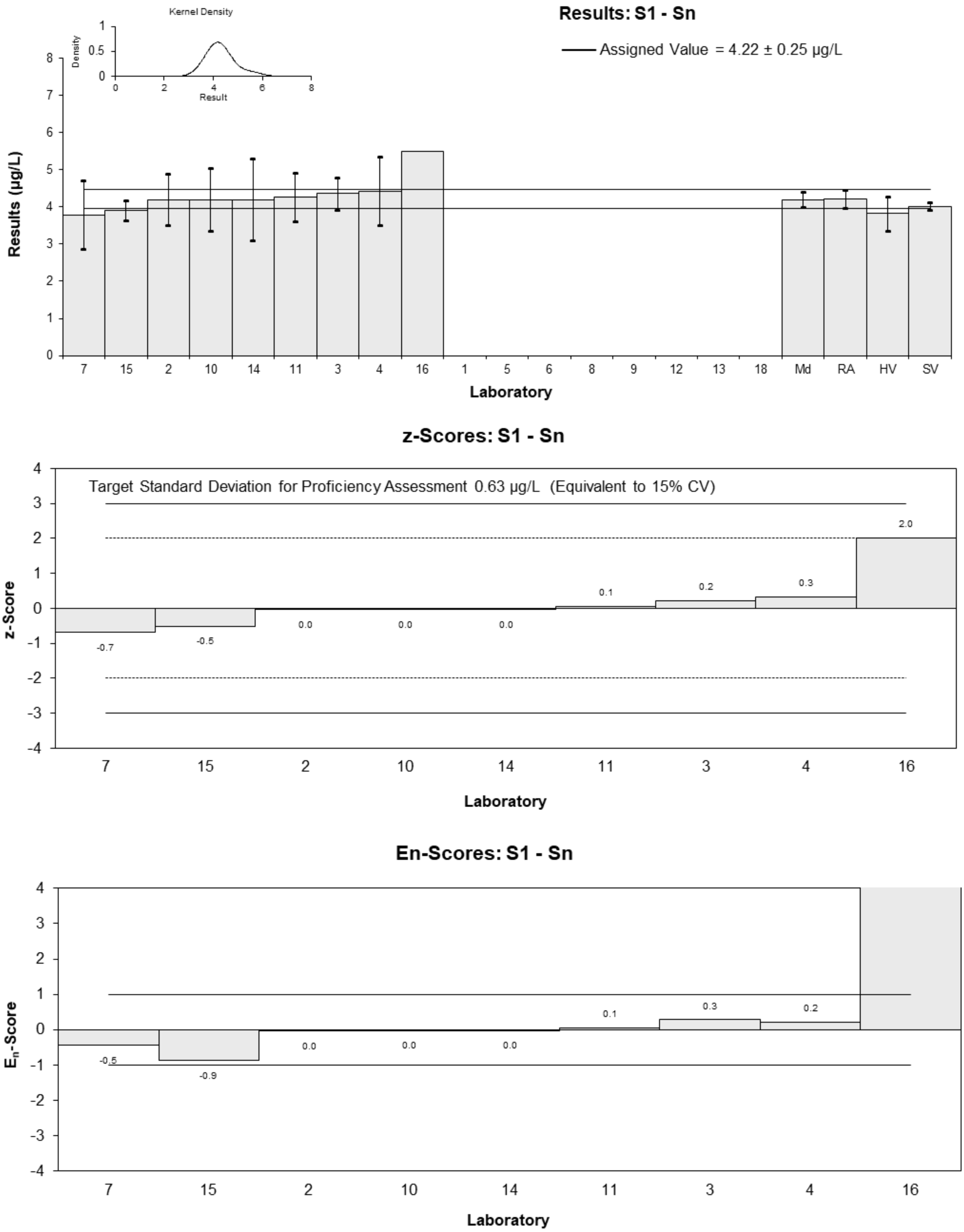

Results: S1 - Sn
Assigned Value = 4.22 ± 0.25 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
15
2
10
14
11
3
4
16
1
5
6
8
9
12
13
18
Md
RA
HV
SV
z-Scores: S1 - Sn
Target Standard Deviation for Proficiency Assessment 0.63 µg/L (Equivalent to 15% CV)
z-Score
-0.7
-0.5
0.0
0.0
0.0
0.1
0.2
0.3
2.0
Laboratory
En-Scores: S1 - Sn
$E_n$-Score
-0.5
-0.9
0.0
0.0
0.0
0.1
0.3
0.2
Laboratory

Figure 17

Table 20

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Tl |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <5 | NR | | |
| **2** | 1.1 | 1.0 | 0.45 | 0.07 |
| **3** | 1.04 | 0.10 | 0.06 | 0.08 |
| **4** | 1.04 | 0.17 | 0.06 | 0.05 |
| **5** | NR | NR | | |
| **6** | 0.88 | 0.18 | -0.97 | -0.76 |
| **7** | 0.93 | 0.22 | -0.65 | -0.43 |
| **8** | NT | NT | | |
| **9** | < 5 | 1 | | |
| **10** | <1 | NR | | |
| **11** | 1.16 | 0.20 | 0.84 | 0.60 |
| **12** | <5 | <1.5 | | |
| **13** | NT | NT | | |
| **14** | 1.1 | 0.5 | 0.45 | 0.14 |
| **15** | 0.98 | 0.05 | -0.32 | -0.53 |
| **16** | 1.0 | NR | -0.19 | -0.38 |
| **18*** | 2.8 | 0.8 | 11.46 | 2.20 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.03 | 0.08 |
| **Spike Value** | 1.01 | 0.03 |
| **Homogeneity Value** | 1.03 | 0.12 |
| **Robust Average** | 1.05 | 0.09 |
| **Median** | 1.04 | 0.07 |
| **Mean** | 1.20 | |
| **N** | 10 | |
| **Max** | 2.8 | |
| **Min** | 0.88 | |
| **Robust SD** | 0.12 | |
| **Robust CV** | 11% | |

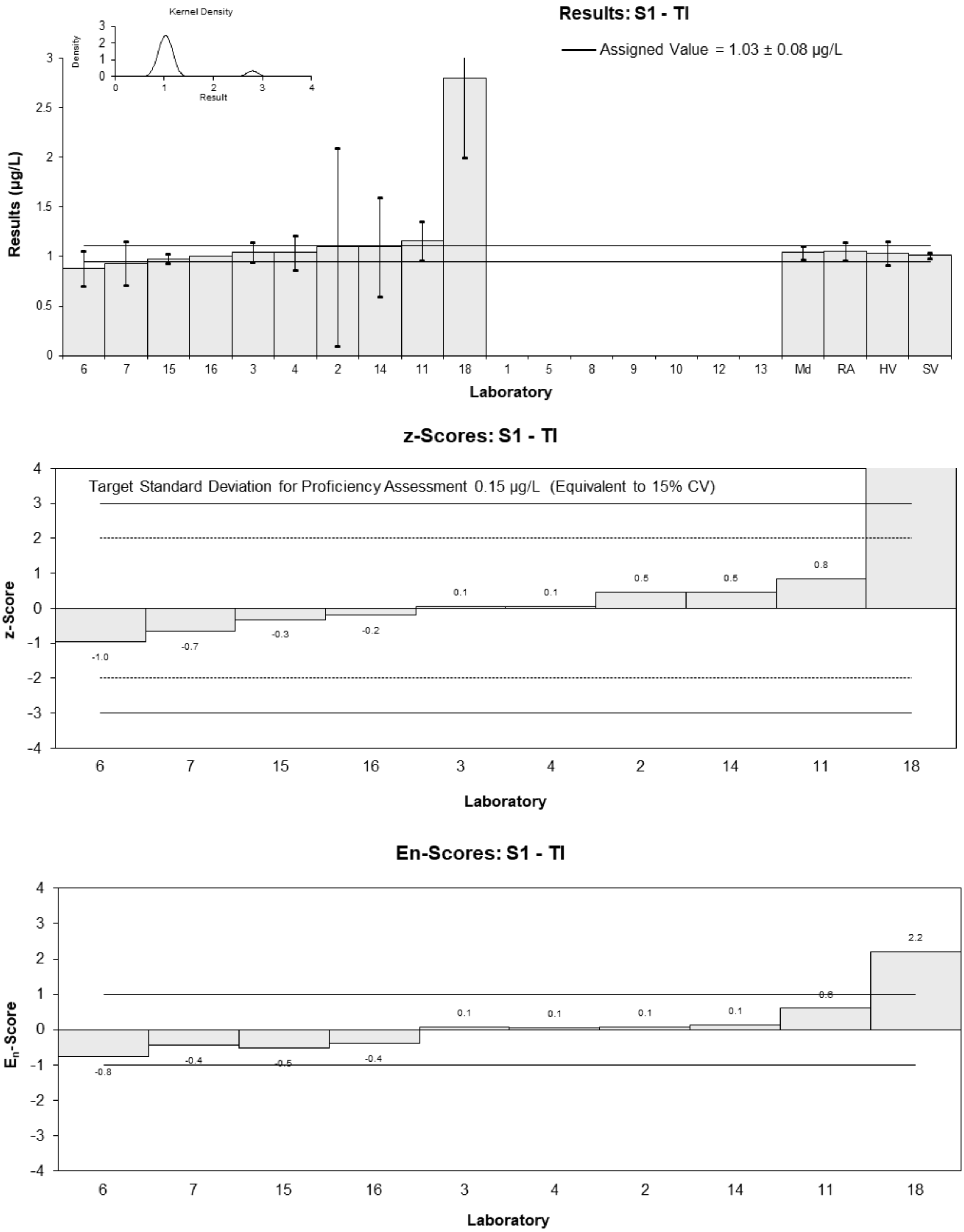

Results: S1 - Tl
Assigned Value = 1.03 ± 0.08 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6 7 15 16 3 4 2 14 11 18 1 5 8 9 10 12 13 Md RA HV SV
z-Scores: S1 - Tl
Target Standard Deviation for Proficiency Assessment 0.15 µg/L (Equivalent to 15% CV)
z-Score
-1.0 -0.7 -0.3 -0.2 0.1 0.1 0.5 0.5 0.8
Laboratory
6 7 15 16 3 4 2 14 11 18
En-Scores: S1 - Tl
$E_n$-Score
-0.8 -0.4 -0.5 -0.4 0.1 0.1 0.1 0.1 0.6 2.2
Laboratory
6 7 15 16 3 4 2 14 11 18

Figure 18

Table 21

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | U |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <5 | NR | | |
| **2** | 2.7 | 1.6 | 0.31 | 0.07 |
| **3** | 2.63 | 0.26 | 0.13 | 0.17 |
| **4** | 2.79 | 0.40 | 0.54 | 0.49 |
| **5** | NR | NR | | |
| **6** | 2.4 | 0.48 | -0.47 | -0.36 |
| **7** | 2.39 | 0.54 | -0.49 | -0.34 |
| **8** | NT | NT | | |
| **9** | < 5 | 1 | | |
| **10** | 2.4 | 0.48 | -0.47 | -0.36 |
| **11** | 2.92 | 0.45 | 0.88 | 0.72 |
| **12** | <5 | <1.5 | | |
| **13** | NT | NT | | |
| **14** | 2.7 | 1.4 | 0.31 | 0.09 |
| **15** | 2.48 | 0.07 | -0.26 | -0.60 |
| **16** | 2.6 | NR | 0.05 | 0.13 |
| **18** | 2.39 | 0.18 | -0.49 | -0.81 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.58 | 0.15 |
| **Spike Value** | 2.44 | 0.42 |
| **Homogeneity Value** | 2.38 | 0.29 |
| **Robust Average** | 2.58 | 0.15 |
| **Median** | 2.60 | 0.21 |
| **Mean** | 2.58 | |
| **N** | 11 | |
| **Max** | 2.92 | |
| **Min** | 2.39 | |
| **Robust SD** | 0.20 | |
| **Robust CV** | 7.8% | |

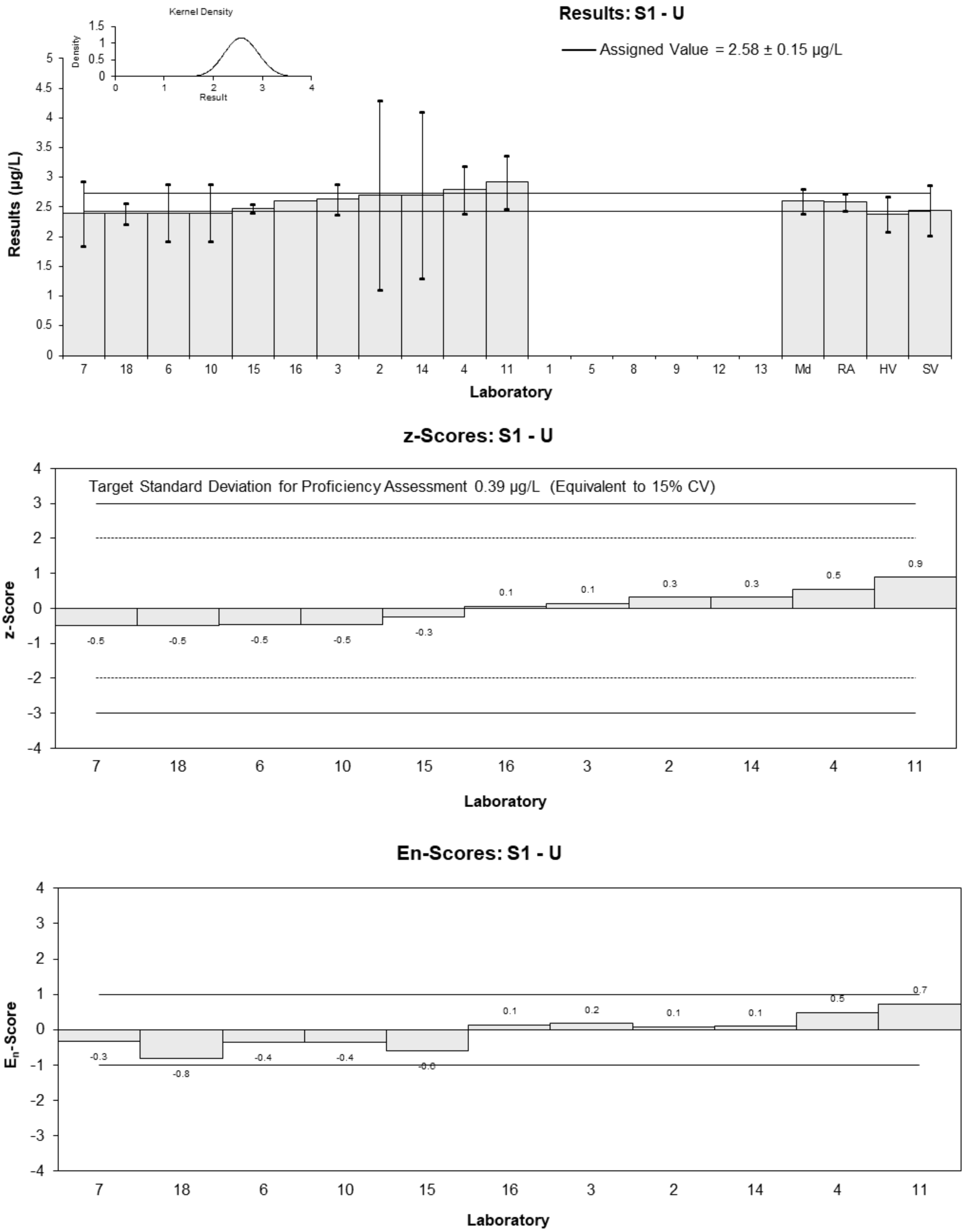

Results: S1 - U
Assigned Value = 2.58 ± 0.15 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
18
6
10
15
16
3
2
14
4
11
1
5
8
9
12
13
Md
RA
HV
SV
z-Scores: S1 - U
Target Standard Deviation for Proficiency Assessment 0.39 µg/L (Equivalent to 15% CV)
z-Score
-0.5
-0.5
-0.5
-0.5
-0.3
0.1
0.1
0.3
0.3
0.5
0.9
Laboratory
En-Scores: S1 - U
$E_n$-Score
-0.3
-0.8
-0.4
-0.4
0.1
0.2
0.1
0.1
0.5
0.7
Laboratory

Figure 19

Table 22

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | V |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <50 | NR | | |
| **2** | 3.3 | 1.2 | -0.20 | -0.08 |
| **3** | 3.68 | 0.37 | 0.55 | 0.65 |
| **4** | 3.59 | 0.65 | 0.37 | 0.28 |
| **5** | NR | NR | | |
| **6** | 2.5 | 0.50 | -1.76 | -1.65 |
| **7** | 2.77 | 0.79 | -1.24 | -0.77 |
| **8** | NT | NT | | |
| **9** | < 5 | 1 | | |
| **10** | 3.5 | 0.70 | 0.20 | 0.14 |
| **11** | 3.65 | 0.55 | 0.49 | 0.42 |
| **12** | <5 | <1.5 | | |
| **13** | NT | NT | | |
| **14** | 3.4 | 0.9 | 0.00 | 0.00 |
| **15** | 3.24 | 0.19 | -0.31 | -0.55 |
| **16** | 3.5 | 1.9 | 0.20 | 0.05 |
| **18** | 3.6 | 0.7 | 0.39 | 0.27 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 3.40 | 0.22 |
| **Spike Value** | 3.92 | 0.31 |
| **Homogeneity Value** | 3.16 | 0.38 |
| **Robust Average** | 3.40 | 0.22 |
| **Median** | 3.50 | 0.17 |
| **Mean** | 3.34 | |
| **N** | 11 | |
| **Max** | 3.68 | |
| **Min** | 2.5 | |
| **Robust SD** | 0.29 | |
| **Robust CV** | 8.5% | |

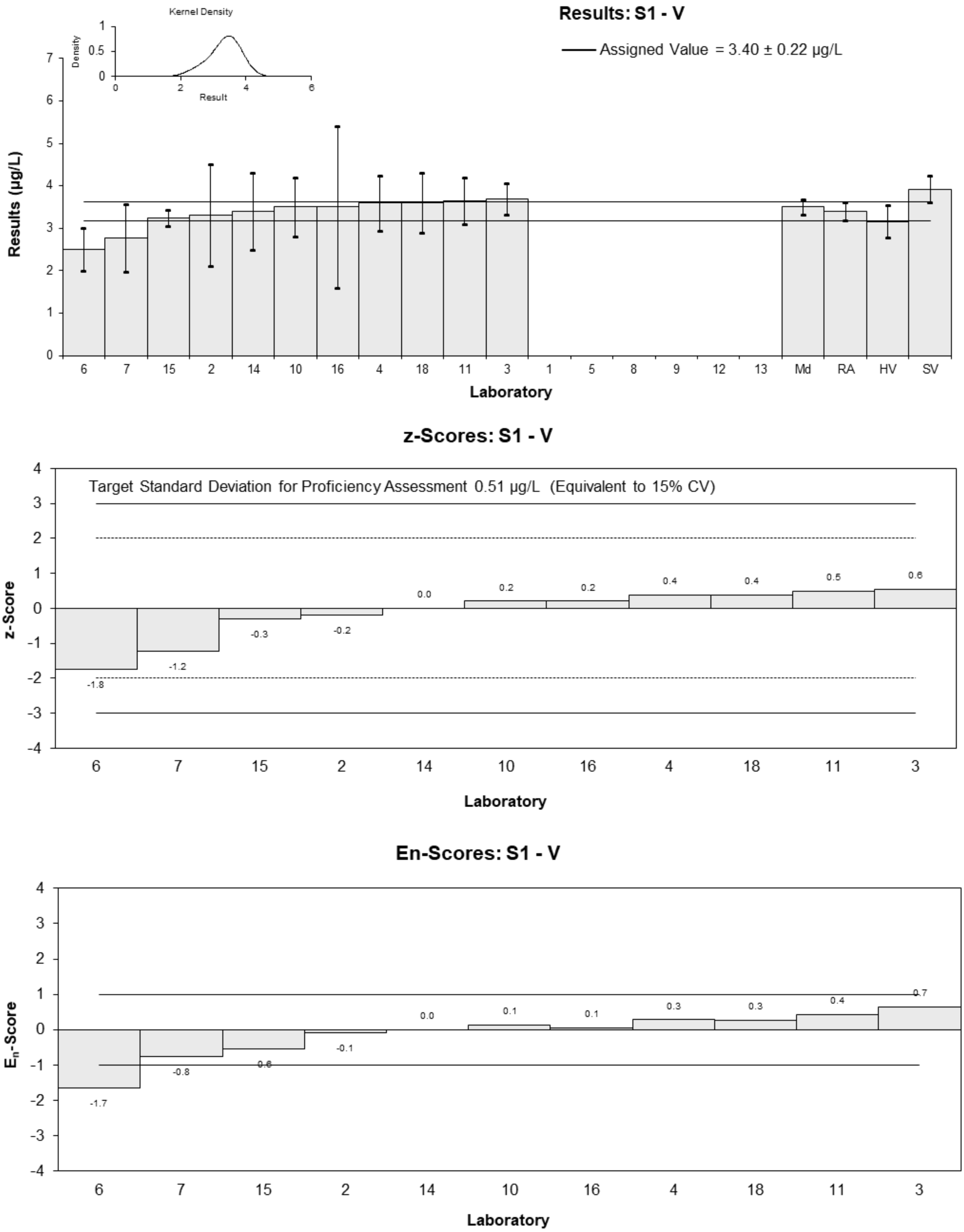

Results: S1 - V
Assigned Value = 3.40 ± 0.22 µg/L
Kernel Density
Density
Result
Results (µg/L)
6 7 15 2 14 10 16 4 18 11 3 1 5 8 9 12 13 Md RA HV SV
Laboratory
z-Scores: S1 - V
Target Standard Deviation for Proficiency Assessment 0.51 µg/L (Equivalent to 15% CV)
z-Score
-1.8 -1.2 -0.3 -0.2 0.0 0.2 0.2 0.4 0.4 0.5 0.6
6 7 15 2 14 10 16 4 18 11 3
Laboratory
En-Scores: S1 - V
$E_n$-Score
-1.7 -0.8 -0.6 -0.1 0.0 0.1 0.1 0.3 0.3 0.4 0.7
6 7 15 2 14 10 16 4 18 11 3
Laboratory

Figure 20

Table 23

**Sample Details**

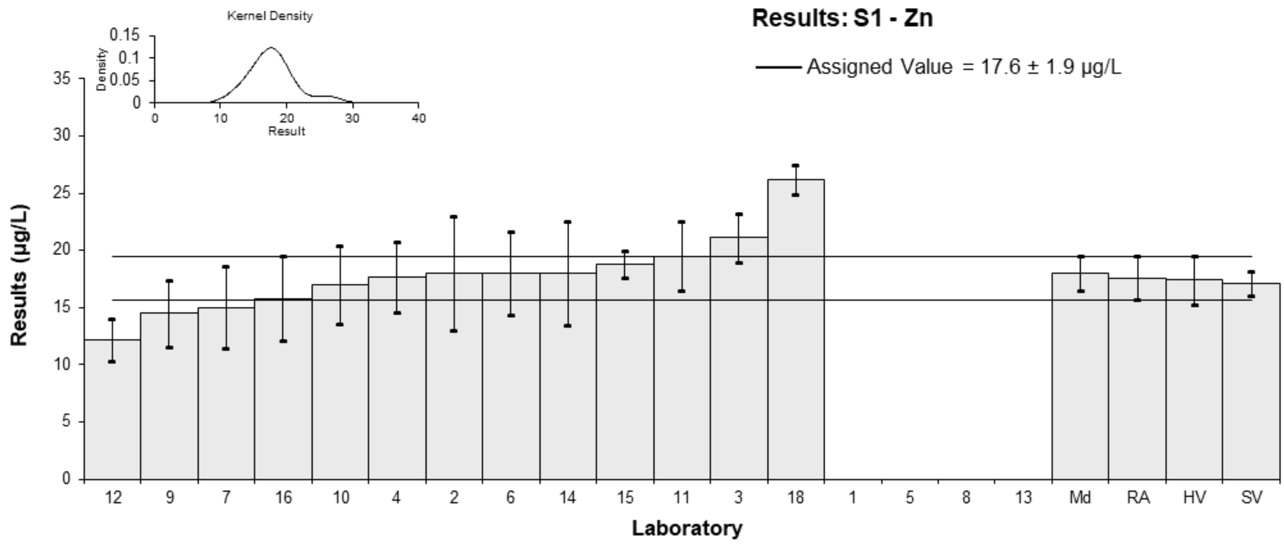
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Zn |
| **Unit** | µg/L |

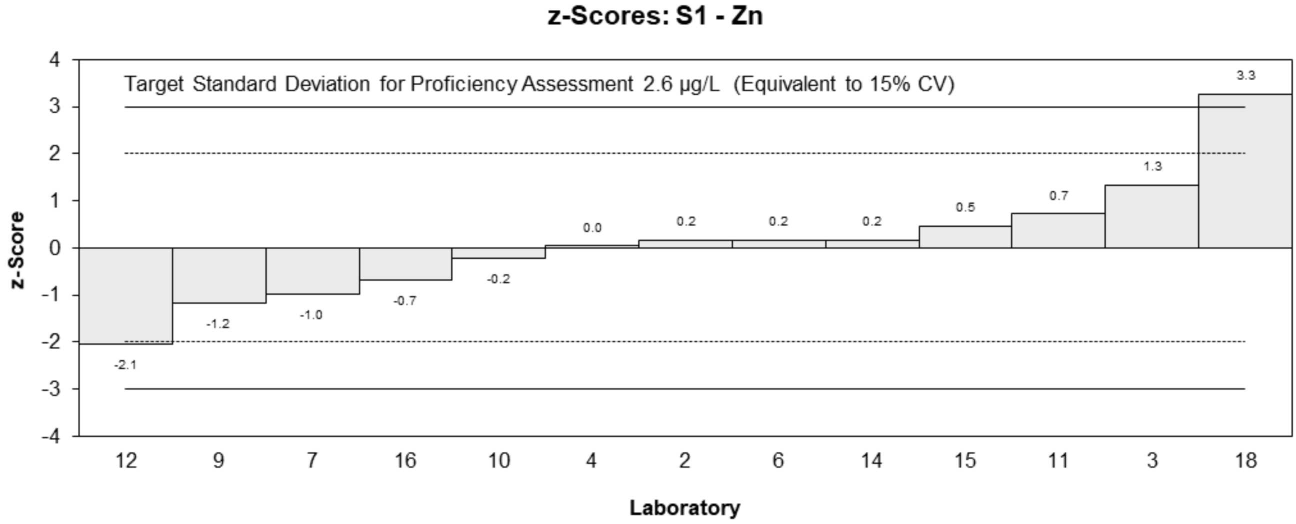
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <25 | NR | | |
| **2** | 18 | 5 | 0.15 | 0.07 |
| **3** | 21.1 | 2.1 | 1.33 | 1.24 |
| **4** | 17.7 | 3.1 | 0.04 | 0.03 |
| **5** | NR | NR | | |
| **6** | 18 | 3.6 | 0.15 | 0.10 |
| **7** | 15.0 | 3.6 | -0.98 | -0.64 |
| **8** | NT | NT | | |
| **9** | 14.5 | 2.90 | -1.17 | -0.89 |
| **10** | 17 | 3.4 | -0.23 | -0.15 |
| **11** | 19.5 | 3.0 | 0.72 | 0.54 |
| **12** | 12.2 | 1.83 | -2.05 | -2.05 |
| **13** | NT | NT | | |
| **14** | 18 | 4.5 | 0.15 | 0.08 |
| **15** | 18.8 | 1.20 | 0.45 | 0.53 |
| **16** | 15.8 | 3.7 | -0.68 | -0.43 |
| **18** | 26.2 | 1.3 | 3.26 | 3.74 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 17.6 | 1.9 |
| **Spike Value** | 17.1 | 1.1 |
| **Homogeneity Value** | 17.4 | 2.1 |
| **Robust Average** | 17.6 | 1.9 |
| **Median** | 18.0 | 1.5 |
| **Mean** | 17.8 | |
| **N** | 13 | |
| **Max** | 26.2 | |
| **Min** | 12.2 | |
| **Robust SD** | 2.8 | |
| **Robust CV** | 16% | |


Results: S1 - Zn
Assigned Value = 17.6 ± 1.9 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12 9 7 16 10 4 2 6 14 15 11 3 18 1 5 8 13 Md RA HV SV


z-Scores: S1 - Zn
Target Standard Deviation for Proficiency Assessment 2.6 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
12 9 7 16 10 4 2 6 14 15 11 3 18

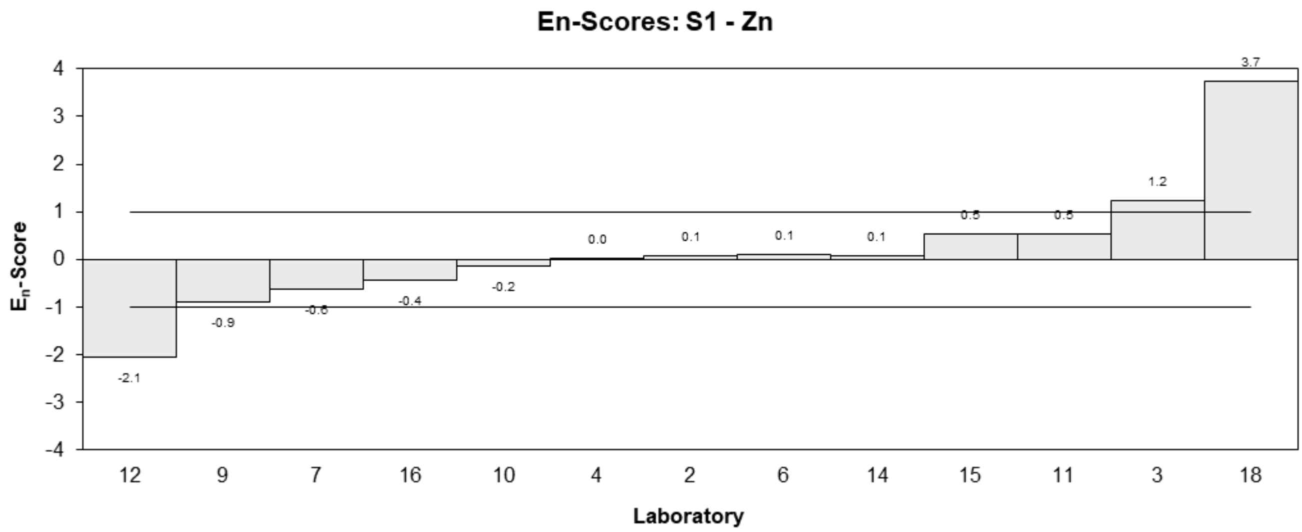

En-Scores: S1 - Zn
En-Score
Laboratory
12 9 7 16 10 4 2 6 14 15 11 3 18

Figure 21

Table 24

**Sample Details**

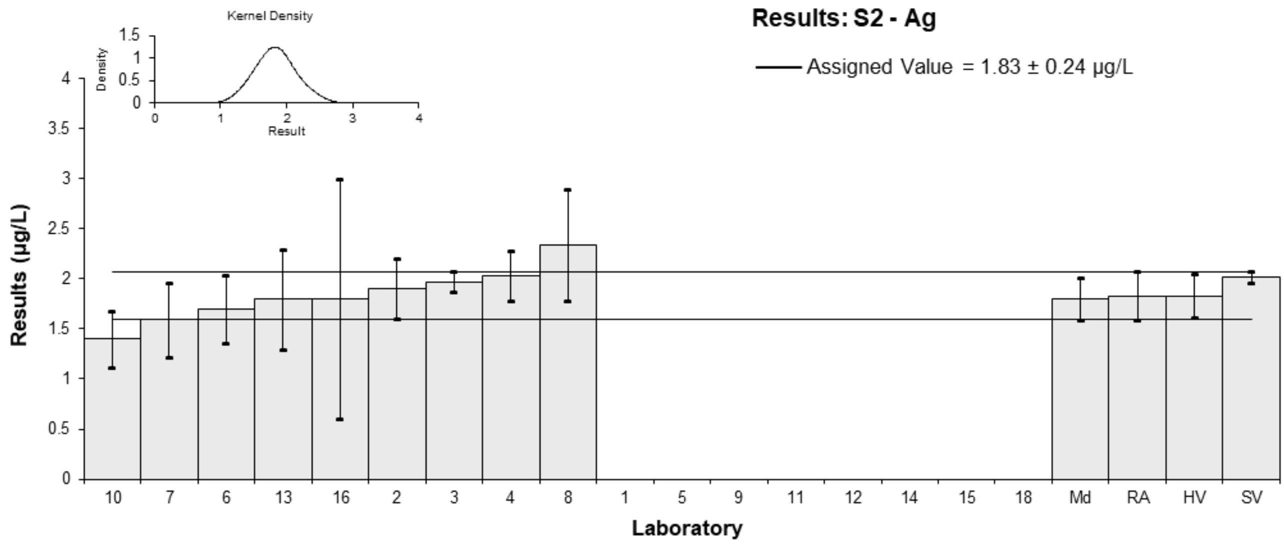
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Ag |
| **Unit** | µg/L |

**Participant Results**

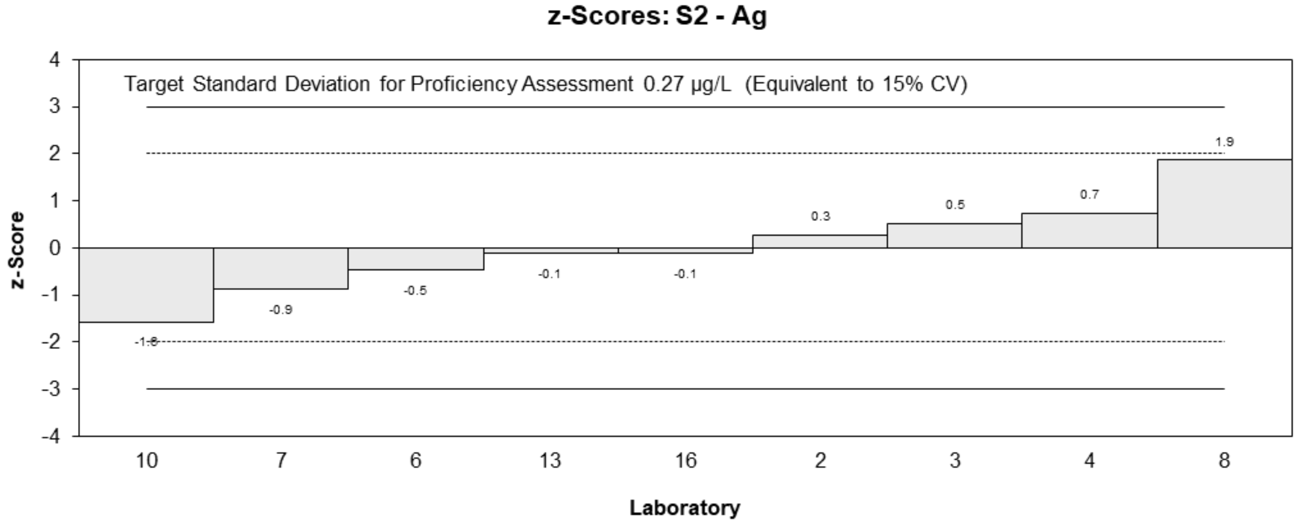
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <1 | NR | | |
| **2** | 1.9 | 0.3 | 0.26 | 0.18 |
| **3** | 1.97 | 0.10 | 0.51 | 0.54 |
| **4** | 2.03 | 0.25 | 0.73 | 0.58 |
| **5** | NT | NT | | |
| **6** | 1.7 | 0.34 | -0.47 | -0.31 |
| **7** | 1.59 | 0.37 | -0.87 | -0.54 |
| **8** | 2.34 | 0.56 | 1.86 | 0.84 |
| **9** | < 5 | 1 | | |
| **10** | 1.4 | 0.28 | -1.57 | -1.17 |
| **11** | NT | NT | | |
| **12** | <5 | <1.5 | | |
| **13** | 1.8 | 0.5 | -0.11 | -0.05 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 1.8 | 1.2 | -0.11 | -0.02 |
| **18** | NT | NT | | |

**Statistics**

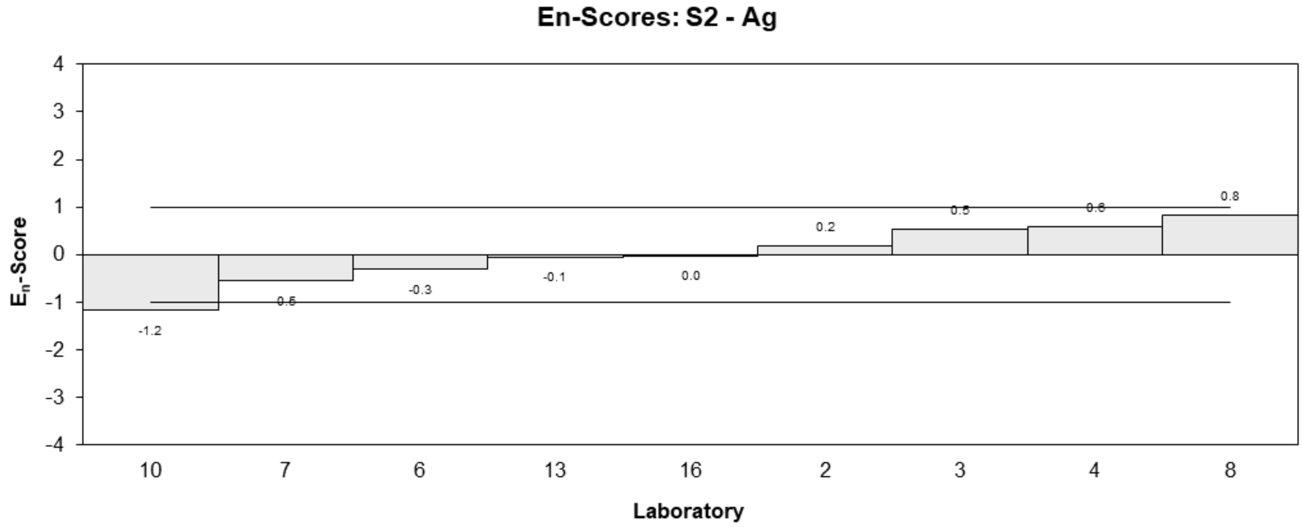
| | | |
|---|---|---|
| **Assigned Value** | 1.83 | 0.24 |
| **Spike Value** | 2.02 | 0.06 |
| **Homogeneity Value** | 1.83 | 0.22 |
| **Robust Average** | 1.83 | 0.24 |
| **Median** | 1.80 | 0.21 |
| **Mean** | 1.84 | |
| **N** | 9 | |
| **Max** | 2.34 | |
| **Min** | 1.4 | |
| **Robust SD** | 0.28 | |
| **Robust CV** | 16% | |



Results: S2 - Ag
Assigned Value = 1.83 ± 0.24 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
10
7
6
13
16
2
3
4
8
1
5
9
11
12
14
15
18
Md
RA
HV
SV

z-Scores: S2 - Ag
Target Standard Deviation for Proficiency Assessment 0.27 μg/L (Equivalent to 15% CV)
z-Score
-1.6
-0.9
-0.5
-0.1
-0.1
0.3
0.5
0.7
1.9
Laboratory
10
7
6
13
16
2
3
4
8

En-Scores: S2 - Ag
$E_n$-Score
-1.2
-0.5
-0.3
-0.1
0.0
0.2
0.5
0.6
0.8
Laboratory
10
7
6
13
16
2
3
4
8


Figure 22

Table 25

**Sample Details**

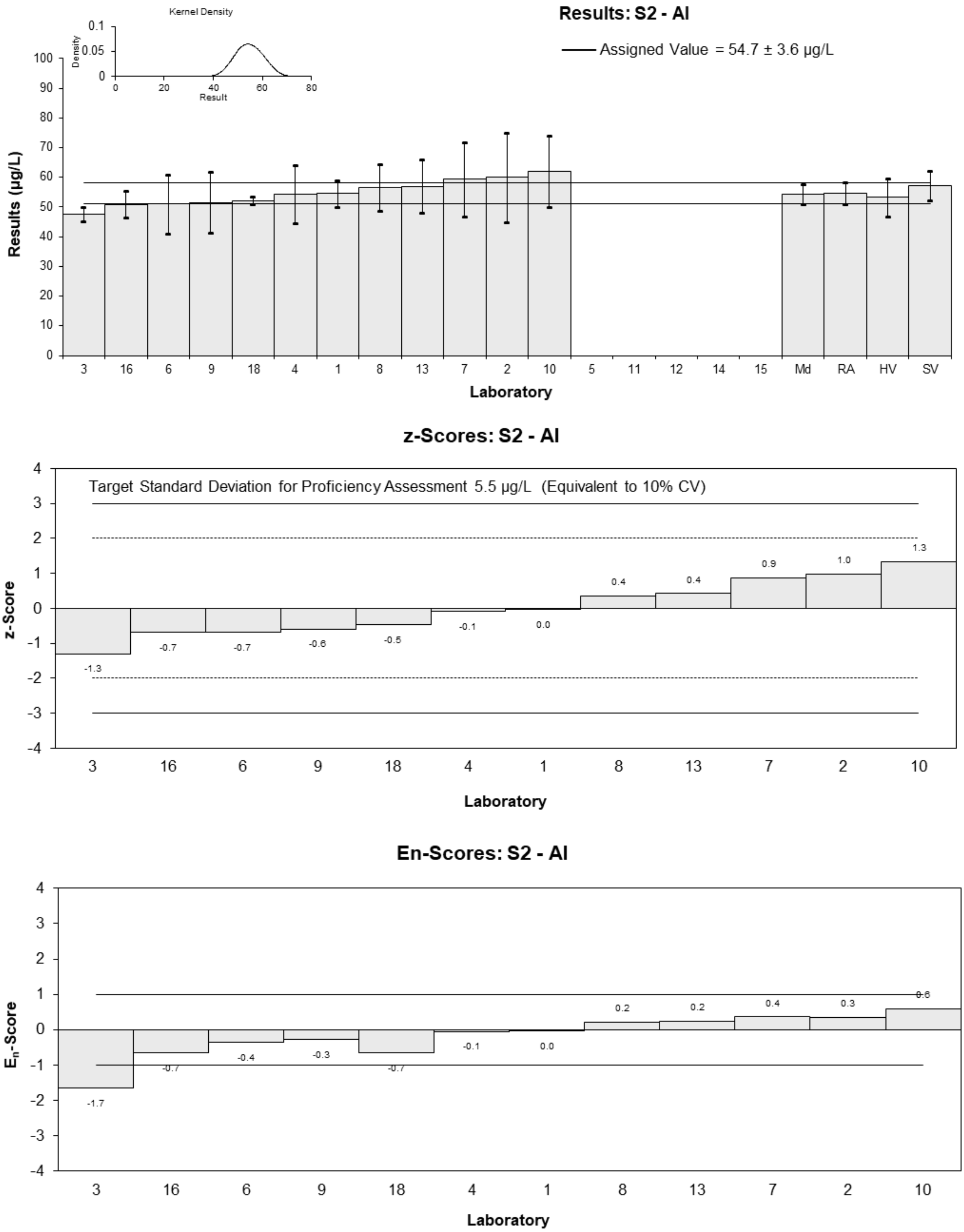
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Al |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 54.48 | 4.37 | -0.04 | -0.04 |
| **2** | 60 | 15 | 0.97 | 0.34 |
| **3** | 47.6 | 2.38 | -1.30 | -1.65 |
| **4** | 54.2 | 9.8 | -0.09 | -0.05 |
| **5** | NT | NT | | |
| **6** | 51 | 10 | -0.68 | -0.35 |
| **7** | 59.4 | 12.5 | 0.86 | 0.36 |
| **8** | 56.61 | 7.9 | 0.35 | 0.22 |
| **9** | 51.5 | 10.3 | -0.59 | -0.29 |
| **10** | 62 | 12 | 1.33 | 0.58 |
| **11** | NT | NT | | |
| **12** | <50 | <15 | | |
| **13** | 57 | 9 | 0.42 | 0.24 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 50.9 | 4.5 | -0.69 | -0.66 |
| **18** | 52.2 | 1.2 | -0.46 | -0.66 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 54.7 | 3.6 |
| **Spike Value** | 57.2 | 5.1 |
| **Homogeneity Value** | 53.2 | 6.4 |
| **Robust Average** | 54.7 | 3.6 |
| **Median** | 54.3 | 3.3 |
| **Mean** | 54.7 | |
| **N** | 12 | |
| **Max** | 62 | |
| **Min** | 47.6 | |
| **Robust SD** | 4.9 | |
| **Robust CV** | 9% | |



Results: S2 - Al
Assigned Value = 54.7 ± 3.6 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3 16 6 9 18 4 1 8 13 7 2 10 5 11 12 14 15 Md RA HV SV
z-Scores: S2 - Al
Target Standard Deviation for Proficiency Assessment 5.5 µg/L (Equivalent to 10% CV)
z-Score
-1.3 -0.7 -0.7 -0.6 -0.5 -0.1 0.0 0.4 0.4 0.9 1.0 1.3
3 16 6 9 18 4 1 8 13 7 2 10
Laboratory
En-Scores: S2 - Al
$E_n$-Score
-1.7 -0.7 -0.4 -0.3 -0.7 -0.1 0.0 0.2 0.2 0.4 0.3 0.6
3 16 6 9 18 4 1 8 13 7 2 10
Laboratory


Figure 23

Table 26

**Sample Details**

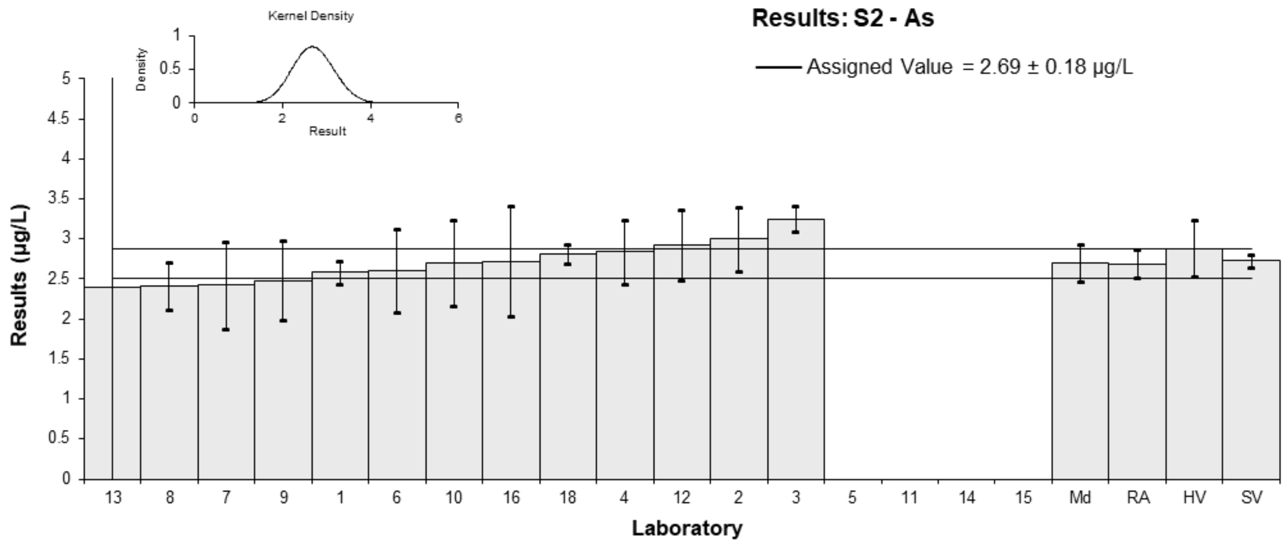
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | As |
| **Unit** | µg/L |

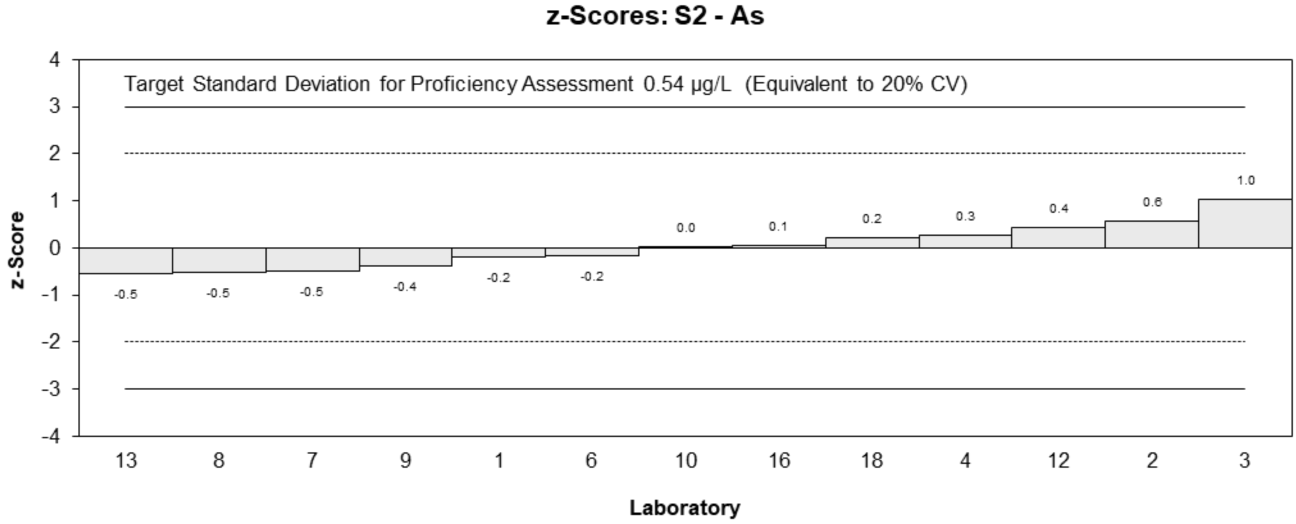
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2.58 | 0.14 | -0.20 | -0.48 |
| **2** | 3.0 | 0.4 | 0.58 | 0.71 |
| **3** | 3.25 | 0.16 | 1.04 | 2.33 |
| **4** | 2.84 | 0.40 | 0.28 | 0.34 |
| **5** | NT | NT | | |
| **6** | 2.6 | 0.52 | -0.17 | -0.16 |
| **7** | 2.42 | 0.54 | -0.50 | -0.47 |
| **8** | 2.41 | 0.29 | -0.52 | -0.82 |
| **9** | 2.48 | 0.496 | -0.39 | -0.40 |
| **10** | 2.7 | 0.54 | 0.02 | 0.02 |
| **11** | NT | NT | | |
| **12** | 2.92 | 0.438 | 0.43 | 0.49 |
| **13** | 2.4 | 5 | -0.54 | -0.06 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 2.72 | 0.69 | 0.06 | 0.04 |
| **18** | 2.81 | 0.12 | 0.22 | 0.55 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.69 | 0.18 |
| **Spike Value** | 2.73 | 0.08 |
| **Homogeneity Value** | 2.88 | 0.35 |
| **Robust Average** | 2.69 | 0.18 |
| **Median** | 2.70 | 0.23 |
| **Mean** | 2.70 | |
| **N** | 13 | |
| **Max** | 3.25 | |
| **Min** | 2.4 | |
| **Robust SD** | 0.26 | |
| **Robust CV** | 9.7% | |


Results: S2 - As
Assigned Value = 2.69 ± 0.18 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
13 8 7 9 1 6 10 16 18 4 12 2 3 5 11 14 15 Md RA HV SV


z-Scores: S2 - As
Target Standard Deviation for Proficiency Assessment 0.54 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
13 8 7 9 1 6 10 16 18 4 12 2 3
-0.5 -0.5 -0.5 -0.4 -0.2 -0.2 0.0 0.1 0.2 0.3 0.4 0.6 1.0

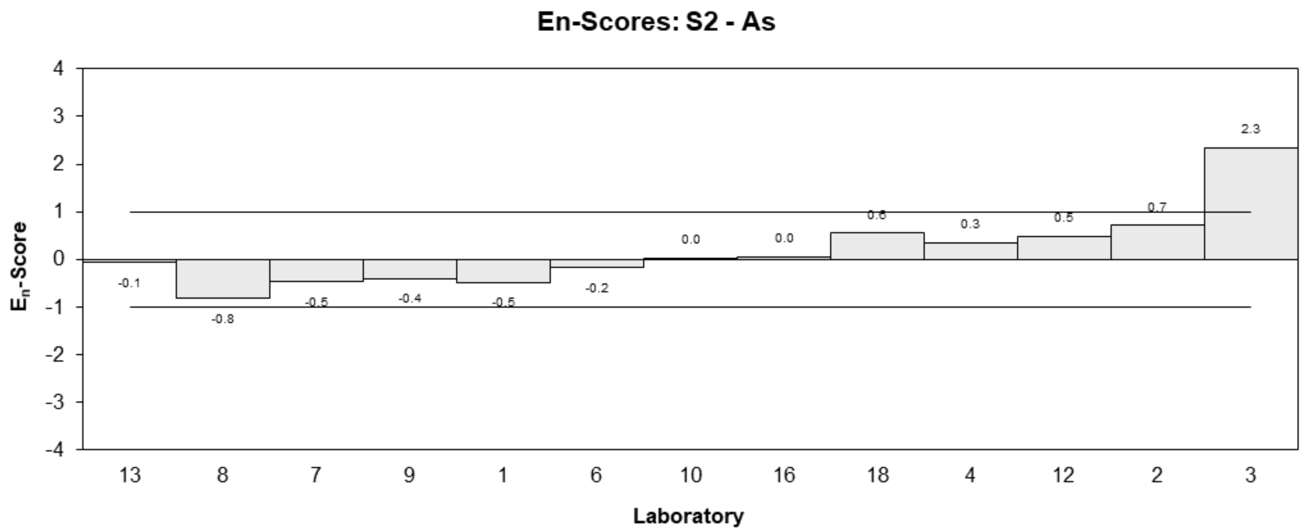

En-Scores: S2 - As
En-Score
Laboratory
13 8 7 9 1 6 10 16 18 4 12 2 3
-0.1 -0.8 -0.5 -0.4 -0.5 -0.2 0.0 0.0 0.6 0.3 0.5 0.7 2.3

Figure 24

Table 27

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Be |
| **Unit** | µg/L |

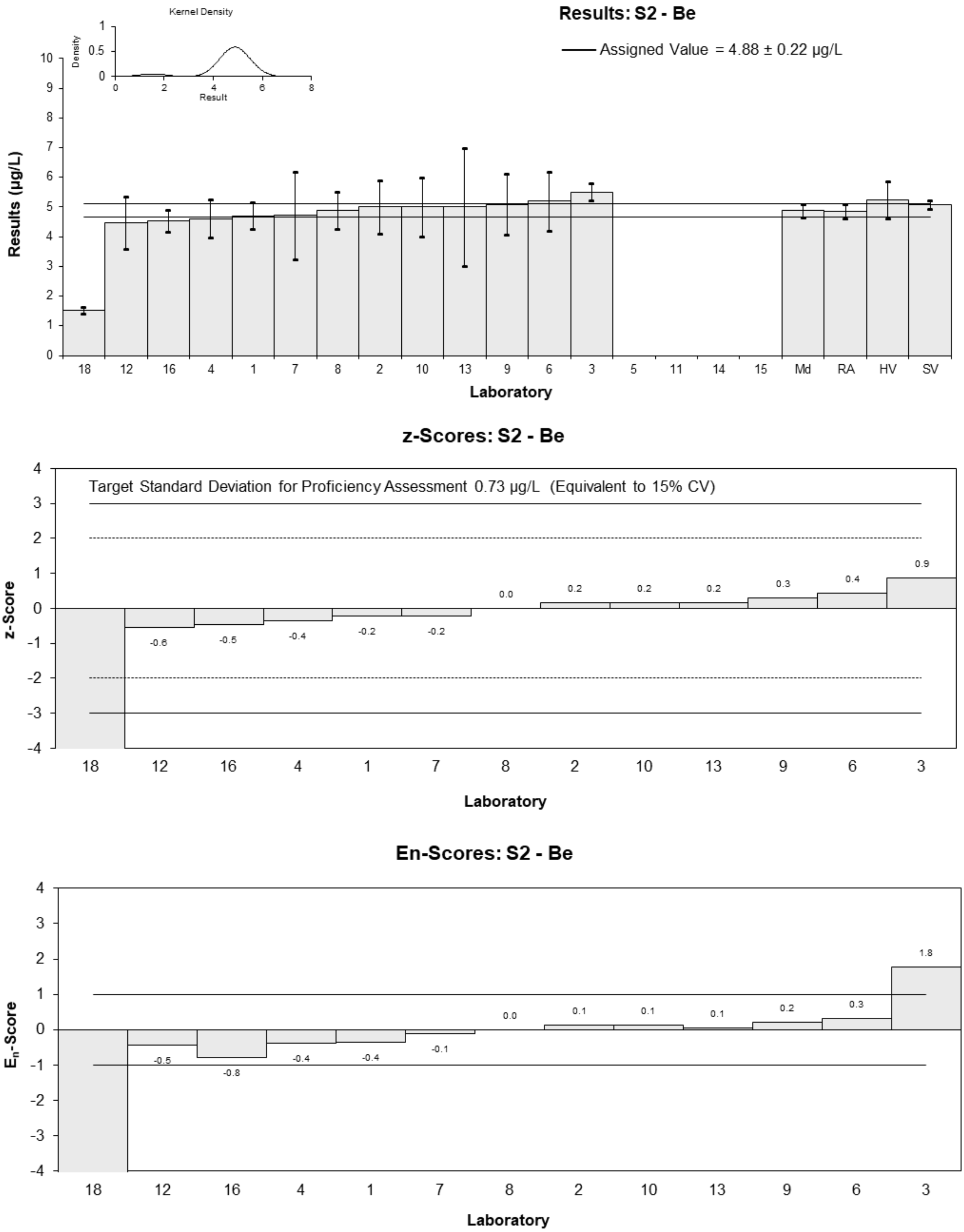
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 4.71 | 0.44 | -0.23 | -0.35 |
| **2** | 5.0 | 0.9 | 0.16 | 0.13 |
| **3** | 5.51 | 0.28 | 0.86 | 1.77 |
| **4** | 4.61 | 0.65 | -0.37 | -0.39 |
| **5** | NT | NT | | |
| **6** | 5.2 | 1.0 | 0.44 | 0.31 |
| **7** | 4.72 | 1.48 | -0.22 | -0.11 |
| **8** | 4.88 | 0.63 | 0.00 | 0.00 |
| **9** | 5.09 | 1.02 | 0.29 | 0.20 |
| **10** | 5.0 | 1.0 | 0.16 | 0.12 |
| **11** | NT | NT | | |
| **12** | 4.47 | 0.894 | -0.56 | -0.45 |
| **13** | 5 | 2 | 0.16 | 0.06 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 4.54 | 0.37 | -0.46 | -0.79 |
| **18*** | 1.52 | 0.10 | -4.59 | -13.90 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.88 | 0.22 |
| **Spike Value** | 5.08 | 0.14 |
| **Homogeneity Value** | 5.23 | 0.63 |
| **Robust Average** | 4.84 | 0.24 |
| **Median** | 4.88 | 0.22 |
| **Mean** | 4.63 | |
| **N** | 13 | |
| **Max** | 5.51 | |
| **Min** | 1.52 | |
| **Robust SD** | 0.35 | |
| **Robust CV** | 7.2% | |



Kernel Density
Density
Result
Results: S2 - Be
Assigned Value = 4.88 ± 0.22 µg/L
Results (µg/L)
18 12 16 4 1 7 8 2 10 13 9 6 3 5 11 14 15 Md RA HV SV
Laboratory
z-Scores: S2 - Be
Target Standard Deviation for Proficiency Assessment 0.73 µg/L (Equivalent to 15% CV)
z-Score
-0.6 -0.5 -0.4 -0.2 -0.2 0.0 0.2 0.2 0.2 0.3 0.4 0.9
18 12 16 4 1 7 8 2 10 13 9 6 3
Laboratory
En-Scores: S2 - Be
En-Score
-0.5 -0.8 -0.4 -0.4 -0.1 0.0 0.1 0.1 0.1 0.2 0.3 1.8
18 12 16 4 1 7 8 2 10 13 9 6 3
Laboratory


Figure 25

Table 28

**Sample Details**

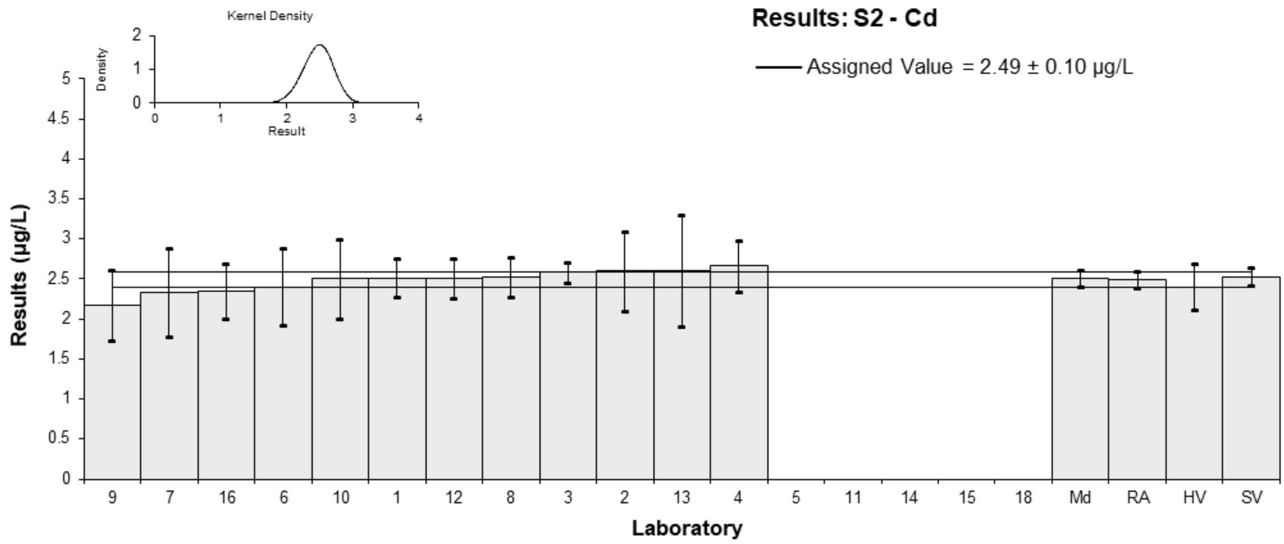
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Cd |
| **Unit** | µg/L |

**Participant Results**

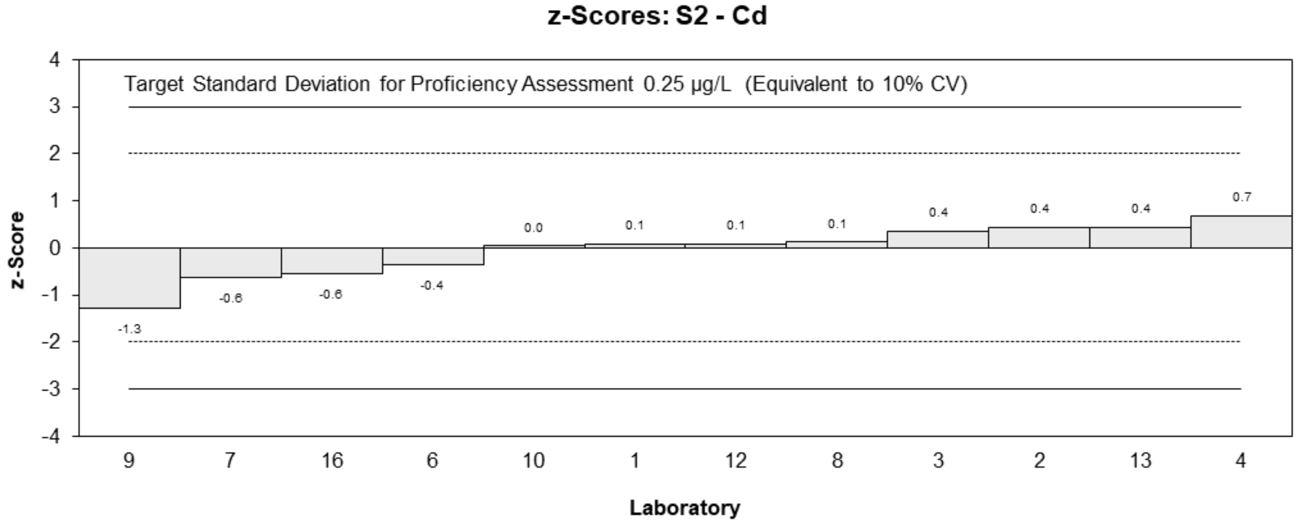
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2.51 | 0.24 | 0.08 | 0.08 |
| **2** | 2.6 | 0.5 | 0.44 | 0.22 |
| **3** | 2.58 | 0.13 | 0.36 | 0.55 |
| **4** | 2.66 | 0.32 | 0.68 | 0.51 |
| **5** | NT | NT | | |
| **6** | 2.4 | 0.48 | -0.36 | -0.18 |
| **7** | 2.33 | 0.55 | -0.64 | -0.29 |
| **8** | 2.52 | 0.25 | 0.12 | 0.11 |
| **9** | 2.17 | 0.434 | -1.29 | -0.72 |
| **10** | 2.5 | 0.50 | 0.04 | 0.02 |
| **11** | NT | NT | | |
| **12** | 2.51 | 0.251 | 0.08 | 0.07 |
| **13** | 2.6 | 0.7 | 0.44 | 0.16 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 2.35 | 0.34 | -0.56 | -0.40 |
| **18** | NT | NT | | |

**Statistics**

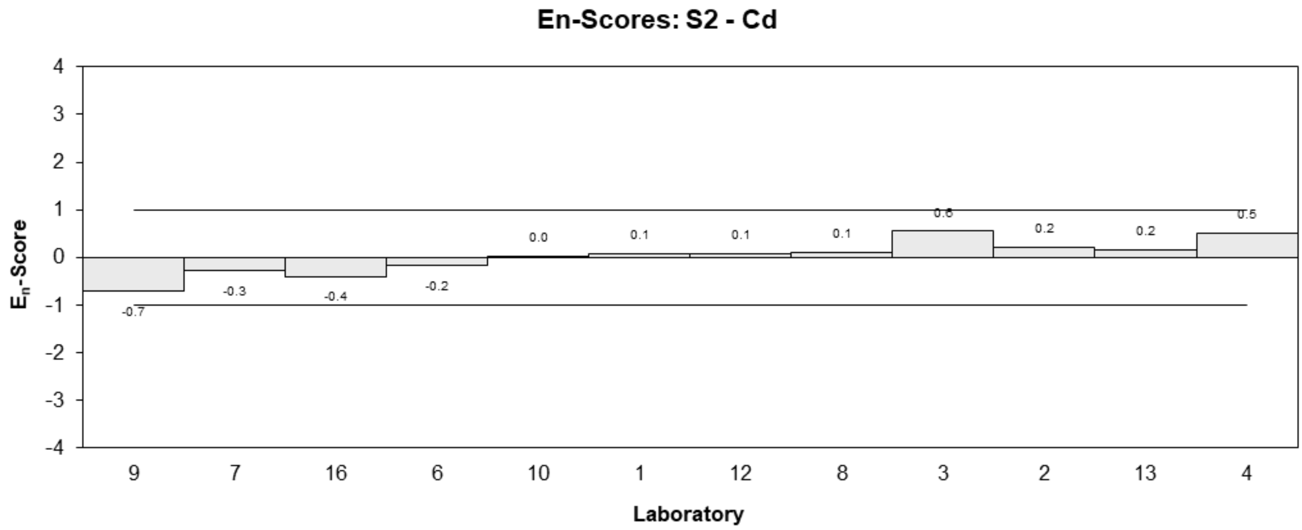
| | | |
|---|---|---|
| **Assigned Value** | 2.49 | 0.10 |
| **Spike Value** | 2.53 | 0.11 |
| **Homogeneity Value** | 2.40 | 0.29 |
| **Robust Average** | 2.49 | 0.10 |
| **Median** | 2.51 | 0.10 |
| **Mean** | 2.48 | |
| **N** | 12 | |
| **Max** | 2.66 | |
| **Min** | 2.17 | |
| **Robust SD** | 0.14 | |
| **Robust CV** | 5.5% | |



Results: S2 - Cd
Assigned Value = 2.49 ± 0.10 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
9
7
16
6
10
1
12
8
3
2
13
4
5
11
14
15
18
Md
RA
HV
SV

z-Scores: S2 - Cd
Target Standard Deviation for Proficiency Assessment 0.25 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.3
-0.6
-0.6
-0.4
0.0
0.1
0.1
0.1
0.4
0.4
0.4
0.7
9
7
16
6
10
1
12
8
3
2
13
4

En-Scores: S2 - Cd
$E_n$-Score
Laboratory
-0.7
-0.3
-0.4
-0.2
0.0
0.1
0.1
0.1
0.6
0.2
0.2
0.5
9
7
16
6
10
1
12
8
3
2
13
4


Figure 26

Table 29

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Co |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <1 | NR | | |
| **2** | 1.2 | 0.6 | 0.95 | 0.25 |
| **3** | 1.16 | 0.06 | 0.70 | 1.10 |
| **4** | 1.11 | 0.24 | 0.38 | 0.24 |
| **5** | NT | NT | | |
| **6** | 1.0 | 0.20 | -0.32 | -0.23 |
| **7** | 0.97 | 0.24 | -0.51 | -0.32 |
| **8** | 1.07 | 0.11 | 0.13 | 0.15 |
| **9** | < 1 | 0.2 | | |
| **10** | 1.0 | 0.20 | -0.32 | -0.23 |
| **11** | NT | NT | | |
| **12** | <1 | <0.3 | | |
| **13** | <1 | 1 | | |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 1.00 | 0.14 | -0.32 | -0.31 |
| **18** | 0.977 | 0.018 | -0.46 | -0.89 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.05 | 0.08 |
| **Spike Value** | 1.02 | 0.03 |
| **Homogeneity Value** | 0.99 | 0.12 |
| **Robust Average** | 1.05 | 0.08 |
| **Median** | 1.00 | 0.04 |
| **Mean** | 1.05 | |
| **N** | 9 | |
| **Max** | 1.2 | |
| **Min** | 0.97 | |
| **Robust SD** | 0.096 | |
| **Robust CV** | 9.1% | |

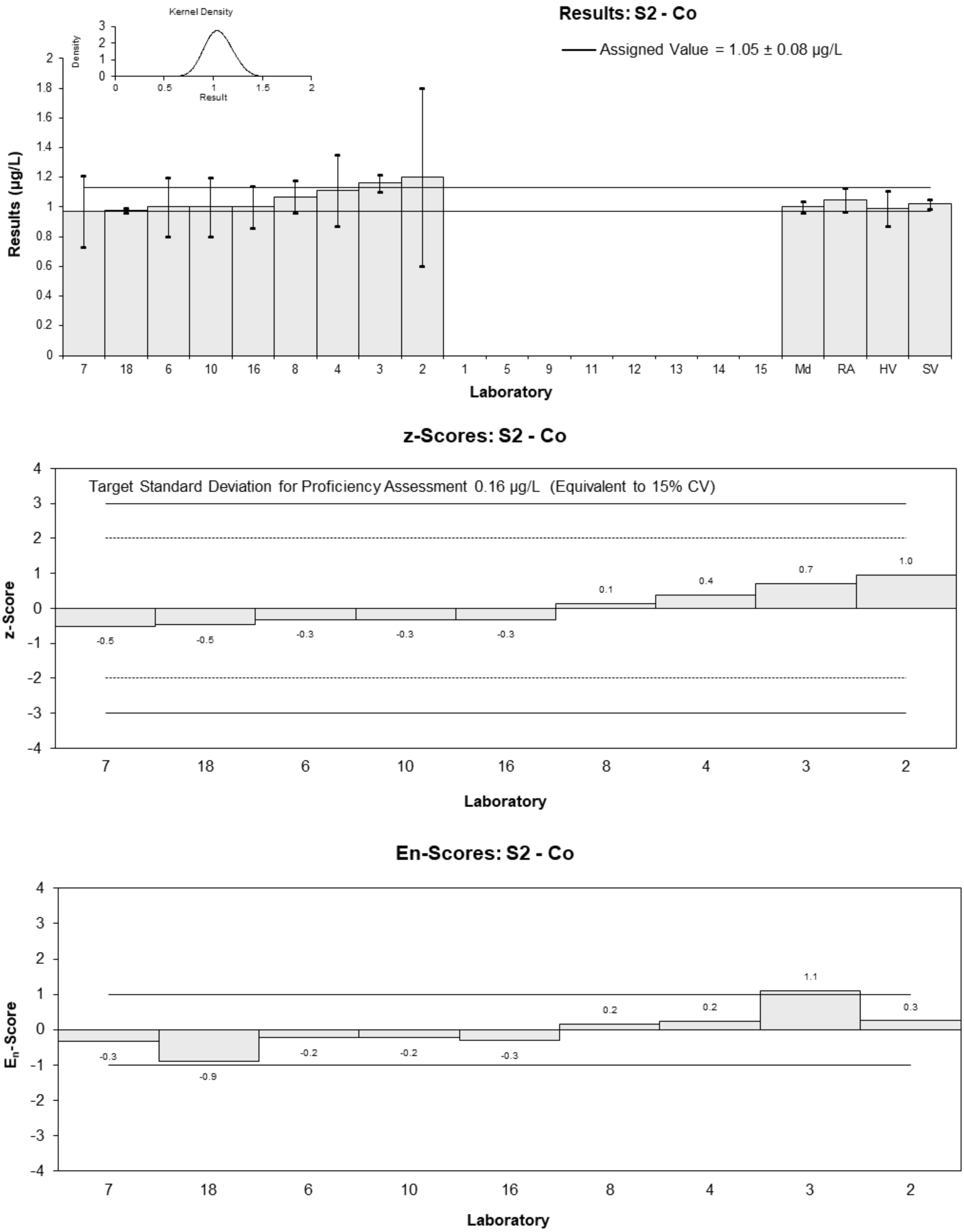

Results: S2 - Co
Assigned Value = 1.05 ± 0.08 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
18
6
10
16
8
4
3
2
1
5
9
11
12
13
14
15
Md
RA
HV
SV
z-Scores: S2 - Co
Target Standard Deviation for Proficiency Assessment 0.16 µg/L (Equivalent to 15% CV)
z-Score
-0.5
-0.5
-0.3
-0.3
-0.3
0.1
0.4
0.7
1.0
Laboratory
En-Scores: S2 - Co
En-Score
-0.3
-0.9
-0.2
-0.2
-0.3
0.2
0.2
1.1
0.3
Laboratory

Figure 27

Table 30

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Cr |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2.03 | 0.18 | 0.85 | 0.90 |
| **2** | 2.0 | 1.3 | 0.74 | 0.15 |
| **3** | 1.00 | 0.05 | -2.96 | -4.28 |
| **4** | 1.94 | 0.30 | 0.52 | 0.40 |
| **5** | NT | NT | | |
| **6** | 1.8 | 0.36 | 0.00 | 0.00 |
| **7** | 1.75 | 0.48 | -0.19 | -0.10 |
| **8** | 1.93 | 0.19 | 0.48 | 0.50 |
| **9** | 1.64 | 0.328 | -0.59 | -0.43 |
| **10** | 1.7 | 0.34 | -0.37 | -0.26 |
| **11** | NT | NT | | |
| **12** | 1.29 | 0.1935 | -1.89 | -1.93 |
| **13** | 1.7 | 1.2 | -0.37 | -0.08 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 1.87 | 0.37 | 0.26 | 0.17 |
| **18** | 2.5 | 0.4 | 2.59 | 1.60 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.80 | 0.18 |
| **Spike Value** | 1.97 | 0.07 |
| **Homogeneity Value** | 1.98 | 0.24 |
| **Robust Average** | 1.80 | 0.18 |
| **Median** | 1.80 | 0.14 |
| **Mean** | 1.78 | |
| **N** | 13 | |
| **Max** | 2.5 | |
| **Min** | 1 | |
| **Robust SD** | 0.27 | |
| **Robust CV** | 15% | |

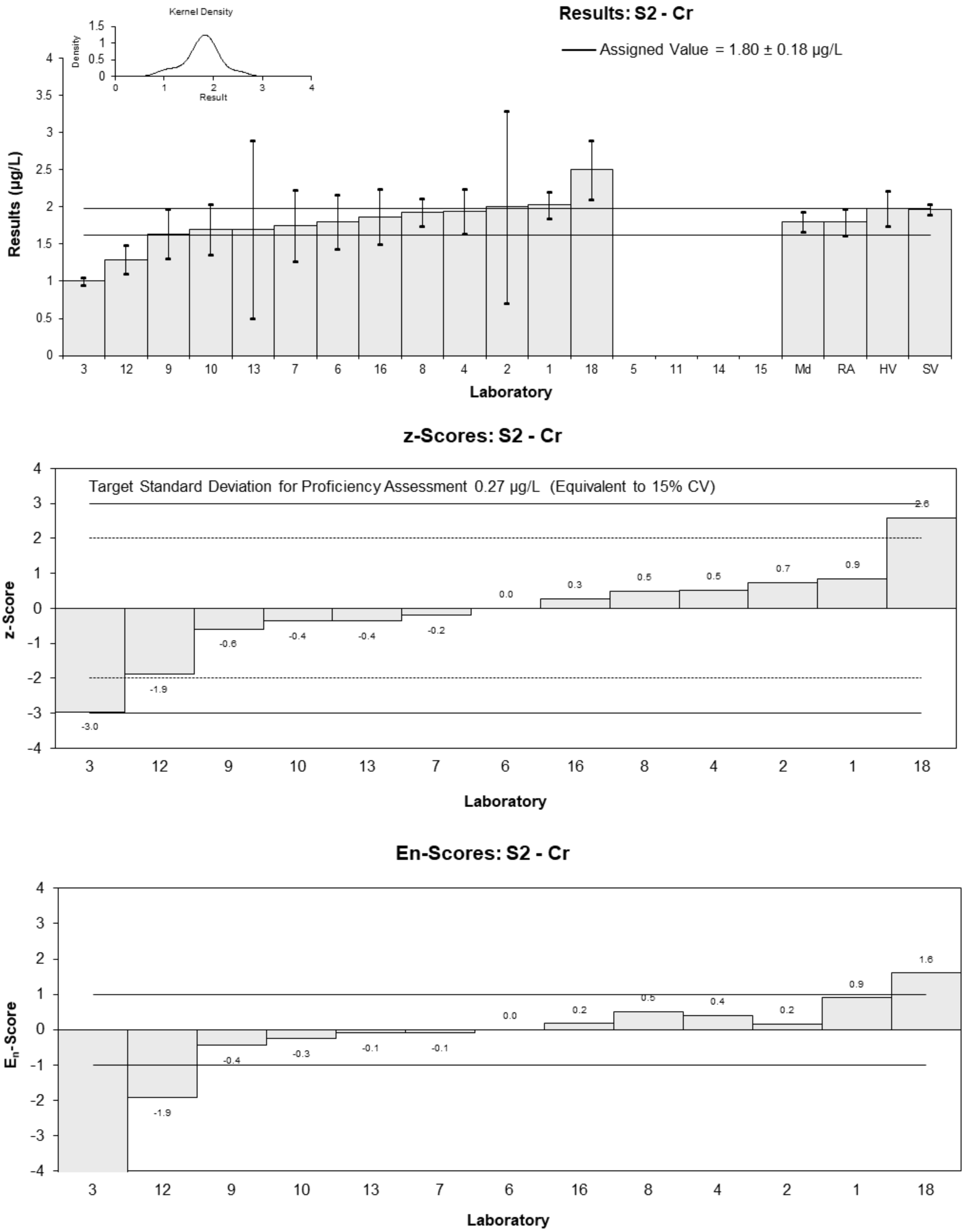

Results: S2 - Cr
Assigned Value = 1.80 ± 0.18 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3 12 9 10 13 7 6 16 8 4 2 1 18 5 11 14 15 Md RA HV SV
z-Scores: S2 - Cr
Target Standard Deviation for Proficiency Assessment 0.27 µg/L (Equivalent to 15% CV)
z-Score
-3.0 -1.9 -0.6 -0.4 -0.4 -0.2 0.0 0.3 0.5 0.5 0.7 0.9 2.6
3 12 9 10 13 7 6 16 8 4 2 1 18
Laboratory
En-Scores: S2 - Cr
$E_n$-Score
-1.9 -0.4 -0.3 -0.1 -0.1 0.0 0.2 0.5 0.4 0.2 0.9 1.6
3 12 9 10 13 7 6 16 8 4 2 1 18
Laboratory

Figure 28

Table 31

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Cu |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 27.68 | 2.19 | 0.14 | 0.14 |
| **2** | 29 | 5 | 0.62 | 0.33 |
| **3** | 31.86 | 1.59 | 1.67 | 2.09 |
| **4** | 29.7 | 4.8 | 0.88 | 0.48 |
| **5** | NT | NT | | |
| **6** | 27 | 5.4 | -0.11 | -0.05 |
| **7** | 27.4 | 6.4 | 0.04 | 0.02 |
| **8** | 25.66 | 2.6 | -0.60 | -0.55 |
| **9** | 25.9 | 5.19 | -0.51 | -0.26 |
| **10** | 25 | 5.0 | -0.84 | -0.44 |
| **11** | NT | NT | | |
| **12** | 24 | 4.8 | -1.21 | -0.66 |
| **13** | 27 | 2 | -0.11 | -0.12 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 26.9 | 2.5 | -0.15 | -0.14 |
| **18** | 29.0 | 1.5 | 0.62 | 0.80 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 27.3 | 1.5 |
| **Spike Value** | 27.8 | 1.6 |
| **Homogeneity Value** | 27.0 | 3.2 |
| **Robust Average** | 27.3 | 1.5 |
| **Median** | 27.0 | 1.4 |
| **Mean** | 27.4 | |
| **N** | 13 | |
| **Max** | 31.86 | |
| **Min** | 24 | |
| **Robust SD** | 2.1 | |
| **Robust CV** | 7.8% | |

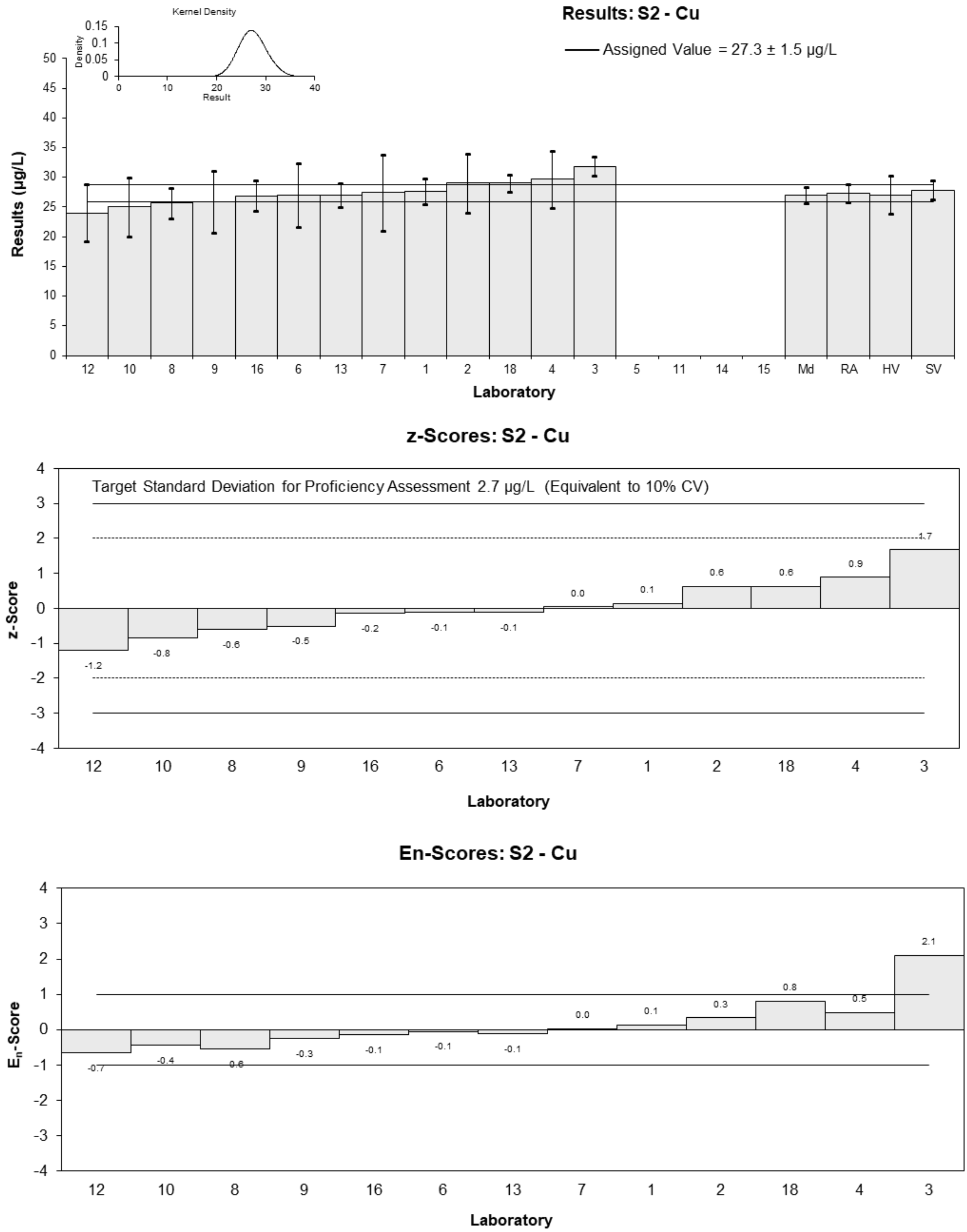

Results: S2 - Cu
Assigned Value = 27.3 ± 1.5 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12
10
8
9
16
6
13
7
1
2
18
4
3
5
11
14
15
Md
RA
HV
SV
z-Scores: S2 - Cu
Target Standard Deviation for Proficiency Assessment 2.7 µg/L (Equivalent to 10% CV)
z-Score
-1.2
-0.8
-0.6
-0.5
-0.2
-0.1
-0.1
0.0
0.1
0.6
0.6
0.9
1.7
En-Scores: S2 - Cu
En-Score
-0.7
-0.4
-0.6
-0.3
-0.1
-0.1
-0.1
0.0
0.1
0.3
0.8
0.5
2.1

Figure 29

Table 32

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Fe |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 375.9 | 35.34 | -0.39 | -0.34 |
| **2** | 430 | 50 | 1.00 | 0.69 |
| **3** | 427.5 | 21.38 | 0.93 | 1.08 |
| **4** | 410 | 62 | 0.49 | 0.28 |
| **5** | NT | NT | | |
| **6** | 365 | 73 | -0.66 | -0.34 |
| **7** | 430 | 103 | 1.00 | 0.37 |
| **8** | 406.52 | 57 | 0.40 | 0.25 |
| **9** | 376 | 75.1 | -0.38 | -0.19 |
| **10** | 410 | 82 | 0.49 | 0.22 |
| **11** | NT | NT | | |
| **12** | 352 | 52.8 | -1.00 | -0.66 |
| **13** | 327 | 33 | -1.64 | -1.52 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 371 | 29 | -0.51 | -0.51 |
| **18** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 391 | 26 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 348 | 42 |
| **Robust Average** | 391 | 26 |
| **Median** | 391 | 25 |
| **Mean** | 390 | |
| **N** | 12 | |
| **Max** | 430 | |
| **Min** | 327 | |
| **Robust SD** | 36 | |
| **Robust CV** | 9.3% | |

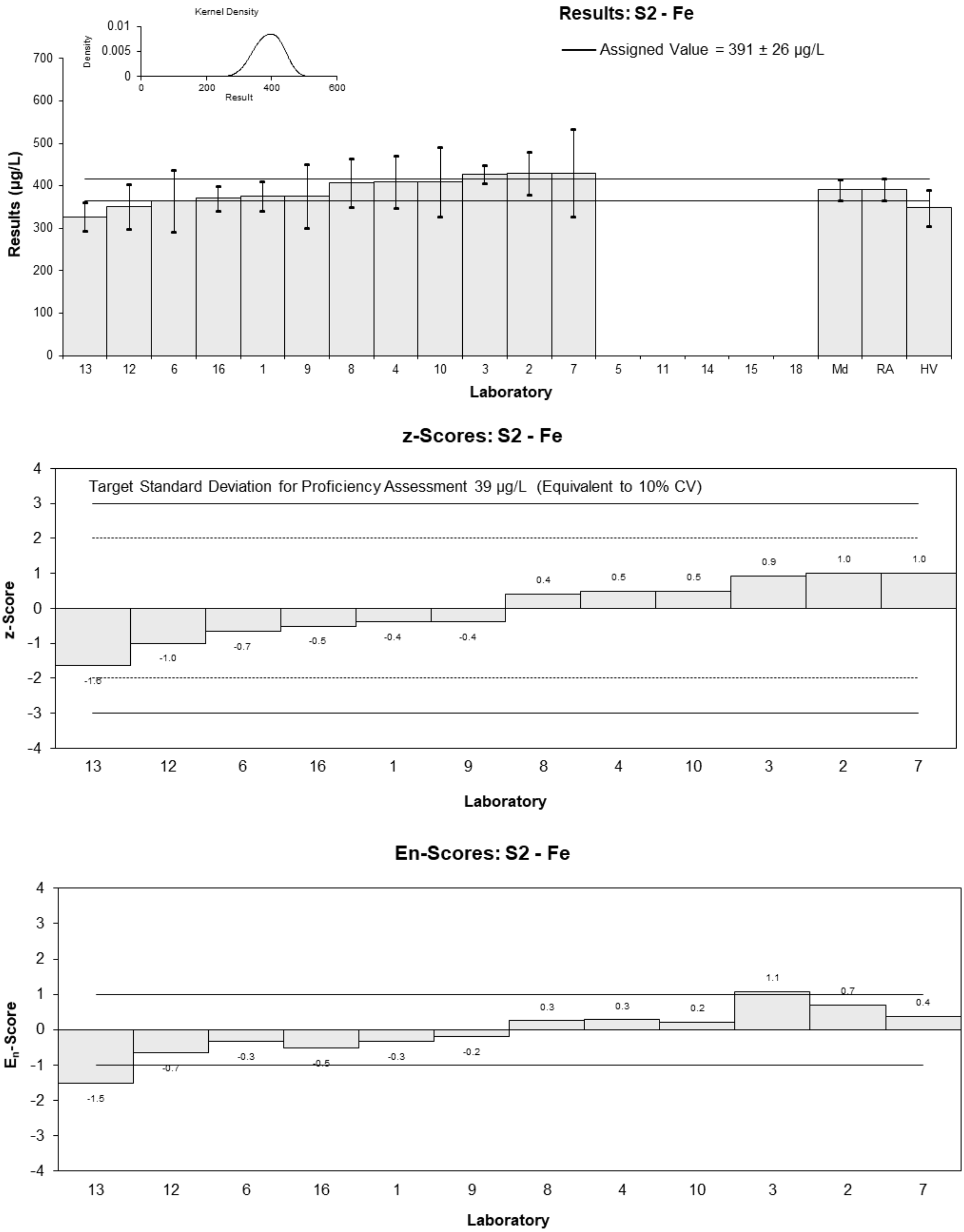

Results: S2 - Fe
Assigned Value = 391 ± 26 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
13 12 6 16 1 9 8 4 10 3 2 7 5 11 14 15 18 Md RA HV
z-Scores: S2 - Fe
Target Standard Deviation for Proficiency Assessment 39 µg/L (Equivalent to 10% CV)
z-Score
-1.6 -1.0 -0.7 -0.5 -0.4 -0.4 0.4 0.5 0.5 0.9 1.0 1.0
13 12 6 16 1 9 8 4 10 3 2 7
Laboratory
En-Scores: S2 - Fe
$E_n$-Score
-1.5 -0.7 -0.3 -0.5 -0.3 -0.2 0.3 0.3 0.2 1.1 0.7 0.4
13 12 6 16 1 9 8 4 10 3 2 7
Laboratory

Figure 30

Table 33

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Hg |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.464 | 0.081 | 0.10 | 0.08 |
| **2** | 0.51 | 0.04 | 0.77 | 1.09 |
| **3** | 0.51 | 0.03 | 0.77 | 1.29 |
| **4** | 0.463 | 0.093 | 0.09 | 0.06 |
| **5** | NT | NT | | |
| **6** | <0.5 | NR | | |
| **7** | 0.44 | 0.09 | -0.25 | -0.18 |
| **8** | 0.47 | 0.08 | 0.19 | 0.15 |
| **9** | 0.47 | 0.094 | 0.19 | 0.13 |
| **10** | 0.44 | 0.09 | -0.25 | -0.18 |
| **11** | NT | NT | | |
| **12** | 0.408 | 0.0816 | -0.71 | -0.57 |
| **13** | 0.42 | 0.08 | -0.54 | -0.44 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 0.437 | 0.075 | -0.29 | -0.25 |
| **18** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.457 | 0.028 |
| **Spike Value** | 0.530 | 0.051 |
| **Homogeneity Value** | 0.445 | 0.053 |
| **Robust Average** | 0.457 | 0.028 |
| **Median** | 0.463 | 0.026 |
| **Mean** | 0.457 | |
| **N** | 11 | |
| **Max** | 0.51 | |
| **Min** | 0.408 | |
| **Robust SD** | 0.037 | |
| **Robust CV** | 8.1% | |

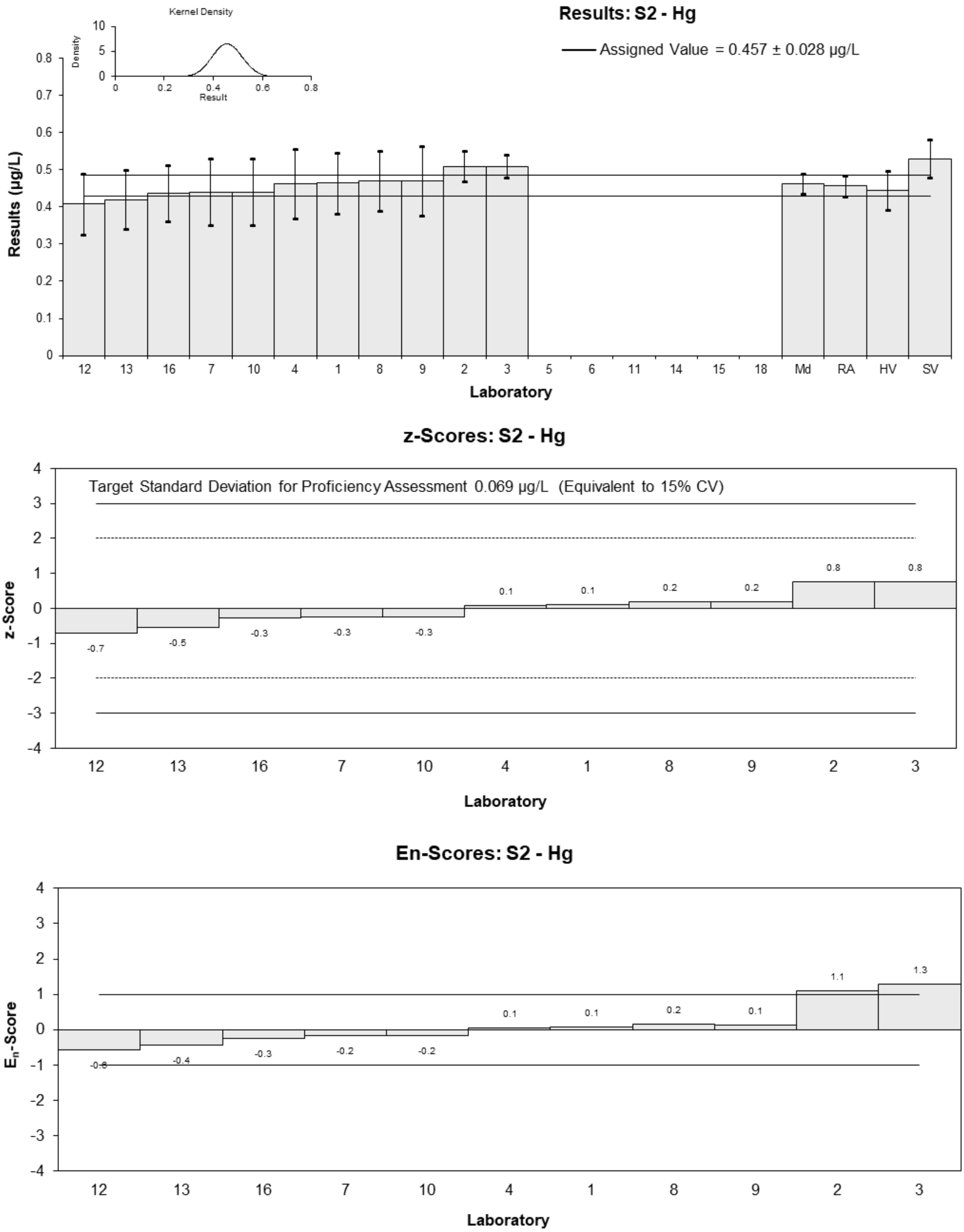

Results: S2 - Hg
Assigned Value = 0.457 ± 0.028 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12
13
16
7
10
4
1
8
9
2
3
5
6
11
14
15
18
Md
RA
HV
SV
z-Scores: S2 - Hg
Target Standard Deviation for Proficiency Assessment 0.069 µg/L (Equivalent to 15% CV)
z-Score
-0.7
-0.5
-0.3
-0.3
-0.3
0.1
0.1
0.2
0.2
0.8
0.8
Laboratory
En-Scores: S2 - Hg
En-Score
-0.6
-0.4
-0.3
-0.2
-0.2
0.1
0.1
0.2
0.1
1.1
1.3
Laboratory

Figure 31

Table 34

**Sample Details**

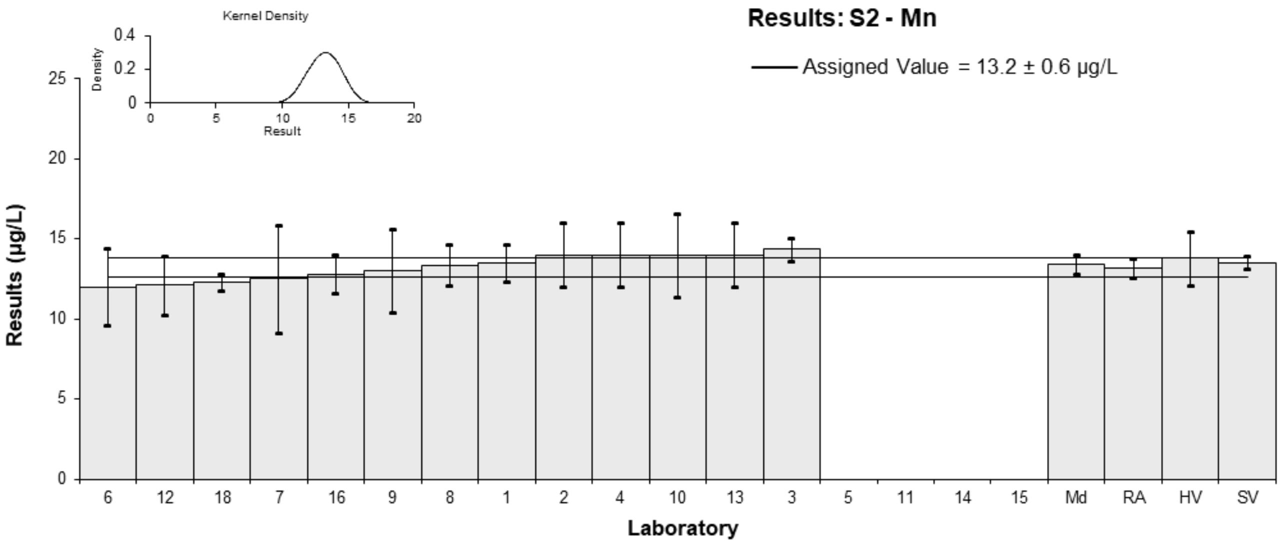
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Mn |
| **Unit** | µg/L |

**Participant Results**

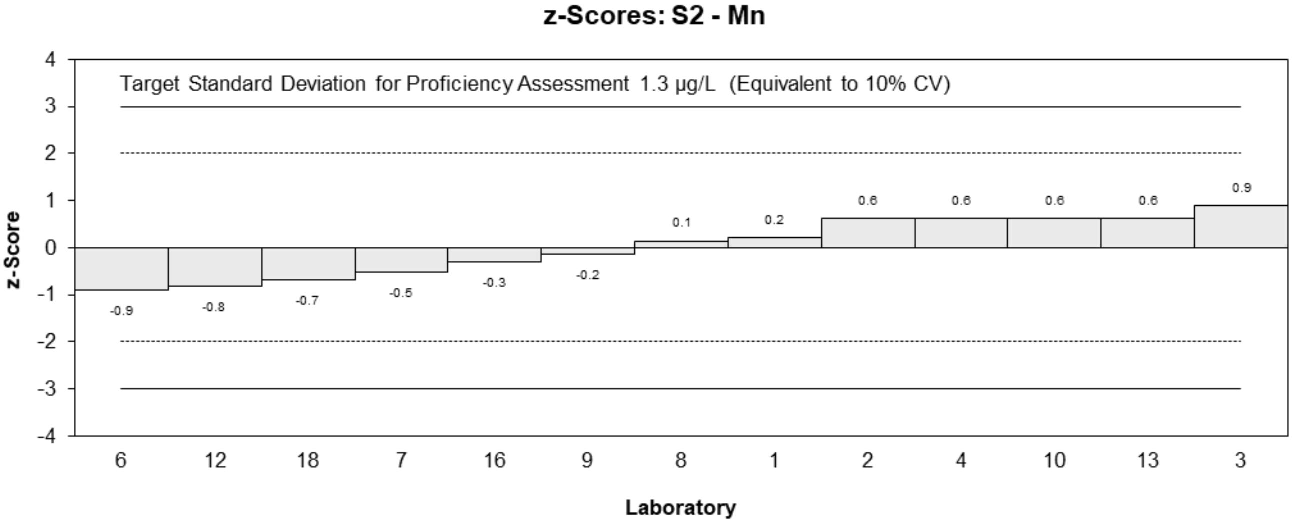
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 13.47 | 1.16 | 0.20 | 0.21 |
| **2** | 14 | 2 | 0.61 | 0.38 |
| **3** | 14.36 | 0.72 | 0.88 | 1.24 |
| **4** | 14.0 | 2.0 | 0.61 | 0.38 |
| **5** | NT | NT | | |
| **6** | 12 | 2.4 | -0.91 | -0.49 |
| **7** | 12.5 | 3.4 | -0.53 | -0.20 |
| **8** | 13.37 | 1.3 | 0.13 | 0.12 |
| **9** | 13.0 | 2.60 | -0.15 | -0.07 |
| **10** | 14 | 2.6 | 0.61 | 0.30 |
| **11** | NT | NT | | |
| **12** | 12.1 | 1.815 | -0.83 | -0.58 |
| **13** | 14 | 2 | 0.61 | 0.38 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 12.8 | 1.2 | -0.30 | -0.30 |
| **18** | 12.3 | 0.5 | -0.68 | -1.15 |

**Statistics**

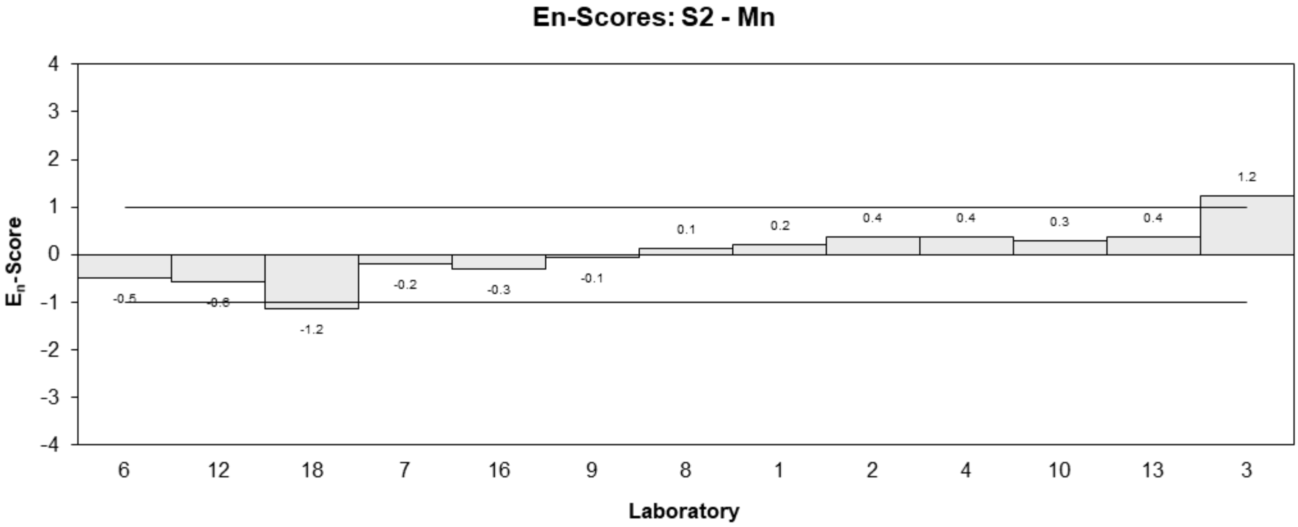
| | | |
|---|---|---|
| **Assigned Value** | 13.2 | 0.6 |
| **Spike Value** | 13.5 | 0.4 |
| **Homogeneity Value** | 13.8 | 1.7 |
| **Robust Average** | 13.2 | 0.6 |
| **Median** | 13.4 | 0.6 |
| **Mean** | 13.2 | |
| **N** | 13 | |
| **Max** | 14.36 | |
| **Min** | 12 | |
| **Robust SD** | 0.93 | |
| **Robust CV** | 7.1% | |



Results: S2 - Mn
Assigned Value = 13.2 ± 0.6 µg/L
Kernel Density
Density
Result
Results (µg/L)
6 12 18 7 16 9 8 1 2 4 10 13 3 5 11 14 15 Md RA HV SV
Laboratory

z-Scores: S2 - Mn
Target Standard Deviation for Proficiency Assessment 1.3 µg/L (Equivalent to 10% CV)
z-Score
-0.9 -0.8 -0.7 -0.5 -0.3 -0.2 0.1 0.2 0.6 0.6 0.6 0.6 0.9
6 12 18 7 16 9 8 1 2 4 10 13 3
Laboratory

En-Scores: S2 - Mn
En-Score
-0.5 -0.6 -1.2 -0.2 -0.3 -0.1 0.1 0.2 0.4 0.4 0.3 0.4 1.2
6 12 18 7 16 9 8 1 2 4 10 13 3
Laboratory


Figure 32

Table 35

**Sample Details**

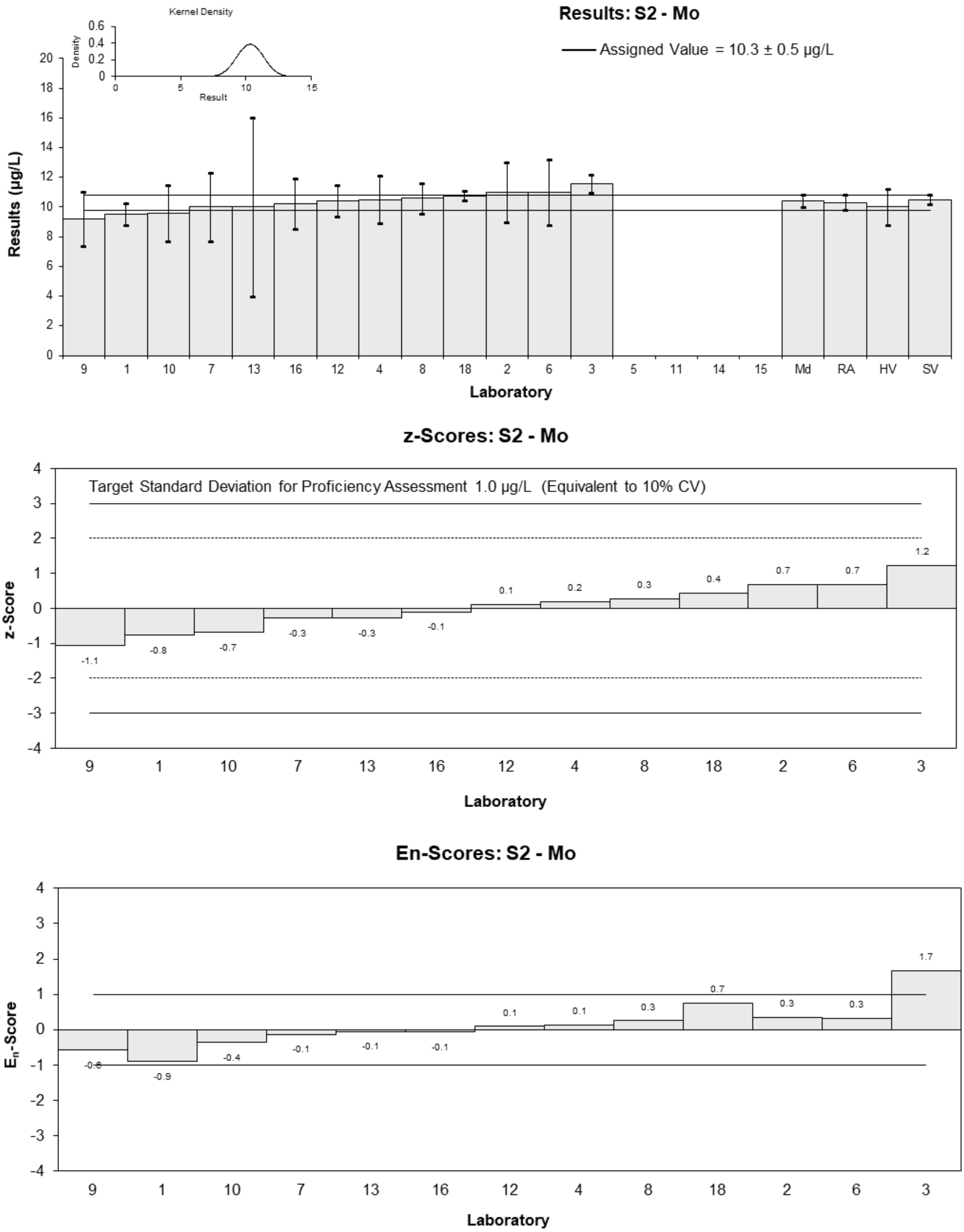
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Mo |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 9.51 | 0.73 | -0.77 | -0.89 |
| **2** | 11 | 2 | 0.68 | 0.34 |
| **3** | 11.57 | 0.58 | 1.23 | 1.66 |
| **4** | 10.5 | 1.6 | 0.19 | 0.12 |
| **5** | NT | NT | | |
| **6** | 11 | 2.2 | 0.68 | 0.31 |
| **7** | 10.0 | 2.3 | -0.29 | -0.13 |
| **8** | 10.58 | 1.0 | 0.27 | 0.25 |
| **9** | 9.2 | 1.84 | -1.07 | -0.58 |
| **10** | 9.6 | 1.9 | -0.68 | -0.36 |
| **11** | NT | NT | | |
| **12** | 10.4 | 1.04 | 0.10 | 0.09 |
| **13** | 10 | 6 | -0.29 | -0.05 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 10.2 | 1.7 | -0.10 | -0.06 |
| **18** | 10.74 | 0.32 | 0.43 | 0.74 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 10.3 | 0.5 |
| **Spike Value** | 10.5 | 0.3 |
| **Homogeneity Value** | 10.0 | 1.2 |
| **Robust Average** | 10.3 | 0.5 |
| **Median** | 10.4 | 0.4 |
| **Mean** | 10.3 | |
| **N** | 13 | |
| **Max** | 11.57 | |
| **Min** | 9.2 | |
| **Robust SD** | 0.73 | |
| **Robust CV** | 7.1% | |



Results: S2 - Mo
Assigned Value = 10.3 ± 0.5 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
9 1 10 7 13 16 12 4 8 18 2 6 3 5 11 14 15 Md RA HV SV
z-Scores: S2 - Mo
Target Standard Deviation for Proficiency Assessment 1.0 µg/L (Equivalent to 10% CV)
z-Score
-1.1 -0.8 -0.7 -0.3 -0.3 -0.1 0.1 0.2 0.3 0.4 0.7 0.7 1.2
Laboratory
9 1 10 7 13 16 12 4 8 18 2 6 3
En-Scores: S2 - Mo
$E_n$-Score
-0.6 -0.9 -0.4 -0.1 -0.1 -0.1 0.1 0.1 0.3 0.7 0.3 0.3 1.7
Laboratory
9 1 10 7 13 16 12 4 8 18 2 6 3


Figure 33

Table 36

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Ni |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 3.67 | 0.33 | 0.05 | 0.07 |
| **2** | 4.0 | 1 | 0.66 | 0.35 |
| **3** | 4.25 | 0.21 | 1.12 | 1.83 |
| **4** | 4.00 | 0.56 | 0.66 | 0.58 |
| **5** | NT | NT | | |
| **6** | 3.5 | 0.70 | -0.26 | -0.19 |
| **7** | 3.47 | 0.78 | -0.31 | -0.21 |
| **8** | 3.96 | 0.40 | 0.59 | 0.67 |
| **9** | 3.54 | 0.708 | -0.18 | -0.13 |
| **10** | 3.6 | 0.72 | -0.07 | -0.05 |
| **11** | NT | NT | | |
| **12** | 3.15 | 0.63 | -0.90 | -0.72 |
| **13** | 3 | 3 | -1.17 | -0.21 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 3.54 | 0.36 | -0.18 | -0.23 |
| **18** | 3.66 | 0.15 | 0.04 | 0.07 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 3.64 | 0.26 |
| **Spike Value** | 3.80 | 0.15 |
| **Homogeneity Value** | 3.70 | 0.44 |
| **Robust Average** | 3.64 | 0.26 |
| **Median** | 3.60 | 0.13 |
| **Mean** | 3.64 | |
| **N** | 13 | |
| **Max** | 4.25 | |
| **Min** | 3 | |
| **Robust SD** | 0.37 | |
| **Robust CV** | 10% | |

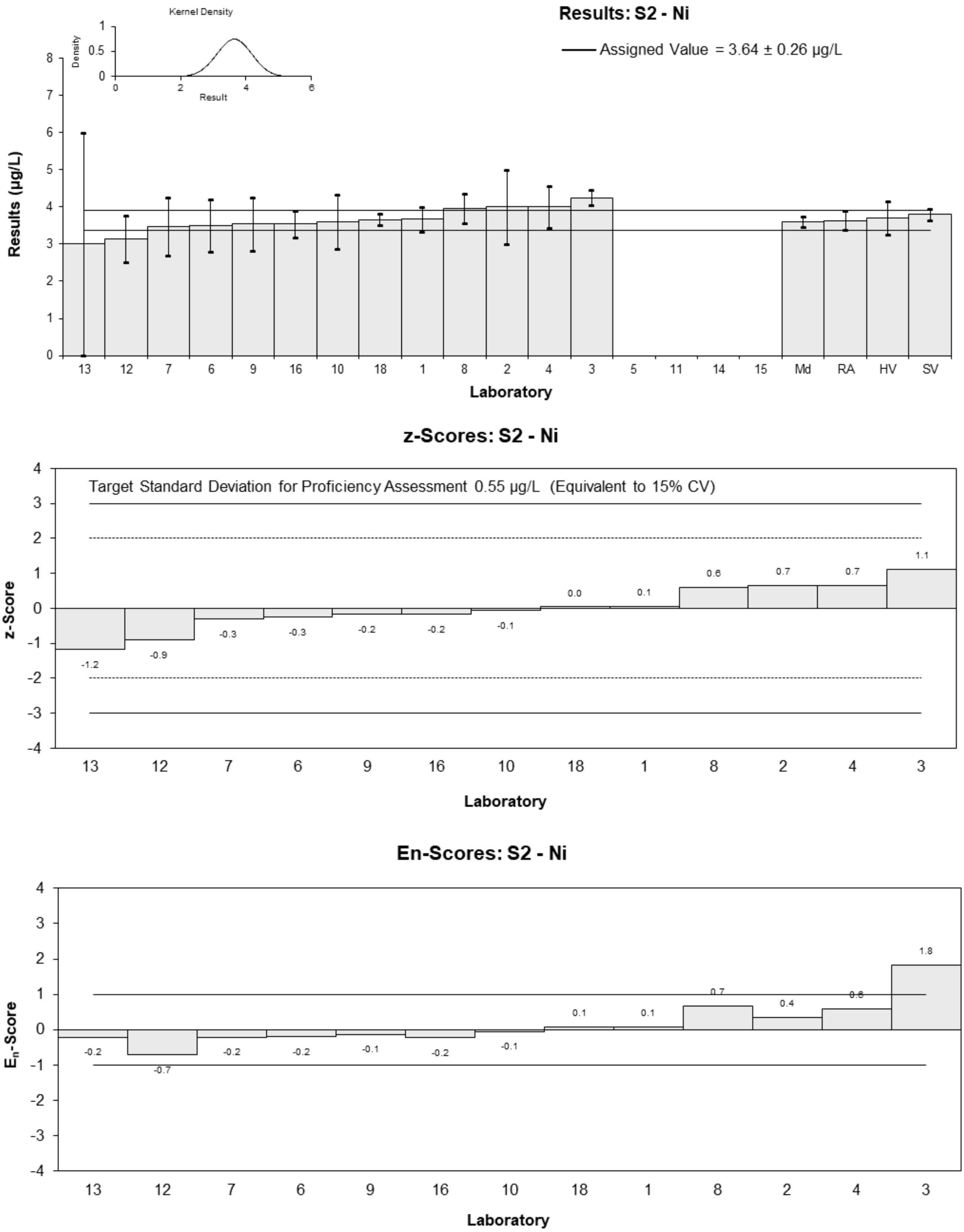

Results: S2 - Ni
Assigned Value = 3.64 ± 0.26 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
z-Scores: S2 - Ni
Target Standard Deviation for Proficiency Assessment 0.55 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S2 - Ni
En-Score
Laboratory

Figure 34

Table 37

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Pb |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 3.12 | 0.25 | 0.37 | 0.35 |
| **2** | 3.0 | 0.5 | -0.03 | -0.02 |
| **3** | 3.38 | 0.17 | 1.23 | 1.45 |
| **4** | 3.33 | 0.60 | 1.06 | 0.51 |
| **5** | NT | NT | | |
| **6** | 2.8 | 0.56 | -0.70 | -0.36 |
| **7** | 2.93 | 0.65 | -0.27 | -0.12 |
| **8** | 3.26 | 0.36 | 0.83 | 0.61 |
| **9** | 2.73 | 0.546 | -0.93 | -0.48 |
| **10** | 3.2 | 0.64 | 0.63 | 0.28 |
| **11** | NT | NT | | |
| **12** | 2.67 | 0.4005 | -1.13 | -0.77 |
| **13** | 2.8 | 3 | -0.70 | -0.07 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 2.78 | 0.21 | -0.76 | -0.81 |
| **18** | 3.132 | 0.031 | 0.41 | 0.63 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 3.01 | 0.19 |
| **Spike Value** | 3.04 | 0.10 |
| **Homogeneity Value** | 2.90 | 0.35 |
| **Robust Average** | 3.01 | 0.19 |
| **Median** | 3.00 | 0.21 |
| **Mean** | 3.01 | |
| **N** | 13 | |
| **Max** | 3.38 | |
| **Min** | 2.67 | |
| **Robust SD** | 0.28 | |
| **Robust CV** | 9.1% | |

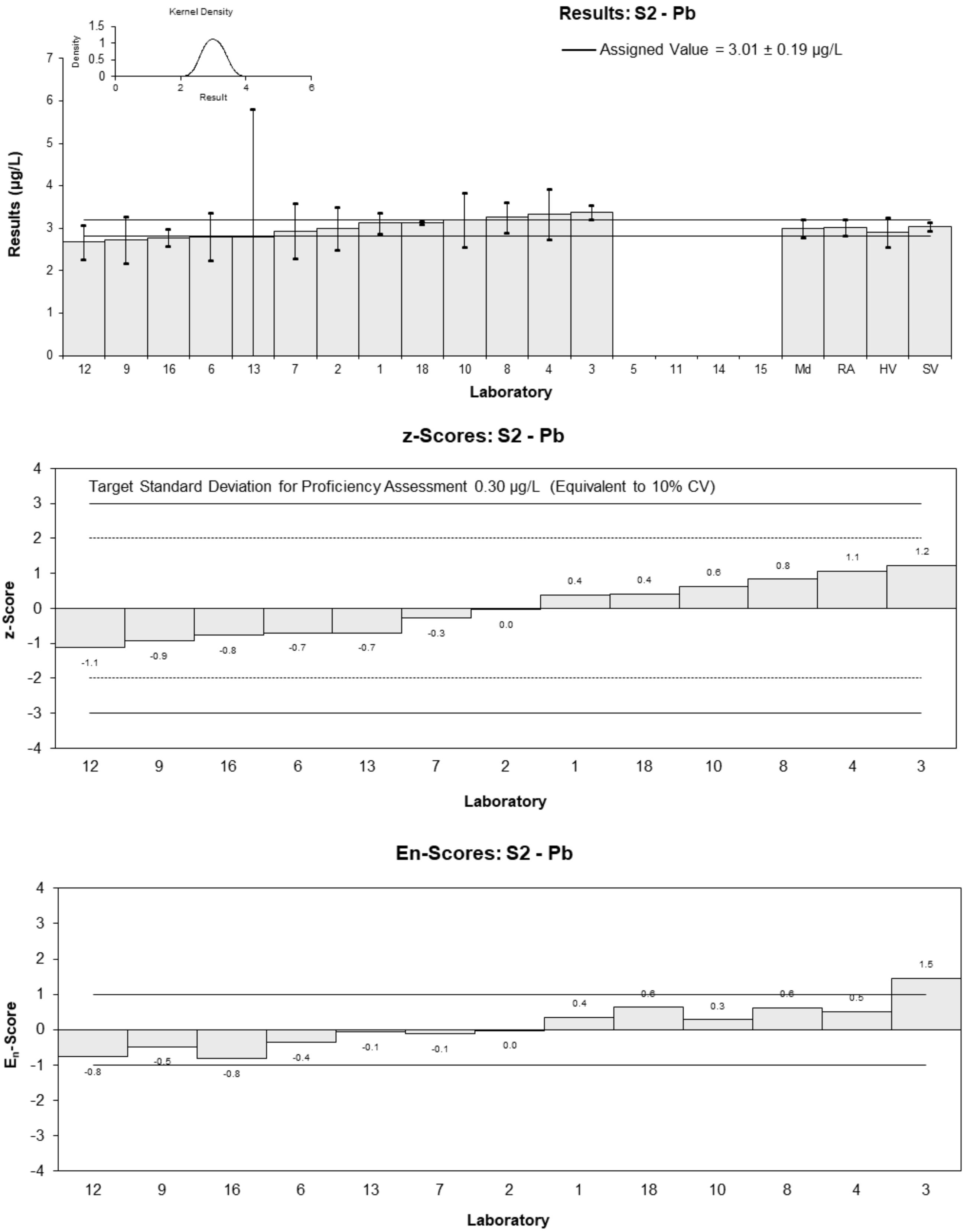

Results: S2 - Pb
Assigned Value = 3.01 ± 0.19 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12 9 16 6 13 7 2 1 18 10 8 4 3 5 11 14 15 Md RA HV SV
z-Scores: S2 - Pb
Target Standard Deviation for Proficiency Assessment 0.30 µg/L (Equivalent to 10% CV)
z-Score
-1.1 -0.9 -0.8 -0.7 -0.7 -0.3 0.0 0.4 0.4 0.6 0.8 1.1 1.2
12 9 16 6 13 7 2 1 18 10 8 4 3
Laboratory
En-Scores: S2 - Pb
$E_n$-Score
-0.8 -0.5 -0.8 -0.4 -0.1 -0.1 0.0 0.4 0.6 0.3 0.6 0.5 1.5
12 9 16 6 13 7 2 1 18 10 8 4 3
Laboratory

Figure 35

Table 38

**Sample Details**

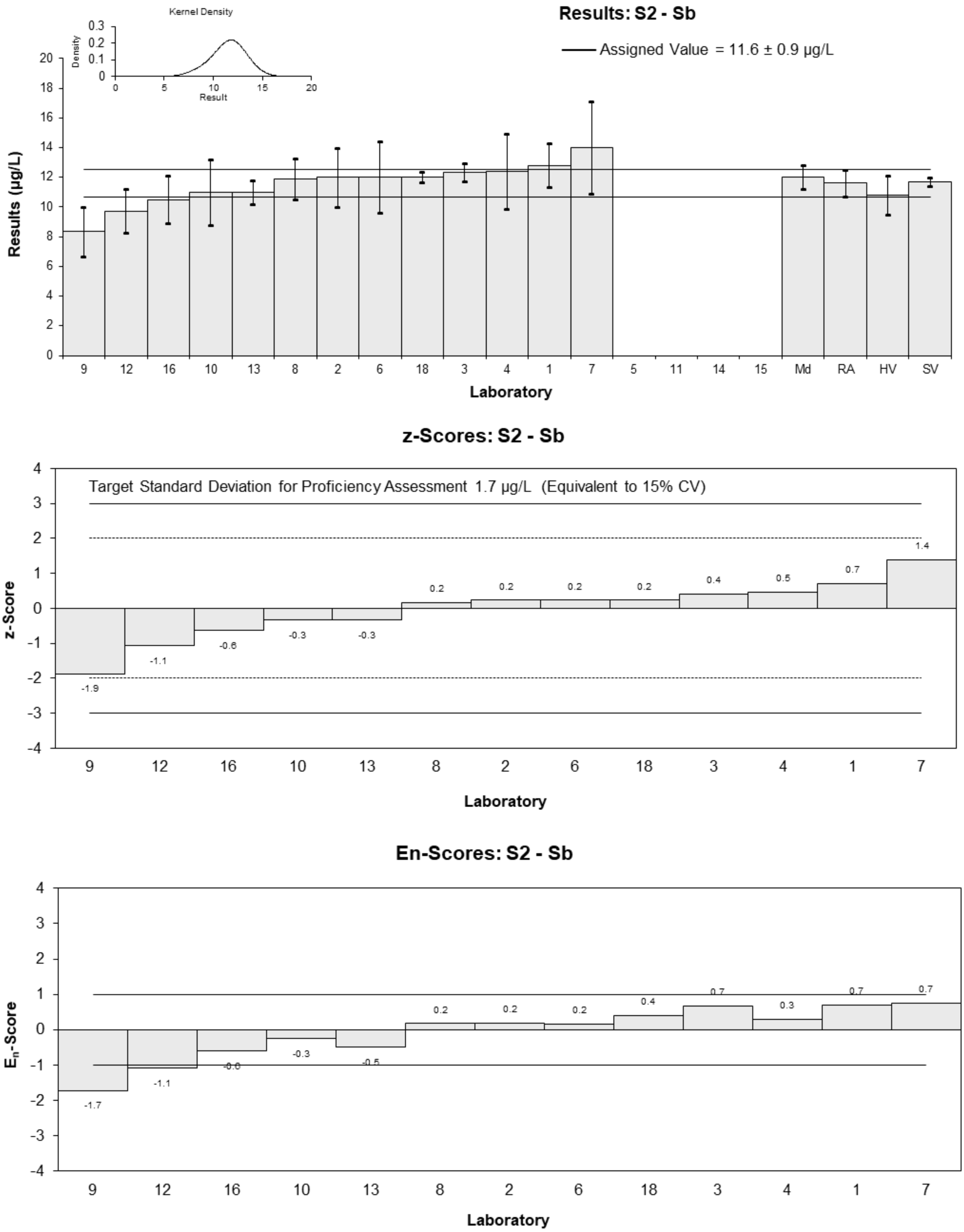
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Sb |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 12.81 | 1.47 | 0.70 | 0.70 |
| **2** | 12 | 2 | 0.23 | 0.18 |
| **3** | 12.32 | 0.62 | 0.41 | 0.66 |
| **4** | 12.4 | 2.5 | 0.46 | 0.30 |
| **5** | NT | NT | | |
| **6** | 12 | 2.4 | 0.23 | 0.16 |
| **7** | 14.0 | 3.1 | 1.38 | 0.74 |
| **8** | 11.88 | 1.4 | 0.16 | 0.17 |
| **9** | 8.34 | 1.67 | -1.87 | -1.72 |
| **10** | 11 | 2.2 | -0.34 | -0.25 |
| **11** | NT | NT | | |
| **12** | 9.74 | 1.461 | -1.07 | -1.08 |
| **13** | 11 | 0.8 | -0.34 | -0.50 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 10.5 | 1.6 | -0.63 | -0.60 |
| **18** | 12.00 | 0.35 | 0.23 | 0.41 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 11.6 | 0.9 |
| **Spike Value** | 11.7 | 0.3 |
| **Homogeneity Value** | 10.8 | 1.3 |
| **Robust Average** | 11.6 | 0.9 |
| **Median** | 12.0 | 0.8 |
| **Mean** | 11.5 | |
| **N** | 13 | |
| **Max** | 14 | |
| **Min** | 8.34 | |
| **Robust SD** | 1.3 | |
| **Robust CV** | 11% | |



Results: S2 - Sb
Assigned Value = 11.6 ± 0.9 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
9 12 16 10 13 8 2 6 18 3 4 1 7 5 11 14 15 Md RA HV SV
z-Scores: S2 - Sb
Target Standard Deviation for Proficiency Assessment 1.7 µg/L (Equivalent to 15% CV)
z-Score
-1.9 -1.1 -0.6 -0.3 -0.3 0.2 0.2 0.2 0.2 0.4 0.5 0.7 1.4
9 12 16 10 13 8 2 6 18 3 4 1 7
Laboratory
En-Scores: S2 - Sb
$E_n$-Score
-1.7 -1.1 -0.6 -0.3 -0.5 0.2 0.2 0.2 0.4 0.7 0.3 0.7 0.7
9 12 16 10 13 8 2 6 18 3 4 1 7
Laboratory


Figure 36

Table 39

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Se |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <10 | NR | | |
| **2** | 3.4 | 0.9 | 0.35 | 0.23 |
| **3** | 3.45 | 0.17 | 0.42 | 0.78 |
| **4** | 3.19 | 0.64 | 0.02 | 0.01 |
| **5** | NT | NT | | |
| **6** | 2.9 | 0.58 | -0.44 | -0.43 |
| **7** | 2.88 | 0.71 | -0.47 | -0.39 |
| **8** | 3.15 | 0.50 | -0.05 | -0.05 |
| **9** | 3.1 | 0.62 | -0.13 | -0.12 |
| **10** | 2.6 | 0.52 | -0.91 | -0.97 |
| **11** | NT | NT | | |
| **12** | 3.6 | 0.54 | 0.66 | 0.68 |
| **13** | 4 | 3 | 1.29 | 0.27 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 2.94 | 0.72 | -0.38 | -0.31 |
| **18** | NT | NT | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 3.18 | 0.30 |
| **Spike Value** | 3.01 | 0.09 |
| **Homogeneity Value** | 2.83 | 0.34 |
| **Robust Average** | 3.18 | 0.30 |
| **Median** | 3.15 | 0.28 |
| **Mean** | 3.20 | |
| **N** | 11 | |
| **Max** | 4 | |
| **Min** | 2.6 | |
| **Robust SD** | 0.40 | |
| **Robust CV** | 12% | |

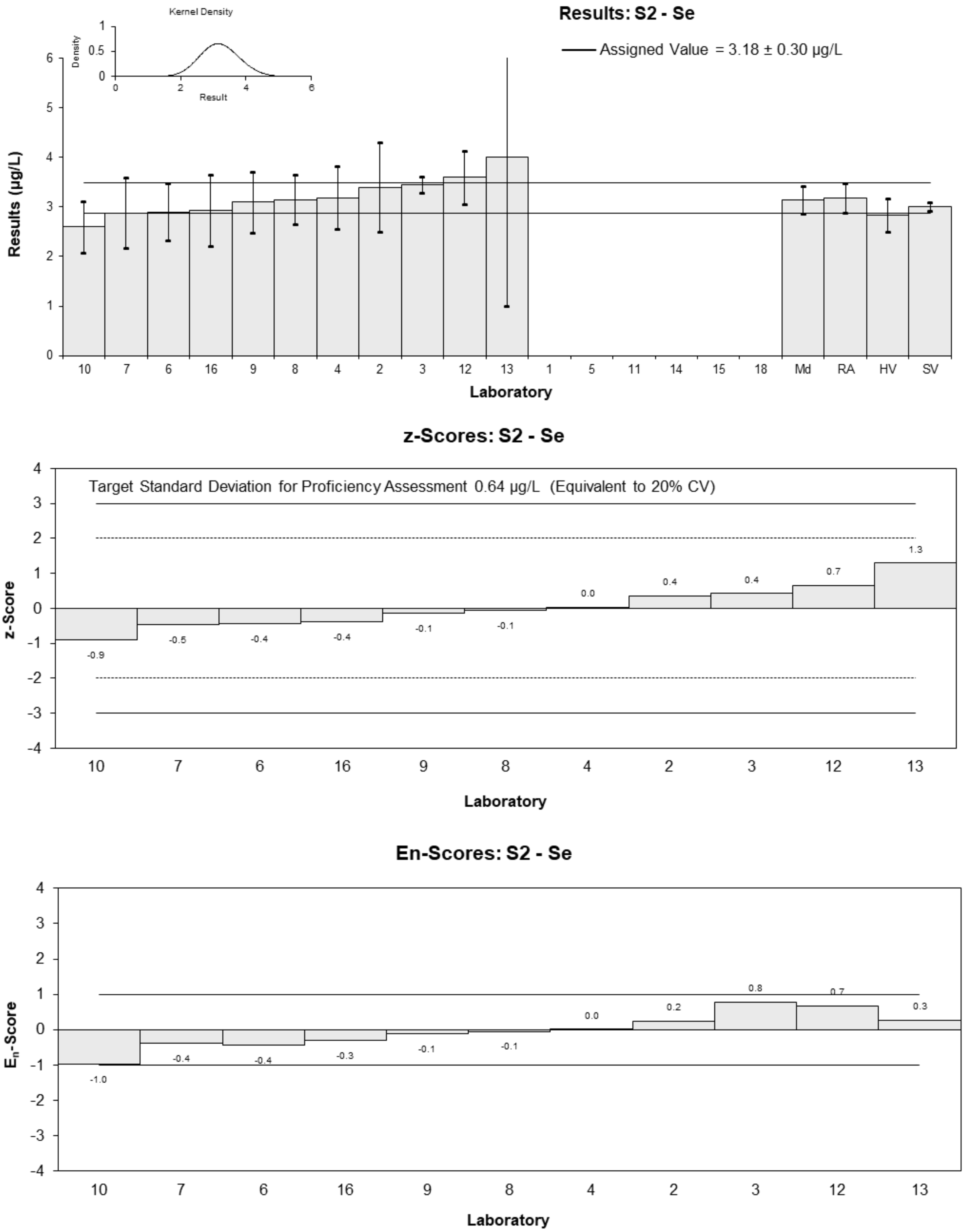

Results: S2 - Se
Assigned Value = 3.18 ± 0.30 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
10 7 6 16 9 8 4 2 3 12 13 1 5 11 14 15 18 Md RA HV SV
z-Scores: S2 - Se
Target Standard Deviation for Proficiency Assessment 0.64 µg/L (Equivalent to 20% CV)
z-Score
-0.9 -0.5 -0.4 -0.4 -0.1 -0.1 0.0 0.4 0.4 0.7 1.3
10 7 6 16 9 8 4 2 3 12 13
Laboratory
En-Scores: S2 - Se
$E_n$-Score
-1.0 -0.4 -0.4 -0.3 -0.1 -0.1 0.0 0.2 0.8 0.7 0.3
10 7 6 16 9 8 4 2 3 12 13
Laboratory

Figure 37

Table 40

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Tl |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <1 | NR | | |
| **2** | 1.0 | 0.5 | -0.07 | -0.02 |
| **3** | 1.14 | 0.06 | 0.86 | 1.53 |
| **4** | 1.07 | 0.18 | 0.40 | 0.32 |
| **5** | NT | NT | | |
| **6** | 1.0 | 0.20 | -0.07 | -0.05 |
| **7** | 0.89 | 0.21 | -0.79 | -0.55 |
| **8** | 1.02 | 0.10 | 0.07 | 0.09 |
| **9** | < 5 | 1 | | |
| **10** | 1.0 | 0.20 | -0.07 | -0.05 |
| **11** | NT | NT | | |
| **12** | <5 | <1.5 | | |
| **13** | 1.0 | 1 | -0.07 | -0.01 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 0.931 | 0.053 | -0.52 | -0.99 |
| **18** | 1.063 | 0.030 | 0.35 | 0.79 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.01 | 0.06 |
| **Spike Value** | 1.04 | 0.03 |
| **Homogeneity Value** | 0.96 | 0.11 |
| **Robust Average** | 1.01 | 0.06 |
| **Median** | 1.00 | 0.05 |
| **Mean** | 1.01 | |
| **N** | 10 | |
| **Max** | 1.14 | |
| **Min** | 0.89 | |
| **Robust SD** | 0.072 | |
| **Robust CV** | 7.2% | |

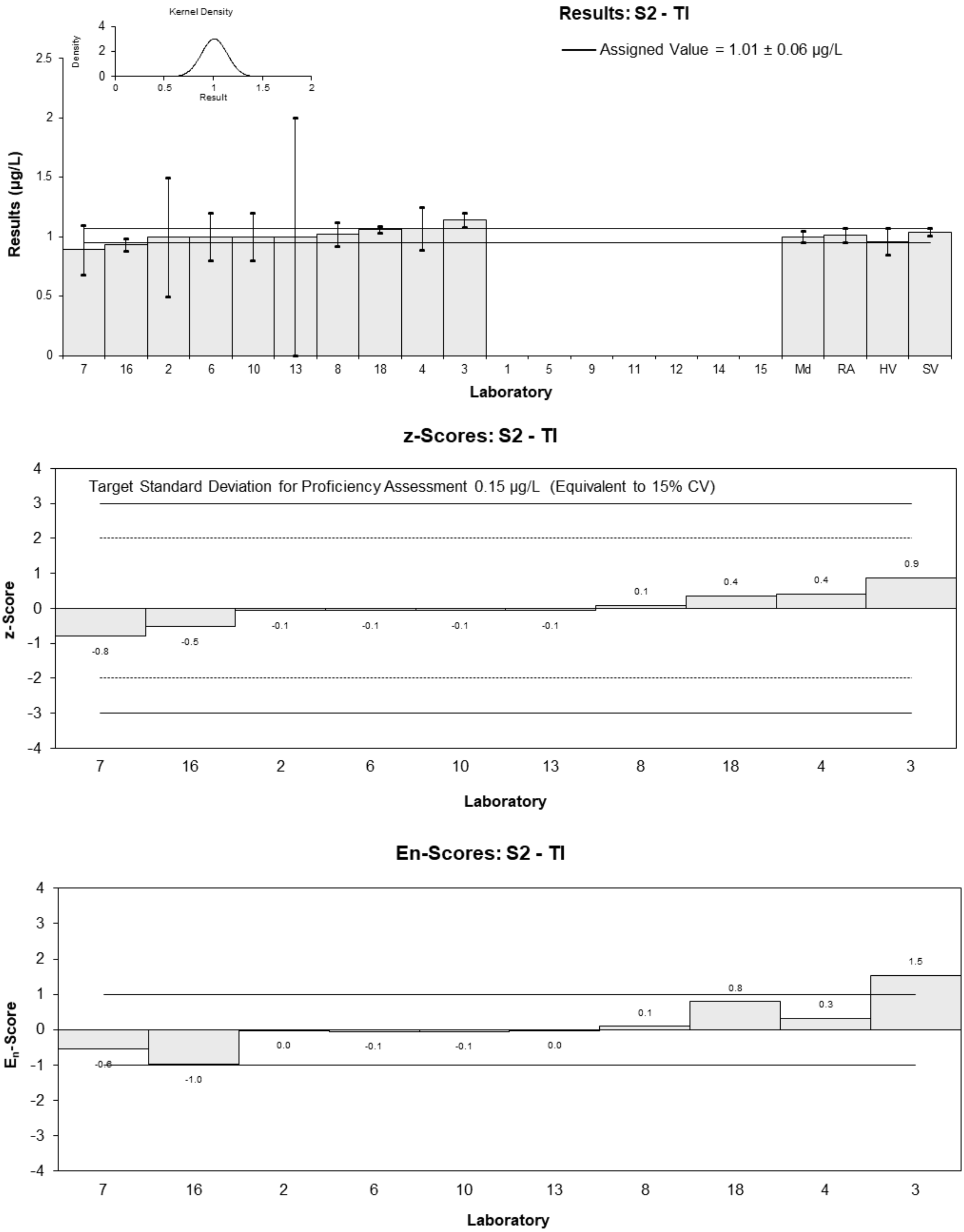

Results: S2 - Tl
Assigned Value = 1.01 ± 0.06 µg/L
Kernel Density
Density
Result
Results (µg/L)
7 16 2 6 10 13 8 18 4 3 1 5 9 11 12 14 15 Md RA HV SV
Laboratory
z-Scores: S2 - Tl
Target Standard Deviation for Proficiency Assessment 0.15 µg/L (Equivalent to 15% CV)
z-Score
-0.8 -0.5 -0.1 -0.1 -0.1 -0.1 0.1 0.4 0.4 0.9
7 16 2 6 10 13 8 18 4 3
Laboratory
En-Scores: S2 - Tl
En-Score
-0.6 -1.0 0.0 -0.1 -0.1 0.0 0.1 0.8 0.3 1.5
7 16 2 6 10 13 8 18 4 3
Laboratory

Figure 38

Table 41

**Sample Details**

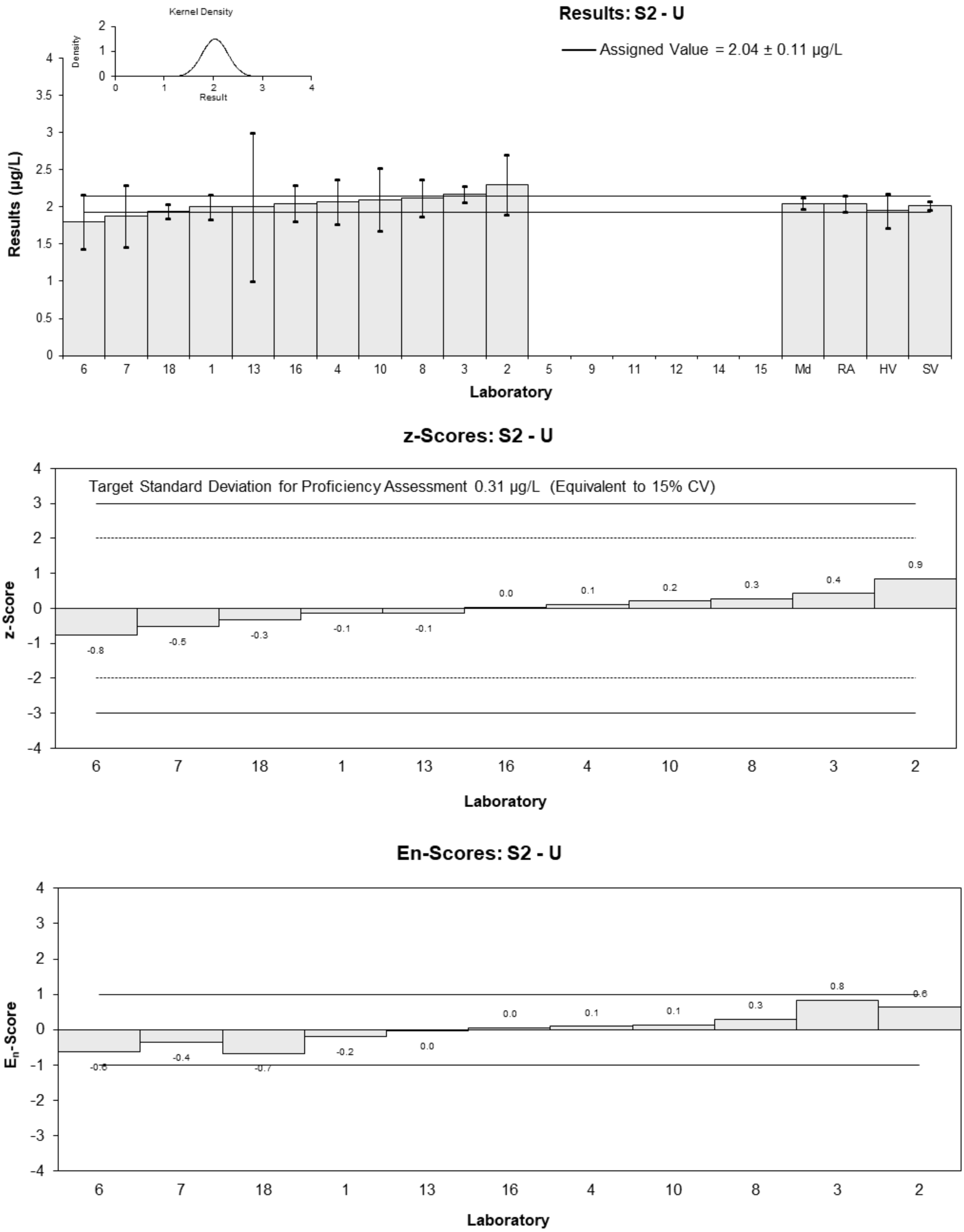
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | U |
| **Unit** | µg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2 | 0.17 | -0.13 | -0.20 |
| **2** | 2.3 | 0.4 | 0.85 | 0.63 |
| **3** | 2.17 | 0.11 | 0.42 | 0.84 |
| **4** | 2.07 | 0.30 | 0.10 | 0.09 |
| **5** | NT | NT | | |
| **6** | 1.8 | 0.36 | -0.78 | -0.64 |
| **7** | 1.88 | 0.42 | -0.52 | -0.37 |
| **8** | 2.12 | 0.25 | 0.26 | 0.29 |
| **9** | < 5 | 1 | | |
| **10** | 2.1 | 0.42 | 0.20 | 0.14 |
| **11** | NT | NT | | |
| **12** | <5 | <1.5 | | |
| **13** | 2 | 1 | -0.13 | -0.04 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 2.05 | 0.24 | 0.03 | 0.04 |
| **18** | 1.94 | 0.10 | -0.33 | -0.67 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2.04 | 0.11 |
| **Spike Value** | 2.02 | 0.06 |
| **Homogeneity Value** | 1.95 | 0.23 |
| **Robust Average** | 2.04 | 0.11 |
| **Median** | 2.05 | 0.08 |
| **Mean** | 2.04 | |
| **N** | 11 | |
| **Max** | 2.3 | |
| **Min** | 1.8 | |
| **Robust SD** | 0.14 | |
| **Robust CV** | 7% | |



Results: S2 - U
Assigned Value = 2.04 ± 0.11 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6 7 18 1 13 16 4 10 8 3 2 5 9 11 12 14 15 Md RA HV SV
z-Scores: S2 - U
Target Standard Deviation for Proficiency Assessment 0.31 µg/L (Equivalent to 15% CV)
z-Score
-0.8 -0.5 -0.3 -0.1 -0.1 0.0 0.1 0.2 0.3 0.4 0.9
6 7 18 1 13 16 4 10 8 3 2
Laboratory
En-Scores: S2 - U
$E_n$-Score
-0.6 -0.4 -0.7 -0.2 0.0 0.0 0.1 0.1 0.3 0.8 0.6
6 7 18 1 13 16 4 10 8 3 2
Laboratory


Figure 39

Table 42

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | V |
| **Unit** | µg/L |

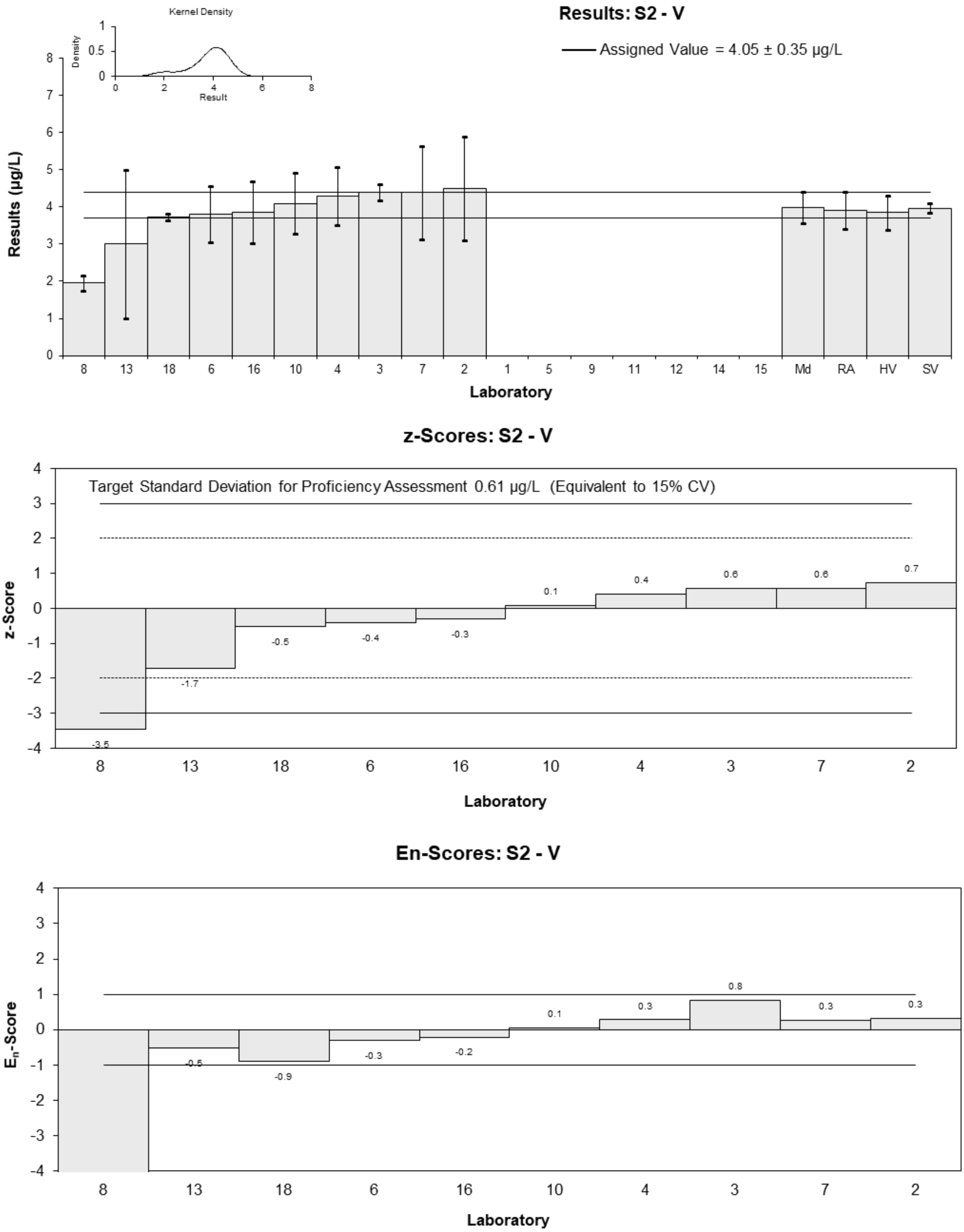
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <10 | NR | | |
| **2** | 4.5 | 1.4 | 0.74 | 0.31 |
| **3** | 4.39 | 0.22 | 0.56 | 0.82 |
| **4** | 4.29 | 0.78 | 0.40 | 0.28 |
| **5** | NT | NT | | |
| **6** | 3.8 | 0.76 | -0.41 | -0.30 |
| **7** | 4.39 | 1.26 | 0.56 | 0.26 |
| **8*** | 1.95 | 0.20 | -3.46 | -5.21 |
| **9** | < 5 | 1 | | |
| **10** | 4.1 | 0.82 | 0.08 | 0.06 |
| **11** | NT | NT | | |
| **12** | <5 | <1.5 | | |
| **13** | 3 | 2 | -1.73 | -0.52 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 3.86 | 0.83 | -0.31 | -0.21 |
| **18** | 3.73 | 0.09 | -0.53 | -0.89 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.05 | 0.35 |
| **Spike Value** | 3.97 | 0.13 |
| **Homogeneity Value** | 3.85 | 0.46 |
| **Robust Average** | 3.90 | 0.50 |
| **Median** | 3.98 | 0.42 |
| **Mean** | 3.80 | |
| **N** | 10 | |
| **Max** | 4.5 | |
| **Min** | 1.95 | |
| **Robust SD** | 0.63 | |
| **Robust CV** | 16% | |



Results: S2 - V
Assigned Value = 4.05 ± 0.35 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
8 13 18 6 16 10 4 3 7 2 1 5 9 11 12 14 15 Md RA HV SV
z-Scores: S2 - V
Target Standard Deviation for Proficiency Assessment 0.61 µg/L (Equivalent to 15% CV)
z-Score
-3.5 -1.7 -0.5 -0.4 -0.3 0.1 0.4 0.6 0.6 0.7
8 13 18 6 16 10 4 3 7 2
Laboratory
En-Scores: S2 - V
$E_n$-Score
-0.5 -0.9 -0.3 -0.2 0.1 0.3 0.8 0.3 0.3
8 13 18 6 16 10 4 3 7 2
Laboratory


Figure 40

Table 43

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | River Water |
| **Analyte** | Zn |
| **Unit** | µg/L |

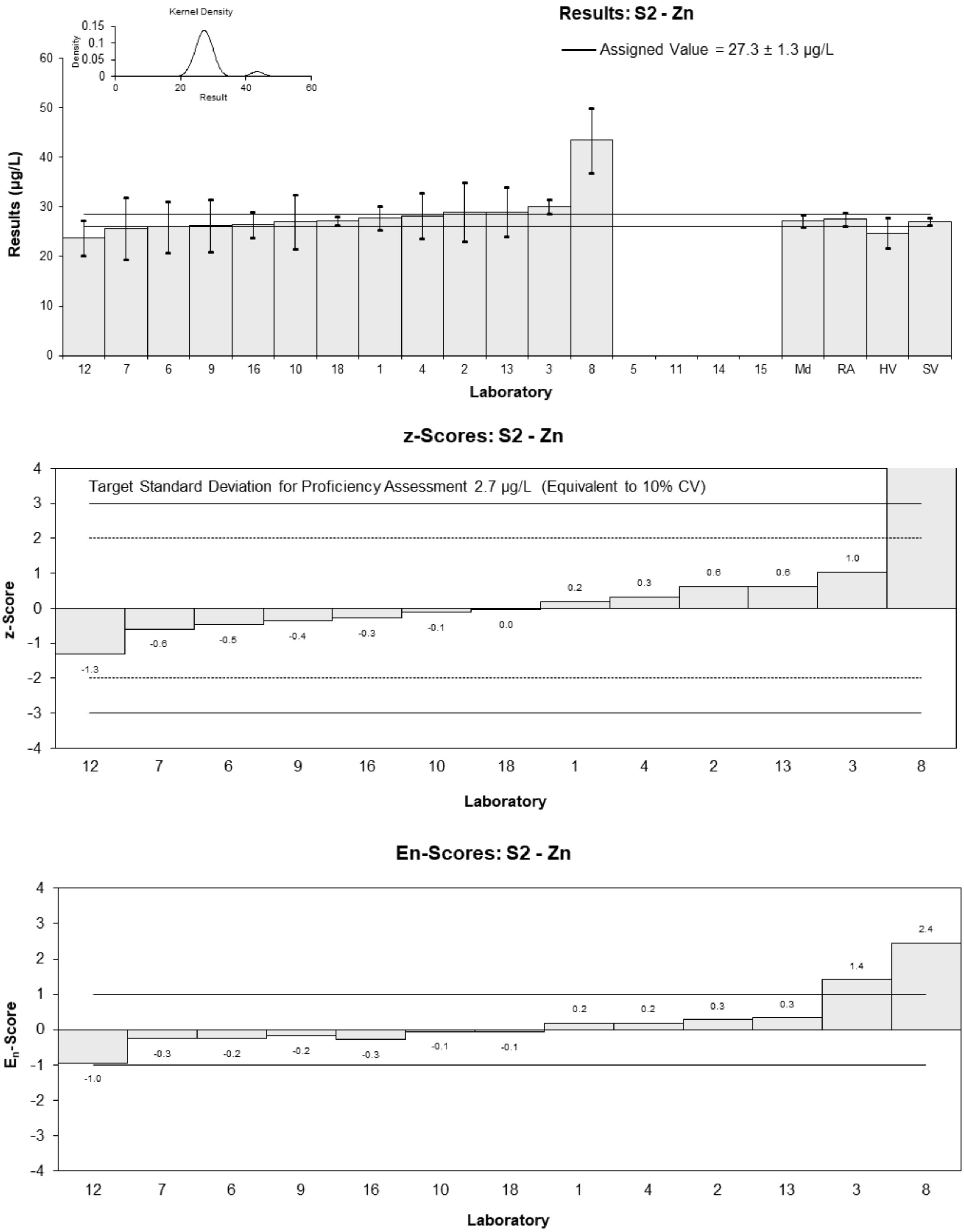
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 27.78 | 2.39 | 0.18 | 0.18 |
| **2** | 29 | 6 | 0.62 | 0.28 |
| **3** | 30.11 | 1.51 | 1.03 | 1.41 |
| **4** | 28.2 | 4.6 | 0.33 | 0.19 |
| **5** | NT | NT | | |
| **6** | 26 | 5.2 | -0.48 | -0.24 |
| **7** | 25.7 | 6.2 | -0.59 | -0.25 |
| **8*** | 43.45 | 6.5 | 5.92 | 2.44 |
| **9** | 26.3 | 5.26 | -0.37 | -0.18 |
| **10** | 27 | 5.4 | -0.11 | -0.05 |
| **11** | NT | NT | | |
| **12** | 23.7 | 3.555 | -1.32 | -0.95 |
| **13** | 29 | 5 | 0.62 | 0.33 |
| **14** | NT | NT | | |
| **15** | NT | NT | | |
| **16** | 26.5 | 2.6 | -0.29 | -0.28 |
| **18** | 27.2 | 0.9 | -0.04 | -0.06 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 27.3 | 1.3 |
| **Spike Value** | 27.1 | 0.7 |
| **Homogeneity Value** | 24.8 | 3.0 |
| **Robust Average** | 27.5 | 1.4 |
| **Median** | 27.2 | 1.2 |
| **Mean** | 28.5 | |
| **N** | 13 | |
| **Max** | 43.45 | |
| **Min** | 23.7 | |
| **Robust SD** | 2.0 | |
| **Robust CV** | 7.4% | |



Results: S2 - Zn
Assigned Value = 27.3 ± 1.3 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
z-Scores: S2 - Zn
Target Standard Deviation for Proficiency Assessment 2.7 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S2 - Zn
$E_n$-Score
Laboratory


Figure 41

## 6 DISCUSSION OF RESULTS

### 6.1 Assigned Value

**Sample S1** was filtered sea water while **Sample S2** was filtered river water. To both a known amount of single element standard solutions was added.

**Assigned Values** were the robust average of participants' results. The robust averages and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2022. Results less than 50% and more than 150% of the robust average were excluded prior to the calculation of each assigned value.[7] Appendix 2 sets out the calculation for the robust average of Fe in Sample S1 and its associated uncertainty.

The assigned values, spike values and homogeneity values were in agreement with each other within their estimates of uncertainty for all elements of interest.

**Traceability** The consensus of participants' results (robust average) is not traceable to any external reference. So although expressed in SI units, the metrological traceability of these assigned values has not been established.

### 6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 468 numerical results, 462 (99%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 1% to 208% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.[9 – 14]

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded uncertainties are presented in the bar charts for each analyte (Figure 2 to 41). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 13 laboratories reported results for Pb in S2. The uncertainty of the assigned value estimated from the robust standard deviation of the 13 laboratories' results is 0.19 µg/L (see equation 4, Appendix 2). If Laboratory 18 result is coming from one measurement then they might have under-estimated its expanded measurement uncertainties reported for Pb in S2 (0.031 µg/L) as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 13 measurements. Alternatively, estimates of uncertainties for As in S1 larger than 1.45 µg/L (the uncertainty of the assigned value, 0.35 µg/L plus the allowable variation from the assigned value, the target standard deviation of 0.55 µg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainties reported by laboratory 2 for As in S1 (2.6 µg/L) might have been over-estimated.

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[10] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 3.

Laboratories 3 and 18 should review their calculation procedure for estimating measurement uncertainty as most of their uncertainties were very low.

Laboratories 13 and 14 should also review their procedure for estimating measurement uncertainty. Most of the uncertainties they reported were over-estimated.

Laboratory 9 attached estimates of the expanded measurement uncertainty to results reported as being less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

Laboratory 13 reported an estimate of expanded uncertainty for some measurement results equal to or larger than the results themselves.

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 106.7 ± 21.3 µg/L, it is better to report 107 ± 21 µg/L or instead of 2.102 ± 0.21 µg/L, it is better to report 2.10 ± 0.21 µg/L.[9]

### 6.3 z-Score

The z-score compares the participant's deviation from the assigned value with the target standard deviation set for proficiency assessment.

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 10% to 20% PCV were used to calculate z-scores. Unlike the standard deviation based on between laboratories CV, setting the target standard deviation as a realistic, set value enables z-scores to be used as fixed reference value points for assessment of laboratory performance, independent of group performance.

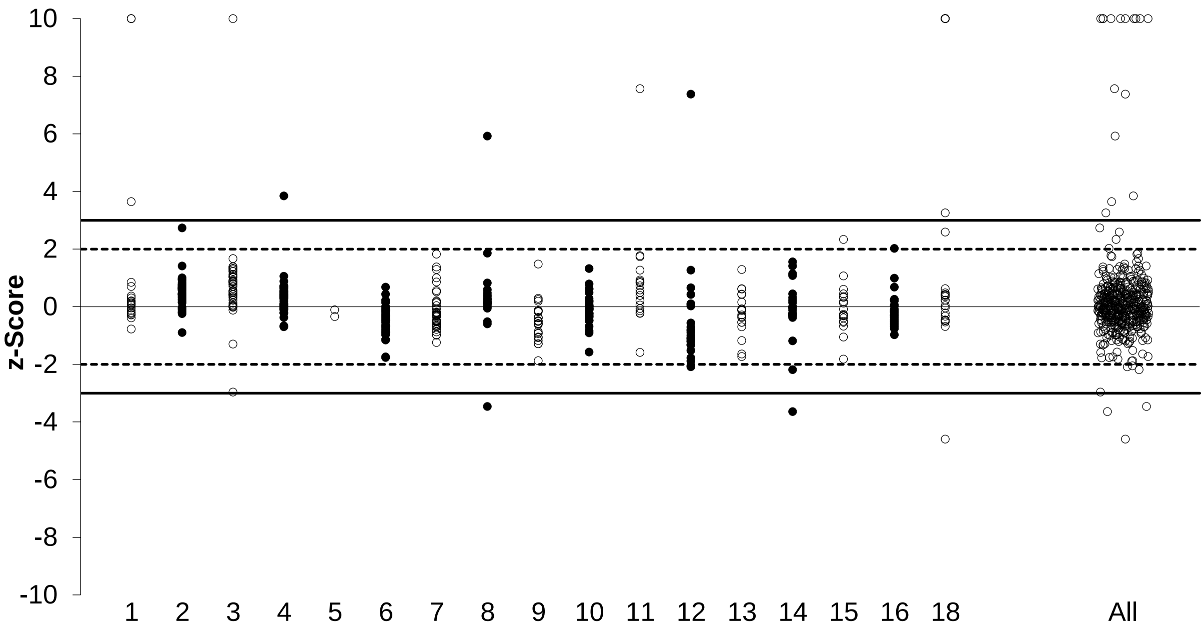
The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 44.

Table 44 Between Laboratory CV of this Study, Thompson CV and Set Target CV

| Sample | Test | Assigned value (µg/L) | Between Laboratories CV* | Thompson/ Horwitz CV | Target SD (as CV) |
|---|---|---|---|---|---|
| S1 | Ag | 1.50 | 12% | 22% | 15% |
| S1 | Al | 27.3 | 25% | 22% | 20% |
| S1 | As | 2.76 | 18% | 22% | 20% |
| S1 | Be | 1.45 | 15% | 22% | 15% |
| S1 | Cd | 0.784 | 12% | 22% | 15% |
| S1 | Cr | 1.89 | 6.5% | 22% | 15% |
| S1 | Cu | 11.2 | 10% | 22% | 15% |
| S1 | Fe | 42.2 | 11% | 22% | 15% |
| S1 | Hg | 0.316 | 14% | 22% | 15% |
| S1 | Mn | 5.50 | 11% | 22% | 15% |
| S1 | Ni | 2.86 | 12% | 22% | 15% |
| S1 | P | 122 | 27% | 22% | 20% |
| S1 | Pb | 1.55 | 15% | 22% | 15% |
| S1 | Sb | 5.72 | 8% | 22% | 15% |
| S1 | Se | 3.04 | 22% | 22% | 20% |
| S1 | Sn | 4.22 | 7.1% | 22% | 15% |
| S1 | Tl | 1.03 | 9.8% | 22% | 15% |
| S1 | U | 2.58 | 7.8% | 22% | 15% |
| S1 | V | 3.40 | 8.5% | 22% | 15% |
| S1 | Zn | 17.6 | 16% | 22% | 15% |
| S2 | Ag | 1.83 | 16% | 22% | 15% |

| Sample | Test | Assigned value (µg/L) | Between Laboratories CV* | Thompson/ Horwitz CV | Target SD (as CV) |
|---|---|---|---|---|---|
| S2 | Al | 54.7 | 9% | 22% | 10% |
| S2 | As | 2.69 | 9.7% | 22% | 20% |
| S2 | Be | 4.88 | 6.3% | 22% | 15% |
| S2 | Cd | 2.49 | 5.5% | 22% | 10% |
| S2 | Co | 1.05 | 9.1% | 22% | 15% |
| S2 | Cr | 1.80 | 15% | 22% | 15% |
| S2 | Cu | 27.3 | 7.8% | 22% | 10% |
| S2 | Fe | 391 | 9.3% | 18% | 10% |
| S2 | Hg | 0.457 | 8.1% | 22% | 15% |
| S2 | Mn | 13.2 | 7.1% | 22% | 10% |
| S2 | Mo | 10.3 | 7.1% | 22% | 10% |
| S2 | Ni | 3.64 | 10% | 22% | 15% |
| S2 | Pb | 3.01 | 9.1% | 22% | 10% |
| S2 | Sb | 11.6 | 11% | 22% | 15% |
| S2 | Se | 3.18 | 12% | 22% | 20% |
| S2 | Tl | 1.01 | 7.2% | 22% | 15% |
| S2 | U | 2.04 | 7% | 22% | 15% |
| S2 | V | 4.05 | 10% | 22% | 15% |
| S2 | Zn | 27.3 | 6.5% | 22% | 10% |

The dispersal of participants' z-scores is presented in Figure 42 (by laboratory code) and in Figure 44 (by test). Of 468 results for which z-scores were calculated, 441 (94%) returned a satisfactory score of $|z| \leq 2.0$ and 8 (2%) were questionable of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.




Scores of >10 or <-10 have been plotted as 10 or -10.

Figure 42: z-Score Dispersal by Laboratory

A summary of participants' performance is presented in Figure 45**.**

**Laboratory 7** reported results for all 40 tests and all returned satisfactory z-scores and $E_n$-scores.

Laboratory **4** returned satisfactory results for 39 tests out of a total of 40 reported.

Of 40 tests for which z-scores were calculated Laboratory **10** reported results for 39 of them, all of which returned satisfactory z-scores.

Laboratory **3** returned satisfactory results for 38 tests out of a total of 40 reported.

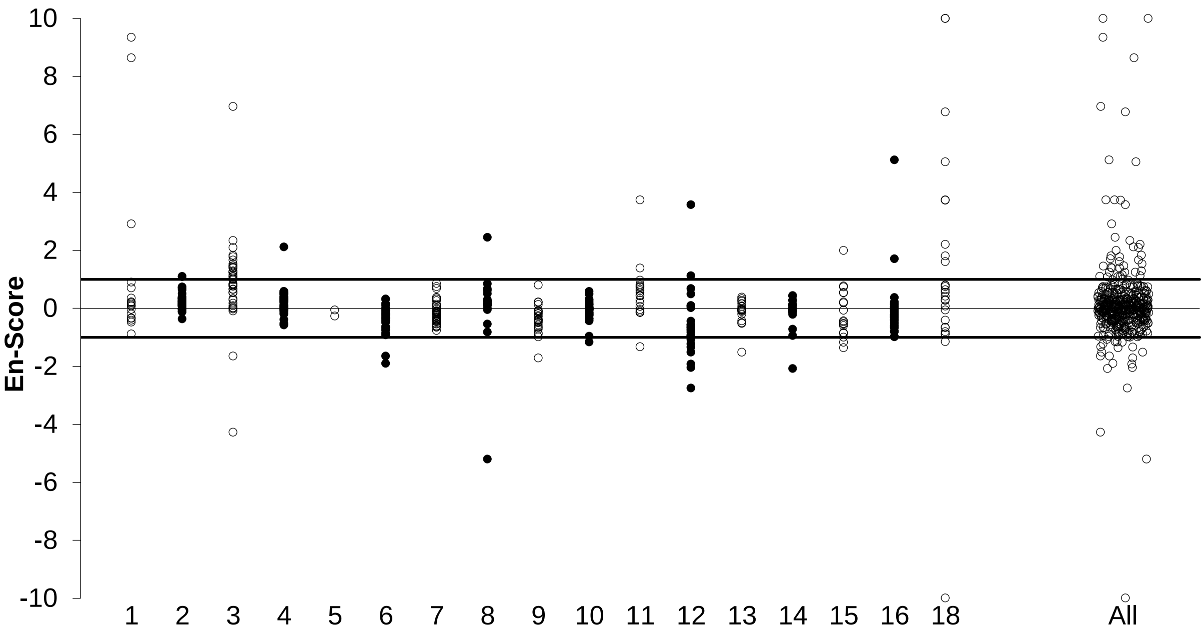
All results reported by Laboratories **6** (35), **9** (27), **13** (19) and **5** (2) returned satisfactory z-scores.

### 6.4 $E_n$-score

$E_n$-score can be interpreted only in conjunction with z-scores. The $E_n$-score indicates how closely a result agrees with the assigned value taking into account the respective uncertainties. An unsatisfactory $E_n$ score for an analyte can either be caused by an inappropriate measurement, an inappropriate estimation of measurement uncertainty, or both.

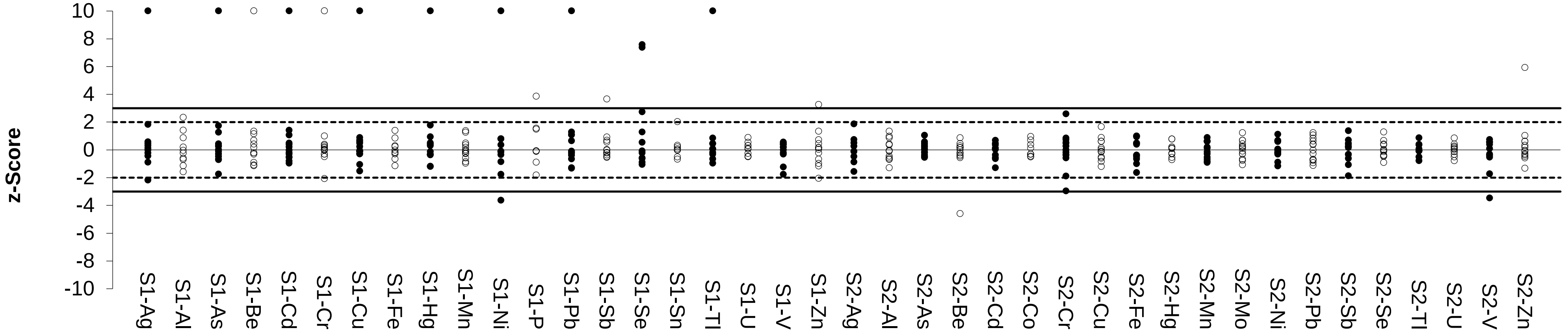
The dispersal of participants' $E_n$-scores is graphically presented in 3. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the $E_n$-score.

Of 468 results for which $E_n$-scores were calculated, 405 (87%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.




Scores of >10 or <-10 have been plotted as 10 or -10.

Figure 43 $E_n$-Score Dispersal by Laboratory




Scores of >10 or <-10 have been plotted as 10 or -10.

Figure 44 z-Score Dispersal by Analyte

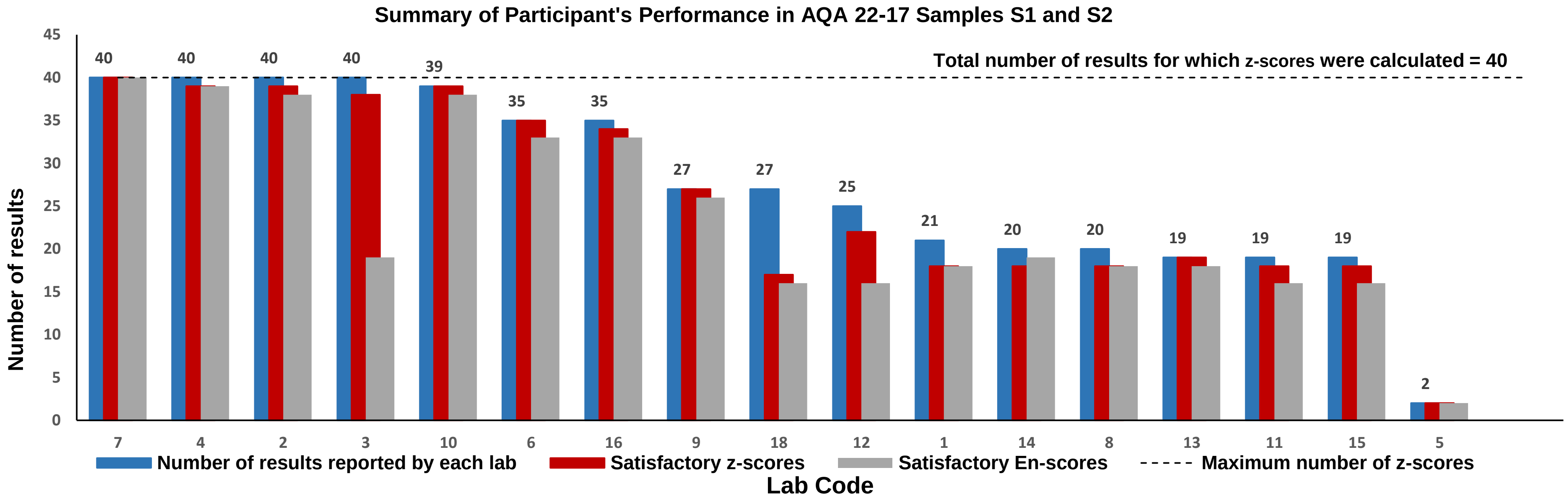



Figure 45: Summary of Participants Performance in AQA 21-18

## Table 45 Summary of Participants' Results and Performance for Sample S1

| Lab Code | Ag (µg/L) | Al (µg/L) | As (µg/L) | Be (µg/L) | Cd (µg/L) | Cr (µg/L) | Cu (µg/L) | Fe (µg/L) | Hg (µg/L) | Mn (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| A.V. | 1.50 | 27.3 | 2.76 | 1.45 | 0.784 | 1.89 | 11.2 | 42.2 | 0.316 | 5.50 |
| H.V. | 1.40 | NA | 2.41 | 1.56 | 0.762 | 1.92 | 12.6 | 43.2 | 0.363 | 6.24 |
| 1 | 24.1 | <50 | <5 | <5 | 8 | <5 | 10.72 | <50 | 0.33 | 5.28 |
| 2 | 1.6 | 26 | 3.0 | 1.6 | 0.95 | 2.0 | 12 | 41 | 0.36 | 5.4 |
| 3 | 1.57 | 32 | 2.77 | 1.74 | 0.84 | 1.89 | 12.7 | 51 | 1.25 | 6.64 |
| 4 | 1.45 | 23.5 | 2.92 | 1.54 | 0.782 | 1.88 | 12.4 | 38.0 | 0.336 | 5.42 |
| 5 | NR | NR | 2.7 | NR | NR | NR | NR | NR | 0.3 | NR |
| 6 | 1.3 | 21 | 1.8 | 1.2 | 0.72 | 1.8 | 11 | 35 | <0.5 | 4.8 |
| 7 | 1.91 | 28.4 | 2.37 | 1.38 | 0.67 | 1.93 | 10.7 | 40.9 | 0.34 | 5.64 |
| 8 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 9 | < 5 | < 50 | 2.9 | 1.25 | 0.724 | 1.75 | 9.44 | < 50 | 0.31 | 5.02 |
| 10 | 1.5 | 27 | 2.5 | 1.4 | 0.75 | 1.9 | 11 | 44 | 0.30 | 5.5 |
| 11 | 1.63 | 18.6 | 3.72 | 1.4 | 0.83 | 1.95 | 11.1 | 47.5 | 0.4 | 6.55 |
| 12 | <5 | <50 | 3.46 | 1.21 | 0.69 | 1.3 | 8.65 | <50 | 0.259 | <5 |
| 13 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 14 | 1.01 | 35 | 2.6 | 1.7 | 0.81 | 1.8 | 11 | 42 | 0.26 | 5.3 |
| 15 | 1.53 | 40.0 | 2.39 | 1.49 | 0.91 | 1.98 | 12.2 | 40.3 | NR | 5.79 |
| 16 | 1.4 | 24 | <4 | NT | 0.76 | 2.17 | 11.6 | 43.7 | 0.299 | 4.70 |
| 18 | NT | NT | 24.5 | 5.39 | NT | 5.5 | 140 | NT | NT | 5.9 |

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, NA = Not Available

Table 45 Summary of Participants' Results and Performance for Sample S1 (continued)

| Lab Code | Ni (µg/L) | P (µg/L) | Pb (µg/L) | Sb (µg/L) | Se (µg/L) | Sn (µg/L) | Tl (µg/L) | U (µg/L) | V (µg/L) | Zn (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| A.V. | 2.86 | 122 | 1.55 | 5.72 | 3.04 | 4.22 | 1.03 | 2.58 | 3.40 | 17.6 |
| H.V. | 3.03 | 100 | 1.58 | 6.17 | 3.08 | 3.82 | 1.03 | 2.38 | 3.16 | 17.4 |
| 1 | <5 | <1000 | <5 | 8.85 | <50 | <5 | <5 | <5 | <50 | <25 |
| 2 | 3.2 | 100 | 1.7 | 6.2 | 4.7 | 4.2 | 1.1 | 2.7 | 3.3 | 18 |
| 3 | 3.2 | 119 | 1.80 | 5.70 | 3.82 | 4.36 | 1.04 | 2.63 | 3.68 | 21.1 |
| 4 | 3.01 | 216 | 1.53 | 5.54 | 3.37 | 4.43 | 1.04 | 2.79 | 3.59 | 17.7 |
| 5 | NR | NT | NR | NR | NR | NR | NR | NR | NR | NR |
| 6 | 2.8 | NT | 1.4 | NT | 2.5 | NT | 0.88 | 2.4 | 2.5 | 18 |
| 7 | 2.71 | 120 | 1.85 | 5.54 | 2.68 | 3.79 | 0.93 | 2.39 | 2.77 | 15.0 |
| 8 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 9 | 2.49 | 158 | 1.25 | < 5 | 2.66 | < 5 | < 5 | < 5 | < 5 | 14.5 |
| 10 | 3.2 | 120 | 1.5 | 5.3 | 3.0 | 4.2 | <1 | 2.4 | 3.5 | 17 |
| 11 | 2.8 | NT | 1.5 | 6.51 | 7.64 | 4.26 | 1.16 | 2.92 | 3.65 | 19.5 |
| 12 | 2.1 | NT | 1.24 | 5.74 | 7.53 | <5 | <5 | <5 | <5 | 12.2 |
| 13 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 14 | 1.3 | 160 | 1.8 | 5.4 | 2.9 | 4.2 | 1.1 | 2.7 | 3.4 | 18 |
| 15 | 2.82 | 77.6 | 1.46 | 5.26 | 2.40 | 3.90 | 0.98 | 2.48 | 3.24 | 18.8 |
| 16 | <7 | NT | 1.52 | 6.3 | <4 | 5.5 | 1.0 | 2.6 | 3.5 | 15.8 |
| 18 | 8.9 | NT | 4.7 | 5.53 | NT | NT | 2.8 | 2.39 | 3.6 | 26.2 |

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value

## Table 46 Summary of Participants' Results and Performance for Sample S2

| Lab Code | Ag (µg/L) | Al (µg/L) | As (µg/L) | Be (µg/L) | Cd (µg/L) | Co (µg/L) | Cr (µg/L) | Cu (µg/L) | Fe (µg/L) | Hg (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| A.V. | 1.83 | 54.7 | 2.69 | 4.88 | 2.49 | 1.05 | 1.80 | 27.3 | 391 | 0.457 |
| H.V. | 1.83 | 53.2 | 2.88 | 5.23 | 2.40 | 0.99 | 1.98 | 27.0 | 348 | 0.445 |
| 1 | <1 | 54.48 | 2.58 | 4.71 | 2.51 | <1 | 2.03 | 27.68 | 375.9 | 0.464 |
| 2 | 1.9 | 60 | 3.0 | 5.0 | 2.6 | 1.2 | 2.0 | 29 | 430 | 0.51 |
| 3 | 1.97 | 47.6 | 3.25 | 5.51 | 2.58 | 1.16 | 1.00 | 31.86 | 427.5 | 0.51 |
| 4 | 2.03 | 54.2 | 2.84 | 4.61 | 2.66 | 1.11 | 1.94 | 29.7 | 410 | 0.463 |
| 5 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 6 | 1.7 | 51 | 2.6 | 5.2 | 2.4 | 1.0 | 1.8 | 27 | 365 | <0.5 |
| 7 | 1.59 | 59.4 | 2.42 | 4.72 | 2.33 | 0.97 | 1.75 | 27.4 | 430 | 0.44 |
| 8 | 2.34 | 56.61 | 2.41 | 4.88 | 2.52 | 1.07 | 1.93 | 25.66 | 406.52 | 0.47 |
| 9 | < 5 | 51.5 | 2.48 | 5.09 | 2.17 | < 1 | 1.64 | 25.9 | 376 | 0.47 |
| 10 | 1.4 | 62 | 2.7 | 5.0 | 2.5 | 1.0 | 1.7 | 25 | 410 | 0.44 |
| 11 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 12 | <5 | <50 | 2.92 | 4.47 | 2.51 | <1 | 1.29 | 24 | 352 | 0.408 |
| 13 | 1.8 | 57 | 2.4 | 5 | 2.6 | <1 | 1.7 | 27 | 327 | 0.42 |
| 14 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 15 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 16 | 1.8 | 50.9 | 2.72 | 4.54 | 2.35 | 1.00 | 1.87 | 26.9 | 371 | 0.437 |
| 18 | NT | 52.2 | 2.81 | 1.52 | NT | 0.977 | 2.5 | 29.0 | NT | NT |

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value

Table 46 Summary of Participants' Results and Performance for Sample S2 (continued)

| Lab Code | Mn (µg/L) | Mo (µg/L) | Ni (µg/L) | Pb (µg/L) | Sb (µg/L) | Se (µg/L) | Tl (µg/L) | U (µg/L) | V (µg/L) | Zn (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| A.V. | 13.2 | 10.3 | 3.64 | 3.01 | 11.6 | 3.18 | 1.01 | 2.04 | 4.05 | 27.3 |
| H.V. | 13.8 | 10.0 | 3.70 | 2.90 | 10.8 | 2.83 | 0.96 | 1.95 | 3.85 | 24.8 |
| 1 | 13.47 | 9.51 | 3.67 | 3.12 | 12.81 | <10 | <1 | 2 | <10 | 27.78 |
| 2 | 14 | 11 | 4.0 | 3.0 | 12 | 3.4 | 1.0 | 2.3 | 4.5 | 29 |
| 3 | 14.36 | 11.57 | 4.25 | 3.38 | 12.32 | 3.45 | 1.14 | 2.17 | 4.39 | 30.11 |
| 4 | 14.0 | 10.5 | 4.00 | 3.33 | 12.4 | 3.19 | 1.07 | 2.07 | 4.29 | 28.2 |
| 5 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 6 | 12 | 11 | 3.5 | 2.8 | 12 | 2.9 | 1.0 | 1.8 | 3.8 | 26 |
| 7 | 12.5 | 10.0 | 3.47 | 2.93 | 14.0 | 2.88 | 0.89 | 1.88 | 4.39 | 25.7 |
| 8 | 13.37 | 10.58 | 3.96 | 3.26 | 11.88 | 3.15 | 1.02 | 2.12 | 1.95 | 43.45 |
| 9 | 13.0 | 9.2 | 3.54 | 2.73 | 8.34 | 3.1 | < 5 | < 5 | < 5 | 26.3 |
| 10 | 14 | 9.6 | 3.6 | 3.2 | 11 | 2.6 | 1.0 | 2.1 | 4.1 | 27 |
| 11 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 12 | 12.1 | 10.4 | 3.15 | 2.67 | 9.74 | 3.6 | <5 | <5 | <5 | 23.7 |
| 13 | 14 | 10 | 3 | 2.8 | 11 | 4 | 1.0 | 2 | 3 | 29 |
| 14 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 15 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 16 | 12.8 | 10.2 | 3.54 | 2.78 | 10.5 | 2.94 | 0.931 | 2.05 | 3.86 | 26.5 |
| 18 | 12.3 | 10.74 | 3.66 | 3.132 | 12.00 | NT | 1.063 | 1.94 | 3.73 | 27.2 |

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value

### 6.5 Participants' Results and Analytical Methods for Dissolved Elements

**Sample S1** was filtered sea water and **Sample S2** was filtered river water. The concentration of Ag, As, Cr, Se, Tl and U in the two study samples was similar. This study design was aimed at helping laboratories to investigate the effect of sample matrices on their performance.

Sea water contains significant quantities of dissolved salts, especially sodium chloride and sulphates. Molecular ions originated from dissolved salts can frequently cause severe interference in ICP-MS measurements because these molecular ions have similar mass to the isotopes used in elemental determination. As a result, false positives, and concentrations much higher than the true values are frequently obtained by conventional quadrupole ICP-MS which does not have the resolution required to separate molecular ions from the isotope of interest. The isotopes most frequently affected in salt water analysis are $^{52}Cr$, $^{58}Ni$, $^{60}Ni$, $^{63}Cu$, $^{65}Cu$, $^{64}Zn$, $^{66}Zn$, $^{75}As$, $^{78}Se$, $^{82}Se$. Overall, the between-laboratory CVs of the river water Sample S2 were lower than those of the sea water sample S1.

As and Se in sea water were the tests which challenged most participants analytical techniques when compared to the river water sample. The between laboratories CVs for these tests in S1 were almost double of S2.

Low level P and Se in S1 were the tests which presented the most analytical difficulty to participating laboratories with CVs of 27% and 22% respectively.

A summary of participants' results and performance in the two study samples is presented in Tables 45 and 46 and in Figures 42 to 44.

**Individual Element Commentary**

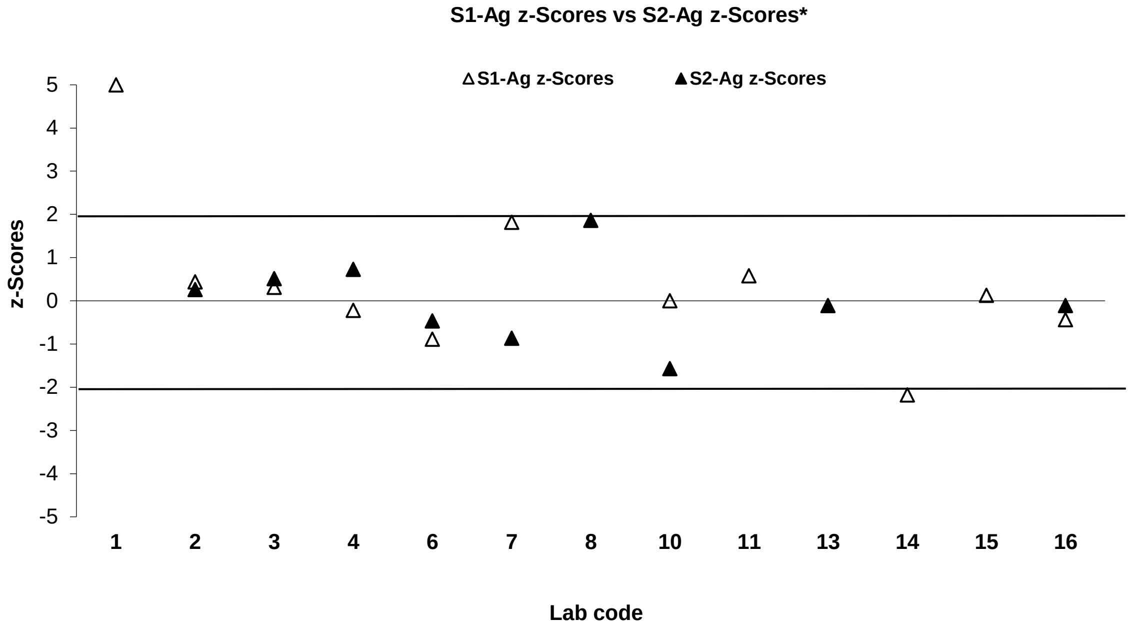
Participants were requested to analyse the two water samples for dissolved elements using their normal test methods and to report a single result as they would normally report to a client. The method descriptions provided by participants are presented in Tables 1 and 3 and instrumental conditions are presented in Appendix 5.

Of 17 participants who reported results, 6 performed digestion. No significant difference was observed between the performances of participants who performed digestion and the ones who did not conduct a digestion procedure on the test samples. Instrumental measurement was one of the main factors that influenced results in the two water samples. However, participants' performance does not reflect instrumental performance alone, but also the performance of the analyst and of the analytical method used by the testing laboratory. Thus, these results should not be construed as an evaluation of a particular instrument.

Most laboratories reported using ICP-MS with a collision/reaction cell; some used ICP-OES and some ICP-MS in standard mode. One participant reported using ICP-MS/MS in standard, collision, or reaction mode with He, $O_2$ or $NH_3$. Most laboratories used Sc, Y or Rh as internal standard. Laboratory 1 reported using Sc, Ir or Rh while Laboratories 8 and 18 used multiple internal standards (Y, Ce, Ga, Ge, Ir, Ho, Sc, Tb, Th, Rh, In or Bi). Plots of participants' results and performance versus instrumental techniques used are presented in Figures 46 to 61.

**Silver** in the river and sea water sample was at similar level. Participants' performance in the two study samples are presented in Figure 46. Silver measurements in water presented difficulties to Laboratory 1 in S1, their reported result returned an unsatisfactory z-score while in S2 they reported a result of less than 1 when the assigned value for this test in the river water sample was 1.83 µg/L.

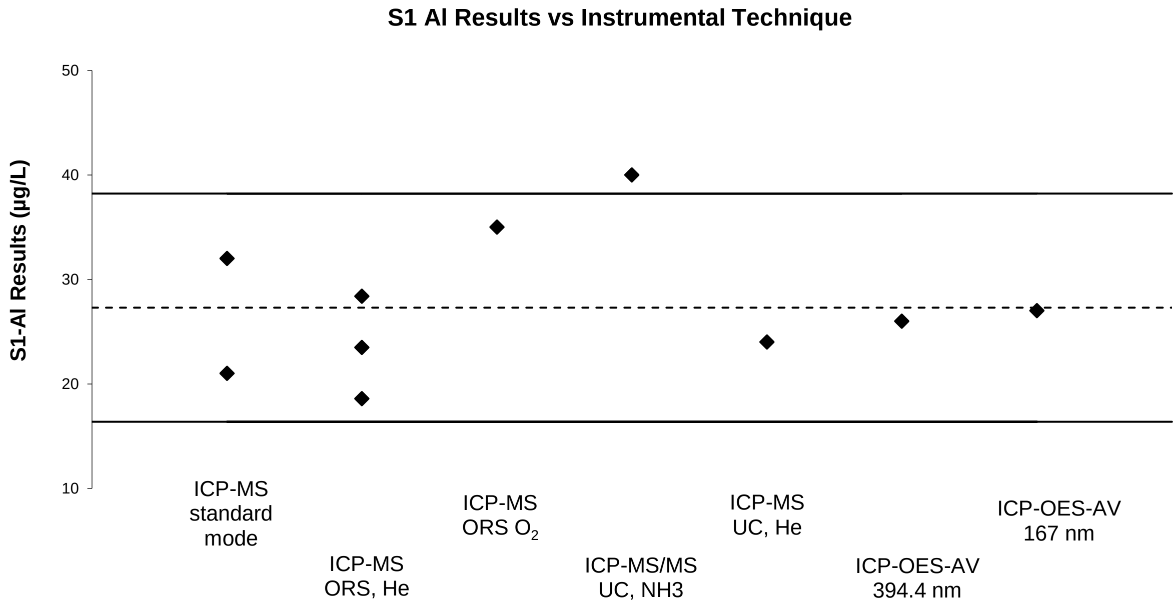
All participants used ICP-MS but one. Laboratory 18 reported using ICP-MS/MS in standard mode.




*The z-Score >5 has been plotted as 5.

Figure 46 S1 and S2 Ag z-Scores vs Laboratory Code

**Aluminium** level in S1 was low, at 27.3 µg/L and was among the most challenging tests for participating laboratories, with a between-laboratory CV of 25%. Plots of instrumental techniques versus results are presented in Figure 47.

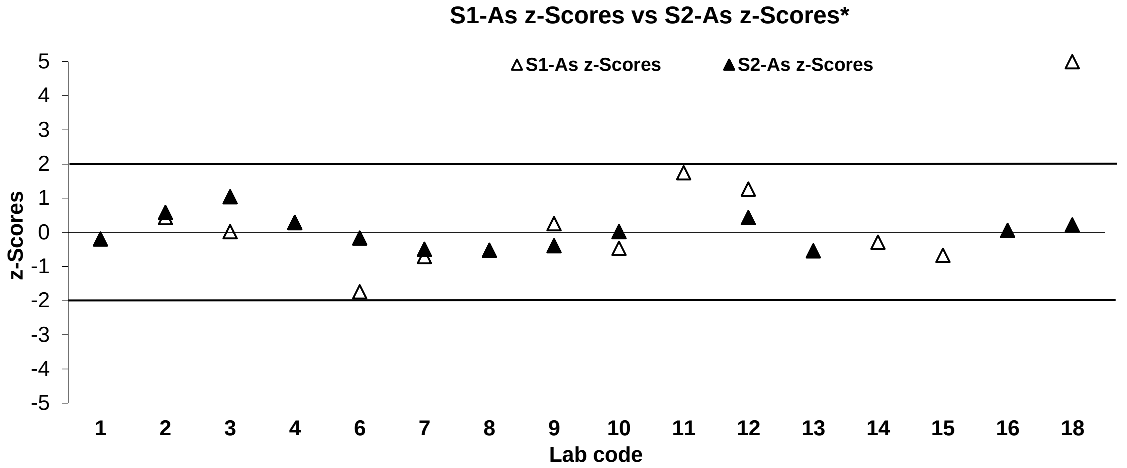



Horizontal lines on chart are the results corresponding to z-scores of 2 and -2

Figure 47 S1-Al Results vs Instrumental Technique

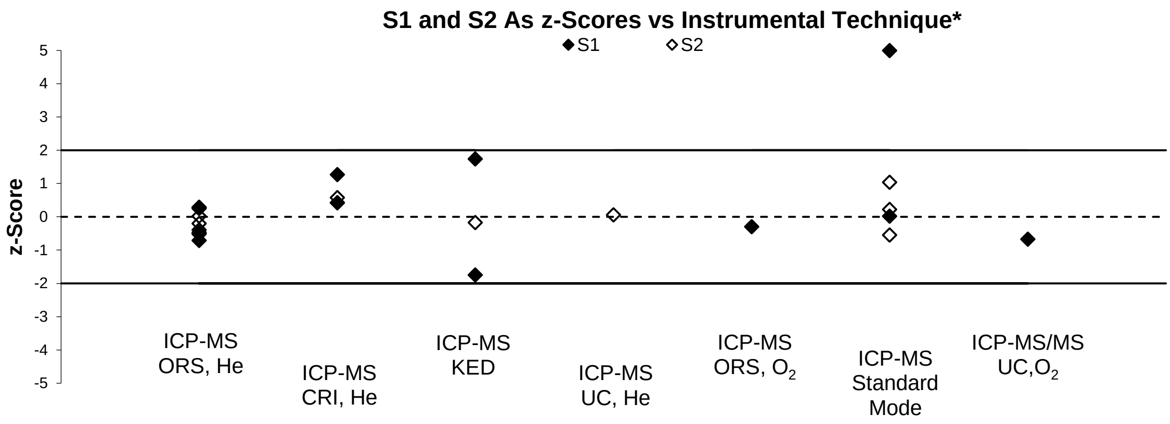
**Arsenic** was at similar level in both the sea water and river water samples at 2.76 µg/L and 2.69 µg/L respectively. Although of 12 reported results for As in S1 and S2 all returned satisfactory z-scores except for one, reported results for the sea water were more variable than in river water; the between-laboratory CV in S1 was 18% while in S2 it was almost half of this, at 9.7% (Table 44 and Figure 48).

For As measurements participants reported using ICP-MS in collision or reaction mode with He or $O_2$ as collision/reaction gases (Figure 49).




*The z-Score >5 has been plotted as 5.

Figure 48 S1 and S2 As z-Scores vs Laboratory Code

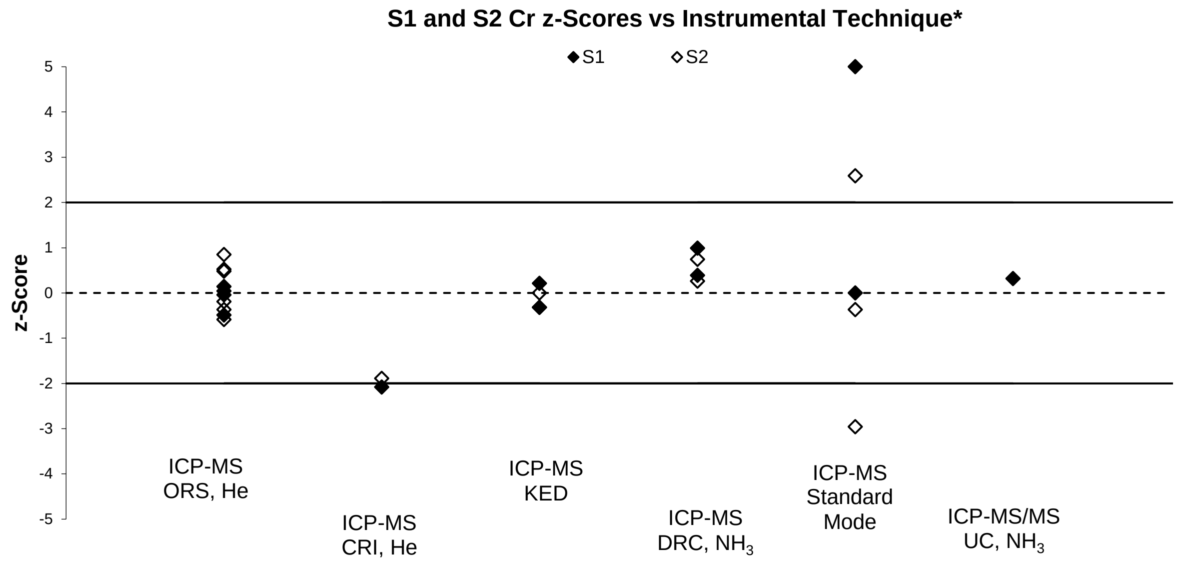



*The z-Score >5 has been plotted as 5.

Figure 49 S1 and S2 As z-Scores vs Instrumental Technique


*The z-Score >5 has been plotted as 5.

Figure 50 S1 and S2 Cr z-Scores vs Laboratory Code



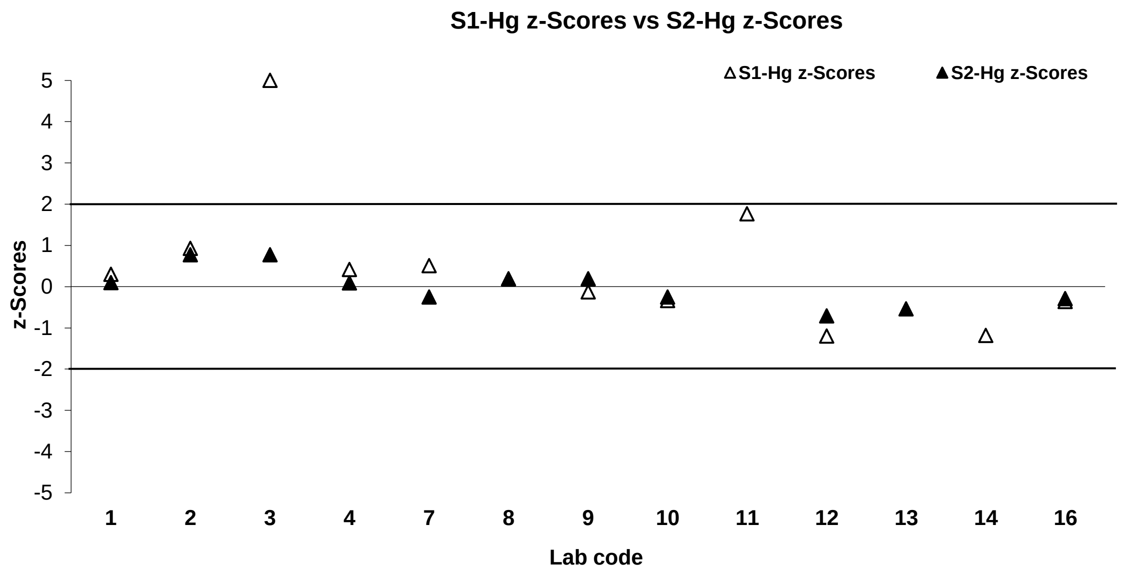

*The z-Score >5 has been plotted as 5.

Figure 51 S1 and S2 Cr z-Scores vs Instrumental Technique

**Chromium** level in S1 was 1.89 µg/L and in S2 was 1.80 µg/L. The results in the river water sample were more variable than those in sea water. The between-laboratory CV in S1 was 6.5% while in S2 it was more than double, at 15%. The high carbon content in the river water may explain the discrepancy as $^{52}Cr$ can have significant interferences from $^{40}Ar^{12}C$ when measured by ICP-MS.

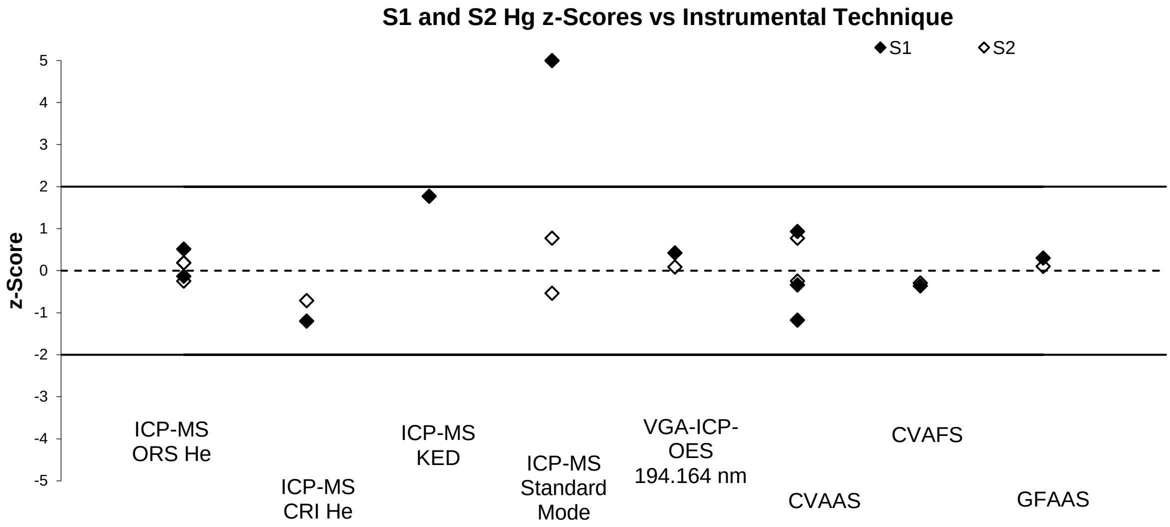
Participants' performance in the two water samples are presented in Figure 50. Laboratories 12 and 18 should check for method bias as the results reported by them were too low and too high respectively.

Plots of participants' performance in the two water samples versus instrumental technique used are presented in Figure 51.




*The z-Score >5 has been plotted as 5.

Figure 52 S1 and S2 Hg z-Scores vs Laboratory Code




*The z-Score >5 has been plotted as 5

Figure 53 S1 and S2 Hg z-Scores vs Instrumental Technique

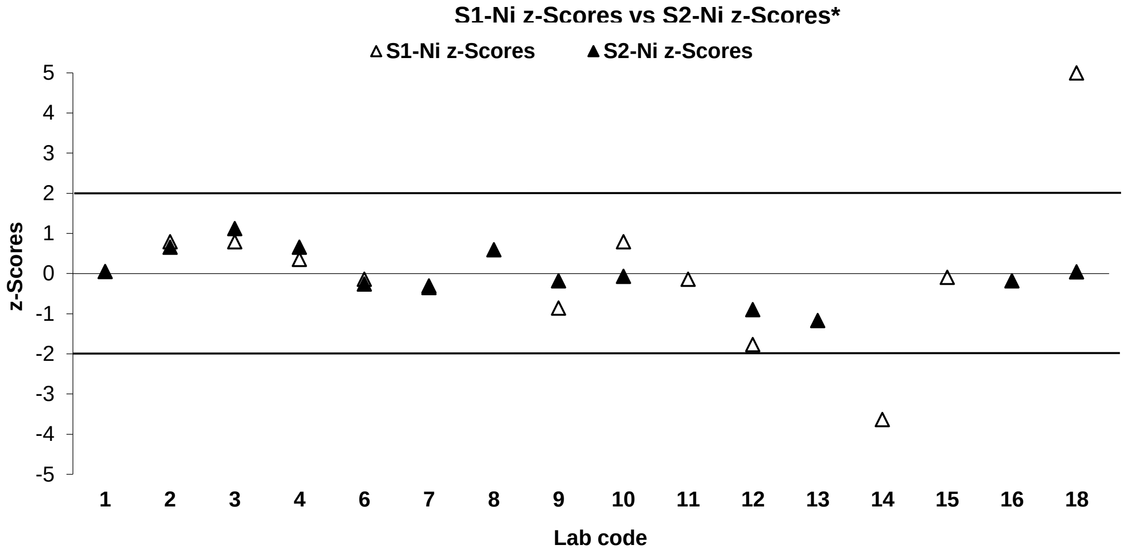
**Mercury** level in S1 was 0.316 g/L and in S2 was 0.457 µg/L. All results reported for Hg in the two study samples returned satisfactory z-scores but one (Figure 52).

Participants used a wide variety of instrumental techniques for Hg measurements in the two water samples and all produced compatible results (Figure 53).

CV-AAS was the most popular instrumental technique used for the measurement of low level Hg in sea water. One participant used ICP-OES with hydride generation accessory and a wavelength of 194.164 nm.

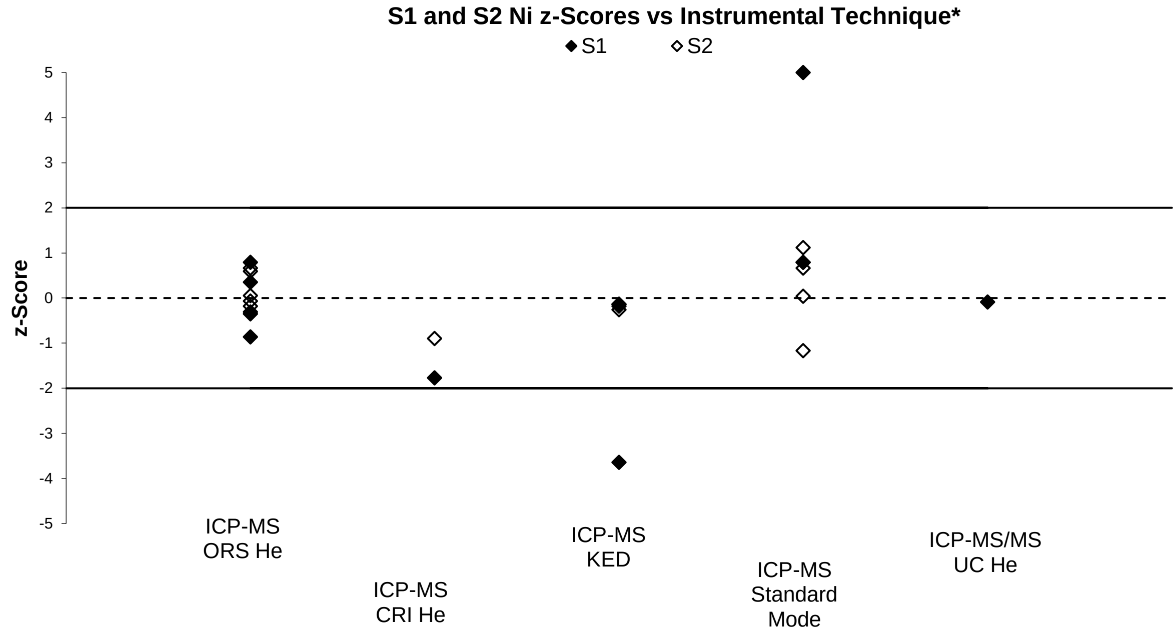
**Nickel** Of 12 participants who reported results for Ni in S1, 10 performed satisfactorily. In S2, of 13 reported results all returned satisfactory z-scores (Figure54).

The high unsatisfactory result for Ni in S1 from ICP-MS measurements in standard mode may be an indication of unsolved interference problems (Figure 55).




*The z-Score >5 has been plotted as 5.

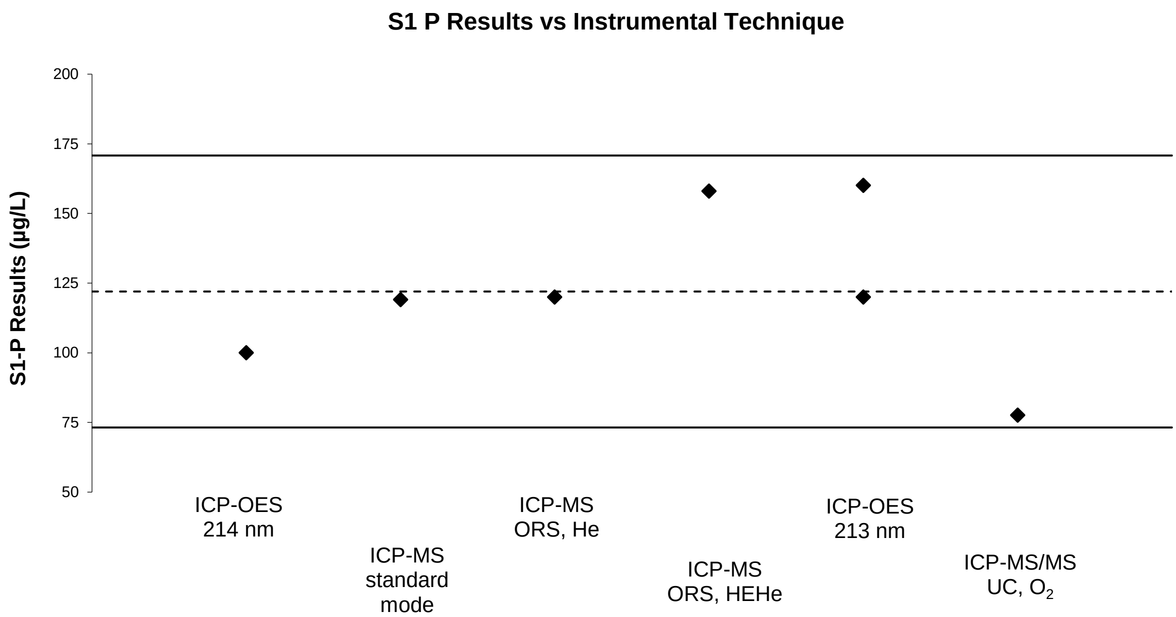
Figure 54 S1 and S2 Ni z-Scores vs Laboratory Code




*The z-Score >5 has been plotted as 5

Figure 55 S1 Ni Results vs Instrumental Technique

**Phosphorus** A limited number of laboratories had the capability to measure P in sea water at this level. Only eight participants reported results for this test and all but one were compatible with each other. Participants used various instrumental techniques: ICP-OES with wavelength 213 nm or 214 nm or ICP-MS in collision, reaction mode or standard mode (Figure 56).




Horizontal lines on chart are the results corresponding to z-scores of 2 and -2

Figure 56 S1 P Results vs Instrumental Technique

**Selenium** analysis in sea water is challenging due to there being multiple sources of significant interference. This is especially problematic at low levels where any unresolved interference can have a more significant effect on results. 11 laboratories reported Se results in S1 and S2; while all reported results in the river water sample returned satisfactory z-scores, only 7 were satisfactory in the sea water sample. Participants who reported satisfactory Se results in S2 but high unsatisfactory results in S1 might not have overcome the interference problem in the sea water sample (Figure 57).

Plots of participants' performance for Se in S1 and S2 versus instrumental technique used are presented in Figure 58.

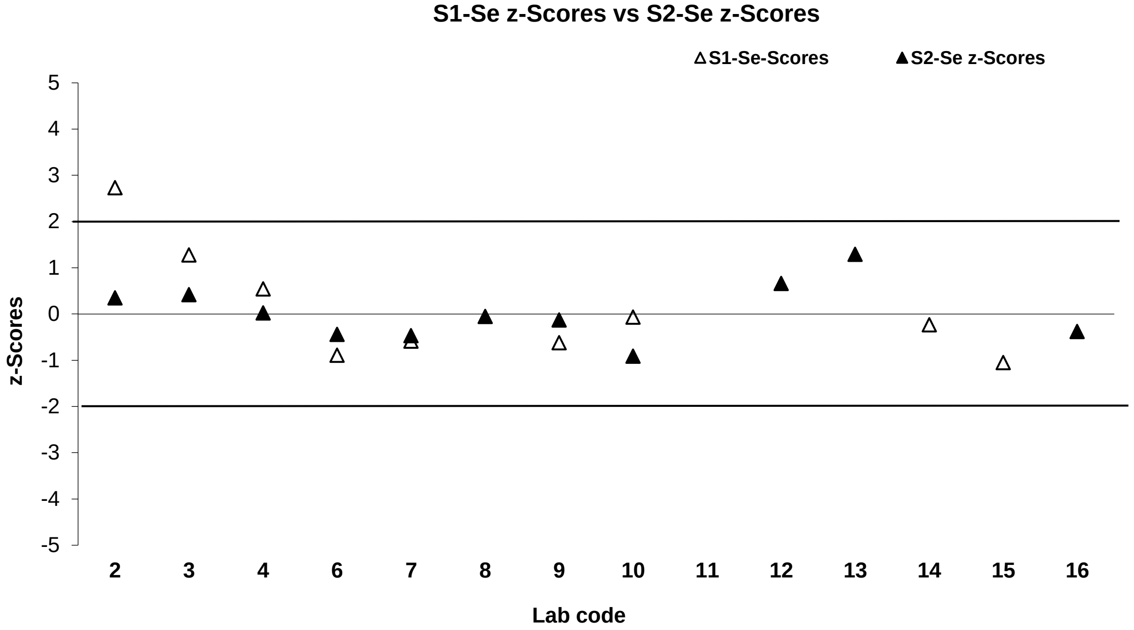



Figure 57 S1 and S2 Se z-Scores vs Laboratory Code

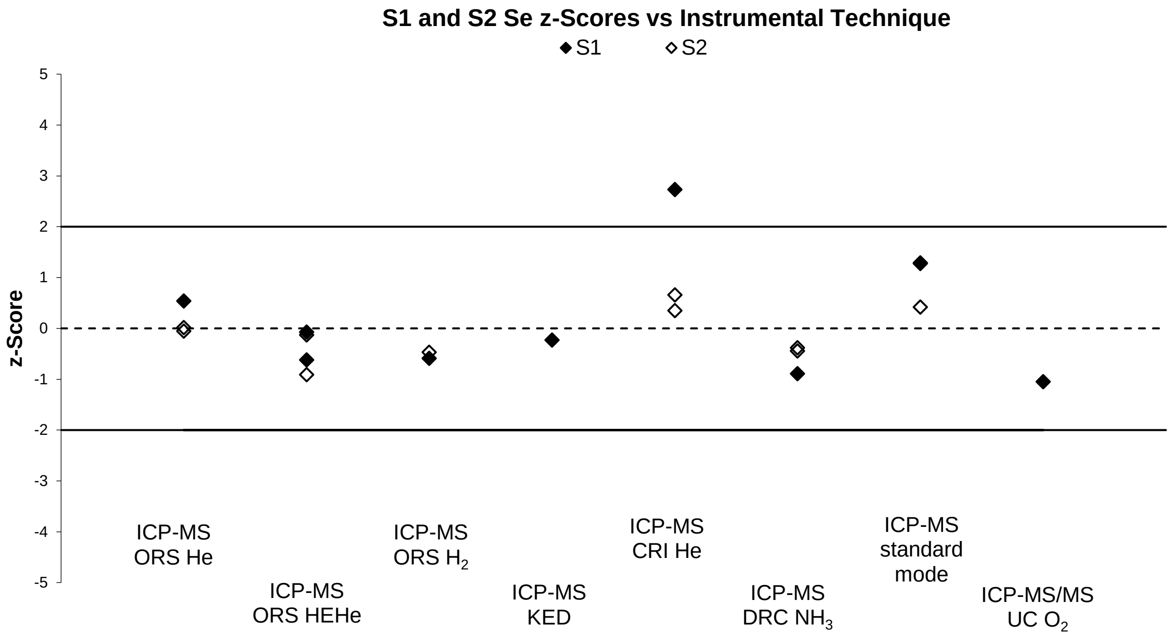



Figure 58 S2 Se Results vs Instrumental Technique

**Antimony** level in S1 was 5.72 µg/L and in S2 was 11.6 µg/L. All results reported for Sb in the two study samples returned satisfactory z-scores but one (Figure 59).

ICP-MS in collision mode was the preferred instrumental technique.

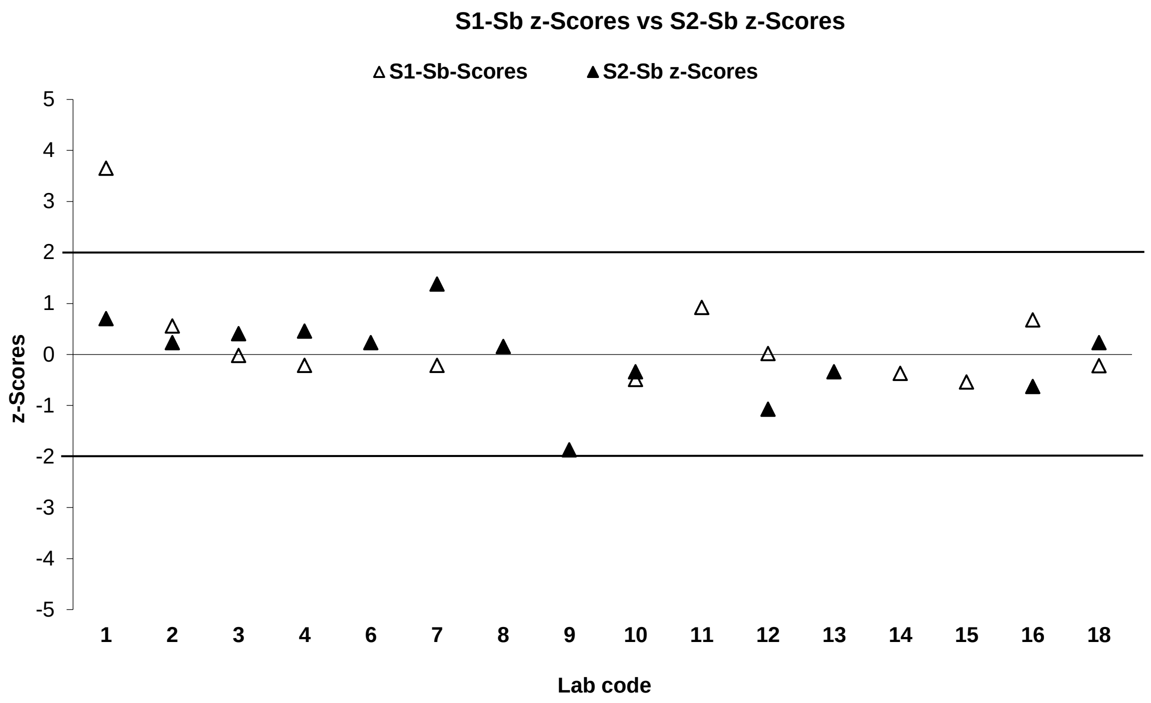



Figure 59 S1 and S2 Sb z-Scores vs Laboratory Code

**Vanadium** Thirteen laboratories reported results for V in S1 and/or in S2. All performed satisfactorily but one (Figure 60). Problems with the calculation/reporting procedure might explain this laboratory unsatisfactory result. The results reported by them for V in S1 was half of the assigned value while the result reported for Zn was double.

Using a matrix matched control sample which is to be taken through every single step of the analytical process together with the routine sample will also help to check the calculation/reporting procedure.

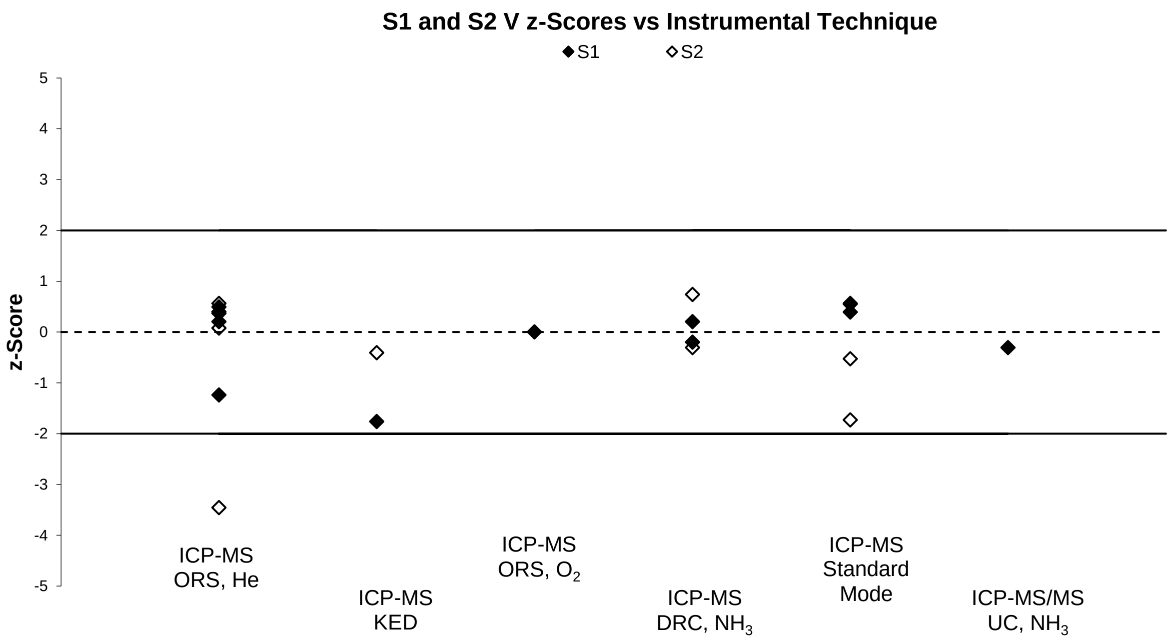
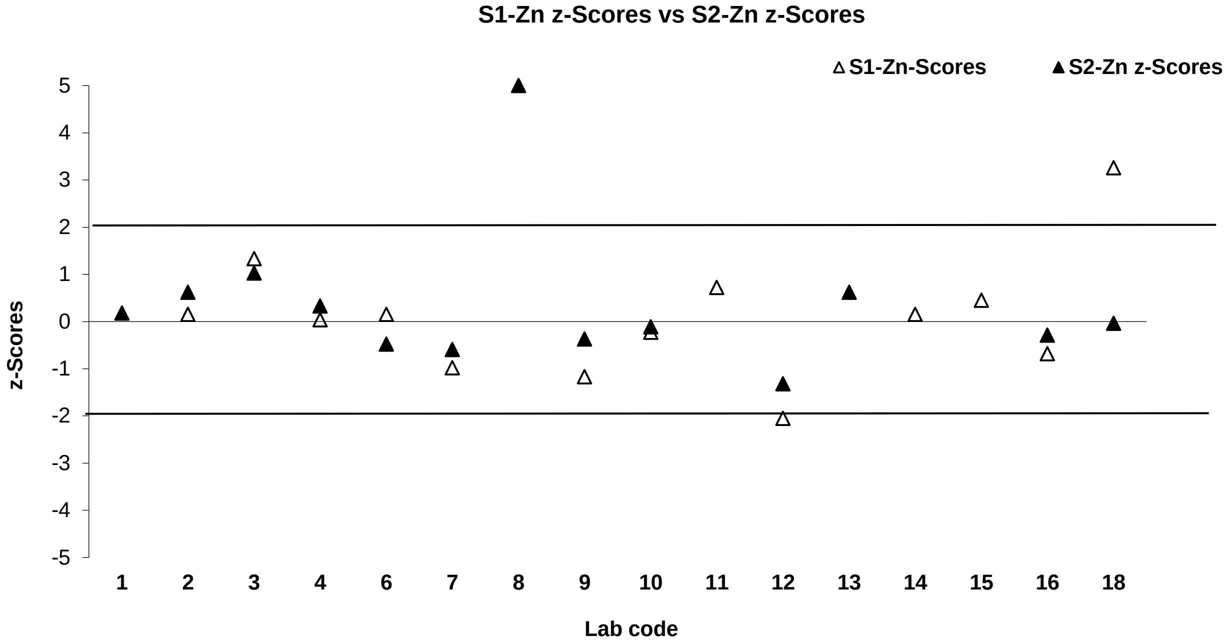



Figure 60 S1 and S2-V z-Scores vs Instrumental Technique

**Zinc** is known to be ubiquitous in the environment; hence, special precautions (e.g. special gloves) are necessary in order to avoid contamination. Plots of participants' performance in the two types of water samples versus laboratory code number are presented in Figure 61.

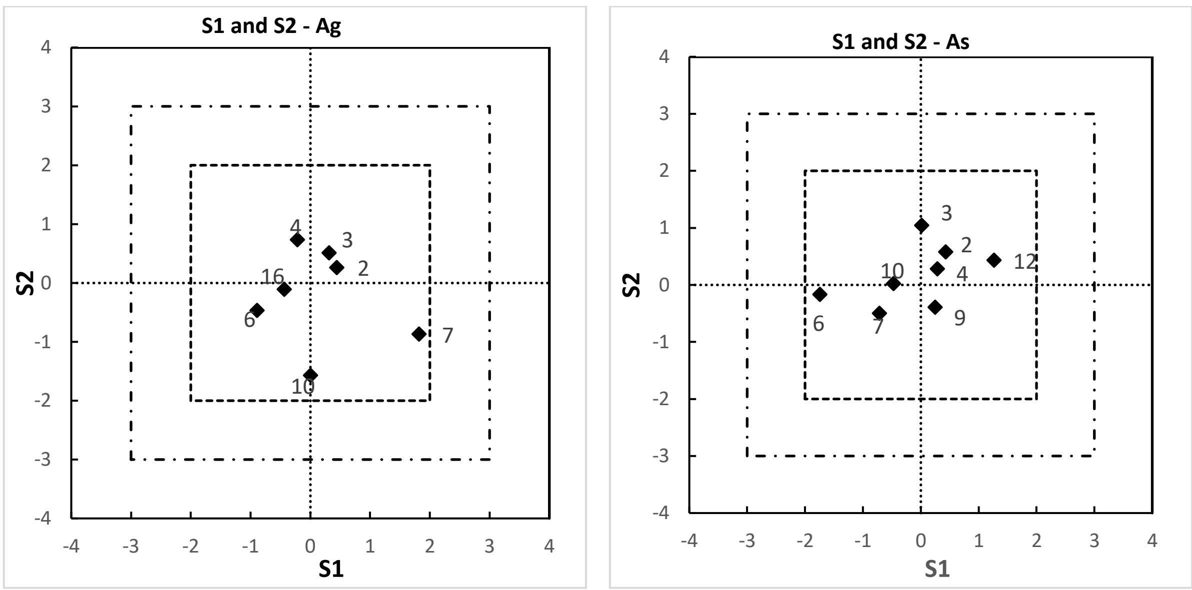



*The z-Score >5 has been plotted as 5.

Figure 61 S1 and S2 Zn z-Scores vs Laboratory Code

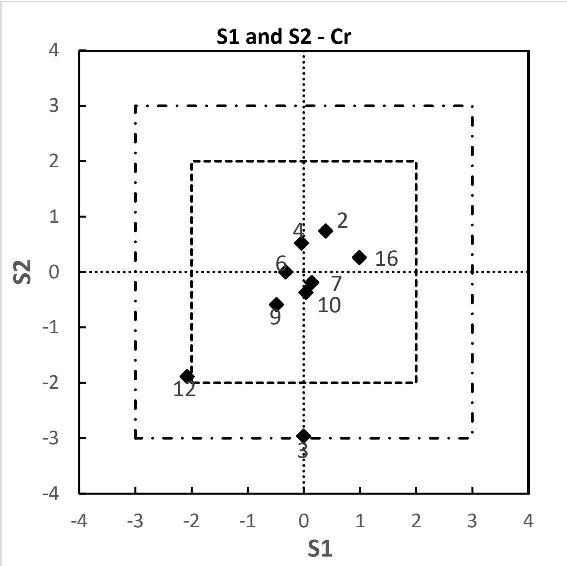
### 6.6 z-Score Scatter plots

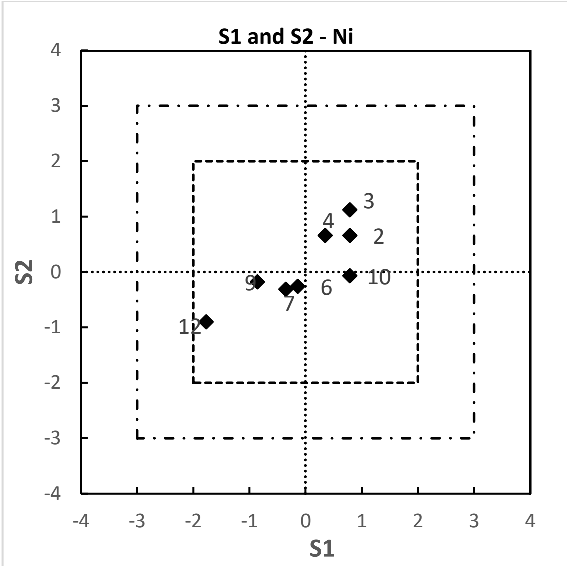
Scatter plots of z-scores for all analytes present in both study samples at a similar level are presented in Figure 62. Scores are predominantly in the upper right and lower left quadrants, indicating that laboratory bias is the major contributor to the variability of results. Points close to the diagonal axis demonstrate excellent repeatability, while points close to the zero demonstrate excellent repeatability and accuracy.




Laboratory 18 is off scale

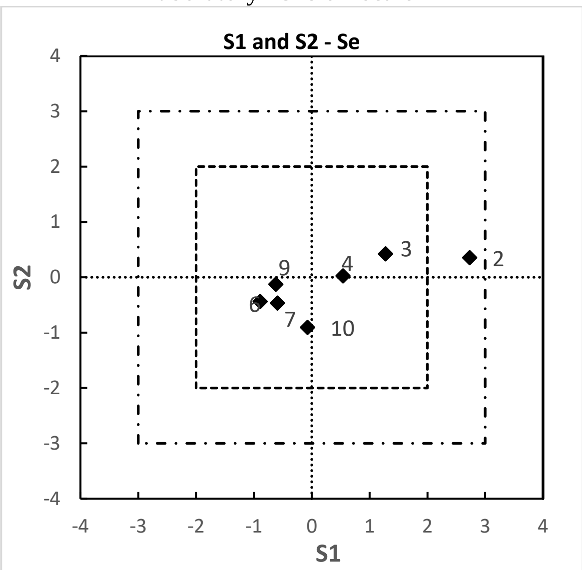
Figure 62 Scatter Plots of: z-Score for S1 and S2

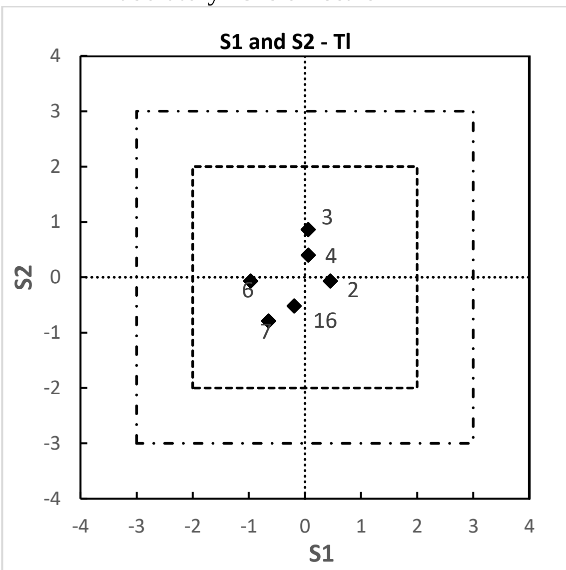



Laboratory 18 is off scale

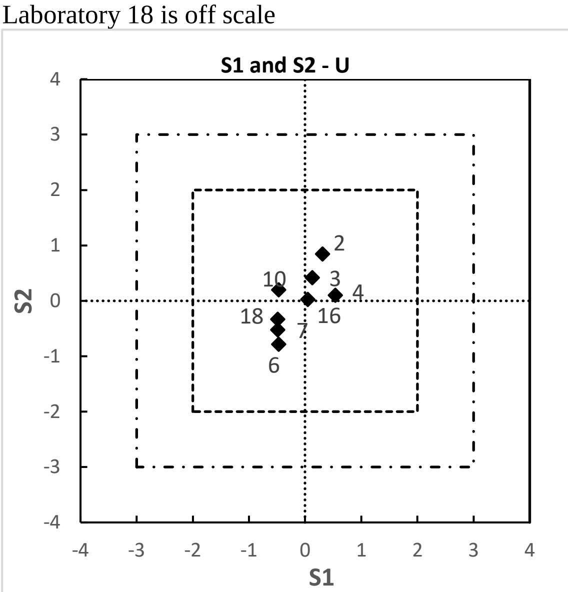
Laboratory 18 is off scale




Laboratory 18 is off scale

Laboratory 18 is off scale



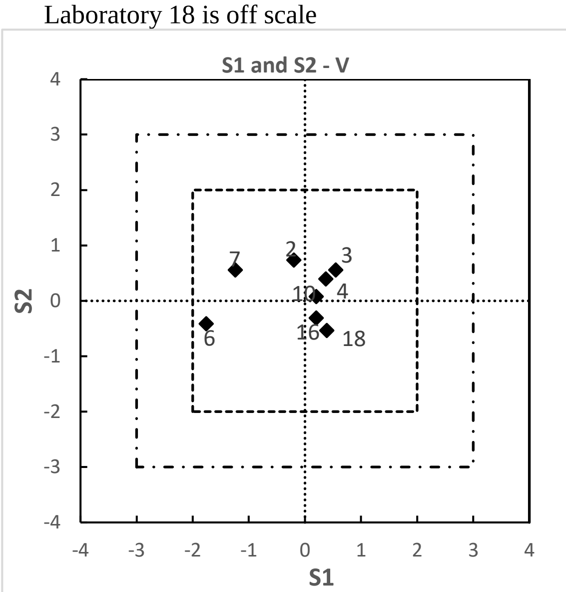




Figure 62: Scatter Plots of: z-Score for S1 and S2 (continued)

## 6.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 22-17 is the 31st NMI proficiency study of metals in water. Participants' performance in the measurement of trace elements in water (river water, seawater, wastewater and potable water) over the last ten years is presented in Figure 63. Over this period, the average proportion of satisfactory scores was 91% for z-scores and 83% for $E_n$-scores.

Over time, laboratories should expect at least 95% of their scores to lay within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ occasionally can occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line is an indication of method or laboratory bias.

Individual performance history reports are emailed to each participant at the end of the study; the consideration of z-scores for an analyte over time provides much more useful information than a single z-score.

## 6.8 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 47).

Table 47 Control Samples Used by Participants

| Lab. Code | Description of Control Samples |
|---|---|
| 1 | CRM |
| 2 | CRM |
| 4 | SS |
| 5 | I641e- Hg |
| 6 | CWW-TM-B and CWW-TM-C (river water) NASS 7, CASS 6 and NMI MX014 (seawater) |
| 7 | SS |
| 9 | CRM |
| 10 | CRM |
| 11 | CRM - IV-16951 |
| 12 | SS |
| 13 | CRM – HPS CRMs |
| 14 | CRM – High Purity Standards – Multi components Standards |
| 15 | MX014 |
| 16 | SS |
| 18 | Elemental check standards sourced from LGC Standards (ISO 17034:2016 accredited Reference Materials Producer, A2LA Certificate No. 2848.02) |

Matrix matched control samples taken through all steps of the analytical process, are most valuable quality control tools for assessing the methods' performance.

Some laboratories reported using certified reference materials. These materials may not meet the internationally recognised definition of a Certified Reference Material:

> *'* ***a 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'*[16]

A certified reference material for trace elements in sea water (MX014) is available from NMI.

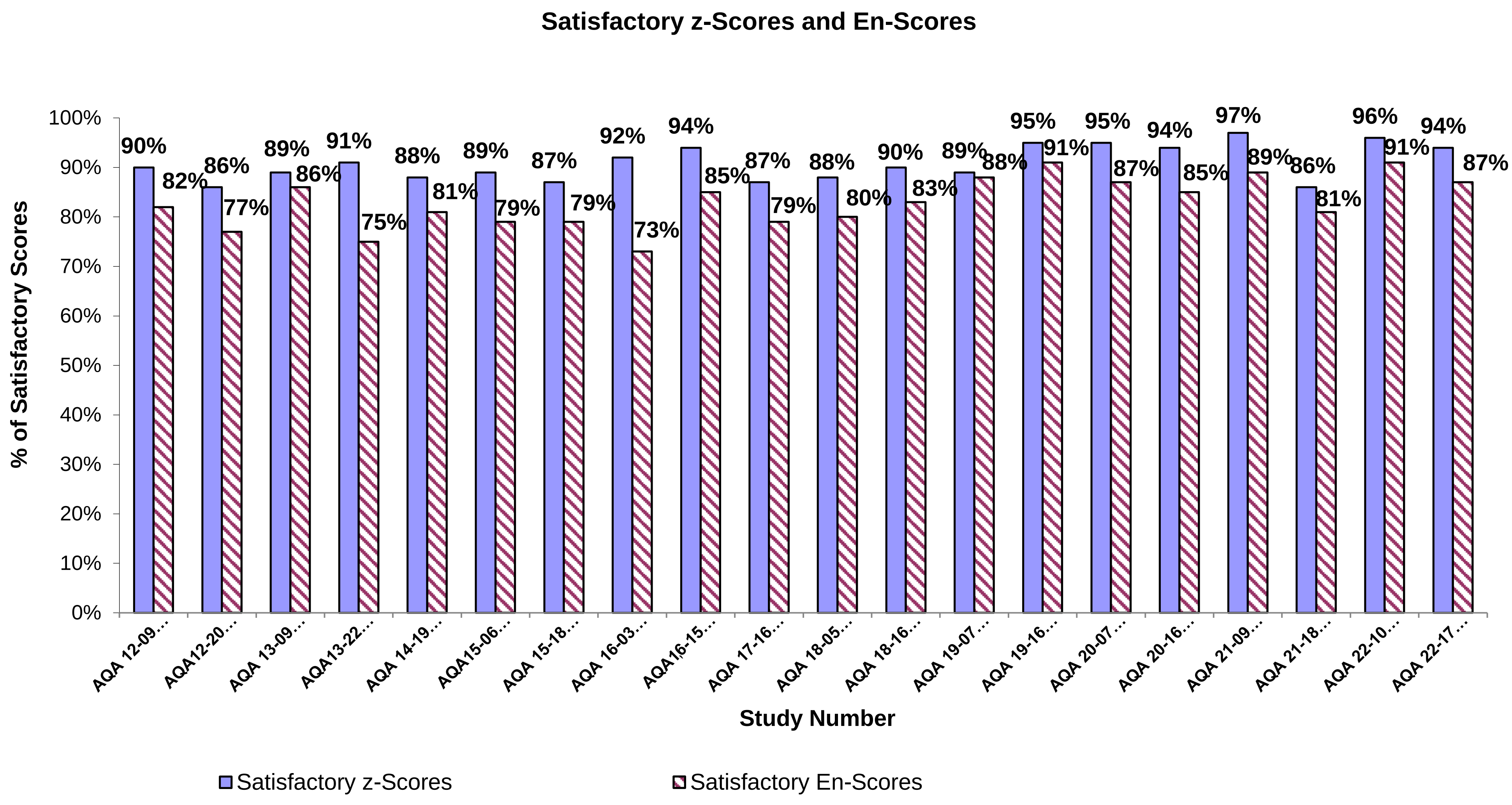



Figure 63 Participants' Performance in Metals in Sea water PT Studies over Last Thirteen Years

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## APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

### Sample Preparation

**Sample S1** was prepared from sea water. Approximately 5 L of sea water was filtered through a 0.45 µm pore size filter, stabilised by adding 2% (v/w) nitric acid and further fortified for 19 elements.

**Sample S2** was prepared by filtering 5 L of river water through a 0.45 µm pore size filter and then stabilised it by adding 2% (v/w) nitric acid and 0.01% (v/w) HCl. The acidified and filtered river water was then further fortified for 19 elements.

### Sample Analysis and Homogeneity Testing

With the exception of Al in S1, a partial homogeneity test was conducted for all analytes of interest. Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

### Sample Analysis for Dissolved Elements

For analyses of dissolved elements in Samples S1 a test portion of 1 mL was transferred to a 14 mL graduated polypropylene centrifuge tube and diluted to 10 mL with milli-Q water

For analyses of dissolved elements in Sample S2, a test portion of 7.5 mL was transferred to a 14 mL graduated polypropylene centrifuge tube and diluted to 10 mL with milli-Q water.

Testing involved measurements using ICP-MS. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates, sample matrix spikes and control samples (MX014, AQA 20-16 S1 and AQA 21-18 S1) was carried through the same set of procedures and analysed simultaneously with the samples. A summary of the ion/wavelength and instrument conditions used for each analyte is presented in Table 48 for S1 and in Table 49 for S2.

Table 48 Instrumental Techniques used for Dissolved Elements in S1

| Analyte | Instrument | Internal Standard | Reaction/ Collision Cell | Cell Mode/Gas | Final Dilution Factor | Ion / Wavelength |
|---|---|---|---|---|---|---|
| Ag | ICP-MS | Rh | ORS | He | 10 | 107 m/z |
| As | ICP-MS | Rh | ORS | He | 10 | 75 m/z |
| Be | ICP-MS | Rh | ORS | He | 10 | 9 m/z |
| Cd | ICP-MS | Rh | ORS | He | 10 | 114 m/z |
| Cr | ICP-MS | Rh | ORS | He | 10 | 52 m/z |
| Cu | ICP-MS | Rh | ORS | He | 10 | 65 m/z |
| Fe | ICP-MS | Rh | ORS | He | 10 | 56 m/z |
| Hg | ICP-MS | Ir | ORS | He | 10 | 202 m/z |
| Mn | ICP-MS | Rh | ORS | He | 10 | 55 m/z |
| Ni | ICP-MS | Rh | ORS | He | 10 | 60 m/z |
| P | ICP-MS | Rh | ORS | HEHe | 10 | 31 m/z |
| Pb | ICP-MS | Ir | ORS | He | 10 | 208 m/z |
| Sb | ICP-MS | Rh | ORS | He | 10 | 121 m/z |
| Se | ICP-MS | Rh | ORS | HEHe | 10 | 78 m/z |
| Sn | ICP-MS | Rh | ORS | He | 10 | 118 m/z |
| Tl | ICP-MS | Rh | ORS | He | 10 | 205 m/z |
| U | ICP-MS | Ir | ORS | He | 10 | 238 m/z |
| V | ICP-MS | Rh | ORS | He | 10 | 51 m/z |
| Zn | ICP-MS | Rh | ORS | He | 10 | 66 m/z |

Table 49 Instrumental Techniques used for Dissolved Elements in S2

| Analyte | Instrument | Internal Standard | Reaction/ Collision Cell | Cell Mode/Gas | Final Dilution Factor | Ion / Wavelength |
|---|---|---|---|---|---|---|
| Ag | ICP-MS | Rh | ORS | He | 1.3 | 107 m/z |
| Al | ICP-MS | Rh | ORS | He | 1.3 | 27 m/z |
| As | ICP-MS | Rh | ORS | He | 1.3 | 75 m/z |
| Be | ICP-MS | Rh | ORS | He | 1.3 | 9 m/z |
| Cd | ICP-MS | Rh | ORS | He | 1.3 | 114 m/z |
| Co | ICP-MS | Rh | ORS | He | 1.3 | 59 m/z |
| Cr | ICP-MS | Rh | ORS | He | 1.3 | 52 m/z |
| Cu | ICP-MS | Rh | ORS | He | 1.3 | 65 m/z |
| Fe | ICP-MS | Rh | ORS | He | 1.3 | 56 m/z |
| Hg | ICP-MS | Ir | ORS | He | 1.3 | 202 m/z |
| Mn | ICP-MS | Rh | ORS | He | 1.3 | 55 m/z |
| Mo | ICP-MS | Rh | ORS | He | 1.3 | 95 m/z |
| Ni | ICP-MS | Rh | ORS | He | 1.3 | 60 m/z |
| Pb | ICP-MS | Ir | ORS | He | 1.3 | 208 m/z |
| Sb | ICP-MS | Rh | ORS | He | 1.3 | 121 m/z |
| Se | ICP-MS | Rh | ORS | HEHe | 1.3 | 78 m/z |
| Tl | ICP-MS | Rh | ORS | He | 1.3 | 205 m/z |
| U | ICP-MS | Ir | ORS | He | 1.3 | 238 m/z |
| V | ICP-MS | Rh | ORS | He | 1.3 | 51 m/z |
| Zn | ICP-MS | Rh | ORS | He | 1.3 | 66 m/z |

## APPENDIX 2 – ASSIGNED VALUE, Z-SCORE AND $E_N$ SCORE CALCULATION

The assigned value was calculated as the robust average using the procedure described in 'ISO13258:2022, Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.[6] The uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 50.

Table 50 Uncertainty of Assigned Value for Fe in Sample S1

| | |
|---|---|
| No. results (p) | 10 |
| Robust Average | 42.2 µg/L |
| $S_{rob\ av}$ | 4.8 µg/L |
| $u_{rob\ av}$ | 1.9 µg/L |
| $k$ | 2 |
| $U_{rob\ av}$ | 3.8 µg/L |

The assigned value for **Fe** in Sample S1 is **42.2 ± 3.8 µg/L.**

**z-Score and $E_n$-score**

For each participant's result a z-score and $E_n$-score are calculated according to Equation 2 and Equation 3 respectively (see page 7).

A worked example is set out below in Table 51.

Table 51 z-Score and $E_n$-score for Fe result reported by Laboratory 2 in S1

| Ag Result µg/L | Assigned Value µg/L | Set Target Standard Deviation | z-Score | $E_n$-Score |
|---|---|---|---|---|
| 41 ± 9 | 42.2 ± 3.8 | 15% as CV or 0.15 x 42.2 = = 6.3 µg/L | $z = \frac{(41 - 42.2)}{6.3}$ z = -0.19 | $En = \frac{(41 - 42.2)}{\sqrt{9^2 + 3.8^2}}$ $E_n$ = -0.12 |

## APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.[10, 12] Between 2007 and 2022, NMI carried out 31 proficiency tests for metals in water. These studies involved analyses of dissolved or total elements at low and high levels in potable, fresh (river), saline water, ground water and waste water. Laboratory X participated and submitted satisfactory results in 21 of these PTs. This data can be separated into two ranges of results: 0.0005 to 0.01 mg/L and 0.01 to 0.10 mg/L. Results are presented in Tables 52 and 53.

Table 52 Laboratory X Reported Results for Ni at 0.0005 to 0.01 mg/L Level

| Study No. | Sample | Laboratory result* mg/L | Assigned value mg/L | Robust CV of all results (%) | Number of Results |
|---|---|---|---|---|---|
| AQA 11-07 | Fresh | 0.0015 ± 0.0003 | 0.00100 ± 0.00001 | 24 | 15 |
| | Fresh | 0.0039 ± 0.00078 | 0.00306 ± 0.00016 | 18 | 19 |
| | Fresh | 0.0039 ± 0.00078 | 0.00306 ± 0.00016 | 9.6 | 19 |
| AQA 12-20 | Saline | 0.0039 ± 0.0008 | 0.00370 ± 0.00028 | 13 | 19 |
| AQA 13-09 | Fresh | 0.0044 ± 0.0009 | 0.00409 ± 0.00017 | 7.9 | 15 |
| AQA 13-22 | Saline | 0.00170 ± 0.00034 | 0.00165 ± 0.00014 | 13 | 14 |
| | Saline | 0.00384 ± 0.00077 | 0.00378 ± 0.00012 | 13 | 14 |
| AQA 15-06 | Sea | 0.00180 ±0.0004 | 0.00177 ± 0.00021 | 28 | 12 |
| | Sea | 0.00172 ± 0.0004 | 0.00177 ± 0.00021 | 28 | 11 |
| AQA 15-18 | Surface | 0.002 ± 0.0003 | 0.00196 ± 0.00013 | 7.8 | 10 |
| AQA 16-03 | Waste | 0.0041 ± 0.0008 | 0.00398 ± 0.00031 | 8.6 | 9 |
| AQA 16-15 | Sea | 0.0070 ± 0.0010 | 0.00652 ± 0.00038 | 9.4 | 16 |
| AQA 17-16 | Sea | 0.0015 ± 0.0003 | 0.00143 ± 0.00029 | 22 | 10 |
| AQA 18-16 | Sea | 0.0022 ± 0.0005 | 0.00206 ± 0.00015 | 11 | 14 |
| AQA 19-07 | Fresh | 0.0018 ± 0.0004 | 0.00187 ± 0.00009 | 5.3 | 10 |
| AQA 19-16 | Sea | 0.0021 ± 0.0004 | 0.00168 ± 0.00037 | 25 | 8 |
| AQA 20-16 | Sea | 0.0013 ± 0.0003 | 0.00178 ± 0.00034 | 24 | 10 |
| AQA 21-09 | River | 0.0007 ± 0.0002 | 0.000756 ± 0.000059 | 8.9 | 8 |
| AQA 21-18 | Saline Water | 0.0029 ± 0.0006 | 0.00298 ± 0.00031 | 13 | 6 |
| AQA 22-10 | Potable | 0.007 ± 0.0011 | 0.00845 ± 0.00036 | 6.1 | 13 |
| AQA 22-17 | Sea Water | 0.0028 ± 0.00056 | 0.00286 ± 0.00027 | 12 | 15 |
| AQA 22-17 | River Water | 0.0035 ± 0.00027 | 0.00364 ± 0.00026 | 10 | 13 |
| Average | | | | 14** | |

*Expanded uncertainty at approximately 95% confidence. ** The mean value of Robust CV was used.

Table 53 Laboratory X Reported Results for Ni at 0.01 to 0.10 mg/L Level

| Study No. | Sample | Laboratory result* mg/L | Assigned value mg/L | Robust CV of all results (%) | Number of Results |
|---|---|---|---|---|---|
| AQA 11-17 | Waste | 0.10 ± 0.009 | 0.099 ± 0.001 | 2 | 15 |
| | Waste | 0.10 ± 0.009 | 0.098 ± 0.001 | 2 | 15 |
| AQA 12-09 | Potable | 0.047 ± 0.007 | 0.045 ± 0.002 | 6.7 | 19 |
| | Potable | 0.055 ± 0.008 | 0.053 ± 0.002 | 7.4 | 19 |
| AQA 12-20 | Saline | 0.0415 ± 0.0083 | 0.0384 ± 0.0021 | 11 | 22 |
| AQA 13-09 | Fresh | 0.0393 ± 0.0040 | 0.0361 ± 0.0010 | 4.8 | 16 |
| | Fresh | 0.0258 ± 0.0030 | 0.0272 ± 0.0025 | 15 | 15 |
| AQA 14-08 | Ground | 0.019 ± 0.004 | 0.0191 ± 0.0007 | 7.9 | 13 |
| AQA 14-19 | Potable | 0.019 ± 0.004 | 0.0183 ± 0.0013 | 11 | 14 |

Table 53 Laboratory X Reported Results for Ni at 0.01 to 0.10 mg/L Level (continued)

| Study No. | Sample | Laboratory result* mg/L | Assigned value mg/L | Robust CV of all results (%) | Number of Results |
|---|---|---|---|---|---|
| AQA 15-18 | Surface | 0.036 ± 0.0035 | 0.0336 ± 0.0013 | 5.1 | 13 |
| AQA 16-03 | Waste | 0.042 ± 0.0045 | 0.0352 ± 0.0050 | 19 | 11 |
| AQA 16-15 | Sea | 0.0456 ± 0.0060 | 0.0409 ± 0.0029 | 12 | 17 |
| AQA 17-16 | Sea | 0.0116 ± 0.0012 | 0.0101 ± 0.0023 | 27 | 9 |
| AQA 18-05 | Potable | 0.017 ± 0.002 | 0.0172 ± 0.0010 | 8.7 | 16 |
| AQA 18-16 | Sea | 0.015 ± 0.0030 | 0.0138 ± 0.0014 | 15 | 15 |
| AQA 19-07 | Fresh | 0.029 ± 0.0035 | 0.0283 ± 0.0009 | 4.3 | 11 |
| AQA 20-07 | Potable | 0.010 ± 0.002 | 0.0106 ± 0.0004 | 6 | 16 |
| AQA 21-09 | Waste | 0.014 ± 0.0021 | 0.0143 ± 0.0006 | 8.1 | 21 |
| Average | | | | 9.6** | |

*Expanded uncertainty at 95% confidence level. **The mean value of Robust CV was used

Taking the average of the robust CVs over these PT samples for each concentration range gives estimates of the relative standard uncertainty of 14% and 9.6% respectively. Using a coverage factor of two gives relative expanded uncertainties of 28% and 20% respectively, at a level of confidence of 95% level.

Table 54 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the ranges 0.0005 – 0.01 mg/L and 0.01 – 0.10 mg/L.

Table 54 Uncertainty of Ni results estimated using PT data

| Results mg/L | Uncertainty mg/L |
|---|---|
| 0.00050 | 0.00014 |
| 0.00100 | 0.00028 |
| 0.0100 | 0.0020 |
| 0.100 | 0.020 |
| 0.150 | 0.030 |

The estimates of 28% and 20% relative passes the test of being reasonable, and the analysis of the thirty-three different PT samples over ten years can be assumed to include all the relevant uncertainty components (different matrices, operators, reagents, calibrators etc.), and so complies with ISO 17025.[8]

# APPENDIX 4 - ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| APHA | American Public Health Association |
| CITAC | Cooperation on International Traceability in Analytical Chemistry |
| CRI | Collision Reaction Interface |
| CRM | Certified Reference Material |
| CV | Coefficient of Variation |
| $CV_{rob}$ | Robust Coefficient of Variation |
| CVAAS | Cold Vapour Atomic Absorption Spectrometry |
| CVAFS | Cold Vapour Atomic Fluorescence Spectrometry |
| DRC | Dynamic Reaction Cell |
| GFAAS | Graphite Furnace Atomic Absorption Spectrometry |
| GUM | Guide to the Expression of Uncertainty in Measurement |
| HEHe | High energy He mode |
| H.V. | Homogeneity Value |
| HR-ICP-MS | High Resolution Inductively Coupled Plasma – Mass Spectrometry |
| IDMS | Isotope Dilution Mass Spectrometry |
| ICP-MS | Inductively Coupled Plasma – Mass Spectrometry |
| ICP-MS/MS | Inductively Coupled Plasma – Tandem Mass Spectrometry |
| ICP-OES | Inductively Coupled Plasma – Optical Emission Spectrometry |
| ISO/IEC | International Organisation for Standardisation / International Electrotechnical Commission |
| IUPAC | International Union of Pure and Applied Chemists |
| KED | Kinetic Energy Discrimination |
| Max | Maximum value in a set of results |
| Md | Median |
| Min | Minimum value in a set of results |
| MU | Measurement Uncertainty |
| N | Number of Participants |
| NIST | National Institute of Standards and Technology |
| NMI | National Measurement Institute (of Australia) |
| NR | Not Reported |
| NT | Not Tested |
| ORS | Octopole Reaction System |
| PCV | Performance Coefficient of Variation |
| PT | Proficiency Test |
| RM | Reference Material |
| SA-ICP-MS | Standard Addition Inductively Coupled Plasma – Mass Spectrometry |
| $SD_{rob}$ | Robust Standard Deviation |
| SI | The International System of Units |
| SS | Spiked sample |
| S.V. | Spiked or formulated concentration of a PT sample |
| $s^2_{sam}$ | Sampling variance |
| $s_a/\sigma$ | Analytical standard deviation divided by the target standard deviation |
| Target SD | Target standard deviation (symbol: $\sigma$) |
| UC | Universal Cell |
| VGA-ICP-OES | Vapour Generation Accessory – Inductively Coupled Plasma – Optical Emission Spectrometry |

## APPENDIX 5 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 55 Instrument Conditions Ag

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 107 |
| **2** | ICP-MS | In | NA | | 10 | 1 | 107 |
| **3** | ICP-MS | | | | | | 109 |
| **4** | ICP-MS | 103 | ORS | He | 1 | 1 | 107 |
| **6** | ICP-MS | Rh | NA | NA | 1 | 1 | 109 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 107 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 107 |
| **9** | ICP-MS | 103 Rh | DRC | He | 1 | 1 | m/z 107 |
| **10** | ICP-MS | Rh | ORS | He | 10 | NA | 107 |
| **11** | ICP-MS | Rh | | He | 1 | NA | 107 |
| **12** | ICP-MS | Rh | CRI | He | 1 | 1 | 107 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Y | KED | | 10 | NA | 107 |
| **15** | ICP-MS/MS | Rh103 | UC | standard mode | 20 | NA | 107 |
| **16** | ICP-MS | Rh | KED | He | 20 | 1 | 109 |

Table 56 Instrument Conditions Al

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 27 |
| **2** | ICP-OES-AV-buffer | Y | NA | | 1 | 1 | 394.401 |
| **3** | ICP-MS | | | | | | 27 |
| **4** | ICP-MS | 45 | ORS | He | 1 | 1 | 27 |
| **6** | ICP-MS | Sc | NA | NA | 1 | 1 | 27 |
| **7** | ICP-MS | Ge | ORS | He | 1.05 | 1.05 | 27 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 27 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 27 |
| **10** | ICP-OES-AV | Y | NA | NA | NA | 2 | 167.019 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 27 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 27 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Li6 | | O2 | 10 | NA | 27 |
| **15** | ICP-MS/MS | Sc45 | UC | NH3 | 20 | NA | 27 |
| **16** | ICP-MS | Sc | KED | He | 20 | 1 | 27 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 27 |

Table 57 Instrument Conditions As

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 75 |
| **2** | ICP-MS | Ga | CRI | He | 10 | 1 | 75 |
| **3** | ICP-MS | | | | | | 75 |
| **4** | ICP-MS | 72 | ORS | He | 1 | 1 | 75 |
| **6** | ICP-MS | Rh | KED | He | 1 | 1 | 75 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 75 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 75 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 75 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 75 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 75 |
| **12** | ICP-MS | Rh | CRI | He | 1 | 1 | 75 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Y | | O2 | 10 | NA | 75 |
| **15** | ICP-MS/MS | Rh103 | UC | O2 | 20 | NA | 91 |
| **16** | ICP-MS | Te | KED | He | 20 | 1 | 75 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 75 |

Table 58 Instrument Conditions Be

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | NA | | | 9 |
| **2** | ICP-MS | In | NA | | 10 | 1 | 9 |
| **3** | ICP-MS | | | | | | 9 |
| **4** | ICP-OES-AV-buffer | Lu | | | 1 | 1 | 313.107 |
| **6** | ICP-MS | Sc | NA | NA | 1 | 1 | 9 |
| **7** | ICP-MS | Ge | ORS | He | 1.05 | 1.05 | 9 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 9 |
| **9** | ICP-MS | 45 Sc | DRC | NA | 1 | 1 | m/z 9 |
| **10** | ICP-MS | Rh | ORS | He | 10 | NA | 9 |
| **11** | ICP-MS | Sc | | standard mode | 1 | NA | 9 |
| **12** | ICP-MS | Sc | CRI | NA | 1 | 1 | 9 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Li6 | KED | | 10 | NA | 9 |
| **15** | ICP-MS/MS | Sc45 | UC | standard mode | 20 | NA | 9 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 9 |

## Table 59 Instrument Conditions Cd

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 111 |
| **2** | ICP-MS | In | NA | | 10 | 1 | 111 |
| **3** | ICP-MS | | | | | | 111 |
| **4** | ICP-MS | 103 | ORS | He | 1 | 1 | 114 |
| **6** | ICP-MS | Rh | NA | NA | 1 | 1 | 111 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 111 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 111 |
| **9** | ICP-MS | 103 Rh | DRC | He | 1 | 1 | m/z 111 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 111 |
| **11** | ICP-MS | Rh | | He | 1 | NA | 111 |
| **12** | ICP-MS | Rh | CRI | He | 1 | 1 | 111 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | In | KED | | 10 | NA | 111 |
| **15** | ICP-MS/MS | Rh103 | UC | O2 | 20 | NA | 114 |
| **16** | ICP-MS | Rh | KED | He | 20 | 1 | 111 |

## Table 60 Instrument Conditions Co

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | NA | | 59 |
| **2** | ICP-MS | In | NA | | 10 | 1 | 59 |
| **3** | ICP-MS | | | | NA | | 59 |
| **4** | ICP-MS | 103 | ORS | He | 1 | 1 | 59 |
| **6** | ICP-MS | Rh | KED | He | NA | 1 | 59 |
| **7** | ICP-MS | In | ORS | He | NA | 1.05 | 59 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 59 |
| **9** | ICP-MS | 45 Sc | DRC | He | NA | 1 | m/z 59 |
| **10** | ICP-MS | Rh | ORS | He | NA | 10 | 59 |
| **12** | ICP-MS | Sc | CRI | He | NA | 1 | 59 |
| **13** | ICP-MS | | | | NA | | |
| **16** | ICP-MS | Ga | KED | He | NA | 1 | 59 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | NA | 10 | 59 |

## Table 61 Instrument Conditions Cr

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 52 |
| **2** | ICP-MS | Ga | DRC | NH3 | 10 | 1 | 52 |
| **3** | ICP-MS | | | | | | 52 |
| **4** | ICP-MS | 72 | ORS | He | 1 | 1 | 52 |
| **6** | ICP-MS | Sc | KED | He | 1 | 1 | 52 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 52 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 52 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 52 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 52 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 52 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 52 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Sc | KED | | 10 | NA | 52 |
| **15** | ICP-MS/MS | Sc45 | UC | NH3 | 20 | NA | 52 |
| **16** | ICP-MS | Ga | DRC | NH3 | 20 | 1 | 52 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 52 |

## Table 62 Instrument Conditions Cu

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 63 |
| **2** | ICP-MS | | CRI | | 10 | 1 | 63 |
| **3** | ICP-MS | | | | | | 63 |
| **4** | ICP-MS | 103 | ORS | He | 1 | 1 | 65 |
| **6** | ICP-MS | Rh | KED | He | 1 | 1 | 65 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 63 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 65 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 63 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 63 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 63 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 63 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Sc | KED | | 10 | NA | 63 |
| **15** | ICP-MS/MS | Rh103 | UC | He | 20 | NA | 65 |
| **16** | ICP-MS | Ga | KED | He | 20 | 1 | 63 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 63 |

## Table 63  Instrument Conditions Fe

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 56 |
| **2** | ICP-OES-AV-buffer | Y | | | 1 | 1 | 239.562 |
| **3** | ICP-MS | | | | | | 57 |
| **4** | ICP-MS | 72 | ORS | He | 1 | 10 | 56 |
| **6** | ICP-MS | Sc | KED | He | 1 | 1 | 56 |
| **7** | ICP-MS | Ge | ORS | He | 1.05 | 1.05 | 56 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 57 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 56 |
| **10** | ICP-OES-AV | Y | NA | NA | 2 | 2 | 238.204 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 56 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 56 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Sc | KED | | 10 | NA | 56 |
| **15** | ICP-MS/MS | Rh103 | UC | NH3 | 20 | NA | 54 |
| **16** | ICP-MS | Ga | DRC | NH3 | 20 | 1 | 54 |

## Table 64  Instrument Conditions Hg

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | GFAAS | NA | NA | NA | | | 253.7 |
| **2** | CVAAS | | | | 2 | 2 | 253.7nm |
| **3** | ICP-MS | | | | | | 201 |
| **4** | VGA-ICP-OES | | | | 1 | 1 | 194.164 |
| **6** | ICP-MS | Ir | NA | NA | 1 | 1 | 201 |
| **7** | ICP-MS | Ir | ORS | He | 1.05 | 1.05 | 202 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 202 |
| **9** | ICP-MS | 175 Lu | DRC | He | 1 | 1 | m/z 201 |
| **10** | CVAAS | | | | | 2 | |
| **11** | ICP-MS | Lu | | He | 1 | NA | 202 |
| **12** | ICP-MS | Lu | CRI | He | 1 | 1 | 201 |
| **13** | ICP-MS | | | | | | |
| **14** | CVAAS | SnCl2 | KED | | | NA | |
| **15** | ICP-MS/MS | | | | 20 | NA | |
| **16** | CVAFS | NA | NA | NA | 5 | 5 | NA |

## Table 65  Instrument Conditions Mn

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 55 |
| **2** | ICP-MS | | CRI | | 10 | 1 | 55 |
| **3** | ICP-MS | | | | | | 55 |
| **4** | ICP-MS | 72 | ORS | He | 1 | 1 | 55 |
| **6** | ICP-MS | Sc | KED | He | 1 | 1 | 55 |
| **7** | ICP-MS | Ge | ORS | He | 1.05 | 1.05 | 55 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 55 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 55 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 55 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 55 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 55 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Sc | KED | | 10 | NA | 55 |
| **15** | ICP-MS/MS | Rh103 | UC | NH3 | 20 | NA | 55 |
| **16** | ICP-MS | Sc | KED | He | 20 | 1 | 55 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 55 |

## Table 66  Instrument Conditions Mo

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | NA | | 95 |
| **2** | ICP-MS | | NA | | 10 | 1 | 95 |
| **3** | ICP-MS | | | | NA | | 95 |
| **4** | ICP-MS | 72 | ORS | He | 1 | 1 | 98 |
| **6** | ICP-MS | Rh | NA | NA | NA | 1 | 95 |
| **7** | ICP-MS | Rh | ORS | He | NA | 1.05 | 95 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 98 |
| **9** | ICP-MS | 45 Sc | DRC | He | NA | 1 | m/z 95 |
| **10** | ICP-MS | Rh | ORS | He | NA | 10 | 95 |
| **12** | ICP-MS | Rh | CRI | He | NA | 1 | 95 |
| **13** | ICP-MS | | | | NA | | |
| **16** | ICP-MS | Rh | KED | He | NA | 1 | 98 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | NA | 10 | 98 |

## Table 67 Instrument Conditions Ni

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 60 |
| **2** | ICP-MS | | CRI | | 10 | 1 | 60 |
| **3** | ICP-MS | | | | | | 60 |
| **4** | ICP-MS | 103 | ORS | He | 1 | 1 | 60 |
| **6** | ICP-MS | Rh | KED | He | 1 | 1 | 60 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 60 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 60 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 60 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 60 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 60 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 60 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Sc | KED | | 10 | NA | 60 |
| **15** | ICP-MS/MS | Rh103 | UC | He | 20 | NA | 60 |
| **16** | ICP-MS | Ga | KED | He | 20 | 1 | 60 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 60 |

## Table 68 Instrument Conditions P

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-OES-AV | Eu | NA | NA | | NA | 185.827 |
| **2** | ICP-OES-AV-buffer | Y | | | 1 | NA | 214.914 |
| **3** | ICP-MS | | | | | NA | 31 |
| **6** | ICP-MS | Sc | KED | He | 1 | NA | 31 |
| **7** | ICP-MS | Ge | ORS | He | 1.05 | NA | 31 |
| **9** | ICP-MS | 45 Sc | DRC | HEHe | 1 | NA | m/z 31 |
| **10** | ICP-OES-AV | Y | NA | NA | 2 | NA | 213.618 |
| **13** | ICP-MS | | | | | NA | |
| **14** | ICP-OES-AV | Yb | KED | | 50 | NA | 213nm |
| **15** | ICP-MS/MS | ScO61 | UC | O2 | 20 | NA | 47 |

## Table 69 Instrument Conditions Pb

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 208 |
| **2** | ICP-MS | | NA | | 10 | 1 | 208 |
| **3** | ICP-MS | | | | | | 208 |
| **4** | ICP-MS | 193 | ORS | He | 1 | 1 | 208 |
| **6** | ICP-MS | Ir | NA | NA | 1 | 1 | 206+207+208 |
| **7** | ICP-MS | Ir | ORS | He | 1.05 | 1.05 | 208 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 206,207,208 |
| **9** | ICP-MS | 89 Y | DRC | He | 1 | 1 | m/z 208 |
| **10** | ICP-MS | Ir | ORS | He | 10 | 10 | 208 |
| **11** | ICP-MS | Lu | | He | 1 | NA | 208 |
| **12** | ICP-MS | Lu | CRI | He | 1 | 1 | 208 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Ir | KED | | 10 | NA | 206 |
| **15** | ICP-MS/MS | Ir193 | UC | standard mode | 20 | NA | 208 |
| **16** | ICP-MS | Tb | KED | He | 20 | 1 | 206+207+208 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 208 |

## Table 70 Instrument Conditions Sb

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 121 |
| **2** | ICP-MS | | NA | | 10 | 1 | 121 |
| **3** | ICP-MS | | | | | | 121 |
| **4** | ICP-MS | 72 | ORS | He | 1 | 1 | 121 |
| **6** | ICP-MS | Rh | NA | NA | 1 | 1 | 121 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 121 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 121 |
| **9** | ICP-MS | 89 Y | DRC | He | 1 | 1 | m/z 121 |
| **10** | ICP-MS | Rh | ORS | He | NA | 10 | 121 |
| **11** | ICP-MS | Rh | | He | 1 | NA | 121 |
| **12** | ICP-MS | Rh | CRI | He | 1 | 1 | 123 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | In | KED | | 10 | NA | 121 |
| **15** | ICP-MS/MS | Rh103 | UC | standard mode | 20 | NA | 121 |
| **16** | ICP-MS | Rh | KED | He | 20 | 1 | 121 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 121 |

## Table 71 Instrument Conditions Se

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | HEHe | | | 78 |
| **2** | ICP-MS | | CRI | | 10 | 1 | 82 |
| **3** | ICP-MS | | | | | | 82 |
| **4** | ICP-MS | 103 | ORS | He | 1 | 1 | 78 |
| **6** | ICP-MS | Rh | DRC | NH3 | 1 | 1 | 82 |
| **7** | ICP-MS | In | ORS | H2 | 1.05 | 1.05 | 78 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 82 |
| **9** | ICP-MS | 45 Sc | DRC | HEHe | 1 | 1 | m/z 78 |
| **10** | ICP-MS | Rh | ORS | HEHe | 10 | 10 | 77 |
| **11** | ICP-MS | Sc | | HEHe | 1 | NA | 78 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 78 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Y | KED | | 10 | NA | 78 |
| **15** | ICP-MS/MS | Rh103 | UC | O2 | 20 | NA | 96 |
| **16** | ICP-MS | Te | DRC | NH3 | 20 | 1 | 82 |

## Table 72 Instrument Conditions Sn

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | NA | 118 |
| **2** | ICP-MS | | NA | | 10 | NA | 118 |
| **3** | ICP-MS | | | | | NA | 118 |
| **4** | ICP-MS | 115 | ORS | He | 1 | 1 | 118 |
| **7** | ICP-MS | Ir | ORS | He | 1.05 | NA | 118 |
| **9** | ICP-MS | 89 Y | DRC | He | 1 | NA | m/z 118 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 118 |
| **11** | ICP-MS | Rh | | He | 1 | NA | 118 |
| **12** | ICP-MS | Rh | CRI | He | 1 | NA | 118 |
| **13** | ICP-MS | | | | | NA | |
| **14** | ICP-MS | In | KED | | 10 | NA | 118 |
| **15** | ICP-MS/MS | Rh103 | UC | standard mode | 20 | NA | 118 |
| **16** | ICP-MS | Rh | KED | He | 20 | NA | 120 |

## Table 73 Instrument Conditions Tl

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 205 |
| **2** | ICP-MS | | NA | | 10 | 1 | 203 |
| **3** | ICP-MS | | | | | | 205 |
| **4** | ICP-MS | 193 | ORS | He | 1 | 1 | 205 |
| **6** | ICP-MS | Ir | NA | NA | 1 | 1 | 205 |
| **7** | ICP-MS | Ir | ORS | He | 1.05 | 1.05 | 205 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 203 |
| **9** | ICP-MS | 89 Y | DRC | He | 1 | 1 | m/z 205 |
| **10** | ICP-MS | Ir | ORS | He | 10 | NA | 205 |
| **11** | ICP-MS | Lu | | He | 1 | NA | 205 |
| **12** | ICP-MS | Lu | CRI | He | 1 | 1 | 205 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Ir | KED | | 10 | NA | 205 |
| **15** | ICP-MS/MS | Ir193 | UC | standard mode | 20 | NA | 205 |
| **16** | ICP-MS | Tb | KED | He | 20 | 1 | 205 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 205 |

## Table 74 Instrument Conditions U

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 238 |
| **2** | ICP-MS | | NA | | 10 | 1 | 238 |
| **3** | ICP-MS | | | | | | 238 |
| **4** | ICP-MS | 193 | ORS | He | 1 | 1 | 238 |
| **6** | ICP-MS | Ir | NA | NA | 1 | 1 | 238 |
| **7** | ICP-MS | Ir | ORS | He | 1.05 | 1.05 | 238 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 238 |
| **9** | ICP-MS | 89 Y | DRC | He | 1 | 1 | m/z 238 |
| **11** | ICP-MS | Lu | | He | 1 | NA | 238 |
| **12** | ICP-MS | Lu | CRI | He | 1 | 1 | 238 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Ir | | O2 | 10 | NA | 238 |
| **15** | ICP-MS/MS | Ir193 | UC | standard mode | 20 | NA | 238 |
| **16** | ICP-MS | Tb | KED | He | 20 | 1 | 238 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 238 |

## Table 75 Instrument Conditions V

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 51 |
| **2** | ICP-MS | | DRC | NH3 | 10 | 1 | 51 |
| **3** | ICP-MS | | | | | | 51 |
| **4** | ICP-MS | 45 | ORS | He | 1 | 1 | 51 |
| **6** | ICP-MS | Sc | KED | He | 1 | 1 | 51 |
| **7** | ICP-MS | Ge | ORS | He | 1.05 | 1.05 | 51 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 51 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 51 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 51 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 51 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 51 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Sc | | O2 | 10 | NA | 51 |
| **15** | ICP-MS/MS | Sc45 | UC | NH3 | 20 | NA | 51 |
| **16** | ICP-MS | Sc | DRC | NH3 | 20 | 1 | 51 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 51 |

## Table 76 Instrument Conditions Zn

| Laboratory Code | Instrument | Internal standard | Reaction Cell | Reaction Gas | S1 Final Dilution Factor | S2 Final Dilution Factor | Wavelength (nm)/ Ion(m/z)/ Absorbance(nm) |
|---|---|---|---|---|---|---|---|
| **1** | ICP-MS | Sc, Ir, Rh | ORS | He | | | 66 |
| **2** | ICP-MS | | CRI | | 10 | 1 | 66 |
| **3** | ICP-MS | | | | | | 66 |
| **4** | ICP-MS | 115 | ORS | He | 1 | 1 | 66 |
| **6** | ICP-MS | Rh | KED | He | 1 | 1 | 66 |
| **7** | ICP-MS | In | ORS | He | 1.05 | 1.05 | 66 |
| **8** | ICP-MS | Y, Ce, Ga, Ge, Ph, Ir, Ho, Sc | NA | He | NA | 10 | 66 |
| **9** | ICP-MS | 45 Sc | DRC | He | 1 | 1 | m/z 66 |
| **10** | ICP-MS | Rh | ORS | He | 10 | 10 | 66 |
| **11** | ICP-MS | Sc | | He | 1 | NA | 66 |
| **12** | ICP-MS | Sc | CRI | He | 1 | 1 | 66 |
| **13** | ICP-MS | | | | | | |
| **14** | ICP-MS | Y | KED | | 10 | NA | 66 |
| **15** | ICP-MS/MS | Rh103 | UC | NH3 | 20 | NA | 66 |
| **16** | ICP-MS | Te | KED | He | 20 | 1 | 66 |
| **18** | ICP-MS | Virtual Internal Standard (Sc, Y, Rh, In, Tb, Bi, Th) | | | 10 | 10 | 66 |

# END OF REPORT