Australian Government
Department of Industry, Science and Resources

National Measurement Institute

# Proficiency Test Final Report AQA 24-18 Nutrients and Anions in Sea and River Water

March 2025

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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 24-18 Nutrients and Anions in Sea and River Water. The study focused on the measurement of pH and electrical conductivity at 25ºC, alkalinity to pH 4.5 (as $CaCO_3$), ammonia-N, bromide, chloride, dissolved organic carbon (as dNPOC), fluoride, nitrate-N, nitrite-N, NOx as N (nitrate-N + nitrite-N), orthophosphate-P, silica (as $SiO_2$), sulphate, total hardness (as $CaCO_3$), total dissolved nitrogen, total dissolved phosphorus, total Kjeldahl nitrogen, total nitrogen, total organic carbon (as NPOC) and dissolved B, Ca, K, Mg and Na in river water and sea water.

The sample set consisted of two sea water samples and two river water samples.

Twenty-three laboratories registered to participate, and all submitted results.

The assigned values were the robust average of participants' result. The associated uncertainties were estimated from the robust standard deviation of the 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;*

Of 530 z-scores, 486 (92%) returned an acceptable score of $|z| \le 2.0$.

Of 530 $E_n$ scores, 443 (84%) returned an acceptable score of $|E_n| < 1.0$.

**Laboratories 5**, **18** and **22** reported results for all 37 tests for which a z-score was calculated. **Laboratories 1** (36 out of 36 reported) and **22** (36 out of 37 reported) returned the highest number of acceptable z-scores.

**Laboratory 5** had the highest number of acceptable $E_n$ scores with 36 out of 37 reported.

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

Low level nitrite-N in river water was the test that most challenged participants' analytical techniques. Only four laboratories reported results.

Low level silica in sea water also challenged participants' analytical techniques. Most of the unsatisfactory results were produced by laboratories that used an ICP method

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

Despite differences in matrices and concentrations, on average, participants' performance remained consistent over time.

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

Of 534 numerical results, 518 (97%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0% to 1333% of the reported value. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 4.

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

The study samples were checked for homogeneity and stability during the study conduct and are well characterised, both by in-house testing and from the results of the proficiency round. Surplus test samples from the present study are available for sale.

# 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;
- chlorophyll a in water; and
- controlled drug assay.

AQA 24-18 is the 19$^{th}$ NMI proficiency study of nutrients, anions and physical tests 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 nutrients, anions and physical tests in river water and sea water;
- compare the performance of participant laboratories with their past performance
- develop the practical application of 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 17043:2023 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 38 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

Twenty-three laboratories participated and all submitted results.

The timetable of the study was:

| | |
|---|---|
| Invitation issued: | 23 September 2024 |
| Samples dispatched: | 21 October 2024 |
| Results due: | 15 November 2024 |
| Interim report issued | 22 November 2024 |
| Preliminary report issued: | 26 November 2024 |

### 2.3 Laboratory Code

All participant laboratories were assigned a confidential code number.

### 2.4 Test Material Specification

Four samples were provided for analysis:

**Sample S1** was two identical bottles of 200 mL of frozen sea water;

**Sample S2** was two identical bottles of 200 mL of chilled sea water;

**Sample S3** was two identical bottles of 200 mL of frozen river water;

**Sample S4** was 200 mL of frozen river water.

### 2.5 Sample Preparation, Analysis and Homogeneity Testing

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. However, a partial homogeneity test was conducted for all tests, with the exception of alkalinity and silica in S2, and fluoride and nitrite-nitrogen in S3. The results of partial homogeneity testing are reported in this study as the homogeneity value.

The preparation and analysis are described in Appendix 1.

### 2.6 Stability of Analytes

A stability study was conducted for the less stable analytes (low level Ammonia-N, DOC, Nitrate-N, and Nitrite-N) in S1 and S3 to address issues associated with holding time and holding conditions. The stability study was covered the entire period of the PT study conduct. The set-up of this study together with the results are presented in Appendix 2.

### 2.7 Sample Storage, Dispatch and Receipt

Samples S1, S3 and S4 were frozen whilst S2 was refrigerated.

The samples were dispatched by courier on 21 October 2024.

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.
- If analyses cannot be commenced on the day of receipt, please store samples S1, S3 and S4 frozen and sample S2 chilled.
- Prior to testing, thaw samples S1, S3 and S4 completely.

Participants are asked to report results in units of mg/L except for pH and EC (µS/cm).

| **SAMPLE S1**<br>**2 x 200 mL frozen sea water** | | **SAMPLE S3**<br>**2 x 200 mL frozen river water** | |
|---|---|---|---|
| **Test** | **Estimated Value mg/L** | **Test** | **Estimated Value mg/L** |
| Ammonia-N | 0.005-0.2 | Ammonia-N | 0.05-2 |
| Nitrate-N + Nitrite-N | 0.005-0.2 | Fluoride | 0.05-2 |
| Chloride | >10000 | Nitrate-N | 0.5-20 |
| Fluoride | 0.05-2 | Nitrite-N | 0.05-5 |
| Sulphate | 100-4000 | Bromide | 0.05-5 |
| Dissolved Organic Carbon (as dNPOC) | 100-4000 | Chloride | 5-200 |
| Orthophosphate-P (FRP) | 0.005-0.2 | Sulphate | 5-200 |
| Total Dissolved Nitrogen | 0.05-2 | Dissolved Organic Carbon (as dNPOC) | 0.5-20 |
| Total Dissolved Phosphorus | 0.005-0.2 | Orthophosphate-P | 0.005-0.2 |
| **SAMPLE S2**<br>**2 x 200 mL chilled sea water** | | Total Dissolved Nitrogen | 0.5-20 |
| **Test** | **Estimated Value mg/L** | Total Dissolved Phosphorus | 0.005-0.2 |
| B (dissolved) | 0.5-20 | B (dissolved) | 0.5-20 |
| Ca (dissolved) | 100-4000 | Ca (dissolved) | 0.5-50 |
| K (dissolved) | 0.5-20 | K (dissolved) | 0.5-20 |
| Mg (dissolved) | 0.5-20 | Mg (dissolved) | 0.5-20 |
| Na (dissolved) | 5-200 | Na (dissolved) | 5-200 |
| Silica (as SiO2) | 0.05-2 | **SAMPLE S4**<br>**200 mL frozen river water** | |
| Alkalinity to pH 4.5 (as CaCO3) | 5-200 | **Test** | **Estimated Value mg/L** |
| Hardness, total (CaCO3) | 1000-40000 | Total Kjeldahl Nitrogen | 0.05-5 |
| EC (at 25 °C, µS/cm) | 2000-80000 | Total Nitrogen | 0.5-20 |
| pH (at 25 °C) | 0.5-20 | Total Organic Carbon (as NPOC) | 0.5-20 |

- 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 mg/L).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.
- Please return the completed results sheet by 15 November 2024.

The results due date was extended to 21 November 2024 due to some labs experiencing instrument difficulties.

## 2.9 Interim and Preliminary Reports

An interim report was emailed to participants on 22 November 2024. A preliminary report was issued on 26 November 2024. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and En-scores for each analyte tested by participants.

No data has been changed from the Preliminary Report in this Final Report.

## 3 PARTICIPANT LABORATORY INFORMATION

### 3.1 Methodology for S1, S2, S3 and S4

Measurement methods and instrumental techniques used for the tests in Samples S1, S2, S3 and S4 are presented in Appendices 6, 7, 8 and 9 respectively.

### 3.2 Additional Information

Participants had the option to report additional information for each sample analysed. These are transcribed in Table 1.

Table 1 Additional Information

| Lab Code | Additional Information |
|---|---|
| 7 | Sample S1: Phosphate sample was diluted with low-nutrient seawater with dilution factor of 2 (1:1), and ammonia sample was diluted with low-nutrient seawater with dilution factor of 5 (1:4). |
| 10 | Sample S1: Phosphate sample was diluted with low-nutrient seawater with dilution factor of 2 (1:1), and ammonia sample was diluted with low-nutrient seawater with dilution factor of 5 (1:4). |
| 19 | Sample S1 : Phosphate and ammonium sample was diluted with low-nutrient seawater with dilution factor of 5 (1:4). |

### 3.3 Basis of Participants' Measurement Uncertainty Evaluation

Participants were requested to provide information about the basis of their uncertainty evaluation (Table 2).

Table 2 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<br>Coverage factor not reported | Control Samples | Recoveries of SS | |
| 2 | Standard deviation of replicate analyses multiplied by 2 or 3<br>Coverage factor not reported | Control Samples - CRM<br>Duplicate Analysis | CRM<br>Instrument Calibration<br>Recoveries of SS | Eurachem/CITAC Guide |
| 3 | Coverage factor not reported | Control Samples - RM<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration | |
| 4 | Coverage factor not reported | | | |
| 5 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Control Samples | Recoveries of SS | ISO/GUM |
| 6 | Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)<br>Coverage factor not reported | Duplicate Analysis<br>Instrument Calibration | CRM | ISO/GUM |
| 7* | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control Samples - CRM | CRM | NMI Uncertainty Course |
| 8 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Control Samples - CRM<br>Duplicate Analysis | CRM | Nordtest Report TR537 |
| 9* | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control Samples - RM<br>Duplicate Analysis | | |

| Lab. Code | Approach to Estimating MU | Information Sources for MU Estimation[a] | | Guide Document for Estimating MU |
|---|---|---|---|---|
| | | Precision | Method Bias | |
| 10* | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control Samples - CRM | CRM | NMI Uncertainty Course |
| 11 | Professional judgment<br>Coverage factor not reported | | | |
| 12 | Standard deviation of replicate analyses multiplied by 2 or 3<br>Coverage factor not reported | Control Samples<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Recoveries of SS | ISO/GUM |
| 13 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Control Samples - SS | Recoveries of SS | |
| 14 | Standard deviation of replicate analyses multiplied by 2 or 3<br>k = 2 | Standard deviation from PT studies only | | ISO/GUM |
| 15 | Standard deviation of replicate analyses multiplied by 2 or 3<br>Coverage factor not reported | Control Samples - RM<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration<br>Recoveries of SS | |
| 16 | Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)<br>Coverage factor not reported | Control Samples - CRM<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration<br>Laboratory Bias from PT Studies | Eurachem/CITAC Guide |
| 17 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control Samples - CRM<br>Duplicate Analysis<br>Instrument Calibration | CRM<br>Instrument Calibration<br>Recoveries of SS | ISO/GUM |
| 18 | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control Samples - CRM<br>Duplicate Analysis | CRM<br>Instrument Calibration<br>Recoveries of SS | Nordtest Report TR537 |
| 19* | Top Down - precision and estimates of the method and laboratory bias<br>k = 2 | Control Samples - CRM | CRM | NMI Uncertainty Course |
| 20 | Professional judgment<br>Coverage factor not reported | Control Samples - CRM | CRM<br>Recoveries of SS | Inhouse Method |
| 21 | Standard deviation of replicate analyses multiplied by 2 or 3<br>Coverage factor not reported | Control Samples - SS<br>Duplicate Analysis | | |
| 22 | Top Down - precision and estimates of the method and laboratory bias<br>Coverage factor not reported | Duplicate Analysis<br>Instrument Calibration | CRM<br>Recoveries of SS | NMI Uncertainty Course |
| 23 | Top Down - reproducibility (standard deviation) from PT studies used directly<br>k = 2 | Standard deviation from PT studies only<br>Instrument Calibration | CRM<br>Instrument Calibration | NATA Technical Report |

[a] RM = Reference Material, CRM = Certified Reference Material, SS = Spiked Samples. *Additional Information in Table 3

## Table 3 Additional Information for Basis of Uncertainty Estimate

| Lab Code | Additional Information |
|---|---|
| 7 | Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval) |
| 9 | UoM is based on ISO 17025 Specific Criteria and EURACHEM/CITAC Guide |
| 10 | Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval) |

| | |
|---|---|
| 19 | Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval) |

## 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. Participants' comments are reproduced in Table 4.

Table 4 Participants' Comments

| Lab Code | Participants' Comments | Study Co-ordinator's Response |
|---|---|---|
| 6 | S1, S2, S3 – Analysis require sharing of single bottle across two different sections;<br>DOC/TOC we usually require separate container for analysis (limited volume) | Sample S1 was *two identical* bottles of 200 mL of frozen sea water;<br>Sample S2 was *two identical* bottles of 200 mL of chilled sea water;<br>Sample S3 was *two identical* bottles of 200 mL of frozen river water;<br>Sample S4 was *one bottle* of 200 mL of frozen river water.<br>DOC was included in S2 while TOC was included in S4.<br>To assist with future studies' design we invite participant laboratories to provide information on recommended sample size and any other requirements. |
| 7, 10 and 19 | We normally report our results as molecules in micromol/L. For this PT, we have converted our micromol/L results into mg/L by using MW of the element and we are reporting the element in mg/L. | Thank you for your feedback. We have to design our studies based on the most popular methods used by laboratories and on the report, format used by the majority. |
| 7, 10 and 19 | The samples for ammonium and phosphate are very high in concentration compared to our conditional analysis range. For this PT, phosphate and ammonium sample was diluted with low-nutrient seawater with dilution factor of dilution factor of 5 (1:4). It would be preferable if phosphate and ammonia samples are available in low range for the future PT to avoid the necessity of dilution. | Thank you for your feedback. We will include samples at a lower level in our next studies. The other participants are invited to comment. |

## 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 4.1 Results Summary

Participant results are listed in Tables 5 to 41 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 39. An example chart with an interpretation guide is shown in Figure 1.

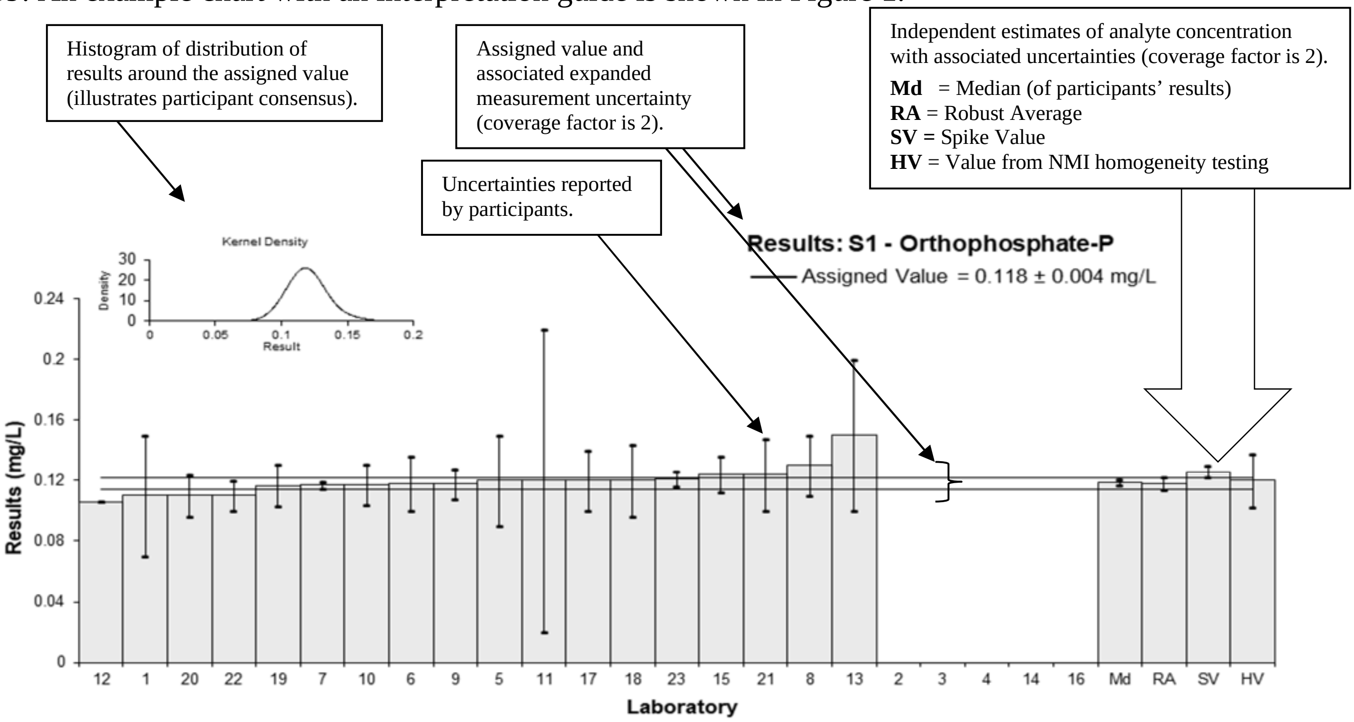



Figure 1 Guide to Presentation of Results

### 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 were obvious blunders, such as those with incorrect units, decimal errors, or results from a different proficiency test item (gross errors) and were removed from 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 3. 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'. 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.[6]

### 4.5 Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment ($\sigma$) 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.

$\sigma = (X) * PCV$ 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 3. 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|):

- $|z| \leq 2.0$ is acceptable;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \geq 3.0$ is unacceptable.

### 4.7 En-Score

An example of $E_n$-score calculation using data from the present study is given in Appendix 3. 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 a 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 ($|E_n|$):

- $|E_n| < 1.0$ is acceptable;
- $|E_n| \geq 1.0$ is unacceptable.

### 4.8 Traceability and Measurement Uncertainty

Laboratories accredited to 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 5

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Ammonia-N |
| **Unit** | mg/L |

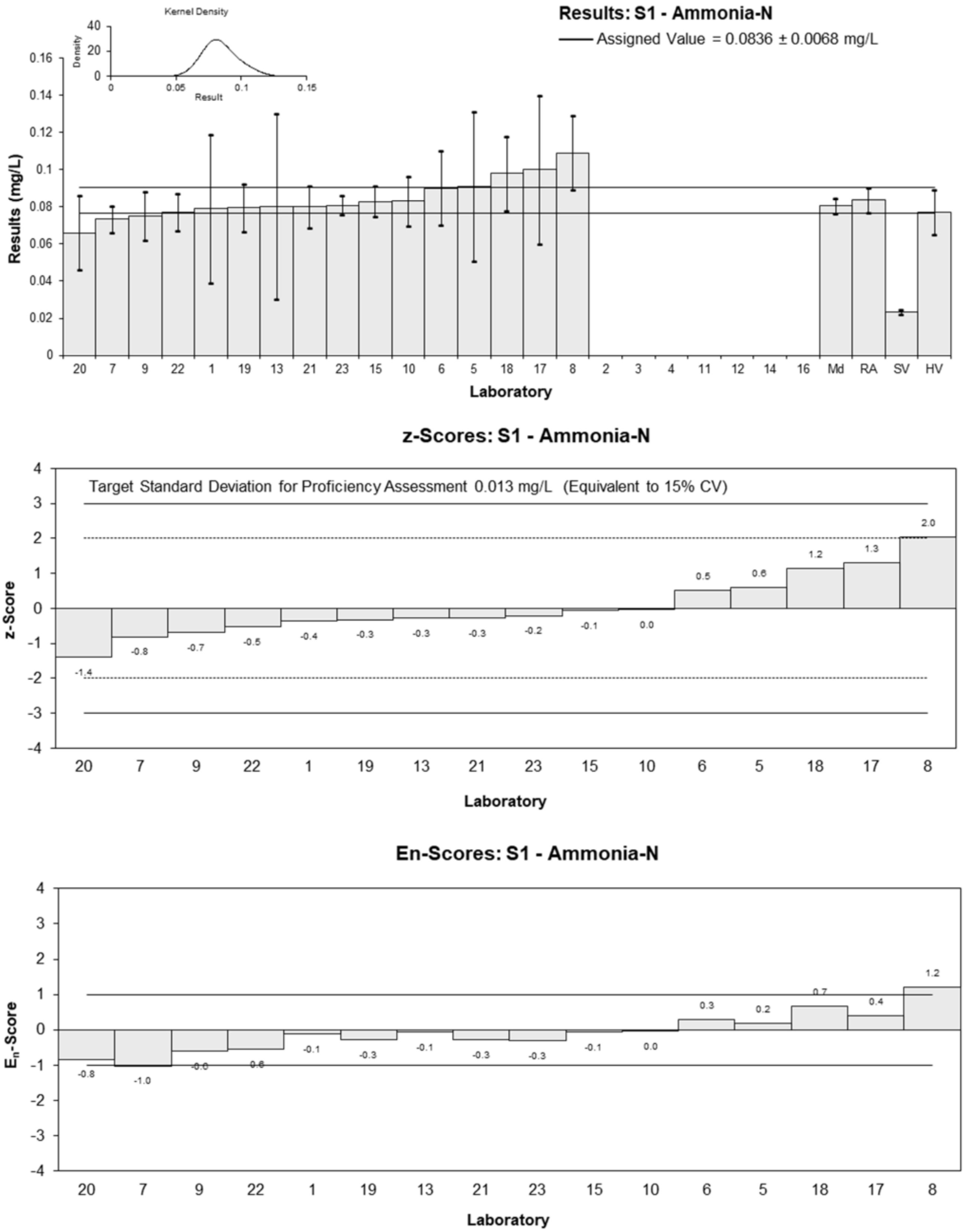
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.079 | 0.04 | -0.37 | -0.11 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.091 | 0.04 | 0.59 | 0.18 |
| **6** | 0.09 | 0.02 | 0.51 | 0.30 |
| **7** | 0.0734 | 0.0073 | -0.81 | -1.02 |
| **8** | 0.109 | 0.02 | 2.03 | 1.20 |
| **9** | 0.075 | 0.013 | -0.69 | -0.59 |
| **10** | 0.0831 | 0.0135 | -0.04 | -0.03 |
| **11** | NR | NR | | |
| **12** | NR | NR | | |
| **13** | 0.08 | 0.05 | -0.29 | -0.07 |
| **14** | NT | NT | | |
| **15** | 0.083 | 0.008 | -0.05 | -0.06 |
| **16** | <0.2 | 1.12 | | |
| **17** | 0.1 | 0.04 | 1.31 | 0.40 |
| **18** | 0.098 | 0.02 | 1.15 | 0.68 |
| **19** | 0.0796 | 0.0129 | -0.32 | -0.27 |
| **20** | 0.066 | 0.02 | -1.40 | -0.83 |
| **21** | 0.0800 | 0.0112 | -0.29 | -0.27 |
| **22** | 0.077 | 0.010 | -0.53 | -0.55 |
| **23** | 0.081 | 0.005 | -0.21 | -0.31 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0836 | 0.0068 |
| **Spike Value*** | 0.0233 | 0.0012 |
| **Homogeneity Value** | 0.077 | 0.012 |
| **Robust Average** | 0.0836 | 0.0068 |
| **Median** | 0.0805 | 0.0042 |
| **Mean** | 0.0841 | |
| **N** | 16 | |
| **Max** | 0.109 | |
| **Min** | 0.066 | |
| **Robust SD** | 0.011 | |
| **Robust CV** | 13% | |

*Incurred value not included



Results: S1 - Ammonia-N
Assigned Value = 0.0836 ± 0.0068 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
z-Scores: S1 - Ammonia-N
Target Standard Deviation for Proficiency Assessment 0.013 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - Ammonia-N
En-Score
Laboratory


Figure 2

Table 6

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Chloride |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 22000 | 6000 | 0.19 | 0.07 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 22000 | 4000 | 0.19 | 0.10 |
| **6** | 21400 | 1540 | -0.09 | -0.12 |
| **7** | NT | NT | | |
| **8** | 22659 | 2270 | 0.49 | 0.46 |
| **9** | 27900 | 1700 | 2.92 | 3.56 |
| **10** | NT | NT | | |
| **11** | 21400 | 4280 | -0.09 | -0.05 |
| **12** | 21592 | 432 | 0.00 | -0.01 |
| **13** | 22000 | 4000 | 0.19 | 0.10 |
| **14** | NT | NT | | |
| **15** | 19500 | 2300 | -0.97 | -0.89 |
| **16** | 21108 | 2110 | -0.23 | -0.23 |
| **17** | 21000 | 2100 | -0.28 | -0.28 |
| **18** | 20000 | 3000 | -0.74 | -0.53 |
| **19** | NT | NT | | |
| **20** | 22000 | 2750 | 0.19 | 0.14 |
| **21** | 22400 | 2700 | 0.37 | 0.29 |
| **22** | 21400 | 1500 | -0.09 | -0.13 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 21600 | 500 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 20000 | 3000 |
| **Robust Average** | 21600 | 500 |
| **Median** | 21600 | 400 |
| **Mean** | 21900 | |
| **N** | 15 | |
| **Max** | 27900 | |
| **Min** | 19500 | |
| **Robust SD** | 850 | |
| **Robust CV** | 3.9% | |

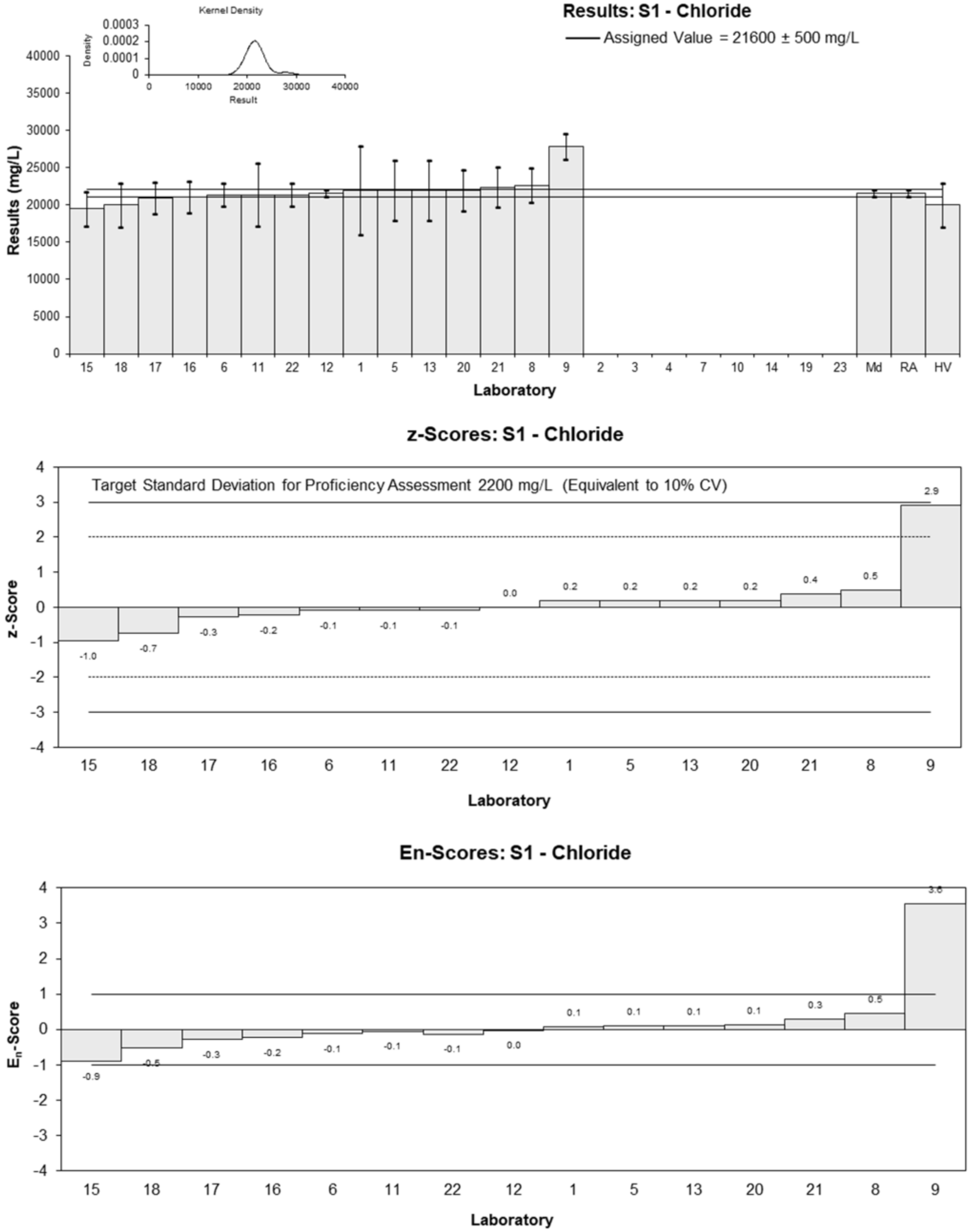

Results: S1 - Chloride
Assigned Value = 21600 ± 500 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15 18 17 16 6 11 22 12 1 5 13 20 21 8 9 2 3 4 7 10 14 19 23 Md RA HV
z-Scores: S1 - Chloride
Target Standard Deviation for Proficiency Assessment 2200 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
15 18 17 16 6 11 22 12 1 5 13 20 21 8 9
-1.0 -0.7 -0.3 -0.2 -0.1 -0.1 -0.1 0.0 0.2 0.2 0.2 0.2 0.4 0.5 2.9
En-Scores: S1 - Chloride
En-Score
Laboratory
15 18 17 16 6 11 22 12 1 5 13 20 21 8 9
-0.9 -0.5 -0.3 -0.2 -0.1 -0.1 -0.1 0.0 0.1 0.1 0.1 0.1 0.3 0.5 3.6

Figure 3

Table 7

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | DOC |
| **Unit** | mg/L |

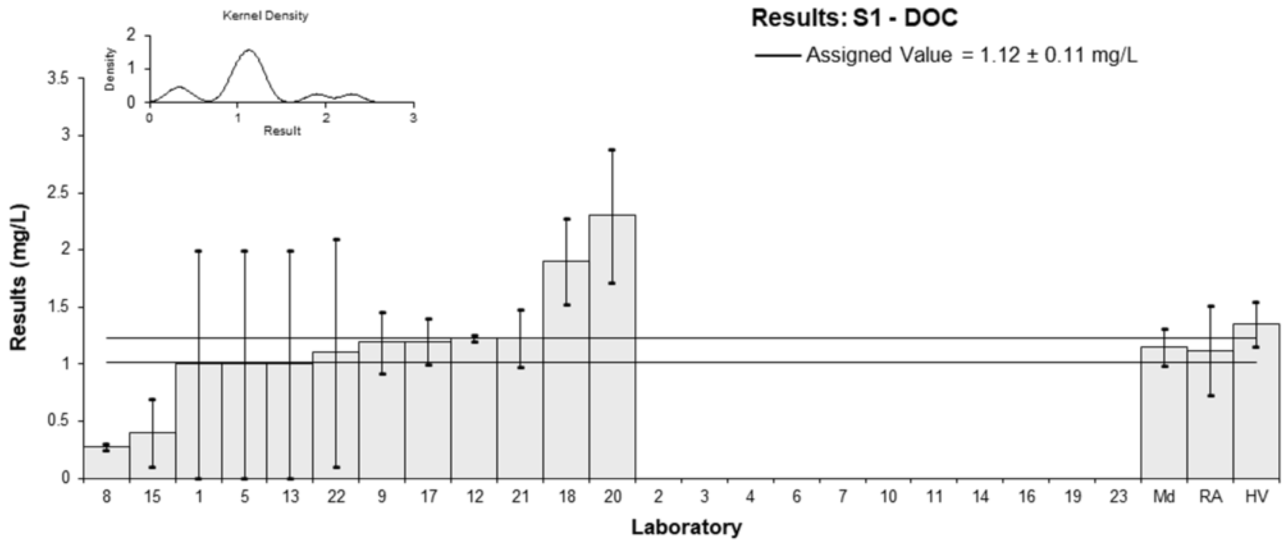
**Participant Results**

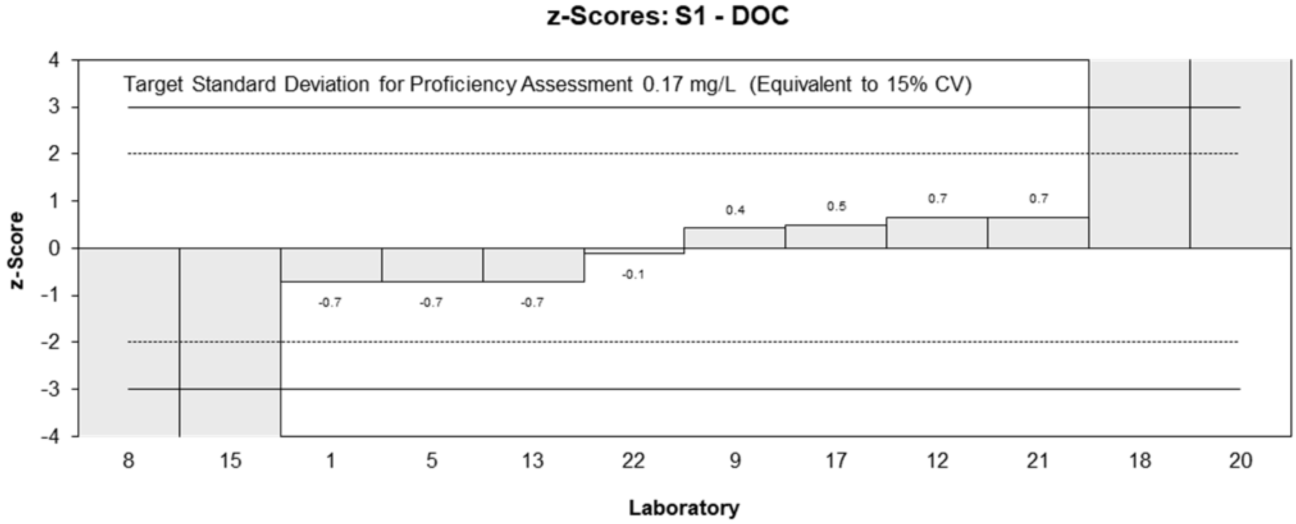
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1 | 1 | -0.71 | -0.12 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 1.0 | 1 | -0.71 | -0.12 |
| **6** | NR | NR | | |
| **7** | NT | NT | | |
| **8*** | 0.274 | 0.03 | -5.04 | -7.42 |
| **9** | 1.19 | 0.27 | 0.42 | 0.24 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 1.23 | 0.025 | 0.65 | 0.98 |
| **13** | 1 | 1 | -0.71 | -0.12 |
| **14** | NT | NT | | |
| **15*** | 0.4 | 0.3 | -4.29 | -2.25 |
| **16** | NT | NT | | |
| **17** | 1.2 | 0.2 | 0.48 | 0.35 |
| **18*** | 1.9 | 0.38 | 4.64 | 1.97 |
| **19** | NT | NT | | |
| **20*** | 2.3 | 0.58 | 7.02 | 2.00 |
| **21** | 1.23 | 0.25 | 0.65 | 0.40 |
| **22** | 1.1 | 1 | -0.12 | -0.02 |
| **23** | NR | NR | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.12 | 0.11 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 1.35 | 0.20 |
| **Robust Average** | 1.12 | 0.39 |
| **Median** | 1.15 | 0.16 |
| **Mean** | 1.15 | |
| **N** | 12 | |
| **Max** | 2.3 | |
| **Min** | 0.274 | |
| **Robust SD** | 0.54 | |
| **Robust CV** | 48% | |


Results: S1 - DOC
Assigned Value = 1.12 ± 0.11 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 15 1 5 13 22 9 17 12 21 18 20 2 3 4 6 7 10 11 14 16 19 23 Md RA HV


z-Scores: S1 - DOC
Target Standard Deviation for Proficiency Assessment 0.17 mg/L (Equivalent to 15% CV)
z-Score
-0.7
-0.7
-0.7
-0.1
0.4
0.5
0.7
0.7
Laboratory
8 15 1 5 13 22 9 17 12 21 18 20

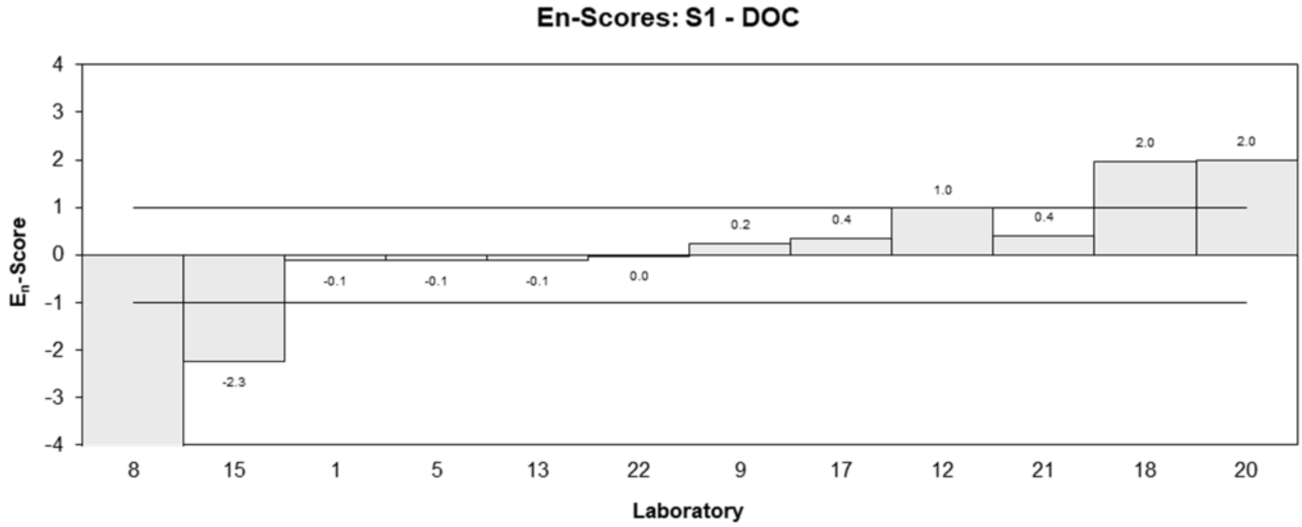

En-Scores: S1 - DOC
En-Score
-2.3
-0.1
-0.1
-0.1
0.0
0.2
0.4
1.0
0.4
2.0
2.0
Laboratory
8 15 1 5 13 22 9 17 12 21 18 20

Figure 4

Table 8

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Fluoride |
| **Unit** | mg/L |

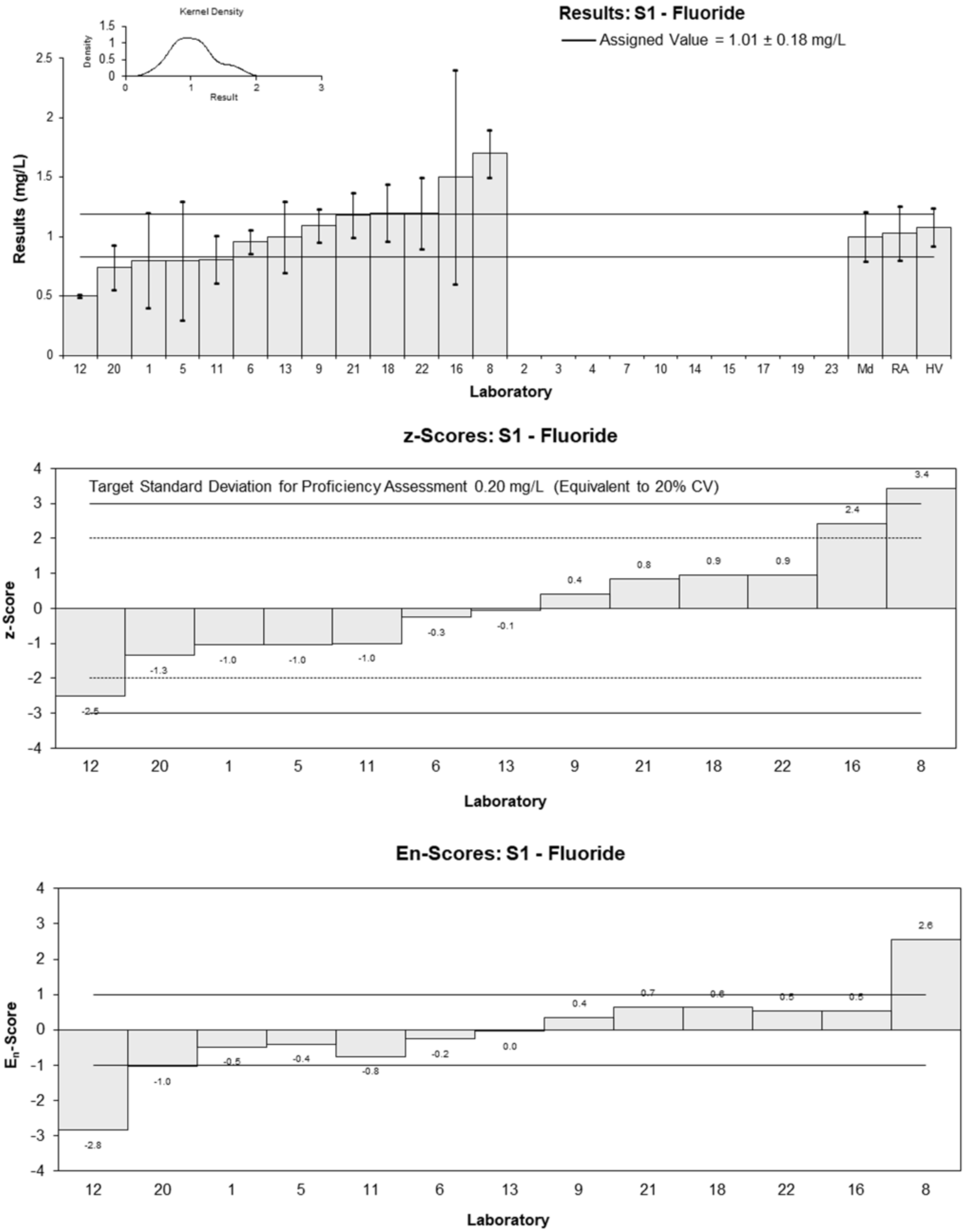
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.8 | 0.4 | -1.04 | -0.48 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.8 | 0.5 | -1.04 | -0.40 |
| **6** | 0.96 | 0.10 | -0.25 | -0.24 |
| **7** | NT | NT | | |
| **8*** | 1.7 | 0.2 | 3.42 | 2.56 |
| **9** | 1.09 | 0.14 | 0.40 | 0.35 |
| **10** | NT | NT | | |
| **11** | 0.808 | 0.2 | -1.00 | -0.75 |
| **12*** | 0.50 | 0.01 | -2.52 | -2.83 |
| **13** | 1 | 0.3 | -0.05 | -0.03 |
| **14** | NT | NT | | |
| **15** | <10 | NR | | |
| **16** | 1.5 | 0.9 | 2.43 | 0.53 |
| **17** | <10 | NR | | |
| **18** | 1.2 | 0.24 | 0.94 | 0.63 |
| **19** | NT | NT | | |
| **20** | 0.74 | 0.19 | -1.34 | -1.03 |
| **21** | 1.18 | 0.19 | 0.84 | 0.65 |
| **22** | 1.2 | 0.3 | 0.94 | 0.54 |
| **23** | NR | NR | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.01 | 0.18 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 1.08 | 0.16 |
| **Robust Average** | 1.03 | 0.23 |
| **Median** | 1.00 | 0.21 |
| **Mean** | 1.04 | |
| **N** | 13 | |
| **Max** | 1.7 | |
| **Min** | 0.5 | |
| **Robust SD** | 0.34 | |
| **Robust CV** | 33% | |



Results: S1 - Fluoride
Assigned Value = 1.01 ± 0.18 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
12 20 1 5 11 6 13 9 21 18 22 16 8 2 3 4 7 10 14 15 17 19 23 Md RA HV
z-Scores: S1 - Fluoride
Target Standard Deviation for Proficiency Assessment 0.20 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
12 20 1 5 11 6 13 9 21 18 22 16 8
En-Scores: S1 - Fluoride
En-Score
Laboratory
12 20 1 5 11 6 13 9 21 18 22 16 8


Figure 5

Table 9

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Nitrate-N +Nitrite-N |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.065 | 0.03 | 0.44 | 0.13 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.060 | 0.02 | -0.11 | -0.05 |
| **6** | 0.06 | 0.02 | -0.11 | -0.05 |
| **7** | 0.0587 | 0.0009 | -0.25 | -0.84 |
| **8** | 0.069 | 0.01 | 0.87 | 0.77 |
| **9** | 0.0597 | 0.0080 | -0.14 | -0.15 |
| **10** | 0.0624 | 0.0025 | 0.15 | 0.39 |
| **11*** | 0.301 | 0.1 | 26.23 | 2.40 |
| **12** | 0.057 | 0.002 | -0.44 | -1.22 |
| **13** | 0.057 | 0.05 | -0.44 | -0.08 |
| **14** | NT | NT | | |
| **15** | 0.058 | 0.006 | -0.33 | -0.46 |
| **16** | NT | NT | | |
| **17** | 0.062 | 0.012 | 0.11 | 0.08 |
| **18** | 0.056 | 0.011 | -0.55 | -0.44 |
| **19** | 0.0597 | 0.0023 | -0.14 | -0.37 |
| **20** | 0.063 | 0.015 | 0.22 | 0.13 |
| **21** | 0.0666 | 0.0133 | 0.61 | 0.41 |
| **22** | 0.058 | 0.010 | -0.33 | -0.29 |
| **23** | 0.070 | 0.007 | 0.98 | 1.21 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0610 | 0.0026 |
| **Spike Value*** | 0.0224 | 0.0011 |
| **Homogeneity Value** | 0.0648 | 0.0097 |
| **Robust Average** | 0.0617 | 0.0029 |
| **Median** | 0.0600 | 0.0024 |
| **Mean** | 0.075 | |
| **N** | 18 | |
| **Max** | 0.301 | |
| **Min** | 0.056 | |
| **Robust SD** | 0.0050 | |
| **Robust CV** | 8.1% | |

*Incurred value not included

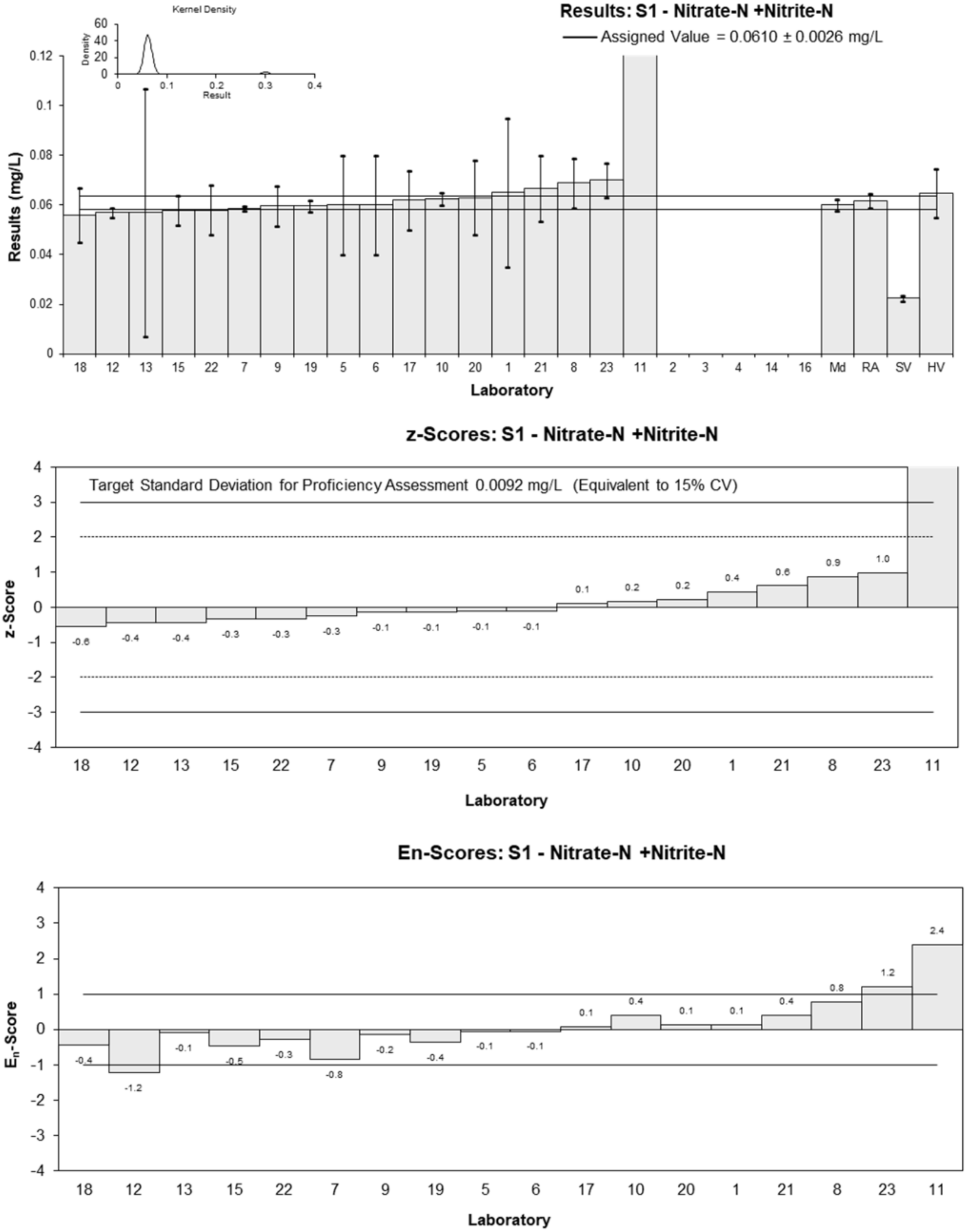

Results: S1 - Nitrate-N +Nitrite-N
Assigned Value = 0.0610 ± 0.0026 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
18 12 13 15 22 7 9 19 5 6 17 10 20 1 21 8 23 11 2 3 4 14 16 Md RA SV HV
z-Scores: S1 - Nitrate-N +Nitrite-N
Target Standard Deviation for Proficiency Assessment 0.0092 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
18 12 13 15 22 7 9 19 5 6 17 10 20 1 21 8 23 11
-0.6 -0.4 -0.4 -0.3 -0.3 -0.3 -0.1 -0.1 -0.1 -0.1 0.1 0.2 0.2 0.4 0.6 0.9 1.0
En-Scores: S1 - Nitrate-N +Nitrite-N
En-Score
Laboratory
18 12 13 15 22 7 9 19 5 6 17 10 20 1 21 8 23 11
-0.4 -1.2 -0.1 -0.5 -0.3 -0.8 -0.2 -0.4 -0.1 -0.1 0.1 0.4 0.1 0.1 0.4 0.8 1.2 2.4

Figure 6

Table 10

**Sample Details**

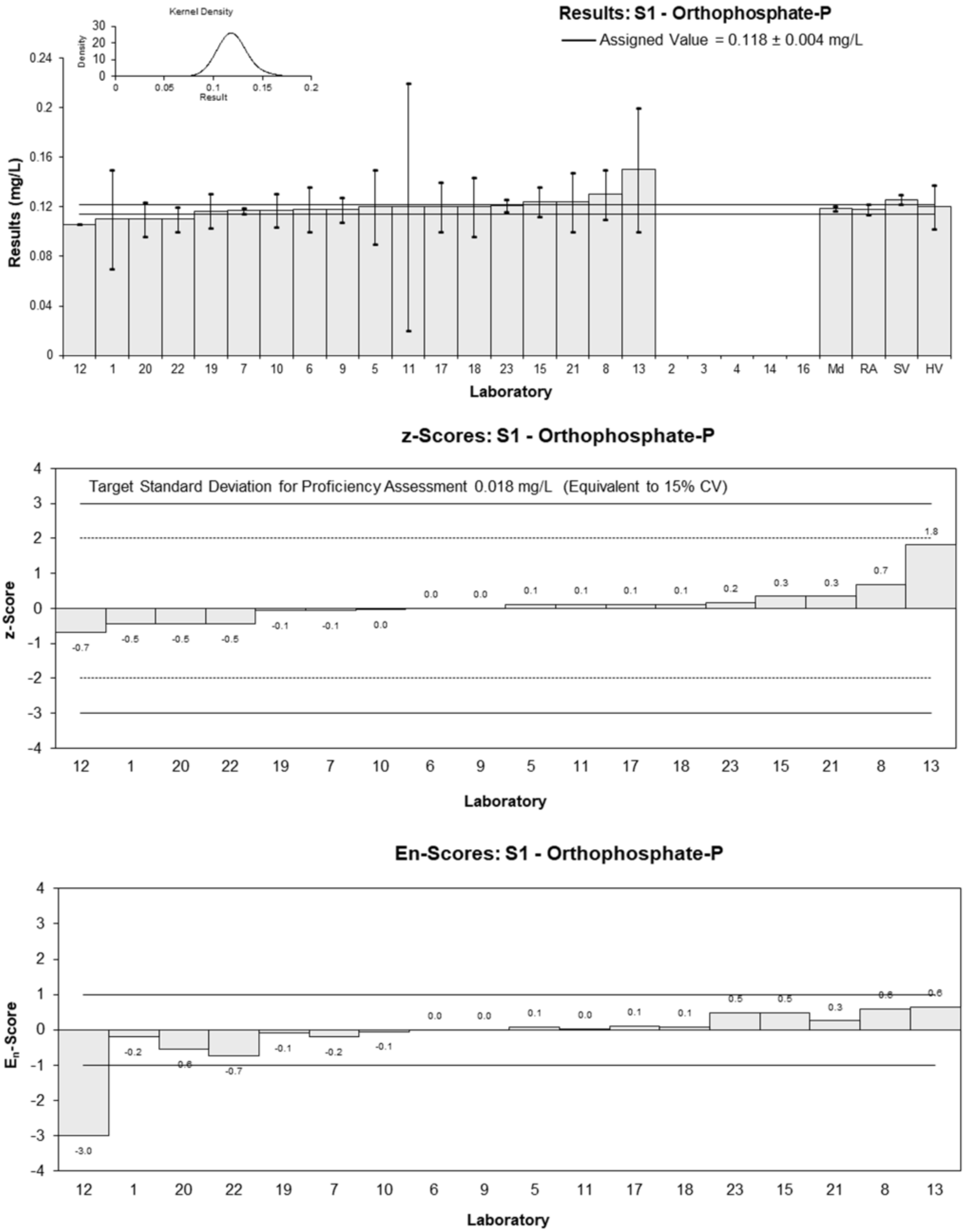
| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Orthophosphate-P |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.11 | 0.04 | -0.45 | -0.20 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.12 | 0.03 | 0.11 | 0.07 |
| **6** | 0.118 | 0.018 | 0.00 | 0.00 |
| **7** | 0.1171 | 0.0022 | -0.05 | -0.20 |
| **8** | 0.130 | 0.02 | 0.68 | 0.59 |
| **9** | 0.118 | 0.010 | 0.00 | 0.00 |
| **10** | 0.1173 | 0.0138 | -0.04 | -0.05 |
| **11** | 0.120 | 0.1 | 0.11 | 0.02 |
| **12** | 0.106 | 0.00 | -0.68 | -3.00 |
| **13** | 0.15 | 0.05 | 1.81 | 0.64 |
| **14** | NT | NT | | |
| **15** | 0.124 | 0.012 | 0.34 | 0.47 |
| **16** | NT | NT | | |
| **17** | 0.12 | 0.02 | 0.11 | 0.10 |
| **18** | 0.12 | 0.024 | 0.11 | 0.08 |
| **19** | 0.1168 | 0.0137 | -0.07 | -0.08 |
| **20** | 0.11 | 0.014 | -0.45 | -0.55 |
| **21** | 0.124 | 0.024 | 0.34 | 0.25 |
| **22** | 0.11 | 0.01 | -0.45 | -0.74 |
| **23** | 0.121 | 0.005 | 0.17 | 0.47 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.118 | 0.004 |
| **Spike Value** | 0.126 | 0.004 |
| **Homogeneity Value** | 0.120 | 0.018 |
| **Robust Average** | 0.118 | 0.004 |
| **Median** | 0.119 | 0.002 |
| **Mean** | 0.120 | |
| **N** | 18 | |
| **Max** | 0.15 | |
| **Min** | 0.106 | |
| **Robust SD** | 0.0068 | |
| **Robust CV** | 5.7% | |



Kernel Density
Density
Result
Results: S1 - Orthophosphate-P
Assigned Value = 0.118 ± 0.004 mg/L
Results (mg/L)
12 1 20 22 19 7 10 6 9 5 11 17 18 23 15 21 8 13 2 3 4 14 16 Md RA SV HV
Laboratory
z-Scores: S1 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 0.018 mg/L (Equivalent to 15% CV)
z-Score
12 1 20 22 19 7 10 6 9 5 11 17 18 23 15 21 8 13
Laboratory
En-Scores: S1 - Orthophosphate-P
$E_n$-Score
12 1 20 22 19 7 10 6 9 5 11 17 18 23 15 21 8 13
Laboratory


Figure 7

Table 11

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | Sulphate |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 2800 | 800 | -0.41 | -0.15 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 2900 | 600 | -0.07 | -0.03 |
| **6** | 3039 | 170 | 0.41 | 0.48 |
| **7** | NT | NT | | |
| **8** | 3185 | 320 | 0.91 | 0.72 |
| **9** | 3750 | 230 | 2.84 | 2.84 |
| **10** | NT | NT | | |
| **11** | 4020 | 800 | 3.77 | 1.34 |
| **12** | 2831 | 57 | -0.30 | -0.47 |
| **13** | 2900 | 600 | -0.07 | -0.03 |
| **14** | NT | NT | | |
| **15** | 2760 | 400 | -0.55 | -0.36 |
| **16** | 3002 | 300 | 0.28 | 0.23 |
| **17** | 2400 | 240 | -1.78 | -1.73 |
| **18** | 2500 | 375 | -1.44 | -1.01 |
| **19** | NT | NT | | |
| **20** | 2900 | 360 | -0.07 | -0.05 |
| **21** | 2880 | 490 | -0.14 | -0.08 |
| **22** | 2910 | 350 | -0.03 | -0.03 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 2920 | 180 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 2580 | 390 |
| **Robust Average** | 2920 | 180 |
| **Median** | 2900 | 100 |
| **Mean** | 2990 | |
| **N** | 15 | |
| **Max** | 4020 | |
| **Min** | 2400 | |
| **Robust SD** | 270 | |
| **Robust CV** | 9.4% | |

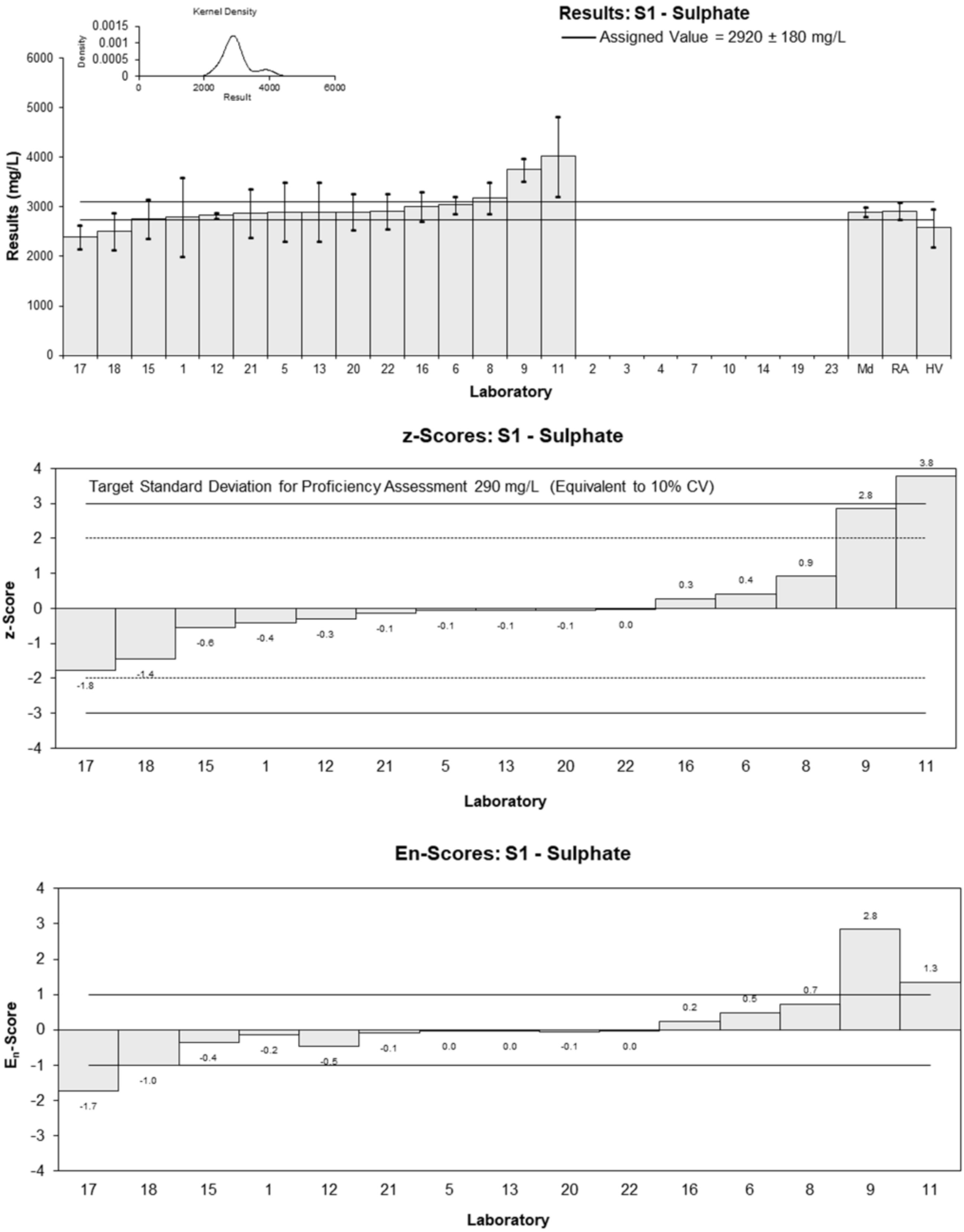

Results: S1 - Sulphate
Assigned Value = 2920 ± 180 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17 18 15 1 12 21 5 13 20 22 16 6 8 9 11 2 3 4 7 10 14 19 23 Md RA HV
z-Scores: S1 - Sulphate
Target Standard Deviation for Proficiency Assessment 290 mg/L (Equivalent to 10% CV)
z-Score
-1.8 -1.4 -0.6 -0.4 -0.3 -0.1 -0.1 -0.1 -0.1 0.0 0.3 0.4 0.9 2.8 3.8
Laboratory
17 18 15 1 12 21 5 13 20 22 16 6 8 9 11
En-Scores: S1 - Sulphate
En-Score
-1.7 -1.0 -0.4 -0.2 -0.5 -0.1 0.0 0.0 -0.1 0.0 0.2 0.5 0.7 2.8 1.3
Laboratory
17 18 15 1 12 21 5 13 20 22 16 6 8 9 11

Figure 8

Table 12

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | TDN |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.2 | 0.1 | -0.43 | -0.18 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.17 | 0.1 | -1.12 | -0.47 |
| **6** | 0.27 | 0.03 | 1.16 | 1.26 |
| **7** | NT | NT | | |
| **8** | 0.205 | 0.03 | -0.32 | -0.35 |
| **9** | <0.3 | 0.064 | | |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 0.190 | 0.004 | -0.66 | -1.06 |
| **13** | 0.2 | 0.2 | -0.43 | -0.09 |
| **14** | NT | NT | | |
| **15** | 0.23 | 0.1 | 0.25 | 0.11 |
| **16** | NT | NT | | |
| **17** | 0.26 | 0.03 | 0.94 | 1.02 |
| **18** | 0.21 | 0.042 | -0.21 | -0.18 |
| **19** | NT | NT | | |
| **20*** | 0.39 | 0.098 | 3.90 | 1.68 |
| **21** | 0.216 | 0.045 | -0.07 | -0.06 |
| **22** | 0.29 | 0.06 | 1.62 | 1.08 |
| **23** | 0.2 | 0.06 | -0.43 | -0.29 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.219 | 0.027 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 0.165 | 0.025 |
| **Robust Average** | 0.226 | 0.031 |
| **Median** | 0.210 | 0.021 |
| **Mean** | 0.233 | |
| **N** | 13 | |
| **Max** | 0.39 | |
| **Min** | 0.17 | |
| **Robust SD** | 0.045 | |
| **Robust CV** | 20% | |

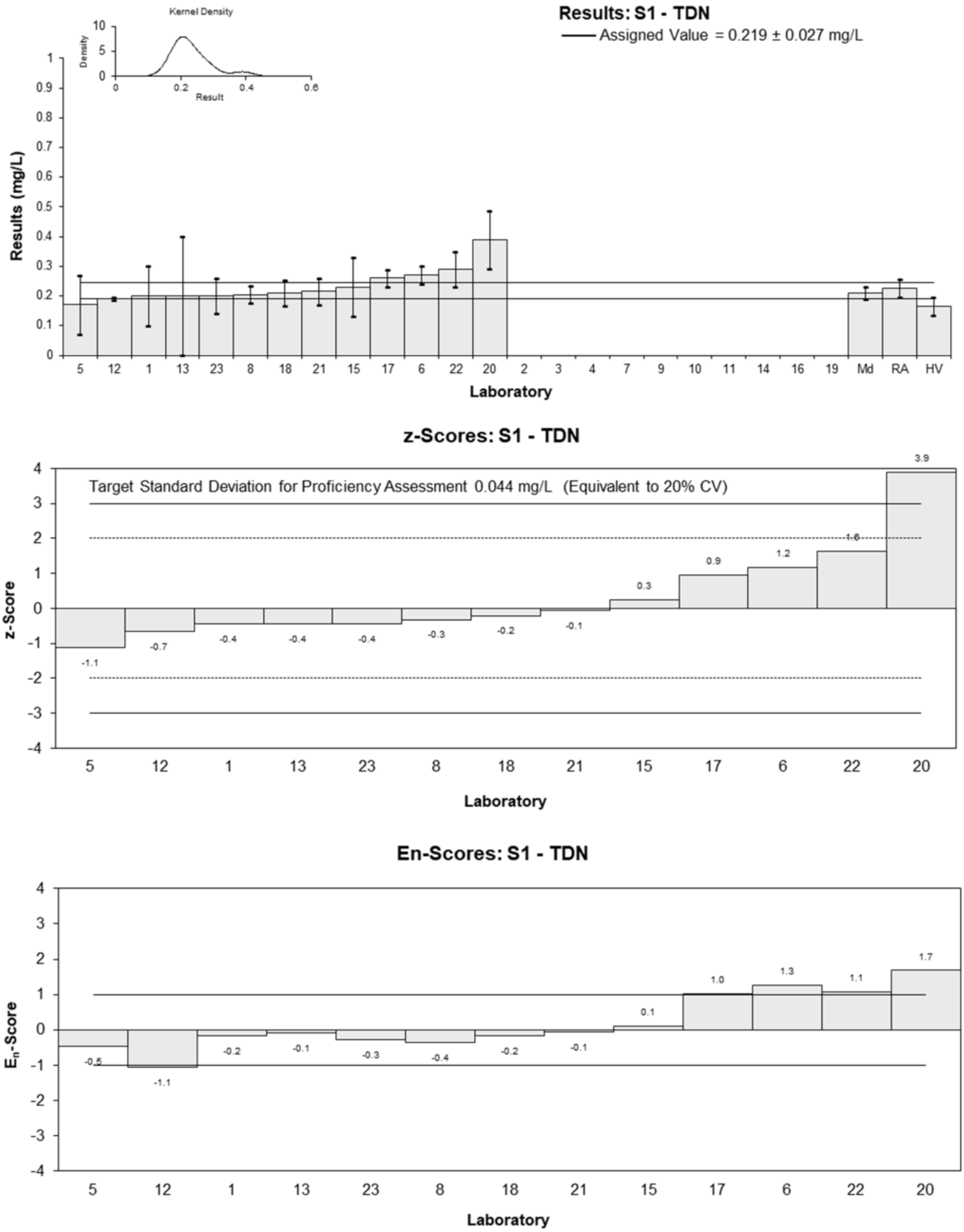

Kernel Density
Density
Result
Results: S1 - TDN
Assigned Value = 0.219 ± 0.027 mg/L
Results (mg/L)
Laboratory
5
12
1
13
23
8
18
21
15
17
6
22
20
2
3
4
7
9
10
11
14
16
19
Md
RA
HV
z-Scores: S1 - TDN
Target Standard Deviation for Proficiency Assessment 0.044 mg/L (Equivalent to 20% CV)
z-Score
-1.1
-0.7
-0.4
-0.4
-0.4
-0.3
-0.2
-0.1
0.3
0.9
1.2
1.6
3.9
Laboratory
En-Scores: S1 - TDN
En-Score
-0.5
-1.1
-0.2
-0.1
-0.3
-0.4
-0.2
-0.1
0.1
1.0
1.3
1.1
1.7
Laboratory

Figure 9

Table 13

**Sample Details**

| | |
|---|---|
| **Sample No.** | S1 |
| **Matrix** | Sea Water |
| **Analyte** | TDP |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.13 | 0.1 | 0.10 | 0.02 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.15 | 0.1 | 1.15 | 0.22 |
| **6** | 0.119 | 0.018 | -0.47 | -0.43 |
| **7** | NT | NT | | |
| **8** | 0.148 | 0.02 | 1.04 | 0.88 |
| **9** | 0.1159 | 0.0043 | -0.63 | -1.02 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | NR | NR | | |
| **13** | 0.12 | 0.1 | -0.42 | -0.08 |
| **14** | NT | NT | | |
| **15** | 0.129 | 0.019 | 0.05 | 0.05 |
| **16** | NT | NT | | |
| **17** | 0.12 | 0.01 | -0.42 | -0.54 |
| **18** | 0.12 | 0.024 | -0.42 | -0.30 |
| **19** | NT | NT | | |
| **20** | 0.15 | 0.038 | 1.15 | 0.56 |
| **21** | 0.134 | 0.020 | 0.31 | 0.26 |
| **22** | 0.11 | 0.03 | -0.94 | -0.56 |
| **23** | 0.12 | 0.005 | -0.42 | -0.66 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.128 | 0.011 |
| **Spike Value** | 0.126 | 0.004 |
| **Homogeneity Value** | 0.120 | 0.018 |
| **Robust Average** | 0.128 | 0.011 |
| **Median** | 0.120 | 0.009 |
| **Mean** | 0.128 | |
| **N** | 13 | |
| **Max** | 0.15 | |
| **Min** | 0.11 | |
| **Robust SD** | 0.015 | |
| **Robust CV** | 12% | |

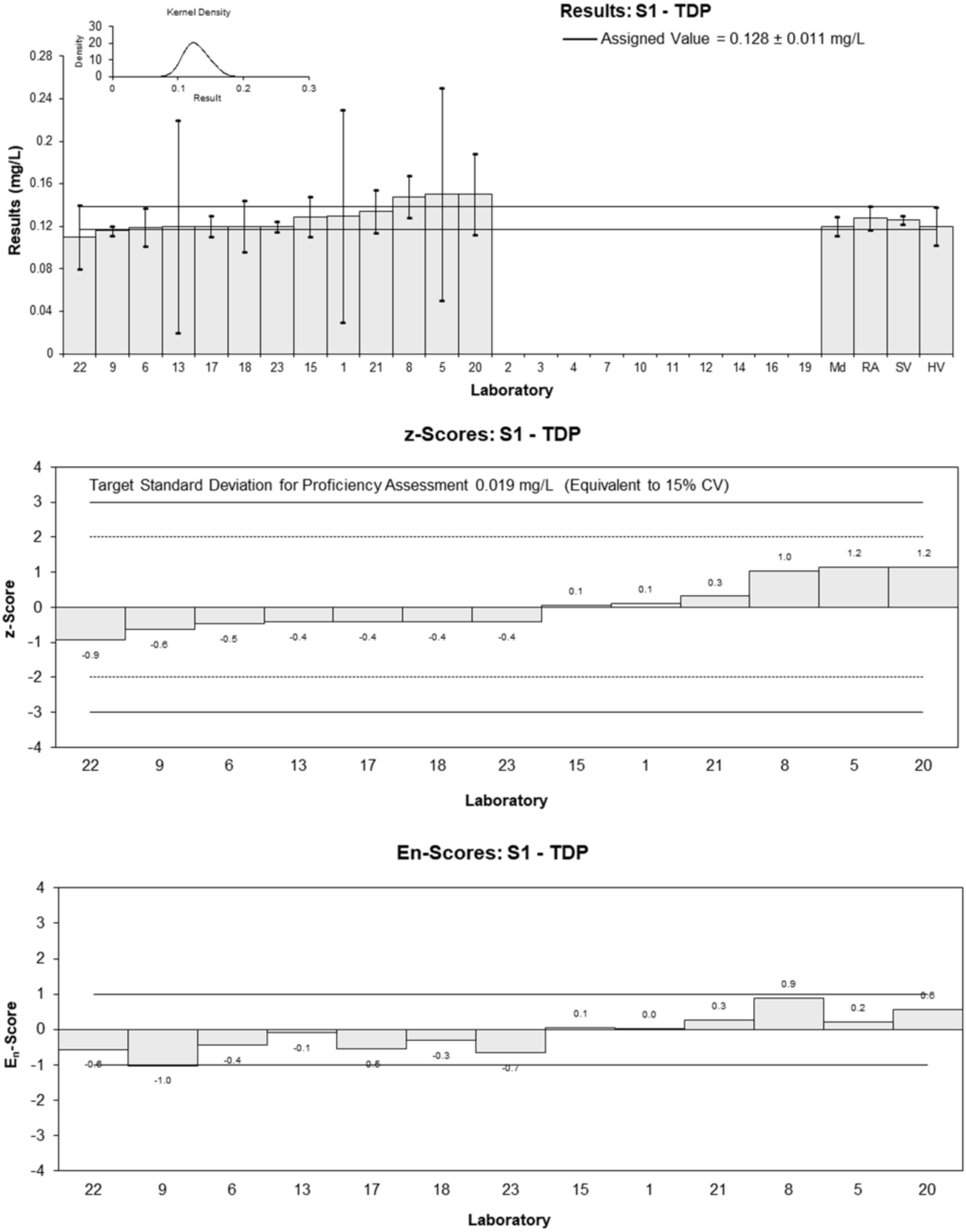

Results: S1 - TDP
Assigned Value = 0.128 ± 0.011 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
22 9 6 13 17 18 23 15 1 21 8 5 20 2 3 4 7 10 11 12 14 16 19 Md RA SV HV
z-Scores: S1 - TDP
Target Standard Deviation for Proficiency Assessment 0.019 mg/L (Equivalent to 15% CV)
z-Score
-0.9 -0.6 -0.5 -0.4 -0.4 -0.4 -0.4 0.1 0.1 0.3 1.0 1.2 1.2
22 9 6 13 17 18 23 15 1 21 8 5 20
Laboratory
En-Scores: S1 - TDP
$E_n$-Score
-0.6 -1.0 -0.4 -0.1 -0.5 -0.3 -0.7 0.1 0.0 0.3 0.9 0.2 0.6
22 9 6 13 17 18 23 15 1 21 8 5 20
Laboratory

Figure 10

Table 14

**Sample Details**

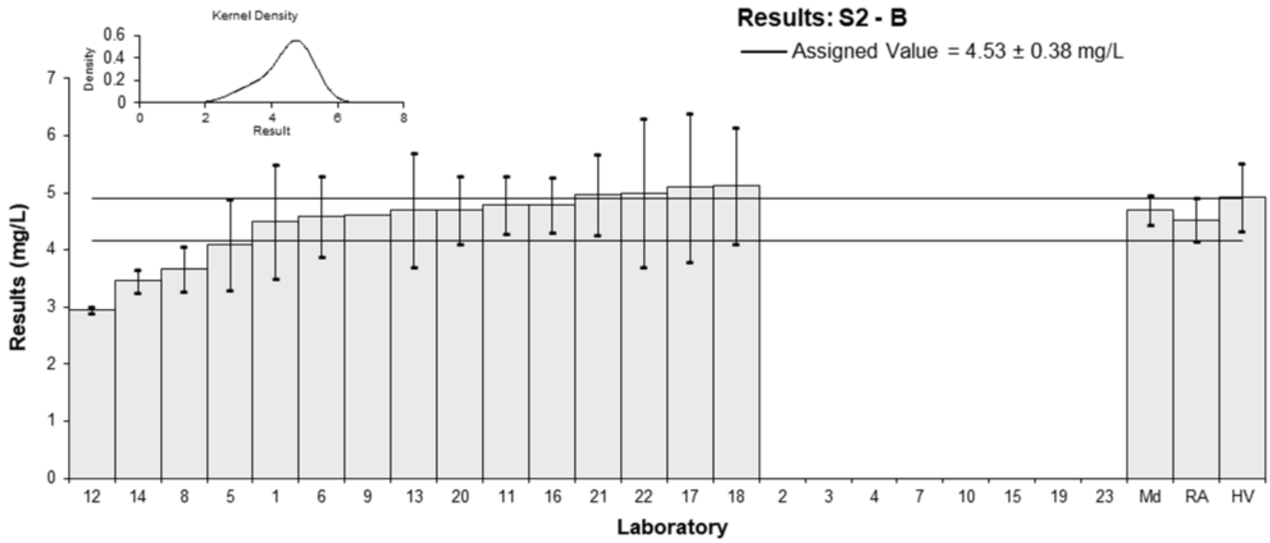
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | B |
| **Unit** | mg/L |

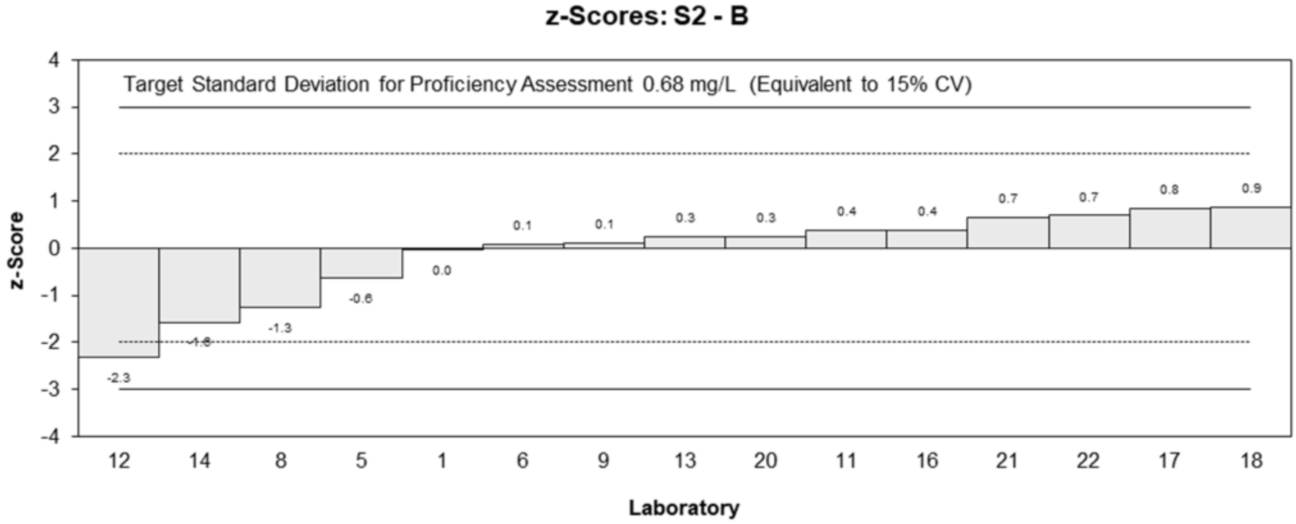
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 4.5 | 1 | -0.04 | -0.03 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 4.1 | 0.8 | -0.63 | -0.49 |
| **6** | 4.58 | 0.71 | 0.07 | 0.06 |
| **7** | NT | NT | | |
| **8** | 3.67 | 0.4 | -1.27 | -1.56 |
| **9** | 4.6 | NR | 0.10 | 0.18 |
| **10** | NT | NT | | |
| **11** | 4.79 | 0.5 | 0.38 | 0.41 |
| **12** | 2.95 | 0.06 | -2.33 | -4.11 |
| **13** | 4.7 | 1 | 0.25 | 0.16 |
| **14** | 3.46 | 0.2 | -1.57 | -2.49 |
| **15** | NT | NT | | |
| **16** | 4.79 | 0.479 | 0.38 | 0.43 |
| **17** | 5.1 | 1.3 | 0.84 | 0.42 |
| **18** | 5.12 | 1.02 | 0.87 | 0.54 |
| **19** | NT | NT | | |
| **20** | 4.7 | 0.59 | 0.25 | 0.24 |
| **21** | 4.97 | 0.70 | 0.65 | 0.55 |
| **22** | 5.0 | 1.3 | 0.69 | 0.35 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.53 | 0.38 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 4.92 | 0.59 |
| **Robust Average** | 4.53 | 0.38 |
| **Median** | 4.70 | 0.26 |
| **Mean** | 4.47 | |
| **N** | 15 | |
| **Max** | 5.12 | |
| **Min** | 2.95 | |
| **Robust SD** | 0.59 | |
| **Robust CV** | 13% | |


Results: S2 - B
Assigned Value = 4.53 ± 0.38 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
12
14
8
5
1
6
9
13
20
11
16
21
22
17
18
2
3
4
7
10
15
19
23
Md
RA
HV


z-Scores: S2 - B
Target Standard Deviation for Proficiency Assessment 0.68 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.3
-1.6
-1.3
-0.6
0.0
0.1
0.1
0.3
0.3
0.4
0.4
0.7
0.7
0.8
0.9

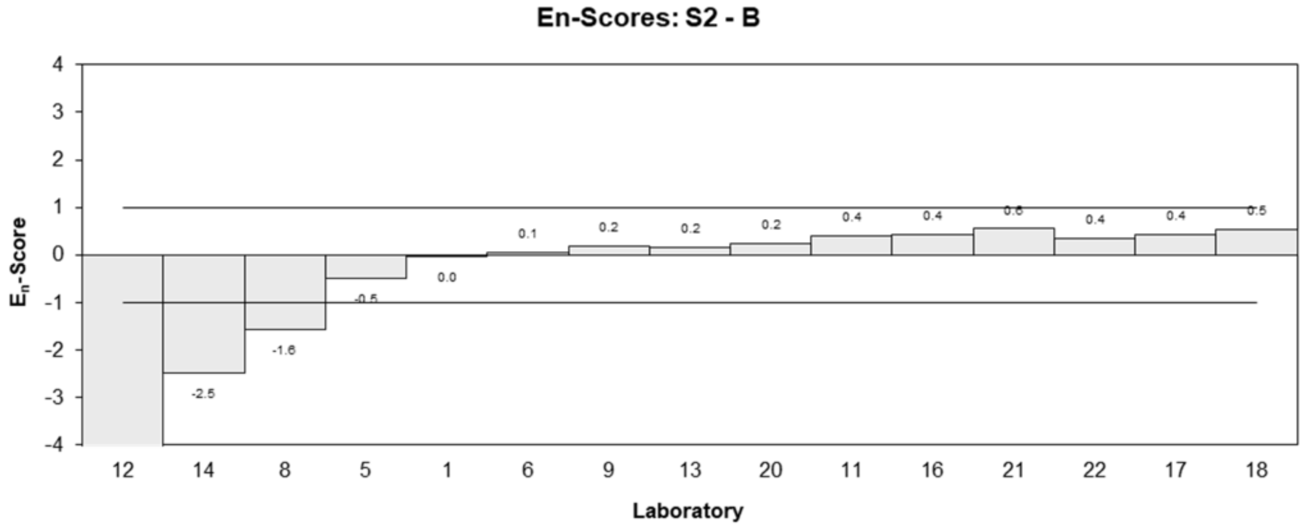

En-Scores: S2 - B
En-Score
Laboratory
-2.5
-1.6
-0.5
0.0
0.1
0.2
0.2
0.2
0.4
0.4
0.6
0.4
0.4
0.5

Figure 11

Table 15

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | Ca |
| **Unit** | mg/L |

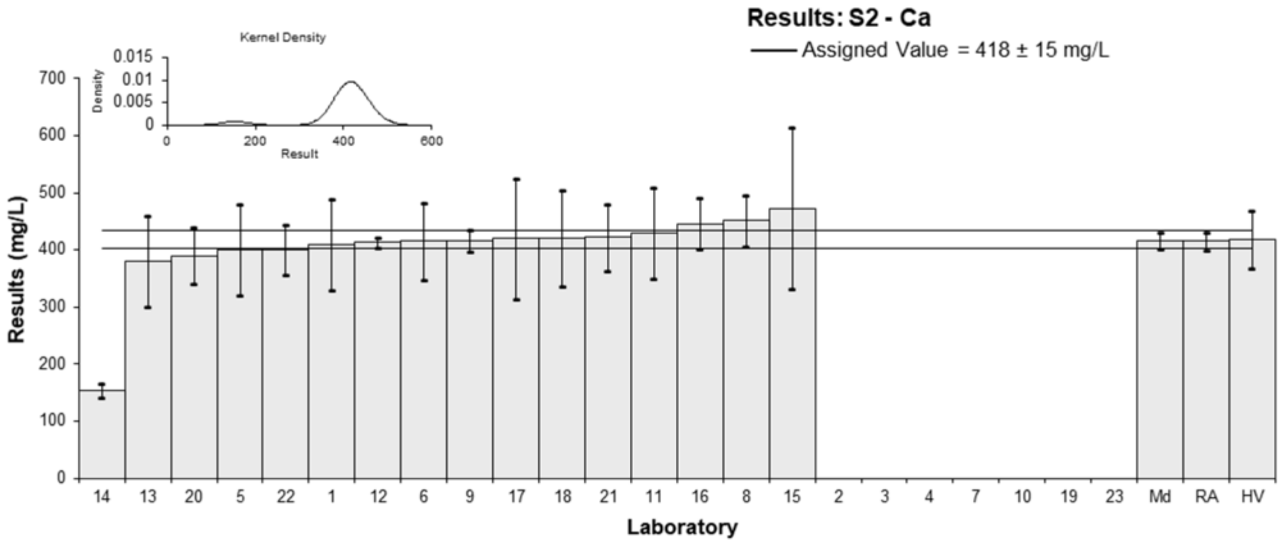
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 410 | 80 | -0.19 | -0.10 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 400 | 80 | -0.43 | -0.22 |
| **6** | 415 | 68 | -0.07 | -0.04 |
| **7** | NT | NT | | |
| **8** | 451 | 45 | 0.79 | 0.70 |
| **9** | 417 | 19 | -0.02 | -0.04 |
| **10** | NT | NT | | |
| **11** | 430 | 80 | 0.29 | 0.15 |
| **12** | 413 | 8.3 | -0.12 | -0.29 |
| **13** | 380 | 80 | -0.91 | -0.47 |
| **14*** | 154.07 | 11.98 | -6.31 | -13.75 |
| **15** | 473 | 142 | 1.32 | 0.39 |
| **16** | 446 | 44.6 | 0.67 | 0.60 |
| **17** | 420 | 105 | 0.05 | 0.02 |
| **18** | 420 | 84 | 0.05 | 0.02 |
| **19** | NT | NT | | |
| **20** | 390 | 50 | -0.67 | -0.54 |
| **21** | 422 | 59 | 0.10 | 0.07 |
| **22** | 400 | 44 | -0.43 | -0.39 |
| **23** | NR | NR | | |

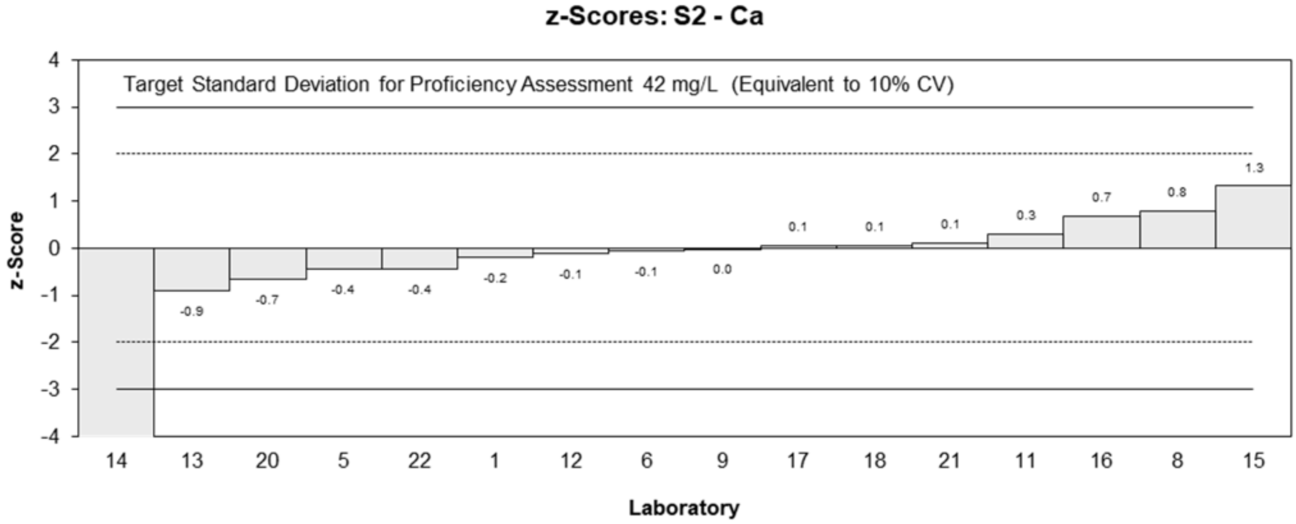
* Outlier, see Section 4.2

**Statistics**

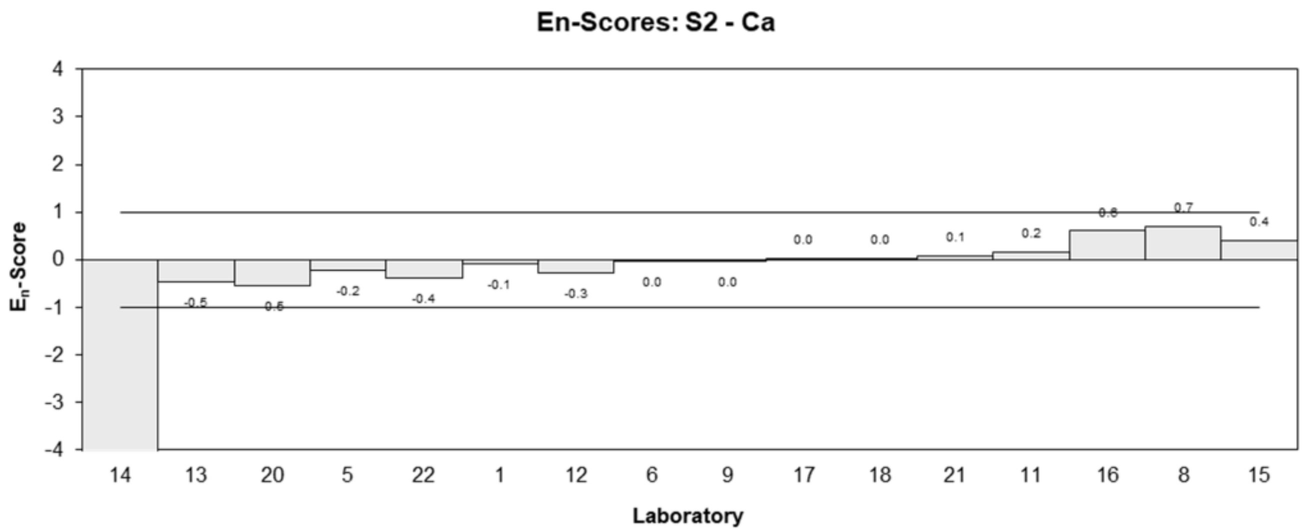
| | | |
|---|---|---|
| **Assigned Value** | 418 | 15 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 418 | 50 |
| **Robust Average** | 415 | 16 |
| **Median** | 416 | 14 |
| **Mean** | 403 | |
| **N** | 16 | |
| **Max** | 473 | |
| **Min** | 154.07 | |
| **Robust SD** | 26 | |
| **Robust CV** | 6.3% | |



Results: S2 - Ca
Assigned Value = 418 ± 15 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
14 13 20 5 22 1 12 6 9 17 18 21 11 16 8 15 2 3 4 7 10 19 23 Md RA HV

z-Scores: S2 - Ca
Target Standard Deviation for Proficiency Assessment 42 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
14 13 20 5 22 1 12 6 9 17 18 21 11 16 8 15

En-Scores: S2 - Ca
En-Score
Laboratory
14 13 20 5 22 1 12 6 9 17 18 21 11 16 8 15


Figure 12

Table 16

**Sample Details**

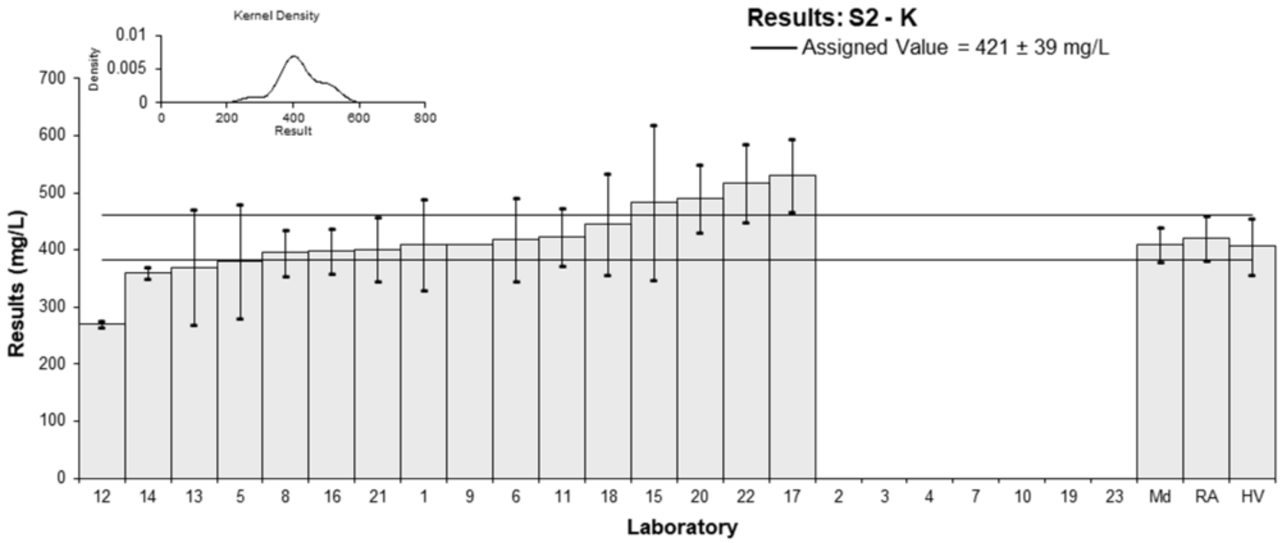
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | K |
| **Unit** | mg/L |

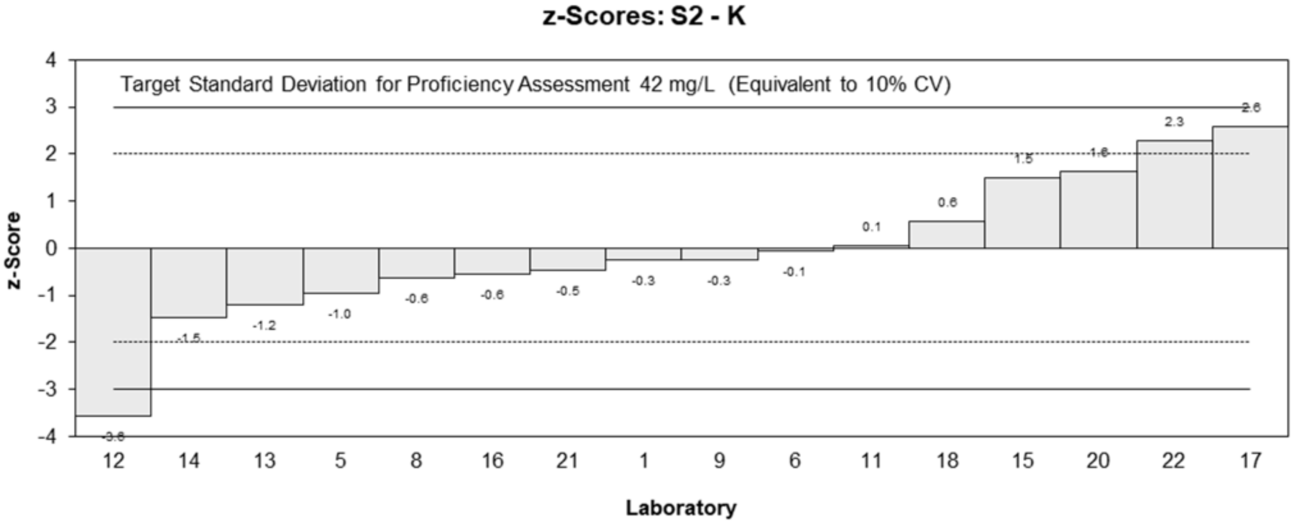
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 410 | 80 | -0.26 | -0.12 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 380 | 100 | -0.97 | -0.38 |
| **6** | 419 | 73 | -0.05 | -0.02 |
| **7** | NT | NT | | |
| **8** | 395 | 40 | -0.62 | -0.47 |
| **9** | 410 | NR | -0.26 | -0.28 |
| **10** | NT | NT | | |
| **11** | 423 | 50 | 0.05 | 0.03 |
| **12** | 271 | 5.42 | -3.56 | -3.81 |
| **13** | 370 | 100 | -1.21 | -0.48 |
| **14** | 359.21 | 10.30 | -1.47 | -1.53 |
| **15** | 484 | 136 | 1.50 | 0.45 |
| **16** | 398 | 39.8 | -0.55 | -0.41 |
| **17** | 530 | 64 | 2.59 | 1.45 |
| **18** | 445 | 89 | 0.57 | 0.25 |
| **19** | NT | NT | | |
| **20** | 490 | 60 | 1.64 | 0.96 |
| **21** | 401 | 56 | -0.48 | -0.29 |
| **22** | 517 | 69 | 2.28 | 1.21 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 421 | 39 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 406 | 49 |
| **Robust Average** | 421 | 39 |
| **Median** | 410 | 30 |
| **Mean** | 419 | |
| **N** | 16 | |
| **Max** | 530 | |
| **Min** | 271 | |
| **Robust SD** | 63 | |
| **Robust CV** | 15% | |


Kernel Density
Density
Result
Results: S2 - K
Assigned Value = 421 ± 39 mg/L
Results (mg/L)
Laboratory
12 14 13 5 8 16 21 1 9 6 11 18 15 20 22 17 2 3 4 7 10 19 23 Md RA HV


z-Scores: S2 - K
Target Standard Deviation for Proficiency Assessment 42 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
12 14 13 5 8 16 21 1 9 6 11 18 15 20 22 17

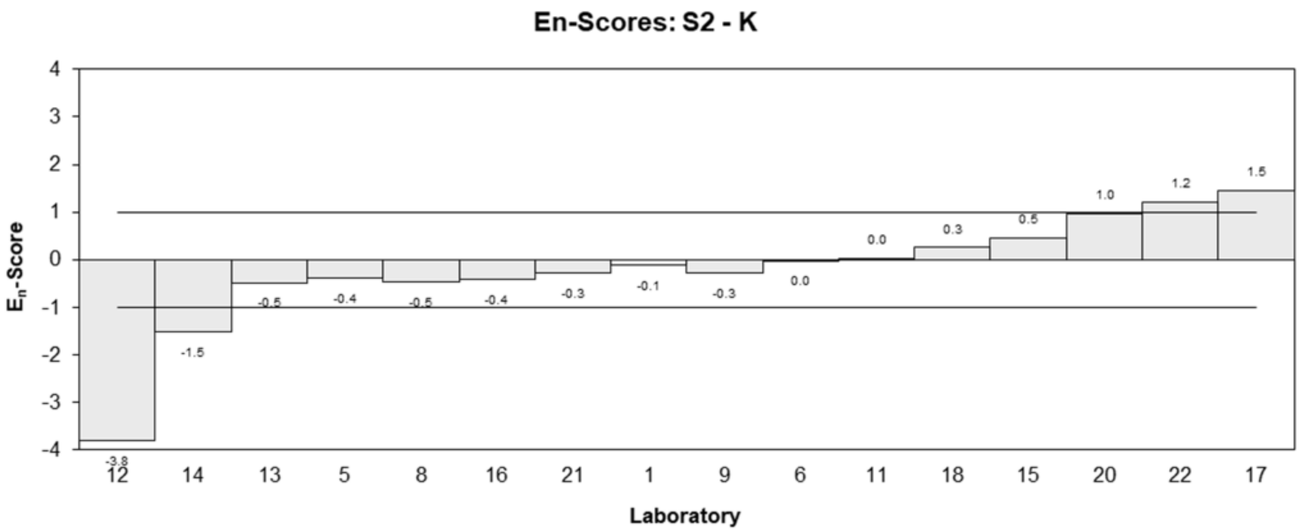

En-Scores: S2 - K
$E_n$-Score
Laboratory
12 14 13 5 8 16 21 1 9 6 11 18 15 20 22 17

Figure 13

Table 17

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | Mg |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1300 | 300 | -0.08 | -0.03 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 1300 | 300 | -0.08 | -0.03 |
| **6** | 1252 | 170 | -0.44 | -0.33 |
| **7** | NT | NT | | |
| **8** | 1309 | 130 | -0.01 | -0.01 |
| **9** | 1280 | 120 | -0.23 | -0.23 |
| **10** | NT | NT | | |
| **11** | 1340 | 150 | 0.23 | 0.19 |
| **12** | 1194 | 24 | -0.89 | -2.09 |
| **13** | 1200 | 300 | -0.84 | -0.36 |
| **14** | 1351.68 | 72.80 | 0.32 | 0.47 |
| **15** | 1440 | 346 | 0.99 | 0.37 |
| **16** | 1418 | 141.8 | 0.82 | 0.72 |
| **17** | 1300 | 260 | -0.08 | -0.04 |
| **18** | 1300 | 260 | -0.08 | -0.04 |
| **19** | NT | NT | | |
| **20** | 1300 | 160 | -0.08 | -0.06 |
| **21** | 1230 | 180 | -0.61 | -0.43 |
| **22** | 1390 | 150 | 0.61 | 0.51 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1310 | 50 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 1320 | 160 |
| **Robust Average** | 1310 | 50 |
| **Median** | 1300 | 40 |
| **Mean** | 1310 | |
| **N** | 16 | |
| **Max** | 1440 | |
| **Min** | 1194 | |
| **Robust SD** | 77 | |
| **Robust CV** | 5.9% | |

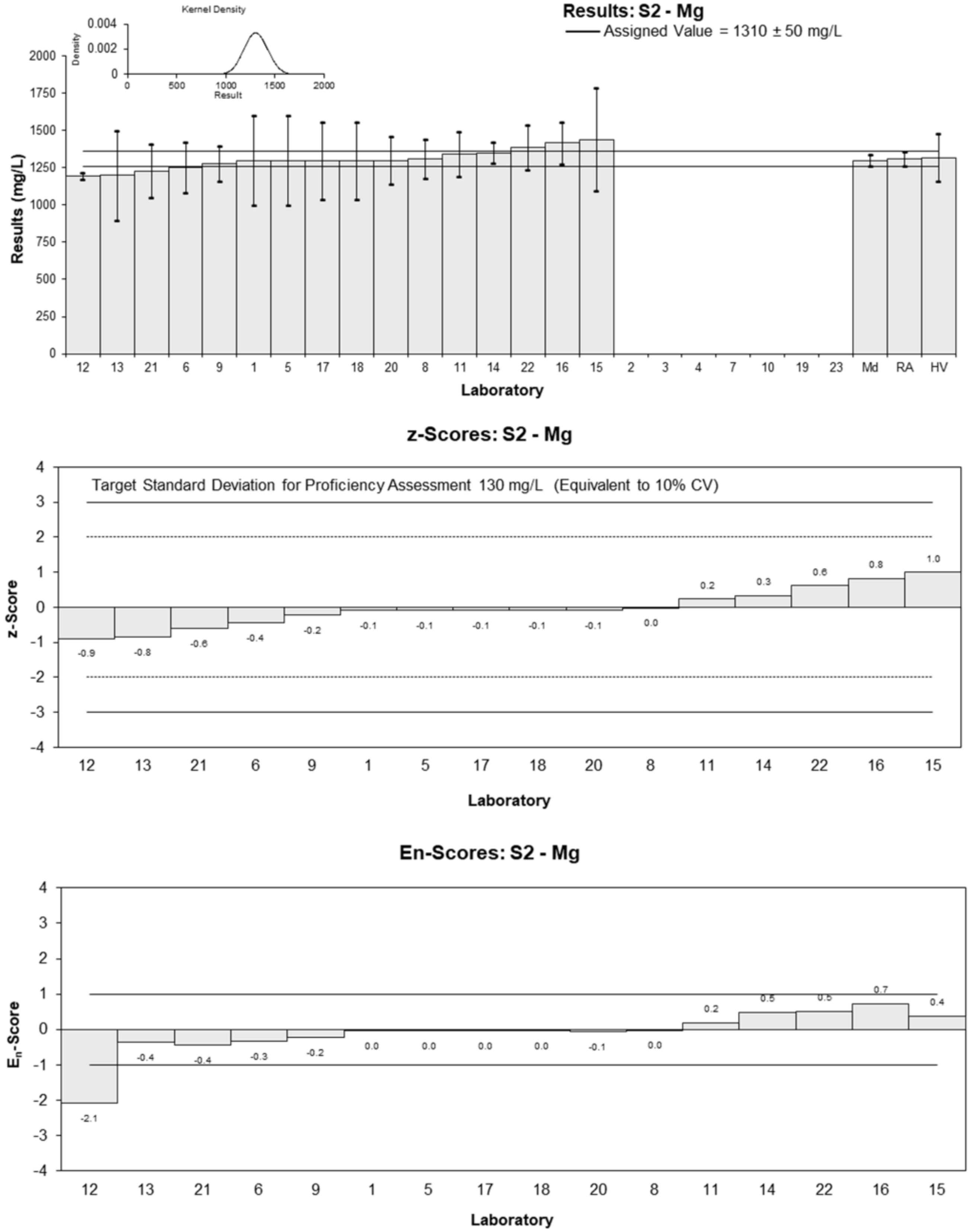

Results: S2 - Mg
Assigned Value = 1310 ± 50 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
12 13 21 6 9 1 5 17 18 20 8 11 14 22 16 15 2 3 4 7 10 19 23 Md RA HV
z-Scores: S2 - Mg
Target Standard Deviation for Proficiency Assessment 130 mg/L (Equivalent to 10% CV)
z-Score
-0.9 -0.8 -0.6 -0.4 -0.2 -0.1 -0.1 -0.1 -0.1 -0.1 0.0 0.2 0.3 0.6 0.8 1.0
Laboratory
12 13 21 6 9 1 5 17 18 20 8 11 14 22 16 15
En-Scores: S2 - Mg
$E_n$-Score
-2.1 -0.4 -0.4 -0.3 -0.2 0.0 0.0 0.0 0.0 -0.1 0.0 0.2 0.5 0.5 0.7 0.4
Laboratory
12 13 21 6 9 1 5 17 18 20 8 11 14 22 16 15

Figure 14

Table 18

**Sample Details**

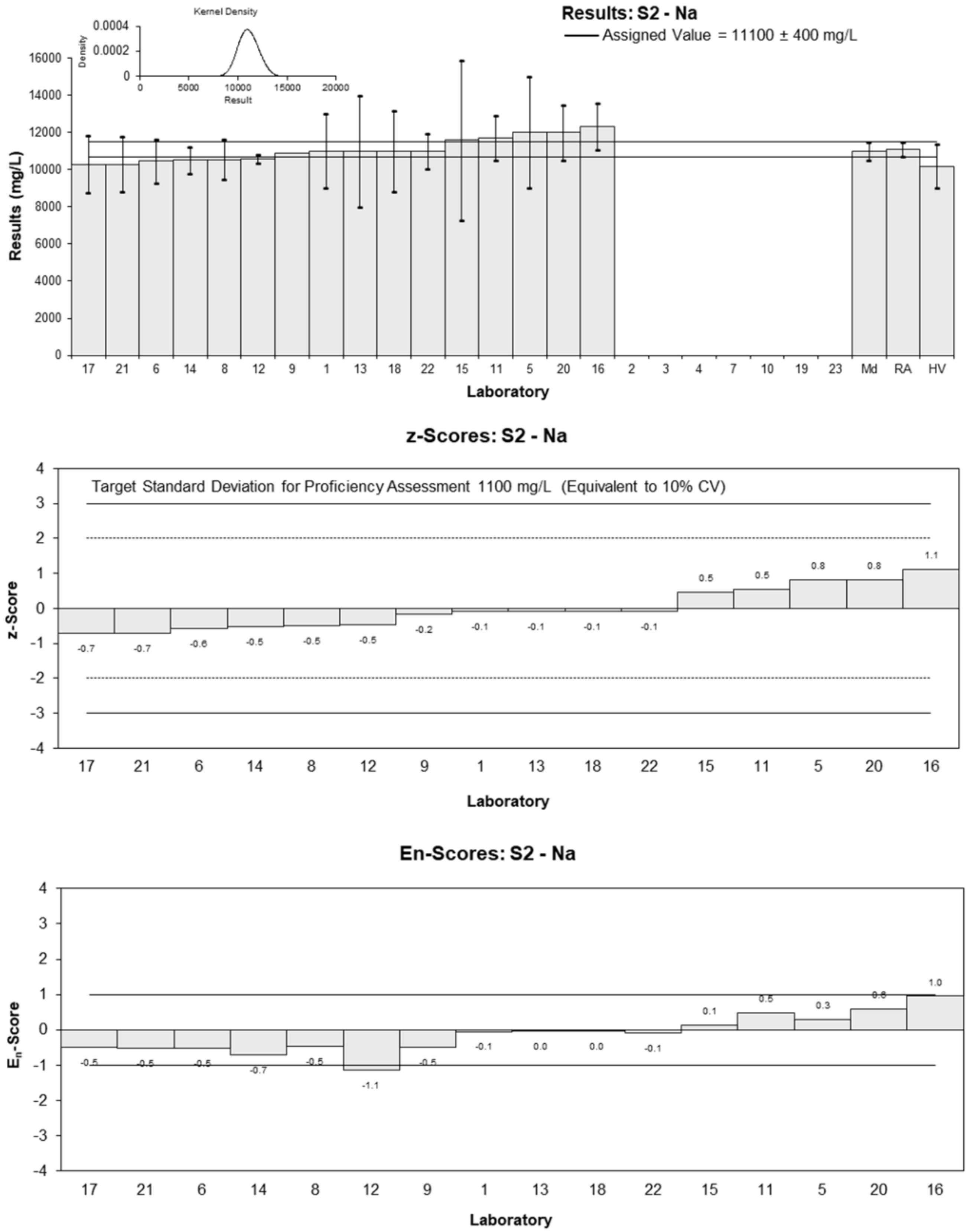
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | Na |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 11000 | 2000 | -0.09 | -0.05 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 12000 | 3000 | 0.81 | 0.30 |
| **6** | 10460 | 1170 | -0.58 | -0.52 |
| **7** | NT | NT | | |
| **8** | 10559 | 1100 | -0.49 | -0.46 |
| **9** | 10900 | NR | -0.18 | -0.50 |
| **10** | NT | NT | | |
| **11** | 11700 | 1200 | 0.54 | 0.47 |
| **12** | 10590 | 212 | -0.46 | -1.13 |
| **13** | 11000 | 3000 | -0.09 | -0.03 |
| **14** | 10511.29 | 734.44 | -0.53 | -0.70 |
| **15** | 11600 | 4300 | 0.45 | 0.12 |
| **16** | 12330 | 1233 | 1.11 | 0.95 |
| **17** | 10300 | 1545 | -0.72 | -0.50 |
| **18** | 11000 | 2200 | -0.09 | -0.04 |
| **19** | NT | NT | | |
| **20** | 12000 | 1500 | 0.81 | 0.58 |
| **21** | 10300 | 1500 | -0.72 | -0.52 |
| **22** | 11000 | 950 | -0.09 | -0.10 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 11100 | 400 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 10200 | 1200 |
| **Robust Average** | 11100 | 400 |
| **Median** | 11000 | 500 |
| **Mean** | 11100 | |
| **N** | 16 | |
| **Max** | 12330 | |
| **Min** | 10300 | |
| **Robust SD** | 710 | |
| **Robust CV** | 6.5% | |



Results: S2 - Na
Assigned Value = 11100 ± 400 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17 21 6 14 8 12 9 1 13 18 22 15 11 5 20 16 2 3 4 7 10 19 23 Md RA HV
z-Scores: S2 - Na
Target Standard Deviation for Proficiency Assessment 1100 mg/L (Equivalent to 10% CV)
z-Score
-0.7 -0.7 -0.6 -0.5 -0.5 -0.5 -0.2 -0.1 -0.1 -0.1 -0.1 0.5 0.5 0.8 0.8 1.1
17 21 6 14 8 12 9 1 13 18 22 15 11 5 20 16
Laboratory
En-Scores: S2 - Na
$E_n$-Score
-0.5 -0.5 -0.5 -0.7 -0.5 -1.1 -0.5 -0.1 0.0 0.0 -0.1 0.1 0.5 0.3 0.6 1.0
17 21 6 14 8 12 9 1 13 18 22 15 11 5 20 16
Laboratory


Figure 15

Table 19

**Sample Details**

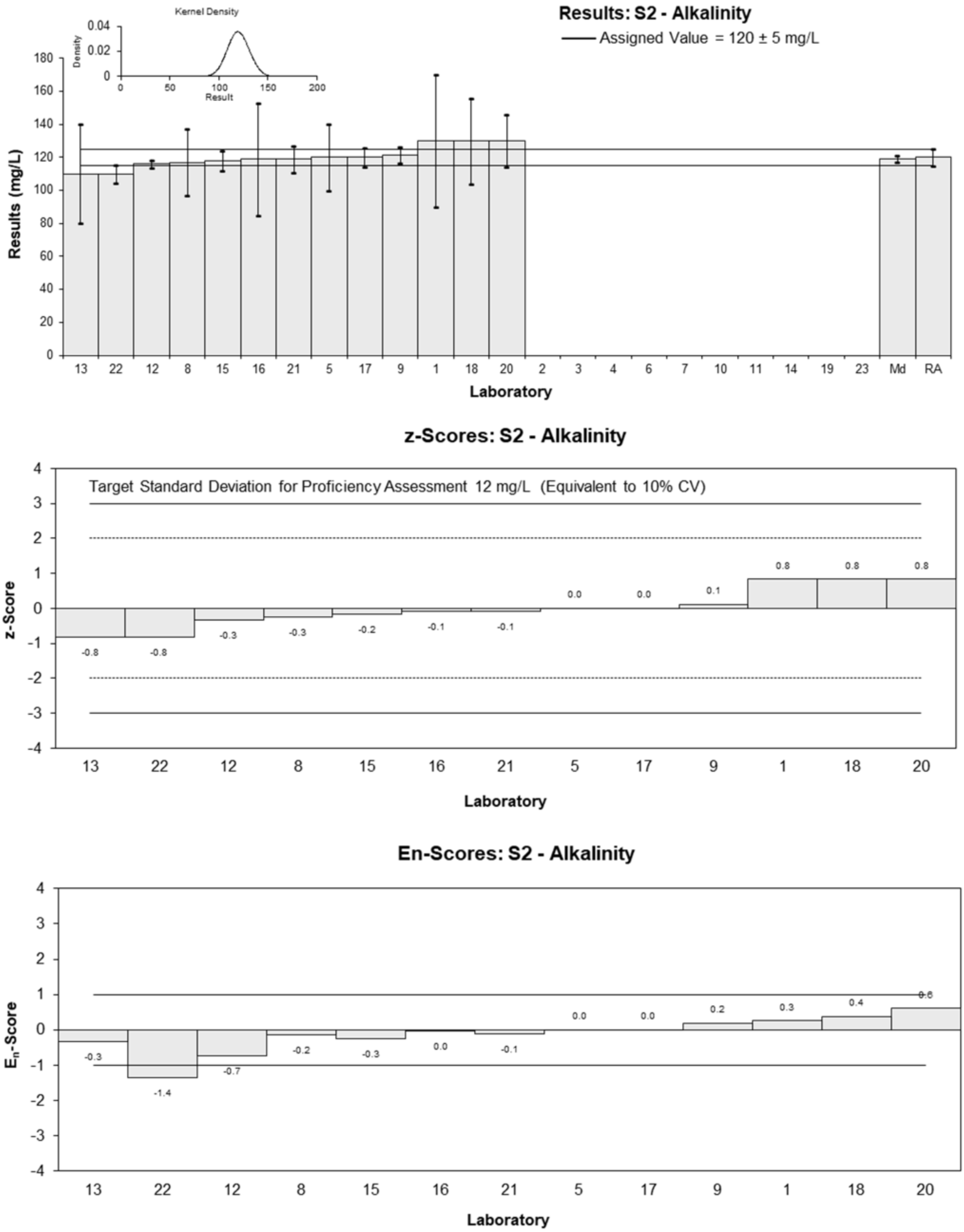
| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | Alkalinity |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 130 | 40 | 0.83 | 0.25 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 120 | 20 | 0.00 | 0.00 |
| **6** | NR | NR | | |
| **7** | NT | NT | | |
| **8** | 117 | 20 | -0.25 | -0.15 |
| **9** | 121.3 | 4.9 | 0.11 | 0.19 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 116 | 2.3 | -0.33 | -0.73 |
| **13** | 110 | 30 | -0.83 | -0.33 |
| **14** | NT | NT | | |
| **15** | 118 | 6 | -0.17 | -0.26 |
| **16** | 119 | 34 | -0.08 | -0.03 |
| **17** | 120 | 6 | 0.00 | 0.00 |
| **18** | 130 | 26 | 0.83 | 0.38 |
| **19** | NT | NT | | |
| **20** | 130 | 16 | 0.83 | 0.60 |
| **21** | 119 | 8 | -0.08 | -0.11 |
| **22** | 110 | 5.5 | -0.83 | -1.35 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 120 | 5 |
| **Spike Value** | Not Spiked | |
| **Robust Average** | 120 | 5 |
| **Median** | 119 | 2 |
| **Mean** | 120 | |
| **N** | 13 | |
| **Max** | 130 | |
| **Min** | 110 | |
| **Robust SD** | 7.6 | |
| **Robust CV** | 6.3% | |



Results: S2 - Alkalinity
Assigned Value = 120 ± 5 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
13 22 12 8 15 16 21 5 17 9 1 18 20 2 3 4 6 7 10 11 14 19 23 Md RA
z-Scores: S2 - Alkalinity
Target Standard Deviation for Proficiency Assessment 12 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.8 -0.3 -0.3 -0.2 -0.1 -0.1 0.0 0.0 0.1 0.8 0.8 0.8
13 22 12 8 15 16 21 5 17 9 1 18 20
Laboratory
En-Scores: S2 - Alkalinity
En-Score
-0.3 -1.4 -0.7 -0.2 -0.3 0.0 -0.1 0.0 0.0 0.2 0.3 0.4 0.6
13 22 12 8 15 16 21 5 17 9 1 18 20
Laboratory


Figure 16

Table 20

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | EC |
| **Unit** | µS/cm |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 52000 | 15000 | -0.33 | -0.12 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 51000 | 10000 | -0.52 | -0.27 |
| **6** | NR | NR | | |
| **7** | NT | NT | | |
| **8** | 58300 | 5830 | 0.84 | 0.72 |
| **9** | 53200 | 1100 | -0.11 | -0.24 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 54560 | 1092 | 0.14 | 0.31 |
| **13** | 59000 | 10000 | 0.97 | 0.51 |
| **14** | 50400 | 250.5 | -0.63 | -1.54 |
| **15** | 52500 | 2600 | -0.24 | -0.38 |
| **16** | 66500 | 6650 | 2.36 | 1.81 |
| **17** | 53800 | 5380 | 0.00 | 0.00 |
| **18** | 54000 | 8100 | 0.04 | 0.02 |
| **19** | NT | NT | | |
| **20** | 51000 | 6400 | -0.52 | -0.41 |
| **21** | 53500 | 2700 | -0.06 | -0.09 |
| **22** | 50900 | 3100 | -0.54 | -0.76 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 53800 | 2200 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 53000 | 4200 |
| **Robust Average** | 53800 | 2200 |
| **Median** | 53400 | 1800 |
| **Mean** | 54300 | |
| **N** | 14 | |
| **Max** | 66500 | |
| **Min** | 50400 | |
| **Robust SD** | 3300 | |
| **Robust CV** | 6.1% | |

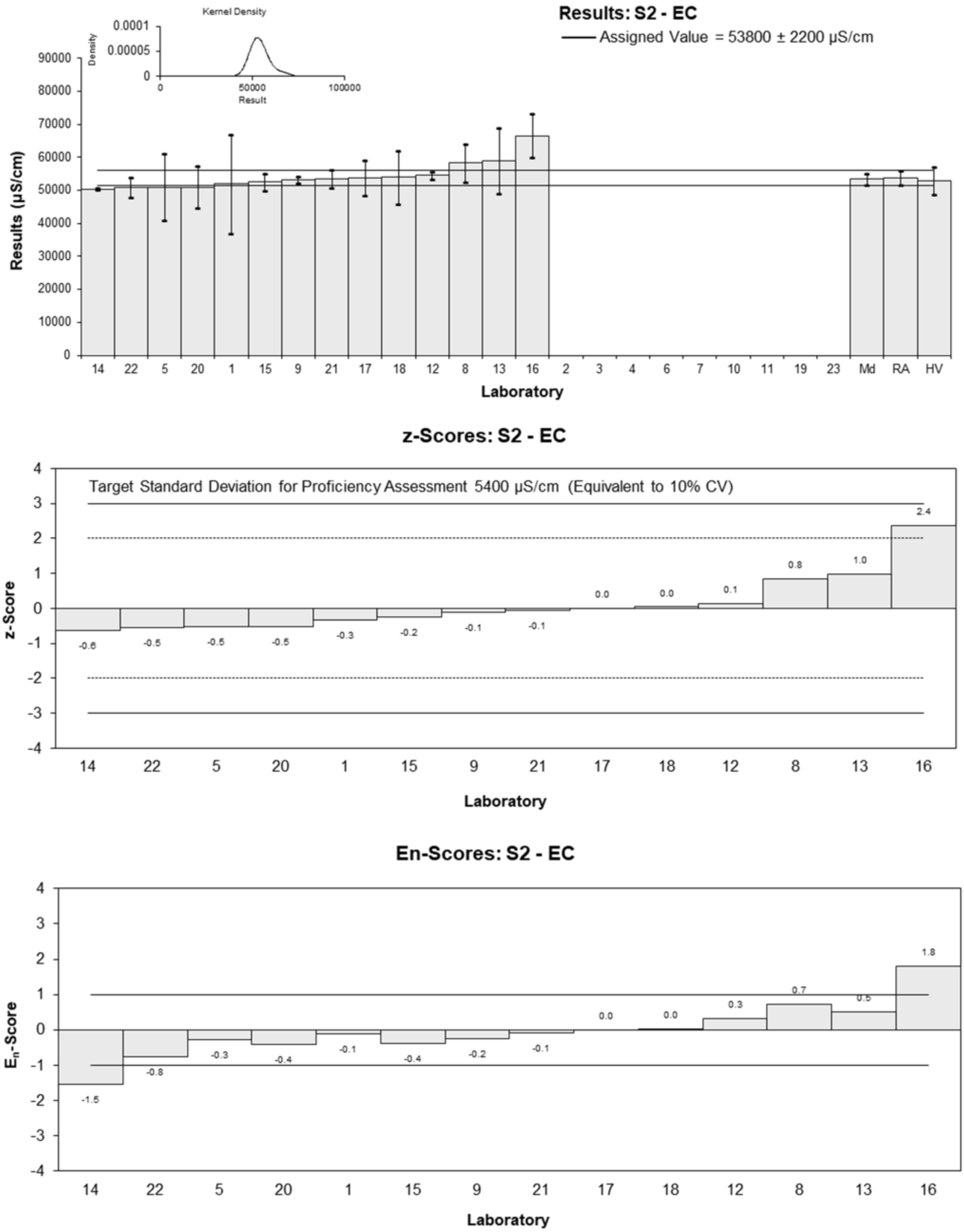

Kernel Density
Density
Result
Results: S2 - EC
Assigned Value = 53800 ± 2200 µS/cm
Results (µS/cm)
14 22 5 20 1 15 9 21 17 18 12 8 13 16 2 3 4 6 7 10 11 19 23 Md RA HV
Laboratory
z-Scores: S2 - EC
Target Standard Deviation for Proficiency Assessment 5400 µS/cm (Equivalent to 10% CV)
-0.6 -0.5 -0.5 -0.5 -0.3 -0.2 -0.1 -0.1 0.0 0.0 0.1 0.8 1.0 2.4
z-Score
14 22 5 20 1 15 9 21 17 18 12 8 13 16
Laboratory
En-Scores: S2 - EC
-1.5 -0.8 -0.3 -0.4 -0.1 -0.4 -0.2 -0.1 0.0 0.0 0.3 0.7 0.5 1.8
En-Score
14 22 5 20 1 15 9 21 17 18 12 8 13 16
Laboratory

Figure 17

Table 21

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | pH |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 7.6 | 0.2 | -1.36 | -1.45 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 7.8 | 0.2 | -0.64 | -0.69 |
| **6** | 8.10 | 0.06 | 0.43 | 0.67 |
| **7** | NT | NT | | |
| **8** | 8.00 | 0.2 | 0.07 | 0.08 |
| **9** | 8.1 | 0.2 | 0.43 | 0.46 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 7.68 | 0.15 | -1.07 | -1.32 |
| **13** | 7.5 | 0.2 | -1.72 | -1.83 |
| **14** | 8.46 | 0.05 | 1.72 | 2.71 |
| **15** | 8.1 | 0.1 | 0.43 | 0.61 |
| **16** | 8.2 | 0.17 | 0.79 | 0.92 |
| **17** | 8.1 | NR | 0.43 | 0.71 |
| **18** | 8.0 | 1.6 | 0.07 | 0.01 |
| **19** | NT | NT | | |
| **20** | 8.0 | 0.2 | 0.07 | 0.08 |
| **21** | 8.2 | 0.2 | 0.79 | 0.84 |
| **22** | 7.9 | 0.4 | -0.29 | -0.18 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 7.98 | 0.17 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 8.00 | 0.24 |
| **Robust Average** | 7.98 | 0.17 |
| **Median** | 8.00 | 0.10 |
| **Mean** | 7.98 | |
| **N** | 15 | |
| **Max** | 8.46 | |
| **Min** | 7.5 | |
| **Robust SD** | 0.26 | |
| **Robust CV** | 3.2% | |

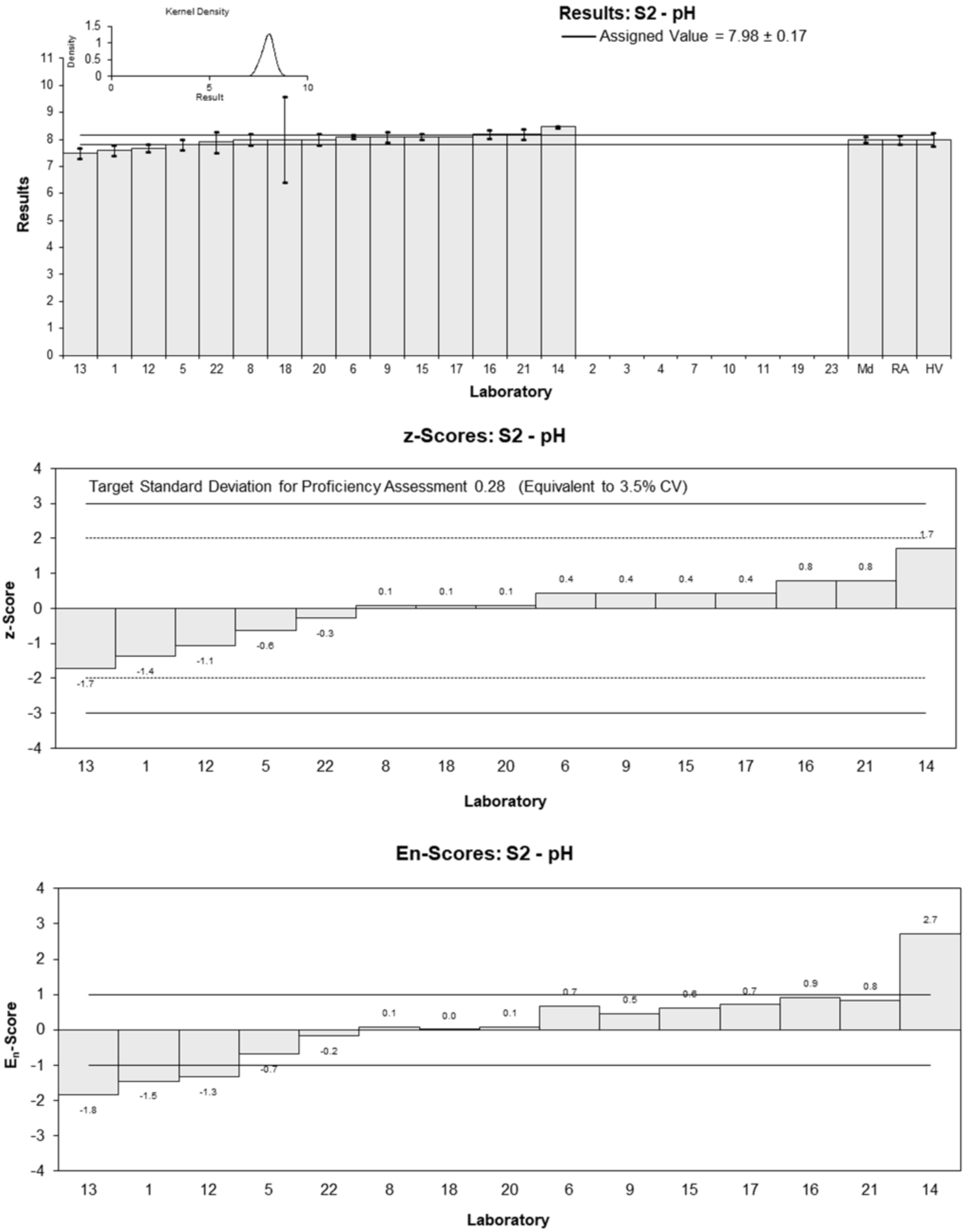

Results: S2 - pH
Assigned Value = 7.98 ± 0.17
Kernel Density
Density
Result
Results
Laboratory
13 1 12 5 22 8 18 20 6 9 15 17 16 21 14 2 3 4 7 10 11 19 23 Md RA HV
z-Scores: S2 - pH
Target Standard Deviation for Proficiency Assessment 0.28 (Equivalent to 3.5% CV)
z-Score
Laboratory
13 1 12 5 22 8 18 20 6 9 15 17 16 21 14
-1.7 -1.4 -1.1 -0.6 -0.3 0.1 0.1 0.1 0.4 0.4 0.4 0.4 0.8 0.8 1.7
En-Scores: S2 - pH
En-Score
Laboratory
13 1 12 5 22 8 18 20 6 9 15 17 16 21 14
-1.8 -1.5 -1.3 -0.7 -0.2 0.1 0.0 0.1 0.7 0.5 0.6 0.7 0.9 0.8 2.7

Figure 18

Table 22

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | Silica (as SiO2) |
| **Unit** | mg/L |

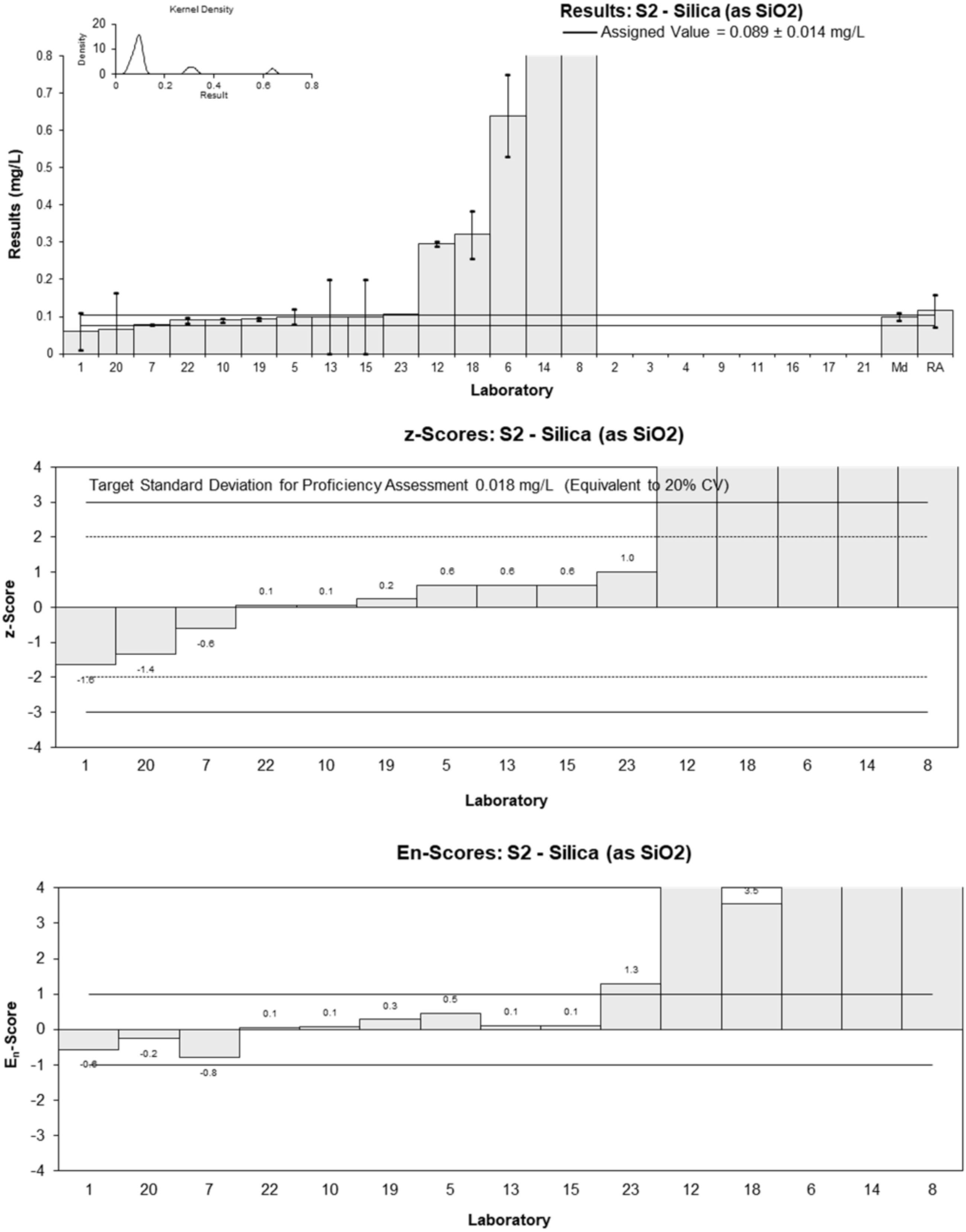
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.06 | 0.05 | -1.63 | -0.56 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.1 | 0.02 | 0.62 | 0.45 |
| **6*** | 0.64 | 0.11 | 30.96 | 4.97 |
| **7** | 0.0781 | 0.0012 | -0.61 | -0.78 |
| **8**** | 13.0 | 2.0 | 725.34 | 6.46 |
| **9** | <1.0 | 0.064 | | |
| **10** | 0.0901 | 0.0042 | 0.06 | 0.08 |
| **11** | NR | NR | | |
| **12*** | 0.296 | 0.006 | 11.63 | 13.59 |
| **13** | 0.1 | 0.1 | 0.62 | 0.11 |
| **14**** | 1.40 | 0.11 | 73.65 | 11.82 |
| **15** | 0.1 | 0.1 | 0.62 | 0.11 |
| **16** | NT | NT | | |
| **17** | <0.1 | NR | | |
| **18*** | 0.321 | 0.064 | 13.03 | 3.54 |
| **19** | 0.0931 | 0.0044 | 0.23 | 0.28 |
| **20** | 0.065 | 0.1 | -1.35 | -0.24 |
| **21** | NT | NT | | |
| **22** | 0.090 | 0.008 | 0.06 | 0.06 |
| **23** | 0.107 | NR | 1.01 | 1.29 |

* Outlier, ** Extreme Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.089 | 0.014 |
| **Spike Value** | Not Spiked | |
| **Robust Average** | 0.116 | 0.043 |
| **Median** | 0.100 | 0.010 |
| **Mean** | 0.165 | |
| **N** | 13 | |
| **Max** | 0.64 | |
| **Min** | 0.06 | |
| **Robust SD** | 0.062 | |
| **Robust CV** | 54% | |



Results: S2 - Silica (as SiO2)
Assigned Value = 0.089 ± 0.014 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 20 7 22 10 19 5 13 15 23 12 18 6 14 8 2 3 4 9 11 16 17 21 Md RA
z-Scores: S2 - Silica (as SiO2)
Target Standard Deviation for Proficiency Assessment 0.018 mg/L (Equivalent to 20% CV)
z-Score
-1.6 -1.4 -0.6 0.1 0.1 0.2 0.6 0.6 0.6 1.0
Laboratory
1 20 7 22 10 19 5 13 15 23 12 18 6 14 8
En-Scores: S2 - Silica (as SiO2)
$E_n$-Score
-0.6 -0.2 -0.8 0.1 0.1 0.3 0.5 0.1 0.1 1.3 3.5
Laboratory
1 20 7 22 10 19 5 13 15 23 12 18 6 14 8


Figure 19

Table 23

**Sample Details**

| | |
|---|---|
| **Sample No.** | S2 |
| **Matrix** | Sea Water |
| **Analyte** | Total Hardness |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 6400 | 2000 | -0.02 | 0.00 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 6400 | 1000 | -0.02 | -0.01 |
| **6** | 6200 | 1310 | -0.33 | -0.16 |
| **7** | NT | NT | | |
| **8** | 6800 | 680 | 0.61 | 0.53 |
| **9** | 6330 | 480 | -0.12 | -0.14 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 5947 | 119 | -0.72 | -1.48 |
| **13** | 5900 | 2000 | -0.80 | -0.25 |
| **14** | 5951 | 329.70 | -0.72 | -1.05 |
| **15** | 7120 | 2140 | 1.11 | 0.33 |
| **16** | 6955 | 695 | 0.85 | 0.72 |
| **17** | NT | NT | | |
| **18** | 6402 | 1280 | -0.01 | -0.01 |
| **19** | NT | NT | | |
| **20** | 6300 | 790 | -0.17 | -0.13 |
| **21** | NT | NT | | |
| **22** | 6700 | 810 | 0.45 | 0.34 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 6410 | 290 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 6360 | 950 |
| **Robust Average** | 6410 | 290 |
| **Median** | 6400 | 310 |
| **Mean** | 6420 | |
| **N** | 13 | |
| **Max** | 7120 | |
| **Min** | 5900 | |
| **Robust SD** | 430 | |
| **Robust CV** | 6.6% | |

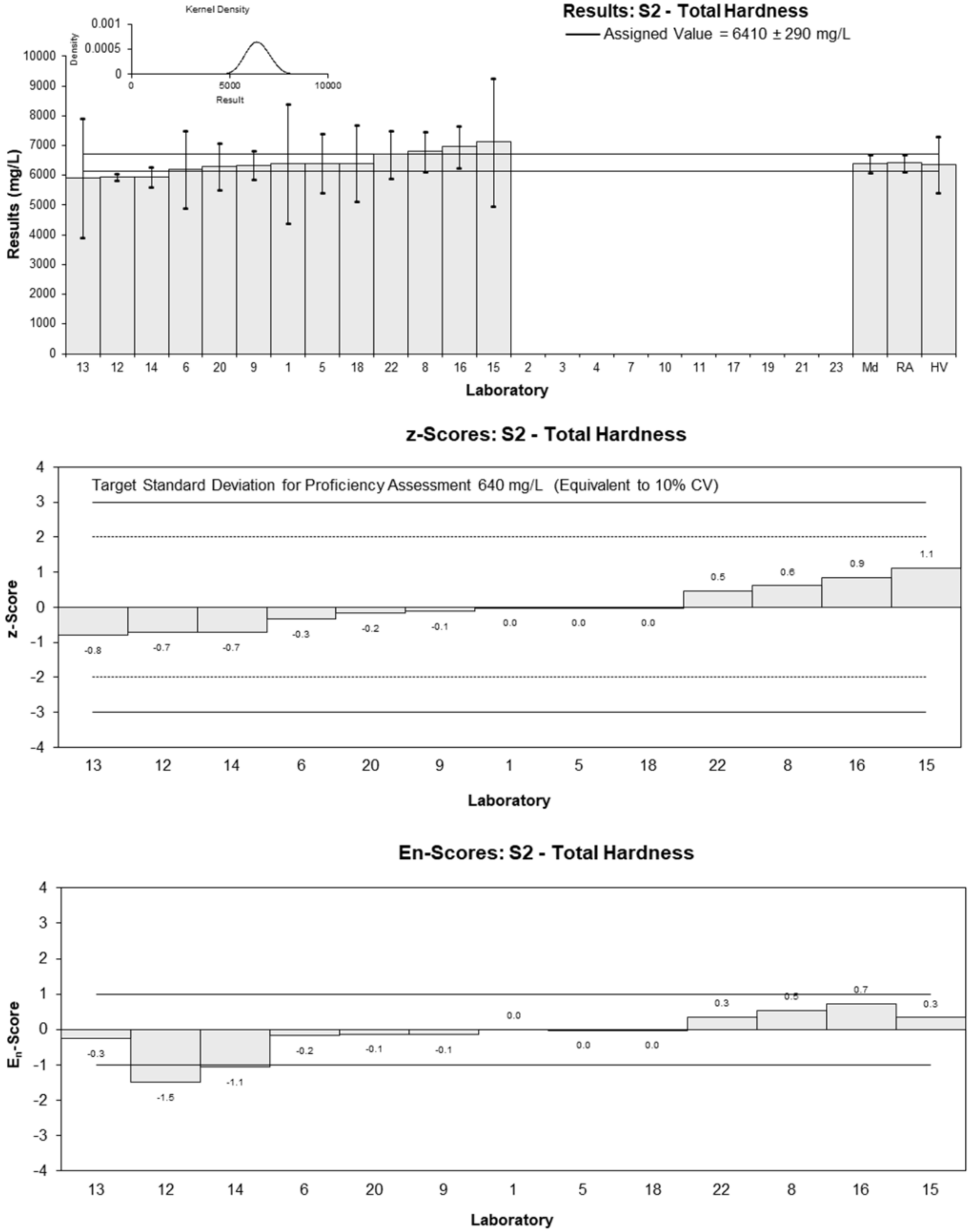

Results: S2 - Total Hardness
Assigned Value = 6410 ± 290 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
13 12 14 6 20 9 1 5 18 22 8 16 15 2 3 4 7 10 11 17 19 21 23 Md RA HV
z-Scores: S2 - Total Hardness
Target Standard Deviation for Proficiency Assessment 640 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.7 -0.7 -0.3 -0.2 -0.1 0.0 0.0 0.0 0.5 0.6 0.9 1.1
13 12 14 6 20 9 1 5 18 22 8 16 15
Laboratory
En-Scores: S2 - Total Hardness
$E_n$-Score
-0.3 -1.5 -1.1 -0.2 -0.1 -0.1 0.0 0.0 0.0 0.3 0.5 0.7 0.3
13 12 14 6 20 9 1 5 18 22 8 16 15
Laboratory

Figure 20

Table 24

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | B |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.7 | 0.2 | -0.77 | -0.44 |
| **2** | 0.866 | 0.05 | 0.63 | 0.99 |
| **3** | NT | NT | | |
| **4** | NR | NR | | |
| **5** | 0.76 | 0.2 | -0.26 | -0.15 |
| **6** | 0.82 | 0.13 | 0.24 | 0.20 |
| **7** | NT | NT | | |
| **8** | 0.675 | 0.07 | -0.98 | -1.29 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 0.798 | 0.1 | 0.06 | 0.06 |
| **12** | 0.693 | 0.014 | -0.83 | -1.67 |
| **13** | 0.79 | 0.2 | -0.01 | 0.00 |
| **14** | NT | NT | | |
| **15** | NR | NR | | |
| **16** | 0.739 | 0.07 | -0.44 | -0.58 |
| **17** | 0.86 | 0.22 | 0.58 | 0.30 |
| **18** | 0.832 | 0.166 | 0.35 | 0.23 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.854 | 0.120 | 0.53 | 0.47 |
| **22** | 0.90 | 0.23 | 0.92 | 0.46 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.791 | 0.057 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 0.799 | 0.096 |
| **Robust Average** | 0.791 | 0.057 |
| **Median** | 0.798 | 0.061 |
| **Mean** | 0.791 | |
| **N** | 13 | |
| **Max** | 0.9 | |
| **Min** | 0.675 | |
| **Robust SD** | 0.083 | |
| **Robust CV** | 10% | |

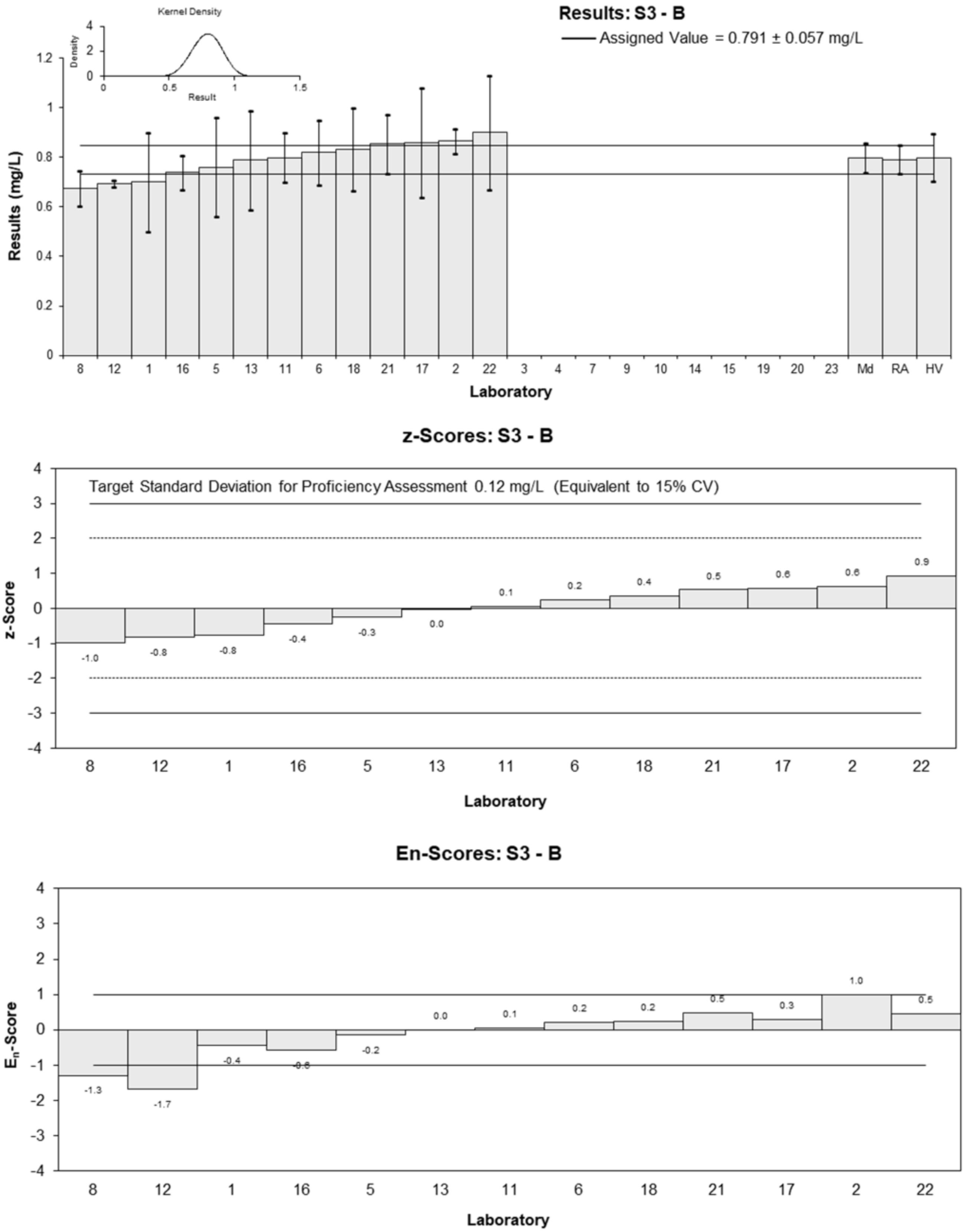

Results: S3 - B
Assigned Value = 0.791 ± 0.057 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 12 1 16 5 13 11 6 18 21 17 2 22 3 4 7 9 10 14 15 19 20 23 Md RA HV
z-Scores: S3 - B
Target Standard Deviation for Proficiency Assessment 0.12 mg/L (Equivalent to 15% CV)
z-Score
-1.0 -0.8 -0.8 -0.4 -0.3 0.0 0.1 0.2 0.4 0.5 0.6 0.6 0.9
8 12 1 16 5 13 11 6 18 21 17 2 22
Laboratory
En-Scores: S3 - B
$E_n$-Score
-1.3 -1.7 -0.4 -0.6 -0.2 0.0 0.1 0.2 0.2 0.5 0.3 1.0 0.5
8 12 1 16 5 13 11 6 18 21 17 2 22
Laboratory

Figure 21

Table 25

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Ca |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 18 | 4 | 0.11 | 0.05 |
| **2** | 18.3 | 0.95 | 0.28 | 0.38 |
| **3*** | 6.28 | 0.04 | -6.47 | -12.79 |
| **4** | 14.7 | NR | -1.74 | -3.44 |
| **5** | 17 | 4 | -0.45 | -0.20 |
| **6** | 19.0 | 3.1 | 0.67 | 0.37 |
| **7** | NT | NT | | |
| **8** | 19.5 | 2.0 | 0.96 | 0.78 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 18.6 | 4 | 0.45 | 0.20 |
| **12** | 18.31 | 0.37 | 0.29 | 0.52 |
| **13** | 18 | 4 | 0.11 | 0.05 |
| **14** | NT | NT | | |
| **15** | 18.3 | 3.66 | 0.28 | 0.13 |
| **16** | 16 | 3 | -1.01 | -0.57 |
| **17** | 13 | 3 | -2.70 | -1.53 |
| **18** | 19.2 | 3.84 | 0.79 | 0.35 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 17.4 | 2.4 | -0.22 | -0.16 |
| **22** | 18.1 | 2.0 | 0.17 | 0.14 |
| **23** | NR | NR | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 17.8 | 0.9 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 19.4 | 2.3 |
| **Robust Average** | 17.5 | 1.1 |
| **Median** | 18.1 | 0.7 |
| **Mean** | 16.9 | |
| **N** | 16 | |
| **Max** | 19.5 | |
| **Min** | 6.28 | |
| **Robust SD** | 1.8 | |
| **Robust CV** | 10.0% | |

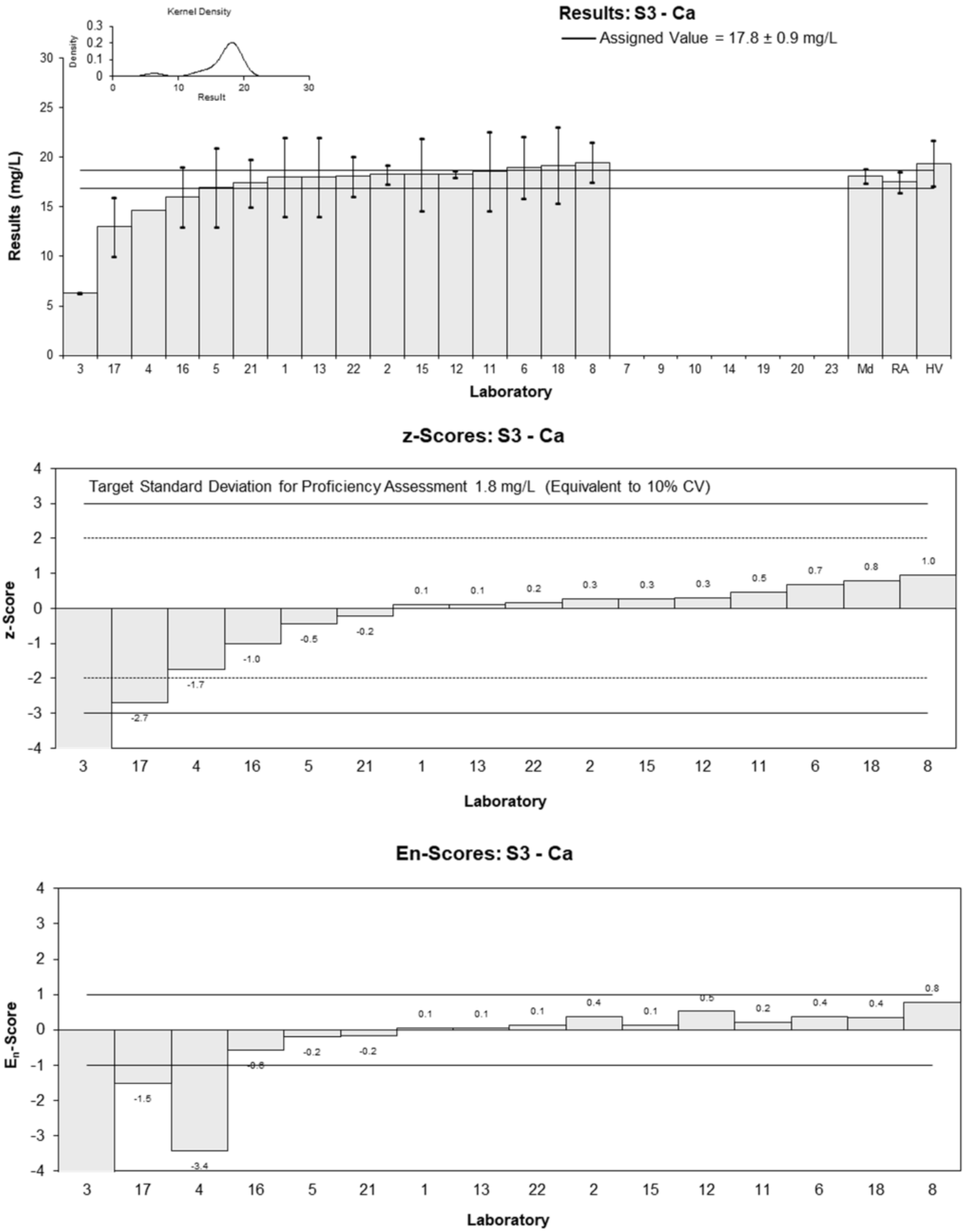

Results: S3 - Ca
Assigned Value = 17.8 ± 0.9 mg/L
Kernel Density
Density
Result
Results (mg/L)
3 17 4 16 5 21 1 13 22 2 15 12 11 6 18 8 7 9 10 14 19 20 23 Md RA HV
Laboratory
z-Scores: S3 - Ca
Target Standard Deviation for Proficiency Assessment 1.8 mg/L (Equivalent to 10% CV)
z-Score
-2.7 -1.7 -1.0 -0.5 -0.2 0.1 0.1 0.2 0.3 0.3 0.3 0.5 0.7 0.8 1.0
3 17 4 16 5 21 1 13 22 2 15 12 11 6 18 8
Laboratory
En-Scores: S3 - Ca
En-Score
-1.5 -3.4 -0.6 -0.2 -0.2 0.1 0.1 0.1 0.4 0.1 0.5 0.2 0.4 0.4 0.8
3 17 4 16 5 21 1 13 22 2 15 12 11 6 18 8
Laboratory

Figure 22

Table 26

**Sample Details**

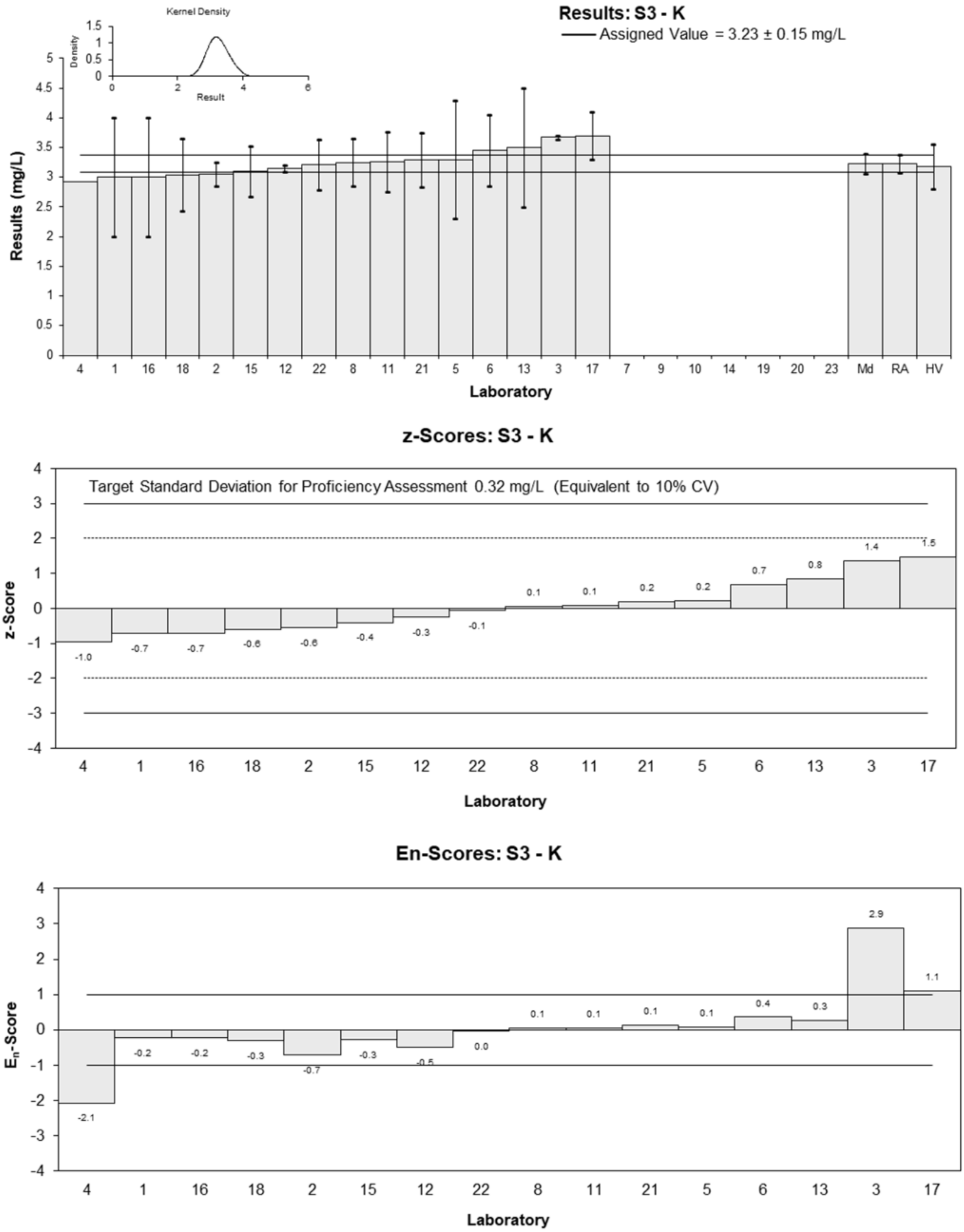
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | K |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 3 | 1 | -0.71 | -0.23 |
| **2** | 3.05 | 0.20 | -0.56 | -0.72 |
| **3** | 3.67 | 0.03 | 1.36 | 2.88 |
| **4** | 2.92 | NR | -0.96 | -2.07 |
| **5** | 3.3 | 1 | 0.22 | 0.07 |
| **6** | 3.45 | 0.60 | 0.68 | 0.36 |
| **7** | NT | NT | | |
| **8** | 3.25 | 0.4 | 0.06 | 0.05 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 3.26 | 0.5 | 0.09 | 0.06 |
| **12** | 3.15 | 0.06 | -0.25 | -0.50 |
| **13** | 3.5 | 1 | 0.84 | 0.27 |
| **14** | NT | NT | | |
| **15** | 3.1 | 0.43 | -0.40 | -0.29 |
| **16** | 3 | 1 | -0.71 | -0.23 |
| **17** | 3.7 | 0.4 | 1.46 | 1.10 |
| **18** | 3.04 | 0.608 | -0.59 | -0.30 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 3.29 | 0.46 | 0.19 | 0.12 |
| **22** | 3.21 | 0.43 | -0.06 | -0.04 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 3.23 | 0.15 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 3.18 | 0.38 |
| **Robust Average** | 3.23 | 0.15 |
| **Median** | 3.23 | 0.17 |
| **Mean** | 3.24 | |
| **N** | 16 | |
| **Max** | 3.7 | |
| **Min** | 2.92 | |
| **Robust SD** | 0.24 | |
| **Robust CV** | 7.6% | |



Results: S3 - K
Assigned Value = 3.23 ± 0.15 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
4 1 16 18 2 15 12 22 8 11 21 5 6 13 3 17 7 9 10 14 19 20 23 Md RA HV
z-Scores: S3 - K
Target Standard Deviation for Proficiency Assessment 0.32 mg/L (Equivalent to 10% CV)
z-Score
-1.0 -0.7 -0.7 -0.6 -0.6 -0.4 -0.3 -0.1 0.1 0.1 0.2 0.2 0.7 0.8 1.4 1.5
Laboratory
4 1 16 18 2 15 12 22 8 11 21 5 6 13 3 17
En-Scores: S3 - K
En-Score
-2.1 -0.2 -0.2 -0.3 -0.7 -0.3 -0.5 0.0 0.1 0.1 0.1 0.1 0.4 0.3 2.9 1.1
Laboratory
4 1 16 18 2 15 12 22 8 11 21 5 6 13 3 17


Figure 23

Table 27

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Mg |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 7 | 2 | -0.40 | -0.14 |
| **2** | 7.56 | 0.40 | 0.37 | 0.53 |
| **3** | 6.36 | 0.04 | -1.28 | -2.98 |
| **4** | 7.10 | NR | -0.26 | -0.61 |
| **5** | 6.9 | 1 | -0.53 | -0.37 |
| **6** | 8.05 | 1.09 | 1.04 | 0.67 |
| **7** | NT | NT | | |
| **8** | 7.47 | 0.8 | 0.25 | 0.21 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 7.49 | 1 | 0.27 | 0.19 |
| **12** | 7.29 | 0.15 | 0.00 | 0.00 |
| **13** | 7.5 | 2 | 0.29 | 0.10 |
| **14** | NT | NT | | |
| **15** | 7.2 | 1.5 | -0.12 | -0.06 |
| **16** | 8 | 1 | 0.97 | 0.68 |
| **17** | 6.5 | 1.3 | -1.08 | -0.59 |
| **18** | 7.02 | 1.40 | -0.37 | -0.19 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 7.35 | 1.03 | 0.08 | 0.06 |
| **22** | 7.69 | 0.83 | 0.55 | 0.45 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 7.29 | 0.31 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 7.41 | 0.89 |
| **Robust Average** | 7.29 | 0.31 |
| **Median** | 7.32 | 0.25 |
| **Mean** | 7.28 | |
| **N** | 16 | |
| **Max** | 8.05 | |
| **Min** | 6.36 | |
| **Robust SD** | 0.49 | |
| **Robust CV** | 6.8% | |

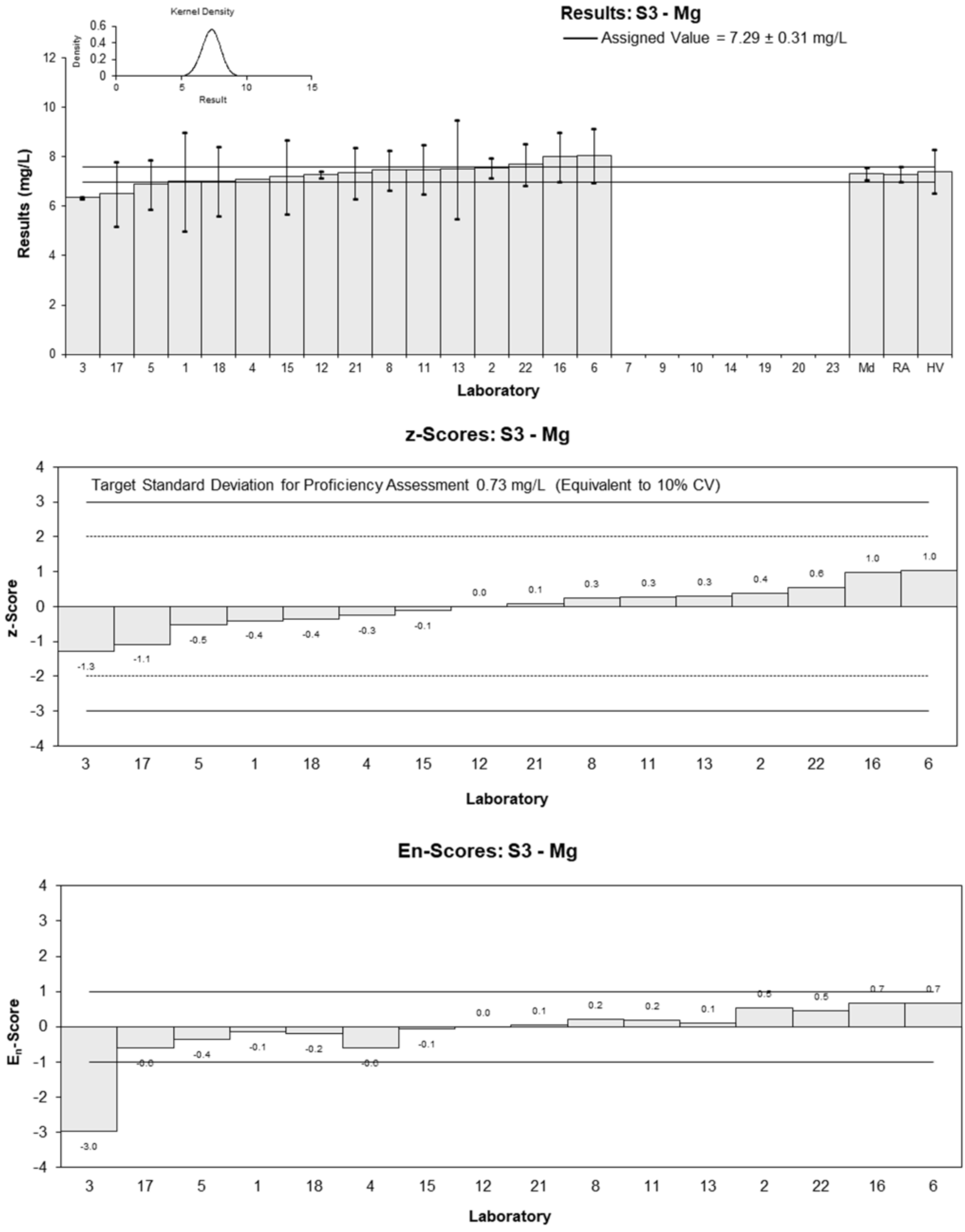

Results: S3 - Mg
Assigned Value = 7.29 ± 0.31 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
3 17 5 1 18 4 15 12 21 8 11 13 2 22 16 6 7 9 10 14 19 20 23 Md RA HV
z-Scores: S3 - Mg
Target Standard Deviation for Proficiency Assessment 0.73 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S3 - Mg
En-Score
Laboratory

Figure 24

Table 28

**Sample Details**

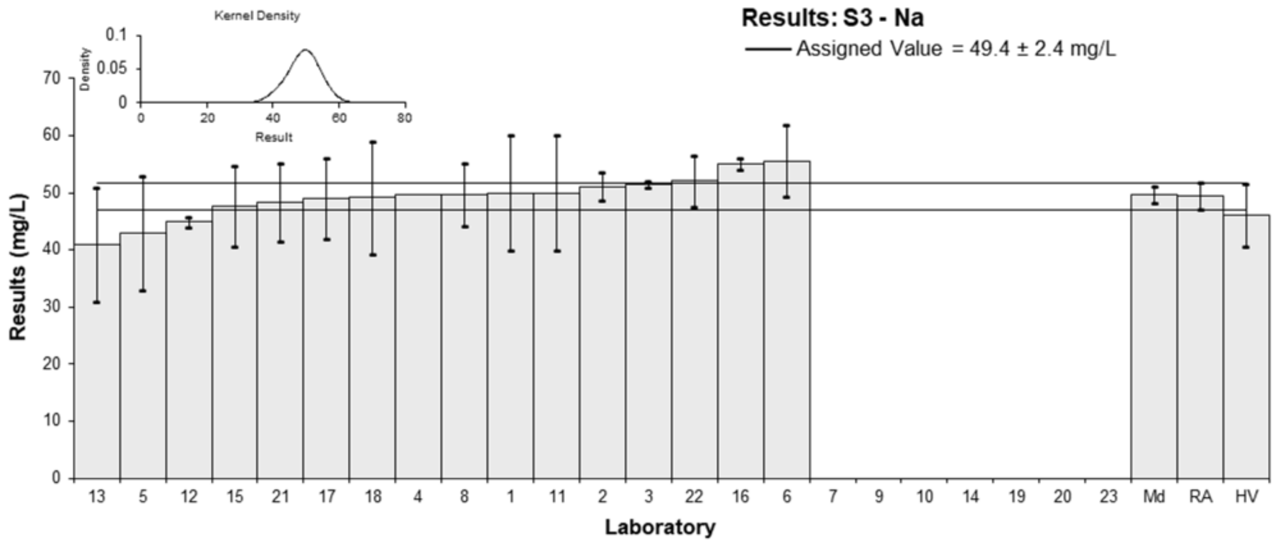
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Na |
| **Unit** | mg/L |

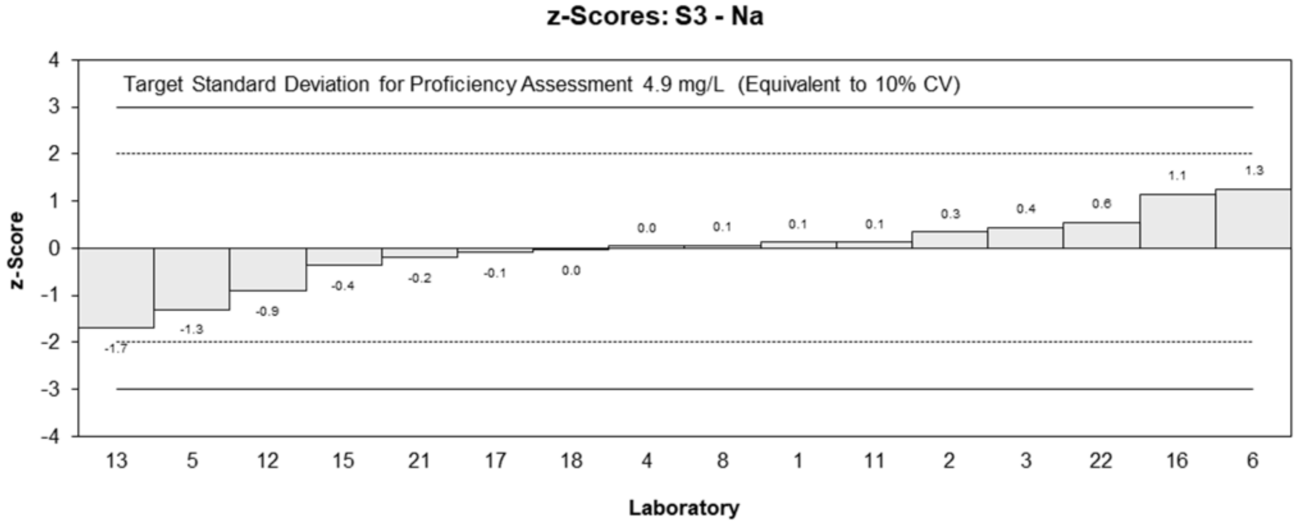
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 50 | 10 | 0.12 | 0.06 |
| **2** | 51.1 | 2.50 | 0.34 | 0.49 |
| **3** | 51.53 | 0.54 | 0.43 | 0.87 |
| **4** | 49.6 | NR | 0.04 | 0.08 |
| **5** | 43 | 10 | -1.30 | -0.62 |
| **6** | 55.6 | 6.2 | 1.26 | 0.93 |
| **7** | NT | NT | | |
| **8** | 49.7 | 5.5 | 0.06 | 0.05 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 50 | 10 | 0.12 | 0.06 |
| **12** | 44.94 | 0.9 | -0.90 | -1.74 |
| **13** | 41 | 10 | -1.70 | -0.82 |
| **14** | NT | NT | | |
| **15** | 47.6 | 7.1 | -0.36 | -0.24 |
| **16** | 55 | 1 | 1.13 | 2.15 |
| **17** | 49 | 7 | -0.08 | -0.05 |
| **18** | 49.2 | 9.84 | -0.04 | -0.02 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 48.4 | 6.8 | -0.20 | -0.14 |
| **22** | 52.1 | 4.5 | 0.55 | 0.53 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 49.4 | 2.4 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 46.1 | 5.5 |
| **Robust Average** | 49.4 | 2.4 |
| **Median** | 49.7 | 1.5 |
| **Mean** | 49.2 | |
| **N** | 16 | |
| **Max** | 55.6 | |
| **Min** | 41 | |
| **Robust SD** | 3.8 | |
| **Robust CV** | 7.7% | |


Results: S3 - Na
Assigned Value = 49.4 ± 2.4 mg/L
Kernel Density
Density
Result
Results (mg/L)
13
5
12
15
21
17
18
4
8
1
11
2
3
22
16
6
7
9
10
14
19
20
23
Md
RA
HV
Laboratory


z-Scores: S3 - Na
Target Standard Deviation for Proficiency Assessment 4.9 mg/L (Equivalent to 10% CV)
z-Score
-1.7
-1.3
-0.9
-0.4
-0.2
-0.1
0.0
0.0
0.1
0.1
0.1
0.3
0.4
0.6
1.1
1.3
13
5
12
15
21
17
18
4
8
1
11
2
3
22
16
6
Laboratory

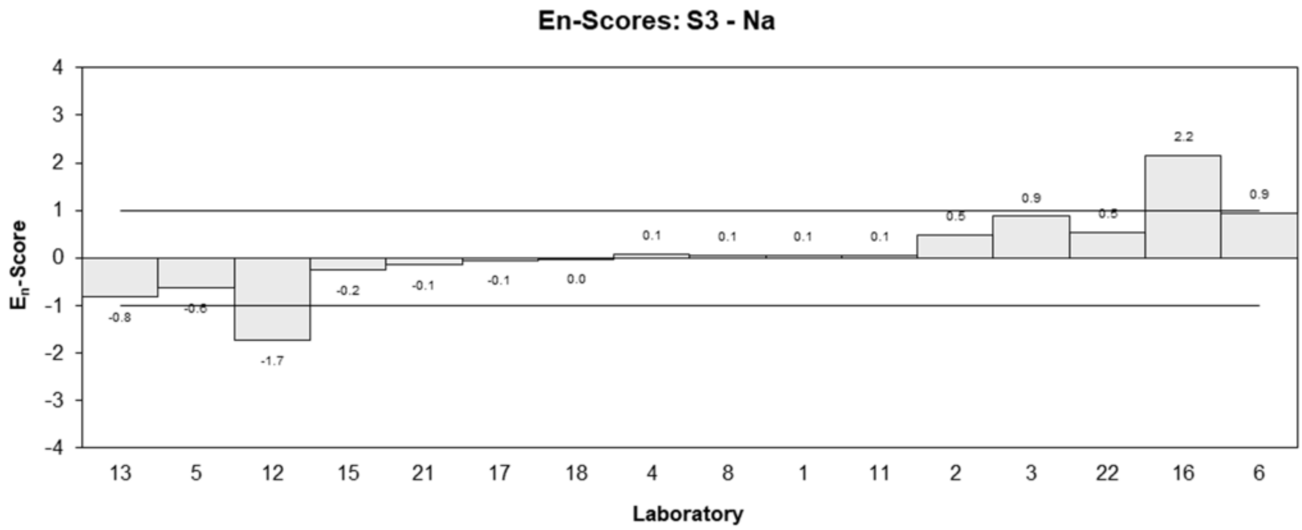

En-Scores: S3 - Na
$E_n$-Score
-0.8
-0.6
-1.7
-0.2
-0.1
-0.1
0.0
0.1
0.1
0.1
0.1
0.5
0.9
0.5
2.2
0.9
13
5
12
15
21
17
18
4
8
1
11
2
3
22
16
6
Laboratory

Figure 25

Table 29

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Ammonia-N |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.04 | 0.02 | -0.66 | -0.22 |
| **2** | NT | NT | | |
| **3** | <1 | 0.1 | | |
| **4*** | 0.099 | NR | 8.20 | 16.55 |
| **5** | 0.06 | 0.03 | 2.34 | 0.52 |
| **6** | 0.04 | 0.01 | -0.66 | -0.42 |
| **7** | NT | NT | | |
| **8** | 0.047 | 0.01 | 0.39 | 0.25 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12*** | 0.139 | 0.003 | 14.20 | 21.21 |
| **13** | 0.04 | 0.02 | -0.66 | -0.22 |
| **14** | NT | NT | | |
| **15** | 0.045 | 0.6 | 0.09 | 0.00 |
| **16** | <0.2 | 1.12 | | |
| **17** | 0.042 | 0.015 | -0.36 | -0.16 |
| **18** | 0.046 | 0.009 | 0.24 | 0.17 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.0494 | 0.0069 | 0.75 | 0.65 |
| **22** | 0.046 | 0.010 | 0.24 | 0.15 |
| **23** | 0.042 | 0.005 | -0.36 | -0.40 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0444 | 0.0033 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 0.0502 | 0.0075 |
| **Robust Average** | 0.0477 | 0.0064 |
| **Median** | 0.0460 | 0.0041 |
| **Mean** | 0.057 | |
| **N** | 13 | |
| **Max** | 0.139 | |
| **Min** | 0.04 | |
| **Robust SD** | 0.0092 | |
| **Robust CV** | 19% | |

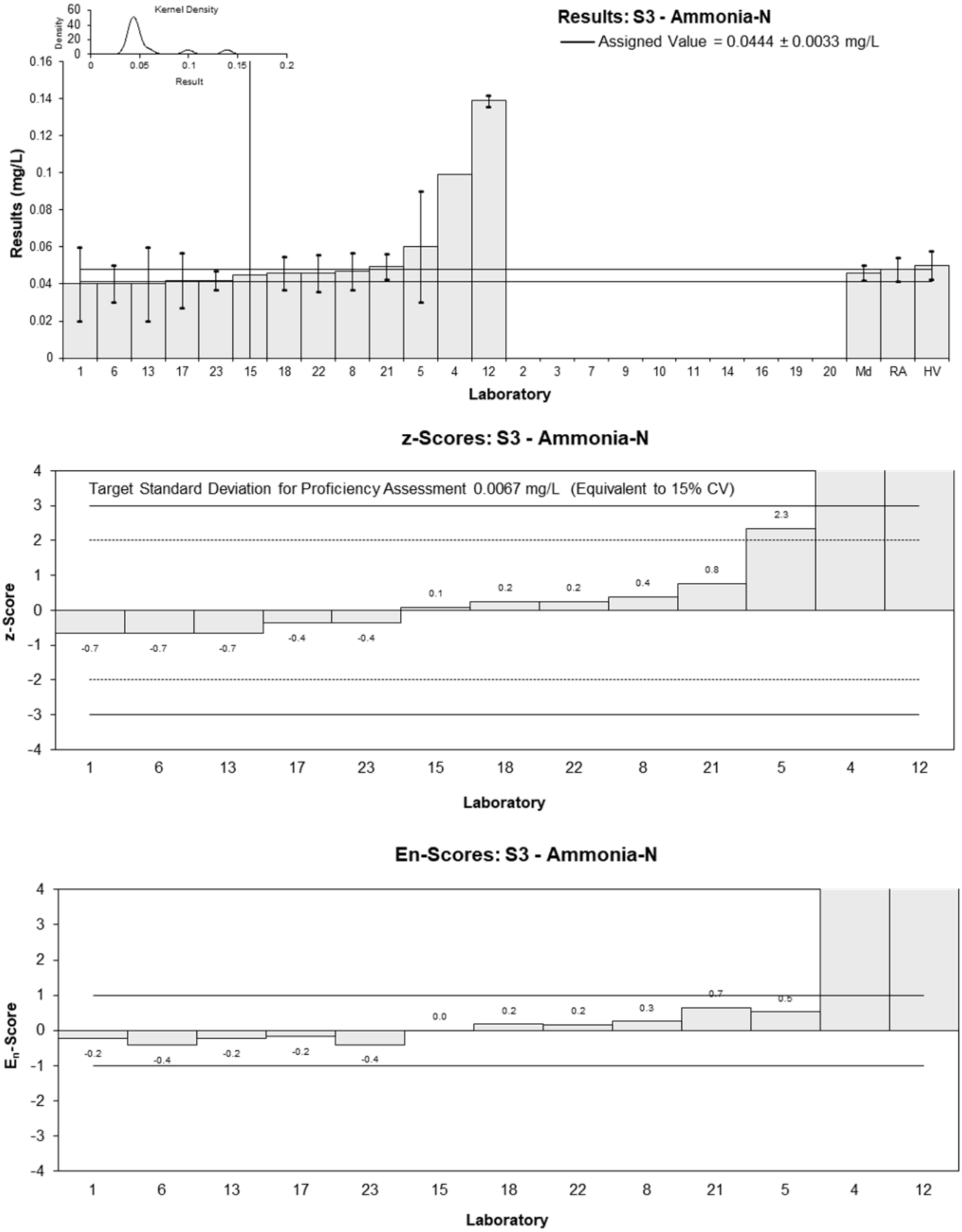

Results: S3 - Ammonia-N
Assigned Value = 0.0444 ± 0.0033 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 6 13 17 23 15 18 22 8 21 5 4 12 2 3 7 9 10 11 14 16 19 20 Md RA HV
z-Scores: S3 - Ammonia-N
Target Standard Deviation for Proficiency Assessment 0.0067 mg/L (Equivalent to 15% CV)
z-Score
-0.7 -0.7 -0.7 -0.4 -0.4 0.1 0.2 0.2 0.4 0.8 2.3
1 6 13 17 23 15 18 22 8 21 5 4 12
Laboratory
En-Scores: S3 - Ammonia-N
En-Score
-0.2 -0.4 -0.2 -0.2 -0.4 0.0 0.2 0.2 0.3 0.7 0.5
1 6 13 17 23 15 18 22 8 21 5 4 12
Laboratory

Figure 26

Table 30

**Sample Details**

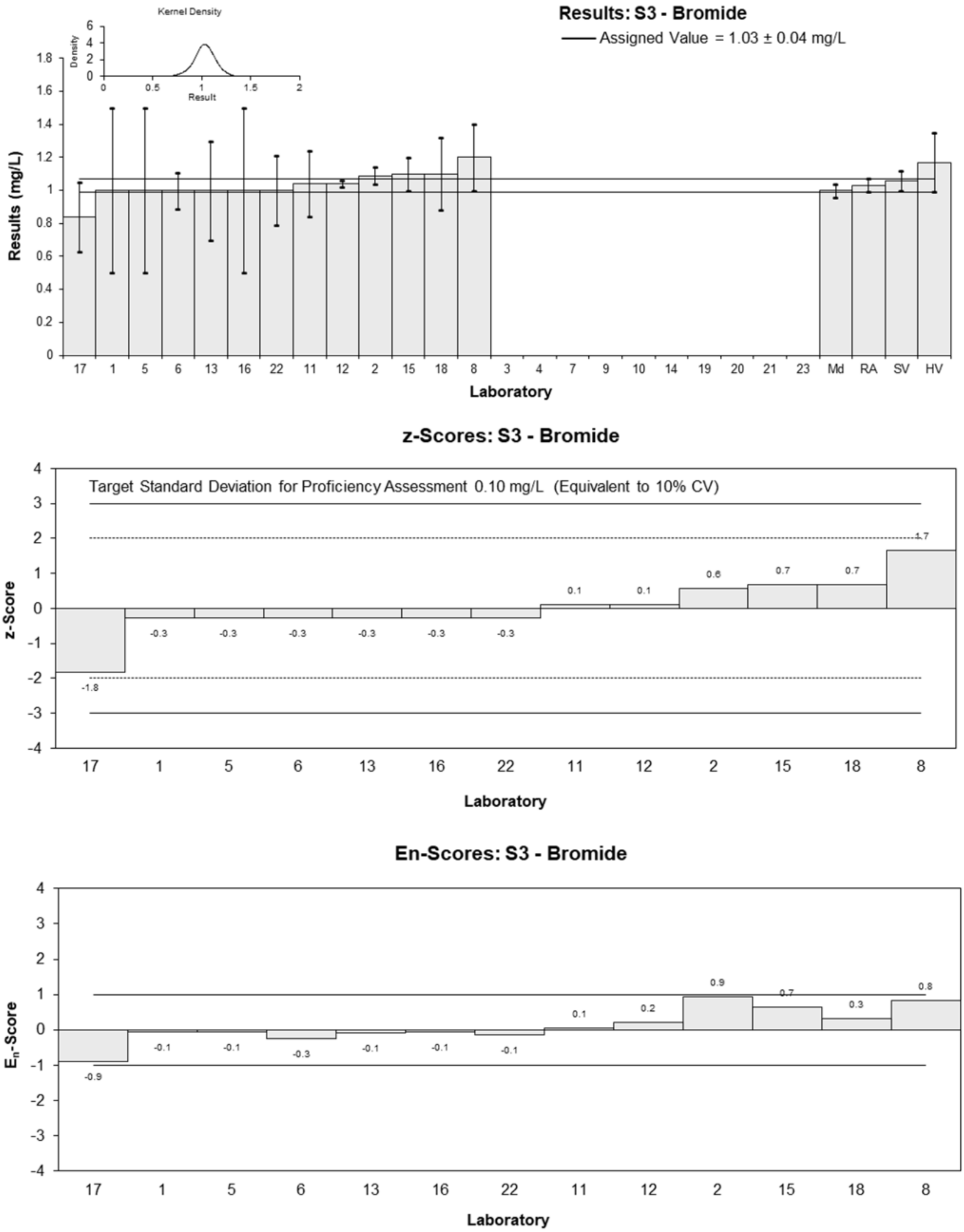
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Bromide |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 1 | 0.5 | -0.29 | -0.06 |
| **2** | 1.09 | 0.05 | 0.58 | 0.94 |
| **3** | NT | NT | | |
| **4** | NR | NR | | |
| **5** | 1.0 | 0.5 | -0.29 | -0.06 |
| **6** | 1.00 | 0.11 | -0.29 | -0.26 |
| **7** | NT | NT | | |
| **8** | 1.20 | 0.2 | 1.65 | 0.83 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 1.04 | 0.2 | 0.10 | 0.05 |
| **12** | 1.04 | 0.021 | 0.10 | 0.22 |
| **13** | 1 | 0.3 | -0.29 | -0.10 |
| **14** | NT | NT | | |
| **15** | 1.1 | 0.1 | 0.68 | 0.65 |
| **16** | 1 | 0.5 | -0.29 | -0.06 |
| **17** | 0.84 | 0.21 | -1.84 | -0.89 |
| **18** | 1.1 | 0.22 | 0.68 | 0.31 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | NT | NT | | |
| **22** | 1.0 | 0.21 | -0.29 | -0.14 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 1.03 | 0.04 |
| **Spike Value** | 1.06 | 0.06 |
| **Homogeneity Value** | 1.17 | 0.18 |
| **Robust Average** | 1.03 | 0.04 |
| **Median** | 1.00 | 0.04 |
| **Mean** | 1.03 | |
| **N** | 13 | |
| **Max** | 1.2 | |
| **Min** | 0.84 | |
| **Robust SD** | 0.062 | |
| **Robust CV** | 6% | |



Kernel Density
Results: S3 - Bromide
Assigned Value = 1.03 ± 0.04 mg/L
Results (mg/L)
Laboratory
z-Scores: S3 - Bromide
Target Standard Deviation for Proficiency Assessment 0.10 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S3 - Bromide
$E_n$-Score
Laboratory


Figure 27

Table 31

**Sample Details**

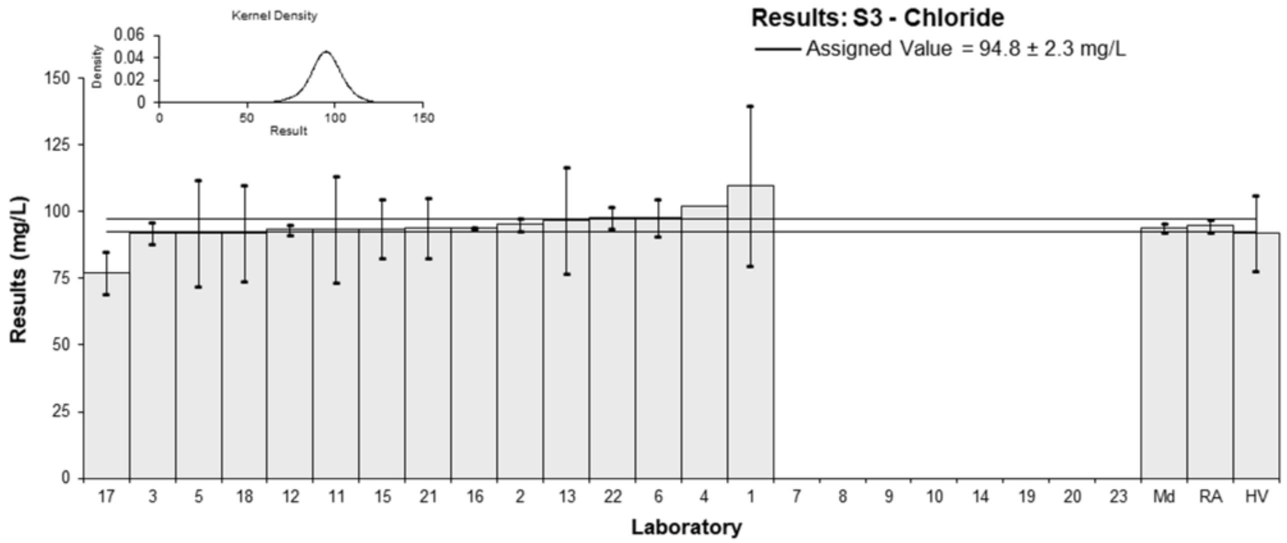
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Chloride |
| **Unit** | mg/L |

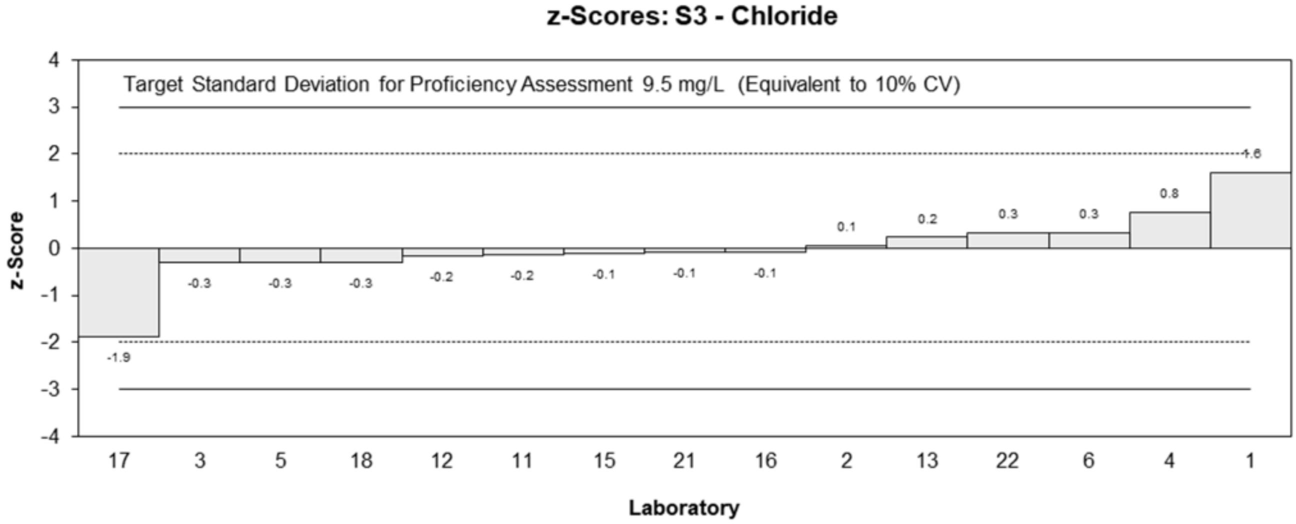
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 110 | 30 | 1.60 | 0.51 |
| **2** | 95.3 | 2.4 | 0.05 | 0.15 |
| **3** | 92 | 4 | -0.30 | -0.61 |
| **4** | 102 | NR | 0.76 | 3.13 |
| **5** | 92 | 20 | -0.30 | -0.14 |
| **6** | 97.9 | 7.0 | 0.33 | 0.42 |
| **7** | NT | NT | | |
| **8** | NR | NR | | |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 93.4 | 20 | -0.15 | -0.07 |
| **12** | 93.3 | 1.87 | -0.16 | -0.51 |
| **13** | 97 | 20 | 0.23 | 0.11 |
| **14** | NT | NT | | |
| **15** | 93.7 | 11 | -0.12 | -0.10 |
| **16** | 94 | 0.3 | -0.08 | -0.34 |
| **17** | 77 | 8 | -1.88 | -2.14 |
| **18** | 92 | 18 | -0.30 | -0.15 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 93.9 | 11.3 | -0.09 | -0.08 |
| **22** | 97.8 | 4.1 | 0.32 | 0.64 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 94.8 | 2.3 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 92 | 14 |
| **Robust Average** | 94.8 | 2.3 |
| **Median** | 93.9 | 1.8 |
| **Mean** | 94.8 | |
| **N** | 15 | |
| **Max** | 110 | |
| **Min** | 77 | |
| **Robust SD** | 3.6 | |
| **Robust CV** | 3.8% | |


Results: S3 - Chloride
Assigned Value = 94.8 ± 2.3 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17 3 5 18 12 11 15 21 16 2 13 22 6 4 1 7 8 9 10 14 19 20 23 Md RA HV


z-Scores: S3 - Chloride
Target Standard Deviation for Proficiency Assessment 9.5 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
17 3 5 18 12 11 15 21 16 2 13 22 6 4 1
-1.9 -0.3 -0.3 -0.3 -0.2 -0.2 -0.1 -0.1 -0.1 0.1 0.2 0.3 0.3 0.8 1.6

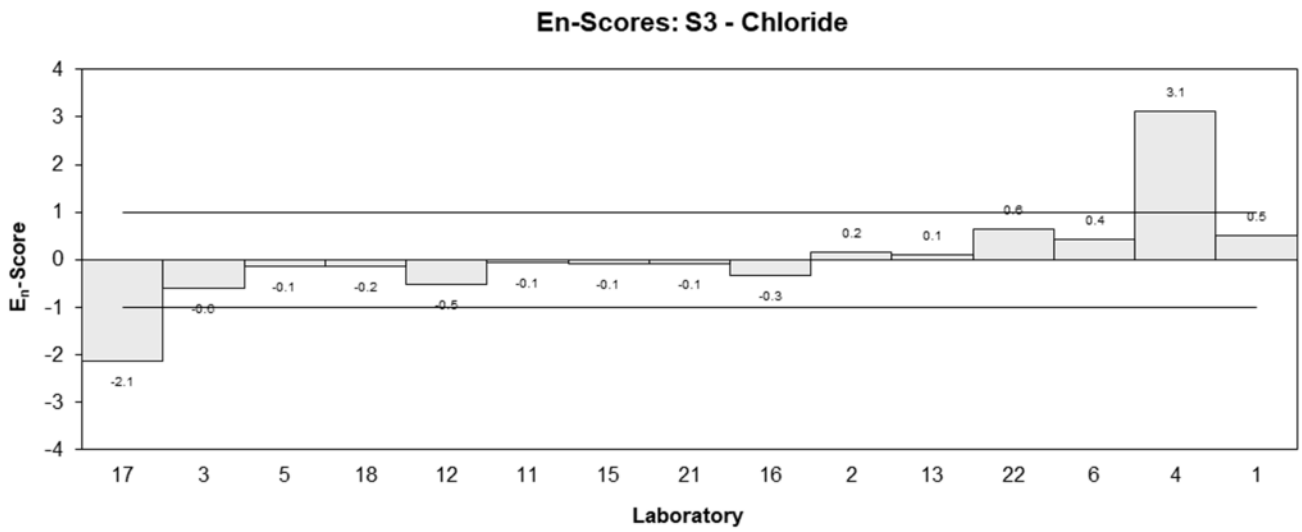

En-Scores: S3 - Chloride
En-Score
Laboratory
17 3 5 18 12 11 15 21 16 2 13 22 6 4 1
-2.1 -0.6 -0.1 -0.2 -0.5 -0.1 -0.1 -0.1 -0.3 0.2 0.1 0.6 0.4 3.1 0.5

Figure 28

Table 32

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | DOC |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 5 | 2 | 0.86 | 0.28 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NR | NR | | |
| **5** | 5 | 2 | 0.86 | 0.28 |
| **6** | NR | NR | | |
| **7** | NT | NT | | |
| **8** | 3.79 | 0.4 | -0.96 | -1.06 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 4.82 | 0.1 | 0.59 | 0.85 |
| **13** | 5 | 2 | 0.86 | 0.28 |
| **14** | NT | NT | | |
| **15** | 3.9 | 0 | -0.80 | -1.18 |
| **16** | NT | NT | | |
| **17** | 4.2 | 0.8 | -0.35 | -0.25 |
| **18** | 4.6 | 0.92 | 0.26 | 0.17 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 4.11 | 0.62 | -0.48 | -0.42 |
| **22** | 3.9 | 1.0 | -0.80 | -0.48 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 4.43 | 0.45 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 3.82 | 0.57 |
| **Robust Average** | 4.43 | 0.45 |
| **Median** | 4.40 | 0.59 |
| **Mean** | 4.43 | |
| **N** | 10 | |
| **Max** | 5 | |
| **Min** | 3.79 | |
| **Robust SD** | 0.57 | |
| **Robust CV** | 13% | |

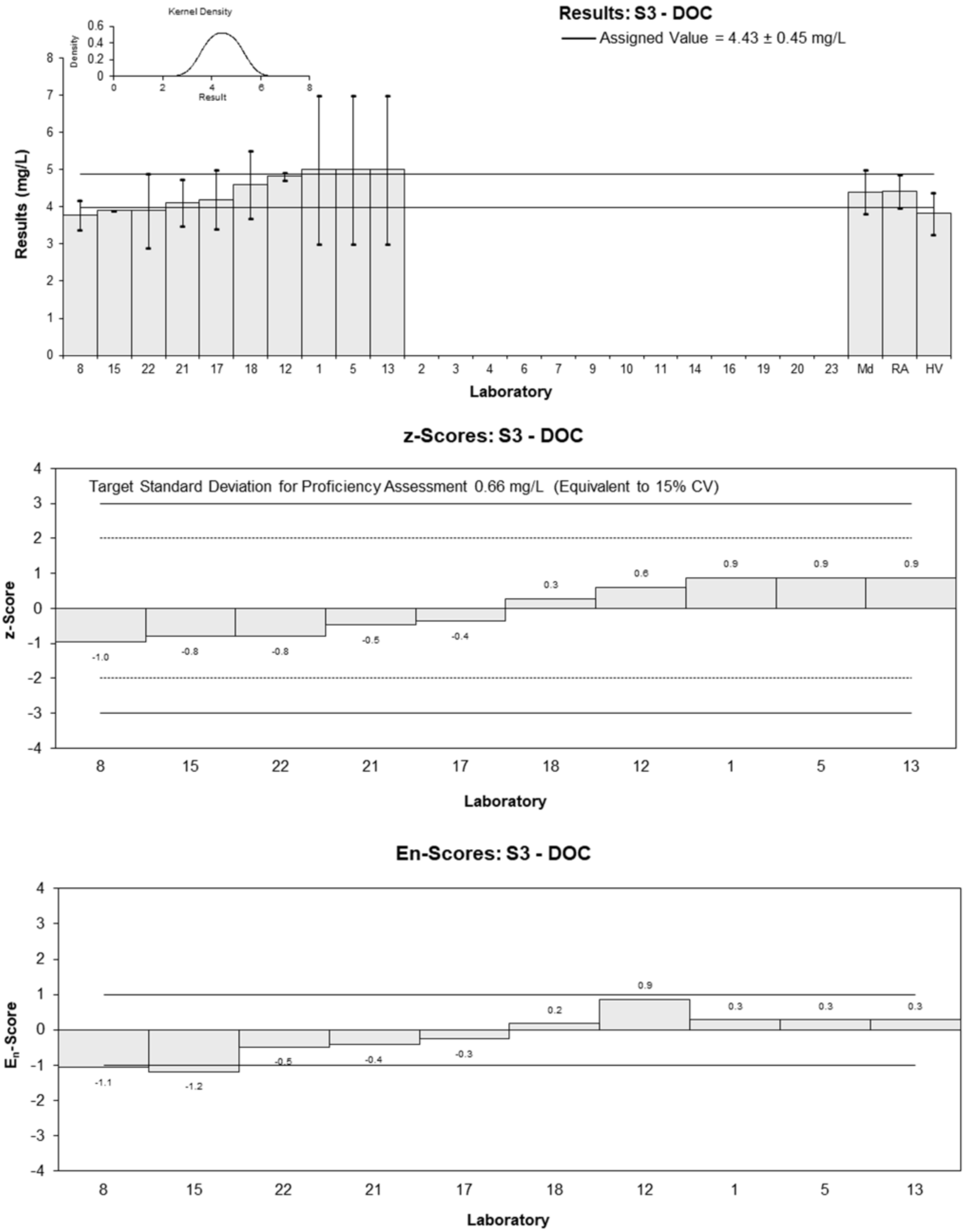

Results: S3 - DOC
Assigned Value = 4.43 ± 0.45 mg/L
Kernel Density
Density
Result
Results (mg/L)
8 15 22 21 17 18 12 1 5 13 2 3 4 6 7 9 10 11 14 16 19 20 23 Md RA HV
Laboratory
z-Scores: S3 - DOC
Target Standard Deviation for Proficiency Assessment 0.66 mg/L (Equivalent to 15% CV)
z-Score
-1.0 -0.8 -0.8 -0.5 -0.4 0.3 0.6 0.9 0.9 0.9
8 15 22 21 17 18 12 1 5 13
Laboratory
En-Scores: S3 - DOC
$E_n$-Score
-1.1 -1.2 -0.5 -0.4 -0.3 0.2 0.9 0.3 0.3 0.3
8 15 22 21 17 18 12 1 5 13
Laboratory

Figure 29

Table 33

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Fluoride |
| **Unit** | mg/L |

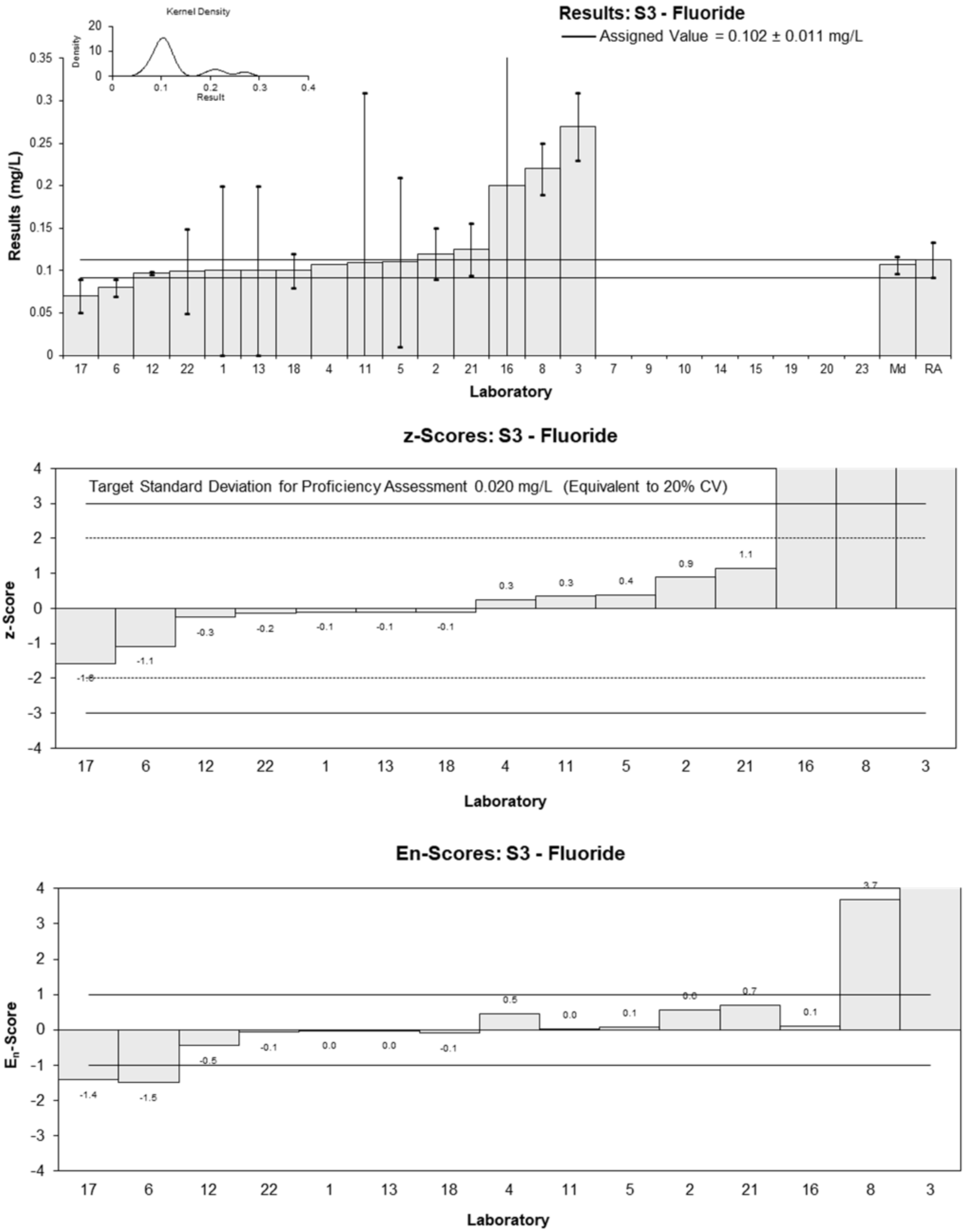
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.1 | 0.1 | -0.10 | -0.02 |
| **2** | 0.12 | 0.03 | 0.88 | 0.56 |
| **3*** | 0.27 | 0.04 | 8.24 | 4.05 |
| **4** | 0.107 | NR | 0.25 | 0.45 |
| **5** | 0.11 | 0.1 | 0.39 | 0.08 |
| **6** | 0.08 | 0.01 | -1.08 | -1.48 |
| **7** | NT | NT | | |
| **8*** | 0.22 | 0.03 | 5.78 | 3.69 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 0.109 | 0.2 | 0.34 | 0.03 |
| **12** | 0.097 | 0.002 | -0.25 | -0.45 |
| **13** | 0.1 | 0.1 | -0.10 | -0.02 |
| **14** | NT | NT | | |
| **15** | <0.15 | NR | | |
| **16*** | 0.2 | 0.9 | 4.80 | 0.11 |
| **17** | 0.07 | 0.02 | -1.57 | -1.40 |
| **18** | 0.1 | 0.02 | -0.10 | -0.09 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.125 | 0.031 | 1.13 | 0.70 |
| **22** | 0.099 | 0.050 | -0.15 | -0.06 |
| **23** | NR | NR | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.102 | 0.011 |
| **Spike Value** | Not Spiked | |
| **Robust Average** | 0.113 | 0.021 |
| **Median** | 0.107 | 0.010 |
| **Mean** | 0.127 | |
| **N** | 15 | |
| **Max** | 0.27 | |
| **Min** | 0.07 | |
| **Robust SD** | 0.032 | |
| **Robust CV** | 28% | |



Results: S3 - Fluoride
Assigned Value = 0.102 ± 0.011 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17 6 12 22 1 13 18 4 11 5 2 21 16 8 3 7 9 10 14 15 19 20 23 Md RA
z-Scores: S3 - Fluoride
Target Standard Deviation for Proficiency Assessment 0.020 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
En-Scores: S3 - Fluoride
$E_n$-Score
Laboratory


Figure 30

Table 34

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Nitrate-N |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.05 | 0.02 | 1.29 | 0.39 |
| **2** | NT | NT | | |
| **3*** | 0.2 | 0.1 | 25.16 | 1.58 |
| **4** | 0.034 | NR | -1.26 | -1.55 |
| **5** | 0.050 | 0.02 | 1.29 | 0.39 |
| **6** | 0.04 | 0.01 | -0.30 | -0.17 |
| **7** | NT | NT | | |
| **8** | 0.049 | 0.01 | 1.13 | 0.63 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 0.0407 | 0.01 | -0.19 | -0.11 |
| **12** | 0.04 | 0.001 | -0.30 | -0.37 |
| **13** | 0.04 | 0.02 | -0.30 | -0.09 |
| **14** | NT | NT | | |
| **15*** | 0.082 | 0.008 | 6.38 | 4.23 |
| **16** | 0.03 | 0.14 | -1.89 | -0.08 |
| **17** | 0.033 | 0.007 | -1.42 | -1.03 |
| **18** | 0.038 | 0.008 | -0.62 | -0.41 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.0433 | 0.0087 | 0.22 | 0.14 |
| **22** | 0.048 | 0.010 | 0.97 | 0.54 |
| **23** | 0.050 | 0.007 | 1.29 | 0.94 |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0419 | 0.0051 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 0.0397 | 0.0060 |
| **Robust Average** | 0.0439 | 0.0060 |
| **Median** | 0.0420 | 0.0070 |
| **Mean** | 0.054 | |
| **N** | 16 | |
| **Max** | 0.2 | |
| **Min** | 0.03 | |
| **Robust SD** | 0.0096 | |
| **Robust CV** | 22% | |

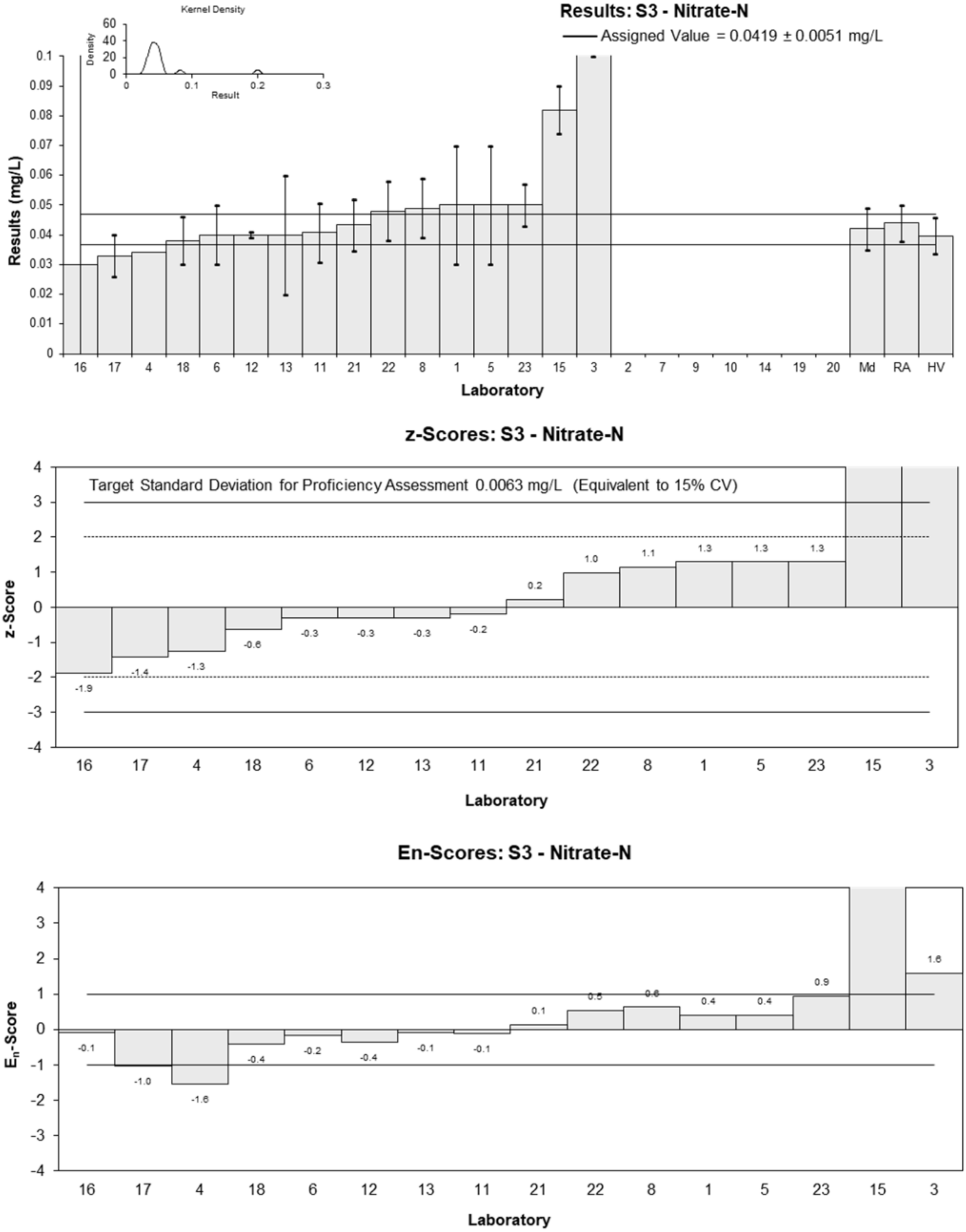

Results: S3 - Nitrate-N
Assigned Value = 0.0419 ± 0.0051 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
16 17 4 18 6 12 13 11 21 22 8 1 5 23 15 3 2 7 9 10 14 19 20 Md RA HV
z-Scores: S3 - Nitrate-N
Target Standard Deviation for Proficiency Assessment 0.0063 mg/L (Equivalent to 15% CV)
z-Score
-1.9 -1.4 -1.3 -0.6 -0.3 -0.3 -0.3 -0.2 0.2 1.0 1.1 1.3 1.3 1.3
Laboratory
16 17 4 18 6 12 13 11 21 22 8 1 5 23 15 3
En-Scores: S3 - Nitrate-N
$E_n$-Score
-0.1 -1.0 -1.6 -0.4 -0.2 -0.4 -0.1 -0.1 0.1 0.5 0.6 0.4 0.4 0.9 1.6
Laboratory
16 17 4 18 6 12 13 11 21 22 8 1 5 23 15 3

Figure 31

Table 35

**Sample Details**

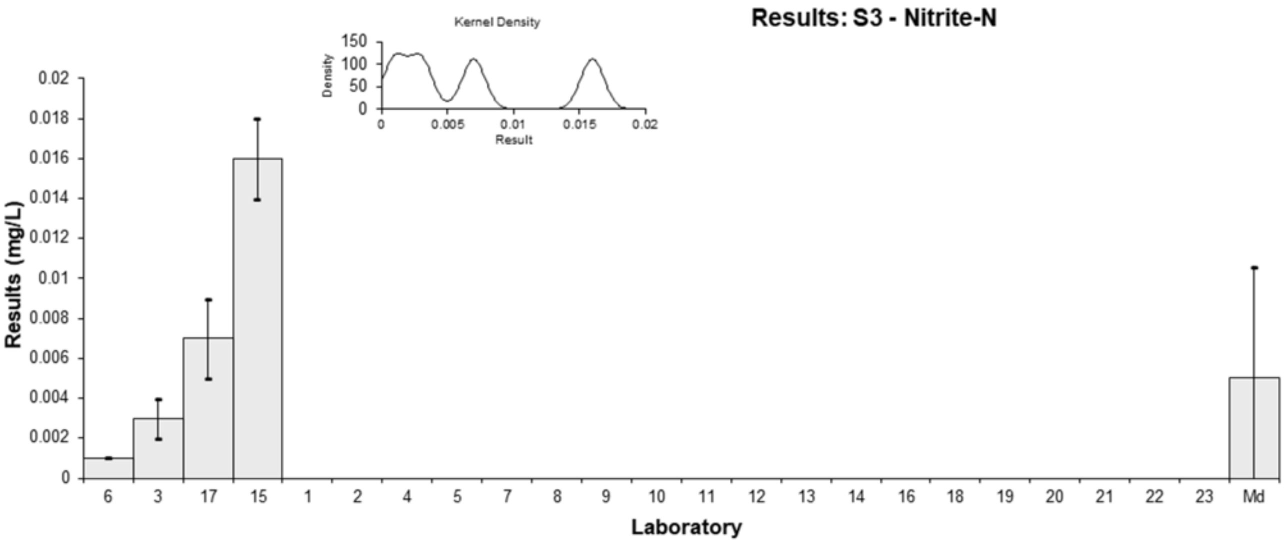
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Nitrite-N |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty |
|---|---|---|
| **1** | <0.005 | NR |
| **2** | NT | NT |
| **3** | 0.003 | 0.001 |
| **4** | < 0.01 | NR |
| **5** | <0.005 | NT |
| **6** | 0.001 | 0.000 |
| **7** | NT | NT |
| **8** | <0.005 | NR |
| **9** | NT | NT |
| **10** | NT | NT |
| **11** | <0.01 | 0.01 |
| **12** | NR | NR |
| **13** | <0.005 | NR |
| **14** | NT | NT |
| **15** | 0.016 | 0.002 |
| **16** | NT | NT |
| **17** | 0.007 | 0.002 |
| **18** | <0.005 | 0.001 |
| **19** | NT | NT |
| **20** | NT | NT |
| **21** | <0.002 | NR |
| **22** | <0.010 | 0.010 |
| **23** | <0.002 | 0.007 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | Not Set | |
| **Spike Value** | Not Spiked | |
| **Robust Average** | NA (N<6) | |
| **Median** | 0.0050 | 0.0056 |
| **Mean** | 0.00675 | |
| **N** | 4 | |
| **Max** | 0.016 | |
| **Min** | 0.001 | |
| **Robust SD** | NA (N<6) | |
| **Robust CV** | NA (N<6) | |



Results: S3 - Nitrite-N
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6
3
17
15
1
2
4
5
7
8
9
10
11
12
13
14
16
18
19
20
21
22
23
Md


Figure 32

Table 36

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Orthophosphate-P |
| **Unit** | mg/L |

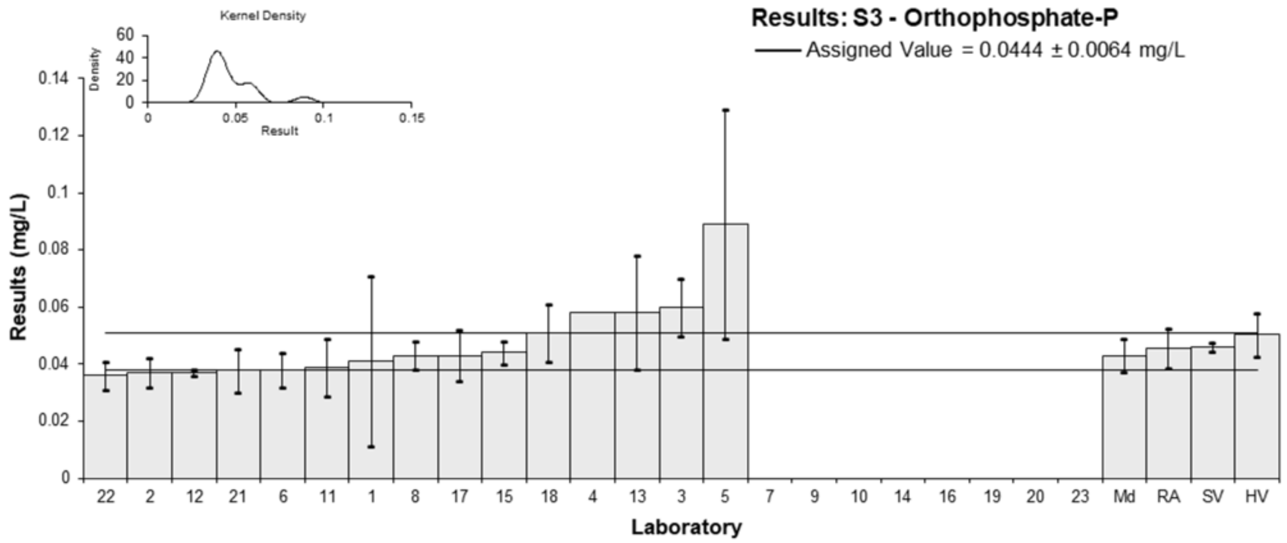
**Participant Results**

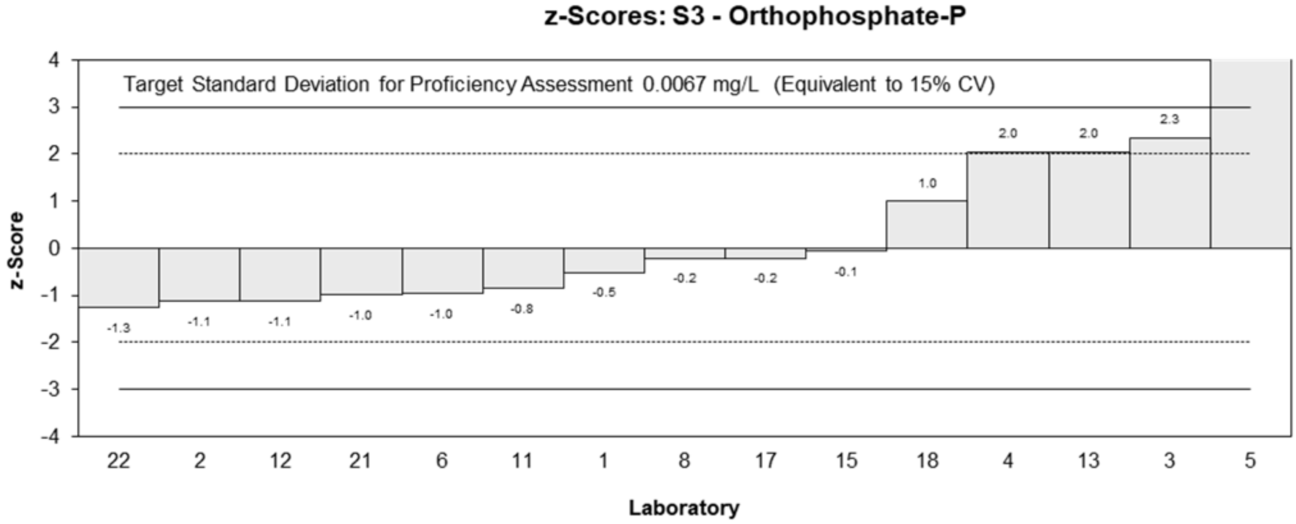
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.041 | 0.03 | -0.51 | -0.11 |
| **2** | 0.037 | 0.005 | -1.11 | -0.91 |
| **3** | 0.06 | 0.01 | 2.34 | 1.31 |
| **4** | 0.058 | NR | 2.04 | 2.12 |
| **5*** | 0.089 | 0.04 | 6.70 | 1.10 |
| **6** | 0.038 | 0.006 | -0.96 | -0.73 |
| **7** | NT | NT | | |
| **8** | 0.043 | 0.005 | -0.21 | -0.17 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 0.0388 | 0.01 | -0.84 | -0.47 |
| **12** | 0.037 | 0.001 | -1.11 | -1.14 |
| **13** | 0.058 | 0.02 | 2.04 | 0.65 |
| **14** | NT | NT | | |
| **15** | 0.044 | 0.004 | -0.06 | -0.05 |
| **16** | NT | NT | | |
| **17** | 0.043 | 0.009 | -0.21 | -0.13 |
| **18** | 0.051 | 0.01 | 0.99 | 0.56 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.0378 | 0.0076 | -0.99 | -0.66 |
| **22** | 0.036 | 0.005 | -1.26 | -1.03 |
| **23** | NR | 0.005 | | |

* Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0444 | 0.0064 |
| **Spike Value** | 0.0460 | 0.0016 |
| **Homogeneity Value** | 0.0503 | 0.0076 |
| **Robust Average** | 0.0456 | 0.0069 |
| **Median** | 0.0430 | 0.0057 |
| **Mean** | 0.0474 | |
| **N** | 15 | |
| **Max** | 0.089 | |
| **Min** | 0.036 | |
| **Robust SD** | 0.011 | |
| **Robust CV** | 23% | |


Results: S3 - Orthophosphate-P
Assigned Value = 0.0444 ± 0.0064 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
22 2 12 21 6 11 1 8 17 15 18 4 13 3 5 7 9 10 14 16 19 20 23 Md RA SV HV


z-Scores: S3 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 0.0067 mg/L (Equivalent to 15% CV)
z-Score
-1.3 -1.1 -1.1 -1.0 -1.0 -0.8 -0.5 -0.2 -0.2 -0.1 1.0 2.0 2.0 2.3
Laboratory
22 2 12 21 6 11 1 8 17 15 18 4 13 3 5

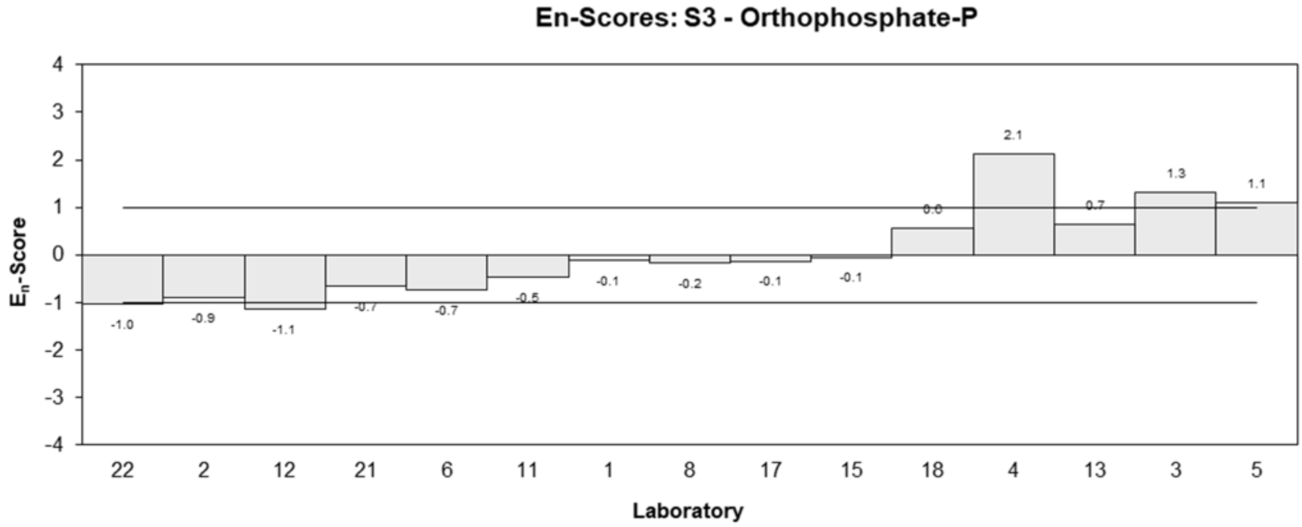

En-Scores: S3 - Orthophosphate-P
En-Score
-1.0 -0.9 -1.1 -0.7 -0.7 -0.5 -0.1 -0.2 -0.1 -0.1 0.6 2.1 0.7 1.3 1.1
Laboratory
22 2 12 21 6 11 1 8 17 15 18 4 13 3 5

Figure 33

Table 37

**Sample Details**

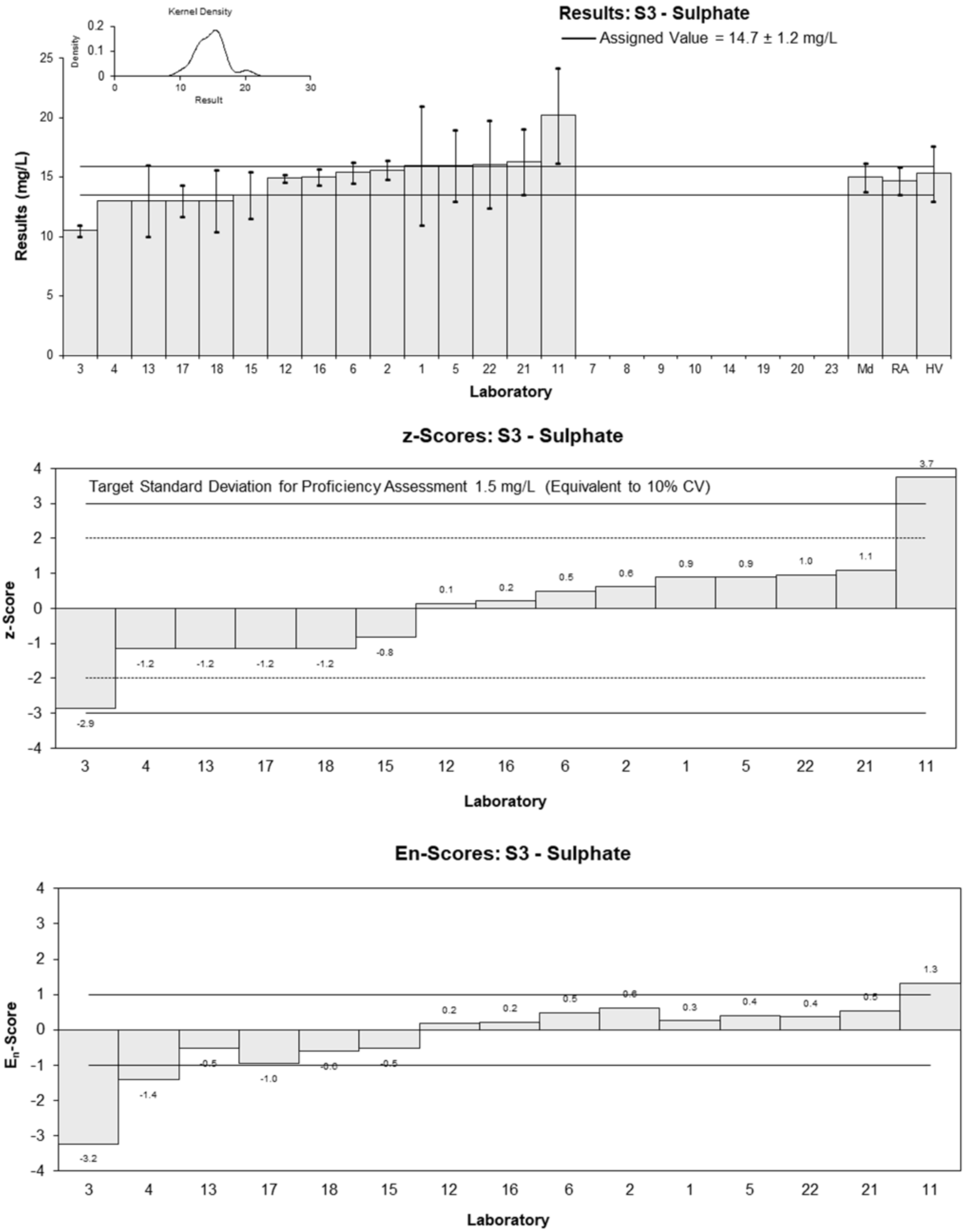
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | Sulphate |
| **Unit** | mg/L |

**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 16 | 5 | 0.88 | 0.25 |
| **2** | 15.6 | 0.80 | 0.61 | 0.62 |
| **3** | 10.5 | 0.5 | -2.86 | -3.23 |
| **4** | 13.0 | NR | -1.16 | -1.42 |
| **5** | 16 | 3 | 0.88 | 0.40 |
| **6** | 15.4 | 0.9 | 0.48 | 0.47 |
| **7** | NT | NT | | |
| **8** | NR | NR | | |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | 20.2 | 4 | 3.74 | 1.32 |
| **12** | 14.91 | 0.3 | 0.14 | 0.17 |
| **13** | 13 | 3 | -1.16 | -0.53 |
| **14** | NT | NT | | |
| **15** | 13.5 | 2 | -0.82 | -0.51 |
| **16** | 15 | 0.7 | 0.20 | 0.22 |
| **17** | 13 | 1.3 | -1.16 | -0.96 |
| **18** | 13 | 2.6 | -1.16 | -0.59 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 16.3 | 2.8 | 1.09 | 0.53 |
| **22** | 16.1 | 3.7 | 0.95 | 0.36 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 14.7 | 1.2 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 15.3 | 2.3 |
| **Robust Average** | 14.7 | 1.2 |
| **Median** | 15.0 | 1.2 |
| **Mean** | 14.8 | |
| **N** | 15 | |
| **Max** | 20.2 | |
| **Min** | 10.5 | |
| **Robust SD** | 1.9 | |
| **Robust CV** | 13% | |



Results: S3 - Sulphate
Assigned Value = 14.7 ± 1.2 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
3 4 13 17 18 15 12 16 6 2 1 5 22 21 11 7 8 9 10 14 19 20 23 Md RA HV
z-Scores: S3 - Sulphate
Target Standard Deviation for Proficiency Assessment 1.5 mg/L (Equivalent to 10% CV)
z-Score
-2.9 -1.2 -1.2 -1.2 -1.2 -0.8 0.1 0.2 0.5 0.6 0.9 0.9 1.0 1.1 3.7
3 4 13 17 18 15 12 16 6 2 1 5 22 21 11
Laboratory
En-Scores: S3 - Sulphate
En-Score
-3.2 -1.4 -0.5 -1.0 -0.6 -0.5 0.2 0.2 0.5 0.6 0.3 0.4 0.4 0.5 1.3
3 4 13 17 18 15 12 16 6 2 1 5 22 21 11
Laboratory


Figure 34

Table 38

**Sample Details**

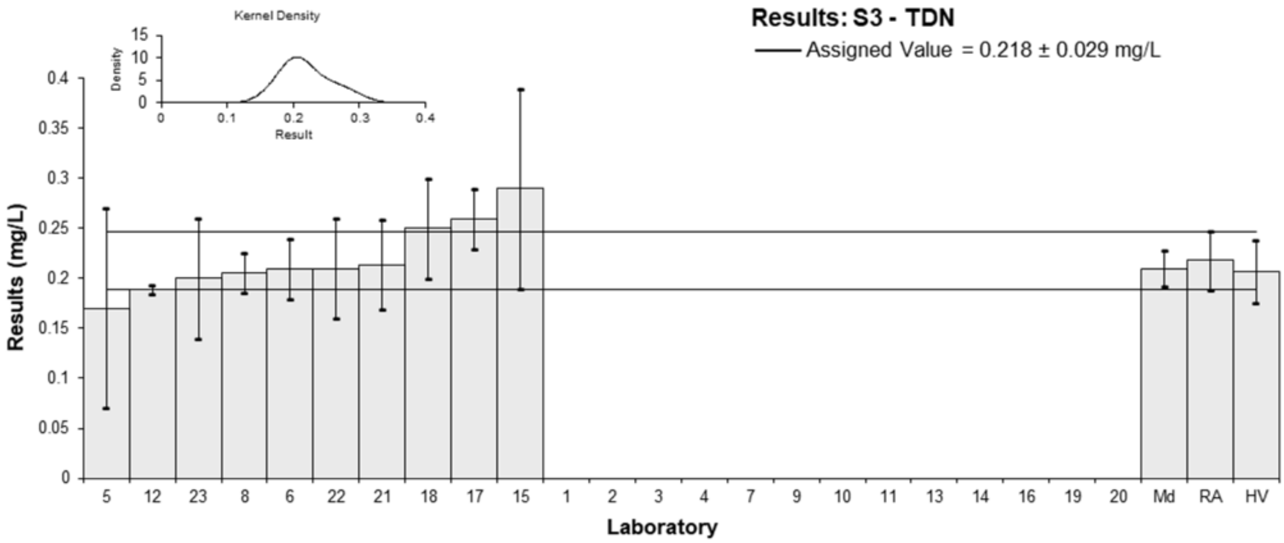
| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | TDN |
| **Unit** | mg/L |

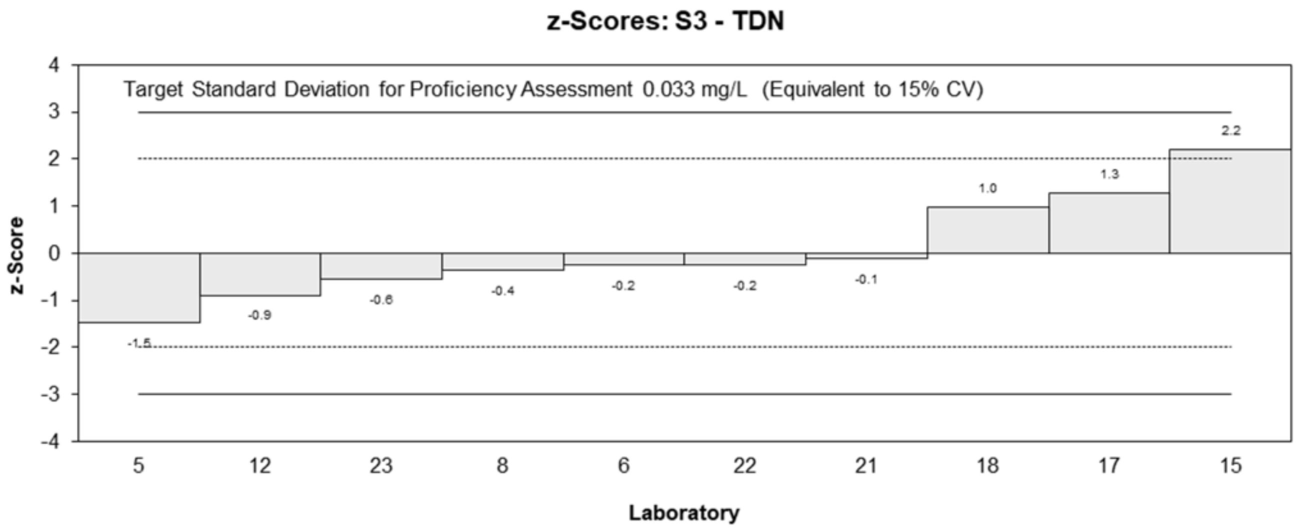
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | <0.1 | NR | | |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NR | NR | | |
| **5** | 0.17 | 0.1 | -1.47 | -0.46 |
| **6** | 0.21 | 0.03 | -0.24 | -0.19 |
| **7** | NT | NT | | |
| **8** | 0.206 | 0.02 | -0.37 | -0.34 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 0.189 | 0.004 | -0.89 | -0.99 |
| **13** | <0.1 | NR | | |
| **14** | NT | NT | | |
| **15** | 0.29 | 0.1 | 2.20 | 0.69 |
| **16** | NT | NT | | |
| **17** | 0.26 | 0.03 | 1.28 | 1.01 |
| **18** | 0.25 | 0.05 | 0.98 | 0.55 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.214 | 0.045 | -0.12 | -0.07 |
| **22** | 0.21 | 0.05 | -0.24 | -0.14 |
| **23** | 0.2 | 0.06 | -0.55 | -0.27 |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.218 | 0.029 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 0.207 | 0.031 |
| **Robust Average** | 0.218 | 0.029 |
| **Median** | 0.210 | 0.018 |
| **Mean** | 0.220 | |
| **N** | 10 | |
| **Max** | 0.29 | |
| **Min** | 0.17 | |
| **Robust SD** | 0.037 | |
| **Robust CV** | 17% | |


Results: S3 - TDN
Assigned Value = 0.218 ± 0.029 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5
12
23
8
6
22
21
18
17
15
1
2
3
4
7
9
10
11
13
14
16
19
20
Md
RA
HV


z-Scores: S3 - TDN
Target Standard Deviation for Proficiency Assessment 0.033 mg/L (Equivalent to 15% CV)
z-Score
-1.5
-0.9
-0.6
-0.4
-0.2
-0.2
-0.1
1.0
1.3
2.2
5
12
23
8
6
22
21
18
17
15
Laboratory

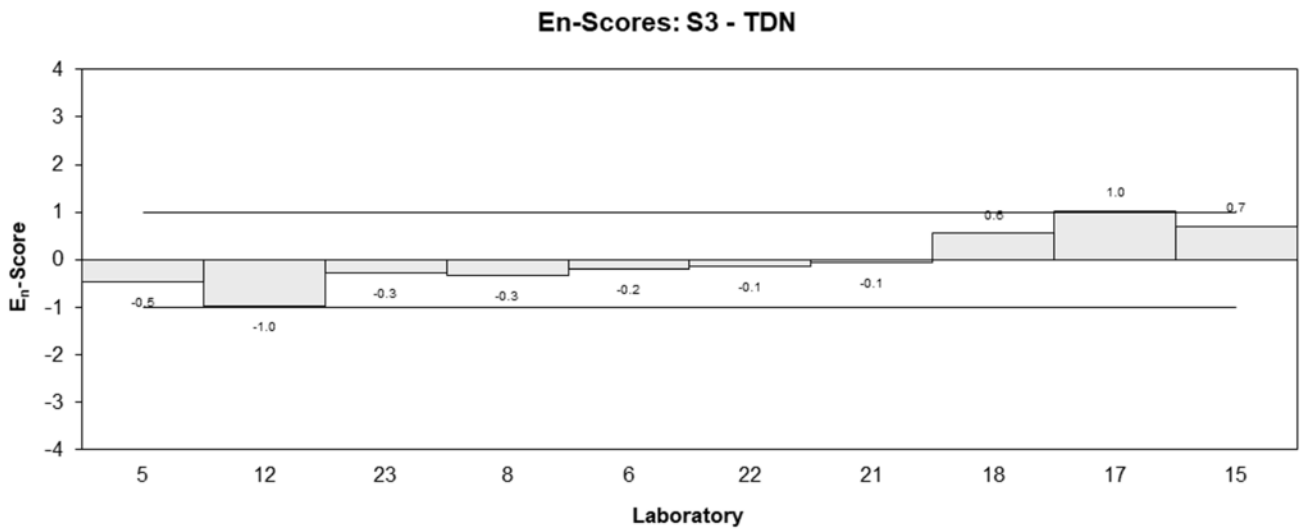

En-Scores: S3 - TDN
$E_n$-Score
-0.5
-1.0
-0.3
-0.3
-0.2
-0.1
-0.1
0.6
1.0
0.7
5
12
23
8
6
22
21
18
17
15
Laboratory

Figure 35

Table 39

**Sample Details**

| | |
|---|---|
| **Sample No.** | S3 |
| **Matrix** | River Water |
| **Analyte** | TDP |
| **Unit** | mg/L |

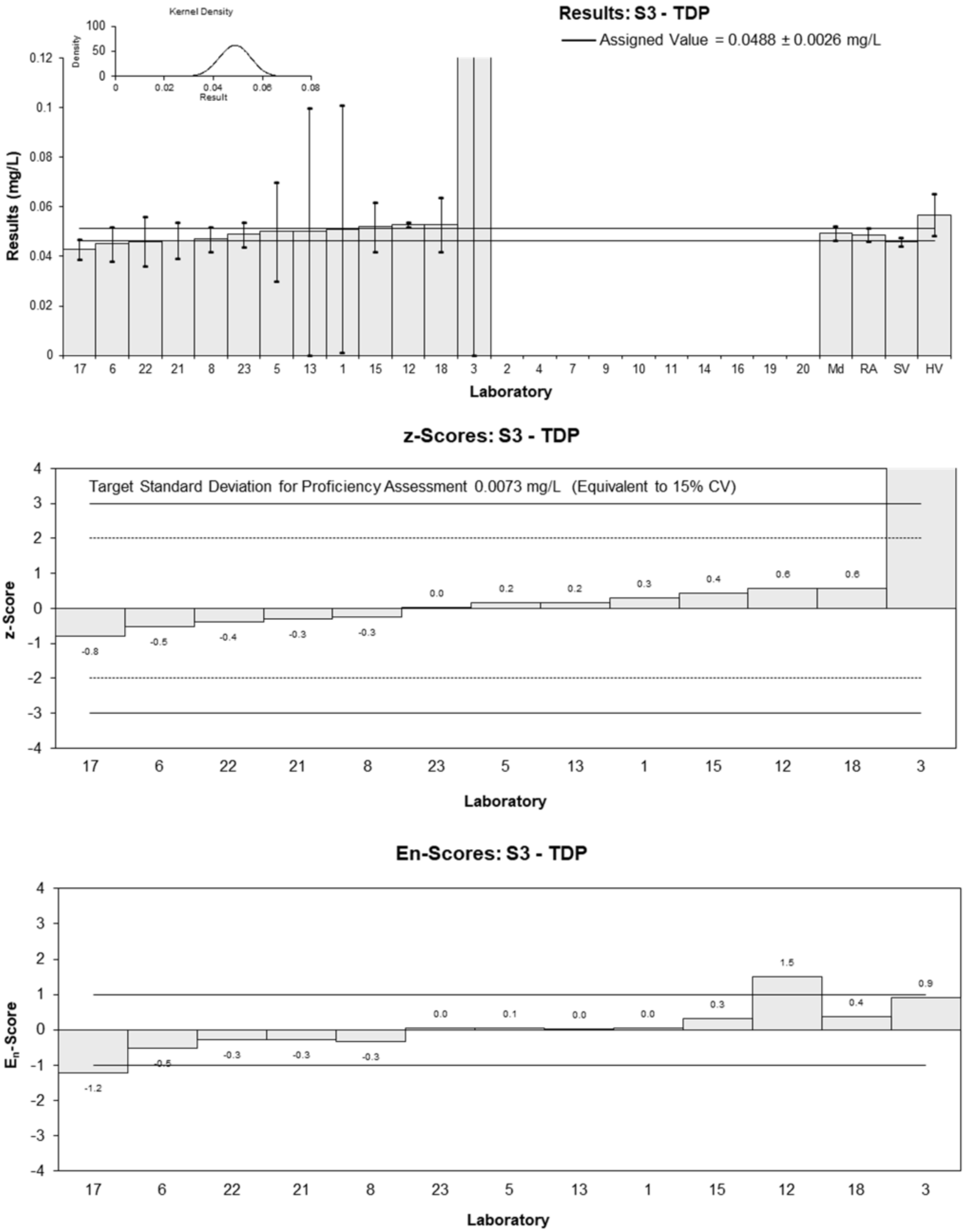
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.051 | 0.05 | 0.30 | 0.04 |
| **2** | NT | NT | | |
| **3**** | 0.60 | 0.6 | 75.30 | 0.92 |
| **4** | NR | NR | | |
| **5** | 0.05 | 0.02 | 0.16 | 0.06 |
| **6** | 0.045 | 0.007 | -0.52 | -0.51 |
| **7** | NT | NT | | |
| **8** | 0.047 | 0.005 | -0.25 | -0.32 |
| **9** | NT | NT | | |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 0.053 | 0.001 | 0.57 | 1.51 |
| **13** | 0.05 | 0.05 | 0.16 | 0.02 |
| **14** | NT | NT | | |
| **15** | 0.052 | 0.01 | 0.44 | 0.31 |
| **16** | NT | NT | | |
| **17** | 0.043 | 0.004 | -0.79 | -1.22 |
| **18** | 0.053 | 0.011 | 0.57 | 0.37 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.0465 | 0.0074 | -0.31 | -0.29 |
| **22** | 0.046 | 0.010 | -0.38 | -0.27 |
| **23** | 0.049 | 0.005 | 0.03 | 0.04 |

** Extreme Outlier, see Section 4.2

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.0488 | 0.0026 |
| **Spike Value** | 0.0460 | 0.0016 |
| **Homogeneity Value** | 0.0568 | 0.0085 |
| **Robust Average** | 0.0488 | 0.0026 |
| **Median** | 0.0495 | 0.0029 |
| **Mean** | 0.0488 | |
| **N** | 12 | |
| **Max** | 0.053 | |
| **Min** | 0.043 | |
| **Robust SD** | 0.0036 | |
| **Robust CV** | 7.5% | |



Kernel Density
Density
Result
Results: S3 - TDP
Assigned Value = 0.0488 ± 0.0026 mg/L
Results (mg/L)
Laboratory
z-Scores: S3 - TDP
Target Standard Deviation for Proficiency Assessment 0.0073 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S3 - TDP
$E_n$-Score
Laboratory


Figure 36

Table 40

**Sample Details**

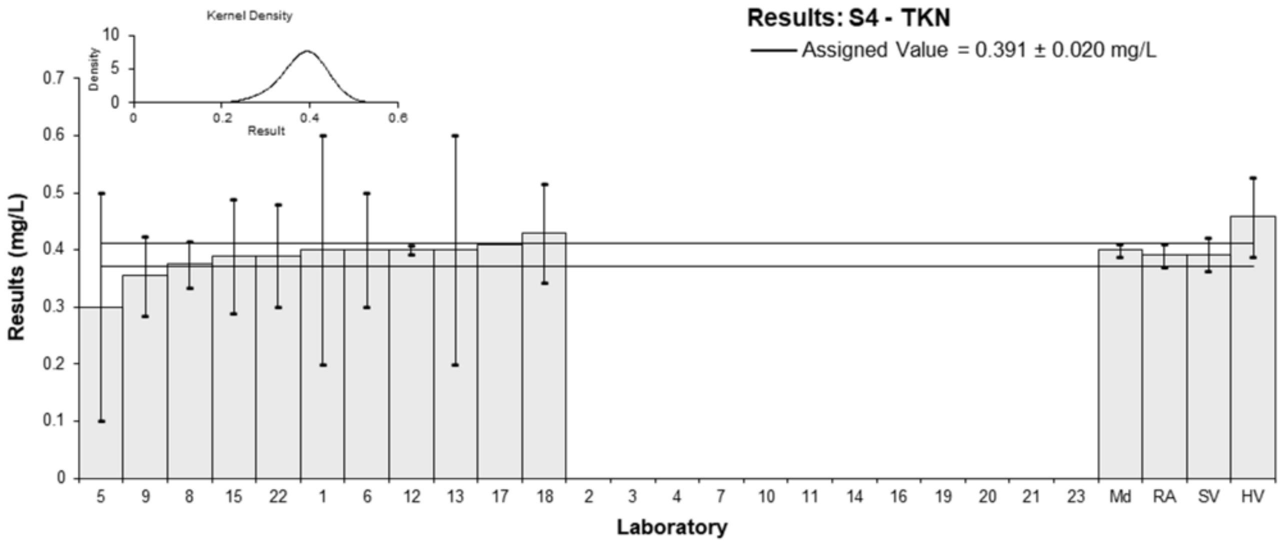
| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | River Water |
| **Analyte** | TKN |
| **Unit** | mg/L |

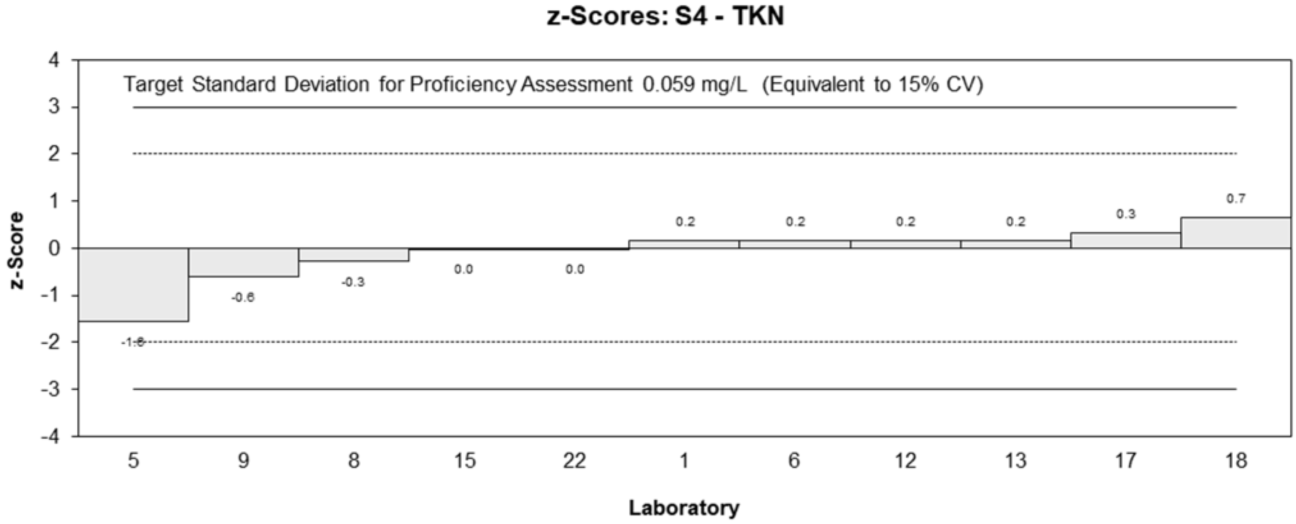
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.4 | 0.2 | 0.15 | 0.04 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.3 | 0.2 | -1.55 | -0.45 |
| **6** | 0.40 | 0.10 | 0.15 | 0.09 |
| **7** | NT | NT | | |
| **8** | 0.375 | 0.04 | -0.27 | -0.36 |
| **9** | 0.355 | 0.070 | -0.61 | -0.49 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 0.4 | 0.008 | 0.15 | 0.42 |
| **13** | 0.4 | 0.2 | 0.15 | 0.04 |
| **14** | NT | NT | | |
| **15** | 0.39 | 0.1 | -0.02 | -0.01 |
| **16** | NT | NT | | |
| **17** | 0.41 | NR | 0.32 | 0.95 |
| **18** | 0.43 | 0.086 | 0.66 | 0.44 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | NT | NT | | |
| **22** | 0.39 | 0.09 | -0.02 | -0.01 |
| **23** | NR | NR | | |

**Statistics**

| | | |
|---|---|---|
| **Assigned Value** | 0.391 | 0.020 |
| **Spike Value** | 0.392 | 0.029 |
| **Homogeneity Value** | 0.458 | 0.069 |
| **Robust Average** | 0.391 | 0.020 |
| **Median** | 0.400 | 0.011 |
| **Mean** | 0.386 | |
| **N** | 11 | |
| **Max** | 0.43 | |
| **Min** | 0.3 | |
| **Robust SD** | 0.026 | |
| **Robust CV** | 6.7% | |


Results: S4 - TKN
Assigned Value = 0.391 ± 0.020 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5 9 8 15 22 1 6 12 13 17 18 2 3 4 7 10 11 14 16 19 20 21 23 Md RA SV HV


z-Scores: S4 - TKN
Target Standard Deviation for Proficiency Assessment 0.059 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.6 -0.6 -0.3 0.0 0.0 0.2 0.2 0.2 0.2 0.3 0.7
5 9 8 15 22 1 6 12 13 17 18

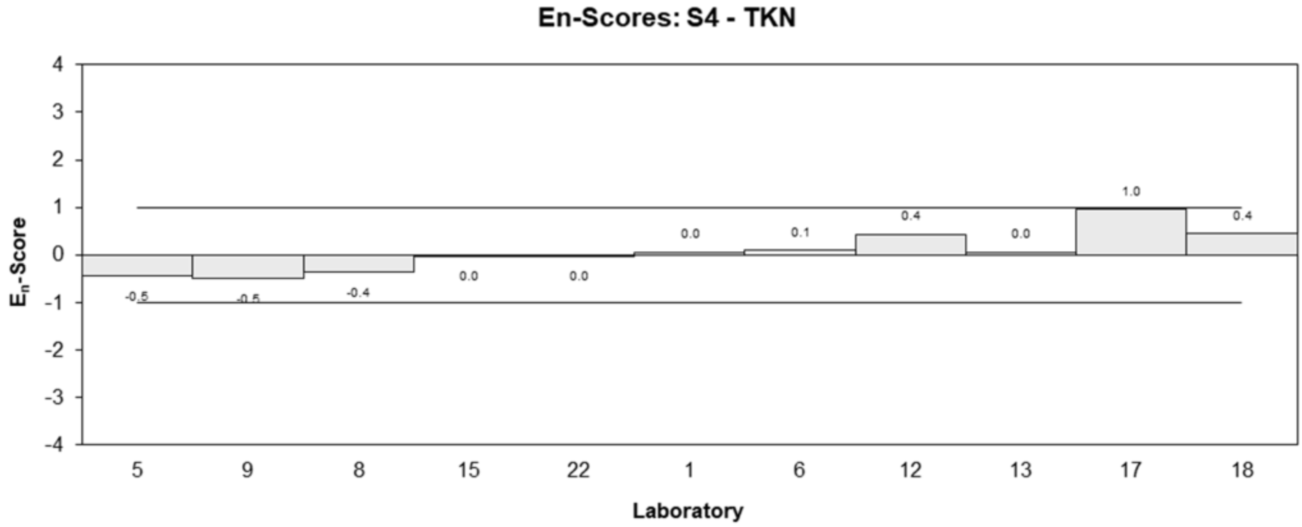

En-Scores: S4 - TKN
$E_n$-Score
Laboratory
-0.5 -0.5 -0.4 0.0 0.0 0.0 0.1 0.4 0.0 1.0 0.4
5 9 8 15 22 1 6 12 13 17 18

Figure 37

Table 41

**Sample Details**

| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | River Water |
| **Analyte** | TN |
| **Unit** | mg/L |

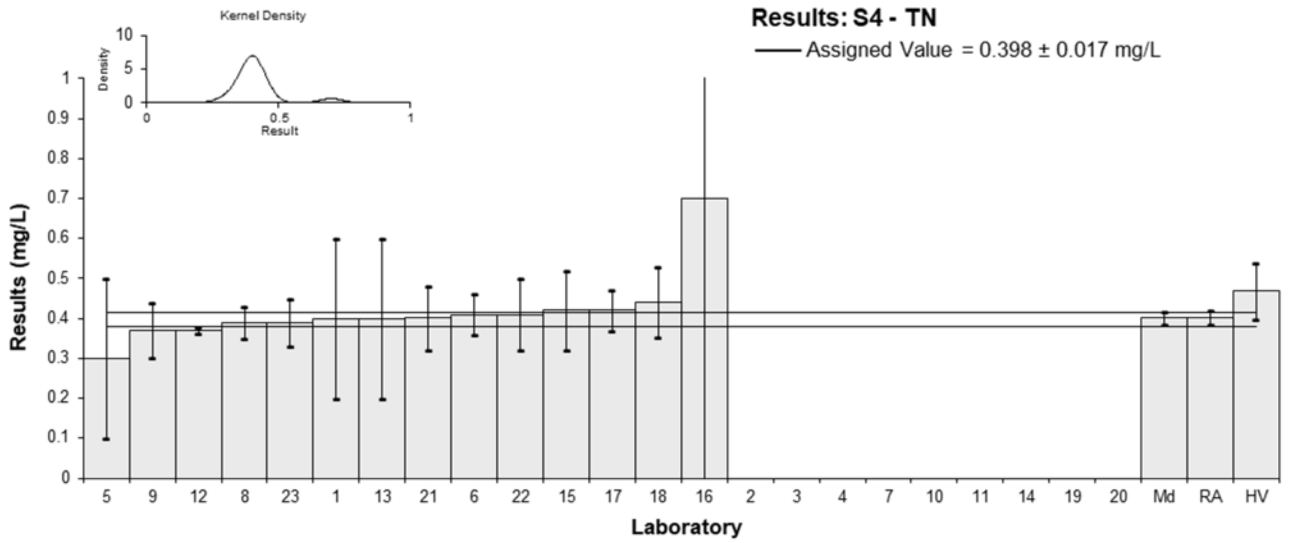
**Participant Results**

| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 0.4 | 0.2 | 0.03 | 0.01 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 0.3 | 0.2 | -1.64 | -0.49 |
| **6** | 0.41 | 0.05 | 0.20 | 0.23 |
| **7** | NT | NT | | |
| **8** | 0.390 | 0.04 | -0.13 | -0.18 |
| **9** | 0.370 | 0.070 | -0.47 | -0.39 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 0.37 | 0.008 | -0.47 | -1.49 |
| **13** | 0.4 | 0.2 | 0.03 | 0.01 |
| **14** | NT | NT | | |
| **15** | 0.42 | 0.1 | 0.37 | 0.22 |
| **16*** | 0.7 | 1.2 | 5.06 | 0.25 |
| **17** | 0.42 | 0.05 | 0.37 | 0.42 |
| **18** | 0.44 | 0.088 | 0.70 | 0.47 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 0.401 | 0.080 | 0.05 | 0.04 |
| **22** | 0.41 | 0.09 | 0.20 | 0.13 |
| **23** | 0.39 | 0.06 | -0.13 | -0.13 |

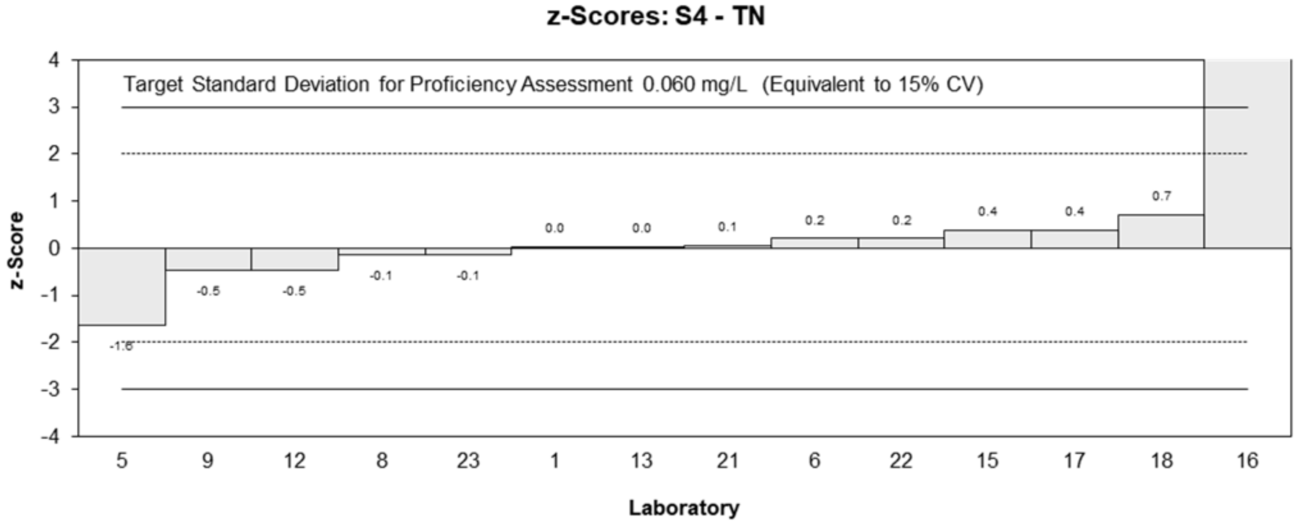
* Outlier, see Section 4.2

**Statistics**

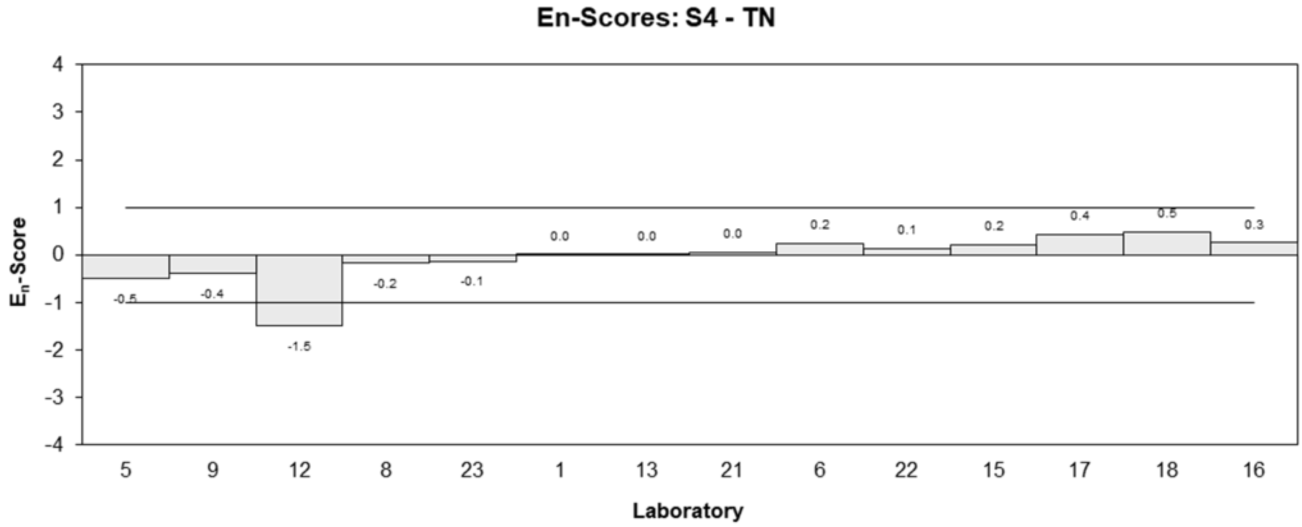
| | | |
|---|---|---|
| **Assigned Value** | 0.398 | 0.017 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 0.468 | 0.070 |
| **Robust Average** | 0.402 | 0.019 |
| **Median** | 0.401 | 0.015 |
| **Mean** | 0.416 | |
| **N** | 14 | |
| **Max** | 0.7 | |
| **Min** | 0.3 | |
| **Robust SD** | 0.028 | |
| **Robust CV** | 7.1% | |



Results: S4 - TN
Assigned Value = 0.398 ± 0.017 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5 9 12 8 23 1 13 21 6 22 15 17 18 16 2 3 4 7 10 11 14 19 20 Md RA HV

z-Scores: S4 - TN
Target Standard Deviation for Proficiency Assessment 0.060 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
5 9 12 8 23 1 13 21 6 22 15 17 18 16
-1.6 -0.5 -0.5 -0.1 -0.1 0.0 0.0 0.1 0.2 0.2 0.4 0.4 0.7

En-Scores: S4 - TN
$E_n$-Score
Laboratory
5 9 12 8 23 1 13 21 6 22 15 17 18 16
-0.5 -0.4 -1.5 -0.2 -0.1 0.0 0.0 0.0 0.2 0.1 0.2 0.4 0.5 0.3


Figure 38

Table 42

**Sample Details**

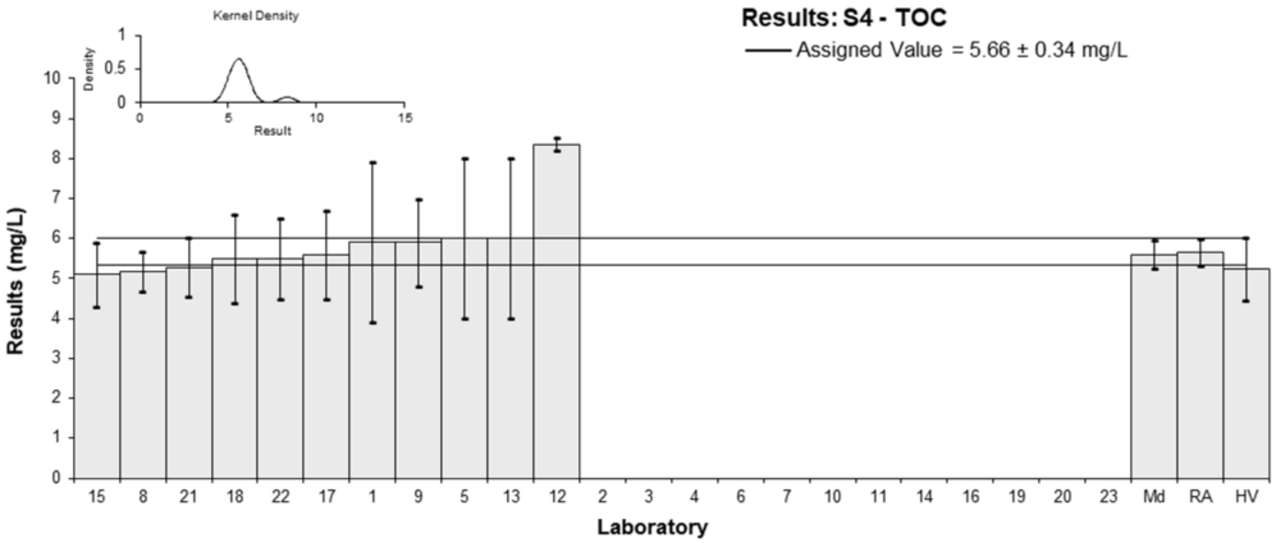
| | |
|---|---|
| **Sample No.** | S4 |
| **Matrix** | River Water |
| **Analyte** | TOC |
| **Unit** | mg/L |

**Participant Results**

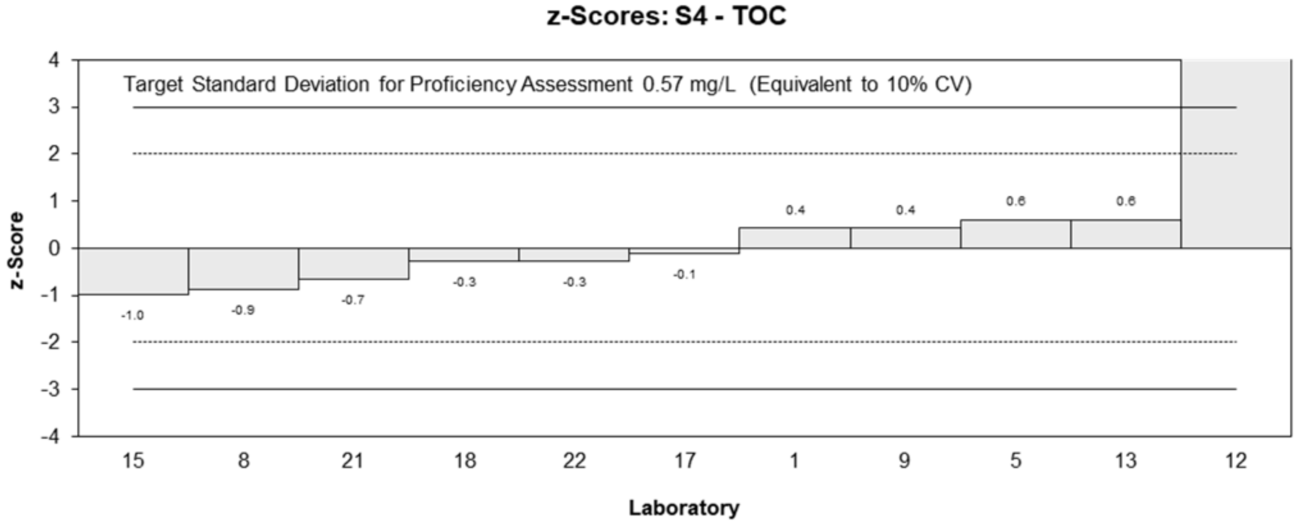
| Lab. Code | Result | Uncertainty | z | $E_n$ |
|---|---|---|---|---|
| **1** | 5.9 | 2 | 0.42 | 0.12 |
| **2** | NT | NT | | |
| **3** | NT | NT | | |
| **4** | NT | NT | | |
| **5** | 6 | 2 | 0.60 | 0.17 |
| **6** | NR | NR | | |
| **7** | NT | NT | | |
| **8** | 5.17 | 0.5 | -0.87 | -0.81 |
| **9** | 5.9 | 1.1 | 0.42 | 0.21 |
| **10** | NT | NT | | |
| **11** | NR | NR | | |
| **12** | 8.36 | 0.17 | 4.77 | 7.10 |
| **13** | 6 | 2 | 0.60 | 0.17 |
| **14** | NT | NT | | |
| **15** | 5.1 | 0.8 | -0.99 | -0.64 |
| **16** | NT | NT | | |
| **17** | 5.6 | 1.1 | -0.11 | -0.05 |
| **18** | 5.5 | 1.1 | -0.28 | -0.14 |
| **19** | NT | NT | | |
| **20** | NT | NT | | |
| **21** | 5.28 | 0.74 | -0.67 | -0.47 |
| **22** | 5.5 | 1.0 | -0.28 | -0.15 |
| **23** | NR | NR | | |

**Statistics**

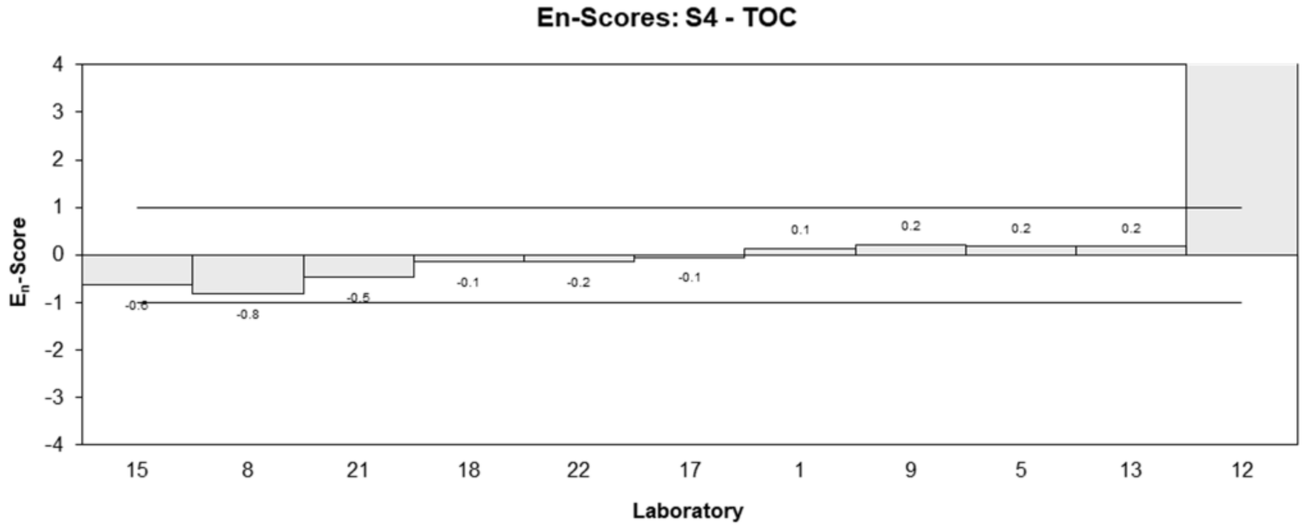
| | | |
|---|---|---|
| **Assigned Value** | 5.66 | 0.34 |
| **Spike Value** | Not Spiked | |
| **Homogeneity Value** | 5.23 | 0.79 |
| **Robust Average** | 5.66 | 0.34 |
| **Median** | 5.60 | 0.36 |
| **Mean** | 5.85 | |
| **N** | 11 | |
| **Max** | 8.36 | |
| **Min** | 5.1 | |
| **Robust SD** | 0.45 | |
| **Robust CV** | 7.9% | |



Results: S4 - TOC
Assigned Value = 5.66 ± 0.34 mg/L
Kernel Density
Density
Result
Results (mg/L)
15 8 21 18 22 17 1 9 5 13 12 2 3 4 6 7 10 11 14 16 19 20 23 Md RA HV
Laboratory

z-Scores: S4 - TOC
Target Standard Deviation for Proficiency Assessment 0.57 mg/L (Equivalent to 10% CV)
z-Score
-1.0 -0.9 -0.7 -0.3 -0.3 -0.1 0.4 0.4 0.6 0.6
15 8 21 18 22 17 1 9 5 13 12
Laboratory

En-Scores: S4 - TOC
En-Score
-0.6 -0.8 -0.5 -0.1 -0.2 -0.1 0.1 0.2 0.2 0.2
15 8 21 18 22 17 1 9 5 13 12
Laboratory


Figure 39

## 6 DISCUSSION OF RESULTS

### 6.1 Assigned Value

**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, Statistical methods for use in proficiency testing by inter-laboratory comparisons'. Results less than 50% and more than 150% of the robust average were removed before calculation of each assigned value.[6] Appendix 3 sets out the calculation for the assigned value of K in Sample S3 and its associated uncertainty.

No assigned value was set for nitrite-N in S3 because the reported results were too few. Participants may still compare their reported result for nitrite-N with other participants' results.

**Spiked Value** where applicable, includes both the incurred value and the fortified value. The incurred values for Ammonia-N and Nitrate-N + Nitrite-N in S1 are not available.

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

### 6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an evaluation of the expanded measurement uncertainty associated with their results. Of 534 numerical results, 518 (97%) were reported with an expanded measurement uncertainty, indicating that laboratories have addressed this requirement of ISO 17025.[8] The magnitude of these expanded uncertainties was within the range 0% to 1333% of the reported value. The participants used a wide variety of procedures to evaluate the expanded measurement uncertainty. These are presented in Table 2.

Approaches to evaluating measurement uncertainty include standard deviation of replicate analyses, 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 evaluation of uncertainty is. Results and expanded uncertainties are presented in the bar charts for each analyte (Figure 2 to 39). As a simple rule of thumb, when the uncertainty 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, 16 laboratories reported results for Na in S3. The uncertainty of the assigned value as determined from the robust standard deviation of the 16 laboratories' results is 2.4 mg/L (5% of the assigned value). Laboratory 3 reported an uncertainty of 0.54 mg/L (1% of their reported value) which may have been underestimated, as an uncertainty evaluated from one measurement cannot be smaller than the uncertainty evaluated from 16 measurements in different laboratories.
Alternatively, reported uncertainties for fluoride in S3 larger than 0.0518 mg/L (the uncertainty of the assigned value, 0.011 mg/L, plus the allowable variation from the assigned value, the target standard deviation of 0.0204 mg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainty reported by Laboratory 5 for fluoride in S3 (0.1 mg/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 evaluate the uncertainty of their measurement results.[10] An example of evaluating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Laboratory 12 should assess their procedure used for evaluating measurement uncertainty, as most of their reported uncertainties were under-estimated.

Laboratories 1, 3, 5, 11, 13, 15, 16 and 20 all reported at least one measurement uncertainty greater than or equal to their reported result.

Further, Laboratories 3, 9, 11, 16, 18, 22, and 23 all reported measurement uncertainty with one or more non-numerical value. An uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

In some cases, the results were reported with an inappropriate number of significant figures. The recommended format is to write the 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 2990 ± 228 mg/L, it is better to report 2990 ± 230 mg/L or, instead of 4.60 ± 0.5 mg/L, it is better to report 4.6 ± 0.5 mg/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 acceptable performance in a proficiency test. Target standard deviations equivalent to 3.5% to 20% PCV were used to calculate z-scores. A set target standard deviation 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 (outliers removed) resulted in this study are presented for comparison in Table 43.

The dispersal of participants' z-scores is presented in Figure 40 (by laboratory code) and in Figure 42 (by analyte).

Of 530 results for which z-scores were calculated, 486 (92%) returned an acceptable score of $|z| \leq 2.0$ and 16 (3%) were questionable at $2.0 < |z| < 3.0$.

Participants with multiple z-scores greater than 2 or less than -2 should check for laboratory bias (Figure 40).

Laboratories **5**, **18**, and **22** reported results for all 37 tests for which a z-score was calculated. Laboratories **1** and **22** returned the highest number of acceptable z-scores (36).

All results reported by laboratories **1** (36), **21** (33), **23** (11), **2** (10), **7** (4), **10** (4) and **19** (4) also returned acceptable z scores.

Summary of participants' performance is presented in Figure 43.

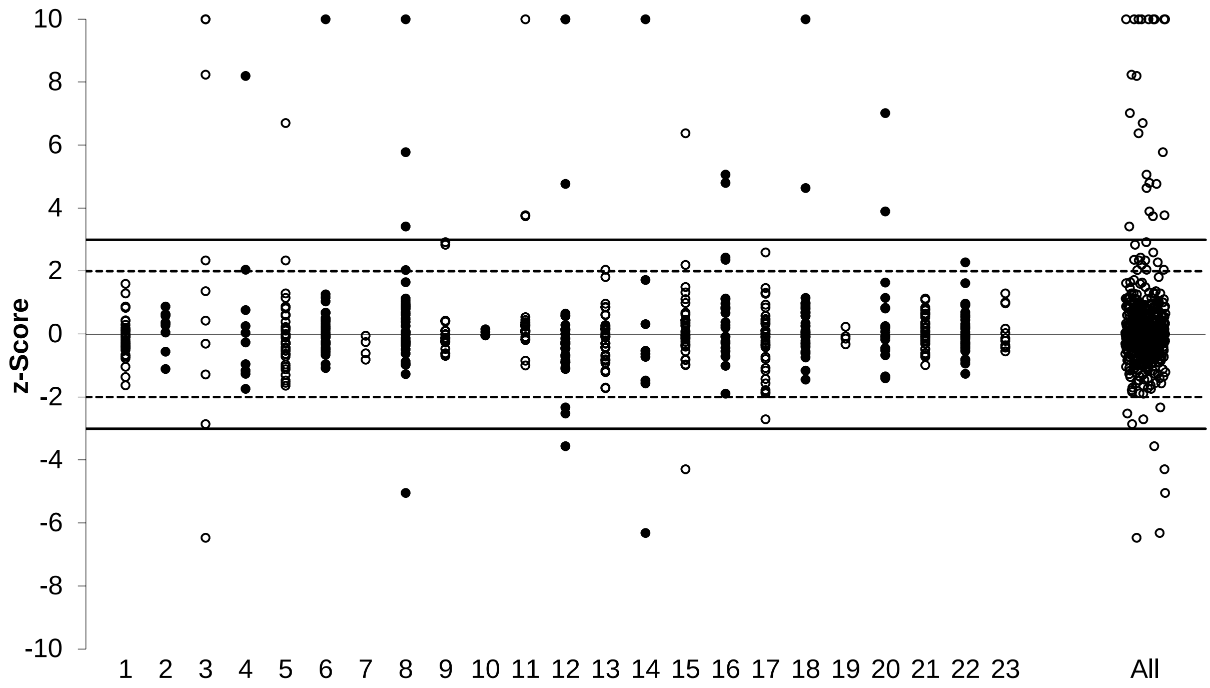
### 6.4 $E_n$-score

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

The dispersal of participants' $E_n$-scores is graphically presented in Figure 41. 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.

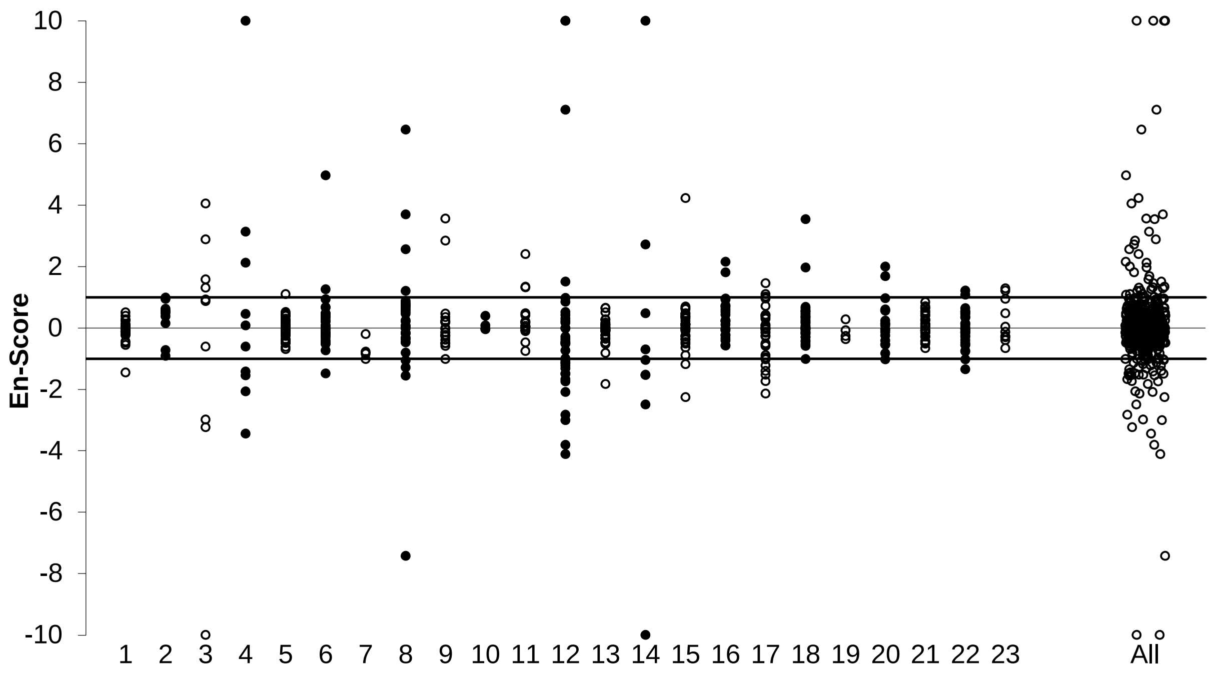
Of 530 results for which $E_n$-scores were calculated, 443 (84%) returned an acceptable score of $|E_n| < 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

Laboratory **5** returned the highest number of acceptable $E_n$-scores (36). All results reported by Laboratories **21** (33), **2** (10), **10** (4) and **19** (4) returned acceptable $E_n$-scores.




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

Figure 40 z-Score Dispersal by Laboratory



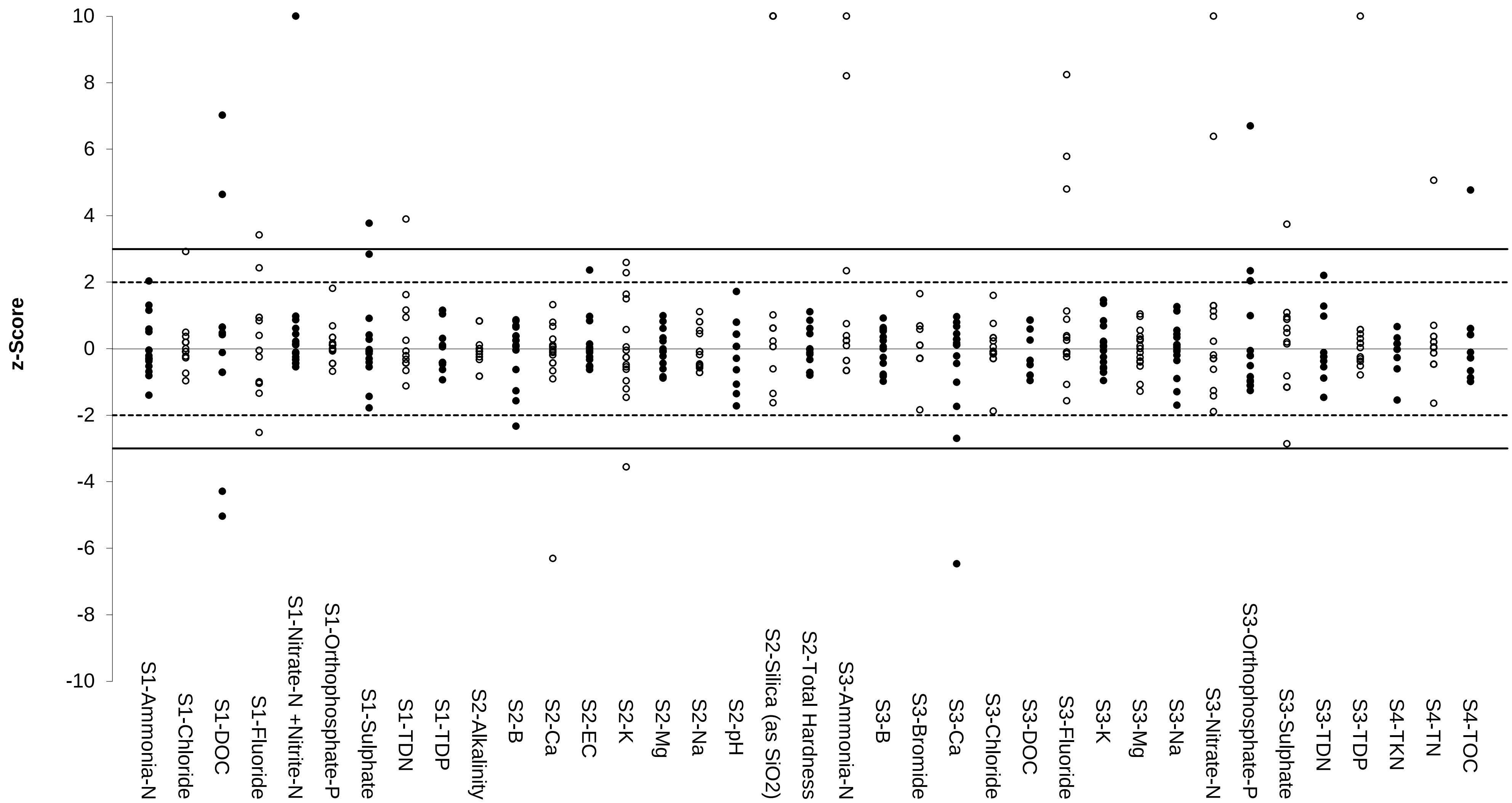

Scores of >10 or < -10 have been plotted as 10 or -10.

Figure 41 $E_n$-Score Dispersal by Laboratory

Table 43 Between Laboratory CV of this study, Thompson CV and Set Target CV

| Sample | Test | Assigned value (mg/L) | Between Laboratories CV* | Thompson/ Horwitz CV | Target SD (as PCV) |
|---|---|---|---|---|---|
| S1 | Ammonia-N | 0.0836 | 13% | 22% | 15% |
| S1 | Chloride | 21600 | 3.9% | 3.6% | 10% |
| S1 | DOC | 1.12 | 11% | 16% | 15% |
| S1 | Fluoride | 1.01 | 24% | 16% | 20% |
| S1 | Nitrate-N +Nitrite-N | 0.0610 | 6.9% | 22% | 15% |
| S1 | Orthophosphate-P | 0.118 | 5.7% | 22% | 15% |
| S1 | Sulphate | 2920 | 9.4% | 4.8% | 10% |
| S1 | TDN | 0.219 | 17% | 20% | 20% |
| S1 | TDP | 0.128 | 12% | 22% | 15% |
| S2 | B | 4.53 | 13% | 13% | 15% |
| S2 | Ca | 418 | 5.6% | 6.4% | 10% |
| S2 | K | 421 | 15% | 6.4% | 10% |
| S2 | Mg | 1310 | 5.9% | 5.4% | 10% |
| S2 | Na | 11100 | 6.5% | 3.9% | 10% |
| S2 | Alkalinity | 120 | 6.3% | 7.8% | 10% |
| S2 | EC | 53800 µS/cm | 6.1% | 3.1% | 10% |
| S2 | pH | 7.98 | 3.2% | 12% | 3.5% |
| S2 | Silica (as SiO2) | 0.089 | 19% | 22% | 20% |
| S2 | Total Hardness | 6410 | 6.6% | 4.3% | 10% |
| S3 | B | 0.791 | 10% | 17% | 15% |
| S3 | Ca | 17.8 | 7.6% | 10% | 10% |
| S3 | K | 3.23 | 7.6% | 13% | 10% |
| S3 | Mg | 7.29 | 6.8% | 12% | 10% |
| S3 | Na | 49.4 | 7.7% | 8.9% | 10% |
| S3 | Ammonia-N | 0.0444 | 9.9% | 22% | 15% |
| S3 | Bromide | 1.03 | 6.0% | 16% | 10% |
| S3 | Chloride | 94.8 | 3.8% | 8.1% | 10% |
| S3 | DOC | 4.43 | 13% | 13% | 15% |
| S3 | Fluoride | 0.102 | 15% | 22% | 20% |
| S3 | Nitrate-N | 0.0419 | 18% | 22% | 15% |
| S3 | Nitrite-N | Not Set | NA | NA | Not Set |
| S3 | Orthophosphate-P | 0.0444 | 22% | 22% | 15% |
| S3 | Sulphate | 14.7 | 13% | 11% | 10% |
| S3 | TDN | 0.218 | 17% | 20% | 15% |
| S3 | TDP | 0.0488 | 7.5% | 22% | 15% |
| S4 | TKN | 0.391 | 6.7% | 18% | 15% |
| S4 | TN | 0.398 | 6.2% | 18% | 15% |
| S4 | TOC | 5.66 | 7.9% | 12% | 10% |

NA = Not Available, *Robust between Laboratories CV with outliers removed.




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

Figure 42 z-Score Dispersal by Analyte

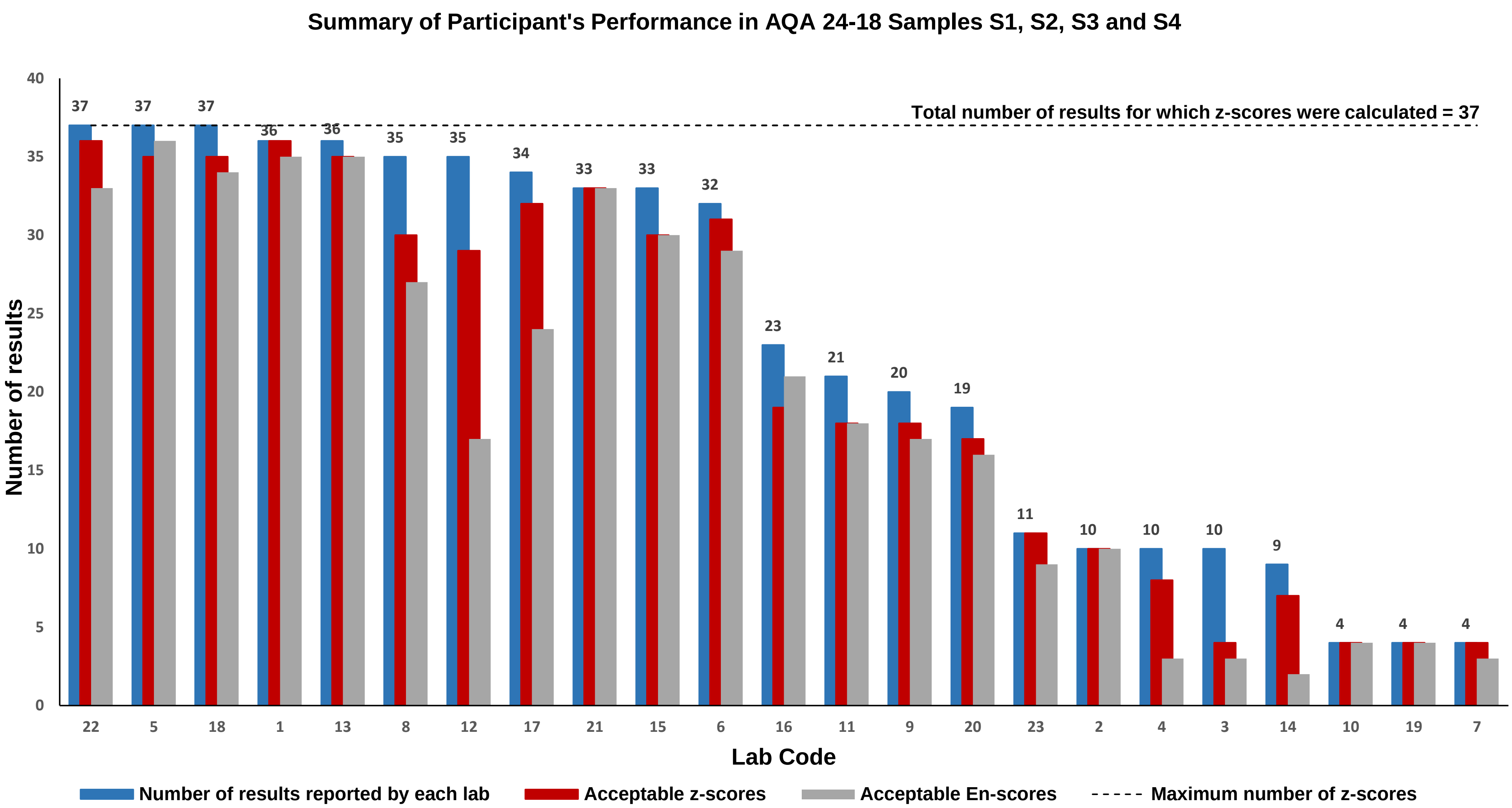



Figure 43 Summary of Participants' Performance

## Table 44 Summary of Participants' Results and Performance for Sample S1

| Lab Code | Ammonia-N (mg/L) | Chloride (mg/L) | DOC (mg/L) | Fluoride (mg/L) | Nitrate-N +Nitrite-N (mg/L) | Orthophosphate-P (mg/L) | Sulphate (mg/L) | TDN (mg/L) | TDP (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| AV | 0.0836 | 21600 | 1.12 | 1.01 | 0.0610 | 0.118 | 2920 | 0.219 | 0.128 |
| HV | 0.077 | 20000 | 1.35 | 1.08 | 0.0648 | 0.120 | 2580 | 0.165 | 0.120 |
| 1 | 0.079 | 22000 | 1 | 0.8 | 0.065 | 0.11 | 2800 | 0.2 | 0.13 |
| 2 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 3 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 4 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 5 | 0.091 | 22000 | 1.0 | 0.8 | 0.060 | 0.12 | 2900 | 0.17 | 0.15 |
| 6 | 0.09 | 21400 | NR | 0.96 | 0.06 | 0.118 | 3039 | 0.27 | 0.119 |
| 7 | 0.0734 | NT | NT | NT | 0.0587 | 0.1171 | NT | NT | NT |
| 8 | 0.109 | 22659 | 0.274 | 1.7 | 0.069 | 0.130 | 3185 | 0.205 | 0.148 |
| 9 | 0.075 | 27900 | 1.19 | 1.09 | 0.0597 | 0.118 | 3750 | <0.3 | 0.1159 |
| 10 | 0.0831 | NT | NT | NT | 0.0624 | 0.1173 | NT | NT | NT |
| 11 | NR | 21400 | NR | 0.808 | 0.301 | 0.120 | 4020 | NR | NR |
| 12 | NR | 21592 | 1.23 | 0.50 | 0.057 | 0.106 | 2831 | 0.190 | NR |
| 13 | 0.08 | 22000 | 1 | 1 | 0.057 | 0.15 | 2900 | 0.2 | 0.12 |
| 14 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 15 | 0.083 | 19500 | 0.4 | <10 | 0.058 | 0.124 | 2760 | 0.23 | 0.129 |
| 16 | <0.2 | 21108 | NT | 1.5 | NT | NT | 3002 | NT | NT |
| 17 | 0.1 | 21000 | 1.2 | <10 | 0.062 | 0.12 | 2400 | 0.26 | 0.12 |
| 18 | 0.098 | 20000 | 1.9 | 1.2 | 0.056 | 0.12 | 2500 | 0.21 | 0.12 |
| 19 | 0.0796 | NT | NT | NT | 0.0597 | 0.1168 | NT | NT | NT |
| 20 | 0.066 | 22000 | 2.3 | 0.74 | 0.063 | 0.11 | 2900 | 0.39 | 0.15 |
| 21 | 0.0800 | 22400 | 1.23 | 1.18 | 0.0666 | 0.124 | 2880 | 0.216 | 0.134 |
| 22 | 0.077 | 21400 | 1.1 | 1.2 | 0.058 | 0.11 | 2910 | 0.29 | 0.11 |
| 23 | 0.081 | NR | NR | NR | 0.070 | 0.121 | NR | 0.2 | 0.12 |

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, HV = Homogeneity Value, SV = Spike Value, NT = Not Tested, NR = Not Reported, NA = Not Available

## Table 45 Summary of Participants' Results and Performance for Sample S2

| Lab Code | B (mg/L) | Ca (mg/L) | K (mg/L) | Mg (mg/L) | Na (mg/L) | Alkalinity (mg/L) | EC (µS/cm) | pH | Silica (mg/L) | Total Hardness (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| AV | 4.53 | 418 | 421 | 1310 | 11100 | 120 | 53800 | 7.98 | 0.089 | 6410 |
| HV | 4.92 | 418 | 406 | 1320 | 10200 | NA | 53000 | 8.00 | NA | 6360 |
| 1 | 4.5 | 410 | 410 | 1300 | 11000 | 130 | 52000 | 7.6 | 0.06 | 6400 |
| 2 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 3 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 4 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 5 | 4.1 | 400 | 380 | 1300 | 12000 | 120 | 51000 | 7.8 | 0.1 | 6400 |
| 6 | 4.58 | 415 | 419 | 1252 | 10460 | NR | NR | 8.10 | 0.64 | 6200 |
| 7 | NT | NT | NT | NT | NT | NT | NT | NT | 0.0781 | NT |
| 8 | 3.67 | 451 | 395 | 1309 | 10559 | 117 | 58300 | 8.00 | 13.0 | 6800 |
| 9 | 4.6 | 417 | 410 | 1280 | 10900 | 121.3 | 53200 | 8.1 | <1.0 | 6330 |
| 10 | NT | NT | NT | NT | NT | NT | NT | NT | 0.0901 | NT |
| 11 | 4.79 | 430 | 423 | 1340 | 11700 | NR | NR | NR | NR | NR |
| 12 | 2.95 | 413 | 271 | 1194 | 10590 | 116 | 54560 | 7.68 | 0.296 | 5947 |
| 13 | 4.7 | 380 | 370 | 1200 | 11000 | 110 | 59000 | 7.5 | 0.1 | 5900 |
| 14 | 3.46 | 154.07 | 359.21 | 1351.68 | 10511.29 | NT | 50400 | 8.46 | 1.40 | 5951 |
| 15 | NT | 473 | 484 | 1440 | 11600 | 118 | 52500 | 8.1 | 0.1 | 7120 |
| 16 | 4.79 | 446 | 398 | 1418 | 12330 | 119 | 66500 | 8.2 | NT | 6955 |
| 17 | 5.1 | 420 | 530 | 1300 | 10300 | 120 | 53800 | 8.1 | <0.1 | NT |
| 18 | 5.12 | 420 | 445 | 1300 | 11000 | 130 | 54000 | 8.0 | 0.321 | 6402 |
| 19 | NT | NT | NT | NT | NT | NT | NT | NT | 0.0931 | NT |
| 20 | 4.7 | 390 | 490 | 1300 | 12000 | 130 | 51000 | 8.0 | 0.065 | 6300 |
| 21 | 4.97 | 422 | 401 | 1230 | 10300 | 119 | 53500 | 8.2 | NT | NT |
| 22 | 5.0 | 400 | 517 | 1390 | 11000 | 110 | 50900 | 7.9 | 0.090 | 6700 |
| 23 | NR | NR | NR | NR | NR | NR | NR | NR | 0.107 | NR |

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, HV = Homogeneity Value, NT = Not Tested, NR = Not Reported, NA = Not Available

Table 46 Summary of Participants' Results and Performance for Samples S3 and S4

| Lab Code | S3-B (mg/L) | S3-Ca (mg/L) | S3-K (mg/L) | S3-Mg (mg/L) | S3-Na (mg/L) | S3-Ammonia-N (mg/L) | S3-Bromide (mg/L) | S3-Chloride (mg/L) | S3-DOC (mg/L) | S3-Fluoride (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| AV | 0.791 | 17.8 | 3.23 | 7.29 | 49.4 | 0.0444 | 1.03 | 94.8 | 4.43 | 0.102 |
| HV | 0.799 | 19.4 | 3.18 | 7.41 | 46.1 | 0.0502 | 1.17 | 92 | 3.82 | NA |
| 1 | 0.7 | 18 | 3 | 7 | 50 | 0.04 | 1 | 110 | 5 | 0.1 |
| 2 | 0.866 | 18.3 | 3.05 | 7.56 | 51.1 | NT | 1.09 | 95.3 | NT | 0.12 |
| 3 | NT | 6.28 | 3.67 | 6.36 | 51.53 | <1 | NT | 92 | NT | 0.27 |
| 4 | NR | 14.7 | 2.92 | 7.10 | 49.6 | 0.099 | NR | 102 | NR | 0.107 |
| 5 | 0.76 | 17 | 3.3 | 6.9 | 43 | 0.06 | 1.0 | 92 | 5 | 0.11 |
| 6 | 0.82 | 19.0 | 3.45 | 8.05 | 55.6 | 0.04 | 1.00 | 97.9 | NR | 0.08 |
| 7 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 8 | 0.675 | 19.5 | 3.25 | 7.47 | 49.7 | 0.047 | 1.20 | NR | 3.79 | 0.22 |
| 9 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 10 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 11 | 0.798 | 18.6 | 3.26 | 7.49 | 50 | NR | 1.04 | 93.4 | NR | 0.109 |
| 12 | 0.693 | 18.31 | 3.15 | 7.29 | 44.94 | 0.139 | 1.04 | 93.3 | 4.82 | 0.097 |
| 13 | 0.79 | 18 | 3.5 | 7.5 | 41 | 0.04 | 1 | 97 | 5 | 0.1 |
| 14 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 15 | NR | 18.3 | 3.1 | 7.2 | 47.6 | 0.045 | 1.1 | 93.7 | 3.9 | <0.15 |
| 16 | 0.739 | 16 | 3 | 8 | 55 | <0.2 | 1 | 94 | NT | 0.2 |
| 17 | 0.86 | 13 | 3.7 | 6.5 | 49 | 0.042 | 0.84 | 77 | 4.2 | 0.07 |
| 18 | 0.832 | 19.2 | 3.04 | 7.02 | 49.2 | 0.046 | 1.1 | 92 | 4.6 | 0.1 |
| 19 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 20 | NT | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 21 | 0.854 | 17.4 | 3.29 | 7.35 | 48.4 | 0.0494 | NT | 93.9 | 4.11 | 0.125 |
| 22 | 0.90 | 18.1 | 3.21 | 7.69 | 52.1 | 0.046 | 1.0 | 97.8 | 3.9 | 0.099 |
| 23 | NR | NR | NR | NR | NR | 0.042 | NR | NR | NR | NR |

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, HV = Homogeneity Value, NT = Not Tested, SV = Spike Value, NR = Not Reported, NA = Not Available

Table 46 Summary of Participants' Results and Performance for Samples S3 and S4 (continued)

| Lab Code | S3-Nitrate-N (mg/L) | S3-Nitrite-N (mg/L) | S3-Orthophosphate-P (mg/L) | S3-Sulphate (mg/L) | S3-TDN (mg/L) | S3-TDP (mg/L) | S4-TKN (mg/L) | S4-TN (mg/L) | S4-TOC (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| AV | 0.0419 | Not Set | 0.0444 | 14.7 | 0.218 | 0.0488 | 0.391 | 0.398 | 5.66 |
| HV | 0.0397 | NA | 0.0503 | 15.3 | 0.207 | 0.0568 | 0.458 | 0.468 | 5.23 |
| 1 | 0.05 | <0.005 | 0.041 | 16 | <0.1 | 0.051 | 0.4 | 0.4 | 5.9 |
| 2 | NT | NT | 0.037 | 15.6 | NT | NT | NT | NT | NT |
| 3 | 0.2 | 0.003 | 0.06 | 10.5 | NT | 0.60 | NT | NT | NT |
| 4 | 0.034 | < 0.01 | 0.058 | 13.0 | NR | NR | NT | NT | NT |
| 5 | 0.050 | <0.005 | 0.089 | 16 | 0.17 | 0.05 | 0.3 | 0.3 | 6 |
| 6 | 0.04 | 0.001 | 0.038 | 15.4 | 0.21 | 0.045 | 0.40 | 0.41 | NR |
| 7 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 8 | 0.049 | <0.005 | 0.043 | NR | 0.206 | 0.047 | 0.375 | 0.390 | 5.17 |
| 9 | NT | NT | NT | NT | NT | NT | 0.355 | 0.370 | 5.9 |
| 10 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 11 | 0.0407 | <0.01 | 0.0388 | 20.2 | NR | NR | NR | NR | NR |
| 12 | 0.04 | NR | 0.037 | 14.91 | 0.189 | 0.053 | 0.4 | 0.37 | 8.36 |
| 13 | 0.04 | <0.005 | 0.058 | 13 | <0.1 | 0.05 | 0.4 | 0.4 | 6 |
| 14 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 15 | 0.082 | 0.016 | 0.044 | 13.5 | 0.29 | 0.052 | 0.39 | 0.42 | 5.1 |
| 16 | 0.03 | NT | NT | 15 | NT | NT | NT | 0.7 | NT |
| 17 | 0.033 | 0.007 | 0.043 | 13 | 0.26 | 0.043 | 0.41 | 0.42 | 5.6 |
| 18 | 0.038 | <0.005 | 0.051 | 13 | 0.25 | 0.053 | 0.43 | 0.44 | 5.5 |
| 19 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 20 | NT | NT | NT | NT | NT | NT | NT | NT | NT |
| 21 | 0.0433 | <0.002 | 0.0378 | 16.3 | 0.214 | 0.0465 | NT | 0.401 | 5.28 |
| 22 | 0.048 | <0.010 | 0.036 | 16.1 | 0.21 | 0.046 | 0.39 | 0.41 | 5.5 |
| 23 | 0.050 | <0.002 | NR | NR | 0.2 | 0.049 | NR | 0.39 | NR |

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, HV = Homogeneity Value, NT = Not Tested, SV = Spike Value, NR = Not Reported, NA = Not Available

### 6.5 Participants’ Results and Analytical Methods

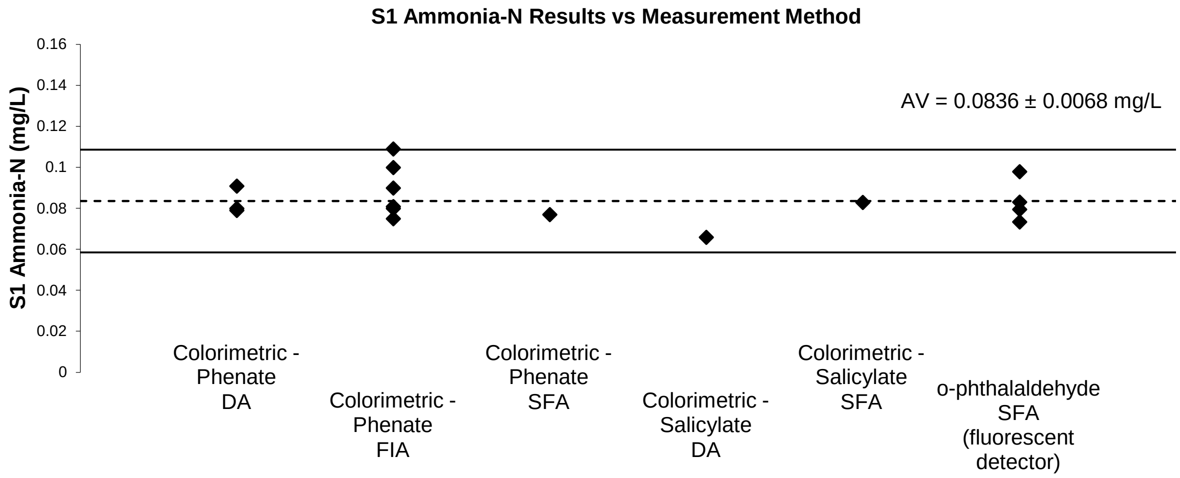
Samples S1 and S2 were sea water samples while Samples S3 and S4 were river water samples. Participants were asked to analyse the samples using their normal test method. The measurement methods and instrumental techniques used are presented in Appendices 6 to 9. Overall, the between-laboratory CVs of the sea water samples and river water samples were comparable.

Low level nitrite-N in S3 was the test that most challenged participants’ analytical techniques. Only four laboratories reported results.

Low level silica in S2 and low-level orthophosphate-P in S3 also challenged participants’ analytical techniques. Of 23 participants, only 15 reported results for these tests. Of the 15 results reported for silica in S2 and orthophosphate-P in S3, 5 and 4 respectively returned unsatisfactory z-scores.

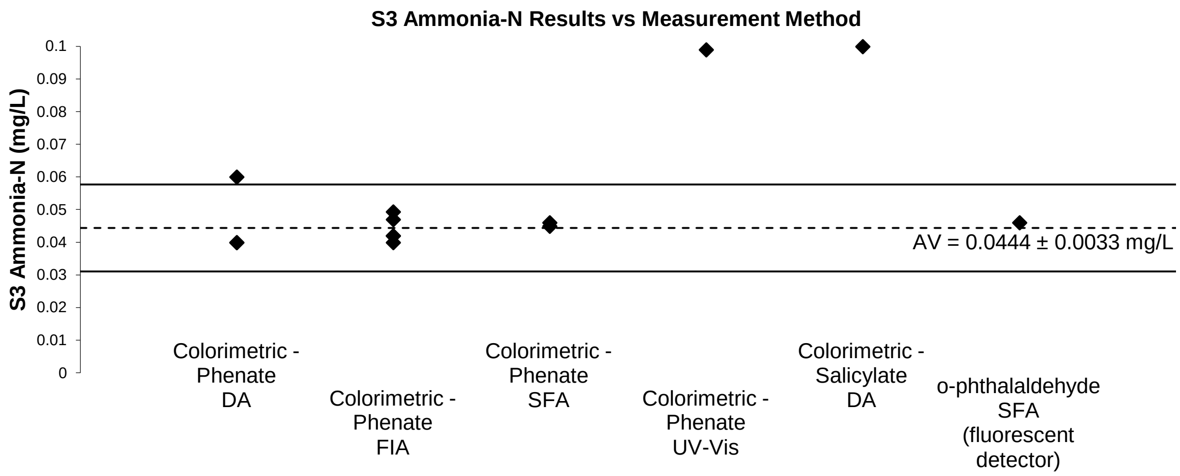
**Individual Test Commentary**

**Alkalinity to pH 4.5 as ($CaCO_3$)** Participants used auto-titration or manual titration to measure alkalinity in S2, and all performed satisfactorily.




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

Figure 44 S1-Ammonia-N Results vs. Measurement Method




Laboratory 12’s result of 0.139 mg/L has been plotted as 0.1 mg/L Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 45 S3-Ammonia-N Results vs. Measurement Method

**Ammonia-Nitrogen** level in the sea water sample S1 was 0.0836 mg/L and in the river water sample S3 was half that, at 0.0444 mg/L. Participants' performance in the two types of water samples was similar.

Plots of participants' results in sea water and river water versus methods used for ammonia–N measurements are presented in Figures 44 and 45. Most participants used the colorimetric-phenate method with FIA determination.

**Bromide** Results produced using the ICP-MS were higher than those from IC measurements (Figure 46).

During ozonation or chlorination, the by-product bromate is formed in water containing bromide. Caution should be exercised when bromide is measured by ICP-MS because it measures both bromide and bromate as bromine. However, there are some technical difficulties when bromine is measure by ICP-MS, because it has only two isotopes, $^{81}Br$ and $^{79}Br$ that typically suffer significant interferences from $^{40}Ar^{40}Ar^{+}$ dimer.

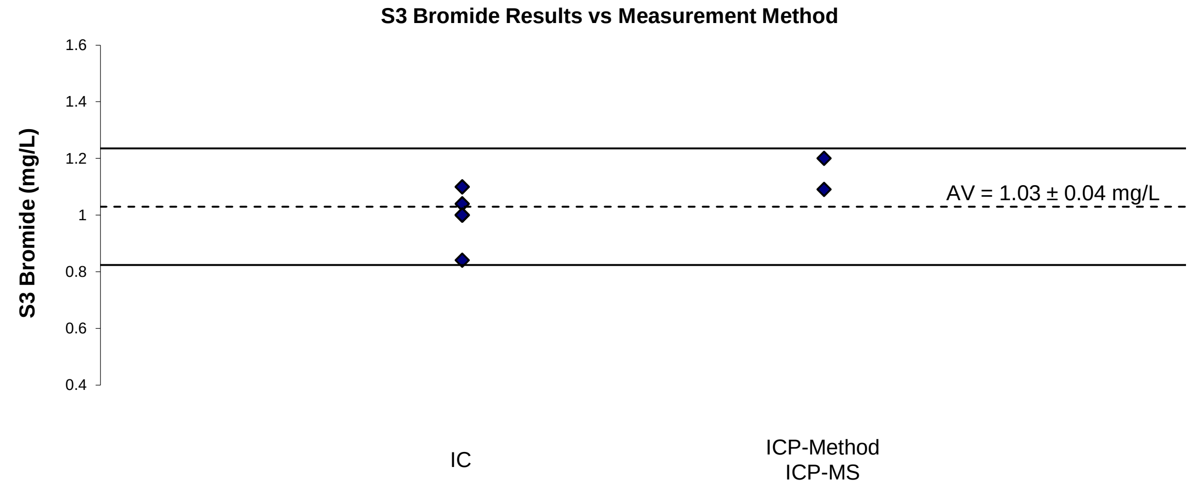
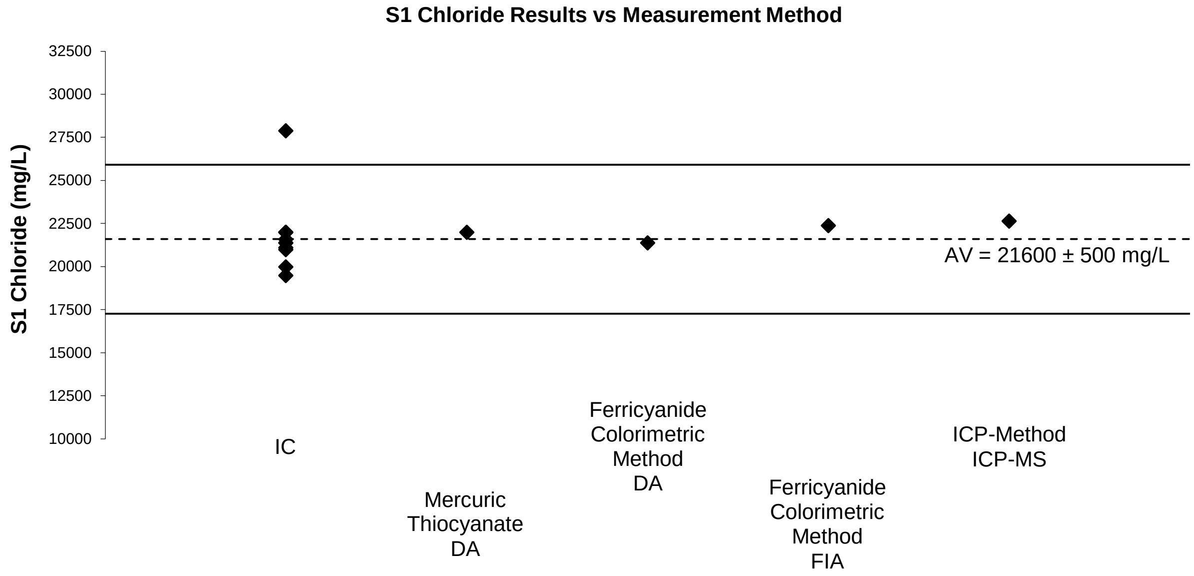
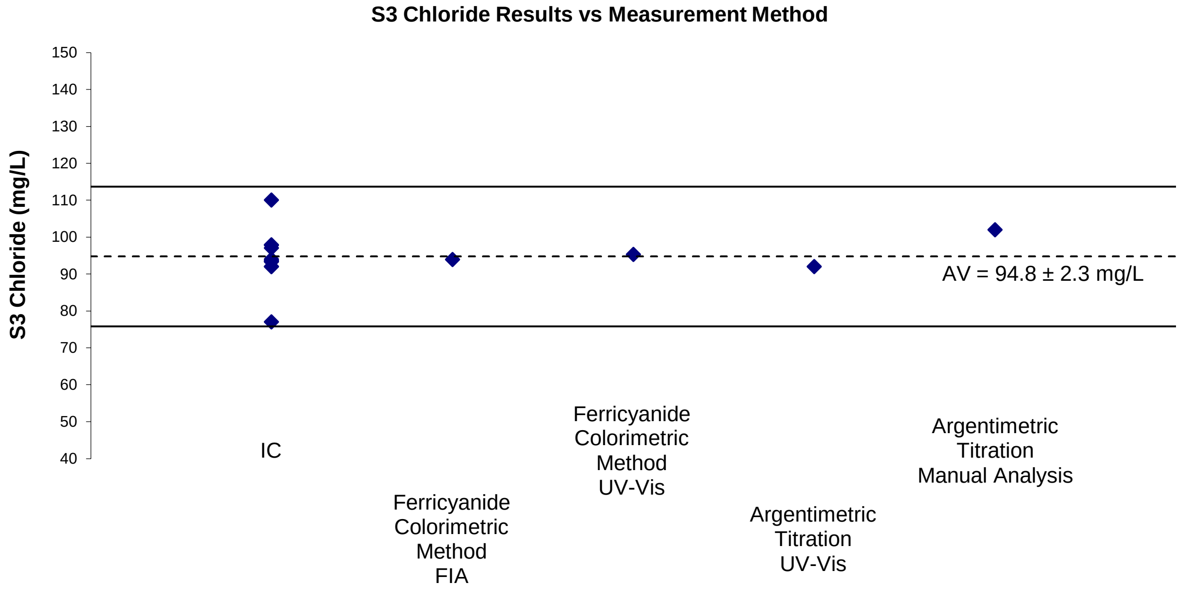



Figure 46 S3-Bromide Results vs. Measurement Method




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

Figure 47 S1-Chloride Results vs. Measurement Method




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

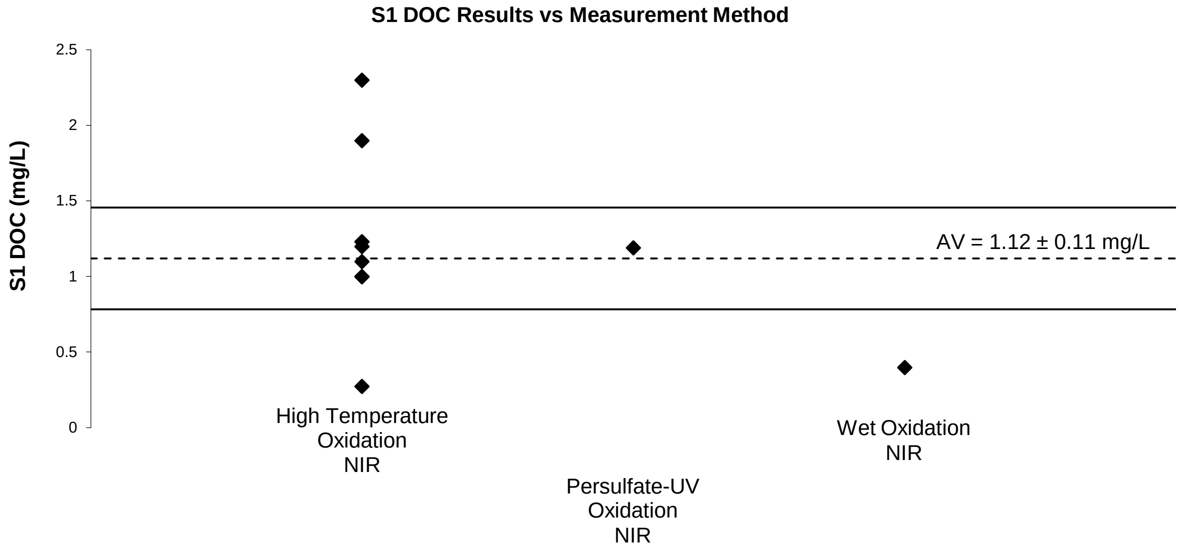
Figure 48 S3-Chloride Results vs. Measurement Method

**Chloride** level in the sea water sample S1 was 21600 mg/L and in S3 was 94.8 mg/L. All the chloride results reported in river water and in sea water returned acceptable results except for one (Figures 47 and 48).

### Dissolved Organic Carbon as dNPOC

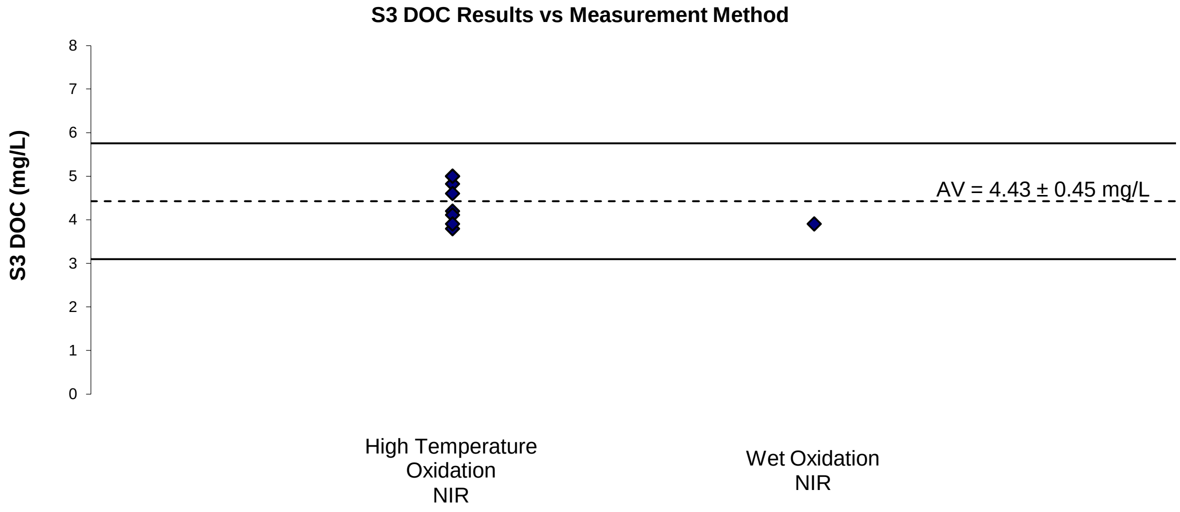
While all the results reported for DOC in Sample S3 river water returned acceptable z- scores, 4 of the 11 reported results in Sample S1 sea water returned unacceptable z-scores (Figures 49 and 50).

Chloride in sea water can interfere in the persulfate oxidation process of the organic molecules. Sample dilution and increased digestion time can help to overcome this problem.[15]



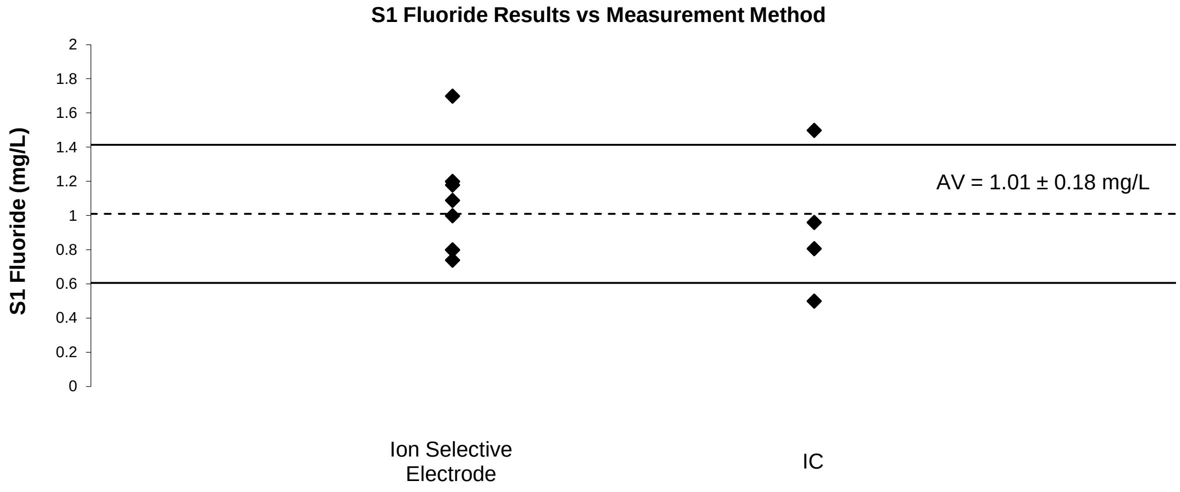

Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 49 S1-DOC Results vs. Measurement Method



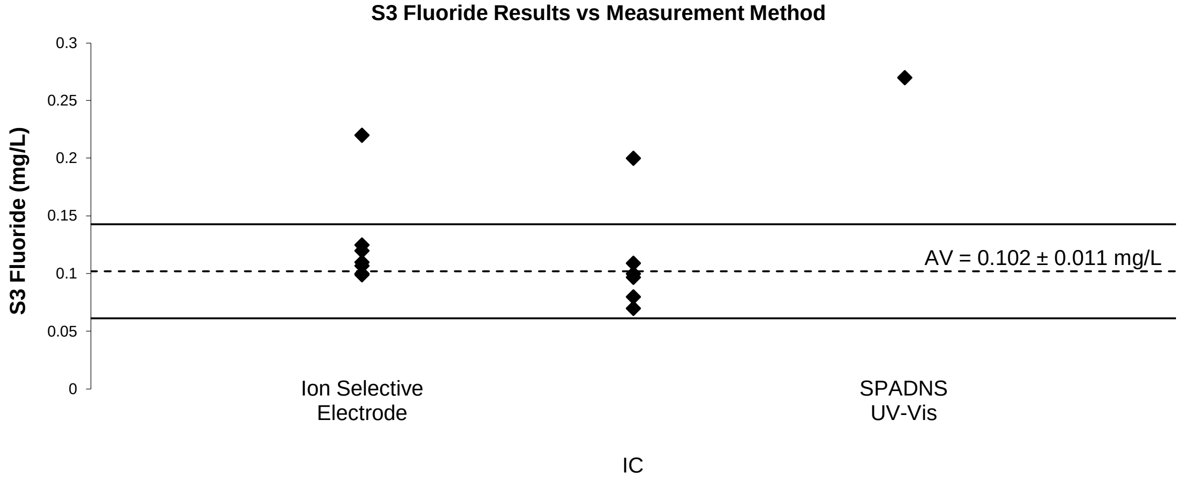

Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 50 S3-DOC Results vs. Measurement Method




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

Figure 51 S1-Fluoride Results vs. Measurement Method




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

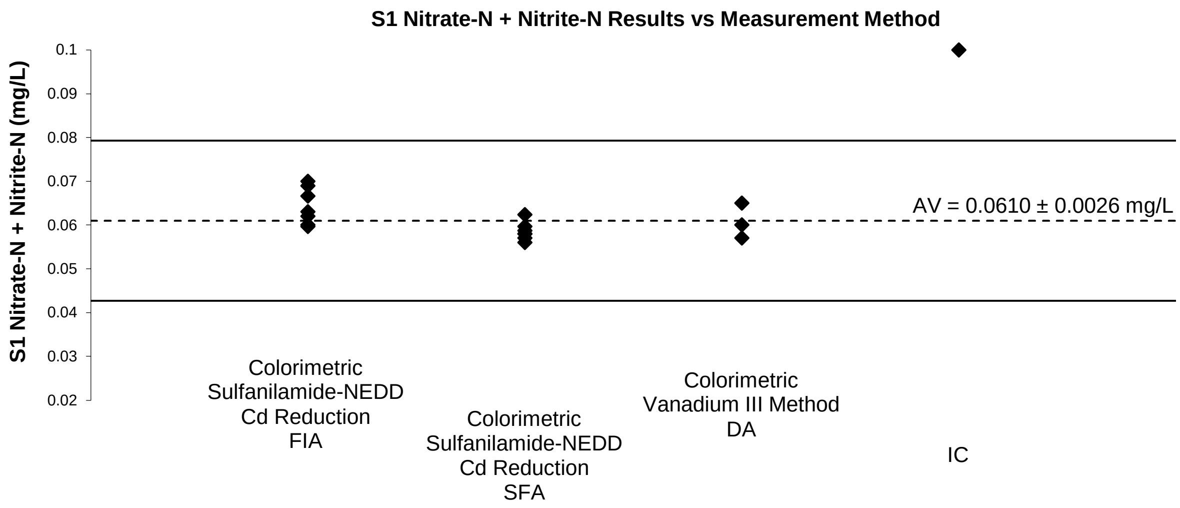
Figure 52 S3-Fluoride Results vs. Measurement Method

**EC** results in sample S2 were in good agreement with each other with only one laboratory not receiving an acceptable z-score. The between-laboratory CV was 6.1%.

**Fluoride** Plots of participants z-scores versus the measurement technique used are presented in Figures 51 and 52.

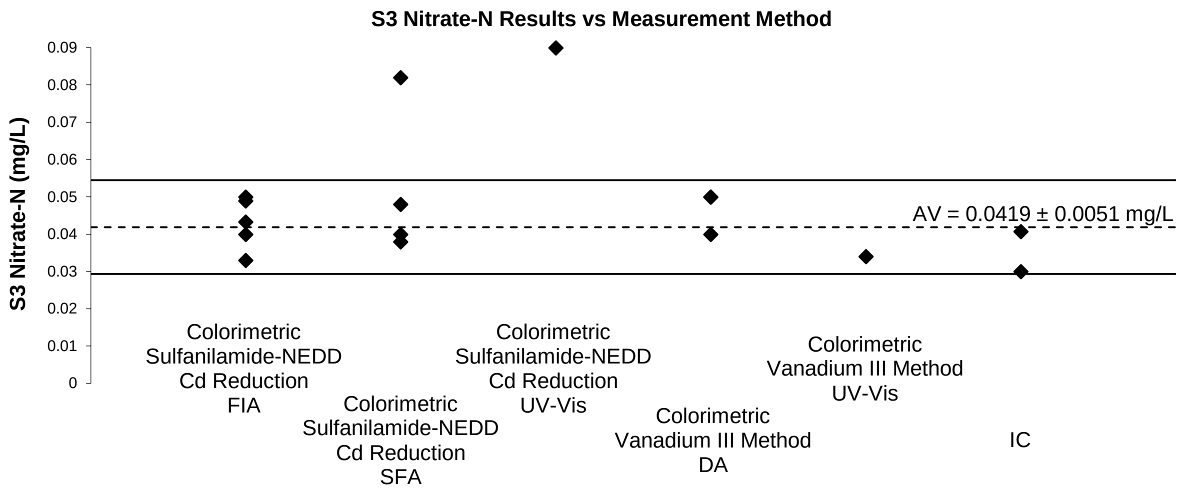
Caution should be exercised when the ion chromatographic method is used for low level fluoride measurements. Fluoride has a low molecular weight and valence charge and is not retained by the columns in the normal elution times like for the other ions. Low level fluoride may be difficult to quantify due to negative contribution of the "water dip" (corresponding to elution of water) or due to interference from the simple organic acids which may elute close to fluoride.[15]

**Nitrate-Nitrogen + Nitrite-Nitrogen** level in the sea water sample S1 was 0.0610 mg/L. Seventeen laboratories reported results and all performed acceptably, but one. Most laboratories used the colorimetric-sulfanilamide-NEDD Cd reduction method with either FIA or SFA (Figure 53).




Laboratory 11 result of 0.301 mg/L has been plotted as 0.1 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 53 S1-Nitrate-N+Nitrite-N Results vs. Measurement Method

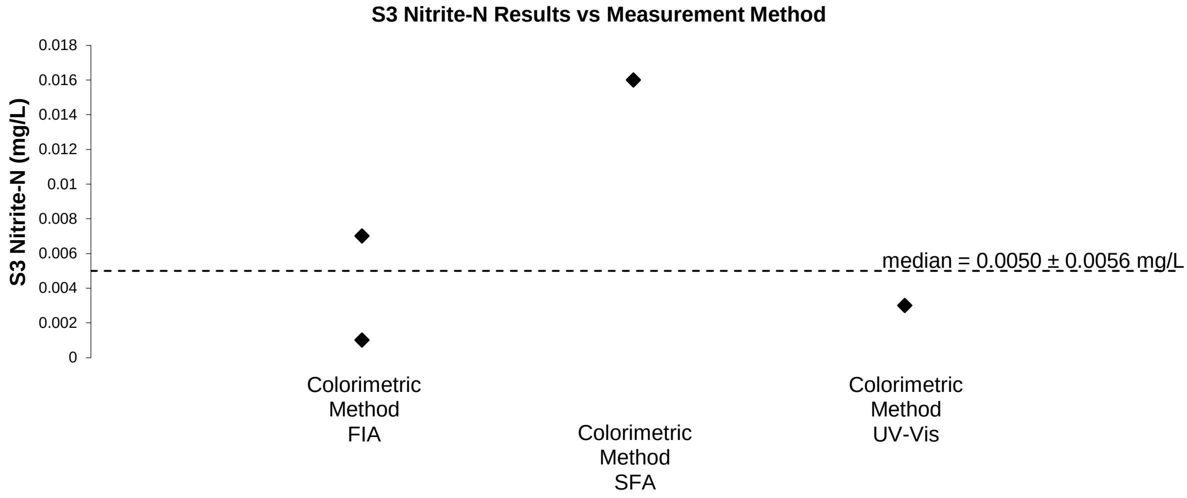



Laboratory 3 result of 0.2 mg/L was plotted as 0.09 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 54 S3 Nitrate-N Results vs. Measurement Method

Nitrate-N and Nitrite-N level in S3 was the incurred level. The assigned value for $NO_3$-N was 0.0419 mg/L. Sixteen participants reported results for $NO_3$-N in S3 and all performed acceptably but two. Most participants reported using a sulfanilamide-NEDD Cd reduction to convert $NO_3$-N to $NO_2$-N and measuring $NO_2$-N by FIA, SFA or UV-Vis (Figure 54).

Nitrite-N level in S3 was below the level of reporting of many participants. Four laboratories reported results for this test, with results varying from 0.001 mg/L to 0.016 mg/L (Figure 55).



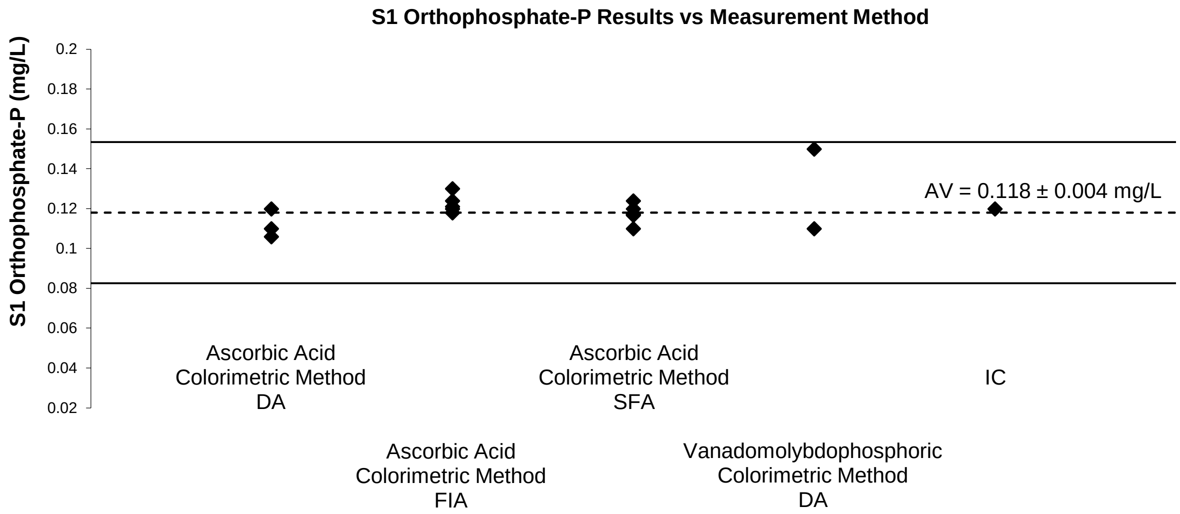

Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 55 S3- Nitrite-N Results vs. Measurement Method

**Orthophosphate-P** level in in the sea water sample S1 was 0.118 mg/L and in the river water sample S3 was 0.0444 mg/L.

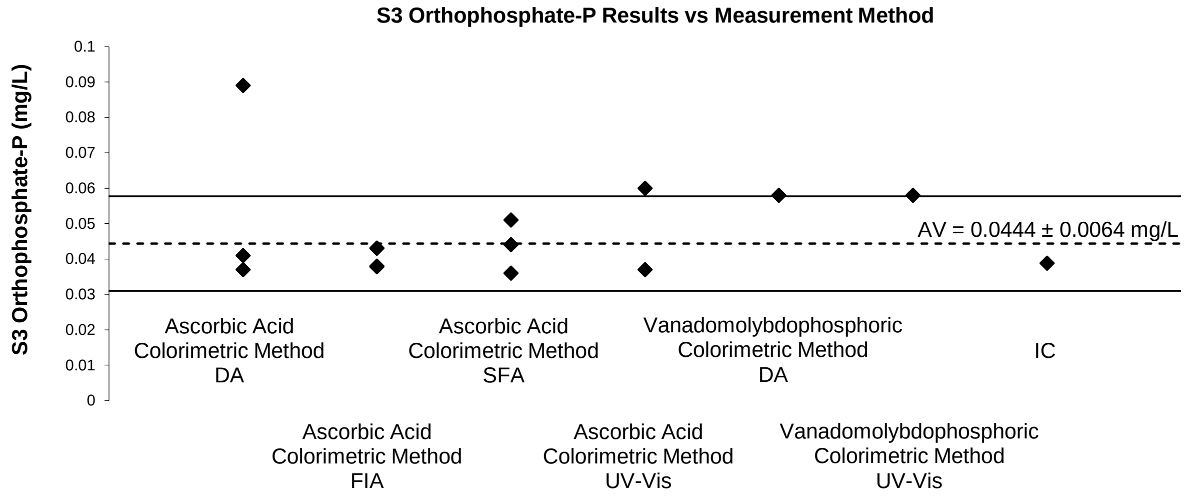
All results reported for orthophosphate-P in S1 returned acceptable z-scores. The river water was more challenging with only 11 out of 15 participants reporting acceptable results.

Ascorbic acid colorimetric method with FIA was the preferred method of measurement (Figures 56 and 57).



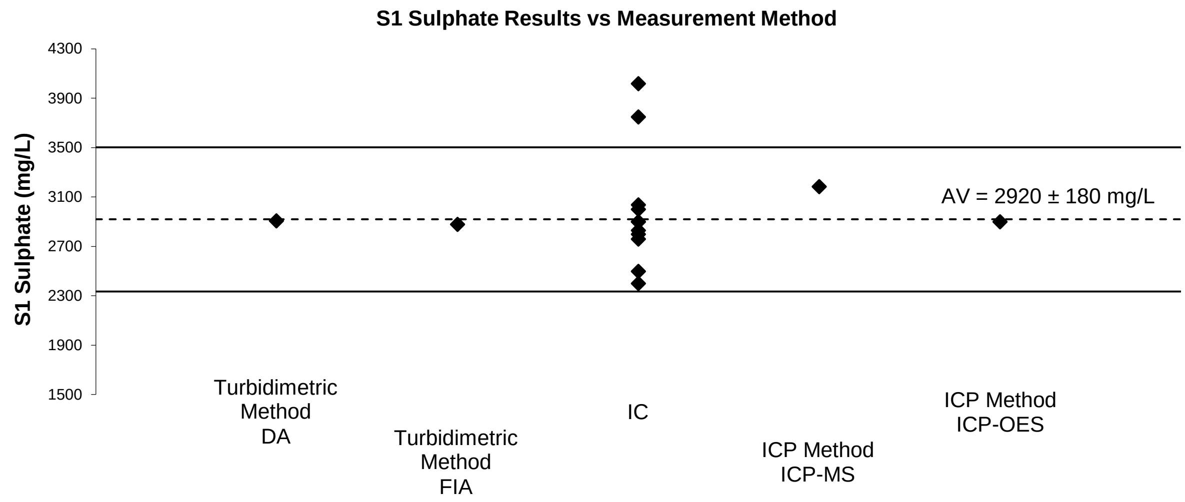

Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 56 S1-Orthophosphate-P Results vs. Measurement Method



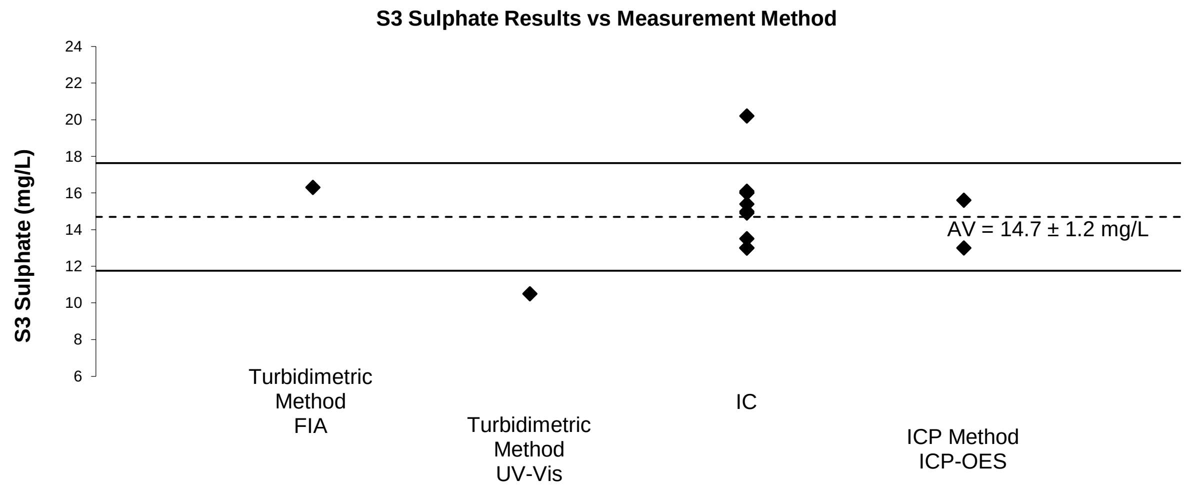

Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 57 S3-Orthophosphate-P Results vs. Measurement Method




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

Figure 58 S1-Sulphate Results vs. Measurement Method



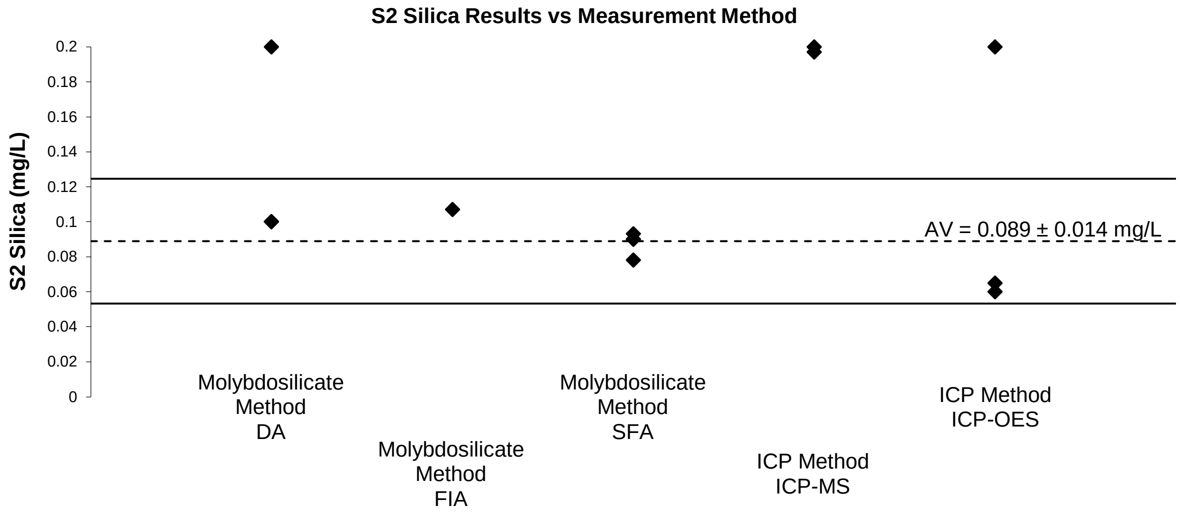

Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 59 S3-Sulphate Results vs. Measurement Method

**Sulphate** Of 15 participants who reported results for sulphate in S1 and S3, 13 performed acceptably in both samples. Laboratories used various methods, and most produced similar results (Figures 58 and 59). Laboratory 11 should check for method bias, as both of their results reported for sulphate in S1 and S3 were higher than assigned value by exactly the same factor, of 1.37.

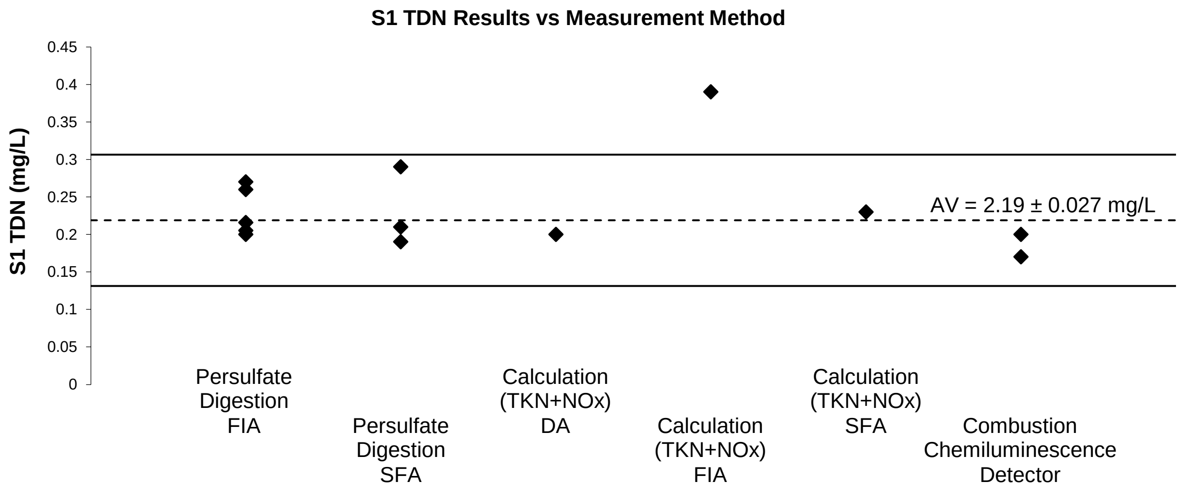
**Silica (as $SiO_2$)** The silica level in seawater sample S1 was low (0.089 mg/L), and this may have posed challenges for some participants' analytical techniques. Most of the unsatisfactory results were produced by an ICP method (Figure 60). Seawater contains high concentrations of dissolved salts, which can cause signal suppression in ICP-MS or ICP-OES analysis. To mitigate this, significant dilution (up to 10 times) is required. However, this can also reduce the silica concentration in the sample to a level that can fall outside the optimal calibration range for these techniques.

The high silica results from ICP determination may be also of indication of measuring total silicon instead of reactive silica- silica species that react with molybdate.



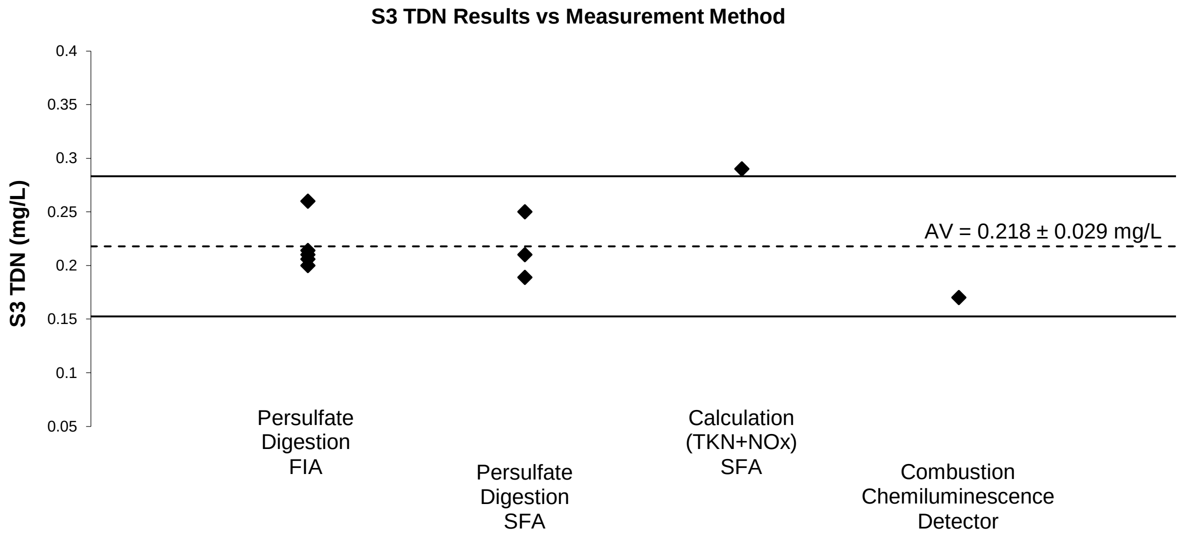

Laboratory 6 result of 0.64 mg/L, Laboratory 8 result of 13 mg/L, Laboratory 12 result of 0.296 mg/L, and Laboratory 18 result of 0.321 mg/L were plotted as 0.2 mg/L or 0.1497 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 60 S2-Silica Results vs. Measurement Method




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

Figure 61 S1-TDN Results vs. Measurement Method



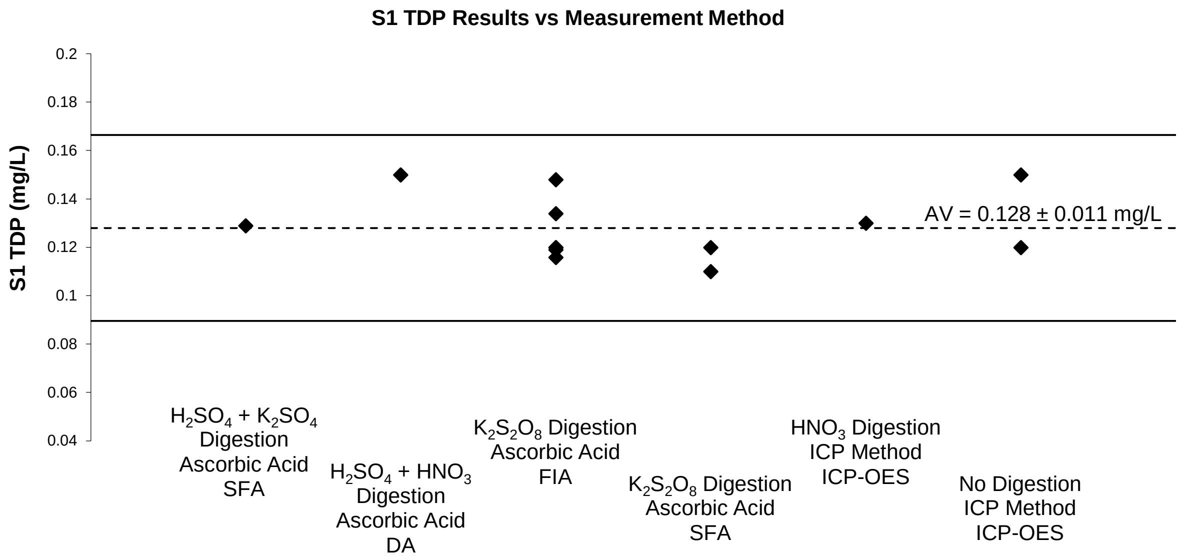

Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 62 S3-TDN Results vs. Measurement Method

**Total Dissolved Nitrogen** level in S1 and S3 was similar at 0.219 mg/L and 0.218 mg/L respectively. Participants used the same method for TDN measurements in the two study samples; these are presented in Figures 61 and 62.

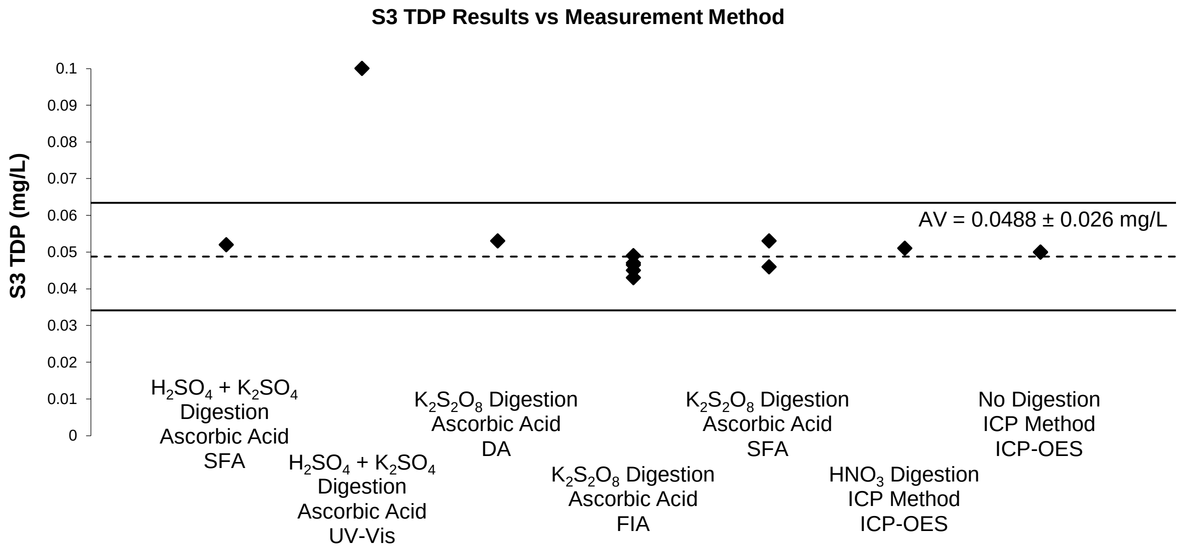
Two laboratories reported a result for TDN in S3 as being less than their level of reporting (0.1 mg/L). They may need to review their method and LOR for TDN measurements in the river water samples.

**Total Dissolved Phosphorus** in the sea water Sample S1 was 0.128 mg/L whilst in the river water sample S3, 0.0488 mg/L. All reported results returned acceptable z-scores with the exception of one. The most popular method used involved potassium persulphate digestion followed by FIA determination (Figures 63 and 64).




Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 63 S1-TDP Results vs. Measurement Method

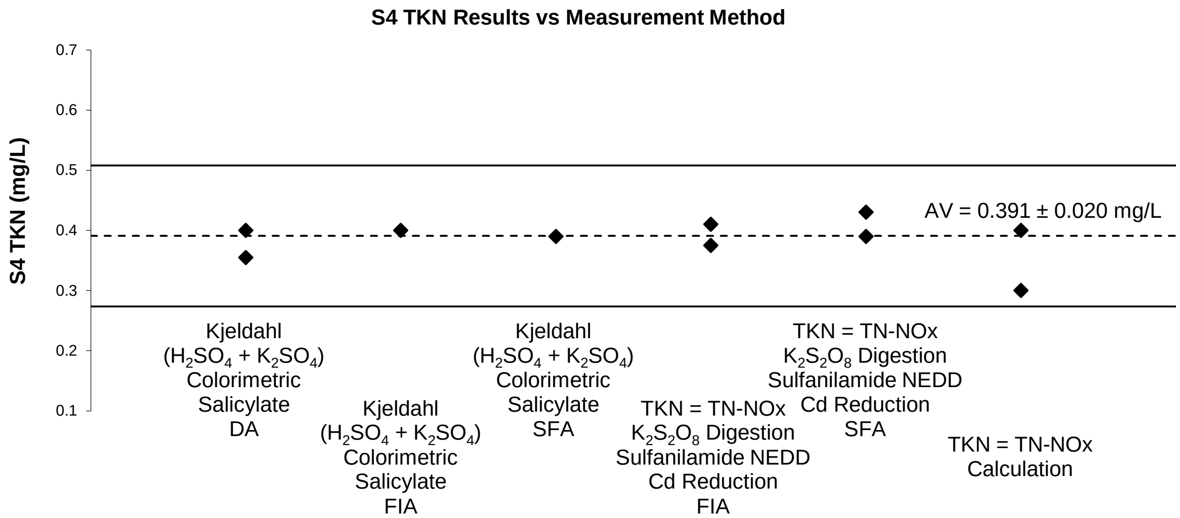



Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 64 S3-TDP Results vs. Measurement Method

**Total Kjeldahl Nitrogen** measurements in the river water sample S4 did not challenge participants' analytical techniques. The between-laboratory CV was 6.7%.

Plots of participants' results versus the measurement method used are presented in Figure 65.



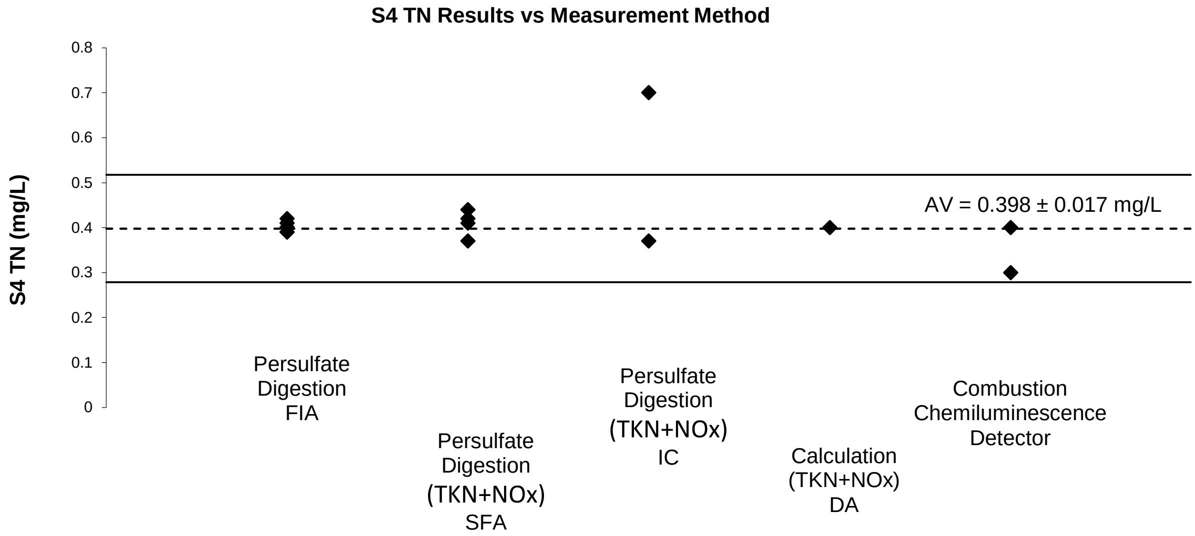

Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 65 S4-TKN Results vs. Measurement Method

**Total Nitrogen** Fourteen laboratories reported results for TN in S4, and all but one returned acceptable z-scores.

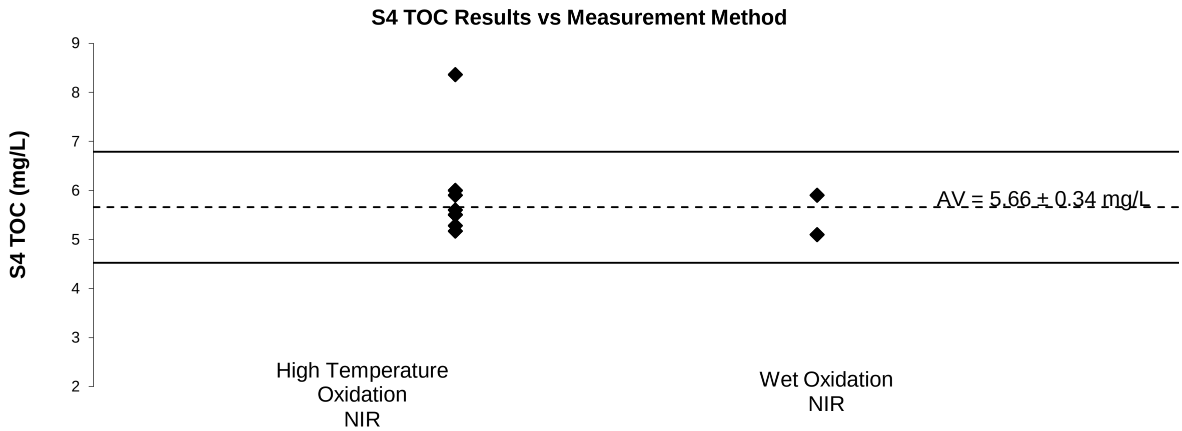
Plots of participants' results versus the instrumental technique used are presented in Figure 66. The most popular method was persulfate digestion with FIA determination

**Total Organic Carbon**. Participants performed well for TOC measurements in S4, with a robust between laboratory CV of 7.9%. All but one participant reported acceptable results (Figure 67).



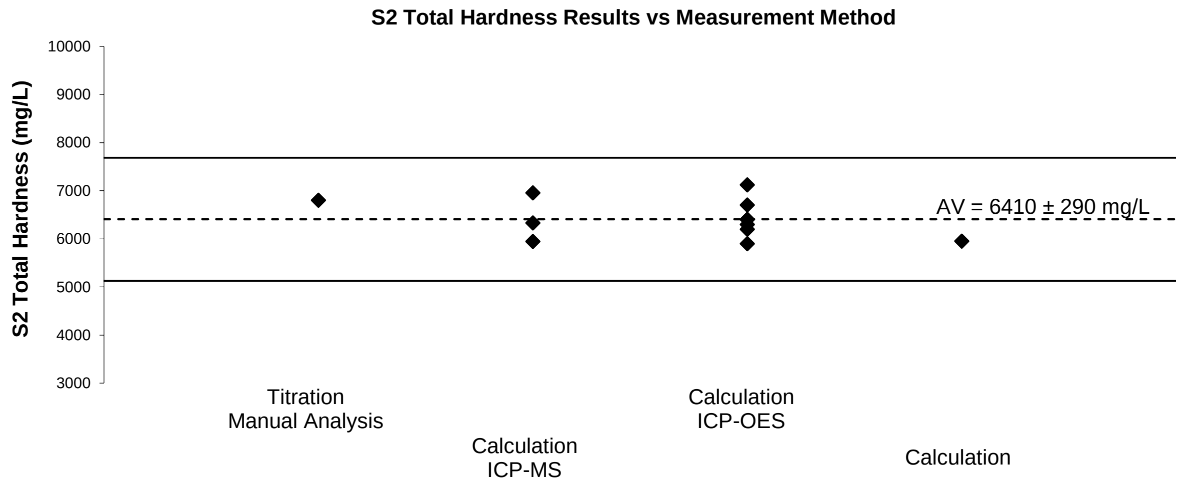

Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 66 S4-TN Results vs. Measurement Method




Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 67 S4-TOC Results vs. Measurement Method



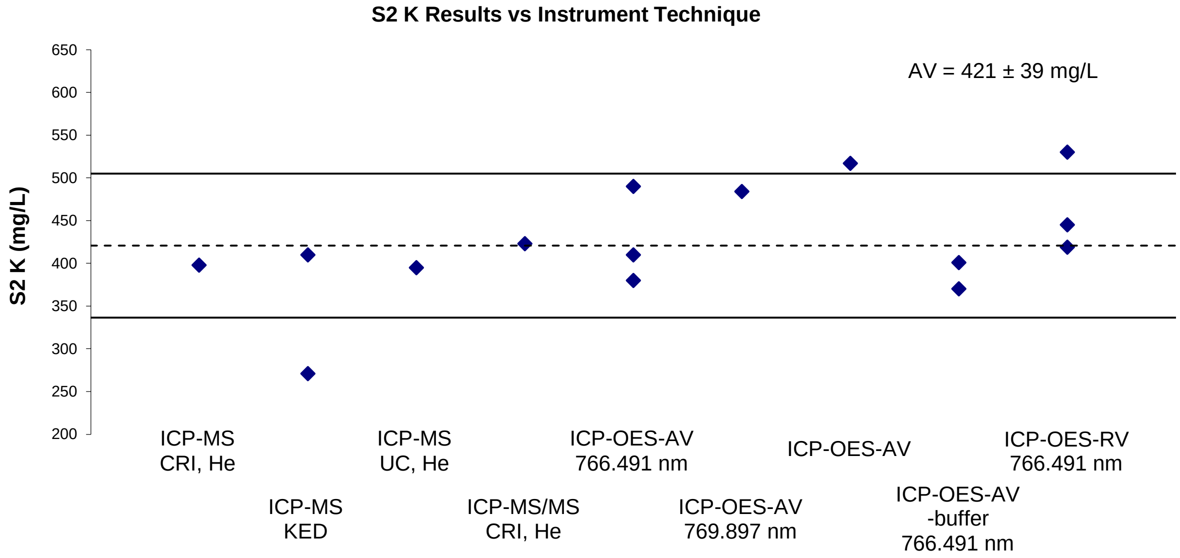

Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 68 S2-Total Hardness Results vs. Measurement Method

**Total Hardness** All reported results for total hardness in S2 returned acceptable results. ICP-OES was the preferred measurement technique (Figure 68).

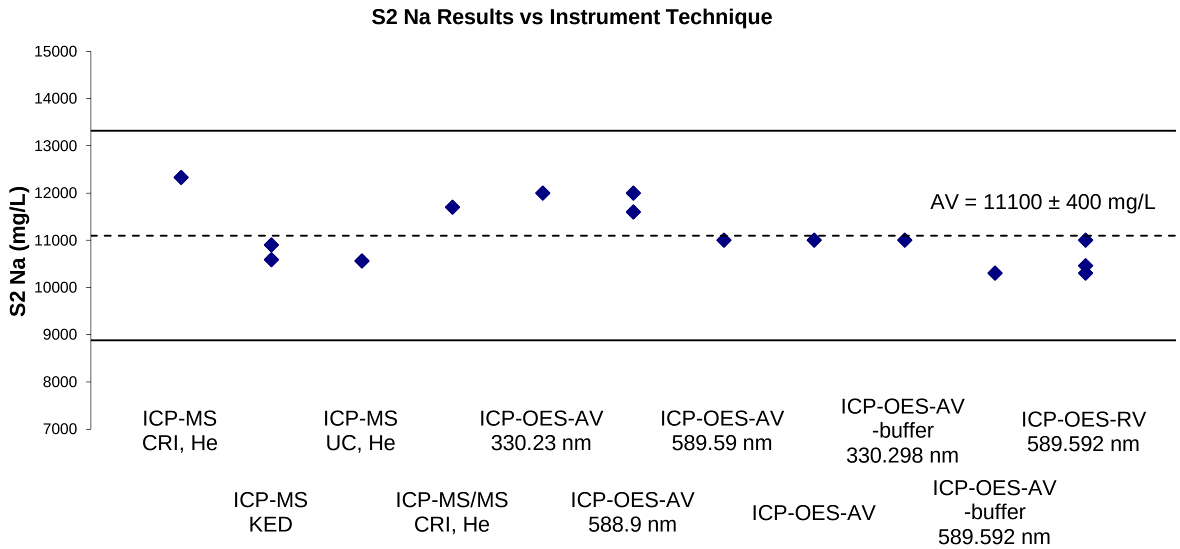
**Potassium and Sodium** Participants used various instrumental techniques for K and Na measurement in S2 (Figures 69 and 70). All results returned acceptable z-scores except for three K results (Figures 69 and 70).

ICP-OES was the preferred instrumental technique. Potassium emission signals are significantly enhanced in the presence of other easily ionised elements such as: Na, Al and Mg. Concentrations much higher than the true values are frequently obtained for K when measurements are made by ICP-OES with axial view plasma (ICP-OES-AV) without an ionisation buffer or correction equation.[16]




Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 69 S2-K Results vs. Instrument Technique




Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 70 S2-Na Results vs. Instrument Technique

## 6.6 Comparison with Previous NMI Proficiency Tests of Water Characteristics

AQA 24-18 is the 19th NMI proficiency test of water characteristics. Figure 71 presents participant performance over time. Despite different matrices and analytes' concentrations, on average, participant performance has remained consistent over time, with an average acceptable z-score rate of 92%, and an average acceptable En-score rate of 83%.

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.

## 6.7 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 | SS |
| 2 | CRM – GWS-6 (in-house reference standard), CRM-TMDW |
| 3 | RM |
| 5 | SS |
| 6 | CRM – Ammonium: ICNNH41, LOT: U2-NH736769. Nitrate: ICNNO31, LOT: T2-NOX72937. Nitrite: ICNNO21, LOT T2-NOX721185. Phosphorus: CGP1, LOT: U2-P728267 |
| 7 | CRM – KANSO Certified Reference Material lot CR (low range) was used for all samples while lot CP (medium range) was also used for silicate and phosphate. Bulk internal QC samples were also used for all samples. |
| 8 | CRM – CWW-TM-A, B and C (metals) Minerals 1 and 2 (salts) |
| 9 | RM |
| 10 | CRM – KANSO Certified Reference Material lot CR (low range) was used for all samples while lot CP (medium range) was also used for silicate and phosphate. Bulk internal QC samples were also used for all samples. |
| 12 | CRM, SS |
| 13 | SS |
| 15 | RM, CRM |
| 16 | CRM – WQC-ALK (HPS CRM) FOR ALKALINITY, NSI STANDARD FOR AMMONIA, PH EC ACCUSPEC CRM |
| 17 | CRM, SS |
| 18 | CRM, SS |
| 19 | CRM – KANSO Certified Reference Material lot CR (low range) was used for all samples. Bulk internal QC samples were also used for all samples. |
| 20 | CRM – Inorganic Venture-QCP MIN and Sulfur Standard, SS |
| 21 | SS |
| 22 | CRM, SS |
| 23 | RM – AQA 21-10 s2, AQA24-08 s1, AQA 22-11 S1, AQA 21-19 S2, AQA 22-18 S1 |

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’*[17]

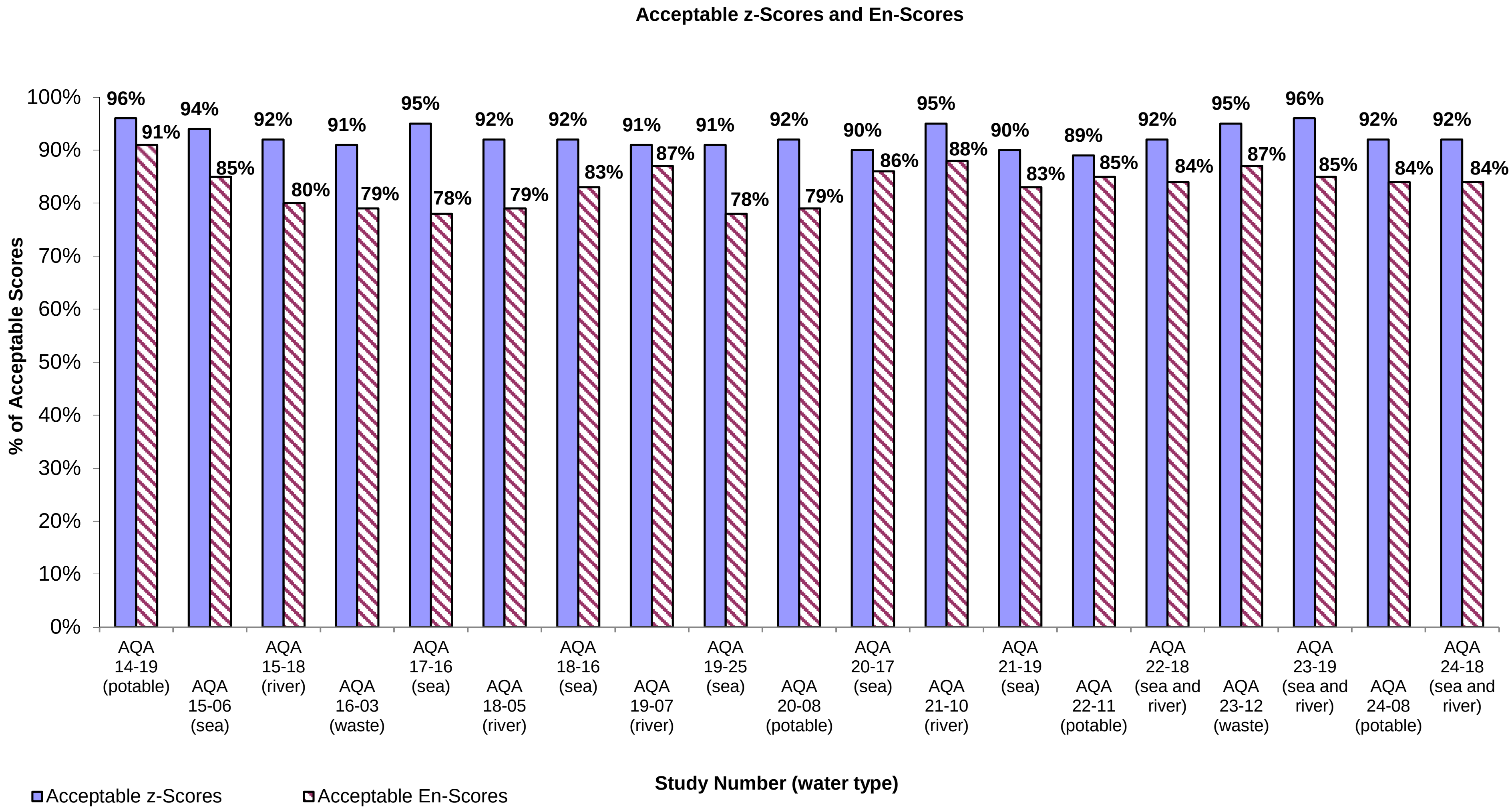



Figure 71 Participant Performance in Nutrients, Anions and Physical Tests in Water PT Studies over Time

## 7 REFERENCES

Note: For all undated references, the latest edition of the referenced document (including any amendments) applies.


[1] ISO17043, Conformity assessment – *General requirements for proficiency testing.*

[2] NMI, *Study Protocol for Proficiency Testing*, viewed February 2025, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf >.

[3] NMI, *Chemical Proficiency Testing Statistical Manual*, viewed February 2025, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

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

[5] National Environmental Protection Council, Schedule B1 Guidelines on the Investigation Levels for Soil and Groundwater, viewed February 2025, <https://www.legislation.gov.au/Details/F2013C00288/Html/Volume_2>.

[6] ISO13528, *Statistical methods for use in proficiency testing by inter laboratory comparisons.*

[7] Thompson, M, 2000, ‘Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing’, *Analyst,* vol 125, pp 385-386.

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

[9] Eurachem/CITAC Guide CG4, QUAM 2012, *Quantifying Uncertainty in Analytical Measurement*, 3rd ed., viewed February 2025, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[10] Bertil, M, 2004, *Nordtest Report Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories TR 537,* 4th Edition, Nordest Tekniikantie, Finland, Esopo.

[11] Hibbert, B 2007, *Quality Assurance for the Analytical Chemistry Laboratory*, Oxford University Press.

[12] ISO (2008), *Guide to the Expression of Uncertainty in Measurement (GUM)*, Geneva, Switzerland.

[13] Eurolab 2002, Technical Report No 1/2002 - Measurement Uncertainty in Testing.

[14] NMI, *Estimating Measurement Uncertainty for Chemists* – viewed, <https://www.industry.gov.au/client-services/training-and-assessment>.

[15] American Public Health Association, American Water Works Association, & Water Environmet Federation, *Standard Methods for the Examination of Water and Wastewater, 24th edition*

[16] Dubuisson, C. Poussel, E. (1997), Comparison of axially viewed and radially viewed inductively coupled plasma atomic emission spectrometry in terms of signal-to background ratio and matrix effects Journal of Analytical Atomic Spectrometry 12, 281-286.

[17] JCGM 200:2012, International vocabulary of metrology – Basic and General Concepts and Associated Terms (VIM), 3rd edition.

[18] National Measurement Institute, Method Number NT2.47: Determination of Total Acid Extractable Metals and Dissolved Elements in Water using Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry.

[19] NMI, *AQA 21-19 Nutrients, Anions and Physical Tests in Sea Water,* viewed February 2025, https://www.industry.gov.au/publications/proficiency-test-reports-2021.

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

### Sample Preparation

**Sample S1** was prepared from approximately 19 L of sea water fortified for four analytes of interest before being mixed thoroughly and dispensed into 200 mL portions each.

**Sample S2** was prepared from approximately 20 L of unspiked sea water dispensed into 200 mL portions each.

**Sample S3** was prepared from approximately 20 L of river water. The water was fortified for three analytes of interest, mixed thoroughly, and dispensed into 200 mL portions each.

**Sample S4** was 10 L of river water fortified for one analyte of interest, mixed thoroughly before being dispensed in portions of 200 mL each.

### Sample Analysis and Homogeneity Testing

Apart from alkalinity and silica in S2, and fluoride in S3 a partial homogeneity test was conducted for all other 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

The analysis for partial homogeneity were conducted by the CRV section of NMI as per method NT2.47. [19] A test portion of 0.5 mL or 2.5 mL for S2, and 8 mL for S3 was diluted to 10 mL with 2% $HNO_3$. 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 (AQA 23-19 S2 and AQA 23-19 S3) was carried through the same set of procedures and analysed simultaneously with the samples.

A summary of the wavelength and instrument conditions used for each analyte is presented in Table 48 for S2 and S3.

Table 48 Methodology for Dissolved Elements

| Analyte | Instrument | Internal Standard | Reaction/ Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength |
|---|---|---|---|---|---|---|
| S2-B | ICP-OES | Y | NA | NA | 4 | 249.678 nm |
| S2-Ca | ICP-OES | Y | NA | NA | 400 | 422.673 nm |
| S2-K | ICP-OES | Y | NA | NA | 4 | 766.491 nm |
| S2-Mg | ICP-OES | Y | NA | NA | 400 | 279.078 nm |
| S2-Na | ICP-OES | Y | NA | NA | 400 | 588.995 nm |
| S3-B | ICP-OES | Y | NA | NA | 1.25 | 249.678 nm |
| S3-Ca | ICP-OES | Y | NA | NA | 1.25 | 422.673 nm |
| S3-K | ICP-OES | Y | NA | NA | 1.25 | 766.491 nm |
| S3-Mg | ICP-OES | Y | NA | NA | 1.25 | 279.078 nm |
| S3-Na | ICP-OES | Y | NA | NA | 1.25 | 588.995 nm |

### Methodology for Tests Other Than Dissolved Elements

Analyses for all the tests other than dissolved elements were conducted by NMI Inorganics section. A summary of the measurement methods and instrumental techniques is presented in Table 49.

Table 49 Methodology for Tests Other Than Dissolved Elements

| Test | Measurement Method | Instrument |
|---|---|---|
| Ammonia-N | Fluorometric Determination – OPA Method | SFA |
| Bromide | Ion Chromatographic Method | IC |
| Chloride | Ion Chromatographic Method | IC |
| Dissolved Organic Carbon | High-Temperature Oxidation | NIR-detector |
| Fluoride | Ion Chromatographic Method | IC |
| Nitrate-N | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA |
| Orthophosphate-P | Ascorbic Acid Colorimetric Method | DA |
| Sulphate | Ion Chromatographic Method | IC |
| Total Dissolved Nitrogen | Persulfate Digestion | SFA |
| Total Dissolved Phosphorus | $K_2S_2O_8$ Digestion; Ascorbic Acid Colorimetric Method | SFA |
| Total Kjeldahl Nitrogen | TKN = TN-NOx (K2S2O8 Digestion) | SFA |
| Total Nitrogen | Persulfate Digestion | SFA |
| Total Organic Carbon | High Temperature Oxidation | NIR-detector |

## APPENDIX 2 - STABILITY STUDY

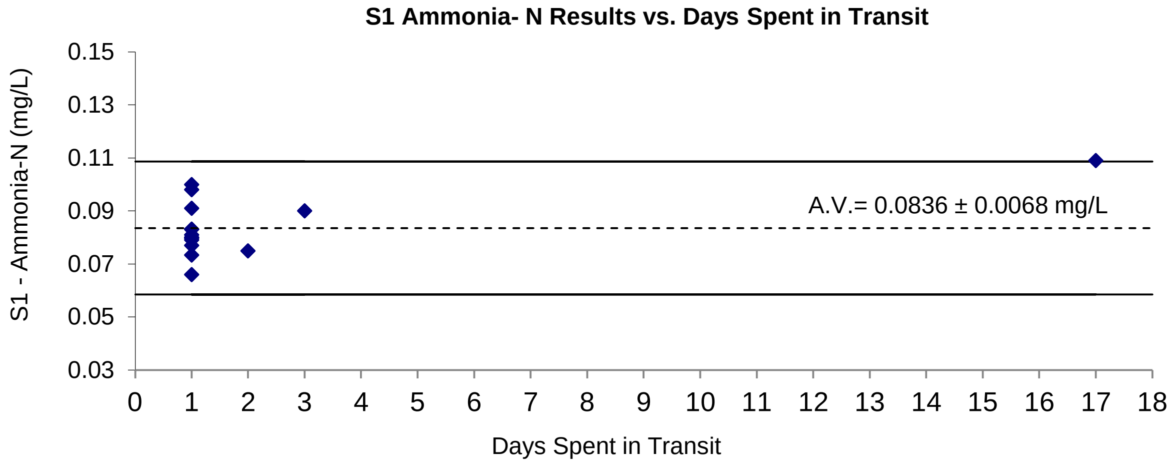
The tests samples were dispatched on 21 October 2024. Participants were advised to store the samples S1, S3 and S4 frozen, if unable to commence analysis on the day of receipt. Samples' condition on receipt and the date when the samples were received and analysed by participants are presented in Table 50.

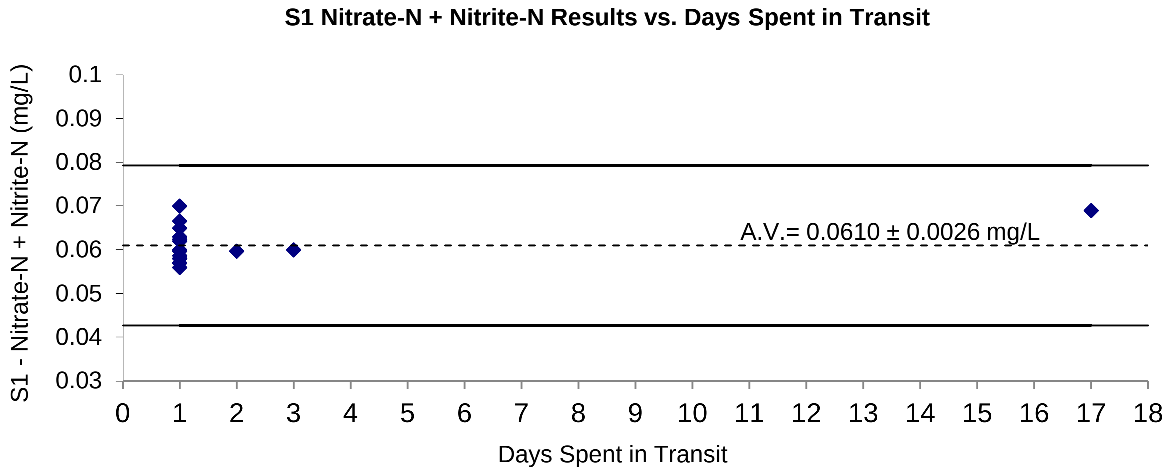
Table 50 Sample S1, S3 and S4 Condition on Receipt and the Date When the Sample was Received and Analysed

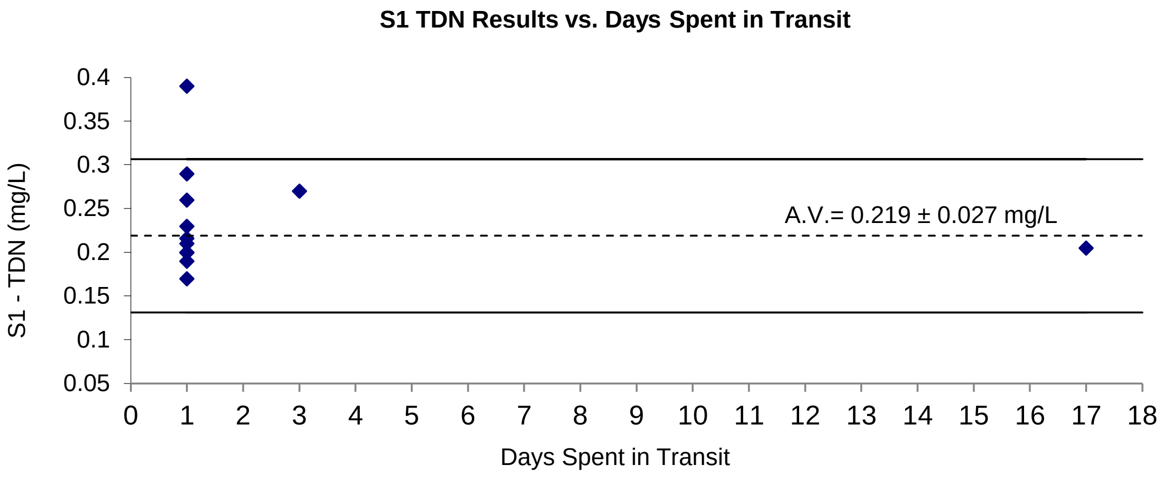
| Lab Code | Received Date | S1 | | S3 | | S4 | |
|---|---|---|---|---|---|---|---|
| | | Condition on Receipt | Date of Analysis | Condition on Receipt | Date of Analysis | Condition on Receipt | Date of Analysis |
| **1** | 22/10/2024 | frozen | 24/10/2024 | frozen | 24/10/2024 | frozen | 24/10/2024 |
| **2** | 25/10/2024 | NA | NA | frozen | 04/11/2024 | NA | NA |
| **3** | 29/10/2024 | NA | NA | Chilled. Inner Ice packs not frozen but the box had been refrigerated before collection | 14/11/2024 | NA | NA |
| **4** | 22/10/2024 | NA | NA | frozen | 23/10/2024 | NA | NA |
| **5** | 22/10/2024 | cold | 22/10/2024 | cold | 22/10/2024 | cold | 22/10/2024 |
| **6** | 24/10/2024 | Cold | 25/10/2024 | Cold | 25/10/2024 | Cold | 25/10/2024 |
| **7** | 22/10/2024 | 70% frozen | 31/10/2024 | NA | NA | NA | NA |
| **8** | 7/11/2024 | cold | 13/11/2024 | cold | 13/11/2024 | cold | 14/11/2024 |
| **9** | 23/10/2024 | frozen | 25/10/2024 | NA | NA | frozen | 25/10/2024 |
| **10** | 22/10/2024 | 70% frozen | 07/11/2024 | NA | NA | NA | NA |
| **11** | 22/10/2024 | frozen | 12/11/2024 | frozen | 12/11/2024 | NR | NR |
| **12** | 22/10/2024 | frozen | 22/10/2024 | frozen | 22/10/2024 | frozen | 22/10/2024 |
| **13** | 22/10/2024 | frozen | 24/10/2024 | frozen | 24/10/2024 | frozen | 24/10/2024 |
| **14** | 22/10/2024 | NA | NA | NA | NA | NA | NA |
| **15** | 22/10/2024 | frozen | NR | frozen | NR | frozen | NR |
| **16** | 23/10/2024 | frozen | 24/10/2024 | frozen | 24/10/2024 | frozen | 24/10/2024 |
| **17** | 22/10/2024 | Partially defrosted | 28/10/2024 | frozen | 28/10/2024 | frozen | 28/10/2024 |
| **18** | 22/10/2024 | frozen | 23/10/2024 | frozen | 23/10/2024 | frozen | 23/10/2024 |
| **19** | 22/10/2024 | 70% frozen | 13/11/2024 | NA | NA | NA | NA |
| **20** | 22/10/2024 | frozen | 24/10/2024 | NA | NA | NA | NA |
| **21** | 22/10/2024 | Frozen | NR | Frozen | NR | Frozen | NR |
| **22** | 22/10/2024 | frozen | 01/11/2024 | frozen | 01/11/2024 | frozen | 04/11/2024 |
| **23** | 22/10/2024 | frozen | 29/10/2024 | frozen | 29/10/2024 | frozen | 29/10/2024 |

NA = Not Applicable, NR = Not Reported.

No relationship between participants' results reported for less stable analytes (ammonia-N, NOx-N, TDN), samples' condition on receipt or the number of days spent in transit, were evident (Figures 72 and 73).

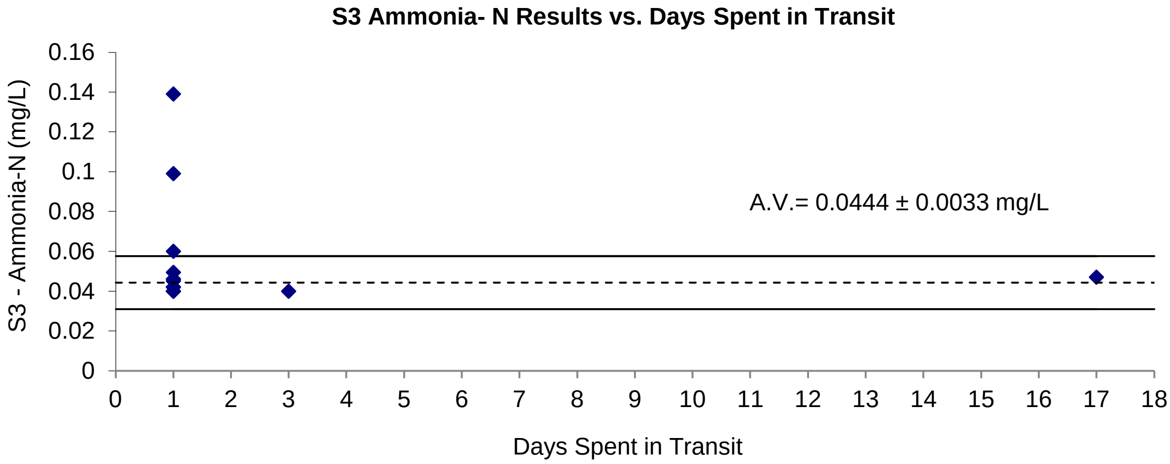


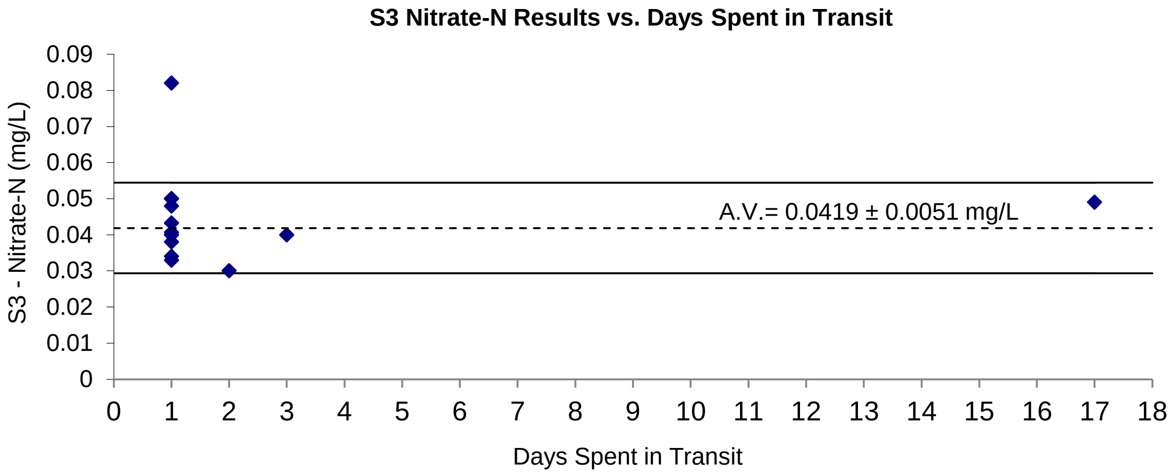



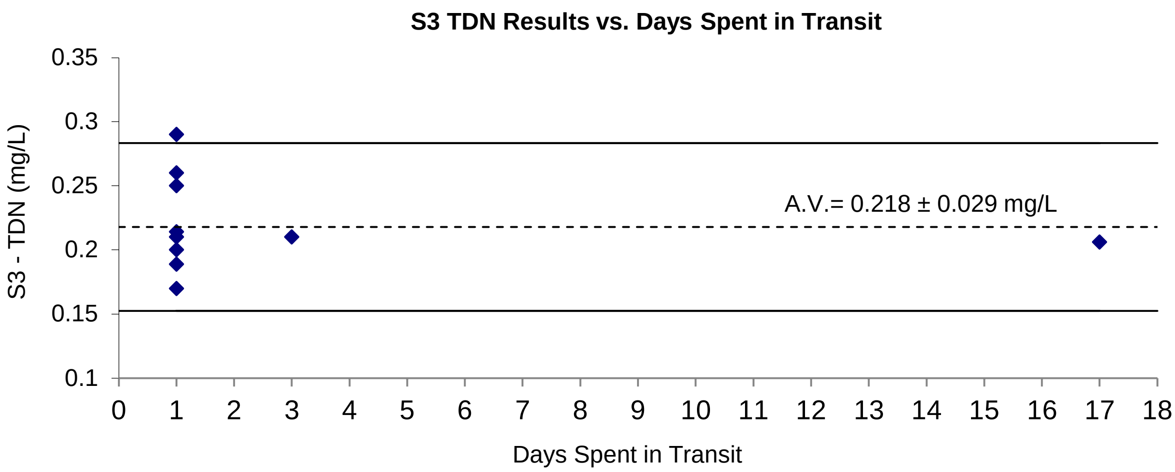




Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 72 Results vs Days Spent in Transit

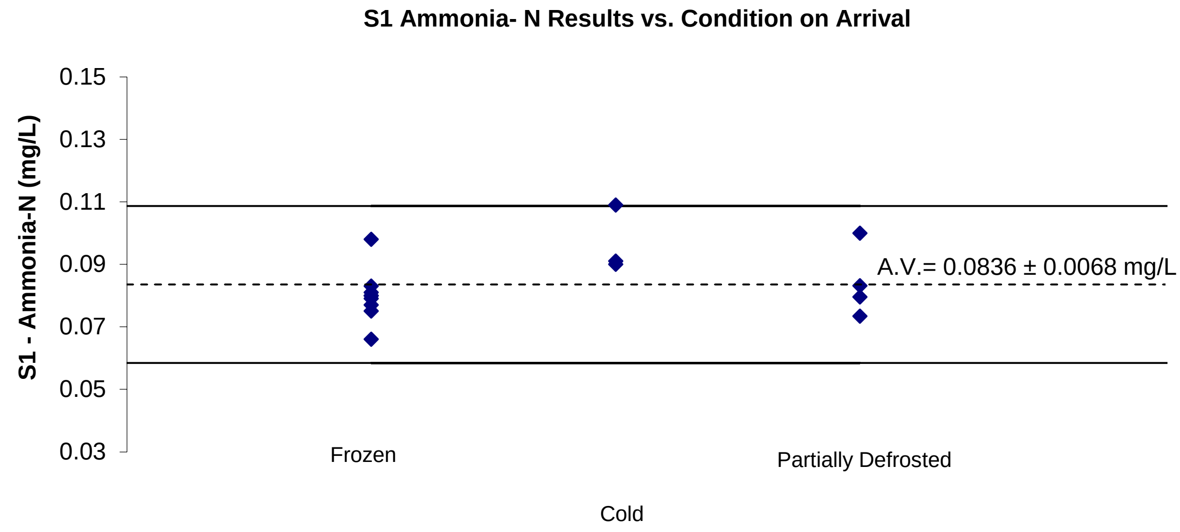


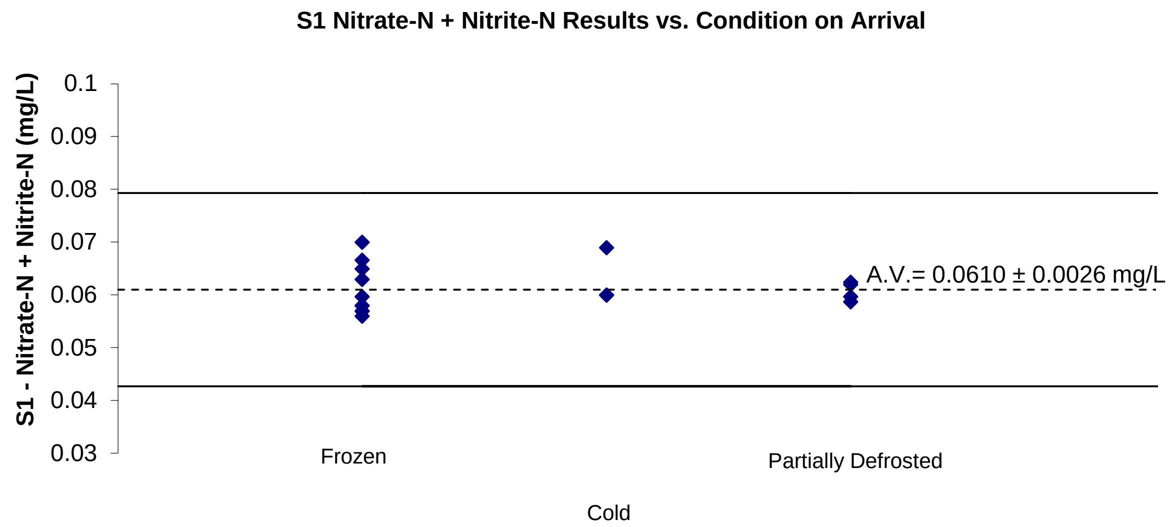



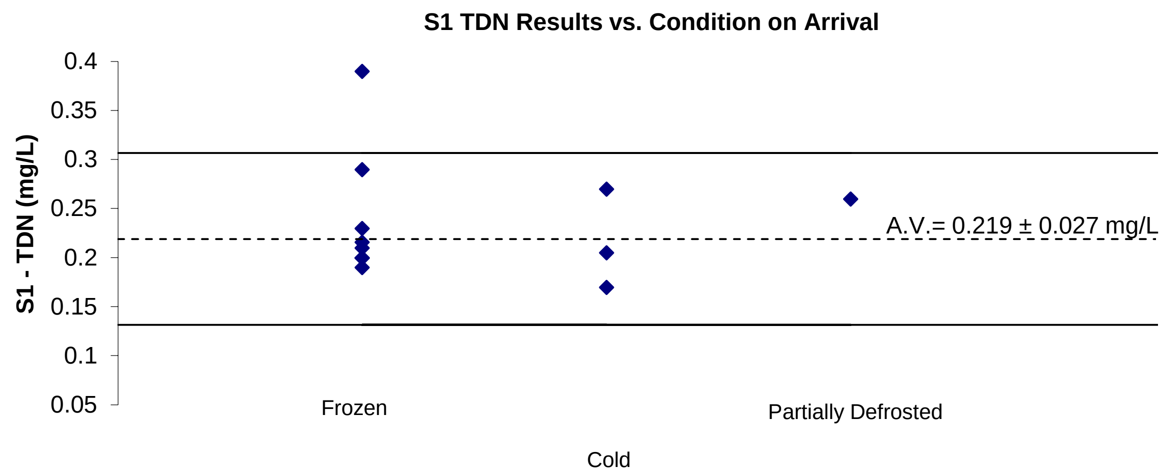




Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 72 Results vs Days Spent in Transit (continued)

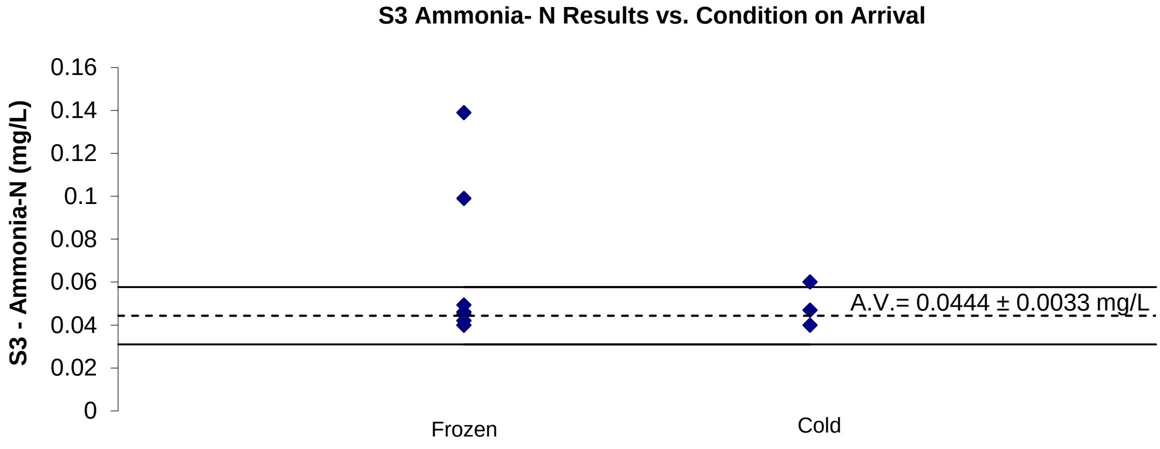


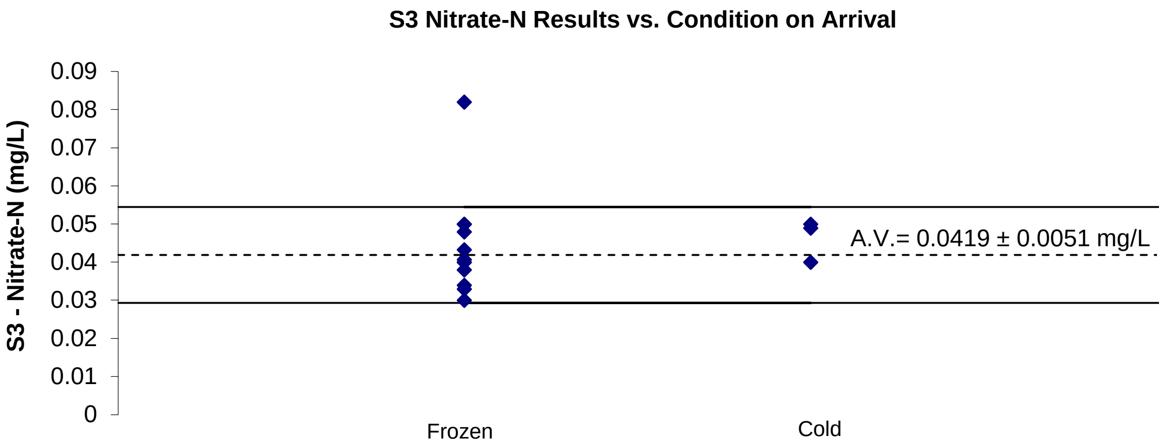



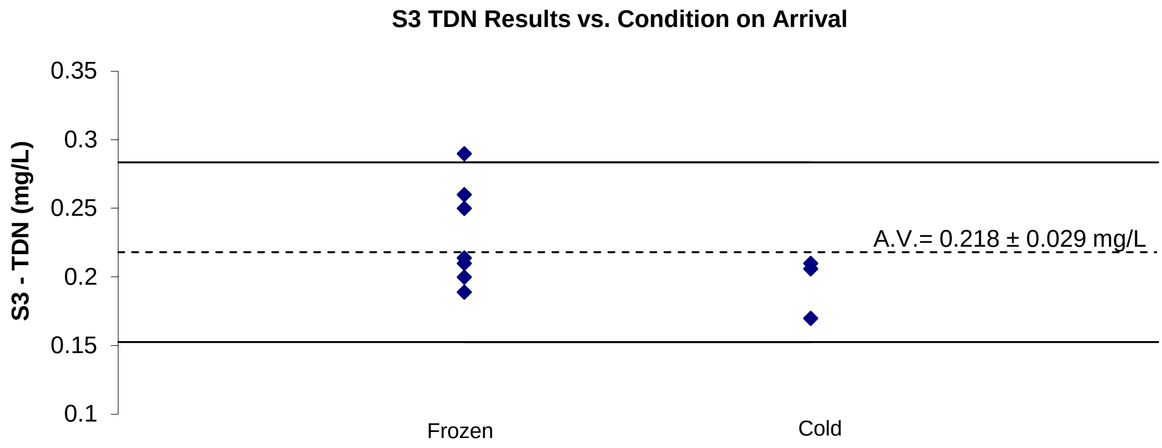




Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 73 Results vs Condition on Arrival




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

Figure 73 Results vs Condition on Arrival (continued)

The same packing and dispatching procedure were followed in the present study as in PT study AQA 21-19. In this study one set of samples, sent overseas, spent eight days in transit. To assess analytes' stability during transport, results from the "transport set of samples" with eight days in transit (T8) were compared with results from a set of samples sent to the same laboratory but with only two days in transit (T2). The results from this study are presented in Figure 74. The two sets of results were in good agreement with each other within their stated uncertainties.[19]

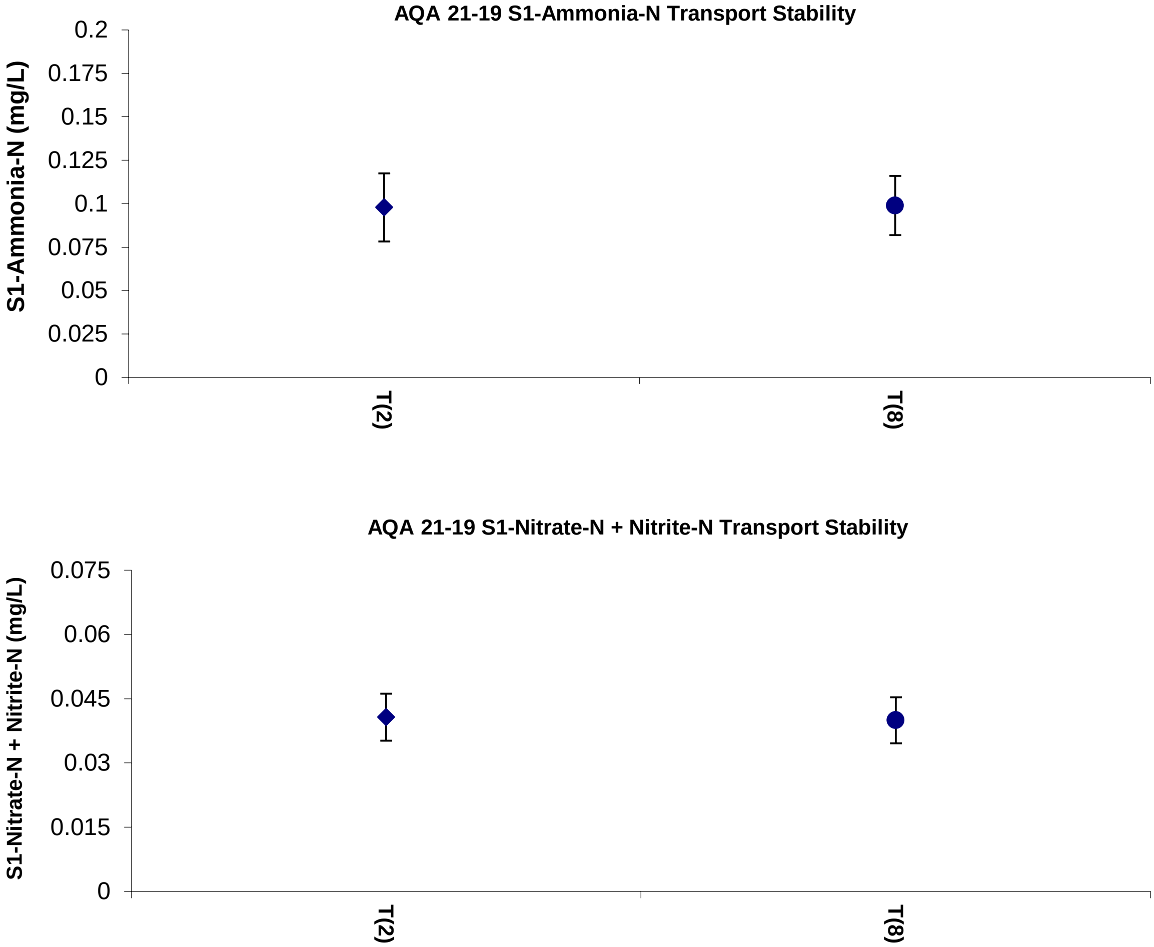



Figure 74 AQA 21-19 Transport Stability Results

**Stability Study**

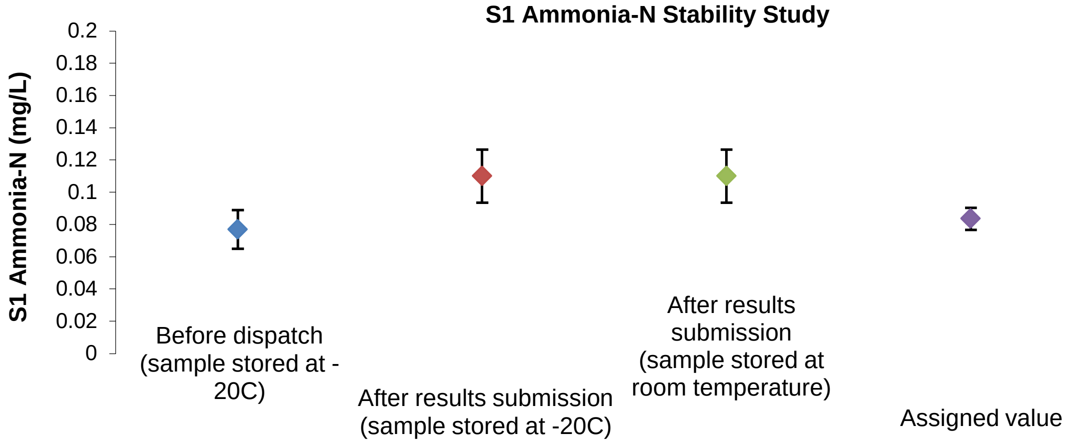
In previous PT studies, stability studies conducted for nutrients and physical tests in water found no significant changes in any of the analytes' concentrations. However, a stability study was still conducted in the present study for the less stable analytes: ammonia-N, NOx-N in S1 and ammonia-N and $NO_3$-N in S3.

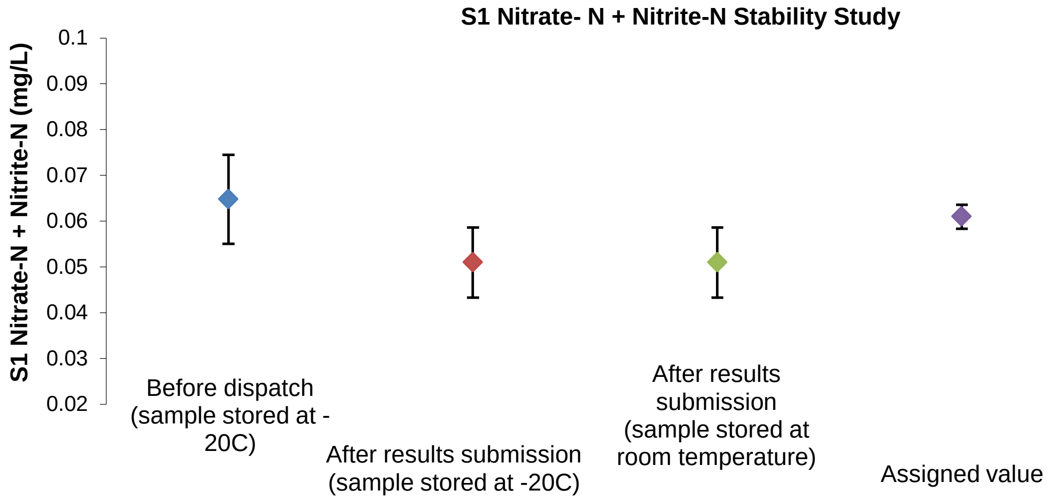
Two main factors were considered to affect the stability of these tests in water: storage condition and time.

To test for storage stability, the results from a sample stored at -20°C (reference samples) was compared with the results from one sample left out on a laboratory table for four days (room). These samples were analysed at the same time.

To check sample stability during the study conduct, a comparison was conducted of the results from samples analysed before the samples' dispatch (T0) versus those analysed at the end of the study, after submission of results (T1). Each sample was analysed in duplicate together with a set of quality control samples consisting of blanks, blank matrix spikes, control samples, duplicates and sample matrix spikes.

Results from both studies were in good agreement with each other and the assigned value were within their stated uncertainties (Figure 75).



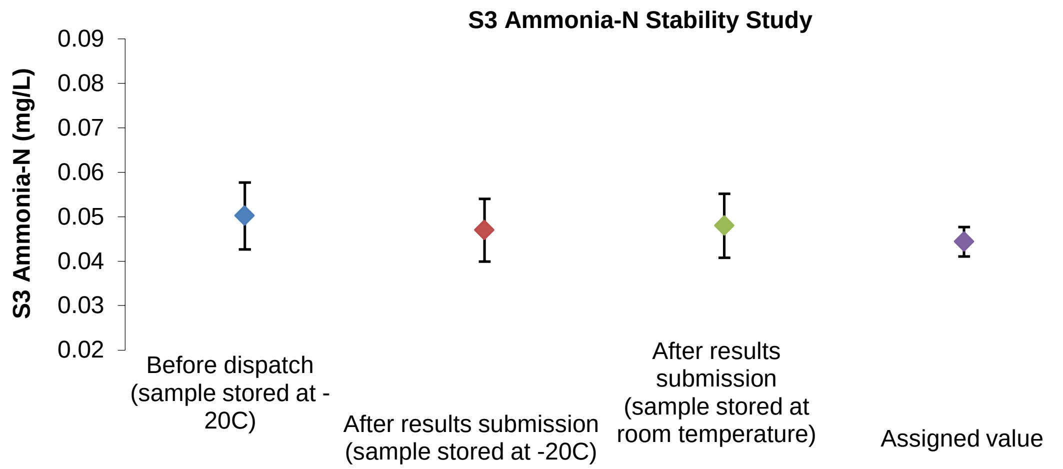




Figure 75 Stability Study Results

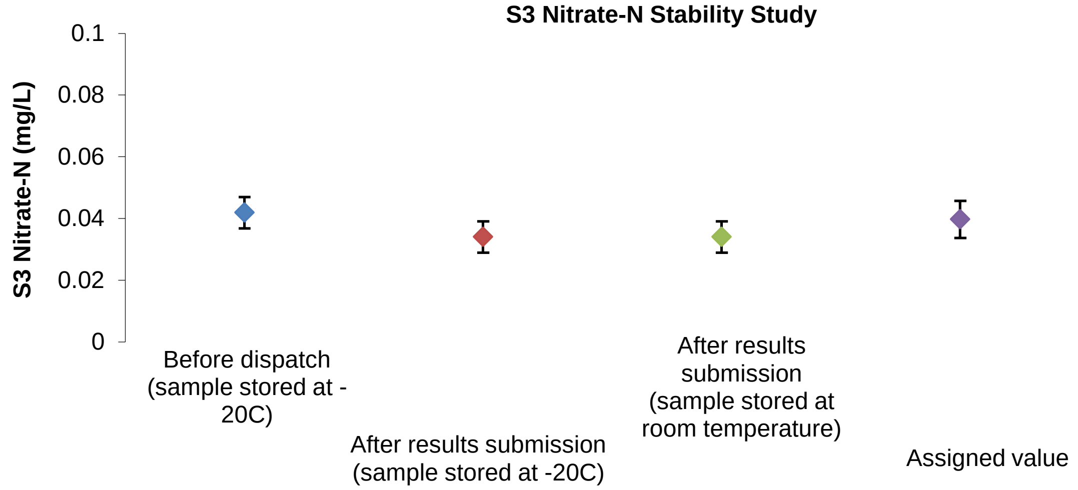



Figure 75 Stability Study Results (continued)

## APPENDIX 3 – ASSIGNED VALUE, Z-SCORE AND $E_N$ SCORE CALCULATION

The assigned value was calculated as the robust average using the procedure described in 'ISO13528:2015(E), 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 51.

Table 51 Uncertainty of Assigned Value for K in Sample S3

| | |
|---|---|
| No. results (p) | 16 |
| Robust Average | 3.23 mg/L |
| $S_{rob\ av}$ | 0.245 mg/L |
| $u_{rob\ av}$ | 0.077 mg/L |
| $k$ | 2 |
| $U_{rob\ av}$ | 0.15 mg/L |

The assigned value for **K** in Sample S3 is **3.23 ± 0.15 mg/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 9).

A worked example is set out below in Table 52.

Table 52 z-Score and $E_n$-score for the K result reported by Laboratory 21 in S3

| Result mg/L | Assigned Value mg/L | Set Target Standard Deviation | z-Score | $E_n$-Score |
|---|---|---|---|---|
| 3.29 ± 0.46 | 3.23 ± 0.15 | 10% as CV or 0.1 x 3.23 = = 0.323 mg/L | $z = \frac{(3.29 - 3.23)}{0.323}$ z = 0.19 | $En = \frac{(3.29 - 3.23)}{\sqrt{0.46^2 + 0.15^2}}$ $E_n$ = 0.12 |

## APPENDIX 4 - USING PT DATA FOR UNCERTAINTY EVALUATION

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 evaluate the uncertainty of their measurement results.[10, 12] An example is given in Table 53. Between 2014 and 2024, NMI carried out 18 proficiency tests for nutrients, anions and physical tests in water. These studies involved measurements of these analytes in potable, fresh (river), waste and seawater.

Laboratory X participated and submitted acceptable results for all studies with chloride in these PTs. This data can usefully be separated into two ranges of results 0.5 to 1000 mg/L and greater than 1000 mg/L (Tables 53 and 54).

Table 53 Laboratory X Reported Results for Chloride at 0.5 to 1000 mg/L Level

| Study No. | Sample | Laboratory result mg/L | Assigned value mg/L | Number of Results | Robust CV of all results (%) |
|---|---|---|---|---|---|
| AQA 14-19 | Potable | 51.9 ± 10 | 55.4 ± 1.4 | 8 | 2.9 |
| AQA 15-18 | River | 65.7 ± 10 | 70.3 ± 3.6 | 10 | 6.5 |
| AQA 18-05 | River | 68 ± 8.0 | 71.3 ± 1.5 | 17 | 3.4 |
| AQA 19-07 | River | 57.0 ± 12 | 53.7 ± 2.0 | 10 | 4.7 |
| AQA 20-08 | Potable | 33.4 ± 7.0 | 41.6 ± 1.9 | 13 | 6.7 |
| AQA 21-10 | River | 81 ± 10 | 86.3 ± 2.7 | 20 | 5.7 |
| AQA 22-11 | Potable | 22.3 ± 5.0 | 25.5 ± 0.8 | 19 | 5.5 |
| AQA 22-18 | River | 60 ± 10 | 62.3 ± 1.5 | 19 | 4.1 |
| AQA 23-12 | Waste | 152 ± 20 | 142 ± 6 | 16 | 6.3 |
| AQA 23-19 | River | 39.8 ± 4.5 | 39.8 ± 2.6 | 11 | 8.7 |
| AQA 24-08 | Potable | 33.3 ± 5.0 | 28.9 ± 1.0 | 19 | 6.3 |
| | | | | Average | 5.5* |
| $\boldsymbol{pooled\ s}\% = \sqrt{\frac{(\mathbf{8-1})\times\mathbf{2.9^2}+(\mathbf{10-1})\times\mathbf{6.5^2}+\cdots\cdots\cdots+(\mathbf{19-1})\times\mathbf{6.3^2})}{\mathbf{162-11}}}$ | | | | | 5.7 |

* The pooled standard deviation was used.

Table 54 Laboratory X Reported Results for Chloride at >1000 mg/L Level

| Study No. | Sample | Laboratory result mg/L | Assigned value mg/L | Number of Results | Robust CV of all results (%) |
|---|---|---|---|---|---|
| AQA 16-03 | Waste | 3099 ± 320 | 2990 ± 170 | 8 | 6.3 |
| AQA 17-16 | Sea | 13100 ± 1300 | 12800 ± 420 | 10 | 4.1 |
| AQA 18-16 | Sea | 16600 ± 1600 | 17300 ± 1600 | 13 | 13 |
| AQA 19-25 | Sea | 20000 ± 2000 | 20500 ± 1000 | 13 | 2.2 |
| AQA 20-17 | Sea | 9800 ± 980 | 10700 ± 400 | 10 | 4.9 |
| AQA 21-19 | Sea | 19440 ± 1950 | 20100 ± 600 | 9 | 3.8 |
| AQA 22-18 | Sea | 14073 ± 1400 | 13800 ± 500 | 14 | 5.3 |
| AQA 23-19 | Sea | 17132 ± 1750 | 16800 ± 500 | 12 | 4.2 |
| AQA 24-18 | Sea | 22659 ± 2270 | 21600 ± 500 | 15 | 3.9 |
| | | | | Average | 5.3* |
| $\boldsymbol{pooled\ s}\% = \sqrt{\frac{(\mathbf{8-1})\times\mathbf{6.3^2}+(\mathbf{10-1})\times\mathbf{4.1^2}+\cdots\cdots\cdots+(\mathbf{15-1})\times\mathbf{3.9^2})}{\mathbf{104-9}}}$ | | | | | 6.1 |

* The pooled standard deviation was used.

Taking the pooled standard deviation of these PT samples for each concentration range gives estimates of the relative standard uncertainty of 5.7% and 6.1% respectively. Using a coverage factor of two gives a relative expanded uncertainty of 12% at 0.5 – 1000 mg/L level, and 13% at >1000 mg/L level, at a level of confidence of approximately 95%.

Table 55 sets out the expanded uncertainty for results of the measurement of Chloride in potable, fresh, waste or sea water over the range 0.5 – 30000 mg/L.

Table 55 Uncertainty of Chloride results estimated using PT data

| Results mg/L | Uncertainty mg/L |
|---|---|
| 20.0 | 2.4 |
| 500 | 60 |
| 1000 | 130 |
| 7500 | 980 |
| 15000 | 2000 |
| 30000 | 3900 |

The MU evaluation made using PT data is close to Laboratory X's uncertainty reported with their PT results. The evaluation of 12% and 13% passes the test of being reasonable, and the analysis of the four different matrices over eleven years can safely be assumed to include all the relevant uncertainty components (different operators, reagents, calibrants etc), and so complies with ISO 17025:2018.[8]

## APPENDIX 5 - 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 |
| DA | Discreet Analyser |
| dNPOC | Dissolved non-purgeable organic carbon |
| FIA | Flow Injection Analyser |
| GUM | Guide to the Expression of Uncertainty in Measurement |
| HV | Homogeneity Value |
| IC | Ion Chromatograph |
| ICP | Inductively Coupled Plasma |
| ICP-MS | Inductively Coupled Plasma - Mass Spectrometry |
| ICP-MS/MS | Inductively Coupled Plasma - Tandem Mass Spectrometry |
| ICP-OES | Inductively Coupled Plasma - Optical Emission Spectrometry |
| ICP-OES-AV | Inductively Coupled Plasma - Optical Emission Spectrometry- axial view |
| ICP-OES-AV-buffer | Inductively Coupled Plasma - Optical Emission Spectrometry- axial view with buffer |
| ICP-OES-RV | Inductively Coupled Plasma - Optical Emission Spectrometry- radial view |
| Max | Maximum Value in a Set of Results |
| Md | Median |
| Min | Minimum Value in a Set of Results |
| MU | Measurement Uncertainty |
| NEDD | N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride) |
| NEPM | National Environment Protection Measures |
| NIR | Near-infrared |
| NMI | National Measurement Institute (of Australia) |
| NOx | Nitrous Oxides |
| NR | Not Reported |
| NT | Not Tested |
| OPA | Orthophtaldialdehyde |
| ORS | Octopole Reaction System |
| PCV | Performance Coefficient of Variation |
| PT | Proficiency Test |
| RA | Robust Average |
| RM | Reference Material |
| Robust CV | Robust Coefficient of Variation |
| Robust SD | Robust Standard Deviation |
| SV | Spiked or Formulated Concentration of a PT Sample |
| SFA | Segment Flow Analyser |
| SI | The International System of Units |
| SPADNS | 1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid |
| SS | Spiked Samples |
| $s_a/\sigma$ | Analytical Standard Deviation Divided by the Target Standard Deviation |
| Target SD | Target Standard Deviation |

| | |
|---|---|
| σ | Target Standard Deviation |
| TKN | Total Kjeldahl Nitrogen |
| UC | Universal Cell |
| USEPA | United Stated Environmental Protection Agency |
| UV-Vis | Ultraviolet and Visible Spectroscopy |

## APPENDIX 6 - METHODOLOGY FOR S1

Table 56 Measurement Methods and Instrument Techniques for Ammonia-N

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Colorimetric - Phenate Method | DA | APHA |
| 5 | Colorimetric - Phenate Method | DA | APHA |
| 6 | Colorimetric - Phenate Method | FIA | APHA |
| 7 | Fluorometric Determination - OPA Method | SFA | Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57) |
| 8 | Colorimetric - Phenate Method | FIA | |
| 9 | Colorimetric - Phenate Method | FIA | APHA4500-NH3 |
| 10 | Fluorometric Determination - OPA Method | SFA | Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57) |
| 13 | Colorimetric - Phenate Method | DA | |
| 15 | Colorimetric - Salicylate Method | SFA | In house |
| 16 | Ion Selective Electrode Method | Ion Selective Electrode | APHA 4500 |
| 17 | Colorimetric - Phenate Method | FIA | Lachat QuikChem |
| 18 | Fluorometric Determination - OPA Method | SFA | SFA |
| 19 | Fluorometric Determination - OPA Method | SFA | Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57) |
| 20 | Colorimetric - Salicylate Method | DA | APHA4500NH3 |
| 21 | Colorimetric - Phenate Method | FIA | Inhouse |
| 22 | Colorimetric - Phenate Method | SFA | APHA |
| 23 | Colorimetric - Phenate Method | FIA | APHA |

Table 57 Measurement Methods and Instrument Techniques for Chloride

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ion Chromatographic Method | IC | APHA |
| 5 | Ion Chromatographic Method | IC | APHA |
| 6 | Ion Chromatographic Method | IC | Inhouse |
| 8 | ICP-Method | ICP-MS | In house |
| 9 | Ion Chromatographic Method | IC | APHA4110B(modified) |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Ion Chromatographic Method | IC | |
| 13 | Ion Chromatographic Method | IC | |
| 15 | Ion Chromatographic Method | IC | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Ion Chromatographic Method | IC | APHA |
| 18 | Ion Chromatographic Method | IC | APHA |
| 20 | Mercuric Thiocyanate | DA | APHA4500Cl- |
| 21 | Ferricyanide Colorimetric Method | FIA | Inhouse |
| 22 | Ferricyanide Colorimetric Method | DA | APHA |

## Table 58 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | High-Temperature Oxidation | NIR-detector | APHA |
| 5 | High-Temperature Oxidation | NIR-detector | APHA |
| 8 | High-Temperature Oxidation | Shimadzu TOC-L | |
| 9 | Persulfate-Ultraviolet Oxidation | NIR-detector | APHA5310C(modified) |
| 12 | High-Temperature Oxidation | NIR-detector | |
| 13 | High-Temperature Oxidation | NIR-detector | |
| 15 | Wet-Oxidation | NIR-detector | In house |
| 17 | High-Temperature Oxidation | NIR-detector | APHA |
| 18 | High-Temperature Oxidation | NIR-detector | APHA |
| 20 | High-Temperature Oxidation | NIR-detector | APHA5310B |
| 21 | High-Temperature Oxidation | NIR-detector | Inhouse |
| 22 | High-Temperature Oxidation | NIR-detector | APHA |

## Table 59 Measurement Methods and Instrument Techniques for Fluoride

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ion Selective Electrode Method | Ion Selective Electrode | APHA |
| 5 | Ion Selective Electrode Method | Ion Selective Electrode | APHA |
| 6 | Ion Chromatographic Method | IC | Inhouse |
| 8 | Ion Selective Electrode Method | Ion Selective Electrode | |
| 9 | Ion Selective Electrode Method | Ion Selective Electrode | APHA4500-F-C |
| 11 | Ion Chromatographic Method | Ion Chromatographic Method | |
| 12 | Ion Chromatographic Method | IC | |
| 13 | Ion Selective Electrode Method | Ion Selective Electrode | |
| 15 | Ion Chromatographic Method | IC | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Ion Chromatographic Method | IC | APHA |
| 18 | Ion Selective Electrode Method | Ion Selective Electrode | APHA |
| 20 | Ion Selective Electrode Method | Ion Selective Electrode | APHA4500F |
| 21 | Ion Selective Electrode Method | Ion Selective Electrode | Inhouse |
| 22 | Ion Selective Electrode Method | Auto Titration | APHA |

Table 60 Measurement Methods and Instrument Techniques for Nitrate-N + Nitrite-N

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Colorimetric -vanadium III method | DA | APHA |
| 5 | Colorimetric -vanadium III method | DA | APHA |
| 6 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | APHA |
| 7 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 8 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | |
| 9 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | APHA-4500NO3(modified) |
| 10 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 11 | Ion Chromatographic Method | Ion Chromatographic Method | |
| 12 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | |
| 13 | Colorimetric -vanadium III method | DA | |
| 15 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | Lachat QuikChem |
| 18 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | SFA |
| 19 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 20 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | APHA4500NO32 |
| 21 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | Inhouse |
| 22 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | APHA |
| 23 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | APHA |

Table 61 Measurement Methods and Instrument Techniques for Orthophosphate-P

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ascorbic Acid Colorimetric Method | DA | APHA |
| 5 | Ascorbic Acid Colorimetric Method | DA | APHA |
| 6 | Ascorbic Acid Colorimetric Method | FIA | APHA |
| 7 | Ascorbic Acid Colorimetric Method | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 8 | Ascorbic Acid Colorimetric Method | FIA | |
| 9 | Ascorbic Acid Colorimetric Method | FIA | APHA4500-PG |
| 10 | Ascorbic Acid Colorimetric Method | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 11 | Ion Chromatographic Method | Ion Chromatographic Method | |
| 12 | Ascorbic Acid Colorimetric Method | DA | |
| 13 | Vanadomolybdophosphoric Colorimetric Method | DA | |
| 15 | Ascorbic Acid Colorimetric Method | SFA | In house |
| 17 | Ascorbic Acid Colorimetric Method | FIA | Lachat QuikChem |
| 18 | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 19 | Ascorbic Acid Colorimetric Method | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 20 | Vanadomolybdophosphoric Colorimetric Method | DA | APHA4500P |
| 21 | Ascorbic Acid Colorimetric Method | FIA | Inhouse |
| 22 | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 23 | Ascorbic Acid Colorimetric Method | FIA | APHA |

Table 62 Measurement Methods and Instrument Techniques for Sulphate

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ion Chromatographic Method | IC | APHA |
| 5 | Ion Chromatographic Method | DA | APHA |
| 6 | Ion Chromatographic Method | IC | Inhouse |
| 8 | ICP Method | ICP-MS | In House |
| 9 | Ion Chromatographic Method | IC | APHA4500-PG |
| 11 | Ion Chromatographic Method | Ion Chromatographic Method | |
| 12 | Ion Chromatographic Method | IC | |
| 13 | Ion Chromatographic Method | IC | |
| 15 | Ion Chromatographic Method | IC | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Ion Chromatographic Method | IC | APHA |
| 18 | Ion Chromatographic Method | IC | APHA |
| 20 | ICP Method | ICP-OES | APHA3120B |
| 21 | Turbidimetric Method | FIA | Inhouse |
| 22 | Turbidimetric Method | DA | APHA |

Table 63 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Calculation (TKN+NOx) | DA | APHA |
| 5 | COMBUSTION | Other | |
| 6 | Persulfate digestion | FIA | APHA |
| 8 | Persulfate digestion | FIA | |
| 9 | Calculation (TKN+NOx) | | |
| 12 | Persulfate digestion | SFA | |
| 13 | Combustion analyser | | |
| 15 | Calculation (TKN+NOx) | SFA | In house |
| 17 | Persulfate digestion | FIA | Lachat QuikChem |
| 18 | Persulfate digestion | SFA | APHA |
| 20 | Calculation (TKN+NOx) | Not Applicable | NA |
| 21 | Persulfate digestion | FIA | Inhouse |
| 22 | Persulfate digestion | SFA | APHA |
| 23 | Persulfate digestion | FIA | APHA |

Table 64 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

| Lab. Code | Measurement Method | | Instrument | Method Reference |
|---|---|---|---|---|
| 1 | HNO3-Digestion | ICP Method | ICP-OES | USEPA 6010c |
| 5 | No Digestion | ICP Method | ICP-OES | APHA |
| 6 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | APHA |
| 8 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | |
| 9 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | APHA4500-PH |
| 13 | | ICP Method | ICP-OES | |
| 15 | H2SO4+K2SO4-Digestion | Ascorbic Acid Colorimetric Method | SFA | In house |
| 17 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | Lachat QuikChem |
| 18 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 20 | H2SO4+HNO3-Digestion | Ascorbic Acid Colorimetric Method | DA | APHA1500P |
| 21 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | Inhouse |
| 22 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 23 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | APHA |

## APPENDIX 7 - METHODOLOGY FOR S2

Table 65 Instrument Techniques for Boron

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | Neat | 208.956 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 2 | 208.956 mm |
| 6 | ICP-OES-AV | Lu | | | 15.8 | 208.956 |
| 8 | ICP-MS | Sc | NA | NA | 1 | 10 |
| 9 | ICP-MS | Sc | KED | He | 20 | 10 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 11 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 5 | 208.956 |
| 15 | ICP-OES-AV | Y 371.029 | | | | 208.889 |
| 16 | ICP-MS | Sc | NA | Standard Mode | 10 | |
| 17 | ICP-OES-AV | | | | | |
| 18 | ICP-OES-AV | Y | NA | | 2 | 249.678 |
| 20 | ICP-OES-AV | Yb | | | 10 | 249.772 nm |
| 21 | ICP-OES-AV-buffer | Lu | | | | 249.678 |
| 22 | ICP-OES-AV | | | | | |

Table 66 Instrument Techniques for Calcium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 20 | 315.88 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 2 | 315.887 mm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 422.673 |
| 8 | ICP-MS | Sc | UC | He | 1 | 44 |
| 9 | ICP-MS | Sc | KED | He | 20 | 43 |
| 11 | ICP-MS/MS | Ge | ORS | O2 | 100 | 42 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 5 | 315.887 |
| 15 | ICP-OES-AV | Y 371.029 | | | | 430.253 |
| 16 | ICP-MS | Sc | CRI | He | 10 | |
| 17 | ICP-OES-RV | | | | | |
| 18 | ICP-OES-RV | Y | NA | | 100 | 422.673 |
| 20 | ICP-OES-AV | Yb | | | 10 | 317.93 nm |
| 21 | ICP-OES-AV-buffer | Lu | | | | 430.253 |
| 22 | ICP-OES-AV | | | | | |

## Table 67 Instrument Techniques for Potassium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 20 | 166.491 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 20 | 766.491 mm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 766.491 |
| 8 | ICP-MS | Sc | UC | He | 1 | 39 |
| 9 | ICP-MS | Sc | KED | He | 20 | 39 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 39 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Rb | NA | NA | 5 | 766.491 |
| 15 | ICP-OES-AV | Y 371.029 | | | | 769.897 |
| 16 | ICP-MS | Sc | CRI | He | 10 | |
| 17 | ICP-OES-RV | | | | | |
| 18 | ICP-OES-RV | Y | NA | | 100 | 766.491 |
| 20 | ICP-OES-AV | Yb | | | 10 | 766.491 nm |
| 21 | ICP-OES-AV-buffer | Lu | | | | 766.491 |
| 22 | ICP-OES-AV | | | | | |

## Table 68 Instrument Techniques for Magnesium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 20 | 279.8 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 2 | 279.800 mm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 285.213 |
| 8 | ICP-MS | Sc | UC | He | 1 | 25 |
| 9 | ICP-MS | Sc | KED | He | 20 | 25 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 24 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 5 | 278.412 |
| 15 | ICP-OES-AV | Y 371.029 | | | | 277.983 |
| 16 | ICP-MS | Sc | CRI | He | 10 | |
| 17 | ICP-OES-AV | | | | | |
| 18 | ICP-OES-RV | Y | NA | | 100 | 279.078 |
| 20 | ICP-OES-AV | Yb | | | 10 | 383.23nm |
| 21 | ICP-OES-AV-buffer | Lu | | | | 279.078 |
| 22 | ICP-OES-AV | | | | | |

## Table 69 Instrument Techniques for Sodium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 400 | 589.59 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 20 | 588.955 mmm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 589.592 |
| 8 | ICP-MS | Sc | UC | He | 1 | 23 |
| 9 | ICP-MS | Sc | KED | He | 20 | 23 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 23 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 5 | 330.298 |
| 15 | ICP-OES-AV | Y 371.029 | | | | 588.995 |
| 16 | ICP-MS | Sc | CRI | He | 1000 | |
| 17 | ICP-OES-RV | | | | | |
| 18 | ICP-OES-RV | Y | NA | | 100 | 589.592 |
| 20 | ICP-OES-AV | Yb | | | 10 | 330.23 nm |
| 21 | ICP-OES-AV-buffer | Lu | | | | 589.592 |
| 22 | ICP-OES-AV | | | | | |

## Table 70 Measurement Methods and Instrument Techniques for Alkalinity

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Titration | Auto Titration | APHA |
| 5 | Titration | Auto Titration | APHA |
| 8 | Titration | Auto Titration | |
| 9 | Titration | Auto Titration | APHA2320B |
| 12 | Titration | Auto Titration | |
| 13 | Titration | Auto Titration | |
| 15 | Titration | Auto Titration | In house |
| 16 | Titration | Manual Analysis | APHA 2320-Alkalinity |
| 17 | Titration | Auto Titration | APHA |
| 18 | Titration | Auto Titration | APHA |
| 20 | Titration | Auto Titration | APHA2320 |
| 21 | Titration | Manual Analysis | Inhouse |
| 22 | Titration | | |

Table 71 Measurement Methods and Instrument Techniques for Silica

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | ICP-Method | ICP-OES | USEPA |
| 5 | Molybdosilicate Method | DA | APHA |
| 6 | ICP-Method | ICP-MS | Inhouse |
| 7 | Molybdosilicate Method | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 8 | ICP-Method | ICP-MS | |
| 9 | Heteropoly Blue Method | FIA | APHA4500-SiO2F modified |
| 10 | Molybdosilicate Method | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 12 | Molybdosilicate Method | DA | |
| 13 | Molybdosilicate Method | DA | |
| 15 | Molybdosilicate Method | DA | In house |
| 17 | ICP-Method | ICP-OES | |
| 18 | ICP-Method | ICP-OES | USEPA |
| 19 | Molybdosilicate Method | SFA | Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) “Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing.” Limnol. Oceanogr: Methods |
| 20 | ICP-Method | ICP-OES | APHA3120 |
| 22 | Molybdosilicate Method | | |
| 23 | Molybdosilicate Method | FIA | APHA |

Table 72 Measurement Methods and Instrument Techniques for Total Hardness

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Calculation | ICP-OES | |
| 5 | Calculation | ICP-OES | APHA |
| 8 | Titration | Manual Analysis | |
| 9 | Calculation | | |
| 12 | Calculation | Not Applicable | |
| 13 | Calculation | ICP-OES | |
| 15 | Calculation | ICP-OES | In house |
| 16 | Calculation | ICP-MS | APHA 2340 B-Hardness |
| 18 | Calculation | ICP-OES | APHA |
| 20 | Calculation | | |
| 22 | Calculation | | |

## APPENDIX 8 – METHODOLOGY FOR S3

Table 73 Instrument Techniques for Boron

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 2 | 208.956 |
| 2 | ICP-OES-AV | Lu | | | | 208 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 1 | 208.956 mm |
| 6 | ICP-OES-AV | Lu | | | 15.8 | 208.956 |
| 8 | ICP-MS | Sc | NA | NA | 1 | 10 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 11 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 1 | 208.956 |
| 15 | ICP-MS/MS | Sc45 | ORS | He | | 11 |
| 16 | ICP-MS | Sc | NA | Standard Mode | 10 | |
| 17 | ICP-OES-AV | | | | | |
| 18 | ICP-OES-AV | Y | NA | NA | 2 | 249.678 |
| 21 | ICP-OES-AV-buffer | Lu | | | | 249.678 |
| 22 | ICP-OES-AV | | | | | |

Table 74 Instrument Techniques for Calcium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 50 | 315.88 |
| 2 | ICP-OES-AV | Lu | | | | 317 |
| 3 | Other | ION 96.4/ARD-01 | NA | Other | 1 | 422.7 |
| 4 | ICP-OES-AV | | | | | 317.93 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 1 | 315.887 mm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 422.673 |
| 8 | ICP-MS | Sc | UC | He | 1 | 44 |
| 11 | ICP-MS/MS | Ge | ORS | O2 | 100 | 42 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 1 | 422.673 |
| 15 | ICP-MS/MS | Sc45 | ORS | He | | 44 |
| 16 | ICP-MS | Sc | CRI | He | 10 | |
| 17 | ICP-OES-RV | | | | | |
| 18 | ICP-OES-RV | Y | NA | NA | 2 | 422.673 |
| 21 | ICP-OES-AV-buffer | Lu | | | | 430.253 |
| 22 | ICP-OES-AV | | | | | |

## Table 75 Instrument Techniques for Potassium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 50 | 166.491 |
| 2 | ICP-OES-AV | Lu | | | | 766 |
| 3 | Other | ION 96.4/ARD-02 | NA | Other | 1 | 766.5 |
| 4 | ICP-OES-AV | | | | | 766.49 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 1 | 766.491 mm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 766.491 |
| 8 | ICP-MS | Sc | UC | He | 1 | 39 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 39 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 1 | 766.491 |
| 15 | ICP-MS/MS | Sc45 | ORS | He | | 39 |
| 16 | ICP-MS | Sc | CRI | He | 10 | |
| 17 | ICP-OES-RV | | | | | |
| 18 | ICP-OES-RV | Y | NA | NA | 2 | 766.491 |
| 21 | ICP-OES-AV-buffer | Lu | | | | 766.491 |
| 22 | ICP-OES-AV | | | | | |

## Table 76 Instrument Techniques for Magnesium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 50 | 279.8 |
| 2 | ICP-OES-AV | Lu | | | | 280 |
| 3 | Other | ION 96.4/ARD-03 | NA | Other | 10 | 285.2 |
| 4 | ICP-OES-AV | | | | | 285.212 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 1 | 279.800 mm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 285.213 |
| 8 | ICP-MS | Sc | UC | He | 1 | 25 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 24 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 1 | 285.213 |
| 15 | ICP-MS/MS | Sc45 | ORS | He | | 24 |
| 16 | ICP-MS | Sc | CRI | He | 10 | |
| 17 | ICP-OES-AV | | | | | |
| 18 | ICP-OES-RV | Y | NA | NA | 2 | 279.078 |
| 21 | ICP-OES-AV-buffer | Lu | | | | 279.078 |
| 22 | ICP-OES-AV | | | | | |

## Table 77 Instrument Techniques for Sodium

| Lab. Code | Instrument | Internal Standard | Reaction/Collision Cell | Cell Mode/Gas | Final Dilution Factor | Wavelength (nm)/ Ion (m/z)/ Absorbance (nm) |
|---|---|---|---|---|---|---|
| 1 | ICP-OES-AV | Lutetium | NA | NA | 1000 | 589.59 |
| 2 | ICP-OES-AV | Lu | | | | 588 |
| 3 | Other | ION 96.4/ARD-04 | NA | Other | 10 | 589 |
| 4 | ICP-OES-AV | | | | | 589.592 |
| 5 | ICP-OES-AV | Lutetium | NA | NA | 1 | 588.995 mm |
| 6 | ICP-OES-RV | Lu | | | 15.8 | 589.592 |
| 8 | ICP-MS | Sc | UC | He | 1 | 23 |
| 11 | ICP-MS/MS | Ge | CRI | He | 100 | 23 |
| 12 | ICP-MS | | | | | |
| 13 | ICP-OES-AV-buffer | Lu | NA | NA | 1 | 589.592 |
| 15 | ICP-MS/MS | Sc45 | ORS | He | | 23 |
| 16 | ICP-MS | Sc | CRI | He | 1000 | |
| 17 | ICP-OES-RV | | | | | |
| 18 | ICP-OES-RV | Y | NA | NA | 2 | 589.592 |
| 21 | ICP-OES-AV-buffer | Lu | | | | 589.592 |
| 22 | ICP-OES-AV | | | | | |

## Table 78 Measurement Methods and Instrument Techniques for Ammonia-N

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Colorimetric - Phenate Method | DA | APHA |
| 3 | Colorimetric - Salicylate Method | UV-Vis Spectrophotometer | |
| 4 | Colorimetric - Phenate Method | UV-Vis Spectrophotometer | |
| 5 | Colorimetric - Phenate Method | DA | APHA |
| 6 | Colorimetric - Phenate Method | FIA | APHA |
| 8 | Colorimetric - Phenate Method | FIA | |
| 12 | Colorimetric - Salicylate Method | DA | |
| 13 | Colorimetric - Phenate Method | DA | |
| 15 | Colorimetric - Phenate Method | SFA | In house |
| 16 | Ion Selective Electrode Method | Ion Selective Electrode | APHA 4500 |
| 17 | Colorimetric - Phenate Method | FIA | Lachat QuikChem |
| 18 | Fluorometric Determination - OPA Method | SFA | SFA |
| 21 | Colorimetric - Phenate Method | FIA | Inhouse |
| 22 | Colorimetric - Phenate Method | SFA | APHA |
| 23 | Colorimetric - Phenate Method | FIA | APHA |

Table 79 Measurement Methods and Instrument Techniques for Bromide

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ion Chromatographic Method | IC | APHA |
| 2 | Other | ICP-MS | |
| 5 | Ion Chromatographic Method | IC | APHA |
| 6 | Ion Chromatographic Method | IC | Inhouse |
| 8 | ICP Method | ICP-MS | |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Ion Chromatographic Method | IC | |
| 13 | Ion Chromatographic Method | IC | |
| 15 | Ion Chromatographic Method | IC | In house |
| 16 | Colorimetric Method | IC | APHA 411 B |
| 17 | Ion Chromatographic Method | IC | APHA |
| 18 | Ion Chromatographic Method | IC | APHA |
| 22 | Ion Chromatographic Method | IC | APHA |

Table 80 Measurement Methods and Instrument Techniques for Chloride

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ion Chromatographic Method | IC | APHA |
| 2 | Ferricyanide Colorimetric Method | UV-Vis Spectrophotometer | 4500 Cl- E (APHA) |
| 3 | Argentometric Titration | UV-Vis Spectrophotometer | 8225 HACH |
| 4 | Argentometric Titration | Manual Analysis | |
| 5 | Ion Chromatographic Method | IC | APHA |
| 6 | Ion Chromatographic Method | IC | Inhouse |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Ion Chromatographic Method | IC | |
| 13 | Ion Chromatographic Method | IC | |
| 15 | Ion Chromatographic Method | IC | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Ion Chromatographic Method | IC | APHA |
| 18 | Ion Chromatographic Method | IC | APHA |
| 21 | Ferricyanide Colorimetric Method | FIA | Inhouse |
| 22 | Ion Chromatographic Method | IC | APHA |

Table 81 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | High-Temperature Oxidation | NIR-detector | APHA |
| 5 | High-Temperature Oxidation | NIR-detector | APHA |
| 8 | High-Temperature Oxidation | Shimadzu TOC-L | |
| 12 | High-Temperature Oxidation | NIR-detector | |
| 13 | High-Temperature Oxidation | NIR-detector | |
| 15 | Wet-Oxidation | NIR-detector | In house |
| 17 | High-Temperature Oxidation | NIR-detector | APHA |
| 18 | High-Temperature Oxidation | NIR-detector | APHA |
| 21 | High-Temperature Oxidation | NIR-detector | Inhouse |
| 22 | High-Temperature Oxidation | NIR-detector | APHA |

Table 82 Measurement Methods and Instrument Techniques for Fluoride

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ion Selective Electrode Method | Ion Selective Electrode | NEPM |
| 2 | Ion Selective Method | Ion Selective Electrode | 4500 F- C (APHA) |
| 3 | SPADNS Colorimetric Method | UV-Vis Spectrophotometer | 8029 HACH |
| 4 | Ion Selective Electrode Method | Ion Selective Electrode | |
| 5 | Ion Selective Electrode Method | Ion Selective Electrode | APHA |
| 6 | Ion Chromatographic Method | IC | Inhouse |
| 8 | Ion Selective Electrode Method | Ion Selective Electrode | |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Ion Chromatographic Method | IC | |
| 13 | Ion Selective Electrode Method | Ion Selective Electrode | |
| 15 | Ion Chromatographic Method | IC | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Ion Chromatographic Method | IC | APHA |
| 18 | Ion Chromatographic Method | IC | APHA |
| 21 | Ion Selective Electrode Method | Ion Selective Electrode | Inhouse |
| 22 | Ion Selective Electrode Method | Auto Titration | APHA |

## Table 83 Measurement Methods and Instrument Techniques for Nitrate-N

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Colorimetric -vanadium III method | DA | APHA |
| 3 | Colorimetric-Sulfanilamide-NEDD Cd reduction | UV-Vis Spectrophotometer | 8171 HACH |
| 4 | Colorimetric -vanadium III method | UV-Vis Spectrophotometer | |
| 5 | Colorimetric -vanadium III method | DA | APHA |
| 6 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | APHA |
| 8 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Calculation | Not Applicable | |
| 13 | Colorimetric -vanadium III method | DA | |
| 15 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | Lachat QuikChem |
| 18 | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | APHA |
| 21 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | Inhouse |
| 22 | Calculation | SFA | APHA |
| 23 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | APHA |

## Table 84 Measurement Methods and Instrument Techniques for Nitrite-N

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Colorimetric Method | DA | APHA |
| 3 | Colorimetric Method | UV-Vis Spectrophotometer | 8507 HACH |
| 4 | Colorimetric Method | UV-Vis Spectrophotometer | |
| 5 | Colorimetric Method | DA | APHA |
| 6 | Colorimetric Method | FIA | APHA |
| 8 | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Colorimetric Method | SFA | |
| 13 | Colorimetric Method | DA | |
| 15 | Colorimetric Method | SFA | In house |
| 17 | Colorimetric Method | FIA | Lachat QuikChem |
| 18 | Colorimetric Method | SFA | APHA |
| 21 | Colorimetric Method | FIA | Inhouse |
| 22 | Colorimetric Method | SFA | APHA |
| 23 | Colorimetric Method | FIA | APHA |

Table 85 Measurement Methods and Instrument Techniques for Orthophosphate-P

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ascorbic Acid Colorimetric Method | DA | APHA |
| 2 | Ascorbic Acid Colorimetric Method | UV-Vis Spectrophotometer | 4500-P E (APHA) |
| 3 | Ascorbic Acid Colorimetric Method | UV-Vis Spectrophotometer | 8048 HACH |
| 4 | Vanadomolybdophosphoric Colorimetric Method | UV-Vis Spectrophotometer | |
| 5 | Ascorbic Acid Colorimetric Method | DA | APHA |
| 6 | Ascorbic Acid Colorimetric Method | FIA | APHA |
| 8 | Ascorbic Acid Colorimetric Method | FIA | |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Ascorbic Acid Colorimetric Method | DA | |
| 13 | Vanadomolybdophosphoric Colorimetric Method | DA | |
| 15 | Ascorbic Acid Colorimetric Method | SFA | In house |
| 17 | Ascorbic Acid Colorimetric Method | FIA | Lachat QuikChem |
| 18 | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 21 | Ascorbic Acid Colorimetric Method | FIA | Inhouse |
| 22 | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 23 | Ascorbic Acid Colorimetric Method | FIA | APHA |

Table 86 Measurement Methods and Instrument Techniques for Sulphate

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Ion Chromatographic Method | IC | APHA |
| 2 | ICP Method | ICP-OES | |
| 3 | Turbidimetric Method | UV-Vis Spectrophotometer | 8051 HACH |
| 4 | ICP Method | ICP-OES | |
| 5 | Ion Chromatographic Method | IC | APHA |
| 6 | Ion Chromatographic Method | IC | Inhouse |
| 11 | Ion Chromatographic Method | IC | |
| 12 | Ion Chromatographic Method | IC | |
| 13 | Ion Chromatographic Method | IC | |
| 15 | Ion Chromatographic Method | IC | In house |
| 16 | Ion Chromatographic Method | IC | APHA 411 B |
| 17 | Ion Chromatographic Method | IC | APHA |
| 18 | Ion Chromatographic Method | IC | APHA |
| 21 | Turbidimetric Method | FIA | Inhouse |
| 22 | Ion Chromatographic Method | IC | APHA |

Table 87 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Calculation (TKN+NOx) | DA | APHA |
| 5 | COMBUSTION | Other | |
| 6 | Persulfate digestion | FIA | APHA |
| 8 | Persulfate digestion | FIA | |
| 12 | Persulfate digestion | SFA | |
| 13 | Combustion | Chemiluminescence detector | |
| 15 | Calculation (TKN+NOx) | SFA | In house |
| 17 | Persulfate digestion | FIA | Lachat QuikChem |
| 18 | Persulfate digestion | SFA | APHA |
| 21 | Persulfate digestion | FIA | Inhouse |
| 22 | Persulfate digestion | SFA | APHA |
| 23 | Persulfate digestion | FIA | APHA |

Table 88 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

| Lab. Code | Measurement Method | | Instrument | Method Reference |
|---|---|---|---|---|
| 1 | HNO3-Digestion | ICP Method | ICP-OES | USEPA 6010c |
| 3 | H2SO4+K2SO4-Digestion | Ascorbic Acid Colorimetric Method | UV-Vis Spectrophotometer | 8190 HACH |
| 5 | No Digestion | ICP Method | ICP-OES | USEPA 6010c |
| 6 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | APHA |
| 8 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | |
| 12 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | DA | |
| 13 | No Digestion | ICP Method | ICP-OES | |
| 15 | H2SO4+K2SO4-Digestion | Ascorbic Acid Colorimetric Method | SFA | In house |
| 17 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | Lachat QuikChem |
| 18 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 21 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | Inhouse |
| 22 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | SFA | APHA |
| 23 | K2S2O8-Digestion | Ascorbic Acid Colorimetric Method | FIA | APHA |

## APPENDIX 9 – METHODOLOGY FOR S4

Table 89 Measurement Methods and Instrument Techniques for Total Kjeldahl Nitrogen

| Lab. Code | Measurement Method | | Instrument | Method Reference |
|---|---|---|---|---|
| 1 | Kjeldahl (H2SO4+K2SO4 digestion) | Colorimetric - salicylate method | DA | APHA |
| 5 | Other | CALCULATION | Not Applicable | |
| 6 | Kjeldahl (H2SO4+K2SO4 digestion) | Colorimetric - salicylate method | FIA | APHA |
| 8 | TKN=TN-NOx (K2S2O8 digestion) | | FIA | |
| 9 | Kjeldahl (H2SO4+K2SO4 digestion) | Colorimetric - salicylate method | DA | APHA4500_N.orgD modified |
| 12 | Other | Other | Not Applicable | |
| 13 | | Calculation | | |
| 15 | Kjeldahl (H2SO4+K2SO4 digestion) | Colorimetric - salicylate method | SFA | In house |
| 17 | TKN=TN-NOx (K2S2O8 digestion) | Colorimetric-Sulfanilamide-NEDD Cd reduction | FIA | |
| 18 | TKN=TN-NOx (K2S2O8 digestion) | Calculation from TN and NOX | SFA | APHA |
| 22 | TKN=TN-NOx (K2S2O8 digestion) | Colorimetric-Sulfanilamide-NEDD Cd reduction | SFA | APHA |

Table 90 Measurement Methods and Instrument Techniques for Total Nitrogen

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | Calculation (TKN+NOx) | DA | APHA |
| 5 | COMBUSTION | Other | |
| 6 | Persulfate digestion | FIA | APHA |
| 8 | Persulfate digestion | FIA | |
| 9 | Calculation (TKN+NOx) | IC | |
| 12 | Persulfate digestion | SFA | |
| 13 | Combustion | Chemiluminescence detector | |
| 15 | Calculation (TKN+NOx) | SFA | In house |
| 16 | Persulfate digestion | IC | ASTM D8001-16e1 |
| 17 | Persulfate digestion | FIA | Lachat QuikChem |
| 18 | Persulfate digestion | SFA | APHA |
| 21 | Persulfate digestion | FIA | Inhouse |
| 22 | Persulfate digestion | SFA | APHA |
| 23 | Persulfate digestion | FIA | APHA |

Table 91 Measurement Methods and Instrument Techniques for Total Organic Carbon

| Lab. Code | Measurement Method | Instrument | Method Reference |
|---|---|---|---|
| 1 | High-Temperature Oxidation | NIR-detector | APHA |
| 5 | High-Temperature Oxidation | NIR-detector | APHA |
| 8 | High-Temperature Oxidation | Shimadzu TOC-L | |
| 9 | Super critical persulphate oxidation | NIR-detector | APHA5310C modified |
| 12 | High-Temperature Oxidation | NIR-detector | |
| 13 | High-Temperature Oxidation | NIR-detector | |
| 15 | Wet-Oxidation | NIR-detector | In house |
| 17 | High-Temperature Oxidation | NIR-detector | APHA |
| 18 | High-Temperature Oxidation | NIR-detector | APHA |
| 21 | High-Temperature Oxidation | NIR-detector | Inhouse |
| 22 | High-Temperature Oxidation | NIR-detector | APHA |

# END OF REPORT